

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.

Correlating electrons via adiabatic connection approach

Łódź April 18-20 2023

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Single reference model: electrons are distributed among orbitals in a single way (single Slater determinant WF) Single reference

$$
\Psi = \hat{a}_1^{\dagger} \hat{a}_2^{\dagger} \dots \hat{a}_N^{\dagger} |vac\rangle
$$

Single reference model: electrons are distributed among orbitals in a single way (single Slater determinant WF) Single reference

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Multireference model: WF is represented as a linear a few Slater determinan $\overline{}$ compination of a rew Slater determinants of pa
importance for a problem under consideration combination of a few Slater determinants of particular Single reference Mulitereference WF

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\Psi = \sum_{Q} D_{Q} \hat{a}_{q_1}^{\dagger} \hat{a}_{q_2}^{\dagger} \dots \hat{a}_{q_N}^{\dagger} |vac\rangle
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Single reference model: electrons are distributed among orbitals in a single way (single Slater determinant WF) Single reference

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$$

prrelatio \overline{a} energ • 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.

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

one-electron reduced function: **one-electron density matrix** *γ* Electron-nuclei interaction energy interaction energy in the set of the set of

> 1-RDM contains information about electron correlation vanio imprinduoni dobat cicculon cont

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 1-electron contraction pumperators and electron and electron \mathcal{A} spin-summed diagonal part of \mathcal{A}

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

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

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

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

Electron correlation (dynamic or static) is manifested in the pattern of natural occupation numbers. #pq = h%0j# p $\frac{1}{2}$

Natural occupation numbers: eigenvalues of the one-electron reduced density matrix are distoired into distoired into distribution of active (np = 1), in the network of active (n 1-electron reduced matrix operators and elements in a basis set of orthonormal spinor- \overline{p} \mathcal{A} spin-summed diagonal part of \mathcal{A}

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$$
\n
$$
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\n
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$$

Natural occupation numbers are nonnegative and not greater than 1 2-electron reduced density matrix operator and the matrix read nat occup numbers of the state o
The state of the st

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

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

Single determinantal WF:
$$
\Psi = \hat{a}_1^\dagger \hat{a}_2^\dagger \dots \hat{a}_{14}^\dagger \ket{vac}
$$

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

Suppose the differential WF:
$$
\Psi = \hat{a}_1^\dagger \hat{a}_2^\dagger \dots \hat{a}_{14}^\dagger \, |vac\rangle
$$

\nUsing the determinantal WF: $\Psi = \hat{a}_1^\dagger \hat{a}_2^\dagger \dots \hat{a}_{14}^\dagger \, |vac\rangle$

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No correlation

Natural occupation numbers of nitrogen molecule N₂ as a function of interatomic distance

Exact (fully correlated) wavefunction

Natural occupation numbers of nitrogen molecule N₂ as a function of interatomic distance

Exact (fully correlated) wavefunction

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

Exact (fully correlated) wavefunction

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

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

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

How to find the correlation correlation energy? Let fpqrsg be general indices of spinorbitals in the assumed basis set. DeÖne spin-summed $\frac{1}{2}$

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

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 $=$ Eq.

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 $|C_0| \approx |C_1| \approx \ldots \approx |C_m|$ Strong correlation: $|C_0| \approx |C_1| \approx \ldots \approx |C_m|$

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Introduce a model Hamiltonian Hamiltonian Hamiltonian Hamiltonian Hamiltonian Hamiltonian Hamiltonian Hamiltonia How to find the correlation correlation energy? Let fpqrsg be general indices of spinorbitals in the assumed basis set. DeÖne spin-summed $\frac{1}{2}$

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Strong correlation can be efficiently captured by multireference wavefunction (MR-WF) models. Strong correlation can be emiciently $\mathbf{F} = \mathbf{F} \mathbf{F} \mathbf{F}$ DET $=$ $\frac{1}{2}$ $\frac{1}{2$ Mulitereference WF

 $=$ Eq.

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 $=$ Eq.

