

The relationship between chemistry and physics from the perspective of Bohmian mechanics

Sebastian Fortin – Olimpia Lombardi – Juan Camilo Martínez González*

CONICET – Universidad de Buenos Aires

1.- Introduction

Although during the last decades the philosophy of chemistry has greatly extended its thematic scope, the problem of the relationship between chemistry and physics still attracts a great interest in the area. In particular, the main difficulties appear in the attempt to link the chemical description of atoms and molecules and the description supplied by quantum mechanics.

In the practice of chemistry, the problems are set aside or even ignored under the assumption that the link between the chemical and the physical domains is gradual and continuous: chemistry, with its concepts and regularities, would arise as the result of applying different approximations to the quantum descriptions. However, during the last years many authors have stressed the *conceptual breakdown* between the two domains (Woolley 1978, Primas 1983, 1998, Amann 1992, Lombardi and Labarca 2005, Labarca and Lombardi 2010). More recently, Hinne Hettema (2012, p. 368) recognizes the “ontological discontinuity” between chemistry and physics: certain terms, used both in chemistry and in physics, refer to different items in the two disciplines. According to this author, such discontinuity is “one of the central problems in the philosophy of chemistry, around which many other problems, such as that of reduction, revolve.” (Hettema 2012, p. 368).

The debates about the relationship between chemistry and physics are almost always conducted in the framework of standard quantum mechanics (SQM), which, independently of the particular interpretation adopted, is the formalism that prevails almost exclusively in the practice of physics. Perhaps for this reason, the fact that there exists another formalism able to explain quantum phenomena is usually not reminded in the philosophy of chemistry: Bohmian mechanics (BM) is not an interpretation of the standard formalism, but a different theory with the same

* This work is fully collaborative: the order of the names is alphabetical and, therefore, does not imply priority.

predictive power as SQM.

Besides the formal differences, BM is a quantum theory of motion that refers to an ontology much closer to the classical –Newtonian or relativistic– ontology than that referred by SQM. Nevertheless, both theories are empirically equivalent (Goldstein 2016); then, in principle, BM could account for chemical phenomena as well as SQM. For this reason, even if not used in practice, BM should be taken into account when conceptual and philosophical matters are considered.

The aim of the present paper is to analyze how the difficulties that threaten the continuous conceptual link between molecular chemistry and quantum mechanics can be overcome or, at least, moderated from the perspective of BM. With this purpose, in Section 2 the foundational incompatibility between chemical and SQM descriptions will be briefly recalled. Section 3 will be devoted to explain the main features of BM. In Section 4, the consequences of the empirical equivalence between SQM and BM will be discussed. Finally, in the Conclusions, after summarizing the argumentation of the paper, we will stress the scope of the obtained conclusions and the philosophical difficulties that still remain even after adopting BM for foundational purposes.

2.- The quantum-mechanical challenges

The foundational incompatibility between the chemical descriptions and the descriptions supplied by SQM has different manifestations. In this section we will briefly consider some of them.

2.a.- The notion of orbital

‘Orbital’ is one of those terms that, as Hettrema correctly points out, are used both in chemistry and in physics, but refer to different items in the two disciplines (Scerri 2000, Labarca and Lombardi 2010, Mulder 2011). According to the *Oxford Dictionary of Chemistry*, both the wave function and its corresponding spatial region of high electron density can be called ‘orbital’ (Daintith 2004).

In fact, in the context of SQM, the term is used as a synonym of ‘*wave function* of a single electron.’ As Eric Scerri (2001) points out, in this context the role of orbitals is to serve as basis sets in terms of which the wavefunction of an atom, ion or molecule can be decomposed

(independently of the still lively debate among philosophers of physics on the interpretation of the wave function; see, *e.g.*, Ney and Albert 2013).

On the other hand, in recent chemistry books the concept of orbital is also introduced in mathematical terms: an orbital is a one-electron wavefunction for an electron in an atom or molecule (Atkins and de Paula 2010, p. 330). Of course, endowing a mathematical entity with a spatial shape makes no sense: it is a category mistake. Nevertheless, from referring a mathematical entity, the concept of orbital is rapidly substantialized, and the talk of “the shape of an orbital” enters the scene: the shape of an orbital turns out to be the shape of a *spatial region* of high *electronic density*, where the electron density is a measure of the probability of an electron being present at a definite spatial place, and can be computed as the square of the electron’s wavefunction. In other words, the spatial region of high electronic density is the *region of space* where the electron is very likely to be found, typically with a probability of 0.90-0.95.

If the shape of an orbital is the shape of a spatial region of high electronic density, it is not difficult to see that in chemistry the meaning of the term ‘orbital’ has mutated from denoting a mathematical entity to referring a *spatial region of high electronic density*. As Peter Mulder stresses, “the point should be clear that the understanding of orbitals as regions of electron density is pervasive in chemistry.” (Mulder 2011, p. 31). And this is true not only in the case of textbooks, but also in research literature, where it is said, for instance, that “the spatial volume occupied by an atom depends on its electronic density”, and that such a region can be visualized (Grosso *et al.* 2015, p. 1; see also Zuo *et al.* 1999, Litvinyuk *et al.* 2000; Pascual *et al.* 2000; Brion *et al.* 2001; Itatani *et al.* 2004). It is worth emphasizing that orbitals, understood as spatial regions, supply the basis to explain the shape of molecules (we will come back to this point below).

In the practice of molecular chemistry, it is assumed that the link between the two meanings of the term ‘orbital’ is gradual and can be explained in terms of approximations. Some philosophers of chemistry support the same position; for instance, Mulder claims that “the meaning of ‘orbital’ as a region of high probability density follows quite straightforwardly from its meaning as a wave function; it is obtained by squaring the wave function and subsequently identifying the region in which the electron is highly likely to be found. The two concepts are therefore continuous with one another.” (Mulder 2011, p. 33). Of course, the mathematical

procedure of squaring the wave function involves no difficulty; but the discontinuity between the two meanings of ‘orbital’ is not mathematical but belongs to the conceptual level. Moreover, difficulties do not depend on the shortcomings of the electron configuration model, arising in many-electron systems (see Mulder 2010): the discontinuity is present already in the hydrogen atom, since it is not the result of approximations.

