



Nuclear Magnetic Shieldings and Molecular Structure

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EVALUATION OF CHEMICAL SHIFTS IN SOLID STATE NMR BY ELECTRONEGATIVITY EQUALIZATION PRINCIPLE

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The principle of the chemical shifts evaluation in solid state NMR relies on the atoms charge estimation in a lattice. The way those charges are calculated uses the electronegativity equalization principle¹:

$$\chi_i = \chi_i^0 + \eta_i q_i + \frac{e^2}{4\pi\epsilon_0} \sum V_{i,j} q_j = \langle \chi \rangle \quad i \in [1, n], \text{ with the charge conservation, } \sum_{i=1}^n q_i = 0$$

The electronegativities and hardnesses χ_i^0 and η_i are evaluated from Bratsch². The potential V_{ij} is due to all the charges of the lattice and is evaluated following Bertaut³. Identification of the global hardness to the difference in energy between the HOMO and the LUMO orbitals has been proposed by Pearson⁴. We propose to identify this hardness η to the mean excitation energy ΔE of the second-order perturbation theory of the chemical shift.

This global hardness is given by $\frac{1}{\eta} = \frac{1}{M} \sum_{i=1}^n \frac{1}{\eta_i}$ following Yang et al.⁵. Therefore, the system of equations

equalizing the electronegativity can be solved, and provides the charges q_i for each atom, the mean electronegativity $\langle \chi \rangle$, the mean hardness $\langle \eta \rangle = \Delta E$. It is therefore possible to try to explicit the dependancies of the chemical shift as a function of the charges. If we use the Jameson Gutowsky relation of the paramagnetic contribution:

$$\sigma^p = k \cdot \frac{\langle r^{-3} \rangle_p P_u}{\Delta E}$$

then, we can describe some limit cases.

In the case of C3S (3CaO.SiO₂), there are 83 inequivalent atoms. The X-ray structure is known and has been used to estimate the charges. The ²⁹Si MAS spectrum shows off the nine different silicons. The chemical shifts have then been plotted as a function of the charge. Actually the δ range is very small, and in such a small domain, this ranking of the chemical shifts shall be legitimate. A linear relation is obtained: $\delta = -96.3q - 13.2$ ppm. The following assignment of the sites can therefore be proposed as Si9, Si1, Si2, Si3, Si7, Si5, Si8 and Si4 in order of decreasing chemical shift with increasing the partial charge.

In the case of a series of oxides the chemical shifts of which have been published^{6,7} and the structures known, ΔE has been evaluated. A plot of the chemical shift versus these ΔE values provides the following relationship: $\delta = -2416 + 21970/\Delta E$ (ΔE in eV).

Some other relations have been tested where $\langle r^{-3} \rangle$, P_u and ΔE are expressed as functions of the charge of the atom chosen for chemical shift evaluation⁸.

This method provides then the possibility to calculate the charges as a function of the entire lattice and to estimate locally the effect of the charges on each component defining the chemical shift. The only necessary inputs are a correct X-ray structure and an electronegativity scale.

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