Multiresolution Coupled-Cluster

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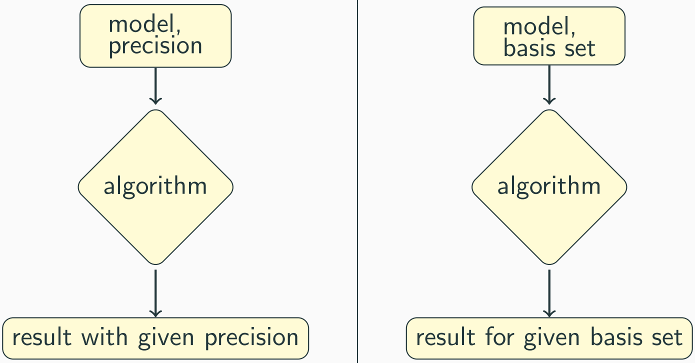
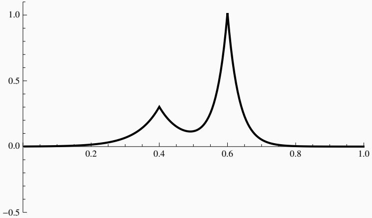
Introduction

Multiresultion | Fixed-Basis



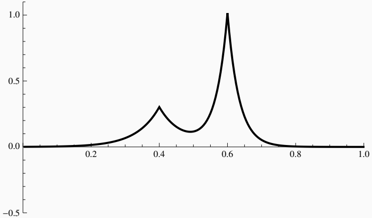
MRA - Multiresolution Analysis

MRA - Basic Idea

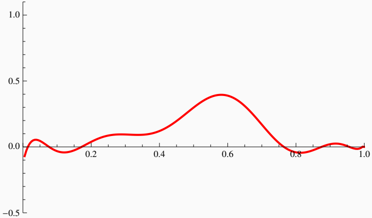


polynomials as universal basis

MRA - Basic Idea



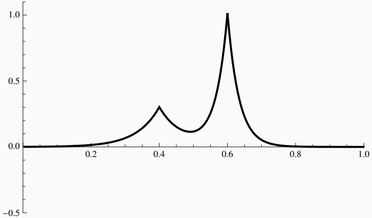
10 basis functions

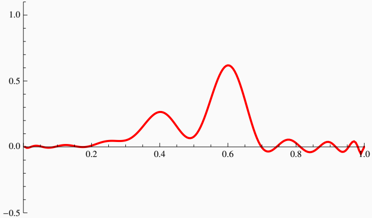


polynomials as universal basis

MRA - Basic Idea

20 basis functions





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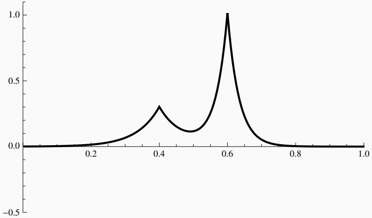
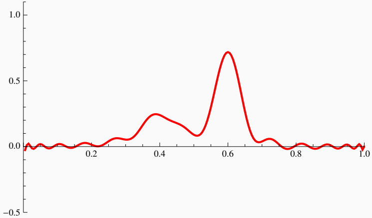


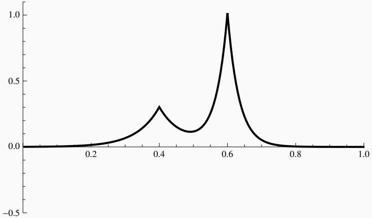
30 basis functions

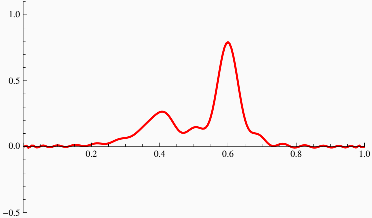


polynomials as universal basis

MRA - Basic Idea

40 basis functions





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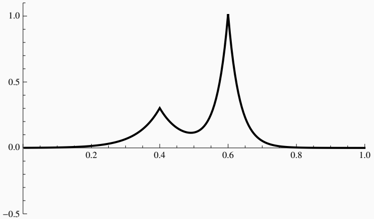
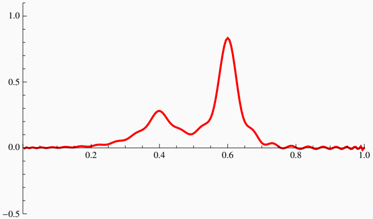


