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Theoretical and Physical Aspects of Nuclear Shielding

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1 Introduction

This chapter primarily reviews calculations of nuclear shielding and such experimental data as components of shielding tensors, vibrational-rotational, and intermolecular effects, which are of interest to theoreticians. Papers published in the period June 1980 to May 1981 are included. Although paramagnetic systems are not normally covered in this chapter, theoretical aspects of chemical shifts in paramagnetic systems are considered relevant and have been included this year. Isotope effects on nuclear shielding have been widely applied; theoretical aspects and such data as may be considered fundamental to its understanding are covered here. The first Section deals entirely with calculations. However, all calculations which pertain to rovibrational, isotope, and intermolecular effects are deferred until the second Section.

2 Theoretical Aspects of Nuclear Shielding

A. General Theory.—The diamagnetic shielding, $\sigma^d(N)$, of nucleus N in a molecule with n electrons, which is represented by:

$$\sigma^d(N) = (\mu_0 e^2 / 12\pi m) \langle \psi | \sum_i^n (1/r_{Ni}) | \psi \rangle \quad (1)$$

at the equilibrium configuration, has been shown¹ to be given by

$$\sigma^d(N) = (\mu_0 e^2 / 12\pi m) \left[- \left(\frac{\partial W_e}{\partial Z_N} \right)_{Z_N, Q} + \mu + \sum_{N \neq N'} \frac{Z_{N'}}{R_{NN'}^e} \right] \quad (2)$$

where $R_{NN'}^e$ are the equilibrium distances in the molecule, μ is the negative of the electronegativity of the molecule (as defined by Parr *et al.*²),

$$\mu = \left(\frac{\partial W}{\partial n} \right)_{Z_N, R_{NN'}} \quad (3)$$

W is the total Born-Oppenheimer energy of the molecule as a function of the atomic numbers $Z_{N'}$ and the net molecular charge Q , and e denotes the equilibrium configuration. The formula given by equation (2) is exact; it enables the calculation of $\sigma^d(N)$ if $W_e(Z_N, Z_{N'}, Q)$, μ , and the equilibrium geometry are known. Ray and Parr demonstrate the use of equation (2) for calculations of the diamagnetic

¹ N. K. Ray and R. G. Parr, *J. Chem. Phys.*, 1980, **73**, 1334.

² R. G. Parr, R. D. Donnelly, M. Levy, and W. Palke, *J. Chem. Phys.*, 1978, **68**, 160.

shielding of atoms in molecules by computing $\sigma^d(N)$ for a series of molecules and comparing their results with those of *ab initio* calculations. The results are very good even when the electronegativity is neglected. Since the individual atom is a special case,

$$\sigma^d(\text{atom}) = (\mu_0 e^2 / 12\pi m) [-(\partial E / \partial Z_N)_Q + \mu_{\text{atom}}]. \quad (4)$$

We can in fact express the diamagnetic shielding in the molecule as

$$\sigma^d(N) \approx \sigma^d(\text{atom}) + \sum_{N' \neq N} (Z_{N'} / R_{NN'})^6 \quad (5)$$

by neglecting the derivative of the dissociation energy. Equation (5) is a commonly used method of estimating the diamagnetic shielding in molecules.³

It has been shown that the second-order energy of the coupled Hartree–Fock theory can also be written in a simple sum-over-states perturbation formula.⁴ Fukui, Yoshida, and Miura⁵ have used this expression to write a formula for the nuclear shielding tensor that should be equivalent to the coupled Hartree–Fock formulae.⁶ The components of the diamagnetic term for the α component of μ_N and the β component of the applied field are as usual,

$$\sigma_{\alpha\beta}^d = 53.251\,325 \times 10^{-6} \sum_i^{\text{occ}} \langle i | (\mathbf{r}_0 \cdot \mathbf{r}_N \delta_{\alpha\beta} - r_{0\alpha} r_{N\beta}) r_N^{-3} | i \rangle \quad (6)$$

where \mathbf{r}_0 denotes the distance vector from the gauge origin to an electron and \mathbf{r}_N is that from the nucleus N of interest to the electron; $|i\rangle$ is the i^{th} molecular orbital obtained by solving the Hartree–Fock equation. Components of the paramagnetic shielding tensor, $\sigma_{\alpha\beta}^p$, are given by

$$\sigma_{\alpha\beta}^p = 53.251\,325 \times 10^{-6} \sum_n^{\text{occ}} \sum_{ij}^{\text{unocc}} \sum_{ab} T_n^{-1} V_{i \rightarrow a, n} V_{j \rightarrow b, n} \times \\ \times (\langle i | r_N^{-3} 1_{N\alpha} | a \rangle \langle b | l_{0\beta} | j \rangle + \langle i | l_{0\alpha} | a \rangle \langle b | r_N^{-3} 1_{N\beta} | j \rangle) \quad (7)$$

where the summation, n , runs over all excited singlet states, $|n\rangle$, with excitation energies T_n . $V_{i \rightarrow a, n}$ is the coefficient of the singlet excitation $i \rightarrow a$ in the above excited state $|n\rangle$. T_n and $|n\rangle$ are given as the n^{th} eigenvalue and eigenvector, respectively, of the Hamiltonian matrix whose elements are defined as follows:

$$H_{i \rightarrow a, j \rightarrow b} = \langle {}^1\Psi_{i \rightarrow a} | H_0 | {}^1\Psi_{j \rightarrow b} \rangle - \langle {}^1\Psi_0 | H_0 | {}^1\Psi_{i \rightarrow a} \rangle - \delta_{ij} \delta_{ab} \langle {}^1\Psi_0 | H_0 | {}^1\Psi_0 \rangle \quad (8)$$

where ${}^1\Psi_{i \rightarrow a}$ is the doubly excited singlet configuration

$$| \dots i a j b (\alpha \beta \alpha \beta - \alpha \beta \beta \alpha - \beta \alpha \alpha \beta + \beta \alpha \beta \alpha) / 2 \dots | |.$$

The l_N and l_0 operators in equation (7) are defined as $\mathbf{r}_N \times \nabla$ and $\mathbf{r}_0 \times \nabla$, respectively. Using the SCF MO energies, ϵ_i , associated with the molecular orbitals ψ_i , and the molecular electron repulsion integrals, Fukui *et al.*⁵ rewrite the matrix elements of H as

$$H_{i \rightarrow a, j \rightarrow b} = \delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i) - [ij|ab] + [ib|ja] \quad (9)$$

³ W. H. Flygare and J. Goodisman, *J. Chem. Phys.*, 1968, **49**, 3122.

⁴ H. Nakatsuji, *J. Chem. Phys.*, 1974, **61**, 3728.

⁵ H. Fukui, H. Yoshida, and K. Miura, *J. Chem. Phys.*, 1981, **74**, 6988.

⁶ W. N. Lipscomb, in 'Advances in Magnetic Resonance', Academic Press, New York, 1967, Vol. 2.

where

$$|ij|ab\rangle = \int \psi_i^*(1)\psi_j^*(1)r_{12}^{-1}\psi_a(2)\psi_b(2)d\tau_1d\tau_2. \quad (10)$$

The real symmetric matrix H is diagonalized to give the diagonal matrix T by the orthogonal matrix V , whose n^{th} column vector gives the coefficients $V_{i \rightarrow a,n}$ in equation (7). Thus, $HV = VT$.

The general concept of a density function for a molecular electronic property was considered and the origin dependence of some electric and magnetic property densities investigated, the nuclear magnetic shielding density function being used as a typical example, by Jameson and Buckingham.⁷ Density difference functions have been defined and calculated for some simple cases. For example, the shielding density difference function due to molecular bond formation is the function resulting by taking differences at each point in space of the shielding density for a nucleus in the molecule and the nucleus in the free atom. This function, when plotted, provides a way of viewing the polarizations and distortions in the shielding density upon molecule formation, and provides a basis for discussion of contributions to the nuclear shielding change from various parts of the molecule. When integrated over all space this difference function results in a single number: the shielding difference between the molecule and the free atom. Density difference maps are also shown for the HF molecule upon bond extension, that is for HF at $R_e + 0.1$ a.u. minus that for HF at the equilibrium distance, for both ^1H and ^{19}F shielding. This difference map provides a physical interpretation of the derivative $(\partial\sigma/\partial\Delta R)_e$.

B. *Ab Initio* Calculations.—The most accurate calculations (to date) of the nuclear magnetic shielding constants for the hydrides of the elements of the first and second rows of the periodic table have been recently carried out.^{8,9} These are coupled Hartree–Fock calculations using basis sets that are satisfactory with respect to gauge invariance. Some of the results are summarized in Tables 1 and 2. Closure relations for choosing an optimum gauge origin for nuclear shielding were tested.^{11,12} For the heavy-atom shielding, the origin of the best gauge is situated on the heavy atom and for ^1H it is found to be very close to the heavy atom. If a

Table 1 ^1H nuclear magnetic shielding in hydrides of the first and second rows of the periodic table,^{8,9} in p.p.m.

	LiH	BeH ₂	BH ₃	CH ₄	NH ₃	H ₂ O	HF
σ_{av}	26.61	28.11	24.17	31.39	31.41	30.13	27.85
$\Delta\sigma$	2.37	4.33	−9.64	10.46	−6.58	−0.57	24.32
	NaH	MgH ₂	AlH ₃	SiH ₄	PH ₃	H ₂ S	HCl
σ_{av}	29.46	26.90	26.57	27.85	28.73	29.87	29.90
$\Delta\sigma$	4.48	6.65	4.99	7.82	−2.36	1.90	23.32

⁷ C. J. Jameson and A. D. Buckingham, *J. Chem. Phys.*, 1980, **73**, 5684.

⁸ R. Höller and H. Lischka, *Mol. Phys.*, 1980, **41**, 1017.

⁹ R. Höller and H. Lischka, *Mol. Phys.*, 1980, **41**, 1041.

