First Principles NMR Calculations by Fragmentation

Adrian M. Lee and Ryan P. A. Bettens*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

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The nuclear magnetic shielding tensor is a molecular property that can be computed from first principles. In this work we show that by utilizing the fragmentation approach, one is able to accurately compute this property for a large class of molecules. This is of great significance because the computational expense required in the evaluation of the shielding tensor for all nuclei in a large molecule is now subject to near linear scaling. On the basis of previous studies and this work, it is also very likely that all molecular properties that can be expressed as derivatives of the total energy of the system are also amenable to accurate evaluation via fragmentation. If only the chemical shifts for nuclei in a small part of a large molecule are of interest, then only those molecular fragments containing those nuclei need to have their shielding tensors evaluated. Further, the fragmentation approach allows one to construct a database of molecular fragments that could, in principle, be used in the NMR characterization of molecules and at the same time provide possible three-dimensional representations of these molecules.

1. Introduction

There are two basic approaches available for predicting NMR chemical shifts: the first approach is empirical[1−6] and the second is from first principles.[7−16] In the empirical approach, measured chemical shifts are used from large sets of known structures to parametrize various constants that are then utilized in additivity models[1,2] or neural networks[3−6] to predict the chemical shifts of, most often, ^{1}H and ^{13}C in new structures. The former approach is adopted in many commercial software suites today, but both are available from a myriad of software packages. However, this approach is clearly limited by the extent of the database used in the parametrization and the flexibility of the model adopted. While attempts have been made to account for the fact that chemical shifts depend on the three-dimensional shape of the target molecule, difficulties arise because almost always the "structures" used in the parametrization and prediction are the two-dimensional projections familiar to all chemists.

The advantages of being able to predict accurately chemical shifts of any nucleus in any molecule from first principles are obvious. However, such predictions are computationally expensive being of the same order as a frequency calculation. It is therefore clear that if NMR predictions from first principles are to be used in structural elucidation of large molecules, linear-scaling techniques necessarily must be applied. While there are a significant number of near linear-scaling fragmentation techniques available presently (density-matrix methods[17−24] and energy-based methods[25−34]), few easily and simply allow for the possibility of determining the second mixed derivative of the total energy of the molecule with respect to applied magnetic field and nuclear magnetic moment for any molecular configuration. Such a requirement is necessary because this second mixed derivative provides the nuclear magnetic shielding tensor from which the chemical shift is derived.

Very recently it has been shown for many molecular systems that the ground-state total first-principles electronic energy of a large molecule can accurately, to the milli-Hartree or less level, be re-expressed as a linear combination of the ground-state total electronic energies of smaller fragment molecules.[25−34] The ability to express the energy of a large molecule in this way enables near linear scaling in the computational expense with respect to molecular size. Furthermore such methods are amenable to large scale parallelization additionally improving computational efficiency. Because the total energy of the system can be expressed as a linear combination of energies of smaller fragments, so too can any derivative of the energy. In this work we show that isotropic absolute magnetic shielding constants for the nuclei in a molecule can be accurately computed using fragmentation.

2. Method

A detailed description of our fragmentation approach has been given elsewhere,[32] so only a brief description will be provided here. Many molecules can be broken down into separate fragment molecules by applying a set of rules. The rules followed never break anything other than a formal single bond in order to form a fragment, and in our method, the bond broken is replaced by a valence bonded hydrogen. Additionally, the fragment structures are exactly identical (bond lengths, angles and dihedrals) to the parent molecule from which they are derived. Following Deev and Collins,[30] we have adopted a hierarchal approach for the fragmentation of a molecule that are designated by "levels", with higher levels of fragmentation producing more accurate total energies. (Note that a typographical error appears in the last line of Table 1 in ref 32. Fragment coefficient −12/3 should be −5/3.)