50 basis functions



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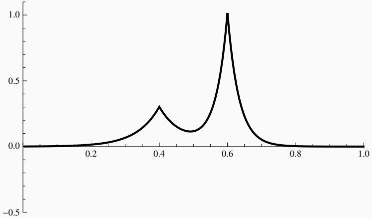
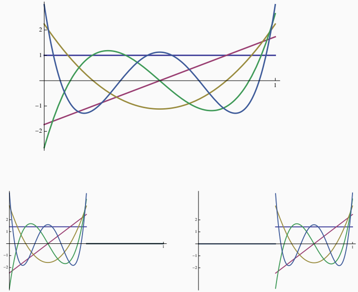
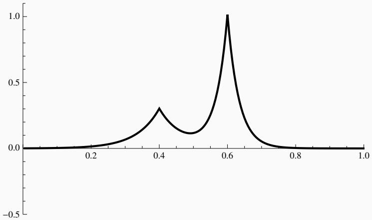




polynomials as universal basis

or piecewise polynomials

MRA - Basic Idea



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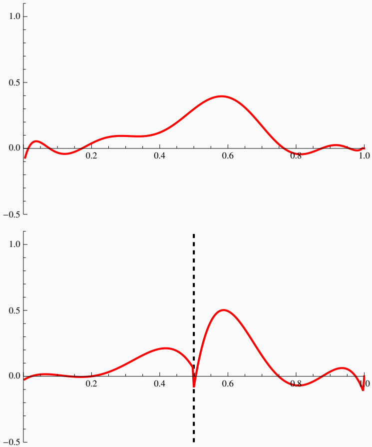

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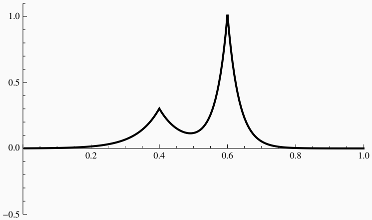

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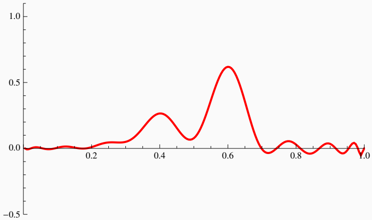

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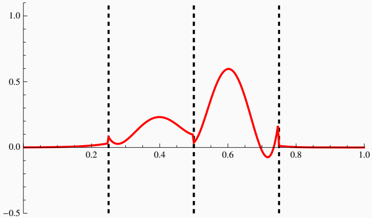

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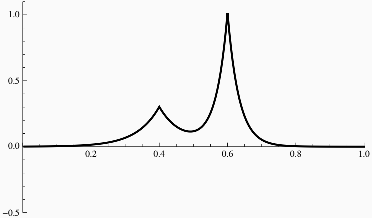

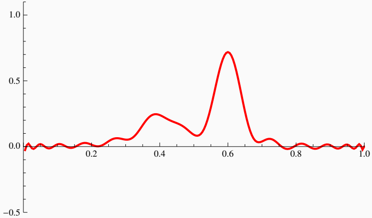

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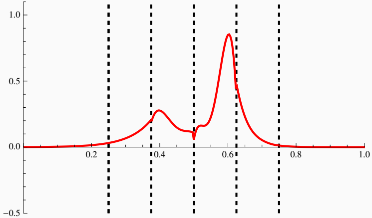

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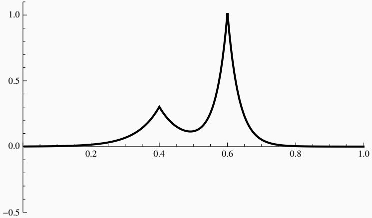

