Review

Searching for the Best Values of NMR Shielding and Spin-Spin Coupling Parameters: $CH_{4-n}F_n$ Series of Molecules as the Example

Karol Jackowski *[ORCID] **and Mateusz A. Słowiński** [ORCID]

Laboratory of NMR Spectroscopy, Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
* Correspondence: kjack@chem.uw.edu.pl

Abstract: Attempts at the theoretical interpretation of NMR spectra have a very long and fascinating history. Present quantum chemical calculations of shielding and indirect spin-spin couplings permit modeling NMR spectra when small, isolated molecules are studied. Similar data are also available from NMR experiments if investigations are performed in the gas phase. An interesting set of molecules is formed when a methane molecule is sequentially substituted by fluorine atoms—$CH_{4-n}F_n$, where n = 0, 1, 2, 3, or 4. The small molecules contain up to three magnetic nuclei, each with a one-half spin number. The spectral parameters of $CH_{4-n}F_n$ can be easily observed in the gas phase and calculated with high accuracy using the most advanced ab initio methods of quantum chemistry. However, the presence of fluorine atoms makes the calculations of shielding and spin-spin coupling constants extremely demanding. Appropriate experimental ^{19}F NMR parameters are good but also require some further improvements. Therefore, there is a real need for the comparison of existing NMR measurements with available state-of-the-art theoretical results for a better understanding of actual limits in the determination of the best shielding and spin-spin coupling values, and $CH_{4-n}F_n$ molecules are used here as the exceptionally important case.

Keywords: NMR spectroscopy; fluoromethanes; nuclear magnetic shielding; spin-spin coupling

1. Introduction

Nuclear magnetic moments have been known since Rabi's molecular beam experiments [1,2], which were performed before World War II. Later, in 1945, two research groups in the USA independently discovered nuclear magnetic resonance (NMR) in macroscopic samples [3,4]. A new physical method was considered a useful tool for the determination of nuclear magnetic moments though its results were dependent on selected samples [5]. In 1950, Proctor and Yu [6] proved the existence of ^{14}N chemical shifts for NH_4^+ and NO_3^- ions. Independently, Dickinson [7] found ^{19}F chemical shifts for a range of fluorine-containing compounds, and both the above publications appeared in the same issue of *Physical Review*. The chemical shifts are due to the magnetic shielding of nuclei by electrons, and this phenomenon was theoretically described first by Ramsey [8–10]. Meanwhile, the indirect interactions of nuclear magnetic moments were also found and carefully analyzed [11–13]. A new analytical method of chemical compounds was born and fast became recognized as very important for chemistry [14] although at the beginning, it was still limited to the observation of nuclei with high natural abundances such as protons or fluorine-19.

Small organic molecules containing halogen atoms (F, Cl, Br, or I) have been extensively used in nuclear magnetic resonance (NMR) spectroscopy for over 70 years. Nowadays, such liquids are mostly applied as solvents for NMR experiments, e.g., tetrachloromethane (CCl_4), chloroform ($CHCl_3$), or deuterated chloroform ($CDCl_3$), but 1,1,1-trichloro-2,2,2-trifluoroethane ($C_2F_3Cl_3$, also known as freon 113) was among other fluorine compounds selected for the first observation of ^{19}F NMR chemical shifts [7] and corresponding medium effects [15]. From the beginning, ^1H and ^{19}F NMR spectra were immediately adopted for

the identification of organic compounds, but the first measurements of proton and fluorine chemical shifts were often unstable and dependent on the selected solvent. Consequently, halogen-containing solvents were also applied for the studies of medium effects in chemical shifts [16–20]; examples of such early investigations are given in the Pople, Schaefer, and Schneider monography [14], and an early review of liquid and gaseous results was completed by Rummens [21]. ^{13}C spectra were available a bit later because of the low natural abundance of carbon-13 isotope [22], and the appropriate medium effects in ^{13}C NMR were successfully studied when the Fourier-transform (FT) technique [23] was applied to standard NMR spectrometers. The early ^{13}C measurements of shielding and spin-spin coupling in gaseous fluoromethanes were performed in 1977 [24].

Let us note that halogen-containing molecules were also used for the standardization of proton chemical shifts, e.g., $CHCl_3$ in Buckingham et al.'s work [20]. This idea was slightly changed when Thiers suggested using tetramethylsilane (TMS, $(CH_3)_4Si$) for internal referencing of proton chemical shifts [25]. TMS as the reference standard remains obligatory also today with the modification that deuterated chloroform (CD_3Cl) is the solvent for the measurements of ^1H, ^{13}C, and ^{29}Si NMR chemical shifts [26,27]. Generally, all the chemical shifts (δ_i) are determined relative to the shielding of a selected reference standard, and the chemical shift is expressed as follows:

$$\delta_i = (\sigma_{ref} - \sigma_i)/(1 - \sigma_{ref}), \tag{1}$$

where σ_{ref} and σ_i are the shielding constants of the observed nuclei in reference and investigated compounds, respectively. δ_i is usually multiplied by 10^6 and given in parts per million (ppm). Earlier, a slightly different scheme was applied for the referencing of ^1H chemical shifts, known as the *τ-scale* [28]. In the *τ-scale*, the TMS signal was assigned exactly 10.00 ppm, ^1H chemical shifts were defined as $\tau_i = 10.00—\sigma_i$, and the ^1H measurements were performed for diluted solutions in CCl_4. Actually, the *τ-scale* convention is not in use, but this concept should be remembered for all older measurements of chemical shifts that were defined in the opposite direction than δ_i values: in the actual scale, δ_i values increase with the decrease of magnetic shielding, and previously, chemical shifts and shieldings have been defined in the same direction [14].

Equation (1) contains the shielding parameter (σ), which is dependent on the electronic structure of molecules and can be calculated using approximate methods of quantum chemistry [29–31]. It is the second-rank tensor, but due to the free reorientation of molecules in gases and liquids, we observe only the averaged σ value of shielding, often called the shielding constant. In fact, the σ parameter is never constant, as it is dependent on many factors such as variable medium effects or temperature. However, this colloquial name is so frequently used in the scientific literature that we cannot completely ignore it, especially when σ_i is strictly defined for external conditions. Precise calculations of magnetic shielding are usually performed for isolated molecules, and it is expected that NMR experiments can also deliver similar results for comparison. Practically, it is possible only for NMR measurements in the gas phase, and for this purpose, fluoromethanes ($CH_{4-n}F_n$) are really a very good group of chemical compounds that allow performing the precise verification of calculated NMR spectral parameters in isolated molecules.

All fluoromethanes ($CH_{4-n}F_n$) are gaseous compounds at room temperature. They can contain three different magnetic nuclei with a one-half nuclear spin and various natural abundances: ^1H 99.9885%, ^{13}C 1.07%, and ^{19}F 100% [26]. Methane (CH_4) is included here just for the comparison of variable NMR parameters upon the following substitution of fluorine atoms. The three molecules of fluoromethanes are polar, having permanent dipole moments [32]: CH_3F 1.858 ± 0.002 D, CH_2F_2 1.9785 ± 0.01 D, and CHF_3 1.6515 D. It is important because these polar molecules can strongly interact even in the gas phase due to intermolecular hydrogen bonds [33–35]. In NMR spectra of fluoromethanes, there is the possibility of observing the distinct indirect spin-spin couplings across one and two chemical bonds: $^1J(^1H-^{13}C)$, $^1J(^{13}C-^{19}F)$, and $^2J(^1H-^{19}F)$, respectively. The absolute values of spin-spin coupling constants are directly measured from NMR spectra, and they are

generally less dependent on medium effects than shielding, but sometimes, this dependence is well marked, as it was shown for $^1J(^{19}F-^{29}Si)$ in SiF_4 [36] or $^1J(^{19}F-^{33}S)$ in SF_6 [37]. In the present review, all the spin-spin couplings in fluoromethane molecules are discussed in a similar way as shielding parameters.

2. NMR Spectral Parameters of Isolated Molecules

2.1. Chemical Shifts and Magnetic Shielding

NMR spectra are mostly observed for liquids, and chemical shifts are measured relative to the reference signal as defined by Equation (1). It shows that we can easily obtain an unknown shielding constant (σ_i) if the reference value (σ_{ref}) is available. In practice, this procedure is quite complex due to medium effects that can influence both the shielding parameters (σ_i and σ_{ref}) in Equation (1) [15,38–41]. It was clear that smaller medium effects could be still present in nuclear shielding even in the gas phase [17]. Thus, there is a question of how can we obtain the most accurate shielding in isolated molecules. As shown by Raynes, Buckingham, and Bernstein [42], this problem could be solved by extrapolating ^1H shielding of gaseous molecules to the zero density point and explaining it as follows:

$$\sigma^A = \sigma_0^A + \sigma_1^A \rho_A + \sigma_2^A \rho_A^2 + \ldots, \tag{2}$$

where σ^A is the nuclear magnetic shielding of A molecule in the gas phase; σ_0^A represents the same shielding at zero density, which is equivalent to the value of an isolated molecule; and ρ_A is for gas density. σ_1^A and σ_2^A, are the second and third coefficients of the above expansion (2), and they are parameters dependent on A-A bimolecular and A-A-A trimolecular collisions, respectively. Let us note that the linear dependence of shielding on gas density is usually observed in NMR spectra for low-density measurements. Then Equation (2) is simplified to the following:

$$\sigma^A = \sigma_0^A + \sigma_1^A \rho_A \tag{3}$$

and can be extended even on gas solutions if a small amount of compound A is observed in another B gas, which is used as a solvent [43]:

$$\sigma^A = \sigma_0^A + \sigma_1^{AB} \rho_{AB} \tag{4}$$

In the last equation, σ_1^{AB} describes A-B molecular interactions, and ρ_B is the gas solvent density. Due to Equations (1)–(3) we are able to determine the nuclear magnetic shielding in an isolated molecule, σ_0^A, which is also known as the shielding constant. This parameter is still dependent on temperature and is usually determined at the fixed standard temperature, 300 K [44].

