Supplementary Material for: The significance of negativity of the target density in Frozen-Density Embedding Theory based simulations

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S1. PROOF THAT $M[\rho_B - \rho^o_{AB}] \leq P[\rho^o_A + \rho_B - \rho^o_{AB}]$

We start with the obvious equality,

$$\int \rho^o_A + \rho_B - \rho^o_{AB} = 0, \tag{S1}$$

from which it follows that:

$$\int\limits_{\rho^o_{AB}<\rho^o_A+\rho_B} \rho^o_A + \rho_B - \rho^o_{AB} = \int\limits_{\rho^o_{AB}>\rho^o_A+\rho_B} \rho^o_{AB} - \rho^o_A - \rho_B. \tag{S2}$$

The above relation used in the definition of P leads to:

$$\begin{aligned} P[\rho^o_A + \rho_B - \rho^o_{AB}] =& \frac{1}{2}\int |\rho^o_A + \rho_B - \rho^o_{AB}| \\ =& \frac{1}{2}\int\limits_{\rho^o_{AB}<\rho^o_A+\rho_B} \rho^o_A + \rho_B - \rho^o_{AB} + \\ & \frac{1}{2}\int\limits_{\rho^o_{AB}>\rho^o_A+\rho_B} \rho^o_A + \rho_B - \rho^o_{AB} \\ =& \int\limits_{\rho^o_{AB}<\rho^o_A+\rho_B} \rho^o_A + \rho_B - \rho^o_{AB}. \end{aligned} \tag{S3}$$

Splitting the domain of integration of the final integral above leads to:

$$\begin{aligned} P[\rho^o_A + \rho_B - \rho^o_{AB}] =& \int\limits_{\rho^o_{AB}<\rho_B} \rho^o_A + \rho_B - \rho^o_{AB} + \\ & \int\limits_{\rho_B\leq\rho^o_{AB}<\rho_B+\rho^o_A} \rho^o_A + \rho_B - \rho^o_{AB} \end{aligned} \tag{S4}$$

$$\begin{aligned} =& \int\limits_{\rho^o_{AB}<\rho_B} \rho_B - \rho^o_{AB} + \\ & + \int\limits_{\rho^o_{AB}<\rho_B} \rho^o_A + \int\limits_{\rho_B\leq\rho^o_{AB}<\rho_B+\rho^o_A} \rho^o_A + \rho_B - \rho^o_{AB} \end{aligned} \tag{S5}$$

The first integral in the right-hand-side of the equation above is equal to $M[\rho^o_{AB} - \rho_B]$ whereas the second and third are non-negative. As a result:

$$P[\rho^o_A + \rho_B - \rho^o_{AB}] \geq M[\rho^o_{AB} - \rho_B], \tag{S6}$$

which ends the proof.

S2. DATA

complex	ρ_B	$E_k[\Delta\rho^c_{v'_A}, \rho'_A, \rho_B]$ [a]	$E_k[\Delta\rho^c_{v'_B}, \rho'_B, \rho_A]$ [a]	$E_{int}^{FDET(\rho_B)}$ [b]	E_{int}^{ref} [c]	Δ_{CP} [d]	M [e]	P [f]	P_{cmpl} [g]
7HQ-2MeOH	ρ_B^{isol}	0.092		-10.983	-0.028	0.009	0.121	0.228	0.362
7HQ-2MeOH	ρ_B^{FAT}	0.081	0.127	-14.269	-0.028	0.009	0.007	0.059	0.362
7HQ-formate	ρ_B^{isol}	0.020		-23.037	-0.058	0.006	0.206	0.316	0.670
7HQ-formate	ρ_B^{FAT}	-0.008	0.068	-33.325	-0.058	0.006	0.007	0.066	0.670
uracil-5H_2O	ρ_B^{isol}	0.224		-32.065	-0.062	0.012	0.234	0.426	0.633
uracil-5H_2O	ρ_B^{FAT}	0.204	0.236	-39.695	-0.062	0.012	0.014	0.114	0.633
PyrBnz-2HCOOH	ρ_B^{isol}	0.160		-26.948	-0.058	0.012	0.184	0.416	0.600
PyrBnz-2HCOOH	ρ_B^{FAT}	0.131	0.164	-34.894	-0.058	0.012	0.013	0.104	0.600

[a] defined in Eq. **??** in the manuscript

[b] defined in Eq. **??**, and Eq. **??** in the manuscript for ρ_B^{isol} and ρ_B^{FAT} respectively.

[c] Counterpoise corrected, i.e. $E_{int}^{ref} = E_{AB}^{(AB)} - E_A^{(AB)} - E_B^{(AB)}$, where all values are obtained with MP2, the subscript denotes the subsystem, and the superscript denotes the centres involved in the basis set expansion.

[d] Counterpoise correction: $\Delta_{CP} = E_A^{(A)} + E_B^{(B)} - E_A^{(AB)} - E_B^{(AB)}$, where all values are obtained with MP2, the subscript denotes the subsystem, and the superscript denotes the centres involved in the basis set expansion.

