Supporting Information:

Exploring the Limits of Second- and Third-Order Møller-Plesset Perturbation Theory for Non-Covalent Interactions: Importance of Regularization and Reference Orbitals

Matthias Loipersberger,[†] Luke W. Bertels,[†,‡] Joonho Lee,[*,†,¶] and Martin Head-Gordon[*,†,§]

†Department of Chemistry, University of California, Berkeley, California 94720, USA

‡Present Address: Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, USA

¶Present Address: Department of Chemistry, Columbia University, NY

§Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

E-mail: jlee7@berkeley.edu; mhg@cchem.berkeley.edu

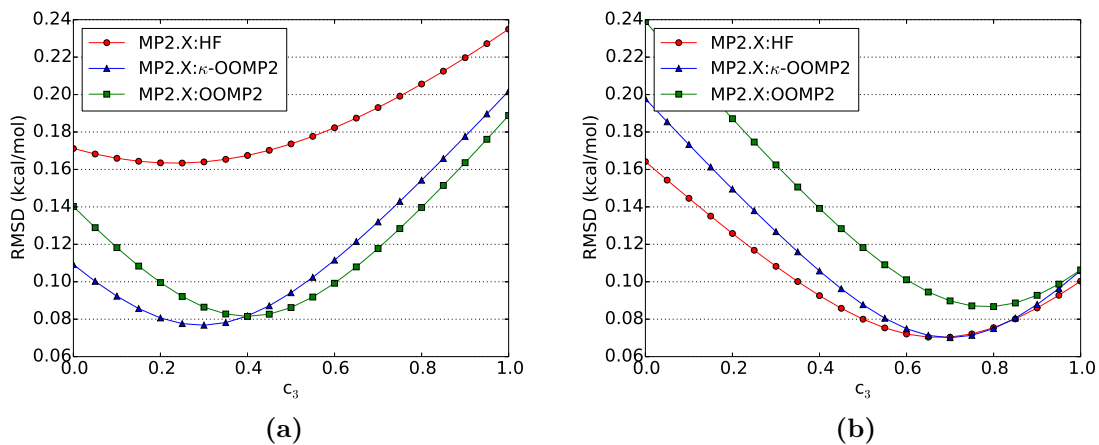# 1 Optimal c_3 Coefficients

Figure S1: Dependence of the the root-mean square deviation on the scaling of the third-order energy (c_3) in the A24 data set aTZ with CBS reference (a); aTZ with aTZ reference (b); RMSD in kcal/mol; four scaled MP2.X methods (MP2.X, MP2.X:OOMP2, MP2.X:κ-OOMP2).
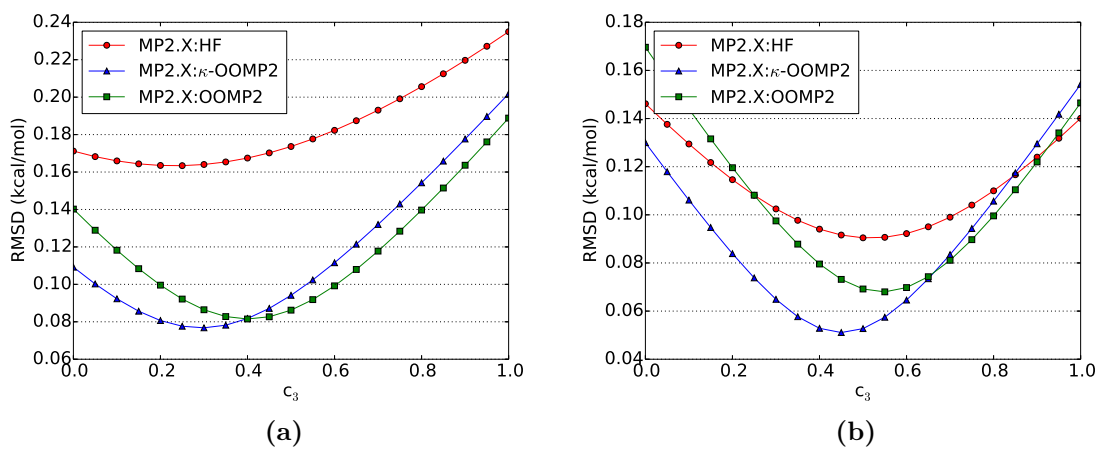
