Ab-initio modeling of an anion $C_{60}^-$ pseudopotential for fullerene-based compounds.

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Abstract. A pseudopotential of $C_{60}^-$ has been constructed from ab-initio quantum-mechanical calculations. Since the obtained pseudopotential can be easily fitted by rather simple analytical approximation it can be effectively used both in classical and quantum molecular dynamics of fullerene-based compounds.

1 Introduction

Fullerene $C_{60}$ is the most studied and widely used among all fullerenes because of the availability, high symmetry and low price [1]. Some of the most promising fields of application of these novel materials are artificial photosynthesis, non-linear optics and the preparation of photoactive films and nanostructures (see, for example [2]). Because of high electron affinity and small rearrangement energy fullerenes, in particular $C_{60}$, play a role of electron-acceptors in such systems and produce very stable radical pairs. In particular, it was demonstrated that a π-conjugated polymer was able to efficiently transfer electrons to the $C_{60}$ core giving rise to long-lived charge-separated states. For example the donor-acceptor compound $[C_{60}]$PCBM [3] is the most known and effectively used in organic solar photoelectric cells for the last time. But, due to the difficulties in the modeling extended and possible nanostructured materials as $[C_{60}]$PCBM an isolated molecular limit is preferable, so the investigations of the isolated anions and radical anions of fullerenes, in particular $C_{60}^-$, seems to be actual.

The anions and radical anions of fullerenes have been an object of intensively investigations during last two decade [4,5]. The anionic fullerenes have been observed in ion cyclotron resonance traps [6], storage rings [7] and electrospray mass spectrometry [8]. The theoretical systematic study of the stability of highly charged anionic fullerenes has been performed within different levels of theory [9,10]. But for the developing efficient quantum simulation methods, which allow us to predict the optimized geometry of the fullerene $C_{60}$ compounds with reasonable computer cost and accuracy, we suggest to construct a pseudopotential of $C_{60}^-$. In this paper the pseudopotential of $C_{60}^-$ has been constructed on the basis of the Hartree-Fock and density functional theory (DFT) calculations by ROHF/6-31G(d) and B3LYP/6-31G(d) levels respectively. Then within the optimized geometry the ab-initio calculations of the electronic structure and the total charge density of $C_{60}^-$ have been performed at the same levels of theory, which is shown to provide reasonable results for small carbon clusters [13] and fullerenes [10,14], both charged and neutral. Although the inclusion of diffuse functions is usually important to obtain accurate absolute energies for anions, it has recently been shown that the 6-31G(d) and 6-31G+(d) basis sets give similar results for geometries, charge distributions, and relative energies of anionic $C_{60}$ and $C_{70}$ fullerenes [15,16].

The important point of the ab-initio calculations of the total charge density is to apply the corresponding key in the input of the FireFly program like AIM PAC = 1 to obtain the practical information about molecular orbital wave functions which are used in the next step of construction of the pseudopotential of $C_{60}^-$. 

2 Method of calculation

2.1 Ab-initio calculations

All ab-initio computations are performed by using the FireFly QC package [12]. For the first the fully optimized geometry and the total energy of $C_{60}$ have been obtained from the Hartree-Fock and density functional theory (DFT) calculations by ROHF/6-31G(d) and B3LYP/6-31G(d) levels respectively. Then within the optimized geometry the ab-initio calculations of the electronic structure and the total charge density of $C_{60}^-$ have been performed at the same levels of theory, which is shown to provide reasonable results for small carbon clusters [13] and fullerenes [10,14], both charged and neutral. Although the inclusion of diffuse functions is usually important to obtain accurate absolute energies for anions, it has recently been shown that the 6-31G(d) and 6-31G+(d) basis sets give similar results for geometries, charge distributions, and relative energies of anionic $C_{60}$ and $C_{70}$ fullerenes [15,16].

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2.2 Pseudopotential construction

The pseudopotential of $C_{60}^-$ can be constructed on the basis of the total electrostatic potential. The latter is presented as a sum of two summands: the potential of nuclei $U_n(r)$, which depends on positions of sixty carbon atoms, and the potential created by electron density $\rho(r)$ of 361 electrons $U_{el}(r)$:

$$
U_{tot}(r) = U_n(r) + U_{el}(r) = 
- \sum_{i=1}^{60} \frac{6}{|\mathbf{r} - \mathbf{R}_i|} + \int \frac{\rho(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'.
$$

(1)

