Targeting Real chemical accuracy at the EXascale

Acknowledgement

Targeting Real Chemical Accuracy at the Exascale project has received funding from the European Union Horizon 2020 research and innovation programme under Grant Agreement **No. 952165.**

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Correlating electrons via adiabatic connection approach

Łódź April 18-20 2023

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Multireference model: WF is represented as a linear combination of a few Slater determinants of particular importance for a problem under consideration

$$\Psi = \sum_Q D_Q \hat{a}_{q_1}^{\dagger} \hat{a}_{q_2}^{\dagger} \ldots \hat{a}_{q_N}^{\dagger} \left|vac\right\rangle$$

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$$\Psi = \sum_Q D_Q \hat{a}_{q1}^\dagger \hat{a}_{q2}^\dagger \ldots \hat{a}_{qN}^\dagger \left|vac\right\rangle$$

- The energy error is called correlation energy

$$E_{corr} = E_{exact} - E_{ref}$$

$$E_{ref} = \left\langle \Psi \hat{H} \Psi \right\rangle$$

- The concept of electron correlation does not have a sharp definition (multireference WF definitely accounts for some part of correlation).
- Taking into account a structure of the wavefunction we distinguish, in general, between

Dynamic electron correlation: included by allowing excitations to many unoccupied orbitals

Static (non-dynamic) correlation: accounted for by including in the wavefunction expansion nearly degenerate states.

One-electron reduced density matrix (1-RDM)

$$\underline{\gamma(\mathbf{r}_1, \mathbf{r}_1')} = N \int d\sigma \int d\tau_2 ... \int d\tau_N \; \Psi^*(\mathbf{r}_1, \sigma, \tau_2, ..., \tau_N)\Psi(\mathbf{r}_1', \sigma, \tau_2, ..., \tau_N)$$

one-electron reduced function: **one-electron density matrix** γ

1-RDM contains information about electron correlation

Electron correlation (dynamic or static) is manifested in the pattern of natural occupation numbers.

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Natural occupation numbers: eigenvalues of the one-electron reduced density matrix

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

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

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

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Natural occupation numbers are nonnegative and not greater than 1

$$\forall p \quad 0 \le n_p \le 1$$

Natural occupation numbers of nitrogen molecule N_2 as a function of interatomic distance

Single determinantal WF: $\Psi = \hat{a}_1^\dagger \hat{a}_2^\dagger \ldots \hat{a}_{14}^\dagger \left|vac\right\rangle$

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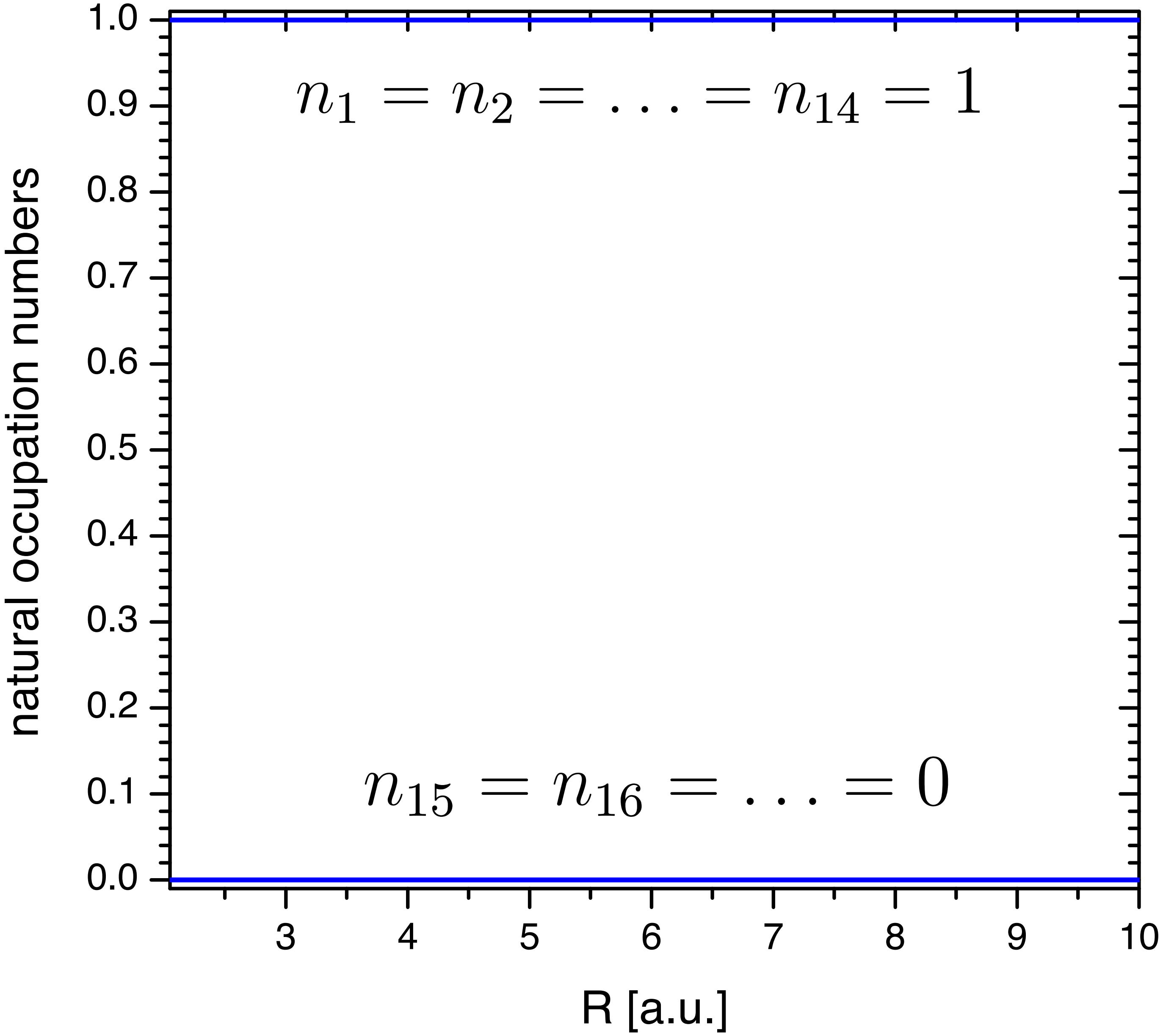