In chemistry, the electronic density is interpreted as a kind of mean value of the definite positions occupied by the electron in its motion around the nucleus: “If a series of measurements could be made of x without disturbing the motion of the particle, the resulting distribution would be ρ . The latter would then reflect the motion of the particle in the same way in which the density of the image on a long-exposure photograph reflects the motion of a macroscopic object.” (Nelson 1990, p. 643). This picture is based on conceiving electrons as traditional individual objects, with definite positions and velocities, whose only difference with respect to classical particles is that their behavior is not governed by classical equations of motion but by an equation that determines their position only in a statistical way. But this view is incompatible with the Heisenberg principle of SQM, according to which quantum “particles” have no trajectories.

The word ‘uncertainty’, usually applied to the Heisenberg principle, suggests an epistemic reading of the principle’s content: the particle is in some definite position, but we do not know which one. This might lead to believe that the impossibility of ascribing simultaneously precise values to position and momentum –or, in general, to incompatible observables– is a limitation of quantum mechanics itself, which could be remediated by adding the necessary complement to the theory (*e.g.*, hidden variables). But in 1967, Simon Kochen and Ernst Specker (1967) presented a fundamental theorem that proves that any assignment of definite values to all the observables of a quantum system leads to *contradiction*: SQM is essentially *contextual*, that is, definite values can be consistently assigned only in a context, determined by the observables that share a same eigenbasis. This means that it is not the case that the particle has a definite momentum but we do not know its position: any assignment of a definite momentum and a definite position is *logically* forbidden by the very structure of the theory. As a consequence, according to SQM, a quantum “particle” is not an *individual* object in the traditional sense, since it always has some properties –represented by certain observables– that have no definite value; and this is not a merely epistemic limitation, but an ontological fact ingrained in the formalism of the theory itself.

2.b.- The components of the atom

Another manifestation of the fact that, in the framework of SQM, quantum systems are not traditional individual objects arises when the subsystems of a composite system are tried to be identified. It is not necessary to consider many-electron systems to develop this argument, since the fact is manifested even in the simplest system, whose equation has a completely analytical solution: the hydrogen atom.

As it is well-known, in SQM a quantum system is represented by a Hilbert space. For instance, a free electron and a free proton are two quantum systems represented by \mathcal{H}_e and \mathcal{H}_p , respectively, each one with its own Hamiltonian. But in the hydrogen atom the two particles interact through a Coulombic potential; so, the Hamiltonian of the atom reads

$$H = \frac{P_e^2}{2m_e} + \frac{P_p^2}{2m_p} - \frac{e^2}{|Q_e - Q_p|} \quad (1)$$

where e is the electric charge of the electron, m denotes the mass of the particle, Q its position, P its momentum, and the subscripts e and p refer to the electron and the proton respectively. However, the Hamiltonian of the atom can also be expressed as $H = K + W$, where K is the kinetic energy and W is the internal energy, by means of a change of variables in terms of the center of mass coordinates Q_C and P_C , and the relative coordinates Q_R and P_R :

$$Q_C = \frac{m_e Q_e + m_p Q_p}{m_e + m_p} \quad Q_R = Q_e - Q_p \quad (2)$$

$$P_C = M \dot{Q}_C = P_e + P_p \quad P_R = \mu \dot{Q}_R = \frac{m_p Q_e - m_e Q_p}{m_e + m_p} \quad (3)$$

where $M = m_e + m_p$ is the total mass, and $\mu = m_e m_p / (m_e + m_p)$ is the reduced mass. In this new coordinate system, the Hamiltonian can be written as

$$H = \frac{P_C^2}{2M} + \frac{P_R^2}{2\mu} - \frac{e^2}{|Q_R|} = K + W \quad (4)$$

where:

$$K = \frac{P_C^2}{2M} \quad W = \frac{P_R^2}{2\mu} - \frac{e^2}{|Q_R|} \quad (5)$$

Up to this point, this seems a mere change of variables, as that used in classical

mechanics. But now the specifically quantum feature appears: since the kinetic energy K only depends on the total momentum, and the internal energy W only depends on differences of positions and, eventually, on their derivatives, then $[K, W] = 0$ and, as a consequence, the total Hamiltonian H of the atom can be expressed as

$$H = K + W = H_K \otimes I_W + I_K \otimes H_W \quad (6)$$

where H_K is a kinetic Hamiltonian acting on a Hilbert space \mathcal{H}_K , H_W is an internal energy Hamiltonian acting on a Hilbert space \mathcal{H}_W , and I_K and I_W are the identity operators of the respective spaces. Moreover, in a reference frame at rest with respect to the center of mass, $\dot{Q}_C = 0$ and, then, $P_C = 0$ and $K = 0$: the Hamiltonian of the atom results $H = W = I_K \otimes H_W$.

Therefore, it can be supposed that there are two equivalent ways of conceiving the hydrogen atom: one, as an electron and a proton in interaction, and the other as a single system characterized by the internal energy and represented by the Hilbert space \mathcal{H}_W . However, the two pictures are not equivalent: it can be proved that the single-system picture is the objective representation, since only this description is invariant under the symmetry group of the theory, that is, the Galilean group (see Ardenghi, Castagnino and Lombardi 2009). This means that, after the interaction between electron and proton, the hydrogen atom becomes a single system S_W , represented by the Hilbert space \mathcal{H}_W . And in the objective (invariant under the Galilean group) system S_W , electron and proton are no longer recognizable, but are inextricably “mixed” to constitute a new entity.

This result agrees with the conclusion of the previous section: quantum “particles” are not individual objects in the traditional sense. The category of individual requires some “principle of individuality” that makes an individual object distinct from others, and that reidentifies it through time (French and Krause 2006). Quantum “particles”, by contrast, do not preserve their identity after interaction, and this fact does not depend on the complexity of the system, but on the very nature of SQM.

