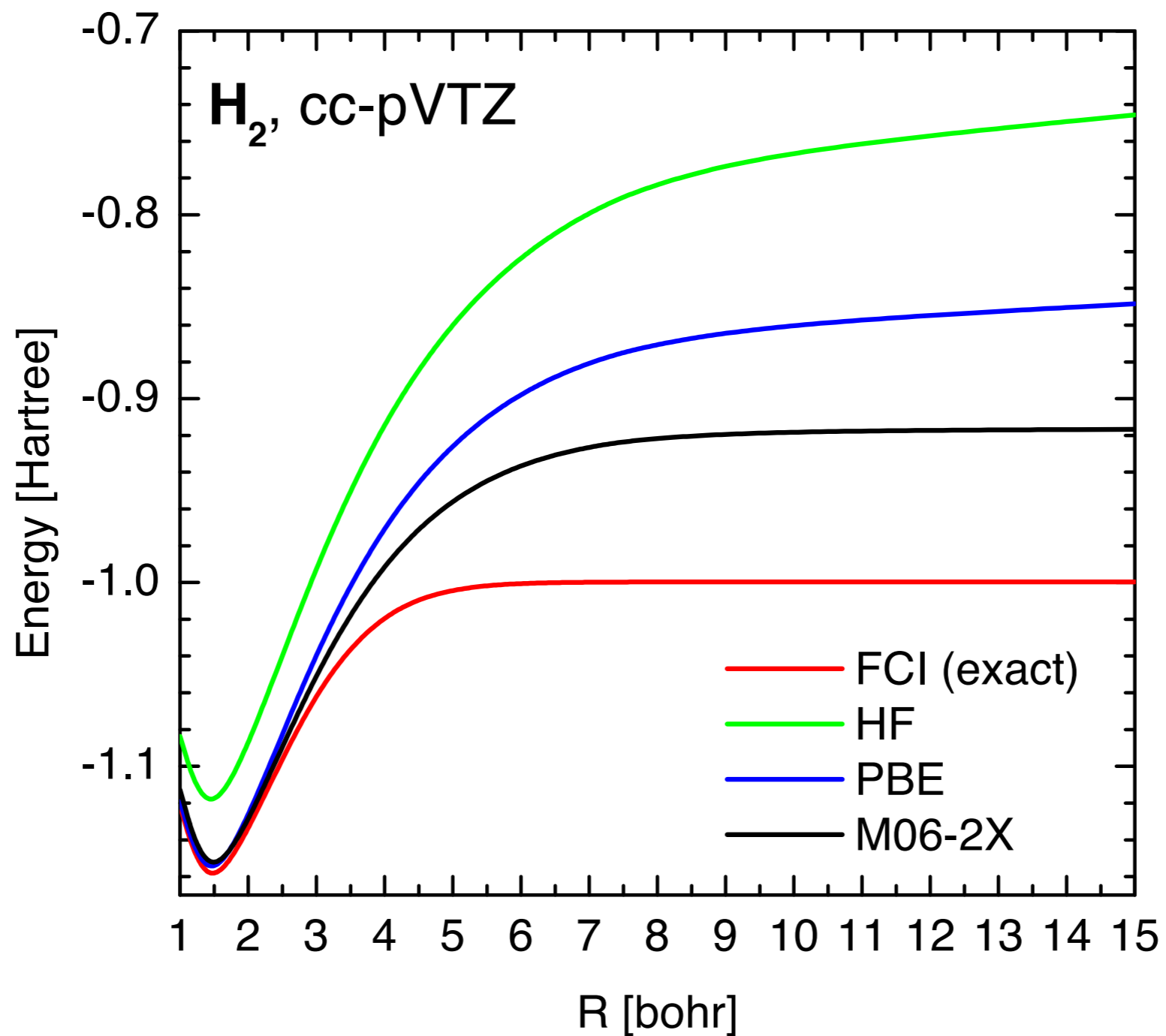# A computationally efficient geminal-based method for accurate description of chemical systems

Katarzyna Pernal

Institute of Physics
Lodz University of Technology, Poland

Nondynamic (static) correlation

- In the dissociation limit one-electron methods break down!

- Static correlation is missing.

APSG model

- The APSG ansatz (antisymmetrized product of strongly orthogonal geminals) for a closed-shell *N*-electron system reads

$$\Psi(x_1, \ldots, x_N) = \hat{\mathcal{A}} \prod_{P=1}^{N/2} \phi_P(x_{2P-1}, x_{2P})$$

  where each geminal is normalized and antisymmetric

$$\phi_P(x_1, x_2) = -\phi_P(x_2, x_1)$$

- Originally formulated for closed shell systems but extensions to the open-shell systems are available.

A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, *Proc. R. Soc. London*, Ser. A **220**, 446 (1953).

W. Kutzelnigg, *J. Chem. Phys.* **97**, 1474 (1964).

V. A. Rassolov, J. Chem. Phys. **117**, 5978 (2002).

APSG model

- In the APSG model each geminal is a two-electron FCI function, i.e.

$$\phi_P(\mathbf{x}_1, \mathbf{x}_2) = 2^{-1/2} \sum_{p \in P} c_p \psi_p(\mathbf{r}_1) \psi_p^*(\mathbf{r}_2) [\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)]$$

- The strong orthogonality requirement

$$\underset{Q \neq P}{\forall} \; \underset{\mathbf{x}_1, \mathbf{x}_1'}{\forall} \; \int \phi_P(\mathbf{x}_1, \mathbf{x}_2) \phi_Q(\mathbf{x}_1', \mathbf{x}_2) d\mathbf{x}_2 = 0$$

implies that the sets of orbitals belonging to individual geminals are disjoint.

T. Arai, *J. Chem. Phys.* **33**, 95 (1960).

- In the representation of the natural spinorbitals

$$c_p^2 = n_p$$

- The spin-summed expression for the electron energy takes a simple form

$$E^{APSG} = 2 \sum_p n_p h_{pp} + \sum_I \sum_{\substack{pq \\ I_p=I_q=I}} c_p c_q \langle pp|qq \rangle + \sum_{I \neq J} \sum_{\substack{pq \\ I_p=I, I_q=J}} n_p n_q [2 \langle pq|pq \rangle - \langle pq|qp \rangle]$$

where I_p stands for the index of a geminal which the pth orbital belongs to.

Ground state energy functional in the APSG model

- In the representation of the natural spinorbitals

$$c_p^2 = n_p$$

- The spin-summed expression for the electron energy takes a simple form

$$E^{APSG} = 2 \sum_p n_p h_{pp} + \sum_I \sum_{\substack{pq \\ I_p = I_q = I}} c_p c_q \langle pp|qq \rangle + \sum_{I \neq J} \sum_{\substack{pq \\ I_p = I, I_q = J}} n_p n_q [2 \langle pq|pq \rangle - \langle pq|qp \rangle]$$

only Coulomb and exchange interactions between geminals

where I_p stands for the index of a geminal which the pth orbital belongs to.

