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Foundations and applications of the orbital theory in chemistry: A philosophical perspective

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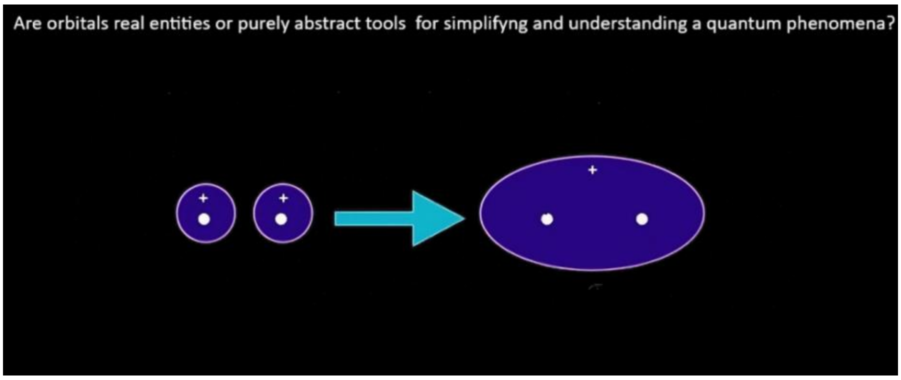
Abstract

The concept of atomic and molecular orbitals has been a fundamental pillar in modern chemistry, shedding light on the structures and reactivity of chemical compounds. This article examines the evolution and significance of orbital theory, its applications in chemistry, and the ongoing debate about the existence of orbitals from both physics and chemistry perspectives. Philosophical aspects related to the ontology of orbitals are explored, emphasizing the complex interplay between mathematical abstractions and tangible reality. The multifaceted nature of orbitals, their role in quantum mechanics, and their implications for understanding the quantum realm are discussed. While the debate surrounding the ontological status of orbitals remains ongoing, it highlights the profound nature of inquiries into the fundamental essence of reality. This exploration underscores the significance of continuous research and discourse in advancing our understanding of these fundamental constituents of the quantum world.



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Highlights

- Concepts of atomic and molecular orbitals are foundational in modern chemistry.
- The orbital theory evolution and significance are crucial to understanding chemistry.
- The intricate mathematical abstraction and tangible reality balance are explored.
- The orbitals' multifaceted nature and significance in quantum mechanics are discussed.
- The existence of orbitals in physics and chemists' perspectives is addressed.

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1. Introduction

Indisputably, the introduction of a theory aimed at elucidating atomic and molecular orbitals has sparked a profound revolution in modern chemistry. This groundbreaking concept has granted us a deeper understanding of the intricate structures and reactivity patterns inherent to atoms and chemical compounds (Levine, 2017; Pauling, 1931; Smith and March, 2006). In the current chemistry landscape, the distribution of electrons within these orbitals governs the physical and chemical attributes of compounds, including their geometric arrangements, polarity, and bond energies. Scientific inquiry, particularly in the disciplines of quantum chemistry and physics, regards orbitals as a subject of perpetual discourse, offering varied perspectives that fuel ongoing debates (Bader, 1990; Ogilvie, 1990; McWeeny, 2002; Shaik and Hiberty, 2008). These mathematical representations play a fundamental role in facilitating our understanding of the microcosmic architecture and dynamic behavior of matter.

For example, Pauling (1931) introduced the Valence Bond Theory, which brought forth the innovative concept of orbital hybridization to elucidate the geometries of molecules and the intricacies of chemical bonding. Subsequently, in the 1950s, the Crystal Field Theory provided insights into the phenomena of coloration and magnetic properties within transition compounds (Levine, 2017; Smith and March, 2006). It becomes unmistakable that the theory of atomic and molecular orbitals is a cornerstone of modern chemistry, bestowing upon us the ability to unravel the structural intricacies and reactivity patterns of chemical compounds at the microscopic scale.

