

Ab initio calculation of electrostatic potentials for C₆₀ and C₈₀

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Abstract

Ab initio calculations of electrostatic potentials of C₆₀ and C₈₀ have been performed at the B3LYP/6-31G(d) level. Comparisons of the present calculations with phenomenological models and other *ab initio* results demonstrate that the new proposed electrostatic potentials give a better description of the confining effect than square potential well models. The present calculated electrostatic potentials are fitted with the Lorentz function. The electrostatic potentials obtained are expected to be useful for modelling atomic dynamic processes, such as photoionization and elastic scattering of endohedral fullerenes, and simulation of the interaction between energetic ions and fullerenes.

Keywords: electrostatic potential, fullerene, photoionization

1. Introduction

Endohedral fullerenes, A@C₆₀, where an atom or small molecule is embedded inside the fullerene, have attracted considerable interest in recent years [1–3]. Effective experimental methods to study such confined atoms are photoionization [4–6] and elastic scattering [7, 8]. Confinement resonances produced in the photoionization of Xe@C₆₀ have been demonstrated in the notable breakthrough experiment by Kilcoyne and co-workers [4, 5]. Meanwhile, extensive calculations have been carried out [9–17] to analyze the observed resonance structures. However, big discrepancies still exist between theoretical and experimental values, as well as between different theories. One possible reason is the electrostatic potential (ESP) used to model the confining effect of the fullerene cage on an embedded atom/molecule. Various phenomenological potential wells were proposed (see [18, 19], and references therein), where a square potential well $U_s(r)$ was commonly adopted [16]:

$$U_s(r) = \begin{cases} -U_0, & \text{if } r_c \leq r \leq r_c + \Delta \\ 0, & \text{otherwise} \end{cases} \quad (1)$$

For the endohedrally confined atom, a diffuse potential is more realistic than a discontinuous square-well pseudo-

potential $U_s(r)$ [20, 21]. Dolmatov *et al* [20] introduced a diffuse potential which was combined by two Woods–Saxon potentials. Another form of such a diffuse model was the attractive short-range spherical Gaussian-type potential, which was introduced by Nascimento *et al* [21]. In 2012, Verkhovtsev and co-workers [22] calculated the ESP for C₆₀, which was based on the density functional theory (DFT) using the Gaussian 09 package and a modified jellium model. The newly proposed ESP was adopted by Li *et al* [17] to calculate the photoionization cross section of Xe@C₆₀, and they found that the new model gave better overall agreement for both the resonance position and width than the square potential well $U_s(r)$. Verkhovtsev *et al*'s work was extended by Vrabel *et al* [23, 24] to C₆₀[−], C₆₀ and C₆₀⁺ with the FireFly package in 2016 and 2018. The question posed here is based on the fact that the calculated ESP of C₆₀ by Verkhovtsev *et al* [22], using a SPL DFT functional with the Slater exchange functional and the local Perdew functional (SPL), has a relatively large difference to the B3LYP hybrid functional and the Slater exchange and Vosko–Wilk–Nusair correlation functional (SVWN) DFT by Vrabel *et al* [24].

In this paper, we start from the ESP of C₆₀ to check the validity of DFT methods by comparing with the second order Møller–Plesset theory (MP2). Then, we extended the calculation to C₈₀. Also, the present calculated ESPs are fitted to the

Lorentz function. The data obtained are expected to be useful for studying endohedral fullerenes, for atomic dynamical processes such as photoionization and elastic scattering. These ESPs are also needed in molecular dynamic simulation of the interaction between energetic ions and fullerenes.

