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Theoretical
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Perspective

Perspective on Norman Ramsey's theories of NMR chemical shifts and nuclear spin–spin coupling

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Abstract. The theories connecting the observed NMR chemical shifts and nuclear spin–spin coupling constants to electronic wave functions were published by Norman Ramsey in eight connected *Physical Review* papers from 1950 to 1953. At the nonrelativistic limit these expressions still stand as the final answer.

Key words: Ramsey's theories – NMR spin – spin coupling – NMR chemical shift – Relativistic effects

1 Introduction

NMR is currently one of the most important forms of chemical spectroscopy. The two main spectroscopic parameters are the chemical-shift tensor, σ, and the nuclear spin–spin coupling tensor, $\mathbf{J}$. The connection between these two quantities and the electronic wave functions of the molecule was described in a series of five papers [1–5] published between 1950 and 1953. These five papers should be regarded as a whole. Together they are among the most influential ones in the quantum chemistry of the twentieth century. A sixth paper [6] pointed out a second-order magnetic self-coupling term, looking like the electric quadrupole interaction. The spin–spin coupling paper [5] had a precursor by Ramsey and Purcell [7]. In rotating molecules further chemical-shift terms occur from zero-point vibrations and "Thomas precession" [8].

2 The original papers

2.1 The NMR Hamiltonian

The NMR spectrum of a molecule containing the magnetic nuclei $\mathbf{I}_i$ is determined in the absence of electric quadrupole effects by the magnetic spin Hamiltonian

$$H = -\mathbf{B} \cdot \sum_i \hbar\gamma_i (1 - \sigma_i) \cdot \mathbf{I}_i + \sum_{i>j} h \mathbf{I}_i \cdot \mathbf{J}_{ij} \cdot \mathbf{I}_j \ . \tag{1}$$

Usually the components of σ are expressed in parts per million (ppm) and those of $\mathbf{J}$ in hertz. The nuclear magnetic moment is $\mu = \hbar\gamma\mathbf{I} = g_N \beta_n \mathbf{I}$; $\beta_n = e\hbar/2m_{\mathrm{p}}c$ is the nuclear magneton.

We consider closed-shell molecules and also neglect here the direct, through-space nuclear spin–spin interactions. For a rotating molecule in vacuum one has to add the spin-rotation term

$$H_{\mathrm{sr}} = -h \sum_N \mathbf{I}_N \cdot C_N \cdot \mathbf{K} \ , \tag{2}$$

where $\mathbf{C}_N$ (in hertz) is the spin-rotation coupling tensor of nucleus N and $\mathbf{K}$ is the rotational angular momentum operator of the molecule.

2.2 Chemical shifts

In his first paper Ramsey [1] showed that the isotropic chemical-shift formula of Lamb [9],

$$\sigma_{\mathrm{d}} = \left(e^2/3mc^2\right)\langle 0|\tfrac{1}{r}|0\rangle \ , \tag{3}$$

where $|0\rangle$ is the total electronic wave function, had to be completed by a term related to the spin-rotation constant:

$$\sigma_{\mathrm{p}} = \frac{1}{6}\frac{\alpha^2(a_0 a^2)}{\beta_n m/M}\left[\frac{2Z(\beta_n m/M)}{a^3} - \frac{m_{\mathrm{r}}}{M} B_N\right] \ . \tag{4}$$

Here m and M are the electronic and nuclear masses, respectively, while m_{r} is the reduced mass, $\alpha = e^2/hc$ is the fine-structure constant and a is the bond length of the molecule. B_N is the magnetic flux density at nucleus

N arising from molecular rotation. For the proton in H_2 σ_d and σ_p were estimated to be 32.4 and -5.3 ppm respectively [1].

In the derivation of the latter term the infinite summation over excited electronic states could be avoided by expressing it in terms of the experimentally known constant, B_N.

