

Why orbitals do not exist?

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Abstract In this paper we will address the problem of the existence of orbitals by analyzing the relationship between molecular chemistry and quantum mechanics. In particular, we will consider the concept of orbital in the light of the arguments that deny its referring character. On this basis, we will conclude that the claim that orbitals do not exist relies on a metaphysical reductionism which, if consistently sustained, would lead to consequences clashing with the effective practice of science in its different branches.

Keywords Orbital · Wavefunction · Molecular chemistry · Quantum mechanics

Introduction

In September of 1999, a news shocked the chemical and the physical communities. In its front page, the prestigious journal *Nature* announced that atomic *d*-orbitals of Cu_2O had been imaged for the first time (Zuo et al. 1999). After almost 10 years since that event, now the story is well-known. That first claim was immediately followed by a number of comments, and the images obtained by the Arizona State University group were uncritically identified with atomic orbitals as presented in textbooks (Jacoby 1999; Humphreys 1999). The result was ever rated as one of the most significant events in chemistry for 1999 (Zurer 1999) and one of the highlights of the year in physics (Yam 1999).

By contrast with those optimistic claims, other authors expressed serious reservations concerning the interpretation of the experiments. In particular, in the philosophical community different arguments were put forward to conclude that the visualization of orbitals is impossible on conceptual grounds. Even John Spence, the leader of the team responsible for the experience, conceded that point (Spence et al. 2001): any similarity between the reported images and textbook orbitals was completely fortuitous. Although the

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philosophical debate seemed to be theoretically decided in favor of the non-observability of orbitals, experimentalists continued to report visualization of orbitals, even of molecular orbitals (Litvinyuk et al. 2000; Pascual et al. 2000; Brion et al. 2001; Itatani et al. 2004).

In this paper we will take the claim of the observation of orbitals as the starting point for analyzing the relationship between molecular chemistry and quantum mechanics from an ontological viewpoint. In particular, we will consider the concept of orbital in the light of the arguments that deny its referring character. On this basis, we will conclude that the claim that orbitals do not exist relies on a metaphysical reductionism which, if consistently sustained, would lead to consequences clashing with the effective practice of science in its different branches.

The context of the debate

The problem of the relationship between chemistry and physics is one of the most discussed topics in the philosophy of chemistry, because it points at the heart of the question about the autonomy of chemistry. Traditionally, the problem was addressed from an epistemological viewpoint, on the basis of the concept of epistemological reduction. At present there is a wide agreement about the impossibility of reducing the whole of chemistry to physics: the concepts and laws of chemistry cannot be completely translated nor reduced to the concepts and laws of quantum mechanics (see, for instance, Primas 1983). However, ontological matters were almost ignored under the assumption of ontological reduction: chemical entities, when properly analyzed, are nothing else than extremely complex physical entities (Wooley 1982; Vemulapalli and Byerly 1999).

The general context of the debate begun to change since the announcement in *Nature*. Whereas the discussions about the meaning of the term ‘orbital’ could be comfortably confined to the epistemological sphere up to 1999, the report of the observation of atomic orbitals led the debate directly to the ontological field: now the problem turned out to be the question of deciding whether atomic orbitals exist or not.

In two papers published shortly after the announcement, Eric Scerri (2000, 2001) decidedly faces the new ontological question and expresses his opinion clearly. According to him, the experiments reported as “visualization of orbitals” were misinterpreted because orbitals are not observable. And such inobservability does not depend on experimental shortcomings, but on the plain fact that ‘orbital’ is a non-referring term: orbitals cannot be observed because, strictly speaking, they do not exist.

Although somewhat different objections to the experimental report have been raised (Wang and Schwarz 2000; Schwarz 2006), and the non-existence of orbitals has been stressed by other authors (Matta and Gillespie 2002; Jenkins 2003), here we will follow Scerri’s argumentation because the author never evades the ontological question by conflating it with epistemological matters. In those first papers, the author supports his conclusion on the basis of two arguments which, even if pointing to the same direction, are grounded on different premises.