Ground state energy functional in the APSG model

- In the representation of the natural spinorbitals

$$c_p^2 = n_p$$

- The spin-summed expression for the electron energy takes a simple form

$$E^{APSG} = 2 \sum_p n_p h_{pp} + \sum_I \sum_{\substack{pq \\ I_p = I_q = I}} c_p c_q \langle pp|qq \rangle + \sum_{I \neq J} \sum_{\substack{pq \\ I_p = I, I_q = J}} n_p n_q [2 \langle pq|pq \rangle - \langle pq|qp \rangle]$$

only Coulomb and exchange interactions between geminals

where I_p stands for the index of a geminal which the pth orbital belongs to.

- The ground state energy is obtained upon minimization with respect to the orbitals and the coefficients c_p under constraints of orbitals orthogonality and normalization of the coefficients.

$$\forall_P \quad \sum_{p \in P} c_p^2 = 1$$

Example: asymmetric water dissociation with APSG

H₂O, cc-pVDZ

FCI
APSG
HF
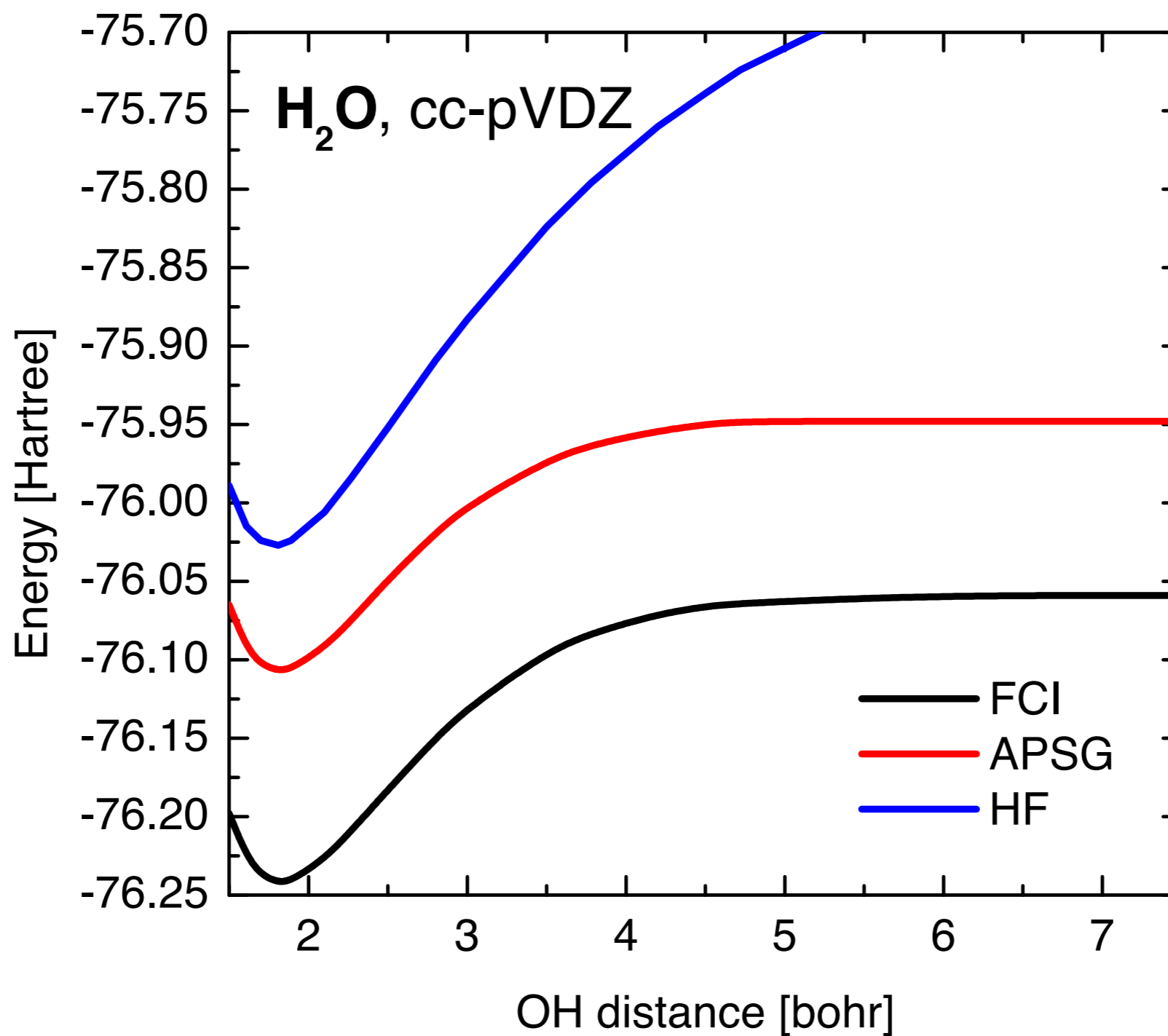
In APSG a large portion of dynamic correlation is missing but static correlation is accounted for.

- The APSG model

  - exact ground state energy of singlet two-electron systems,

  - a qualitative picture of a single bond dissociation,

  - size-extensive,

  - geminals localized on two-electron bonds or lone pairs,

  - computationally efficient: $(M_{basis})^4 M_{geminal}$ scaling,

P.R. Surján, Top. Curr. Chem. **203**, 63–88 (1999).

V. Rassolov, *J. Chem. Phys*. **117**, 5978 (2002) and the references cited therein.

P.R. Surján, A. Szabados, P. Jeszenszki, and T. Zaboki, *J Math Chem*. **50**, 534 (2012).

- The APSG model

  - exact ground state energy of singlet two-electron systems,

  - a qualitative picture of a single bond dissociation,

  - size-extensive,

  - geminals localized on two-electron bonds or lone pairs,

  - computationally efficient: $(M_{basis})^4 M_{geminal}$ scaling,

  but

  - intergeminal correlation is missing (energies are too high),

  - dispersion interaction is missing (van der Waals complexes are not bound),

  - inaccurate energy barriers,

  - incorrect products of multiple-bond dissociation.

P.R. Surján, Top. Curr. Chem. **203**, 63–88 (1999).
V. Rassolov, *J. Chem. Phys.* **117**, 5978 (2002) and the references cited therein.
P.R. Surján, A. Szabados, P. Jeszenszki, and T. Zaboki, *J Math Chem.* **50**, 534 (2012).

- The electron-electron interaction is determined by the pair density

$$E_{ee} = \frac{1}{2} \int \int \rho^{(2)}(x_1, x_2)|\mathbf{r}_1 - \mathbf{r}_2|^{-1} dx_1 dx_2$$

- The pair density can be written in terms of a density and a density fluctuation operator

$$\rho(x) = \langle 0|\hat{\rho}(x)|0\rangle$$

$$\delta\hat{\rho}(x) = \hat{\rho}(x) - \langle 0|\hat{\rho}(x)|0\rangle$$

as

$$\rho^{(2)}(x_1, x_2) = \langle \delta\hat{\rho}(x_1)\delta\hat{\rho}(x_2)\rangle + \rho(x_1)\rho(x_2) - \delta(x_1 - x_2)\rho(x_1)$$

- The first term ties a fluctuation at x_1 to a fluctuation at x_2 and this gives rise to electron correlation.

