

Do molecules have structure in isolation?¹

How models can provide the answer

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

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(..) if a model represents, then it can instruct us about reality because (at least some of) the model's parts or aspects have corresponding parts or aspects in the world. (Frigg and Hartmann 2020)

1. Introduction

The way quantum mechanics describes molecular structure has received considerable attention in the philosophy of chemistry as it plays a central role in understanding not only the nature of molecular structure, but also chemistry's relation to quantum mechanics.³ An issue that has been of particular concern is that the quantum mechanical description does not identify structure in isolated molecules unless certain assumptions are made about the examined system. This issue has been expressed in different ways in the literature, considered for specific types of molecules (such as isomers and chiral molecules), and invoked as evidence for different philosophical positions (such as anti-reduction, pluralism, and strong emergence (for example see Chang 2015; Hendry 2010a; Lombardi 2014)). In this paper I offer a new way of expressing this issue by invoking concepts and ideas from the literature on models in science.⁴

Specifically, it is uncontroversial that molecules are described in quantum mechanics by an array of mathematical models. Based on this, the issue is as follows: some quantum models identify structure for isolated molecules, whereas other models do not. Formulating the issue in this way allows us to raise the following questions. Why do some quantum models identify structure, whereas others don't? What is the main difference between those two sets of models? And, which quantum models are faithful representations of molecular structure?

³ 'Molecular structure' refers to the spatial arrangement of the particles that constitute the molecule. This definition is in line with how molecular structure is understood in the relevant literature (such as Chang 2015; Fortin et al. 2016; Hendry 2010a; Lombardi 2014; Lombardi & Castagnino 2008; Primas 1981; Woolley 1978; Woolley and Sutcliffe 1977). I do not consider conceptual issues regarding molecular structure (see for example Hendry 2016).

⁴ I do not claim that this is the only correct way of expressing this issue; existing analyses have contributed greatly in understanding molecular structure and its quantum mechanical description.

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I focus on the latter question.⁵ I argue that the models that do not identify structure are more faithful representations of isolated molecules. This is for two reasons. First, experimental evidence is consistent with there being no structure in isolation: assuming that an isolated molecule has structure is an idealisation. Secondly, the models that identify structure in isolation only do so because they assume information from observations of the relevant molecule in non-isolation.

That isolated molecules may not have structure is something that philosophers should seriously consider as it affects our understanding of molecular structure, but also of the relation between chemistry and quantum mechanics. Very briefly, if isolated molecules do not have structure, then this raises questions about what sort of property molecular structure is. For example, molecular structure could be a relational property which is instantiated only in relation to the environment (see section 6). Moreover, the absence of structure in isolation also affects how one understands the identity of molecules. Given that structure is a defining characteristic of molecules in chemistry, can we maintain that molecules exist in isolation (at least in the way standardly understood in chemistry)? All in all, not having structure in isolation prompts novel and interesting questions about chemical entities and properties vis à vis the literature on the metaphysics of identity, properties, and relations.

Furthermore, such an understanding of molecular structure can potentially undermine existing accounts about chemistry's relation to quantum mechanics. Specifically, certain antireductionist and emergentist theses are based on the implicit assumption that molecules have structure in isolation. Under this assumption, the failure of *ab initio* quantum mechanics to identify structure shows that chemistry is not reduced to quantum mechanics, or that structure strongly emerges. So by challenging that isolated molecules have structure, these accounts can be to some extent undermined (see section 6).⁶

⁵ The other questions are pertinent to this discussion, so they will also be investigated to some extent.

⁶ I do not claim that my claim implies the *in toto* rejection of anti-reduction or strong emergence. I only point out that to the extent that any philosophical account is contingent on the assumption that isolated molecules have structure, such accounts face a problem that needs to be addressed.

