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Accounting for dynamical effects in *ab initio* NMR calculations MARK ROBINSON, University of Cambridge, UK, PETER HAYNES, Imperial College London, UK — The *ab initio* calculation of chemical shifts using density functional theory (DFT) is now routine. For many rigid crystals and molecules isotropic chemical shifts have been computed agreeing with experiment to better than 1ppm. However systems that exhibit greater dynamical motion, such as in biological systems, the computed shifts are found to be in error. We study an example of one such system, an L-Alanine molecular crystal, using the NMR-CASTEP code. A straightforward calculation results in a discrepancy between computed and experimental chemical shifts of nearly 4ppm. Previous work by Dumez and Pickard has shown that dynamics are a contributing factor to this error [1]. To incorporate dynamics into the calculation of the chemical shifts we average over an ensemble of configurations representational of the motion of the system. These configurations are generated using molecular dynamics (MD). This can pose a problem for *ab initio* MD since the time scale of such dynamics can be of the order of a picosecond. We overcome this by fitting a force field to DFT forces for the system under study. Classical MD is then used to generate uncorrelated configurations from which the chemical shifts are averaged. Using this procedure we are able to improve the computed chemical shifts for L-Alanine significantly. [1] J-N. Dumez and C.J. Pickard, J. Chem. Phys., 130 (2009) 104701.

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