

The dual descriptor to measure local reactivity on Buckminster fullerenes: an analysis within the framework of conceptual DFT

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Abstract The Buckminster fullerene C_{60} molecule was analyzed from the point of view of global and local reactivity. In particular, the dual descriptor—a local reactivity descriptor derived from conceptual density functional theory—was used to describe local reactivity in this molecule. One of the main advantages of using such a descriptor is the simplicity of obtaining accurate information about the local reactivity required to form covalent bonds without needing to perform calculations at higher levels of theory. The descriptor was adapted to the correct symmetry of this molecule in equilibrium so that the isosurface belongs to the totally symmetrical irreducible representation of the respective group of symmetry. Unlike global and some other local reactivity descriptors, correlation effects and basis sets are not critically important when using the dual descriptor because local reactivity is conserved at a qualitative level.

Keywords Buckminster fullerene · Conceptual DFT · Local reactivity descriptors · Dual descriptor · Fukui functions

Introduction

Since its discovery by Kroto et al. [1], and synthesis by Kräschmer et al. [2], much of the attention paid to Buckminster fullerene (or C_{60} ; Fig. 1) has focused on the pursuit of technology innovation. In parallel, in order to better understand the theory of C_{60} reactivity, a number of

experimental and theoretical approaches have been taken. Experimentally, multiphoton ionization [3], low-energy electron attachment [4], photoinduced charge transfer in excited fullerene [5], photoconductivity measurements of C_{60} and C_{60} -doped poly(vinylchloride) [6], along with fabrication and electron-beam-induced polymerization of C_{60} nanoribbon [7] have been carried out, and apparent electrocatalysis has been observed on C_{60} film-modified electrodes [8]. Hasobe et al. [9] experimented with composite nanoclusters made of porphyrines and fullerenes with gold nanoparticles for use in designing photovoltaic cells. Additionally, in order to modify the molecular structure of C_{60} , its functionalization through the use of organometallic reagents has been established by Champeil et al. [10]; this will help multiply and extend the uses of this molecule in many other fields. These latter modified C_{60} structures constitute fundamental bases because, as explained by Barszcz et al. [11], to optimize the process of photo-induced electron transfer from electron donors [e.g., an organic chromophore molecule or π -conjugated polymer] to an electron acceptor such as the C_{60} molecule, the contact between both species must be very close and the best way to achieve this is to covalently bond the chromophore to the C_{60} . This work is oriented towards the design of solar cells [11]. Peralta-Inga et al. [12] have characterized the surface electrostatic potentials of some nanotubes—molecular structures related to fullerenes. More work focused on the local reactivity on fullerenes by examining molecular electrostatic potentials has been carried out by Politzer and coworkers [13].

There are many more experimental examples highlighting the increasing importance of C_{60} and its derivatives in the development of exciting new technologies [14–16]. From the above, it will be apparent to the reader that understanding of C_{60} reactivity is essential; pursuit of this

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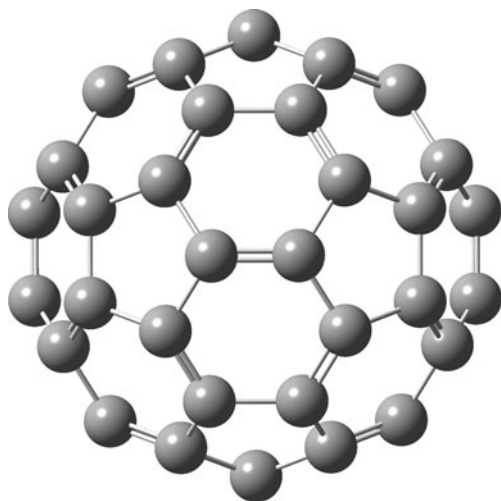


