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CORRELATIONS IN NUCLEAR MAGNETIC SHIELDING, PART II

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I. Introduction

Nuclear magnetic shielding in molecules depends on the currents induced by the magnetic field in the conductor formed by the molecular electronic atmosphere. This is no simple matter, and in suitably chosen compounds the chemical shifts may correlate with a variety of other physical, spectroscopic, and chemical properties of the molecule (which here includes ions and extended structures). Such correlations form the subject of this article, which, like Part I (*111a*), aims to describe physical models and chemical and spectroscopic relationships of interest to the inorganic chemist.

II. Diamagnetic and Paramagnetic Currents

A first approximation in nuclear magnetic shielding is to quasi-spherical symmetry, such that the molecular electrons circulate in the

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applied field in their ground-state atomic or molecular orbitals, without constraint by the other nuclei (a ring current in an aromatic molecule is of this type). Such a shielding term gives a poor approximation to the observed shielding of a nucleus in a molecule. It is known as the molecular *diamagnetic shielding term* $\sigma_d(A)$, so called because the field induced by the free precession opposes the applied field. Its use is to enable us to separate the more complex *paramagnetic term* $\sigma_p(A)$, which arises from the asymmetry of the charge, due to the presence of the other nuclei.

We are concerned only with diamagnetic molecules (to exclude the larger effects of the spin of unpaired electrons). In these, the electrostatic field of the neighboring nuclei quenches the orbital angular momentum about the observed nucleus (by lifting orbital degeneracies present in the free atom) so that there is no net circulation of electrons, in zero magnetic field. But the stationary waves are equivalent to superposed running waves, with the appropriate directionality and phase. Thus a p_x and a p_y electron together form two countercurrents ($m = \pm 1$, i.e., with moments of ± 1 Bohr magneton) circulating the z axis (*29*). If we apply a magnetic field in the z direction one sense of rotation is favored, and there is a net magnetic moment. This now augments the applied field, i.e., the current is "paramagnetic." The instantaneous fields due to the orbital motion, which normally cancel, are very large, and a slight polarization gives us the nuclear magnetic shielding we observe.

In Section VI, we shall be concerned with low-spin transition-metal complexes, in which (as is well known) the quenching of the orbital angular momentum by the ligand field leads to an energy difference Δ (the ligand field splitting) between the π- or nonbonding orbitals, which point between the ligands, and the σ^* orbitals, which point toward them. If the σ^* orbitals are unoccupied, a magnetic field can induce $\pi \rightarrow \sigma^*$ currents of the *d* electrons. These are usefully imagined as virtual excitations, with energy Δ. On molecular orbital (MO) theory, the orbitals distort in the applied field to allow the circulation, by the mixing in of excited states. The smaller the excitation energy, the larger the current and the deshielding of the metal, other things being equal. We may then expect to find correlations of the NMR shift with the spectrochemical series of the ligands, and these can be observed in cobalt(III) complexes.

The deshielding is greater, the smaller the radius of the circulating electrons. Therefore in complexes in which covalent bonding is important, and the *d* electrons are delocalized on the ligands (and for smaller variations in excitation energies), we may look for correlations of the NMR shifts with the nephelauxetic (electron-cloud expanding) series of the ligands. This is found, for example, in platinum complexes. These correlations are discussed in Section VI.

The inorganic chemist is accustomed to think of orbital angular momentum as a property of an electron, if rotation about some axis transforms its orbital into another of the same energy and shape (and if both orbitals do not contain equal numbers of electrons of the same spin). In a magnetic field, however, paramagnetic currents can circulate between *any p*, *d*, *f*... orbitals, if they are appropriately oriented, incompletely filled, and not too far apart in energy. Since the mixing of orbitals and the electron current is the greater the smaller the energy separation ΔE, the largest deshielding is caused by nonbonding (n) or loosely held (π, sometimes σ) electrons, circulating in low-lying orbitals, as close as possible to the resonant nucleus.

Such "paramagnetic" currents located on other groups can have a shielding or a deshielding effect at a nucleus A, depending on the orientation (as in the familiar "neighbor anisotropy" approximation) (*142*). In proton shielding, neighboring currents may well overwhelm the tiny current of the proton's own electrons. A dramatic example is the high shielding observed for many or most transition metal hydrides, in which paramagnetic circulations of d electrons which deshield the metal, shield a proton attached to it (Section VI).

III. Shielding Terms

A. THE RAMSEY THEORY

The shielding of a nucleus (A) was described by Ramsey (*143*, *144*) as the sum of two molecular terms, derived, respectively, by first-order and second-order perturbation theory. [Analogous results have been obtained by valence bond theory (*63*, *151*) by variation methods (*33*), or by the finite perturbation theory discussed below.] The Ramsey equations (in SI units) for the averaged shielding are

$$\sigma(\mathrm{A}) = \sigma_{\mathrm{d}}(\mathrm{A}) + \sigma_{\mathrm{p}}(\mathrm{A}) \tag{1}$$

$$\sigma_{\mathrm{b}}(\mathrm{A}) = \frac{\mu_0}{4\pi}\frac{e^2}{3m}\left\langle 0\left|\sum_j r_j^{-1}\right|0\right\rangle \tag{2}$$

$$\sigma_{\mathrm{p}}(\mathrm{A}) = \frac{-\mu_0}{4\pi}\frac{e^2}{3m^2}\sum_j\left[\frac{\left\langle 0\left|\sum_j \mathbf{L}_j\right|n\right\rangle\left\langle n\left|\sum_j (L_j r_j^{-3})\right|0\right\rangle + \text{c.c.}}{(E_n - E_0)}\right] \tag{3}$$

where μ_0 is the permeability of free space, e and m are the electronic charge and mass, and E_n is the energy of the nth excited state, sums being taken over all electrons j and states n except the ground state $n = 0$. **L** and **r** are the angular momentum and position vectors of the jth electron, and $\mathbf{L} = \mathbf{r} \times (\hbar/i)\nabla$, the gradient operator ∇ being equal to $\partial/(\partial x)$ for rotation about the x axis; c.c. stands for complex conjugate. Expressions for the tensor elements are given by Raynes (*146*).

Since we are interested in the chemical phenomena, and their physical basis, we take the gauge origin at the observed nucleus A. In MO calculations the paramagnetic term, and the errors therein, may be reduced by taking the molecular electronic centroid as the origin of coordinates [*25*; (cf. also Sadlej (*150*)]. Change of axes gives rise to equal and opposite changes in σ_d and σ_p, in principle, but gauge invariance in MO calculations is achieved only in the limit of a complete basis set.

The diamagnetic term is straightforward to calculate. Semiempirical methods give reasonably good results, as also does the Ramsey–Flygare or extended Flygare approximation, discussed in Section III,C.

In Eq. (3) each $\langle 0|L|n\rangle/(E_n - E_0)$ term corresponds to a paramagnetic current at a distance r from A, and the related $\langle n|L(r^{-3})|0\rangle$ term represents the translation of the magnetic field due to this current to the nucleus A. Net shielding terms vanish for electrons tightly bound to "distant" nuclei, and the paramagnetic term vanishes for electrons in closed shells on the atom A, so errors may be reduced by confining the summation to valence electrons (*143*). All the same, we cannot sum accurately over the excited states, because of lack of knowledge of the wave functions and energies. This general problem of second-order perturbation theory is commonly evaded by recourse to the closure approximation: the series of excitation energies $(E_n - E_0)$ is replaced by an effective excitation energy ΔE, so that the sum in Eq. (3) may be replaced by a ground-state expectation value, using the law of matrix multiplication (*143*).

$$\sigma_p = \frac{-\mu_0 \mu_B{}^2}{3\pi(\Delta E)} \langle 0|L_j \cdot L_k(r_k{}^{-3})|0\rangle \tag{4}$$

where $\mu_B = (e\hbar)/(2m)$ is the Bohr magneton.

This expression does not give accurate results: it depends on the second derivative of the wave function, and is very sensitive to errors in it. Another general problem (*102*) is that contributions from all the excited states do not necessarily have the same sign [this problem arises in spin–spin coupling calculations also (*72*)]. Particular care is needed with delocalized systems. The deshielding contributions usually dominate, but sometimes they do not, as in ClF, shown by Cornwell (*28*) and Santry (*152a*) to have a positive value of $\sigma_p(A)$. [The term "Cornwell effect" was suggested in Part I for positive "paramagnetic" contributions; or confusion may be avoided by calling the paramagnetic term the high-frequency term (*33*), following Van Vleck (*169*).]

The theory of nuclear magnetic shielding has been based on that of diamagnetic susceptibility, since this depends on the same paramagnetic and diamagnetic currents and has been known much longer. Just as Van Vleck added a high-frequency term χ_p, the "temperature-independent paramagnetism," to the Langevin term for the diamagnetic susceptibility (*169*), so Ramsey added the paramagnetic term σ_p to the Lamb term σ_d for the nuclear magnetic shielding (*143*). The significant difference between χ_p and σ_p is in the radial factor $\langle r^{-3}\rangle$, which appears only in the shielding, since the nucleus samples the magnetic field from its vantage point:

$$\chi = \chi_d + \chi_p \tag{5}$$

$$\chi_d = (-N\mu_0/4\pi)(2e^2\langle r^2\rangle/3m)$$

$$\chi_p = \frac{N\mu_0}{4\pi}\frac{2\mu_B{}^2}{3}\sum\left[\frac{\langle 0|L|n\rangle\langle n|L|0\rangle}{E_n - E_0}\right] \tag{6}$$

so that, approximately

$$\begin{aligned}\sigma_d &= -2\langle r^{-3}\rangle\chi_d/N\\ \text{and}\qquad \sigma_p &= -2\langle r^{-3}\rangle\chi_p/N\end{aligned} \tag{7}$$

where N is the Avogadro constant. (The susceptibility is the ratio of the induced field to the applied field, and so is negative for diamagnetic currents. These usually dominate the molecular susceptibility, because of the importance of distant currents, with large r). Some diamagnetic compounds, however, show a weak paramagnetism because of very low excitation energies [examples are $MnO_4{}^-$ (*169*) and $(NO)_2$ (*107*)] and this should correlate with resonance at very low field.

A practical though approximate method of evaluating the sum over excited states in nuclear magnetic shielding is to use susceptibility measurements, as in the atomic approximation described below. In the familiar neighbor anisotropy approximation, the shielding effect of a neighboring group is estimated from the anisotropy of the diamagnetic susceptibility (*142*).