Orbitals may be succinctly defined as localized regions surrounding an atom or molecule, within which the likelihood of containing one or more electrons is notably high (Bader, 1990; Ogilvie, 1990; Pauling, 1931; Levine, 2017; McWeeny, 2002; Shaik and Hiberty, 2008; Smith and March, 2006). Within the realm of quantum chemistry, an orbital is a mathematical and spatial representation of the likelihood of encountering one or more electrons in the vicinity of an atomic nucleus or an assembly of nuclei within a molecule. These structures are derived from the equations of quantum mechanics and delineate not only the electrons' location but also their energy and angular momentum.

In simpler terms, an orbital takes the form of a three-dimensional nebula enveloping an atomic nucleus or a cluster of nuclei, demarcating the realm where the presence of an electron is astoundingly probable. Each orbital possesses a unique configuration and orientation, orchestrating the symphony of electron distribution in the spatial expanse around the nucleus. Orbitals are categorized into types such as s and p orbitals, each with distinctive shapes and used to describe the spatial distribution of electrons across varying energy levels and sublevels of an atom.

It is imperative to understand that orbitals do not represent precise trajectories or orbital pathways for electrons, as envisioned in the older Bohr atomic model. Instead, they depict territories where the likelihood of encountering an electron is elevated, and pinpointing the exact location of an electron within an orbital is a conundrum due to the probabilistic nature of quantum mechanics. Orbitals form the bedrock of comprehending the electronic architecture of atoms and molecules in contemporary chemistry.

In recent years, chemistry has witnessed significant progress, thanks to the emergence of Electron Density Theory, known as Density Functional Theory (DFT) (Parr and Yang, 1989; Sordo, 2014). DFT has become an indispensable tool for chemists, enabling the simulation and analysis of intricate molecular systems at the subatomic level. This theory pivots on the distribution of electron density within a molecular environment, granting the power to predict reactivity patterns and the architectural traits of chemical compounds. DFT harmoniously complements the concept of orbitals, which chronicles the spatial likelihood of finding electrons within atoms and molecules. In essence, DFT elevates the foundational concepts of orbitals and electron distribution to new heights. Through DFT, scientists gain a profound understanding of electron density, enabling predictions of not only the electrons' locations but also their behavior within molecular landscapes. This revelation bears significant weight in unraveling the intricacies of chemical reactions, molecular bonds, and the electronic characteristics of diverse substances. Together, orbitals and DFT have revolutionized the way chemists apprehend and manipulate matter at the atomic and molecular level. Their alliance empowers us to forge groundbreaking materials, forecast reaction mechanisms, and optimize chemical processes with unparalleled precision. This marriage of theoretical and computational instruments has opened new vistas in the exploration of the microscopic world of chemistry, infusing excitement into this dynamic and promising field, rich with potential for further discoveries and innovations.

On a broader scale, the prevailing definition of orbital posits that these entities fundamentally arise from solutions to Schrödinger's equation for the hydrogen atom, resulting in a set of wave functions. This definition enjoys a unanimous consensus within the scientific community and stands as a testament to its remarkable precision. Notably, Schrödinger referred to these functions, particularly when they exist independently of time, as amplitude rather than wave functions (Schrödinger, 1926).

At its core, it is imperative to understand that orbitals are fundamentally mathematical abstractions closely intertwined with the realm of quantum chemistry. These abstract constructs lack direct, observable attributes, establishing a foundational concept that every chemist must firmly grasp. However, this concept delves deep into philosophical realms, prompting a fundamental question: do orbitals represent genuine, objective entities, existing independently of our powers of observation and mathematical modeling, or are they purely abstract tools utilized to simplify and fathom quantum phenomena? This inquiry navigates the intricate intersection of metaphysics and quantum theory, emphasizing the enduring philosophical enigma woven into the fabric of orbitals.

