1 Introduction
During this review period (June 1982 to May 1983) several papers on the relativistic theory of nuclear shielding have appeared. It is therefore appropriate that a large part of the section on general theory is devoted to this. Further developments in the shielding of conjugated systems, which yield some definitive conclusions on the physical aspects of the ring current, are described in Section 2B. Initial attempts at modelling the nuclear shielding of molecules (CO in particular) adsorbed on a surface are reported in Section 3D. A review of calculations of nuclear shielding has appeared.¹

2 Theoretical Aspects of Nuclear Shielding
A. General Theory. – In Volume 12 of this Series we reviewed the relativistic theory for magnetic susceptibilities and shielding formulated by Kolb, Johnson, and Shorer² in terms of Dirac–Fock wavefunctions. In the solution of the coupled equations, the relativistic random phase approximation was used (which in the non-relativistic static field limit reduces to CHF theory). Applications were reported on some closed shell atoms and ions up to \( Z = 80 \). In this review period, apparently unaware of the work of Kolb et al., Pykko³ and Pyper⁴ independently report formulations of relativistic theory of nuclear shielding.

We recall that in non-relativistic theory, the effective one-electron Hamiltonian in the absence of external fields and nuclear moment is

\[
\mathcal{H}_{NR}(0) = \frac{p^2}{2m} + V + V_X
\]

in the local potential \( V \) and the nonlocal exchange potential \( V_X \). In a field this becomes

\[
\mathcal{H}_{NR}(\mathbf{B}) = \frac{(p + eA)^2}{2m} + V + V_X
\]

where \(-e\) is the charge electron, and \( \mathbf{A} = \mathbf{A}(r) \) is the combined vector potential of the external magnetic field and the nuclear magnetic moment

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\[
\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B}_0 \times \mathbf{r} + \frac{\mu_0}{4\pi} \left( \frac{\mathbf{\mu} \times (\mathbf{r} - \mathbf{R})}{|\mathbf{r} - \mathbf{R}|^3} \right) = \mathbf{A}_B + \mathbf{A}_N
\]

which can be written in terms of (1) and the remainder as a perturbation:

\[
\mathcal{H}_{NR}(\mathbf{B}) = \mathcal{H}_{NR}(0) + \mathcal{H}'
\]

\[
\mathcal{H}' = \left( \frac{e}{m} \right) \mathbf{p} \cdot \mathbf{A} + \left( \frac{e}{m} \right)^2 \mathbf{A}^2
\]

In relativistic theory the Dirac Hamiltonian is

\[
\mathcal{H}_{REL}(0) = \mathbf{\alpha} \cdot \mathbf{p} + \mathbf{\beta} \mathbf{m} + V
\]

where \( \mathbf{\alpha} \) and \( \mathbf{\beta} \) are \( 4 \times 4 \) matrices, which becomes

\[
\mathcal{H}_{REL}(\mathbf{B}) = \mathbf{\alpha} \cdot (\mathbf{p} + e\mathbf{A}) + \mathbf{\beta} \mathbf{m} + V = \mathcal{H}_{REL}(0) + \mathcal{H}'
\]

The perturbation is now

\[
\mathcal{H}' = e \mathbf{\alpha} \cdot \mathbf{A} + \Delta
\]

where \( \Delta \) constitutes the change in the electrostatic potential due to the \( B_0 \) field induced changes in the charge distribution of the orbitals.

If the electronic ground state \( |0\rangle \) and the excited states \( |n\rangle \) are described by Dirac–Fock wavefunctions, \( i.e. \), single Slater determinants of four component molecular orbitals \( \phi_i \), each of which satisfy one-electron Dirac equations [equation (9)]. To calculate the shielding, we need to consider energy terms that are linear in \( B_0 \) and in \( \mathbf{\mu} \), \( i.e. \), those terms in \( \mathbf{A}_B \cdot \mathbf{A}_N \) coming from \( \mathbf{p} \cdot \mathbf{A} \) in non-relativistic theory or from \( \mathbf{\alpha} \cdot \mathbf{A} \) in relativistic theory. In nonrelativistic theory such terms arise in first order from \( (e/m)^2 \mathbf{A}^2 \), so-called diamagnetic, and in second order from the product of matrix elements of \( \mathbf{p} \cdot \mathbf{A}_B \) and \( \mathbf{p} \cdot \mathbf{A}_N \), so-called paramagnetic. In relativistic theory such terms arise in second order only, from the product of the matrix element of \( \mathbf{\alpha} \cdot \mathbf{A}_B \) with a matrix element of \( \mathbf{\alpha} \cdot \mathbf{A}_N \). Thus, after decomposition of the relativistic current operator \( -e\mathbf{\alpha} \) for both diagonal and off-diagonal matrix elements, the Dirac current \( \mathbf{j} = -e\mathbf{\alpha} \) has been exactly decomposed into (i) a convection current \( -e\mathbf{\beta} (\mathbf{p} + e\mathbf{A}_B) \), which includes a magnetic field induced diamagnetic current, and (ii) an electron spin current \( -(e\mathbf{\beta}/2m) \mathbf{\Sigma} \times \mathbf{V} \). Both these currents interact with the nuclear vector potential in the usual dot product \( \mathbf{j} \cdot \mathbf{A}_N \). The matrix elements of \( \mathbf{\alpha} \cdot \mathbf{A}_B \) can be written as

\[
\langle e | \mathbf{\alpha} \cdot \mathbf{A}_B | a \rangle = \langle e | \frac{1}{2m} \mathbf{\beta} (1 + \mathbf{\Sigma}) \cdot \mathbf{B}_0 | a \rangle + \frac{1}{2m} (e_a - e_e) \langle e | \mathbf{\alpha} \cdot \mathbf{A}_B \mathbf{\beta} | a \rangle
\]

\[
+ \frac{1}{2m} \langle e | [\mathbf{\alpha} \cdot \mathbf{A}_B \mathbf{\beta}, \mathbf{K}] | a \rangle
\]

where \( K \) is the relativistic exchange operator. By a careful analysis of shielding in Dirac–Fock theory Pyper has shown that it predicts the nuclear shielding to consist of five terms:
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(1) The diamagnetic term $\sigma^{d}$. It differs from the non-relativistic term in that an extra factor of $\beta$ is present. To lowest order in $1/c^2$ this extra factor of $\beta$ arises from the reduction of the electron Larmor precession frequency caused by the velocity induced relativistic increase of electron mass. Although in relativistic theory there is no $A^2$ term, such as that which gives rise to $\sigma^{d}$ in non-relativistic theory, its counterpart arises from the relativistic equation when the positron-like states are summed over.

(2) The paramagnetic term $\sigma^{pA}$, which arises from the $(1 + \Sigma) \cdot B_0$ interaction. This is the exact analogue of Ramsey's $\sigma^p$ in non-relativistic theory. It differs from the latter in only three respects: (a) in the substitution of relativistic for non-relativistic wavefunctions, (b) in the presence of factors of $\mathbf{p}$ (4 x 4 matrix) involving the change in the Bohr magneton caused by the relativistic increase in electron mass, and (c) in the presence of contributions from the interactions of the electron spin with both the external magnetic field, $B_0$, and the nuclear vector potential, $A_N$. The spin terms (c) vanish in the non-relativistic limit because a relativistic wavefunction for a closed shell system, unlike its non-relativistic analogue, is not an eigenstate of the total electron spin, although the expectation values of all components of the electron spin do vanish. Hence the spin as well as the orbital angular momentum can be partially unquenched by the $B_0$ field, thus creating a magnetic field at the nucleus contributing to the shielding.

