Transcorrelation in a bi-orthonormal framework: a hidden gem for QMC ?

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- **TC** or **VMC** ?

VMC: pros and cons

- **Pros: can handle any WF**
  - Variational optimization+probablistic approach: **8**

    Safe measure of the quality of any WF
    No need for semi analytical integrals
    Handles any forms of correlation factors
    Allow to try many forms of **compact** WF

- **Cons: statistical noise**
  - Stochastic optimization of many parameters ($> 10^5$): **8**

    Need to compute many gradients/hessian
    Small quantities → need to have small stat. error
    Hard to handle lengthy CI/CC expansions
  - Core electrons: **8**

    High-energy regions→ large variance of $E_{loc}(\mathrm{r})$
    Complex parametrization of $u(\mathrm{r}_1, \mathrm{r}_2)$ to adapt to the core
    Core electrons are often just spectators of chemistry
    Often use pseudo potentials (localization approximation)

TC: pros and cons

- **Pros: deterministic framework**
  - Non-hermitian → "Simple" Hamiltonian: **8**

    "No more" than 3-body integrals
    Can rely on "pure" numerical integrals ($R^6 \times N^p$)
    Can use any form of correlation factor
  - Deterministic calculations: **8**

    "Standard" second-quantized approaches (CI/CC etc)
    Orbital optimization
    Can handle very lengthy parametrization ($\approx 10^8$)
- **Cons: non variational8**
  - Hard to know the "true" quality of WF
  - Hard to optimize the correlation factor
  - Core electrons:

    No clear core-valence splitting in real-space
    High-density regions are very sensitive
    Can cause "catastrophic" breakdown
    Need for complex $u(r_1, r_2)$ in the core regions

The aim of this talk: best of both world ?

- **Deterministic optimization of the Slater part**
  - TC Selected CI

    multi-configurational wave function
    coupling with dominant weak-correlation effects
  - Bi-orthonormal orbital framework

    Optimize both left- and right-eigenvectors
    Improves the SCI+PT2 convergence
    Enables frozen-core calculations

- **Variational Monte Carlo for Jastrow**
  - Safely optimize correlation factors
  - Few parameters Jastrow
  - Transferable from atoms to molecules

Connection between QMC and TC: the right eigenvectors

- Φ is the left- and right-eigenvector of $\tilde{H}_{\mathrm{VMC}} = e^J H e^J$ (hermitian)

$$e^J H e^J \Phi = E_{\mathrm{VMC}} e^J e^J \Phi \Leftrightarrow \tilde{H}_{\mathrm{VMC}} \Phi = E_{\mathrm{VMC}} S_{\mathrm{VMC}} \Phi$$

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- E_{TC} is **not necessarily variational ... 8**

Transcorrelation in a nutshell (Boys, Handy, 1969)

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Application to VMC: optimizing lengthy CI expansion

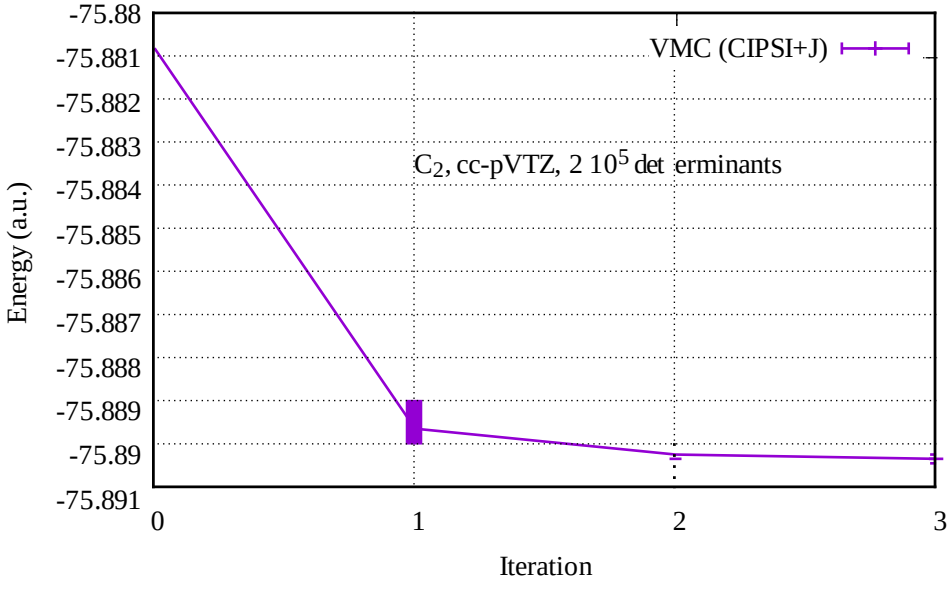
- Consider the $\Psi = e^J \Phi = e^J \sum_i c_i \varphi_i$
- The correlation factor J **is fixed**
- Goal: **re-optimize** lengthy CI expansions ($\approx 10^5$) for J
- Use **TC to optimise** Φ

