The off-center endohedrally-confined Hydrogen molecule

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In this study, we address the problem of the C_{60} endohedrally confined Hydrogen molecule through a Configuration-Interaction approach to the electronic dynamics. Modeling the confinement by means of a combination of two Woods-Saxon potentials, we analyze the stability of the system as a function of the nuclei position through the behavior of the electronic spectrum. After studying the convergence of two different partial wave expansions, one related to the molecular Coulomb centers and the other related to the off-centering of the C_{60} well, we found that the second approach provides a more accurate description of the system. Furthermore, we observed that the inter-atomic distance changes on the position of the atoms inside to the cavity. Thus, the most favourable energetic configuration for the molecule is for it to be positioned inside the cavity next to the structure, where it decreases size.

1   Introduction

In recent years there has been an increasing interest in the study of confined systems and their applications in several fields owing to modifications in their chemical and physical properties[1–14]. Some examples of these applications are the use of molecular cages as nanocontainers[15], the design of materials with specific optical properties[16–20], the development of rechargeable ion batteries[21], the fabrication of gas sensors to detect pollutant gases[22], the study of quantum-chemical models of enzyme active sites[23], the use of nanocarriers as drug delivery systems for tumor treatments[24], the improvement of nanoelectronics devices[25], or the understanding of certain modifications in the properties of atoms and ions in a plasma environment[26,27]. In particular, the storage and transport of hydrogen has gained a great deal of attention due to its use as a clean source of energy[28,29], and several theoretical and experimental works have focused on this subject under different confining situations[30–43].

The properties of confined systems have been studied using various confinement models depending on the applications considered. Some of the most frequently studied are the spherical hard wall[44–48], the finite barrier[49–51], the gaussian-well potential[52–54], the square-well potential[55,56] or a combination of Woods-Saxon potentials[57,58]. Moreover, these models usually consider the system to be at the center of the cavity as an initial approximation, however to achieving to a more realistic analysis

other possible positions should also be taken into account to see how this affects energy levels and other properties of the confined species.

In this paper we address the problem of the hydrogen molecule in off-centered spherical confinement. We have analyzed the effect of the off-center position in the fullerene cage on the potential energy curve of the molecule. Different potentials have been employed for fullerene cages, mainly the square-well or the combination of two Woods-Saxon[55–58], with the latter being more suitable because its diffuse but compact borders are more realistic than the infinitely sharp edges of the former, therefore we use the combination of two Woods-Saxon potentials to model a C_{60} fullerene cage as the confining cavity[58,59]. The convergence of the partial wave expansion in two different reference systems is studied: a) the one associated to the confining cavity, and b) the one related to one of the molecule's Coulomb centers. The solution of the Schrödinger equation is computed using a configuration-interaction approach with generalized Sturmian functions[60].

The article is organized as follows: in Sec. 2, we outline the theoretical approach used to describe the confined hydrogen molecule under different reference systems; in Sec. 3, we present a convergence analysis of the H_2 electronic ground state energy as a function of its displacement in relation to the origin of the reference system and the partial wave order, and we show the main results of the present study; finally, in Sec. 4 some conclusions are drawn. Atomic units are used throughout this work.

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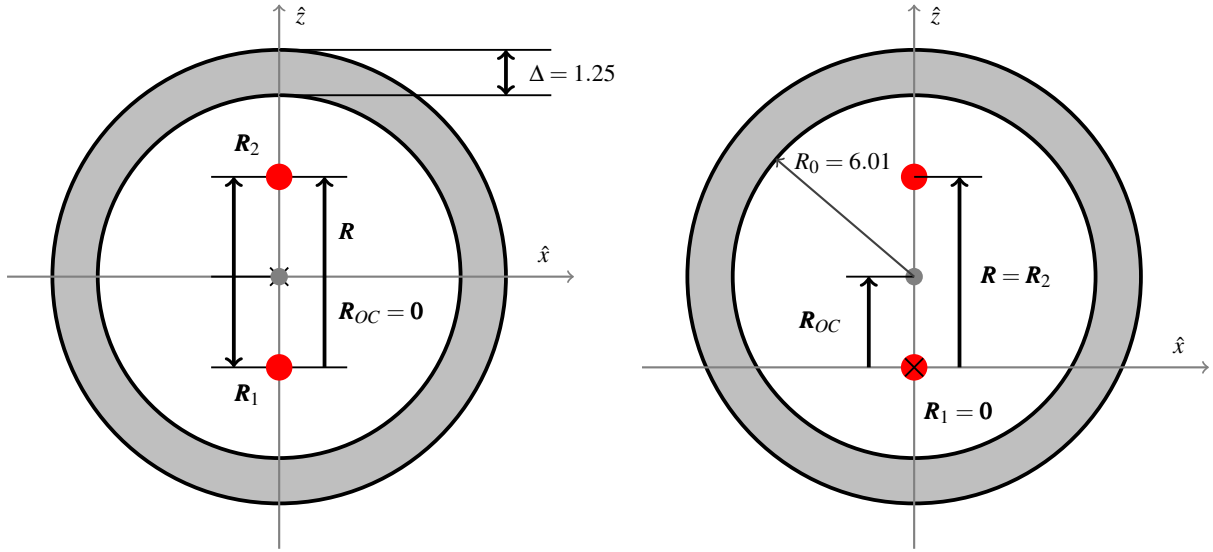[*] Corresponding author: fa1sarua@uco.es

