Direct dipole-dipole coupling and the magic angle as they pertain to solid state NMR

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Abstract:

Direct dipole-dipole coupling and magic angle spinning (MAS) are two very important concepts in solid state NMR. Some of the most common pulse sequences used in solid state NMR often take advantage of the dipolar coupling in order to gather unique spatial or dynamical information about the sample. MAS allows for a much better resolution in most of the NMR experiments due to the motional averaging of the dipolar interactions, and the chemical shift anisotropy.

Direct dipole-dipole coupling:

Direct dipole-dipole couplings between spins arise due to the fact that each nuclear spin generates a magnetic field, which can in turn interact the magnetic field generated by other nuclei. This is a direct, through space interaction between nuclear spins and does not involve the electron clouds,[1] as the example shows below in Figure 1. This is an interaction of interest for NMR because the Larmor frequency of a nuclear spin, given by Equation 1, depends directly on the magnetic field that the nuclear spin is experiencing.[2]

$$\omega_0 = -\gamma B_0 \qquad (1)$$

Where ω_0 is the Larmor frequency in rad/s, γ is the gyromagnetic ratio of the nucleus, and B_0 is the strength of the magnetic field.

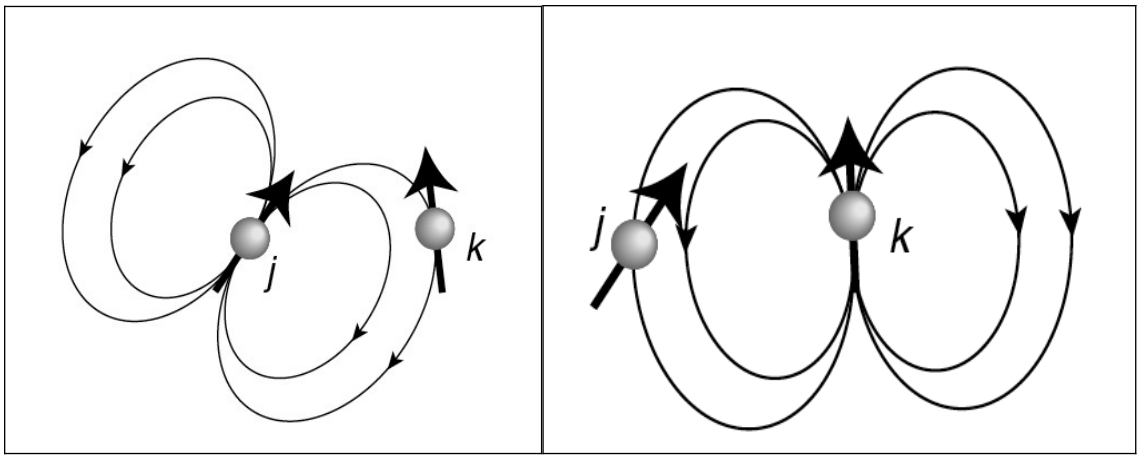

Figure 1. Diagram of how the magnetic fields generated by two nuclear spins can interact with each other. The left diagram shows how spin j interacts with spin k, and the right diagram shows how spin k interacts with spin j. (Reproduced from reference 1.)

Taking direct dipole-dipole couplings into account is more important in samples in the solid state than in the liquid state, due to the fact that in an isotropic liquid the dipole-dipole couplings average to zero. This averaging is mostly due to the random motion of the nuclei when in an isotropic liquid environment. The full Hamiltonian describing dipole-dipole coupling between spins $\mathbf{I}_j$ and $\mathbf{I}_k$ is shown below[1]:

$$H_{jk}^{DD,full} = b_{jk}(3(\mathbf{I}_j \cdot \mathbf{e}_{jk})(\mathbf{I}_k \cdot \mathbf{e}_{jk}) - \mathbf{I}_j \cdot \mathbf{I}_k) \quad (2)$$

Where $\mathbf{e}_{jk}$ is the unit vector connecting spins $\mathbf{I}_j$ and $\mathbf{I}_k$ (as shown below in Figure 2) and b_{jk} is the dipole-dipole coupling constant given by the following expression:

$$b_{jk} = -\frac{\mu_0}{4\pi}\frac{\gamma_j \gamma_k h}{r_{jk}^3} \quad (3)$$

Where μ_0 is the magnetic constant, γ_j and γ_k are the gyromagnetic ratios of the spins and r_{jk} is the distance between the two spins.[1] This dipole-dipole coupling constant is responsible for the magnitude of the dipole-dipole interaction.

