Efficient Bosonic and Fermionic Sinkhorn Algorithms for Non-Interacting Ensembles in One-body Reduced Density Matrix Functional Theory in the Canonical Ensemble

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Code: https://www.github.com/DerkKooi/bfsinkhorn

See also Sarina Sutter her talk and arXiv:2209.11663 by S.M. Sutter and K.J.H. Giesbertz

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- When using a (non-interacting) reference system: canonical reference may be "closer" to interacting system than grand canonical reference

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  - Use (canonical) entropy to model correlation energy[4]

4. J. Wang and E.J. Baerends. Phys. Rev. Lett. ***128****, 013001 (2022), DOI: 10.1103/PhysRevLett.128.013001*

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- Furthermore, for any interaction (also no interaction):[3, 5] $h \leftrightarrow \gamma$

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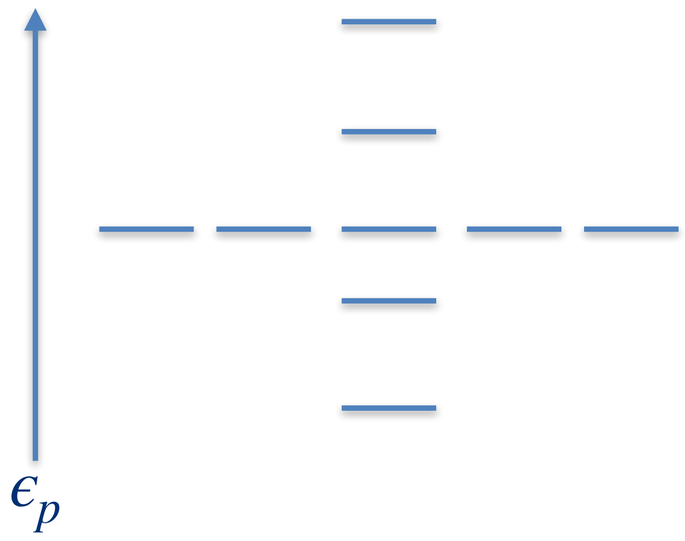

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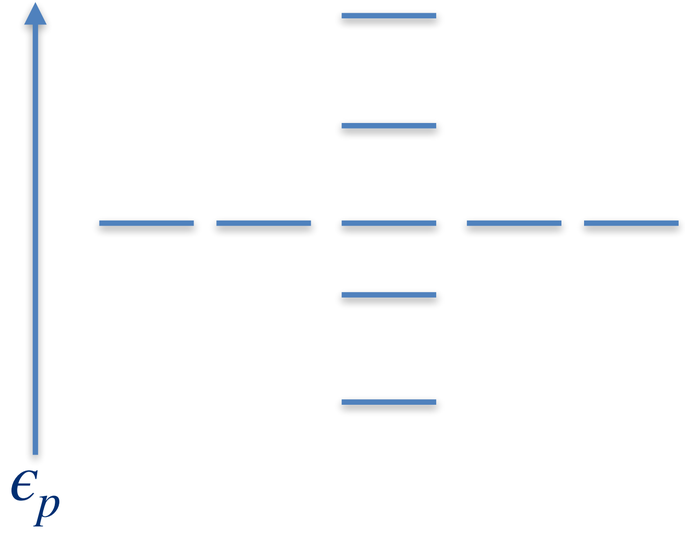

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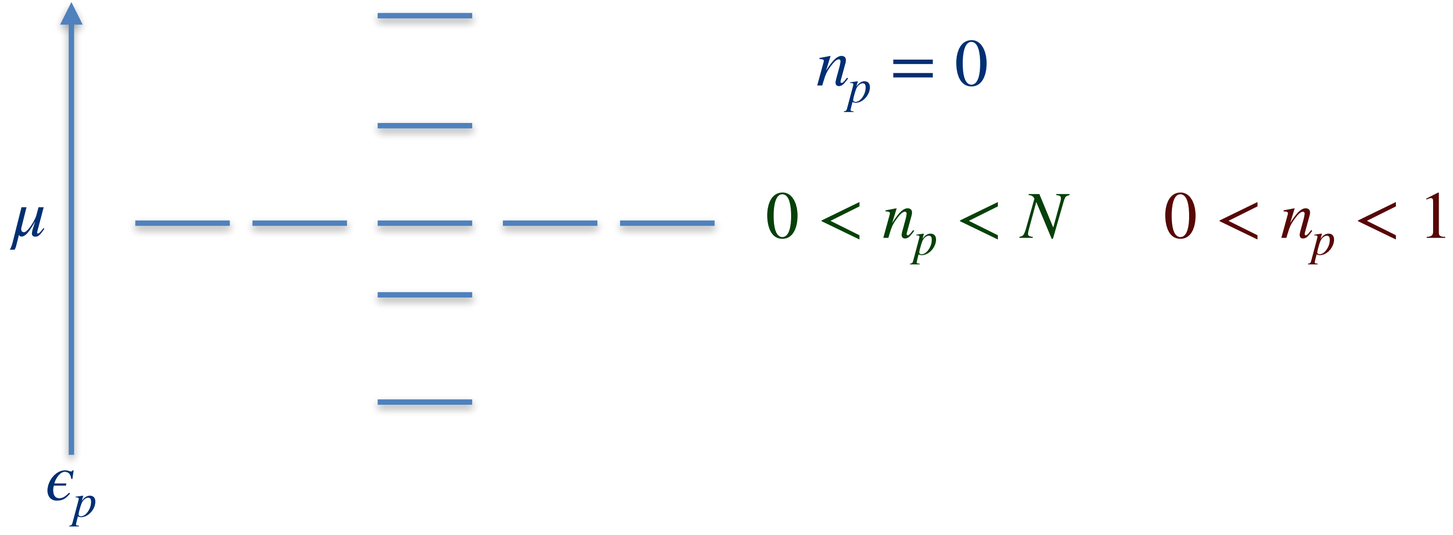

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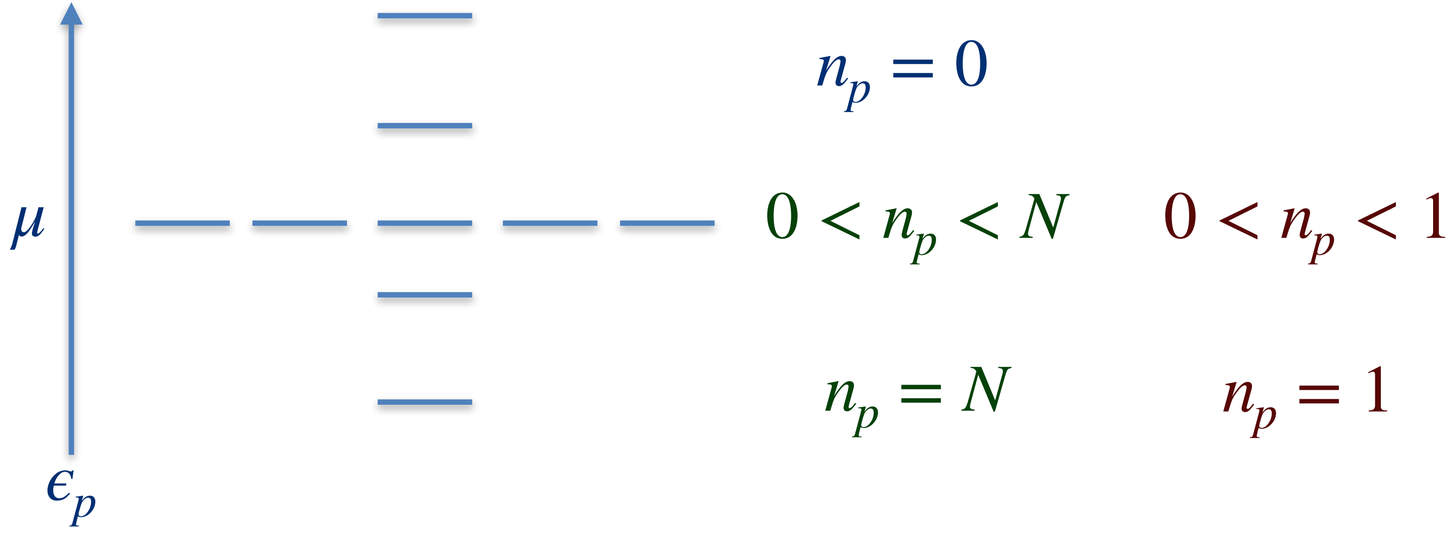

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  no more single Slater Determinant
- For 1-RDMFT:

$$A^{\beta}_{\text{int}}[\gamma] = \min_{\hat{\Gamma}\to\gamma}\left(\cancel{\mathrm{Tr}\left(\hat{\Gamma}\hat{W}\right)} + \frac{1}{\beta}\mathrm{Tr}\left(\hat{\Gamma}\log(\hat{\Gamma})\right)\right)$$

$$\min_{\hat{\Gamma}_0^{\beta}\to\gamma}\frac{1}{\beta}\mathrm{Tr}\left(\hat{\Gamma}_0^{\beta}\log(\hat{\Gamma}_0^{\beta})\right) = \frac{1}{\beta}\min_{\hat{\Gamma}_0\to\gamma}\mathrm{Tr}\left(\hat{\Gamma}_0\log(\hat{\Gamma}_0)\right) = -\frac{1}{\beta}S_0[\{n_p\}]$$

$$\hat{H}_0^{\beta} = \sum_p \epsilon_p^{\beta}[\{n_q\}]\hat{n}_p \qquad \epsilon_p^{\beta} = \frac{\beta'}{\beta}\epsilon_p^{\beta'}$$

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- Note that the functional for the (grand) canonical ensembles are not the same: constrained search over different Hilbert space

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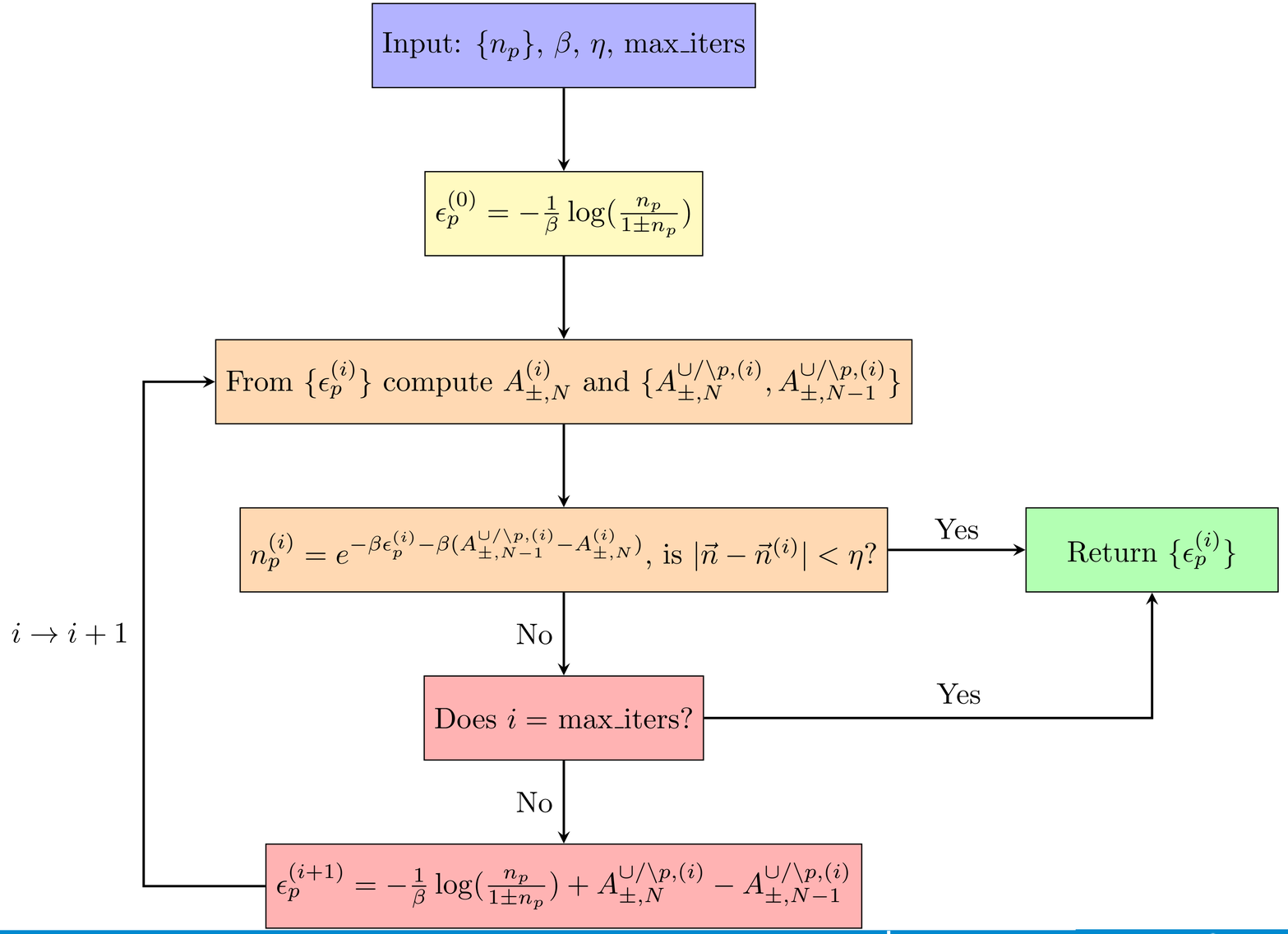
Practical Algorithm



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For numerical stability,
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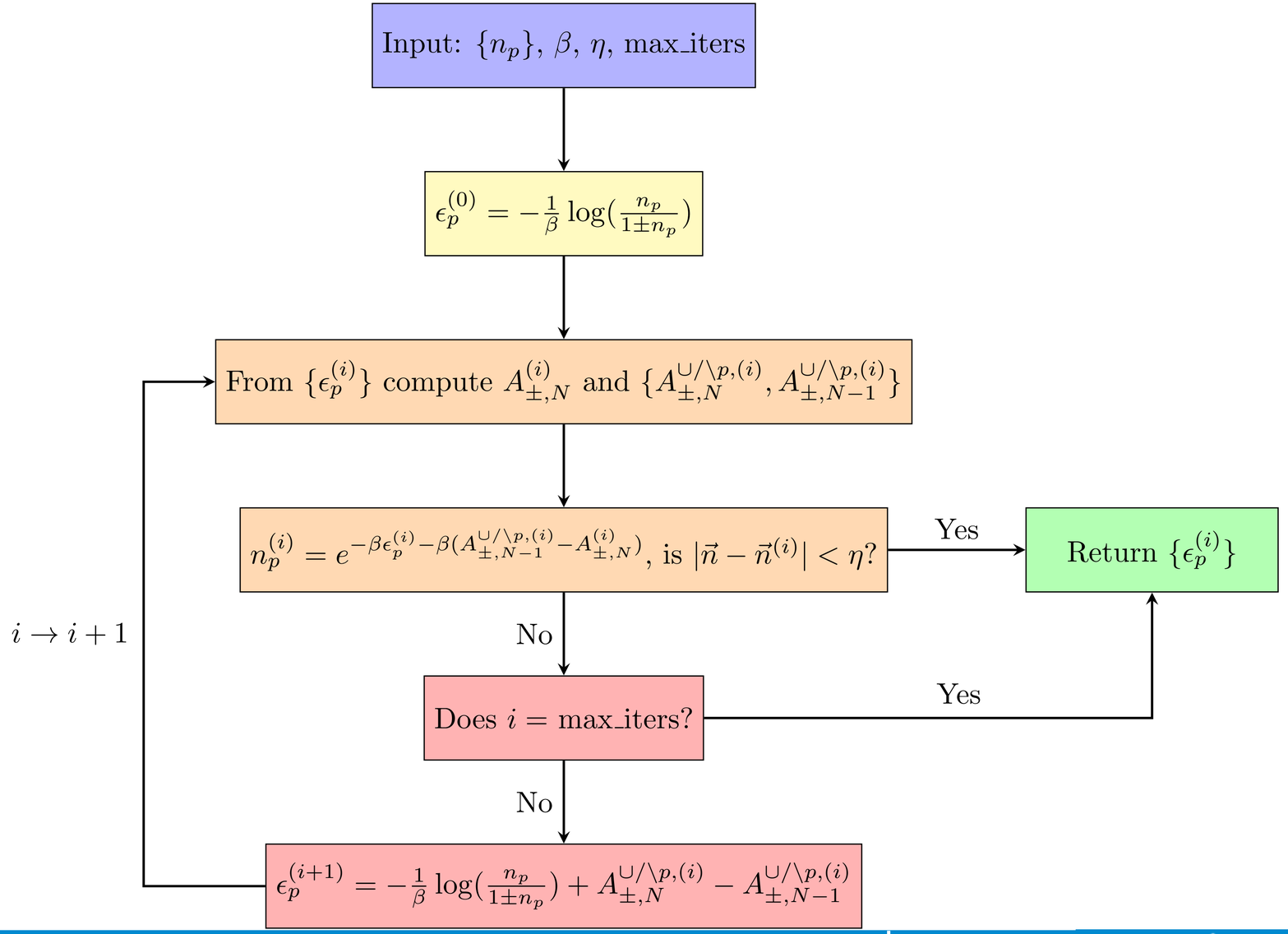

