Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Reliability of Interacting Quantum Atoms (IQA) Data Computed from Post-HF Densities: Impact of Approximation Used

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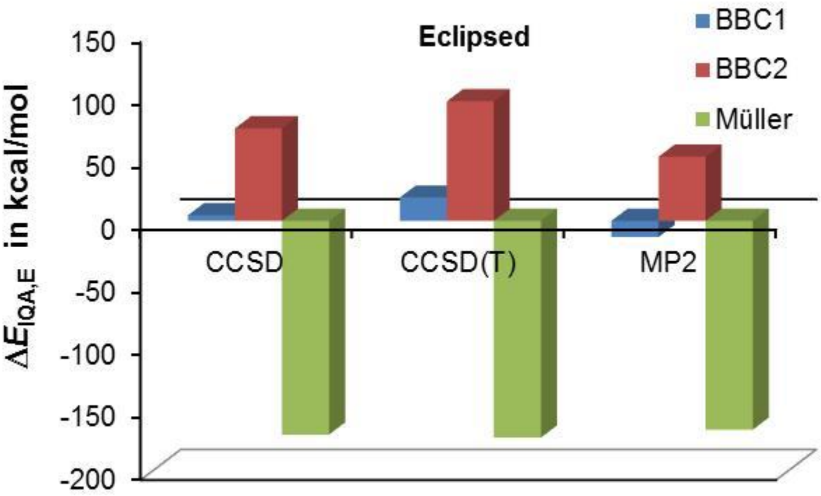
Electronic Supplementary Information



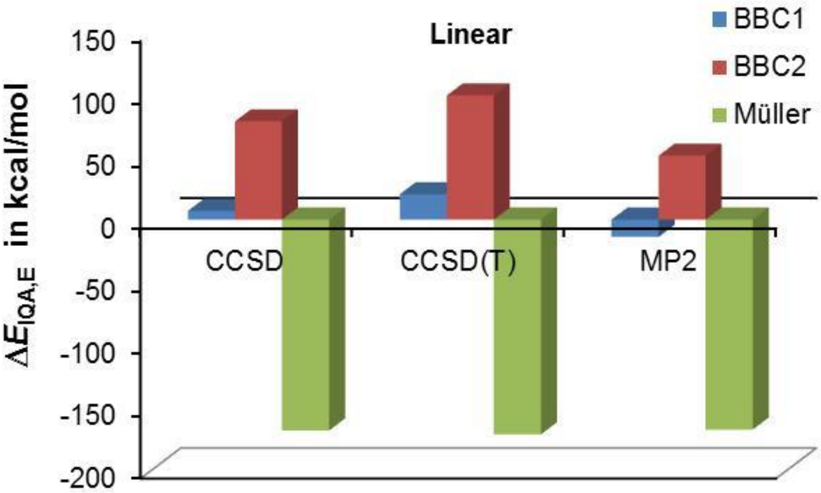
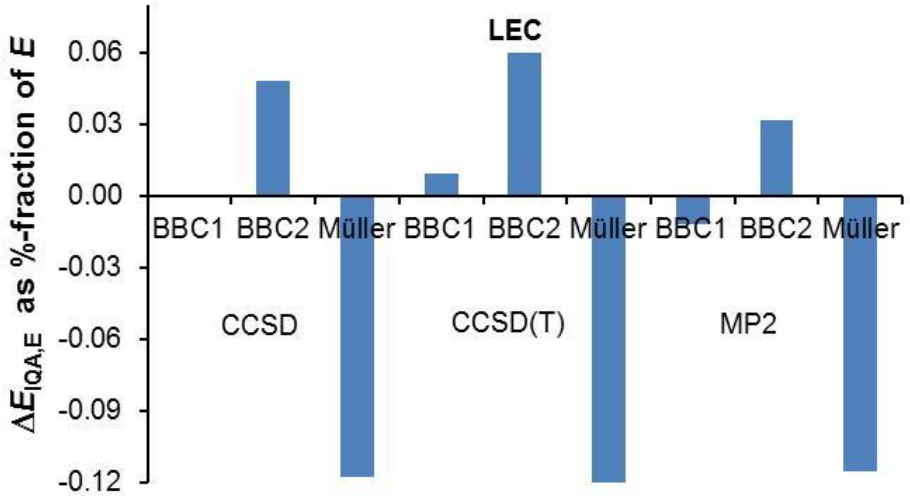
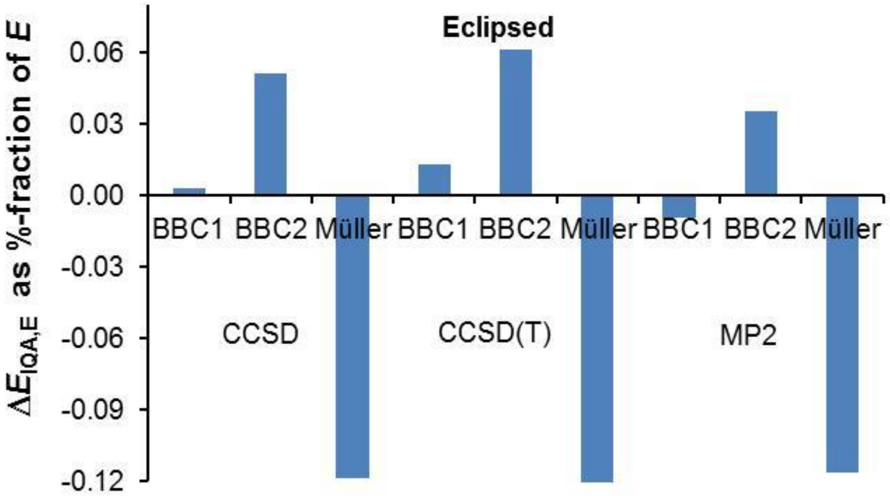


Figure S1. Pictorial presentation of the computed $\Delta E_{\mathrm{IQA,E}} = E(\mathrm{IQA}) - E$ values for the Eclipsed and Linear conformers of glycol at the indicated levels of theory and approximation.





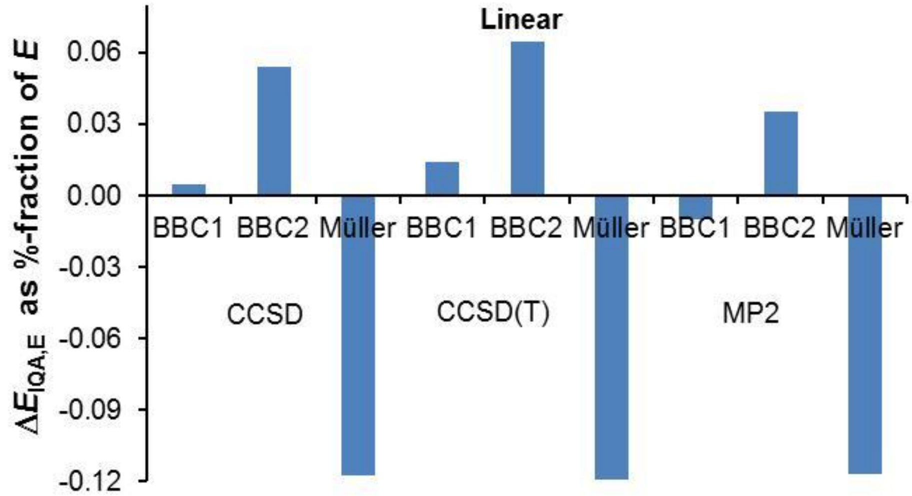


Figure S2. Variation in the $\Delta E_{\mathrm{IQA,E}}$ values expressed as the %-fraction of a molecular energy of each conformer of glycol at indicated levels of theory and approximation.

Very much the same trends are observed for all conformers in Figure S2 and, as an example, we obtained $\Delta E_{\mathrm{IQA,E}}$ values as 2.6×10^{-4} , 4.8×10^{-2} and 1.2×10^{-1}% of molecular energy E for the **LEC** when BBC1, BBC2 and Müller approximation was used, respectively. In principle, it mimics the general trends seen in Figure 2 or Table 1 in the main body of the text. However, we have noted that the trends in the %-fractions are not the same at each level of theory, e.g., we found $(\%\text{-fraction})_{\mathrm{CCSD}} < (\%\text{-fraction})_{\mathrm{CCSD(T)}} < (\%\text{-fraction})_{\mathrm{MP2}}$ for the **LEC** but $(\%\text{-fraction})_{\mathrm{CCSD}} < (\%\text{-fraction})_{\mathrm{MP2}} < (\%\text{-fraction})_{\mathrm{CCSD(T)}}$ for **Ecl** and **Lin** when BBC1 was used.

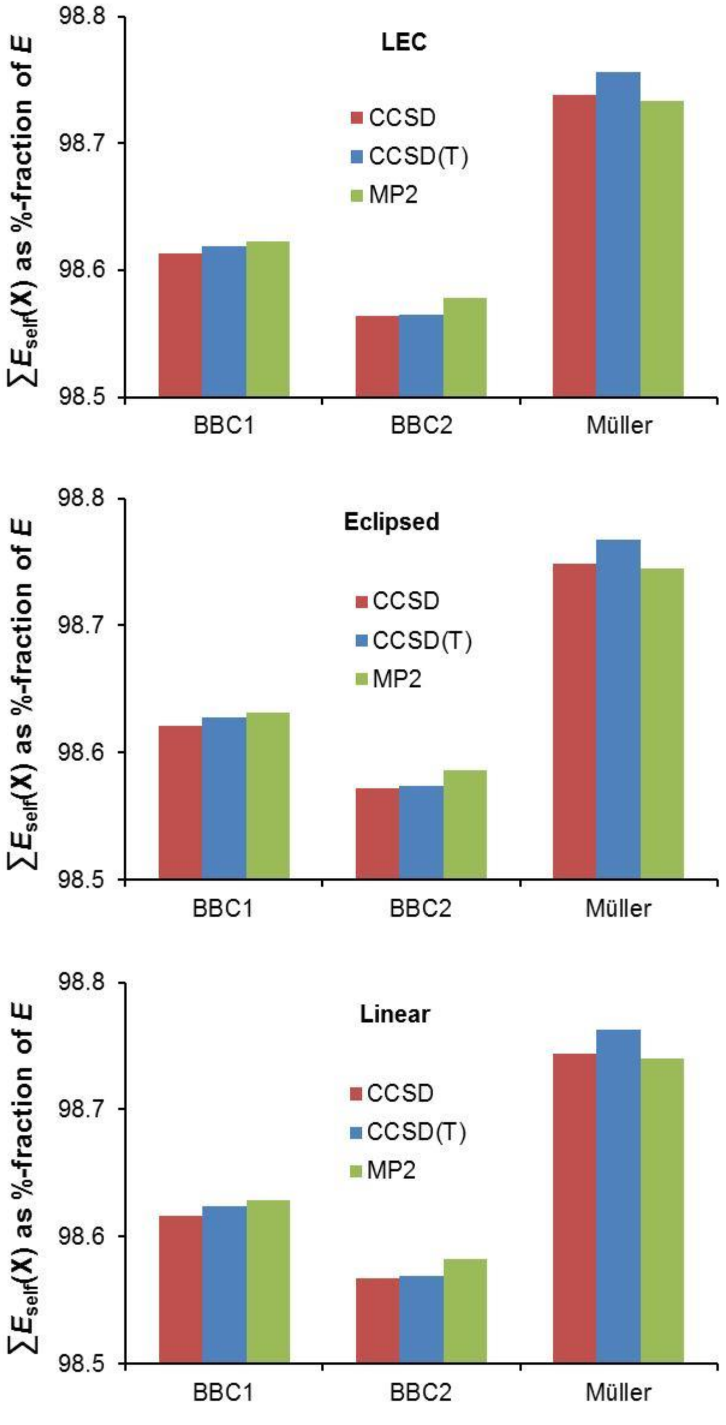


Figure S3. Variation, with the LoT/LoA combination, in the computed total self-molecular energy expressed as a %-fraction of a molecular energy of the indicated conformers of glycol.