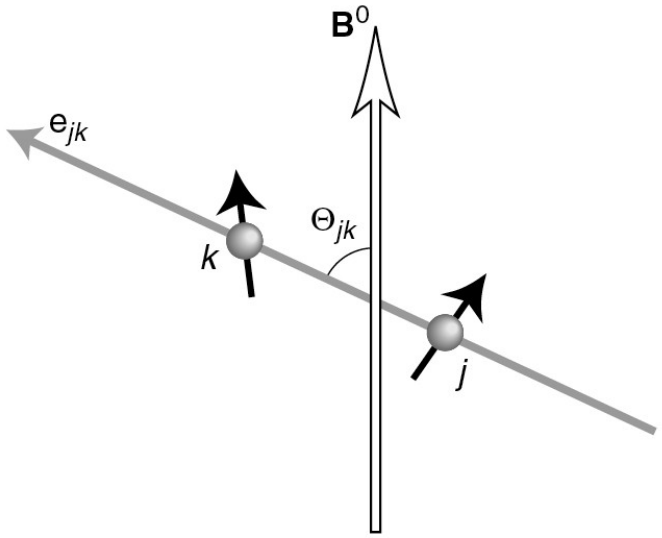

Figure 2. A graphical representation of two spins j and k in the presence of a magnetic field B^0.

When moving to deal with many spin systems it becomes necessary to deal with the secular dipole-dipole coupling rather than the direct dipole-dipole coupling between each pair of spins. This secular coupling's magnitude is determined by the tern d_{jk} which is given by the following expression:

$$d_{jk} = b_{jk}\frac{1}{2}(3cos^2\Theta_{jk} - 1) \tag{4}$$

Where b_{jk} is the previously defined direct dipole-dipole coupling constant, and Θ_{jk} is the angle that the vector $\mathbf{e}_{jk}$ connecting the spins of interest makes with the magnetic field B^0 (as shown above in Figure 2.) The dependence of the secular dipolar coupling on the distance between the 2 interacting spins is shown below in Figure 3. This plot shows that there is a very rapid drop off of dipolar coupling

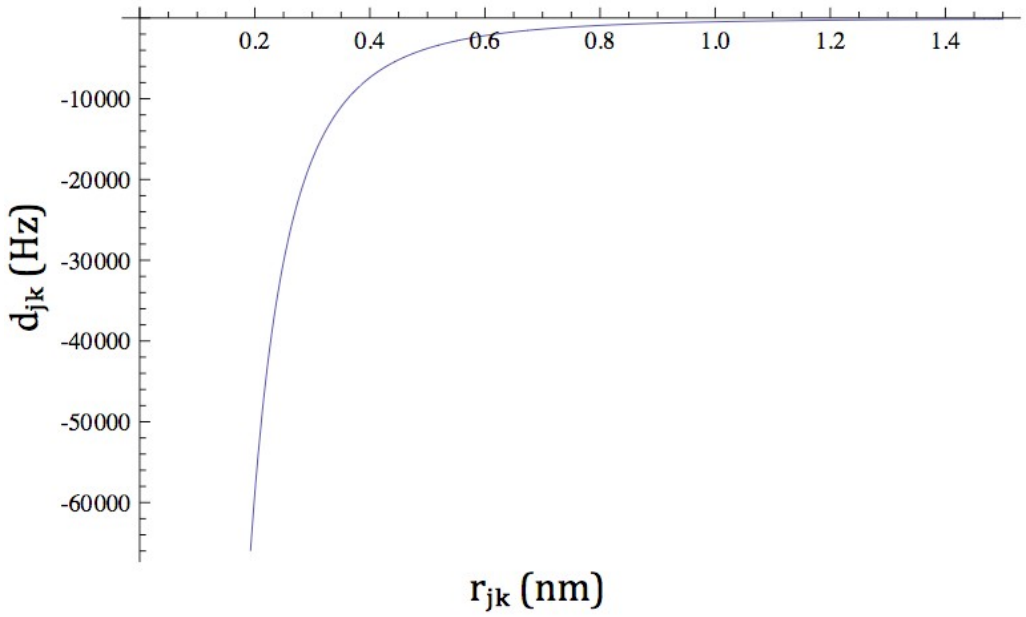

Figure 3. A plot of the secular dipolar coupling constant as a function of distance between the interacting spins.

