Dynamic correlation for strongly orthogonal geminals

Katarzyna Pernal

Instytut Fizyki
Politechnika Łódzka

Uncorrelated strongly orthogonal electron pairs approximation

- Many-electron wavefunction is given as an antisymmetrized product of two-electron functions (strongly orthogonal geminals)

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

- Each geminal is of the form (APSG)

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

where

$$\forall_q \quad (c_q)^2 = n_q \in (0, 1)$$

- Geminals are strongly orthogonal

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

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).

PP-GVB (perfect-pairing generalized valence bond)
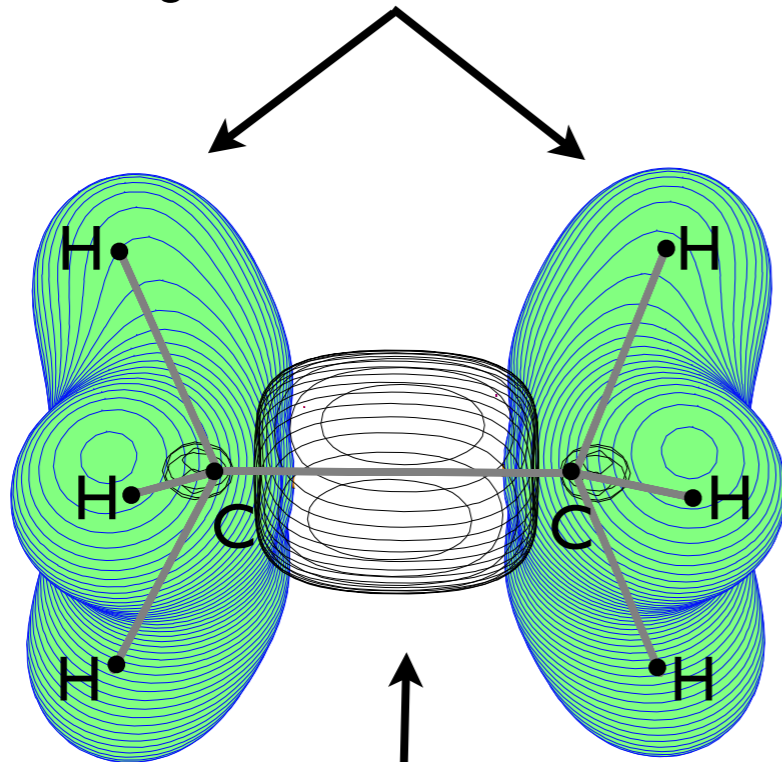
- Each geminal is of the form

$$\forall_P \quad \phi_P^{GVB}(\mathbf{r}_1, \mathbf{r}_2) = c_{1_P}\psi_{1_P}(\mathbf{r}_1)\psi_{1_P}(\mathbf{r}_2) + c_{2_P}\psi_{2_P}(\mathbf{r}_1)\psi_{2_P}(\mathbf{r}_2)$$
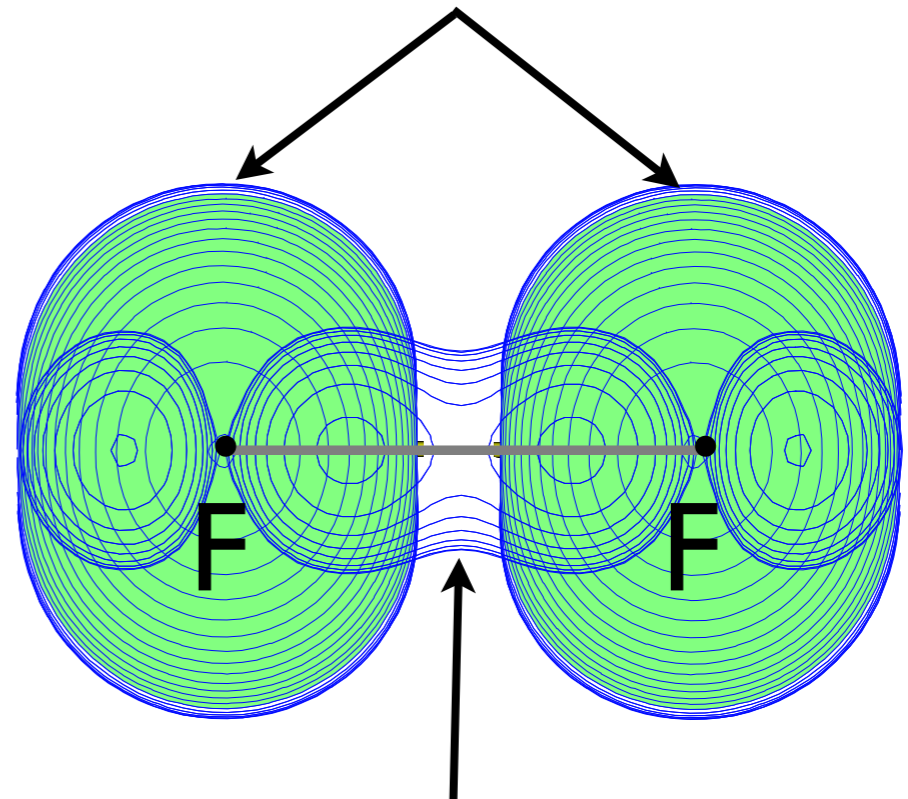
where

