

Why molecular structure cannot be strictly reduced to quantum mechanics

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1.- Introduction

Perhaps the hottest topic in the philosophy of chemistry is that of the relationship between chemistry and physics. The problem finds one of its main manifestations in the debate about the nature of molecular structure, given by the spatial arrangement of the nuclei in a molecule. The debate focuses not on an auxiliary or secondary notion, but on a central concept of molecular chemistry: molecular structure is the main factor in the explanation of reactivity, it 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 the concept seems to find no place in the theoretical framework of quantum mechanics. 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. Although this problem has been widely discussed, the debate is far from settled.

Some authors consider that the impossibility of deriving molecular structure from quantum mechanics is not the result of a conceptual obstacle, but the consequence of our partial knowledge of the molecular systems in the theoretical framework of quantum mechanics. This is the case of Guy Woolley and Brian 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) adopts 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. For the author, the problem lies, at least partially, in the scarce impact that the recent developments in quantum chemistry, such as

the “Quantum Theory of Atoms in Molecules” (Bader 1994), have had in the present day philosophy of chemistry. Another reductionist strategy is that adopted by those who rely on the concept of 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 (Troost and Hornberger 2009, Scerri 2011, 2013).

From an opposite position, some authors point out the difficulties of explaining molecular structure in exclusively quantum terms. For instance, in his works of the 70’s and the 80’s, Woolley discusses the implications of the approximation Born-Oppenheimer in a specifically chemical context. According to the author, by means of the description of a molecule from “first principles”, “*one cannot even calculate the most important parameters in chemistry, namely, those that describe the molecular structure*” (Woolley 1978, p. 1074). Woolley 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).

Hans Primas highlights non-locality as a specific feature of quantum mechanics that excludes the spatial concept of molecular structure: “*the holistic correlations between the nuclei and electrons are suppressed, so the description of a molecule reduces to the description of the motion in the electrical field of a classical nuclear framework*” (Primas 1998, p. 91; see also Primas 1983). Others also stress that, in order to conceive the molecule as an individual object with its own spatial structure, it is necessary to ignore quantum correlations: “*The shape of a molecular state should of course not show holistic correlations to other molecular quantities and hence be unambiguously defined*” (Amann 1992, p. 32). In turn, if the state of the molecule determines its properties, the possibility of superpositions has to be dismissed; for instance, in the case of chemical isomers: “*What is the shape of the hypothetical superposition of these two species? Is there a proper reason to exclude such superpositions? What reason can be given –from a quantum-mechanical point of view– for chemical systematics?*” (Amann 1992, p. 32).

From this perspective, Primas (1998) rejects the traditional concept of reduction by showing the need to identify precisely the auxiliary conditions required for one theory to be rigorously and completely deduced from another. These auxiliary conditions are the context that defines the validity domain of the deduced theory: “*In this mathematically precise sense, one*

can speak of the emergence of novelty in descriptions of a higher level” (Primas 1998, p. 86). Following Primas’ ideas, Robert Bishop (2005) also considers the limitations of quantum mechanics to account for molecular structure, and points out that proper attention to the context relevant to a particular situation can resolve otherwise intractable problems (see also Bishop and Atmanspacher 2006).

Robin Hendry (2004, 2008, 2010) has largely treated the issue of molecular structure in the context of the problem of reduction. He clearly distinguishes between the intertheoretic and the metaphysical aspects of the reduction debate. 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.

Summing up, the claim that molecular structure cannot be reduced to quantum mechanics is not new. Different chemical examples are appealed to for supporting it. The case of optical isomerism is perhaps the clearest challenge to a reductive stance: *“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): how can chiral molecules exist?

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. As Hendry (1998) stresses, in the quantum theoretical domain no directional properties can be assigned to an isolated molecule in a general energy eigenstate. For example, the hydrogen chloride molecule has an asymmetrical charge distribution that explains its acidic behavior and its boiling point; however, according to quantum mechanics, the expectation value of the dipole moment of the molecule in an arbitrary eigenstate of the full molecular Hamiltonian is always zero. On this basis, he concludes that “*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).