Figure S2: Dependence of the the root-mean square deviation on the scaling of the third-order energy (c_3) in the A24 data set aTZ with CBS reference (a); aQZ with CBS reference (b); RMSD in kcal/mol; four scaled MP2.X methods (MP2.X, MP2.X:OOMP2, MP2.X:κ-OOMP2).
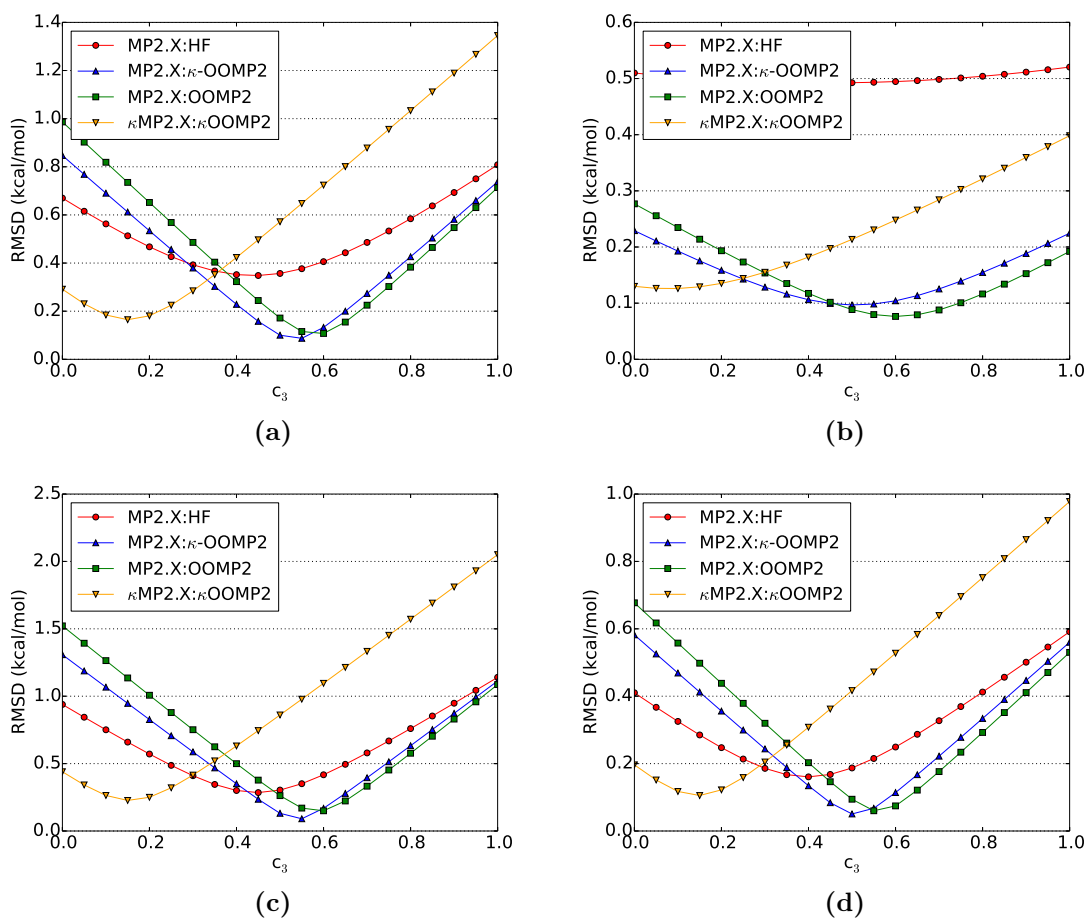
Figure S3: Dependence of the the root-mean square deviation on the scaling of the third-order energy (c_3) in the S66 data set (a) and the three subgroups hydrogen bonding (b), dispersion (c) and mixed (d); RMSD in kcal/mol; four scaled MP2.X methods (MP2.X, MP2.X:OOMP2, MP2.X:κ-OOMP2, κMP2.X:κ-OOMP2).
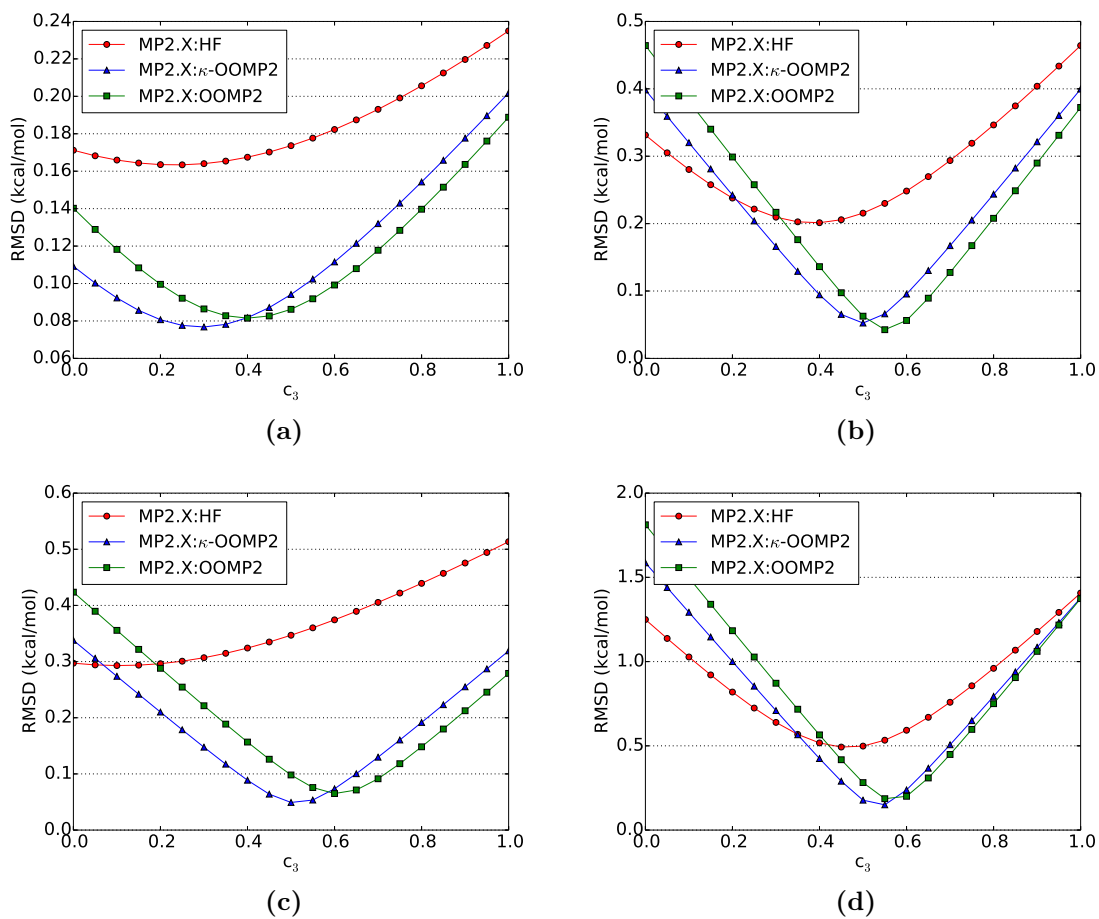
Figure S4: Dependence of the the root-mean square deviation on the scaling of the third-order energy (c_3) in the A24 (a), DS14 (b), HSG (c) and S22 (d) data sets; RMSD in kcal/mol; four scaled MP2.X methods (MP2.X, MP2.X:OOMP2, MP2.X:κ-OOMP2, κMP2.X:κ-OOMP2).
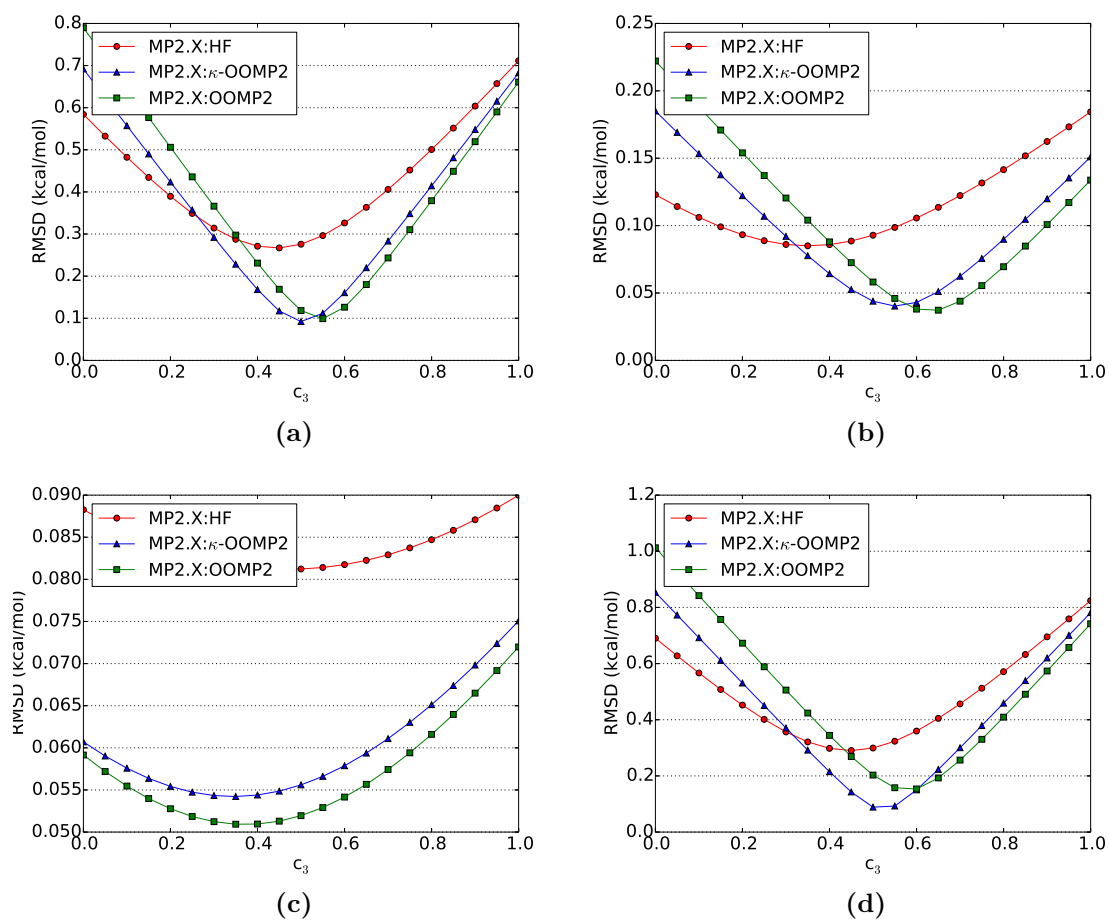
Figure S5: Dependence of the the root-mean square deviation on the scaling of the third-order energy (c_3) in the X40 (a), HW30 (b), NC15 (c) and AlkBind12 (d) data sets; RMSD in kcal/mol; four scaled MP2.X methods (MP2.X, MP2.X:OOMP2, MP2.X:κ-OOMP2, κMP2.X:κ-OOMP2).
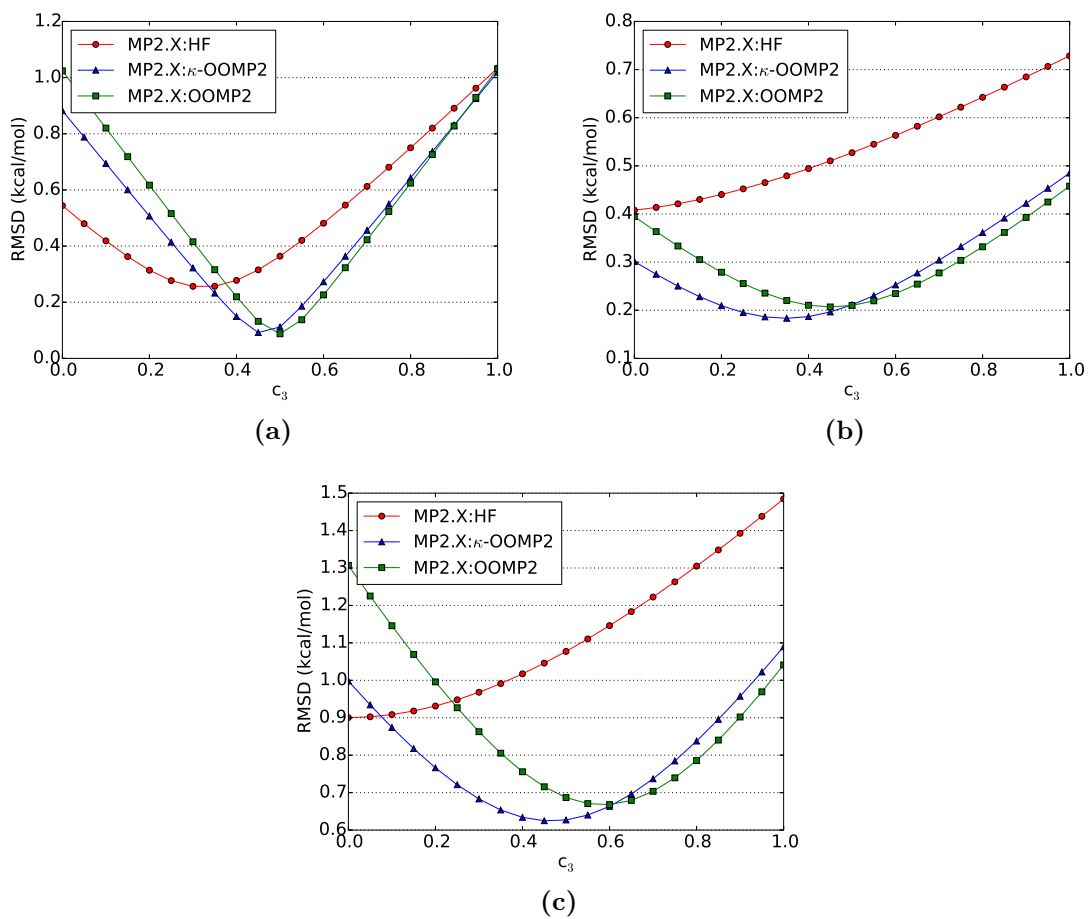
(a)