Ramsey pointed out also the connection between nuclear magnetic shielding in an applied magnetic field, and the spin-rotation interaction of the nuclear spin with the magnetic field generated by the rotation of the molecule (*144*). (The effects of the positive and negative charges do not cancel, since the electrons slip relative to the nuclei, except for the valence electrons, which are shared between atoms.) Observation of this interaction in molecular beam or microwave experiments on small molecules allows direct measurement of the molecular paramagnetic term σ_p, which is particularly useful in establishing absolute scales for nuclear magnetic shielding, as discussed in Part I (*40*, *144*). Thus a scale for chlorine can now be based on the molecular beam measurements on HCl (*35*, *69*) together with a calculated diamagnetic term (*22*, *103*) and an accurate measurement of the chemical shift in HCl gas (*89*).

The magnetic moment of a molecule that arises from its rotation is described by the molecular *g* value tensor, which is related to the magnetic susceptibility tensor, as well as to other electrical and magnetic properties of the molecule, such as the electric dipole and quadrupole moments. In recent years the molecular Zeeman effect in diamagnetic molecules has been investigated by microwave spectroscopy, notably by Flygare (*40*) and co-workers, and their measurements and correlations (some of which we return to below) have greatly extended our understanding of magnetic interactions in diamagnetic molecules.

B. THE "ATOM IN A MOLECULE" APPROXIMATION

Ramsey's shielding terms, like Van Vleck's susceptibilities, were summed over the whole molecule, but subsequent workers, beginning with Saika and Slichter (*151*), have found it more convenient to use local (atomic) shielding terms. These are more readily compared, for a particular nucleus in different molecules, as Saika and Slichter compared fluorides (Section IV). They are also much simpler to calculate; LCAO-MO theory is based on atomic orbitals; and magnetic susceptibility tensor elements can be obtained as a sum of atomic terms (*40*, *49*).

In the Pople LCAO–MO theory of diamagnetism of the early 1960s (*138*, *139*) the susceptibility tensor was calculated as a sum of atomic contributions χ^A, each the sum of a diamagnetic and a paramagnetic term, χ_d and χ_p. These are related in rather complex fashion to the

Pascal constants, which give the molar susceptibility as a sum of atomic and constitutive terms (*40*, *157*). The atomic shielding terms $\sigma_d{}^A$ and $\sigma_p{}^A$ were derived from $\chi_d{}^A$ and $\chi_p{}^A$ as in Eq. (7) above: for the second-row elements with which the theory was concerned, the radial term $\langle r^{-3}\rangle$ is the expectation value for the $2p$ electrons. Such atomic terms can be expressed by the Ramsey Eqs. (2) and (3), but with the summations restricted to the electrons on the atom A. Additional terms σ^{AB} represent the shielding at A due to the currents on the other atoms B (strictly $\sigma_d{}^A$, $\sigma_p{}^A$, should be $\sigma_d{}^{AA}$, $\sigma_p{}^{AA}$). Ring currents need a further term but are unimportant in the shielding of nuclei other than hydrogen. Thus

$$\sigma(A) = \sigma_d{}^A + \sigma_p{}^A + \sum \sigma^{AB} \tag{8}$$

The so-called gauge-invariant atomic orbitals (GIAO) of London (*93*) were used to avoid large and canceling shielding terms (*57*, *139*). (These orbitals are in fact gauge dependent, since the phase of the wave functions is so chosen that the origin of vector potential for each atom is at its own nucleus.) In the paramagnetic term the sum over excited states may be retained, or it may be avoided by the use of an effective energy ΔE, as in the Karplus–Pople expression for second-row elements (*73*)

$$\sigma_p{}^A = \frac{-\mu_0 \mu_B{}^2}{2\pi(\Delta E)} \langle r^{-3}\rangle \sum Q \tag{9}$$

The Q terms express the imbalance of charge in the valence shell and are obtained from the charge densities and bond orders.

Jameson and Gutowsky have given a more general expression (*63*):

$$\sigma_p{}^A = \frac{-2\mu_0 \mu_B{}^2}{\pi(\Delta E)} [\langle r^{-3}\rangle_{np} P_u + \langle r^{-3}\rangle_{nd} D_u] \tag{10}$$

where P_u and D_u represent the imbalance of the valence electrons in p and d orbitals on the atom A. P_u has a maximum value of 2, when two p orbitals are filled and one is not (or vice versa). The maximum achieved, however, depends on the element. For fluorine, with only one bonding (p) orbital, the highest value is 1, and for carbon it is 3/2. In d orbitals the maximum D_u is 12, in low-spin d^6 octahedral or d^4 tetrahedral complexes, with the t_{2g} orbitals filled and the e_g unfilled, or vice versa (in principle). Equation (10) gives the same results as the Griffith and Orgel expression (Section VI).

In this approximation, the diamagnetic term is an extension of the Lamb term for the free atom (*85*). The "atom in a molecule" is considered to have spherical symmetry, but to be acted upon by the inductive effects of the ligands (*138*):

$$\sigma_d{}^A = \frac{\mu_0}{4\pi}\frac{e^2}{3m}\sum_{\lambda}^{A} P_{\lambda\lambda}\langle r^{-1}\rangle \tag{11}$$

where the $P_{\lambda\lambda}$ terms are the electron populations of the atomic orbitals λ on the atom A, and r is the average electron distance from the nucleus. Electronegative ligands reduce the valence-shell electron population, but by increasing the effective nuclear charge of the atom A, they reduce r also. The net result is that the atomic diamagnetic term changes rather little for a given atom in different molecules: how much it changes can be estimated by X-ray photoelectron spectroscopy, as discussed in the next section. The result is that variation in $\sigma_d{}^A$ is usually neglected in comparison with the much larger variation (and uncertainty) in $\sigma_p{}^A$.

The neighbor contributions σ^{AB} are estimated by the neighbor anisotropy approximation (*142*), from which they appear to be small: so these, too, are commonly neglected. The net result is that variations in chemical shift are taken as variations in $\sigma_p{}^A$, or as so often in the literature, as variations in "the" paramagnetic term. In truth "the" paramagnetic term is the molecular term, as measured in the spin-rotation interaction. The atomic paramagnetic term $\sigma_p{}^A$ cannot be observed without neighbor contributions that are difficult to quantify. It is true that distant paramagnetic and diamagnetic contributions to the shielding cancel, but those from the nearest neighbors in general do not, and these are worst served by the neighbor anisotropy approximation, which assumes point dipoles [or by extensions of this to finite dipoles (*7*)]. The atomic approximation clearly breaks down when there are heavy-atom substituents, for which the diamagnetic and paramagnetic contributions to the shielding of the atom A are large and noncanceling, as discussed in later sections (cf. *120a*).

Generally speaking, however, the "atom in a molecule" model has the advantage of ease of application, with concomitant loss of accuracy. The approximate equations for $\sigma_p{}^A$, such as Eqs. (9) and (10), are particularly valuable when one low-lying excitation dominates the shielding, as in transition-metal complexes when there are strong paramagnetic currents of the *d* electrons. The equations are also readily modified to take some account of important influences of the ligands that are neglected in the simple theory (Section VI). More generally, they are important in demonstrating physical characteristics of the shielding, such as the dependence on excitation energies and on the radial term, on which our qualitative understanding of chemical shifts is based. Useful results can also be obtained by the use of ΔE as a semiempirical parameter, in appropriate series of molecules.

C. THE DIAMAGNETIC TERM AND THE XPES CONNECTION

Someone has remarked that X-ray photoelectron spectroscopy (Xpes, ESCA) will correlate with every chemist's favorite property. This is not very surprising since the core-binding energy reflects the atomic charge. Only a partial correlation is possible with NMR, since the paramagnetic term depends on other factors as well; but a direct connection can be made with the local diamagnetic term $\sigma_d{}^A$ *(10, 154)*. In its original formulation this was a purely theoretical construct, as mentioned in Section III,B, an extension of Lamb's term for the free atom. Lamb pointed out that $\sigma_d{}^A$ depends directly on the electrostatic potential $V(\mathrm{O})$ produced at the nucleus by the atomic electrons *(85)*:

$$\sigma_d{}^A = \frac{\mu_0}{4\pi}\frac{e^2}{3m} V(\mathrm{O}) \tag{12}$$

In Xpes, the energy to remove the core electron depends on its electrostatic potential energy within the atom (V'), and at the atomic site (V'') arising from the surrounding charges in the molecule or lattice. The observed core binding energy E_b depends also on the relaxation of the other electrons, which speeds the parting electron; but for broad correlations, we may assume Koopmans' theorem (frozen orbitals).

Measured core-binding energies, it is found, can be fitted to an equation of the type (*65*, *160*)

$$E_b = kQ_A + V'' + l \tag{13}$$

where k and l are empirical constants, Q^A is the (calculated) net atomic charge of the ionizing atom A, and V'' is the (calculated) molecular or Madelung potential $\sum_B (Q_B/r_{AB})$ due to the surrounding charges Q_B at distance r_{AB} from A. Since kQ_A represents the atomic potential V', k is an (r^{-1}) term; l depends on the reference level. The connection can then be made with the extended Ramsey–Flygare equation for the molecular diamagnetic term (*41*, *49*)

$$\sigma_d(\mathrm{A}) = \sigma_d{}^{\mathrm{A}} + \frac{\mu_0}{4\pi}\frac{e^2}{3m}\sum_{\mathrm{B}}(Z_{\mathrm{B}}/r_{\mathrm{AB}}) \tag{14}$$

As an approximation for $\sigma_d{}^{\mathrm{A}}$, Flygare suggested the use of the Lamb term for the free atom, for which tabulated (Hartree–Fock) values are available (*104*). In the "extended Flygare method," $\sigma_d{}^{\mathrm{A}}$ is obtained by interpolation of the Hartree–Fock values of σ_d for free atoms and ± ions, using atomic charges calculated by semiempirical methods. The second term is related to V'' and is a molecular or Madelung potential term, in which the sum runs over all the other nuclei, with atomic number Z, and at a distance r_{AB} from A. This "distant contribution" figures in the molecular diamagnetic term, but not in the atomic term, since it roughly cancels with a similar contribution (σ_{nuc}) in the molecular paramagnetic term.