Even with very large *m* the expansion is not long enough (not even DMRG) to retrieve all important correlation. $\mathbf{F}_{\mathbf{p}}$. $\frac{1}{2}$ is not long anough (not $\mathbf{F}_{\mathbf{c}}$ P $\overline{}$ and $\overline{}$ and $\overline{}$ e expansion is not long enough (not even DMRG) to
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 from the prostupe of a Correlation energy from the perturbation theory

• If a Hamiltonian is known for an assumed reference WF, i.e. ned re \overline{a}

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

perturbation theory can be applied to recover correlation energy for
the perturbation operator the perturbation operator \mathfrak{p} (0) ref \mathfrak{p} = Eq. (1) ref \mathfrak{p} = Eq. (1) a annlied to rec H

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

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

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

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

• If

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

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

MP2, CASPT2 or NEVPT2

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MP2, CASPT2 or NEVPT2

• 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)

intruder state problem (close-lying states)

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intruder state problem (close-lying states)

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

> CASPT2 or NEVPT2 methods become very expensive (3rd- and 4thorder 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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General formalism of the adiabatic connection (AC) method

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 adiabatic connection (AC) expression for the correlation energy deÖned II. AC CORRELATION ENERGY AND LONGITUDE AND LONGITUDE AND LONGITUDE AND LONGITUDE AND LONGITUDE AND LONGITUDE

• Derivation of the AC expression for the correlation energy (for a given reference WF) \bullet Derivation of the AC expression for the correlation energy (for a given

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

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

is based on defining the AC Hamiltonian

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

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

Adiabatic Connection (AC) formula for the Correlation Energy $H^{\left(n \right)}$ formula it (8) C) formula for the Correlation Energy

• The coupling parameter (alpha) switches between partial-correlation and it assumes that at α -0.000 α -0.000 α

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

 \mathbf{F} the adiabatic connection parameter \mathbf{F} and full correlation limits full-interaction electronic Hamiltonic Hamilto and full correlation limits

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

$$
\hat{H}^\alpha \Psi^\alpha_\nu = E^\alpha_\nu \Psi^\alpha_\nu
$$

• From the Hellmann-Feynman theorem

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

• From the Hellmann-Feynman theorem **Example Hollmann** Founman theorem

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

Integration of the left-hand-side of Eq.(17) and employees of Eq.(17) and employees E Integration of the left-hand-side of Eq.(7) and employing Eq.(??) yield on one hand

$$
\int_0^1 \frac{\partial E_0^{\alpha}}{\partial \alpha} d\alpha = \int_0^1 \left\langle \Psi_0^{\alpha} | \hat{H}' | \Psi_0^{\alpha} \right\rangle d\alpha
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$$

on the other on the other

$$
\int_0^1 \frac{\partial E_0^{\alpha}}{\partial \alpha} d\alpha = E_0^{\alpha=1} - E_0^{\alpha=0}
$$

= $E_{exact} - \langle \Psi_{ref} | \hat{H}^{(0)} | \Psi_{ref} \rangle$
= $E_{exact} - \langle \Psi_{ref} | \hat{H} - \hat{H}' | \Psi_{ref} \rangle$
= $E_{exact} - E_{ref} + \langle \Psi_{ref} | \hat{H}' | \Psi_{ref} \rangle$
= $E_{corr} + \langle \Psi_{ref} | \hat{H}' | \Psi_{ref} \rangle$

• From the Hellmann-Feynman theorem **Example Hollmann** Founman theorem nan theor an th \overline{O} \overline{a} n

 \int

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= $E_{corr} + \langle \Psi_{ref} | \hat{H}' | \Psi_{ref} \rangle$

and we have Finally

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

• From the Hellmann-Feynman theorem **Example Hollmann** Founman theorem nan theor an th \overline{O} \overline{a} n

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on the other on the other

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= $E_{exact} - \langle \Psi_{ref} | \hat{H}^{(0)} | \Psi_{ref} \rangle$
= $E_{exact} - \langle \Psi_{ref} | \hat{H} - \hat{H}' | \Psi_{ref} \rangle$
= $E_{exact} - E_{ref} + \langle \Psi_{ref} | \hat{H}' | \Psi_{ref} \rangle$
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$$

 S^2 far exact in proprieted. (exact but not practical)