$$\forall_q \quad (c_q)^2 = n_q \in (0,1)$$

Localization on bonds and lone pairs of geminal densities

densities of geminals localized on C-H bonds

densities of geminals localized on atoms

a geminal localized on bond

a geminal localized on bond

Ground state energy functional in the APSG model

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

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

intrageminal electron interaction

Coulomb and exchange intergeminal interaction

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 (1) the orbitals, (2) the coefficients c_p under normalization constraint, and (3) Arai subspaces.

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

Lack of pair-pair correlation results in failure in capturing dispersion interaction

He$_2$, aug-cc-pVTZ

exact
PP-GVB
HF

Interaction energy [mHartree]

Internuclear distance [bohr]
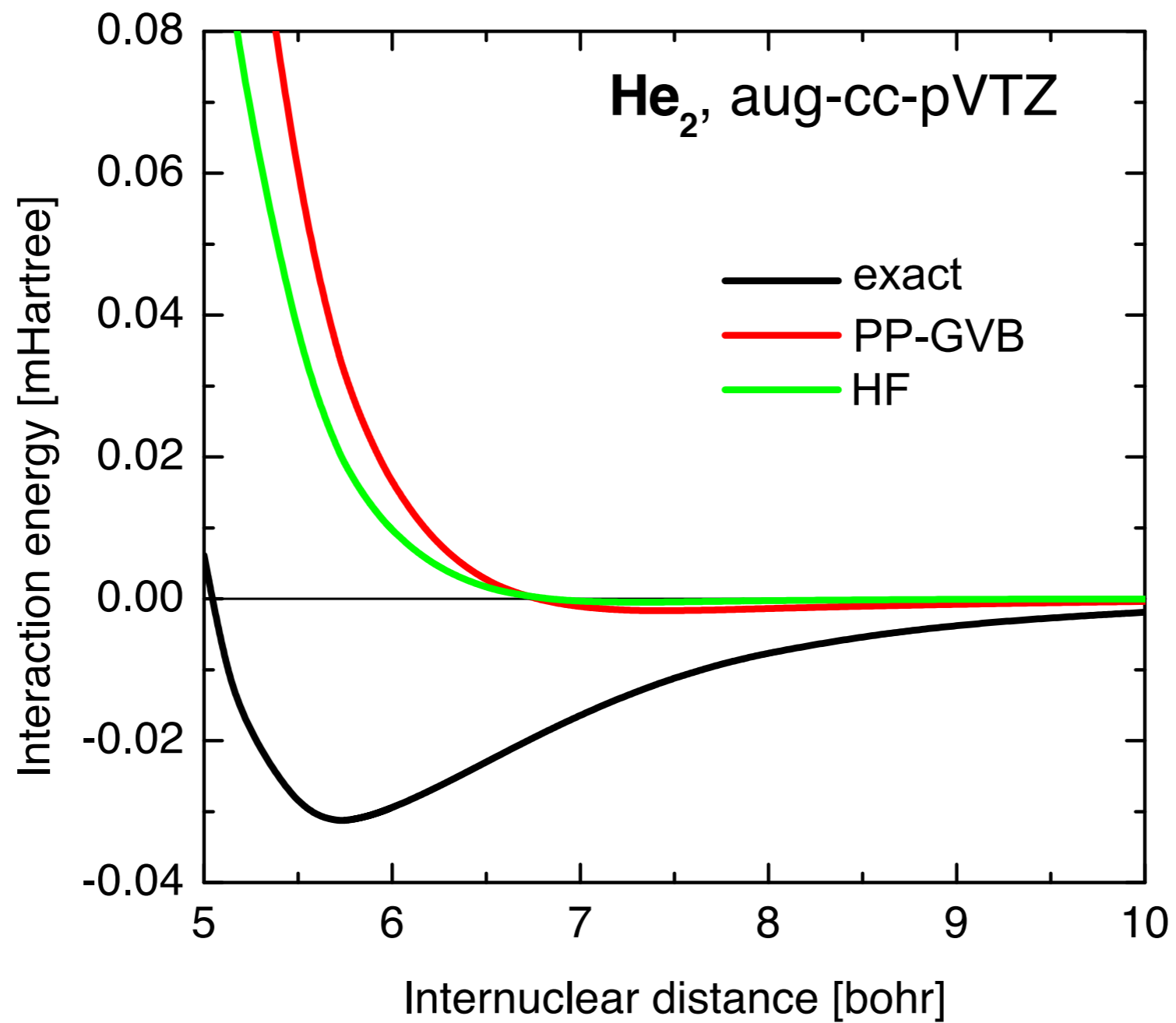
Inter-pair correlation energy

