

Matters are not so clear on the physical side

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Abstract According to ontological reductionism, molecular chemistry refers, at last, to the quantum ontology; therefore, the ontological commitments of chemistry turn out to be finally grounded on quantum mechanics. The main problem of this position is that nobody really knows what quantum ontology is. The purpose of this work is to argue that the confidence in the existence of the physical entities described by quantum mechanics does not take into account the interpretative problems of the theory: in the discussions about the relationship between chemistry and physics, difficulties are seen only on the side of chemistry, whereas matters highly controversial on the side of physics are taken for granted. For instance, it is usually supposed that the infinite mass limit in the Born-Oppenheimer approximation leads by itself to the concept of molecular framework used in molecular chemistry. We will argue that this assumption is implicitly based on an interpretative postulate for quantum mechanics, which, in turn, runs into difficulties when applied to the explanation of the simplest model of the hydrogen atom.

Keywords Molecular chemistry · Quantum mechanics · Born-Oppenheimer approximation · Quantum ontology

Introduction

According to ontological reductionism, chemical entities, when analyzed in depth, are nothing else than very complex physical entities. In other words, molecular chemistry refers, at last, to the quantum ontology; therefore, the ontological commitments of

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The purpose of this work is to argue that the confidence in the existence of the physical entities described by quantum mechanics does not take into account the interpretative problems of the theory: in the discussions about the relationship between chemistry and physics, difficulties are seen only on the side of chemistry, whereas matters highly controversial on the side of physics are taken for granted. For instance, it is usually supposed that the infinite mass limit in the Born-Oppenheimer approximation leads by itself to the concept of molecular framework used in molecular chemistry. We will argue that this assumption is implicitly based on an interpretative postulate for quantum mechanics, which, in turn, runs into difficulties when applied to the explanation of the simplest model of the hydrogen atom.

Molecular chemistry and quantum mechanics

Chemistry and physics are scientific disciplines that embrace a number of different theories, each one of them with its own concepts and laws. Although both disciplines are in contact in several points, the problem of the relationship between them is manifested mainly in the links between molecular chemistry and quantum mechanics: it is in this case where ontological reductionism is usually assumed.

Many authors have stressed the conceptual discontinuity between quantum mechanics and molecular chemistry. In fact, a quantum system is a contextual entity, described by its non-separable state vector, and maintaining non-local correlations with other quantum systems. In molecular chemistry, on the contrary, a molecule is an individual entity, with definite properties—as its shape—and without non-local correlations with other molecular entities (see, for instance, Amann 1992, Primas 1994). The nuclei of the atoms in the molecule behave as classical particles that constitute the nuclear framework; “*so the description of a molecule reduces to the description of the motion of electrons in the electrical field of a classical nuclear framework*” (Primas 1998, p. 91).

For certain authors, this conceptual breakdown implies the impossibility of explaining certain chemical concepts in terms of ontologically referring concepts of quantum mechanics. And, under the assumption of the priority of quantum mechanics over molecular chemistry, they conclude the non-existence of the referents of those chemical concepts. For instance, orbitals are quantum wavefunctions and, then, they do not exist (Scerri 2000, 2001); molecular shape is only a “*powerful and illuminating metaphor*” (Woolley 1982, p. 4) because quantum mechanics does not account for it. However, physicists and quantum chemists in general do not perceive the conceptual breakdown between molecular chemistry and quantum mechanics, or do not consider it as an obstacle to ontological reductionism, under the assumption that there exists an adequate reductive relationship linking both conceptual domains. In particular, the Born-Oppenheimer approximation is supposed to supply the conditions for the desired relationship. Let us see the issue in detail.

A molecule is a complex system composed by nuclei and electrons, all of which interact with each other. According to quantum mechanics, the molecule is a composite system, where nuclei and electrons have only a contextual but not an independent existence. Moreover, due to the indeterminacy principle, a quantum particle cannot be simultaneously assigned a definite position and a definite momentum (for the indeterminacy principle and the contextuality of quantum mechanics, see e.g., Hughes 1989). According to molecular

chemistry, on the contrary, the nuclei are classical particles, at rest (definite momenta) in definite positions: they supply a classical nuclear framework producing the electrical field where the electrons move. Therefore, if the ontological reductionist wants to maintain that the molecule is what quantum mechanics says about it, he has to show that the molecular-chemistry picture can be given in quantum-mechanical terms: the classicality of the nuclei at rest at definite positions is the property that should be explained in terms of the contextual system that inhabits the quantum ontology. The Born-Oppenheimer approximation is supposed to supply such an explanation: by separating the wavefunction of the molecule into its electronic and its nuclear components, the approximation makes it possible to compute the energy levels and the molecular wavefunction of very complex molecules. Proposed in the early days of quantum mechanics by Born and Oppenheimer (1927), the approximation is still an indispensable tool in molecular chemistry. Its success depends on the high ratio between nuclear and electronic masses; nevertheless, even in the cases where it does not lead to good enough predictions, the Born-Oppenheimer approximation is used as a departing point for computations.