(3) The paramagnetic term $\sigma^{pE}$. This is purely relativistic in origin and does not have a non-relativistic counterpart. It involves expectation values over the Dirac–Fock ground state wavefunction only.

(4) The paramagnetic term $\sigma^{pX}$ (the exchange term). This is also purely relativistic in origin involving orbital exchange operators.

(5) The self-consistency term $\sigma^{\Delta}$, which also occurs in non-relativistic theory, arises from the perturbation, $\Delta$, constituting the change in the electrostatic potential due to the $B_0$-field-induced changes in the charge distributions of the orbitals.

In addition to these five main terms, there are the Breit interaction terms,\(^5\) the Breit interaction being the leading relativistic correction to the Coulomb repulsion between a pair of electrons.\(^6\) The additional relativistic corrections to the nuclear shielding, which arise because the interaction between the orbital motion of the electrons and $B_0$ causes the velocities of the electrons to change, thereby changing the Breit energy in a field-dependent way, have been derived by Pyper. The leading Breit corrections to the nuclear shielding are of the order of $(1/c^2)$ and can be interpreted as corrections to the relativistic orbit–orbit and spin–other orbit interaction. Terms up to the order of $(1/c^2)^2$ have been derived.\(^5\)

Earlier unpublished work on this subject has been described in abstracts of a symposium.\(^7\) A partial relativistic theory in which only some of the lowest order (to the order of $1/c^2$) relativistic corrections are included, was formulated


earlier, by carrying Ramsey's treatment to third order perturbation theory, involving products of matrix elements of spin–orbit coupling, the interaction of the orbital angular momentum with the field $B_0$ and the electron spin–nuclear spin coupling in the field-free molecular states. Even earlier was a partial relativistic theory of nuclear magnetic shielding in which only the larger two of the four component wavefunction are used. The application of this to a H-like atom gives a relativistic correction that is $(-1/15)$ times the non-relativistic shielding for the ground state. The relativistic theory of nuclear shielding for the $H_2$ molecule ion has been previously reviewed here.

The nuclear magnetic shielding tensor is represented, in general, by an asymmetric second rank tensor with nine independent components, since $\sigma_{\alpha\beta} = [\partial^2 E/\partial \mu_\alpha \partial B_\beta]_{\mu, B=0}$, whereas $\sigma_{\beta\alpha} = [\partial^2 E/\partial \mu_\beta \partial B_\alpha]_{\mu, B=0}$. These two expressions are not necessarily equivalent, as was pointed out by Buckingham and Pople in 1963 and by Buckingham and Malm in 1971. By inspection of Ramsey's formulae it becomes obvious that the diamagnetic term can be represented by a symmetric second-rank tensor with a maximum of six components, with $\sigma^d_{\alpha\beta} = \sigma^d_{\beta\alpha}$. However, the paramagnetic part is not necessarily symmetric. Following Buckingham's suggestion, the $\sigma$ tensor can be written as the sum of an isotropic part, a traceless symmetric part, and a traceless antisymmetric part [equation (11)]. The isotropic part is observed as the

$$\sigma_{\alpha\beta} = \bar{\sigma} \delta_{\alpha\beta} + \sigma_{\alpha\beta}^s + \sigma_{\alpha\beta}^a$$

where

$$\bar{\sigma} = (1/3)\sigma_{\gamma\gamma} \quad (1 \text{ component})$$

$$\sigma_{\alpha\beta}^s = \frac{1}{2}(\sigma_{\alpha\beta} + \sigma_{\beta\alpha}) - \sigma \delta_{\alpha\beta} = \sigma_{\beta\alpha}^s \quad (5 \text{ components})$$

$$\sigma_{\alpha\beta}^a = \frac{1}{2}(\sigma_{\alpha\beta} - \sigma_{\beta\alpha}) = -\sigma_{\beta\alpha}^a \quad (3 \text{ components})$$

scalar shift in liquids. If the resonance frequency is measured as a function of rotation angles about three mutually orthogonal axes fixed in a single crystal, the observed angular dependence of the frequency shift [equation (12)] yields

$$\Delta \nu(\phi)/\nu_0 = (A + B \cos 2\phi + C \sin 2\phi)^{1/2} - 1$$

A, B, and C, which are, in general, quadratic functions of the shielding tensor components. It has been shown that if only terms which are linear in $\sigma_{ij}$ are included in the analysis of the angular variation of the resonance frequency, relying on the argument that $\sigma_{ij} \ll 1$ and $\sigma_{ij}^2 \ll \sigma_{ij}^3$, then only the six components (the isotropic plus the traceless symmetric part) influence the results. This is due to the fact that the antisymmetric part of the shielding...
tensor affects the resonance position only in the second order.\textsuperscript{14–16} Conversely, information about the antisymmetric part is lost. It has been suggested that some spin–lattice relaxation time measurements may yield the sum of the squared antisymmetric components.\textsuperscript{17} The spin–lattice relaxation equation due to chemical shielding interactions is expressed in equation (13).

\[
\frac{1}{T_1} = \omega_c^2 \tau_c \{2[(\sigma_{12})^2 + (\sigma_{23})^2 + (\sigma_{13})^2] + \frac{1}{6} (\Delta \sigma)^2 (1 + \frac{1}{3} \eta^2)\}
\]

where

\[
\begin{align*}
\Delta \sigma &= \sigma_{33} - \frac{1}{2}(\sigma_{22} + \sigma_{11}) \\
\eta &= (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \bar{\sigma})
\end{align*}
\]

In order for \(Z(O_2^+)\) to be extracted from \(T_1\) measurements, the sum of \((\sigma^a)^2\) terms must not be negligible compared to the \((\Delta \sigma)^2\) terms. A recent calculation\textsuperscript{18} of the antisymmetric components gives the following results. Since the diamagnetic shielding is a symmetric tensor, the antisymmetric part \(\sigma^a\) can be obtained from equation (14), where \(\sigma^D\) is the transpose of \(\sigma^a\).

\[
\begin{align*}
\sigma^a &= \frac{1}{2} (\sigma^P - \sigma^D) \\
\sigma^P.
\end{align*}
\]

The results are shown in Table 1. The ratios of the \((\sigma^a)^2\) terms to the \((\Delta \sigma)^2\) terms are \(2.2 \times 10^{-2}\), \(5.6 \times 10^{-4}\), and \(4.2 \times 10^{-4}\) for \(^{13}\text{C}\) in CHFCICH\(_3\), CH\(_3\)CHO, and NH\(_2\)CHO, respectively. This calculation seems to indicate that the antisymmetric part of the shielding tensor may be too small to measure even for the heavy nuclei.

The effects of electron correlation on nuclear shielding can be calculated using a theory at the configuration interaction (CI) level. This was presented by Daborn and Handy,\textsuperscript{19} (reported in Volume 12 of this Series) and more recently by Fukui.\textsuperscript{20} For the F nucleus in HF, electron correlation has a shielding effect (+30 p.p.m.), and for the H nucleus in the same molecule, a deshielding effect (−0.7 p.p.m.).