- Inter-domain correlation between I and J domains results from coupling density-density fluctuations

$$\rho_{IJ}^{(2)}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{2}[\langle \delta\hat{\rho}_I(\mathbf{x}_1)\delta\hat{\rho}_J(\mathbf{x}_2)\rangle + \langle \delta\hat{\rho}_J(\mathbf{x}_1)\delta\hat{\rho}_I(\mathbf{x}_2)\rangle]$$

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

$$E_{corr}^{IJ} = \frac{1}{2}\sum_{\sigma_1,\sigma_2}\int\int \frac{\rho_{IJ}^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}d\mathbf{r}_1 d\mathbf{r}_2$$

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

K. Pernal, Phys. Chem. Chem. Phys., **18**, 21111 (2016).

- It is more convenient to write the Inter-Geminal (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).
K. Pernal, Phys. Chem. Chem. Phys., **18**, 21111 (2016).

Equation of motion

- 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 equations for excitation energies

$$(\mathbf{A}+\mathbf{B})\ (\mathbf{X}+\mathbf{Y})\ =\ \omega\ \mathcal{N}\ (\mathbf{Y}-\mathbf{X})$$
$$(\mathbf{A}-\mathbf{B})\ (\mathbf{Y}-\mathbf{X})\ =\ \omega\ \mathcal{N}\ (\mathbf{X}+\mathbf{Y})$$

The eigenvectors are related to the transition density matrix elements

$$\forall_{p>q}\ (n_p - n_q)[(Y_\nu)_{pq} - (X_\nu)_{pq}] = (T_\nu)_{pq}\ + (T_\nu)_{qp}$$

$$(T_\nu)_{pq} = \left\langle 0|\hat{a}^\dagger_q\hat{a}_p|\nu\right\rangle$$
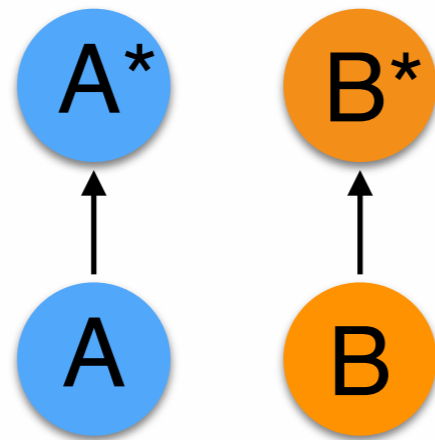
D. J. Rowe, *Rev. Mod. Phys.* **40**, 153 (1968).
K. Chatterjee and K. Pernal, *J. Chem. Phys.* **137**, 204109 (2012).
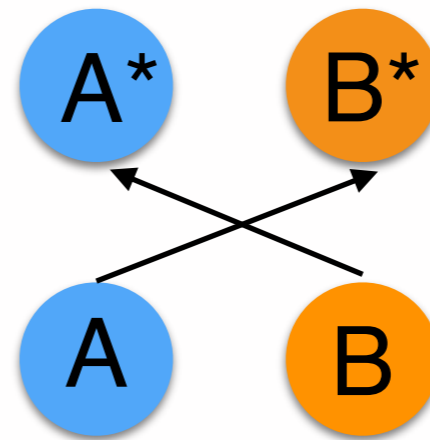K. Pernal, K. Chatterjee, and P. H. Kowalski, *J. Chem. Phys.* **140**, 014101 (2014).

