NMR second moments of nuclei with restricted motion

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In calculating powder NMR second moments M_2 of interacting nuclei with restricted hopping motion in crystals one has to find

$$K_{ij} = \langle \langle (3\cos^2\theta_{ij} - 1)/r_{ij}^3 \rangle_n^2 \rangle_p \ , \tag{1}$$

where we first average the coupling between nuclei i and j over the possible configuration vectors $\mathbf{r}_{ijn}$ with angles θ_{ijn} relative to H_0, then square the result and take the powder average.

Direct use of Eq. (1) can be rather tedious in the general case of restricted motion, but the calculations can be simplified by the addition theorem and the orthogonality relation for spherical harmonics as indicated by Miller and Gutowsky.[1] However, their result Eq. (A3) for PF_6^- interaction is not valid in the general case. We find

$$\begin{aligned} K_{ij} = \frac{1}{5n^2}\Bigg[& \left(\sum_n \frac{(3\cos^2\theta'_{ijn} - 1)}{r_{ijn}^3}\right)^2 \\ & + 3\left(\sum_n \frac{\sin 2\theta'_{ijn}\cos\phi'_{ijn}}{r_{ijn}^3}\right)^2 + 3\left(\sum_n \frac{\sin 2\theta'_{ijn}\sin\phi'_{ijn}}{r_{ijn}^3}\right)^2 \\ & + 3\left(\sum_n \frac{\sin^2\theta'_{ijn}\cos 2\phi'_{ijn}}{r_{ijn}^3}\right)^2 + 3\left(\sum_n \frac{\sin^2\theta'_{ijn}\sin 2\phi'_{ijn}}{r_{ijn}^3}\right)^2 \Bigg] \end{aligned} \tag{2}$$

and $\sum_j K_{ij}$ should replace $(\frac{4}{5})\sum_j r_{ij}^{-6}$ in the rigid lattice M_2 formulas for powders[2] to give the effect of the motion.

The advantage of Eq. (2) is that the new polar angles θ'_{ijn} and ϕ'_{ijn} of $\mathbf{r}_{ij}$ can be calculated in any convenient coordinate system fixed in the lattice, and K_{ij} is independent of this choice. If position coordinates of nuclei in tumbling complexes are given, Eq. (2) can be used directly to give a general computer program. However, for hand calculations it is advantageous to use whatever symmetry there is to reduce the number of terms. For instance, with the particular symmetry of interacting PF_6^- complexes in $NaPF_6$ Eq. (2) reduces to two terms if the P–P direction is taken as the z' axis.[1]

Checking some limiting cases of Eq. (2) we find as required: (a) rigid lattice, $n = 1$, gives $K_{ij} = \frac{4}{5}r_{ij}^{-6}$ by adding the terms; (b) reorientation of a complex about an n-fold axis with $n \geq 3$ gives the intracomplex $K_{ij} = (3\cos^2\gamma_{ij} - 1)^2/5r_{ij}^6$, where γ_{ij} is the angle of $\mathbf{r}_{ij}$ relative to the rotation axis[3] since all but the first term average to zero.

[1] G. R. Miller and H. S. Gutowsky, J. Chem. Phys. **39**, 1983 (1963).
[2] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).
[3] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. **18**, 162 (1950).

