Localized Resolution of Identity

Accurate and efficient evaluation of the Coulomb operator for advanced electronic structure methods

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MAX-PLANCK-GESELLSCHAFT

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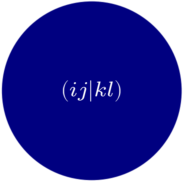
FHI-aims Developers' and Users' Meeting

Why do we need four-center integrals?

$$(ij|kl) = \iint \frac{\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})\varphi_k(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'$$



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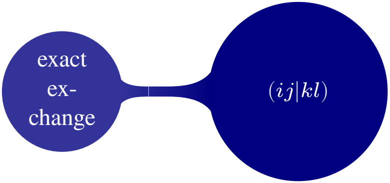

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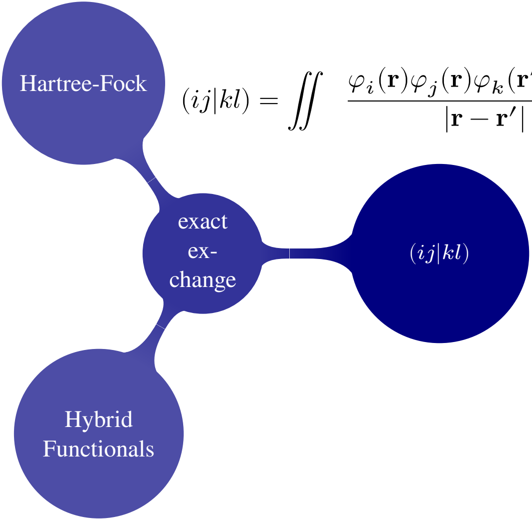

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$$\Sigma^x_\sigma(\mathbf{r},\mathbf{r}') = -\sum_m^{\text{occ}} \frac{\psi_{m\sigma}(\mathbf{r})\psi^*_{m\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$E^x = \frac{1}{2}\sum_{n\sigma}^{\text{occ}} \iint \psi^*_{n\sigma}(\mathbf{r})\Sigma^x_\sigma(\mathbf{r},\mathbf{r}')\psi_{n\sigma}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

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$$\Sigma^x_{ij\sigma} = -\sum_{kl}\sum_{m\sigma}^{\text{occ}} c^{k}_{m\sigma}c^{l*}_{m\sigma} \iint \frac{\varphi^*_i(\mathbf{r})\varphi_k(\mathbf{r})\varphi^*_l(\mathbf{r}')\varphi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$$

$$= -\sum_{kl} D_{kl\sigma}\,(ik|lj)$$

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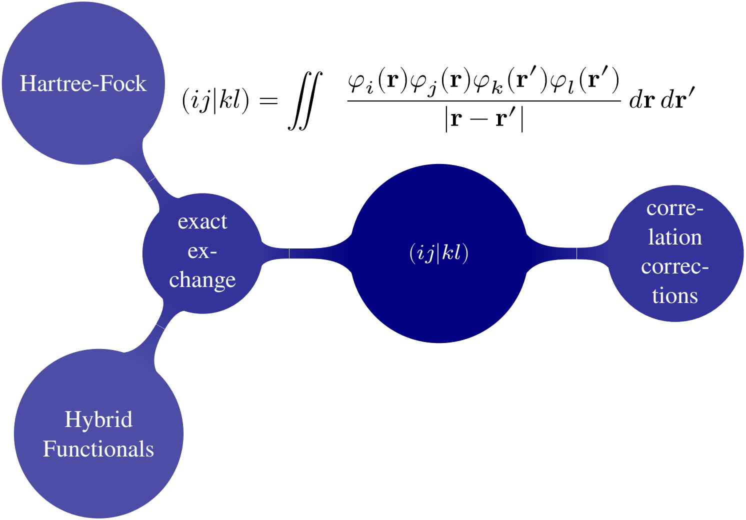

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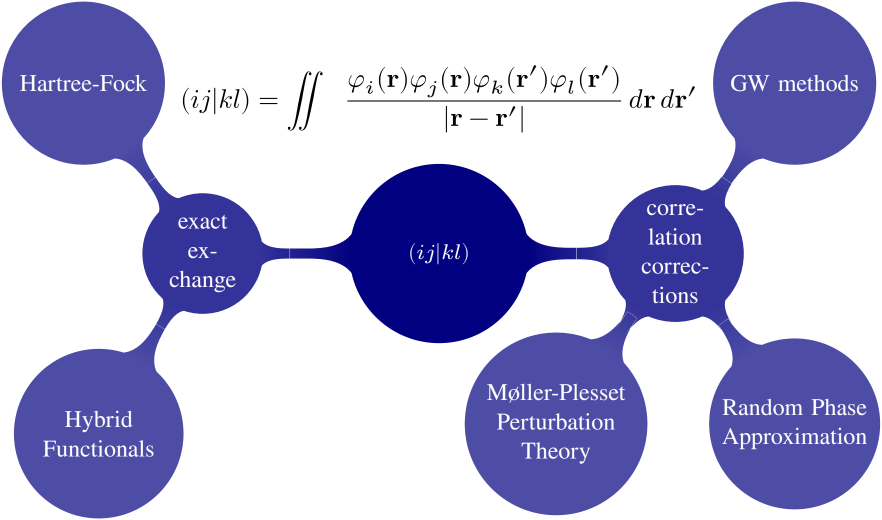

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Hartree-Fock

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GW methods

Numeric atom-centered Orbitals

-strict localization at given radius
-can include correct near-nuclear behavior
-can include correct asymptotic behavior
-no analytic solutions for four-center integrals

Hybrid Functionals

Møller-Plesset Perturbation Theory

Random Phase Approximation

Theoretical framework: RI-V[1]

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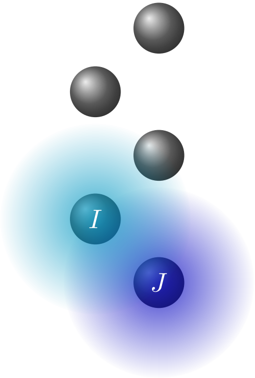
$$\rho_{ij}(\mathbf{r}) = \varphi_i(\mathbf{r})\varphi_j(\mathbf{r})$$



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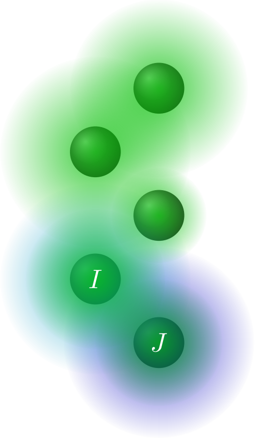

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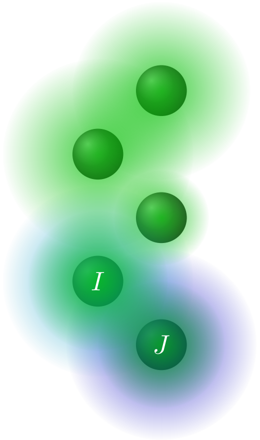