The full paper on chemical shifts [2] builds on an analogy of Van Vleck's theory of magnetism. The theory starts from the substitution

$$\mathbf{p} \rightarrow \pi = \mathbf{p} + e\mathbf{A}/c \ , \tag{5}$$

with $e < 0$ and the magnetic vector potential

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \times (\mathbf{r}_{kn} - \mathbf{R}_{kl}) + \mu \times \mathbf{r}_{kN}/r_{kN}^3 \ . \tag{6}$$

Here $\mathbf{r}_{kN}$ is the distance to electron k from the nucleus N and $\mathbf{R}_{kl}$ is the distance from a gauge origin. The final expression is

$$\begin{aligned}\sigma_{zz} = {} & \left(e^2/2mc^2\right)\langle 0|\left(x^2+y^2\right)/r^3|0\rangle \\ & + 2\sum_n{}' \left[\langle 0|m_z|n\rangle\langle n|m_z/r_k^3|0\rangle + \text{c.c.}\right]/(E_0 - E_n)\end{aligned} \ , \tag{7}$$

with $m_z = \beta l_z$. This equation still stands as the correct one at the nonrelativistic limit. The connection with the spin-rotation constant is now discussed in more detail and the result for a linear molecule becomes

$$\sigma = \left(e^2/3mc^2\right)\langle 0|\frac{1}{r}|0\rangle - \frac{\alpha^2 a_0 I}{6\beta_n}\left(\sum_N \frac{2Z_N\beta_n}{Ia_N} - \frac{B_N}{KM}\right) \ . \tag{8}$$

Here I is the moment of inertia and M is the nuclear mass. The dependence of the shielding on the M_K quantum number of the rotational state $|KM_K\rangle$ for a linear molecule is discussed in Ref. [3].

In Ref. [4] Ramsey discussed the chemical shifts of a general polyatomic molecule or a solid. It was further shown that the paramagnetic term arising from tightly bound electrons on a distant atom, L, can be made to vanish by setting the gauge origin $\mathbf{R}_{kL} = 0$. The possible contributions from thermally accessible excited states were also discussed.

2.3 Spin–spin coupling

The fifth paper [5] formulates the theory of spin–spin coupling in molecules starting from the hyperfine Hamiltonians

$$h_1 = \sum_k \frac{1}{2m}\left[\left(\mathbf{p}_k + \frac{e}{c}\sum_N \mathbf{A}_N\right)^2 - \mathbf{p}_k^2\right] \ , \tag{9}$$

$$h_2 = \sum_{kN} g g_N \beta\beta_n \left[3(\mathbf{S}_k\cdot\mathbf{r})(\mathbf{I}_N\cdot\mathbf{r})r^{-5} - \mathbf{S}_k\cdot\mathbf{I}_N r^{-3}\right] \ , \tag{10}$$

$$h_3 = \sum_{kN} -\frac{8\pi}{3} g g_N \beta\beta_n \mathbf{S}_k\cdot\mathbf{I}_N\delta(\mathbf{r}) \ . \tag{11}$$

Here $\mathbf{r}$ is the vector from the nucleus N to the electron k. Ramsey derived the expressions for the full spin–spin coupling tensor $\mathbf{J}$ and its scalar part J between the nuclei N and N'.

$$h\mathbf{J}^{(1\mathrm{a})} = \frac{e^2\beta_n^2 g_N g_{N'}}{mc^2}\left\langle 0\left|\frac{\mathbf{1}\mathbf{r}_{kN}\cdot\mathbf{r}_{kN'} - \mathbf{r}_{kN}\mathbf{r}_{kN'}}{r_{kN}^3 r_{kN'}^3}\right|0\right\rangle \ , \tag{12}$$

$$hJ^{(1\mathrm{a})} = \frac{2}{3}\frac{e^2\beta_n^2 g_N g_{N'}}{mc^2}\left\langle 0\left|\frac{\mathbf{r}_{kN}\cdot\mathbf{r}_{kN'}}{r_{kN}^3 r_{kN'}^3}\right|0\right\rangle \ , \tag{13}$$

$$\begin{aligned}hJ^{(1\mathrm{b})} = {} & -\frac{8}{3}\beta^2\beta_n^2 g_N g_{N'}\sum_n{}'\left\langle 0\left|\frac{\mathbf{r}_{kN}\times\nabla}{r_{kN}^3}\right|n\right\rangle \\ & \cdot\left\langle n\left|\frac{\mathbf{r}_{kN'}\times\nabla}{r_{kN'}^3}\right|0\right\rangle/(E_0 - E_n)\end{aligned} \ , \tag{14}$$

