The Electron Bubble and the $He_{60}$ Fullerene: A First-Principles Approach

R. Santamaria¹ · J. Soullard¹ · R. G. Barrera¹

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Abstract
Helium has a light atomic mass and, as a closed shell element, shows minimal interaction with other particles of the environment. Such properties favor the capture of an electron by liquid helium, leading to the formation of an electron bubble. The helium bubbles are of theoretical importance since different levels of quantum mechanical models can be tested for the correct prediction of a single quantum particle trapped in a cage. In this work, we propose a first-principles model of the electron bubble that takes, for the first time, the electronic structure of the cage into consideration. The model consists of a fullerene-type cage made of $He$ atoms with an additional electron. The solution of the many-body Schroedinger equation is then performed using density functional theory, with a small and an extra-large atomic basis set. Several major improvements over the model of a particle in a rigid or soft spherical potential are assessed in this way, such as the localization and delocalization of the electron in the helium bubble, the transition of the electron to the continuum, the polarization of the $He$ atoms building the wall, the ionic state of the electron bubble, besides the determination of relations of the volume-pressure type.

Keywords Electron bubble · Confinement of an electron · Electronic properties · Localized–delocalized states · Density functional theory

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1 Introduction

It is by now accepted that an excess electron in liquid helium forms by itself a large spherical cavity, due essentially to both, the strong repulsive interaction between the electron and the helium atoms, and the light mass of helium atoms that makes them liable to be reaccommodated. The cavity, referred to as an electron bubble, may show a radius as large as 15–20 Å at zero pressure. When the bubble moves slowly through the liquid, it drags a hydrodynamic mass of approximately 100–200 helium atomic masses [1–4]. With such characteristics, the electron bubble is regarded as an interesting quantum object. After the pioneering experiments of Sommer [5], involving the injection of electrons into liquid helium, the model of an electron within a bubble started to being devised. In this respect, a large amount of mobility [6–11] and spectroscopic studies [12–18] of theoretical and experimental nature have been performed to determine, as accurate as possible, the transport and quantum properties of the electron bubble, with special attention on helium in the superfluid state [4,12,13,19–21]. Possible applications are currently explored [22]. Yet, some fundamental questioning on the integrity of the electron, like a possible splitting of the bubble with a single electron into two smaller bubbles, remains without a definite answer [20,21].

The simplest model of the electron in the bubble considers an electron in a spherical potential barrier of infinite strength. By using elementary quantum mechanics, the ground state energy of the electron as a function of the bubble radius is calculated. The bubble radius is determined from a macroscopic pressure-balance equation, that equates the external pressure to the pressure coming from the kinetic energy of the electron, that tries to increase the radius of the bubble, minus the pressure arising from the bubble surface tension, that tries to decrease it. Assuming that the surface tension is independent of the bubble radius, reasonable values of the bubble size are obtained in this way. The calculation of the energy levels of the electron is straightforward when the equilibrium radius has been determined. The energy values of the first two excited states of the electron agree reasonably well with results of infrared-absorption experiments [14,15]. Such a simple model can be improved in different forms, for example, by assuming a finite strength of the potential barrier, by considering more realistic values of the surface tension, and also by introducing (in the pressure-balance equation) the effects of a finite temperature. In principle, the results can be compared with the ones obtained from a wide variety of experiments performed at different pressures and temperatures [18].

The above potential barrier model, what we will call empirical model, is not satisfactory due to its phenomenological origin. Clearly, a more fundamental approach to justify the existence and behavior of the electron bubble is welcomed. An attempt in such a direction has used density functional theory in the context of inhomogeneous liquid theory [12,23]. In this approach, one regards the liquid as a continuum, and the objective is to establish an appropriate expression of the free energy in terms of the liquid density. The excess electron is included by introducing in the free energy the interaction energy of the electron with the liquid. The dynamic equations are derived from the functional dependence on the liquid helium density of the grand potential. The approach yields two coupled equations, one for the cavity as an inhomogeneity in the liquid density and a Schroedinger-like equation for the electron in a cavity-shaped

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potential generated by this same inhomogeneity. The results, among others, of the radius dependence on the external pressure are quite satisfactory, as well as the dependence of the first- and second-excited energy states of the electron as a function of the external pressure. Although this model is, no doubt, more satisfactory than the potential barrier model, it is fair to ask whether the properties of the electron bubble can be actually derived as a legitimate solution of the many-body Schrödinger equation that takes account of the electronic structure of the cavity wall.

The purpose of the present work is, precisely, to investigate within a many-body quantum-mechanical approach, the properties of a single electron in the helium bubble. A realistic microscopic approach to treat the electron bubble would require a molecular model of the liquid itself, and this is not an easy task. Instead, we will assume that due to the strong repulsive interaction between the electron and the helium atoms, the electron will interact only with the first layer of atoms forming the bubble, and therefore, we will simplify the electron bubble system and take up the quantum-mechanical problem of an electron in a helium cage. Furthermore, we will take for the cage the highly symmetric $He_{60}$ fullerene, a polyhedron with 12 pentagons and 20 hexagons all with edges of length $d$, that resembles well a spherical cavity. From thermodynamic data of the molar volume of liquid $He$, at different pressures and temperatures [24], one can infer that at 1.5 K, the average interatomic distance is about 3.56 Å at 1 atm down to 3.37 Å at 25 atm. At atmospheric pressure, this number agrees with the estimate obtained from neutron-scattering data [25]. In the $He_{60}$ fullerene, one locates the helium nuclei at the vertices of the polyhedron, thus the average interatomic distance in the liquid, would correspond to the length $d$ of the edges. We now define the radius $R$ of the fullerene cavity as the radius of a sphere with the same area as the polyhedron, and one gets the following relationship: $R = 2.403726 \, d$. Thus, the radius $R$ of the $He_{60}$ cavity, with length of its edges equal to the average interatomic distance in liquid helium, is $R = 8.56$ Å at atmospheric pressure and $R = 8.10$ Å at 25 atm. Since the radius of the electron bubble at zero pressure is close to 18 Å, our model will give an insight to its electronic properties only for radii around 8 Å, where the interatomic distance at the cage resembles the one in liquid $He$. A more realistic model would require cages with different geometries for each radius, a geometry in which the average length of the edges were equal to the interatomic distance in the liquid, at the corresponding radii. Even so, one would be also neglecting the presence of the second layer of atoms of the bubble surface. This can be justified a posteriori by realizing that the overlap of the electron density within the bubble and the electron density at the cage is small and does not go beyond the first layer.

