



Accuracy of RPA for Large Weakly Interacting Systems

Brian D. Nguyen, Matthew M. Agee, Absjörn M. Burrow, Guo P. Chen, and Filipp Furche
Department of Chemistry, Natural Sciences II, University of California, Irvine, CA 92697-2025, USA

Introduction

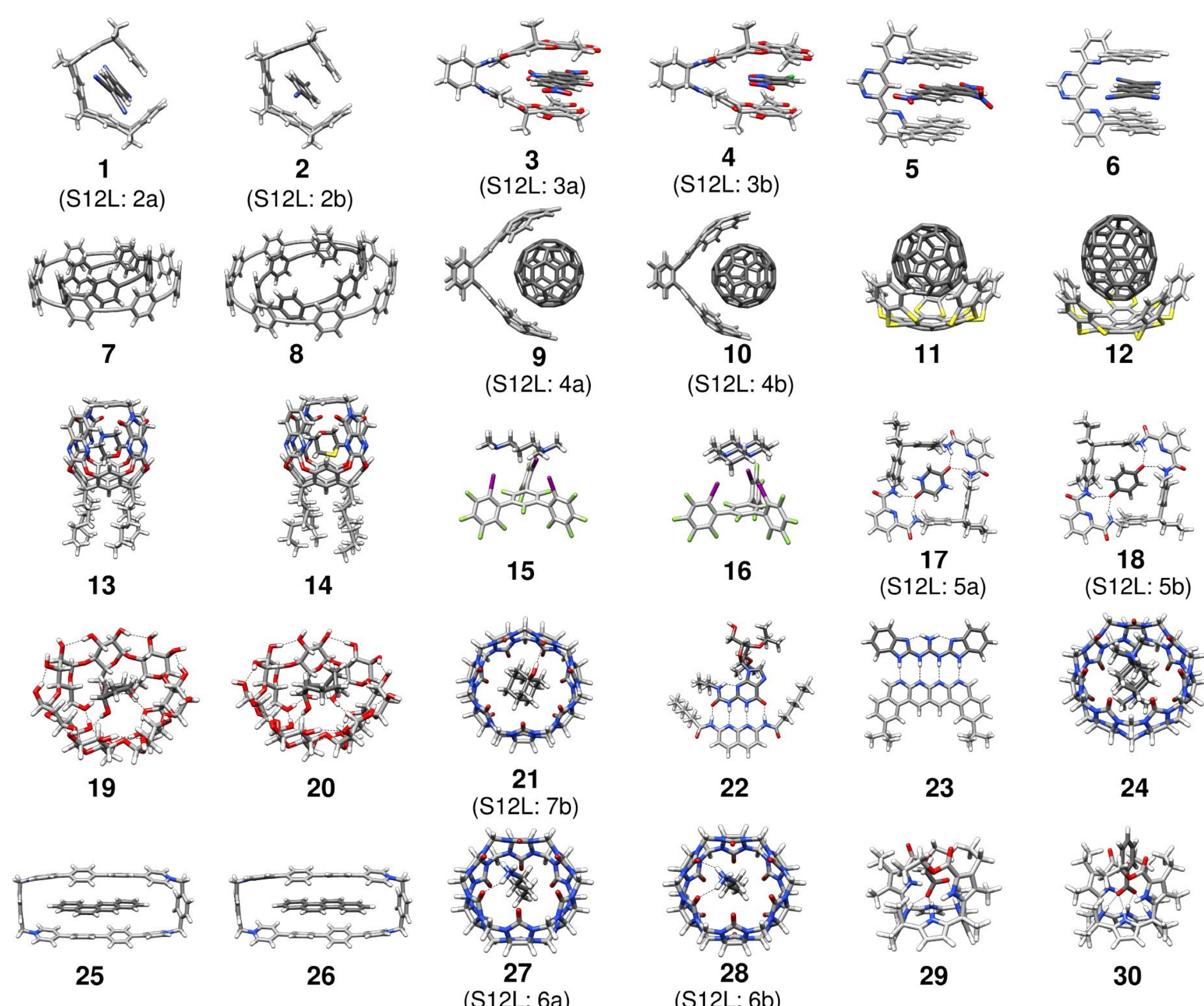


Figure 1. The 30 supramolecular complexes contained in the S30L test set.¹

Accurate predictions of noncovalent interactions (NI) in large and complex chemical systems remain challenging for electronic structure theory. Here we assess the performance of the random phase approximation (RPA) for NIs of large supramolecular complexes (Fig. 1).¹

