Novel approaches towards constructing reduced density matrix functionals within random phase approximation framework

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Outline

- Part 1

  Factorization of 2-RDM in terms of one-electron reduced functions

- Part 2

  Linear response equations, Rowe equation of motion, (Extended)RPA

- Part 3

  Direct approach: density matrix functional based on factorization formula and (Extended)RPA

- Part 4

  Employing Adiabatic Connection construction, Multireference Wavefunction gets in.

Part 1

Factorization of 2-RDM in terms of 1-electron functions

A. D. McLachlan, M. A. Ball, Rev Mod Phys **36**, 844 (1964).

J. Dobson, in *Time-Dependent Density Functional Theory*; Marques, M. A. L., et al., Eds.; Springer: Berlin, 2006; pp 443-462.

Density matrices and density functions

- One-electron reduced density matrix (1-RDM): operator, matrix, and function

$$\hat{\gamma}_{pq} = \hat{a}_q^\dagger \hat{a}_p$$

$$\gamma_{pq} = \langle \Psi_0 | \hat{\gamma}_{pq} | \Psi_0 \rangle$$

$$\gamma\left(x, x'\right) = \sum_{pq} \gamma_{pq} \varphi_p(x) \varphi_q(x')^*$$

- Spinorbitals which diagonalize 1-RDM are called natural spinorbitals

- Diagonal elements of 1-RDM in the representation of the natural spinorbitals are called natural occupation numbers

$$\gamma_{pq} = n_p \delta_{pq}$$

- A spin-summed diagonal part of 1-RDM is simply electron density

$$\rho(\mathbf{r}) = \sum_\sigma \gamma\left(x, x\right)$$

Density matrices and density functions

- Two-electron reduced density matrix (2-RDM): an operator, a matrix, and a function

$$\hat{\Gamma}_{pqrs} = \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_p$$

$$\Gamma_{pqrs} = \left\langle \Psi_0 | \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_p | \Psi_0 \right\rangle$$

$$\Gamma(x_1, x_2; x_1' x_2') = \sum_{pqrs} \Gamma_{pqrs} \varphi_p(x_1) \varphi_q(x_2) \varphi_r(x_1')^* \varphi_s(x_2')^*$$

- A spin-summed diagonal part of 2-RDM is simply a pair density function

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\sigma_1, \sigma_2} \Gamma(x_1, x_2; x_1 x_2)$$

Electronic Hamiltonian and electronic energy

- Electronic Hamiltonian includes only one- and two-particle operators

$$\hat{H} = \sum_{pq} \hat{a}_q^\dagger \hat{a}_p h_{qp} + \frac{1}{2} \sum_{pqrs} \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_p \langle rs|pq\rangle$$

$$h_{qp} = \int \varphi_q(x)^* \left[\hat{t} + \hat{v}_{ext}\right] \varphi_p(x) dx$$

$$\langle pq|rs\rangle = \int\int \varphi_p(x_1)^* \varphi_q(x_2)^* r_{12}^{-1} \varphi_r(x_1) \varphi_s(x_2) dx_1 dx_2$$

- Its expectation value (electronic energy) is determined by 1- and 2-RDM

$$E = \left\langle \Psi_0 | \hat{H} | \Psi_0 \right\rangle = \sum_{pq} \gamma_{pq} h_{qp} + \frac{1}{2} \sum_{pqrs} \Gamma_{pqrs} \langle rs|pq\rangle$$

$$= E_{one} + E_{ee}$$

Writing 2-RDM operator in terms 1-RDM operators

- Anticommutation relations for fermionic creation and anihilation operators

$$\hat{a}_s^\dagger \hat{a}_p = -\hat{a}_p \hat{a}_s^\dagger + \delta_{ps}$$

$$\hat{a}_q^\dagger \hat{a}_p^\dagger = -\hat{a}_p^\dagger \hat{a}_q^\dagger$$

$$\hat{a}_q \hat{a}_p = -\hat{a}_p \hat{a}_q$$

- By using anticommutation relations 2-RDM operator can be expressed in terms of 1-RDM operators

$$\hat{\Gamma}_{pqrs} = \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_p = -\hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_p \hat{a}_q = -\hat{a}_r^\dagger \left(-\hat{a}_p \hat{a}_s^\dagger + \delta_{ps}\right) \hat{a}_q = \hat{a}_r^\dagger \hat{a}_p \hat{a}_s^\dagger \hat{a}_q - \hat{a}_r^\dagger \hat{a}_q \delta_{ps}$$

$$= \hat{\gamma}_{pr} \hat{\gamma}_{qs} - \hat{\gamma}_{qr} \delta_{ps}$$

Writing 2-RDM operator in terms 1-RDM operators

- 2-RDM elements read therefore

$$\Gamma_{pqrs} = \left\langle \Psi_0 | \hat{\Gamma}_{pqrs} | \Psi_0 \right\rangle = \langle \Psi_0 | \hat{\gamma}_{pr} \hat{\gamma}_{qs} | \Psi_0 \rangle - \gamma_{qr} \delta_{ps}$$

- A set of states $|\Psi_v\rangle$ is complete. Use resolution of identity

$$\hat{1} = \sum_{\nu} |\Psi_\nu\rangle \langle \Psi_\nu| = |\Psi_0\rangle \langle \Psi_0| + \sum_{\nu \neq 0} |\Psi_\nu\rangle \langle \Psi_\nu|$$

to get

$$\begin{aligned}
\Gamma_{pqrs} &= \langle \Psi_0 | \hat{\gamma}_{pr} |\Psi_0\rangle \langle \Psi_0 | \hat{\gamma}_{qs} | \Psi_0 \rangle + \sum_{\nu \neq 0} \langle \Psi_0 | \hat{\gamma}_{pr} |\Psi_v\rangle \langle \Psi_\nu | \hat{\gamma}_{qs} | \Psi_0 \rangle - \gamma_{qr} \delta_{ps} \\
&= \gamma_{pr} \gamma_{qs} + \sum_{\nu \neq 0} \gamma_{pr}^{0\nu} \gamma_{qs}^{\nu 0} - \gamma_{qr} \delta_{ps}
\end{aligned}$$

Writing 2-RDM operator in terms 1-RDM operators

- 2-RDM matrix elements are now expressed as

$$\Gamma_{pqrs} = \gamma_{pr}\gamma_{qs} + \sum_{\nu \neq 0} \gamma_{pr}^{0\nu}\gamma_{qs}^{\nu 0} - \gamma_{qr}\delta_{ps}$$

i.e. in terms of transition density matrix for excitation to a excited state

$$\gamma_{pr}^{0\nu} = \langle \Psi_0 | \hat{\gamma}_{pr} | \Psi_\nu \rangle$$

$$\gamma_{pr}^{\nu 0} = \langle \Psi_\nu | \hat{\gamma}_{pr} | \Psi_0 \rangle = \left(\gamma_{rp}^{0\nu}\right)^*$$

This relation is exact.

Electron interaction energy in terms of one-electron reduced functions

- So we have we have arrived at electron interaction energy written in terms of one-electron density functions

$$E_{ee} = \frac{1}{2}\sum_{pqrs}\Gamma_{pqrs}\left\langle rs|pq\right\rangle$$

$$= J[\gamma] + \frac{1}{2}\sum_{pqrs}\left(\sum_{\nu\neq 0}\gamma_{pr}^{0\nu}\gamma_{qs}^{\nu 0} - \gamma_{qr}\delta_{ps}\right)\left\langle rs|pq\right\rangle$$

$$J[\gamma] = \frac{1}{2}\sum_{pqrs}\gamma_{pr}\gamma_{qs}\left\langle rs|pq\right\rangle = \frac{1}{2}\int\int\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1 d\mathbf{r}_2$$

Part 2

Linear response equations, TD-RDMFT, Rowe's equation of motion, (Extended)RPA

D. J. Rowe, Rev. Mod. Phys. 40, 153 (1968).

K. Pernal, K. Giesbertz, O. Gritsenko, and E.J. Baerends, *J. Chem. Phys.* 127, 214101 (2007).

K. Chatterjee and K. Pernal, J. Chem. Phys. 137, 204109 (2012).

TD-RDMFT

- The linear response equations read

$$\sum_{rs} \delta\gamma_{rs}(\omega)[\omega\ \delta_{pr}\delta_{qs} - \delta_{pr}h_{qs} + \delta_{qs}h_{rp} - K_{pqrs}(\omega)] = (n_p - n_q)\, v_{qp}(\omega)$$

and they involve the frequency-dependent coupling matrix

$$\forall_{pqvw} \quad K_{pqvw}(\omega) = 2 \int e^{-i\omega\,(t-t')} \times \frac{\partial \sum_{rst} \{\Gamma_{prst}[\gamma](t)\langle\varphi_q\varphi_r|\varphi_s\varphi_t\rangle - \Gamma_{tsrq}[\gamma](t)\ \langle\varphi_t\varphi_s|\varphi_r\varphi_p\rangle\}}{\partial\gamma_{vw}(t')}\bigg|_{\gamma=\gamma^{(0)}} d(t-t')$$

K. Pernal, K. Giesbertz, O. Gritsenko, and E.J. Baerends, *J. Chem. Phys.* **127**, 214101 (2007).

Adiabatic approximation to TD-RDMFT equations

$$\forall_{pqvw} \quad K_{pqvw} = \left. \frac{\partial \left\{ \sum_{rs} (W^*_{rs}[\gamma] - W_{sr}[\gamma]) U^*_{rp} U_{sq} \right\}}{\partial \gamma_{vw}} \right|_{\gamma=\gamma^{(0)}}$$

- For a functional being natural orbital and natural occupation numbers functional

$$E_{ee}[\gamma] = \frac{1}{2} \sum_{pqrs} \Gamma_{rspq}[\boldsymbol{n}] \langle pq|rs \rangle$$

$$W_{pq} = \left\langle \frac{\delta E_{ee}[\gamma]}{\delta \varphi_p} \varphi_q \right\rangle = \sum_{ptrs} \Gamma_{ptrs}[\boldsymbol{n}] \langle rs|qt \rangle$$