Here, we will consider instead the geometry of the $He_{60}$ as given, and although this is not a fully realistic model of the electron bubble in liquid helium, it captures the main essence of the bubble, that is, the pressure exerted on the walls of the cage due to the energetically favorable existence of a “free” electron within the cage. Furthermore, the quantum-mechanical treatment of the helium cage plus one extra electron—$He_{60}^{-}$—is by itself, an interesting quantum object, and we report here a full study of its electronic and mechanical properties. To do this, we use density functional theory (DFT) on a system that consists of an electron immersed in a helium cage with a well-defined atomic structure, implementing a first-principles electronic structure methodology on a system of molecular nature. Notice that in our approach, one loses track of the
wavefunction of the electron within the bubble and the concept of an effective potential felt by this electron, the many-body wavefunctions that we calculate are antisymmetric with respect to exchange of any pair of electrons; thus, the identity of each electron is completely lost. The only quantities that sustains its physical significance are the electron density and the total energy of the electron system.

The report is structured as follows. In the following section, we briefly present the molecular model of $He_{60}^-$ and, in the next section, the level of DFT theory is discussed and its accuracy is analyzed. In subsequent sections, the $PV(T = 0\, K)$ cold equation of state of $He_{60}^-$ is analyzed, as well as the isoelectron density maps, and relevant many-body molecular orbital energies. The final section remarks the importance of this work.

## 2 A Molecular Model of $He_{60}^-$

An electron in the fullerene-like cage builds a molecular system, here, the molecular model is denoted in the form $He_{60}^-$. In relation to the electron bubble, this molecular model differs from other bubble models where the confining walls are simulated either by a rigid potential or through a continuum approximation including no atomic structure [23]. It is important to mention the limitations of the present model, like the absence of the liquid environment around the bubble. In principle, the $He$ bubble proposed in this work is unstable in the gas phase, as it would spontaneously break apart. However, in a rather simplified way, the $He$ cage is supposed to be stable after considering the pressure from the liquid, keeping the bubble intact in the form proposed in this work. Thus, as in the empirical models, the bubble and the excess electron within are assumed to be in mechanical and thermodynamic equilibrium with the surrounded liquid. In relation to the dynamics of the electrons, this equilibrium state allows us to consider the $He$ nuclei as stationary and makes it possible to evaluate the interactions among all nuclei and electrons departing from a first-principles methodology.

### 2.1 First-Principles Method

In the Kohn–Sham (KS) version of DFT, the wavefunction is represented by a single determinant of occupied many-body molecular orbitals. Such a representation ensures the indistinguishability of the 121 electrons, and their treatment under equal hierarchical status. The additional electron in the cage, like any other electron of the molecular system, is supposed to be immersed in the average field of the other electrons plus the electrostatic field created by all the nuclei. The KS approach leads to what is known as the one-electron KS equations [26].

$$\left[ -\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \phi_i = \varepsilon_i \phi_i$$

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{nuc}}(\mathbf{r}) + v_{\text{coul}} + v_{\text{xc}}(\mathbf{r})$$

The functions $\phi_i$ are the molecular orbitals, and the subscript $i$ runs from 1 to the total number of electrons, $N$. The effective potential $v_{\text{eff}}$ acts on the $i$th electron, it is
constituted by the nuclear potential, a Coulombic potential (of classical type), and an exchange-correlation potential, both depending on the rest of the molecular orbitals, under an integral sign. A set of equations is required for the $\alpha$-spin electrons and another for the $\beta$-spin electrons. Thus, the one-electron KS equations constitute a set of coupled integro-differential equations, which are solved numerically in a self-consistent manner. The number of equations depends on the size and choice of the orbital basis set. By solving the one-electron KS equations, the many-body molecular orbitals are obtained. There are occupied and virtual (non-occupied) molecular orbitals. Once the orbitals are calculated, the wavefunction in the form of a determinant is established, and it is used to evaluate the energetic features, as well as the mechanical properties of the system under consideration.

The DFT–KS approach is capable to provide accurate structures and the correct energetics of molecular systems, when the appropriate exchange and correlation functionals are chosen, in combination with an adequate orbital basis sets. Thus, based on previous results on confined molecules using fullerene-type cages, we consider the Becke expression ($B_{88}$) for the exchange functional [27], and the Lee–Yang–Parr expression ($LYP$) for the correlation functional [28]. The DFT–KS/$B88LYP$ level of theory is classified as a gradient-corrected approach of DFT and has shown excellent results in the case of hydrogen molecules under confinement within fullerene-like cages [29–31]. The choice for the $B88LYP$ functional is additionally supported by the results of a study on the performances of a large number of DFT functionals [32].

In relation to the van der Waals forces, not included in the $B88LYP$ functional, let us recall that these forces are originated from the quantum fluctuations between induced electric dipoles in the atoms. In our electron bubble model, there is an electron at the center of the cage, with no positive charge; thus, an electric dipole cannot be induced to account for a van der Waals interaction between the excess electron and the $He$ atoms. On the one hand, there is a van der Waals contribution among the interacting $He$ atoms of the cage when the radius is large, yet, it is a negligible contribution, especially when one calculates energy differences. On the other hand, the electron density at the bubble center is expected to have spherical symmetry, and one can regard this electron as an electric monopole able to induce a radial polarization on the shell of $He$ atoms. This weak $e−He$ polarization is taken into consideration in our calculations.