2.2. Referencing of Shielding

There is one more problem with NMR measurements in gases: the shielding of the reference compound (TMS or its solution in $CDCl_3$) must be known with satisfactory precision when Equation (1) is applied for the determination of σ^A (gas). Fortunately, the shielding parameters in single TMS molecules (σ_{ref}) are already well known: 30.783(5) ppm for ^1H, 188.04(10) ppm for ^{13}C, and 376.4(20) ppm for ^{29}Si [45]. In this, the σ_{ref} data are also established for liquid TMS and for 1% TMS solution in liquid $CDCl_3$. It may be interesting that the above standard shielding values are already not so crucial in NMR experiments because we can alternatively use a new universal shielding standard suitable for all the magnetic nuclei: an isolated ^3He atom [46], for which its nuclear magnetic shielding was calculated with great precision, i.e., $\sigma_0(^3He)$ = 59.96743 ppm [47]. Combining this result with the new values of nuclear magnetic moments [48,49] and the measurements

of absolute resonance frequencies, the direct measurement of nuclear magnetic shielding in NMR spectra σ_X is possible according to the following relationship [50,51]:

$$\sigma_X = 1 - \frac{\nu_X}{\nu_{He}} \cdot \frac{|\mu_{He}|}{|\mu_X|} \cdot \frac{I_X}{I_{He}}(1 - \sigma_{He}), \tag{5}$$

where ν_X and ν_{He} are the absolute resonance frequencies of X and ^{3}He samples, and μ_X and μ_{He} the nuclear magnetic moments of X and ^{3}He nuclei together with their spin numbers I_X and I_{He}, respectively. Let us add that the shielding parameters can be transferred from the ^{3}He atom on liquid-deuterated solvents [51,52], so there is no need for the use of gaseous helium-3 in every NMR measurement of shielding. It makes this method of shielding measurement easy because deuterated solvents are usually applied for the lock system of standard NMR spectrometers. Knowing the absolute resonance frequencies ν_i measured by the NMR spectrometer, one can determine the absolute shielding of many various nuclei [50–52]. As seen, the reading of nuclear magnetic shielding is easily available, and the precise comparison of experimental and calculated values can be performed at least for small molecules.

2.3. Indirect Spin-Spin Coupling

Between magnetic nuclei in a molecule, spin-spin coupling occurs, which is observed as the splitting of NMR signals. In contrast to shielding, spin-spin couplings do not require any reference standard, and their absolute values $^nJ_{AB}$ are often available directly from NMR spectra. $^nJ_{AB}$ means the spin-spin coupling constant via n chemical bonds [14], but again, the $^nJ_{AB}$ parameter is the averaged value of the second-rank tensor, and it is never constant for the same reason as the shielding parameter σ. Spin-spin couplings are also modified by intermolecular interactions [53] and by temperature though such effects in $^nJ_{AB}$ parameters are less significant than in shielding. Similarly, the measurements of $^nJ_{AB}$ in gases can be performed, and the results can be studied for example by exploring the following equation:

$$^nJ_{AB} = (^nJ_{AB})_0 + (^nJ_{AB})_1 \rho_A \tag{6}$$

and one can determine the indirect spin-spin coupling constant in an isolated molecule, $(^nJ_{AB})_0$ [36,54]. Fluoromethanes contain only the nuclei with the spin $I = \frac{1}{2}$ (^{1}H, ^{13}C, and ^{19}F), and their NMR spectra give fairly sharp lines due to the relatively long lifetimes of appropriate magnetic states. It allows the reading of such spin-spin coupling constants with high precision. In gases at low pressure, the lifetimes are considerably shortened, and the observation of $^nJ_{AB}$ is less precise due to the efficient spin-rotation mechanism of relaxation. However, the measurements of $^nJ_{AB}$ performed according to the idea of Equation (5) deliver usually well-marked linear dependence on density, which gives a more precise reading of $(^nJ_{AB})_0$. This result can be additionally confirmed by observing spectra from two different nuclei, namely A and B. In the next section, we present the comparison of experimental and calculated values for both the NMR spectral parameters, i.e., shielding σ_0 and spin-spin coupling $^nJ_0$ values in isolated molecules.

3. Experimental vs. Calculated NMR Spectral Parameters

Calculations of NMR shielding and spin-spin coupling in a molecule are rather complex, and they always consist of a few steps. The first step belongs to the optimization of molecular geometry at the lowest possible energy level (equilibrium geometry), and the calculation of a spectral parameter (σ_0 or $^nJ_0$) is the next task. The treatment of electron correlation is certainly the most important factor at the latter level. Let us also add that four different mechanisms of spin-spin coupling must be taken into account, and therefore, the calculations of shielding are always a bit easier than the modeling of spin-spin coupling. After completing the calculation of the spectral parameter (σ_0 or $^nJ_0$) at the equilibrium geometry, one must add the corrections for molecular vibrations: they are called ZPV (zero point vibration) corrections at the lowest vibrational level. Further corrections are

required for the rovibrational motion of a molecule with the temperature increase and also for the relativistic effects in molecules containing heavy atoms, i.e., for atoms with Z < 36 [31,55,56]. Altogether, the calculations of NMR spectral parameters are difficult and time-consuming. Varieties of different calculation schemes are applied to solve the above problems, and they are summarized in numerous review publications, e.g., ref. [29–31]. Looking for the most accurate calculations, we should consider first of all the modern ab initio GIAO (Gauge Included Atomic Orbitals) methods proposed by Gauss and Stanton and named the coupled-cluster calculations [57,58], cf. CCSD (Coupled Cluster Singles and Doubles) or CCSD(T) (Coupled Cluster Singles and Doubles with Perturbative Triples Corrections) methods. They can deliver very accurate results of NMR spectral parameters but can be applied to relatively small, isolated molecules. At present, large molecular objects are theoretically studied rather by DFT (Density-Functional Theory) methods, which use approximate potentials. They are really efficient, but their results for small molecules are not as accurate as the others from state-of-the-art GIAO methods [59]. DFT calculations are extremely effective when contracted basis sets are specially designed for the calculations of shielding [60] or spin-spin coupling constants [61] and obviously require less time for computing. Considerably easier are also calculations of NMR spectral parameters for molecules in solids and liquids with the use of the GIPAW (Gauge Including Projector Augmented Waves) method [62]. Calculations of indirect spin-spin coupling constants are much more complex than the modeling of shielding and often require other than CCSDT methods based on MCSCF (Multi-Configurational Self-Consistent Field) or SOPPA (Second-Order Polarization-Propagator Approximation) models [30,63] and other basis sets, as mentioned above [61].

3.1. Chemical Shifts

Modeling of chemical shifts by quantum chemistry methods is very popular and useful in chemistry. It is due to the significance of NMR in the chemical analysis of organic compounds. According to Equation (1), the theoretical value of chemical shift can be precisely obtained when two shielding constants (σ_{ref} and σ_i) are determined with sufficient accuracy. Let us verify this idea with a modest example taken from the literature on calculated ^{19}F chemical shifts of fluoromethanes [64]. Table 1 displays the fluorine chemical shifts that were calculated using the DFT (B3LYP-GIAO) method and verified with ^{19}F NMR measurements performed for pure liquids. Note that the results cited here are not complete and represent only the use of two basis sets from ref. [64]: 6-31G(d,p) and 6-31G++(d,p), but the same problem exists in the majority of other chemical shift calculations.

Table 1. An example of the GIAO-DFT calculated ^{19}F chemical shifts for fluoromethanes; the selected data are cited from Ref. [64].