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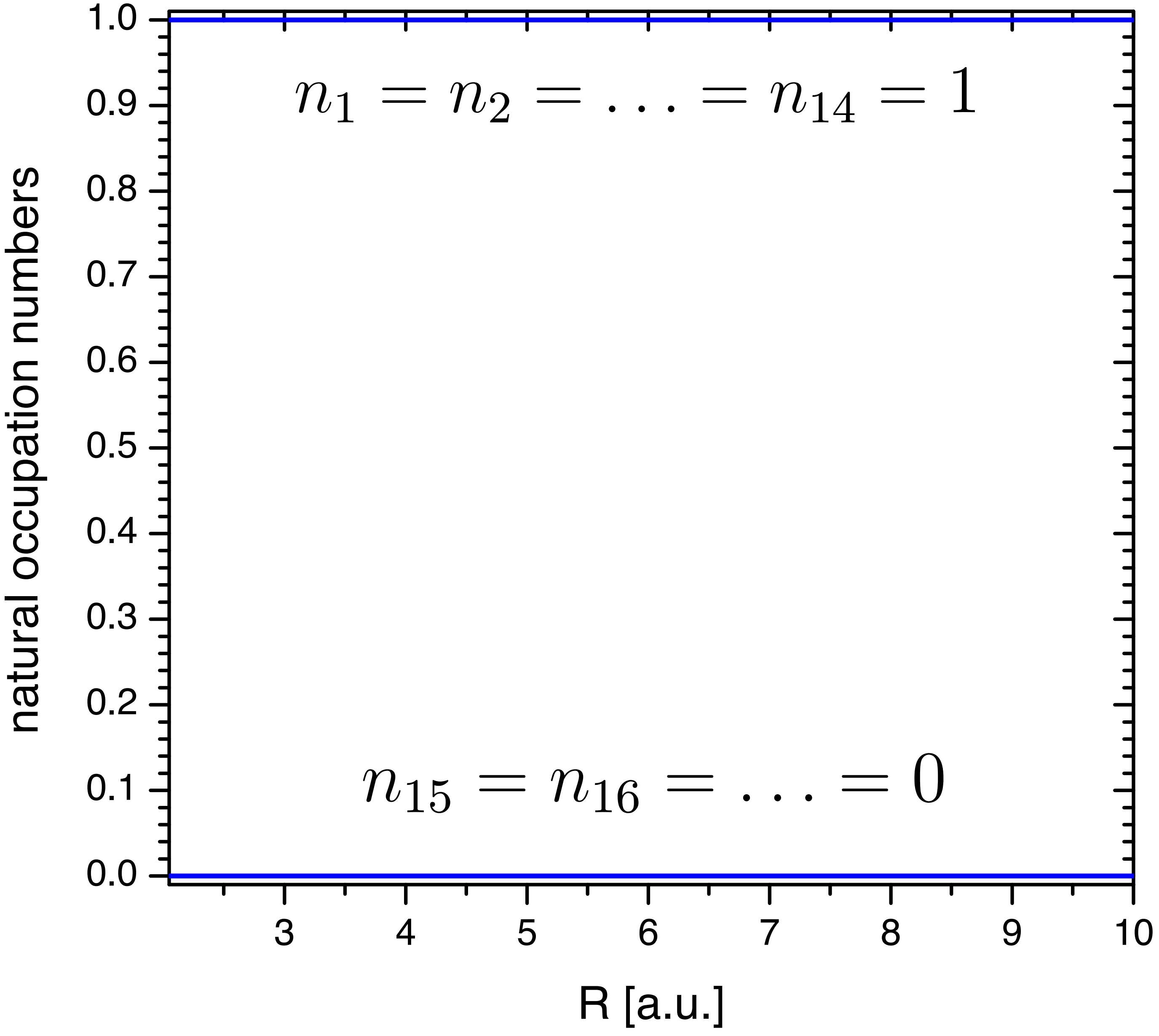


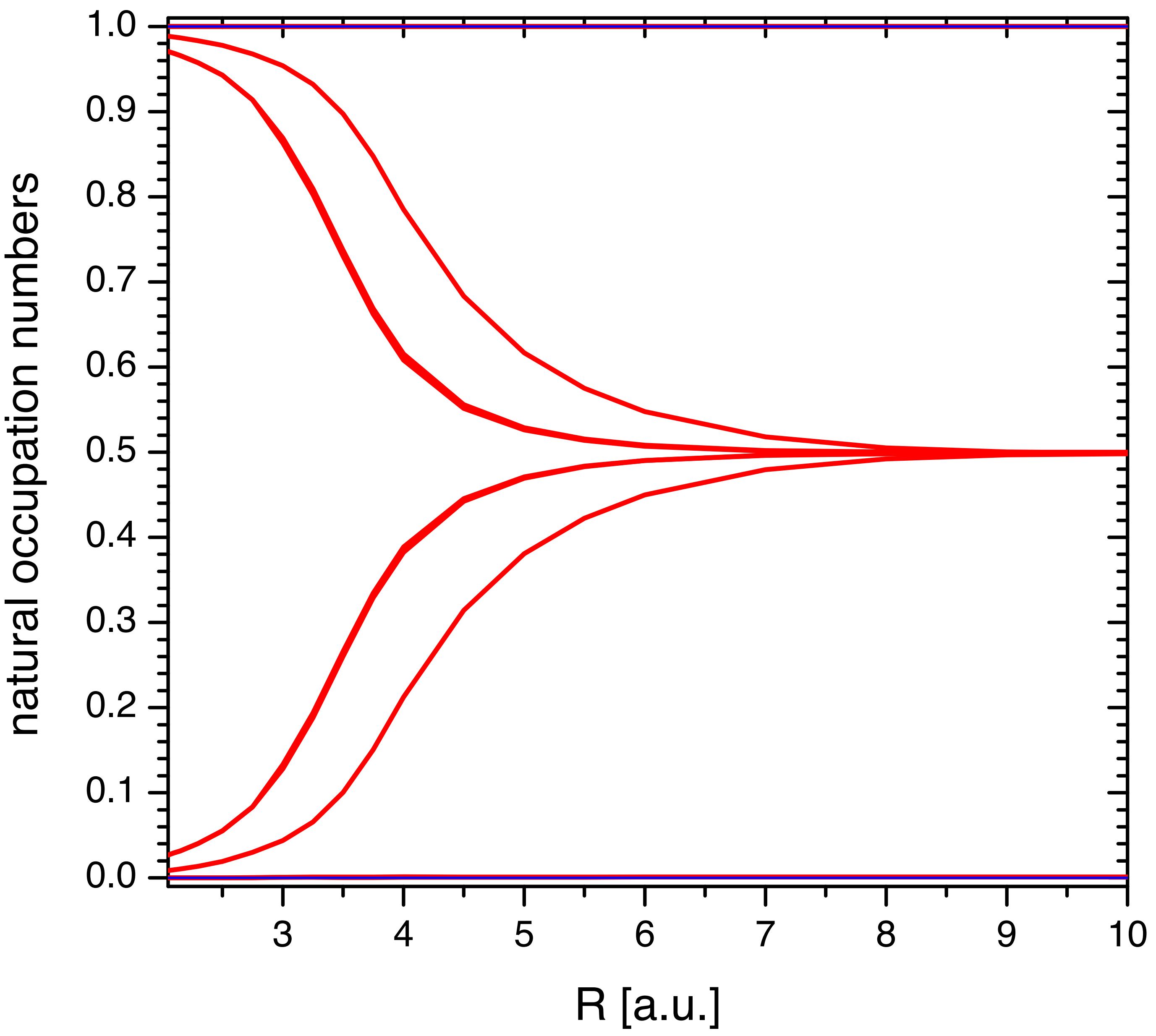
$n_1 = n_2 = \ldots = n_{14} = 1$

$n_{15} = n_{16} = \ldots = 0$

No correlation

Natural occupation numbers of nitrogen molecule N_2 as a function of interatomic distance

