Supplementary Information

Reference MP2/CBS and CCSD(T) quantum-chemical calculations on stacked adenine dimers. Comparison with DFT-D, MP2.5, SCS(MI)-MP2, M06-2X, CBS(SCS-D) and force field descriptions.

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Table S1: Structural parameters of parallel (P) and non-parallel (NP) dimers.

Dimer	Struct. N°	ω [°]	Δx [Å]	Δy [Å]	Δz [Å]*	α [°]	γ [°]
P1	1-12	0.0	0.0	0.0	2.9-4.0	0.0	0.0
P2	13-24	0.0	1.5	0.0	2.9-4.0	0.0	0.0
P3	25-36	0.0	0.0	1.5	2.9-4.0	0.0	0.0
P4	37-48	180.0	0.0	0.0	2.9-4.0	0.0	0.0
P5	49-60	180.0	1.5	0.0	2.9-4.0	0.0	0.0
P6	61-72	180.0	-1.5	0.0	2.9-4.0	0.0	0.0
P7	73-84	180.0	0.0	1.5	2.9-4.0	0.0	0.0
P8	85-96	180.0	0.0	-1.5	2.9-4.0	0.0	0.0
P9	97-101	30.0-150.0	0.0	0.0	3.3	0.0	0.0
NP1	102-111	180.0	0.0	0.0	3.5-4.4	10.0	25.0
NP2	112-121	180.0	0.0	2.0	3.6-4.5	10.0	25.0
NP3	122-131	180.0	1.5	2.0	3.6-4.5	10.0	25.0

(*) Δz ≡ r

Computational methods

MP2/CBS calculations corrected by the CCSD(T) method with a small basis set (abbreviated as CBS(T)). The MP2/CBS and CCSD(T) calculations have been performed with the Molpro 2006.1 software package, applying the frozen-core approximation. In the case of MP2, we have also applied the density-fitting approximation. The Helgaker *et al*. extrapolation scheme (Equations 1 and 2) has been used to extrapolate the Hartree-Fock (HF) and the correlation energies.

$$E_X^{HF} = E_{CBS}^{HF} + Ae^{-\alpha X} \tag{1}$$

$$E_X^{CORR} = E_{CBS}^{CORR} + BX^{-3} \tag{2}$$

In these equations E_X is the energy for the basis set with the largest angular momentum X, E_{CBS} is the energy for the complete basis set, and α is a parameter that was fitted in their original work. Herein we have used the aug-cc-pVDZ→aug-cc-pVTZ extrapolation. Since higher-order correlation-energy contributions cannot be neglected, the CCSD(T)/CBS estimate of the interaction energies have been obtained with Equation 3. CCSD(T)/CBS interaction energies estimated according to this equation are also known as CBS(T) data.

$$\Delta E_{CBS}^{CCSD(T)} \approx \Delta E_{CBS}^{MP2} + \left(\Delta E^{CCSD(T)} - \Delta E^{MP2} \right)\Big|_{cc-pVDZ} \tag{3}$$

Behind this equation is the assumption that the difference between the CCSD(T) and MP2 interaction energies is basically basis-set independent, and can in consequence be computed with a small- or medium-size basis set. The second term in the r.h.s of Equation 3 is sometimes abbreviated as ΔCCSD(T).

AMBER non-bonded empirical potential. The empirical-potential calculations have been performed with a local code, employing the van der Waals (vdW) and Coulombic terms of the AMBER force field. The atom-centered point charges were obtained by an electrostatic potential (ESP) fitting at the MP2/aug-cc-pVDZ level of theory using the Merz-Kollman approach as implemented in the Gaussian 03 software package. The reasons why this level of theory has been chosen for the derivation of the point charges can be found in the literature. This non-bonded potential is analogous to the one employed in AMBER, with the only exception that condensed-phase simulations with AMBER are carried out with charges derived in a RESP fitting at the HF/6-31G*

level of theory.

DFT augmented with an empirical dispersion term (DFT-D). The DFT-D calculations have been performed with the TurboMole 5.8 software package in combination with a local code that computes the empirical dispersion correction, following the approach developed by Jurečka *et al.*, who parameterized the method by a fitting procedure against the CCSD(T) interaction-energy data for the S22 training set. In this approach a pair-wise additive potential is used to account for long-range dispersion effects that are not properly described with common density functionals. This empirical correction (E_{disp}) is then added to the Kohn-Sham DFT energy (E_{KS-DFT}) according to Equation 4.

$$E_{DFT-D} = E_{KS-DFT} + E_{disp} \qquad (4)$$

The empirical dispersion correction has been evaluated as in the original work of Jurečka *et al.*, where the exact mathematical form of this correction can be found. All of the parameters used in the present work for the evaluation of the dispersion correction are the same as those used by these authors. For the DFT part of the calculation we have used the TPSS/6-311++G(3df,3pd) level of theory and the RI approximation, also known as density fitting. This level of theory augmented with the dispersion correction will hereafter be referred to as DFT-D. When discussing the performance of the DFT-D method we refer exclusively to the approach of Jurečka *et al.*, without claiming that the results are valid for other methods that also combine DFT with an empirical correction for dispersion interactions.

SCS-MP2 for molecular interactions (SCS(MI)-MP2). The SCS(MI)-MP2 calculations have been performed with the Molpro 2006.1 software package, applying the frozen-core and density-fitting approximations. This method relies on an empirical scaling of the same- (SS) and opposite-spin (OS) components of the MP2 energy ($E_{MP2} = c_{OS}E_{OS} + c_{SS}E_{SS}$), aiming at a good description of intermolecular interactions. The opposite- and same-spin parameters (c_{OS} and c_{SS} respectively) were obtained in the original work by a fitting procedure against the CCSD(T) interaction-energy data for the S22 training set. Here we calculate the SCS(MI)-MP2 interaction energies using the cc-pV(DT)Z extrapolation (cc-pVDZ→cc-pVTZ), for which the same- and opposite-spin optimized parameters are 1.46 and 0.29 respectively. The MP2/CBS limit is approximated according to the following extrapolation scheme:

$$E_{XY} = E_{SCF,Y} + \frac{X^3 E_{CORR,X} - Y^3 E_{CORR,Y}}{X^3 - Y^3} \qquad Y > X \tag{5}$$

where $X=2$ and $Y=3$ for the D→T extrapolation used in this work.

DFT-symmetry adapted perturbation theory (DFT-SAPT). The DFT-SAPT calculations have been performed with the Molpro 2006.1 software package. In this method the interaction energy is decomposed into a sum of first- and second-order energies, plus the δHF term. The first-order energy includes the electrostatic and exchange-repulsion contributions, while the second-order energy includes the induction, exchange-induction, dispersion, and exchange-dispersion contributions. The δHF term is an estimate of higher-order Hartree-Fock contributions and is BSSE dependent. The interaction energy is given by Equation 6, and the electrostatic, induction, dispersion, and exchange contributions are defined in Equations 7–10.

$$E_{int} = E_{pol}^{(1)} + E_{ex}^{(1)} + E_{ind}^{(2)} + E_{ex-ind}^{(2)} + E_{disp}^{(2)} + E_{ex-disp}^{(2)} + \delta HF \tag{6}$$

$$E_{elec} = E_{pol}^{(1)} \tag{7}$$

$$E_{ind} = E_{ind}^{(2)} + E_{ex-ind}^{(2)} \tag{8}$$

$$E_{disp} = E_{disp}^{(2)} + E_{ex-disp}^{(2)} \tag{9}$$

$$E_{exch} = E_{ex}^{(1)} \tag{10}$$

The decomposition has been carried out using the LPBE0AC XC potential with the pure ALDA kernel for both the static and dynamic response, in combination with the aug-cc-pVDZ basis set. The density-fitting approximation has also been used. The ionization potential (IP) of the monomer and the energy of the highest occupied molecular orbital (HOMO), which are required to evaluate the shift parameter, have been calculated at the PBE0/aug-cc-pVDZ level of theory. The aug-cc-pVDZ basis set is sufficient to get an idea about the relative magnitude of the interaction energy components, and its use for the IP calculations does not affect the shift values dramatically.

MP2/CBS plus MP3 corrections (MP2.5). The MP2/CBS calculations have been performed with the Molpro 2006.1 software package, applying the frozen-core and the density-fitting approximations, whereas the calculations needed for the third-order correction have been performed with a recently developed module of the MOLCAS 7 software package, taking advantage of the Cholesky decomposition of the two-electron integrals. The MP2.5 method is a linearly-interpolated MP method where the third-order correction is damped by 50%. The interaction energy is simply obtained by adding a scaled third-order energy contribution to the MP2/CBS interaction energy, as shown in Equation 11. This contribution has been computed with the aug-cc-pVDZ basis set.

$$\Delta E_{CBS}^{MP2.5} = \Delta E_{CBS}^{MP2} + 0.5\left(\Delta E^{MP3} - \Delta^{MP2}\right)\Big|_{aug-cc-pVDZ} \tag{11}$$

Table S2: Interaction energies (kcal mol⁻¹) for the parallel dimers, calculated with the AMBER, DFT-D, SCS(MI)-MP2, MP2.5, and CBS(T) methods.