Writing 2-RDM operator in terms of 1-RDM paratar in tary

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

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

$$
\Gamma_{pqrs}=\left\langle\Psi_{0}|\hat{\Gamma}_{pqrs}|\Psi_{0}\right\rangle=\langle\Psi_{0}|\hat{\gamma}_{pr}\hat{\gamma}_{qs}|\Psi_{0}\rangle-\gamma_{qr}\delta_{ps}
$$

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 given in Eq. (1), whereas the energy is given by a sum of the energy is giv $\mathsf{relation}$

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

in the adiabatic connection correlation energy expression in the adiabatic connection correlation energy expression

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

 n allows one to express the correlation energy in terms of the one-electron and in Eq. (9). A derivation employe ie to express the correlation energy in terms of the one-e discomed to derive an adiabatic straightforward to derive an adiabatic straight ϵ pleuse ane to express the estralation energy in terms of the ane electron allows one to express the correlation energy in terms of the one-electron reduced functions:

$$
\gamma^\alpha \;=\; \langle \Psi_0^\alpha | \hat{\gamma} | \Psi_0^\alpha \rangle \qquad \text{ one-electron reduced density matrix (1-RDM)}
$$

i for transitions between a ground state and excited states ís, reading

 $\gamma^{\alpha,0\nu} \,=\, \langle \Psi_0^\alpha | \hat{\gamma} | \Psi_\nu^\alpha \rangle \qquad \text{transition one-electron RDM}$

Adiabatic Connection (AC) formula for the Correlation Energy

The exact AC expression for the correlation energy reads The exact AC expression for the correlation energy reads \hat{C} ex proboth for the boltelation energy reads

$$
E_{corr}^{AC} = \int_0^1 (W^{\alpha} + \Delta^{\alpha}) d\alpha ,
$$

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

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

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

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W^{\alpha} = \frac{1}{2} \sum_{pqrs'} \left(\sum_{\nu \neq 0} \gamma_{pr}^{\alpha,0\nu} \gamma_{qs}^{\alpha,\nu} + \gamma_{ps}^{\alpha=0} \gamma_{qr}^{\alpha=0} - \gamma_{qr}^{\alpha=0} \delta_{ps} \right) \langle rs|pq \rangle
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\Delta^{\alpha} = \sum_{I} \sum_{p \in I} \sum_{J \neq I} \sum_{q \in J} h'_{pq} \int_0^1 (\gamma_{qp}^{\alpha} - \gamma_{qp}^{\alpha=0}) d\alpha
$$

(still exact but still not practical) (still allowed values of the para-

Complete Active Space (CAS) model

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

$$
\psi^{\rm DET} = \psi^{\rm DET}[\left\{\varphi_p\right\}_{p\in \rm inactive}] \quad \text{si}
$$

ingle determinant

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

FCI in a reduced space

Complete Active Space (CAS) model

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

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

single determinant

space

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

Complete Active Space (CAS) model

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

$$
\psi^{\rm DET} = \psi^{\rm DET}[\{\varphi_p\}_{p\in \rm inactive}] \quad \text{sir}
$$

ngle determinant

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

Dynamic correlation energy outside CAS is missing $=$ $\frac{1}{2}$

First approximation: Approximation

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

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

First approximation: Approximation approxii

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

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

Consequently,

 \overline{a} $\Delta^{\alpha}=0$

First approximation $A = \frac{1}{\sqrt{2}}$ approxii

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

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

Consequently,

$$
\Delta^{\alpha} = 0
$$

 n k for example of the N_2 molecule Subityfy correlated electrons, think for example of the tyz molecule ... poor approximation if a single determinantal WF were used for a system with ... poor approximation if a single determination vir were used for a
strongly correlated electrons, think for example of the N₂ molecule

First approximation $A = \frac{1}{\sqrt{2}}$ approxii

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strongly correlated electrons, think for example of the N₂ molecule

A spin-summer 2-RDM operators p r a^^s a^^q + ^a^y p r a^^s a^^q + ^a^y p r a^^s a^^q + ^a^y p r a^^s a^^q (33) ... but the approximation is justified if the reference wavefunction is multiconfigurational.

