PRAGMATIC REALISM IN CHEMISTRY

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Resumen: *Como resultado de su rechazo del realismo metafísico con su "perspectiva desde el ojo de Dios", Roberto Torretti abogó por un* realismo pragmático *que se ajusta a la forma de trabajar de los científicos en la práctica cotidiana. Para argumentar en favor de su postura, Torretti toma como ejemplos algunos casos en el campo de la física, en los cuales los físicos no han dudado en combinar teorías incompatibles para obtener sus resultados. El objetivo del presente artículo es añadir un nuevo ejemplo en favor del realismo pragmático, pero en este caso procedente de la química: el uso de la aproximación Born-Oppenheimer en el campo de la química cuántica, y su rol en la explicación de la estructura molecular.*

Palabras clave: *Realismo metafísico, realismo pragmático, química cuántica, aproximación de Born-Oppenheimer, estructura molecular.*

Abstract: *As the result of his rejection of metaphysical realism and its "God's eye perspective", Roberto Torretti advocated for a* pragmatic realism *that fits the way scientists work in everyday practice. To argue for his position, Torretti takes some cases in the field of physics as examples, in which physicists have not hesitated to combine incompatible theories in order to obtain their results. The aim of the present article is to add a new example in favor of pragmatic realism, but in this case coming from chemistry: the use of Born-Oppenheimer approximation in the field of quantum chemistry and its role in the explanation of molecular structure.*

Keywords: *Metaphysical realism, pragmatic realism, quantum chemistry, Born-Oppenheimer approximation, molecular structure.*

1. Introduction

The term 'polymath' comes from the Greek 'πολυμαθής' ('polimathós') and means "who knows many things". It was coined in the Renaissance and was paradigmatically applied to Leonardo Da Vinci for well-known reasons. In today's world of hyper-specialization, extremely few individuals embody the ideal of the Renaissance man and his polymathy: one such exceptional case is Roberto Torretti. His overwhelming intellectual power allowed him not only to be self-taught in multiple and dissimilar areas, but also to excel in all of them.

It is impossible to cover all or even many of the aspects that Torretti developed during his academic life. Therefore, those of us who admire him so much can only take a specific issue and try to contribute to his work with some detail. This is the strategy I will adopt in this article. In particular, I will take as a starting point Torretti's defense of what he called, following Hilary Putnam, "pragmatic realism", as well as the particular examples, coming from physics, that he presented to support his position. The aim of the present article is to add a new example, but in this case coming from chemistry: the use of Born-Oppenheimer approximation in the field of quantum chemistry. For this purpose, the paper is organized as follows. In Section 2, I will recall pragmatic realism as conceived by Torretti, and the two examples to which he resorts: Hawking's explanation for black hole evaporation, and the account of the precession of Mercury's perihelion. Section 3 will be devoted to introducing an overview of what has been perhaps the central problem of the philosophy of chemistry since its inception: the relationship between chemistry and physics, in particular quantum mechanics. This presentation will allow me, in Section 4, to explain the problem of molecular structure as a particular case of the above problem. On this basis, in Section 5 the role of the Born-Oppenheimer approximation in the account of molecular structure will be discussed, showing how this case points to the same direction as Torretti's examples. Finally, in Section 6, I will make some closing remarks.

2. Torretti's pragmatic realism

In his article "«Scientific realism» and scientific practice" (2000), Torretti expresses his firm rejection of *metaphysical realism*, which supposes the possibility of knowing the world as it is in itself, from the God's eye perspective. This kind of realism becomes *scientific realism* when the thesis that science is the privileged means of attaining that knowledge is added. In his words:

> "«Scientific realists» believe that reality is well-defined, once and for all, independently of human action and human thought, in a way that can be adequately articulated in human discourse. They also believe that the primary aim of science is to develop just the sort of discourse which adequately articulates reality —which, as Plato said, «cuts it at its joints»—, and that modern science is visibly approaching the fulfilment of this aim." (Torretti, 2000, p.114)

