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Possibility of Field-Dependent Nuclear Magnetic Shielding

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The possibility of an observable field dependence of the nuclear magnetic shielding in NMR experiments is discussed. It is shown that in most molecules such an effect should be unobservably small. However, in some molecules, especially where the magnetic shielding is abnormally large, it is possible that the field dependence of the shielding could be large enough to be observable. In NMR experiments of high accuracy in strong magnetic fields, the proportionality of the resonance frequency to the magnetic field should therefore not be automatically assumed, but should be experimentally verified.

I. INTRODUCTION

When a single nuclear magnetic resonance line is observed with liquids, it is generally presumed that the resonance frequency is exactly proportional to the external magnetic field. This presumption has indeed been supported by those past experiments in which the proportionality has been tested. However, in many of the highest-resolution NMR experiments on chemical shifts, a small field dependence of the magnetic shielding would escape notice since the resonances are often measured at only a single magnetic field. It is the purpose of this paper to point out that as nuclear resonance experiments are performed with greater precision and in higher magnetic fields, there is reason in some cases to expect small departures from exact proportionality between the resonance frequency and the magnitude of the external magnetic field H_0.

II. FIELD-DEPENDENT NUCLEAR MAGNETIC SHIELDING

Departures from simple proportionality between the resonance frequency and the field can arise from a magnetic field dependence of the nuclear magnetic shielding.[1] Thus, if σ^T represents the total magnetic shielding and if σ is the usual field-independent shielding, the total shielding should be field-dependent and given by

$$\sigma^T = \sigma + \tau H_0^2 + \cdots , \qquad (1)$$

where τ is a molecular coefficient defined by the above relation. The odd powers of H_0 in Eq. (1) vanish by the symmetry requirement that the magnitude of the shielding must be independent of the direction of the magnetic field. The term in H_0^2 in Eq. (1) will give rise to a cubic dependence of the angular resonance frequency ω upon H_0 since

$$\omega = (1 - \sigma^T)\gamma H_0 = (1 - \sigma)\gamma H_0 - \tau\gamma H_0^3 . \qquad (2)$$

It should be noted that although the value of σ can not be empirically obtained by observations of the dependence of ω upon H_0, the value of τ can be found in this manner.

Quadratic terms in the magnetic shielding would be expected both from higher-order perturbation shifts of the energy levels of specific molecular states and from slight shifts in the distribution of population among the different states upon application of the magnetic field. As discussed previously,[1] the perturbation with the external field H_0 and the relevant magnetic moment μ taken parallel to the z axis is given by

$$\mathcal{3C}^{(1)} + \mathcal{3C}^{(2)} = -\sum_k (H_0 + 2\mu/r_k^3)m_{zk}^0$$
$$+ (e^2/8mc^2)\sum_k (H_0 + 2\mu/r_k^3)^2(x_k^2 + y_k^2) , \qquad (3)$$

where m_{zk}^0 is the z-component orbital magnetic moment operator.[1] With this, the fourth-order perturbation calculation of the energy can be carried out in the usual manner.[2] If W_λ' represents

the sum of all such fourth-order terms which are proportional to μH^3 and if τ_1 is the perturbation theory contribution to τ, then we obtain

$$\tau_1 = (W_\lambda''/\mu H_0^3) \ . \tag{4}$$

The large number of terms involved in the fourth-

order calculation are directly given by the general perturbation-theory expressions[2] and will not be listed here. It has not been feasible to calculate reliable numerical values for τ_1. However, its general magnitude can be estimated by considering a typical term. Such a typical term τ_1' would be[2]

$$\tau_1' = -2\frac{(0\lambda \,|\sum_k m_{zk}^0|\,n'\lambda')(n'\lambda'\,|\sum_k m_{zk}^0|\,n''\lambda'')(n''\lambda''\,|\sum_k m_{zk}^0|\,n'''\lambda''')(n'''\lambda'''\,|\sum_k(m_{zk}^0/r_k^3)|\,0\lambda)}{(E_{n'}-E_0)(E_{n''}-E_0)E_{n'''}-E_0)} \ . \tag{5}$$

One way of estimating the magnitude of a typical term τ_1' is to approximate the matrix elements of m_{zk}^0 to the Bohr magneton β and to assume that the energy differences in the denominator are each approximately equal to the same value Δ, in which case

$$\tau_1' H_0^2 \approx -2\beta^4 H_0^2/r^3\Delta^3 = -2(\beta^2/r^3\Delta)^3(H_0 r^3/\beta)^2 \ . \tag{6}$$

The analogous approximations in evaluating a typical term σ' in the magnetic shielding σ give

$$\sigma' \approx -2\beta^2/r^3\Delta \ . \tag{7}$$

Consequently, we have

$$\tau_1' H_0^2/\sigma' \approx (\beta^2/r^3\Delta)^2(H_0 r^3/\beta)^2 \ . \tag{8}$$

If we take $r = a_0$, $\Delta = e^2/2a_0$, and $\beta = \frac{1}{2}e\,\alpha a_0$, we obtain

$$\tau_1' H_0^2/\sigma' \approx \tfrac{1}{4}\alpha^4(H_0 a_0^3/\beta)^2 \approx 7.1\times10^{-10} \ , \tag{9}$$

where in the last step we have taken $H_0 a_0^3/\beta$ equal to 1, as it would for a field of 62 600 G.