J.F. Dobson in "Time-Dependent Density Functional Theory", M.A.L. Marques et al. ed., Springer 2006, p.443-463 and references there.

- Intergeminal correlations should result from coupling of geminal density fluctuations.

- Define an intergeminal pair correlation function - a contribution to a pair density from intergeminal correlations:

$$\rho_{IGcorr}^{(2)}(x_1, x_2) = \frac{1}{2} \sum_{\substack{I,J \\ I>J}} [\langle 0|\delta\hat{\rho}_I(x_1)\delta\hat{\rho}_J(x_2)|0\rangle + \langle 0|\delta\hat{\rho}_J(x_1)\delta\hat{\rho}_I(x_2)|0\rangle]$$

where a geminal density of the geminal *I* and the fluctuation operator read

$$\hat{\rho}_I(x) = \sum_{p,q \in I} \hat{a}_q^\dagger \hat{a}_p \ \varphi_q(x)^* \varphi_p(x)$$

$$\delta\hat{\rho}_I(x) = \hat{\rho}_I(x) - \rho_I(x)$$

- The intergeminal electron correlation energy follows from

$$E_{IGcorr} = \frac{1}{4} \sum_{\substack{I,J \\ I>J}} \int \int [\langle 0|\delta\hat{\rho}_I(x_1)\delta\hat{\rho}_J(x_2)|0\rangle + \langle 0|\delta\hat{\rho}_J(x_1)\delta\hat{\rho}_I(x_2)|0\rangle]|\mathbf{r}_1 - \mathbf{r}_2|^{-1}dx_1 dx_2$$

- A fluctuation-dissipation theorem for geminals leads to the following intergeminal (IG) correlation energy expression

$$E_{IGcorr} = -\frac{1}{4\pi} \sum_{\substack{I,J \\ I>J}} \int dx_1 \int dx_2 \int_0^\infty d\omega \left[\chi_{IJ}(x_1, x_2, i\omega) + \chi_{JI}(x_2, x_1, i\omega) \right] |\mathbf{r}_1 - \mathbf{r}_2|^{-1}$$

- It is more convenient to write the IG correlation in terms of the transition density matrix elements

$$(T_\nu)_{pq} = \left\langle 0 | \hat{a}_q^\dagger \hat{a}_p | \nu \right\rangle$$

$$E_{IGcorr} = \frac{1}{2} \sum_{\substack{I,J \\ I>J}} \sum_{pq \in I} \sum_{rs \in J} \sum_{\nu \neq 0} (T_\nu)_{qp} (T_\nu)_{rs}^* \ \langle pr | qs \rangle$$

K. Pernal, *J. Chem. Theory Comput.* **10**, 4332 (2014).

- A fluctuation-dissipation theorem for geminals leads to the following intergeminal (IG) correlation energy expression

$$E_{IGcorr} = -\frac{1}{4\pi} \sum_{\substack{I,J \\ I>J}} \int dx_1 \int dx_2 \int_0^\infty d\omega \left[\chi_{IJ}(x_1, x_2, i\omega) + \chi_{JI}(x_2, x_1, i\omega)\right] |\mathbf{r}_1 - \mathbf{r}_2|^{-1}$$

- It is more convenient to write the IG correlation in terms of the transition density matrix elements

$$(T_\nu)_{pq} = \langle 0|\hat{a}_q^\dagger \hat{a}_p|\nu\rangle$$

$$E_{IGcorr} = \frac{1}{2} \sum_{\substack{I,J \\ I>J}} \sum_{pq\in I} \sum_{rs\in J} \sum_{\nu\neq 0} (T_\nu)_{qp}(T_\nu)_{rs}^* \ \langle pr|qs\rangle$$

How to express $\mathbf{T}_\nu$ in terms of the APSG ground state properties?

K. Pernal, *J. Chem. Theory Comput.* **10**, 4332 (2014).

- By considering the Rowe's equation of motion and the ERPA (**extended random phase approximation**) excitation operator

$$\hat{O}^{\dagger}_{ERPA} = \sum_{p>q}(X_{\nu})_{pq}(\hat{a}^{\dagger}_{p_{\alpha}}\hat{a}_{q_{\alpha}} + \hat{a}^{\dagger}_{p_{\beta}}\hat{a}_{q_{\beta}}) + \sum_{p>q}(Y_{\nu})_{pq}(\hat{a}^{\dagger}_{q_{\alpha}}\hat{a}_{p_{\alpha}} + \hat{a}^{\dagger}_{q_{\beta}}\hat{a}_{p_{\beta}})$$

where p,q pertain to the natural spinorbitals, we have obtained the equations for excitation energies

$$\begin{pmatrix} \mathbf{0} & \mathbf{A}^{+} \\ \mathbf{A}^{-} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \tilde{\mathbf{Y}}_{\nu} \\ \tilde{\mathbf{X}}_{\nu} \end{pmatrix} = \omega_{\nu} \begin{pmatrix} \tilde{\mathbf{Y}}_{\nu} \\ \tilde{\mathbf{X}}_{\nu} \end{pmatrix}$$

The eigenvectors are related to the transition density matrix elements

$$\forall_{p>q} \quad (c_p + c_q)(\tilde{Y}_{\nu})_{pq} = (T_{\nu})_{pq} + (T_{\nu})_{qp}$$

K. Chatterjee and K. Pernal, *J. Chem. Phys.* **137**, 204109 (2012).
K. Pernal, K. Chatterjee, and P. H. Kowalski, *J. Chem. Phys.* **140**, 014101 (2014).

- Including all possible intergeminal correlation interactions leads to the energy functional

$$E^{ERPA-APSG} = E^{APSG} + \sum_{p>q}\sum_{r>s}(1 - \delta_{I_pI_q}\delta_{I_rI_s}\delta_{I_pI_r})$$

$$\times \left[2(c_p + c_q)(c_r + c_s)\sum_\nu(\tilde{Y}_\nu)_{pq}(\tilde{Y}_\nu)_{rs} - [c_p^2(1 - c_q^2) - c_q^2(1 - c_s^2)]\delta_{pr}\delta_{qs}\right]\langle pr|qs\rangle$$

where I_p corresponds to a geminal which an orbital p belongs to.