On the contrary, as he had already emphasized in *Creative Understanding* (1990) from his Kantian perspective, all knowledge, even the most observational, is based on a categorical-conceptual structure that comes from the knowing subject. However, this does not imply, as scientific realists fear, that knowledge is a mere human invention without a real substrate. As Torretti clearly emphasizes, Kant repeatedly points out that the very term 'phenomenon' carries with it a reference to something that in itself is not a phenomenon, something that participates in an effective way in the constitution of the object of knowledge:

> "the purely phenomenal character of the objects of experience does not exclude but rather implies a transcendent reality that serves as their basis and that, although unknowable, is no less effective for that reason. [...] phenomenal objects are not mere insubstantial phantoms, [...] the perception in which their presence manifests itself reveals an effective existence." (Torretti, 2005, pp. 676-677, my translation[1])

Although Kant compares our access to reality to that of a judge, who forces witnesses to answer the questions that he himself decides to propose, the Kantian view does not force the responses: independent reality must answer in the same language in which the questions were formulated, but it can always answer negatively, making its effective presence manifest.

Despite his Kantian filiation, Torretti does not fail to recognize a limitation of Kant's thought:

> "Although [Kant] rightly compares the scientist with an investigating judge who directs his questions to nature and fixes the terms in which the answer has to be conceived, he never considers the case that, frustrated because the answers contradict with each other, the inquiries get complicated and stuck and, in general, do not seem to lead anywhere, the investigating judge rethinks his questions, modifies the categories in which the answers must be framed, and even changes the goals of the research or the criteria to evaluate their results." (Torretti, 2007, p. 199; my translation[2])

In other words, the conceptual framework with which we construct knowledge is not fixed, as Kant supposed. In turn, if the framework changes, the categorial-conceptual relativity of

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1 ˝el carácter puramente fenoménico de los objetos de la experiencia no excluye sino más bien implica una realidad trascendente que les sirve de base y que, aunque incognoscible, no es por ello menos efectiva. [...] los objetos fenoménicos no son meros fantasmas insustanciales, [...] la percepción en que se manifiesta su presencia revela una existencia efectiva˝

2 ˝Aunque [Kant] compara atinadamente al científico con un juez instructor que dirige sus preguntas a la naturaleza y fija los términos en que tiene que venir concebida la respuesta, no se pone nunca en el caso de que, frustrado porque las respuestas se contradicen, las indagaciones se complican y atascan, y en general no parecen estar llegando a nada, el juez instructor repiense sus preguntas, modifique las categorías en que deben encuadrarse las respuestas e incluso cambie las metas de la investigación o los criterios para evaluar sus resultados.˝

scientific knowledge must be admitted. On this basis, he adopts what Putnam (1987) called pragmatic realism, an expression that Torretti considers an "emphatic pleonasm" (2000, p. 114) since there is no other way to be seriously realistic than from a pragmatic viewpoint. It is precisely in support of this position that Torretti provides two examples:

> "A few examples drawn from past and present scientific practice will, I hope, clarify these ideas and substantiate my contention that it is pragmatic realism, not the nostalgic kryptotheology of «scientific realism», that best expresses the real facts of human knowledge and the working scientist's understanding of reality." (Torretti, 2000, p. 115)

The first example refers to Hawking radiation (Torretti, 2000, p. 117). Black holes are cosmological objects predicted by general relativity: they are regions of space-time where the gravitational field is so strong that all matter and radiation entering them can no longer come out. However, in 1974 Stephen Hawking published a paper in which he argued that, if matter inside a black hole obeys the laws of quantum physics, there is a non-zero probability that it escape by tunneling. Thus, over time the black hole will lose its mass and, consequently, will shrink. Torretti points out that, in order to explain this phenomenon, known as "black hole evaporation", Hawking needed to appeal to two theories: general relativity, which accounts for the possible existence of black holes, and quantum mechanics, which explains the tunneling effect that allows a particle trapped inside a potential well to have a finite probability of passing through the surrounding potential barriers. These two theories, as is well known, have not yet been unified under a quantum gravity framework in a complete way, and the basic theoretical difficulties that hinder unification still persist. Moreover, some authors consider that there is a deep incompatibility between the two theories that leads to a foundational obstacle to the formulation of a quantum theory of gravity: the difference between the notions of time in quantum theory and in general relativity, a theory invariant under general coordinate transformations (see, e.g., Kuchař, 1991; Isham, 1993). However, this did not prevent Hawking from using both theories simultaneously to explain the phenomenon of black hole evaporation, nor did it prevent the physicists of the time from accepting Hawking's argument as scientifically sound.