Fig. 1 Schematic representation of the position of the H_2 atomic centers (red circles) and the center of mass of the C_{60} fullerene potential (gray circle) in the different reference systems. On the left, the coordinate system origin is located at the center of the confinement, while on the right it coincides with the position of one of the atoms.

2 Methodology

2.1 One-body Hamiltonians

In this section we board the problem of the lack of spherical symmetry of a molecule located at an arbitrary region in a spherical confinement. In doing so, we study two different reference systems for the partial wave expansion of the non-spherical components of the potential: a) one with the origin at the center of the confinement potential; b) the other with the origin located at one of nuclei.

In both cases, we have assumed that the positions $\mathbf{R}_1$ and $\mathbf{R}_2$ of the two atomic nuclei are aligned in the z axis with the center of the confinement. Our first approach was to use a partial-wave expansion for the Coulomb interaction between each electron and the nuclei. Thus, the single–electron Hamiltonian, $H_{(a)}$, can be written as

$$H_{(a)}(\mathbf{r}) = -\frac{1}{2}\nabla_{\mathbf{r}}^2 + V_c(r) - \sum_{l=0}^{\infty}\left(\frac{r_{1,<}^l}{r_{1,>}^{l+1}}P_l(\cos\theta_1) + \frac{r_{2,<}^l}{r_{2,>}^{l+1}}P_l(\cos\theta_2)\right) \quad (1)$$

where $r_{i,>} \equiv \text{Max}[r,R_i]$, $r_{i,<} \equiv \text{Min}[r,R_i]$ and θ_i is the angle between $\mathbf{r}$ and $\mathbf{R_i}$ (note that θ_i is either θ_i or $\pi - \theta_i$, $i = 1,2$); $V_c(r)$ is the confinement potential (spherically symmetric in this coordinate system) and P_l are the Legendre polynomials[61].

The second approximation is addressed in a similar way except that we have considered the center of the coordinate system coinciding with the position of one of the Hydrogen atoms, and a partial wave decomposition for the off-centered Coulomb center

and the confinement potential. Thus, $H_{(b)}$ reads

$$H_{(b)}(\mathbf{r}) = -\frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{r}$$
$$+ \sum_{l=0}^{\infty}\left(f_l(r,R_{OC})P_l(\cos\theta_c) - \frac{r_{2,<}^l}{r_{2,>}^{l+1}}P_l(\cos\theta_2)\right), \quad (2)$$

where $\{R_{OC},\theta_c,\varphi_c\}$ are now the coordinates of the center of the spherical potential V_c in the system centered at the first atom, which without a loss of generality we can choose $\theta_c = \varphi_c = 0$, and $f_l(r,R_{OC})$ is given by

$$f_l(r,R_{OC}) = \frac{2l+1}{2}$$
$$\times \int_0^{\pi} d\theta \, \sin\theta \, P_l(\cos\theta) \, V_c\left(\sqrt{r^2 + R_{OC}^2 - 2rR_{OC}\cos\theta}\right). \quad (3)$$

