

*Supporting Information for*

**“Noncovalent interactions from models for the  
Møller-Plesset adiabatic connection”**

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**Table S1:** MAEs in kcal/mol of MP2, SPL, MPACF-1 and SPL2 for the three subsets of the S66 dataset.

method	H-bonds	dispersion	others
MP2	0.18	0.82	0.41
SPL	0.42	0.42	0.19
MPACF-1	0.15	0.45	0.17
SPL2	0.19	0.30	0.12

**Table S2:** MAEs of 3 different reference calculations relative to each other, as well as the MAEs of MP2, SPL, SPL2, MPACF-1 relative to each of the three references for the L7 dataset. Regardless of the reference, SPL gives improvement over MP2 and SPL2 and MPACF-1 give improvements over SPL. Data from ref. 1 for L7 were obtained from DLPNO-CCSD(T) and a newly developed CBS extrapolation scheme,<sup>1</sup> ref. 2 using QCISD(T)/CBS<sup>2</sup> and ref. 3 using LNO-CCSD(T)/CBS(Q,5)) (Local Natural Orbital).<sup>3</sup> We used ref. 1 of Grimme and co-workers in the main paper. For interaction energies of individual complexes, see Fig. S2

MAE	ref. 1	ref. 2	ref. 3
ref. 1	0	1.70	0.77
ref. 2	1.70	0	1.36
ref. 3	0.77	1.36	0
MP2	8.74	7.20	8.55
SPL	3.83	2.59	3.74
SPL2	0.89	1.26	0.95
MPACF-1	2.32	1.50	2.42

