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Theoretical and Physical Aspects of Nuclear Shielding

BY CYNTHIA J. JAMESON

1 Introduction

This chapter reviews the papers published during the period June 1st 1981 to May 31st 1982. The first part deals with general theory and calculations of the components of nuclear magnetic shielding. The second part reviews experimental data on the anisotropy of the shielding tensor, effects of rotation and vibration, isotope effects, intermolecular effects, and the theoretical calculations in support of these physical aspects. Several new developments in the theory of nuclear shielding are discussed in Section 2A (gauge invariant techniques, relativistic calculations, and inclusion of correlation effects on σ by perturbed configuration interaction methods). All examples given are *ab initio* calculations which are also discussed in this section. Other *ab initio* calculations using standard methods are reviewed in Section 2B. The theoretical treatment of the variation of nuclear magnetic shielding with internal co-ordinates (bond lengths and bond angles) is discussed in Section 3B since this is intimately connected with the rotational and vibrational averaging which gives rise to the temperature dependence of nuclear magnetic shielding in the isolated molecule and the mass dependence of this rovibrational average (isotope shifts).

2 Theoretical Aspects of Nuclear Shielding

A. General Theory.—It has been shown that it is possible to obtain very accurate values of the nuclear magnetic shielding provided that the computation is carried out using a very large AO basis set. Some examples of these were reviewed in Chapter 1 of Volume 11 of this series. In principle, σ is gauge invariant, that is, its value is independent of the choice of origin if Ramsey's theory is carried out with a complete basis set, and if the energies used in the perturbation expansion are obtained by diagonalizing exactly the exact electronic Hamiltonian with zero external fields (*i.e.*, if the wavefunctions used are exact Hartree–Fock functions).[1] In practice, of course, a truncated basis set is used and the energies are obtained in some approximate way. The approximations to σ, obtained with finite LCAO bases, converge very slowly when these bases are enlarged. Therefore, calculations carried out in the standard manner (by the coupled Hartree–Fock method) lead to different results for different choices of gauge origin and these differences (gauge dependence) are especially pronounced when the basis set used is small. It has been

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[1] R. M. Stevens, R. M. Pitzer, and W. N. Lipscomb, *J. Chem. Phys.*, 1963, **38**, 550.

found that with a judicious choice of gauge origin, for example the centre of electronic charge, the results are in better agreement with experiment. Tests for gauge dependence have been devised to determine *a priori* the 'goodness' of a shielding calculation, that is, the adequacy of the basis set used, without resorting to comparison with experiment. For example, the sum rules $(P_\alpha, P_\beta) = \delta_{\alpha\beta}N$, where N is the number of electrons, or $(L_\alpha/r^3, P_\beta) = -(L_\beta/r^3, P_\alpha)$, *etc.*[2, 3] can be applied.

A different approach proposed by Ditchfield[4] avoided the choice of gauge origin altogether by using field-dependent atomic orbitals (GIAO). It now becomes clear that this approach is only one of several possible approaches to a gauge independent calculation. These are gauge-independent in the sense that (a) the gauge origins are predetermined, and (b) not a single origin is chosen but several origins. Three different approaches have been used:

(1) different gauge origins for different atomic orbitals – GIAO, by Ditchfield;[4]

(2) different gauge origins for different localized molecular orbitals – IGLO, by Schindler and Kutzelnigg;[5]

(3) different gauge origins for different pairs of orbitals (AOs or MOs), by Levy and Ridard.[6]

The first is well known by its many applications to various small molecules. The last two have been reported during this review period.

The physical basis for the improvement in these methods over the standard CHF method has not been demonstrated. The improvements probably result because an appropriate gauge origin choice reduces both the diamagnetic and paramagnetic contributions to shielding, thereby minimizing the paramagnetic part which is more difficult to calculate accurately. Thus, by choosing in each instance (for each AO or for each localized MO) an appropriate origin, the total error can be reduced. In these approximations to Ramsey's theory the nuclear magnetic shielding is calculated using a single configuration (Slater determinant) for the unperturbed wavefunction.

In the method of Schindler and Kutzelnigg,[5, 7, 8] individual gauge for localized orbitals (IGLO), calculations are carried out with a new molecular orbital ψ_k that is related to ϕ_k (molecular orbitals which are expanded in powers of field strength, $\phi_k = \phi_{k0} + i\phi_{k1} + \phi_{k2} + \ldots$) by the following relationship: $\phi_k = e^{i\Lambda_k}\psi_k$ where Λ_k is some local multiplicative operator proportional to the field strength.

For comparison we show here the general form of the expression for the nuclear magnetic shielding in Schindler and Kutzelnigg's method and the standard CHF method.[9] In the standard CHF method the shielding of a nucleus with magnetic moment μ at the position ρ is:

$$\sigma_{\alpha\beta} = \frac{\delta^2}{\delta\mu_\alpha\,\delta B_\beta}\,2\left\{\sum_k^n\left[<\phi_{k0}|h_2|\phi_{k0}> - 2<\phi_{k0}|h_1|\phi_{k1}>\right]\right\} \qquad (1)$$

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[2] G. P. Arrighini, M. Maestro, and R. Moccia, *J. Chem. Phys.*, 1968, **49,** 882.

[3] G. P. Arrighini, M. Maestro, and R. Moccia, *J. Chem. Phys.*, 1970, **52,** 6411.

[4] R. Ditchfield, *J. Chem. Phys.*, 1972, **56,** 5688; *Chem. Phys. Lett.*, 1972, **15,** 203.

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

[6] B. Levy, and J. Ridard, *Mol. Phys.*, 1981, **44,** 1099.

[7] W. Kutzelnigg, *Isr. J. Chem.*, 1980, **19,** 193.

[8] M. Schindler, Thesis, 1980, Universität Bochum, West Germany.

[9] W. N. Lipscomb, in 'Advances in Magnetic Resonance,' Academic Press, New York, 1966, Vol. 2, p. 137.

where

$$h_2 = \frac{\mu_0}{4\pi}\frac{\mathrm{e}^2}{2m}\left\{\mathbf{B}\times(\mathbf{r}-\mathbf{R})\right\}\left\{\frac{\boldsymbol{\mu}\times(\mathbf{r}-\mathbf{P})}{|\mathrm{r}-\mathrm{p}|^3}\right\} \tag{2}$$

$$h_1 = \frac{\mu_0}{4\pi}\frac{\mathrm{e}}{mi}\frac{\mathbf{u}\times(\mathbf{r}-\mathbf{p})\cdot\mathbf{P}}{|\mathrm{r}-\mathrm{p}|^3} \tag{3}$$

ϕ_{k0} are the occupied molecular orbitals of the ground electronic state of the $2n$ electron system and are eigenfunctions of the Fock operator with eigenvalues ε_k. ϕ_{k1} are the molecular orbitals $\phi_{k1} = \sum_p C_{pk}{}^{(1)}\phi_{p0}$ with $C_{pk}{}^{(1)}$ being the coefficients obtained by solving the simultaneous equations (the coupled Hartree–Fock equations):

$$(\varepsilon_p-\varepsilon_i)C_{pi}{}^{(1)}+(h_B)_{pi}+\sum_{j=1}^{\mathrm{occ}}\sum_{q=n+1}^{\mathrm{unocc}}[(qi|pj)-(ji|pq)]C_{qj}{}^{(1)} = 0 \tag{4}$$

where

$$h_B = \frac{\mathrm{e}}{2mi}\{\mathbf{B}\times(\mathbf{r}-\mathbf{R})\}\cdot\mathbf{P} \tag{5}$$

and $(qi|pj)$ are the two electron repulsion integrals. Note that the common gauge origin is at **R**. Schindler and Kutzelnigg's analogous expression for the shielding is:[5]

$$\sigma_{\alpha\beta} = \frac{\delta^2}{\delta\mu_\alpha\delta B_\beta}2\left\{\sum_k^n[<\psi_{k0}|\tilde{h}_{2k}|\psi_{k0}> -2<\psi_{k0}|h_1|\psi_{k1}>]\right\} \tag{6}$$

where

$$\tilde{h}_{2k} = \frac{\mu_0}{4\pi}\frac{\mathrm{e}^2}{2m}\left\{\mathbf{B}\times(\mathbf{r}-\mathbf{R}_k)\right\}\left\{\frac{\boldsymbol{\mu}\times(\mathbf{r}-\mathbf{P})}{|\mathrm{r}-\mathrm{p}|^3}\right\} \tag{7}$$

$$h_1 = \frac{\mu_0}{4\pi}\frac{\mathrm{e}}{mi}\left[\frac{\mathbf{u}\times(\mathbf{r}-\mathbf{p})\cdot\mathbf{P}}{|\mathrm{r}-\mathrm{p}|^3}\right] \tag{8}$$

