

Density-functional theory calculation of the nuclear magnetic resonance indirect nuclear spin–spin coupling constants in C₆₀

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(Received 13 September 2002; revised version accepted 20 November 2002)

Density-functional theory is used to study the nuclear magnetic resonance (NMR) indirect nuclear spin–spin coupling constants in C₆₀. Knowledge of these coupling constants may help in the analysis of future experimental NMR studies of ¹³C-enriched C₆₀. At the Becke 3-parameter Lee–Yang–Parr (B3LYP) Kohn–Sham level, the one-bond couplings within pentagons and between pentagons are 62 Hz and 77 Hz, respectively; the corresponding geminal couplings are 7 Hz and 1 Hz, respectively. Except for the vicinal couplings (about 4 Hz), the long-range couplings are all 1 Hz or smaller. This is the largest theoretical calculation to date of the complete set of indirect nuclear spin–spin coupling constants of a molecular system; it has been made possible by solving the response equations only for the perturbing operators related to one nuclear magnetic moment, making the calculation feasible.

1. Introduction

Ever since the first experimental evidence for the existence of the ‘bucky-ball’ C₆₀ [1] and the subsequent verification that the molecule consists of sixty equivalent carbon atoms by the use of nuclear magnetic resonance (NMR) spectroscopy [2, 3], C₆₀ has attracted a great deal of experimental and theoretical interest—see for instance [4]. However, although several applications have been proposed for the class of molecules labelled fullerenes, the commercial application of these molecules remains elusive. In part, this situation is due to the lack of a proper understanding of the electronic structure and reactions of the fullerenes. For example, only recently was a complete route presented for the systematic synthesis of C₆₀ [5]. Nevertheless, even though a complete synthesis is now available, the yield of the synthetic route is low and the complete reaction mechanisms remain unclear. Thus, the elucidation of which reaction paths and combinations of the molecular framework are essential in the fullerene synthesis may help the understanding of how to make fullerenes more efficiently—in particular, how to

synthesize functionalized fullerenes containing one or more dopant atoms such as nitrogen [5].

One way to achieve this may be through the ¹³C enrichment of the reagents involved in the synthesis. A non-symmetrical arrangement of ¹³C atoms results in a lowering of the molecular symmetry of C₆₀. The magnetic moments of these carbon atoms, whose indirect spin–spin interaction is mediated by the electrons, leads to NMR multiplet patterns that depend on the relative positions of the ¹³C atoms. Following sufficient ¹³C enrichment, NMR may thus prove to be a useful diagnostic tool for distinguishing between possible reaction paths, provided these lead to different arrangements of the ¹³C atoms.

In this work, we consider the possibility of using the indirect NMR spin–spin coupling constants as a tool for investigating the arrangement of ¹³C atoms in C₆₀. We do this by performing density-functional theory (DFT) calculations of the indirect spin–spin coupling constants of C₆₀ using the 3-parameter Becke Lee–Yang–Parr (B3LYP) functional [6, 7]. From a knowledge of the calculated NMR coupling constants, an experimental NMR spectrum can thus be assigned to a particular ¹³C arrangement. From a knowledge of this arrangement, the reaction mechanisms of fullerene formations may in turn be elucidated.

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In addition to providing a set of NMR coupling constants that may be useful in fullerene chemistry, this work represents the largest theoretical calculation to date of the complete set of indirect nuclear spin–spin coupling constants of a molecular system. This calculation thus illustrates nicely the recent progress in the area of theoretical spin–spin calculations, which a few years ago could only accurately calculate the spin–spin coupling constants of systems containing no more than ten atoms.

In section 2, we briefly describe the theoretical calculation of the indirect spin–spin coupling constants, focusing in particular on the computational reductions possible when only the couplings to a limited number of nuclei are needed. Next, in sections 3 and 4, we summarize the computational details, present our results, and discuss their relevance.

2. Theory

The perturbation-theory approach for calculating indirect nuclear spin–spin coupling constants was developed by Ramsey more than 50 years ago [8]. However, because of the many difficulties facing practical calculations of these properties—that is, the large number of perturbing operators, the triplet nature of the Fermi-contact and spin–dipolar interactions, and the dependence of the properties on the electron density close to the nucleus—the practical application of Ramsey’s theory was, until very recently, restricted to rather small molecular systems. In particular, the role of electron correlation has been known to be important since the work of Roos and co-workers in the early 1970s [9], which means that Hartree–Fock results are often unreliable.

