

# *What is the electron density?*

Sebastian Fortin and Olimpia Lombardi

*CONICET – UBA, Argentina.*

## **1.- Introduction**

Although the electron density can be calculated with the formal resources of quantum mechanics, in physics it does not play the leading role that the quantum state does. In contrast, the concept of electron density is central in quantum chemistry, in any of its different approaches: the Hartree-Fock Method, the Density Functional Theory, and the Quantum Theory of Atoms in Molecules.

There is no doubt about how the electron density is computed in terms of the wave function of an atom or molecule. However, when the interpretation of the concept is at stake, there is no general agreement. In this article we will analyze the two main interpretations of the concept of electron density: the Born-style probability density interpretation and the Schrödinger-style charge density interpretation. In particular, we will examine their differences, their relations with quantum mechanics and the consequences that each of them entails from a strictly quantum point of view.

With this purpose, the article is organized as follows. In Section 2 we will recall how the electron density is usually computed, and in Section 3 we will introduce the two main interpretations of the concept of electron density: as a mathematical field—a probability density—and as a matter field—a charge density. Section 4 will be devoted to stress the difficulties involved in conceiving of electron density as a matter field in the light of quantum mechanics. In Section 5 we will point out how the attempts to make both interpretations compatible by means of different average strategies require thinking of electrons as point particles, an ontological picture that conflicts with quantum mechanics in most of its versions. In Section 6 Bohmian Mechanics will be considered as a theoretical framework that could accommodate the way in which quantum chemists conceive the electron density. Finally, in Section 7 the reductive assumptions that underlie the attempts of compatibilization will be critically examined.

## 2.- Computing the electron density

According to the usual presentations, the electron density is computed as follows. In the case of a single electron with wave function  $\psi(\mathbf{r},s)$ , the electron density  $\rho(\mathbf{r})$  is defined as proportional of the square of the wave function's amplitude as

$$\rho(\mathbf{r}) = (-e)|\psi(\mathbf{r},s)|^2. \quad (1)$$

Let us consider a system with  $N$  electrons, whose wave function is  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, s_1, s_2, \dots, s_N)$ . In this case, the electron density  $\rho(\mathbf{r})$  is computed as the sum of the contributions of each electron, obtained by integrating over the coordinates of the other electrons:

$$\begin{aligned} \rho(\mathbf{r}) = & (-e) \sum_{s_1, s_2, \dots, s_N} \int |\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, s_1, s_2, \dots, s_N)|^2 d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N + \\ & (-e) \sum_{s_1, s_2, \dots, s_N} \int |\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, s_1, s_2, \dots, s_N)|^2 d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N + \dots + \\ & (-e) \sum_{s_1, s_2, \dots, s_N} \int |\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, s_1, s_2, \dots, s_N)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 \dots \end{aligned} \quad (2)$$

But electrons are indistinguishable and, since they are fermions, their wave function must be anti-symmetric. As a consequence, each electron contributes equally to the total electron density and eq. (2), after normalizing as a non-dimensional quantity, can be written as

$$\rho(\mathbf{r}) = (-N) \sum_{s_1, s_2, \dots, s_N} \int |\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, s_1, s_2, \dots, s_N)|^2 d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N. \quad (3)$$

Let us notice that the indistinguishability of the electrons is what allows passing from an abstract function  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, s_1, s_2, \dots, s_N)$  on the configuration space of  $3N$  dimensions to a real-valued function  $\rho(\mathbf{r})$  on a space of three dimensions that, therefore, can be thought as representing the physical space. In what follows, the spin of the electrons will be ignored for simplicity. Now the question is how to interpret this function  $\rho(\mathbf{r})$ .

## 3.- Interpreting the electron density

Despite the consensus on how to calculate the electron density, and that it is an observable accessible from experimentation (Bader and Zou 1992, Bader and Matta 2013), there is no agreement on the conceptual meaning of the magnitude thus obtained. In particular, two clearly different interpretations can be distinguished.

According to the *Born-style probability density interpretation (PDI)*, the electron density is the probability density of finding an electron at each specific location in space. More precisely,  $\rho(\mathbf{r})$  is the density of probability of finding an electron in an infinitesimal region around  $\mathbf{r}$ . The “finding an electron” can be understood in two different ways. From a realist perspective,  $\rho(\mathbf{r})$  encodes the probability of an electron being located at position  $\mathbf{r}$ . From an instrumentalist perspective,  $\rho(\mathbf{r})$  encodes the probability of an electron being found at position  $\mathbf{r}$  through measurement. Nevertheless, in both cases the electron density is a *mathematical field* that refers to probabilities. This is the interpretation usually adopted in physics, following Born’s probabilistic reading of quantum mechanics.

According to the *Schrödinger-style charge density interpretation (CDI)*, the electron density is a density of charge distributed over the entire three-dimensional physical space. It is a kind of “cloud” of negative charge spread throughout space. In this case the electron density is a physical field, in particular, a *material field* of negative charge.