$\psi_{k0} = \phi_{k0}$ are the occupied molecular orbitals but are not necessarily eigenfunctions of the Fock operator, $\psi_{k1} = \mathrm{e}^{-i\Lambda_k}\phi_{k1}$ are the solutions to a set of simultaneous equations which may be considered as analogues of equation (4) with operators transformed by $e^{i\Lambda_k}$ and matrix elements constructed in ψ_k. Note that the gauge origin is at $\mathbf{R}_k$, a different origin for each molecular orbital ϕ_k. The advantage of switching from the ϕ_k to the ψ_k orbitals becomes obvious when Λ_k is chosen so that one has the optimum gauge origin for ψ_k. With the choice

$$\Lambda_k(\mathbf{r}) = \frac{\mathrm{e}}{2\hbar}(\mathbf{R}_k\times\mathbf{B})\cdot\mathbf{r} \tag{9}$$

in which **r** is the usual electron position vector in the molecular co-ordinate system, and $\mathbf{R}_k$ is taken as the position vector of the centroid of charge of the molecular orbital $\psi_{k0} = \phi_{k0}$, one has a much better gauge origin for this orbital than a common origin for all orbitals. Consequently, one gets 'local' diamagnetic and paramagnetic contributions, of which the latter are rather small. In the standard CHF calculation, with a common gauge origin for all the orbitals, large diamagnetic and paramagnetic contributions are obtained which cancel each other to a large extent. The advantage of having 'local' terms with small errors in Schindler and Kutzelnigg's theory comes at the expense of having to calculate many additional terms. Expressions for these 'exchange corrections' and 'resonance corrections' are given and further approximations are made in their calculations.

The results of Schindler and Kutzelnigg are very encouraging; some of them are given in Tables 1 and 2 for comparison with other theoretical calculations reported during this review period. In addition, these authors carried out calculations for the following systems: BH, BH_3, B_2H_6, CH_4, H_2CO, NH_3, and F_2 all at the equilibrium geometry; $(H_2)_2$ in the D_{2h} configuration, as a function of distance between H_2 bond centers, CH_3^+ in the C_{3v} configuration as a function of angle and bond length.[5]

In the third method, different gauge origins are used for different pairs of orbitals (AOs or MOs) by Levy and Ridard.[6] The second order energy is written in terms of pair contributions. In the diamagnetic term there are only two orbital indices involved so that the pairs are chosen uniquely. In the paramagnetic term there are four orbital indices and an arbitrary choice of pairs is made [equation (10)]. The

$$E^{(2)}=\boldsymbol{\mu}\cdot\boldsymbol{\sigma}\cdot\mathbf{B}=\sum_{ij}E_{ij}=\sum_{ij}(E_{ij}^{(\mathrm{d})}+E_{ij}^{(\mathrm{p})}) \qquad (10)$$

different pair contributions are not physical observables so that the theory is not gauge invariant. If each pair contribution is calculated with a specific gauge origin, G_{ij}, using a truncated basis set, then the value of the pair contribution obtained using the specific gauge origin G_{ij}, $E_{ij}(G_{ij})$, is related to the value E_{ij} obtained using a common gauge origin, by $E_{ij}=E_{ij}(G_{ij})+\rho_{ij}$, with a non-vanishing correction ρ_{ij} for each pair. Levy and Ridard then give a recipe for computing the sum of the pair corrections. In practice, they compute the second order energy in some basis in a standard (CHF) way and then subtract the value of the correction $\sum_{ij}\rho_{ij}$ obtained by use of the orbital pair model in this basis. It is hoped that doing this subtraction will correct to a large extent the effect of the truncated basis and thus will give a result nearly equivalent to that obtained by using a very large basis set. The numerical test was carried out on PH_3. From previous calculations (reported in Volume 10 of this Series) the ^{31}P and ^{1}H shielding values from 78- and 83-function basis sets provide a standard large basis calculation. The present calculation uses 37 basis functions. The individual gauge origins G_{ij} are chosen at the midpoint between the centres of the main components ϕ_i and ϕ_j. The results show that the agreement between the calculated values using 37 functions with pair correction and those using 78 and 83 functions is good. Three different calculations with the 37 basis functions using a common origin in each calculation are carried out. Results obtained for ^{1}H are 88.0, 25.0, and 3.1 p.p.m. with the origin at H, at P and at 1.8 a_0 above P along the symmetry axis respectively, using standard CHF theory. With the orbital pair theory the values obtained are 31.6, 22.4, and 19.1 respectively. The experimental value is 28.3 p.p.m. We note that this model does not make an adequate correction; the corrected values still show some gauge dependence.

In all the methods discussed above, one is solving directly either by iterative techniques or by matrix solution of simultaneous equations, for that part of an electronic energy eigenfunction $\Psi^{(1)}$ (in terms of MOs ϕ_{k1}) which is first order in the uniform magnetic field B. A different approach is suggested by Parker:[10] find a way of transforming the equation for $\Psi^{(1)}$ into an equation for a new unknown function f which, unlike $\Psi^{(1)}$, is independent of the choice of gauge. The transformation[11] depends on the physical assumption that when B is applied parallel to one of the principal axes of the dipole magnetizability tensor ($\boldsymbol{\chi}$), the induced current density tends to be perpendicular to the magnetic field. This method is applied to a calculation of χ in the context of the independent electron approximation.[12] The equation to be solved in the function f is in terms of the normalized zero-field probability density obtained from a non-degenerate real zero-field eigenfunction Ψ_0, a 3-dimensional density $P_0\ (x,y,z)$:

$$\nabla_t\cdot\{P_0{}^{-1}\nabla_t(f_\alpha P_0)\}=2 \tag{11}$$

where ∇_t is the transverse gradient, that part of ∇ which is perpendicular to $\mathbf{B}$, the magnetic field along principal axis α. For calculations of nuclear shielding, this equation is transformed further to an equivalent form which is not too sensitive to errors in f_α near the shielded nucleus at $r=0$. The 3-dimensional density $P_0\,(x,y,z)$ is replaced by a series of 2-dimensional densities $R(x_s, y, z)$ characteristic of slices through a molecule perpendicular to the axis α at positions $x_s=x_1, x_2, \ldots$, so that $R(x_s, y, z)\mathrm{d}y\mathrm{d}z$ is the conditional probability of finding the electron in $\mathrm{d}y\mathrm{d}z$ given that it is in the slice at x_s. The results for H_2, using a 2-term function and a 5-term function, give shielding values which are in very good agreement with those of a 48-function calculation[13] (see Table 1). The advantage of this method appears to be that the shielding calculation carried out with a P_0 value taken from a very high quality SCF (or better) wavefunction, is no more complicated than one with a P_0 value from a small basis set. Byproducts of the calculation (from solving the equation for f_α in slices) are contour maps of the modulus and the direction of current densities in the molecule for a magnetic field along a principal axis.

The CHF technique has been generalized to treat atoms and ions of high nuclear charge where the relativistic effects as well as correlations are expected to be important.[14] The method is the relativistic random phase approximation (RRPA) which in the non-relativistic limit reduces to the random phase approximation with exchange. The latter theory describes the linear response of an atom to a dynamic external field, and reduces to the CHF theory in a static uniform field. The magnetic shielding for closed shell atoms Xe, Pd, Kr, Ar, Ne, He as well as their closed shell ions with the same number of electrons: 46, 36, 18, 10, 2 [for example Xe(0), Xe(+8), Xe(+18), Xe(+44) and Xe(+52)] have been reported together with the entire Ne ioselectronic sequence, from Ne(0) ($\sigma=558.6\times10^{-6}$) to U(+82) ($\sigma=1.744\times10^{-2}$). The non-relativistic approximation to σ is also shown for these systems. For Ne(0) and U(+82) they are 553.4×10^{-6} and $0{\cdot}8225\times10^{-2}$, respectively. We note that the relativistic calculations become necessary for highly charged ions of moderate atomic number Z as well as atoms of high Z.

