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IN THE ENDOHEDRAL FULLERENE He₂@C₆₀¹**

For more than twenty years, the endohedral fullerene cavity is attracting a permanent attention of experimenters and theorists, computational chemists and physicists, who apply their efforts to simulate encapsulated atoms and molecules in the fullerene cavity on computers and analyze the arising phenomena of atomic bonding. In this work, recent developments concerning the endohedral fullerene He₂@C₆₀, in particular, its experimental observation and relevant computational works, are reviewed. On the one hand, the dihelium He₂ embedded into the C₆₀ cavity is observed experimentally. On the other hand, the computer simulation shows that each of the He atoms is characterized by an insignificant charge transfer to C₆₀, so that the He dimer exists as a partially charged (He^{+δ})₂ entity. The key issue of the work concerns the existence of a bond between those two helium atoms. Since the bond is created between two particles, we assert that it suffices to define the bond on the basis of the molecular Löwdin's postulate and use it to study the He dimer in the C₆₀ cavity in terms of the He–He potential energy well. It was analytically demonstrated that this well can contain at least one bound (ground) state. Therefore, according to Löwdin's postulate, which is naturally anticipated in quantum theory, the conclusion is drawn that the (He^{+δ})₂ entity is a diatomic molecule, in which two heliums are bound with each other. On the basis of those arguments, the concept of endohedral fullerene stability is proposed to be extended.

Keywords: fullerene, endohedral fullerene, He@C₆₀, He₂@C₆₀, bond, molecule, Löwdin's postulate.

1. Reminiscences

One of the co-authors of this work, E.S.K., recalls that he got acquaintance with G. Puchkovska due to Prof. Therese Zeegers-Huyskens from the Catholic University of Leuven (Belgium). At that time, all the three were studying the theory of hydrogen bonding². It was a period, when the paradigm in the theory of hydrogen bonding was changed. This paradigm touched the fundamentals of chemistry as a science, which was discussed by T. Kuhn in his famous work [4].

The paradigm change essence was as follows. It is known that the characteristic feature of the H...Y hydrogen bond formation in the complex X–H...Y

is the elongation of the X–H bond, which is accompanied by the so-called “red shift”

$$\Delta\nu(\text{X–H}) = \nu(\text{X–H}\cdots\text{Y}) - \nu(\text{X–H}) < 0, \quad (1)$$

where $\nu(\text{X–H}\cdots\text{Y})$ and $\nu(\text{X–H})$ are the frequencies of the X–H valence vibrations in the complex X–H...Y and in X–H, respectively. However, in the late 1990s and at the beginning of the 2000s, a number of unordinary, “improper” or “blue-shifted”, hydrogen bonds³ were revealed both experimentally and in computer experiments, in which the X–H bond length becomes

¹ Dedicated to the memory of Galyna Oleksandrivna Puchkovska (1934–2010).

² The works made by G. Puchkovska during that period are cited in works [1–3].

³ For many years, a discussion was continued: How correctly is to classify such bonds to hydrogen ones?

shorter, and the frequency of the valence X–H vibration shifts toward the blue spectral section, i.e. for which $\Delta\nu(\text{X–H}) > 0$ (see works [5–7] and references therein).

In our opinion, this “change of the paradigm”, being artificial to some extent, was induced by the controversial foundations of the chemistry itself [8, 9]. Let us explain our standpoint using the hydrogen bonding as an example. The classical concept of hydrogen bond was proposed by Moore and Winnill [10], Huggins [11, 12], Latimer and W.H. Rodebush [13], and Pauling [14] at the beginning of the 20th century⁴. However, only a century later, in 2014, the International Union of Basic and Applied Chemistry (IUPAC) proposed the definition of hydrogen bond⁵ and published it in the so-called IUPAC Gold Book [17, 18]. The definition is formulated as follows.

The hydrogen bond “*is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group represented by X–H···Y–Z, wherein the three dots denote the bond. X–H represents the hydrogen bond atom in the same or a different molecule, in which there is evidence of the bond formation. A typical hydrogen bond may be a donor. The receptor may be an atom, an anion Y, a fragment, or a molecule Y–Z, wherein Y is bonded to Z*”.

What does it mean: “There is evidence of bond formation”? Here lies the cornerstone of philosophy in chemistry. This issue was discussed by G.R. Desiraju [9, p. 2489], who believed that “... it is practically impossible to describe a hydrogen bond in terms of what it is, perhaps the more practical way out is to describe it in terms of what it does”. In essence, this is a definition of hydrogen bond like those given in works [19, 20], namely, on the basis of the magnitude of the red (or blue) shift, the proton displacement, and so on. As G.R. Desiraju marked further, this is a point where the reductionism and holism in chemistry conflict with the concept of reality (i.e. with our ability to imagine this reality; see, e.g., work [21]). Moreover, as was recently emphasized by W.H.E. Schwarz *et*

al. [22], “explanations and interpretations in the complicated domain of chemistry are ambiguous. Various interpretations can all be logically consistent”. The cited authors faced this dilemma when studying “the evidence of bonding” between He atoms in the so-called endofullerene He₂@C₆₀ on the basis of the definition from the mentioned IUPAC Gold Book [23]:

“*When forces acting between two atoms or groups of atoms lead to the formation of a stable independent molecular entity, a chemical bond is considered to exist between these atoms or groups. The principal characteristic of a bond in a molecule is the existence of a region between the nuclei of constant potential contours that allows the potential energy to improve substantially by atomic contraction at the expense of only a small increase in kinetic energy. Not only directed covalent bonds characteristic of organic compounds, but also bonds such as those existing between sodium cations and chloride anions in a crystal of sodium chloride or the bonds binding aluminium to six molecules of water in its environment, and even weak bonds that link two molecules of O₂ into O₄, are to be attributed to chemical bonds.*”

This issue is discussed below.

2. Introduction. Endofullerenes

Nature abhors a vacuum.

ARISTOTLE

In 1985, Kroto, Curl, Smalley *et al.* [24–26] experimentally discovered a C₆₀ cluster composed of sixty carbon atoms, which they called buckminsterfullerene or buckyball (the short form is fullerene) due to the similarity of its structure to the soccer ball. Later, in 1996, they won the Nobel Prize in chemistry [27]. The story of C₆₀ discovery was rather instructive and not very short, especially if the year of 1970 is taken as a reference point, when Osawa [28] predicted the existence of C₆₀ and its high stability in the form of a truncated icosahedron belonging to the point group I_h (see Fig. 1). In three years, Bochvar and Galperin [29] performed first quantum-chemical calculations of this structure. Finally, fullerenes were revealed in nature and in interstellar space, where they manifested themselves in the absorption bands of carbon-rich giant red stars and comet tails [30–32].

Owing to its properties, C₆₀ still remains the subject of numerous studies [46–51], including the study of diffuse interstellar bands [52]. One of its properties

⁴ More precisely, the idea of a weak nonspecific interaction with a directly engaged hydrogen atom can also be found in works by Nernst *et al.* (see review [15]). Probably, the term “hydrogen bond” was first referred to by Lewis in 1923 [16].

⁵ In no case, this means that such definitions were not proposed earlier (see, e.g., works [19, 20]).

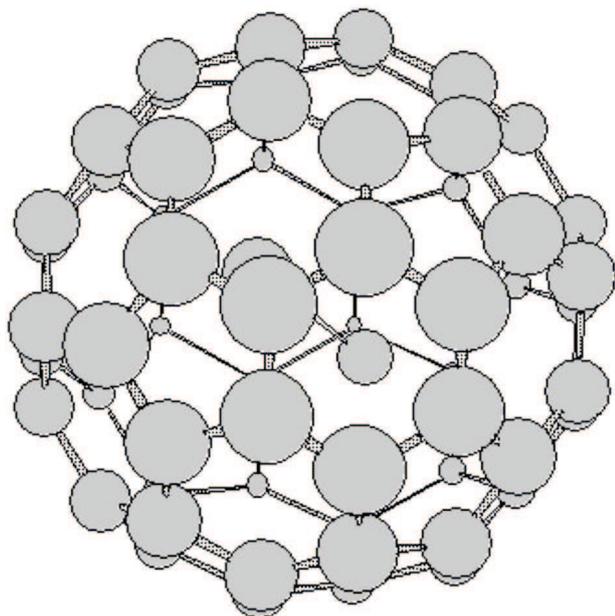


Fig. 1. Structure of $C_{60}(I_h)$ [reproduced from *Acc. Chem. Res.* **25**, 30 (1992)]. According to the X-ray diffraction experiment, the average diameter d_{60} of the C_{60} cavity amounts to 0.714 Å [43–45]. C_{60} is a polyhedron with 20 hexagonal and 12 pentagonal faces

follows from a tendency to hold the “foreign” atom or molecule in the fullerene cavity as in a “cage”. This ability was confirmed within a week after the discovery of C_{60} when synthesizing the so-called lanthanum endofullerene⁶ $La@C_{60}$, where the symbol “@” means that the La atom is located inside C_{60} [43, 53]. Later, a lot of other endofullerenes were discovered. Of special interest among them are those, which encapsulate atoms of noble gases, $Ng_n@C_m$, where $n \geq 1$ and $m = 20, 28, \dots, 84, 240, \dots, 720, \dots, 1500, 2160$, and so on.

