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A Philosophical Analysis of the Relation between Chemistry and Quantum Mechanics

The case of a single inert molecule

Vanessa A. Seifert

A dissertation submitted to the University of Bristol in accordance with the requirements for award of the degree of Doctor of Philosophy in the Faculty of Arts.

Department of Philosophy

September 2018

Word length: 60,289

Abstract

This thesis investigates the epistemological and metaphysical relations between chemistry and quantum mechanics. These relations are examined with respect to how chemistry and quantum mechanics each describe a single inert molecule. A review of how these relations are understood in the literature shows that there is a proliferation of positions which focus on how chemistry is separate from quantum mechanics. This proliferation is accompanied by a tendency within the philosophy of chemistry community to connect the legitimacy of the field with the autonomy of chemistry. First, it is argued that this connection should not be made. Secondly, it is argued that chemistry and quantum mechanics are unified in accordance with Harold Kincaid's model of non-reductive unity because the two theories exhibit particular epistemic and metaphysical interconnections. Thirdly, a metaphysical account is examined which is incompatible with Kincaid's model of unity; namely strong emergence as understood by Robin Hendry. According to Hendry, the structure of a single inert molecule strongly emerges from its quantum mechanical entities in the sense that there is downward causation. However, Hendry's defense of this account faces certain problems. Moreover, the putative empirical evidence for his understanding of strong emergence can be explained without invoking strong emergence. This is shown by considering how quantum mechanics assumes an idealized understanding of a molecule's stability and structure. In the light of the philosophical literature on idealizations, this idealization can be interpreted in two different ways, both of which explain why quantum mechanics describes the structure of a single molecule the way it does, without assuming strong emergence in Hendry's sense. Each interpretation has philosophical implications regarding the nature of chemical properties, and the relation of chemistry and quantum mechanics. These implications are consistent with Kincaid's model of unity and thus further support chemistry's unity with quantum mechanics (as per Kincaid).

Acknowledgements

First, I would like to thank James Ladyman who gave me the opportunity to do a PhD under his supervision. His continuous support and advice far exceeded his obligations as a supervisor and were truly invaluable. Secondly, I would like to thank the Darwin Trust of Edinburgh which funded my research for three years, as well as the Royal Institute of Philosophy which funded the last year of completing the thesis. Also, I would like to thank Nick Norman and Fred Manby of the department of chemistry at the University of Bristol, who were kind enough to clarify certain aspects in theoretical chemistry. Lastly, I would like to thank the following people who, in different ways each, gave me academic assistance during this period: Tami Spector, Olimpia Lombardi, Nicos Stylianou, Geoffrey Blumenthal, Hasok Chang, Karoliina Pullkinen, Hinne Hettema, Elay Shech, Sean Gryb, Karim Thebault, Ana Cretu, Niall Paterson, Chiara Ambrosio, Tudor Baetu and Juan Camilo Martínez González.

The ruling is acknowledged from the Faculty of Arts that this dissertation is under the 2017-18 rules, in that the text count excludes abstract, footnotes, references, bibliography, table of contents, list of images and list of abbreviations.

Statement on publications by author

Chapter 4 is an altered and expanded version of ‘An alternative approach to unifying chemistry with quantum mechanics’, by Vanessa Seifert, published in Foundations of Chemistry, 2017, 19(3): 209-222. A large part of section 4.2, as well as small parts of sections 4.1, 4.3, and 4.4 are reproduced from this paper.

Author's Declaration

I declare that the work in this dissertation was carried out in accordance with the requirements of the University's *Regulations and Code of Practice for Research Degree Programmes* and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. In addition, helpful comments have been provided on all the chapters by James Ladyman. Any views expressed in the dissertation are those of the author.

SIGNED: .... DATE:..........................

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List of Abbreviations

BO	Born-Oppenheimer
DC	Downward Causation
CCP	Causal Closure Principle
IUPAC	International Union of Pure and Applied Chemistry
UP	Ubiquity of Physics

1. Introduction

Phenomena that are standardly regarded as belonging to the subject matter of chemistry have been discussed in philosophy since ancient times. For example, Aristotle did a systematic analysis of phenomena and of concepts that nowadays are regarded within the purview of chemistry.[1] However, the philosophy of chemistry as an organized research study is a relatively new field that flourished in the past 20 years. One of the key events that signified the formation of this field was the foundation of the International Society for the Philosophy of Chemistry which organizes annual conferences since 1997 and established the journal *Foundations of Chemistry* in 1999.[2]

The philosophy of chemistry examines two sorts of issues:

> In the first, conceptual issues arising within chemistry are carefully articulated and analyzed. Such questions which are internal to chemistry include the nature of substance, atomism, the chemical bond, and synthesis. In the second, traditional topics in philosophy of science such as realism, reduction, explanation, confirmation, and modeling are taken up within the context of chemistry. (Hendry et al. 2011)

This thesis focuses on issues of the second sort (though they overlap a little with some of the first sort). Specifically, it is concerned with:

(1) the epistemological relation between chemistry and quantum mechanics; and,

(2) the relation between the entities, properties, etc. that are postulated by chemistry and quantum mechanics respectively.

For brevity this thesis refers to (1) and (2) as respectively the epistemic and metaphysical relations between chemistry and quantum mechanics.

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[1] See the following works of Aristotle: *On Generation and Corruption*, *Meteorology*, *Physics*, and *On the Heavens* (Barnes 1984). See also (Hendry et al. 2011: Section 1.1) and (Needham 2006).

[2] Moreover, books and collections of papers are continuously published on the philosophy of chemistry (see, for example, (Primas 1983), (Scerri and McIntyre 2015), and (van Brakel 2000)). Philosophy of science journals such as *Philosophy of Science* and the *British Journal for the Philosophy of Science* publish papers on issues concerning the philosophy of chemistry (for example (Scerri 1994) and (Hendry and Needham 2007)). The presence of the philosophy of chemistry has also expanded online. Most notable examples are the electronic journal *HYLE: International Journal for Philosophy of Chemistry* and the entry 'Philosophy of Chemistry' in the *Stanford Encyclopedia of Philosophy* (Hendry et al. 2011). For a detailed analysis of the history of the field see (Scerri and Fisher 2015: 3-5).

The rest of this chapter sets the parameters for the investigation of (1) and (2). First, it is important to define the subject matter of chemistry and of quantum mechanics. Chemistry is concerned with how 'matter is composed, the investigation of their properties and reactions, and the use of such reactions to form new substances' ("chemistry, n.1.", OED Online 2018). The description, explanation, and prediction of the composition and reaction of matter is achieved within chemistry by reference to entities, properties, etc. that the theory postulates. In other words, chemistry uses concepts which are characteristic of the chemical description and which allegedly refer to entities, properties, etc. that determine how matter is composed and reacts. Phenomena that are within the purview of chemistry are the rusting of metals, the properties of atoms and molecules, the boiling of water and the volatility of mercury.[3]

Quantum mechanics is 'the non relativistic theory for the description of microscopic systems' (Palgrave Macmillan Ltd 2004: 1863). It is distinguished from relativistic quantum mechanics which is 'a Lorentz-covariant formulation of quantum mechanics' (Palgrave Macmillan Ltd 2004: 1945). Quantum mechanics is also distinguished from quantum field theory which is a 'relativistic quantum theory for describing elementary particles and their interactions, which is based on the wave character of matter and introduces the particle aspect through the quantization of the corresponding, relativistically formulated, classical field theory' (Palgrave Macmillan Ltd 2004: 1848). The description, explanation, and prediction of microscopic systems is achieved within quantum mechanics by reference to entities, properties, etc. that the theory postulates. Phenomena that are within the purview of quantum mechanics are black-body radiation, the double-slit experiment, and the behavior of a free particle under a magnetic field.

This chapter presents the two issues addressed in this thesis and sets the parameters for the examination of them. Section 1.1 explicates the naturalistic approach that is followed here. Given this naturalistic approach, three features of the thesis' investigation are specified. First, it is important, prior to making any claims about the relation between chemistry and quantum mechanics, that one specifies the relevant domain with respect to which this relation is examined. In light of this, this thesis investigates this relation with respect to how chemistry and quantum mechanics describe a single inert molecule. Secondly, it is also important to specify the relevant scale of the two theories. In light of this, the section specifies the relevant scales of chemistry and of quantum mechanics. Lastly, this thesis assumes a definition of phenomena which is consonant to how scientists implicitly understand phenomena. It is noted that this understanding of

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[3] This is a very brief and incomplete analysis of the subject matter of chemistry. A more complete analysis of chemistry requires reference to issues such as the role of the periodic table in chemistry, the tools of representation employed in chemistry, the subject matter of chemistry's sub-disciplines (such as physical chemistry, analytic chemistry, organic chemistry and quantum chemistry) and the role of synthetic design. An informative analysis of chemistry is provided by (Chang 2017) as well as by collections of papers, such as (Baird et al. 2006).

phenomena implies a pragmatic realist approach towards unobservable entities. Section 1.2 briefly presents the main claims that are made in each chapter of this thesis.

1.1 The two issues

The first issue that is investigated in this thesis is the epistemic relation between chemistry and quantum mechanics. This issue is an epistemological one because it focuses on the relation between two distinct scientific theories. The term 'scientific theory' is understood here in a naive manner, as referring to any sort of description or representation that is employed by working scientists in order to describe, explain, and predict some set of phenomena.[4] Scientific theories are in the business of describing, explaining, and predicting phenomena by, among other things, postulating theoretical entities, properties, etc..[5]

Also, note that two scientific theories are understood here as being distinct in the sense that the scientific community regards them as being two separate (but not necessarily independent) theories. This section assumes this understanding of 'distinct' in order to avoid presupposing the existence of some sort of epistemic relation between the two theories. Since the goal of this thesis is to examine whether and what sort of epistemic relation exists between the two theories, the term 'distinct' cannot be understood here in a way that predetermines the existence or nature of such a relation.[6]

The relation between distinct scientific theories can concern scientists and philosophers alike. Scientists are interested in them primarily because investigating them can raise novel and interesting research questions. For example, considering the relation between chemistry and quantum mechanics led to the research question of understanding the structure of the periodic table in terms of atomic orbits ((Scerri 2012b: 74-76), see also (Scerri 2007c) and (Gavroglu and Simões 2012b: 48-60)). Philosophers are interested in the relations

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[4] No particular position regarding the structure, composition, or function of scientific theories is assumed here. Chapter 4, which supports the unity between chemistry and quantum mechanics, specifies how scientific theories are understood in the context of its proposed account of unity. Also, the end of this section specifies what is meant here by 'phenomena'.

[5] The role of phenomena in the confirmation of theories is not examined here. For an overview of how philosophy examines the confirmation of scientific theories see (Salmon et al. 1992: 42–103) and (Crupi 2015).

[6] Also, note that this understanding of 'distinct' is a rather naive and intuitive one in the sense that it is not based on a more nuanced or philosophically informed understanding of 'distinctness' in relation to scientific theories or disciplines. For example, Hasok Chang provides a historically and philosophically informed account of what renders chemistry 'a separate scientific discipline' (2017: 360).

between theories because they are relevant to the investigation of issues such as the nature of theory change, confirmation, explanation, reduction and scientific realism (see for example (Curd and Cover 1998)).[7]

The relation between scientific theories can be investigated for pairs of theories that belong to different disciplines, and for pairs that 'belong' to the same discipline.[8] For example, scientific theories that are regarded as belonging to the general discipline of physics are often examined with respect to their relation; these include equilibrium statistical mechanics and thermodynamics (for example (Nagel 1979)), classical mechanics and quantum mechanics (Bokulich 2008b), and classical mechanics and the special theory of relativity (Nickles 1975). On the other hand, there are pairs of theories which are considered to belong to different scientific disciplines, whose relation is also examined. This includes the relation between psychology and biology (for example (Bickle 2006: 412)), psychology and physics (Lewis 1966), biology and physics (Kitcher 1984), and chemistry and physics (Scerri 2007a).

This thesis draws extensively (especially in chapters 4 and 5) on the philosophy of science literature about inter-theory relations, as a valuable source that contributes to understanding and resolving debates that concern the relation between chemistry and quantum mechanics and which are discussed in the philosophy of chemistry literature.

The second issue that is examined in this thesis is the relation between the entities postulated by chemistry and quantum mechanics respectively.[9] This is a metaphysical issue because it examines a particular aspect of how the world is, and not of how it is described. This thesis examines this issue in a naturalistic context.[10] According to naturalism, 'philosophical theorizing about the natural world should be consonant with scientific facts and theses, concerning both scientific subject and scientific methodology' (Wilson 2005: 438). This requires that 'one's philosophical methodology and results be "commensurable" (connoting: having a common measure) or "consonant" (connoting: being in agreement or harmony) with scientific facts and

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[7] Perhaps one of the most widely discussed relations in science and in philosophy is that between equilibrium statistical mechanics and thermodynamics. For a scientific account of the relation between these two theories see, for example, (Attard 2002). Philosophical discussions about the relation of equilibrium statistical mechanics and thermodynamics can be found in (Nagel 1979) and (Sklar 1993).

[8] This point applies to the investigation of the metaphysical relation as well. Moreover, 'discipline' is understood here in a manner consonant to how scientists understand and identify scientific disciplines.

[9] The term 'entities' is used here broadly to refer to entities, properties, processes, collections of entities, etc.. That is, the term refers to 'any relevant ontological category (property, event, substantial particular, etc.)' (Wilson 2010: 280).

[10] The epistemic relation between chemistry and quantum mechanics is also investigated in a naturalistic context because this investigation is, by definition, based on the analysis of the best current theories.

theses, as these are presently reasonably taken to be' (Wilson 2005: 439). Based on this, the investigation of the relation between the entities postulated by chemistry and quantum mechanics 'should be consonant with scientific facts and theses' (Wilson 2005: 438).

Note that if 'scientific facts and theses' postulate some relation between two theories, then such facts should also be taken into consideration when investigating the relation between the two theories' postulated entities. For example, it is a scientific fact that molecules are made of atoms.[11] The term 'made up' has no direct philosophical implications; for example, it does not imply whether the molecule is, say, type or token identical to a collection of atoms, or whether it is composed of atoms in a different sense. These are possible metaphysical interpretations. Nevertheless, the naturalistic method is to seek the right philosophical interpretation from close consideration of the available scientific facts.

Note that scientific facts such as the above often indicate that the relevant scientific theories are somehow epistemically related. However, a naturalist requires that the metaphysical relation that is defended is consistent only with the scientific facts, and not with the epistemic interpretation of these facts. Primarily, this is because there is usually more than one available interpretation of how two theories are epistemically related. For example, the epistemic relation can be philosophically interpreted as an indication of epistemic reduction, emergence, unity, etc. In light of this, the nature of the metaphysical relation is not decisively settled by investigating the epistemic relation between the relevant theories. Secondly, even if a particular epistemic relation is supported, the existence and nature of the metaphysical relation is not decisively settled by the support of this epistemic relation. This is because it is possible that the postulated epistemic relation is consistent with more than one position about the metaphysical relation between the two theories' postulated entities. For example, it is consistent with the epistemic reduction of chemistry to quantum mechanics to support type identity, token identity, or some other sort of identity relation between atoms and molecules (see section 3.2). Therefore, while a naturalistic approach towards the investigation of the metaphysical relation is informed by the available positions regarding the epistemic relation between the respective theories, the defense of a particular epistemic relation does not determine the relevant metaphysical relation.

Given the naturalistic approach followed in this thesis, it is important to clarify that the epistemic and metaphysical relations between chemistry and quantum mechanics are examined within the purview of a specific domain of scientific inquiry. Specifically, the thesis focuses on how chemistry and quantum mechanics each describe, explain, and predict a single inert molecule (and its properties). That is, the epistemic relation between chemistry and quantum mechanics is examined with respect to how the chemical

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[11] See any current scientific textbook on the matter: for example (Atkins and Friedman 2005), (Atkins and Jones 2010), (Feynman et al. 1965) and (Jewett and Serway 2010).

and quantum mechanical descriptions of a single inert molecule relate to each other. The metaphysical relation between chemistry and quantum mechanics is examined with respect to how the respective entities, properties, etc. that are postulated for the description of a single inert molecule, are related to each other. An inert molecule is a stable and unreactive molecule under specified conditions (IUPAC 2014: 729).[12]

Note that the way chemistry and quantum mechanics relate to each other with respect to other domains of inquiry, is not investigated here.[13] For example, the thesis does not examine how chemistry is related to quantum mechanics when it comes to their descriptions of a non-inert molecule. Moreover, the claims that are supported in this thesis are supported only for the examined domain of inquiry. That is, the thesis' claims are not necessarily correct with respect to other domains of inquiry.[14]

Specifying the domain of inquiry is important in a naturalized context for the following reasons. First, any account of the relation between two scientific theories is specific to a certain domain of inquiry. For example, the relation between biology and neurophysiology can be examined in the context of how they both describe and explain particular behaviors of living organisms; the relation of equilibrium statistical mechanics and thermodynamics can be examined in the context of how they both describe and explain the behavior of large systems; whereas the relation of macroeconomics and microeconomics can be examined in the context of how they both describe and explain, say, the fluctuation of stock markets.

Secondly, the postulated epistemic relation between a pair of scientific theories largely depends on the particular domain with respect to which those theories are examined. This is because the particular domain determines the scientific evidence that is used for the support of a particular relation between two theories. For example, Eleanor Knox defends a certain kind of reductive relation between biology and neurophysiology by examining a particular phenomenon; namely 'the characteristic output patterns of the stomatogastric ganglion of a lobster' (2017: 124). This illustrates not only that the relation between two theories can be examined in more than one domain, but also that the particular postulated relation is contingent on the specific domain in which it is examined.

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[12] The definitions of stability and reactivity are stated in chapter 2. Chapter 2 provides a concise presentation of how chemistry and quantum mechanics each describe a single inert molecule.

[13] For example, Hinne Hettema examines the relation between chemistry and physics with respect to how chemistry, quantum chemistry, and statistical mechanics contribute to the description and explanation of chemical reaction rates (2017: 69-86).

[14] For example, chapter 4 argues that chemistry and quantum mechanics are unified when it comes to how they describe a single inert molecule. Whether chemistry and quantum mechanics are also unified (in the manner argued for in chapter 4) with respect to other domains of inquiry, is not investigated in this thesis.

Thirdly, in inter-theory relations, the domains must be explicitly specified because the particular energy, length, or time within which the examined phenomena occur, has an impact on how two theories relate to each other. For example, the reduction of thermodynamics to equilibrium statistical mechanics is allegedly problematic when one focuses on the particular range of energy that corresponds to the critical point of the examined system (Berry 2001: 43). Therefore, the postulated relation between two theories is contingent not only on which phenomena are considered, but potentially also on the particular range of energy, length, or time within which those phenomena occur.

Since the examined phenomena occur at some scale, it is important when investigating the epistemic and metaphysical relations between two theories to specify the scale (or range of scale) of application of each theory. The 'scale of a theory' refers to the particular time, length and/or energy scale at which the theory's postulated entities, etc. are found.[15] Before explaining why specifying the scales of two theories is important to the investigation of the two theories' relation, two general points are made about scale.

First, the scale of theories that are taken to belong to the natural sciences (i.e. physics, chemistry, biology, etc.) can be directly specified because most of the postulated entities are quantitatively measured and assigned to specific measurement units of time, length and/or energy (or some combination of those units). Interestingly, although scale can be determined by the unit in which a theory's entities are measured, the scales of theories are not explicitly stated in terms of such measurable quantities. This would amount to saying, for example, that the length scale of chemistry falls within a range of 10^{-15} m - 10^{-9} m, the length scale of quantum mechanics falls within 10^{-35} m to 10^{-16} m, and the length scale of astronomy falls within a range of 10^{6} m - $10^{10\wedge 10\wedge 122}$ m.[16] Instead, the length scale of a theory is indirectly specified in terms of the spatially defined or measurable properties of the postulated entities, such as the size of atoms and molecules in chemistry, of subatomic particles in quantum mechanics, etc..[17] A similar point applies for the specification of the energy and time scale of a theory.

Concerning theories that are not taken to belong to the natural sciences (such as economics, psychology, and sociology), their scale is not specified in the way just outlined because most of the postulated entities are not

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[15] 'Scale' is distinct here from 'level' which often carries strong philosophical connotations. For example, Jonathan Schaffer defines levels as a metaphor of, among other things, 'a mereological structure, ordered by a part-whole relation', 'a supervenience structure', and 'a realisation structure, ordered by functional relations' (Schaffer 2003: 500).

[16] The numerical values are from (Wikipedia 2018). The accuracy of these values does not play any role in the validity of the claim.

[17] For example, the size of atoms is empirically identified by measuring, among other things, their radius (which for all types of atoms is in average 10^{-10} m (Dingdi et al. 2013:1)).

defined or measured in terms of units of length, time, and/or energy. However, the scale of such theories can still be specified because the postulated entities are relevant to a particular time, length, and/or energy scale. For example, the fluctuation of stock prices is relevant to a particular scale of time; stock price changes are determined in economics through the value of stock prices from one day, month, or year to the next, and not through the value of stock prices from one second or nanosecond to the next. Similarly, the length scale of sociology is that to which towns, cities, or small groups of people are relevant.

Secondly, note that while the scales of two theories could be the same, these scales may be specified via completely different sets of entities. For example, the length scales relevant to electromagnetism and to biology are partially the same; the wavelengths of X-rays fall within the same approximate range as that of the diameter of the DNA-helix.[18] However, this does not imply that the wavelength of X-rays and the diameter of the DNA-helix are otherwise related.

The specification of the scales of two theories is central to the investigation of their epistemic and metaphysical relations for two reasons. First, the epistemic or metaphysical relation that is advocated for a particular pair of theories is partially determined by the comparative analysis of the scales at which the two theories' entities are found. Very simply, if the entities of two theories are found at partially distinct energy, length, and/or time scales, then the advocated relation might be different compared to the one advocated between entities that are found at identical scales. For example, the role of scale is often taken as a central problem regarding how to account for the macroscopic behavior of a material from knowledge about its constituents (Robert Batterman refers to this problem as the 'tyranny of scales' (2012: 255)).[19]

This point also becomes apparent if one considers the distinction between higher and lower-level theories. This distinction is most commonly assigned to theories that postulate entities that are found at partially distinct scales.[20] The terms 'higher' and 'lower-level theories' refer to pairs of theories which postulate entities that are found at respectively larger and smaller energy, time and/or length scales. If the theories whose (metaphysical or epistemic) relation is examined, are considered as a pair of higher and lower-level

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[18] Specifically, the average range of X-ray wavelengths is 10^{-8} m to 10^{-12} m (Jewett and Serway 2010: 999) and the average diameter of a DNA-helix is $2 * 10^{-9}$ m (Travers and Muskhelishvili 2015: 2283).

[19] See also (Ladyman and Ross 2007) and (Bursten 2018).

[20] Many accounts on inter-theory relations do not state this explicitly and often use terms other than 'scale' in order to distinguish higher from lower-level theories. For example, Alisa Bokulich distinguishes between higher and lower-level theories in terms of 'levels of descriptions' and not scales, even though she employs the term 'scales' when discussing particular examples of theories ((Bokulich 2008b: 25-27), see also (O'Connor and Churchill 2010)). Nevertheless, to the knowledge of the present author, there is no reference in the literature which explicitly denies the relevance of scale to the distinction between higher and lower-level theories.

theories, then the postulated relation is usually referred to as 'synchronic'; i.e. 'a relation between two concurrent theories that belong to two different levels of description' (Bokulich 2008b: 6). If the theories are not considered as being synchronically related, then the investigated relation is usually referred to as 'diachronic'; i.e. 'a relation between a historical predecessor theory and its successor' (Bokulich 2008b: 6).

Secondly, the sort of metaphysical relation that is advocated between particular sets of entities of two theories informs one's metaphysical understanding of scale. Put differently, the question of the metaphysical relation between entities that are found at partially distinct scales, can be transformed to the question of the metaphysical understanding of scale. For example, James Ladyman and Don Ross 'offer a theory of ontology to unify physics and the special sciences' that, among other things, includes the claim that '(o)ntology is scale relative in respect of both space and time' ((Ladyman 2017: 148, 152), see also (Ladyman and Ross 2007)). Therefore, specifying the relevant scale of two theories while investigating the two theories' metaphysical relation, raises questions regarding scale relativity.

This thesis does not focus on how the metaphysical relation between chemistry and quantum mechanics informs questions about scale relativity. Nevertheless, three points are made here about chemistry's and quantum mechanics' scales. First, the scale of chemistry is quite wide. This is because chemistry postulates entities, properties, etc. of substantially different time and length scales; atoms, molecules, and electrons are found at a substantially different time and length scale compared to, say, grams of iron reacting with oxygen gas. All these entities, etc. specify the scale of chemistry. On the other hand, the entities that are postulated by quantum mechanics and that specify the scale of the theory, are the subatomic particles and their relevant properties (including electrons, protons, and neutrons).

Secondly, note that the scales of chemistry and of quantum mechanics are distinct but partially overlap. Their scales partially overlap because chemistry and quantum mechanics postulate an identical set of entities (i.e. electrons, protons, neutrons). However, their scales are distinct because chemistry postulates entities that are found at a larger length and time scale than those postulated by quantum mechanics. For example, chemistry postulates chemical species, chemical substances, and mixtures, all of which are found at a larger length scale than subatomic particles.[21] In light of this and following Bokulich's specification of

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[21] Chemical species are '(a)n ensemble of chemically identical molecular entities that can explore the same set of molecular energy levels on the time scale of the experiment' (IUPAC 2014: 264). Chemical substances are '(m)atter of constant composition best characterized by the entities (molecules, formula units, atoms) it is composed of' (IUPAC 2014: 265). A mixture is a '(p)ortion of matter consisting of two or more chemical substances' (IUPAC 2014: 941).

synchronically related theories (see above), the chemical and quantum mechanical scales indicate that the corresponding theories are a pair of higher and lower-level theories.[22]

Thirdly, the scales that are relevant to the thesis' investigation of the epistemic and metaphysical relations between chemistry and quantum mechanics, are those that are specified via the entities, etc. that are postulated by the two theories for the description of a single inert molecule. This chapter does not explicitly state the scale that is of relevance to the current investigation. Nevertheless, chapter 2 presents the main entities, properties, etc. that are postulated by chemistry and by quantum mechanics for the description of a single inert molecule. This presentation provides an abstract understanding of the relevant scales and is sufficient for the thesis' analysis of the two theories' relations.

As already noted, this thesis investigates how chemistry and quantum mechanics relate to each other with respect to how they each describe a single inert molecule. This means that the phenomenon that the thesis focuses on and which chemistry and quantum mechanics describe is that of the behavior of a single inert molecule. In accordance with a naturalistic approach, this section assumes a definition of phenomena that accurately captures what scientists regard as phenomena.[23]

One notion of phenomena goes as follows: a phenomenon is 'something that is shown, or revealed, or manifest in experience. (…) More generally, the phenomenal aspects of things are the aspects that show themselves, rather than the theoretical aspects that are inferred or posited in order to account for them' (Blackburn 2008: 274). In this context, phenomena occur (and are thus observed) either without any interference from the part of the observer (like the movement of the stars) or by manipulating a particular system (i.e. via experimentation). Under this definition of phenomena, chemistry is in the business of describing, explaining, and predicting phenomena such as the peaks of NMR spectroscopy, the change of color of a chunk of matter, and the boiling of water. However, this definition is rejected for the purposes of the current thesis because it does not accurately capture the set of phenomena that chemists regard as belonging to their domain of inquiry. Specifically, this definition disregards the fact that many phenomena are expressible with reference to theoretical terms. For example, explaining why the temperature of a liquid

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[22] It can be argued that chemistry is also a predecessor theory to quantum mechanics because it precedes quantum mechanics (that is, the two theories are diachronically related). Bokulich refers to pairs of theories which are both synchronically and diachronically related as 'mixed cases' (2008b: 6). This is not further examined here.

[23] Note that this section does not examine issues regarding the perception of phenomena and the objectivity of observations (such as phenomenalism), the linguistic form and analysis of observation, the structure of scientific theories and their relation to observation, the relation between observation and experimentation, or theories of reference (see, for example, (Bogen 2017), (Hacking 1983), (Hesse 1958), (Kripke 1980), (van Fraassen 2008) and (Winther 2015)).

rises involves reference to the term ‘temperature’ and ‘liquid’. In addition, this definition excludes phenomena that are regarded as such by science, even though they are, under Blackburn’s definition, unobservable. For example, chemistry explains why certain materials change colors by invoking the chemical properties of organic compounds (Raman and Bhagavantam 1929). However, chemistry is also in the business of describing, predicting, and explaining the properties of those organic compounds (see for example (Bird and Kuhn 1981)). Therefore, the behavior of organic compounds is a phenomenon that chemistry is in the business of describing.

Given the above, this section assumes a definition of phenomena that takes into account that science takes phenomena to include ‘inferred or posited’ entities and properties. That is, phenomena are understood here as concrete events and processes in the world and their properties. According to this definition, a single inert molecule and its properties is a phenomenon that chemists are in the business of describing, explaining, and predicting. While a particular molecule and its properties (such as its structure) are not ‘directly observable’ in the manner that Blackburn requires phenomena to be, molecules and their properties belong to the set of phenomena that chemistry investigates. This definition of phenomena also accurately captures the set of events and processes that quantum mechanics describes and explains. For example, such a phenomenon is the movement of an isolated particle within a magnetic field.

Lastly, the definition of phenomena that is assumed here presupposes a pragmatic realist position about unobservable entities, and in particular about molecules and their properties.[24] What this means here is that since the behavior of a single inert molecule requires reference to theoretical entities, properties, etc., it follows that these entities are taken seriously (for else, why would scientists investigate their behavior, and why would a naturalist examine their metaphysical relation?). However, this should not be understood as presupposing a strong metaphysical commitment towards these entities. Rather, it is part of a naturalistic methodology of making the best sense of inter-theory relations, to regard the entities posited by the two examined theories as seriously as the relevant scientists do. Put differently, this thesis assumes a philosophically naive understanding of ‘reality’ which is consonant with how scientists understand the reality of these unobservable entities (namely of atoms, molecules, and their properties).[25]

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[24] This pragmatic realist position should not be conflated with existing realist positions in the philosophy of science literature, such as Hilary Putnam’s ‘internal or pragmatic realism’ ((Sosa 1993: 612), see also (Putnam 1987: 17) and (Putnam 1983)).

[25] Recall that the thesis assumes a similar understanding of the terms ‘distinct’ and ‘discipline’ (see above).

The history of science specifies how chemists and physicists arrived at a consensus regarding the reality of atoms and molecules. A detailed analysis of how physicists and chemists came to agree upon the existence of atoms and molecules is not pursued here.[26] Nevertheless, it is worth noting that Jean Perrin was one of the key figures which contributed in cementing the scientists' acceptance of the existence of atoms and molecules:

> The role of Jean Perrin in the definition of the atomic-molecular hypothesis as a physical hypothesis capable of experimental demonstration and his successful verification of that hypothesis by his numerous experiments, most notably those on Brownian movement, is irrefutably central to the resolution of these controversies of the nineteenth century and to the development of the chemistry and physics of the twentieth century. (Nye 1972: 169)

As already stated, this pragmatic realist position should not be understood as suggesting that the question of the reality of atoms, molecules, and their properties is settled. This realist question is partially independent of the question of the epistemic and metaphysical relations between chemistry and quantum mechanics and requires extensive investigation.[27] This thesis does not examine this realist question. It merely takes a pragmatic realist stance towards molecules and their properties and leaves it open whether and in what manner molecules and their properties exist.

All the above set the context in which this thesis investigates the relation between chemistry and quantum mechanics. Specifically, the thesis investigates this relation with respect to a specific domain of inquiry; namely with respect to how chemistry and quantum mechanics describe a single inert molecule. The phenomenon under investigation is that of the behavior of a single inert molecule, and while the molecule and its properties are not assumed here as being real (in accordance to a particular realist account), the thesis takes a pragmatic realist approach towards molecules and their properties.

1.2 The structure of this thesis

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[26] See, for example, (Nye 1972) which presents in detail how scientists in the nineteenth century arrived at an agreement that atoms and molecules exist. See also (Pais 1982: 79-107).

[27] This does not mean that the investigation of the epistemic and metaphysical relations between the two theories cannot inform the investigation of the realist question. For example, chapter 7 presents how a realist position can be consistently defended if one accepts the existence of a particular epistemic and metaphysical relation between the two theories.

The thesis is divided into six chapters, excluding this introduction and the conclusion. Each chapter examines a particular issue that is relevant to the investigation of the epistemic and metaphysical relations between chemistry and quantum mechanics. This section briefly presents the content of each chapter.

Chapter 2 briefly presents how chemistry and quantum mechanics each describe a single inert molecule. The basic concepts that are employed in the chemical and quantum mechanical descriptions are defined and specified, as well as the basic postulates that underwrite each of the two theories' descriptions of a single inert molecule. Presenting chemistry's and quantum mechanics' descriptions of a single inert molecule is particularly important, given the naturalistic approach followed in this thesis.

Chapter 3 reviews how the philosophy of chemistry literature investigates the epistemic and metaphysical relations between chemistry and quantum mechanics. The chapter divides the existing positions in the literature into those that support a unity thesis, and those that support a disunity thesis. A unity thesis is any position that primarily focuses on how chemistry is related or dependent on quantum mechanics. A disunity thesis is any position that primarily focuses on how chemistry is separate or autonomous from quantum mechanics. Two claims are made in this chapter. First, the chapter argues that there is a proliferation of disunity theses in the philosophy of chemistry literature which is accompanied by a tendency within the relevant community to connect the legitimacy of the philosophy of chemistry with the autonomy of chemistry itself. Secondly, the investigation of the relation between chemistry and quantum mechanics often involves the historical investigation of the two theories. This illustrates the importance of taking into account historical considerations in the investigation of this relation.

Having reviewed the existing positions in the philosophy of chemistry literature, chapter 4 presents an account from the philosophy of science literature which was initially proposed for the epistemic and metaphysical relations between biology and chemistry. This is Harold Kincaid's model of non-reductive unity and can be understood as a form of unity thesis. The chapter argues that Kincaid's model successfully applies to the relation between chemistry and quantum mechanics. Based on Kincaid's understanding of unity, the two theories are unified with respect to their descriptions of a single inert molecule because they exhibit the required metaphysical and epistemic interconnections and dependencies.

Chapter 5 examines a position which is extensively discussed in the philosophy of chemistry literature and which poses a challenge to the model of unity that is supported in the previous chapter. This position is strong emergence, as this is understood by Robin Hendry for the case of the relation between chemistry and quantum mechanics. According to Hendry, the structure of a single inert molecule strongly emerges from its quantum mechanical entities in the sense that it exhibits downward causal powers. Chapter 5 presents

Hendry’s account and argues that the manner in which Hendry supports his understanding of strong emergence in terms of downward causation faces certain problems.

Chapter 6 examines how chemistry and quantum mechanics describe a single inert molecule. Specifically, it argues that chemistry and quantum mechanics both make an idealization which has not been identified as such in the philosophy of chemistry literature. Specifically, when chemistry and quantum mechanics describe a single isolated molecule, they assume that the molecule is stable and has structure. This chapter explains why regarding a single isolated molecule as being stable and having structure is an idealization. Moreover, it presents how idealizations are understood and discussed in the philosophy of science literature, and briefly presents how this particular idealization in chemistry and in quantum mechanics, can contribute to the investigation of the relation between chemistry and quantum mechanics.

Chapter 7 argues that the idealization that is presented in the previous chapter can be interpreted in two ways, both of which can solve the problem of molecular structure. The ‘problem of molecular structure’ refers to the consensus in the philosophy of chemistry that the manner in which quantum mechanics describes a molecule’s structure is problematic for the defense of a reductionist or physicalist position about the relation of chemistry with quantum mechanics. Given the philosophical literature on idealizations, it is possible to interpret the quantum mechanical description of a single inert molecule in two ways (namely via the epistemic and the referential interpretations of idealizations). Each of the two interpretations solves the problem of molecular structure in a particular way. The chapter presents the two interpretations and argues that both interpretations are preferable to Hendry’s account of strong emergence because they solve the problem of molecular structure in a way that doesn't require the postulation of downward causal relations. The two interpretations also contribute to the examination of the nature of molecular structure and to the analysis of the relation between chemistry and quantum mechanics.

2. The Chemical and Quantum Mechanical Descriptions of a Single Inert Molecule

Chapter 2 presents how chemistry and quantum mechanics each describe a single inert molecule. This provides a more precise specification of (i) the domain of inquiry with respect to which the relations between the two theories are examined, and (ii) the relevant scales of the two theories (see chapter 1). This chapter makes no philosophical claims about the relation between the two theories, their historical development, the conceptualization of scientific terms, and the interpretation of quantum mechanics. This chapter is an incomplete, yet sufficient for the purposes of this thesis, presentation of the two scientific descriptions. To avoid repetition, there are certain parts of the chemical and quantum mechanical descriptions of a single inert molecule which are not mentioned or presented in detail in this chapter.[28] These parts are presented in other chapters of this thesis because they are invoked as putative empirical evidence for the support of particular philosophical claims (see in particular chapters 4, 5, 6 and 7).

Section 2.1 presents the chemical description of a single inert molecule and section 2.2 presents the quantum mechanical description of a single inert molecule.

2.1 The chemical description of a single inert molecule

This section presents the main terms that are employed in the chemical description of a single inert molecule. These terms are based on IUPAC's *Compendium of Chemical Terminology,* also known as the *Gold Book* (IUPAC 2014).[29] IUPAC (i.e. the International Union of Pure and Applied Chemistry) is one of the leading authorities regarding chemical nomenclature, the definition of chemical terms, and 'the resolution of critical global issues that involve every aspect of chemistry' (IUPAC 2018b). It was founded in 1919 and provides a common database regarding different aspects of chemical theory and practice, that informs the scientific and chemical communities worldwide.

Based on the highly regarded status of IUPAC, it is safe to assume that the glossary provided by the *Gold Book* is more or less accepted by the entire chemical community. The terms and their respective definitions in the *Gold Book* have been rigorously reviewed and published in chemistry journals (IUPAC 2018a). This chapter employs the *Gold Book* in order to provide a well-accepted and uniform account of the chemical

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[28] Of course, it is unavoidable that certain parts of the two descriptions are repeated in the other chapters of this thesis.

[29] The *Gold Book* is an online resource which 'collects together terminology definitions from IUPAC recommendations already published in' other books and journals (IUPAC 2018a).

description of a single inert molecule. This would not be easily achieved if this chapter employed terms or definitions from multiple chemical or philosophical sources. This is because different sources often employ either different terms, and/or varying definitions of terms.

Note that this is not a complete presentation of chemistry's description of a single inert molecule. For example, the different classifications of molecules are not presented (such as polymers, macromolecules, hydrogen molecule (H_2), etc.). Also, this chapter does not examine how these terms have been defined, specified, explained, confirmed or empirically examined throughout the history of chemistry (see, for example, (Nye 1972) and (Pullman 1998)). Moreover, it does not examine the conceptualization of chemical terms or whether particular chemical terms are well-defined (such as 'element', 'substance', 'simple substance', 'basic substance', and 'mixture') (see for example (Scerri 2012b) and (Hendry 2008)).

2.1.1 Definition of main chemical terms

A molecule is an 'electrically neutral entity consisting of more than one atom' (IUPAC 2014: 958). A molecule is a molecular entity, where molecular entity is '(a)ny constitutionally or isotopically distinct atom, molecule, ion, (..), etc., identifiable as a separately distinguishable entity' (IUPAC 2014: 950). The term 'single' is not defined by the *Gold Book*. However, based on the *Gold Book's* definition of molecular entities and of molecules, a single molecule is defined here as any one separately distinguishable molecule.[30]

Note that molecules are distinct from chemical species. This is because, as already mentioned in chapter 1, a chemical species is an 'ensemble of chemically identical molecular entities that can explore the same set of molecular energy levels on the time scale of the experiment' (IUPAC 2014: 264).[31] Chemical substances are distinct from chemical species and they denote '(m)atter of constant composition best characterized by the entities (molecules, formula units, atoms) it is composed of' (IUPAC 2014: 265). A '(p)ortion of matter consisting of two or more chemical substances' is called a mixture (IUPAC 2014: 941).

IUPAC defines 'inert' with respect to chemical species and not to single molecules. Specifically, a chemical species is inert if it is 'stable and unreactive under specified conditions' (IUPAC 2014: 729). Stability

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[30] A single molecule is often regarded as a system, where system is an '(a)rbitrarily defined part of the universe, regardless of form or size' (IUPAC 2014: 1509).

[31] This definition of chemical species should be distinguished from the definition of 'chemical species of an element' which is a '(s)pecific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure' (IUPAC 2014: 264). The latter definition is currently disregarded.

'expresses a thermodynamic property' of chemical species 'which is quantitatively measured by relative molar standard Gibbs energies', G (IUPAC 2014: 1432). For example, a 'chemical species A is more stable than its isomer B if $\Delta_r G^o > 0$ for the (real or hypothetical) reaction A -> B, under standard conditions' (IUPAC 2014: 1432). A chemical species is stable with respect to 'some explicitly stated or implicitly assumed standard' (IUPAC 2014: 1432).[32] A chemical species is unstable if it 'has a higher molar Gibbs energy than some assumed standard' (IUPAC 2014: 1581).

The term 'stability' should not be conflated with 'reactivity' which is a kinetic property of chemical species: a 'species is said to be more reactive or to have a higher reactivity in some given context than some other (reference) species if it has a larger rate constant for a specified elementary reaction' (IUPAC 2014: 1261). A chemical species is said to be unreactive if it fails 'to react with a specified chemical species under specified conditions. The term should not be used in place of stable, since a relatively more stable species may nevertheless be more reactive than some reference species towards a given reaction partner' (IUPAC 2014: 1581).

Based on the definitions of stability and reactivity, inertness is defined in chemistry as a property of chemical species, and not of a single molecule. Therefore, when one refers to the inertness of a molecule that is part of a chemical species, what is meant is that the molecule is part of an inert chemical species. Put differently, a molecule is stable and unreactive in the sense that it is part of a stable and unreactive chemical species. On the other hand, when it comes to a single molecule that is in isolation, talk of a molecule's reactivity becomes redundant since there is nothing with which an isolated molecule reacts.[33] Moreover, given that stability is defined as being a property of chemical species, it follows that stability cannot be understood in this instance as a property which a molecule has in virtue of being part of a chemical species (this is because the molecule is in isolation and thus not part of a chemical species). This proves particularly important in the discussion of the relation of chemistry and quantum mechanics and it will be discussed in detail in chapters 6 and 7.[34]

In chemistry, a molecule is taken to be constituted of atoms. IUPAC defines constitution as '(t)he description of the identity and connectivity (…) of the atoms in a molecular entity (omitting any distinction arising from

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[32] What is meant by this is explained in chapter 6.

[33] A molecule is in isolation if it is far removed from any other system (and thus doesn't interact with other molecular entities) and, if its total energy is conserved. Chapter 6 discusses in detail how chemists understand the properties of an isolated molecule.

[34] Note that wherever this thesis uses the term 'inert' as a property of an isolated molecule, the term is understood only in the sense of the molecule being stable (whatever that means in chemistry- see chapter 6).

their spatial arrangement)' (IUPAC 2014: 325). In light of this definition of constitution, a molecule is fully described when one specifies the following features of the molecule:

i. The identity of the atoms in the molecule: This includes the specification of atomic properties (such as atomic mass, atomic number, etc.), but also the specification of the particles that constitute the atom (including their arrangement and interactions within the atom).
ii. The connectivity between atoms: This includes information about which atoms interact with which (in terms of bonds), 'without any indication or implication concerning the spatial direction of bonds' (IUPAC 2014: 841).
iii. The spatial arrangement of the atoms within the molecule: This is determined by the specification of the intramolecular interactions and includes information about the spatial direction of bonds.

The remainder of section 2.1 presents how each of these clauses are specified in chemistry.

2.1.2 The identity of atoms

First, an atom is the '(s)mallest particle still characterizing a chemical element. It consists of a nucleus of a positive charge (Z is the proton number and e the elementary charge) carrying almost all its mass (more than 99.9%) and Z electrons determining its size' (IUPAC 2014: 121).[35] The nucleus consists of protons and neutrons. A proton is a 'nuclear particle of charge number +1, spin quantum number 1/2 and rest mass of 1.007276470(12) u' (IUPAC 2014: 1195). A neutron is a 'nuclear particle of zero charge, spin quantum number 1/2 and a mass of 1.008664904(14) u' (IUPAC 2014: 989). The electron is an '(e)lementary particle not affected by the strong force' with 'spin quantum number 1/2, a negative elementary charge and a rest mass of 0.000548579903(13) u' (IUPAC 2014: 477).