The traditional strategy underlying these arguments is to consider chemical cases that challenge the reducibility of molecular structure to quantum mechanics. Instead of taking that top-down strategy, in this paper we will adopt a bottom-up argumentation: if the problems are consequences of the foundational incompatibility between quantum systems and molecular systems, it is worth considering in detail the conceptual features of quantum mechanics that obstruct reduction. For this purpose, in Section 2 we will recall the contextuality of quantum mechanics, which challenge the category of individual for quantum systems. On this basis, in Section 3 we will show how the individuality of quantum particles gets lost even in the simplest system: the hydrogen atom. Section 4 will be devoted to develop an analysis of certain assumptions that, although adopted acritically in quantum chemistry, are highly conflictive from the quantum perspective. In Section 5 we will discuss what kind of approximation is the Born-Oppenheimer approximation, stressing in what sense it involves a conceptual breakdown regarding the underlying domain. Finally, in the Conclusions we will review how the peculiar features of quantum mechanics are foundational obstacles to the reduction of molecular structure, and we will consider the possible ways out of this conceptual situation.

2.- The nature of the quantum object

Let us begin by recalling the traditional formalism of quantum mechanics in the Dirac-von Neumann version (Dirac 1930, von Neumann 1932) based on Hilbert spaces, because in this framework the foundational features of the theory are clearly expressed. In this formalism, a quantum system is represented by a Hilbert space \mathcal{H} : the pure states of the system are represented by the vectors (written as kets of the form $|\varphi\rangle$) belonging to \mathcal{H} , and the

observables are represented by Hermitian operators acting on those vectors. Any observable A can be defined by its eigenstates $|a_i\rangle$ and its eigenvalues a_i (strictly speaking, eigenvectors and eigenvalues of its representing operator), which are related to each other as follows:

$$A|a_i\rangle = a_i|a_i\rangle \quad (1)$$

where the a_i represent the possible values of the observable A . If the observable is not degenerate (if all its eigenvalues are different from each other), its eigenstates form a basis $\{|a_i\rangle\}$ of the Hilbert space \mathcal{H} (usually called “eigenbasis” of A). When the state of the system is $|\varphi\rangle$, the probability that the observable A acquires the value a_k is given by the Born rule:

$$\Pr(a_k, |\varphi\rangle) = |\langle\varphi|a_k\rangle|^2 \quad (2)$$

where $\langle\varphi|a_k\rangle$ can be thought as the projection of the vector $|\varphi\rangle$ onto the direction of the vector $|a_k\rangle$.

Although in quantum chemistry it is usual to work with wavefunctions in the position representation, this formalism and the Hilbert space formalism are equivalent and can be easily correlated. In fact, for every state $|\psi\rangle \in \mathcal{H}$, a wavefunction $\psi(q) = \psi(x, y, z) = \langle q|\psi\rangle$ can be defined, where the $|q\rangle \in \mathcal{H}$ are the eigenstates of the position operator Q . In this formalism, the probability of finding a particle in the position $q_k = (x_k, y_k, z_k)$ is the square of the amplitude of the wavefunction in that position: $|\psi(x_k, y_k, z_k)|^2$. The correspondence between state vectors and wavefunctions can also be understood intuitively. A vector can be represented by an array of numbers, say, $\vec{v} = (v_1, v_2, v_3) \in V$, where v_i with $i = 1, \dots, 3$ is a discrete function representing the components of the vector, and V is the vector space in which addition, scalar product and inner product are defined. A first generalization is to consider vector spaces of infinite dimension: in this case, $i = 1, \dots, \infty$. A further generalization is to admit a continuum for the components of the vector: in this case, the originally discrete index $i \in \mathbb{Z}$ becomes a continuous index $x \in \mathbb{R}$, and the v_i become a continuous function $v(x)$ that represents the components of the vector. This allows to conceive functions as vectors, and to use the powerful mathematical apparatus developed in vector algebra.

Now we can recall the model of the free particle studied in the first courses of quantum mechanics. The quantum free particle is represented by a wavepacket whose square represents the probability of finding the particle at each position. Although the wavepacket may be highly peaked in one point, it has a non-zero value in all space. Moreover, according to the Heisenberg uncertainty principle, the product of the standard deviations of position and of momentum (by

considering the wavefunction in the momentum representation), Δq and Δp , are bounded by a constant value:

$$\Delta q \Delta p \geq \hbar / 2 \quad (3)$$

The very name of the Heisenberg principle, ‘*uncertainty principle*’, suggests an epistemic reading of its content: the particle is in some determinate position, but we do not know which one. The limitation is viewed as merely predictive: “*if the momentum is specified precisely, it is impossible to predict the location of the particle*” (Atkins and de Paula 2010, p. 276). This reading was already implicit in the so called “Heisenberg microscope”, a thought experiment proposed by Werner Heisenberg (1930), according to which the measurement of the position of the particle disturbs its momentum and vice versa.