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Note that other philosophers have also considered that isolated molecules do not have structure (for example Lombardi and Castagnino 2008; Woolley 1978; Franklin and Seifert 2020). Such considerations are based on a close examination of foundational issues in quantum mechanics.⁷ For example, Lombardi and Castagnino 2008 argue that the modal Hamiltonian interpretation of quantum mechanics implies that molecular structure is a relational property. This paper differs from such accounts in that it considers this possibility from the perspective of models: it provides epistemic- rather than ontological- grounds for believing that molecules have no structure in isolation. While some may regard epistemic grounds as insufficient for supporting ontological claims, I take such an analysis to be justified by the fact that philosophers (especially of a naturalistic mentality) often invoke models in support of metaphysical claims. Moreover, I take my analysis to complement- rather than compete with- similar claims about molecular structure in the sense that I offer epistemic grounds for believing that isolated molecules do not have structure.⁸

The quantum mechanical description of molecular structure has been considered before from the perspective of models. For example, Hendry 1998 also draws conclusions about molecular structure by invoking ideas about models (see Hettema 2017 for a similar approach with respect to chemical bonds). So this paper is very much in the same spirit. Nevertheless, it differs in two important respects. First, the quantum mechanical description is examined here exclusively in terms of models and idealisations. This is different from Hendry 1998 where it is primarily examined in terms of the relation between models and the theory of quantum mechanics (see section 2). Secondly, the conclusions drawn here about molecular structure are quite different.

The structure of the paper is as follows. In section 2, I explain why it is helpful to consider the quantum mechanical description of molecular structure from the perspective of models in science. In section 3, I

⁷ Such as the debate around the different interpretations of quantum mechanics, the measurement problem, and the issue of the classical-quantum divide.

⁸ This implies that I do not offer an explanation as to why (and in what way) molecules do not have structure in isolation. That is, I do not provide ontological grounds for believing this claim. Nevertheless, I take accounts that provide such explanations to further enforce my claim that there is no structure in isolation (though I leave it open about which particular explanation is the right one- see sections 4 and 5).

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distinguish between the quantum models that identify structure in isolated molecules from those that do not, and I point out the main epistemic difference between them. In section 4, I show that it is an idealisation to assume that isolated molecules have structure. I argue that this gives us epistemic grounds for believing that there is no structure in isolation. In section 5, I discuss a possible objection against this claim and offer a way out of it. In section 6, I point out some novel questions that arise in the context of my proposal.

2. Setting the framework: some ideas about models

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

There is a proliferation of accounts on models which makes it difficult to pin down a uniform and widely accepted definition of models. But, very broadly, we could say that models are a means through which scientists represent some aspect of the world and make inferences about it.⁹ The aspect of the world that a model is taken to represent is called the target system. The target system could be anything: an object, a state, a phenomenon, etc. For the purposes of this paper, specifying the nature of plausible targets is not important; here the target system is the isolated molecule.

⁹ Note that there are also other means of representation that are not always understood as models. Also, there is debate about whether models are a specific kind of scientific representation and whether all scientific representations are models (see Frigg and Nguyen 2020). Given that it makes no substantial difference to the current discussion, I assume for simplicity that models are at least a kind of scientific representation. In this context, the above definition of models suffices to broadly characterise models (this definition is largely based on Suarez's (2003) definition of scientific representations).

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That quantum chemistry represents isolated molecules via models is a fairly uncontroversial fact.¹⁰ The models I have in mind are the mathematical models that are employed in quantum chemistry in order to describe the properties of atoms and molecules.¹¹ Specifically, quantum chemistry describes atoms and molecules via the Schrödinger equation. Complex computational methods are employed to solve the equation and these methods follow specific mathematical strategies and make different assumptions, approximations, and idealisations.¹² This results in an abundance of quantum models which vary in how predictively and explanatorily successful they are in identifying the properties of different types of atoms and molecules.

All the above prompt interesting philosophical questions about models in quantum chemistry. For example, how are these models related to the exact quantum mechanical equations and the overall theory of quantum mechanics (see for example Hendry 1998 for such an analysis)?¹³ What type of models are they, given the different types that have been identified in philosophy, such as “(p)robing models, phenomenological models, computational models” and others (Frigg and Hartmann 2020; Weisberg 2007)? What is the ontology of these models? I do not examine any of these questions here. Instead, I focus on a different question which in its generality can be stated as follows: what is the relation of quantum models to their target system? In particular, when quantum models are employed for the description of isolated molecules, how faithfully do they represent their structure?

These questions are related to investigations of the representational function of models. As happens with any philosophical topic, there is a vast literature on this topic and there are different conceptions of scientific

¹⁰ Gavroglu and Simões call quantum chemistry “a sub-discipline that is not quite physics, not quite chemistry, and not quite applied mathematics” (2012: viii). More precisely, it is the “branch of theoretical chemistry in which the methods of quantum mechanics are applied to chemical problems” (Palgrave Macmillan Ltd 2004: 1845).