$$\begin{aligned}h\mathbf{J}^{(2)} = {} & 2g^2\beta^2\beta_n^2 g_N g_{N'}\sum_n{}'\left\langle 0\left|\frac{\mathbf{S}_k}{r_{kN}^3} - \frac{3(\mathbf{S}_k\cdot\mathbf{r}_{kN})r_{kN}}{r_{kN}^5}\right| n\right\rangle \\ & \cdot\left\langle n\left|\frac{\mathbf{S}_k}{r_{kN'}^3} - \frac{3(\mathbf{S}_k\cdot\mathbf{r}_{kN'})r_{kN'}}{r_{kN'}^5}\right| 0\right\rangle/(E_0 - E_n)\end{aligned} \ , \tag{15}$$

$$\begin{aligned}hJ^{(3)} = {} & 2\left(\frac{8\pi}{3}\right)^2 g^2\beta^2\beta_n^2 g_N g_{N'}\sum_n{}'\langle 0|\mathbf{S}\delta(\mathbf{r}-\mathbf{r}_N)|n\rangle \\ & \times\langle n|\mathbf{S}\delta(\mathbf{r}-\mathbf{r}_{N'})|0\rangle/(E_0 - E_n)\end{aligned} \ . \tag{16}$$

These four contributions 1a, 1b, 2, and 3 are called the diamagnetic, orbital, dipole, and Fermi contact terms, respectively. For the anisotropic part of the spin–spin coupling tensor, a dipolar-contact cross term $\mathbf{J}^{(2,3)}$ was obtained. The gauge origin for $\mathbf{A}_N$ was here placed on the nucleus N. Numerical values were estimated for J in HD using the closure approximation and an effective energy denominator, ΔE, for $J^{(2)}$ and $J^{(3)}$. Again, Eqs. (12)–(16) remain exact at the non-relativistic limit.

2.4 Later developments

The quoted papers still form the basis of our understanding of σ and $\mathbf{J}$ in molecules studied by condensed-phase NMR. No new terms were found later. Ramsey [2] had cautiously thought that his terms "at least partially and perhaps completely" explained the chemical shifts. For freely rotating molecules in the gas phase, the small "Thomas precession" chemical-shift term of Ramsey [8] was later improved by Reid and Chu [10] and by Rebane and Volodicheva [11]. For the latest references to it, see Ref. [12].

An important aspect for practical numerical calculations by the practising quantum chemist turned out to be the effect of the chosen gauge origin, $\mathbf{R}_{kl}$, on the chemical shift σ. A common way to secure this is to use the so-called London orbitals [13] or "gauge-including atomic orbitals (GIAO)". Initially the acronym stood for "Gauge-invariant" ones. Other, potentially more economical alternatives exist, such as the "individual gauge origins for local orbitals" by Kutzelnigg [14] or the "localized orbital/local origin" one [15]. These methods are now a standard part of quantum chemical NMR chemical-shift packages. Without them correct results can be obtained but the basis-set convergence would be much slower.

3 Relativistic effects

Ramsey's theories, like their Van Vleck analogues for magnetism, were entirely nonrelativistic. They were originally only applied to compounds of light elements. In treatises on NMR, such as that of Abragam [16], only this nonrelativistic theory was discussed.

It had been shown early on by Breit [17] and Racah [18] that the relativistic corrections to magnetic dipole hyperfine interactions can be substantial. For later references, see, for instance, Refs. [19–21]. For the 6*s* valence orbital of an element such as mercury this correction is roughly a factor of 3. Hence the J(HgHg) coupling constant is increased by an order of magnitude due to relativistic effects.

More subtle are the spin–orbit-induced "heavy-atom chemical shifts" at the atom nearest to the heavy one, or at more remote nuclei. If one uses the same Hamiltonians as Ramsey, one must go to third-order perturbation theory, with one Zeeman, one hyperfine, and one spin–orbit matrix element [22]. For a recent discussion on the nature of this shift, see Ref. [23]. It was also noted that an analogous effect, a "heavy-atom shift on the heavy atom" can occur, for instance on the Pb(II) nucleus in PbR_3^- compounds. The early semiempirical calculations suggested that the Zeeman–SO–Fermi contact cross term, zero in Ramsey's theory, could then become the dominant contribution to the Pb chemical shift [24].

If relativistic wave functions are used, second-order perturbation theory is enough. The ultimate goal, of course, remains a fully relativistic theory of both **J** and σ. The analogues to Ramsey's theories for them using the Dirac equation were formulated in Ref. [25] and in Refs. [26–28], respectively. The first numerical applications are now starting to appear, see, for example, the two conference proceedings [29, 30].