Despite the widespread of this epistemic reading of the Heisenberg principle, the Hilbert space formalism clearly shows that the principle has nothing to do with measurements and unavoidable disturbances. The Heisenberg principle is the consequence of a formal feature of quantum mechanics: the existence of incompatible observables, that is, observables represented by non-commuting operators,

$$AB \neq BA \quad (4)$$

This non-commutativity has a clear manifestation in the framework of the Hilbert space: if $\{|a_i\rangle\}$ and $\{|b_i\rangle\}$ are the eigenbases of the non-commuting (non-degenerate) observables A and B respectively, then the two bases are rotated with respect to each other. Therefore, if the system is in a state $|\varphi\rangle$, the probabilities for the values a_i and for the states b_i are mathematically related in a definite way. Moreover, if the state $|\varphi\rangle$ is one of the states $|a_i\rangle$, say $|\varphi\rangle = |a_k\rangle$, then it is clear that it is not one of the states $|b_i\rangle$: the mathematical structure only gives the probabilities, in this case certainly less than one, that the observable B has each of the possible values b_i .

Although non-commutativity is a much deeper feature than mere epistemic uncertainty, somebody might still believe that the impossibility of ascribing simultaneously precise values to incompatible observables is a limitation of the laws of quantum mechanics itself, which could be remediated by adding the necessary complements to the theory. This was Einstein’s original idea when, in his paper on non-locality (Einstein, Podolsky and Rosen 1935), presented an argument precisely designed to prove the incompleteness of quantum mechanics. This gave rise to the hope of completing the theory with some kind of “hidden variables”, which would assign

definite values to all the observables of a quantum system. But in 1967, Simon Kochen and Ernst Specker (1967) presented a fundamental theorem that proves, in the context of the Hilbert space formalism, that any assignment of a definite value to all the observables of a quantum system leads to *contradiction*. In other words, the Kochen-Specker theorem demonstrates that quantum mechanics is essentially *contextual*: definite values can be consistently assigned only in a context, that is, to observables that share the same eigenbasis.

The contextuality of quantum mechanics shows that it is not the case that the quantum system has definite properties but we do not know which; in fact, any non-contextual attempt to complete the assignment of properties, no matter how, leads to contradiction. It is not the case that the particle has a definite momentum but we do not know its position: any assignment of a definite position and a definite position is *logically* forbidden by the very structure of the theory. Therefore, quantum mechanics challenges the traditional principle of omnimode determination, “*quodlibet existens est omnimode determinatum*”, that appears in the works of Wolff (1728), in the famous treatise on the calculus of probabilities by Bernoulli (1713), and is also repeated several times by Kant in his lectures on metaphysics dating from the 1760s to the 1790s (see the edition of 1902). A quantum “particle” is not an *individual* in the traditional sense, since it has properties –those represented by its observables– that have no definite value; and this is not a merely epistemic limitation, but an ontological fact described by the theory. As we will see in the next section, this feature of quantum mechanics is not a mere philosophical curiosity, but has specific manifestations in physical models.

3.- The components of the hydrogen atom

In the discussions about molecular structure, reductionists usually rely on the complexity of the molecules and the insolubility of exact equations. However, the idea of molecules whose structure is given by certain individual objects, the nuclei, approximately localized and spatially related with each other is untenable, not because of mathematical intractability, but due to the conceptual breakdown regarding the very concept of individual in the quantum realm. And this breakdown is manifested even by the simplest system, whose equation has a complete analytical solution: the hydrogen atom.

Let us begin by recalling that the symmetry group of quantum mechanics is the Galilean group, a Lie group defined by ten symmetry generators that represent the basic magnitudes of

the theory: the energy H representing time-displacement, the three momentum components P_i representing space-displacements, the three angular momentum components J_i representing space-rotations, and the three components G_i representing velocity-boosts (see Lévy-Leblond 1963, Ballentine 1998). In turn, a Casimir operator of a Lie group is an operator that commutes with all the generators of the group and, therefore, is invariant under all its transformations. The Galilean group has three Casimir operators: the mass operator M , the operator S^2 , and the internal energy operator W . The eigenvalues of the Casimir operators label the irreducible representations of the group; so, in each irreducible representation, the Casimir operators are multiples of the identity: $M = mI$, $S^2 = s(s+1)I$ and $W = wI$, where m is the mass, s is the eigenvalue of the spin, and w is the scalar internal energy.