Note that the first column in Figure S3 (data produced by CCSD/BBC1) represents the expectation value one should obtain for any other LoT/LoA combination provided no errors are present in the computed self-molecular energy.

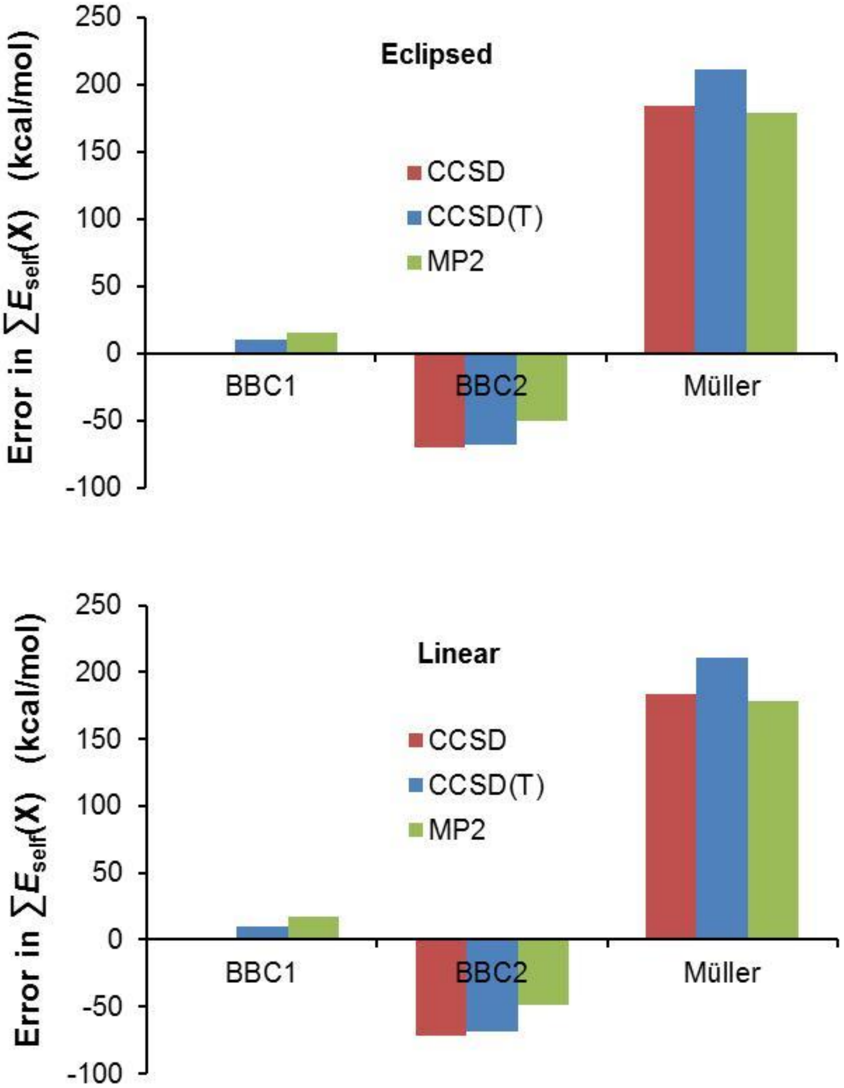


Figure S4. Errors (as $-\Delta_{\text{self}}^{\text{Tot}}$ values in Table 2 of the main body of the text) in the computed total self-molecular energy of the Eclipsed and Linear conformers at the indicated LoT/LoA combination.

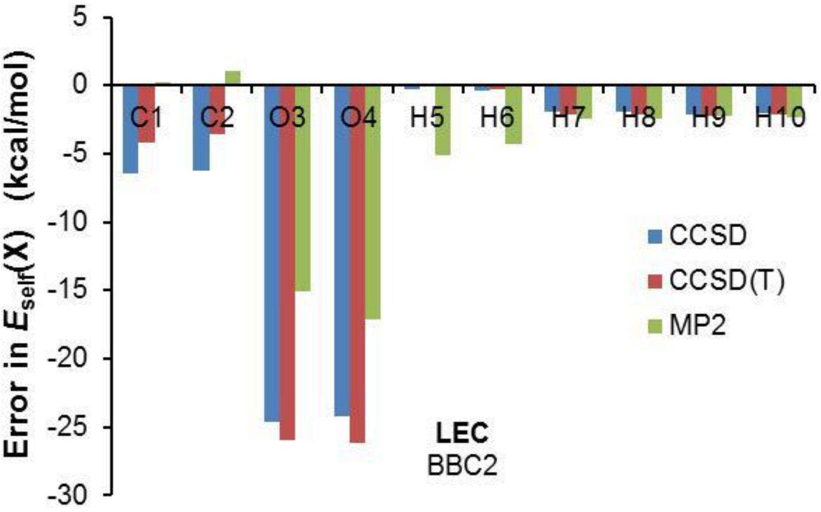


Figure S5. Relative to CCSD/BBC1 data, errors in computed self-atomic energies of the LEC of glycol at the indicated LoTs using BBC2 approximation.

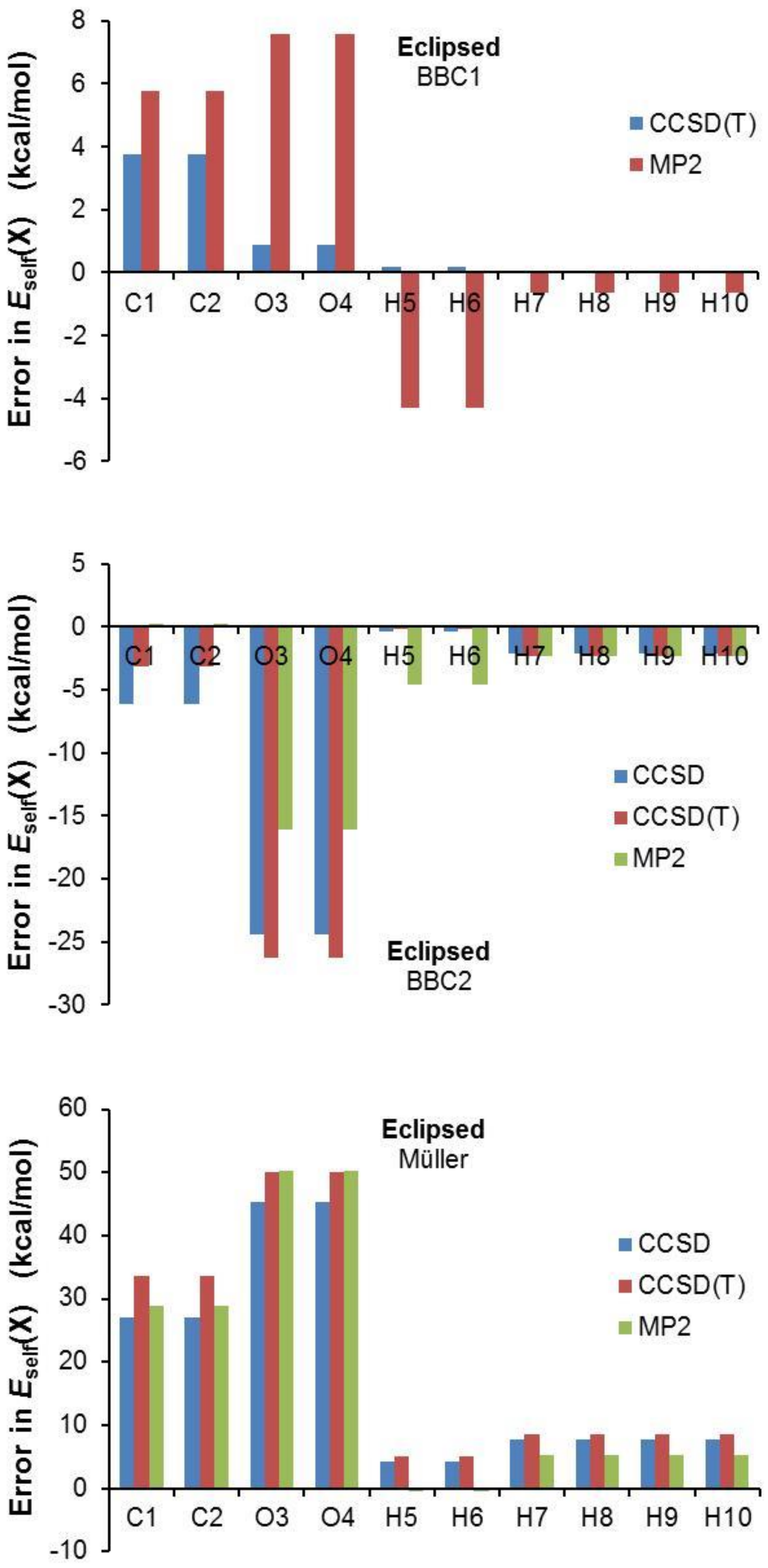


Figure S6. Relative to CCSD/BBC1 data, errors in computed self-atomic energies of the Eclipsed conformer of glycol at the indicated LoT/LoA combination.