2. Theoretical method

In the present work, DFT calculations are performed using the hybrid density functional method of B3LYP [25–27]. An additional benchmark calculation for C_{60} was carried out using the MP2 [28]. Then, the total ESP that an electron feels can be expressed as the sum of the ESP generated by the nuclei and the ESP generated by the electrons [22]:

$$U_{tot}(r) = U_{nuc}(r) + U_{ele}(r) = -\sum_A \frac{Z_A}{|r - R_A|} + \int \frac{\rho(r')}{|r - r'|} dr' \quad (2)$$

here, $U_{tot}(r)$ is the total ESP, $U_{nuc}(r)$ is the ESP generated by the nuclei, $U_{ele}(r)$ is the ESP generated by electrons and $\rho(r')$ is the electron density. Since the systems we calculated are highly symmetrical, close to spherically, we averaged the total ESP in the r direction. *Ab initio* calculations were performed using the Gaussian 09 package [29], and the total ESP was further calculated using a multi-functional wave function analyzer (Multiwfn) [30].

The atomic units were used throughout the paper.

3. Results and discussion

For C_{60} , the confining potential was commonly described by the square potential well $U_s(r)$ in equation (1), where $U_0 = 8.22$ eV is the depth of the well and was obtained by fitting the experimental electron affinity energy of C_{60} [31]. Here, $r_c = 5.8$ a.u. is the inner radius of the shell and $\Delta = 1.9$ a.u. is its thickness, which were obtained by fitting the photoabsorption cross section of C_{60} [32]. We performed optimization calculations using B3LYP/6-31G(d) and MP2/6-31G(d). The SPL/6-311 + G(d) was also adopted to compare with the previous calculations. We compare our results and previous results in figure 1. Our DFT and MP2 results are in good agreement with the results calculated by [24]. The SPL/6-311 + G(d) result reported in [22] differs from the other results. There are small differences in the depth of the potential, which is generally a reflection of electron affinity energy. However, such a difference will have very little influence on atomic dynamic processes such as photoionization and hence can be ignored. It also confirms that the B3LYP/6-31G(d) has a good description of fullerene, and this method was adopted for further calculations on C_{80} .

A photoionization cross section of $Lu_3N@C_{80}^{q+}$ ($q = 1, 2, 3$) has been measured by employing the photon-ion merged-beam technique [33]. The fragmentation dynamics of

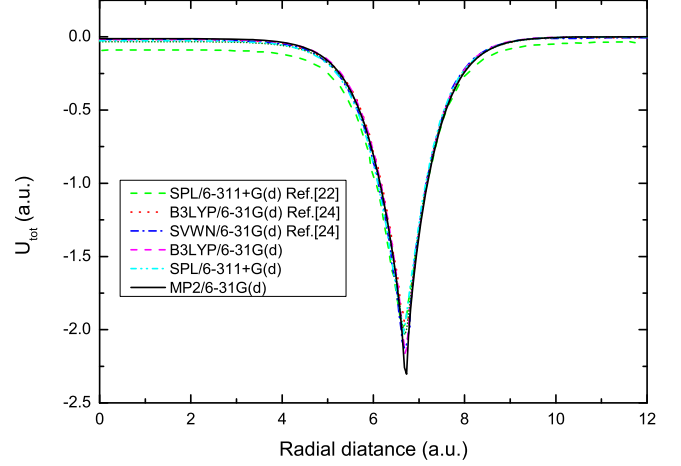


Figure 1. A comparison of the ESPs for C_{60} between the present calculations and previous results: SPL/6-311 + G(d) is the result from [22] (dash, green); B3LYP/6-31G(d) (dot, red) and SVWN/6-31G(d) (dash dot, blue) are the results from [24]; the present results are B3LYP/6-31G(d) (dash, magenta), SPL/6-311 + G(d) (dash dot dot, cyan) and MP2/6-31G(d) (solid, black).

