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Ameer A Ali
 Department of Chemistry,
 College of Science, University
 of Tikrit, Tikrit, Iraq

Faiz M AL-Abady
 Department of Chemistry,
 College of Science, University
 of Tikrit, Tikrit, Iraq

Corresponding Author:
Ameer A Ali
 Department of Chemistry,
 College of Science, University
 of Tikrit, Tikrit, Iraq

Calculating theoretical octane numbers of various petroleum derivatives using quantum mechanical DFT methods

Ameer A Ali and Faiz M AL-Abady

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Abstract

This research included calculating the octane number of a group of chemical compounds using the (DFT) method by using multiple regression analysis of the relationship between the practical octane number values with the theoretically calculated physical variables, where a number of variables were calculated including the calculation of energy functions, including the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LOMO), hardness (η), chemical potential (μ), and spherical electrophilic index (W), and the thermodynamic functions (ΔG , ΔH , ΔS , ΔE) and dipole moment were calculated. They were evaluated from the correlation coefficient relationship (R^2). Through the four-way statistical analysis, we obtained the best correlation coefficient for the variables calculated using the DFT method, where (R^2) showed the highest values for the following variables: ($\Delta E + \text{HOMO} + \Delta G + \mu$) ($R^2=0.793$) ($\Delta S + \text{LOMO} + \Delta G + W$) ($R^2=0.753$). Through the single and multiple statistical analysis, the most influential variable on the octane number values is (HOMO).

Keywords: DFT Method, octane number, quantum

Introduction Octane Number

It is a measure of the ignition quality or ignition ability of gasoline. Research Octane Number (RON) refers to normal road performance under moderate inlet temperature (65.6 °C) and rpm (600 rpm). Engine octane number (MON) refers to high-speed performance under severe inlet temperatures (148.9 °C) and 900 rpm. Research Octane Number (RON) and Engine Octane Number (MON) are evaluated using ASTM D2699 and ASTM D2700, respectively [1, 2].

Computational chemistry

Computational chemistry is one of the branches of physical chemistry, including quantum mechanics and molecular mechanics. Its purpose is to find the most important properties of chemical compounds and compare them with practical values. It is one of the main branches of research used in the analysis, diagnosis, and support of scientific research [3]. Computational chemistry depends on the use of computers instead of chemicals and the creation of effective mathematical methods to solve theoretical problems through advanced computational methods. John People is considered the first to introduce computers into quantum chemistry in the fifties of the last century by creating new integrated algorithms, highly efficient in calculations, and then marketing computational programs such as the Gaussian program [4]. Computational chemistry is characterized by the fact that its calculations are easy to perform compared to In experiments that are often difficult to perform and involve the risks of chemicals as well as less expensive because they do not require chemicals, and can be performed on any system even if it is not present, while experiments are limited to relatively stable molecules, however, computational chemistry is not an alternative to experimental methods, but it plays an important role in knowing the properties of chemical compounds [5].

The term computational chemistry is used when the mathematical method has been developed sufficiently to be applied using computer programs [6].

Density Function Theory (DFT)

The first to use and develop this theory were the researchers (Hohenberge-Kohn) in 1964 AD, and it later became one of the important components related to the basic analysis methods that were used extensively in theoretical studies, especially after the development in the field of electronic computers. This theory is based on finding the electronic properties of the molecule in the stable state, which are found using the electronic density. The advantage of this theory is that it includes finding the approximate electronic correlations with the same The accuracy calculated by the well-known method (Hartree-Fock) (HF) is usually faster than the experimental method and is considered the most accurate method in calculations, so it can be used as one of the basic calculation methods (Ab-initio). It is similar to the basic calculations and semi-empirical calculations in terms of its reliance on the Schrodinger equation, but it differs from the two methods in that it does not calculate a wave function but derives the distribution of electrons (electron density function) directly, where the electron density is expressed as the square of the function. Wave, the basis of this method is to simulate the actual distribution of the electron density of the system, so the larger the set of functions used to model the electrons, the more accurate the calculations become, and the results are much better, as they have been developed by introducing electronic exchange and correlation functions that increase the accuracy of the calculations. There are many approximations used in this method, including:

- **LDAM:** Local Density Approximation.
- **LSDA:** Local spin Density Approximation.
- **GCM:** Gradient Corrected Method.