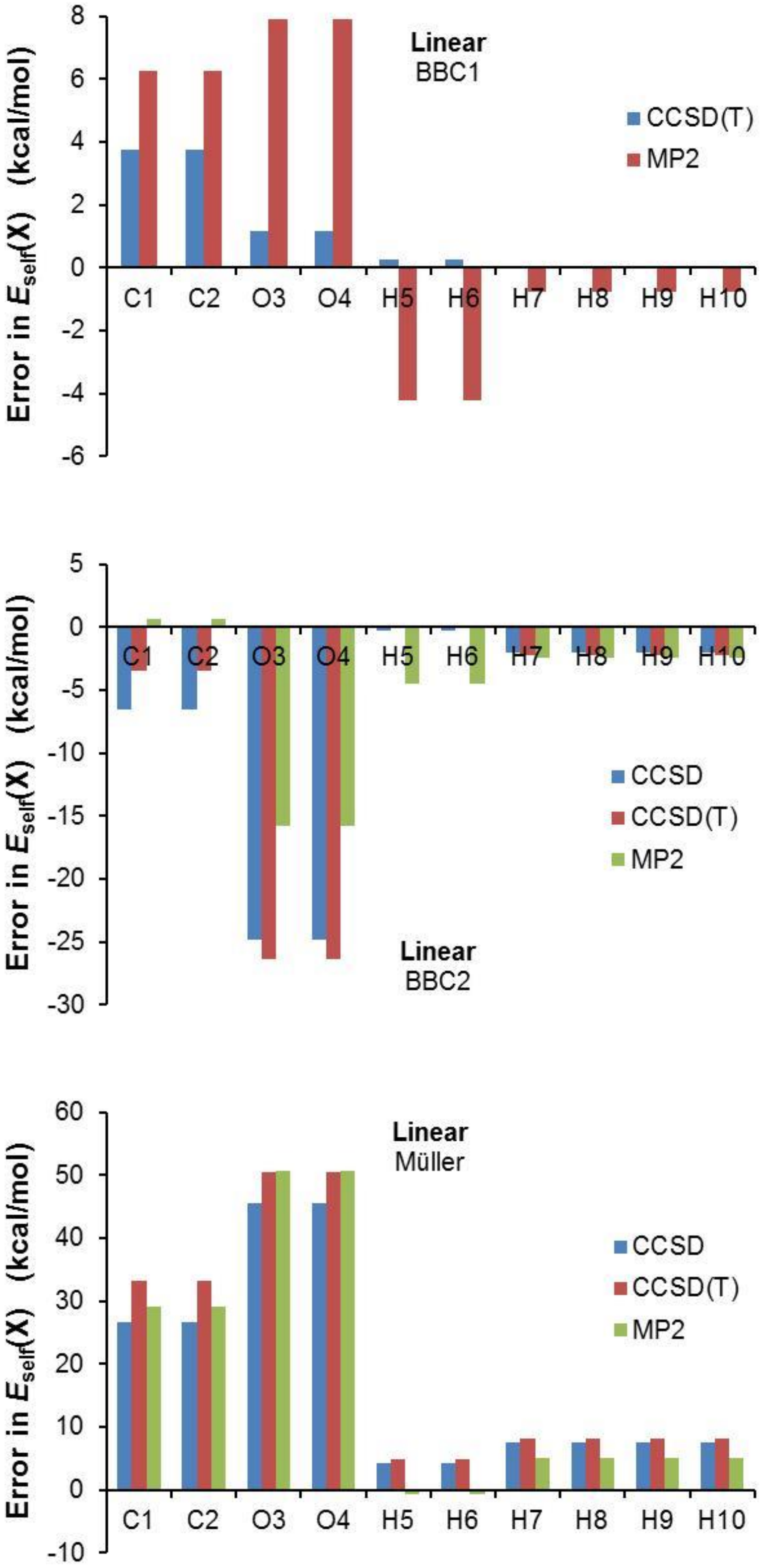


Figure S7. Relative to CCSD/BBC1 data, errors in computed self-atomic energies of the Linear conformer of glycol at the indicated LoT/LoA combination.

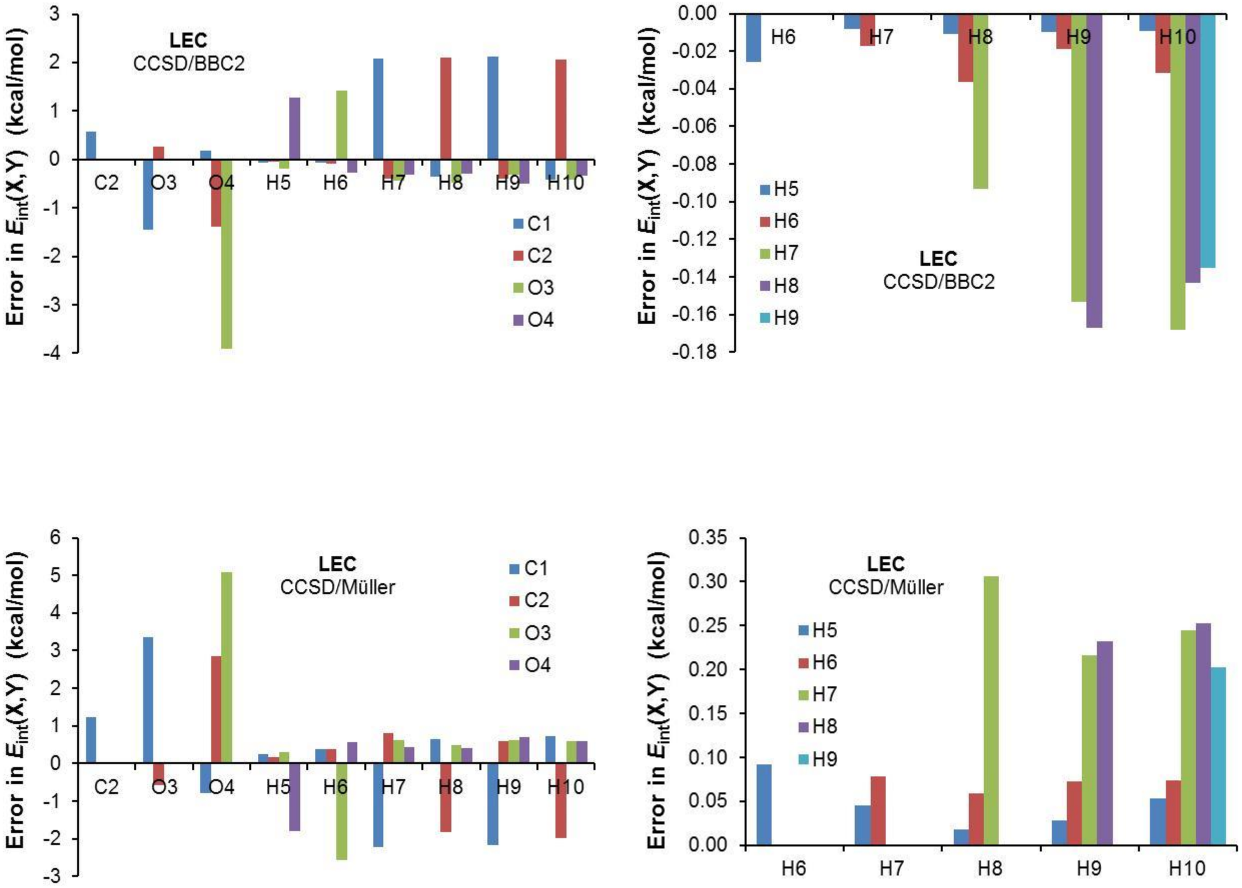


Figure S8. Relative to CCSD/BBC1, errors in the computed diatomic interactions in the **LEC** of glycol at CCSD using the BBC2 and Müller approximations.

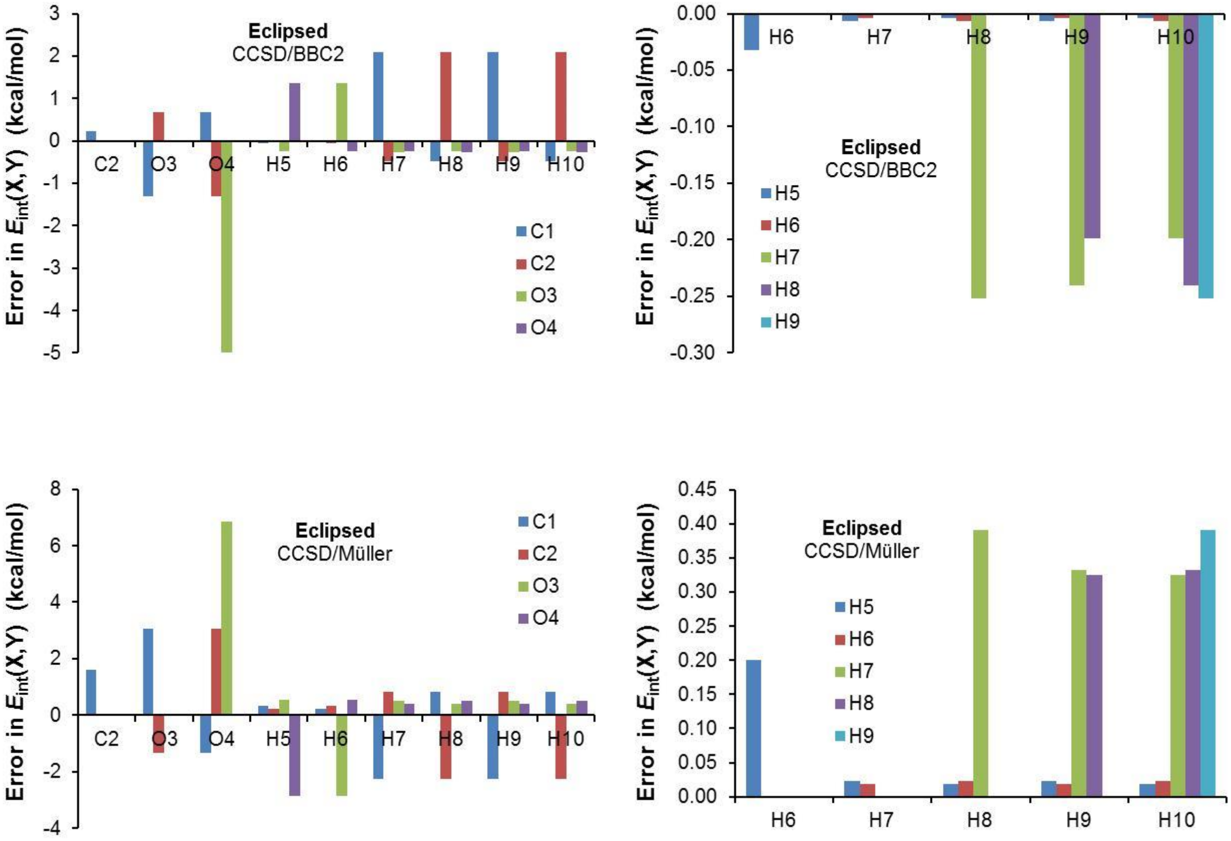


Figure S9. Relative to CCSD/BBC1, errors in the computed diatomic interactions in the Eclipsed conformer of glycol at CCSD using the BBC2 and Müller approximations.

