Low-scaling *GW* with localized basis sets

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Contents

1. Introduction
2. Space-time with localized basis sets
3. Other techniques for scaling reduction
4. Conclusion

Localized basis sets

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▷ traditionally used in quantum chemistry codes, but also now in solid-state codes

Slater-type orbitals (STOs)

$$\phi^{\mathsf{STO}}(\mathbf{r}) = N r^{n-1} \exp(-\alpha r) Y_{lm}(\Omega)$$

Gaussian type orbitals (GTOs)

$$\phi^{\mathsf{GTO}}(\mathbf{r}) = N r^{l} \exp(-\alpha r^2) Y_{lm}(\Omega)$$

Numeric atom-centered orbitals (NAOs)

$$\phi^{\mathsf{NAO}}(\mathbf{r}) = \frac{u(r)}{r} Y_{lm}(\Omega)$$

- $u(r)$ radial part, numerically tabulated on dense grids
- STOs and GTOs are a special form of an NAO

Why localized basis sets?

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Advantages

- inherent locality can be exploited for low-scaling
- compact virtual space
- excellent for 2D materials → no vacuum "penalty"
- all-electron treatment

Disadvantages

- basis set optimization not trivial
- extrapolation schemes for correlated methods

Why localized basis sets?

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Disadvantages

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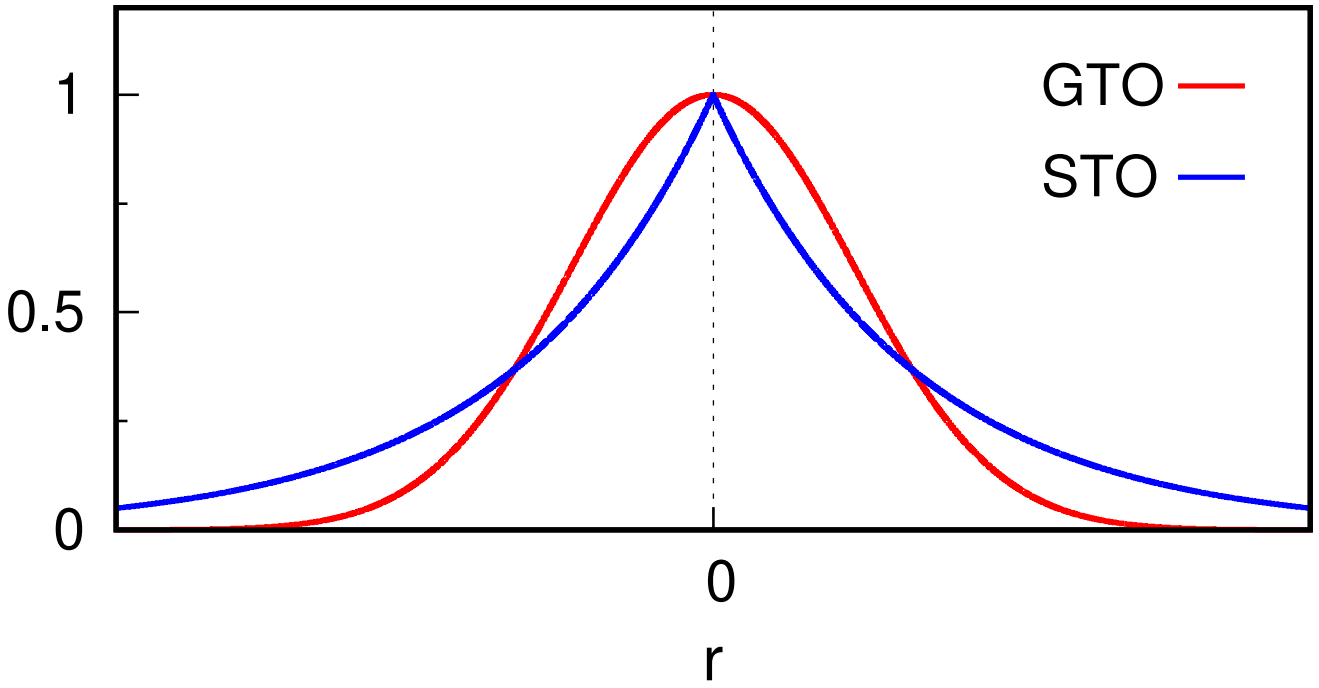
- extrapolation schemes for correlated methods

STOs vs GTOs



- STOs: reasonable "shape", correct cusp behavior and exponential decay
- GTOs: shape wrong, but easy analytic evaluation of Gaussian integrals (Gaussian product theorem)

NAOs

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Radial shape for native NAOs

▷ solve radial Schrödinger equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+v_i(r)+v_{cut}(r)\right]u_i(r)=\epsilon_i u_i(r)$$

Radial shape for e.g. GTOs treated as NAO

▷ tabulate nummerically

$$u(r)=N^{-1}r^{l+1}\exp\left(-\alpha r^2\right)$$

- correct shape of radial part
- compact
- numerical integration

FHI-aims The ab initio materials simulation package

Blum *et al.* Comp. Phys. Comm. 180 (**2009**), 2175

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Space-time method

Original scheme

$$\chi^0(\mathbf{r},\mathbf{r}'+\mathbf{R},i\tau) \longrightarrow \chi^0_{\mathbf{GG}'}(\mathbf{q},i\omega) \longrightarrow \epsilon_{\mathbf{GG}'}(\mathbf{q},i\omega) = \delta_{\mathbf{GG}'} - v_{\mathbf{GG}'}(\mathbf{q})\chi^0_{\mathbf{GG}'}(\mathbf{q},i\omega) \longrightarrow W_{\mathbf{GG}'}(\mathbf{q},i\omega) = \epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},i\omega)v_{\mathbf{GG}'}(\mathbf{q})$$

$$\downarrow$$

$$\Sigma_n(\omega) \xleftarrow{\text{AC}} \Sigma_n(i\omega) \longleftarrow \Sigma(\mathbf{r},\mathbf{r}'+\mathbf{R},i\tau) = iG(\mathbf{r},\mathbf{r}'+\mathbf{R},i\tau)W(\mathbf{r},\mathbf{r}'+\mathbf{R},i\tau) \longleftarrow W(\mathbf{r},\mathbf{r}'+\mathbf{R},i\tau)$$

Rojas, Godby, Needs, PRL, 74 (**1995**), 1827

Space-time method

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Original scheme

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Why change to $\mathbf{G},\mathbf{G}'$ basis?

$$\epsilon(\mathbf{r},\mathbf{r}',i\omega) = \delta(\mathbf{r},\mathbf{r}') - \int d\mathbf{r}''\, v(\mathbf{r},\mathbf{r}'')\,\chi^0(\mathbf{r}'',\mathbf{r}',i\omega)$$

$$\epsilon^{-1}(\mathbf{r},\mathbf{r}',i\omega) = \delta(\mathbf{r},\mathbf{r}') + \int d\mathbf{r}''\, v(\mathbf{r},\mathbf{r}'')\,\chi^0(\mathbf{r}'',\mathbf{r}',i\omega) + \ldots$$