Dimer	n	r [Å]*	AMBER	DFT-D	SCS(MI)-MP2	MP2.5	CBS(T)
P1	1	2.9	19.52	16.32	14.83	15.03	14.18
	2	3.0	9.63	9.15	8.21	8.48	7.73
	3	3.1	3.57	4.39	3.72	4.06	3.38
	4	3.2	-0.09	1.32	0.77	1.12	0.53
	5	3.3	-2.22	-0.59	-1.11	-0.77	-1.31
	6	3.4	-3.40	-1.71	-2.24	-1.90	-2.38
	7	3.5	-3.97	-2.32	-2.84	-2.52	-2.94
	8	3.6	-4.16	-2.63	-3.10	-2.80	-3.17
	9	3.7	-4.13	-2.74	-3.13	-2.84	-3.18
	10	3.8	-3.96	-2.74	-3.02	-2.75	-3.05
	11	3.9	-3.71	-2.67	-2.82	-2.58	-2.84
	12	4.0	-3.43	-2.54	-2.58	-2.36	-2.59
P2	13	2.9	5.25	1.07	-1.58	-0.71	-1.42
	14	3.0	-0.11	-1.90	-3.75	-2.98	-3.62
	15	3.1	-3.21	-3.74	-4.98	-4.30	-4.88
	16	3.2	-4.90	-4.73	-5.56	-4.97	-5.50
	17	3.3	-5.70	-5.06	-5.71	-5.18	-5.66
	18	3.4	-5.95	-4.95	-5.57	-5.11	-5.54
	19	3.5	-5.88	-4.63	-5.26	-4.86	-5.24
	20	3.6	-5.61	-4.30	-4.86	-4.51	-4.86
	21	3.7	-5.24	-4.03	-4.41	-4.10	-4.41
	22	3.8	-4.82	-3.75	-3.95	-3.68	-3.96
	23	3.9	-4.39	-3.42	-3.51	-3.27	-3.52
	24	4.0	-3.97	-3.07	-3.08	-2.89	-3.11
P3	25	2.9	6.01	0.45	-1.49	-0.64	-1.62
	26	3.0	0.54	-2.40	-3.71	-2.97	-3.84
	27	3.1	-2.66	-4.12	-4.98	-4.33	-5.11
	28	3.2	-4.43	-4.99	-5.59	-5.02	-5.71
	29	3.3	-5.31	-5.26	-5.77	-5.26	-5.88
	30	3.4	-5.63	-5.16	-5.65	-5.21	-5.76
	31	3.5	-5.61	-4.89	-5.36	-4.96	-5.45
	32	3.6	-5.40	-4.56	-4.97	-4.61	-5.05
	33	3.7	-5.07	-4.21	-4.53	-4.22	-4.60
	34	3.8	-4.69	-3.87	-4.07	-3.80	-4.14
	35	3.9	-4.29	-3.56	-3.62	-3.39	-3.69
	36	4.0	-3.89	-3.24	-3.20	-2.99	-3.26

Table S2 (Cont.): Interaction energies (kcal mol^{-1}) for the parallel dimers, calculated with the AMBER, DFT-D, SCS(MI)-MP2, MP2.5, and CBS(T) methods.

Dimer	n	r [Å]*	AMBER	DFT-D	SCS(MI)-MP2	MP2.5	CBS(T)
P4	37	2.9	7.99	-0.44	-3.14	-2.02	-3.08
	38	3.0	0.78	-3.88	-5.84	-4.86	-5.81
	39	3.1	-3.47	-5.95	-7.37	-6.51	-7.37
	40	3.2	-5.86	-6.99	-8.09	-7.34	-8.10
	41	3.3	-7.07	-7.37	-8.28	-7.62	-8.29
	42	3.4	-7.55	-7.32	-8.10	-7.55	-8.15
	43	3.5	-7.58	-6.99	-7.71	-7.23	-7.76
	44	3.6	-7.35	-6.51	-7.19	-6.77	-7.24
	45	3.7	-6.97	-6.03	-6.62	-6.25	-6.66
	46	3.8	-6.51	-5.61	-6.02	-5.70	-6.06
	47	3.9	-6.02	-5.21	-5.44	-5.17	-5.49
	48	4.0	-5.52	-4.79	-4.90	-4.65	-4.93
P5	49	2.9	4.08	-0.36	-2.67	-1.77	-2.97
	50	3.0	-1.73	-3.38	-5.13	-4.37	-5.41
	51	3.1	-5.04	-5.21	-6.52	-5.87	-6.77
	52	3.2	-6.79	-6.18	-7.18	-6.62	-7.41
	53	3.3	-7.58	-6.59	-7.35	-6.86	-7.56
	54	3.4	-7.78	-6.62	-7.20	-6.78	-7.39
	55	3.5	-7.63	-6.37	-6.85	-6.49	-7.02
	56	3.6	-7.28	-5.95	-6.39	-6.08	-6.56
	57	3.7	-6.83	-5.52	-5.88	-5.62	-6.04
	58	3.8	-6.32	-5.16	-5.35	-5.13	-5.49
	59	3.9	-5.81	-4.81	-4.84	-4.64	-4.97
	60	4.0	-5.31	-4.43	-4.35	-4.18	-4.47
P6	61	2.9	1.52	-1.14	-3.57	-2.52	-3.20
	62	3.0	-3.40	-3.97	-5.75	-4.82	-5.45
	63	3.1	-6.15	-5.61	-6.95	-6.15	-6.73
	64	3.2	-7.54	-6.40	-7.48	-6.78	-7.30
	65	3.3	-8.10	-6.67	-7.56	-6.95	-7.41
	66	3.4	-8.14	-6.58	-7.35	-6.82	-7.24
	67	3.5	-7.89	-6.25	-6.96	-6.51	-6.88
	68	3.6	-7.46	-5.82	-6.48	-6.08	-6.41
	69	3.7	-6.95	-5.42	-5.94	-5.60	-5.89
	70	3.8	-6.41	-5.07	-5.41	-5.12	-5.37
	71	3.9	-5.87	-4.69	-4.88	-4.64	-4.86
	72	4.0	-5.35	-4.29	-4.39	-4.18	-4.37

Table S2 (Cont.): Interaction energies (kcal mol^{-1}) for the parallel dimers, calculated with the AMBER, DFT-D, SCS(MI)-MP2, MP2.5, and CBS(T) methods.

Dimer	n	r [Å]*	AMBER	DFT-D	SCS(MI)-MP2	MP2.5	CBS(T)
P7	73	2.9	5.75	1.15	0.00	0.48	-0.53
	74	3.0	0.19	-1.94	-2.73	-2.30	-3.20
	75	3.1	-3.05	-3.81	-4.39	-4.00	-4.80
	76	3.2	-4.83	-4.84	-5.29	-4.95	-5.66
	77	3.3	-5.72	-5.30	-5.67	-5.37	-6.00
	78	3.4	-6.05	-5.39	-5.72	-5.45	-6.01
	79	3.5	-6.04	-5.27	-5.54	-5.31	-5.80
	80	3.6	-5.83	-5.02	-5.23	-5.03	-5.46
	81	3.7	-5.51	-4.72	-4.85	-4.68	-5.06
	82	3.8	-5.14	-4.42	-4.43	-4.29	-4.62
	83	3.9	-4.74	-4.12	-4.02	-3.90	-4.19
	84	4.0	-4.35	-3.81	-3.62	-3.52	-3.77
P8	85	2.9	6.75	1.85	0.10	0.65	-0.11
	86	3.0	0.35	-1.94	-3.13	-2.61	-3.26
	87	3.1	-3.43	-4.25	-5.13	-4.62	-5.17
	88	3.2	-5.57	-5.52	-6.26	-5.77	-6.24
	89	3.3	-6.66	-6.11	-6.79	-6.31	-6.72
	90	3.4	-7.10	-6.28	-6.91	-6.47	-6.82
	91	3.5	-7.14	-6.20	-6.77	-6.36	-6.66
	92	3.6	-6.94	-5.92	-6.46	-6.09	-6.35
	93	3.7	-6.61	-5.56	-6.06	-5.71	-5.94
	94	3.8	-6.20	-5.21	-5.62	-5.30	-5.49
	95	3.9	-5.76	-4.87	-5.16	-4.87	-5.04
	96	4.0	-5.32	-4.53	-4.71	-4.44	-4.59
P9	97	30.0	-5.33	-5.11	-5.73	-5.19	-5.88
	98	60.0	-7.12	-6.89	-7.46	-6.78	-7.43
	99	90.0	-7.04	-6.88	-7.50	-6.84	-7.43
	100	120.0	-6.13	-5.73	-6.36	-5.80	-6.36
	101	150.0	-5.77	-5.30	-5.94	-5.36	-5.92

(*) For P9 the values correspond to the twist angle ω.