(b)

(c)

Figure S6: Dependence of the the root-mean square deviation on the scaling of the third-order energy (c_3) in the CO2Nitrogen16 (a), HB49 (b) and Ionic43 (c) data sets; RMSD in kcal/mol; four scaled MP2.X methods (MP2.X, MP2.X:OOMP2, MP2.X:κ-OOMP2, κMP2.X:κ-OOMP2).
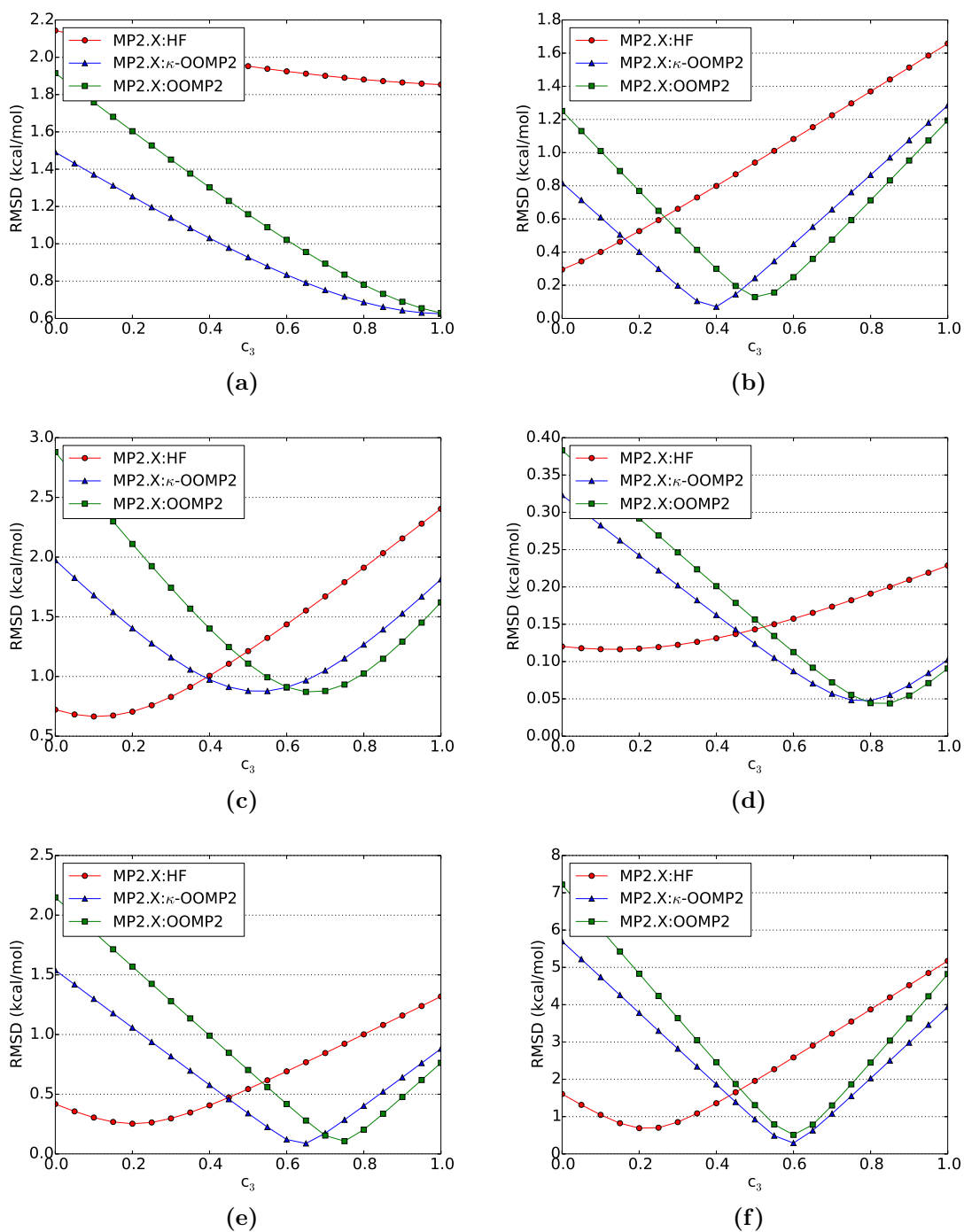
Figure S7: Dependence of the the root-mean square deviation on the scaling of the third-order energy (c_3) in the TA13 (a), HB49 (b), Bauza30 (c), CT20 (d) data sets, XB51 (e) and Orel26rad (f); RMSD in kcal/mol; four scaled MP2.X methods (MP2.X, MP2.X:OOMP2, MP2.X:κ-OOMP2, κMP2.X:κ-OOMP2).
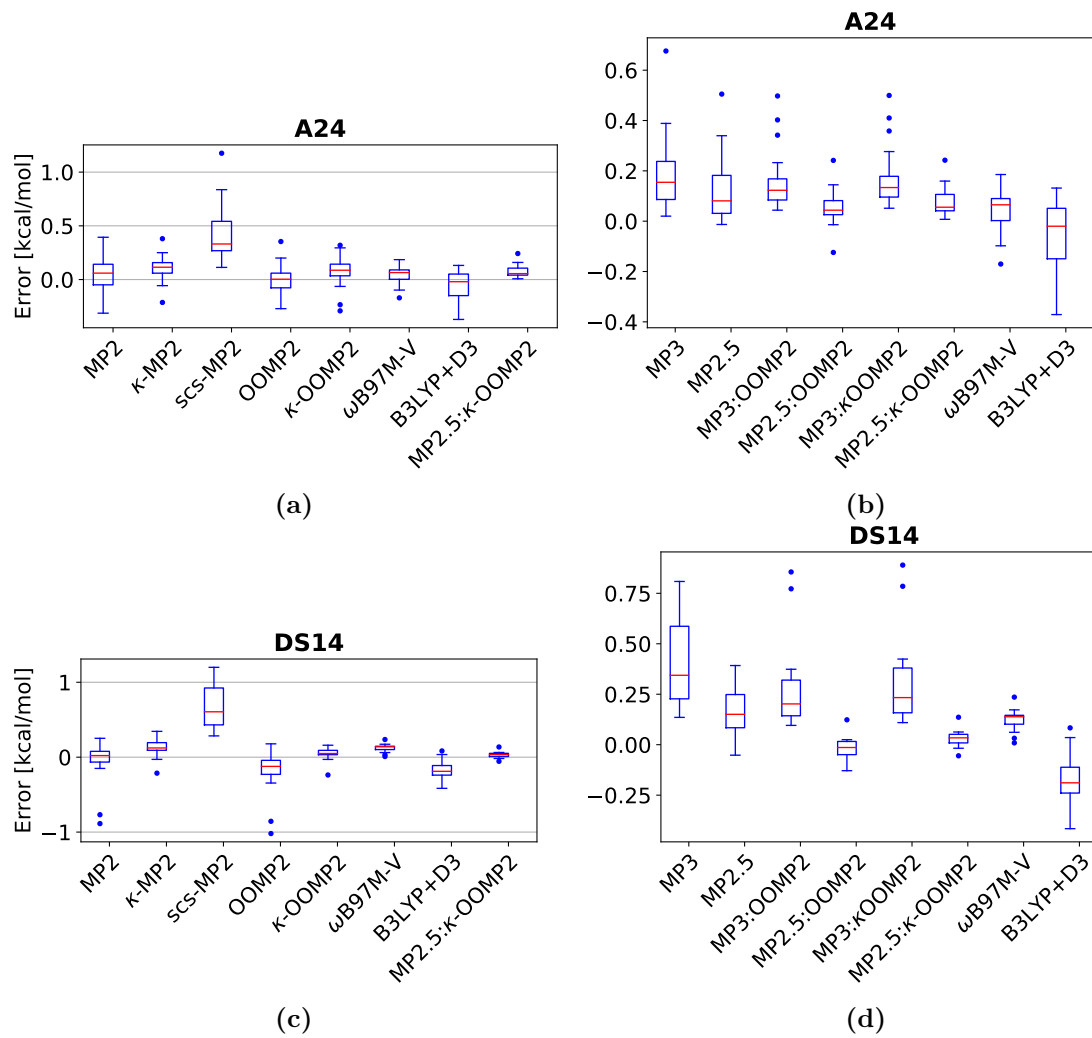
2 Box Plots

