ADVANCED ANALYSIS OF TOTAL ENERGIES OF FULLERENES

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Abstract
A comparison study has been conducted to compare the accuracy of the used methods, the global and local definitions, in order to calculate the cage radii of fullerene, by which the total energies of fullerene have been analyzed. It was found that the local definition method is more accurate in calculating the cage radii of fullerene than the global definition basing on correlation coefficients and standard deviation values in addition to the agreement of the elasticity theory predictions with local definition method results.

I. INTRODUCTION
It is generally agreed that Carbon is one of the most widely studied elements due to the fact that it is the basis of all life forms on our planet. Since fullerene forms with graphite and diamond the allotropes of carbon, any study about these materials is very important for the previous reason [1].

Fullerene can be defined as a molecule which consists of an even number of carbon atoms in the form of a hollow sphere, an ellipsoid or a tube [2]. With regard to the structure, they are similar to graphite but they differ in that graphite is composed of stacked graphene sheets of linked hexagonal rings and fullerene contains pentagonal rings in addition to hexagonal rings, which prevents the sheet of fullerene from being planar. It is widely accepted that Fullerene is represented by the formula (C_N), where (N) is the number of carbon atoms in the structure. There are many forms of fullerenes such as (C_{60}, C_{70}, C_{76}, C_{78}, C_{82}, and C_{84}) but the most abundant and studied fullerene is C_{60}, it is called [60] fullerene or buckminsterfullerene due to the fact that its molecule has a similar shape to the geodesic dome popularized by the noted architect Richard Buckminster Fuller [3].

Fullerenes can be insulators, conductors, semiconductors or even superconductors when they
doped with other atoms or molecules. As a result of that, they have many different applications, in addition to fullerene compounds that are still under study in all areas of sciences.

Due to the fact that fullerenes involved in many important applications, we analyzed fullerenes energies in order to know more about the properties this material and to employ the obtained data to be a reference in the researchers in this field. This study was based on analyzing the energies of (115) type of fullerenes. The best method which have been used to calculate fullerenes energies was the density functional theory (DFT), it consider an ab initio method but it is different from other ab initio approaches because in order to describe a molecule, it uses electron density instead of the wave function[4]. The main problem of the (DFT) is that the exact for exchange and correlation are not known. Therefore, the most accurate expression for them is the B3LYP functional is used in our calculations in conjunction with finite basis set. There are many types of basis set such as STO-3G, 6-31G and 6-311G etc. one of them mainly B3LYP/6-31G* is used in our calculations of fullerenes energies [5]. The calculated energies using the previous expression are very small, which are expressed in the atomic units, so it is necessary to convert the computed total energies to the standard enthalpies of formation using conversion equations[6,7].

The obtained fullerenes energies will be analyzed geometrically using local and global definitions, the global definition simply involves the distances of carbon atoms from the center of mass whereas the local definition (based upon spheres passed through quartets of carbon atoms) reflects the local curvature of the cage as we processed to get through both of them.

II. METHODOLOGIES

A. Global Definition of Cage Radii

It is generally agreed that the radius is the distance between any point on surface and the center of sphere or circle.

\[ R_i = \sqrt{(x_i-x_0)^2 + (y_i-y_0)^2 + (z_i-z_0)^2} \]  

This formula can be used to calculate the radius of the fullerene due to the to the fact that the radii are the same for all the 60 carbon atoms which is differ from the other fullerene types in that the distance between the center of the molecule and each carbon atom is different. However, the cage radius is can be obtained by the average of the individual radii:

\[ \langle R \rangle = \frac{1}{N} \sum_{i=1}^{N} R_i \]  

Where (N) is the number of carbon atoms. Also, the average powers of global radii are computed in analogous way:

\[ \langle R^k \rangle = \frac{1}{N} \sum_{i=1}^{N} R_i^k \]  

B. Local Definition of Cage Radii and Curvature

Another approach which can be used to calculate the radius of fullerenes cage, that is, the

\[ (1) \]

\[ (2) \]

\[ (3) \]
local definition of the cage radii. The approach has been obtained from the Cartesian coordinates, \((x_i, y_i\) and \(z_i\)), \((x_j, y_j\) and \(z_j\)), \((x_k, y_k\) and \(z_k\)) and \((x_l, y_l\) and \(z_l\)) of the four connected atoms (i.e. atoms \(j, k,\) and \(l\) connected to the \(i\) atom) that suffice to determine the sphere radius \((r_i)\) by solving the following system of equations:

\[
(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 = r_i^2
\]  \(4\)

\[
(x_i - x_k)^2 + (y_i - y_k)^2 + (z_i - z_k)^2 = r_i^2
\]  \(5\)

\[
(x_i - x_l)^2 + (y_i - y_l)^2 + (z_i - z_l)^2 = r_i^2
\]  \(6\)