There should be a direct correlation therefore between chemical shifts in the core-binding energy (ΔE_b) and in the atomic diamagnetic term ($\Delta\sigma_{\mathrm{A}}$), since both depend directly on the potential inside the valence shell, imagined as a hollow charged sphere (*159*); this potential depending on Q/r, as in Eq. (11) for $\sigma_d{}^{\mathrm{A}}$. (The summation over electrons in $\sigma_d{}^{\mathrm{A}}$ includes the core electrons, but their contribution to the potential at the nucleus does not change with the chemical environment.) Thus ΔE_b and $\Delta\sigma_d{}^{\mathrm{A}}$ both depend on the changes in the valence shell, induced by the ligands. For any atom A,

$$\Delta\sigma_d{}^{\mathrm{A}}/\mathrm{ppm} = (-17.75/27.21)E_b/\mathrm{eV} \tag{15}$$

As mentioned above, diamagnetic terms are not difficult to calculate. The tabulated values for free atoms and ions (*104*) afford an estimate of the range of $\sigma_d{}^{\mathrm{A}}$ for a given element: thus for nitrogen, $\sigma_d{}^{\mathrm{A}}$ varies by 18 ppm from N^+ to N^-, compared with 12 ppm for phosphorus from P^+ to P^-, or 9 ppm for fluorine from F to F^-. In the periodic table the range decreases down the group and seems to be largest for nitrogen. The value of the Xpes correlation is to connect calculated $\sigma_d{}^{\mathrm{A}}$ values with physical measurements on atoms in molecules, or ions in lattices. For carbon (*112*), the range of variation of $\sigma_d{}^{\mathrm{A}}$ is about 7–8 ppm from C_2H_2 to CF_4, or 10 ppm if one includes negative ions, such as CN^- (Interestingly, carbon is more positively charged in CF_4 than in Me_3C^+.) For nitrogen, the range is about 13 ppm from ONF_3 to negative ions, such as CN^- (*113*). For covalent fluorine the range is only 2–3 ppm, increasing perhaps to 10 ppm if ionic solids are included. As yet the observed core binding energies are not directly comparable for gases and solids, because of uncertainties in work function, charging, and surface effects in solid samples. For comparable compounds, however, a calibration of free atom/ion values for $\sigma_d{}^A$ can perhaps be obtained from empirical values of the coefficient k in Eq. (13), since this expresses the decrease in core electron-binding energy for the gain of one valence electron ($Q_A = 1$). For a suitable set of related compounds, such as the xenon fluorides, experimental values can be obtained for k and the atomic charges from simultaneous Eqs. (13) for the core-binding energies of the different atoms (*24*). Experimental values of k for atoms in molecules are larger than the free atom or ion values, which may be interpreted by contraction of the orbitals on compound formation (*137*). Thus the ranges for $\sigma_d{}^A$ given above may be underestimated.

In detailed comparisons of ΔE_b and $\sigma_d{}^A$ it may be necessary to correct for relaxation processes. This was found to improve the correlation for nitrogen compounds (*113*), but to be less important for carbon (*112*). (Chemical shifts in the relaxation energy can dominate the variation of E_b for progressive substitution by heavier ligands; thus in the series $NH_4{}^+$ to Me_4N^+, $E_b(N-1s)$ reflects the relaxation process, rather than inductive effects, which are small.)

As mentioned above, there is no general δ/E_b correlation, of NMR and core binding energy shifts. Thus core-binding energies correlate well with electronegativities, and NMR shifts do not. Several workers (*14*, *26*, *116*, *177*) have tried to demonstrate linear correlations for groups of closely related molecules. Of these, the correlation of ^{13}C and $E_b(C - 1s)$ shifts in certain halomethanes was found to break down when a fuller range was compared, by Gelius and co-workers (*45*, *46*), who have also compared large numbers of NMR and Xpes shifts for boron and fluorine. They pointed out that correlation is only to be expected if the NMR shift reflects the local charge density, as in aromatic systems. It occurs only to a limited degree for the substituted methanes.

Gelius has pointed out that there is a good correlation between nuclear magnetic shielding, the E_b chemical shift, and the spin-rotation constant (*45*). The $E_b/\sigma_d{}^A$ correlation does not extend to the *molecular* diamagnetic term (or the atom-plus-ligand term discussed in Section III,D) because this includes the "distant" contribution, given in the Ramsey–Flygare Eq. (14) by the summation over Z/r. However, a (roughly) equal and opposite term σ_{nuc} (arising from the motion of the other nuclei) balances the molecular paramagnetic term (arising from the motion of the electrons) in the spin-rotation interaction (between the nuclear spin and the magnetic field due to the rotation of the molecule):

$$\sigma_{sr}(A) = \sigma_p(A) - \sigma_{nuc} \tag{16}$$

Combination of this equation with the extended Flygare equation and the Ramsey Eq. (1) gives

$$\sigma = \sigma_d{}^A + \sigma_{sr} \tag{17}$$

Thus spin-rotation constants can be deduced from E_b and the observed shielding.

D. OTHER RESTRICTED TERM APPROXIMATIONS

The "atom in a molecule" approximation has found extensive use in inorganic chemistry, as shown in later sections. It does not, however, give good results in comparisons of molecules having ligand atoms from different rows of the Periodic Table, or differing numbers of such ligands, particularly when the observed nucleus is from the second row. Unexplained high-field shifts appear for multiple substitution by heavier ligand atoms, as shown in the familiar U-shaped or "sagging" curves (Section IV,C). Thus CI_4 is red, and $\Delta E(\sigma \rightarrow \sigma^*)$ is likely to be low, as is the radial term $\langle r^{-3} \rangle_{2p}$, but all the same the ^{13}C line is 280 ppm upfield of methane. Similar high shielding of the central atom is found in other iodides ($BI_4{}^-$, $AlI_4{}^-$, SiI_4, GeI_4, SnI_4, PbI_4, and transition-metal complexes).

Such heavy ligand atom effects can be traced, at least in part, to neglect of the ligand contributions to the nuclear magnetic shielding. This neglect is in a sense an artifact of the "atom in a molecule" approximation. In this the variation in the local diamagnetic term $\sigma_d{}^A$, as defined, is small, and so are values of the neighbor contributions as given by the dipole approximation. This means that variations in the chemical shift have to be accounted for by the local paramagnetic term, and in the event it fails to do so, for many substituent effects are much larger than the theory predicts [even for less heavy ligand atoms, as shown by the ^{13}C alkyl substituent parameters (*110*)].

A less severe approximation is to include the ligand atoms L in the diamagnetic and paramagnetic shielding terms, as in the "atom-plus-ligand" (AL) approximation (Part I). Like the atomic terms, the AL terms have the advantage over the Ramsey (molecular) terms of being easier to estimate, and directly comparable in related compounds, since the "distant" contributions cancel: but the more distant contributions can now more safely be neglected. As described in Part I, the AL diamagnetic term is readily calculated by the Ramsey–Flygare approximation (or its extended form, which takes account of inductive effects on the atom A). The AL paramagnetic term can be calculated, or obtained by difference from the absolute shielding, given by the observed shift referred to an absolute scale based on spin rotation or other measurement of the (molecular) paramagnetic term.

A useful approach is to regard the AL diamagnetic term as a simple physical correction that allows us to identify significant chemical relationships of the paramagnetic term. Thus the molecular paramagnetic term was found to vary periodically with the atomic number of the ligand, in proton (*108*) and fluorine (*109*) resonance. This periodicity is shown clearly by the AL term also, but not by the chemical shift, nor by the local paramagnetic term, which varies as the chemical shift.

Effects of multiple substitution, which are often additive, emerge clearly only after separation of the diamagnetic and paramagnetic terms, since substituents contribute to both in different ways. Thus in the substituted methanes CX_4, the ^{13}C shielding increases in the order $F < Cl < OR < Me < Br < I$. With separation of the diamagnetic and paramagnetic terms, both are seen to increase (numerically) in the order $Me < OR < F < Cl < Br$ ($<I$ for the diamagnetic term, but $Br \lesssim I$ for the paramagnetic term, showing the emergence of some other heavy-atom substituent effect). This order for the paramagnetic term is in better accord with expectation based on the relative excitation energies.

The AL (or Ramsey) diamagnetic correction changes the sequence drastically in comparisons of ligands from different rows of the Periodic Table, in comparisons involving progressive substitution by a heavier ligand, and in comparisons of different coordination numbers. High coordination numbers may correlate with higher shielding not only because of the higher symmetry [reducing $\sigma_p(A)$], but because of the increase in the number of ligands (increasing $\sigma_d(A)$]. In such comparisons, therefore, the "chemical" correlations (with ΔE, with the radial factor, or with other factors), or spectroscopic correlations, are obscured in the observed shifts, and revealed by a diamagnetic correction.

E. FINITE PERTURBATION THEORY

A powerful method that can be used to avoid the difficult summation over excited states, or an arbitrary choice of excitation energy, is to allow the magnetic field to perturb the Roothaan–Hartree–Fock equations, modifying the orbital coefficients. As Lipscomb has shown (*92*, *166*), expressions so obtained for the diamagnetic susceptibility or the nuclear magnetic shielding correspond to those obtained by Ramsey using Rayleigh–Schrödinger perturbation theory. Pople's finite perturbation method (*38*, *141*) gives similar equations and has made the method more accessible. The equations can be used to obtain molecular shielding terms, or local terms, and can be used at any level of approximation (*37*, *44*, *83*, *84*). Better results are obtained with gauge-dependent atomic orbitals, as in Ditchfield's *ab initio* calculations (*37*). Reparameterization is advisable for best results with semiempirical methods, such as INDO (*44*). With Eqs. (1) and (2) as before,

$$\sigma_{\mathrm{p}}(\mathrm{A}) = \frac{-\mu_0\mu_{\mathrm{B}}}{3\pi}\sum_{\mu,\nu}\left(\frac{\partial P_{\mu\nu}(H_\alpha)}{\partial H_\alpha}\right)_{\mathrm{H}=0}\langle\phi_\mu|Lr^{-3}|\phi_\nu\rangle \tag{18}$$

for orbitals ϕ_μ and ϕ_ν. The $P_{\mu\nu}(H_\alpha)$ terms are elements of the density matrix with the perturbation due to the magnetic field. They are obtained by solving the Roothaan equation with the perturbed Fock matrix $F_{\mu\nu}(H_\alpha)$, which contains the additional (perturbation) term $-\mu_{\mathrm{B}}\sum_\alpha H_\alpha\langle\phi_\mu|L|\phi_\nu\rangle$, generating paramagnetic currents. The differential coefficients $\{[\partial P(H_\alpha)]/\partial H_\alpha\}_{\mathrm{H}=0}$ can be replaced numerically by $\mathrm{Im}[P_{\mu\nu}(H_\alpha)]/H_\alpha$, where $\mathrm{Im}[P_{\mu\nu}(H_\alpha)]$ is the imaginary part of the density matrix H_α.

The results can be interpreted in terms of excitation energies, as for the Ramsey theory. In the finite perturbation method, the bond parameter β (the matrix element corresponding to the resonance integral of Hückel theory) may be reduced (becoming less negative), allowing some recovery of orbital angular momentum quenched by the molecular field (*83*). This amounts to destabilization of the occupied MOs, and decrease in excitation energies, facilitating paramagnetic currents.

The finite perturbation method is well suited also to calculation of neighbor contributions to nuclear magnetic shielding, as in recent work by Kondo and co-workers on the effects on proton shielding of paramagnetic currents on neighboring carbon (*84*). Their results are relevant to the study of proton shielding in inorganic hydrides, including the transition-metal hydrides discussed in Section VI.