**B. Ab Initio Calculations.** – Ab initio calculations of nuclear shielding for molecules larger than benzene have previously only been possible with Ditchfield’s GIAO method.\textsuperscript{21,22} The IGLO (individual gauge for localized

Table 1. Calculated principal values and antisymmetric parts of \(^{13}\text{C}\) shielding tensors in p.p.m.\textsuperscript{18}

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(\sigma_{11})</th>
<th>(\sigma_{22})</th>
<th>(\sigma_{33})</th>
<th>(\sigma_{12}^a)</th>
<th>(\sigma_{13}^a)</th>
<th>(\sigma_{23}^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHFCICH(_3)</td>
<td>333.1</td>
<td>288.8</td>
<td>227.1</td>
<td>-2.354</td>
<td>2.563</td>
<td>0.2895</td>
</tr>
<tr>
<td>MeCHO</td>
<td>-87.14</td>
<td>29.97</td>
<td>241.4</td>
<td>-1.758</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NH(_2)CHO</td>
<td>235.2</td>
<td>109.3</td>
<td>-44.71</td>
<td>0</td>
<td>0</td>
<td>1.289</td>
</tr>
</tbody>
</table>

Nuclear Magnetic Resonance

orbitals) method (reviewed in Volume 12 of this Series) has been applied to the calculation of nuclear shielding (and magnetic susceptibilities) in hydrocarbons and other organic molecules.\(^{23}\) In this method, the gauge origin for the position vector \(\mathbf{r}\) of an electron in a field-dependent molecular orbital is chosen at the centre of gravity \(\mathbf{R}_k\) of the localized orbital to which it is related by the factor \(e^{i\mathbf{k} \cdot \mathbf{r}}\). That is, \(\lambda_k = (e/2\hbar)(\mathbf{R}_k \times \mathbf{B}) \cdot \mathbf{r}\). The local paramagnetic contributions calculated with these individual gauge origins are small since the localized molecular orbitals are nearly spherical, thus the errors in them have only a small effect on the final \(\sigma\), which is obtained as the sum of a local diamagnetic term, \(\sigma^d\) and a local paramagnetic term, \(\sigma^P\). The results of IGLO calculations of \(^1\)H and \(^{13}\)C shieldings in about a hundred compounds are reported.\(^{23}\) Only chemical shifts relative to CH\(_4\) in the gas phase, rather than absolute shielding values, are shown. In most cases, the agreement with experiment appears to be better than that provided by other calculations. A particularly promising result of this paper is the apparent transferability of orbital contributions. Since the nuclear shielding is obtained by the IGLO method directly as sums over contributions of the localized orbitals, it is possible to assign specific contributions from various parts of the molecule and develop an \textit{ab initio} incremental system for shielding. For \(^1\)H, the most important contribution is from the bonding orbital to the carbon to which the proton is attached. One order of magnitude smaller are the contributions of those bonds that directly involve this carbon; all other contributions are smaller by two orders of magnitude, except in cyclic systems. Of course, empirical incremental systems have been in use for some time, but this paper shows that increments with a definite physical meaning can be defined. The IGLO method can be very useful in gaining insight into the shielding tensor by looking at the individual contributions from localized orbitals in selected molecules, more so than in reproducing large numbers of experimental data. For example, it would be instructive to see the \textit{ab initio} increments which make up the components of the shielding tensors in the H\(_3\)C–CH\(_3\), H\(_2\)C=CH\(_2\), and HC≡CH series and the CH\(_n\)F\(_{4-n}\) and C\(_2\)H\(_n\)F\(_{4-n}\) series.

Application of Ditchfield’s GIAO method to the shielding (and magnetic susceptibilities) of the six-electron systems BH, BeH\(^-\), and CH\(^+\)\(^{24}\) using double zeta split-valence contracted Gaussian basis sets \([3s2p]\) for B, Be, and C, and \([2s]\) for H, over-estimates values for \(\chi(\text{BH})\) compared to previous reports using extended basis sets. This may indicate that the calculated \(\sigma\) values for BH and the other molecules in the series are not reliable. One may well wonder about the rationale behind applying a well-tested method to a six-electron system with a relatively limited basis set.

Ditchfield’s GIAO method has also been used in the calculations of shielding tensors for acetylene, ethylene, formaldehyde, formamide, imidazole and


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cytosine.\textsuperscript{25} The results for the three simplest molecules are not as good as those calculated by using IGLO.\textsuperscript{23} The shielding anisotropies are particularly disappointing in comparison with experiment, for example, 208 p.p.m. (calc.) vs. 245 p.p.m. (expt.) for \textsuperscript{13}C in HC≡CH.

Nakatsuji’s SOS–CI\textsuperscript{26} approach to the calculation of second order properties is reviewed in Volume 11 of this Series. This method has been shown to be equivalent to the CHF and FPT methods and exactly reproduces the FPT results for a series of test molecules (HF, H\textsubscript{2}O, NH\textsubscript{3}, CH\textsubscript{4}).\textsuperscript{27,28} Further applications, to calculations of \(\sigma\) (as well as \(\chi\) and \(J\)) for first and second row hydrides using the centre of mass as the gauge origin, show that the SOS–CI method can mimic the CHF results with the same basis set quality, using less computational time.\textsuperscript{29} SOS–CI therefore appears to be a convenient alternative to the FPT and CHF methods.

Several other theoretical investigations of \(\chi\) and \(\sigma\) for unsaturated hydrocarbons, with specific attention to delocalized or ring currents or other special effects due to the \(\pi\)-electrons, have been reported, some with definite conclusions about the physical reality of ‘ring currents’.\textsuperscript{25,30–35} Pesquer \textit{et al.}\textsuperscript{30,31} apply the extended London theory\textsuperscript{36} to calculate the magnetic susceptibility tensors of several (twenty-four) unsaturated hydrocarbons ranging from acetylene to anthracene, including five-, six-, and seven-membered rings.\textsuperscript{31} The extended London theory consists of solving the secular equations of the extended Hückel theory in the presence of a magnetic field. The agreement with experimental values, where available, is quantitatively good for the average \(\chi\) and somewhat less so for \(\Delta\chi\), although all the signs and overall trends are also reproduced for the latter. The structure of the extended London theory allows the principal \(\chi_{\alpha\alpha}\) to be split up into sums of six terms, one of which represents the contribution due to the \(1s^2\) core electrons of the carbon atoms.\textsuperscript{30} Examination of the constitutive terms reveals that, although the \(\pi\)-electron contributions are different for aromatic and non-aromatic compounds (benzene \textit{vs.} fulvene, for example), the other terms are of the same order of magnitude as the London contribution and cannot be neglected. In fact, the London contribution to \(\Delta\chi\) represents only half the total anisotropy of the aromatic compounds.\textsuperscript{30}

In Volume 12 of this Series we reviewed the major findings of a large-scale (198 contracted Gaussian orbitals) investigation of the magnetic properties of the benzene molecule\textsuperscript{37} \textit{vis-à-vis} the ‘unnecessary and unphysical ring current

\begin{thebibliography}{99}
\end{thebibliography}
hypothesis' applied to the estimation of $\chi$, and the $\sigma^{(13)}C$, and $\sigma^{(1)}H$ tensors. The succeeding paper, by the same authors, plots the modulus and direction of the quantum-mechanical current density vector in the benzene molecule in an attempt to visualize the actual electron currents induced by a uniform external magnetic field.\(^{33,34}\) The findings lend some support to the idea of $\pi$ interatomic currents as an important cause of deshielding for protons. However, whereas the ring current model assumes a mobile $\pi$ cloud flowing with equal intensity in every point of a loop, the intensity of the $\pi$ current density is significantly reinforced in the environment of the carbon nuclei. In addition, the intensity of the $\sigma$-electron current densities localized about C–C bonds is almost equal to that of the $\pi$ stream. Sigma-electrons also give rise to delocalized currents that are diamagnetic in the outer regions and paramagnetic about the centre of the molecule. The authors conclude that the existence of the paramagnetic interatomic current loop within the molecular hexagon forming an axial vortex rotating around the centre of the ring is characteristic of planar aromatic molecules and is predetermined by topological considerations.\(^{34}\) Their results on the cyclopropenyl cation (the simplest aromatic ring) and cyclopropane give similar conclusions: the central paramagnetic axial vortex is expected as a consequence of the nodal topology of the wavefunction, which is entirely determined by symmetry considerations.\(^{32}\) These results should put to rest any further speculations on the reality of the ring current.