The second example concerns the precession of Mercury's perihelion (Torretti, 2000, pp. 118-119). Newton theory predicts that, if Mercury were the only planet around the Sun, its orbit should be a closed ellipse with the Sun located at one focus and the major axis always pointing in the same direction in space. However, the gravitational interaction with the other planets adds a small force to the primary force due to the Sun. The result is that the motion of Mercury is not a closed ellipse because the major axis of the ellipse slowly rotates about the Sun: Mercury's perihelion –the nearest point of Mercury's orbit around the Sun– advances each year by less than 1 minute of arc, and this effect is known as "precession". The theory of Newton, taking into account all the effects from the other planets (as well as a very

slight deformation of the sun due to its rotation) and the fact that the Earth is not an inertial frame of reference, predicts a precession of 5557 seconds of arc per century; but there is a discrepancy of 43 seconds of arc per century that Newton's theory cannot account for. It is usually accepted that such a discrepancy was successful explained by general relativity, and this has thereafter been regarded as one of the "three classic tests" of Einstein's theory. However, Torretti stressed that nobody was in a position to even approximately solve the Einstein field equations for the solar system. Then, in order to face the problem of Mercury's perihelion, relativists simply ignored the precession of 5557 seconds of arc per century under the assumption that this can be accounted for by Newton's laws. If one assumed that general relativity is the "final" physical theory, then one could safely assume that it would yield predictions agreeing with the Newtonian predictions within an acceptable margin of error when applied to the whole solar system. But if general relativity is not the final theory, as everybody today accepts, this example shows again how physicists appeal to different and incompatible theories to deal with their problems without worrying about their incompatibility.

According to Torretti, both examples serve as an illustration of the way in which scientists solve an unmanageable problem

"by bringing to bear on it two conceptually very different theories, irreconcilable in God's eye, none of which can be true of reality in the strong scientific realist's sense." (Torretti, 2000, p. 119)

He even says about the work of physicists that it

"combines disparate theories, I dare say, outrageously." (Torretti, 2000, p. 119)

In the next sections I will introduce another example of this outrageous scientific strategy. Given his expertise in the philosophy of physics, most of the scientific cases that Torretti mentions throughout his works come from physics. Here I will appeal to an example coming from chemistry, which will show that the combination of incompatible theories is at the very heart of quantum chemistry, one of the most recent and successful discipline of chemical sciences.

3. Chemistry and its philosophy

Before introducing the promised example, I will make a brief detour to recall the origins and main themes of the philosophy of chemistry.

Compared to the philosophy of physics, the philosophy of chemistry is a subfield of the philosophy of science that has emerged only very recently: there are very few journals specialized in the philosophical issues derived from chemistry, and the community of philosophers of chemistry is still extremely reduced in comparison with the communities of

philosophers of other special sciences. This situation, clearly described by Eric Scerri and Lee McIntyre (1997), is particularly surprising in the light of the long and successful history of chemistry and its relevant place in the context of current science. Why chemistry has been ignored by philosophers for so long?

Part of the answer of this question relies on the traditional assumption about the relationship between chemistry and physics: despite the fact that chemistry has historically evolved independently of physics, since the impressive success of quantum mechanics the reduction of chemistry to physics has been widely assumed. In other words, chemistry has been conceived as a scientific discipline that deals with complex systems or particular processes which, nevertheless, could "in principle" be described and explained by means of quantum theory. Dirac's famous statement has become a commonplace in this line of thinking: "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry [are] completely known from quantum mechanics" (Dirac 1929: 714). Under this strongly reductionist stance it is not difficult to recognize that scientific realism which assumes that science "cuts reality by its joints": from the perspective of the eye of God there is only one true theory, the one that describes reality in itself, and that theory belongs to physics.