K. Pernal, *J. Chem. Theory Comput.* **10**, 4332 (2014).
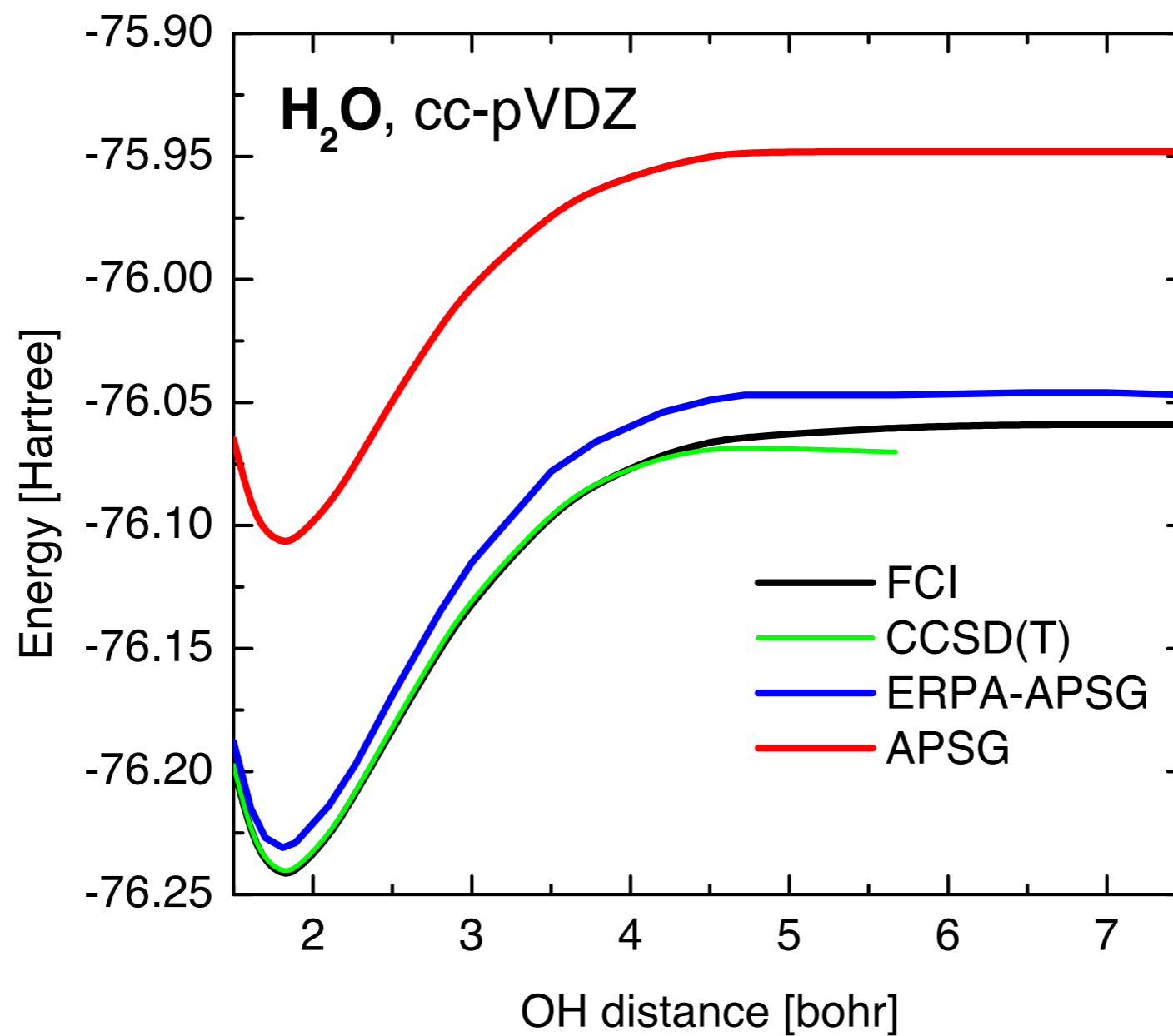
ERPA-APSG method

- Optimize the APSG energy

$$E^{APSG}[\{c_p\}, \{\varphi_p\}] = 2 \sum_p c_p^2 \, h_{pp} + \sum_{pq} \delta_{I_p I_q} \, c_p c_q \, \langle pp|qq \rangle$$

$$+ \sum_{pq} (1 - \delta_{I_p I_q}) \, c_p^2 c_q^2 \, [2 \langle pq|pq \rangle - \langle pq|qp \rangle] \quad .$$

- Solve the ERPA eigenequations

$$\left[\left(\mathbf{A}^+ \right)^{1/2} \mathbf{A}^- \left(\mathbf{A}^+ \right)^{1/2} \right] \left(\mathbf{A}^+ \right)^{-1/2} \mathbf{Y}_\nu = \omega_\nu^2 \left(\mathbf{A}^+ \right)^{-1/2} \mathbf{Y}_\nu$$

- Find the intergeminal correlation and add it to the APSG energy.

E. Pastorczak and K. Pernal, *Phys. Chem. Chem. Phys.* **17**, 8622 (2015).

Asymmetric dissociation of water molecule

H$_2$O, cc-pVDZ

FCI
CCSD(T)
ERPA-APSG
APSG

	FCI	APSG	ERPA-APSG
$E_{corr}(R_{eq})$	100%	37%	95%
D_e [Hartree]	0.183	0.159	0.184

Symmetric dissociation of water molecule

H$_2$O, cc-pVDZ

FCI
CCSD(T)
ERPA-APSG
APSG

Energy [Hartree]