Fig. 1 Molecular structure of Buckminster fullerene, also known as C_{60}

knowledge can be approached from different angles, for example via computational chemistry through the use of quantum chemical calculations. Indeed, some theoretical studies have already been carried out on C_{60} and its derivitized molecular structures. Since 1991, different kinds of theoretical calculations have started to characterize fullerenes. Lüthi and Almöf [17] performed ab-initio studies on the thermodynamic stability of the icosahedral C_{60} molecule; meanwhile, Scuseria [18] predicted the equilibrium geometries of C_{60} , $C_{60}H_{60}$ and $C_{60}F_{60}$ from an ab-initio theoretical point of view; Koga et al. [19] analyzed the Jahn-Teller distortion and electronic structure in the C_{60} anion radical by means of ab-initio calculations; De Proft et al. [23] used conceptual density functional theory (conceptual DFT) to study the influence of electrostatic effects and hardness of the endohedral complexes of C_{60} , Si_{60} , and Ge_{60} with monoatomic ions [21] and magnetic interaction between C_{60} anion radicals [22]. However, to date, research conducted on C_{60} global and local reactivity based on conceptual DFT is still insufficient [23]. Since C_{60} remains the focus of intense interest, any research that helps explain the reactivity of this molecule will be useful in the synthesis of new devices and molecules based on it. The aim of this paper was to establish a proper level of theory to depict a specific tool for C_{60} , i.e., a local reactivity descriptor revealing sites that will be attacked by nucleophilic and electrophilic species.

Theoretical background

Reactivity is a key concept in chemistry because it is associated with reaction mechanisms. Understanding of reactivity facilitates the comprehensive understanding of

chemical reactions, thus improving synthesis procedures to develop novel molecules or materials. A branch of DFT [24, 25] called qualitative density-functional theory of chemical reactivity—also called conceptual DFT [23, 26, 27]—has been developed and used in chemistry; conceptual DFT is characterized by a set of global and local descriptors that measure the reactivity of molecular systems. These reactivity descriptors will be defined in the following sections.

Global reactivity descriptors

Conceptual DFT [23, 28] has provided a set of reactivity descriptors based on the fact that, in the canonical ensemble, electronic energy E can be written as a function of N , the total number of electrons, and as a functional of $v(\mathbf{r})$, the external potential; then $E \equiv E[N, v(\mathbf{r})]$.

Chemical potential, molecular hardness and electrophilicity index

Assuming differentiability of E with respect to N and $v(\mathbf{r})$, a series of response functions emerge: the chemical potential that characterizes the tendency of electrons to escape from the equilibrium system is defined as [23, 29]:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(\mathbf{r})}, \quad (1)$$

the molecular hardness, the resistance to charge transfer, is defined as [23, 30]:

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\mathbf{r})} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(\mathbf{r})}. \quad (2)$$

Both μ and η are global properties that are involved in the reactivity of molecular systems [23]. A three-point finite difference approximation leads to the following working equations for these quantities [23, 28]

$$\mu \approx -\frac{1}{2}(I + A) \quad (3)$$

$$\eta \approx \frac{1}{2}(I - A), \quad (4)$$

where I and A are the first vertical ionization potential and the first electronic affinity of the neutral molecule, respectively. Further approximation using the Koopmans' theorem [31] from the closed-shell Hartree-Fock theory [32] ($I \approx -\epsilon_{\text{HOMO}}$ and $A \approx -\epsilon_{\text{LUMO}}$) allows one to write μ and η in terms of energies of the lower unoccupied

molecular orbital LUMO ($\varepsilon_{\text{LUMO}}$) and higher occupied molecular orbital HOMO ($\varepsilon_{\text{HOMO}}$):

$$\mu \approx \frac{1}{2}(\varepsilon_{\text{LUMO}} + \varepsilon_{\text{HOMO}}), \quad (5)$$

$$\eta \approx \frac{1}{2}(\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}), \quad (6)$$

Following Parr et al. [33] the square of the chemical potential of a chemical species divided by two times its chemical hardness, defines its electrophilicity index [33]:

$$\omega = \frac{\mu^2}{2\eta} \quad (7)$$

The electrophilicity index measures the energetic stabilization when the system gains electrons from its surroundings.

Local reactivity descriptors

Electronic density, Fukui function and dual descriptor

After establishing the functional derivatives of the energy functional $E[N, v(\mathbf{r})]$ with respect to the external potential $v(\mathbf{r})$, the electronic density $\rho(\mathbf{r})$ is obtained at the first order [23], the Fukui function $f(\mathbf{r})$ is obtained at the second order [23, 30] and the dual descriptor $\Delta f(\mathbf{r})$ is obtained at the third order [34, 35]. These are known as local reactivity descriptors. In the canonical ensemble, along with the global reactivity descriptors, site selectivity is characterized by local reactivity descriptors. In the first place the electronic density $\rho(\mathbf{r})$ is useful as a local descriptor when reactions involves ionic compounds [34]:

$$\left[\frac{\delta E}{\delta v(\mathbf{r})} \right]_N = \rho(\mathbf{r}), \quad (8)$$

so that net atomic charges provide a good description of the way in which the electronic density distribution of a molecular system interacts with other molecules.