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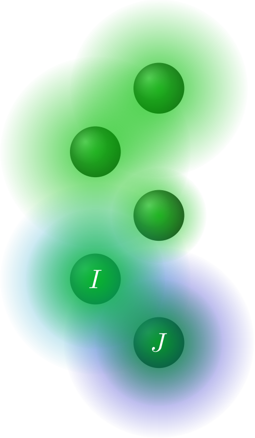

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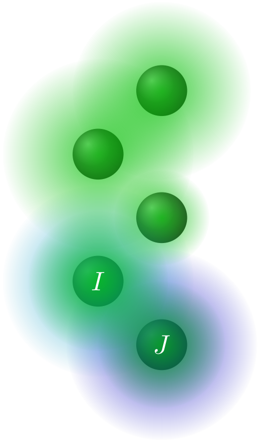

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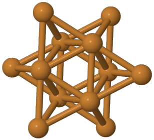

Example: Cu_{12} cluster

(40 basis functions per atom)

$(ij\|kl)$:	395.5 GB
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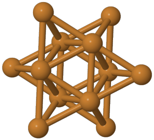

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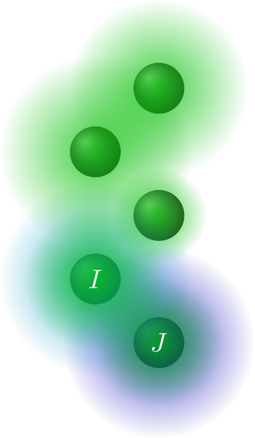

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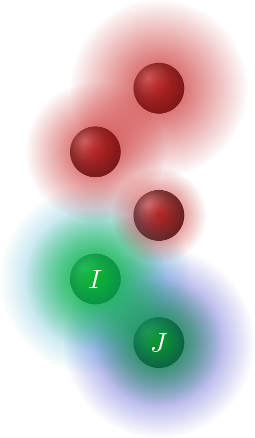

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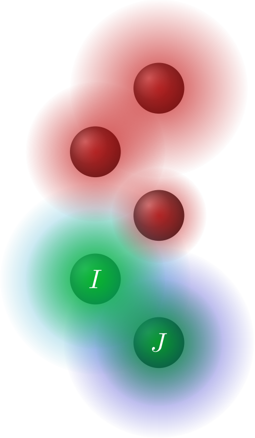

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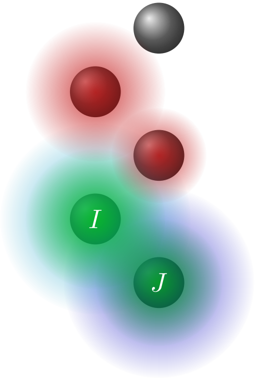

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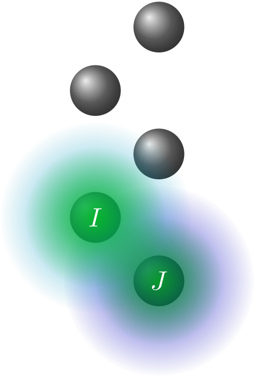

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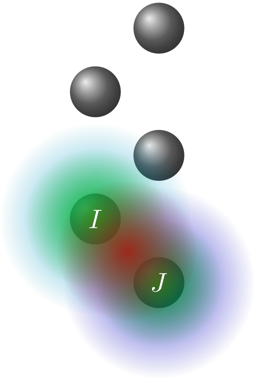

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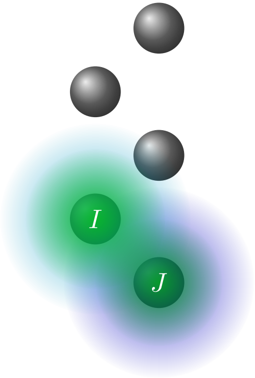

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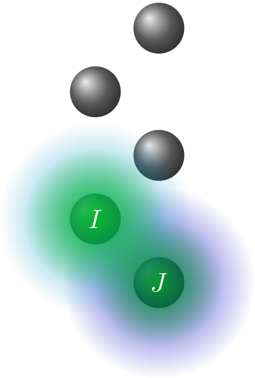

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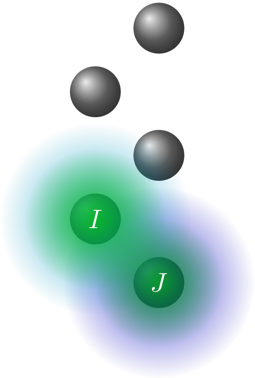

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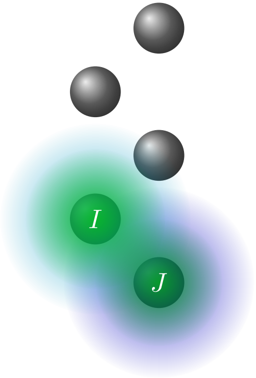
RI-V: $(ij|kl) \approx \sum_{\mu,\nu} (ij|\mu)\, V_{\mu\nu}^{-1}\,(\nu|kl)$



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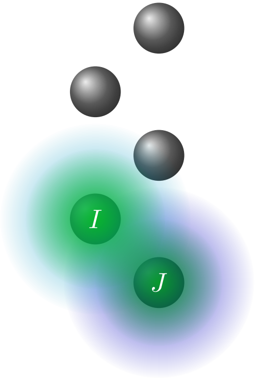
RI-V: $(ij|kl) \approx \sum_{\mu,\nu} (ij|\mu) \, V^{-1}_{\mu\nu} \, (\nu|kl)$



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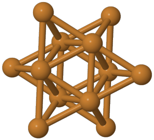

Example: Cu_{12} cluster
(40 basis functions per atom)

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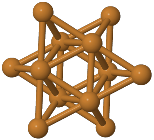
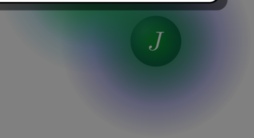
$(ij\|\mu)$ and $(\mu\|\nu)$:	4.2 GB
sparse $(ij\|\mu)$ and $(\mu\|\nu)$:	0.7 GB



$\mu\nu\lambda\sigma \in \mathcal{P}(IJ)$



$$\text{RI-V: } (ij|kl) \approx \sum_{\mu,\nu} (ij|\mu)\, V^{-1}_{\mu\nu}\, (\nu|kl)$$

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Theoretical framework: Auxiliary Basis Construction[1]

radial basis functions $u_{skl}(r)$ of orbital basis set (OBS)

s: species index
k: function index
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→ onsite radial products $u_{sk_1l_1}(r) \cdot u_{sk_2l_2}(r)$

→ maximal angular momenta l_s^{max} per species

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Gram-Schmidt orthonormalization to remove linear dependencies