There are essentially two steps in our method for obtaining the total energy of a molecule via fragmentation. The first involves following a set of rules, as mentioned, that breaks a larger molecule down into smaller fragment molecules. The total energy obtained for the entire molecule from these fragments is denoted as the fragment bonded energy, because the fragments are derived by considering the valence bonding in the molecule. In the second step, the remaining interactions not accounted

* Corresponding author. E-mail: chmbrpa@nus.edu.sg. Phone: +65 6516 2846. Fax: +65 6779 1691.

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for in the bonded fragmentation treatment are dealt with. In our previous paper, this was done very simply by interacting all groups pairwise that were not included together in the same bonded fragment. In this case the correction to the bonded fragmentation energy is the sum of all these pairwise nonbonded interactions.

Regardless of fragmentation level and whether or not the nonbonded interactions are included, the energy of a molecule, E, can be approximated as

$$E = \sum_{i=1}^{N_{\text{fragments}}} c_i E_i \tag{1}$$

where E_i is the energy of a molecular fragment and c_i is a fragment coefficient, typically either 1 or −1. Essentially, the higher the level of fragmentation, the larger the molecular fragments and the overlaps between them, the more accurate the total energy. Equation 1 can be applied for any molecular configuration of the system. Thus, it follows that if eq 1 is true for any configuration, then so must also be the higher derivatives of the energy with respect to atomic displacements. That is

$$\frac{\partial}{\partial \mathbf{X}} E = \sum_{i=1}^{N_{\text{fragments}}} c_i \frac{\partial}{\partial \mathbf{X}} E_i \text{ (and higher derivatives)} \tag{2}$$

where $\mathbf{X}$ is the vector of Cartesian coordinates of all the atoms in the system. Indeed, it has been shown previously that excellent agreement is achieved for equilibrium[30,34] and transition state structures, as well as harmonic frequencies using fragmentation.[30]

Further, other molecular properties like dipole moments and polarizabilities[35] are well reproduced using fragmentation. This is of significance because for these properties the energy derivatives are not with respect to Cartesian displacements, but are with respect to an applied external electric field. The nuclear magnetic shielding tensor, $\boldsymbol{\sigma}_{\mathbf{n}}$, for nucleus, n, is defined as the mixed second derivative of the energy with respect to an applied external magnetic field, $\mathbf{B}$, and the magnetic moment of the nucleus, $\mathbf{m}_{\mathbf{n}}$:

$$\boldsymbol{\sigma}_{\mathbf{n}} = \frac{\partial^2 E}{\partial \mathbf{B} \partial \mathbf{m}_{\mathbf{n}}} \tag{3}$$

A third of the trace of this tensor is the isotropic absolute magnetic shielding constant for nucleus n and is linearly related to the familiar chemical shift used in NMR spectroscopy. By applying the mixed second derivative of eq 3 to eq 1, we find that this tensor is also subject to evaluation via fragmentation (as is any property of the molecule that can be expressed as an energy derivative, assuming, of course, that eq 1 is accurate), i.e.

$$\boldsymbol{\sigma}_{\mathbf{n}} = \sum_{i=1}^{N_{\text{fragments}}} c_i \frac{\partial^2 E_i}{\partial \mathbf{B} \partial \mathbf{m}_{\mathbf{n}}} \tag{4}$$

and below we provide a trivial example to illustrate the procedure. Note that we have neglected capping hydrogens from eq 4; however, their effect is small.

As an example we have chosen the conformation of 3-fluorooctane illustrated in Figure 1. All calculations in this paper were performed using the Gaussian 03 suite of programs.[36] In this example we optimized the geometry and performed all calculations at the HF/6-31G level. The NMR method used was Gauge-Independant Atomic Orbital (GIAO).[7−10]

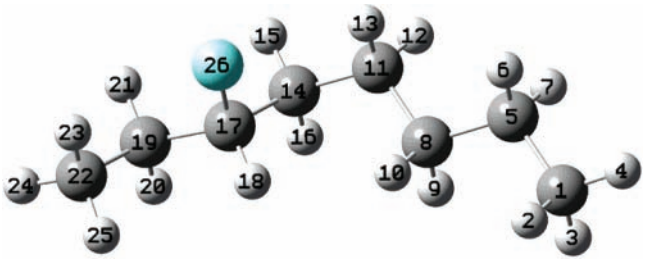

Figure 1. The conformation used for 3-fluorooctane showing the atoms labels used in Table 1.