Furthermore, the significance of orbitals transcends mere philosophical contemplation. In the domain of chemistry, the theory of molecular orbitals assumes a vital role, elucidating the stability and reactivity of organic and inorganic compounds. It also provides insights into the intricacies of regioselectivity and stereoselectivity in chemical reactions (Atkins, 2010; Kaskel, 2016; Smith and March, 2006). This holistic comprehension, rooted in the theory of orbitals, empowers chemists to unlock the mysteries of chemical compound structures and reactivity. It serves as the foundation for the design and synthesis of innovative materials, enriched with enhanced properties. Notably, it underpins the creation of molecular catalysts, enabling selective and efficient chemical reactions, all based on a profound understanding of electronic structure and its intricate interaction with chemical reactivity. This narrative underscores how orbitals move beyond philosophical musings to become indispensable tools shaping the world of chemistry (Armarego, 2003; Fujiwara, 2009; Vivas-Reyes, 2008).

Since the introduction of orbital theory, it has evolved and refined, giving rise to various tools and concepts that have transformed chemistry as a discipline. This evolution is evident in the textbooks in the field of chemistry, emphasizing the utilization of orbitals and the theories that underpin them (Atkins, 2010;

Levine, 2017; Kaskel, 2016; Smith and March, 2006). Undoubtedly, these recent advances in electron density theory and the simulation of complex molecular systems have opened new possibilities for the design and synthesis of materials with specific properties and for understanding fundamental chemical processes (Burke, 2012; Frisch et sl., 2016; Popelier, 2000).

However, despite the apparent usefulness of the orbital concept in chemistry, it remains a subject of controversy. Its applications sometimes vary, leading to differing interpretations. Some view orbitals as purely mathematical constructs arising from the solution of the Schrödinger equation. From this standpoint, orbitals are not seen as tangible entities in the physical world; instead, they serve as abstract tools for explaining the properties of atoms and molecules in different contexts. This contrast will be thoroughly examined in this text (Boys, 1950; Scerri, 2000a; Scerri, 2006).

2. Fundamentals of orbital theory

This section explores the foundational principles of atomic and molecular orbitals, elucidating their origins and intricate relationship with the electronic structure of atoms and molecules. Orbital theory constitutes a cornerstone in the realm of chemistry, facilitating a precise comprehension of the structures and properties of atoms and molecules (Bader, 1990; McQuarrie, 2008). Each orbital is defined by a set of quantum numbers that convey information about its energy, shape, and spatial orientation. Orbitals are categorized into sublevels s, p, d, and f based on their energy levels and shapes, and each sublevel corresponds to different values of quantum numbers, determining the maximum number of electrons that a particular orbital can accommodate (Levine, 2017; Shaik and Hiberty, 2008).

Molecular Orbitals emerge through the amalgamation of atomic orbitals stemming from the constituent atoms of a molecule. Electrons within molecular orbitals interact with one another, giving rise to molecular properties like structure, polarity, and chemical reactivity (Szabo, 1996).

The theory of orbitals originated from quantum mechanics, a fundamental theory of physics that describes the behavior of subatomic particles such as electrons. Quantum mechanics allows for the calculation of electron properties in orbitals, such as their energy and position, and predicts how these properties affect the structure and properties of atoms and molecules. The electronic structure of atoms and molecules is closely related to orbitals. Atoms with a complete electron configuration in their outermost orbitals are more stable and less reactive than atoms with unpaired electrons in their outermost orbitals. Similarly, the electronic structure of molecules determines their physical and chemical properties. Quantum mechanics is the fundamental theory that enables the calculation of electron properties in orbitals and predicts how these properties affect the structure and properties of atoms and molecules. Furthermore, orbital theory is essential in fields such as organic chemistry, inorganic chemistry, biochemistry, and materials chemistry, as it allows us to understand the properties and reactivities of molecules in these fields (Bader, 1990; Ogilvie, 1990; McQuarrie, 2008; Szabo, 1996).

Orbital theory has played an essential role in our understanding of the electronic structure of atoms and molecules. However, a contentious debate lingers regarding the existence and significance of orbitals in the domains of physics and chemistry, sparking ongoing discussions within the scientific community (Bensaude-Vincent, 2008; Labarca, 2010; Scerri, 2000a; Scerri, 2004). From some scientific perspectives, orbitals are seen as purely mathematical constructs, emerging as solutions to the Schrödinger equation, and not possessing a concrete presence in the physical world. They are abstract tools used to describe the properties of atoms and molecules. In the eyes of physicists, orbitals serve as valuable mathematical abstractions for unravelling electronic structures but should not be considered as actual physical entities (Perdew, 2001).