OH distance [bohr]
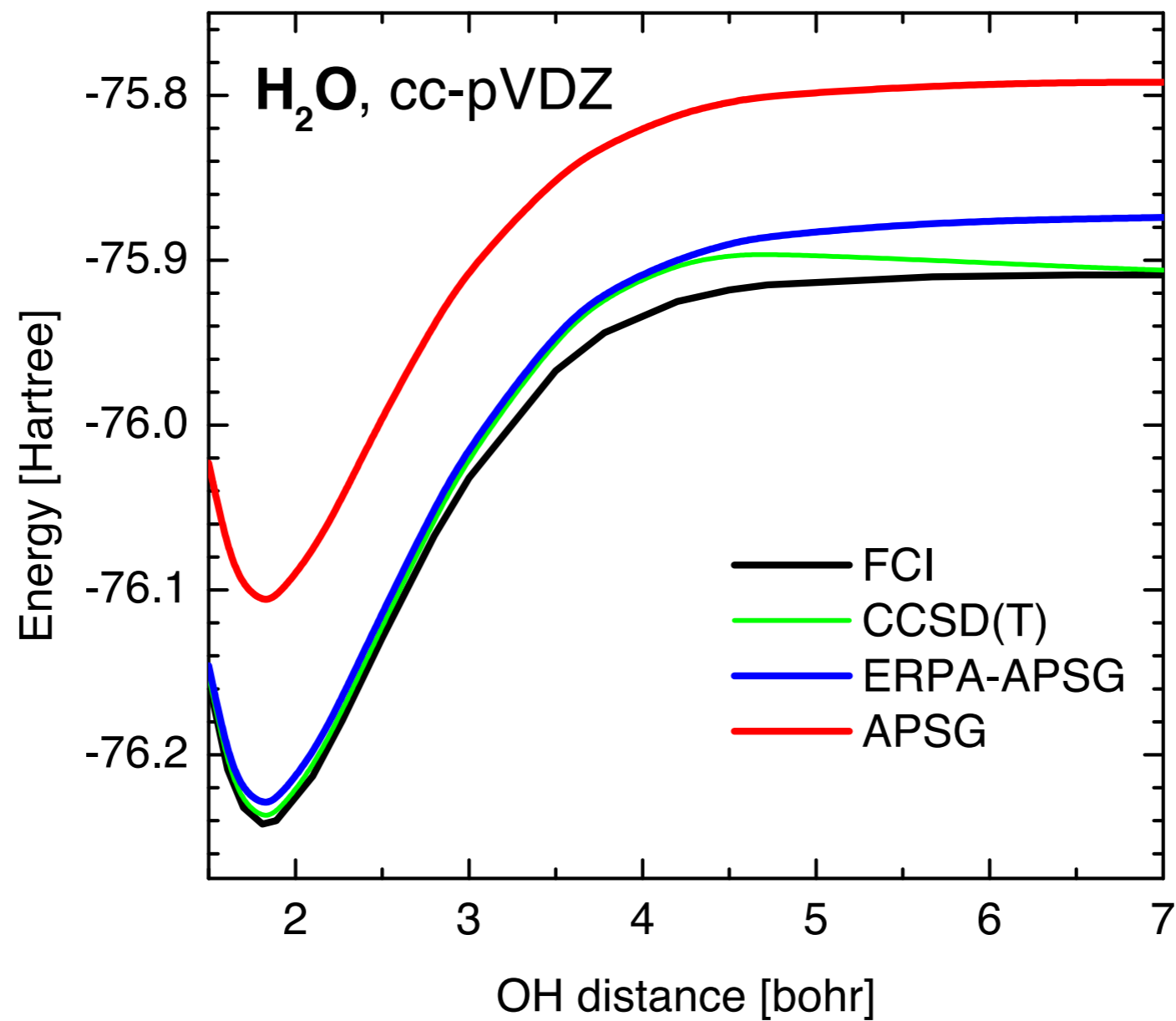
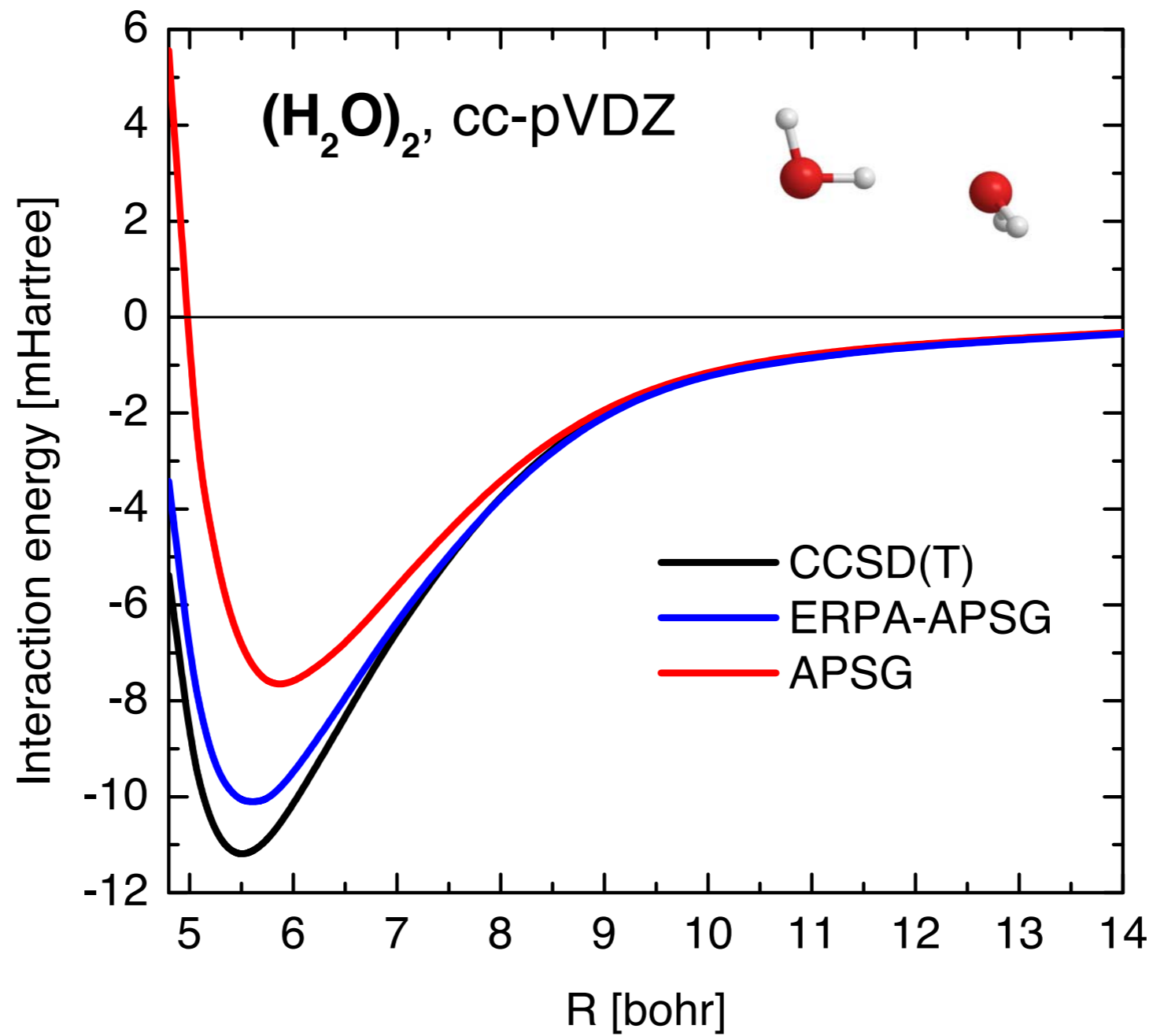|	FCI	APSG	ERPA-APSG
$E_{corr}(R_{eq})$	100%	37%	95%
D_e [Hartree]	0.333	0.315	0.356

