Calculation of the Chemical Shift of N-15 by Quantum Mechanics

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ABSTRACT
This study aims to develop a new set of added variables to calculate the chemical shift N-15 based on quantum mechanics methods for a number of periodic compounds using theoretical chemistry (Gaussian V.12, 2010). The relationship between the experimental N-15 was conducted with two mechanical variables, such as SPSS V 2019. The relationship between the theoretical chemical shift values of the N-15 atom nucleus and practical values in literature was examined. Two quantitative mechanical methods are used to extract information to calculate the N-15 chemical shift, the traditional method, the other AB Initio method, and the DFT job theory. The success of the method is determined in terms of the values of the correlation coefficient (R) and the standard error (SE), as well as the material meaning of the specified variables. A good consensus is seen between practical and theoretical values. A comparison was made between the two methods to find out the best in the chemical transformation account. The DFT method gave better results.

KEYWORDS
Correlation analysis, Traditional method, DFT method, N-15 chemical shift

1. Introduction
1.1 Nuclear magnetic resonance (NMR)
Magnetic resonance is a physical phenomenon that depends on magnetic properties. It is a phenomenon that you can find in the radioactive navicular gap of a certain frequency and the presence of an influence from an external magnetic and building these works based on the Muslim properties of the different cores [Pavia, 2008]. There are no elements in the periodic table or in the purification. So it bears a subject whose axis is the main axis. This torque is called the spin quantum number, which refers to the set of values based on the nuclear properties of the isotopes [AL-Abady, 2001]. Where the number (0) indicates the number of spinning that these notes have no rotation, the quantum is determined by this spin (μ) [Al-Hyali, 2022], and this can be studied for the nuclear resonance spectra of an atom such as.

1.2 Nuclear Magnetic Resonance Spectroscopy for N15
Nitrogen belongs to a few elements found in the general structure of organic and bio-organic molecules, and the functional groups containing nitrogen atoms are of great importance in organic and biochemical reactions [Burrell, 2010]. Electrons in the outer shell of the valence of the atom. Thus, nitrogen, according to the concept of the octet rule, has a triple valence in most of its compounds and has an oxidation number from -3 to 5, most of which are covalent. Nitrogen is the only element that can bond with itself in its group. The bond length for nitrogen between its atoms is N≡N (109.76 pm).
Figure (1-1) is the length of the bond of the nitrogen molecule

In nature, there are two isotopes, N-14 and N-15, but the percentages in them differ, as the ratio of N-14 is the highest at 99.635, while the other isotope has a very small percentage, which is about 0.365, and there are other artificial isotopes whose atomic number is between (12-19), but the age of Half of it is very small, ranging from minutes to seconds. Nitrogen has a spin number; if nitrogen has 14 spins, \( I = 1 \)

While the isotope of 15 has a spin number of \( \frac{1}{2} \). The two isotopes can give a magnetic spectrum. But the spectrum is the most important according to the studies that have been conducted. The spectrum of [5] N-14 has been shown to be unstable and cannot be used for large particles. The isotope 15 was used in nuclear resonance because of its ease of use, and it is used for all small and large molecules. In addition, it has an important and beneficial effect, which is the Aforhauser effect of High-intensity magnets [Al-Abady, 2022].

Alternatively, this problem can be solved by transferring the polarization from sensitive, fast-relaxing nuclei such as (H, F). The use of large-sized samples in the middle of a high magnetic field has helped to overcome the problems facing N-15 in spectroscopy, which has poor sensitivity and also takes a long time to obtain the sample and is not suitable for analytical applications in synthetic and biochemistry [Perinua, 2014].