Molecule	6-31G(d,p)	6-31G++(d,p)	Experiment
CH_3F	−278.22 ppm	−279.16 ppm	276.3 ppm
CHF_3	−93.91 ppm	−87.13 ppm	−84 ppm
CF_4	−80.71 ppm	−70.43 ppm	−69 ppm
$CFCl_3$	*179.41 ppm*	*179.16 ppm*	*188.7 ppm*

The two columns of chemical shifts are obtained with the above-mentioned basis sets, while the last one presents experimental chemical shifts. It is not bad if we check the calculated 31G++(d,p) chemical shifts with the experimental shifts determined for pure liquids [64], but let us verify it with Equation (1) and the σ_{ref} value in there. The numerical values of $CFCl_3$ reference are given in Table S2 of the Supplementary Materials attached to the original work [64] and shown in the last row of our mini-table. The calculated chemical shifts of fluoromethanes seem better than the direct comparison of calculated shielding available for $CFCl_3$. Probably, many inaccuracies of shielding calculations were accidentally canceled in the final results of fluoromethane chemical shifts. However, on the basis of such
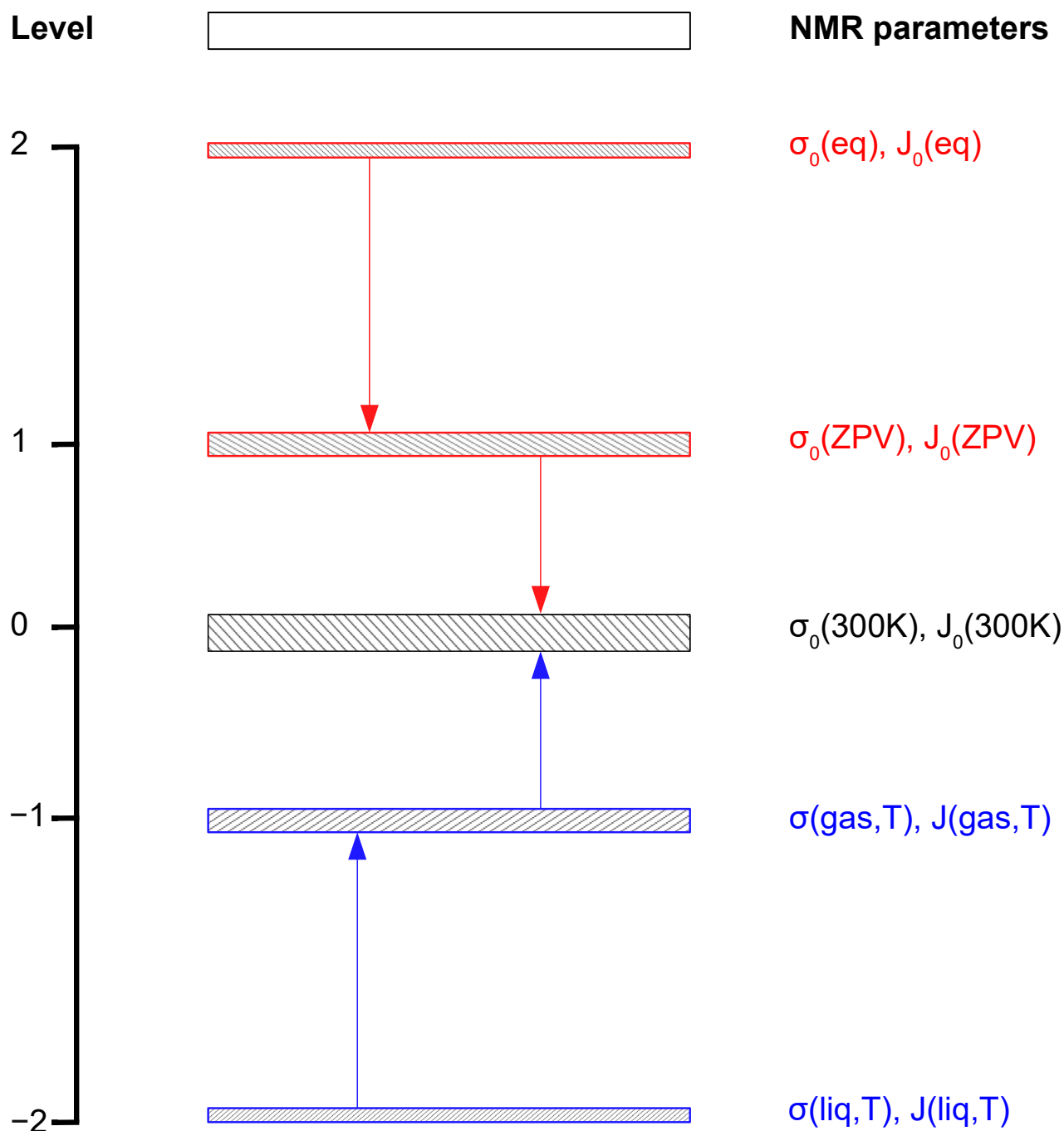
calculated ^{19}F chemical shifts, we can properly assign NMR signals to particular chemical compounds. It looks as though the approximate calculations can be still useful in analytical practice, but their accuracy remains uncertain. It is quite common in the literature that some DFT-estimated chemical shifts have unusually high precision, which cannot be obtained for shielding constants, cf. ^{19}F chemical shifts relative to SiF_4, as presented in ref. [65]: calc. -107.96 ppm vs. exp. -107.71 ppm for CH_3F, 88.40 vs. 89.06 ppm for CHF_3, and 103.87 vs. 104.21 ppm for CF_4. As seen, the accuracy of these calculated chemical shifts must be rather artificial because the experimental σ_{ref} value of SiF_4 is known only with ± 6 ppm accuracy from the ^{19}F measurement of HF and SiF_4 gases at the zero-density limit [66]. The numerical values of $\sigma_{ref}(SiF_4)$ are not given in ref. [65].

As mentioned, the calculated chemical shifts can be useful in chemical analysis, and therefore, their applications are widely discussed in numerous review articles [55,67–72], from the semiempirical IGLO (Individual Gauge for Localized Orbitals) approximation [67] to the modern methods with relativistic corrections to shielding [55,71,72]. The most recent studies in this field have been reviewed by Kupka [73,74]. Below, we come back to the problem of accuracy in the calculated nuclear magnetic shielding and indirect spin-spin coupling parameters. Having reliable shielding constants, we are always able to determine also reliable chemical shifts according to Equation (1).

3.2. Nuclear Magnetic Shielding and Indirect Spin-Spin Coupling

Shielding is the most sensitive parameter of NMR spectra; its measurement is possible [50–52] but only with limited precision. The same is true for indirect spin-spin coupling constants. Their absolute values can be obtained from NMR spectra with likewise limited precision. Moreover, the sign of coupling constant must be determined using, for example, a double NMR resonance experiment [75] or calculated with the advanced quantum-chemical method [76,77]. Figure 1 shows the correct way of comparison between the experimental and calculated NMR parameters for molecules: shielding (σ) and spin-spin coupling (^{n}J). First, let us consider only those nuclei with the one-half spin number (I = $^1/_2$) in liquids: their lifetime on magnetic levels is long, and the observation of the natural line-with of their NMR signals is possible; then, the sharp signals allow for the most precise determination of the signal positions. It is represented by Level 2 in Figure 1, where the precision of measurement can be limited only by Heisenberg's uncertainty principle [78]. At present, the exact comparison of experimental and calculated parameters (σ_{liq} and J_{liq}) on Level 2 is practically impossible because it requires giant quantum mechanical calculations for all possible interactions between molecules in the liquid state. NMR signals in liquids are significantly modified by the medium effects and by temperature. Evaluation of the medium effects in liquids on shielding [21] and spin-spin coupling [53] is possible using the model of reaction field, but it is only the estimation with low accuracy. Level 1 regards the NMR measurements of gaseous compounds, and the precision of reading signals (σ_{gas} and J_{gas}) is lower on Level 1 than on Level 2 because of the fast rotation of molecules in gases. However, it is a step in the right direction; the medium effects in the gas phase are considerably smaller than in liquids, and the measurement of the molecular σ parameter in a molecule is more accurate. The studies of shielding as the function of gas density permit the extrapolation of results to the zero-density point, and this way, we can gain shielding and spin-spin constants for isolated molecules (σ_0 and J_0) at Level 0. It was first done for the shielding of protons [42], next for ^{19}F [43], and a bit later also for ^{13}C [79]. A similar procedure was applied for the observed spin-spin couplings in gases, and the J_0 parameters were determined for many gaseous compounds [36,54]. The precision of σ_0 and J_0 reading seems to be better than for the single measurements of σ_{gas} and J_{gas} values, but one should remember that it is true only when all the experimental procedures are perfectly completed. Moreover, the σ_0 and J_0 parameters are extrapolated but not directly observed. It is better to assume that the precision of their determination is considerably limited, as shown in Figure 1 at Level 0.

Level

NMR parameters

2

σ_0(eq), J_0(eq)

1

σ_0(ZPV), J_0(ZPV)

0

σ_0(300K), J_0(300K)

−1

σ(gas,T), J(gas,T)

−2

σ(liq,T), J(liq,T)

Figure 1. Comparison of experimental and calculated NMR spectral parameters σ and nJ. The thickness of Levels illustrates the increasing uncertainty of determining parameters from −2 to 0 for experiments and from 2 to 0 for calculations.

Levels 1 and 2 in Figure 1 are exclusively reserved for the theoretical results of σ_0 and $(^nJ_{AB})_0$ parameters. Their values can be calculated first for the equilibrium geometry: (eq) on Level 2. Adding the vibrational corrections Level 1 is reached, and the calculated parameters have the σ_0(ZPV) and J_0(ZPV) values equivalent to exactly their state at 0 K temperature. The precision (not the accuracy) of calculations is slightly lower on Level 1 than on Level 2 because the calculations are just more complex. The result of Level 1 still requires improvements because the NMR measurements needed for comparison cannot be performed in very low temperatures. The next correction is needed for temperature effects, which are due to the rovibrational motion of molecules in gases. Finally, Level 0 is also

reached for the calculations where the experimental and theoretical data can be compared at the standard temperature, usually at 300 K. The complete procedure of such a comparison is not easy because both the experimental and calculated results introduce some error bars, as shown in Figure 1.