Hybrid functional function

In this, the functional function theory (DFT) is combined with the Hartree-Fock theory (HF) to describe the functional function of the exchange energy, including:

- **B3LYP:** Becke's 3 parameter exchange correlation functional, which uses 3 Parameters and LYP, the Lee, Yang and Parr correlation functional.

This function is considered the most used in calculations due to the accuracy of the results that can be obtained. However, new functions are constantly being developed to increase the accuracy of calculations [7, 8].

Theoretical calculation

Quantum mechanics methods were used in this study, represented by the DFT method, by using these theoretical methods to find the values of the octane number by the (Chem. Office) program [9]. And the (Gaussian program Gauss View 06 Gaussian 09) program. The programs used in the calculations are one of the modern methods in theoretical calculation chemistry to accomplish theoretical research and support practical research. The information obtained from using the (Gaussian 09) program is numerous, including the following:

1. Energy of atomic orbitals (LUMO, HOMO).
2. Dipole moment.
3. Heat of formation.

4. Bond lengths.
5. Angles between atoms.
6. Bond dissociation energy.
7. Total energy.
8. Atomic charges.
9. Thermodynamic functions.
10. Potential and electrostatic energy.
11. Transition state structures and their energies.

Gaussian 09 was used as it contains a huge amount of information, and this is considered a distinctive thing in calculations using multiple theories in order to conduct a comprehensive search for theoretical methods in the fields of computational chemistry to choose the best of these theories and methods to obtain the best theoretical values for the Octane Number (ON). In this study, by using quantum mechanics represented by Ab-initio methods (DFT), The following variables were calculated:

1. Dipole moment.
2. Thermodynamic functions (ΔH , ΔG , ΔS , ΔE).
3. Energy values of atomic orbitals (HOMO, LOMO).
4. The values of the energy functions that were calculated from the values of (HOMO, LOMO) are (hardness, chemical electron potential, and spherical electrophilic index).

The calculations were performed using the following methods

1. Ab-initio methods (DFT).

Gaussian 09 program

Steps of theoretical calculations for the compounds under study using Gaussian 09:

1. Drawing the molecular formula of the compounds using the (Chem. Office) program.
2. Transferring the compound drawn in the (Chem. Office) program to the (Chem. 3D) program.
3. Save the compound in the (Chem. 3D) program in the file format (Input File).
4. Open the program (Gaussian 0.6) then open the file saved in (Input File) format.
5. Select the (Calculate) button, then select (Gaussian Calculation Setup).
6. From the Job Type button, select (Optimization), then select (Minimum) to obtain the lowest energy, which will be more stable and have the best spatial shape.
7. After that, from the (Method) button, select the theoretical method and determine the basis set.
8. After that, select (Submit) to perform the calculations in the (Gaussian 09W) program.
9. After finishing and completing the results, they will be saved via (Notepad).
10. The statistical analysis is performed using the SPSS program.

Statistical analysis

The statistical analysis was conducted between the selected and calculated variables (HOMO, LOMO, dipole moment, hardness, electronic potential, spherical electrophilic index, ΔH , ΔG , ΔS , ΔE) using theoretical methods with the practical Octane Number (ON) values calculated using SPSS

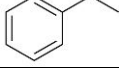
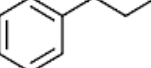
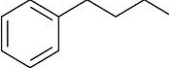
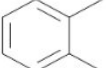
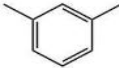
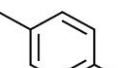
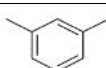
Program

The correlation coefficient (R^2) values were adopted as a reference for this purpose to know the strength and type of

relationship between the calculated variables and the practical Octane Number (ON) values, as the statistical analysis was conducted between the variables with each other and with the practical Octane Number (ON) values using the methods used, where each method was taken separately and with the following steps:

1. The calculated variables of the studied compounds (HOMO, LOMO, dipole moment, Hardness, electron potential, spherical electrophilic index, ΔH , ΔG , ΔS , ΔE) were entered as non-dependent variables with the practical octane number values that are dependent variables.
2. The variables were analyzed through a series of steps in the SPSS program using the following steps: (Linear + regression + analysis).
3. The values of the correlation coefficient (R^2) are then obtained, since knowing the values of (R^2) determines the variables that have a significant effect on the Octane Number (ON) in the simple regression analysis.
4. We then conduct the process of multiple statistical analysis to determine the strength of the relationship between the variables that were used with each other and with the scientific octane number values obtained from the literature.