In the light of these results, Gomes\(^{35}\) redefines the ring current as a delocalized current that is made up of the sum over all natural orbitals (with the respective occupations) of only those lines of current which encircle the axis of the molecule. The remainder of the orbital probability current densities he assigns to 'local' currents. The defined delocalized current then behaves as the ring current of unsophisticated models. In this context, part of the delocalized current may be due to $\sigma$-electrons, and part of the 'local' currents are due to $\pi$-electrons. This sounds a bit contrived and is an artificial separation of a part of the current intensity, invoked solely for the purpose of preserving the idea of a 'physical reality' of the ring current.

C. Semi-empirical Calculations. – Finite perturbation calculations using field-dependent atomic orbitals (GIAO) at the INDO, CNDO/S, and Extended Huckel molecular orbital levels of approximation are reported for nuclear shielding in elements of the first row of the periodic table.\(^{38-42}\) The INDO calculations of $^{13}C$ shielding in a series of sixteen $sp^2$- and $sp$-carbons give an average deviation of 5 p.p.m. from experimental values. Only the isotropic shielding is reported. Three-centre terms are included, which for protons range from 1 part in 50 to 1 part in 5. Calculations of shielding for $^1H$ and the nuclei from B to F, with optimization of parameters so as to fit experimental chemical shifts, show that two- and three-centre items are essential for


\(^{42}\) L. Ducasse, J. Hoarau, and M. Pesquer, THEOCHEM, 1982, 5, 61.
quantitative treatment of substituent effects. In a series of ureas, CNDO/S parametrization gives a linear relationship between the calculated $^{15}$N chemical shifts and the calculated C-N bond orders, except in sterically crowded molecules. Results of extended Hückel calculations of $^{13}$C shielding in which only one-centre and some two-centre terms are included in the paramagnetic contribution can account for some general trends in $^{13}$C chemical shifts. The $X_{\alpha}$ scattered wave MO method has been applied to $^{13}$C shielding; the results correlate well with experiment if the atomic sphere radii are properly chosen. The primary advantage of this method for shielding calculations is that the scattered wave solutions are excellent near the nuclei.

Approximate calculations using the Pople–Karplus formalism with a mean excitation energy have been applied to $^{13}$C shielding in transition-metal carbonyls and in four substituted benzenes.

D. Calculations in Paramagnetic Systems. - A non-relativistic calculation of the energies of the $H_2^+$ molecular ion in a magnetic field of arbitrary strength as a function of the internuclear separation and the angle between the molecular axis and the field $B$ reveals the effects of strong fields on the rotation, vibration, and equilibrium bond length of the molecule. The interaction with the magnetic field is explicitly included in the Hamiltonian by replacing $p$ by $p - eA$ for the two protons and $p + eA$ for the electron, and the Schrödinger equation is solved variationally. The solution to the electronic problem is cast in terms of a dimensionless parameter $\gamma$, which measures the strength of the magnetic field [$\gamma = \mu_B B/R$, where $R$ is the Rydberg $(e^2/2a_0)$]. For the hydrogen atom ground state the energy is $-1.0R$. Magnetic fields of intermediate or high strength correspond to $\gamma \approx 1$ ($\gamma = 1$ when $B = 2.35 \times 10^5$ T in a vacuum). Note that for nuclear charge $Z$, $\gamma = 1$ when $B \approx 10^5$ T/$Z^2$. The potential $V$ in which the rovibrational motion takes place depends upon the field strength and orientation, since the electronic wavefunction is altered by the field. $V(\theta)$ is found to have its minimum at $\theta = 0$, the molecule in its ground rotational state tends to align with the field. In the presence of a field of arbitrary strength at an arbitrary angle to the molecular axis, in the Born–Oppenheimer approximation, the $H_2^+$ molecule does not rotate freely in its lowest-lying rotational states but rather oscillates like a pendulum pivoted at the molecular centre of mass. Simultaneously, the molecule vibrates along the molecular axis. In magnetic fields of intermediate or high strength the electronic wavefunction is compressed, producing increased charge between the protons and drawing them together. Thus, with an increase in $B$ the vibrational frequencies increase substantially. At large fields the energy of the pendular motion is considerably greater than that of the vibration in the ground rotation–vibration state. The diamagnetic susceptibility is calculated as a function of the field strength and internuclear separation; unfortunately, the proton shielding itself is not calculated. However, with the results of this paper it is possible to add the magnetic vector potential of the nuclear moments as a small correction, and to carry out the

calculation of the proton-shielding as a function of field strength and internuclear separation, averaging the shielding over the rotational and vibrational motion, which this paper also gives as a function of the field strength.

Calculations of chemical shifts for 4d² systems, and also for an f-electron in a crystal field of octahedral symmetry, have been reported. The hyperfine integrals are given in analytical form and the pseudo-contact shift for a 4d¹ system in a strong crystal field of octahedral symmetry is calculated exactly and in a multipole expansion. The R⁻⁷ term contributes dominantly to the shift. The general treatment for an f-electron in an octahedral crystal field is also compared with a multiple expansion and various other approximations.

3 Physical Aspects of Nuclear Shielding

A. Anisotropy of the Shielding Tensor. ¹⁹F shielding tensors for the CF₃X (X = Cl, Br, I) molecules have been experimentally determined in the enclathrated molecules in D₂O hydrates in order to minimize intermolecular broadening. The ¹⁹F shielding tensors for these molecules are not axially symmetric about the C–F bond, although the σ₃₃ principal axis lies very close to the C–F bond direction. This component decreases as X is changed from F to Cl to I. The most shielded (σ₂₂) direction lies in the XCF plane perpendicular to the C–F bond, and σ₂₂ is relatively insensitive to X. The least shielded (σ₁₁) direction is perpendicular to the XCF plane and like σ₃₃, σ₁₁ decreases as X is changed from F to Cl to I. The results are shown in Table 2. Anisotropies of ¹⁹F shieldings in fluoranil and hexafluorobenzene have been measured in the partially oriented molecules in liquid crystalline solutions. For both molecules the direction of largest shielding is perpendicular to the molecular plane. For fluoranil (2,3,5,6-tetrafluoro-p-quinone) σ₂₂ = 1/2(σₓₓ + σᵧᵧ) = 185 p.p.m. and (σₓₓ − σᵧᵧ) = −41 p.p.m. For hexafluorobenzene σ₂₂ = 1/2(σₓₓ + σᵧᵧ) = 158 ± 2 p.p.m. in various smectic and nematic liquid crystalline solutions. For both molecules, liquid crystal and solid state data are in agreement.

