1

Theoretical and Physical Aspects of Nuclear Shielding

BY CYNTHIA J. JAMESON

1 Theoretical Aspects of Nuclear Shielding

A. *Ab Initio* Calculations. – As discussed in the previous volume of this series, calculations of shielding of nuclei of high atomic number have to be done with a relativistic theory. The detailed results of relativistic random phase approximation calculations described in a paper reviewed earlier[1] are provided in tables for atoms and ions with closed 1*s*, 2*p*, 3*p*, 3*d*, 4*p*, 4*d*, and 5*p* shells. The tables include all ions in these sequences with nuclear charge up to $Z = 56$ and a representative selection of ions with $56 < Z \leqslant 92$.[2]

Further applications are reported using the Individual Gauge for Localized (molecular) Orbitals (IGLO) method described earlier,[3] which is essentially a coupled Hartree–Fock type of calculation but one in which different gauge origins are chosen for different localized molecular orbitals.[4] The use of localized molecular orbitals allows the contributions to the total shielding to be partitioned into orbital contributions, so that the specific role played by the lone pairs on the atom in question and orbitals centred on neighbouring atoms can be discerned. In the most recent application, all shielding tensors are calculated with fairly good basis sets for N_2, HCN, CO, C_2H_2, CO_2, NNO, OF_2, O_3, and FNO molecules. There is still some tendency to overestimate the paramagnetic term in several instances.

In addition to the values calculated at r_e, shown in Tables 1 and 2, shielding values have been calculated for configurations slightly displaced from the equilibrium one, from which one can calculate derivatives of nuclear shielding. For N_2 and CO the nuclear shielding is calculated at two internuclear separations r_0 and r_e, which values the authors unfortunately failed to include in their tables. For CO $r_0 = 1.1308$ and $r_e = 1.1283$ Å, so we may calculate $(\partial\sigma^C/\partial\Delta r)_e = -600$ p.p.m. Å^{-1} (which may be compared with the value obtained from temperature dependent chemical shift measurements in the gas phase taken to the zero pressure

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[1] D. Kolb, W. R. Johnson, and P. Shorer, *Phys. Rev. A*, 1982, **26**, 19.

[2] W. R. Johnson, D. Kolb, and K. N. Huang, *At. Data Nucl. Data Tables*, 1983, **28**, 333.

[3] M. Schindler and W. Kutzelnigg, *J. Chem. Phys.*, 1982, **76**, 1919.

[4] M. Schindler and W. Kutzelnigg, *Mol. Phys.*, 1983, **48**, 781.

Table 1 *Results of theoretical calculations of nuclear shielding in linear molecules,*[4] *compared with experiment*

Molecule	*Nucleus*	$\sigma_{\parallel}$	$\sigma_{\perp}$	$\bar{\sigma}$	$\bar{\sigma}$	$\Delta\sigma$	$\Delta\sigma$
			theoretical		*expt.*	*theor.*	*expt.*
N_2	N	338.8	−332.0	−108.4	−101 ± 20[a], −102[b], −61.6[c]	670.8	657 ± 20[a], 630 ± 28[d]
CO	C	271.0	−171.3	−23.8	3.20 ± 0.27[e]	442.2	~400[f], 384 ± 10[g], 406 ± 30[h]
	O	410.5	−331.5	−84.1	−16 ± 20[b], −61 ± 5[i]	742.0	680[j]
HCN	H	39.17	23.55	28.76	28.32[k]	15.62	
	C	276.9	−29.1	72.9	77.23[l]	306.0	280 ± 30[m]
	N	336.9	−237.4	−46.0	−20.4[c]	574.4	577 ± 20[i]
NNO	N (end)	342.0	−50.62	80.25	105 ± 12[n], 99.5[c]	392.62	376 ± 12[n]
	N (cen)	349.82	−240.56	−43.77	−24 ± 31[o], −44 ± 15[n], 11.3[c]	590.38	508 ± 10[p]
	O	418.15	45.56	169.76		372.59	
HC≡CH	H	41.01	24.14	29.76	29.26[q]	16.87	22.2 ± 2[r]
	C	278.6	34.8	116.1	120 ± 10[j]	243.8	240 ± 5[s]
CO_2	C	281.7	−64.8	50.7	60.9[t]	346.5	334.9[t]
	O	414.4	128.3	223.7		286.2	

[a] S. I. Chan, M. R. Baker, and N. F. Ramsey, *Phys. Rev. A*, 1964, **136**, 1224; [b] T. D. Gierke and W. H. Flygare, *J. Am. Chem. Soc.*, 1972, **94**, 7277; [c] C. J. Jameson, A. K. Jameson, D. Oppusunggu, S. Wille, P. M. Burrell, and J. Mason, *J. Chem. Phys.*, 1981, **74**, 81; [d] L. M. Ishol and T. A. Scott, *J. Magn. Reson.*, 1977, **27**, 23; [e] D. B. Neumann and J. W. Moskowitz, *J. Chem. Phys.*, 1969, **50**, 2216; [f] T. M. Duncan, J. T. Yates, and R. W. Vaughan, *ibid.*, 1979, **71**, 3129; [g] I. Ozier, L. M. Crapo, and N. F. Ramsey, *ibid.*, 1968, **49**, 2314; [h] A. A. V. Gibson and T. A. Scott, *J. Magn. Reson.*, 1977, **27**, 29; [i] ref. 4; [j] B. R. Appleman and B. P. Dailey, *Adv. Magn. Reson.*, 1974, **7**, 231; [k] W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, 1958, **28**, 601; [l] R. M. Garvey and F. C. DeLucia, *J. Mol. Spectrosc.* 1974, **50**, 38; [m] F. Millett and B. P. Dailey, *J. Chem. Phys.*, 1971, **54**, 5434; [n] J. M. L. J. Reinartz, W. L. Meerts, and A. Dymanus, *Chem. Phys.*, 1978, **31**, 19; [o] K. H. Casleton and S. K. Kukolich, *J. Chem. Phys.*, 1975, **62**, 2696; [p] P. K. Bhattacharyya and B. P. Dailey, *ibid.*, 1973, **59**, 5820; [q] S. Mohanty, *Mol. Phys.*, 1973, **25**, 1173; [r] S. Mohanty, *Chem. Phys. Lett.*, 1973, **18**, 581; [s] K. W. Zilm, R. T. Conlin, D. M. Grant, and J. Michl, *J. Am. Chem. Soc.*, 1980, **102**, 6672; [t] K. Jackowski and W. T. Raynes, *Mol. Phys.*, 1977, **34**, 465.