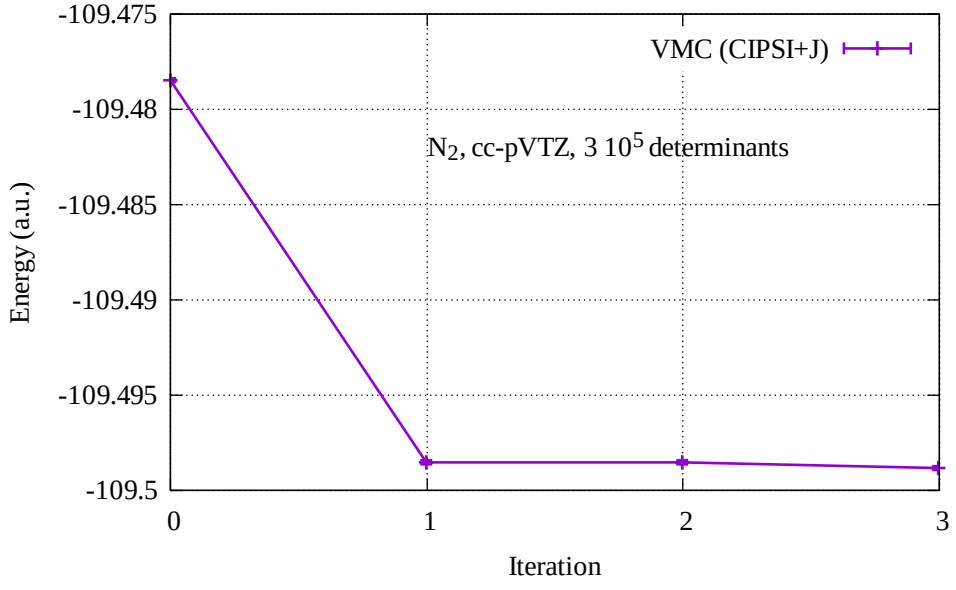
$$(H + \hat{\Delta}_U)\Phi = E\Phi$$

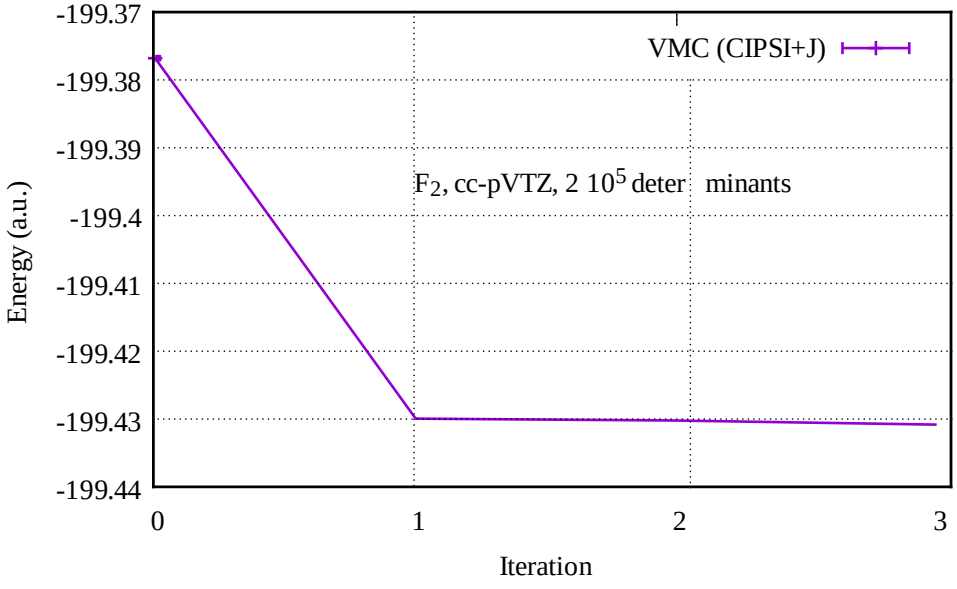
- We chosed a generic one- and two-body correlation factor
- Technicalities: **iterative hermitian dressing**
  - Dressing inspired from MRCC work (JCP, 2016)
  - $H\Phi$ computed analytically (usual CI vector)
  - Sampling of a single vector $\hat{\Delta}_U\Phi =$ in VMC
  - $\hat{\Delta}_U\Phi$: small fluctuations
  - Zero variance with analytical integrals of simple U
  - Strong reduction of variance
  - **Could be done purely deterministically and linearly**