Figure S8: Box-plots of the data-sets A24: (a) MP2 methods, (b) MP3 methods; DS14: (c) MP2 methods, (d) MP3 methods. Red lines mark the median deviation, boxes bound the central 50% of the data, whiskers enclose all data points within 1.5 times the inter-quartile range of the box edges, and points denote outlying data.
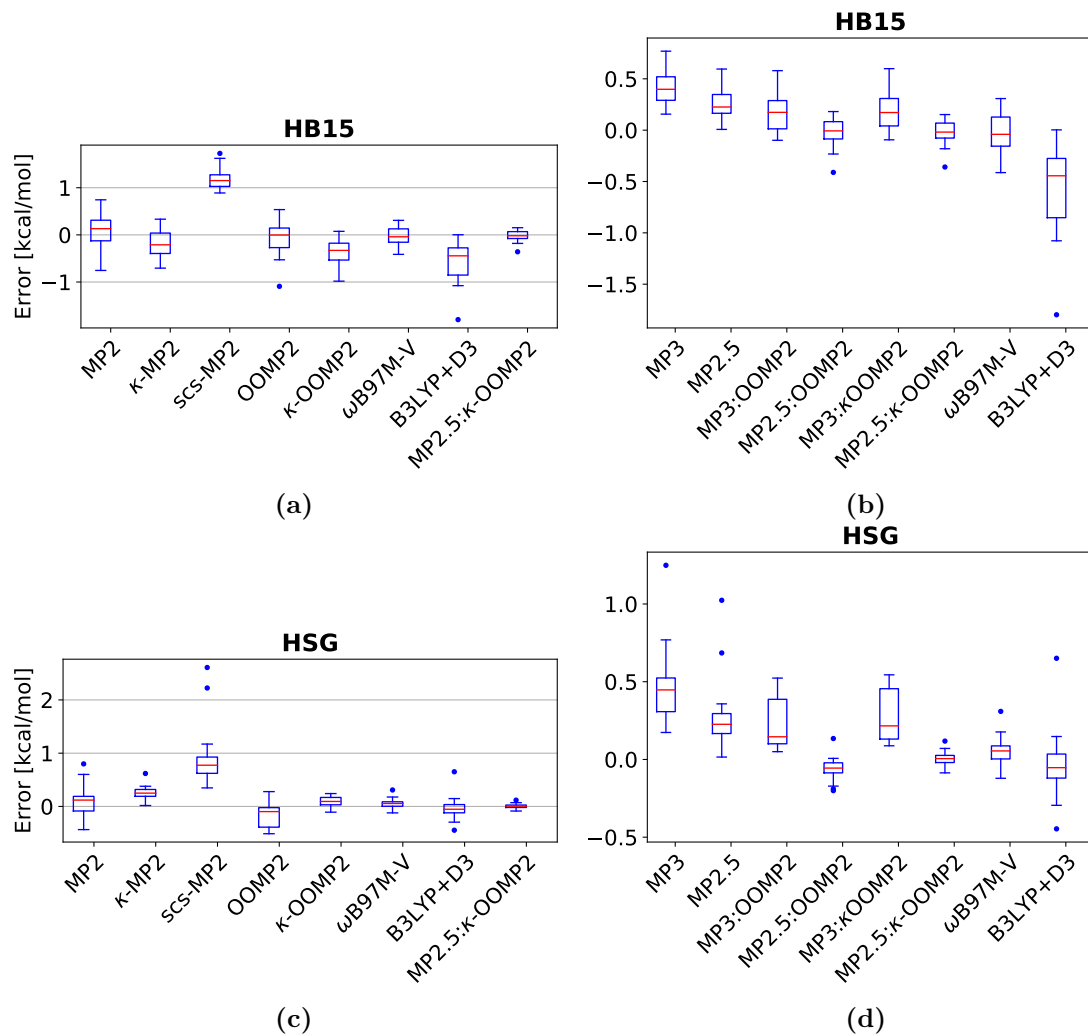
(a)

(b)

(c)

(d)