Table 2 *Results of theoretical calculations of nuclear shielding in bent triatomic molecules.*[4] *The molecular plane is as shown*

Molecule	*Nucleus*	σ_{xx}	σ_{yy}	σ_{zz}	$\bar{\sigma}$	$\bar{\sigma}$
			theoretical			*expt.*
O_3 (yz)	O(end)	−139	−5564	−3037	−2914	
	O(cen)	139	−6332	−2258	−2817	
FNO (xy)	F	−957.6	339.4	−175.1	−264.4	−290.3[a]
	N	49.9	−820.4	−162.1	−310.9	−247.8 ± 5[b,c], −236.8 ± 10
	O	−992.8	−1071.1	90.4	−657.8	
OF_2 (xy)	F	368.3	162.7	−473.7	19.1	
(C_2 along y)	O	−401.8	−641.4	−311.7	−451.7	

[a] J. R. Holmes, B. B. Stewart, and J. S. MacKenzie, *J. Chem. Phys.*, 1962, **37**, 2728; [b] A. M. Qureshi, J. A. Ripmeester, and F. Aubke, *Can. J. Chem.*, 169, **47**, 4247; [c] L. O. Andersson, J. Mason, and W. Van Bronswizk, *J. Chem. Soc. A*, 1970, 296.

limit: -225 ± 45 p.p.m. $Å^{-1}$)[5] and $(\partial\sigma^{O}/\partial\Delta r)_e = -1200$ p.p.m. $Å^{-1}$. A similar value of $r_0 - r_e$ for N_2 gives $(\partial\sigma^{N}/\partial\Delta r)_e = -1000$ p.p.m. $Å^{-1}$ (which may be compared with -775 ± 90 p.p.m. $Å^{-1}$ from gas phase measurements[5]). For ozone, the variation of the calculated ^{17}O shielding with bond length the bond angle is unusually large $(\partial\sigma^{O}/\partial\Delta r)_e = -2.01 \times 10^4$ and -1.89×10^4 p.p.m. $Å^{-1}$ for the end and central oxygen respectively. The variation with angle is not obtained at the equilibrium bond length, nevertheless, $(\partial\sigma^{O}/\partial\Delta\alpha) = -600$ and -1750 p.p.m. rad^{-1} at $r = 1.2$ Å for the end and central oxygen respectively. The authors also note that in O_3 the paramagnetic contributions come mainly from the lone pairs on the respective oxygen atoms, unlike CO_2 and NNO in which they result mainly from the bonds interacting with the antibonding π^* and only a little from the lone pairs. Ozone appears to be an exceptional molecule. Experimental data in the zero pressure limit together with a good absolute shielding scale for ^{17}O are essential in order to check the predictions of the theory. For ^1H nuclei and for some ^{13}C nuclei in these molecules, agreement with experimental shielding is quite good. However, for others, discrepancies between calculated and experimental values indicate that the paramagnetic contributions tend to be overemphasized by the theory.

The coupled Hartree–Fock and the self-consistent configuration interaction (SCF-CI) methods have been applied to the H_2O, H_3O^+, and OH^- systems.[6] In the SCF-CI scheme,[7] both the unperturbed zeroth order wavefunction and the first order wavefunction are expanded in all singly and doubly excited singlet configuration state functions. ^1H shieldings in

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

[6] H. Fukui, K. Miura, and F. Tada, *J. Chem. Phys.*, 1983, **79**, 6112.

[7] H. Fukui, *Int. J. Quantum Chem.*, 1983, **23**, 633.

H_2O, H_3O^+, and OH^- are respectively 29.3, 20.7, and 41.4 p.p.m. with the SCF-CI method; ^{17}O shielding values are respectively 295.8, 330.4, and 231.1 p.p.m. The CHF method gives somewhat smaller shieldings for both ^1H and ^{17}O. Theory predicts that the ^1H and ^{17}O resonance signals shift in opposite directions in the series H_3O^+, H_2O, OH^-. Comparison with experiment is not straightforward since no gas-phase data in the zero-pressure limit are available, nor are there any spin-rotation constants measured in a molecular beam or in the gas phase. Condensed phase chemical shifts cannot easily be corrected for H_3O^+–solvent (or OH^-–solvent) interactions and for the contributions from counterions and H_2O molecules in the hydration sphere. From the spin-rotation constant, ^1H shielding in the H_2O molecule is 30.052 ± 0.015 p.p.m. With an estimated gas-to-liquid shift, the approximate value for ^{17}O shielding in the H_2O molecule is 334 ± 15 p.p.m.[8] These are to be compared with the theoretical values of 29.3 p.p.m. and 295.8 p.p.m., respectively. Other calculated values for shielding in H_2O were reviewed in Volume 12 of this series. In this connection, P. Lazzeretti has kindly brought attention to this reporter's error in the comparison of the off-diagonal components for ^1H shielding in that volume. When the different directions of the axes used by the authors are properly taken into consideration, after the transposition and change in sign, the two sets of numbers can be compared. The σ_{xz} and σ_{zx} components are -8.97 and -10.12 p.p.m. by Höller and Lischka's calculations,[9] to be compared with -8.872 and -10.247 p.p.m. by Lazzeretti and Zanasi.[10] The agreement is excellent.

Another CI approach to the calculation of nuclear shielding involves a sum over states (SOS-CI).[11] This perturbation technique considers all singly excited configurations and, at the same time, introduces doubly excited configurations in a restricted way. Application of this method to several molecules gives mixed results.[12,13]

For the compounds HN=NH, HP=NH, HP=PH and HAs=AsH, there is a strong geometrical dependence of the paramagnetic term in the shielding of all nuclei.[13] The N or P nucleus in the *trans* isomer is less shielded than in the *cis*. The ^1H in the *trans* is less shielded than in the *cis* isomer for hydrogens bonded to N; the reverse is true for hydrogens bonded to P. In all cases, the N and P nuclei are deshielded relative to the bare nucleus. Unfortunately, there are no experimental values to compare with. Related molecules with various substituents replacing H are known; for example, $(SiMe_3)_3C{-}As{=}As{-}C(SiMe_3)_3$ is a stable molecule. In the diazenes, diphosphenes, and phosphazenes, (RN=NR′, RP=PR′, RN=PR′) the N and P nuclei are drastically deshielded relative to NH_3

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[8] W. T. Raynes, Vol. 8 of this series.

[9] R. Höller and H. Lischka, *Mol. Phys.*, 1980, **41**, 1017.

[10] P. Lazzeretti and R. Zanasi, *J. Chem. Phys.*, 1978, **68**, 1523.

[11] H. Nakatsuji, *J. Chem. Phys.*, 1974, **61**, 3728.

[12] V. Galasso, *THEOCHEM*, 1983, **10**, 201.

[13] V. Galasso, *Chem. Phys.*, 1984, **83**, 407.

and PH_3, respectively, which agrees qualitatively with the theoretical results. However, observed relative shieldings in *cis* and *trans* isomers for R, R′ ≠ H go in the opposite direction to that predicted by the calculations. The authors attribute this to substituent effects.