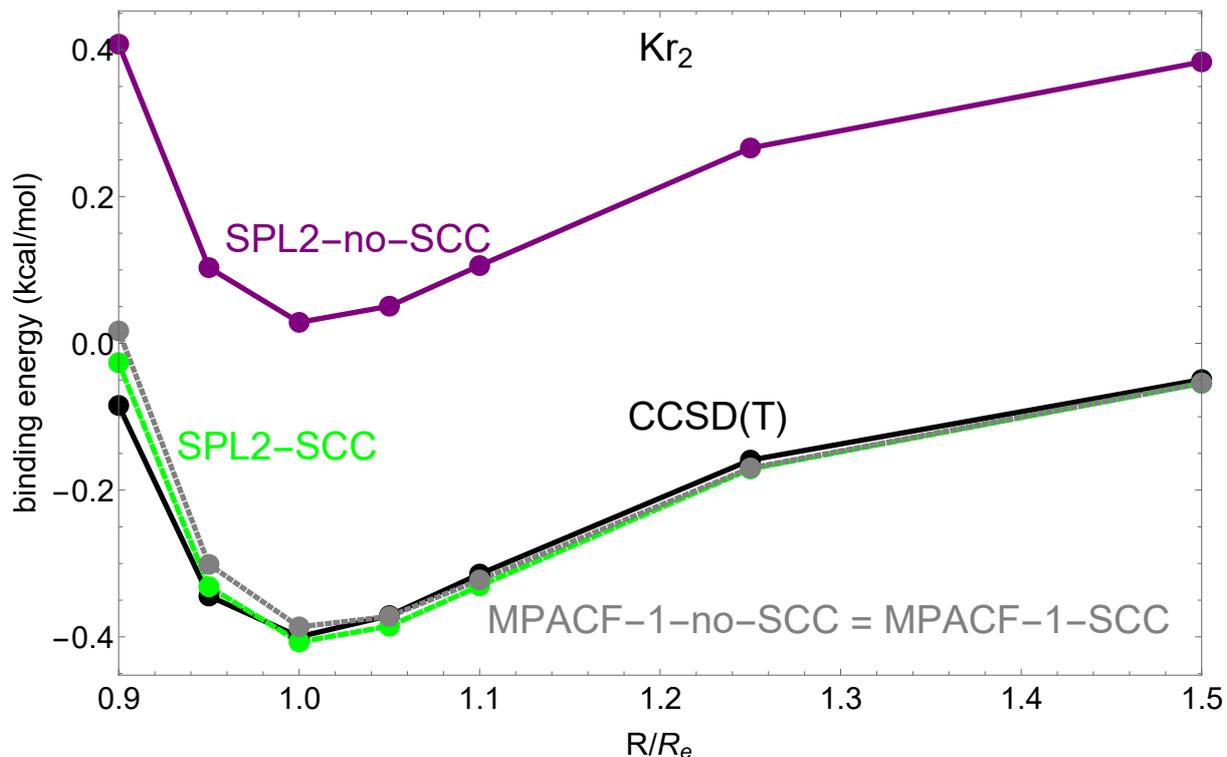


Figure S1: The SPL2 with and without size consistency corrections (SCC) plotted for the  $\text{Kr}_2$  vs the MPACF-1 method with and without SCC and the reference CCSD(T) data. For a complex composed by identical fragments  $A$ , the following equation,  $W^{\text{model}}(N\mathbf{W}(A)) = NW^{\text{model}}(\mathbf{W}(A))$ , is a size-extensivity requirement for adiabatic connection model functions,  $W^{\text{model}}$ , with  $\mathbf{W}(A) = \{W_1(A), \dots, W_i(A)\}$  being a compact notation for the  $i$  input ingredients for fragment  $A$  and  $N$  the number of fragments.<sup>4</sup> SPL2 violates this equation, while MPACF-1 obeys it. Because of that, without the SCC, interaction energies of SPL2 do not vanish even for systems that dissociate into equal fragments as it can be seen from the  $\text{Kr}_2$  example here. Since MPACF-1 is size-extensive, the addition of the SCC does not change the  $\text{Kr}_2$  dissociation curve, as it is already correct in the dissociation limit. In any case, all our models must be used with the SCC as it ensures that the interaction energies vanish in the dissociation limits (at least for systems dissociating into fragments with non-degenerate ground-state). Without the SCC, meaningless interaction energies would be obtained in some instances [see Ref. 4].