A method of calculation of second-order magnetic properties at the configu-

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[10] G. W. Parker, *Mol. Phys.*, 1982, **46**, 183.
[11] G. W. Parker, *Phys. Rev. Lett.*, 1978, **40**, 1556.
[12] G. W. Parker and J. D. Memory, *Phys. Rev. A*, 1980, **23**, 2099.
[13] A. J. Sadlej and W. T. Raynes, *Mol. Phys.*, 1978, **35**, 101.
[14] D. Kolb, W. R. Johnson, and P. Shorer, *Phys. Rev. A*, 1982, **26**, 19.

ration interaction (CI) level of accuracy has been presented.[15] A general CI perturbation theory is developed based on the CHF scheme that second-order properties may most easily be calculated by defining them to be first order changes in expectation values.[16] A zeroth order CI wavefunction has to be calculated [equation (12)], where $\Phi_I^{(0)}$ are the configurations in the CI, each being a linear

$$\Psi_{CI}^{(0)} = \sum_{I=1}^{M} C_I^{(0)}\Phi_I^{(0)} \tag{12}$$

combination of determinants of molecular orbitals. Then the first-order changes in the CI wavefunction have to be calculated [equation (13)], in which $\Phi_I^{(1)}$ are the

$$\Psi_{CI}^{(1)} = \sum_{I=1}^{M} (C_I^{(0)}\Phi_I^{(1)} + C_I^{(1)}\Phi_I^{(0)}) \tag{13}$$

first-order changes in the configurations due to the first-order changes in the molecular orbitals $\phi_i^{(1)} = \sum_K c_{ik}^{(1)}\phi_k^{(0)}$. The paramagnetic contribution to the shielding is then given by:

$$\begin{aligned}\sigma_{\alpha\beta}^{\mathrm{p}} &= 2\sum_{IJ} C_I^{(0)}\, C_J^{(1)\beta} < \Phi_I^{(0)}|h_{1\alpha}|\Phi_J^{(0)} > \\ &\quad + \sum_{IJ} C_I^{(0)}\, C_J^{(0)}\, [< \Phi_I|h_{1\alpha}|\Phi_J >]_\beta^{(1)}\end{aligned} \tag{14}$$

The first term uses the first-order CI vector due to the perturbation h_B along the β principal axis in conjunction with the molecular orbital integrals for h_1 along the α axis. The second term uses the zeroth-order CI vector in conjunction with the first-order changes in the matrix elements of the $h_{1\alpha}$ due to the perturbation of $h_{B\beta}$. In the second term the first-order changes in the matrix elements are calculated using the first-order changes in the molecular orbitals c_{ik}. The diamagnetic term can of course be calculated using the zeroth-order CI wavefunction. This method was applied to LiH. The results for LiH[15] are not too exciting because the correlation contributions in this molecule are small. They are shown in Table 1 together with the other calculations.

B. *Ab Initio* Calculations.—The results of applying the newly developed theoretical treatments discussed in the previous section to the classic test cases H_2, LiH, and HF, are shown in Table 1. We note that the agreement with experiment is excellent when rovibrational averaging is included.[17]

Recent results of *ab initio* calculations for H_2O[5, 23, 24] justify a summary of the calculated shielding tensor components in this molecule in Table 2. As Buckingham and Malm[34] point out, the nuclear magnetic shielding tensor is an asymmetric second-rank tensor, and that for ^1H in H_2O has 5 independent components. The two other non-zero components for ^1H shielding have been calculated by Fowler[23] ($\sigma_{xz} = +17.738$ and $\sigma_{zx} = +5.809$ p.p.m.), by Holler and Lischka[21] ($\sigma_{xz} = +8.97$, $\sigma_{zx} = +10.12$ p.p.m.), by Lazzeretti and Zanasi[29] ($\sigma_{xz} = -10.247$ and $\sigma_{zx} = -8.872$ p.p.m.), and by Thomsen and Swanstrom[26] ($\sigma_{xz} = -5.8$ and $\sigma_{zx} = -7.8$ p.p.m.). [As

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[15] G. T. Daborn and N. C. Handy, *Chem. Phys. Lett.*, 1981, 201.
[16] G. T. Daborn, W. I. Ferguson, and N. C. Handy, *Chem. Phys.*, 1980, **50**, 255.
[17] R. Ditchfield, *Chem. Phys.*, 1981, **63**, 185.

Table 1 *Results of recent calculations of shielding tensors in small molecules*

	$\sigma_{\parallel}$	$\sigma_{\perp}$	$\Delta\sigma$	σ_e	$\sigma_0(300)$	*Ref.*
^{1}H in H_2	27.7056	26.0223	1.6833	26.5834	26.202	Ditchfield[17]
	27.826	25.580	2.246	26.329		Sadlej and Raynes[13]
	27.82	25.77	2.05	26.45		Parker[10]
	27.70	26.59	1.11	26.96		Parker[10]
	28.182	25.948	2.234	26.693		Cook, *et al.*[18]
					26.26 ± 0.15	Experiment[19, 20]
^{1}H in LiH	28.3655	25.3210	3.0445	26.3358	26.213	Ditchfield[17]
	28.12	25.79	2.33	26.59		Schindler *et al.*[5]
					26.73	Daborn and Handy[15]
	28.19	25.82	2.37	26.61		Holler and Lischka[21]
					$25.84 \pm 0{\cdot}5$	Experiment[a]
^{7}Li in LiH	101.607	88.9281	12.6789	93.1544	93.233	Ditchfield[17]
	101.41	83.81	17.60	89.67		Schindler *et al.*[5]
				89.53		Daborn and Handy[15]
	101.4	83.6	17.8	89.5		Holler and Lischka[21]
					89.18 ± 1.2	Experiment[a]
^{1}H in HF	44.2187	21.2063	23.0124	28.8771	28.486	Ditchfield[17]
	44.08	20.03	24.05	28.05		Schindler *et al.*[5]
	44.06	19.74	24.32	27.85		Holler and Lischka[21]
				29.2 ± 0.5		deduced from expt.[22]
					28.8 ± 0.5	Experiment[22]
					28.51 ± 0.20	Recom. by Raynes[19]
^{19}F in HF	482.118	395.981	86.137	424.697	413.463	Ditchfield[17]
	481.7	379.4	102.3	413.5		Schindler *et al.*[5]
	481.6	381.7	99.9	415.0		Holler and Lischka[21]
				419.7 ± 0.3		deduced from expt.[22]
					410.0 ± 6	Experiment[22]

[a] These values are obtained by using the CI-level σ^d from Daborn and Handy[15] and the values $\sigma_H{}^p = -13.8 \pm 0.5$ p.p.m., $\sigma_{Li}{}^p = -18.7 \pm 1.2$ p.p.m. calculated for ^{7}LiH ($v = 0$) by Stevens and Lipscomb,[1] based on the values of spin-rotation constants from molecular beam results of L. Wharton, L. Gold, and W. Klemperer, *J. Chem. Phys.*, 1962, **37,** 2149: $C_H = -8 \pm 1$ and $C_{Li} = +10 \pm 1$ MHz. More recent values of $C_H = -9.05 \pm 0.05$ and $C_{Li} = +10.025 \pm 0.075$ MHz reported by E. Rothstein, *J. Chem. Phys.*, 1969, **50,** 1899, will change these somewhat.

shown in equation (1), the convention is as follows: the first index refers to the nuclear magnetic moment, the second index to the external magnetic field. The z axis is the symmetry axis, the x axis is perpendicular to it and in the plane of the molecule.] The large discrepancy between these sets of calculations has not been

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[18] D. B. Cook, A. M. Davies, and W. T. Raynes, *Mol. Phys.*, 1971, **21,** 113.

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

[20] W. D. Phillips, W. E. Cooke, and D. Kleppner, *Phys. Rev. Lett.*, 1975, **35,** 1619.

[21] R. Holler and H. Lischka, *Mol. Phys.*, 1980, **41,** 1017.

[22] D. K. Hindermann and C. D. Cornwell, *J. Chem. Phys.*, 1968, **48,** 4148.

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[24] P. W. Fowler and W. T. Raynes, *Mol. Phys.*, 1981, **43,** 65.

[25] J. Verhoeven and A. Dymanus, *J. Chem. Phys.*, 1970, **52,** 3222.

[26] K. Thomsen and P. Swanstrom, *Mol. Phys.*, 1973, **26,** 751.

[27] U. T. Lamanna, G. Guidoti, and G. P. Arrighini, *J. Chem. Phys.*, 1977, **67,** 604.

[28] P. Swanstrom, W. P. Kraemer, and G. H. F. Diercksen, *Theor. Chim. Acta*, 1977, **44,** 109.