The effect of an external electric field on nuclear shielding is usually calculated in a multiple perturbation scheme, involving the magnetic field, the nuclear moment, and the electric field.[14,15] A simple approach to this problem is suggested, in which only the paramagnetic shielding term is included.[16] For nucleus A in a diatomic molecule AB at internuclear separation R, with the internuclear vector along the direction of the electric field, E:

$$\sigma_A^p(R, E) = \sigma_A^{(0)} + \sigma_A^{(1)}E + (1/2!)\sigma_A^{(2)}E^2 + (1/3!)\sigma_A^{(3)}E^3 + \ldots \quad (1)$$

in which

$$\sigma_A^{(0)}(R) = \mathrm{const}(ab) \quad (2)$$

$$\sigma_A^{(1)}(R) = \mathrm{const}[-ac + \mu_1(R)b] \quad (3)$$

$$\sigma_A^{(2)}(R) = \mathrm{const}[-a(1/e^2Z_A)(\mathrm{d}\mu_1/\mathrm{d}R) - 2\mu_1(R)c + \mu_2(R)b] \quad (4)$$

where

$$a = \mu_0(R) - eZ_BR \quad (5)$$

$$b = Z_B/R^2 + (1/e^2Z_A)(\mathrm{d}W_0/\mathrm{d}R) \quad (6)$$

$$c = (1/e^2Z_A)(\mathrm{d}\mu_0/\mathrm{d}R) + (1/e) \quad (7)$$

and const stands for a factor involving only fundamental constants. Note that all of the contributions are expressible in terms of $\mathrm{d}W_0/\mathrm{d}R$, (the derivative of the adiabatic potential in the absence of an electric field), the dipole moment μ of the molecule, and its derivatives with respect to bond extension:

$$\mu(R, E) = \mu_0(R) + \mu_1(R)E + (1/2!)\mu_2(R)E^2 + (1/3!)\mu_3(R)E^3 + \ldots \quad (8)$$

Here, μ_0, μ_1, and μ_2 can be identified as the permanent dipole moment in the absence of the field, the longitudinal polarizability ($\alpha_\parallel$), and the longitudinal first and second hyperpolarizabilities of the molecule in a field along the direction of the internuclear axis, and $\mathrm{d}\mu_0/\mathrm{d}R$, $\mathrm{d}\mu_1/\mathrm{d}R$, and $\mathrm{d}\mu_2/\mathrm{d}R$, are the derivatives with respect to bond extension.

The equations (1)–(4) depend on the adoption of a magnetic vector potential with the gauge origin at the centre of gravity of the electron cloud of the molecule. Equation (2) is a generalized form of the formula of Chan and Das.[17] The advantage of the simple approach is that the effects of an

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[14] B. Day and A. D. Buckingham, *Mol. Phys.* 1976, **32**, 343.
[15] A. J. Sadlej and W. T. Raynes, *Mol. Phys.*, 1978, **35**, 101.
[16] M. I. Volodicheva and T. K. Rebane, *Theor, Exp. Chem.*, 1983, **19**, 357.
[17] S. I. Chan and T. P. Das, *J. Chem. Phys.*, 1962, **37**, 1527.

external electric field on the nuclear shielding are expressed entirely in terms of other molecular properties, which are functions of the internuclear separation. Further equations (1)–(4) can be expressed in terms of $R_e(E)$, (the equilibrium internuclear distance itself depends on the electric field) and the derivatives $(d\mu_0/dR)_{R_e(0)}$ and $(d^2W_0/dR^2)_{R_e(0)}$, quantities which may be obtained directly from experiment or from *ab initio* calculations which do not involve the perturbation by external fields. This method is applied by the authors to ^1H in H_2, HF, HCl, HBr, and HI and the agreement with experiment is reasonable for the paramagnetic terms in the absence of an electric field: -6.3, -86.6, -119.5, -226.8, -305 p.p.m. (calculated),[16] to be compared with -5.8, -79.7, -110.9, -214.0, -283 p.p.m. (experimental).[18] There are no experimental values for the shielding terms which are linear and quadratic in the electric field, which are also calculated. It should be noted that this method calculates only the paramagnetic term. There are contributions due to the effects of the electric field on the diamagnetic term in the shielding as well.

Maps of nuclear magnetic shielding density, showing the values of the nuclear shielding density function in a plane (not necessarily a molecular plane), especially in a 3-D perspective view, permit visualization of the regions of molecular space where shielding or deshielding effects arise.[19] Such maps are plotted for ^1H shielding in benzene molecule, calculated by the CHF method, using a very large basis set (198 contracted gaussians).[20] The pictures unequivocally demonstrate that the immediate region surrounding a proton is largely responsible for its nuclear shielding. Deshielding effects arise almost entirely from the nearest carbon and the C—H bond, and there is no appreciable deshielding contribution from the region of the C—C bonds. Thus, the maps fully explain the observed deshielding of ^1H in benzene in terms of local contributions, in terms of C and C—H magnetic anisotropy. This supports Musher's localized model[21] for the interpretation of proton shifts in aromatic compounds, and suggests the ring current model as physically incorrect. A topological description of the electron current density field in molecules in an external homogeneous magnetic field is presented for the many-electron current density and also for its one-electron (orbital) components.[22] The description is applied to the magnetically induced current densities in the cyclopropenyl cation.[23] This qualitative description involves identification of domains of physical space associated with vortices and is presented with the possible application to the distinction between local and nonlocal effects in electronic properties of molecules. Its utility remains to be seen.

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[18] J. Mason, *J. Chem. Soc., Dalton Trans.*, 1975, 1422.

[19] C. J. Jameson and A. D. Buckingham, *J. Chem. Phys.*, 1980, **73**, 5684.

[20] P. Lazzeretti and R. Zanasi, *Chem. Phys. Lett.*, 1983, **100**, 67.

[21] J. I. Musher, *J. Chem. Phys.*, 1965, **43**, 4081; 1967, **46**, 1219; *Adv. Magn. Reson.*, 1966, **2**,177.

[22] J. A. N. F. Gomes, *Phys. Rev. A.*, 1983, **28**, 559.

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The ^{31}P in deoxyribonucleoside monophosphates tends to be less shielded for those systems having large values of $^3J(PH)$ to 3′ and 5′ protons, which indicates a dependence of the ^{31}P shielding on the torsion angles about the P—O ester bond. Calculations on a model compound (dimethylphosphate anion) for different values of the torsion angles about the P—O ester bond and different orientations of the methyl groups, show that both types of conformational parameters affect the value of ^{31}P shielding.[24] The highest shielding is obtained when the methyl groups are staggered with respect to the P—O bond, the least shielding for the eclipsed arrangement.

B. Semi-empirical Calculations. – Average bond lengths tend to increase with increasing temperature as a result of anharmonic vibrations and centrifugal distortion. The same intramolecular dynamics tend to result in longer averge bond lengths when one of the atoms involved in the bond is replaced by a lighter one. Nuclear shielding varies with these changes in molecular geometry. This is the basis for the observation of a temperature dependence of nuclear shielding in the gas phase at the zero-pressure limit, and the observation of a mass dependence of nuclear shielding (the n.m.r. isotope shift). Interpretation of these experiments require nuclear shielding calculations for molecular configurations slightly displaced from the equilibrium one. These nuclear shielding values form a surface in configuration space which correspond to the global minimum in the potential energy surface, and the rovibrational average over the surface leads to the observed thermal average shielding. Some calculations are reported for portions of the shielding surfaces of B, C, N, F, P, and Si nuclei in the following molecules: BF_3, CF_4, SiF_4, NF_3, PF_5, CH_4, and PH_3.[25] One important finding is that in every case the variations in bond length and bond angle lead to neglibible changes in the diamagnetic shielding contributions. Thus, the paramagnetic terms are responsible for $(\delta\sigma/\delta\Delta r)_e$ and $(\partial\sigma/\partial\Delta\alpha)_e$. Although other more accurate calculations of $(\partial\sigma/\partial\Delta r)_e$ have been carried out for diatomic molecules, the methods used normally do not allow the separate contributions to be identified when gauge-dependent orbitals are used. These semi-empirical calculations show that the nuclear shielding decreases with increasing internuclear separation in these polyatomic molecules. This is consistent with all previous calculations for a variety of nuclei in diatomic molecules and in H_2O. Thus far, only Li nuclear shielding in LiH has been found to increase with increasing bond length.[26,27]

The variation of N and P shielding as the pyramidal bond angle is changed in NH_3, NF_3, PH_3, and PF_3 is also reported.[25] Except for a previous calculation of $(\partial\sigma/\partial\Delta\alpha)_e$ in H_2O,[28] this aspect of nuclear shielding

[24] C. Giessner-Prettre, B. Pullman, and F. Ribas-Prado, *Biopolymers*, 1984, **23**, 377.