It is evident that C_{60} can capture an Ng atom only if its cavity has a sufficient volume. Otherwise, their interaction will be repulsive and energetically disadvantageous. Saunders, Schwartz *et al.* (later, Thiel *et al.*) [54–58] demonstrated that all atoms of noble gases up to Xe can exist in the C_{60} cavity. Furthermore, it was recently shown that more atoms of

⁶ The etymology of the word “endo” means “inside, in, inner”. It comes from the Greek words $\epsilon\nu\delta\omicron\nu$ [endon], which means “in, inside”, and $\epsilon\delta\rho\alpha$ [hedra], which means a face of a geometric form.

inert gases are required to achieve such an internal pressure, at which C_{60} is destroyed [59]. The first experimentally observed $Ng@C_{60}$ was $He@C_{60}$ produced in 1993 in an amount that was sufficient for registration⁷ using the high pressure/high temperature method (fullerene was heated up in the presence of a Ng gas to a temperature of 650°C and under a pressure of 3000 atm [60]. $He@C_{60}$ was detected with the help of mass spectroscopy [61]. In the 3He case, an NMR signal of He^3 was observed [62].

Another practical method for detecting such complexes is the rotational-vibrational spectroscopy, which allows some nonstandard peculiarities in the spectra to be revealed [63]. In 1997, Saunders *et al.* experimentally observed $He_2@C_{60}$ [64] (see also works [65, 66]); and, later, $Ng_n@C_{60}$ with $n = 2$ [67–70]. The researchers emphasized that endohedral fullerenes with clusters of three or more inert-gas atoms had not been revealed, although their existence had been predicted by computational methods.

The mentioned endohedral fullerenes $Ng_n@C_{60}$ ($n \geq 2$), in particular $He_2@C_{60}$, comprise a rather specific research domain, because of a long holding time of inert-gas atoms. The latter are highly inert systems. They never participate in the chemical bonding, but two exceptions: van der Waals interactions and, as it predicted, the binding with a fullerene cavity. This viewpoint was changed in 1962, when Bartlett synthesized $Xe^+[PtF_6]^-$ [71, 72].

Since 1997, the interest in endohedral fullerenes of noble gases $Ng_n@C_{60}$ and, partially, $He_2@C_{60}$ is growing, because it was unclear how the atoms of inert gases inside fullerenes would interact with one another and whether it is the confinement that causes the binding between the atom and the fullerene “cage”, and between the atoms themselves in such van der Waals molecules. Here, under the term “confinement”, we mean the existence of a barrier beyond a certain space region, the C_{60} surface, i.e. the “wall” potential

$$V_{\text{confinement}} = \begin{cases} 0 & r \leq R, \\ V_0 & r > R, \end{cases} \quad (2)$$

where $R = d_{60}/2$ is the radius of the C_{60} spherical “cage”. On the other hand, if $Ng@C_{60}$ does exist, this complex must be very stable, because the Ng atom

⁷ Approximately one of every 650000 C_{60} “cages” contains a helium atom [54–56].

cannot leave the cavity until a few edges of the “cage” have been destroyed. The encapsulation of the inert-gas atom into the fullerene cavity can reveal crucially different properties of the atom, e.g., its ability to the binding [53, 73–77]. Of course, the bond concept formed the basis of chemistry. That is why, in this work, with the help of a computational technique, which is briefly discussed in the next section, all arguments pro and contra the existence of the binding between two He atoms in the C₆₀ cavity are analyzed.

3. Calculation Technique

The equilibrium structures C₆₀(I_h) and He₂@C₆₀ were obtained similarly to our previous works (see works [78, 79] and references therein) using the geometry optimization. This procedure was carried out with the help of the GAUSSIAN software package [80]. In calculations, we used the meta exchange-correlation density functional (DF) M06-2X, which makes a correction for van der Waals interactions [81, 82]⁸ and the set of basic functions 6-31G(d) [80].

The structure of He₂@C₆₀ is depicted in Fig. 2. In this complex, two He atoms are located at a distance of 1.979 Å (unlike 1.948 Å, as in work [90]) from each other. Each He atom is located at a distance of about 2.507 Å (2.671 Å in work [90]) from the C–C bond in the C₆₀ pentagon. The Mulliken charge of an He atom equals $\delta = +0.011$ e. The calculated frequency $\nu(\text{He–He}) = 69.6$ cm^{−1} describes the motion of the diatomic dumbbell-like complex He–He, which was also mentioned earlier in work [90, p. 8260]⁹. The He–He stretching is observed at a frequency of 531.0 cm^{−1}. Changes in the diagonal quadrupole moment, when two He atoms are introduced into C₆₀, are as follows: $Q_{xx} = -2.5$ D Å, $Q_{yy} = -2.4$ D Å, and $Q_{zz} = -2.3$ D Å. We assume that the latter circumstance may testify to a weak polarization of atoms. Note that the theory at the level M06-2X/6-31G (d)

⁸ The importance of taking the dispersion interactions into account, when studying fullerenes and endohedral fullerenes, was first shown by Dodziuk and Dolgonos [83–86], and Grimme *et al.* [87–89].

⁹ The corresponding fragment: “We conclude that there is a near free precession movement of diatomic Ng₂ around its midpoint in the C₆₀ cage, with the possible exception of Xe₂ dimer”. If we adopt that “a near free precession movement of diatomic Ng₂ around its midpoint in the C₆₀ cage” is a motion of the dumbbell type, then what is the “handle” of this dumbbell? The bond?

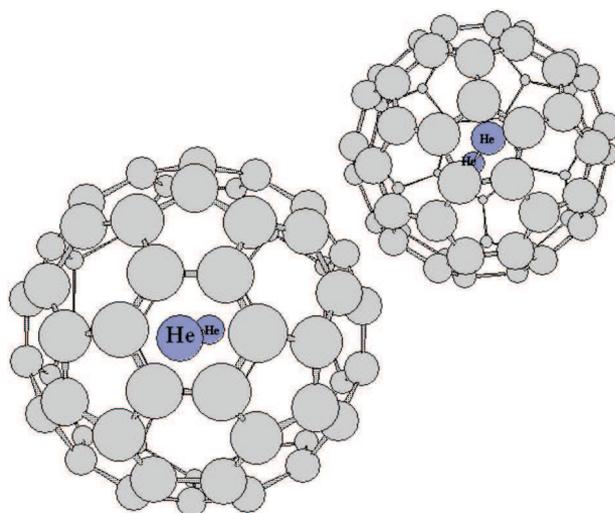


Fig. 2. Optimized structure of endofullerene He₂@C₆₀. Carbon atoms are marked grey, and helium atoms blue. The top-right insert demonstrates two He atoms inside He₂@C₆₀. The latter is oriented so that the observer looks through the C₆₀ pentagonal face “window”

gives $r_5 = 1.452$ Å for the length of the edge common for the pentagon and hexagon ($r_5 = 1.495$ Å in C₆₀) and $r_6 = 1.388$ Å for the length of the common edge of two neighbor hexagons ($r_6 = 1.391$ Å in C₆₀).

4. History of the Problem

Let us begin to discuss the history of the problem formulated above by considering old works dealing with the behavior of the inert helium atom interacting with other molecules. First of all, a few comments should be made concerning the bond concept [91, 92], with the starting point being undoubtedly quantum-mechanical, irrespective of the binding type. It is evident that the bonding between a pair of interacting atoms assumes the formation of a diatomic molecule. On the one hand, the molecule is an embodiment of the bond (bonds) and vice versa. On the other hand, an existing molecule is more energetically stable than its atoms. In other words, the molecule has a lower energy than its atoms. More specifically, the ground-state energy of a molecule must be compared with the energies of its atoms. Vice versa, the corresponding energy shift determines the energy required to break the bond.

As an example, consider the HeH system, which is the simplest neutral heteroatomic molecule. In the

Table 1. Calculation results for a He₂ dimer obtained at the levels MP2/aug-cc-pV5Z and M06-2X/aug-cc-pV5Z with the help of the MOLPRO 2010.1 (M) [98, 99] and Gaussian09 (G09) [80] software codes. The values obtained for $\Delta_{\text{ZPE}}E(\text{He}_2)$ are in good agreement with the results of Luo *et al.* [100–102], Gdanitz [103], Zhao and Truhlar [104], and Szalewicz *et al.* [105, 106]. For example, $\Delta_{\text{ZPE}}E(\text{He}_2) = -10.980 \pm 0.004$ K at $R(\text{He} - \text{He}) = 2.9634$ Å [103] and $\Delta_{\text{ZPE}}E(\text{He}_2) = -11.0006(2)$ K at $R(\text{He} - \text{He}) = 2.9634$ Å [105] (see Tabl. 2)

Levels	$R(\text{He-He}), \text{Å}$	$\Delta E(\text{He}_2), \text{kcal/mol}$	ZPE, kcal/mol	$\Delta_{\text{ZPE}}E(\text{He}_2), \text{K}$
MP2/aug-cc-pV5Z M	3.0496	-0.01402	0.04048	-13.3
MP2/aug-cc-pV5Z G09	3.0682	-0.01406	0.03815	-12.2
CCSD(T)/aug-cc-pV5Z M	2.9801	-0.02041	0.04695	-13.4
M06-2X/aug-cc-pV5Z G09	2.8880	-0.11440	0.11900	-2.3

ground electron state $X^2\Sigma^+$, its potential energy curve (PEC) is very shallow (see works [93, 94] and references therein). It has the van der Waals minimum $D_e = 4.720 \text{ cm}^{-1} = 6.79$ K at the equilibrium interatomic H-He distance $R_e = 3.548$ Å. It was proved [93, 94] that the small depth of a potential well cannot provide the existence of any bound state, including the ground one. Therefore, the ground electron state $X^2\Sigma^+$ of the HeH system is unstable.