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l: angular momentum

onsite radial products $u_{sk_1l_1}(r) \cdot u_{sk_2l_2}(r)$

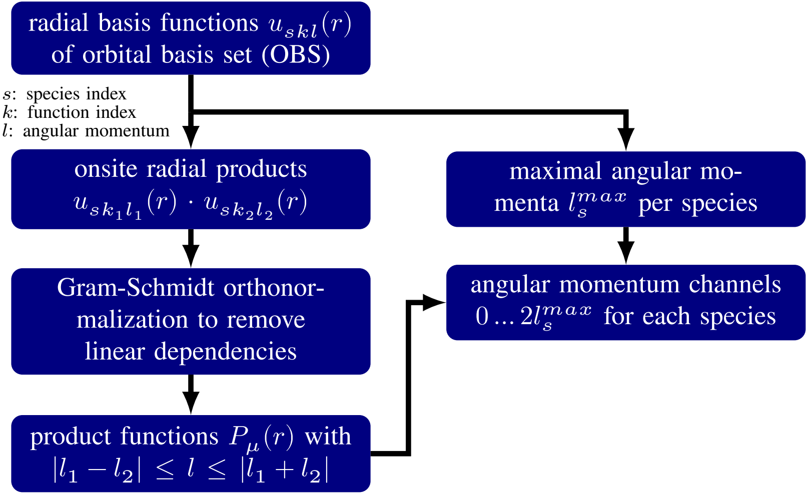
Gram-Schmidt orthonormalization to remove linear dependencies

product functions $P_\mu(r)$ with $|l_1 - l_2| \leq l \leq |l_1 + l_2|$

maximal angular momenta l_s^{max} per species

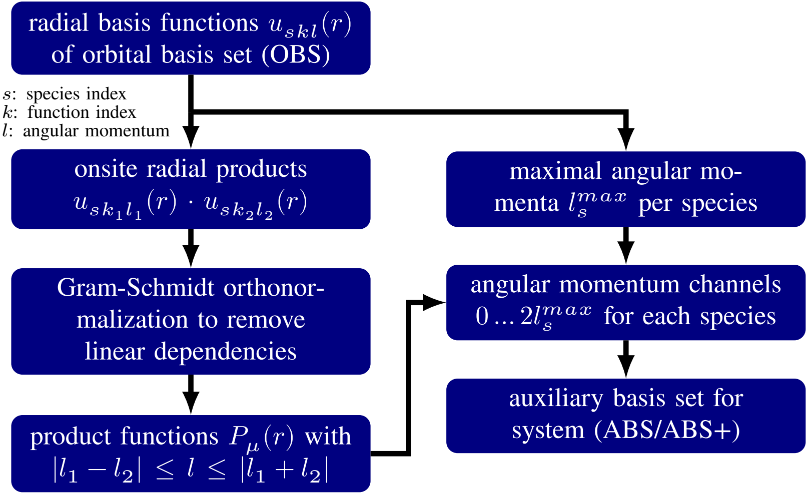
[1] Xinguo Ren et al., *New Journal of Physics* 5, (2012).

Theoretical framework: Auxiliary Basis Construction[1]



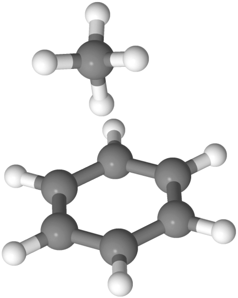
[1] Xinguo Ren et al., *New Journal of Physics* 5, (2012).

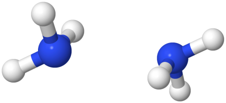
Theoretical framework: Auxiliary Basis Construction[1]

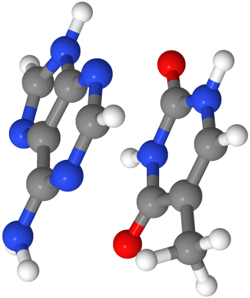


[1] Xinguo Ren et al., *New Journal of Physics* 5, (2012).

Accuracy I - The S22 test set

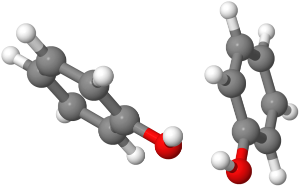


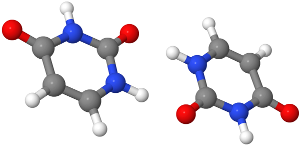




Accuracy Analysis I

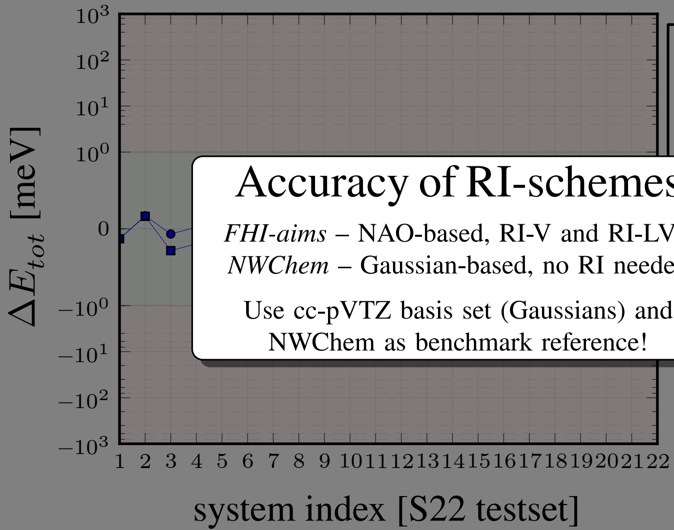
The S22[1] test set





[1] Petr Jurečka et al., *Phys. Chem. Chem. Phys.* 17, (2006).

Accuracy of RI schemes in FHI-aims with a cc-pVTZ basis



Accuracy of RI-schemes

FHI-aims – NAO-based, RI-V and RI-LVL

NWChem – Gaussian-based, no RI needed

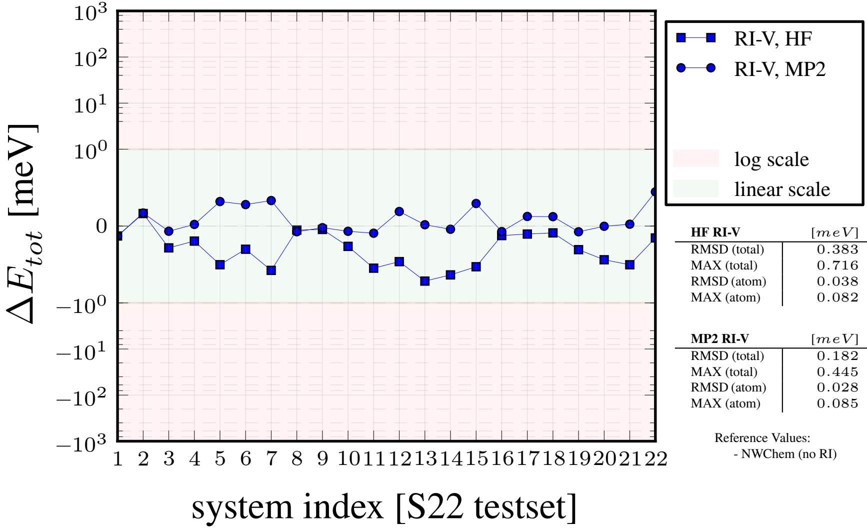
Use cc-pVTZ basis set (Gaussians) and NWChem as benchmark reference!