Historically, the CDI was the first interpretation to appear. It was formulated by Schrödinger (1926a, 1926b), who defined the electron density as a continuous distribution of *electricity* in the physical space, perhaps in resonance with his idea of the wave function as a field in physical space. According to him, the wave function  $\psi$  should not be directly used to interpret quantum phenomena, since it is a function in configuration space and not in physical space. Instead, he advocates for appealing to  $\psi$  only to obtain the quantity  $\psi^* \psi$ , since

*“the charge of the electron is not concentrated in a point, but is spread out through the whole space, proportional to the quantity  $\psi^* \psi$ ”* (Schrödinger 1926b: 1066).

Schrödinger is then interested in the electron charge density,  $e\rho(\mathbf{r})$ , where  $e$  is the charge of the electron and  $\rho(\mathbf{r})$  is the electron density.

When it became clear that the wave function could not be conceived of as a physical field in three-dimensional space, Schrödinger’s interpretation of the electron density was also rejected. Today, the PDI is the commonly adopted interpretation in physics: Born’s probabilistic reading of the wave function and, derivatively, of the electron density, is unreservedly admitted in this context.

By contrast, the CDI is a very common interpretation of the concept of electron density in the domain of quantum chemistry. This view of the electron density as referring to a “stuff” of negative charge spread out in physical space and represented by a scalar field is explicitly

adopted by Richard Bader and Chérif Matta in the framework of the Quantum Theory of Atoms in Molecules (QTAIM) when they say:

*“The electronic charge, unlike that of the more massive nuclei, is spread throughout space, and matter is made up of point-like nuclei embedded in the relatively diffuse spatial distribution of electronic charge. The distribution of electronic charge is described by the electron density that determines the amount of negative charge per unit volume.”* (Bader and Matta 2013: 255).

Bader explicitly retrieves Schrödinger’s interpretation to claim that the electron density is not a probability density: from his view, it acquires materiality since describes the kind of stuff of which atoms and molecules are made.

It is worth stressing that the coexistence of these two interpretations leads to a conceptual tension: taken at face value, the CDI and the PDI are incompatible since, in principle, the same magnitude cannot be a mathematical field and a material field at the same time. In the case of the CDI, the electron density refers to a material “cloud” occupying the physical space, while in the case of the PDI, it refers to an abstract probability. Suppose, for example, that the value of the electron density at a point in space is 0.8 (multiplied by the electron charge). According to the PDI, this means that the probability of finding an electron at that point when a measurement is performed is 80% and, therefore, when the measurement is effectively performed, the electron may or may not be found at that point. On the contrary, according to the CDI, there is an amount of charge at that point regardless of the result of the measurement and even whether the measurement is performed or not. It is quite clear that the two situations are completely different. In the next sections some possible strategies for dealing with this tension will be discussed.

#### **4.- Taking the idea of charge density seriously**

If the conceptual incompatibility between the CDI and the PDI is accepted, why not definitively set aside the PDI and resolutely embrace the CDI? In other words, why not adopt Schrödinger’s position seriously? This alternative has an immediate puzzling feature: the charge distribution, even in the case of a single electron, does not display electrostatic self-interaction. It could be argued that the absence of self-interaction is a peculiar characteristic of the quantum world. However, as we will see below, conceiving the electron density as a material field of negative charge leads to different difficulties in the light of certain general tenets of quantum mechanics.

#### 4.1.- How the charge density changes during measurement

Let us imagine that  $\rho(\mathbf{r})$  really represents a material field of charge density. In a hydrogen atom that material field would be a radially symmetric charge field distributed around the nucleus. However, when the electron is measured, it is detected at a definite position. This means that, upon measurement, the original distributed charge density must instantaneously, or almost instantaneously, “collapse” to become a charge density represented by a Dirac delta distribution centered at the electron position. This picture leads to two undesirable consequences.

First, if collapse is instantaneous, it should produce infinitely strong currents at the collapse time. And if collapse is not instantaneous but occurs within a very short interval of time, the currents will be very strong but not infinite: the difficulty here is that no such currents have ever been detected.

Second, if the charge density vanishes around the nucleus to concentrate at a single position, then the local conservation of charge is violated: suddenly the charge disappears from one location to appear at another. These criticisms are not new: they have been directed to some Spontaneous-Collapse Interpretations of quantum mechanics, according to which the wave function of each fundamental particle independently undergoes spontaneous collapses, which are random in time (see Ghirardi and Bassi 2020). Independently of the mechanism and the details of the collapses, these interpretations have been conceived in terms of a “mass density” that fills the space and concentrates instantaneously at a defined position during collapse. In this case the criticisms point to the non-detected mass flow and to the violation of the local conservation of mass. But it is clear that these objections can be transferred in a direct way to the CDI of the electron density.