There are additional properties of the atom that need to be specified in order to provide its complete description. For example, one central property of atoms is the mass number which is the '(t)otal number of heavy particles (protons and neutrons jointly called nucleons) in the atomic nucleus' (IUPAC 2014: 885). This should be distinguished from atomic mass which is the '(r)est mass of an atom in its ground state' (IUPAC 2014: 123).

An important aspect of chemistry's description of the atom involves reference to the quantum mechanical description of atoms. This is because quantum mechanics specifies how the particles that constitute an atom, behave and interact. Although the quantum mechanical description of molecules is discussed in the next section, it is important, given the naturalistic approach followed in this thesis (chapter 1), to present how

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[35] The 'number of protons in the atomic nucleus' is referred to as the 'atomic number' (IUPAC 2014: 123).

quantum mechanical terms are defined and employed in the chemical description of atoms and molecules. Those terms are presented here in accordance to how they are understood and employed in chemistry (and not necessarily in quantum mechanics). Specifically, the definitions that are presented below are drawn from IUPAC's *Gold Book*.

Chemists describe the constitution of atoms by specifying their electronic configuration. The electronic configuration is 'a distribution of the electrons of an atom or a molecular entity over a set of one-electron wavefunctions called orbitals, according to the Pauli principle' (IUPAC 2014: 317). An orbital, whether atomic or molecular, is a '(w)avefunction depending explicitly on the spatial coordinates of only one electron' (IUPAC 2014: 1034). An atomic orbital is a '(o)ne-electron wavefunction obtained as a solution of the Schrödinger equation for an atom' (IUPAC 2014: 124). Given that orbitals depend on the spatial coordinates of electrons, the electronic configuration of an atom provides a representation of the distribution of electrons in the atom. This is particularly important in chemistry because it serves as a basis for the explanation and prediction of the type of bonds that are formulated between atoms.

The electronic configuration of an atom is specified in chemistry by following the Aufbau principle which is a 'rule for building up the electronic configuration of atoms and molecules. It states that a maximum of two electrons are put into orbitals in the order of increasing orbital energy: the lowest-energy orbitals are filled before electrons are placed in higher-energy orbitals' (IUPAC 2014: 128). The Aufbau principle specifies the building process that needs to be followed in order to determine the electronic configuration of many-electron atoms and molecules. Complementary to the Aufbau principle is the Pauli exclusion principle, according to which 'a maximum of two electrons can occupy an orbital and then only providing that the spins of the electrons are paired, i.e. opposed' (IUPAC 2014: 1071).

Calculating the electron density P(x, y, z) is central to the specification of the electronic configuration of an atom.[36] The electron density is the 'probability of finding an electron in the volume element dxdydx at the point of a molecular entity with coordinates x, y, z' (IUPAC 2014: 480). Based on the electron density, chemists construct pictorial representations of the spatial region in which an electron of an atom most probably resides:

> To clarify the concept of electron probability it is helpful to do a hypothetical experiment in which we take a set of instantaneous pictures of an electron with a specific energy moving around a nucleus. If all these imaginary sequential pictures were superimposed, with the electron appearing as a small dot in each picture, a "cloud" (..)

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[36] The electron density is also referred to as 'electron probability' (for example (DeKock and Gray 1980: 23).

> would result. This picture is called an electron-density (..) representation. The density of dots in a given spatial region is a pictorial representation of the *probability density* in that region. (DeKock and Gray 1980: 23)[37]

Although this cloud is 'fuzzy' in the sense that it does not possess definite boundaries, chemists employ it to construct pictorial representations of the spatial region in which an electron resides. This is achieved by assuming the existence of 'an arbitrary boundary' which is specified by 'a surface along which the probability density is some constant value' (DeKock and Gray 1980: 24). This surface determines the shape of the electron density and is taken to pictorially represent the atomic orbital. It should be noted that identifying the areas in which the electron density is zero restricts the set of possible orbitals over which the electrons of an atom are distributed. This is another reason why electron density is central in the determination of an atom's electronic configuration.

The aforementioned analysis is by no means a complete presentation of how chemistry identifies atoms and their constitution. However, it is sufficient for the purpose of this chapter; namely to identify those chemical terms that are required for a sufficient description of a single inert molecule. The next subsection presents how chemistry specifies the connectivity of atoms in molecules.

2.1.3 The connectivity of atoms in molecules

In chemistry, atoms are taken to be connected within a molecule in the sense that they interact with each other in a particular manner. By 'connectivity' chemists refer to 'the information content of a line formula, but omitting any indication of bond multiplicity' (IUPAC 2014: 323). The line formula is a 'two-dimensional representation of molecular entities in which atoms are shown joined by lines representing single or multiple bonds, without any indication or implication concerning the spatial direction of bonds' (IUPAC 2014: 841).[38] In order to present the information content of a line formula, this subsection presents the different types of interactions that are invoked for the description of the connectivity of atoms.

In general, interactions are distinguished between intermolecular and intramolecular.[39] An intermolecular interaction is 'any process that involves (..) interactions between two or more molecular entities', whereas an

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[37] The italics are in the original text.

[38] Subsection 2.1.4 presents the various representational tools that are employed in chemistry for the specification of the spatial arrangement of atoms in molecules.

[39] The nature of interactions invoked for the explication of the connectivity of atoms isn't of particular concern here (see 4.2.2). However, it should be noted that such interactions are identified in chemistry as being electrostatic, caused by the attractive and repulsive forces that are exerted between the particles (i.e. protons and electrons).

intramolecular interaction is 'any process that involves a transfer (..) or interactions between different parts of the same molecular entity' (IUPAC 2014: 746, 753).

Intramolecular interactions are distinguished between bonded and non-bonded interactions. Non-bonded interactions are 'intramolecular attractions or repulsions between atoms that are not directly linked to each other, affecting the thermodynamic stability of the chemical species concerned' (IUPAC 2014: 1007). Moreover, there are certain interactions which are not specified as non-bonded by IUPAC, which nevertheless capture some form of indirect intramolecular interaction. There are, for example, van der Waals forces which include 'dipole–dipole, dipole-induced dipole and London (..) forces' (IUPAC 2014: 1588).

Bonded interactions are intramolecular attractions or repulsions between atoms that are directly linked to each other.[40] Bonded interactions are most commonly referred to as a 'chemical bond'. The *Gold Book* defines chemical bonds as follows:

> When forces acting between two atoms or groups of atoms lead to the formation of a stable independent molecular entity, a chemical bond is considered to exist between these atoms or groups. The principal characteristic of a bond in a molecule is the existence of a region between the nuclei of constant potential contours that allows the potential energy to improve substantially by atomic contraction at the expense of only a small increase in kinetic energy. (IUPAC 2014: 257)

Below are some of the basic types of chemical bonds that are invoked in chemistry.[41]

- Covalent bond: 'A region of relatively high electron density between nuclei which arises at least partly from sharing of electrons and gives rise to an attractive force and characteristic internuclear distance' (IUPAC 2014: 344).
- Ionic bond: 'The bond between atoms with sharply different electronegativities. In strict terms, an ionic bond refers to the electrostatic attraction experienced between the electric charges of a cation and an

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[40] IUPAC doesn't provide a definition of bonded interactions; however, it is safe to assume that they are understood as an opposite to non-bonded interactions; i.e. as intramolecular interactions that directly link atoms.

[41] This is not a complete enumeration of the different types of chemical bonds that are postulated in chemistry. Chemists, for example, postulate metallic bonds which aren't defined in the *Gold Book*. Also, some types of chemical bonds (for example, hydrogen bonds) are taken to occur not only intramolecularly, but also intermolecularly. This seems to contradict IUPAC'S distinction between bonded and non-bonded interactions. This is not examined further.

anion, in contrast with a purely covalent bond. In practice, it is preferable to consider the amount of ionic character of a bond rather than referring to purely ionic or purely covalent bonds' (IUPAC 2014: 767).[42]

- Hydrogen bond: 'A form of association between an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom. It is best considered as an electrostatic interaction, heightened by the small size of hydrogen, which permits proximity of the interacting dipoles or charges. (..) Hydrogen bonds may be inter-molecular or intramolecular' (IUPAC 2014: 697).
- Multi-center bonds: 'Representation of some molecular entities solely by localized two-electron two-centre bonds appears to be unsatisfactory. Instead, multi-centre bonds have to be considered in which electron pairs occupy orbitals encompassing three or more atomic centres. Examples include the three-centre bonds in diborane, the delocalized π-bonding of benzene and bridged carbocations' (IUPAC 2014: 968).

The above concepts are central when specifying the connectivity of atoms within a single inert molecule. The next subsection presents the main chemical terms that are employed for the specification of the spatial arrangement of atoms within a molecule.

2.1.4 The spatial arrangement of atoms

The initial step in describing the spatial arrangement of atoms involves identifying which atoms are connected with which and what sort of connections are developed between them. The line formula shows which atoms directly interact with each other, and thus provides information about the sequence in which atoms within a molecule are connected. However, this is not sufficient for the specification of the spatial arrangement of atoms. Additionally, the spatial arrangement of the atoms is specified by:

i. the properties that are assigned to the intramolecular interactions of atoms;
ii. the properties that are based on the quantum mechanical description of molecules;
iii. representing the spatial arrangement of atoms through pictorial models of the molecule; and,
iv. examining the structural differences between molecules.

First, the spatial arrangement of atoms is partially specified through the properties that are assigned to the particular interactions that exist between atoms. In general, depending on the chemical species under examination and on the type of intramolecular interaction that is postulated, one can specify the following

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[42] It is not possible to state the definitions of all the chemical terms that are mentioned here. Nevertheless, it is useful to state at least the definition of electronegativity: 'Concept introduced by L. Pauling as the power of an atom to attract electrons to itself' (IUPAC 2014: 486).

properties of intramolecular interactions: bond length, bond number, bond order, bond energy, bond dissociation energy, bond migration, electron-deficient bond, etc.[43] Certain of these properties specify the spatial arrangement of atoms, and thus contribute to the overall specification of a molecule's structure.[44] For example, bond length (namely 'the distance between atomic centers involved in a chemical bond') provides information about the spatial arrangement of the two atoms involved in a particular bond (namely the distance between them) (IUPAC 2014: 175).

Secondly, the spatial arrangement of atoms is specified by reference to properties that are based on the quantum mechanical description of molecules. Similarly to the identification of atoms, chemists specify a molecule's electronic configuration (see previous subsection). In this case, the orbitals over which the distribution of a molecule's electrons is specified are not atomic, but molecular orbitals; i.e. a 'one-electron wavefunction describing an electron moving in the effective field provided by the nuclei and all other electrons of a molecular entity of more than one atom. (..) Molecular orbitals can also be described, in terms of the number of nuclei (or "centres") encompassed, as two-centre, multi-centre, etc. molecular orbitals, and are often expressed as a linear combination of atomic orbitals. An orbital is usually depicted by sketching contours on which the wavefunction has a constant value (contour map) or by indicating schematically the envelope of the region of space in which there is an arbitrarily fixed high (say 96%) probability of finding the electron occupying the orbital (..)' (IUPAC 2014: 953).

By a similar process to specifying the electronic configuration of atoms, it is possible to specify the electronic configuration of a molecule. Moreover, by specifying the bonding and anti-bonding molecular orbitals, it is possible to distinguish between the different possible energetic states of a molecule and thus specify which particular electronic configuration corresponds to the molecule's ground state.[45] The ground state is 'the state of lowest Gibbs energy of a system' (IUPAC 2014: 646).

Thirdly, another important element of the specification of the spatial arrangement of atoms involves the construction of pictorial representations. This includes not only the line formula, but also the Lewis formula, the Kekulé structure, and different projection formulae. Of particular interest is the stereochemical formula (i.e. a subcategory of projection formulae) which is a 'three-dimensional view of a molecule either as such or

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[43] The scope of this thesis does not allow to present the definition of these chemical terms. See (IUPAC 2014).

[44] Molecular structure is discussed in detail in chapter 6. Very briefly, by 'molecular structure' this thesis refers to the spatial arrangement of atoms in a molecule.

[45] Anti-bonding molecular orbitals are molecular orbitals whose 'occupation by electrons decreases the total bonding of a molecule' (IUPAC 2014: 98). On the other hand, bonding molecular orbitals are those whose 'occupation by electrons increases the total bonding of a molecule' (IUPAC 2014: 178).

in a projection' (IUPAC 2014: 1447). The projection of a stereochemical formula can be represented in various forms such as the Fischer projection, the Newman projection, the sawhorse projection, the wedge projection and the zig-zag projection.[46] Moreover, with the advent of computational chemistry, graphic visualization technics have been developed that provide a graphic three-dimensional representation of molecules. Below are some examples of the different representations of molecules and their structure.

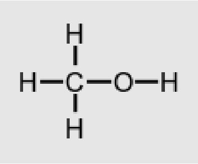

Image 1. Line formula
(IUPAC 2014: 841)

Image 2. Lewis formula
(IUPAC 2014: 833)

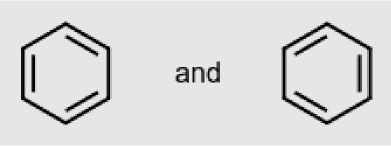

Image 3. Kekulé structures
(IUPAC 2014: 803)

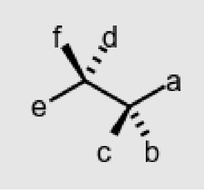

Image 4. Three-dimensional stereochemical formula (IUPAC 2014: 990)

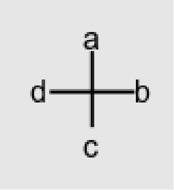

Image 5. Fischer projection
(IUPAC 2014: 565)

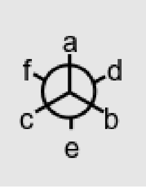

Image 6. Newman projection
(IUPAC 2014: 990)

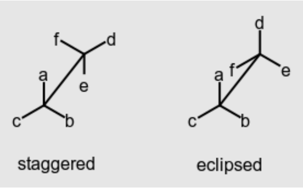

Image 7. Sawhorse projection
(IUPAC 2014: 1335)

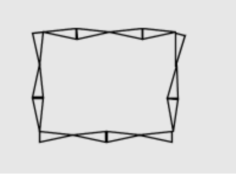

Image 8. Wedge projection
(IUPAC 2014: 1604)

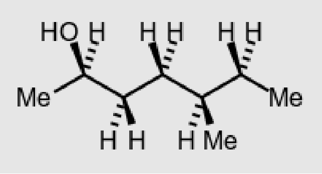

Image 9. Zig-zag projection
(IUPAC 2014: 1620)

Lastly, the specification of the spatial arrangement of atoms involves the examination of the structural differences between molecules that are constituted by the same number and type of atoms, but which differ either in terms of how those atoms are connected (i.e. in terms of their line formulae), or (only) in terms of the spatial arrangement of atoms. Although such structural differences can be specified through the pictorial representation of molecules, chemistry also employs a set of concepts that differentiates molecules in terms of such structural differences. The central concept employed for the structural differentiation of molecules is

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[46] Which projection is the most suitable representation of a molecule's structure depends on the type of molecule that is under examination. For example, the Kekulé structure is suitable only for the representation of aromatic molecular entities, i.e. of 'cyclically conjugated molecular entities' (IUPAC 2014: 109).

‘isomerism’. Isomers are ‘one of several species (or molecular entities) that have the same atomic composition (molecular formula) but different line formulae or different stereochemical formulae and hence different physical and/or chemical properties’ (IUPAC 2014: 784). Molecules that have different line formulae are called constitutional isomers, and molecules that have different stereochemical formulae are called stereoisomers.

The kind of isomerism that is of particular interest when investigating the relation of chemistry and quantum mechanics is stereoisomerism, and in particular enantiomerism (see chapters 4 and 6). Stereoisomers are sets of molecules which ‘possess identical constitution’ (that is, they have the same type, number, and connectivity of atoms) but which ‘differ in the arrangement of their atoms in space’ (IUPAC 2014: 1450).[47] An enantiomer is ‘one of a pair of molecular entities which are mirror images of each other and non-superposable’ (IUPAC 2014: 499). Superposability is ‘(t)he ability to bring two particular stereochemical formulae (or models) into coincidence (or to be exactly superposable in space, and for the corresponding molecular entities or objects to become exact replicas of each other) by no more than translation and rigid rotation’ (IUPAC 2014: 1488). A common way to understand enantiomers in chemistry is through the analogue of two human hands. A left hand is the mirror image of a right hand, yet it is not identical to the former. Based on this rudimentary understanding of chirality, chemists usually refer to any pair of enantiomers as the ‘left-handed’ and the ‘right-handed molecule’ (Image 10).

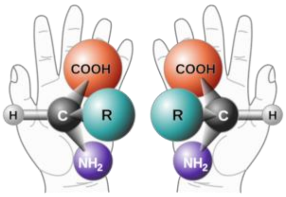

Image 10. A generic form of an amino acid that is chiral (Psychonautwiki 2017)

An enantiomer is said to possess the property of chirality with respect to the molecule that is its non-superposable mirror image. Chirality is a ‘geometric property of a rigid object (or spatial arrangement of points or atoms) of being non-superposable on its mirror image (..). If the object is superposable on its mirror image the object is described as being achiral’ (IUPAC 2014: 269). For the case of a single molecule, a molecule is said to have the property of being chiral when its mirror molecule is not identical to itself. However, the property of chirality can also be assigned to an assembly of molecules that have the same chirality sense; i.e. all share the same enantiomeric form (IUPAC 2014: 271). Such an assembly is called enantiomerically pure or enantiopure (IUPAC 2014: 501). An enantiopure should be distinguished from a racemate which is an ‘equimolar mixture of a pair of enantiomers’ (IUPAC 2014: 1223).

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[47] In general, there are three main types of stereoisomers: enantiomers, diastereoisomers, and cis-trans isomers.

This concludes the brief presentation of the chemical description of a single inert molecule. The next section presents how quantum mechanics describes a single inert molecule.

2.2 The quantum mechanical description of a single inert molecule

This section briefly presents the mathematical formalism of quantum mechanics which constitutes the basis of quantum chemistry.[48] Quantum chemistry is the 'branch of theoretical chemistry in which the methods of quantum mechanics are applied to chemical problems' ((Palgrave Macmillan Ltd 2004: 1845), see also (Gavroglu and Simões 2012b)).[49] In this context, quantum mechanics is taken as a framework of physics that is applicable to individual particles and composite systems. In quantum chemistry, the electromagnetic interactions among particles are described by classical field theory. Note that quantum mechanics is not the most fundamental quantum theory because it does not describe quantized fields. 'Quantum theory' is the umbrella term which refers to the 'physical theories for the behaviour of micro-objects, the theories resting upon the experimentally established wave-particle dualism and contain Planck's quantum of action as a fundamental new constant of nature' (Palgrave Macmillan Ltd 2004: 1871).[50] The primary references of this section's presentation are (Griffiths 2005), (Bransden and Joachain 1989), (Ney and Albert 2013) and (Palgrave Macmillan Ltd 2004).

Any collection of particles can in principle be described with quantum mechanics and any such collection is henceforth referred to as a 'quantum system'. A quantum system can be studied either in isolation or with respect to how it interacts with its environment, and it can be in a number of different possible dynamical states (Bransden and Joachain 1989: 189).

In classical physics, the dynamical state of a system 'is determined at each instant of time by the knowledge of the physical quantities- dynamical variables- such as the position vectors and the momenta of the particles which constitute the system' (Bransden and Joachain 1989: 189). In classical physics, all dynamical variables may be determined simultaneously and with equal precision. The same doesn't apply to the quantum mechanical description of a system's dynamical states. According to Heisenberg's uncertainty principle,

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[48] This section doesn't provide a complete presentation of the quantum mechanical formalism nor does it discuss the different interpretations of quantum mechanics (see for example (Sklar 1993)).

[49] As mentioned in chapter 1, quantum mechanics is distinguished from relativistic quantum mechanics and from quantum field theory.

[50] This feature of quantum mechanics is not further discussed here.

there is ‘a limit to the precision with which “complementary” dynamical variables can be measured simultaneously’ (Bransden and Joachain 1989: 189).

A state can be mathematically represented in quantum mechanics in two equivalent ways (Ney and Albert 2013: 5). First, it can be represented as a state vector, $|\Im(t)\rangle$, in Hilbert space. This is also known as the Dirac notation. Secondly, it can be represented as a wavefunction, Ψ, ‘from elements of a configuration space to (complex) numbers’ (Ney and Albert 2013: 5). This is also known as the Schrödinger or wavefunction notation. The two representations are regarded as equivalent because it is possible to analyze a quantum system by focusing only (but not necessarily) on one notation and not on the other. However, the two representations are not distinct; they are part of one overall representation. Specifically, the state of a system is represented by a vector, $|\Im(t)\rangle$, that ‘lives “out there in Hilbert space”, but we can *express* it with respect to any number of different *bases*’ (Griffiths 2005: 119).[51] This is because the wavefunction is ‘actually the coefficient in the expansion of’ the state vector, $|\Im(t)\rangle$, in some basis set (Griffiths 2005: 119). Specifically, if the basis set is that of position eigenfunctions, then the wavefunction is the position wavefunction $\Psi(\mathbf{x}, t)$, where $\Psi(\mathbf{x}, t) = \langle \mathbf{x} | \Im(t)\rangle$.[52] If the basis is that of momentum eigenfunctions, then the wavefunction is the momentum space wavefunction $\Psi(\mathbf{p}, t)$ (where $\Psi(\mathbf{p}, t) = \langle \mathbf{p} | \Im(t)\rangle$), whereas if one expands the state vector $|\Im(t)\rangle$ in the basis of energy eigenfunctions, then the wavefunction is the energy wavefunction (Griffiths 2005: 119). These wavefunctions represent the quantum state of a system in terms of different basis sets, just like any vector in, say, two-dimensional space is represented in terms of different sets of axes. Put differently, the wavefunctions contain the same information regardless of the basis set in which they are expressed (Griffiths 2005: 119).

This section presents the quantum mechanical formalism in terms of its position wavefunction, $\Psi(\mathbf{x},t)$. The position wavefunction $\Psi(\mathbf{x}, t)$ (henceforth wavefunction) of a single particle is a complex function of its position vector, $\mathbf{x}$, at any time, t. The position wavefunction of a system that consists of more than one particle (i.e. N particles) is a complex wavefunction $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t)$ ‘which depends on the position vectors $\mathbf{r}_1, \ldots, \mathbf{r}_N$ of the particles and on the time t’ (Bransden and Joachain 1989: 191). The wavefunction represents the state of a system because it ‘plays the role of a probability amplitude’ (Bransden and Joachain 1989: 54). This is based on the Born interpretation of a particle’s wavefunction, according to which, for an interval [a,

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[51] Italics in (Griffiths 2005: 119). The definition and mathematical understanding of bases is derived from linear algebra. A vector can be expressed in terms of different sets of linearly independent vectors. A linear combination of vectors is an expression of the form ‘$a|\alpha\rangle + b|\beta\rangle + c|\gamma\rangle + \ldots$’. If a set of linearly independent vectors can express any vector, then that set is called a basis. ‘The number of vectors in any basis is called the dimension of the space’ (Griffiths 2005: 437).

[52] Eigenfunctions are presented later in this section.

b], the integral of $|\Psi(\mathbf{x}, t)|^2$ in terms of dx equals the 'probability of finding the particle between a and b, at time t' (Griffiths 2005: 2).

Based on Born's interpretation of the wavefunction, it is possible to calculate the expectation value of all dynamical variables of a state of a system (Griffiths 2005: 17). Given that each wavefunction represents a particular state of a system, the expectation value of the system's position and momentum in that state is defined respectively as follows (Griffiths 2005: 17):

$\langle \mathbf{x} \rangle = \int \Psi^*(x)\Psi dx$, integrated between $[-\infty, +\infty]$, where Ψ^*: the complex conjugate of Ψ; and,
$\langle \mathbf{p} \rangle = \int \Psi^* (-\hbar\, i\, \partial/\partial x)\, \Psi\, dx$, integrated between $[-\infty, +\infty]$

Based on position and momentum, it is possible to calculate the expectation value of all the other dynamical variables of the state of a system. This is because all dynamical variables (such as the kinetic energy) can be expressed in terms of position and momentum (Griffiths 2005: 17).

A central concept in quantum mechanics is the operator. In general, an operator is 'an instruction to do something to the function that follows it' (Griffiths 2005: 17).[53] For example, (d/dx) is an operator that applies to a function f(x) and it instructs to differentiate f(x) in terms of x; i.e. d(f(x))/dx. Operators are usually denoted in quantum mechanics by upper case letters of the form; $\hat{A}$, $\hat{H}$, etc.[54] A linear operator, $\hat{A}$, is an operator with the following property:

$\hat{A}(c_1f_1 + c_2f_2) = c_1(\hat{A}f_1) + c_2(\hat{A}f_2)$, where f_1, f_2: functions and c_1, c_2: complex constants

A Hermitian operator is a linear mapping of a subspace of Hilbert space in Hilbert space (Palgrave Macmillan Ltd 2004: 1088). A Hermitian operator has the following property (Griffiths 2005: 97):

$\langle f | \hat{A}g \rangle = \langle \hat{A}f | g \rangle$, for all functions f(x) and g(x).[55]

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[53] So, for example, the calculation of the expectation value of position requires the application of the operator (x) on the wavefunction Ψ, whereas the calculation of the expectation value of momentum requires the application of the operator $(-\hbar\, i\, \partial/\partial x)$ on Ψ.

[54] For example, one could define the operator $\hat{A}$ as $\hat{A} = d/dx$.

[55] This involves the application of the inner product $\langle f | g \rangle$ which is defined as: $\langle f | g \rangle = \int f(x)^* g(x) dx$ in the interval between [a, b], where $f(x)^*$: the conjugate function of f(x), and f(x): a complex function (Griffiths 2005: 95).

In the quantum mechanical description of physical systems such as molecules, specified Hermitian operators are taken to represent observables; namely particular dynamical variables of a system's determinate state.[56] For example, if one knows the wavefunction of the determinate state of a system (i.e. $\psi(x)$), it is possible to calculate the value of all the dynamical variables of that state (i.e. observables) by applying the appropriate operator on the wavefunction. Put differently, the value that is produced as a result of the operator's application to a wavefunction, corresponds to a physical measurement that is made on a particular determinate state of that system. That is:

$\hat{A}\psi = \alpha\psi$, where $\hat{A}$: the Hermitian operator applied to the wave function $\psi(x)$
α: a real number

This equation is often called the 'eigenvalue equation for the operator $\hat{A}$', ψ is called the 'eigenfunction of $\hat{A}$', and α is the eigenvalue of $\hat{A}$. When the operator applies to all the possible eigenfunctions of a system (i.e. to all states of the system), then the 'collection of all the eigenvalues of an operator is called its spectrum' (Griffiths 2005: 99). When two or more linearly independent eigenfunctions (ψ_1, ψ_2, .., ψ_N) share the same eigenvalue, α, the spectrum is said to be degenerate (Griffiths 2005: 99).[57]

If an operator corresponds to an observable, then the eigenstates of the former correspond to the definite states of the latter. This is because generally 'when you measure an observable (..) on an ensemble of identically prepared systems, all in the same state Ψ, you do not get the same result each time- this is the indeterminacy of quantum mechanics' (Griffiths 2005: 98). However, it is possible 'to prepare a state such that every measurement of (an observable) is certain to return the same value' (Griffiths 2005: 98). Such states are called determinate states and examples of determinate states are stationary states as defined below.

In order to find the wavefunctions that represent all the states of a system, one solves the Schrödinger equation for that system. This chapter only focuses on the non-relativistic Schrödinger equation of a quantum system since this is the one that is standardly employed for the description of a single molecule. The Schrödinger equation is the 'equation of motion for the wave function' which describes 'the state of a quantum-mechanical system' (Palgrave Macmillan Ltd 2004: 2029). The time-dependent Schrödinger equation is a linear partial second-order differential equation with respect to position and a partial first-order differential equation with respect to time. Its solutions $\Psi(x, t)$ are (potentially) the wavefunctions of the system under examination (i.e. of an electron, atom, molecule etc.). Being a differential equation of this

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[56] Determinate states are defined below.

[57] The corresponding states of the system are also called degenerate.

form, the Schrödinger equation provides an infinite number of solutions. Moreover, according to the superposition principle, 'if one possible state of an ensemble of identical systems is described by a wave function Ψ_1 and another state of this ensemble by a wave function Ψ_2, then any linear combination $\Psi = c_1\Psi_1 + c_2\Psi_2$ (…) is also a wave function describing a possible state of the ensemble' (Bransden and Joachain 1989: 56).

The generic form of the time-dependent Schrödinger equation is the following:

$i\hbar\, \partial\Psi(x,t)/ \partial t = - (\hbar^2/2m)(\partial^2\Psi(x,t)/\partial x^2) + V\Psi(x,t)$, where $\Psi(x,t)$: a system's wavefunction
$\hbar$: Planck's constant
m: the system's mass
x: position
t: time
V: potential energy

If one assumes that a system's potential energy is independent of time, then it is possible to solve the Schrödinger equation using the method of separation of variables (Griffiths 2005: 24). In this context, the solutions that are produced are wavefunctions of the following form (Griffiths 2005: 24):

$\Psi(x,t) = \psi(x)\varphi(t)$, where ψ: a function of position
φ: a function of time

Based on the ability to separate the variables of the Schrödinger equation in this way, it is possible to formulate the time-independent Schrödinger equation, which is an equation independent of time and whose solutions are a system's time-independent wavefunctions, $\psi(x)$. These wavefunctions correspond to the stationary states of the system under examination. The time-independent Schrödinger equation has the following generic form:

$- (\hbar^2/2m)\, (d^2\psi(x)/dx^2) + V\psi(x) = E\psi(x)$, where E: the total energy of the system

Notice that the time-independent Schrödinger equation is not a partial differential equation (like the initial time-dependent one). This makes its solution much easier. Moreover, the time-independent Schrödinger equation does not yield one unique solution; i.e. one wavefunction. In fact, 'the general solution is a linear combination of separable solutions' (Griffiths 2005: 27). It yields an infinite number of solutions ($\psi(x_1)$, $\psi(x_2)$, …), each of which corresponds to a different state of the system under examination. Note that, in accordance with the superposition principle (see above), any linear combination of the solutions of the time-independent Schrödinger equation is also regarded as a wavefunction that represents a possible state of the system (Griffiths 2005: 27).

The stationary state of a system (through its wavefunction $\psi(x)$) provides useful information about the total state of the system, $\Psi(x, t)$. First, the probability density $\Psi(x, t)$ equals $|\psi(x)|^2$. This means that knowledge of just the stationary state of a system (through the solution of the time-independent Schrödinger equation) provides the probability of finding the system at a particular region in space.

Secondly, it is possible to calculate the expectation value of any dynamical variable of a state of the system through the stationary state of the system alone.

> Every expectation value is constant in time; we might as well drop $\varphi(t)$ altogether, and simply use ψ in place of Ψ. (Griffiths 2005: 26)

From this it follows that stationary states are states of definite total energy, E (Griffiths 2005: 26). The expectation value of the total energy is constant in time, and thus can be calculated with the use of the stationary state's wavefunction alone. That is, if one applies the Hamiltonian operator to the time-independent wavefunction of a system and, assuming that the wavefunction is known (i.e. the stationary state of the system is known), it can provide the total energy of the state of the system. Each solution to the time-independent Schrödinger equation is associated with a particular allowed total energy of the system (E_1, E_2, …).

The wavefunction that is associated with the minimum total energy corresponds to the ground state of the system, whereas the wavefunctions whose total energies are larger correspond to the excited states of the system. The ground state of a single molecule is taken to correspond to the stable state of the molecule, where stability is understood in a manner consonant to chemistry's understanding (a detailed analysis of this feature of quantum mechanics is provided in chapter 5, so this is not further discussed here).

Based on the above, the time-independent Schrödinger equation for a single isolated molecule provides an infinite number of solutions (i.e. wavefunctions) each of which corresponds to different stationary states of the molecule. A stable isolated molecule, in virtue of being stable, is said to be in the ground state. From this it follows that it is represented by the wavefunction that is associated with the system's ground state and that it has the minimum total energy. Put differently, the wavefunction that corresponds to the ground state of a molecule is taken to be the correct quantum mechanical description of a stable isolated molecule.

Moreover, the Hamiltonian operator plays a central role in the solution of the time-independent Schrödinger equation for quantum systems, and isolated molecules in particular. This is because one can formulate the time-independent Schrödinger equation in the following way:

$\hat{H}\psi = E\psi$, where $\hat{H}$: the Hamiltonian operator
ψ: the wavefunction of a state of the system
E: the total energy of a state of the system

The Hamiltonian operator is the sum of two operators; the kinetic energy operator and the potential energy operator. Below is its generic form:

$\hat{H} = - (\hbar^2/2m) (d^2/dx^2) + \hat{U}$, where $(\hbar^2/2m)(d^2/dx^2)$: the kinetic energy operator
and $\hat{U}$: the potential energy operator

When the system under examination is a molecule, the Hamiltonian operator corresponds to the total energy of the molecule (i.e. its eigenvalues is the total energy of each state of the molecule); hence it is called the molecular Hamiltonian. In principle, the molecular Hamiltonian operator should include all the factors that determine the kinetic and dynamic energy of the molecule. That is, it should take into account the kinetic energy of each nucleus and electron in the system, the repulsion between each pair of electrons and between each pair of nuclei, and the attraction between each pair of electron and nucleus.

Because of the mathematical complexity involved in the formulation of the Hamiltonian operator, molecular systems are examined within the framework of the Born-Oppenheimer approximation (henceforth BO approximation).[58] 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). Peter Atkins explicates nicely the importance of the BO approximation to the quantum mechanical description of a single molecule:

> 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,

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[58] The BO approximation is also referred to as the adiabatic approximation (IUPAC 2014: 179). This section does not consider cases where the approximation is not justified (see for example (IUPAC 2014: 179)).

> 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 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)

Within the BO approximation, one can in principle formulate the Hamiltonian operator by positioning the nuclei at all the possible fixed positions. Each set of nucleonic positions corresponds to different quantum states of the system (hence to different wavefunctions) and to different values of the total energy, E, of the molecule. However, in practice this process is not followed. By having prior knowledge of the quantum system that is under examination (in this case, by knowing the chemical and structural properties of a molecule), only particular nucleonic conformations are considered when constructing the Hamiltonian operator. This is a crucial characteristic of the quantum mechanical description of molecules that is extensively discussed in the philosophy of chemistry with respect to chemistry's relation to quantum mechanics (see chapters 5 and 7).

At this point, it should be noted that, even when the nucleonic conformation is fixed (in the manner represented by the BO approximation), calculating the solution of the Schrödinger equation remains a complicated task. First, each nucleonic conformation is compatible with different quantum states of the system (and thus different wavefunctions). This is compatible with chemistry's understanding of molecules because, even if the nuclei are fixed at particular positions, the electrons may behave in more than one possible way within that molecule. Secondly, solving the Schrödinger equation and finding the wavefunction that corresponds to the ground state of the system (i.e. the state of the stable isolated molecule) is not straightforward for one additional reason. There are two unknowns in the equation; namely the total energy of the system, E, and the wavefunction of the corresponding quantum state of the system. That means that one must solve one single equation with two unknown variables.

In light of the above, the Schrödinger equation is not solved analytically for all molecules. As Hendry states:

> 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. (Hendry 2010a: 212)

Instead, various approximate methods have been developed to solve the Schrödinger equation, most of which employ the BO approximation. In general, the development of computation has led to the proliferation of complex computational methods that solve the equation by following different mathematical strategies and by making different assumptions. This includes the Valence Bond Approach, the Molecular Orbital Approach, and the Hartree-Fock Method.[59]

2.3 Summary

The naturalistic approach requires that the investigation of the epistemic and metaphysical relations between two theories is consonant with what those theories postulate and claim (see chapter 1). Moreover, in the context of a naturalistic approach, it is important to specify the domain of inquiry and the scale of the two relevant theories. In light of this, chapter 2 briefly presented how chemistry and quantum mechanics each describe a single inert molecule. The main concepts and definitions of chemistry and of quantum mechanics were stated so as to specify the domain of inquiry with respect to which the epistemic and metaphysical relations between the two theories are examined. Furthermore, by outlining the main entities and properties that are postulated by the two theories, it is possible to understand in a general manner what the relevant scales are.

All the above set the framework in which the thesis examines the epistemic and metaphysical relations between chemistry and quantum mechanics. The next chapter reviews the existing positions regarding the relations between the two theories. Chapter 4 argues in favour of the unity of the two theories (in terms of Kincaid's model of unity), while chapter 5 critically examines an existing metaphysical position regarding the two theories (namely Hendry's account of strong emergence). Chapter 6 focuses on specific aspects of the chemical and quantum mechanical descriptions of a single inert molecule. By closely examining these aspects, it is argued that chemistry and quantum mechanics assume an idealised understanding of the structure and stability of a single isolated molecule. The existence of this idealisation in quantum mechanics explains why quantum mechanics describes molecular structure the way it does. This explanation is consistent with Kincaid's model of unity and does not require the acceptance of Hendry's account of strong emergence.

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[59] This is a very brief and incomplete presentation of the quantum models that are employed in quantum chemistry for the description of atoms and molecules. For a more complete overview of these models see, for example, (Atkins and Friedman 2005).

3. The Relation of Chemistry and Quantum Mechanics in the Philosophy of Chemistry Literature

This chapter reviews the philosophy of chemistry literature. The main positions that have been proposed are presented, to inform the later discussion of the particular accounts that are the focus of the current thesis (see chapters 4 and 5).

This chapter divides the positions into those that support disunity whether explicitly or not (these are henceforth referred to as disunity theses), and those that support unity (these are henceforth referred to as unity theses).[60] Disunity theses primarily focus on how chemistry is separate or autonomous from quantum mechanics. Disunity theses are argued for by pointing out the two theories' epistemic and/or ontological differences or incompatibilities. Unity theses primarily focus on how chemistry is related or dependent on quantum mechanics. They are argued for by pointing out the two theories' epistemic and/or ontological connections.

Section 3.1 discusses disunity theses and shows that there is a proliferation of such positions in the philosophy of chemistry literature. It is shown that this proliferation is accompanied by a tendency within the community to connect the legitimacy of the field with the autonomy of chemistry itself. It is argued that this connection should not be made. Section 3.2 discusses unity theses and points out two interesting characteristics of such positions in the literature. Section 3.3 points out that the investigation of the relation between chemistry and quantum mechanics often involves the historical investigation of the relevant fields. This further clarifies the manner in which the relation between the two theories is currently investigated and illustrates the importance of taking into account historical considerations in the investigation of this relation.

3.1 Disunity theses

Since the development of the philosophy of chemistry as a research field, there has been a proliferation of accounts in the literature which primarily focus on the formulation and support of disunity theses

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[60] As mentioned in chapter 1, there are accounts which examine the relation between the two theories with respect to different domains of inquiry. For example, there are accounts which examine this relation with respect to the periodic table (Scerri 2012b: 75-76), with respect to molecular structure (Hendry 2010b), with respect to orbitals (Villani et al. 2018), or with respect to chemical reaction rates (Hettema 2017: 69-86). While this thesis focuses on how chemistry and quantum mechanics describe a single inert molecule, this chapter does not distinguish the existing accounts with respect to the domain of phenomena that they focus on.

concerning the relation between chemistry and quantum mechanics.[61] This proliferation is accompanied by an attitude, held by some members of the relevant community, to connect the autonomy of chemistry with the legitimacy of the philosophy of chemistry. Here disunity thesis is any account of the relation between chemistry and quantum mechanics according to which chemistry is autonomous. The autonomy of chemistry from quantum mechanics is characterized in ways such as:

- *denying particular epistemic relations between the two theories*

  For example, it is argued that chemistry fails to epistemically reduce to quantum mechanics (see for example (Bogaard 1978), (Primas 1983), (Scerri 1991), (Scerri 1994), (van Brakel 2000) and (Woolley 1976)).

- *pointing out the difference in the methodologies, tools, or concepts that are employed by chemistry and quantum mechanics, as well as the explanatory and predictive success of chemistry (over quantum mechanics) with respect to a particular set of phenomena* (see for example (Schummer 2014) and (Llored 2012))

- *denying the existence of a particular ontological relation between the two theories*

  For example, it is argued that chemistry fails to ontologically reduce to quantum mechanics (Labarca and Lombardi 2005: 140).

- *making an ontological claim about chemical entities, properties, etc.*

  For example, it is argued that chemical entities are distinct from quantum mechanics entities because chemical entities possess distinct causal powers that partially determine the interactions between quantum mechanical entities. This argument can be explicated in terms of downward causation and strong emergence (Hendry 2006). For different accounts regarding the ontological autonomy of chemistry see (Labarca and Lombardi 2006), (Labarca and Lombardi 2007,) and (Scerri 2007b).

While the autonomy of chemistry is not entailed by such considerations, they are taken to somehow support it. For example, although the denial of ontological reduction does not imply that chemistry is autonomous, Martín Labarca and Olimpia Lombardi explicitly argue from the former to the latter:

> although the failure of the epistemological reduction of chemistry to physics can preserve the autonomy of the chemists' everyday activity, it is not sufficient for eliminating the traditional conception of chemistry as a

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[61] As mentioned in chapter 1, an overview of the history of the philosophy of chemistry is provided in (Scerri and Fisher 2015: 3-5).

> secondary, merely phenomenological discipline: only the rejection of ontological reduction can reverse such a traditional assumption. (2005: 146)

These various understandings of the autonomy of chemistry from quantum mechanics may not be compatible or consistent with each other, and clearly the idea of the autonomy of chemistry from quantum mechanics can be understood in many different senses.[62] Of course, there are disunity theses which are similar in further respects beyond the general idea of autonomy. Moreover, disunity theses do not always deny that there is any relation between chemistry and quantum mechanics. For example, Hendry, who defends the strong emergence of chemistry and thus formulates a disunity thesis, accepts that supervenience holds between the chemical and quantum mechanical properties of a molecule (2006a: 173-176). Nevertheless, all disunity theses primarily focus on presenting the differences or incompatibilities between chemistry and quantum mechanics.

The philosophy of chemistry literature includes many disunity theses. This proliferation of disunity theses is accompanied by an attitude held by some members of the philosophy of chemistry community to connect the legitimacy of its field with the autonomy of chemistry from quantum mechanics. This attitude partially explains why there is such a proliferation of disunity theses. While each disunity thesis should be critically examined on philosophical, empirical, or historical grounds, the underlying attitude within the community should be rejected. Let us explain this in more detail.

The philosophy of chemistry is a relatively new field of philosophical inquiry (Scerri and Fisher 2015: 3-5). Particular members of the respective community, in their effort to establish the legitimacy of the philosophy of chemistry as a novel, interesting, and fruitful field of study, express the view that if chemistry is shown to be autonomous from quantum mechanics, then this would suffice to establish that the philosophy of chemistry is a field that should be regarded as autonomous from other fields (such as the philosophy of physics and the philosophy of science) (for example (Scerri and Fisher 2015: 3) and (Labarca and Lombardi 2005: 126)). In fact, it is implicitly assumed that the autonomy of the philosophy of chemistry is undermined if chemistry is understood as merely providing examples and case studies for the investigation of issues that are the primary concern of the philosophy of science (Scerri and Fisher 2015: 3). This implicit assumption explains to a degree why the philosophy of chemistry literature has exhibited such a proliferation of disunity theses. This is because the support of some sort of disunity thesis about chemistry, is taken to assure that the philosophy of chemistry is a legitimate field in the sense that it:

(i) poses interesting philosophical questions that deserve inquiry; and,

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[62] See, for example, section 4.4 which discusses different understandings of autonomy.

(ii) poses philosophical questions which primarily require the examination of chemistry and therefore cannot be addressed by other fields of inquiry, such as the philosophy of physics, of science, of biology, etc.