Below, we present the comparison of experimental and theoretical $\sigma_0(300\ K)$ and $J_0(300\ K)$ values for the choice of $CH_{4-n}F_n$ molecules in Tables 2 and 3. We have tried to select only the best available results in order to verify the quality of the comparison if selected shielding and spin-spin coupling constants come from different laboratories but are limited to the same group of molecules. We hope that the choice of $CH_{4-n}F_n$ compounds is suitable for our task.

Table 2. Selected shielding constants for CH4-nFn isolated molecules available from gas-phase NMR experiments [a] and advanced ab initio calculations of quantum chemistry [b].

Parameter	^1H Shielding (ppm)		^{13}C Shielding (ppm)		^{19}F Shielding (ppm)	
Molecule	$\sigma_0^H(exp)$	σ_0^H (calc)	$\sigma_0^C(exp)$	σ_0^C (calc)	$\sigma_0^F(exp)$	σ_0^F (calc)
CH_4	30.633(6) [c] 30.611(24) [g]	31.41 [d] 31.6 [q] 31.4 [w] 31.93 [z]	195.01 [e] 195.1 [h] 195.15 [i]	195.2 [j] 196.2 [f] 193.6 [d] 197.52 [z]		
CH_3F	26.635(8) [c] 26.62 [l]	26.59 [k] 26.90 [l] 27.52 [d]	116.83 [l] 116.69 [o] 116.8 [h] 116.3 [s]	118.30 [k] 118.8 [f] 122.0 [d] 120.3 [l]	470.98(1) [m] 471.0 [P]	472.9 [n] 475.85 [r] 482.0 [d]
CH_2F_2	25.331(3) [t]	25.24 [k] 26.58 [d]	77.726(4) [t] 77.6 [s]	78.87 [k] 89.6 [d]	338.935(2) [t] 339.1 [u]	340.7 [n] 358.40 [r] 363.7 [d]
CHF_3	24.583(10) [c]	24.55 [k] 25.80 [d]	68.738(8) [v] 68.5 [s]	69.28 [k] 82.6 [d]	273.988(4) [v] 274.1 [P]	275.2 [n] 298.03 [r] 302.0 [d]
CF_4			64.5 [h] 64.5 [s]	63.9 [l] 79.1 [d]	258.80 [o] 259.0 [u]	259.5 [n] 278.0 [d] 281.22 [r]

[a] Extrapolated to the zero-density point and otherwise as marked; [b] GIAO calculations as described; [c] ref. [80]; [d] HF (Hartee–Fock), ref. [81]; [e] ref. [82]; [f] MP2 (Møller–Plesset Perturbation Theory (second order)) including ZPV, ref. [83]; [g] ref. [84]; [h] ref. [85]; [i] ref. [79]; [j] CCSD(T) ref. [58], including −3.695 ppm for the rovibrational correction given in ref. [86]; [k] DFT and CCSD(T) jointly, ref. [87]; [l] ref. [88]; [m] ref. [89]; [n] CCSD(T) including ZPV and temperature corrections, ref. [90]; [o] ref. [91]; [P] ref. [92]; [q] CCSD(T) ref. [58]; [r] HF, including ZPV, Ref. [93]; [s] low-density gas without extrapolation, ref. [24]; [t] ref. [94]; [u] ref. [95]; [v] ref. [96]; [w] MP2, ref. [97]; [z] HF, ref. [98].

Table 3. Selected indirect spin-spin coupling constants for $CH_{4-n}F_n$ isolated molecules available from gas-phase NMR experiments [a] and advanced ab initio calculations of quantum chemistry [b].

Parameter	$^1J(^{13}C-^1H)$ Coupling (Hz)		$^1J(^{13}C-^{19}F)$ Coupling (Hz)		$^2J(^{19}F-^1H)$ Coupling (Hz)	
Molecule	$^1J_0(exp)$	$^1J_0(calc)$	$^1J_0(exp)$	$^1J_0(calc)$	$^2J_0(exp)$	$^2J_0(calc)$
CH_4	125.304 [c] 125.31 [d]	125.65 [e] 124.26 [f] 120.61 [g]				
CH_3F	147.37(5) [h] 149.15 [i]	148.09 [g] 145.62 [f] 141.5 [k]	−163.10(5) [h] −163.00(2) [k] −160.2 [l]	−160.8 [f] −156.6 [k]	46.64(5) [h]	46.81 [f] 46.3 [k]

Table 3. *Cont.*

| Parameter	$^1J(^{13}C-^1H)$ Coupling (Hz)		$^1J(^{13}C-^{19}F)$ Coupling (Hz)		$^2J(^{19}F-^1H)$ Coupling (Hz)	
CH_2F_2	180.42(5) [m]	179.85 [f]	−234.55(5) [m]	−224.52 [f]	50.24(5) [m]	50.25 [f]
	180.38(4) [k]	175.7 [k]	−233.91(11) [k]	−220.7 [k]		
			−232.7[l]			51.9 [k]
CHF_3	235.63(5) [n]	235.63 [f]	−272.29(5) [n]	−238.28 [f]	79.92(5) [n]	79.18 [f]
	235.26(9) [k]	236.8 [k]	−272.18(7) [k]	−242.1 [k]		79.3 [k]
			−272.4 [l]			
CF_4			−258.32(9) [h]	−272.84 [g]		
			−259.4 [l]			

[a] Extrapolated to the zero-density point and otherwise as marked; [b] ab initio calculations or as described; [c] ref. [99]; [d] ref. [100]; [e] CCSD, ref. [100]; [f] DFT and CCSD(T) jointly, ref. [87]; [g] MP2 or experimental geometry and CCSD, ref. [101]; [h] ref. [91]; [i] ref. [102]; [k] MCSCF LR (Multi-Configuration Self-Consistent-Field Linear Response), ref. [103]; [l] low-density gas without extrapolation, ref. [24]; [m] ref. [94]; [n] ref. [96].

4. Experimental and Calculated Spectral Parameters for Isolated $CH_{4-n}F_n$ Molecules

4.1. ^1H, ^{13}C, and ^{19}F Nuclear Magnetic Shielding

Table 2 presents selected experimental σ_0(exp) and calculated σ_0(calc) results for ^1H, ^{13}C, and ^{19}F shielding constants observed for isolated $CH_{4-n}F_n$ molecules. The measured results are from NMR experiments performed in the gas phase and extrapolated to the zero-density limit. The calculated shielding constants are chosen from a great number of calculations, and only the most advanced data are placed in Table 2. As seen, it is not a review of all the available results but only the selection of reliable data according to our best knowledge. Extrapolated shielding constants (σ_0(exp)) are consistent within experimental error bars for the studied nuclei in $CH_{4-n}F_n$ molecules. Note that the measurements come from many various laboratories [24,79,80,82,84,85,88,89,91,92,95–97], and it proves that we have reliable experimental ^1H, ^{13}C, and ^{19}F shielding constants. This result is graphically presented in Figure 2, where the sequential substitution of CH_4 by strongly electronegative (4.0) fluorine atoms leads to the decrease of all the observed nuclei, including ^{19}F as well.

In contrast, the calculated shielding constants (σ_0(calc)) are not as consistent as the experimental parameters. It is due to different methods of calculations applied in the preparation of σ_0(calc) values. We have tried to place the best results in the first lines for each molecule, and it is easy to check that the data come mostly from the advanced quantum-mechanical calculations, usually from CCSD, CCSD(T), or CCSDT methods with large basis sets. The method of each calculation can be verified in the original publications, but it is also well marked in Table 2. For example, we can observe the obvious discrepancy between the theoretical and experimental data for proton shielding in the CH_4 molecule, but it points out the lack of the rovibrational correction in proton shielding. Generally, this discrepancy of 1 ppm only in the proton shielding must be considered rather large; ±1 ppm in ^{13}C or ^{19}F shielding is fairly meaningless. Thus, for the rest of the presented data, the importance is the excellent agreement between the most advanced calculations and NMR measurements of σ_0(300 K) shielding constants. It proves that the applied methods of shielding calculations are fantastic, and they can deliver reliable results.
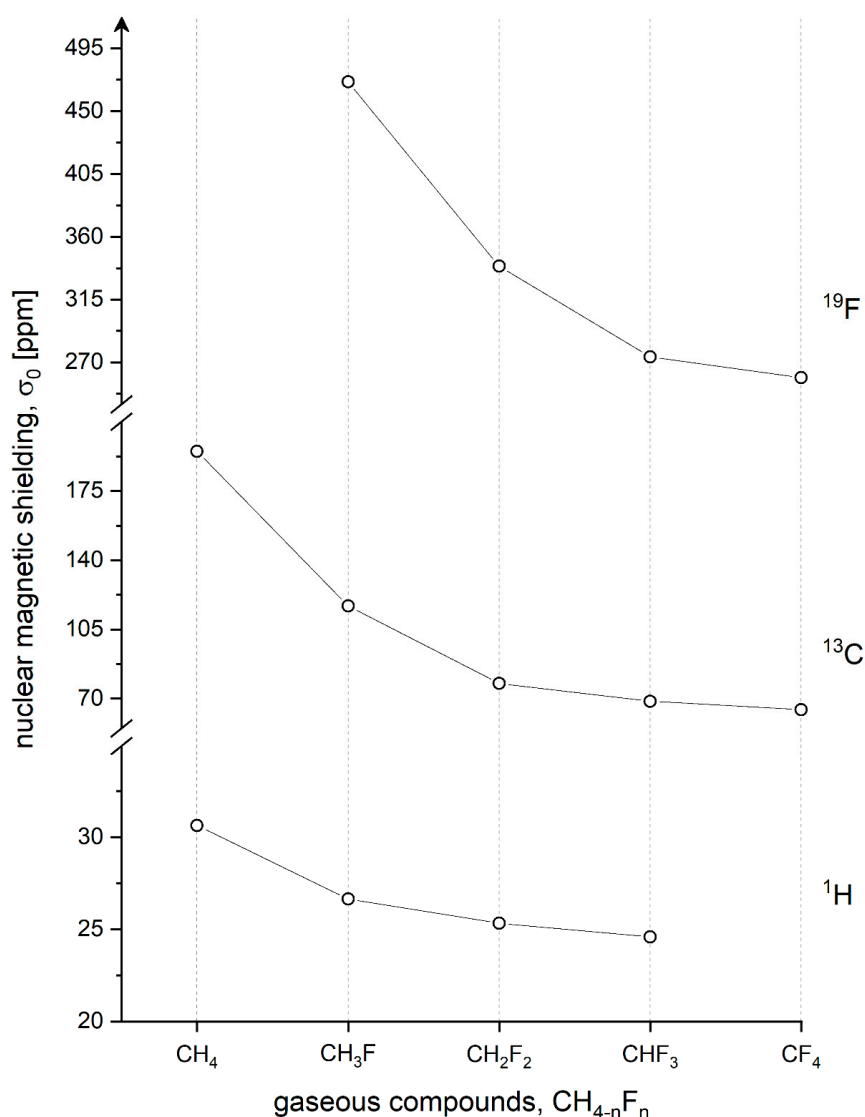
Figure 2. Experimental ^{19}F, ^{13}C, and ^{1}H NMR shielding values in isolated molecules of fluoromethanes. Each substitution of an electronegative fluorine atom leads to significant deshielding effects for all the nuclei in fluoromethane molecules. Note: The scale of shielding is different for ^{19}F, ^{13}C, and ^{1}H nuclei for better visualization.

