Extrapolating to the basis set limit using PNO-MP2 pair energies

Kesha Sorathia and David Tew

Max Planck Institute for Solid State Research, Stuttgart

Abstract

The use of pair natural orbitals (PNOs) in the virtual space offers a way to control the accuracy of the electronic correlation energy through occupation number threshold. Exploiting this feature of PNOs we introduce using a single basis set and different PNO thresholds a two-point extrapolation scheme to approach the basis set limit of the pair correlation energies. We employ an extrapolation for pair correlation energies computed using PNO-MP2 with cc-pVxZ and cc-pVxZ-F12 basis sets on a set of 106 molecules reported in [1] and 105 arbitrary reactions involving those molecules for which the basis set limit MP2 valence pair correlation energies are known. We first studied the behaviour of error in total pair correlation energies with respect to the basis set limit as a function of average number of PNOs and also the behaviour of error in individual pair correlation energies as a function of number of PNOs on a test set of molecules for which the basis set limits with different methods are reported by Klopper [2]. For our extrapolation we use an expression which is related to the linear energy convergence behaviour of the basis sets and involves the number of PNOs N and a fitting parameter c: $E_{corr} = E(N) + cN^{-1}$. Two sequential occupation number threshold points are used in this scheme. The results are comparative with another two point method proposed by Helgaker et al [3] which involves extrapolation using correlation energies obtained from calculations with two correlation-consistent basis sets.

References

[1] D. Bakowies, "Extrapolation of electron correlation energies to finite and complete basis set targets," *The Journal of Chemical Physics*, vol. 127, no. 8, p. 084105, 2007.

[2] W. Klopper, "Highly accurate coupled-cluster singlet and triplet pair energies from explicitly correlated calculations in comparison with extrapolation techniques," *Molecular Physics*, vol. 99, no. 6, pp. 481–507, 2001.

[3] T. Helgaker, W. Klopper, H. Koch, and J. Noga, "Basis-set convergence of correlated calculations on water," *The Journal of Chemical Physics*, vol. 106, no. 23, pp. 9639–9646, 1997.