S30L Benchmark Results

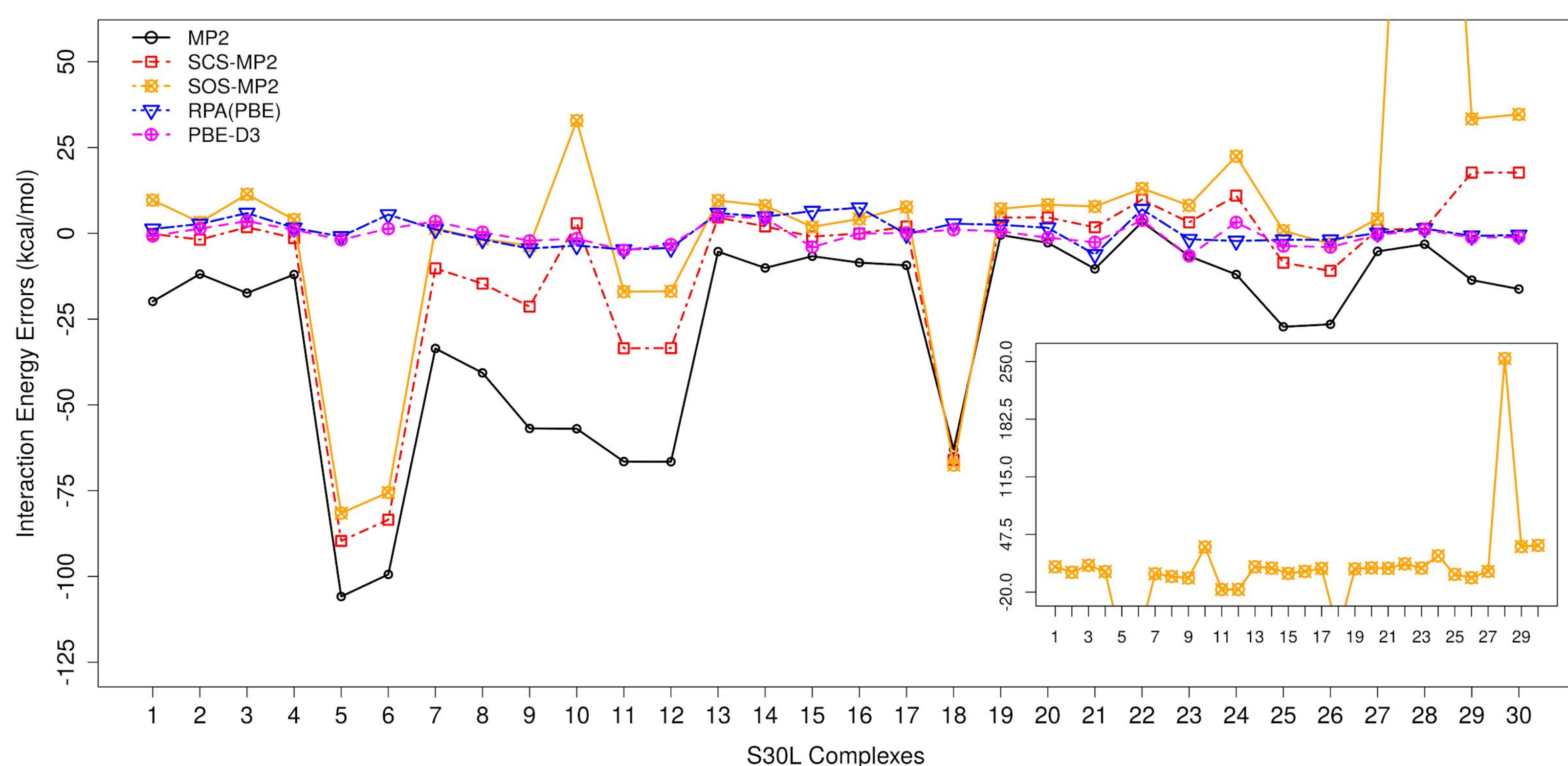


Figure 3. A comparison of the accuracy of MP2, SCS-MP2, SOS-MP2, RPA, and dispersion corrected³ PBE to the S30L test set. MP2 and RPA were computed using the Ahlrichs basis set for the Hartree exchange term and the Dunning basis set for correlation. 3-4 extrapolation and 50% counterpoise correction were applied to the correlation energy.

The calculations show that MP2 and different flavors of MP2 significantly overbinds for the π - π stacking complexes (5 - 12). In comparison, the three-body empirical dispersion (D3) corrected PBE and RPA yielded similar errors throughout the S30L test set (Fig 3). From Table 1, RPA performs on par with the highly empirical and best performing PW6B95-D3 functional.¹

Table 1. Mean absolute error (MAE), mean error (ME), and standard deviation (STD) in kcal/mol of S30L test set for various methods

Method	ME	MAE	STD
MP2	-27.06	27.28	29.23
SCS-MP2	-9.67	15.41	26.73
SOS-MP2	7.35	25.14	54.15
RPA(PBE)	0.76	3.11	3.78
PBE-D3	1.83	2.75	3.22
PW6B95-D3	-0.12	2.42	3.15