K. Giesbertz, K. Pernal, O.V. Gritsenko, and E.J. Baerends, *J. Chem. Phys.* **130**, 114104 (2009).

- no response of the occupation numbers in the adiabatic approximation

$$\delta n_p(\omega) = 0$$

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- The linear response equations in the adiabatic approximation

$$\begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{B} & \mathcal{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^\nu \\ \mathbf{Y}^\nu \end{pmatrix} = \omega_\nu \begin{pmatrix} -\mathcal{N} & \mathbf{0} \\ \mathbf{0} & \mathcal{N} \end{pmatrix} \begin{pmatrix} \mathbf{X}^\nu \\ \mathbf{Y}^\nu \end{pmatrix}$$

$$\mathcal{A}_{pqrs} = \mathcal{B}_{pq,sr} = (n_r - n_s)(\delta_{pr} h_{qs} - \delta_{qs} h_{rp} + K_{pqrs})$$

$$\mathcal{N}_{pqrs} = (n_p - n_q)\delta_{pr}\delta_{qs}$$

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- Transition density matrix elements

$$\forall_{p>q} \quad \gamma^{0\nu}_{qp} = (n_q - n_p) Y^\nu_{pq}$$

$$\forall_{p<q} \quad \gamma^{0\nu}_{qp} = (n_p - n_q) X^\nu_{qp}$$

$$\forall_{p} \quad \gamma^{0\nu}_{pp} = 0$$

Rowe's equations-of-motion

- Consider an eigenequation of the Hamiltonian

$$\hat{H}\left|0\right\rangle = E_0\left|0\right\rangle$$

$$\hat{H}\left|\nu\right\rangle = E_\nu\left|\nu\right\rangle$$

$$\omega_\nu = E_\nu - E_0$$

The Rowe's equations-of-motion formalism is based on the concept of excitation and dexcitation operators

$$O_\nu^+\left|0\right\rangle = \left|\nu\right\rangle$$

$$O_\nu\left|0\right\rangle = 0$$

$$\left\langle 0\right|\left[\delta O,\left[H,O^+\right]\right]\left|0\right\rangle = \omega_\nu\left\langle 0\right|\left[\delta O,O^+\right]\left|0\right\rangle$$

D. J. Rowe, *Rev. Mod. Phys.* **40**, 153 (1968).

Extended Random Phase Approximation

- Only single excitations in the excitation operator

$$O_\nu^\dagger = \sum_{p>q} \left(X_{pq} a_p^\dagger a_q + Y_{pq} a_q^\dagger a_p \right)$$

K. Chatterjee and K. Pernal, *J. Chem. Phys.* **137**, 204109 (2012).

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$$\begin{aligned} \forall_{pqrs} \quad \mathcal{A}_{rspq} = \mathcal{B}_{rsqp} &= (n_r - n_s)(\delta_{pr} h_{sq} - \delta_{sq} h_{pr}) \\ &+ \sum_{tu} \Gamma_{purt} \langle st||qu\rangle + \sum_{tu} \Gamma_{stqu} \langle up||tr\rangle \\ &+ \sum_{tu} \Gamma_{turq} \langle ps|tu\rangle + \sum_{tu} \Gamma_{sptu} \langle tu|qr\rangle \\ &+ \delta_{sq} \sum_{twu} \Gamma_{wurt} \langle tp|wu\rangle + \delta_{pr} \sum_{tuw} \Gamma_{swtu} \langle tu|wq\rangle \end{aligned}$$

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only 1- and 2-RDM's are needed!

K. Chatterjee and K. Pernal, *J. Chem. Phys.* **137**, 204109 (2012).

TD-RDMFT vs. ERPA

- If the electron repulsion functional is of the general form

$$E_{ee}[\gamma] = \frac{1}{2} \sum_{pqrs} \Gamma_{rspq}[\boldsymbol{n}] \langle pq|rs\rangle$$

$$\mathcal{A}^{TD-RDMFT} = \mathcal{A}^{ERPA}(\gamma, \Gamma)$$

$$\mathcal{B}^{TD-RDMFT} = \mathcal{B}^{ERPA}(\gamma, \Gamma)$$

Adiabatic TD-RDMFT equations are identical to those of ERPA.

Part 3

Direct approach: density matrix functional based on the factorization formula for 2-RDM and ERPA

K. Pernal, Int. J. Quant. Chem., DOI: 10.1002/qua.25462 (2017).

Reconstruction of 2-RDM via ERPA(=adiabatic TD-RDMFT)

Here is the idea:

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- Electron interaction in terms of 1-electron functions

$$E_{ee} = \frac{1}{2}\sum_{pqrs}\Gamma_{pqrs}\,\langle rs|pq\rangle$$

$$= J[\gamma] + \frac{1}{2}\sum_{pqrs}\left(\sum_{\nu\neq 0}\gamma^{0\nu}_{pr}\gamma^{\nu 0}_{qs} - \gamma_{qr}\delta_{ps}\right)\langle rs|pq\rangle$$

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- Transition reduced density matrices from linear response (ERPA=adiabatic kernel)

$$\begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{B} & \mathcal{A} \end{pmatrix}\begin{pmatrix} \mathbf{X}^\nu \\ \mathbf{Y}^\nu \end{pmatrix} = \omega_\nu \begin{pmatrix} -\mathcal{N} & \mathbf{0} \\ \mathbf{0} & \mathcal{N} \end{pmatrix}\begin{pmatrix} \mathbf{X}^\nu \\ \mathbf{Y}^\nu \end{pmatrix}$$

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Reconstruction of 2-RDM via ERPA(=adiabatic TD-RDMFT)

$$\mathcal{A} = \mathcal{A}(\gamma, \tilde{\Gamma})$$

$$\mathcal{B} = \mathcal{B}(\gamma, \tilde{\Gamma})$$

$$\Gamma^{ERPA}$$

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2-RDM from ERPA should account for correlation effects not included in the input 2-RDM. For example dispersion interactions.

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Sum rule and the normalization condition are satisfied

$$\sum_{q} \Gamma^{ERPA}_{pqrq}(\gamma, \tilde{\Gamma}) = (N-1)\, n_p \delta_{pr}$$

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the reconstructed 2-RDM does not modify 1-RDM

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the reconstructed 2-RDM does not modify 1-RDM

but N-representability conditions (e.g. symmetry rules) are violated.

H_2 test case

What is the error introduced by ERPA equations if exact 1,2-RDM's are used?

$$\Gamma^{ERPA}(\Gamma^{exact}, \gamma^{exact}) \neq \Gamma^{exact}$$

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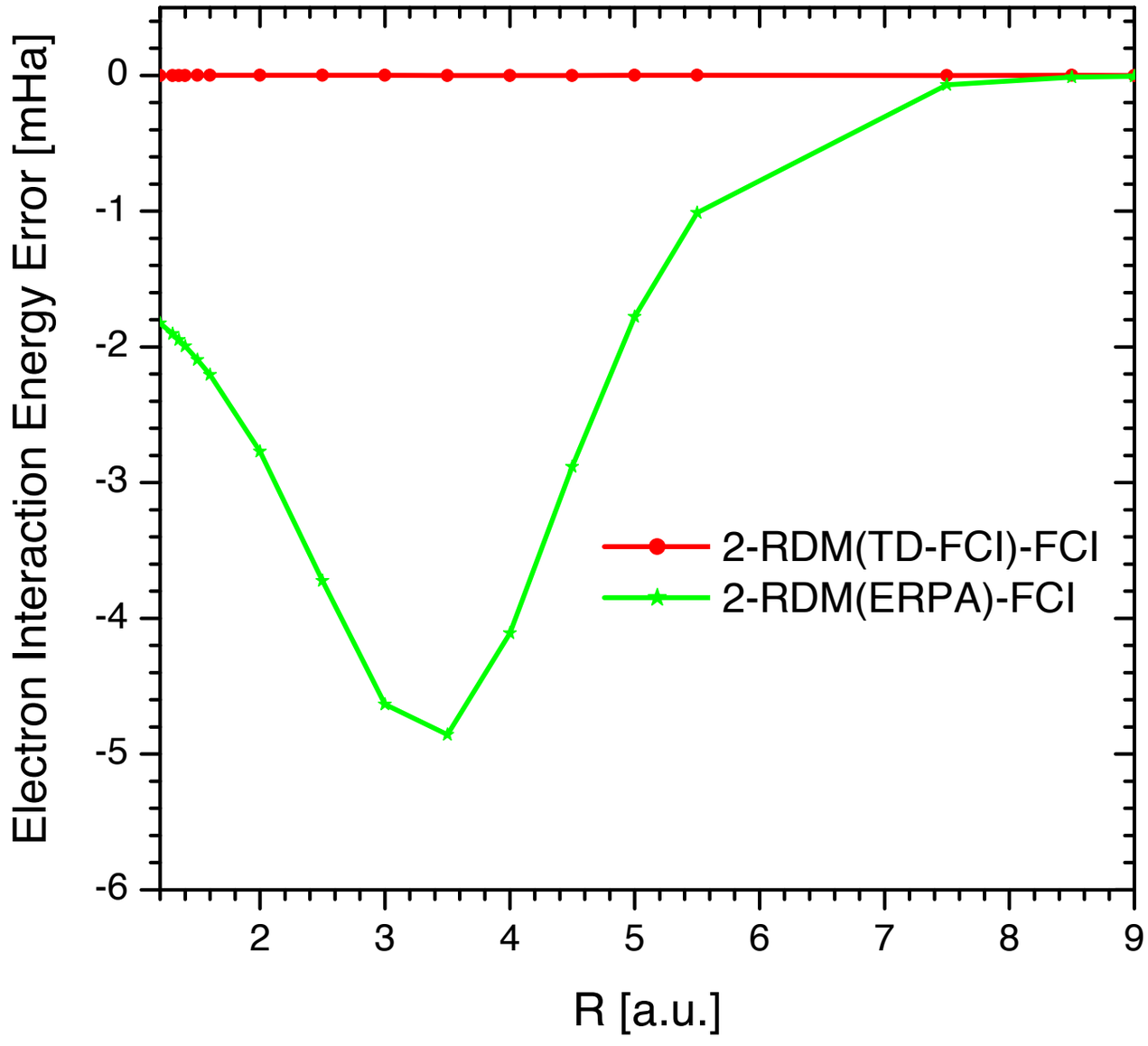

2-RDM(ERPA)-FCI: ERPA equations solved for the exact (FCI) 1- and 2-RDM's.