This traditional reductionist assumption, which spread rapidly among physicists and philosophers (see van Brakel, 2000, Chapter 5), deprives the philosophy of chemistry of legitimacy as a field of philosophical inquiry: the philosophical problems of chemistry, when considered in depth, are problems belonging to the philosophy of physics (see discussion in Lombardi and Labarca, 2005). In this context, it is not surprising that one of the hottest issues in the philosophy of chemistry since its inception has been the relationship between chemistry and physics, in particular, quantum mechanics. The problem of molecular structure is one of the most debated topics in connection with this relationship.

4. The problem of molecular structure

The problem of molecular structure, which stands at the heart of the discussions about the relationship between physics and chemistry, is whether molecular structure can be accounted for exclusively by means of the concepts and the laws of quantum mechanics. It is relevant to emphasize that the debate focuses not on an auxiliary or secondary notion, but on a central concept of molecular chemistry: molecular structure is the main ingredient in the explanation of reactivity, it is "the central dogma of molecular science" (Woolley, 1978, p. 1074). As Hans Primas says: "the alpha and omega of molecular chemistry is the doctrine that molecules exist as individual objects and that every molecule has a shape, characterized by its molecular frame" (Primas, 1994, p. 216). According to Robin Hendry, "molecular structure is so central to chemical explanation that to explain molecular structure is pretty much to explain the whole of chemistry" (Hendry, 2010, p. 183). In fact, many properties of chemical substances are explained in terms of the structure of their molecules.

The concept of molecular structure is characterized in several ways in chemistry. In the framework of molecular chemistry, the term 'molecular structure' refers to the spatial arrangement of the atoms in the molecule and the chemical bonds that hold them together. When the molecular system is analyzed from a more detailed viewpoint, it is conceived as a system in physical space, composed by nuclei surrounded by inert inner-shell electrons, placed in definite positions, and bonds explained in terms of interacting "bonding" electrons; the structure of this system is defined by these elements in their spatial arrangement. From a perspective closer to quantum mechanics, a molecule is a system in which the nuclei, placed in definite positions, create a potential in which quantum electrons move; the structure of this system is defined by these elements in their spatial arrangement. The important point to note here is that, in all cases, the concept involves a strong spatial connotation related, at least, to the positions of the nuclei. It is this feature of molecular structure that prevents it from finding a comfortable place in the theoretical context of quantum mechanics.

The discussions about the difficulties in reducing molecular structure to quantum mechanics are not new. For instance, in his works of the 70's and the 80's, the eminent quantum chemist Guy Woolley stresses that, by appealing only to "first principles", "one cannot even calculate the most important parameters in chemistry, namely, those that describe the molecular structure" (Woolley, 1978, p.1074). He considers that the impossibility of determining the geometry of a molecule by means of quantum mechanics is a proof of the fact that molecular structure is only a "powerful and illuminating metaphor" (Woolley, 1982, p. 4).

Several chemical examples have been invoked to illustrate these difficulties. The case of optical isomerism is perhaps the best known: "the existence of isomers, and the very idea of molecular structure that rationalizes it, remains a central problem for chemical physics." (Woolley, 1998, p.3). The structures of the members of a pair of optical isomers are chiral, which means that they are non-superimposable mirror-images of each other: they can be macroscopically distinguished by their optical activity, that is, their ability to rotate plane-polarized light by equal amounts but in opposite directions. Friedrich Hund's "paradox" (Hund, 1927) expresses the central problem of optical isomerism when trying to explain it in quantum-mechanical terms: given that the chiral states are not eigenstates of the parity-invariant Hamiltonian, and none of them corresponds to the ground state, why certain chiral molecules display an optical activity that is stable in time? More recently, Hund's paradox was formulated in a slightly stronger version (Berlin, Burin, and Goldanskii, 1996): how can chiral molecules exist?