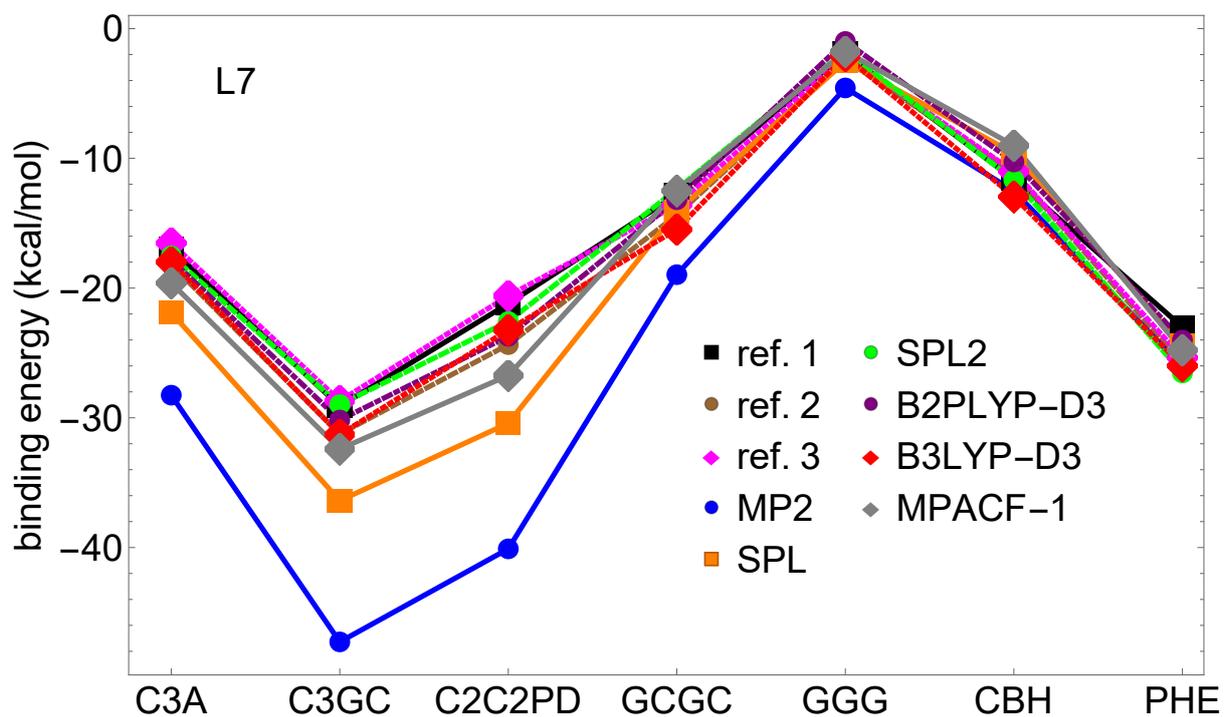


Figure S2: Interaction energies of MP2, SPL, SPL2, B3LYP-D3 and B2PLYP as well as three different reference (ref. 1 is Grimme et al.,<sup>1</sup> ref. 2 is Sedlak et al.,<sup>2</sup> and ref. 3 is Al-Hamdani et al.<sup>3</sup>) data plotted for all 7 complexes of the L7 dataset. For further details on these references, see Table S1.

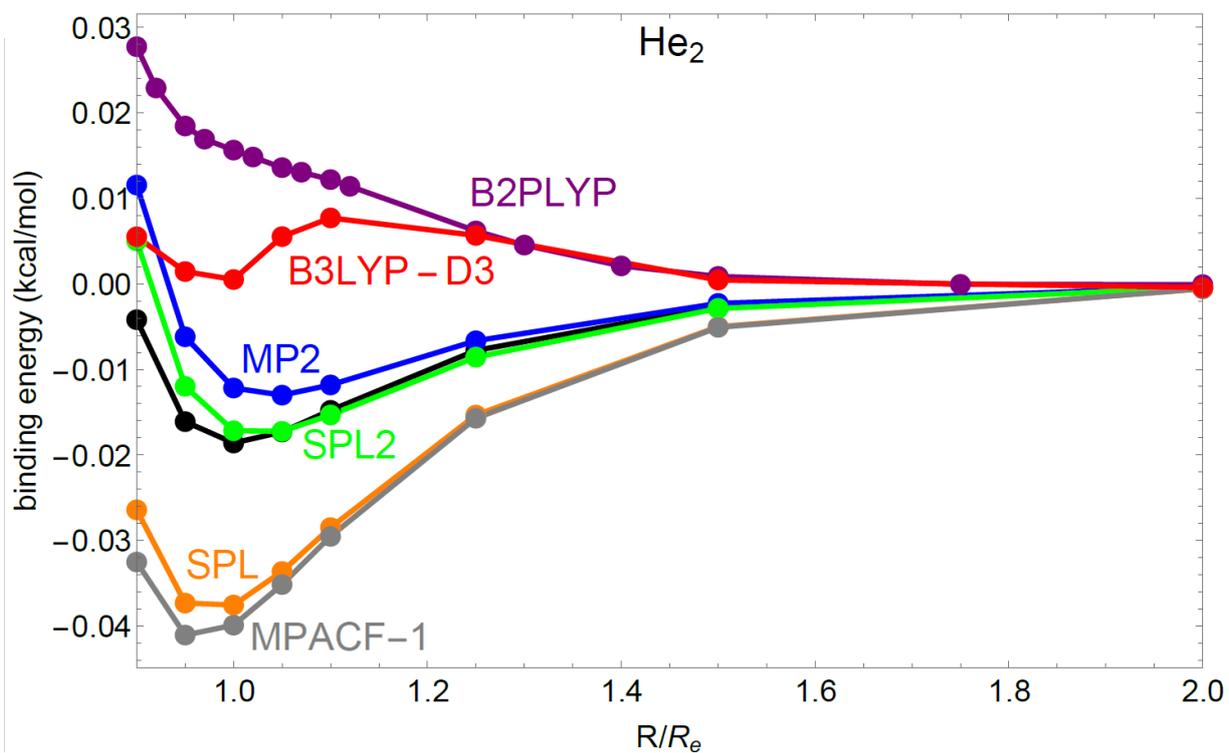


Figure S3: The interaction energies of MP2, SPL, SPL2, MPACF-1, B3LYP-D3 and B2PLYP as well as reference CCSD(T) curves for  $\text{He}_2$ . B3LYP even upon addition of D3 is producing an unphysical curve.