H_2 test case

Use Hartree-Fock 1- and 2-RDM's in ERPA equations

$$\mathcal{A} = \mathcal{A}(\gamma^{HF}, \Gamma^{HF})$$
$$\mathcal{B} = \mathcal{B}(\gamma^{HF}, \Gamma^{HF}) \quad \Rightarrow \quad \Gamma^{ERPA}$$

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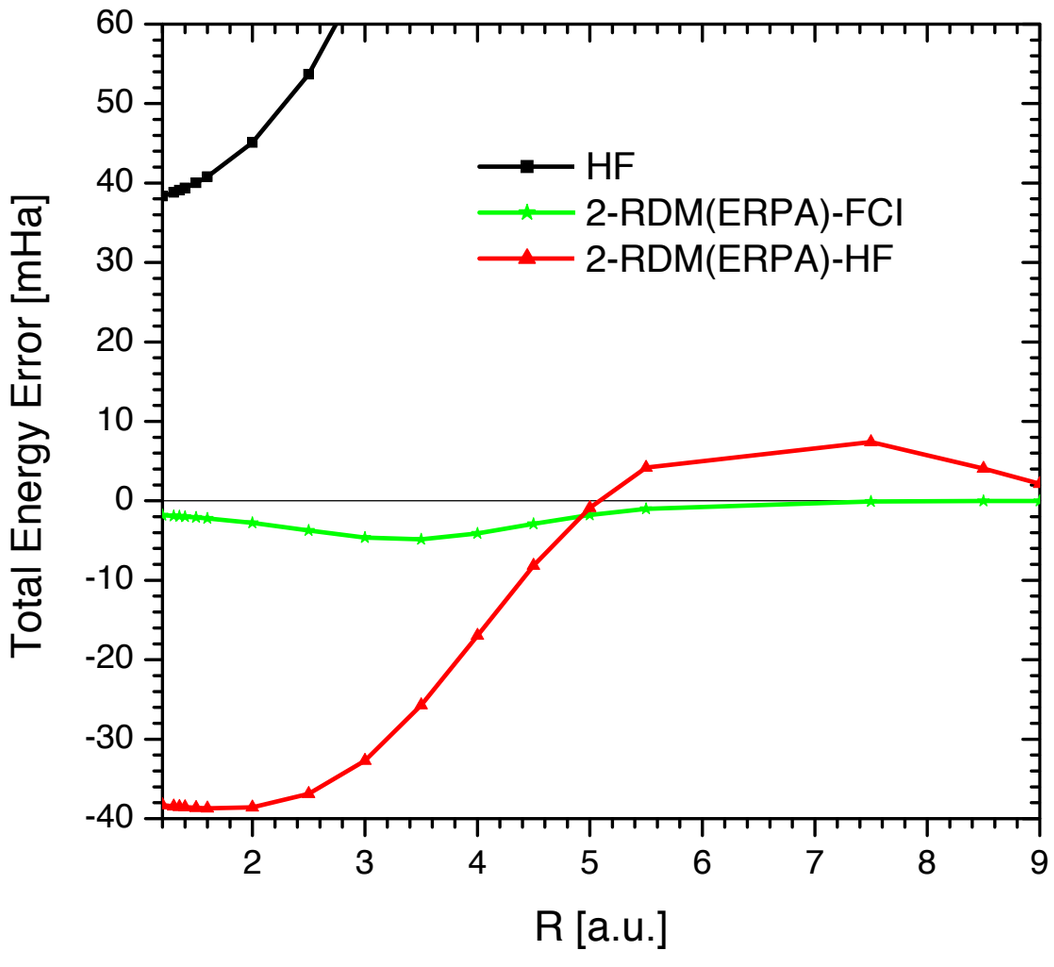

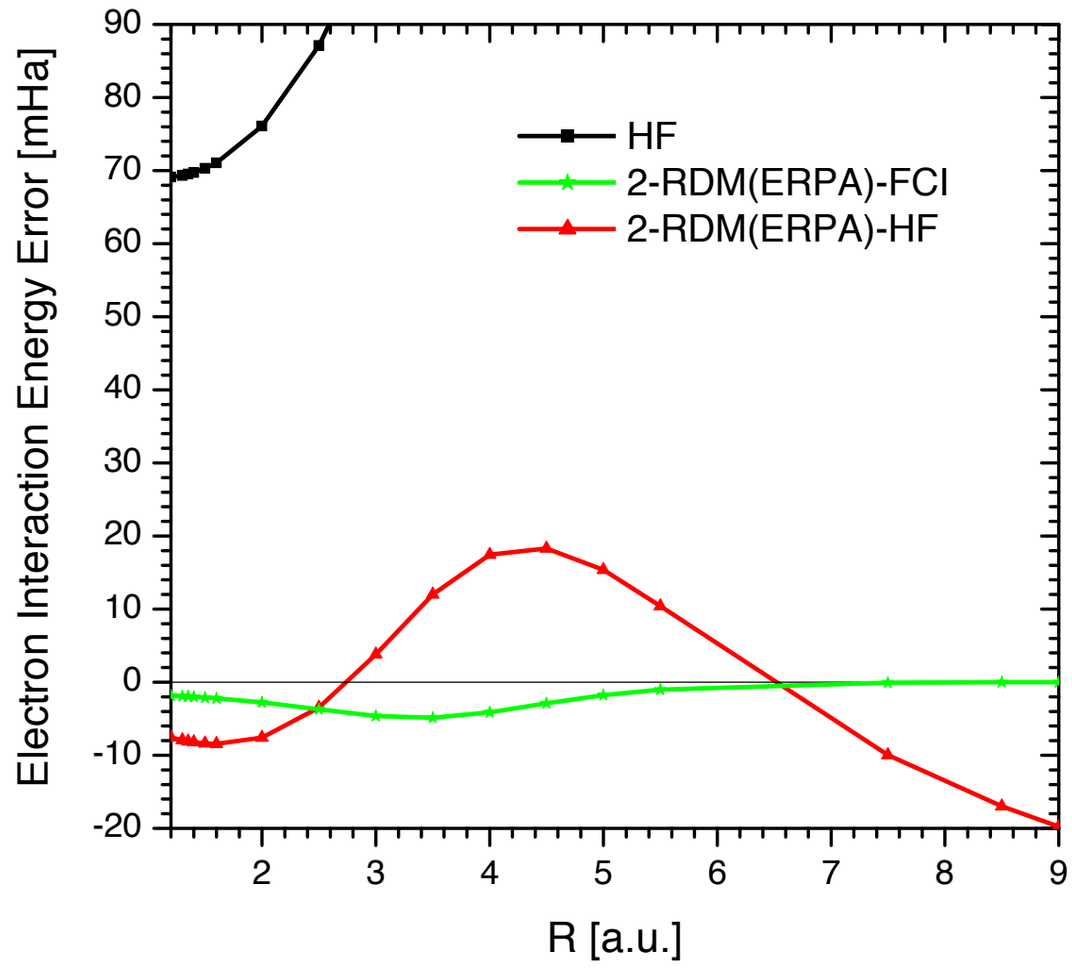

2-RDM(ERPA)-HF: ERPA equations solved for the HF 1- and 2-RDM's

$$E_{one} = E_{one}[\gamma^{HF}]$$

$$E_{ee} = E_{ee}[\Gamma^{ERPA}]$$

BB kernel

Use of BB functional gives rise to a BB kernel in TD-DMFT

$$E_{ee}^{BB} = \frac{1}{2}\sum_{pq} n_p n_q \langle pq|pq\rangle - \frac{1}{2}\sum_{pq}\sqrt{n_p n_q}\,\langle pq|pq\rangle$$

M. A. Buijse and E. J. Baerends, *Mol. Phys*. **100**, 401 (2002).

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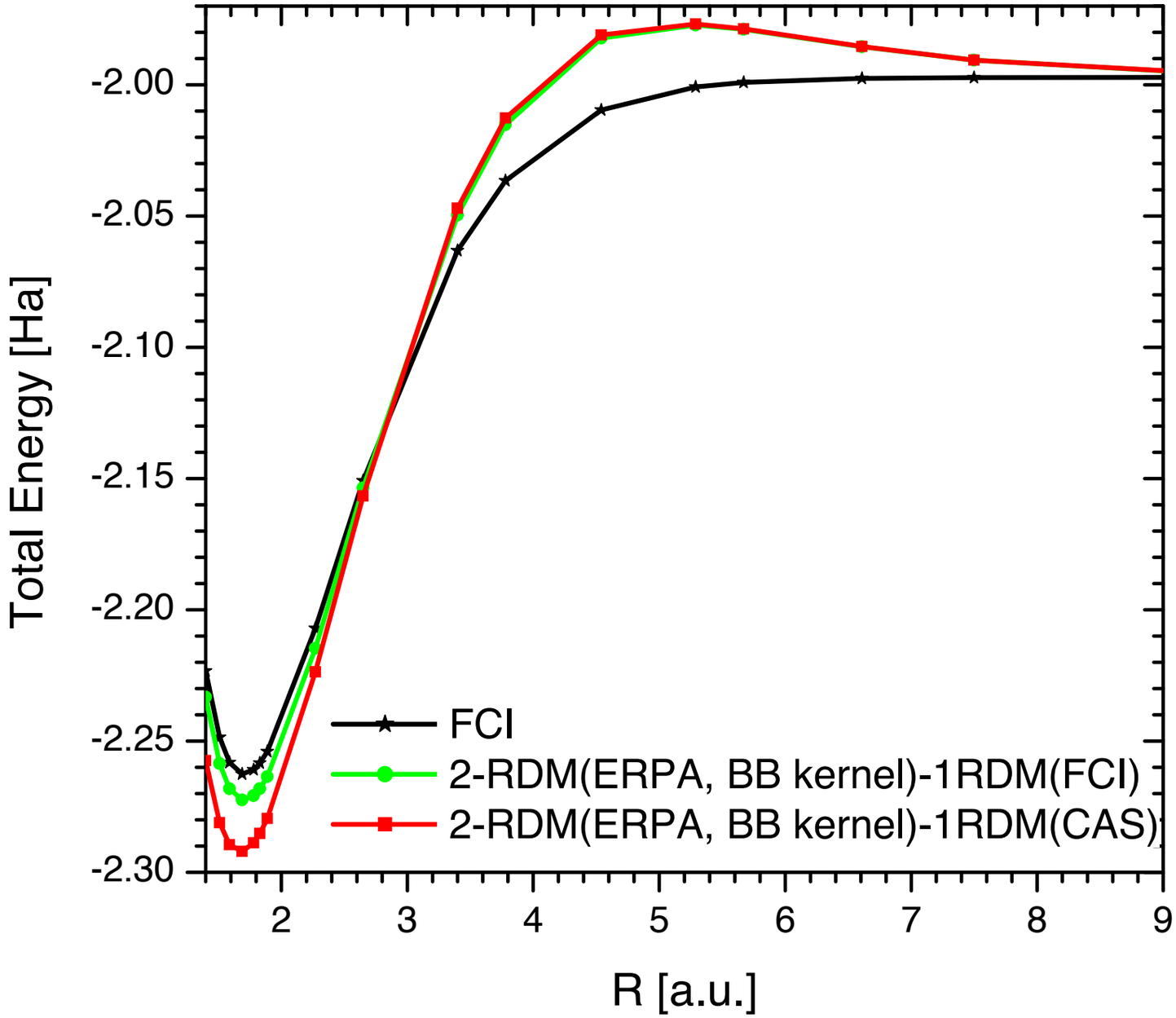
ERPA (=TD-DMFT) equations will be solved with accurate 1-RDM and BB 2-RDM