Exact (fully correlated) wavefunction



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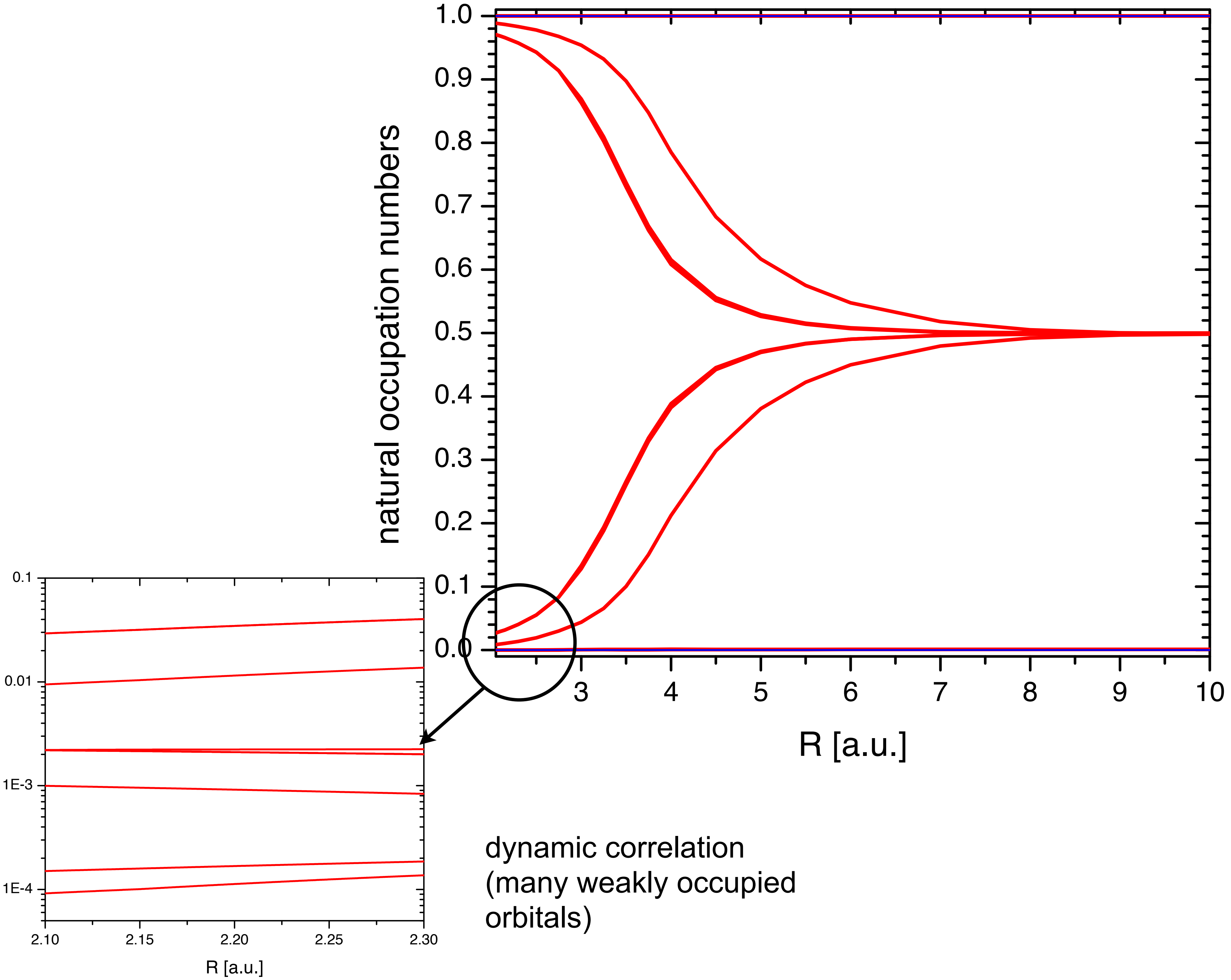

dynamic correlation
(many weakly occupied
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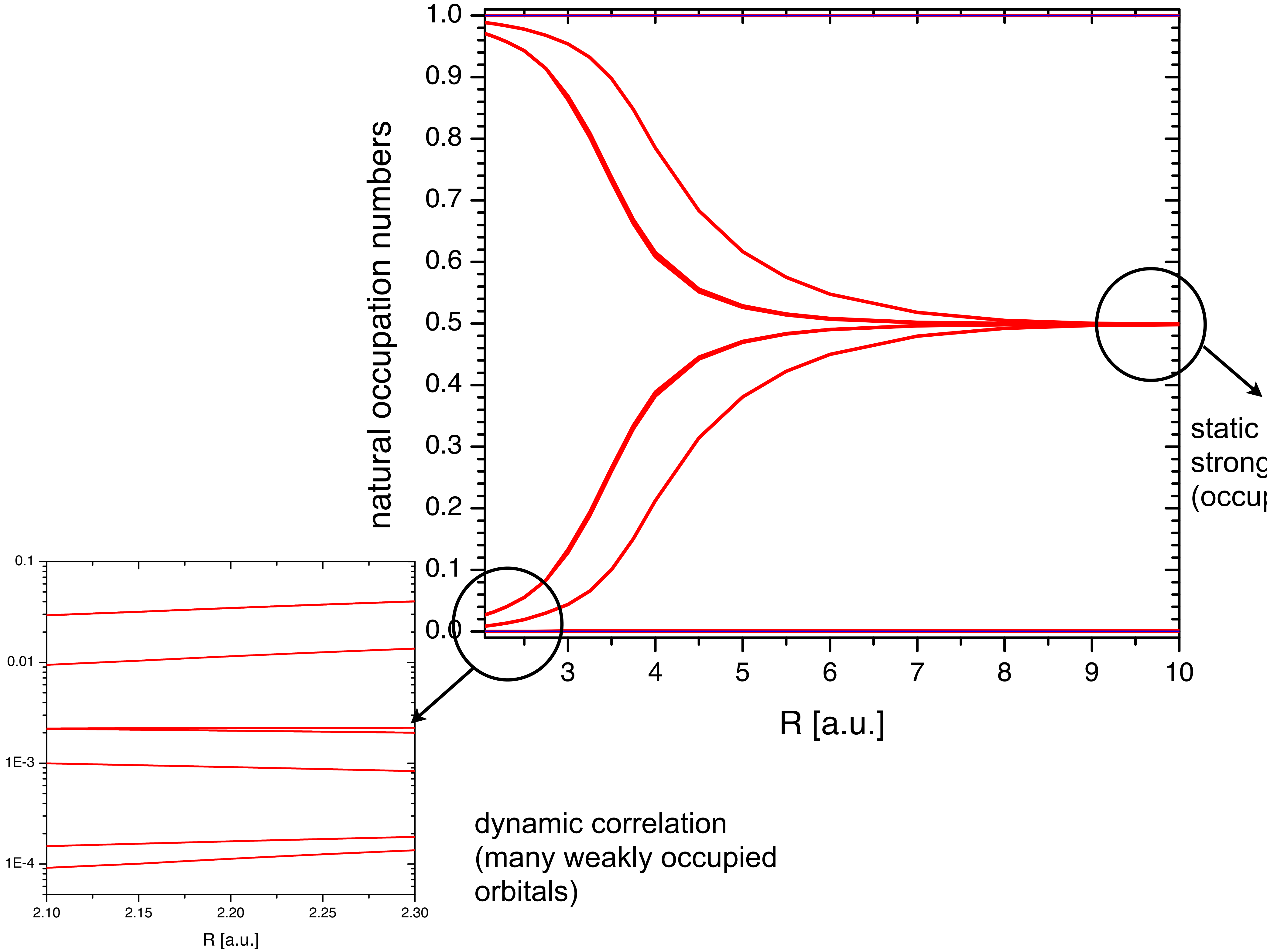

static correlation: six strongly correlated electrons (occupancy = 1/2)

dynamic correlation (many weakly occupied orbitals)

Weak versus strong correlation

$$\Psi = C_0\psi_0 + C_1\psi_1 + C_2\psi_2 + \ldots C_m\psi_m + \ldots$$

$$E_{ref} = \left\langle \Psi \hat{H} \Psi \right\rangle$$

$$E_{corr} = E_{exact} - E_{ref}$$

How to find the correlation correlation energy?

Weak versus strong correlation

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Weak correlation: $|C_0| \gg |C_1|, |C_2|, \ldots$

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Strong correlation can be efficiently captured by multireference wavefunction (MR-WF) models.

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Even with very large *m* the expansion is not long enough (not even DMRG) to retrieve all important correlation.

$$E_{ref} = \left\langle \Psi \hat{H} \Psi \right\rangle$$

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How to find the correlation correlation energy?