$\rightarrow$ grows as N^3_{grid}; in PW basis $O(N^2)$

Rojas, Godby, Needs, PRL, 74 (**1995**), 1827

Scaling of original space-time method

$$G(\mathbf{r},\mathbf{r}',i\tau) = \begin{cases} i\sum_{i}^{\text{occ}} \psi_i(\mathbf{r})\psi_i(\mathbf{r}')\exp(\varepsilon_i\tau)\,, & \tau > 0 \\ -i\sum_{a}^{\text{virt}} \psi_a(\mathbf{r})\psi_a(\mathbf{r}')\exp(\varepsilon_a\tau)\,, & \tau < 0 \end{cases}$$

$$\mathcal{O}(N_{\text{grid}}^2(N_{\text{occ}} + N_{\text{virt}})) = \mathcal{O}(N^3)$$

$$\chi^0(\mathbf{r},\mathbf{r}',i\tau) = -iG(\mathbf{r},\mathbf{r}',i\tau)G(\mathbf{r},\mathbf{r}',-i\tau)$$

$$\mathcal{O}(N_{\text{grid}}^2) = \mathcal{O}(N^2)$$

$$\chi^0(\mathbf{r},\mathbf{r}',i\omega) = \text{FT}\left[\chi^0(\mathbf{r},\mathbf{r}',i\tau)\right]$$

$$\mathcal{O}(N_{\text{grid}}^2) = \mathcal{O}(N^2)$$

Figure adapted from: J. Wilhelm, P. Seewald, D. Golze, JCTC, 17 (**2021**), 1662

Adaptation to localized basis sets

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What stays the same?

- $i\tau$ / $i\omega$ and $i\omega$ / $i\tau$ transformations
- $\mathbf{R}$ / $\mathbf{q}$ transformations

Difference

- projection of ϵ, W in localized basis
- projection of G, χ^0 dependent on algorithm

Adaptation to localized basis sets

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Strategy 1 Projection of all quantities in localized basis

a) Global RI with local metric
Wilhelm, Golze, Talirz, Hutter, Pignedoli, JPCL, 9 (**2018**), 306
Wilhelm, Seewald, Golze, JCTC, 17 (**2021**), 1662
M. Graml, J. Wilhelm et al.,arxiv 2306.16066 **(2023)**

b) Local RI
Förster, Visscher, JCTC, 16 (**2020**), 7381
LibRPA by Ren et al. arXiv:2307.12029

$$\chi^0_{PQ}(i\tau) \longrightarrow \chi^0_{PQ}(i\omega) \longrightarrow \epsilon_{PQ}(i\omega) \longrightarrow W_{PQ}(i\omega) \longrightarrow W_{PQ}(i\tau)$$

Strategy 2 Introduction of additional $\mathbf{r}_k$ grid for χ^0
Duchemin, Blase, JCTC, 17 (**2021**), 2383

$$\chi^0(\mathbf{r}_k, \mathbf{r}'_k, i\tau) \longrightarrow \chi^0_{PQ}(i\tau) \longrightarrow \chi^0_{PQ}(i\omega) \longrightarrow \epsilon_{PQ}(i\omega) \longrightarrow W_{PQ}(i\omega) \longrightarrow W_{PQ}(i\tau)$$

Strategy 1: All quantities in localized basis

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Expansion of KS orbitals $\{\psi_n\}$ in atomic orbitals (AOs) $\{\phi_\mu\}$

$$\psi_n(\mathbf{r}) = \sum_\mu C_{n\mu}\phi_\mu(\mathbf{r})$$

Project of G in localized basis

$$G_{\mu\nu}(i\tau) = \begin{cases} i\sum_n^{\text{occ}} C_{n\mu}C_{n\nu}\exp(\varepsilon_n\tau)\,, & \tau > 0\,, \\ -i\sum_n^{\text{virt}} C_{n\mu}C_{n\nu}\exp(\varepsilon_n\tau)\,, & \tau < 0\,. \end{cases}$$

where $G(\mathbf{r},\mathbf{r}',i\tau) = \sum_{\mu\nu}\phi_\mu(\mathbf{r})\,G_{\mu\nu}(i\tau)\,\phi_\nu(\mathbf{r}')$.

Global resolution of the identity (RI)

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Expression of AO products $\phi_\mu \phi_\nu$ as

$$\phi_\mu \phi_\nu \approx \sum_P A^P_{\mu\nu} \varphi_P(\mathbf{r})$$

Expansion coefficients

$$A^R_{\mu\nu} = \sum_P (\mu\nu|P) M^{-1}_{PR} \quad \text{with} \quad M_{PQ} = \int d\mathbf{r}\, d\mathbf{r}'\, \varphi_P(\mathbf{r})\, m(\mathbf{r},\mathbf{r}')\, \varphi_Q(\mathbf{r}')$$

3c integral

$$(\mu\nu|P)_m = \int d\mathbf{r}\, d\mathbf{r}'\, \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r})\, m(\mathbf{r},\mathbf{r}')\, \varphi_P(\mathbf{r}')$$

Choice of metric

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Overlap metric (RI-SVS)

$$m_{\mathrm{O}}(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$$

Wilhelm, Golze, Talirz, Hutter, Pignedoli, JPCL, 9 (**2018**), 306

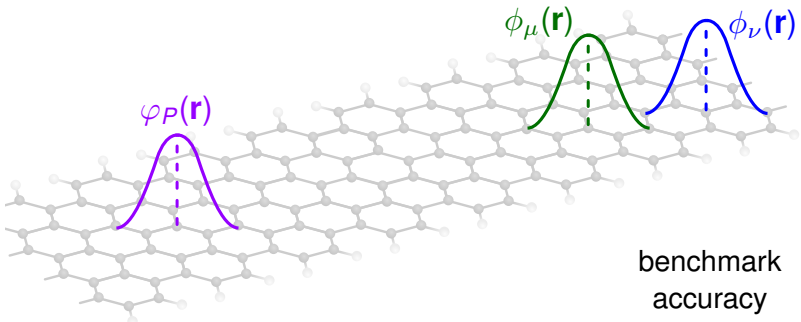
Coulomb metric (RI-V)

$$m_{\mathrm{C}}(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

Truncated Coulomb metric (RI-tC)

$$m_{r_{\mathrm{c}}}(\mathbf{r},\mathbf{r}') = \begin{cases} \dfrac{1}{|\mathbf{r}-\mathbf{r}'|} & \text{if } |\mathbf{r}-\mathbf{r}'| < r_{\mathrm{c}}\,, \\ 0 & \text{else} \end{cases}$$

