CORRELATIONS IN NUCLEAR MAGNETIC SHIELDING. PART I

JOAN MASON

Open University, Milton Keynes, Buckinghamshire, England

I. Introduction

A quarter of a century has elapsed since Proctor and Yu (*74*) found "an annoying ambiguity," in Bloch's phrase (*6*), in their determination of the magnetic moment of ^{14}N using an ammonium nitrate solution, and since Ramsey (*75*) proposed the theory of magnetic screening, based on Van Vleck's (*91*) theory of magnetic susceptibility. In the 1950s and early 1960s, useful approximations were developed, notably the local term approximation (*58*, *69*, *81*) which made it easier to interpret NMR shifts in chemical terms. But it has often been found difficult to make detailed interpretations and progress has been slow toward a physical model for nuclear magnetic screening comparable to the models with which the chemist understands other forms of spectroscopy, such as vibrational or electronic spectra. Perhaps as a result, the enthusiasm of the inorganic chemist for measuring shifts, particularly those of the less accessible nuclei, has diminished.

However, with the development of methods for the study of ^{13}C in natural abundance, the measurement of these shifts has become much easier. Pulse Fourier transform spectroscopy with decoupling and spectral accumulation has greatly increased sensitivity and speed of measurement and can produce simple spectra for difficult nuclei in complex molecules. Multiple pulsing can eliminate dipolar and quadrupolar effects in solids and give an accurate measure of shielding anisotropies (*94*). At the same time, other physical techniques, notably molecular beam, electric and magnetic resonance (*7*) and microwave spectroscopy (*28*, *90*) are providing information on absolute shielding that can fill important gaps in our knowledge obtained from conventional NMR spectroscopy. In this article we collect evidence from the physical and chemical literature with which we can relate nuclear magnetic screening to molecular structure via the periodic table.

II. NMR Measurements and the Periodic Table

Figure 1 shows a periodic table of magnetic nuclei all of which have been observed by NMR except those shown in parentheses. Nuclei may be difficult to observe because of low sensitivity, which is proportional to the third power of the magnetic moment, because of low natural abundance, or because of quadrupolar or other broadening of the resonance lines. For the nuclei without electric quadrupole moments, Table I gives the order of diminishing *receptivity*, which is the product of the fractional natural abundance and the sensitivity relative to the proton at constant field. Table I shows that many nuclei of considerable interest, such as those of Sn, Pt, Pb, Hg, and Si, compare favorably in receptivity with ^{13}C, and shifts have been measured for a number of their compounds. Several complexes of Rh and W have been measured, and even $^{107,\,109}Ag$ (*8*) and ^{57}Fe have been observed; the measurement of the ^{57}Fe resonance in $Fe(CO)_5$ took 20 hr on a high-sensitivity pulse spectrometer (*83*).

For quadrupolar nuclei, rapid pulsing can improve the signal-to-noise ratio. They are often most readily measured by wide-line techniques however, as for example ^{17}O (*84*) and ^{14}N (*79*). Many more wide-line measurements have been made of ^{14}N, which is quadrupolar, than high-resolution measurements of ^{15}N, which has spin $\frac{1}{2}$ but is expensive. The broadening increases with the nuclear quadrupole moment, which is small for ^{2}H (2.8×10^{-3}), ^{6}Li (4.6×10^{-4}), and ^{17}O (-4×10^{-3}), and fairly small, between 10^{-2} and 10^{-1}, for ^{9}Be, ^{11}B, ^{14}N, ^{33}S, ^{35}Cl, and ^{37}Cl (the units are $e \times 10^{-24}$ cm^2, where e is the electronic charge) (*20*, *70*). The broadening increases with asymmetry of the nuclear environment; thus, the line width increases a thousand-fold from the relatively sharp line

TABLE I

ORDER OF DECREASING RECEPTIVITY OF NUCLEI OF SPIN $\frac{1}{2}$

Nucleus	Natural abundance (%)	Sensitivity at constant field relative to an equal number of protons	Receptivity[a]
^{1}H	99.98	1	1
^{3}H	—	1.21	—
^{19}F	100	0.833	0.833
^{205}Tl	70.48	0.192	0.135
^{31}P	100	6.64×10^{-2}	6.64×10^{-2}
^{129}Xe	26.24	2.12×10^{-2}	5.56×10^{-3}
^{119}Sn	8.68	5.18×10^{-2}	4.50×10^{-3}
^{195}Pt	33.7	9.94×10^{-3}	3.35×10^{-3}
^{125}Te	7.03	3.16×10^{-2}	2.22×10^{-3}
^{207}Pb	21.11	9.13×10^{-3}	1.93×10^{-3}
^{113}Cd	12.34	1.09×10^{-2}	1.34×10^{-3}
^{199}Hg	16.86	5.72×10^{-3}	9.64×10^{-4}
^{171}Yb	14.27	5.50×10^{-3}	7.85×10^{-4}
^{169}Tm	100	5.51×10^{-4}	5.51×10^{-4}
^{77}Se	7.50	6.97×10^{-3}	5.23×10^{-4}
^{29}Si	4.70	7.85×10^{-3}	3.69×10^{-4}
→ ^{13}C	1.11	1.59×10^{-2}	1.76×10^{-4}
^{89}Y	100	1.17×10^{-4}	1.17×10^{-4}
^{109}Ag	48.65	1.01×10^{-4}	4.91×10^{-5}
^{103}Rh	100	3.12×10^{-5}	3.12×10^{-5}
^{183}W	14.28	6.98×10^{-5}	9.97×10^{-6}
^{15}N	0.365	1.04×10^{-3}	3.80×10^{-6}
^{57}Fe	2.245	3.38×10^{-5}	7.59×10^{-7}
^{3}He	10^{-6}	0.442	4.42×10^{-9}
^{239}Pu	—	2.9×10^{-3}	—

[a] The receptivity is the product of the natural abundance (expressed as a fraction) and the sensitivity at constant field (relative to an equal number of protons).

for aqueous Cl^- to covalently bound chlorine, which may be difficult to observe. (This difference is turned to advantage in the "halogen probe" technique used in biological studies.) In many important fields of study, sharp lines are observed for quadrupolar nuclei because of symmetry about the nucleus, e.g., in complexes of ^{59}Co(III) or ^{105}Pt(II,IV). Broadening because of coupling to a quadrupolar nucleus can, of course, be removed by double resonance.

Paramagnetic broadening, due to unpaired electrons, is usually much greater than quadrupolar broadening, and the nuclear resonance

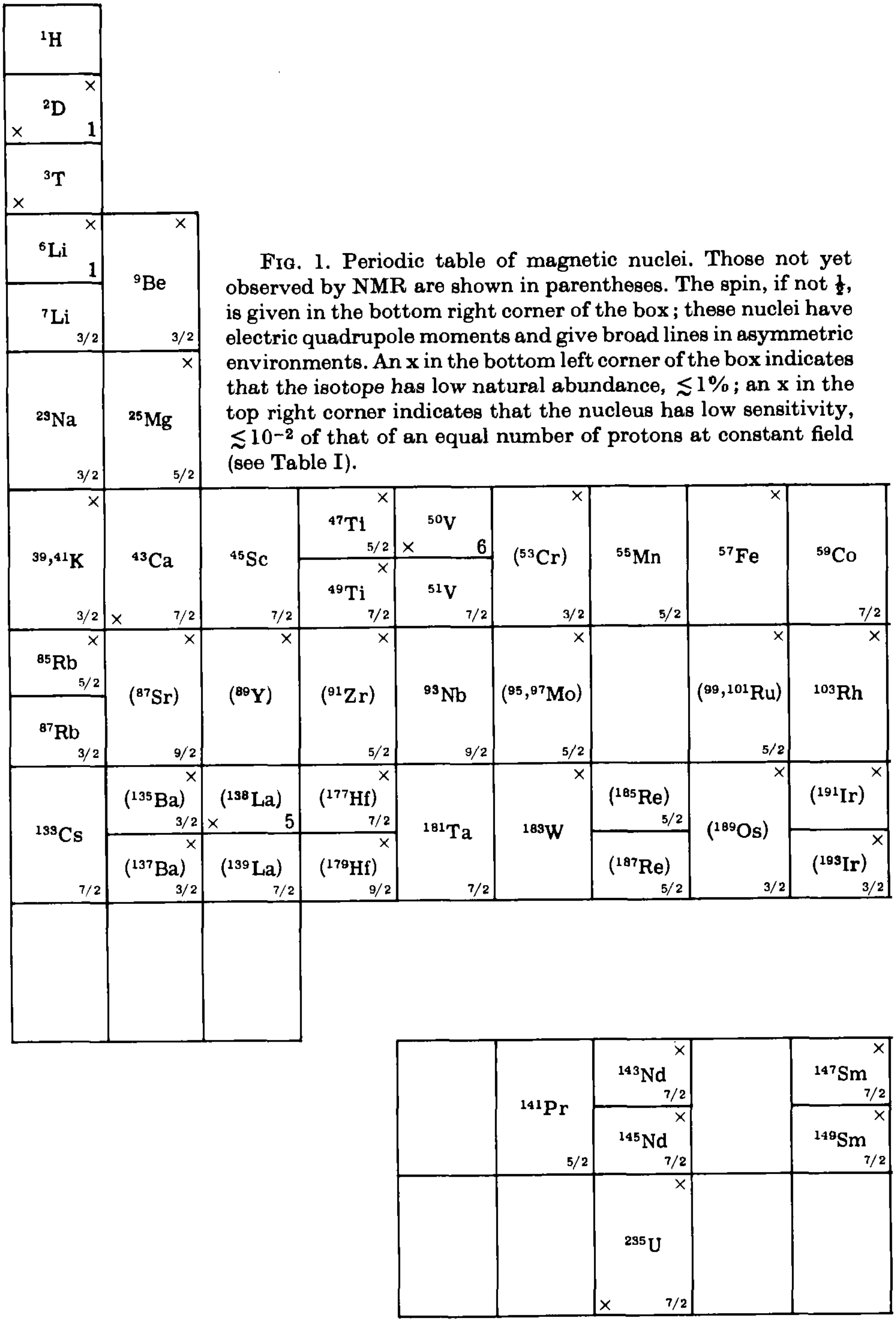

FIG. 1. Periodic table of magnetic nuclei. Those not yet observed by NMR are shown in parentheses. The spin, if not ½, is given in the bottom right corner of the box; these nuclei have electric quadrupole moments and give broad lines in asymmetric environments. An x in the bottom left corner of the box indicates that the isotope has low natural abundance, ≲1%; an x in the top right corner indicates that the nucleus has low sensitivity, $\lesssim 10^{-2}$ of that of an equal number of protons at constant field (see Table I).