In stark contrast, chemists argue that orbitals are more than mere mathematical constructs. To them, orbitals are tangible entities with a real presence, and they view orbitals as indispensable tools for comprehending chemistry from a quantum perspective. Chemists see orbitals as actual components that enable the understanding of molecular structure and chemical properties (M. Morrison, 2006; Lombardi, 2005).

The divergence of opinion among some scientists has sparked extensive debates within the scientific community. Philosophers of chemistry, such as Scerri, suggest that the dispute regarding orbitals highlights a deeper contention between the realms of physics and chemistry regarding the role of mathematics in representing physical reality. According to Scerri, chemistry maintains its distinct identity, separate from physics, and this distinctiveness becomes evident in its approach to comprehending chemical phenomena in the context of molecular structure, reactivity, and physical characteristics (Scerri, 2004; Scerri, 2006; Van Brakel, 1999).

In the pursuit of a deeper understanding of modern chemistry, orbital theory has been recognized as an essential tool. By elucidating the electronic structure of atoms and molecules, this theory allows us to discern the chemical properties inherent to them. Quantum chemistry and the orbital approximation are being examined for their alignment with either a realistic or anti-realistic viewpoint concerning theoretical terms (Scerri, 2000a). This ongoing debate underscores the intricacy of the relationship between the abstract realm of mathematics and the tangible world of chemical reality (Bruice, 2017; Klein, 2017; R. Morrison, 1987; Vivas-Reyes, 2009).

The evolution of the Pauli Principle provides a concrete example of the ongoing debate regarding orbitals. Initially, this principle dictated that no two electrons within an atom or molecule could possess identical sets of four quantum numbers. However, this principle transformed when it was generalized to assert that the wave function for a system of fermions becomes anti-symmetric upon the interchange of any two electrons. Consequently, the traditional interpretation of the Pauli Principle, which assigned four quantum numbers to individual electrons, became obsolete. As Scerri affirms, this transformation led to the emergence of the concept known as the ‘orbital fallacy.’ In essence, it is no longer valid to claim the physical existence of atomic orbitals in systems with multiple electrons, except for one-electron systems. Many-electron orbitals are now regarded as ontologically redundant (Scerri, 2000b).

Despite the philosophical questions surrounding the existence of orbitals, their use remains fundamental in the practice of chemistry at all levels. The tension between the foundational status of orbitals and their continued utility in chemistry poses a philosophical dilemma that recent studies have begun to address. Quantum chemistry and the orbital approximation are being examined for their alignment with either a realistic or anti-realistic viewpoint concerning theoretical terms (Scerri, 2000b). This ongoing debate underscores the intricacy of the relationship between the abstract realm of mathematics and the tangible world of chemical reality.

3. Ontology of Orbitals

The debate surrounding the existence of atomic and molecular orbitals within the realm of the philosophy of chemistry is an intellectually captivating topic that delves deep into fundamental questions about the very nature of reality. Philosophers find themselves divided on whether orbitals represent actual ontological entities or are simply valuable mathematical tools employed to describe the behavior of electrons (Mulder, 2011, Perdew, 2001; Scerri, 2001).

To grasp the depth of this issue, it is crucial to differentiate between ontology, which concerns itself with the nature of reality in its essence, and ontics, which deals with the specific objects and entities within that reality. In the context of atomic orbitals, the debate primarily revolves around ontics, aiming to ascertain whether orbitals possess a genuine existence. Some proponents argue fervently that they do indeed exist as integral components of atomic structure, while others view them as mathematical constructs, akin to numbers or equations, contingent on our human representation (van Brakel,1999, van Brakel, 2000; Esfeld, 2013; Ladyman et al., 2007).

