

Analytic DFT calculations of anharmonic force constants

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We present a recursive scheme for the analytic calculation of cubic and quartic force constants at the density functional level of theory[1] based on an open-ended, atomic-orbital-based scheme for calculating higher-order molecular properties.[2] All possible rules for eliminating response parameters using the $k(2n+1)$ rules[3] have been implemented, allowing for a stringent test of the correctness of the code and allowing us to explore the computational costs of different approaches for calculating higher-order molecular properties. The use of recursive programming allows for an open-ended, compact code, and we will present results for the sextic force constants at the Hartree–Fock level of theory.

The evaluation of one- and two-electron integrals differentiated with respect to geometrical perturbations follows the approach of Reine, Tellgren and Helgaker[4], integrating the differentiated integrals in Hermite rather than Cartesian orbital basis, as implemented in the Gen1Int[5] and a local two-electron integral program.[6] The contributions arising from derivatives of the exchange–correlation kernel are evaluated using automatic differentiation.[7]

In addition to outlining the key features of the approach for calculating analytic DFT cubic and quartic force fields, results for anharmonic force constants obtained both for small molecules and for molecular systems containing up to 10-20 atoms will be presented. The main focus of the discussion will be on the analysis of the importance of electron correlation, as described by DFT, on cubic and quartic force constants.

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