

He₂@C₆₀: Thoughts of the Concept of a Molecule and of the Concept of a Bond in Quantum Chemistry

Eugene S. Kryachko^{*[a]} and Tymofii Yu. Nikolaenko^[b]

We present a broad palette of discussions of the concepts of a molecule and a chemical bond that always lay down behind all computational modeling in quantum chemistry and of the endohedral fullerene He₂@C₆₀ in particular. For this purpose, we offer the definition of quantum chemistry as composed of three ingredients. Each of them is illustrated by its particular concept, either that of a molecule or a bond. The third, computational ingredient is tackled to resolve the bonding mani-

fold of He₂@C₆₀ and to demonstrate that van-der-Waals binding of He—He is converted within He₂@C₆₀ into a stronger bond due to that C₆₀ acts as an electronic buffer and [He₂] moiety mimics a fractionally charged He₂^{δ+}. Experimental fingerprints of He₂@C₆₀ are computed. © 2015 Wiley Periodicals, Inc.

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"In exact sciences, every theory has a philosophical, mathematical and empirical content. All these aspects are equally important; if we neglect one of them, we sooner or later get into difficulties."

Hans Primas ^[2]

how the foundation was laid. It is never too late to become reasonable and wise; but if the knowledge comes late, there is always more difficulty in starting a reform."

Immanuel Kant ^[8], p. 4)

Foreword

Writing on the special occasion is always a welcomed and pleasant work as it allows to explore some more unusual ideas, thoughts, and concepts that may not be fully appropriate for the standard mode of scientific paper.^[3–7] Some such speculative notions are perfectly suitable for the Festschrift publication and the authors do not necessarily need to worry of being carried away too far on their, if any, wings of imagination and wings of thoughts.

In this work, we intend to take the full advantage of the aforementioned authors' freedom that any Festschrift kindly offers and address the topics that we have been thinking for quite some time on and off. We can only hope that Erkki Brändas, whose 75th birthday this Festschrift is honorably dedicated to, will not be so displeased with our contribution. Bearing in mind this apology, we will now begin to expose our thoughts about the science and quantum chemistry in particular.

On Science in General and on Quantum Chemistry in Particular

"After all, there is nothing extraordinary in the elaboration of science that, when men begin to wonder how far it has advanced, the question should at last occur whether and how such a science is possible at all. Human reason so delights building that it has several times built up a tower and then razed it to see

The following background is behind our thoughts. Aristotle began his book "Metaphysics"* dated to 350 B.C. with the famous words:

"All men by nature desire to know."

From Webster's Dictionary we learn that "to know is to have knowledge, as of fact" (facts), "to have information, as about something." This gives the birth to the word "science" that was originated from the Latin word "scientia" meaning "knowledge."

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[a] E. S. Kryachko
Bogolyubov Institute for Theoretical Physics, Kiev, 03680, Ukraine
E-mail: eugene.kryachko@ulg.ac.be

[b] Tymofii Yu. Nikolaenko
Faculty of Physics, Taras Shevchenko National University of Kyiv, Kyiv, 01601, Ukraine

Faithfully dedicated to Erkki Brändas on the occasion of his 75th birthday. Among his recent works are highly worth of mentioning the works on the application of Gödel's incompleteness theorem to complex self-organized, primarily biological and living, systems.^[1]

*In fact, Aristotle did not name his book this way—he called it "First Philosophy." Actually, the origin of the term "metaphysics" is accidental. In 1 B.C., the Greek scientist and philosopher Andronicus of Rhodes decided to re-edit Aristotle's works and placed Aristotle's books on the first philosophy and placed them right after another work "Physics," calling them thus as "ταμετα" "ταφεικος" "βιβλια" meaning "the books that come after the physics." Latin scholiasts misread the latter and thought that it is meant "the science of what is beyond the physics," though "φεικος" physics, means "nature."⁹

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Science aims to create a new knowledge—as a set of Truths—of the nature, the world that daily surrounds us, or the Universe. To us, the latter appears through act of appearance, or phenomenon. The latter word originated from the Greek one “φαινόμενον” meaning “phainomenon” which is formed by the verb φαίνειν (phainein) meaning “to show, appear, shine, to be manifested, or manifest itself.”