This ongoing philosophical discourse primarily centers on the challenge of directly observing orbitals through empirical experiments. While they may lack a tangible physical existence, their utility lies in elucidating the intricate behavior of electrons. What can be empirically observed is the electron density distribution, a tangible representation of the likelihood of encountering electrons in specific regions of space. This empirical observation forms the foundational basis for the descriptions and explanations of orbitals (Esfeld, 2013; van Brakel, 2000).

This philosophical discourse underscores the intricate and multifaceted nature of the topic, carrying profound implications not only for theoretical physics but also for practical applications in the field of chemistry. The question of whether orbitals exist as tangible physical entities or remain as valuable abstractions persists as a dynamic and ongoing philosophical debate that has yet to find a definitive resolution. However, irrespective of this debate, orbitals continue to play an irreplaceable and pivotal role in chemistry, serving as indispensable tools in both theoretical and practical contexts. This expanded version further explores the philosophical aspects of the debate regarding the existence of atomic and molecular orbitals.

4. Development and challenges in the interpretation of orbitals in chemistry

Unifying the profound role of orbitals in understanding complex systems is essential. Additionally, it is crucial to emphasize the concept of “perspective” when rationalizing these systems through phenomenological models, as chemistry and physics converge in adopting first-principles-based approaches, as evident in the prominence of orbital theory in modern textbooks on organic and inorganic chemistry.

Throughout this text, we have consistently emphasized that orbitals are foundational concepts, serving as essential instruments for describing and manipulating the structures, properties, and processes of actual molecules, crystals, and a variety of other systems. The characterization of orbitals is influenced by the intrinsic nature of molecules and the specific aspects that researchers aim to highlight through experimental investigations and theoretical analyses. (Schwarz, 2006)

Moreover, it is worth noting that many interpretations related to the concept of orbitals often arise due to a “lack of familiarity with the concept” rather than implying philosophical problems or adherence to a specific philosophy of thought. Many scientists may employ this concept without delving into its meaning in detail. Linus Pauling, a pioneer in these matters, provides a notable example by interpreting linear combinations of atomic orbitals (LCAO) while considering the most significant coefficients of the wave function. This approach led to the development of a coherent, understandable, and applicable model for the common chemist of the time, which constituted a significant success. The widespread use of hybridization persists and is successfully applied today, as evidenced in the case of the tetra valence of carbon, which was successfully explained using concepts from Valence Bond Theory (Chen, 2023; Lamoureux and Ogilvie, 2021).

In general terms, chemistry has approached the concept of orbitals qualitatively. Through this perspective, models have been developed to facilitate the understanding and modelling of chemical reactions and other concepts. Some concepts such as electronegativity and their correlated properties have been successfully integrated into a quantum framework. Similarly, non-linear reactions, which often pose challenges for mathematical interpretation outside the linear region, allow for a reasonable appreciation from a qualitative point of view. In the context of discussions about orbitals, the chemical perspective is associated qualitatively with the most significant LCAO coefficient, as evident in resonance studies described by the straightforward Hückel theory (Pauling, 1931).

Paradoxically, obtaining quantum results with extremely precise chemical resolution poses an intriguing challenge in interpreting the individual terms used in the Linear Combination of Atomic Orbitals (LCAO) approach. This approach involves a comprehensive qualitative description combined with a rigorous mathematical solution obtained through a specific methodology. However, one of the most notable challenges is the generation of multiple dissociated descriptions, particularly in complex chemical systems. When applying this approach, several different models or explanations that seem valid for specific aspects of these systems can be obtained. Each of these descriptions sheds light on certain specific aspects, but collectively, they fail to consolidate into a coherent and comprehensive theory. This fragmentation is evident in the procedures applied in organic chemistry, where rules are established for specific homologous molecules based on the highest LCAO coefficients, although these rules accumulate numerous exceptions. The central issue lies in determining the point of reasonableness in these fragmented descriptions (Chen, 2023; Lamoureux and Ogilvie, 2021; Schwarz, 2006).

Undoubtedly, chemistry is a highly complex discipline, and chemical thinking has proven capable of anticipating results described by equally complex theories. Therefore, the chemical perspective must remain in constant evolution. These points represent areas that the author could consider developing in greater depth.