Some of members of the field state this quite explicitly. For example, Eric Scerri and Grant Fisher state that:

> the philosophy of chemistry had been mostly ignored as a field, in contrast to that of physics and, later, biology. This seems to have been due to a rather conservative, and at times implicitly reductionist, philosophy of physics whose voice seemed to speak for the general philosophy of science. It has taken an enormous effort by dedicated scholars around the globe to get beyond the idea that chemistry merely provides case studies for established metaphysical and epistemological doctrines in the philosophy of physics. These efforts have resulted in both definitive declarations of the philosophy of chemistry to be an autonomous field of inquiry and a number of edited volumes and monographs. (2015: 3)

Labarca and Lombardi state something very similar regarding the ‘traditional assumption’ of reduction:

> this traditional assumption not only deprives the philosophy of chemistry of legitimacy as a field of philosophical inquiry, but also counts against the autonomy of chemistry as a scientific discipline: whereas physics turns out to be a ‘fundamental’ science that describes reality in its deepest aspects, chemistry is conceived as a mere ‘phenomenological’ science, that only describes phenomena as they appear to us. (2005: 126)

Labarca and Lombardi claim that this attitude within the community has influenced the sort of positions proposed with respect to the relation between chemistry and quantum mechanics:

> In recent years some authors have begun to challenge these traditional assumptions in order to recover the autonomy of chemistry and, as a consequence, the legitimacy of the philosophy of chemistry. (2005: 126)

While Labarca and Lombardi suggest that the formulation of disunity theses has been driven by the intention to legitimize the philosophy of chemistry, it cannot be argued here that any particular disunity thesis has been formulated with such an explicit intention. Nevertheless, the quotes above illustrate that some members of the field have connected the indispensability of the philosophy of chemistry with the success to argue for a disunity thesis.[63] Put differently, there is an attitude held by some members of the relevant community, not necessarily advocated by all members of the field, that if the relation between chemistry and quantum mechanics is undermined, then this assures not only the autonomy of chemistry (from quantum mechanics), but also the importance of philosophizing about chemistry.

This attitude within the philosophy of chemistry community is based on the acceptance of the following assumption. If the autonomy of chemistry is established, then the philosophy of chemistry is legitimized as a field of study. However, this is a mistaken assumption. The investigation of the relation between chemistry and quantum mechanics should neither be connected to, nor is it necessary for, the support of the indispensability of the philosophy of chemistry. This is for two main reasons.

First, the examination of any philosophical issue pertaining to chemistry should not be driven by an interest to 'save' either chemistry, or the philosophy of chemistry. If quantum mechanics proves to successfully describe, predict, and explain all chemical phenomena, and if chemistry proves to be no longer useful in any sense, then so be it.[64] The same applies to the philosophy of chemistry; philosophy of chemistry is a legitimate field only in so far as it contributes to the examination of philosophical issues pertaining to chemistry, as well as to other scientific disciplines.

Secondly, the legitimacy of the philosophy of chemistry is not threatened by the support of a reductionist or unificatory account against which these disunity theses are addressed. This is for the following reasons:

(i) There are many interesting philosophical questions that could arise even within a unificatory or reductionist framework. The work of the philosophers of chemistry would not end if it is somehow proven that chemistry is reduced to or unified with quantum mechanics. For example, the question of whether chemical entities, properties, etc. are real, is not settled within a reductionist or unificatory framework. Even if chemistry is reduced to quantum mechanics, there would still be a question of whether chemical entities are real in virtue of their relation to quantum mechanical entities, or whether they should be eliminated from our overall understanding of what sort of entities occupy the world.

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[63] In fact, Scerri, Labarca and Lombardi, and Schummer have defended some sort of disunity thesis concerning the relation between chemistry and quantum mechanics. See, for example, (Scerri 1994), (Labarca and Lombardi 2005), (Labarca and Lombardi 2007) and (Schummer 2014). It should be noted that Scerri has recently stated that he is no longer inclined to defending so strongly non-reductionism with respect to chemistry and quantum mechanics (Scerri and Fisher 2015: 135-37).

[64] The author of this thesis highly doubts that chemistry will ever become fruitless or redundant, but still cannot preclude the logical possibility of this happening in the future.

(ii) There are many interesting philosophical questions that concern chemistry which are at least partially independent of the question of chemistry's relation to quantum mechanics. These include questions regarding theory change, mereology, the role of experimentation, the reality of chemical entities, and many others. For example, the philosophical analysis of the Chemical Revolution with respect to the topic of theory change is independent of the way chemistry is related to quantum mechanics (see for example (Blumenthal 2013) and (Chang 2012)). The philosophy of chemistry can provide useful insight into such questions.

The fact that the legitimacy of the philosophy of chemistry is independent from any discussion concerning chemistry's relation to quantum mechanics, can be further supported by comparing the philosophy of chemistry with other fields of philosophy. Consider, for example, the philosophy of physics and of biology. The development and legitimacy of the philosophy of physics is not based on the fact that physics is the most fundamental science. In fact, making such claims remains highly contestable in the respective literature (see for example (Ney 2017)). What does it mean to be fundamental? And which physics is one referring to when it is claimed that physics is the most fundamental science? These are open questions and the legitimacy of the philosophy of physics is not dependent on the assumption that physics reduces all other sciences. Moreover, regardless of the 'verdict' concerning such issues, there are other issues within the philosophy of physics that are largely independent from physics' relation to other sciences. Consider, for example, the arrow of time, the measurement problem in quantum mechanics, the issue of non-locality, the nature of space-time, the role of experiment in physics and determinism. Furthermore, regarding the philosophy of biology, this field of research has developed greatly during the last decades. The development of the philosophy of biology is not due to the fact that the autonomy of biology from physics or chemistry is settled. Rather, the philosophy of biology has flourished as a research field because of the rapid development of biology itself, and the consequent creation of novel issues and questions regarding biological phenomena. Based on this brief examination of the philosophy of physics and of biology, it is safe to argue that the legitimacy of the philosophy of chemistry should be understood in a similar manner.

The critical analysis of how certain members in the philosophy of chemistry community understand and defend the legitimacy of the field, contributes to understanding the general context in which the relation between chemistry and quantum mechanics is investigated. Moreover, while this chapter rejects the attitude which accompanies the formulation of disunity theses, it does not in principle reject any of the disunity theses that have been presented in the literature. These accounts contribute to the discussion concerning the relation between chemistry and quantum mechanics and point out important features of this relation. Lastly, it should be noted that reductionist and unificatory accounts are also discussed in the philosophy of chemistry literature (section 3.2). This suggests that the community is open to discussing alternative positions about chemistry's relation to quantum mechanics. This openness should be reinforced by a rejection of the aforementioned attitude.

3.2 Unity theses

Unity theses include here any account that focuses on those features of chemistry's relation to quantum mechanics that illustrate the unity or dependence of chemistry to quantum mechanics. This unity or dependence of chemistry to quantum mechanics is characterized in ways such as:

- *supporting a particular sort of epistemic relation between the two theories*

  For example, Eugen Schwarz argues that quantum mechanics can in principle derive the electronic structure of atoms (Schwarz 2007). Hettema argues for the 'union' of chemistry and quantum mechanics by proposing an amended understanding of Nagelian reduction (2017). Richard Bader formulated the so-called Quantum Theory of Atoms in Molecules and suggested that, through this theory, quantum mechanics predicts the 'properties of atoms in molecules' ((Bader 1990: vi), see also (Hettema 2012), (Hettema 2013), (Bader and Matta 2013) and (Causá et al. 2014)). Moreover, Paul Dirac's famous claim that '(t)he fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known', could also be regarded as a unity thesis (1929: 714).[65] Other accounts that could be regarded as advocating a unity thesis are those that point out the methodological, explanatory, heuristic and/or confirmatory dependence of chemistry to quantum mechanics (see for example (Needham 2010) and (Seifert 2017)).

- s*upporting the existence of a particular sort of ontological relation between the respective entities, properties, etc. that are postulated by the two theories*

  For example, Robin Le Poidevin argues for the 'ontological reduction' of chemistry to quantum mechanics (2005) (see also McLaughlin 1992).

Note that, as with the case of disunity theses, the term 'unity theses' groups together accounts that differ in various respects. Specifically, unity theses propose different understandings of the relation between chemistry and quantum mechanics, which may not be compatible or consistent with each other. For example, some positions propose an amended understanding of epistemic reduction (such as (Hettema 2017), whereas others advocate a non-reductive unificatory view (such as (Le Poidevin 2005) and (Seifert

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[65] Whether Dirac's view should be understood as a 'firm expectation that a "full reduction" of chemistry can one day be achieved' is not examined here (Hettema 2017: 3). For example, Hettema argues that Dirac was not so 'confident' about the epistemic reduction of chemistry to quantum mechanics (2017: 3).

2017)). On the other hand, it may be the case that different unity theses in the literature are similar in some respect other than the one that is invoked here. However, the only similarity that is invoked (and according to which all these accounts are grouped together) is that they formulate a variation of unity thesis regarding the relation between chemistry and quantum mechanics.

Moreover, unity theses do not necessarily reject that chemistry is somehow autonomous or separate from quantum mechanics. For example, there are unity theses which acknowledge that chemistry is autonomous from quantum mechanics in the sense that the former employs distinct methodologies and has independent research goals (see, for example, (Needham 2010) and (Seifert 2017: 221)). Moreover, there are unity theses which accept that chemistry is epistemically distinct from quantum mechanics (in the sense of being non-reducible in a strict Nagelian manner) but argue that there is a particular ontological relation between the postulated entities of the respective theories (Le Poidevin 2005).[66] Nevertheless, all unity theses primarily focus on presenting the connections or dependencies between chemistry and quantum mechanics.

There are two interesting characteristics of the existing unity theses in the philosophy of chemistry literature. First, most unity theses accept that a strict Nagelian reduction fails with respect to the examined pair of theories. As Hettema states, ‘the idea that chemistry stands in a reductive relationship to physics still is a somewhat unfashionable doctrine in the philosophy of chemistry’ (2017: 1).[67] While reduction is understood differently by different accounts in the literature, it is safe to say that both unity and disunity theses take that a strict Nagelian reduction at least requires the (in principle) derivation or deduction of chemistry from quantum mechanics ((Needham 2010: 164) and (Hettema 2017: 7)). A strict Nagelian reduction consists of two ‘formal’ requirements; i.e. the ‘connectability and derivability’ of the two theories ((Scerri 1994: 160), see also (Hettema 2017: 7)). Moreover, the reduction of chemistry to quantum mechanics would fall under the cases of heterogeneous reductions. This is because ‘some typically chemical terms cannot be found in the quantum mechanical language’, thus requiring the existence of bridge laws (Scerri 1994: 160). With respect to the examined pair of theories, a successful reduction would sufficiently be supported if the properties of atoms and molecules can (at least in principle) be calculated ‘entirely from first principles, without recourse to any experimental input whatsoever’ (Scerri 1994: 162).[68]

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[66] What is meant by reduction in ‘a strict Nagelian manner’ is specified below as well as in the next chapter.

[67] A possible exception is the position, advocated primarily by Bader, that ‘the Quantum Theory of Atoms in Molecules forms a proper, (reductionist) basis for chemistry’ ((Hettema 2013: 311), see also (Bader and Matta 2013) and (Shahbazian 2013)). Whether Bader’s position should be considered as one that supports strict Nagelian reduction in the sense specified here, is not examined further. Another possible exception is (Schwarz 2007).

[68] The use of the term ‘Nagelian’ with reference to such an understanding of reduction is to an extent misleading because, as Hettema argues, Nagel was not so strict in his account of reduction: ‘Reduction is too often conceived of as a

A strict Nagelian reduction along these lines has been rejected within the philosophy of chemistry literature for a variety of reasons. For example, strict Nagelian reduction allegedly fails for the examined pair of theories because quantum mechanics employs approximations and models in order to describe chemical phenomena. This argument assumes that a strict Nagelian reduction does not permit the use of models and approximations by the reducing theory (in this case by quantum mechanics). For example, Paul Needham states that '(a)s originally conceived, Nagel's conception of reduction takes no account of approximate reasoning and this failure has certainly restricted its applicability, perhaps to the point of making it unrealistic as a model of reduction in science' (Needham 2010: 163). Moreover, Scerri argues that even if reduction is understood as allowing the use of approximations, it still fails for the examined pair of theories (Scerri 1994: 168). Another problem that has been raised against the tenability of a strict Nagelian reduction with respect to chemistry's relation to quantum mechanics is that 'chemistry is a *field*, whereas reduction tends to be a relation between individual theories, or between laws and theories' (Hettema 2017: 1).[69]

Nevertheless, contrary to the existing disunity theses, unity theses do not take that the failure of strict Nagelian reduction supports the claim that the two theories are in some way disunified (in the manner specified in the previous section). There are two main ways in which unity theses support unity despite the alleged failure of strict Nagelian reduction. First, there are theses which propose an amended understanding of Nagelian reduction. For example, Hettema proposes 'a suitable *paraphrase* of the Nagelian reduction programme' which is 'reinforced by a modern notion of both connectibility and derivability' (Hettema 2017: 24).[70] Needham also proposes a more liberal understanding of Nagelian reduction that permits and takes into account the use of approximations in science (Needham 2010: 168-169). Secondly, there are theses which defend the unity of chemistry and quantum mechanics by defending the existence of an ontological relation that does not require a strict Nagelian reduction between the respective theories (Le Poidevin 2005).

Another interesting point regarding existing unity theses is that there are many available non-reductive positions in the philosophy of science literature that, to this day, are not extensively discussed by the philosophy of chemistry community. Positions such as non-reductive physicalism and weak emergence that

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straightforward derivation or deduction of the laws and concepts of the theory to be reduced to a reducing theory, notwithstanding Nagel's insistence that heterogeneous reduction simply does not work that way' ((Hettema 2017: 1-2), see also (Nagel 1979)). Nevertheless, since 'Nagelian' is often employed with reference to this understanding of (strict) reduction, this section retains it in order to differentiate it from amended understandings of reduction that are formulated in the philosophy of chemistry literature.

[69] Italics are in the original text.

[70] Italics are in the original text.

could potentially be understood as defending some sort of unity thesis, have not been examined with respect to the relation between chemistry and quantum mechanics.[71] The neglect of such positions in the philosophy of chemistry is not unexpected considering the current attitude held by some members of the philosophy of chemistry community to focus on defending (or at least investigating) the autonomy of chemistry from quantum mechanics. Nevertheless, it also shows that much more can be said about the relation between the two theories.

3.3 The integration of history and philosophy of chemistry

This section illustrates how philosophical positions regarding the relation between chemistry and quantum mechanics are supported by historical considerations. There are two characteristics of chemistry that often render the consideration of history essential for the philosophical analysis of issues pertaining to chemistry. First, chemistry is a science that is driven not only by theoretical considerations, but also to a large degree by the economic and social benefits that can be gained through the discovery of new elements and processes, as well as through the production of novel chemical substances.[72]

Secondly, the experimental tools that are available at a particular time, as well as the methodological decisions that are made by particular chemists during their examination of chemical phenomena, have partially determined the way in which chemical theories and concepts are formulated. For example, the classification of the elements and the development of the periodic table were influenced by the specific experimental means that were available at the time, as well as by the particular classificatory goals of the scientists involved (for example (Scerri 2007c) and (Tobin and Ambrosio 2016)).
In sum, history illuminates:

(i) the influence of the economic and social context in which chemistry is being practiced at particular times; and,
(ii) the role particular chemists have played in the development of chemical theories.

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[71] For example, this includes accounts such as non-reductive physicalism formulated in terms of degrees of freedom (Wilson 2010), and 'realization physicalism' (Melnyk 2003). It is not argued here that any of these accounts successfully apply to the examined pair of theories. Instead, these accounts are mentioned in order to point out that there is a rich bibliography in the philosophy of science (and potentially other fields of philosophy, such as the philosophy of biology) that could contribute to the examination of unity theses in the philosophy of chemistry.

[72] For a very brief overview of how efficient chemistry has been in the production of novel chemical substances, see (Madrigal 2009). Also, the Chemical Abstracts Service (CAS) which is a division of the American Chemical Society, has founded the CAS registry which enumerates all the known chemical substances (more than 133 million chemical substances thus far) (CAS 2018).

Based on the above, history plays an important role in the analysis of philosophical issues such as theory change, mereology, conceptual analysis, and the relation of chemistry with other sciences.[73] For example, the Chemical Revolution and other events within chemistry have served as case studies to the philosophical examination of how scientific theories change over time (for example (Kuhn 2012) and (Hoyningen-Huene 2008)). Moreover, the understanding of central chemical concepts (such as the atom and the classification of elements) has been articulated within historical accounts about the main players involved in the development of those concepts.[74] As a result, the history of chemistry has influenced the conceptual analysis of the atom, the chemical bond, and other chemical terms.[75]

The investigation of the relation between chemistry and other sciences (such as quantum mechanics, mathematics, thermodynamics, biological sciences, etc.) is informed by mapping the historical affiliations between chemistry and those sciences.[76] In fact, there are numerous examples of unity and disunity theses which invoke historical facts and events in order to support their position regarding the relation of chemistry and quantum mechanics (for example (Llored 2014) and (Schummer 2014)).

An example of a disunity thesis that focuses on the historical investigation of chemistry, quantum mechanics, and quantum chemistry is (Llored 2012). In this paper, Jean-Pierre Llored presents and supports his account of emergence by looking at how '(f)rom the Twenties to nowadays, quantum chemical methods have been *constitutively* concerned with the links between the molecule and its parts' (2012: 257).[77] For example, he presents and analyses the debate between Linus Pauling and Robert Mulliken who both 'focused on the description and the understanding of the molecule, its reactivity, and thus its transformations' (Llored 2012: 257). On the other hand, an example of a unity thesis that focuses on the historical investigation of chemistry and of quantum mechanics is (Hettema 2017). Hettema presents the history of the reaction rate theory (by presenting, among other things, the views of Eugene Wigner) in order to explicate his account of unity (2017: 71-81). Moreover, Needham examines whether historical developments in chemistry and physics are consonant with how reduction tells us that two theories are related (2010: 170).

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[73] See, for example, (Blumenthal 2013), (Blumenthal and Ladyman 2017), and (Chang 2009).

[74] For a historical account of the image of the atom see, for example, (Pullman 1998). For a historical account concerning the discovery of particular chemical elements see, for example, (Scerri 2013).

[75] For the conceptual analysis of the atom see, for example, (Scerri and Fisher 2015: 15- 36). For the conceptual analysis of the chemical bond see, for example, (Hendry 2008), (Sutcliffe 1996), and (Weisberg 2008).

[76] For the case of the relation between chemistry and quantum mechanics see, for example, (Gavroglu and Simões 2012b). For a historical analysis of the relation of chemistry with mathematics see (Gavroglu and Simões 2012a).

[77] The italics are in the original text.

3.4 Summary

This chapter briefly presented how the relation of chemistry and quantum mechanics is investigated in the philosophy of chemistry literature. It understood the relevant positions as falling into two general groups; i.e. as disunity or unity theses. Concerning disunity theses, it argued that there is a proliferation of such positions which emphasize the autonomy of chemistry and its separateness from quantum mechanics. Moreover, this chapter commented on how the philosophy of chemistry community has defended the legitimacy of its field. It specified that it is crucial to identify and reject the attitude held by some members of the philosophy of chemistry community to connect the autonomy of chemistry with the legitimacy of the philosophy of chemistry. The identification and rejection of this attitude accommodates the further development and advancement of the philosophy of chemistry as a legitimate field of study. Concerning unity theses, this chapter argued that while most accounts reject strict Nagelian reduction, they advocate the unity of chemistry with quantum mechanics by either proposing an amended understanding of reduction, or by focusing on the metaphysical relation between the two theories. However, there are available accounts in the philosophy of science literature which are not extensively considered in the literature (namely non-reductive accounts) and which could contribute to the further understanding of the relation between the two theories within the framework of a unity thesis. Lastly, this chapter pointed out that the history of chemistry and of quantum mechanics have (and can) contribute to the understanding of the relation between the two theories.

In light of the above, chapter 4 investigates the applicability of a position that is discussed in the philosophy of science literature. This position is Harold Kincaid's model of non-reductive unity and can be understood as proposing a unity thesis. The two main reasons why Kincaid's model is examined here is that (1) it is largely based on the historical analysis of the two theories, and (2) it is an account which supports unity in a non-reductive framework. These two features of Kincaid's model render the model a novel contribution to the discussion of chemistry's relation to quantum mechanics.

4. Unifying Chemistry with Quantum Mechanics

Harold Kincaid in *Individualism and the Unity of Science* presents a model of unity-without-reduction in order to describe the relation between biology and chemistry. He argues that 'the two theories are linked by (..) an integrated interlevel theory' which unifies them 'by employing explanations and confirmation procedures invoking both levels and by providing evidence that the events and entities of one theory depend upon and are constituted from those of the other' (1997: 66).[78]

This chapter argues that Kincaid's model successfully applies to the relation between chemistry and quantum mechanics.[79] The two theories are unified with respect to their mutual descriptions of a single inert molecule, and are linked by an integrated interlevel theory, namely quantum chemistry.

4.1 Introducing Kincaid's model

Kincaid's model is appealing for several reasons. First, Kincaid's model defines unity in terms of particular metaphysical and epistemic 'interconnections and dependencies' which do not entail a strict Nagelian reduction of one theory to another (Kincaid 1997: 65).[80] Moreover, it allows the theories to exhibit epistemic differences (such as methodological or conceptual differences) without this implying that the two theories are disunified (in the manner specified in chapter 3).

Furthermore, Kincaid's model is in line with some work in the philosophy of chemistry on the unity of chemistry and quantum mechanics. For example, a similar view of unity is examined by Paul Needham (2010):

> unity surely does not require reduction, intuitively understood as the incorporation of one theory within another. (..) Consistency, requiring the absence of contradiction, and more generally in the sense of the absence of conflicts, tensions and barriers within scientific theory, would provide weaker, though apparently adequate, grounds for unity. (Needham 2010: 163)[81]

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[78] For chemistry and biology, the relevant 'integrated interlevel theory' is molecular biology (Kincaid 1997: 65).

[79] A shorter and modified version of this chapter is published in (Seifert 2017).

[80] Strict Nagelian reduction was defined in the previous chapter. Additional comments are made in section 4.3.

[81] Needham investigates Duhem's views on unity in order to critically examine Nagel's understanding of reduction (Needham 2010: 164-66). This aspect of Needham's work is not considered here.

In this paper, Needham presents Pierre Duhem's 'scheme' of 'unity without reduction' in a manner that resembles in some respects Kincaid's understanding of unity in terms of an 'integrated interlevel theory' (Needham 2010: 166):

> From the Duhemian perspective, there is no preconceived notion of "fundamental law" or "basic property". Microscopic principles complement macroscopic theory in *an integrated whole*, with no presumption of primacy of the one over the other. (Needham 2010: 167)[82]

Another reason why Kincaid's unity is appealing has to do with the existence and success of quantum chemistry. Quantum chemistry is regarded as a distinct sub-discipline of chemistry that applies quantum models for the description, prediction, and explanation of chemical phenomena. These phenomena primarily concern the 'structure and bonding of atoms and molecules' (Hendry 2010a: 212). By 'quantum models' this chapter refers to the semi-empirical methods, models and approximations that have been developed on the basis of quantum mechanics.[83] The existence, development, and empirical success of quantum chemistry indicates that there is a sense in which the two theories are indeed unified. In light of this, the goal of this chapter is to propose a philosophical account of unity which takes into account the existence and success of quantum chemistry. Kincaid's model accommodates this goal.

Lastly, Kincaid's model is partially supported by reference to historical facts and events pertaining to chemistry and quantum mechanics. Considering that historical events are often invoked in the philosophy of chemistry literature in order to support both the unity and disunity of the two theories (see section 3.3), Kincaid's model is a novel example of how historical evidence can be employed for the defense of unity.

Although Kincaid proposed his model of unity for different pairs of theories, it is possible to apply it to the case of chemistry's relation to quantum mechanics.[84] This is because, similarly to biology and chemistry, the examined pair has the following characteristics:

(i) They describe a common set of phenomena; and,

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[82] The italics are added here in order to highlight the particular element of Duhem's view that resembles Kincaid's understanding of unity. Note that Kincaid would not agree with Duhem that there is no kind of primacy. This becomes apparent by the way Kincaid specifies his proposed model of unity (see section 4.2).

[83] Among those methods are the Valence Bond method, the Molecular Orbital approach, the Hartree-Fock method of approximation and any other method and model that is found in textbooks of quantum chemistry (for example see (Atkins and Friedman 2005: chapters 8 and 9), see also section 2.2).

[84] Kincaid also discusses his model of unity with respect to individualism and macroeconomics (1997).

(ii) They postulate entities that are found at (at least) partially distinct scales.[85]

Kincaid's model is comprised of two parts.[86] The first part consists of seven requirements for the examined pair of theories to exhibit unity. As Kincaid states:

> When these requirements are met, then the two theories are linked by, or perhaps incorporated in, an *integrated interlevel theory*. (1997: 66)[87]

Hence, if chemistry and quantum mechanics satisfy the seven requirements with respect to their descriptions of a single inert molecule, then they are 'linked or incorporated' in an integrated interlevel theory. Moreover, this chapter concludes one more thing from the successful application of Kincaid's model. If the two theories satisfy the model, then this means that they provide a unified body of knowledge about the behavior of a single inert molecule. The term 'body of knowledge' is taken from Needham (2010) who employs it in a manner that closely resembles the general idea of unity that is supported in this chapter:

> Put another way, mechanics is expanded by the addition of concepts and principles from thermodynamics, and *the whole new body of knowledge is integrated in a systematic new theory*. All the old mechanics is incorporated, but in addition there is provision for the explanation of new phenomena. (2010: 166)[88]

The second part of Kincaid's model concerns the rejection of reduction. According to Kincaid, the rejection of reduction follows from the meeting of the seven requirements; Kincaid's model of 'unity basically involves interconnections and dependencies between theories that nonetheless do not allow for one theory to replace the other' (Kincaid 1997: 65). It is not merely that the seven requirements do not imply reduction (which is also the case); they are incompatible with reduction. What Kincaid takes as reduction and the reasons for which reduction is incompatible with the model, are explained in section 4.3.

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[85] Chapter 1 specified in detail how these two clauses hold for the case of chemistry and quantum mechanics. Note that chemistry and quantum mechanics are also referred to here as the 'higher' and 'lower-level theory' respectively. Higher and lower-level theories were defined by reference to scale in chapter 1.

[86] Kincaid does not organize the model into these two parts. This chapter organizes the model into two parts for reasons of simplicity and clarity.

[87] The italics are of Kincaid.

[88] The italics are added here.

It should be clarified that there are certain elements of the model that this chapter either amends or specifies in more detail, compared to Kincaid's analysis. For example, this chapter specifies what constitutes sufficient support in order for the requirements to hold for the particular pair of theories.[89] It also specifies certain terms that are not sufficiently specified by Kincaid, such as 'token identity' (see 4.2.1), 'composition' (4.2.1), and 'supervenience' (4.2.2).

Another example concerns the definition of scientific theories. Kincaid defines theories as 'sets of statements' (Kincaid 1997: 63) without explicating any further what he means by that. One possible way to define theories in more detail, is by examining their structure (as, for example, per the syntactic, semantic, or pragmatic view of scientific theories).[90] Such an approach is not pursued here. Instead, this chapter defines theories in the following manner. Theories include not only sets of statements, but also the relevant models, visual representations, experimental and semi-empirical methods that are employed for the description, explanation, and prediction of a phenomenon. This definition is more accurate than Kincaid's because it captures all those aspects that render, according to Kincaid, two theories unified.[91] Specifically, the interconnections and dependencies that he invokes for the support of unity are not merely connections between sets of statements of two theories; they also include connections between the respective models, visual representations, etc. (this becomes particularly evident by the last three criteria of the model- see 4.2.5, 4.2.6, and 4.2.7). In this context, defining theories as just sets of statements is misleading because it disregards a central characteristic of the proposed unity; namely of a unity which is partially supported and instantiated by the connections between the models, etc. of two theories.

Lastly, it should be noted that this chapter does not critically examine whether Kincaid's model is an accurate understanding of unity. For example, it does not examine whether each of the seven criteria are

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[89] For example, section 4.2 defines 'heuristic interdependence' and 'logical compatibility' in a manner that is specific to the examined pair.

[90] For a general overview of these views see (Winther 2015). For an overview with respect to chemistry's relation to quantum mechanics see (Villani et al. 2018: 90-91).

[91] Note that the definition of theories that is proposed in this section, resembles the pragmatic view which 'does not deny the effectiveness of logic-linguistic analysis and mathematic models', yet 'considers that the scientific enterprise relies on a wide spectrum of cognitive tools that includes non formal tools' (Villani et al. 2018: 91). Interestingly, the pragmatic view is defended in the literature with respect to chemistry's and quantum mechanics' 'conception of orbitals' (Villani et al. 2018: 90-92). The work in (Villani et al. 2018) indicates that the understanding of theories that is proposed here, is appropriate when examining the application of Kincaid's model for the case of chemistry's relation to quantum mechanics. However, this chapter does not further elaborate on this issue, mainly because a sufficient analysis requires the critical examination of the pragmatic view (and its rivals). This goes beyond the scope of this thesis.

necessary and/or sufficient requirements for unity. Nevertheless, section 4.4 examines the model's epistemic and metaphysical implications.

4.2 The seven criteria of Kincaid's model

This section presents the seven criteria that need to be satisfied for the examined pair of theories to be unified according to Kincaid's model. Note that these criteria, apart from being the formal requirements of this model of unity, also explain how unity is understood by Kincaid. Following Kincaid, the criteria are presented in 'increasing order of significance' (1997: 65).

4.2.1 Chemical entities may be composed of or token identical to quantum mechanical entities

Kincaid formulates the first criterion as follows:

> The ontology of one theory may exhaust that of the other- every entity described by the one theory may be composed of or token identical to some entity described by the other. (1997: 66)

This is a metaphysical criterion; it requires the existence of a particular relation between the entities that are postulated by two theories. For Kincaid, this is the least important criterion of the model. This is evident from the way Kincaid formulates the criterion (notice the use of the term 'may') and from the fact that it is presented first (1997: 65). The chapter takes that the way Kincaid presents the seven criteria indicates that the first criterion is not necessary for the model to hold. That is, even if there is a relevant higher-level entity that is not composed of or token identical to some lower-level entity, the model as a whole is not decisively rejected. As long as the higher-level entities comply to the more important metaphysical criteria of the model (namely supervenience- see subsection 4.2.3), the model is not sufficiently challenged by the rejection of only this criterion.[92] Nevertheless, if the criterion is satisfied, then this is a positive indication that the model may hold.

Before explicating why the criterion holds for the examined pair of theories, it is important to specify the main terms that are employed in the formulation of this criterion. First, 'entity' is not defined by Kincaid. This subsection takes that 'entity' refers to those things that the higher-level theory, via the relevant scientific textbooks, regards as such. Given such an understanding of 'entity', this subsection examines the criterion

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[92] Recall that the importance of each criterion is determined by the order in which Kincaid presents them.

with respect to those things that chemistry regards as entities (namely atoms, molecules, and (possibly) chemical bonds). This is a philosophically naive understanding and analysis of entities, which disregards certain metaphysical issues that concern the nature and identity of entities.[93] Nevertheless, it sufficiently accommodates the analysis of this criterion.

Moreover, 'token identity' is defined as an identity relation between particular entities at a particular instance. For example, claiming that a particular segment of DNA is token identical to a particular gene 'means that in this instance this particular gene is that sequence of bases' (Kincaid 1997: 78). According to token identity, a particular entity may be identical to either a particular lower-level entity, or to a sum of particular lower-level entities (Kincaid 1997: 78).

'Composition' is not explicitly defined by Kincaid. In fact, he employs different terms when referring to this relation; namely 'constitution' and 'realization' (1997: 78). He invokes this relation in cases where it 'is often unclear, for example, with what physical token we should identify complex objects such as universities' (Kincaid 1997: 78). What he means by this, is that token identity does not accurately describe how certain entities are related to each other. Based on the example that Kincaid invokes (see quote above), one could explicate Kincaid's use of the notion of composition by means of the following example. The University of Bristol at a particular instance is not just a particular set of academic staff, buildings, and books. It is also the interactions amongst its staff, the research programs undertaken by the relevant academics, the classes that are given to students, etc. In this context, token identity does not accurately describe the relation between the University of Bristol and such entities, because it takes into account only the entities, and not the relevant processes and interactions that are instantiated or performed by them.[94]

In light of this, 'composition' is defined here as a part-whole relation that is not merely aggregative, but that also takes into account that the whole may be partially determined by the interactions between the relevant parts. These interactions are contingent on the particular parts to which they are assigned. For example, if one refers to atoms or electrons as being the parts of say, a magnet, then the interactions that are involved are the physical ones (i.e. primarily electromagnetic, but also gravitational, strong nuclear, and weak nuclear interactions). If one refers to individuals as being the parts of, say, a society, then the relevant interactions are those that are instantiated by individuals (such as psychological or social interactions).[95]

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[93] For a discussion of the nature of entities and their properties see, for example, (Lowe 2002).

[94] It is not argued here that the correct way to understand the relation between the University of Bristol and some set of lower-level entities is in terms of composition. This is merely an example that illustrates the difference between token identity and composition.

[95] See (Ladyman and Ross 2007) and (Ladyman 2017) for a similar understanding of composition as dynamical.

Note that this definition is very general and employs a concept that is discussed extensively in the philosophy of science literature; namely part-whole relations (see for example (Varzi 2016) and (Hüttemann and Papineau 2005)). In light of this, it is evident that composition can be further specified with reference to different positions that examine the relation between higher and lower-level entities, and/or the relation between (physical) parts and wholes. Which positions are relevant to the further specification of composition depends on the particular theories that are of interest. For example, if one examines Kincaid's model of unity (and thus composition) with respect to thermodynamics and statistical mechanics, then the relevant literature discusses how physical parts are related to physical wholes. On the other hand, if one examines the relation of a special science theory with a physical one (as in this case), then the relevant literature about composition is the one which discusses how special science entities are related to physical ones.[96]

In light of the above, composition with respect to chemical and quantum mechanical entities can be further specified by accounts such as the following. First, it can be specified in terms of reductive physicalism (see, for example, (Kim 2005) and (Papineau 2002)). Moreover, one could specify composition by reference to 'degrees of freedom', as this is defined by Wilson's account of non-reductive physicalism (2010). Lastly, emergentist accounts also propose a particular understanding of composition (see for example (Wilson 2015: 363-364)).

This section does not support any of the above accounts. Instead, it takes that any position about composition is admissible within Kincaid's model, as long as it complies to the following constraints:

i. It does not entail nor require reduction, as this is defined by Kincaid; and,
ii. It does not go against the main tenet of Kincaid's first criterion- namely that the 'ontology of one theory may exhaust that of the other' (Kincaid 1997: 66).

While these constraints may be satisfied by different understandings of 'composition', they also exclude some positions. For example, reductive physicalism is excluded if it entails the sort of reduction that Kincaid

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[96] This does not necessarily mean that questions regarding the relation between physical parts and wholes are independent from questions regarding the relation between special science and physical entities. If they are not independent, then obviously there is a lot more that can be said about composition that goes beyond the scope of this model. On the other hand, Andreas Hüttemann and David Papineau argue that the relation between physical parts and wholes, and the relation between special science and physical entities are issues that are and should be understood as independent (2005: 33). While the present author does not agree with Hüttemann and Papineau, this disagreement is not elaborated or justified here.

rejects.[97] Strong emergence is also excluded, if it denies that the higher-level ontology is exhausted by the lower-level one.[98]

It should be noted that Kincaid does not specify what he means by 'the ontology of one theory exhausting that of the other' (Kincaid 1997: 66). Therefore, it is not possible to decisively state whether he would regard the model as being incompatible to strong emergence. For example, if one understands Kincaid's criterion as defending the causal closure of the physical, then strong emergence is inconsistent with Kincaid's model (for example, Hendry's understanding of strong emergence is inconsistent with the causal closure (Hendry 2010b)).[99] On the other hand, if one understands the criterion as being in accordance to the principle of the 'ubiquity of physics', then strong emergence is compatible with the criterion.[100] Adding to this uncertainty, this criterion is somewhat hedged by Kincaid (see beginning of this section). In light of the above, this section assumes that since strong emergence (as presented in the philosophy of chemistry by Hendry) is a disunity thesis (see chapter 3), it is incompatible with Kincaid's model of unity, regardless of whether it is consistent with the first criterion.

The remainder of this subsection employs the general definition of composition (i.e. understood as a part-whole relation that is not merely aggregative) in order to support the claim that atoms, molecules, and chemical bonds, as they are described in chemistry, are composed of entities postulated by quantum mechanics. While it is possible to examine this criterion for other entities that are postulated by chemistry, this subsection examines it only with respect to the three most common entities that are postulated by chemistry in the description of a single inert molecule.

First, consider how chemistry defines an atom. As already mentioned in chapter 2, an atom is defined in chemistry as a particle which consists of a nucleus and electrons (IUPAC 2014: 121). The nucleus consists of protons and neutrons. A proton is a '(n)uclear particle of charge number +1' and 'spin quantum number 1/2'

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[97] Section 4.4 discusses in more detail the compatibility or incompatibility of Kincaid's model with other accounts on inter-theory relations in the philosophical literature.

[98] Note that section 4.3 argues that reduction is not well-supported for the examined pair of theories. Chapters 5 and 6 argue that Hendry's account of strong emergence is not sufficiently supported either. These points collectively support the successful application of Kincaid's model to the examined pair of theories.

[99] One should be careful with how to understand Kincaid's first criterion because its understanding must be such that it doesn't imply reduction (the latter would make the first criterion incompatible with Kincaid's model). The causal closure of the physical is discussed in chapter 5.

[100] According to the 'ubiquity of physics', 'physical principles constrain the motions of particular systems though they may not fully determine them (Hendry 2010b: 188). Hendry takes the ubiquity of physics to be compatible with strong emergence. Hendry's account of strong emergence is discussed in detail in chapter 5.

(IUPAC 2014: 1195) and a neutron is a '(n)uclear particle of zero charge' and 'spin quantum number 1/2' (IUPAC 2014: 989). The electron is an elementary particle with spin quantum number 1/2 and a 'negative elementary charge' (IUPAC 2014: 477).

Based on these definitions, chemistry understands atoms as being composed of the lower-level entities that are postulated by physics, and whose properties and behavior is described by quantum mechanics; namely protons, neutrons, electrons as well as their respective interactions. In fact, chemistry not only accepts that such entities compose the atom, but also accepts the manner in which quantum mechanics takes those entities to compose it. For example, it accepts that electrons move in a wave-like manner around the nucleus of an atom, and that electrons are confined to have particular energies (i.e. to be quantized) (Urch 1970: 12).

Concerning the molecule, chemistry defines it as an 'electrically neutral entity consisting of more than one atom' (IUPAC 2014: 958). It is understood as being composed by a group of atoms that are arranged in a particular manner and that are held together via chemical bonds. Based on the fact that the atom is composed of entities postulated by physics, it follows that the molecule is also composed of these entities; namely of protons, neutrons, electrons, and their respective interactions.

Concerning the chemical bond, IUPAC's definition does not explicitly refer to chemical bonds as entities (see subsection 2.1.3). In fact, there is an ongoing debate about whether the chemical bond refers to an entity or to a property. Hendry presents this debate by distinguishing between the structural and the energetic conception of the chemical bond (2006b). The structural conception takes chemical bonds to be entities; namely 'material parts of the molecule that are responsible for spatially localized submolecular relationships between individual atomic centers' (Hendry 2008: 917). The energetic conception remains agnostic as to whether the chemical bond is an entity; instead, it focuses on the specification of 'chemical bonding' as a property of molecules that signifies 'facts about energy changes between molecular or supermolecular states' (Hendry 2008: 919). This section does not defend a particular conception of the chemical bond; it argues that, under both, Kincaid's criteria are satisfied.

Specifically, if one accepts the structural conception then the chemical bond is a higher-level entity and, as such, it should be examined with respect to the first criterion.[101] According to the structural conception, 'a bond must be individuated by the atomic centers it links' and 'electrons participate physically in the bond'

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[101] Under the energetic conception, Kincaid's model requires that the chemical bond satisfies the criterion of supervenience and not of token identity/composition. Subsection 4.2.3 defends supervenience with respect to chemical properties in general. This suffices for the investigation of the energetic conception with respect to its compatibility with Kincaid's model.

(Hendry 2008: 918). Quantum mechanics takes electrons to participate in these bonds 'as the occupancies of non arbitrary partitions of the full electronic wave function that can be associated with the bond' (Hendry 2008: 918). This formulation of the structural conception shows that chemical bonds (as entities) are composed of quantum mechanical entities and their interactions.

This subsection argued that three entities which are central in the chemical description of a single inert molecule, are composed of quantum mechanical entities. This partially supports the first criterion with respect to the examined pair of theories. The next subsection examines the second (and more important) criterion of this model.

4.2.2 Chemistry and quantum mechanics are logically compatible

Kincaid states this requirement as follows:

> Two theories may be irreducible yet logically compatible in that neither explicitly or implicitly uses or presupposes statements at odds with those from the other theory. (1997: 66)

This is an epistemic requirement which is understood here as demanding that chemistry and quantum mechanics do not make contradictory claims. Note that logical compatibility should not be confused with other sorts of compatibilities, like conceptual or methodological compatibility.[102] To the extent that conceptual, methodological, or any other epistemic incompatibility does not imply the two theories' logical incompatibility, the former incompatibilities are permissible by the model.

This criterion is supported by two claims. First, if chemistry assumed forces that are not postulated by quantum mechanics, i.e. forces that are independent and different from the four main forces postulated in the totality of physics (namely electromagnetic, gravitational, strong nuclear and weak nuclear forces), then this would suffice to claim that chemistry is incompatible with quantum mechanics. Since there are no such chemical forces, then this indicates that there is no such logical incompatibility.[103] On the contrary, the forces postulated by chemistry in the explanation of phenomena are all physical (in particular electrostatic forces).

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[102] Joachim Schummer for example argues that chemistry and quantum mechanics are methodologically and conceptually incompatible (2014).

[103] According to the totality of physics, there are no other fundamental forces in nature. Therefore, if chemistry postulated the existence of a chemical force that is distinct and irreducible to these fundamental physical forces then this would contradict the claim of physics that there are no other fundamental forces in nature and thus would render chemistry logically incompatible with physics. Special thanks to James Ladyman for specifying this point.

Secondly, the historical development of quantum chemistry- that is, 'of a sub discipline that is not quite physics, not quite chemistry, and not quite applied mathematics' (Gavroglu and Simões 2012b: viii)- shows that the two theories are logically compatible. First, it is unclear how quantum chemistry would be evaluated with respect to its empirical accuracy and success, if the two main theories that are involved in its development made contradictory claims. Secondly, there is historical evidence which indicates that whenever the two theories were logically incompatible, the relevant scientific communities would either amend or reject some element of one of the two theories, or they would at least recognize the existence of an anomaly in one of them.

The most striking example of this is how chemistry's image of the atom significantly changed with the incorporation of quantum mechanics' postulations about the wave-like manner of entities, the quantization of energy levels, and spin.[104] Specifically, quantum mechanics' postulations of the wave-like manner of entities affected and influenced chemistry's image of the atom.[105] The proposition that entities do not only behave as particles but also as waves, had a direct effect on the way atoms were perceived and on how their inner structure was described in chemistry.[106] For example, Erwin Schrödinger formulated the equation that describes the behavior of a particle in terms of its wave-like characteristics (see section 2.2). In this context, electron behavior is now described in terms of the Schrödinger equation which is the mathematical representation of the trajectory of electrons. Added to this is the de Broglie relation which calculates the wave length of the electrons, and relates it to their momentum via Planck's constant, $\hbar$.

Moreover, Max Planck's proposal that the amount of energy emitted from a blackbody in thermal equilibrium is discrete and not continuous, had a significant effect on the model of the atom as well. Specifically, Niels Bohr incorporated Planck's conclusion in his model of the atom, by postulating stable electron orbits around the nucleus and by suggesting that, when an electron occupying a specific orbit 'jumps' onto another orbit, it either releases or absorbs a discrete amount of energy (Pullman 1998: 262-269). Lastly, the Schrödinger equation brought in a natural way Bohr's image of the atom, since it generated and specified Bohr's three quantum numbers (Pullman 1998: 277). Bohr's quantum numbers that were

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[104] See for example (Pullman 1998), (Gavroglu and Simões 2012b), (Nye 1972), and (Pais 1982) for an analysis of the historical events that occurred during the relevant period.