The mathematical argument

The first argument used by Scerri to deny the existence of orbitals relies on the approximations necessary to describe many-electron atoms. In fact, only the atom as a whole possesses a well defined stationary quantum state represented by its total wavefunction,

which results from the interactions between the nucleus and each electron, and between the electrons to each other. As a consequence of the interactions between electrons, the total Hamiltonian of the atom cannot be obtained as the mere addition of the Hamiltonians of the component electrons. Then, in general the Schrödinger equation cannot be analytically solved: there is no sense in which the electrons can be conceived as having individual and dynamically independent states and, then, defined quantum numbers cannot be independently assigned to them. Any decomposition of the total wavefunction of the atom as a product of electron wavefunctions neglects the electrons interaction and, as a consequence, is a mere approximation.

According to Scerri (2001, p. S79), the only value of orbitals lies in their serving as basis sets, or as a form of coordinate system, with which the wavefunction of an atom, ion, or molecule can be expanded mathematically to any degree of accuracy dictated by the available computational power. On this basis, the author concludes that the orbital model has no physical significance: in spite of its usefulness in many applications, orbitals “are strictly non-referring in that they do not pick out any entity which may be said to physically exist in the same sense that a planetary orbit exists” (Scerri 2001, p. S84).

This last quote is particularly interesting because it suggests the analogy with the three-body problem in classical mechanics. As it is well-known, in a classical system of $n \geq 3$ bodies interacting gravitationally, the equations of motion are non-separable and, then, they have no analytical solution. For instance, in the Solar system each planet cannot be strictly endowed with an independent equation of motion: the separability of the full equation is based on neglecting the gravitational interactions between the planets and, so, involves an approximation. However, here the issue is not epistemological but ontological: the point is to decide whether this mathematical limitation implies the inexistence of the planetary orbits. Of course, if we supposed that ‘planetary orbit’ means ‘the trajectory that the planet would follow around the Sun in absence of the other planets’, then orbits would not exist: they would be only mathematical fictions useful for computations. However, this interpretation not only “ontologizes” a mathematical limitation, but also deprives us of a term to name the trajectory effectively followed by the planet, a trajectory whose existence cannot be denied in classical mechanics. When, more reasonably, we use ‘planetary orbit’ to denote the sequence of positions effectively occupied by a planet over time as a consequence of its interactions with the remaining bodies of the system, the non-separability of the equations of motion does not imply the inexistence of planetary orbits.

It has to be clear that here we are neither proposing a planetary model of the atom nor assuming definite trajectories for the electrons: the argument must be understood by analogy. As the non-separability of the classical equations of motion does not imply the inexistence of planetary orbits, in the same sense the non-separability of the wavefunction of the atom does not imply the inexistence of orbitals understood as the spatial regions where the location of the electrons is more probable. As in the classical n -bodies case, where the description in terms of independent equations of motion is only an approximation, in the atomic case the factorization of the wavefunction of the atom is also an approximation: strictly, the spatial region where the probability of finding the electrons around the nucleus is higher has to be computed with the complete wavefunction of the atom. Of course, in a many-electron atom the shape of that region is not the mere superposition of the shapes corresponding to the orbitals of independent electrons, but “it will correspond to a composite shape due to contributions from the shapes of all the orbitals” (Scerri 2001, p. S82). But, as the fact that the planetary orbits around the Sun have complex shapes due to the interactions between planets does not imply the inexistence of planetary orbits, the complex shape of the electronic orbitals due to the

interactions between electrons neither implies that orbitals -the spatial regions where the location of the electrons is more probable- do not exist. And it even less implies the inexistence of the spatial region where the probability of finding all the electrons of the atom is higher. The relevance of this fact relies on that it is precisely in terms of the shape of this whole spatial region that the bonds between atoms and the shapes of the molecules are explained.

Since the computations based on the factorization of the atomic wavefunction are approximations, it should be not surprising that the results so obtained be not sufficiently accurate in certain situations. What sounds surprising is that this fact be used as an argument to deny the existence of orbitals. For instance, Jenkins claims that this rejection of orbitals relies in experimental grounds, not on metaphysical grounds: “We reject orbitals in particular cases because they do not predict experimental results with an accuracy sufficient for those particular cases” (Jenkins 2003, p. 1059). If we adopted Jenkins’s position, when the mathematical technique used in a description is not sufficiently accurate, we should consider all the concepts involved in such a description as non-referring. Again, this amounts to turn a mathematical limitation into an ontological fact. But even worst: if the limit of an approximation implied the non-referring character of the involved concepts, we would be left in a completely non-referring science. As Ostrosky (2005) points out, when we say that the exact solution of the Schrödinger equation can only be obtained for the hydrogen atom, we are talking of a non-relativistic description. But the Schrödinger equation itself is an approximation since it does not account for relativistic effects. An exact solution can also be obtained from the Dirac equation, which takes relativistic effects into account: it ensures a better agreement with experiments but, again, it is an approximation. If we want to achieve higher accuracy by considering the atomic interaction with the electromagnetic field, we have to turn to quantum electrodynamics. And so on. Summing up, “physics is nothing else than a hierarchy of approximations [...]. This is not a pitiful temporary drawback that might be removed in the course of time. It will continue forever, since it reflects the essence of the approach of physics to describing nature” (Ostrosky 2005, p. 104), and the same holds for any other discipline. Therefore, if approximation implied non-reference, as Jenkins seems to claim, not only orbitals would not exist, but the entire world described by science would vanish as a whole.