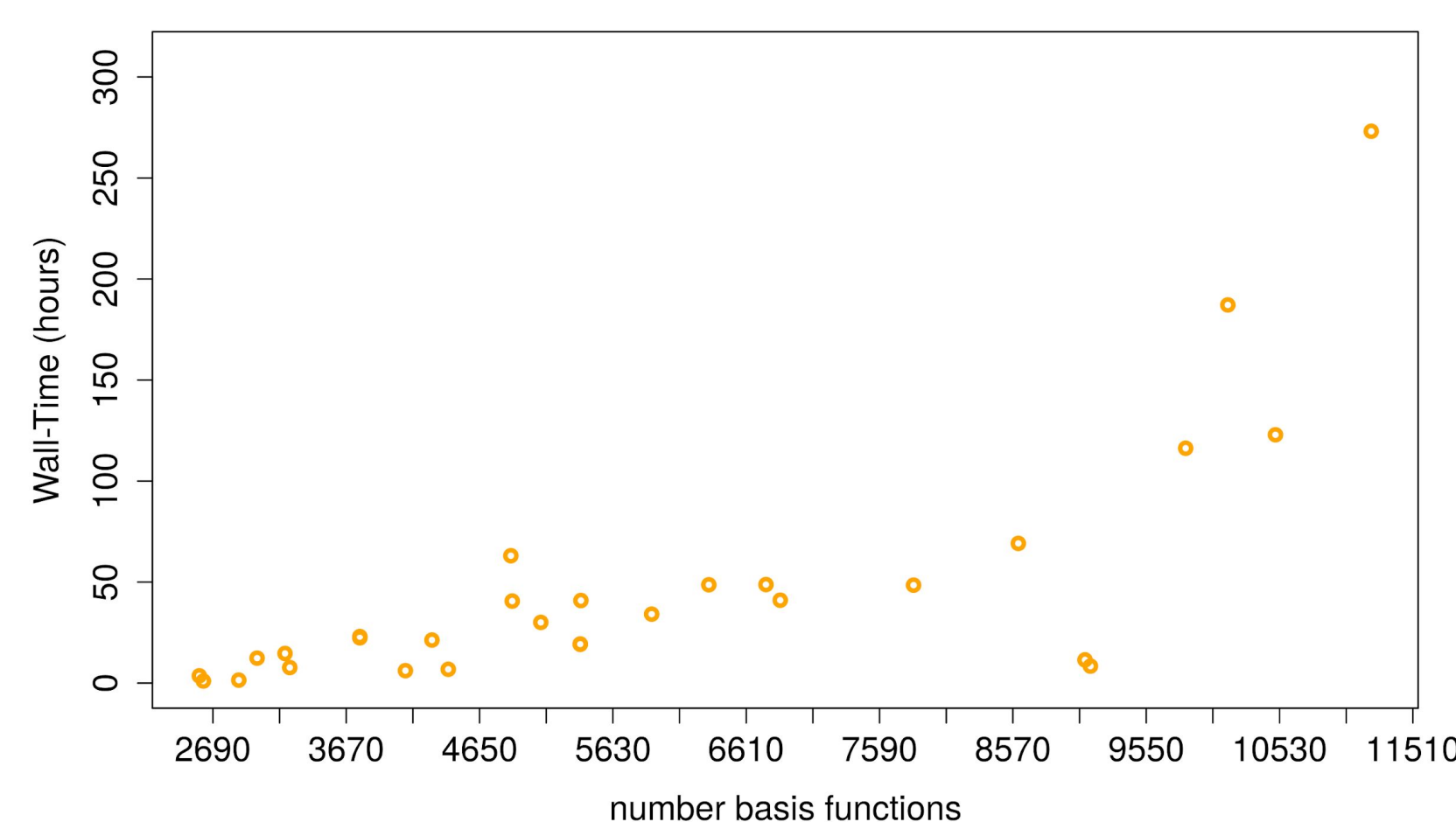


Figure 4. Reported timings of RIRPA single point energy calculations as a function of basis functions using up to 20 CPUs and 250GB memory.

Conclusion

RPA interaction energies for the S30L benchmark exhibit relative errors on par with dispersion corrected semilocal Density Functional Approximation (DFA). The magnitude of the RPA errors is independent of the system size illustrated by the L7⁵, S66⁶, and S30L¹ benchmarks. For MP2, the error increases with the system size. RPA calculations were demonstrated to be feasible for systems with hundreds of atoms on computer clusters and may be used to calibrate dispersion corrected DFAs for real systems.

Computational Method

$$\Delta E = E(\text{Complex}) - E(\text{Host}) - E(\text{Guest})$$

$$E^{\text{RPA}} = \langle \Phi | \hat{H} | \Phi \rangle + E^{\text{C RPA}}$$

$$E^{\text{C RPA}} = - \int_0^1 d\alpha \Im \int_0^\infty \frac{d\omega}{2\pi} \left\langle \mathbf{V} [\mathbf{n}_\alpha^{\text{RPA}}(\omega) - \mathbf{n}_0(\omega)] \right\rangle$$

$$\mathbf{n}_\alpha^{\text{RPA}}(\omega) = \mathbf{n}_0(\omega) + \alpha \mathbf{n}_0(\omega) \mathbf{V} \mathbf{n}_0(\omega) + \alpha^2 \mathbf{n}_0(\omega) \mathbf{V} \mathbf{n}_0(\omega) \mathbf{V} \mathbf{n}_0(\omega) + \dots$$