Table S3: Interaction energies (kcal mol^{-1}) for the non-parallel dimers, calculated with the AMBER, DFT-D, SCS(MI)-MP2, MP2.5, and CBS(T) methods.

Dimer	n	r [Å]	AMBER	DFT-D	SCS(MI)-MP2	MP2.5	CBS(T)
NP1	102	3.5	5.20	1.67	0.98	1.22	0.41
	103	3.6	0.48	-0.75	-1.17	-0.95	-1.68
	104	3.7	-2.25	-2.33	-2.53	-2.33	-2.98
	105	3.8	-3.75	-3.31	-3.33	-3.15	-3.74
	106	3.9	-4.48	-3.84	-3.73	-3.58	-4.10
	107	4.0	-4.76	-4.04	-3.87	-3.73	-4.20
	108	4.1	-4.75	-4.02	-3.82	-3.71	-4.13
	109	4.2	-4.57	-3.87	-3.66	-3.57	-3.94
	110	4.3	-4.31	-3.66	-3.44	-3.36	-3.69
	111	4.4	-4.01	-3.43	-3.17	-3.12	-3.41
NP2	112	3.6	9.26	5.00	3.85	3.94	3.60
	113	3.7	3.44	1.94	1.10	1.18	0.86
	114	3.8	0.03	-0.19	-0.72	-0.65	-0.96
	115	3.9	-1.92	-1.65	-1.88	-1.82	-2.10
	116	4.0	-2.97	-2.57	-2.56	-2.50	-2.76
	117	4.1	-3.47	-3.09	-2.91	-2.85	-3.09
	118	4.2	-3.64	-3.33	-3.04	-2.98	-3.20
	119	4.3	-3.61	-3.37	-3.01	-2.96	-3.16
	120	4.4	-3.47	-3.26	-2.90	-2.84	-3.02
	121	4.5	-3.26	-3.08	-2.73	-2.68	-2.84
NP3	122	3.6	6.78	3.39	2.75	2.62	2.16
	123	3.7	2.09	0.58	0.24	0.14	-0.27
	124	3.8	-0.72	-1.36	-1.39	-1.45	-1.82
	125	3.9	-2.34	-2.58	-2.39	-2.43	-2.76
	126	4.0	-3.21	-3.26	-2.95	-2.98	-3.28
	127	4.1	-3.62	-3.57	-3.22	-3.24	-3.50
	128	4.2	-3.74	-3.66	-3.28	-3.29	-3.52
	129	4.3	-3.69	-3.61	-3.21	-3.21	-3.42
	130	4.4	-3.54	-3.47	-3.06	-3.06	-3.24
	131	4.5	-3.33	-3.27	-2.86	-2.86	-3.02