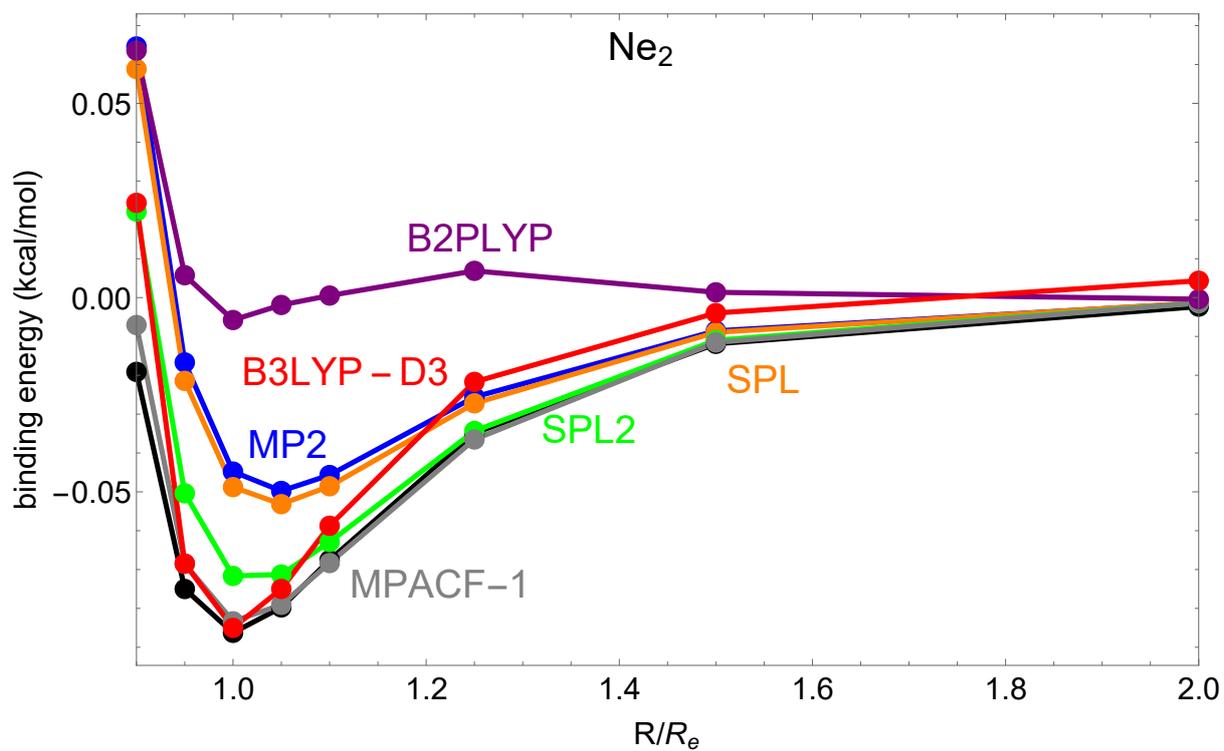


Figure S4: The interaction energies of MP2, SPL, SPL2, MPACF-1, B3LYP-D3 and B2PLYP as well as reference CCSD(T) curves for Ne<sub>2</sub>.