…I-V	$[meV]$
…D (total)	0.383
… (total)	0.716
…D (atom)	0.038
… (atom)	0.082

…RI-V	$[meV]$
…MSD (total)	0.182
MAX (total)	0.445
RMSD (atom)	0.028
MAX (atom)	0.085

Reference Values:
- NWChem (no RI)

Accuracy of RI schemes in FHI-aims with a cc-pVTZ basis

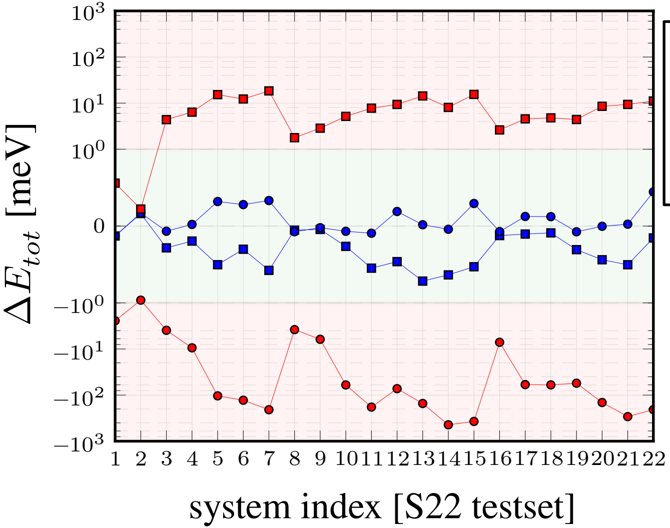


HF RI-V	$[meV]$
RMSD (total)	0.383
MAX (total)	0.716
RMSD (atom)	0.038
MAX (atom)	0.082

MP2 RI-V	$[meV]$
RMSD (total)	0.182
MAX (total)	0.445
RMSD (atom)	0.028
MAX (atom)	0.085

Reference Values:
- NWChem (no RI)

Accuracy of RI schemes in FHI-aims with a cc-pVTZ basis

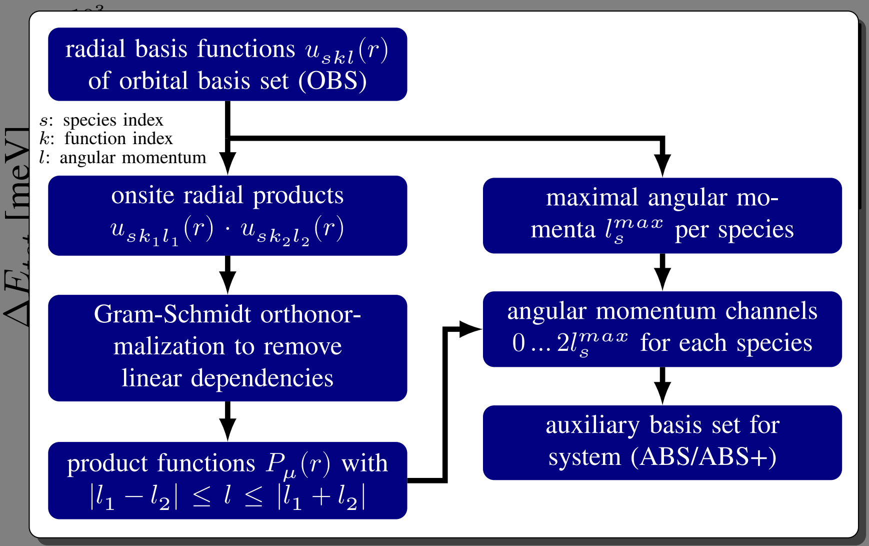


HF RI-LVL	$[meV]$
RMSD (total)	9.129
MAX (total)	18.423
RMSD (atom)	0.743
MAX (atom)	1.062

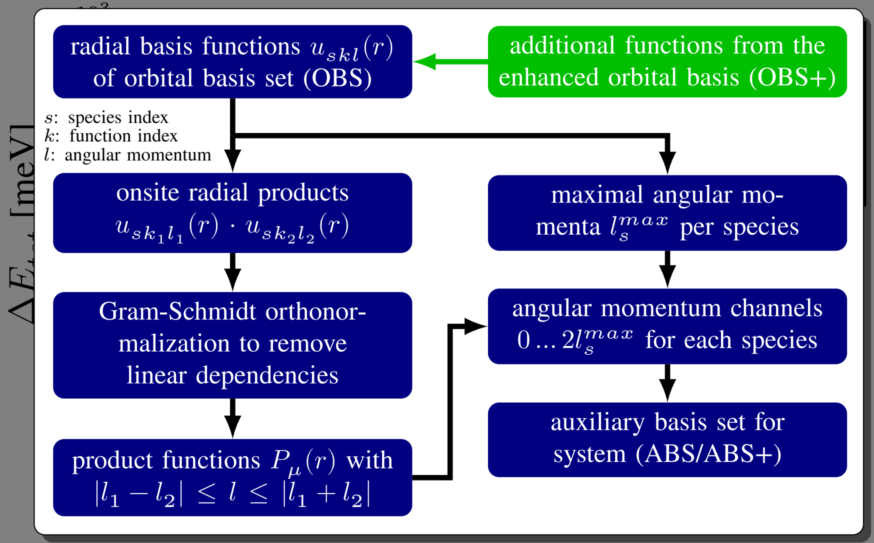
MP2 RI-LVL	$[meV]$
RMSD (total)	168.995
MAX (total)	440.565
RMSD (atom)	11.432
MAX (atom)	29.371

Reference Values:
- NWChem (no RI)

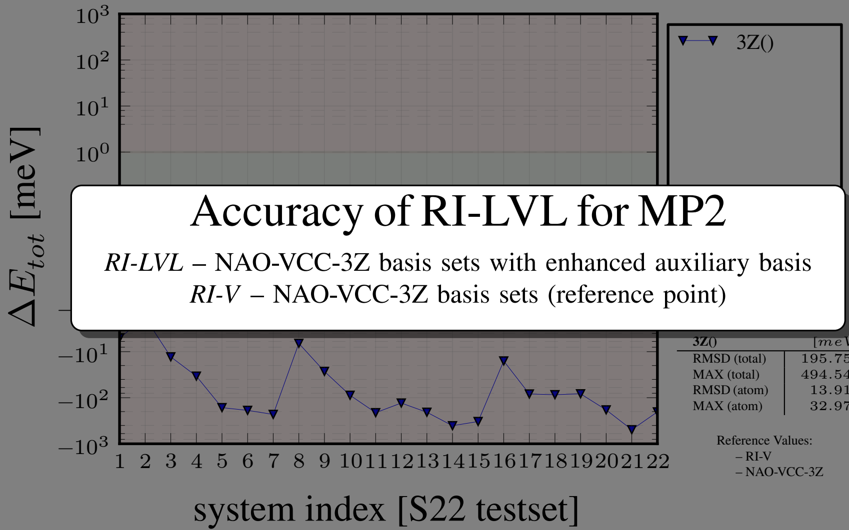
Accuracy of RI schemes in FHI-aims with a cc-pVTZ basis