Let us note that this argument only applies to many-electron atoms, since only in these cases the atomic wavefunction is non-separable; but the hydrogen atom and other one-electron atoms are immune to it: “the scientific term ‘orbital’ is strictly non-referring with the exception of when it applies to the hydrogen atom or other one-electron system” (Scerri 2001, p. S79). This sounds rather curious since one would expect that, if orbitals do not exist, such a conclusion should apply to any kind of atoms. As we will see in the next section, when the problem is addressed in conceptual terms, arguments are not confined to the many-electron situation.

The conceptual argument

In spite of having devoted a significant part of his 2001 paper to emphasize the approximate nature of orbitals, close to the end of that work Scerri recognizes that “the fact that orbitals might only provide an approximation to the motion of many-electron systems is not a sufficient reason for the complete denial that they or something related to orbitals can possibly exist” (Scerri 2001, p. S87). So, he proposes a second argument, which he claims to be the most decisive one: “Orbitals depict a quantity called probability amplitude, which

has been known to be inobservable in principle since the birth of quantum mechanics as distinct from the old quantum theory” (Scerri 2001, p. S87). The point is that electrons have no defined trajectories: the electron wavefunction only allows us to compute a density of probability. If one admits that an orbital is a wavefunction, orbitals are in principle inobservable because they are complex functions that include the imaginary number $i = \sqrt{-1}$; therefore, “one can only observe the square of an atomic orbital rather than the atomic orbital itself” (Scerri 2001, p. S87).

This second strategy does not appeal to approximations. Now the reason for denying the existence of orbitals is purely conceptual: the concept of orbital does not refer due to its own nature. But this new argument relies on an essential premise: the identification between ‘orbital’ and ‘wavefunction’. The clue is, then, to ask whether this is the concept of orbital used in chemistry to talk about orbital shapes or to explain bonding. Since this argument is not based on the approximations for many-electron atoms, let us consider the hydrogen atom: What does ‘orbital’ mean in this case?

In physics the description of the atom is only a particular case of application of quantum mechanics, that is, a theory referred to systems composed by subatomic entities. In this context, the orbital of the hydrogen atom is the *wavefunction* of its single electron, that is, a mathematical item that does not have an ontological reference in spite of being the orbital of a one-electron atom. This should not be surprising: since the first days of quantum mechanics it was clear that the wavefunction is not a wave in physical space, but only one of the many possible representations of a state vector belonging to a Hilbert space. By contrast with the classical state, due to the existence of non-commuting observables, the quantum state of a system does not assign a definite value to all its observables. This result was originally interpreted as a limitation of the theory, which could be removed by means of definite-valued “hidden variables”. But the hope of recovering a classical picture vanished when Kochen and Specker (1967) proved the contextuality of quantum mechanics: it is not possible to assign a precise value to all the observables of the system with no contradiction. In this way, quantum mechanics strongly challenges the philosophical notion of *individual*, according to which there is some principle of individuation (substance or “essential” properties) that makes an object different than the others and preserves its identity over time (see French and Krause 2006). Another central feature of quantum mechanics is non-locality, as manifested by EPR-type experiments (Einstein et al. 1935): the behavior of a quantum system cannot be accounted for independently of the correlations with all the other systems with which it interacted in the past, in spite of the fact that those interactions have ended, and no matter how far those systems are at present (see Berkovitz 1998). Non-locality is a serious obstacle to the traditional notion of *local* object, that is, to the idea that an entity can be identified by its definite spatial position at each time. The inapplicability of spatial properties to identify quantum entities is forgotten when the quantum components of a molecule are supposed to be endowed with spatial features: “The only spatial entities at hand are electrons and nuclei, which are at the same level of organization” (Jenkins 2003, p. 1061). These conceptual puzzles of quantum mechanics, which have perturbed many physicists and philosophers through decades, show that no classical picture of objects fits into the quantum domain: whatever quantum systems be, they are not the *local individuals* of non-quantum science.

