Quantum Dynamical Effects on ^{3}He NMR in Endohedral Fullerenes

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The presence of a cavity inside fullerenes allows the introduction of guest atoms or small molecules inside the cage, *e.g.*, noble gas atoms such as ^{3}He [1], forming the so-called endohedral fullerenes. Experimentally observed ^{3}He NMR shift differences for fullerenes with one and two helium atoms [2] are here treated with path-integral Monte Carlo (PIMC) simulations of He and He_2 in neutral C_{60} and C_{70}, as well as their hexa-anions [3]. The potential energy (PES) and ^{3}He chemical shift surfaces are modelled at first-principles SCS-MP2 and DFT levels, respectively. The method provides information about the quantum dynamical effects of both helium and carbon atoms on ^{3}He NMR shifts at different temperatures.

With the efficient PIMC implementation, these pre-parametrised energy and NMR property surfaces also enable the study of *negative* thermal expansion (thermal contraction) of the C_{60} fullerene [3]. We can show that the effect is clearly observable in the ^{3}He NMR shift and we propose endohedral noble gas NMR as a complementary method to investigate the thermal expansion of fullerenes and other nanostructures with cavities in addition to Raman and infrared spectroscopies as well as noble gas EXAFS [4,5].

References

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