The quantum electrodynamical corrections to these Dirac-level results are small. The leading one is the correction factor of 1.001 159 652 193(4) to the free-electron g-factor of -2.

4 Conclusion

Ramsey's theories turned out to be virtually complete, when applied to compounds of light elements. A huge number of applications have been built on them. Among the excellent reviews, we mention the latest ones [31, 32]. Ramsey's theories undoubtedly belong to the classics of twentieth-century science. Corrections to them are required for compounds containing heavier elements.

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Appendix

In order to maintain historical continuity we have used the Gauss-cgs systems of units, used in the original papers of Ramsey. In this system $\epsilon_0 = \mu_0 = 1$ with a Coulomb potential $V = Q/r$. The transition to atomic units is made with $e = m_e = \hbar = 1$. Apart from units of cm for l, g for m, and s for t, yielding the energy unit erg $= \mathrm{cm^2\,g s^{-2}} = 10^{-7}$ J some electromagnetic units are as follows:
charge Q: $\mathrm{cm^{3/2}\,g^{1/2}\,s^{-1}} = 1$ esu; magnetic moment μ: $\mathrm{cm^{5/2}\,g^{1/2}\,s^{-1}}$; magnetic flux density **B**: $\mathrm{g^{1/2}\,cm^{-1/2}\,s^{-1}} = 1$ gauss; magnetic vector potential **A**: $\mathrm{g^{1/2}\,cm^{1/2}\,s^{-1}}$.

References

1. Ramsey NF (1950) Phys Rev 77: 567
2. Ramsey NF (1950) Phys Rev 78: 699–703
3. Ramsey NF (1951) Phys Rev 83: 540–541
4. Ramsey NF (1952) Phys Rev 86: 243–246
5. Ramsey NF (1953) Phys Rev 91: 303–307
6. Ramsey NF (1953) Phys Rev 89: 527
7. Ramsey NF, Purcell EM (1952) Phys Rev 85: 143–144
8. Ramsey NF (1953) Phys Rev 90: 232
9. Lamb W (1941) Phys Rev 60: 817
10. Reid RV Jr, Chu AH-M (1974) Phys Rev A 9: 609
11. Rebane TK, Volodicheva MI (1974) Vestn Leningr Univ 22: 55
12. Sundholm D, Gauss J, Schäfer A (1996) J Chem Phys 105: 11051
13. London F (1937) J Phys Radium 8: 397
14. Kutzelnigg W (1980) Isr J Chem 19: 193
15. Hansen AaE, Bouman TD (1985) J Chem Phys 82: 5035
16. Abragam A (1961) Principles of nuclear magnetism, Clarendon, Oxford
17. Breit G (1930) Phys Rev 35: 1447
18. Racah G (1931) Z Phys 71: 431
19. Pyykkö P, Pajanne E, Inokuti M (1973) Int J Quantum Chem 7: 785
20. (a) Lindgren I, Rosén A (1974) Case Stud At Phys 4: 93; (b) Lindgren I, Rosén (1974) Case Stud At Phys 4: 197
21. Pyykkö P, Wiesenfeld L (1981) Mol Phys 43: 557
22. Nomura Y, Takeuchi Y, Nakagawa N (1969) Tetrahedron Lett 8: 639
23. Kaupp M, Malkina OL, Malkin VG, Pyykkö P (1998) Chem Eur J 4: 118
24. Edlund U, Lejon T, Pyykkö P, Venkatachalam TK, Buncel E (1987) J Am Chem Soc 109: 5982
25. Pyykkö P (1977) Chem Phys 22: 289
26. Pyykkö P (1983) Chem Phys 74: 1
27. (a) Pyper NC (1983) Chem Phys Lett 96: 204 (b) Pyper NC (1983) Chem Phys Lett 96: 211
28. Zhang ZC, Webb GA (1983) J Mol Struct 104: 439
29. ACS Conf Proc (1999)
30. J Comput Chem (1999)
31. Jameson CJ, de Dios AC (1999) In: Webb GA (ed) Specialist periodical reports. Nuclear magnetic resonance, vol 28. The Royal Society of Chemistry, Cambridge (in press)
32. Helgaker T, Jaszuński M, Ruud K (1999) Chem Rev 99: 293