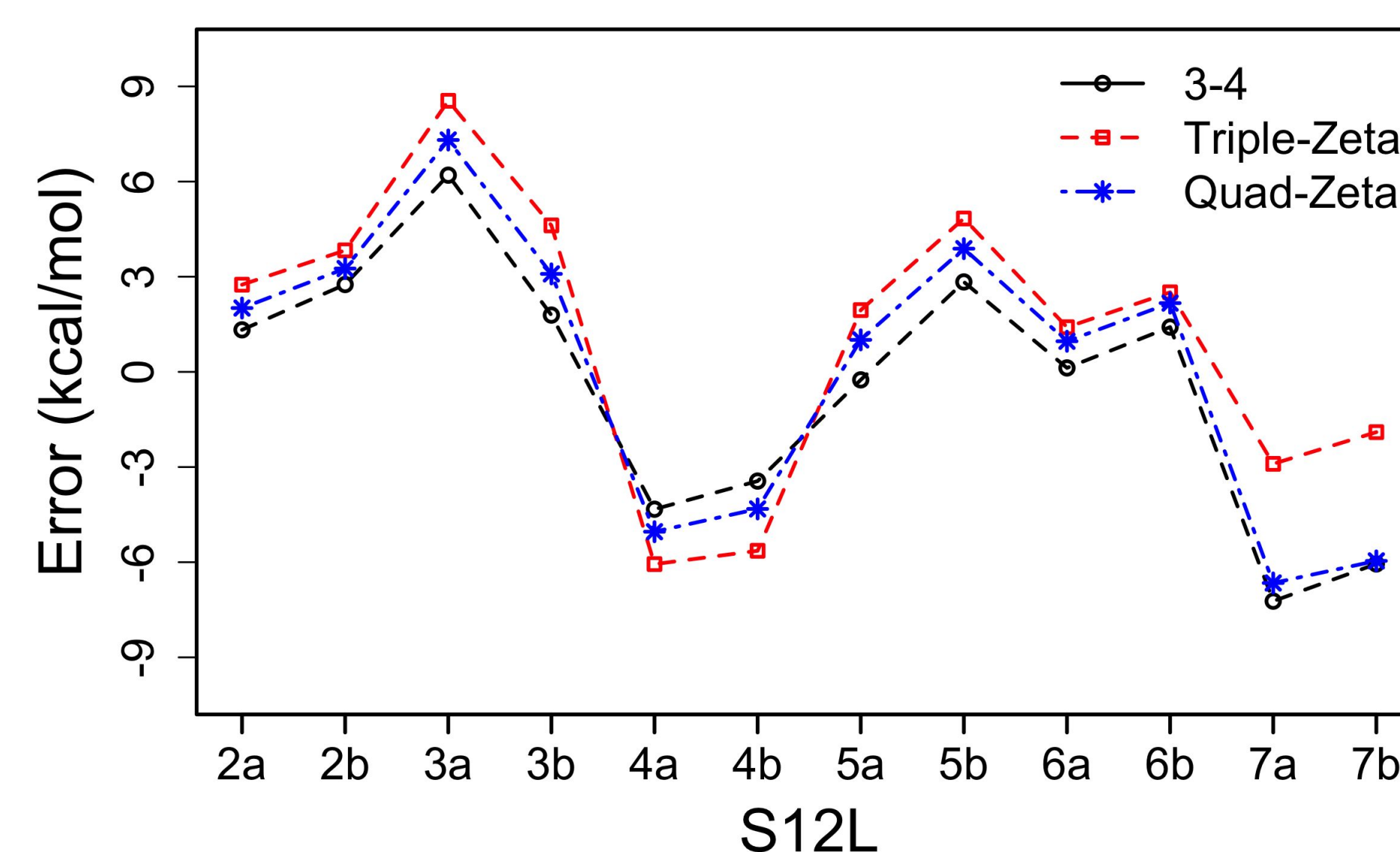


Figure 2. The basis set convergence of RIRPA single point energy calculations demonstrated with the S12L test set.² Energies were computed by treating the Hartree exchange with the Ahlrichs basis set and the correlation with the Dunning basis set including 50% counterpoise correction. The 3-4 energies are the extrapolated triple-zeta and quadruple-zeta correlation energy.³

RPA energies were obtained from Kohn-Sham (KS) orbital reference using PBE with gridsize m5. RIRPA module from TURBOMOLE 7.2⁴ used resolution-of-the-identity (RI) approximation and imaginary frequency integration to compute $E^{\text{C RPA}}$.