#### 4.2.- How the charge density behaves without collapse

Let us now consider how the charge density behaves in the context of a non-collapse interpretation of quantum mechanics. In this case, what happens when the wave function is a superposition of macroscopically distinguishable states?

The paradigmatic example of this situation is Schrödinger’s cat, whose wave function  $\psi$  is a superposition of the wave functions “dead cat”  $\psi_d$  and “alive cat”  $\psi_a$ . If equiprobability is assumed, then  $\psi = 1/\sqrt{2}(\psi_d + \psi_a)$ . In turn, the dead cat and the alive cat are two different systems of many electrons, so that their respective electron densities  $\rho_d$  and  $\rho_a$  can be computed in terms of  $\psi_d$  and  $\psi_a$ , respectively. But if the concept of electron density is interpreted as describing a charge density, in this case there are two charge densities spread throughout the same three-dimensional physical space. In the terms of Valia Allori, Sheldon Goldstein, Roderich Tumulka, and Nino Zanghì, this means that the two “cats” coexist in the same space, as “*ghosts we do not perceive*” (Allori et al. 2011: 8); the authors use another

metaphor:

*“the universe [...] resembles the situation of a TV set that is not correctly tuned, so that one always sees a mixture of several channels.”* (Allori et al. 2011: 8)

To escape from this image of different “worlds” coexisting in the same space, it is necessary to appeal to the Many Worlds Interpretation (MWI) of quantum mechanics, according to which, although there is no collapse, in each measurement event the entire universe bifurcates into different branches, each of which contains one of the components of the superposition (see Vaidman 2021). If this interpretation is accepted, the two charge densities do not correspond to a single “world”, but each will inhabit its own universe.

This interpretation, besides sounding extravagant to the ears of most quantum chemists, still entails certain conceptual problems: the problem of the probability and the problem of the preferred basis. If the splitting of the universe cancels superposition, it is not clear how superpositions with different pairs of probabilities are distinguished. On the other hand, despite the appeal to decoherence, it is still not clear why we see apparent collapses into a certain basis of states and not others. These questions continue to be discussed despite the efforts to answer them by the proponents of the MWI.

Furthermore, if the electron density is conceived as a material density, the Many Worlds Interpretation introduces an additional difficulty. At each split of the entire universe, the total charge in each branch decreases with respect to the total charge of the universe before the split (see Allori et al. 2014). Although this effect has no observable consequences, it is something the quantum chemist has to accept in order to adopt the CDI of the electron density.

## **5.- Searching for compatibility**

If the ontological picture, proper to CDI, of a physical field of charge on three-dimensional space causes so many problems, it may be worthwhile to try to make both interpretations compatible. Perhaps on the basis of the uncritical acceptance of this idea of compatibility, some authors oscillate between CDI and PDI without explanation. For example, in a well-known quantum chemistry text one reads:

*“If we have an electron described by the spatial wave function  $\psi_a(\mathbf{r})$ , then the probability of finding that electron in a volume element  $d\mathbf{r}$  at a point  $\mathbf{r}$  is  $|\psi_a(\mathbf{r})|^2 d\mathbf{r}$ . The probability distribution function (charge density) is  $|\psi_a(\mathbf{r})|^2$ .”*  
(Szabo and Ostlund 1989: 138).

The strategies to achieve the compatibility between the CDI and the PDI appeal to the idea of average.

### 5.1.- The space-average strategy

Sometimes, the electron density is also defined as a measure of the number of electrons per unit volume of space: the physical space is divided into small cells and each cell is assigned a charge value proportional to the number of electrons it contains. This view leads to understanding the electron density from the CDI perspective. The link between charge density and probability is given by assuming that the probability of finding an electron in a given cell is proportional to the number of electrons in that cell.

This idea of a “cloud” of electrons can be associated to the CDI, that is, to a cloud of negative charge only if the number of electrons tends to infinity. For this reason, the space-average strategy may approximately work for systems of a high number of electrons; but for systems with few electrons this strategy is very hard to be sustained. For this reason, the time-average strategy is more common in the literature.

### 5.2.- The time-average strategy

According to the time-average strategy, the electron density  $\rho(\mathbf{r})$  is interpreted as representing a kind of mean value of the definite positions occupied by the electron in its motion around the nucleus. This idea had already appeared in Linus Pauling’s famous book originally published in 1939:

*“We can accordingly describe the normal hydrogen atom by saying that the electron moves in and out about the nucleus, remaining usually within a distance of about  $0.5 \text{ \AA}$ , with a speed that is variable but is of the order of magnitude of  $v_0$ . Over a period of time long enough to permit many cycles of motion of the electron the atom can be described as consisting of the nucleus surrounded by a spherically symmetrical ball of negative electricity (the electron blurred by a time exposure of its rapid motion)”* (Pauling 1960: 14-15).