However, the introduction of DFT for the calculation of indirect spin–spin coupling constants [10, 11]—in particular, in the fully analytical, complete implementations presented independently by Sychrovský, Gräfenstein and Cremer [12] and by Helgaker, Watson and Handy [13] in 2000—has paved the way for routine calculations of these properties even for fairly large molecules. Although we do not go into the details of our DFT implementation here [13], we shall briefly sketch our approach to the calculation of indirect spin–spin coupling constants, focusing on some improvements that we have made to the calculation of the coupling constants in the Dalton program [14].

According to the non-relativistic theory of Ramsey [8], there are four interaction mechanisms that contribute to the indirect spin–spin coupling constants. These interactions arise from the second-order diamagnetic spin–orbit (DSO) operators

$$h_{KL}^{\text{DSO}} = \alpha^4 \sum_i \frac{(\mathbf{r}_{iK} \cdot \mathbf{r}_{iL})(\mathbf{M}_K \cdot \mathbf{M}_L) - (\mathbf{r}_{iK} \cdot \mathbf{M}_K)(\mathbf{r}_{iL} \cdot \mathbf{M}_L)}{r_{iK}^3 r_{iL}^3} \quad (1)$$

with $K > L$, and from the first-order paramagnetic spin–orbit (PSO), spin–dipole (SD), and Fermi-contact (FC) interaction operators:

$$h_K^{\text{PSO}} = \alpha^2 \sum_i \frac{\mathbf{l}_{iK} \cdot \mathbf{M}_K}{r_{iK}^3}, \quad (2)$$

$$h_K^{\text{SD}} = \alpha^2 \sum_i \frac{r_{iK}^2 \mathbf{m}_i \cdot \mathbf{M}_K - 3(\mathbf{m}_i \cdot \mathbf{r}_{iK})(\mathbf{r}_{iK} \cdot \mathbf{M}_K)}{r_{iK}^5}, \quad (3)$$

$$h_K^{\text{FC}} = -\frac{8\pi\alpha^2}{3} \sum_i \delta(\mathbf{r}_{iK}) \mathbf{m}_i \cdot \mathbf{M}_K. \quad (4)$$

In these equations we have used atomic units, α is the fine-structure constant, and we have introduced the permanent magnetic moments of the nuclei \mathbf{M}_K and of the electrons $\mathbf{m}_i = -\mathbf{s}_i$. For a more detailed description of the theory, see [15].

Of the four interaction mechanisms equations (1)–(4), only the DSO contribution is bilinear in the nuclear magnetic moments. As such, it can be evaluated from the ground-state density as an expectation value. For the three operators that are linear in the nuclear magnetic moments, the mechanism of the interaction can be depicted by assuming that we analyse the value of one operator while another is perturbing the electronic structure of the molecule. We thus need to compute linear response functions [16, 17] of the type $\langle\langle A; B \rangle\rangle$, where A and B are tensor components of the perturbation operators equations (2)–(4).

Since the PSO operator equation (2) is of singlet spin symmetry and the SD and FC operators equations (3) and (4) are triplet operators, the PSO operator will only interact with itself—that is, with the wave function perturbed by the PSO operator, determined by solving the singlet linear response equations [16], schematically written as:

$$\frac{\partial^2 \mathcal{E}}{\partial \lambda_S \partial \lambda_S} \frac{\partial \lambda_S}{\partial \mathbf{M}_L} = -\frac{\partial^2 \mathcal{E}}{\partial \lambda_S \partial \mathbf{M}_L}. \quad (5)$$

Here \mathcal{E} is the molecular energy, λ_S is a vector containing the singlet orbital-rotation parameters in the Kohn–Sham formulation of DFT, and $\partial \lambda_S / \partial \mathbf{M}_L$ represents the first-order PSO-perturbed wave function.

Since the triplet FC operator is purely isotropic and the triplet SD operator purely anisotropic, there is no mixed FC–SD contribution to the isotropic part of the coupling constant—that is, the only isotropic contributions are FC–FC and SD–SD. The FC and SD first-order perturbed wave functions are obtained by solving a triplet linear response equation [17] in a manner

similar to equation (5):

$$\frac{\partial^2 \mathcal{E}}{\partial \lambda_T \partial \lambda_T} \frac{\partial \lambda_T}{\partial \mathbf{M}_L} = - \frac{\partial^2 \mathcal{E}}{\partial \lambda_T \partial \mathbf{M}_L}, \quad (6)$$

where the vector λ_T contains triplet orbital-rotation parameters. Explicit expressions for the matrix elements in the response equations, equations (5) and (6), can be found in [16, 17].