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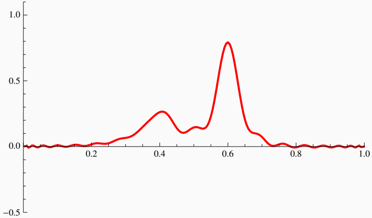

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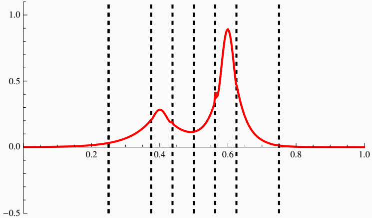

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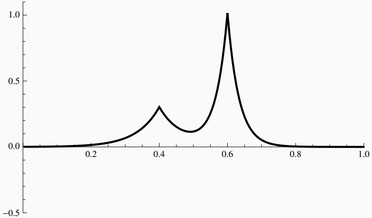

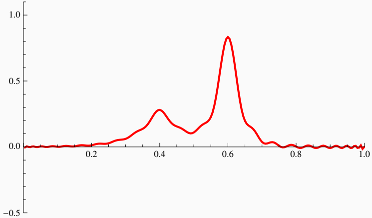

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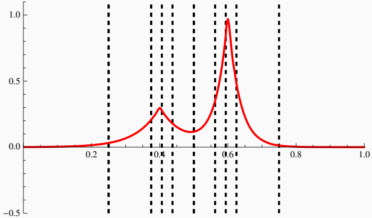
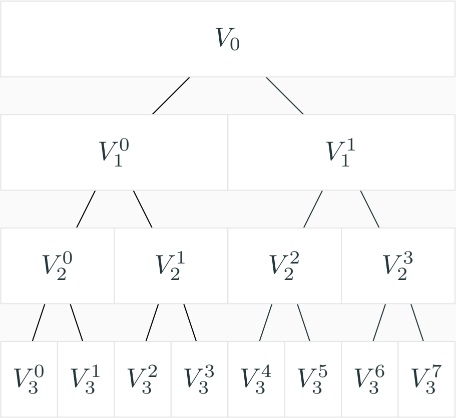


MRA - Tree Structure

$$V_0 \subset V_1 \subset V_2 \subset \cdots \subset \mathbf{L}^2$$

$$V_n = \bigoplus_{l=0}^{l=2^n-1} V_n^l$$

$$V_{n+1} = V_n \oplus W_n$$

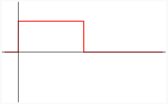
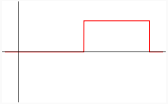


MRA - Tree Structure

$$V_0 \subset V_1 \subset V_2 \subset \cdots \subset \mathbf{L}^2$$

Haar Wavelets

$$V_n = \bigoplus_{l=0}^{l=2^n-1} V_n^l$$

$V_1 =$ ( , )

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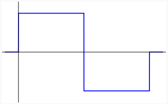
$V_1 =$ ( , )

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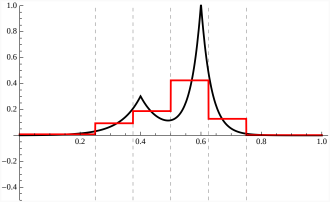
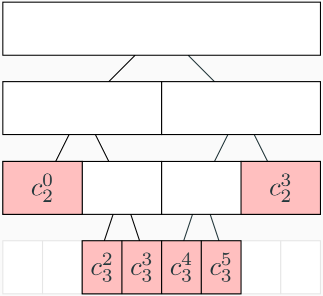
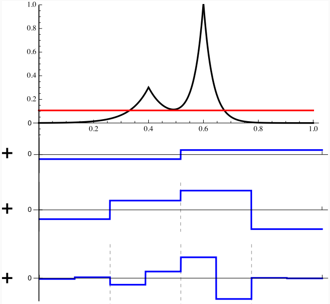




$$|f\rangle = \sum_{nl} c_n^l |\varphi_n^l\rangle$$

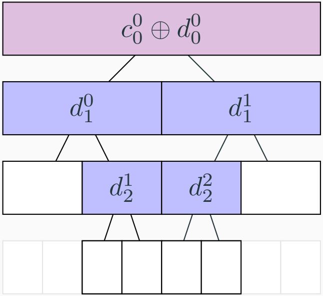
reconstructed representation

MRA - Tree Structure



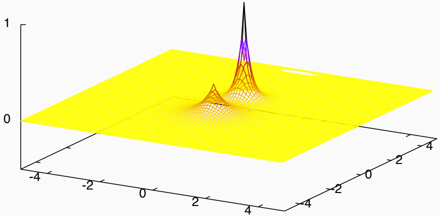
$$|f\rangle = c_0|\varphi_0\rangle + \sum_{nl} d_n^l |\psi_n^l\rangle$$