The same strategy is adopted in much more recent works. For instance, in a paper published in a journal of chemical education, Peter Nelson uses the following image:

*“if a series of measurements could be made of  $x$  without disturbing the motion of the particle, the resulting distribution would be  $\rho$ . The latter would then reflect the motion of the particle in the same way in which the density of the image on a*

*long-exposure photograph reflects the motion of a macroscopic object”* (Nelson 1990: 643).

The same picture appears more recently in a textbook by Ira Levine:

*“The rapid motion of electrons causes the sluggish nuclei to ‘see’ the electrons as a charge cloud rather than as discrete particles.”* (Levine 2014: 430).

The idea is the following. Let us consider a hydrogen atom. The electron moves very fast around the nucleus so that, in average, it forms a cloud of negative charge surrounding the nucleus. If the physical space is divided into small cells, the time spent by the electron in each cell can in principle be computed. Under the assumption that the time spent by the electron in each cell is proportional to the volume of the cell, such a volume turns out to be proportional to the probability of finding the electron in that cell.

This idea is not new. Already at the end of the 19th century Boltzmann appealed to the motion of particles to account for the emergence of probability in classical statistical mechanics. A central element of his proposal was the acceptance of the so-called “ergodic hypothesis”, according to which the orbit of the representative point of a system in the phase space of microstates eventually goes through all points on the surface of constant energy; this fact is what guarantees that the time spent by the system in some region of the phase is proportional to the volume of this region, which, in turn, is proportional to the probability that the system is in a microstate belonging to that region. Recently, Shan Gao appeals precisely to ergodicity to explain the physical origin of the electron density conceived as a charge density:

*“It is argued that the charge distribution of a quantum system is effective, that is, it is formed by the ergodic motion of a localized particle with the charge of the system.”* (Gao 2018: 146)

According to the author, this picture may explain the non-existence of electrostatic self-interaction for the charge distribution of a single quantum system. Moreover, the picture of ergodic motion of a single particle can be extended to many particles.

### **5.3.- Requirements for the average strategies**

The average strategies implicitly assume that electrons are particles, that is, tiny objects that occupy definite positions in space. In particular, the time-average strategy is based on the assumption that electrons have definite trajectories around the nucleus. In other words, electrons are conceived as individual objects, with definite positions and velocities, whose main difference with respect to classical particles is that their behavior is not governed by



classical equations of motion but by an equation that determines their position only in a statistical way.

The problem with this view is that it is in conflict with the conceptual structure of quantum mechanics in several senses. First, it is incompatible with the Heisenberg principle, according to which quantum systems cannot possess definite position and definite momentum simultaneously and, consequently, do not describe trajectories like classical objects. Second, the Kochen-Specker theorem (Kochen and Specker 1967) proves the impossibility of ascribing precise values to *all* the observables of a quantum system simultaneously while preserving the functional relations between commuting observables. It follows that quantum mechanics is essentially *contextual*: definite values can be consistently assigned to observables only in a context, determined by the observables that share the same eigenbasis (see Martínez González, Fortin, and Lombardi 2019). The theorem proves that the fact that a quantum system always has some non-definite-valued properties is not a limitation of our knowledge but an ontological fact resulting from the formalism of the theory. Third, the quantum domain admits surprising non-local correlations between the properties of distant non-interacting systems, such as those of the famous Einstein-Podolsky-Rosen paradox. These EPR-correlations link systems between which no light signal can travel but, nevertheless, they do not allow sending information at a superluminal velocity. For this reason, non-locality is usually conceived as holism, the characteristic of some physical objects that are indivisible wholes (see Healey and Gomes 2022). Fourth, elementary “particles” are essentially indistinguishable, i.e., each of them cannot be labeled, nor can they be counted when they form aggregates (see French 2019). This indistinguishability is manifested by the fact that they do not follow Maxwell-Boltzmann statistics, but are collectively described by Bose-Einstein statistics (for bosons, like photons) or by Fermi-Dirac statistics (for fermions, like electrons).

All these features point to the same direction: quantum systems are not particles in any reasonable sense of the term ‘particle’. Elementary quantum systems are not *individual* objects according to the traditional meaning of the term ‘individual’ (see Lombardi 2023). In fact they lack synchronic and diachronic individuality: they cannot be discerned by their space-time positions, and they cannot be reidentified over time by the continuous trajectory traced by their motion. Moreover, due to their indistinguishability, they cannot be counted nor can they be reidentified when forming an aggregate, like individual objects. They are contextual, meaning that they always have properties that are not definite.

All these characteristics that orthodox quantum mechanics ascribes to quantum systems constitute an obstacle to the time-average strategy. The idea that the electron density  $\rho(\mathbf{r})$  represents a kind of mean value of the definite positions occupied by the electron in its motion around the nucleus requires conceiving electrons as particles with individuality and defined

trajectories, an ontological picture that is challenged by the quantum theory.

