1 Introduction

1.1 Perturbation

1.2 Electric Properties

In electric field $\mathbf{F}$:

$$E(\mathbf{F}) = E_0 - \mathbf{F}^{\mathrm{T}}\mathbf{d}_0 - \frac{1}{2}\mathbf{F}^{\mathrm{T}}\alpha\mathbf{F} + \mathcal{O}(\mathbf{F}^3) \tag{1}$$

where the molecular properties: permanent dipole moment $\mathbf{d}_0$ and polarisability tensor α are:

$$\mathbf{d}_0 = -\frac{\mathrm{d}E}{\mathrm{d}\mathbf{F}}\Big|_{\mathbf{0}} \tag{2}$$

$$\alpha = -\frac{\mathrm{d}^2E}{\mathrm{d}\mathbf{F}^2}\Big|_{\mathbf{0}} \tag{3}$$

1.3 Magnetic Properties (Closed-Shell)

For an NMR experiment on closed-shell systems, we have:

- Closed-shell system
- Static external magnetic field $\mathbf{B}$
- a set of nuclear magnetic moments $\mathbf{M}_K$

With these conditions:

$$E(\mathbf{B}, \mathbf{M}_K) = E_0 + \frac{1}{2}\mathbf{B}^{\mathrm{T}}\mathbf{E}^{(20)}\mathbf{B} + \sum_K \mathbf{B}^{\mathrm{T}}\mathbf{E}_K^{(11)}\mathbf{M}_K + \sum_{K>L} \mathbf{M}_K^{\mathrm{T}}\mathbf{E}_{KL}^{(02)}\mathbf{M}_L \tag{4}$$

No first-order term since it vanishes for closed-shell systems (explained in section 4), and the higher order properties are neglected. The properties:

- magnetisability tensor (direct interaction of the system with external field $\mathbf{B}$):

$$\mathbf{E}^{(20)} = \xi = -\frac{\mathrm{d}^2E}{\mathrm{d}\mathbf{B}^2}\Big|_{\mathbf{0}} \tag{5}$$

- coupling of magnetic moment $\mathbf{M}_K$ to field $\mathbf{B}$:

$$\mathbf{E}_K^{(11)} = \frac{\mathrm{d}^2E}{\mathrm{d}\mathbf{M}_K\,\mathrm{d}\mathbf{B}} = -\mathbf{I}_3 + \sigma_K \tag{6}$$

  where σ_K is the nuclear magnetic shielding tensor

- coupling between nuclear magnetic moments:

$$\mathbf{E}_{KL}^{(02)} = \frac{\mathrm{d}^2E}{\mathrm{d}\mathbf{M}_K\,\mathrm{d}\mathbf{M}_L}\Big|_0 = \frac{\mu_0}{4\pi}\frac{R_{KL}^2\mathbf{I}_3 - 3\mathbf{R}_{KL}\mathbf{R}_{KL}^{\mathrm{T}}}{R_{KL}^5} + \mathbf{K}_{KL} \tag{7}$$

  the first term is the classical direct dipole-dipole interaction between $\mathbf{M}_K$ and $\mathbf{M}_L$ and the second term is the indirect nuclear spin-spin coupling tensor