Size Dependence and Dispersion

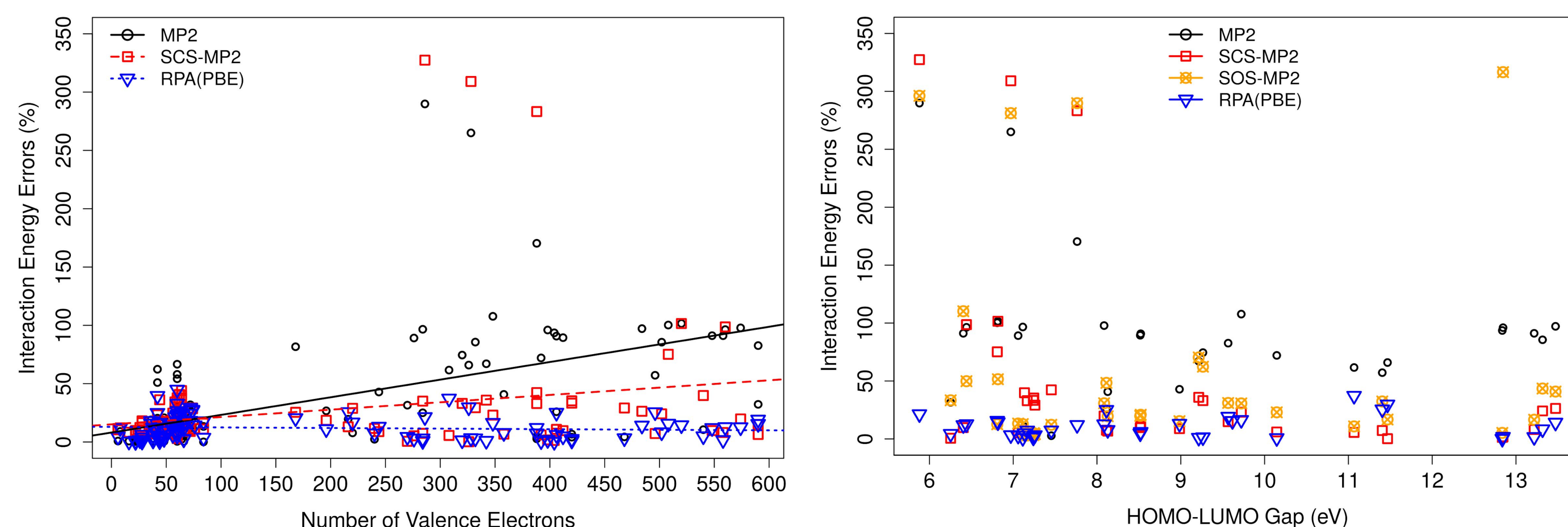


Figure 5. These are reported MP2, SCS-MP2, SOS-MP2, and RPA interaction energy errors of the L7⁵, S66⁶, and S30L⁷ test sets. Energies were computed by treating the Hartree exchange with the Ahlrichs basis set, and the correlation with the Dunning basis set including 50% counterpoise correction and 3-4 extrapolated.⁴

For the L7⁵, S66⁶, and S30L¹ test sets, the accuracy of MP2 deteriorates as the system size grows while the accuracy of RPA remain relatively consistent (Fig 5).

Expansion of the $E^{\text{C RPA}}$ Term

$$E_{AB}^{\text{RPA}} - E_A^{\text{RPA}} - E_B^{\text{RPA}} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \left\langle \ln (1 - \mathbf{n}_A(i\omega) \mathbf{V}_{AB} \mathbf{n}_B(i\omega) \mathbf{V}_{BA}) \right\rangle$$

$$\|\mathbf{n}_A(i\omega) \mathbf{V}_{AB} \mathbf{n}_B(i\omega) \mathbf{V}_{BA}\| < 1$$