## 6.- A Bohmian ontology for quantum chemistry

If, in the framework of orthodox quantum mechanics, the average strategies face the problem that quantum systems are not individual particles, then perhaps the way out is to change the theoretical framework. The natural choice for the framework change is Bohmian Mechanics (BM, see de Broglie 1928, Bohm 1952; in its contemporary version, Dürr, Goldstein, and Zanghì 2013), according to which quantum systems are particles of the same nature as classical ones: particles always have definite positions and velocities and, therefore, also definite trajectories. From the Bohmian perspective, then, probabilities are not objective, but only express the ignorance of the observer about the definite positions of the particles. Perhaps the fact that this ontological picture is more akin to the chemist's way of thinking partially explains a certain revival of the interest in BM since the 1980s for the description of atoms and molecules.

### 6.1.- The standard application of BM to atoms and molecules

In the Bohmian formalism, the motion of a quantum particle is determined by its wavefunction  $\psi(\mathbf{x}, t)$ :

$$\psi(\mathbf{x}, t) = R(\mathbf{x}, t) e^{iS(\mathbf{x}, t)/\hbar}, \quad (4)$$

where  $R$  is the amplitude and  $S$  is the phase of the wavefunction and both are real-valued. Then, the momentum is computed as

$$\mathbf{p} = \nabla S. \quad (5)$$

In the description of the 1s state of the electron in a hydrogen atom, eq. (5) predicts that, since  $\nabla S = 0$ , the electron remains at rest. Although the exact position of the electron cannot be computed because the initial condition is unknown, the distance between the electron and the proton can be calculated and the result is that such a distance is equal to the Bohr radius (see Holland 1993: 148). In turn, when the  $\sigma$  bonding orbital of the hydrogen molecule is described with BM, calculations show that the electrons remain at rest in the region close to the middle point of the line joining the two nuclei (see Holland 1993: 319). Surprisingly, BM offers a picture of the chemical bond similar to the Lewis bond, but in the present case on the basis of a fully articulated physical theory and of detailed computations (see Fortin, Lombardi, and Martínez González 2017).

David Bohm himself explained, in his original works on his proposal (Bohm 1952, 1953), how the electron density arises on the basis of this ontological image. In order to obtain the electron density of, for instance, a hydrogen atom in its ground state it is necessary to perform many measurements of the electron position in one of the two following situations. In one

situation, the measurement is repeated on the same atom in such a way that each interaction necessarily perturbs the position of the electron which, in the following measurement, will be in a new initial condition, different from the original one. In the other situation, a measurement is made on an ensemble of atoms, all of them in the same quantum state but whose electrons are initially in different positions. In both cases, the distribution of positions yields the same electron density as in the orthodox calculations, which is not surprising since orthodox quantum mechanics and BM are empirically equivalent. However, according to the Bohmian ontological picture, the electron density of an atom or a molecule can be meaningfully interpreted as the average of the electrons' definite positions for different initial conditions, in a way that is reconcilable with the way quantum chemists conceive their ontology. Moreover, the quantum probability involved in the concept of electron density has the same status as the probability in classical statistical mechanics: it measures ignorance about the precise configuration of the particles.

## 6.2.- The role of spin in BM

Despite the interesting results obtained in the application of BM to chemistry, the image of electrons at rest in atoms and molecules looks strange to the eyes of certain chemists, who are used to thinking of electrons as “orbiting” around nuclei. This difficulty has been tackled by some more recent applications of BM, which provide results that are more familiar, and even more useful, for chemists.

Peter Holland (1999), strong advocate of the BM, pointed out that eq. (5) is valid only for spin-0 particles. However, for particles with spin, the condition of Lorentz covariance of the Schrödinger law of motion implies that the momentum of a particle of spin  $s$  is given by

$$\mathbf{p} = \nabla S + \nabla \rho \times \mathbf{s}, \quad (6)$$

where  $\rho = \psi^* \psi$ . On the basis of this idea, Caroline Colijn and Edward Vrscaj (2003a) computed the trajectories of the electron of the hydrogen atom in different energy eigenstates by taking into account the spin. The authors prove that the momentum of the electron is perpendicular to the direction of the steepest increase of  $\rho$  and, then, its trajectories lie in the level surfaces of  $\rho$ . On the other hand, the momentum of the electron is also perpendicular to the direction of the spin, say,  $z$ . Therefore, the shape of the Bohmian trajectories of the electron can be obtained from the intersection between the level surfaces of  $\rho$  and the planes of constant  $z$ . This analysis allows Colijn and Vrscaj to conclude that the Bohmian trajectories are circular orbits about the direction of the spin in orbitals 1s and 2s and periodic orbits for 2p orbitals. Moreover, by numerically integrating the trajectories corresponding to the wavefunction  $\psi_{2p_x}$  for several initial conditions in the  $xz$ -plane, the authors also show a good qualitative agreement between these trajectories and the shapes of the  $2p_x$  orbitals as usually depicted in textbooks. In a second part of their paper, they also describe the

trajectories of the electron of the hydrogen atom when the wavefunction is a linear combination of  $1s$  and  $2p_0$  eigenstates evolving in time under the atom's Hamiltonian. From a chemical viewpoint, this work offers an internal detail of what an electron does within an orbital resulting from an  $sp$  hybridization.