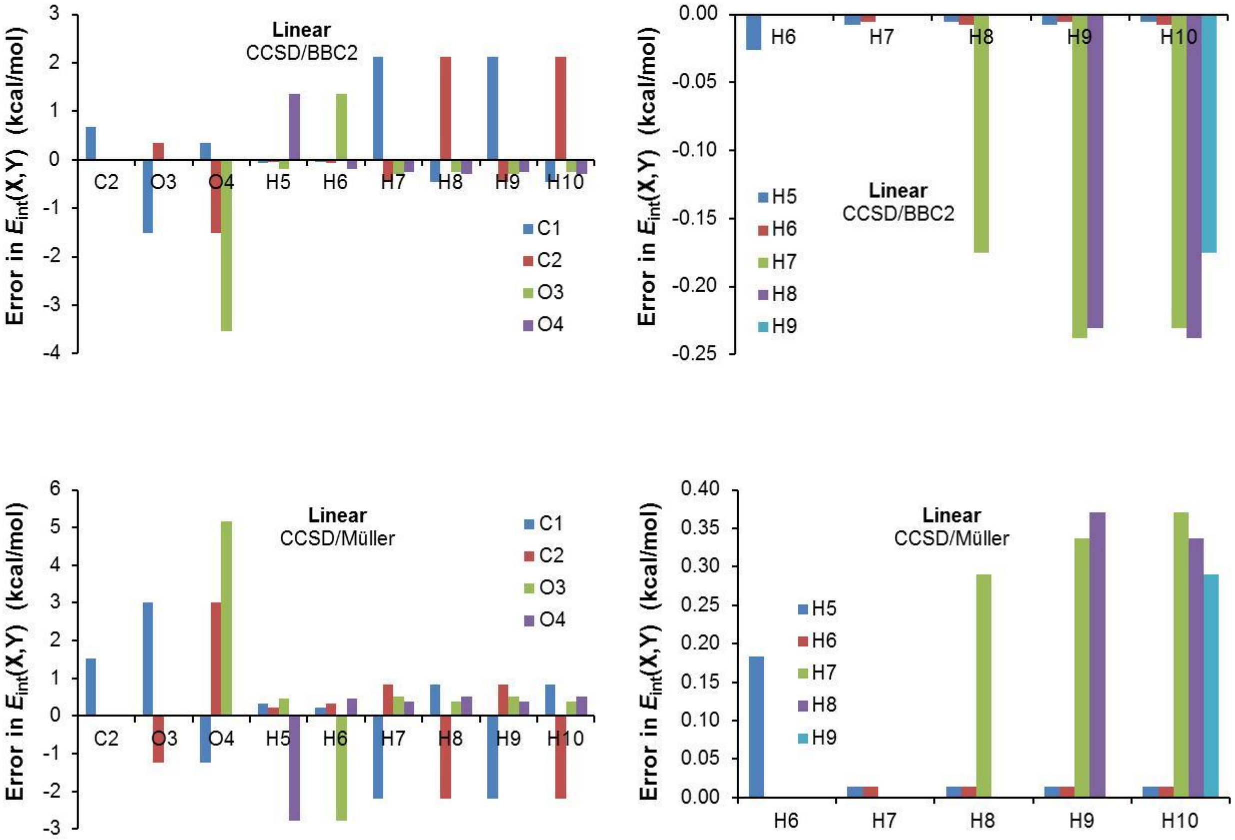


Figure S10. Relative to CCSD/BBC1, errors in the computed diatomic interactions in the Linear conformer of glycol at CCSD using the BBC2 and Müller approximations.

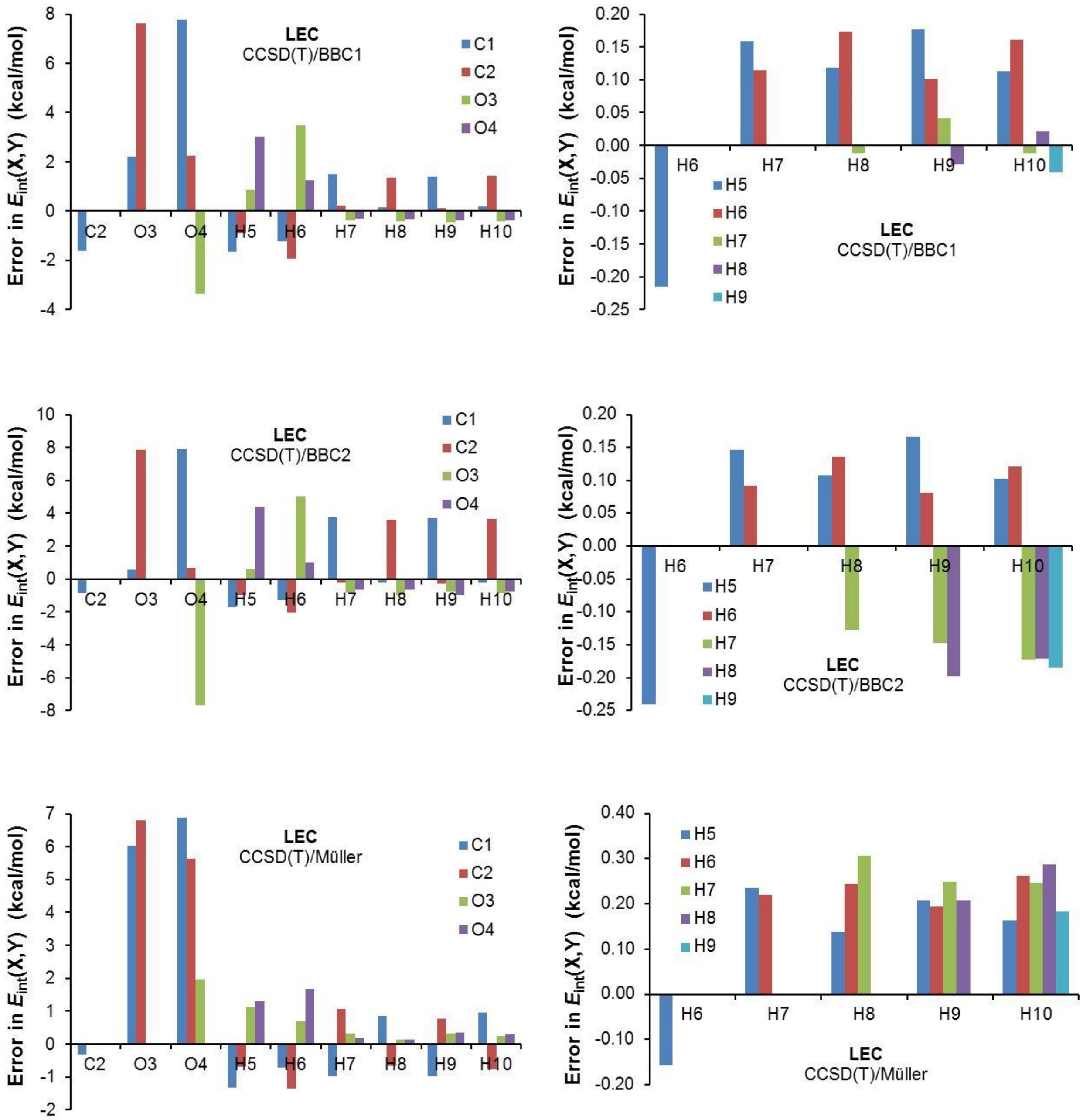


Figure S11. Relative to CCSD/BBC1, errors in the computed diatomic interactions in the **LEC** of glycol at CCSD(T) using the BBC1, BBC2 and Müller approximations.

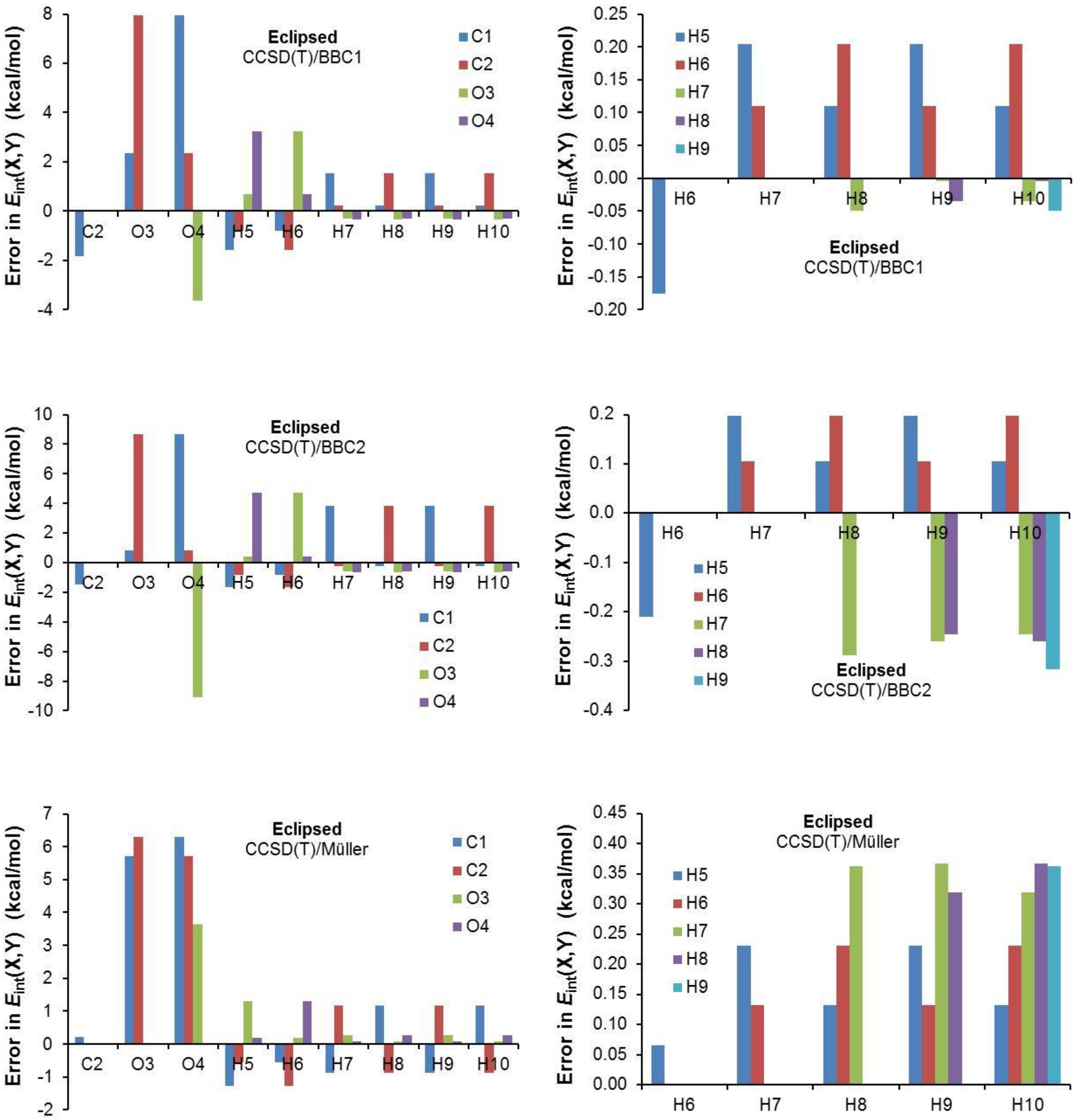


Figure S12. Relative to CCSD/BBC1, errors in the computed diatomic interactions in the Eclipsed conformer of glycol at CCSD(T) using the BBC1, BBC2 and Müller approximations.