Obtained expression for the inter-pair correlation involves pairwise terms representing interactions of transition densities from A and B electron pairs
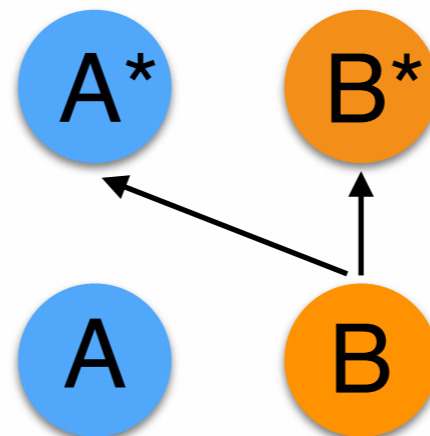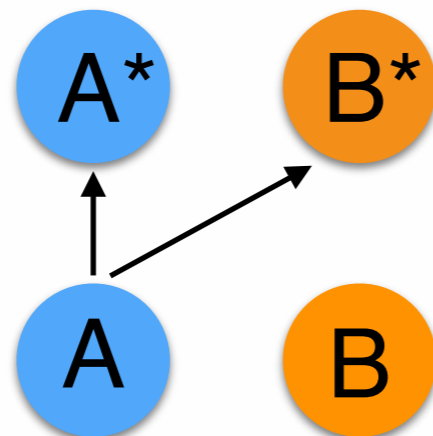
Dispersion

Exchange-Dispersion

Charge transfer

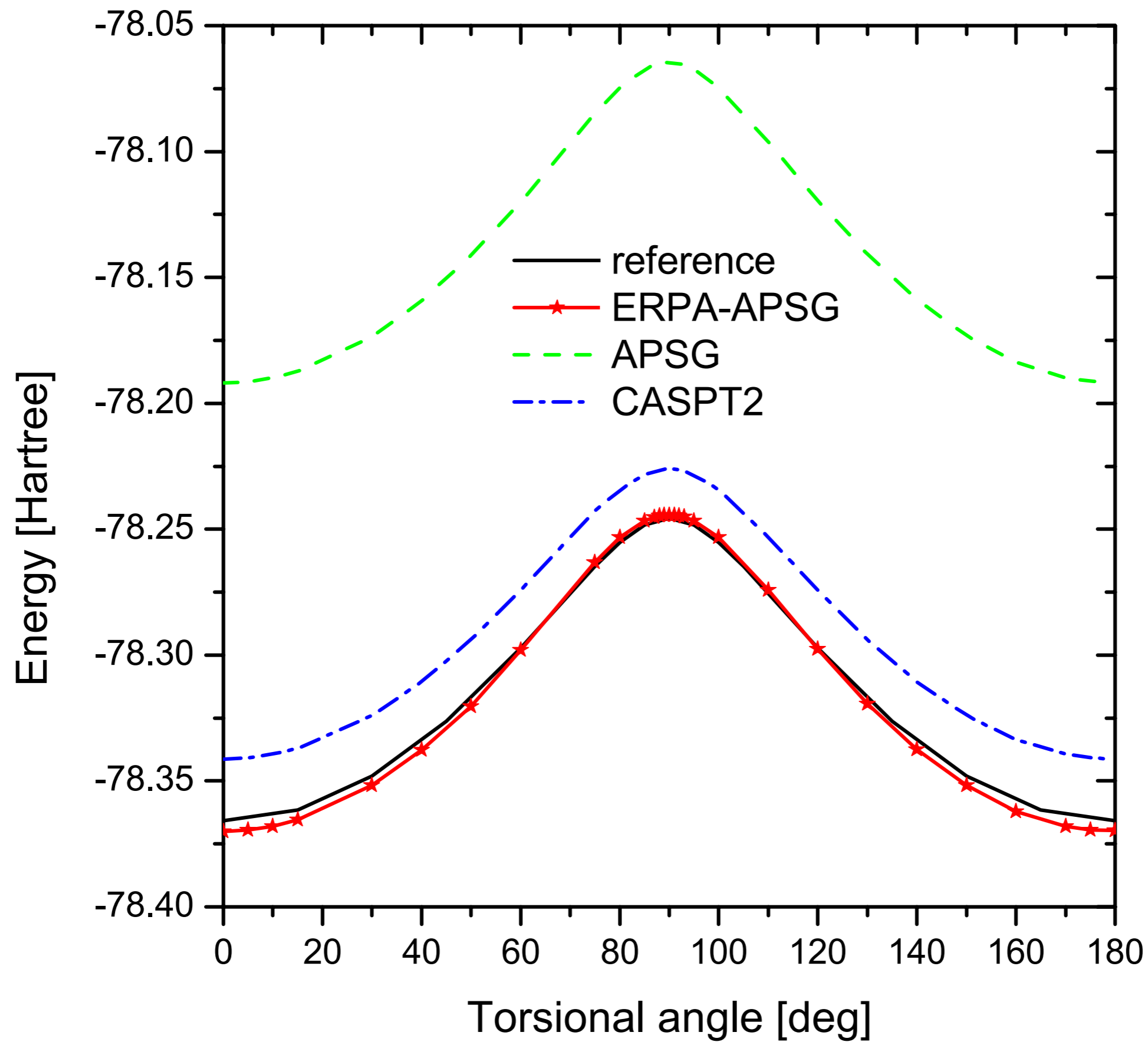# Many-body correlation terms in ERPA-GVB