4.2. $^{1}J_{CH}$, $^{1}J_{CF}$, and $^{2}J_{FH}$ Indirect Spin-Spin Coupling Constants

Table 3 contains the experimental and theoretical spin-spin coupling constants for $CH_{4-n}F_n$ molecules. We can observe similar consistency of experimental data from various laboratories if the results were determined for isolated molecules and, generally, also good modeling of spin-spin coupling constants. It is incredible because the calculations of spin-spin couplings are much more complex than shielding modeling. Therefore, some calculation methods are mixed, and such a mixture delivers extraordinarily good results, cf., for example, ref. [87]. The authors optimized molecular geometry for investigated molecules with the use of the DFT method and completed the rest of the calculations applying CCSD, CCSD(T), and CCSDT advanced modeling. The latter results of shielding and spin-spin couplings (shown in Tables 2 and 3) are really very good and only a bit worse than the complete state-of-the-art calculations [99,100]. Coming back to Table 3, we note that the comparison of calculated and measured spin-spin coupling constants is good in the case of $^{1}J_{CH}$ but a little worse for $^{1}J_{CF}$. One can presume that it is the influence of electronegative fluorine atom, but the consistency between experimental and calculated $^{2}J_{FH}$ is again almost ideal in every case. It may also be an effect of the fluorine atom, which lasts

only across one chemical bond. The experimental results of Table 3 are presented graphically in Figure 3. As shown, the spin-spin coupling constants of $^1J_{CH}$ and $^2J_{HF}$ in isolated molecules are increased with the substitution of fluorine atoms. However, negative values of $^1J_{CF}$ do not further maintain this dependence by increasing for CF_4. It is a really interesting case of spin-spin coupling that was first observed in the gas phase already 45 years ago [24]. Actually, it is well confirmed by numerous advanced calculations, as seen in Table 3.
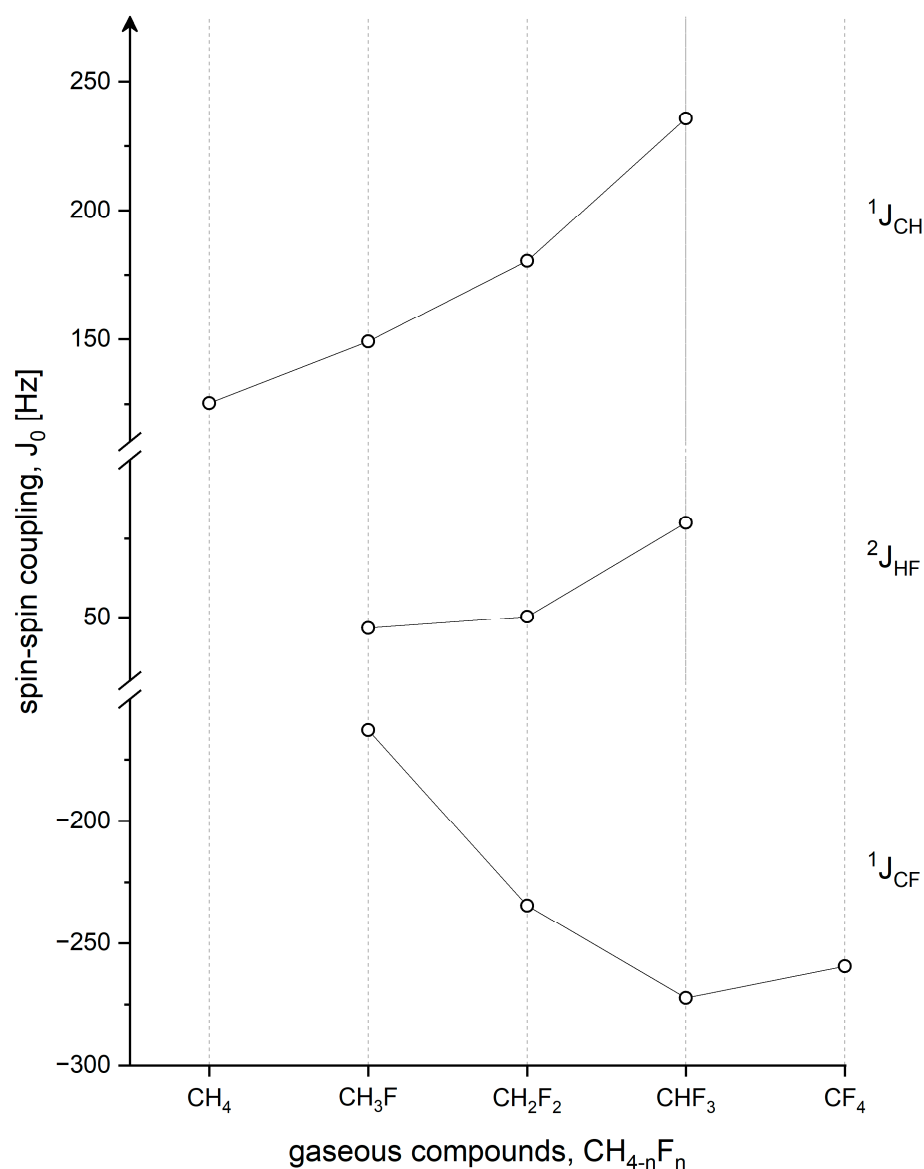
Figure 3. Spin-spin couplings of fluoromethanes without the influence of intermolecular interactions as seen in ^{19}F, ^{13}C, and ^1H NMR measurements. The opposite signs of $^1J_{CH}$ and $^1J_{CF}$ coupling constants were first found in double-resonance experiments [104].

5. Conclusions

It is remarkable how the new magnetic properties of atomic nuclei that were discovered from physical experiments, considered exotic at the time [1,2], quickly became a fundament for the new spectroscopy method [3,4]. Currently, this NMR spectroscopy is one of the most important techniques used in numerous fields in physics, chemistry, biology, and medicine (MRI, magnetic resonance imaging). The whole development of NMR can occur during

one person's lifetime, especially if we consider the period since the first NMR spectra were obtained [6,7].

Due to the modern development of computing systems, we can model the σ_0 and J_0 spectral parameters. As shown in this review, the present results for $CH_{4-n}F_n$ molecules from various laboratories are quite consistent and can be used for the verification of calculated shielding and spin-spin coupling constants. The quality of the theoretical NMR parameters depends on the applied method of calculations, and in the near future, we can certainly expect further progress in this field. This progress should lead to the exact modeling of molecular interactions in condensed phases, i.e., liquids and solids. For this purpose, one must investigate molecular interactions between two molecules spatially oriented to average the results gained from their different orientations. The first steps of such studies were completed already in 1978 [105,106]. Nowadays, the accurate treatment of this subject is possible but still time-consuming, as shown for the shielding in the N_2 pair of molecules [107].