Correlation energy from the perturbation theory

- If a Hamiltonian is known for an assumed reference WF, i.e.

$$\hat{H}^{(0)}\Psi_{ref} = E^{(0)}\Psi_{ref}$$

perturbation theory can be applied to recover correlation energy for the perturbation operator

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

$$E_{exact} = E^{(0)} + E^{(1)} + E^{(2)} + \ldots$$

- If

$$\left\langle \Psi_{ref} | \hat{H} | \Psi_{ref} \right\rangle = E^{(0)} + E^{(1)}$$

the correlation energy (or rather a part of it) is obtained as

$$E_{corr} = E^{(2)} + \ldots$$

- Perturbation approaches have been established for single-reference and multireference methods, the examples are

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- Problems of the perturbation methods:

  not general: for each reference WF it may be necessary to figure out a zeroth-order Hamiltonian, which is not unique

  one stops at 2nd-order correction (increasing cost and possible lack of convergence if higher-orders are included)

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- Perturbation approaches designed for multireference WF's suffer from additional problems:

  CASPT2 or NEVPT2 methods become very expensive (3rd- and 4th-order reduced density matrices are needed) when the number of active electron and orbitals increases

  often not accurate enough (2nd-order only)

  corrected energies do not show monotonic convergence to the FCI value with the expansion of the number of active electrons and orbitals

Part 2

General formalism of the adiabatic connection (AC) method

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The adiabatic connection formalism has been already proposed in the framework of DFT as a way of accounting for correlation energy

D. Langreth and J. Perdew, Phys. Rev. B **15**, 2884 (1977)

and together with the Random Phase Approximation has recently led to emergence of a new family of orbital-dependent DF correlation functionals (RPA and its variants)

H. Eshuis, J. Bates, and F. Furche, Theor. Chem. Acc. **131**, 1084 (2012)
X. Ren, P. Rinke, C. Joas, and M. Scheffler, J. Mater. Sci. **47**, 7447 (2012)

Adiabatic Connection (AC) formula for the Correlation Energy

- Derivation of the AC expression for the correlation energy (for a given reference WF)

$$E_{corr} \equiv E_{exact} - E_{ref}$$

$$E_{ref} = \left\langle \Psi_{ref} | \hat{H} | \Psi_{ref} \right\rangle$$

is based on defining the AC Hamiltonian

$$\forall_{0 \leq \alpha \leq 1} \quad \hat{H}^{\alpha} = \hat{H}^{(0)} + \alpha \hat{H}'$$

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

Adiabatic Connection (AC) formula for the Correlation Energy

- The coupling parameter (alpha) switches between partial-correlation

$$\Psi_0^{\alpha=0} = \Psi_{ref} \ , \quad E_0^{\alpha=0} = \left\langle \Psi_{ref} | \hat{H}^{(0)} | \Psi_{ref} \right\rangle$$

and full correlation limits

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

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

- From the Hellmann-Feynman theorem

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

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on one hand

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on the other

$$\begin{aligned}
\int_0^1 \frac{\partial E_0^\alpha}{\partial \alpha} d\alpha &= E_0^{\alpha=1} - E_0^{\alpha=0} \\
&= E_{exact} - \left\langle \Psi_{ref} | \hat{H}^{(0)} | \Psi_{ref} \right\rangle \\
&= E_{exact} - \left\langle \Psi_{ref} | \hat{H} - \hat{H}' | \Psi_{ref} \right\rangle \\
&= E_{exact} - E_{ref} + \left\langle \Psi_{ref} | \hat{H}' | \Psi_{ref} \right\rangle \\
&= E_{corr} + \left\langle \Psi_{ref} | \hat{H}' | \Psi_{ref} \right\rangle
\end{aligned}$$

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Finally

$$\boxed{E_{corr} = \int_0^1 \left\langle \Psi_0^\alpha | \hat{H}' | \Psi_0^\alpha \right\rangle d\alpha - \left\langle \Psi_{ref} | \hat{H}' | \Psi_{ref} \right\rangle}$$

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(exact but not practical)

Writing 2-RDM operator in terms of 1-RDM

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

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

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

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

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

Use the resolution of identity $\hat{1} = \sum_{\nu} |\Psi_\nu\rangle \langle \Psi_\nu| = |\Psi_0\rangle \langle \Psi_0| + \sum_{\nu \neq 0} |\Psi_\nu\rangle \langle \Psi_\nu|$

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

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

Using the relation

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

in the adiabatic connection correlation energy expression

$$E_{corr} = \int_0^1 \left\langle \Psi^{\alpha}_0 | \hat{H}' | \Psi^{\alpha}_0 \right\rangle d\alpha - \left\langle \Psi_{ref} | \hat{H}' | \Psi_{ref} \right\rangle$$

allows one to express the correlation energy in terms of the one-electron reduced functions:

$$\gamma^{\alpha} = \left\langle \Psi^{\alpha}_0 \middle| \hat{\gamma} \middle| \Psi^{\alpha}_0 \right\rangle$$ 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

The exact AC expression for the correlation energy reads

$$E^{AC}_{corr} = \int_0^1 (W^\alpha + \Delta^\alpha) \; d\alpha \quad ,$$

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

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

$$\Delta^\alpha = \sum_I \sum_{p \in I} \sum_{J \neq I} \sum_{q \in J} h'_{pq} \int_0^1 (\gamma^\alpha_{qp} - \gamma^{\alpha=0}_{qp}) d\alpha$$

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(still exact but still not practical)

Complete Active Space (CAS) model

$$\Psi^{\mathrm{CAS}} = \hat{A}[\psi^{\mathrm{DET}} \; \Psi^{\mathrm{FCI}}]$$

$$\psi^{\mathrm{DET}} = \psi^{\mathrm{DET}}[\{\varphi_p\}_{p\in\mathrm{inactive}}]$$

single determinant

$$\Psi^{\mathrm{FCI}} = \Psi^{\mathrm{FCI}}[\{\varphi_p\}_{p\in\mathrm{active}}]$$

FCI in a reduced space

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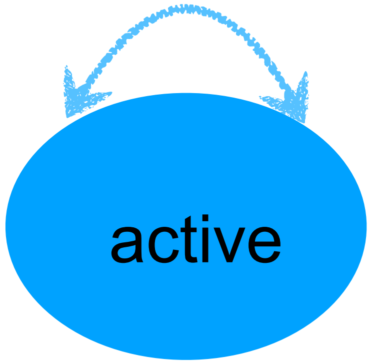
FCI in a reduced space



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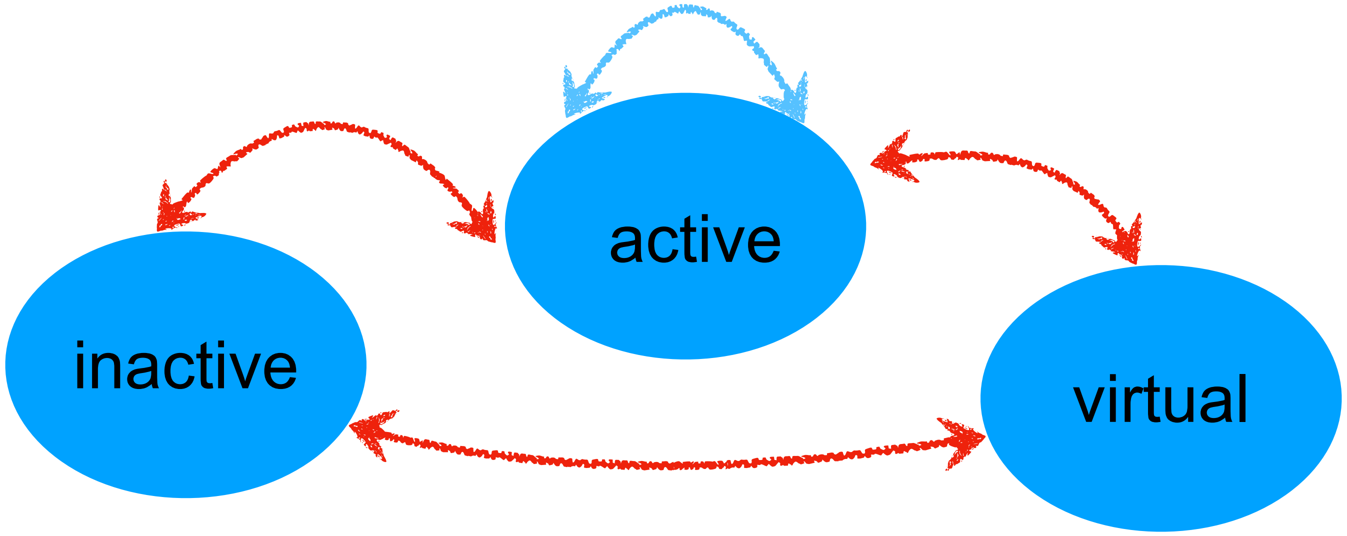
$$\psi^{\mathrm{DET}} = \psi^{\mathrm{DET}}[\{\varphi_p\}_{p\in\mathrm{inactive}}]$$ single determinant

$$\Psi^{\mathrm{FCI}} = \Psi^{\mathrm{FCI}}[\{\varphi_p\}_{p\in\mathrm{active}}]$$ FCI in a reduced space



