Nuclear Multipole Moments - A Torturous Way for Quantum Chemistry

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This talk gives an overview over different techniques to determine nuclear multipole moments indirectly from quantum chemical calculations of electric field gradients and higher derivatives for atoms, molecules and the solid state. For scalar relativistic calculations the recently developed point charge nuclear quadrupole moment (PCNQM) model in our group avoids the picture- change-error error for electric field gradients (EFG) which can be as high as the relativistic effects itself for heavy elements. The method is numerically stable and in perfect agreement with analytically derived expectation values. Hence for atoms and molecules including heavy elements accurate nuclear quadrupole moments can now be obtained. For the solid state the situation is less satisfying since currently the only reasonably accurate method is the density functional approximation. Here different density functionals lead to substantially different field gradients especially for transition element containing compounds. This rather erratic behaviour can be traced back to small errors in the molecular charge distribution caused by the exchange part of the functional. The many claims where a coupling between the electric third derivative (4th order tensor) and the nuclear hexadecapole moment has been observed turn out to be unsubstantiated. Such couplings are in the mHz range similar to parity violation effects and it will be difficult to observe such effects by rotational or NMR spectroscopy.