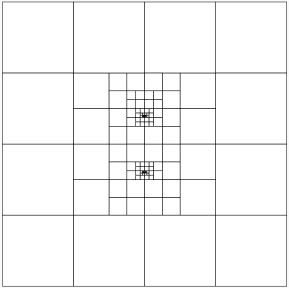
$$\varphi_n^l \in V_n^l, \quad \psi_n^l \in W_n^l$$



compressed representation

MRA - Beyond One Dimension





N-dimensional MRA with k scaling functions :

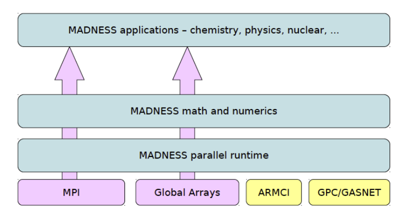
2^N children for each box $\rightarrow$ Regularization

k^N coefficients for each box $\rightarrow$ Low-Rank decomposition

MADNESS

$$\left(-\frac{\Delta}{2}+\hat{\mathrm{V}}\right)|\Psi\rangle = E|\Psi\rangle$$

MADNESS (www.github.com/m-a-d-n-e-s-s)[1]



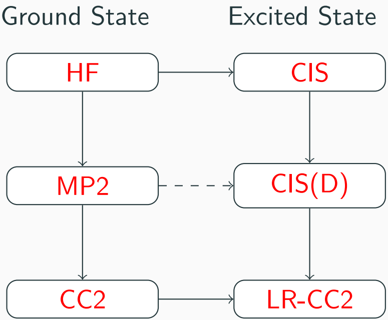
$$\Psi\left(x\right) = -2\int \mathrm{d}x\, G\left(x-x'\right)\left(\hat{\mathrm{V}}\Psi\right)\left(x'\right)$$

$$\left(\Delta-2E\right)G\left(x\right)=\delta\left(x\right)$$

Lecture notes online[2]

[1] R. J. Harrison *et al.*, *SIAM J. Sci. Comput.*,38:5, **2016**.
[2] https://sites.google.com/view/numericalquantumchemistry2018/lecture-notes

MADNESS



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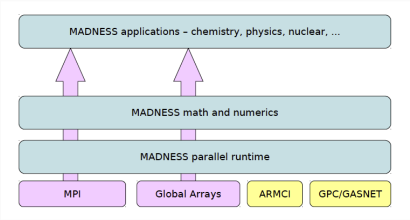

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Real-Space Coupled-Cluster

Real-Space Coupled-Cluster

$$\mathcal{H}|0\rangle = E|0\rangle$$

Reference Wavefunction $|0\rangle$

$$\mathcal{H} = e^{-\hat{\mathcal{T}}_1 - \hat{\mathcal{T}}_2 - \dots} \hat{\mathrm{H}} e^{\hat{\mathcal{T}}_1 + \hat{\mathcal{T}}_2 + \dots}$$

Cluster-Operators $\hat{\mathcal{T}}_1,\ \hat{\mathcal{T}}_2, \dots$

Real-Space Coupled-Cluster - First Quantized Formalism

Conventional coupled-cluster: Solve for amplitudes

$$t_i^a, t_{ij}^{ab} \in \mathbb{R}$$

Real-space form of coupled-cluster: Solve for cluster-functions[1]

$$|\tau_i\rangle \in L^2\left(\mathbb{R}^3\right), \qquad |\tau_{ij}\rangle \in L^2\left(\mathbb{R}^6\right)$$