The idea of inter-pair (two-body interaction) has been generalized to include

- 1-body (intra-pair) correlation

- 2-body correlation (density fluctuations of two pairs are coupled)

- 3-body correlation (density fluctuations of three pairs are coupled)

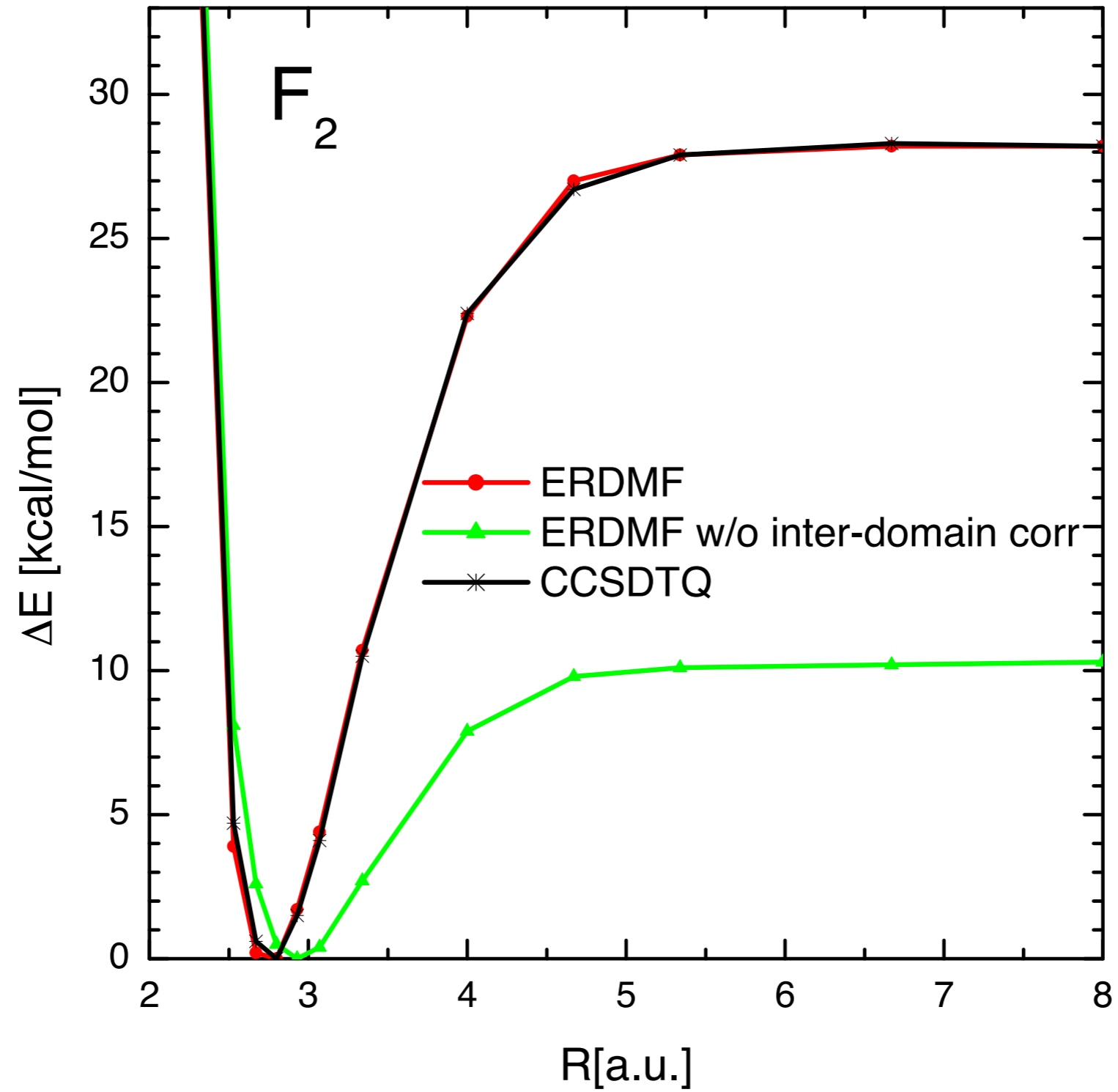- 4-body correlation (density fluctuations of four pairs are coupled)