2.c.- The concept of molecular structure

The problem of the relationship between chemistry and physics finds one of its main manifestations in the debate about the nature of molecular structure. The debate focuses not on an

auxiliary or secondary notion, but on a central concept of molecular chemistry: molecular structure is “the central dogma of molecular science” (Woolley 1978, p. 1074). As Robin Hendry claims, “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). The problem consists in the fact that whereas “[t]he alpha and omega of molecular chemistry is the doctrine that molecules exist as individual objects and that every molecule has a shape, characterized by its molecular frame” (Primas 1994, p. 216), the classical idea of definite spatial position for the atomic nuclei, conceived as individual objects, is, at least, strongly conflictive in the quantum context.

Already in his works of the 70’s and the 80’s, Guy Woolley stressed that, in the context of SQM, talking about the size or shape of an atom or molecule makes no sense, and this is a proof of the fact that molecular structure is only a “powerful and illuminating metaphor” (Woolley 1982, p. 4, see also Woolley 1978). During the last decades, Robin Hendry (2004, 2008, 2010) has largely treated the issue of molecular structure in the context of the problem of reduction. By taking an anti-reductionist stance, Hendry considers that the relationship between molecular structure and the quantum components of the molecule must be conceived in terms of emergence.

Perhaps the clearest challenge to the reduction of molecular structure to SQM is the case of optical isomerism: “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). Friedrich Hund’s “paradox” expresses that central problem: given that the chiral states are not eigenstates of the parity-invariant Hamiltonian, and none of them corresponds to the basal state, why certain chiral molecules display an optical activity that is stable in time, associated to a well-defined chiral state, and they are not in a superposition of the two possible chiral states? (Hund 1927). During the last decades, Hund’s paradox was formulated in a slightly stronger version (Berlin, Burin and Goldanskii 1996): why chiral molecules have a definite chirality? (for a criticism of the solution based on decoherence, see Fortin, Lombardi and Martínez González 2016).

The problem of isomerism is a particular case of what can be called, following Woolley and Sutcliffe (1977), the *symmetry problem*: if the interactions embodied in the Hamiltonian of the molecule are Coulombic, the solutions of the Schrödinger equation are spherically symmetrical; however, the asymmetry of polyatomic molecules is essential in the explanation of their chemical

behavior. In other words, in the quantum theoretical domain no directional properties can be assigned to an isolated molecule in a general energy eigenstate: “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 1998).

A central element in the discussion about molecular structure is the role played by the Born-Oppenheimer (B-O) approximation. As Hendry (1998, 2010) points out, the “proxy” defense of B-O models is based on the assumption that using them instead of the exact solution 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). In fact, the B-O strategy is based on the so-called *clamped nuclei approximation*: electrons are conceived as moving in the Coulomb potential produced by nuclei at rest, “clamped” at definite positions. This move simplifies calculations, but at the cost of contradicting the Heisenberg principle, according to which a quantum particle cannot simultaneously have definite values of position and of momentum: “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.” (Chang 2015, p. 198; for a detailed analysis of the assumptions underlying the B-O approximation, see Lombardi and Castagnino 2010).

3.- Bohmian mechanics

If the above manifestations of the incompatibility between molecular chemistry and SQM are considered from a general viewpoint, it is not difficult to see that the ultimate roots of the problem is the contextual nature of quantum systems: they are not individual objects in the traditional sense; they are not individualized by their positions in space and time and, as a consequence, they do not follow definite trajectories. Therefore, a quantum theory that attempts to restore a classical ontological picture deserves to be seriously taken into account. This quantum theory is BM.

3.a.- Bohm's formalism

During the last decades, the formalism of BM has begun to attract interest, mainly in the field of the foundations of physics. Many authors have studied the ideas of Bohm and have proposed different corrections to the formalism and interpretation for the original theory. As a consequence, there is not a single BM but a variety of formalisms that attempt to describe the quantum phenomena by appealing to quantum particles with well-defined position and momentum; just some examples are the Quantum Theory in Terms of Hidden Variables (Bohm 1952), the Quantum Theory of Motion (Holland 1993) and Quantum Hydrodynamics (Wyatt 2005). In this section we will present a simplified formalism following the original paper (Bohm 1952), since this will be sufficient for the purpose of this paper.

Classical mechanics

There are many equivalent formulations of classical mechanics. The most widespread is that learnt in school and known with the name of “Newton’s laws”. According to Newton’s second law, the acceleration of an object is proportional to the net force applied to the object and inversely proportional to its mass. Mathematically, the law leads to a differential equation, whose solution represents the trajectory of the object, that is, its position and velocity for all times. However, this is not the only way to formulate classical mechanics. For instance, the Lagrangian mechanics is a reformulation of the theory where the trajectory of a system is derived by solving the Lagrange equations. In turn, in the Hamiltonian mechanics the central mathematical item is the Hamiltonian H , which is the sum of the kinetic and the potential energies; with H , the trajectory of the system can be obtained by solving the Hamilton equations (see, e.g., Goldstein *et al.* 2002).