$$\left.\begin{aligned}\mathcal{A} &= \mathcal{A}(\gamma^{FCI}, \Gamma^{BB}) \\ \mathcal{B} &= \mathcal{B}(\gamma^{FCI}, \Gamma^{BB})\end{aligned}\right\} \Rightarrow \Gamma^{ERPA}$$

$$\Gamma^{BB}_{pqrs} = n_p n_q \delta_{pr}\delta_{qs} - \sqrt{n_p n_q}\delta_{ps}\delta_{qr}$$

H_4 linear chain dissociation

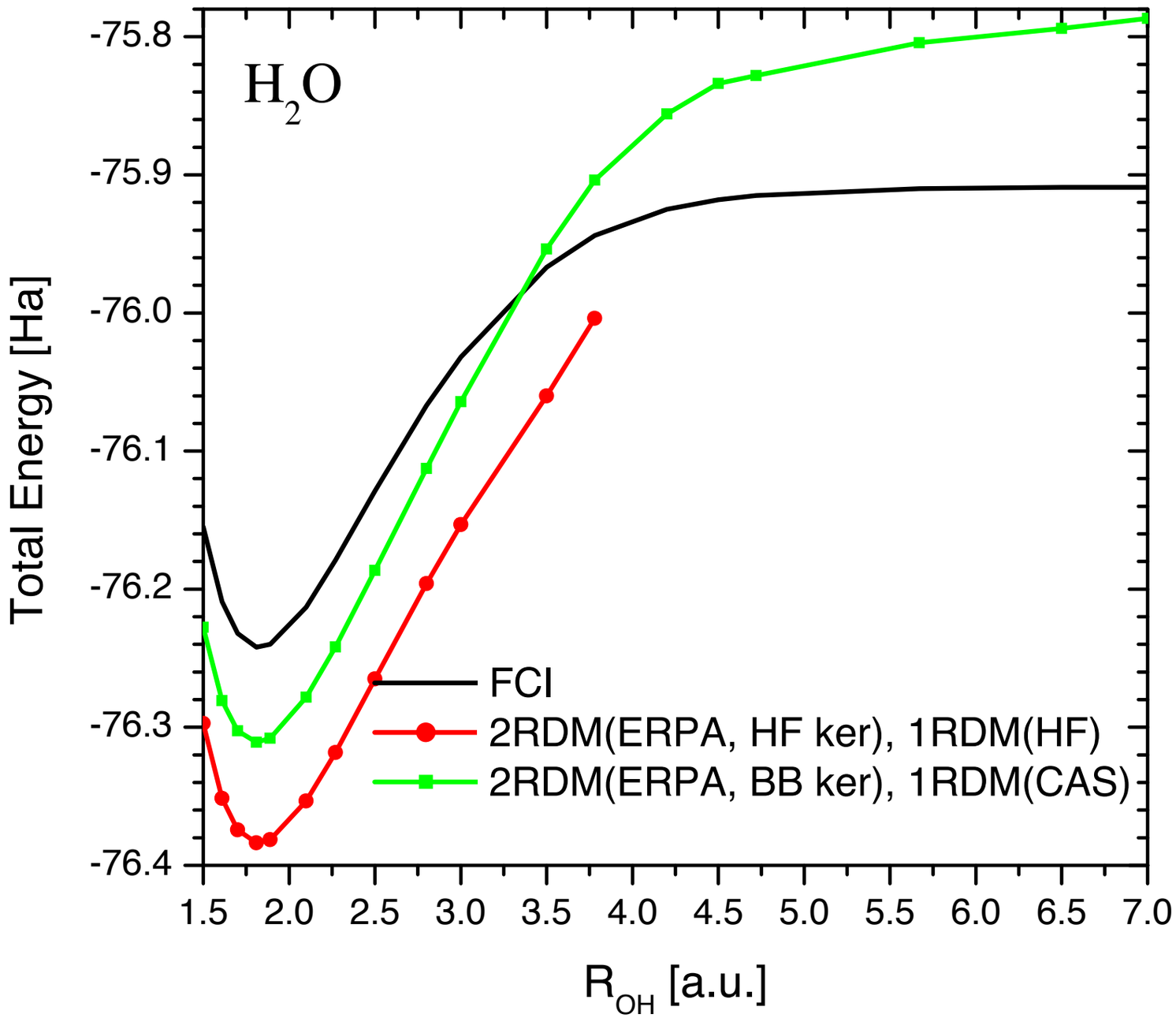
FCI or CAS 1-RDM, BB kernel in ERPA equations



$$E_{one} = E_{one}[\gamma^{FCI}]$$

$$E_{ee} = E_{ee}[\Gamma^{ERPA}]$$

H_2O symmetric (both O-H bonds) dissociation



Part 3 - conclusions

The naive reconstruction of the full 2-RDM from 1-RDM and approximate transition density matrices from ERPA

$$\mathcal{A} = \mathcal{A}(\gamma, \tilde{\Gamma})$$

$$\mathcal{B} = \mathcal{B}(\gamma, \tilde{\Gamma})$$

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$$\begin{aligned} \forall_{p>q} \quad & \gamma^{0\nu}_{qp} = (n_q - n_p) Y^\nu_{pq} \\ \forall_{p<q} \quad & \gamma^{0\nu}_{qp} = (n_p - n_q) X^\nu_{qp} \\ \forall_{p} \quad & \gamma^{0\nu}_{pp} = 0 \end{aligned}$$

$$\Gamma_{pqrs} = \gamma_{pr}\gamma_{qs} + \sum_{\nu \neq 0} \gamma^{0\nu}_{pr}\gamma^{\nu 0}_{qs} - \gamma_{qr}\delta_{ps}$$

Part 3 - conclusions

The naive reconstruction of the full 2-RDM from 1-RDM and approximate transition density matrices from ERPA

$$\mathcal{A} = \mathcal{A}(\gamma, \tilde{\Gamma})$$

$$\mathcal{B} = \mathcal{B}(\gamma, \tilde{\Gamma})$$

$$\begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{B} & \mathcal{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^\nu \\ \mathbf{Y}^\nu \end{pmatrix} = \omega_\nu \begin{pmatrix} -\mathcal{N} & \mathbf{0} \\ \mathbf{0} & \mathcal{N} \end{pmatrix} \begin{pmatrix} \mathbf{X}^\nu \\ \mathbf{Y}^\nu \end{pmatrix}$$

$$\begin{aligned} \forall_{p>q} \quad & \gamma^{0\nu}_{qp} = (n_q - n_p) Y^\nu_{pq} \\ \forall_{p<q} \quad & \gamma^{0\nu}_{qp} = (n_p - n_q) X^\nu_{qp} \\ \forall_{p} \quad & \gamma^{0\nu}_{pp} = 0 \end{aligned}$$

$$\Gamma_{pqrs} = \gamma_{pr}\gamma_{qs} + \sum_{\nu \neq 0} \gamma^{0\nu}_{pr}\gamma^{\nu 0}_{qs} - \gamma_{qr}\delta_{ps}$$

... does not work with approximate kernels (2-RDM's) used in ERPA equations.

Part 4

Employing Adiabatic Connection construction, Multireference Wavefunction gets in.

Employing the Adiabatic Connection (AC) formalism together with the ERPA equations results in the (dynamic) Electron Correlation expression for the Multireference Wavefunction

Multireference methods

Multireference methods

- A multireference wavefunction is assumed in a form of a linear combination of at least two Slater determinant.

- The long-range electron correlation (static correlation), responsible i.g. for correct description of bond dissociation, is already accounted for by the form of a wavefunction.

Multireference methods

- A multireference wavefunction is assumed in a form of a linear combination of at least two Slater determinant.

- The long-range electron correlation (static correlation), responsible i.g. for correct description of bond dissociation, is already accounted for by the form of a wavefunction.