								^{3}He ×
			× ^{10}B 3 ^{11}B 3/2	× ^{13}C ×	× ^{14}N × ^{15}N ×	^{17}O ×	^{19}F	× (^{21}Ne) × 3/2
			^{27}Al 5/2	× ^{29}Si	^{31}P	× ^{33}S × 3/2	× ^{35,37}Cl 3/2	
× (^{61}Ni) × 3/2	^{63,65}Cu 3/2	× (^{67}Zn) 5/2	^{69,71}Ga 3/2	× ^{73}Ge 9/2	^{75}As 3/2	× ^{77}Se	^{79,81}Br 3/2	× (^{83}Kr) 9/2
× (^{105}Pd) 5/2	× ^{107,109}Ag	× ^{111,113}Cd	^{113,115}In 9/2	^{117,119}Sn	^{121}Sb 5/2 ^{123}Sb 7/2	(^{123}Te) × ^{125}Te	^{127}I 5/2	^{129}Xe × (^{131}Xe) 3/2
× ^{195}Pt	× (^{197}Au) 3/2	× ^{199}Hg × ^{201}Hg 3/2	^{203}Tl ^{205}Tl	× ^{207}Pb	(^{209}Bi) 9/2			

^{151,153}Eu 5/2	× ^{155,157}Gd 3/2	^{159}Tb 3/2	× ^{161,163}Dy 5/2	^{165}Ho 7/2	× ^{167}Er 7/2	× ^{169}Tm	× ^{171}Yb × ^{173}Yb 5/2	^{175}Lu 7/2 ^{176}Lu 6

may be lost; or it may be detectable by wide-line techniques, as for example the ^{14}N resonance in liquid N_2O_4 at 10°C, at which temperature it is brown with NO_2, and exchanging with this as well (*1*).

III. Theory and Physical Models of Nuclear Magnetic Shielding

A. MOLECULAR SHIELDING TERMS

Ramsey gave the magnetic screening of a nucleus in a diamagnetic molecule as the resultant of a diamagnetic (σ_d) and a paramagnetic term σ_p (*75*). Lamb had shown (*45*) that a magnetic field induces electronic currents in a free atom that oppose the field and shield the nucleus (following Lenz's law, the Biot-Savart law, and Larmor's theorem). For an atom in a molecule, σ_d gives the shielding due to the rotation with the Larmor angular velocity of all the electrons of the molecule about the chosen origin, which we take at the nucleus of interest. This rotation is largely fictitious because of restraint by the other nuclei. Then σ_p represents similarly fictitious circulations of the valence electrons that reinforce the applied field. These arise from the slight unquenching in the magnetic field of the orbital angular momentum of the valence electrons which is quenched by directional bonding. The paramagnetic circulations are of $p_x \rightarrow p_y{}^*$, $d_x \rightarrow d_y{}^*$, etc., type (x and y refer to different directions) allowed by the mixing in with the ground state by the magnetic field of excited states that have angular momentum, i.e., $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, $\pi^* \rightarrow \sigma^*$, $\sigma_x \rightarrow \sigma_y{}^*$, and so on. Although the diamagnetic and paramagnetic terms tend to cancel in conventional NMR experiments, σ_p can be measured directly for an isolated molecule in molecular beam or microwave experiments, as described below.

Ramsey obtained σ_d by first-order and σ_p by second-order perturbation theory (*76*); variational treatments give similar results (*14*, *71*, *73*). The term σ_p is sometimes called the second-order paramagnetic term and sometimes the high-frequency term (*14*), because of the dependence of the (temperature-independent) paramagnetism in molecules on the high-frequency matrix elements of the orbital moments (*91*).

The average values of the screening tensors for a particular nucleus can be written as

$$\sigma = \sigma_d + \sigma_p$$

with

$$\sigma_d = \frac{e^2}{3mc^2}\left\langle \psi^0 \middle| \sum_i \mathbf{r}_i{}^{-1} \middle| \psi^0 \right\rangle \tag{1}$$

and

$$\sigma_p = \frac{-e^2}{3mc^2} \sum_k \left[\frac{\left\langle \psi^0 \middle| \sum_i \mathbf{L}_i \middle| \psi^k \right\rangle \left\langle \psi^k \middle| \sum_i \mathbf{L}_i \mathbf{r}_i^{-3} \middle| \psi^0 \right\rangle + \text{c.c.}}{\Delta E_k} \right] \tag{2}$$

where e and m are the electron charge and mass, respectively, c is the speed of light, ψ^0 is the wave function of the molecule in the ground state, ψ^k that in the kth excited state with energy ΔE_k above the ground state, and c.c. stands for complex conjugate. The factor 3 in the denominator arises from the averaging of the components of the shielding tensor about the three axes, i.e., $\sigma_{\text{av}} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$. The $\mathbf{L}$ and $\mathbf{r}$ vectors are, respectively, the angular momentum and position of the ith electron relative to the origin, and sums are taken over all electrons i and excited states k. σ_d and σ_p thus increase indefinitely with molecular size. The magnitude of each depends on the choice of gauge origin but the sum is invariant, as for the two parts of the magnetic susceptibility (*91*).

Values of σ_d are not very difficult to calculate, for Eq. (1) involves only ground-state wave functions. Furthermore, Flygare and Goodisman (*25*) have shown that Eq. (3) gives values of σ_d that are reasonably accurate (within 1 to 2 ppm), using tabulated values of the free atom (Lamb) term (*7*, *55*, *56*) and a knowledge of the molecular geometry:

$$\sigma_d = \sigma_d\,(\text{free atom}) + \frac{e^2}{3mc^2} \sum_\alpha \frac{Z_\alpha}{r_\alpha} \tag{3}$$

where α runs over all nuclei except the nucleus of interest, Z_α is the atomic number of the αth nucleus, and r_α its distance from the origin. [Ramsey has given a corresponding relationship (*78*). The error is small, being given by the Hellman–Feynman theorem as the ratio of the bonding energy of an atom to the total electronic energy of the atom.] The term σ_d can, therefore, be treated as a physical correction applied to the resultant shielding to obtain the paramagnetic term from conventional NMR experiments; or applied to the paramagnetic term from spin-rotation experiments to obtain the total shielding.

Because of the $\langle r^{-1} \rangle$-dependence of σ_d, the innermost electron shells make the largest contribution, but the fall-off is fairly gradual, as we shall see in examples below. For free atoms, σ_d increases steadily with the number of electrons, as shown in Fig. 2, but the increase is periodic in molecules, as shown in Figs. 6–8 for the binary hydrides and fluorides.

Equation (2) shows that σ_p vanishes for electrons without angular momentum (symmetrically distributed), e.g., in *s* orbitals, closed shells, free atoms, or monatomic ions; similarly, $\sigma_p{}^{\parallel}$ vanishes in linear molecules. The value of σ_p is larger the more asymmetric the distribution of

p, d, or f electrons, the closer they are to the origin ($\langle r^{-3}\rangle$ large), and the lower the energy of the excited states involving a rotation of charge $[(\Delta E)^{-1}$ large]. When there are low-lying $n \rightarrow \pi^*$ excited states, for example, σ_p correlates with the visible or ultraviolet absorption, the line shifting upfield as the absorption goes to shorter wavelengths (*2*, *23*, *32*).

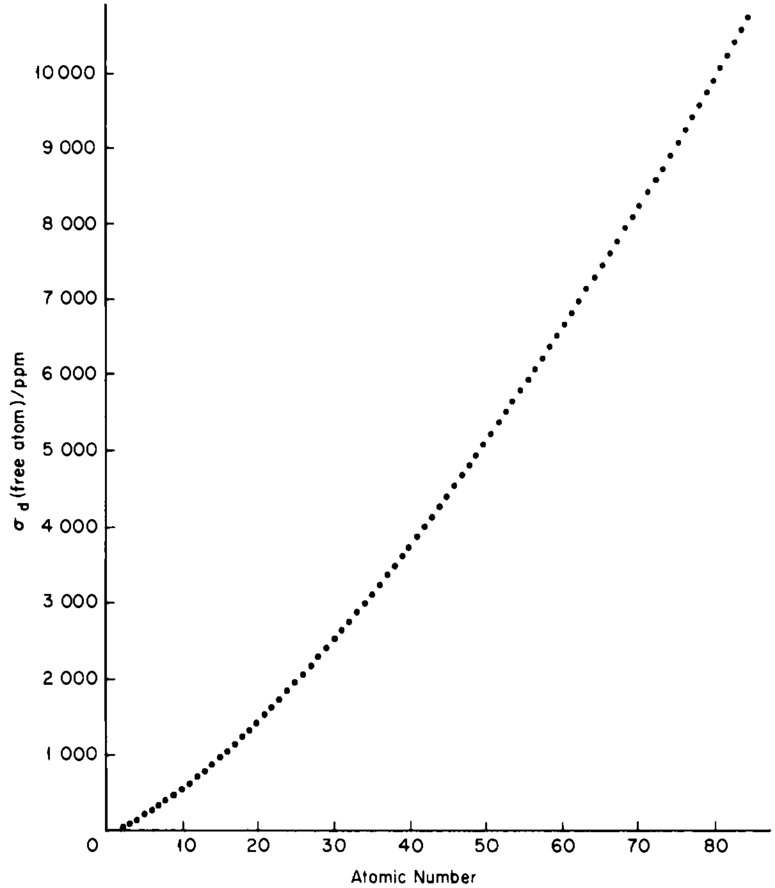

FIG. 2. Variation of σ_d (free atom) with atomic number Z (*7*, *55*, *56*).

A crude physical interpretation of Eq. (2) is that the factor $(\mu B/\Delta E)$ $\langle\psi^0|\mathbf{L}|\psi^k\rangle$ represents the applied field (B is the magnetic flux density and μ the Bohr magneton) driving the angular momentum and inducing a paramagnetic current, and the factor $\langle\psi^k|\mathbf{L}r^{-3}|\psi^0\rangle$ represents the transmission of the magnetic field due to the current to the nucleus at a distance r (*3*).

The $\langle r^{-3}\rangle$ dependence imposes a periodicity on the variation of the paramagnetic term with atomic number Z of the nucleus if the molecular environments are similar. Figure 3 shows the variation with Z of $\langle r^{-3}\rangle$ for the valence p electrons, obtained from observed atomic spin-orbit splittings (*5*), to be compared in later sections with periodic variations of σ_p.

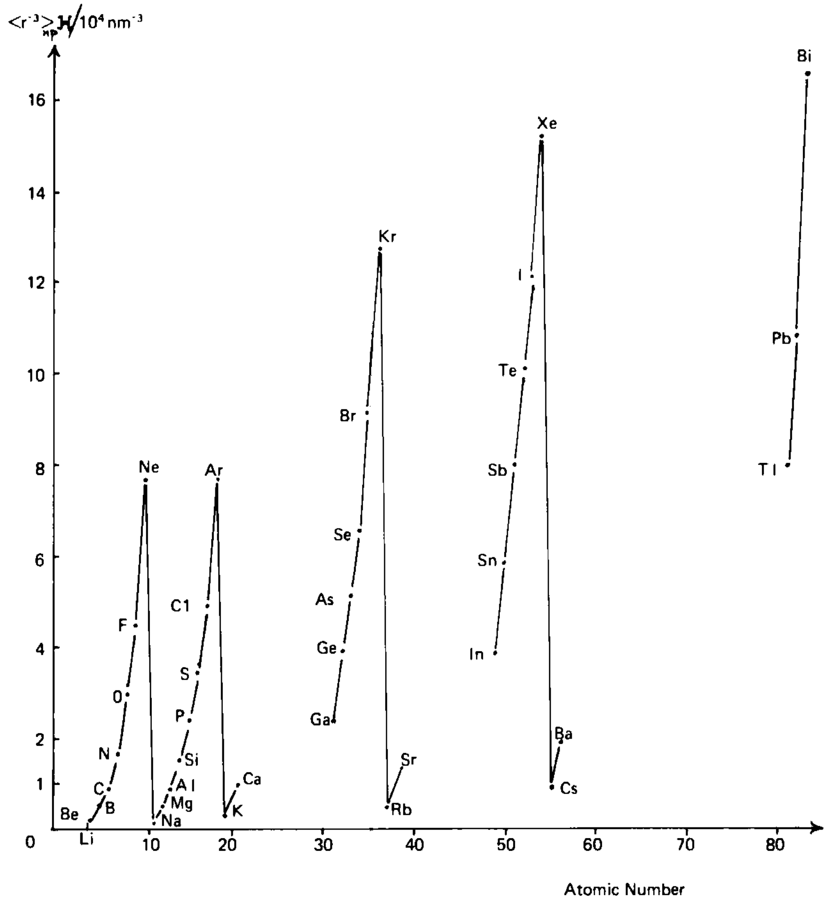

FIG. 3. Variation of $\langle r^{-3}\rangle_{np}\mathscr{H}$ for the valence p electrons with atomic number Z, as determined from spin-orbit splittings in atomic spectra (*5*). The $\mathscr{H}$ is a small relativistic correction, important mainly for heavy atoms ($Z > 50$). The values for the elements with the p^3 configuration (N, P, As, Sb) were obtained by interpolation. (Taken from Barnes and Smith (*5*), appeared also in Jameson and Gutowsky (*35*)].