In this work we use a combination of two Woods-Saxon potentials to model a C_{60} fullerene cage as the confining cavity[58,59]

$$V_c(r) = \begin{cases} \frac{U_0}{1+e^{(R_0-r)/\eta}} & \text{for} \quad r \leq R_0 + \frac{1}{2}\Delta, \\ \frac{U_0}{1+e^{(r-R_0-\Delta)/\eta}} & \text{for} \quad r > R_0 + \frac{1}{2}\Delta, \end{cases} \quad (4)$$

where R_0 as the inner radius of the potential, Δ is its width, U_0 represents the depth of the potential, and η is the smoothing parameter. Here, we have used fixed values of the potential height $U_0 = -0.422$ a.u., width $\Delta = 1.25$ a.u., inner radius $R_0 = 6.01$ a.u. and smoothing parameter $\eta = 0.1$ a.u. in order to model a C_{60} fullerene cage[58,59,62]. Figure (1) shows a schematic representation of the approaches and confinement used here.

Figure (2) shows the radial components of the partial-wave decomposition of the potential given by Eq. (4), together with $V_c(r)$.
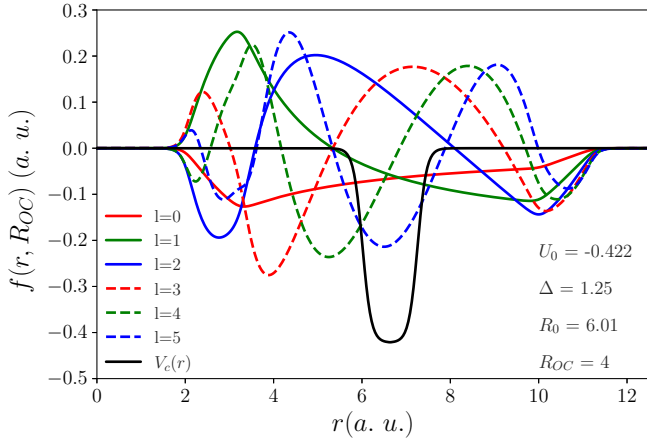
Fig. 2 Fullerene potential given by Eq. (4) (black line) and partial-wave terms $f_l(r, R_{OC})$ given by Eq. (3) of its off-centered description, for $R_{OC} = 4$ a.u. and as a function of the radial distance.

Note that all the radial components expand over a radial range that goes from $R_0 + \frac{1}{2}\Delta - R_{OC}$ to $R_0 + \frac{1}{2}\Delta + R_{OC}$.

2.1.1 Sturmian functions.

As a basis for the expansion of the H_2 two-electron wavefunctions, we used for each radial electron coordinate a set of solutions of the spherical Sturmian equation. With the aim of improving convergence, these functions are defined in terms of the radial differential equation which takes into account some of the one-body interactions which are present in the Hamiltonian[63]. For the Hamiltonians with off-centered terms, these can be defined as

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + V_c(r) - \frac{1}{\text{Max}[r, R_1]} - \frac{1}{\text{Max}[r, R_2]} - E_s \right] s_{n,l}^{(a)}(r)$$

$$= -\beta_{n,l}^{(a)} V(r) s_{n,l}^{(a)}(r) \quad (5)$$

and

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r} - \frac{1}{\text{Max}[r, R_2]} - E_s \right] s_{n,l}^{(b)}(r)$$

$$= -\beta_{n,l}^{(b)} V(r) s_{n,l}^{(b)}(r) \quad (6)$$

depending on the reference system employed. In the above equations, E_s is a parameter while β is the eigenvalue. In this work, we have only considered the $l = 0$ term in the partial wave expansions of the off-centered potentials in the Sturmian equations.

The generating potential $V(r)$ on the right-hand sides of Eqs. (5) and (6), together with the value of E_s, modulate the region over which we want to concentrate the oscillations of the basis to improve convergence. In general, we chose a short-range potential[63,64], although for negative energies it is also possible to set them as Coulombic, as is the case in Coulomb Sturmian Func-

tions[65], especially if we do not have any prior knowledge of the spatial extension of the electronic states. In this work we have used

$$V(r) = \frac{1}{\text{Max}[r, R_1]} + \frac{1}{\text{Max}[r, R_2]}, \quad (7)$$

with $R_1 = 0$ when the system is centered on the first atom.

Spherical harmonics are used for the angular coordinates, and the complete one-body elements can be written as

$$S_{n,l,m}^{(x)}(\mathbf{r}) = \frac{s_{n,0}^{(x)}(r)}{r} Y_l^m(\hat{\mathbf{r}})$$

where x is either a or b.