The above level of theory is combined with the $aug−cc−pV5Z$ orbital basis sets. Such a basis set considers quintuple-zeta functions with correlation-consistent polarized valence-only ($cc−pV$) orbital features. The acronym $aug$ is the nomenclature for the augmented version of the $cc−pV5Z$ basis set with diffuse functions included. The $aug−cc−pV5Z$ functions are sufficiently large, minimize basis-set superposition errors, produce relatively low spin contamination, render the proper energetics of molecular systems, show a reliable picture of the electron distribution in the cases of molecular bonding, and are capable to describe localized and delocalized electrons. In addition, we use a single Gaussian orbital basis set with the goal of assessing the faithfulness representation of the electron densities and energies of the DFT–KS/$B88LYP/aug−cc−pV5Z$ level of theory considered in this work (more details are provided later). The convergence threshold of both the electron density and the energy in the self-consistent cycles is $10^{−5}$ au. The computations are performed as implemented in the $NWChem$ [33] and $Gaussian$ packages [34].
Table 1  Non-relativistic ground state energy and ionization potential of the He atom

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Property</th>
<th>This work [au]</th>
<th>Ref. [35,36]</th>
</tr>
</thead>
<tbody>
<tr>
<td>aug − cc − PV2Z</td>
<td>E(He)</td>
<td>−2.90066</td>
<td>−2.90372</td>
</tr>
<tr>
<td>aug − cc − PV2Z</td>
<td>IP [eV]</td>
<td>24.78</td>
<td>24.59</td>
</tr>
<tr>
<td>aug − cc − PV5Z</td>
<td>E(He)</td>
<td>−2.90702</td>
<td></td>
</tr>
<tr>
<td>aug − cc − PV5Z</td>
<td>IP [eV]</td>
<td>24.81</td>
<td></td>
</tr>
</tbody>
</table>

The accuracy of the DFT method in chemical reactions, which involve energy differences, is estimated to be 0.04 eV ≃ 0.002 au using a large basis set, like the aug − cc − pV5Z orbital basis set.

We start our calculation procedure by assuming that the additional electron is enclosed in the He cage, behaving as a confined particle. Due to the symmetry of the cage, the basis set describing the imprisoned electron is located at the center of the cage using a hydrogen ghost center with zero mass and zero electric charge. We calculate first the total energy of the molecular system containing the extra electron that we label $E(He_{60}^-)$ and then the total pressure on the walls of the cage is simply given by:

$$P_{\text{tot}} = -\frac{\partial E(He_{60}^-)}{\partial V} = -\frac{1}{4\pi R^2} \frac{\partial E(He_{60}^-)}{\partial R}$$

(2)

where $R$ and $V$ are the cage radius and cage volume, respectively.

### 2.2 Method Performance

The level of theory DFT–KS/B88LY P/aug − cc − pV5Z plays a fundamental role in the first-principles description of the electron imprisoned in the cage. In this respect, the level of theory is first tested on an isolated atomic helium by computing the non-relativistic ground state energy of the neutral atom, $E(He)$, and its ionization potential given in the form $IP = E(He) - E(He^+)$. Table 1 shows such energies. There, we also include energy values using a smaller basis set, namely, the aug − cc − pV2Z orbital basis set (it differs from the aug − cc − pV5Z orbital basis set by reducing the number of valence polarization functions from 5s, 4p, 3d, 2f, 1g to 2s, 1p). All the energies compare fairly well with other values of the literature.

In the “Appendix” we estimate the deviations produced by dispersion effects in the energy. Also, we evaluate the deviations attributed to the use of other exchange-correlations functionals there. The results from the “Appendix” indicate no noticeable energy changes by the inclusion of the dispersion effects. It is also observed that the energy differences obtained with different functionals amount to an order of magnitude smaller than the energies of the He bubble reported here. In short, the DFT level of theory previously described is sufficiently accurate to describe the different states of the electron bubble.
3 Results

In the following sections, the energetic features of the confined electron are analyzed. We include electronic properties such as the electron density and population charges in the analysis to gather evidence on the encapsulation of a localized electron density within the He cage.

3.1 Calculation with an Ample Basis Set

The system consists of 60 doubly charged nuclei, fixed at their corresponding fullerene positions, plus 121 electrons, 2 per each helium atom of the cage plus the additional electron. First, we investigate the energetic features of the molecular He$_{60}^-$ cage with and without an imprisoned electron, using a high-level theory with an ample basis set. The encapsulated electron is described as a quantum particle by including in the basis set a hydrogen ghost center (with zero mass and zero electric charge). We employ a basis set of the type aug − cc − pV5Z, in such a way that all the electrons of the molecular system are described on equal terms. This level of theory is referred to with the name 5Z.

The energy eigenvalues of the Kohn-Sham equations, in the selected basis set, are associated with 60 doubly-occupied orbitals, orbital 61 singly occupied, plus a set of unoccupied virtual orbitals (with no physical interpretation here). At this stage, it is tempting to associate orbital 61 to the behavior of the additional electron, if not quantitatively at least qualitatively. In Table 2, we report the representative results of this calculation for different radii of the cage. In the left column, one has the radius of the cage (in Å). In the second column, one finds a bona fide Kohn–Sham quantity, the total energy of the system (in au), and in parenthesis the corresponding total energy of the system without the additional electron. In the third column, one has the spin density of orbital 61 that gives a qualitative estimate of the probability density of finding an electron in orbital 61. In the next two columns one finds, respectively, the eigenvalue energy and kinetic energy of orbital 61, and in parenthesis the corresponding energies of orbital 60 for the system without the additional electron. Looking in Table 2 at the spin density column of orbital 61, one could interpret that the additional electron is found inside the cage with high probability for radii lower than 12.5 Å, but the electron is delocalized and found with high probability at the cage shell for radii greater than 12.5 Å. From an energetic perspective, we see, in the second column of Table 2, that the total energy $E(\text{He}_{60}^-)$ of the system decreases as the radius of the cage increases, but around 12.5 Å, it goes through a slope discontinuity and it starts to increase for radii greater than 12.5 Å, as shown in Fig. 1a, where we plot the total energy $E(\text{He}_{60}^-)$, in au, as a function of the cage radius $R$, in Å. One can see that for $R > 12.5$ Å the total energy increases as the radius increases, yielding, according to Eq. (2), a negative pressure. Thus, the slope discontinuity as well as the presence of a negative pressure signify a manifest signature of a mechanical instability. We interpret this as the transition between two electronic states: a localized state in which the probability of finding the additional electron lies within the cage, and a delocalized state in which this probability lies somewhere on the atoms of the helium cage. Now we use Eq. (2) to
Table 2  Energies of the He cage with and without electron