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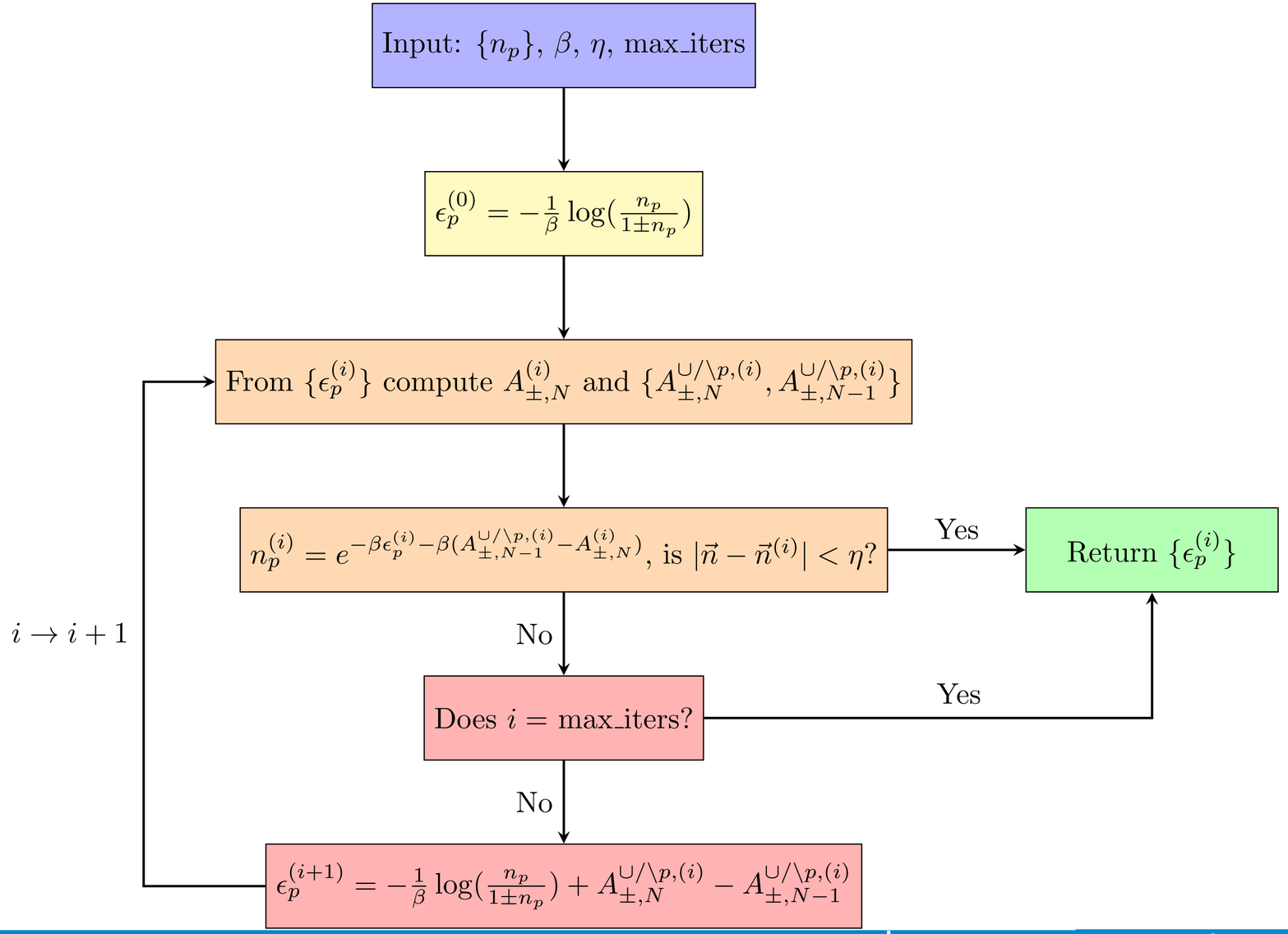

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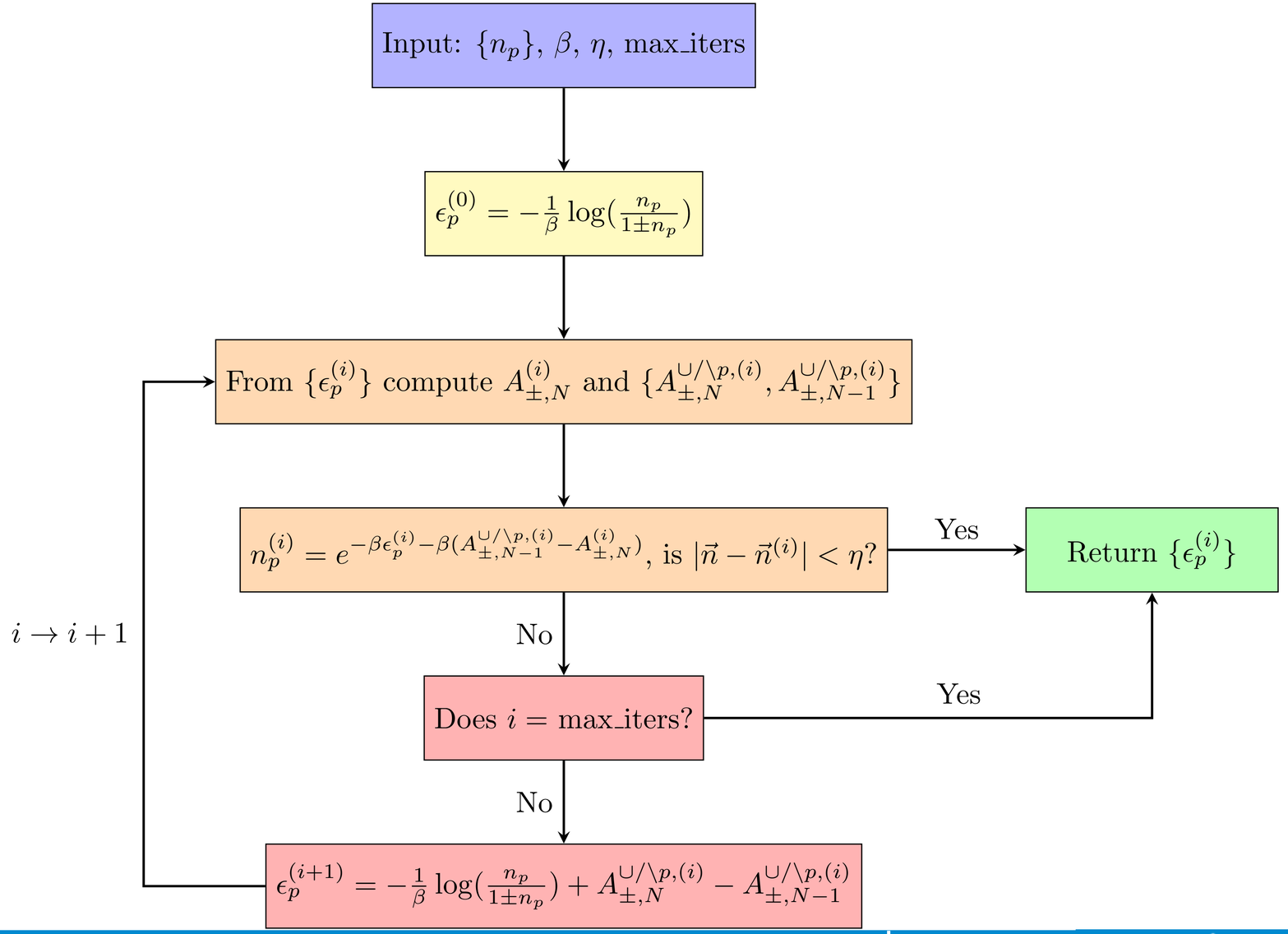

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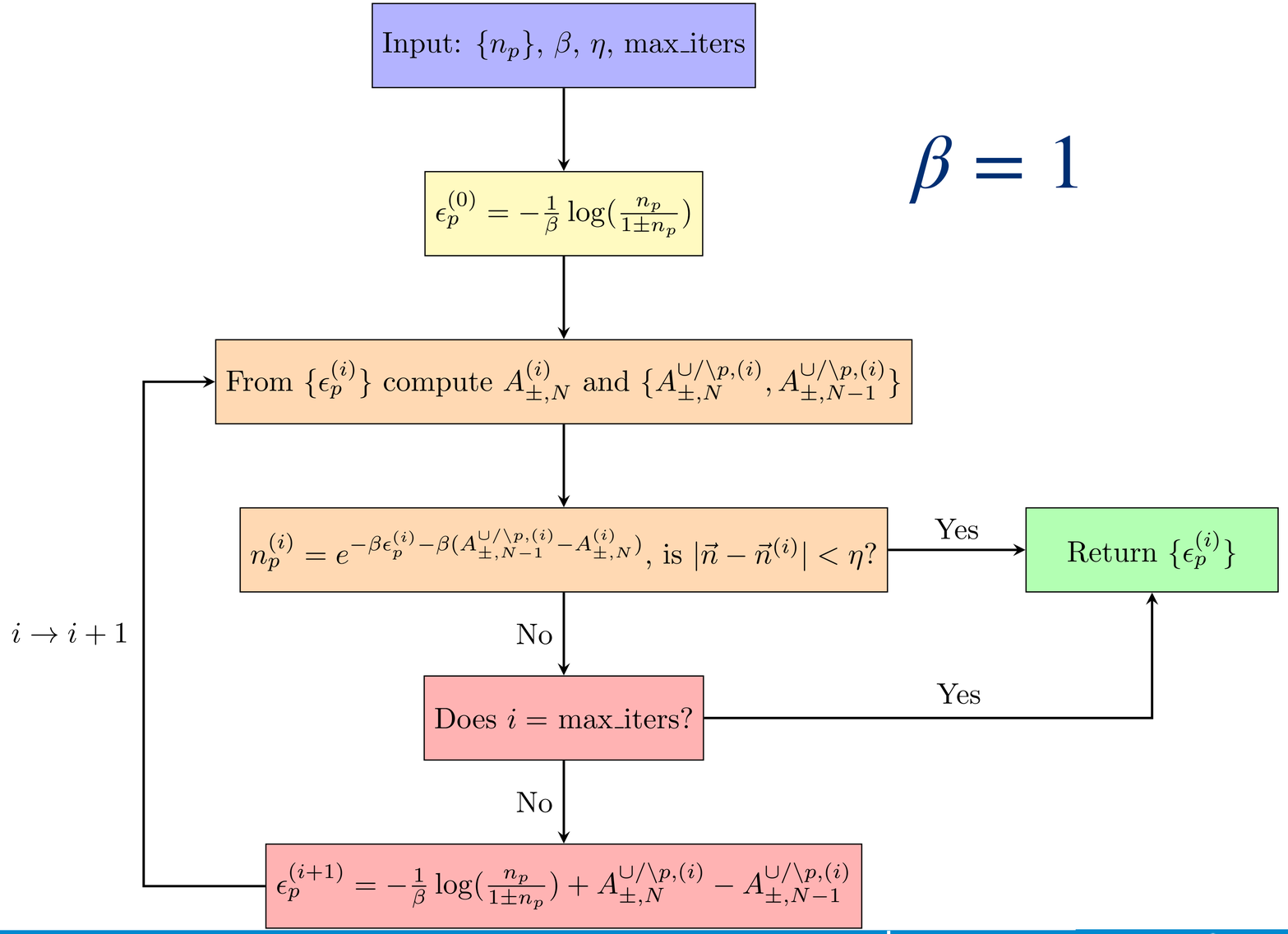

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Convergence 20 bosons in 10 orbitals

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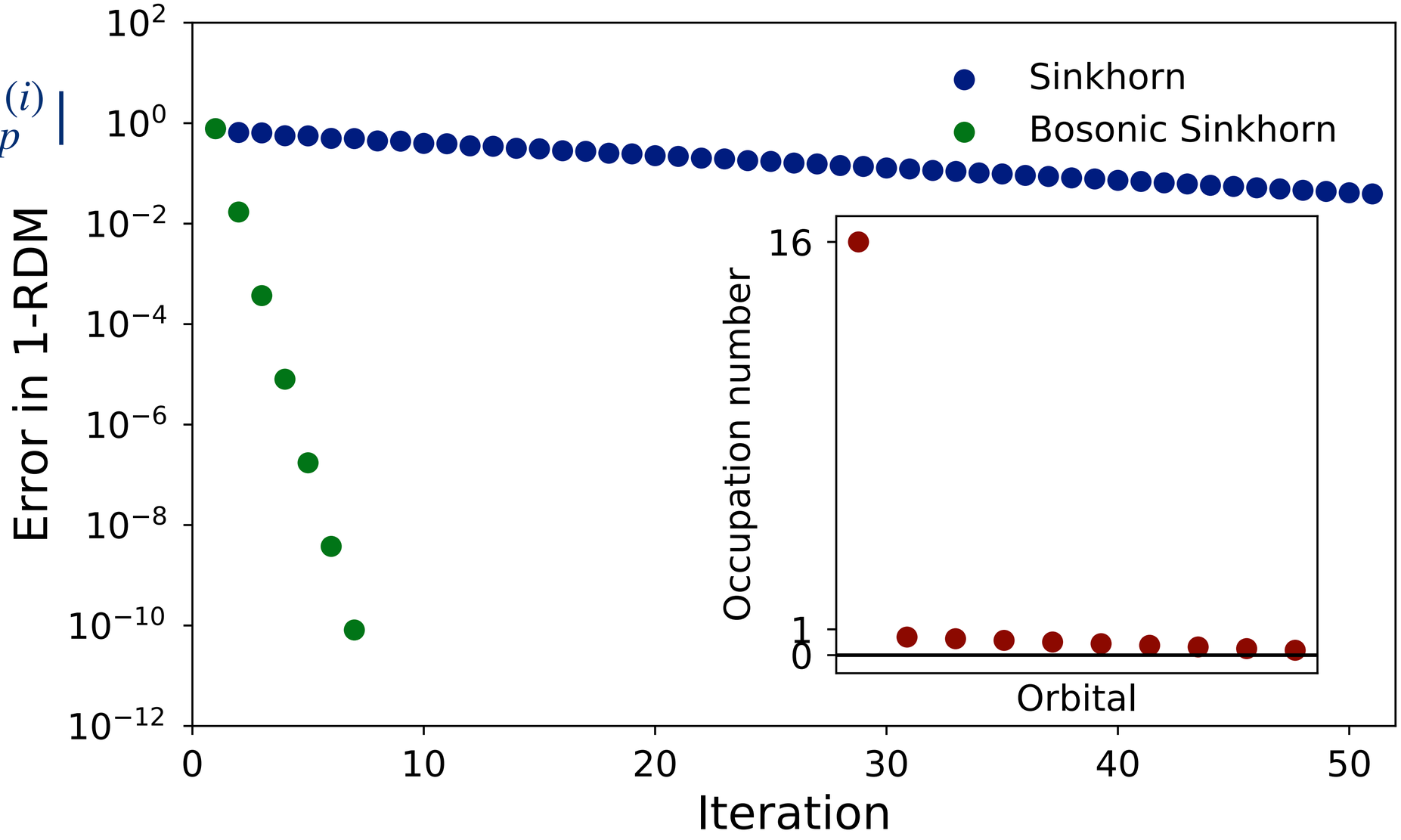

