

# Simulating NMR spectrum of $C_{60}Cl_6$ through Ab Initio method

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**ABSTRACT:** The NMR spectrum of different  $C_{60}Cl_6$  has been calculated through ab initio method. The simplest structure of  $C_{60}Cl_6$  molecule has sixty carbon nuclei reside on a sphere and six chloride atoms attached with six carbon atoms of fullerene. The structures of  $C_{60}Cl_6$  are very sensitive to electron correlation treatment with basis set that are employed. When the average simulation peak of  $C_{60}Cl_6$  compared with the available average  $C_{60}Cl_6$  NMR data peak, this comparison gives 15% error with the experimental NMR data. The error may be arising due to two facts. Firstly the experimental sample  $^{13}C_{60}Cl_6$  might not possess all  $^{13}C$  and  $^{35}Cl$  during the NMR experiment. This reduces the number of NMR peaks of  $C_{60}Cl_6$  that could obtain in NMR spectrum experimentally. Secondly experimental  $C_{60}Cl_6$  having thirty two peaks instead of sixty-six peaks so this increase the error percentage of simulation data.

**KEYWORDS:** NMR spectrum,  $C_{60}Cl_6$

## I. INTRODUCTION

The compound ( $C_{60}Cl_6$ ) chlorofullerene synthesis and structural characterization was reported in 1993 and this compound was among the first halides discovered for fullerene. [1] Chloro-fullerene is considerable interest because it has a prospective originator for the sample preparation of fullerenes derivatives. Chloro-fullerenes were poorly investigated in comparison with other halogenated fullerenes. Single crystal X-ray crystallography has been synthesized and structurally characterized  $C_{60}$  chlorinated derivatives such as  $C_{60}Cl_{24}$  ( $T_h$ ),  $C_{60}Cl_{28}$  ( $C_1$ ),  $C_{60}Cl_{30}$  ( $C_2$ ) and  $C_{60}Cl_{30}$  ( $D_{3d}$ ) [2-4]. The production of  $C_{60}Cl_6$  was reported and this chloride was utilized for the preparation of organic derivatives of  $C_{60}$ . [5-9] In the past decade, considerable progress has been made in the understanding of fullerene derivatives. Although the preparation of  $C_{60}Cl_6$  was described previously but the addition of six chlorine atoms to the fullerene cage could be understood with the help of  $^{13}C$  NMR spectroscopy. [10-12] In this paper we systematically examine NMR of  $C_{60}Cl_6$  using ab initio Hartree-Fock method.

## II. COMPUTATIONAL DETAILS

The simplest structure of  $C_{60}Cl_6$  molecule has sixty carbon nuclei reside on a sphere and six chloride atoms attached with six carbon atoms of as shown in figure -1. The  $C_{60}Cl_6$  structure has  $C_1$  symmetry and the bond length of each carbon-carbon is 1.35 Å and the bond length of carbon-chloride atom is 2.08 Å. The two different C-C bond lengths in C indicate that the  $\pi$  electrons are evenly delocalized over all bonds. The green colour and blue colour represent the carbon and chloride atoms respectively.

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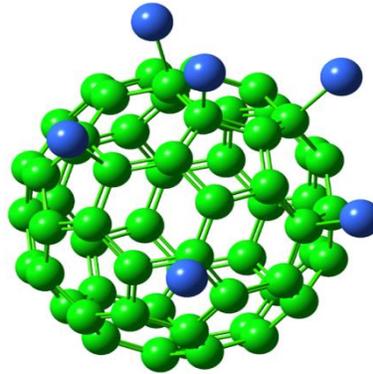


Figure 1 shows C<sub>60</sub>Cl<sub>6</sub> structure configurations

### III CALCULATION

Calculations of NMR shielding tensors have been published from many years [13-16]; these methods are all applicable to calculate the magnetic shielding function of different molecules. The time-dependent Schrodinger equation is given by

$$H\psi(r,t) = -i\frac{\partial}{\partial t}\psi(r,t) \quad (1)$$

It is needed to derive an expression for the current. Differentiating the time-dependent density

$$\rho(r,t) = N \int_{-\infty}^{\infty} dr_2 \dots dr_N |\psi(r, r_2, \dots, r_N, t)|^2 \quad (2)$$

with respect to the time coordinate gives together with Eq. (1) the continuity equation

$$\frac{\partial}{\partial t}\rho(r,t) = -\nabla J(r,t) \quad (3)$$

where  $J(r,t)$  is the flux, or the probability current

$$J(r,t) = \frac{1}{2i} \int_{-\infty}^{\infty} dr_2 \dots dr_N (\psi^* \nabla \psi - \nabla \psi \psi^*) \quad (4)$$