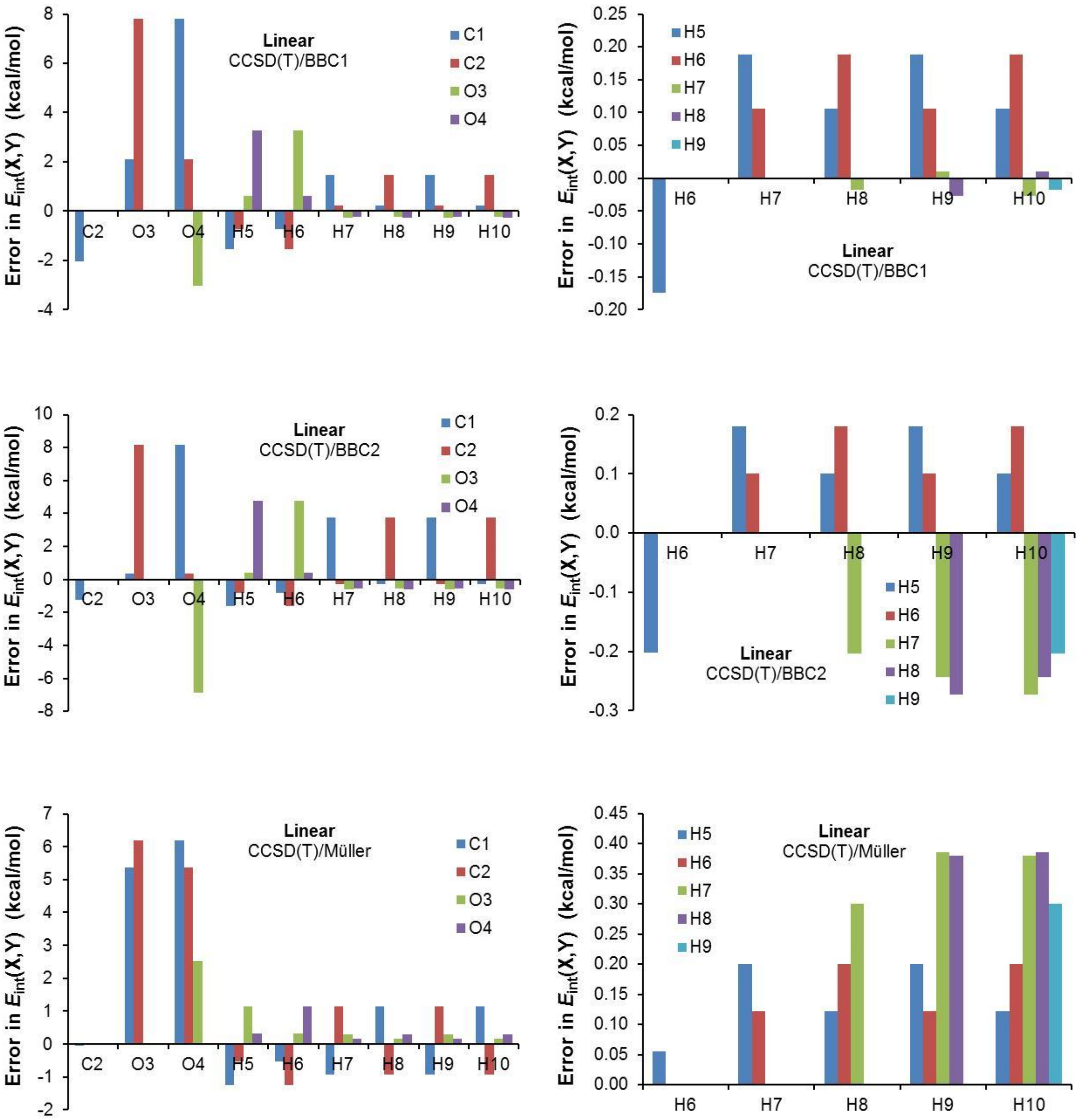


Figure S13. Relative to CCSD/BBC1, errors in the computed diatomic interactions in the Linear conformer of glycol at CCSD(T) using the BBC1, BBC2 and Müller approximations.

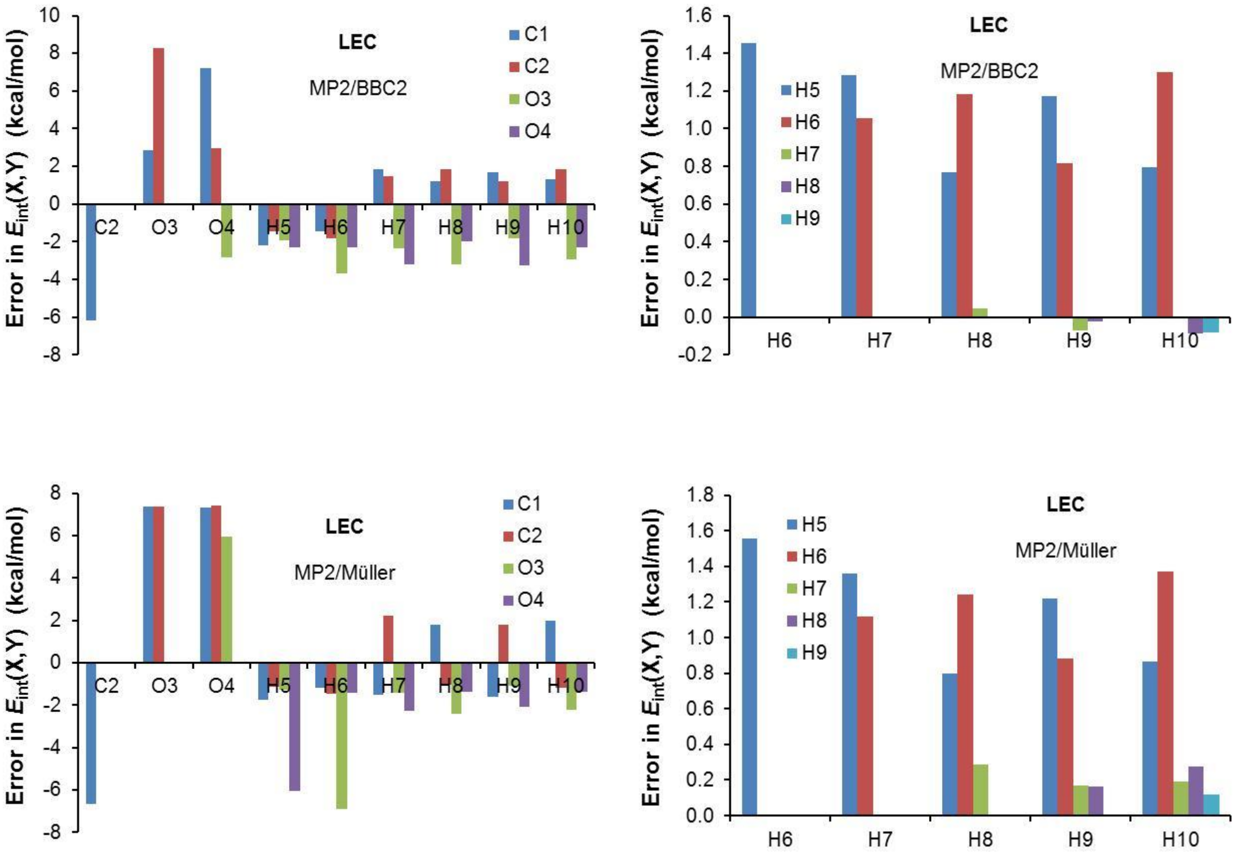


Figure S14. Relative to CCSD/BBC1, errors in the computed diatomic interactions in the **LEC** of glycol at MP2 using the BBC2 and Müller approximations.

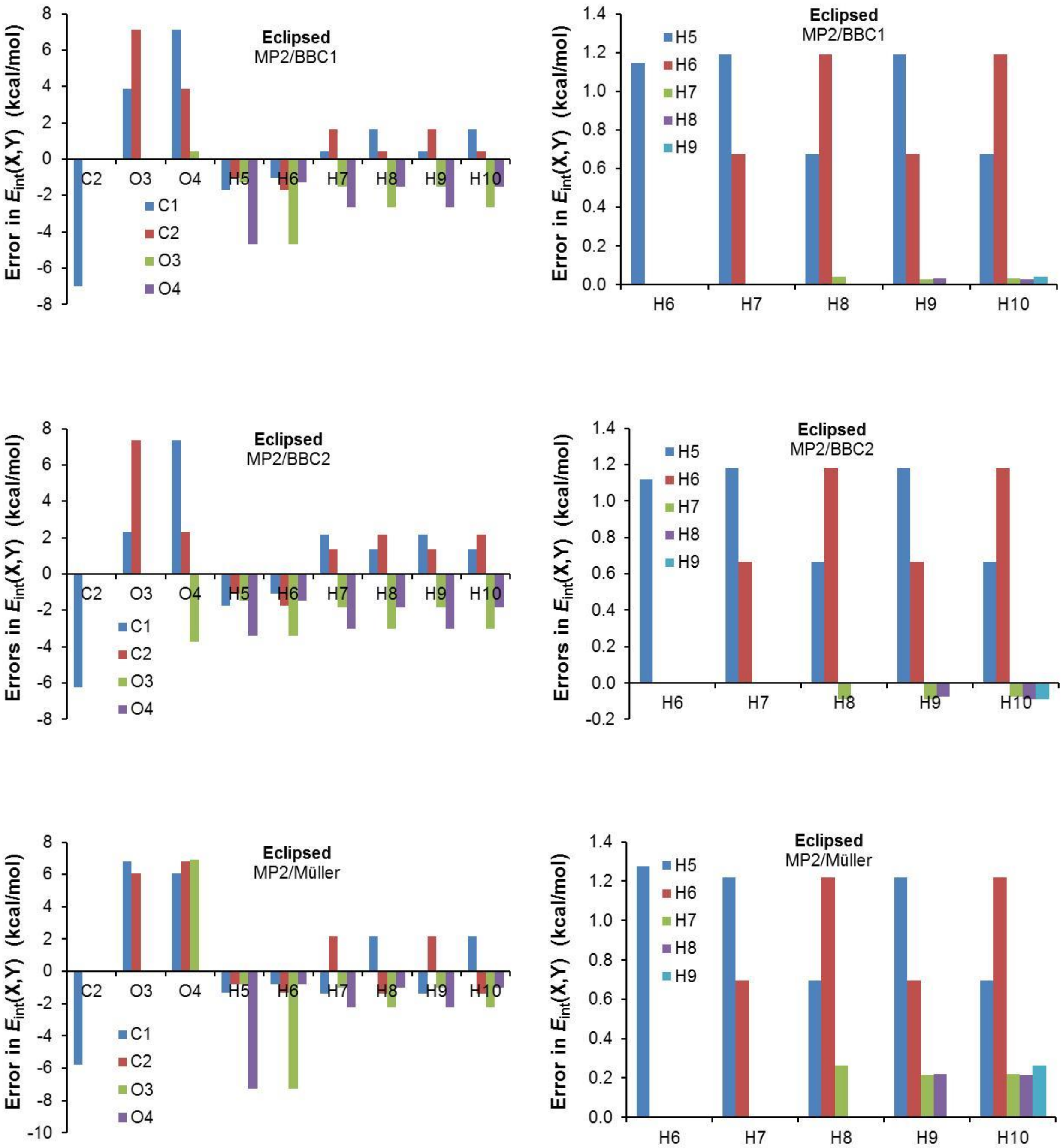


Figure S15. Relative to CCSD/BBC1, Errors in the computed diatomic interactions in the Eclipsed conformer of glycol at MP2 using the BBC1, BBC2 and Müller approximations.