The problem of isomerism is a particular case of what can be called, following Woolley and Brian Sutcliffe (1977), "the symmetry problem": since the interactions embodied in the full Hamiltonian of the molecule are Coulombic, the solutions of the Schrödinger equation have several symmetries; however, the corresponding asymmetries of polyatomic molecules are essential in the explanation of their chemical behavior. For example, the solutions of the Schrödinger equation are spherically symmetric. Therefore,

according to quantum mechanics, the expectation value of the electric dipole moment of the molecule in an arbitrary eigenstate of the full molecular Hamiltonian is always zero. But, according to chemistry, the hydrogen chloride molecule has an asymmetrical charge distribution that explains its acidic behavior and its boiling point. As Hendry clearly states, "if the acidic behaviour of the hydrogen chloride molecule is conferred by its asymmetry, and the asymmetry is not conferred by the molecule's physical basis according to physical laws, then surely there is a prima facie argument that ontological reduction fails." (Hendry, 2010, p.186; see also Hendry, 1998).

Some authors retain an ontologically reductionistic view by conceiving the problem of molecular structure as a result of deep epistemic limitations; this is the case of Woolley and Sutcliffe when they say: "We have never claimed that molecular structure cannot be reconciled with or reduced to quantum mechanics, or that there is something 'alien' about it; our claim is much more modest. We do not know how to make the connection." (Sutcliffe and Woolley, 2011, p. 94; see also Sutcliffe and Woolley, 2012). Hinne Hettema (2012, Chap. 3) takes an explicitly reductionist stance by considering that the inter-theoretic relationship between molecular chemistry and quantum mechanics has not been properly formulated in present-day philosophy of chemistry, due to the scarce impact that the Quantum Theory of Atoms in Molecules (QTAIM) (Bader 1994, Bader and Matta, 2013) have had in this philosophical field (for the limitations of QTAIM to solve the problem of molecular structure, see Lombardi and Matta, 2022).

Another reductionist strategy is based quantum decoherence: conceived as the process that accounts for the classical limit of quantum mechanics (Zurek, 1991; 2003), environment induced decoherence would supply the necessary link between the classical concepts of molecular chemistry and the quantum domain (Trost and Hornberger, 2009; Scerri, 2011; 2013). However, the authors specialized in decoherence agree in that it does not solve the measurement or the classical limit problem of quantum mechanics, but only selects the preferred basis, given by the physical quantities perceived as determinate (see, e.g., Schlosshauer, 2004). As a consequence, decoherence does not provide a way out the problem of molecular structure (Fortin, Lombardi, and Martínez González, 2016).

More recently it has been argued that the problem of molecular structure is just a special case of the quantum measurement problem; therefore, insofar as the measurement problem is solved, the problem of molecular structure is resolved as well (Franklin and Seifert, 2020). However, this claim has also been challenged. It is true that, if a solution is given to the quantum measurement problem, an answer can be given to the symmetry problem, for example, by explaining why a definite value of electric dipole moment or the chirality of a molecule is observed (Fortin, Lombardi, and Martínez González, 2018). But there are many different ways to being, e.g., a chiral molecule: there are many different geometrical configurations of the nuclei that realize, say, a left-handed molecule. This means that solving the symmetry problem only accounts for the definite value of a quantity –e.g.,

electric dipole moment or chirality–, but is still far from solving the problem of molecular structure, which requires explaining, at least, the positions of all the nuclei in the molecule (Fortin and Lombardi, 2021).

From a completely different viewpoint, several authors have claimed that molecular structure cannot be strictly explained by quantum mechanics not due to epistemic limitations, but for strictly conceptual reasons (see, e.g., Primas 1983, 1998, Amann, 1992). In particular, by adopting a bottom-up argumentative strategy, it has been argued that there is a deep conceptual breakdown between quantum mechanics and molecular chemistry. The theoretical peculiarities of quantum mechanics stand against the possibility of accounting for molecular structure, defined in terms of the spatial relations of nuclei conceived as individual localized objects. According to quantum mechanics, quantum "particles" are not individuals that can be identified as different from others and that can be re-identified through time; therefore, they do not have the ontological stability necessary to maintain the relations that can lead to a spatially definite system with an identifiable shape (Martínez González, Fortin, and Lombardi, 2019).