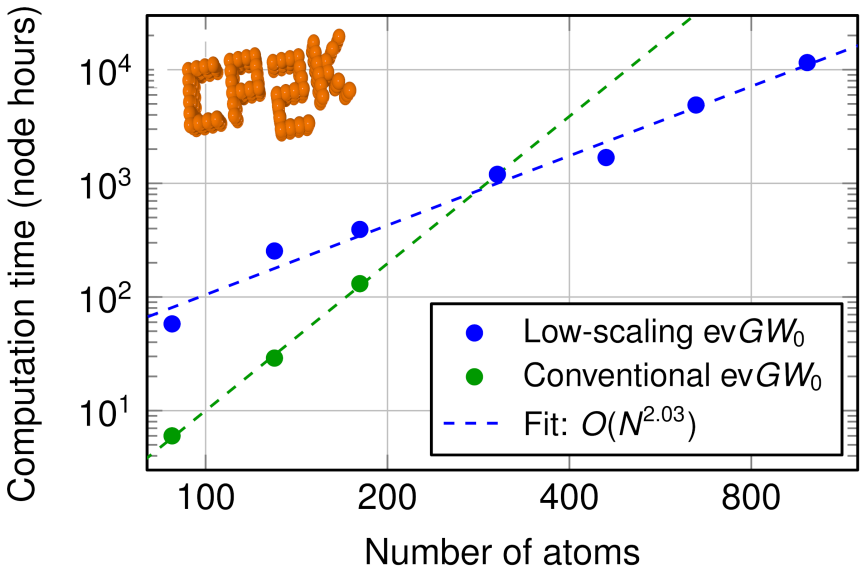
Wilhelm, Seewald, Golze, JCTC, 17 (**2021**), 1662



		benchmark accuracy
overlap metric:	$(\mu\nu\|P)_m \approx 0$	✗
Coulomb metric:	$(\mu\nu\|P)_m \gg 0$	✓
truncated Coulomb metric:	$(\mu\nu\|P)_m \approx 0$	✓

▷ local metric required for low-scaling

Strategy 1a: Global RI with local metric



- highly accurate (<10 meV error)
- up to 1000 atoms

J. Wilhelm, P. Seewald, D. Golze, JCTC, 17 (2021), 1662
M. Graml, J. Wilhelm et al.,arxiv 2306.16066 **(2023)**

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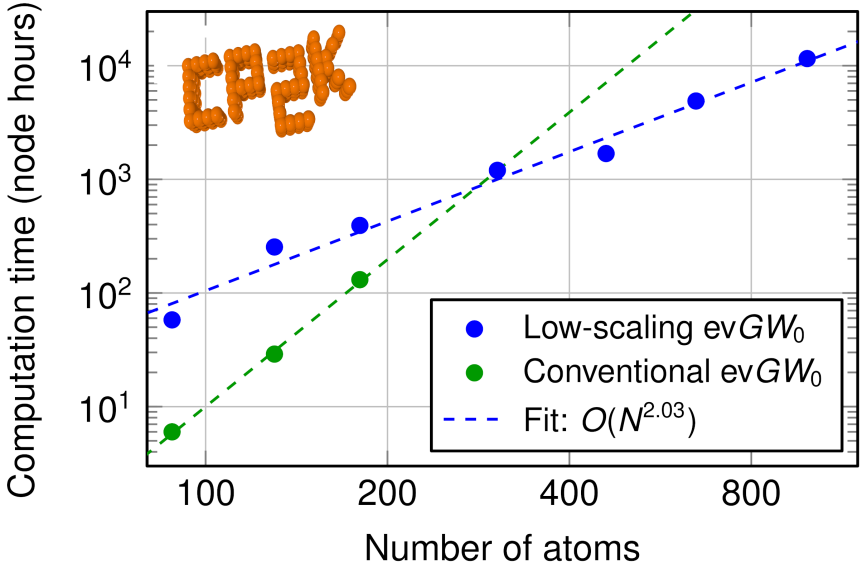

Local RI metric (m = overlap or truncated Coulomb)

$$X_{\mu\sigma P} = \sum_{\lambda} (\underline{\lambda\sigma}|P)_m \, G_{\underline{\mu\lambda}}(i\tau) \qquad \underline{\mathcal{O}(N^2)}$$

$$Y_{\mu\sigma Q} = \sum_{\nu} (\underline{\mu\nu}|Q)_m \, G_{\underline{\nu\sigma}}(-i\tau) \qquad \underline{\mathcal{O}(N^2)}$$

$$\chi^0_{PQ}(i\tau) = -i \sum_{\mu\sigma} X_{\mu\sigma \underline{P}} Y_{\mu\sigma \underline{Q}} \qquad \underline{\mathcal{O}(N^2)}$$

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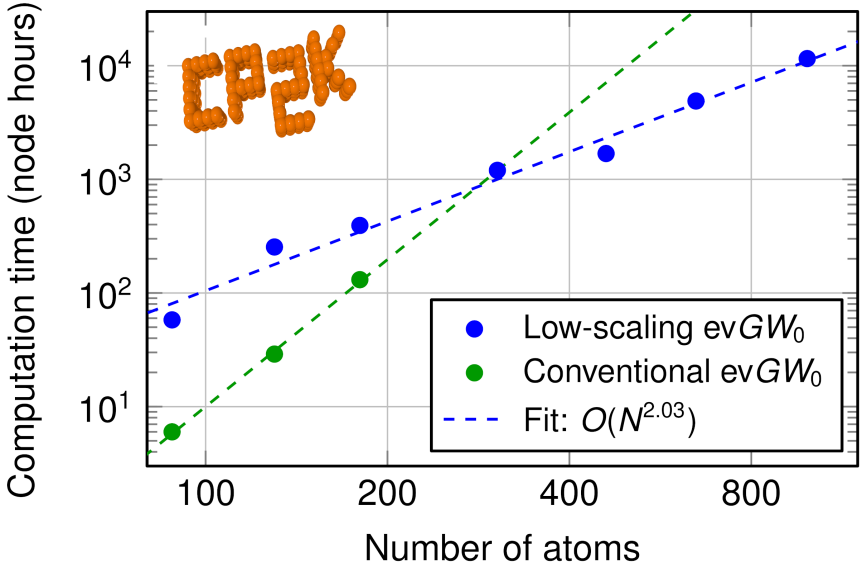

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Sparse tensor-tensor multiplication ☹

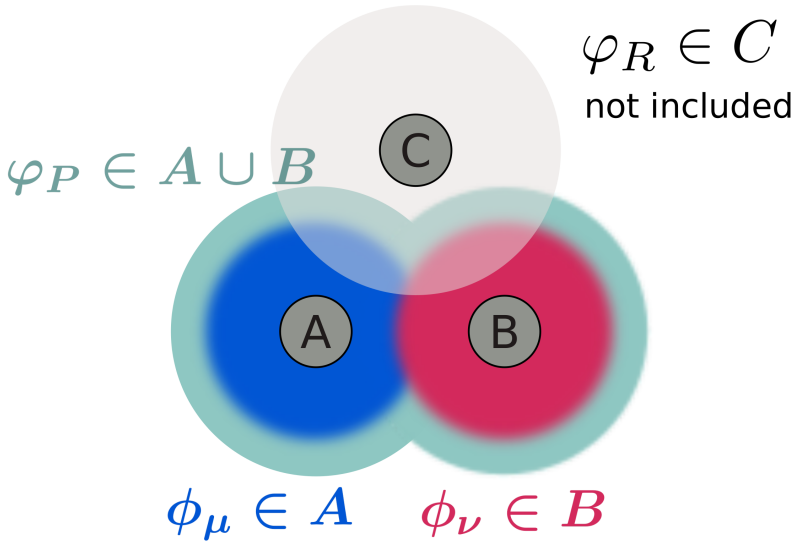
J. Wilhelm, P. Seewald, D. Golze, JCTC, 17 (2021), 1662
M. Graml, J. Wilhelm et al.,arxiv 2306.16066 **(2023)**