2.2 Two-body Hamiltonians

Using the definitions given in Eqs. (1) and (2), the equation for the two-electron wavefunction in any of the approximations reads

$$\left[H_{(x)}(\mathbf{r}_1) + H_{(x)}(\mathbf{r}_2) + \frac{1}{r_{12}} + \frac{1}{|\mathbf{R_1} - \mathbf{R_2}|} - E \right] \Psi_\alpha^{(x)}(\mathbf{r}_1, \mathbf{r}_2) = 0 \quad (8)$$

where x is either a or b and α represents the quantum numbers of the eigenstate.

The expansion of the two electron wavefunction reads

$$\Psi_\alpha^{(x)}(\mathbf{r}_1, \mathbf{r}_2) = \sum_\nu a_{\alpha,\nu}^{(x)} \psi_\nu^{(x)}(\mathbf{r}_1, \mathbf{r}_2) \quad (9)$$

with

$$\psi_\nu^{(x)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left(S_{n_1, l_1, m_1}^{(x)}(\mathbf{r}_1) S_{n_2, l_2, m_2}^{(x)}(\mathbf{r}_2) \right.$$

$$\left. + (-1)^S S_{n_1, l_1, m_1}^{(x)}(\mathbf{r}_2) S_{n_2, l_2, m_2}^{(x)}(\mathbf{r}_1) \right) \quad (10)$$

where ν comprises the indexes $\{n_i, l_i, m_i\}$ ($i = 1, 2$) and S is the total spin quantum number. The values of l_1 and l_2 run from 0 to a certain L_{max}, and m_i from $-l_i$ to l_i ($i = 1, 2$).

By replacing the expansion given in Eq. (9) into Eq. (8) and projecting to the left using the complete set of basis functions, we obtained a generalized eigenvalue problem for the eigenenergies and eigenvectors given by the coefficients $a_{\alpha,\nu}^{(x)}$. The reason why it corresponds to a generalized eigenvalue problem and not a standard one is because the two-electron basis elements in Eq. (10) are not orthonormal in the indexes n_i ($i = 1, 2$). Instead, the orthogonality relations for the radial components follow the properties of the Sturmian functions[63].

3 Results and discussion

We first analyzed the differences between the ground state energy in each of the approaches considered in Sec. 2. To achieve this, we fixed the inter-atomic distance R to 1.4 a.u., with the three centers (the two atoms and the center of the cage) aligned with the $\hat{z}$ axis, and performed the calculation for several configurations in each approach, firstly moving down one of the nuclei, and secondly moving up the confinement. In Fig. (3) we com-
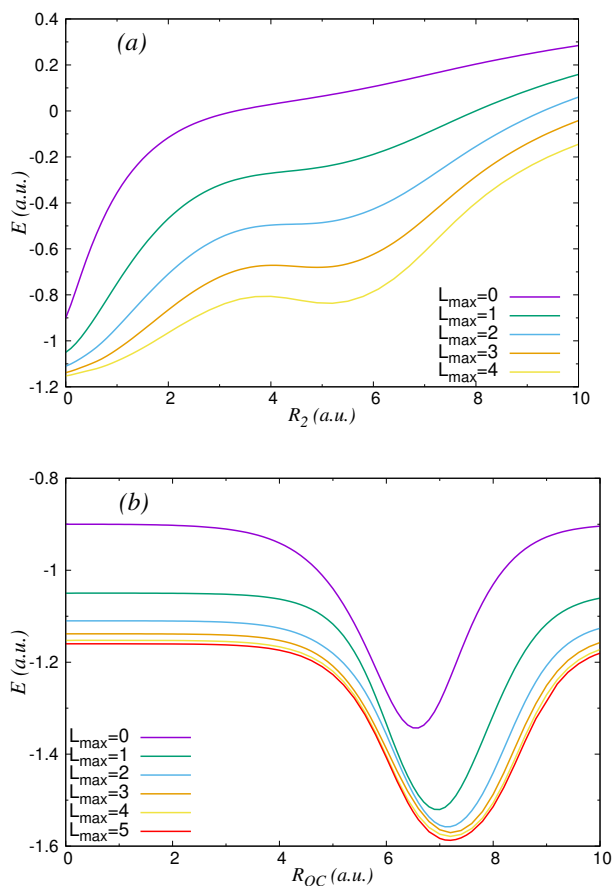
Fig. 3 Upper panel: Electronic ground state energy of the H_2 molecule inside C_{60} as a function of the distance, R_2, from nucleus 2 to the cavity center, for different values of the maximum number of partial waves L_{max} per electron. Lower panel: Electronic ground state energy of H_2 inside C_{60} as a function of R_{OC}, the distance from the of the center of the cavity to nucleus 1, where the origin of the coordinate system is located, for different values of the maximum number of partial waves L_{max} per electron. In both figures, the inter-atomic distance is fixed at $R = 1.4$ a.u.