[25] B. T. Hamdi, D. J. Reynolds, and G. A. Webb, *Org. Magn. Reson.*, 1984, **22**,90.

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[27] R. Ditchfield, *Chem. Phys.*, 1981, **63**, 185.

[28] P. W. Fowler, G. Riley, and W. T. Raynes, *Mol. Phys.*, 1981, **42**, 1463.

has not been previously explored. The N and P shielding decreases with the increasing bond angle in NH_3, NF_3, and PH_3, P shielding increases with increasing bond angle in PF_3. These results are consistent with earlier approximate calculations of P shielding in PZ_3-type molecules,[29] in which the electronegativity of Z was arbitrarily varied and the variation of P shielding with bond angle changes direction as the electronegativity of Z increases. Unfortunately, these recent calculations cannot easily lead to conclusions about the bond angle deformation contributions to the thermal average shielding. While the increase of the bond length with temperature is fairly well established experimentally and theoretically, the thermal average bond angle is not so well known, it may be greater or less than the equilibrium bond angle.

Since *ab initio* calculations have shown that local contributions from the atom in question, from the immediate carbon atom, and from the bond to it, are largely responsible for nuclear shielding of a proton in a ring system, it may be possible to approximate these contributions from superpositions of shielding due to localized fragments described by two electron orbitals (geminals). This method of approximation has been applied to some hydrocarbons.[30] The same wavefunctions for the C—C and C—H bonds are used for all the molecules. The shielding due to each bond is calculated at various points, leading to an isoshielding map. CH_4 is constructed as a superposition of four such C—H bonds and the contributions from the individual bonds at a particular ^1H are added together. Cyclohexane is constructed in the same fashion, and the shielding of an axial and an equatorial proton are estimated. It is found that the axial proton is more shielded than the equatorial one by 0.9 p.p.m., to be compared with the experimental value of 0.55 p.p.m. The trends in the shifts of *exo* and *endo* protons of bicyclo[2.2.1]heptanols are also predicted qualitatively. The authors do not state the method of choosing the parameters for their C—H and C—C geminals, perhaps these were optimized for the best agreement with experiment. In any case, the method cannot be expected to work for protons in molecules in which there are significant effects transmitted through bonds.

An application of the equations of Jameson and Gutowsky[31] to include contributions from orbitals centred on atoms other than the observed nucleus, but still including only one-centre integrals and still using a mean energy approximation has been employed with CNDO-SCF wavefunctions in calculations of ^{13}C chemical shift increments for alkanes.[32] The calculated contributions to the α carbon shielding arising from primary, secondary, tertiary, and quaternary types of neighbouring carbons are, respectively, 10.01, 15.11, 22.40, and 28.63 p.p.m., in reasonably good agreement with empirical values 9.10, 17.64, 25.76, 30.07 p.p.m.

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[29] J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, 1966, **44**, 815.
[30] R. M. Aminova and Y. Y. Samitov, *Teor. Eksp. Khim.*, 1983, **19**, 209.
[31] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1964, **40**, 1714.
[32] J. M. Riera and J. Marine, *Int. J. Quantum Chem.*, 1984, **25**, 715.

CNDO/2 calculations of ^{13}C shielding with modified parameters using an SOS scheme give qualitative agreement with experimental chemical shifts relative to benzene for CH_4, CH_3CH_3, $CH_2{=}CH_2$, $HC{\equiv}CH$, CO, CO_2, CH_3COCH_3, $CH_3{-}CH{=}CH{-}CH_3$ (*cis* and *trans*), $CH_3{-}CH{=}CH_2$, $(CH_3)_2C{=}CH_2$, $CH_3CH_2CH{=}CH_2$.[33] The standard parametrization gives the worst results. None of the parameters reproduce the relative order of ^{13}C chemical shifts in the CH_4, CH_3CH_3, $CH_2{=}CH_2$, $HC{\equiv}CH$ series. Gauge-dependent orbitals with PCILO , EHT, or CNDO/2 wavefunctions are used to calculate proton chemical shifts in aliphatic, olefinic, and aromatic compounds with results which are of the right order of magnitude but the small differences between compounds could not be reproduced.[34] SOS calculations of ^{13}C and ^{15}N shielding using CNDO/S-parametrized wavefunctions are significantly improved by inclusion of two-centre integrals in the paramagnetic terms.[35]

INDO calculations using gauge-dependent atomic orbitals in a finite perturbation method (FPT) previously described[36] have been applied to ^{13}C and ^{15}N shielding in a large number of molecules containing H, C, and N atoms.[37] Except for a couple of isolated cases the calculated nitrogen shifts differ from experiment by 10–30 p.p.m., the carbon shifts differ by less than 5 p.p.m. The formalism adopted here allows the separation of σ into paramagnetic and diamagnetic parts, local and distant contributions. For a nucleus M involved in a bond to atom K, in a molecule with other pairs of bonded atoms AB, the shielding is partitioned into the following terms:

$$\sigma = \sigma^d(M) + \sigma^d(K) + \sigma^p(M) + \sigma^p(K) + \sigma(MK) + \sigma(M, AB) \tag{9}$$

There are implied sums in the above representation, over all M—K bonds and all other bonds A—B (not involving M). This partitioning allows the examination of various contributions to the shielding, for a better understanding of the role of contributions from other atoms. The findings are as follows: distant atoms have only a minor effect on the shielding of C or N; the *total* dia- and para-magnetic contributions of all atoms *but M* from AOs centred on K, [*i.e.*, $\sigma^d(K) + \sigma^p(K) + \sigma(MK)$] is roughly constant. For ^{15}N this sum is 30.6 ± 6 p.p.m., and for ^{13}C it is 19.6 ± 4 p.p.m. for all cyclic compounds and 13.8 ± 4 p.p.m. for noncyclic molecules. Thus, the sum of all the contributions other than the local one [*i.e.*, $\sigma^d(M) + \sigma^p(M)$] is nearly invariant, 20.5 ± 5.5 p.p.m. for ^{13}C and 33.1 ± 4 p.p.m. for ^{15}N. The local diamagnetic part, $\sigma^d(M)$, is virtually constant. Therefore, it appears that the total variation in shielding is almost entirely determined by that of the local paramagnetic term, *i.e.*,

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$$\delta \simeq [\sigma^{p}(M)]_{ref} - [\sigma^{p}(M)]. \quad (10)$$

The plots of equation (10) give very good straight lines passing through the origin, for a range of about 160 p.p.m. for ^{13}C and about 400 p.p.m. for ^{15}N, in a large and diverse set of molecules. Equation (10) is assumed in the early calculations of nuclear shielding for heavy nuclei;[31] however the use of FPT-INDO with gauge-dependent orbitals to obtain $\sigma^{p}(M)$ is a significant improvement over the SOS or mean energy approximation methods. This result again emphasizes the local nature of nuclear shielding.