Reactions involving non-charged species are governed by interactions due to orbital overlapping. Thus, in such cases, the Fukui function [23, 36], $f(\mathbf{r})$, properly describes the local reactivity. Site selectivity, which describes the local changes occurring in the electronic density $\rho(\mathbf{r})$ of the system due to changes in the total number of electrons N , is characterized through this function; through a Maxwell relation, it measures the sensitivity of a system's chemical potential μ to an external perturbation $v(\mathbf{r})$ at point \mathbf{r} :

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})} = \left[\frac{\delta \mu}{\delta v(\mathbf{r})} \right]_N. \quad (9)$$

The function $f(\mathbf{r})$ reflects the ability of a molecular site to accept or donate electrons. High values of $f(\mathbf{r})$ are related to a high reactivity at point \mathbf{r} [23, 36].

Since the number of electrons, N , is a discrete variable, right and left derivatives of $\rho(\mathbf{r})$ with respect to N have emerged. By applying a finite difference approximation to Eq. 9, two definitions of Fukui functions depending on total electronic densities are obtained:

$$f^+(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})}^+ = \rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r}), \quad (10)$$

$$f^-(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})}^- = \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r}), \quad (11)$$

where $\rho_{N+1}(\mathbf{r})$, $\rho_N(\mathbf{r})$ and $\rho_{N-1}(\mathbf{r})$ are the electronic densities at point \mathbf{r} for a system with $N + 1$, N and $N - 1$ electrons, respectively. The first one $f^+(\mathbf{r})$ has been associated to reactivity for a nucleophilic attack so that it measures the intramolecular reactivity at site \mathbf{r} toward a nucleophilic reagent. The second one, $f^-(\mathbf{r})$, has been associated to reactivity for an electrophilic attack so that this function measures the intramolecular reactivity at site \mathbf{r} toward an electrophilic reagent [37].

The densities of frontier molecular orbitals (FMOs), $\rho_{\text{LUMO}}(\mathbf{r})$ and $\rho_{\text{HOMO}}(\mathbf{r})$, now come into the picture since it has been shown [37, 38] that when the frozen orbitals approximation (FOA) is used, this lead to a direct relation between $f^{+/-}(\mathbf{r})$ with the density of the appropriate FMO, thus avoiding the need for calculations of the system with $N + 1$ and $N - 1$ electrons:

$$f^+(\mathbf{r}) \approx \rho_{\text{LUMO}}(\mathbf{r}), \quad (12)$$

$$f^-(\mathbf{r}) \approx \rho_{\text{HOMO}}(\mathbf{r}), \quad (13)$$

Using Eqs. 12 and 13 instead of 10 and 11 allows the computational cost to be diminished without losing the qualitative picture of local reactivity, but this approach should be always checked by comparison of these two pairs of working equations.

Condensation to atoms is achieved through integration within the k^{th} -atomic domain Ω_k [39, 40]:

$$f_k^{+/-} = \int_{\Omega_k} f^{+/-}(\mathbf{r}) d\mathbf{r}. \quad (14)$$

$f_k^{+/-}$ is now an atomic index that is used to characterize the electrophilic/nucleophilic power of atom k .

More recently, a new dual descriptor [$f^{(2)}(\mathbf{r}) \equiv \Delta f(\mathbf{r})$] for chemical reactivity has been proposed [34, 35]. It is defined in terms of the derivative of $f(\mathbf{r})$ with respect to N ; through a Maxwell relation, the same descriptor is interpreted as the variation of η with respect to $v(\mathbf{r})$:

$$\Delta f(\mathbf{r}) = \left(\frac{\partial f(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})} = \left[\frac{\delta \eta}{\delta v(\mathbf{r})} \right]_N. \quad (15)$$

According to the expressions given by Eqs. 10 and 11, this is written as the difference between nucleophilic and electrophilic Fukui functions [34]:

$$\Delta f(\mathbf{r}) \approx f^+(\mathbf{r}) - f^-(\mathbf{r}) = \rho_{N+1}(\mathbf{r}) - 2\rho_N(\mathbf{r}) + \rho_{N-1}(\mathbf{r}). \quad (16)$$

The use of FMO densities provides an easier-to-compute working equation:

$$\Delta f(\mathbf{r}) \approx \rho_{\text{LUMO}}(\mathbf{r}) - \rho_{\text{HOMO}}(\mathbf{r}). \quad (17)$$

The computational cost is decreased owing to the use of FMO densities from the system with N electrons only.