The term “phenomenon” entered philosophy due to I. Kant’s major work, the “Critique of Pure Reason” (1781, ^[10]). Each phenomenon is observable and can be detectable, either by means of man’s senses or measured by instruments made by man. The former manner of observations is rather limited, simply for physical reasons: as example, our senses are incapable to tell us whether the Earth is revolving relative to its axis and around the Sun, about the nature of the forces keeping planets on their orbits, about electromagnetic fields, death and so on. The truth, Nature, Universe, is presumed to exist independently on any observation implying, therefore, that a “real phenomenon,” or object, is not identical to an “observed phenomenon” or subject. This demonstrates that the classical relationship between the observer (subject) and the observed phenomenon (system, object) is no longer valid.[†] To emphasize his point of view on phenomenon, Kant contrasted it with “noumenon” (in German: “Ding an sich,” “thing-in-itself,” or “thing per se”) [8], which, by definition, is not directly accessible to observation: “a thing that is not thought of as an object of the senses but rather as a thing in itself.” A rough English equivalent of “noumenon” is “something that is thought” or “the object of an act of thought,” “a transcendent object.” The concept of a “noumenon,” as wrote Kant in [Kant contrasted it with that of “noumenon” using the term Ding an sich, “thing-in-itself (thing per se),” which, by definition, is not directly accessible to observation: “a thing that is not thought of as an object of the senses but rather as a thing in itself.” According to Wikipedia, a rough English equivalent is “something that is thought” or “the object of an act of thought,” “a transcendent object.” The concept of a noumenon, as wrote Kant in the aforementioned Ref. [8], “is necessary to prevent sensible intuition from being extended to things in themselves, and thus to limit the objective validity of sensible knowledge.” The Oxford Essential Dictionary of Foreign Terms (American Edition, Berkley Books, NY, 1999) defines: “noumenon – German ‘Ding an sich.’ An object of purely intellectual intuition, devoid of all phenomenal attributes.”].

Let imagine that we gather some fact(s) about a given phenomenon under study. Assume that the axioms chosen to prove whether this fact is true are incomplete. Therefore, according to Gödel’s theorem,^[12] it is undecidable—that is, neither provable nor disprovable. As we cannot state that this fact is the Truth about the phenomenon under study, the latter has to be treated as noumenon.

[†]Trivial example: a toad enables to see only oblong objects. In this regard, Werner Heisenberg wrote: “Some physicists would prefer to come back to the idea of an objective real world whose smallest parts exist objectively in the same sense as stones or trees exist independently of whether we observe them. This however is impossible.”^[11]

One of the authors (ESK): reminiscences

“Chemistry, until my childhood, not that long ago, was regarded as a calculating device. Because you couldn’t reduce to physics. So it’s just some way of calculating the result of experiments. The Bohr atom was treated that way.”

Noam Chomsky

By fate, when I was the 4-year student of theoretical physics in the Kharkov State University, Department of Theoretical physics that now bears the name of Ilya M. Lifshits, the former Head, there was translated into Russian and published the book “Quantum Mechanics of Molecules” by Roy McWeeny and Brian Sutcliffe. It really impressed me, precisely speaking, I was “burned” by this science of “molecular quantum mechanics” and excited of the world of atoms and molecules - the world that actually composes the area of quantum chemistry.⁵ Though, in school, I never liked chemistry, but successfully took part in regional olympiads in chemistry.

When I worked at the LMU (Munich), in the Lab of Georg Zundel, as the Alexander von Humboldt postdoc fellow, Jean-Louis Calais invited me to visit Uppsala. Uppsala for me was like the Mecca of quantum chemistry founded by Per-Olov Löwdin and all time I dreamed of visiting it. So, I arrived in Uppsala in July of 1990 and suddenly appeared at the birthday party of Erkki Brändas. He was then 50-years old.



About quantum chemistry

What is quantum chemistry? Surprisingly, it appears to be rather difficult to define, except probably N. N. Semenov’s chemical-physics-type of definition: “Quantum chemistry is what quantum chemists are making.” By one definition, quantum chemistry is quantum mechanics of chemical structure of matter, or “quantum mechanics as applied to chemistry.”^[17] According to E. Bright Wilson, quantum chemistry began in 1926. As mentioned in Ref. [16a], speaking of the rise of quantum chemistry, Friedrich Hund said that there were three, Heitler, London, and Mulliken who began quantum chemistry in 1927. Two-years later Paul Adrien Maurice Dirac made his famous forecast in the opening paragraph of his 1929-year paper^[18]: “The general theory of quantum

⁵There exists the solid opinion that Hans G. A. Hellmann (1903–1938) was the founder, the “pioneer” of quantum chemistry. His books: “Quantum Chemistry” (the Russian Edition: ONTI, Moscow, 1937, 546 pp.) and “Einführung in die Quantenchemie” (the German Edition, Deuticke, Leipzig and Wien, 1937, 350 pp.) were the first on this discipline [for more details see: W. H. E. Schwarz, D. Andrae, S. R. Arnold, J. Heidberg, H. Hellmann, Jr., J. Hinze, A. Karachailos, M. A. Kovner, P. C. Schmidt, L. Züllicke, Hans G. A. Hellmann (1903–1938) Part I. A Pioneer of Quantum Chemistry. Part II. A German Pioneer of Quantum Chemistry in Moscow, Bunsen-Magazin 1999 (1) 10–21, (2) 60–70] (see also Ref. [16]). On the history of quantum chemistry see: M. J. Nye, From Chemical Philosophy to Theoretical Chemistry: Dynamics of Matter and Dynamics of Disciplines, 1800–1950. (University of California Press, Berkeley, 1993). p. 227–261; and K. Gavroglu, A. Simões, Historical Studies in the Physical Sciences, 25, 47–110 (1994).

mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. **The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.** It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

Another definition is that quantum chemistry is "a discipline that is not quite physics, not quite chemistry, and not quite applied mathematics."^{[19,20]a} In the other words, we, therefore, may define:

$$(\text{Quantum}) \text{ Physics} \cap \text{Chemistry} \cap \text{Computational Modeling} = \text{Quantum Chemistry} \quad (1)$$

We discuss all these ingredients below.



First ingredient in Eq. (1)

"In the history of science, this century's exploration of the world of atoms has hardly any parallel in so far as the progress of knowledge and the mastery of that nature of which we ourselves are part are concerned."

N. Bohr^[21]

The left-hand-side ingredient in Eq. (1) is of clear meaning: Quantum chemistry prehistorically began with the discovery of **the atom** as its first key element. It was the time—precisely, the end of the nineteenth century—when on Friday, of the 27th of April, 1900, Lord Kelvin (William Thomson) gave a speech "Nineteenth-Century Clouds over the Dynamical Theory of Heat and Light"^[22] that summarized the nineteenth-century's physics and started with the words: "The beauty and clearness of the dynamical theory, which asserts heat and light to be modes of motion, is at present obscured by two clouds." These are two clouds on the horizon of knowledge of physics were, first, the inability to detect the ether and the failure of the Michelson-Morley experiment and, second, the black body radiation effect known as the ultraviolet catastrophe.

Then, quantum mechanics only made its first steps in the minds of mankind and in the beginning of the Universe of the simplest atom, the hydrogen atom H.[†] Ever as Leukippos—this was the 5th century B.C.—the atom was imagined

as the smallest indivisible and discrete particle: in fact, the word "atom" came from the Greek *ατομ* which means "indivisible." This concept of the atom was further developed by pupils of Demokritos of Abdera, and later generalized by Copernicus, Kepler, Galileo, Descartes, and the others. In the XIXth century, Kelvin and Helmholtz proposed models of the atom, though they were either mechanical or hydrodynamic. We miss the important decade at the end of the XIXth century when J. J. Thompson discovered the "electron corpuscles" which Stony renamed in the "electricity atom" or "electron," for what, or precisely, for "recognition of his theoretical and experimental studies devoted to conduction of electricity by gases" was awarded by the Nobel Prize in physics in 1906.

By this time all the prerequisites to set the structure of the "indivisible" atom were available, and led Thomson to his model of the "plum pudding" ^[24] (see also Ref. [25]) which, however, lasted only for about 5 years. In this model, the atom was regarded as positively charged "soup," "jelly" in which electrons are embedded to balance the positive charge of jelly, like raisins in pudding. Electrons in jelly traffic on closed orbits.^{**} According to Earnshaw theorem^[31] (for details see Ref. [32] [Problem 3, p. 25] and^[33] [§ 19, p. 94]), that bears the name of Samuel Earnshaw, English clergyman, physicist and mathematician,^[31] the question of the stability of the atom remained open. In fact, Earnshaw theorem denied the existence of the atom as the Thomson's static charge and led to the planetary model.

It was also the time of discovering radioactivity that seemed a very mysterious phenomenon. However, its nature was disclosed that earned Rutherford the 1908th-year Nobel Prize in Chemistry.^{††} It was then thought that radioactivity can be explained within the model Thomson's "pie."^[24]

Let mention that this was also the time when there were no any accelerators and colliders, and the experimentalists used only radioactive isotopes as the sources of α - and β -particles. Thus, alpha-particles arising from the decay of radium and some other elements and is essentially fully ionized helium atom ${}^4\text{He}^{2+}$. In collisions with the atoms, the α - and β -particles deviate from the desired direction. The former, as being faster, can penetrate into the interior of atoms that is definitely the cause of the observed deviations. It is naturally

[†]Abraham Pais wrote about these times^[23]: "Times were not yet ripe for tackling the theory of atomic structure when the twentieth century began. As one physicist has written: "It is perhaps not unfair to say that, for the average physicist of that time, speculations about atomic structure were something like speculations about life on Mars—very interesting for those who like that kind of thing, but without much hope of support from convincing scientific evidence and without much bearing on scientific thought and development."