[105] Bernard Pullman provides a detailed historical analysis of how chemists and physicists understood the atom (1998).

[106] This section does not do justice to all the scientists that, through their work, influenced how chemistry understands the atom. That is, it does not examine in detail how the relevant historical events occurred. Instead, it very brief presents the main postulates of quantum mechanics that contributed to chemistry's image of the atom.

‘associated with the size, shape, and spatial orientation’ of the orbits, are now inferred by quantum mechanics instead of merely being postulated (Pullman 1998: 268).

One could argue that while the above incompatibilities have been overcome, there are still persisting issues that illustrate the logical incompatibility between chemistry and quantum mechanics. For example, chemistry is a classical theory in the sense that it postulates distinguishable entities that have definite properties. On the other hand, quantum mechanics raises the measurement problem and the indistinguishability of entities (see (Albert 1992) and (Sklar 1993)). This can be regarded as a logical incompatibility between the two theories. How this incompatibility could be resolved is not currently discussed. This is an example of a more general issue that concerns the classical-quantum divide. However, the manner in which this incompatibility is scientifically and philosophically investigated indicates that it is an anomaly which is recognized by the relevant communities and that there is a continuous effort to resolve it.[107] This suffices in order to support the logical compatibility of the two theories.

This last point illustrates an interesting feature of the criterion and of the overall understanding of Kincaid’s unity. Logical compatibility is a historically informed and time-dependent requirement. This implies that two theories need not be logically compatible from the outset of their formulation in order for the present criterion to be satisfied. Rather, the criterion requires that, even when contradictory claims are made, the relevant communities acknowledge them as anomalies that require resolution. This, in turn, indicates that the advocated unity is one that is historically informed and time-dependent. Kincaid’s model does not propose an all-or-nothing view of unity. Instead, it understands unity as a continuous process during which two theories *unify*, in the sense that they are continuously building interconnections and dependencies, and that they are in a process of resolving any logical incompatibilities that may arise.[108]

4.2.3 Chemistry supervenes on quantum mechanics

The next criterion of this model concerns supervenience. Kincaid understands supervenience in the following manner. ‘Fixing or determining’ a set of lower-level ‘facts or properties’ also fixes some higher-level ‘fact or property’ (Kincaid 1997: 72). What Kincaid means by ‘fix’, ’determine’,’fact’ and ‘property’ is not entirely clear, so this subsection assumes an understanding of supervenience that is compatible with Kincaid’s model. Specifically, it presents the basic points that make up Kincaid’s understanding of supervenience and provides a compatible definition.

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[107] There is a vast literature on these issues. An interesting example is (Bokulich 2008b) which explicitly investigates the so-called ‘classical-quantum relation’.

[108] Special thanks to Hasok Chang for pointing out this feature of Kincaid’s model of unity.

Kincaid makes the following points about supervenience:

I. Supervenience does not ensure the existence of bridge laws, identity relations, or definitions that connect lower-level with higher-level properties. It is not required that one is able to describe the specific relationship between chemical and quantum mechanical properties. Supervenience does not require that there is a systematic way of describing such relations; it merely postulates that some sort of relation between the quantum and chemical ontology exists (Kincaid 1997: 70-71).

II. Kincaid employs different terms to refer to the relata of the supervenience relation. These include 'facts', 'properties', 'predicates', 'entities', 'processes' and 'theories'. For reasons of clarity, this section employs the term 'properties'. Properties henceforth refer to any set of entities, properties, processes, or any other sort of thing that is postulated by the relevant theory (Kincaid 1997: 74).

III. While it is possible to specify on which set of lower-level properties a particular higher-level property supervenes, supervenience is not refuted if one is unable to make such a specification for every higher-level property. This is because the predicates which describe these higher and lower-level properties may 'cut up the world differently', in the sense that they 'have extensions that only overlap' (Kincaid 1997: 73).

IV. Supervenience is not refuted if the description of lower-level properties is formulated on the basis of information that is provided by the description of higher-level properties (Kincaid 1997: 90).

V. Multiple realizability is permissible. That is, it is possible for two systems to differ with respect to their lower-level properties, while not differing with respect to their higher-level properties (Kincaid 1997: 50-51).

VI. It is not required that a change in the chemical properties necessitates a specific change in the quantum mechanical properties. Supervenience merely postulates that there is a change in the lower-level properties, whenever there is a change in the higher-level properties. Put differently, Kincaid's understanding of supervenience is compatible with various interpretations of its modal force.[109]

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[109] Kincaid does not explicitly state this but since he does not discuss modality with respect to supervenience, it is safe to make this assumption.

Based on the above, supervenience postulates a relation such that when any chemical property of a molecule changes, then it is always the case that one or more of the molecule's quantum mechanical properties have changed as well. However, supervenience does not require such a relation to be epistemically describable by chemistry or quantum mechanics (point I). Moreover, it is not required that one is able to specify which specific set of quantum mechanical properties changes when a chemical property changes.

One way to lend support to supervenience is by showing that when the complete chemical description of a molecule changes, then its relevant complete quantum mechanical description changes as well. However, this rests on the assumption that both descriptions are complete in their characterization of a molecule. That is, neither chemistry nor quantum mechanics miss out in describing some entity, property, process or interaction that is relevant to the respective scale. However, this may not be the case (see subsection 7.2.2). Therefore, this subsection supports supervenience differently, by arguing that the rejection of supervenience is not scientifically well-supported.

Let us suppose that supervenience does not hold. If so, then there would be at least one chemical property whose change is not accompanied by a change in the molecule's quantum mechanical properties; the molecule remains invariant with respect to its quantum mechanical properties. Epistemically, this is reflected by the fact that the complete quantum mechanical description of the molecule would remain the same as before the change of its (complete) chemical description. Moreover, the rejection of supervenience implies that there is at least some set of higher-level properties that is not determined or realized by its lower-level entities and their respective interactions. This subsection has not explicitly defined supervenience in terms of realization, determination or a similar concept. Nevertheless, Kincaid understands supervenience in a manner that involves such a metaphysical idea.[110] For chemical properties this idea can be stated as follows: there is at least one chemical property of a molecule that is not determined by the existence, interactions, and properties of its composing electrons and nuclei. It is not only that the change in a chemical property is not accompanied by some change in the quantum mechanical description; such a change is not determined by any set of lower-level properties.

The problem with rejecting supervenience is that our current physics and chemistry do not support such a view of molecules (as specified in the previous paragraph). For example, the success of quantum mechanics in the prediction and explanation of chemical phenomena is at odds with the rejection of supervenience. This oddity becomes also apparent if we consider the success in overcoming logical incompatibilities between the two theories. As argued in the previous subsection, even when chemistry and quantum mechanics made

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[110] This becomes evident by his use of the terms 'fix', 'determine' and 'realize' (1997: 72). This subsection takes these terms as primitives and leaves it open how these terms can be specified.

incompatible claims, the scientific community managed to resolve them. The success in overcoming such logical compatibilities would be odd if supervenience is false.

While this argument raises interesting questions about how to reconcile the possible falsity of supervenience with the success of our current scientific theories, of course it does not entail supervenience. Supervenience is a metaphysical claim and as such its truth/falsity is independent from how successfully our best current science describes and explains phenomena. Nevertheless, there is no scientific evidence that molecules behave in a manner that is independent from their quantum mechanical description; rather the contrary. For most changes in the chemical description of a molecule, it is possible to show that the relevant quantum mechanical description has changed as well. Note that the formulation of the quantum mechanical description almost always involves the use of ad hoc assumptions that are drawn from chemistry. However, this is not a problem for supervenience, as the latter is understood by Kincaid (point IV above). The manner in which the quantum mechanical description changes when particular chemical properties are considered to have changed, is discussed in detail in the next two chapters.

One last argument in favor of supervenience is provided in the next criterion.

4.2.4 It is possible to inductively support supervenience

This criterion requires that there is scientific evidence that inductively supports supervenience. Specifically, it requires that 'we can cite some of the mechanisms that realise or bring about higher-level kinds' (Kincaid 1997: 66).[111] Kincaid does not require that there is a specifiable set of mechanisms that 'realises or brings about' *all* higher-level properties. In fact, he takes that there is no such set because, if there were specifiable mechanisms that 'realise or bring about' *all* higher-level properties, then this would suffice for the defense of reduction (see also subsection 4.3). He supports this point by looking at the best current sciences:

> there is no general demand for lower-level mechanisms if we are to have good science. Some of our best science explains in ignorance of details at lower-levels. Nor is information about lower-level processes always crucial. (1997: 144)

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[111] What Kincaid means by the term 'kinds' and whether Kincaid's meaning of kinds relates to the discussion of natural kinds (as this is examined in the philosophy of science literature), is not currently examined. See for example (Beebee and Sabbarton-Leary 2010).

While he makes reference to causal mechanisms in various parts of his book, Kincaid does not provide a definition of mechanisms. Given this ambiguity in Kincaid's understanding of mechanisms, this section takes that Stuart Glennan's definition of 'minimal mechanism' is compatible with Kincaid's model:

> A mechanism for a phenomenon consists of entities (or parts) whose activities and interactions are organized so as to be responsible for the phenomenon. (Glennan 2017: 17)

Glennan's definition is picked here because, according to Glennan, (i) the definition is 'broad enough to capture most of the wide range of things scientists have called mechanisms', and (ii) 'mechanisms in this minimal sense constitute the causal structure of the world' (2017: 17-18). Both clauses are prima facie in a similar spirit with Kincaid's understanding of causal mechanisms and of how sciences are related. Of course, this justification does not sufficiently support that Glennan's understanding of mechanisms is correct. Nevertheless, to the extent that this definition accommodates the specification of this criterion, it serves the purposes of the current subsection.[112]

Also, note that this subsection does not examine questions pertaining to mechanisms. For example, it does not examine the ontological status of mechanisms. It takes that scientific theories often make reference to such mechanisms in order to explain, confirm, or predict some set of phenomena. Moreover, mechanisms are taken to be represented via models or methods. Whether mechanisms exist and, consequently, whether the respective models specify and represent them accurately, is not examined. It suffices that there are some examples of models or methods employed by any of the two theories, which represent some sort of mechanism in order to explain, confirm, or predict some set of higher-level phenomena.

Based on the above, the criterion requires the citation of models that describe a particular chemical phenomenon by specifying a mechanism that consists of quantum mechanical entities and their respective properties. The most striking example of such a mechanism is the one employed to specify the orbital structure of atoms in chemistry. This mechanism is based on Schrödinger's specification of the three quantum numbers, and on Pauli's exclusion principle that specifies the fourth quantum number. It outlines the building rules with which chemists are able to specify the electron configuration of atoms, and consequently it provides the basis for specifying what kind of bonds different types of atoms can form, and with what type of atoms that could be.[113]

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[112] Given this approach, it is left open whether there is a more suitable understanding of mechanisms for the purposes of Kincaid's model.

[113] These building rules were also mentioned in chapter 2 in terms of the Aufbau principle.

The electron configuration of an atom is a 'list of all its occupied orbitals, with the number of electrons that each one contains' (Atkins and Jones 2010: 33). This list is completed by following certain building rules that are based on Schrödinger's solution of the wave function and on Pauli's Principle. Specifically, atomic orbitals refer to one-electron orbital eigenfunctions which are 'based on the attraction of the nucleus for the electron we are considering plus the average repulsion of all the other electrons' (Mulliken 1967: 13). The shape and size of the area that the electron is most probably occupying around the nucleus, is designated by the four quantum numbers.

The first quantum number is the principle quantum number, which represents the energy and size of the atomic shell.[114] This classification of orbitals into atomic shells is further sub-divided because an electron can occupy an atomic shell by orbiting around in various forms. These different forms are captured by the notion of subshell, and each subshell is represented by the angular momentum quantum number, l. In chemistry, one writes down the shell and subshell that an electron occupies, in terms of the value of the principle quantum number (n) and the letters s,p,d,f that correspond to the values of the angular momentum quantum number (l). So, for example, 1s represents a subshell of the s-form that occupies the lowest atomic shell, 2p represents the p subshell in the second atomic shell, etc.

Moreover, from the quantum calculation of the probability density of finding an electron at a particular subshell, it turns out that not all atomic shells allow all forms of subshells (Atkins and Jones 2010: 33). This is because, for example, the wave function of a p-electron vanishes at its nucleus. This explains why, for example, in shell-1 an electron will be found to occupy only an s-subshell, and not a p- or f- subshell. Keeping this in mind, quantum mechanics posits that, depending on how many electrons an atom has, the subshells which are occupied by the available electrons can be found by following the sequence below:

1s, 2s, 2p, 3s, 3p, 3d, …

The third feature that is required to specify the orbital of an electron is the magnetic quantum number, m_l. The value of m_l specifies the individual orbitals within a subshell and represents the different direction of each orbital within that subshell.

The last element for the complete specification of the electrons' orbitals, is derived from Pauli's Principle. Pauli introduced a rule according to which a maximum of two electrons can occupy one orbital; namely an orbital with a specific set of (n,l, m_l) numbers. These two electrons are viewed as if moving on opposite

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[114] The technical notation is from (Atkins and Friedman 2005) and (Atkins and Jones 2010).

directions on the orbital, and they are represented uniquely in chemistry by one more quantum number, namely spin (which takes two possible values; +1/2, -1/2).

In sum, the possible values of the three quantum numbers, together with their subshell ranking and the Pauli Principle, act as building rules that chemists use in order to specify the electron configuration of an atom. By following those rules, it is possible to represent the orbitals that the electrons of a particular atom will occupy in terms of them having particular size, shape and orientation. So, for example, the hydrogen atom has one electron. It must be the case that the lowest energy shells are occupied first; so hydrogen's electron occupies shell-1. Also, we know that in shell-1 the electron moves in an s-subshell, namely spherically around the nucleus. So, the electron of a hydrogen atom occupies orbital 1s. For the carbon atom, which has six electrons, two electrons will occupy shell-1 on an s-subshell with opposite spin (due to Pauli's Principle), two more will occupy shell-2 on an s-subshell, and the other two will occupy shell-2 on a p-subshell.[115]

This method of specifying the electronic configuration of atoms shows the mechanism which is responsible for the structure of atoms. Specifically, the number of electrons that fill the last atomic orbital and the particular characteristics of the atomic orbital (in terms of the quantum numbers that specify it), determine the overall structure of the atom, and subsequently its chemical behavior. This is particularly important for the chemical description of atoms and molecules since, specifying the structure of each atom explains the particular bonds that are formed with other atoms within the molecule, and thus contributes to the explanation and prediction of the structure and reactivity of the molecule. Given how Kincaid's criterion is formulated here, the aforementioned method inductively supports that chemical properties supervene on quantum mechanical properties.

4.2.5 Chemistry and quantum mechanics heuristically depend on each other

For the two theories to be considered heuristically dependent on each other, it should be the case that both quantum mechanics and chemistry:

i. have enriched or influenced the research questions that concern the other; and,
ii. have developed methods or models that have accommodated the research questions of the other.

Indeed, chemistry and quantum mechanics have enriched the research questions of each other. For example, quantum mechanics led chemists to further investigate the structure of atoms and to incorporate in the chemical description quantum mechanical postulations about the structure of atoms (see for example

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[115] Which subshell must be filled first is indicated by the designated sequence (i.e. 1s, 2s, 2p, 3s, 3p, 3d, …).

(Pullman 1998)). Conceptual issues, such as the nature of the chemical bond, still maintain a lively debate among chemists and physicists, because quantum mechanics reveals the existence of factors that affect the conceptual understanding of basic chemical concepts ((Hendry 2008), (Sutcliffe 1996), and (Weisberg 2008)). Chemistry also raised questions that enriched quantum mechanical research. For example, different quantum models are continuously being developed in order to expand the quantum mechanical description to various kinds of entities (i.e. atoms, diatomic molecules, polyatomic molecules, metals, etc.) that are standardly examined in chemistry (see for example (Hayward 2002: 136- 166) and (Becke and Dickson 1990)).

Moreover, the history of chemistry, quantum mechanics, and quantum chemistry provide evidence that chemistry and quantum mechanics have exchanged tools, methods and models. Chemists have gained a substantial amount of quantitative and qualitative information concerning molecular structure by quantum models that solve, via approximations and idealizations, the Schrödinger equation for different types of atoms or molecules. Certain techniques manage to give us accurate descriptions of small molecules, whereas others are more successful in describing larger (polyatomic) molecules, or types of matter (such as metals) (Hofmann 1990). Moreover, through the development of the Molecular Orbital approach, quantum chemists developed novel visual representations of molecular orbitals that enriched chemistry's understanding of molecular structure in organic chemistry (see for example (Dewar 1952) and (Fleming 2009)).[116]

All in all, the history of chemistry, quantum mechanics and quantum chemistry illustrate how the theories have utilized each other's models in order to expand their research and accommodate their explanatory, heuristic, and predictive needs (Gavroglu and Simões 2012b). Currently, this interdependence between chemistry and quantum mechanics has been extended to a wide range of sub-disciplines where quantum mechanical models are used (such as material science, drug design, etc.) (Matta 2013: 245). Based on all the above, Kincaid's criterion is satisfied.

4.2.6 Chemistry and quantum mechanics confirmationally depend on each other

Another important requirement is that the two theories confirmationally depend on each other. Kincaid does not provide a general specification of this requirement such that could underwrite any pair of theories; rather he examines it with respect to particular pairs (i.e. biology and chemistry, and individualism and macroeconomics). In light of this, this subsection presents how this requirement is understood and supported for the case of chemistry and quantum mechanics. This subsection disregards philosophical

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[116] Andrea Woody also points out that quantum mechanical models derive 'contemporary algebraic and diagrammatic representations of molecular systems' (2000: S612).

discussions about confirmation and problems related to this notion (such as the problem of induction). Nevertheless, confirmation is broadly understood here as referring to the support of a theory or hypothesis by any data or evidence, as this is understood by the relevant scientists.

First, the results of chemical experimentation have played a vital role both in the development and in the evaluation of quantum models:

> It is not unfair to say that (…) in practically the whole of theoretical chemistry, the form in which the mathematics is cast is suggested, almost inevitably, by experimental results. This is not surprising when we recognize how impossible is any exact solution of the wave equation for a molecule. Our approximations to an exact solution ought to reflect the ideas, intuitions and conclusions of the experimental chemist. (Coulson 1961: 113–14)

What Coulson's quote suggests is that the quantitative results of quantum models are compared with experimental results in order to evaluate the accuracy of those models, and determine what changes are required so as to minimize error (see for example (Becke and Dickson 1990)). Those experimental results are provided through the work of experimental chemists who, with the use of spectroscopic and other techniques, calculate chemical properties. This aspect of confirmational interdependence is also illustrated by Michael Weisberg, who evaluates the predictive success of different quantum models, by comparing the calculation of the dissociation energy and the equilibrium distance of atomic nuclei in quantum models, with the respective results of chemists' experimental calculation of the dissociation energy and bond length (2008: 936-940).

Secondly, novel predictions of chemical phenomena have been made with the help of quantum mechanics. For example, the specification of atomic structure by quantum mechanics helped chemists understand spectroscopic results and thus predict novel elements, in accordance to the periodic table (Needham 2004: 213). Moreover, quantum models have made novel predictions about, among others, pericyclic reactions (Hendry 2004: 1057), large molecules, and metals. These predictions enriched chemical knowledge and contributed to the confirmation of chemistry's theoretical postulations.

These two points show how the two theories confirmationally depend on each other. The following subsection presents the last (and thus most important) criterion in Kincaid's model.

4.2.7 Chemistry and quantum mechanics explanatorily depend on each other

Kincaid does not assume a particular philosophical model of explanation (such as deductive nomological, SR model, causal mechanical, etc.; see for example (Curd and Cover 1998)) (1997: 80). He defines explanation to be 'an answer to a why-question' that 'must be specified according to contextual parameters' (1997: 78-79). Specifying the contextual parameters is necessary for Kincaid, because a why-question can take different possible answers. Therefore, picking the relevant answer requires that one specifies 'why the topic of the question arose', what factors are taken to be relevant to the question, and what are the particular background assumptions that are made when raising the question (Kincaid 1997: 79).

Having specified explanation in this manner, Kincaid states that the explanatory power of a theory can be evaluated by (i) 'its ability to answer any given, fully specified question' and (i) 'the number of relevant questions it can answer' (1997: 79). Based on this, he argues that lower-level theories provide only incomplete and partial explanations to why-questions. This is because there are why-questions that are specified in terms of concepts postulated by higher-level theories. There is no way to provide an answer to such questions by employing only concepts or predicates of the lower-level theory.

> As a result, lower-level theories will necessarily leave a great many questions unanswered. (Kincaid 1997: 81)

This does not imply that lower-level theories do not contribute to the explanation of higher-level events; 'supervenience and realisation can ensure, at least under some conditions, that lower-level theories do explain higher-level events' (Kincaid 1997: 86).

Based on Kincaid's analysis of explanation, the relevant criterion holds if the following is the case. There is a non-empty set of why-questions that a theory can answer 'fully', only if it makes reference to concepts, postulates, or explanations of the other theory. That is, if one theory does not make reference to the other, then its answer to certain why-questions is incomplete and partial.

Indeed, there is evidence which shows that this is the case with respect to chemistry and quantum mechanics. Specifically, advances in quantum mechanics have enriched chemical explanations of molecular behavior and at times even led to their revision. Also, chemical explanations have been used in the development of quantum models and have guided quantum chemists towards a more accurate interpretation of the mathematical description of atoms and molecules (namely via the Schrödinger equation). In fact, genuine explanatory differences both between different quantum models, and between quantum models and chemistry have raised discussions in order to consolidate or review the explanatory account of one or both theories.

Consider the following examples:

- As already illustrated, quantum mechanics provides chemists a mechanism to specify and explain atomic structure in terms of electron configuration (subsection 4.2.4). This proves particularly helpful in the explanation of the periodic table and of its success in classifying chemical elements according to similar chemical and physical properties. Despite the fact that the periodic table was constructed long before the advent of quantum mechanics, quantum mechanics explains why chemical elements that belong in specific vertical and horizontal columns in the periodic table, exhibit particular similarities.[117]

- Quantum mechanics has contributed to chemistry's explanations of molecular structure. For example, the development of the Molecular Orbital approach in quantum mechanics has revealed the effect of electron delocalisation on the overall stability of a molecule. Modern versions of the Molecular Orbital approach, like the Hartree-Fock method and the Configuration Interaction approach, take into account the repulsion of electrons, the ionic character of chemical bonds, and the mixing of higher energy states, thus enriching chemistry's understanding of a molecule's structure (Weisberg 2008: 939-943).

- Quantum mechanical models that are employed for the solution of the Schrödinger equation for complex atoms and molecules, have been calibrated or corrected by employing postulations, theoretical assumptions, and explanations from chemistry (Hendry 2010b: 183). To the extent that these models contribute to the explanation of the atoms and molecules which they are describing, it follows that chemistry contributes, in the aforementioned manner, to the formulation of these explanations.

Concluding this section, there is sufficient evidence that supports the heuristic, confirmational, and explanatory interdependence of quantum mechanics and chemistry. This epistemic interdependence, together with the satisfaction of composition/token identity, supervenience and the logical compatibility of the two theories, define unity and support that quantum mechanics and chemistry are unified.

The next section presents how Kincaid defines reduction and briefly presents the grounds on which he rejects it.

4.3 Kincaid's rejection of reduction

Together with presenting a particular model of unity, Kincaid also examines the tenability of reduction. This is a sensible thing to do when looking at the appropriate understanding of the relation between two theories. If reduction is successful, then there is no need to investigate alternative understandings of unity. This is

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[117] The history of how the periodic table is presented in (Scerri 2007c).

because reduction is standardly regarded as the strongest unificatory relation. Therefore, if it is successful then any postulated relation that is weaker, is obsolete.

Kincaid understands reduction as follows:

> one theory reduces another when it can do all the explanatory work of the reduced theory (1997: 5)

According to Kincaid, a (necessary but not sufficient) requirement for reduction is that there are 'lawlike mappings from each' chemical description to a quantum mechanical one that 'allow us to deduce the true or well-confirmed explanations of' chemistry in such a way that chemical 'explanations are completely replaced by' quantum mechanical ones (1997: 14). Kincaid argues that reduction must at least include the idea that the lower-level theory can 'do all the explanatory work of the reduced theory' (1997: 5). According to Kincaid, any notion of reduction that does not require or entail 'explanatory completeness' (in the sense just specified) is not a genuine and interesting reductive thesis (1997: 5):

> To claim reduction while admitting explanatory incompleteness is to make the issue a trivial semantic one. (1997: 5)

Based on Kincaid's understanding of reduction, alternative theses that are labelled as reductions do not challenge Kincaid's unity because in the context of Kincaid's analysis, they do not represent genuine reduction. Nevertheless, this does not mean that such theses are necessarily rejected by the model. For example, one could argue that the correct thesis of reduction is a particular account of ontological reduction. In light of the above, Kincaid would reject calling such an account a reduction (or he would argue that it collapses to his own understanding of reduction). Nevertheless, if this account of ontological reduction is consistent with the criteria of the model and if it does not imply Kincaid's understanding of reduction, then it can be considered as a further contribution to the model's postulated metaphysical relationship.[118]

Returning to Kincaid's understanding of reduction, he identifies three basic 'problems' to reduction. The first is multiple realizability ((1997: 50-51), see also subsection 4.2.3). The second is 'the problem of context sensitivity' (1997: 51). According to this, 'it might well be that events described in lower-level terms are not uniquely correlated with some higher-level description, depending on the context' (1997: 51).[119] The third

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[118] For example, it would be interesting to examine whether Kincaid's rejection of reduction is compatible with Paul Oppenheim's and Hilary Putnam's unity thesis (Oppenheim and Putnam 1958).

[119] This problem is not examined here.

problem is that of 'presupposing higher-level explanations' for the construction of lower-level explanations (1997: 51).

This section accepts without further inquiry that these three problems represent an obstacle to reduction on Kincaid's understanding of that term. That is, if there is empirical evidence that any of the three problems occur, then this suffices to reject reduction, as the latter is formulated and understood by Kincaid.[120] Notice that these problems to reduction are not only permissible, but also part of Kincaid's model of unity. For example, multiple realizability is compatible with the model because supervenience is defined in such a way that permits it. Moreover, the use of higher-level explanations in the formation of lower-level ones is explicitly required by the last criterion (see 4.2.7).

Regarding chemistry and quantum mechanics, this section argues that the problem of 'presupposing higher-level explanations' occurs with respect to chemistry and quantum mechanics. Showing that this problem occurs, suffices to reject reduction for the examined pair of theories. The problem of 'presupposing higher-level explanations' occurs with respect to chemistry and quantum mechanics, for three main reasons.

First, notice that the use of higher-level explanations in the formation of lower-level ones is explicitly required by the last criterion (see 4.2.7). In this context, 'presupposing higher-level explanations' has already been shown to apply for the examined pair of theories, via the examples that were presented in order to support the last criterion of the model. Secondly, there is one more example that further supports the existence of this problem with respect to chemistry and quantum mechanics. According to Kincaid, one way in which the problem of presupposing higher-level explanations occurs is if the lower-level theory uses 'higher-level information in its explanations' (1997: 51). Indeed, this is the case with the quantum mechanical description of a single inert molecule. The quantum mechanical description of a single inert molecule describes (and explains) all the molecule's properties only after it has incorporated information regarding that molecule's structure. This is done via the Born-Oppenheimer approximation, which fixes the nuclear geometry of the examined molecule in order to then solve the relevant Schrödinger equation. The nuclear geometry that is assumed, is taken from chemistry's analysis of the molecule and its structure.[121]

Thirdly, the manner in which Kincaid understands reduction closely resembles how the philosophy of chemistry literature understands strict Nagelian reduction (see chapter 3). Recall that strict Nagelian reduction at least requires the (in principle) derivation or deduction of chemistry from quantum mechanics ((Needham 2010: 164) and (Hettema 2017: 7)). Therefore, the success of strict Nagelian reduction would

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[120] Kincaid explains why these issues pose a problem to reduction (1997: 50-51).

[121] This assumption is examined in detail in the next two chapters, as well as in section 2.2.

imply the deduction of chemical explanations from quantum mechanics (as specified by Kincaid's notion of reduction). Since there is a consensus in the philosophy of chemistry that such a reduction fails, this section does not examine the evidence that supports this claim. Instead, it takes as decisive the objections that have been raised in the literature against the tenability of strict Nagelian reduction. This further reinforces the rejection of Kincaid's understanding of reduction, and thus of his proposed model of unity.

4.4 A critical analysis of Kincaid's model

This section evaluates Kincaid's model by addressing three questions. First, what sort of unity does the model involve? Secondly, can two theories be regarded as autonomous given such unity? Thirdly, what is the main difference between Kincaid's model of unity and positions involving unity of some kind that have been presented in the philosophy of chemistry literature?

Kincaid's model is primarily an epistemic position; it provides an understanding of how the theories are unified. This is evident given the nature of the criteria that define his sort of unity. Logical compatibility, as well as the explanatory, heuristic and confirmational interdependence are epistemic requirements that concern how a single inert molecule is described. On the other hand, the criteria of composition/token identity and of supervenience are metaphysical requirements about the relation between the postulated entities, properties, etc. In the light of this, Kincaid's model of unity is a metaphysical position as well.

Nevertheless, there are various aspects of the epistemic and metaphysical relations between the two theories that are not specified by Kincaid's model. Therefore, any epistemic or metaphysical position that specifies in more detail some aspect of their relation and which is compatible with the model, ought to be acceptable within Kincaid's overall framework. For example, the relation between the postulated properties could be as in non-reductive physicalism, if the latter position is compatible with the criteria of the model (see section 4.2). As another example, consider 'local reduction' as this is explicated by Kim (1992) in the sense of making 'local or contextual identifications' between particular higher and lower-level kinds (van Riel and Van Gulick: section 3.3). Specifically, 'if we individuate the high-level kinds in a more fine-grained way, we can save a weaker form of type-identity theory', despite higher-level kinds being multiply realized (van Riel and Van Gulick: section 3.3.). This account is prima facie compatible with Kincaid's less specific account, provided it satisfies the latter's criteria.[122]

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[122] Obviously, this section does not do justice to the vast literature that could further specify Kincaid's model of unity. Nevertheless, this section illustrates that Kincaid's understanding of unity can be illuminated or specified by looking at how the philosophy of science literature examines unity (as well as disunity, as it is shown below).

A similar approach can be followed with respect to pluralist positions, in particular, those that defend 'a plurality of theories or models in describing the *same* (single) domain of phenomena' (Bokulich 2008b: 9).[123] For example, Kincaid's model may be compatible with the view that science is a pluralist enterprise that consists of multiple different subcultures, each of which focuses on investigating a particular set of research questions and employs partially distinct tools, concepts, methodologies, and experiments (see for example (Schummer 2014) for the presentation of such a position with respect to chemistry).[124] However, the model is incompatible with any pluralist position according to which these disagreements or differences in methods, tools, etc. constitute sufficient reason to regard the theories as disunified.

Moreover, Kincaid's model is inconsistent with pluralist positions which either implicitly or explicitly contradict the seven requirements of the model.[125] For example, Paul Feyerabend supports the following position:

> introducing a new theory involves changes of outlook both with respect to the observable and with respect to the unobservable features of the world, and corresponding changes in the meaning of even the most "fundamental" terms of the language employed. (1962: 29)

This position is incompatible with Kincaid's model. This is because Kincaid's model can only support the logical compatibility and the explanatory (but also confirmational) interdependence of two theories if the meaning of the terms (of these theories) which are involved in the support of the model's criteria, are at least to some extent invariant (Feyerabend 1962: 30). Moreover, positions of metaphysical pluralism, such as those advocated by Nancy Cartwright (1999) and by John Dupré (1993), are not prima facie consistent with Kincaid's metaphysical requirements and, thus, with his advocated unity. In general, Kincaid's unity is not compatible with pluralist theses which support the following view:

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[123] According to Bokulich, there is a 'family of approaches' that can be understood as defending some sort of pluralist position. She distinguishes between three 'types' of positions. Type-I 'defends the necessity of multiple scientific theories or models in describing *different* domains of phenomena' (2008b: 8). Type-II was just defined in the main text of this section. Type-III argues for both type-I and type-I (2008b: 8-9).

[124] This section does not support these positions; it merely outlines what sort of positions may be consistently supported if one accepts Kincaid's unity. Also note that this is a very brief overview of the alternative positions that could be examined with respect to Kincaid's unity. Alternative pluralist positions can be found in (Kellert et al. 2006), (Fodor 1974) and (Fodor 1997).

[125] Another 'thesis of incommensurability' is proposed by Thomas Kuhn ((Kuhn 2012) - see also (Bokulich 2008b: 9) for a brief overview of what she labels as 'theoretical pluralism').

> What begins to emerge from these defences of theoretical pluralism is a view of science as "radically fractured" with distinct scientific communities whose respective members have difficulty communicating with each other. The image that Cartwright uses to illustrate her pluralism is one in which scientific theories are likened to isolated balloons- tethered to the empirical world- but not intimately interconnected with each other. If each theory has its own proper domain, then it would seem that the search for intertheoretic relations and interdependencies is fundamentally misguided. (Bokulich 2008b: 11-12)

In light of all the above, it is evident that there are many open questions that require investigation even if we accept Kincaid's model. This is because this model is not a complete account of how the postulated ontologies are related, nor of whether (and on what grounds) the higher-level entities, etc. are real. Moreover, there are various aspects of the model that have not been specified in much detail. This includes not only the specification of composition, but also the specification of mechanisms (4.2.4), of confirmation (4.2.6), and of explanation (4.2.7). Nevertheless, the model provides a context in which unity-without-reduction can be discussed.

How does the model affect one's view of the autonomy of the two theories? This depends on the particular understanding of autonomy. If autonomy requires that the relevant theories (i) postulate properties that have no ontological connection, (ii) employ and develop independent confirmatory tools and methods, and/or (iii) propose independent explanations of some common set of phenomena, then chemistry and quantum mechanics are not autonomous.[126]

On the other hand, if autonomy is defined in the sense that the two theories achieve distinct and (partially) independent research goals (whilst allowing epistemic and metaphysical interconnections and dependencies), then chemistry and quantum mechanics, as well as the sub-disciplines that are formulated within each, are autonomous. How autonomy can be defined and what its requirements are, is an issue that deserves a more detailed analysis than the present one. Nevertheless, the present analysis provides some direction to how this issue can be addressed within Kincaid's model of unity.[127] For example, Kincaid's non-reductive unity may be compatible with a notion of autonomy that posits 'far more in the way of local rules, cultures, ontologies, and epistemologies than a reductionist account, which sees scientific practice as (at

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[126] This section does not examine 'explanatory autonomy' as this is investigated by Philip Kitcher (1984: 371-372).

[127] For more on this issue see, for example, (Dupré 2016: 183), (Radder 2010: 18-19), (Strevens 2016: 153-181) and (Woodward 2016). In the philosophy of chemistry literature see (Hettema 2017: 274-278) and (Needham 2010).

bottom) unified' (Strevens 2016: 172).[128] Moreover, the defense of autonomy does not necessitate the support of a pluralist position (as mentioned above). In fact, the pluralists' understanding of autonomy may be partially accommodated within a unificatory framework, such as that proposed by Kincaid.

Turning to where Kincaid's unity is positioned with respect to other positions on unity in the philosophy of chemistry literature, the most relevant work is that of Needham and Hettema who specifically consider the unity between chemistry and quantum mechanics. According to the former, positions on unity can be distinguished into four groups:

> (i) unity in virtue of reduction, with no autonomous areas, (ii) unity in virtue of consistency and not reduction, but still no autonomy because of interconnections, (iii) unity in virtue of consistency and not reduction, with no autonomous areas, and (iv) disunity. (Needham 2010: 163-164)

Hettema (2017) adds two more groups in order to specify where his proposed position of unity falls. He states that his position is a reductive account which, contrary to (i), primarily understands reduction in a 'loose' sense and also advocates the existence of autonomous areas. Hettema's position is taken to 'occasionally' 'spill-over' to another form of unity which advocates for a notion of 'para-consistency' and reductionism (this last form of Hettema's unity is not further examined here) (2017: 277).

Based on the above, the first form of unity (i.e. (i)) is on a par with Kincaid's unity because the latter rejects the sort of reduction that is advocated by (i); namely 'reductionism in which derivation is strict and reduction postulates are identities' ((Hettema 2017: 277), see also section 4.3). The third form of unity (i.e. (iii)) is also on a par with Kincaid's model of unity because, contrary to Kincaid's model, it disregards the 'idea that one science may fruitfully explain aspects of another' (Hettema 2017: 278). Disunity (i.e. (iv)) is understood with reference to Dupré and, therefore, is contrary to Kincaid's model (Hettema 2017: 277).

One way to understand Kincaid's model is in terms of the second form of unity (i.e. (ii) above). This is because Kincaid's unity is a non-reductive position which supports the consistency of the two theories and proposes particular interconnections between them. Hettema argues that this form of unity, as it is presented by Needham, faces certain challenges. For example, in this form of unity 'the nature of the "interconnections" is (..) not well specified in Needham's scheme' (Hettema 2017: 277). Moreover, 'the theories of chemistry and physics are not as strongly dependent on each other as implied (though not stated)

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[128] This point is by no means sufficiently supported here; it is made to provide an example of how autonomy might be defended if one accepts Kincaid's model of unity.

in position (ii) in the scheme' (Hettema: 277-278). In light of these objections, this chapter takes that Kincaid's model is a better version of Needham's second form of unity, because it specifies these interconnections. This makes it a valuable contribution to the philosophy of chemistry.

Another way to understand Kincaid's model is in terms of Hettema's form of unity which proposes a 'loose' sense of reduction and the autonomy of the respective theories (see above). Since Kincaid's model rejects only a strict reduction (as specified in the previous section), it is prima facie compatible with Hettema's 'loose' understanding of reduction. This section does not further examine the compatibility of Hettema's position with Kincaid's model, which would require a detailed analysis of the former.[129] In any case, Kincaid's model is an alternative to Hettema's position because, contrary to the latter, it does not employ additional terms and concepts in order to specify the relation between the two theories. For example, Hettema's position is formulated in terms of 'linkages', 'networks', and 'nets' (2017). On the other hand, Kincaid's model employs concepts that are common in the philosophy of science literature; i.e. explanation, confirmation, supervenience, composition, etc. This makes it a simpler model because it accommodates the specification of the two theories' relation within the context of the standard literature.

4.5 Summary

Kincaid's model of unity successfully applies to the relation between chemistry and quantum mechanics. Specifically, chemistry and quantum mechanics are unified in the sense that they exhibit particular metaphysical and epistemic interconnections and dependencies. Moreover, a central feature of this model of unity is that it neither entails, nor requires the strict reduction of one theory to another. Lastly, the model may be compatible with additional epistemic and/or metaphysical claims regarding the two theories.

The next chapter critically examines one disunity thesis that is discussed extensively in the philosophy of chemistry literature; namely Robin Hendry's account of strong emergence. Since it is assumed here that Kincaid's unity is incompatible with strong emergence (see 4.2.1), it is crucial to investigate whether there is sufficient evidence for strong emergence, as the latter is understood by Hendry. Chapter 5 argues that Hendry's strong emergence with respect to chemistry and quantum mechanics faces problems. This further supports the unity (as per Kincaid) of the two theories.

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[129] For example, one would need to examine whether Hettema's loose understanding of reduction (as he calls it) implies Kincaid's understanding of reduction (even if prima facie this does not seem to be the case). If, however, this is the case, then Hettema's account is not compatible with Kincaid's model of unity.

5. Strong Emergence

Robin Hendry argues that the structure of a single inert molecule strongly emerges from its quantum mechanical entities. He specifies this with reference to downward causation, according to which, ‘the emergent behavior of complex systems must be viewed as determining, but not being fully determined by, the behavior of their constituent parts’ (Hendry 2006: 180).

The previous chapter argued that strong emergence is incompatible with Kincaid’s model of unity (see subsection 4.2.1). If this is correct and if strong emergence is a coherent and tenable position, then Kincaid’s model might not apply to the case of chemistry’s relation to quantum mechanics. This chapter argues that strong emergence is not tenable and, therefore, Kincaid’s model is compatible with the actual epistemic and metaphysical relations between the two theories.

It should be noted that Kincaid’s model may be challenged by alternative emergentist accounts which are different from Hendry’s position. Such accounts are not examined in this thesis. This is because there is no unique account of emergence that one could investigate and thus contrast to Kincaid’s model (see section 5.1). Instead, there is a proliferation of many different and sometimes incompatible accounts of emergence. In this context, the question of whether there is a tenable emergentist position that challenges Kincaid’s model remains to an extent open. Nevertheless, since Hendry’s strong emergence is the most prevalent position regarding the examined pair of theories, it is sensible to focus on this.[130]

Section 5.1 outlines how emergence is discussed in the philosophy of science and identifies the main disagreements that make it difficult to agree upon a standard account of emergence. Section 5.2 presents strong emergence and defines downward causation (DC), as this is argued for with respect to the examined pair of theories. Section 5.3 examines downward causation in the context of Kim’s distinctions between diachronic and synchronic, and between reflexive and non-reflexive DC. In the context of these distinctions, the chapter argues that DC is problematic and so Hendry’s account of strong emergence is not plausible.

5.1 Emergence

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[130] Another emergentist position which is defended with respect to chemistry’s relation to quantum mechanics is contextual emergence (as presented in (Bishop and Atmanspacher 2006), see also (Hettema 2017: 55)). This position is not examined here mainly because there is not a lot of literature in the philosophy of chemistry which discusses this position.

The term 'emergence' is used in the philosophy of science to describe a relation:

- between scientific theories, descriptions, or representations (this is usually labelled as 'epistemic' or 'weak' emergence, see for example (Clayton and Davies 2006: 244 -255)); or,
- between entities, properties, etc. that occupy at least partially distinct levels or scales of ontology (this is usually labelled as 'ontological', 'metaphysical', or 'strong' emergence).[131]

While the distinction between epistemic and metaphysical emergence is to an extent accepted in the literature, any further attempt to specify emergence falls short of wide agreement.[132] In general, there is no single, standard, and widely accepted account of emergence. As Paul Humphreys states:

> In the case of emergence, there are too many different uses of the term "emergence" that are entrenched across various fields for a single comprehensive definition to be possible at this point in time or, perhaps, ever. (2016: 26)

In fact, there are six kinds of disagreements in the current literature that obstruct the acceptance of a standard account of emergence.[133] First, it is often assumed that emergence is understood differently in philosophy and differently in the sciences.[134] For example, according to Elanor Taylor, discussing emergence becomes 'difficult when we turn to scientific uses of the concept of emergence, which are often taken to be radically discontinuous with philosophical approaches' (2015: 654).[135] Interestingly, this difference between

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[131] The term 'weak emergence' is also taken to refer to a metaphysical position. For example, Umut Baysan and Jessica Wilson take that 'accounts of metaphysical emergence (…) are typically characterized as either "weak" or "strong", reflecting whether or not the emergence at issue is supposed to be compatible with physicalism' (Baysan and Wilson 2017: 51). In order to avoid confusion, this chapter uses the terms 'epistemic' and 'metaphysical emergence' in order to distinguish (emergentist) views about the relation between scientific theories/descriptions/representations from views about the relation between entities, etc.

[132] An exception is Humphreys' account which presents a taxonomy of emergence that doesn't involve the distinction between epistemic and metaphysical emergence (2016). A detailed analysis of the current disagreements about emergence is provided in (Wilson 2015).

[133] These may not be the only kinds of disagreements in the literature. Nevertheless, the disagreements that are presented here sufficiently illustrate why a standard account of emergence does not currently exist.

[134] This section does not necessarily agree that this sort of difference between the philosophical and scientific understanding of emergence, indeed exists. The point here is to highlight that such a disagreement exists in the relevant literature.

[135] Taylor challenges the existence of such a discontinuity between the scientific and philosophical use of 'emergence' by arguing that the two notions are continuous. Specifically, she argues that there are certain elements (i.e. unpredictability,

the philosophical and the scientific use of the concept is not unique to 'emergence'. For example, discussions concerning reduction may differ in the two communities as well. The way physicists understand reduction is different from certain philosophical accounts of inter-theoretic reduction (see for example (Nickles 1975), (Batterman 2002) and (Batterman 2010)). However, while there is a difference between the scientific and philosophical use of the term 'reduction', it is not a stretch to say that Nagel's account of reduction is regarded as a standard understanding of reduction within the philosophical literature (Nagel 1979).[136] The same cannot be said about emergence.