- The missing part of (mostly dynamic) correlation is included via:
  - excitation of electrons to virtual orbitals (configuration interaction CI methods)
  - applying perturbative corrections (e.g. CASPT2, NEVPT2 methods)
  - **adiabatic connection formula**

Group Product Function Ansatz in the second quantization

- We consider states given as

$$|\Psi\rangle = \prod_I \hat{\psi}_I^\dagger \, |vac\rangle$$

a group-creating operator creates multireference N_I-electron state

$$\hat{\psi}_I^\dagger = \sum_{\mathcal{Q}} D_{\mathcal{Q}}^I \; \hat{a}_{q_1}^\dagger \hat{a}_{q_2}^\dagger \ldots \hat{a}_{q_{N_I}}^\dagger$$

$$q_1, q_2, \ldots, q_{N_I} \in I$$

- Subspaces of orbitals (forming groups) are disjoint

$$I \cap J = \emptyset$$

E. Rosta and P. Surjan, *J. Chem. Phys.* **116**, 878 (2002).

Group Product Function - Special Cases

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Hartree-Fock approximation: one-electron groups

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Generalized Valence Bond or APSG: two-electron groups (electron pairs)

$$GVB:$$

$$\psi_I = \psi_I(x_1, x_2)$$

$$I = \{\varphi_{I_1}, \varphi_{I_2},\} \quad \text{- each group contains only two orbitals}$$

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$$I = \{\varphi_{I_1}, \varphi_{I_2},\} \quad \text{- each group contains only two orbitals}$$

Multireference wavefunctions (CASSCF, DMRG)

$$MCSCF,\ CASSCF:$$

$$I_1 = \text{inactive orbitals}$$

$$I_2 = \text{active orbitals}$$

$$I_3 = \text{secondary (virtual) orbitals}$$

Correlation Energy

- The expectation value of the electronic energy

$$E_{\mathrm{Ref}} = \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle = \sum_{I} \langle \psi_I | \sum_{i=1}^{N_I} \hat{h}(\mathbf{x}_i) + \sum_{i<j}^{N_I} r_{ij}^{-1} | \psi_I \rangle + \sum_{I>J} E_{Coul-Exch}^{IJ}$$

where

$$E_{Coul-Exch}^{IJ} = \int\int \frac{\rho_I(\mathbf{x}_1)\rho_J(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 - \int\int \frac{\gamma_I(\mathbf{x}_1,\mathbf{x}_2)\gamma_J(\mathbf{x}_2,\mathbf{x}_1)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2$$

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- Correlation energy is defined with respect to the exact ground state value

$$E_{corr} \equiv E_0 - E_{\mathrm{Ref}}$$

Schrödinger Equations for Group Wavefunctions

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- A group function satisfies the equation

$$\hat{H}_I \psi_I = E_I \psi_I$$

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$$\hat{H}_I \psi_I = E_I \psi_I$$

$$\hat{H}_I = \sum_{pq \in I} h_{pq}^{eff} \; \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs \in I} \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_p \, \langle rs|pq \rangle$$

$$\forall_{pq \in I} \quad h_{pq}^{eff} = h_{pq} + \left\langle p \middle| \hat{v}_{HX}^I \middle| q \right\rangle \quad ,$$

$$\left\langle p \middle| \hat{v}_{HX}^I \middle| q \right\rangle = \sum_{J \neq I} \sum_{r \in J} n_r \left[\langle pr|qr \rangle - \langle pr|rq \rangle \right]$$

Electrons in a given group are embedded in the field of electrons of other groups and interact with them in averaged (SCF) manner.

Adiabatic Connection (AC) formula for the Correlation Energy

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- A group product wavefunction is an eigenfunction of the 0th-order Hamiltonian

$$\hat{H}^{(0)} = \sum_{I} \hat{H}_I$$

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- A group product wavefunction is an eigenfunction of the 0th-order Hamiltonian

$$\hat{H}^{(0)} = \sum_I \hat{H}_I$$

- Define the adiabatic connection Hamiltonian

$$\hat{H}^{\alpha} = \hat{H}^{(0)} + \alpha \hat{H}'$$

$$\hat{H}' = \hat{H} - \hat{H}^{(0)}$$

$$\hat{H}^{\alpha} \Psi_{\nu}^{\alpha} = E_{\nu}^{\alpha} \Psi_{\nu}^{\alpha}$$

Adiabatic Connection (AC) formula for the Correlation Energy

Adiabatic Connection (AC) formula for the Correlation Energy

- The coupling parameter switches between no-group-correlation and full correlation

$$\hat{H}^{\alpha=0} = \hat{H}^{(0)}, \quad \Psi_0^{\alpha=0} = \Psi, \quad E_0^{\alpha=0} = \sum_I E_I$$

$$\hat{H}^{\alpha=1} = \hat{H}, \quad \Psi_0^{\alpha=1} = \Psi_0, \quad E_0^{\alpha=1} = E_0$$

Adiabatic Connection (AC) formula for the Correlation Energy

- From the Hellmann-Feynman theorem

$$\frac{\partial E_0^\alpha}{\partial \alpha} = \left\langle \Psi_0^\alpha \middle| \hat{H}' \middle| \Psi_0^\alpha \right\rangle$$

- Integration of the left hand side yields

$$\begin{aligned}\int_0^1 \frac{\partial E_0^\alpha}{\partial \alpha} d\alpha &= E_0 - \sum_I E_I \\ &= E_0 - E_{Ref} - \frac{1}{2} \sum_I \sum_{p \in I} \sum_{J \neq I} \sum_{q \in J} n_p n_q \left[\langle pq|pq\rangle - \langle pq|qp\rangle \right]\end{aligned}$$

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$$= E_0 - E_{Ref} - \frac{1}{2} \sum_I \sum_{p \in I} \sum_{J \neq I} \sum_{q \in J} n_p n_q \left[\langle pq|pq \rangle - \langle pq|qp \rangle \right]$$

$$E_{corr} = \int_0^1 \left\langle \Psi_0^\alpha \middle| \hat{H}' \middle| \Psi_0^\alpha \right\rangle d\alpha + \frac{1}{2} \sum_I \sum_{p \in I} \sum_{J \neq I} \sum_{q \in J} n_p n_q \left[\langle pq|pq \rangle - \langle pq|qp \rangle \right]$$

$$= \int_0^1 \left\langle \Psi_0^\alpha \middle| \hat{H}' \middle| \Psi_0^\alpha \right\rangle d\alpha - \int_0^1 \left\langle \Psi \middle| \hat{H}' \middle| \Psi \right\rangle d\alpha \quad .$$

Adiabatic Connection (AC) formula for the Correlation Energy

Use the exact relation

$$\Gamma^{\alpha}_{pqrs} = \gamma^{\alpha}_{pr}\gamma^{\alpha}_{qs} + \sum_{\nu\neq 0} \gamma^{\alpha,0\nu}_{pr}\gamma^{\alpha,\nu 0}_{qs} - \gamma^{\alpha}_{qr}\delta_{ps}$$

$$\Gamma^{\alpha} = \left\langle \Psi^{\alpha}_{0} \middle| \hat{\Gamma} \middle| \Psi^{\alpha}_{0} \right\rangle$$ two-electron reduced density matrix (2-RDM)

$$\gamma^{\alpha} = \left\langle \Psi^{\alpha}_{0} \middle| \hat{\gamma} \middle| \Psi^{\alpha}_{0} \right\rangle$$ one-electron reduced density matrix (1-RDM)

$$\gamma^{\alpha,0\nu} = \left\langle \Psi^{\alpha}_{0} \middle| \hat{\gamma} \middle| \Psi^{\alpha}_{\nu} \right\rangle$$ transition one-electron RDM

Adiabatic Connection (AC) formula for the Correlation Energy

and employ the assumption

$$\forall_{\alpha\in[0,1]} \quad \gamma^{\alpha}_{pq} = \delta_{pq} n_p$$

Adiabatic Connection (AC) formula for the Correlation Energy

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$$\forall_{\alpha\in[0,1]} \quad \gamma^{\alpha}_{pq} = \delta_{pq} n_p$$

to obtain

$$E^{AC}_{corr} = \int_0^1 W^{\alpha}\, d\alpha$$

$$W^{\alpha} = \frac{1}{2} {\sum_{pqrs}}' \left(\sum_{\nu\neq 0} \gamma^{\alpha,0\nu}_{pr} \gamma^{\alpha,\nu 0}_{qs} + (n_p - 1) n_q \delta_{rq} \delta_{ps} \right) \langle rs|pq\rangle$$

prime indicates that terms corresponding to spinorbitals p, q, r, s belonging to the same group are excluded.

α-Extended Random Phase Approximation (α-ERPA)

$$\begin{pmatrix} \mathcal{A}_\alpha & \mathcal{B}_\alpha \\ \mathcal{B}_\alpha & \mathcal{A}_\alpha \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu^\alpha \\ \mathbf{Y}_\nu^\alpha \end{pmatrix} = \omega_\nu \begin{pmatrix} -\mathcal{N} & \mathbf{0} \\ \mathbf{0} & \mathcal{N} \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu^\alpha \\ \mathbf{Y}_\nu^\alpha \end{pmatrix}$$

$$\mathcal{A}_\alpha = \mathcal{A}_\alpha[\mathbf{h}^\alpha, \mathbf{g}^\alpha, \gamma, \{\mathbf{\Gamma}^I\}]$$

$$\mathcal{B}_\alpha = \mathcal{B}_\alpha[\mathbf{h}^\alpha, \mathbf{g}^\alpha, \gamma, \{\mathbf{\Gamma}^I\}]$$

$$(\mathcal{N})_{pq,rs} = (n_p - n_q)\delta_{pr}\delta_{qs}$$

$$\forall_{p>q} \quad \left[\gamma^{\alpha,0\nu}\right]_{qp} = (n_q - n_p)\left[\mathbf{Y}_\nu^\alpha\right]_{pq}$$

$$\forall_{q>p} \quad \left[\gamma^{\alpha,0\nu}\right]_{qp} = (n_p - n_q)\left[\mathbf{X}_\nu^\alpha\right]_{qp}$$