Following the strategy of considering the spin of the electron, in a second paper Colijn and Vrscay (2003b) compute the trajectory of the electron of the hydrogen atom when it undergoes the transition from state  $1s$  to state  $2p_0$  as the result of the action of an oscillating electron field. More recently, and as an explicit continuation of the just mentioned works, Jeff Timko and Vrscay (2009) obtain the Bohmian trajectories for the two electrons of a helium atom.

Independently of their technical details, these works reveal that BM provides chemists with a picture that agrees with the way in which they conceptualize their object of study (see Fortin and Lombardi 2024). BM describes electrons that not only orbit around nuclei, but move in a definite way as they make transitions to higher energy states. Those processes, which can only be described in probabilistic terms in orthodox quantum mechanics, in the Bohmian framework acquire a space-time representation that facilitates chemists' conceptual understanding. And, regarding the problem of how the concept of electron density can be understood, from the Bohmian viewpoint there is no conceptual obstacle to conceive the electron density as an average over the positions of point particles with definite trajectories.

### **6.3.- Other Bohmian variants**

In a recent paper primarily directed to physicists, Charles Sebens (2021) addresses the issue of the interpretation of the electron density. There he mentions two variants of Bohm's ideas, which would make it possible to keep particles in the ontology and, thus, to conceive of electron density in average terms.

As mentioned above, Gao (2018) adopts the time-average strategy and appeals to ergodicity to explain the physical origin of the electron density conceived as a charge density. He bases his position on the assumption that electrons are particles with definite positions. However, instead of accepting the Bohmian picture of continuous and deterministic trajectories, he rescues Bohr's idea of quantum jumps and proposes that electrons move in a discontinuous and indeterministic way:

*“It turns out that microscopic particles such as electrons are indeed particles, but their motion is never continuous but always discontinuous and random. Moreover, the wave function represents the state of random discontinuous motion of particles”* (Gao 2015: 146).

According to Gao, his view has the advantage that it is not necessary to wait a finite time

interval to the ergodic motion of the electrons lead to the charge density corresponding to the electron density: with random jumps, the correct probability density and charge density obtain at an infinitesimal interval about each time.

Sebens, in turn, proposes what he calls “Newtonian quantum mechanics” (Sebens 2015), which lies somewhere in between Bohmian Mechanics and the Many Worlds Interpretation: it also retains the concept of particle with definite position but combines it with a multiplicity of worlds. According to this view, there are many worlds such that in each of them particles have precise locations:

*“Particles feel ordinary classical forces (such as electrostatic attraction and repulsion) from other particles in the same world and quantum forces from interactions between worlds.”* (Sebens 2021: 32)

According to this view, the electron density turns out to be a charge density across the worlds. For instance, a hydrogen atom has copies in the different worlds. In each one of them, the electron is placed in a different position. But the distribution of positions across the worlds is such that it leads to a charge density that agrees with the standard electron density of the hydrogen atom. In other words, the charge density is not distributed in each world, but it is concentrated in the electron’s position; but the electron density can still be interpreted as a distributed charge density across the worlds.

## **7.- Coda: A new ontology for quantum chemistry?**

Let us recapitulate. It is an undoubted fact that electron density is a central observable magnitude of quantum chemistry. However, although there is no disagreement about how to calculate it, there are two possible interpretations of the concept: the Bohr-style PDI, which is used explicitly in physics, and the Schrödinger-style CDI, to which quantum chemists implicitly appeal. As has been pointed out, adopting the CDI so that the electron density represents a true matter field brings several difficulties in the light of quantum mechanics. Therefore, different average strategies are used in the attempt to make both interpretations compatible. But these strategies require conceiving electrons as point particles, an ontological picture at odds with quantum mechanics in most of its versions. For this reason appealing to BM in some of its variants seems reasonable.

What has not been said so far is that all these problems are the result of the attempt to explain the quantum-chemical picture of the electron density as a matter field (the Schrödinger-style CDI) in terms of the quantum-physical picture of the electron density as a mathematical field (the Bohr-style PDI). This attempt is based on the assumption that chemistry must be explainable in terms of physics: charge density arises as some kind of average over quantities

proper to the underlying physical level. The requirement that chemistry “must be explainable” hides a reductionist assumption according to which the entities of chemistry are nothing more than very complex physical entities. From this reductionist perspective, quantum mechanics is the fundamental theory that should be able to explain in principle all chemistry, as Dirac claimed in his famous dictum:

*“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry [are] completely known from quantum mechanics”* (Dirac 1929: 714).

For this reason, from this reductionist standpoint, if difficulties are found in the attempt to reduce, say, the electron density to the ontology of quantum mechanics, perhaps it is necessary to review the theory that describes the underlying fundamental level, as Gao and Sebens propose.