Table 1: Structures of the compounds under study and their names with octane number (ON) values

No.	ON	Nameclature	Structure
1.	102	Benzene	
2.	122	Toluen	
3.	130	Ethyl benzene	
4.	110	Propyl benzene	
5.	92	Butyl benzene	
6.	145	O- Xylene	
7.	140	M- Xylene	
8.	136	P- Xylene	
9.	166	Mesitylene	

Theoretical calculations

In this research, the compounds were studied theoretically and the Octane Number (ON) values were extracted theoretically, as a set of variables were calculated, including the thermodynamic functions (ΔH , ΔG , ΔS , ΔE), dipole moment and orbital energy (HOMO, LOMO), and energy

functions (hardness η , electron-chemical potential μ , spherical electrophilic index W). The octane number values were calculated for a number of compounds to obtain the best relationship between the variables and the octane number values.

Table 2: Calculating thermodynamic functions and dipole moment using DFT method

No	Dipole moment	ΔH Hartee/Particle	ΔS Cal.K ⁻¹ .mol ⁻¹	ΔG Hartee/Particle	$E\Delta$ Cal.K ⁻¹ .mol ⁻¹
1.	0.0000	0.106936	68.753	0.074269	66.511
2.	0.3305	0.136366	79.424	0.098629	84.979
3.	0.4188	0.177212	85.512	0.136583	110.610
4.	0.4375	0.196839	91.934	0.153158	122.926
5.	0.4596	0.242561	99.332	0.195365	151.617
6.	0.5825	0.165920	83.979	0.126019	103.524
7.	0.3936	0.165859	90.219	0.122993	103.486
8.	0.0004	0.164896	86.637	0.123732	102.881
9.	0.0983	0.195317	100.371	0.147628	121.971

Table 3: Calculating the energy values of the studied compounds using the DFT method

No	HOMO e.v	LOMO e.v	H e.v	μ e.v	W e.v
1.	0.25191-	0.00546	0.128685	-0.123225	0.059022273
2.	0.23900-	0.00580	0.012240	-0.11660	0.055537418
3.	0.18242-	0.09655	0.139485	-0.042935	0.660792997
4.	0.23793-	0.00761	0.122770	-0.11516	0.054010853
5.	0.18145-	0.09740	0.139425	-0.042025	0.00633514793
6.	0.23202-	0.00884	0.120430	-0.11159	0.051699444
7.	0.23357-	0.00599	0.119780	-0.11379	0.054049775
8.	0.22756-	0.00583	0.116695	-0.110865	0.052663086
9.	0.22873-	0.00965	0.119190	-0.10954	0.050335647

(Table 4) shows the descriptive statistics of the variables studied using the DFT method. The table shows that the average octane number of the studied samples is 127, and the average polar moment of the studied materials is about 0.3024. The enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) changes are around the average values of 87.3512, 0.1724, and 0.1309 respectively, while the average energy

change (ΔE) of the studied materials is about 107.6117. For the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LOMO), the average values are -0.2238 and 0.0270, respectively. The average transport efficiency (η) of the studied materials is 0.1132, and the average polarity (μ) is -0.0984.