Twisting of the CC bond in ethylene
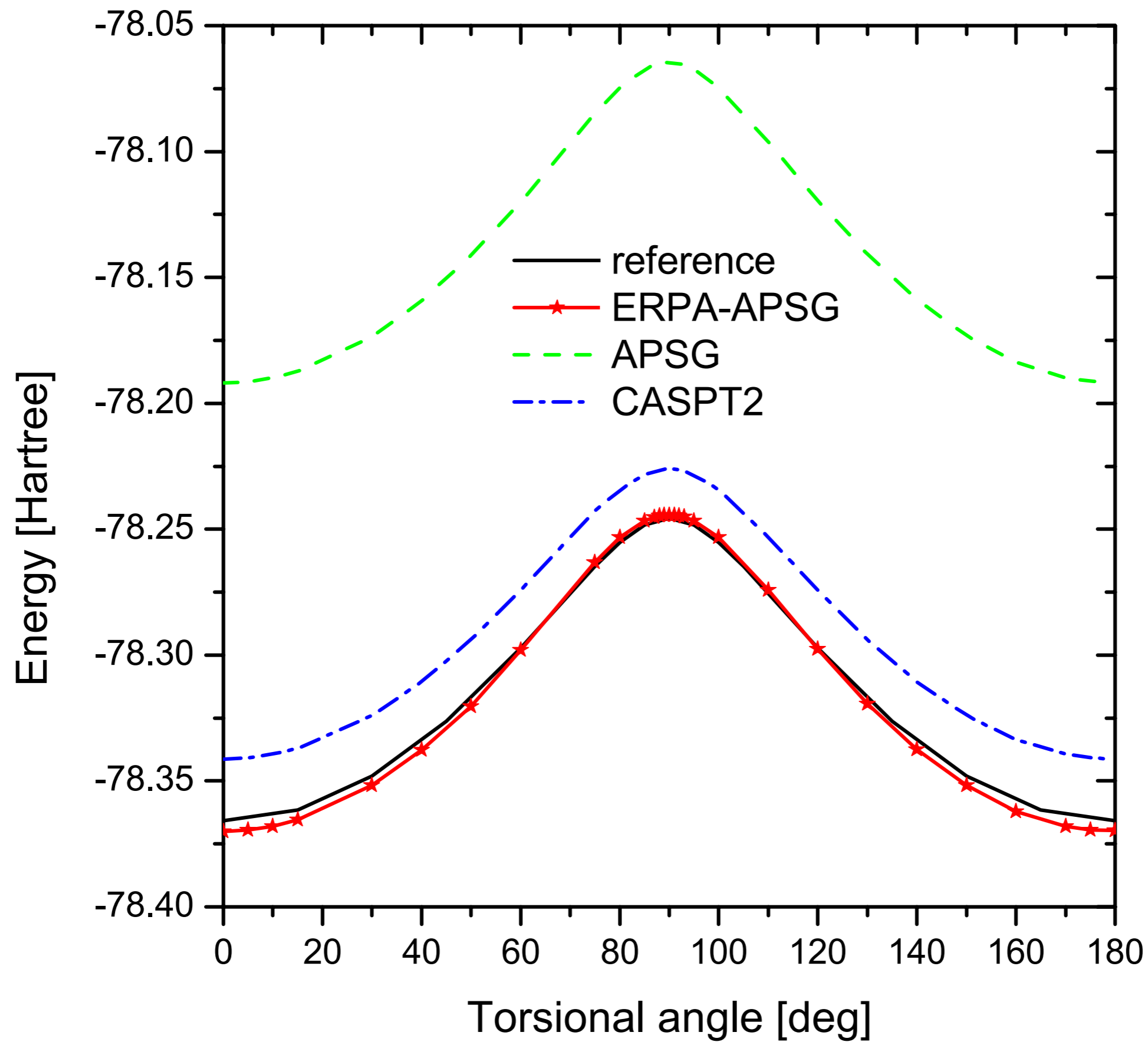
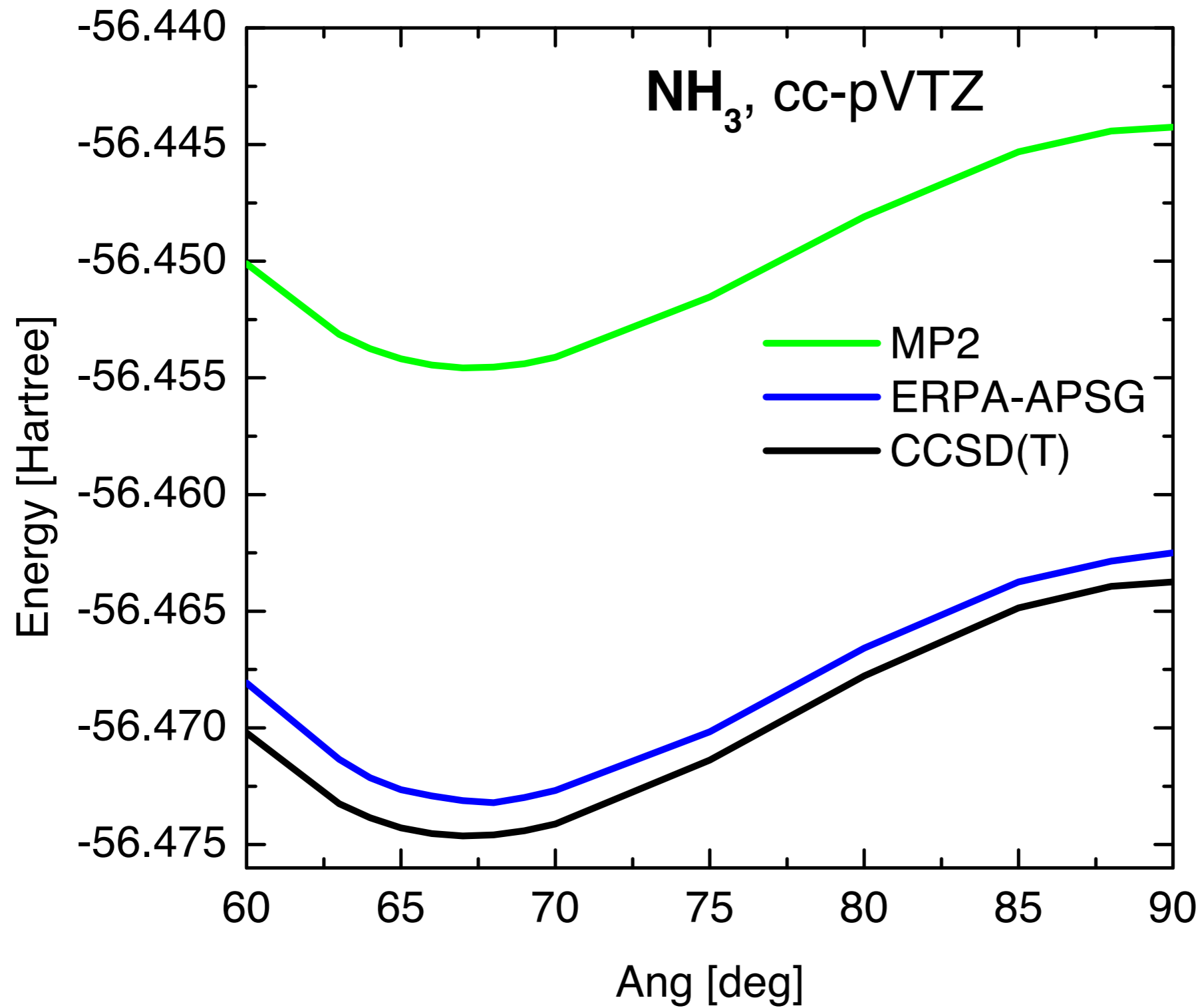ERPA-APSG: exact asymptotic of the interaction energy for the helium dimer

