WP12

Theoretical Methods for Condensed Matter

Part II

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1 Partitioning Noncovalent Interactions

The interactions in weakly bound dimers were investigated using the symmetry-adapted perturbation theory[1] (SAPT) as implemented in the MOLPRO2012 program package.[2] By using the SAPT ansatz, the first and second order contributions to the complexation energy can be obtained as

$$E_{\text{SAPT}} = E_{\text{pol}} + E_{\text{exch}} + E_{\text{ind}} + E_{\text{exch}-\text{ind}} + E_{\text{disp}} + E_{\text{exch}-\text{disp}} \ , \tag{1}$$

Therefore, a monomer description via HF or DFT is required.

1.1 Interactions in the argon, water and uracil dimers

Here, the interactions in the argon, water and uracil dimers were calculated and partitioned on the HF-SAPT/aug-cc-pVTZ[3,4] and AC-PBE0[5]/aug-cc-pVTZ level of theory. In case of PBE0, an asymptotic correction (AC) to the monomer exchange-correlation potential is added to obtain reasonable results. DFT-based SAPT needs experimental and theoretical ionization energies as input for the dimer calculation. The experimental ones were obtained from the NIST webpage.[6] For the theoretical ones a monomer calculation was performed, subsequently using the negative HOMO energy as the negative ionization potential according to Koopman's theorem. For the uracil dimer a smaller aug-cc-pVDZ basis set was used to reduce the computational effort. Note that with the decreasing basis set size larger basis set incompleteness (BSIE) error arise. It is important to mention that within the SAPT ansatz, there is per definition no basis set superposition error (BSSE) since no calculation of the full dimer is carried out.

The obtained energies are displayed in Table 1. The first order polarization energy E_{pol}^1 as well as the second order induction E_{ind}^2 and dispersion E_{disp}^2 energies are negative throughout all the calculations. This is reasonable since these processes are per definition attractive. Opposed to that, the first order exchange energy E_{exch}^1 and the second order induction-exchange $E_{\text{ind}-\text{exch}}^2$ and dispersion-exchange $E_{\text{disp}-\text{exch}}^1$ contribute positively and hence repulsively. Taking a look to the summed energy contributions E_{tot}^1 and E_{tot}^2 one can see that the second order energy is negative for all cases. In case of the unpolar argon dimer, this can be explained by the large contribution of the dispersion energy which is a second order quantity. In case of the water and uracil dimers, dispersion still gives a large part of the energy, but the induction energy is slightly larger for water and significantly larger for uracil which can be deduced to the polar nature of the latter dimers as compared to argon. Since the summed second order contributions are close to each other w.r.t the comparison between HF and PBE0, the differences in the binding energy are produces by the differences in the summed first order energy contributions which are mainly caused by the first order exchange energy. The summed first order energies are positive in case of argon (missing dispersion as explained before). For water and uracil, they strongly differ between HF and PBE0 resulting even in opposite signs in case of uracil. The more repulsive nature of the DFT energy is deduced to the wrong PBE0 potential which is

Table 1: Contributions to the binding energies of the argon, water and uracil dimers obtained by SAPT. Energies are given in E_{h}.