pare the electronic ground state energy as a function of: in Fig. (3) (a), the distance R_2 of nucleus 2 (always above nucleus 1 in our choice of the coordinate system) to the origin of the coordinates and considering positions of nucleus 2 in the negative $\hat{z}$-axis; and in Fig. (3) (b), the distance, R_{OC}, from the origin of the coordinate system to the center of the confining cavity located in the positive $\hat{z}$-axis. As can be seen, although both figures show similar behavior with minima around the same region, the convergence is faster in the second scheme. This is because the convergence of the energy is dominated by the interaction between the electrons and the nuclei, and the off-center description of s-like cusp conditions is poor with the limited number of partial waves in the system centered in the cage. When we refer the coordinate system to one of the ions, we still have an off-centered ion, but we can see that the difference in the energy curves decreases rapidly with L_{max}, which gives us a much more accurate description from this phenomenological point of view. The results reported have been obtained by fixing one of the atoms to the center of the co-
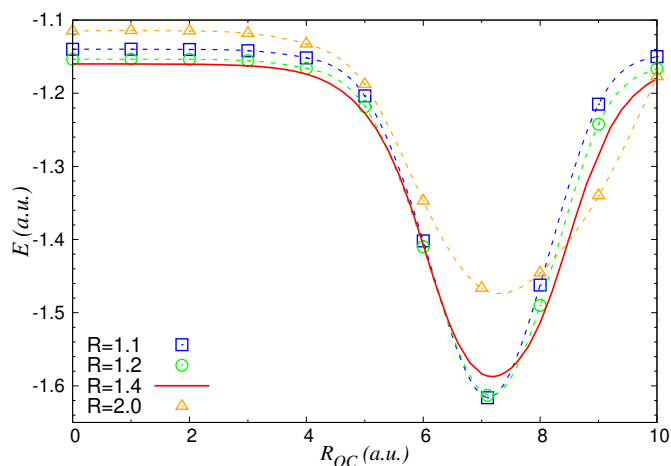

Fig. 4 Electronic ground state energy of H_2 as a function of the position of the center of the confining cavity, R_{OC}, for different values of the nuclear separation, R.

ordinate system and considering different positions of the cage center and using $L_{max} = 5$ in the partial wave expansion of the potential.

As it is seen in Fig. (3) (b), the total decrease in energy with respect to the free case is ~ 0.5 a.u., which indicates a strong coupling between the atoms of the molecule mediated by the interaction with the fullerene surface. This coupling will lead to substantial changes in the molecular structure, such as, for example, differences in the equilibrium nuclear distances. This is shown in Fig. (4), where we plot the ground state energy as a function of the position of the center of the cage, R_{OC}, for different values of the nuclear separation, R. It can be observed that lower energies are obtained for smaller nuclear separations as the molecule approaches the inner surface of the fullerene. The effect of the C_{60} potential is negligible when R_{OC} is below 4 a.u., while a significant decrease in energy is observed for greater distances, reaching a minimum for $R_{OC} = 7.1$ a.u. These results show that confinement effects become important for distances of 0.5 a.u. or less from the inner surface of the fullerene. The minimum is reached when the molecule is inside the shell of the cage, which is 1.25 a.u. wide in our model, while at larger distances from the center, the energy rises and approximates that of the free H_2 molecule.

To shed further light on this behavior, in Fig. (5) we show the equilibrium inter-atomic distance, R_{eq}, and energy, E_{eq}, as a function of the confinement potential position, R_{OC}, calculated using a minimization process.