He$_2$, aug-cc-pVTZ

APSG
ERPA-APSG
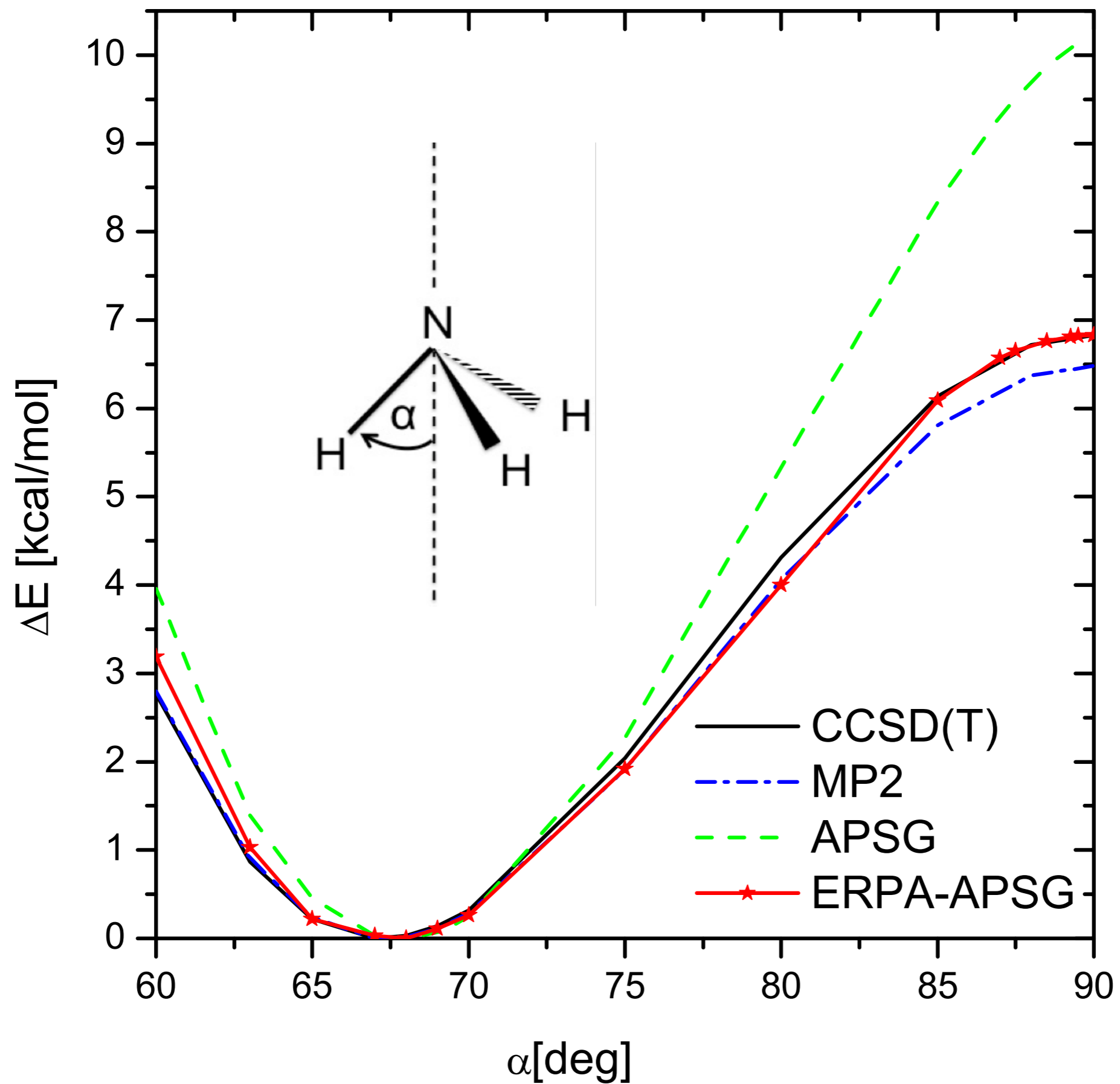CCSD(T)

Interaction energy [mHartree]

Internuclear distance [bohr]
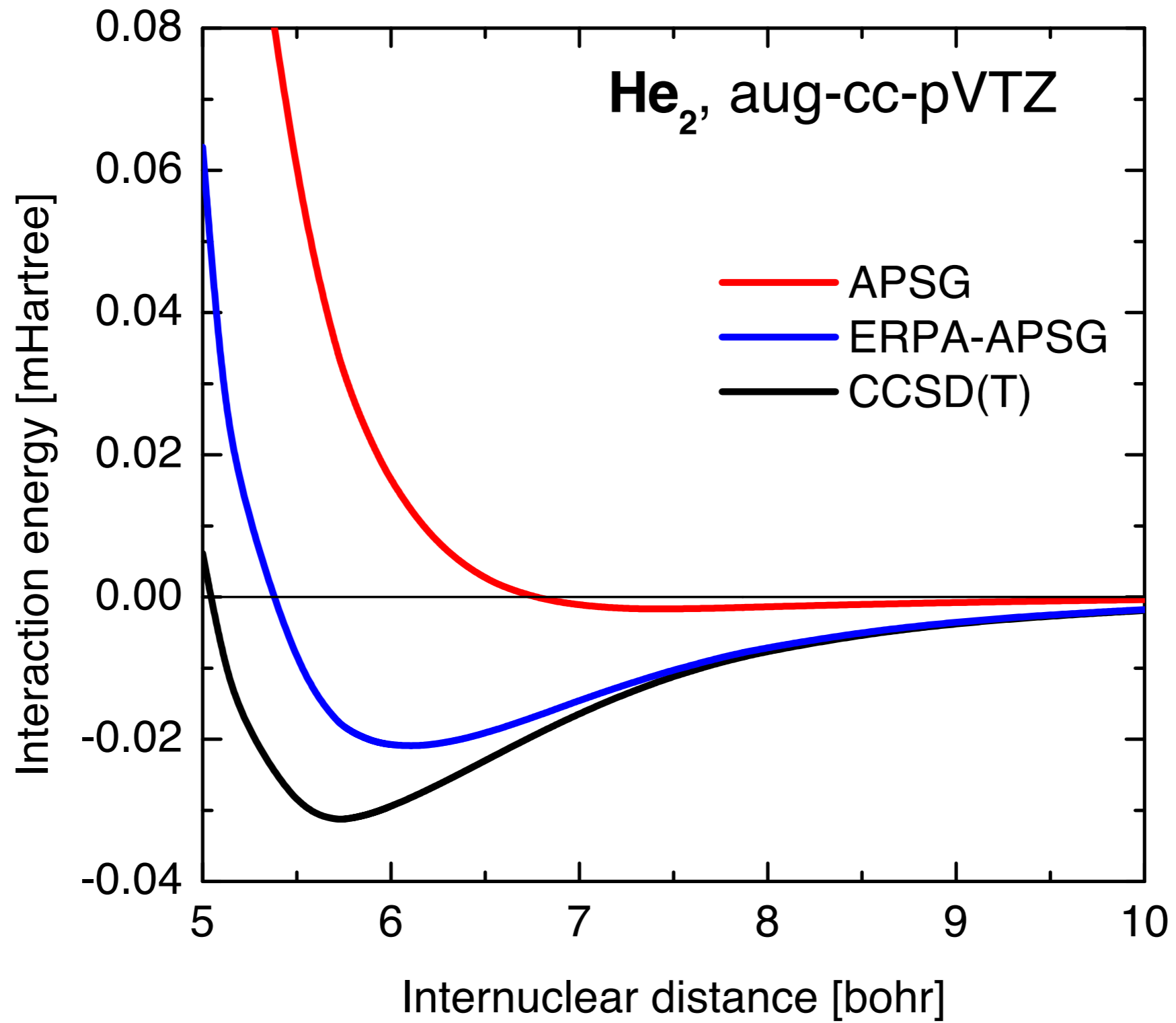
Interaction energy for water dimer