¹⁰ G. Malli and C. Froese, *Int. J. Quantum Chem.*, 1967, **1S**, 95.

¹¹ A. Sadlej, *Chem. Phys. Lett.*, 1975, **36**, 129.

¹² R. Yaris, *Chem. Phys. Lett.*, 1976, **38**, 460.

Table 2 X nuclear magnetic shielding^{8,9} in hydrides XH_n of the first and second rows of the periodic table compared to the diamagnetic shielding of the free atom,¹⁰ in p.p.m.

	LiH	BeH ₂	BH ₃	CH ₄	NH ₃	H ₂ O	HF
σ_{av}	89.5	87.68	96.7	195.8	266.1	328.1	415.0
$\Delta\sigma$	17.8	91.69	171.7	0	-40.4	-22.75	99.9
σ_{atom}	101.45	149.26	201.99	260.74	325.47	395.11	470.71
	NaH	MgH ₂	AlH ₃	SiH ₄	PH ₃	H ₂ S	HCl
σ_{av}	566.3	472.2	352.8	481.8	584.9	716.5	951.5
$\Delta\sigma$	92.4	350.3	120.7	0	-36.4	-242.5	295.6
σ_{atom}	628.90	705.60	789.88	874.09	961.14	1050.47	1142.64

reasonable gauge origin (as given by the closure relations) is chosen, much smaller basis sets can be used. The nuclear magnetic shielding tensors for the simplest hydrocarbons are reported.⁸ The results are shown in Table 3 and compared with experimental data and other theoretical calculations. The *z* axis is taken to be the unique axis. In the case of ethylene *z* is along the C—C bond and the *x* axis is perpendicular to the plane of the molecule. The magnetic susceptibility tensors for some hydrides and hydrocarbons are also reported.⁸ There has been some ambiguity about the magnitude and sign of the anisotropy of the magnetic susceptibility tensor, which has been used for empirical calculations of neighbour magnetic anisotropy contributions to nuclear shielding. The results shown in Table 3 for the components of the magnetic susceptibility tensor are probably the most accurate calculations available for these quantities and better than the available experimental values.

The semi-classical approach for calculation of the nuclear magnetic shielding and magnetic susceptibility tensors presented by Schmiedel^{24,25} for which a finite element method of numerical solution has been demonstrated²⁶ (reviewed in Volume 10), has been applied to polyatomic molecules.^{17,27} The procedure is a gauge-invariant calculation, which only requires a knowledge of the unperturbed electron density. The numerical solution is based on a partitioning of the electron density into localized parts. Since the basis set for the unperturbed electron densities used for the first attempt to apply this semi-classical method to polyatomic molecules is a relatively limited one, the results cannot be expected to be very good.

¹³ W. T. Raynes, in 'Nuclear Magnetic Resonance', ed. R. J. Abraham (Specialist Periodical Reports), The Royal Society of Chemistry, London, 1978, Vol. 7, p. 1.

¹⁴ R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789.

¹⁵ P. Lazzeretti and R. Zanasi, *J. Chem. Phys.*, 1978, **68**, 832.

¹⁶ B. Appleman, T. Tokuhito, G. Fraenkel, and C. Kern, *J. Chem. Phys.*, 1974, **60**, 2574.

¹⁷ U. Sternberg, K. Salzer, and H. Pfeifer, *Monatsh. Chem.*, 1980, **111**, 505.

¹⁸ G. Arrighini, M. Maestro, and R. Moccia, *Chem. Phys. Lett.*, 1970, **7**, 351.

¹⁹ S. Gordon and B. P. Dailey, *J. Chem. Phys.*, 1961, **34**, 1084.

²⁰ W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, 1958, **28**, 601.

²¹ K. Jackowski and W. T. Raynes, *Mol. Phys.*, 1977, **34**, 465.

²² R. Ditchfield and P. D. Ellis, *Chem. Phys. Lett.*, 1972, **17**, 342.

²³ D. B. Neumann and J. W. Moskowitz, *J. Chem. Phys.*, 1969, **50**, 2216.

²⁴ H. Schmiedel, *Phys. Status Solidi B*, 1975, **67**, K27.

²⁵ K. Salzer and H. Schmiedel, *Ann. Phys. (Leipzig)*, 1977, **34**, 415.

²⁶ K. Salzer, *Ann. Phys. (Leipzig)*, 1979, **36**, 91.

²⁷ K. Salzer, *Ann. Phys. (Leipzig)*, 1980, **37**, 271.

Table 3 Nuclear magnetic shielding and magnetic susceptibility tensor components of some simple hydrocarbons^{8*}

<i>¹H nuclear shielding:</i>							
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{av}	$\sigma_{av}(expt.)$	$\sigma_{av}(other\ calc.)$	
CH ₄	27.90	27.90	38.36	31.39	30.611 ± 0.024 ¹³	32.73 ¹⁴	30.96, ¹⁵ 30.45, ¹⁶ 34.89 ¹⁷
C ₂ H ₆	34.78	26.13	30.99	30.63	29.26 ^a	32.38 ¹⁴	34.80 ¹⁷
C ₂ H ₄	24.66	23.13	28.47	25.42	25.43 ^a	27.12 ¹⁴	34.97 ¹⁷
C ₂ H ₂	24.23	24.23	41.09	29.85	29.86 ^a	31.48 ¹⁴	32.68 ¹⁷
<i>¹³C nuclear shielding:</i>							
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{av}	$\sigma_{av}(expt.)$	$\sigma_{av}(other\ calc.)$	
CH ₄	195.8	195.8	195.8	195.8	197.35 ± 0.34 ^b	193.9 ¹⁸	204.8 ¹⁴ 239.0 ¹⁶
C ₂ H ₆	182.7	182.7	193.1	186.2	183.1 ± 0.33 ^b	197.4 ¹⁴	244.6 ¹⁶
C ₂ H ₄	177.9	-81.1	84.3	60.4	66.76 ± 0.35 ^b	74.0 ¹⁴	118 ¹⁶
C ₂ H ₂	39.0	39.0	279.4	119.1	121.35 ^b	129.6 ¹⁴	149 ¹⁶
<i>Magnetic susceptibility</i>							
	χ_{xx}	χ_{yy}	χ_{zz}	χ_{av}			
CH ₄	-18.95	-18.95	-18.95	-18.95			
C ₂ H ₆	-33.14	-33.14	-33.59	-33.29			
C ₂ H ₄	-30.16	-23.47	-21.36	-25.00			
C ₂ H ₂	-22.59	-22.59	-24.59	-23.50			

* The z axis is the unique axis. In C₂H₄ z is along the C—C bond and x is perpendicular to the plane of the molecule. Experimental values are for gases extrapolated to zero density except for C₂H₂.

^a Based on shifts from CH₄ quoted in refs. 19 and 20. ^b Based on shifts from CO given in ref. 13; original data from refs. 21 and 22. $\sigma_0(\text{CO}) = 3.20 \pm 0.27$ p.p.m. from ref. 23.

Small differences in unperturbed electron densities can lead to significant differences in the magnetic susceptibility and shielding tensors calculated from them by this semi-classical approach. Only the results for proton shielding are included in Table 3. The ¹³C shielding calculations do not give results that are comparable to the quality of the other theoretical values shown in Table 3. The relationship of the semi-classical approach to uncoupled Hartree–Fock perturbation theory and to the variational method of Rebane²⁸ is also shown.²⁷

Ab initio calculations of the one-electron properties, including the diamagnetic shielding for all nuclei, have been carried out for the COF₂, SO₂F₂, and SOF₂ molecules.²⁹ For COF₂ the paramagnetic shielding for ¹⁹F has been calculated previously from the spin–rotation constant obtained from hyperfine structure in the rotational transitions measured in a molecular beam maser spectrometer.³⁰ This result combined with the ¹⁹F diamagnetic shielding²⁹ yields the following components of the ¹⁹F shielding tensor in COF₂: $\sigma_{zz} = 178.62$, $\sigma_{yy} = 281.88$, and $\sigma_{xx} = 230.46$ p.p.m., where z is parallel to the C=O direction and x is perpendicular to the plane of the molecule. The error limits on σ are determined by the precision of the spin–rotation data, of course, which translates to ± 10 p.p.m. in the nuclear

²⁸ T. K. Rebane, *Zh. Eksp. Teor. Fiz.*, 1960, **38**, 963.

²⁹ G. de Brouckere, R. Broer, W. C. Nieuwpoort, and G. Berthier, *Mol. Phys.*, 1980, **41**, 729.

³⁰ J. H. S. Wang and S. G. Kukolich, *J. Am. Chem. Soc.*, 1973, **95**, 4138.

shielding components. The estimates of σ^d ,³⁰ obtained by using the Flygare method,³¹ can be compared with these recent values: $\sigma_{xx} = 637.64$ p.p.m., *ab initio* (633.5 p.p.m., Flygare), $\sigma_{yy} = 543.59$ (542.4), $\sigma_{zz} = 584.91$ (582.3). We see that the approximate method of Flygare, which is easily applied, given only the equilibrium geometry of the molecule, continues to hold up as a very good approximation.