The principal values of the ¹³C shielding tensors for the tropilium cation, benzene, and the cyclopentadienide anion (all six-π-electron ring systems) are

<table>
<thead>
<tr>
<th></th>
<th>σ₁₁</th>
<th>σ₂₂</th>
<th>σ₃₃</th>
<th>̅σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₄</td>
<td>213</td>
<td>213</td>
<td>351</td>
<td>259</td>
</tr>
<tr>
<td>CF₃Cl</td>
<td>142</td>
<td>262</td>
<td>262</td>
<td>222</td>
</tr>
<tr>
<td>CF₃Br</td>
<td>128</td>
<td>258</td>
<td>242</td>
<td>210</td>
</tr>
<tr>
<td>CF₃I</td>
<td>104</td>
<td>260</td>
<td>217</td>
<td>194</td>
</tr>
</tbody>
</table>

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Table 3 Components of the $^{13}$C shielding tensors in six-π-electron ring systems, in p.p.m. relative to TMS$^{52}$

<table>
<thead>
<tr>
<th>System</th>
<th>$\sigma_{11}$</th>
<th>$\sigma_{22}$</th>
<th>$\sigma_{33}$</th>
<th>$\sigma$</th>
<th>(liq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_7$</td>
<td>280</td>
<td>168</td>
<td>22</td>
<td>167</td>
<td>156.3</td>
</tr>
<tr>
<td>C$_6$H$_8$</td>
<td>234</td>
<td>146</td>
<td>9</td>
<td>130</td>
<td>128.7</td>
</tr>
<tr>
<td>C$_2$H$_5$</td>
<td>182</td>
<td>114</td>
<td>21</td>
<td>106</td>
<td>103.0</td>
</tr>
</tbody>
</table>

obtained using cryogenic techniques.$^{52}$ The values obtained are shown in Table 3. The $\sigma_{11}$ value is identified with the C–H bond axis, $\sigma_{22}$ with an axis in the molecular plane perpendicular to the C–H bond, and $\sigma_{33}$ with the axis perpendicular to the molecular plane. The value of $\sigma_{33}$ is characteristic of saturated carbon atoms, which is not unexpected since it is determined primarily by the properties of electrons in the σ-bonds. Both $\sigma_{11}$ and $\sigma_{22}$ lie in the molecular plane and both have a linear dependence on the calculated π-electron charge. This work supports the importance of using the tensor components as opposed to the isotropic average in attempting to understand the relationships between the electronic structure of molecules and nuclear shielding.

A similar conclusion on the usefulness of three-dimensional chemical shift data is reached in the interpretation of $^{13}$C shielding tensors of metal carboxyls.$^{53}$ From the results shown in Table 4, the tensors of terminally bound CO groups can be seen to be highly anisotropic (380 ± 60 p.p.m.) and nearly axially symmetric, varying only slightly with the transition-metal. On the other hand, the $^{13}$C shielding tensors of CO groups that bridge two or more metal atoms are much less anisotropic. These tensors are distinct from those in organic carboxyls, indicating that the bonding in metal-bridging CO groups is different from that in organic compounds, which is not apparent from a comparison of isotropic $^{13}$C chemical shifts.

Inequivalence of molecular sites in a crystal lead to inequivalence of shielding tensors. Two recent examples are the $^{13}$C (carboxyl) shielding tensors in calcium formate and in ammonium tartrate. In the case of calcium formate there are two types of ion in each unit cell, for which the $^{13}$C shielding anisotropies are $(\sigma_{33} - \sigma_{11}) = 123.0 \pm 2$ and 133.0 ± 2 p.p.m. and $(\sigma_{22} - \sigma) = -9.0 \pm 0.5$ and $-8.1 \pm 0.5$ p.p.m., respectively.$^{54}$ In ammonium tartrate the shielding tensors of the two carboxyls in each tartrate ion are different (partly due to hydrogen-bonding to NH$_4^+$ ions): the components are $\sigma_{11} = -111.6$ and $-109.4$ p.p.m., $\sigma_{22} = -64.9$ and $-58.5$ p.p.m., and $\sigma_{33} = 22.5$ and 20.7 p.p.m. (relative to external benzene).$^{55}$

The shielding anisotropies of $^{23}$Na$^+$ ions in single crystals of NaNO$_3$, NaClO$_3$, and NaBrO$_3$ are $0 \pm 2, 12 \pm 1$, and $17 \pm 1$ p.p.m. respectively,$^{56}$ before

---

Table 4 $^{13}$C shielding tensors for metal carbonyls, in p.p.m. relative to TMS$^{53}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\sigma_{11}$</th>
<th>$\sigma_{22}$</th>
<th>$\sigma_{33}$</th>
<th>$\tilde{\sigma}$</th>
<th>$\Delta \sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)$_6$</td>
<td>+ 70</td>
<td>- 353</td>
<td>- 353</td>
<td>- 212</td>
<td>423</td>
</tr>
<tr>
<td>Mo(CO)$_6$</td>
<td>+ 75</td>
<td>- 343</td>
<td>- 343</td>
<td>- 203</td>
<td>417</td>
</tr>
<tr>
<td>W(CO)$_6$</td>
<td>+ 71</td>
<td>- 324</td>
<td>- 324</td>
<td>- 192</td>
<td>395</td>
</tr>
<tr>
<td>Ru$^2$(CO)$_{12}$</td>
<td>+ 63</td>
<td>- 319</td>
<td>- 348</td>
<td>- 201</td>
<td>397</td>
</tr>
<tr>
<td>Os$^4$(CO)$_{12}$</td>
<td>+ 55</td>
<td>- 292</td>
<td>- 292</td>
<td>- 176</td>
<td>347</td>
</tr>
<tr>
<td>Ir$<em>7$(CO)$</em>{12}$</td>
<td>+ 53</td>
<td>- 277</td>
<td>- 277</td>
<td>- 167</td>
<td>322</td>
</tr>
<tr>
<td>Rh$<em>6$(CO)$</em>{16}$</td>
<td>terminal</td>
<td>+ 80</td>
<td>- 305</td>
<td>- 315</td>
<td>- 181</td>
</tr>
<tr>
<td></td>
<td>bridging</td>
<td>- 102</td>
<td>- 296</td>
<td>- 296</td>
<td>- 231</td>
</tr>
<tr>
<td></td>
<td>(η$^2$-C$_5$H$_4$)$_2$Fe$_2$(CO)$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>terminal</td>
<td>+ 85</td>
<td>- 354</td>
<td>- 354</td>
<td>- 211</td>
</tr>
<tr>
<td></td>
<td>bridging</td>
<td>- 179</td>
<td>- 309</td>
<td>- 328</td>
<td>- 272</td>
</tr>
<tr>
<td>Fe$<em>6$(CO)$</em>{12}$</td>
<td>+ 6</td>
<td>- 316</td>
<td>- 325</td>
<td>- 212</td>
<td>327</td>
</tr>
<tr>
<td>CO$^a$</td>
<td>+ 90</td>
<td>- 316</td>
<td>- 316</td>
<td>- 181</td>
<td>406</td>
</tr>
<tr>
<td>Ni(CO)$_4$</td>
<td>+ 69</td>
<td>- 326</td>
<td>- 326</td>
<td>- 194</td>
<td>395</td>
</tr>
<tr>
<td>Fe(CO)$_5$</td>
<td>+ 70</td>
<td>- 355</td>
<td>- 355</td>
<td>- 213</td>
<td>425</td>
</tr>
<tr>
<td>Rh$_2$(CO)$_3$Cl$_2$</td>
<td>+ 99</td>
<td>- 299</td>
<td>- 306</td>
<td>- 186</td>
<td>402</td>
</tr>
</tbody>
</table>


the shielding of Na$^+$ had been assumed to be isotropic. The degree of trigonal deformation of the octahedral symmetry of the sodium ion site in these crystals determines the anisotropy.

The shielding tensor of $^{35}$Cl in a $p$-dichlorobenzene single crystal has been determined from Zeeman-split n.q.r. spectra, with the magnetic field applied along the principal axis-direction of the electric field gradient tensor:$^{57} \sigma_{xx} = 0 \pm 200$ p.p.m., $\sigma_{yy} = -2900 \pm 500$ p.p.m., and $\sigma_{zz} = -800 \pm 200$ p.p.m. (There are actually two inequivalent sites.) The $x$-axis is perpendicular to the molecular plane, the $y$-axis lies in the molecular plane perpendicular to the C–Cl bond, and the $z$-axis is the axis along the C–Cl bond. As for the F shielding tensor in fluorobenzenes, the direction of largest shielding is found to be perpendicular to the molecular plane.