Dynamic correlation energy outside CAS is missing

First approximation

Approximation: the one-body density matrix is constant along the AC path

$$\forall_{\alpha\in[0,1]} \quad \gamma_{pq}^{\alpha} = \gamma_{pq}^{\alpha=0}$$

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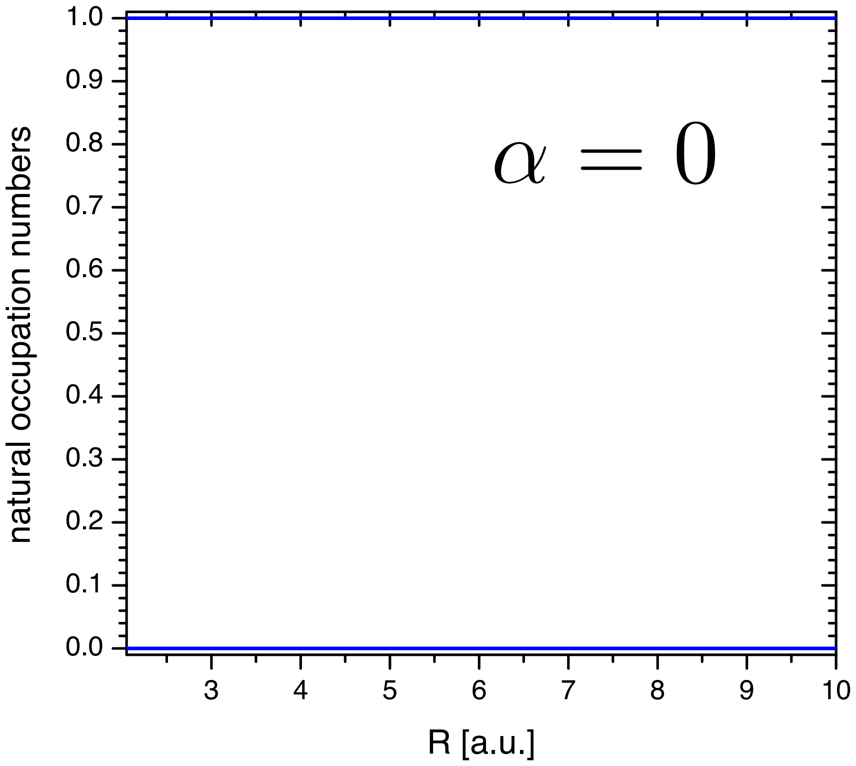
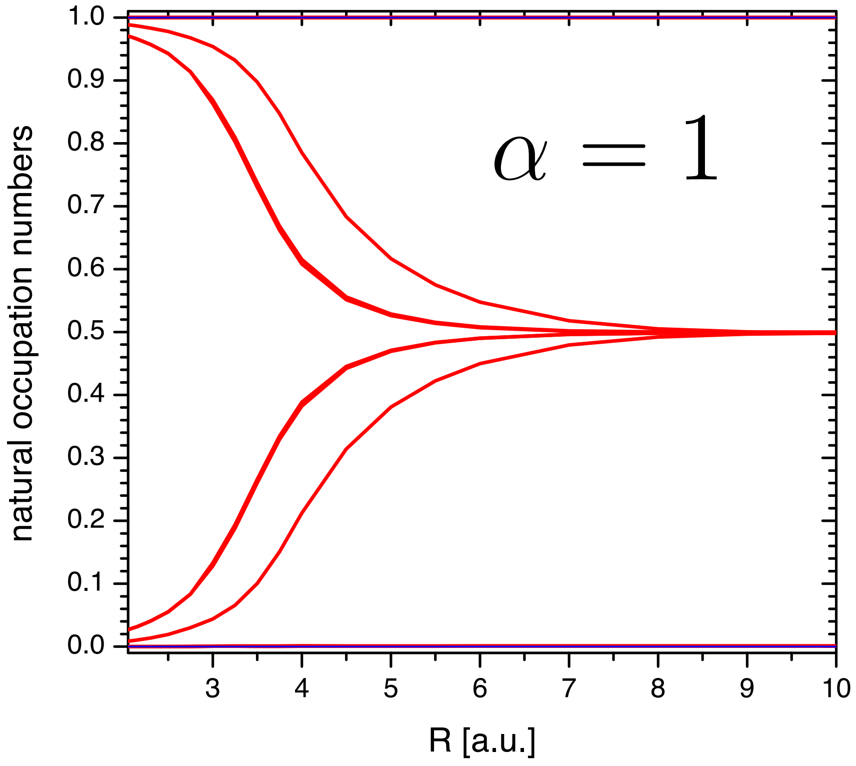
... poor approximation if a single determinantal WF were used for a system with strongly correlated electrons, think for example of the N_2 molecule





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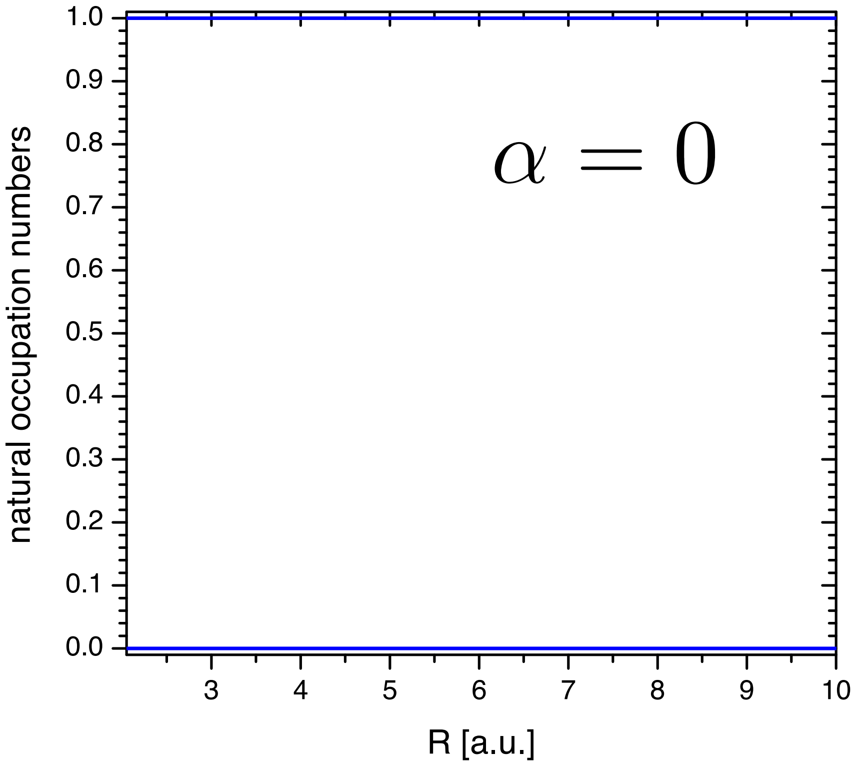