C. Semi-empirical Calculations.—The relationship of the paramagnetic term in the shielding (with the gauge origin at the nucleus of interest) to the nuclear quadrupole coupling constant (which is a measure of the electric-field gradient at the nucleus) was expressed in 1954.³² Both are essentially dependent upon the ‘fraction of the unbalanced *p* electrons on the atom in question’. It is not surprising then that ²³Na chemical shifts for each of the (Na⁺)L_{*n*}L’_{4-*n*} species, where L are various ligands, are directly proportional to the square root of the observed linewidths normalized to unit viscosity.³³ In this case linewidths depend on the electric-field gradient, which shares a common origin with σ^p : namely injection of electrons donated by the ligands into 3*p* orbitals on the Na⁺ ion, according to a theoretical interpretation of the ²³Na chemical shifts.^{34, 35}

In the past several years a variety of carbocations in solution have been prepared and characterized. Differentiation between carbocations with classical or non-classical structures by a range of physical methods may or may not lead to unequivocal conclusions. For a pair of degenerate equilibrating classical carbonium ions, the observed nuclear shieldings are averages of the shielding for various geometries from one extreme static structure to the other. For non-classical ions, however, the observed shielding is merely averaged over the very small displacements undergone by any rotating-vibrating molecule. N.m.r. allows the unambiguous determination of the cation structure provided its spectrum corresponds to an asymmetrical classical structure. Some cations, however, have spectra characteristic of a symmetrical structure down to the lowest temperature of observation, so that either a non-classical symmetrical structure or rearrangements of classical structures with a frequency exceeding the frequency difference of the averaged n.m.r. lines are possible interpretations. It could be concluded that an ion has a non-classical spectrum if its spectrum differs from the average spectra of classical structures. The problem in applying this criterion is that the n.m.r. spectra of the limiting unobserved classical structures are not known and the nature of the averaging motion has to be assumed. Thus, calculations of nuclear shielding will allow, in principle, the differentiation to be made. One calculation for the non-classical structure, calculations for the limiting classical structures and for an assumed character of the motion, and calculations for the structures through which one limiting classical structure passes into the other one need to be carried out. Cheremisin and Schastnev³⁶ have carried out semi-empirical (INDO) calculations of ¹³C nuclear shielding in some typical carbonium ions with this strategy as the ideal approach. In practice, only the average between the ¹³C shieldings in the two

³¹ T. D. Gierke, H. C. Tigelaar, and W. H. Flygare, *J. Am. Chem. Soc.*, 1972, **94**, 330.

³² A. Saika and C. P. Slichter, *J. Chem. Phys.*, 1954, **22**, 26.

³³ C. Deverell, *Mol. Phys.*, 1969, **16**, 491.

³⁴ A. Delville, C. Detellier, A. Gerstmans, and P. Laszlo, *J. Am. Chem. Soc.*, 1980, **102**, 6558.

³⁵ A. Delville, C. Detellier, A. Gerstmans, and P. Laszlo, *J. Magn. Reson.*, 1981, **42**, 14.

³⁶ A. A. Cheremisin and P. V. Schastnev, *Org. Magn. Reson.*, 1980, **14**, 327.

limiting structures is reported. Since there are usually several ^{13}C nuclear sites whose shieldings relative to CH_4 can be compared with experiment, there is some possibility of success. In some cases they arrive at definite conclusions that agree with evidence from other physical methods. In others no definite assignment is made. The classes of cations considered include the 2-norbornyl, 7-norbornenyl, 7-norbornadienyl, bicyclohexyl, and cyclopropyl cations, as well as some simpler cations. The validity of their conclusions may be affected in part by solvent effects, which are unaccounted for, and the improper averaging of just the two limiting structures in the cations undergoing rearrangement. In addition, the bond lengths and angles of the non-classical cations may be incorrectly estimated and the method of summation over states in the INDO approximation may be inadequate for the sometimes subtle distinctions in ^{13}C shieldings being made.

In approximate calculations of nuclear magnetic shielding it is customary to consider the total shielding as being partitioned into separate contributions, *e.g.*, ring currents, electric field, and magnetic anisotropy effects from various parts of the molecule. Calculations of only one or two contributions are then undertaken for a series of related compounds, in which all other contributions, if this is to be believed, remain the same. The approach is to try to find a dominant varying contribution that is independent of the varying structural details of the molecules in the series. This seems to work when the series of compounds studied are sufficiently similar and when the shielding changes are indeed largely due to the contribution upon which attention is being fixed. This seems to be a sensible approach for long-range effects. In this review period several calculations of this nature have been reported. Cheremisin and Schastnev³⁷ have introduced a method of calculating the contributions to the nuclear shielding from spin-orbit interactions by third-order perturbation theory. Allowing for the perturbation terms in $L \cdot S$, $L \cdot B$, and $S \cdot B$ [interaction between spin and orbital angular momentum, between orbital (or spin) angular momentum and the magnetic field] in the molecular Hamiltonian, the wavefunction of the ground state $\psi'(B)$ depends on the external magnetic field and owing to the spin-orbital interaction the singlet ground state has a small admixture of triplet components. The hyperfine contribution to the energy of the system can be obtained by averaging the hyperfine interaction operator (contact and dipolar terms in the interaction of electron spin with nuclear spin angular momentum) over the wavefunction $\psi'(B)$. In the case of the halogen hydrides, HBr and HI, the spin-orbital contributions to the ^1H shielding have been shown to be comparable with the diamagnetic and paramagnetic contributions.^{38,39} In the case of ^{13}C shielding in halogen-substituted methanes, $\text{CH}_n\text{X}_{4-n}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), the above method, applied in the INDO approximation using gauge-dependent atomic orbitals, leads to contributions which are not additive; for example, 6.2, 15.2, 35.6, and 76.3 p.p.m. in going from CH_3Br to CBr_4 . These contributions constitute a large fraction of the total ^{13}C shielding relative to CH_4 in the cases of Br and I substitution. The results obtained describe quantitatively ^{13}C shielding changes in the halomethanes of the type $\text{CH}_n\text{X}_{4-n}$ as n is varied. It would have been interesting to see if the data on the mixed halomethanes ($\text{CX}_n\text{Y}_{4-n}$; $\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) could

³⁷ A. A. Cheremisin and P. V. Schastnev, *J. Magn. Reson.*, 1980, **40**, 459.

³⁸ I. Morishima, K. Endo, and T. Yonezawa, *J. Chem. Phys.*, 1973, **59**, 3356.

³⁹ M. I. Volodochova and T. K. Rebane, *Theor. Exp. Chem. (USSR)*, 1978, **14**, 447.

also be reproduced. Perhaps the authors are already working on these. Nearly all the spin-orbit contribution comes from the contact or isotropic term rather than the dipolar one.

A factor analysis of the ^{13}C shielding in methyl halides and other aliphatic and alicyclic halides has been carried out.⁴⁰ Each halogen atom is assigned three substituent-effect terms, which are intrinsic parameters characteristic of each halogen, attenuated by coefficients assumed to be sensitive to the site of the halogen in the molecule. The intrinsic parameters are found to be linearly related to bond polarizabilities, atomic contributions to molar diamagnetic susceptibility, *etc.* Unfortunately the authors have failed to include halomethanes of the type $\text{CH}_n\text{X}_{4-n}$ or $\text{CX}_n\text{Y}_{4-n}$ except for CH_3X . They would surely have found large deviations owing to the large deviations from additivity of substituent effects, as shown by the calculations of Cheremisin and Schastnev.³⁷ The effects of substituents on ^{13}C , ^{29}Si , and ^{31}P nuclear magnetic shielding have also been interpreted by CNDO and extended Hückel calculations.⁴¹

The electric field and magnetic anisotropy contributions are considered in the following reports, generally treated as through-space effects due to nitrile groups,⁴² C—F bonds in fluorostyrenes,⁴³ and various C—X bonds (X = F, Cl, Br, OH, Me) in steroids.⁴⁴ The use of the ring-current concept continues to be advocated.⁴⁵ Ducasse *et al.*⁴⁶ have calculated ^1H chemical shielding in hydrocarbons using extended Hückel theory and gauge-dependent atomic orbitals. The two-centre integrals of the angular-momentum operators are evaluated analytically using formulae given by Barfield and Grant.⁴⁷ Adjustable parameters are used in evaluating tricentric integrals in terms of products of overlap integrals and two-centre integrals in the angular-momentum operators. An attempt is made to separate out the ring-current effect. The calculated ^1H shieldings in hydrocarbons reproduce experimental values within 1 p.p.m. The contribution due to the π -electron ring currents, separated out in this calculation, is only -0.26 p.p.m., which is small when compared to the theoretical difference between the ethylene and benzene shielding constants (-1.65 p.p.m.). It is not clear that the whole of this difference can be attributed to the ring-current effect, as is usually done. Calculations at the CNDO/INDO level for ^{13}C and ^1H shielding in hydrocarbons have also been reported.^{48–50}

Parameterizing the atomic β values in a semi-empirical calculation of chemical shifts of a given atom in a molecule, based on the level of agreement between theory and experiment for a limited number of representative molecules, appears to yield good agreement upon application to calculations of shieldings of the same nucleus in unrelated molecules. Ellis *et al.* have extended this parameterization method,

40 K. B. Wiberg, W. E. Pratt, and W. F. Bailey, *J. Org. Chem.*, 1980, **45**, 4936.

41 R. Wolf and R. Radeaglia, *Z. Phys. Chem. (Leipzig)*, 1980, **261**, 726.

42 M. Rouillard, S. Geribaldi, J. Khazarian, and M. Azzaro, *Org. Magn. Reson.*, 1980, **13**, 323.

43 W. F. Reynolds, V. G. Gibb, and N. Plavac, *Can. J. Chem.*, 1980, **58**, 839.

44 W. Gschwendtner and H. J. Schneider, *J. Org. Chem.*, 1980, **45**, 3507.

45 J. A. N. F. Gomes, *Mol. Phys.*, 1980, **40**, 765.

46 L. Ducasse, J. Hoarau, and M. Pesquer, *Mol. Phys.*, 1980, **40**, 1249.

47 M. Barfield and D. M. Grant, *J. Chem. Phys.*, 1977, **67**, 3322.

48 F. W. Whitehurst, Ph. D. Thesis, Duke Univ., USA, 1980, from *Diss. Abstr. Int. B*, 1980, **41**, 1387.

49 I. F. Tupitsyn and A. A. Kane, *Zh. Obshch. Khim.*, 1980, **50**, 653.

50 D. B. Chestnut and F. W. Whitehurst, *J. Comput. Chem.*, 1980, **1**, 36.

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which they developed for ^{13}C calculations, to ^{11}B .⁵¹ The results predict the correct order for the boron nuclear shielding values, but also the appropriate magnitude of shielding differences between structurally unrelated molecules. Overall agreement with experimental boron chemical shifts is indicated by a least-squares line with a slope of 0.92 and a standard deviation of 9.44 p.p.m. for shielding values ranging from -60 to 90 p.p.m. relative to the free atom (202 p.p.m.). The results are better than those from MINDO/3 calculations reported in the previous reviewing period.⁵²