This becomes apparent by the second kind of disagreement about emergence. Specifically, there are philosophical accounts that define and describe emergence by reference to sets of terms that are at least partially distinct. This makes it difficult to compare alternative accounts of emergence. Jaegwon Kim makes this point as follows:

> those discussing emergence, even face to face, more often than not talk past each other. Sometimes one gets the impression that the only thing that the participants share is the word emergence. (2006: 548)

For example, Michael Silberstein argues that metaphysical emergence can be specified in four different ways; namely in terms of 'non-elimination', 'non-identity', 'mereological emergence/holism', or 'nomological emergence' (2002: 90). Moreover, epistemic emergence can be specified either in terms of 'predictive/explanatory emergence', or in terms of 'representational emergence' (Silberstein 2002: 92). On the other hand, Humphreys' classification is 'two dimensional' (2016: 38). The first ('relational') dimension consists of 'ontological emergence', 'inferential emergence', and 'conceptual emergence' (2016: 38-39). The second ('temporal') dimension consists of 'synchronic and diachronic emergence' (2016: 39).

A third kind of disagreement arises with respect to how the postulated (epistemic or metaphysical) relation is specified. Its specification varies to such an extent that it is often not possible to compare alternative accounts of emergence. For example, Wilson outlines four alternative understandings of the relation regarding metaphysical emergence; namely in terms of 'material composition, modal covariation, causation or causal dependence, and functional or other realisation' (2015: 363). Each of these understandings can be further specified by use of alternative terms (Wilson 2015: 364-372). Another point of disagreement has to do with the role of time in the specification of the relation. For example, the relation may be considered only

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failure of deducibility, underivability, unexplainability) that are regarded by the scientific community as signs of emergence (possibly even of the metaphysical kind) and which illustrate some level of continuity with the philosophical accounts of emergence (2015: 656-658).

[136] This doesn't mean that all philosophers endorse such an account of reduction.

diachronically (Kim 1999: 31), whereas others allow a synchronic understanding as well (Humphreys 2016: 39).

A fourth kind of disagreement lies in the specification of the relata that participate in the postulated relation. Regarding metaphysical emergence, philosophers speak of emergence between parts and wholes, properties, events and processes, causal capacities, laws, entities (Silberstein 2002: 90), features (Wilson 2015: 373), or phenomena (Batterman 2011: 1031). Most commonly, philosophers use some set of the aforementioned notions interchangeably, without implying a change in content (for example (Wilson 2015: 349)). In this context, it is implicitly assumed that the relata that primarily participate in the postulated relation are properties, and that the respective entities, phenomena, etc. are emergent in virtue of the emergent properties (Bedau 2002: 7). There are however accounts of emergence that disagree on this point. For example, Batterman argues that emergence in terms of properties is 'a mistake' when examining emergence with respect to physical theories, and that emergence should be discussed in terms of emergent phenomena (2011: 1031). Moreover, regarding epistemic emergence, the relata can vary as well, including for example emergent concepts, theories, models, frameworks, or laws (Silberstein 2002: 90).

A fifth disagreement concerns the appropriate criteria that need to be satisfied in order to support emergence. For example, some accounts take 'explanatory irreducibility' to be the deciding criterion for emergence ((Bedau 2002: 48) and (Kim 1999: 21)). Other criteria include epistemic/conceptual novelty ((Butterfield 2011a) and (Butterfield 2011b)), the irreducibility of theories, or unpredictability (Batterman 2011: 1031). Humphreys sets out his own criteria for emergence which include novelty, autonomy, and holism (2016: 26).

Lastly, emergentist accounts often differ in that they are formulated with respect to different domains of inquiry. Some accounts are restricted to investigating emergence with respect to physical theories or physical phenomena (Batterman 2011: 1031). For example, this includes the examination of non-linear thermodynamic phenomena (Baysan and Wilson 2017: 52). Other accounts focus on the special sciences and/or their postulated entities, properties, etc. For example, Mark Bedau examines weak emergence in relation to cellular automata (Bedau 2002: 44) and Robin Hendry examines strong emergence in relation to molecular structure (Hendry 2006). Also, note that certain accounts support emergence only for a specific domain of theories or phenomena (for example (Hendry 2006)), whereas others make claims about emergence that allegedly underwrite a larger domain of phenomena or theories (for example (Humphreys 2016) and (Wilson 2015)).

Based on the above, the literature is highly divergent with respect to how emergence is understood, specified, and supported. In reply to this divergence, some philosophers propose a unified understanding of emergence either by arguing that there is a specific set of notions that underwrite all accounts, or by showing how all existing accounts are compatible with their proposed unified account of emergence. For example, Wilson argues that all the different accounts and understandings of metaphysical emergence conform to either 'Weak' or 'Strong emergence'; i.e. a proposed schema of metaphysical emergence that she argues is complete and exhaustive ((Wilson 2015: 348), see also (Taylor 2015)).[137] Others present novel concepts that allegedly specify more accurately emergence. For example, Carl Gillett introduces the concept of machresis; i.e. 'The non-productive determinative relation between composed and component entities such that composed entities determine some of the powers of their components through role-shaping or role-constraining' (2016: 359).

This chapter does not follow any of the aforementioned strategies in order to examine emergence. Instead, it examines the account which is explicitly invoked by Hendry in the case of chemistry's relation to quantum mechanics, and which is strong emergence in terms of downward causation (see (Hendry 2006), (Hendry 2010a)). Other accounts of metaphysical emergence, as these were specified above, are not examined. This also includes accounts that primarily focus on the relation between physical parts and wholes, and accounts that deny the existence of a dependence relation (namely dualist accounts, such as (Hasker 1999)). Epistemic emergence is not investigated either. However, elements of epistemic emergence (i.e. irreducibility, unpredictability, etc.) are considered to the extent that they are relevant to the examined metaphysical claim. Finally, the nature of the relata, whether only properties, or also entities, phenomena, systems, or processes that are taken to participate in the postulated relation, is not considered here. As with supervenience (see previous chapter), this chapter takes entities and properties to be the relata for the purposes of the discussion. This should be understood rather loosely to refer to any sort of thing that, in a particular domain of phenomena, allegedly emerges. For example, in the case under examination what allegedly emerges is molecular structure. While the latter is intuitively understood as a property of molecules, this is not examined in detail.

Obviously, this is an incomplete analysis of emergence with respect to chemistry, but this is unavoidable in the light of the extensive disagreements that were explained above. Hendry's account of strong emergence in terms of downward causation is the most widely discussed account of emergence with respect to chemistry and quantum mechanics.

5.2 Strong emergence in terms of downward causation

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[137] According to this schema, strong emergence 'requires that higher-level features have more token powers than their dependence base features', whereas weak emergence 'requires that higher-level features have a proper subset of the token powers of their dependence base features' (Wilson 2015: 343).

There are three core elements that underwrite Hendry's understanding of strong emergence. These are:

(i) A hierarchy of levels;
(ii) the existence of a dependence relation; and,
(iii) the causal autonomy of the higher-level.[138]

(i) suggests that the entities postulated by the examined pair of theories reside in different levels of ontology. As Humphreys states, 'there is an ontology that is divided into an ordered hierarchy of levels, with the more fundamental entities occurring toward the bottom of that hierarchy' (2016: 8). Whether the postulation of a hierarchy of levels is necessary for strong emergence, is not examined; it is taken for granted as being one of its core elements.[139] Moreover, a discussion concerning how 'levels' should be understood isn't pursued here.[140] The thesis takes 'levels' to refer to distinct energy, length, and/or time scales.[141] In this context, strong emergence takes nature to be divided into distinct scales of ontology that the physical and special science theories specify by postulating entities, properties, etc. that are found at distinct (yet possibly overlapping) energy, length, and/or time scales.[142]

(ii) involves the postulation of a dependence relation between higher and lower-level entities. While there are alternative understandings of this dependence relation, this chapter understands it in terms of supervenience (see for example (Wilson 2015: 347)). That is, the higher-level properties participate in a dependence relation with lower-level properties in the sense that the former supervene on the latter. The previous chapter defined supervenience with respect to the relation between chemical and quantum mechanical properties, and in accordance to Kincaid's understanding of the notion.[143] According to this definition, supervenience postulates the existence of a relation between chemical and quantum mechanical

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[138] While the presented account of strong emergence is based on Hendry's work, its current explication makes reference to other philosophers that have also examined this account (namely (Wilson 2015), (Humphreys 2016), (Kim 1999) and (Kim 2006)). Their understanding of strong emergence is not incompatible with Hendry's account and it contributes to a more specific understanding of his account of strong emergence.

[139] Humphreys, for example, examines the possibility of there being no levels (2016).

[140] See, for example, the discussion of levels in terms of mechanisms in (Bechtel 2017) and (Eronen 2013). Also, note that this chapter does not examine whether there is a final, fundamental lower level.

[141] Although the existence of a hierarchy of levels is not explicitly stated by Hendry, this section takes it to be compatible with how he understands strong emergence.

[142] See chapter 1 for a detailed analysis of scales.

[143] This implies that strong emergence is consistent with Kincaid's criterion of supervenience. However, it is not consistent with Kincaid's overall unity thesis (see 4.2.1).

properties, such that when any chemical property of a single inert molecule changes, then it is always the case that one or more of its quantum mechanical properties have changed as well. This understanding is compatible with Hendry's explication of the dependence relation:

> Roughly, a group of properties, A (the supervenient group), supervenes on another, B (the subvenient, or base group) when there cannot be variation in respect of A without variation in respect of B. (1999: 120)

(iii) postulates the causal autonomy of the higher level.[144] The higher level is causally autonomous because, according to strong emergence, there is some set of higher-level entities, properties, etc. that possess causal powers which are distinct from the powers possessed by the lower-level entities, etc. on which the former depend (in accordance to clause ii).[145] These powers are distinct in the sense that they are not token identical to any set of powers possessed by the lower-level entities, etc. (Wilson 2015: 362).

Whether this understanding of causal autonomy is the sort of causal autonomy that Hendry has in mind when presenting strong emergence is not entirely clear. This is because Hendry does not employ the term 'causal autonomy' in his work on strong emergence (as this is reviewed in (Hendry 1999), (Hendry 2006), (Hendry 2010a), (Hendry 2010b) and (Hendry 2017)). Nevertheless, this seems a compatible understanding of causal autonomy. This is because Hendry states that 'the emergentist sees (special-science properties) as distinct and non-reducible just because the causal powers they confer are *not* exhausted by those conferred by their physical bases' ((Hendry 2010b: 185)- italics are added here).

The acceptance of the causal autonomy of the higher-level, together with the postulation of a dependence relation, is allegedly problematic if one also accepts the Causal Closure of the Physical (CCP). The CCP states that 'every lower-level physically acceptable effect has a purely lower-level physically acceptable cause' (Wilson 2015: 352). Or, as Hendry puts it, following Papineau (2002), 'physical effects are brought about solely by physical causes via physical laws' (Hendry 2010b: 185). The CCP is relevant to the current discussion because, regarding chemistry's relation to quantum mechanics, quantum mechanics is assumed

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[144] This chapter does not examine what sort of things (i.e. entities, properties, etc..) possess causal powers. This is left open for further investigation and does not affect the current discussion. For simplicity, the remainder of this chapter mentions entities and properties as the possessors of causal powers. However, this should be understood loosely as referring to any sort of thing that might possess causal powers.

[145] For now, the chapter follows Wilson in taking powers in a rather 'neutral' manner: 'the notion of "power" here is metaphysically almost entirely neutral, reflecting commitment just to the plausible thesis that what causes an entity may potentially bring about (perhaps only contingently) are associated with how the entity is- that is, with its features' (Wilson 2015: 348). Nevertheless, the nature of causation in strong emergence is evaluated later on in more detail.

to be the physical theory that specifies the 'physically acceptable causes and effects' regarding the behavior of a single inert molecule.[146]

The causal autonomy of the higher-level, together with supervenience, lead to the conclusion that there are effects that are caused by higher-level token powers. However, if one accepts the CCP then this leads to the overdetermination problem (Kim 2005: 39-51). Applied to the case of chemistry and quantum mechanics, the overdetermination problem is presented here as follows:

Due to the causal autonomy of the chemical level, it follows that:

a. A chemical entity M sufficiently causes another chemical entity M*.
b. M is distinct from any set of quantum mechanical entities P in the sense that it possesses novel causal powers.

Supervenience states that:

c. The chemical entity M* supervenes on some set of quantum mechanical entities P*.

Due to the CCP it follows that:

d. For any quantum mechanical entity P*, there is a set of quantum mechanical entities P that sufficiently causes P*.

From (a), (b), and (c) it follows that:

e. M sufficiently causes P*, by causing M*.

From (d) and (e):

f. M causes P*, and P causes P*.

=> P* is causally overdetermined.

The acceptance of the causal autonomy of the chemical level, together with the acceptance of supervenience and the CCP, lead to the conclusion that quantum mechanical effects have more than one cause (i.e. the overdetermination problem).[147] According to Wilson, there are four ways to deal with this problem (2015: 353):

1. One could deny the causal autonomy of the chemical level and maintain that only the quantum mechanical level is causally efficacious. Specifically, one could deny causal autonomy by denying either a. or b. For example, one could argue that chemical causal powers are (at least) token identical to quantum mechanical causal powers (i.e. deny b.), or that only quantum mechanical causal powers are

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[146] This assumption is not criticized here.

[147] There are alternative formulations of this problem (which is also referred to as the Exclusion Problem or the Causal Exclusion Problem, see (Block 2003)). For example, the overdetermination problem can be stated in the sense that chemical effects are overdetermined (i.e. M causes M* and P causes M*) (Wilson 2015: 352).

sufficient to cause effects (i.e. deny a.), or that there are no real chemical entities to possess powers (i.e. deny the existence of chemical entities, etc. and subsequently their causal autonomy). Whichever justification is proposed, it follows that only P causes P* and M doesn't cause P*.

2. One could deny the existence of a dependence relation between chemical and quantum mechanical entities (i.e. deny supervenience).
3. One could argue that overdetermination is not a problem. That is, one could 'allow that there is overdetermination, but deny that it is of the firing squad variety that would be intuitively problematic as generally characterizing higher-level causation' (Wilson 2015: 353).
4. One could reject the CCP and deny that P sufficiently causes P* (i.e. deny d.). That is, there are quantum mechanical effects that are necessarily, and even perhaps sufficiently, caused by some chemical cause. Put differently, for at least one quantum mechanical entity P*, there is no set of quantum mechanical entities P that sufficiently causes P*.[148]

Strong emergence addresses the overdetermination problem by rejecting the CCP (option 4 above). That is, it 'avoids overdetermination by denying that every lower-level physically acceptable effect has a purely lower-level physically acceptable cause' (Wilson 2015: 353). Strong emergence, as per Hendry, maintains that there are quantum mechanical effects that require the exertion of powers that are not token identical to any set of powers possessed by the quantum mechanical entities on which the chemical entities supervene ((Wilson 2015: 353) and (Hendry 2010b:188)).

Hendry discusses the CCP with respect to various issues. For example, he argues that its rejection does not 'involve the violation of physical laws', and that strong emergence is compatible with an 'alternative principle of universality, the ubiquity of physics' (2010b: 188). This feature of the CCP and of strong emergence is discussed in section 5.5.

There are various ways in which one can specify the causal autonomy of the higher level. This chapter examines Hendry's understanding of causal autonomy (and thus of strong emergence), which is specified in terms of downward causation. That is, the higher level is causally autonomous iff it exhibits downward causal powers. Put differently, causal autonomy is established via the support of downward causation.

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[148] Although the rejection of the CCP entails that there are effects that are not sufficiently caused by physical causes, this does not imply that in such cases physical causes do not participate as partial causes (i.e. it does not imply that they are not necessary for the occurrence of such effects). The denial of the CCP merely implies that there are certain effects that are not sufficiently caused by physical token powers. Whether Hendry identifies this implication of the denial of the CCP is briefly discussed in the following pages of this section and in subsection 5.5.4.

Downward causation is invoked in order to explicate statements such as the following:

- ‘Conditions in a cell, such as its phase in the cell cycle, constrain which genes are expressed’ (Bechtel 2017: 253).
- ‘a body regulates its own processes’ (Paoletti and Orilia 2017: 1).
- ‘the motions of (..) electrons and nuclei’ are ‘constrained by the molecule of which they are part’ (Hendry 2006: 183).

Hendry defines strong emergence in terms of downward causation as follows:

> the emergentist sees (special-science properties) as distinct and non-reducible just because the causal powers they confer are not exhausted by those conferred by their physical bases. The additional causal powers are exerted in downward causation.(..) Emergentism invokes downward causation- the special-science properties sometimes push their physical supervenience bases around. (2010b: 185)

Based on this, this section takes Hendry’s understanding of downward causation to consist of the following claim:

- The higher-level causal powers produce effects at the lower level. That is, they determine certain properties of the lower-level entities of the system under examination.

Hendry does not explicitly state what notion of causation he has in mind with reference to downward causation. Nevertheless, he proposes a ‘nomological formulation of emergentism’ which suggests that DC is at least supported (if not understood) in terms of nomological sufficiency (2010a: 218). On the other hand, Hendry examines DC with respect to Kim’s examination of the overdetermination problem and of the CCP. However, Kim’s analysis of the overdetermination problem and of the CCP is based on an understanding of ‘(c)ausation as generation, or effective production and determination’ (Kim 2005: 18). Kim does not provide a more detailed understanding of causation as production, so this chapter accepts Christian List and Peter Menzies’ point that Kim, following Elizabeth Anscombe, ‘treats productive causation as primitive’ ((List and Menzies 2007: 10), see also (Anscombe 1971)). In light of this, this chapter formulates DC in terms of Kim’s notion of production as a primitive (without further clarifying this notion), and then examines how Hendry supports DC in terms of nomological sufficiency.

Moreover, Hendry does not specify whether the higher-level causal powers that participate in the downward causal relation, are necessary or sufficient in producing particular lower-level effects. If they are necessary, then this doesn't exclude lower-level causal powers in participating in the determination of lower-level effects. On the other hand, if they are required to be sufficient by DC, then this means that the higher-level causal powers determine certain lower-level effects without the involvement of lower-level causal powers. The ambiguity of this aspect of DC is a weakness of Hendry's formulation that requires specification because depending on this, the requirements for downward causation may be different. For example, subsection 5.5.4 examines whether it is tenable to consider higher-level causal powers as being sufficient in determining lower-level effects. It argues that this is not tenable.

Furthermore, Hendry investigates DC with respect to Kim's distinctions between synchronic and diachronic DC, and between reflexive and non-reflexive DC ((Kim 1999) and (Hendry 2010b: 188-189)). These distinctions result in four notions of downward causation; namely reflexive synchronic, non-reflexive synchronic, reflexive diachronic and non-reflexive diachronic DC.

Very briefly, reflexive DC postulates that there is 'some activity or event involving a whole W' which 'is a cause or has a causal influence on, the events involving its own micro-constituents' (Kim 1999: 26). Non-reflexive DC takes that a whole W is a cause or has a causal influence on events that involve the micro constituents of another distinct whole, S. Synchronic DC postulates a causal relation between 'states or conditions occurring at the very same time' (Kim 1999: 28). In this context, the question is 'how things and phenomena at different levels hang together in a temporal cross section of the world, or over small time intervals' (Kim 1999: 20). Diachronic DC postulates a causal relation which holds for states or conditions that do not occur at the same time. Instead, the relata of this causal relation occur at t and t+ Δt (Kim 1999: 30).

It is not entirely clear which of the four notions of DC Hendry assumes with respect to chemistry. He has explicitly supported diachronic DC and has accepted Kim's objections against a synchronic notion (Hendry 2010b: 189). However, it is not clear whether he supports a reflexive or non-reflexive understanding of diachronic DC. On the one hand, he argues that 'Kim is premature in dismissing cases of non-reflexive downward causation and diachronic downward causation as mundane or unremarkable' (Hendry 2010b: 189). Based on this, it would seem that he examines strong emergence in terms of non-reflexive diachronic DC. On the other hand, when he contrasts the case of a falling vase with that of a molecule's structure and how in the two cases the higher-level properties emerge from the lower-level ones, he states that there is 'a clear difference' between the two cases, 'whether the molecule's causal powers are exerted internally or externally (that is, *reflexively or non-reflexively*)' (Hendry 2010b: 189).[149] Therefore, it is not clear whether he assumes a reflexive or non-reflexive understanding of diachronic DC.

Based on this ambiguity regarding DC, the remainder of this chapter examines Hendry's understanding of strong emergence in the context of all four notions of DC. It argues that each of the four notions of

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[149] The italics were added here.

downward causation are, for different reasons each, untenable and that, therefore, unless additional clarifications are provided, Hendry's account should be rejected with respect to the emergence of the structure of a molecule.

5.3 Reflexive synchronic downward causation

This section argues that reflexive synchronic DC should be rejected because synchronicity is incoherent given the 'causal-power actuality principle' (Kim 1999: 29).

Reflexive synchronic DC, as a form of strong emergence of molecular structure, is stated as follows. Molecular structure exhibits reflexive synchronic DC with respect to its quantum mechanical entities. Specifically, at t, there is at least one non-empty set of token causal powers:

- possessed by the chemical entities which define system W's structure (i.e. the structure of a single inert molecule);
- which is not token identical to any set of causal powers possessed by the quantum mechanical entities of W; and,
- which produces certain aspects of the quantum mechanical entities of system W.[150]

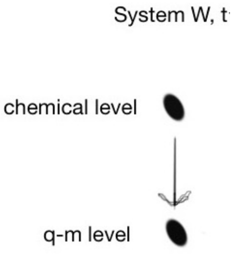

Image 11. An abstract representation of reflexive synchronic downward causation

Two objections against reflexive synchronic DC are considered here. First, following Kim, synchronic reflexive DC goes against what he defines as the 'causal-powers actuality principle'. The principle states the following:

> for an object, x, to exercise, at time t, the causal/determinative powers it has in virtue of having property P, x must *already* possess P at t. When x is caused to acquire P at t, it does not already possess P at t and is not capable of exercising the causal/determinative powers inherent in P. (Kim 1999: 29)[151]

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[150] Although supervenience is stated here as holding between properties, this should be understood rather loosely as referring to a relation between any set of entities, properties, processes, etc. (see also 4.2.3).

[151] The italics are in the original text.

In the case under examination, this means that, if the chemical entities that specify the molecule's structure possess token causal powers that produce certain of the quantum mechanical properties, then certain properties of the quantum mechanical entities do not yet exist at that moment. This means that DC cannot be a synchronic causal relation between the token causal powers of the chemical entities of a molecule and the molecule's quantum mechanical properties. Therefore, the notion of reflexive synchronic DC is incoherent. Further support to Kim's 'causal-powers actuality principle' is not provided here, and in any case, Hendry accepts this as a plausible principle and objection to DC:

> Now the causal-power actuality principle looks plausible, and whether or not it fully captures Kim's 'uneasy feeling' about synchronic reflexive downward causation, I think that the emergentist could accept it as a constraint on their understanding of downward causation without undermining the metaphysical interest of downward causation, or its incompatibility with reductive physicalism. (Hendry 2010b: 189)

Secondly, it is interesting to note that the causal-powers actuality principle implies that synchronic reflexive DC is incoherent in a further respect, not identified by Kim. Supervenience is a synchronic dependence relation between the lower-level and higher-level properties of a system. If the higher-level properties determine some set of lower-level properties, then the latter set does not yet exist at t (this is based on the causal-powers actuality principle). However, synchronic DC supposes that the supervening chemical properties exist at t, since it claims that certain of its token causal powers produce quantum mechanical properties at t. Therefore, we arrive at the incoherent result that the supervenient chemical properties exist at t, whereas the complete set of the respective properties on which they supervene is not instantiated at t. Thus, supervenience cannot hold at t. This is contradictory to one of the core elements of Hendry's understanding of strong emergence, namely that supervenience holds at t.

5.4 Non-reflexive diachronic and non-reflexive synchronic downward causation

This section examines both non-reflexive diachronic and non-reflexive synchronic DC. This is because both notions of DC are rejected on the same grounds.

Non-reflexive diachronic DC, as a form of strong emergence of molecular structure, is stated as follows. There is at least one non-empty set of token causal powers:

- possessed by the chemical entities, etc. which define system W 's structure (i.e. the structure of a single inert molecule) at t_1;

- which is not token identical to any set of causal powers possessed by the quantum mechanical entities, etc. of W at t_1; and,
- which produces certain aspects of the quantum mechanical entities, etc. of system S (distinct from W) at t_2.

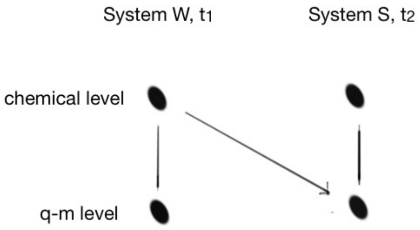

Image 12. An abstract representation of non-reflexive diachronic downward causation

Moreover, non-reflexive synchronic DC, as a form of strong emergence of molecular structure, is stated as follows. Molecular structure exhibits non-reflexive synchronic DC with respect to its quantum mechanical entities. Specifically, at t, there is at least one non-empty set of token causal powers:

- possessed by the chemical entities, etc. which define system W 's structure (i.e. the structure of a single inert molecule);
- which is not token identical to any set of causal powers possessed by the quantum mechanical entities of W; and,
- which produces certain aspects of the quantum mechanical entities of system S, distinct from W.

Both forms of DC (i.e. non-reflexive synchronic and non-reflexive diachronic DC) cannot serve as a form of strong emergence because they don't reflect the idea that the structure of a molecule causally produces lower-level effects on its *own* quantum mechanical entities.

This point is illustrated by contrasting the case under examination with a case that both Kim and Hendry consider as a characteristic example of non-reflexive diachronic DC; namely that of a falling vase ((Kim 1999: 26) and (Hendry 2010b: 189)). A vase of, say, 1 kg is thrown towards a window at t_1, and at t_2 both the window and the vase break. In this context, assume that one focuses on the relation between the two following systems.

- System W at t_1: This is described in terms of entities, properties, etc. that are found at the macroscopic level, and it includes all and only the entities and properties of the unbroken vase (i.e. its particular shape, its weight of 1kg etc.). Suppose that these macroscopic properties supervene on properties that are found at a microscopic level at t_1, and also suppose that at least certain of the macroscopic entities, etc. possess causal powers at t_1 that are not token identical to any set of causal powers possessed by the entities, etc. on which they supervene.

- System S at t_2: This is described in terms of entities, properties etc. that are found at the microscopic level and it includes all and only the molecules and relevant properties of the broken window. Suppose that the properties that describe the broken window at the macroscopic level at t_2 supervene on the properties of the microscopic level (i.e. the molecules and their properties).

The falling vase produced a number of changes at the molecular level of its surrounding environment and changed the molecular properties of the objects with which it collided (i.e. the window); 'these effects are surely micro and lower-level in relation to the fall of an object with a mass of 1 kilogram' (Kim 1999: 26). Assuming that the vase's macroscopic properties (weight, shape, etc.) supervene on its molecular properties, and that certain of the vase's causal powers are not token identical to any set of powers possessed by its molecules at t_1, then one could argue that this is a case of non-reflexive diachronic DC. This is because, there are certain molecular properties of a distinct system (i.e. system S) that have been produced at t_2 by the falling of the vase at t_1 (i.e. system W).

Regardless of whether these assumptions are well supported, the aforementioned example illustrates that the case of the structure of a single inert molecule does not fall under the set of cases that are (allegedly) genuine examples of non-reflexive DC (either diachronic or synchronic). This is because Hendry posits a causal relation between a molecule's *own* properties (namely between its structure and its quantum mechanical properties).

5.5 Reflexive diachronic downward causation

There is one last notion of DC that requires examination; i.e. reflexive diachronic DC. This can be formulated as a form of strong emergence of molecular structure as follows. There is at least one non-empty set of token causal powers:
- possessed by the chemical entities which define system M 's structure (i.e. the structure of a single inert molecule) at t_1;
- which is not token identical to any set of causal powers possessed by the quantum mechanical entities of M at t_1; and,
- which determines certain aspects of the quantum mechanical entities of M at t_2, in the sense that it produces a change in some set of the entities of M of t_1.

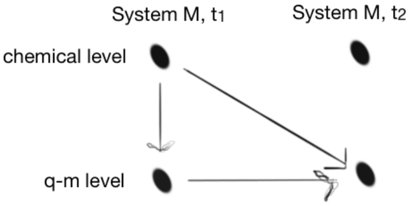

Image 13. An abstract representation of reflexive diachronic downward causation

This section first examines whether this notion of DC is compatible with the causal-power actuality principle. Secondly, this section examines whether the arguments provided in the literature for the support of this notion of DC are tenable. In order to accommodate this examination, this section distinguishes between two sets of exemplary cases of diachronic reflexive DC.[152] The first set includes examples such as:

- A vase falling and breaking;
- 'I fall from the ladder and break my arm' (Kim 1999: 30);
- 'I walk to the kitchen for a drink of water and ten seconds later, all my limbs and organs have been displaced from my study to the kitchen' (Kim 1999: 30); and,
- A 'bird flies into the blue yonder, and all of the bird's cells and molecules, too, have gone yonder' (Kim 1999: 30).

The second set includes examples such as:

- The structure of a single inert molecule determines aspects of its quantum mechanical behaviour;
- 'a cell constrains what happens to its own constituents' (Paoletti and Orilia 2017: 1);
- 'a body regulates its own processes' (Paoletti and Orilia 2017: 1); and,
- 'two atoms, when they are appropriately related, make it the case that their own electrons are distributed in certain ways' (Paoletti and Orilia 2017: 1).

Concerning the first set, the case of the vase falling and breaking is formulated as follows. Consider a vase of, say, 1 kg which is thrown to a window at t_1, and at t_2 breaks. Assume that one focuses on the relation between the two following systems.

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[152] The first set of examples are explicitly examined by Kim in relation to diachronic reflexive DC. Regarding the second set of examples, as already noted, it is not clear which particular notion of DC Hendry assumes with respect to molecular structure. Whether a similar ambiguity exists in the literature concerning the other examples of the second set, is not currently considered. Instead, it is assumed here that, since the examples of the second set have been regarded as being similar to that of the case of molecular structure, and since the other notions of DC have been rejected in the previous sections, then the only remaining alternative is to consider these examples in terms of diachronic reflexive DC.

- M-at-t_1: This is described in terms of entities, properties etc. that are found at the macroscopic scale and it includes all and only the entities and properties of the unbroken vase (i.e. its particular shape, its weight of 1kg etc.) that are relevant to that scale.
- M-at-t_2: This is described in terms of entities, properties etc. that are found at the microscopic scale and it includes all and only the molecules and relevant properties of the broken vase that are relevant to that scale.

The relation between the two systems could be formulated in terms of a relation between the causal powers possessed by higher-level entities of system M-at-t_1, and some set of the lower entities that describe M-at-t_2. Assuming that the vase's macroscopic properties (weight, shape, etc.) supervene on its molecular properties at t_1, and that certain of the vase's causal powers are not token identical to any set of powers possessed by its molecules at t_1, one could argue that this is a case of reflexive diachronic DC. Specifically, the causal powers of the macroscopic entities of the falling vase at t_1 produce changes to its lower-level molecular entities, in such a way that determines aspects of how the molecules behave at the state in which the vase is broken (at t_2). Similar arguments can be formulated for all cases of the same set.

Concerning the second set, the case of the single inert molecule could be formulated in terms of diachronic reflexive DC as well. Consider a molecule that is in isolation. The molecule is considered to be stable, and thus, unless no external change is imposed on it (i.e. unless it is no longer isolated), it will remain unchanged in terms of its chemical identity.[153] This implies that, although the molecule undergoes continuous dynamical change at the quantum mechanical scale, there is no change in its chemical identity. In this context, the examined case focuses on the relation between the two following systems.
- M-at-t_1: This is described in terms of entities, etc. that are found at the chemical scale and it includes all the entities, etc. of the molecule at t_1.
- M-at-t_2: This is described in terms of entities, etc. that are found at the quantum mechanical scale and it includes all the quantum mechanical entities, etc. of the molecule at t_2.

Assuming that the molecule's chemical entities supervene on its quantum mechanical ones at t_1, and that certain of the molecule's causal powers are not token identical to any set of powers possessed by its quantum mechanical entities at t_1, then one could argue that this is a case of reflexive diachronic DC. That is, the causal powers of the chemical entities of the molecule at t_1 produce changes to its quantum mechanical entities, in such a way that determines aspects of how the quantum mechanical entities behave at t_2. Similar arguments can be formulated for all examples of the second set.

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[153] Chapter 2 presents how chemistry and quantum mechanics describe a single inert molecule. Also, the notion of stability in relation to a single isolated molecule is discussed in chapter 6.

Regarding these two sets of cases, this section makes the following points. First, the formulation of both sets of cases in terms of diachronic reflexive DC is coherent. Unlike any notion of synchronic DC, a diachronic notion of causation 'allows' for the higher-level causal powers to be instantiated at t_1, prior to being 'exercised' in any way that produces a change at t_2. Therefore, the notion is coherent given the causal-powers actuality principle.

Consider now the notion's tenability with respect to each set of cases. Concerning the first set, Kim considers them to be cases of unproblematic causal statements:

> It doesn't seem to me that these cases present us with any special mysteries rooted in self-reflexivity, or that they show emergent causation to be something special and unique. (1999: 30)

According to Kim, what possesses the causal powers at t_1 and produces the respective lower-level effects at t_2, are the lower-level entities of the system at t_1 on which the higher-level entities supervene. Therefore, while he accepts the formulation of statements such as the 'falling vase at t_1 caused its molecules to scatter at t_2', he suggests that such statements signify the existence of a genuine causal relation *only* at the lower-level of ontology, and *not* a downward causal one. Put differently, he denies that these are genuine cases of diachronic reflexive DC because, unlike how diachronic reflexive DC is defined, there are no causal powers possessed by the higher-level entities that are not token identical to the causal powers possessed by lower-level entities.[154]

Kim states that most emergentists would agree with such an interpretation of causal statements regarding the first set of cases (1999: 31). This is also accepted by Hendry (2010b: 189). However, Hendry denies that the second set of cases are not genuine instances of downwards causation. This is because, according to Hendry, in these instances the higher-level entities possess causal powers that are:
(i) novel; and,
(ii) causally sufficient for the production of lower-level effects.[155]

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[154] Given the three core elements of strong emergence (section 5.2), Kim's point challenges strong emergence because he denies the causal autonomy of the higher-level.

[155] By 'novel' this chapter takes that causal powers possessed by higher-level entities etc. are not token identical to any set of causal powers possessed by the respective lower-level properties on which the higher-level properties supervene.

Before considering whether these conditions hold for the case of molecular structure, it is worth noting why Kim interprets the second set of examples as he does. He takes it that there is no sufficient evidence that higher-level systems possess novel causal powers. He supports this by considering three alternative notions of causation; i.e. causation as nomological sufficiency, counterfactual causation, and causation as a 'causal chain' (Kim 1999: 32).[156] For example, with respect to nomological sufficiency, Kim argues:

> [F]or if causation is understood as nomological (law-based) sufficiency, P, as M's emergence base, is nomologically sufficient for it, and M, as P*'s cause, is nomologically sufficient for P*. Hence, P is nomologically sufficient for P* and hence qualifies as its cause. (1999: 32)

Put differently, while he admits that there are higher-level token causal powers that are nomologically sufficient for the production of lower-level effects, they are not novel.

Kim's argument can be formulated as follows:

a. If the system's lower-level entities, etc. at t_1 are nomologically sufficient for the production of its lower-level entities, etc. at t_2; and,

b. If the system's higher-level entities, etc. supervene on the lower-level ones at t_1;

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c. Then the higher-level causal powers at t_1 are (at least) token identical to the lower-level causal powers;

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d. Therefore, there is no genuine downward causal relation between the higher-level entities, properties, etc. at t_1 and the respective lower-level ones at t_2.

This section does not examine whether Kim's argument is sound, or how it is argued against. However, it is worth noting that it is only valid if it is assumed that supervenience implies token identity (which is denied for example by (Ladyman 2006)). In what follows, it is explained how Hendry denies the conclusion, by denying the first premise in the instance of molecular structure.

Hendry formulates a 'counternomic criterion for downward causation' (2010b: 189). According to this criterion, 'a system exhibits downward causation if its behavior would be different were it determined by

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[156] It is worth noting that Kim's analysis of DC in terms of these three notions of causation makes it even more difficult to understand which notion of causation Kim assumes with respect to DC. On the one hand, Kim examines these three alternative notions of causation (i.e. nomological sufficiency, counterfactual causation, and causation as causal chain). On the other hand, he challenges DC by invoking the overdetermination problem which is formulated by assuming a notion of causation as production (see (List and Menzies 2007)).

the more basic laws governing the stuff of which it is made' (Hendry 2010b: 189). He claims this criterion is satisfied in the case of molecular structure given how quantum mechanics describes it, which is as follows:

(i) A molecule is described in a complete and exact manner by the Coulombic Schrödinger equation. The Coulombic Schrödinger equation is constructed by employing the so-called 'resultant Hamiltonian' (Hendry 2010a: 210-211). The Coulombic Schrödinger equation is a complete and exact description because the relevant resultant Hamiltonian takes into account all the intra-molecular interactions, and it is constructed using as input only fundamental physical interactions and the value of the physical properties of the entities (i.e. masses, charges etc.) (Hendry 2010a: 210-211).
(ii) A resultant Hamiltonian is in practice never used for the solution of the Schrödinger equation. This is primarily due to the equation's mathematical complexity. Nevertheless, if the Coulombic Schrödinger (i.e. the Schrödinger equation that employs the resultant Hamiltonian) were to be solved, it would not distinguish between different molecular structures (specifically that of isomers), and it would not explain the symmetry properties of a single isolated molecule.
(iii) Instead, quantum explanations of molecular structure are based on the construction of 'configurational Hamiltonians' for the solution of the Schrödinger equation of a molecule (Hendry 2010a: 210-211).
(iv) Configurational Hamiltonians are constructed on the basis of ad hoc assumptions which impose on the Schrödinger equation the molecular structure that is supposed to be derived from that equation.
(v) The aforementioned situation satisfies the counternomic criterion. This is because we did not recover a molecule's 'structure from the "resultant" Hamiltonian, given the charges and masses of the various electrons and nuclei; rather we viewed the motions of those electrons and nuclei as constrained by the molecule of which they are part' (Hendry 2006: 183).

The counternomic criterion implies that it is in principle impossible to specify all the properties of a system based solely on its quantum mechanical description. If this is taken to support DC, then it must be assumed that there are certain properties which do not exist at the scale describable by quantum mechanics. According to Hendry then, the molecule's structure should be taken to be in principle impossible to specify quantum mechanically, and thus does not exist at the relevant scale.

There is a very subtle, but important aspect to Hendry's reasoning. Hendry's account shouldn't be understood as suggesting that quantum mechanics is incomplete. Rather, quantum mechanics is not a 'theory of everything'. Hendry states this as follows:

> non-relativistic quantum mechanics is assumed to be a sort of "theory of everything" for the motions of electrons and nuclei, and therefore for any molecule. Physicists and philosophers (..) usually mean a theory that could- in principle- explain everything that happens in a system to which it is applied, to the extent that it can be

> explained. Think of Newton's laws applied to the planetary motions: natural philosophers since Newton's time have imaged a God's-eye-view application of his laws which could be used to predict all future planetary positions, if only we had accurate enough access to their current positions and momenta, plus large enough computers to cope with very detailed and accurate mathematical models of the solar system. (…) The question of whether molecular structure is strongly emergent is, I think, best understood as the question of whether we have good reasons to think that, from a God's-eye-view, non-relativistic quantum mechanics is a "theory of everything" in this sense, or whether some looser relationship between the dynamics and the evolution of the system is better supported. (2017: 153)

This should not be understood as meaning that quantum mechanics doesn't specify fully the entities, properties, etc. of a system at the quantum mechanical scale, at a particular point in time.[157] Instead, quantum mechanics is not a 'theory of everything' in the sense that the quantum mechanical description of a system at t_1 cannot in principle specify its quantum mechanical description at a later time t_2. This is because the system possesses entities, properties, etc. at t_1 that belong to a different scale. These entities, in virtue of existing at a distinct scale, cannot be recovered within a lower-level complete description. Nevertheless, they partially determine how the lower-level entities will behave later. Therefore, the quantum mechanical description of the system at t_1 is not nomologically sufficient to specify how the system is at t_2. With regard to a molecule's structure, this does not merely mean that the quantum mechanical description (via the resultant Hamiltonian) cannot specify the system's structure at t_1; rather there is no structure at the quantum mechanical scale at t_1.[158] The system possesses structure only at the chemical scale and, as such, it partially determines the entities, etc. found at the quantum mechanical scale at t_2.

Quantum mechanics not being a theory of everything is compatible with Hendry's proposed principle of universality; namely the 'ubiquity of physics' (UP):

> Under the ubiquity of physics, physical principles constrain the motions of particular systems though they may not fully determine them. (Hendry 2010b: 188)

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[157] The completeness of quantum mechanics is also discussed in chapter 7.

[158] This is a natural interpretation of Hendry's account of strong emergence which is further supported by the following quote: '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).

This principle acts as a substitute for the causal closure of the physical (CCP) which Hendry rejects and which is incompatible with his notion of strong emergence. UP allows for the physical principles (as these are formulated via the physical laws and theories) to 'apply universally without accepting that they fully determine the motions of the systems they govern' (Hendry 2010b: 188). According to Hendry, unlike UP, the CCP is not well supported by physics itself, which he follows Robert Bishop in thinking 'does not imply its own causal closure' (Bishop 2006: 45).

Hendry supports downward causation by presenting how quantum mechanics describes particular types of molecules. The following subsection presents the examples from chemistry which he takes to support downward causation empirically.

5.5.1 The empirical support of strong emergence

The first example concerns the quantum mechanical description of isomers. 'Isomers' refers to any set of molecules that contain the same number and kind of atoms, but whose atoms are arranged differently.[159] Isomers have distinct chemical descriptions, and their existence is vital for the explanation of a variety of physical and chemical phenomena. If one is to describe an isomer via the use of its resultant Hamiltonian, then the Schrödinger equation is identical with the Schrödinger equations that describe the other relevant isomers (Hendry 2017: 153). On the other hand, if one is to describe an isomer via the use of its configurational Hamiltonian, then the Schrödinger equation that is subsequently constructed, is not identical to those that describe the other relevant isomers. According to Hendry, this means that this example satisfies the counternomic criterion. He thinks it illustrates that the molecule's behavior, as this is described 'by the more basic laws governing the stuff of which it is made' (i.e. via the resultant Hamiltonian) is different from its behavior, as this is described by assuming certain chemical properties (namely its structure) via the configurational Hamiltonian.

The second example that Hendry takes as empirical support for downward causation involves the symmetry properties of molecules. Similarly to the case of isomers, one cannot derive the different chemical symmetry properties from the quantum mechanical description:

> the only force appearing in molecular Schrödinger equations is the electrostatic or Coulomb force: other forces are negligible at the relevant scales. But the Coulomb force has spherical symmetry. How, from this slim basis, do

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[159] See also chapter 2 which presents in more detail chemistry's understanding of isomers.

> we get the great variety of different symmetry properties (chiral (asymmetrical), cylindrical, hexagonal and many more) exhibited in real molecules? (Hendry 2017: 154)

Both examples are taken by Hendry to satisfy the counternomic criterion. It follows that the resultant Hamiltonian of a molecule at t_1 is not nomologically sufficient to specify it at t_2. According to Hendry, this is because the molecule at t_1 does not possess structural properties at the quantum mechanical scale; instead, it possesses structure only at the chemical scale. Hence, it satisfies the conditions for downward causation above.

5.5.2 Objection 1: Incoherence with respect to supervenience

The remainder of section 5.5 presents three objections that undermine Hendry's grounds for the strong emergence of molecular structure, as he understands it in terms of downward causation. First, it is argued that there is an incoherence between Hendry's acceptance of supervenience and how he empirically supports downward causation.