IV. Patterns of Shielding in Inorganic Molecules

The interplay of the factors that determine chemical shifts can be observed in the fluorine molecule, for which the strong deshielding, compared with fluorine in HF, or fluoride ion, was interpreted by Saika and Slichter, early in the history of NMR. A $2p_x$ electron is considered to be missing at a given instant from the valence shell on each fluorine (with the x axis along the bond). A magnetic field applied in the z direction may then unquench angular momentum between the (filled) $2p_y$ and (half-filled) $2p_x$ orbital, to bring up the $\sigma^*(^1\pi_g)$ state, and a degree of paramagnetism (151).

The fluorine shielding is observed to increase in the order $F_2 < HF < F^-$. For the fluoride ion there is a closed shell, so that (weak) paramagnetic currents arise only by interaction with the solvent. In gaseous HF the ionic character ($i \approx 0.43$) reduces the deshielding compared with F_2 by a factor $(1 - i)$, since i equal to 1 corresponds to a closed shell. The fluorine chemical shift was thus expected (*151*) to correlate with the ionic character of the E—F bond, and this is true to a degree (*28*); however, effects of covalency, including π bonding, are important also (*63*).

In the fluorine molecule the virtual excitation is from the highest occupied orbital [π^*, formed from nonbonding (n) orbitals], to the lowest unoccupied orbital, i.e., $\pi^* \rightarrow \sigma^*$. HF, however, has no π orbitals, and the lowest excitation ($n \rightarrow \sigma^*$) has a higher energy. The effect of the radial term is rather small; an estimate using Slater orbitals shows an increase of 4.5% in $\langle r^{-3}\rangle_{2p}$ from HF to F_2, equivalent to about 30 ppm in NMR shift.

Patterns of nuclear magnetic shielding are thus determined by the relative importance, in the compounds considered, of the effective excitation energy ΔE, the local symmetry, and the radial term (r^{-3}). These factors are not independent, as we have seen in the simple example of F_2 compared with HF, but frequently one can be seen to dominate. A further factor may be variation in the diamagnetic term, notably for heavier ligands, for multiple substitution, or for both of these.

A. EXCITATION ENERGIES

Relatively high-field ^{13}C and ^1H resonances are observed for the alkanes, which have no loosely held electrons or low-lying excited states, and similarly for the other second-row atoms in BH_4^-, NH_4^+, NH_3, H_2O, and HF. Bonds to hydrogen are particularly strong for the nonmetals, and this may account for the high shielding observed for the heavy atom in PH_3, AsH_3, H_2S, H_2Se, HCl, etc.

Low-field resonances are observed when ΔE is small, and linear δ/λ correlations are observed between the chemical shifts δ and the wavelength λ of the lowest energy electronic absorption band, in appropriate compounds. They are well known for groupings with $n \rightarrow \pi^*$ transitions, as in nitrosyl or azo (*3*, *114*) or keto groups (since the bands lie at longer wavelengths than for excitations of bonding electrons). They are better known for nitrogen than for oxygen since $n_N \rightarrow \pi^*$ excitations have components that are magnetic and electric dipole allowed, so the bands are of reasonable intensity. (In bent R—N=X compounds the lone pair is usually sp^2 hybridized; the $s \rightarrow p\pi^*$ part of the $n \rightarrow \pi^*$ excitation is optically allowed and magnetically inactive, and the reverse is true for the $p \rightarrow p\pi^*$ part. The lowest $n_O \rightarrow \pi^*$ excitation in $X_2C{=}O$ compounds is however from a pure *p* orbital.) If charge rotates without translation the excitation is electric dipole forbidden, and so may be difficult to locate in the electronic spectrum, as, for example, the $\sigma \leftrightarrow \pi$ excitations in the ethene spectrum in the presence of the strong but magnetically inactive $\pi \rightarrow \pi^*$ band. The problem is not made any easier by the bands appearing in the vacuum ultraviolet region. In ethene, however, the most important excitation is $\pi \rightarrow \sigma^*$, and a measure of the excitation energy in ethene and substituted ethenes can be obtained from the photoelectron spectrum in the form of the first ionization energy $I_1(\pi)$ (*113a*). Other correlations involving excitation energies are discussed in later sections (correlations of transition-metal chemical shifts with $d \rightarrow d$ wavelengths in Section VI).

B. THE RADIAL FACTOR, AND THE ELECTRIC FIELD GRADIENT; THE NQCC AND MÖSSBAUER CONNECTION

Since we are dealing with a dipolar field, the paramagnetic term falls off as (r^{-3}), that is, fairly steeply. The periodicity of the radial factor $\langle r^{-3}\rangle_{np}$ for the valence *p* electrons (*9a*), which arises from its dependence on the effective nuclear charge, is reflected in the ranges of chemical shifts of the elements (*63*). As the resonant atom moves across the row of the periodic table the range increases with increase in $\langle r^{-3}\rangle_{np}$, and also in the number of nonbonding electrons, which reduce ΔE and may reduce the local symmetry. Down the group also the range increases with increase in $\langle r^{-3}\rangle_{np}$, and also with decrease in ΔE as bond lengths increase and orbitals proliferate.

Parallelisms of chemical shifts can be found for neighboring elements in the periodic table, if similarly bonded, with the shifts in the ratio of the radial factors: thus the ^{77}Se and ^{125}Te shifts in analogous compounds are closely related by a line of this slope (*98a*), and similarly (though more approximately) for ^{14}N and ^{17}O (*2a*) or ^{13}C and ^{17}O (*113a*) in the same chromophore. For cadmium and mercury, however, or tin and lead (*77a*), the shifts for the heavier atom are larger than can be accounted for by the increase in radial factor, suggesting perhaps that more orbitals come into play for these heavier elements.

Because of the (r^{-3}) fall-off, correlations may be found with bond lengths to the ligands—for example, in proton resonance, in which neighbor effects are important; particularly in transition-metal hydrides, in which the neighbor effects are large (*7a*, *19*).

Electronegative ligands increase the radial term, and thus the paramagnetic term, by increasing the effective nuclear charge of the atom A, pulling in the electrons involved in the paramagnetic circulation (*31*). For carbon, the radial term nearly doubles from C^- to C^+, and for nitrogen it increases by a factor of 1.7 from N^- to N^+. Thus the radial factor tends to increase as the neighbor atom moves to the right in the Periodic Table: and this applies also if the resonant nucleus is a ligand atom (H, C, F, etc.) and the neighbor moves across the row of the transition metals, for comparable compounds.

When ligands from different rows of the Periodic Table are being compared, an important effect may be the greater availability in the larger ligands of *d* orbitals, in which electrons from the resonant atom may be delocalized. This, with the greater bond length, acts to reduce the effectiveness of paramagnetic currents. The decrease in the radial factor as the ligand or neighbor moves down the group of the Periodic Table must contribute to the high-field shifts observed with heavy-atom substituents. The radial factor is decreased also by π-delocalization onto ligands such as CO, CN^-, or PR_3, although an important part is played also by the σ-donation, and the concomitant increases in ΔE. Radial factors are frequently overwhelmed by larger changes in excitation energies.

A correlation that will become increasingly fruitful as more measurements are made is that of NMR shifts with the ground-state electronic charge distribution, as revealed by interaction with a quadrupolar nucleus and as studied by microwave, NQR, or Mössbauer spectroscopy. Thus for nuclei such as ^{14}N, ^{35}Cl, ^{55}Mn, or ^{59}Co the paramagnetic shielding tensor can be related to the nuclear quadrupole coupling constant (nqcc) e^2qQ/h, since the electric field gradient (efg) tensor represented by q has a similar (r^{-3})-dependence on the p or d electron charge distribution. In appropriate molecules we may find σ_p proportional to the nqcc if ΔE is sufficiently constant, or proportional to the ratio nqcc/ΔE if ΔE varies, and if an effective excitation energy can be identified. In studies of inorganic (*64*, *115*) and organic (*152*) chlorides, δ/nqcc comparisons were limited by the difficulty of estimating appropriate excitation energies; for the covalent inorganic chlorides, including some of transition metals, ΔE was estimated from the nqcc/δ ratio (*64*). In nitroso or nitrosyl compounds XNO, however, the nitrogen shift (or σ_p^{AL}) correlates well with the nitroso $(n \rightarrow \pi^*)$ excitation energy, which can be used for ΔE (*3*), and nqcc data are available from microwave measurements for X = hal, Me, NMe_2, OMe, etc. A linear correlation is observed of δ or σ_p^{AL} with the nqcc/ΔE ratio, and a poor correlation with the nqcc alone. There is also a reasonably linear correlation with $\eta/\Delta E$, where η is the ^{14}N asymmetry parameter (*111*).

Such correlations are particularly useful when components of the shielding tensor and of the efg tensor can be compared, and effects of the different paramagnetic circulations isolated, as in combined NMR/NQR measurements of crystalline solids. Important studies of this type include those of complexes of manganese (*8, 119, 120, 161, 165*), rhenium (*120*), and cobalt (*18, 86, 118, 119, 163, 164*).

In Mössbauer spectroscopy the quadrupole splitting arises from the interaction of the nuclear quadrupole with the electric field gradient [the isomer shift being related to the electron density at the nucleus (*126*)]. As yet there has been little direct correlation with nuclear magnetic shielding. For ^{57}Fe, the most useful Mössbauer nucleus, NMR studies are in their infancy (*155*); nuclei such as ^{119}Sn may be more promising (*75, 162*) but the Mössbauer sensitivity is low (*131*). Many general conclusions, however, are of interest, together with those from NQR studies, and can provide useful insights into NMR shielding, for example, on questions of ionic versus covalent bonding, on the Townes–Dailey model (*18, 115*).

An important consideration for NMR shielding in metal complexes is that of additivity (or otherwise) of ligand effects. We have on the one hand the spectroscopic evidence as to excitation energies, and now, from NQR and Mössbauer studies, the concept of partial field gradients (pfg) with which we can quantify the crystal field and observe direct effects of changes in σ and π orbital populations. ^{57}Fe and ^{119}Sn Mössbauer splittings, it is found, can be interpreted in terms of a (tensor) sum of pfg parameters characteristic of individual ligands (*131*), and this model has been applied to ^{55}Mn and ^{59}Co, for both of which NQR and NMR data can be compared. Thus in low-spin d^6 octahedral complexes, the cobalt nqcc is little changed from the monosubstituted $[CoA_5X]$ to the *cis*-$[CoA_4X_2]$ complex, but it is doubled in *trans*-$[CoA_4X_2]$, where A = amine and X = Cl (*18*). Deviations from additivity are likely to arise, however, if there is direct interaction between ligands, asymmetry of the ligand about the M–L axis, etc.