$$
E_{corr}^{ERPA-GVB} = \overset{1-body}{\sum_{A}} E_A^{corr} + \overset{2-body}{\sum_{AB}} E_{AB}^{corr} + \overset{3-body}{\sum_{ABC}} E_{ABC}^{corr} + \overset{4-body}{\sum_{ABCD}} E_{ABCD}^{corr}
$$

where A,B,C,D stand for geminals.

K. Chatterjee, E. Pastorczak, K. Jawulski, and K. Pernal, *J. Chem. Phys.* **145**, 244111 (2016).
K. Pernal, *Phys. Chem. Chem. Phys*. **18**, 21111 (2016).
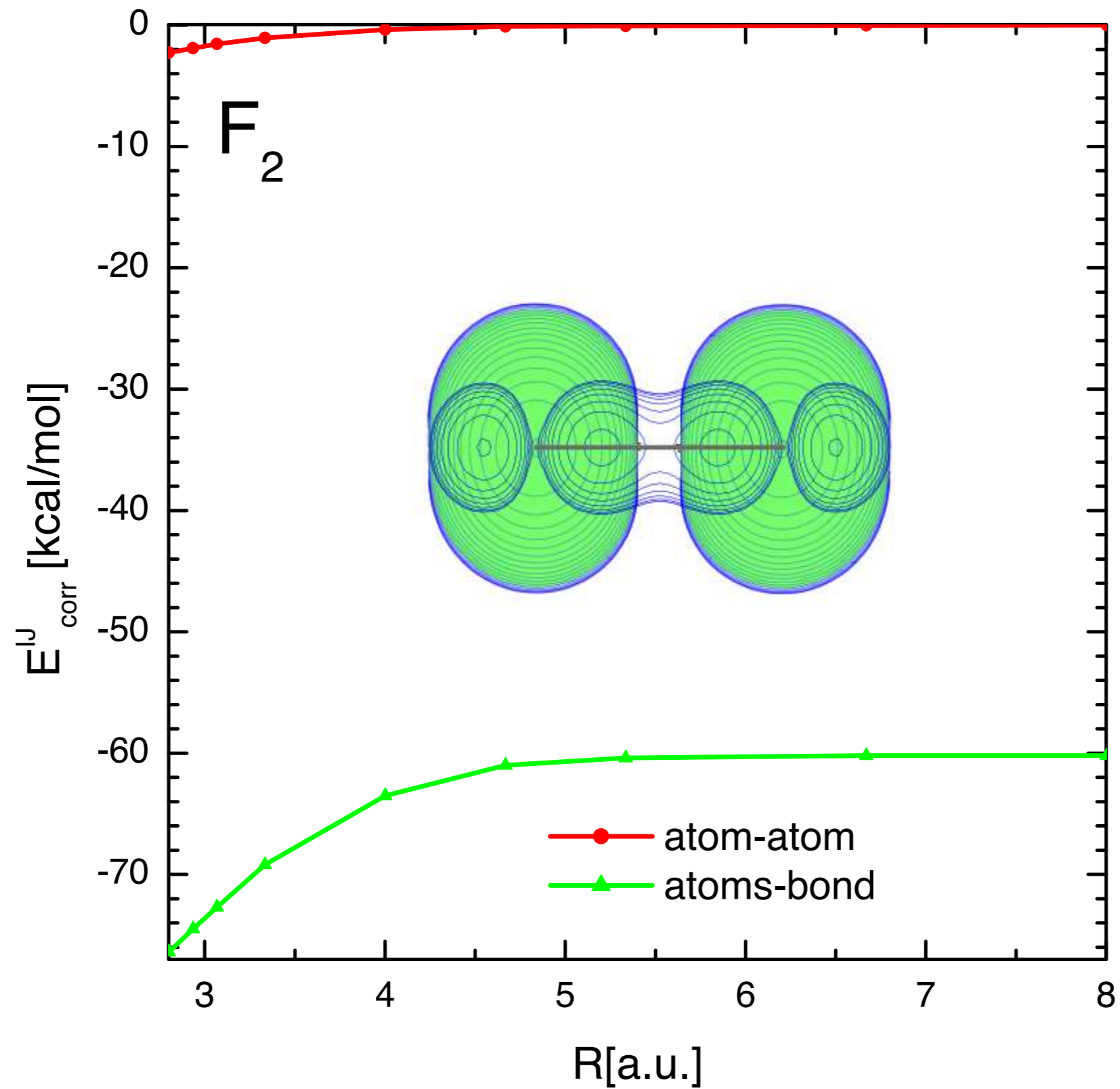
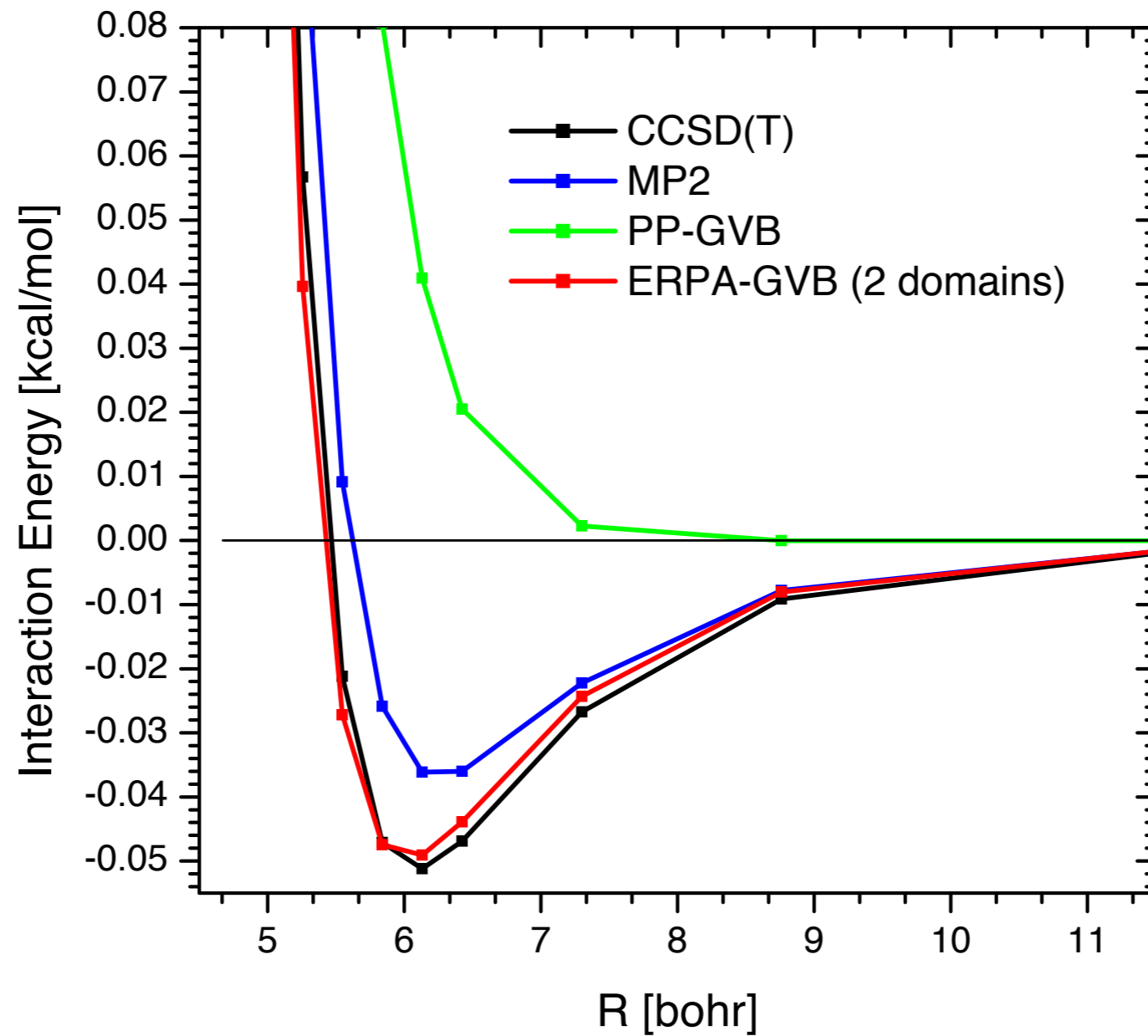Twisting of the CC bond in ethylene