The problem of the origin of the chemical shielding difference between *syn* and *anti* ^{13}C nuclei in *NN*-disubstituted amides has been examined.⁵³ In the great majority of cases, $\sigma_{\text{syn}} > \sigma_{\text{anti}}$. Since the difference is only slightly solvent dependent, it is probably not intermolecular in origin. It is found that calculated values of electric-field contributions to this *syn-anti* anisochrony are all about a factor of 4–10 too small. Other possible contributions are dismissed as likewise unimportant. Thus, the origin of the difference is still not understood in terms of through-space effects. Another interesting *syn versus anti* shielding problem is the extraordinary deshielding of ^{31}P nuclei in phosphines of the *syn-7*-phosphanorbornene system.⁵⁴ The ^{31}P shielding values are about 100 p.p.m. lower than those for the corresponding *anti* isomers. The double bond appears to be essential for the large deshielding since the ^{31}P nuclei in corresponding saturated compounds do not exhibit the same deshielding. Nuclear shielding of heavy nuclei such as ^{51}V and ^{93}Nb can usually be interpreted only approximately, using a mean energy approximation in the calculation of the paramagnetic term.^{55, 56} The local diamagnetic contribution to vanadium shielding in carbonyl-substituted phosphine vanadium complexes amounts to 1712 p.p.m. and is considered almost constant for all vanadium compounds. The difference in the paramagnetic term is explained in terms of changes in the energy separation between the highest occupied and lowest unoccupied molecular orbitals as the degeneracy is lifted.⁵⁶

Calculations of ^{13}C shielding in hydrocarbons⁵⁷ has led to a very useful method of providing information about the micro-structure of polymers. Relative to an unsubstituted carbon, each carbon substituent in the α and β position produces a deshielding effect of about -10 p.p.m. On the other hand a γ -carbon substituent shields the observed carbon by $+2$ to $+3$ p.p.m. The latter requires that the observed and γ carbons must be in a *gauche* arrangement. It is this contribution to carbon nuclear magnetic shielding that is sensitive to polymer-chain conformation. Calculations of ^{13}C shielding in polymers have been recently reviewed⁵⁸ and applied to ethylene-vinyl chloride copolymers and polypeptides.^{59, 60} The effect of geometry

⁵¹ P. D. Ellis, Y. C. Chou, and P. A. Dobosh, *J. Magn. Reson.*, 1980, **39**, 529.

⁵² M. Jallali-Heravi and G. A. Webb, *J. Mol. Struct.*, 1979, **55**, 113.

⁵³ C. Piccinni-Leopardi and J. Reisse, *J. Magn. Reson.*, 1981, **42**, 60.

⁵⁴ L. D. Quin and K. A. Mesch, *J. Chem. Soc., Chem. Commun.*, 1980, 959.

⁵⁵ V. P. Tarasov, S. M. Sinityna, V. D. Kopanev, V. G. Khleboarov, and Y. A. Buslaev, *Koord. Khim.*, 1980, **6**, 1568.

⁵⁶ H. Schmidt and D. Rehder, *Trans. Met. Chem.*, 1980, **5**, 214.

⁵⁷ D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, 1964, **86**, 2984.

⁵⁸ I. Ando and T. Asakura, in 'Annual Reports on NMR Spectroscopy', ed. G. A. Webb, Academic Press, London, 1980, Vol. 10A, p. 81.

⁵⁹ A. E. Tonelli and F. C. Schilling, *Macromolecules*, 1981, **14**, 74.

⁶⁰ A. E. Tonelli, *J. Am. Chem. Soc.*, 1980, **102**, 7635.

modifications on ^{13}C shielding is investigated using INDO and Gaussian 70 calculations.⁶¹ The latter give poor absolute shielding values but compare well with reparameterized INDO calculations of variations in shielding with changes in geometry.

D. Calculations in Paramagnetic Systems.—Golding and Stubbs continue their theoretical treatment of the pseudocontact contribution to nuclear shielding in d^1 and d^2 transition-metal ion systems. In this latest work⁶² formulae are presented for a d^1 system without assuming a strong crystal field. A compact general expression is developed to obtain analytical expressions for all of the required matrix elements for any d^n system. The shielding shifts in a d^2 system in a strong crystal field of octahedral symmetry are determined and the effect of configurational mixing examined in detail. Through this work and earlier work, these authors have made very clear the complex pattern of these shifts in various regions of the paramagnetic molecule, as shown by isoshielding diagrams.⁶³ In some regions, the shielding due to the electron orbital angular momentum and the electron-spin dipolar–nuclear-spin angular momentum interactions changes very rapidly with distance. All of these calculations are on systems with fixed nuclei. Recently Golding and Pascual considered the effect of vibronic coupling in these transition-metal ion paramagnetic systems.⁶⁴ The specific case of a d^1 transition-metal ion vibrating in a strong crystal field of octahedral symmetry is examined. The results show that in some regions the vibronic coupling may have a substantial effect, for example, a shielding change of -1.19 p.p.m. compared to a no coupling case of -0.90 p.p.m. and 8.63 p.p.m. compared with the no coupling case of 9.67 p.p.m. The effect of vibronic coupling is important in those regions where the isoshielding contours for the rigid system are closely spaced (shielding changing rapidly with distance).

3 Physical Aspects of Nuclear Shielding

A. Anisotropy of the Shielding Tensor.—Cross-polarization n.m.r. spectroscopy of molecules isolated in argon matrices at low temperatures (*ca.* 20–30 K) has been developed.⁶⁵ By observing dilute molecules in the nearly isotropic argon matrix, the technique greatly reduces intermolecular contributions to the shielding, which may lead to changes in both orientation and magnitude of the tensor elements. The technique is applied to a series of small olefins and other small molecules.^{66–68} The values of the components of the shielding tensors so obtained are given in Table 4. Comparison of theoretical values with the components of the shielding tensor provides a more stringent test of the theory than comparison with the isotropic average which is measured in gases, liquids, or solutions. In fact, examination of the components of shielding in the olefins has already provided some interesting

⁶¹ D. B. Chesnut and A. L. Helms, *Theor. Chim. Acta*, 1981, **58**, 163.

⁶² R. M. Golding and L. C. Stubbs, *J. Magn. Reson.*, 1980, **40**, 115.

⁶³ R. M. Golding and L. C. Stubbs, *J. Magn. Reson.*, 1979, **33**, 627.

⁶⁴ R. M. Golding and R. O. Pascual, *Mol. Phys.*, 1980, **41**, 421.

⁶⁵ K. W. Zilm, D. M. Grant, R. T. Conlin, and J. Michl, *J. Am. Chem. Soc.*, 1978, **100**, 8038.

⁶⁶ K. W. Zilm, A. J. Beeler, D. M. Grant, J. Michl, T.-C. Chou, and E. L. Allred, *J. Am. Chem. Soc.*, 1981, **103**, 2119.

⁶⁷ K. W. Zilm and D. M. Grant, *J. Am. Chem. Soc.*, 1981, **103**, 2913.

⁶⁸ K. W. Zilm, R. T. Conlin, D. M. Grant, and J. Michl, *J. Am. Chem. Soc.*, 1980, **102**, 6672.

Table 4 ^{13}C nuclear magnetic shielding tensors measured by cross-polarization spectroscopy at about 30 K in an argon matrix. Values were originally reported as p.p.m. from TMS.^{66–68} They are converted to absolute shielding values based on ^{13}C in CO = 3.20 ± 0.27 .²³ On this shielding scale ^{13}C in liquid TMS at room temperature is 185.4 p.p.m.⁶⁹ Estimated errors are ± 2.5 p.p.m. except where indicated

Olefinic Carbons	σ_{11}	σ_{22}	σ_{33}
ethylene	-53.6	56.4	156.4
trans-but-2-ene	-46.6	72.4	148.4
cis-but-2-ene	-46.6	66.4	163.4
trans-cyclo-octene	-52.6	58.4	148.4 ± 5
cis-cyclo-octene	-54.6	62.4	157.4 ± 5
cycloheptene	-59.6	59.4	158.4 ± 5
cyclohexene	-50.6	62.4	162.4 ± 5
cyclopentene	-49.6	67.4	146.4
cyclobutene	-58.6	47.4	155.4 ± 5
cyclopropene	-53.6	106.4	180.4
acetylene	35.4	35.4	275.4 ± 5
<i>Aliphatic Carbons</i>			
trans-but-2-ene	158.4	158.4	180.4
cis-but-2-ene	157.4	179.4	178.4
cyclopentene C_{α}	133.4	155.4	173.4
cyclopentene C_{β}	146.4	163.4	178.4
cyclobutene	142.4	152.4	162.4
cyclopropene	145.4	156.4	144.4
cyclopropane	163.4	183.4	221.4
<i>Others</i>			
CH ₃ F	80.4 ± 10	80.4 ± 10	170.4 ± 10
CH ₃ CHO C ₁	-99.6	-45.6	101.4
CH ₃ CHO C ₂	132.4	145.4	186.4

results.⁶⁸ Variations in the three tensor components can cancel each other and thereby reduce the overall range of isotropic shifts. It is interesting to compare the experimental results given here with the calculated shielding values in Table 3 for C₂H₄ and C₂H₂. For C₂H₄ the calculated values σ_{zz} (C—C bond), σ_{xx} (\perp to plane of molecule), σ_{yy} are 84.3, 177.9, -81.1 p.p.m., respectively.⁸ The experimental values are 56.4, 156.4, -53.6 p.p.m.⁶⁷ The assignments of the tensor components agree with theory. For C₂H₂ the calculated values for σ_{\parallel} and σ_{\perp} are 279.4 and 39.0, respectively, which agree quite well with the experimental values of 275.4 and 35.4 p.p.m.⁶⁷

Shielding tensors for protons involved in very strong hydrogen bonds have been obtained in single crystals. The shielding anisotropy, $\Delta\sigma$, results for potassium hydrogen-oxydiacetate,⁷⁰ -dicrotonate,⁷⁰ and -malonate⁷¹ are respectively 28.3 ± 0.9 , 28.9 ± 0.9 , and 27.6 ± 0.6 p.p.m. The anisotropy of the deuterium shielding tensor in α -oxalic acid dihydrate⁷² and in potassium bicarbonate⁷³ are

⁶⁹ J. Mason, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1671.