A method of estimating the diamagnetic part of the shielding from gross orbital and gross atomic electron populations, using three adjustable parameters characteristic of each nucleus, has been proposed.[38] The parameters are found to be greatly dependent on the basis set used to calculate the populations. It would be interesting to find out whether the same set of parameters reproduces the individual components of the diamagnetic shielding, rather than just the isotropic average. The simple and straightforward Flygare method is more convenient to use for this purpose and requires neither wavefunctions nor adjustable parameters.[39]

Estimation of ^{59}Co chemical shifts in octahedral Co complexes using a set of ligand parameters is suggested in the following form:

$$\delta = \frac{1}{3}\left(\frac{1}{S_1 + S_2} + \frac{1}{S_3 + S_4} + \frac{1}{S_5 + S_6}\right), \quad (11)$$

in which δ is the chemical shift in p.p.m. relative to $Co(CN)_6^{3-}$. S_1 and S_2 are parameters characteristic of the ligands on the x axis, S_3 and S_4 of ligands on the y axis, and so on. A total of 9 parameters are used to fit 39 chemical shifts. The standard deviation is 108 p.p.m. in a total range of 14 070 p.p.m.[40] Approximate calculations of Co shifts in these complexes have been carried out independently, in which the shifts are interpreted in terms of $\langle r^{-3}\rangle_{3d}$ and ΔE variations.[41] An appreciation of the empirical S_1, S_2, *etc.* parameters, at the level of approximation used in the latter paper (in terms of their contributions to the variation of $\langle r^{-3}\rangle$ and ΔE) or at a higher level of sophistication would be useful. The form of equation (11) is intriguing, indicating an additivity of shielding due to sets of ligands which are *trans* to one another. The theoretical basis for this empirical form will contribute much to our understanding of nuclear shielding of transition metal nuclei.

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2 Physical Aspects of Nuclear Shielding

A. Anisotropy of the Shielding Tensor. – The principal values of the shielding tensor provide a more sensitive and complete characterization of the local electronic environment than the isotropic shielding. The unique relationship between the components of the paramagnetic part of the shielding tensor and the components of the spin–rotation interaction constant, together with easily calculated diamagnetic components yield the complete shielding tensor. Molecular beam electric (MBER) spectroscopy measurements on H_2S, HDS, and D_2S[42] and NaCN[43] have resulted in spin–rotation tensors for ^1H, ^{23}Na, and ^{14}N nuclei in these respective molecules. For H_2S $\sigma^p(^1H) = -104.84\,(40)$ p.p.m. is calculated from these. No statistically significant difference is observed in the spin–rotational tensors calculated from the H or D couplings in H_2S, HDS, and D_2S, indicating that the primary and secondary isotope effect on ^1H shielding upon D substitution is within the experimental errors. The components of the ^1H paramagnetic shielding in H_2S (with the gauge origin on the proton, in the principal axes of inertia system) calculated from these are: $\sigma^p = (-71, -88, -154$ p.p.m.) where the 2-axis is coincident with the two-fold symmetry axis and the 3-axis is perpendicular to the plane of the molecule. Similarly the ^{23}Na and ^{14}N paramagnetic shielding contributions in NaCN can be calculated from the spin–rotation constants:[43]

$$M_{bb}(^{23}Na) = 1.09\,(20)\,\text{kHz} \qquad M_{aa}(N) = 13.7\,(3.5)\,\text{kHz}$$

$$M_{cc}(^{23}Na) = 0.96\,(31)\,\text{kHz} \qquad M_{cc}(N) = 1.88\,(42)\,\text{kHz}.$$

The ^{29}Si shielding anisotropy in a Si=Si bond is comparable to that for ^{13}C in a C=C bond:(180, 27, −15 p.p.m. relative to Me_4Si) in tetramesityldisilene,[44] and (234, 120, 24 p.p.m. relative to Me_4Si) in ethylene. The 2-axis is along the double bond, the 1-axis is in the molecular plane and perpendicular to it. The shielding anisotropies in $Cs_2GeF_6 \cdot 4HF$ ($\Delta\sigma^H = 39 \pm 7$ p.p.m., $\Delta\sigma^F = 86 \pm 4$ p.p.m.)[45] are close to the values for HF ($\Delta\sigma^H = 24$ p.p.m., $\Delta\sigma^F = 108$ p.p.m.).[46] In hydrogen-bonded dimers of tetrafluoroterephthalic acid [$C_6F_4(COOH)_2$] the ^1H shielding tensor components are −20.5, −9.4, and +3.0 p.p.m. relative to liquid water, showing an unusually large asymmetry factor.[47] The ^{19}F shielding tensors for the inequivalent fluorines are (+65, −99, −117) and (+63, −104, −126) p.p.m. relative to CaF_2. The *z* component is along the C—F bond, the *x* axis being normal to the ring.

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^{19}F shielding tensors for CF_3 groups bonded to carbon in CF_3CN, CF_3CCl_3, CF_3COOD, and CF_3CD_2OD,[48] show only minor differences (the three components are 180–197, 279–287, and 335–341 p.p.m. absolute shielding). In UF_6, $\sigma_\parallel = +73$, $\sigma_\perp = -1137$ p.p.m. relative to gaseous F_2.[49] This converts to an isotropic shielding of -967 p.p.m., based on the ^{19}F absolute shielding scale.[46,50] This appears to be one of the most deshielded F environments. ^{19}F and ^{31}P shielding tensors in a variety of phosphates have been reported: in K_2PO_3F, $(NH_4)_2PO_3F \cdot H_2O$, Ag_2PO_3F, $BaPO_3F$, and $PbPO_3F$,[51] and in h-P_4O_{10}, K_3PO_4, $K_4P_2O_7$, $K_5P_3O_{10}$, $K_3P_3O_9$, and $(KPO_3)_x$.[52] In the condensed phosphates, there are four types of PO_4 units: isolated PO_4 end groups, PO_4 middle groups, and PO_4 branching groups. With increasing number of bridging oxygen atoms of a PO_4 group, the average ^{31}P shielding increases. The ^{31}P shielding tensors of the end PO_4 groups and the triply linked (branching) group are axially symmetric within experimental errors. This axial symmetry is consistent with the three-fold symmetry around the ^{31}P of the single and triply linked PO_4 which have 3 terminal oxygen atoms and 3 bridging oxygen atoms. The direction of the σ principal axis belonging to the PO_4 end groups is identical with the long and weaker P—O bond to the bridging oxygen ($\sigma_\parallel = -84$ p.p.m.) whereas in the branching PO_4 groups $\sigma_\parallel$ lies along the short (stronger) P—O bond to the terminal oxygen ($\sigma_\parallel = +240$ p.p.m.), both relative to 85% H_3PO_4.[52] ^{31}P shielding tensors in substituted phosphonic acid diester models of biologically active compounds have also been reported.[53]