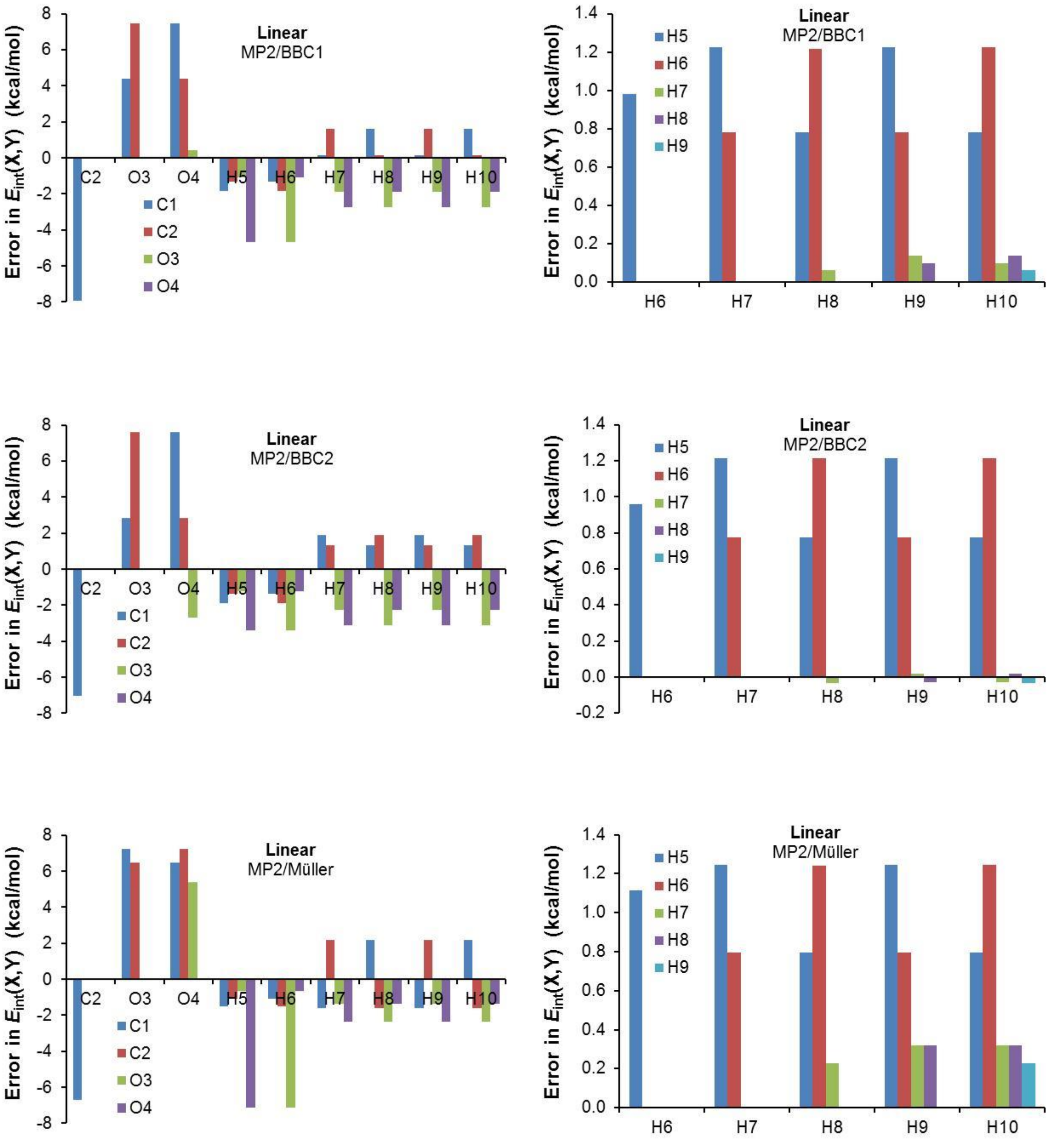


Figure S16. Relative to CCSD/BBC1, errors in the computed diatomic interactions in the Linear conformer of glycol at MP2 using the BBC1, BBC2 and Müller approximations.

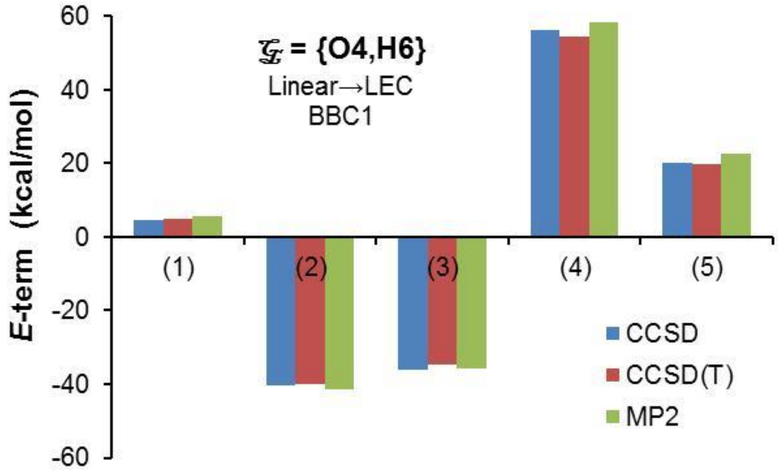


Figure S17. Energy terms, $\Delta E_{\text{self}}^{\mathcal{G}}$ as (1), $\Delta E_{\text{int}}^{\mathcal{G}}$ as (2), $E_{\text{attr-loc}}^{\mathcal{G}}$ as (3), $\Delta E_{\text{int}}^{\mathcal{G}\mathcal{H}}$ as (4) and $E_{\text{attr-mol}}^{\mathcal{G}}$ as (5), computed for the $\mathcal{G}$ = {O4,H6} fragment at the indicated levels of theory using the BBC1 approximation for the **Lin→LEC** structural change of glycol.

Table S1. FAMSEC-based description of the {O3–H6···O4} molecular fragment in the **LEC** showing the $\Delta E_{\text{self}}^{\mathcal{G}}$, $\Delta E_{\text{int}}^{\mathcal{G}}$, $E_{\text{attr-loc}}^{\mathcal{G}}$, $\Delta E_{\text{int}}^{\mathcal{G},\mathcal{H}}$, and $E_{\text{attr-mol}}^{\mathcal{G}}$ indices computed on the **Lin→LEC** structural change at the CCSD, CCSD(T) and MP2 levels of theory using the BBC1, BBC2 and Müller approximations. All values in kcal/mol.

Level of theory	$\Delta E_{\text{self}}^{\mathcal{G}}$	$\Delta E_{\text{int}}^{\mathcal{G}}$	$E_{\text{attr-loc}}^{\mathcal{G}}$	$\Delta E_{\text{int}}^{\mathcal{G}\mathcal{H}}$	$E_{\text{attr-mol}}^{\mathcal{G}}$
			BBC1		
CCSD	7.0	-11.0	-4.0	-5.6	-9.5
CCSD(T)	7.4	-10.4	-3.0	-7.5	-10.5
MP2	8.5	-11.8	-3.3	-3.1	-6.3
Avr:	7.6	-11.1	-3.4	-5.4	-8.8
Std.Dev.	0.8	0.7	0.5	2.2	2.2
			BBC2		
CCSD	6.2	-11.4	-5.1	-6.7	-11.8
CCSD(T)	6.5	-10.9	-4.4	-8.6	-13.0
MP2	7.3	-12.4	-5.2	-3.3	-8.4
Avr:	6.7	-11.6	-4.9	-6.2	-11.1
Std.Dev.	0.5	0.8	0.4	2.7	2.4
			Müller		
CCSD	9.3	-10.8	-1.4	-2.2	-3.6
CCSD(T)	9.6	-10.6	-1.1	-2.5	-3.5
MP2	10.1	-11.0	-0.9	-1.4	-2.3
Avr:	9.7	-10.8	-1.1	-2.0	-3.1
Std.Dev.	0.4	0.2	0.3	0.5	0.7

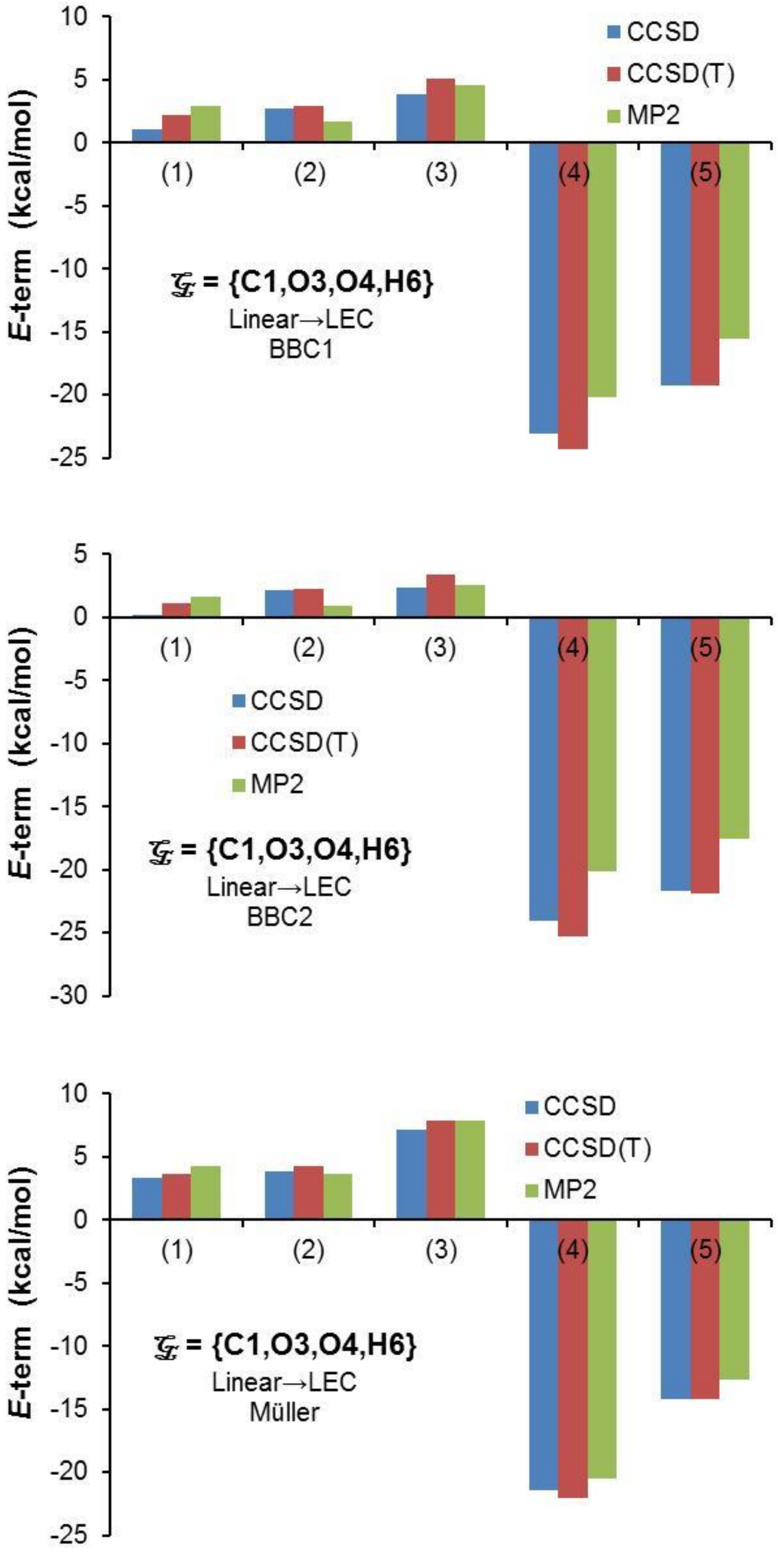


Figure S18. Energy terms, $\Delta E^{\mathcal{G}}_{\mathrm{self}}$ = (1), $\Delta E^{\mathcal{G}}_{\mathrm{int}}$ = (2), $E^{\mathcal{G}}_{\mathrm{attr\text{-}loc}}$ = (3), $\Delta E^{\mathcal{G}\mathcal{H}}_{\mathrm{int}}$ = (4) and $E^{\mathcal{G}}_{\mathrm{attr\text{-}mol}}$ = (5), computed for the $\mathcal{G}$ = {C1,O3,O4,H6} fragment at the indicated level of theory and approximation for the **Lin→LEC** structural change of glycol.