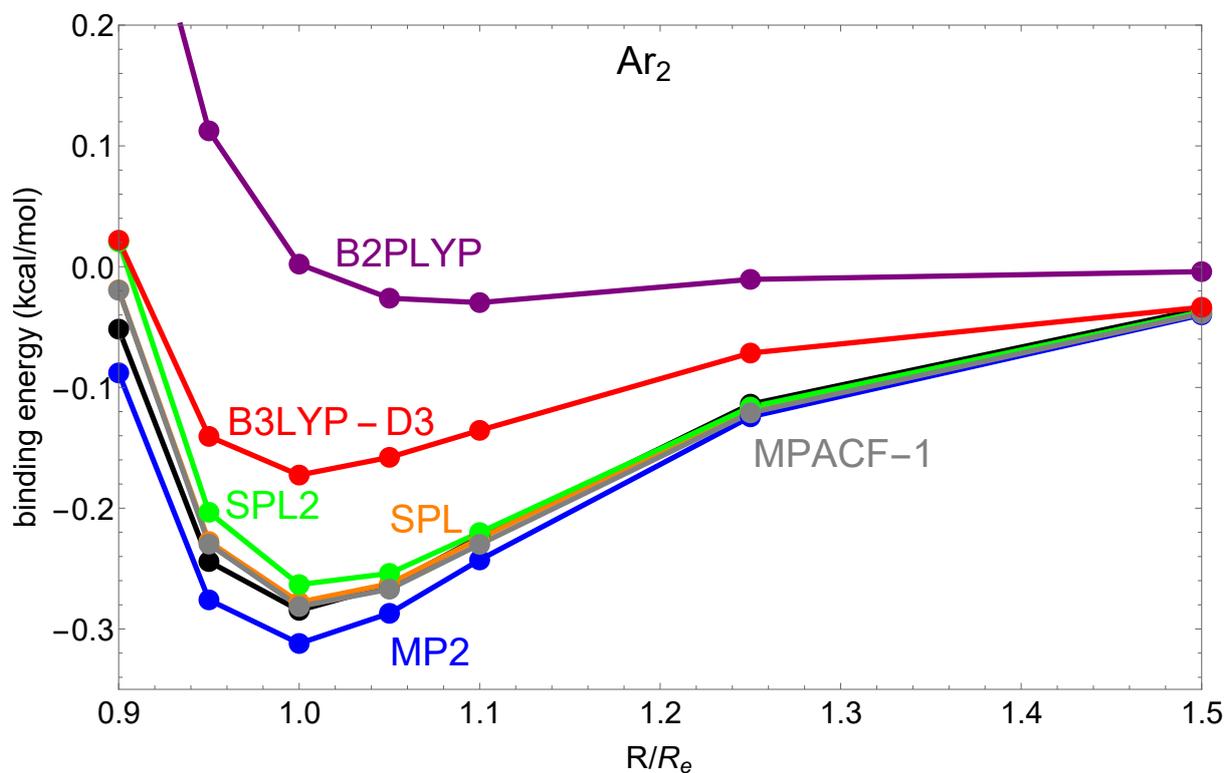


Figure S5: The interaction energies of MP2, SPL, SPL2, MPACF-1, B3LYP-D3 and B2PLYP as well as reference CCSD(T) curves for Ar<sub>2</sub>.

