Supporting Information

On generalized Partition Methods for Interaction Energies

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In general, when *n* fragments (F) are present, E_{int}^{frg} is the sum of *n*(*n*-1)/2 inter-fragment interactions.

$$E_{int}^{frg} = \frac{1}{2} \sum_{\substack{F^i \neq F^j \\ F^i,F^j,\ldots,F^n \in M}} E_{int}^{F^i,F^j} = \frac{1}{2} \sum_{\substack{F^i \neq F^j \\ F^i,F^j,\ldots,F^n \in M}} \left(\sum_{A \in F^i} \sum_{B \in F^j} E_{int}^{AB} \right) \qquad S(1)$$

$$\Delta E_{int}^{G,H} = E_{int}^{frg} + \Delta E_{Dint}^{F^i} + \ldots + \Delta E_{Dint}^{F^n} = \frac{1}{2} \left(\sum_{\substack{A \neq B \\ A,B \in M}} E_{int}^{AB} - \sum_{\substack{A \neq B \\ A,B \in F^i}} E_{int,vac}^{AB} - \ldots - \sum_{\substack{A \neq B \\ A,B \in F^n}} E_{int,vac}^{AB} \right) \qquad S(2)$$

$$\Delta E_{Dself}^{frg} = \sum_{F \in M} \Delta E_{Dself}^{F} \qquad S(3)$$

While $E_{int}^{F^i,F^j}$ is the interaction energy between the basin A of the fragment F^i with the basin B of the fragment F^j. This summation runs over all the *n* fragments of the molecule (M).

Coupling equations (S2) with (S3), the global energy binding contribution ΔE_{bind}^{frg} of many interacting fragments is obtained.

$$\Delta E_{bind}^{frg} = \Delta E_{int}^{frg} + \Delta E_{Dself}^{frg} \qquad S(4)$$

Table S1. Nomenclature of IQA energy terms computed with AIMALL.

E	Partition terms	AIMALL terms
E_{self}^{A}	V_{ne}^{A}	$V_{ne}(A,A)$
	V_{C}^{A}	$V_{eeC}(A,A)$
	V_{xc}^{A}	$V_{eeXC}(A,A)$
	T^{A}	$T(A)$
	V_{nn}^{AB}	$V_{nn}(A)$
E_{int}^{AB}	$V_{neen}^{AB} = V_{en}^{AB} + V_{ne}^{AB}$	$V_{neen}^{AB}(A,A)$
	V_{C}^{AB}	$V_{eeC}(A,A)$
	V_{xc}^{AB}	$V_{eeXC}(A,A)$

Table S2. Energy terms form EDA and IQA for the H_3E---ZH_3 donor-acceptor interaction.

	BH_3						AlH_3					
	NH_3		PH_3		AsH_3		NH_3		PH_3		AsH_3	
	PIE/EDA	RS-IQA	PIE/EDA	RS-IQA	PIE/EDA	RS-IQA	PIE/EDA	RS-IQA	PIE/EDA	RS-IQA	PIE/EDA[a]	RS-IQA
ΔE_{bind}	-41.7	-41.9	-34.5	-33.5	-24.6	-24.4	-30.2	-30.4	-15.5	-15.8	-12.3 (-10.9)	-12.2
$\Delta E_{Kinetic}$	77.6	70.4	44.6	37.9	22.0	24.4	58.9	49.2	16.9	15.4	5.5 (7.0)	11.0
$\Delta E_{Classic}$	-70.1	-64.7	-27.7	-23.1	-8.5	-11.4	-53.1	-47.4	-10.9	-11.2	-0.8 (-2.5)	-6.7
ΔE_{XC}	-49.2	-47.6	-51.3	-48.4	-38.1	-37.4	-36.0	-32.3	-21.5	-19.9	-17.0 (-15.3)	-16.4
%Classic	58.8	57.6	35.1	32.3	18.2	23.4	59.6	59.5	33.5	36.1	4.4 (14.3)	29.0
%XC	41.2	42.4	64.9	67.7	81.8	76.6	40.4	40.5	66.5	63.9	95.6 (85.7)	71.0
ΔE_{Pauli}	110.2		119.7		90.3		58.6		41.2		33.0 (34.5)	
ΔE_{els}	-77.1		-61.7		-45.6		-58.5		-30.6		-23.1 (-23.0)	
ΔE_{orb}	-74.8		-92.5		-69.3		-30.4		-26.1		-22.2 (-22.4)	
$\%\Delta E_{els}$	50.8		40.0		39.7		65.8		53.9		50.9 (50.6)	
$\%\Delta E_{orb}$	49.2		60.0		60.3		34.2		46.1		49.1 (49.4)	

[a] Values in parenthesis refer to energy terms computed with the level of theory BLYP/TZP

Table S3. Energy terms form EDA and IQA for the $M^n(CO)_4$transition metal carbonyl compounds.

	$[Cu(CO)_4]^+$		$Ni(CO)_4$		$[Co(CO)_4]^-$		$[Fe(CO)_4]^{2-}$	
	PIE/EDA	**RS-IQA**	**PIE/EDA**	**RS-IQA**	**PIE/EDA**	**RS-IQA**	**PIE/EDA**	**RS-IQA**
ΔE_{bind}	-21.4	-21.5	-30.8	-31.1	-53.570	-54.1	-78.2	-81.2
$\Delta E_{Kinetic}$	8.2	7.3	64.8	69.3	136.8	138.9	227.4	214.7
$\Delta E_{Classic}$	-29.9	-28.5	-80.1	-84.1	-147.0	-149.7	-200.1	-206.2
ΔE_{XC}	0.3	-0.2	-15.5	-16.3	-43.3	-43.4	-105.5	-89.7
%Classic	101.2	99.2	83.8	83.8	77.2	77.5	65.5	69.7
%XC	-1.2	0.8	16.2	16.2	22.8	22.5	34.5	30.3
ΔE_{Pauli}	60.2		116.1		154.446		169.9	
ΔE_{els}	-50.6		-90.4		-117.909		-124.8	
ΔE_{orb}	-30.9		-56.6		-90.107		-123.3	
$\%\Delta E_{els}$	62.1		61.5		56.683		50.3	
$\%\Delta E_{orb}$	37.9		38.5		43.3		49.7	

Table S4. Energy terms form EDA (basis-set ATZ2P) and IQA (basis-set 6-311+G(d,p) and aug-cc-PVQZ) tested with functionals B3LYP and M06-2X, for the H_3N---BH_3 interaction.

	H_3N---BH_3				
	B3LYP			**M06-2X**	
	PIE/EDA ATZ2P	RS-IQA 6-311+G(d,p)	RS-IQA aug-cc-PVQZ	PIE/EDA ATZ2P	RS-IQA 6-311+G(d,p)
ΔE_{bind}	-41.7	-41.9	-42.2	-45.4	-45.2
$\Delta E_{Kinetic}$	77.6	70.4	77.7	74.8	66.5
$\Delta E_{Classic}$	-70.1	-64.7	-70.2	-68.6	-62.6
ΔE_{XC}	-49.2	-47.6	-49.6	-51.6	-49.2
%Classic	58.8	57.6	58.6	57.1	56.0
%XC	41.2	42.4	41.4	42.9	44.0
ΔE_{Pauli}	110.2			108.5	
ΔE_{els}	-77.1			-80.3	
ΔE_{orb}	-74.8			-73.6	
$\%\Delta E_{els}$	50.8			52.2	
$\%\Delta E_{orb}$	49.2			47.8	