For Hendry, downward causation is supported by how the Coulombic Schrödinger equation (via the resultant Hamiltonian) describes a molecule. Hendry disregards the success of the configurational Hamiltonian in distinguishing molecules in terms of their structure (like isomers). This is because, '(w)ithout a quantum-mechanical justification for the attributions of structure (and the lower symmetry)' configurational Hamiltonians 'simply assume the facts about molecular structure that ought to be explained' (Hendry 2010b:186).

This leads to incoherence in Hendry's account, because, it equally undermines the grounds for thinking supervenience holds, which is one of the core elements of Hendry's understanding of strong emergence.[160] Consider, for example, the two isomers ethanol and methoxymethane; they are chemically distinct and thus have different chemical descriptions (Hendry 2010a: 214). The resultant Hamiltonians, and thus the Coulombic Schrödinger equations which quantum mechanically describe the two isomers, are the same. Therefore, if ethanol changes into methoxymethane, then its higher-level description would change, whereas its lower-level description (as specified by the Coulombic Schrödinger equation) would remain the same. In sum, if as Hendry recommends we disregard a molecule's configurational Hamiltonian, then it follows that there are molecules (namely isomers) whose chemical descriptions are different, whereas their quantum

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[160] Recall that supervenience postulates a relation such that when any chemical property of a molecule changes, then it is always the case that one or more of the molecule's quantum mechanical properties have changed as well. Hendry does not provide specific empirical evidence that supervenience holds, even though he says it does (see section 5.2).

mechanical descriptions (in terms of the resultant Hamiltonian) are the same. So, supervenience would not hold.

Note that, according to Kincaid's understanding of supervenience, the quantum mechanical description of isomers in the form of the resultant Hamiltonian does not undermine supervenience. This is because supervenience is defined by Kincaid in such a manner that allows the use of ad hoc information drawn from the higher-level theory. Since the configurational Hamiltonians of ethanol and methoxymethane provide different Schrödinger equations for each molecule, then this suffices to support supervenience in this particular instance, regardless of the fact that the configurational Hamiltonians are constructed on the basis of ad hoc assumptions. Such an understanding of supervenience is not explicitly accepted by Hendry.

Based on the above, Hendry needs to justify whether and why the configurational Hamiltonian is used as putative empirical evidence for supervenience. If Hendry accepts the use of the configurational Hamiltonian for the empirical support of supervenience, then he needs to justify why the configurational Hamiltonian can be used as putative empirical evidence for supervenience, but not as putative empirical evidence for the existence of structure at the quantum mechanical scale. Put differently, why is the resultant Hamiltonian not taken into account when examining the validity of supervenience, while it is regarded as decisive evidence for the support of downward causation? On the other hand, if Hendry argues that the configurational Hamiltonian of a molecule cannot be invoked for the empirical support of supervenience, then he needs to explain why, despite the fact that the resultant Hamiltonian describes different isomers in an identical manner, supervenience is accepted within his understanding of strong emergence.

5.5.3 Objection 2: Ad hoc assumptions in quantum mechanics and chemistry

The previous objection brings forward a general issue regarding the use of ad hoc assumptions in science. On what grounds and under which particular instances should the use of ad hoc assumptions be taken as sufficiently supporting a particular metaphysical claim? This is a particularly pressing question if one takes into account that the use of ad hoc assumptions is the norm, rather than the exception, in the process of scientific inquiry.

Hendry refers to the fact that quantum mechanics cannot describe a molecule without the use of ad hoc assumptions regarding the molecule's structure. This is an epistemic claim which is taken to support a metaphysical one; namely that the things that are assumed (rather than derived) by quantum mechanics (i.e. structure) strongly emerge at a distinct scale. Hendry argues that this 'complaint' does not merely stem from the fact that the configurational Hamiltonian employs ad hoc assumptions regarding structure; the 'complaint' is allegedly more pressing than that:

> The complaint is not that there are no explanations of empirically determined molecular shapes, or even that the explanations are ad hoc, or of poor quality. Rather it is that the explanation is conditioned on determinate nuclear positions: if electronic motions are constrained by a stable nuclear backbone, then the energy dependence is such that such-and-such is the lowest energy configuration. (Hendry 2006: 184-185)

It is not very clear how this complaint is based on something more than the use of a particular ad hoc assumption; namely that the nuclei which comprise a molecule have determinate positions. Nevertheless, what is suggested by Hendry's account is that this assumption, apart from being an addition to quantum mechanics, is in some sense 'unacceptable' for the tenability of non-emergentist (namely reductive or physicalist) accounts. However, based on the philosophy of science literature, it is not evident why this is the case.

One way to clarify this is by considering what renders a hypothesis ad hoc. Based on the relevant literature, this subsection argues that while the particular case is a hypothesis which is neither derived nor required by the theory in which it is assumed, it is not ad hoc in the sense of being an 'unacceptable', 'arbitrary', 'contrived', or 'strange' hypothesis (Hunt 2012: 11). In this context, Hendry needs to clarify why this particular example in quantum mechanics is a case of an 'unacceptable' ad hoc hypothesis.

Christopher Hunt states that 'few things are spoken of more derisively in science or philosophy of science than ad hoc hypotheses' (2012: 2). However, as he points outs, it is not very clear what constitutes a hypothesis ad hoc, and in what instances it is 'unacceptable' for the theory that assumes it. In the philosophy of science literature, various definitions and requirements are presented that constitute a hypothesis ad hoc. For example, Karl Popper (1965) takes that a hypothesis H is ad hoc if the following is the case:

> Suppose that there exists a theory T that is "saved" from an observation F by tacking onto it a hypothesis H to make a new theory TH. If the only difference between T and TH is F, according to Popper, H should be considered ad hoc. (Hunt 2012: 5)

According to Carl Hempel (1966), this definition does not successfully distinguish between ad hoc and non-ad hoc hypotheses (see also (Hunt 2012: 5)). In light of this, Hempel proposes a modified definition of ad hoc hypotheses: a hypothesis is ad hoc if it does not have any observational consequences that are significantly or interestingly different from the observational result for which this hypothesis was initially employed in the theory (Hunt 2012: 5).

Based on this modified definition, a hypothesis is not ad hoc simply because it is an addition to the theory. Instead, a hypothesis is ad hoc if certain requirements are met. However, '(w)hat counts as a legitimate addition to the theory and what is an illegitimate ad hoc change may be a matter of debate' (Darden 1995: 147). Due to the scope of this thesis, this is a topic which is not examined in detail here. Nevertheless, certain points can be drawn from the relevant literature which challenge the 'complaint' that the case under examination is an ad hoc hypothesis of the 'unacceptable' sort.

First, the addition of this hypothesis sometimes allows the quantum mechanical description to make predictions about the behavior of the examined molecule, including its structural properties. These predictions have not only contributed to the empirical verification of the theory, but also to the formulation of novel explanations about the relevant phenomena. In fact, as chapter 4 pointed out, to the extent that quantum mechanics has contributed to the advancement of chemistry (as specified via the confirmational, heuristic, and explanatory interdependence of the two theories), this hypothesis has played a central role in chemistry's advancement as well. This undermines the claim that this is an 'unacceptable' assumption to make in the theory. In fact, Hunt, following Adolf Grünbaum, claims that if 'an auxiliary hypothesis turns out to make a novel prediction about which the progenitor of the idea was not aware', it should not be considered ad hoc in the unacceptable sense of the term ((Hunt 2012: 3), see also (Grünbaum 1964: 1409)).[161]

Secondly, the hypothesis that the examined molecule has 'determinate nuclear positions' (and thus that it has structure), is something that is supported by empirical evidence which is independent from the empirical verification and analysis of quantum mechanics. Specifically, the assumption that molecules have an average stable structure has been experimentally supported in chemistry. This provides independent support to the hypothesis of molecular structure. In fact, this suggests that this hypothesis comes in contrast to examples which have been standardly understood as cases of ('unacceptable') ad hoc hypotheses. This is because, according to Mary Hesse, one thing that renders hypotheses ad hoc is that they are 'in principle unobservable' (Hunt 2012: 4). For example, the hypothesis of the FitzGerald-Lorentz contraction was assumed in order to explain why 'the velocity Michelson and Morley measured for the "ether wind" was essentially zero' (Hunt 2012: 2). According to Hesse, this was an ad hoc hypothesis not merely because it was not independently testable, but 'because it entailed that motion in the aether is in principle unobservable' (Hesse 1961: 228). This is not the case with the hypothesis of molecular structure because scientists regard molecular structure an in principle observable property.[162]

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[161] Grünbaum calls such hypotheses 'psychologically ad hoc' (1964: 1409).

[162] For example, molecular spectroscopy techniques are standardly employed in order to observe the structure of molecules (see for example (Aruldhas 2008) and (Barnwell 1983)).

A possible reply to the above is that the presented literature examines the acceptability of an ad hoc hypothesis with respect to the validity of the theory in which it is added, and not with respect to the theory's metaphysical implications. While the above arguments correctly explicate that quantum mechanics is not challenged (as an accurate description of some set of phenomena) by the use of this hypothesis, from this it does not follow that the use of this hypothesis is not consistent with an emergentist understanding of structure.

Indeed, in a naturalistic context, this is a sensible way to support metaphysical claims in the following sense. Hendry's account of strong emergence is not supported on a priori grounds, but by taking into account the manner in which scientific theories describe the world. Put differently, supporting downward causation by reference to the use of ad hoc assumptions is consistent with the naturalistic approach. Nevertheless, whenever a particular metaphysical claim is based on the evaluation of how science is done, it is important to also take into account the general context in which scientific theories are formulated. Specifically, it is important to take into account the general role and prevalence of ad hoc assumptions in science, when evaluating the metaphysical claims that are supported via those scientific practices. Three points are presented here which illustrate that the use of ad hoc assumptions in this particular instance requires a more detailed analysis when it is used to support strong emergence.

First, quantum mechanics more often than not employs information from classical physics or the special sciences in order to describe a domain of phenomena. Depending on the particular system which it is set to describe, quantum mechanics draws information from the relevant classical or special science theories, in order to derive the properties of the system in a manner consonant to experimental evidence. An example which illustrates the prevalence of ad hoc assumptions in quantum mechanics is the case of wavefunction scarring, as discussed by Bokulich (2008a). She examines how semiclassical mechanics explains quantum phenomena in classical systems which are chaotic (2008a: 219). Similarly to the case of molecular structure, the explanation of the behavior of quantum systems is provided by reference to classical structures. This is allegedly problematic because 'the classical structure that they appeal to do not, strictly speaking, exist in these quantum systems' (Bokulich 2008a: 217). Another example concerns quantum electrodynamics. In this context, '(i)t has become conventional to interpret experiments on the electromagnetic properties of leptons in terms of ad hoc modifications introduced in the formulas of quantum electrodynamics' (Kroll 1966: 65).

In light of the above, the supporter of strong emergence could say that these are further examples of strong emergence.[163] On this view, it is not only molecular structure which strongly emerges; various higher-level

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[163] Special thanks to Robin Hendry for pointing this out.

properties of a system, as these are described by classical physics or the special sciences, strongly emerge from its quantum mechanical behavior. On the other hand, one could say that the prevalence of such examples indicates that something not so special is going on; this is merely how scientific explanations are derived from our theories. For example, Bokulich argues that while a purely quantum mechanical explanation of the phenomenon (i.e. 'without reference to classical structures') is 'in some sense deficient', 'the classical trajectories do not cause the scarring' (2008a: 219 and 228).[164] If strong emergence is to be supported by the ad hoc assumptions about molecular structure, then the overall use of ad hoc assumptions in quantum mechanics has to be addressed.[165]

Another point against the idea that the use of ad hoc assumptions gives empirical support to strong emergence, concerns the role of ad hoc assumptions in the construction of the resultant Hamiltonian of a single molecule. Hendry's argument for strong emergence assumes that the Coulombic Schrödinger equation (via the resultant Hamiltonian) is the only 'exact' description, because it makes no prior assumptions about the system that it describes, and it is based only on the main postulates of quantum mechanics (Hendry 2010a: 212- 213). However, the Coulombic Schrödinger equation is not an exact description in the manner that Hendry assumes. The construction of the Coulombic Schrödinger equation is based on prior knowledge about the behavior of particles. For example, the fact that the equation is spherically symmetric is something that is not derived from basic principles of physics, but is an ad hoc assumption that is made in order to formulate the equation.[166] Therefore, the claim that there is no structure at the quantum mechanical scale because one needs to employ ad hoc assumptions in order to break the spherical symmetry of the Coulombic Schrödinger equation and thus accurately describe the structure of a molecule, is undermined (see subsection 5.5.1) because the spherical symmetry of the Coulombic Schrödinger equation is an ad hoc assumption as well.

One last issue which further undermines the manner in which Hendry supports strong emergence, concerns the role of ad hoc assumptions in chemistry. If molecular structure does not exist at a particular scale because in that scale structure is describable only via the use of ad hoc assumptions, then it follows that molecular structure exists at a scale which is not describable via the use of ad hoc assumptions. Since Hendry takes that structure exists at the chemical scale, then chemistry should derive without the use of ad hoc assumptions the structure of a molecule (or at least, there should be an indication that chemistry could

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[164] This section does not present the alternative positions that can be proposed for explicating the use of ad hoc assumptions in quantum mechanics. The next two chapters will propose such a position for the case of molecular structure.

[165] Special thanks to James Ladyman, Karim Thebault and Sean Gryb for making this point.

[166] Special thanks to Karim Thebault for making this point.

in principle do so). However, this seems to be too demanding of chemistry. Chemistry is primarily a non-mathematical theory, and as such it seems untenable that chemistry describes (even in principle) the behavior of molecules, without making some sort of assumption about them. This feature of chemistry is not further examined here. Nevertheless, the nature, role, and existence of ad hoc assumptions in chemistry is an issue that needs to be addressed, if Hendry is to coherently support downward causation. All in all, he needs to explain why the use of ad hoc assumptions *only* in the configurational Hamiltonian, and not in the resultant Hamiltonian and (potentially) in the chemical description, is taken as decisive evidence for the support of strong emergence.

5.5.4 Objection 3: The nature of causation in downward causation

Section 5.2 assumed an understanding of causation in terms of a primitive notion of production. It pointed out that Hendry does not explicitly state which notion of causation he assumes when referring to downward causation. Nevertheless, Hendry presents a counternomic criterion which, according to him, sufficiently supports downward causation. Specifically, Hendry takes it that this criterion supports DC because the quantum mechanical description is nomologically sufficient for specifying the structure of a molecule, only after the use of ad hoc assumptions. Put differently, downward causation is understood by Hendry as a relation of nomological sufficiency.

The problem with such an understanding of DC is that, even if the quantum mechanical system at t_1 is not nomologically sufficient for the occurrence of the quantum mechanical system at t_2 (as Hendry argues), this does not necessarily imply that the chemical system at t_1 determines the quantum mechanical system at t_2. For DC to be tenable, it must also be argued that the chemical entities, etc. at t_1 are nomologically sufficient for the determination of the quantum mechanical entities, etc. at t_2. That is, the chemical system must go through the same level of scrutiny that the quantum mechanical system at t_1 goes through and allegedly fails. For that to be the case, it must be that the chemical description *alone* is nomologically sufficient for the occurrence of the quantum mechanical system at t_2.[167]

This section argues that the chemical entities, etc. at t_1 are not nomologically sufficient for the determination of the quantum mechanical entities, etc. at t_2. It introduces Ned Hall's account of 'causation as production'

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[167] This objection can be challenged if strong emergence requires that the chemical description is nomologically necessary, and not sufficient, for the occurrence of the quantum mechanical system (see also section 5.2). However, this is something that needs to be explicitly clarified. In fact, the defender of strong emergence needs to explain why the nomological necessity of the higher level implies the existence of a downward causal relation.

and argues that, within Hall's account, the chemical entities, etc. are not nomologically sufficient at t_1 for the determination of the quantum mechanical ones at t_2 (Hall 2004).

According to Hall (2004), a system M, understood as a set of all the entities, properties, processes, etc. that define M, sufficiently produces a system M′, just in case M′ follows from:

(i) the laws;
(ii) the premise that all the members of M occur at t_1; and,
(iii) the premise that no other events occur at t_1.[168]

Hall does not examine 'causation as production' with respect to systems that are described within different scales, so this subsection makes three clarifications. First, since the description of all systems is scale dependent, the laws that are employed in order to describe each system must include all and only those concepts, theoretical postulations, explanatory mechanisms and laws of nature that are relevant to that specific scale. Secondly, the members of M are taken to include all and only those entities, properties, causal powers, etc. which completely specify the system at the relevant scale.[169] That is, neither the laws nor the entities, properties, etc. should belong to a different scale from that in which the respective system is specified. Thirdly, in the case under examination, there are two systems that are taken to be causally related via diachronic reflexive DC. The first system is that of a single inert isolated molecule at t_1 (i.e. system M). M is the set of all and only those chemical entities, properties, causal powers, etc. that occur at t_1 and specify the molecule.[170] The second system M′ occurs at t_2, and is the set of the quantum mechanical entities, properties, etc. at t_2. Notice that the change that has been produced to the quantum mechanical entities, etc. from t_1 to t_2 has not led to a change in the chemical properties of the molecule at t_2. The structural properties of the single inert molecule produce changes to certain of its quantum mechanical properties in such a way that does not

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[168] Certain modifications are made to Hall's understanding of causation as production in order to maintain uniformity with respect to the terms employed in the examination of DC. First, Hall's account is originally stated in terms of a causal relation between events c and e, not systems M and M′. Secondly, this subsection disregards the fact that Hall's account has been formulated in accordance to John Mackie's INUS conditions (Mackie 1965). Specifically, Hall takes that an event/system M′ can be produced by a number of different and distinct events M, none of which are necessary for the occurrence of M′, each of which however is sufficient for M′. The advantage of such an analysis of the causal relation between two events/systems is that, while M is a sufficient set that produces an event M′, this set M is not necessarily the only set that could lead up to event M′. That is, it is possible to have more than one sufficient set M that independently produces event M′. This subsection takes this to be an unproblematic aspect of Hall's account and does not examine it with respect to DC.

[169] The same applies for the effect/system M′ as well, regardless of the fact that M is not explicitly defined as a set.

[170] This includes its molecular structure.

change those structural properties. Put differently, the structure of the entire molecule produces certain aspects of the behavior of the electrons and nuclei in such a way that maintains that structure.

In order for M to causally produce a reflexive diachronic change, it must be the case that the set M, in accordance with the chemical laws, are sufficient for a change at the quantum mechanical level to occur at t_2. This must follow from:

(i) the chemical laws;

(ii) all the members of M that occur at t_1; and,

(iii) no other events outside of M occurring at t_1.

However, the chemical laws, together with the set M at t_1, are not sufficient for determining the quantum mechanical description of the system at t_2. This is for two reasons. First, it is not possible to derive the quantum mechanical description of system M′ at t_2 from the chemical description of system M at t_1, and the relevant chemical laws. The chemical laws and chemical entities, etc. cannot derive the sort of fine-grained description required for the full specification of the quantum mechanical system at t_2. Therefore, this model of production collapses and, consequently, diachronic reflexive DC in terms of production is not epistemically supported.

A possible reply to this objection is that, although it is not possible to derive the quantum mechanical description of the system at t_2 from the chemical description, laws, etc. of the system at t_1, this doesn't preclude the possibility that chemical systems cause quantum mechanical changes. This reply to the first objection leads to the second objection against DC. Due to multiple realizability, it is possible that a single inert molecule, as this is described in chemistry, supervenes on more than one quantum mechanical state. Put differently, there are more than one possible quantum mechanical states of M′ on which the single inert molecule (both at t_1 and at t_2) supervenes. In light of this, it is not possible that the chemical system alone, without 'taking into account' the particular lower-level entities that occur 'within' it at that particular time, can determine the state of its lower-level entities, etc.

A possible reply to this objection is that the set M includes all possible members of the basis on which M supervenes, and not only the actual set of entities, properties, etc. on which the single inert molecule supervenes at that particular time. If M is understood this way, then the set M suffices for the production of the quantum mechanical change.[171] However, this would not be equivalent to stating that a molecule at t_1 produces quantum mechanical changes on its supervenience basis at t_2, but rather that the molecule together with its supervenience basis at t_1 produce such changes at t_2.

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[171] This however also requires the inclusion of the quantum mechanical laws that specify the supervenience basis at t_1.

Based on the above analysis, the chemical system at t_1 is not nomologically sufficient for the production of the quantum mechanical system at t_2. It should be noted that, in the context of Hall's account, the configurational Hamiltonian and its respective Schrödinger equation cannot be regarded as the higher-level description that supports the nomological sufficiency of the chemical system. The configurational Hamiltonian that is used for formulating the quantum mechanical description of a molecule, is neither a chemical description of that molecule at t_1, nor is it based on the application of chemical laws pertaining to the molecule. Indeed, some assumptions and approximations that are used in order to construct the configurational Hamiltonian have been based on the relevant chemical description of the system at t_1. However, the configurational Hamiltonian is still part of a quantum mechanical description because the entities, properties, etc. that are postulated, as well as the interactions that are described, are found at the quantum mechanical scale.

A possible way out for Hendry is to support a different notion of causation. This however requires a detailed presentation of how his proposed notion of causation supports the metaphysical claims that:

- the quantum mechanical entities, etc. at t_1 do not determine certain aspects of the system's quantum mechanical behavior at t_2; and *also,* that,
- the chemical entities, etc. at t_1 determine certain aspects of the system's quantum mechanical behavior at t_2.

In a naturalistic context, this also requires that one specifies the epistemic criteria that sufficiently support the existence of such a causal relation.

4.6 Summary

This chapter showed that three notions of DC are either incoherent or inapplicable to the case of a single inert molecule. While diachronic reflexive DC seems to be the most appropriate candidate for the case under examination, the defender of strong emergence in terms of downward causation needs to specify which notion of DC is assumed out of the fourfold classification of DC.

With respect to diachronic reflexive DC, there are three objections against strong emergence:

- The empirical evidence presented for strong emergence for the support of downward causation equally undermines supervenience. Supervenience is one of the main tenets of strong emergence. Therefore, it is important to clarify this point.
- Hendry argues that making ad hoc assumptions in order to recover structural information from the quantum mechanical description is consistent with the view that structure strongly emerges. However, the use of ad hoc assumptions is a very common practice across all sciences, including chemistry.

Therefore, one needs to address why in this particular instance it is considered as an indication of strong emergence.

- It is crucial to specify how causation is understood when referring to downward causation. If one takes nomological sufficiency as adequately supporting the existence of a downward causal relation, then it does not suffice to only show that the quantum mechanical entities at t_1 are not nomologically sufficient for the occurrence of the quantum mechanical entities at t_2. One must also show that the higher-level entities, etc. at t_1 are nomologically sufficient for the occurrence of the lower-level entities, etc. at t_2. In the context of Hall's account of causation, this chapter showed that this is not the case; the chemical entities, etc. at t_1 are not nomologically sufficient for the occurrence of the quantum mechanical entities at t_2.

An additional issue that requires examination concerns the putative empirical evidence employed in order to support strong emergence. Despite the philosophical weaknesses of strong emergence (as specified above), the analysis of the quantum mechanical description of a single inert molecule is indeed consistent with an emergentist understanding of molecular structure. However, there are alternative positions which are equally compatible with how quantum mechanics describes molecular structure and that, thus, undermine the tenability of strong emergence.

The goal of the next two chapters is to analyze in detail the quantum mechanical description of molecular structure, and to propose two alternative interpretations of this description, neither of which posit strong emergence. Specifically, chapter 6 claims that both chemistry and quantum mechanics assume an idealized understanding of a molecule's stability and structure. Based on this claim, chapter 7 argues that this idealization in quantum mechanics can be interpreted in two alternative ways, each of which explains why quantum mechanics describes molecular structure the way it does, without positing strong emergence.

6. The Role of Idealizations in Describing a Single Molecule

When chemistry and quantum mechanics describe a single isolated molecule, both assume that the molecule is stable and has structure. These assumptions are examined in the light of the literature on idealizations in science. Doing so raises interesting philosophical questions and helps resolve disagreements in the philosophy of chemistry literature.[172]

Section 6.1 briefly presents how idealizations are understood and discussed in the philosophy of science literature. Section 6.2 explains why regarding a single isolated molecule as being stable and having structure is an idealization. When it comes to describing a single isolated molecule, both chemistry and quantum mechanics make this idealization. Section 6.3 presents how this idealization contributes to the investigation of various philosophical issues, including those concerning the relation between chemistry and quantum mechanics.

6.1 The philosophical investigation of idealizations

Making idealizations is one of the most common practices in science and numerous cases can be invoked as examples. '(F)rictionless planes, point masses, infinite velocities, isolated systems, omniscient agents, and markets in perfect equilibrium' are regarded as idealizations that are made in the relevant theories or models (Frigg and Hartmann 2012: section 1.1). Assuming that gas molecules are infinitely small, or that light consists of 'one-dimensional beams rather than waves' are also examples of idealizations (Strevens 2017: 2).

The philosophy of science examines various questions regarding idealizations.[173] For example, it examines the nature of idealizations and whether there are distinct kinds of idealizations in science (see for example (McMullin 1985) and (Weisberg 2007a)). Moreover, it examines how particular figures in the history of science have understood idealizations. This is because idealizations are crucial to the work of central figures such as Aristotle, Galileo, and Newton (McMullin 1985: 240-262). For example, Ernan McMullin analyses Galileo's understanding of idealizations in order to distinguish a particular type of idealization; namely Galilean idealization (1985). Furthermore, the use of idealizations in science is often examined in relation to

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[172] Chapter 7 presents one particular problem that is extensively discussed in the philosophy of chemistry literature and explains how this idealization resolves it.

[173] Note that this section only briefly presents how idealizations are discussed in the philosophy of science literature. For a concise presentation of idealizations see (Ladyman 2008). See also (Batterman 2011), (Frigg and Hartmann 2012), (Hartmann 2005), (Liu 2004), (McMullin 1985), (Norton 2012), (Strevens 2017), (Thébault et al. 2018), (Weisberg 2007a), (Weisberg 2007b) and (Wimsatt 2007).

philosophical topics such as scientific realism, emergence, models in science, representation and explanation (Ladyman 2008: 360-365). For example, the use of idealizations in science is used as putative evidence for antirealism ((Weisberg 2007a: 657), see also (Cartwright 1983)). On the other hand, it is also argued that idealizations can support scientific realism ((Weisberg 2007a: 657) and (Norton 2012: 211)). Also, Batterman proposes the notion of 'infinite idealizations' in order to support an emergentist position regarding critical phenomena and phase transitions ((Batterman 2010), see also (Strevens 2017)).

Perhaps as is to be expected, there is no standardly accepted single account of idealizations. As Weisberg states:

> Philosophers of science increasingly recognize the importance of idealization (…). Yet this recognition has not yielded consensus about the nature of idealization. The literature of the past thirty years contains disparate characterizations and justifications, but little evidence of convergence towards a common position. (2007a: 639)

The lack of a common position about idealizations becomes apparent from the fact that numerous definitions of idealizations are given. For example, Roman Frigg and Stephan Hartmann propose the following definition:

> An idealization is a deliberate simplification of something complicated with the objective of making it more tractable. (2012: section 1.1)

McMullin defines idealizations in a similar manner; namely as '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' (1985: 248). John Norton argues that idealizations should be taken to 'refer to new systems some of whose properties approximate some of those of the target system' (Norton 2012: 207), whereas Weisberg defines idealizations as 'the intentional introduction of distortion into scientific theories' (Weisberg 2007a: 639). The above definitions illustrate that idealizations are 'a feature of both the formulation of laws and theories and of their application to the world' (Ladyman 2008: 358). For example, Weisberg understands idealizations as a feature of scientific theories, whereas Norton understands them as a feature of the system or phenomenon that scientific theories describe.[174]

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[174] McMullin, as well as Frigg and Hartmann, formulate a definition which allows both understandings of idealizations; namely as a feature of theories and as a feature applied to systems or phenomena in the world.

A question which is raised about idealizations concerns their function in science. According to Frigg and Hartmann, the function of idealizations is to make ‘something’ more ‘tractable’ (2012: section 1.1). Other philosophers specify in more detail the function of idealizations. For example, idealizations are used in order to:

(i) ‘reduce the complexity of the model’, by either ‘making the mathematics more tractable or by reducing the empirical demands of the model’ (Strevens 2017: 3);

(ii) identify the ‘core or primary causal factors that give rise to the phenomenon of interest (Weisberg 2007a: 651); and,

(iii) construct ‘a single model for a particular target or class of target phenomena’ (Weisberg 2007a: 655).

Moreover, a particular notion of idealization is often supported with respect to the description of a particular phenomenon. For example, Batterman proposes the notion of ‘infinite idealizations’ with respect to phase transitions and critical phenomena (2011: 1033).[175] Weisberg proposes the notion of ‘multiple models idealization’ regarding the description of global weather patterns (2007a: 646). McMullin argues that the application of geometry for the specification of the movement of planets is an example of ‘mathematical idealization’ (1985: 248-254).

There are disagreements about several issues regarding idealizations. For example, some argue that idealizations are distinct from approximations, whereas others use the two terms interchangeably.[176] Also, there are particular examples of theories, models, or representations for which it is not very clear whether idealizations or some other notion (such as analogues) accurately specifies their ‘representational styles’ (Frigg and Hartmann 2012: section 1.1). Specifically, ‘some scale models would also qualify as idealized models and it is not clear where exactly to draw the line between idealized and analogue models’ (Frigg and Hartmann 2012: section 1.1).[177] Another issue that is discussed concerns the categorization of idealizations. For example, Frigg and Hartmann argue that there are two main kinds of idealizations; i.e. ‘Galilean’ and ‘Aristotelian idealizations’ (2012: section 1.1). McMullin distinguishes between ‘mathematical’, ‘Galilean’ (which are further distinguished into ‘construct’ and ‘causal idealizations’), ‘material’, ‘formal’ and ‘subjunctive idealizations’ ((McMullin 1985), see also (Ladyman 2008: 361-362)). Weisberg argues that there are three kinds of idealizations; namely ‘Galilean’, ‘minimalist’, and ‘multiple-models idealizations’ (2007a).

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[175] This is also referred to as ‘asymptotic idealization’ (Wayne 2012: 344).

[176] The former is supported by Norton (2012). An example of the latter is (Wayne 2012: 343). A similar issue arises with respect to the distinction between idealizations and abstractions (see for example (Cartwright 1989) and (Ladyman 2008: 362-363)).

[177] This question requires a detailed analysis of models and representations in science and is not further examined here (see for example (Ladyman 2008: 360-364)).

Michael Strevens examines ‘asymptotic’ and ‘simple idealizations’ (2017). Whether there is a unique classification that underwrites all proposed kinds of idealizations is not examined here.[178] Regardless of the exact characterization of ‘idealization’ and its various species and cognates, the way chemistry and quantum mechanics describe the stability and structure of a single isolated molecule counts as idealization of some kind in the sense of all the accounts above.[179]

Lastly, it is interesting to note that a number of examples from chemistry and quantum mechanics have been invoked when discussing idealizations in science. For example:

i. The use of approximate wavefunctions in order to calculate the properties of molecules, is regarded as an example of Galilean idealization (Weisberg 2007a: 641).
ii. Treating ‘the vibrating bond as spring-like with a natural vibrational frequency’ in order to calculate the vibrational properties of a covalent bond, is regarded as a minimalist idealization (Weisberg 2007a: 644).
iii. The description of atoms and molecules via the Molecular Orbital or the Valence Bond approach is regarded as an example of Weisberg’s third kind of idealization; i.e. the multiple-models idealization (Weisberg 2007a: 646).
iv. The Bohr image of the atom is regarded as an example of Galilean idealization (McMullin 1985: 260).
v. The Lewis electron pair model of chemical bonding is also regarded an idealization (Weisberg 2007a: 650).

While this chapter does not examine the general role of idealizations in chemistry and in quantum mechanics, the above examples illustrate that both chemistry and quantum mechanics employ various idealizations of possibly different types. Moreover, some of the above examples illustrate that there are particular features of the quantum mechanical description of a single molecule which have been examined in terms of the notion of idealizations. Nevertheless, there is a particular feature of quantum mechanics (and of chemistry) that has not been identified as an idealization in either the philosophy of science or the philosophy of chemistry literature; namely the assumption that a single isolated molecule is stable and has structure.

6.2 Stability and structure in chemistry and quantum mechanics

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[178] Weisberg argues that his classification underwrites the different kinds or notions of idealizations that have been proposed in the literature (2007a: 639).

[179] The particular example may be alternatively identified as an abstraction or approximation, and not as an idealization. This is not examined here.

Chemistry and quantum mechanics each make the assumption that a single molecule in isolation is stable and has structure independent of time. This is correctly construed as an idealization for two main reasons. First, stability and structure are partially determined by factors that concern the context in which a single molecule is considered (i.e. thermodynamic conditions, time-range of experiment, environment, etc.). Secondly, the stability and structure of a molecule can only be empirically identified with reference to those factors.

This section presents how stability and structure are defined, understood, and empirically identified. This analysis explicates in more detail why the assumption of a single isolated molecule with stability and structure is an idealization. Note that a particular account of idealizations regarding their nature, function, etc. (as presented in 6.1), is not currently assumed.[180] The aim of this section is to present the scientific evidence which supports the claim that this assumption is an idealization. The next section will then discuss this assumption in terms of the philosophical literature on idealizations.

6.2.1 Stability

This subsection distinguishes three cases in which stability is considered in chemistry, namely:

a. the stability of chemical species;
b. the stability of a single molecule when considered as being part of an ensemble (i.e. of a chemical species); and,
c. the stability of a single molecule in isolation.[181]

This subsection presents each case separately. The stability of chemical species is examined because it is the only case for which IUPAC provides a definition of stability. The stability of a single molecule is not defined by IUPAC (2014) and, in fact, such a notion of stability is implicitly considered within the context of particular idealizations.[182]

a. The stability of chemical species

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[180] Chapter 7 examines the assumption presented here in terms of two different understandings of the notion of idealization.

[181] I would like to thank Nick Norman and Fred Manby for clarifying how chemists understand stability and structure.

[182] See also chapter 2.

A chemical species is '(a)n ensemble of chemically identical molecular entities that can explore the same set of molecular energy levels on the time scale of the experiment' (IUPAC 2014: 264).[183] Given this definition, stability with reference to chemical species is defined in the following way:

> As applied to chemical species, the term expresses a thermodynamic property, which is quantitatively measured by relative molar standard Gibbs energies. A chemical species A is more stable than its isomer B if $\Delta_r G^o > 0$ for the (real or hypothetical) reaction A -> B, under standard conditions. If for the two reactions:
>
> P -> X + Y ($\Delta_r G^o{}_1$)
>
> Q -> X + Z ($\Delta_r G^o{}_2$)
>
> $\Delta_r G^o{}_1 > \Delta_r G^o{}_2$, P is more stable relative to the product Y than is Q relative to Z.
>
> Both in qualitative and quantitative usage the term stable is therefore always used in reference to some explicitly stated or implicitly assumed standard. (IUPAC 2014: 1432)

Based on this definition, the stability of a chemical species is relative to the following factors:

- The particular reaction(s) with respect to which the stability of a chemical species is considered. For example, while a chemical species P is more stable relative to Y when considered with respect to how stable Q is relative to Z (see above), P is less stable relative to Y when considered with respect to how stable A is relative to T (for the hypothetical reaction A -> X + T, $\Delta_r G^o{}_3$, where $\Delta_r G^o{}_3 > \Delta_r G^o{}_1$) .

- The particular chemical species with which a chemical species' stability is relative. For example, while P is more stable relative to Y (when considered with the reaction Q -> X + Z), it is less stable relative to M (when considered with the reaction Q -> X + Z), if it is the case that there is a hypothetical reaction P -> X + M (with $\Delta_r G^o{}_4$) such that $\Delta_r G^o{}_4 < \Delta_r G^o{}_2$.

- The thermodynamic conditions in which those reactions are performed.[184] The relative molar Gibbs energies are calculated and compared under the assumption that the considered reactions are performed under standard thermodynamic conditions. However, if the thermodynamic conditions are different (i.e.

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[183] A molecular entity is '(a)ny constitutionally or isotopically distinct atom, molecule, ion, (..), etc., identifiable as a separately distinguishable entity' (IUPAC 2014: 950).

[184] Usually, the thermodynamic conditions in which stability is considered are the standard conditions. For gases, standard conditions are temperature T = 273,15 K and pressure P = 10^5 Pa.

the temperature or pressure of the examined systems are different), then it is possible that the relevant molar Gibbs energies are different, and thus that the stability of the chemical species is different.[185]

- The environment in which that particular set of reaction(s) is assumed to be performed. This includes the specification of the type of solution or background gas within which the reactions are performed. For example, there are polymers which 'are reported to be stable in air up to 500°C and to nearly 800°C in nitrogen' (Marvel 2009: 361).

It should be noted that the stability of a chemical species is measured only after the examined set of reaction(s) has (at least hypothetically) reached chemical equilibrium; i.e. the molar Gibbs energy is measured after sufficient time has elapsed so as the concentration of the reactants and the products give the appearance of remaining (in average) constant (IUPAC 2014: 258).[186] Assuming that the examined reactions have reached chemical equilibrium and that there is no change in the thermodynamic conditions, then, in theory, time is not a factor that influences the stability of a chemical species. Put differently, if the system under examination does not exchange matter with the environment, and if there is no change in the thermodynamic conditions in which it is considered, then it will remain (on average) chemically unchanged for an indefinite amount of time.

Furthermore, it should not be assumed that a chemical species, in virtue of being stable, is also static. The molecules that make up the ensemble (i.e. the chemical species) do not remain static in space over time. This is because these molecules move and interact with each other. Therefore, while the probability of finding a stable chemical species in an unstable state at a particular point in time is very small, it is nevertheless non-zero. This illustrates the role of time in the empirical identification of the stability of a chemical species, since it is possible that, at an arbitrary point in time, the examined chemical species is found to be unstable.

Based on the above, the stability of a chemical species is a relational property. This section assumes Ney's definition of relational properties, according to which relational properties are properties objects have 'in relation to other things' (Ney 2014: 285).[187] Given this definition, the stability of a chemical species is a

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[185] For example, (Marvel 2009) examines stability with respect to various thermodynamic factors, including temperature.

[186] Chemical equilibrium is said to be reached when 'the rates in both directions' of a reversible process 'are identical, so that the system gives the appearance of having a static composition at which the Gibbs energy, G, is a minimum' (IUPAC 2014: 258).

[187] Ney's definition of relational properties provides a rather general understanding of relational properties because it does not specify what renders an object in relation to something else. Nevertheless, this understanding of relational properties suffices in order to support the claim that the stability of a chemical species is not a property that the chemical

relational property because it is a property that chemical species have in relation to other chemical species, as well as in relation to particular thermodynamic conditions, to a set of reaction(s), and to the environment in which the chemical species is assumed to be found.

b. The stability of a single molecule when considered as part of an ensemble (i.e. of a chemical species)

First, it is important to justify the distinction between the stability of a single molecule which is part of a chemical species, and the stability of a single molecule in isolation. IUPAC (2014) does not provide a definition of stability with reference to a single molecule. However, chemists understand stability not only as a property of chemical species, but also as a property of a single molecule. Concerning the latter, with the advent of quantum mechanics and the analysis of the structure of atoms, stability is standardly understood as referring to that state of a molecular entity which corresponds to its ground state. This understanding of stability is henceforth referred to as stability simpliciter, because it does not specify whether the molecular entity to which it refers is considered as being part of an ensemble or as being in isolation. In this context, a molecule is understood as being stable simpliciter in the sense that it is in its ground state.

It should be noted that stability simpliciter does not contradict IUPAC's definition of stability with reference to chemical species, because the ground state of a molecule is defined as 'the state of lowest Gibbs energy' (IUPAC 2014: 646).[188] The ground state of a molecule is taken to correspond to a particular internal structure of that molecule. This structure corresponds to the average nucleonic and electronic configurations of the atomic nuclei and electrons within the molecule and is determined by their respective interactions. Based on this, one could assume that, unlike the stability of chemical species, the stability simpliciter of a molecule is independent of the conditions in which that molecule is considered. That is, stability simpliciter is as an intrinsic property of a single molecule.[189] However, this is not an accurate understanding of stability because it disregards:

i. the factors that influence the stability of a single molecule when that molecule is part of an ensemble (i.e. of a chemical species); and,

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species has in and of itself. Chapter 7 examines in more detail the nature of stability as a relational property, so a more specified understanding of relational properties is not assumed in the current chapter.

[188] Interestingly, this illustrates an ambiguity with respect to the use of thermodynamic concepts when referring to a single molecule. This is because a single molecule does not have temperature, pressure, etc. However, one could assume the use of equilibrium statistical mechanics in spelling out thermodynamic concepts in a way that is meaningful for a single molecule. This aspect of the chemical description is not examined here.

[189] Intrinsic properties are 'properties objects have just in virtue of how they are in themselves, not how they are in relation to other things' (Ney 2014: 285). See also section 7.3.

ii. the manner in which the stability of a single molecule is empirically identified.

Therefore, stability simpliciter does not accurately capture the nature of this property when referring to a single molecule. In order to specify accurately the nature of stability, one needs to specify first whether it refers to a single molecule which is considered as part of an ensemble, or to one considered in isolation.

Regarding the stability of a single molecule that is part of an ensemble, it is stable in virtue of being part of a stable chemical species. This is because the molecule that is part of an ensemble is neither static, nor always fixed at its ground state. The molecules of a stable chemical species interact both intermolecularly and intramolecularly. Therefore, the conformation of each molecule that is part of a stable species dynamically changes over time. In fact, each molecule might, at indefinite points in time, be in a state that doesn't correspond to its ground state.[190] Needham explains this as follows:

> What appears macroscopically as an unchanging state of affairs is thus the scene of rapid change at the microlevel. Although the changes balance to maintain steady concentrations when dynamic equilibrium is established, the fixed concentrations are not constituted by fixed quantities of matter. The half-life of the dissociation of water (time for half of a given amount of water to decompose) is about 20ms (20 x 10^{-6}s). So after a very short time on the human scale, say half a second, an appreciable proportion of the water molecules in any given quantity of water will have been dissociated and the ions from any particular molecule will have recombined, though not necessarily with one another. (2017: 134)

In light of this, the stability of a single molecule which is part of a stable chemical species is partially determined by the set of chemical species with which its respective chemical species is compared (in terms of their relative molar standard Gibbs energy), by the thermodynamic conditions in which it is considered, by the (actual or hypothetical) set of reaction(s) that are considered, and by the environment in which the chemical species is assumed to be found.[191]

Based on the above, the stability of a single molecule that is part of an ensemble is a relational property of that molecule. This is because, whilst it is partially determined by the arrangements and interactions of the

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[190] The term 'conformation' standardly applies to molecules which exhibit different stereoisomeric structures. A conformation corresponds to 'the spatial arrangement of the atoms affording distinction between stereoisomers which can be interconverted by rotations about formally single bonds' ((IUPAC 2014: 319), see also chapter 2). However, it is also understood more broadly as referring to the different possible spatial arrangements of the atoms that comprise a molecular entity (see subsection 6.2.3). The latter understanding of conformation is assumed here.

[191] See also the aforementioned presentation of stability with reference to chemical species.

entities that comprise it, it is also determined by factors that concern the relation of that molecule with its surroundings.

c. The stability of a single molecule in isolation

The other case is a single molecule in isolation. Contrary to a single molecule which is part of an ensemble, one would expect the stability of a single isolated molecule to be an intrinsic property which is only determined by its composing entities and interactions. In this case, the stability of a single molecule in isolation would refer to stability simpliciter; i.e. to the ground state of the molecule. However, the in principle impossibility of empirically identifying any property of an isolated system, entails that this model of the stability of a single isolated molecule is highly idealized.

First, let us define what is meant by 'isolation' here. The term is understood in science in various ways; i.e. there is thermodynamic isolation, material isolation, radiative isolation, etc. (see for example (Jewett and Serway 2010)). Given how science understands 'isolation', a single molecule is understood as a system in isolation when the following requirements are met:

- It is far removed from any other system and thus doesn't interact with other molecular entities (i.e. with other atoms, molecules, ions, etc.); and,
- The total energy of the system is conserved.[192]

This is a highly idealized representation of a single molecule, for two main reasons. First, it is very difficult to empirically examine a single molecule's properties in an environment in which the molecule doesn't interact with other molecular entities. In practice, when it comes to the empirical support of chemical properties, the experiments are performed on chemical substances and not on a single molecular entity.[193] Given this, it is common in chemical practice to assign chemical properties to a single molecule by measuring properties of samples of matter. The experiments are performed in such conditions that it is safe to assume that the behavior of each molecule of an ensemble, closely resembles the behavior of a single molecule when in isolation.[194]

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[192] To the knowledge of the present author, there is no reference in chemistry or quantum chemistry which specifies what renders a molecule in isolation (see for example (IUPAC 2014)). However, based on how chemists and quantum chemists describe an isolated molecule and on how physics defines isolation, this chapter takes this to be a correct definition of an isolated molecule.