Shielding anisotropies for the ^{205}Tl nucleus in the compounds TlI, Me_2TlBr, and Me_2TlNO_3 indicate significant covalent bonding in these compounds, estimated to be about 10% covalency in the iodide.[54] $\sigma_\parallel$ and $\sigma_\perp$ are $(-602, -485)$, $(+480, +1530)$, $(+5915, +5430)$, and $(+6389, +4414)$ p.p.m. relative to Tl(I) in an infinitely dilute aqueous solution, in $TlClO_4$, TlI, Me_2TlBr, and Me_2TlNO_3, respectively. ^{113}Cd shielding tensors in $Cd(NO)_3)_2 \cdot 4H_2O$ and $3CdSO_4 \cdot 8H_2O$ do not exhibit axial symmetry, although the asymmetries are small.[55] These two compounds are examples of a Cd nucleus in an all oxygen environment with co-ordination numbers of 8 and 6 respectively. In the nitrate the principal components are $(-174.4, -154.3$, and $22.2)$ p.p.m. with respect to solid $Cd(ClO_4)_2$. In the sulphate there are two symmetry related tensors which have the principal elements $(-93.1, -76.7$, and 25.5 p.p.m.) and $(-95.6, -85.3$,

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and -3.4 p.p.m.). The least shielded tensor elements are aligned nearly perpendicular to planes containing water oxygen. The more shielded elements are oriented perpendicular to the longer Cd–O bonds.

Shielding anisotropies of nuclei in molecules dissolved in liquid crystals compare well with solid state data. For $^{15}N_2$ $\sigma_{\parallel} - \sigma_{\perp} = 590 \pm 50$ p.p.m. is obtained in a nematic phase,[56] to be compared with 603 ± 28 p.p.m. obtained in the solid.[57] ^{13}C shielding components in ethylene dissolved in various liquid crystals (-132.7 ± 1.1, 109.1 ± 1.1, and 23.6 ± 0.4 p.p.m. relative to the isotropic shielding)[58] compared with (-102 ± 3, 108 ± 3, and -6 ± 2.9 p.p.m.)[59] obtained in a solid Ar matrix. ^{1}H shielding components in ethylene are also reported (-1.6 ± 0.1, -0.9 ± 0.1, and 2.5 ± 0.1 p.p.m. relative to the isotropic shielding) in the same work.[58] Comparison with theoretical values shows reasonably good agreement: (-141.5, 117.5, and 23.9) p.p.m. for ^{13}C,[60] and (-2.29, -0.76, and 3.05) p.p.m. for ^{1}H,[60] or (-3.65, 0.42, and 3.23) p.p.m.,[58] all relative to the isotropic shielding. The principal axes of the ^{1}H shielding tensor are slightly tilted (by about 10°) from the ^{13}C principal axes in the molecular plane. ^{1}H and ^{13}C shielding anisotropies in $CH_3—C{\equiv}C—CH_3$ dissolved in liquid crystals are: $\Delta\sigma(^{1}H) = 1.61 \pm 0.10$, $\Delta\sigma(^{13}C \text{ in } CH_3) = 17.4 \pm 1.1$ and $\Delta\sigma(^{13}C \text{ in } —C{\equiv}C—) = 227.0 \pm 1.0$.[61] The $\Delta\sigma$ for the acetylenic carbon compares reasonably well with semi-empirical theoretical calculations: 237.6 p.p.m.[62] and 202.6 p.p.m.,[63] by INDO and CNDO/S methods respectively. ^{13}C shielding tensors in benzonitrile dissolved in liquid crystal solution[64] indicate very similar electronic environments in the CN groups of HCN, CH_3CN, and C_6H_5CN. In the latter, the principal elements are (-88, 231, and 213) p.p.m. relative to TMS, showing nearly axial symmetry, compared with $\sigma_{\parallel}, \sigma_{\perp} = (-71, 211)$ and (-90, 221) p.p.m. for HCN and CH_3CN respectively. The shielding components of the aromatic carbons at the *ortho* and *meta* positions in C_6H_5CN are quite similar. As usual, the most shielded direction is along the CH axis, the least shielded perpendicular to the ring. ^{1}H and ^{13}C shielding anisotropies have also been reported for several substituted benzenes: 1,3,5-tribromobenzene and 1,3,5-trinitrobenzene, as well as for methyl isocyanate.[65]

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A new spinning technique, switching-angle sample spinning (SASS) for obtaining individual powder pattern spectra of chemically distinct nuclei has been reported independently by two groups,[66,67] and used to determine the ^{13}C shielding tensor elements in 3,4-dimethoxybenzaldehyde[66] and *p*-dimethoxybenzene.[67]

Shielding anisotropies in both the methyl and carboxyl carbons in ten metal acetates are reported.[68] A typical one is the cadmium salt, with carboxyl principal elements (-100, -79, and 24 p.p.m.) and methyl elements (84, 102, and 129 p.p.m.) relative to external liquid benzene. The values for other acetates differ from these by only a few p.p.m. The carboxyl tensor is not axially symmetric and the anisotropy is quite large, $\Delta\sigma = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2 = 92$ to 121 p.p.m., and similar to those found in other carboxylates. The most shielded component lies in the range 11–28 p.p.m. The inplane components show considerably more variation among the acetates. The methyl group is not axially symmetric even in a motionally averaged situation; the anisotropy is small but the asymmetry is large.

The shielding tensor elements of ^{13}C in *cis* and *trans* polyacetylene are quite typical for a long conjugated system with alternating double bonds. For the *cis* form the principal components are (-227.8, -138.6, and -17.4) and for the *trans* (-234.1, -145.5, and -33.8) p.p.m. relative to TMS.[69] The 3-axis is taken to be perpendicular to the plane of the C=C bond and the 2-axis is nearly parallel to the C=C bond, by analogy with other systems. All ^{13}C tensor elements in poly(methyl methacylate) have been obtained.[70]

There has recently been some interest in characterizing the shielding tensors of amino acids, peptides, and nucleic acids. For glycine-d_5,[71] l-threonine,[72] and l-serine monohydrate[73] and ^2H and ^{13}C shielding tensors have been obtained in the single cystals. The ^{13}C tensors in a single crystal of the simplest dipeptide, glycylglycine, recently reported,[74] provides an example from which information concerning the peptide carbon orientations may be based. Likewise the ^{31}P shielding tensor in the single crystal of deoxycytidine 5′-monophosphate[75] serves as a simple example of a structure closely related to the ^{31}P environment in nucleic acids.