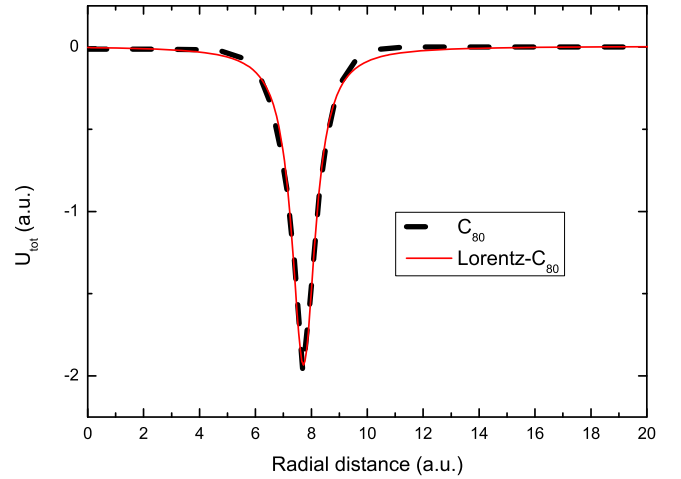


Figure 2. The calculated ESP (dash, black) for C_{80} together with the fitted curve using the Lorentz function (solid, red).

$Sc_3N@C_{80}$, using a synchrotron soft-x-ray photon at the advanced light source (ALS) [34], and of $Ho_3N@C_{80}$, using femtosecond near-infrared laser pulses [35], were reported recently. The ESP of C_{80} is required to calculate the photoionization cross section and fragmentation dynamics. We performed optimization calculations using the B3LYP/6-31G(d) method and calculated the ESP of C_{80} , which is shown in figure 2 together with the fitted curve using the Lorentz function.

The calculated ESPs are fitted using the Lorentz function. The general formula is as follows:

$$U_{tot}(r) = U_0 + \frac{2A}{\pi} \frac{W}{4(r - r_c)^2 + W^2}. \quad (3)$$

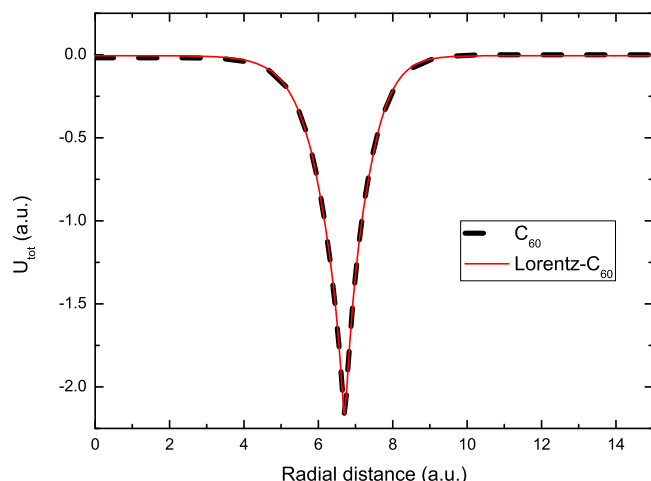


Figure 3. The calculated ESP (dash, black) for C_{60} together with the fitted curve using the Lorentz function (solid, red).

Table 1. Coefficients of the Lorentz function used for fitting the ESPs.

Coefficients	C_{60}	C_{80}
U_0	0.014 12	0.004 88
r_c	6.675 42	7.717 53
W	1.031 76	1.022 05
A	-3.171 99	-3.111 84

The fitting coefficients are given in table 1 and are plotted for C_{60} in figure 3.

4. Conclusion

In this paper, the total ESPs of C_{60} have been calculated using the DFT and MP2 theory employing the Gaussian 09 package. We confirm that B3LYP/6-31G(d) has a good description of fullerene, and this method has been extended to calculate the ESP of C_{80} . The total ESP we calculated is more realistic than the discontinuous square potential well model. We fitted the total ESPs with the Lorentz function. The fitting formula can be used for other molecular dynamics tasks. Looking ahead much remains to be done. (i) There are many derivatives of C_{60} whose geometries are non-spherically symmetric. We need to introduce a new ESP model to account for deformation effects. (ii) If we look through the photoionization milestone experiment of $Xe@C_{60}$ [7], we notice that the system is actually Xe inside a C_{60}^+ cage instead of C_{60} . This is also the case in the photoionization experiment of $Lu_3N@C_{80}^{q+}$ ($q = 1, 2, 3$). Further studies on the effects of a charged shell $C_n^{z\pm}$ are needed.

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