It is important to realize that the computational cost of calculations of indirect spin–spin constants is dominated almost exclusively by the cost of solving the singlet and triplet response equations. The construction of the right-hand sides of equations (5) and (6) involves only one-electron terms, and can therefore be made with little or no computational effort. Because of the interchange theorem, we may choose which nuclear magnetic moments perturb our wave function, and thus for which nuclei we should solve response equations. For a highly symmetric molecule such as C_{60} , in which all carbon atoms are equivalent, it suffices to solve the response equations for only one set of perturbing operators—that is, for PSO, SD and FC related to a single nucleus. All coupling constants can then be calculated at little or no extra cost.

However, since point-group symmetry is used in our calculations, we need to solve response equations for symmetry-adapted nuclear magnetic moments. In general, therefore, little reduction in the number of response equations that must be solved is obtained by invoking the interchange theorem. In practice, Dalton, like many other programs, can only exploit the symmetry of D_{2h} and its subgroups. For C_{60} in the D_{2h} subgroup, the carbon nuclei fall into two classes—one with four symmetry-related atoms and one with eight symmetry-related atoms. Since these two classes are equivalent in the full icosahedral point group, we choose to solve only the response equations for the class containing four symmetry-related atoms. In this manner, we can determine all 23 symmetry-distinct indirect spin–spin coupling constants (*vide infra*) by solving only 12 singlet and 28 triplet response equations, noting that there are three tensor components for each PSO operator, six for each SD operator, and one for each FC operator.

We have in Dalton implemented the option of calculating all possible indirect coupling constants to a single atom from the wave-function response determined for that atom. This scheme provides a very convenient approach to the calculation of indirect spin–spin coupling constants even for fairly large molecules, and in particular when combined with the DFT formalism, which appears to give good results for such properties.

3. Computational details

In our calculations of indirect nuclear spin–spin couplings of C_{60} , we have used the B3LYP functional [6, 7]. As demonstrated by Helgaker, Watson and Handy [13] and by Lantto, Vaara, and Helgaker [18], the hybrid B3LYP functional performs considerably better than the local-density approximation and the generalized gradient approximation for the calculation of spin–spin coupling constants of the considered organic molecules. The geometry of C_{60} was taken from [19].

In calculations on a system as large as C_{60} , it is important to choose a basis set that represents a good compromise between size and quality. We have used here a [9s5p1d/5s4p1d] basis taken from Huzinaga’s compilations [20] with the polarization functions suggested by van Wüllen [21], giving a total of 1320 contracted Gaussians for C_{60} . This basis is at the same time one of the smallest basis sets expected to give reasonable results for spin–spin couplings [22] and one of the largest basis sets we can handle for a molecule of this size. DFT calculations on small organic molecules indicate that this basis gives coupling constants that differ from the basis-set limit by less than 10% [23].

4. Results and discussion

There are 23 distinct coupling constants in C_{60} . We describe these here by recalling that C_{60} is built from 12 non-adjacent pentagons. We first select a reference pentagon and its antipode; between these pentagons, there are two concentric shells, each containing five non-adjacent pentagons, symmetrically located about the axis connecting the reference pentagon and its antipode.

Within each pentagon, there are two distinct coupling constants. Next, there are nine distinct coupling constants between the reference pentagon and the carbon nuclei in the first concentric shell, and likewise nine couplings with the carbon nuclei in the second shell. Finally, there are three distinct couplings between the reference pentagon and its antipode, giving a total of 23 distinct coupling constants in C_{60} . In table 1, we have listed the coupling constants in this particular sequence, also specifying the numbering of the atoms according to figure 1. The numbers in this Schlegel diagram follow standard nomenclature, see [24].

To discuss the spin–spin coupling constants, we have provided some auxiliary data in table 1. Thus, we have listed the carbon–carbon distance (different for each unique coupling constant), the number of bonds in the shortest interconnecting pathway (n in ${}^n J$), and a specification of this pathway (along the pentagon or hexagon edges, with preference to pentagons, and its arrangement). This specification is perhaps less important for the interpretation of the coupling constants

Table 1. Definitions and total values of the distinct indirect nuclear spin-spin coupling constants in C_{60} . Separations in pm and couplings in Hz. The numbering of nuclei is according to figure 1.