Strategy 1b: Local RI

$$\phi_\mu \phi_\nu \approx \sum_{P \in A} A^P_{\mu\nu} \varphi_P(\mathbf{r}) + \sum_{P \in B} A^P_{\mu\nu} \varphi_P(\mathbf{r})$$

- metric: Coulomb
- significantly smaller number of 3c integrals
- no library for sparse tensor multiplications required
- space-time GW codes:
  - ADF (STOs)
  - libRPA (NAOs)

RI-LVL scheme



$$\phi_\mu(\mathbf{r}) \cdot \phi_\nu(\mathbf{r}) = \sum_{P \in A \cup B} A^P_{\mu\nu} \varphi_P(\mathbf{r})$$

Strategy 2: separable RI or real-space RI (RI-RS)

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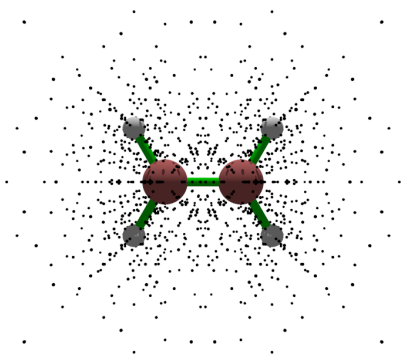
RI-RS expansion coefficients

$$A^P_{\mu\nu} = \sum_k Z_{Pk} \phi_\mu(\mathbf{r}_k) \phi_\nu(\mathbf{r}_k)$$



- r_k... pre-optimized atomic real-space grid
- inspired by interpolative separable density fitting (ISDF)

Obtaining Z_{Pk} coefficients

$$\underset{Z}{\text{argmin}} \sum_{\mu\nu} \sum_P \left([A^P_{\mu\nu}]_{\text{RI-RS}} - [A^P_{\mu\nu}]_{\text{RI-V}} \right)^2$$

RI-RS: Duchemin and Blase, JCP, 150 (**2019**), 174120; JCTC, 17 (**2021**), 2383
ISDF review: JCTC, 19 (2023) 679

Strategy 2: Space-time method with RI-RS

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Polarizability in real-space basis

$$\chi^0_{kk'}(i\tau) = iG(\mathbf{r}_k, \mathbf{r}'_k, i\tau)G(\mathbf{r}'_k, \mathbf{r}_k, -i\tau)$$

Polarizability in auxiliary (NAO) basis

$$\chi^0_{PQ}(i\tau) = \sum_{kk'} M_{Pk}\chi^0(\mathbf{r}_k, \mathbf{r}'_k, i\tau)M_{k'Q} \qquad \text{with} \qquad M_{kP} = \sum_Q Z_{kQ}V^{1/2}_{QP}$$

- matrix-matrix multiplications
- RI-RS coefficients: matrix-matrix multiplications and inversion
- implemented in Fiesta (GTOs) and FHI-aims (NAOs)

Duchemin, Blase, JCTC, 17 (**2021**), 2383

Atomization energies and QP energies using RI-RS

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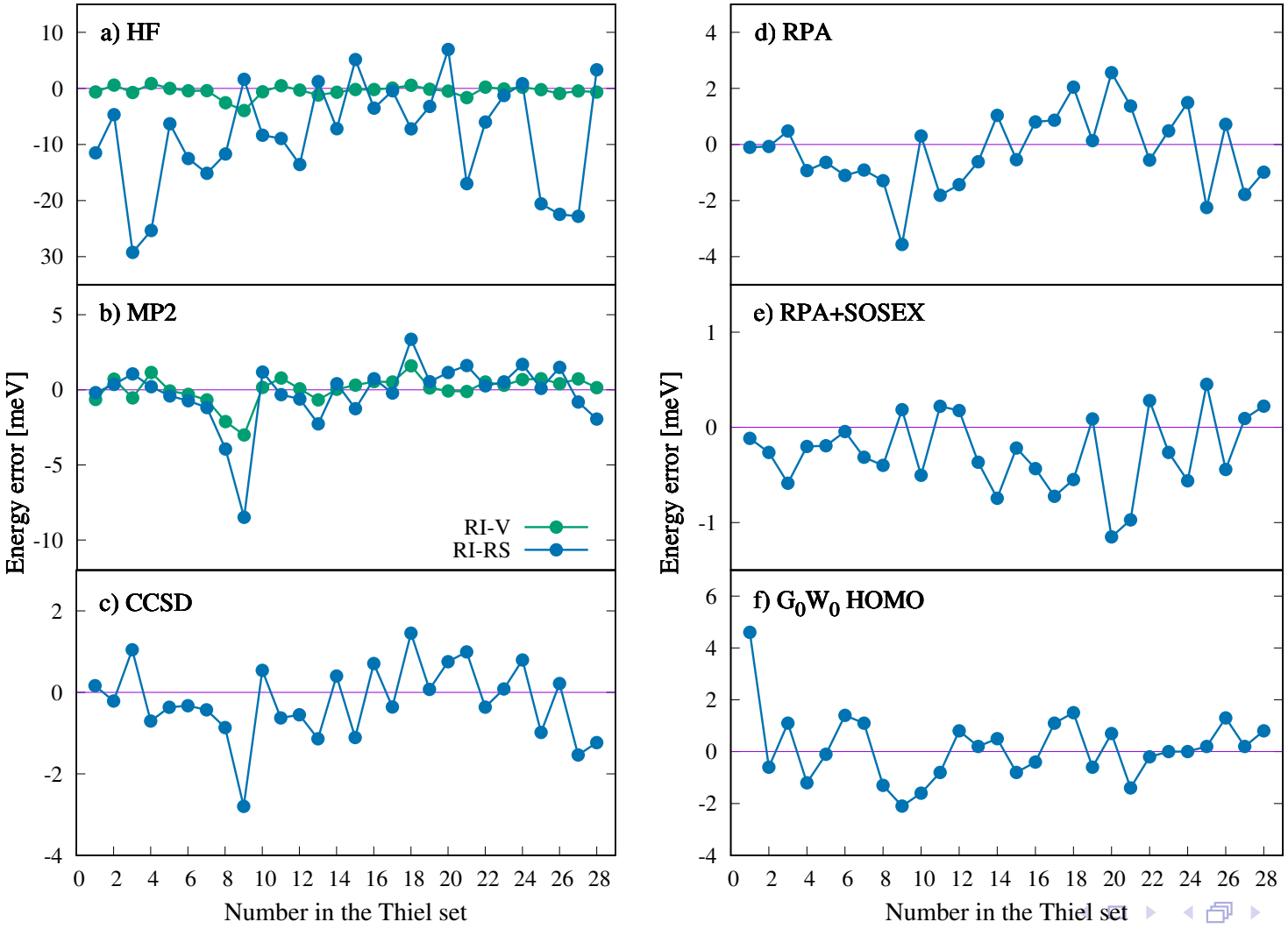
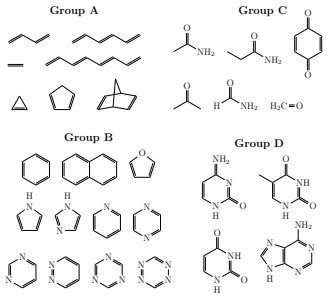
▷ How accurate is the RI-RS approach?