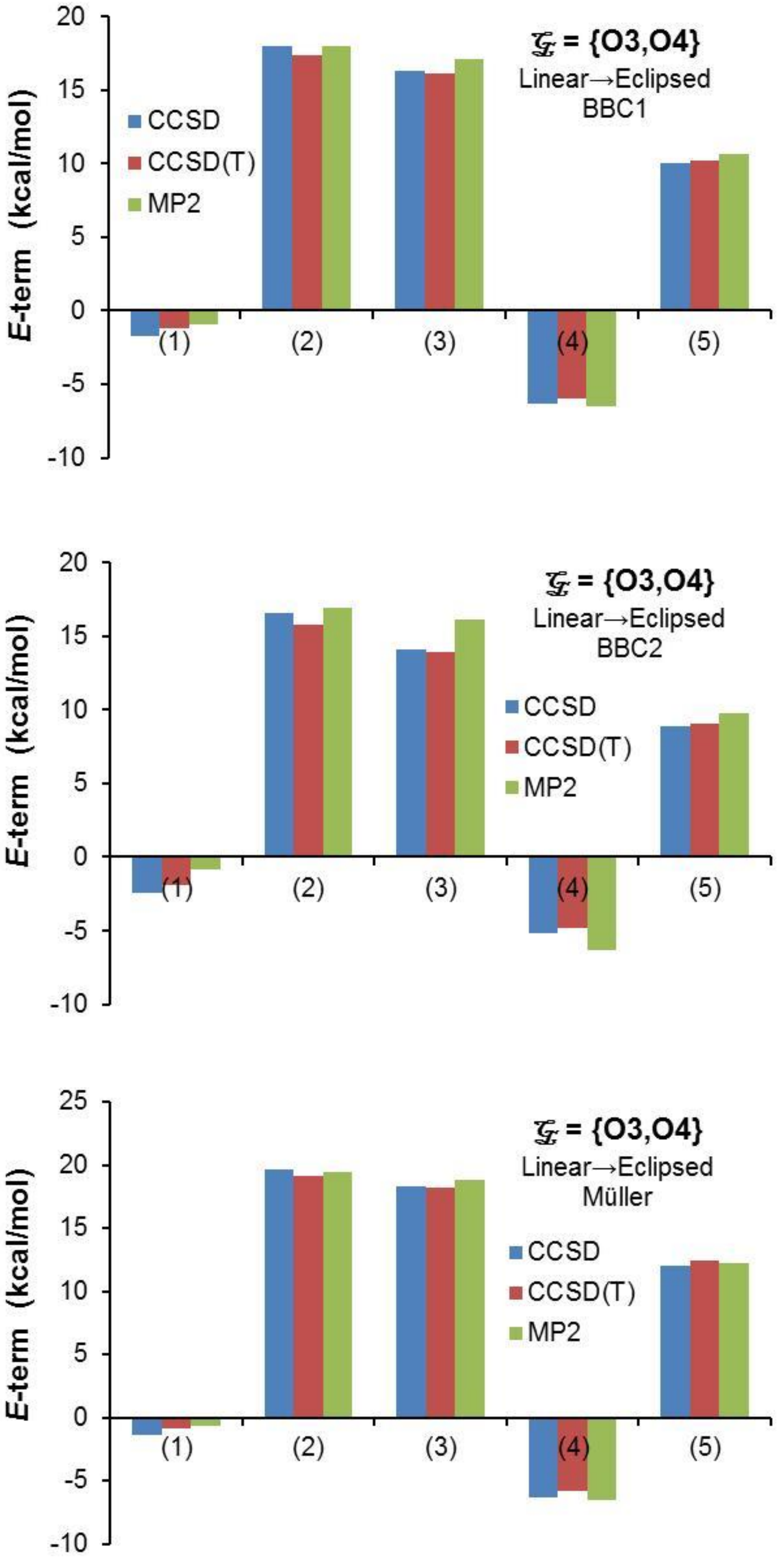


Figure S19. Energy terms, $\Delta E^{\mathcal{G}}_{\text{self}}$ as (1), $\Delta E^{\mathcal{G}}_{\text{int}}$ as (2), $E^{\mathcal{G}}_{\text{attr-loc}}$ as (3), $\Delta E^{\mathcal{G}\mathcal{H}}_{\text{int}}$ as (4), and $E^{\mathcal{G}}_{\text{attr-mol}}$ as (5), computed for the molecular fragment $\mathcal{G}$ = {O3,O4} at the indicated level of theory and approximation for the **Lin→Ecl** structural change of glycol.

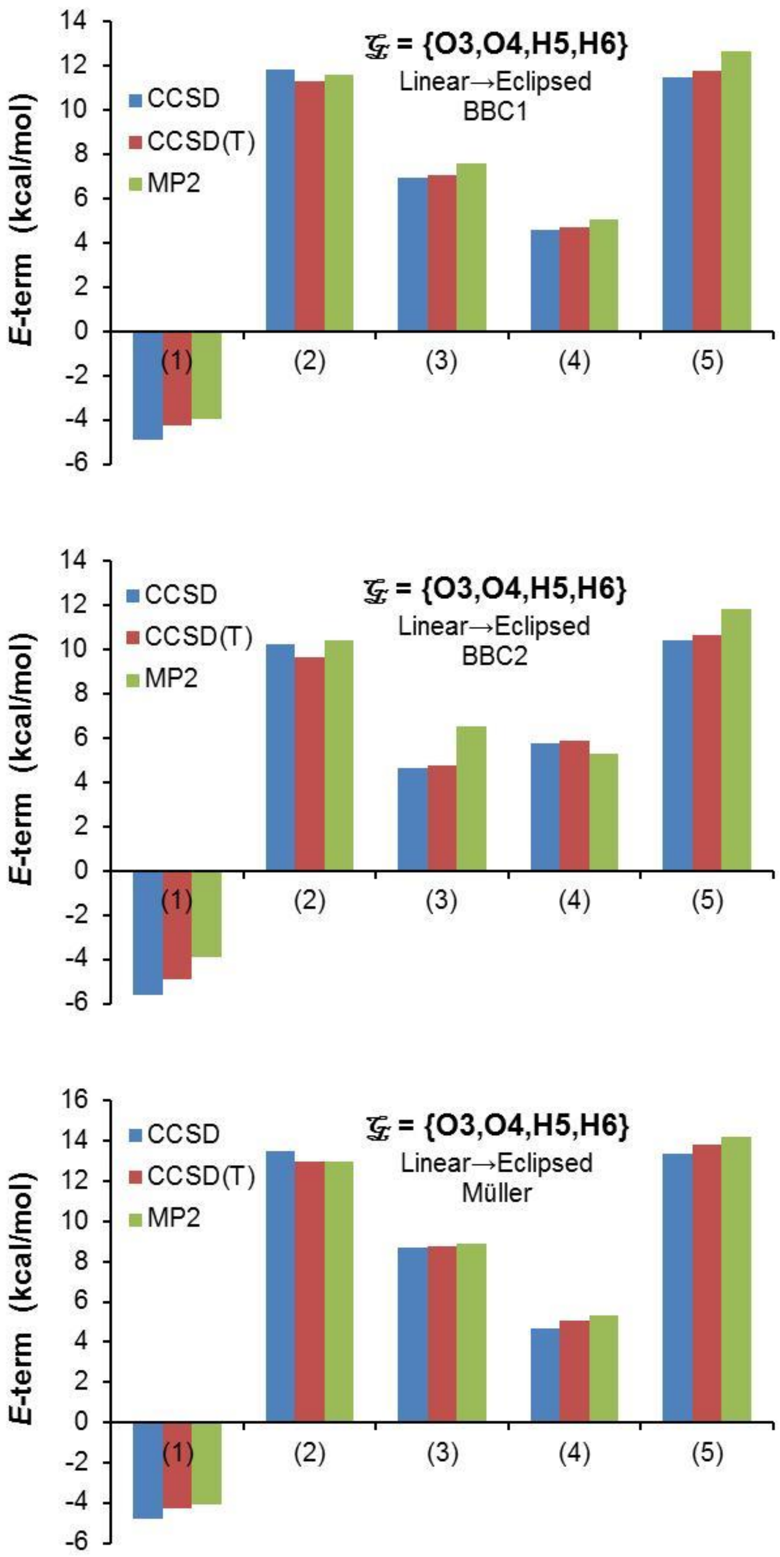


Figure S20. Energy terms, $\Delta E_{\text{self}}^{\mathscr{G}}$ as (1), $\Delta E_{\text{int}}^{\mathscr{G}}$ as (2), $E_{\text{attr-loc}}^{\mathscr{G}}$ as (3), $\Delta E_{\text{int}}^{\mathscr{G}\mathscr{H}}$ as (4), and $E_{\text{attr-mol}}^{\mathscr{G}}$ as (5), computed for the molecular fragment $\mathscr{G}$ = {O3,O4,H5,H6} at the indicated level of theory and approximation for the **Lin→Ecl** structural change of glycol.

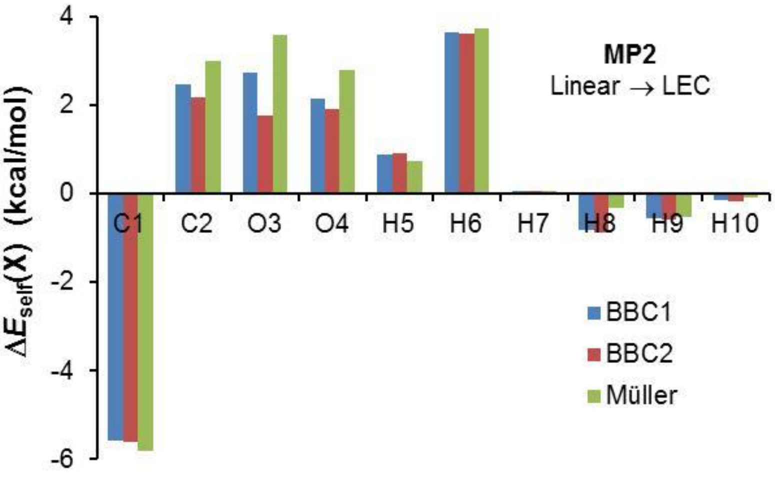


Figure S21. Change in self-atomic energy at MP2 on the **Lin→LEC** structural change obtained using indicated approximations.