Accuracy of RI schemes in FHI-aims with a cc-pVTZ basis



RI-LVL convergence for MP2



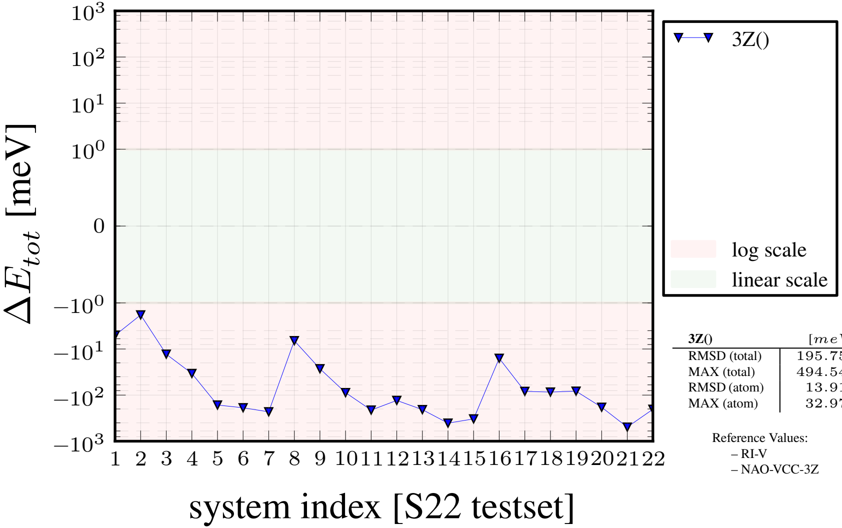
Accuracy of RI-LVL for MP2

RI-LVL – NAO-VCC-3Z basis sets with enhanced auxiliary basis
RI-V – NAO-VCC-3Z basis sets (reference point)

3Z()	$[meV]$
RMSD (total)	195.751
MAX (total)	494.545
RMSD (atom)	13.919
MAX (atom)	32.970

Reference Values:
– RI-V
– NAO-VCC-3Z

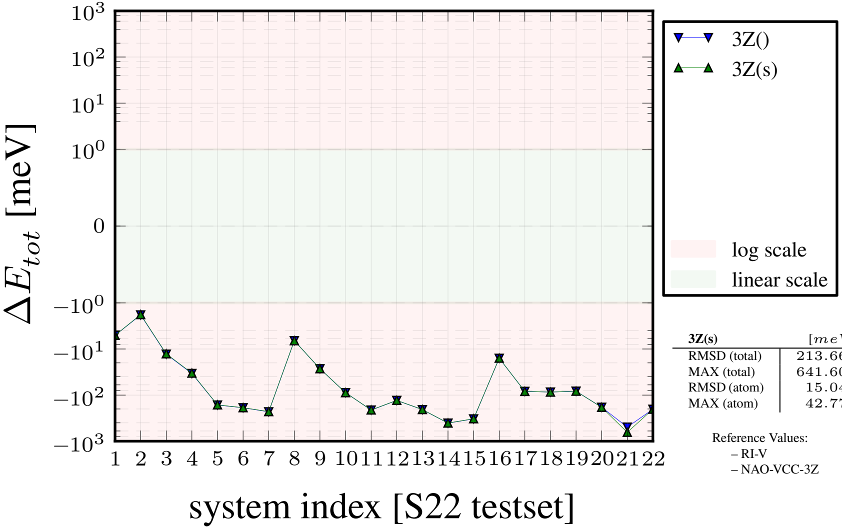
RI-LVL convergence for MP2



3Z()	$[meV]$
RMSD (total)	195.751
MAX (total)	494.545
RMSD (atom)	13.919
MAX (atom)	32.970

Reference Values:
- RI-V
- NAO-VCC-3Z

RI-LVL convergence for MP2

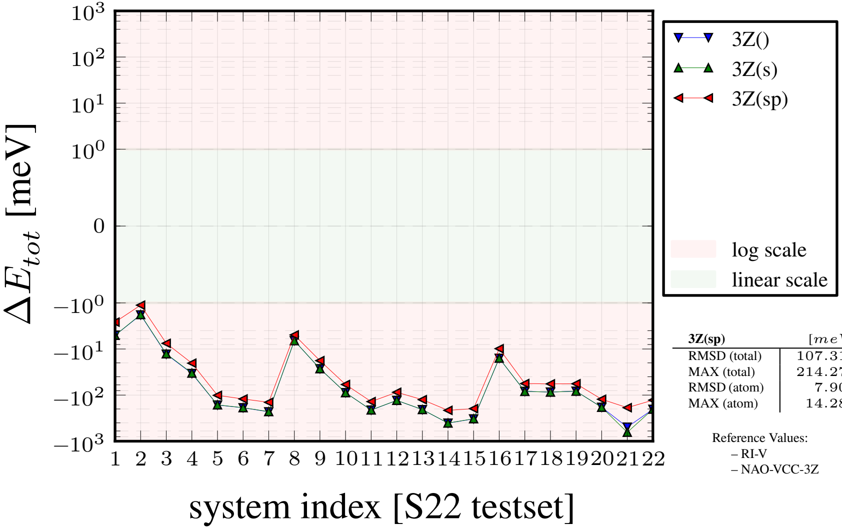


3Z(s)	$[meV]$
RMSD (total)	213.662
MAX (total)	641.604
RMSD (atom)	15.049
MAX (atom)	42.774

Reference Values:

- RI-V
- NAO-VCC-3Z

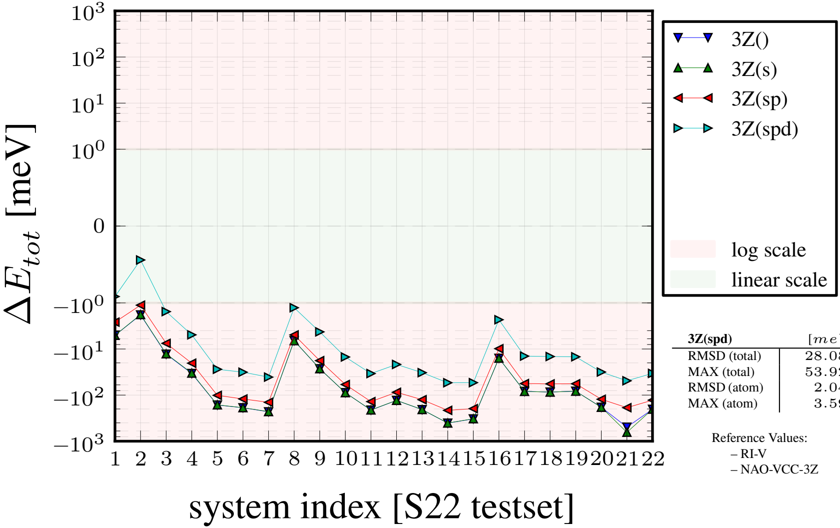
RI-LVL convergence for MP2



3Z(sp)	$[meV]$
RMSD (total)	107.315
MAX (total)	214.279
RMSD (atom)	7.905
MAX (atom)	14.285