The question is why this assumption, which has already been challenged from different perspectives, should be uncritically accepted. Somebody might claim that the electron density is an item belonging to the quantum ontology, which emerges from the underlying quantum-mechanical domain but cannot be reduced to it (Matta et al. 2020, Lombardi and Matta 2022; for a defense of the emergence of molecular chemistry from a more general point of view, see Hendry 2010). Or one can also adopt a pluralist position, according to which the ontological priority of the physical world turns out to be a mere metaphysical prejudice: concepts like electron density, bonding, and molecular structure refer to items belonging to the chemical ontology, which only depends on the theory that constitutes it (see Lombardi and Labarca 2005, 2006, Lombardi 2015).

Whichever anti-reductionist alternative is adopted, in both cases it is admitted that quantum chemistry has its own ontology. From this perspective, and independently of the formal proposal embodied in the QTAIM, Bader’s insistence on considering the electron density as the fundamental quantity of quantum chemistry would make sense. The fact that the electron density can be defined in terms of the wave function does not mean that it is just a quantum concept. The term ‘electron density’ refers to a charge density that emerges from the quantum domain but is not reduced to it and, as a consequence, preserves its ontological autonomy. Or, from a pluralistic perspective, the charge density referred to by that term belongs to the ontological domain of chemistry; it does not owe its existence to an ontologically more fundamental level of reality, but to the fact that it is an essential ingredient of theories with immense predictive and creative power.

In summary, we consider the anti-reductionist philosophical stance to be the most fruitful for quantum chemists in their daily theoretical and experimental practice. For that reason, this paper can be read as a plea in favor of a specific ontology for quantum chemistry, free from the constraints imposed by quantum mechanics in its different versions.

## References

- Allori, V., Goldstein, S., Tumulka, R., and Zanghì, N. (2011). “Many worlds and Schrödinger’s first quantum theory”. *The British Journal for the Philosophy of Science*, **62**: 1-27.
- Allori, V., Goldstein, S., Tumulka, R., and Zanghì, N. (2014). “Predictions and primitive ontology in quantum foundations: A study of examples”. *The British Journal for the Philosophy of Science*, **65**: 323-352.
- Bader, R. F. W. and Matta, C. F. (2013). “Atoms in molecules as non-overlapping, bounded, space-filling open quantum systems”. *Foundations of Chemistry*, **15**: 253-276.
- Bader, R. F. W. and Zou, P. F. (1992). “An atomic population as the expectation value of a quantum observable”. *Chemical Physics Letters*, **191**: 54-58.
- Bohm, D. (1952). “A suggested interpretation of the quantum theory in terms of ‘hidden’ variables”. *Physical Review*, **85**: 166-179, 180-193.
- Bohm, D. (1953). “Proof that probability density approaches  $|\psi|^2$  in causal interpretation of the quantum theory”. *Physical Review*, **89**: 458-466.
- Colijn, C. and Vrscay, E. R. (2003a). “Spin-dependent Bohm trajectories associated with an electronic transition in hydrogen”. *Journal of Physics A*, **36**: 4689-4702.
- Colijn, C. and Vrscay, E. R. (2003b). “Spin-dependent Bohm trajectories for Pauli and Dirac eigenstates of hydrogen”. *Foundations of Physics Letters*, **16**: 303-323.
- de Broglie, L. (1928). “La nouvelle dynamique des quanta”. Pp. 105-132 in *Electrons et photons. Rapports et discussions du cinquième Conseil de Physique tenu à Bruxelles du 24 au 29 octobre 1927 sous les auspices de l’Institut International de Physique Solvay*. Paris: Gauthier-Villars. English translation: (2009), pp. 341-371 in G. Bacciagaluppi and A. Valentini (eds.), *Quantum Theory at the Crossroads. Reconsidering the 1927 Solvay Conference*. Cambridge: Cambridge University Press.
- Dirac, P. A. M. (1929). “Quantum mechanics of many-electron systems”. *Proceedings of the Royal Society A*, **338**: 714-733.
- Dürr, D., Goldstein, S., and Zanghì, N. (2013). *Quantum Physics without Quantum Philosophy*. Berlin: Springer.
- Fortin, S. and Lombardi, O. (2024). “Bohmian Mechanics for quantum chemistry”. In Andrea Oldofredi (ed.), *Guiding Waves in Quantum Mechanics*, Oxford: Oxford University Press, forthcoming.
- Fortin, S., Lombardi, O., and Martínez González, J. C. (2017). “The relationship between chemistry and physics from the perspective of Bohmian mechanics”. *Foundations of Chemistry*, **19**: 43-59.

