

Current Research Interests.

(last update 1/10-2014)

Developments of New Basis Sets for Electronic Structure Methods.

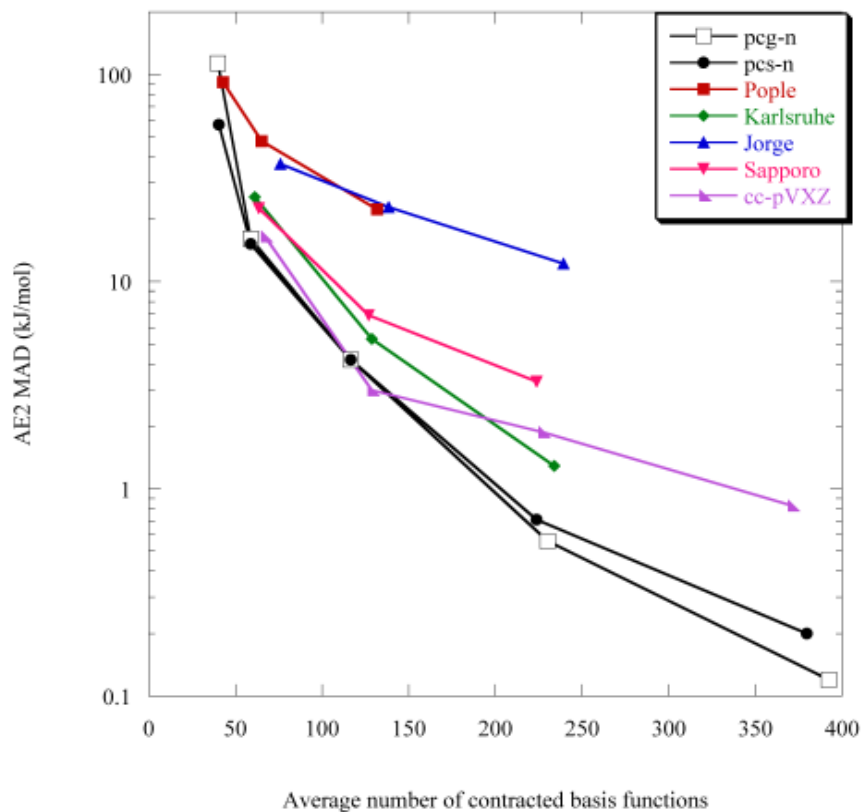
The electron correlation converges as an inverse power series in the highest angular momentum L included in the basis set.

$$\Delta E_{corr} = \frac{A}{L^3} + \frac{B}{L^4} + \frac{C}{L^5} + \dots$$

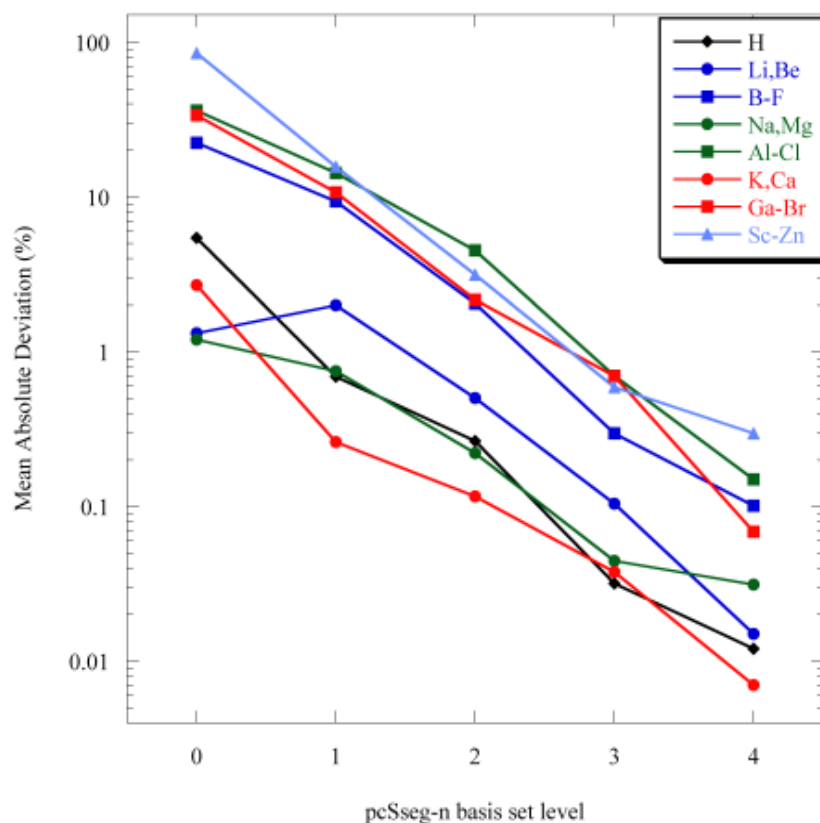
The corresponding convergence of Hartree-Fock (HF) and Density Functional Theory (DFT) energies is exponential-square-root.