|	E_{pol}^1	E_{exch}^1	E_{ind}^2	$E_{\mathrm{ind-exch}}^2$	E_{disp}^2	$E_{\mathrm{disp-exch}}^2$	E_{tot}^1	E_{tot}^2	$E_{\mathrm{tot}}^1 + E_{\mathrm{tot}}^2$
Ar$_2$/HF	-0.1195	0.4005	-0.1469	0.1442	-0.5018	0.0355	0.2811	-0.4692	-0.1881
Ar$_2$/PBE0	-0.1249	0.4120	-0.1544	0.1513	-0.5236	0.0382	0.2871	-0.4886	-0.2016
(Uracil)$_2$/HF	-26.8849	25.3701	-12.8279	6.2995	-8.7528	1.5528	-1.5147	-13.7284	-15.2431
(Uracil)$_2$/PBE0	-25.7862	29.4175	-15.6878	9.4262	-9.6500	1.9399	3.6314	-13.9717	-10.3403
(H$_2$O)$_2$/HF	-7.3830	5.4955	-2.3656	1.2402	-2.2502	0.3952	-1.8875	-2.9804	-4.8679
(H$_2$O)$_2$/PBE0	-7.0930	6.3003	-2.7487	1.6166	-2.4950	0.4730	-0.7927	-3.1542	-3.9469
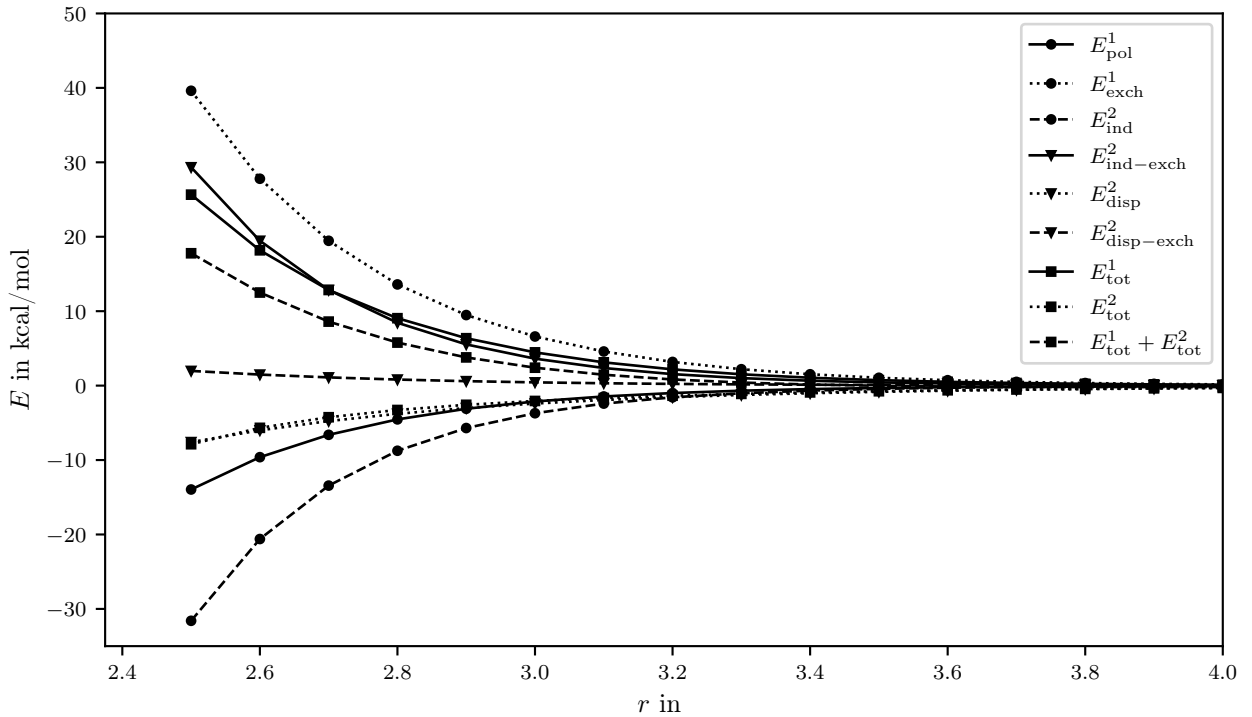
Figure 1: Distance-dependent partitioning of the noncovalent interactions in the argon dimer.

asymptotically corrected but still wrong.

The polarity of the molecules increases in the order argon < water < uracil leading to shorter distances between the monomers. Accordingly, the short-ranged exchange becomes more important and heavily contributes to the binding energy. Hence, the too repulsive DFT potential causes deviations as compared to the overbinding HF in the above-mentioned order.

1.2 Potential energy surface of the argon dimer

The potential energy surface of the argon dimer was computed between 2.5 and 4.0 Å on the HF-SAPT/aug-cc-pVTZ level of theory. The distance dependency of all contributions to the binding energy is displayed in Figure 1.