▷ Thiel set



Francisco Antonio Delesma

Prefactor for RI-RS

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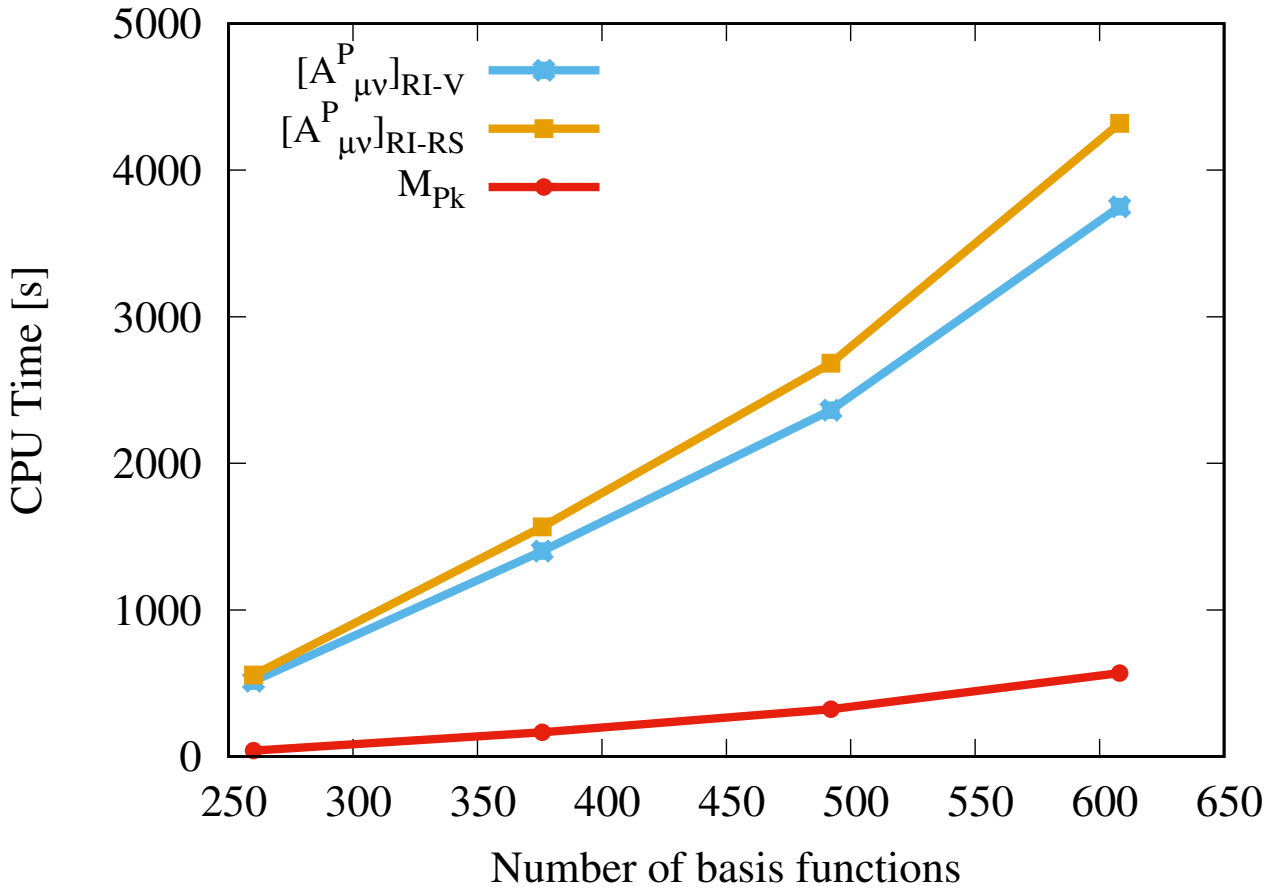
▷ alkane chains with cc-pVTZ basis



FHI-aims The ab initio materials simulation package

F. A. Delesma, D. Golze, P. Rinke, arXiv:2310.11058 **2023**

RI with truncated Coulomb potential (RI-tC)