¹¹ Some philosophers have identified specific types of models in quantum chemistry (see Weisberg 2007). This is outside the scope of this paper.

¹² These models include the Valence Bond Approach, the Molecular Orbital Approach, and the Hartree-Fock Method.

¹³ This question may also involve investigating the structure of scientific theories (in terms of -say- the syntactic or semantic view; see Winther 2016 for an overview). This issue is not investigated here.

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

Consider for example Thomson's and Bohr's models of the atom.¹⁴ It is now an incontestable scientific fact that Bohr's model is a more faithful representation of atomic structure, compared to Thomson's model. That is, atoms- should we accept they exist- have a structure that is more faithfully represented by Bohr's model (rather than Thomson's).¹⁵ This fact is not contingent on a particular account of models or scientific representations. Whether one holds a structural, fictional, or inferential conception of representations does not determine whether Bohr's or Thomson's model faithfully represent the atom. Rather, we should demand that this fact holds under any sensible account on scientific representations.

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

¹⁴ According to Thomson's model (also known as the plum pudding model), atoms are uniform spheres of positive charge where electrons are embedded. On the other hand, Bohr's model takes positive charge to be concentrated in the nucleus and electrons to move in dynamically stable orbits around the nucleus. Bohr's model was very much based on Rutherford's model of the atom (for an overview of the different models of the atom see Cushing 1998 and Pullman 2001).

¹⁵ This does not mean that Bohr's model of the atom is the most faithful representation of atomic structure. In fact, scientists have identified various respects in which this model is not a faithful representation.

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

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

Significant work has been done in identifying idealisations in quantum models. For example, Weisberg argues that it is an idealisation to treat “the vibrating bond as spring-like with a natural vibrational frequency” when calculating the vibrational properties of covalent bonds (2007: 644). Hendry has also offered a rigorous analysis of the idealisations made in the molecular Schrödinger equation: this includes the disregard of relativistic effects as well as the distortion of some of the interactions and motions of the subatomic particles that constitute a molecule (1998: 125).¹⁶

¹⁶ Interestingly, Hendry also identifies the assumption of structure in isolation as an idealisation. He states: “the Hamiltonians are usually relevant only to isolated molecules, of which there are none in the real world” (1998: 125). However, in his analysis of quantum models he does not further consider whether the application of this idealisation has any effect on the faithfulness of the relevant models.

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

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

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

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

3. Rephrasing the Debate about Molecular Structure

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There is wide consensus in philosophy of chemistry that ab initio quantum mechanics does not identify structure in isolated molecules.¹⁷ As Woolley states:

if one starts from a description of a molecule as an isolated, dynamical system consisting of the number of electrons and nuclei implied by the stoichiometric formula that interact via electromagnetic forces, one cannot even calculate the most important parameters in chemistry, namely, those that describe the molecule structure. (1978: 1074)

What quantum chemists do in order to identify molecular structure is apply the Born-Oppenheimer approximation (henceforth BO approximation) to the molecular Schrödinger equation.¹⁸ The BO approximation is a “(r)epresentation of the complete wavefunction as a product of an electronic and a nuclear part $\Psi(r,R) = \Psi_e(r,R) \Psi_N(R)$ ” (IUPAC 2014: 179). The validity of the BO approximation is “founded on the fact that the ratio of electronic to nuclear mass (...) is sufficiently small and the nuclei, as compared to the rapidly moving electrons, appear to be fixed” (IUPAC 2014: 179). The importance of the BO approximation to quantum mechanics is clearly expressed as follows:

The practical effect of the approximation is that it is possible to simplify both the discussion and the calculation of molecular electronic structures. Instead of having to treat all the particles in the molecule on an equal footing, it is possible, according to the approximation, to set the nuclei into a frozen conformation, and then to calculate the electronic energy and distribution corresponding to it.

The nuclei can then be moved to a new conformation, and the electronic calculation repeated. In this

¹⁷ Quantum mechanics is characterised as ‘ab initio’ when the description is formulated from first principles, without appeal to ad hoc assumptions (including chemical facts), and by taking into account only the number and types of physical entities that make up the examined system (see for example Scerri 2004 and IUPAC 2014 under the term ‘ab initio’). Moreover, a molecule is in isolation when (i) it is far removed from any other system and thus doesn't interact with other entities; and, (ii) the total energy of the molecule is conserved (Seifert 2019: 21).