Another example concerns the ground state of the dimer He₂. Since 1928, when Slater performed the first calculation of the potential well depth $\Delta E = -8.9$ K for He₂ in the ground state [95], this value is reproduced by almost each quantum chemist.

In order to continue our discussion, let us consider the ground state of a He dimer at two theoretical levels: MP2/aug-cc-pV5Z (see work [96], as well as work [90]) and M06-2X/aug-cc-pV5Z. The both are available in the Gaussian software package [80]. The results of corresponding calculations are summarized in Table 1. They demonstrate that the only contribution to ΔE is given by the energy of zero vibrations, so that ΔE reaches 2.4 K at a He-He distance of about 3 Å [97]. Of course, this energy is rather low, being not sufficient to maintain even a single bound state, which is required for a stable molecule to exist (see works [107, 108]).

Almost till 1994, it was not clear whether a stable He₂ dimer can exist [107–109]. However, the diffraction experiments carried out in 1994, unambiguously proved that ${}^2\text{He}^4$ does exist. This is a stable diatomic molecule characterized by the average bond length $\langle R \rangle = 52$ Å and $\Delta E = 1,3$ mK [107, 108]. Certainly, this averaged bond length considerably exceeds the diameter d_{60} of the C₆₀ cavity, which is equal to

Table 2. Experimental and computational results for a helium dimer: $\langle R \rangle$ is the averaged bond length, D_o the dissociation energy

Source	$\langle R \rangle, \text{Å}$	D_o
Diffraction experiments [107, 108]	52	151.9 ± 13.3 neV
Luo <i>et al.</i> [100]	62 ± 10	0.65–1.30 K
Gdanitz [103], $(r_{12})\text{MR-CI}$	46.4 ± 1.4	1.67 ± 0.11 K
Szalewicz <i>et al.</i> [106], four-electron correlated set of basis functions ^a	47.50 ± 0.46	136.6 ± 2.9 neV

^a In work [106], it was also shown that the dimer ${}^4\text{He}_2$ has only one weakly bound vibrational state. This is an example of a quantum “halo” state, in which atoms predominantly move in the classically forbidden tunnel region of the configuration space.

7.14 Å (see the figure caption in Fig. 1). Therefore, this cavity may turn out insufficient to arrange the He₂ dimer, thereby excluding that the He₂ dimer is still bound in C₆₀. As was asserted in work [79], the He-He binding in He₂@C₆₀ is a result of the following mechanism. The repulsive interaction between two helium atoms moves them away from the C₆₀ center and closer to the C₆₀ surface. In addition, it establishes the charge transfer between He and C₆₀.

5. Arguments Pro and Contra the Bond

Let us proceed from the intriguing problem about the existence of a He-He bond in He₂@C₆₀. According to work [111],

“...Ng-Ng bond is present only in Xe₂@C₆₀ while He₂@C₆₀ and Ne₂@C₆₀ are weakly bonded van der Waals complexes. In the former case of the heavy no-

ble gas, there is a considerable charge transfer between the guest and the host cavity. This effect, which is thought to be responsible for the bonding in endohedral metal complexes, is considered to be responsible for the Xe–Xe bonding in the complex with C₆₀. In view of a relatively close distance between He and Ne atoms inside C₆₀ and changes in properties of the host and guests after the complexation, one often speaks about the He₂@C₆₀ [59] and Ne₂@C₇₀ [87] complexes, in which the noble gases form weakly bound van der Waals molecules. In any case, the latter complexes illustrate the impact the encapsulation can have on a guest”.

Let us first consider the formation mechanism of Ng_n@C₆₀ complexes with $n = 1, 2$ by the example of He. Its three stages can be distinguished. At stage I, a He atom approaches C₆₀ from the infinity and participates in the formation of the exohedral complex He–C₆₀ [112]. At stage II, the He atom, with the help of the so-called “window mechanism” [113–118], overcomes the corresponding “window barrier” and penetrates into the C₆₀ “cage” [119]. The experimentally determined height of this barrier is approximately 90 kcal/mol [120], whereas the estimates calculated at the theoretical level B3LYP//MNDO [121, 122] are more than twice as large: 229–262 kcal/mol. In this work, the height of the “window barrier” for the penetration of a He atom into C₆₀ was put to equal about 240.2 kcal/mol.

Stage III completes the formation of He@C₆₀. This complex is stable, because the energy of its formation or binding, which can be denoted as

$$\Delta E[\text{He}@C_{60}] := E[\text{He}@C_{60}] - E[C_{60}] - E[\text{He}],$$

where $E[X]$ is the total energy of the given system X ($X = \text{He}@C_{60}$, C₆₀, and He) in its equilibrium geometry, is negative and varies by absolute value from 0.1 to 2.1 kcal/mol depending on the theoretical level used in calculations [121, 123, 124]. The quantity $\Delta E[\text{He}@C_{60}]$ is illustrated in Fig. 3, in which it was emphasized that, from the viewpoint of quantum-mechanical theory, for the complex He@C₆₀ to be stable, there must be at least one bound state in the interval $\Delta E[\text{He}@C_{60}]$. The energy $\Delta_{\text{ZPE}} E[\text{He}@C_{60}]$, which includes a correction for the energy of zero vibrations, can be determined analogously. Note that the charge of a He atom located inside He@C₆₀ equals zero, as follows from the results of calculations at the theoretical level MP2/6-31G//HF/6-31G [125] (see

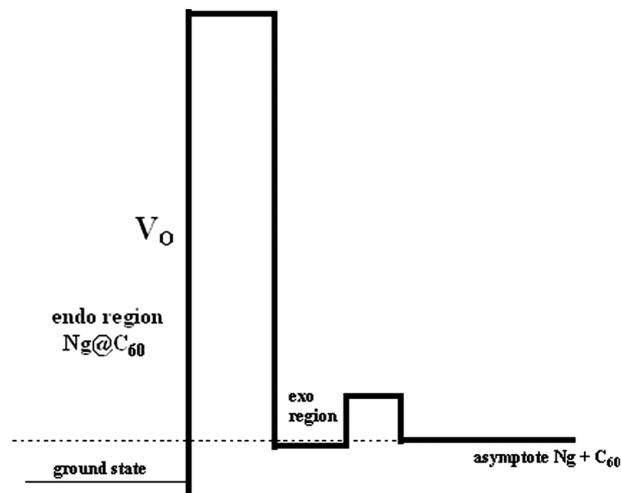


Fig. 3. Schematic diagram of the potential energy profile describing the formation of He@C₆₀, when a He atom approaches C₆₀ from infinity. The energy difference between the lower left and right lines equals $\Delta E[\text{He}@C_{60}]$. The solid line (marked as “ground state”) within this interval demonstrates the position of the ground-state level, which is a quantum-mechanical attribute of the He@C₆₀ stability. In other words, He@C₆₀ is stable if and only if there is such a ground state between the two indicated asymptotes (see the discussion in Section 6)

work [126]), which testifies to the absence of charge transfer, when He@C₆₀ is formed.

The endohedral fullerene He₂@C₆₀ is a completely different case. Actually, it is observed experimentally. It undoubtedly exists *in silico*: the recent work carried out at the theoretical level SCS-MP2/TZVPP//BP86/TZVPP by Krapp and Frenking [90] predicts the following parameters for the ground state of the complex He₂@C₆₀: the symmetry D_{3d} , the binding energy $\Delta E[\text{He}_2@C_{60}] = -1.25$ kcal/mole, the equilibrium distance $r(\text{He–He}) = 1.953$ Å, and $\inf_{V \in C_{60}} r(\text{He–C}) = 2.696$ Å.

In this work, we propose our arguments concerning the existence of the He–He bond in C₆₀. Our key idea is as follows. All what is always said about He₂@C₆₀ concerns neutral He atoms. However, as was shown in Section 3, the encapsulation of He into fullerene C₆₀ reveals an interesting quantum behavior: all atoms belonging to the fullerene surface within the monoatomic thickness partially ionize the He atoms, which enables them to be dimerized into a dimer (He^δ)₂ ($\delta = +0.01|e|$). This dimer has the following characteristics: the He–He distance

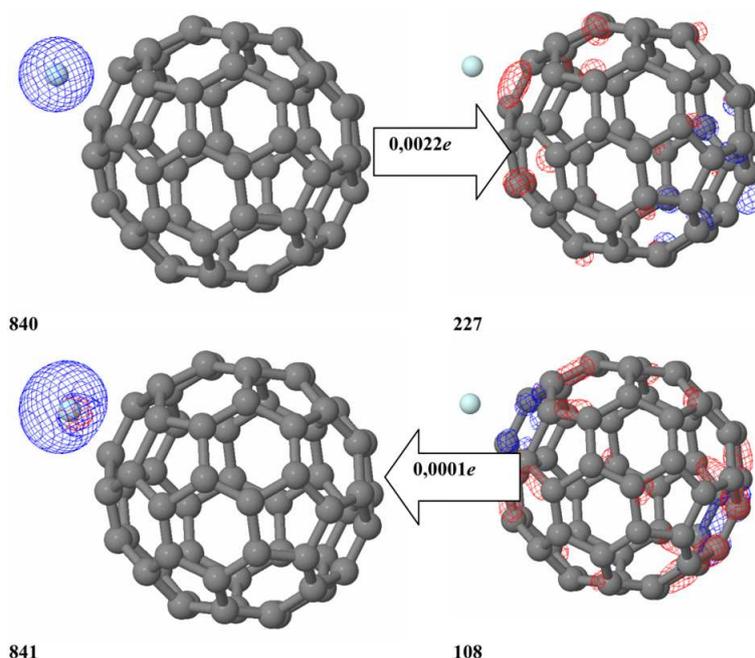


Fig. 4. Isosurfaces of orbitals that give the largest charge transfer. The numbers near the figures correspond to the orbital enumeration used in Tables 2 and 3: orbitals 840 and 227 are quoted in Table 2, and orbitals 108 and 841 in Table 3

equals 1.979 Å, and the He–He stretching frequency 531.0 cm^{-1} . The approach proposed in this work consists of two stages. At the first stage (Section 5.5.1), we use a model to describe a small charge transfer between He and C_{60} .