Second approximation

Transition density matrices for each coupling constant ea $\frac{1}{2}$ $\mathsf{instant}$

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

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

Not Rays Res Mad Rhys 43,458,4888) 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 *Here H H E E Here Concept of EXAMPLE EXAMPLE EXAMPLE EXAMPLE EXAMPLE EXAMPLE THE EXAMPLE T* The Rowe's equations-of-motion formalism is based on the concept of

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

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

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

Extended Random Phase Approximation

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

Extended Random Phase Approximation EXtended F
ons in the e $\frac{1}{2}$

• Only single excitations in the excitation operator ϵ tion operator 204109 (2012) read

$$
O^{\dagger}_{\nu} = \sum_{p>q} \left(X_{pq} a^{\dagger}_p a_q + Y_{pq} a^{\dagger}_q a_p \right)
$$

$$
\left(\begin{array}{c}\mathcal{A}&\mathcal{B}\\\mathcal{B}&\mathcal{A}\end{array}\right)\left(\begin{array}{c}\mathbf{X}^{\nu}\\\mathbf{Y}^{\nu}\end{array}\right)=\omega_{\nu}\left(\begin{array}{cc}-\mathcal{N}&\mathbf{0}\\\mathbf{0}&\mathcal{N}\end{array}\right)\left(\begin{array}{c}\mathbf{X}^{\nu}\\\mathbf{Y}^{\nu}\end{array}\right)
$$

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

K. Chatterjee and K. Pernal, *J. Chem. Phys.* **137**, 204109 (2012). or if the matrices are written explicitely in terms of $2-$ RDM their (spin-summed) elements of $2-$

Extended Random Phase Approximation and on property with a context of the cont EXtended F
ons in the e

xienueu Nanuonn Filase A
ns in the evcitation operator • Only single excitations in the excitation operator ϵ tion operator 204109 (2012) read

$$
O^{\dagger}_{\nu} = \sum_{p>q} \left(X_{pq} a^{\dagger}_p a_q + Y_{pq} a^{\dagger}_q a_p \right)
$$

$$
\left(\begin{array}{c}\mathcal{A}&\mathcal{B}\\\mathcal{B}&\mathcal{A}\end{array}\right)\left(\begin{array}{c}\mathbf{X}^{\nu}\\\mathbf{Y}^{\nu}\end{array}\right)=\omega_{\nu}\left(\begin{array}{cc}-\mathcal{N}&\mathbf{0}\\\mathbf{0}&\mathcal{N}\end{array}\right)\left(\begin{array}{c}\mathbf{X}^{\nu}\\\mathbf{Y}^{\nu}\end{array}\right)
$$

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

$$
\forall_{pqrs} \quad \mathcal{A}_{rspq} = \mathcal{B}_{rsqp} = (n_r - n_s)(\delta_{pr}h_{sq} - \delta_{sq}h_{pr})
$$

+ $\sum_{tu} \Gamma_{purt} \langle st || qu \rangle + \sum_{tu} \Gamma_{stqu} \langle up || tr \rangle$
+ $\sum_{tu} \Gamma_{turq} \langle ps | tu \rangle + \sum_{tu} \Gamma_{sptu} \langle tu | qr \rangle$
+ $\delta_{sq} \sum_{tuv} \Gamma_{wurt} \langle tp | wu \rangle + \delta_{pr} \sum_{tuv} \Gamma_{swtu} \langle tu | wq \rangle$

K. Chatterjee and K. Pernal, *J. Chem. Phys.* **137**, 204109 (2012). or if the matrices are written explicitely in terms of $2-$ RDM their (spin-summed) elements of $2-$

α-Extended Random Phase Approximation (α-ERPA) Eq.(15). By following derivation of the ERPA equations shown in Ref.??? with the fully ^ V. Extended Dandem Phace An

to the following set of $\mathcal{L}_\mathcal{S}$ equations $\mathcal{L}_\mathcal{S}$ equations $\mathcal{L}_\mathcal{S}$ equations $\mathcal{L}_\mathcal{S}$ Derive the ERPA equations for the AC Hamiltonian Derive the LINFA equations for the AC Hamiltonian r