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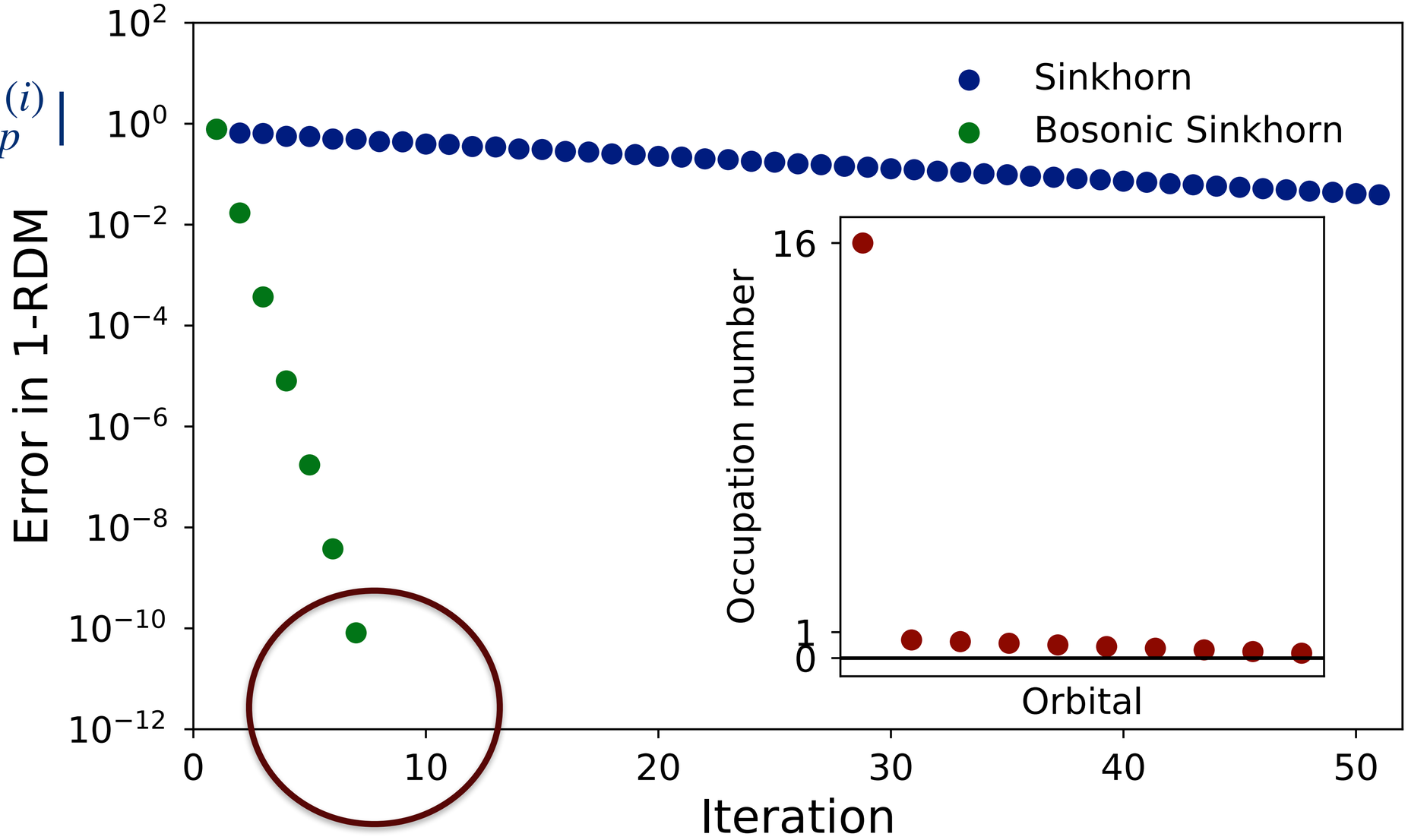

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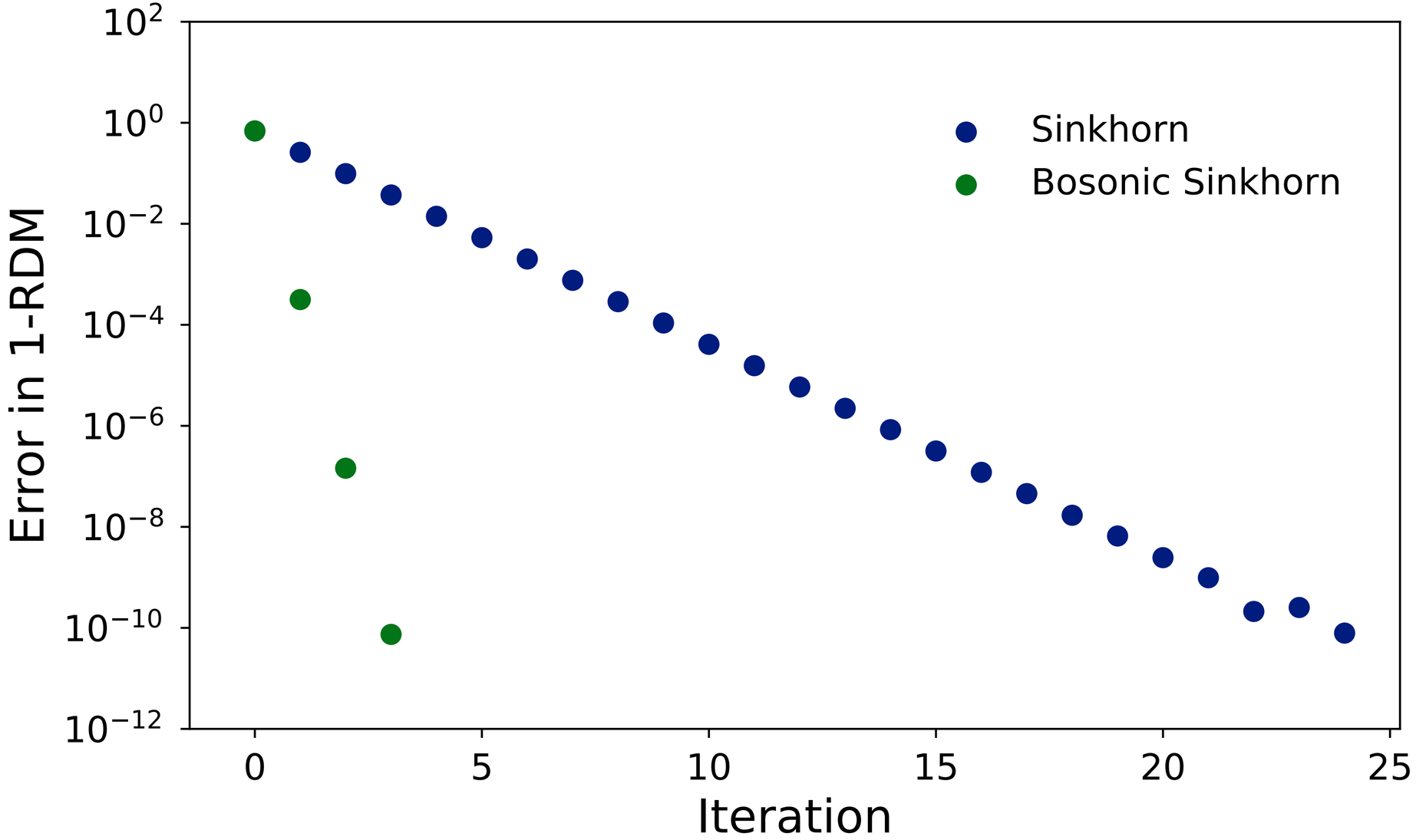

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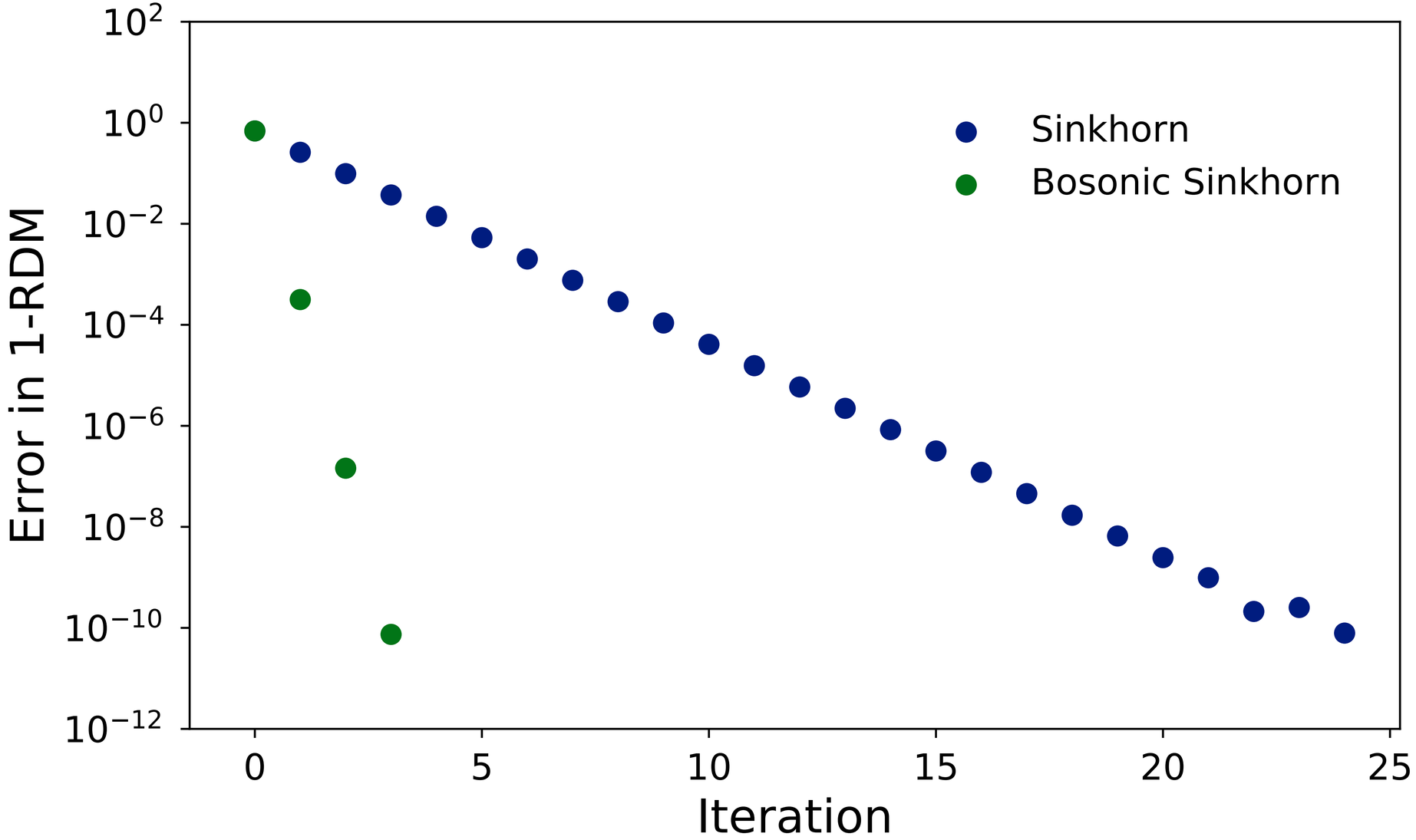
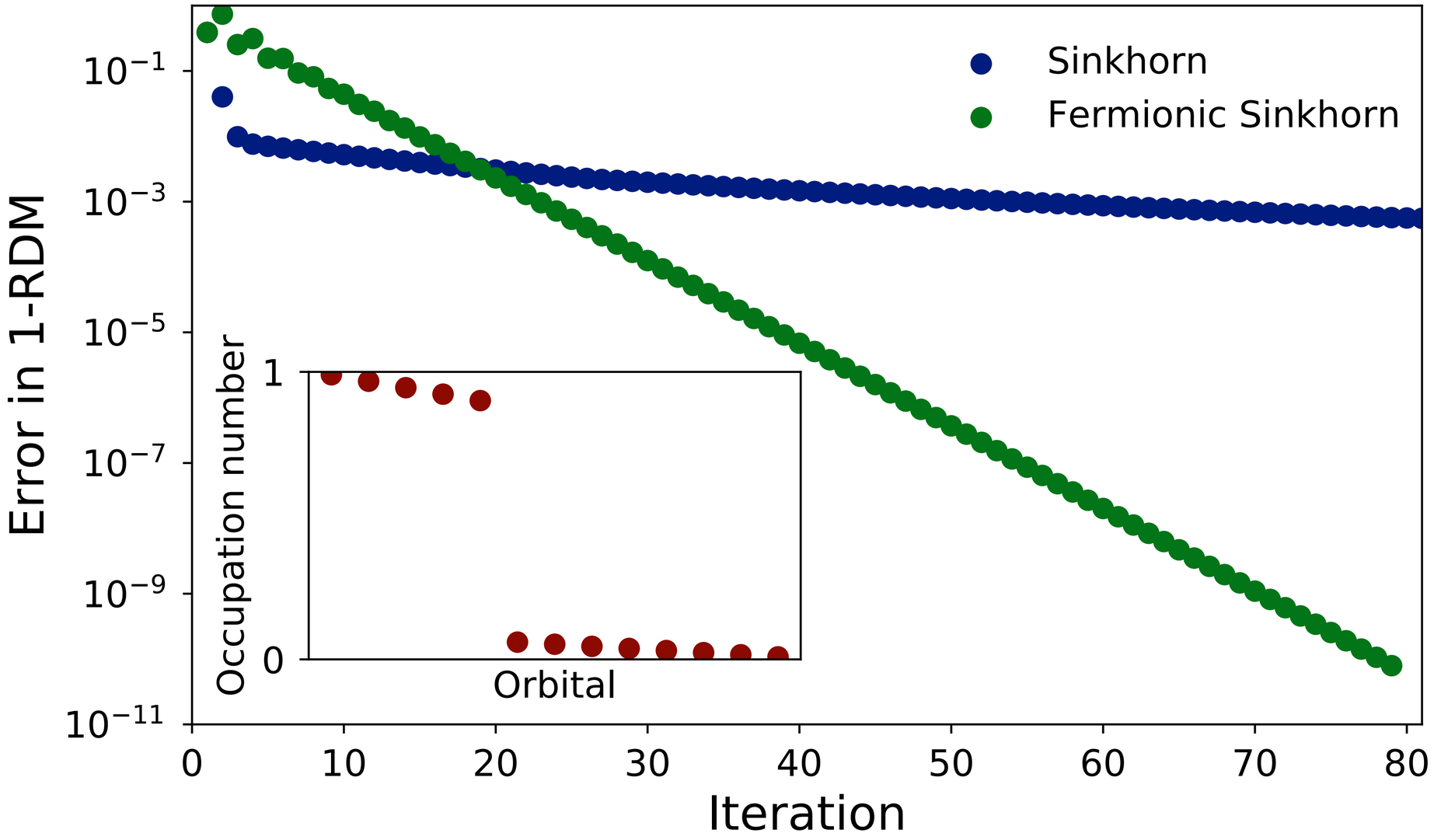


(Few seconds)

Convergence 5 fermions in 13 orbitals



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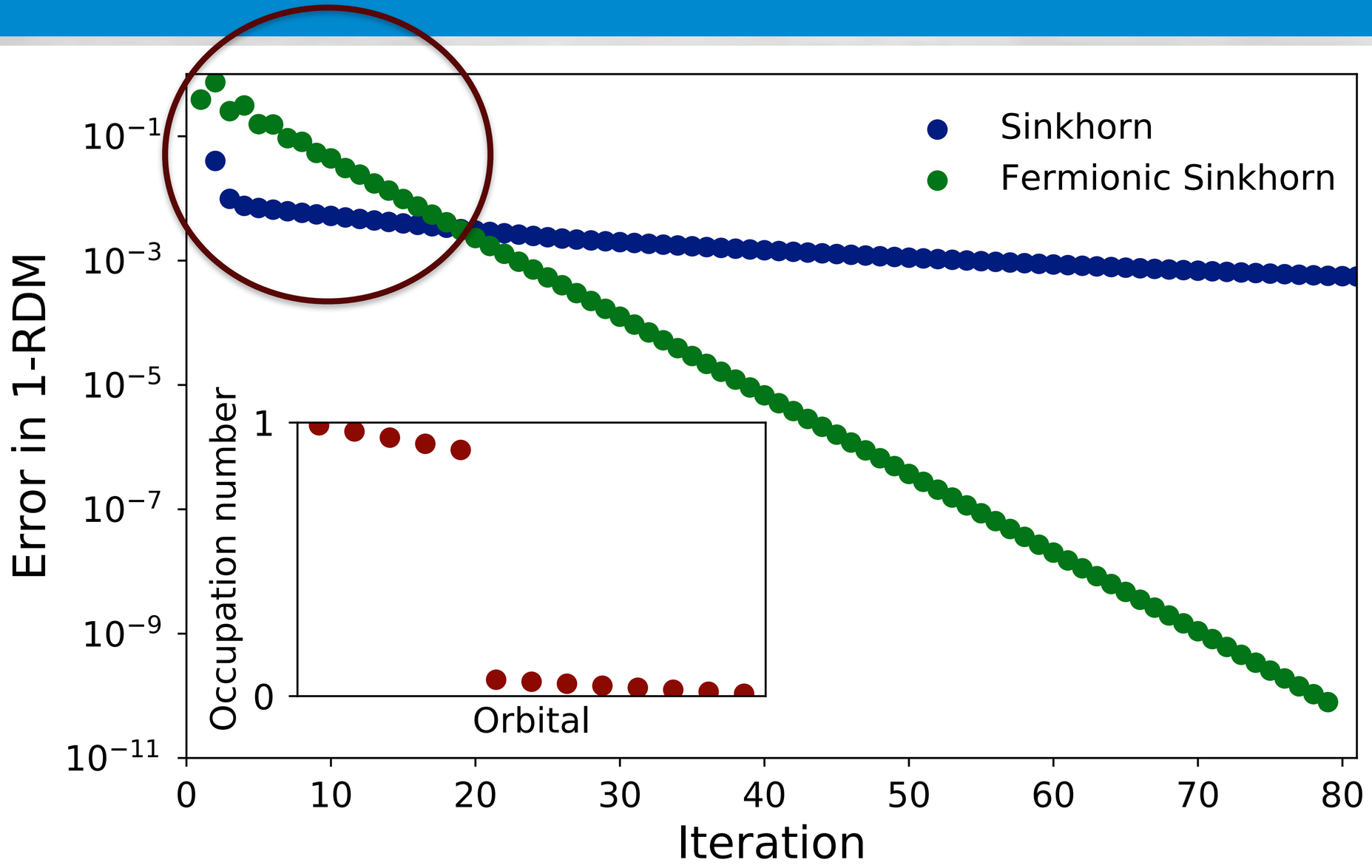