Figure S1: Interaction-Energy Gradient of P1
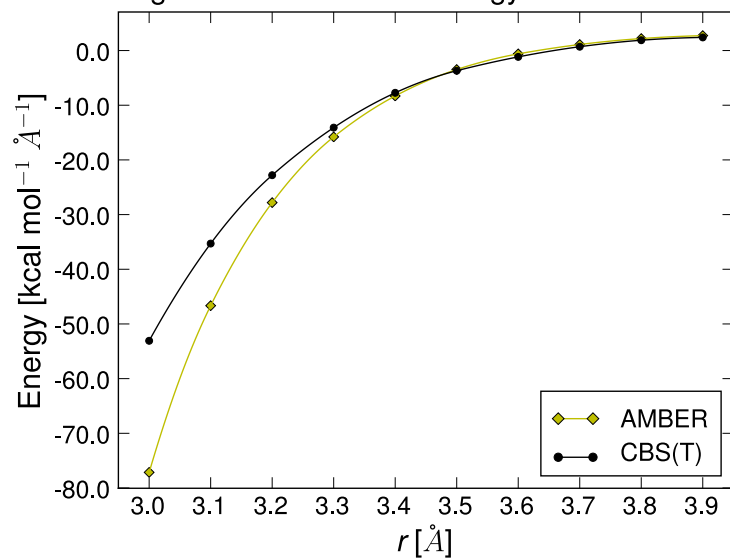
Figure S2: Interaction-Energy Gradient of P2
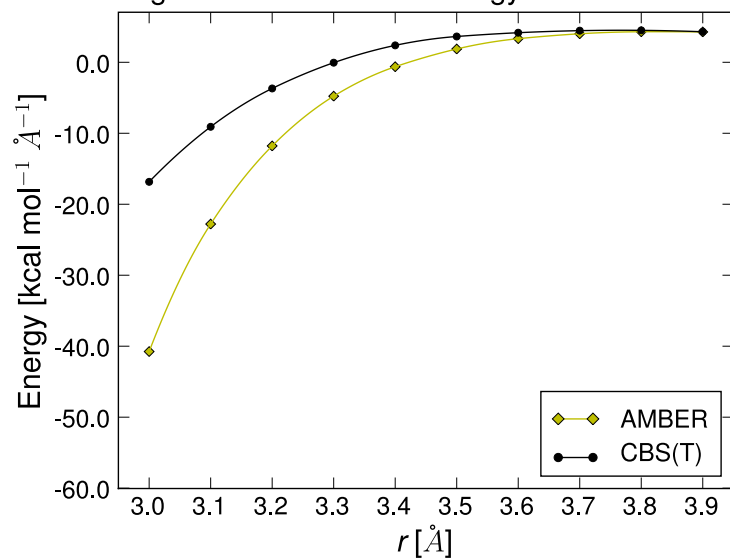
Figure S3: Interaction-Energy Gradient of P3
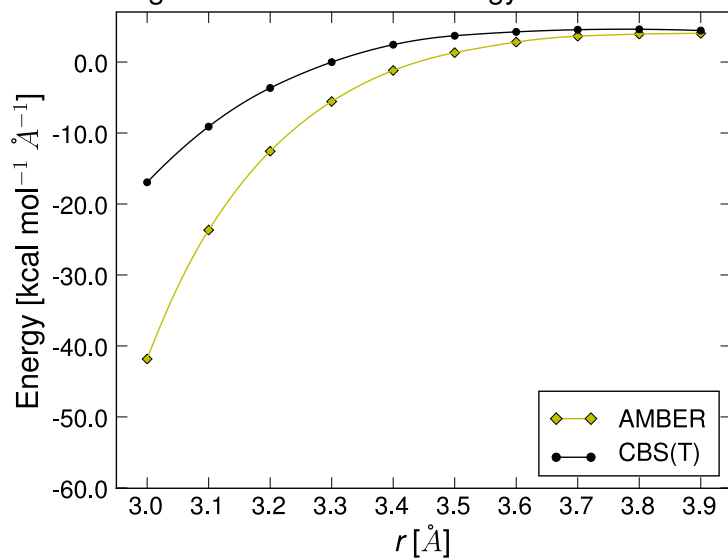
Figure S4: Interaction-Energy Gradient of P5
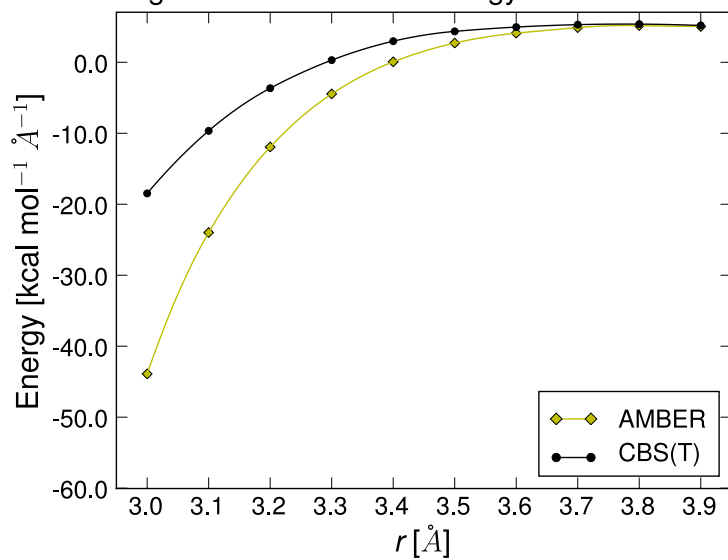
Figure S5: Interaction-Energy Gradient of P6
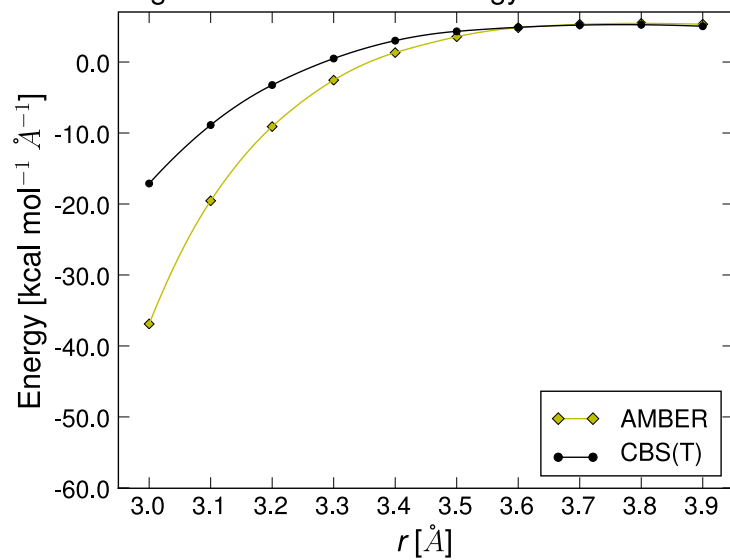
Figure S6: Interaction-Energy Gradient of P7
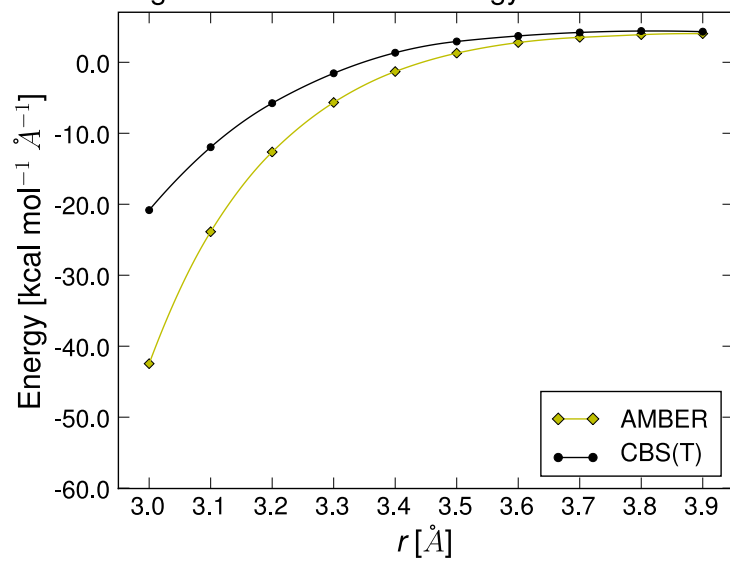
Figure S7: Interaction-Energy Gradient of P8
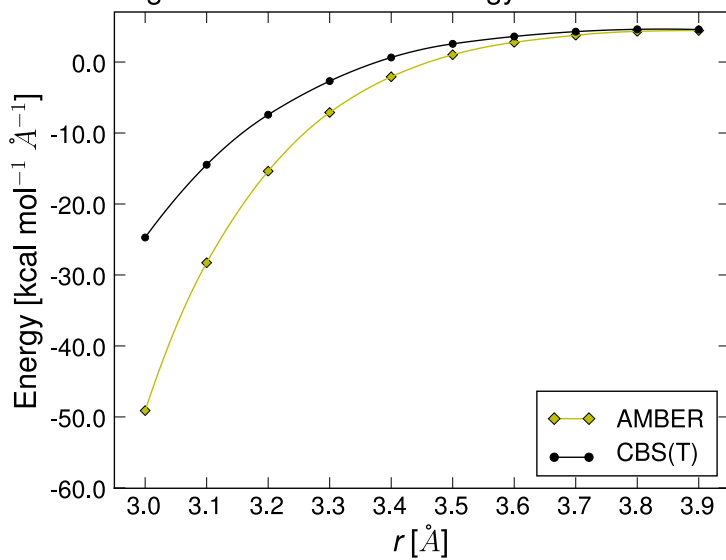
Figure S8: Interaction-Energy Gradient of NP1