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Idea

- avoid N^2 to N^3 scaling of RI-V
- replace RI-V reference in RI-RS with RI-tC

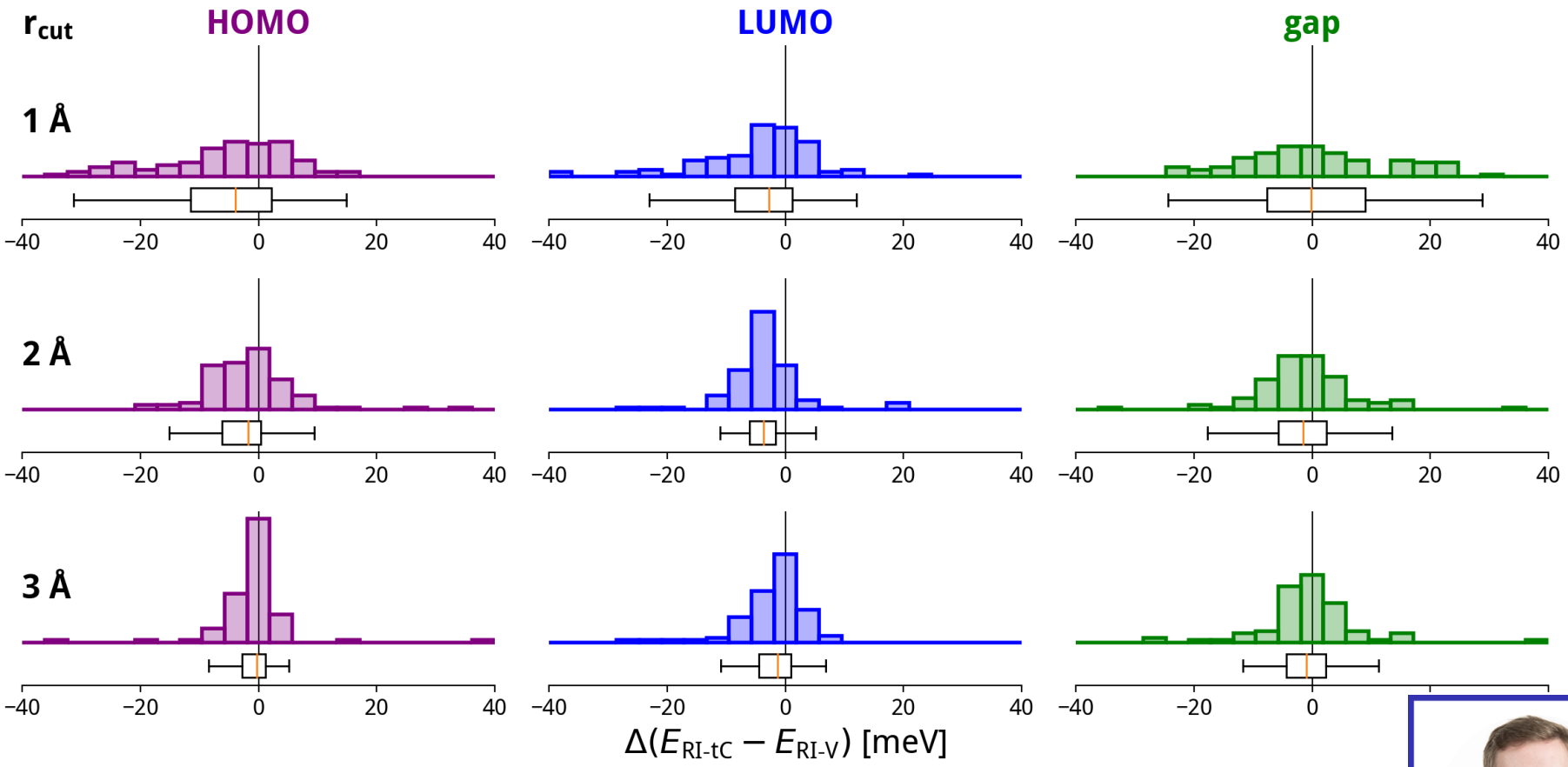
RI-tC metric

$$m_{r_c}(\mathbf{r},\mathbf{r}') = \begin{cases} \dfrac{1}{|\mathbf{r}-\mathbf{r}'|} & \text{if } |\mathbf{r}-\mathbf{r}'| < r_c \\ 0 & \text{else} \end{cases}$$

Alternatives

- attenuated Coulomb
- Yukawa potential

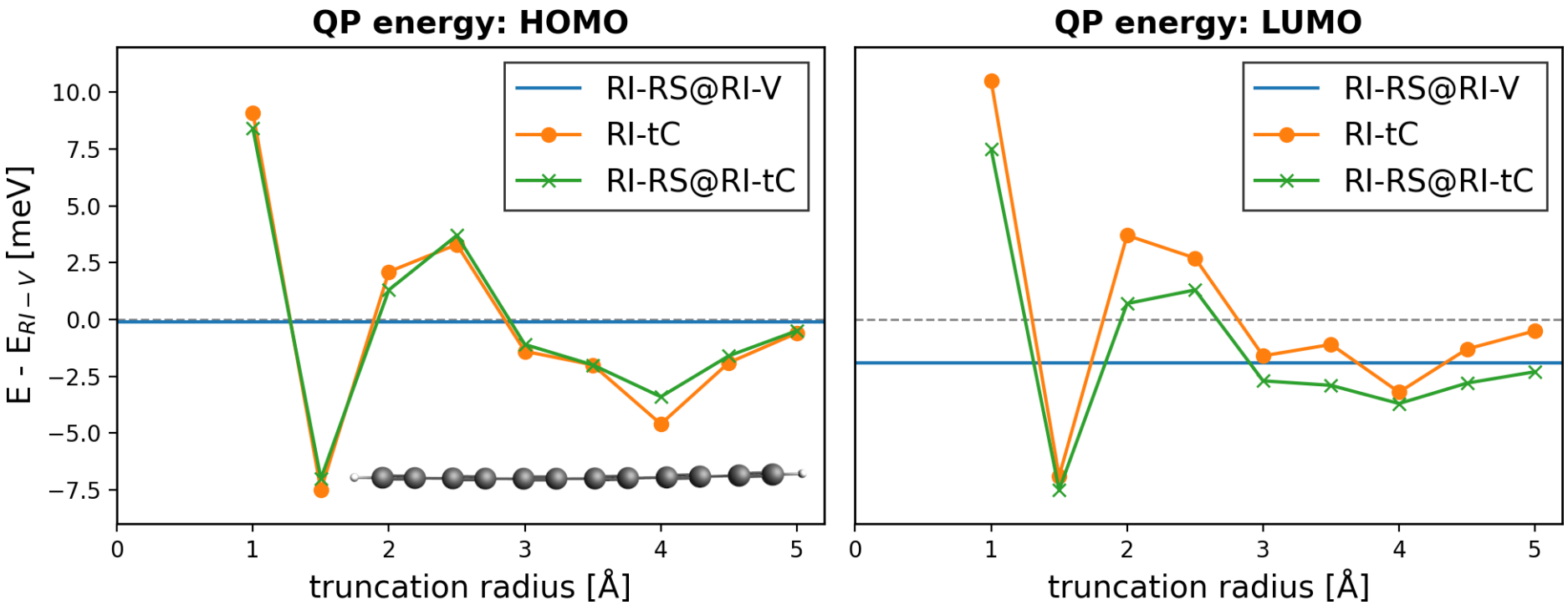
Performance of RI-tC: GW100 test set



- conventional-scaling G_0W_0 with RI-V as reference

Moritz Leucke

Performance of RI-tC: alkene chain



- conventional-scaling G_0W_0 with RI-V as reference
- replacement of RI-V coefficient with RI-tC or RI-RS ones

Moritz Leucke

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Scaling-reduction for core levels