There is still another formulation of classical mechanics based on the Hamilton-Jacobi formalism (see, e.g., Landau and Lifshitz 1975). In this formulation the motion is governed by the Hamilton-Jacobi equation,

$$\frac{\partial S}{\partial t} + \frac{1}{2m}(\nabla S)^2 + V = 0 \quad (7)$$

where S is the action and V the potential. With this equation, the function S can be computed, and with it, the Hamilton-Jacobi formalism can be applied to compute the position and momentum of the object for all times. For example, the momentum is computed with the equation

$$\bar{p} = \bar{\nabla}S \quad (8)$$

Bohmian mechanics

The Hamilton-Jacobi equation (7) is very relevant to quantum mechanics because it has a remarkable relation with the Schrödinger equation. The canonical way to write the Schrödinger equation is

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \bar{\nabla}^2 \psi + V\psi \quad (9)$$

where V is the potential of the forces involved in the problem and ψ the wavefunction. Since ψ is a complex function, we can write it as

$$\psi = \sqrt{P} \cdot e^{i\frac{S}{\hbar}} \quad (10)$$

where P is the module of ψ and S is its phase. If we introduce eq. (10) into (9), we obtain two equations for P and S :

$$\frac{\partial P}{\partial t} + \bar{\nabla} \cdot \left(P \frac{\bar{\nabla}S}{m} \right) = 0 \quad (11)$$

$$\frac{\partial S}{\partial t} + \frac{(\bar{\nabla}S)^2}{2m} + V - \frac{\hbar^2}{4m} \left(\frac{\bar{\nabla}^2 P}{P} - \frac{1}{2} \frac{(\bar{\nabla}P)^2}{P^2} \right) = 0 \quad (12)$$

Eq. (11) is a continuity equation, which states that probability is conserved. The second equation, eq. (12), embodies the dynamics of the quantum system. By comparing it with eq. (7) of classical mechanics, it is easy to see that eq. (12) includes a term added to the potential V . Then, it is possible to imagine that this term plays the role of a new potential: the so-called *quantum potential* U_q can be defined as:

$$U_q = -\frac{\hbar^2}{4m} \left(\frac{\bar{\nabla}^2 P}{P} - \frac{1}{2} \frac{(\bar{\nabla}P)^2}{P^2} \right) \quad (13)$$

Therefore, if the total potential $V_{Total} = V + U_q$ is introduced in eq. (12), an equation completely analogous to the classical Hamilton-Jacobi eq. (7) is obtained:

$$\frac{\partial S}{\partial t} + \frac{(\bar{\nabla}S)^2}{2m} + V_{Total} = 0 \quad (14)$$

It is important to notice that this eq. (14) is an exact equation: there is no approximation

involved and it is equivalent to the Schrödinger equation. But when it is compared with the Hamilton-Jacobi eq. (7), it is very easy to see that the two equations have the same mathematical form. On this basis, the idea of David Bohm was to appeal to the Hamilton-Jacobi formalism in order to compute trajectories for quantum systems; for example, eq. (8) can be used to compute the momentum of the system. From this perspective, there is only one difference between quantum mechanics and classical mechanics: now the quantum potential must be considered.

Relation between Bohmian mechanics and quantum mechanics

By means of eq. (14), the trajectory of a quantum particle could be computed if one counted with the initial conditions. The problem is that we cannot know the exact initial conditions of a quantum particle. For this reason, it is necessary to apply a statistical treatment to the possible initial conditions and, as a consequence, to the possible trajectories. The Bohmian Measurement Theory (Bohm 1953, Holland 1993, Wyatt 2005) explains why the probability of finding the particle in a region of space is $|\psi|^2$. Thus, according to BM, quantum phenomena are the result of a statistical analysis over the possible trajectories of a particle.

In this way, the new theory can reproduce all the results of SQM, but with the addition that now both precise position and precise momentum can be simultaneously assigned to quantum systems. This theory supplies correct predictions for the results of measurements, but offers a novel “classical” view of quantum phenomena. The price to be paid for accepting this theory is the introduction of a new strange force. Strange and “uncomfortable” because it is a non-local force, that is, it depends instantaneously on the positions and the velocities of all the particles of the universe.

It is important to emphasize that SQM and BM are *empirically equivalent*, that is, they reproduce the same results to be obtained in measurements. Nevertheless, in order to compute the trajectories of quantum systems, BM adds new equation coming from the Hamilton-Jacobi formalism. This is the reason why BM is not an interpretation of the standard formalism, but a different theory with the same predictive power as SQM.

3.b.- Applications of Bohmian mechanics

The theory has been developed in different directions in the field of both theoretical physics and applied physics. Here we will only consider some results that may be of interest to the philosophy

of chemistry.

Hydrogen atom

When BM is applied to the hydrogen atom, the state 1s for the electron results:

$$\psi = f(r)e^{-i\frac{E}{\hbar}t} \quad (15)$$

where E is the energy. Then, the “action” in this case is $S = -Et$. By means of eq. (8), the momentum of the electron can be computed as $\bar{p} = \bar{\nabla}S = 0$. In other words, the momentum is zero, and this means that the electron is at rest. Of course, we cannot compute the exact position of the electron because we do not know its initial condition: we can only calculate the statistical distribution of positions. However, it is possible to compute the distance between the electron and the proton (see Holland 1993, p. 148): the result is that the electron is at a distance equal to the Bohr radius. It is easy to understand this result in classical terms. There are two kinds of interactions: the electromagnetic force, that is repulsive, and the quantum force, that is attractive. The point where the two forces exactly cancel with each other is at a distance of the proton equal to the Bohr radius.

For the other orbitals, the function S is not a constant in space, but depends on the angle ϕ . Then, the momentum of the electron, obtained as $\bar{p} = \bar{\nabla}S$, is not zero. The result of the computation is (Holland 1993, p. 158)

$$r = r_0, \quad \theta = \theta_0, \quad \phi = \phi_0 + m \frac{\hbar}{m_e r_0^2 \sin^2(\theta_0)} t \quad (16)$$

where (r, θ, ϕ) are the spherical polar coordinates, (r_0, θ_0, ϕ_0) are the initial coordinates, m is the azimuthal quantum number, and m_e is the electron mass. The result of eqs. (16) means that the electron moves in an orbit around the nucleus. Nevertheless, the picture is different from the primitive Bohr model, in which an electron moves in a circle in the equatorial plane; in the result obtained with BM, the orbit of the electron is not in the equatorial plane.

Hydrogen molecule

According to the traditional way of speaking in chemistry, two hydrogen atoms can be linked by a covalent bond to form a molecule H_2 . But the problem is to make sense of the bond in the context of SQM.