$^{113}$Cd shielding tensors are found to be axially symmetric in Cd–TPP (TPP = tetraphenylporphyrin); $\Delta \sigma = \sigma_\parallel - \sigma_\perp = -341 \pm 3$ p.p.m., and in its pyridine adduct, $\Delta \sigma = -105 \pm 2$ p.p.m.$^{58}$ The value of $\sigma_\parallel$ (unique axis) is increased by $124 \pm 5$ p.p.m. whereas that of $\sigma_\perp$ (the in-plane component) is decreased by $112 \pm 5$ p.p.m. when pyridine adds as a fifth ligand to Cd–TPP. These dramatic changes are not reflected by the decrease in isotropic shielding, which is a mere 33 p.p.m.

$^{205}$Tl shielding tensors in ionic environments and in thallium salts have been reported.$^{59}$ In mixed salts of TlNO$_3$ with LiNO$_3$, NaNO$_3$, or AgNO$_3$, the Tl spectra are identical to those of pure TlNO$_3$; with KNO$_3$ a non-

axially symmetric Tl shielding tensor is observed. In these ionic environments the anisotropy of Tl shielding is 50–90 p.p.m.; this is quite large for a Tl⁺ ion which, if isolated, would be isotropic. Tl shieldings in fatty acid salts are axially symmetric and have anisotropies of ±780±80 p.p.m.; here σ₁ is along the symmetry axis of the head group of the fatty acid (TIOOC₁₂₇).^60^

**B. The Effects of Rotation and Vibration.** The accurate spin–rotation constants from molecular beam results of Ramsey for the H₂, HD, and D₂ molecules in low rotational states^61^ have been used along with the temperature-dependent deuterium n.m.r. isotope shifts in the gas phase^62^ to yield the nuclear magnetic shielding function for an isolated H₂ molecule. From the spin–rotation data, Raynes and Panteli obtain σ_e^0(1), and from the isotope shift data they evaluate σ_e(1) in the shielding function:

\[
\sigma/p.p.m. = \sigma_e^0 + \sigma_e^{(1)}\xi + \sigma_e^{(2)}\xi^2 + \ldots
\]

\[
= 26.689(±0.003) - 8.974(±0.047)\xi + \ldots \tag{15}
\]

where \(\xi\) is the dimensionless parameter that is a measure of bond extension, \(\xi = (R - R_e)/R_e\). They calculate values of \(\sigma\) for various rotational levels of the \(v = 0\) states of the six isotopomers of H₂. The zero-point vibrational motion produces chemical shifts (relative to the equilibrium configuration shielding) of 0.17 p.p.m. for T₂ and 0.30 p.p.m. for H₂. The centrifugal distortion reduces the shielding further with rotational excitation. A thermal average is also calculated with this shielding function and yields the best value for the shielding of hydrogen gas at zero density and 34°C:

\[
\sigma_0(H₂, 34°C) = 26.363(±0.004) \text{ p.p.m.} \tag{16}
\]

At any density \(\rho\), the intermolecular shielding terms \(\sigma_1(34°C)\rho + \sigma_2(34°C)\rho^2 + \ldots\) further decrease the shielding.

**C. Isotope Effects.** Fowler continues his general approach to rotational and vibrational averaging of molecular electronic properties, with specific applications to nuclear shielding. He has adapted the contact transformation method, an operator form of perturbation theory developed in the 1930s, to the double perturbation level, leading to equations (his eq. 38–43) which had been dervied earlier by Secroun et al. and have been in use by vibrational spectroscopists for some time. He then derives the
average value of the isotope shift of an electronic property, such as shielding, in terms of the vibration-rotation parameters of a single isotopomer of an asymmetric top. When applied to the shielding differences between the various isotopomers of H$_2$O, he calculates the following isotopic shifts (where 1 p.p.b. refers to 1 part in $10^9$):

$$\Delta^1H(^{17/16}O) = \sigma_H(H_2^{16}O) - \sigma_H(H_2^{17}O) = -1 \text{ p.p.b.}$$

(17)

$$\Delta^2H(^{2/1}H) = \sigma_H(H_2^{16}O) - \sigma_H(HD^{16}O) = -50 \text{ p.p.b.}$$

(18)

$$\Delta^0H(^{2/1}H) = \sigma_H(H_2^{16}O) - \sigma_D(HD^{16}O) = -70 \text{ p.p.b.}$$

(19)

$$\Delta^{17}O(^{2/1}H) = \sigma_O(H_2^{17}O) - \sigma_O(D_2^{17}O) = -3.1 \text{ p.p.m.}$$

(20)

These may be compared with the observed isotope shifts in H$_2$O, which are $\Delta^{17}O(^{2/1}H) = -3.08 \pm 0.20$ p.p.m. ($-1.54$ p.p.m. per D) at 299 K, in excellent agreement with Fowler's calculations, and $\Delta^1H(^{2/1}H)$ less than $-20$ p.p.b. smaller than the calculated $-50$ p.p.b.

In the above, we have adopted the notation for secondary isotope shifts suggested by Gompler, in which the masses are in the order $M > m$:

$$n\Delta X(M/mY) = [\nu_X \text{ (in molecule with } M/Y) - \nu_X \text{ (in molecule with } m/Y)]/\nu_0$$

$$= \delta_X(M/Y) - \delta_X(m/Y) = \sigma_X \text{ (with } M/Y) - \sigma_X \text{ (with } M/Y)$$

(21)

with $n$ being the number of bonds separating the observed nucleus from the isotopic substitution site. Because of the additivity of isotope shifts upon substitution in equivalent sites, the number quoted is usually p.p.m. per atom substituted. The definition can be extended, in theory, to primary isotope shifts by using the same notation with $n = 0$. In practice, of course, the primary isotope shifts cannot be measured in this way. This notation is consistent in sign with the IUPAC sign convention for chemical shifts, being derived from differences in frequencies (rather than shielding parameters). The usual sign of the n.m.r. isotope shift defined in this way is negative, that is, substitution with a heavier atom leads to a lower resonance frequency.

In Volume 10 of this Series we noted the dependence of the isotope shift on bond order, hybridization, and electronegativity of substituents. It has previously been observed that the magnitude of isotope shifts increases roughly in line with the range of chemical shifts of the resonant nucleus. In this review period, measurement of isotope shifts in analogous Se and Te compounds give further insight into this aspect. It is well known that $^{77}$Se and $^{125}$Te chemical shifts for corresponding compounds give a straight line plot with a slope of 1.8. Gompler reports that the one-bond $^{13}$C-induced

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$^{125}$Te and $^{77}$Se isotope shifts in (CF$_3$)$_2$X$_2$, (CF$_3$)$_2$X, and Me$_2$X are, respectively, $-0.320$ vs. $-0.175$, $-0.330$ vs. $-0.191$, and $-0.341$ vs. $-0.228$ p.p.m. for $\Delta^{125}$Te($^{13/12}$C) vs. $\Delta^{77}$Se($^{13/12}$C). The ratios $\Delta^{125}$Te/$\Delta^{77}$Se in these compounds are 1.8, 1.7, and 1.5, which are close to the $\delta^{(125}$Te)/$\delta^{(77}$Se) slope of 1.8.

Another interesting general trend in isotope shifts is typified by the value of $\Delta^{15}$N($^{18/16}$O) in NO$_3$ (planar symmetrical) compared to that of NO$_2$ (bent); these are, respectively, $-0.056$ p.p.m. and $-0.138$ p.p.m. per O substitution.$^{71,72}$ Both the electronic and dynamic parts of the isotope shift in the highly symmetrical environment contribute to smaller shifts. The more symmetrical electronic distribution means smaller changes in the paramagnetic term with bond extension, compared with the less symmetrical environment. In addition, there are more totally symmetric vibrational modes in the less symmetrical molecules, involving both bond extension and angle deformation, e.g., in pyramidal NH$_3$ compared to tetrahedral NH$_4^+$, or in bent NO$_2$ compared to planar symmetric NO$_3$.