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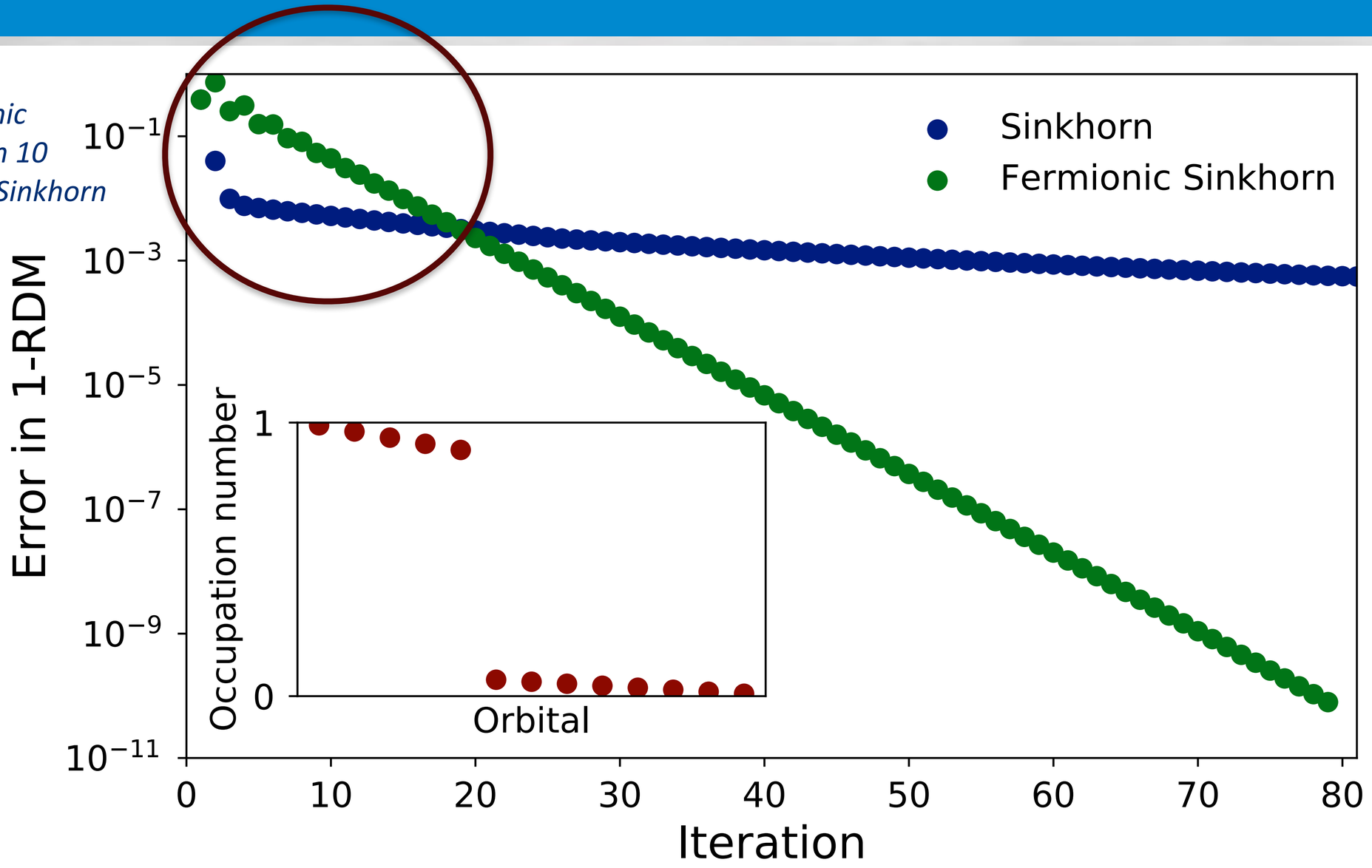
Hot-start Fermionic Sinkhorn with 10 iterations of Sinkhorn



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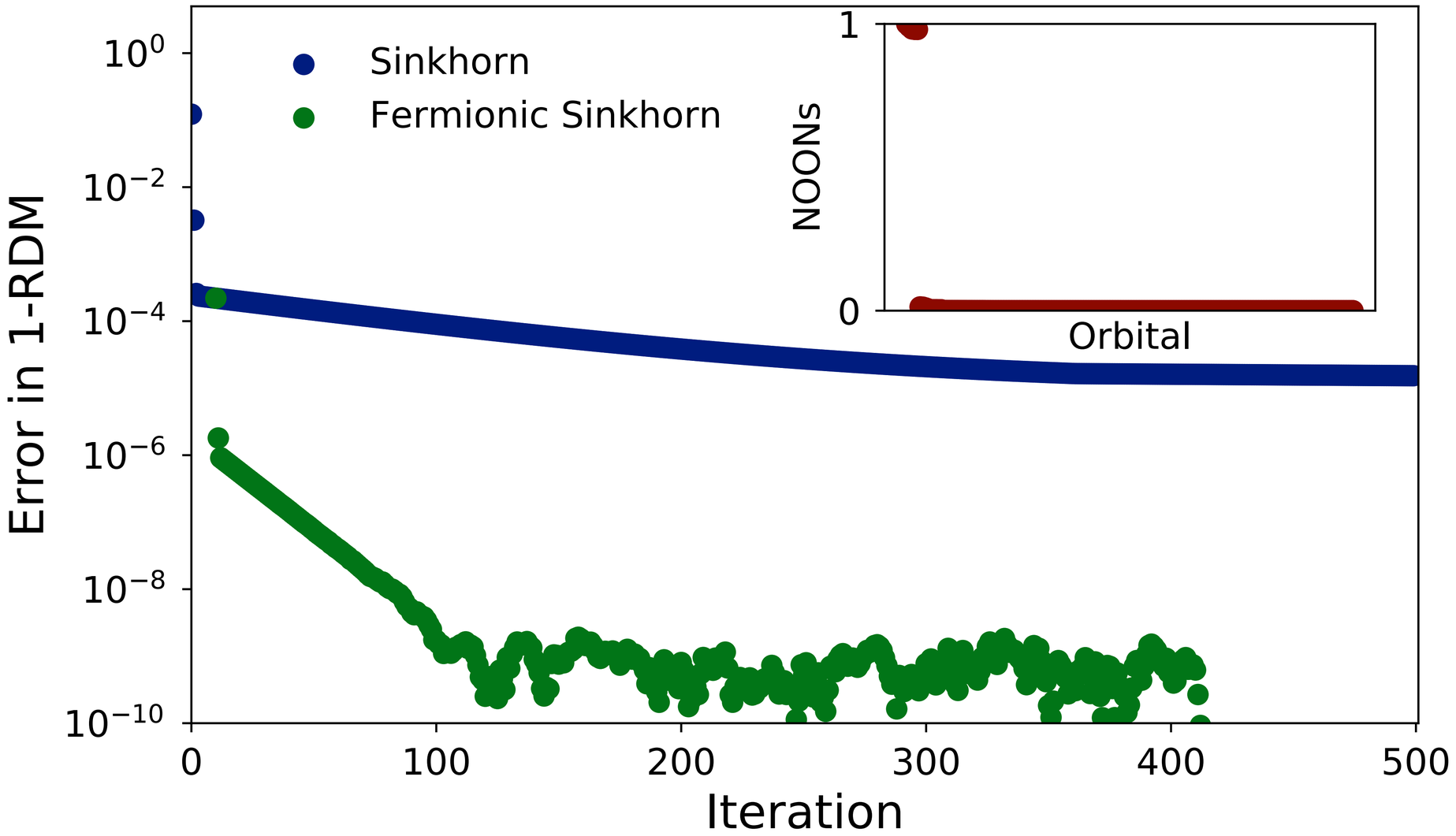

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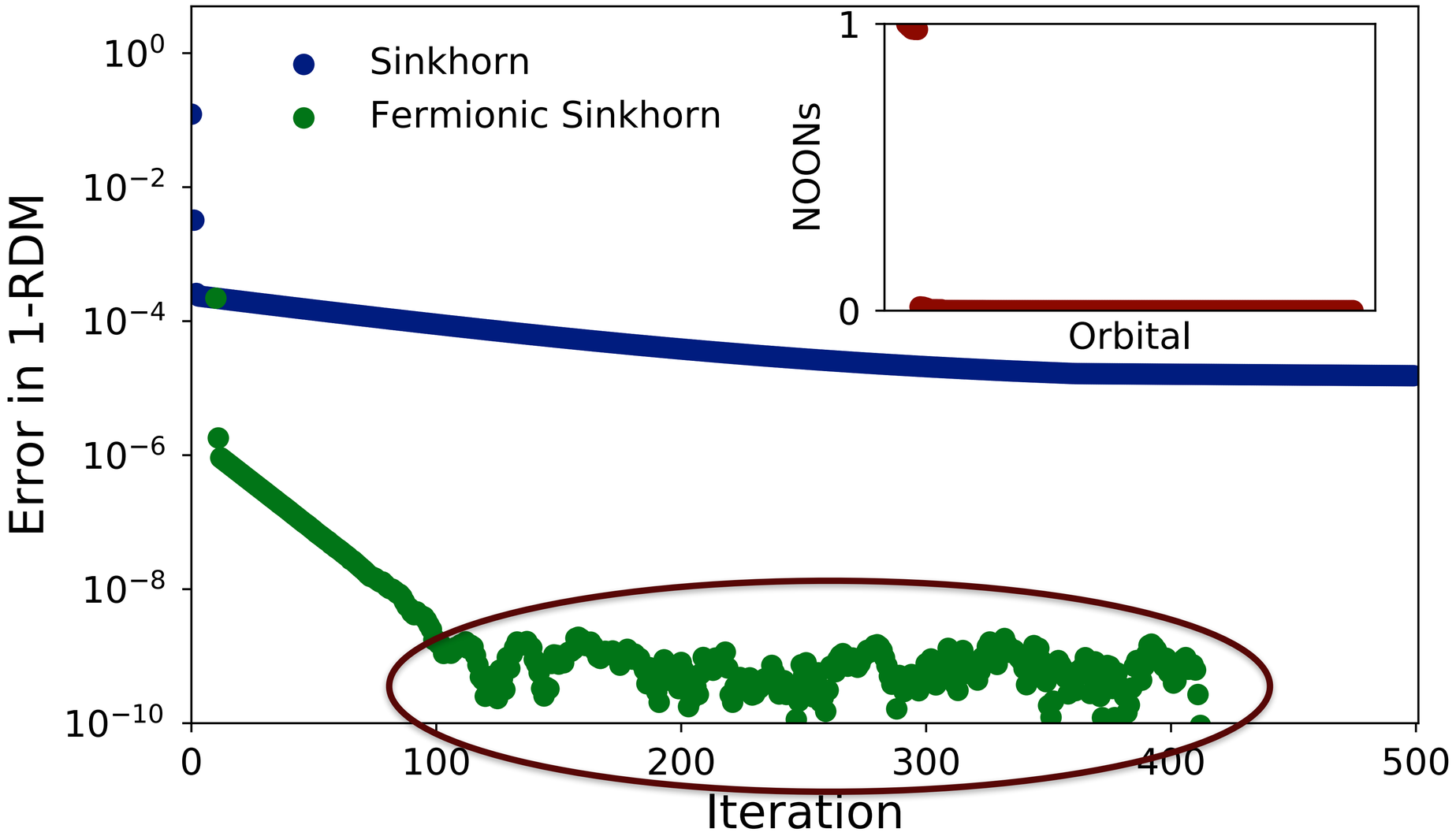

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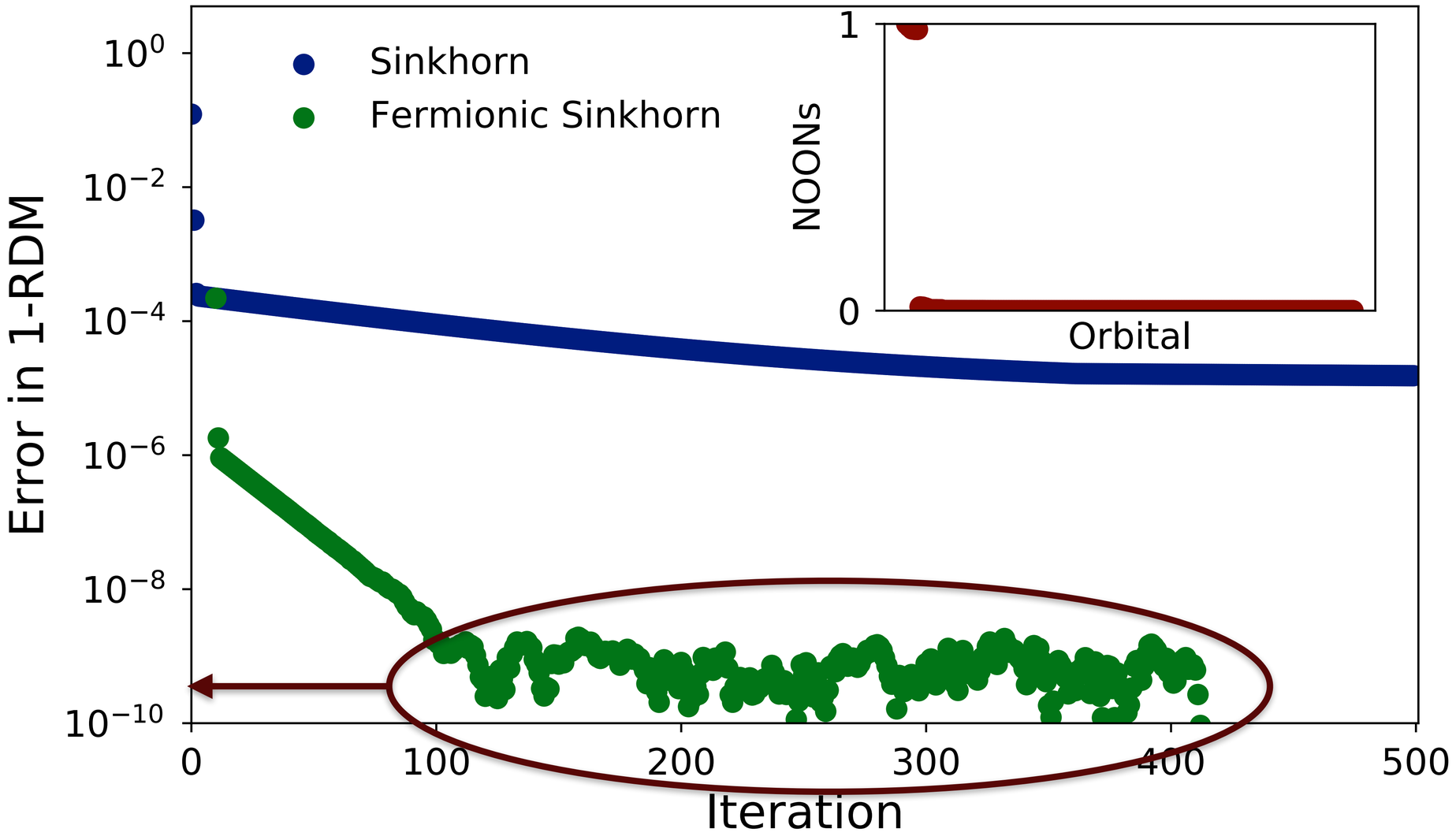