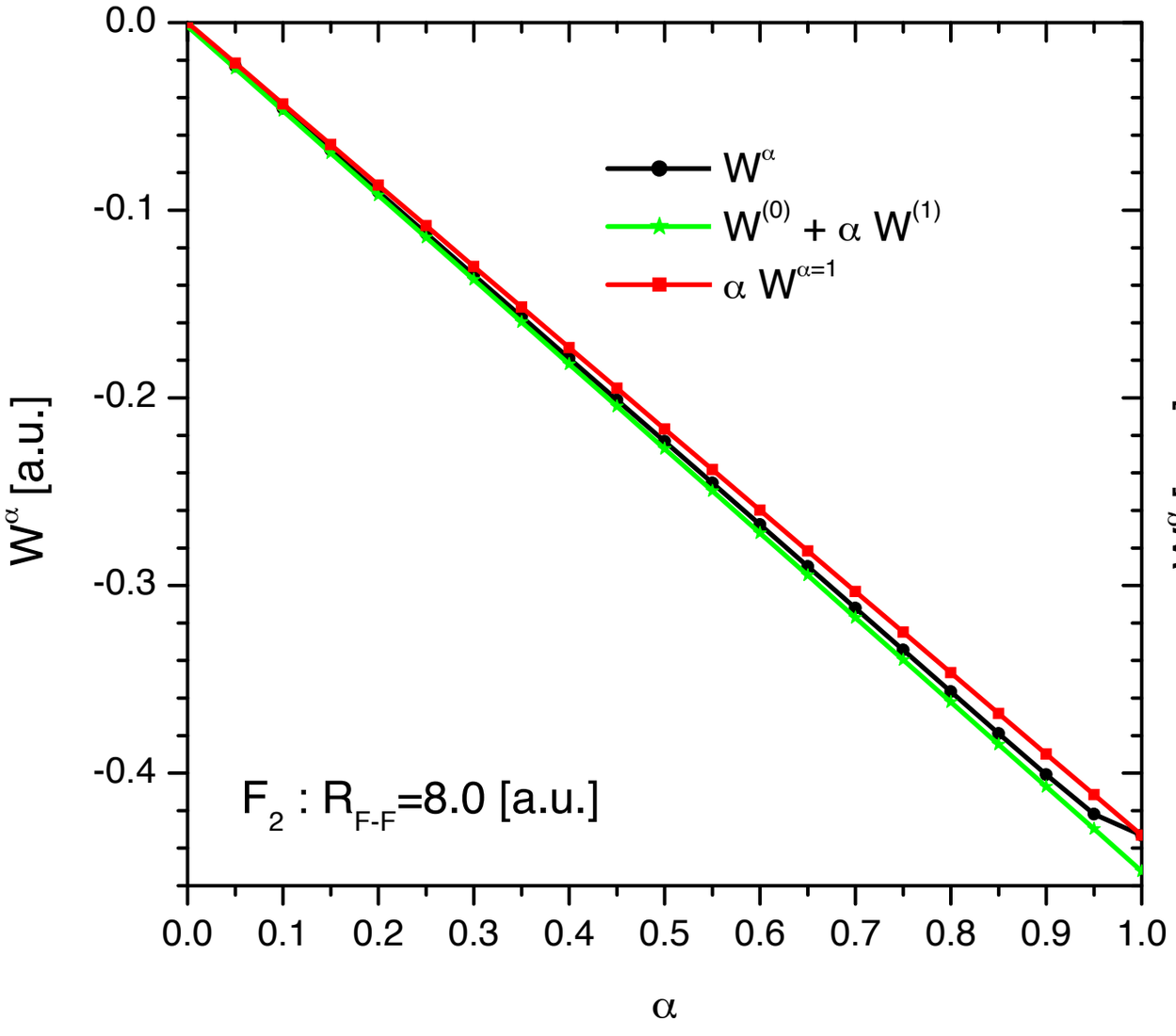
A final spin-summed working form of the AC integrand

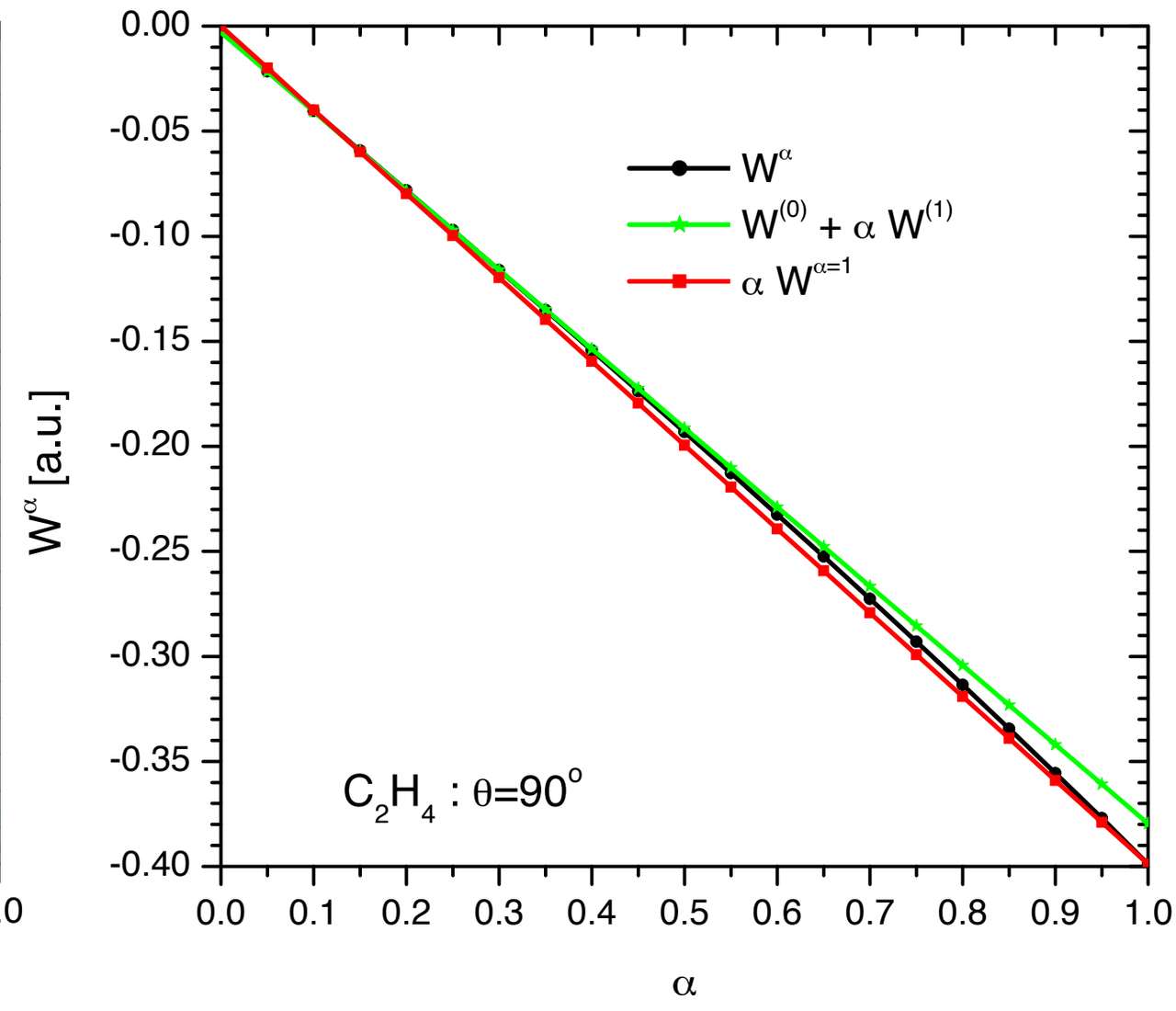
$$W^{\alpha} = 2 \sum_{p>q,r>s}{}' \{(n_p - n_q)(n_r - n_s) \times \sum_{\nu} ([\mathbf{Y}^{\alpha}_{\nu}]_{pq} - [\mathbf{X}^{\alpha}_{\nu}]_{pq})([\mathbf{Y}^{\alpha}_{\nu}]_{rs} - [\mathbf{X}^{\alpha}_{\nu}]_{rs}) - \frac{1}{2}[n_p(1-n_q) + n_q(1-n_p)]\delta_{pr}\delta_{qs}\} \langle pr|qs\rangle$$

$$E^{AC}_{corr} = \int_0^1 W^{\alpha}\, d\alpha$$

K. Pernal, submitted (2017).

High degree of linearity of the coupling constant integrand (**GVB reference**) even for systems with **strongly correlated electrons**





Linear extrapolation from the α=1 limit

- Linear approximation for the AC integrand

$$W^{\alpha} = \alpha W^{\alpha=1}$$

$$E_{corr}^{AC1} = \frac{1}{2} W^{\alpha=1}$$

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- **ERPA equations are solved only once (only 1-RDM and 2-RDM from the reference wavefunction are needed)**

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- **ERPA equations are solved only once (only 1-RDM and 2-RDM from the reference wavefunction are needed)**

- For the GVB (or APSG) reference wavefunction AC1 is identical to the recently proposed ERPA-GVB (ERPA-APSG).

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

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

K. Chatterjee, E. Pastorczak, K. Jawulski, and K. Pernal, *J. Chem. Phys.* **145**, 244111 (2016).

Linear extrapolation from the α=0 limit

- First-order expansion of the AC integrand

$$W^{\alpha} = W^{\alpha=0} + \left.\frac{dW^{\alpha}}{d\alpha}\right|_{\alpha=0} \alpha = W^{(0)} + W^{(1)}\ \alpha$$

$$E_{corr}^{AC0} = W^{(0)} + \frac{1}{2}W^{(1)}$$

Linear extrapolation from the α=0 limit

$$W^{(1)} = \sum_{p>q,r>s}{}' \langle pr|qs\rangle \times \frac{\left(\mathcal{A}^{(1)}+\mathcal{B}^{(1)}\right)_{pq,rs} - a_{pq}\left(\mathcal{A}^{(1)}-\mathcal{B}^{(1)}\right)_{pq,rs}a_{rs}}{\omega^{+}_{pq}+\omega^{+}_{rs}}$$

$$\forall_{\substack{\nu=(pq)\\ p>q\\ p\in I\ q\in I}} \quad \omega^{+}_{\nu} = \frac{\varepsilon_\nu}{(c_p+c_q)^2}$$

$$\varepsilon_\nu = \left[\mathcal{A}^{(0)}+\mathcal{B}^{(0)}\right]_{pq,pq}$$

Linear extrapolation from the α=0 limit

$$W^{(1)} = \sum_{p>q,r>s}{}' \langle pr|qs\rangle \times \frac{\left(\mathcal{A}^{(1)}+\mathcal{B}^{(1)}\right)_{pq,rs} - a_{pq}\left(\mathcal{A}^{(1)}-\mathcal{B}^{(1)}\right)_{pq,rs} a_{rs}}{\omega^{+}_{pq}+\omega^{+}_{rs}}$$

$$\forall_{\substack{\nu=(pq)\\ p>q\\ p\in I\ q\in I}} \quad \omega^{+}_{\nu} = \frac{\varepsilon_\nu}{(c_p+c_q)^2}$$

$$\varepsilon_\nu = \left[\mathcal{A}^{(0)}+\mathcal{B}^{(0)}\right]_{pq,pq}$$

- **No need to solve ERPA equations.**
- **Closed-form expressions.**
- **Correlation energy obtained at MP2 cost!**