Beyond the mathematical definition of a group, it is important to stress the physical meaning of a symmetry transformation. A continuous transformation, as in the case of those belonging to the Galilean group, admits two interpretations. Under the active interpretation, the transformation corresponds to a change from a system to another –transformed– system; under the passive interpretation, the transformation consists in a change of the viewpoint –the reference frame– from which the system is described (see Brading and Castellani 2007). Nevertheless, in both cases the invariance of the fundamental law of a theory under its symmetry group implies that the behavior of the system is not altered by the application of the transformations: in the active interpretation language, the original and the transformed systems are equivalent; in the passive interpretation language, the original and the transformed reference frames are equivalent.

From the viewpoint of the passive interpretation, the invariance of the dynamical laws under the Galilean group amounts to the equivalence among inertial reference frames (time-translated, space-translated, space-rotated or uniformly moving with respect to each other). In other words, Galilean transformations do not introduce a modification in the physical situation, but only amount to *a change in the perspective from which the system is described*. The group-theoretical language expresses mathematically the natural idea according to which objectivity should not depend on the particular perspective used for the description: what is objective according to a theory is what is invariant under the symmetry group of the theory (Nozick 2001).

Now we can consider the case of the hydrogen atom, conceived as a two-body system consisting of an electron and a proton interacting with each other through a Coulombic potential. So, relative to a reference frame RF the Hamiltonian reads

$$H = \frac{P_e^2}{2m_e} + \frac{P_p^2}{2m_p} - \frac{e^2}{|Q_e - Q_p|} \quad (5)$$

where e is the electric charge of the electron, and the subscripts e and p refer to the electron and the proton respectively. Of course, we can operate with this Hamiltonian to solve the time-independent Schrödinger equation as usual. But if we want to know which are the objective magnitudes of the system, we have to rewrite the Hamiltonian of eq. (5) under the form $H = K + W$, where K is the kinetic energy and W is the internal energy. Since the value of the kinetic energy K is modified by a boost, K is a non-objective magnitude that changes with the mere change of the descriptive perspective. In particular, when the system is described in the reference frame at rest with respect to its center of mass, then $P = 0$ and the kinetic energy disappears from the description. This agrees with the fact that energy is defined up to a constant value: the objective information about the energy spectrum of the system is contained in its internal energy W , which is a Casimir operator of the Galilean group and, therefore, is invariant under all its transformations.

In order to express the Hamiltonian under the form $H = K + W$, it is necessary to introduce a change of variables in terms of the center of mass coordinates and the relative coordinates:

$$Q_C = \frac{m_e Q_e + m_p Q_p}{m_e + m_p} \quad Q_R = Q_e - Q_p \quad (6)$$

$$P_C = M \dot{Q}_C = P_e + P_p \quad P_R = \mu \dot{Q}_R = \frac{m_p Q_e - m_e Q_p}{m_e + m_p} \quad (7)$$

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

$$H = \frac{P_C^2}{2M} + \frac{P_R^2}{2\mu} - \frac{e^2}{|Q_R|} = K + W \quad (8)$$

where:

$$K = \frac{P_C^2}{2M} \quad W = \frac{P_R^2}{2\mu} - \frac{e^2}{|Q_R|} \quad (9)$$

In fact, 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 becomes equal to the internal energy, $H = W$. This shows that the term $P_R^2/2\mu$, although having the form of a kinetic energy, is really a part of the internal energy W .

Up to this point this seems a mere change of variables, as those used in classical mechanics. But now the specifically quantum feature appears. The kinetic energy K only depends on the total momentum relative to RF , and the internal energy W does not depend on the position and the momentum relative to RF , but only depends on differences of positions and, eventually, on their derivatives. These features of K and W guarantee that $[K, W] = 0$ and, as a consequence, H can be expressed as

$$H = K + W = H_K \otimes I_W + I_K \otimes H_W \quad (10)$$

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 Hilbert spaces (Ardenghi, Castagnino and Lombardi 2009). This means that, after the interaction between the electron and the proton, the hydrogen atom becomes a composite system, but not composed of the electron and the proton: now the subsystems are a system \mathcal{S}_W represented by the Hilbert space \mathcal{H}_W , and a system \mathcal{S}_K represented by the Hilbert space \mathcal{H}_K . And in the objective (invariant under the Galilean group) system \mathcal{S}_W , electron and proton are no longer recognizable, but are inextricably “mixed” to constitute a new entity.