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

Table 2 *Components of the shielding tensors in* H_2O (z *axis is the symmetry axis,* x *axis perpendicular to it in the plane of the molecule*)

	Gauge	σ_{xx}	σ_{yy}	σ_{zz}	σ_e	σ_0(400 K)	*Ref.*
^1H	O	38.108	21.935	29.424	29.823	29.240	Fowler[23, 24]
	ec	39.1	23.3	29.5	30.6		Thomsen *et al.*[26]
	H	40.29	25.55	33.25	33.03		Lamanna *et al.*[27]
	O				30.21		Lamanna *et al.*[27]
	ec	38.6	22.5	29.5	30.2		Swanstrom *et al.*[28]
	cm	38.349	22.265	29.421	30.011		Lazzeretti *et al.*[29]
	O	36.52	20.60	27.57	28.23		Arrighini *et al.*[31]
	loc	38.74	22.83	30.09	30.56		Schindler *et al.*[5]
	opt	38.31	22.33	29.75	30.13		Holler and Lischka[21]
	H	−37.3	−108.3	−71.3	(σ^p only)		Verhoeven *et al.*[25]
						30.052 ± 0.015	based on exptl. σ^p given above[19]
^{17}O	O	362.762	304.529	309.839	325.710	311.830	Fowler[23, 24]
	loc	364.6	305.0	312.7	327.4		Schindler *et al.*[5]
	ec	354.2	282.7	293.7	310.2		Thomsen *et al.*[26,a]
	O	362.19	304.97	307.21	324.79		Lamanna *et al.*[27]
	ec	364.0	303.6	310.0	325.9		Swanstrom *et al.*[28]
	cm	364.672	303.995	310.930	326.533		Lazzeretti *et al.*[29]
	O	360.89	307.00	325.29	331.06		Arrighini *et al.*[30]
	loc	355.4	308.8	320.1	328.1		Ditchfield[33]
	opt	366.0	305.3	312.9	328.1		Holler and Lischka[21]
						334 ± 15	Experiment[32,b]

[a] Corrected values from P. Swanstrom, as cited by R. B. Mallion in Volume 4 of this series, pp. 22—23; [b] W. T. Raynes reviewed this result in Volume 8 of this series. With the gas-to-liquid shift correction he believes this value could be as high as 370 p.p.m. for a rovibrationally averaged H_2O monomer.

explained. Perhaps the off-diagonal components of the tensor are more sensitive to basis set truncation than are the diagonal components.

The magnetic properties of benzene and other aromatic systems are usually rationalized in terms of the ring-current model. The model is a very simple one: a uniform magnetic field perpendicular to the molecular plane induces an interatomic current in the mobile pi-electron system. Since the ring current makes a contribution to the diamagnetic susceptibility only in the direction perpendicular to the plane of the ring this provides a contribution to the anisotropy of χ which is peculiar to aromatic systems. The ring-current model has been used in interpretation of the chemical shifts of nuclei in the vicinity of the aromatic ring. The ring current produces an effective magnetic field which is in the same direction as the external field if the nucleus is in the plane and outside of the ring, as the protons in benzene, a deshielding effect resulting in a shift to higher frequency. On the other hand a nucleus in a solute molecule dissolved in an aromatic solvent is on the average either above or below the ring, and thereby experiences an effective field which is in a direction opposite to that of the external field, a shielding effect, resulting in shifts to lower frequency. This model is very successful and there is little

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[30] G. P. Arrighini, M. Maestro, and R. Moccia, *Chem. Phys. Lett.*, 1970, **7**, 351.

[31] G. P. Arrighini, M. Maestro, and R. Moccia, *J. Chem. Phys.*, 1970, **52**, 6411.

[32] B. R. Appleman, T. Tokuhiro, G. Fraenkel, and C. W. Kern, *J. Chem. Phys.*, 1974, **60**, 2574.

[33] R. Ditchfield, cited by B. R. Appleman and B. P. Dailey in 'Advances in Magnetic Resonance,' ed. J. S. Waugh, Academic Press, New York, 1974, Vol. 7, p. 231.

[34] A. D. Buckingham and S. M. Malm, *Mol. Phys.*, 1971, **22**, 1127.

question as to its utility. The controversy arises only with respect to its physical basis and the tendency of some authors to take a literal interpretation of the model.

The controversy was opened by Musher who refuted the existence of delocalized circulations.[35, 36] A large number of papers have been published in defence of the reality of the ring current. We noted in Volume 10 of this Series that Blustin[37—39] has succeeded in computing fairly accurate shifts using a localized pi-bond model and thus providing an alternate model which is just as useful but does not require delocalization to give rise to a shift of the same direction and magnitude as the ring-current model does.

The questions which have been raised are (a) is there indeed a current density vector line which follows the carbon skeleton in a plane above and below the ring of carbon nuclei?, (b) when the total diamagnetic susceptibility is partitioned into localized and delocalized contributions, is the anisotropy of χ accounted for nearly entirely by delocalized π contributions?, and (c) are the nuclear magnetic shielding components (not just the isotropic average) consistent with a ring current effect?

Lazzeretti and Zanasi answer these questions with two calculations;[40, 41] the simplest aromatic hydrocarbon cyclopropenyl cation $C_3H_3^+$ and benzene. The smaller molecule yields more reliable results from the point of view of size of basis set, whereas the latter is more typical of the systems to which the model has been applied. Contributions to magnetic properties arising from the π and σ electrons are reported separately. The results are as follows in $C_3H_3^+$:[40]

(1) Diamagnetic electron current densities in the molecular plane are essentially localized on carbon atoms and C–C bonds. Delocalized diamagnetic currents are found only in the tail regions of the molecular space, (which is a general feature of symmetric systems, such as atomic hydrogen) and are negligible with respect to the σ currents in the molecular plane.

(2) The large magnetic susceptibility anisotropy is almost entirely due to σ electrons; in fact the π contributions to $\Delta\chi$ almost cancel.

(3) π electrons give a larger fraction to the *in-plane* components of χ, which is hard to reconcile with the ring-current model.

(4) The nuclear magnetic shielding component σ_{zz} is comparable in magnitude with σ_{xx}. The ring current model predicts a large $(\sigma_{zz}-\sigma_{xx})$. The total induced magnetic field, $B_z^{\text{ind}} = -\sigma_{zz}B_z^{\text{ext}}$, has the *opposite* direction to the external field at the proton, contrary to the ring-current model. The incremental π contribution to the induced magnetic field is very small and in the same direction as the external field.

(5) The π electrons do not provide a deshielding effect on the protons, as predicted by the ring-current model, actually they provide a shielding effect which is $+1.4$ p.p.m.

Thus, the results for $C_3H_3^+$ demonstrate the non-physical character of the model and its theoretical inconsistency. The calculations on benzene are somewhat less reliable because of the larger number of electrons involved, the 198-basis orbital

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[35] J. I. Musher, *J. Chem. Phys.*, 1965, **43,** 4081.

[36] J. I. Musher, in 'Advances in Magnetic Resonance', Academic Press, New York, 1966, Vol. 2, p. 177.

[37] P. H. Blustin, *Mol. Phys.*, 1980, **39,** 565.

[38] P. H. Blustin, *Mol. Phys.*, 1978, **36,** 1441.

[39] P. H. Blustin, *Chem. Phys. Lett.*, 1979, **64,** 507.

[40] P. Lazzeretti and R. Zanasi, *Chem. Phys. Lett.*, 1981, **80,** 533.

[41] P. Lazzeretti and R. Zanasi, *J. Chem. Phys.*, 1981, **75,** 5019.

calculation on benzene is not comparable to the 105 basis calculation on $C_3H_3^+$. Nevertheless, the results are illuminating:[41]

(1) The π electron contribution to the in plane diamagnetic susceptibility is roughly 11%, and 44% for the out-of-plane component. Unfortunately, because of the discrepancy between the experimental paramagnetic term and the calculated one, it cannot be ascertained whether the π electrons are predominant contributors to the anisotropy of χ.

(2) The calculated proton shielding tensor components are $\sigma_{xx} = 27.21$ (along the CH bond), $\sigma_{yy} = 18.20$, and $\sigma_{zz} = 15.99$ p.p.m. (perpendicular to the plane). The π electron contributions to this are -1.30, 12.13, and -3.31 p.p.m. respectively, which are not consistent with the ring-current model which would predict a negative π contribution to the zz component but not to the xx component. In summary, the results for benzene show that there is a sizeable π electron contribution to the out of plane magnetic susceptibility. Other than this, the results are not sufficiently accurate to draw the same conclusions as in $C_3H_3^+$ with equal confidence.