<table>
<thead>
<tr>
<th>Radius (Å)</th>
<th>Total energy (au)</th>
<th>Spin density</th>
<th>Orbital 61 (60) total energy (au)</th>
<th>Orbital 61 (60) kinetic energy (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.253</td>
<td>−174.3617 (−174.3918)</td>
<td>0.918</td>
<td>0.0786 (−0.5686)</td>
<td>0.0725 (1.5432)</td>
</tr>
<tr>
<td>6.582</td>
<td>−174.3730 (−174.4002)</td>
<td>0.866</td>
<td>0.0731 (−0.5730)</td>
<td>0.0739 (1.5213)</td>
</tr>
<tr>
<td>6.911</td>
<td>−174.3805 (−174.4051)</td>
<td>0.820</td>
<td>0.0680 (−0.5762)</td>
<td>0.0744 (1.5038)</td>
</tr>
<tr>
<td>7.240</td>
<td>−174.3857 (−174.4083)</td>
<td>0.777</td>
<td>0.0639 (−0.5785)</td>
<td>0.0748 (1.4898)</td>
</tr>
<tr>
<td>7.569</td>
<td>−174.3898 (−174.4105)</td>
<td>0.744</td>
<td>0.0602 (−0.5803)</td>
<td>0.0743 (1.4787)</td>
</tr>
<tr>
<td>7.898</td>
<td>−174.3927 (−174.4124)</td>
<td>0.710</td>
<td>0.0574 (−0.5816)</td>
<td>0.0751 (1.4699)</td>
</tr>
<tr>
<td>8.474</td>
<td>−174.3962 (−174.4148)</td>
<td>0.663</td>
<td>0.0539 (−0.5831)</td>
<td>0.0768 (1.4587)</td>
</tr>
<tr>
<td>8.721</td>
<td>−174.3972 (−174.4157)</td>
<td>0.645</td>
<td>0.0529 (−0.5835)</td>
<td>0.0781 (1.4551)</td>
</tr>
<tr>
<td>8.968</td>
<td>−174.3978 (−174.4164)</td>
<td>0.622</td>
<td>0.0521 (−0.5839)</td>
<td>0.0806 (1.4522)</td>
</tr>
<tr>
<td>9.214</td>
<td>−174.3983 (−174.4171)</td>
<td>0.604</td>
<td>0.0514 (−0.5842)</td>
<td>0.0825 (1.4497)</td>
</tr>
<tr>
<td>9.544</td>
<td>−174.3990 (−174.4179)</td>
<td>0.592</td>
<td>0.0505 (−0.5845)</td>
<td>0.0834 (1.4470)</td>
</tr>
<tr>
<td>9.790</td>
<td>−174.3992 (−174.4183)</td>
<td>0.580</td>
<td>0.0501 (−0.5847)</td>
<td>0.0846 (1.4454)</td>
</tr>
<tr>
<td>10.04</td>
<td>−174.3993 (−174.4187)</td>
<td>0.565</td>
<td>0.0497 (−0.5848)</td>
<td>0.0865 (1.4441)</td>
</tr>
<tr>
<td>11.00</td>
<td>−174.3995 (−174.4198)</td>
<td>0.540</td>
<td>0.0484 (−0.5852)</td>
<td>0.0883 (1.4407)</td>
</tr>
<tr>
<td>12.00</td>
<td>−174.3995 (−174.4204)</td>
<td>0.521</td>
<td>0.0471 (−0.5853)</td>
<td>0.0885 (1.4390)</td>
</tr>
<tr>
<td>12.25</td>
<td>−174.3996 (−174.4204)</td>
<td>0.520</td>
<td>0.0468 (−0.5853)</td>
<td>0.0880 (1.4388)</td>
</tr>
<tr>
<td>12.50</td>
<td>−174.3996 (−174.4205)</td>
<td>0.521</td>
<td>0.0466 (−0.5854)</td>
<td>0.0874 (1.4386)</td>
</tr>
<tr>
<td>12.60</td>
<td>−174.3952 (−174.4205)</td>
<td>0.053</td>
<td>0.0473 (−0.5854)</td>
<td>0.1475 (1.4385)</td>
</tr>
<tr>
<td>12.75</td>
<td>−174.3948 (−174.4205)</td>
<td>0.018</td>
<td>0.0425 (−0.5854)</td>
<td>0.1498 (1.4384)</td>
</tr>
<tr>
<td>13.00</td>
<td>−174.3947 (−174.4206)</td>
<td>0.012</td>
<td>0.0423 (−0.5854)</td>
<td>0.1496 (1.4382)</td>
</tr>
<tr>
<td>14.00</td>
<td>−174.3937 (−174.4206)</td>
<td>0.000</td>
<td>0.0421 (−0.5854)</td>
<td>0.1489 (1.4379)</td>
</tr>
<tr>
<td>15.00</td>
<td>−174.3920 (−174.4207)</td>
<td>0.000</td>
<td>0.0429 (−0.5854)</td>
<td>0.1508 (1.4377)</td>
</tr>
</tbody>
</table>

The numbers in parenthesis are for the empty bubble. The spin density indicates the average population of the molecular orbital 61 associated with the encapsulated electron at the cage center. The level of theory DFT–KS/B88LYP/aug–cc-pV5Z, charge = −1, multiplicity = 2 is employed for the bubble with confined electron. The level of theory for the cage is similar to that of the bubble with the trapped electron (for instance, it also includes the ghost atomic center), except for the charge = 0 and multiplicity = 1.

calculate the total pressure exerted by the whole system of electrons, upon the system of nuclei, balanced by an external agent that has to keep them at the fixed fullerene positions.

In order to compute the derivatives of the total energy to calculate $P_{tot}$, we find convenient to use an analytical fit to $E(He_{60})$ in terms of the radius $R$ that can be written as:

$$E(He_{60}) = E_1 + \exp(-\beta R)/\exp(-\beta R_0)$$

$$E_1 = -174.4 ; \quad \beta = 1.02638 ; \quad R_0 = 3.07226$$

(3)

It is valid for $R < 12.5$ Å and accurate within $3 \times 10^{-4}$ au. In Fig. 1b, we plot the total pressure, in atm, as a function of the cage radius, in Å. Note that for a cage of small radius, the pressure can be extremely large, which can be interpreted as due to
Fig. 1  In a, the total energy of the bubble in terms of its radius is shown. In b, the total pressure in terms of the bubble radius is shown. The red arrow indicates the bubble radius where a null pressure is obtained. The inset in this last figure plots in a magnified scale the radius interval 11.4–12.5 Å and pressure 1–6 atm for better appreciation (Color figure online)

the kinetic energy of the imprisoned electron. In the inset of Fig. 1b, we show how the pressure approaches zero, becoming negative after $R = 12.5$ Å (not shown in the figure).