[e] $M = M[\rho^{ref} - \rho_B^{FDET(FAT)}]$ with $M[\rho]$ defined in Eq. **??** in the manuscript

[f] $P_{cmpl} = P[\rho_A^{isol} + \rho_B^{isol} - \rho^{ref}]$ (cf. Eq. **??**), with $P[\rho]$ defined in Eq. **??** in the manuscript

[g] $P = P[\rho^{ref} - \rho_{tot}^{FDET(FAT)}]$ with $P[\rho]$ defined in Eq. **??** in the manuscript

[h] $E_{int}^{FDET(FAT)}$ is given in Eq. **??** in the manuscript

TABLE S1. Supplementary data for *supermolecular expansion* results. Energies are given in kcal/mol and quantities related to electron densities are given in atomic units.

complex	ρ_B	$E_k[\Delta\rho^c_{v'_A}, \rho'_A, \rho_B]$ [a]	$E_k[\Delta\rho^c_{v'_B}, \rho'_B, \rho_A]$ [a]	$E_{int}^{FDET(\rho_B)}$ [b]	E_{int}^{ref} [c]	Δ_{CP} [d]	M [e]	P [f]	P_{cmpl} [g]
7HQ-2MeOH	ρ_B^{isol}	0.087		-10.702	-17.473	5.632	0.123	0.231	0.368
7HQ-2MeOH	$\rho_B^{pp(Mulliken)}$	0.084		-10.688	-17.473	5.632	0.121	0.221	0.368
7HQ-2MeOH	$\rho_B^{pp(ChelPG)}$	0.084		-13.492	-17.473	5.632	0.037	0.118	0.368
7HQ-2MeOH	ρ_B^{FAT}	0.081	0.128	-13.181	-17.473	5.632	0.013	0.073	0.368
7HQ-formate	ρ_B^{isol}	0.021		-22.927	-36.485	3.522	0.205	0.316	0.673
7HQ-formate	$\rho_B^{pp(Mulliken)}$	0.016		-27.202	-36.485	3.522	0.148	0.242	0.673
7HQ-formate	$\rho_B^{pp(ChelPG)}$	0.015		-28.678	-36.485	3.522	0.096	0.186	0.673
7HQ-formate	ρ_B^{FAT}	0.011	0.117	-28.028	-36.485	3.522	0.036	0.114	0.673
uracil-5H_2O	ρ_B^{isol}	0.212		-31.629	-38.620	7.839	0.237	0.427	0.643
uracil-5H_2O	$\rho_B^{pp(Mulliken)}$	0.201		-35.221	-38.620	7.839	0.173	0.305	0.643
uracil-5H_2O	$\rho_B^{pp(ChelPG)}$	0.205		-38.010	-38.620	7.839	0.058	0.206	0.643
uracil-5H_2O	ρ_B^{FAT}	0.196	0.234	-37.182	-38.620	7.839	0.024	0.129	0.643
PyrBnz-2HCOOH	ρ_B^{isol}	0.161		-25.795	-36.532	7.318	0.185	0.419	0.606
PyrBnz-2HCOOH	$\rho_B^{pp(Mulliken)}$	0.141		-31.448	-36.532	7.318	0.152	0.281	0.606
PyrBnz-2HCOOH	$\rho_B^{pp(ChelPG)}$	0.146		-32.291	-36.532	7.318	0.057	0.215	0.606
PyrBnz-2HCOOH	ρ_B^{FAT}	0.139	0.164	-32.418	-36.532	7.318	0.016	0.127	0.606

[a] defined in Eq. **??** in the manuscript

[b] defined in Eq. **??**, and Eq. **??** in the manuscript for ρ_B^{isol} and ρ_B^{FAT} respectively, and in Eq. **??** for $\rho_B^{pp(Mulliken)}$ and $\rho_B^{pp(ChelPG)}$

[c] Counterpoise corrected, i.e. $E_{int}^{ref} = E_{AB}^{(AB)} - E_A^{(AB)} - E_B^{(AB)}$, where all values are obtained with MP2, the subscript denotes the subsystem, and the superscript denotes the centres involved in the basis set expansion.

[d] Counterpoise correction: $\Delta_{CP} = E_A^{(A)} + E_B^{(B)} - E_A^{(AB)} - E_B^{(AB)}$, where all values are obtained with MP2, the subscript denotes the subsystem, and the superscript denotes the centres involved in the basis set expansion.

[e] $M = M[\rho^{ref} - \rho_B^{FDET(FAT)}]$ with $M[\rho]$ defined in Eq. **??** in the manuscript

[f] $P_{cmpl} = P[\rho_A^{isol} + \rho_B^{isol} - \rho^{ref}]$ (cf. Eq. **??**), with $P[\rho]$ defined in Eq. **??** in the manuscript

[g] $P = P[\rho^{ref} - \rho_{tot}^{FDET(FAT)}]$ with $P[\rho]$ defined in Eq. **??** in the manuscript

[h] $E_{int}^{FDET(FAT)}$ is given in Eq. **??** in the manuscript

TABLE S2. Supplementary data for *monomer expansion* results. Energies are given in kcal/mol and quantities related to electron densities are given in atomic units.