For this example we have chosen to fragment the molecule at level 3, which produces an energy error in the total electronic energy of 0.2 milli-Hartrees. Using the atom labels on each carbon to represent the carbon and valence bonded hydrogens and/or fluorine, the level-3 fragments are given as the headings of columns 2−10 in Table 1 with the fragment coefficients, c_i, provided in the second row. Note that the capping hydrogens are not included in Table 1.

It is clear from Table 1, that the shielding constant for each nucleus is well reproduced by fragmentation at level 3, which we recommend as the lowest level of fragmentation to be used for NMR calculations. Of note is that it is often the case that for a given nucleus in a specific fragment the computed shielding constant differs significantly from that in the full calculation, yet upon taking the appropriate linear combination of the shielding constants for the specific nucleus in each fragment produces an accurate net result. This is particularly evident for the fluorine nucleus, which appears in 5 of the 9 fragments with shielding constants ranging from 409.3 to 453.9; yet the final value of the shielding constant computed with the fragments differs by only −0.5 ppm (−0.1% error) from the value computed in the entire molecule. Note also for carbon nucleus 8, all fragment shielding constants are significantly larger than its value in the entire molecule; yet upon summing the fragment shielding constants appropriately, it differs by only 0.8 ppm.

It should also be clear from this example that if one is interested in the chemical shift of a specific nucleus in a much larger molecule then only those fragments that contain the nucleus of interest need be computed because only those fragments will contribute to the net value of the shielding constant.

3. Results and Discussion

Table 2 provides a list molecules studied in this work and the largest number of heavy atoms found in a fragment at levels 3 and 4. These molecules were chosen from our previous study,[32] where it was noted that only in taxol were the nonbonded interactions large (of the order of 25 milli-Hartrees at level 4). These molecules have a wide variety of group connectivities, such that the range of heavy atoms in the largest fragments should be representative of the number that would be seen in any organic molecule, no matter the size. Thus, the size of the fragments generated by the technique used in this study is independent of the size of the target molecule. Fragment size is dependent upon the size of the groups defined (group definitions are discussed in our previous work as well as in the Supporting Information) and the degree of interconnectivity within the molecule.

Table 3 provides a list of the levels of theory and basis sets used for the molecules studied in this work. Table 4 lists the rms errors between the full calculation of the absolute shielding constant for ^{1}H in each molecule and the same calculated at

TABLE 1: Computed Isotropic Absolute Shielding Constants (σ) in ppm for the Fragments Given in Columns 2−10 Using the Atom Labels as Shown in Figure 1[a]

	1−11	5−14	8−17	11−19	14−22	5−11	8−14	11−17	14−19	obs	obs − calc
c_i[b]	1	1	1	1	1	−1	−1	−1	−1		
1	193.0									193.0	−0.04
2	32.7									32.6	−0.05
3	32.7									32.7	0.00
4	32.5									32.5	−0.04
5	185.0	192.8				192.0				186.2	0.44
6	32.4	32.7				32.7				32.3	−0.09
7	32.4	32.7				32.7				32.4	−0.01
8	185.4	185.7	196.6			193.6	192.8			180.5	−0.82
9	32.4	32.4	32.9			32.3	32.7			32.7	−0.03
10	32.4	32.3	32.2			32.4	32.6			32.1	0.02
11	193.5	185.1	193.4	198.1		192.7	193.4	198.5		185.1	−0.34
12	32.7	32.4	32.3	32.6		32.7	32.3	32.6		32.5	0.04
13	32.7	32.4	31.7	31.9		32.7	32.3	31.8		31.7	−0.01
14		193.9	180.3	179.8	186.6		193.2	186.1	186.2	174.7	−0.60
15		32.5	31.6	32.0	32.1		32.5	31.7	32.1	31.9	0.00
16		32.7	32.8	32.5	32.8		32.7	32.5	32.8	32.6	−0.04
17			131.6	122.4	121.6			128.2	126.1	120.6	−0.68
18			28.9	29.0	29.1			29.1	28.8	29.1	0.01
19				186.3	180.0				185.9	180.5	0.07
20				32.8	32.5				32.8	32.6	0.04
21				32.1	32.0				32.0	32.0	−0.01
22					196.6					196.5	−0.09
23					31.9					31.9	0.00
24					32.6					32.6	0.01
25					32.7					32.7	−0.01
26			453.9	420.3	419.5			452.4	409.3	431.6	−0.50