In summary, when a classical or quantum composite system is described in the reference frame of its center of mass, in both cases its internal energy is represented by a Casimir operator of the Galilean group and, since invariant under all the transformations of the group, the internal energy is an objective property of the composite system. However, this agreement does not undermine the deep difference between the two cases. In the classical case, the component particles can be reidentified in the composite system: they are individuals whose identity can be traced off through their trajectories even after the interaction. In the quantum case, on the contrary, there are no trajectories that identify each particle as an individual different from the others, since contextuality prevents them to simultaneously have definite values of position and momentum. Therefore, quantum systems are identified by the structure of properties represented in a given Hilbert space. But in a quantum composite system, the internal energy is an objective property corresponding to a single Hilbert space, indecomposable into the Hilbert spaces of

component systems. In other words, the objective description of a quantum composite system shows that it can no longer be analyzed in terms of the quantum systems that existed before the interaction: after the interaction, a quantum “composite” system is not really composite since it does not have objective components.

This result agrees with the conclusion of the previous section: quantum “particles” are not individuals in the traditional sense. The category of individual requires some “principle of individuality” that makes an individual different than other individuals and that re-identifies it through time (French and Krause 2006). Quantum “particles”, by contrast, do not preserve their identity after interaction, and this does not depend on the complexity of the system, but on the very nature of quantum mechanics.

4.- Why the basis of the energy?

As stressed above, a quantum system is represented by a Hilbert space \mathcal{H} . In this vector space, all the bases are equivalent: there is no theoretical reason to prefer a basis over the others. However, chemistry always works in the basis of the energy: the interest is always focused on the possible values of the energy and the possible eigenstates of the Hamiltonian. Why?

Another way of stressing this point is to notice that it is usual to talk about the *time-independent Schrödinger equation*:

$$H_{tot}|\Psi_i\rangle = E_i|\Psi_i\rangle \quad (11)$$

Thus, the Hamiltonian seems to have a privilege in the description of molecules not only regarding their dynamics, but also synchronically, since it is contained in a “time-independent law”. However, in the context of quantum mechanics, the Schrödinger equation is the dynamical postulate of the theory, that is, the law that rules the time evolution of the system. Therefore, talking of a dynamical postulate that is “independent of time” sounds, at least, strange from a physical viewpoint. Strictly speaking, eq. (11) is not a time-independent law, but the eigenstate-eigenvalue equation of the Hamiltonian. Although in general chemists are interested in the energy levels of the molecule, from the quantum viewpoint this is a merely practical matter, since any other observable of the molecule has an equally legitimate eigenstate-eigenvalue equation, and this also holds for observables that do not commute with the Hamiltonian and, as a consequence, define different bases. Therefore, once eq. (11) is deprived from its status of quantum law, the privilege conferred to the Hamiltonian to refine the preferred basis of the

Hilbert space needs to be justified. Forgetting this point may lead to some reconstructions of the theory that restrict the space of observables to a single observable, the Hamiltonian (see Hettema 2012, pp. 264-265), depriving quantum mechanics from its specificity, strongly related to the existence of incompatible observables.

A possible answer to this requirement of justification is that chemists are mainly interested in the *stationary* states of the molecule (eigenstates of the Hamiltonian) and in the energy of the molecule in those states. But this supposes that energy is a definite-valued property. However, this is not an innocent assumption since, as stressed in Section 2, the Kochen-Specker theorem teaches us that not all the observables of the system may have definite values simultaneously. From this perspective, the need for the justification of the privilege of energy takes the form of the need for the justification of the definite-valuedness of the Hamiltonian.

Once the problem is expressed in this way, one can see that it is not the formalism of quantum mechanics what usually offers the desired justification, but a traditional interpretative postulate known as the “*eigenstate-eigenvalue link*”. According to this postulate, when a quantum system is in a state $|\varphi\rangle$, an observable A is definite-valued iff $|\varphi\rangle$ is an eigenvector of A (see, e.g., Bub 1997). On this basis, the justification runs easily: since the molecule is in a stationary state, its state $|\Psi\rangle$ is an eigenvector of H_{tot} ; since $|\Psi\rangle$ is an eigenvector of H_{tot} , according to the eigenstate-eigenvalue link, H_{tot} is definite-valued.