The dual descriptor allows one to obtain simultaneously the nucleophilic and the electrophilic behavior of the system at point \mathbf{r} . The dual descriptor can also be condensed through an appropriate integration within the k^{th} -atomic domain Ω_k :

$$\int_{\Omega_k} \Delta f(\mathbf{r}) d\mathbf{r} = \Delta f_k. \quad (18)$$

When $\Delta f_k > 0$ the process is driven by a nucleophilic attack on atom k and then that atom acts an electrophilic species; conversely, when $\Delta f_k < 0$ as a consequence the process is driven by an electrophilic attack over atom k and therefore atom k acts as a nucleophilic species.

Particular attention has been paid to the dual descriptor, $\Delta f(\mathbf{r})$, because this descriptor has been demonstrated to be a robust tool to correctly predict specific sites of nucleophilic and electrophilic attacks much more efficiently than with the Fukui function by itself. Thus, several studies remarking on the powerfulness of the $\Delta f(\mathbf{r})$ descriptor and all of those based on it [43–47] have been published. Martínez [48] proposed a simple procedure to take into account FMO degeneration when using Koopmans' theorem [31], so that $\Delta f(\mathbf{r})$ and any other local reactivity descriptor depending on $\Delta f(\mathbf{r})$ can be properly depicted, thus allowing a local reactivity isosurface adapted to the molecule symmetry to be obtained. Since the symmetry of

the C_{60} is I_h [49], any local reactivity descriptor should satisfy the symmetry requirement. In this case, the dual descriptor should belong to the totally symmetrical irreducible representation of the I_h group of symmetry, A_g .

Computational methods

The C_{60} molecule shown in Fig. 1 was optimized geometrically in the ground state according to the Schlegel algorithm [52] at the Hartree-Fock and DFT levels of theory; in particular, the functionals used in the present calculations based on the DFT methodology were the Becke-3 for exchange and Lee-Yang-Parr (LYP) for correlation [53, 54]. The STO-3G (900 primitive functions), 6-31G (1,320 primitive functions), 6-311G (1,560 primitive functions) and 6-311G(d) (1,920 primitive functions) basis sets [50, 55, 56] were used in both levels of theory. All calculations were carried out using the Gaussian 03 [58] code. Koopmans' theorem was used to obtain μ , η and ω through the use of Eqs. 5 and 6 with the respective level of theory and basis set. The selection of degenerate FMOs is based on the assumption that a difference in molecular orbital energy lower than 1×10^{-4} hartree is enough to be considered as a case of molecular orbital degeneration. All isosurfaces of the dual descriptor are depicted at 1×10^{-4} a.u.

Results and discussion

All global reactivity descriptor values used in this work are listed in Table 1. The influence of the basis set on the global reactivity descriptors was analyzed according to the number of primitive functions as an independent variable. When analyzing local reactivity, these influences were analyzed by simple inspection of the respective dual descriptor isosurface for each level of theory and basis set.

Table 1 Global reactivity descriptors from Koopmans' theorem through the use of $\varepsilon_{\text{HOMO}}$ and $\varepsilon_{\text{LUMO}}$: μ chemical potential, η molecular hardness, ω electrophilicity. All values in eV with the exception of primitives

Basis set	Number of primitives	μ/eV	η/eV	ω/eV
Hartree-Fock				
STO-3G	900	-1.29037	4.32855	0.19234
6-31G	1,320	-4.25889	3.76908	2.46617
6-311G	1,560	-4.47563	3.75262	2.66897
6-311G(d)	1,920	-4.26936	3.67071	2.48283
DFT-B3LYP				
STO-3G	900	-2.67966	1.61378	2.22477
6-31G	1,320	-4.81251	1.43446	8.07281
6-311G	1,560	-5.18721	1.43446	9.37885
6-311G(d)	1,920	-5.03074	1.36888	9.24420