And

\[
(x_i - x_0)^2 + (y_i - y_0)^2 + (z_i - z_0)^2 = r_i^2
\]  \(7\)

Substituting Eqs. 5), 6), and 7) from 4) get

\[
(x_j - x_0)^2 - (x_i - x_0)^2 + (y_j - y_0)^2 - (y_i - y_0)^2 + (z_j - z_0)^2 - (z_i - z_0)^2 = 0
\]  \(8\)

\[
(x_k - x_0)^2 - (x_i - x_0)^2 + (y_k - y_0)^2 - (y_i - y_0)^2 + (z_k - z_0)^2 - (z_i - z_0)^2 = 0
\]  \(9\)

And

\[
(x_l - x_0)^2 - (x_i - x_0)^2 + (y_l - y_0)^2 - (y_i - y_0)^2 + (z_l - z_0)^2 - (z_i - z_0)^2 = 0
\]  \(10\)

These three equations can be written as:

\[
2(x_j - x_i)x_0 + 2(y_j - y_i)y_0 + 2(z_j - z_i)z_0 = x_j^2 - x_i^2 + y_j^2 - y_i^2 + z_j^2 - z_i^2
\]  \(11\)

\[
2(x_k - x_i)x_0 + 2(y_k - y_i)y_0 + 2(z_k - z_i)z_0 = x_k^2 - x_i^2 + y_k^2 - y_i^2 + z_k^2 - z_i^2
\]  \(12\)

And

\[
2(x_l - x_i)x_0 + 2(y_l - y_i)y_0 + 2(z_l - z_i)z_0 = x_l^2 - x_i^2 + y_l^2 - y_i^2 + z_l^2 - z_i^2
\]  \(13\)

In order to solve them, one uses Kramer's rule which yields the matrix equation:
Let \((D)\) be the main determinant of the above matrix:
\[
\begin{vmatrix}
2(x_j - x_i) & 2(y_j - y_i) & 2(z_j - z_i) \\
2(x_k - x_i) & 2(y_k - y_i) & 2(z_k - z_i) \\
2(x_l - x_i) & 2(y_l - y_i) & 2(z_l - z_i)
\end{vmatrix} = \begin{bmatrix} x_0 \\ y_0 \\ z_0 \end{bmatrix}
\]

(14)

And \(D_x, D_y\), and \(D_z\) be the determinants formed by replacing its \(x, y\) and \(z\) columns,
\[
D_x = \begin{vmatrix}
x_j^2 - x_i^2 + y_j^2 - y_i^2 + z_j^2 - z_i^2 & 2(y_j - y_i) & 2(z_j - z_i) \\
x_k^2 - x_i^2 + y_k^2 - y_i^2 + z_k^2 - z_i^2 & 2(y_k - y_i) & 2(z_k - z_i) \\
x_l^2 - x_i^2 + y_l^2 - y_i^2 + z_l^2 - z_i^2 & 2(y_l - y_i) & 2(z_l - z_i)
\end{vmatrix}
\]

(15)

\[
D_y = \begin{vmatrix}
x_j^2 - x_i^2 + y_j^2 - y_i^2 + z_j^2 - z_i^2 & 2(z_j - z_i) \\
x_k^2 - x_i^2 + y_k^2 - y_i^2 + z_k^2 - z_i^2 & 2(z_k - z_i) \\
x_l^2 - x_i^2 + y_l^2 - y_i^2 + z_l^2 - z_i^2 & 2(z_l - z_i)
\end{vmatrix}
\]

(16)

\[
D_z = \begin{vmatrix}
x_j^2 - x_i^2 + y_j^2 - y_i^2 + z_j^2 - z_i^2 \\
x_k^2 - x_i^2 + y_k^2 - y_i^2 + z_k^2 - z_i^2 \\
x_l^2 - x_i^2 + y_l^2 - y_i^2 + z_l^2 - z_i^2
\end{vmatrix}
\]

(17)