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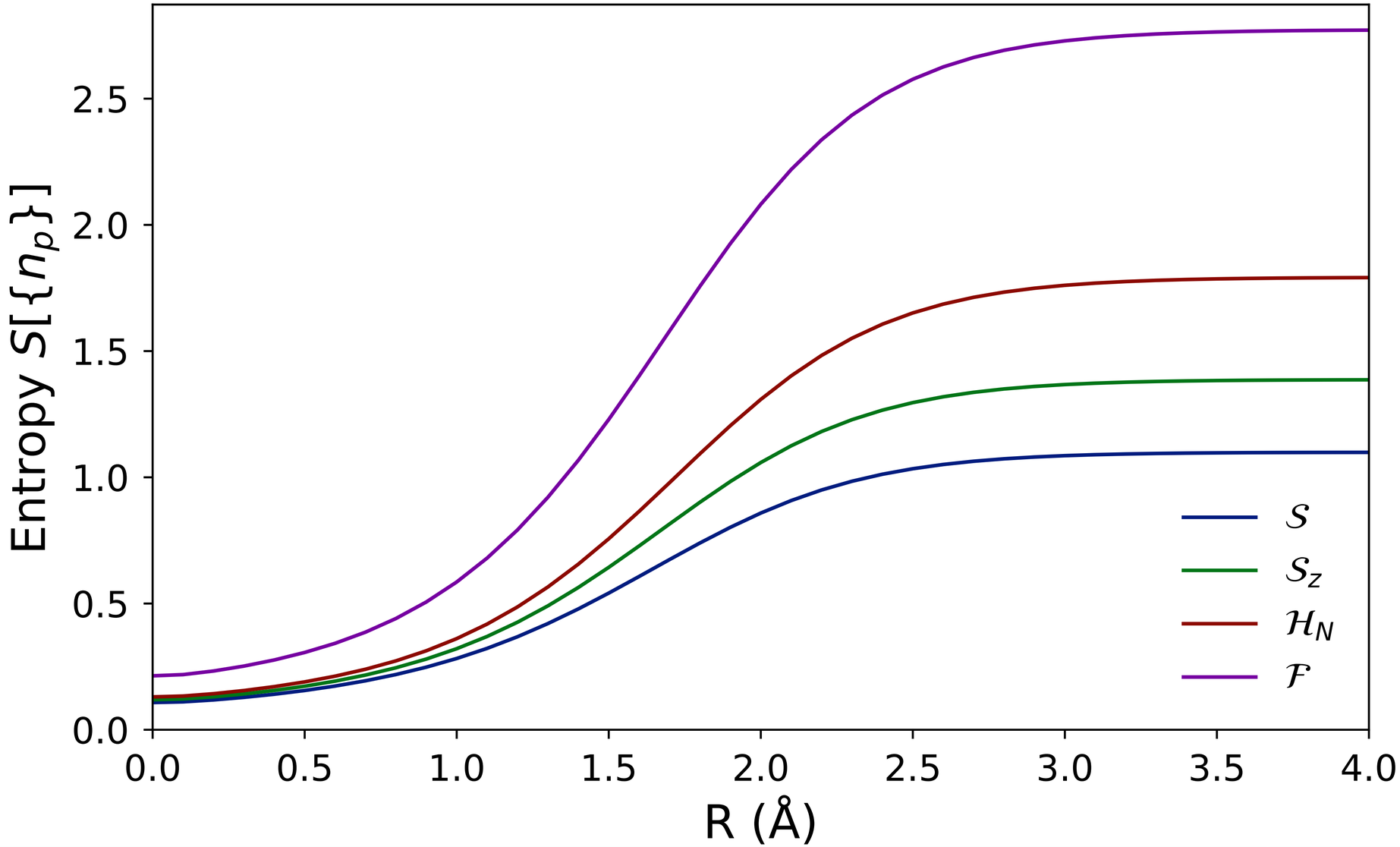
H_2 dissociation, CISD (exact), aug-cc-pVQZ



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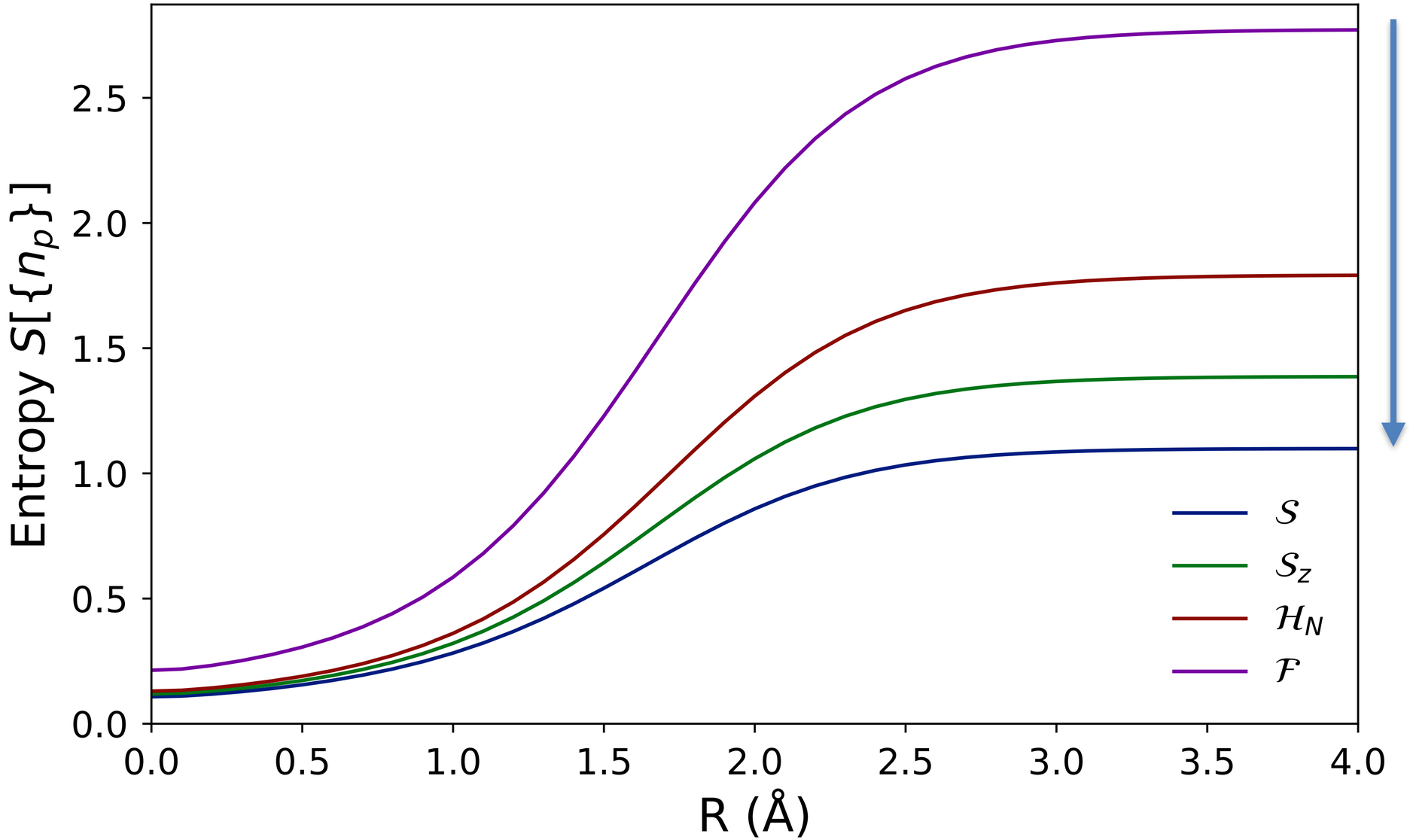

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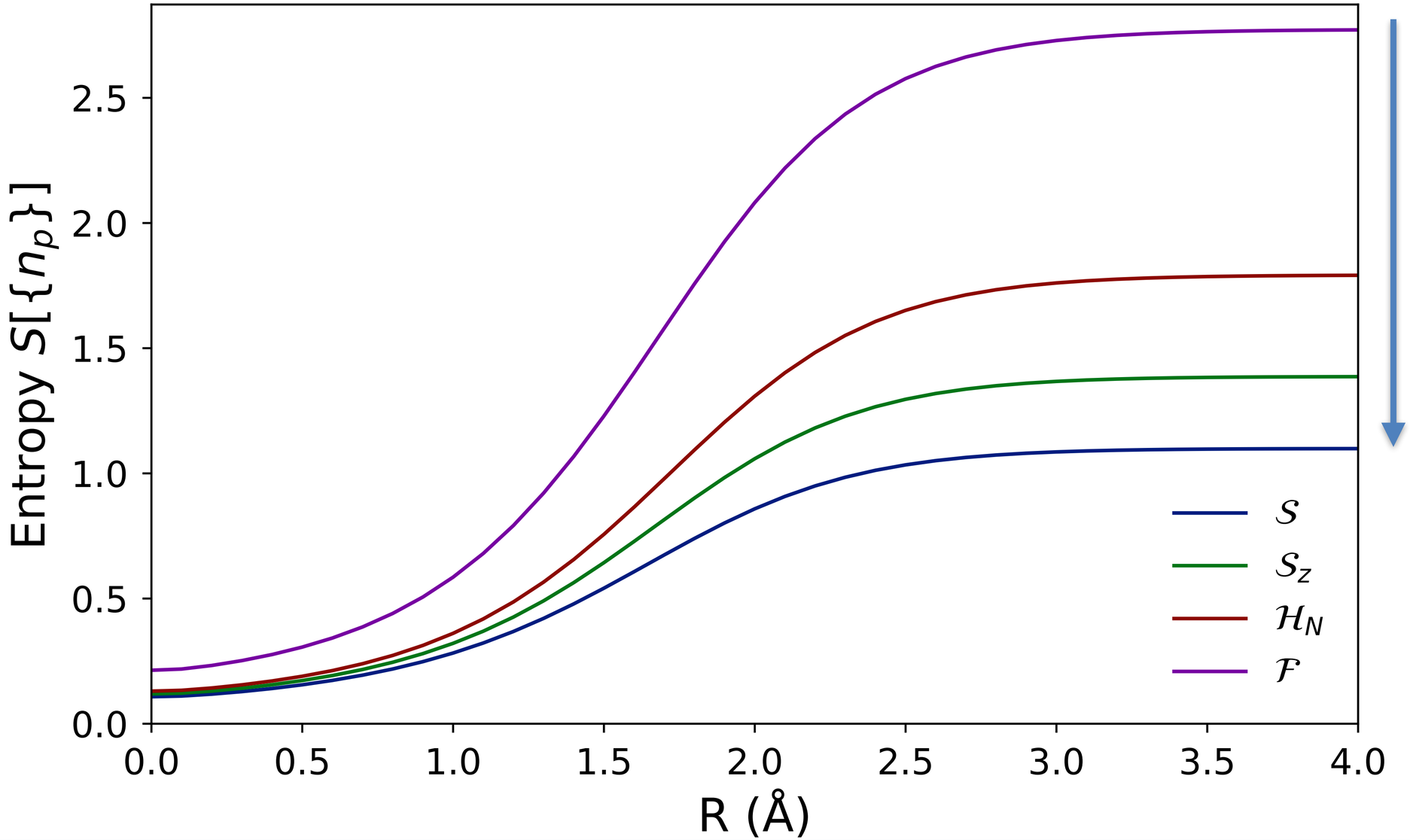

Less variational freedom

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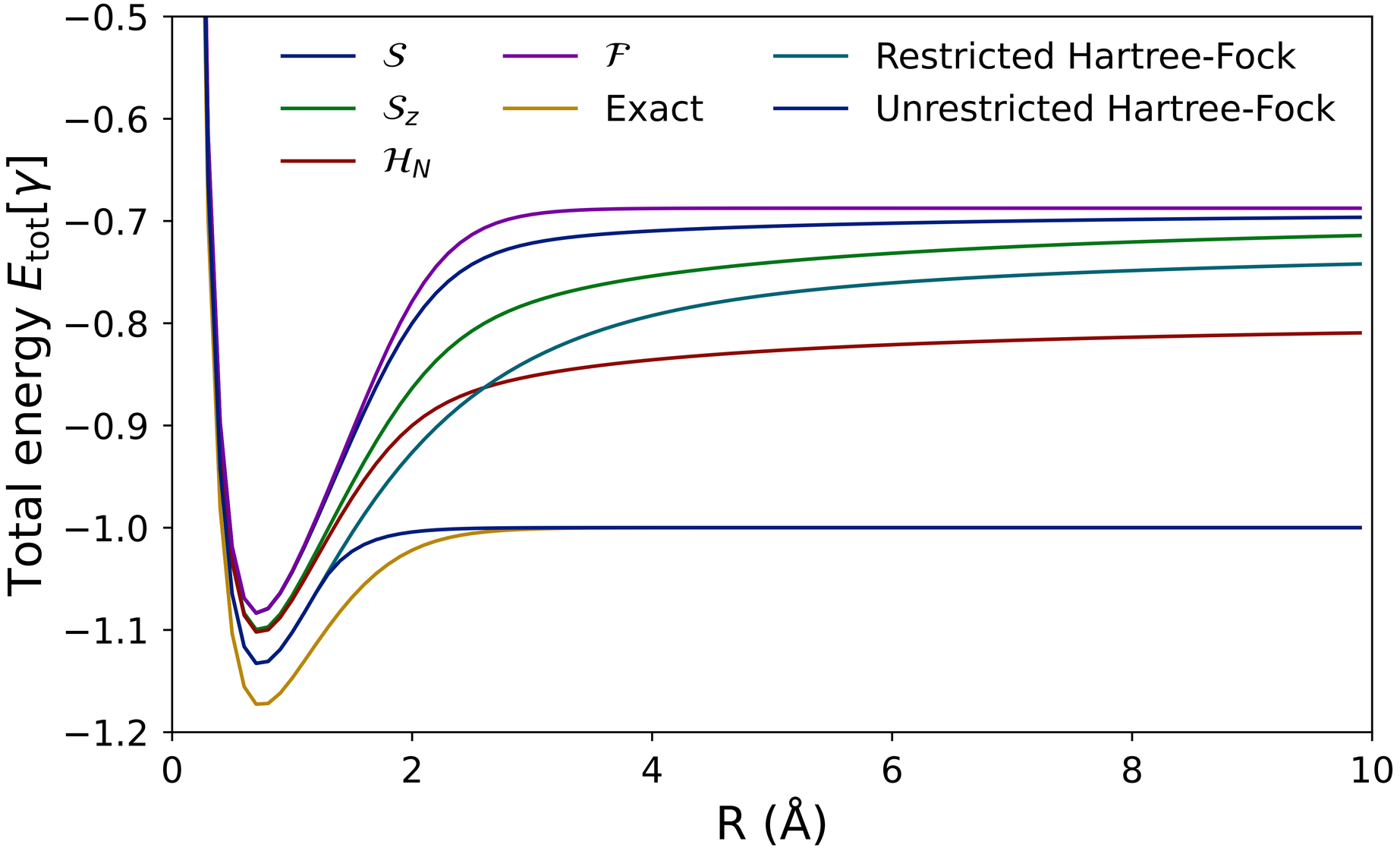