¹⁸ Of course quantum chemists apply a number of additional assumptions and approximations in order to arrive at a computationally tractable and useful description of the target system. Nevertheless, it seems incontestable in the literature that in practice the BO approximation is always applied in order to identify structure.

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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.

(1974: 29)

As becomes evident from Atkins' quote, the application of the BO approximation amounts to presupposing facts about the molecule's structure. While these facts do not completely specify the molecule's structure (because- among other things- they leave undetermined how the electrons behave), they involve information about the spatial position of nuclei.

In philosophy, this methodological feature of quantum mechanics has been invoked in support of anti-reductionism and of strong emergence (among others). For example, Fortin et. al. state that:

(..) from the viewpoint of reduction, the Born–Oppenheimer approximation faces some difficulties. First, it introduces the molecular structure into the quantum description from the very beginning, when the positions of the nuclei are established with the appeal to classical geometric considerations. Second, the assumption of the nuclei at rest in fixed spatial positions is in contradiction with the Heisenberg principle, which prevents quantum systems from having definite values of position and velocity simultaneously. (2016: 227)¹⁹

Hendry invokes this feature of quantum mechanics in order to argue against (reductive and non-reductive) physicalism and in favour of the strong emergence of molecular structure. Specifically, he takes the application of the BO approximation to undermine the tenability of even an approximate form of reduction between the two sciences (he calls such accounts of reduction the 'proxy defence' (Hendry 2010a: 208)). Moreover, he claims that the form of the Schrödinger equation prior the application of the BO approximation is consistent with the view that molecular structure emerges at a level of ontology that is in-principle undescrivable by the lower-level (i.e. quantum mechanical) theory. As he states:

¹⁹ The issue of classicality and Heisenberg's uncertainty principle is another problem in defending chemistry's reduction (see also Chang 2015 and section 4).

In the Born–Oppenheimer approximation, the spherical symmetry that is expected of exact solutions to the full Schrödinger equation is simply replaced by a less symmetrical structure that is compatible with the asymmetrical charge distribution. Molecular structures cannot be recovered from the Coulomb Schrödinger equations, but not because of any mathematical intractability. The problem is that they are not there to begin with. (Hendry 2010a: 213)

Based on the above, we can distinguish between two general groups of quantum models; those that identify structure and those that do not.²⁰ What differentiates those two sets of models is the application of the BO approximation: The quantum models that do not apply the BO approximation, do not identify structure; whereas the models that do apply the approximation, identify structure.²¹

One could argue that my proposed distinction does not frame the investigation of molecular structure correctly as the problem does not lie in how different quantum models describe molecular structure, but rather in how the theory of quantum mechanics relates to actual solutions of the Schrödinger equation. On this view, the description that does not employ the BO approximation refers to the exact equation of the theory. What is meant by ‘exact’ is not entirely clear but based on the literature, it is safe to say that it refers to a description that is constructed using as input only fundamental physical interactions and the value of the physical properties of the entities (i.e. masses, charges etc), without presupposing any chemical facts about the target system (Hendry 1999: 130; Hendry 2010a: 210-211; Hendry 2010b: 183-184; Woody 2000:

²⁰ My proposed distinction of quantum models is an oversimplification as there are differences and similarities between those two sets of models, as well as alternative categorisations of quantum models, that are completely disregarded here. For example, scientists standardly distinguish models in terms of whether they apply the Valence Bond or the Molecular Orbital approach (for an overview see Weisberg 2008). Nevertheless, I believe this is a useful way to rephrase the debate about molecular structure as it illuminates previously unexplored epistemic features of quantum mechanics that are closely relevant to the discussion of molecular structure.

²¹ In the next section I show that it is *because* of the BO approximation that models can identify structure.

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S613; Woolley 1976: 34-35).²² In this context, the appropriate way to examine molecular structure is by looking at how it is described by the exact theory and the quantum models respectively. For example, notice how Hendry frames the discussion:

There is an *exact analytical solution* to the non-relativistic Schrödinger equation for the hydrogen atom and other one-electron systems, but these are special cases on account of their simplicity and symmetry properties. (...) To solve the Schrödinger equations for more complex atoms, or for any molecule, quantum chemists apply a battery of *approximate methods and models*. (2010a: 212)²³

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

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

4. Idealising molecular structure in Quantum Mechanics

²² It seems to me that 'exact' is just an alternative term for 'ab initio'- though I leave it open that there is an alternative definition of 'exact' that I am not aware of.