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B. Isotope Effects on Nuclear Shielding. – One of the observed effects of the averaging of nuclear shielding over the rotational and vibrational motions of the nuclei in a molecule is a shift of the nuclear resonance when one of the nuclei is replaced by an isotope; substitution by a heavy atom generally leads to increased shielding and substitution by a lighter atom leads to deshielding. These effects are fairly well understood in terms of centrifugal stretching of the bonds and anharmonic vibration leading to increased bond lengths compared to the equilibrium rigid structure. The excursions of a lighter atom during vibration tend to be of greater amplitude than those of heavier atoms, leading to longer average bond lengths. When combined with the theoretically established tendency of the nuclear shielding to decrease with increasing bond length, this averaging over the nuclear motions leads to increased shielding upon heavy isotopic substitution. These effects leading to the one bond isotope shift are most directly explained, since nuclear shielding is a strong function of the length of the bond directly involving the observed nucleus. However, for *n*-bond isotope shifts where $n \geqslant 2$ (${}^{n}\Delta$, *i.e.*, shifts due to isotopic substitution *n* bonds away from the observed nucleus), the explanation becomes less straightforward. There is a change in the nuclear shielding due to the extension of a bond far removed from the observed nucleus. This is expected to be smaller than the variation due to extension of bonds involving the nuclear site. In addition, there is a secondary isotope effect on the length of a bond far removed from the isotope substitution site. Thus, the ${}^{n}\Delta X({}^{m'/m}Y)$ for $n > 1$ comes from two types of terms. The first involves a primary dynamic effect on the bond length at the substitution site transmitted by a secondary electronic effect on shielding at the nuclear site. The second involves a secondary dynamic effect on the bond length at the nuclear site with a primary electronic effect on the nuclear shielding. The secondary effects are generally smaller and tend to (but not always) be in the same direction as the primary effects. With the increasing use of higher magnetic fields, these very small secondary effects become observable. Isotope effects at nuclear sites 3–5 bonds away are not uncommonly observed, especially in conjugated systems. Note that the mechanism discussed here for long range isotope shifts is the same as the general interpretation of one bond isotope shifts. Only the magnitudes of the secondary effects are different.

Alternative explanations have been advanced for long range deuterium induced ${}^{13}C$ shifts each one somewhat specific in nature, depending on the molecular systems studied. (*a*) One is known as 'isotopic perturbation of resonance,' used to explain the unusual sign of a 0.17 p.p.m. 3-bond isotope shift in cyclohexenyl cation.[76] This necessitates a breakdown in the Born–Oppenheimer separation of electronic and nuclear motion, *i.e.*, it involves a change in the electronic distribution due to a change in mass of one of the atoms in the molecule. (*b*) Another is the different ability of

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hydrogen-bonding of OD and OH groups.[77] An isotope effect on ^{13}C transmitted through a hydrogen bond is fairly small, $^{2}\Delta^{13}C(^{2/1}H) = -15$ p.p.b.[78] (*c*) Still another explanation is the supposed less efficient hyperconjugative electron donating ability of deuterium atoms compared to protons at a CH, CH_2, or CH_3 group next to a resonance system.[79,80] This mechanism also requires a Born–Oppenheimer breakdown. A relationship is proposed for $^{n}\Delta$ based on this mechanism:

$$^{n}\Delta = a\langle\sin^2\theta\rangle + b \qquad (12)$$

where θ is the angle between the plane of the ring and the plane containing the (C_{ring})—C—D bond, and the average of $\sin^2\theta$ depends on the barrier to rotation. For $^{5}\Delta$, constants *a* and *b* are found by using the dependence of ^{6}J(HH) on $\langle\sin^2\theta\rangle$ and the observed empirical correlation between $^{5}\Delta$ and ^{6}J, applied to $^{5}\Delta^{13}C(^{2/1}H)$ in toluene, ethylbenzene, and cumene.[81] This mechanism has also been used to explain the dependence of $^{3}\Delta$ on the π bond order, the effect of deuteration on the *ortho* carbons of benzylic hydrocarbons.[82] Indeed a straight line described by

$$^{3}\Delta^{13}C(^{2/1}H) = 88.4P_{\pi} - 54.9\ \text{p.p.m.} \qquad (13)$$

is found for seven carbons, and only two cases fall substantially away from this line. These isotope shifts are −16 to +20 p.p.b. in these compounds. (*d*) Still another proposed mechanism is a 'through-space' or 'steric' isotope effect proposed in paracyclophanes in which non-bonded interactions between deuterons and carbon atoms are assumed to be responsible for the shifts.[80]

None of these specific mechanisms applies to the long range (up to 6 bonds) ^{13}C isotope shifts in naphthalene and azulene.[83] In these compounds, $^{1}\Delta^{13}C(^{2/1}H)$ values are −322 and −246 p.p.b., $^{2}\Delta$ values are −96, −108, and −111 p.p.b., $^{5}\Delta = -7$ to 10 p.p.b., $^{6}\Delta = -4.5$ to −7.5 p.p.b $^{3}\Delta$ and $^{4}\Delta$ appear to be of unusual (+) sign, at least for some carbons. The labels are not unique because in ring systems multiple paths exist between the deuteron and the observed carbon. Nevertheless, there are three cases of unusual sign, +13 p.p.b., +27 p.p.b. (where the closest path is along three bonds) and +9 p.p.b. for a nominally 4-bond isotope effect. The separate paths are not independent or additive. Given a vibrationally averaged configuration of a ring, the three bonds to an sp^2-type carbon have some average lengths and these three determine the isotope shift, in part. The other part has to do with the change in shielding at the carbon upon a change in the C—H length at the deuterium substitution

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site. Unusual signs of $^2\Delta$ have also been observed for a carbonyl carbon D—C—C=O, in cyclodecanones: $^2\Delta = +39, +80$, as well as for ring carbons: $^7\Delta$ and $^8\Delta = +26, +31$ p.p.b.[84] These unusual signs pose a challenge to the theoretician. It remains to be seen whether this is largely dynamic or electronic in nature. The correlation with π bond order seems to indicate an electronic origin.

All signs of $^n\Delta^{13}C(^{2/1}H)$ are normal in the deuteriated stilbenes.[85] $^1\Delta = -340$ p.p.b. at the ethylenic carbons and $-310, -220$ p.p.b. at ring carbons. $^2\Delta = -70$ to -100 p.p.b., $^3\Delta$ are small.

Other isotope shifts reported include $^n\Delta^{13}C(^{18/16}O)$, for $n = 1,2,3$, respectively, $-46, -31$, and -7 p.p.b.[86] ^1H and ^{19}F shifts induced by ^{13}C have been measured for $n = 1$ up to 4.[87,88] For example, in fluorobenzene $^n\Delta^{19}F(^{13/12}C) = -87.2, -25.6, -5.6$, and -2.1 p.p.b., respectively, for $n = 1$ to 4.[88] Proton shifts are considerably smaller: $-2.44, -1.34, -0.51$, and -0.33 p.p.b.[87] $^1\Delta^{31}P(^{15/14}N)$ is greater for the shorter equatorial than for the longer axial P—N bonds in a phosphorinane.[89] This is consistent with other previous correlations of the magnitudes of $^1\Delta$ isotope shifts with bond length.[90] ^{18}O induced isotope effects on ^{13}C, ^{15}N, and ^{31}P shifts have been reviewed.[91,92] $^1\Delta^{31}P(^{18/16}O)$ correlates linearly with the spin–spin coupling $^1J(PO)$,[93] reminiscent of the linear relation found between $^1\Delta^{19}F(^{13/12}C)$ and $^1J(CF)$. Such correlations are useful in systems where only one of the two parameters can be measured. However, they are even more useful from a theoretical point of view. Since the coupling is a purely electronic quantity, whereas the isotope shift is a combination of dynamic and electronic factors, the observed correlations indicate the nature of the electronic factors in the isotope shifts.