The calculation of σ_p is very difficult for molecules that are more complicated than hydrogen because of the summation over all excited states (including the continuum) and the sensitivity to the wave functions used. Since σ_d and σ_p are quite large for molecules of any size and are opposite in sign, errors in σ_p bulk large in the resultant shielding, and one is weighing the ship with and without the captain. For these reasons, direct measurement of σ_p, where this is possible, is particularly important; and local-term approximations (with or without an average-energy approximation) have been extensively used in discussions of nuclear magnetic shielding. Both of these topics are considered in detail below.

B. THE CORNWELL EFFECT

Although the diamagnetic term must be positive (shielding), the paramagnetic term is not always negative. The best-known example of a positive value for σ_p is that of the fluorine shielding in chlorine monofluoride ClF, for which the resonance is well upfield of the fluoride ion (*11*); σ_p has now been measured (through the spin-rotation interaction) as +68 ppm (*16*). This unusual observation has been explained by Cornwell (*11*), and also by Santry (*82*). In ClF, the $\pi^* \rightarrow \sigma^*$ excitation produces circulations in opposite senses on the two atoms. The circulation is normal on chlorine (for which σ_p is found to be negative) but reversed on fluorine because it arises from an antibonding orbital, in which the chlorine terms are dominant because fluorine is the more electronegative partner. The reversed circulation on fluorine results in a positive contribution to σ_p which is large because of the relatively low energy (36,400 cm^{-1}) of the $\pi^* \rightarrow \sigma^*$ excitation. In the bonding orbitals, the coefficients for the fluorine terms are the greater and the $\pi \rightarrow \sigma^*$ circulation is normal, but the resulting negative contribution to σ_p is now smaller because of the higher energy of excitation from the π than from the π^* orbital. It serves, however, to cancel part of the positive contribution.

This phenomenon of antiparamagnetic paramagnetic terms clearly needs a name and is called here the *Cornwell effect* (ideally the Cornwell-Santry effect). Positive contributions to σ_p (which may or may not be positive overall) are expected in heteronuclear diatomics if they have a π^* state; this excludes, e.g., HF, InF, and TlF. In homonuclear diatomics, the $\pi^* \rightarrow \sigma^*$ excitation is symmetry-forbidden. The possibility has been mentioned for XeF_2 (*34*), although, from the chemical shift and calculated values of σ_d, the resultant σ_p (^{19}F) is negative in XeF_2 and KrF_2 (cf. Fig. 7). Another candidate is $FC{\equiv}CH$, from the evidence of the fluorine chemical shift and spin-rotation interaction (*96*). According to this interpretation there should be a substantial upfield shift of the ^{13}C

resonance for the carbon attached to fluorine, compared to carbon attached to hydrogen.

Low-energy circulations between π^* orbitals on fluorine and σ^* (e_g^*) *d* orbitals on the metal are possible in the (spin-paired) d^6 complex fluorides, NiF_6^{2-}, PdF_6^{2-}, and PtF_6^{2-}, and Cornwell's description of ClF has been invoked (*62*) in discussion of the fluorine resonance in these ions, which is at particularly high field compared with earlier transition metal fluorides (cf. Fig. 8). The ^{17}O resonance in $Co(acac)_3$, and the ^{14}N resonances in the hexammines of Co(III), Rh(III), and Ir(III) are at similarly high field.

C. THE (ATOMIC) LOCAL-TERM APPROXIMATION

Because of the problems described above of the Ramsey shielding terms, a useful approximation is to take advantage of the rough cancellation of the long-range diamagnetic and paramagnetic contributions to the shielding of the nucleus A, and to represent this by local terms σ_d^{A} and σ_p^{A}, which are calculated by Ramsey's theory applied only to the electrons on A (*81*, *85*). Contributions σ^{AB} from circulations on other atoms B are added as required. The σ_p^{A} term is obtained by valence bond (*35*, *81*) or molecular orbital methods (*35*, *69*).

For proton shielding, variations in all three terms σ_d^{A}, σ_p^{A} and σ^{AB} are important because of the small range of proton shifts, and because of the proximity of circulations on nearest neighbors, which are included in σ^{AB}; Fig. 6 shows this graphically (*58*). Well-known exceptions to generalizations about proton shifts can be traced to neglect of one or two of these terms. Contributions σ^{AB} may be obtained (*51*, *68*) by replacing a "distant" atomic current by a point dipole at that distance; the strength of the dipole is proportional to the magnetic susceptibility, which may be estimated as the sum of atomic contributions. The resulting shielding contribution is then proportional to the anisotropy of the susceptibility. Here too high-resolution microwave spectroscopy can contribute. Zeeman effect measurement of the molecular susceptibility tensor in formamide has given an estimate of the neighboring group anisotropy effect of the α-proton in a polypeptide link, which was used to show that the chemical shift in the transition from the helix to the random coil in poly-(L-alanine) is a solvation effect (*89*).

Interatomic or ring currents also may contribute to σ^{AB} in hydrogen, and much work has been done on these (*63*).

For nuclei other than hydrogen, with a much larger range of chemical shifts, σ_d^{A} is not very different from the free-atom term, σ^{AB} terms are relatively small and often neglected, and chemical shift relationships are ascribed to variation in $\sigma_p{}^{\mathrm{A}}$. (We discuss the limitations of this approach below.) A further more drastic approximation is to avoid the summation over excited states in $\sigma_p{}^{\mathrm{A}}$ by the use of an average energy ΔE (*38*, *69*):

$$\sigma_p{}^{\mathrm{A}} = \frac{-e^2\hbar^2\langle r^{-3}\rangle_{2p}}{2m^2c^2(\Delta E)}\left[Q_{\mathrm{AA}} + \sum_{\mathrm{B}\neq\mathrm{A}} Q_{\mathrm{AB}}\right] \tag{4}$$

Equation (4) applies to second-row elements, $\langle r^{-3}\rangle$ being the expectation value of the inverse cube of the radius of the $2p$ orbitals on atom A. The theory has been extended to lower rows of the periodic table by the inclusion of d orbitals (*35*, *48*). The average energy ΔE is usually used as an adjustable parameter to rationalize observed shifts (note that this approximation presupposes that contributions from all excited states have the same sign). The Q terms express the imbalance (in the ground state) of the $2p$ electrons, which depends on the nature of the bonding and of the immediate ligands B. The Q_{AA} term depends on electron density, whereas Q_{AB} depends on π-bonding at A.

If we take ^{13}C magnetic resonance as an example, ΣQ_{AB} is 0 for C—C and C≡C, increasing to 0.44 for C═C and to 0.77 for C═**C**═C, and this helps to place the resonance at high field in alkanes and alkynes, at medium field in alkenes and arenes, and at low field for the middle carbon in allenes. In addition, σ_p tends to be increased for unsaturated relative to saturated carbon by the lower excitation energies in the former. Doubly bonded carbon is deshielded by $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ circulations (when the magnetic field is perpendicular to the double bond and in the molecular plane), the middle carbon in allene being doubly deshielded in this way. Corresponding arguments apply to other nuclei; e.g., the middle nitrogen in the azide ion is less shielded than the end nitrogens.

In ^{19}F NMR, Q_{AA} is usually the more important term, although the π electrons may be very important in shielding, e.g., in aromatic fluorine compounds, or as we have seen in ClF. Both Q_{AA} and $\langle r^{-3}\rangle_{2p}$ depend on the electron density on the atom A and increase with increasing electronegativity of the ligands. So, however, does ΔE, and this is dominant when there are low-lying excited states, as for the nitrogen shielding in nitroso, nitro or azo compounds (*2*, *60*, *61*).

This qualitative theory is helpful in the physical and chemical interpretation of chemical shifts in covalent molecules and ions and may be used semiquantitatively in some comparisons of closely related species. It is, however, a fairly gross approximation, predicting, for example, that all alkane carbons have the same chemical shift. For ^{14}N and ^{17}O shielding the average energy approximation may be less appropriate (than for ^{13}C shielding) because of the large variation in excitation energies with nonbonding electrons present. When Cornwell effects are large the average energy approximation breaks down, of course.

D. THE ATOM-PLUS-LIGAND LOCAL-TERM APPROXIMATION

The local-term approximation described in the previous section, without the hazards of the average energy approximation (*52*), can, in principle, give an accurate account of the shielding if the long-range diamagnetic and paramagnetic contributions cancel or if noncancelling contributions can be determined reliably. The first condition holds for contributions from sufficiently distant atoms as the paramagnetic contribution then becomes $\langle r^{-1} \rangle$-dependent (as is the diamagnetic contribution), since angular momentum about the origin increases with distance and there are two factors depending on angular momentum in Eq. (2); the $\langle r^{-2} \rangle$-dependent terms are 0 for distant dipoles (*51*). However, the inclusion with the distant atoms of the immediate ligands is a source of trouble since they may well be too close to be treated as dipoles. Near atom A the molecular diamagnetic term falls off more slowly than the paramagnetic term. As we see below, contributions by the immediate ligands to the molecular diamagnetic term in second-row elements may change by 100 ppm or so, even in compounds that are closely related chemically. But the local (atomic) term σ_d^{A} varies by no more than about 20 ppm, often much less, for second-row elements (*69*). Occasional voices have been heard suggesting that variations in the local diamagnetic term should be taken more seriously, e.g., Davies says "The possibility of variations in σ_d for ^{19}F has been mentioned only to be dismissed" (*13*), and Chan says "for fluorine shielding, changes in the Lamb term are not as negligible as they are often assumed to be" (*10*). Lambert and Roberts (*46*) noted large changes in σ_d (^{14}N), e.g., 150 ppm from NH_4^+ to NO_3^-, when nearest neighbors were taken into account.