²³ Italics added here.

When a system is in isolation this implies that one cannot empirically verify its properties.²⁴ This is because the mere act of observing the target system renders it in non-isolation. So all we ever know about any system is how it behaves in non-isolation. Of course this is by no means sufficient to support that molecules don't have structure in isolation. The fact that - strictly speaking- we will never experimentally verify its structure doesn't necessarily imply that the molecule doesn't have one. Nevertheless, by pointing this out we are reminded that an isolated molecule with no structure is empirically possible.

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

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

Regarding an isolated molecule, it becomes evident that, in virtue of being isolated, there are no molecules around to partially determine its structure. However, it is not entirely accurate to infer from this that an

²⁴ See footnote above for a definition of isolation.

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isolated molecule's structure can be solely determined by the interactions of the subatomic particles that make up the molecule. The structure of an isolated molecule refers to an idealised state of the molecule which can never be empirically identified and whose existence is assumed rather than empirically verified. Given that the environment, time and thermodynamic conditions play a causal role in determining its structure, we should not reject the possibility that in the absence of these factors, structure is no longer a meaningful property.

Simply put, the structure of an entity A is empirically identified when A is examined with respect to a set of entities B and in conditions C. In this context, the structure of A is determined not only by the nature of A, but also by the presence of B and the conditions C. Whenever the structure of A is empirically examined, it is observed to be determined by B and C. This implies that there is no empirical evidence that A is structured when B and C do not exist (i.e. when A is in isolation); whenever structure is observed, it is always partially determined by factors external to A.

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

Consider as an analogy Alan's politeness. How polite Alan is, is empirically identified when one examines Alan with respect to the presence of people P in an environment C. In this context, whether Alan is polite or rude is determined by the people with which Alan interacts and by the environment in which their interaction occurs. Now consider Alan in isolation. It doesn't make sense to talk about Alan's politeness

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independently of other people and of the context in which he is considered.²⁵ This is not merely because one cannot empirically verify whether Alan is polite in such a context, but because Alan doesn't instantiate the property of being rude or polite when there is no one around.

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

Nevertheless, that something is an idealisation of this sort does not make it always false. It is common place in science to infer that a system has a certain property under conditions that cannot be empirically tested and that disregard causally relevant factors (Cartwright 1989). So while being an idealisation gives us grounds for being sceptical, it is not sufficient to reject its truthfulness. As Ladyman states for two standard cases of idealisations:

(...) a perfectly reversible (or maximally efficient) Carnot engine is impossible to build in practice, and yet is considered a respectable part of the subject matter of thermodynamics. On the other hand, a perpetual motion machine of the second kind, the sole effect of which is the complete conversion of heat into work, is regarded as fundamentally impossible. What is the difference between an impossibility that can be considered possible in ideal circumstances and an impossibility that remains so no matter how idealised the scenario we envisage? (Ladyman 2008: 360-361)

What Ladyman's quote reveals is that being an idealisation is not sufficient to decide whether the relevant assumption is possible or not. Both a perfectly reversible Carnot engine and a perpetual motion machine are idealisations, but only one of the two is physically impossible and false. So, similarly stating that the

²⁵ Obviously this analogy can be philosophically challenged and debated. Nevertheless, this doesn't undermine the possibility of understanding such properties in this manner.

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assumption of isolated molecules with structure is an idealisation, is not enough. What is also required to convincingly support this, is an ontological story that explains why isolated molecules don't have structure.

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

Scientists have observed that under particular conditions (which seem to resemble the conditions of isolation) molecules exhibit non-classical behaviour in the sense of exhibiting interference effects, non locality, and entanglement.²⁶ Moreover, there are types of molecules (namely chiral molecules) for which the quantum mechanical description predicts that the most stable state is that which corresponds to a superposition of structures (this is standardly referred to as Hund's paradox- see Bahrami and Shafiee 2011; Berlin, Burin, and Goldanskii 1996; Hund 1927; Trost and Hornberger 2009). Philosophers have also pointed out that Heisenberg's uncertainty principle implies that subatomic particles do not hold fixed spatial positions (Chang 2015; González, Fortin, and Lombardi 2019). This purportedly comes in contrast with chemistry's understanding of molecular structure which assumes that nuclei hold fixed positions in space.