Other *ab initio* calculations are reported on the diamagnetic shielding of nuclei in cyclobutanone (C_4H_6O), trimethylene oxide (C_3H_6O), trimethylene sulphide (C_3H_6S),[42] and the larger molecules, cyclopentadiene (C_5H_6), pyrrole (C_4H_5N), furan (C_4H_4O), thiophene (C_4H_4S), and dihydrothiophene (C_4H_6S)[43] using an extended basis set, including *d*-type polarization functions, that provides a reasonable description of the molecular charge distribution and at the same time allows calculations on large systems. A GIAO calculation of the H, C, N, and O nuclear shielding in cytosine[44] and in formamide, hydrated formamide, and *N*-methylformamide[45] have been carried out using a split valence shell basis set. Qualitative trends (chemical shifts) within the molecule are correctly reproduced.

Calculations of high accuracy for the magnetic susceptibility of LiH[15], CO, HF, HCl, and CH_3F[46] and relativistic atoms and ions[14, 47] have been reported. These are relevant because calculations of nuclear shielding are subject to the same general difficulties as are calculations of χ. The LiH calculation is at the CI level.[15]

C. Semi-empirical Calculations.—The ring-current model has been applied to the calculation of proton chemical shifts in linear acenes.[48] If benzene is used as a convenient standard, the quantity $(B'_r/B'_{\text{benzene}})$, sometimes referred to as the sigma ratio of the rth proton, can be calculated. Here B'_r is the secondary magnetic field at the rth proton due to the ring currents in all rings of an n-cyclic molecule, and B'_{benzene} is the corresponding secondary field calculated by the same method, to be experienced by a standard benzene proton because of the ring current in benzene. This sigma ratio can be written as a sum over rings:

$$(B'_r/B'_{\text{benzene}}) = \sum_{\substack{\text{rings}\\ i=1}}^{n} (J_i/J_{\text{benzene}}) \times (K_i^r/K_{\text{benzene}}) \qquad (15)$$

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[42] G. de Brouckere and R. Broer, *Mol. Phys.*, 1981, **43,** 1139.

[43] G. de Brouckere, W. C. Nieuwpoort, R. Broer, and G. Berthier, *Mol. Phys.*, 1982, **45,** 649.

[44] C. Giessner-Prettre and B. Pullman, *J. Am. Chem. Soc.*, 1982, **104,** 70.

[45] F. Ribas-Prado, C. Giessner-Prettre, A. Pullman, J. F. Hinton, D. Harpool, and K. R. Metz, *Theor. Chim. Acta*, 1981, **59,** 55.

[46] R. D. Amos, *Chem. Phys. Lett.*, 1982, **87,** 23.

[47] J. P. Desclaux, L. Laaksonen, and P. Pyykko, *J. Phys. B*, 1981, **14,** 419.

[48] C. W. Haigh and R. B. Mallion, *J. Chem. Phys.*, 1982, **76,** 4063.

where J is the ring current intensity calculated on the basis of McWeeny's 'test-dipole' formalism.[49] (K_i^r/K_{benzene}) is a purely geometric factor that depends only on the physical position in space of the rth proton with respect to the ith ring, its magnitude is a measure of the effect that the ring current in ring i of the n-cyclic molecule has on the secondary magnetic field at the rth proton. These sigma ratios can then be converted directly into proton chemical shifts by application of an empirical relationship.[50] These calculations show that in the linear acenes, predictions of proton chemical shifts are in qualitative agreement with those of Blustin's localized π-bond model.[39] The ring-current model has been applied to the conjugated rings of the amino-acids of porphyrin,[51] of nucleic acid bases, and the conjugated parts of some intercalating agents.[52] The intensities of the ring currents, the radii of the conjugated rings, and the atomic contributions to local magnetic anisotropy have been calculated to provide the contributions to the nuclear shielding for any nucleus located at any point in space in the plane of the conjugated ring or above this plane. The goal is to provide a semi-empirical calculation of contributions to shielding from neighbouring groups in a large (ultimately macromolecular) system.

Other semi-empirical calculations of proton shielding have been reported.[53–55] Proton chemical shifts are correlated with the charges on the hydrogen atom which have been calculated by a method known as 'partial equalization of orbital electronegativity' which gives atomic charges that are different from those obtained by a Mulliken population analysis.[53] The correlation is a good one, with a correlation coefficient of 0.990 and a standard deviation of 0.15 p.p.m. for a single correlation line for a great variety of compounds. The conclusion drawn by the authors is that proton chemical shifts are largely determined by electronic effects. MINDO and INDO methods have been used to calculate the geometrical dependence of the proton shielding in some small molecules.[54] Proton shielding in alanine oligopeptides is calculated[55] approximately by a sum of terms: $\sigma = \sigma^E + \sigma^{\text{ani}}$, the electric field and magnetic anisotropy terms, respectively. The CNDO/2 method has been used to calculate the charges at various amide atoms and Buckingham's formula $\sigma^E = -2.0 \times 10^{-12}\, E_z - 10^{-18}\, E^2$ [56] was used, neglecting the E^2 term. The magnetic anisotropy contribution to the shielding is estimated from the anisotropy of the bond magnetic susceptibility, parameters which are fixed for the C=O, C–N bonds, *etc*. With these electric field and anisotropy terms the proton chemical shifts for all α-CH protons and all NH protons in a series of alanine oligomers with up to 6 alanine residues are calculated and compared with the experimental proton spectra. The agreement is good with the anti-parallel β pleated-sheet structure although there are some small discrepancies. The solvent effect is assumed to be the same for all protons. These promising results seem to indicate that such calculations may be useful in studying the solution conformation of oligopeptides and polypeptides.

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[49] R. McWeeny, *Mol. Phys.*, 1958, **1**, 311.
[50] C. W. Haigh, R. B. Mallion, and E. A. G. Armour, *Mol. Phys.*, 1970, **18**, 751.
[51] C. Giessner-Prettre and B. Pullman, *Biochem. Biophys. Res. Commun.*, 1981, **101**, 921.
[52] F. Ribas-Prado and C. Giessner-Prettre, *Theochem.*, 1981, **1**, 81.
[53] J. Gasteiger and M. Marsili, *Org. Magn. Reson.*, 1981, **15**, 353.
[54] M. B. Ferraro, M. V. Carrilho, J. C. Facelli, and R. H. Contreras, *Theochem.*, 1981, **3**, 63.
[55] T. Asakura, *Makromol. Chem.*, 1981, **182**, 1097.
[56] A. D. Buckingham, *Can. J. Chem.*, 1960, **38**, 300.

Discussions of the anisotropy of ^{13}C, ^{29}Si, and ^{31}P shielding were reported in a series of papers by Radeglia and co-workers[57—60] using CNDO/2 and the average excitation energy approximation for the following molecules: PH_3, POF_3, $POCl_3$, $POMe_3$, $Si_2O_7^{6-}$, ethylene and benzene. Similar interpretations of ^{15}N and ^{31}P shieldings in cyclotetraphosphazenes and that for ^{13}C in three tricarbonylcyclodienyl iron(1+) cations are given.[61, 62] The anisotropy of the ^{31}P shielding tensor in PH_3, POF_3, $POCl_3$, and $POMe_3$ is calculated[63] with a PCILO wavefunction and compared with experiment. All the calculated values are too small, from 1/3 to 2/3 of the experimental ones.

3 Physical Aspects of Nuclear Shielding

A. Anisotropy of the Shielding Tensor.—The individual components of the σ tensor are of interest because they represent a more stringent test of theoretical calculations than its trace and provide more information on the influence of structural and chemical factors on shielding. A review of ^{13}C shielding tensors in organic single crystals[64] describes how the components are determined from proton enhanced ^{13}C spectra for a single crystal rotated with respect to the external magnetic field. The cross polarization method[65] removes line broadening due to ^{13}C–^{1}H dipolar interaction and enhances the intrinsically low n.m.r. sensitivity of ^{13}C spins while leaving the ^{13}C shielding tensor unperturbed. Furthermore, line broadening due to ^{13}C–^{13}C dipolar interactions is negligible due to the large distances between the dilute ^{13}C spins. The review compares the shielding tensors of aromatic ring, carbonyl, carboxyl, and methyl carbons. A recent addition to the ^{13}C data from single crystal studies is that of dimethylmaleic anhydride and acrylamide.[66]