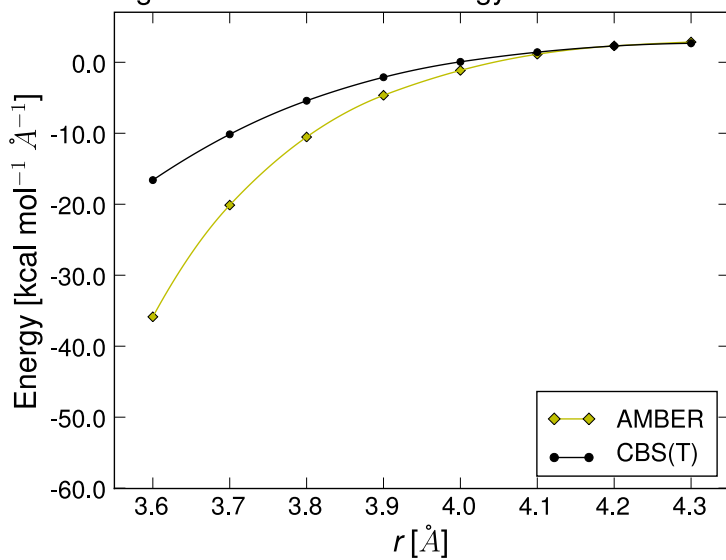
Figure S9: Interaction-Energy Gradient of NP2
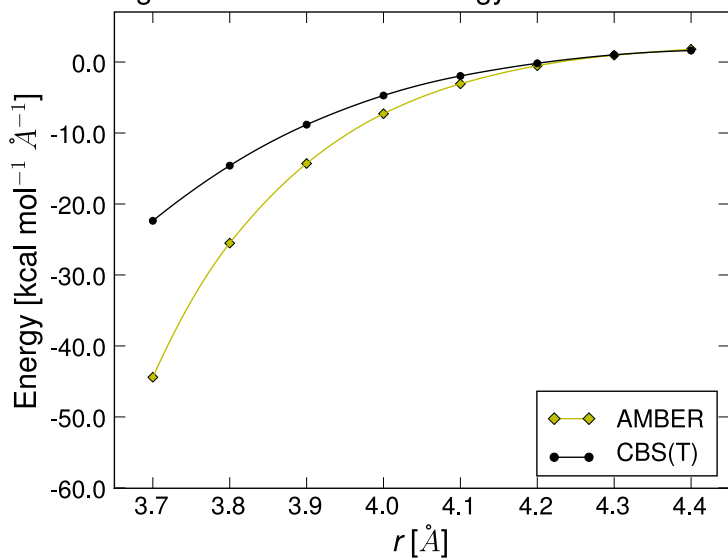
Figure S10: Interaction-Energy Gradient of NP3
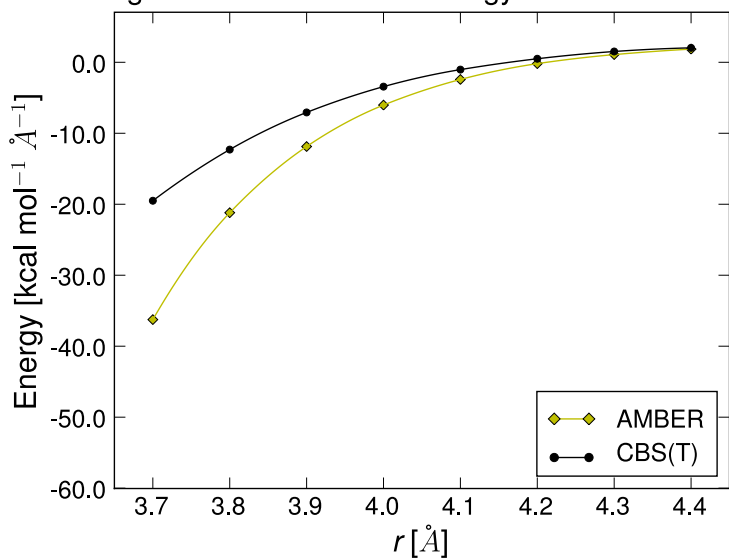
Figure S11: DFT-SAPT Energy Terms of P1
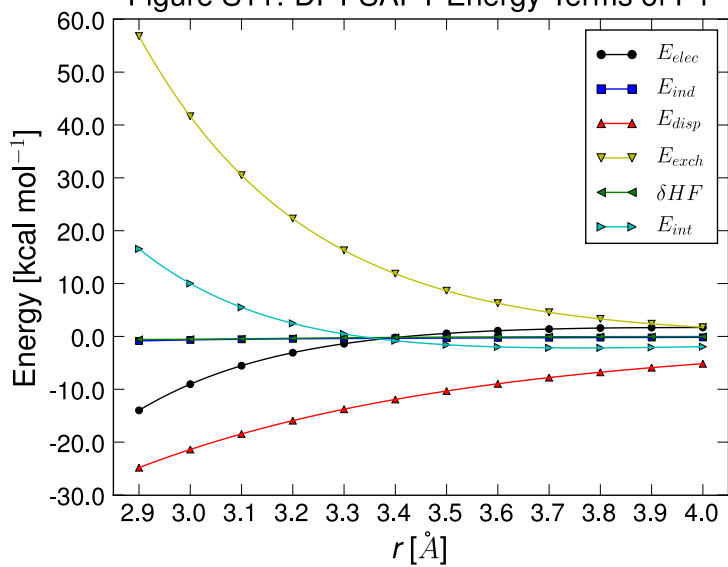
Figure S12: DFT-SAPT Energy Terms of P2
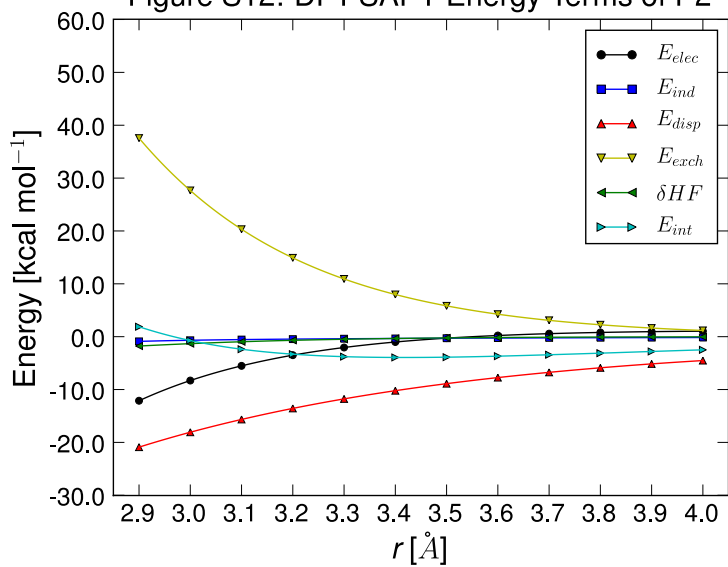
Figure S13: DFT-SAPT Energy Terms of P3
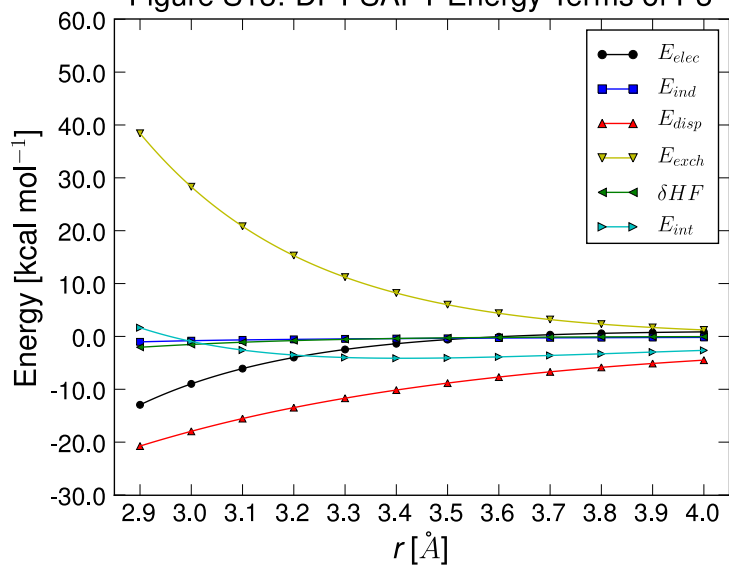
Figure S14: DFT-SAPT Energy Terms of P4
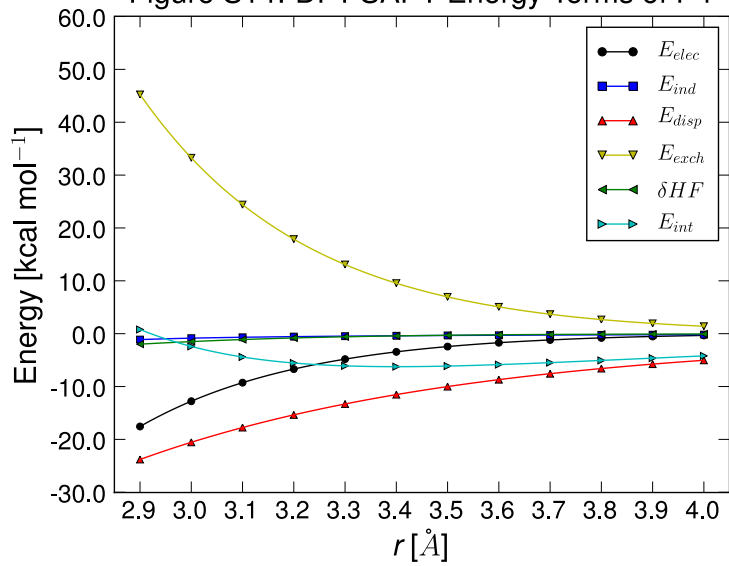
Figure S15: DFT-SAPT Energy Terms of P5
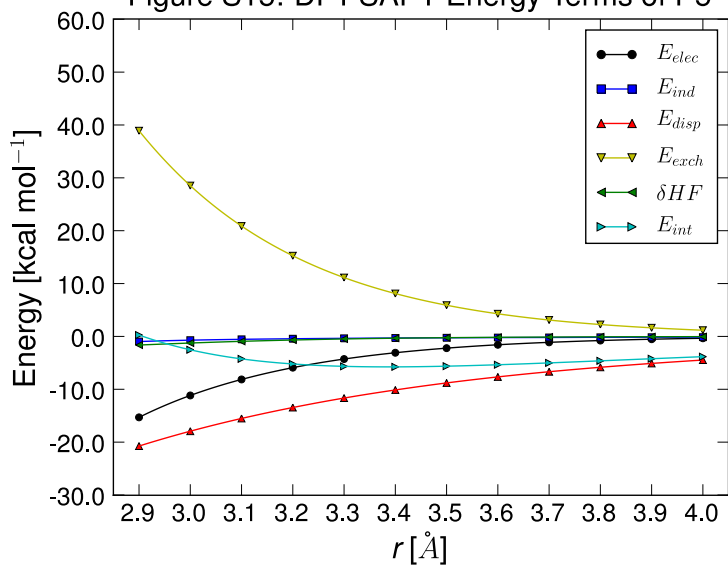
Figure S16: DFT-SAPT Energy Terms of P6