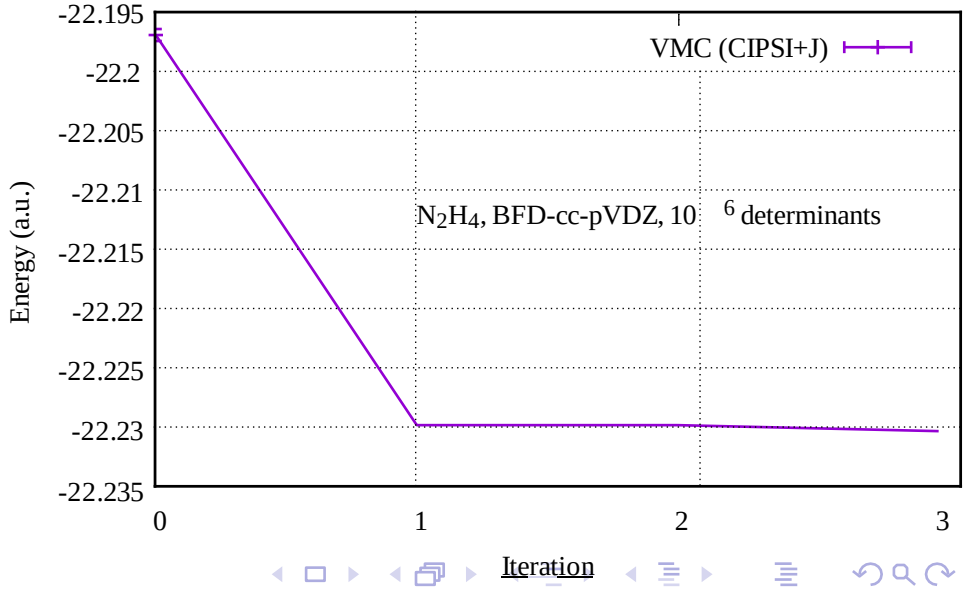
Application to VMC: optimizing lengthy CI expansion

TC can indeed lower the VMC Energy !









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- Stabilize the PT2 energy corrections

$$E_\alpha^{(2)} = \frac{\langle\chi^{(0)}|V|D_\alpha\rangle\langle D_\alpha|V|\Phi^{(0)}\rangle}{\tilde{E}^{(0)} - \epsilon_\alpha}, \quad E^{(2)} = \sum_\alpha E_\alpha^{(2)},$$

$$E_{\text{TC-FCI}} \approx E^{(0)} + E^{(2)}, \quad E^{(0)} \approx E_{\text{TC-FCI}} - E^{(2)}$$

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- Stabilize the PT2 energy corrections

$$E_\alpha^{(2)} = \frac{\langle\chi^{(0)}|V|D_\alpha\rangle\langle D_\alpha|V|\Phi^{(0)}\rangle}{\tilde{E}^{(0)} - \epsilon_\alpha}, \quad E^{(2)} = \sum_\alpha E_\alpha^{(2)},$$

$$E_{\text{TC-FCI}} \approx E^{(0)} + E^{(2)}, \quad E^{(0)} \approx E_{\text{TC-FCI}} - E^{(2)}$$

- Select Slater determinants based on $|E_\alpha^{(2)}|$

How to choose the Jastrow factor ?

Two kinds of $u(r_i, r_j)$?