Overall, it can be observed that the contributions decay to zero with increasing monomer
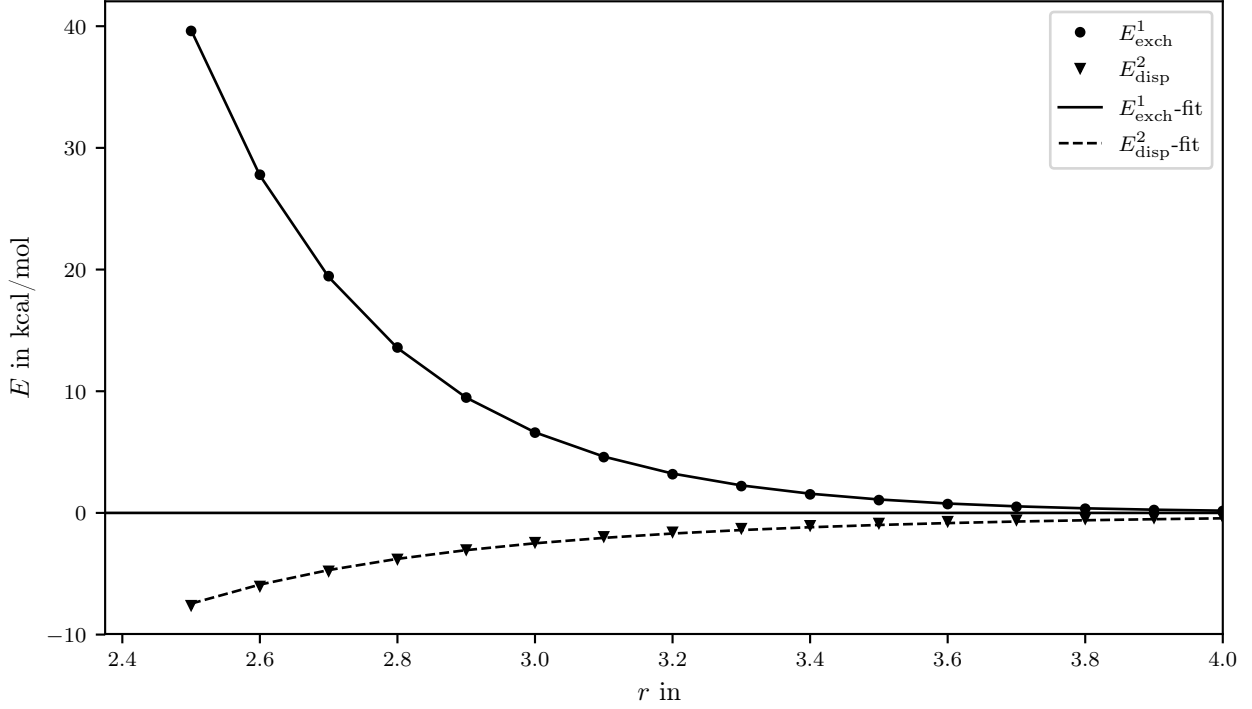
Figure 2: Distance-dependency of the first order exchange E^1_{exch} and second order dispersion energy E^2_{disp} and suitable fits (e^{-r} and r^{-6}, respectively) in the argon dimer @/.

distance. Note that their convergence behavior is different and will be exemplary discussed below. First order polarization as well as second order induction and dispersion contribute attractively, whereas the mixed second order terms and the first order exchange energy contribute repulsively. The magnitude of the contributions at the equilibrium distance of $3.76\,\text{Å}$ is shown in Table 1. At smaller distances, most of the contributions – except for $E_{\text{disp}-\text{exch}}$ – become very large.

The analytical distance dependencies of the first order exchange and second order dispersion energy are e^{-r} and r^{-6}, respectively as shown in Figure 2.

2 Supermolecular Approaches

The binding energy of a system AB consisting out of two fragments A, B is (in the supermolecular approach) defined by the energy difference between the AB system E_{AB} and the (summed) fragments E_{A}, E_{B}:

$$E_{\text{bind}} = E_{\text{AB}} - (E_{\text{A}} + E_{\text{B}}) \,. \tag{2}$$

The total energy E_{tot} of an arbitrary system is composed of the SCF energy E_{SCF} and correlation energy E_{corr}. Knowing the convergence behavior of E_{SCF} and E_{corr} w.r.t. the basis set size X, one can extrapolate the energies to the basis set limit (CBS) via

$$E^{(\infty)}_{\text{SCF}} = E^{(\text{X})}_{\text{SCF}} + A \cdot \text{e}^{-\alpha\sqrt{\text{X}}} \,, \tag{3}$$

Table 2: Hartree–Fock energies E_{RHF}, correlation energies E_{corr} and total energies E_{tot} (all in E_{h}) of the water and argon monomer and dimer. **XZ** refers to aug-cc-pV**XZ**.

(a) Energies of water.

	Monomer			Dimer		
	E_{RHF}	E_{corr}	E_{tot}	E_{RHF}	E_{corr}	E_{tot}
MP2/TZ	-76.060707	-0.268399	-76.329106	-152.126933	-0.539404	-152.666337
MP2/QZ	-76.066089	-0.285972	-76.352061	-152.137665	-0.574415	-152.712080
CCSD(T)/TZ	-76.060707	-0.281761	-76.342468	-152.126933	-0.566184	-152.693117

(b) Energies of argon.