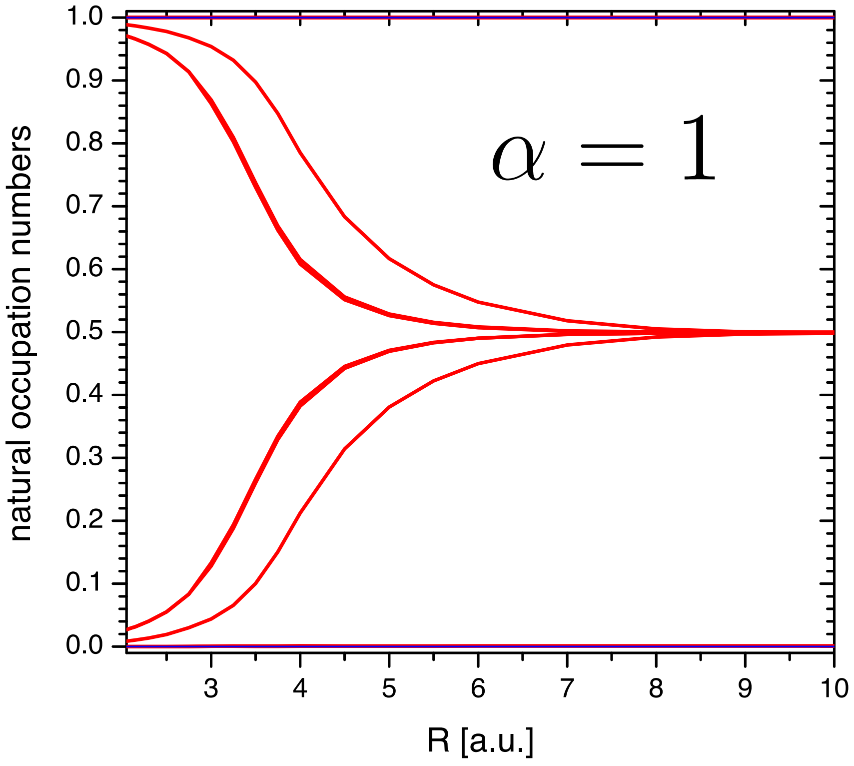

... but the approximation is justified if the reference wavefunction is multiconfigurational.

Second approximation

Transition density matrices for each coupling constant

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

are obtained within the Extended Random Phase Approximation.

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

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

Rowe's equations-of-motion

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

Consider an eigenequation of the Hamiltonian

$$\hat{H}\,|0\rangle = E_0\,|0\rangle$$

$$\hat{H}\,|\nu\rangle = E_\nu\,|\nu\rangle$$

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

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

$$O_\nu^+\,|0\rangle = |\nu\rangle$$

$$O_\nu\,|0\rangle = 0$$

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

Extended Random Phase Approximation

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

Extended Random Phase Approximation

- Only single excitations in the excitation operator

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

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

$$A_{rspq} = B_{rsqp} = \left\langle 0 | [\hat{a}_r^\dagger \hat{a}_s, [\hat{H}, \hat{a}_q^\dagger \hat{a}_p]] | 0 \right\rangle$$

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

only 1- and 2-RDM’s are needed!

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

α-Extended Random Phase Approximation (α-ERPA)

Derive the ERPA equations for the AC Hamiltonian

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

$$\forall_{\substack{p>q \\ r>s}} \quad \mathcal{N}_{pqrs} = (n_p - n_q)\delta_{pr}\delta_{qs}$$

$$\forall_{\substack{p>q \\ r>s}} \quad [\mathcal{A}^\alpha]_{pqrs} = A_{pqrs}(h^\alpha, g^\alpha, \gamma, \Gamma)$$

$$\forall_{\substack{p>q \\ r>s}} \quad [\mathcal{B}^\alpha]_{pqrs} = B_{pqrs}(h^\alpha, g^\alpha, \gamma, \Gamma)$$

We only know 1- and 2-electron reduced density matrices for alpha=0, so we use them in the ERPA equations.

Transition density matrix elements from α-ERPA

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

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

The eigenvectors are normalized

$$\left[\mathbf{Y}_\nu^\alpha\right]^T \mathcal{N} \mathbf{Y}_\nu^\alpha - \left[\mathbf{X}_\nu^\alpha\right]^T \mathcal{N} \mathbf{X}_\nu^\alpha = \frac{1}{2}$$

Adiabatic Connection (AC) formula for the Correlation Energy

A final spin-summed working form of the AC integrand

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

$$
\boxed{E_{corr}^{AC} = \int_0^1 W^{\alpha} \, d\alpha}
$$

K. Pernal, Phys. Rev. Lett. **120**, 013001 (2018).

Correlation energy from the Adiabatic Connection approximation: a summary

- Compute the energy for an assumed model (reference) and find one- and two-electron reduced density matrices.

K. Pernal, Phys. Rev. Lett. **120**, 013001 (2018).

Correlation energy from the Adiabatic Connection approximation: a summary

- For a given coupling constant the ERPA equation is solved (the main matrix requires only 1- and 2-RDM's obtained form a reference WF)

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

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- The eigenvectors are used as approximate transition density matrices

$$W^\alpha = W^\alpha(\{\mathbf{Y}_\nu^\alpha\}, \{\mathbf{X}_\nu^\alpha\})$$

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- The eigenvectors are used as approximate transition density matrices

$$W^\alpha = W^\alpha(\{\mathbf{Y}_\nu^\alpha\}, \{\mathbf{X}_\nu^\alpha\})$$

- The AC integrand is computed and the correlation energy obtained. The correlation energy is added to the reference energy.

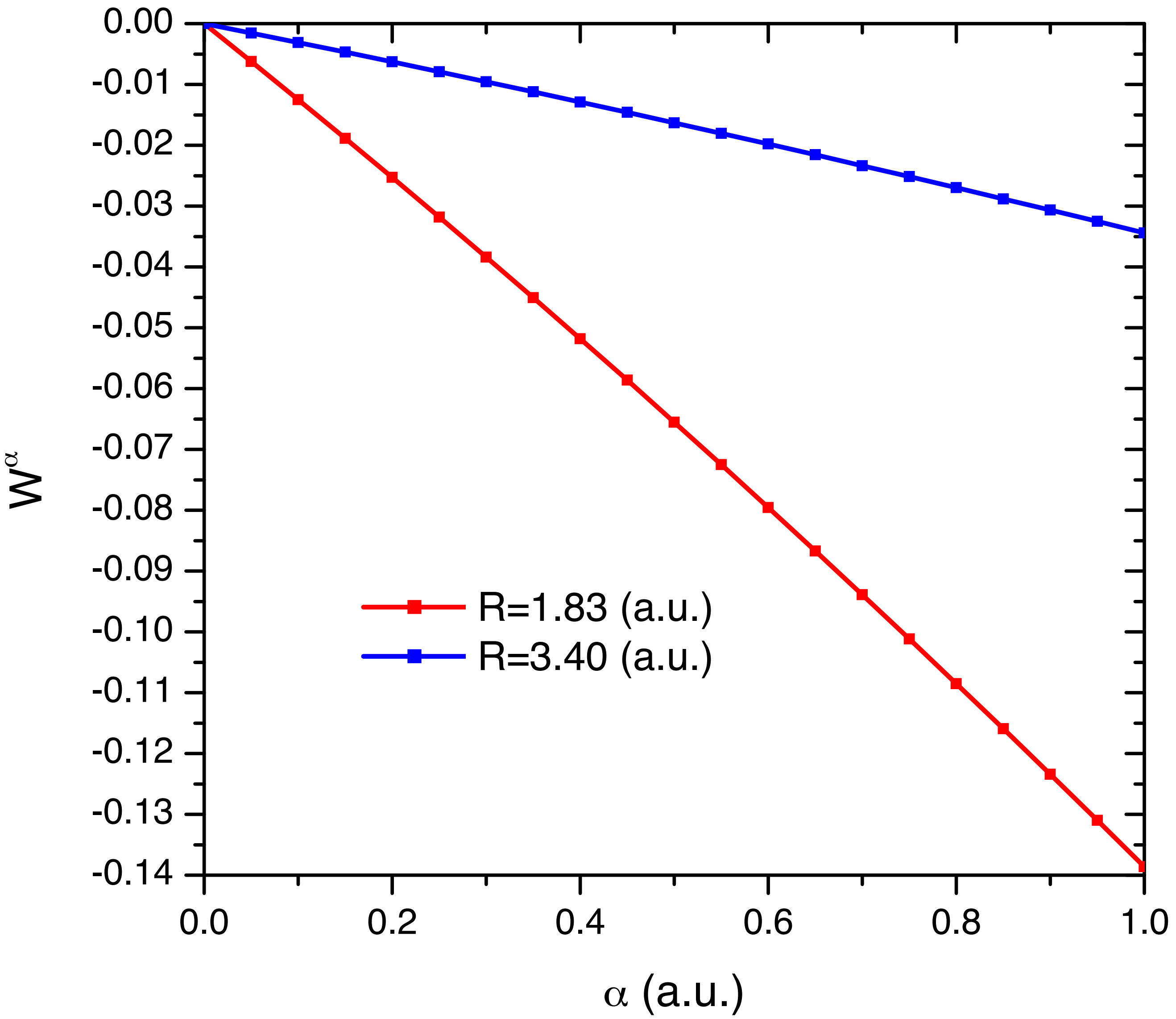
$$E_{corr}^{AC} = \int_0^1 W^\alpha \, d\alpha$$

