Modeling of $C_{60}$ pseudopotential with the different basis sets

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Abstract. As a result of ab-initio-based calculations, we can propose the description of the fullerene $C_{60}$ in terms of pseudopotential. In the paper, the results of calculations based on the basis set composed of atomic orbitals and plane waves basis set have been compared. Also, the pseudopotential was approximated by an analytical function, which can be applied in future calculations.

1. Introduction
Fullerene $C_{60}$ is being extensively researched all over the world from the first prediction [1] due to its unique properties and wide availability of such compounds. Because of the high affinity to electron, $C_{60}$ can play the role of electron acceptor in the complex systems. The fullerenes can act as a semiconductor, conductor and superconductor under specific conditions. Fullerenes can display the photochromic effect, which is a change in light transmission based on intensity.

Modeling of extended nanostructured systems that contain $C_{60}$ is very difficult, and for some applied problems a simple analytical description of fullerene potential is highly desirable. Modeling of $C_{60}$ potential starts from introducing the jelly model [2, 3] and still stays actual. Due to the fact that the fullerene symmetry is close to spherical, the natural choice of the effective potential is the angular averaged total electrostatic potential that obtained from ab-initio calculations.

2. Details of calculation and results
Ab-initio calculations were performed in 2 ways: with basis set of atomic orbitals and basis set of plane wave that can be seen from figure 1. First of all, the role of electronic correlation effects to the total electrostatic potential of $C_{60}$ should be investigated. For this purpose we carried out calculation with atomic orbitals within the hybrid Becke-Lee-Yang-Parr three-parameter [4] (B3LYP) density functional treatment. That includes HF-type exchange and exchange-correlation functionals formulated within the Generalized Gradient Approximation (GGA). Moreover, the attractive dispersion corrections to the DFT treatment via the
B3LYP-D3 [5] approach was taken into account since dispersion-corrected DFT is the current standard. Total electrostatic potential was averaged over a solid angle to clarify the radial dependence.

Ab-initio computations within atomic orbitals were performed with the FireFly quantum-chemistry package [6]. The initial optimization of the structure was realized through the semi-empirical PM3 approach [7]. The resulting geometry was used as a zero-order approximation for calculation in B3LYP/6-31G(d) and B3LYP-D3/6-31G(d) treatments (Popple notation).

\[
U_{\text{tot}}(r) = U_n(r) + U_{\text{el}}(r) = -\sum_{i=1}^{60} \frac{6}{|r-R_i|} + \int \frac{\rho(r')}{|r-r'|} dr' \tag{1}
\]

Figure 1. The histograms of distances between the center of \( C_{60} \) and positions of carbon nuclei obtained with atomic orbital (AO) basis and wave function (WF) basis.

As it was mentioned above the pseudopotentials of \( C_{60} \) and were constructed on the basis of the corresponding total electrostatic potentials. The latter was presented as a sum of two terms: the potential of nuclei \( U_n(r) \), which depends on the positions of sixty carbon atoms, and the potential \( U_{\text{el}}(r) \) created by electron density \( \rho(r) \):

\[
U_{\text{pseudo}}(r) = U_{\text{tot}}(r) = U_n(r) + U_{\text{el}}(r) \tag{2}
\]

\[
U_i(r) = \frac{1}{4\pi} \int U_i(r)d\Omega \quad (i=\text{tot, n, el})
\]

Calculations within plane wave basis set were performed with Quantum Espresso package [8-9] also with DFT and similar approximations.

DFT-based approximations lead to an increase of the effective radius \( C_{60} \) that associated with the accounting of the electronic correlations and the B3LYP-D3 approach within atomic orbital basis set.
produces the lowest total energy. The account of electron correlations makes potential deeper keeping its width. Also the position of pseudopotential minimum is shifted to the larger radial distances when correlations are taken into consideration. Since the sharp shape of potential leads to very high sensitivity of the electronic level position, even this small discrepancy should be treated carefully. Thus, the result of B3LYP-D3 calculations should be used for construction of analytical approximation of pseudopotential of C\textsubscript{60}.

For the future purposes, numerical solution was approximated by the analytical Chesler-Cram peak function [8, 9] that generally used for fitting of chromatographic peaks.

\begin{align}
    y &= y_0 + A\left(e^{-\frac{(x-x_{c1})^2}{2w}} + B\left[1 - 0.5\left(1 - \tanh(k_2(x - x_{c2}))\right)\right]e^{-0.5k_3(|x - x_{c3}| + (x - x_{c3}))}\right) \quad (3),
\end{align}

where $x$ is the radial distance. The sets of constants allowing to achieve accurate approximation are, $y_0=-0.01239$, $x_{c1}=6.66442$, $A=-0.15527$, $w=0.04559$, $B=27.94053$, $k_2=0.89397$, $x_{c2}=6.85974$, $k_3=2.25645$, $x_{c3}=6.71233$ are the constants of approximation.

Figure 2. Color map of the pseudopotentials C\textsubscript{60} obtained within the approximation of B3LYP-D3. The considered fullerene exhibit the strong attraction near the fullerene radius and have weak attraction force far from fullerene cage.
Figure 3. Chesler-Cram approximation for pseudopotentials obtained from ab-initio B3LYP-D3 calculations. Chesler-Cram peak function fits well within C_{60} pseudopotential at any distance.

Conclusion
We have calculated the electronic and spatial structure of the fullerene C_{60}. By averaging the total electrostatic potential, the radial dependent pseudopotential were constructed. The calculated pseudopotential have been fitted by the analytical Chesler-Cram peak function and can be applied for further tasks.

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