Hendry (2004, 2008, 2010), who has repeatedly discussed the problem of molecular structure, distinguishes between the intertheoretic and the metaphysical aspects of the debate on reduction. In fact, reductionists and non-reductionists agree that classical intertheoretic reductions of chemistry are not currently available, but differ in how they interpret the situation: "the issue is essentially future directed –both sides must wait and see, even if they would bet different ways. But why do the two sides make different bets? Perhaps the answer concerns their different underlying metaphysical views." (Hendry, 2010, p.184). On this basis, Hendry considers that the reduction debate must turn to consider the ontological relationships between the entities, processes, and laws studied by different sciences. In particular, the relationship between quantum mechanics and molecular chemistry, embodied in the way in which the molecular structure of a system of several electrons and nuclei is explained, must be conceived in terms of emergence.

In summary, the problem of molecular structure has given rise to heated debates, both in chemistry and in the philosophy of chemistry, which are far from being settled. In the context of this discussion, a central role is played by the Born-Oppenheimer approximation.

5. The Born-Oppenheimer approximation

In the vast majority of cases, quantum chemists are interested in the stationary states of the molecule, that is, the eigenstates of the full Hamiltonian. For this reason, they try to solve the time-independent Schrödinger equation,

$$\hat{H}\left|\Psi_i\right\rangle = E_i \left|\Psi_i\right\rangle ,\tag{1}$$

where the $\left|\Psi_i\right\rangle$ are the eigenstates of the full Hamiltonian and the E_i are the corresponding values of energy. But this equation is always too complex to be solved analytically. Therefore, it is necessary to resort to approximations, among which the Born-Oppenheimer approxi-

mation (BOA) is the first to be appealed to. Originally proposed by Max Born and J. Robert Oppenheimer (1927), it is based on the assumption that the wave functions of atomic nuclei and of electrons in a molecule can be treated separately, based on the fact that the masses of the nuclei are much larger than those of the electrons (for an analysis of this assumption in the context of quantum mechanics, see Lombardi and Castagnino, 2010). Let us see how the BOA works.

Given a molecular system, its *full* Hamiltonian can be expressed as:

$$\hat{H} = \hat{T}_N\left(\hat{P}_\alpha\right) + \hat{V}_{NN}\left(\hat{R}_\alpha\right) + \hat{T}_e\left(\hat{p}_i\right) + \hat{V}_{ee}\left(\hat{r}_i\right) + \hat{V}_{eN}\left(\hat{r}_i, \hat{R}_\alpha\right), \tag{2}$$

where $\hat{T}_N$ is the nuclear kinetic energy (function of the nuclear momenta $\hat{P}_\alpha$), $\hat{V}_{NN}$ is the potential due to the interactions between the nuclei (function of the nuclear positions $\hat{R}_\alpha$), $\hat{T}_e$ is the electronic kinetic energy (function of the electronic momenta $\hat{p}_i$), $\hat{V}_{ee}$ is the potential due to the interactions between the electrons (function of the electronic positions $\hat{r}_i$), and $\hat{V}_{eN}$ is the potential due to the interactions between the electrons and the nuclei (function of the $\hat{r}_i$, and the $\hat{R}_\alpha$). The first step of the BOA is the so-called "*clamped nuclei*" approximation: the nuclei are "clamped" at definite positions, and the electrons move in the Coulomb potential produced by those fixed particles. If the nuclei are at rest at definite positions, the nuclear positions are no longer represented by quantum operators $\hat{R}_\alpha$, but by classical parameters $\boldsymbol{R}_\alpha$. As a consequence, the classical nuclear kinetic energy $T_N\left(P_\alpha\right)$, now function of the classical nuclear momenta P_α, is zero, and the classical nuclear potential $V_{NN}\left(\boldsymbol{R}_\alpha\right)$ is just a constant that shifts the eigenvalues of the new Hamiltonian only by some constant amount and, therefore, can be neglected. As a result, the electronic Hamiltonian turns out to be

$$\hat{H}_e = \hat{T}_e\left(\hat{p}_i\right) + \hat{V}_{ee}\left(\hat{r}_i\right) + \hat{V}_{eN}\left(\hat{r}_i, \boldsymbol{R}_\alpha\right) = \hat{H}_e\left(\hat{r}_i, \boldsymbol{R}_\alpha\right). \tag{3}$$