Projectors to ensure orthogonality to reference states ϕ_i

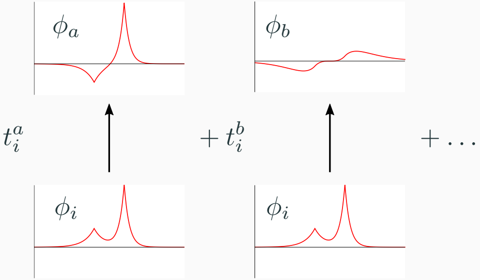
$$\mathcal{Q} = 1 - \sum_i |\phi_i\rangle\langle\phi_i|$$

[1] R. Bukowski, B. Jeziorski and K. Szalewicz, *J. Chem. Phys.*, 110(9), **1999**.

Fixed-basis formalism

Reference calculation: occupied orbitals and also virtual orbitals

$\hat{\mathcal{T}}_n$ replaces
n occupied orbitals
by
n virtual orbitals



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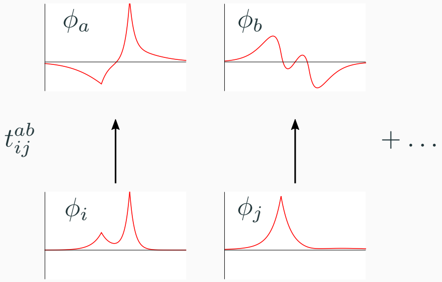

Real-space formalism

Reference calculation: occupied orbitals

$\hat{\mathcal{T}}_n$ replaces
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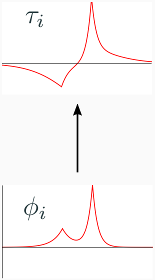

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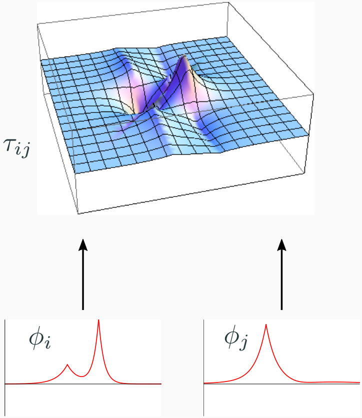


Real-Space Coupled-Cluster - First Quantized Formalism

cluster-functions and amplitudes

$$|\tau_i\rangle = \sum_a t_i^a |a\rangle$$

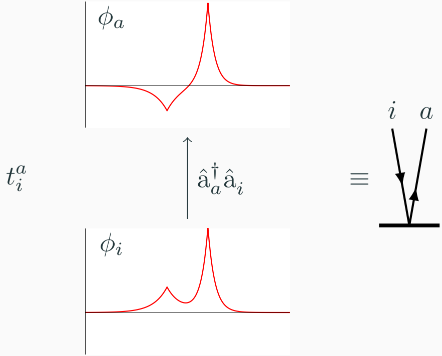
$$|\tau_{ij}\rangle = \sum_{ab} t_{ij}^{ab} |ab\rangle$$

$$\vdots$$

Diagrammatic Expansion

$$|a\rangle = \mathcal{Q}|a\rangle, \quad \langle a|\tau_i\rangle \equiv t_i^a, \quad \langle a|a'\rangle \equiv \delta_{aa'}$$

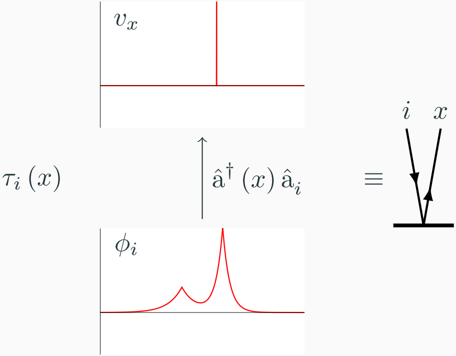
$$\hat{\mathcal{T}}_1 = \sum_{ia} t_i^a \hat{a}_a^\dagger \hat{a}_i$$



Diagrammatic Expansion

$$|v_x\rangle = \mathcal{Q}|x\rangle, \quad \langle x|\tau\rangle = \tau(x), \quad \langle x'|x\rangle = \delta(x - x')$$