When the wave function is real, then the system is independent of time so the current must vanish. As eqn. (3) represents a conservation law i.e. a change in the density in some region must be compensated by flux in or out of that region. The magnetic field is initiated into the quantum mechanical framework through minimal substitution of the magnetic vector potential,  $A$ , into the kinetic energy operator

$$p \rightarrow \pi = p + \frac{e}{c} A \quad (5)$$

where  $p = -i\nabla$ ,  $c$  is the speed of light (in atomic units  $c = 137.035987$ ) and  $e$  is the electron charge. It is feasible to explain that this gives the correct form for the Hamiltonian by considering the Lagrangian for the Lorentz force of an

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electron in an electromagnetic field [19]. The interested magnetic vector potential of consists of two contributions,  $A=A^B+A^{m_l}$ . The first term express a uniform, time-independent external magnetic field.

$$A^B(r) = \frac{1}{2} B \times (r - R_o) \tag{6}$$

where  $R_o$  is the chosen as the magnetic field origin and the second term is due to the magnetic moments of the nuclei

$$A^{m_l}(r) = \sum_l m_l \times \frac{r - R_l}{|r - R_l|^3} \tag{7}$$

where  $m_l$  is the magnetic moment of the  $l^{\text{th}}$  nucleus with  $R_l$  the nuclear position vector.

The current density  $\vec{j}(\vec{r})$  of a fullerene derivative molecule in a stationary external magnetic field  $\vec{B}^{ext}$  in the electronic ground state with the corresponding wave function is given by

$$\vec{j}(\vec{r}) = \frac{i}{2} \left[ \vec{\nabla} \psi_0^* \psi_0 - \psi_0^* (\vec{\nabla} \psi_0) \right] - \frac{1}{c} \vec{A} \psi_0^* \psi_0 \tag{8}$$

where  $\vec{A}$  is the vector potential of the external magnetic field. The induced field  $\vec{B}^{ind}$  at any position  $\vec{r}_k$  of a molecule in an external magnetic field  $\vec{B}^{ext}$  can be computed using Biot-Savart's law.

$$\vec{B}^{ind}(\vec{r}_k) = \frac{1}{c} \int \frac{\vec{j}(\vec{r}) \times \vec{r}_k}{r_k^3} d^3 r \tag{9}$$

Alternatively to the induced field, a tensorial shielding function  $\overline{\overline{\sigma}}(\vec{r}_k) (\overline{\overline{\sigma}} \leftrightarrow \sigma_{\alpha\beta})$  may bring in to explain the response of the electronic system in a molecule to the external magnetic field

$$\left( \vec{B}^{ind} \right)_\alpha = - \sum_{\beta=1}^3 \sigma_{\alpha\beta} \left( \vec{B}^{ext} \right)_\beta \tag{10}$$

This shielding function works just the generalization of the shielding tensor in NMR spectroscopy, where the induced field, respectively, the shielding field, is needed only at a few specific positions of the nuclei in space.

$$\overline{H} = \sum_{k=1}^N \left[ \frac{p_k^{-2}}{2} - \frac{1}{2c} A \cdot p_k^{-2} + \frac{1}{2c^2} \vec{A}^{-2} \right] + V \tag{11}$$

Where  $V$  represents for the electron nucleus with electron-electron interaction potential, and  $\vec{p}$  is the momentum operator respectively.  $\vec{A}$  is the vector potential of the external magnetic field, for which the Coulomb gauge is taken.

$$\vec{A}(\vec{r}) = \frac{1}{2} (\vec{B} \times \vec{r}) \tag{12}$$

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Moreover, it has been considered that  $\vec{\nabla} \cdot \vec{A} = 0$ . Thinking of only linear terms in the magnetic field (“weak perturbation”),

the perturbation operator of the external magnetic field  $\vec{H} \left( \vec{H} = \vec{H}^{(0)} + \vec{H}^{(1)} \right)$  is given by

$$\vec{H} = -\frac{i}{2c} \left( \vec{B}_{ext} \times \vec{r} \right) \cdot \vec{\nabla} = \frac{1}{2c} \vec{B}_{ext} \cdot \vec{L} \quad (13)$$

where  $\vec{L}$  denotes the angular momentum operator. The current density  $\vec{j}(\vec{r})$  can be expanded in a Taylor series in  $\vec{B}_{ext}$ .