The results presented in Tables 2 and 3 confirm the capability of the precise modeling of shielding and spin-spin coupling constants by ab initio methods. The calculated results are good in every case but are not perfect. Some effects in these calculations were fully neglected, e.g., relativistic corrections. They are probably quite small even for shielding in fluorine atoms (in a range of 1 ppm), but they exist. On the other hand, the calculated results of ^{19}F shielding are more accurate than the experimental data, which give the absolute shielding with the error bar ± 6 ppm [66]. This is due to the difficulty of experimental work with extremely aggressive hydrogen fluoride (HF) gas. Most accurate NMR measurements are carried out in glass, but it is not possible for hydrogen fluoride. It is worth underlining that such good calculations of ^{19}F shielding in $CH_{4-n}F_n$ molecules shown in Table 2 permit us to limit the error bar in the absolute scale of ^{19}F shielding to the range of ± 2 ppm, which is consistent with earlier estimation obtained by DFT calculations [65]. Altogether, the choice of $CH_{4-n}F_n$ molecules for the verification of the present capability of theoretical prediction of multinuclear shielding and spin-spin coupling seems to be good because it gives us insight into the accuracy of state-of-the-art calculations of spectral NMR parameters for isolated molecules.

References

1. Rabi, I.I. Space Quantization in a Gyrating Magnetic Field. *Phys. Rev.* **1937**, *51*, 652–654. [CrossRef]
2. Rabi, I.I.; Millman, S.; Kusch, P.; Zacharias, J.R. A New Method of Measuring Nuclear Magnetic Moment. *Phys. Rev.* **1938**, *53*, 318. [CrossRef]
3. Purcell, E.M.; Torrey, H.C.; Pound, R.V. Resonance Absorption by Nuclear Magnetic Moments in a Solid. *Phys. Rev.* **1946**, *69*, 37–38. [CrossRef]
4. Bloch, F.; Hansen, W.W.; Packard, M.E. Nuclear Induction. *Phys. Rev.* **1946**, *69*, 127. [CrossRef]
5. Ramsey, N.F. The Internal Diamagnetic Field Correction in Measurements of the Proton Magnetic Moment. *Phys. Rev.* **1950**, *77*, 567. [CrossRef]
6. Proctor, W.G.; Yu, F.C. The Dependence of a Nuclear Magnetic Resonance Frequency upon Chemical Compound. *Phys. Rev.* **1950**, *77*, 717. [CrossRef]
7. Dickinson, W.C. Dependence of the F19 Nuclear Resonance Position on Chemical Compound. *Phys. Rev.* **1950**, *77*, 736–737. [CrossRef]
8. Ramsey, N.F. Magnetic Shielding of Nuclei in Molecules. *Phys. Rev.* **1950**, *78*, 699–703. [CrossRef]

9.   Ramsey, N.F. Dependence of Magnetic Shielding of Nuclei upon Molecular Orientation. *Phys. Rev.* **1951**, *83*, 540–541. [CrossRef]
10.   Ramsey, N.F. Chemical Effects in Nuclear Magnetic Resonance and in Diamagnetic Susceptibility. *Phys. Rev.* **1952**, *86*, 243–246. [CrossRef]
11.   Proctor, W.G.; Yu, F.C. On the Nuclear Magnetic Moments of Several Stable Isotopes. *Phys. Rev.* **1951**, *81*, 20–30. [CrossRef]
12.   Gutowski, H.S.; McCall, D.W. Nuclear Magnetic Resonance Fine Structure in Liquids. *Phys. Rev.* **1951**, *82*, 748–749. [CrossRef]
13.   Hahn, E.L.; Maxwell, D.E. Chemical Shift and Field Independent Frequency Modulation of the Spin Echo Envelope. *Phys. Rev.* **1951**, *84*, 1246–1247. [CrossRef]
14.   Pople, J.A.; Schneider, W.G.; Bernstein, H.J. *High-Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, NY, USA, 1959.
15.   Dickinson, W.C. The Time Average Magnetic Field at the Nucleus in Nuclear Magnetic Resonance Experiments. *Phys. Rev.* **1951**, *81*, 717–731. [CrossRef]
16.   Bothner-By, A.A.; Glick, R.E. Specific Medium Effects in Nuclear Magnetic Resonance Spectra of Liquids. *J. Am. Chem. Soc.* **1956**, *78*, 1071–1072. [CrossRef]
17.   Buckingham, A.D.; Schaefer, T.; Schneider, W.G. Solvent Effects in Nuclear Magnetic Resonance Spectra. *J. Chem. Phys.* **1960**, *32*, 1227–1233. [CrossRef]
18.   Bothner-By, A.A. Medium Effects in the NMR Spectra of Liquids. *J. Mol. Spectrosc.* **1960**, *5*, 52–61. [CrossRef]
19.   Abraham, R.J. A Proton Magnetic Resonance Investigation of Some Weak Interactions in Solutions. *Mol. Phys.* **1961**, *4*, 369–383. [CrossRef]
20.   Buckingham, A.D.; Schaefer, T.; Schneider, W.G. Solvent Effects in Nuclear Magnetic Resonance. *J. Chem. Phys.* **1961**, *34*, 1064–1065. [CrossRef]
21.   Rummens, F.H.A. Van der Waals Forces in NMR Intermolecular Shielding Effects. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer: New York, NY, USA, 1975; Volume 10.
22.   Lauterbur, P.C. C^{13} Nuclear Magnetic Resonance Spectra. *J. Chem. Phys.* **1957**, *26*, 217–218. [CrossRef]
23.   Ernst, R.R.; Anderson, W.A. Application of Fourier Transform Spectroscopy to Magnetic Resonance. *Rev. Sci. Instrum.* **1966**, *37*, 93–102. [CrossRef]
24.   Jackowski, K.; Raynes, W.T. Carbon-13 Magnetic Shielding in the Methyl Halides. *J. Chem. Res. (S)* **1977**, 66–67.
25.   Tiers, G.D.V. Proton Nuclear Resonance Spectroscopy: I. *Reliable Shielding Values by Internal Referencing with Tetramethylsilane, J. Phys. Chem.* **1958**, *62*, 1151–1152.
26.   Harris, R.K.; Becker, E.D.; Cabral de Menezes, S.M.; Goodfellow, R.; Granger, P. NMR Nomenclature. Nuclear Spin Properties and Conventions for Chemical Shifts (IUPAC Recommendations 2001). *Pure Appl. Chem.* **2001**, *73*, 1795–1818, Erratum in *Magn. Reson. Chem.* **2002**, *40*, 489–405.. [CrossRef]
27.   Harris, R.K.; Becker, E.D.; Cabral de Menezes, S.M.; Granger, P.; Hoffman, R.E.; Zilm, K.W. Further Conventions for NMR Shielding and Chemical Shifts (IUPAC Recommendations). *Pure Appl. Chem.* **2008**, *80*, 59–84, Erratum in *Magn. Reson. Chem.* **2008**, *46*, 582–598.. [CrossRef]
28.   Emsley, J.W.; Feeney, J.; Sutcliffe, L.H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Appendix B; Pergamon Press: Oxford, UK, 1966; Volume 2, pp. 1115–1129.
29.   Antušek, A.; Jaszuński, M. Accurate Non-Relativistic Calculations of NMR Shielding Constants. In *New Developments in NMR*; Chapter 6 in Gas Phase, N.M.R., Price, W.S., Jackowski, K., Jaszuński, M., Eds.; Royal Society of Chemistry: Cambridge, UK, 2016; pp. 186–217.
30.   Faber, R.; Kaminsky, J.; Sauer, S.P.A. Rovibrational and Temperature Effects in Theoretical Studies of NMR Parameters. In *New Developments in NMR*; Chapter 7 in Gas Phase, N.M.R., Price, W.S., Jackowski, K., Jaszuński, M., Eds.; Royal Society of Chemistry: Cambridge, UK, 2016; pp. 218–266.
31.   Repisky, M.; Komorovsky, S.; Bast, R.; Ruud, K. Relativistic Calculations of Nuclear Magnetic Resonance Parameters. In *New Developments in NMR*; Chapter 8 in Gas Phase, N.M.R., Price, W.S., Jackowski, K., Jaszuński, M., Eds.; Royal Society of Chemistry: Cambridge, UK, 2016; pp. 267–303.
32.   Haynes, W.M.; Lide, D.R.; Bruno, T.J. (Eds.) *CRC Handbook of Chemistry and Physics*; Edition 2012–2013; Taylor and Francis Group: Boca Raton, NJ, USA, 2012; Volume 93, pp. 9–59.
33.   Yonker, C.R.; Palmer, B.J. Investigation of CO_2/Fluorine Interactions through the Intermolecular Effects on the ^1H and ^{19}F Shielding of CH_3F and CHF_3 at Various Temperatures and Pressures. *J. Phys. Chem. A* **2001**, *105*, 308–314. [CrossRef]
34.   Blanco, S.; López, J.C.; Lesarri, A.; Alonso, J.L. A Molecular-Beam Fourier Transform Microwave Study of Difluoromethane Dimer. *J. Mol. Struct.* **2002**, *612*, 255–260. [CrossRef]
35.   Tsuzaki, S.; Uchimaru, T.; Mikami, M.; Urata, S. Ab Initio Calculations of Intermolecular Interaction of CHF_3 Dimer: Origin of Attraction and Magnitude of CH/F Interaction. *J. Phys. Chem. A* **2003**, *107*, 7962–7968. [CrossRef]
36.   Jameson, A.K.; Reger, J.P. A Gas-Phase Density-Dependent Directly Bonded Coupling Constant. *J. Phys. Chem.* **1971**, *78*, 437–439. [CrossRef]
37.   Jackowski, K.; Wilczek, M.; Makulski, W.; Koźmiński, W. Effects of intermolecular interactions on ^{33}S magnetic shielding in gaseous SF_6. *J. Phys. Chem. A* **2002**, *106*, 2829–2832. [CrossRef]
38.   Marshall, T.W.; Pople, J.A. Nuclear Magnetic Shielding of a Hydrogen Atom in an Electric Field. *Mol. Phys.* **1958**, *1*, 199–202. [CrossRef]
39.   Stephen, M.J. The Effect of Molecular Interaction on Magnetic Shielding Constants. *Mol. Phys.* **1958**, *1*, 223–232. [CrossRef]