With this Hamiltonian, the time-independent Schrödinger equation reads

$$\hat{H}_e\left(\hat{r}_i, \boldsymbol{R}_\alpha\right)\psi_n\left(\hat{r}_i, \boldsymbol{R}_\alpha\right) = E_n\left(\boldsymbol{R}_\alpha\right)\psi_n\left(\hat{r}_i, \boldsymbol{R}_\alpha\right), \tag{4}$$

where the $|\psi_n\left(\hat{r}_i, \boldsymbol{R}_\alpha\right)$ are the electronic eigenstates and the $E_n\left(\boldsymbol{R}_\alpha\right)$ are the electronic eigenvalues for fixed $\boldsymbol{R}_\alpha$, with $n=0$ corresponding to the electronic ground state. If this calculation is repeated by varying $\boldsymbol{R}_\alpha$, an effective potential $E_n\left(\boldsymbol{R}_\alpha\right)$ is obtained, where now the $\boldsymbol{R}_\alpha$ are no longer classical parameters but classical variables. Electrons supposedly move on such a potential $E_n\left(\boldsymbol{R}_\alpha\right)$. The second step of the BOA consists in turning back the nuclear positions into operators so that, for the nuclear degrees of freedom, a nuclear Hamiltonian $\hat{H}_{Nn}$ for the nth effective potential can be constructed:

$$\hat{H}_{Nn}\left(\hat{R}_\alpha\right) = \hat{T}_N\left(\hat{P}_\alpha\right) + \hat{E}_n\left(\hat{R}_\alpha\right). \tag{5}$$

On this basis, the *effective* Hamiltonian for the molecule can be defined as

$$\hat{H}_{eff}\left(\hat{r}_i, \hat{R}_\alpha\right) = \hat{H}_e\left(\hat{r}_i, \boldsymbol{R}_\alpha\right) + \hat{H}_{Nn}\left(\hat{R}_\alpha\right). \tag{6}$$

This effective Hamiltonian is no longer Coulombic and, as a consequence, does not have the symmetries of the full Hamiltonian: "the conventional product of the electronic wavefunctions (from the clamped-nuclei Hamiltonian) and associated nuclear wavefunctions lack the symmetry properties of Coulomb Hamiltonian eigenfunctions and this difference has not been explained." (Sutcliffe and Woolley 2021: 200). In this way, quantum chemistry overcomes the foundational problem of symmetry.

The use of the Born-Oppenheimer approximation is pervasive in quantum chemistry, and this fact must not be questioned: its justification relies on its own success. Here the question is how the entire strategy is viewed from the perspective of quantum mechanics.

The first point to note is that, in the context of quantum mechanics, a quantum system is identified by its own Hamiltonian: changing the Hamiltonian amounts to changing the identity of the quantum system itself. So, if one decides to replace a set of the variables by fixed numbers and associate these numbers with infinite mass and the same charge as the variables replaced, one gets a new conceptual problem (Sutcliffe and Woolley, personal communication). In fact, from a strict quantum viewpoint, the only Hamiltonian of the quantum molecule is the full one. The effective Hamiltonian represents a different quantum system: a system of quantum electrons interacting between them and moving in an effective non-Coulombic potential endowed with the asymmetries required by quantum chemistry. In this sense, Hendry (1998, 2010) points out that the "proxy" defense of Born-Oppenheimer models is based on the assumption that using them instead of the full Hamiltonian makes only a small difference to the energy. However, from a theoretical viewpoint, those models "simply assume the facts about molecular structure that ought to be explained" (Hendry, 2010, p. 186).

The second and most relevant point about the BOA is that the fact that nuclei are placed at rest at definite positions contradicts the Heisenberg principle. Somebody might replay that the nuclear kinetic energy $\hat{T}_n\left(\hat{P}_\alpha\right)$ tends to zero because nuclear masses tend to infinity (when compared with electronic masses) and not because the nuclear momenta tend to zero; then, it is not necessary to suppose that the nuclei are at rest. However, from a strict quantum perspective, if the positions $\hat{R}_\alpha$ of the nuclei have precise values, the values of the momenta $\hat{P}_\alpha$ are completely indefinite. In other words, assuming that the nuclei are placed at definite positions and that the values of their momenta are bounded to meaningfully make that $\hat{T}_n\left(\hat{P}_\alpha\right)$ tends to zero also contradicts the Heisenberg principle, which establishes a finite bound to the corresponding uncertainties.