$$\vec{j}(\vec{r}) = \vec{j}^{(0)}(\vec{r}) + \vec{j}^{(1)}(\vec{r}) + \dots \quad (14)$$

$$\vec{j}^{(1)}(\vec{r}) = \vec{B}_{ext} \cdot \vec{j}^{(1)}(\vec{r}) \quad (15)$$

with

$$\left( \vec{j}^{(1)}(\vec{r}) \right)_{\alpha\beta} = \frac{\partial \left( \vec{j}(\vec{r}) \right)_{\alpha}}{\partial \left( \vec{B} \right)_{\beta}}$$

where  $\vec{j}^{(1)}(\vec{r})$  is the current density in a molecule with no external magnetic field. It finishes for molecules without a permanent magnetic moment. With a corresponding expansion of the wave function:

$$\psi_j = \psi_j^{(0)} + i \vec{B}_{ext} \cdot \vec{\psi}_j^{(1)} + \dots \quad (16)$$

the current density up to linear terms in the magnetic field might then be written as:

$$\vec{B}_{ext} \cdot \vec{j}^{(1)}(\vec{r}) = \frac{i}{2} \left\{ \vec{B}_{ext} \left[ \psi_0^{(0)} \left( \vec{\nabla} \cdot \vec{\psi}_0^{(1)} \right) - \vec{\psi}_0^{(1)} \cdot \left[ \vec{\nabla} \psi_0^{(0)} - \frac{1}{c} \vec{A} \left| \psi_0^{(0)} \right|^2 \right] \right] \right\} \quad (17)$$

By only these linear terms in Biot-Savart’s law, one obtains for the shielding function:

$$\vec{\sigma}(\vec{r}) = \frac{1}{2c} \left\langle \psi_0^{(0)} \left| \frac{\left( \vec{r}, \vec{r}_k \right) \vec{I} - \vec{r}_k \otimes \vec{r}}{r_k^3} \right| \psi_0^{(0)} \right\rangle - \frac{2}{c} \left\langle \psi_0^{(0)} \left| \frac{\vec{L}}{r_k^3} \right| \vec{\psi}_0^{(1)} \right\rangle \quad (18)$$

Where  $\vec{I}$  denotes the identity matrix. As for the NMR shielding tensors, the first term is called the diamagnetic contribution to  $\vec{\sigma}$ , whereas the second term is called the paramagnetic contribution.

The first-order perturbed wave function  $\vec{\psi}_0^{(1)}$  is traditionally expanded in terms of excited states of the unperturbed system

$$\vec{\psi}_0^{(1)} = \sum_{n \neq 0} \vec{C}_n^{(1)} \psi_n^{(0)} \quad (19)$$

This directs to the same expressions as originally derived for the NMR shielding tensors by Ramsey, [17] when  $\vec{r}_k$  is restricted to the nuclear positions  $\vec{r}_k = \vec{R}_k$

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$$\bar{\sigma}(\vec{r}_k) = \frac{1}{2c} \left\langle \psi_0^{(0)} \left| \frac{(\vec{r} \cdot \vec{r}_k) \vec{I} - \vec{r}_k \otimes \vec{r}}{r_k^3} \right| \psi_0^{(0)} \right\rangle - \frac{2}{c} \sum_{n \neq 0} \frac{1}{E_n - E_0} \left\langle \psi_0^{(0)} \left| \frac{\vec{L}}{r_k^3} \right| \psi_0^{(1)} \right\rangle \otimes \left\langle \psi_n^{(0)} \left| \vec{L} \right| \psi_0^{(0)} \right\rangle \quad (20)$$

Computations of the shielding function using eqn. (20) would require the knowledge of the complete set of the solutions of the unperturbed (without external magnetic field) many-particle Schrodinger equation  $\psi_0^{(0)}, \psi_1^{(0)}, \psi_2^{(0)} \dots$  with the corresponding energies  $E_0^{(0)}, E_1^{(0)}, E_2^{(0)} \dots$ . Although, concerning the Coulomb interactions between the electrons, only approximate solutions of the Schrodinger equation can be obtained in principle. Within the Hamiltonian of eqn. (22), the magnetic field acts only in the kinetic energy part. Therefore, one might expect that the shielding function can simply be calculated by application of eqn (20), just by using approximate solutions for  $\psi_0^{(0)}, \psi_1^{(0)}, \psi_2^{(0)} \dots$  and  $E_0^{(0)}, E_1^{(0)}, E_2^{(0)} \dots$ . However, even in the single determinant (Slater determinant) ansatz for the wave function (HF), it turns out that the problem is more involved. Within HF theory, the single particle wave functions (orbitals)  $\psi_j$  of the Slater determinant are solutions of single particle-like equations (HF equations)