40. Buckingham, A.D. Chemical Shifts in the Nuclear Magnetic Resonance Spectra of Molecules Containing Polar Groups. *Can. J. Chem.* **1960**, *38*, 300–307. [CrossRef]

41. Bothner-By, A.A. Medium Effects in the Nuclear Magnetic Resonance of Liquids. 4. Nature of the Effects. *J. Mol. Spectrosc.* **1960**, *5*, 52–61. [CrossRef]

42. Raynes, W.T.; Buckingham, A.D.; Bernstein, H.J. Medium Effects in Proton Magnetic Resonance. I. Gases. *J. Chem. Phys.* **1962**, *36*, 3481–3488. [CrossRef]

43. Petrakis, L.; Bernstein, H.J. Medium Effects in NMR. III. Fluorine Resonance in Gases. *J. Chem. Phys.* **1963**, *38*, 1562–1568. [CrossRef]

44. Jameson, C.J. Fundamental Intramolecular and Intermolecular Information from NMR in the Gas Phase. In *Gas Phase NMR—New Developments in NMR*; Price, W.S., Jackowski, K., Jaszuński, M., Eds.; Royal Society of Chemistry: Cambridge, UK, 2016; pp. 1–51, Chapter 1.

45. Makulski, W.; Jackowski, K. ^{1}H, ^{13}C and ^{29}Si Magnetic Shielding in Gaseous and Liquid Tetramethylsilane. *J. Magn. Reson.* **2020**, *313*, 106716. [CrossRef]

46. Jackowski, K.; Jaszuński, M.; Kamieński, B.; Wilczek, M. NMR Frequency and Magnetic Dipole Moment of ^{3}He Nucleus. *J. Magn. Reson.* **2008**, *193*, 147–149. [CrossRef]

47. Rudziński, A.; Puchalski, M.; Pachucki, K. Relativistic, QED, and Nuclear Mass Effects in the Magnetic Shielding of ^{3}He. *J. Chem. Phys.* **2009**, *130*, 244102. [CrossRef]

48. Antušek, A.; Jackowski, K.; Jaszuński, M.; Makulski, W.; Wilczek, M. Nuclear Magnetic Dipole Moments from NMR Spectra. *Chem. Phys. Lett.* **2005**, *411*, 111–116. [CrossRef]

49. Jackowski, K.; Jaszuński, M. Nuclear Magnetic Moments from NMR Spectra—Experimental Gas Phase Studies and Nuclear Shielding Calculations. *Concepts Magn. Reson. A* **2007**, *30*, 246–260. [CrossRef]

50. Jackowski, K.; Jaszuński, M.; Wilczek, M. Alternative Approach to the Standardization of NMR Spectra. Direct Measurements of Nuclear Magnetic Shielding in Molecules. *J. Phys. Chem. A* **2010**, *114*, 2471–2475. [CrossRef]

51. Jaszuński, M.; Antušek, A.; Garbacz, P.; Jackowski, K.; Makulski, W. The Determination of Accurate Nuclear Magnetic Dipole Moments and Direct Measurements of NMR Shielding Constants. *Prog. Nucl. Magn. Reson. Spectrosc.* **2012**, *67*, 49–63. [CrossRef]

52. Garbacz, P.; Jackowski, K. Referencing of ^{1}H and ^{13}C NMR Shielding Measurements. *Chem. Phys. Lett.* **2019**, *728*, 148–152. [CrossRef]

53. Barfield, M.; Johnson, M.D., Jr. Solvent Dependence of Nuclear Spin-Spin Coupling Constants. *Chem. Rev.* **1973**, *12*, 53–73. [CrossRef]

54. Jackowski, K. Gas–Phase Studies of Spin-Spin Coupling Constants. *Int. J. Mol. Sci.* **2003**, *4*, 135–142. [CrossRef]

55. Aucar, G.A.; Aucar, A.I. Recent Developments in Absolute Shielding Scales for NMR Spectroscopy. *Annu. Rep. NMR Spectrosc.* **2019**, *96*, 77–141. [CrossRef]

56. Melo, J.I.; Ruiz de Azua, M.C.; Giribet, C.G.; Aucar, G.A.; Romero, R.H. Relativistic Effects on the Nuclear Magnetic Shielding Tensor. *J. Chem. Phys.* **2003**, *118*, 471–486. [CrossRef]

57. Gauss, J.; Stanton, J.F. Coupled-Cluster Calculations of Nuclear Magnetic Resonance Chemical Shifts. *J. Chem. Phys.* **1995**, *103*, 3561–3577. [CrossRef]

58. Gauss, J.; Stanton, J.F. Perturbative Treatment of Triple Excitations in Coupled-Cluster Calculations of Nuclear Magnetic Shielding Constants. *J. Chem. Phys.* **1996**, *104*, 2574–2583. [CrossRef]

59. Krivdin, L.B. Computational Protocols for Calculating ^{13}C NMR Chemical Shifts. *Prog. Nucl. Magn. Reson. Spectrosc.* **2019**, *112–113*, 103–156. [CrossRef] [PubMed]

60. Jensen, F. Segmented Contracted Basis Sets Optimized for Nuclear Magnetic Shielding. *J. Chem. Theory Comput.* **2015**, *11*, 132–138. [CrossRef] [PubMed]

61. Jensen, F. The Optimum Contraction of Basis Sets for Calculating Spin-Spin Coupling Constants. *Theor. Chem. Acc.* **2010**, *126*, 371–382. [CrossRef]

62. Picard, C.J.; Mauri, F. All-Electron Magnetic Response with Pseudopotentials: MNR Chemical Shifts. *Phys. Rev. B* **2001**, *63*, 245101. [CrossRef]

63. Helgaker, T.; Jaszuński, M.; Pecul, M. The Quantum-Chemical Calculation of NMR Indirect Spin-Spin Coupling Constants. *Prog. Nucl. Magn. Reson. Spectrosc.* **2008**, *53*, 249–268. [CrossRef]

64. Fukuya, H.; Ono, T. DFT-GIAO Calculations of ^{19}F NMR Chemical Shifts for Perfluoro Compounds. *J. Compt. Chem.* **2003**, *25*, 51–60. [CrossRef]

65. Shaghaghi, H.; Ebrahimi, H.; Tafazzoli, M.; Jalali-Heravi, M. A survey of wave function effects on theoretical calculation of gas phase ^{19}F NMR chemical shifts using factorial design. *J. Fluor. Chem.* **2010**, *131*, 47–52. [CrossRef]

66. Hindermann, D.K.; Cornwell, C.D. Vibrational Corrections to the Nuclear-Magnetic Shielding and Spin–Rotation Constants for Hydrogen Fluoride. Shielding Scale for ^{19}F. *J. Chem. Phys.* **1968**, *48*, 4154–4161. [CrossRef]

67. Kutzelnigg, W.; Fleischer, U.; Schindler, M. The IGLO-Method. Ab-Initio Calculation and Interpretation of NMR Chemical Shifts and Magnetic Susceptibilities. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer: New York, NY, USA, 1991; Volume 23, pp. 165–262.

68. Jameson, C.J. Chemical Shift Scales on an Absolute Basis. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D.M., Harris, R.K., Eds.; John Wiley: London, UK, 1996; pp. 1273–1281.

69. Gryff-Keller, A. Theoretical Modeling of ¹³C NMR Chemical Shifts—How to Use the Calculation Results. *Concepts Magn. Reson. A* **2011**, *38*, 289–307. [CrossRef]

70. Fedorov, S.V.; Rusakov, J.J.; Krivdin, L.B. Quantum-Chemical Calculations of NMR Chemical Shifts of Organic Molecules: XII. Calculation of the ¹³C NMR Chemical Shifts of Fluoromethanes at the DFT Level. *Russ. J. Org. Chem.* **2014**, *50*, 160–164. [CrossRef]

71. Samultsev, D.O.; Rusakov, Y.Y.; Krivdin, L.B. Normal Halogen Dependence of ¹³C NMR Chemical Shifts of Halomethanes Revisited at the Four-Component Relativistic Level. *Magn. Reson. Chem.* **2016**, *54*, 787–792. [CrossRef] [PubMed]

72. Krivdin, L.B. Computational Aspects of ¹⁹F NMR. *Russ. Chem. Rev.* **2020**, *89*, 1040–1073. [CrossRef]

73. Kupka, T. Theory and Computation of Nuclear Shielding. *Nucl. Magn. Reson.* **2021**, *46*, 1–33. [CrossRef]

74. Kupka, T. Theory and Computation of Nuclear Shielding. *Nucl. Magn. Reson.* **2022**, *48*, 1–15. [CrossRef]

75. Muller, N.; Carr, D.T. Carbon-13 Splittings in Fluorine Nuclear Magnetic Resonance Spectra. *J. Phys. Chem.* **1963**, *67*, 112–115. [CrossRef]

76. Kaupp, M.; Bühl, M.; Malkin, V.G. *Calculation of NMR and EPR Parameters—Theory and Applications*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2004.