$$\Delta E_{HF/DFT} = Ae^{-B\sqrt{L}}$$

This difference in convergence means that optimum basis sets for electron correlation and independent particle models (HF/DFT) are different. We have developed a hierarchy of new basis sets aimed at DFT methods, denoted *polarization consistent* (pc- n), where n (= 0,1,2,3,4) indicates the level of polarization beyond the isolated atom. The pc- n basis sets can be considered as HF/DFT equivalents of the correlation consistent basis sets cc-pVXZ for electron correlation methods. We have recently shown how general and segmented contraction can be unified, and this allowed construction of segmented contracted versions denoted pcseg- n . These basis set are currently defined for all atoms up to Kr and provide faster convergence than other basis sets for DFT energies.



Energy optimized basis sets, like cc-pVXZ and pcseg-*n*, are not necessarily optimum for calculating molecular properties. We have shown how the basis set errors for NMR properties (shielding and spin-spin coupling constants) can be substantially improved by adding selected tight basis functions and redefining the contraction, leading to the pcS-*n* and pcJ-*n* basis sets, and the former has recently been redefined in a segmented contracted version pcSseg-*n* for all atoms up to Kr.

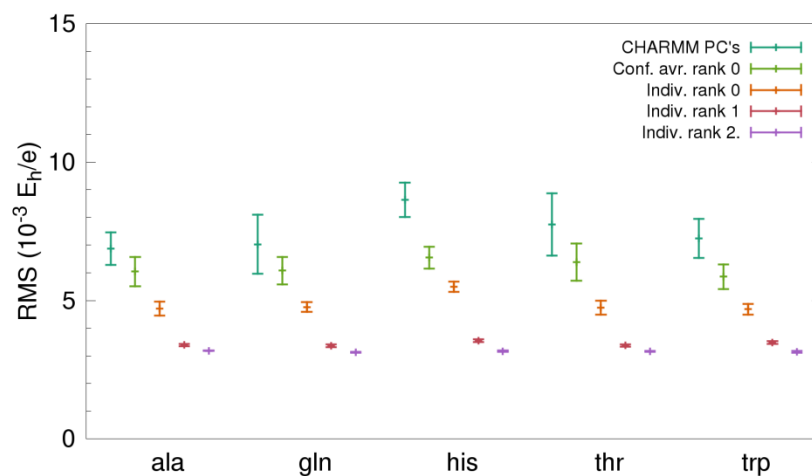


We may pick up on other molecular properties at some point.

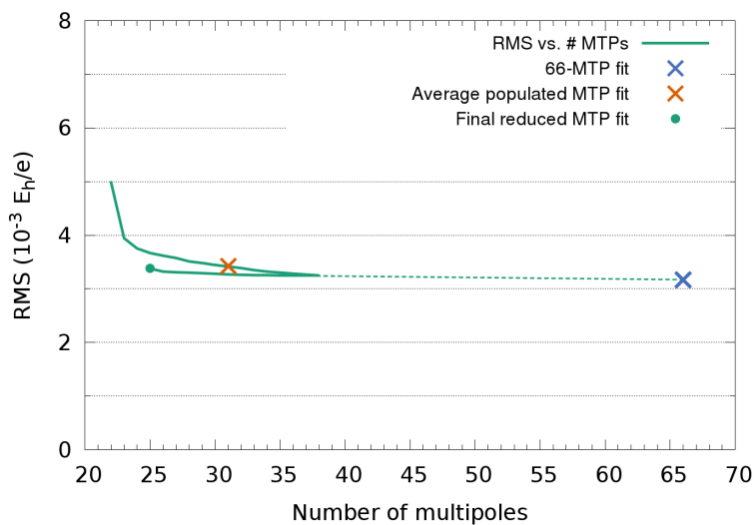
Developing Improved Force Fields.

All production type force fields (CHARMM, AMBER, GROMOS, OPLS) for simulations are class-I force fields employing fixed partial atomic charges for representing the electrostatic interactions. The neglect of higher order multipole moments and polarization is known to be the major source of error in simulations. This, among other things, leads to inaccurate relative energies for conformations and associated conformational transition states, which affects the dynamics.

The extension to include higher order atomic multipole moments and polarization is formally straightforward, but the convergence properties are largely unknown. Inclusion of atomic dipoles and quadrupoles reduces the fitting error of the electrostatic potential to roughly half, but it is unclear how to make further progress.



The large(r) number of parameters furthermore forms a near-redundant set, and we have recently shown that at least half of the charge/dipole/quadrupole moments can be removed with essentially zero penalty.



We are currently working on different strategies to derive a concise and non-redundant set of parameters for representing the electrostatic interaction, and hopefully that strategy can be used also for the other parameters in a force field.