Before turning to the second stage, we must adopt a rigorous and general – “working” – definition of the bond. Our concept of chemical bonding is based on the following speculations. The bond is a two-particle formation between two atoms. We define this formation as a (diatomic) molecule. Evidently, if the diatomic molecule is defined rigorously, the definition will be valid for its bond as well. Hence, in order to operate with the bond concept, we must choose a “working” definition of molecule. As such, we choose the Löwdin postulate [127–133]:

“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 ”.

It is evident that the Löwdin definition (or postulate) is consistent with the definition adopted in the IUPAC Gold Book [23]:

“molecule. An electrically neutral entity consisting of more than one atom ($n > 1$). Rigorously, a molecule, in which $n > 1$ must correspond to a depression on the potential energy surface that is deep enough to confine at least one vibrational state”.

We always consider a molecule as a combination or set of $n > 1$ atoms, in which the atomic pairs are linked by bonds. In Section 5.2, we demonstrate that the He–He potential curve corresponding to dragging apart two He atoms inside C_{60} has at least a bound state. In the sense of the Löwdin postulate, this means that there is a bond between the helium atoms in $He_2@C_{60}$. Surely, the logic is quite clear here.

5.1. Substantiation 1. Charge transfer between He and C_{60}

In order to estimate the charge transferred between the helium atoms and C_{60} in the endofullerene $He_2@C_{60}$, let us apply the model described in Appendix A. According to it, the total charge transfer from a helium atom to fullerene equals 0.01134 e (Table 2), whereas the charge transfer backward from

Table 3. Orbitals that participate in the charge transfer from He to C₆₀ and give contributions not less than 0.5% to the total charge transfer. Estimates of changes in orbital energies at the given charge transfer are quoted in columns 4, 6, and 7

Transferred charge $Q_{i \rightarrow j}$	Contribution (in %) of this pair of orbitals to the total value of transferred charge	Donor-orbital number	Donor-orbital energy $\varepsilon_i^{\text{He}}$ in a.u.	Acceptor-orbital number	Acceptor-orbital energy $\varepsilon_j^{\text{C}_{60}}$ in a.u.	Orbital energy change owing to charge transfer, kcal/mol
0.00037	3.30	840	-0.64559	182	-0.12898	-0.12
0.00043	3.80	840	-0.64559	188	-0.0459	-0.16
0.0001	0.90	840	-0.64559	191	-0.04195	-0.04
0.00008	0.70	840	-0.64559	202	0.03975	-0.04
0.00006	0.50	840	-0.64559	206	0.075	-0.03
0.00021	1.90	840	-0.64559	212	0.12441	-0.1
0.00103	9.10	840	-0.64559	217	0.16106	-0.52
0.00221	19.50	840	-0.64559	227	0.20223	-1.18
0.00025	2.20	840	-0.64559	230	0.22539	-0.13
0.00103	9.10	840	-0.64559	236	0.25462	-0.58
0.0003	2.60	840	-0.64559	240	0.25833	-0.17
0.00057	5.00	840	-0.64559	241	0.26798	-0.33
0.00046	4.00	840	-0.64559	248	0.29236	-0.27
0.00025	2.20	840	-0.64559	253	0.3168	-0.15
0.00007	0.60	840	-0.64559	264	0.35369	-0.04
0.00021	1.90	840	-0.64559	282	0.39112	-0.14
0.00049	4.30	840	-0.64559	284	0.39274	-0.32
0.00039	3.50	840	-0.64559	285	0.39474	-0.26
0.00072	6.30	840	-0.64559	287	0.39753	-0.47
0.0005	4.40	840	-0.64559	293	0.42719	-0.34
0.0001	0.80	840	-0.64559	301	0.463	-0.07
0.00022	2.00	840	-0.64559	315	0.49353	-0.16
0.00042	3.70	840	-0.64559	328	0.53598	-0.32
0.00007	0.60	840	-0.64559	330	0.5386	-0.05
0.00012	1.00	840	-0.64559	341	0.56555	-0.09
Total: 0.01134 e						

fullerene to the helium atom equals 0.00116 e (Table 3). Thus, in total, the helium atom loses 0.01018 e, which is in good agreement with the NPA charge of a helium atom (+0.01014 e). The isosurfaces of orbitals giving the largest contributions to the charge transfer between the components of the complex (about 20% of the total charge transfer in the He → C₆₀ case and about 11% in the C₆₀ → He case) are shown in Fig. 4.

To summarize, we emphasize that, when talking about the charge transfer from a helium atom to fullerene, no separate fullerene orbital¹⁰ can be dis-

tinguished, the charge transfer onto which dominates. In other words, the charge transferred from the helium atom is proportionally distributed among a lot of fullerene orbitals.

5.2. Substantiation 2: The Ground State of He-He in He₂@C₆₀

In order to satisfy the Löwdin postulate for the He-He bond in He₂@C₆₀, let us first approximate the potential energy curve (PEC) of the dimer He...He embedded into C₆₀ by an analytical function. Afterward, we should solve the Schrödinger equation with the help of perturbation theory. All details of this

¹⁰ For the definition of such orbitals used in our model, see Appendix A.

Table 4. Orbitals that participate in the charge transfer from C₆₀ to He and give contributions not less than 0.5% to the total charge transfer. Estimates of changes in orbital energies at the given charge transfer are quoted in columns 4, 6, and 7

Transferred charge $Q_{i \rightarrow j}$	Contribution (in %) of this pair of orbitals to the total value of transferred charge	Donor-orbital number	Donor-orbital energy $\varepsilon_i^{\text{He}}$ in a.u.	Acceptor-orbital number	Acceptor-orbital energy $\varepsilon_j^{\text{C}_{60}}$ in a.u.	Orbital energy change owing to charge transfer, kcal/mol
0.00001	0.70	68	-0.90317	841	1.30114	-0.01
0.00001	1.20	75	-0.83122	841	1.30114	-0.02
0.00004	3.30	84	-0.76233	841	1.30114	-0.05
0.00002	1.30	92	-0.70333	841	1.30114	-0.02
0.00006	5.40	95	-0.65985	841	1.30114	-0.08
0.00002	1.30	98	-0.63012	841	1.30114	-0.02
0.00002	2.00	104	-0.60441	841	1.30114	-0.03
0.00013	10.80	108	-0.55479	841	1.30114	-0.15
0.00003	2.70	116	-0.51876	841	1.30114	-0.04
0.00008	6.70	119	-0.49599	841	1.30114	-0.09
0.00001	0.60	120	-0.49072	841	1.30114	-0.01
0.00008	7.10	122	-0.47099	841	1.30114	-0.09
0.00007	5.60	127	-0.46154	841	1.30114	-0.07
0.00001	1.10	132	-0.45011	841	1.30114	-0.01
0.00007	6.30	136	-0.43375	841	1.30114	-0.08
0.00007	5.70	146	-0.41434	841	1.30114	-0.07
0.00002	1.90	148	-0.39496	841	1.30114	-0.02
0.00007	6.40	151	-0.36924	841	1.30114	-0.08
0.0001	8.50	165	-0.33964	841	1.30114	-0.1
0.00001	0.70	172	-0.27836	842	1.84189	-0.01
0.00001	0.70	173	-0.27832	843	1.85778	-0.01
0.00009	7.90	174	-0.27172	841	1.30114	-0.09
0.00001	0.90	178	-0.22934	842	1.84189	-0.01
0.00001	0.80	179	-0.22932	843	1.85778	-0.01
Total: 0.00116 e						

approach are described in Appendix B. The He–He PEC in the interval of He–He distances from 1.45 to 2.89 Å is shown in Fig. 5. At the ends of this interval, the energy amounts to about 15 kcal/mole. Table 4, in which the eigenstates of the system, i.e. the solutions of the corresponding Schrödinger equations, are summarized, demonstrates that the considered interval of He–He distances includes at least 10 bound states. Thus, we arrive at the conclusion that, according to the Löwdin postulate, the He–He bond in He₂@C₆₀ does exist, Q.E.D.