2. Computational chemistry

It is a branch of chemistry sciences (theoretical chemistry), and its main objective of it is to obtain some characteristics of the compounds under study and compare these results with the values of the information previously. It can be a bit dangerous. Through this branch, which is known as theoretical chemistry, the information we need to complete scientific research is calculated and obtained. Calculation of the rate constant for chemical reactions [Ibrahim, 2020]. Such as atomic charges, dipole moment, total energy, Raman spectrum, IR spectrum, and some thermochemical properties, including enthalpy, gypsum free energy, entropy, and NMR [Leach, 2001], as computational chemistry is one of the basic branches used in analytical and diagnostic research [Ibrahim, 2006]. The importance of this type of branch of computational chemistry lies in a variety of uses, including [Jensen, 2007] Calculation of the frequency of the impedance, the calculation of the charge and the electronic distribution, and computational chemistry (theoretical) was divided into two main parts, namely molecular mechanics and quantum mechanics [Lashkaripour, 2021].

3. Programs a used

It was used in this study (Gaussian V.12/2010), which is a multi-use molecular model simulation program for many molecules, where it is possible to make calculations for molecules that need time and effort if they are calculated manually. It is also possible to access the physical properties of molecules and know their structures’ transitional state. As it became possible to perform important calculations on personal computers due to the availability of qualified software for this purpose [Samuel, 2017]. The calculation was carried out using two methods. The first is a traditional method of calculating the chemical shift from the relationship between the number of carbon atoms in positions and the number of protons in positions relative to the carbon atom of the compounds under study [Dalling, 1974]. The second method was studied by using computational methods by simulating the studied chemical molecules at different levels, as this method includes the use of basic quantum mechanics methods (DFT) [Lashkaripour, 2021].
Table (1-2) of the compounds under study in the research

|   | Compound                                | Molecular Structure | Value |
|---|-----------------------------------------|---------------------|-------|
| 1 | 1-methylpiperidine                      | ![1-methylpiperidine](image1) | 37.4  |
| 2 | 1,4-dimethylpiperidine                  | ![1,4-dimethylpiperidine](image2) | 48.9  |
| 3 | (S)-1,2-dimethylpiperidine              | ![S-1,2-dimethylpiperidine](image3) | 36.4  |
| 4 | (R)-1,3-dimethylpiperidine              | ![R-1,3-dimethylpiperidine](image4) | 37    |
| 5 | 1,3,3-trimethylpiperidine Cis           | ![1,3,3-trimethylpiperidine Cis](image5) |       |
| 6 | (2R,6S)-1,2,6-trimethylpiperidine Cis   | ![2R,6S-1,2,6-trimethylpiperidine Cis](image6) | 62.1  |

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| Page | Compounds                                      | Chemical Shift |
|------|-----------------------------------------------|----------------|
| 7    | (2S,6S)-1,2,6-trimethylpiperidine             | 32.6           |
| 8    | Piperidien                                    | 37.7           |
| 9    | (S)-2-methylpiperidine                       | 54.9           |
| 10   | (R)-3-methylpiperidine                       | 37             |
| 11   | 4-methylpiperidine                           | 36.5           |
| No. | Compound                           | Chemical Shift |
|-----|-----------------------------------|----------------|
| 12  | Trans -2,6-di Me- pp              | 63.8           |
| 13  | Cis- 3,5 –di Me- pp               | 37.5           |
| 14  | Trans -3,5 di Me –pp              | 26.7           |
| 15  | 3,3-di Me- pp                     | 30.4           |
| 16  | 2,2,6,6-Tetra Me- PP              | 81.7           |

4. Results and Discussion

1-Traditional way

These variables are similar to the method adopted by Krant [Leach, 2001] in calculating the chemical shift of cyclohexane compounds from the representation of the factor (P) by the number of carbon atoms of a type (α, β, γ, ..., etc.) relative to the carbon atoms under study and the proton interactions with the number of hydrogen atoms in these locations as well, and the difference What we have adopted here is the addition of variables representing the location of the CH3 group (relative to the studied nitrogen atom because this group is expected to have a significant impact on the chemical shift of the nitrogen atom, and these variables have been applied to a group of compounds under study collectively and as shown in Table No. Table (1-2) results were obtained after calculating the variables, as we went through previously in the methods of work.
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2-Method DFT

During our study in quantitative methods, a number of values of physical variables were calculated, including the physical represented (Total Energy, Density, Angle............. etc.) for a group of cyclohexane and cyclohexane compounds. Some energy value variables (HOMO, LUMO, χ, M, W) were also calculated. This process has been accomplished using four methods of quantum mechanics and two methods of basic calculations (DFT) if the following results are obtained, as mentioned in the tables below.