Reference Values:
- RI-V
- NAO-VCC-3Z

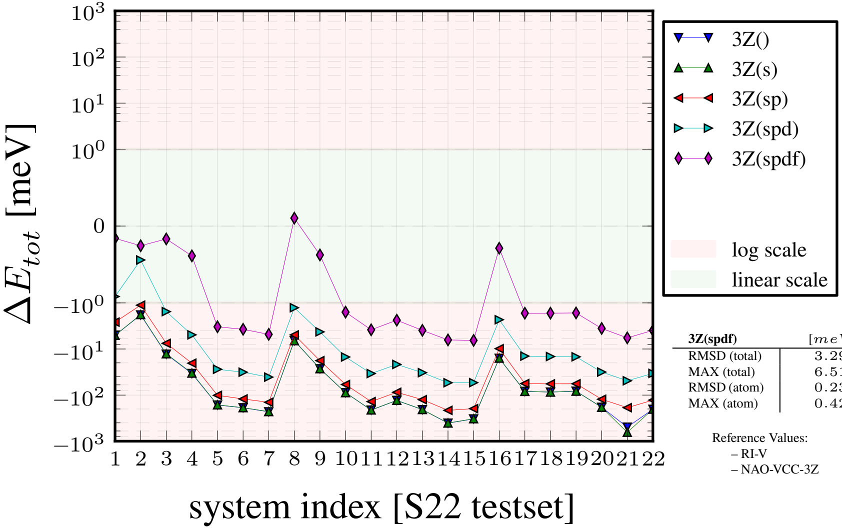
RI-LVL convergence for MP2



3Z(spd)	$[meV]$
RMSD (total)	28.086
MAX (total)	53.926
RMSD (atom)	2.043
MAX (atom)	3.595

Reference Values:
- RI-V
- NAO-VCC-3Z

RI-LVL convergence for MP2

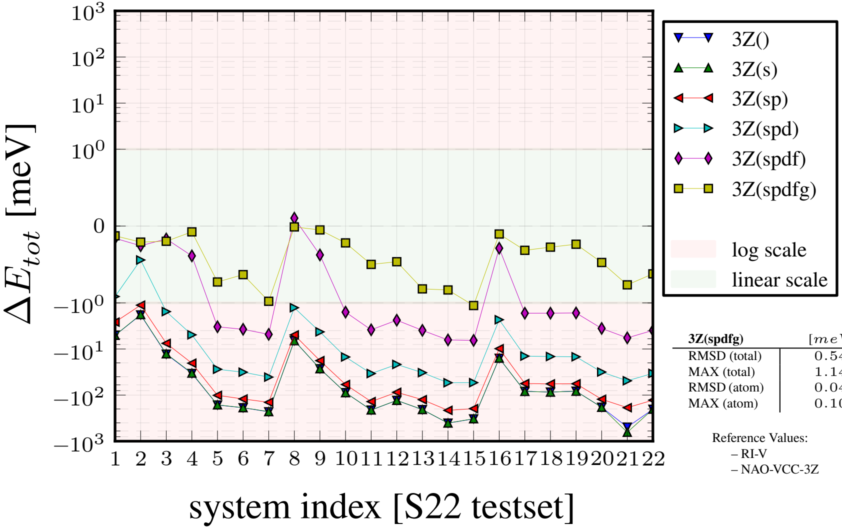


3Z(spdf)	$[meV]$
RMSD (total)	3.299
MAX (total)	6.511
RMSD (atom)	0.238
MAX (atom)	0.424

Reference Values:

- RI-V
- NAO-VCC-3Z

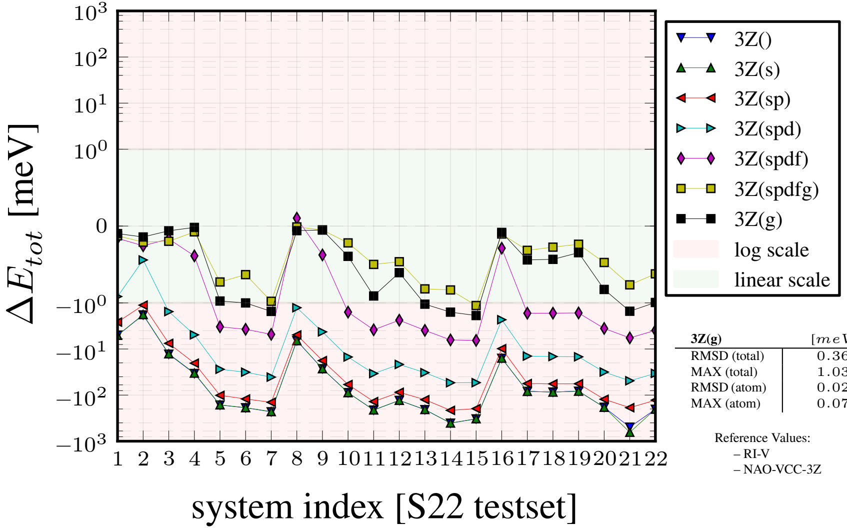
RI-LVL convergence for MP2



3Z(spdfg)	$[meV]$
RMSD (total)	0.548
MAX (total)	1.141
RMSD (atom)	0.047
MAX (atom)	0.104

Reference Values:
- RI-V
- NAO-VCC-3Z

RI-LVL convergence for MP2

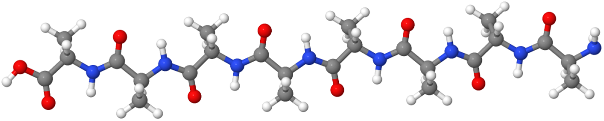


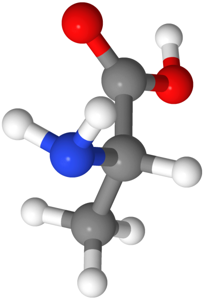
3Z(g)	$[meV]$
RMSD (total)	0.364
MAX (total)	1.035
RMSD (atom)	0.028
MAX (atom)	0.074

Reference Values:

- RI-V
- NAO-VCC-3Z

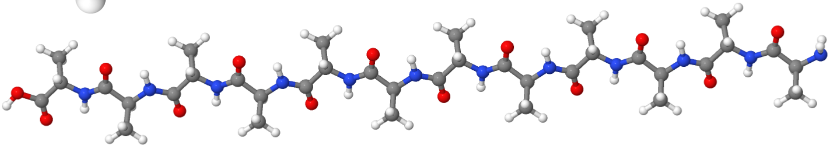
Fully Extended Polyalanine - A scaling prototype



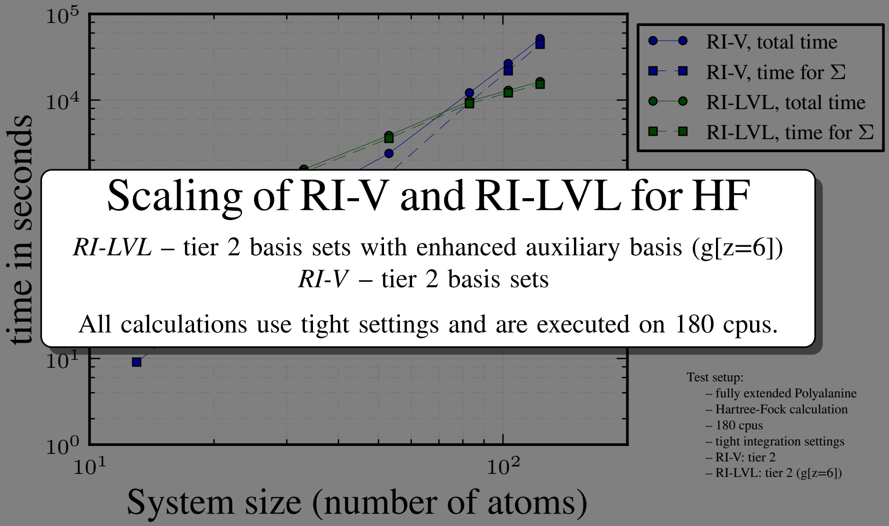


Scaling Analysis:

HF for Fully Extended Polyalanine



Total Computational Time and Exchange Matrix Evaluation



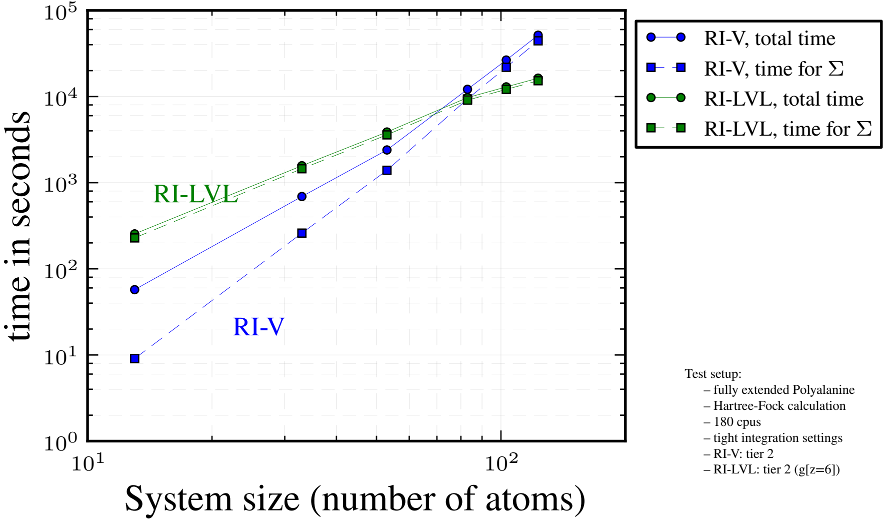
Scaling of RI-V and RI-LVL for HF

RI-LVL – tier 2 basis sets with enhanced auxiliary basis (g[z=6])
RI-V – tier 2 basis sets

All calculations use tight settings and are executed on 180 cpus.

Test setup:
- fully extended Polyalanine
- Hartree-Fock calculation
- 180 cpus
- tight integration settings
- RI-V: tier 2
- RI-LVL: tier 2 (g[z=6])

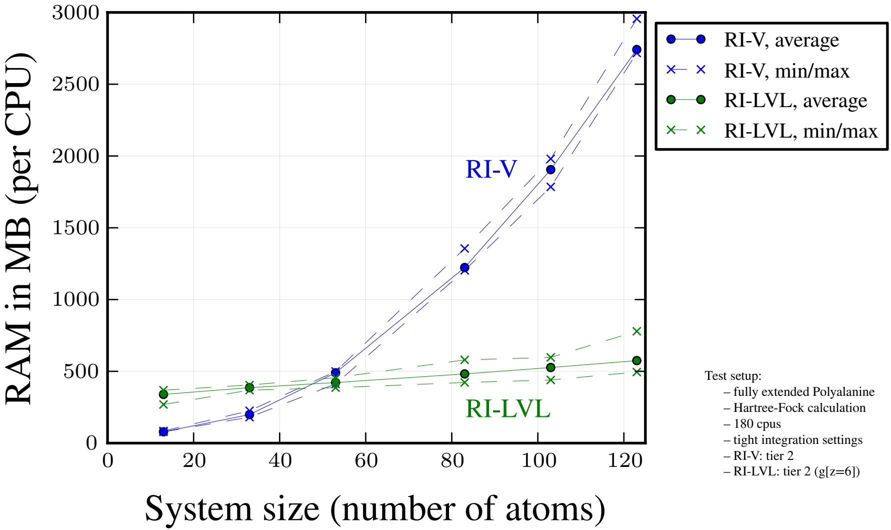
Total Computational Time and Exchange Matrix Evaluation



Test setup:

- fully extended Polyalanine
- Hartree-Fock calculation
- 180 cpus
- tight integration settings
- RI-V: tier 2
- RI-LVL: tier 2 (g[z=6])

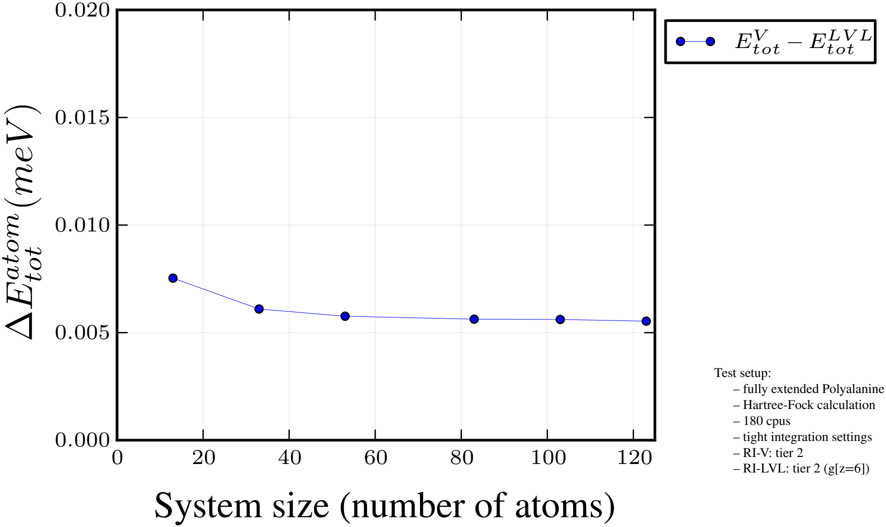
Memory Consumption



Test setup:

- fully extended Polyalanine
- Hartree-Fock calculation
- 180 cpus
- tight integration settings
- RI-V: tier 2
- RI-LVL: tier 2 (g[z=6])

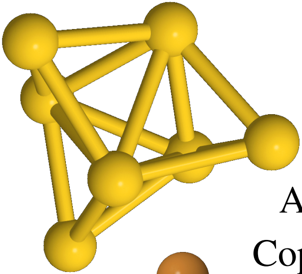
Total Energy Errors

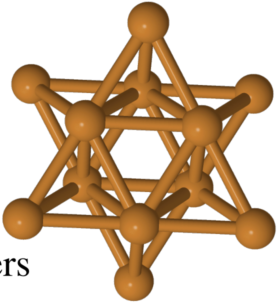


Test setup:

- fully extended Polyalanine
- Hartree-Fock calculation
- 180 cpus
- tight integration settings
- RI-V: tier 2
- RI-LVL: tier 2 (g[z=6])

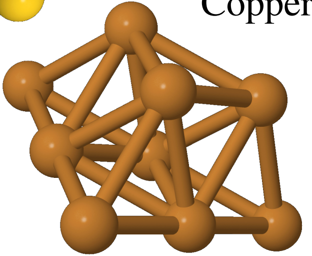
Accuracy II - Heavy Elements

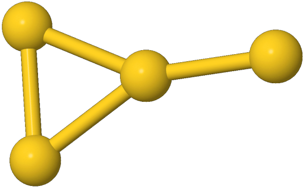




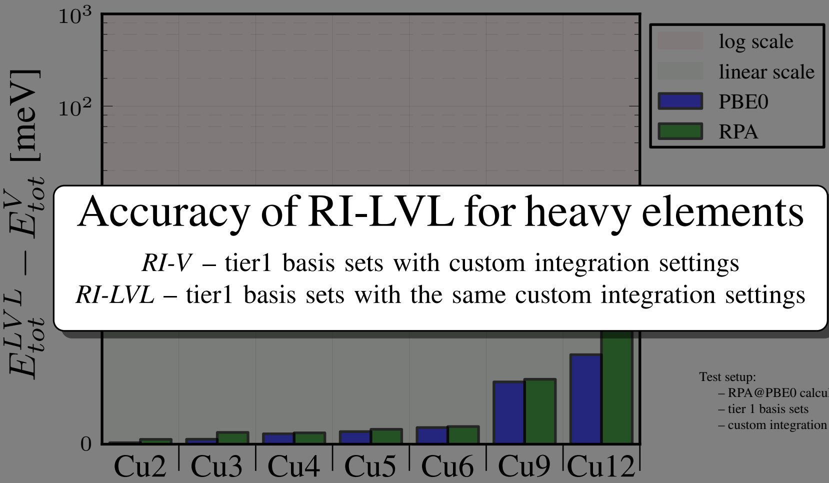
Accuracy Analysis II

Copper and Gold clusters





Accuracy for Copper clusters



Accuracy of RI-LVL for heavy elements

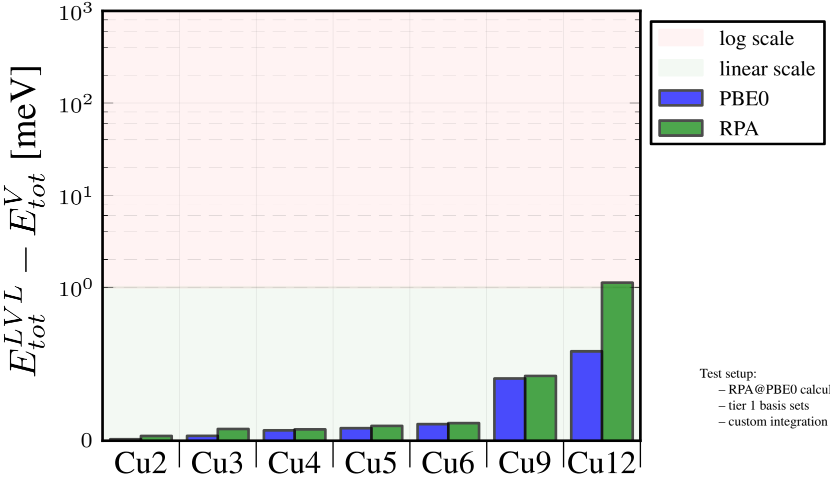
RI-V – tier1 basis sets with custom integration settings

RI-LVL – tier1 basis sets with the same custom integration settings

Test setup:

- RPA@PBE0 calculations
- tier 1 basis sets
- custom integration settings

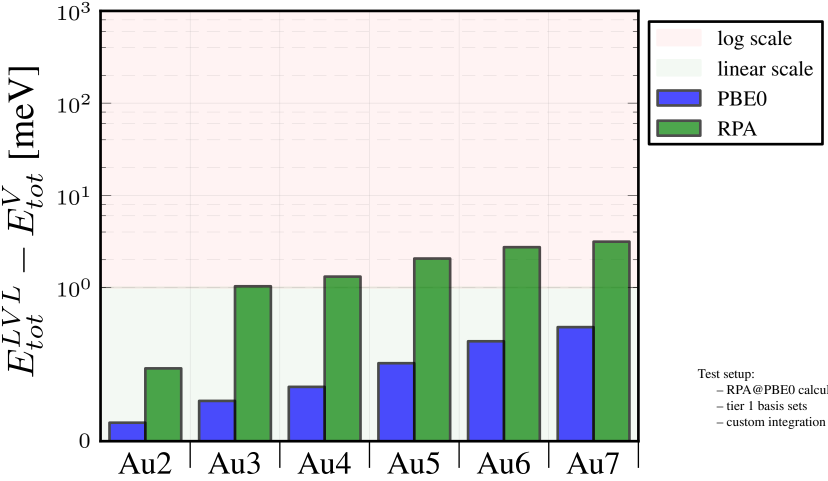
Accuracy for Copper clusters



Test setup:

- RPA@PBE0 calculations
- tier 1 basis sets
- custom integration settings

Accuracy for Gold clusters



Test setup:

- RPA@PBE0 calculations
- tier 1 basis sets
- custom integration settings

Summary and Conclusions

- Results
  - RI-LVL in combination with a suitably chosen auxiliary basis gives very accurate results for light elements
  - RI-LVL is very accurate for heavier elements, even without modifications of the auxiliary basis
  - explicit use of the sparsity exhibits superior scaling, as shown for exact exchange
- Outlook
  - implement RI-LVL for RPA and GW

Thank you for your attention!