⁷⁰ B. Berglund, J. Allison, D. G. Carson, and R. W. Vaughan, *J. Magn. Reson.*, 1980, **40**, 475.

⁷¹ B. Berglund, D. G. Carson, and R. W. Vaughan, *J. Chem. Phys.*, 1980, **72**, 824.

⁷² A. M. Achlama, *J. Magn. Reson.*, 1980, **41**, 374.

⁷³ A. M. Achlama, *J. Chem. Phys.*, 1981, **74**, 3623.

28.6 ± 0.5 and 26.4 ± 0.5 p.p.m., respectively. Correlations between proton shielding tensors and bond distances for hydrogen bonds in solids have been discussed⁷⁴ in terms of Ditchfield's calculated results in a $\text{H}_2\text{O}-\text{H}_2\text{O}$ hydrogen bond system.⁷⁵ The conclusion is that the variation in the experimental isotropic shielding and the anisotropy is consistent with the results of the theoretical calculations. The variation in the isotropic proton shielding is almost totally due to internal variations in an $\text{O}-\text{H}\cdots\text{O}$ bond, whereas the anisotropy is also strongly dependent on the geometrical arrangement about the bond. σ_{\perp} appears to be sensitive to the degree of hydrogen-bonding, whereas σ_{\parallel} appears to be essentially unaffected.

The ^1H and ^{13}C nuclear magnetic shielding tensors in pyromellitic acid dihydrate and malonic acid have been determined in the single crystal. The total experimental shielding tensor for ^1H has been divided between intra- and inter-molecular contributions. When corrections are made on the basis of a simple model for the intermolecular contributions, the remaining shielding tensor conforms more closely to the symmetry of the molecule. Like other hydrogen-bonded systems, the carboxyl proton in pyromellitic acid dihydrate shows an increase in shielding anisotropy with decreasing hydrogen-bond length. The ^{13}C shielding tensor components for the ring carbons and the carboxyl carbons in this compound and in malonic acid are largest normal to the plane of the ring or carboxyl group.⁷⁶ In calcium and lead formate, intermolecular shielding contributions lead to different proton tensors for four different environments in the single crystal.⁷⁷ Correction for these intermolecular contributions leads to a tensor whose orientation relative to the formate ion is similar in all four sites and can therefore be identified with the shielding of the proton in an isolated formate ion. The C—H bond direction is the most, and the normal to the formate ion is the least, shielded principal direction, with $\Delta\sigma = 5 \pm 1$ p.p.m. The formate ion is a small enough species for very good theoretical calculations. However, see the section on intermolecular interactions (p. 18) for calculations on the effect of Ca^{2+} ions on the formate ion.

The ^{13}C shielding tensors for the carboxyl-, methyl-, and α -carbons in L-alanine have been measured in the single crystal.⁷⁸ The carboxyl carbon shielding has a large anisotropy with the most shielded direction being perpendicular to the plane ($\sigma_{11}, \sigma_{22}, \sigma_{33} = -114.4$ p.p.m., -55.0 p.p.m., 21.8 p.p.m.). The methyl carbon and the α -carbon shieldings have a small anisotropy. The results are CH_3 (98.2 p.p.m., 107.1 p.p.m., 120.2 p.p.m.) and C_{α} (63.4 p.p.m., 72.0 p.p.m., 97.2 p.p.m.). All values are relative to liquid benzene.

Shielding tensors have also been reported in various polycrystalline materials. Carbon shielding tensors in metal sandwich compounds, Fe, Ru, and Mg bis(cyclopentadienyl) complexes and bis(benzene) chromium.⁷⁹ The shielding anisotropy is very sensitive to the nature of the ring-metal interactions, $\Delta\sigma$ varies from 76 to 155 p.p.m., which is to be compared with 174 p.p.m. for benzene itself. The ^{31}P tensor in four cyclic organophosphorus compounds of different sizes, where

⁷⁴ B. Berglund and R. W. Vaughan, *J. Chem. Phys.*, 1980, **73**, 2037.

⁷⁵ R. Ditchfield, *J. Chem. Phys.*, 1976, **65**, 3123.

⁷⁶ J. Tegenfeldt, H. Feucht, G. Ruschitzka, and U. Haeberlen, *J. Magn. Reson.*, 1980, **39**, 509.

⁷⁷ H. Post and U. Haeberlen, *J. Magn. Reson.*, 1980, **40**, 17.

⁷⁸ A. Naito, S. Ganapathy, K. Akasaka, and C. A. McDowell, *J. Chem. Phys.*, 1981, **74**, 3190.

⁷⁹ D. E. Wemmer and A. Pines, *J. Am. Chem. Soc.*, 1981, **103**, 34.

the phosphorus atom has the same local environment, has been determined. The effect of the geometry of the rest of the molecule on the P-shielding tensor is found to be substantial, leading to $\Delta\sigma$ values that range over 50 p.p.m.⁸⁰ The ³¹P tensor in sodium triphosphate has an anisotropy of 182 p.p.m.⁸¹ The ²⁹Si shielding tensor in silicates appears to be related to the length of the Si—O bond, the most shielded direction corresponding to the shortest Si—O bond. The relation between the character of the Si—O bond and the Si shielding tensor is the same as that observed for P—O bonds and ³¹P shielding.⁸² The principal components of the ¹¹³Cd shielding tensors in some cadmium sulphate hydrates have been reported. Anisotropies range from 84 to 189 p.p.m., which are to be compared with the very small ¹¹³Cd anisotropy found in CdO.⁸³

Some anisotropy measurements in liquid crystals, clathrates, and in hydrated liquid-crystalline phospholipid bilayers have also been reported. The ¹³C shielding anisotropies of acetylenic carbons in acetylene, methyl-, and dimethyl-acetylene are found⁸⁴ to be as follows: HC≡CH (269 ± 11 p.p.m.), CH₃C≡CH (191 ± 10 p.p.m. for C—H and 251 ± 9 p.p.m. for C—CH₃), CH₃C≡CCH₃ (160 ± 7 p.p.m.). The acetylene ¹³C shielding anisotropy can be compared with the experimental value obtained by matrix isolation (240 p.p.m.)⁶⁷ and the theoretical value (240.4 p.p.m.).⁸ In contrast, the ¹³C anisotropies in the carbonyl groups of the γ - and β -chains in phospholipid bilayers are small: -25 ± 2 p.p.m. and -5 ± 2 p.p.m., respectively.⁸⁵ It is postulated that the chains undergo different sorts of motion over which the carbon shielding tensors become averaged and the anisotropies become almost eliminated. ¹⁹F shieldings in SF₆, SeF₆, and TeF₆ in clathrate deuteriohydrates are reported.⁸⁶ The $\Delta\sigma$ values are 310 ± 30 p.p.m. for SF₆, 370 ± 20 p.p.m. for SeF₆, and 215 ± 25 p.p.m. for TeF₆. The isotropic shielding and the spin-rotation constants for ¹⁹F in these compounds are calculated from the measured anisotropies and the calculated diamagnetic terms using the method of Gierke and Flygare.³¹ For SF₆, comparison of the derived spin-rotation constant with the literature values shows that previous values of the anisotropy of the spin-rotation tensor in SF₆ may have been too large. ¹⁹⁹Hg shielding anisotropy has been derived from T_1 measurements on diphenyl mercury. A very large value of $\Delta\sigma$ (6800 ± 680 p.p.m.) is calculated.⁸⁷

B. The Effects of Rotation and Vibration.—The effects of intramolecular dynamics (rotational and vibrational motion) on nuclear magnetic shielding have been reviewed recently.⁸⁸ The available observed temperature dependence of nuclear shielding in isolated molecules (measurements in the gas extrapolated to zero density) are summarized. Presently, data of this type are available for ¹⁹F, ¹⁵N, ¹¹B, ¹³C, ³¹P, and ¹H in a variety of small molecules (F₂, CO, HCl, HBr, ClF, NNO, CO₂, BF₃, NF₃, PH₃, NH₃, PF₃, CH₄, CF₄, SiF₄, CF₃H, CH₃F, CF₃Cl, CF₃Br, POF₃,

⁸⁰ J. P. Dutasta, J. B. Robert, and L. Wiesenfeld, *Chem. Phys. Lett.*, 1981, **77**, 336.

⁸¹ E. R. Andrew, D. J. Bryant, E. M. Cashell, and B. A. Dunell, *Chem. Phys. Lett.*, 1981, **77**, 614.

⁸² A. R. Grimmer, R. Peter, E. Fechner, and G. Molgedey, *Chem. Phys. Lett.*, 1981, **77**, 331.

⁸³ P. D. Murphy and B. C. Gerstein, *J. Am. Chem. Soc.*, 1981, **103**, 3282.

⁸⁴ K. Hayamizu, O. Yamamoto, and I. Ando, *J. Magn. Reson.*, 1980, **39**, 343.

⁸⁵ B. A. Cornell, *Chem. Phys. Lett.*, 1980, **72**, 462.

⁸⁶ S. K. Garg, J. A. Ripmeester, and D. W. Davidson, *J. Magn. Reson.*, 1980, **39**, 317.

⁸⁷ D. G. Gillies, L. P. Blaauw, G. R. Hays, R. Huis, and A. D. H. Clague, *J. Magn. Reson.*, 1981, **42**, 420.