Since the interatomic distances of the helium atoms increase as the cage radius increases, one could understand this transition as a weakening of the repulsive confining cage potential, allowing the additional electron to get closer to the helium nuclei, and by polarizing the $He$ atoms in the cage, an additional fraction of an external electron is integrated to the electron density of each $He$ atom. The final result in this situation is the migration of the central electron to the bubble surface.
The orbital energies represent an interesting property of the He$^{-60}$ system. The purpose here is to briefly discuss the many-body molecular orbital energies of the system in terms of the cage radius. Since the many-body wavefunction is obtained as the antisymmetric product of the molecular orbitals given by the solution of the KS equations, and only two electrons with opposite spins can occupy each orbital, the orbital energies span, at small cage radius, an energy band as in a solid, meaning that the electrons are not confined within each atom, but they have a finite probability to be found at any atom of the cage. Figure 2 shows that behavior. The orbital energies of the molecular system become degenerate when the cage radius (indicated in that figure) is sufficiently large, and the interactions among the helium atoms are negligible. In this case, the 60 orbitals only differ in their spatial orientations, while the energies are expected to tend to the unique value of the electronic orbital energy of atomic $He$, once the additional electron is gone. On the other hand, the energy of the highest occupied molecular orbital, $e_{\text{HOMO}}$, corresponds to the additional electron and is positive (Fig. 2), indicating a “free” electron in the helium cage. The difference between $e_{\text{HOMO}}$
The 3D electron density difference $\rho(He_{60}^-) - \rho(He_{60})$ of the electron bubble is pasted (from a given perspective) onto the 2D figure shown above. The He atoms are depicted in blue color, the ghost atom center in yellow color, and the electron density in red color. The size of the atoms in blue color and the ghost atom center in yellow color have no physical significance (they are depicted just for visualization purposes).

In the left inset, the radius of the bubble is 9.214 Å and the electron density isosurface is $2 \times 10^{-7}$ Bohr$^{-3}$. In this case, the additional electron is observed to be trapped at the center of the cage (it is in a localized state), and the central electron induces a polarization of the bubble electron clouds. In the right inset, the radius of the bubble is 14.000 Å and the electron density isosurface is $3 \times 10^{-7}$ Bohr$^{-3}$. In this case, the additional electron is observed mainly on the bubble cage (it is in a delocalized state as the electron is found along the “bond lengths” of the atomic nuclei, and a tiny residual amount at the cage center). The level of theory is DFT - KS/B88LYP using the basis set aug-cc-pV5Z and ultrafine grids in the numerical computations (Color figure online)

and the lowest unoccupied molecular orbital energy, $e_{\text{LUMO}}$, defines the energy gap, $E_{\text{GAP}}$.

$$E_{\text{GAP}} = e_{\text{HOMO}} - e_{\text{LUMO}}$$

In going from a small radius to a large radius, the energy gap is slowly closed. Such a process allows the additional electron to change from a localized state to a delocalized state (Fig. 3). When the electron is on the cage surface, the energy gap is sufficiently small and the electron has the possibility to escape to the continuum. Interestingly, the hydrogen clusters under similar circumstances exhibit the opening of the energy gap [37]. Thus, the gap closings occur in different directions of compression: for confined hydrogen clusters it occurs in the direction of high compression rates, and for the He$_{60}^-$ system, it occurs in the direction of low compression rates. In principle, the opening/closing of the energy gap in these cases may be associated with nonbonded/bonded electrons, respectively.

We further characterize the additional electron on the He cage by performing 3D plots of the electron density. Figure 3 shows plots of the electron density difference $\rho(He_{60}^-) - \rho(He_{60})$. When the cage radius is 9.214 Å, the electron is found trapped at the center of the cage, and when the cage radius is 14.000 Å, the electron is found on the bubble cage. We have also focussed attention on the region close to the center of the cage using 2D plots of the electron density (not exhibited in Fig. 3). In these plots, for $R = 8.227$ Å and $R = 10.037$ Å, and recalling that the electron density has radial symmetry, one can see a rise up at the edges corresponding to the presence of the
electrons in the walls of the cage, while the profile around the center is associated with the additional electron. However, a peculiar rippled shape of the density profile close to the cage center is observed. It is probably due to the specific structure of the multi-Gaussian basis set, and this non-smooth bending yields, most probably, non-physical contributions to the kinetic energy of the additional electron. Also, as $R$ increases, the density piles up around the center, keeping its non-smooth profile, and at $R \geq 12.5\,\text{Å}$ it drops down almost to zero, leaving an empty cage. We identify this behavior with the transition to the delocalized state, where the electron is shared by all the helium atoms in the walls of the cage.

### 3.3 A Single Gaussian Describing the Additional Electron of $\text{He}_{60}^-$

In trying to overcome the non-physical characteristics of the density profile mentioned above, we briefly review the basic idea of the empirical model in order to look for a more adequate basis set to describe the additional electron at the center of the cage. In the empirical model of the electron bubble, an electron is trapped within a spherical well of infinite strength. In this case, the ground state wavefunction of the electron is given by:

$$
\psi_0(r) = \sqrt{\frac{\pi}{2}} \frac{1}{2} j_0(\pi r/R)
$$

where $j_0$ is the spherical Bessel function of order 0, and the 1s ground state energy is:

$$
E_{1s}(R) = \frac{\hbar^2}{2m} \frac{\pi^2}{R^2}
$$

where $m$ is the electron mass. One can see that the energy increases when $R$ decreases. The rate of energy change of the electron when the volume is reduced can be interpreted as an internal pressure exerted by the electron on the cavity walls, that is:

$$
P_e = -\frac{\partial E_{1s}}{\partial V} = \frac{1}{4\pi R^2} \frac{\partial E_{1s}}{\partial R}
$$

where $V$ is the volume of the sphere. There is also a pressure $P_\gamma = 8\pi R\gamma$, coming from the surface tension that tends to collapse the bubble. Here, $\gamma$ denotes the surface tension. Mechanical equilibrium is attained when the sum of these two pressures is balanced by an external pressure. The equilibrium radius $R_0$, at zero external pressure, is the one corresponding to the direct balance between the pressure coming from the electron and the one coming from the surface tension. Taking $\gamma$ as a quantity independent of $R$ and equal to 0.34 dynes/cm [15], one gets $R_0 = 19.34\,\text{Å}$, as an estimate of the equilibrium radius at zero pressure.