Additivity of ligand pfg contributions has been tested also in the cobaloximes (*86*), which are model compounds for vitamin B_{12}. The field gradient tensor can be defined in terms of two pfg parameters, N, for the four nitrogens in the plane, and X, the average for the two axial ligands. In this system the N and X parameters are not independent, since the sum is roughly constant, although the individual contributions vary quite widely over the range of ligand atoms (C, N, S, P, As, Br, Cl). A reasonably linear δ/efg correlation was then found, the cobalt resonance moving upfield (over a range of 3600 ppm), with decrease in N/X, that is, with increase in the ligand field of the axial ligands, since the equatorial ligands are constant.

Cobalt NQR measurements have also been used to obtain information on σ–π donor–acceptor properties of the ligands, with which to compare the NMR shifts. In trigonal bipyramidal cobalt(I) complexes such as $\{Co[P(OMe)_3]_5\}^+$ the field gradient, which depends largely on the $3d$ orbital populations, can be correlated with that in the isostructural iron complex $[Fe(CO)_5]$, from Mössbauer spectra, and $[Mn(CO)_5]^-$, from manganese NQR, to provide information on the parent compound $[Co(CO)_5]^+$ (*18*). The substituted carbonyls $[Co(CO)_4L]$ were then compared for a range of ligand atoms (Si, Ge, Sn, Pb, Hg) with organo- and halosubstituents. Larger quadrupole coupling constants are observed for ligands that are relatively poor σ-donors and/or strong π-acceptors (such as $SnCl_3$), and vice versa (e.g., $SnMe_3$). This can be explained on the assumption that the d_{xy} and $d_{x^2-y^2}$ orbitals are more highly populated than the d_{z^2} and d_{xz}, d_{yz}; a strong π-acceptor reduces the d_{xz}, d_{yz} population, increasing q_{zz} (whereas a strong σ-donor would increase the d_{z^2} population, restoring the balance). It is of course difficult to separate the σ and π effects. NMR studies of single crystals (*164*) showed the z component of the cobalt shielding to be constant within the $[Co(CO)_4(MX_3)]$ series, as expected, and showed the variation of the x and y components with the ligands: the results suggesting that among the group IV ligands, π-bonding effects are strongest for the cobalt–tin bond (*164, 174*). The NQR/NMR correlation was particularly valuable here since the $d \rightarrow d$ bands could not be observed, being obscured in the electronic spectrum by strong ligand transitions. Correlations are found also of the nqcc with the highest frequency CO stretching mode (*18*).

Similarly detailed work has been done on the corresponding manganese complexes (*9*). The manganese shielding increases with increase in σ-donor ability of the ligand, correlating also with Graham's σ parameter (*51*).

Yet another correlation that emerges in studies of quadrupolar nuclei is between the chemical shift and $\sqrt{\Delta B}$, where ΔB is the line width in units of magnetic field (*8, 23, 64, 126, 174*). Quadrupolar relaxation dominates the spin-lattice relaxation time T_1, which in the extreme narrowing case is given by

$$1/T_1 = \frac{3}{40}\frac{(2I+3)}{I^2(2I-1)}(1+\eta^2/3)(e^2qQ/\hbar)^2\tau_q$$

where I is the nuclear spin quantum number and τ_q the correlation time for molecular reorientation (*1*). As we have seen, the paramagnetic shielding term is proportional to the nqcc, if excitation energies do not change overmuch.

C. LOCAL SYMMETRY, SUBSTITUENT EFFECTS, AND THE SHIELDING TENSOR

Since paramagnetic currents require an imbalance of charge in the valence shell, correlations arise of increased shielding with increase in local symmetry, although it is often difficult to disentangle the operative factors.

Among the lighter elements, low-field resonance is observed for planar molecules, because of deshielding by $\sigma \leftrightarrow \pi$ circulations. Carbon is most strongly deshielded in carbocations R_3C^+ and in carbene ligands in metal complexes (*15,27*), and boron in BMe_3 and BH_3 (*123*), in which charge can circulate from σ bonds into the underoccupied π orbital; the shielding increases with π-donor ligands (*15, 30*) (Section V). Boron is more highly shielded when 4-coordinate, and in apical positions in boranes, such as pentaborane. Similarly, in ethene and perhaps in NO_3^-, carbon and nitrogen are deshielded by circulations of π electrons in σ^* orbitals, and deshielding is stronger still for $n \rightarrow \pi^*$ circulations, as in NO_2^- or ozone.

In linear molecules, however, resonance may be at relatively high field, since there is no paramagnetic circulation about the C_∞ or D_∞ axis (as in the free atom), the classic example being acetylenic carbon. But resonance may be at low field when the perpendicular circulations are particularly effective, as in F_2, or PN in phosphorus shielding [studied by molecular-beam electric resonance (*6, 145*)].

Among the medium-to-heavy main-group elements (discussed in Section V), higher shielding is observed for higher local symmetry (for comparable ligands), that is planar < tetrahedral < octahedral. There is a pleasing sequence in chlorophosphorus compounds, in which the phosphorus shielding increases $PCl_3 < PCl_4^+ < PCl_5 < PCl_6^-$ (*54*). Theoretical analysis of ^{31}P shifts in a wide range of compounds showed their sensitivity to asymmetric electronic loading of phosphorus (*91*).

In transition-metal complexes, however, the metal may be more shielded in a less symmetrical ligand field, because of the smaller ligand field splitting. Examples are rhodium and platinum, which are more highly shielded in square-planar than in octahedral complexes (*17, 39, 62, 78, 98, 176*).

The question of substituent effects is a complicated one (and will not be considered in detail). Heavy-ligand-atom effects are not well understood. In proton shielding, a plot of the molecular diamagnetic and paramagnetic terms against the atomic number of the ligand in the binary hydrides shows that $\sigma_d(H)$ and $\sigma_p(H)$ both increase fairly symmetrically, and in periodic fashion, but for heavier ligands the diamagnetic term increases slightly faster (*108*). The rationale may be along familiar lines, or there may be special effects, e.g., of spin-orbit coupling (*143*), as suggested in ^{13}C studies of CH_3I (*120a*); there has been little investigation of this.

There have been many studies of multiple substitution, and this again is a complicated question, since the diamagnetic and paramagnetic effects of the substituent are usually opposed, and within the paramagnetic term, ΔE and radial (and charge density) factors may be opposed. Characteristic U-shaped or "sagging" curves are often observed for the shielding of the central atom with progressive substitution, e.g., of hydrogen or methyl by halogen, NMe_2, OR, or other groups, as shown originally by Lauterbur for carbon in substituted methanes (*88*), and now demonstrated for aluminum (*79*), silicon (*153*), tin (*59, 162*), phosphorus (*90*), and others. Frequently the shielding decreases with the first, and perhaps the second, substituent, then increases with further substitution. For carbon in the methanes it was shown (in the AL approximation) that the sagging results largely from the opposition of the diamagnetic and paramagnetic terms. Each term separately gives a monotonic curve, but only the diamagnetic term is linearly additive, and this increases faster than the paramagnetic term for multiple substitution by a heavier ligand, giving the upfield turn to the U-shaped curve (Part I). With heavier atoms particularly, there is a pronounced sagging in the plot of the paramagnetic term, and we then have to explain the larger paramagnetic contribution for the partially substituted molecules.

For substituents differing in electronegativity, the overall variation of the paramagnetic term is strongly influenced by the changes with substitution in the radial term and in the valence *p* orbital population on the central atom (*75*). But in addition to this, the excitation energies themselves form a U- (or W-) shaped curve, since the energy levels which are degenerate in the unsubstituted AX_4 and AY_4 molecules are split in the less symmetrical AX_3Y, AX_2Y_2, and AXY_3 molecules, and this splitting introduces some lower energy excitations. Lyubimov and Ionov (*96a*) have relaxed the severity of the Karplus–Pople average energy approximation, following Cornwell (*28*), to take account of the additional magnetically allowed excitations in the C_{3v} and C_{2v} molecules (for A = Al, Si, Sn; X/Y = F/Cl, F/Br, Cl/Br, Cl/I, H/OH). The calculations are difficult because of the many uncertainties, but they achieve some qualitative agreement with observed deviations from additivity. Again, it seems that lower symmetry correlates with lower shielding. This approach is applicable also to other symmetries (octahedral, trigonal, etc.); and to π-bonding or electron delocalization among the ligands, as in polyfluoro compounds in which the lone pairs interact at close approach, or polybromo or iodo compounds in which there are steric interactions.

The information from experiment that we need in order to understand these relationships is increasingly becoming available now from various sources, in the form of individual elements of the shielding tensor, or anisotropies. Cross-correlation of NMR and NQR results has already been mentioned, and molecular beam and microwave methods that give the elements of the paramagnetic shielding tensor were referred to in Part I. Many studies have used liquid crystals (*95*). Recent years have seen important advances in techniques for high-resolution NMR spectroscopy with solid (preferably single crystal) samples, removing the dipolar interactions that broaden the resonance lines, sometimes by several kilohertz (*105*). An early technique to impose motional narrowing, which also removes quadrupolar broadening, is to rotate the solid at the magic angle (α) at which the dipolar interaction $\frac{1}{2}(3\cos^2\alpha - 1)$ is zero (*5*); but the shielding tensor elements are then averaged to the isotropic value. A powerful method for obtaining the full shielding tensor in a high-resolution spectrum is to hold the single crystal still, and rotate the nuclear spin system by a special sequence of 90° pulses, with Fourier transform of the free induction decay. The WAHUHA sequence of Waugh, Huber, and Haeberlen (*171*) magnetizes the sample for equal periods of time along each of the axes in the rotating reference frame in alteration. This removes interactions between like nuclei, but not between unlike nuclei, for which multiple resonance (or magic axis rotation) can be used. The phosphorus shielding tensors in α-$Ca_2P_2O_7$ have been measured in this way (*81*), and proton shielding tensors (with and without hydrogen bonding) (*87*), for example.

An important extension of the multipulse technique enables "rare" spins (which may be chemically or isotopically dilute), such as ^{13}C, ^{15}N, or ^{17}O, to be studied in the presence of an abundant spin such as ^{1}H or ^{19}F. This is used to cross-polarize the rare spin (*61*), as in Waugh's proton-enhanced nuclear induction (alias NMR) spectroscopy (*48*, *134*, *135*). The shielding tensor has been obtained in this way for ^{13}C in $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ (which is a one-dimensional conductor) (*167*), in calcium formate (*168*), and in several organic molecules; for ^{15}N in NH_4NO_3 (*47*), etc; and for ^{29}Si in some organosilicon compounds (*48*). This technique has now been extended so that nuclei such as ^{25}Mg and

^{43}Ca of low gyromagnetic ratio, as well as low natural abundance (*13*), can be studied under high resolution in solid samples.

Such methods are in their infancy (and are expensive). Their potential for inorganic chemistry is enormous. Degrees of ionicity can be quantified (since σ_p is zero for a free ion), as in ^{19}F studies of the group II difluorides (*170*), which can be compared with results obtained for the alkali metals in their halides (*156*). Suggestions of π bonding can be tested, by reference to observed anisotropies about the bonds in question; and so on.