Upon inspection of this equation it can be seen that there will be values for Θ_{jk} which will result in the magnitude of the dipolar coupling to be zero. The solution to this geometric problem is called the "magic angle" and is defined below:

$$3cos^2\Theta_{jk} - 1 = 0 \tag{5}$$

$$\Theta_{MA} = arctan\sqrt{2} = 54.74^o \tag{6}$$

This result can also be observed graphically, as shown below in Figure 4. The two interceptions of the x-axis represent the angles at which the secular dipolar coupling constant is zero.

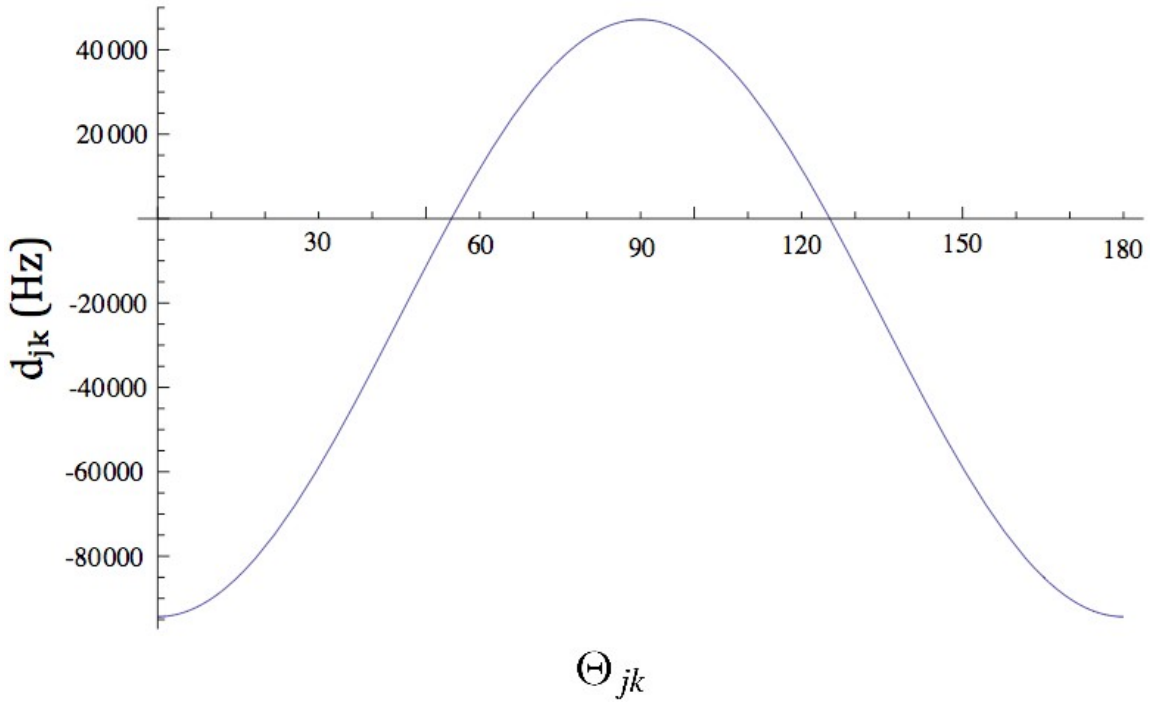

Figure 4. A plot of the secular dipolar coupling constant as a function of the angle between the vector connecting the two interacting spins and the magnetic field (Θ_{jk}); which is defined graphically in Figure 2.

The important application of the magic angle in solid state NMR is the implementation of magic angle spinning.[3] Due to the logistical inability to effectively spatially average these interactions completely isotropically, emulating a liquid, the sample is spun about an axis. This allows for the rotational averaging of dipolar interactions in all of the directions except for interactions parallel with the spinning axis. If this spinning sample is tilted such that it axis of rotation is at the magic angle with respect to the magnetic field, then the non-averaged interactions along the spinning axis of the sample will drop to zero.

References:

[1].) Levitt, M. H. Spin Dynamics: 2nd Edition. **2008,** John Wiley and Sons, Ltd. West Sussex, UK.
[2].) Keeler, J. Understanding NMR spectroscopy: 2nd Edition. **2010,** John Wiley and Sons, Ltd.
[3].) Jaing, Y. J.; Harper, J. K. *Concepts Magn. Reson.* **2009,** *35A*, 249-263.