In order to study the formation of a hydrogen molecule by means of BM, it is necessary to begin by considering two hydrogen atoms initially far apart. In each atom, the electron is in the state 1s; therefore, according to the previous result, the electrons are at rest in fixed positions.

When we study the formation of a hydrogen molecule with quantum mechanics, we first consider two atoms initially far apart. The electrons in each atom are in the state 1s, then the electrons are at rest in a fixed positions. When the atoms are brought closer, the wavefunction of the whole system can be computed by means of the Schrödinger equation independent of time:

$$\left[-\frac{\hbar^2}{2m_e}(\bar{\nabla}_1^2 + \bar{\nabla}_2^2) - \frac{\hbar^2}{2M}(\bar{\nabla}_A^2 + \bar{\nabla}_B^2) + V \right] \psi = E\psi \quad (17)$$

where $\psi = \psi(\bar{x}_1, \bar{x}_2, \bar{r}_A, \bar{r}_B)$, with \bar{x}_i , $i = 1, 2$ the coordinates of the electrons, \bar{r}_j , $j = A, B$ the coordinates of the nuclei. Moreover, the factor enclosed in squared brackets is the Hamiltonian, where the potential V is

$$V = -\frac{e^2}{r_{A1}} - \frac{e^2}{r_{B2}} - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B1}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{AB}} \quad (18)$$

m_e is the electron mass, M is the proton mass and $\bar{r}_{\alpha\beta}$ are the distances between the particles. Eq. (17) can be solved with the usual approximations: as well-known, it has a bonding and an antibonding solution.

If we consider the σ orbital of this molecule in the light of BM, the result is not less surprising than that of the hydrogen atom. For the case of nuclei, there are two kinds of interactions: electromagnetic (repulsive) and quantum (attractive). Then, there is an equilibrium point where electromagnetic and quantum forces cancel with each other (for detailed computations, see Holland 1993, p. 316). So, the quantum force is the responsible for the attraction between atoms and the formation of a stable bond. For the electrons, calculations show that they are at rest in the region close to the middle point of the line joining the two nuclei (see Holland 1993, p. 319). Surprisingly, BM offers a picture of chemical bond similar to the Lewis bond, but in this case on the basis of a fully articulated theory and of detailed computations.

3.c.- Solving foundational problems

Although precise results can be obtained in the framework of BM, this fact can be considered insufficient to advocate for a different quantum theory in the everyday practice of chemistry.

Nevertheless, BM deserves to be seriously taken into account in the context of the philosophy of chemistry, since it sheds a new light on the traditional foundational problems of the discipline.

The notion of orbital

Let us consider the example of the hydrogen atom. According to SQM, when the atom is in the ground state, the electron is in the state $1s$. But if we ask for the position and the momentum of the electron, the answer is: if it has a value of momentum, it is nowhere; if it has a definite position, it has no value of velocity. As explained in Section 2, according to the formalism a quantum “particle” is not an *individual* object in the traditional sense, since it always has some properties that have no definite value.

BM, by contrast, offers a completely different and less conflictive view of the hydrogen atom: the electron always has definite properties of position and velocity, so it can be conceived as a localized particle. In the ground state, the electron is at rest at a distance equal to the Bohr radius. This fact justifies the size of the atom that chemists write in the periodic table. Additionally, this picture offers an alternative explanation for the stability of matter; in Holland words: “if the particle is at rest relative to the nucleus, it is evidently not accelerating, and hence does not radiate. Therefore, it does not lose energy and it will not spiral into the nucleus, the famous outcome predicted by classical electrodynamics. When the atom is in an excited state the electron is in an orbit around the nucleus.” (Holland 1993, p. 153).

The components of the atom

As discussed in Section 2, in the context of SQM quantum “particles” do not preserve their identity after the interaction that leads to a composite system. In the case of the hydrogen atom, electron and proton are no longer recognizable, but constitute a new entity where they cannot be reidentified.

The ontological picture supplied by BM is completely different, and closer to classical physics: Bohmian quantum particles are individual objects in the traditional sense. They preserve their identity through time to the extent that they follow definite trajectories. They also preserve their identity as components of a composite system: for instance, the hydrogen atom is always composed by a proton in a fixed position and an electron at a definite distance of it. In this sense, this picture is in agreement with the ontological view of atoms implicit in chemistry: the components of an atom are conceived as traditional objects, with definite positions and velocities,

whose only difference with respect to classical particles is that their behavior is not governed by the classical equations of motion.

The concept of molecular structure

Chemistry textbooks usually explain the stability of the molecule in terms of the minimum of the potentials involved in the system. For instance, in the case of the hydrogen molecule, Figure 1 shows the total potential V_{Total} produced by the nuclei in function of the distance r_{AB} between the nuclei: V_{Total} has a minimum for the σ bonding orbital, but is monotonically decreasing for the σ antibonding. Figures of this kind are commonly found in chemistry textbooks (see, for instance, Atkins and de Paula 2010, pp. 363, 371, 455, and others). The reason is that molecular structure and molecular spectroscopy is explained by assuming that the electrons occupy the minimum of the potential. This kind of figures, which represent the potential in function of the distances between the nuclei of a molecule, are obtained on the basis of the assumption of the clamped nuclei strategy underlying the B-O approximation. But, as explained in Section 2, that strategy contradicts the Heisenberg principle, according to which a quantum particle cannot simultaneously have definite values of position and of momentum.

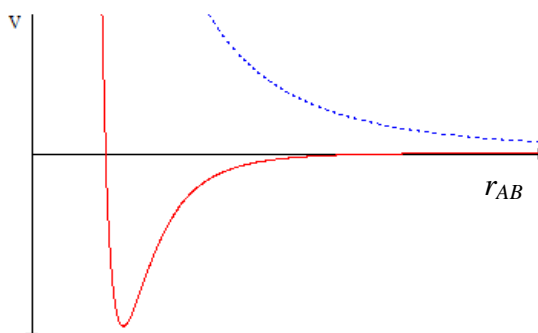


Figure 1. Potential energy for σ orbitals, bonding (solid) and antibonding (dot).