In chemistry, on the contrary, the basic entity is not the atom but the *molecule*: “chemistry is not the science of atoms, [...] but the science of molecules” (Liegener and Del Re 1987a, p. 27; see also 1987b). The main purpose of molecular chemistry consists in identifying the different kinds of molecules and in studying their individual and collective properties. A central feature of a molecule is its shape, which plays an essential role in the

understanding of the physico-chemical properties of matter. As Wooley (1978, p. 1074) claims, the notion of molecular shape is “the central dogma of molecular science”. This notion is a spatial, classical notion: the shape of the molecule is explained in terms of the spatial relationships among the component atoms and the shape of its orbitals. So, the term ‘orbital’ needs to have a spatial content in order to account for the geometrical dispositions of the atoms in the molecule. Therefore, in molecular chemistry the orbital of the hydrogen atom is understood as the *region of space* where the single electron of the atom is most likely to be located.

In the chemical context, molecules are non-quantum objects in an individual and local sense: they have definite properties at any time, preserve their identity through the change of properties, and always possess not only a definite position but also a definite shape. As Primas (1994, p. 216) says: “The alpha and omega of molecular chemistry is the doctrine that molecules exist as individual objects and that every molecule has a shape, characterized by its molecular frame”. The notion of molecular frame is also a classical concept, since it relies on the assumption of the unambiguous positions and momenta of the nuclei, assumption that contradicts quantum contextuality. On the other hand, the non-locality of quantum mechanics excludes the spatial concept of molecular shape (Primas 1983, 1994, 1998). Then, in order to conceive the molecule as an individual object with its own shape 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, the state of the molecule determines its properties, as in classical physics; molecular chemistry does not include the possibility of superpositions in Hilbert space. For instance, if chemical isomers, with their own shape, correspond to different state vectors, then superposition makes sense from the quantum-mechanical viewpoint: “What is the shape of the hypothetical superposition of (state vectors corresponding to) 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).

These and other arguments have been used to stress that the molecule studied by molecular chemistry is a local individual, “which exists separately and independently in the sense that it can consistently said to ‘have’ certain properties, whether or not it interacts with anything else” (Wooley 1978, p. 1074). In this classical ontology, the shape of the molecule depends on the spatial disposition of its local and individual atoms, whose locations are given by the definite positions of the classical-like nuclei; and although the electrons do not follow definite orbits, they are also individuals located in a region of space close to the nuclei, with a probabilistic distribution given by the total wavefunction. In other words, the molecule is constituted by classical nuclei and semi-classical electrons, that is, individuals whose behavior is not governed by classical equations of motion but by an equation that determines their position only in a statistical way. This picture is completely alien to quantum mechanics, where one could strictly speak only of the molecule-system, described by its whole non-separable state vector, maintaining its quantum correlations with other quantum systems, and whose components are not classical individuals but quantum subsystems with the same quantum features, that is, contextuality and non-locality.

The traditional strategy to link the chemical and the quantum descriptions of molecules usually appeals to the Born–Oppenheimer approximation, which in general supplies good predictions because the mass M of the nucleus is much greater than the mass m of the electrons. From a formal viewpoint, the approximation is an asymptotic expansion about the singular limit $m/M \rightarrow 0$. This means that the relationship between both descriptions is

strictly valid for infinite nuclear masses; only in this case “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). But masses are never infinite: the Born–Oppenheimer approximation implies a “qualitative change in the theory which is expressed in the mathematics by a discontinuous approximation” (Wooley 1978, p. 1076). As Amann (1992, p. 30) claims, the innocent-looking Born–Oppenheimer approximation actually amounts to a “declaration” that molecular chemistry smuggles into quantum mechanics: “the nuclei of the involved molecule are declared to behave like classical particles”. Therefore, the link between the chemical and the quantum description of the molecule is not a mere reductive relationship, to the extent that it involves a qualitative discontinuity between the related concepts. In fact, as Woolley and Primas point out, the Born–Oppenheimer approximation is analogous to the quasi-classical WKB approximation, with its corresponding limit $\hbar \rightarrow 0$. Such an analogy becomes natural when the issue is viewed from a more general perspective: both approximations are attempts to answer the still unsolved problem of the classical limit of quantum mechanics, that is, the problem of explaining how the local individuals of classical science arise from the non-local and contextual domain described by quantum mechanics.