This is another cloud, not even a "cloud!"

^{**}Bertrand theorem^[26–30] states that the only central potentials which are functions of the distance r and which permit, independently on the initial conditions, the closed orbits for bound particles are the Coulomb potentials, $\sim 1/r^2$, and the isotropic harmonic oscillator (i.e., Hooke's law, $\sim r$). See in this regard the comment by Ehrenfest^[28] about the exception of 3D dimension compared to the other.

^{††}Note that Rutherford, who considered himself a physicist, not a chemist, has been widely cited as having said: "The whole science - or physics, or collectible stamps."

Table 1. Theoretical scattering data of alpha-particle on the foil of gold.

$\theta(^{\circ})$	15	30	45	60	75	105	120	135	150
ΔN	132,000	7800	1435	477	211	69.5	51.9	43.0	33.1
C, Eq.(4)	38.4	35.0	30.8	29.8	29.1	27.5	29.0	31.2	28.8

assumed that these deviations occur due to the electric field existing inside the atom, and therefore, they can provide some information about the charge distribution in the atom.^[34] As the mass of an alpha-particle m_{α} exceeds the mass of the electron in approximately 7300 times, one can definitely ignore the influence of the electron on scattering of alpha particles and on a significant change in its direction. Therefore, only a positively charged region of the atom significantly impacts on the movement of alpha particles bearing the charge $z_{\alpha} = +2$.

In 1909, Hans Geiger, young German physicist, and Ernest Marsden, student of the University of Manchester, conducted experiments where alpha particles bombard the target consisted of a plate of gold foil ¹⁹⁷Au.^{[35]††} Gold was chosen for the reason that as the most precious metal among so-called "coinage" metals, it is substantially inert in the bulk.^{[39–42]§§} Then, Geiger and Marsden observed the following behavior of alpha particles which were dispersed by a gold foil, namely:

- There was quite a wide angular distribution which cannot be explained in terms of the Thomson model of the atom in which "N negatively charged particles located in the same number of positively charged particles of jelly evenly distributed in a sphere."^[22] Thus, approximately one of 8000 alpha particles, passed throughout the gold foil of a thickness of 0.00004 cm, are scattered at an angle $\theta > 90^{\circ}$ (a so called "back scattering").
- The most probable scattering angles of the α -particles on a gold foil of a thickness of 1.7×10^{-4} cm fall around 1.40° .^[44,89]

The answer of the theory on these experiments is the following. Consider the alpha-particle that moves from infinity with a velocity v_{∞} and is scattered at a point-like positive charge Ze of mass M (where e is the positive charge equal, by the absolute value, that of the electron). The energy U of Coulomb interaction is $U = z_{\alpha}Ze^2/r$ where r is the distance between particles. Then the differential cross-section is given by the Rutherford formula^[34,45]

$$\frac{d\sigma}{d\Omega} = \left(\frac{z_{\alpha}Ze^2}{\mu v_{\infty}^2} \right)^2 \csc^4 \left(\frac{\theta}{2} \right) \quad (2)$$

where $\mu = m_{\alpha}M/(m_{\alpha} + M)$ is the reduced mass. Then the number of scattered particles which are detected at the angle θ is

$$\Delta N = \frac{d\sigma}{d\Omega} N_{Au} / \Delta \Omega \quad (3)$$

where N_{Au} is the number of centers that scatter on alpha-particles and l is a thickness of foil. Comparing Eqs. (2) and (3), we obtain

$$\Delta N \sin^4 \left(\frac{\theta}{2} \right) = \text{const} \equiv C \quad (4)$$

The results of Eq. (4) are compared in Table 1 with the experimental data for gold. It then directly follows that the product of $\Delta N \sin^4(\theta/2)$ varies slightly in the interval (15° , 150°) and thus the model of scattering of alpha particles on the nucleus with charge $\sim Ze$ approximately describes the data of the Geiger–Marsden experiment. We may assume that this approximation arises due to, first, the fact that the formula (2) itself is approximate (see e.g., Refs. [46–48]) and neglect the effect of electronic subsystem that is a part of the atom and that shields the effective positive charge.

Using his formula, Rutherford^[34] concluded that the scattering angle satisfies the inequality $\theta > 90^{\circ}$ if the scattering occurs between alpha particles and a highly charged particle with a concentrated mass. Therefore, the atom has a massive center with charge Ze surrounded by a sphere of a negative charge. This model of the atom is called "planetary."^[34] Thus, the atom, according to Rutherford, is a system in which all the positive charge of the bulk of the atom, which is located within a sufficiently small volume - the so-called center of the atom, or nucleus, and negatively charged particles, electrons, move around the nucleus at rather large distances. Rutherford showed in Ref. [34] that his formula is in good agreement with the experimental data of Geiger and Marsden and that the value of the positive charge of the atom is approximately proportional to its atomic weight A (in the case of atoms heavier than aluminum). For instance, the gold atom which atomic weight $A = 197$ possesses the charge Z , approximately equal to 100.