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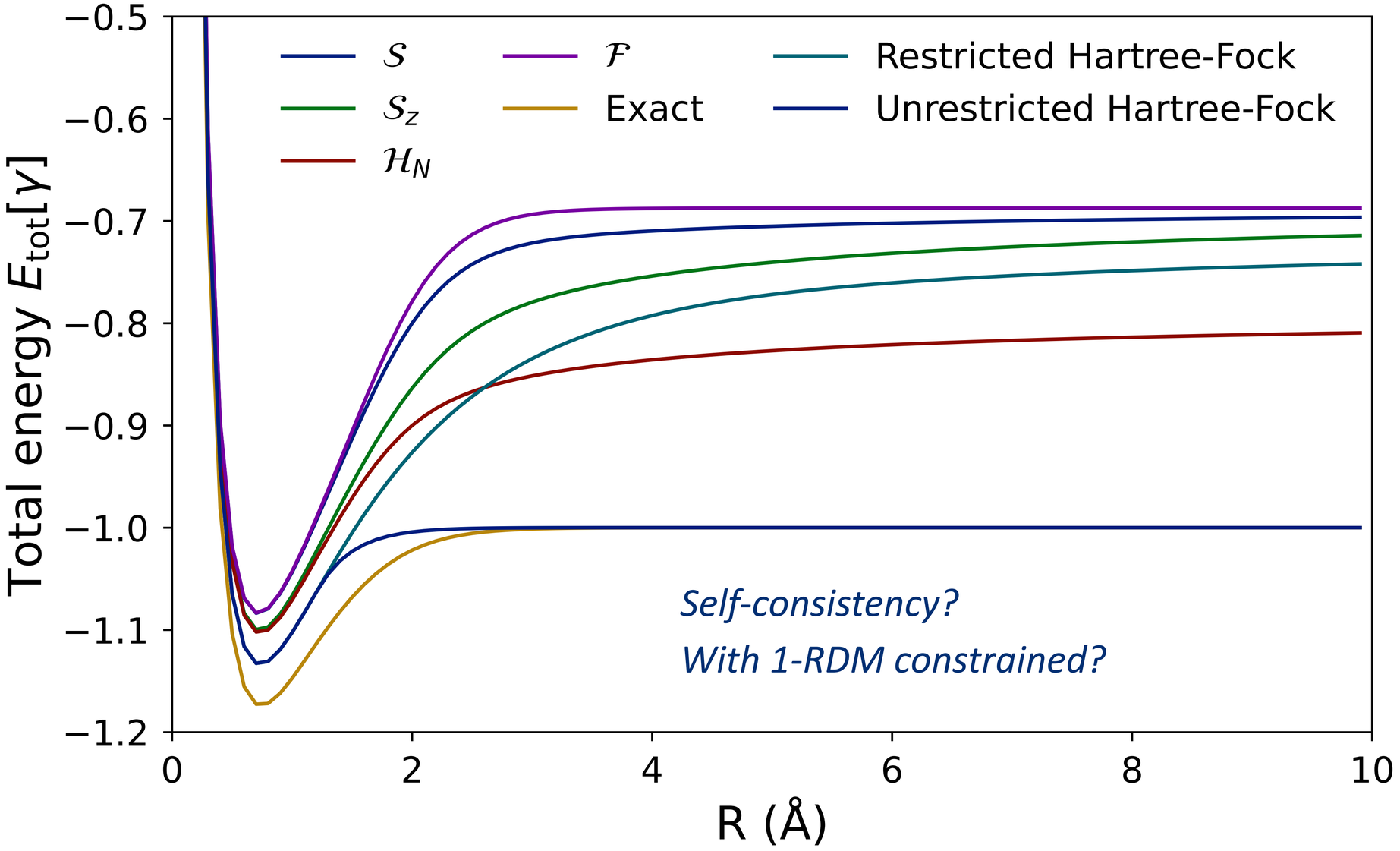

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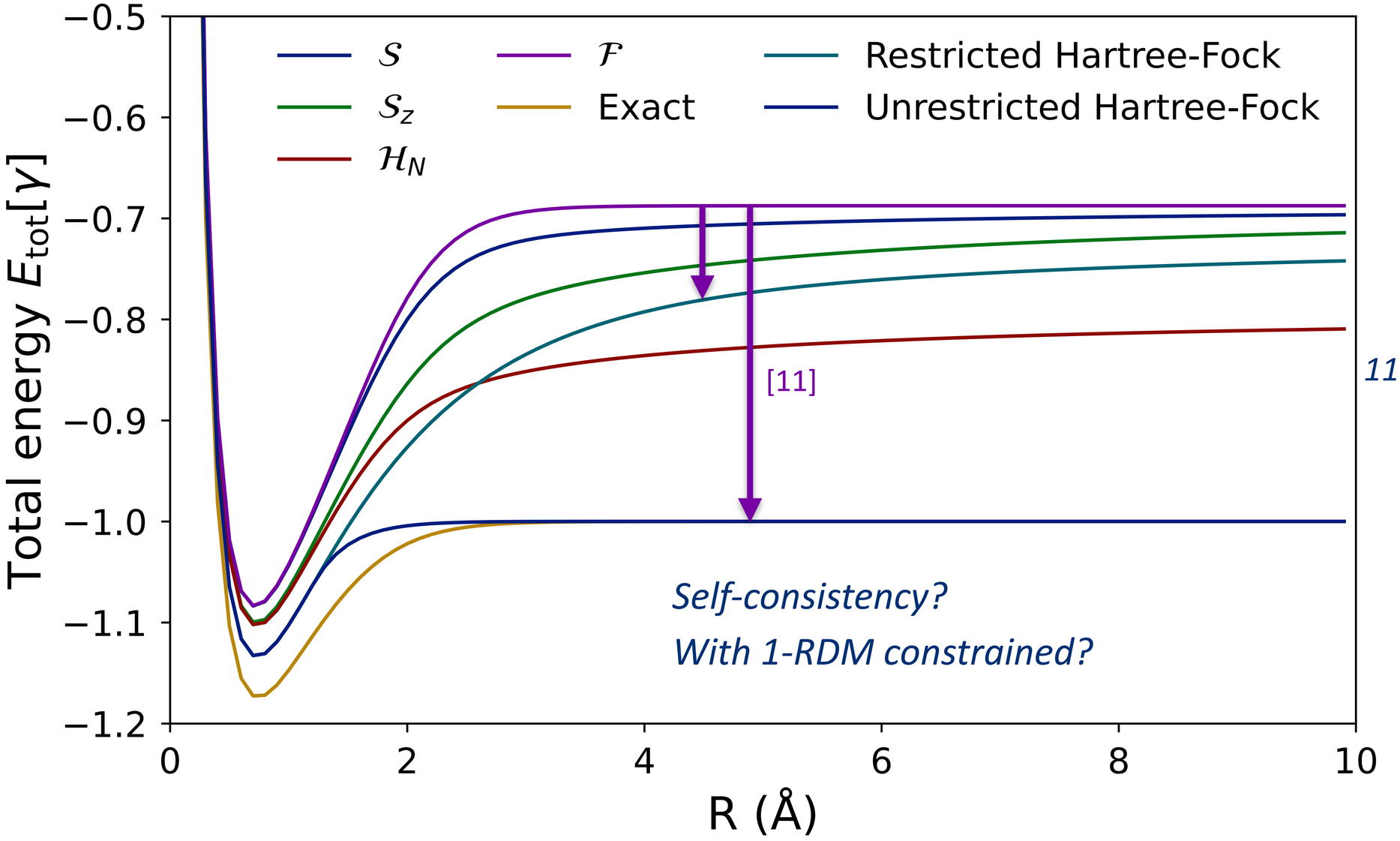

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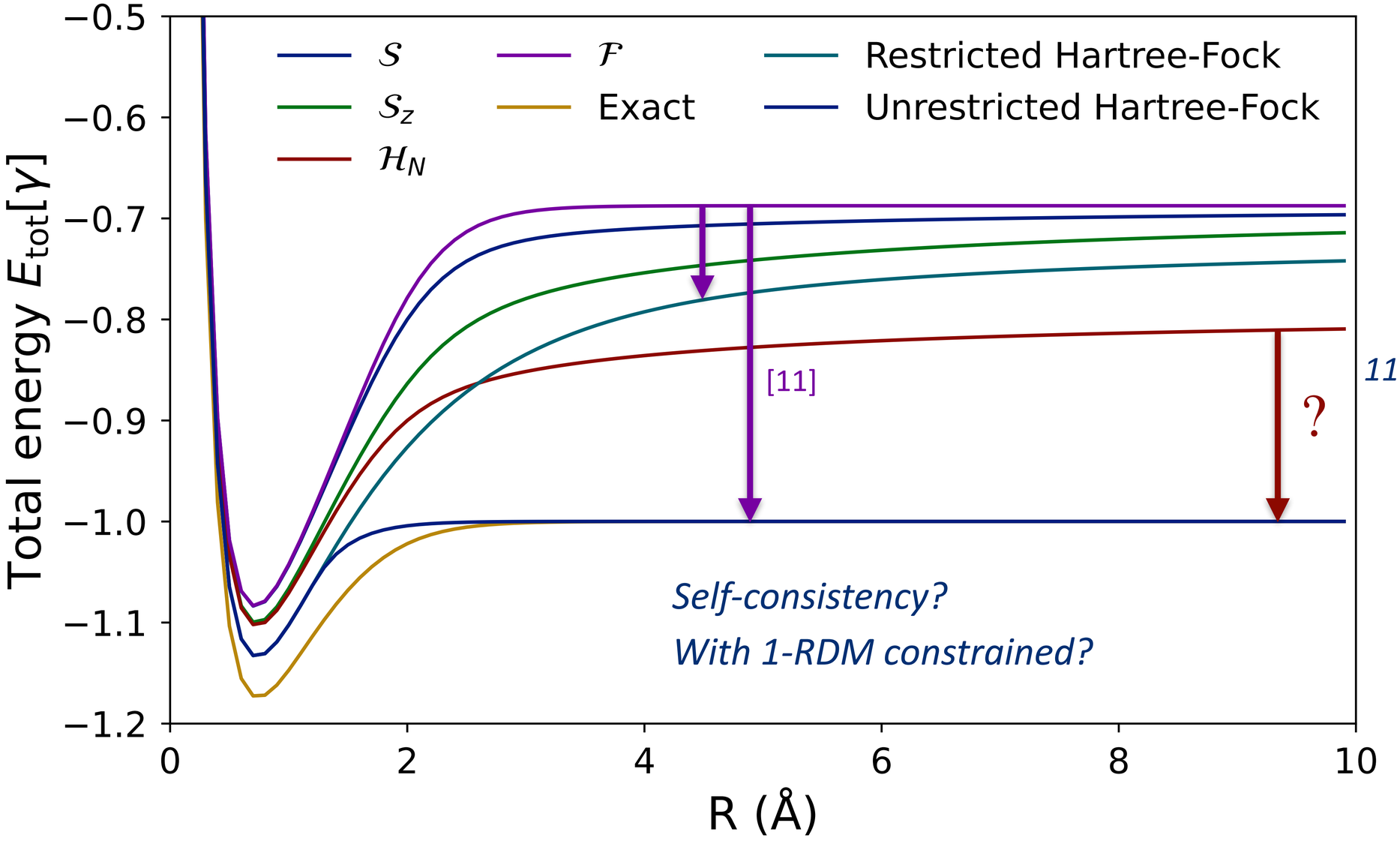

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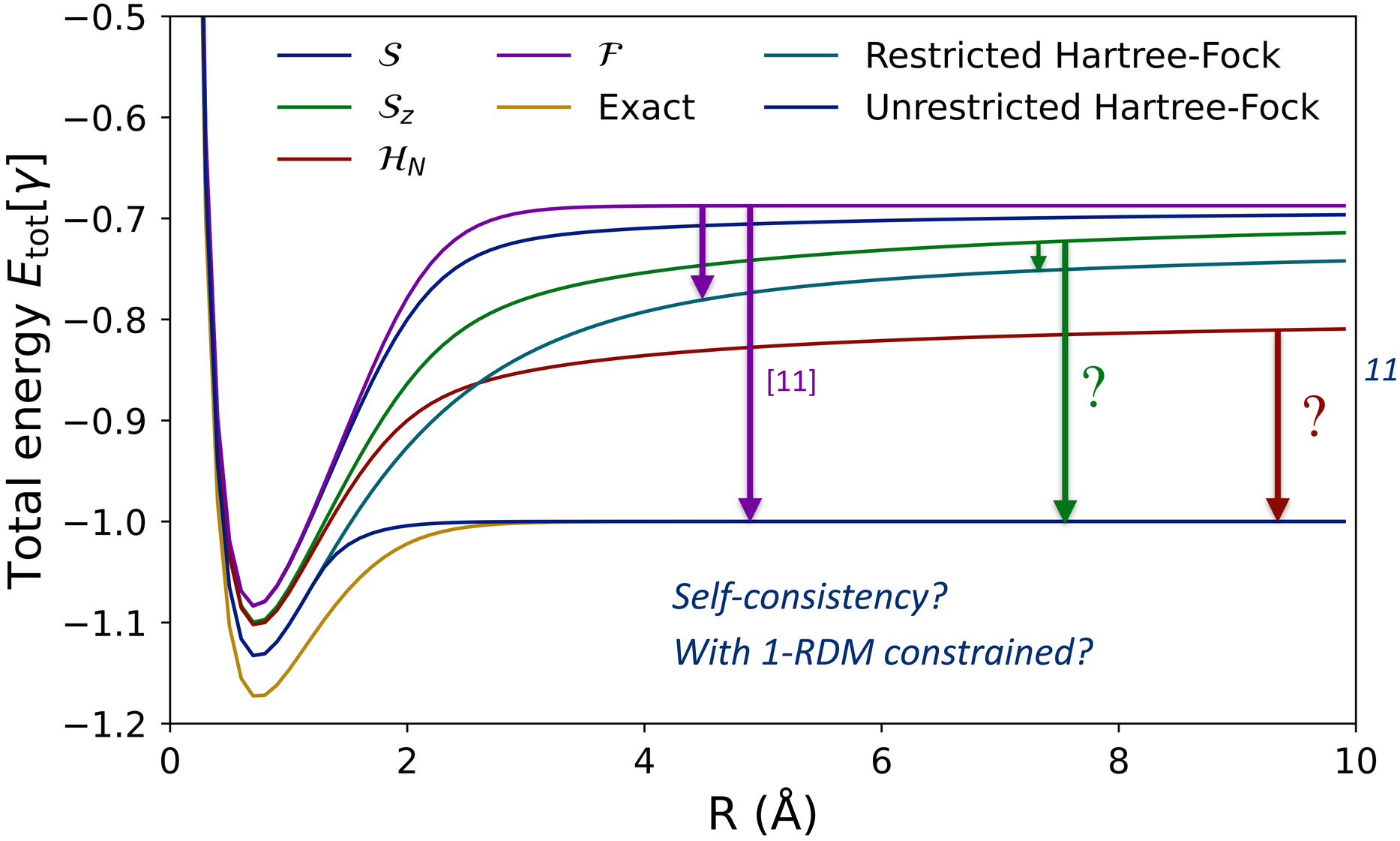

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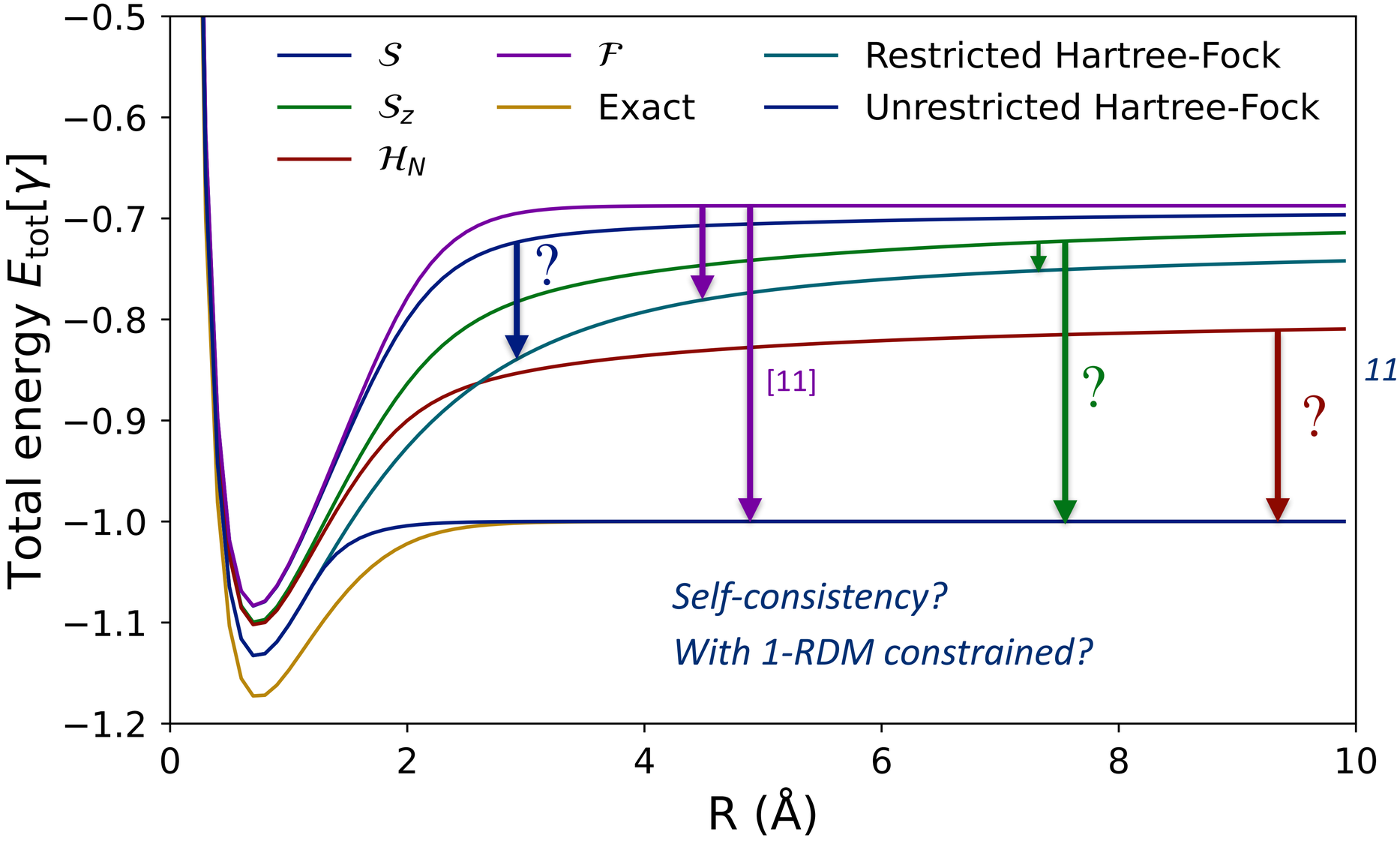