The eigenstate-eigenvalue link supplies an adequate answer in this case and accounts for many situations encountered in practice. However, it does not always work as well as one would expect: its shortcomings come to the light already in the simplest atomic model: the free hydrogen atom (see Lombardi and Castagnino 2010). As it is well known, the principal quantum number n , the orbital angular momentum quantum number l and the magnetic quantum number m_l label the wavefunctions Ψ_{nlm_l} , solutions of the time-independent Schrödinger equation:

$$H \Psi_{nlm_l} = E_n \Psi_{nlm_l} \quad (12)$$

with $n = 0, 1, 2, \dots$, $l < n$, and $-l \leq m_l \leq l$. The wavefunctions Ψ_{nlm_l} are the configuration representations of the vectors $|\Psi_{nlm_l}\rangle$ belonging to the Hilbert space of the system. In the Hilbert space formalism, the quantum numbers correspond to the eigenvalues of the observables H , L^2 and L_z respectively, where L is the orbital angular momentum, and L_x , L_y , L_z are its components:

$$H \left| \Psi_{nlm_l} \right\rangle = E_n \left| \Psi_{nlm_l} \right\rangle \quad (13)$$

$$L^2 \left| \Psi_{nlm_l} \right\rangle = l(l+1)\hbar^2 \left| \Psi_{nlm_l} \right\rangle \quad (14)$$

$$L_z \left| \Psi_{nlm_l} \right\rangle = m_l \hbar \left| \Psi_{nlm_l} \right\rangle \quad (15)$$

Since each vector $\left| \Psi_{nlm_l} \right\rangle$ is an eigenstate of the three observables H , L^2 and L_z , according to the eigenstate-eigenvalue link, these three observables should be definite-valued. However, this conclusion is not physically admissible.

Although $\left| \Psi_{nlm_l} \right\rangle$ depends on the three quantum numbers, the free hydrogen atom is symmetric under space-rotation, and this makes the selection of the spatial direction z a completely arbitrary decision: since space is isotropic, we could choose a different direction z' . In other words, $\{H, L^2, L_z\}$ and $\{H, L^2, L_{z'}\}$ supply both equally “good” descriptions of the system. Therefore, according to the eigenstate-eigenvalue link, the observable $L_{z'}$ should also be definite-valued. Since z and z' are any two directions in space, they can be orthogonal; in this case, $[L_z, L_{z'}] \neq 0$. But the two non-commuting observables cannot have both definite values. This means that, by contrast with the eigenstate-eigenvalue prescription, the nature of the system itself precludes the definite value of L_z , for any spatial direction z .

In fact, the wavefunctions Ψ_{nlm_l} of the atom (orbitals) are labeled as ‘ $X\alpha$ ’, where X is the principal quantum number n , and α is replaced with s, p, d, f , etc., corresponding to the value of the angular momentum quantum number l : $1s, 2s, 2p, 3s, 3p, 3d$, etc. The magnetic quantum number m_l is not included in those labels, and this is justified by the fact that there is no experimental evidence for m_l in the free hydrogen atom: the energy spectrum of the atom does not depend on m_l , in complete agreement with the arbitrariness in the selection of the z -direction for defining the observable L_z . The empirical evidence for m_l is obtained by means of the application of a magnetic field B along the z -direction, which breaks the isotropy of space and, as a consequence, the space-rotation symmetry of the Hamiltonian: the spectral lines split into multiple closely spaced lines (Zeeman effect). In this situation, L_z is not arbitrarily chosen but is selected by the direction of the magnetic field. But now the atom is no longer free; it is a new system with a Hamiltonian that includes the magnetic field and whose eigenvalues depend explicitly on m_l (see Ballentine 1998, p. 326).

In this section, it was shown how different arguments designed to justify the privilege usually conferred to the Hamiltonian basis cannot be justified in terms of bare quantum

mechanics. Appealing to the role played by the Hamiltonian in the so-called “time-independent Schrödinger equation” is not adequate, since this is not a law but the eigenstate-eigenvalue equation for the Hamiltonian, an equation that can be formulated for any other observable of the system. The argument that relies on the interest in the energy of the stationary states of the molecule requires the Hamiltonian to be definite-valuedness, which cannot be guaranteed a priori. Appealing to the eigenstate-eigenvalue link to guarantee that definite-valuedness is not a successful strategy since, as it was shown, the fact that the state of a system is the eigenstate of an observable does not guarantee that such an observable is definite-valued: as shown in the free hydrogen atom, although the state of the system is an eigenstate of the component z of the orbital angular momentum, that component cannot have a definite value; it acquires a definite value only when a magnetic field is applied but, in this case, the system is no longer a free hydrogen atom. Summing up, the privilege of the Hamiltonian basis, although pragmatically justified by many successful applications, finds no theoretical support in quantum mechanics: the definite value of the energy does not count with a strictly quantum justification.

6.- The Born-Oppenheimer approximation

A central element in the discussion about molecular structure is the role played by the Born-Oppenheimer approximation. As Hendry (1998, 2010) points out, the “proxy” defense of Born-Oppenheimer 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). Let us consider this claim in detail.