For $R_{OC} < 6.0$ a.u, $R_{eq} = 1.4$ a.u., just like in the free case although E_{eq} decreases compared to the unconfined energy. The most bounded value is $E_{eq} = -1.616$ a.u., obtained for $R_{eq} = 1.1$ a.u. at $R_{OC} = 7.1$ a.u., as noted above, which shows us that the molecule shrinks. This occurs when one of the nuclei is inside the shell and the other on the inner surface which produces the lowest energy among the different configurations of the molecule and suggests that the molecule will tend to be close to the structure of the cavity.
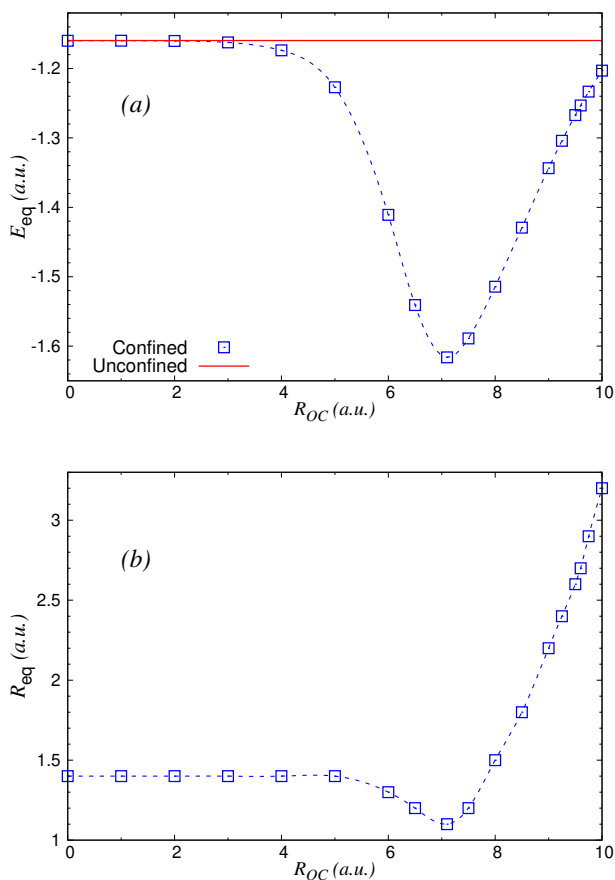
Fig. 5 Upper panel: Energy for the equilibrium bond length, E_{eq}, of the H_2 as a function of the position of the center of the confining cavity, R_{OC} (blue squares), compared with the unconfined value (red line). Lower panel: Equilibrium bond length, R_{eq}, of the H_2 for different positions of the center of the confining cavity, R_{OC}.

Fig. 6 Upper panel: Electronic ground state energy of the H_2 molecule as a function of the internuclear distance, R, for $R_{OC} = 3.0$, 6.0 and 7.1 a.u. Lower panel: The same for $R_{OC} = 7.1$, 8.5 and 10.0 a.u. The minimum energy is marked with a cross on each curve. The unconfined energy is also plotted in the panels for the sake of comparison.

On the other hand, for more distant cavity positions such as $R_{OC} = 9.0$ a.u., the minimum energy is obtained for $R_{\text{eq}} = 2.2$ a.u., a configuration where one atom lies in the shell and the other outside the fullerene, which corresponds to a greater inter-atomic separation than that of the free molecule, reaching values above 3.0 a.u. for $R_{OC} = 10.0$ a.u. Consequently, if one nucleus is inside the shell and the other is outside the fullerene, the molecule increases in size and energy in contrast to the behavior observed, with one nucleus inside the shell and the other in the interior cavity, where both the energy and the size decrease.

In Fig. (6), we plot the ground state energy as a function of the inter-atomic distance for different values of R_{OC}, in order to observe the differences between the confined and unconfined values for different positions of the cavity and the changes in the configuration of the molecule described above; the result for the unconfined case is also shown. Two different figures are included to analyze the different regimes: in Fig. (6) (a), curves for R_{OC} of 7.1 a.u. and below are displayed, while in Fig. (6) (b), energy curves for $R_{OC} = 7.1$ a.u. and above are shown.