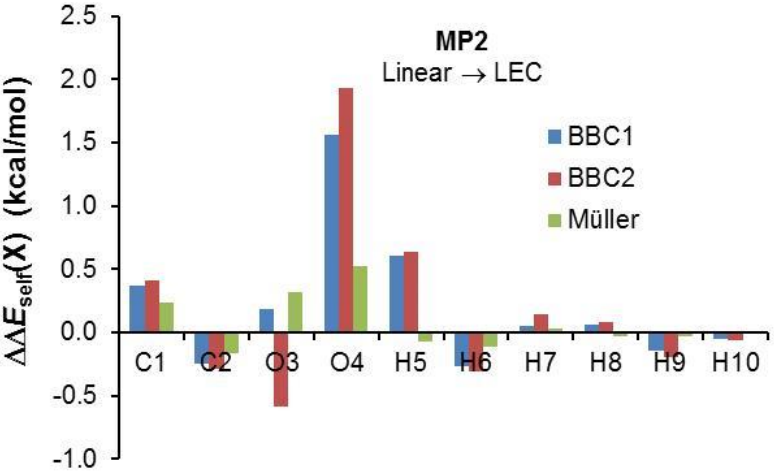
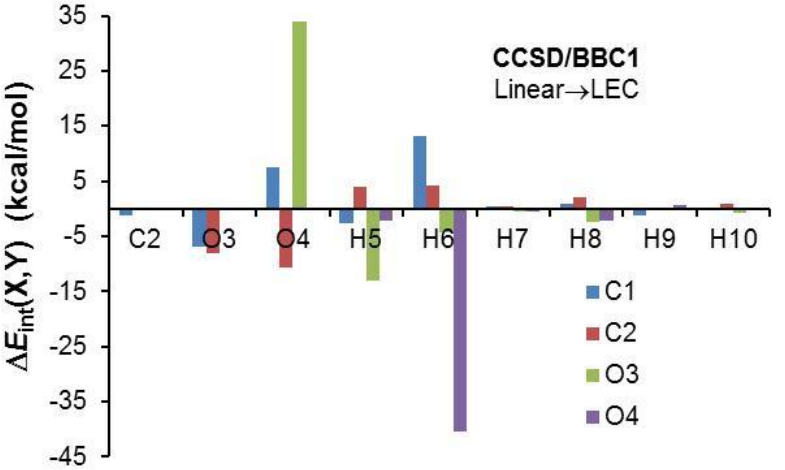


Figure S22. Relative to CCSD/BBC1, differences in computed at MP2/LoA level changes in self-atomic energies on the **Lin→LEC** structural change.



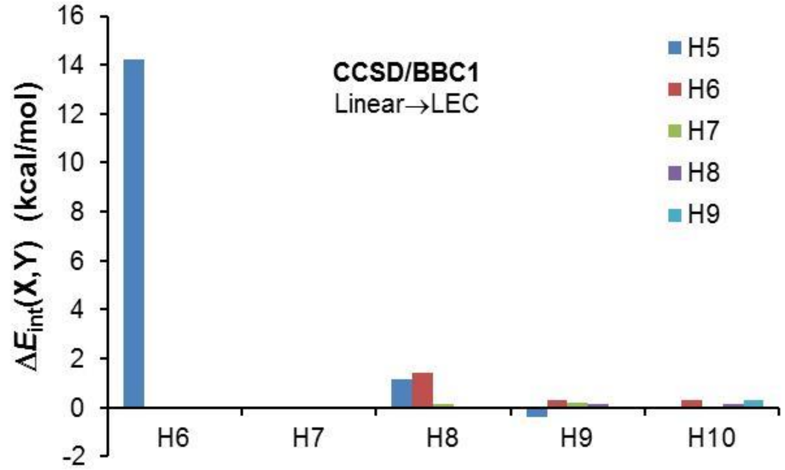
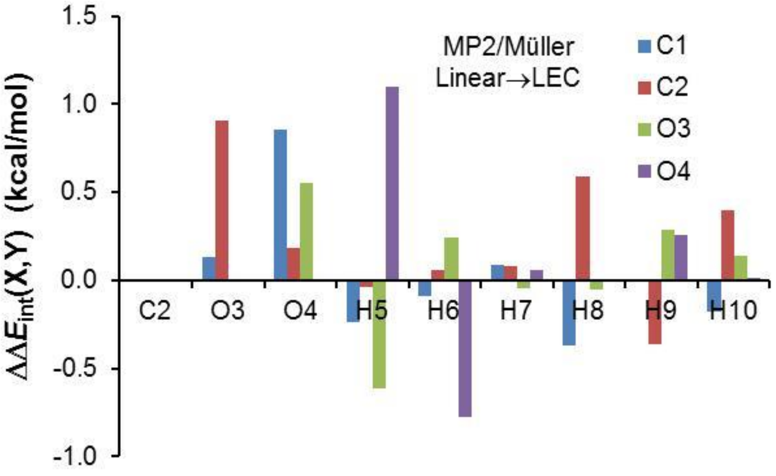


Figure S23. Change in diatomic interaction energies on the **Lin→LEC** structural change obtained at the CCSD/BBC1 level.



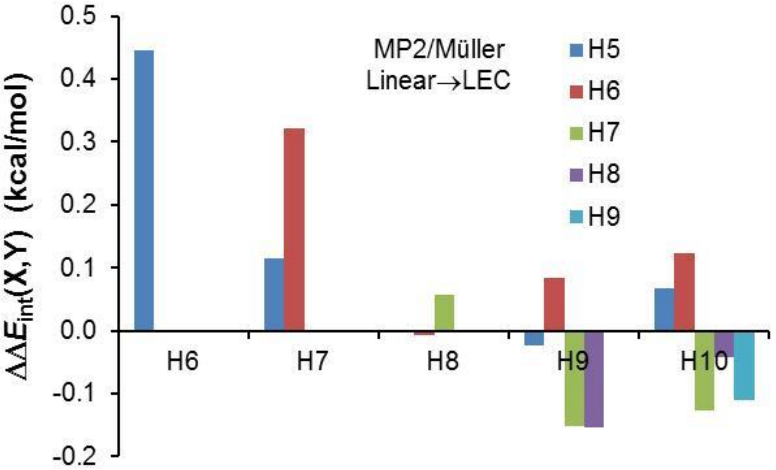


Figure S24. Relative to CCSD/BBC1, differences in computed at the MP2/Müller level changes in diatomic interaction energies on the **Lin→LEC** structural change.

Importance of ΔE(IQA) ≈ 0 in the FAMSEC analysis

It is suggested that the departure of $\Delta E_{\mathrm{IQA,E}}$ from zero might be tolerated in comparative analysis, such as FAMSEC, provided that the difference between E(IQA) computed for the *fin*-state and *ref*-state of the molecular system approaches zero.

This suggestion can be supported by making use of expressions that incorporate unavoidable computational errors. Just as an example, let us start with the self-molecular energy for which largest errors were obtained, but the same reasoning applies to individual self-atomic as well as interaction energy terms. For the final state of a molecular system we can write

$$(E_{\mathrm{self}}^{\mathrm{Tot}})_{fin\text{-state}} = \left(E_{\mathrm{self}}^{\mathrm{Tot}}\right)_{fin-\mathrm{state}}^{\#} + (err_{\mathrm{self}}^{\mathrm{Tot}})_{fin\text{-state}} \quad . \tag{S1}$$

Exactly the same expression can be written for the *ref*-state (recall that # refers to the exact and, in principle, unknown value). In comparative analysis, the main focus is on the change in the selected property when the transformation from the *ref*-state to *fin*-state takes place. Hence, in this specific example we would monitor

$$\Delta(E_{\mathrm{self}}^{\mathrm{Tot}}) = (E_{\mathrm{self}}^{\mathrm{Tot}})_{fin\text{-state}} - (E_{\mathrm{self}}^{\mathrm{Tot}})_{ref\text{-state}} \; . \tag{S2}$$

This work has demonstrated that due to the same (i) level of theory and approximation and (ii) parameters selected in the IQA calculations used for the two molecular states, the errors of almost the same value are generated,

$$(err_{\mathrm{self}}^{\mathrm{Tot}})_{fin\text{-state}} \approx (err_{\mathrm{self}}^{\mathrm{Tot}})_{ref\text{-state}} \tag{S3}$$

Hence, on computing the *change* in self-molecular energies when *ref*-state → *fin*-state, cancellation of errors takes place and, as a result, the computed difference can be seen as acceptable approximation of variation in the exact self-molecular energies,

$$\Delta(E_{\mathrm{self}}^{\mathrm{Tot}}) \approx \left(E_{\mathrm{self}}^{\mathrm{Tot}}\right)_{fin-\mathrm{state}}^{\#} - \left(E_{\mathrm{self}}^{\mathrm{Tot}}\right)_{ref-\mathrm{state}}^{\#} \; . \tag{S4}$$

The difference in IQA molecular energies between the two molecular states, ΔE(IQA) = E(IQA)$_{fin\text{-state}}$ – E(IQA)$_{ref\text{-state}}$, can be written as

$$\begin{aligned}\Delta E(\mathrm{IQA}) = {} & \left(E_{\mathrm{self}}^{\mathrm{Tot}}\right)_{fin-\mathrm{state}}^{\#} + \left(E_{\mathrm{int}}^{\mathrm{Tot}}\right)_{fin-\mathrm{state}}^{\#} + (err_{\mathrm{self}}^{\mathrm{Tot}})_{fin\text{-state}} + (err_{\mathrm{int}}^{\mathrm{Tot}})_{fin\text{-state}} \\ & - \left(E_{\mathrm{self}}^{\mathrm{Tot}}\right)_{ref-\mathrm{state}}^{\#} - \left(E_{\mathrm{int}}^{\mathrm{Tot}}\right)_{ref-\mathrm{state}}^{\#} - (err_{\mathrm{self}}^{\mathrm{Tot}})_{ref\text{-state}} - (err_{\mathrm{int}}^{\mathrm{Tot}})_{ref\text{-state}}\end{aligned} \tag{S5}$$

Eq. S5 demonstrates that when the IQA-generated errors in *fin*- and *ref*-state of a molecule are nearly the same then the Δ*E*(IQA) should be very close to the difference in electronic energy of the two molecular states, such as two conformers. Clearly, the smaller difference between Δ*E*(IQA) and $\Delta E = E_{fin\text{-state}} - E_{ref\text{-state}}$, hence when $\Delta(\Delta E_{\mathrm{IQA,E}}) = (\Delta E_{\mathrm{IQA,E}})_{fin\text{-state}} - (\Delta E_{\mathrm{IQA,E}})_{ref\text{-state}} \rightarrow 0$, then the better quality (more reliable) FAMSEC-defined energy terms are.