Note here that until 1911, the atomic number Z as the number of electrons of the element of the Periodic Table did not exist: the chemical elements were still determined by atomic weights. Rutherford first introduced the concept of the "atomic number," it was done in 1913, although a month ahead was the Dutch amateur physicist Antonius Johannes van den Broek, who published an article in Nature^[44] (see also Refs. [49,50]) one-month later the appearance of the corresponding article of Rutherford. Van den Broek believed that atomic number determines the positive charge of the Rutherford atom. True, the Rutherford model of atom was not ideal: difficulties arose with interpreting Balmer's series^[51] and the

††100-years later, a similar experiment was conducted by Antoine Lemasson with the colleagues from France, India, Poland and the United States on the accelerator SPIRAL (France).^[36–38]

§§Generally speaking, this statement is not entirely true. For example, in the 16th century, the catalytic properties of gold - the so-called "drinkable gold" ("aurum potabile"), in particular - have been known due to the work by the alchemist David de Campo (David de Planis Campy), physician French surgeon to the King Louis XIII, and his Treatise "The true, unique, great, and universal medicine of old; so-called drinking recens or addition to clean gold containing the large nature mirror"^[43] and famous alchemist Philip Aureolus Teofrastusa Bombastusa v. Hohenheim (Philippus Aureolus Theophrastus Bombastus von Hohenheim), better known as Paracelsus.

regularities discovered by Rydberg and Ritz.^[52] N. Bohr comprehended all these difficulties and one hundred and one years ago, in his trilogy,^[53] proposed the following postulates:

1. **"The quantum postulate"** "An atomic system based on Rutherford's model can only exist in certain *stationary states* (orbits) having energies

$$\{\varepsilon_1, \varepsilon_2, \varepsilon_3 \dots\} \quad (5)$$

and can be partially described by the laws of Classical Mechanics.

2. The *emission* (or *absorption*) of electromagnetic radiation occurs only due to transitions between two stationary orbits, in such a way that the frequency (ν) of the emitted (or absorbed) radiation is given by

$$\frac{\nu = |\varepsilon_f - \varepsilon_i|}{h} \quad (6)$$

where h is Planck's constant and ε_f and ε_i are, respectively, the energy values of the two orbits involved in the transition. In other words, the energy (ε) of the emitted or absorbed photon is given by Planck's law $\varepsilon = h\nu$.

These postulates were well-grounded later, within the Schrodinger's picture of quantum theory with the total Hamiltonian

$$H = -\frac{1}{2}\Delta_0 + Z \sum_{i=1}^n \frac{e^2}{r_i} + \sum_{i,j=1;i < j}^n \frac{e^2}{r_{ij}} \quad (7)$$

where Δ_0 is the Laplace operator on R^{3n} , $r_{ij} = r_i - r_j$, r_i is the radii-vector of the i th electron, and Z is the aforementioned atomic number.

$$\psi \quad \psi \quad \psi$$

Second ingredient in Eq. (1)

"Chemistry matters."

**A wise quantum chemistry folklore
(probably from Uppsala)**

The second ingredient in Eq. (1) is chemistry. To define chemistry, let address to some classics:

Linus Pauling^[54]: "Chemistry is the science of substances: their structure, their properties, and the reactions that change them into other substances."

Jean-Marie Lehn^[55]: "Chemistry is progressively unraveling the processes that underlie the evolution of matter towards states of higher complexity and the generation of novel features along the way by self-organization under the pressure of information."

As, in our opinion, there definitely exists some confusion in chemistry regarding terminology, it is prudent to begin with some elementary definitions to claim the presented statements unambiguously.

A substance, matter is composed of molecules. In quantum chemistry, there definitely exist two categories, say, **U** and **A**, of definitions of a molecule.

- Category **U** asserts

DEFINITION 1. That, similarly to that of atom, defines a molecule as a **unit** by itself. **Definition 1** was shared by R. S. Mulliken, one of the founders of theoretical quantum chemistry (see Ref. [20]a), p. 387^[6]). Another definition of molecule belongs to P.-O. Löwdin:

DEFINITION 2. (Löwdin^[56], see also Refs. [57,58] and references therein).

"A system of electrons and atomic nuclei is said to form a *molecule* if the Coulombic Hamiltonian H – with the centre of mass motion removed – has a discrete ground state energy E_0 ."