$$E_{tot} = E_{ref} + E_{corr}^{AC}$$

K. Pernal, Phys. Rev. Lett. **120**, 013001 (2018).

Computation cost reduction - linearization of the AC integrand

The AC integrand is almost linear if the multireference reference wavefunction is employed



Plot of the AC integrand for the H_8 linear chain, R - a distance between adjacent hydrogen atoms. CAS(8,8) reference wavefunction.

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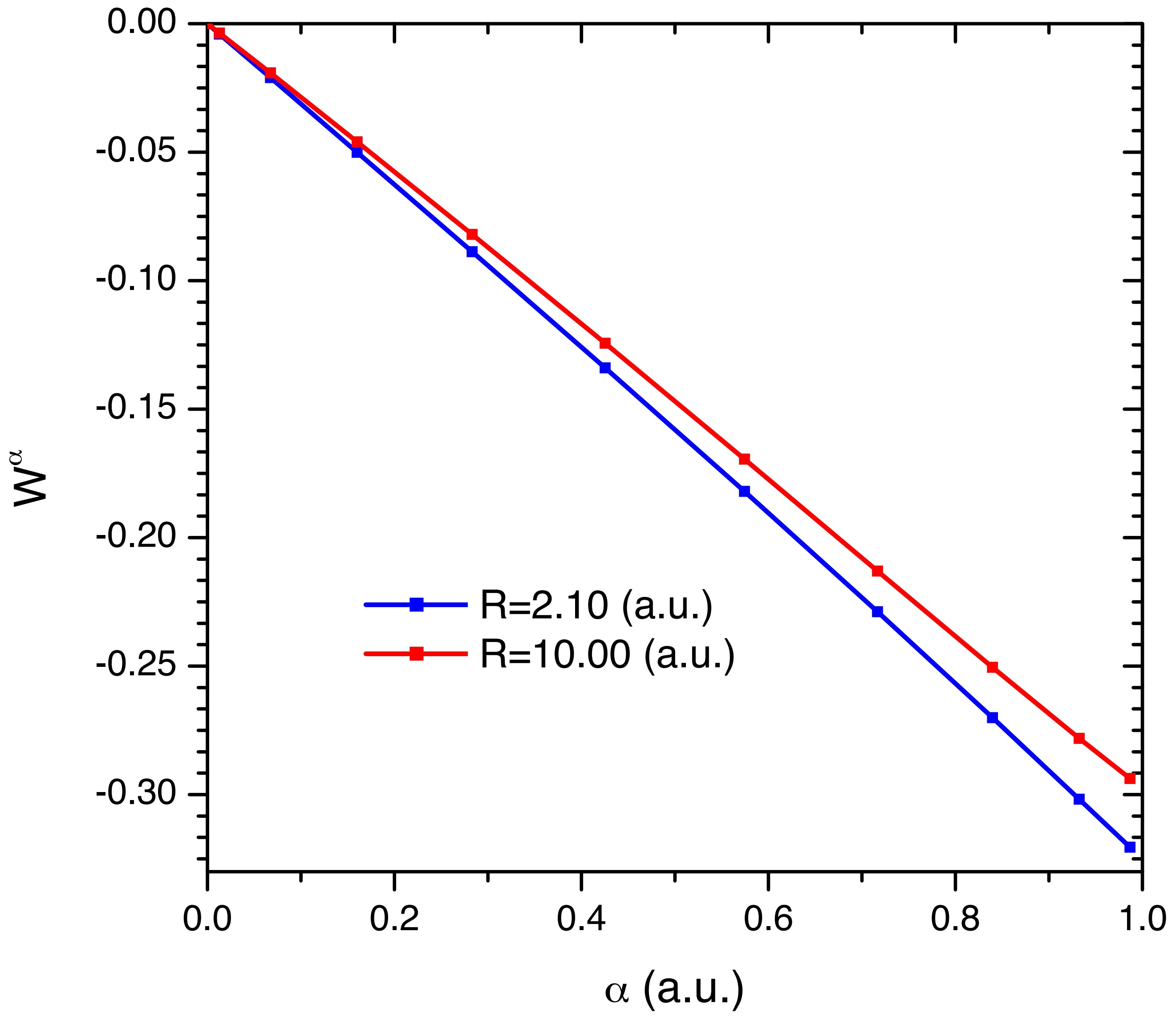

Plot of the AC integrand for the N_2 molecule, R - a distance between nitrogen atoms. CAS(6,6) reference wavefunction.

Linear extrapolation from the α=0 limit

- First-order expansion of the AC integrand

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

$$E_{corr}^{AC0} = \int_0^1 W^{(1)}\alpha \; d\alpha = \frac{W^{(1)}}{2}$$

- First-order corrections to the ERPA eigenvectors are found from perturbation theory. No need to diagonalize full ERPA matrix (only small blocks).

ACn

$$E_{\mathrm{corr}}^{\mathrm{AC}_{\mathrm{n_{max}}}} = \frac{2}{\pi}\mathrm{Tr}\left[\left(\int_0^{\infty} \mathrm{d}\omega \sum_{n=1}^{\mathrm{n_{max}}} \frac{\bar{\mathbf{C}}(\omega)^{(n)}}{n!(n+1)}\right)\mathbf{D}^2\right]$$

- ✓ high-order in α
- ✓ m^5 scaling with the system size
- ✓ n^6 scaling (only) with the number of active orbitals
- ✓ avoids instabilities

D. Drwal, P. Beran, M. Hapka, M. Modrzejewski, A. Sokol, L. Veis, K. Pernal, J. Phys. Chem. Lett. **13**, 4570 (2022)

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- Size-consistent

CASSCF (or DMRG) reference

$$E^{AC-CAS} = E_{CASSCF} + E^{AC}_{corr}$$

$$E^{AC0-CAS} = E_{CASSCF} + E^{AC0}_{corr}$$

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

2. Compute the AC correlation energy, which accounts for correlation among ***active***, ***inactive*** and ***secondary*** orbitals.