Table (1-3) of the results obtained from the quantum mechanics method using the DFT method

| Num | Name                              | Pri  | Sec  | Tir  | qur  | PH   | SH   | TH   | QH   |
|-----|-----------------------------------|------|------|------|------|------|------|------|------|
| 1   | N-Me-PP                           | 1    | 2    | 0    | 0    | 3    | 4    | 0    | 0    |
| 2   | N-2 diMe PP                       | 1    | 2    | 0    | 0    | 3    | 4    | 0    | 0    |
| 3   | N,3-di Me pp                      | 1    | 1    | 1    | 0    | 3    | 2    | 1    | 0    |
| 4   | N,4-di Me pp                      | 1    | 2    | 0    | 0    | 3    | 4    | 0    | 0    |
| 5   | N (Cis-3,5)-tri Me pp             | 1    | 0    | 2    | 0    | 3    | 0    | 2    | 0    |
| 6   | N(Cis-3,5)-tri Me pp              | 1    | 0    | 2    | 0    | 3    | 4    | 0    | 0    |
| 7   | 1,2,6-trimethylpiperidine         | 1    | 2    | 0    | 0    | 3    | 4    | 0    | 0    |
| 8   | Piperidiene                       | 0    | 2    | 0    | 0    | 0    | 4    | 0    | 0    |
| 9   | (S)-2-methylpiperidine            | 0    | 1    | 1    | 0    | 0    | 2    | 1    | 0    |
| 10  | (R)-3-methylpiperidine            | 0    | 2    | 0    | 0    | 0    | 4    | 0    | 0    |
| 11  | 4-methylpiperidine                | 0    | 2    | 0    | 0    | 0    | 4    | 0    | 0    |
| 12  | Trans -2,6-di Me- pp              | 0    | 0    | 2    | 0    | 0    | 0    | 2    | 0    |
| 13  | Cis- 3,5 -di Me- pp               | 0    | 2    | 0    | 0    | 0    | 4    | 0    | 0    |
| 14  | Trans -3,5 di Me-pp               | 0    | 2    | 0    | 0    | 0    | 4    | 0    | 0    |
| 15  | 3,3-di Me- pp                     | 0    | 2    | 0    | 0    | 0    | 4    | 0    | 0    |
| 16  | 2,2,6,6-Tetra Me- PP              | 0    | 0    | 0    | 2    | 0    | 0    | 0    | 0    |

HOMO, LUMO, μ, η, W(GEI), Stretched, S/B, Torsion, nonVDW, VDW, Energy tot, Angle, Density

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5. Statistical analysis
A simple and multiple statistical analysis was conducted to reach the results obtained in the mentioned tables (1-3 and 1-4) below for the methods used in this research after conducting the statistical analysis.[Shorter, 1973]. The best factors that are directly affected by chemical shifts were reached, and these variables were used in a theoretical equation to reach the theoretical values, as shown below [Berenson, 2012].

1- The traditional way

After conducting a statistical analysis, the best result was obtained.

Table (1-4) the best values for the variables in the traditional method

| Var    | Coef |
|--------|------|
| BataH  | 3.679|
| GamaH  | 0.122|
| Data   | -2.684|
| Constant | 24.597|
| R      | 0.982|
| S.E    | 3.165|

After reaching good values, the following equation was used to obtain the chemical shift values for the compounds under study.