To avoid the confusion to which this topic is prone we should define a local-term approximation which gives the total shielding $\sigma(\mathrm{A})$ of the nucleus A in terms of the shielding σ^{AL} due to electronic circulations on A and on its directly bonded neighbors (ligands) L, i.e.,

$$\sigma(\mathrm{A}) = \sigma_d^{\mathrm{AL}} + \sigma_p^{\mathrm{AL}} + \sigma^{\mathrm{C}}$$

where (5)

$$\sigma_d^{\mathrm{AL}} = \sigma_d^{\mathrm{A}} + \sigma_d^{\mathrm{L}} \qquad \text{and} \qquad \sigma_p^{\mathrm{AL}} = \sigma_p^{\mathrm{A}} + \sigma_p^{\mathrm{L}}$$

where σ_d^{A} and σ_p^{A} are the atomic terms of the conventional local-term approximation, and σ_d^{A} and σ_p^{L} the diamagnetic and paramagnetic contributions to the screening of the nucleus A, from circulations on the ligand atoms. The σ^{C} term then represents the remaining long-range contributions, which we now with more confidence expect to be negligible or small. As before, the diamagnetic terms can be obtained with little difficulty, for example by Flygare and Goodisman's equation. It would be difficult to calculate $\sigma_p{}^{L}$, but less difficult to calculate $\sigma_p{}^{AL}$. Values of $\sigma_p{}^{AL}$ may be obtained, however, by subtracting $\sigma_d{}^{AL}$ from σ (A) obtained by referring the observed shift to an absolute scale (as discussed below). Alternatively, relative values can be used for the shielding parameters; the resonance of the simple hydride (CH_4, $NH_4{}^+$) may be a useful reference point since other resonances are normally downfield of this.

The atom-plus-ligand local-term approximation has been justified *a posteriori* for ^{14}N *(30)* and ^{13}C *(57)* shielding, since certain expected relationships of chemical shifts, such as additivity of substituent effects, were found to be absent for the observed shifts, but were fulfilled for $\sigma_p{}^{AL}$, i.e., after correction for the atom-plus-ligand diamagnetic term. Some examples are given in the following sections.

E. ADDITIVITY OF SUBSTITUENT EFFECTS IN NUCLEAR MAGNETIC SHIELDING

There are many examples of the linear additivity of substituent shifts. Shoolery's constants predict methylene proton shifts in disubstituted methanes for a wide range of substituents including the halogens, OR, SR, NO_2, and singly, doubly, and triply bonded carbon *(67)*. Additivity is found extensively in ^{13}C shifts *(88)*. Pairwise additivity, attributed to interaction between neighboring substituents, has been demonstrated in ^{11}B *(87)*, ^{27}Al *(53)*, ^{73}Ge *(41)*, $^{47,49}Ti$ *(40)*, and ^{93}Nb *(42)*, as well as in ^{13}C resonance *(54)*. The interactions have been expressed as perturbations of the McWeeny group wave functions of the substituents; the additivity rules fail when the perturbation is large, examples being drawn from ^{1}H, ^{11}B, and ^{19}F shifts *(93)*.

Table II shows that the observed *(29)* ^{13}C shifts δ (taken as positive downfield) show a degree of linear additivity in the methyl-substituted methanes, with a shortfall for neopentane. Table II shows also the division of the shielding into atom-plus-ligand diamagnetic and paramagnetic parts, relative to methane for which σ_d is 295 ppm. The diamagnetic terms were calculated by Flygare's method *(25)*. With each substitution of hydrogen by carbon, $\sigma_d{}^{AL}$ for the central carbon increases by 28 ppm but $|\sigma_p|$ increases by about 37 ppm, and the line moves 9 ppm downfield. Analogous relationships have been demonstrated for ^{14}N shielding in methyl-substituted NH_3 and $NH_4{}^+$ *(30)*. Table II shows that the shortfall at neopentane is in the paramagnetic term.

Unexpected support for the atom-plus-ligand diamagnetic correction

TABLE II

^{13}C SHIELDING TERMS FOR THE CENTRAL CARBON IN METHYL-SUBSTITUTED METHANES[a]

	δ	σ_d^{AL} (ppm)	σ_p^{AL} (ppm)
CH_4	0	Say 0	Say 0
CH_3CH_3	8.0 (*8*)	28 (*28*)	−36 (*−36*)
$\mathit{C}\mathrm{H_2(CH_3)_2}$	18.2 (*10*)	56 (*28*)	−74 (*−38*)
$\mathit{C}\mathrm{H(CH_3)_3}$	27.3 (*9*)	85 (*29*)	−111 (*−37*)
$\mathit{C}\mathrm{(CH_3)_4}$	29.7 (2.4)	112 (26)	−142 (*−31*)

[a] The numbers in parentheses are differences with successive substitution.

has come from arithmetic relationships of ^{13}C shifts in the hydrocarbons (*57*). Linear additivity in the observed shifts finds expression in the well-known substituent parameters (α—ϵ) which are used to assign ^{13}C resonances in alkanes and alkyl groups (*29*). The α parameter, about 9 ppm, gives the increase in chemical shift (positive downfield) for each substituent carbon α to the nucleus of interest, and similarly for the parameters (β—ϵ). However, eight additional parameters were found to be necessary in order to include carbons at or next to branching positions, making a total of thirteen independent parameters (of which two are small). After the atom-plus-ligand diamagnetic correction, the ^{13}C shifts relative to methane are given satisfactorily for linear and branched acyclic alkanes, and for simple cycloalkanes, by only four parameters (*57*) (Fig. 4).* Similarly, anomalies in ^{13}C resonances at bridgehead positions in polyphenyls and fused arenes, which are found to be well upfield of the positions predicted by molecular orbital theory, can be attributed to the diamagnetic part of the ligand contribution (*57*).

The empirical substituent parameters that give the values of the corrected shift for the unhindered alkanes are $\alpha = 35.4$, $\beta = 8.4$, $\gamma = -1.5$, and $\delta = 1.4$ (it is a general observation that the γ contribution is upfield). Support for the neglect of the long-range terms σ^C [Eq. (5)] for the γ- and δ-carbons is given by the small magnitude of these parameters, to which motional averaging may contribute as well. The rather large value of the β parameter demonstrates the noncancellation of the diamagnetic and paramagnetic contributions at that distance.

* Steric restrictions lead to irregularities; e.g., the methyl cyclohexane parameters vary with conformation, and the ^{13}C line in cyclopropane is significantly upfield of the predicted shift.

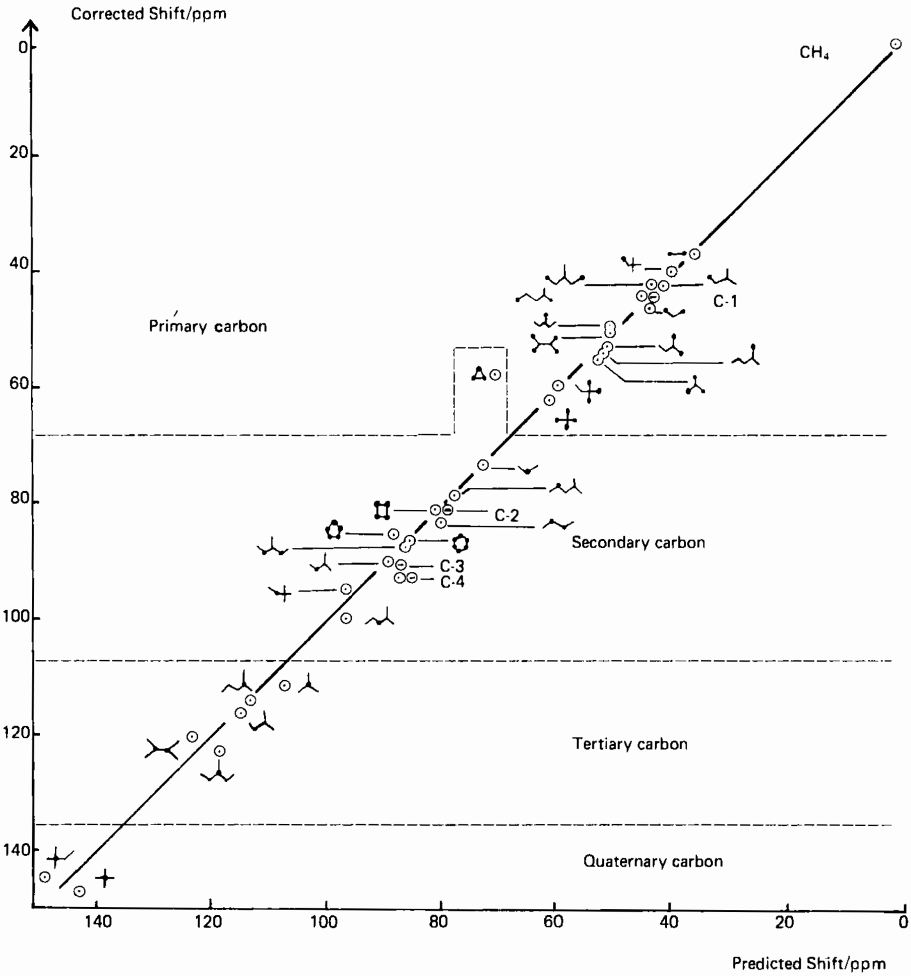

FIG. 4. ^{13}C Shifts in alkanes: plot of corrected shift against values predicted using four empirical parameters. [Appeared in Mason (57).]

Although the observed shifts are reasonably additive for methyl-substitution in methane, this is not true for other substituents, and the top half of Fig. 5 contains an up-dated version of the well-known plot (47) of ^{13}C shifts in substituted methanes against the number of substituents. The lower half of Fig. 5 shows that the large increase in σ_d^{AL} with successive substitution accounts for most of the upfield turn of the plots. The residual shortfall in σ_p^{AL} increases with degree of substitution and