[a] "obs" is the σ for the full calculation and "obs − calc" is the difference between the σ's for the full calculation and that calculated using fragmentation. [b] Fragment coefficient.

TABLE 2: Largest Number of Heavy Atoms Found in a Fragment at Levels 3 and 4 for the Molecules Studied in this Work

molecule	level 3	level 4	full
cholesterol	13	15	28
DDT	10	17	19
folic Acid	12	15	32
hexenal	6		7
linamarin	8	9	17
moronic acid	12	15	33
ranitidine	8	9	18
taxol	12	16	62
vitamin A	11	14	21
VX gas	7	9	16
average	9.9	13.2	NA

TABLE 3: Molecules Studied in this Work,[a] Method and Basis Sets Used

molecule	method	basis
cholesterol	HF	6-31G(d) (5d)
DDT	MPW1PW91	6-311+G(2d, p)
folic Acid	HF	6-311G(2d, p)
hexenal	HF	6-311G(2d, p) (5d)
hexenal	MP2	6-311G(2d, p) (5d)
hexenal	B3LYP	6-311G(2d, p) (5d)
linamarin	B3LYP	6-31G(d, p) (5d)
moronic acid	B3LYP	6-31G(d) (5d)
ranitidine	B3LYP	6-31G(d, p) (5d)
taxol(A)	B3LYP	6-31G(d) (5d)
taxol(A)	MPW1PW91	6-31G(d) (5d)
taxol(B)	MPW1PW91	6-31G(d) (5d)
vitamin A	B3LYP	6-311+G(2d, p) (5d)
VX gas	B3LYP	6-311+G(2d, p)

[a] Cartesian coordinates, energies, and shielding constants are available in the Supporting Information.

fragmentation levels 3 and 4 both not including and including the nonbonded interactions. Table 5 is analogous to Table 4, except we report the rms errors for the absolute shielding constant for ^{13}C. Table 6 is a summary of the rms errors in the absolute shielding constants for the H, C, N and O nuclei in all our molecules except taxol.

Examination of Tables 4 and 6 reveals that, apart from taxol, the ^{1}H chemical shifts are well reproduced at level 3, and improved by almost a factor of 3 at level 4 when only the bonded interaction is considered. Inclusion of the nonbonded interaction into the fragmentation scheme improves the level 3 bonded results almost by a factor of 2, but does not significantly improve the results obtained at level 4. Excluding taxol, at level 4 ^{1}H chemical shifts are reproduced to within 0.1 ppm. Note that we have no results for hexenal at level 4 because the molecule is too small to be fragmented at this level.

Again, examination of Tables 5 and 6 clearly shows that when taxol is excluded ^{13}C chemical shifts can be reproduced very well with bonded interactions only at levels 3 and 4. The rms error is within 2 ppm at level 3 and about 0.5 ppm at level 4. Inclusion of nonbonded interactions has almost no effect at level 3, and provides no improvement at level 4. We also note from Table 6 that the chemical shifts for the small number of N and O nuclei in our data set, excluding taxol, are also reasonably well reproduced at level 3 and improved by nearly a factor of 2 at level 4 for the bonded interactions. Inclusion of the nonbonded interactions for these nuclei either makes no impact or worsens the rms considerably.