When the two theories involved in the discussion about orbitals are clearly identified, it is easy to see that the problem of the reference of the term ‘orbital’ is rooted on a deep conceptual breakdown. Whereas in quantum mechanics ‘orbital’ is a non-referring term, in molecular chemistry orbitals exist as spatial regions on the basis of which the shape of the local and individual molecules can be explained. As we have shown, many authors recognize not only the non-reducibility of molecular chemistry to quantum mechanics, but also the *conceptual discontinuity* between the two theories. The question is now to decide what *ontological* conclusion can be drawn from this conceptual breakdown.

The underlying ontological reductionism

Let us consider two theories T_1 and T_2 , both containing a term ‘ C ’, which is non-referring in T_1 , but refers to the entity C in T_2 . Moreover, T_2 cannot be epistemologically reduced to T_1 . For what reason can we say that the entity C does not exist *simpliciter*? Since epistemological reduction fails, the entity C described in T_2 does not exist only under the assumption that T_1 is the “true” theory or, at least, the theory most appropriate to describe reality. This assumption underlies Scerri’s claim: “it is essential for scientists to be more discerning in attributing physical reality to entities which are theoretically defined and which the theory itself informs us do not exist physically” (Scerri 2001, p. S81). Which is the theory that informs us that orbitals do not exist? Quantum mechanics, of course. But why we do not ask molecular chemistry about the matter? What privilege does quantum mechanics carries for becoming the clue witness about what exists and does not exist in the world? There seems to be no other grounds for that privilege than an ontologically reductionistic attitude, according to which quantum mechanics is the best theory to describe the only “true” ontology: any description that disagrees with the quantum picture in unavoidably confined to a strictly non-referring realm.

Certainly, there is no logical contradiction in ontological reductionism, but it is interesting to see the consequences implied by a coherent defense of it. If quantum mechanics were the only theory that describes (at least, approximately) reality, it would say what exists in the world, and it would be entitled to deny the existence of all the entities referred

to by non-quantum theories (the local individuals of non-quantum science, see Section “[The conceptual argument](#)”). Then, not only chemical orbitals would not exist: all the entities referred to by non-quantum theories would also be non-existing. Then, we would see to vanish from reality molecules with their shapes, gases with their temperatures, planets with their orbits, biological organisms with their cells, and so on. If the observation of chemical orbitals implied “an outright refutation of quantum mechanics” (Scerri 2001, p. S76), then the observation of any entity not belonging to the domain of quantum mechanics would also refute it; nevertheless, all non-quantum science is supported by those observations. According to Scerri, orbitals do not exist and, then, “they cannot be observed, period” (Scerri 2000, p. 1494). Let us replace in this sentence the term ‘orbital’ with any other term not belonging to quantum mechanics—‘molecule’, ‘cell’, ‘planet’, ‘virus’, ‘galaxy’, etc.—: a coherent reductionist should accept the statement resulting from that replacement.

Conclusion and perspectives

In previous works (Lombardi and Labarca 2005, 2006) we have defended the ontological autonomy of chemistry from an ontologically pluralistic perspective, according to which different ontologies may coexist with no reduction or priority relationships among them. In this Kantian rooted philosophical framework, since any ontology results from the synthesis between the “noumenal” independent reality and the conceptual scheme of a theory, the quantum ontology is not a conceptually independent domain but a realm as constituted as the realm of molecular chemistry. Therefore, the quantum world has no priority over the world of molecular chemistry: chemical entities do not need the support of quantum entities to legitimate their objective existence. From this perspective, orbitals exist in the ontology of molecular chemistry, in spite of the fact that they do not exist in the quantum world.

This pluralistic position does not amount to charge ontological reductionism with an unacceptable self-contradiction, but to conceive it as a metaphysical thesis in a Kantian sense: it is beyond any possible evidence. In fact, formal, historical and pragmatic evidence, far from supporting ontological reductionism, provides further arguments for ontological pluralism. But the discussion of those arguments is beyond the limits of the present paper and will be the subject of a future work.

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