Figure S9: Box-plots of the data-sets HB15: (a) MP2 methods, (b) MP3 methods; HSG: (c) MP2 methods, (d) MP3 methods. Red lines mark the median deviation, boxes bound the central 50% of the data, whiskers enclose all data points within 1.5 times the inter-quartile range of the box edges, and points denote outlying data.
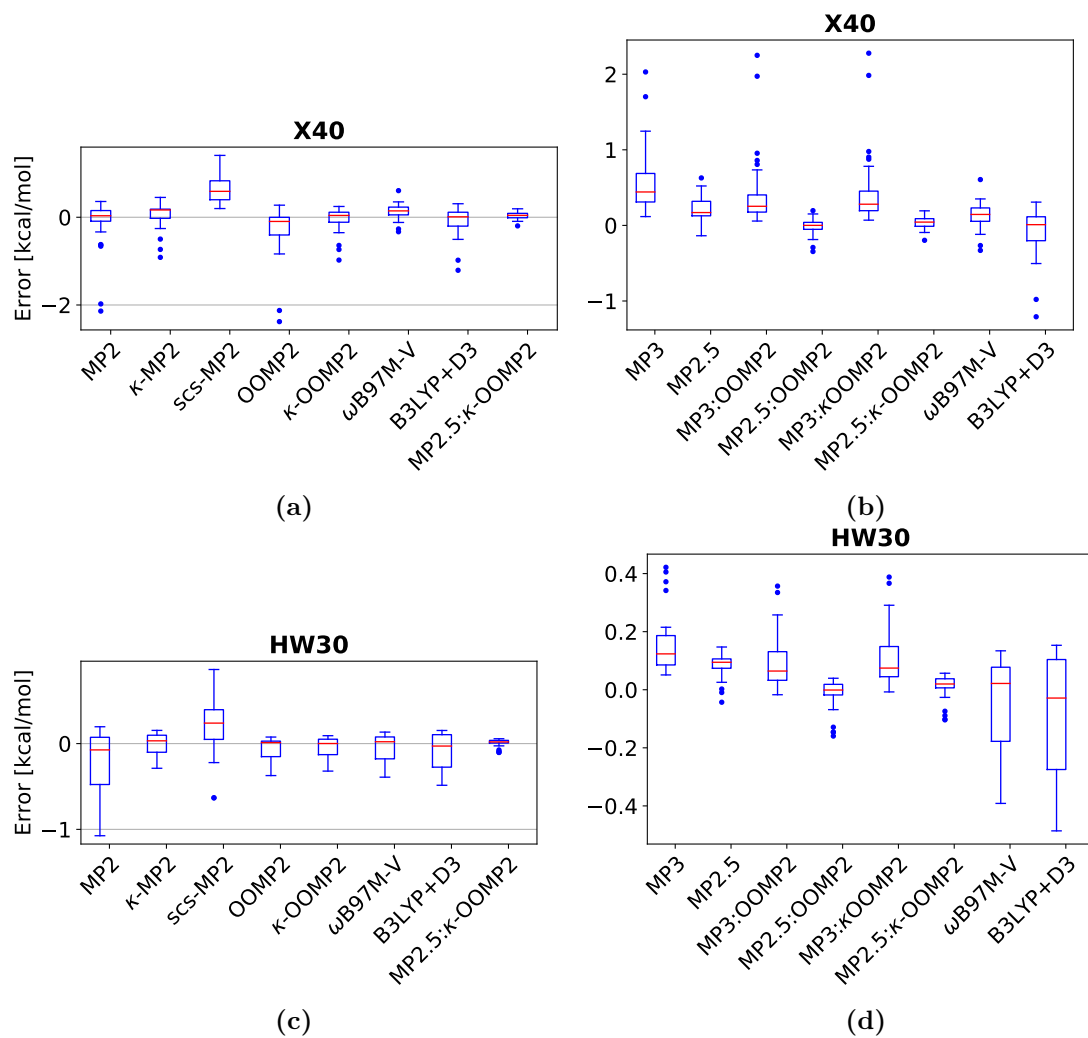
Figure S10: Box-plots of the data-sets X40: (a) MP2 methods, (b) MP3 methods; HW30: (c) MP2 methods, (d) MP3 methods. Red lines mark the median deviation, boxes bound the central 50% of the data, whiskers enclose all data points within 1.5 times the inter-quartile range of the box edges, and points denote outlying data.
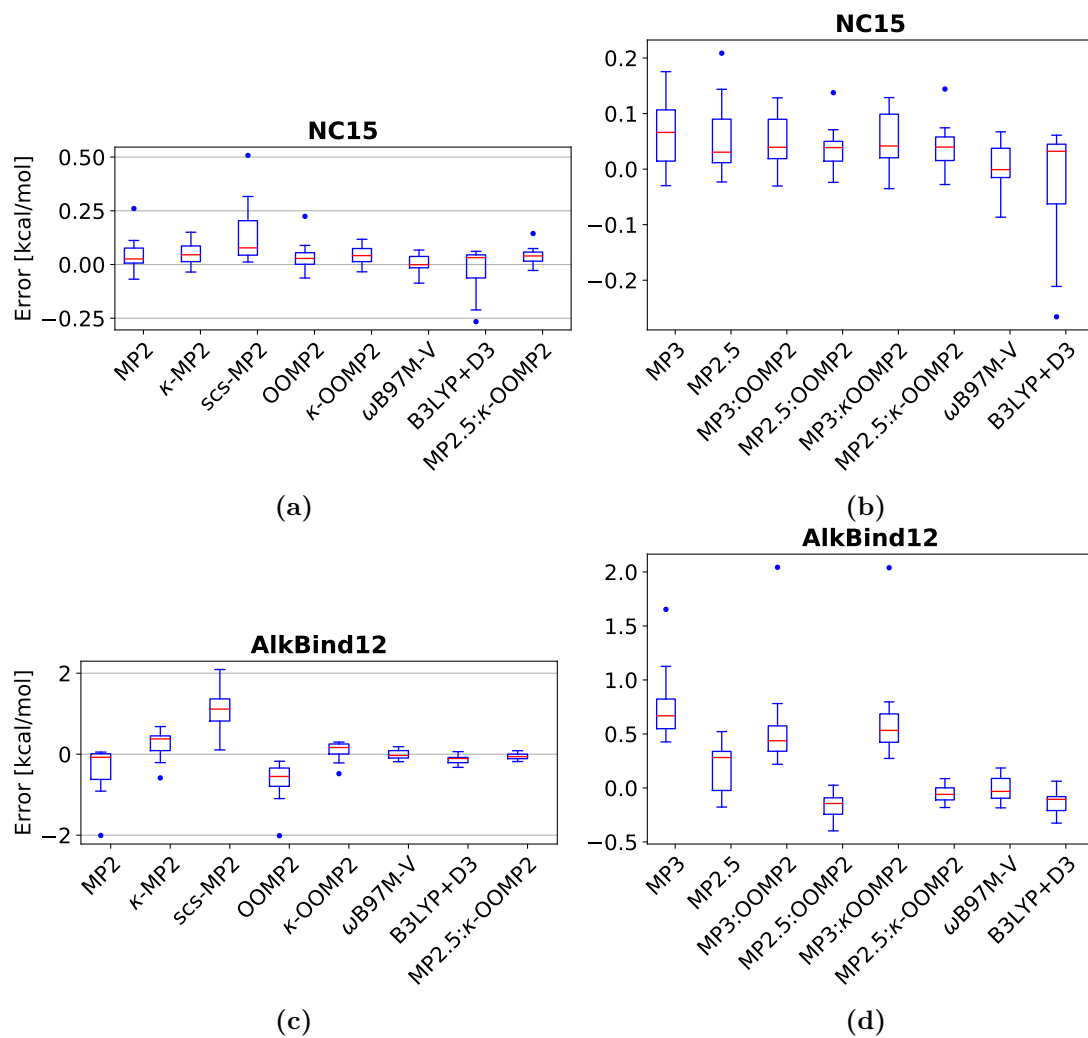