Two points are very clear through close examination of Tables 4−6. The first is that when the molecule possesses no significant nonbonded interactions not already included in the bonded fragments the chemical shielding constant is very well reproduced by our fragmentation method. The second point is that when nonbonded interactions not already included in the bonded fragments are significant, as is the case in taxol, our, apparently, overly simplified approach to the treatment of these interactions performs poorly. For both ^{1}H and ^{13}C, the rms errors are significantly larger than for the remaining molecules, and when

TABLE 4: RMS and Maximum Differences between the Full and Fragmentation Calculations, Including Only Bonded Interactions (B) and Bonded Plus Nonbonded Interactions (B + N) for ^{1}H Absolute Chemical Shifts (ppm)

		level 3				level 4			
molecule	nH[a]	rms (B)	rms (B + N)	max (B)	max (B + N)	rms (B)	rms (B + N)	max (B)	max (B + N)
cholesterol	46	0.11	0.07	0.50	0.19	0.03	0.03	0.13	0.13
DDT	9	0.16	0.15	0.31	0.28	0.06	0.05	0.12	0.09
folic Acid	19	0.16	0.20	0.43	0.65	0.06	0.06	0.13	0.14
hexenal[b]	10	0.03	0.01	0.05	0.02				
hexenal[c]	10	0.02	0.01	0.03	0.03				
hexenal[d]	10	0.02	0.02	0.03	0.04				
linamarin	17	0.50	0.16	1.78	0.32	0.13	0.06	0.31	0.15
moronic acid	46	0.18	0.13	0.59	0.28	0.05	0.05	0.17	0.13
ranitidine	18	0.07	0.07	0.13	0.17	0.06	0.06	0.11	0.11
taxol(A[d])	51	0.47	0.27	1.99	1.09	0.46	0.31	1.98	1.39
taxol(A[e])	51	0.46	0.26	1.94	1.02	0.45	0.29	1.90	1.29
taxol(B)	51	0.38	0.25	1.67	0.66	0.37	0.29	1.50	1.32
aitamin A	30	0.08	0.09	0.33	0.36	0.10	0.09	0.22	0.21
VX gas	26	0.10	0.10	0.22	0.30	0.05	0.05	0.13	0.13

[a] Number of hydrogen atoms. [b] HF. [c] MP2. [d] B3LYP. [e] mPW1PW91.

TABLE 5: RMS and Maximum Differences between the Full and Fragmentation Calculations, Including Only Bonded Interactions (B) and Bonded Plus Nonbonded Interactions (B + N) for ^{13}C Absolute Chemical Shifts (ppm)

		level 3				level 4			
molecule	nC[a]	rms (B)	rms (B + N)	max (B)	max (B + N)	rms (B)	rms (B + N)	max (B)	max (B + N)
cholesterol	27	0.90	1.35	2.71	4.96	0.12	0.12	0.32	0.31
DDT	14	3.08	3.22	6.71	7.23	0.53	0.52	1.04	1.04
folic Acid	19	1.16	1.10	2.94	2.76	0.68	0.57	1.99	2.06
hexenal[b]	6	0.10	0.10	0.14	0.12				
hexenal[c]	6	0.09	0.09	0.15	0.15				
hexenal[d]	6	0.09	0.09	0.17	0.17				
linamarin	10	2.85	2.67	4.94	5.53	0.60	0.59	1.20	1.15
moronic acid	30	2.40	1.28	10.5 0	5.51	0.26	0.35	0.51	1.03
ranitidine	12	0.85	0.62	1.90	1.32	0.94	0.77	1.99	1.67
taxol(A[d])	47	2.24	2.88	6.71	5.96	2.16	2.22	9.55	9.20
taxol(A[e])	47	2.22	2.80	6.65	5.94	2.09	2.14	9.06	8.70
taxol(B)	47	2.00	2.49	5.95	6.00	1.83	1.95	7.52	7.29
vitamin A	20	1.36	1.47	4.02	4.54	0.65	0.73	1.49	1.61
VX gas	11	2.49	1.87	3.86	3.67	0.46	0.56	0.93	1.03

[a] Number of carbon atoms. [b] HF. [c] MP2. [d] B3LYP. [e] mPW1PW91.