E. Pastorczak and K. Pernal, *J. Phys. Chem. Lett.* **9**, 5534 (2018)
E. Pastorczak, M. Hapka, L. Veis, and K. Pernal, J. Phys. Chem. Lett. **10**, 4668 (2019)
P. Beran, M. Matousěk, M. Hapka, K. Pernal, and L. Veis, J. Chem. Theory Comput. **17**, 7575 (2021)
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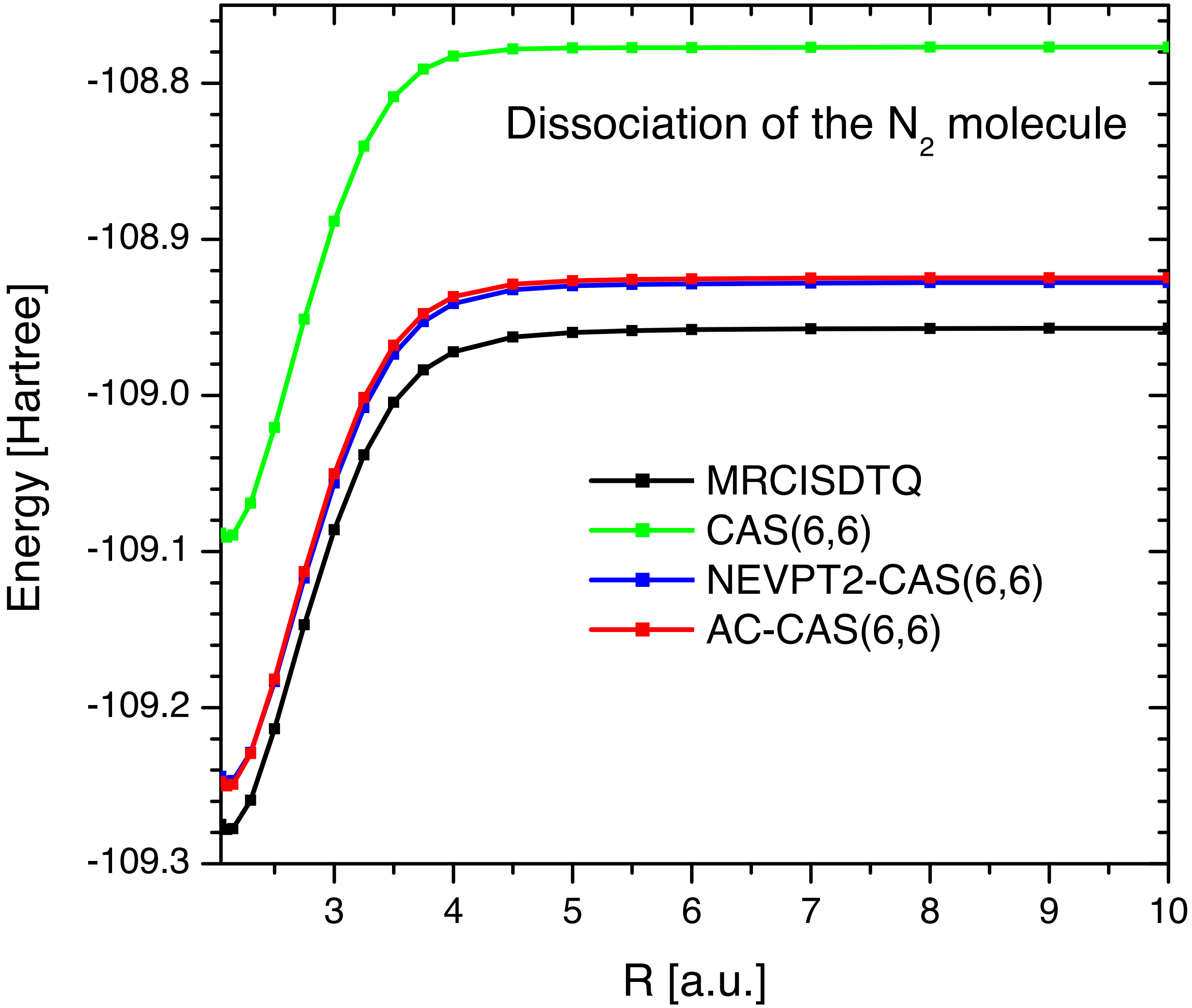
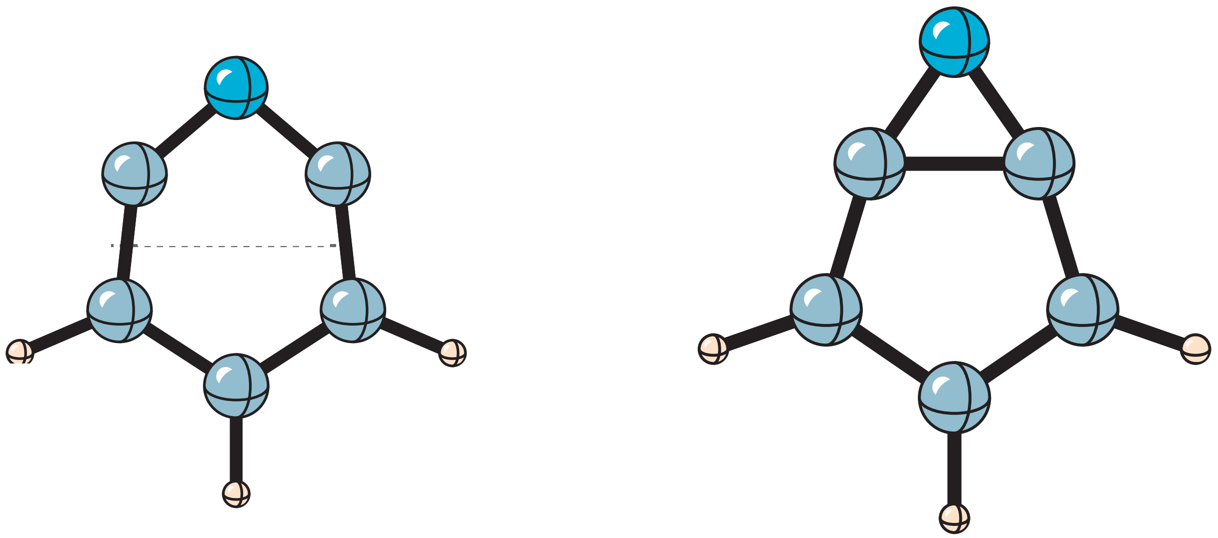


	NEVPT2-CAS(6,6)	AC-CAS(6,6)	NEVPT2-CAS(6,12)	AC-CAS(6,12)	NEVPT2-CAS(10,10)	AC-CAS(10,10)
R_{N2}=2.1 [a.u.]	30.7	27.8	30.1	24	20.1	16
R_{N2}=10.0 [a.u.]	29.3	32.4	23.1	27.2	31.4	16.6
E_{diss}	-1.4	4.6	-6.9	3.3	11.3	0.7

Errors of the total energy and the dissociation energy in mHa w.r.t MRCISDTQ(*) values for the N_2 molecule in cc-pVDZ.

(*)M. Hanauer, A. Koehn, J. Chem. Phys. **136**, 204107 (2012).

Energy difference between mono- and bicyclic forms of the 2,6-pyridyne (C_6NH_3) diradical



	NEVPT2-CAS(8,8)	AC-CAS(8,8)	AC0-CAS(8,8)	NEVPT2-CAS(10,10)	AC-CAS(10,10)	AC0-CAS(10,10)
E_{bi}-E_{mono}	7.4	7.8	7.3	10.8	9.1	10.4
error	-1.4	-1	-1.5	2	0.3	1.6

Energy differences and energy barrier errors in kcal/mol. Errors of the energy barriers computed with respect to the multireference CCSD(T) - Mk-MRCCSD(T) - value, 8.8 kcal/mol, from F.A. Evangelista et al. J. Chem. Phys. 132, 074107 (2010).

Adiabatic Connection (AC) vs. PT2 (CASPT2, NEVPT2)

No shifts in AC unlike in CASPT2

AC scales with the 6th power with the number of active orbitals - large active spaces can be treated, unlike in CASPT2/NEVPT2

Accuracy comparable to NEVPT2 but sometimes better

We have examples for which AC shows more systematic improvements with enlarging active space than NEVPT2

GAMM
COR

`https://github.com/pernalk/GAMMCOR`