Global reactivity level

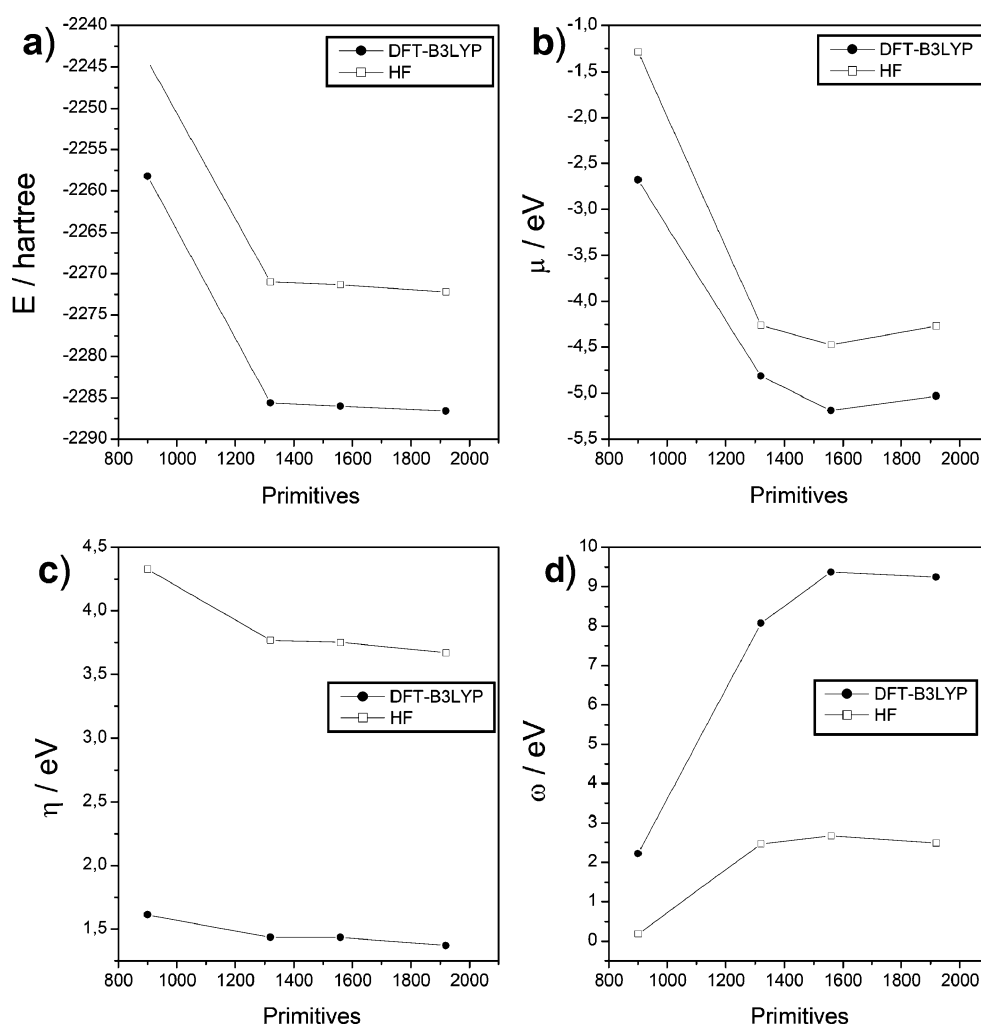
In general, a basis set such as 6–31G should be sufficient to generate a suitable optimized molecular structure of Buckminster fullerene (as indicated in Fig. 2a), because the difference in energy in both types of calculations (Hartree-Fock and DFT) can be attributed solely to the lack of electronic correlation of the Hartree-Fock methodology. On the other hand, using the STO-3G basis set, the chemical potential, μ , is the least affected global reactivity descriptor due to the lack of electronic correlation (Fig. 2b). In the second place, the molecular hardness, η , is also affected (Fig. 2c) and, finally, the electrophilicity, ω , is the most affected global reactivity descriptor due to the lack of electronic correlation (Fig. 2d). This is due to the combined effect of μ and η to obtain ω . The asymptotic behavior of ω in the 6-311G basis set indicates that this is an appropriate basis set to describe the global reactivity of C_{60} . At present, a rapid procedure used to obtain qualitative information about global reactivity at an acceptable level of theory is to

consider the 6-31G basis set for geometrical optimization and the 6-311G basis set, at least, at the Hartree-Fock (HF) or DFT levels of theory for single point calculations to obtain global and local descriptor values. However, the use of geometrical optimization at the HF/6-311G level and a single point calculation at the B3LYP/6-311G level of theory provides a suitable procedure with which to obtain confident values of these global reactivity descriptors.