With the availability of higher resolution in high field spectrometers, isotope shifts due to substitution in parts of the molecule remote from the resonant nucleus are being observed. For example, values of $n\Delta^{13}$C($^{2/1}$H) have been reported for $n = 1$–12.$^{73}$ The magnitude drops off very rapidly with an increase in $n$ for $n > 2$; nevertheless, some isotope shifts in the p.p.b. range have been reported. For $n = 3$, a stereochemical dependence is observed in $^{13}$C$^{74}$ as well as in $^{119}$Sn isotope shifts.$^{75}$ The value of $\Delta^{13}$C($^{2/1}$H) varies with the dihedral angle, $\phi$, between the bonds connecting the resonant nucleus with the heavy atom substitution site: $\Delta^{13}$C($^{2/1}$H) = $-0.080$ for $\phi = 0$, $-0.050$ for $\phi = 30$, $< [0.020]$ for $\phi = 90$, and $-0.021$ to $-0.043$ for $\phi = 60$ in glucosides.$^{76}$ The analogous $\Delta^{119}$Sn($^{2/1}$H) results indicate that a sign change occurs at $\phi \approx 120$, the usual sign for $\phi \approx 180$, and positive (unusual) sign for $\phi \approx 0$.$^{77}$ There is also a report of what appears to be an isotopic shift due to steric effects [$^{4}\Delta^{13}$C($^{2/1}$H) = +0.02 and +0.01 p.p.m. per D (sign is unusual)] in bicyclodecanone.$^{77}$ This is explained$^{78}$ in the context of the model for calculating the $\gamma$ effects on $^{13}$C chemical shifts from the steric compression between CH groups. Since a CD$_2$ group is effectively smaller (smaller amplitudes of vibration) than a CH$_2$ group, this compression is smaller in the deuteriated molecule, leading to a high frequency shift due to less steric compression.$^{77}$ Other $\Delta^{13}$C($^{2/1}$H) data have been reported: $-0.275$ to $-0.279$ p.p.m. per D for sp$^2$-carbon$^{73}$ and $-0.275$ to $-0.4344$ p.p.m. per D for sp$^3$-carbon.$^{79}$ The isotope shifts $\Delta^{13}$C($^{2/1}$H) in the following

$^{73}$ S. Berger and H. Kuenzer, Angew. Chem. 1983, 95, 321.
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molecules, which show the effect of electronegative substituents, have been determined more accurately: $-0.04900(5)$ p.p.m. per D in CD$_3$I, $-0.14780(5)$ in CD$_3$CN, $-0.2026(5)$ in CDCl$_3$, $-0.2281(16)$ in CD$_3$NO$_2$, $-0.2502(1)$ in (CD$_3)_2$CO, $-0.2831(1)$ in CD$_3$OD, and $-0.3029(4)$ in (CD$_3)_2$SO. All the values agree with the ones previously reported within the latter's estimated errors. $^2\Delta^{13}C(2/1 H)$ values are generally smaller than the one-bond isotope shifts. Values of the order of $-0.0811$ to $-0.1094$ for $sp^3$-$sp^3$-D-carbons, 78, 79 and $-0.0296$ to $-0.0341$ for $sp^2$-CD$_3$-carbons 79 are reported.

$^1\Delta^{13}C(18/16O)$ shifts in a series of substituted acetophenones have been found to correlate with bond order, giving a linear plot for isotope shifts of $-0.0440$ to $-0.04856$ p.p.m. Values typical of alcohols, epoxides, and ethers ($-0.019$ to $-0.042$) have been reported. 83-86 Some exceptional values of $^1\Delta^{13}C(13/12C)$ have been observed in small-ring compounds: $-0.003$ to $-0.048$ and $+0.005$ to $+0.011$. 87 The nature of the vibrational averaging of framework atoms (including ring puckering) in ring compounds does not preclude either sign for isotope shifts in cases where the resonant nucleus and substitution site are both on the ring. The other unusual aspect of these small ring shifts is that the values of $^2\Delta$ are of the same order of magnitude as those of $^1\Delta$. Again this comes as no surprise when the dynamics of the problem are considered.

$^1\Delta^{13}C(15/14N)$ values equal to $-0.025$ to $-0.030$ p.p.m. in oximato complexes are comparable to those for C=N in cyano complexes, although the CN bond order in the former is closer to 2. $^1\Delta^{15}N(13/12C)$ results in cyano complexes are $-0.067$ to $-0.101$, 89 from the $^{13}$C and the $^{15}$N shifts in these complexes, empirical derivatives $(\partial\sigma_N/\partial\Delta r)_e = -872 \pm 160$ p.p.m./Å and $(\partial\sigma_C/\partial\Delta r)_e = -473 \pm 90$ p.p.m./Å have been deduced. These are not significantly different from the corresponding empirical derivatives found in $^{15}$N$_2$ and $^{13}$CO by analysis of the temperature-dependence of the $^{15}$N and $^{13}$C shifts in the zero-pressure limit.

One-bond isotope shifts for the heavier nuclei are correspondingly larger, which is in parallel with their larger chemical shift ranges. For example, $^1\Delta^{99}$Tc(18/17/16O) = $-0.22$ p.p.m. per mass number in TcO$_4$, $^1\Delta^{119}$Sn(2/1H) = $-1.62$ p.p.m. in Bu$_3$SnH, 75 and $^1\Delta^{199}$Hg(13/12C) and $^1\Delta^{199}$Hg(29/28Si) are $+0.34$ to $+0.39$ and $+0.06$ to $+0.07$, respectively.

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(note that the signs are unusual). On the other hand, $^1$H isotope shifts are very small, the values of $n\Delta^1H(^{13/12}C)$ being $-2.44$, $-1.34$, $-0.51$, and $-0.33$ p.p.b. for $n = 1$-$4$ bonds separating the resonant proton from the substitution sites. Isotope effects transmitted through intramolecular hydrogen-bonds, $^2\Delta^1H(2H)$ in O–D ... O–H vs. O–H ... O–H, are about 0.01 p.p.m. and of either sign. Deuterium substitution of hydrogen-bonds can either weaken or strengthen the bond; this may help to explain the observation of both signs.

**D. Intermolecular Effects.** – Theoretical calculations of intermolecular effects on shielding that have been reported include model calculations for adsorbed species, the (HCN)$_2$ dimer, and hydrated formaldehyde and imidazole. The experimentally observed large shifts (30–100 p.p.m.) of the $^{13}$C n.m.r. signals of CO molecules upon adsorption in decationated zeolites, and much smaller shifts (less than 5 p.p.m.) in zeolites containing alkali ions, have prompted the calculation of $^{13}$C shieldings in the system Li$^+$ ... CO, Na$^+$ ... CO, and Al$^{3+}$ ... CO. The results are in qualitative agreement with experiment. *Ab initio* CHF calculations, with large bases of contracted Gaussian orbitals (for example, 10s6p2d on C, O, Na), yield the following interesting results: The Al ... C ... O arrangement gives a 117–122 p.p.m. shift to higher shielding in $\sigma^C$, and 89–99 p.p.m. to lower shielding in $\sigma^O$, whereas the Al ... O ... C gives a shift of 95–100 p.p.m. to lower shielding in $\sigma^C$ and 280–284 p.p.m. to higher shielding in $\sigma^O$, compared to the isolated CO molecule. The values of $\sigma^C$ and $\sigma^O$ vary only slightly in the investigated cases, which is understandable since the parallel shielding components have no paramagnetic contribution. The T-shaped arrangement (Al approaching perpendicular to the CO molecular axis) gives no energetically stable configuration. If the experimentally observed shift, upon adsorption, to lower $^{13}$C shielding is compared with these calculations, one would conclude that the most probable adsorption arrangement is linear Al ... O ... C. The Al$^{3+}$ shielding tensors have also been calculated. In the Li$^+$/CO and Na$^+$/CO complexes, the calculations indicate that if the ion approaches CO on the O side, a small shift of the electronic charge from the C to the O atom occurs, which is in agreement with the high frequency shift of the $^{13}$C and the low frequency shift of the $^{17}$O n.m.r. signals in adsorbed CO relative to isolated CO. However, the same correlation between electronic charge and chemical shift holds if the ion approaches CO on the C side.