The purely dynamical factor shows up in the analysis of the one bond isotope shifts, $^1\Delta^{77}Se(^{m'/m}Se)$ in R_1—^{77}Se—$^{m'/m}Se$—R_2.[94] This is a very nice set of molecular systems (R_1, R_2 = CH_3, CF_3) because there are four related electronic environments for the ^{77}Se nucleus and there are 6 selenium masses which are involved. The mass effect is observed in parallel in the 4 electronic environments and the behaviour is expected; the larger fractional mass change leads to larger isotope shifts. This is a purely dynamical effect. An interesting feature of these compounds is the larger magnitudes of shifts for ^{77}Se next to CH_3 compared to that bonded to CF_3,

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with the group R_2 modifying these isotope shifts in a non-negligible way. These are purely electronic factors.

Two interesting reports on isotope shifts of systems which are amenable to theoretical explanation are the deuterium induced isotope effect on ^{14}N shielding in the NH_4^+ ion,[95] and the ^{13}C induced ^{59}Co isotope shift in $[Co(CN)_6]^{3-}$.[96] The former is -0.293 p.p.m. per ^2H with slight deviations from additivity, and the latter is $-(0.888 \pm 0.005)$ per ^{13}C. A comprehensive review of isotope shift data published after 1965 has recently appeared.[97]

C. Intermolecular Effects on Nuclear Shielding. – *Ab initio* calculations of the variation of nuclear magnetic shielding with intermolecular separation are reported for $H_2O—H_2O$ and $CH_4—CH_4$ molecular systems.[98] To calculate the effect of intermolecular interactions on nuclear shielding, it is necessary to have the variation of nuclear shielding with intermolecular separation and orientation, $\sigma(R, \Omega_1, \Omega_2)$, as well as the intermolecular potential surface, $V(R, \Omega_1, \Omega_2)$. The latter is not yet well known for the systems of interest here, although there are some approximate spherical potentials $V(R)$ and some parts of the anisotropic terms have been estimated. The *ab initio* calculation of $\sigma(R, \Omega_1, \Omega_2)$ is similar to that of the calculation of $V(R, \Omega_1, \Omega_2)$ in that the shielding is calculated in the isolated molecule and in the molecular pair treated as a supermolecule. A partitioning of the σ function in terms of various contributions provides some insight into the physical aspects of the problem, thus, the calculation is carried out in such a way as to be able to identify these contributions.[98] Morokuma[99] has provided a means of doing this for V and this method has been applied to σ.[98]

The contributions are the following: (1) The 'geometric' or direct contribution arises from the shielding of nucleus N in molecule A due only to the electrons of molecule B in the absence of any interaction between them. (2) The polarization contribution utilizes polarized wavefunctions for A and B, as defined by Morokuma. These polarized wavefunctions are obtained by an SCF calculation which takes into account the presence of the other molecule but neglects completely intermolecular overlap. The Hamiltonians used contain explicitly the intermolecular nuclear attraction and electronic repulsion. These polarized wavefunctions are used as the zeroth order wavefunctions in the perturbation calculation of the nuclear shielding. (3) The exchange plus charge transfer contribution is what remains after the sum of the above two contributions are subtracted from

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the perturbation calculation of shielding in the supermolecule. This takes into account the overlap of the two wavefunctions (exchange or repulsion) and introduces in the shielding calculation the intermolecular excitations (occupied orbitals of A to unoccupied orbitals of B and *vice versa*) which are responsible for the charge transfer interactions. (4) The van der Waals contributions which are due to electron correlation are not included since these calculations do not include correlation effects. All the conclusions with respect to the importance of individual contributions relative to the whole are therefore invalid, since the magnitude of the correlation effects on the electron distribution (and to the shielding) are not included. However, comparisons between the calculated contributions (*e.g.*, which ones may be neglected relative to the others) should be permissible.

The results for H_2O—H_2O indicate that the polarization contribution is not negligible even for those nuclei not engaged in the hydrogen bond. The charge transfer plus exchange effect is found to be extremely sensitive to the basis set and, for non-hydrogen atoms, very sensitive to the intermolecular orientation. This means that calculations for fixed molecular orientations, varying only the intermolecular separation, may lead to incorrect conclusions. Of the calculated terms, the short range (exchange plus charge transfer) effects can be the largest ones. Approximate treatments which neglect these[100] may be in error. In the case of polar molecules the polarization contribution remains important for large distances for all nuclei.

Previous calculations of $\sigma(R, \Omega_1, \Omega_2)$[101-106] have neglected the counterpoise correction. This correction is the difference between the magnetic shielding of nucleus N in molecule A calculated with *the total basis set* of the molecular pair AB and that calculated for the molecule A with the basis set for molecule A. Since finite basis sets are used, part of the shielding obtained in the supermolecule calculation is due simply to basis set expansion and not a real shielding contribution. This correction is found to be negligible for protons and also for C in CH_4—CH_4. However, in general, for non-hydrogen nuclei, it should be taken into account.[107]

Modeling of adsorbed molecule–surface interactions leading to shifts in the resonance signals of the nuclei in the absorbed species has been prompted by experimental data, especially of molecules adsorbed on

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zeolites. The effect of various cations preset in some adsorption sites in zeolites is investigated with Na^+—CH_2=CH_2 or Na^+/Li^+—CH_3CN systems.[108,109] Semi-empirical (PCILO, CNDO/2, and CNDO/S) results for ^{13}C in CH_2=CH_2 itself are so poor compared with experiment[59] or *ab initio* calculations,[60] that the differences between isolated CH_2=CH_2 and the CH_2=CH_2 in the presence of Na^+ ion may not be meaningful.

The effects of hydrogen bonding on the ^1H shielding in RCOOH and ROH dimers and on N shielding in some heterocycles are reported and compared with experiment.[104,110] The computed directions of the principal axes are in excellent agreement with those observed in hydrogen bonded systems.[104] The dependence of the isotropic ^1H shifts on the O—O distance in the model compounds mimic the empirical dependence observed.[111]

Intermolecular effects on ^1H and ^{19}F nuclear shielding in the gas phase have been measured for CF_2=CH_2 in various buffer gases: Xe, SF_6, Kr, SiF_4, CH_4, CF_4.[112] The second virial coefficient, σ_1, in the following equation,

$$\sigma(T, \varrho) = \sigma_0(T) + \sigma_1(T)\varrho + \ldots$$

is reported for ^1H and ^{19}F for CF_2=CH_2 in these CF_2=CH_2/buffer pairs. The magnitudes are in the above order, with Xe being the most effective perturber. For CF_2=CH_2 in C_2H_6, HCl, and CO_2, the absolute σ_1 values decrease in this order. An alternative model to the nuclear site effect on σ_1[113] is proposed to arise from 'molecular buffeting' of isotropic solute molecules in liquid solvents.[114]

The larger intermolecular effects on measurements in condensed phases may lead to errors in the quantities deduced from chemical shift studies, such as barriers to internal rotation in amides or chemical equilibrium constants for keto–enol tautomerism and (*E*)–(*Z*) isomerism. Thus, n.m.r. measurements in the dilute gas phase are desirable. Some results are reported of such gas-phase studies.[115,116] Standard free energies of activation for internal rotation in amides are at least 1 to 2.3 kcal mol^{-1} lower than values obtained in liquid solutions.[115]

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