GVB reference

$$E^{AC-GVB} = E^{GVB} + \int_0^1 W^{\alpha} d\alpha$$

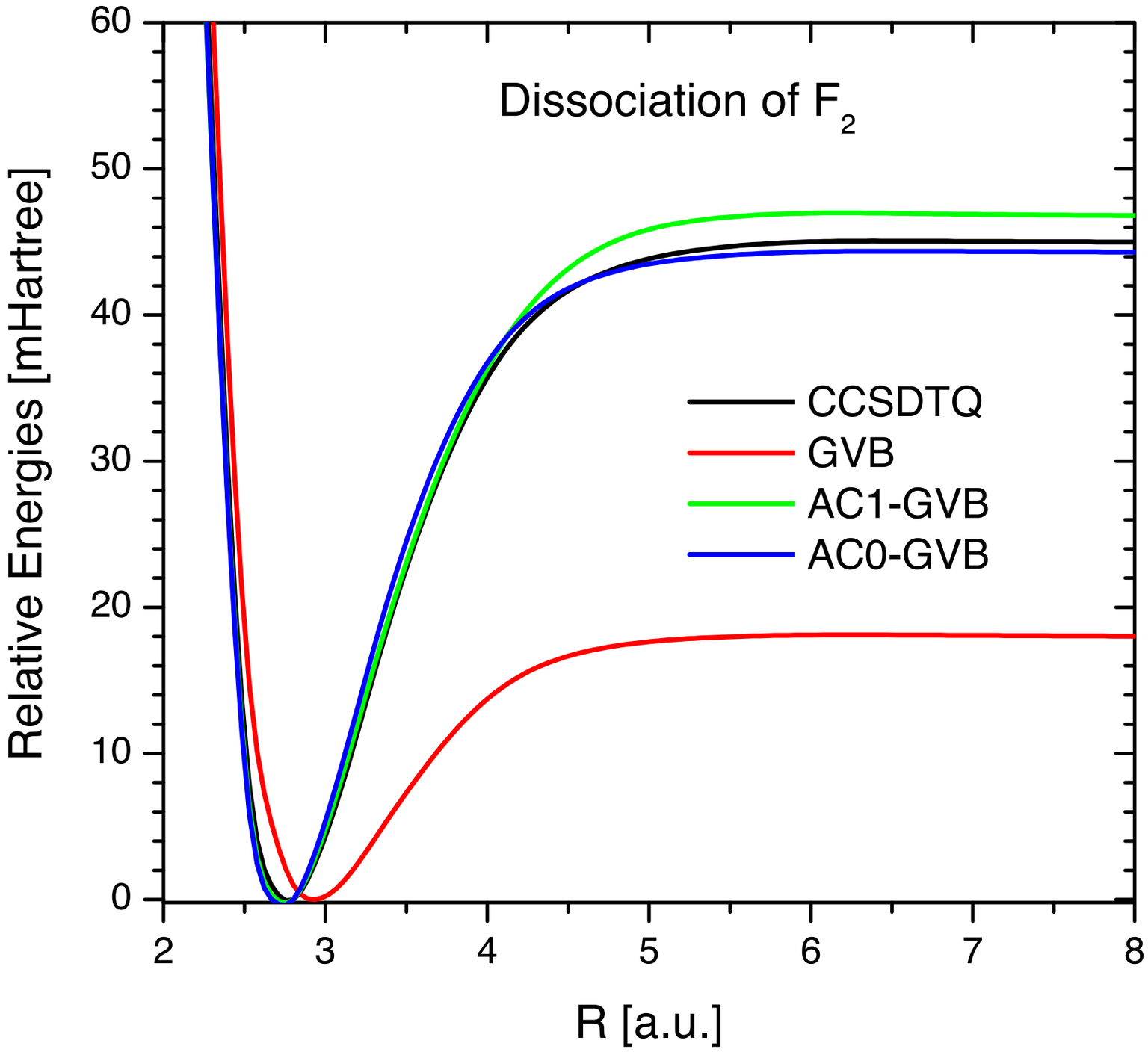
$$E^{AC1-GVB} = E^{GVB} + \frac{1}{2} W^{\alpha=1} = E^{ERPA-GVB}$$

$$E^{AC0-GVB} = E^{GVB} + W^{(0)} + \frac{1}{2} W^{(1)}$$

Molecule	Method	E_{eq}	E_{diss}	ΔE
F_2	Reference	-199.104	-199.059	0.045
$R_{eq} = 2.80$	AC-GVB	-199.071	-199.032	0.040
$R_{diss} = 8.00$	AC0-GVB	-199.080	-199.036	0.044
	AC1-GVB	-199.072	-199.025	0.047
H_2O	Reference	-76.242	-75.909	0.333
$R_{eq} = 1.81$	AC-GVB	-76.227	-75.886	0.341
$R_{diss} = 7.00$	AC0-GVB	-76.234	-75.888	0.346
	AC1-GVB	-76.227	-75.878	0.349
H_8	Reference	-4.495	-4.130	0.365
$R_{eq} = 1.83$	AC-GVB	-4.462	-4.104	0.358
$R_{diss} = 3.40$	AC0-GVB	-4.454	-4.103	0.351
	AC1-GVB	-4.467	-4.101	0.365

Energy values and bond lengths in [a.u.].

Dissociation of F_2 in cc-pVDZ basis set



CCSDTQ results from: M. Musial and R. J. Bartlett, *J. Chem. Phys*. **135**, 044121 (2011).

CASSCF (or DMRG) reference

$$E^{AC1-CASSCF} = E^{CASSCF} + \frac{1}{2} W^{\alpha=1}$$

1. Find CASSCF solution (for assumed spaces of ***active***, ***inactive*** and ***secondary*** orbitals).

2. Solve ERPA equations (only 1- and 2-RDM are needed).

3. Compute correlation energy, which accounts for correlation among ***active***, ***inactive*** and ***secondary*** orbitals.

$$W^{a=1} = 2 \sum_{\substack{p>q \\ r>s}}{}' \{ (n_p - n_q)(n_r - n_s) \sum_{\nu} \left[(Y^{\nu})_{pq} - (X^{\nu})_{qp} \right] \left[(Y^{\nu})_{rs} - (X^{\nu})_{sr} \right]$$
$$- \frac{1}{2} [n_p(1 - n_q) + n_q(1 - n_p)] \delta_{pr} \delta_{qs} \} \langle pr | qs \rangle$$

CASSCF (or DMRG) reference

$$\begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{B} & \mathcal{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^\nu \\ \mathbf{Y}^\nu \end{pmatrix} = \omega_\nu \begin{pmatrix} -\mathcal{N} & \mathbf{0} \\ \mathbf{0} & \mathcal{N} \end{pmatrix} \begin{pmatrix} \mathbf{X}^\nu \\ \mathbf{Y}^\nu \end{pmatrix}$$

$$\mathcal{A} = \mathcal{A}(\gamma^{CAS}, \Gamma^{BB}(\gamma^{CAS}))$$

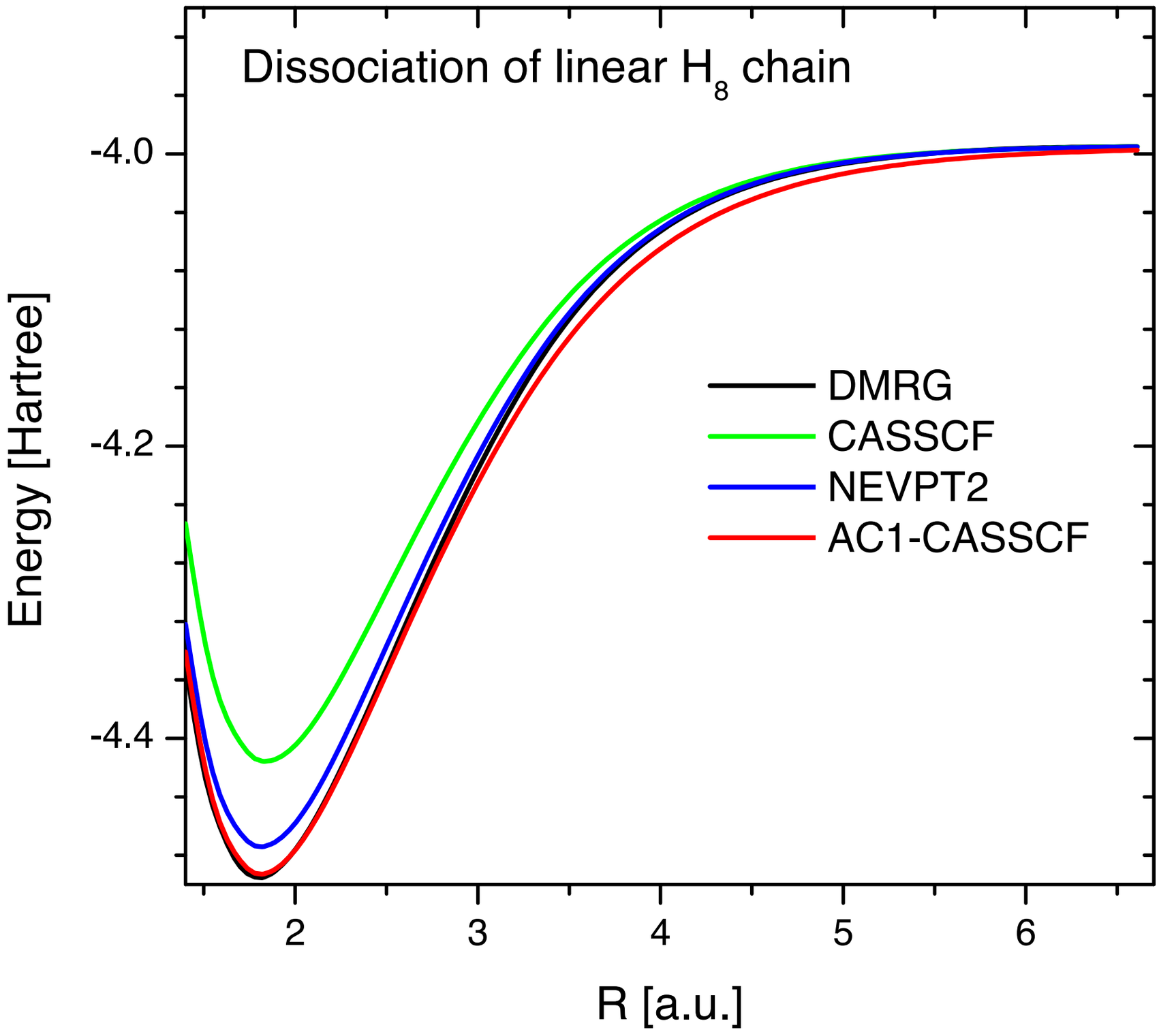
$$\mathcal{B} = \mathcal{B}(\gamma^{CAS}, \Gamma^{BB}(\gamma^{CAS}))$$

