

Supermolecular calculations of intermolecular interaction effects on NMR properties: Examples on liquid water and gaseous xenon

Juha Vaara,^a Teemu S. Pennanen,^{ab} Matti Hanni^{ab} and Perttu Lantto^b

^aLaboratory of Physical Chemistry and Center of Excellence in Computational Molecular Science, Department of Chemistry, University of Helsinki, Finland

^bNMR Research Group, Department of Physical Sciences, University of Oulu, Finland
E-mail: juha.t.vaara@helsinki.fi

One of the challenges of experiment-oriented quantum-chemical modelling of nuclear magnetic resonance (NMR) parameters is the fact that experimental data are taken in liquid solution, solid state, or at best from the point of view of theory, in a low-pressure gas phase, making it necessary to include intermolecular interaction effects. The analytical reaction field model fails to provide satisfactory modification of NMR data, due to its inability to describe the short-range, specific solvation. This leaves the supermolecular method as a conceptually simple approach whereby both local and long-range environmental effects on NMR properties can be captured. In order to model the effects of solvation dynamics it is mandatory to average over configurations taken from, *e.g.*, a molecular dynamics (MD) simulation trajectory.

In my talk I will describe two applications of the supermolecule method to environmental effects on NMR parameters, investigated in my group. In the first project [1], finite clusters sampled from a density-functional theory-based Car-Parrinello MD trajectory of liquid water at ambient conditions are fed into a hybrid reaction-field model to capture the gas-to-liquid shifts of ¹/₂H and ¹⁷O NMR shielding and quadrupole coupling. By the use of the Eckart coordinate frame it is possible to obtain, for the first time, dynamically averaged solvation effects for the individual components of the property tensors. Two-, three-, four-, and five-fold coordinated water molecules present in the liquid are analysed separately to shed light on the effect of the local coordination and hydrogen bonding pattern on the local probe furnished by NMR.

NMR of guest noble gas atoms, particularly that of ¹²⁹Xe, is used as a non-invasive probe of the local structure of different host materials: liquids, liquid crystals, molecular sieves, clathrates, and solid surfaces. Principles of the adsorption and solvation shifts of ¹²⁹Xe are largely unknown, and even the prototype system of pure xenon gas poses a challenge to quantum-chemical modelling. In the second project to be discussed in the talk [2], the second virial coefficient of ¹²⁹Xe shielding in the low-pressure gas phase — where pairwise interaction effects provide the leading deviation from the ideal gas behaviour — is investigated using a hierarchy of *ab initio* methods for both the inter-atomic potential energy curve and the binary shielding function. The hitherto best agreement with the existing, very accurate experimental data is obtained at coupled-cluster level of theory, greatly surpassing what can be achieved at the density-functional theory level. As a by-product, the so far most accurate purely theoretical potential energy function is obtained for Xe₂.

- [1] T. S. Pennanen, J. Vaara, P. Lantto, A. J. Sillanpää, K. Laasonen, and J. Jokisaari, *Journal of the American Chemical Society* **126**, 11093 (2004).
- [2] M. Hanni, P. Lantto, N. Runeberg, J. Jokisaari, and J. Vaara, *Journal of Chemical Physics* **121**, 5908 (2004).