$$\bar{F} \psi_j = \epsilon_j \psi_j \quad (21)$$

The Fock operator,  $\bar{F}$ , the orbitals,  $\psi_j$ , and the orbital energies,  $\epsilon_j$ , are also be expanded in a Taylor series similar manner as in eqn (7) :

$$\begin{aligned} \psi_j &= \psi_j^{(0)} + i \bar{B}_{ext} \cdot \psi_j^{(1)} + \dots \\ \epsilon_j &= \epsilon_j^{(0)} + i \bar{B}_{ext} \cdot \epsilon_j^{(1)} + \dots \\ \bar{F}_j &= \bar{F}_j^{(0)} + i \bar{B}_{ext} \cdot \bar{F}_j^{(1)} + \dots \end{aligned} \quad (22)$$

$\bar{F}^{(0)}$  is the Fock operator without an external magnetic field.

$$\bar{F}^{(0)} = \frac{p^2}{2} + V_{ext} + \sum_{j=1}^{N_{occ}} (2J_j^{(0)} - K_j^{(0)}) \quad (23)$$

where  $V_{ext}$  stands for the scalar external potential (electron nucleus potential) as well as  $J_j^{(0)}$  and  $K_j^{(0)}$  are the usual Coulomb and exchange expressions, respectively. The first-order perturbed Fock operator  $\bar{F}^{(1)}$  is, however, not only given by  $\bar{H}^{(1)}$  (eqn. 6). There is no first-order correction to  $J_j$  but there has to be considered one in the exchange part  $K_j$

$$\bar{F}^{(1)} = \bar{B}_{ext} \bar{H}^{(1)} - \sum_{j=1}^{N_{occ}} \bar{K}_j^{(1)} \quad (24)$$

$$\bar{K}_j^{(1)} = \int \left[ \psi_j^{(1)}(\vec{r}) \psi_j^{(0)}(\vec{r}') - \psi_j^{(0)}(\vec{r}) \psi_j^{(1)}(\vec{r}') \right] \frac{1}{|\vec{r} - \vec{r}'|} \psi(\vec{r}') d^3 r' \quad (25)$$

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Inserting expansions (21) into eqn. (21), one can obtain up to first order a set of linear equations, which has to be solved successively

$$\left(\vec{h}^{(0)} - \epsilon_j^{(0)}\right) \psi_j^{(0)} = 0 \quad (26)$$

$$i\left(\vec{h}^{(0)} - \epsilon_j^{(0)}\right) \vec{B}_{\text{ext}} \cdot \vec{\psi}_j^{(1)} = \left[\vec{B}_{\text{ext}} \cdot \left(\vec{\epsilon}_j^{(1)} - \vec{F}^{(1)}\right)\right] \psi_j^{(0)} \quad (27)$$

Because of the exchange part, the first order perturbed eqn. (8) has to be solved iteratively coupled Hartree fock method. [18]

### IV. RESULT AND DISCUSSIONS

The fullerenes derivative ( $C_{60}Cl_6$ ) has 192 degree of freedom. Actually it starts with 198 total degrees of freedom for an isolated  $C_{60}Cl_6$  molecule but subtracting the six degrees of freedom corresponding to three translations and three rotations, results in 192 vibrational degrees of freedom. The rotational constants in x, y, and z axis in the fullerenes derivative ( $C_{60}Cl_6$ ) is 0.06, 0.05 and 0.05 (GHz) respectively. The  $C_{60}Cl_6$  has 354 symmetry adapted basis functions, 1062 primitive gaussians, 354 cartesian basis functions, 231 alpha electrons and 231 beta electrons with the nuclear repulsion energy 12974.07 Hartrees. The fullerenes derivative ( $C_{60}Cl_6$ ) has done SCF E (RHF) = -4970.33 A.U. after 21 cycles with convergence density matrix= 0.4894D-08.

Generally NMR experiment, any  $C_{60}$  molecules having the distribution of  $^{12}C$  to  $^{13}C$  isotopes is in proportion to 75 to 25 percent. It is interesting that about more than half of the molecules in  $C_{60}$  samples experiment are  $^{12}C_{60}$  molecules, which do not give NMR spectrum. Although the isotope effects discussed above are expected to affect the line intensities of the rotational and rotational-vibrational modes significantly in ordinary  $C_{60}$  samples at very low temperatures.