The separation of electron and nuclear motions depends on assuming the nuclei as classical-like particles at rest in a definite position. This approximation can be thought off as formally arising from making the masses of the nuclei infinite, in such a way that the limit $m/M \rightarrow 0$ (where M is the nuclear mass and m is the electronic mass) can be applied. But masses are never infinite: this is what makes the Born-Oppenheimer approximation an approximation and not a precise method. It is on this point that the discussions usually focus: the problem is to determine the applicability limits of the Born-Oppenheimer approximation within the degree of accuracy required in each case. However, an important issue on the side of physics is unnoticed: the fact that the nuclei can be treated as classical-like particles cannot be inferred from the Born-Oppenheimer approximation alone, but also requires an interpretative postulate for quantum mechanics. In other words, from a strictly quantum-mechanical viewpoint, the definite-valued position of the nuclei is not fully explained by the Born-Oppenheimer approximation, even under the assumption of infinite nuclear masses. Let us see the argument that supports this claim.

The Born-Oppenheimer approximation at work

The total Hamiltonian of a molecule reads

$$H_{tot} = T_n(P_x) + V_{nn}(R_x) + T_e(p_i) + V_{ee}(r_i) + V_{en}(r_i, R_x) \quad (1)$$

where T_n is the nuclear kinetic energy (function of the nuclear momenta P_x), V_{nn} is the potential due to the interactions between the nuclei (function of the nuclear positions R_x), 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_x). The Born-Oppenheimer approximation proceeds in two steps.

First step: The nuclear kinetic energy is neglected, that is, $T_n(P_x)$ is subtracted from the total Hamiltonian H_{tot} . The resulting electronic Hamiltonian H_e reads

$$H_e = V_{nn}(R_x) + T_e(p_i) + V_{ee}(r_i) + V_{en}(r_i, R_x) \quad (2)$$

where the nuclear positions R_x play the role of parameters. Therefore, the nuclear potential $V_{nn}(R_x)$ is just a constant that shifts the eigenvalues of H_e only by some constant amount.¹ Thus, the electronic Schrödinger equation

$$H_e \Psi_e(r_i; R_x) = E_e(R_x) \Psi_e(r_i; R_x) \quad (3)$$

is solved, and the electronic energy eigenvalues $E_e(R_x)$, parametrically depending on the R_x , are obtained.

This step is often referred to as the *clamped nuclei approximation*: the electron-nucleus interactions, represented by $V_{en}(r_i, R_x)$, are conceived in terms of electrons in the Coulomb potential produced by nuclei “clamped” at definite positions. The subtraction of $T_n(P_x)$ 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 $M/m \rightarrow \infty$, then $T_n(P_x) \rightarrow 0$.

Second step: The nuclear kinetic energy is reintroduced and the total energy E_{tot} is obtained by solving the nuclear Schrödinger equation,

$$[T_n(P_x) + E_e(R_x)] \Psi_n(R_x) = E_{tot} \Psi_n(R_x) \quad (4)$$

It is clear that the crucial approximation of the Born-Oppenheimer approximation is introduced in the first step, where the relation $M \gg m$ is approximated to $M/m \rightarrow \infty$. Of course, this limit is never strictly true and, therefore, the results so obtained are mere approximations. But this is not the point here. Let us suppose for a moment that the nuclear mass were effectively infinite; according to the usual reading of the Born-Oppenheimer approximation, in this case we could infer that the nuclei are effectively clamped at definite positions. The question is: Why can we 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, here we are not in a classical domain, but in a quantum theoretical framework where, as it is well known, classical intuitions usually do not work.

The usual quantum answer is more adequate than the previous one, because it relies on quantum concepts. Let us recall that the total Hamiltonian H_{tot} of the molecule can be expressed as (see Eqs. 1 and 2)

$$H_{tot} = T_n(P_x) + H_e(p_i, r_i, R_x) \quad (5)$$

where the electronic Hamiltonian H_e is not a function of the nuclear momenta P_x . When $M/m \rightarrow \infty$ and, then, $T_n(P_x) \rightarrow 0$, both Hamiltonians can be considered as equal, $H_{tot} = H_e(p_i, r_i, R_x)$. As a consequence, since R_x commutes with H_e , when $M/m \rightarrow \infty$ R_x also commutes with H_{tot} :

$$H_{tot} = H_e(p_i, r_i, R_x) \Rightarrow [H_{tot}, R_x] = 0 \quad (6)$$

On this basis, the quantum answer reads as follows: since the molecule is in a time-independent state (essentially an axiom of quantum chemistry), its state is an eigenvector of H_{tot} and, as a consequence, it has a definite value of H_{tot} (that is, of its energy). Since the molecule has a definite value of its H_{tot} , then the R_x , commuting with H_{tot} , are also definite-valued, and this means that the nuclei are located at definite positions.