The principal components of the ^{31}P absolute shielding tensor have been systematically determined in a large number of compounds from powder samples.[67] The absolute shielding of ^{31}P in PH_3 is presumed to be known, and it is on this basis that the shifts relative to the reference are placed on an absolute scale. The compounds studied are of the form $O{=}PR_3$, $S{=}PR_3$, $Se{=}PR_3$, with equivalent R groups. The anisotropies are large and follow the order $\Delta\sigma(O{=}PR_3) > \Delta\sigma(S{=}PR_3) > \Delta\sigma(Se{=}PR_3)$; they are generally larger for R = aryl than for R = alkyl. While the isotropic shielding observed in the liquid phase for these compounds covers a range of 80 p.p.m., all the anisotropies exceed 80 p.p.m. The largest component is that along the X = P axis. ^{31}P shielding tensors have also been determined in cyclic thioxophosphonates of different size, 5- to 8-membered rings.[68]

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[57] R. Radeglia, *Z. Naturforsch., Teil A*, 1981, **36,** 763.
[58] R. Radeglia and A. R. Grimmer, *Z. Phys. Chem. (Leipzig)*, 1981, **262,** 718.
[59] R. Radeglia and R. Wolff, *Z. Naturforsch., Teil A*, 1981, **36,** 1177.
[60] R. Radeglia and A. R. Grimmer, *Z. Phys. Chem. (Leipzig)*, 1982, **263,** 204.
[61] B. Thomas, W. Bieger, and G. Grossman, *Z. Chem.*, 1981, **21,** 292.
[62] D. A. Brown, J. P. Chester, and N. J. Fitzpatrick, *Inorg. Chem.*, 1982, **21,** 2111.
[63] T. Weller, D. Deininger, and R. Lochmann, *Z. Chem.*, 1981, **21,** 105.
[64] W. S. Veeman, *Philos. Trans. R. Soc. London, Ser. A*, 1981, **299,** 629.
[65] A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, 1973, **59,** 569.
[66] D. Igner and D. Fiat, *J. Magn. Reson.*, 1982, **46,** 233.
[67] J. B. Robert and L. Wiesenfeld, *Mol. Phys.*, 1981, **44,** 319.
[68] J. P. Dutasta, J. B. Robert, and L. Wiesenfeld, *ACS Symp. Ser.*, 1981, **171,** 581.

The tensors are not axially symmetric and the asymmetry varies with the intracyclic O–P–O bond angle.

Both imidazole ^{15}N shielding tensors in L-histidine hydrochloride monohydrate single crystal are oriented approximately along the molecular symmetry directions of the ring.[69] The largest shielding component is perpendicular to the plane of the imidazole ring. ^{19}F shielding tensors were determined in $Sn^{II}F_2$,[70] fluoranil, and 5-fluorouracil,[71] and in tetrafluoro-1,4-benzoquinone.[72] The ^{19}F shielding anisotropy in hexafluorobenzene is obtained under 6 different conditions and solvents.[73] All values reported are in agreement within the limits of experimental error ($\pm$2—4 p.p.m.). Solute–solvent interactions which affect the geometry as well as the anisotropy of *J*(CF) do not show any effect on the shielding anisotropy. The intermolecular contributions to the ^{13}C shielding anisotropy of benzene are estimated by the ring current model to be of the order of 5—7 p.p.m.[74] This agrees semi-quantitatively with the difference in shielding anisotropy between benzene in the solid state and in liquid crystals.

^{113}Cd anisotropies of axially symmetric shielding tensors have been determined in Cd-substituted porphyrins,[75] in a decanuclear Cd^{II} complex,[76] and in several complexes representing a wide range of co-ordination patterns.[77] A small ^{205}Tl shielding anisotropy, 150 p.p.m., in the Tl^{I} valinomycin complex is interpreted in terms of a weak ion pairing with the anion.[78] These solid-state spectra provide information about Cd^{2+} co-ordination environments which are not complicated by chemical exchange and therefore complement solution n.m.r. spectra. ^{77}Se shielding tensors of the structurally nonequivalent Se nuclei in antiferroelectric single crystals of $CsH_3(SeO_3)_2$ are closely connected with the SeO_3 group geometry, reflecting its degree of distortion.[79] The temperature dependence of the tensor components indicates that the phase transition to the ordered phase is accompanied by an increasing amount of SeO_3 group distortion as the hydrogen bonding protons are ordered. Shielding tensors of ^{35}Cl in *p*-dichlorobenzene,[80] ^{2}H in malonic acid,[81] and ^{23}Na in $NaBrO_3$ [82] single crystals have been determined. For these quadrupolar nuclei, the anisotropy of the shielding as well as the magnitudes of the quadrupole coupling constants, indicate the deviation of the electronic environment from spherical symmetry.

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[69] G. Harbison, J. Herzfeld, and R. G. Griffin, *J. Am. Chem. Soc.*, 1981, **103,** 4752.
[70] M. Le Floch-Durand, U. Haeberlen, and C. Mueller, *J. Phys.* (*Les Ulis, Fr.*), 1982, **43,** 107.
[71] E. E. Burnell, A. L. Mackay, D. C. Roe, and A. G. Marshall, *J. Magn. Reson.*, 1981, **45,** 344.
[72] D. Catalano, C. A. Veracini, G. Chidichimo, and M. Longeri, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77,** 2267.
[73] D. Catalano, L. Marcolini, and C. A. Veracini, *Chem. Phys. Lett.*, 1982, **88,** 342.
[74] T. Barbara, C. F. Wood, and B. P. Dailey, *J. Magn. Reson.*, 1982, **48,** 225.
[75] P. D. Ellis, R. R. Inners, and H. J. Jakobsen, *J. Phys. Chem.*, 1982, **86,** 1506.
[76] P. D. Murphy, W. C. Stevens, T. T. P. Cheung, S. Lacelle, B. C. Gerstein, and D. M. Kurtz, *J. Am. Chem. Soc.*, 1981, **103,** 4400.
[77] P. G. Mennitt, M. P. Shatlock, V. J. Bartuska, and G. E. Maciel, *J. Phys. Chem.*, 1981, **85,** 2087.
[78] J. F. Hinton, K. R. Metz, and F. S. Millett, *J. Magn. Reson.*, 1981, **44,** 217.
[79] A. I. Kriger, Y. N. Moskvich, A. A. Sukhovskii, and O. V. Falaleev, *Phys. Status Solidi A*, 1982, **69,** 455.
[80] M. Ostafin and J. Pietrzak, *Chem. Phys. Lett.*, 1981, **80,** 589.
[81] C. Mueller, S. Idziak, N. Pislewski, and U. Haeberlen, *J. Magn. Reson.*, 1982, **47,** 227.
[82] S. F. Sagnowski and J. Ogar, *Phys. Status Solidi B*, 1981, **107,** K125.

B. The Effects of Rotation and Vibration.—Important progress has been made in this review period towards theoretical studies of the effects of rotation and vibration on nuclear shielding. Ditchfield[17] calculated shielding tensors for the nuclei in H_2, HF, and LiH over a range of internuclear separations. The method used (mentioned in Section 2A) is that of different gauge origins for different atomic orbitals. The shielding surfaces so obtained (in terms of only one co-ordinate in these molecules) are fitted to a power series in the reduced co-ordinate $\xi = (r - r_e)/r_e$, so that the derivatives $\sigma_e' = (d\sigma/d\xi)_e$, $\sigma_e'' = (d^2\sigma/d\xi^2)_e$, *etc.* can be determined. The intramolecular (vibrational) potential function is expressed as a Dunham series in ξ, which allows the expectation values of powers of ξ to be determined for a given vibration–rotation state. Such values are combined with the shielding surface derivatives to calculate rovibrational averages of the tensor components for different vibration–rotation states. With these, the Boltzmann average over the thermally accessible vibration–rotation states may be calculated to yield the isotropic shielding constant at temperature T, $\sigma_0(T)$. For the shielding of the nuclei in H_2 and HF, the agreement between the calculated and experimental values of $\sigma_0(T)$ at 300 K is excellent. In addition, the experimental isotope shifts upon deuteriation are reproduced. The $\sigma_0(T)$ value for ^{19}F in HF is predicted to decrease with increasing temperature. While this has not been observed for HF itself (the monomer is not easy to isolate for such studies), a decrease of $\sigma_0(T)$ with increasing temperature has been reported for ^{19}F in a wide variety of molecules.[83] In contrast, the ^7Li $\sigma_0(T)$ value in LiH is predicted to increase slightly with increasing temperature. This experiment has not yet been carried out; however, there are two instances where the value of $\sigma_0(T)$ has been found to increase with increasing temperature: ^{15}N in NH_3 and ^{31}P in PH_3.[84, 85] All other experimental studies of the temperature dependence of $\sigma_0(T)$ for ^1H, ^{13}C, ^{15}N, ^{19}F, ^{31}P nuclei show a decrease with increasing temperature. It is concluded that the contributions to $\sigma_0(T)$ from σ_e'' and higher derivatives of the shielding function are relatively insensitive to temperature changes in the range accessible in conventional n.m.r. spectrometers. Thus, measurement of the temperature dependence of $\sigma_0(T)$ ought to provide accurate estimates of σ_e'. On the other hand the terms in σ_e'' and higher derivatives contribute significantly to the temperature independent component of $\sigma_0(T)$, thus the latter will not give accurate estimates of σ_e.