The fractional shift of the magnetic shielding implied by Eq. (9) is too small to be observable. On the other hand, it is well known that some substances have a chemical shift in the magnetic shielding much larger than would be obtained by evaluating Eq. (7) with assumptions similar to those used above. The reason for this is presumed to be much lower values for Δ as a result of near degeneracies. If all the energy differences in the denominator of Eq. (5) should be equally small, we could evaluate Eq. (8) by using Eq. (7) to eliminate Δ, in which case

$$\tau_1' H_0^2/\sigma' = \sigma'^2(H_0 r^3/\beta)^2 \approx 10^{-4} \ , \tag{10}$$

where in the last step we have assumed the same value of H_0 as used above in Eq. (9) and have taken for σ' the value of 0.01, the magnitude of the chemical shift experimentally found for the magnetic shielding of some cobalt compounds.[3]

The detection of a magnetic shielding change even smaller than that indicated by Eq. (10) is well

within the sensitivity of present NMR experiments. However, most experiments of high sensitivity are not carried out in widely different magnetic fields, so an observable field dependence of the magnetic shielding could easily escape detection. It is apparent from the above discussion that the field dependence of the magnetic shielding would probably be most easily observable in compounds, such as cobalt, where the chemical shifts in the normal magnetic shielding are unusually large.

Field dependence of the shielding can also arise from the alteration with magnetic fields of the population distribution over the different states. If σ_p is the shielding in the pth state, ξ_p is the diamagnetic susceptibility of that state, and W_p is the energy when H is zero, then we have

$$\sigma = \left[\ \textstyle\sum_p \sigma_p \exp(-W_p + \tfrac{1}{2}\xi_p H_0^2)/kT\right]$$
$$\times \left[\textstyle\sum_p \exp(-W_p + \tfrac{1}{2}\xi_p H_0^2)/kT\right]^{-1} \ . \tag{11}$$

The contributing states may be either low-lying electronic states or states of differently oriented molecular rotation. States which differ only in molecular orientation will not in this way give rise to a magnetic field dependence of the shielding if the molecule or complex is sufficiently symmetrical that ξ and σ are orientation independent, as in the case of most cobalt complexes studied with nuclear magnetic resonance.

Since the bulk magnetic susceptibility of a solution may become field dependent in sufficiently strong magnetic fields, the bulk magnetic susceptibility correction of nuclear magnetic resonance can, in principle, give rise to a departure from proportionality between the resonance frequency and the magnitude of the externally applied field. Such a bulk susceptibility effect can be distinguished from field-dependent magnetic shielding by dissolving the substances being studied and those being used for field calibration in the same sample, so that the bulk susceptibility correction is the same for all.

III. CONCLUSION

Although the field dependence of the nuclear magnetic shielding for most substances should be unobservably small, there is the possibility that such a dependence could be observed for some substances in high-precision experiments in strong magnetic fields. The largest effects would be expected in molecules for which the chemical shifts of the magnetic shielding are abnormally large. As nuclear magnetic resonance experiments are made with greater accuracy and in higher magnetic fields, the proportionality of the resonance frequency to the magnetic field should not be automatically assumed, but should be experimentally verified.

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Birefringent Dispersion and the Nuclear Quadrupole Interaction

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This paper is an addendum to a paper by the author which presented a relation between the gradient of the electric field at the nucleus and dipole matrix elements. A scheme is suggested to take advantage of the result.

The gradient of the electronic electric field at the position of the atomic nucleus is required for an evaluation of nuclear quadrupole moments from the hyperfine B coefficients. Recently,[1] it was shown that this could be expressed by the sum rule

$$\langle 0|q|0\rangle = \frac{-m^2}{\hbar^4 N e^2}\, T(2)\ , \quad q = \sum_{i=1}^{n} \frac{P_2(\cos\theta_i)}{r_i^3}\ . \quad (1)$$

N is the nuclear charge, n the number of electrons, m the electronic mass, and

$$T(j) = \sum_{k}(\epsilon_k - \epsilon_0)^{j+1}$$
$$\times \left(\left|\langle 0|\sum_{i=1}^{n} z_i|k\rangle\right|^2 - \tfrac{1}{3}\left|\langle 0|\sum_{i=1}^{n}\vec{r}_i|k\rangle\right|^2 \right)$$

or the equivalent in terms of dipole momentum or acceleration matrix elements. [We correct Eq. (7) of Ref. 1 by a factor of 2.] As we indicated in the earlier paper, the dipole matrix elements govern radiative transitions, so that $\langle 0|q|0\rangle$ may be deduced if measurements of rates are available. However, experimental techniques are insufficient-

ly developed to apply Eq. (1) immediately. Our purpose in writing the present article is to point out how an approximate value of $T(2)$ may be extracted from a set of dispersion measurements.

The $T(j)$ are analogous in form to the scalar sum rules $S(j)$;

$$S(j) = \tfrac{2}{3}\sum (\epsilon_k - \epsilon_0)^{j+1}\left|\langle 0|\sum_{i=1}^{n}\vec{r}_i|k\rangle\right|^2\ .$$

Some well-known dipole sum rules for atoms are[2]

$$S(-2) = \bar{\alpha}/e^2, \quad \text{average static polarizability} \quad (2)$$

$$S(-1) = \tfrac{2}{3}\langle 0|\left|\sum_{i=1}^{n}\vec{r}_i\right|^2|0\rangle\ , \quad (3)$$

$$S(0) = n\,\hbar^2/m\ , \quad f \text{ sum rule} \quad (4)$$

$$S(2) = 4\pi N e^2 \hbar^4/3m^2 \langle 0|\sum_{i=1}^{n}\delta(\vec{r}_i)|0\rangle\ . \quad (5)$$

Tensor sum rules are not restricted to $T(2)$. For example we have

$$T(-2) = \alpha'/3e^2, \quad \text{tensor static polarizability} \quad (6)$$

$$T(-1) = \langle 0|\left|\sum_{i=1}^{n} z_i\right|^2 - \tfrac{1}{3}\left|\sum_{i=1}^{n}\vec{r}_i\right|^2|0\rangle\ , \quad (7)$$