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

$$
\forall_{\substack{p>q\\r>s}} \mathcal{N}_{pqrs} = (n_p - n_q) \delta_{pr} \delta_{qs}
$$
\n
$$
\forall_{\substack{p>q\\r>s}} \left[\mathcal{A}^{\alpha} \right]_{pqrs} = A_{pqrs} (h^{\alpha}, g^{\alpha}, \gamma, \Gamma)
$$
\n
$$
\forall_{\substack{p>q\\r>s}} \left[\mathcal{B}^{\alpha} \right]_{pqrs} = B_{pqrs} (h^{\alpha}, g^{\alpha}, \gamma, \Gamma)
$$

use them in the ERPA equations. \mathcal{G} We only know 1- and 2-electron reduced density matrices for alpha=0, so we \mathcal{L} follows from Eqs.(50) after replacing one-electron Hamiltonian hamil we only know it and z-electron reduced density matrices for alpha
use them in the ERPA equations.

Transition density matrix elements from α -ERPA

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

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

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 rr elation Ene erg $\overline{}$ Adiabatic Connection (AC) formula for the Correlation Energy

A final spin-summed working form of the AC integrand

^ˆ*[|]* ↵

$$
W^{\alpha} = 2 \sum_{p>q,r>s} \left\{ (n_p - n_q)(n_r - n_s) \times \sum_{p>q,r>s} \left\{ (\mathbf{Y}_{\nu}^{\alpha})_{pq} - [\mathbf{X}_{\nu}^{\alpha}]_{pq} \right\} ([\mathbf{Y}_{\nu}^{\alpha}]_{rs} - [\mathbf{X}_{\nu}^{\alpha}]_{rs} \right\}
$$

$$
- \frac{1}{2} [n_p(1 - n_q) + n_q(1 - n_p)] \delta_{pr} \delta_{qs} \left\{ \langle pr | qs \rangle \right\}
$$

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

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.

Correlation energy from the Adiabatic Connection approximation: a summary transition density matrix elements for the adiabatic connection Hamiltonian H^ given in Eq.(15). By following derivation of the ERPA equations shown in Ref.??? with the fully

• 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)

$$
\left(\begin{array}{cc}\mathcal{A}_{\alpha} & \mathcal{B}_{\alpha} \\ \mathcal{B}_{\alpha} & \mathcal{A}_{\alpha}\end{array}\right)\left(\begin{array}{c}\mathbf{X}_{\nu}^{\alpha} \\ \mathbf{Y}_{\nu}^{\alpha}\end{array}\right)=\omega_{\nu}\left(\begin{array}{cc}-\mathcal{N} & \mathbf{0} \\ \mathbf{0} & \mathcal{N}\end{array}\right)\left(\begin{array}{c}\mathbf{X}_{\nu}^{\alpha} \\ \mathbf{Y}_{\nu}^{\alpha}\end{array}\right)
$$

Correlation energy from the Adiabatic Connection approximation: a summary transition density matrix elements for the adiabatic connection Hamiltonian H^ given in Eq.(15). By following derivation of the ERPA equations shown in Ref.??? with the fully

• 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) $\,$ nt the FRPA equation is solved (the main matrix Etot = Eref + EAC

$$
\left(\begin{array}{cc}\mathcal{A}_{\alpha} & \mathcal{B}_{\alpha} \\ \mathcal{B}_{\alpha} & \mathcal{A}_{\alpha}\end{array}\right)\left(\begin{array}{c}\mathbf{X}_{\nu}^{\alpha} \\ \mathbf{Y}_{\nu}^{\alpha}\end{array}\right)=\omega_{\nu}\left(\begin{array}{cc}-\mathcal{N} & \mathbf{0} \\ \mathbf{0} & \mathcal{N}\end{array}\right)\left(\begin{array}{c}\mathbf{X}_{\nu}^{\alpha} \\ \mathbf{Y}_{\nu}^{\alpha}\end{array}\right)
$$

• The eigenvectors are used as approximate transition density matrices nvectors $\overline{}$ used as approximate transition density matrices

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

Correlation energy from the Adiabatic Connection approximation: a summary transition density matrix elements for the adiabatic connection Hamiltonian H^ given in Eq.(15). By following derivation of the ERPA equations shown in Ref.??? with the fully 2
2
2 nergy from t α ˆ, and ˆ*ext* - an external potential operator. a ground state eigenfunction and the community of the ground state eigenfunction σ ation energy from the Adiabatic Connection approximation: a sum