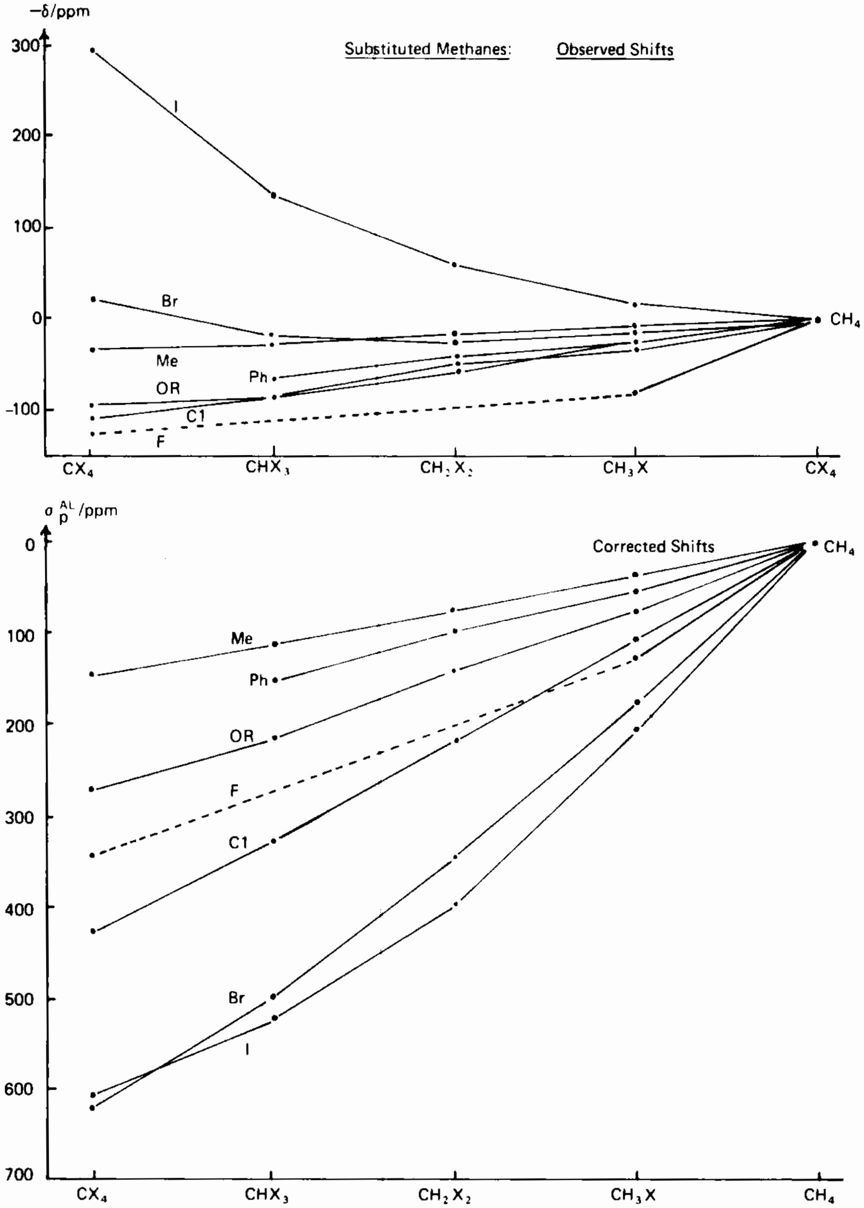

FIG. 5. Plot of ^{13}C shifts in substituted methanes against the number of substituents. The observed shifts are compared with these corrected for the atom-plus-ligand diamagnetic term. [Appeared in Mason (*57*).]

with size of the ligand and, presumably, involves electron delocalization; cf. the anomaly of cyclopropane in the alkane correlations.

Some other types of correlation are improved if observed shifts are corrected for σ_d contributions of the nearest ligands; e.g., the ^{14}N shielding in nitroso compounds XNO is roughly linear with the $n \rightarrow \pi^*$ wavelength [representing $(\Delta E)^{-1}$] when X is a second-row atom, as in RNO, R_2NNO, RONO, and NOF, but the ^{14}N line diverges to high field when X is a third- or fourth-row atom, as in RSNO, NOCl, and NOBr. The divergence is compensated by correction for σ_d^{AL}, which increases by 130 ppm from NOF to NOBr (*2*).

F. *Ab Initio* CALCULATIONS*

Ab initio molecular orbital calculations of ^{13}C, ^{14}N, ^{17}O, and ^{19}F shieldings in a wide range of organic molecules containing up to 3 second-row atoms, but including CF_4, have been reported by Ditchfield, Miller, and Pople (*19*). Because of the expense of large extended basis sets, even for these small molecules, the aim was for reasonable accuracy in shifts from molecule to molecule, since the absolute values depend on the choice of origin when the basis set is incomplete. A finite perturbation method was used to obtain the molecular diamagnetic and paramagnetic shielding parameters with the center of mass as origin. Good agreement with experiment was found so long as the nuclei being compared occupy similar positions relative to the origin, e.g., ^{13}C shifts in CH_3X compounds are fairly well described when X contains 1 second-row atom, but not the relative shifts in methane, ethane, and propane. There is reasonably good agreement, however, for methyl carbons in propane, dimethylamine, and dimethyl ether, or for the central carbons in propane, propene, propyne, allene, acetonitrile, acetaldehyde, and formamide.

The calculations allow some useful conclusions as to "chemical" influences on the shifts, e.g., a large part of the ^{13}C shifts in CH_3X compounds, when X is CH_3, NH_2, OH, or F, depends on the increase in the paramagnetic term with contraction of the carbon orbitals as charge is withdrawn by X (i.e., as $\langle r^{-3} \rangle$ increases).

G. ELECTRONEGATIVITY CORRELATIONS

Correlations of chemical shifts with electronegativity of the substituent are of long standing (*12*, *72*, *86*). In general the ^{1}H, ^{13}C, ^{19}F (or etc.) line goes downfield with increasing electronegativity of the sub-

---

* More recent developments in this important field are described by R. Ditchfield and P. D. Ellis in "Topics in Carbon-13 NMR Spectroscopy" (G. C. Levy, ed.), Wiley, New York, 1974, and by W. T. Raynes in *Chem. Soc. Spec. Per. Rep. NMR* **3**, 8 (1974) and R. B. Mallion, *ibid.* 4, 14 (1975).

stituent, but there are many anomalies. For ^{13}C shielding in Me_nX compounds the line goes downfield as X runs across the second or third row of the typical and post-transition elements, but this trend tends to be reversed in later rows, as shown by a plot of the observed ^{13}C shift against the atomic number of the ligand X (*57*). This variation was compared with the corresponding plot of $\sigma_p{}^{AL}$ (^{13}C), obtained by subtraction of the atom-plus-ligand diamagnetic terms from the observed shifts (all relative to CH_4); the latter plot was found to be more consistently periodic. The corrected shift ($\sigma_p{}^{AL}$) increases numerically as the ligand moves across the row of the periodic table (and its electronegativity increases), but it increases also as the ligand moves down the group (and its electronegativity decreases).

The corresponding periodic correlation of ^{19}F shifts (*59*) is more extensive and informative. This and the corresponding plot for proton shielding (*58*) have been constructed using absolute values of the molecular shielding terms, avoiding the hazards of local-term approximations. Discussion of these periodicities is postponed to Section V.

IV. Absolute Shielding

A. THE SPIN-ROTATION INTERACTION

Theory gives the nuclear magnetic shielding for the gaseous molecule relative to the bare nucleus. In conventional spectrometers the shielding is usually measured in fluid phases, so that intermolecular effects are motionally averaged, and relative to standard compounds because of the difficulty of accurate measurement of field strengths; frequencies are readily measured to 1 part in 10^8. Absolute measurements for comparison with theory can, however, be obtained under favorable circumstances from the spin-rotation interaction. The tumbling of a molecule generates magnetic fields at a nucleus because of the circular motions about it of the other nuclei (which can be calculated in classical terms) and of the electrons, just as the effect of a magnetic field on the electrons is equivalent to that of a molecular rotation (this is Larmor's theorem). In the absence of collisions the spin-rotation interaction can be observed, for simple molecules, as magnetic hyperfine structure either of the nuclear spin resonance or of the rotational spectrum.

This interaction was discovered in 1939 in the hydrogen molecule in studies deriving ultimately from the Stern–Gerlach experiment, which demonstrated the quantization of angular momentum, and was converted into a resonance method by Rabi and his collaborators in the 1930s for the measurement of magnetic moments (*39*). The various approaches to nuclear magnetic shielding were synthesized by Ramsey in 1950 (*75*). Spin-rotation coupling constants C_i are now measured by molecular beam magnetic resonance (*4*, *9*, *77*) or electric resonance (*99*), or by high-resolution microwave spectroscopy (*26*, *31*, *97*) or molecular beam maser, invented by Townes and his collaborators (*28*, *90*); complex spectra are subjected to computer analysis. Perhaps because of the small interest taken in them so far by chemists (with some notable exceptions), spin-rotation constants, which may have been obtained in the pursuit of other molecular information, are often reported in the physical or chemicophysical literature without reference to the shielding information that they contain.

The importance of the spin-rotation interaction is that it monitors a paramagnetic electronic circulation divorced from the diamagnetic circulation that must accompany it when an external field is applied to the molecule. The physical basis for the interaction was examined by Wick (*98*) for the hydrogen molecule and then extended to polyatomic molecules (*21*, *36*). In the rotating molecule, the inner-shell electrons rotate with their nuclei. Closed shells on the nucleus taken as origin produce no field there, nor do closed shells elsewhere (for which the field is cancelled by equivalent positive charges on their own nuclei); these shells have been compared to the chairs on a Ferris wheel that preserve their orientation as the frame rotates. If the valence electrons "slipped" in this way there would be no rotational paramagnetic effect; but since they are associated with more than one nucleus they rotate partially with the molecule. Their angular momentum relative to the molecular frame can be considered to arise, as before, from the mixing in of appropriate excited states, and the resultant field at the nucleus corresponds to the deshielding in an applied field. The important difference in the rotating molecule is that σ_p is opposed only by the effect of the rotating nuclei σ_{nuc}. The resultant is the σ_{sr} term due to the spin-rotation interaction:

$$\sigma_{sr} = \sigma_p - \sigma_{\mathrm{nuc}}$$

compared with (6)

$$\sigma = \sigma_d + \sigma_p$$

in conventional NMR spectroscopy. The σ_{nuc} term due to the motion of the other nuclei about the origin is easily found (following the Biot–Savart law) from the molecular geometry. It is, in fact, the negative of the second term in Eq. (3), because of the balance of forces on a nucleus from the electrons and from the other nuclei. Thus the shielding in conventional NMR experiments can be estimated as the sum of σ_d (free atom) and σ_{sr}.

The value of σ_{sr} is obtained from the spin-rotation constants C_i, which are the components (in units of frequency) of the nuclear spin-rotational tensor, defined by the Hamiltonian

$$\mathscr{H} = -hC_i\mathbf{I}\cdot\mathbf{J}$$

where **I** and **J** are, respectively, the nuclear and rotational angular momenta (the spin-rotation interaction is sometimes called the "I dot J" interaction). This definition embodies Ramsey's sign convention, which is also followed by Flygare; many microwave spectroscopists use the opposite convention. Experiment gives the magnitude but not necessarily the sign of C_i, and this is found from chemical shifts, or by analogy, or from other evidence.

Equations relating σ_{sr} and the spin-rotation constants have been given by Ramsey (*9*, *77*, *78*) for linear molecules and by Flygare (*24*) for symmetric top, spherical top, and asymmetric molecules. A simple expression for the general case, and neglecting vibrational effects, is

$$\sigma_{sr} = \frac{e\pi \Sigma C_{\lambda\lambda} I_{\lambda\lambda}}{3m_e c\hbar\gamma} \tag{7}$$

where γ is the magnetogyric ratio of the nucleus of interest, the I's are the principal moments of inertia referred to axes λ, and the C's the corresponding components of the nuclear spin-rotational tensor. In linear molecules, two of these components are equal ($C^{\perp}$) and the third ($C^{\parallel}$) is zero ($\sigma_p{}^{\parallel}$ being zero) so the sum over $C_{\lambda\lambda}I_{\lambda\lambda}$ reduces to $\frac{2}{3}C^{\perp}I^{\perp}$.

Thus the spin-rotation constants contain the infinite sum over excited states that is so difficult to calculate. The relative contributions of σ_p and σ_{nuc} to σ_{sr} are of interest. For hydrogen, with its small nuclear charge and unusually spherical distribution of electrons, the slip effect is rather large in proportion, and the magnetic field due to the rotating nuclei exceeds that due to the electrons. For all other nuclei the electronic contribution outweighs the nuclear contribution, e.g. for ^{19}F all known values of C_i are negative (on Ramsey's sign convention) except for ClF.