Local reactivity level

Buckminster fullerene has the following characteristics: each carbon atom is shared by two hexagonal and one pentagonal ring. On the other hand, there are two types of bonds, C–C bonds shared by two hexagonal rings, and C–C bonds shared by one hexagonal and one pentagonal ring. Therefore, although there is only one kind of atom in Buckminster fullerene (carbon atom), the molecular structure should exhibit a local reactivity that reveals differences between C–C bonds shared by two hexagonal rings and

Fig. 2 a–d Global properties and their dependence on the basis set. **a** Energy, **b** chemical potential, **c** molecular hardness, **d** electrophilicity



C–C bonds shared by one hexagonal and one pentagonal ring. As a consequence, a good local reactivity descriptor should be able to reveal two kinds of C–C bonds. If so, then such a descriptor would be a suitable tool for describing local reactivity in any other molecular system regardless of whether the compound is metallic or non-metallic in nature.

Independently of the level of calculation used, in the case of the Buckminster fullerene studied here there are five-fold degenerate HOMOs and three-fold degenerate LUMOs, so these are the molecular orbitals that must be considered when building up the dual descriptor. Following the procedure mentioned in the section on local reactivity descriptors and in [48], the dual descriptor of C_{60} is obtained mathematically as follows:

$$\Delta f(\mathbf{r}) \approx \frac{1}{3} \sum_{k=1}^3 \rho_{\text{LUMO}k}(\mathbf{r}) - \frac{1}{5} \sum_{k=1}^5 \rho_{\text{HOMO}k}(\mathbf{r}). \quad (19)$$

As a result, the dual descriptor isosurfaces illustrated in Figs. 3 and 4 were obtained; it can be observed that with Hartree-Fock as well as DFT calculations, the STO-3G basis set is qualitatively sufficient to reproduce an approximated result from a molecular structural point of view, and therefore the local reactivity is also obtained through the use of the dual descriptor; however, a slight difference in lobe shape is observed (cf. Fig. 3d and Fig. 4d).

This is due to the lack of electronic correlation in Hartree-Fock calculations (Fig. 3d), so that the d polarization functions perturb the lobe shapes; this does not occur

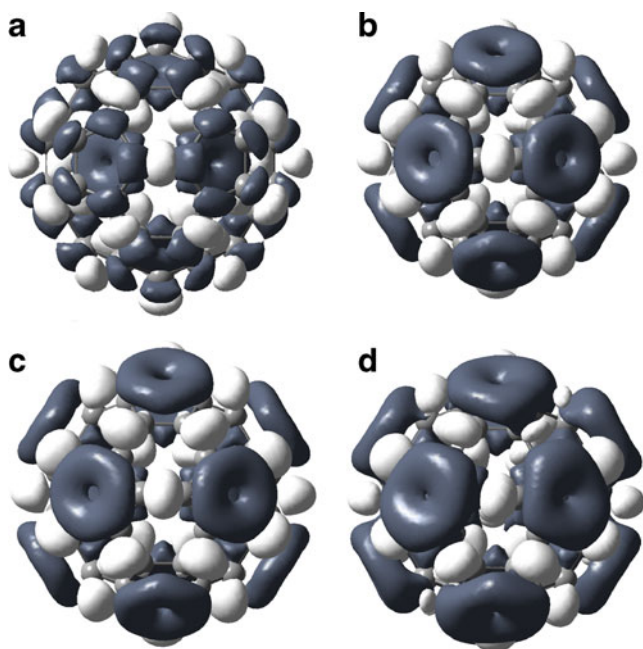


Fig. 3 Dual descriptor isosurfaces obtained at various Hartree-Fock levels of theory: **a** STO-3G, **b** 6-31G, **c** 6-311G, **d** 6-311G(d). All isosurfaces are depicted at 1×10^{-4} a.u. Nucleophilic attacks will be oriented toward dark lobes; electrophilic attacks, toward light lobes