Dissociation curve of F_2 (cc-pVDZ basis set)

Dissociation curve of F_2 - inter-domain contributions
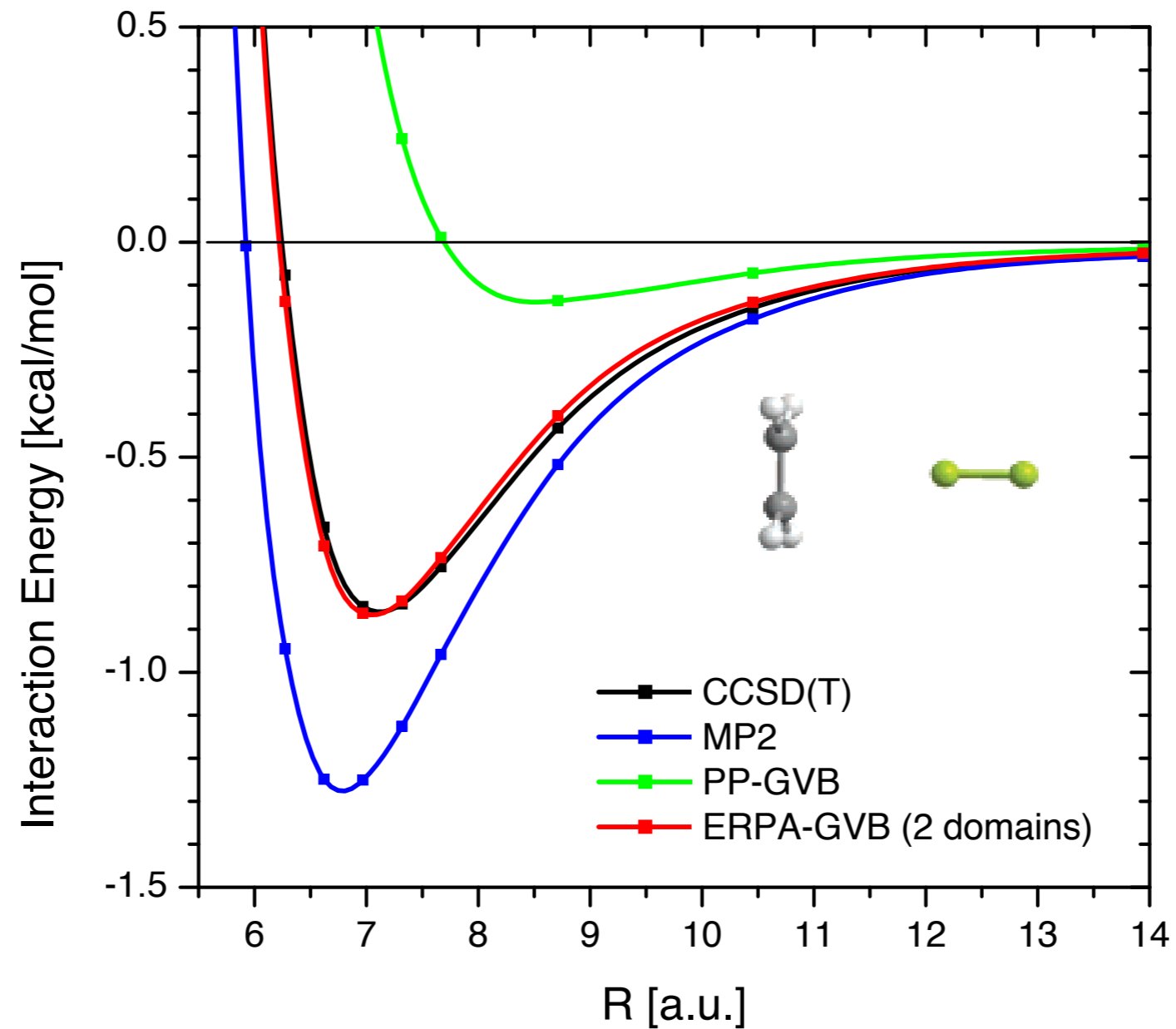
Ne$_2$ (aug-cc-pVDZ)

PP-GVB: no inter-domain correlation

ERPA-GVB (2 domains): intra- and inter-domain ERPA correlation added

C$_2$H$_4$--F$_2$ dimer (aug-cc-pVDZ)

PP-GVB: no intra and inter-domain ERPA correlation

ERPA-GVB (2 domains): intra- and inter-domain ERPA correlation added

Circular H₆ - breakdown for non-Lewis-structure molecule