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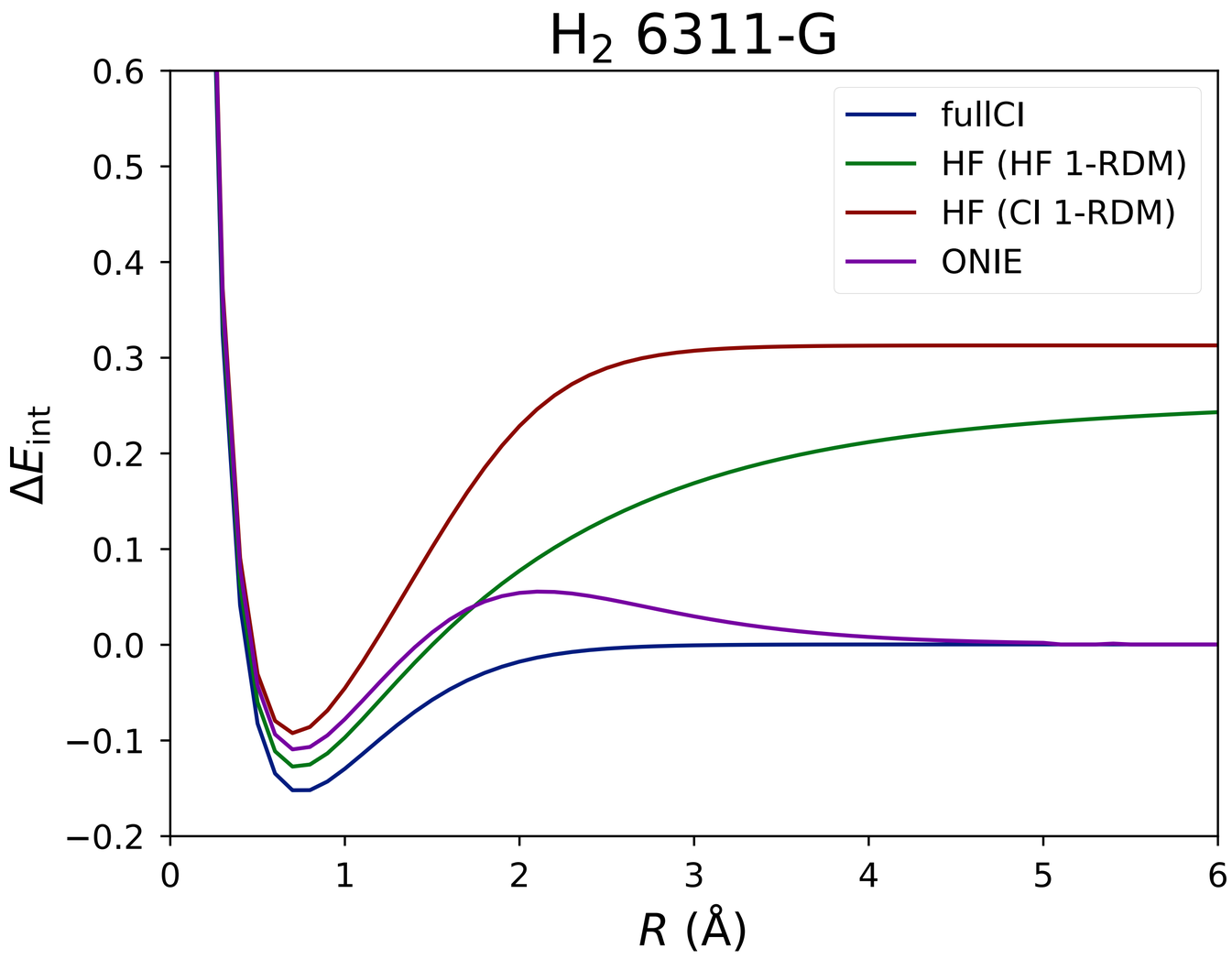

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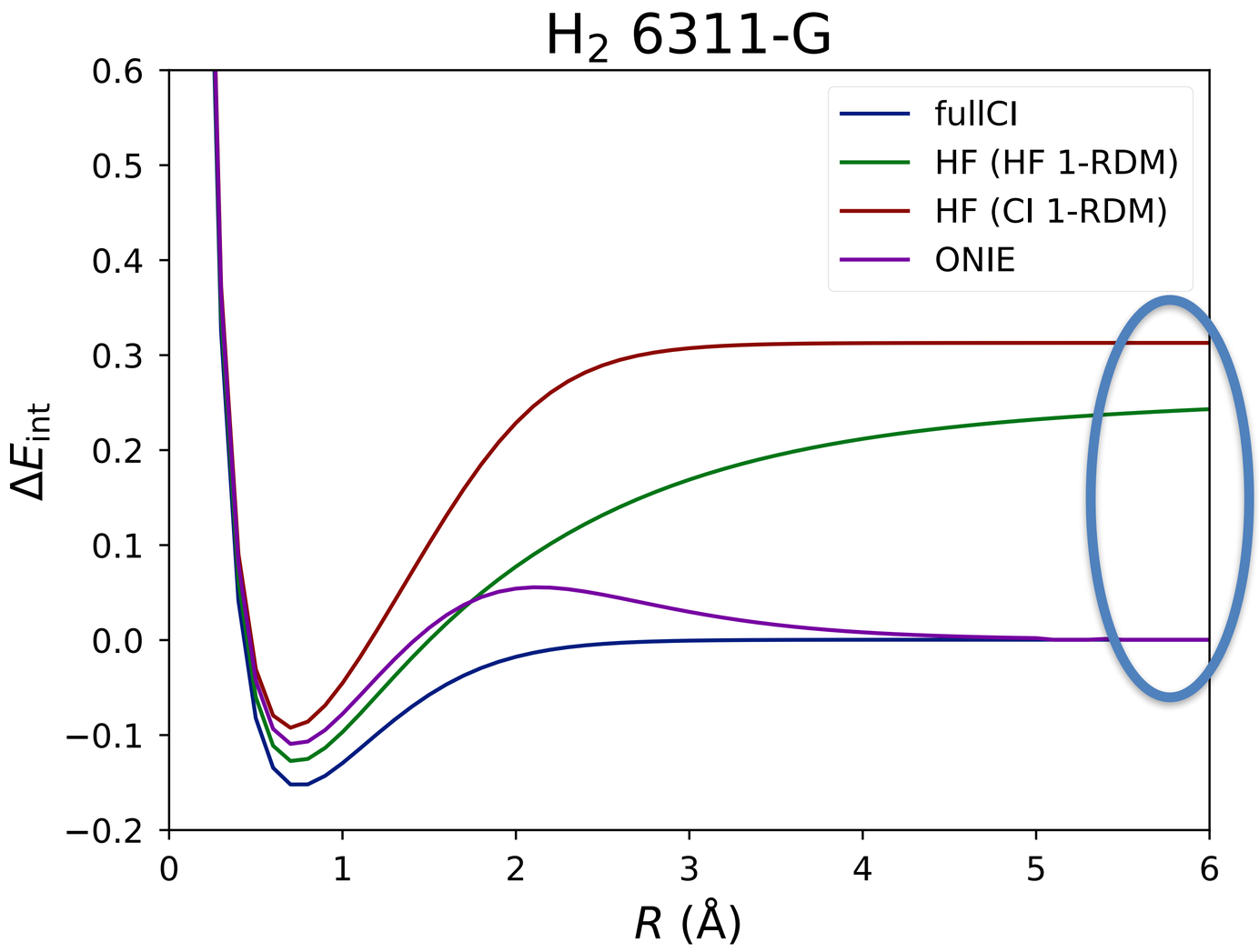

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- A study of the corresponding canonical approximation to the interaction $W_0[\gamma]$ revealed interesting behaviour w.r.t. grand canonical

Thanks

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References

References

- Manuscript: arXiv:2205.15058 (under review)

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- bfsinkhorn: https://www.github.com/DerkKooi/bfsinkhorn

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1-RDM Optimisation

$$h_{pp} - \frac{1}{\beta}\frac{\partial S_0[\{n_q\}]}{\partial n_p} + \frac{\partial W_0[\gamma]}{\partial n_p} + \frac{A_c^{\beta}[\gamma]}{\partial n_p} = 0$$

$$\epsilon_p^{0,\beta(i+1)} = h_{pp}^{(i)} + \frac{\partial W_0[\gamma^{(i)}]}{\partial n_p} + \frac{\partial A_c^{\beta}[\gamma^{(i)}]}{\partial n_p^{(i)}} \longrightarrow n_p^{(i+1)}[\{\epsilon_q^{0,\beta(i+1)}\}]$$

1-RDM Optimisation

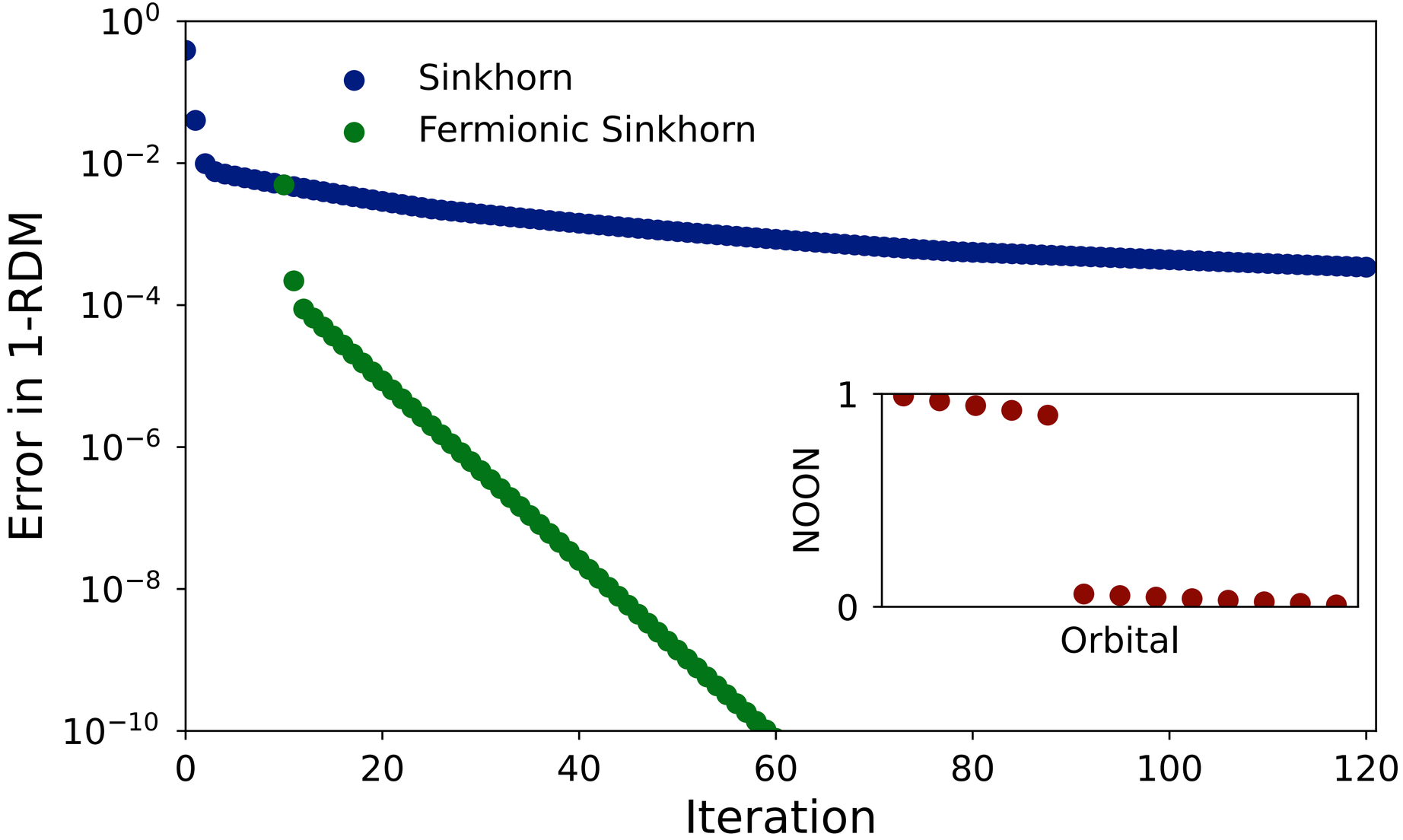
- We need to optimise w.r.t. NOONs $\{n_p\}$ and NOs $\{\phi_p(\mathrm{x})\}$
- Taking the derivative of $A^\beta[\gamma]$ w.r.t. n_p:

$$h_{pp} - \frac{1}{\beta}\frac{\partial S_0[\{n_q\}]}{\partial n_p} + \frac{\partial W_0[\gamma]}{\partial n_p} + \frac{A_c^\beta[\gamma]}{\partial n_p} = 0$$

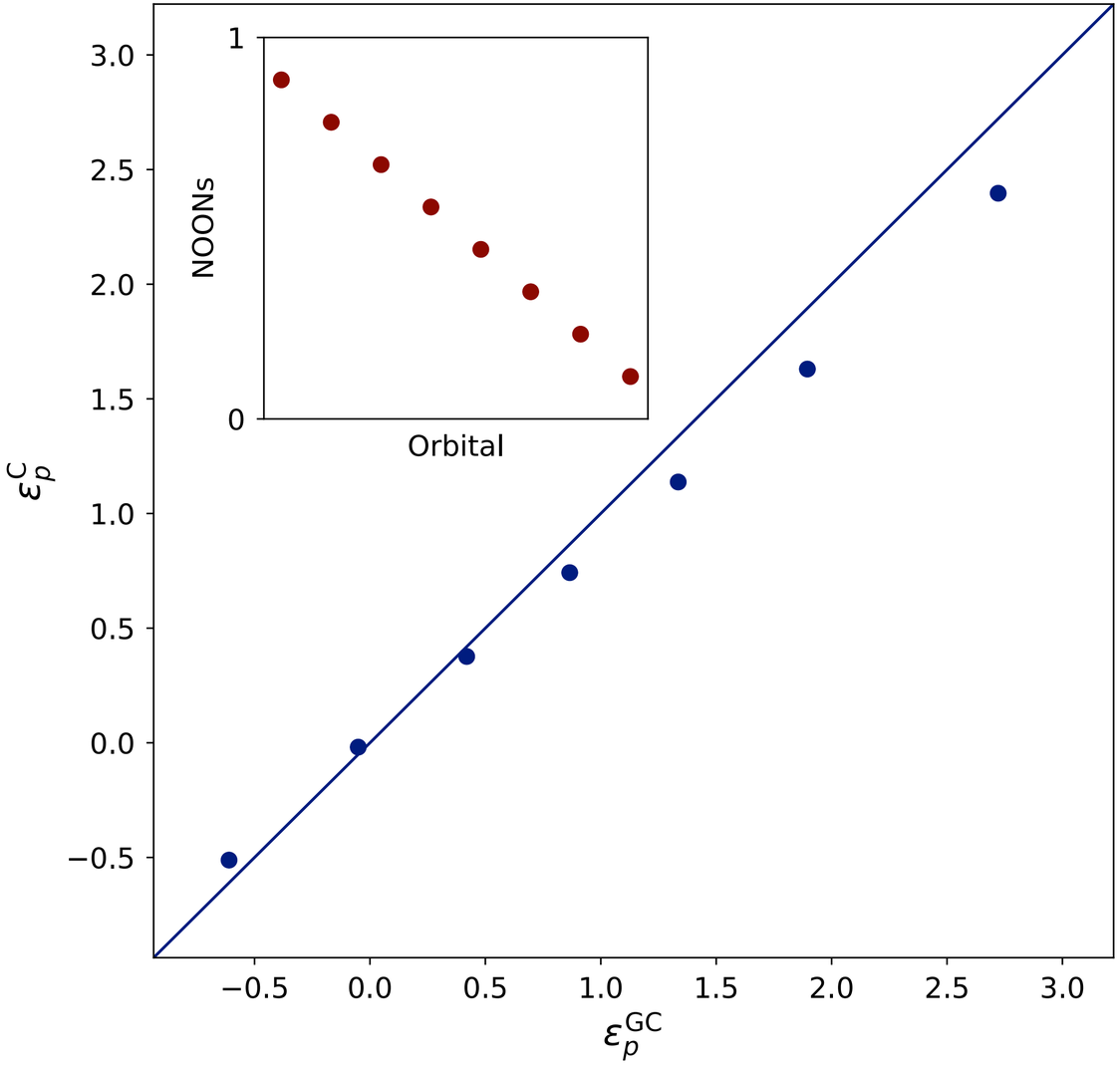
$$\epsilon_p^{0,\beta(i+1)} = h_{pp}^{(i)} + \frac{\partial W_0[\gamma^{(i)}]}{\partial n_p} + \frac{\partial A_c^\beta[\gamma^{(i)}]}{\partial n_p^{(i)}} \longrightarrow n_p^{(i+1)}[\{\epsilon_q^{0,\beta(i+1)}\}]$$