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

²⁶ Specifically, scientific programs are currently under way whose goal is to "explore, to test, and to control the 'strange' quantum properties of non-locality, entanglement, and decoherence, and to apply these features to complex systems including large molecules" (Chatzidimitriou-Dreismann and Arndt 2004: 144; see also Arndt et al. 1999; Wang and Kais 2007).

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quantum mechanics (such as Bahrami et al. 2012; Fortin, Lombardi, and González 2017; 2018; Franklin and Seifert 2020).

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

5. A hurdle: what about the models that identify structure?

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

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

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targets. That is, the best way to explain their success is by the fact that molecules actually have the structure that these models posit.²⁷

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

First, as shown in section 3, the principal epistemic difference between the models that identify structure and those that do not, is the application of the BO approximation. The BO approximation is not just an epistemic feature that one invokes so as to distinguish these two sets of models: it is what makes it possible for quantum models to identify structure.²⁸ This is more eloquently expressed by Woolley:

It is clear that a molecular structure description in the quantum theory of molecules is intimately connected with the Born-Oppenheimer separation of electronic and nuclear motion, for only then can we talk about a potential energy surface and chemical bonds. A corollary of this statement is that molecular structure makes *no* appearance in a quantum treatment of molecules starting from first principles. (1978: 1076)²⁹

The information that is applied via the BO approximation is about the spatial positions of nuclei and it is based on the experimental analysis of the relevant molecules. However, any and all information drawn from

²⁷ Note that the abductive argument just sketched is an example of an Inference to the Best Explanation. I do not examine here the validity of abduction nor consider possible objections that have been made against such arguments, including objections within the debate about scientific realism (see for example Douven 2017; Psillos 2005).

²⁸ Whether the BO approximation is a necessary step to identifying structure through quantum mechanics is not examined here; it may be that the BO is used just because scientists have not yet developed other computational means to describe molecules without it. As things stand however, there is no model which identifies molecular structure without applying this approximation. So I will only draw conclusions based on the present situation in quantum chemistry, and not on how they could potentially be in the future.

²⁹ Italics in original text.

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experimental analysis is information about non-isolated molecules, not isolated ones. This is because any experimental analysis automatically renders the examined system in a state of non-isolation.

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

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

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

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

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

This is where the ontological story becomes again an essential element of the discussion about molecular structure. Based on our best current science, there is mounting evidence that the above is not the case. The properties of isolated systems differ radically from those of their non-isolated counterparts (see for example the case of chiral molecules in Hund's paradox in section 4). If this is indeed the case, then this reinforces my claim that there is no structure in isolation. However, as noted in the previous section, a lot more has to be said about this and further investigation in philosophy of chemistry and quantum mechanics is vital.

6. Philosophical Implications

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

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

Moreover, there is the question whether structure is a relational or intrinsic property of molecules.³⁰ According to Ney, relational properties are properties objects have “in relation to other things” (2014: 285). However, this is a rather general statement that does not specify- among other things- what renders an object in relation to something else. For example, ‘Paris is in love with Helen’ straightforwardly posits the existence of a relational property (i.e. being in love with) between two objects (i.e. Paris and Helen). Can we specify the relata that are involved in the instantiation of structure in a similar manner? Could one argue, for example, that molecule A has structure in relation to molecule B (and under conditions C)? Or, is structure an intrinsic property that is causally determined by external factors?

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

Lastly, how does this discussion inform the investigation of chemistry’s relation to quantum mechanics? As mentioned in the introduction, existing antireductionist and emergentist positions implicitly assume that there is structure in isolation. This is a sensible reading of these positions because the failure of quantum models to identify structure in isolation has been invoked as evidence against the reduction of chemistry. As Hendry states:

³⁰ In light of the previous paragraph, it is evident that one needs to investigate whether relational properties can be consistently regarded as essences, propensities, or potencies. For example, Molnar argues that relational properties cannot be regarded as potencies (2003: 158-162). Bird examines how such a position can be challenged (2007: 166-167).

Although molecular structure cannot be derived directly from exact molecular Schrödinger equations, quantum-mechanical models do assume that molecules have them, for example in the explanation of microwave spectroscopy. (2010a: 213)

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

7. Conclusion

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

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

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