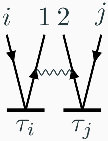
$$\hat{\mathcal{T}}_1 = \sum_i \int \mathrm{d}x \; \tau_i(x)\, \hat{\mathrm{a}}^\dagger(x)\, \hat{\mathrm{a}}_i$$



Diagrammatic Expansion

Real-space interpretation of diagrams:

- Only differs for virtual lines
- Summation over virtual indices → integration over function variable
- Virtual lines carry $\mathcal{Q}$ projectors



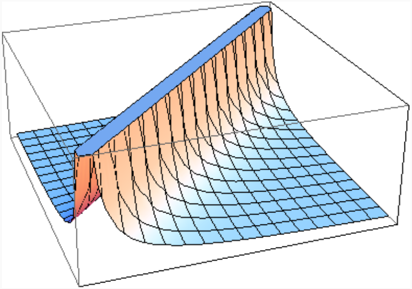
$$= \int \mathrm{d}x_1' \int \mathrm{d}x_2' \mathcal{Q}_{12} \langle x_1 x_2 | \frac{1}{r_{12}} | x_2' x_3' \rangle \tau_i \left(x_1' \right) \tau_j \left(x_2' \right)$$

$$= \mathcal{Q}_{12} \frac{1}{r_{12}} \tau_i \left(x_1 \right) \tau_j \left(x_2 \right)$$

$$r_{12} = \| x_1 - x_2 \|$$

Singularities

- Electron-repulsion: 3D subspace of 6D space

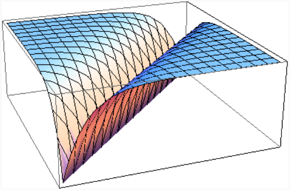


Need regularization to avoid the direct representation of $\dfrac{1}{r_{12}}$

Regularization

$$\left[\hat{\mathrm{T}}_{12}, f_{12}\right] = \mathcal{U}_{12} - \frac{1}{r_{12}}$$ cancels $\frac{1}{r_{12}}$ in the main equations

$$f_{12} = \frac{1}{2}\left(1 - e^{-r_{12}}\right)$$



Similar to explicitly correlated methods in LCAO

W. Kutzelnigg, *Theoret. Chim. Acta*, 68(6), **1985**.
W. Klopper *et al.*. *Int. Rev. Phys. Chem.*, 25:3, **2006**.

Regularization

What about the nuclear potential?

Regularization is not crucial but it still helps

Key ideas are similar

F. A. Bischoff, *J. Chem. Phys.*, 141, **2014**.
F. F. Seelig, *Z. Naturforsch. A*, 21, **1966**.

Formal Scaling

Formal scaling N_{occ}^3

Relaxed orbitals and modified projector

$$|t_i\rangle = |i\rangle + |\tau_i\rangle$$

$$\mathcal{Q}^t = 1 - \sum_k |t_k\rangle\langle k|$$

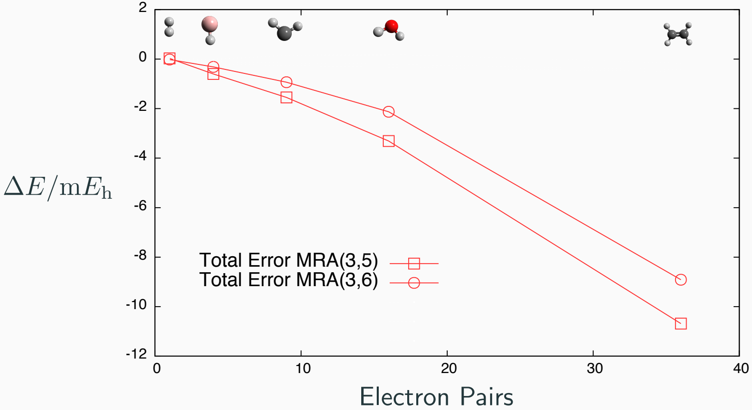
Equivalent to $\hat{\mathcal{T}}_1$ transformed Hamiltonian