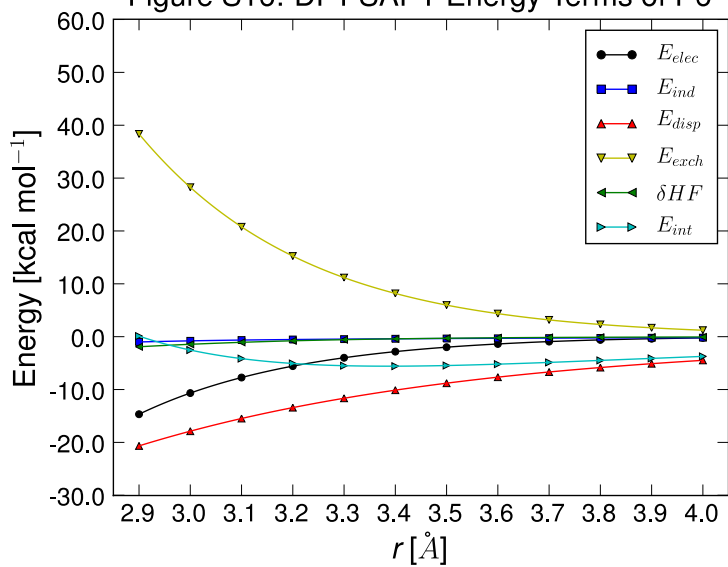
Figure S17: DFT-SAPT Energy Terms of P7
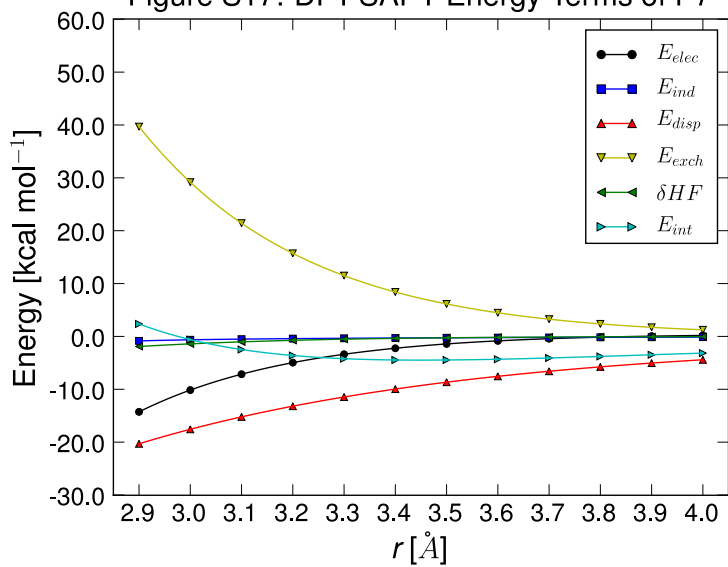
Figure S18: DFT-SAPT Energy Terms of P8
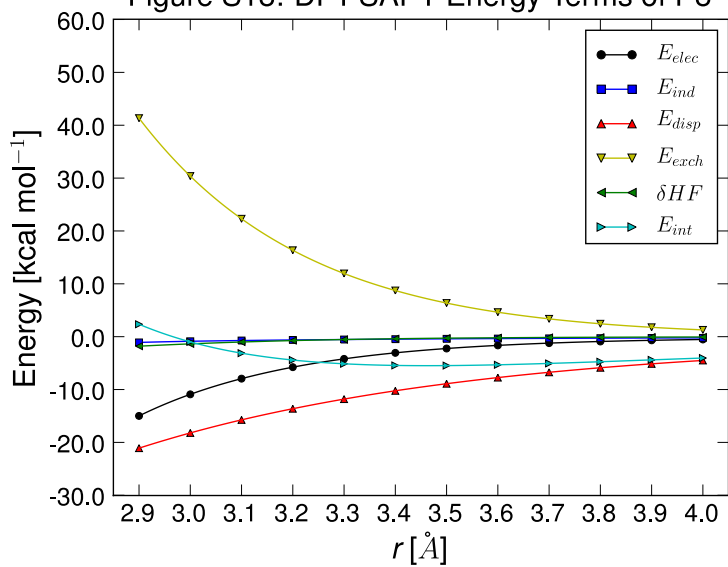
Figure S19: DFT-SAPT Energy Terms of P9
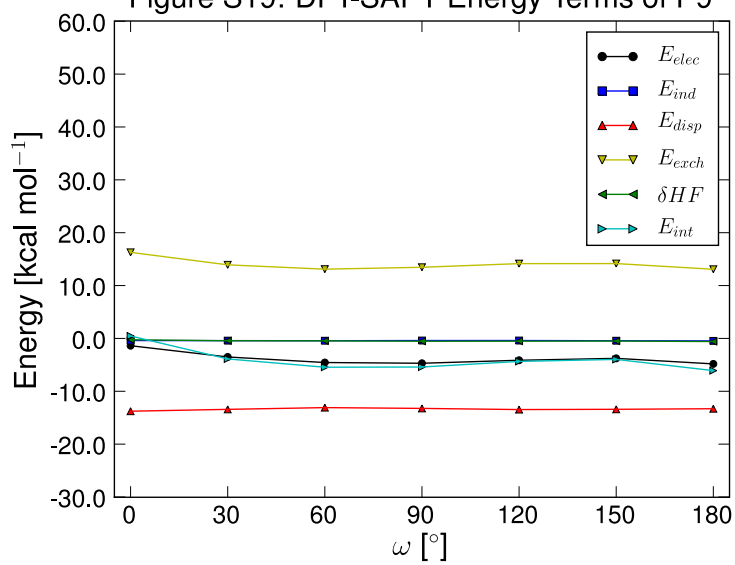
Figure S20: DFT-SAPT Energy Terms of NP1
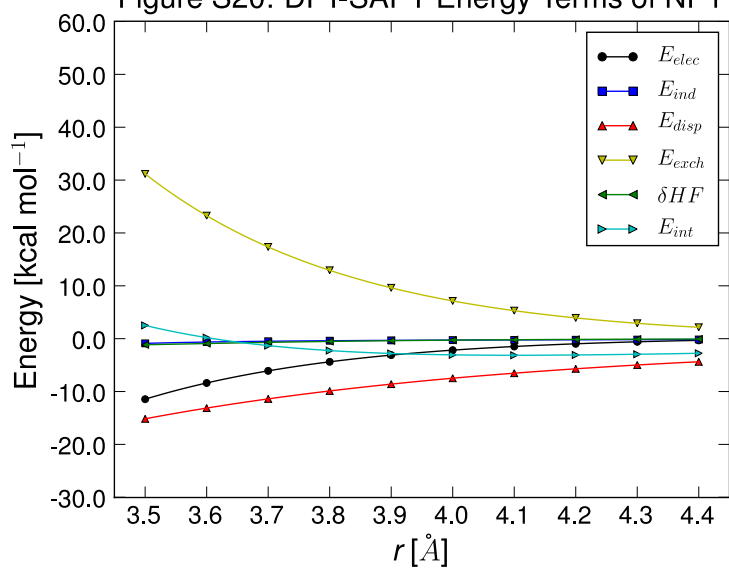
Figure S21: DFT-SAPT Energy Terms of NP2
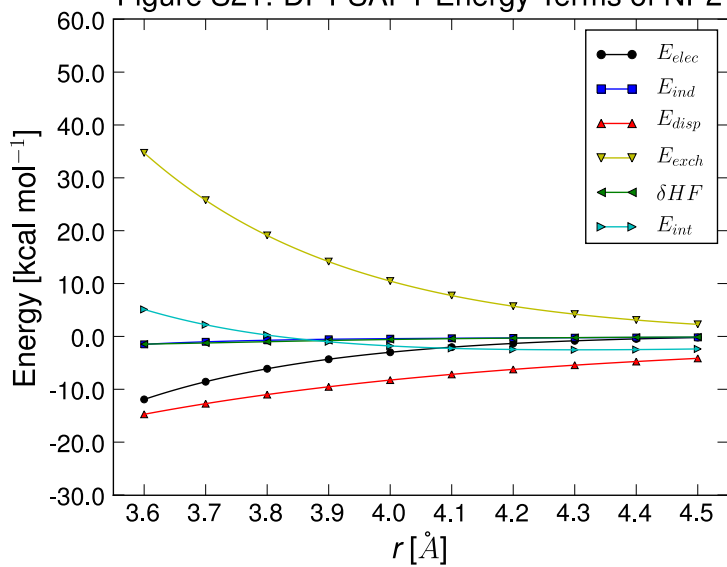
Figure S22: DFT-SAPT Energy Terms of NP3
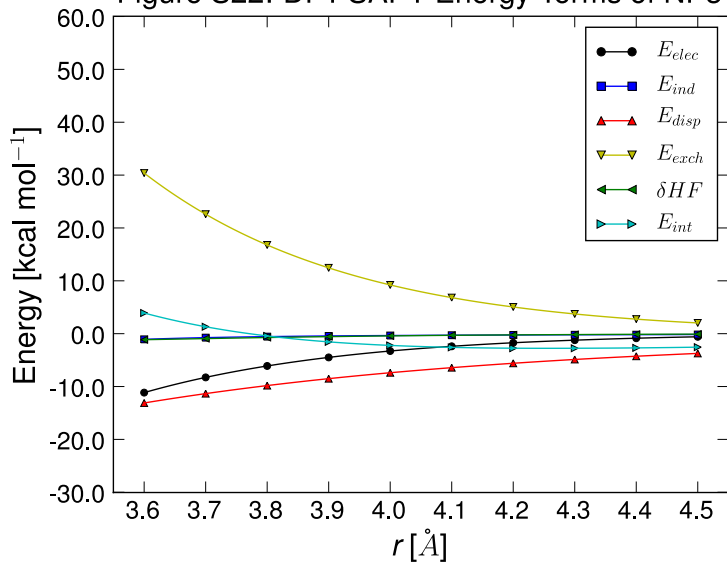
Figure S23: DFT-SAPT electrostatic terms