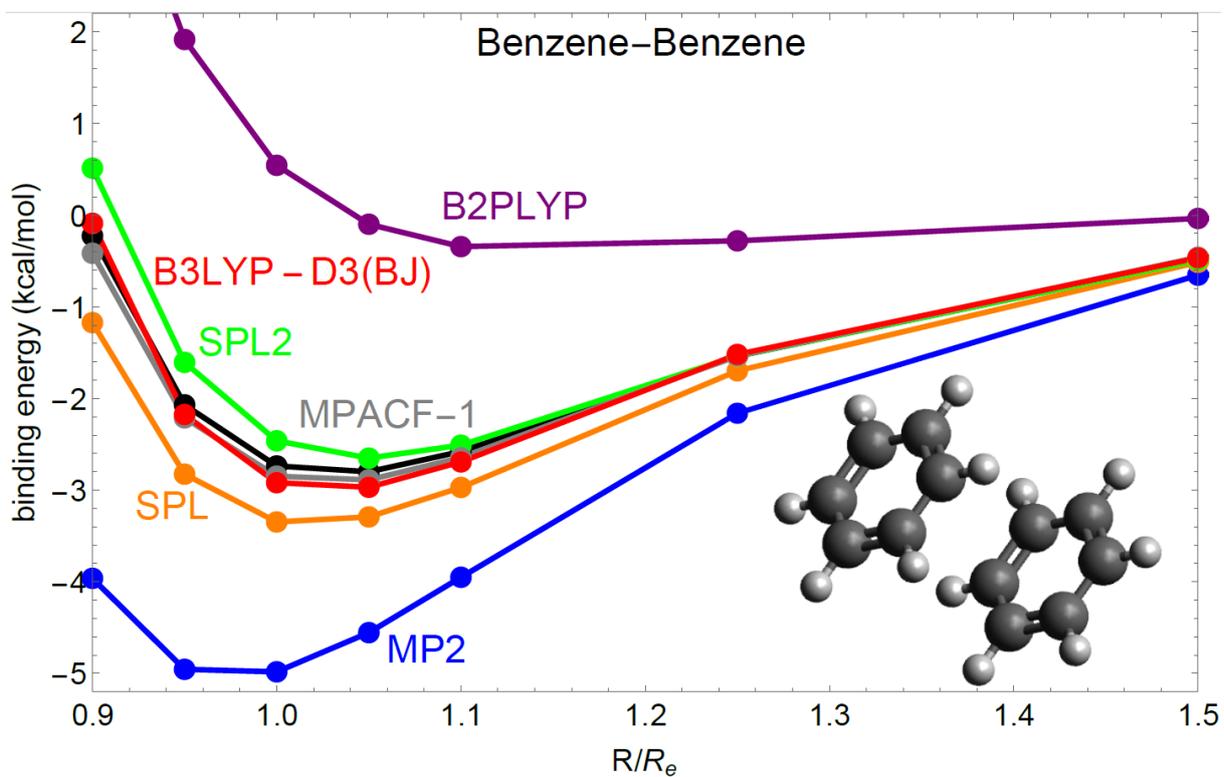


Figure S6: The interaction energies of MP2, SPL, SPL2, MPACF-1, B3LYP-D3(BJ) and B2PLYP as well as reference CCSD(T) curves for Benzene dimer.

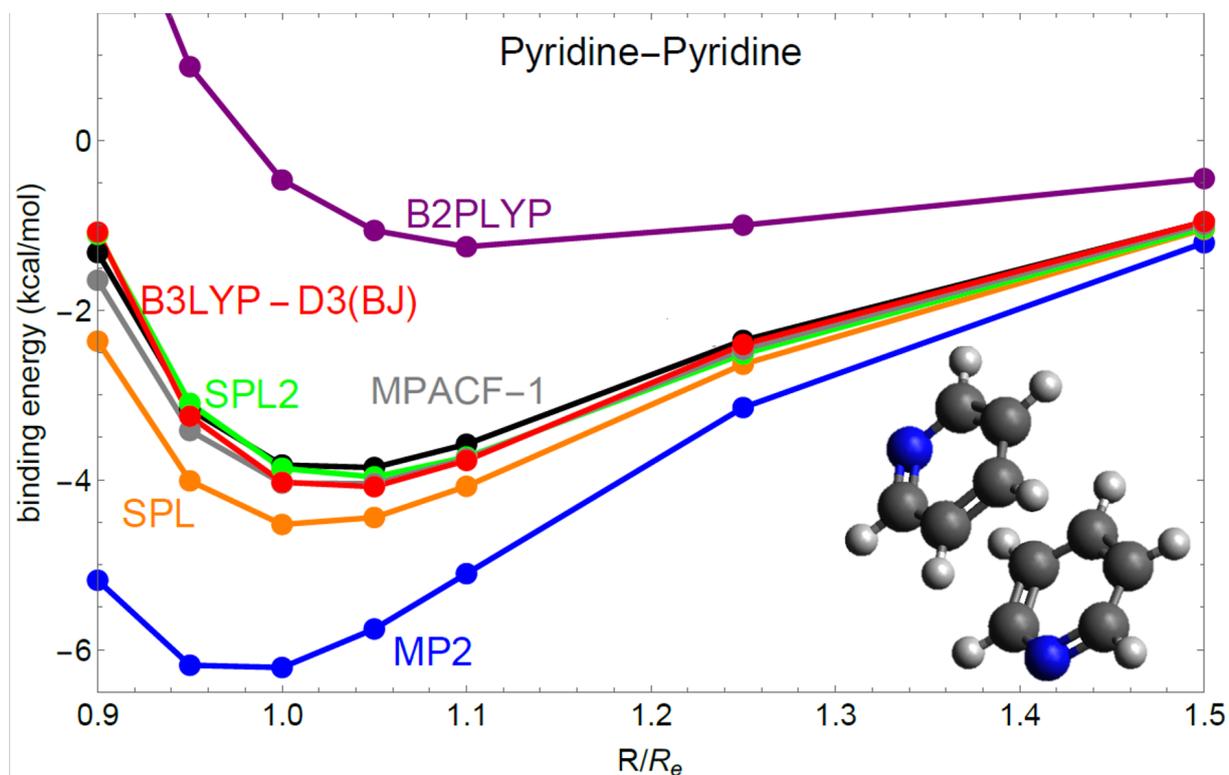


Figure S7: The interaction energies of MP2, SPL, SPL2, MPACF-1, B3LYP-D3(BJ) and B2PLYP as well as reference CCSD(T) curves for Pyridine dimer.