- French, S. (2019). "Identity and individuality in quantum theory". In E. N. Zalta (ed.), *The Stanford Encyclopedia of Philosophy* (Winter 2019 Edition), URL = <https://plato.stanford.edu/archives/win2019/entries/qt-idind/>.
- Gao, S. (2015). "How do electrons move in atoms? From the Bohr model to quantum mechanics". Pp. 450-464 in F. Aaserud and H. Kragh (eds.), *One Hundred Years of the Bohr Atom*. Copenhagen: Scientia Danica.
- Gao, S. (2018). "Is an electron a charge cloud? A reexamination of Schrödinger's charge density hypothesis". *Foundations of Science*, **23**: 145-157.
- Ghirardi, G-C. and Bassi, A. (2020). "Collapse theories". In E. N. Zalta (ed.), *The Stanford Encyclopedia of Philosophy* (Summer 2020 Edition), URL = <https://plato.stanford.edu/archives/sum2020/entries/qm-collapse/>.
- Healey, R. and Gomes, H. (2022). "Holism and nonseparability in physics". In E. N. Zalta and U. Nodelman (eds.), *The Stanford Encyclopedia of Philosophy* (Winter 2022 Edition), URL = <https://plato.stanford.edu/archives/win2022/entries/physics-holism/>.
- Hendry, R. F. (2010). "Ontological reduction and molecular structure". *Studies in History and Philosophy of Modern Physics*, **41**: 183-191.
- Holland, P. (1993). *Quantum Theory of Motion*. Cambridge: Cambridge University Press.
- Holland, P. (1999). "Uniqueness of paths in quantum mechanics". *Physical Review A*, **60**: 4326-4330.
- Kochen, S. and Specker, E. (1967). "The problem of hidden variables in quantum mechanics." *Journal of Mathematics and Mechanics*, **17**: 59-87.
- Levine, I. N. (2014). *Quantum Chemistry*. Boston: Pearson, 7th edition.
- Lombardi, O. (2015). "The ontological autonomy of the chemical world: facing the criticisms". Pp. 23-38 in E. Scerri and L. McIntyre (eds.), *Philosophy of Chemistry: Growth of a New Discipline* (Boston Studies in the Philosophy and History of Science). Dordrecht: Springer.
- Lombardi, O. (2023). "Not individuals, nor even objects: On the ontological nature of quantum systems". Pp. 45-77 in J. R. B. Arenhart and R. W. Arroyo (eds.), *Non-Reflexive Logics, Non-Individuals, and the Philosophy of Quantum Mechanics*. Cham: Springer, Synthese Library.
- Lombardi, O. and Labarca, M. (2005). "The ontological autonomy of the chemical world". *Foundations of Chemistry*, **7**: 125-148.
- Lombardi, O. and Labarca, M. (2006). "The ontological autonomy of the chemical world: A response to Needham". *Foundations of Chemistry*, **8**: 81-92.
- Lombardi, O. and Matta, C. (2022). "Coarse-graining and the Quantum Theory of Atoms in Molecules". Pp. 217-241 in O. Lombardi, J. C. Martínez González, and S. Fortin (eds.), *Philosophical Perspectives in Quantum Chemistry*. Synthese Library, Cham: Springer.
- Martínez González, J. C., Fortin, S., and Lombardi, O. (2019). "Why molecular structure cannot be strictly reduced to quantum mechanics". *Foundations of Chemistry*, **21**: 31-45.
- Matta, C., Lombardi, O., and Jaimes Arriaga, J. (2020). "Two-step emergence: The Quantum Theory of Atoms in Molecules as a bridge between quantum mechanics and molecular chemistry". *Foundations of Chemistry*, **22**: 107-129.



- Nelson, P. (1990). "How do electrons get across nodes?". *Journal of Chemical Education*, **67**: 643-647.
- Pauling, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell University Press (first edition 1939).
- Schrödinger, E. (1926a). "Quatisierung als Eigenwertproblem (Vierte mitteilung)". *Annalen der Physik*, **81**: 437-490. English translation in E. Schrödinger, *Collected Papers on Wave Mechanics*, 1928. London and Glasgow: Blackie & Son Limited.
- Schrödinger, E. (1926b). "An undulatory theory of the mechanics of atoms and molecules". *Physical Review*, **28**: 1049-1070.
- Sebens, C. T. (2015). "Quantum mechanics as classical physics". *Philosophy of Science*, **82**: 266-291.
- Sebens, C. (2021). "Electron charge density: a clue from quantum chemistry for quantum foundations". *Foundations of Physics*, **51**: #75.
- Szabo, A. and Ostlund, N. S. (1989). *Modern Quantum Chemistry*. New York: McGraw-Hill.
- Timko, J. A. and Vrscay, E. R. (2009). "Spin-dependent Bohmian electronic trajectories for helium". *Foundations of Physics*, **39**: 1055-1071.
- Vaidman, L. (2021). "Many-Worlds Interpretation of quantum mechanics". In Edward N. Zalta (ed.), *The Stanford Encyclopedia of Philosophy* (Fall 2021 Edition), URL = <https://plato.stanford.edu/archives/fall2021/entries/qm-manyworlds/>.