Current bottleneck: 6D-MRA for two-body cluster functions

Ground State Correlation Energies

Difference in total correlation energies:

$$\Delta E = \text{MP2-F12/aug-cc-pV6Z} - \text{MP2/MRA(x,k)}$$



Notation: MRA(x,k) $\rightarrow$ MRA threshold of 10^{-x} with k Legendre scaling functions

MP2-F12/aug-cc-pV6Z values obtained with TURBOMOLE

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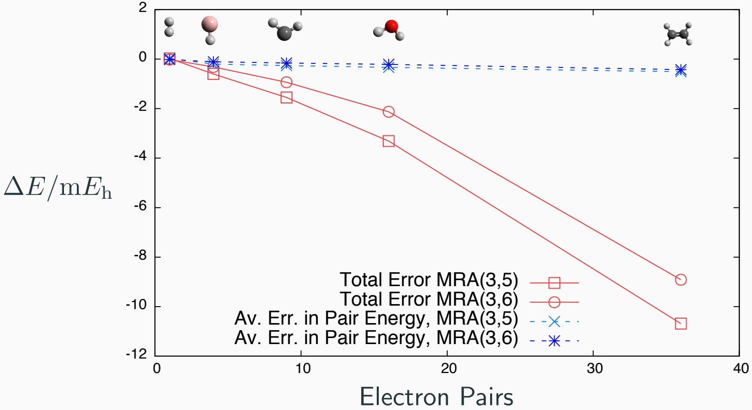

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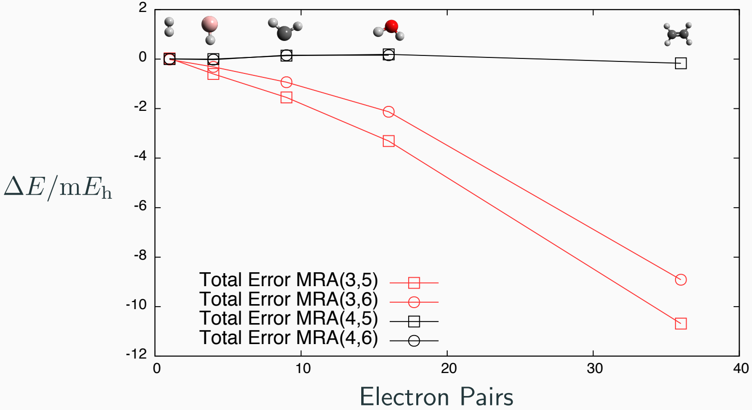
Difference in total correlation energies:

$$\Delta E = \text{MP2-F12/aug-cc-pV6Z} - \text{MP2/MRA(x,k)}$$



Notation: MRA(x,k) $\rightarrow$ MRA threshold of 10^{-x} with k Legendre scaling functions

MP2-F12/aug-cc-pV6Z values obtained with TURBOMOLE

Linear Response CC2

CC2 excitation energies are eigenvalues of the CC2 Jacobian[1,2]

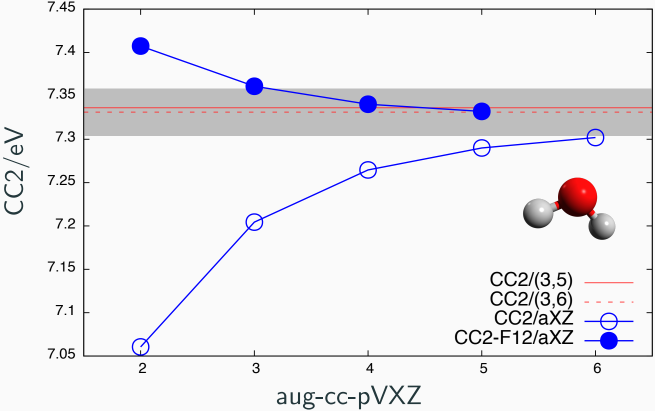
$$\mathbf{A}\mathbf{x} = \omega\mathbf{x}$$

$$\mathbf{A} = \begin{pmatrix} \frac{\partial\Omega_i^a}{\partial t_1} & \frac{\partial\Omega_i^a}{\partial t_2} \\ \frac{\partial\Omega_{ij}^{ab}}{\partial t_1} & \frac{\partial\Omega_{ij}^{ab}}{\partial t_2} \end{pmatrix}$$