Therefore, a molecule is a quantum system $\mathbf{M} := (1, \dots, n)$ of n particles with the corresponding charges e_i and masses m_i , $i = 1, \dots, n$, whose Hamiltonian H , has the following form:

$$H = -\frac{1}{2}\Delta_0 + \sum_{i,j=1;i < j} \frac{e_i e_j}{r_{ij}} \quad (8)$$

where Δ_0 is the Laplace operator on $\mathbb{R}_0 := \{r | r \in R^{3n}, \sum_{i=1}^n m_i r_i = 0\}$, $r_{ij} = r_i - r_j$ and r_i is the radii-vector of the i th particle. Note that the form (8) of H which differs from (7) for the atom asserts the equivalence of the subsystems of nuclei and electrons composing a given molecule. Through this equivalence there passes the borderline between the categories **U** and **A**. Collins English Dictionary^[59] shares the point of view of the latter category defining that "molecule is the simplest unit of a chemical compound that can exist, consisting of two or more atoms held together by chemical bonds." The entire chemistry is primarily laid on the concept of the **bond** which is something that binds two chemical species together via their mutual **bonding**, thus forming a **molecule**. The 1997 definition of IUPAC of the bond is this^[60]: "there is a chemical bond between two atoms or groups of atoms in the case that the forces acting between them are such as to lead to the formation of an aggregation with *sufficient stability* (Italics of the present authors) to make it convenient for the chemist to consider it as an independent 'molecular species.'"

To summarize. First: it is the nature of a chemist to view molecules as a collection of atoms and a condensed state as a collection of molecules, and to interpret the properties of the larger aggregates in terms of their smaller building "stones" and the interactions between them. Second: the bond leads to "the formation of an aggregation with sufficient stability." Full stop.

Hence, the bond can be viewed as the entity that holds a given molecule stable^[61] or, equivalently, prevents it from any

^[6]As mentioned therein, Mulliken "liked to say in the manner of Gertrude Stein that 'a molecule is a molecule is a molecule.'"^[18b]

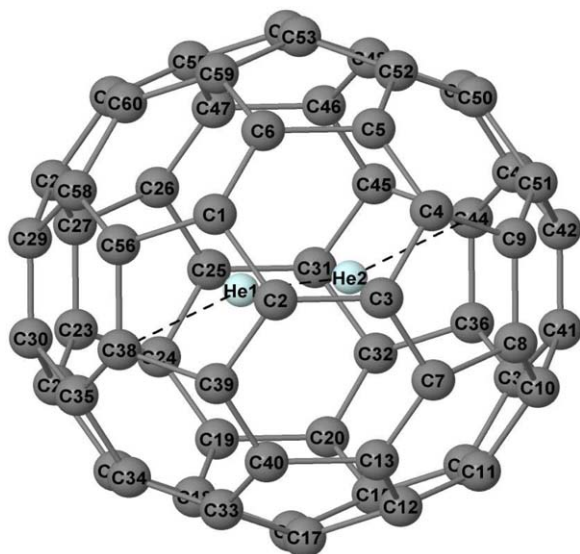


Figure 1. The M06-2X/6–31G(d) structure of the endohedral fullerene $\text{He}_2@C_{60}$. The dashed line connects the atoms linked by a bond path according to the QTAIM analysis of the electron density. The mean-square

radii \bar{R} ($\text{He}_2@C_{60}$) = 3.540 Å where $\bar{R} = \sqrt{\frac{1}{N} \sum_{i=1}^N R_i^2}$ (where R_i is the distance

from the geometrical center to the i -th carbon atom) of a given endofullerene $\text{He}_2@C_{60}$ with $N = 60$ carbon atoms. Note that \bar{R} (C_{60}) = 2.540 Å. The Mulliken atomic charge on each He atom is equal to +0.010 e.

so called cluster partition. Let us now define a cluster partition:

DEFINITION 3. (Ref. [62]). As in **Definition 2**, $\mathbf{M} = (1, \dots, n)$ of n particles. A partition of $\mathbf{M} = (\mathbf{M}_1, \dots, \mathbf{M}_k)$ into mutually nonintersecting, nonempty sets $\{\mathbf{M}_j\}$ such that $\mathbf{M}_j \cap \mathbf{M}_l = \emptyset$ ($j < l = 1, \dots, k$) is called a cluster partition (decomposition): $\mathbf{M} = \mathbf{M}_1 \cup \mathbf{M}_2 \cup \dots \cup \mathbf{M}_k$. Each \mathbf{M}_j is called a cluster.

One of the definitions of stability is that^[63] “a removal of any particle from a given system is unprofitable.” Theorem 1

proved therein (Ref. [63], p. 83) states that “for a given system to be stable, it suffices that a removal of any particle from a given system is unprofitable.”