B. OTHER METHODS FOR THE MEASUREMENT OF ABSOLUTE SHIELDING

A method for obtaining the paramagnetic terms directly, which will become more important now that pulsed NMR provides accurate measurements of shielding anisotropies in solids (*92*, *94*), is to take advantage of the zero parallel component of the paramagnetic term in linear molecules. Because of this the anisotropy $\Delta\sigma_p$ in the paramagnetic term gives the absolute (average) value:

$$\begin{aligned} \Delta\sigma_p &= \sigma_p{}^{\parallel} - \sigma_p{}^{\perp} = -\sigma_p{}^{\perp} \\ \sigma_p &= \tfrac{1}{3}(\sigma_p{}^{\parallel} + 2\sigma_p{}^{\perp}) = -\tfrac{2}{3}\Delta\sigma_p \end{aligned} \tag{8}$$

The anisotropy in the paramagnetic term is obtained by correcting the measured anisotropy for the anisotropy in σ_d, and Gierke and Flygare (*27*) have shown how this may be estimated. This correction is often neglected, but is rarely negligible; e.g., for F_2, $\Delta\sigma_d$ is −75 ppm. If the measured anisotropy for the fluorine molecule (*65*) is corrected in this way, then it gives a value of σ_p which agrees well with values obtained from the spin-rotation interaction and from the chemical shift (*59*).

Another way in which chemical shifts can be related to absolute shielding is by the comparison of the nuclear magnetic moment (measured by the NMR method for an atom in a molecule) with the moment for the free atom. This has been done with considerable accuracy for hydrogen (*80*) and also for lead (*50*).

C. ABSOLUTE SHIELDING SCALES

In the past the difficulties of the absolute measurements have tended to limit their precision; but with modern techniques, and under favorable circumstances, the precision approaches that of the measurement of chemical shifts, and the information can be combined to set up absolute shielding scales. This has been done for hydrogen, as mentioned above, and for fluorine on the basis of spin-rotation measurements on HF (*95*), with vibrational correction of the spin-rotation and shielding constants (*33*). For ^{13}C, measurements on ^{13}CO (*22, 64, 66*) could be used, for ^{14}N,* measurements on NH_3 [by two-cavity molecular beam maser (*43, 44*)] or on HCN (*17*), for ^{31}P, measurements on PH_3 (*15*), and for the halogens, measurements on $H^{35}Cl$ (*37*) and on $H^{79}Br$ and $H^{127}I$ (*18*). This list is by no means exhaustive, and there is now a considerable body of information on absolute shielding that could yield interesting chemical comparisons.

V. Periodicity in Nuclear Magnetic Shielding

The study of periodicity in nuclear magnetic shielding has been neglected in the past, except for one or two isolated studies. Jameson and Gutowsky (*35*) showed that the range of chemical shifts for a particular nucleus (which resembles the diamagnetic term for the free atom) varies periodically with the atomic number of the nucleus, and traced this variation to the dependence of the paramagnetic term on $\langle r^{-3}\rangle$ for the bonding electrons. The periodic variation of $\langle r^{-3}\rangle_{np}$ is shown in Fig. 3.

---

* This has now been done (J. Mason and J. G. Vinter, *J. Chem. Soc., Dalton Trans.*, in press.

As mentioned above, the electronegativity correlation in nuclear magnetic shielding suggests a periodic dependence of nuclear shielding on the atomic number of the ligand. This was explored in a preliminary way (*57*) for ^{13}C shielding in methyl derivatives Me_nX, many of which have now been measured, and the periodicity of the ^{13}C shielding with the atomic number of the ligand X was found to be improved when the paramagnetic part of the shielding (relative to methane) was separated according to the atom-plus-ligand approximation.

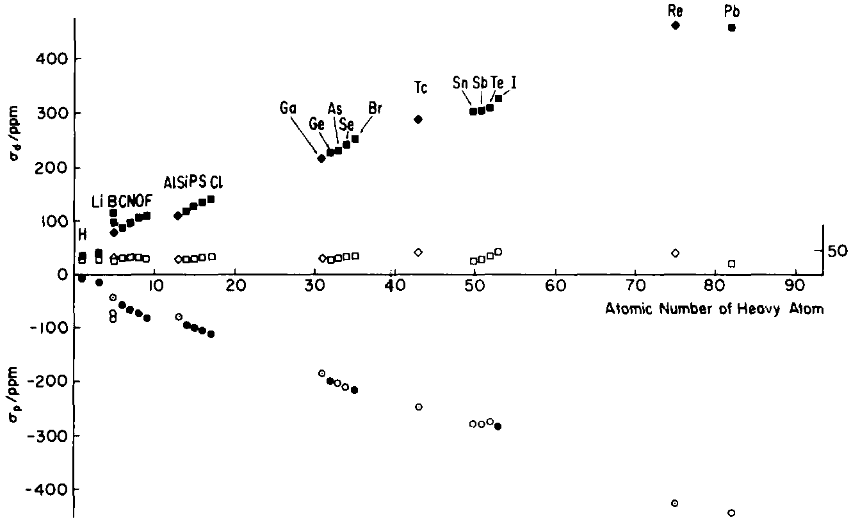

FIG. 6. Proton-shielding parameters for the binary hydrides of the elements plotted against the atomic number of the central atom. Explanation of symbols:

	Molecules	Ions
σ_d(calc.)	■	◆
$\sigma(\delta)$	□	◇
$\sigma_p(\delta)$	○	⊙
σ_p(obs.)	●	

For proton and ^{19}F shielding, a sufficiently large number of the paramagnetic shielding constants have been measured, mostly through the spin-rotation interaction, so that the periodicity can be examined (*58*, *59*) for the Ramsey (all-atom) shielding terms σ_d and σ_p. Many calculated values of σ_d are available in the literature for the binary hydrides and some for the binary fluorides. The rest were calculated by Flygare and Goodisman's method (*25*).

Figure 6 shows the shielding terms σ_d, σ_p, and σ (the resultant shielding) for the proton in the binary hydrides plotted against the atomic

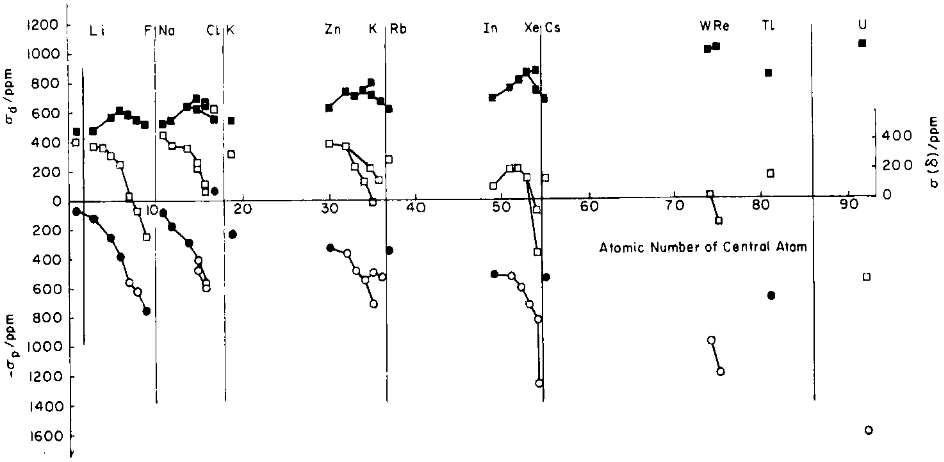

FIG. 7. ^{19}F Shielding parameters for the binary fluorides plotted against the atomic number of the central atom—molecular species. (■)σ_d(calc.); (□)$\sigma(\delta)$; (○)$\sigma_p(\delta)$; (●) σ_p(obs.).

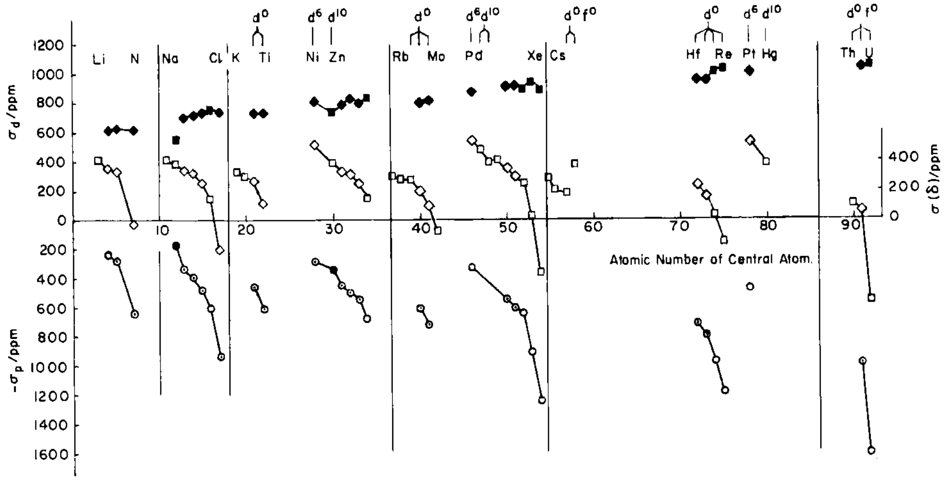

FIG. 8. ^{19}F Shielding parameters for the binary fluorides plotted against the atomic number of the central atom—fluoride anions, solids, and high-oxidation states of the central atom. Explanation of symbols:

	Molecules	Ions
σ_d(calc.)	■	◆
$\sigma(\delta)$	□	◇
$\sigma_p(\delta)$	⊙	○
σ_p(obs.)	●	

number Z of the heavy atom (*58*), and Figs. 7 and 8 are analogous plots (*59*) for the ^{19}F shielding in the binary fluorides (in Fig. 7 are plotted molecular species, and in Fig. 8 mainly fluoride anions, solids, and high-oxidation states of the central atom). The values of σ_p(obs.) plotted as closed circles were obtained from the spin-rotation interaction, apart from some values for linear fluorides for which σ_p was obtained from the shielding anisotropy. The values of σ_d(calc.) are plotted as closed squares. The values of $\sigma(\delta)$, plotted as open squares, are obtained from conventional NMR by referring the chemical shift δ to an absolute scale, as described in the previous section.

It was found for the hydrides and for the fluorides that the values for the resultant shielding obtained by combining σ_p(obs.) and σ_d(calc.) agreed well with those obtained from the chemical shift. (Where agreement was not so good, e.g., for SiH_4 and GeH_4, the discrepancy corresponds to the uncertainty in the spin-rotation constants.) The paramagnetic term for the hydrides and fluorides for which no spin-rotation value was available was therefore estimated by subtracting σ_d(calc.) from $\sigma(\delta)$. The resulting values of $\sigma_p(\delta)$ are plotted as open circles in the Figs. 6 to 11.

The striking feature of the hydride correlation in Fig. 6 is the very similar periodicity in σ_d and σ_p. This is unique to hydrogen, for which all the electrons are valence electrons. The value of σ_d increases with the number of electrons on the heavy atom, and the periodic variation of σ_d with the number of ligands (which rises in the second row to 4 for carbon and then falls to 1 for fluorine) is not evident in the hydride plot, although it can be seen in the fluoride plot in Fig. 7. In Fig. 6, boron–hydrogen shieldings are shown for diborane and BH_4^-. The BH_4^- ion is seen to fit the periodic correlation, as do AlH_4^-, GaH_4^- (for which the chemical shift was estimated from that of related compounds), TcH_9^{2-} and ReH_9^{2-} (d^0). The shielding of hydrogen attached to boron correlates more with molecular topology than with chemical expectation since the electron-deficient bridge proton is not the least shielded, although the electron-affluent terminal proton is the most shielded. (The relative shielding of the bridge and terminal protons follows the increase in σ_d as the proton comes closer to the electrons on two borons, but the proton in BH_4^- is the most shielded because of the smallness of σ_p.)