- **Universal** correlation factors: $u(r_i, r_j) = u(r_{12})$
  - "cheap" integrals
  - same correlation hole everywhere
  - Easy parametrization (Univeral)
- **"3-body"** Jastrow: electron-nucleus dependency
  $u(r_i, r_j) = u(r_{12}, r_{1A}, r_{2A})$
  - usually non analytical integrals: $R^6 \times (N_{AO})^2$ integrals
  - Flexible correlation hole
  - Lots of parameters, not easy optimization

One parameter correlation factor (JCP-2021)

- **Reproduces RS-DFT** interaction at leading order in $1/r_{12}$

$$-\frac{2}{r_{12}}\frac{\partial u(r_{12},\mu)}{\partial r_{12}}+\frac{1}{r_{12}}=\frac{\mathrm{erf}(\mu r_{12})}{r_{12}},$$

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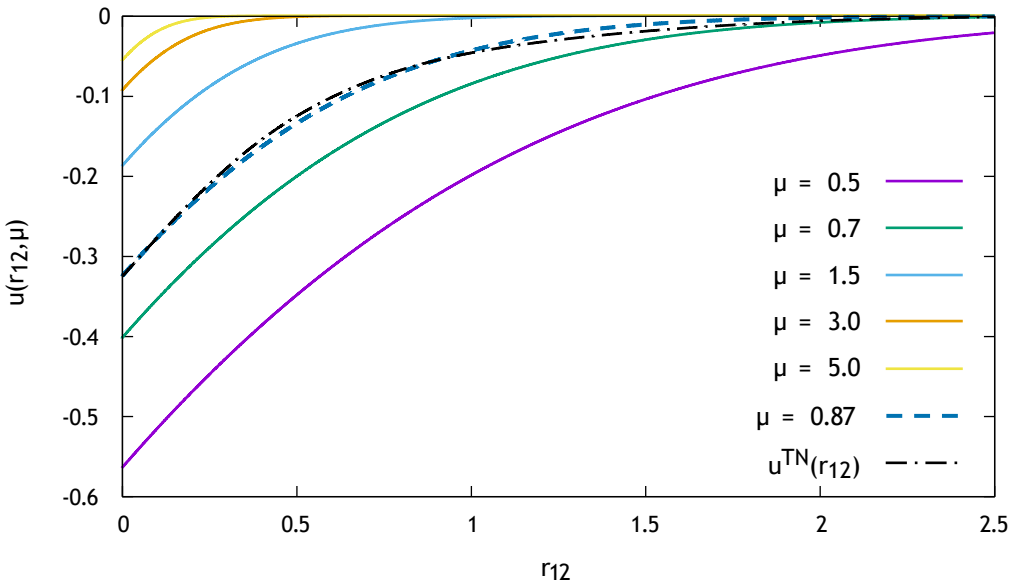