Now we recall that being the Kohn-Sham equations the result of a variational procedure, the main criteria for choosing an alternative basis set to solve them, will be if the alternative choice leads to a lower total energy of the electron system, besides a physically reasonable electron-density profile. In the present section, we use as
a basis set for the ghost at the center of the cage a single Gaussian function. The Gaussian exponent is estimated from an electron density (produced by a Gaussian function) that reproduces the electron density of the \( j_0 \) spherical Bessel function (Eq. 5). Then, the Gaussian function is used to solve self-consistently the \( KS \) equations. During this procedure, the Gaussian function is multiplied by a coefficient through the minimization process. More precisely, the coefficient of the Gaussian is considered the variational parameter in the calculation of the energy. Yet, by introducing the electronic structure of the wall in the present calculations, we shall be able to evaluate the total energy of the \( \text{He}_{60}^- \) system and compare it to the one obtained in the 5Z model, where we used for the central ghost a hydrogen basis set of the type \( \text{aug} - cc - pV5Z \). In case that the total energy turns out to be lower than in the previous case, this solution will be considered more favorable.

The charge density associated with the spherical Bessel wavefunction \( j_0 \) vanishes at the edges of the confining wall, and such a behavior will be to some extent inherited to the Gaussian function, although strictly speaking, a Gaussian tends asymptotically to zero. The expression for the Gaussian is written as:

\[
\exp\left[-\frac{r^2}{(2\sigma^2)}\right]
\]

The values of \( \sigma \) for the various radii of the cage are given in Å in Table 3. The one-electron Kohn–Sham equations are self-consistently solved using the \( \text{aug} - cc - pV5Z \) basis set representation for the \( \text{He} \) atoms, and the single Gaussian basis set described previously for the orbital of the additional electron. This level of theory is referred to with the name 1G. The results using the 1G approach are shown in Table 3.

In the first column, one finds the radii of the cage in Å, and in the second column, the total energy of the \( \text{He}_{60}^- \) system. The third column has the chosen value of the Gaussian exponent \( \sigma \) in Å. The fourth column has the spin density of orbital 61, as a measure of the total probability of finding an electron in this orbital. In the fifth and sixth columns one finds, respectively, the total and kinetic energy of orbital 61 in the \( \text{He}_{60}^- \) system, and in parenthesis, the corresponding energies of orbital 60 in the \( \text{He}_{60}^- \) system. We compare the total energy obtained in this calculation with the energy obtained from the 5Z approach. This comparison is displayed in Fig. 4.

One can see that for \( R \) greater than 7.8 Å, the total energy of the 1G calculation is lower than the one obtained with the 5Z calculation, yielding an energetically more favorable result. Nevertheless, one requires still to explore the stability properties. For this, we calculate the total “pressure” of the electron system exerted on the \( \text{He} \) nuclei located on the walls of the cage, as the derivative of the total energy with respect to volume (Eq. 2). The results of this calculation are shown in Fig. 5, where we plot the total pressure in terms of the cage radius. We also show the corresponding results of both the 5Z calculation and the empirical model.

One can see that in the 1G case, the total pressure goes smoothly to zero as the radius increases. There is no transition to a delocalized state as in the 5Z calculation, where the total pressure goes to zero around 12.5 Å. For comparison, we also plot the results obtained using the empirical model (em) of the electron bubble, using the same value of the surface tension equal to 0.34 dynes/cm for all radii. For easiness in the
Table 3  Energies of the $He$ cage with an excess electron using the 1G basis set