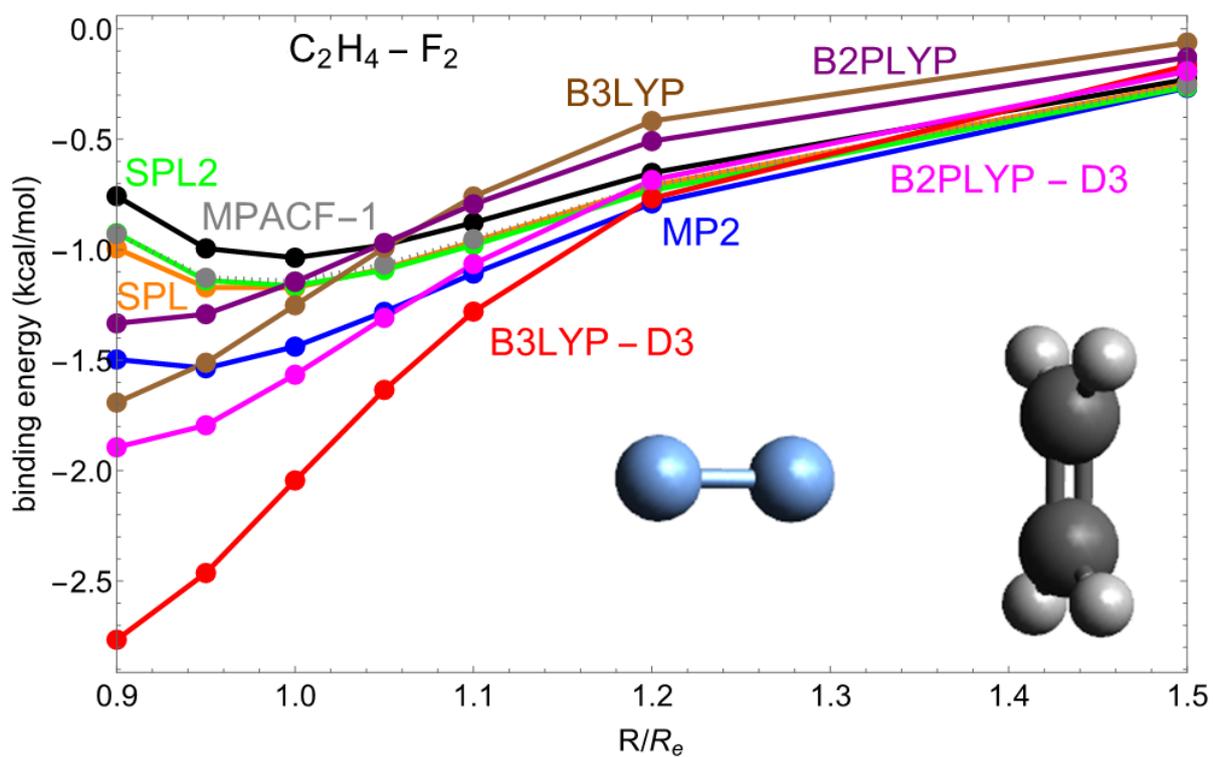


Figure S8: The interaction energies of MP2, SPL, SPL2, MPACF-1, B3LYP-D3 and B2PLYP as well as reference CCSD(T) curves for  $C_2H_4-F_2$