While the shielding surfaces for diatomic molecules are fairly simple, those for bent triatomics are given in terms of three independent internal co-ordinates rather than one. In a series of elegant papers, Fowler and Raynes have extended the calculations discussed above to bent triatomics, in particular to the water molecule.[23, 24, 86] First they calculate the nuclear shielding surfaces for H_2O, then they perform vibrational–rotational averaging of the proton and oxygen shielding using an accurate empirical force field. The same averages are calculated for the electric dipole moment and the magnetizability. There are 18 isotopomers of this asymmetric top molecule. They also calculate the Boltzmann average, $\sigma_0(T)$ for the

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[83] C. J. Jameson, *Bull. Magn. Reson.*, 1981, **3**, 1.
[84] C. J. Jameson, A. K. Jameson, S. M. Cohen, H. Parker, D. Oppusunggu, P. M. Burrell, and S. Wille, *J. Chem. Phys.*, 1981, **74**, 1608.
[85] C. J. Jameson, A. K. Jameson, and H. Parker, *J. Chem. Phys.*, 1978, **68**, 2868.
[86] P. W. Fowler and W. T. Raynes, *Mol. Phys.*, 1982, **45**, 667.

shielding as a function of temperature. They point out that the formula used by Jameson[87] for this thermal average, in terms of coth($hc\omega_i/2kT$), having been obtained using a harmonic oscillator partition function in summing up an anharmonic vibration correction over all thermally accessible vibrational levels, may lead to deviations from the 'exact' thermal average at high temperatures. For H_2O however, the differences between the results using the Jameson formulae and taking the actual sum term by term, are small, 0.002 p.p.m. at 300 K for oxygen, 0.001 p.p.m. and 0.011 p.p.m. for proton and oxygen, respectively, at 500 K where the respective $\sigma_0(T)$ values are 29.230 and 311.681 p.p.m. The convenience of using the coth($hc\omega_i/2kT$) terms becomes obvious when the number of normal modes is much greater than three. Then, carrying out the sum properly involves considering individual terms in a congested vibrational manifold. The predicted temperature dependence of the proton $\sigma_0(T)$ is small and will be very difficult to measure experimentally. However, the predicted $d\sigma_0(T)/dT$ value for ^{17}O in H_2O is large enough to be observed. The isotopic shifts are in good agreement with experiment. Fowler has extended the theoretical formalism to vibration–rotation effects on the electronic properties of symmetric tops and linear molecules.[88] These molecules have doubly degenerate vibrations which necessitate a different approach from that used for the bent triatomic.

A new formulation for the study of the interaction between nuclear magnetic moments and molecular vibrations has been developed.[89, 90] In order to study the effect of intramolecular interactions (molecular vibration) and rotation on properties such as nuclear magnetic shielding, the standard procedure, as discussed above, is to use a Taylor series expansion of the molecular electronic property about the equilibrium geometry. This approach is probably valid in the limit of infinitesimal displacements. The use of a calculated property surface based on Ramsey's theory together with the solutions of the vibration–rotation problem obtained *via* perturbation theory or contact transformations, leads to a rovibrationally averaged electronic property which can be compared with experiment. However, this is a patchwork of perturbations, with truncated expansions being used in several stages. The Ramsey terms in the Hamiltonian expansion are obtained from classical expressions for the energy of a magnetic dipole in a magnetic field, and the nuclear motion terms are based on perturbations of classical harmonic oscillator–rigid rotor systems. The rotational–vibrational spectroscopists are getting hyperfine effects on their spectra, the magnetic resonance spectroscopists are getting rotationally and vibrationally averaged hyperfine or shielding constants, and each group is treating the other as a perturbation. What Michelot has done is to replace Ramsey's simplified theoretical model, based on the classical expressions for the energy of a magnetic dipole in a magnetic field, with a more rigorous, more complete Hamiltonian expansion. He starts with the molecular Hamiltonian developed by Moss[91, 92] and includes all relevant interaction terms involving nuclear magnetic moments. The transformation is made to the

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[87] C. J. Jameson, *J. Chem. Phys.*, 1977, **66**, 4977; **67**, 2814.
[88] P. W. Fowler, *Mol. Phys.*, 1981, **43**, 591.
[89] F. Michelot, *Mol. Phys.*, 1982, **45**, 949.
[90] F. Michelot, *Mol. Phys.*, 1982, **45**, 971.
[91] B. J. Howard and R. E. Moss, *Mol. Phys.*, 1970, **19**, 433.
[92] R. E. Moss, 'Advanced Molecular Quantum Mechanics', Chapman and Hall, London, 1973.

laboratory frame where the fields are defined and the various measurements are made. In order to separate more completely the various types of motion, a frame bound to the molecule is introduced. Equations are given which describe the separation of translational, electronic, and vibrational motions. For neutral molecules, it is possible to suppress the translational dependence of the generalized magnetic vector potentials, thus translation variables can be separated out. The Hamiltonian in molecular co-ordinates, including all electron, nuclear, and electron-nuclear terms, is given explicitly and each term is identified.[89] (Fermi contact interaction, relativistic nuclear dipolar interaction, nuclear spin–vibration–rotation interaction, *etc.*) There are 31 types of term including the effects of the finite dimension of nuclei. In this Hamiltonian the effects induced by molecular vibration appear explicitly so that a precise study of all direct and indirect effects induced by molecular vibration can be possible. The theory is then applied to a non-degenerate electronic state and the adiabatic approximation is used (rather than the Born–Oppenheimer approximation) and non-adiabatic corrections are introduced. Several terms contribute to the interaction between a nuclear magnetic moment and the magnetic field induced at the nucleus site by the molecular vibration and rotation. These are examined. When an external magnetic field is applied this Hamiltonian also allows a systematic study of the vibrational dependence of many molecular parameters (shielding tensor, molecular susceptibility tensor, *etc.*). In the past, several relationships have been established between the coefficients of the hyperfine and Zeeman Hamiltonians *when the effects induced by molecular vibration are neglected.* The well known relations of interest here are those connecting the paramagnetic terms of the rotational g factor and of the magnetic susceptibility, the other is that relating the paramagnetic term of the shielding tensor and the spin-rotation tensor. Michelot shows that the relation established by Flygare[93] between the latter two tensors is only approximate. A relation between these tensors which includes the effects induced by vibration is given.

C. Isotope Effects.—Due to the mass dependence of vibrational motion, the rovibrational average of nuclear shielding is different for different isotopomers. This isotope effect on the nuclear shielding provides information which is complementary to that obtained from the temperature dependence of the chemical shift in the zero-density limit.[17] As discussed in Section 3B, Ditchfield finds that the first derivative $\sigma'_e = (d\sigma/d\xi)_e$ can be accurately determined from the temperature dependence in the zero-density limit for diatomic molecules but the temperature-independent part contains non-negligible rovibrational corrections involving $\sigma''_e = (d^2\sigma/d\xi^2)_e$. Thus, the isotope shift can provide an empirical measure of σ''_e if σ'_e is assumed to be known from the temperature dependence of $\sigma_0(T)$. A more stringent test of theory is the temperature dependence of the isotope shift. Such a measurement has been carried out for the D_2–HD pair of hydrogen isotopomers.[94] The isotope shift in the deuterium resonance, $\sigma(D_2)$–σ(HD) was measured over the temperature range 18–296 K. At 296 K in the zero-density limit the value of the shift is 0.0469 ± 0.0005 p.p.m., an improvement in the uncertainty by nearly 2 orders of

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[93] W. H. Flygare, *J. Chem. Phys.*, 1964, **41**, 793.

[94] J. R. Beckett and H. Y. Carr, *Phys. Rev. A*, 1981, **24**, 144.

magnitude over the previous results,[95] 0.048 ± 0.032. Ditchfield's recent calculations give 0.054 p.p.m.[17] which is in excellent agreement with the old value but is now outside the experimental uncertainty of more recent results.[94] The predicted,[96] but previously unobserved, temperature dependence is found.