The positions of the carbon atoms within the optimized geometry and corresponding charge density have been extracted from results of the *ab-initio* FireFly QC package calculations by using of a Multifunctional Wavefunction Analyzer (Multiwfn) [17] (see for example a color filled map of the electron charge density of the $C_{60}^-$ obtained from *ab-initio* calculations prepared within the Multiwfn [17] software on the Fig. 1). This software has been used for computation of the corresponding electrostatic potentials on a specified grid of the position vector $\mathbf{r}$. After that we have averaged the electrostatic potential obtained from Multiwfn software over the directions of the position vector $\mathbf{r}$ to construct the radial dependence of $C_{60}^-$ pseudopotential $U_{pseudo}(r)$ and to obtain averaged electron density $\rho(r)$:

$$
U_{pseudo}(r) = \overline{U}_{tot}(r) = \overline{U}_n(r) + \overline{U}_{el}(r),
$$

$$
\overline{U}_i(r) = \frac{1}{4\pi} \int U_i(r) d\Omega \quad (i = tot, n, el),
$$

$$
\rho(r) = \frac{1}{4\pi} \int \rho(r) d\Omega.
$$

(2)

3 Results

For the first we have checked the non-applicability of the jellium model for purpose of construction of pseudopotential of $C_{60}^-$. The averaged radial valence electron density $\rho(r)$ of $C_{60}^-$ calculated by *ab-initio* method has been compared with results of the jellium model and *ab-initio* calculations for $C_{60}$ [11]. The Hartree-Fock method has been used for self-consistent calculations in all three cases. Fig. 2 demonstrates the density profiles of valence electrons of $C_{60}$ [11] and $C_{60}$ (present work, ROHF/6-31G(d) level) as a function of radial distance from a center of fullerene. As Fig. 2 indicates, the results of *ab-initio* calculations for fullerene and anion are close, but substantially differ from the results of jellium model calculations for $C_{60}$, which makes this approach non-applicable to solving a problem of determination of $C_{60}^-$ pseudopotential.

The results of the $C_{60}^-$ pseudopotential calculations by Hartree-Fock method (ROHF/6-31G(d)) and within DFT (B3LYP/6-31G(d)) are presented and compared in Fig. 3. Note that the usage of the different approaches for the electronic structure calculations leads to the significant discrepancy of the corresponding one-particle energies results but doesn’t lead to the any noticeable differences in the resulting behavior of pseudopotential (compare blue and red solid line in Fig. 3).

It should be mentioned several important features of the pseudopotential obtained. The first one is the correct asymptotic behavior at the large distances as $1/r$, which is
For purposes of the classical and quantum molecular dynamics of fullerene-based compounds it is reasonable to make the analytical approximation of the numerically obtained pseudopotential. Within the range 0 – 10 a.u. of radial distance the pseudopotential has been approximated by sum (3) of constant and Chesler-Cram single peak function (see Fig. 4). This Chesler-Cram function is applied to approximate experimental results in the processing of chromatographic data. We use this function because it may describe discontinuity point and consists of elementary functions. The general view of our function is presented by the following formula:

$$u(r) = y_0 + A[e^{-\frac{(r-r_{c1})^2}{2w}} + B e^{-\frac{1}{2}k_3(|r-r_{c3}|+(r-r_{c3}))}] \times (1 - 0.5 (1 - \tanh(k_2(r-r_{c2})))),$$  \hspace{1cm} (3)

where \( r \) is the radial distance, \( y_0, A, r_{c1}, w, B, k_2, r_{c2}, k_3, r_{c3} \) are approximation constants. The array of constants that allows to achieve the best result is represented in the table 1.

Table 1. array of constants

| symbol | value  |
|--------|--------|
| \( y_0 \) | 0.10096 |
| \( r_{c1} \) | 6.66092 |
| \( A \) | -1.60691 |
| \( w \) | 4.0523 \times 10^{-3} |
| \( k_2 \) | 0.79686 |
| \( r_{c2} \) | 8.32747 |
| \( B \) | 20.83852 |
| \( k_3 \) | 3.14767 |
| \( r_{c3} \) | 6.66096 |

4 Conclusion

In this work we have constructed the pseudopotential of the fullerene anion \( C_{60}^- \) for molecular dynamic purposes. The method of construction is based on the using of the charge density obtained by the \textit{ab-initio} calculations and on the averaging of the corresponding total electrostatic potential to make the radial dependence of the pseudopotential.

The pseudopotential of the fullerene anion \( C_{60}^- \) obtained has rather simple analytical approximation and then can be effectively used both in classical and quantum molecular dynamics of fullerene-based compounds.

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