Real-space formulation: Take functional derivative of $\Omega\left[\tau\right]$

[1] O. Christiansen, H. Koch and P. Jørgensen. *Chem Phys. Lett.*, 243(5), **1995**
[2] H. Koch, P. Jørgensen, *J. Chem. Phys.*, 93, **1990**

Linear Response CC2 - H_2O Example



CC2 with TURBOMOLE, CC2-F12 with KOALA

Linear Response CC2

- Numerically accurate excitation energies for small molecules
- No error accumulation observed
- No balancing issues between ground and excited state
- Accurate representation of one- and two-body terms

PNO-MRA

PNO-MRA - Key Idea

Represent the pair functions by pair natural orbitals (PNOs)

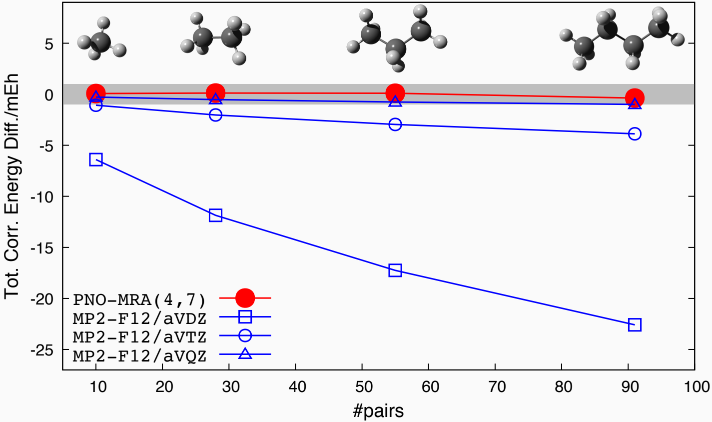
$$|\tau_{ij}\rangle = \sum_{ab} t_{a_{ij}b_{ij}} \left(|a_{ij}\rangle \otimes |b_{ij}\rangle\right)$$

Represent and optimize the PNOs with MRA

in colaboration with E. F. Valeev

PNO-MRA - Correlation Energies

Difference in total correlation energies: Reference is MP2-F12/aug-cc-pV6Z

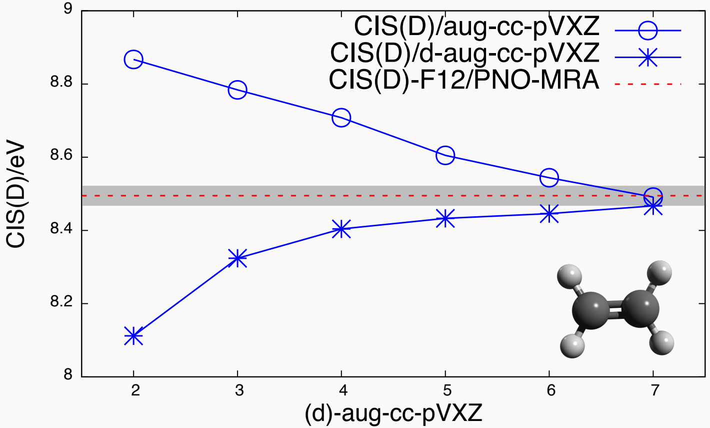


Average PNO ranks:

22 19 17 15

PNO-MRA - Excitation Energies

Adaptive growing of PNO ranks



Average PNO rank: 43 (canon) or 25 (localized)

Conclusion

Conclusion and Outlook

MRA-CC2[1]

Numerical accuracy is black-box

Exact explicit correlation is crucial

Decreased formal scaling but large prefactor (6D-MRA)

PNO-MRA

3D-MRA for all functions

Low ranks with explicit correlation

Extension to higher excitation levels more straightforward

[1] JSK, F. A. Bischoff, *JCCT*, 13, **2017**

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