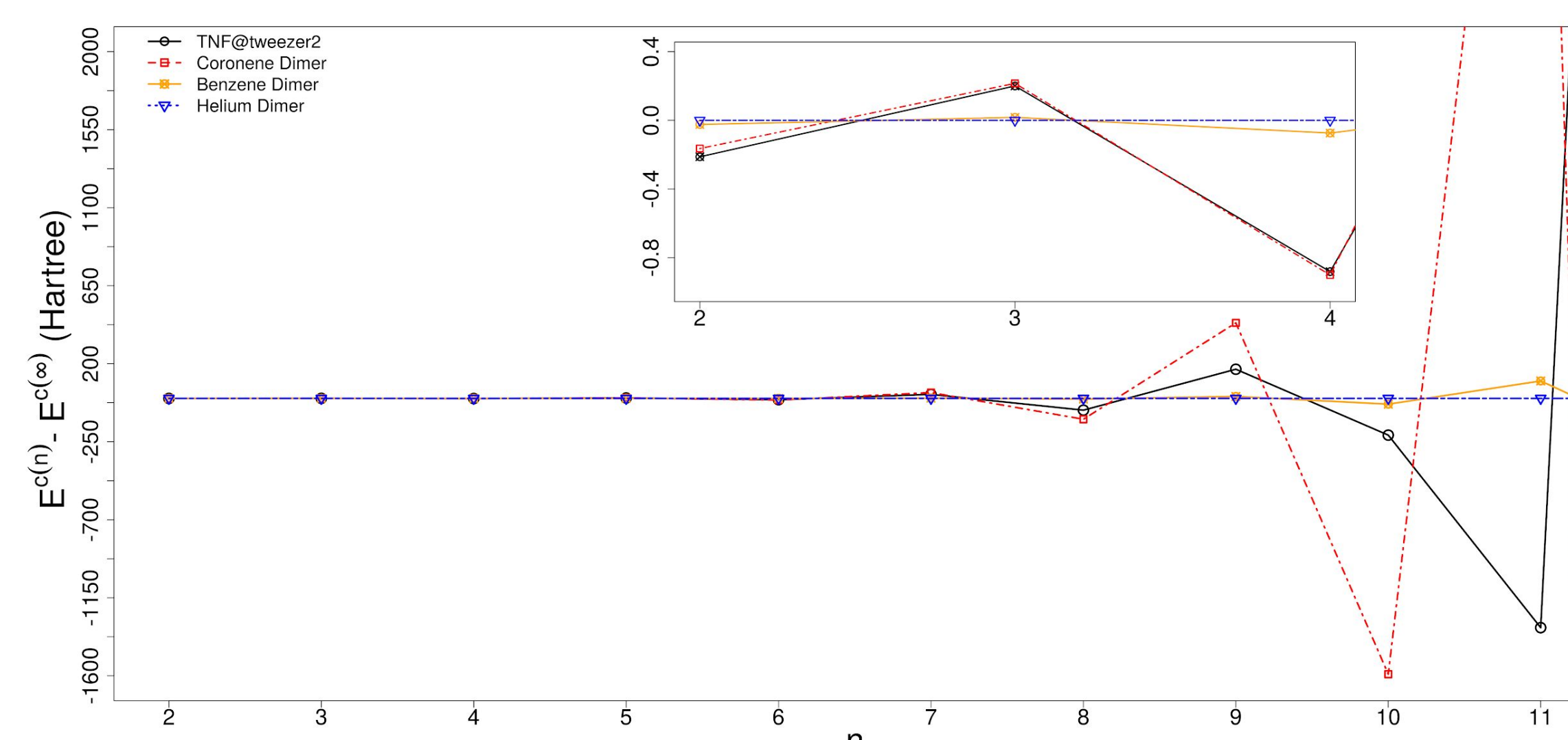


Figure 6. The RPA correlation of the interaction energy is computed at nth order of the Taylor series expansion of the $E^{\text{C RPA}}$ generates intermolecular perturbation series and calculations were performed using the PBE Kohn Sham orbital reference with cc-pVTZ basis set.

Acknowledgement

- This material is based on work supported by the National Science Foundation under CHE-1800431
- TURBOMOLE GmbH; available from <http://www.turbomole.com>

References

1. Sure, R.; Grimme, S. J. Chem. Theory Comput., 2015, 11(8), 3785-3801.
2. Grimme, S. Theory. Chem. Eur. J., 2012, 18, 9955-9964.
3. Eshuis, H.; Furche, F. J. Chem. Phys., 2012, 136(8), 084105.
4. Furche, F.; Ahlrichs, R.; Hättig, C.; Klopper, W.; Weigend, F.; Sierka, M. WIREs Comput. Mol. Sci., 2014, 4, 91-100.
5. Sedlak, R.; Janowski, T.; Pitoňák, M.; Řezáč, J.; Pulay, P.; Hobza, P. J. Chem. Theory Comput., 2013, 9(8), 3364-3374.
6. Riley, K.E.; Pitoňák, M.; Jurečka, P.; Hobza, P. Chem. Rev., 2010, 110(9), 5023-5063.