As to the symmetry of the plot for σ_d and σ_p, we mentioned earlier that the effective r dependence of σ_p may be nearer $\langle r^{-1}\rangle$ than $\langle r^{-3}\rangle$ for "distant" contributions, because of the dependence of the moment of the electron on its distance r. The plot reflects (for σ_p) the increase in the r term across the row of the ligand and the decrease down the group, against the tendency of $(\Delta E)^{-1}$ to decrease across the row and increase down the group. Figures 6 and 9 illustrate the familiar alternation of properties down the group, due to irregularities in atomic structure and the periodic table. The relatively large increase in σ_d and σ_p from the first row (hydrogen) to the second reflects the relatively large increase in the number of electrons on the ligand, and similarly for the large increase from the third row to the post-transition elements of the fourth. However, σ_d and σ_p do not increase at the same rate, and given the steady increase in σ_d with the number of electrons in the molecule, we can ascribe the irregularities in the variation of the proton shielding down the group of the ligand to the smaller increase in σ_p than in σ_d down the later groups.

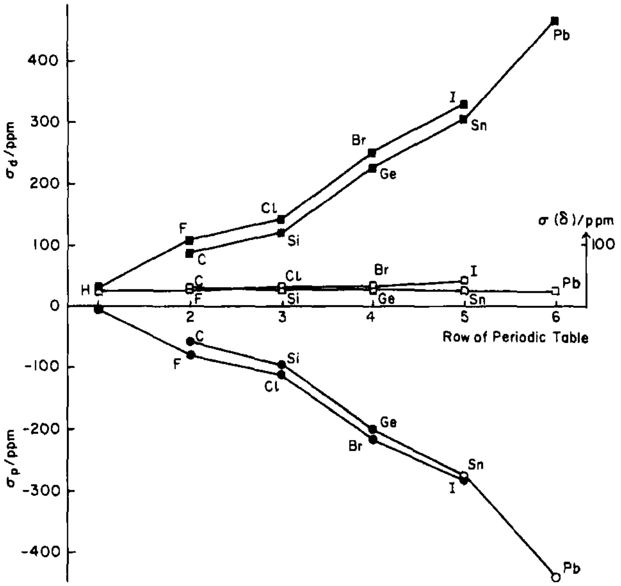

FIG. 9. Variation in the proton shielding parameters down the groups of the heavy atom for Groups IV and VII. (■) σ_d(calc.); (□] $\sigma(\delta)$; (o) $\sigma_p(\delta)$; (●)σ_p(obs.).

Thus, although proton shielding is often described as dominated by the diamagnetic term, the periodic correlation shows that variations in the resultant shielding may be determined by changes in σ_p, as across the second row and down the group of the ligand. Across the third and subsequent rows, the diamagnetic term increases faster than the paramagnetic term, the more so the heavier the central atom, but the margin is relatively small.

Figure 7 shows clearly the periodic variation of σ_d for ^{19}F in fluorides

(*59*) with the number of electrons in the molecule. For the second-row ligands this reaches a maximum at CF_4, but in later rows the maximum is at the end of the row, at the highest fluoride of the halogen or xenon. Both σ_d and σ_p are larger for higher fluorides compared with lower fluorides of the same element. The resultant shielding, although it is higher in the higher-oxidation state for the fluorides of the elements of Groups V and VI, is higher for the *lower* fluorides of the halogens or xenon; a comparative study of Cornwell effects would be of interest here.

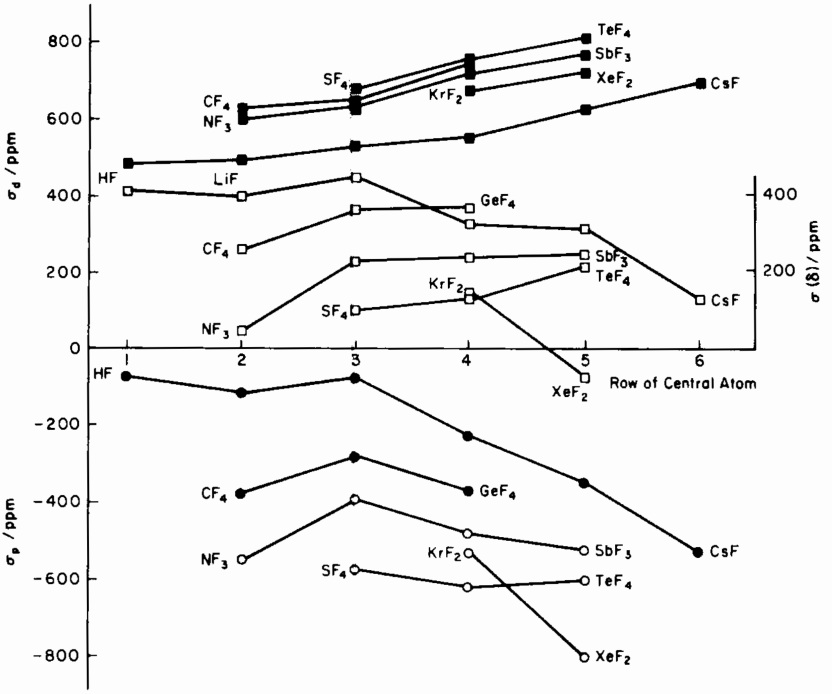

FIG. 10. Variation in ^{19}F shielding down the group of the central atom for Groups O, I, IV, V, and VI. (■) σ_d(calc.); (□) $\sigma(\delta)$; (o) $\sigma_p(\delta)$; (●) σ_p(obs.).

The most striking feature of Figs. 7 and 8, particularly as compared with the hydride plot, is the plunge downfield of the resultant shielding, following the paramagnetic term, across the row of the central atom for the typical elements, and also for the early transition metals (Fig. 8), with ready circulation of fluorine $2p$ electrons into empty t_{2g} orbitals in the d^0 complexes. Fluorine is highly shielded however in the d^6 molecules and ions, and this was discussed in Section III, B as a possible Cornwell effect (*62*).

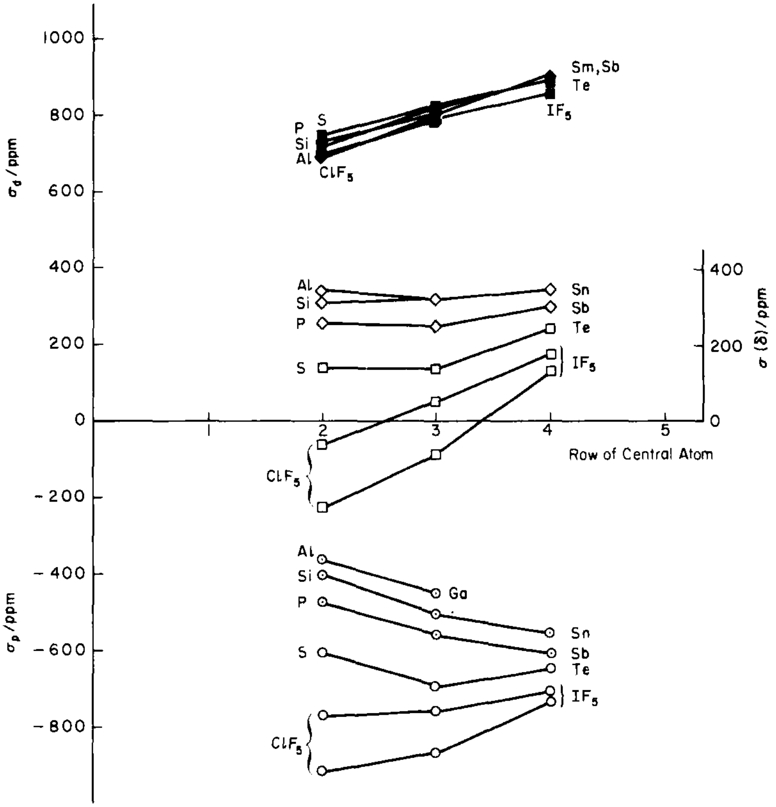

FIG. 11. Variation in ^{19}F shielding down the group of the central atom in hexafluoride ions and molecules and in halogen pentafluorides. Explanation of symbols:

	Molecules	Ions
σ_d(calc.)	■	○
$\sigma(\delta)$	□	◇
$\sigma_p(\delta)$	○	⊙
σ_p(obs.)	●	

The increase in σ_p across the row of the central atom follows the increasing imbalance of the fluorine $2p$ electrons with increasing covalency, the increase in $\langle r^{-3}\rangle_{2p}$ (cf. Fig. 3), and the tendency of $(\Delta E)^{-1}$ to increase [in contrast to the trend in the energy term for the proton (*58*) and ^{13}C shielding (*57*) across the row of the ligand]. Down the group of the central atom (Figs. 10 and 11), σ_p tends to increase with the energy term against the tendency of the radius term to decrease (for the typical elements), although there are important anomalies that, perhaps, show the influence of the radius term; e.g., the large values of σ_p when the central atom belongs to the second row and the radius term is large. Near the bottom of the later groups the increase in σ_p is slowed or reversed so that the resultant shielding increases, and this tendency is evident also in the proton and ^{13}C correlations (*57*, *58*). Figure 11 shows that this is not an effect of change in the molecular shape across the row since it is very marked for the higher fluorides. Figure 10 shows that this tendency in Group VI and VII is not, however, shown by KrF_2 and XeF_2.

Thus, although the hydride and fluoride periodicities look very different at first sight, similar trends can be discerned overall as well as in many of the details, and these trends are evident also in the periodic correlations for the shielding of other nuclei, ^{13}C, for example.

The periodic correlations illustrate the basis in molecular electronic structure for the generalization, "more electrons, more shielding," and for the exceptions to this. Effects of ligand electronegativity in nuclear magnetic shielding are complex, since the excitation energies are influenced by both σ- and π-inductive effects, and so also are the orbital terms, including the radius terms. In the periodic correlations, as in the earlier examples, separation of the diamagnetic and paramagnetic parts often helps in understanding chemical shifts in groups of related compounds.

REFERENCES

1. Andersson, L.-O., and Mason, J., *Chem. Commun.* p. 99 (1968).
2. Andersson, L.-O., Mason, J., and W. van Bronswijk, *J. Chem. Soc., London* p. 296 (1970).
3. Atkins, P. W., "Molecular Quantum Mechanics," p. 441. Oxford Univ. Press (Clarendon), London and New York, 1970.
4. Baker, M. R., Anderson, C. H., and Ramsey, N. F., *Phys. Rev. A* **133**, 1533 (1964).
5. Barnes, R. G., and Smith, W. V., *Phys. Rev.* [2] **93**, 95 (1954).
6. Bloch, F., *Pure Appl. Chem.* **32**, 1 (1972).
7. Bonham, R. A., and Strand, T. G., *J. Chem. Phys.* **40**, 3447 (1964).
8. Bürges, C.-W., Koschmieder, R., Sahm, W., and Schwenk, A., *Z. Naturforsch. A* **28**, 1753 (1973).
9. Chan, S. I., Baker, M. R., and Ramsey, N. F., *Phys. Rev. A* **136**, 1224 (1964).
10. Chan, S. I., and Dubin, A. S., *J. Chem. Phys.* **46**, 1745 (1967).
11. Cornwell, C. D., *J. Chem. Phys.* **44**, 874 (1966); *Abstr. Columbus Symp. Molec. Spectrosc.*, p. 40 (1964).
12. Dailey, B. P., and Shoolery, J. N., *J. Amer. Chem. Soc.* **77**, 3977 (1955).
13. Davies, D. W., *Nature (London)* **207**, 75 (1965).
14. Davies, D. W., "The Theory of the Electric and Magnetic Properties of Molecules," p. 179. Wiley, London and New York, 1967.