Information on magnetic shielding and susceptibility anisotropies has been assembled by Appleman and Dailey (*6*), and the experimental shielding tensor components were compared with (*ab initio*) calculated values, for second-row atoms. Their review contains much of interest to the inorganic chemist; for example, ^{19}F shielding anisotropies in inorganic fluorides (of opposite sign in PtF_6 compared to MoF_6, WF_6, and UF_6); and the small phosphorus anisotropy in PH_3 (as for nitrogen in NH_3), compared with large anisotropies in PN, N_2, and ClCN.

V. Main Group Elements

Like chemical bonding, nuclear magnetic shielding depends on electrons, and there are characteristic variations across the row and down the group of the periodic table. Thus the chemical shifts of boron, carbon, and nitrogen vary in parallel for isoelectronic compounds, such as BR_3 and R_3C^+, or R_3BNH_3 and R_3CCH_3 (*123*); and the resonance of the central atom in borate, carbonate, or nitrate ion appears at relatively low field.

In the comparisons that follow, in which an attempt is made to pick out important factors determining chemical shifts, it is usually difficult to ensure constancy of other factors. This general caveat applies particularly to the heavy substituent effect; thus many or most generalizations have the exception that the iodides (and perhaps bromides, selenides, etc.) appear too far upfield.

In boron resonance the planar alkyl boranes BR_3, with only 6 electrons (formally) in the boron valence shell, appear at lowest field, and the BX_3 line moves upfield over a range of nearly 100 ppm for $X = R < H < SMe < Cl < Br < NMe_2 < OMe < F < I$ (*30, 101, 122–124*). This sequence is roughly as expected for increasing population of the boron $p\pi$ orbital (except for the heavy ligand effect). In support of this rationale, the deshielding of boron in BMe_3 relative to BMe_4^- (or BH_3 relative to BH_4^-) is very large, about 100 ppm, but the difference is only 14 ppm for BF_3 relative to BF_4^-; and a different sequence is observed in the BX_4^- compounds, $Cl \lesssim OH \lesssim NHMe \approx F < Me < Br < H < I$. The BX_3 and BX_4^- sequences overlap, the resonance of BF_3 at medium field being close to those for B_2H_6 and BCl_4^-. (As previously mentioned, relatively high shielding is observed for apical boron in the pentaboranes.) Effects of multiple substitution are evident, since the sequence differs in the Me_2BX compounds, for which the boron shielding increases as $X = Me \approx H < Br < Cl < F < OMe < NMe_2$.

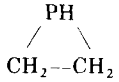
In nitrogen resonance the range is extended to low field by the presence of lone pairs on nitrogen, with strong deshielding from $n_N \rightarrow \pi^*$ circulations as in $XN{=}NX$ (*114*) or $NX{=}O$ compounds (*3*). In ammonia and the amines, however, relatively little deshielding of nitrogen can be attributed to the presence of the lone pair, and a similar pattern is observed for the other nonmetal hydrides (as already mentioned), related to high excitation energies, and small *p* character of the lone pair electrons.

In aluminum resonance (*2*, *79*, *127*), alkyl compounds, such as Al^iBu_3—$Al_2{}^iBu_6$ appear at lowest field. Then follow overlapping sequences of Al_2X_6 and AlX_4^- compounds, in which the aluminum shielding increases, for Al_2X_6 as $X = R < Cl < Br < I$, and for AlX_4^- as $X = Cl < H < OH < Br < F < I$. At highest field are the octahedral complexes $[Al(acac)_3] \sim [Al(H_2O)_6]^{3+} < [Al(NCMe)_6]^{3+}$ (with AlI_4^- among them) (*58*). These relationships, with AlH_4^- at medium field, suggest that $p\sigma \rightarrow d\pi$ circulations may be significant in the shielding. Gallium is a more difficult nucleus to measure: of the compounds studied, GaH_4^- appears at low field and GaI_4^- at high field (*2*). 6-Coordinate gallium(III) (with water or DMF as ligands) is now in the middle of the range, since the highest shielding is observed for Ga^+ in Ga_2Br_4 and Ga_2Cl_4, which are gallium gallates $Ga^+GaX_4^-$.

The group IV elements are well studied by NMR, since all except germanium have spin-$\frac{1}{2}$ nuclei in adequate abundance, and the nuclear quadrupole moment for germanium is not very large. Silicon resonance (*153a*) resembles that of aluminum in that 6-coordinate silicon $[Si(acac)_3$, $SiF_6^{2-}]$ is upfield of 4-coordinate silicon (although SiI_4 appears at highest field). In the SiX_4 compounds, there is some indication of increased shielding with increasing π-donor ability of the ligand, as for BX_3, with the silicon shielding increasing in the order $Me < Cl < NMe_2 < OMe < Br < F$ ($<I$). The order for Me_3SiX compounds is $F < Cl < Br < OMe < I < NMe_2 < Me < Cl < H$. At very low field is the silicon resonance in $Hg(SiMe_3)_2$, and this may be related to Orgel's description (given below) of *d* orbital contributions to deshielding for posttransition metals in $d^{10}s^2$ configurations.

The germanium compounds measured in germanium resonance (*74*, *80*) roughly follow the SiX_4 pattern, and similarly for SnX_4. A wide range of compounds has been measured in tin resonance (*21*, *32*, *59*, *75*, *162*). At high field (apart from SnI_4) are the highly symmetrical ions Sn^{2+}, $SiF_6{}^{2-}$, $Sn(OH)_6{}^{2-}$, and also $[MeSnBr_5]^-$; at low field, $Sn(SMe)_4$.

At high field in phosphorus resonance (*158*) are the hydride species, in which the phosphorus shielding increases with *de*creasing symmetry, $PH_4{}^+ < PH_3 < PH_2{}^-$ (the series is isoelectronic, and excitation energies are high). Unexpectedly high phosphorus shielding is observed in P_4 and in phosphirane



(*170a*). The tetrahedral species ($PO_4{}^{3-}$, etc.) are at medium field, and at lowest field, PX_3 with $X = Br < Cl < I < OMe < NMe_2 < F$ (*90*, *117*). The small number of arsenic compounds that have been measured follow the phosphorus pattern (*8*). Sulfur has been rather little studied because the magnetic nucleus ^{33}S has a low natural abundance (1%) and sensitivity. Shielding increases in the order $SO_4{}^{2-} < Me_2SO <$ thiophene $< CS_2 < Et_2S < S^{2-}$ (*149*). Spin-rotation constants have been measured for $^{16}O^{12}C^{33}S$, so the absolute shielding can be determined (*148*). Selenium is somewhat less difficult. In the oxyacids and anions the shielding increases as the symmetry increases, $HSeO_3{}^- < H_2SeO_3 < SeO_3{}^{2-} < Se(OH)_3{}^+ < H_2SeO_4$ (*82*). Of the compounds that have been studied, H_2Se is at highest field, SeF_6 at medium field, and then the tetrahedral compounds $SeO_4{}^{2-}$, SeF_4, and $SeCl_4$; and the planar $SeOCl_2$ and $SeOBr_2$ molecules at lowest field (*12*).

Fluorine chemical shifts are well known, with the more ionic fluorides (and gaseous HF, LiF, NaF) at high field [and ClF at unexpectedly high field (*28*, *152a*)]. In the xenon fluorides (*50*) the decrease in fluorine shielding $XeF^+ > XeF_2 > XeF_4 > XeF_3{}^+ > (XeF_6)_4 > XeF_5{}^+$ follows the decrease in ionicity of the Xe–F bond, and is accompanied by decrease in the Xe–F coupling constant. The periodicity of the fluorine shift with the atomic number of the ligand (*109*) was discussed in Part I. The fluorine resonance is at very low field in UF_6 in which fluorine nonbonding electrons may circulate in *d* (or *f*) orbitals. It is likely that this can happen even when fluorine is a *β*-substituent on a transition metal, since fluorine in fluorocarbon ligands is deshielded when bonded through carbon to manganese, rhenium, iron, or cobalt in low-spin d^6 complexes, though not when bonded (through carbon) to a main-group element, such as tin or phosphorus. This has been explained in terms of circulation of fluorine lone-pair electrons ($2p_y$) using the metal $nd_{z^2}(\sigma^*)$ orbital (*136*).

For the other halogens, the nuclei are quadrupolar, and the quadrupole moments are large for bromine and iodine. Chlorine is reasonably amenable to NMR study, although sensitivity is low (*64*, *152*). Of the compounds studied in chlorine resonance, Cl^-, HCl, and CH_3Cl are at highest field, and ClO_3^- at lowest. Then follow chlorides and oxychlorides, for which the chlorine shielding increases $ClO_4^- < TiCl_4 < VOCl_3 < SO_2Cl_2 < SOCl_2 < CrO_2Cl_2 < PSCl_3 < CCl_4 < S_2Cl_2 < POCl_3 < PCl_3$; then Cl_2; and at fairly high field $SiCl_4 \approx GeCl_4 < AsCl_3 < SnCl_4$. There is a very rough correlation of the chemical shift with the nqcc if the compounds of the transition metals are ignored; for these the further deshielding can be explained by low-lying *d* orbitals on the metal (*64*).

Orgel (*129*) has accounted for the shielding of posttransition metals in $d^{10}s^2$ configurations in terms of $p_x \rightarrow p_y$ circulations; this applies to Ga(I) to Tl(I), Ge(II) to Pb(II), and As(III) to Bi(III). For the ions in the $d^{10}s^2$ ground state, there are no paramagnetic currents, and Ga^+(as mentioned) resonates at high field. In environments lacking a center of symmetry there is stabilization by *sp* hybridization, and this accounts for the low coordination numbers that are observed in compounds of Pb(II), Sb(III), and Bi(III). The so-called inert pair occupies an orbital with varying proportions of *s* and *p* character, and provides the main contribution to paramagnetic currents—the more, the greater the *p* character. Thus in (solid) red (tetragonal) PbO the lead resonates 3000 ppm downfield of Pb^{2+}, and in the same region as $PbMe_4$. In yellow (rhombic) PbO, however, the lead resonates about 4000 ppm farther downfield. In the tetragonal form the lead is at the apex of a rather flat square pyramid, so that it has four oxygens to one side and the "inert pair" to the other (*172*). The orthorhombic structure contains chains of alternating lead and oxygen, weakly bonded into layers, so that there are two nearer and two more distant oxygen neighbors (*172*) (and presumably more *p* character in the nonbonding electrons on lead). A variety of covalent lead compounds has now been studied (*77*, *77a*, *97*, *133*).