In BM, the difficulties related to the clamped nuclei assumption simply disappear. Since quantum particles are individual objects, they always have definite position and velocity; therefore, the picture of nuclei at rest in precise locations is natural in the Bohmian framework. Therefore, the total potential can be computed without conceptual difficulties, and the stability of the molecule is explained in terms of the minimum of such a potential. In the case of the

hydrogen molecule, the total potential $V_{Total} = V + U_q$ is the result of the combined action of the electromagnetic potential V and the quantum potential U_q : V_{Total} has a minimum at a distance $r_{AB} = r_{eq}$ because the electromagnetic force is repulsive and the quantum force is attractive. In turn, the electrons are traditional individuals localized in the minimum of the total potential, equidistant from the two hydrogen nuclei.

4.- Empirical equivalence and underdetermination

A usual objection to BM is that it makes exactly the same predictions as SQM; therefore, strictly speaking it is not a different theory, but merely a reformulation of SQM. In Werner Heisenberg's words: "Bohm's interpretation cannot be refuted by experiment [...]. From the fundamentally "positivistic" (it would perhaps be better to say "purely physical") standpoint, we are thus concerned not with counter-proposals to the Copenhagen interpretation, but with its exact repetition in a different language." (Heisenberg 1955, p. 18). In more recent times, Anthony Leggett takes the same stance when, regarding the double-slit experiment, he asserts: "No experimental consequences are drawn from [the assumption of definite particle trajectories] other than the standard predictions of the QM formalism, so whether one regards it as a substantive resolution of the apparent paradox or as little more than a reformulation of it is no doubt a matter of personal taste." (Leggett 2002, p. R419). However, as clearly explained in the previous section, BM not only involves a different formalism, but also supplies a completely different picture of the microscopic ontological domain. As Sheldon Golstein stresses, "it is only with a purely instrumental attitude towards scientific theories that Bohmian mechanics and standard quantum mechanics can possibly be regarded as different formulations of exactly the same theory." (Golstein 2016). The relation between BM and SQM illustrates what in general philosophy of science is known as *empirical equivalence* and *underdetermination of theory by evidence*.

Two scientific theories are said to be *empirically equivalent* when they make the very same empirical, observational predictions; therefore, they cannot be better or worse supported by any *possible* body of experimental data. In this sense, Bas van Fraassen emphasizes that even our best scientific theories might have empirical equivalents, that is, theories that make all and only the same predictions; so no evidence will ever permit us to decide between them on experimental grounds. The possibility of empirical equivalence between scientific theories leads to the thesis of

the *underdetermination of scientific theory by evidence* (or by data), which is based on the simple idea that the evidence available to us may be insufficient to determine what beliefs we should hold in response to it. In the field of the philosophy of science, the underdetermination thesis is the claim that empirical (observational, experimental) evidence alone is not sufficient to proof any given scientific theory.

The origin of the underdetermination thesis can be traced back to the works of Pierre Duhem (1914), who stresses the impossibility of testing a scientific hypothesis in isolation: in order to derive observable predictions from a hypothesis it is necessary to conjoin it with many other assumptions about, for instance, other theories, the environment, the measurement devices, etc. Therefore, if the result of an experimental observation is in conflict with the derived predictions, there is no way to be sure whether the hypothesis originally sought to test or one of the additional assumptions is the responsible of the failed prediction. A similar idea was expressed several years later by Willard Quine in the context of his “conformational holism”, according to which “total science is like a field of force whose boundary conditions are experience. A conflict with experience at the periphery occasions readjustments in the interior of the field. But the total field is so underdetermined by its boundary conditions, experience, that there is much latitude of choice as to what statements to reevaluate in the light of any single contrary experience. No particular experiences are linked with any particular statements in the interior of the field, except indirectly through considerations of equilibrium affecting the field as a whole.” (Quine 1951, pp. 42-43). Due to this historical framework, the thesis of underdetermination is usually referred to as the “Duhem-Quine thesis.”

In the field of general philosophy of science, empirical equivalence and theory underdetermination are considered as mere conceptual possibilities that play a relevant role in the debate about realism versus anti-realism regarding scientific theories. However, in his influential book *Quantum Mechanics. Historical Contingency and the Copenhagen Hegemony*, the purpose of James Cushing is “to consider an underdetermination thesis, not just as some in-principle or abstract logical possibility, but as a real and practical problem that should be faced in our most successfully theory to date –quantum mechanics.” (Cushing 1994, p. 207). In his detailed formal and historical study, Cushing shows that the relationship between BM and SQM is an actual, long-standing case of undetermination: “we may have two *actual* (not just fancifully concocted for argument’s sake) empirically indistinguishable scientific theories that have diametrically

opposed ontologies (indeterministic/deterministic laws and nonexistence/existence of particle positions and trajectories).” (Cushing 1994, p. 203). As the author claims, Nature provides (often tight) constraints, but there still remains latitude in theory choice: science, even in its products or laws, remains historical and contingent in an essential manner. Cushing’s book can be seen as an essay directed to show how historical contingency played an important role in the neglect of Bohm’s program.

As Goldstein (2016) points out, despite the empirical equivalence between BM and SQM, there is a variety of experimental situations that do not fit comfortably within the context of SQM, but find a conceptually much better explanation in BM: dwell and tunneling times (Leavens 1996), escape times and escape positions (Daumer *et al.* 1997), scattering theory (Dürr *et al.*, 2000), and quantum chaos (Dürr *et al.* 1992). The conceptual account of the relationship between quantum chemistry and quantum mechanics might count as another conceptual advantage of considering BM as the physical underlying theory.