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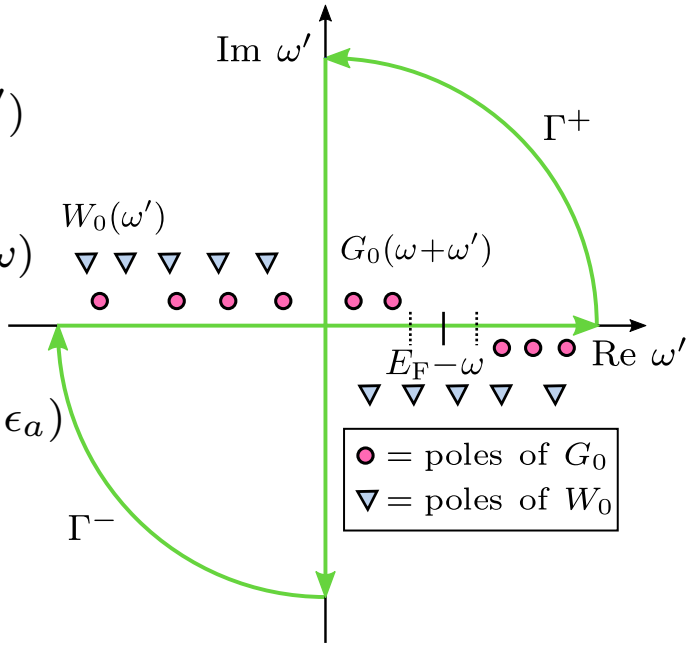
Contour deformation (CD)

$$\Sigma^c(\mathbf{r},\mathbf{r}',\omega) = -\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega' G_0(\mathbf{r},\mathbf{r}',\omega+i\omega')W_0^c(\mathbf{r},\mathbf{r}',i\omega')$$
$$-\sum_i^{\text{occ}} \phi_i(\mathbf{r})\phi_i(\mathbf{r}')W_0^c(\mathbf{r},\mathbf{r}',|\epsilon_i-\omega|+i\eta)\theta(\epsilon_i-\omega)$$
$$+\sum_a^{\text{virt}} \phi_a(\mathbf{r})\phi_a(\mathbf{r}')W_0^c(\mathbf{r},\mathbf{r}',|\epsilon_a-\omega|+i\eta)\theta(\omega-\epsilon_a)$$



Scaling behavior

- integral term: $O(N^4)$
- residue term: $O(N^5)$ for core levels

Golze *et al.*, JCTC, 14 (2018), 4856

FHI-aims The ab initio materials simulation package

Scaling-reduction for core levels

Contour deformation (CD)

$$\Sigma^c(\mathbf{r},\mathbf{r}',\omega) = -\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega' G_0(\mathbf{r},\mathbf{r}',\omega+i\omega')W_0^c(\mathbf{r},\mathbf{r}',i\omega')$$
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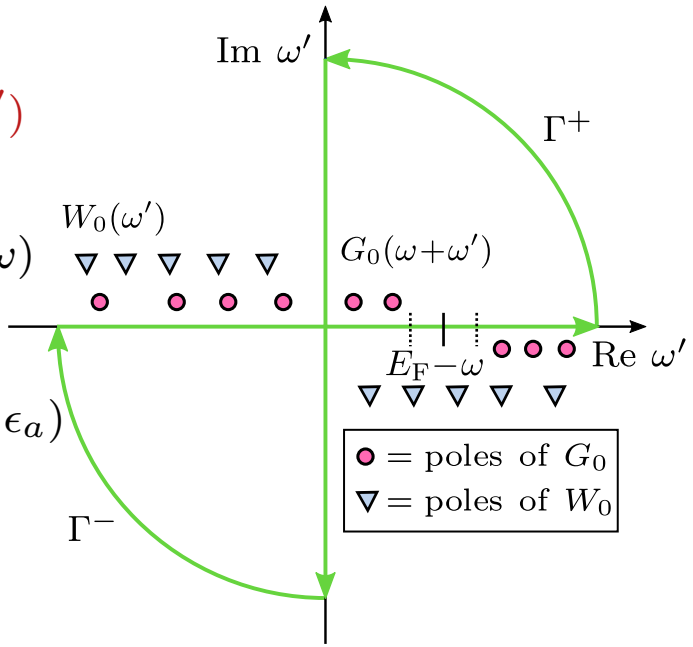

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Scaling-reduction for core levels

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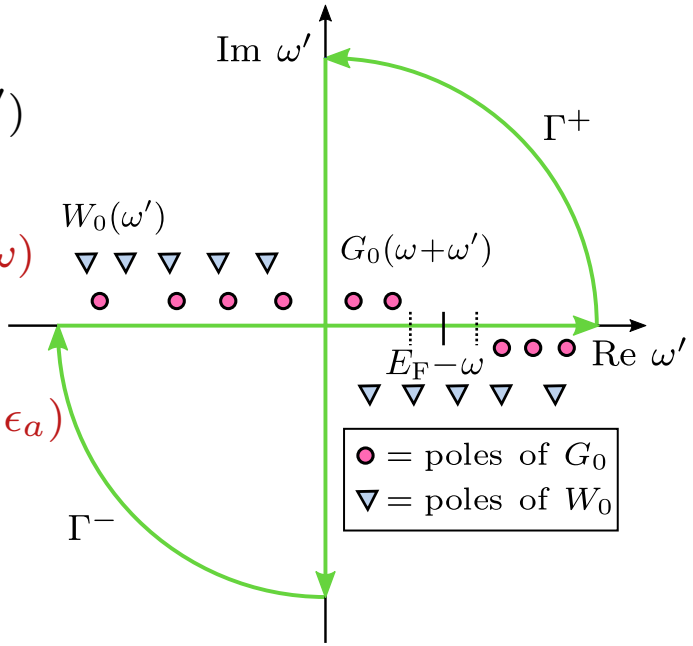
$$+\sum_a^{\text{virt}} \phi_a(\mathbf{r})\phi_a(\mathbf{r}')W_0^c(\mathbf{r},\mathbf{r}',|\epsilon_a-\omega|+i\eta)\theta(\omega-\epsilon_a)$$



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Golze *et al.*, JCTC, 14 (2018), 4856

W analytic continuation (WAC)

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Goal

- find model function for $W_{nm} = \langle nm | W_0^c(\mathbf{r}, \mathbf{r}', \epsilon_m - \omega + i\eta) | mn \rangle$
- overall scaling reduction to $O(N^4)$ for core-levels

Padé approximant

$$W_{nm}(z) \approx \frac{\sum_{i=0}^{(N-1)/2} p_i z^i}{1 + \sum_{i=1}^{N/2} q_i z^i}$$