⁸⁸ C. J. Jameson, *Bull. Magn. Reson.*, 1980, **3**, 3.

PF₅, SF₆). The interpretation of the observed temperature dependence of nuclear shielding in this limit is generally expressed in terms of the variation of nuclear shielding with bond extension and bond-angle deformation, and the temperature dependence of the mean bond displacements, mean-square bond displacements, and so on. Thus, the expansion of the nuclear shielding in terms of the normal co-ordinates is used:

$$\sigma = \sigma_e + \sum_i (\partial\sigma/\partial q_i)q_i + \frac{1}{2} \sum_{ij} (\partial^2\sigma/\partial q_i\partial q_j)q_iq_j + \dots \quad (11)$$

For the diatomic molecule the average of σ reduces to a single co-ordinate:

$$\langle\sigma\rangle = \sigma_e + (\partial\sigma/\partial\xi)_e\langle\xi\rangle + \frac{1}{2}(\partial^2\sigma/\partial\xi^2)_e\langle\xi^2\rangle + \dots \quad (12)$$

This form has been used by many authors for a variety of molecular properties. An empirical form that has been suggested for magnetic electronic properties dependent on the internuclear distance in a diatomic molecule is:

$$\chi_{\perp}^p = \chi_{\perp}^p(R_e)(R/R_e)^n \quad (13)$$

for example, for the perpendicular component of the magnetic susceptibility tensor. A comparison of results obtained with this functional form ($n = 3.8$) with the Taylor expansion form [analogous to equation (12)] and the proper average over the calculated magnetic susceptibility tensor components as a function of internuclear distance from $0.6 a_0$ to $10 a_0$ for the H₂ molecule, shows that equation (13) describes the R dependence for small R adequately, whereas a truncated Taylor series expansion does not.⁸⁹ The same may be true for the σ_{\perp}^p of H₂. The difficulty may be in finding a proper value of n , however.

The temperature dependence of nuclear shielding in the limit of zero density has been reported for ¹⁵N in N₂,⁹⁰ ¹³C in CO,⁹⁰ ¹⁵N and ¹H in NH₃,⁹¹ and ¹⁹F in SF₄ and COF₂.⁹² The temperature dependence of ¹⁵N in N₂ is $\sigma_0(T) - \sigma_0(300 \text{ K}) = -(0.85 \pm 0.10) \times 10^{-3} (T/\text{K} - 300)$ p.p.m. for $T = 200$ – 380 K and for ¹³C in CO, $\sigma_0(T) - \sigma_0(300 \text{ K}) = -(0.2906 \pm 0.4) \times 10^{-3} (T/\text{K} - 300)$ p.p.m. for $T = 380$ K. Since the harmonic frequencies of these diatomic molecules are very high the vibrational contribution to the shielding remains essentially constant over the temperature range of this study. Thus, the observed temperature dependence is entirely due to rotation (centrifugal distortion):

$$\langle\sigma\rangle^T - \langle\sigma\rangle^{300 \text{ K}} \simeq (4k/hc)(B_e/\omega_e^2)(d\sigma/d\xi)_e(T/\text{K} - 300) \quad (14)$$

This allows an empirical value for $(d\sigma/d\xi)_e$ to be determined for ¹³C in CO and ¹⁵N in N₂; they are (-255 ± 50) p.p.m. and (-850 ± 100) p.p.m., respectively. These are compared with the theoretical values of -466.5 ⁹³ and -700.6 p.p.m.,⁹⁴ respectively. The temperature dependence of ¹⁵N shielding in NH₃ at the zero-density limit is $\sigma_0(T) - \sigma_0(300 \text{ K}) = +(6.51 \pm 0.82) \times 10^{-3} (T/\text{K} - 300)$ p.p.m. for $T = 320$ – 380 K.⁹¹ This is very nearly the same as the temperature dependence of ³¹P in PH₃ around 300

⁸⁹ J. Rychlewski and W. T. Raynes, *Mol. Phys.*, 1980, **41**, 843.

⁹⁰ C. J. Jameson, A. K. Jameson, S. Wille, and P. M. Burrell, *J. Chem. Phys.*, 1981, **74**, 853.

⁹¹ C. J. Jameson, A. K. Jameson, S. M. Cohen, H. Parker, D. Oppusunggu, P. M. Burrell, and S. Wille, *J. Chem. Phys.*, 1981, **74**, 1608.

⁹² C. J. Jameson, A. K. Jameson, and S. Wille, *J. Chem. Phys.*, 1981, **74**, 1613.

⁹³ R. M. Stevens and M. Karplus, *J. Chem. Phys.*, 1968, **49**, 1094.

⁹⁴ E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Chem. Phys.*, 1971, **54**, 4269.

K. Both ^{15}N in NH_3 and ^{31}P in PH_3 exhibit an unusual $d\sigma_0/dT > 0$. The ^1H nuclear shielding in NH_3 , however, shows the usual decrease with increasing temperature.⁹¹ $\sigma_0(T) - \sigma_0(300\text{ K}) = -4.08 \times 10^{-4} (T/\text{K} - 300)$ p.p.m. for $T = 300\text{--}370\text{ K}$. ^{19}F in SF_4 under fast exchange at the zero-density limit has a very similar temperature dependence to ^{19}F in SF_6 . For ^{19}F in SF_4 , $\sigma_0(T) - \sigma_0(300\text{ K}) = -1.297 \times 10^{-2} (T/\text{K} - 300) - 0.7047 \times 10^{-3} (T/\text{K} - 300)^2$ p.p.m. for $T = 300\text{--}380\text{ K}$.⁹² For ^{19}F in COF_2 , this function is $-4.332 \times 10^{-3} (T/\text{K} - 300) - 1.3465 \times 10^{-5} (T/\text{K} - 300)^2 + 1.623 \times 10^{-8} (T/\text{K} - 300)^3$ p.p.m. for $T = 230\text{--}380\text{ K}$.⁹²

The temperature dependence of the ^{19}F nuclear shielding in SF_6 has been interpreted in terms of equation (11) truncated after the linear term.⁹⁵ At this level the thermal average of nuclear shielding is given by $\langle \sigma \rangle^T \simeq \sigma_e + B \langle \Delta r \rangle^T$, where

$$B = \sum_i^6 (\partial \sigma / \partial \Delta r_i)_e$$

may be considered as an empirical parameter. The experimentally determined function $\langle \sigma \rangle^T - \langle \sigma \rangle^{300\text{ K}}$ can then be fitted to the function $\langle \sigma \rangle^T - \langle \sigma \rangle^{300\text{ K}} = C + B \langle \Delta r \rangle^T$ where $C = \sigma_e - \langle \sigma \rangle^{300\text{ K}}$. $\langle \Delta r \rangle^T$ has been calculated by two methods; one in terms of the cubic force constant of SF_6 and the other by an approximate method. The value of B obtained, -2200 p.p.m. \AA^{-1} , can be interpreted as being largely due to $(\partial \sigma_{\text{F}_1} / \partial \Delta r_{\text{SF}_1})_e$ since the stretch of the adjacent or opposite S—F bonds should have a much smaller contribution to σ_{F} . This leads to an empirical value of $C = \sigma_e - \langle \sigma \rangle^{300\text{ K}} = 13$ p.p.m. About 90% of the change in nuclear shielding with temperature is due to anharmonic vibration, the remainder is due to rotation.

A different approach to the interpretation of the temperature dependence of nuclear shielding due to vibrational effects is used for the ^{59}Co magnetic shielding in some diamagnetic Co^{III} complexes.⁹⁶ The interpretation is as follows: a temperature increase causes occupation of higher vibrational levels, which causes a decrease in the ligand-field splitting. The effect of temperature on the diamagnetic shielding term is neglected and the effect on the paramagnetic shielding contribution is written in terms of the mean excitation energy approximation, and the ligand-field splitting determines this mean excitation energy. The effect of the ligand type or temperature on $\langle r^{-3} \rangle$ (where r is the distance of the d electron from the cobalt nucleus) is neglected. This approach works reasonably well for the very large ^{59}Co shielding changes that show linear behaviour with the wavelength (related to $1/\Delta E$) of the $^1A_{1g} \rightarrow ^1T_{1g}$ electronic transition under octahedral symmetry.

C. Isotope Effects.—In this review we are only interested in intrinsic isotope effects on nuclear magnetic shielding. Intrinsic isotope effects are those which are characteristic of a particular isolated molecule. Thus, one should study rigid systems, otherwise one cannot separate the intrinsic isotope effect from the isotope effects on chemical or conformational equilibria. Secondly, one should study isotope effects in the gas phase when at all possible, otherwise one cannot separate the intrinsic isotope effect from solvent effects, which may be slightly different on each isotopomer. This can be very pronounced when H_2O is used as a solvent, since

⁹⁵ C. J. Jameson, *Mol. Phys.*, 1980, **40**, 999.

⁹⁶ N. Juranic, *J. Chem. Phys.*, 1981, **74**, 3690.

the structure of liquid H₂O is slightly different from that of liquid D₂O. For example, comparison of resonance frequencies of deuteriated species dissolved in D₂O with that of normal species dissolved in H₂O may include substantial solvent-related shifts. A common experimental method is to observe a neat mixture of the isotopomers, or a solution of the isotopomers in a mixture of isotopomeric solvents. If the measured isotope shift is found to be independent of the variation of the relative concentrations of isotopomers, the isotope effect on the structure of the solvent is probably not significant. However, this does not preclude extrinsic contributions to isotope shifts. The average environment of a nucleus in a molecule with an H atom will necessarily be different from a nucleus in a molecule with a D atom. The wider excursions of the H atom compared to those of the D atom affect the interactions of the observed molecules with the solvent. This contribution to isotope effects was first discussed in 1959.⁹⁷ With this in mind, we now summarize isotope-induced shifts published during this reporting period. All of the data were obtained in condensed phases under various conditions, so the observed shift is not necessarily entirely due to the intrinsic isotope effect on nuclear shielding.