Pentagon	Constant	Separation	Pathway	Coupling
self	$^1J(1-2)$	145.5	p	61.63
	$^2J(1-3)$	235.5	pp	6.94
first shell	$^1J(5-6)$	139.1	h	77.35
	$^2J(1-6)$	246.6	ph	1.00
	$^3J(1-7)$	284.7	php-cis	4.27
	$^3J(1-20)$	369.5	php-trans	3.83
	$^3J(2-6)$	357.6	pph	3.81
	$^4J(2-7)$	411.4	pphp-cis	-0.99
	$^4J(2-20)$	451.2	pphp-trans	0.43
second shell	$^5J(2-22)$	520.2	pphp-cis	0.52
	$^5J(2-21)$	540.2	pphp-trans	-0.07
	$^4J(1-24)$	460.6	hpph	0.27
	$^5J(1-23)$	483.1	hphp-cis	0.55
	$^5J(1-44)$	548.1	hphp-trans	0.21
	$^6J(2-23)$	578.5	phpph-cis	-0.34
	$^6J(2-44)$	606.2	phpph-trans	0.30
	$^6J(1-43)$	613.3	hpphpp	0.15
	$^7J(2-42)$	650.3	phpphpp-cis	0.34
	$^7J(2-43)$	665.7	phpphpp-trans	-0.28
	$^8J(3-43)$	696.1	pphppph	0.33
antipode	$^7J(1-57)$	669.7	hpphpph	-0.08
	$^8J(2-57)$	694.8	phpphpph	0.27
	$^9J(3-57)$	709.9	pphppphh	-0.27

in C_{60} than in other molecules since—in particular, for distant nuclei—various pathways can be equivalent or similar. Still, it allows us to interpret longer pathways as extensions to shorter ones, which is why we have chosen to specify certain pathways instead of other equivalent pathways. Finally, we present in table 2 the individual contributions to the coupling constants.

As expected, the largest coupling constants are the one-bond constants, with the coupling between two hexagons (77.4 Hz) somewhat larger than that within one pentagon (61.6 Hz). However, both these couplings are stronger than the one-bond coupling of 55.8 Hz in benzene [25]. Next, whereas the two geminal couplings in C_{60} are 6.9 Hz (within one pentagon) and 1.0 Hz (between two pentagons), the three vicinal couplings (between two pentagons) are all about 4 Hz. The remaining long-range couplings are all smaller than 1 Hz. Thus, in general, the couplings nJ become smaller with increasing n and increasing internuclear distance. However, there are exceptions with for example the $^2J(1-6)$ coupling being significantly smaller than the $^3J(1-7)$ coupling. This behaviour is similar to that in benzene, where $^2J(CC)$ and $^3J(CC)$ are -2.5 and 10.1 Hz, respectively [25]. For constants across more bonds, there are many such irregularities. For example, the value of the $^4J(1-24)$ coupling is smaller than most of the couplings following it in table 1, all of which can be viewed as couplings along the same pathway.

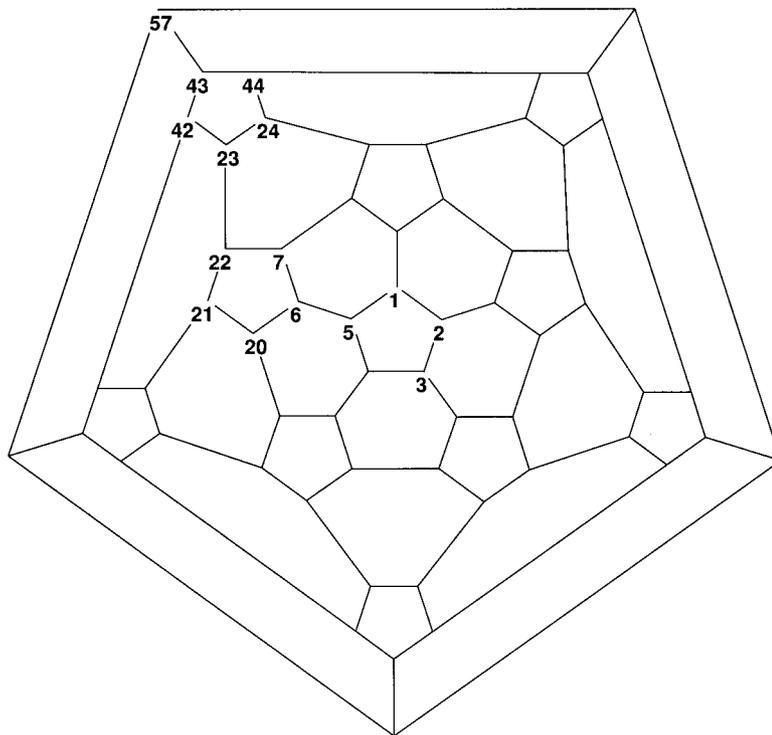


Figure 1. Numbering of the nuclei in C_{60} .