Finally, we note that, according to Table 4, the dependence of the transition energy between vibrational states, for which the vibration quantum num-

bers n differs by one, amounts to 1.52 kcal/mol for the transition $n = 0 \rightarrow n = 1$ in the harmonic approximation (which corresponds to 531.0 cm⁻¹) and to 1.49 kcal/mole (521.8 cm⁻¹), if the anharmonicity is taken into account. The latter transition energy value decreases to 1.25 kcal/mole (437.7 cm⁻¹) for the transition $n = 9 \rightarrow n = 10$.

6. Final comments and Conclusions

Nothing exists except atoms and empty space, everything else is opinion.

DEMOCRITUS

After all the results of this work have been presented above, let us formulate our key speculations and con-

cepts. The early chemistry of endohedral fullerenes He@C₆₀ and He₂@C₆₀¹¹ was based on two issues: the bond and the molecule. Therefore, two corresponding definitions were required in order to describe the physically observed He₂@C₆₀, although the available works, in which He@C₆₀ was considered, dealt with either the He–C₆₀ bond or the same bond in He@adamantane (see, e.g., works [135–137]).

Nevertheless, one may agree with work [136, p. 9107] that “In order to understand the chemical bonding, we must first define the concept of ‘stability’, i.e. we must compare a stable or a metastable system with a reasonably chosen “starting point” with a higher energy”. Therefore, it is natural and reasonable – although we recognize that this is rather a matter of taste – to assume that, if a given molecule does exist, all its bonds also exist. This means that it is natural to propose a single definition for the molecule, as a variant of the general concept, which would serve as a basis for the consideration of endohedral fullerenes with noble gas atoms from the “chemical” viewpoint, i.e. in terms of bonds, charge transport, and related categories. This work is an example of such a study.

We used the experimental observation of He₂@C₆₀ in order to demonstrate, by solving the corresponding Schrödinger equation, that the He₂ dimer¹² exists in the stable form (He^δ)₂ (δ = +0.011 e)¹³ in C₆₀, i.e. it has at least one bound state. We obtained good agreement between the experimental frequency of He–He stretching vibrations, regarded as an indicator of the binding, and the corresponding value obtained numerically. Generally speaking, we proceed from the fact that it is necessary and sufficient to choose only one

¹¹ We exclude He₃@C₆₀ from consideration. Its existence *in silico* was shown in work [121]. Otherwise, it would result in the formation of Efimov states [134] (although the He trimer is surrounded by the carbon atoms of C₆₀), if we assume that the dimer He₂ is unbound.

¹² It will be called dihelium below in accordance with the standard terminology.

¹³ We agree that, from the chemical viewpoint, this charge transfer value is rather insignificant to provide a real charge transfer and a subsequent bonding. However, it should be noted that the smallness of its magnitude directly follows from the well-known “rigid” (or “inertial” in some sense) character of the He atom, which is characterized by the highest ionization energy (24.5874 eV) among all elements of the Periodic table, the low polarizability $\alpha = 0.67 \text{ \AA}^3$, and a rather high electron affinity of C₆₀ (2.66 eV).

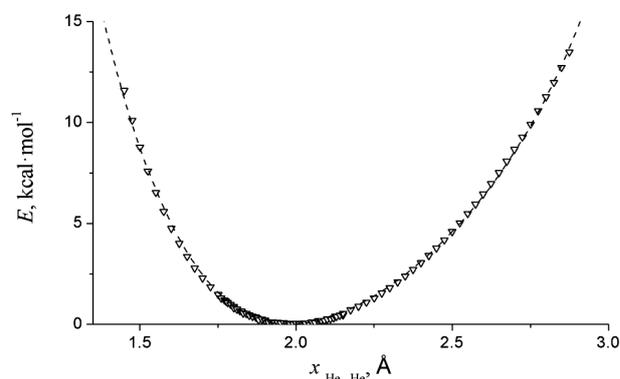


Fig. 5. Dependence of the energy E (in kcal/mol units) of the helium dimer He \cdots He embedded into fullerene C₆₀ on the distance between the helium atoms. Triangles correspond to calculation results obtained at the theoretical level M06-2X/6-31G(d), and the dashed curve $U(x)$ to the approximation of those energy values by the fourth-order polynomial (18) with parameters (19)

Table 5. Ground-state energy and first ten excited vibrational states obtained taking and not taking anharmonic corrections into account

Vibrational state	Energy (in harmonic approximation), kcal/mole	Energy (in anharmonic approximation), kcal/mole
0 (ground state)	0.76	0.76
1	2.28	2.25
2	3.80	3.71
3	5.32	5.15
4	6.83	6.57
5	8.35	7.95
6	9.87	9.31
7	11.39	10.64
8	12.91	11.95
9	14.43	13.22
10	15.95	14.48

definition, e.g., for the molecule, in the spirit of the Löwdin postulate (see Section 5), based on the existence of a single bound state.

Then it becomes trivial that if the given He₂ entity inside C₆₀ is a molecule, then, according to this postulate, the He atoms are also bound by means of a bond. The latter is regarded as a “something” that has already been revealed in previous works as a

manifestation of the “dumbbell handel” allowing one atom to “see” the other owing to the “almost free precessional motion of He₂ around its midpoint in the C₆₀ cage” [90, 124, 138]. The authors of works [90] came to the conclusion about the existence of this bond on the basis of very small energy differences between different He₂ orientations. Evidently, the existence of one (ground) state in the potential well is an appropriate quantum-mechanical element in the Löwdin postulate concerning the molecule as a stable formation. It is quite clear that some hypothetical ideas of the nature of the binding in He₂ embedded into He₂@C₆₀ are urgently needed for the current work to be completed. Putting forward hypotheses on this issue, we would like to mention the so-called dihelium [139, 140], or a partial analog of the dication He₂²⁺ [141]¹⁴, or, finally, various polarization effects in endohedral fullerenes (see, e.g., work [143] and references therein, as well as the discussion on the He₂@C₆₀ quadrupole moment in Section 4).

In our opinion, the definition of stability for endo-fullerenes, which are depicted in Fig. 3, on the basis of the existence of a single bound state agrees well with the rigorous interpretation of endohedral fullerenes that was proposed in this work. As a result, the approach developed in this work and which is a littlegnoseological in some sense becomes substantiated. Nevertheless, we believe that the last word on the existence of a He–He bond in He₂@C₆₀ still belongs to quantum crystallography, which can “improve information ... obtained from a crystallographic experiment [in order to show] the binding nature” [144].

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APPENDIX A.

Model of charge transfer between He and C₆₀ in He₂@C₆₀

The electron charge density in the He₂@C₆₀ system was calculated, by using the software package ORCA 3.0.2 [145], with the

¹⁴ Its stability, despite apparent repulsion, was predicted by L. Pauling [142]

help of the functional B3LYP/G and the set of basis functions Def2-svp [146, 147]. In the density functional theory (DFT), the electron density of a system with closed electron shells can be represented as the sum

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_{\text{occ}}} 2 |\psi_i(\mathbf{r})|^2, \quad (3)$$

where $\psi_i(\mathbf{r})$ are the Kohn–Sham orbitals corresponding to the eigenstate energies ε_i . The functions $\psi_i(\mathbf{r})$ can be expanded, by using the basis function set $b_\mu(\mathbf{r})$:

$$\psi_i(\mathbf{r}) = \sum_{\mu} c_{i\mu} b_{\mu}(\mathbf{r}). \quad (4)$$

The coefficients $c_{i\mu}$ in Eq. (4) can be determined, by solving the following eigenvalue problem:

$$\mathbf{F}\mathbf{c}_i = \varepsilon_i \mathbf{S}\mathbf{c}_i, \quad (5)$$

where \mathbf{F} and \mathbf{S} are matrices, whose matrix elements can be written as follows (in the system of atomic units):

$$F_{\mu\nu} = \left(b_{\mu}, \left(-\frac{1}{2}\Delta + \hat{v}_{\text{KS}}(\mathbf{r}) \right) b_{\nu} \right), \quad (6)$$

$$S_{\mu\nu} = (b_{\mu}, b_{\nu}), \quad (7)$$

where $\hat{v}_{\text{KS}}(\mathbf{r})$ is the Kohn–Sham potential.

The corresponding expressions for the subsystems, namely, the He atom and fullerene C₆₀, which are similar to Eqs. (3) and (5), have the following forms:

$$\rho^{\text{He}}(\mathbf{r}) = \sum_{i=1}^{N_{\text{occ}}} 2 \left(\sum_{\mu \in \text{He}} c_{i\mu}^{\text{He}} b_{\mu}(\mathbf{r}) \right)^2, \quad (8)$$

and

$$\mathbf{F}^{\text{He}} \mathbf{c}_i^{\text{He}} = \varepsilon_i^{\text{He}} \mathbf{S}^{\text{He}} \mathbf{c}_i^{\text{He}}, \quad (9)$$

for He, and analogous expressions for C₆₀. In Eq. (9), \mathbf{S}^{He} is a diagonal submatrix in the overlap matrix \mathbf{S} , in which only those columns and rows were left, which correspond to the indices of basis functions $b_{\mu}(\mathbf{r})$ that are centered at the He atom. If we consider an isolated He atom in the gas phase, the elements of matrix \mathbf{F}^{He} look like

$$F_{\mu\nu}^{\text{He}} = \left(b_{\mu}, \left(-\frac{1}{2}\Delta + \hat{v}_{\text{KS}}^{\text{He}}(\mathbf{r}) \right) b_{\nu} \right).$$

However, when considering the charge transfer between He and C₆₀, it is expedient that a He atom with the Kohn–Sham potential that is realized in the complex with fullerene rather than with the Kohn–Sham potential $\hat{v}_{\text{KS}}^{\text{He}}(\mathbf{r})$ should be chosen as a “reference point”. In this approximation, the both matrices \mathbf{S}^{He} and \mathbf{F}^{He} become diagonal subblocks of the corresponding matrices in expressions (6) and (7). This point is a key approximation for the model proposed in this appendix.