77. Krivdin, L.B. Theoretical Calculations of Carbon-Hydrogen Spin-Spin Coupling Constants. *Prog. Nucl. Magn. Reson. Spectrosc.* **2018**, *108*, 17–73. [CrossRef]

78. Heisenberg, W. Über den anschaulichen Inhalt der quantentheoretischen Kinematik und Mechanik. *Z. Phys.* **1927**, *43*, 172–198. (In German)

79. Jackowski, K.; Raynes, W.T. Density-Dependent Magnetic Shielding in Gas Phase ¹³C N.M.R. *Mol. Phys.* **1977**, *34*, 465–475. [CrossRef]

80. Garbacz, P.; Jackowski, K.; Makulski, W.; Wasylishen, R.E. Nuclear Magnetic Shielding for Hydrogen in Selected Isolated Molecules. *J. Phys. Chem. A* **2012**, *118*, 11896–11904. [CrossRef]

81. Åstrand, P.O.; Mikkelsen, K.V.; Ruud, K.; Helgaker, T. Magnetizabilities and Nuclear Shielding Constants of the Fluoromethanes in the Gas Phase and Solution. *J. Phys. Chem.* **1996**, *100*, 19771–19782. [CrossRef]

82. Makulski, W.; Szyprowska, A.; Jackowski, K. Precise Determination of the ¹³C Nuclear Magnetic Moment from ¹³C, ³He and ¹H NMR Measurements in the Gas Phase. *Chem. Phys. Lett.* **2011**, *511*, 224–228. [CrossRef]

83. Auer, A.A.; Gauss, J. Quantitative Prediction of Gas-Phase ¹³C Nuclear Magnetic Shielding Constants. *J. Chem. Phys.* **2003**, *118*, 10407–10417. [CrossRef]

84. Raynes, W. Theoretical and Physical Aspects of Nuclear Shielding. *Spec. Period. Rep. Nucl. Magn. Reson.* **1977**, *7*, 1–25.

85. Jameson, A.K.; Jameson, C.J. Gas-Phase ¹³C Chemical Shifts in the Zero-Pressure Limit: Refinements to the Absolute Shielding Scale for ¹³C. *Chem. Phys. Lett.* **1987**, *134*, 461–466. [CrossRef]

86. Raynes, W.T.; Fowler, P.W.; Lazzeretti, P.; Zanasi, R.; Grayson, M. The Effects of Rotation and Vibration on the Carbon-13 Shielding, Magnetizabilities and Geometrical Parameters of some Methane Isotopomers. *Mol. Phys.* **1988**, *64*, 143–162. [CrossRef]

87. Dračínský, M.; Kaminský, J.; Bouř, P. Relative Importance of First and Second Derivatives of Nuclear Magnetic Resonance Chemical Shifts and Spin-Spin Coupling Constants for Vibrational Averaging. *J. Chem. Phys.* **2009**, *130*, 094106. [CrossRef] [PubMed]

88. Kantola, A.M.; Lantto, P.; Vaara, J.; Jokisaari, J. Carbon and Proton Shielding Tensors in Methyl Halides. *Phys. Chem. Chem. Phys.* **2010**, *12*, 2679–2692. [CrossRef]

89. Jackowski, K.; Kubiszewski, M.; Makulski, W. ¹³C and ¹⁹F Nuclear Magnetic Shielding and Spin-Spin Coupling in Gaseous Fluoromethane-d₃. *J. Mol. Struct.* **2002**, *614*, 267–272. [CrossRef]

90. Harding, M.E.; Lenhart, M.; Auer, A.A.; Gauss, J. Quantitative Prediction of Gas-Phase ¹⁹F Nuclear Magnetic Shielding Constants. *J. Chem. Phys.* **2008**, *128*, 244111. [CrossRef]

91. Kubiszewski, M. Wpływ Oddziaływań Międzymolekularnych w Fazie Gazowej na Stałe Sprzężenia Spinowo-spinowego i Przesunięcia Chemiczne Fluorowych Pochodnych Metanu. Ph.D.Thesis, University of Warsaw, Warszawa, Poland, 2005. (In Polish).

92. Jameson, C.J.; Jameson, A.K.; Burrell, P.M. ¹⁹F Nuclear Magnetic Shielding Scales from Gas Phase Studies. *J. Chem. Phys.* **1980**, *73*, 6013–6020. [CrossRef]

93. Åstrand, P.O.; Ruud, K. Zero-Point Vibrational Contribution to Fluorine Shieldings in Organic Molecules. *Phys. Chem. Chem. Phys.* **2003**, *5*, 5015–5020. [CrossRef]

94. Kubiszewski, M.; Makulski, W.; Jackowski, K. Intermolecular Effects on Spin-Spin Coupling and Magnetic Shielding Constants in Gaseous Difluoromethane. *J. Mol. Struct.* **2004**, *704*, 211–214. [CrossRef]

95. Jameson, C.J.; Jameson, A.K.; Honarbakhsh, J. ¹⁹F Nuclear Magnetic Shielding Scale from Gas Phase Studies. II. *J. Chem. Phys.* **1984**, *81*, 5266–5267. [CrossRef]

96. Kubiszewski, M.; Makulski, W.; Jackowski, K. ¹H, ¹³C and ¹⁹F Nuclear Magnetic Shielding and Spin-Spin Coupling in Gaseous Trifluoromethane. *J. Mol. Struct.* **2005**, *737*, 7–10. [CrossRef]

97. Zuschneid, T.; Fischer, H.; Handel, T.; Albert, K.; Häfelinger, G. Experimental Gas Phase ¹H NMR Spectra and Basis Set Dependence of ab initio GIAO MO Calculations of ¹H and ¹³C NMR Absolute Shieldings and Chemical Shifts of Small Hydrocarbons. *Z. Naturforsch.* **2004**, *59b*, 1153–1176. [CrossRef]

98. Alkorta, I.; Elguero, J. Ab Initio Calculations of Absolute Nuclear Shieldings for Representative Compounds Containing ¹(²)H, ⁶(⁷)Li, ¹¹B, ¹³C, ¹⁴(¹⁵)N, ¹⁷O, ¹⁹F, ²⁹Si, ³¹P, ³³S, and ³⁵Cl Nuclei. *Struct. Chem.* **1998**, *9*, 187–202. [CrossRef]

99. Bennett, B.; Raynes, W.T.; Anderson, C.W. Temperature Dependences of J(C,H) and J(C,D) in $^{13}CH_4$ and Some of its Deuterated Isotopomers. *Spectrochim. Acta* **1989**, *45A*, 821–827. [CrossRef]

100. Antušek, A.; Kędziera, D.; Jackowski, K.; Jaszuński, M.; Makulski, M. Indirect Spin-Spin Coupling Constants in CH_4, SiH_4 and GeH_4—Gas-phase NMR Experiment and ab initio Calculations. *Chem. Phys.* **2008**, *352*, 320–326. [CrossRef]

101. Kjær, H.; Sauer, S.P.A.; Kongsted, J. Benchmarking NMR Indirect Nuclear Spin-Spin Coupling Constants: SOPPA, SOPPA(CC2), and SOPPA(CCSD) versus CCSD. *J. Chem. Phys.* **2010**, *133*, 144106. [CrossRef]

102. Jokisaari, J.; Hiltunen, Y.; Lounila, J. Methyl Fluoride-^{13}C in Nematic Liquid Crystals: Anisotropy of the Indirect ^{13}C-^{19}F Spin-Spin Coupling and of the ^{1}H, ^{13}C, and ^{19}F Chemical Shieldings. *J. Chem. Phys.* **1986**, *85*, 3198–3202. [CrossRef]

103. Lantto, P.; Kaski, J.; Vaara, J.; Jokisaari, J. Spin-Spin Coupling Tensors in Fluoromethanes. *Chem. Eur. J.* **2000**, *6*, 1395–1406. [CrossRef]

104. Tiers, G.V.D.; Fluorine, N.M.R. Spectroscopy. XII. Proof of Opposite Signs for the "Direct" Carbon-13 Coupling Constants to Hydrogen and to Fluorine. *J. Am. Chem. Soc.* **1962**, *84*, 3972–3973. [CrossRef]

105. Jackowski, K.; Raynes, W.T.; Sadlej, A.J. Intermolecular Effects on the ^{1}H and ^{13}C Magnetic Shielding of Methane. *Chem. Phys. Lett.* **1978**, *54*, 128–131. [CrossRef]

106. Riley, J.P.; Hillier, I.H.; Raynes, W.T. An Ab Initio Coupled Hartree-Fock Calculation of the Nuclear Shielding in the H_2/He Interacting System. *Mol. Phys.* **1978**, *38*, 353–365. [CrossRef]

107. Hapka, M.; Jaszuński, M. The Effect of Weak Intermolecular Interactions on the Nuclear Magnetic Resonance Shielding Constant in N_2. *Magn. Reson. Chem.* **2020**, *58*, 245–248. [CrossRef] [PubMed]