Metals in d^{10} configurations, Cu(I) to Au(I), Hg(II), or Tl(I), can be deshielded by currents of *p* or *d* electrons. The bonding in linear ML_2 groupings has been described by Orgel (*128*) in terms of *sd* hybridization, since the *d*—*s* splitting is small. This allows circulations via d^9s excited states to deshield the metal. Schneider and Buckingham (*153*) have compared the heavy-metal shielding in $HgMe_2$, $TlMe_3$, and $PbMe_4$ in terms of *sp*, sp^2, and sp^3 valence states, respectively, with a large deshielding for incomplete *p* and *d* shells. Thus mercury is strongly deshielded in $HgMe_2$, compared with the aqueous Hg^{2+} ion at high field (*76*). Thallium in $TlMe_3$ is deshielded compared with aqueous Tl^+ at high field; with aqueous Tl^{3+} in between, since this ion has a degree of covalent bonding to water, as $[Tl(H_2O)_4]^{3+}$, with an sp^3 valence state (*97, 153*).

VI. Transition Metals

The approximate (crystal field) theory for transition-metal complexes with incomplete *d* shells is simple. For diamagnetic compounds we are restricted to a limited number of *d*-electron configurations, mainly d^6 (octahedral), d^8 (square planar or trigonal bipyramidal), some d^4 (e.g., h^5-cyclopentadienyl), and a few d^2 (cubic) (*96*). Only one-electron terms and singlet states are involved. Complications then arise, with more detailed considerations of ligand electronegativity, σ and π bonding, asymmetric substitution, and so on (some of these have been considered to some extent in Section IV,C). There are technical limitations to the NMR studies, in that rather few transition metals have abundant isotopes of suitable spin. Most work has been done with cobalt, platinum, tungsten, rhodium, or manganese, but the range is fast increasing as multiple resonance and Fourier–transform techniques are reducing the obstacles. For the quadrupolar nuclei, ^{51}V, ^{55}Mn, and ^{59}Co, there are problems of rapid relaxation (in asymmetric environments), but these are perhaps offset by the availability of NQR techniques as well, as already discussed.

Griffith and Orgel (*54, 55*) applied crystal field theory to the Ramsey shielding theory, in the local term approximation of Saika and Slichter. Their subject was d^6 (low spin) complexes of cobalt(III), but the method is a general one. Neglecting variation in the diamagnetic term, they derived the expression for the paramagnetic term:

$$\sigma = \frac{-\mu_0}{4\pi} \frac{4\mu_B{}^2 \langle r^{-3} \rangle_{3d}}{3\Delta_0} \langle 0|L^2|0 \rangle \qquad (19)$$

for a sum over six *d* electrons in a strong octahedral field, $\langle r^{-3} \rangle_{3d}$ being the average over a single *d* orbital, and Δ_0 the splitting in the octahedral crystal field. Thus the metal nucleus is deshielded by circulation of the t_{2g} (d_{xy}, d_{yz}, d_{xz}) electrons, via e_g orbitals ($d_{x^2-y^2}$, d_{z^2}) unoccupied in the ground state. The theory thus predicts linear δ/Δ^{-1} or δ/λ relationships between the chemical shift and the wavelength of the $d \rightarrow d$ ($^1A_1 \rightarrow {}^1T_{1g}$) absorption. A close correlation was in fact found by Freeman, Murray, and Richards, between the cobalt resonance frequencies and the spectrochemical series of the ligands, for fourteen complexes of cobalt(III) (*42*).

The theory also predicts a small decrease in shielding with increasing temperature, since the increasing population of higher vibrational modes, particularly the bending modes, tends to reduce Δ_0. This has been confirmed for cobalt (*42*), platinum (*98*), and rhodium (*62*); it is not observed for closed *d* shells. The effect of spin-orbit coupling was considered to be negligible. Griffith and Orgel pointed out that neglect of covalent bonding between metal and ligand overestimates the orbital angular momentum, since electron delocalization is underestimated: but that neglect of configuration interaction tends to compensate for this. Betteridge and Golding have made semiquantitative estimates of these effects for cobalt(III) (*11*). As to spin-orbit interaction, mixing in of the $^3T_1$ excited state contributes rather little to σ_p, about 0.3%. Configurational mixing is rather more important, since the effect of mixing the possible configurations of the $^1A_1$, $^3T_1$, and $^1T_1$ states over the crystal range of interest is to lower the shielding term by about 3%. Distortion effects are relatively small and can be allowed for by an orbital reduction term. The largest effect is that of covalent bonding, with a large quenching of the orbital angular momentum, because of transfer of spin to the ligands. We return to this subject below.

Buckingham and Stephens extended the theory of the d^6 octahedral complexes to examine the effect of the *d* electron currents on a proton attached to the transition metal (*19*). They calculated the *d*-electron contribution to the proton shielding, using the Ramsey–Orgel theory, assuming $\delta \simeq 5$ ppm for the other contributions to the proton shielding; and give diagrams showing the variation of the shielding tensor elements with distance R for various values of the Slater orbital exponent k and the principal quantum number n. They show that the $\sigma_{xx}{}^p$ and $\sigma_{yy}{}^p$ tensor elements are positive for circulations about axes perpendicular to the M—H bond axis, at a normal proton distance (*68*) ($R \simeq 3$ a.u.) and for likely values of k (between 3 and 4). These tensor elements are negative for lower values of k, and the paramagnetic term $\sigma_{zz}{}^p$ for circulation about the M—H bond axis is always negative. Thus the average value of the paramagnetic term is positive at the proton, accounting for the high-field resonance observed. The theory predicts a very high anisotropy in the proton shielding ($\sigma_{xx}{}^p - \sigma_{zz}{}^p = -500$ ppm); and predicts also that the paramagnetic term is not very sensitive to the ligand field splitting. For $R = 0$, the expressions for σ_p reduce to Griffith and Orgel's Eq. (19). Only in the limit of an infinite orbital exponent k, i.e., when the metal orbitals are contracted to a point at the nucleus, do the equations give the same (zero) shielding as the neighbor anisotropy approximation for an isotropic near neighbor; that is, a point dipole approximation does little justice to a metal atom at the normal M—H distance.

Buckingham and Stephens extended the theory also to d^8 square-planar complexes, using platinum(II) as example (with diagrams to show the variation of the shielding terms with R and k) (*20*). The paramagnetic circulations of d_{xy}, d_{yz}, and d_{xz} electrons now use the $d_{x^2-y^2}$ σ^* orbital, unoccupied in the ground state. The excitation energies are ΔE_{A} (i.e., ${}^1\mathrm{A}_1 \rightarrow {}^1\mathrm{A}_2$) for the d_{xy} electrons, and ΔE_{E} (i.e., ${}^1\mathrm{A}_1 \rightarrow {}^1E$) for the d_{yz} and d_{xz} electrons, with $\Delta E_{\mathrm{A}} < \Delta E_{\mathrm{E}}$. Once again the paramagnetic term is positive for circulations about the axes perpendicular to the M—H bond axis (with excitation energy ΔE_{E}) and negative for circulation about the M—H bond axis (with excitation energy ΔE_{A}) for $R \simeq 3$ a.u. and k between 3 and 4. The resultant effect is again to shield the proton, although less in general than in the octahedral case. There is the further prediction that protons above the plane should be strongly deshielded.

As before, the equations reduce in the limit of $R = 0$ to those for the d electron contribution to the shielding of the metal nucleus, in d^8 square-planar complexes, that is:

$$\sigma_{xx}{}^{p} = \sigma_{yy}{}^{p} = \frac{-\mu_0}{4\pi}\frac{8\mu_{\mathrm{B}}{}^2\langle r^{-3}\rangle_d}{\Delta E_{\mathrm{E}}} = \frac{-\mu_0}{4\pi}\frac{4\mu_{\mathrm{B}}{}^2k^3}{21\,\Delta E_{\mathrm{E}}}$$

$$\sigma_{zz}{}^{p} = \frac{-\mu_0}{4\pi}\frac{32\mu_{\mathrm{B}}{}^2\langle r^{-3}\rangle_d}{\Delta E_{\mathrm{A}}}$$

The shielding reduces in the limit of $k \rightarrow \infty$ to the value given by the neighbor anisotropy approximation, with the same wave functions; but this now predicts the sign (though not the magnitude) of the metal contribution to the proton shielding correctly, since the paramagnetic susceptibility due to $d \rightarrow d$ excitations is greater (in fact 4 times greater) perpendicular to the plane than in the plane. A pleasing sequel is the near-linear correlation, with negative slope, found by Dean and Green (*34*) between the shielding of the platinum and of the attached proton, in a series of square-planar complexes, *trans*-[PtHL(PEt$_3$)$_2$], with a variety of anionic ligands L.

The subject of coordination shifts is a large one, and will not be considered in detail here. The deshielding observed for fluorine in CF$_2$ or CF$_3$ ligands on a d^6 metal has been mentioned (*136*): the excitation energy for the $2p_y \rightarrow nd_{z^2}$ circulations (about the axes perpendicular to the M—F axis) being given by the difference between the fluoride ionization energy and the ionization energy of the metal in the ligand field, plus the ligand field splitting.

In cobalt shielding, the $(\delta/\Delta_0{}^{-1})$ correlation with the spectrochemical series of the ligands was found to be successful for cobalt(III) complexes with second-row ligand atoms (C, N, O) (*36*, *147*, *175*). Subsequent work showed increased shielding for heavier ligand atoms (S, Se, As, etc.) (*11*, *43*, *71*, *106*), and in appropriate complexes, different correlation lines can be drawn for ligands from different rows of the Periodic Table. Similarly in organo-cobalt complexes, and low oxidation states of cobalt, the crystal field model was found to be inadequate (*118*, *119*, *164*, *165*). Lucken, Noack, and Williams used a ligand field extension of the theory, to account for the shielding in cobalticenium ion, and in cobalt complexes with carbonyl, nitrosyl, hydride, and phosphine ligands. Effective excitation energies were taken from MO correlation diagrams. In the cobalticenium ion, cobalt is deshielded by $\pi \rightarrow \sigma^*$ circulations of d_{z^2}, and d_{xy}, $d_{x^2-y^2}$ electrons into d_{xz}, d_{yz} orbitals. In the carbonyl and phosphine compounds cobalt is relatively highly shielded as the d shell is (formally) closed, and the relative shielding was accounted for in terms of circulations of d electrons in $4p(\pi^*)$ orbitals (*94*).