An elegant demonstration of the application of the n.m.r. isotope shift is the recent measurement of the magnetic moment of the positive muon (μ^+) in units of the magnetic moment of the proton.[97] μ^+ can be considered an isotope of hydrogen. When the μ^+ particle is stopped by a liquid target such as Br_2 or H_2O it forms molecules which are isotopomers of HBr or H_2O, $(\mu^+e^-)Br$ and $(\mu^+e^-)OH$, respectively. The Larmor frequency of μ^+ in these two targets, liquid Br_2 and liquid Br_2 contaminated with H_2O, are measured by a stroboscopic muon spin rotation technique in a field of 0.75 tesla. The frequency of ^1H in the same chemical environments is measured by high resolution n.m.r. The primary isotope shifts for the $(\mu^+e^-)OH/H_2O$ and $(\mu^+e^-)Br/HBr$ isotopomers are calculated. With these corrections the shielding of μ^+ in $(\mu^+e^-)Br$ and $(\mu^+e^-)OH$ are known. By correcting the μ^+ Larmor frequencies with these shielding values the results from the different targets are consistent, giving the magnetic moment of the bare muon in units of the magnetic moment of the proton.

In Volume 10 of this Series, a summary of experimental ^{18}O-induced ^{13}C isotope shifts and their dependence on structure were reported. These isotope shifts have been plotted against the ^{13}C chemical shifts.[98] A linear relationship between the magnitude of the one-bond isotope effect and the chemical shift of the carbon atom is found for carbonyl groups. No such correlation is found for isotopic substitution of the oxygen atoms bound to carbon atoms by single bonds, the scatter being worse for sp^3 carbons than for sp^2 carbons. It was surmised that some undiscovered effects may be obscuring a correlation in the C–O data. A simple explanation can be offered here for these observations. Of the vibrational modes which can contribute to the ^{18}O-induced ^{13}C isotope shift in a C=O group, there will be one which is predominantly a C=O stretch at a characteristic frequency which is fairly constant for a variety of compounds. Thus, the C=O mode is nearly isolated, so that its mass-dependent effects on the average nuclear shielding in fairly uniform C=O bonds [therefore more similar $(\partial\sigma_C/\partial\Delta r_{C=O})$ values] can correlate well with the ^{13}C nuclear shielding. On the other hand the C–O bonds are part of the skeletal structure, and the C–O stretching motion is not separable in the same way. In addition the C–O bond has a more variable electronic structure [therefore more variable $(\partial\sigma_C/\partial\Delta r_{C-O})$ values] than the C=O bond. Thus, it is not surprising that no correlation can be found for these types of carbons.

There are several reports of new ^{18}O-induced ^{13}C isotope shifts.[99–102] Of some interest is the use of spin–echo techniques to resolve these shifts.[101, 102] A spin–echo

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pulse sequence $\{90°-\tau-180°-\tau\text{-acquisition-}t\}$ where $\tau = 1/(2J_{CC})$ is used to resolve isotope shifts from interfering carbon–carbon couplings. The spin–echo Fourier transform (SEFT) technique allows the separation of the uncoupled $^{13}C-^{16}O$ and $^{13}C-^{18}O$ singlets from doublet signals due to ^{13}C coupled to nearby ^{13}C atoms. With this sequence the coupled ^{13}C are in phase, and the uncoupled ^{13}C are out of phase and appear inverted. The theory of the influence of SEFT on signal intensities has not been developed so that this technique may lead to errors in quantitative estimates of isotope ratios from relative signal intensities.

Deuterium-induced ^{13}C isotope shifts have been reported.[103—105] In cyclophanes the intrinsic isotope effects are deshielding for some carbons and shielding for others in the same molecule.[105] They are interpreted in terms of through-bond and through-space effects. Other isotope shifts reported are ^{18}O-induced ^{15}N shifts,[106] ^{13}C-induced ^{19}F shifts,[107] and ^{2}H-induced ^{1}H shifts.[108] In nitrite ion the ^{15}N shift is 0.138 p.p.m. per ^{18}O atom and it is additive.[106] This relatively large isotope shift permits the direct study, by n.m.r., of oxygen-exchange reactions involving nitrogen species. The ^{13}C-induced ^{19}F isotopic shifts measured in monofluorobenzene partially oriented in liquid crystals show the usual attenuation with remoteness of the ^{13}C-substitution site from the observed ^{19}F nucleus.[107] The ratio 8:2:0.5 Hz for 1-bond:2-bonds:3-bonds is preserved in all solvents. An unusual observation in the monodeuteriobenzene ^{1}H spectrum is contrary to the above case. Here the isotope shifts are very small. Nevertheless, the ^{1}H spectrum of liquid benzene-d_1 is completely analyzed as an AB_2C_2X ($X = {}^{2}H$) system. The ^{2}H isotope induced ^{1}H shifts are -1.4 (A), -1.3 (B), and $+0.3$ (C) all in p.p.b.[108]

D. Intermolecular Effects.—Two gas-phase studies of intermolecular effects on nuclear shielding have been reported: one is on the ^{1}H, ^{13}C, and ^{15}N nuclei in HCN,[109] the other on the ^{15}N nucleus in Me_3N.[110] In both studies, the association constant for the complex (the HCN–HCN or the $Me_3N-HCCl_3$) is involved in the interpretation of the results. Liquid phase data are also given. In HCN the ^{15}N shielding appears to be representative of that found in pyridine and acetonitrile, and is markedly different from that found in alkyl amines and NH_3: the effect of intermolecular interactions on ^{15}N in HCN leads to an increase rather than the usual decrease in shielding observed for all other nuclei.[109] The gas phase $Me_3N-HCCl_3$ complex formation constant is 2 orders of magnitude greater than that in solution with cyclohexane as solvent but the ^{1}H chemical shift upon complexation is a factor of 10 less in the gas phase than in cyclohexane.[110]

Hydrogen-bonding has been studied in the solid state and interpreted with semi-empirical and *ab initio* calculations. Holler and Lischka have performed large basis CHF calculations on $(HF)_2$ and $(H_2O)_2$.[111] The changes in the anisotropy of σ

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upon hydrogen-bond formation are larger than the shifts of the average value of σ. In H_2O, $(\sigma_{\text{dimer}} - \sigma_{\text{monomer}})$ values are found to be of opposite signs for the two oxygens, the negative one being the larger. Thus, in a fast-exchanging monomer–dimer equilibrium, an average deshielding will be observed for ^{17}O. Under fast exchange the hydrogens are predicted to be deshielded as well. In HF, the proton involved in the hydrogen bridge is deshielded upon dimer formation, while both fluorines become more shielded. GIAO calculations on ^1H shielding in $(H_2O)_2$, $(H_3O_2)^-$, and $(H_5O_2)^+$ have been reported;[112] agreement with single crystal pulsed n.m.r. experiments is obtained. The proton chemical shift is linearly dependent on the O...O separation. PCILO-level GIAO calculations for ^1H in glycine and its hydrogen-bonded dimer are used for the interpretation of solid state data. When the rotation of the NH_3 groups is taken into account, the qualitative features of the experiment are correctly represented. There is semi-quantitative agreement with the experimental anisotropy and asymmetry of the proton shielding.[113] Experimental studies of hydrogen bonds in carboxylic acid dimers in the solid state have been reported for benzoic acid[114] and *p*-toluic acid.[115]

Theoretical calculations by Jallali-Heravi and Webb with the solvaton model were reported in Volume 11 of this Series. Recent experimental results on ^{13}C and ^{17}O in acetone and acetonitrile have been found to agree with predictions of these calculations for atoms belonging to the polar groups.[116] Discrepancies between theoretical and experimental results in the solvent effects on shifts of methyl carbons are attributed to the predominance of van der Waals interaction effects on shielding. CNDO/2 calculations of ^{13}C shielding tensors in a free benzene molecule and in a benzene interacting with an OH^- group are used to model the ^{13}C n.m.r. spectra of adsorbed benzene molecules.[117] The anisotropy of the ^{13}C shielding tensor in free benzene is semiquantitatively reproduced. The calculated shift upon complexation with OH^- ranges from $+0.7$ to -2.3 p.p.m., which is small compared to the discrepancies between the calculated and experimental components of free benzene. ^{129}Xe nuclei adsorbed on zeolites show a density dependence and increased shielding relative to Xe gas.[118] In the limit of zero density, $(\sigma_{\text{adsorbed}} - \sigma_{\text{free}}) = 58 \pm 4$ p.p.m. and 83 ± 2 p.p.m. for different zeolites. Other studies of intermolecular effects in the solid state involve ^{13}C in n-alkanes,[119] and ^{15}N in histidine and imidazole.[120]

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