In Volume 10 we reviewed the effect of structure on the isotope effect. There is new work along these lines on ketones and alcohols.⁹⁸ Data published during this period support the previous generalizations. Once again it is found that the isotope shift depends on bond order, so that heavy-oxygen-induced shifts of ¹³C for C=O are larger than those for C—O⁹⁹ and ¹⁵N-induced shifts of ¹³C for C≡N are much larger than those for C—N.¹⁰⁰ The isotope shift depends on hybridization,⁹⁸ there is some attenuation in the presence of conjugation,^{101, 98} but there is probably no steric effect on the magnitude of isotope effects.⁹⁹ In alcohols the magnitude of isotope effects on shielding increases in the order primary, secondary, tertiary,^{98, 99} but this may be due to a solvent effect. Solvent effects are suspected in some apparent isotope shifts that have been reported.^{98, 102, 103} Once again additivity of isotope effects has been verified in cases of multiple labelling^{99, 101, 104} and the magnitude of the shift decreases with remoteness of isotopic substitution from the observed nucleus.^{101, 105} Deuterium-induced isotope shifts in the ¹³C shielding of cycloalkanes containing from 3 to 7 carbons have allowed Aydin and Gunther¹⁰⁵ to study this trend systematically; isotope-induced shifts over 3 and 4 bonds are observed. With the available empirical data on the dependence of isotope shifts with structure it has become, and will continue to be, useful as a tool in assigning spectra, analysing products of a reaction, *etc.* The oxygen isotope effect on ³¹P nuclear shielding has provided biochemists with an important new tool to study molecules involved in phosphate reactions.^{106–108} It has also found some use in the classical *vs.*

⁹⁷ H. S. Gutowsky, *J. Chem. Phys.*, 1959, **31**, 1683.

⁹⁸ J. Diakur, T. T. Nakashima, and J. C. Vederas, *Can. J. Chem.*, 1980, **58**, 1311.

⁹⁹ J. M. Riskey and R. L. Van Etten, *J. Am. Chem. Soc.*, 1980, **102**, 6699.

¹⁰⁰ R. E. Wasylshen, D. H. Muldrew, and K. J. Friesen, *J. Magn. Reson.*, 1980, **41**, 341.

¹⁰¹ R. N. Moore, J. Diakur, T. T. Nakashima, S. L. McLaren, and J. C. Vederas, *J. Chem. Soc., Chem. Commun.*, 1981, 501.

¹⁰² T. Yonemitsu and K. Kubo, *J. Chem. Soc., Chem. Commun.*, 1981, 309.

¹⁰³ P. E. Pfeffer, F. W. Parrish, and J. Unruh, *Carbohydr. Res.*, 1980, **84**, 13.

¹⁰⁴ I. M. Ismail, S. J. S. Kerrison, and P. J. Sadler, *J. Chem. Soc., Chem. Commun.*, 1980, 1175.

¹⁰⁵ R. Aydin and H. Gunther, *J. Am. Chem. Soc.*, 1981, **103**, 1301.

¹⁰⁶ M. R. Webb and D. R. Trentham, *J. Biol. Chem.*, 1980, **255**, 1775.

¹⁰⁷ S. L. Buchwald and J. R. Knowles, *J. Am. Chem. Soc.*, 1980, **102**, 6601.

¹⁰⁸ D. G. Gorenstein and R. Rowell, *J. Am. Chem. Soc.*, 1980, **102**, 6165.

non-classical structure assignment for carbocations. Servis and Shue have measured isotope shifts in a large number of carbocations.¹⁰⁹ They find that the α -isotope shifts (one bond removed) are about the same as in the precursors of the cations and about the same for all cations. On the other hand, the β -isotope shifts (two bonds away) vary in magnitude and sign and may be useful as an identifier. The presence of a huge isotope shift (1—100 p.p.m.) with a large temperature dependence is of course a clear indication of an equilibrium isotope effect and is proof for the existence of a rapidly equilibrating pair of classical ions.¹¹⁰ On the other hand, a small isotope effect, that is of the same order as other intrinsic isotope effects, indicates a static non-classical structure.¹¹⁰

An interesting application of the intrinsic isotope effect that has arisen, based on the dependence on structure, is the use of the oxygen isotope effect on phosphorus to determine absolute configuration. The *R*-enantiomer of an inorganic phosphate gives rise to ¹⁸O bridging, whereas the *S*-enantiomer gives rise to a non-bridging ¹⁸O when incorporated into ATP. Since the ³¹P isotope shifts for bridging and non-bridging ¹⁸O atoms are, respectively, ~ 0.021 p.p.m. vs. ~ 0.036 p.p.m., it is possible to distinguish unequivocally between *R*- and *S*-enantiomers of the inorganic phosphate.

Although most of the reported isotope effects are due to ²H or ¹⁸O substitution on ¹³C, there are also data on ³⁷C/³⁵Cl and ⁸¹Br/⁷⁹Br-induced shifts on ¹⁹⁵Pt shielding,¹⁰⁴ which are 0.167 p.p.m. and 0.028 p.p.m. per isotope, respectively; also ²³⁸U/²³⁵U-induced shifts in the ¹⁹F shielding of UF₆.¹¹¹

D. Intermolecular Effects.—There is a recent review on the effects of intermolecular interactions on nuclear shielding, summarizing the pair interactions that have been studied in the gas phase and also some general observations and interpretations of these data.⁸⁸ The ¹⁵N shielding in N₂ interacting with N₂,⁹⁰ ¹⁹F shielding in SF₄ and COF₂ gas,⁹² and ¹⁵N and ¹H shielding in NH₃ gas⁹¹ have been studied as a function of density and temperature. In the virial expansion of nuclear shielding in powers of density, $\sigma = \sigma_0 + \sigma_1\rho + \sigma_2\rho^2 + \dots$, σ_1 gives a measure of the effect of pairwise interactions on nuclear shielding. Values of σ_1 recently reported are $-(4.26 \pm 0.13) \times 10^{-3}$ p.p.m. amagat⁻¹* for ¹⁵N in N₂ interacting with N₂,⁹⁰ $-(8.35 \pm 1.5) \times 10^{-3}$ p.p.m. amagat⁻¹ for ¹⁹F in SF₄ interacting with SF₄,⁹² $-(1.987 \pm 0.14) \times 10^{-2} + 8.907 \times 10^{-5}$ (T/K - 300) $- 7.983 \times 10^{-7}$ (T/K - 300)² p.p.m. amagat⁻¹ for ¹⁹F in COF₂ interacting with COF₂,⁹² -0.041 ± 0.002 p.p.m. amagat⁻¹ and -0.0032 ± 0.0001 p.p.m. amagat⁻¹, respectively, for ¹⁵N and ¹H in NH₃ interacting with NH₃.⁹¹ None of these values have been corrected for bulk susceptibility effects.

Some experimental data in condensed phases have been reported. ¹³C shifts of small probe molecules adsorbed on a solid surface (zeolites) have nearly the same magnitude as the gas-to-liquid shift.¹¹² The ¹⁷O nuclear shielding in liquid and solid CO has been studied over a range of temperatures.¹¹³ The ¹H shielding in biphenyl

¹⁰⁹ K. L. Servis and F. F. Shue, *J. Am. Chem. Soc.*, 1980, **102**, 7233.

¹¹⁰ M. Saunders and M. R. Kates, *J. Am. Chem. Soc.*, 1980, **102**, 6867.

¹¹¹ E. V. Iorga, A. G. Kucheryaev, and V. A. Lebedev, *Koord. Khim.*, 1981, **7**, 145.

¹¹² D. Michel, W. Meiler, A. Gutsche, and A. Wronkowski, *Z. Phys. Chem. (Leipzig)*, 1980, **261**, 953.

¹¹³ F. Li, Ph.D. Thesis, Univ. Florida, Gainesville, USA, *Diss. Abstr. Int. B*, 1980, **41**, 253.

* 1 amagat = 2.687×10^{19} molecules cm⁻³.

in hexane has been studied as a function of pressure (up to 2000 kg cm⁻²).¹¹⁴ The *ortho*-proton shift is interpreted in terms of the decrease in dihedral angle between the rings under increased pressure. The large temperature dependence of ¹³C shielding in liquid alcohols (methanol, ethanol, and isopropanol) is smaller than that in TMS. By comparison both with temperature coefficients of compounds not involving hydrogen bonding and with protonation studies, it is inferred that the temperature dependence of the ¹³C shielding in liquid alcohols is not mainly due to a reduction in hydrogen bonding as the temperature is raised, but largely due to a change in the van der Waals forces.¹¹⁵ Intermolecular effects on ³¹P shielding have been in the literature for decades. Only recently have the solvent effects on the ³¹P shielding in nucleotides been considered as possibly affecting attempts to relate ³¹P shielding changes to the conformational state of the polynucleotides.¹¹⁶ Solvent shifts of the order of 1–3 p.p.m., as a function of the mol fraction of solvent, are observed in the ³¹P shielding of 3',5'-cAMP. The authors conclude that these observations render questionable any interpretation of ³¹P chemical shifts that are attributed solely to changes in the conformation of phosphodiester bonds.^{117, 118} σ_1 values of -0.0023 to -0.266 p.p.m. amagat⁻¹ for ³¹P in the gas phase and 21.1–93.0 p.p.m. shifts of ³¹P in solutions of P₄ in various non-polar solvents clearly indicate that solvent effects for ³¹P cannot be neglected.⁸⁸ Typical magnitudes of intermolecular effects on shielding for a variety of nuclei have been summarized.¹¹⁹ In any application using changes in nuclear shielding, one should consider making corrections for concentration and temperature effects if the shifts being observed are of the same order of magnitude or smaller.