	Monomer			Dimer		
	E_{RHF}	E_{corr}	E_{tot}	E_{RHF}	E_{corr}	E_{tot}
MP2/TZ	-526.813355	-0.210921	-527.024277	-1053.626321	-0.422740	-1054.049060
MP2/QZ	-526.816807	-0.232142	-527.048949	-1053.633199	-0.465215	-1054.098413
CCSD(T)/TZ	-526.813355	-0.235403	-527.048758	-1053.626321	-0.471625	-1054.097946

$$E_{\mathrm{corr}}^{(\infty)} = E_{\mathrm{corr}}^{(\mathrm{X})} + B \cdot \mathrm{X}^{-\beta} \ . \tag{4}$$

The parameters α, β are basis set dependent and were optimized for the present case as $\alpha = 5.79$ and $\beta = 3.05$. To extrapolate CCSD(T) results to the basis set limit, the following formula can be applied:

$$E_{\mathrm{CCSD(T)}}^{(\mathrm{CBS})} = E_{\mathrm{MP2}}^{(\mathrm{CBS})} + (E_{\mathrm{CCSD(T)}}^{(\mathrm{X})} - E_{\mathrm{MP2}}^{(\mathrm{X})}) \ . \tag{5}$$

Table 3: Binding energies of the water and argon dimer in kcal/mol computed on different levels of theory and comparison to the experiment.

	HF/CBS	CCSD(T)/CBS	AC-PBE0-SAPT	Exp.
$(H_2O)_2$	-3.444	-4.967	-3.947	XXX
Ar_2	0.261	-0.290	-0.202	XXX

3 Molecules in Solution

The equilibrium association free energy ΔG_{a} of a host-guest system (molecular tweezer with tetracyanoquinone) at room temperature in toluene is accessed by a supermolecular approach. There are different contributions to this quantity, namely the DFT Energy E_{tot}, the two- and three-body dispersion correction $E_{\mathrm{D3}}^{\mathrm{ATM}}$, the geometrical Counter–Poise correction energy E_{gCP}, the free energy correction in the rigid-rotor-harmonic-oscillator approximation $\Delta G_{\mathrm{RRHO}}^{298}$ and

the solvent free energy correction $\Delta\delta G_{\text{solv}}^{298}$:

$$\Delta G_{\text{a}} = E_{\text{tot}} + E_{\text{D3}}^{\text{ATM}} + E_{\text{gCP}} + \Delta G_{\text{RRHO}}^{298} + \Delta\delta G_{\text{solv}}^{298} \ . \tag{6}$$

Table 4: Contributions to the equilibrium association free energy of the host-guest system. Energies are given in E_{h}, except for the row "Δ" which is given in kcal/mol.

System	E_{tot}	E_{disp}	E_{gCP}	ΔG_{RRHO}^{298}	$\Delta\delta G_{solv}^{298}$
host	-1619.355877	-0.145975	0.037984	0.526756	-0.045041
guest	-678.950769	-0.035501	0.007677	0.082988	-0.023998
complex	-2298.299259	-0.239366	0.047508	0.633091	-0.045983
Δ	4.64	-36.33	1.16	14.65	14.47

$\Delta G_a = -1.41\,\text{kcal/mol}$

4 Organic Solids

The sublimation enthalpy ΔH_{sub} of an organic urea crystal at room temperature is computed. Its defined as the difference between the enthalpies of the two phases H_{gas}, H_{solid} which themselves can be split up into different contributions

$$\Delta H_{\text{sub}} = H_{\text{gas}} - H_{\text{solid}} \tag{7}$$

$$H^i = E_{\text{el}}^i + E_{\text{trans}}^i + E_{\text{rot}}^i + E_{\text{vib}}^i + pV \ , \tag{8}$$

where the E^i denote the electronic, translational, rotational and vibrational energy contributions, respectively. pV is the volume work. The vibrational energy is treated in the harmonic approximation and therefore consists of a constant part – the zero-point vibrational energy ZPVE – and a temperature dependent part.

Table 5: Contributions sublimation enthalpy of urea. Energies are given in kcal/mol.

	$E_{\text{el}}^{\text{TPSS}}$	$E_{\text{el}}^{\text{DFTB}}$	ZPVE	E_{trans}	E_{rot}	$E_{\text{vib}}^{\text{DFTB}}$	pV	H
gas	-1278.15	-7123.36	37.73	0.00	0.00	2.23	0.06	-7083.34
solid	-1293.40	-7150.34	38.81	0.30	0.30	3.29	0.00	-7107.65

Literature

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