15. Davies, P. B., Neumann, R. M., Wofsy, S. C., and Klemperer, W., *J. Chem. Phys.* **55**, 3564 (1971).
16. Davis, R. E., and Muenter, J. S., *J. Chem. Phys.* **57**, 2836 (1967).
17. DeLucia, F. C., and Gordy, W., *Phys. Rev.* **187**, 58 (1969).
18. DeLucia, F. C., Helminger, P., and Gordy, W., *Phys. Rev. A* **3**, 1849 (1971).
19. Ditchfield, R., Miller, D. P., and Pople, J. A., *J. Chem. Phys.* **54**, 4186 (1971).
20. Emsley, J. W., Feeney, J., and Sutcliffe, L. H., "High Resolution NMR Spectroscopy," Appendix A. Pergamon, Oxford, 1965.
21. Esbach, J. R., and Strandberg, M. W. P., *Phys. Rev.* [2] **85**, 24 (1952).
22. Ettinger, R., Blume, P., Patterson, A., and Lauterbur, P. C., *J. Chem. Phys.* **33**, 1547 (1960).
23. Figgis, B. M., Kidd, R. G., and Nyholm, R. S., *Proc. Roy. Soc., Ser. A* **269** 469 (1962).
24. Flygare, W. H., *J. Chem. Phys.* **41**, 793 (1964).
25. Flygare, W. H., and Goodisman, J., *J. Chem. Phys.*, **49**, 3122 (1968).
26. Flygare, W. H., and Weiss, V. W., *J. Chem. Phys.* **45**, 2785 (1966).
27. Gierke, T. D., and Flygare, W. H., *J. Amer. Chem. Soc.* **94**, 7277 (1972).
28. Gordy, W., and Cook, R. L., "Microwave Molecular Spectra," Chapters 9 and 11. Wiley (Interscience), New York, 1970.
29. Grant, D. M., and Paul, E. G., *J. Amer. Chem. Soc.* **86**, 2984 (1964).
30. Grinter, R., and Mason, J., *J. Chem. Soc., London* p. 2196 (1970).
31. Gunther-Mohr, G. R., Townes, C. H., and Van Vleck, J. H., *Phys. Rev.* [2] **94**, 1191 (1954).
32. Herbison-Evans, D., and Richards, R. E., *Mol. Phys.* **6**, 191 (1964).
33. Hindermann, D. K., and Cornwell, C. D., *J. Chem. Phys.* **48**, 4148 (1968).
34. Hindermann, D. K., and Falconer, W. E., *J. Chem. Phys.* **50**, 1203 (1969); **52**, 6198 (ref. 31) (1970).
35. Jameson, C. J., and Gutowsky, H. S., *J. Chem. Phys.* **40**, 1714 (1964).
36. Jen, C. K., *Phys. Rev.* [2] **81**, 197 (1951); *Physica (Utrecht)* **17**, 379 (1951).
37. Kaiser, W., *J. Chem. Phys.* **53**, 1686 (1970).
38. Karplus, M., and Das, T. P., *J. Chem. Phys.* **34**, 1683 (1961); Karplus, M., and Pople, J. A., *ibid.* **38**, 2803 (1963).
39. Kellogg, J. M. B., Rabi, I. I., Ramsey, N. F., and Zacharias, J. R., *Phys. Rev.* [2] **56**, 728 (1939); **57**, 677 (1939).
40. Kidd, R. G., and Spinney, H. G., *J. Amer. Chem. Soc.* **94**, 6686 (1972).
41. Kidd, R. G., and Spinney, H. G., *J. Amer. Chem. Soc.* **95**, 88 (1973).
42. Kidd, R. G., and Spinney, H. G., *Inorg. Chem.* **12**, 1967 (1973).
43. Kukolich, S. G., *Phys. Rev.* [2] **156**, 83 (1967).
44. Kukolich, S. G., and Wofsy, S. C., *J. Chem. Phys.* **52**, 5477 (1970).
45. Lamb, W. E., *Phys. Rev.* [2] **60**, 817 (1941).
46. Lambert, J. B., and Roberts, J. D., *J. Amer. Chem. Soc.* **87**, 4087 (1965).
47. Lauterbur, P. C., *Ann. N.Y. Acad. Sci.* **70**, 840 (1958).
48. Letcher, J. H., and van Wazer, J. R., *J. Chem. Phys.* **44**, 815 (1966).
49. Logan, N., *in* "Nitrogen N.M.R." (M. Witanowski and G. A. Webb, eds.), p. 319. Plenum, New York, 1973.
50. Lutz, O., and Stricker, G., *Phys. Lett. A* **35**, 397 (1971).
51. McConnell, H. M., *J. Chem. Phys.* **27**, 226 (1957).
52. McLachlan, A. D., *J. Chem. Phys.* **32**, 1263 (1960).
53. Malinowski, E. R., *J. Amer. Chem. Soc.* **91**, 4701 (1969).

54. Malinowski, E. R., Vladimiroff, T., and Tavares, R. E., *J. Phys. Chem.* **70**, 2046 (1966).

55. Malli, G., and Fraga, S., *Theor. Chim. Acta* **5**, 275 (1966).

56. Malli, G., and Froese, C., *Int. J. Quantum Chem.* **1s**, 95 (1967).

57. Mason, J., *J. Chem. Soc., London* p. 1038 (1971).

58. Mason, J., *J. Chem. Soc., Dalton Trans.* p. 1422 (1975).

59. Mason, J., *J. Chem. Soc., Dalton Trans.* p. 1426 (1975).

60. Mason, J., and van Bronswijk, W., *J. Chem. Soc. A* p. 1763 (1970).

61. Mason, J., and van Bronswijk, W., *J. Chem. Soc., A* p. 791 (1971).

62. Matwiyoff, N. A., Asprey, L. B., Wageman, W. E., Reisfeld, M. J., and Fukushima, E., *Inorg. Chem.* **4**, 751 (1969).

63. Memory, J. D., "Quantum Theory of Magnetic Resonance Parameters," Chapter 6. McGraw-Hill, New York, 1968.

64. Neumann, D. B., and Moskowitz, J. W., *J. Chem. Phys.* **50**, 2216 (1969).

65. O'Reilly, D. E., Peterson, E. M., El Saffar, Z. M., and Scheie, C. E., *Chem. Phys. Lett.* **8**, 470 (1971).

66. Ozier, I., Crapo, L. M., and Ramsey, N. F., *J. Chem. Phys.* **49**, 2314 (1968).

67. Paudler, W. W., "Nuclear Magnetic Resonance," p. 27. Allyn & Bacon, Boston, 1971.

68. Pople, J. A., *Proc. Roy. Soc., Ser. A* **239**, 541 (1957).

69. Pople, J. A., *J. Chem. Phys.* **37**, 53 and 61 (1962); *Discuss. Faraday Soc.* **34**, 7 (1962); *Mol. Phys.* **7**, 301 (1963–1964).

70. Pople, J. A., Schneider, W. G., and Bernstein, H. J., "High Resolution Nuclear Magnetic Resonance," Appendix A. McGraw-Hill, New York, 1959.

71. Pople, J. A., Schneider, W. G., and Bernstein, H. J., "High Resolution Nuclear Magnetic Resonance," p. 170. McGraw-Hill, New York, 1959.

72. Pople, J. A., Schneider, W. G., and Bernstein, H. J., "High Resolution Nuclear Magnetic Resonance," Chapter 12. McGraw-Hill, New York, 1959.

73. Powles, J. G., *Rep. Progr. Phys.* **22**, 433 (1959).

74. Proctor, W. G., and Yu, F. C., *Phys. Rev.* [2] **77**, 717 (1950).

75. Ramsey, N. F., *Phys. Rev.* [2] **78**, 699 (1950); **90**, 232 (1953).

76. Ramsey, N. F., *Phys. Rev.* [2] **83**, 540 (1951); **86**, 243 (1952).

77. Ramsey, N. F., "Molecular Beams." Oxford Univ. Press (Clarendon), London and New York, 1956.

78. Ramsey, N. F., *Am. Sci.* **49**, 509 (1961).

79. Randall, E. W., and Gillies, D. G., *Progr. NMR Spectrosc.* **6**, 119 (1970).

80. Raynes, W. T., *Chem. Soc., Spec. Per. Rep. NMR* **2**, 4 (1973).

81. Saika, A., and Slichter, C. P., *J. Chem. Phys.* **22**, 26 (1954).

82. Santry, D. P., "Theoretical Chemical Research at the Carnegie Institute of Technology." 1965.

83. Schwenk, A., *Phys. Lett. A* **31**, 513 (1970); *J. Magn. Resonance* **5**, 376 (1971).

84. Silver, B. L., and Luz, Z., *Quart. Rev., Chem. Soc.* **21**, 458 (1967).

85. Slichter, C. P., *Ann. N. Y. Acad. Sci.* **70**, 769 (1958).

86. Spiesecke, H., and Schneider, W. G., *J. Chem. Phys.* **35**, 722 (1961).

87. Spielvogel, B. F., and Purser, J. M., *J. Amer. Chem. Soc.* **93**, 4418 (1971).

88. Stothers, J. B., "Carbon-13 NMR Spectroscopy," p. 390. Academic Press, New York, 1972.

89. Tigelaar, H. L., and Flygare, W. H., *J. Amer. Chem. Soc.* **94**, 343 (1972).

90. Townes, C., and Schawlow, A., "Microwave Spectroscopy," Chapter 8. McGraw-Hill, New York, 1955.

91. Van Vleck, J. H., "Theory of Electric and Magnetic Susceptibilities." Oxford Univ. Press, London and New York, 1932.

92. Vaughan, R. W., Elleman, D. D., Rhim, W.-K., and Stacey, L. M., *J. Chem. Phys.* **57**, 5383 (1972).

93. Vladimiroff, T., and Malinowski, E. R., *J. Chem. Phys.* **46**, 1830 (1967).

94. Waugh, J. S., Wang, C. H., Huber, L. M., and Vold, R. L., *J. Chem. Phys.* **48**, 662 (1968).

95. Weiss, R., *Phys. Rev.* [2] **131**, 659 (1963).

96. Weiss, V. M., Todd, H. D., Lo, M.-K., Gutowsky, H. S., and Flygare, W. H., *J. Chem. Phys.* **47**, 4021 (1967).

97. White, R. L., *Rev. Mod. Phys.* **27**, 276 (1955).

98. Wick, G. C., *Phys. Rev.* [2] **73**, 51 (1948).

99. Wofsy, S. C., Muenter, J. S., and Klemperer, W., *J. Chem. Phys.* **55**, 2014 (1971).