Equation........... (1) \( \eta N=24.597+(3.679\times BataH)+(0.122\times gamaH)+(-2.684\times Data) \)

Table (1-5) Theoretical chemical shift values for the aliphatic nitrogen compounds under study by the traditional method

| No | BataH | gamaH | Data  | Cal | Shift | Exp |
|----|-------|-------|-------|-----|-------|-----|
| 1  | 4     | 2     | 0     | 39.55596 | 37.4 | 2.156 |
| 2  | 7     | 1     | 0     | 50.47127 | 48.9 | 1.5713 |
| 3  | 3     | 2     | 0     | 35.87695 | 36.4 | -0.523 |
| 4  | 4     | 1     | 1     | 36.75 | 37 | -0.25 |
From the results obtained from the regression analysis, the equation that represents the multivariate linear relationship was used, and this equation was used in calculating the chemical shift to obtain a correlation coefficient and a standard deviation. For nitrogen -15 for the compounds studied in theory, the calculated results and the amount of difference from the practical values have been included in Table (1-4). In most cases, they result either from a steric obstruction on the carbon or nitrogen atoms. When the chemical shift values for (1,2) compounds are observed, we find that there is a difference between the values in an observable way from the beginning. As for compound No. (3,4), we find there is also the steric shape that has a role in determining the chemical shift of the two compounds. We note that there are some high chemical shift values, and it appears in a far range from TMS due to the steric shape of the compound, as we find the geometry structure is responsible for the values of this shift and thus increases the effect of the external magnetic field on the central atom and this is shown through the shift values that we obtained Theoretically as well as from the practical value as there is a convergence between the two methods.

Calculation of the chemical shift of aliphatic compounds by DFT method.

| Var    | Coef  |
|--------|-------|
| Angle  | -2.591|
| TE     | 4.980 |
| 1,4nonVDW | -24.525|
| Torsion| -8.836|
| Stretch| -17.512|
| Constant| 290.863|
| R      | 0.962 |
| S.E    | 4.92  |

Then we use the following equation to get the theoretical chemical shift values for the compounds under study.
\[ \eta N-15= 290.863 +(-2.591 \times \text{Angle})+(4.980 \times \text{TE})+(-24.525 \times 1,4\text{nonVDW})+(-8.836 \times \text{Torsion})+(-17.512 \times \text{Stretch}) \]

Table (1-7) values of the practical and theoretically calculated chemical shift of nitrogen and the difference between them using the DFT method

| Stretch | 1,41,4nonVDW | Torsion | Angle | TE | Cal | Abs | Exp |
|---------|--------------|---------|-------|----|-----|-----|-----|
| 1.9282  | -1.1870      | 3.7572  | 110.9529 | 15.5 | 42.6389221 | 37.4 | 5.239 |
| 1.6545  | -1.6008      | 2.0956  | 111.422 | 12.2 | 54.603848 | 48.9 | 5.704 |
| 1.2433  | -0.4856      | 2.4901  | 112.1745 | 14.5 | 40.5562934 | 36.4 | 4.156 |
| 1.6930  | -1.5843      | 3.7550  | 111.5516 | 12.2 | 38.7146222 | 37 | 1.715 |
| 2.3109  | -1.8171      | 3.2917  | 110.2939 | 15.4 | 56.9228996 | 62.1 | -5.18 |
| 3.1474  | -0.7847      | 4.0594  | 109.8315 | 20.5 | 36.8216638 | 36.8 | 0.022 |
| 3.1376  | -0.6691      | 2.6139  | 112.0957 | 18 | 28.5515624 | 32.6 | -4.05 |
| 0.2602  | -0.9866      | 1.9555  | 111.2224 | 5.85 | 34.2408059 | 37.7 | -3.46 |
| 0.3888  | -1.2791      | 3.1519  | 110.0768 | 9.42 | 49.3193999 | 54.9 | -5.59 |
| 0.4166  | -1.3732      | 3.3311  | 111.245 | 8.12 | 40.0638251 | 37 | 3.064 |
| 0.3609  | -1.4062      | 1.9159  | 113.1729 | 6.16 | 39.5823691 | 36.5 | 3.082 |
| 0.497   | -1.7298      | 3.0806  | 116.816 | 12.8 | 58.4782866 | 63.8 | -5.32 |
| 0.5779  | -1.7818      | 5.2951  | 114.1395 | 12 | 41.9643287 | 37.5 | 4.464 |
| 0.5782  | -0.7778      | 5.296   | 111.1335 | 12 | 25.1234557 | 26.7 | -1.58 |
| 0.652   | -1.6341      | 5.0145  | 111.3298 | 8.24 | 27.8330979 | 30.4 | -2.57 |
| 1.1105  | -2.4238      | 4.6433  | 107.3649 | 14.1 | 81.9900795 | 81.7 | 0.29 |