Table 4: Descriptive statistics of the study variables calculated using the DFT method

DFT	ON	Dipole moment	ΔH	ΔS	ΔG	ΔE	HOMO	LOMO	η	μ	W
Mean	127	0.3024	0.1724	87.3512	0.1309	107.6117	-0.2238	0.0270	0.1132	-0.0984	0.1160
Std. Error of Mean	8	0.0715	0.0128	3.2623	0.0114	8.0310	0.0083	0.0132	0.0129	0.0107	0.0683
Median	130	0.3936	0.1659	86.6370	0.1260	103.5240	-0.2320	0.0076	0.1204	-0.1116	0.0540
Std.div.	23	0.2146	0.0384	9.7870	0.0342	24.0930	0.0248	0.0397	0.0388	0.0320	0.2049
Variance	534	0.0460	0.0010	95.7850	0.0010	580.4740	0.0010	0.0020	0.0020	0.0010	0.0420
Range	74	0.5825	0.1356	31.6180	0.1211	85.1060	0.0705	0.0919	0.1272	0.0812	0.6545
Minimum	92	0.0000	0.1069	68.7530	0.0743	66.5110	-0.2519	0.0055	0.0122	-0.1232	0.0063
Maximum	166	0.5825	0.2426	100.371	0.1954	151.6170	-0.1815	0.0974	0.1395	-0.0420	0.6608

Table 5: Pearson correlation coefficient between variables calculated by DFT method

DFT		ON	Dipole moment	ΔH	ΔS	ΔG	ΔE	HOMO	LOMO	η	μ	W
ON	R	1	-0.113	-0.059	0.265	-0.102	-0.059	-0.183	-0.375	-0.056	-0.304	0.083
	p		0.772	0.881	0.49	0.794	0.881	0.637	0.32	0.886	0.427	0.831
Dipole moment	R	-0.113	1	0.438	0.272	0.455	0.438	0.389	0.373	0.02	0.383	0.177
	p	0.772		0.239	0.479	0.219	0.239	0.3	0.323	0.96	0.31	0.649
ΔH	R	-0.059	0.438	1	0.916**	0.999**	1.000**	0.688*	0.573	0.407	0.623	-0.014
	p	0.881	0.239		0.001	0	0	0.04	0.107	0.278	0.073	0.971
ΔS	R	0.265	0.272	0.916**	1	0.893**	0.916**	0.488	0.317	0.294	0.386	-0.114
	p	0.49	0.479	0.001		0.001	0.001	0.183	0.406	0.443	0.304	0.77
ΔG	R	-0.102	0.455	0.999**	0.893**	1	0.999**	0.706*	0.601	0.417	0.647	0
	p	0.794	0.219	0	0.001		0	0.033	0.087	0.265	0.059	0.999
ΔE	R	-0.059	0.438	1.000**	0.916**	0.999**	1	0.688*	0.573	0.407	0.623	-0.014
	p	0.881	0.239	0	0.001	0		0.04	0.107	0.278	0.073	0.971
HOMO	R	-0.183	0.389	0.688*	0.488	0.706*	0.688*	1	0.962**	0.389	0.985**	0.565
	p	0.637	0.3	0.04	0.183	0.033	0.04		0	0.301	0	0.113
LOMO	R	-0.375	0.373	0.573	0.317	0.601	0.573	0.962**	1	0.393	0.994**	0.597
	p	0.32	0.323	0.107	0.406	0.087	0.107	0		0.295	0	0.09
η	R	-0.056	0.02	0.407	0.294	0.417	0.407	0.389	0.393	1	0.395	0.229
	p	0.886	0.96	0.278	0.443	0.265	0.278	0.301	0.295		0.292	0.553
μ	R	-0.304	0.383	0.623	0.386	0.647	0.623	0.985**	0.994**	0.395	1	0.59
	p	0.427	0.31	0.073	0.304	0.059	0.073	0	0	0.292		0.094
W	R	0.083	0.177	-0.014	-0.114	0	-0.014	0.565	0.597	0.229	0.59	1
	p	0.831	0.649	0.971	0.77	0.999	0.971	0.113	0.09	0.553	0.094	

R: Pearson correlation, P: p value *Correlation is significant at the 0.05 level. **Correlation is significant at the 0.01 level.