▷ p_i/q_i calculated from N reference points $(\omega_i, W_{nm}(\omega_i))$

C. Friedrich, PRB, 100 (2019), 075142 and I. Duchemin, X. Blase, JCTC, 16 (2020), 1742

Benchmarks

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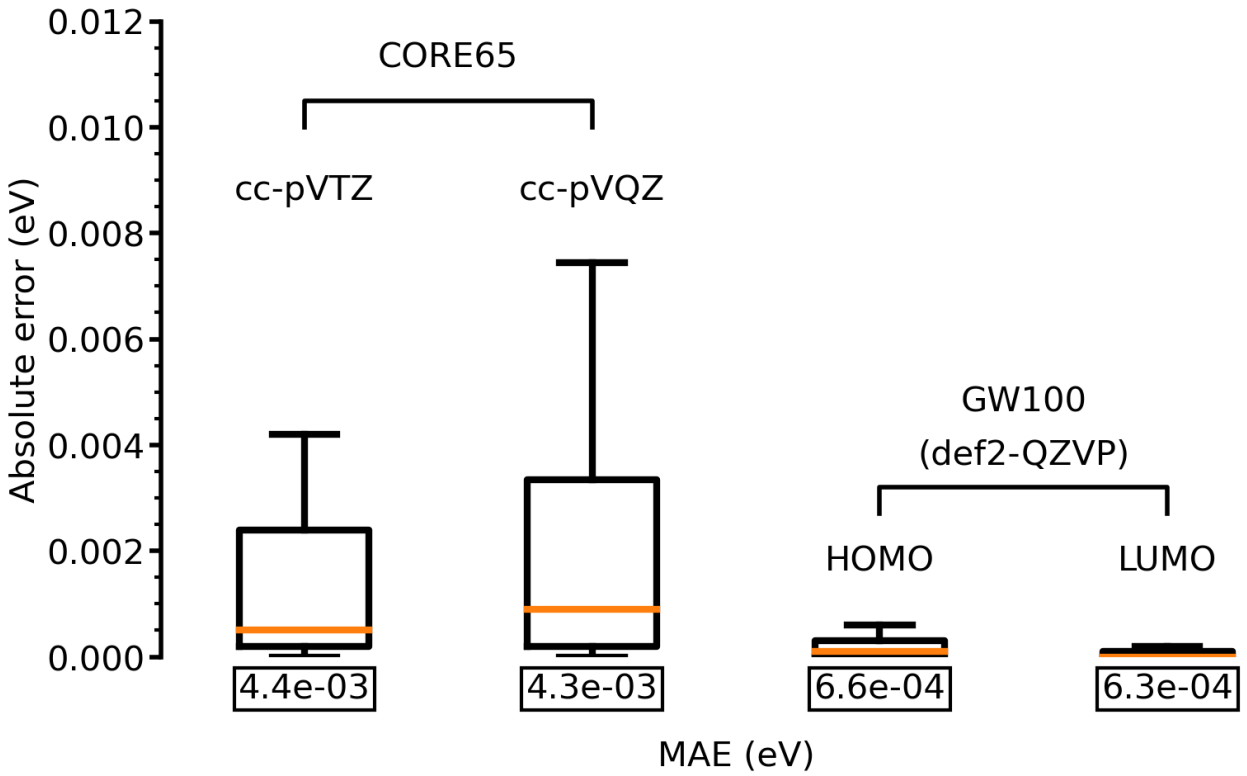
▷ valence and core-level GW benchmark with CD as reference



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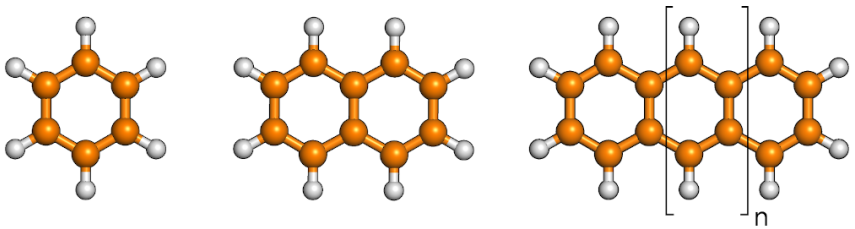
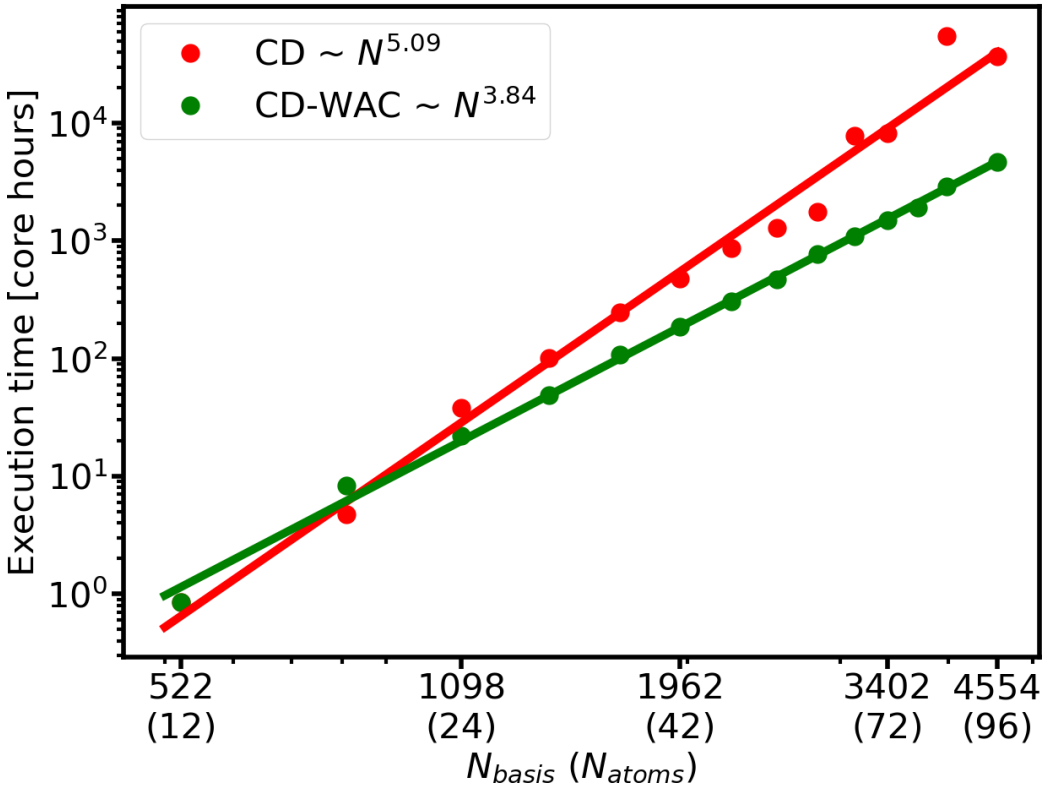
Performance of CD-WAC approach





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2. Space-time with localized basis sets
3. Other techniques for scaling reduction
4. Conclusion

Conclusions

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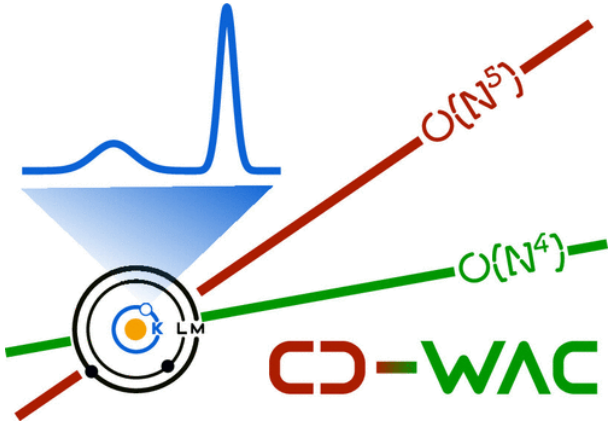
Space-time method & localized basis set

- three different strategies: i) global RI & local metric, ii) local RI & global metric and ii) RI-RS
- up to 1000 atoms; high to good accuracy
- periodic implementations emerging



Other scaling

- CD-WAC: reduction from $O(N^5)$ to $O(N^4)$
- specific to core levels

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