- Optimisation over NOs yields effective one-particle Schrödinger equation
- Analogous for Grand Canonical

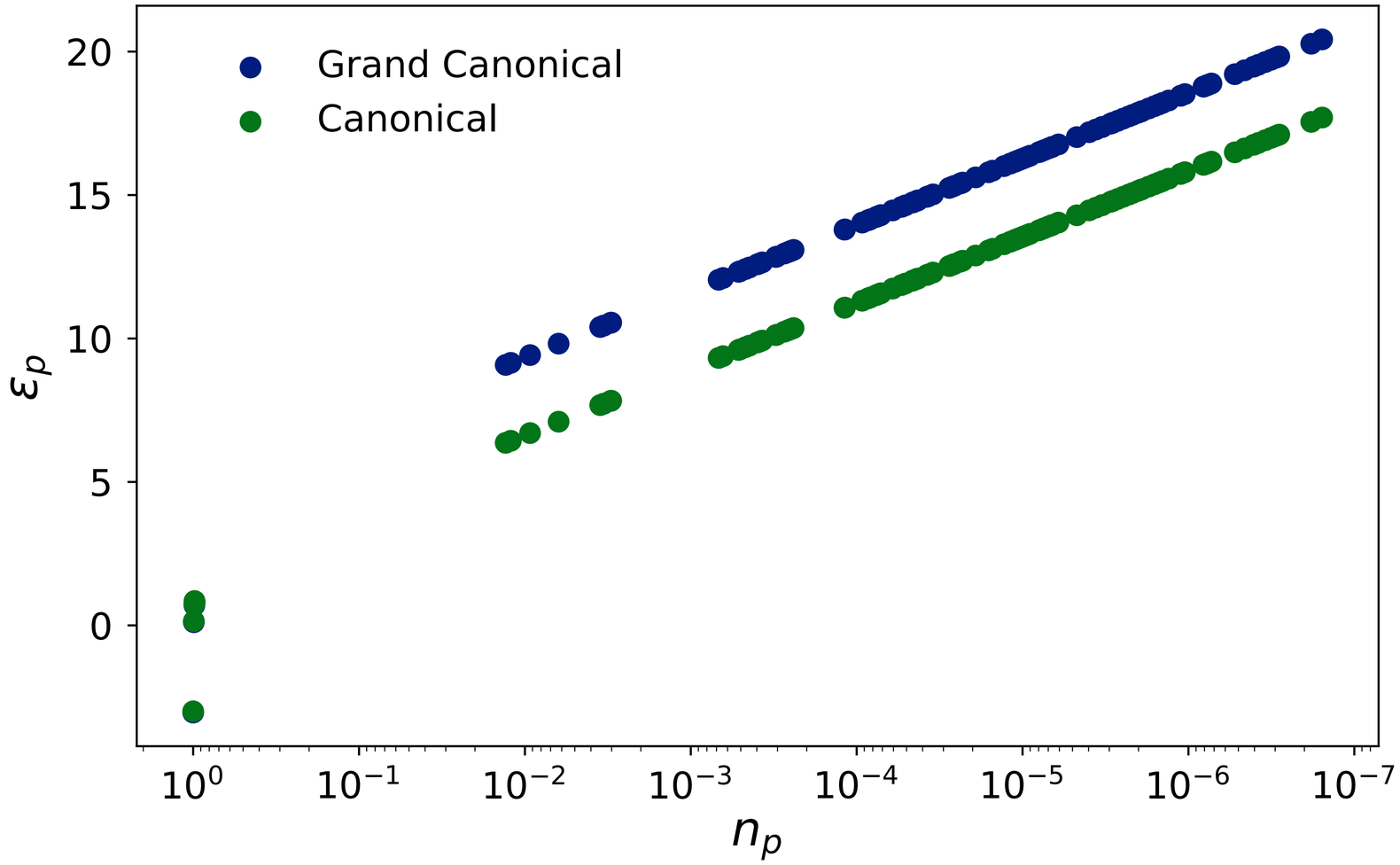
Hotstart convergence 5 fermions in 13 orbitals



Linear NOONs 4 particles in 8 orbitals



Orbital energies H_2O CCSD in cc-pVQZ basis



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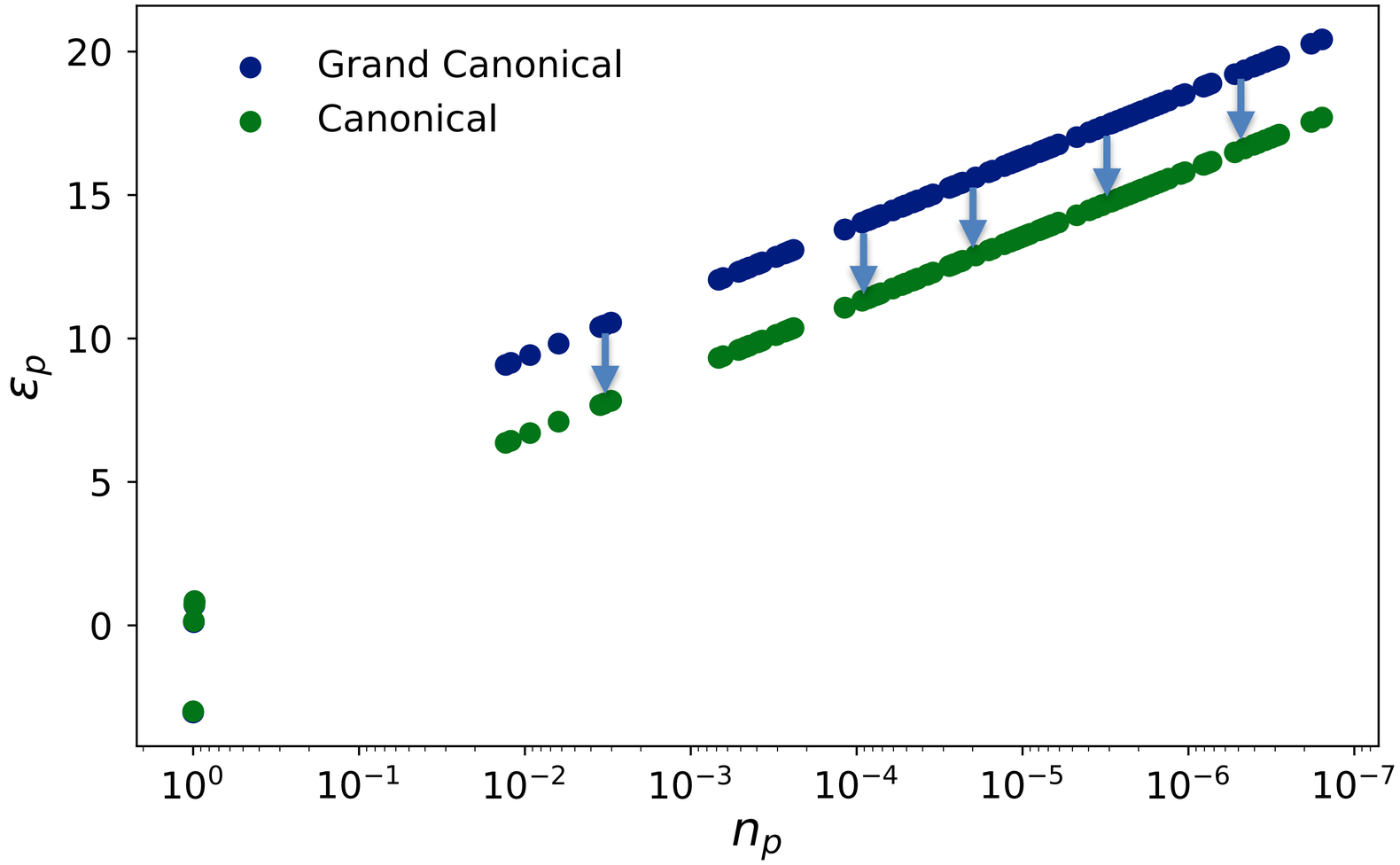
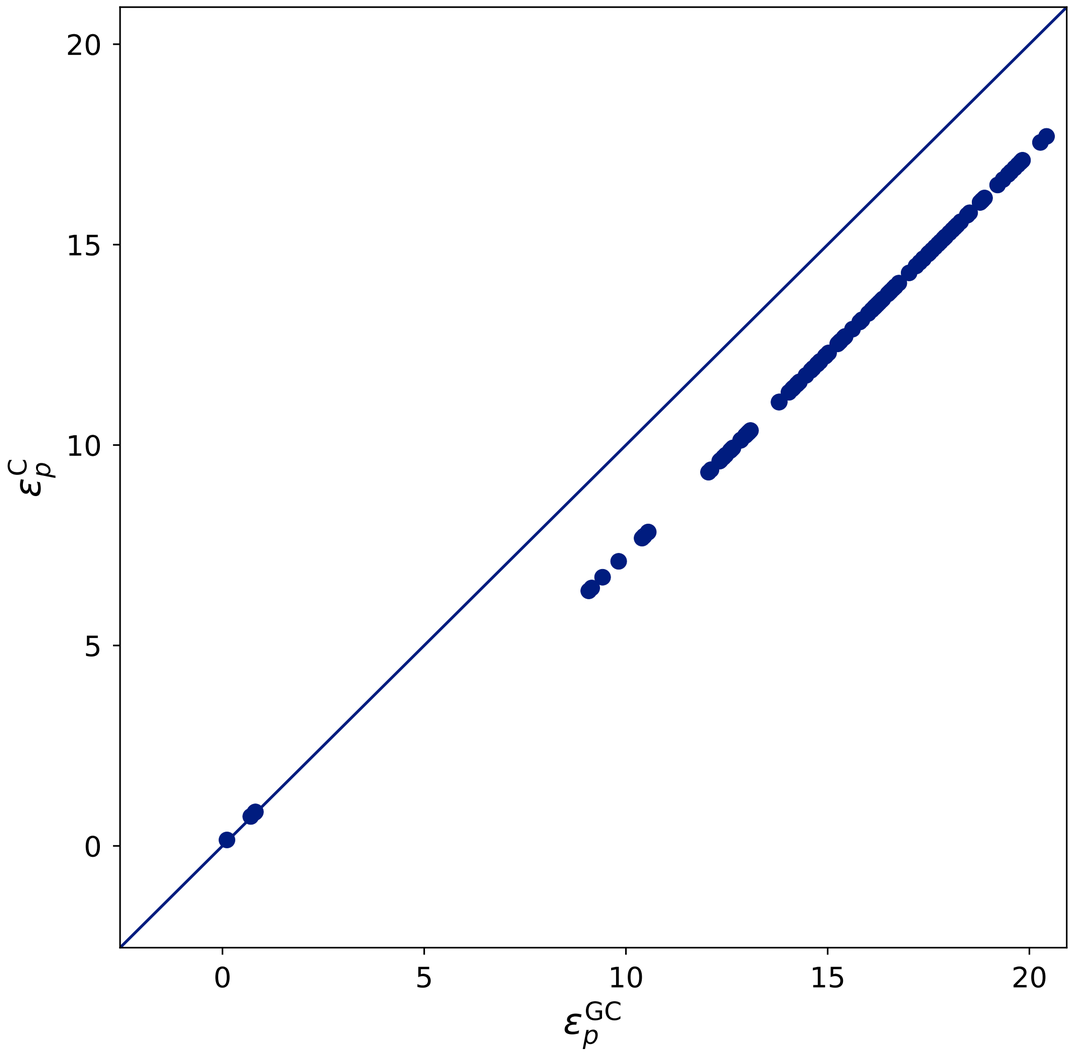
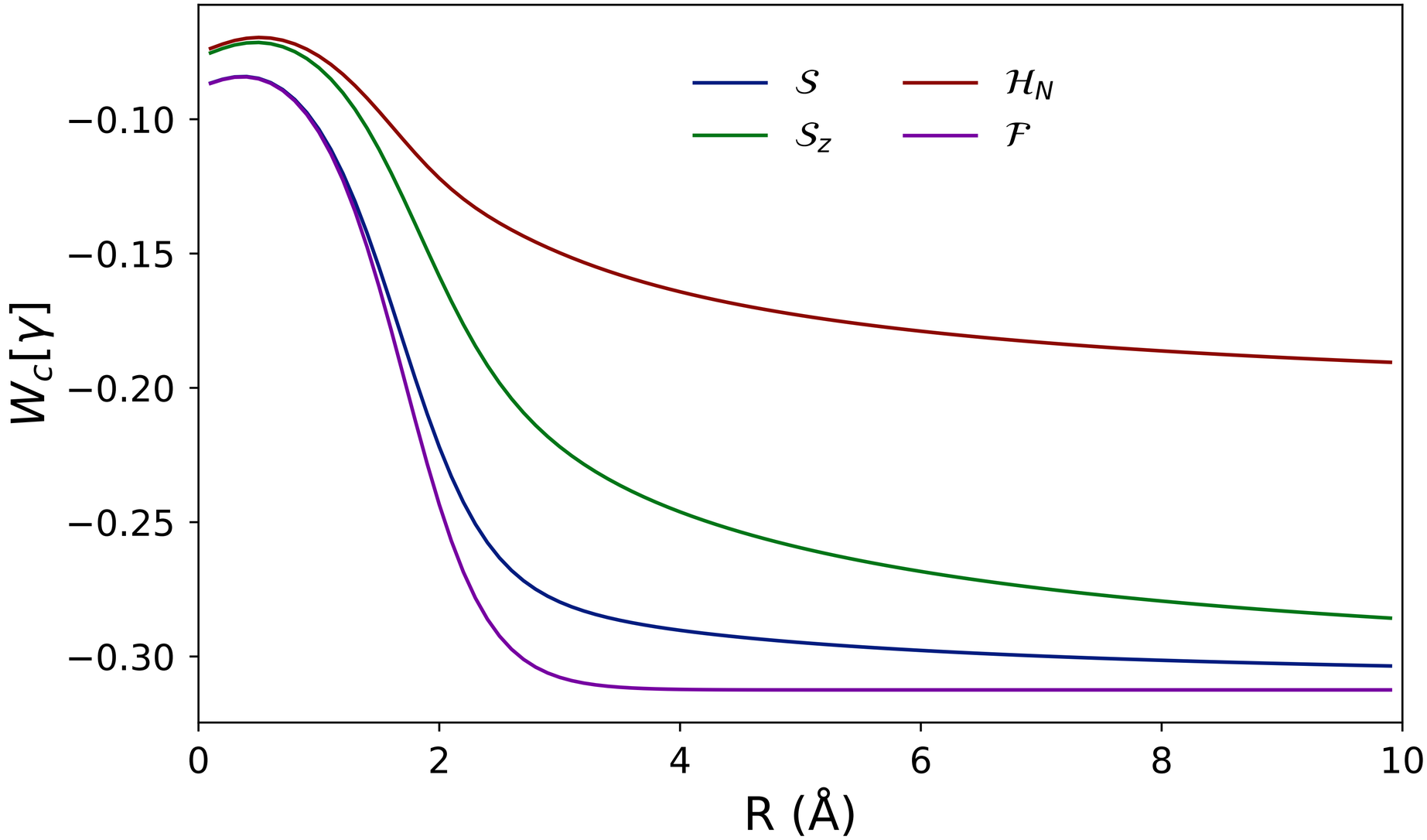


- Shift by a constant and either match the strongly or weakly occupied

Orbital energies H_2O CCSD in cc-pVQZ basis



H_2 dissociation, CISD (exact), aug-cc-pVQZ



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Grand Canonical: $$\mathscr{F} = \bigoplus_{N=0}^{\infty} \mathscr{H}_N \qquad \hat{\Gamma}^{\beta,\mu} \in \mathscr{F} \otimes \mathscr{F}$$

Dump

$$\mathcal{S}_z = \left\{ |\Phi_P\rangle \in \mathscr{H}_N | \quad \hat{S}_z |\Phi_P\rangle = S_z |\Phi_P\rangle \right\}$$

$$\mathcal{S}_z = \left\{ |\Xi_P\rangle \in \mathscr{H}_N | \quad \hat{S}^2 |\Xi_P\rangle = S^2 |\Xi_P\rangle \right\}$$