The total Hamiltonian of a molecule can be written as:

$$H_{tot} = T_n(P_\alpha) + V_{nn}(R_\alpha) + T_e(p_i) + V_{ee}(r_i) + V_{en}(r_i, R_\alpha) \quad (16)$$

where T_n is the nuclear kinetic energy (function of the nuclear momenta P_α), V_{nn} is the potential due to the interactions between the nuclei (function of the nuclear positions R_α), T_e is the electronic kinetic energy (function of the electronic momenta p_i), V_{ee} is the potential due to the interactions between the electrons (function of the electronic positions r_i), and V_{en} is the potential due to the interactions between the electrons and the nuclei (function of the r_i and the R_α). The Born-Oppenheimer strategy is based on the so-called *clamped nuclei approximation*: the electron-nucleus interactions, represented by $V_{en}(r_i, R_\alpha)$, are conceived in terms of electrons

in the Coulomb potential produced by nuclei “clamped” at definite positions. For this purpose, the nuclear kinetic energy is neglected, that is, $T_n(P_\alpha)$ is subtracted from the total Hamiltonian H_{tot} . The resulting electronic Hamiltonian H_e reads

$$H_e = V_{nn}(R_\alpha) + T_e(p_i) + V_{ee}(r_i) + V_{en}(r_i, R_\alpha) \quad (17)$$

where the nuclear positions R_α play the role of parameters. Thus, the electronic time-independent Schrödinger equation, with the Hamiltonian H_e , is solved, and the electronic energy eigenvalues $E_e(R_\alpha)$, parametrically depending on the R_α , are obtained. Only in a second step the nuclear kinetic energy is reintroduced and the total energy E_{tot} is obtained by solving the nuclear time-independent Schrödinger equation.

In the present discussion, the critical step is the clamped nuclei approximation. The subtraction of $T_n(P_\alpha)$ is justified by assuming that $T_n \ll T_e$, which, in turn, relies on the assumption that the nuclear mass is much greater than the electronic mass: $M \gg m$. In particular, if $m/M \rightarrow 0$, then $T_n(P_\alpha) \rightarrow 0$. But, why are we entitled to make this inference? The uncritical answer relies on intuitions coming from classical physics: a body with infinite mass M would have null kinetic energy $T = P^2/2M$ and, as a consequence, it would be at rest in a definite position. However, this is not a classical domain, but a quantum theoretical framework where, as it is well known, classical intuitions frequently do not work.

The usual quantum answer is more appropriate since relying on quantum concepts. The electronic Hamiltonian H_e is not a function of the nuclear momenta P_α (see eq. (17)); then, it commutes with the nuclear positions R_α , $[H_e, R_\alpha] = 0$. In turn, when $M/m \rightarrow \infty$ and, then, $T_n(P_\alpha) \rightarrow 0$, H_e is approximately equal to the total Hamiltonian: $H_{tot} = H_e(p_i, r_i, R_\alpha)$. As a consequence, since R_α commutes with H_e , when $m/M \rightarrow 0$ R_α also commutes with H_{tot} : $[H_{tot}, R_\alpha] = 0$. On this basis, the definite position of the nuclei is explained as follows. When the molecule is in a stationary state, its state is an eigenstate of H_{tot} and, as a consequence, it has a definite value of H_{tot} . Since the molecule has a definite value of its H_{tot} , then the R_α , commuting with H_{tot} , are also definite-valued, and this means that the nuclei are located at definite positions. Although seemingly reasonable, this explanation takes for granted the definite value of H_{tot} , a point that, as argued in the previous section, is far from being clear from a quantum-mechanical viewpoint.

But even letting aside the problem of the definite-valuedness of the energy, it is worth considering what kind of approximation underlies the Born-Oppenheimer strategy. In the

philosophy of science literature it is usual to distinguish between factual and counterfactual limits (Bruer 1982, Rohrlich 1989). For instance, the relationship between special relativity and classical mechanics can be established by means of the factual limit $v/c \rightarrow 0$, that is, an approximation for velocities v much lower than the speed of light c , or by letting $c \rightarrow \infty$, that is, a counterfactual limit given that c has a finite value in the relativistic context. Another case is the classical limit of quantum mechanics, which involves the factual limit $\hbar/S \rightarrow 0$, representing situations in which the action S is much higher than the quantum of action \hbar , but that can also be based on the counterfactual limit $\hbar \rightarrow 0$. It is interesting to notice that a counterfactual limit is legitimate only if it can be replaced by a factual limit. Then, what kind of limit is $m/M \rightarrow 0$? The limit $m \rightarrow 0$ is counterfactual because the mass of the electron is a constant, and the limit $M \rightarrow \infty$ is also counterfactual because, since the masses of the nuclei's components are also constant, it would require an infinite number of components of the nuclei. Despite this, the limit $m/M \rightarrow 0$ can be still thought as a “practical” limit that expresses the high difference between the two masses.