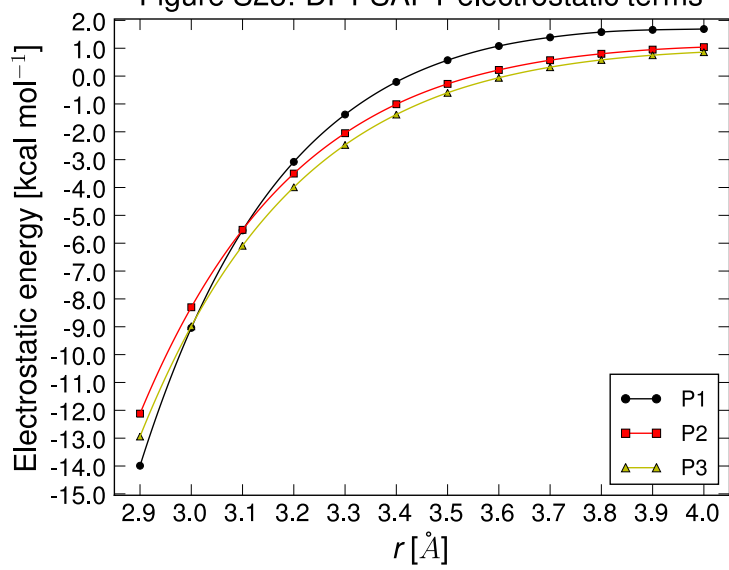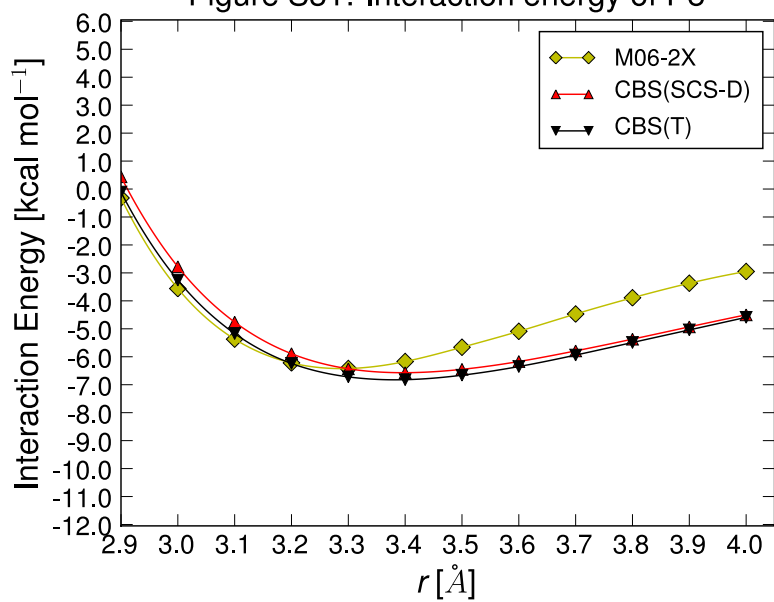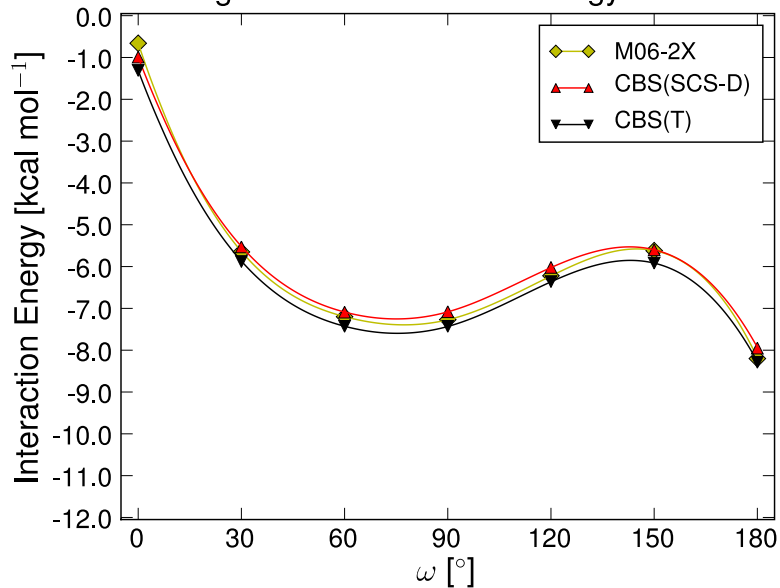
Figure S24: Interaction energy of P1
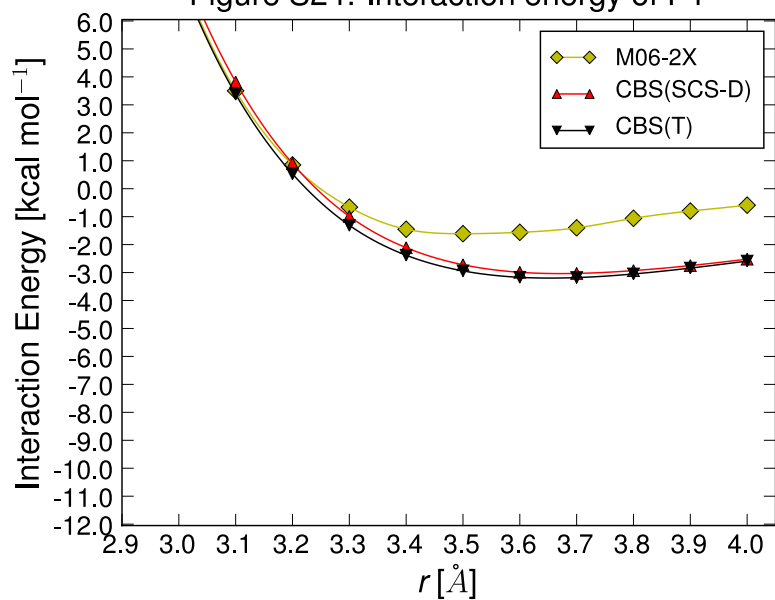
Figure S25: Interaction energy of P2
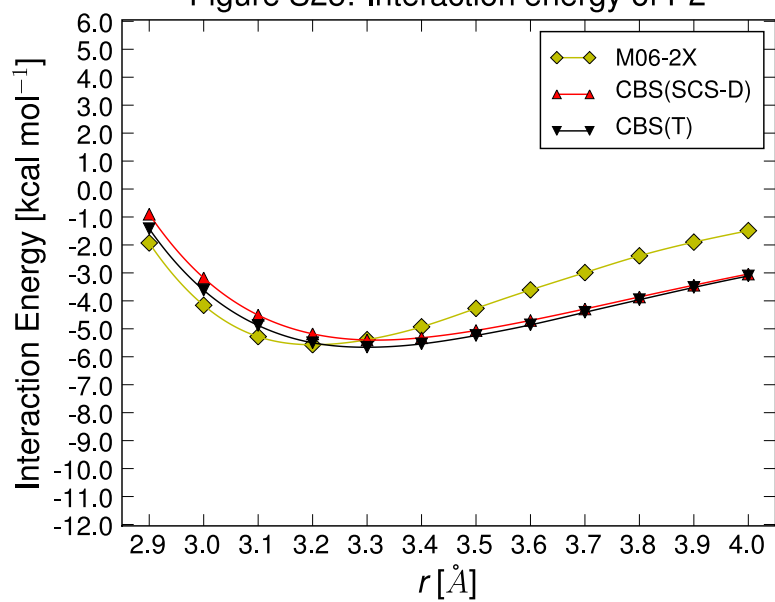
Figure S26: Interaction energy of P3
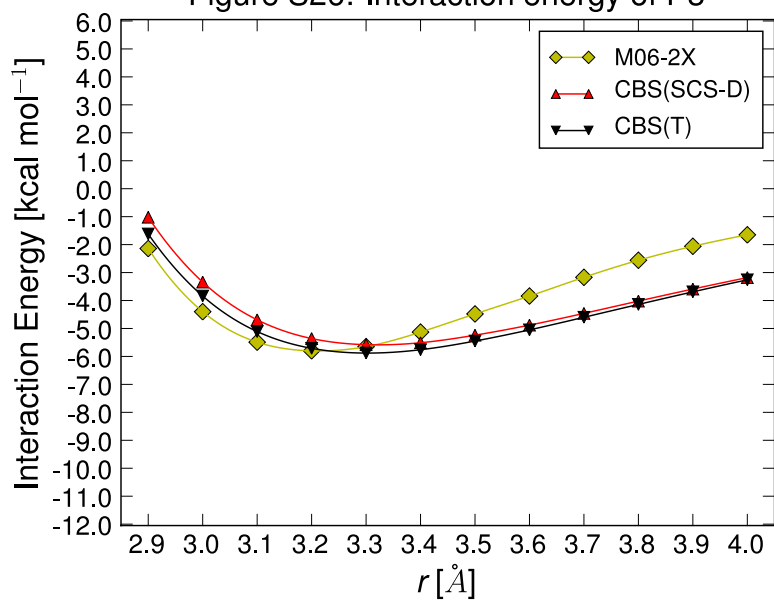
Figure S27: Interaction energy of P4
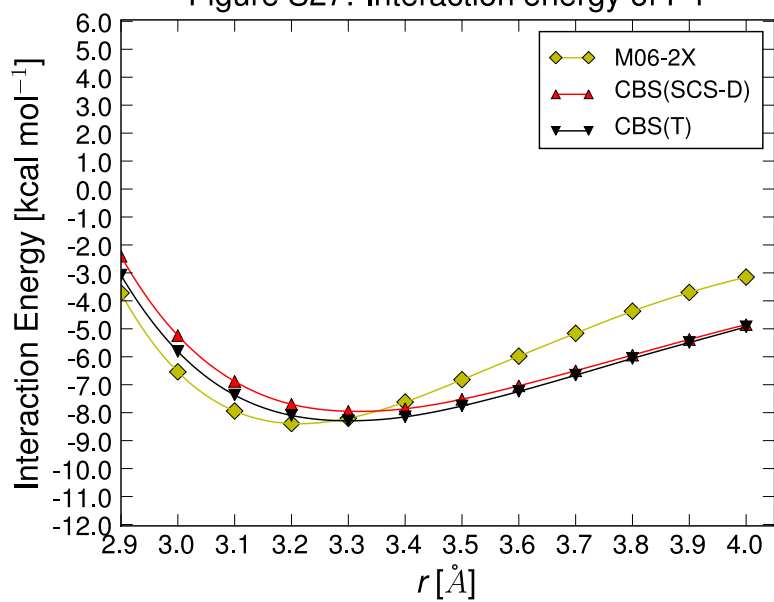
Figure S28: Interaction energy of P5
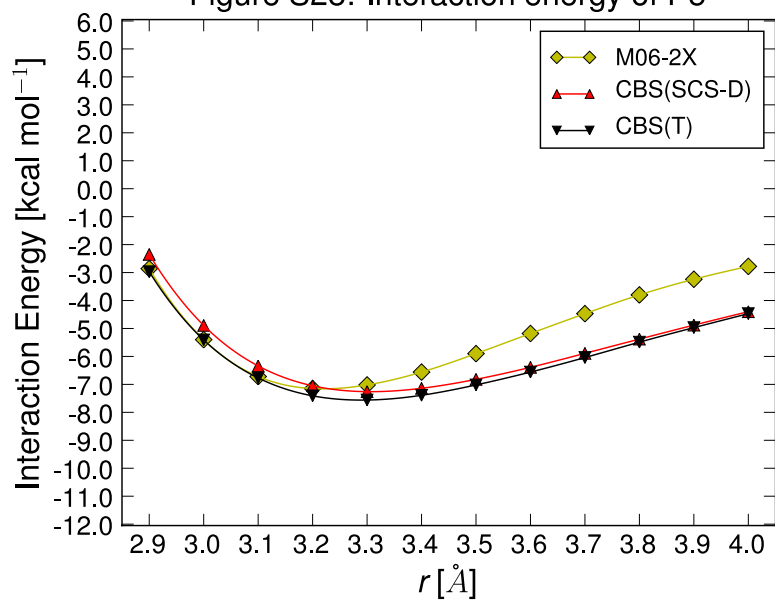
Figure S29: Interaction energy of P6
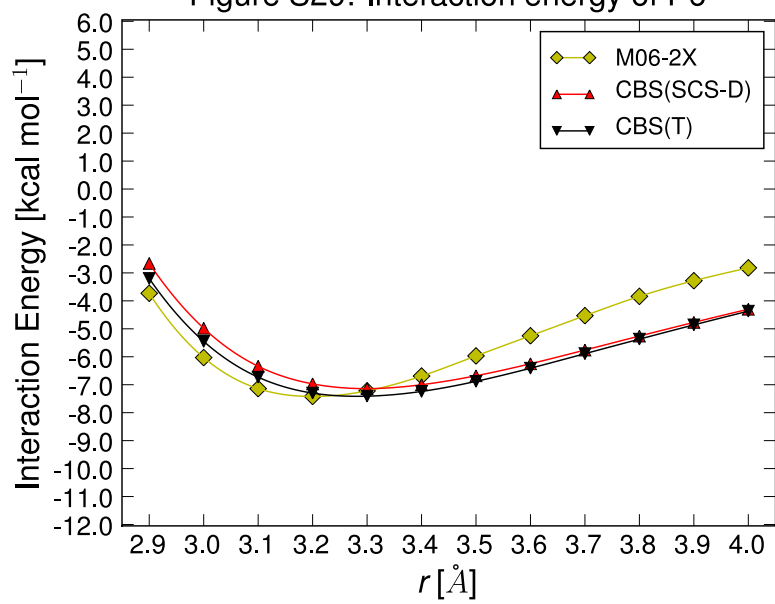
Figure S30: Interaction energy of P7
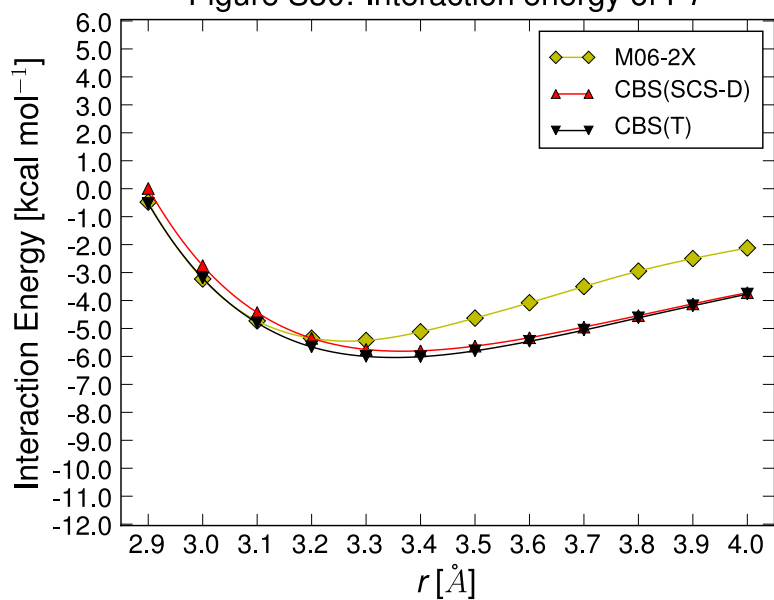
Figure S31: Interaction energy of P8