Table 6: Values of the correlation coefficient (R^2) between the octane number and the variables calculated in the quadratic statistic using the (DFT) method

Model No.	Variables	R^2
1.	HOMO + LOMO + η + W	0.734
2.	HOMO + η + W + μ	0.734
3.	HOMO + η + ΔS + ΔE	0.699
4.	HOMO + η + ΔE + LOMO	0.649
5.	ΔE + HOMO + ΔG + μ	0.793
6.	ΔE + LOMO + μ + W	0.729
7.	ΔE + W + HOMO + ΔG	0.722
8.	LOMO + ΔS + ΔG + W + μ	0.753
9.	W + LOMO + ΔS + ΔH	0.753
10.	W + ΔS + ΔH + HOMO	0.722

Calculating the theoretical octane number values using the DFT method

From (Table 6), Model 5 was identified as the best model for calculating the theoretical octane number values because the R^2 values were the highest value compared to the other models, at 0.793. (Table 7) shows the estimation of the parameters of the quadratic statistical model using the DFT method to calculate the octane number. The table shows the

coefficients for the variables specified by the model, which include the variables: ΔE , HOMO, ΔG , μ . The table also shows the standardized coefficients, which show the effect of each variable in a standard way, where Beta shows the effect of each variable with respect to the dependent variable. The values of Statistical test and p value also show the extent of the effect of each variable with respect to the model statistically.

Table 7: Quadruple statistics of octane number using DFT method

Methods	Model	Coefficients	Unstandardized coefficients		Standardized coefficients	t	Sig.
			B	Std. error	Beta		
DFT	Model 5	(Constant)	460.239	341.223	-	1.349	0.249
		ΔE	10.195	5.935	10.634	1.718	0.161
		HOMO	2899.223	1811.121	3.115	1.601	0.185
		ΔG	-7497.620	4200.794	-11.097	-1.785	0.149
		μ	-2035.772	1407.053	-2.817	-1.447	0.221

(Table 8) reflects the performance of the quadratic model using the DFT method to calculate the octane number. The results show that this model (Model 5) has a strong correlation coefficient ($R = 0.890$), with the value of the square of the correlation coefficient ($R^2 = 0.793$) indicating that 79.3% of the variance in the octane number can be explained by the independent variables used. The values of adjusted R^2 (0.585) reflect the accuracy of the model based

on the number of variables and sample size, while the standard error of the estimate (Standard Error of the Estimate = 14.877) shows the amount of expected deviation between actual values and expectations. Overall, the table shows that the model has an excellent ability to predict the octane number based on the independent variables, with the need to take into account the standard error of the estimate in assessing its accuracy.

Table 8: Characteristics of the quadratic statistical model used to calculate the octane number using the DFT method

Model summary					
Methods	Model	R	R square	Adjusted R square	Std. error of the estimate
DFT	Model 5	0.890	0.793	0.585	14.877