¹ We are grateful to W. H. Eugen Schwarz for drawing our attention on this point.

Although seemingly reasonable, this explanation takes for granted the definite value of H_{tot} , a point that is far from being clear from a quantum-mechanical viewpoint. In fact, a stationary state of the molecule is represented by an eigenvector $|\Psi\rangle$ of H_{tot} :

$$H_{tot}|\Psi\rangle = E|\Psi\rangle \quad (7)$$

But $|\Psi\rangle$, being a vector of a Hilbert space, can be expressed in any basis of the space. The Hamiltonian H_{tot} , if non-degenerate, univocally defines a particular basis through the spectral decomposition theorem (see Ballentine 1998).² But there are many other observables, non-commuting with H_{tot} , which define different bases. Why the eigenbasis of H_{tot} , and not the eigenbasis of any other observable non-commuting with H_{tot} , is selected to express $|\Psi\rangle$? Moreover, the Kochen-Specker theorem (Kochen and Specker 1967) teaches us that all the observables of a quantum system cannot have simultaneously definite values; therefore, a decision about the subset of “privileged” definite-valued observables has to be made. Why the Hamiltonian H_{tot} is one of those privileged observables?

When the quantum answer is analyzed with care, it is not difficult to see that it is implicitly based on 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). Now the quantum answer turns out to be a precise argument:

- 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.
- Since $M/m \rightarrow \infty$, then $[H_{tot}, R_x] = 0$
- Since $|\Psi\rangle$ is an eigenvector of H_{tot} and $[H_{tot}, R_x] = 0$, then $|\Psi\rangle$ is an eigenvector of R_x .
- Since $|\Psi\rangle$ is an eigenvector of R_x , according to the eigenstate-eigenvalue link, R_x is definite-valued, that is, the nuclei are “clamped” at definite positions.

It is quite clear that the formalism of quantum mechanics does not provide, by itself, a rule for selecting the definite-valued observables of a system: an interpretative postulate has to be added to accomplish this task. Why not the eigenstate-eigenvalue link? As we have seen, the link works well in the Born-Oppenheimer approximation when the definite positions of the nuclei are to be accounted for. The problem is that the eigenstate-eigenvalue link does not always work as well as one would expect: its shortcomings come to the light already in the simplest atomic model.

The shortcomings of the eigenstate-eigenvalue link

Let us recall that the model of the free hydrogen atom is a two-particle system consisting of an electron and a proton linked to each other by a Coulombian interaction. The usual strategy for solving the Schrödinger equation is to refer the total Hamiltonian of the atom to the center of mass by means of a canonical transformation, and to write the resulting equation in spherical coordinates (r, θ, ϕ) . With this strategy, the wavefunction can be expressed as the product of two functions, one only depending on the radial coordinate and the other only depending on the angular coordinates: $\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$. By solving the radial and the angular equations, three “good” quantum numbers are obtained: the

² If H_{tot} is degenerate, it does not suffice to univocally define a basis of the Hilbert space, but it is a member of a complete set of commuting observables (CSCO) which univocally defines a basis.

principal quantum number n , the orbital angular momentum quantum number l and the magnetic quantum number m_l . The quantum numbers n , l , and m_l label the wavefunctions Ψ_{nlm_l} , solutions of the Schrödinger equation:

$$H\Psi_{nlm_l} = \omega_n\Psi_{nlm_l} \tag{8}$$

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:

$$H|\Psi_{nlm_l}\rangle = \omega_n|\Psi_{nlm_l}\rangle \tag{9}$$

$$L^2|\Psi_{nlm_l}\rangle = l(l+1)\hbar^2|\Psi_{nlm_l}\rangle \tag{10}$$

$$L_z|\Psi_{nlm_l}\rangle = m_l\hbar|\Psi_{nlm_l}\rangle \tag{11}$$

Therefore, the free hydrogen atom is described in terms of the basis $\{|\Psi_{nlm_l}\rangle\}$ of the Hilbert space, defined by the complete set of commuting observables (CSCO) $\{H, L^2, L_z\}$, and whose vectors are labeled by the three quantum numbers n, l , and m_l .

We know that, if the atom is in a stationary state, such a state is represented by one of the vectors $|\Psi_{nlm_l}\rangle$. In turn, each vector $|\Psi_{nlm_l}\rangle$ is an eigenvector of the three observables H, L^2 and L_z of the CSCO (see Eqs. 9, 10 and 11). Therefore, according to the eigenstate-eigenvalue link, the three observables H, L^2 and L_z should be definite-valued. The problem is that this conclusion is not scientifically reasonable.