Figure S11: Box-plots of the data-sets NC15: (a) MP2 methods, (b) MP3 methods; AlkBind12: (c) MP2 methods, (d) MP3 methods. Red lines mark the median deviation, boxes bound the central 50% of the data, whiskers enclose all data points within 1.5 times the inter-quartile range of the box edges, and points denote outlying data.
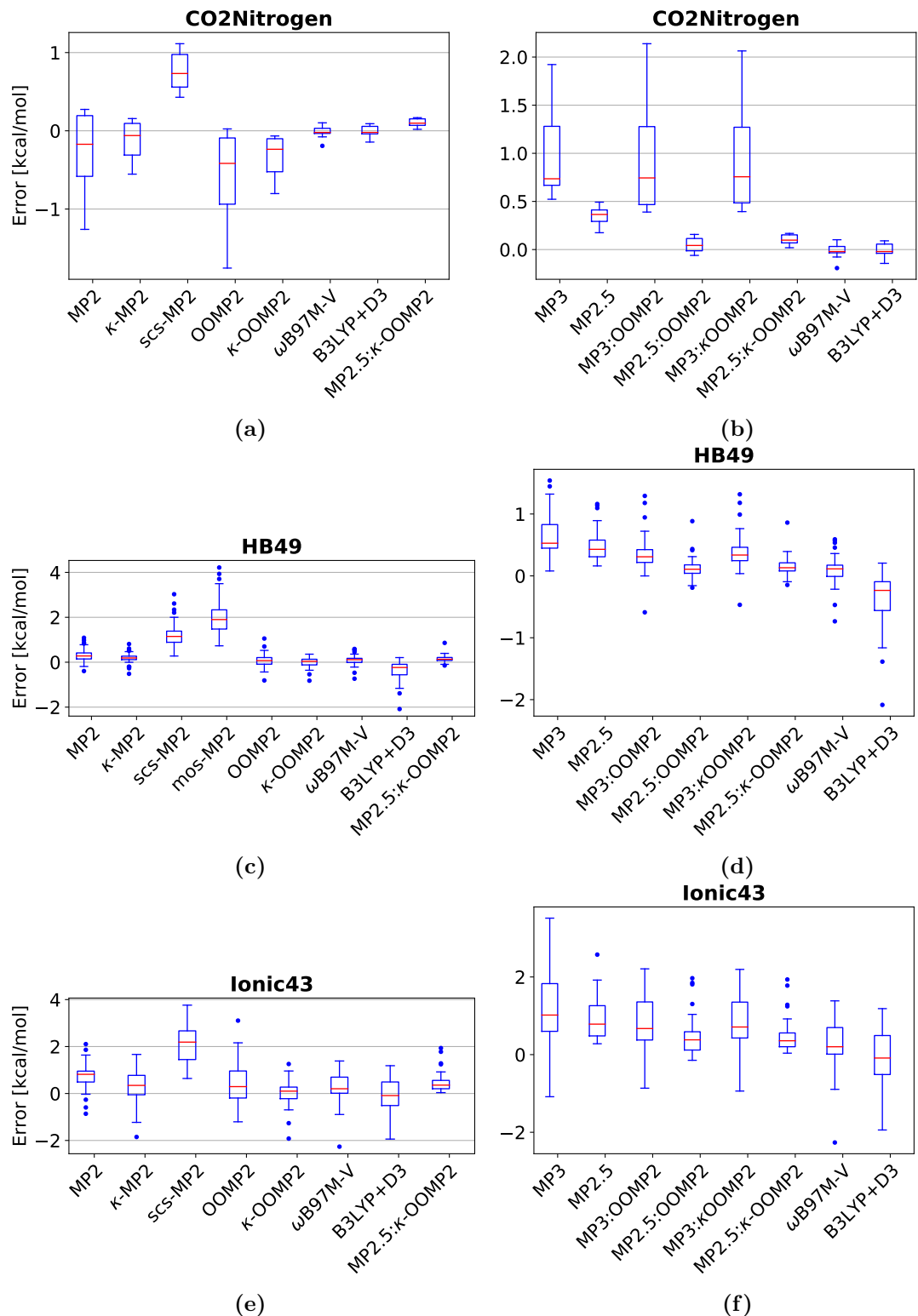
Figure S12: Box-plots of the data-sets CO2Nitrogen16: (a) MP2 methods, (b) MP3 methods; HB49: (c) MP2 methods, (d) MP3 methods; Ionic43: (e) MP2 methods, (f) MP3 methods. Red lines mark the median deviation, boxes bound the central 50% of the data, whiskers enclose all data points within 1.5 times the inter-quartile range of the box edges, and points denote outlying data.