In the philosophy of science literature it is common to distinguish between factual and counterfactual approximations (Bruer, 1982; Rohrlich, 1989); a counterfactual approximation, contradicts a postulate of the theory. For example, the relationship between special relativity and classical mechanics involves the factual approximation $v/c \to 0$, that is, a limit for velocities v much lower than the speed of light c, or the approximation $c \to \infty$, which is counterfactual because the finite value of c is given by a relativistic postulate. Analogously,

the classical limit of quantum mechanics involves the factual approximation $\hbar/S \to 0$, which represents situations in which the action S is much higher than the quantum of action $\hbar$, but it can also be based on the approximation $\hbar \to 0$, which is counterfactual because $\hbar$ is a constant in the context of quantum mechanics. Although it can be used in practice, a counterfactual approximation is only legitimate if it can be replaced by a factual approximation, as in the cases just mentioned. It is quite clear that the BOA is a counterfactual approximation because it contradicts the Heisenberg principle. However, since it requires the substitution of the quantum nuclear positions $\hat{R}_\alpha$ by the classical nuclear positions R_α, the BOA cannot be replaced by a factual approximation that leads to the effective Hamiltonian lacking the symmetries of the full Hamiltonian. As Hasok Chang clearly points out: "In this «clamping-down» approximation, the atomic nuclei are treated essentially as classical particles; […] this picture is non-quantum in a very fundamental way as the simultaneous assignment of fixed positions and fixed momenta (namely, zero) to them violates the Heisenberg uncertainty principle. But without such classical scene-setting, the quantum calculations are quite impossible. The difficulty here is not only about the practicalities of calculation, and the clamping-down of nuclei is not merely an approximation." (Chang, 2015, p. 198).

The BOA, as used in the context of quantum chemistry, is a vivid example of how scientists "outrageously" appeal to incompatible theories in their practice. In this case, quantum chemical models of molecules are obtained by combining classical mechanics to describe the nuclei and quantum mechanics to account for the motion of the electrons. As explained, such a combination is not an innocent strategy that could be circumvented if we had access to a higher level of calculating power. As Sutcliffe and Woolley claim: "it is not, at present, possible to regard the clamped-nuclei Hamiltonian as an approximation to the full Hamiltonian." (2021, p. 173). The BOA introduces molecular features that are conceptually alien to the quantum description. Therefore, it is a strategy completely unacceptable from the viewpoint of scientific realism, and it only makes sense from a pragmatic realist perspective.

Finally, it is interesting to emphasize that this example does neither involve exotic cosmological objects as black holes nor does it account for a slight numerical discrepancy as in the case of the precession of Mercury's perihelion. The BOA is a key part of the real-life quantum analysis of molecules. Although at present there are a very few works that go beyond the BOA to try to account for the behavior of the nuclei in the molecule, the BOA remains the central assumption that underpins practically all the work in quantum chemistry.

5. Final remarks

Much ink has been spilled on the problem of realism in science, making it one of the traditional issues of the contemporary philosophy of science; in fact, it concerns the very nature of scientific knowledge. In this article I recalled the position that Torretti called "pragmatic realism" and the scientific examples he used to support it. The aim was not to analyze this

view on realism: for that purpose I recommend the article "Pragmatic realism", included in a special issue of the *Revista de Humanidades de Valparaíso* in homage to Torretti, in which Chang (2016) gives an extremely clear exposition of pragmatic realism as stated by Torretti himself, and then offers a further development of such a position from his viewpoint. The aim here was to introduce a new example to reinforce pragmatic realism, but this time coming not from physics but from chemistry: the role of the Born-Oppenheimer approximation in the quantum description of molecules.

The problem of molecular structure is the central issue in the foundations of quantum chemistry, and continues to be a source of heated debates. Nevertheless, as always, Torretti's philosophical thinking allows us to approach traditional problems from new and fruitful perspectives.

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