ERPA equations have been solved for the CASSCF 1-RDM and 2-RDM approximated by a Buijse-Baerends form

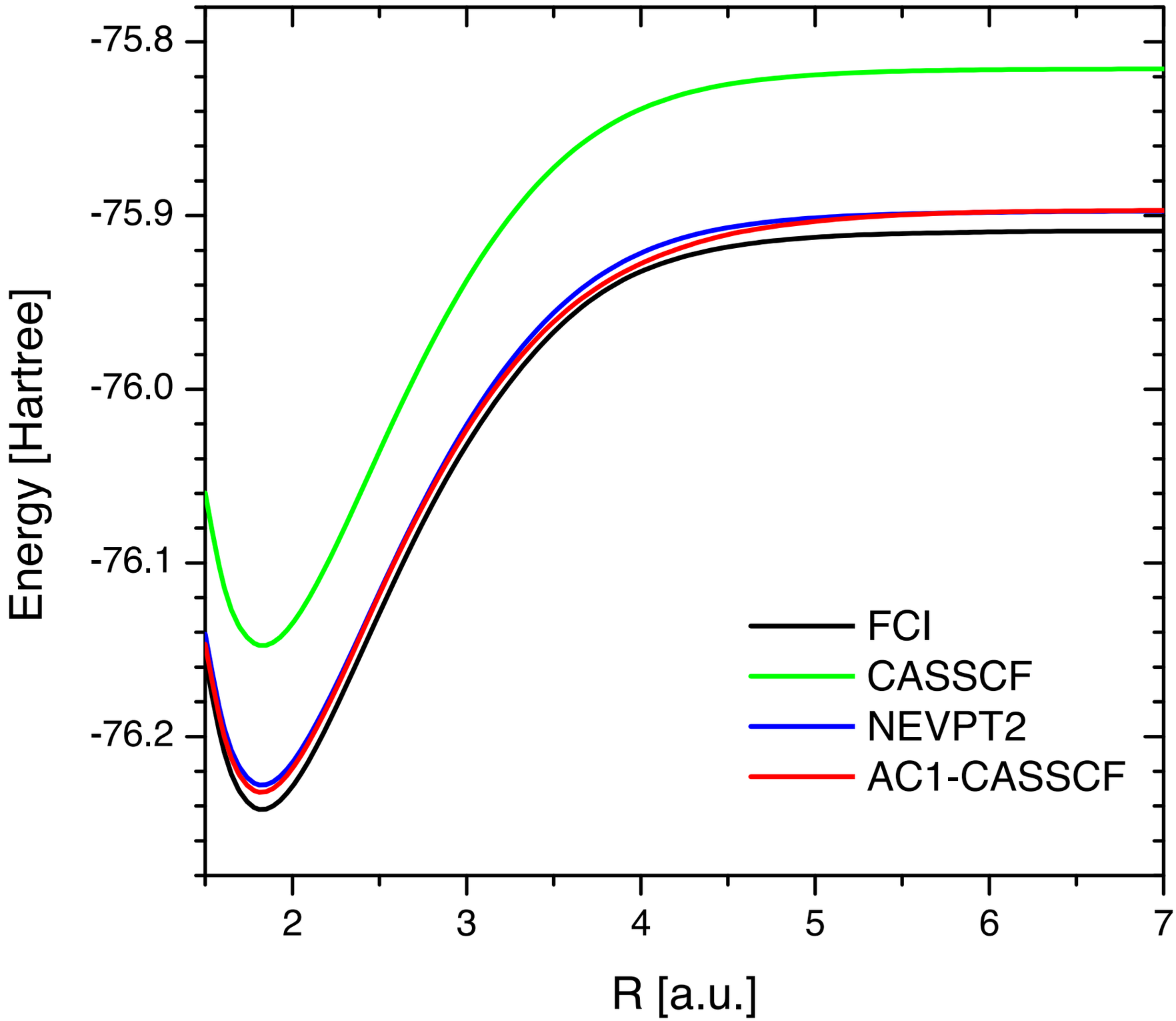
$$\Gamma^{BB}_{pqrs} = n_p n_q \delta_{pr} \delta_{qs} - \sqrt{n_p n_q} \delta_{ps} \delta_{qr}$$

Notice that the correlation energy is determined only by the 1-RDM of the reference wavefunction!

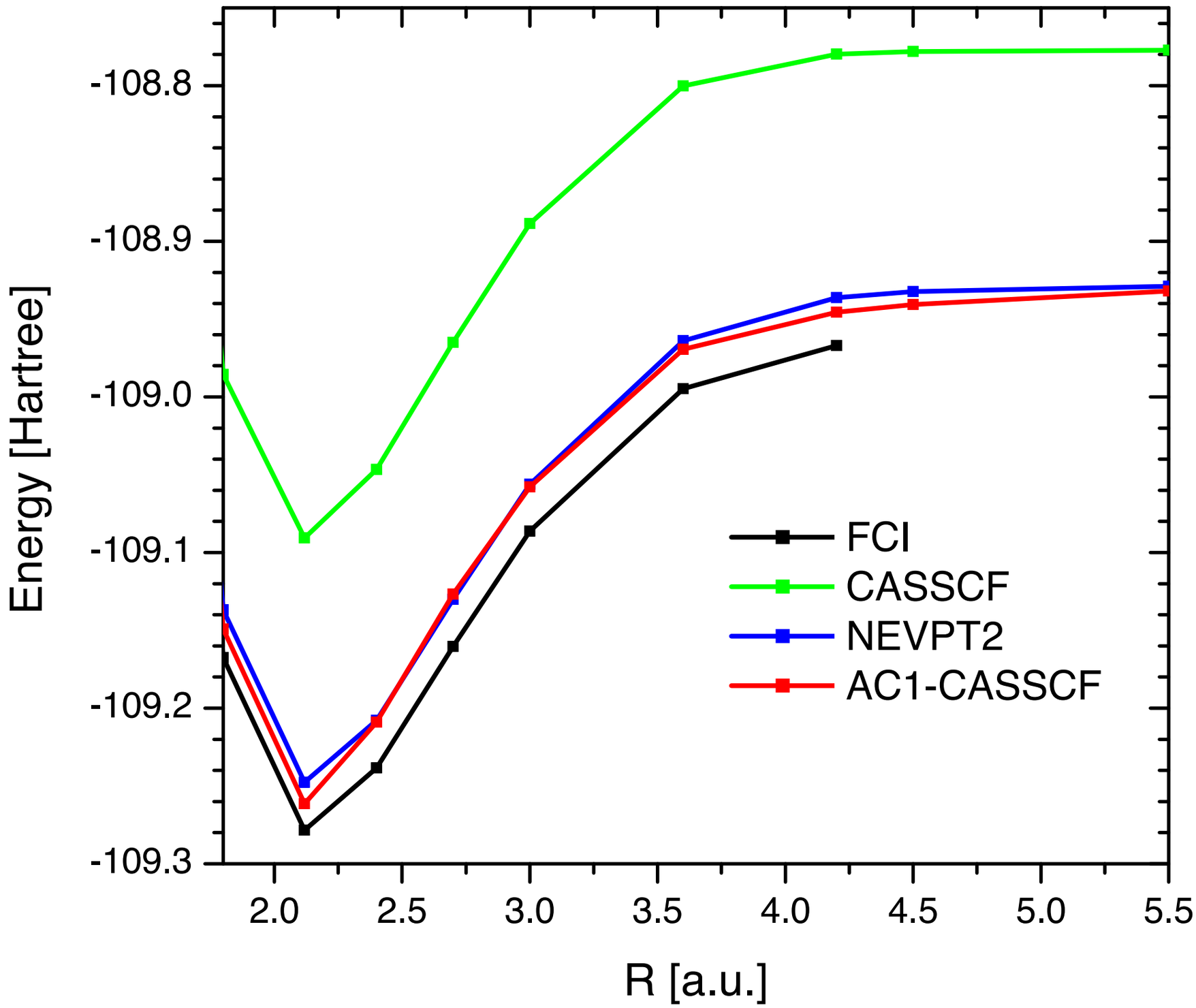
Dissociation of linear H_8 chain in cc-pVDZ basis set
CAS(8,8)



Symmetric dissociation (both OH bonds break) of water in cc-pVDZ basis set, CAS(8,8)



Dissociation of N_2 in cc-pVDZ basis set, CAS(6,6)



Part 4 - conclusions

The adiabatic connection formula together with ERPA equations yields accurate ground state energy for multireference wavefunctions.

Extensions to excited states are straightforward.

For CASSCF or DMRG the method is an attractive alternative (free of the intruder state problem and size-extensive) to the perturbation (PT2) approach.

Part 4 - conclusions

Notice that we have considered partitioning of orbitals space into disjoint subspaces, resulting in partitioning 1- and 2-RDM's as

$$\gamma(x,x') = \gamma^A(x,x') + \gamma^B(x,x') + \gamma^C(x,x') + \dots$$

$$\Gamma = \sum_I \Gamma^I + \sum_{I \neq J} \gamma^I \wedge \gamma^J + \Gamma_{corr}[\{\Gamma^I\}]$$

$$E_{tot} = \sum_I E[\Gamma^I] + \sum_{I \neq J} E_{XC}^{IJ} + E_{corr}[\{\Gamma^I\}]$$

Functionals can be used to describe group energy

$$E[\Gamma^I] = E^{RDMFT}[\gamma^I]$$

$$E[\Gamma^I] = E^{DFT}[\rho^I]$$