Several quantum mechanical calculations of solvent effects on nuclear magnetic shielding have been published during this review period. *Ab initio* calculations of the shielding tensors of ¹H and ¹³C nuclei in formate ion and two formate–Ca adducts show that polarization of the formate anion by Ca²⁺ ions is important in determining the magnitudes of the components of the shielding tensors.¹²⁰ *Ab initio* calculations of the ¹H, ¹³C, and ¹⁵N nuclei of imidazole in the isolated and hydrated molecules indicate that hydrogen bonds produce large changes in the ¹⁵N shielding and the hydrogen-bonded proton, as expected, and also measureable shifts in the shielding of the carbon nuclei.¹²¹ Semi-empirical calculations of solvent effects have been undertaken by Webb *et al.*^{122–124} These calculations employ the 'solvaton' model of Germer.¹²⁵ According to this model, a solute molecule induces a number of charges, the solvatons, in a solvent of dielectric constant ϵ , one solvaton is associated with each atom of the solute and its charge is equal in magnitude but opposite in sign to the net charge of the atom to which it is attached, and there are

¹¹⁴ H. Yamada, Y. Miyata, and T. Kinugasa, *J. Magn. Reson.*, 1980, **39**, 309.

¹¹⁵ K. Jackowski and W. T. Raynes, *Org. Magn. Reson.*, 1980, **13**, 438.

¹¹⁶ D. B. Lerner and D. R. Kearns, *J. Am. Chem. Soc.*, 1980, **102**, 7611.

¹¹⁷ D. G. Gorenstein, J. B. Findlay, R. K. Momii, B. A. Luxon, and D. Kar, *Biochemistry*, 1976, **15**, 3796.

¹¹⁸ D. G. Gorenstein, A. M. Wyrwicz, and J. Bode, *J. Am. Chem. Soc.*, 1976, **98**, 2308.

¹¹⁹ C. J. Jameson, A. K. Jameson, and P. M. Burrell, *J. Chem. Phys.*, 1980, **73**, 6013.

¹²⁰ C. Giessner-Prettre and A. Pullman, *Chem. Phys. Lett.*, 1981, **77**, 444.

¹²¹ F. Ribas-Prado, C. Giessner-Prettre, and B. Pullman, *Org. Magn. Reson.*, 1981, **16**, 103.

¹²² M. Jallali-Heravi and G. A. Webb, *Org. Magn. Reson.*, 1980, **13**, 116.

¹²³ M. Jallali-Heravi, B. N. Lamphun, G. A. Webb, I. Ando, M. Kondo, and S. Watanabe, *Org. Magn. Reson.*, 1980, **14**, 92.

¹²⁴ I. Ando and G. A. Webb, *Org. Magn. Reson.*, 1981, **15**, 111.

¹²⁵ H. A. Germer, *Theor. Chim. Acta*, 1974, **34**, 145.

no interactions between the solvatons. With this model, additional terms in the Hamiltonian containing the induced solvaton charge, and its separation from nuclei and electrons are used to evaluate contributions which are approximated by terms involving the dielectric constant. In this way it is comparable to the reaction field model of solvent effects on shielding. With this model solvent effects on ^{13}C , ^{17}O , and ^{19}F shielding in a very large number of solute-solvent combinations have been calculated.^{122–124} Empirical calculations of ^{13}C shifts in adsorbed molecules have been carried out by assuming some probable structures for the adsorption complexes.¹²⁶

E. Absolute Shielding Scales.—In order to be able to compare theoretical calculations with experiment, nuclear shielding data on the isolated molecule are necessary. By using results of density and temperature studies, ^{19}F n.m.r. frequencies measured in twenty gases of known densities have been reduced to the zero-density limit at 300 K and from these, differences in shielding between rovibrationally-averaged isolated molecules at this temperature are obtained.¹¹⁹ The results for six molecules, previously reported,¹²⁷ are in excellent agreement. The absolute rovibrationally-averaged shielding, σ_0 , of the isolated molecule SiF_4 , as a secondary reference based on the spin-rotation constant in HF as a primary reference, is obtained making all the appropriate corrections.¹²⁷ Thus, the measured shielding differences between the various molecules and SiF_4 in the zero-density limit can be converted to absolute shielding. The ^{19}F shielding scale is shown in

Table 5 ^{19}F absolute shielding (σ_0)¹¹⁹ based on HF as primary reference molecule (410.0 p.p.m.)¹²⁷ at 300 K

Compound	σ_0 , p.p.m.
ClF	637.1
CH ₃ F	471.0
SiF ₄	363.2
BF ₃	327.2
POF ₃	288.2
CF ₃ CF ₃	283.0
CF ₃ CF ₂ Cl	281.9
CF ₃ H	274.1
CF ₂ ClCF ₃	269.7
CF ₂ ClH	267.3
CF ₄	259.0
CF ₃ CH ₃	258.7
PF ₃	228.3
CF ₃ Cl	224.4
COF ₂	221.6
CF ₃ Br	213.8
CF ₃ Cl	202.6
SF ₆	139.6
SF ₄ (av)	118.7
NF ₃	50.3
F ₂	-232.8

¹²⁶ D. Deininger, D. Michel, and D. Heidrich, *Surf. Sci.*, 1980, **100**, 541.

¹²⁷ D. K. Hindermann and C. D. Cornwell, *J. Chem. Phys.*, 1968, **48**, 4148.

Table 5. These values are based on $\sigma_0(\text{SiF}_4) = 363.2$ p.p.m., which is based on $\sigma_0(\text{HF}) = 410.0$ p.p.m.

A similar procedure has been applied to a few ^{15}N systems, thus establishing the nitrogen-shielding scale.¹²⁸ The corrections of the type made by Hinderman and Cornwell¹²⁷ were not carried out on the primary reference molecule (NH_3), however. Nitrogen shielding in NH_3 is taken to be 265.54 p.p.m.,¹²⁹ and N_2 is chosen as the secondary reference. The measured shielding differences between other nuclear environments and N_2 in the zero-density limit provide the values shown in Table 6.

The absolute shieldings for alkali-metal nuclei in diatomic molecules are now available. Huber *et al.* have performed highly precise measurements of nuclear magnetic dipole moments in alkali-metal molecules using atom-molecule exchange optical pumping.¹³⁰ A comparison with the measurement of nuclear moments in free alkali-metal atoms gives the nuclear magnetic shielding differences between atoms and molecules. These are $\sigma(\text{M}_2) - \sigma(\text{M}) = 29 \pm 16$ p.p.m. for ^{23}Na , 99 ± 85 p.p.m. for ^{39}K , 120 ± 17 for ^{87}Rb , and 221 ± 14 p.p.m. for ^{133}Cs . From the theoretical diamagnetic shielding values for the free atoms¹⁰ it is possible to obtain absolute shielding values for these nuclei in the isolated diatomic molecules. They are $\sigma_0 = 658 \pm 16$ p.p.m. in $^{23}\text{Na}_2$, 1428 ± 85 p.p.m. in $^{39}\text{K}_2$, 3487 ± 17 p.p.m. in $^{87}\text{Rb}_2$, and 6001 ± 14 p.p.m. in $^{133}\text{Cs}_2$.

The absolute shielding scale for ^{71}Ga has been established.¹³¹ The ratio of the resonance frequencies of ^{71}Ga to ^2H in solution were measured and extrapolated to a vanishing Ga salt concentration. From this procedure the resonance frequency of the $\text{Ga}(\text{D}_2\text{O})_6^{3+}$ species at infinite dilution relative to that of ^2H in pure D_2O is obtained: 1.986 668 9 (3). Using the known ratio of ^2H to ^1H frequencies in water and the measured magnetic moment of the proton in water¹³² the nuclear moment of ^{71}Ga in $\text{Ga}(\text{D}_2\text{O})_6^{3+}$ at infinite dilution is obtained. The nuclear magnetic moment of ^{71}Ga in the free atom is known from atomic-beam magnetic resonance experiments. Thus, Kodweiss *et al.* have obtained the ^{71}Ga nuclear magnetic shielding difference between the $\text{Ga}(\text{D}_2\text{O})_6^{3+}$ species in infinitely dilute aqueous solution and the free Ga atom: -800 ± 45 p.p.m. The nuclear magnetic shielding of the free Ga atom is 2638.57 p.p.m. from theoretical calculations.¹⁰ Thus, the

Table 6 ^{15}N absolute shielding (σ_0)¹²⁸ based on NH_3 ($\sigma_0 = 264.54$ p.p.m.)¹²⁹ at 300 K

Compound	σ_0 , p.p.m.
N_2	-61.6
NNO	99.5
$\bar{\text{N}}\text{NO}$	11.3
$\text{N}\bar{\text{H}}_3$	264.54
HCN	-20.4

¹²⁸ C. J. Jameson, A. K. Jameson, D. Oppusunggu, S. Wille, P. M. Burrell, and J. Mason, *J. Chem. Phys.*, 1981, **74**, 81.

¹²⁹ S. G. Kukolich, *J. Am. Chem. Soc.*, 1975, **97**, 5704.

¹³⁰ R. Huber, M. Knapp, F. Koenig, H. Reinhard, and H. G. Weber, *Z. Phys. A*, 1980, **296**, 95.

¹³¹ J. Kodweiss, O. Lutz, W. Messner, K. R. Mohn, A. Nolle, B. Stutz, and D. Zepf, *J. Magn. Reson.*, 1981, **43**, 495.

¹³² E. R. Cohen and B. N. Taylor, *J. Phys. Ref. Data*, 1973, **2**, 663.

absolute shielding for ^{71}Ga in $\text{Ga}(\text{D}_2\text{O})_6^{3+}$ in infinitely dilute aqueous solution is 1839 ± 45 p.p.m. Based on this, the absolute shielding of some other Ga ions (GaI_4^- , GaBr_4^- , GaCl_4^- , and GaH_4^-) are 2330, 1770, 1580, and 1140 p.p.m., respectively. Unfortunately the authors only provided a figure, rather than a table of numbers, for the shielding scale including a variety of gallium chemical environments.¹³¹