This approximation is quite similar to the approximation used in the NBO method [148–151], when evaluating the charge transfer (or the electron delocalization) in a real system and in the idealized Lewis structure. However, it is worth noting that,

in the framework of the NBO method, the charge transfer between orbitals localized at one and/or two atoms is considered, as a rule. Instead, in order to solve the problem formulated in this work, it is necessary to research the charge transfer between one- and 60-atomic systems located within the examined complex. Therefore, we present below the calculations bringing us to an expression for the charge transfer that turns out similar to the expression used in the NBO method. At the same time, it is adapted exactly to the system concerned. These calculations may also have some methodological value, because we do not know other literature sources that would contain a rather detailed and consistent derivation of the expression used while calculating the charge transfer magnitude in the framework of the NBO method.

For convenience, we begin from some expressions that are required for studying the charge transfer between He and C₆₀. The elements of all matrices will be considered in the basis of orthonormal functions $(b_\mu, b_\nu) = \delta_{\mu\nu}$ – namely, the so-called natural atomic orbital (NAO) basis set – which were obtained for the examined system using the NAO method [152, 153] and the JANPA software package [153, 154]. In this basis, the overlap matrix \mathbf{S} is a unit matrix, so that it is omitted in the expressions below.

Hence, similarly to the approach applied in the NBO method, we express the matrix \mathbf{F} in the form

$$\mathbf{F} = \begin{pmatrix} \mathbf{F}^{\text{He}} & 0 \\ 0 & \mathbf{F}^{\text{C}_{60}} \end{pmatrix} + \begin{pmatrix} 0 & \mathbf{F}_{12} \\ \mathbf{F}_{12}^T & 0 \end{pmatrix} \equiv \mathbf{F}_0 + \mathbf{V}, \quad (10)$$

where \mathbf{V} is a small correction. The eigenvectors of the matrix \mathbf{F} are constructed from the eigenvectors of matrices \mathbf{F}^{He} and $\mathbf{F}^{\text{C}_{60}}$ using the perturbation method.

Let us denote the μ -components of the j -th eigenvector of the matrices $\begin{pmatrix} \mathbf{F}^{\text{He}} & 0 \\ 0 & 0 \end{pmatrix}$ and $\begin{pmatrix} 0 & 0 \\ 0 & \mathbf{F}^{\text{C}_{60}} \end{pmatrix}$ as $c_{j\mu}^{\text{He}}$ and $c_{j\mu}^{\text{C}_{60}}$, respectively, and the eigenvalues corresponding to those vectors as $\varepsilon_i^{\text{He}}$ and $\varepsilon_j^{\text{C}_{60}}$. In these notations, the following equality is true for any i and j :

$$c_{i\mu}^{\text{He}} c_{j\mu}^{\text{C}_{60}} = 0, \quad (11)$$

because the μ -th component can be non-zero either in the vector $c_{i\mu}^{\text{He}}$ (if the μ -th basis function belongs to the He atom) or in the vector $c_{j\mu}^{\text{C}_{60}}$ (if the μ -th basis function belongs to the carbon atom of fullerene C₆₀), but not in the both vectors simultaneously.

In addition, the set of vectors \mathbf{c}_i^{He} and $\mathbf{c}_j^{\text{C}_{60}}$ can be used to create a unitary matrix that transforms the matrix \mathbf{F} to a form, in which its subblocks \mathbf{F}^{He} and $\mathbf{F}^{\text{C}_{60}}$ are diagonal. Below, we assume that the matrix \mathbf{F} is written in this basis.

By applying the perturbation theory, in a first approximation for the orbital expansion coefficients, we obtain

$$\mathbf{c}_i \approx \begin{cases} \mathbf{c}_i^{\text{He}} + \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{He}} - \varepsilon_j^{\text{C}_{60}}} \mathbf{c}_j^{\text{C}_{60}}, \\ \mathbf{c}_i^{\text{C}_{60}} + \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{C}_{60}} - \varepsilon_j^{\text{He}}} \mathbf{c}_j^{\text{He}}. \end{cases}$$

These vectors are normalized to unity only in the first approximation. Therefore, it is convenient to exactly normalize them to unity by rewriting them in the form

$$\mathbf{c}_i \approx \begin{cases} \left(\mathbf{c}_i^{\text{He}} + \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{He}} - \varepsilon_j^{\text{C}_{60}}} \mathbf{c}_j^{\text{C}_{60}} \right) A_i^{\text{He}}, \\ \left(\mathbf{c}_i^{\text{C}_{60}} + \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{C}_{60}} - \varepsilon_j^{\text{He}}} \mathbf{c}_j^{\text{He}} \right) A_i^{\text{C}_{60}}, \end{cases}$$

where the normalizing constants

$$A_i^{\text{He}} = \left(1 + \sum_{j \neq i} \left(\frac{V_{ij}}{\varepsilon_i^{\text{He}} - \varepsilon_j^{\text{C}_{60}}} \right)^2 \right)^{-1/2} \quad (12)$$

and

$$A_i^{\text{C}_{60}} = \left(1 + \sum_{j \neq i} \left(\frac{V_{ij}}{\varepsilon_i^{\text{C}_{60}} - \varepsilon_j^{\text{He}}} \right)^2 \right)^{-1/2} \quad (13)$$

are introduced. These constants are close to, but a little smaller than unity. Now, according to Eq. (3), the electron charge density in the system can be written in the first approximation as follows:

$$\begin{aligned} \rho(\mathbf{r}) \approx & 2 \sum_i \left(A_i^{\text{He}} \right)^2 \left(\sum_\mu c_{i\mu}^{\text{He}} b_\mu(\mathbf{r}) + \right. \\ & \left. + \sum_\mu b_\mu(\mathbf{r}) \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{He}} - \varepsilon_j^{\text{C}_{60}}} c_{j\mu}^{\text{C}_{60}} \right)^2 + \\ & + 2 \sum_i \left(A_i^{\text{C}_{60}} \right)^2 \left(\sum_\mu c_{i\mu}^{\text{C}_{60}} b_\mu(\mathbf{r}) + \right. \\ & \left. + \sum_\mu b_\mu(\mathbf{r}) \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{C}_{60}} - \varepsilon_j^{\text{He}}} c_{j\mu}^{\text{He}} \right)^2 = \left(\rho^{\text{He}}(\mathbf{r}) + \delta\rho^{\text{He}}(\mathbf{r}) \right) + \\ & + \left(\rho^{\text{C}_{60}}(\mathbf{r}) + \delta\rho^{\text{C}_{60}}(\mathbf{r}) \right) + \delta\rho^0(\mathbf{r}), \end{aligned} \quad (14)$$

where the notations

$$\begin{aligned} \rho^{\text{He}}(\mathbf{r}) &= \sum_i 2 \left(A_i^{\text{He}} \right)^2 \left(\sum_\mu c_{i\mu}^{\text{He}} b_\mu(\mathbf{r}) \right)^2, \\ \rho^{\text{C}_{60}}(\mathbf{r}) &= \sum_i 2 \left(A_i^{\text{C}_{60}} \right)^2 \left(\sum_\mu c_{i\mu}^{\text{C}_{60}} b_\mu(\mathbf{r}) \right)^2 \end{aligned}$$

were introduced for the electron densities of subsystems (He and C₆₀, respectively) regarded as “non-interacting” with each other. Furthermore, the corrections described by the expressions

$$\begin{aligned} \delta\rho^{\text{He}} &= \sum_i 2 \left(A_i^{\text{He}} \right)^2 \left(\sum_\mu b_\mu(\mathbf{r}) \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{He}} - \varepsilon_j^{\text{C}_{60}}} c_{j\mu}^{\text{C}_{60}} \right)^2, \\ \delta\rho^{\text{C}_{60}} &= \sum_i 2 \left(A_i^{\text{C}_{60}} \right)^2 \left(\sum_\mu b_\mu(\mathbf{r}) \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{C}_{60}} - \varepsilon_j^{\text{He}}} c_{j\mu}^{\text{He}} \right)^2, \\ \delta\rho^0(\mathbf{r}) &= \sum_i 4 \left(A_i^{\text{He}} \right)^2 \sum_\mu c_{i\mu}^{\text{He}} b_\mu(\mathbf{r}) \sum_\nu b_\nu(\mathbf{r}) \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{He}} - \varepsilon_j^{\text{C}_{60}}} c_{j\nu}^{\text{C}_{60}} + \\ & + \sum_i 4 \left(A_i^{\text{C}_{60}} \right)^2 \sum_\nu c_{i\nu}^{\text{C}_{60}} b_\nu(\mathbf{r}) \sum_\mu b_\mu(\mathbf{r}) \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{C}_{60}} - \varepsilon_j^{\text{He}}} c_{j\mu}^{\text{He}} \end{aligned}$$

were separated, which characterize the difference between the sum $\rho^{\text{He}}(\mathbf{r}) + \rho^{\text{C}_{60}}(\mathbf{r})$ and the density $\rho(\mathbf{r})$ of the researched system. It should be noted that since we use the orthonormal basis functions $((b_\mu, b_\nu) = \delta_{\mu\nu})$, we have