The calculations (by Ditchfield’s GIAO method) on the $^1$H, $^{13}$C, and $^{15}$N shielding tensors of the HCN dimer, yield results that are in agreement with the isotropic shielding changes observed experimentally in HCN vapour and

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The effect of hydration on the principal values and directions of all the shielding tensors of formaldehyde and imidazole have been calculated (using Ditchfield's GIAO method) with a split-valence shell basis of Gaussian functions. The results indicate that the principal values and the anisotropy of the shielding tensors, but not their directions, are sensitive to hydration, the components in the molecular plane undergoing the largest changes. The anisotropies of all $^1$H shieldings suffer larger changes than the isotropic shielding (in agreement in magnitude and sign with experimental data for the hydrogen atoms participating in the hydrogen-bond).

Gas-phase studies of the density dependence of $^1$H shielding in CH$_4$, C$_2$H$_6$, C$_2$H$_4$, CH$_3$F, CH$_2$F$_2$, CHF$_3$, and H$_2$S$^{99}$ yield values of the second virial coefficient of shielding, $\sigma_1$, as in $\sigma(T, \rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \ldots$. The temperature variation of $\sigma_1$ for $^1$H has been observed and in all cases, as expected, it becomes less negative as the temperature increases. The bulk susceptibility contribution is removed from $\sigma_{1\text{obs}}$, yielding $\sigma_1$ values due to (self) intermolecular interactions, which are uniformly negative. These are, in units of p.p.m. cm$^3$ mol$^{-1}$, $-7.6(\pm 2.2)$ for CH$_4$, $-8.7(\pm 3.3)$ for C$_2$H$_6$, $-20.3(\pm 1.8)$ for C$_2$H$_4$, $-15.9(\pm 3.5)$ for CH$_3$F, $-35.3$ for CH$_2$F$_2$, $-24.3$ for CHF$_3$, and $-60.6$ for H$_2$S. It has been noted that since the true $^1$H $\sigma_1$ values are very small when measured in a cylindrical cell in a spectrometer with a superconducting magnet, the bulk susceptibility term being twice as large and opposite in sign to that measured in an electromagnet, positive values of $\sigma_1$ are actually observed.

Perturbation calculations of the effects of binary dispersive interactions on the shielding lead to the following equation:$^{100}$

$$\delta = \sigma_{\text{pair}} - \sigma_0 = \frac{I_A}{I_A + I_B} \frac{t}{a^3} \frac{\bar{\varepsilon} - 1}{2\bar{\varepsilon} + 1}$$

(22)

to which is added the terms

$$2K'_2 \frac{d}{T^{1/2}} \exp \left(-\frac{\Delta U_2}{RT}\right) (\delta)_2 + 3K'_3 \frac{d^2}{T^{3/2}} \exp \left(-\frac{\Delta U_3}{RT}\right) (\delta)_3$$

which apply when a specific bimolecular complex of molar energy of formation $\Delta U_2$ (with a corresponding $\Delta U_3$ for a termolecular complex) is formed. In the above, the first term takes the usual form of reaction field theory, with ionization energies $I_A$ and $I_B$ for the interacting molecules, and a frequency-dependent dielectric constant $\bar{\varepsilon} = \varepsilon(\bar{\nu})$; $t$ is related to the polarizability; $a$ is a density-independent cavity radius, $d$ is the density; $(\delta)_2$ and $(\delta)_3$ are the chemical shifts of the bimolecular and termolecular complexes relative to the isolated molecule. $K'_2$ and $K'_3$ are collections of molecular constants in the statistical mechanical expressions for the equilibrium constants for bimolecular and termolecular complex formation.


except that the explicit dependence on density, temperature, and \( \exp(-\Delta U/RT) \) have been separated out. The authors apply this theory to the temperature- and density-dependent shielding of \(^{129}\)Xe in Xe gas\(^{101}\) and obtain \((\delta)_{2} = 2237\) p.p.m. as the \(^{129}\)Xe chemical shift between Xe$_2$ and Xe. This appears to be too large, the observed \(^{129}\)Xe gas-to-liquid shift \(\sigma\) (vapour) \(-\sigma\) (liq.) being only \(+200\) p.p.m. at 244 K.\(^{102}\) Another question that arises in this theory is the apparent redundancy between the first term and the second term. The reaction field model has been commonly used as an alternative to the binary interaction model. The first and second terms reported appear to correspond to these two models, respectively. The theory is also applied to the \(^{31}\)P(P$_4$O$_6$) gas-to-solution shifts, which are found to be linearly dependent on the density of the solution; the authors include only the first term in this case, and the cavity radius \(a\) is assumed to be related to the effective co-ordination number. With this, the authors find co-ordination numbers of 12.5 P$_4$O$_6$ molecules, 16 CCl$_4$, and 31.5 CS$_2$ around a P$_4$O$_6$ solute molecule.

The temperature-dependence of the shielding in the reference liquids TMS (\(^1\)H and \(^{13}\)C)\(^{103}\) and Me$_2$Se(\(^{77}\)Se)\(^{104}\) have been reported so that variable temperature chemical shift measurements relative to these references (used externally to the sample but at the same temperature) can be corrected for the temperature variation of the liquid reference itself. The same correction cannot be applied when TMS is used internally, in part because some of the temperature variation is due to the bulk susceptibility variation of neat TMS with temperature; this has prompted a measurement of the bulk susceptibility of neat liquid TMS as a function of temperature.\(^{103}\) However, even when this additional correction is made, the temperature variation of the chemical shift relative to internal TMS still includes in it the undesirable term \[\sigma_p(T) = \sigma_p(T) - \sigma_p(T)\rho_p(T)\] where the \(\sigma_p\rho\) terms are the intermolecular contributions to the TMS temperature-dependence in A and in neat liquid TMS, respectively. This difference varies with temperature, and thus, for temperature-dependent work, the use of an external reference is recommended.

The measurement of kinetic parameters of molecules undergoing internal rotation, ring inversion, or complex formation is adversely affected by solvent effects, which are necessarily present in condensed phases. Gas phase n.m.r. investigations of internal rotation in NN-dimethyltrifluoroacetamide yield activation energies, \(\Delta G^\ddagger\), \(\Delta H^\ddagger\), \(\Delta S^\ddagger\) which are of smaller magnitude than the values obtained in solution.\(^{105}\) On the other hand, the gas-phase studies of the ring inversion of cyclohexane yield activation parameters that are of larger magnitude than those in solution.\(^{106}\) The interpretation of this difference is given in terms of an activation volume that is positive in the first example and negative in the second. The latter is consistent with an increase


in interconversion rate with increasing pressure (1–5000 bar) in several solvents.\textsuperscript{107} For systems with significant volume differences between conformers, or between conformers and transition states, the internal solvent-pressure-effects can significantly change the activation parameters.