5. Conclusions

The theory of atomic and molecular orbitals holds a central place in modern chemistry, bearing paramount significance. These electron distributions, essential in shaping the physical and chemical characteristics of compounds, including geometry, polarity, and bond energy, are pivotal from chemists’ perspectives. The introduction of Density Functional Theory (DFT) has significantly advanced the simulation and in-depth analysis of complex molecular systems at the atomic level.

Moreover, the indispensable role of orbitals in chemistry is beyond dispute. Molecular orbital theory elucidates the stability and reactivity of organic compounds, as well as the regioselectivity and stereoselectivity of chemical reactions. The profound contributions of orbital theory have not only revolutionized the field of chemistry but have also played a key role in innovating and synthesizing novel materials with enhanced properties.

The ongoing debate surrounding the existence of orbitals underscores a profound schism in the perspectives of physicists and chemists concerning the role of mathematics in elucidating the physical world. Physicists regard orbitals as valuable mathematical abstractions, whereas chemists deem them as fundamental instruments for comprehending molecular structure and properties. Despite this enduring disparity, orbital theory remains an indispensable cornerstone of modern chemistry, exerting its influence across diverse domains within the field. In the eloquent words of Hückel, "Today, we possess a map, and that map is quantum mechanics."

From a more quantitative and mathematical perspective, some scientists argue that orbitals offer a valuable representation of a quantum system's wave function. From this perspective, orbitals provide a precise mathematical exposition of the probability distribution for electron localization across diverse spatial regions. In this framework, orbitals emerge as an indispensable mathematical reality, essential for accurately predicting subatomic particle behavior.

The discourse on the ontological existence of atomic and molecular orbitals remains a complex and captivating issue within the philosophy of chemistry. Some argue for their real ontological existence, while others view them as valuable mathematical constructs. This debate ultimately depends on our broader understanding of the nature of reality. It stands as a compelling and ongoing matter that touches upon fundamental aspects of our comprehension of reality. Despite the lack of a definitive resolution, it is imperative to persist in exploration and discourse to advance our understanding of the fundamental nature of reality.

The exploration of orbitals has revealed a profound aspect of quantum mechanics in the realm of atomic and molecular structure. Through various coordinate transformations within the Schrödinger equation, orbitals of varying shapes can be derived, each characterized by distinct quantum numbers. Practical applications have been instrumental in enhancing our comprehension of these orbitals, with the primary aim of obtaining "good quantum numbers" for predictive accuracy.

Furthermore, the duality of obtaining orbitals through both position and momentum descriptions exemplifies the multifaceted nature of these fundamental entities. The position description, intimately linked to spatial location, represents a well-established approach. Nevertheless, the potential for a more profound grasp of the momentum description, connected to concepts of velocity and change, holds promise for enriching our understanding of quantum systems.

The quest for a comprehensive understanding of orbitals, encompassing their existence and mathematical foundations, remains a dynamic and intellectually stimulating field of study that transcends the boundaries of both physics and chemistry. This enduring debate surrounding the ontological status of orbitals highlights the profound nature of our inquiries into the fundamental essence of reality. While a definitive resolution is lacking, the ongoing discourse underscores the significance of unwavering exploration and dialogue in advancing our grasp of the fundamental constituents of the quantum realm.

The examination of the ontological existence of atomic and molecular orbitals presents a complex issue within the realm of philosophical chemistry. Diverse perspectives emerge, with some advocating for their genuine existence, while others regard them as valuable mathematical constructs. This continuous debate is firmly rooted in our broader comprehension of reality and remains a compelling and vital subject in our pursuit of understanding.

The exploration of orbitals remains a dynamic and intellectually stimulating area of research that transcends the boundaries of physics and chemistry. The ongoing debate regarding their ontological status serves as a testament to the depth of our inquiries into the fundamental nature of reality. While a definitive resolution remains elusive, ongoing exploration and discourse are indispensable in advancing our comprehension of the foundational components of the quantum world.

Authors' contributions

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