[193] See 2.1 for the definition of chemical substances.

[194] One could justify this assumption if, for example, the chemical substance is examined in very low pressure.

This is merely an epistemic difficulty which, with the improvement of technological means, could possibly be overcome. In fact, there has been extensive development of techniques and experiments in chemistry which aim at measuring the value of properties of single molecules, instead of inferring the properties of a single molecule by measuring the properties of an ensemble of molecules. This research is often referred to as 'single-molecule chemistry' (see for example (Bai et al. 1999), (Orrit 2015) and (Walter 2008)).

There is, however, a second reason why the description of a single isolated molecule is highly idealized. The empirical identification of a molecule's stability (or of any other property) necessitates the interaction of that molecule with an experimental device, through the emission of light or the imposition of a field to the system. Therefore, the properties of an examined system are necessarily those that the system exhibits when it is in a state of non-conservation of energy. This cannot be overcome; in principle any act of measurement will probe the examined system in such a way that it will cease to be in isolation.

In conclusion, the empirical verification of the stability of a single isolated molecule is (a) to an extent unattainable with the use of current technological means, because one standardly measures the properties of samples of matter, and (b) in principle impossible because any sort of measurement (even if that measurement is performed to a molecule that is far removed from other entities) requires the probing of the system to a state in which it is no longer in isolation. Therefore, the stability of a single isolated molecule refers to a state of a system which can never be empirically identified and whose existence is assumed, rather than empirically verified. This idealization is made both in chemistry and in quantum mechanics, whenever the two theories describe a single stable isolated molecule.

It is important here to clarify that the justification for this idealization does not imply that a single isolated molecule cannot be stable. While the stability of a single molecule in non-isolation is a relational property, it does not follow that an isolated molecule cannot be stable. Put differently, it does not follow from our epistemic impossibility to access a single isolated molecule, that such a molecule does not instantiate this property. Nevertheless, the lack of direct empirical evidence of an isolated molecule, together with the scientific fact that external factors determine the stability of the respective non-isolated molecule, renders the assignment of this property an idealization.

6.2.2 Stability simpliciter versus epistemic stability

There is one additional feature that renders the chemical and quantum mechanical descriptions of a single isolated molecule an idealization, namely the way in which they represent it in time. This becomes evident by distinguishing between two notions of stability. One notion takes into account time (henceforth ‘epistemic stability’), whereas the other regards stability as a time-independent property of systems (henceforth ‘stability simpliciter’).[195]

According to epistemic stability, a system is stable if it is possible empirically to identify it as a separately distinguishable system. Epistemic stability is not a property of the system, but rather an epistemic requirement for the identification and measurement of a system. It states that, in order to identify a system and its particular characteristics, one should be able to empirically identify it and measure its properties. That is, the system should be epistemically stable. The requirement of epistemic stability is crucial for the empirical identification and measurement of a system’s structure. If a system is not stable under some set of conditions and for a measurably adequate amount of time, then one cannot empirically identify it as a separately distinguishable entity, and thus the investigation of its structure is empirically unsupported. Time is a central factor in determining the epistemic stability of a system because this notion is specific to a particular time-range (i.e. the time range of the experiment in which stability is empirically identified).

Epistemic stability does not put any constraints on the nature of the examined system. Any sort of molecular entity could be regarded stable in this sense of the notion. For example, the excited state of an atom or molecule may be epistemically stable if that atom or molecule can be empirically identified and measured under specific conditions and for a sufficient amount of time. Note that, under particular conditions, it is possible that an excited state of a system is more epistemically stable than its ground state because the excited state can be identified and measured for a larger range of time. Moreover, the requirement of epistemic stability is not one that greatly restricts the set of molecular entities whose properties can be empirically examined. For example, with the development of advanced experimental and technological tools, it is possible to empirically identify and measure the structural properties of molecular entities which are stable for very short time ranges or under very extreme conditions (see for example (Hansen et al. 2015)). Nevertheless, the requirement of epistemic stability is essential for the empirical investigation of the properties of molecules. That is, molecules have to be epistemically stable in order to empirically identify them and measure their properties (including their structure).

As already mentioned in 6.2.1, stability simpliciter corresponds to the idealized understanding of stability with reference to a single molecule and is defined in terms of the molecule being in its ground state. The crucial difference between stability simpliciter and epistemic stability is that the former is understood as being a property of a system, and not as an epistemic requirement for a molecule’s empirical identification. However, stability simpliciter is an idealized understanding of the property of stability because, apart from

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[195] ‘Stability simpliciter' has been defined in the previous subsection. This definition is maintained here. The distinction that is presented here should be understood as further specifying the meaning of ‘stability simpliciter’.

not taking into account the factors that determine the stability of an empirically identifiable single molecule (i.e. thermodynamic conditions, presence of chemical species, environment), it does not take into account the range of time in which the system's stability is epistemically identified. This is because stability simpliciter corresponds to the ground state of a molecule, which in turn is a stationary state; namely a state that 'does not evolve with time' (IUPAC 2014: 1443).

Based on the distinction between these two notions of stability, it follows that systems that are epistemically stable may not be stable simpiciter (or vice versa). Molecules that are not in their ground state (in the sense of being in the state of lowest Gibbs energy) may be epistemically stable, if they are empirically identified under specific conditions and for a particular range of time. However, such molecules don't possess the property of stability because they are not found in their ground state. On the other hand, it is possible that a system which is stable in terms of being in its ground state, is not epistemically stable. This may be because, with the available experimental means, it is not epistemically possible to identify that state in a measurable range of time.

The distinction between these two notions of stability raises an interesting question about the nature of stability with respect to a single isolated molecule. Is this a time-independent property? The previous subsections pointed out that, in virtue of being defined as corresponding to the ground state (i.e. as stability simpliciter), stability is understood in an idealized way with reference to a single isolated molecule (see 6.2.1). This is because the factors that determine the stability of an empirically identifiable molecule (thermodynamic conditions, environment, chemical species, etc.) are not taken into account. The stability of a single isolated molecule is further idealized because it is defined as corresponding to a stationary state of the molecule. This representation of an isolated molecule's stability doesn't take into account that the empirical identification of its stability is dependent on the time-range of a particular experiment. However, there is empirical evidence of particular molecules which change from one structure into another in the course of time, suggesting that a molecule may not remain in one stable state indefinitely.[196] So, given that in non-isolation, stability is a time-dependent property, it may be assumed that stability in isolation is a time-dependent property as well. On the other hand, one can assume that the stability of an isolated molecule is time-independent, in accordance to how it is described in quantum mechanics through the stationary states. While both assumptions are consistent with empirical evidence, the above analysis suggests the following. When describing an isolated molecule, chemistry's and quantum mechanics' understanding of stability as a time-independent property is an idealization; namely something that is assumed, rather than empirically verified.

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[196] For example, (Meléndez-Martínez et al. 2014) examine the time-dependence of the different isomeric structures of carotenoids.

The next section argues that a similar idealized understanding is assumed with respect to the structure of a single isolated molecule.

6.2.3 Structure

Molecular structure is a central property of molecules that figures in the explanation of their chemical behavior. The particular structure of a molecule can explain (to a certain degree) the stability and reactivity of that molecule. Also, the structure of a molecule that participates in a particular reaction may partially explain the process through which it transforms into particular products (i.e. the reaction mechanism), as well as the sort of products that are produced during the reaction. Moreover, physical properties of matter may be explained in terms of the structure of the molecules that compose it.

While molecular structure is employed by IUPAC for the definition of other chemical terms (such as molecular modelling and the Lewis formula), the term itself is not defined in (IUPAC 2014). In light of this, this chapter proposes a definition which is based on how the term is broadly understood in chemistry. Moreover, similarly to the examination of stability, this subsection investigates how a molecule's structure is understood and empirically identified for two cases, namely:

a. a single molecule when considered as part of an ensemble (i.e. of a chemical species); and,
b. a single molecule in isolation.

Note that, unlike with the case of stability, there is no definition of structure with reference to chemical species. Instead, structure is taken to refer exclusively to a single molecule.[197]

a. The structure of a single molecule when considered as part of an ensemble

There are two concepts that are often employed when referring to molecular structure; namely 'shape' and 'conformation'. The 'structure of a molecule' is often employed interchangeably with the 'shape of a molecule' or 'molecular shape' (for example (Llored 2012), (Ramsey 1997), (Woolley 1976: 28)). Moreover, depending on the type of molecules that are examined, molecular structure is often referred to in terms of the conformations that a specific molecule can take. Furthermore, the specific structure of a particular molecule is described by specifying the spatial arrangement of the atoms within that molecule.

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[197] The definition of 'the structure of a catalyst' is not relevant to the current discussion, so it is disregarded (IUPAC 2014: 1470).

The structure of a molecule is defined here as the spatial arrangement of the atoms that constitute it. The factors that determine this spatial arrangement are contingent not only on the identity and interactions between the atoms that comprise the examined molecule, but also on the context in which the molecule as a whole is considered. This becomes evident when examining the structure of a single molecule that is considered as being part of an ensemble. In this case, the spatial arrangement of a molecule's atoms is determined by (i) their intramolecular interactions, and (ii) the intermolecular interactions between its atoms and one or more distinct molecular entities. This justifies the aforementioned distinction between the structure of a single molecule considered as part of an ensemble, and the structure of a single molecule in isolation.

Molecular structure is a collective term in the sense that it doesn't refer to one particular and empirically measurable chemical property, but rather to a collection of empirically measurable chemical (but also quantum mechanical) properties of the molecule.[198] In light of this, the properties that specify a molecule's structure when that molecule is part of an ensemble, can be categorized into two sets. The first set includes the information that specifies the interactions between a molecule's own atoms (i.e. the intramolecular interactions). This includes reference to:

- the intramolecular interactions of atoms, both bonding and nonbonding;
- the properties that are assigned to the intramolecular interactions of atoms;
- certain properties that are based on the quantum mechanical description of molecules;
- the pictorial representation of molecules; and,
- the properties that specify the structural differences between molecules.[199]

The intermolecular interactions between a molecule and two or more molecular entities can significantly affect the structure of the molecule. 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).[200] Two water molecules in a water dimer (i.e. $(H_2O)_2$) do not have the same structure and each molecule's

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[198] This seems to be in accordance with intuition. For example, when describing the structure of a box, one specifies its angles, the length of its sides, the distance between its surfaces, etc. There is no one measurable property that fully identifies and describes the structure of a box. The same applies to a molecule's structure. There is a set of properties that need to be specified in order to provide a satisfactory description of molecular structure.

[199] See also section 2.1.

[200] Special thanks to Fred Manby for suggesting these two examples.

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).[201] In light of this, there is a second set of properties which are invoked for the specification of a molecule's structure. This set includes reference to:

- the interactions of the molecule (or of its constituting atoms) with one or more distinct molecular entities (for example hydrogen bonds); and,
- the properties that are assigned to the intermolecular interactions.

This set depends on the identity of the molecule under examination, but also on the identity of the surrounding molecular entities.

Depending on the explanatory, predictive, or heuristic needs of chemistry as well as on the particular type of molecule that is under examination, intermolecular interactions may be disregarded in the description of the molecule's structure. For example, a molecule with aromatic character exhibits unusual epistemic stability due to its structure, regardless of the particular environment in which it is considered (IUPAC 2014: 109). Therefore, its structure and stability are usually explained independently of the environment and conditions in which the molecule may be found. On the other hand, there are also cases where intermolecular interactions play an important role in explaining molecular structure, and thus in the behavior of molecules. For example, the 'abnormal physical properties' of matter composed of NH_3, H_2O or HF is explained with reference to the intermolecular interactions that take place between such molecules (namely in terms of hydrogen bonding) (Needham 2013: 52).

In the light of the above discussion, it is clear that when a single molecule is considered as part of an ensemble then its structure is a relational property, in the sense that a molecule's shape is partially determined by the relations it develops with other molecular entities.

b. The structure of a single molecule in isolation

Concerning a single isolated molecule, it becomes evident that, in virtue of being isolated, intermolecular interactions do not play any role in the determination of the molecule's structure. However, it is not entirely accurate to infer from this that what determines molecular structure are only the intramolecular interactions of an isolated molecule. Just like in the case of stability, molecular structure is empirically supported in the context of chemical species, and not of a single isolated molecule. The terms employed for the description of molecular structure are defined with reference to chemical species and empirically supported by

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[201] Needham raises a similar point regarding the properties of a single molecule in general: 'A molecule in the liquid isn't like a water molecule in isolation (in the gas phase at very low pressure) but will be subject to all the stresses imposed by the ambient medium' (2017: 135).

experiments done on ensembles of molecular entities. Moreover, the structure of a single molecule is partially determined by the thermodynamic conditions in which the molecule is considered, as well as by the environment in which it is found. For example, depending the temperature of the system, the molecule may exhibit different structures (see for example (Xiao et al. 2016)). Therefore, the structure of a single isolated molecule refers to an idealized state of the molecule which can never be empirically identified and whose existence is assumed rather than empirically verified.

Consider, for example, the empirical identification of chirality; namely of the 'geometric property' of a molecule 'of being non-superposable on its mirror image' (IUPAC 2014: 269). A single inert molecule has the property of being chiral when its mirror molecule is not identical to itself. The term enantiomer refers to each molecule of any pair of chiral molecules. The two enantiomers of a pair of chiral molecules are often referred to as the right- and left-handed enantiomers. A chiral molecule is experimentally identified through the measurement of the optical activity of the sample in which that molecule is contained (IUPAC 2014: 1030).[202] Any assembly of chiral molecules that is either enantiomerically pure (i.e. it contains only right or only left-handed enantiomers) or that contains an unequal amount of a pair of enantiomers (i.e. it contains, say, more left- than right- handed enantiomers) is optically active. The measurement of optical activity is performed on a sample of material, i.e. on matter composed of an ensemble of (either chemically distinct or identical) molecular entities. While chemists infer from such experiments that the observed sample contains molecules with specific chiral structure, the observed optical activity is that of the entire sample, and not of a single chiral molecule.

It should be noted that there are advances on single-molecule chemistry concerning the measurement of the polarization of light produced by one single molecule. This is directly relevant to the empirical examination of the chirality of a single molecule (see for example (Chuntonov and Haran 2013)). However, even in single-molecule chemistry, the single molecule whose properties are measured, is considered in a system where it interacts with other molecules. It is not the case that the single molecule is far removed from other molecular entities. Therefore, both the presence of other molecules, as well as the environmental and thermodynamic conditions in which a single molecule is considered, are still relevant to the determination of its structure.

An additional idealization concerning the structure of a single molecule becomes apparent from how structure is pictorially represented. In chemistry, the structure of a molecule is represented statically, as if the molecule and its constituting atoms are not continuously moving and rotating in space. However, the pictorial representation of a molecule's structure only highlights the average shape of a molecule and does

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[202] A 'sample of material able to rotate the plane of polarization of a beam of transmitted plane-polarized light is said to possess optical activity (or to be optically active)' (IUPAC 2014: 1030).

not refer to a static and unchanging structure. This is important because, even if one considers a single isolated molecule, it still remains the case that the particles that comprise an isolated molecule interact with each other and move in space. This is due to the existence of intramolecular interactions which persist even when the total energy of the system is constant (since the angular momentum of its comprising entities is non-zero). Therefore, the structure of a molecule is dynamic in the sense that a molecule (even in isolation) can possess different conformations in time as a result of the continuous interactions of the entities (namely electrons and nuclei) that comprise the system (see for example (Longuet-Higgins 1963: 446)).

There is one additional factor that plays a central role in the understanding of structure. This further illustrates the idealized framework in which one describes the structure of a single isolated molecule. The empirical identification of a molecule's structure is possible only if the examined molecule is epistemically stable. That is, the empirical identification of a molecule's structure necessitates that the molecule is epistemically stable for a particular range of time. If a molecule is not epistemically stable under particular conditions and within a particular environment, then it is not possible to empirically identify its structure. Moreover, time is not only central to the empirical identification of structure. There are types of molecules whose structure change in the course of time (see for example (Meléndez-Martínez et al. 2014)). This suggests that a single molecule's structure is contingent on a particular time range of the experiment in which it is examined. This is not taken into account in quantum mechanics which describes the properties of a molecule by specifying its stationary (i.e. time-independent) states.[203]

6.3 Philosophical implications

The previous section presented the factors that determine a molecule's stability and structure. A molecule's stability and structure are by necessity empirically identified in relation to those factors. Hence, when one describes a single molecule in isolation and independent of time, it is just assumed that it is stable and has structure, because this description (whether chemical or quantum mechanical) disregards the factors that partially determine the stability and structure of an empirically identifiable molecule. Whether this assumption is justified (namely whether an isolated molecule is stable and has structure) is not examined here.[204] The chapter only points out that, given how science empirically identifies these two properties, a single isolated molecule with stability and structure is an assumption.

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[203] Another interesting paper which illustrates the importance of the above factors in determining the structure of a molecule is (Elango et al. 2010).

[204] See the end of this section for more on this point, as well as chapter 7.

Taking into account the philosophical literature on idealizations (see section 6.1), numerous questions can be raised about the assumption that a single isolated molecule is stable and has structure. First, there are various ways in which one could argue that this assumption is an idealization. For example, one could define this as a deliberate simplification/distortion of the description of a single molecule which disregards some of the factors that determine the molecule's properties, in order to achieve one or more goals (i.e. tractability, solubility, simplicity, generality, identification of core causal factors, etc.) (in line with (McMullin 1985) and (Weisberg 2007a)). On the other hand, one could say that chemistry and quantum mechanics refer to a new system (i.e. a single isolated and time-independent molecule) some of whose properties approximate some of those of the target system (i.e. a single non-isolated and time-dependent molecule) (in line with (Norton 2012)). Contrary to both views, it could be argued that there is no interesting difference between these two interpretations of the assumption; both interpretations capture the same understanding of idealization regardless of whether we formulate it in terms of descriptions or in terms of the system to be described. However, there are philosophers who would possibly disagree with this. For example, Norton argues that his proposed understanding of idealization introduces 'reference to a novel system' and thus carries 'a novel semantic import' (2012: 208-209).

Secondly, another question is whether the assumption that is presented here is an example of a particular type of idealization. For example, one could say that this is an example of Galilean idealization as the latter is defined by Weisberg:

> Galilean idealization is the practice of introducing distortions into theories with the goal of simplifying theories in order to make them computationally tractable. One starts with some idea of what a nonidealized theory would look like. Then one mentally and mathematically creates a simplified model of the target. (2007a: 640)

Alternatively, one could say that this is an example of Aristotelian idealization, as defined by Frigg and Hartmann:

> Aristotelian idealization amounts to 'stripping away', in our imagination, all properties from a concrete object that we believe are not relevant to the problem at hand. This allows us to focus on a limited set of properties in isolation. (2012: section 1.1)

While it is possible to argue for different types of idealizations, there are particular types that do not apply to the assumption presented here. For example, the assumption is not a case of an infinite idealization where the latter is defined as 'distortions or misrepresentations (..) in which some parameter takes on an infinite or infinitesimal value' (Shech 2018: 1). In fact, it is not a case of a mathematical idealization, in the sense that some mathematical value that is involved in the description of the system, is set to infinity or zero. Consider for example McMullin's definition of mathematical idealization:

> Mathematical idealisation is a matter of imposing a mathematical formalism on a physical situation, in the hope that the essentials of that situation will lend themselves to mathematical representation. (1985: 254)

That the particular assumption is not a case of an infinite or mathematical idealization is supported as follows. Indeed, quantum mechanics imposes a mathematical formalism on molecules via the Schrödinger equation. The equation assumes that an isolated molecule is stable and has structure by setting the values of some parameters in the Schrödinger equation. However, the same does not apply to chemistry's description of a single molecule. This is because chemistry is not primarily a mathematical description; its description of the relevant phenomena includes non-mathematical vocabulary as well. While it employs mathematical formalisms (from thermodynamics, quantum mechanics, etc.), it also employs a formalism that is non-mathematical.

This issue also raises the question of why this idealization is made in chemistry and in quantum mechanics. Since this idealization is not only made in the mathematical formalism of quantum mechanics, it is inadequate to claim that its function is the mathematical tractability of the system. Perhaps its function is simplicity in general, in the sense that one includes in the descriptions as little as possible (Weisberg 2007a: 650). Alternatively, its function may also be explanatory because the descriptions employ this idealization in order to 'include only the core causal factors which give rise to a phenomenon' (Weisberg 2007a: 642). While this section does not examine and specify in detail what the function of this idealization is, it is evident that this idealization serves more than one function in the relevant descriptions. First, this idealization accommodates the mathematical tractability of the quantum mechanical description of a single molecule. This is because, if quantum mechanics took into account time and the different conditions in which the molecule can be considered, then the relevant mathematical equation would be very difficult, if not impossible, to solve. Moreover, this idealization has also an explanatory function in the following sense. It is much easier for chemists to explain and understand the properties of a molecule, if they consider it in isolation and independent of time. By considering a single molecule in isolation, chemists identify particular properties of the molecule and explain how these properties account for macroscopic properties of the matter in which the molecule is part of. These properties play a large role in understanding why the molecule behaves the way it does, even if these properties are not the only factors which determine its behavior (see also (Weisberg 2007a: 650)).

One more issue that is revealed in light of the literature on idealizations, concerns the nature of stability and structure. If stability and structure are only empirically identifiable when external factors partially determine them, then it is a matter of philosophical debate whether stability and structure are intrinsic or relational properties of a molecule. Put differently, can a single isolated molecule be stable and have structure? Is the assumption of an isolated stable molecule with structure a 'legitimate idealisation' or an 'outright falsehood' (Ladyman 2008: 360)? This is a particularly interesting question, if one considers examples of idealizations in science which are considered as false or impossible:

> For example, 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)

In light of this, a strict empiricist could argue that since we don't have any empirical evidence of a single isolated molecule having stability and structure, then we cannot be certain about whether such a molecule instantiates these properties (see section 7.3). That is, it is possible that this particular idealization is an impossibility; an isolated molecule cannot be stable or have structure. On the other hand, one could argue that the empirical success of chemistry and of quantum mechanics supports the assumption that an isolated molecule possesses these properties. Therefore, this assumption is a legitimate idealization within chemistry and quantum mechanics (see section 7.2).[205]

The next chapter applies two different interpretations of idealizations to the assumption that a single isolated molecule is stable and has structure. Chapter 7 shows that the application of each interpretation contributes to the philosophical analysis of the quantum mechanical description of a single isolated molecule. Recall that the manner in which quantum mechanics describes a single isolated molecule is invoked as putative empirical evidence for Hendry's account of strong emergence (see chapter 5). By considering this assumption as an example of a particular interpretation of idealizations, one can explain why quantum mechanics describes a single molecule the way it does, without positing Hendry's strong emergence. Moreover, each interpretation of idealizations has different philosophical implications regarding the relation between chemistry and quantum mechanics, the reality of molecular structure, and the nature of

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[205] These two positions about the nature of stability and structure are discussed in detail in the next chapter.

stability and structure. These philosophical implications further illustrate that examining the above assumption as a case of an idealization, is useful and informative.

7. The Problem of Molecular Structure

There is a consensus in the philosophy of chemistry literature that the manner in which quantum mechanics describes a molecule's structure is problematic when it comes to specifying the relation between chemistry and quantum mechanics (this is henceforth referred to as the problem of molecular structure).[206] Specifically, two features of the quantum mechanical description of molecular structure are regarded as being problematic in the literature. The first is the use of configurational, instead of resultant, Hamiltonians. This concerns the methodological analysis of how the structural properties of a single inert molecule are described in quantum mechanics.[207] The second is referred to as Hund's paradox. It concerns why, in the case of an isolated inert chiral molecule, the ground state corresponds to the superposition of two distinct enantiomeric structures. Both involve how quantum mechanics describes the structure of a single inert molecule and have been used as putative empirical evidence for the support of different accounts regarding the nature of molecular structure and the relation of chemistry with quantum mechanics.

This chapter argues that the idealizations presented in the previous chapter can be interpreted in two ways so as to solve the problem of molecular structure; namely the epistemic and the referential interpretation. Each interpretation is a novel solution to the problem of molecular structure. In fact, if one accepts the argument from parsimony, then both interpretations are preferable to Hendry's account of strong emergence because they solve the problem of molecular structure in a way that doesn't require the postulation of downward causal relations. The two interpretations also contribute to the examination of the nature of molecular structure and to the analysis of the relation between chemistry and quantum mechanics.

Section 7.1 presents the problem of molecular structure. Sections 7.2 and 7.3 present one of the two proposed interpretations. Each section raises three questions about them. First, how does the interpretation solve the problem of molecular structure? Secondly, how does it avoid strong emergence? Thirdly, how does it contribute to the understanding of the nature of molecular structure, and of the relation between chemistry and quantum mechanics?

7.1 The problem of molecular structure

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[206] A concise presentation of the problem of molecular structure and how it has been addressed in the philosophy of chemistry is provided by Hettema (2017: 49-68).

[207] Chapter 5 explained how the methodological analysis of quantum mechanics is used as putative empirical evidence that molecular structure strongly emerges (as the latter is understood by Hendry).

This section explains why quantum mechanics is regarded as problematic with respect to how it describes a molecule's structure. It also enumerates the existing solutions that have been proposed in the literature, without critically examining them.

7.1.1 The use of configurational, instead of resultant, Hamiltonians

In the philosophy of chemistry literature the use of configurational, instead of resultant, Hamiltonians is posed as a challenge to the recovery of a molecule's structure from its quantum mechanical description.[208] The inability of quantum mechanics to recover a molecule's structure is, in turn, posed as a challenge to the strict Nagelian reduction of chemistry to quantum mechanics, as well as to reductive and non-reductive physicalism.[209] The terminology used here is due to Hendry who makes the distinction between what he labels as 'resultant' and 'configurational Hamiltonians' ((2010a: 210- 211) and (2010b: 185)).

A resultant Hamiltonian is defined as the complete description of the intra-molecular interactions, and it is constructed using as input the fundamental physical interactions and the value of the physical properties of the entities. However, the Coulombic Schrödinger equation, which is defined in terms of a resultant Hamiltonian, is almost never used. Instead, what is used in order to construct the Schrödinger equation and to describe a system, is the configurational Hamiltonian. The configurational Hamiltonian is constructed on the basis of ad hoc assumptions about the nuclear geometry of the examined molecule.[210]

Hendry claims that, regardless of the mathematical complexity involved in solving the Coulombic Schrödinger equation, the resultant Hamiltonian is in principle unable to provide information regarding a

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[208] This has also been presented in chapter 5 so it will not be analyzed in detail here (see the presentation of the 'counternomic claim' in section 5.5). See also (Hendry 1999), (Hendry 2006), (Hendry 2010a), (Hendry 2010b), (Primas 1981), (Scerri 2007a), (Scerri 2012a), (Woolley 1978), (Woolley 1998), (Woolley and Sutcliffe 1977) and (Sutcliffe and Woolley 2012).

[209] Chapter 3 defined strict Nagelian reduction as the position which at least requires the (in principle) derivation or deduction of chemistry from quantum mechanics (see also section 4.3). While there are different accounts of physicalism in the philosophy of science literature, physicalism (whether reductive or non-reductive) is broadly understood here as the 'ontological position according to which the physical facts determine all the facts' (Hendry 1999: 118).

[210] Specifically, this assumption is the Born-Oppenheimer approximation (also referred to as the 'adiabatic approximation' (Hettema 2017: 61), or BO approximation). The Born-Oppenheimer approximation 'takes note of the great difference in masses of electrons and nuclei'; this allows to consider the nuclei 'as fixed in position' (Atkins and Friedman 2005: 249). When the BO approximation is made, the 'fixed nuclear geometry appears as a parameter' in the Schrödinger equation and, thus, the equation is solved only for the electrons that comprise a molecule (Hendry 2010a: 213). Hettema presents the history of the Born-Oppenheimer approximation (2017: 57-61). See also 2.2.

molecule's structure. He supports this claim by considering two examples. The first concerns the quantum mechanical description of isomers ((Hendry 2010a: 213), (Hendry 2010b: 186) and (Woolley 1998: 11)). According to Hendry, distinct isomers are described by an identical resultant Hamiltonian and therefore an identical Coulombic Schrödinger equation. Therefore, it is not possible to differentiate, via the resultant Hamiltonian, molecules that differ in terms of their isomerism. Only the configurational Hamiltonian can differentiate systems that differ only in terms of their structure. The second example concerns the quantum mechanical description of any non-symmetric isolated molecule ((Hendry 2010b: 186) and (Sutcliffe and Woolley 2012: 409)). The quantum mechanical description (in terms of the resultant Hamiltonian) does not describe the asymmetries in the structure of a particular molecule (as specified, for example, by the dipole moment). This is because, 'arbitrary solutions to the Coulombic Schrödinger equations should be spherically symmetrical' (Hendry 2010a: 213). However, 'polyatomic molecules cannot be spherically symmetrical, for their lower symmetries are important in explaining their behavior' (Hendry 2010a: 213). Therefore, one inserts information regarding such asymmetries to the configurational Hamiltonian, in order to construct an accurate description of a molecule's structure.[211]

Is Hendry correct in claiming that the Coulombic Hamiltonian is in principle unable to provide information about a system's structure? Why is it that we employ configurational, instead of resultant, Hamiltonians? Is this merely an epistemic problem, in the sense that we don't yet have the available computational means to solve the Coulombic Schrödinger equation in such a way as to describe the structural properties of a system? Or is this an indication that, in principle, the system has no structure at the quantum mechanical scale?

These questions can be answered in various ways, and some of these answers have interesting metaphysical implications about the nature of molecular structure and about chemistry's relation to quantum mechanics. For example, Hendry argues that the Coulombic Schrödinger equation is in principle unable to describe the structure of the system, because structure strongly emerges at a level of ontology which is not derivable from quantum mechanics. Another answer is that the problem arises solely due to epistemic difficulties regarding the solution of the Coulombic Schrödinger equation. Nevertheless, using the configurational Hamiltonian 'makes only a small difference to the calculated energy of the molecule' and it is 'enough to consider only an equilibrium geometry that is known empirically' (Hendry 2010a: 213).[212] Another account suggests that the reason we employ configurational Hamiltonians is that the resultant Hamiltonian of an

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[211] These two examples are also presented and examined in chapter 5. Moreover, note that a quantum mechanical description is understood here as being accurate if it agrees with how the structure of a molecule is experimentally identified.

[212] This position is referred to by Hendry as the 'proxy defence' of quantum mechanics (see also (Hendry 2006: 183-184) and (Hettema 2017: 54)).

isolated system does not take into account the system's interaction with the environment. The configurational Hamiltonian should be understood as a more accurate description of a single molecule because it can be formulated so as to take into account its interactions with the environment (Hendry 2010b: 186).[213] Lastly, the use of configurational Hamiltonians could be explained by the fact that quantum mechanics is an incomplete description, in the sense that it does not take into account all the interactions that take place at the relevant scale of inquiry.[214]

This chapter does not critically examine any of these accounts. Instead, it argues that a well-supported explanation of the use of configurational Hamiltonians should consider the fact that the quantum mechanical description is an idealization regarding the stability and structure of a single inert molecule. First, the next subsection presents the second feature of quantum mechanics that reveals the problem of molecular structure.

7.1.2 Hund's paradox

Friedrich Hund in 1927 formulated a paradox concerning chiral molecules.[215] Recall that chirality is the 'geometric property of a rigid object (or spatial arrangement of points or atoms) of being non-superposable on its mirror image (..)' (IUPAC 2014: 269). A single inert molecule has the property of being chiral when its mirror molecule is not identical to itself.[216] The term enantiomer refers to each molecule of any pair of chiral molecules. The two enantiomers of a pair of chiral molecules are often referred to as the right- and left-handed enantiomers.

The paradox is that a chiral molecule is observed in one of its two enantiomeric forms despite the fact that, according to the quantum mechanical description of a single isolated chiral molecule:

(i) the two enantiomeric structures are not energy eigenstates of the symmetric molecular Hamiltonian (Bahrami and Shafiee 2011a: 1); and instead,
(ii) the molecule's energy ground state corresponds to the symmetric superposition of the two enantiomeric structures (Trost and Hornberger 2009: 1).

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[213] Hendry argues that this account does not actually solve the problem (2010a: 215).

[214] A position along these lines, though stronger in its claim, is supported by Hans Primas who argues that quantum mechanics is 'incorrect and should be revised, partly because (it) seems incapable of rendering a robust account of concepts such as molecular shape' ((Hettema 2017: 53), see also (Primas 1981)).

[215] See (Bahrami and Shafiee 2011a), (Bahrami and Shafiee 2011b), (Bahrami et.al. 2012), (Berlin et.al. 1996), (Day 2009), (Fortin et al. 2018) and (Trost and Hornberger 2009).

[216] See chapter 2 for more details on chirality.

Hund's paradox is formulated in the context of a model of the chirality of an isolated, single inert molecule as follows. A single isolated chiral molecule is treated as a 'particle in a one-dimensional symmetric double-well potential with the only stationary energy level in each individual well' ((Berlin et al. 1996: 333), see Image 15). In this context:

$|L\rangle$ represents the state of the molecule that corresponds to the left-handed enantiomer

$|R\rangle$ represents the state of the molecule that corresponds to the right-handed enantiomer

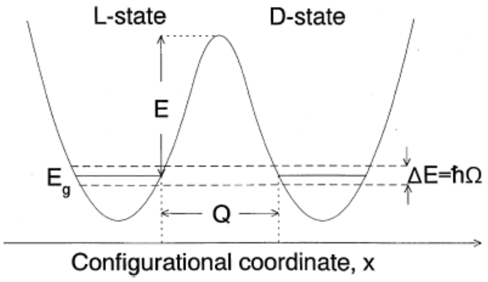

Image 15. The model of an isolated chiral molecule in terms of a one-dimensional symmetrical double-well system. The two enantiomers are described by the L- and D- states of the molecular system. They have the same energy E_g and are splitted due to quantum tunnelling. ΔE is the splitting energy, equal to the product of the Planck constant, h, and the tunnelling frequency Ω. x is the configurational coordinate, E is the height of the potential energy barrier, and Q is the width of the barrier. (Image is from (Berlin et al. 1996: 333))

Each state is related to a wavefunction which is localized in one of the two wells (Image 15). These states have definite chirality, do not have definite parity, and are degenerate in energy (Berlin et al. 1996: 333). However, they are not energy eigenstates of the system because, for a finite barrier, their respective wavefunctions overlap.[217] Due to this overlap, the energy eigenstates of the molecule are symmetric and antisymmetric combinations of the two chiral states, namely:

$$|+\rangle = (|L\rangle + |R\rangle)/\sqrt{2}$$

and

$$|-\rangle = (|L\rangle - |R\rangle)/\sqrt{2}$$

State $|+\rangle$ corresponds to the energetic ground state of the molecule, whereas state $|-\rangle$ is its first energetic excited state (Fischer and Mittelstaedt 1990: 412). Both states have definite parity; the ground state has

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[217] This is also specified by stating that the two wavefunctions are quasi-localized in each of the respective wells (Fischer and Mittelstaedt 1990: 413).

positive parity, whereas the first excited state has negative parity (Fischer and Mittelstaedt 1990: 412). That is, they are respectively symmetric and antisymmetric under the parity transformation, P:[218]

$P|+\rangle = |+\rangle$; and,
$P|-\rangle = -|-\rangle$

The ground state $|+\rangle$ does not have definite chirality; instead it corresponds to the symmetric superposition of the right- and left- handed chiral structures. This implies that the 'molecule will spend equal times in the L- and D- states and will tunnel back and forth between them with a characteristic frequency' (Berlin et al. 1996: 334). However, this comes in contrast with the empirical investigation of the structure of a single chiral molecule, since there are certain chiral molecules which, under specific conditions, are observed to have definite chirality, i.e. they are either in the L- or R- state. This is the paradox.

There are various accounts that have been proposed for either explaining or resolving Hund's Paradox. First, Hund explained the observation of one enantiomer, instead of a superposition of two enantiomeric structures, by the 'possibly very long tunnelling time from a left-handed configuration state $|L\rangle$ to a right-handed one $|R\rangle$' (Trost and Hornberger 2009: 1). Other accounts suggest that environmental decoherence resolves the paradox and specify which particular structure an examined chiral molecule will take under particular environmental conditions ((Bahrami et al. 2012) and (Trost and Hornberger 2009)). Another account proposes a novel interpretation of quantum mechanics in order to resolve the paradox; namely the modal-Hamiltonian Interpretation (MHI) ((Fortin et al. 2018), see also (Fortin et al. 2016)).[219] By assuming this interpretation of quantum mechanics, it follows that a molecule's structural properties (including its chirality) are relational properties that aren't instantiated when examining the molecule in isolation (Fortin et al. 2018: 11). Lastly, other accounts suggest that the 'correct' ground state of a single isolated chiral molecule is not of definite parity (as initially suggested above) ((MacDermott and Hegstrom 2004), (Bahrami and Shafiee 2011a), and (Bahrami and Shafiee 2011b)). This is because there is a 'small parity-violating energy shift' to one of the two possible enantiomers which, if taken into account, results in having a ground state which corresponds to an 'unequal' superposition of the two chiral states (MacDermott and Hegstrom 2004: 56-57). In this context, if one takes into account environmental effects, then it is possible to explain the

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[218] The symmetry under parity transformation of the ground state is also referred to as parity-invariance (Trost and Hornberger 2009: 1).

[219] The thesis does not present in detail this interpretation of quantum mechanics.

empirical identification of a molecule's chiral structure in a way that is consistent with its quantum mechanical description.[220]

Two things are noted here about Hund's paradox. First, it is a special case of the measurement problem, considered in the context of how quantum mechanics describes an isolated, single inert molecule.[221] This is because the primary question Hund's paradox raises is why, prior to the observed structure of a molecule, the description predicts that a single isolated inert molecule is in a superposition of the two structures. In fact, Alexandra MacDermott and Roger Hegstrom explicitly identify the eigenstates of a chiral molecule to 'genuine Schrödinger's cat-like coherent superpositions' (2004: 56). The 'term "Schrödinger's cat" states is appropriate because these molecular vibrational states are coherent superpositions of the familiar classical geometrical structures' (MacDermott and Hegstrom 2004: 56). That Hund's paradox is a special case of the measurement problem is also supported by the fact that some accounts allegedly solve the paradox by proposing a suitable interpretation to quantum mechanics (i.e. in terms of decoherence or the MHI) (see ((Bahrami et al. 2012), (Trost and Hornberger 2009) and (Fortin et al. 2018)).[222]

Secondly, there is at least one sense in which Hund's paradox is relevant to the use of configurational Hamiltonians (though it is not mentioned in this context by Hendry). Hund's paradox can be understood as additional evidence of the general inability of quantum mechanics to describe the structural properties of a single isolated inert molecule from 'first principles' (Trost and Hornberger 2009: 1).[223] That is, Hund's paradox is a special case of the problem of molecular structure which focuses on how quantum mechanics describes a particular structural property of molecules (namely chirality). However, Hund's paradox should

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[220] There are various kinds of environmental effects which are examined in the literature. These include the effect of interactions with phonons of optically inactive solids below a particular temperature (Berlin et al. 1996: 1), the effect of intermolecular interactions and blackbody radiation (Bahrami et al. 2012), and the effect of collisions with a background gas ((Trost and Hornberger 2009) and (Bahrami and Shafiee 2011b)).

[221] A detailed presentation of the measurement problem is not given here. Very briefly, the problem 'lies in the conflict between the predictions of the dynamics of quantum mechanics and simple facts about observation' (Ney and Albert 2013: 22). As David Albert states, 'the postulate of collapse seems to be right about what happens when we make measurements, and the dynamics seems to be bizarrely *wrong* about what happens when we make measurements; and yet the dynamics seems to be *right* about what happens whenever we *aren't* making measurements' (Albert 1992: 79) (italics are in original text).

[222] This does not mean that these accounts indeed solve the measurement problem. For example, Stephen Adler argues that decoherence does not solve the measurement problem (Adler 2003). Nevertheless, they have been proposed as solutions to the measurement problem. For an overview of the proposed solutions to the measurement problem, including decoherence, see (Ney and Albert 2013: 26-36).

[223] While the two problems may be related in a more substantial manner as well, this is not examined here.

not be confused with the issue of the use of configurational Hamiltonians. Unlike Hund's paradox, the issue of the use of configurational, instead of resultant, Hamiltonians underwrites the quantum mechanical description of any molecule (chiral and non-chiral). Therefore, the use of configurational Hamiltonians is a more general and persisting element of the problem of molecular structure.

The next two sections present two novel solutions to the problem of molecular structure. Each solution is based on the fact that quantum mechanics assumes an idealised understanding of stability and structure (see chapter 6). As explicated in the previous chapter, the philosophy of science literature presents a variety of definitions, accounts, and interpretations of idealisations. In light of this, each of the next two sections applies a particular interpretation of idealisations to the case of the quantum mechanical understanding of stability and structure. Each interpretation solves the problem of molecular and contributes to understanding why quantum mechanics describes a molecule the way it does.

7.2 An epistemic interpretation for the problem of molecular structure

The epistemic interpretation of idealizations is based on how Weisberg defines idealizations. As mentioned in section 6.1, he defines idealizations as 'the intentional introduction of distortion into scientific theories' (Weisberg 2007a: 639). This section applies this definition of idealizations to how quantum mechanics understands stability and structure in the following manner. Quantum mechanics is an idealization in the sense that it is a simplified/distorted description of the empirically identifiable molecule. This is because quantum mechanics disregards the factors which determine the stability and structure of that molecule (i.e. environment, thermodynamic conditions, time, etc.). This interpretation of idealizations is labelled here as 'epistemic' because it makes reference to how stability and structure are described in quantum mechanics, and not to the nature of a molecule's stability and structure.

There is an alternative way to formulate the epistemic interpretation. If one assumes Norton's distinction between idealizations and approximations, then the epistemic interpretation states that quantum mechanics is an approximation to (and not an idealization of) the empirically identifiable molecule (Norton 2012: 209). Norton defines an approximation as 'an inexact description of a target system' (Norton 2012: 209). The target system here is the empirically identifiable molecule. In this context, the assumptions that are made about stability and structure render the quantum mechanical description an approximation to the empirically identifiable molecule. According to Norton, this is distinct from regarding the quantum mechanical description an idealization. This is because Norton defines idealizations as 'a real or fictitious system, distinct from the target system, some of whose properties provide an inexact description of some aspects of the target system' (2012: 209).[224]

7.2.1 How this interpretation solves the problem of molecular structure

The problem of molecular structure can be resolved if we take into account that the Schrödinger equation, both in the form of the resultant and in the form of the configurational Hamiltonian, is a distorted description of a single molecule.

It is reasonable that one derives from quantum mechanics different information about a stable molecule's structure, compared to how structure is empirically identified. This is because both the resultant and the configurational Hamiltonians are distorted descriptions of a molecule's stability and structure. In fact, if one understands quantum mechanics in terms of this interpretation of idealizations, then it is possible to explain why the resultant Hamiltonian, unlike the configurational one, does not describe a molecule's structure. The resultant Hamiltonian assumes a more idealized understanding of stability and structure, compared to the configurational Hamiltonian. Put differently, the resultant Hamiltonian is a more distorted description of a molecule's stability and structure, compared to the configurational Hamiltonian.

This is supported by comparing the idealizations assumed in the two descriptions. While both the resultant and the configurational Hamiltonians have assumed an idealized understanding of a molecule, the configurational Hamiltonian has less idealizations than the resultant Hamiltonian in the following sense.[225] The configurational Hamiltonian is formulated for a 'fixed nuclear geometry'. The particular nuclear geometry which is assumed is taken from chemistry's empirical identification of the structure of the examined molecule (Hendry 2010a: 213). Therefore, the configurational Hamiltonian assumes information regarding the target system and thus indirectly takes into account factors that determine the structure and stability of the examined molecule.