In  $C_{60}Cl_6$ ,  $^{13}C$  and  $^{35}Cl$  is considered to evaluate the total NMR effect on  $C_{60}Cl_6$  sample. The simulated  $^{13}C$  NMR spectra of  $C_{60}Cl_6$  contain sixty one lines in each model. In  $^{13}C_{60}Cl_6$ , each  $^{13}C$  atom has a nuclear spin  $\phi = 1/2$  and each molecule thus has  $2^{66}$  nuclear spin states, with  $\phi_{\text{tot}}$  values ranging from  $\phi_{\text{tot}} = 0$  to  $\phi_{\text{tot}} = 66$ . The statistical weight for each irreducible representation of  $C_1$  for all  $2^{66}$  states of  $^{13}C_{60}Cl_6$  is well approximated by the dimension of the irreducible representation. The NMR observed peaks and simulated peaks of each model are given below. The number in the bracket represents the number of NMR peaks obtaining at particular frequency. The observed NMR peaks of  $C_{60}Cl_6$  [14] are 54.93(1), 55.46(2), 66.47(3), 69.42(4), 135.39(5), 140.18(6), 140.51(7), 140.76(8), 141.58(9), 141.82(10), 142.03(11), 142.34(12), 142.78(13), 143.16(14), 143.52(15), 143.97(16), 144.18(17), 146.23(18), 146.365(19), 146.38(20), 146.46(21), 146.93(22), 147.05(23), 147.22(24), 147.555(25), 147.565(26), 147.63(27), 147.64(28), 148.17(29), 148.34(30), 150.96(31), 152.79 (32)

In detail, the calculated NMR peaks shifts of  $C_{60}Cl_6$  are follows (in ppm.): 118.17 (1), 118.26 (2), 119.6 (3), 120.23 (4), 120.38 (5), 120.58 (6), 120.88 (7), 120.92 (8), 121 (9), 121.19 (10), 121.53 (11), 122.17 (12), 122.18 (13), 122.22 (14), 122.56 (15), 122.63 (16), 122.64 (17), 122.71 (18), 122.84 (19), 122.94 (20), 123.06 (21), 123.18 (22), 123.26 (23), 123.33 (24), 123.37 (25), 123.38 (26), 123.53 (27), 123.55 (28), 123.57 (29), 123.72 (30), 123.74 (31), 123.79 (32), 123.82 (33), 123.85 (34), 124.19 (35), 124.61 (36), 124.65 (37), 125.34 (38), 125.49 (39), 125.59 (40), 125.67 (41), 125.68 (42), 125.87 (43), 126.01 (44), 126.03 (45), 129.13 (46), 132.39 (47), 133.26 (48), 133.46 (49), 138.48 (50), 140.44 (51), 146.37 (52), 146.38 (53), 146.46 (54), 146.93 (55), 147.62 (56), 147.72 (57), 148.09 (58), 180.19 (59), 182.28 (60), 186.47 (61), 187.75 (62), 191.12 (63), 636.27 (64), 657.12(65), 694.58 (66)

The average observed [14] NMR of  $C_{60}Cl_6$  is at 134.55 ppm which is nearest the simulated NMR structure configuration 155.85 ppm. When compared with the observed NMR data peak gives 15% error. The error may be due to two reasons. Firstly the experimental sample  $^{13}C_{60}Cl_6$  might not possess all  $^{13}C$  and  $^{35}Cl$  during the NMR experiment. Thus the structure of  $C_{60}Cl_6$  obtained thirty two peaks instead of sixty-six peaks. Secondly slightly changes distortion occurs in many bond lengths of  $C_{60}Cl_6$  due to addition chlorine during  $C_{60}Cl_6$  formation from the fullerene. In  $^{13}C_{60}Cl_6$  structure configuration,

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the bond length and bond angle are taken as ideals in almost two carbon atoms of  $C_{60}$  except where the chlorine atoms of  $C_{60}Cl_6$  attached get changed with carbon atoms of  $C_{60}$ .

## V CONCLUSION

The structures of  $C_{60}Cl_6$  are very sensitive to electron correlation treatment with basis set that are employed. When the average simulation peak of  $C_{60}Cl_6$  compared with the available average  $C_{60}Cl_6$  NMR data peak, this comparison gives 15% error with the experimental NMR data. The error may be arising due to two facts. Firstly the experimental sample  $^{13}C_{60}Cl_6$  might not possess all  $^{13}C$  and  $^{35}Cl$  during the NMR experiment. This reduces the number of NMR peaks of  $C_{60}Cl_6$  that could obtain in NMR spectrum experimentally. Secondly experimental  $C_{60}Cl_6$  having thirty two peaks instead of sixty-six peaks so this increase the error percentage of simulation data.

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