	CCSD(T)	APSG	ERPA-APSG
E_{int} [mHartree]	-11.2	-6.8	-10.1

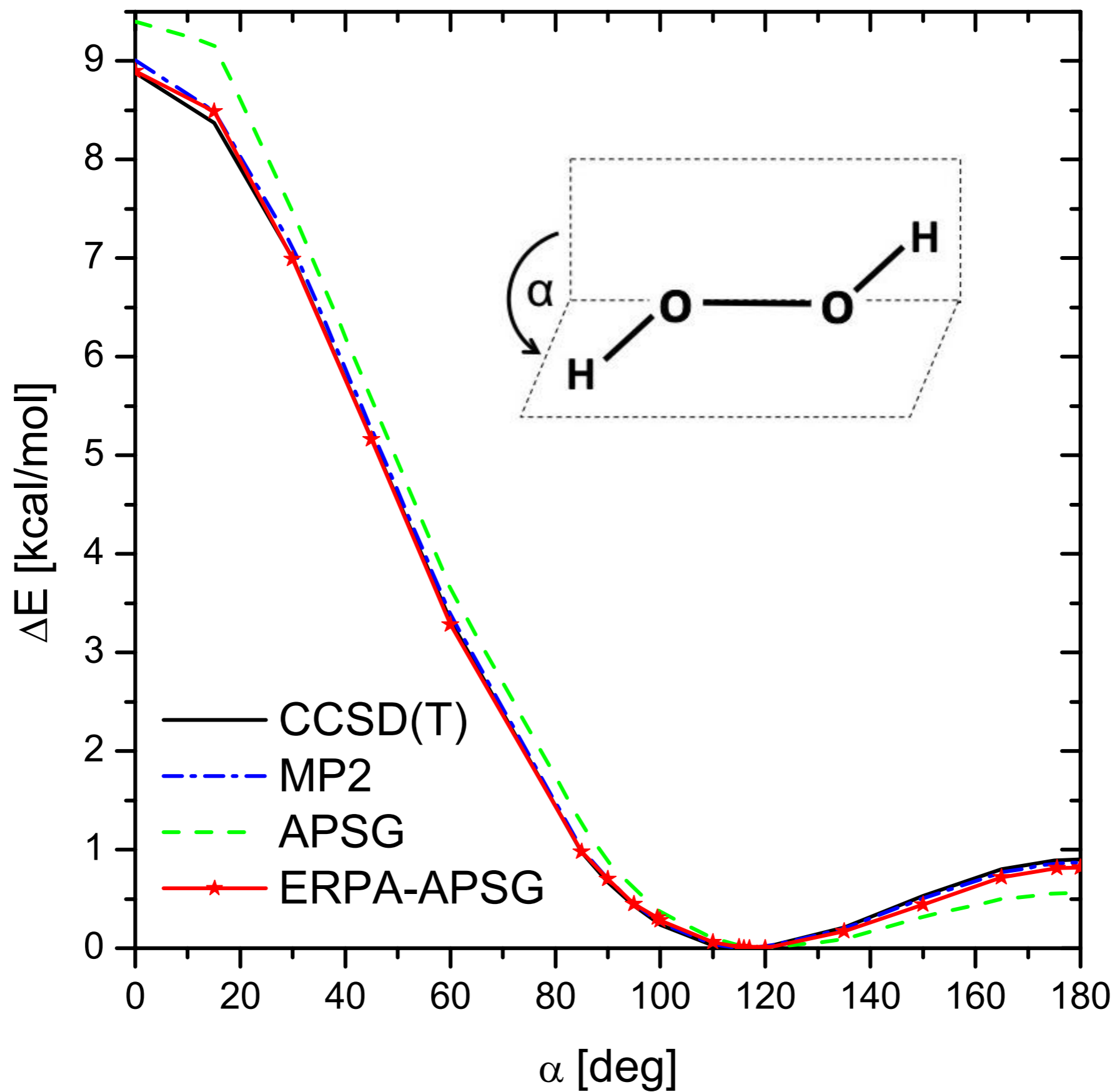Umbrella inversion of the NH₃ molecule in cc-pVTZ basis set

Umbrella inversion energy barriers for NH$_3$

Energy barriers for twisting of the O-O bond in H_2O_2

Inversion barrier of the NH₃ and H₂O molecules in cc-pVTZ basis set

Molecule	Method	Total energy [Ha]		Barrier [kcal/mol]
		Opt. geom.[a]	Linear	
H₂O	CCSD(T)	-76.3339	-76.2785	34.8 (0.0)
	MP2	-76.3205	-76.2663	34.0 (0.8)
	APSG	-76.1569	-76.0886	42.9 (8.1)
	ERPA-APSG	-76.3297	-76.2751	34.2 (0.5)
		Opt. geom.[b]	Planar	
NH₃	CCSD(T)	-56.4746	-56.4637	6.8 (0.0)
	MP2	-56.4546	-56.4442	6.5 (0.3)
	APSG	-56.3258	-56.3095	10.2 (3.4)
	ERPA-APSG	-56.4726	-56.4618	6.8 (0.0)

E. Pastorczak and K. Pernal, *Phys. Chem. Chem. Phys.* **17**, 8622 (2015).

Deprotonation energies in aug-cc-pVDZ basis set

Molecule	Method	ΔE [kcal/mol]
H_2O^a	CCSD(T)	395.5 (0.0)
	MP2	391.6 (3.9)
	APSG	405.1 (9.6)
	ERPA-APSG	397.9 (2.4)
CH_3OH^b	CCSD(T)	393.5 (0.0)
	MP2	390.4 (3.1)
	APSG	404.1 (10.6)
	ERPA-APSG	396.5 (3.0)
$C_2H_5OH^b$	CCSD(T)	389.3 (0.0)
	MP2	386.6 (2.7)
	APSG	401.9 (12.6)
	ERPA-APSG	393.3 (4.0)
$C_3H_7OH^c$	CCSD(T)	390.9 (0.0)
	MP2	388.2 (2.7)
	APSG	403.7 (12.8)
	ERPA-APSG	395.0 (4.1)

Conclusions

- The ERPA-APSG energy takes into account static and short- and long-range dynamic correlation.

- In particular, the method

  - yields exact ground state energy of singlet two-electron systems,

  - reproduces correct potential energy curves (dissociation energies of the same or better accuracy than those of APSG),

  - predicts correct energy barriers,

  - takes into account dispersion energy,

  - improves hydrogen bonds over APSG,

  - is size-extensive,

  - is comparable to RPA in terms of computational efficiency.

Acknowledgment

Ewa Pastorczak, EPFL

Koushik Chatterjee, Lodz University of Technology

Piotr Kowalski, Lodz University of Technology