It should be noted that the configurational Hamiltonian is not rid of all the idealizations that are assumed by the resultant Hamiltonian. For example, the solution of the Schrödinger equation, via the configurational Hamiltonian, describes states that are independent of time. Moreover, the configurational Hamiltonian makes certain idealizations that are not assumed by the resultant Hamiltonian (namely via the Born-Oppenheimer approximation). Nevertheless, the configurational Hamiltonian provides a less idealized

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[224] The next section presents how the problem of molecular structure can be solved if one assumes Norton's definition of idealizations.

[225] Examples of idealizations that are made in the configurational Hamiltonians are briefly mentioned later on in the text.

description of a single molecule, in the sense that it incorporates information that is drawn from the empirical identification of the structure of a molecule. This explains why, unlike the resultant Hamiltonian, the configurational Hamiltonian describes the structure of a molecule in a way consonant to the empirical identification of structure.

This point is further supported by the fact that the configurational Hamiltonian provides accurate and novel information regarding the structure of the examined system. This information is novel in the sense that it is not presupposed for the configurational Hamiltonian's construction, and in the sense that it contributes to the further understanding of a molecule's structure.[226] The predictive and explanatory success of the configurational Hamiltonian further supports the claim that, unlike the resultant Hamiltonian, the configurational Hamiltonian is a less idealized description of the molecule.

Regarding Hund's paradox, the epistemic interpretation is silent on the measurement problem. The fact that quantum mechanics is a distorted description does not explain why the ground state of a chiral molecule corresponds to a symmetric superposition of its two enantiomeric structures. However, the epistemic interpretation explains why, even though quantum mechanics predicts a state of indefinite chirality as being the most stable state of a molecule, one empirically identifies a state of definite chirality.

Hund's paradox is often analyzed in the literature in terms of stability. For example, Mohammad Bahrami and Afshin Shafiee discuss Hund's paradox with respect to the stability of a molecule:

> A great number of molecular properties (e.g., molecular geometries, optical activity and dipole moments which depend on the nuclear configuration) are stable properties of the chiral molecules in many different physical conditions (e.g., temperature, pressure, and the size of molecule). However, the chiral configuration states are not the eigenstates of the symmetric molecular Hamiltonian. (2011a: 1)

This apparent disagreement between the empirical identification of a stable molecule's structure and its quantum mechanical description can be explained by the fact that there is an equivocation between how 'stability' is understood when one empirically identifies it and how 'stability' is understood in quantum mechanics. This equivocation becomes apparent if one considers the distinction between 'epistemic stability' and 'stability simpliciter' (as presented in subsection 6.2.2). Quantum mechanics assumes a notion of

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[226] Chapter 4 provided examples of how quantum models (which are mostly formulated in the context of the Born-Oppenheimer approximation and thus employ configurational Hamiltonians) have contributed to the description and explanation of a molecule's behavior (including its structure) (see subsections 4.2.5, 4.2.6, and 4.2.7).

stability which is defined in terms of the molecule being in the ground state (i.e. stability simpliciter), whereas the empirical identification of a molecule identifies stability as a relational property in the sense of being partially determined by the conditions and time-range in which the molecule is considered (i.e. epistemic stability). In this context, there is no disagreement between quantum mechanics and the empirical identification of a molecule's chirality because, strictly speaking, they involve different notions of stability when describing a chiral molecule.

The solution provided by the epistemic interpretation to the problem of molecular structure is a plausible one if one considers how alternative accounts purport to solve this problem. Recall that some accounts of the problem of molecular structure, in particular those that invoke decoherence, refer to the role of the environment in determining the structure of a single molecule. Such solutions reformulate the quantum mechanical description by considering the effect of a background gas, of different thermodynamic conditions, etc.(see subsection 7.1.2). Irrespective of whether accounts of decoherence successfully provide a solution to the measurement problem, their relative success in quantum mechanically describing the structure of a molecule (including its chirality) reveals the importance of taking into account the factors which have been empirically identified as partially determining the stability and structure of a molecule. In this context, whenever quantum mechanics takes into account those factors, quantum mechanics is a more accurate description because it incorporates an understanding of stability and structure which is consonant with how stability and structure are empirically identified and understood. Therefore, the relative success of decoherence further supports that the mismatch between quantum mechanics and the empirical identification of a molecule's structure, is partially due to the existence of idealizations in quantum mechanics.

It should be clarified that the epistemic interpretation neither implies nor necessitates the acceptance of decoherence as a solution to the measurement problem. However, the relative success of decoherence in providing a more accurate description of chiral molecules at least partially stems from the fact that it takes into account factors that have been empirically verified to determine a molecule's stability and structure. This further supports the tenability of the solution provided via the epistemic interpretation and reinforces the position that the problem of molecular structure in quantum mechanics can be (partially) solved by reference to epistemic factors. Moreover, while this solution is compatible with decoherence accounts, it is distinct because it is based on the analysis of the empirical identification of a single molecule and does not solve problems that pertain exclusively to quantum mechanics (most notable being the measurement problem).

7.2.2 Contra strong emergence

The epistemic interpretation challenges strong emergence as Hendry conceives of it because it denies one of its basic assumptions. Hendry argues that quantum mechanics (in the form of the resultant Hamiltonian) is in principle unable to describe and explain the structure of a single inert molecule. According to Hendry, if the Coulombic Schrödinger equation is in principle unable to describe the structure of a molecule, then this supports the claim that molecular structure strongly emerges. In order for Hendry to argue that the Coulombic Schrödinger equation is in principle unable to describe the structure of a molecule, it must be assumed that this equation is a complete description of the molecule at the relevant scale. If this assumption is not made, then the inability of the Coulombic Schrödinger equation to derive the structure of a molecule is explicable by the fact that it is an incomplete description. This assumption is not explicitly stated by Hendry.

The epistemic interpretation challenges this assumption in the following manner. If quantum mechanics is a distorted description of a molecule then this means that the resultant Hamiltonian is not a complete description of a single molecule. Several examples indicate that the resultant Hamiltonian is not a complete description of a single molecule (or any examined system, whether particle, atom, molecule, etc.). First, the Coulombic Schrödinger equation disregards the factors that partially determine a molecule's stability and structure. Secondly, it disregards the gravitational, weak and strong nuclear forces between particles. Only the electrostatic forces between particles are taken into account when examining the interactions between the entities that comprise the examined system. While this is a sensible assumption in the sense that the electrostatic forces play the most determinant role in the behavior of particles, it nevertheless distorts the descriptions. In fact, certain accounts state that 'the weak interactions result in tiny energy differences between two chiral enantiomers' (Bahrami and Shafiee 2011a: 84), suggesting that the interactions that have been disregarded in the Coulombic Schrödinger equation partially determine (even if minimally) the structure of a molecule. Lastly, the Coulombic Schrödinger equation is a non-relativistic and time-independent description. This is a further distortion which renders the Coulombic Schrödinger equation an incomplete description.

Based on the above, the epistemic interpretation denies the assumption that the Coulombic Schrödinger equation is a complete description. If the Coulombic Schrödinger equation is not a complete description, then there are no sufficient grounds to support strong emergence in Hendry's sense.

7.2.3 Philosophical implications

This subsection examines how the epistemic interpretation informs the discussion regarding the nature of molecular structure, and the relation between chemistry and quantum mechanics. As explained above, it does not make any claim regarding the nature of molecular structure at the quantum mechanical scale, or the relation between chemistry and quantum mechanics. Therefore, it is possibly compatible with more than one positions regarding these two issues. Due to the limited scope of this chapter, a complete analysis of these positions is not pursued here. Instead, this chapter argues that the epistemic interpretation is compatible with:

i. a realist position regarding molecular structure at the quantum mechanical scale; and,
ii. a physicalist position regarding the relation between chemistry and quantum mechanics.

First, this interpretation is compatible with a realist position regarding molecular structure. Specifically, one can argue that a single isolated inert molecule has structure at the quantum mechanical scale by considering how this interpretation solves the problem of molecular structure. Specifically, the previous subsection argued that the Coulombic Schrödinger equation is an incomplete description because it is a distorted (i.e. idealized) description. Based on this, Hendry cannot convincingly argue that the Coulombic Schrödinger equation is a more 'exact' description compared to the one provided by the configurational Hamiltonian. Therefore, one should regard the configurational Hamiltonian at least on an equal footing when examining the nature of molecular structure. In fact, one can invoke the configurational Hamiltonian for the defence of the existence of molecular structure at the quantum mechanical scale. For example, the explanatory, confirmational, and predictive success of configurational Hamiltonians in deriving structural properties supports the claim that there is structure at the relevant scale. Put differently, the best explanation for why the configurational Hamiltonian is so successful in describing structure is that there is structure at the relevant scale.[227]

While the configurational Hamiltonian is constructed with the use of ad hoc assumptions regarding the position of the nuclei within the molecule, it has nevertheless succeeded in predicting and explaining structural properties of the molecule which chemistry does not always predict or explain. As mentioned in chapter 4, the chemical understanding of molecular structure has advanced greatly with the development of quantum mechanical models which assume the BO approximation. This success of the Schrödinger equation (in terms of the configurational Hamiltonian) is best explained by the fact that the use of ad hoc information provides an accurate description of the molecule at the relevant scale. The ad hoc information concerns the structural properties of the examined molecule. Therefore, the molecule has structure at the quantum mechanical scale.

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[227] Note that this argument for the reality of molecular structure is a special case of the following 'well-known argument for scientific realism': 'we ought to infer that scientific theories that are predictively successful are (approximately) true, since their truth would be the best explanation of their success' (Lipton 2004: 184) This realist argument is discussed in detail in the philosophy of science literature. This is often discussed in conjunction with the miracle argument ((Putnam 1975: 73), see also (Lipton 2004)).

Moreover, if one accepts the principle of parsimony (also labelled 'Ockham's Razor'), then the above position is a preferable account of the nature and reality of molecular structure than Hendry's strong emergence. The latter incorporates the reality of molecular structure because of the supposed novel causal powers possessed by the structure of a molecule at the chemical scale. This is based on Alexander's dictum according to which 'the reality of a broadly scientific entity plausibly requires that it has causal powers' (Wilson 2010: 303-304). However, if one assumes the principle of parsimony, then the proposed argument is preferable to strong emergence both with respect to how they respectively solve the problem of molecular structure, and with respect to how they defend the reality of molecular structure. According to the principle of parsimony, 'one should not multiply one's ontological commitments beyond necessity' (Ney 2014: 287). Since the epistemic interpretation solves the problem of molecular structure and defends the reality of molecular structure without postulating downward causal powers, then it is preferable to Hendry's strong emergence.

Note that this is not an adequate defense of this realist position. For example, one should address issues that pertain to the validity of abductive arguments and of the principle of parsimony.[228] Moreover, it is important to examine the implications of this position to the nature of molecular structure.[229] Nevertheless, it overcomes the problem of molecular structure. By overcoming this, the examination of the reality of molecular structure can be pursued within the general and standard framework of this debate in the philosophy of science literature.[230]

Moreover, the use of configurational Hamiltonians is identified by Hendry as one the central problems for physicalists regarding the relation between chemistry and quantum mechanics (2010a: 219). The epistemic interpretation provided an explanation of this problem in a way that does not undermine physicalism, and therefore reinforced the tenability of the latter. However, it neither gives, nor implies a particular understanding of the metaphysical relation between the two descriptions. An adequate defense of a particular physicalist position requires a detailed analysis of what such a position advocates, as well as a specification and support of the requirements that need to be fulfilled for such a position to hold.

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[228] For example, one objection towards the principle of parsimony is that there is no adequate justification of why one should prefer theories, accounts, or hypotheses which are ontologically parsimonious ((Ney 2014: 49-50), see also (Baker 2016)).

[229] For example, it is prima facie consistent with the view that molecular structure is real because it possesses 'a proper subset of the token powers of' the quantum mechanical entities on which it supervenes (Wilson 2015: 343). This does not refute the causal completeness of physics and is in line with Wilson's 'weak emergence' as well as with non-reductive physicalism (see (Wilson 2010) and (Wilson 2015))

[230] See for example (Brock and Mares 2007), (Chakravartty 2017), (Ladyman 2001), (Ladyman 2006), (Psillos 1999), and (Worrall 1989).

Nevertheless, this interpretation explains the use of configurational Hamiltonians in such a manner that the investigation of the relation between the two descriptions can now be pursued within the standard framework of this debate.

One last comment should be made regarding the epistemic interpretation. In order for the current thesis to be self-consistent, any proposed position should be compatible with the other positions that are defended here. For example, chapter 4 defended Kincaid's model of unity regarding the relation between chemistry and quantum mechanics. Therefore, it is important to examine whether the epistemic interpretation is compatible with Kincaid's model of unity. In fact, this is the case. This is because:

i. It requires the rejection of strong emergence.
ii. It is compatible with the criteria that need to be fulfilled for the model of unity to hold. Specifically, it is compatible with supervenience, as well as with the requirement of composition/token identity of the higher and lower-level entities.

Clause i was supported in subsection 7.2.2. Regarding clause ii, the epistemic interpretation supports (and thus is compatible with) supervenience for the following reason. Recall that, for supervenience to hold, it must be the case that whenever the chemical description of a single molecule changes, then its respective quantum mechanical description changes as well. According to the epistemic interpretation, the configurational Hamiltonians should not be disregarded when investigating metaphysical issues, including the question of supervenience. Configurational Hamiltonians support supervenience since, even when a molecule changes just in terms of its structural properties, its configurational Hamiltonian (and thus the solution of the corresponding Schrödinger equation) changes as well. Therefore, supervenience is supported by the epistemic interpretation. Regarding the criterion of token identity and composition, the epistemic interpretation neither supports but nor contradicts this criterion. The specification and defense of token identity is presented in chapter 4 and there is no obvious manner in which this defense comes in contrast to the epistemic interpretation of quantum mechanics. Therefore, the epistemic interpretation is prima facie compatible with this criterion of Kincaid's model. However, it is also compatible with reductive accounts (both epistemic and ontological) regarding the relation between the two descriptions. Kincaid's model of unity requires the rejection of reductive accounts, therefore additional arguments are required that are consistent with this interpretation and that reject reduction. Such arguments are presented in chapter 4 so the current chapter does not examine this further.

7.3 A referential interpretation for the problem of molecular structure

This section presents a second interpretation of idealizations which solves in an alternative manner the problem of molecular structure. This interpretation assumes a different understanding of idealizations; namely as referring to a new system some of whose properties approximate some of those of the target system (in line with (Norton 2012)). It is labelled here 'referential' because, under this interpretation, idealizations, are defined as carrying 'novel semantic import' (Norton 2012: 208).[231]

7.3.1 How this interpretation solves the problem of molecular structure

Chapter 6 argued that stability and structure are only empirically identified with reference to a single non-isolated molecule. In light of this, a single isolated molecule is a distinct system from the one which is empirically identified. Put differently, the latter is an idealization in the following manner:

> An idealisation is a real or fictitious system, distinct from the target system, some of whose properties provide an inexact description of some aspects of the target system. (Norton 2012: 209)

The target system is the non-isolated molecule. Chemistry is in the business of describing and explaining the properties of the target system, including its stability and structure.[232] The idealization is the isolated molecule. Quantum mechanics, via the time-independent Schrödinger equation, describes this idealization. While the two systems are distinct, it is assumed that some of the properties of the idealization 'provide an inexact description of some aspects of the target system' (Norton 2012: 209).

In light of this, the problem of molecular structure can be resolved by considering the following question. Do particular properties of the idealization provide an inexact description of the relevant properties of the target system?

If one assumes that science is in the business of providing an accurate description of the stability and structure of the target system (i.e. of the empirically identifiable, non-isolated molecule), then from the mere existence of the problem of molecular structure, it follows that the idealization does not provide an accurate

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[231] The term 'referential' is not employed by Norton with respect to his proposed understanding of idealizations. As mentioned in the previous section, Norton distinguishes this notion of idealization by contrasting it with the notion of approximation. In the light of the literature on idealizations, this chapter labels Norton's understanding of idealizations as 'referential' in order to distinguish it from alternative understandings of the notion (such as the epistemic interpretation which was presented in section 7.2).

[232] This doesn't mean that chemistry does not include 'inexact descriptions of the target system'; namely approximations in Norton's sense (Norton 2012: 209).

description of the target system. This makes sense if one considers that stability and structure are partially determined by factors that do not present themselves in the idealization. The idealization is defined independently of the factors that partially determine these properties.

This interpretation of idealizations resolves the use of configurational, instead of resultant, Hamiltonians in the following manner. First, both the configurational and the resultant Hamiltonians provide, via the formulation of the relevant Schrödinger equation, descriptions of the idealization; namely of a single isolated molecule. They are inexact descriptions of the idealization because (i) they do not take into account time (unlike the initial time-dependent Schrödinger equation), and because (ii) they disregard certain physical interactions (namely the weak, strong, and gravitational interactions). Nevertheless, both descriptions refer to this idealization.

The resultant Hamiltonian provides a more accurate description of the idealization, compared to the configurational one. This is because the resultant, unlike the configurational, Hamiltonian doesn't (indirectly) incorporate assumptions regarding the structure and stability of the target system. In virtue of incorporating information about the target system, the configurational Hamiltonian provides a more inexact (or distorted) description of the idealization. On the other hand, the properties that are derived from the configurational Hamiltonian provide a more accurate description of the target system. This is because the configurational Hamiltonian incorporates information that is drawn from the empirical identification of the target system, and not of the idealization. This is what renders the properties of the idealization, as these are described by the configurational Hamiltonian, a more accurate (yet inexact) description of the target system. The properties of the idealization (specifically stability and structure) as these are provided by the resultant Hamiltonian, do not accurately describe the relevant properties of the target system, because the resultant Hamiltonian describes the properties of the idealization in a manner that completely disregards certain of the factors that determine the relevant properties of the target system.

This interpretation of idealizations also resolves Hund's paradox. The paradox is problematic only if one assumes that the quantum mechanical and the chemical descriptions refer to the same system. However, as it has become evident, this is not the case. The quantum mechanical description of a chiral molecule refers to the idealization (i.e. a single isolated molecule); it assigns the ground state (i.e. stability simpliciter) of an isolated molecule to the superposition of the molecule's two enantiomeric structures. Similarly, the chemical description refers to the target system; it assigns the most stable state (i.e. epistemic stability) to a particular chiral structure. These are not competing descriptions because they neither refer to the same property of stability, nor do they refer to the same system. In fact, it is not a problem that the properties of the isolated molecule do not accurately describe the relevant properties of the non-isolated chiral molecule. This is because the properties of the latter are partially determined by factors that are not considered when specifying the properties of the former.

The aforementioned solution to the problem of molecular structure is very similar to the one provided via the epistemic interpretation of idealizations. This is because the problem of molecular structure primarily concerns the relation between quantum mechanics and the target system. While this chapter does not examine whether other notions of idealization solve the problem of molecular structure, one can conjecture that, since the problem of molecular structure is solved under both examined notions of idealizations, the problem of molecular structure can be solved under different notions of idealization as well.[233]

Regardless of whether one understands quantum mechanics as an approximation of the target system or as referring to a distinct system, the explication of the problem of molecular structure is similar. This is because, as Norton states, '(a)n idealization can be demoted to an approximation by discarding the idealizing system and merely extracting the inexact description' (2012: 211). Instead, the difference between the two interpretations lies in their respective philosophical implications. This is because, unlike the epistemic interpretation, the referential interpretation of idealizations assumes that idealizations carry 'novel semantic import' (Norton 2012: 208). This raises interesting philosophical questions about the nature and existence of the idealization. Specifically, the next subsection focuses on examining how this interpretation informs the discussion about the nature of stability and of molecular structure.

7.3.2 Philosophical implications (I): the nature of stability and structure

The referential interpretation accommodates the investigation of metaphysical issues regarding idealizations. For example, Norton leaves it open whether the idealization is a fictional or real system:

> The characterisation of idealizations is quite permissive when it comes to the nature of the idealizing system. They may be other real systems or fictitious systems or mathematical objects or even parts of the target system itself. (2012: 209-210)

This raises interesting questions regarding the idealization examined here. Is a single isolated molecule real? Moreover, can stability and structure be meaningfully assigned to a single isolated molecule (i.e. to the idealization)? The first question is not examined in detail here. However, it is worth noting that there are various positions that one could support. For example, an empiricist such as Bas van Fraassen would argue

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[233] See chapter 6 for a brief analysis of the different accounts and notions of idealizations.

that since it is in principle impossible to empirically identify this idealization, we should not support that it is real. The postulates of quantum mechanics are not true, except in what they say about the empirically identifiable target system (i.e. the non-isolated molecule).[234] This is in line with van Fraassen's general empiricist stance:

> So from an empiricist point of view, to serve the aims of science, the postulates need not be true, except in what they say about what is actual and empirically attestable. (van Fraassen 1980: 3)[235]

Regarding the second question, while it is essential to examine the reality of an isolated molecule in order to argue that it instantiates (or not) certain properties, there is a sense in which the second question is independent of the first. For example, whether a tree can instantiate social properties is to an extent independent from the question of whether it exists.[236] In a similar manner, the question of whether stability and structure are instantiated by an isolated molecule can be investigated independently of the realist question.[237]

In light of this, this subsection presents an empiricist interpretation of the nature of stability and structure which is formulated after assuming Norton's notion of idealizations. It is an empiricist interpretation in the sense that it takes as decisive the lack of empirical evidence that could support the existence of these properties with reference to an isolated molecule (i.e. to the idealization, as defined in subsection 7.3.1). Based on the analysis of chapter 6, there is no empirical evidence of a single isolated molecule with structure and stability. Put differently, science has only experimentally identified these properties in a non-isolated and time-dependent manner. More than that, the experimental identification of these properties suggests that the environment and conditions in which a molecule is examined partially determines its stability and structure. This challenges the assumption that stability and structure are properties which can be

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[234] This is a moderate empiricist position in the sense that one could additionally argue that there is no sufficient empirical evidence for the existence of the target system itself. This would amount to supporting a more general antirealist position about molecules. Specifically, antirealists can regard both chemistry and quantum mechanics as 'inexact descriptions without referential success; they are all mere approximations' (Norton 2012: 211). See for example (Cartwright 1983) and (Laudan 1981).

[235] This section does not examine what van Fraassen takes to be 'actual and empirically attestable'. It assumes that there is prima facie a way to understand the empirically identifiable molecule as being 'actual and empirically attestable'.

[236] Wohlleben (2017) claims that trees allegedly feel and communicate. Intuitively, feeling and communicating are regarded as properties that cannot be instantiated by such entities. Therefore, the question of whether trees can instantiate them raises a debate that is at least partially independent of whether trees exist.

[237] This is consistent with the pragmatic realist approach that is assumed from the outset of this thesis (see chapter 1).

instantiated by an isolated molecule. Put differently, it challenges the assumption that stability and structure are intrinsic properties.[238]. If this challenge is correct, then one cannot meaningfully assign these properties to a molecule that is in isolation (i.e. to the idealization).

Consider for example the property of stability. The stability of a molecule is empirically shown to be partially determined by the molecule's environment and thermodynamic conditions (as outlined in chapter 6). There is no empirical evidence that a molecule's stability is independent of such factors. Therefore, it is consistent with empirical evidence to regard stability as a relational property which cannot be instantiated by an isolated molecule. Simply put, the stability of an entity A is defined and empirically identified when A is examined with respect to a set of entities B and in conditions C. In this context, scientific practice claims that the stability of A is determined not only by the nature of A, but also by the presence of B and the conditions C in which it is considered. The stability of A is a relational property in the sense that it is determined with respect to B and C. There is no empirical evidence that A is stable when B and C do not exist (i.e. when A is in isolation).

From this one might conclude that we just don't have the epistemic means to identify the stability of A when in isolation. Nevertheless, it might be argued, it is reasonable to assume that A is stable even in isolation; i.e. the stability of A is determined in such a case from the nature of A alone. For example, the first proposed interpretation implicitly accepts such an assumption (section 7.2). However, it also is consistent with empirical evidence to challenge this assumption and support an empiricist interpretation of stability. Specifically, it could be argued that talk of A's stability doesn't make sense in an isolated context. Stability is a relational property, and as such one cannot identify it when A is in isolation. It is a category mistake to investigate the stability of A 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, the fact that Alan is polite/rude is determined with respect to whom Alan interacts with in a particular environment. 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.[239] This is not merely because one cannot empirically

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[238] Recall that intrinsic properties are 'properties objects have just in virtue of how they are in themselves, not how they are in relation to other things' (Ney 2014: 285). Whether it is justified to understand stability and structure as not being intrinsic properties in this sense, is discussed in subsection 7.3.4.

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

verify whether Alan is polite in such a context, but because being rude or polite is partially determined by the environment and the persons with which Alan interacts.

A similar claim can be supported with respect to 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 assume that structure is a relational property which cannot refer to an isolated molecule (i.e. to the idealization). Put differently, there is no empirical justification that a single molecule in isolation has structure.

Three reasons support this claim about the nature of molecular structure. First, as with stability, whenever structure is empirically examined, it is always partially determined by the conditions and environment in which the molecule is found. If one is an empiricist, then the lack of empirical evidence suffices for challenging that such properties can be instantiated by an isolated molecule. Secondly, it is consonant with our intuitions that this property is not meaningfully describable with reference to an isolated system. Consider for example two molecules which only differ with respect to the fact that one has a left-handed structure, whereas the other has a right-handed structure (i.e. they are chiral molecules). In a universe where the left-handed molecule is in isolation, there is no obvious manner in which the two are different; in isolation the two are exactly the same. It is not merely that one cannot discern between the two (because, say there is no reference point according to which one can specify each molecule's handedness). Neither of the two molecules instantiate in isolation any property that could discern them from one another. Such properties are only instantiated when the molecule is related to something else.[240]

Thirdly, this understanding of stability and structure is supported by how quantum mechanics describes the idealization. According to Hund's paradox, the quantum mechanical description of a single isolated chiral molecule assigns its ground state to the superposition of its two enantiomeric structures. In this context, a single isolated molecule exhibits no structure. The same is indicated by the resultant Hamiltonian of any single molecule. Recall that the more accurate description of the idealization is the one that is provided by the Coulombic Schrödinger equation (i.e. via the resultant Hamiltonian, see subsection 7.3.1). The Coulombic Schrödinger equation suggests that the idealization has no structure:

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[240] Special thanks to James Ladyman for making this point. Note that in this hypothetical case, we assume that an isolated system is stable and can thus have a stable structure. This seems to contradict the overall claim made here that neither stability nor structure are instantiated by an isolated molecule. In this context, this 'intuitive' point should be only regarded as an indication that there is something problematic when considering structure in an isolated context.

> 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)

In light of this, quantum mechanics suggests that the idealization does not instantiate the properties of stability and structure. Just like Alan is neither polite nor rude when he sits in a room by himself, so the molecule is neither stable nor unstable, and neither structured nor unstructured. That molecules exhibit such a 'strange' non-classical behavior is supported by our best current science. For example, 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 and Arndt 2004: 144). This suggests that under particular conditions (which seem to resemble the conditions of isolation) molecules exhibit non-classical behavior in the sense of exhibiting interference effects, non-locality, and entanglement.[241] This further supports the claim that classical properties such as stability and structure are not instantiated by an isolated molecule.

7.3.3 Contra strong emergence

The empiricist interpretation of stability and structure is incompatible with Hendry's strong emergence. On the one hand, this interpretation is similar to the latter in that both theses involve the claim that there is no structure at the quantum mechanical scale. On the other hand, the two interpretations are incompatible for the following reason. According to the empiricist interpretation, structure is not instantiated by the idealization because the idealization is an isolated system. This implies that the property is not instantiated by an isolated molecule, regardless of the scale within which the molecule is found. Put differently, there is no structure either at the quantum or at the chemical scale. This comes in direct opposition to Hendry's strong emergence which involves the claim that structure emerges at the chemical scale. This implies that, according to Hendry's strong emergence, an isolated molecule has structure at the chemical scale.[242]

Also, note that even if one does not support this particular empiricist interpretation regarding stability and structure, the referential interpretation of idealizations by itself undermines the tenability of strong emergence. This is for two reasons. First, it is an added contribution to the explication of the problem of molecular structure. As an additional proposition which is equally consistent to empirical and scientific evidence, it undermines the tenability of the other existing solutions to the problem. Secondly, this is

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[241] See for example (Arndt et al. 1999), (Chatzidimitriou-Dreismann and Arndt 2004), and (Wang and Kais 2007).

[242] While not explicitly stated by Hendry, this is a fairly obvious implication of strong emergence. If an isolated molecule has no structure at the chemical scale, then there is no emergence of structure from the quantum to the chemical scale.

because it explains the empirical evidence that allegedly supports strong emergence, without implying (or at least requiring) metaphysical claims.[243] Similarly to the epistemic interpretation (see section 7.2), the referential interpretation explains the problem of molecular structure in a manner preferable to how strong emergence explains it. Specifically, if one assumes the principle of parsimony then the referential interpretation provides a simpler explanation of the problem in the sense that it does not require the postulation of additional (and downward) causal powers.

7.3.4 Philosophical implications (II)

This subsection examines how the referential interpretation of idealizations, as well as the empiricist interpretation of the nature of stability and structure, inform the discussion regarding the nature of molecular structure, and the relation between chemistry and quantum mechanics.

First, consider the implications of the referential interpretation of idealizations to the question of the relation between chemistry and quantum mechanics. Given the referential interpretation, quantum mechanics is taken to refer to a system which is distinct from the one that is empirically identified. Quantum mechanics refers to a single isolated molecule whereas scientists empirically identify the properties of a single non-isolated molecule. In light of this, if chemistry is taken to be in the business of describing and explaining the properties of the empirically identifiable molecule, then the two descriptions refer to distinct systems.[244] Therefore the investigation of the relation between the two theories has to take into account that, while the two theories are employed for the description and explanation of some common domain of phenomena, each theory provides a description of different systems.

The fact that the two descriptions refer to distinct systems does not render the question of their relation fruitless. First, this is because quantum mechanics makes reference to the same type of entities that chemistry refers to; namely atoms and molecules. In fact, both descriptions agree on the constitution of these entities; namely in terms of electrons, protons, and neutrons (see subsection 4.2.1). Moreover, quantum

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[243] While it is possible for this interpretation to be accompanied by metaphysical claims regarding the ontological status of idealizations, this is not a requirement of this interpretation. This is because, according to Norton, the idealization may be either a fictional or real system (see subsection 7.3.2).

[244] This is a justified assumption regarding the role of chemistry. Recall that chemistry is defined as the science that is concerned with how matter behaves and transforms (see for example the definition of chemistry in (Hendry et al. 2011) and in (Stevenson 2010)). This implies that chemistry is primarily interested in how molecules behave when they are part of matter, and not when they are isolated. In this context, the description and explanation of a single molecule in chemistry is primarily pursued because it accommodates the description and explanation of the behaviour of matter.

mechanics provides valuable insight into the behavior of the system that chemistry refers to (see subsections 4.2.6 and 4.2.7). This suggests that there are properties of the isolated and time-independent molecule which resemble those of the non-isolated and time-dependent molecule. So, the question of the relation between the two descriptions comes down to how closely the properties of a single isolated and time-independent molecule approximate those of the relevant non-isolated and time-dependent molecule.

The referential interpretation is consistent with Kincaid's model of unity for three reasons. First, recall that Kincaid's unity is supported by examining the 'interconnections and dependencies' between sets of statements, but also between the models, visual representations, etc. of the two theories (see section 4.1). In light of this, it is permissible to also examine the role of idealizations in such connections. In fact, the interpretation points at a relation between the quantum mechanical description and the target system which prima facie is not inconsistent with the explanatory, heuristic, and confirmational dependence of the two theories. Secondly, the referential interpretation does not prima facie imply or require metaphysical claims that go against the two metaphysical requirements of Kincaid's model (i.e. supervenience and composition/token identity). Thirdly, to the extent that this interpretation undermines Hendry's strong emergence, it is consistent with Kincaid's model (which in turn rejects Hendry's strong emergence).

Regarding the nature of molecular structure, the referential interpretation of idealizations doesn't imply or require a particular metaphysical claim. This is because, as already mentioned, the idealization may be regarded either as a fiction or as a real system. Therefore, if one accepts only this interpretation, then the question of the nature of molecular structure requires the postulation of additional metaphysical claims. On the other hand, the empiricist interpretation of stability and structure has interesting implications regarding the nature of molecular structure. The remainder of this subsection presents certain relevant questions that can be raised within the framework of the empiricist interpretation.

The first concerns the existence of structure with respect to a single isolated molecule. The previous subsections argued that there is no sufficient empirical evidence of a single isolated molecule having stability and structure. If one is an empiricist, this suffices to prima facie doubt (if not reject) the existence of structure and stability with respect to an isolated molecule. However, the specifics of this claim depend to a large extent on what one means by 'existence', 'property' and 'relational property'. The meaning assigned to these terms requires the investigation of metaphysical issues that go beyond the scope of this thesis.[245] For example, are we justified to regard stability and structure as relational properties (as the empiricist interpretation suggests)? Recall that, according to Ney, relational properties are properties objects have 'in relation to other things' (Ney 2014: 285). However, this is a rather general statement because it does not

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[245] See for example (Hawthorne 2001) and (Orilia and Swoyer 2016).

specify what renders an object in relation to something else. For example, 'Elliot is in love with Helen' posits the existence of a relational property (i.e. being in love with) between two objects (i.e. Elliot and Helen). In a similar manner, one needs to investigate which relata are involved in the relational properties of stability and structure. For example, one could argue that molecule A is stable in comparison with molecule B in conditions C.[246]

Another question is whether relational properties exist even if they are not instantiated by the system. For example, one could argue that while structure and stability are not instantiated by the isolated molecule, this does not mean that these properties, understood as propensities, dispositions or potencies, do not exist when referring to an isolated molecule (see for example (Bird 2007)).[247] Put differently, an isolated molecule has the propensity towards stability and structure regardless of the fact that it does not instantiate them in isolation. This suggests that the examination of the reality of molecular structure with reference to an isolated molecule raises difficult metaphysical issues which can nevertheless be pursued within the general and standard framework in the philosophy of science literature.

Lastly, another question is whether a non-isolated molecule has structure. To the extent that quantum mechanics is employed for the description of a non-isolated molecule, it is a 'false' description of that molecule in the sense that it does not refer to it. However, there is independent empirical evidence from chemistry which could be regarded as sufficiently supporting the existence of structure with reference to the target system. Moreover, while the configurational Hamiltonian does not refer to the empirically identifiable molecule, the structure that it describes successfully approximates the structure of the target system. This could support the claim that a single non-isolated molecule has structure (in a manner similar to how the previous section defended this; namely in terms of an abductive argument). While this is prima facie a tenable position, the above is an incomplete defense of the reality of a non-isolated molecule's structure. Nevertheless, since the problem of molecular structure is overcome, then the examination of the reality of molecular structure can be pursued within the general and standard framework of this debate in the philosophy of science literature.

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[246] If such a formulation of stability and structure as relational properties is not tenable, one could investigate whether there is an alternative understanding of relational properties which does not require the explicit specification of such relata. In any case, this raises metaphysical questions that require a detailed investigation in order to fully specify the empiricist interpretation. See for example (Heil 2003), (Lowe 2002), (Marmodoro and Yates 2016) and (Ney 2014).

[247] Such a view requires investigating whether relational properties can be regarded as 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).

7.4 Summary

This chapter presented the problem of molecular structure and the solutions that have been proposed. It argued that the problem can be solved in two alternative manners, if one takes into account that quantum mechanics assumes an idealized understanding regarding a single molecule's stability and structure. Specifically, the chapter considered two interpretations of this idealization in quantum mechanics; namely the epistemic and the referential interpretation. Under both interpretations, the problem of molecular structure is solved. Moreover, each interpretation has different philosophical implications regarding the nature of molecular structure and the relation between chemistry and quantum mechanics. Both interpretations are inconsistent with Hendry's strong emergence regarding molecular structure and thus further undermine Hendry's position. Lastly, both interpretations are prima facie consistent with Kincaid's model of unity, thus further reinforcing a unificatory view regarding the relation between chemistry and quantum mechanics (in line with Kincaid's model of unity).

8. Conclusion

This chapter recapitulates the main claims of this thesis and points outs some further questions that it raises.

This thesis investigates how chemistry and quantum mechanics are epistemically and metaphysically related, with particular attention to how each theory describes a single inert molecule (chapter 1). It reviews the existing accounts that have been proposed in the philosophy of chemistry regarding the epistemic and metaphysical relations between chemistry and quantum mechanics. It divides those accounts into those that support disunity, and those that support unity. The thesis shows that there is a proliferation of positions that support disunity and argues that this proliferation is accompanied by a tendency within the community to connect the legitimacy of the philosophy of chemistry with the autonomy of chemistry. This connection should not be made (chapter 3).

In light of how the philosophy of chemistry investigates the epistemic and metaphysical relations between chemistry and quantum mechanics, this thesis proposes a novel framework within which one can understand and investigate these relations. This framework is based on Kincaid's model of unity-without-reduction. The thesis argues that chemistry and quantum mechanics exhibit particular epistemic and metaphysical interconnections and dependencies that satisfy Kincaid's conditions for unity. Specifically, the thesis provides historical and scientific evidence that supports the following interconnections between the two theories:

- Particular chemical entities are composed of quantum mechanical entities.
- Chemistry and quantum mechanics are logically compatible with each other.
- Chemical properties supervene on quantum mechanical ones.
- Chemistry and quantum mechanics depend confirmationally, explanatorily, and heuristically on each other (chapter 4).

Given that chemistry and quantum mechanics are unified in accordance with Kincaid's model of unity, one can raise further questions regarding the epistemic and metaphysical relations between the two theories. For example, one question is whether and in what sense chemistry is autonomous from quantum mechanics. Kincaid's model is prima facie consistent with particular understandings of the notion of autonomy (see chapter 4). These understandings of autonomy can be further explored in order to defend the autonomy of chemistry in a manner consistent with chemistry's unity with quantum mechanics (as per Kincaid). Another issue that can be investigated concerns the analysis of the metaphysical relation between chemical and quantum mechanical entities. The notion of composition is not specified in detail by Kincaid's model. This leaves room to further investigate the appropriate understanding of composition consistent with Kincaid's model. This is an issue the investigation of which can be informed by existing metaphysical accounts of the relation between special science and physical entities. Lastly, given the role that the notions of explanation and mechanisms play in specifying Kincaid's model of unity, it is interesting to examine how these two notions can be further specified in a manner that is (i) consistent with Kincaid's model, and (ii) consonant with how explanations and mechanisms are employed and formulated in chemistry and in quantum mechanics.

This thesis assumes that Kincaid's model of unity is incompatible with strong emergence as understood by Hendry in terms of downward causation. Given this assumption, it is crucial to investigate the tenability of Hendry's account. The thesis explicates the core elements of it and examines the coherence and tenability of downward causation in the context of Kim's fourfold distinction between different versions of downward causation. This thesis argues that the only version of DC that could coherently apply to the case of the strong emergence of molecular structure is diachronic reflexive DC. However, diachronic reflexive DC faces three objections that undermine its tenability with respect to the strong emergence of molecular structure. First, the empirical evidence that Hendry invokes for the support of downward causation undermines a core element of Hendry's account, namely supervenience. Secondly, the use of ad hoc assumptions in quantum mechanics is invoked by Hendry as putative evidence that molecular structure strongly emerges. However, the use of ad hoc assumptions is common practice in science, and it is not clear in Hendry's account why the use of ad hoc assumptions in the quantum mechanical description of molecular structure, is indicative of downward causation. Thirdly, according to Hendry's understanding of strong emergence, the structure of a molecule exerts downward causal powers on the quantum mechanical entities of that molecule. This implies the existence of a downward causal relation between particular chemical entities, etc. and quantum mechanical ones. However, the nature of this causal relation is not adequately specified by Hendry. This is problematic because standard understandings of causation, such as Ned Hall's causation as production, are incompatible with the existence of a diachronic reflexive downward causal relation between the chemical entities, etc. at t_1 and the quantum mechanical ones at t_2 (chapter 5).

The examination of Hendry's strong emergence motivates the examination of interesting philosophical questions, all of which cannot be mentioned here. However, it is worth mentioning one particular question whose examination can be informed by Hendry's account of strong emergence. This question is how to defend the causal autonomy of the higher level without postulating the existence of downward causation. If one accepts Alexander's dictum, then Hendry's account of strong emergence implies the reality of higher-level properties (namely of molecular structure) (see chapter 7). This is because Hendry's account of strong emergence supports the causal autonomy of the chemical level. Even though Hendry's account is not tenable, the causal autonomy of the chemical level (and therefore its reality) could still be defended without recourse to downward causation and strong emergence. After all, while the existence of a downward causal relation implies the causal autonomy of the higher level, the causal autonomy of the higher level does not necessarily imply downward causation or strong emergence.[248] Therefore, it is interesting to examine how one can defend the causal autonomy of the chemical level without invoking downward causation and strong emergence. For example, in the philosophy of science literature there are accounts of weak emergence and non-reductive physicalism that could be invoked for the defense of the causal autonomy of chemical entities (for example (Wilson 2010)).[249] Given the other claims of this thesis, such accounts are particularly interesting because they are prima facie consistent with Kincaid's model of non-reductive unity. Therefore, it is interesting to examine whether and how one can defend the reality of chemical entities while maintaining that chemistry is unified with quantum mechanics (in Kincaid's sense of unity).

The last two chapters of this thesis examine how chemistry and quantum mechanics each describe the structure of a single inert molecule. This issue is relevant to how one understands the relation between chemistry and quantum mechanics because the manner in which quantum mechanics describes molecular structure has been used as putative empirical evidence for the rejection of strict Nagelian reduction and physicalism, and for the defense of Hendry's account of strong emergence. The thesis points out that chemistry and quantum mechanics both assume an idealized understanding of stability and structure. That is, when chemistry or quantum mechanics describes a single isolated molecule, it assumes that the molecule is stable and has structure (chapter 6). This is a particularly interesting feature of the chemical and quantum mechanical descriptions of a single inert molecule because it raises interesting philosophical questions about, among other things, the nature of this idealization and its function in the two theories.

Given this idealization, this thesis argues that the manner in which quantum mechanics describes an isolated molecule's structure is not problematic when it comes to specifying the relation between chemistry and quantum mechanics. That is, the so-called problem of molecular structure can be resolved in two alternative ways by applying two different interpretations to the idealization identified above. According to the epistemic interpretation of idealizations, the quantum mechanical description of a molecule's structure is a distorted description of that molecule. This explains why quantum mechanics describes molecular structure the way it does, without positing downward causation (as per Hendry). According to the referential interpretation of idealizations, the quantum mechanical description of a molecule's structure refers to a system which is distinct from the empirically identifiable molecule and its properties. This explains, in a

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[248] This becomes apparent by the literature on causal autonomy which does not make reference to the notion of downward causation or strong emergence. See, for example, (List and Menzies 2007), (Silberstein and McGeever 1999), and (Wilson 2015: 357- 361).

[249] Of course, there are accounts of non-reductive physicalism and weak emergence that reject the causal autonomy of the higher level and thus do not defend the reality of the higher level.

similar but distinct manner to the epistemic interpretation, why quantum mechanics describes molecular structure the way it does, without positing downward causation (chapter 7).

Each interpretation raises interesting questions about the nature of stability and structure, and the relation between chemistry and quantum mechanics. While some of these implications are pointed out in this thesis, there is still a lot more that can be said about them. For example, each interpretation is compatible with different understandings of the nature of stability and structure. The epistemic interpretation is compatible with an understanding of structure and stability as intrinsic properties of a single molecule because, given this interpretation, one can defend that an isolated molecule has structure. On the other hand, the referential interpretation is compatible with an understanding of structure and stability as relational properties. This is because, if one is an empiricist, then it can be argued that an isolated molecule cannot have stability or structure. Based on the above, the two interpretation may imply incompatible understandings of the nature of stability and structure. Therefore, one needs to examine which of the two understandings of stability and structure is tenable.

From the analysis of the chemical and quantum mechanical descriptions of a single inert molecule, the thesis concludes that the problem of molecular structure can be solved in ways which (i) do not imply strong emergence as understood by Hendry, and (ii) are prima facie consistent with a unified understanding of the relation between chemistry and quantum mechanics (as per Kincaid). Nevertheless, as it often happens in philosophy, the investigation of the relation between chemistry and quantum mechanics, and of the problems that are regarded relevant to this relation, raises additional questions which deserve further inquiry.

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