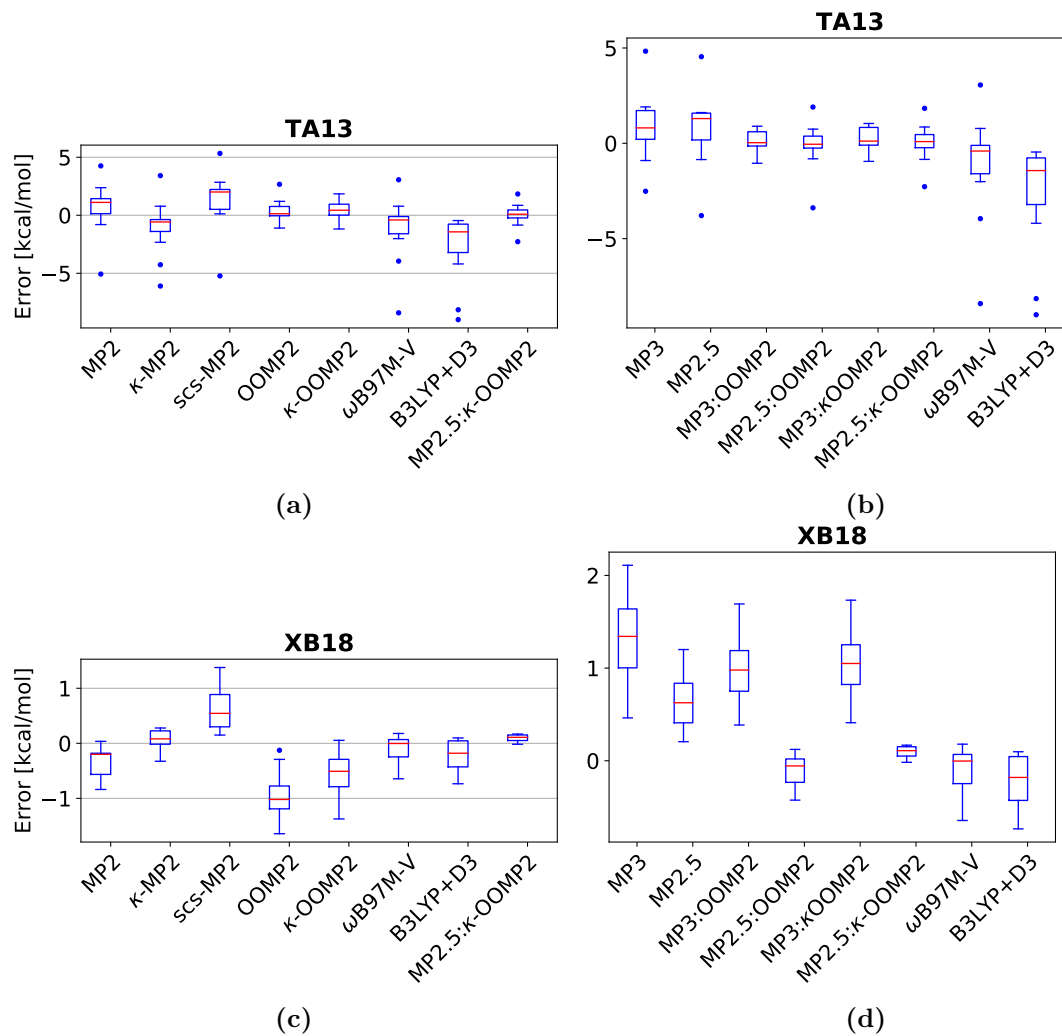
Figure S13: Box-plots of the data-sets TA13: (a) MP2 methods, (b) MP3 methods; XB18: (c) MP2 methods, (d) MP3 methods. Red lines mark the median deviation, boxes bound the central 50% of the data, whiskers enclose all data points within 1.5 times the inter-quartile range of the box edges, and points denote outlying data.
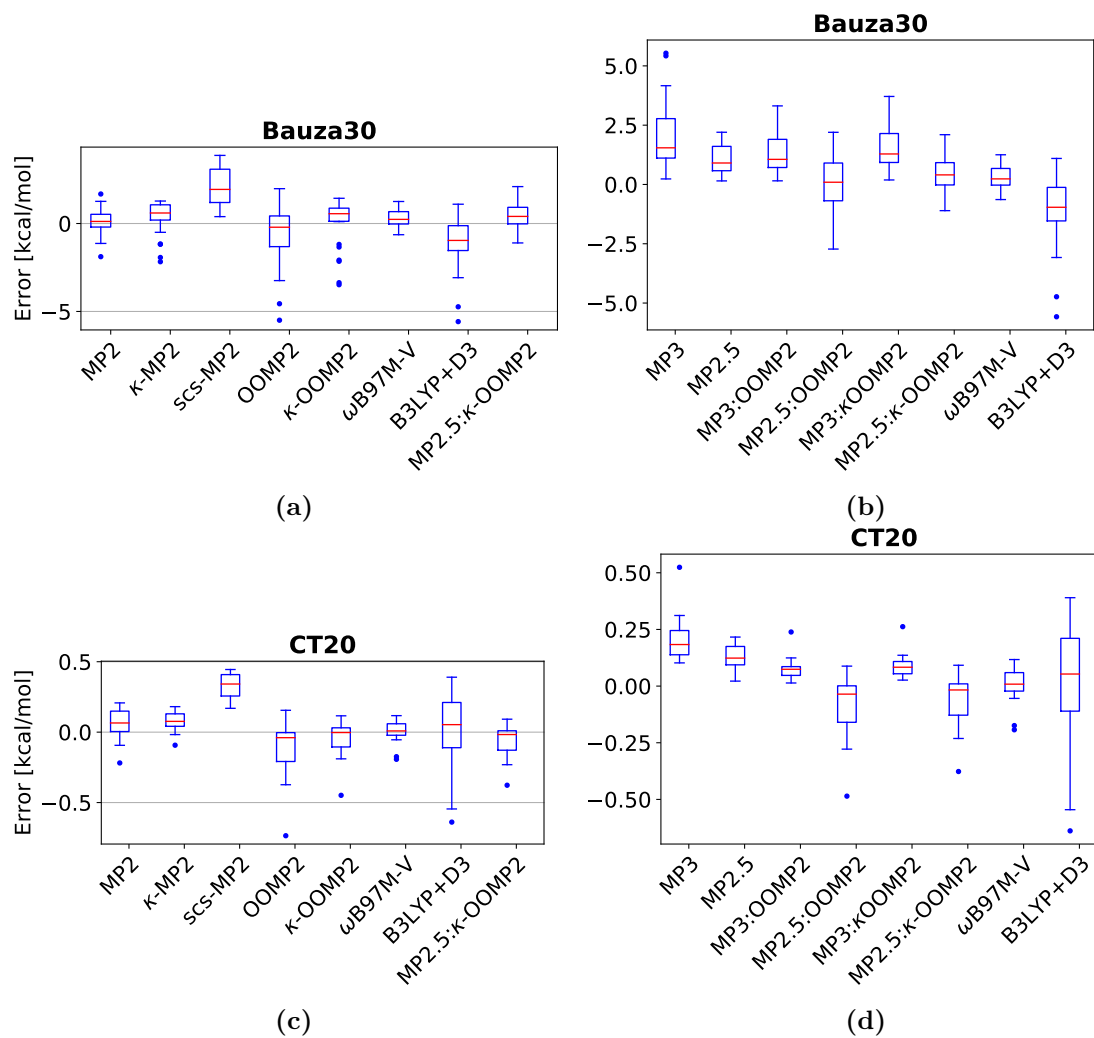
Figure S14: Box-plots of the data-sets Bauza30: (a) MP2 methods, (b) MP3 methods; XB18: (c) MP2 methods, (d) MP3 methods. Red lines mark the median deviation, boxes bound the central 50% of the data, whiskers enclose all data points within 1.5 times the inter-quartile range of the box edges, and points denote outlying data.