When observing the results we obtained, we find a discrepancy between all the methods used in the calculation process for the values of chemical shift between practical and theoretical results, and this is consistent with the literature study by Stefano Chimichi et al.(2018). In Compound No. (1) we find a clear difference between the quantum mechanics methods, and the difference is close to the methods used in the calculations (Alph) used in Grant and Al-Hayali’s studies about the other. Likewise, when we observe compound (2), we also find different values in the chemical shift between practical and theoretical values in all methods except for the (DFT) method. We find the result of this compound close between the process and the theory [Chimichi, 2010]. As for the effect of some compensators on the values of the chemical shift represented by the total methyl, we notice that when the number of atoms of the compensator increases in compound No. 2, we notice a decrease in the electronic density around the central atom. When referring to Table (1-3), the decrease in the electronic density does not generate a steric tension and thus falls under the influence of the external magnetic field, and its effect is clear through the difference in values in the chemical shift between compound No, which carries one compensated while compound No. 2 has two compensated methyl groups. Thus, the shift value is high and appears far from the TMS, which represents the reference and carries a value of zero for the shift [Perinua, 2014]. While in compound No. 3, we note that the shift value is close to compound 1 despite the presence of two groups. This is due to the occurrence of large steric interferences resulting from the effect of the steric shape, as the geometric figure increases the electronic density, unlike what is found in the previous compound, and when the electronic density is increased, the shift values are few because this works to block the external field from reaching the center of the nitrogen atom, so the shift values are few [AL-Hayali, 1994].

To reach the best method among the studied methods is by knowing the relationship between the theoretical and practical shift values and the extent of convergence between them, as shown in the figures below.
Figure (1–1) the relationship between the results of the process and the view of the chemical shift of nitrogen cyclic compounds

![Graph showing the relationship between Pri and DFT with R² values of 0.8474 and 0.9261 respectively.]

After looking at the following figures, we find the best method is the DFT method, which is consistent with the theory presented in the research, as the DFT method is more modern and comprehensive in the process of theoretical calculations.

6. Conclusion
This study can provide researchers with valuable information about geometry and stereochemistry in a quantitative manner. Sixteen compounds were selected for achieving this investigation. The work was carried out using a number of physical variables derived by the traditional method and DFT (B3LYP) at the basis set (3–21G). The variables were selected depending on their relationship with the chemical shifts of N-15. The results showed that chemical shift is affected by the substituted groups on the reaction centers through the steric and inductive effects. These data cannot be provided by traditional laboratory methods. It gives an idea about the structural distortion that can be obtained from the calculation of the difference between the experimental and calculated chemical shifts of the nuclei of nitrogen-15 atoms. The differences between the calculated and the practical chemical shift were found to be a good measure of the amount of structural distortions. Additive parameters were suggested to calculate the N-15 chemical shifts for a number of aliphatic amines using the traditional method and DFT methods. The best set of these two methods in achieving this study is determined by comparing the experimental and calculated chemical shift values in terms of the correlation coefficient (R²) and standard errors (SE). The DFT gave better results in terms of consistency and agreement between the observed and calculated N15 chemical shifts.

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