<table>
<thead>
<tr>
<th>Radius (Å)</th>
<th>Total energy $(au)$</th>
<th>$\sigma$ (Å)</th>
<th>Spin density</th>
<th>Orbital 61 (60) total energy $(au)$</th>
<th>Orbital 61 (60) kinetic energy $(au)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.253</td>
<td>−174.3611</td>
<td>2.9987</td>
<td>0.955</td>
<td>0.0812 (−0.5686)</td>
<td>0.0758 (1.5432)</td>
</tr>
<tr>
<td>6.582</td>
<td>−174.3726</td>
<td>3.1564</td>
<td>0.943</td>
<td>0.0750 (−0.5730)</td>
<td>0.0749 (1.5213)</td>
</tr>
<tr>
<td>6.911</td>
<td>−174.3804</td>
<td>3.3142</td>
<td>0.930</td>
<td>0.0693 (−0.5762)</td>
<td>0.0729 (1.5038)</td>
</tr>
<tr>
<td>7.240</td>
<td>−174.3860</td>
<td>3.4720</td>
<td>0.917</td>
<td>0.0644 (−0.5785)</td>
<td>0.0706 (1.4989)</td>
</tr>
<tr>
<td>7.569</td>
<td>−174.3906</td>
<td>3.6298</td>
<td>0.910</td>
<td>0.0599 (−0.5803)</td>
<td>0.0671 (1.4787)</td>
</tr>
<tr>
<td>7.898</td>
<td>−174.3943</td>
<td>3.7876</td>
<td>0.901</td>
<td>0.0560 (−0.5816)</td>
<td>0.0639 (1.4699)</td>
</tr>
<tr>
<td>8.227</td>
<td>−174.3973</td>
<td>3.9453</td>
<td>0.893</td>
<td>0.0526 (−0.5825)</td>
<td>0.0608 (1.4630)</td>
</tr>
<tr>
<td>8.474</td>
<td>−174.3996</td>
<td>4.0638</td>
<td>0.893</td>
<td>0.0502 (−0.5831)</td>
<td>0.0575 (1.4587)</td>
</tr>
<tr>
<td>8.721</td>
<td>−174.4016</td>
<td>4.1823</td>
<td>0.892</td>
<td>0.0481 (−0.5835)</td>
<td>0.0546 (1.4551)</td>
</tr>
<tr>
<td>8.968</td>
<td>−174.4031</td>
<td>4.3007</td>
<td>0.888</td>
<td>0.0463 (−0.5839)</td>
<td>0.0526 (1.4522)</td>
</tr>
<tr>
<td>9.214</td>
<td>−174.4045</td>
<td>4.4186</td>
<td>0.886</td>
<td>0.0446 (−0.5842)</td>
<td>0.0502 (1.4497)</td>
</tr>
<tr>
<td>9.544</td>
<td>−174.4065</td>
<td>4.5769</td>
<td>0.891</td>
<td>0.0424 (−0.5845)</td>
<td>0.0461 (1.4470)</td>
</tr>
<tr>
<td>9.790</td>
<td>−174.4077</td>
<td>4.6948</td>
<td>0.893</td>
<td>0.0409 (−0.5847)</td>
<td>0.0435 (1.4454)</td>
</tr>
<tr>
<td>10.037</td>
<td>−174.4086</td>
<td>4.8133</td>
<td>0.892</td>
<td>0.0397 (−0.5848)</td>
<td>0.0418 (1.4441)</td>
</tr>
<tr>
<td>11.000</td>
<td>−174.4115</td>
<td>5.2751</td>
<td>0.898</td>
<td>0.0354 (−0.5849)</td>
<td>0.0343 (1.4401)</td>
</tr>
<tr>
<td>11.500</td>
<td>−174.4128</td>
<td>5.5149</td>
<td>0.908</td>
<td>0.0333 (−0.5849)</td>
<td>0.0302 (1.4391)</td>
</tr>
<tr>
<td>12.000</td>
<td>−174.4136</td>
<td>5.7547</td>
<td>0.912</td>
<td>0.0318 (−0.5850)</td>
<td>0.0275 (1.4384)</td>
</tr>
<tr>
<td>13.048</td>
<td>−174.4151</td>
<td>6.2573</td>
<td>0.936</td>
<td>0.0287 (−0.5850)</td>
<td>0.0220 (1.4376)</td>
</tr>
<tr>
<td>14.353</td>
<td>−174.4160</td>
<td>6.8831</td>
<td>0.936</td>
<td>0.0259 (−0.5850)</td>
<td>0.0177 (1.4372)</td>
</tr>
<tr>
<td>15.788</td>
<td>−174.4171</td>
<td>7.5713</td>
<td>0.954</td>
<td>0.0232 (−0.5850)</td>
<td>0.0134 (1.4370)</td>
</tr>
<tr>
<td>16.578</td>
<td>−174.4172</td>
<td>7.9501</td>
<td>0.958</td>
<td>0.0223 (−0.5849)</td>
<td>0.0119 (1.4370)</td>
</tr>
<tr>
<td>17.367</td>
<td>−174.4176</td>
<td>8.3285</td>
<td>0.965</td>
<td>0.0211 (−0.5849)</td>
<td>0.0104 (1.4369)</td>
</tr>
</tbody>
</table>

The numbers in parenthesis are for the empty bubble. The spin density indicates the average population of the encapsulated electron at the cage center. The level of theory employed for the bubble atoms is: DFT-KS/B88LYP/aug-cc-pV5Z, charge $=−1$, multiplicity $=2$. In the present case, a single Gaussian basis function with parameter $\sigma$ was used to describe the encapsulated electron. The level of theory of the empty bubble is similar to that of the bubble with trapped electron (these computations include the ghost center), except for the charge $= 0$ and multiplicity $= 1$.

Fig. 4  The electron bubble energy in terms of its radius. Red: the basis function on the ghost atom is a Gaussian function (the electron density derived from such a Gaussian function was fitted to the electron density obtained from the spherical Bessel function $j_0$), and the basis set on $He$ atoms is aug-cc-pV5Z. Blue: the basis set on the $He$ atoms and on the ghost atom is aug-cc-pV5Z (Color figure online)
The total pressure in terms of the bubble radius is shown. Green: empirical model. Red: the basis function on the ghost atom is a Gaussian function, and the basis set on the $He$ atoms is $aug-cc-pV5Z$. Blue: the basis set on the $He$ atoms and on the ghost atom is $aug-cc-pV5Z$. The blue circle indicates the bubble radius for which a null pressure is obtained (Color figure online).

handling of derivatives, in the energy and pressure plots of Figs. 4 and 5, we used an analytical fit to the total energy given by:

$$E(He_{60}) = E_0 - E_1 \frac{a + bR}{c + dR}$$

where $E_0 = -173.0$, $E_1 = 0.984606$, $a = -5.7099$, $b = 1.17416$, $c = -3.88603$, $d = 0.81087$. The energy parameters $E_0$ and $E_1$ are in atomic units and $R$ in Å. The deviations between the proposed expression and the numerical values are smaller than the accuracy of the DFT method employed.

We discuss two other outcomes of the DFT calculations, they are related to the spin population and orbital energies also reported in Table 3. The molecular orbital number 61 is associated to the basis function describing the central electron. The total orbital energy is positive, characteristic of a free particle in a rigid box. On the other hand, the kinetic energy is an essential part of the total energy, these two energies decrease as the bubble radius increases, following the expectations of a particle in a rigid box. Contrariwise, the orbital number 60 associated with an electron of the cage, exhibits a negative energy, characteristic of a bound electron to an atomic nucleus, and does not depend strongly on the bubble radius (see Table 3).

There is an initial population drop (or a spin density drop, Table 3) of the central electron with bubble radius, followed by an increase when the bubble radius is greater than 10 Å. Apparently, the electron density of the central electron has a small overlap with the electron density of the $He$ atoms at large values of the bubble radius. In spite of that, the present model and the empirical model present a common feature, namely a localized electron at the center of the bubble.