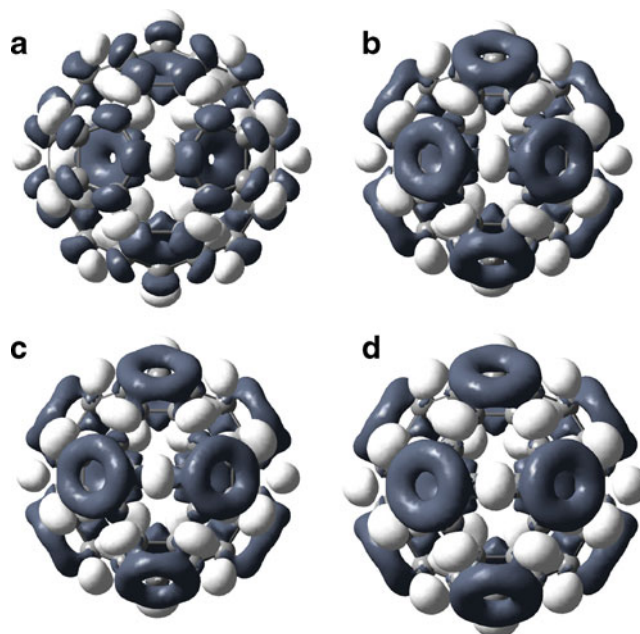


Fig. 4 Dual descriptor isosurfaces obtained at various DFT levels of theory: **a** STO-3G, **b** 6-31G, **c** 6-311G, **d** 6-311G(d). All isosurfaces have been depicted at 1×10^{-4} a.u. Nucleophilic attacks will be oriented toward dark lobes; electrophilic attacks, toward light lobes

with DFT calculations (Fig. 4d) because the dual descriptor keeps its symmetry according to the totally symmetrical irreducible representation given by the I_h group, A_g . Since it has been demonstrated that C_{60} is able to bond to other chemical species [10], carbon atoms from C_{60} should be able to be attacked by nucleophilic and electrophilic reagents. It is important to mention that the dual descriptor will be always a suitable local reactivity descriptor when electron-transfer processes are occurring due to soft reagents, meanwhile the molecular electrostatic potential [57] is a more suitable local reactivity descriptor (not belonging to conceptual DFT) when charge effects are more important because of hard reagents [47]. In general, it can be noted that electronic correlation helps to stabilize the dual descriptor topology.

To better understand this statement, the reader can observe that the electrophilic lobes (dark lobes) are susceptible to attack by nucleophilic reagents (Figs. 3, 4). As can be observed, electrophilic lobes are always localized over five-membered rings so that nucleophilic reagents will be oriented towards the five-membered rings and not towards the six-membered rings of C_{60} . In addition, when comparing HF with B3LYP-DFT calculations, the topology of electrophilic lobes obtained with the latter methodology changes very little as the basis set increases (Figs. 4b–d), i.e., when going from B3LYP/6-31G to B3LYP/6-311G(d); on the other hand, when using HF calculations, the topology of electrophilic lobes changes a little more (Figs. 3b–d) when going from HF/6-31G to HF/6-311G(d). In fact, the dual

descriptor picture from Fig. 3d does not belong to the totally symmetrical irreducible representation of I_h group of symmetry despite being a local reactivity descriptor calculated from an equilibrium C_{60} molecular structure, thus revealing the importance of taking into account the electronic correlation when representing isosurfaces properly.

To sum up, the local reactivity behavior in C_{60} has been well-defined by using the dual descriptor, showing that nucleophilic attacks will be oriented towards those C–C bonds shared by one hexagonal and one pentagonal ring (dark lobes), whereas electrophilic attacks will be oriented towards the C–C bonds shared by two hexagonal rings (light lobes).

Conclusions

This is the first time that a dual descriptor adapted to the symmetry of the C_{60} molecule has been obtained. Global reactivity descriptors depend strongly on the basis set, thus a 1,600 primitive function basis set should be accurate enough to quantify global reactivity; however, the dual descriptor, a relatively new local reactivity descriptor, correctly represents local reactivity at a qualitative level that does not depend heavily on the basis set used and for which it is not mandatory to consider the electronic correlation in order to obtain this kind of local reactivity descriptor. It is, however, recommended that electronic correlation be taken into account when an accurate calculation at a local level is desired to obtain integrated values of the dual descriptor on specific atoms of C_{60} . Polarization functions in non-electronic correlation calculations (e.g., HF) affect the dual descriptor, thus producing a slight distortion on the electrophilic lobes that could affect the values obtained after an integration procedure is carried out. As C_{60} is considered a fundamental molecular system in nanotechnology, further theoretical calculations at the global and local level will be carried out in order to measure the reactivity of derivitized molecules from C_{60} . This will help in characterizing chemical reactions involving these kind of compounds, thus contributing to knowledge related to the chemistry of Buckminster fullerene and its derivatives at a low-cost computational level in order to anticipate experimental results.

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