Figure S32: Interaction energy of P9
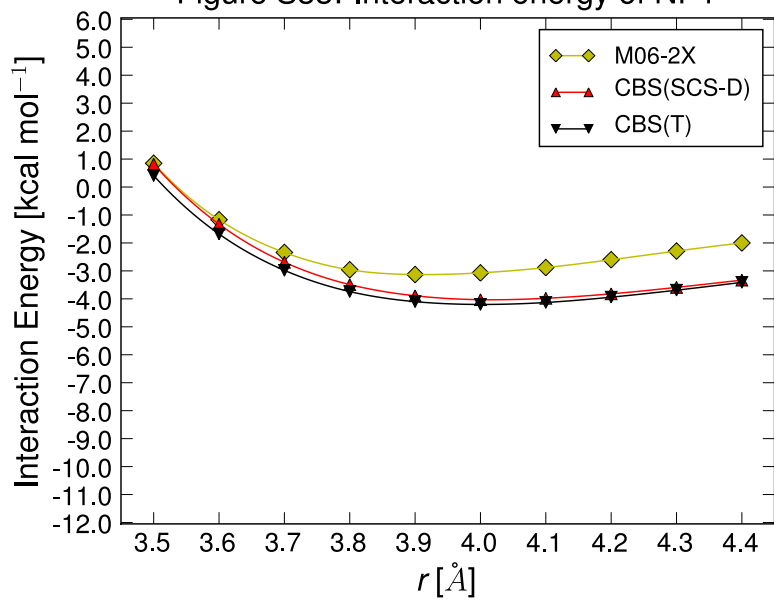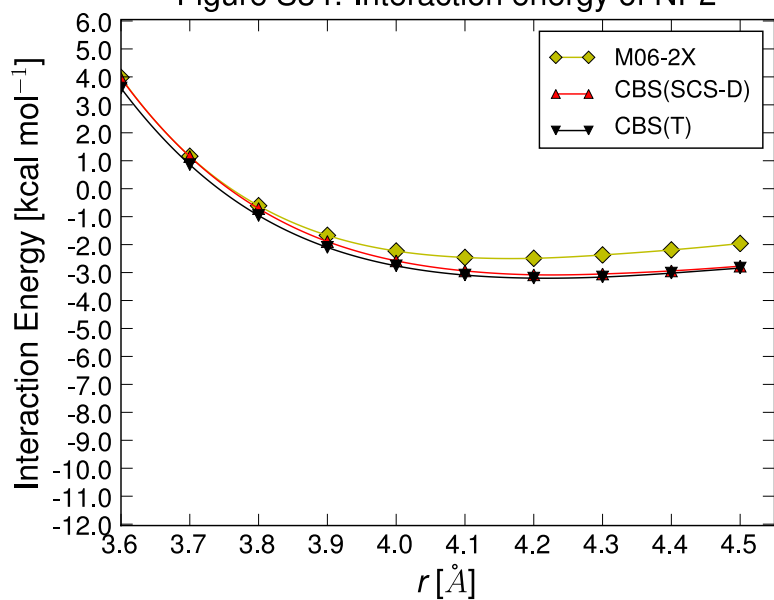

Figure S33: Interaction energy of NP1

Figure S34: Interaction energy of NP2

Figure S35: Interaction energy of NP3