4 Conclusions

The investigation of a single quantum particle under realistic conditions of confinement represents a challenge from a theoretical perspective. In this work, we proposed a novel
model of imprisoning an electron in a $He$ cage, in an attempt to simulate an electron bubble in liquid helium. The model assumes a fullerene-type cage made of helium atoms together with the presence of a “floating” electron. Although the resemblance with the electron bubble is not adequate at all radii of the fullerene cage, the proposed model represents an interesting quantum object by itself. The atomic nature of the model allows to apply density functional theory with regard to molecular structures. The $He$ atoms are described by a large basis set, $aug-cc-pV5Z$. However, the description of the floating electron is performed using in different instances two basis sets. In a first stage, the basis set $aug-cc-pV5Z$ is used giving the opportunity to energetically accommodate the additional electron. In a second stage, a single Gaussian function (with a shape similar to the spherical Bessel function solution of the rigid spherical potential model) is associated with the additional electron in a localized state. A ghost atomic center with no mass, neither electric charge was used to positioning the electron basis set at the center of the $He$ cage. In both situations the predictions were improved over the rigid spherical potential model. Yet, the results obtained from using the large basis set, together with other descriptors such as the spin densities, electron densities and orbital energies, provided evidence of a stable electron inside the $He$ cage for bubble radii below 12.5 Å, and a delocalized electron (this is, distributed on the cage atoms by analyzing different properties of the molecular system) at larger bubble radii. On the other hand, the possibility of building Gaussian basis sets from spherical Bessel functions of a model system of corresponding nature, represents a novel method to describe electrons without being ascribed to any specific nuclei, while maintaining the computational algorithmic structure of DFT without changes.

The helium bubbles with electrons inside have shown interesting promises on technological applications, specially on the fields of quantum computing and quantum information. In principle, the spin of several electrons trapped in a helium bubble may be manipulated with a magnetic field gradient to produce their entanglement. The molecular model presented in this work can be improved in different ways to provide a better understanding of the electron bubble. For example, the presence of the medium is important and should be considered in the near future. The free location of the $He$ atoms to form the bubble also becomes of interest. In spite of that, the results obtained for the $He_{60}$ system in this work show interesting features on the localization and delocalization of the additional electron in the cage.

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**Appendix**

The purpose of this section is to evaluate the dispersion effects on the $He$ bubble energy, and also estimate the accuracy of energy differences by using different DFT energy functionals. To do this, we depart from the fact that an energy functional of DFT is an approximation, whose energies are usually adapted to reproduce the exchange-
correlation and dispersion energies measured in the experiments. There is not an exchange-correlation energy functional or dispersion energy functional exclusively designed for helium. In spite of that, there are functionals specially designed to provide the correct long-range attractive and repulsive interactions. One of these is the \( APF - D \) functional, which includes dispersion effects as an empirical correction to the \( APF \) functional \cite{38}. The dispersion expression contained in the \( APF - D \) functional is shown below.

\[
E_{\text{disp}} = \sum_{A>B} V(R_{AB}); \quad V(R_{AB}) = \begin{cases} 0; & R_{AB} \leq R_{d,AB} \\ \frac{C_{6,AB}}{[R_{AB}^2 - R_{s,AB}^2]^3} f(R_{AB}) g(R_{AB}); & R_{AB} > R_{d,AB} \end{cases}
\]

The dispersion term contains the damping function \( f \) and switching function \( g \) for the attenuation of the Coulomb interactions, and with the purpose of producing continuous derivatives. There are nine parameters \( P_i \) adjusted to reproduce the ionization potentials (\( \varepsilon_i \)), and effective atomic polarizabilities (\( \alpha_i \)) of 15 noble gas dimers (several of them containing \( He \)), plus some hydrocarbon dimers.

\[
C_{6,AB} = \frac{3}{2} P_1 \left( \frac{\varepsilon_{H,A} \varepsilon_{H,B}}{\varepsilon_{H,A} + \varepsilon_{H,B}} \right) \alpha_A \alpha_B \\
R_{s,AB} = \frac{P_i}{\sqrt{-(\varepsilon_{H,A} + \varepsilon_{H,B})/2}}; \quad R_{d,AB} = \frac{P_j}{\sqrt{-(\varepsilon_{H,A} + \varepsilon_{H,B})/2}} - P_6 \\
P_1 = 1.18604; \quad P_6 = 0.234859
\]

The \( P_i \) factor is one of the \( P_2, P_3, P_4, P_5 \) parameters, and the \( P_j \) factor is one of the \( P_7, P_8, P_9 \) parameters (presented in Table 3 of Ref. \cite{38}), decided according to the dimer type \( AB \). The accuracy of the \( APF \)-family of functionals is comparable to that of more refined levels of theory, such as CCSD(T)/aug-cc-pVTZ, and the energy values are found in excellent agreement with experimental measurements.

In the present work, we have been mainly concerned with energy differences (such as the ionization potential, energy gap, pressure, and more). Therefore, we consider the difference between the electron bubble, \( E(He_{60}) \), and the energy of the empty cage, \( E(He_{60}) \), for the evaluation of the dispersion effects. In Table 4, we present a list of energies using the energy functional \( APF - D \), it includes dispersion effects in the energy, and the energy functional \( APF \), which is the counterpart functional that includes no dispersion effects in the energy \cite{38}. The basis set is \( aug - cc - PV5Z \), it was used in the main text. Table 4 also includes the level of theory used in the main text (\( DFT - KS/B88LYP/aug - cc - PV5Z \)) with the purpose of comparing energies. The computations are performed for a helium bubble with radius 8.227 Å.

The results of Table 4 indicate that the energy difference \( E(He_{60}) - E(He_{60}) \) using the functional \( APF - D \), which includes dispersion effects, is 0.0159 Hartree. It is essentially identical to the energy obtained from the functional \( APF \), which includes no dispersion effects. Thereby, there are no noticeable energy changes (by the inclusion of the dispersion effects) up to the fourth significant figure on the bubble energy.
On the other side, we find a value of 0.0191 Hartree of the energy difference \( E(\text{He}^{60}) - E(\text{He}^{60}) \) using the level of theory reported in the body text. There is an absolute difference of 0.0031 Hartree between the energies given by the functionals APF and B88LYP, both without including dispersion effects. In principle, the value 0.0031 Hartree may be considered an upper limit in the error when one uses different energy functionals. Such a number is an order of magnitude smaller than the energy differences presented in the main text. The reason to use the B88LYP functional, instead of the APF functional, in the main text is the relatively rapidity of the energy convergence in the self-consistent process.

## References