$$\int \delta\rho^0(\mathbf{r})d\mathbf{r} = 4 \sum_i (A_i^{\text{He}})^2 \sum_\mu c_{i\mu}^{\text{He}} \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{He}} - \varepsilon_j^{\text{C}_{60}}} c_{j\mu}^{\text{C}_{60}} + 4 \sum_i (A_i^{\text{C}_{60}})^2 \sum_\nu c_{i\nu}^{\text{C}_{60}} \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{C}_{60}} - \varepsilon_j^{\text{He}}} c_{j\nu}^{\text{He}} = 0,$$

where the property $c_{i\mu}^{\text{He}} c_{j\mu}^{\text{C}_{60}} = 0$ mentioned above was also used. Hence, the sums $\rho^{\text{He}}(\mathbf{r}) + \delta\rho^{\text{He}}(\mathbf{r})$ and $\rho^{\text{C}_{60}}(\mathbf{r}) + \delta\rho^{\text{C}_{60}}(\mathbf{r})$ in the first approximation, they satisfy the equality

$$\int \rho(\mathbf{r})d\mathbf{r} = \int (\rho^{\text{He}}(\mathbf{r}) + \delta\rho^{\text{He}}(\mathbf{r}))d\mathbf{r} + \int (\rho^{\text{C}_{60}}(\mathbf{r}) + \delta\rho^{\text{C}_{60}}(\mathbf{r}))d\mathbf{r}$$

– can be interpreted as the electron densities of He and C_{60} , respectively, which interact with each other as the components of endohedral fullerene $\text{He}_2@C_{60}$. In addition, the densities $\rho^{\text{He}}(\mathbf{r})$ and $\rho^{\text{C}_{60}}(\mathbf{r})$ can be considered (in the same approximation) as the densities of the non-interacting He and C_{60} in $\text{He}_2@C_{60}$.

Thus, the quantities $\delta\rho^{\text{He}}(\mathbf{r})$ and $\delta\rho^{\text{C}_{60}}(\mathbf{r})$ have the meaning of the electron charge density that is transferred from fullerene to the He atom and from the He atom to fullerene, respectively, due to their interaction in the $\text{He}_2@C_{60}$ complex. Making allowance for this interpretation, we obtain the value of the total transferred electron charge,

$$\int \rho^{\text{He}}(\mathbf{r})d\mathbf{r} = \sum_i 2 (A_i^{\text{He}})^2 \sum_\mu (c_{i\mu}^{\text{He}})^2,$$

where $(A_i^{\text{He}})^2 < 1$, and $\sum_\mu (c_{i\mu}^{\text{He}})^2 = 1$ or 0 depending on whether the i -th orbital belongs to the He atom or not. Hence, the integral $\int \rho^{\text{He}}(\mathbf{r})d\mathbf{r}$ turns out less than the total electron charge of the He atom. Analogously, $\int \rho^{\text{C}_{60}}(\mathbf{r})d\mathbf{r}$ is less than the total charge of fullerene electrons. At the same time, it should be noted that the expressions for $\delta\rho^{\text{He}}(\mathbf{r})$ and $\delta\rho^{\text{C}_{60}}(\mathbf{r})$ are proportional both to $(A_i^{\text{He}})^2$ and $(A_i^{\text{C}_{60}})^2$, as well as to the squared matrix elements V_{ij} , which, according to the assumption made above, are already small quantities of the first order. Therefore, in order to determine the first-order terms in the expansions of $\delta\rho^{\text{He}}(\mathbf{r})$ and $\delta\rho^{\text{C}_{60}}(\mathbf{r})$ in V_{ij} , we must neglect the dependence of $(A_i^{\text{He}})^2$ and $(A_i^{\text{C}_{60}})^2$ on V_{ij} [see Eqs. (12) and (13)] and put $(A_i^{\text{He}})^2$ and $(A_i^{\text{C}_{60}})^2$ equal to unity.

Then, considering the orthonormal character of basis functions, we obtain the following expression for the complete transferred charge:

$$\int \delta\rho^{\text{He}}d\mathbf{r} = \sum_i 2 \sum_{j \neq i} \frac{V_{ij}}{\varepsilon_i^{\text{He}} - \varepsilon_j^{\text{C}_{60}}} \sum_\mu c_{j\mu}^{\text{C}_{60}} c_{k\mu}^{\text{C}_{60}} \sum_{j \neq i} \frac{V_{ik}}{\varepsilon_i^{\text{He}} - \varepsilon_j^{\text{C}_{60}}} =$$

$$= \sum_i 2 \sum_{j \neq i} \left(\frac{V_{ij}}{\varepsilon_i^{\text{He}} - \varepsilon_j^{\text{C}_{60}}} \right)^2.$$

Here, the orthogonality of eigenvectors, namely,

$$\sum_\mu c_{j\mu}^{\text{C}_{60}} c_{k\mu}^{\text{C}_{60}} = (\mathbf{c}_j^{\text{C}_{60}}, \mathbf{c}_k^{\text{C}_{60}}) = \delta_{jk},$$

was also used. Analogously, we can obtain that

$$\int \delta\rho^{\text{C}_{60}}d\mathbf{r} = 2 \sum_i \sum_{j \neq i} \left(\frac{V_{ij}}{\varepsilon_i^{\text{C}_{60}} - \varepsilon_j^{\text{He}}} \right)^2 = \int \delta\rho^{\text{He}}d\mathbf{r}.$$

Hence, the electron charge transferred between the subsystems is the sum of the components

$$Q_{i \rightarrow j} = 2 \left(\frac{V_{ij}}{\varepsilon_i^{\text{He}} - \varepsilon_j^{\text{C}_{60}}} \right)^2, \quad (15)$$

which can be interpreted as the electron charge transferred from the i -th orbital of He onto the j -th orbital of fullerene in the examined complex. As was marked above, the expression obtained is identical to that used in the standard NBO method [148–151]; namely,

$$Q_{i \rightarrow j}^{\text{CT}} = n_i^0 \cdot \frac{|\langle \varphi_i | \mathbf{F} | \varphi_j \rangle|^2}{(\varepsilon_j^0 - \varepsilon_i^0)^2}, \quad (16)$$

where $n_i^0 = 2, 0$ is the population of the φ_i -orbital in the donor molecule, from which the charge is transferred, $\varepsilon_i^0 = \langle \varphi_i | \mathbf{F} | \varphi_i \rangle$ is the energy of this orbital in the complex provided that it does not interact with other complex components, φ_j is the charge-acceptor orbital, and $\varepsilon_j^0 = \langle \varphi_j | \mathbf{F} | \varphi_j \rangle$ is its energy in the complex provided that it does not interact with other complex components. Concerning expression (16) for $Q_{i \rightarrow j}^{\text{CT}}$, it is worth noting that the elements of the matrix diagonal subblocks do not contribute to the matrix elements \mathbf{F} , because the i -th and j -th orbitals definitely belong to different molecules of the studied complex. We should also mark the expression

$$\Delta E^{(2)} = n_i^0 \cdot \frac{|\langle \varphi_i | \mathbf{F} | \varphi_j \rangle|^2}{\varepsilon_j^0 - \varepsilon_i^0} = Q_{i \rightarrow j}^{\text{CT}} \cdot (\varepsilon_j^0 - \varepsilon_i^0), \quad (17)$$

It is used in the NBO method mentioned above in order to evaluate the decrease in the energy of the donor orbital associated with the charge transfer onto an acceptor orbital that was completely unoccupied in the unperturbed system.

In order to evaluate the charge transfer with the help of expression (15), a software code was developed [155] using the Python programming language. The input data for calculations include only the matrix \mathbf{F} in the basis of NAO-orbitals of the complex. From this matrix, the program separates the diagonal subblocks \mathbf{F}^{He} and $\mathbf{F}^{\text{C}_{60}}$, as well as the correction \mathbf{V} according to Eq. (10). Information about the localization of that or another basis NAO orbital—at the He atom or at fullerene—is also used. Then the matrices \mathbf{F}^{He} and $\mathbf{F}^{\text{C}_{60}}$ are diagonalized in order to calculate the components $c_{j\mu}^{\text{He}}$ and $c_{j\mu}^{\text{C}_{60}}$ of their eigenvectors and the corresponding eigenvalues $\varepsilon_j^{\text{He}}$ and $\varepsilon_j^{\text{C}_{60}}$. Note that the enumeration of eigenvectors and eigenvalues corresponds to their ranging in accordance with the growth of the

energies $\varepsilon_j^{\text{He}}$ and $\varepsilon_j^{\text{C}_{60}}$. These eigenvectors are further used to construct a unitary matrix that transforms the matrix \mathbf{F} into a form, in which its diagonal subblocks \mathbf{F}^{He} and $\mathbf{F}^{\text{C}_{60}}$ are diagonal. Finally, expression (15) is used to determine the value of the transferred electron charge. In addition, the transferred charge value, the change in the orbital energy is also calculated by formula (17). The rest of the program creates output files in the MOLDEN-type format for storing the components of the vectors $c_{j\mu}^{\text{He}}$ and $c_{j\mu}^{\text{C}_{60}}$ of the corresponding orbitals of the He atom and fullerene C₆₀, respectively. Afterward, those files are used to visualize the orbitals that participate in the charge transfer using the JMOL program [156, 157].