It is clear that L_z is a constant of motion of the system, since it commutes with H . However, the free hydrogen atom is symmetric under space-rotation. As a consequence, although $|\Psi_{nlm_l}\rangle$ depends on the three quantum numbers, the space-rotation symmetry of the system makes the selection of the spatial direction z a completely arbitrary decision: since space is isotropic, we could choose a different direction z' to obtain an equally legitimate description of the free atom. In other words, the CSCO's $\{H, L^2, L_z\}$ and $\{H, L^2, L_{z'}\}$ supply both equally “good” descriptions of the free hydrogen atom. Therefore, according to the eigenstate-eigenvalue link, the observable $L_{z'}$ should also be definite-valued. But $[L_z, L_{z'}] \neq 0$: two non-commuting observables cannot have both definite values. On the other hand, if one of them were selected as the definite-valued observable, a physical fact would depend on an arbitrary descriptive decision; but this move would be unacceptable from a scientific viewpoint.

This argument shows that, by contrast with the eigenstate-eigenvalue prescription, the nature of the system itself preclude 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., that is, with letters 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 .

In order to obtain empirical evidence for m_l , a magnetic field B has to be applied to the atom: in this situation, the spectral lines split into multiple closely spaced lines. First observed by Pieter Zeeman in 1896, this phenomenon is known as Zeeman effect. The magnetic field B along the z -direction breaks the isotropy of space and, as a consequence,

the space-rotation symmetry of the Hamiltonian. In turn, this symmetry-breaking removes the energy degeneracy in m_l : L_z is not arbitrarily chosen but it is selected by the direction of the magnetic field. But now the atom is no longer free; it is a new system whose Hamiltonian is approximately (see Ballentine 1998, p. 326)

$$H = H_f + \frac{e}{2m_e c} B \cdot L \quad (12)$$

where H_f is the Hamiltonian of the free atom, and e and m_e are the electric charge and the mass of the electron respectively. The original degeneracy of the $(2l + 1)$ -fold multiplet of fixed n and l is now removed: the energy levels turn out to be displaced by an amount

$$\Delta\omega_{nlm_l} = \frac{e\hbar|B|}{2m_e c} m_l \quad (13)$$

and these energy displacements are the empirical manifestation of m_l .³

Summing up, there are strong theoretical and empirical reasons to consider that the observable L_z should not be definite-valued, in spite of the prescription of the eigenstate-eigenvalue link. This shows that the interpretative postulate that works pretty well for certain purposes—as for justifying the classical-like behavior of the highly massive nuclei of a molecule—, may fail in other simple cases. And this is only one of the many manifestations of that matters are not so clear on the physical side.

Conclusions

The relationship between chemistry and physics is one of the most controversial topics in present-day philosophy of chemistry. In the context of this debate, discussions usually focus on the possibility or impossibility of describing chemical concepts in terms of quantum mechanics, under the assumption that theoretical reduction would supply good arguments for ontological reduction. In other words, the implicit idea behind those discussions is that, if we could refer the concepts used by chemistry to quantum-mechanical concepts, we would gain in conceptual precision and, at the same time, we would discover the real quantum-mechanical nature of chemical entities.

The purpose of this paper has been to challenge this widespread assumption. By analyzing two very simple cases, we have shown that the confidence in quantum mechanics is an uncritical belief, which does not take into account the many interpretative problems of the theory. Therefore, any attempt to explain chemistry in quantum mechanical terms is committed to take charge of the serious difficulties that quantum mechanics has to face to supply a coherent account of the quantum ontology. Here we have not taken a definite position about the relationship between chemistry and physics: we only want to stress that, if one is guided by the belief that physics is the ultimate arbiter of chemical ontology, then he has to acknowledge the difficulties in the ontological interpretation of quantum mechanics. As a consequence, chemical ontology, far from gaining in clarity and precision when referred to the quantum ontology, inherits the unclear features of the supposed underlying quantum world.

Of course, that conclusion does not mean that the study of the relationships between chemistry and physics is a sterile task. On the contrary, we think that the assumption of

³ Recently, we have proposed the modal-Hamiltonian interpretation of quantum mechanics (Lombardi and Castagnino 2008, Castagnino and Lombardi 2008, Ardenghi et al. 2009), which explains the fact that L_z is not definite-valued in the free hydrogen atom, but acquires a definite value in the case of the Zeeman effect.

ontological reductionism is not a necessary condition to find meaningful links between the chemical and the physical domains. Moreover, we consider that philosophy of chemistry and philosophy of physics should cooperate in this task: the convergence of different perspectives on the same problem usually leads to fruitful results. This paper can also be read as an attempt to contribute to the collaboration between both areas.

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