At this point, it is worth clearly stressing that the arguments presented above belong to the field of the foundations and the philosophy of chemistry. By no means is it suggested that SQM should be replaced with BM in the actual practice of molecular chemistry or of quantum chemistry. In fact, the use of BM not only is unnecessary in a field whose practitioners are taught and trained with the formal resources of SQM, but also is not convenient to the extent that the mathematical calculations of BM rapidly become highly intractable with the increase of the system’s complexity. Nevertheless, to the extent that the two theories are empirically equivalent, the strategy of obtaining results with SQM could be safely pursued even if one relied on BM from the foundational viewpoint: SQM would become a mere instrumental tool for prediction, but the conceptual difficulties derived from the link between molecular chemistry and quantum mechanics would be tackled from a Bohmian perspective.

5.- Conclusions

In this paper we have considered the difficulties that challenge the continuous conceptual link between molecular chemistry and SQM. We have stressed that those difficulties ultimately rest on the fact that, in the framework of SQM, quantum systems are not individual systems in the traditional sense of individuality: they lack a “principle of individuality” that makes an individual

different than other individuals and that reidentifies it through time. In fact, due to the Heisenberg principle, quantum systems cannot be individualized by their positions in space and time: there are not trajectories in the SQM realm. For this reason, the existence of BM as a theoretical alternative to SQM deserves to be considered in the field of the philosophy of chemistry.

Although empirically equivalent to SQM, BM is a quantum theory of motion that refers to an ontology much closer to the classical –Newtonian or relativistic– ontology than the standard formalism: the building blocks of the BM ontology are individual particles, with precise values of position and velocity and, as a consequence, with precise trajectories. Quantum probabilities are not irreducible probabilities but are measures of the unavoidable ignorance of the observer about those precise values. This picture supplies an ontological framework much friendlier for molecular chemistry than that given by SQM, to the extent that molecular chemistry is a “hybrid” field: although it incorporates the Schrödinger equation to compute energy levels, it is still based on the assumption of traditional individuals with definite locations in space and time, which preserve their individuality through interactions.

In spite of the conceptual advantages that BM may offer in the field of the philosophy and the foundations of chemistry, certain shortcomings cannot be ignored. Perhaps the main difficulty is to account for the quantum potential, which is the responsible for the highly non-classical effects on the motion of the particles (interference, non-locality) but, by contrast with any other physical potential, has no clear physical source. Of course, this fact does not affect the empirical equivalence between BM and SQM; however, it is a feature that makes Bohmian ontology unpalatable for many physicists, who are used to link any potential with a field, and the field with its source or to the interaction that generates it. Therefore, we are faced with the following alternative: the BM ontology of classical individuals interacting through a non-local field with no source, or the SQM ontology with standard fields but populated by contextual and non-individual entities. The first one is more suitable to apply quantum resources to molecular chemistry; the second one stands in better agreement with the physical view of fields and interactions. As always, there is no absolute and definitive answer in the philosophy of science.

Acknowledgements:

This article was made possible through the support of Grant 57919 from the John Templeton

Foundation and Grant PICT-2014-2812 from the National Agency of Scientific and Technological Promotion of Argentina.

References

- Ardenghi, J., Castagnino, M. and Lombardi, O. (2009). “Quantum mechanics: Modal interpretation and Galilean transformations.” *Foundations of Physics*, **39**: 1023-1045.
- Amann, A. (1992). “Must a molecule have a shape?” *South African Journal of Chemistry*, **45**: 29-38.
- Atkins, P. and de Paula, J. (2010). *Physical Chemistry*. Oxford: Oxford University Press.
- Berlin, Y., Burin, A. and Goldanskii, V. (1996). “The Hund paradox and stabilization of molecular chiral states.” *Zeitschrift für Physik D*, **37**: 333-339.
- Bohm, D. (1952). “A suggested interpretation of the quantum theory in terms of hidden variables.” *Physical Review*, **85**: 166-179.
- Bohm, D. (1953). “Proof that probability density approaches $|\psi|^2$ in causal interpretation of the quantum theory.” *Physical Review*, **89**: 458-466.
- Brion, C., Cooper, G., Zheng, Y., Litvinyuk, L. and McCarthy, I. (2001). “Imaging of orbital electron densities by electron momentum spectroscopy – a chemical interpretation of the binary ($e, 2e$) reaction.” *Chemical Physics*, **70**: 13-30.
- Chang, H. (2015). “Reductionism and the relation between chemistry and physics.” In T. Arabatzis, J. Renn and A. Simoes (eds.), *Relocating the History of Science: Essays in Honor of Kostas Gavroglu*. New York: Springer.
- Cushing, J. (1994). *Quantum Mechanics. Historical Contingency and the Copenhagen Hegemony*. Chicago: The University of Chicago Press.
- Daintith, J. (2004). *Oxford Dictionary of Chemistry*. New York: Oxford University Press.
- Daumer, M., Dürr, D., Goldstein, S. and Zanghì, N. (1997). “On the quantum probability flux through surfaces.” *Journal of Statistical Physics*, **88**: 967-977.
- Duhem, P. (1914). *La Théorie Physique: Son Objet et sa Structure*. Paris: Marcel Riviera & Cie. English translation by P. Wiener (1954). *The Aim and Structure of Physical Theory*. Princeton: Princeton University Press.