Table S3: The  $W_{c,\lambda}$  and  $E_c$  forms of the three different methods (SPL, SPL2 and MPACF-1) as well as their fixed and empirical parameters. For all forms,  $E_x$  and  $E_c^{MP2}$  are the exact exchange energy and the MP2 correlation energy respectively, whereas  $W_\infty^{\text{PC}}[\rho^{\text{HF}}]$  is a GEA functional ('PC model') evaluated on the HF density, which takes the following integral form:  $W_\infty^{\text{PC}}[\rho^{\text{HF}}] = \int \left[ A\rho^{\text{HF}}(\mathbf{r})^{4/3} + B\frac{|\nabla\rho^{\text{HF}}(\mathbf{r})|^2}{\rho^{\text{HF}}(\mathbf{r})^{4/3}} \right] d\mathbf{r}$  with  $A = -1.451$  and  $B = 5.317 \times 10^{-3}$ . In SPL,  $W_{c,\infty}$  form results from the PC model approximation to  $W_{c,\infty}^{\text{DFT}}$  as done in Ref. 4. In SPL2,  $W_{c,\infty}$  has been approximated in terms of the form containing  $\alpha$  and  $\beta$  parameters, which have been determined empirically. The form of  $W_{c,\infty}$  in MPACF-1 has been fixed by the large  $\lambda$  limit of the MP AC for the uniform electron gas.

	SPL	SPL2	MPACF-1
$W_{c,\lambda}$	$W_{c,\infty} \left( 1 - \frac{1}{\sqrt{1+b\lambda}} \right)$	$C_1 - \frac{m_1}{\sqrt{1+b_1\lambda}} - \frac{m_2}{\sqrt{1+b_2\lambda}}$	$g \left( \frac{(h+1) \left( h\sqrt{d_1^2\lambda+1} (3d_2^4\lambda+4) + 2(d_1^2\lambda+2) (d_2^4\lambda+1)^{3/4} \right)}{4\sqrt{d_1^2\lambda+1} (d_2^4\lambda+1)^{3/4} \left( \sqrt{d_1^2\lambda+1} + h\sqrt[4]{d_2^4\lambda+1} \right)^2} - 1 \right)$
$E_c = \int_0^1 W_{c,\lambda} d\lambda$	$W_{c,\infty} \left( \frac{2+b-2\sqrt{1+b}}{b} \right)$	$C_1 - \frac{2m_1(\sqrt{1+b_1}-1)}{b_1} - \frac{2m_2(\sqrt{1+b_2}-1)}{b_2}$	$-g + \frac{g(h+1)}{\sqrt{d_1^2+1} + h\sqrt[4]{d_2^4+1}}$
$W_{c,\infty}$	$W_\infty^{\text{PC}}[\rho^{\text{HF}}] - E_x$	$\alpha W_\infty^{\text{PC}}[\rho^{\text{HF}}] + \beta E_x$	$\alpha W_\infty^{\text{PC}}[\rho^{\text{HF}}] + \beta E_x$
Fixed params.	$b = \frac{4E_c^{\text{MP2}}}{W_{c,\infty}}$	$C_1 = W_{c,\infty}$ , $b_1 = \frac{b_2}{m_2 - W_{c,\infty}^{E_c^{\text{MP2}}}}$ , $m_1 = W_{c,\infty} - m_2$	$g = -W_{c,\infty}$ , $h = \frac{4E_c^{\text{MP2}} - 2d_1^2W_{c,\infty}}{-4E_c^{\text{MP2}} + d_2^4W_{c,\infty}}$
Emp. params.	-	$b_2 = 0.117$ , $m_2 = 10.68$ , $\alpha = 1.1472$ , $\beta = -0.7397$	$d_1 = 0.294$ , $d_2 = 0.934$ $\alpha = 1$ , $\beta = 1$

## References

- (1) Grimme, S.; Brandenburg, J. G.; Bannwarth, C.; Hansen, A. Consistent structures and interactions by density functional theory with small atomic orbital basis sets. *The Journal of Chemical Physics* **2015**, *143*, 054107.
- (2) Sedlak, R.; Janowski, T.; Pitoňák, M.; Řezáč, J.; Pulay, P.; Hobza, P. Accuracy of Quantum Chemical Methods for Large Noncovalent Complexes. *Journal of Chemical Theory and Computation* **2013**, *9*, 3364–3374.
- (3) Al-Hamdani, Y. S.; Nagy, P. R.; Barton, D.; Kállay, M.; Brandenburg, J. G.; Tkatchenko, A. Interactions between Large Molecules: Puzzle for Reference Quantum-Mechanical Methods. 2020.
- (4) Vuckovic, S.; Gori-Giorgi, P.; Della Sala, F.; Fabiano, E. Restoring size consistency of approximate functionals constructed from the adiabatic connection. *J. Phys. Chem. Lett.* **2018**, *9*, 3137–3142.