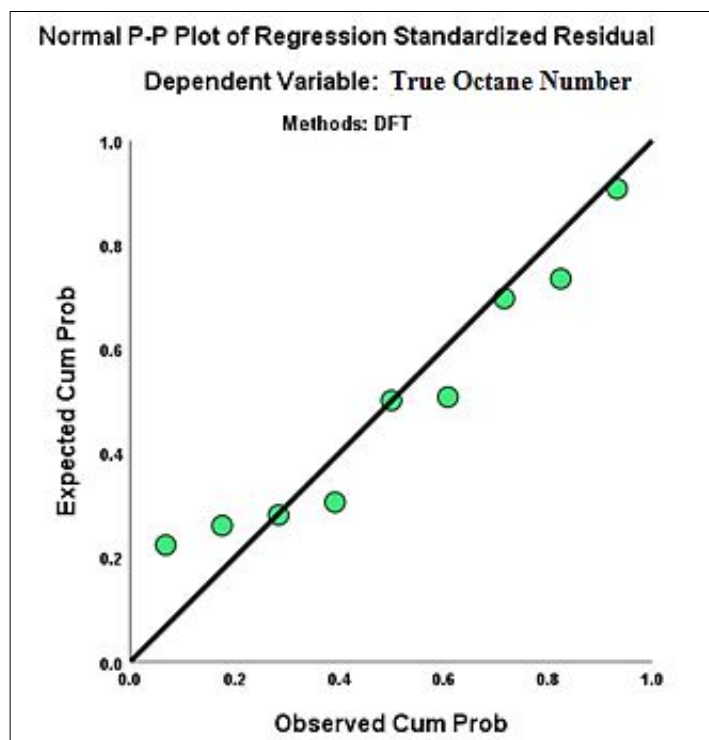


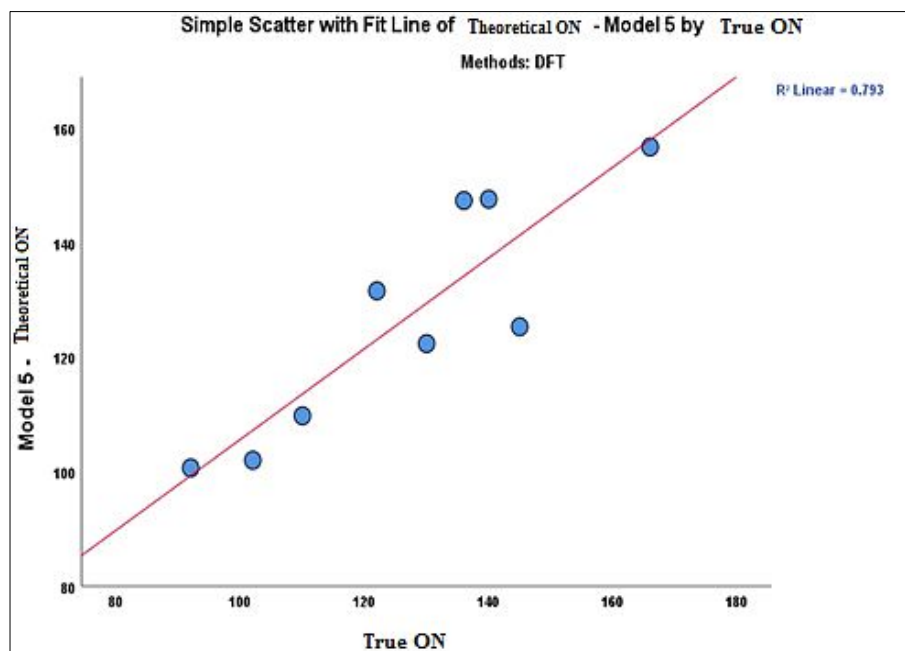
Fig 1: Normal P-P plot of regression standardized residual

Therefore, the statistical model equation is obtained by substituting the Model 5 estimators into Equation 1 as follows:

$$\text{Theoretical Octane No} = 460.239 + (10.195 \cdot \Delta E) + (2899.223 \cdot \text{HOMO}) - (7497.620 \cdot \Delta G) - (2035.772 \cdot \mu) + \text{error}$$

Table 9: Theoretical octane number values for DFT method

Compound	ΔE	HOMO	ΔG	μ	Theoretical octane number	True octane number	Δ
1.	66.511	-0.25191	0.074269	-0.123225	102	102	0
2.	84.979	-0.23900	0.098629	-0.116600	132	122	10
3.	110.61	-0.18242	0.136583	-0.042935	122	130	8
4.	122.926	-0.23793	0.153158	-0.115160	110	110	0
5.	151.617	-0.18145	0.195365	-0.042025	101	92	9
6.	103.524	-0.23202	0.126019	-0.111590	125	145	20
7.	103.486	-0.23357	0.122993	-0.113790	148	140	8
8.	102.881	-0.22756	0.123732	-0.110865	147	136	11
9.	121.971	-0.22873	0.147628	-0.109540	157	166	9

**Fig 2:** Simple scatter plot with fit line for model 5

It is noted from the attached (Table 9) and from the results of the regression analysis, that there is a significant correlation between the practical octane number values obtained from the literature with the theoretically calculated octane number values, with some differences in some compounds for the four methods used. This is evidence of the strength of the proposed variables for calculating the octane number values for some gasoline derivatives^[10]. This study opens up broad horizons in the field of software chemistry (computational chemistry).

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