A useful approach is to introduce some allowance for covalency into the simple crystal field model, in which the e_g and t_{2g} orbitals are taken to be pure d orbitals. Freeman, Murray, and Richards gave the shielding, following the Orgel theory, as $\sigma = A - B/\Delta$, with A and B effectively constant among their octahedral complexes. A is the diamagnetic term σ_d, and

$$\sigma_p = -B_0/\Delta_0 = \frac{-32\mu_B{}^2\langle r^{-3}\rangle_{3d}}{\Delta_0}$$

Effects of covalent bonding may be simulated by an orbital reduction factor $k_{\sigma\pi}$ between the t_{2g} and e_g orbitals (*11*, *43*, *54*, *70*, *106*, *130*):

$$\sigma_p = \frac{-32\mu_B{}^2 k_{\sigma\pi}{}^2\langle r^{-3}\rangle_{nd}}{\Delta_0}$$

The problem is then to find separate estimates of $k_{\sigma\pi}$ and $\langle r^{-3}\rangle_{nd}$, since the discussion becomes circular when these, or their products, are deduced from the observed shifts. An argument for taking the $\langle r^{-3}\rangle_{nd}$ factor as effectively constant is that its relative importance is greatest near the nucleus, where it is least affected by the ligands. Betteridge and Golding have calculated values of the orbital reduction factor k

(from the chemical shift and Δ_0) for cobalt(III) complexes as 0.85 for first-row ligands (C, N, O), decreasing to 0.72 for second-row ligands (Si, P, S, Cl), and 0.67 for third row (As, Se); the corresponding values of the percentage spin transferred to the ligands being 2.86, 5.35, and 6.31. A problem in this approach is that near-constancy of the $\langle r^{-3} \rangle$ and the $k^2\langle r^{-3} \rangle$ factors, e.g., for C, N, and O ligand atoms implies that k has similar values for π-acceptor ligands such as CN, and for π-donor ligand atoms nitrogen and oxygen, as the k^2 and $\langle r^{-3} \rangle$ factors would not be expected to vary inversely. Some comparisons were made (*11*) with independent estimates of k from ESR studies (*56*).

An alternative formulation, in adapting the crystal field theory to allow for covalency, is to insert a $C_M{}^2$ factor into the expression for the paramagnetic term, where C_M is the coefficient of the metal orbital in the molecular orbital, as defined (*52*) by Gray and Ballhausen. Platinum shifts have been discussed in this way, and correlated with other measures of covalency, as discussed below (*34*, *132*); and similarly for vanadium and manganese in octahedral complexes (*121a*).

Effects of the radial factor ($k^2\langle r^{-3} \rangle_{nd}$, $C_M{}^2\langle r^{-3} \rangle_{nd}$, etc.) can usefully be considered in general terms. In general, increase in d electron radius, as by π-delocalization on the ligands, may be expressed as an increase in nephelauxetic (electron cloud-expanding) (*66*, *67*) effect, which corresponds to a reduced paramagnetic term, since the electron circulation is farther away from the metal nucleus. Values of $k^2\langle r^{-3} \rangle_{3d}$ in cobalt complexes, as determined from the chemical shifts and ligand field splittings, were found to be 35–55% smaller than in the free ion, and this was interpreted by radial expansion of the e_g orbitals, as a consequence of covalent bonding. Smaller radial factors are found for heavier ligand atoms (*43*).

In square-planar complexes of platinum(II) (d^8), with a smaller variation in the ligand field splitting, it is possible to trace correlations with the nephelauxetic series of the ligands, in particular series of compounds, as well as with the spectrochemical series. The Δ_s term is taken as a linear combination of the ${}^1A_{2g}$ and the ${}^1E_g$ energies. In $[PtX_2L_2]$ complexes, where X is halogen and L a ligand bonded through nitrogen, oxygen, phosphorus, arsenic, etc., Pidcock, Richards, and Venanzi (*132*) found that the platinum shifts follow the spectrochemical series of the ligands L if the halogen is the same. For changes in the halogen, however, the radial factor $C_M{}^2\langle r^{-3} \rangle_{5d}$ dominates, the shielding increasing Cl < Br < I (although the ligand field splitting decreases Cl > Br > I). The nephelauxetic series was followed also in a series of square-planar platinum hydride complexes with *trans*-phosphine ligands and a fourth anionic ligand L = halide, $NO_2{}^-$,

NO_3^-, etc. (*34*). The order of increasing platinum shielding is L = $RCOO^- < NO_3^- < NO_2^- < Cl^- < SCN^- < Br^- < CN^- < I^-$, which differs from the nephelauxetic order only in the placement of CN^-, and is quite different from the spectrochemical order, in which the shielding increases I < Br < Cl. The conclusion is that the more polarizable ligands reduce the deshielding by reducing the coefficient C_M (subsuming the radial term $\langle r^{-3}\rangle_{5d}$). This conclusion is confirmed in more recent work, on platinum shielding in square-planar complexes (*51a*, *78*): a plot of the shielding against λ_{av} gives different lines for chlorides, bromides, and iodides, with the polarizable ligands (Sb, Te) below the lines (this corresponds to increased shielding) and the less polarizable ones (N, C) above. Some correspondence is observed also between the chemical shifts and other measures of ligand covalency, such as ligand dissociation equilibrium constants, and the pK_a of the acid HL. The high covalency attributed to the Pt—I bond is in keeping with other spectroscopic observations, such as low infrared intensity and high Raman intensity of the bands for Pt-I stretching vibrations.

Broad correlations are possible, therefore, for compounds with a given *d* electron configuration, and between the different configurations; despite the complications of opposing factors, such as increasing covalency (σ or $\sigma + \pi$) increasing the excitation energies as well as decreasing the radial factor. In general the spectrochemical series correlation is likely to be observed for less polarizable (hard, class A) ligands, and higher oxidation states of the metal, whereas the nephelauxetic pattern is observed in complexes of polarizable or ($\sigma + \pi$)-bonding ligands, with metals in low oxidation states. Relevant studies (including many already referred to) are those of vanadium (*121a*, *146a*), manganese (*9*, *23*, *121a*, *125*, *126*), molybdenum (*96*), tungsten (*53*, *99*, *100*), rhodium (*17*, *62*), and platinum (*78*, *98*, *176*), and reviews of heavy-atom shielding (*97*, *173*).

VII. Correlations with Spectroscopic and Other Properties

As we have seen, linear δ/λ or δ/IE (ionization energy) correlations (*113a*) can be observed in appropriate series of compounds. Near-linear δ/J (spin–spin coupling constant) correlations have been reported also, in fluorides of carbon (*121*), boron (*60*), xenon (*50*), etc. and in hydride complexes of platinum (*7a*), for example. In the xenon fluorides and oxyfluorides and their cations (*50*) the relation between δ(F) and J(XeF) was attributed to the importance of a mean excitation energy ΔE in the paramagnetic shielding term and in the Fermi contact contribution, which is assumed to be dominant in the Xe—F spin–spin coupling. The excitations are different in the paramagnetic term and in the Fermi contact term, since the latter is concerned with *s* orbitals and triplet states (*140*); but all the same, the energies may vary in parallel. In the platinum hydride complexes (*7a*) *trans*-$[PtHL(PEt_3)_2]$, with 26 different carboxylate ligands L, the different factors contributing to the Fermi contact term were examined. This term depends directly on the amount of platinum 6*s* orbital involved in the Pt—H bond, the magnitude of this orbital at the nucleus, and the mean triplet excitation energy $^3\Delta E$. Since changes in the carboxylate ligands produced negligible changes in the electronic spectrum, it was concluded that the variation in J_{PtH} was unlikely to be with $^3\Delta E$, and more likely to be with the increase in *s*-character of the bond. This is accomplished by a shortening of the bond, which should increase the proton shielding, in the theory of Buckingham and Stephens (Section VI). In other square-planar platinum complexes the chemical shifts are found to correlate more with covalency of the bonds to the ligands, and with the nephelauxetic series, than with the spectrochemical series. However, in a series of platinum hydride complexes with inorganic acido-ligands (L = hal^-, NO_3^-, etc.) the spin-spin coupling constant was found to follow the order of the spectrochemical series for the *trans*-ligand (*7a*).

In the platinum hydride carboxylate complexes linear correlations were found also between the chemical shift of the hydride ligand and the Pt—H stretching frequency, and the pK_a of the parent carboxylic acid (*7a*). δ/ν (vibration frequency) correlations are not uncommon. Correlations are found also with bond energies, as in a study of ^{13}C shifts in methyl- and phenylmercury(II) compounds, in which the effective excitation energy is $\sigma \rightarrow \sigma^*$, so that deshielding correlates with a decrease in the C—Hg bond dissociation energy (*16*). In the range of Xe-F compounds mentioned above, the Xe—F bond length correlates inversely with J, ν, and with the nuclear magnetic shielding (*50*).

Since nuclear magnetic shielding depends on the number of electrons, chemical shifts may correlate with charge densities, with Hammett substituent parameters, or with pK_a or pK_b values, if other factors involved in the shielding remain sufficiently constant.

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NOTE ADDED IN PROOF

Now that definitive studies of ^{129}Xe resonance in the element and its compounds are available (*1A*,*2A*), it is interesting to examine the pattern of chemical shifts for this heavy atom. The familiar effects of local symmetry and effective nuclear charge are evident in the sequence of the fluoride species in xenon resonance. The xenon shielding decreases $\mathrm{Xe} \ggg \mathrm{XeF_2} > (\mathrm{FXe\cdots F\cdots XeF})^+ > \mathrm{XeF^+} > (\mathrm{XeF_6})_4 > \mathrm{XeF_5}^+ > \mathrm{XeF_4} > \mathrm{XeF_3}^+$, with the free atom and then the linear molecule XeF_2 at highest field, and at lowest field the T-shaped ion XeF_3^+ and then the square planar molecule XeF_4. The shielding decreases also with increase in oxidation number of zenon from 0 to VIII (increasing the $\langle r^{-3}\rangle_{5p,d}$ terms), with XeF_4 and XeF_3^+ out of line, because of their lower symmetry.

Xenon is strongly deshielded with increase in oxygen substitution in the sequence $\mathrm{XeF_5}^+ > \mathrm{XeOF_4} > \mathrm{XeO_2F_2} > \mathrm{XeO_3} > \mathrm{XeOF_3}^+ > \mathrm{XeF_4} > \mathrm{XeF_3}^+ > \mathrm{XeO_2F}^+ \gg \mathrm{XeO_6}^{4-}$. Interestingly, the highly symmetrical perxenate ion resonates at very low field. This is found for other oxyanions [such as ClO_4^- (*64*)] and may be associated with low excitation energies.

In the series of linear complexes of XeF_2 with Lewis acids (A) of increasing acid strength, from F–Xe–F via AF··Xe··F to $^+$Xe–F, the xenon line goes downfield as the (terminal) fluorine line goes upfield, as the terminal Xe–F bond shortens, and with increase in $^1J(\mathrm{XeF})$.

In these results the theory of Jameson and Gutowsky (*3A,63*) for the xenon fluorides and $XeOF_4$, in terms of localized bonds using xenon s, p, and d orbitals, is well confirmed. It seems that the "atom in a molecule" description is rather well suited to the shielding of a heavy atom with lighter ligands, as ligand atom contributions can then more safely be neglected.

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