Intermolecular interaction energies from fourth order many-body perturbation theory. Impact of individual electron correlation contributions.

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The performance of Møller-Plesset perturbation theory methods for describing intermolecular interaction energies is investigated with the focus on illuminating the impact of individual electron correlation energy contributions in fourth order. While it is observed that for reproducing high level fifth order or coupled cluster interaction energies the inclusion of fourth order triples is mandatory, the decomposition of the fourth order singles (S), doubles (D), triples (T) and quadruples (Q) terms into their corresponding subterms revealed that individual terms from each excitation class can have a huge impact on the energy that is much larger than the total fourth order correlation contribution. A partial summation of S, D and Q terms can be derived that can reproduce the full fourth order interaction energies with a good accuracy and which does not include the computationally expensive triples energy term.