APPENDIX B.

Determination of the Ground Vibrational State of the He Dimer Inside He₂@C₆₀ Using the Perturbation Method

With the help of the Gaussian 09 software package [80], a relaxed scanning of the He–He potential energy curve was performed at the theoretical level M06-2X/6-31G*. The scanning was carried out within the interval of He–He distances $R_{\text{He–He}}$ from 1.45 to 2.89 Å. In total, 101 pairs of values for $x = R_{\text{He–He}}$ and the corresponding energies $E_{\text{PE}} = E_{\text{PE}}(x)$ were obtained. The obtained dependence $E_{\text{PE}}(x)$ was approximated by the fourth-order polynomial

$$U(x) = V_0 + \frac{k}{2}(x - x_0)^2 + \alpha(x - x_0)^3 + \beta(x - x_0)^4, \quad (18)$$

where the fitting parameters x_0 , k , α , and β were determined using the least-squares method. The corresponding values are as follows:

$$\begin{aligned} x_0 &= 1.98 \text{ \AA}, \\ k &= 47.9 \text{ kcal/mole}^{-1} \cdot \text{\AA}^{-2}, \\ \alpha &= -21.7 \text{ kcal/mole}^{-1} \cdot \text{\AA}^{-3}, \\ \beta &= 15.7 \text{ kcal/mole}^{-1} \cdot \text{\AA}^{-4}. \end{aligned} \quad (19)$$

The both potential energy curves, $E_{\text{PE}}(x)$ and $U(x)$, are shown in Fig. 5. The mean-square deviation of the approximation $U(x)$ amounts to only 0.1 kcal/mole. Therefore, below, we neglect the difference between $E_{\text{PE}}(x)$ and $U(x)$.

Let us consider the system He₂@C₆₀, in which the fullerene (i) creates an external potential describing by polynomial (18) and (ii) contains the helium dimer. Let us analyze the dimer motion in this field. The dihelium consists of two atoms and, hence, has only six degrees of freedom. The latter can be selected as follows: the coordinates of the dimer's center of mass (three degrees of freedom), the dimer orientation in space (two degrees of freedom), and the distance between the atoms in the dimer (the variable x , which was introduced above). Neglecting the motion of the dimer as a whole, assuming that its center of mass coincides with the center of mass of fullerene, and taking into account an almost spherical symmetry of fullerene molecule, we regard the system energy to be actually independent of the dimer orientation. In this approximation, the

stationary states of the dimer in the fullerene field correspond to the stationary states of a one-dimensional oscillator in the anharmonic potential $U(x)$. Let us consider those states using the perturbation method.

The Ox -axis is selected to be directed along the dimer axis, so that the coordinates of dimer atoms are x_1 and x_2 . Now, by introducing the coordinate of the center of mass $x_c = \frac{x_1 + x_2}{2}$ and the relative coordinate $x = x_2 - x_1$ (the inverse relations are $x_1 = x_c - x/2$ and $x_2 = x_c + x/2$), we can obtain a classical expression for the kinetic energy of the dimer

$$T_x = \frac{m_{\text{He}}}{2} \left(\left(\frac{dx_1}{dt} \right)^2 + \left(\frac{dx_2}{dt} \right)^2 \right),$$

where m_{He} is the mass of helium atom, in the form

$$T_x = \frac{2m_{\text{He}}}{2} \left(\left(\frac{dx_c}{dt} \right)^2 \right) + \frac{\mu}{2} \left(\left(\frac{dx}{dt} \right)^2 \right),$$

where $\mu = m_{\text{He}}/2$ is the reduced mass corresponding to the motion along the relative coordinate x introduced above.

Hence, in the approximations of the stationary center of mass and the spherically symmetric potential field for the fullerene atoms, the Hamiltonian for the He dimer acquires the form

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + U(x) + \hat{T}_{\text{rot}}, \quad (20)$$

where \hat{T}_{rot} is the operator of the rotational kinetic energy of the dimer (we consider the rotational and vibrational motions to be independent). The stationary states of the dimer rotation are known from both the quantum-mechanical problem of the symmetric-top rotation (see, e.g., work [158, p. 103]).

Now, let us proceed to the solution of the problem concerning the energies of dimer vibrational states. For this purpose, it is convenient to use the quantum-mechanical perturbation theory. We adopt a system with the Hamiltonian

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + V_0 + \frac{k}{2}(x - x_0)^2, \quad (21)$$

as an undisturbed one and consider the other summands

$$\nu(x) = \alpha(x - x_0)^3 + \beta(x - x_0)^4$$

in potential (18) as a perturbation. In this case, the calculation of corrections in the framework of the second-order perturbation theory gives rise to the following formula for the energy of stationary states (the corresponding calculations can be found in work [158, section 38, exercise 3]:

$$\begin{aligned} E_n &= \hbar\omega \left(n + \frac{1}{2} \right) - \\ &- \frac{15}{4} \frac{\alpha^2}{\hbar\omega} \left(\frac{\hbar}{m\omega} \right)^3 \left(n^2 + n + \frac{11}{30} \right) + \\ &+ \frac{3}{2} \beta \left(\frac{\hbar}{m\omega} \right)^2 \left(n^2 + n + \frac{1}{2} \right), \end{aligned} \quad (22)$$

where $\omega = \sqrt{\frac{k}{\mu}} = \sqrt{\frac{2k}{m_{\text{He}}}}$ is the frequency of dimer vibrations in the harmonic approximation. Note that a similar approach is

used in spectroscopy to determine the influence of the anharmonicity on the vibration frequency of polyatomic molecules [159, 160]. For the given values of potential parameters, it is easy to obtain that the vibration frequency of the dimer in the harmonic approximation equals 531 cm^{-1} (more accurately, 531.177 cm^{-1}), which coincides with a frequency of 531 cm^{-1} obtained by quantum-chemical calculations of the $\text{He}_2@\text{C}_{60}$ vibrational spectra (see section 2). By rearranging the summands in Eq. (22), we ultimately obtain

$$E_n = \varepsilon_0 + \hbar\omega \left(n + \frac{1}{2}\right) - \hbar\omega x_e \left(n + \frac{1}{2}\right)^2, \quad (23)$$

where $n = 0, 1, 2, \dots$ is the ordinal number of vibrational state. For the values of potential parameters indicated above [Eq. (19)], we obtain

$$\varepsilon_0 = V_0 + \frac{3}{2}\beta b^4 - \frac{7}{2} \frac{\alpha^2 b^6}{\hbar\omega} = 0.002 \text{ kcal/mole},$$

where $b = \sqrt{\frac{\hbar}{2m\omega}} = 0.126 \text{ \AA}$ is the amplitude of zero vibrations, $\hbar\omega = 1,52 \text{ kcal/mole}$, and $x_e = \frac{1}{\hbar\omega} \left(30 \frac{\alpha^2 b^6}{\hbar\omega} - 6\beta b^4\right) = 0.0088$ is the anharmonicity constant. Its small, in comparison with unity, value means that the anharmonic correction (18) is substantial only if the value of $x_e(n + 1/2)^2$ is comparable with unity, i.e. starting from the 10-th excited vibrational state. To illustrate these results, the ground-state energy and the energies of the first 10 excited vibrational states calculated by the formula $E_n = V_0 + \hbar\omega \left(n + \frac{1}{2}\right)$, i.e. in the framework of the harmonic approximation, and by formula (22), i.e. making allowance for the anharmonism, are quoted in Table 4.

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ДО ПИТАННЯ He–He ЗВ'ЯЗКУ
У ЕНДОЕДРАЛЬНОМУ ФУЛЕРЕНІ He₂@C₆₀

Резюме

Вже минуло двадцять років відтоді як порожнина ендоедрального фулерену безперервно привертає увагу експериментаторів та теоретиків, хіміків і фізиків, що обчислюють та спрямовують свої зусилля на комп'ютерне моделювання інкапсульованих атомів і молекул у порожнину фулеренів та розгадають явища зв'язування атомів, які при цьому ви-

никають. Ми подаємо огляд останніх досягнень, які стосуються ендоедральних фулеренів He₂@C₆₀, їх експериментальних спостережень та пов'язаних обчислювальних робіт. Два останні аспекти становлять головну проблему, що розглядається в даній роботі: з одного боку, дигеліум He₂, вбудований в порожнину C₆₀, спостерігається експериментально, а, з іншого (обчислювального) боку, кожен із атомів He в порожнині характеризується незначним перенесенням заряду на C₆₀, внаслідок чого дигеліум існує як частково заряджений (He^{+δ})₂. Чи існує зв'язок між двома атомами гелію є ключовим питанням даної роботи. Оскільки зв'язок є двочастинковим утворенням, ми стверджуємо, що достатньо означити зв'язок на основі постулату Льовдіна щодо молекули, і використати його для вивчення згаданого дигеліуму у порожнині C₆₀ в термінах потенціальної ями взаємодії He–He. Аналітично показано, що ця потенціальна яма дозволяє вмістити щонайменше один зв'язаний (основний) стан, і тому, згідно з постулатом Льовдіна, який природно передбачається у квантовій теорії, ми приходимо до висновку, що (He^{+δ})₂ є молекулою, а саме двоатомною, у якій два атоми гелію зв'язані один з другим. Використовуючи ці аргументи, ми також пропонуємо розширити поняття стабільності ендоедральних фулеренів.