As R_{OC} rises up to 7.1 a.u., the ground state energy decreases and the minimum of the potential energy curve is shifted to the left, i.e., the equilibrium bond length decreases, and the molecule
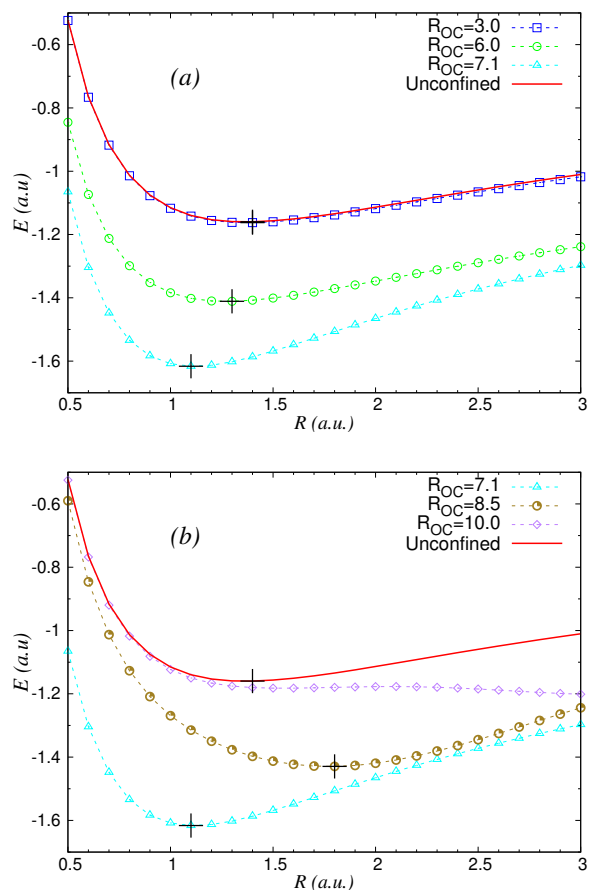
therefore shrinks. On the other hand, for $R_{OC} > 7.1$ a.u., the energy rises and approximates unconfined values. However, due to the fact mentioned above that in this regime, the most favorable configuration feature one nucleus trapped inside the shell and the other outside the cage, the potential energy curve flattens for higher values of inter-atomic distance. Consequently, the minimum is not defined and cannot be appreciated in the scale of the figure.

4 Conclusions

In this paper, we have addressed the problem of the Hydrogen molecule under off-centered spherical confinement, with a combination of two Woods-Saxon potentials to model a C_{60} fullerene cage as a confining cavity, and a configuration interaction approach with generalized Sturmian functions for the electronic structure of the molecule. Two different choices for the origin of the reference system have been studied: a) in the center of the cavity, b) at the position of one nucleus. After analyzing the convergence of the electronic ground state energy of the molecule in both systems, it is clear that the one related to the Coulomb charge is the most suitable for the problem here considered.

Using this reference system, we have obtained the electronic ground state energy for different inter-atomic distances, R, and positions, R_{OC}, of the H_2 molecule within the fullerene. When the molecule is close to the center of the cavity, $R_{OC} \leq 3$ a.u., the effect of the cavity is negligible. As the distance to the center of the cavity increases, $3 \leq R_{OC} \leq 7.1$ a.u., the energy presents a minimum for an equilibrium bond length lower than that of the free molecule. For greater separations from the cavity center, $R_{OC} > 7.1$ a.u., the energy rises and approaches the potential energy curve of the unconfined H_2 molecule, but with one important difference: the minimum tends to disappear because the curve flattens when the molecule is located far from the center of the cavity. This has been interpreted in terms of the relative position of the atoms in the cavity. Thus, when the nuclei are inside the interior cavity and far from its inner surface, the confining potential has a perturbative effect on the system, while when they become closer to the inner surface, the attraction by the structure causes a significant decrease in energy and equilibrium bond length. The minimum is obtained when one nucleus is inside the shell and the other one is on the inner surface. For greater separations from the center, the situation changes, and one nucleus lies outside the fullerene while the other is trapped within its shell, in such a way that the potential energy curve is practically flat. Therefore the most favorable configuration is with one atom inside the shell and close to the outer surface and the other located at a great distance. Finally, it is worth mentioning that a more complete description of the structure of the molecule inside C_{60} must address the situation in which the atoms are not aligned with the center of the cage. We hope to present the results of this study in a future publication.

Author contributions

J.M.R. and A.J.S. conceived the idea and the model, J.M.R. designed the computational framework; J.M.R. and M.F. M.-A. carried out the implementation; M.F. M-A. performed the calculations; M.F. M-A. and J.M. A.-P. contributed to the analysis of results; M.F. M.-A., J.M. A.-P. and J.M.R. wrote the initial version of the manuscript; all the authors contributed to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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