- Dürr, D., Goldstein, S., Teufel, S. and Zanghì, N. (2000). "Scattering theory from microscopic first principles." *Physica A*, **279**: 416-431.
- Dürr, D., Goldstein, S. and Zanghì, N. (1992). "Quantum chaos, classical randomness, and bohmian mechanics." *Journal of Statistical Physics*, **68**: 259-270.
- Fortin, S., Lombardi, O. and Martínez González, J. C. (2016). "Isomerism and decoherence." *Foundations of Chemistry*, on line first.
- French, S. and Krause, D. (2006). *Identity in Physics: A Historical, Philosophical and Formal Analysis*. Oxford: Oxford University Press.
- Goldstein, H., Poole, C. P., Safko, J. L. (2002). *Classical Mechanics* (3rd ed.). San Francisco: Addison Wesley.
- Goldstein, S. (2016). "Bohmian mechanics." In E. Zalta (ed.), *The Stanford Encyclopedia of Philosophy* (Fall 2016 Ed.), <http://plato.stanford.edu/archives/fall2016/entries/qm-bohm/>.
- Grosso, B., Cooper, V., Pine, P., Hashibon, A., Yaish, Y. and Adler, J. (2015). "Visualization of electronic density." *Computer Physics Communications*, **195**: 1-13.
- Heisenberg, W. (1955). "The development of the interpretation of the quantum theory." In W. Pauli (ed), *Niels Bohr and the Development of Physics*. London: Pergamon.
- Hendry, R. F. (1998). "Models and approximations in quantum chemistry." In N. Shanks (ed.), *Idealization in Contemporary Physics*. Amsterdam-Atlanta: Rodopi.
- Hendry, R. F. (2004). "The physicists, the chemists, and the pragmatics of explanation." *Philosophy of Science*, **71**: 1048-59.
- Hendry, R. F. (2008). "Two conceptions of the chemical bond." *Philosophy of Science*, **75**: 909-920.
- Hendry, R. F. (2010). "Ontological reduction and molecular structure." *Studies in History and Philosophy of Modern Physics*, **41**: 183-191.
- Hettema, H. (2012). *Reducing Chemistry to Physics. Limits, Models, Consequences*. Groningen: University of Groningen.
- Holland, P. (1993). *Quantum Theory of Motion*. Cambridge: Cambridge University Press.
- Hund, F. (1927). "Zur Deutung der Molekelspektren. III." *Zeitschrift für Physik*, **43**: 805-826.

- Itatani, J., Levesque, J., Zeidler, D., Niikura, H., Pépin, H., Kieffer, J., Corkum, P. and Villeneuve, D. (2004). “Tomographic imaging of molecular orbitals.” *Nature*, **432**: 867-871.
- Kochen, S. and Specker, E. (1967). “The problem of hidden variables in quantum mechanics.” *Journal of Mathematics and Mechanics*, **17**: 59-87.
- Labarca, M. and Lombardi, O. (2010). “Why orbitals do not exist?” *Foundations of Chemistry*, **12**: 149-157.
- Landau, L. D. and Lifshitz, E. M. (1975). *Mechanics*. Amsterdam: Elsevier.
- Leavens, C. (1996). “The ‘tunneling-time problem’ for electrons.” In J. Cushing, A. Fine and S. Goldstein (eds.), *Bohmian Mechanics and Quantum Theory: An Appraisal* (Boston Studies in the Philosophy of Science, Volume 184). Boston: Kluwer Academic Publishers.
- Leggett, A. (2002). “Testing the limits of quantum mechanics: motivation, state of play, prospects.” *Journal of Physics: Condensed Matter*, **14**: R415-R451.
- Litvinyuk, I., Zheng, Y. and Brion, C. (2000). “Valence shell orbital imaging in adamantane by electron momentum spectroscopy and quantum chemical calculations.” *Chemical Physics*, **253**: 41-50.
- Lombardi, O. and Castagnino, M. (2010). “Matters are not so clear on the physical side.” *Foundations of Chemistry*, **12**: 159-166.
- Lombardi, O. and Labarca, M. (2005). “The ontological autonomy of the chemical world.” *Foundations of Chemistry*, **7**: 125-148.
- Mulder, P. (2010). “On the alleged non-existence of orbitals.” *Studies in History and Philosophy of Modern Physics*, **41**: 178-182.
- Mulder, P. (2011). “Are orbitals observable?” *Hyle—International Journal for Philosophy of Chemistry*, **17**: 24-35.
- Nelson, P. (1990). “How do electrons get across nodes?” *Journal of Chemical Education*, **67**: 643-647.
- Ney, A. and Albert, D. (eds) (2013). *The Wave Function*. Oxford: Oxford University Press.
- Pascual, J., Gómez-Herrero, J., Rogero, C., Baró, A., Sánchez-Portal, D., Artacho, E., Ordejón, P. and Soler, J. (2000). “Seeing molecular orbitals.” *Chemical Physical Letters*, **321**: 78-82.
- Primas, H. (1983). *Chemistry, Quantum Mechanics and Reductionism*. Berlin: Springer.

- Primas, H. (1994). "Hierarchic quantum descriptions and their associated ontologies." In K. V. Laurikainen, C. Montonen and K. Sunnarborg (eds.), *Symposium on the Foundations of Modern Physics 1994*. Gif-sur-Yvette: Editions Frontières.
- Primas, H. (1998). "Emergence in exact natural sciences." *Acta Polytechnica Scandinavica*, **91**: 83-98.
- Quine, W. (1951). "Two dogmas of empiricism." Reprinted in *From a Logical Point of View*, 2nd Ed. Cambridge: Harvard University Press.
- Scerri, E. (2000). "The failure of reduction and how to resist disunity of the sciences in the context of chemical education." *Science & Education*, **9**: 405-425.
- Scerri, E. (2001). "The recently claimed observation of atomic orbitals and some related philosophical issues." *Philosophy of Science*, **68**: S76-S88.
- Woolley, R. G. (1978). "Must a molecule have a shape?" *Journal of the American Chemical Society*, **100**: 1073-1078.
- Woolley, R. G. (1982). "Natural optical activity and the molecular hypothesis." *Structure and Bonding*, **52**: 1-35.
- Woolley, R. G. (1998). "Is there a quantum definition of a molecule?". *Journal of Mathematical Chemistry*, **23**: 3-12.
- Woolley, R. G. and Sutcliffe, B. T. (1977). "Molecular structure and the Born-Oppenheimer approximation." *Chemical Physics Letters*, **45**: 393-398.
- Wyatt, R. (2005). *Quantum Dynamics with Trajectories: Introduction to Quantum Hydrodynamics*. New York: Springer.
- Zuo, J. Kim, M., O'Keefe, M. and Spence, J. (1999). "Direct observation of *d*-orbital holes and Cu-Cu bonding in Cu₂O." *Nature*, **401**: 49-52.