• 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) • For a given coupling constant the ERPA equation is solved (the main matrix Etot = Eref + EAC **Example 3** r a given coupling constant the FRPA equation is solved (the ma derivation of the additional tend to the advertise the manufacture interestion of the addition of the connectio
In tires only 1- and 2-RDM's obtained form a reference WF) \mathbf{r} and \mathbf{r} and \mathbf{r} and \mathbf{r} relation between an exact relation between \mathbf{r}

$$
\left(\begin{array}{cc}\mathcal{A}_{\alpha} & \mathcal{B}_{\alpha} \\ \mathcal{B}_{\alpha} & \mathcal{A}_{\alpha}\end{array}\right)\left(\begin{array}{c}\mathbf{X}_{\nu}^{\alpha} \\ \mathbf{Y}_{\nu}^{\alpha}\end{array}\right)=\omega_{\nu}\left(\begin{array}{cc}-\mathcal{N} & \mathbf{0} \\ \mathbf{0} & \mathcal{N}\end{array}\right)\left(\begin{array}{c}\mathbf{X}_{\nu}^{\alpha} \\ \mathbf{Y}_{\nu}^{\alpha}\end{array}\right)
$$

• The eigenvectors are used as approximate transition density matrices nvectors $\overline{}$ • The eigenvectors are used as approximate transition density matrices *y*envectors are used as approximate transition density matrix

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

rne Ao megrand is computed and the correlation energy obtained. a
A • The AC integrand is computed and the correlation energy obtained. The 22
82
1920 - Paul Barnett, prinse amerikansk politiker
1920 - Paul Barnett, politiker
1920 - Paul Barnett, politiker he AC integrand is computed and the correlation energy obtaine orrelation energy

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

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

K. Pernal, Phys. Rev. Lett. **120**, 013001 (2018). $\overline{1}$ K. Pernal, Phys. Rev. Le *p* \overline{p} $\frac{1}{2}$ 120 $\overline{1}$ *pr* ↵*,*⌫⁰ *qs* + (*n^p* 1)*nqrqps* 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.

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

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 $\alpha=0$ limit

• First-order expansion of the AC integrand Etot = Eref + EAC

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

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

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

ACn ACn

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

 $\sqrt{}$ high-order in α

- √ m⁵ scaling with the system size
- $\sqrt{n^6}$ 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)

ACn approximation

• Great computational saving: the cost scales only with the 6th power of the number of the active orbitals.

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• The overall cost of the ACn approximation is close to MP2 method if the number of virtual orbitals is much larger than the number of the active orbitals (which is a typical case).

• Great computational saving: the cost scales only with the 6th power of the number of the active orbitals.

• The overall cost of the ACn approximation is close to MP2 method if the number of virtual orbitals is much larger than the number of the active orbitals (which is a typical case).

• Size-consistent

CASSCF (or DMRG) reference

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

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

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

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

> EAC = W. d'Alexandre de l'Alexandre de l'Alexandre de l'Alexandre de l'Alexandre de l'Alexandre de l'Alexandre de l'
De l'Alexandre de l E. Pastorczak and K. Pernal, *J. Phys. Chem. Lett.* **9**, 5534 (2018)

0 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)

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

Errors of the total energy and the dissociation energy in mHa w.r.t MRCISDTQ^(*) values for the N2 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 ₃) diradical

barriere compated with reepoot to the matthererence electer(1) with the monocyclic forms of the MRCCSD(T) - value, 8.8 kcal/mol, from F.A. Evangelista et al. J. Chem. a-CCSD a-CCS
Terrenormalismus a-CCSD a-- valuc, l
'1107 *(*21 Energy differences and energy barrier errors in kcal/mol. Errors of the energy barriers computed with respect to the multireference CCSD(T) - Mk-Phys. 132, 074107 (2010).

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

No shifts in AC unlike in CASPT2 and Gw with numeric atom-centered orbital basis functions. And CASPT2 and CASPT2

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

Accuracy comparable to NEVPT2 but sometimes better

We have examples for which AC shows more systematic improvements with enlarging active space than NEVPT2 *Phys.* 2015, *113*, 3085–3127.

https://github.com/pernalk/GAMMCOR