TABLE 6: RMS between the Full and Fragmentation Calculations for All Molecules Studied except Taxol, Including Only Bonded Interactions (B) and Bonded Plus Nonbonded Interactions (B + N) for H, C, N, and O Absolute Chemical Shifts (ppm)

	level 3			level 4		
	no.	rms (B)	rms (B + N)	no.	rms (B)	rms (B + N)
H	241	0.18	0.11	211	0.07	0.06
C	161	1.85	1.62	143	0.53	0.52
N	11	1.74	1.68	11	0.93	3.37
O	25	2.61	4.26	22	1.71	1.44

we consider the results for the bonded calculations we note that on going from level 3 to 4 there is little to no improvement in the rms error. Again, this is largely due to nonbonded interactions, usually involving O atoms, dominating the rms. When we include our simple approach to computing these interactions, we see some improvement in the ^{1}H shielding constants, but none in the ^{13}C. Furthermore, while not shown here, the shielding constants of several oxygen atoms are very poorly reproduced (see Supporting Information).

The inability of properly describing nonbonded interactions by simply interacting two groups is born out when we changed our method for computing the energy of taxol to mPW1PW91 from B3LYP in our original paper. While the energy of taxol was well reproduced at level 4 including the nonbonded interactions using the latter hybrid method, we find that when using mPW1PW91 the fragmentation energy of taxol, including nonbonded interactions is in error by 11 and 13 milli-Hartrees (see Supporting Information) for taxol A and B respectively. Thus, it is imperative that a more accurate method be found for the determination of the nonbonded interaction energy, particularly when H-bonding is involved. We are presently working on improving our treatment of nonbonded interactions in a manner that does not lead to an increase in the current size of our fragments.

4. Conclusions

We have shown that our fragmentation method can be directly applied to the evaluation of the nuclear magnetic shielding tensor with high accuracy (and our results equally apply to 2D NMR), at least for systems with no significant nonbonded interactions not already included in the bonded fragments. Nonbonded interactions have been treated accurately by other authors, but at a cost of significantly larger fragment sizes.[28,33,34] It is our opinion that it is possible to treat nonbonded interactions accurately without significantly increasing the fragment size, and in so doing enable the accurate calculation of the shielding tensor for any molecular system using small fragments. It has been previously shown that the fragmentation technique is accurate for reproducing equilibrium geometries, harmonic frequencies, dipole moments and polarizabilities.[31,35] Provided

that eq 1 is accurate, the fragmentation approach will also be accurate for computing all molecular properties that can be written as derivatives of the total energy of the system. Aside from the properties already mentioned, these include the following:[37] electric multipole moments; magnetic multipole moments; electric hyperpolarizability (first, second etc.); magnetizability and hypermagnetizability (first, second, etc.); hyperfine coupling constants; spin−spin coupling (for different nuclei); infrared absorption and Raman intensities including those for overtone and combination bands; circular dichroism; magnetic circular dichroism (Faraday effect[38]); all anharmonic corrections to vibrational frequencies; and, of course, the Voigt (Cotton−Mouton) effect.[39,40]

Because the shielding tensor can be accurately computed for a large number of molecular systems using fragmentation, it is clear that if only a single nucleus is of interest then only those fragments containing that nucleus need have their shielding tensors evaluated. Furthermore, it is quite possible to envisage a situation whereby a database of fragments in various conformations containing pre-computed shielding constants is called upon whenever an NMR spectrum of a new molecule is required. Only for those fragments not in the database would computation be required. Such a situation would aid significantly in the spectral characterization of molecules as well as provide possible three-dimensional representations of these species.

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Supporting Information Available: An algorithm for assigning groups in a molecule. Cartesian coordinates, shielding constants and total energies of all molecules studied in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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