Figure S15: Box-plots of the data-sets XB51: (a) MP2 methods, (b) MP3 methods; Orel26rad: (c) MP2 methods, (d) MP3 methods. Red lines mark the median deviation, boxes bound the central 50% of the data, whiskers enclose all data points within 1.5 times the inter-quartile range of the b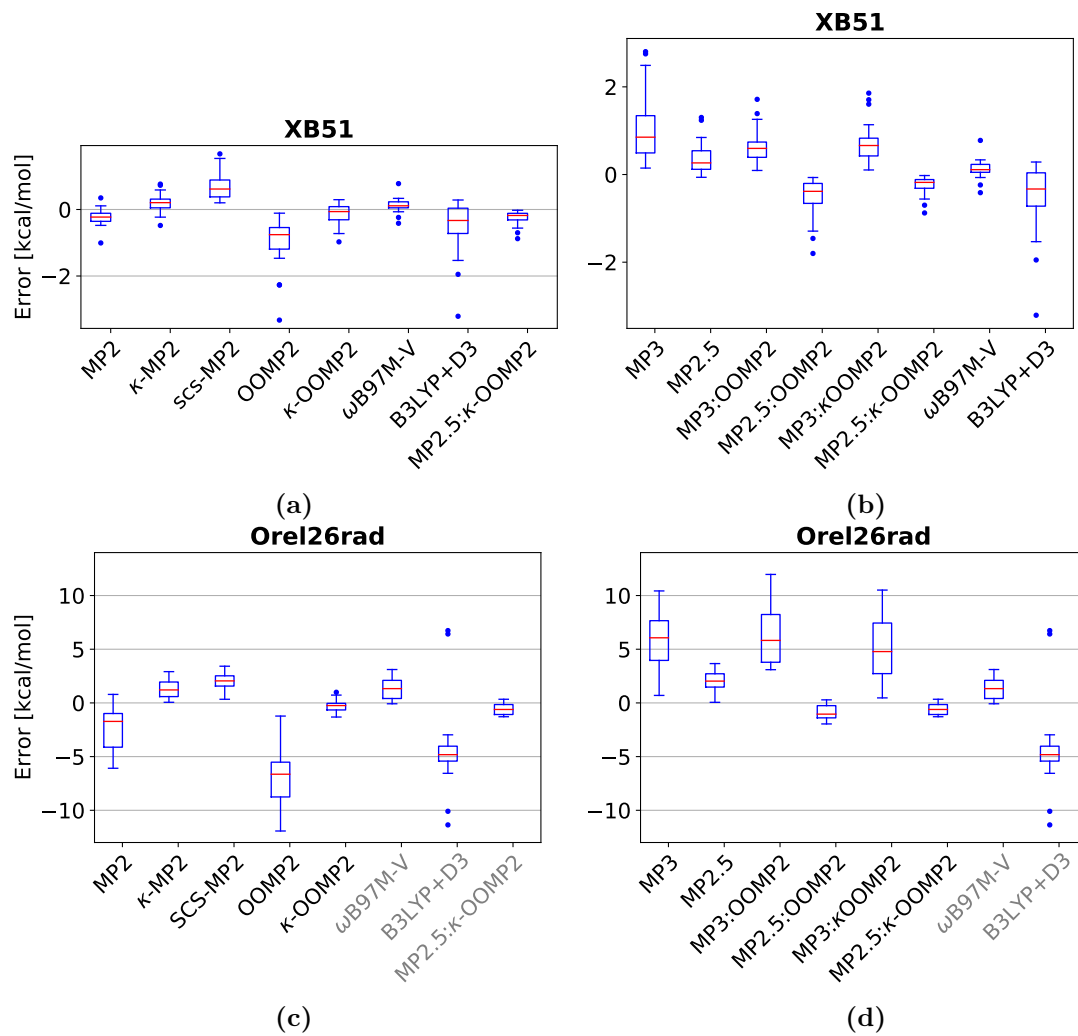ox edges, and points denote outlying data.