Table 2. Contributions to the indirect nuclear spin–spin coupling constants in C_{60} (in Hz). The numbering of nuclei is according to figure 1.

Pentagon	Constant	FC	SD	PSO	DSO	Total
self	$^1J(1-2)$	64.64	0.25	−3.69	0.43	61.63
	$^2J(1-3)$	7.04	−0.01	−0.26	0.16	6.94
first shell	$^1J(5-6)$	82.18	0.42	−5.68	0.43	77.35
	$^2J(1-6)$	1.11	−0.04	−0.20	0.13	1.00
	$^3J(1-7)$	4.30	0.06	−0.21	0.12	4.27
	$^3J(1-20)$	3.92	−0.01	−0.11	0.03	3.83
	$^3J(2-6)$	3.67	−0.05	0.16	0.03	3.81
	$^4J(2-7)$	−1.00	0.01	−0.03	0.02	−0.99
	$^4J(2-20)$	0.41	−0.02	0.03	0.01	0.43
	$^5J(2-22)$	0.53	0.00	0.00	0.00	0.52
	$^5J(2-21)$	−0.06	0.00	−0.01	0.00	−0.07
	second shell	$^4J(1-24)$	0.24	−0.01	0.03	0.01
$^5J(1-23)$		0.58	−0.04	0.01	0.01	0.55
$^5J(1-44)$		0.21	0.00	0.01	0.00	0.21
$^6J(2-23)$		−0.34	0.00	0.00	0.00	−0.34
$^6J(2-44)$		0.33	0.00	−0.02	0.00	0.30
$^6J(1-43)$		0.15	0.00	0.00	0.00	0.15
$^7J(2-42)$		0.34	0.00	0.00	0.00	0.34
$^7J(2-43)$		−0.28	0.00	0.00	0.00	−0.28
$^8J(3-43)$		0.34	0.00	0.00	−0.01	0.33
antipode		$^7J(1-57)$	−0.08	0.00	0.00	0.00
	$^8J(2-57)$	0.26	0.00	0.01	0.00	0.27
	$^9J(3-57)$	−0.26	−0.01	0.00	−0.01	−0.27

As shown in table 2, the values of the coupling constants for C_{60} are also dominated by the FC contribution, the other contributions being rather small, even in relative terms. The largest non-FC contribution is the PSO contributions to the one-bond couplings, which are -3.7 Hz within one pentagon and -5.7 Hz between two pentagons. These contributions should be compared with the FC contributions of 64.6 and 82.2 Hz, respectively. The dominance of the FC contribution appears to be more consistent in C_{60} than in other molecules and for couplings between nuclei other than carbon. This observation may be used to simplify future calculations of spin–spin coupling constants—either in more advanced calculations on C_{60} or for other fullerenes—recalling that the FC contribution has only one tensor component and therefore is relatively fast to compute.

The magnitudes of the computed coupling constants in C_{60} cover a wide range. We believe that the larger couplings at least are sufficiently large and different from one another to enable an assignment of an experimental spectrum. For ^{13}C -enriched C_{60} in specific (e.g., three non-equivalent) positions, the experiment is, in principle, feasible. In particular, with a group of ^{13}C nuclei close to one another, we can expect differences in the shielding

constants because of rovibrational effects, and the corresponding large coupling constants should then be observable. For example, it should be possible experimentally to distinguish between two C_{60} isotopomers, one including three neighbouring ^{13}C nuclei in a pentagon and one with the ^{13}C nuclei in a hexagon.

5. Conclusions

We have calculated the NMR indirect nuclear spin–spin coupling constants of C_{60} by DFT, at the hybrid level of theory using the B3LYP functional. The one-bond couplings within a single pentagon and between neighbouring pentagons are 62 Hz and 77 Hz, respectively. The geminal couplings are much smaller: 7 Hz within one pentagon and 1 Hz between neighbouring pentagons. Except for the vicinal couplings, which are all about 4 Hz, the long-range couplings are 1 Hz or smaller. Knowledge of these couplings may help in unravelling the spectrum of ^{13}C -enriched C_{60} .

We are indebted to Ola Berg Lutnæs for his program for selecting the distinct spin–spin coupling constants. MJ acknowledges helpful discussions with Dr Slawomir Szymański. This project was supported by the

Norwegian Research Council through a travel grant to MJ (Grant No. 141932) and for computer time through the Programme for Supercomputing.

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