Let $\mathbf{M} = (1, \dots, n)$ be a system of n particles, and $\mathbf{M} = (\mathbf{M}_1, \dots, \mathbf{M}_k)$ be its arbitrary cluster partition into sets \mathbf{M}_j , $j = 1, \dots, k$. Each \mathbf{M}_j can be considered as a system with its own sub-Hamiltonian built similarly to Eq. (8). If the conditions of **Definition 2** are satisfied for these sub-Hamiltonians, each cluster is actually a molecule. Hunziker–Van Winter–Zhislin (HVZ) theorem^[63,64] then links the essential spectra $\sigma_{\text{ess}}(H)$ of these sub-Hamiltonians of infinitely separated clusters with the Hamiltonian (8) of \mathbf{M} and states that $\sigma_{\text{ess}}(H)$ is bounded below by the lowest possible energy which two independent subsystems can have. In fact, the HVZ theorem ensures the criteria of “boundness”^[65] and thus, in the other words, laid down the foundation of quantum chemistry.

Computational Modeling: $\text{He}_2@C_{60}$ Is Not a Molecule

This section on the third ingredient of quantum chemistry in Eq. (1), we begin with the titles of René Magritte works “This is not a Pipe” and “This is not an Apple,” thereby addressing the questions of whether $\text{He}_2@C_{60}$ is the molecule and of whether do He_2 form a bond in $\text{He}_2@C_{60}$?****

To answer on the above questions, we invoke the following computational methodology.

ψ ψ ψ

Computational methodology excerpts

The computational level invoked in the present work uses Gaussian-09 package of programs^[69] with the keyword Int = UltraFine and uses the density functional approach^[66] based on the M06-2X meta exchange-correlation density functional that takes into account a van-der-Waals-correction^[67,70,71] and that was recently used in Ref. [72] for the analogous tasks.

Quantum Theory of Atoms and Molecules (QTAIM)^[73–75] is applied to study the bonding manifold in the endohedral fullerene $\text{He}_2@C_{60}$.^{†††} It is worth noticing that although QTAIM itself provides only a *definition* of a topological atom and does not provide a formal proof for its relevance to “chemical” atoms, numerous examples demonstrate the fruitfulness of equating these concepts. In particular, bond paths have been shown to be a universal indicator of bonded interactions.^{[75]c,d} Using Gaussian package, we obtained the electron density distributions at the corresponding computational level using the keyword “output = wfn” and analyzed it with AIMAll package^[77] to reveal all (3,–1)-type critical points and bond paths

****At the first sight, the latter question seems to be meaningless: according to the long-established chemical principle the He atoms, as the noble gas (Ng) ones, are inert and do not participate in formation of the chemical bond. Nevertheless, two works^[66,67] addressed this question and the fact of existence of the Ng–Ng (Ng=He–Kr) bond by inspecting the precession of Ng_2 within $\text{Ng}_2@C_{60}$ (see also Ref. [68]).

†††In the recent work on QTAIM,^[76] it was revealed some “conceptual incompatibilities in H_2 ” resulting in “that QTAIM localization and delocalization indices should not be estimated from interpretations of the valence bond wave function in terms of the Lewis model.”

Table 2. QTAIM analysis of the electron density distribution in $\text{He}_2@C_{60}$.

Bond (A...B)	R_{AB} (Å)	$\rho^{\text{CP}} \cdot 10^2$, e/a_B^3	Bond ellipticity
$\text{He}_1 \cdots \text{He}_2$	1.979 ^[a]	1.26	$3 \cdot 10^{-6}$
Other works:			
BP86/TZVPP	1.948 ^[79]		
M05-2X/6–311G(d)	2.035 ^[80]		
$\text{He}_2^+(\sum_u^+)$:			
Present work	1.1881 ^[b]		
MR-CI ^[81]	1.0816		
B3LYP ^[82]	1.1454 ^[c]		
BLYP ^[82]	1.1830 ^[d]		
Expt. ^[83,84]	1.0806 ^[e]		
CI ^[84,85]	1.08056		
$\text{C}_{38} \cdots \text{He}_1$	2.588	1.07	1.21
$\text{C}_{44} \cdots \text{He}_2$	2.588	1.07	1.21