Nevertheless, although relevant, the difference between factual and counterfactual limit does not take into account the consequences of the approximation. For this purpose a new distinction is in order: whether the approximation has consequences consistent or inconsistent with the theory on which it is applied. For instance, in the framework of classical mechanics one may suppose that the friction on a body in motion on a surface is zero. The assumption is likely false, because a surface perfectly smooth surely does not exist in the real world. However, the assumption is compatible with classical mechanics: the existence of such a surface would not contradict the postulates of the theory. The situation is completely different if one supposes, in the context of special relativity, that two spatially separated objects interact instantaneously: this assumption contradicts one of the postulates of the theory, in particular, that which fixes c as the speed limit of any physical interaction.

As pointed out above, by considering that the R_α commute with the definite-valued H_{tot} , the Born-Oppenheimer approximation supposes the nuclei to be placed at definite positions. On the other hand, $T_n(P_\alpha) \rightarrow 0$ may lead to assume that the nuclei are at rest. In this way, the two ingredients necessary to define molecular structure are obtained. But at the cost of contradicting the Heisenberg principle, according to which quantum particle cannot simultaneously have definite values of position and of momentum.

Somebody might retort that $T_n(P_\alpha) \rightarrow 0$ obtains because $M \rightarrow \infty$, and not because $P_\alpha \rightarrow 0$; then, it is not necessary to suppose that the nuclei are at rest. However, if the positions R_α of the nuclei have precise values, the momenta P_α are completely indefinite; therefore, there is a non-zero probability that $P_\alpha \rightarrow 0$ does not hold and, as a consequence, that $T_n(P_\alpha) \rightarrow 0$ does not hold either. In other words, assuming that the nuclei are placed at definite positions and that the values of their momenta are bounded to make $T_n(P_\alpha) \rightarrow 0$, also contradicts the Heisenberg principle, which establishes a finite bound to the corresponding uncertainties.

These arguments show that the Born-Oppenheimer approximation, with its clamped nuclear assumption, is not a mere innocent approximation that admits a proxy defense in a reductionist context. It not only puts molecular structure by hand, in a way that cannot be derived from quantum mechanics. What the approximation adds to the fundamental theory contradicts this very theory, which supposedly serves as the basis of the reduction.

6.- Conclusions

In this paper we have addressed the problem of the reduction of molecular structure to quantum mechanics from a bottom-up perspective: our aim was to show how the theoretical peculiarities of quantum mechanics stand against the possibility of molecular structure, defined in terms of the spatial relations of the nuclei conceived as individual localized objects. According to the theory, 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. On the other hand, although quantum chemists use the resources supplied by quantum mechanics with successful results, this does not mean reduction: their “approximations” add certain assumptions not justified in the context of quantum mechanics or even inconsistent with the very formal structure of the theory.

Of course, these conclusions do not force the abandonment of the ideal of reduction. The insistent reductionist still has two possible strategies. One is to expect the deep revision of chemistry, which in the future would dispense with any concept not perfectly translatable to the underlying quantum theory and, for this reason, considered with no ontological reference. The other is to wait for a replacement of quantum mechanics in its traditional version with another theory better suited to intertheoretic links. One candidate for the replacement is Bohmian

mechanics, since it describes a world much closer to the classical ontology; however, this implies to take charge of the widely discussed difficulties of this alternative theory.

On the other hand, for those without a particularly strong reductionist temperament, the arguments developed above serve to support a non-reductionist view of the relations between molecular chemistry and quantum mechanics. In this line there are also different options. For instance, one may consider that the chemical concepts non reducible to physics, such as molecular structure, denote emergent items that, although existentially depending on the underlying physical realm, populate the ontology of chemistry (Hendry 2006, 2010). Or one may take an ontological pluralist position, according to which chemical concepts refer to items whose existence is guaranteed by the success of chemistry and, therefore, do not need of being referred to a fundamental physical domain (Lombardi and Labarca 2005, 2006, Lombardi 2014). Nevertheless, from any of both non-reductionist perspectives, the conceptual fissure between molecular chemistry and quantum mechanics is acknowledged, and it turns out to be clear that it cannot be filled by the traditional reductionist arguments without a deep modification of the disciplines involved in the debate.

7.- References

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