Since it is complicated to calculate the values of \((D, D_x, D_y\) and \(D_z\)) by hand, we use a specific code using FORTRAN software to find values of these determinants. According to Kramer's rule, it was found that the values of \((x_0, y_0\) and \(z_0\)) as the following:
\[
x_0 = \frac{D_x}{D}
\]

(19)

\[
y_0 = \frac{D_y}{D}
\]

(20)

And
\[
z_0 = \frac{D_z}{D}
\]

(21)

By substituting the values of \((x_0, y_0\) and \(z_0\)) which obtained from the Equations (1-19), (1-20), and (1-21) respectively in one of equations (1-4), (1-5), (1-6), or (1-7), we get the local radius \((r_i)\). The local curvature \((p_i)\) is a reciprocal of \((r_i)\) by analogy with Eq. (1-3), the average powers of local radii are obtained as the following:
\[
\langle r^k \rangle = \frac{1}{N} \sum_{i=1}^{N} r_i^k
\]

(22)
III. RESULTS

A. Dependence of fullerene stability on the average global cage radius

In order to uncover the main factors influencing stabilities, the correlations between the standard enthalpies of formations per atom $\Delta H^{o}/N$ and the average powers of cage radii $(R^k)$ were determined. The selected values of the power $(k)$ were (-3, -2, -1, -0.5, 0.5, 1, 2, 3), then the obtained correlations values have been represented vs the selected power values $(k)$ in order to obtain the power value $(k)$ at which the best correlation value can be obtained (which is should be the nearest value to 1). After representing the data, it was found that $\Delta H^{o}/N$ correlates the best with $(R^{-1/2})$, i.e. the average inverse square root of the global cage radius. In this case, the correlation coefficient amounts to $r^2 = 0.8607$ and the standard deviation equals 0.78 [KJ/mol.]. The correlations are substantially worse for other values of $(k)$.

One way to improve these results is to add the measure of variation of $R_i$ for a given fullerene cage as the second variable in linear correlation. A convenient measure of this kind is given by the equation:

$$h_K = (R^{2K}) - (R^K)^2$$  \hspace{1cm} (23)

Inclusion of $h_K$ in the correlations, i.e. estimating $\Delta H^{o}/N$ according to the following equation:

$$\Delta H^{o}/N \approx A + B(R^K) + C h_K$$  \hspace{1cm} (24)

The equation vastly improves the quality of stability predictions, the correlation coefficient increasing to $r^2 = 0.9322$ for $k = (-0.5)$ and the respective standard deviation dropping to 0.54 [KJ/mol.]. The following figures (1), (2) show the correlation values vs power values $(k)$ and the standard deviation vs power values $(k)$ before and after correction process.

![Figure (1). The Squared Correlation Values Vs Power Values (k)](image-url)
B. Dependence of Fullerene Stability on the Average local Cage Radius

This section deals with the correlations between the standard enthalpy of formation per carbon atom ΔHf°/N and average powers of the cage radii (r^K) stemming with local definition. The same procedure which been used in the previous section have been used in here. Inspection of the obtained figures reveals that for a given they correlations involving (r^K) are markedly better than those with RK.

The best linear regression is obtained for (K=-2) for which (r²) = 0.9041 and the standard deviation equals 0.65 [KJ/mol]. Unlike in the case of global cage radii, inclusion of the radius variations Eq. (1-23) improves this correlation only marginally, increasing to (r²) to 0.9105 and decreasing the standard deviation to 0.63 [KJ/mol]. However, the following figure (3) and (4) show the correlation values vs power values (K) and the standard deviation vs power values (K) before and after correction process.

In summary, the analysis presented clearly that establishes the advantage of using the radii obtained from the local definition over the global one.

![The Standard Deviation Vs The Powers](image1.png)

**Figure (2). The Standard Deviation Values Vs Power Values (k).**

![The Correlation Coefficient Vs The Powers](image2.png)

**Figure (3): The Squared Correlation Values Vs Power Values (K).**
IV. CONCLUSION

It turns out that the best prediction of the standard enthalpies of formation of fullerenes (per carbon atom) emerge from a correlation involving the average inverse square of the local cage radius, which is equivalent to the average square of the local curvature. Such an expression agrees with the predictions of the elasticity theory, according to which the bending energy of an elastic membrane is proportional to the surface integral of the square of the local curvature. On the other hand, the best correlation (corresponding to the inverse square root of the radii) obtained for the global definition of the cage radii has not obvious theoretical basis.

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