R_{AB} is the A...B-intermolecular distance, $\rho^{\text{CP}} \equiv \rho(r_{\text{CP}})$, the charge density at the (3,–1) bond critical point CP, and a_B is the Bohr radius, and ρ^{CP} qualitatively measures a strength of a noncovalent interaction. [a] $\nu(\text{He} \cdots \text{He})$ stretch in $\text{He}_2@C_{60}$: is centered at 531.0 cm^{-1} . [b] The calculated frequency in $\text{He}_2^+ = 1293 \text{ cm}^{-1}$. [c] $\nu(\text{He} \cdots \text{He})$ stretch = 1359.9 cm^{-1} . [d] $\nu(\text{He} \cdots \text{He})$ stretch = 1192.8 cm^{-1} . [e] $\nu_{\text{expt}}(\text{He} \cdots \text{He})$ stretch = 1698.5 cm^{-1} .^[83]

of the electron charge density distribution. A bond ellipticity that defines a measure of the extent to which a charge is preferentially accumulated in a given plane^[78] was calculated as $\varepsilon = \lambda_1/\lambda_2 - 1$, where λ_1 and λ_2 are negative eigenvalues ($|\lambda_1| \geq |\lambda_2|$) of the Hessian matrix $H_{ij} = \frac{\partial^2 \rho}{\partial x_i \partial x_j}$ ($i, j = 1, 2, 3$) evaluated at the bond critical point. When possible transformations of a given molecular graph represented by a set of molecular bond paths are considered, it can be shown that “the ellipticity of the bond which is to be broken increases dramatically and becomes infinite at the geometry of the bifurcation point” so that “a structure possessing a bond with an unusually large ellipticity is potentially unstable.”^[74] Therefore, the value of bond ellipticity can be considered as the measure of bond stability.



Computational results

The resultant structure of $\text{He}_2@\text{C}_{60}$ obtained at the computational level M06-2X/6-31G(d) is shown in Figure 1. The QTAIM analysis reveals three bond paths in its bonding manifold: one lies between two helium atoms, and the other two between He_1 and C_{38} and between He_2 and C_{44} (see Fig. 1). Their properties are illustrated in Table 2.



Summary

All the computations we carried in the present work portray the endohedral fullerene $\text{He}_2@\text{C}_{60}$ as a molecule which bonding manifold comprises of three bonds: one that is formed between the encapsulated helium atoms, and the other two between each atom of He and the carbon atom of C_{60} . The problem with the He–He interaction earlier discussed in Refs. [68,79,80] and seemingly paradoxical due to the inertness of He has been definitely resolved by the (Mulliken) atomic charges on these atoms which, altogether, demonstrate a fractionally charged $[\text{He}_2]$ moiety with the total charge of +0.02 e. This implies that within the C_{60} -void, He_2 represents itself a slightly fractionally charged analogue of He_2^+ rather the neutral He_2 van-der-Waals dimer—their comparison is given in Table 2. The former is definitely covalently bonded and characterized by the $\nu(\text{He-He})$ stretching mode which can serve as its experimental fingerprint.

Thoughts and Conclusions

“Quantum chemistry does not claim any more than all chemical and physical material properties to be capable of purely theoretical precalculation, simply on the basis of one single mathematical law [and] of creating a theoretical reconstruction of the chemical world.”

Hans Hellmann^[86]

Let us embark on this section by returning to Eq. (1) which two former—lhs—ingredients define the first principles and

fundamental concepts of quantum chemistry. Among the latter is the concept of a bond. Both, explicitly and implicitly, we have approached this concept in on science in general and on quantum chemistry in particular section : (i) implicitly: whether a bond is a noumenon? and (ii) explicitly: to which degree a term “bond” is euphemism of that of “stability”?

We always believe that these principles and these concepts are absorbed in the Hamiltonian H (8). True, solving this Hamiltonian exactly for many molecules is meaningless. The third part of Dirac’s forecast that states: “It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation” thus enters into the force. Together with the computational doctrine of quantum chemistry that all molecules which are computable do exist—are molecules in a non-Magritte sense and cannot be taken for granted—and hence are measurable and experimentally identified, this forecast form the foundation of computational quantum chemistry. Experiments play the primary role in identifying a real molecule with its computational image. It is obvious that such a comparison is worth to conduct only if a given molecule self-behaves under the conditions of experiment and weakly depends on environment. To these experiments naturally belong those on diffraction which allow to obtain the information on a molecular structure and the spectroscopic ones which are of importance because, according to the Bohr’s second postulate, molecules “cannot do anything except absorb or electromagnetic radiation.”^[87] It was hence the reason we have taken in computational modelling: $\text{He}_2@\text{C}_{60}$ is not a molecule section into account to identify the bonding in a fractionally charged $[\text{He}_2]$ moiety as identical to the bonding in He_2^+ , taking into account on a difference of a positive charge of $[\text{He}_2]$ moiety. The formation of this moiety is a consequence of the charge transfer from the encapsulated He dimer to the carbon C_{60} fullerene which is simply dictated by so called ionic model of interaction^[88] that explained the first isolation of $\text{La}@\text{C}_{82}$ in 1991.^[78]

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Keywords: quantum chemistry • molecule • bond • $\text{He}_2@\text{C}_{60}$ endohedral fullerene • DFT

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