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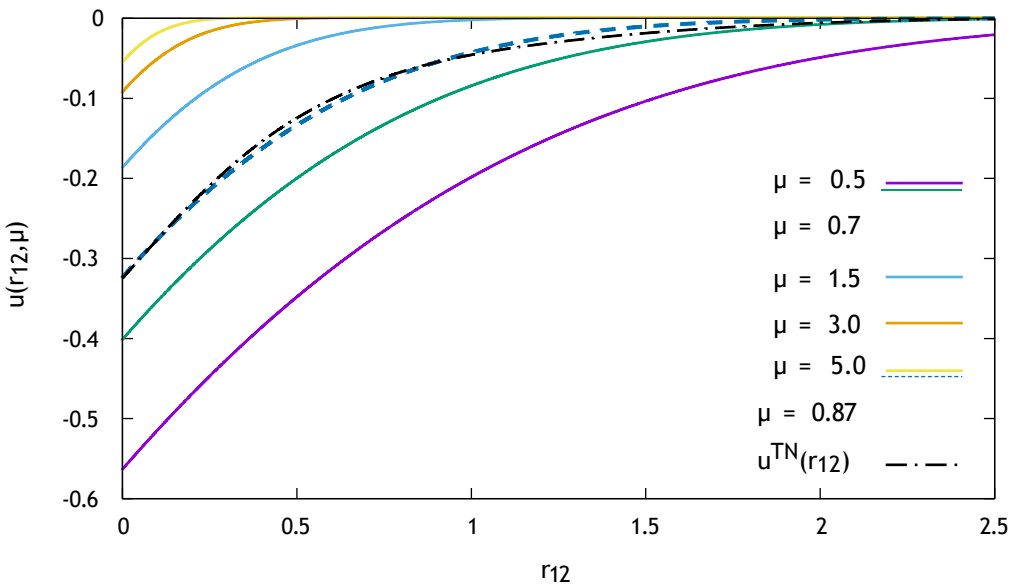
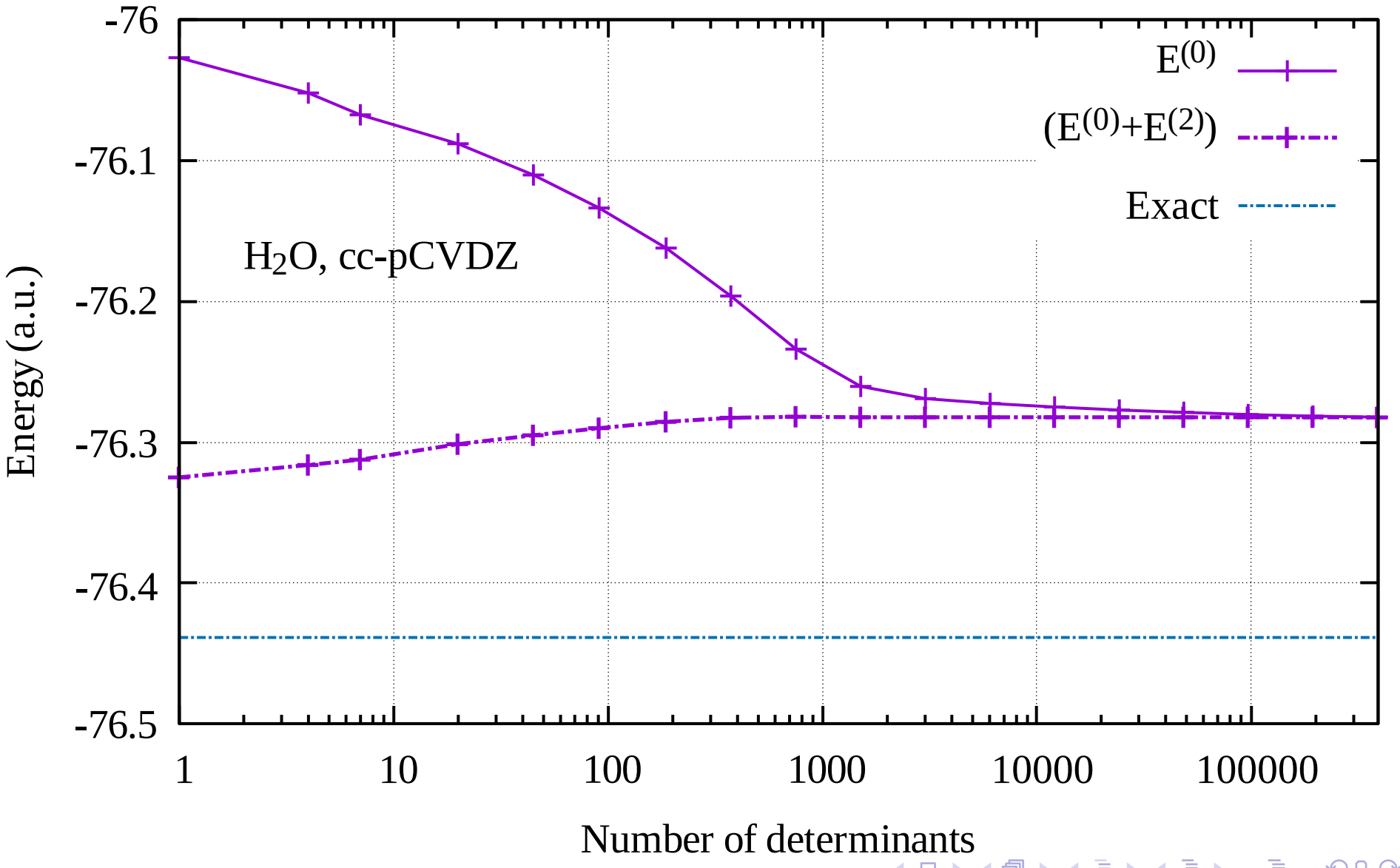
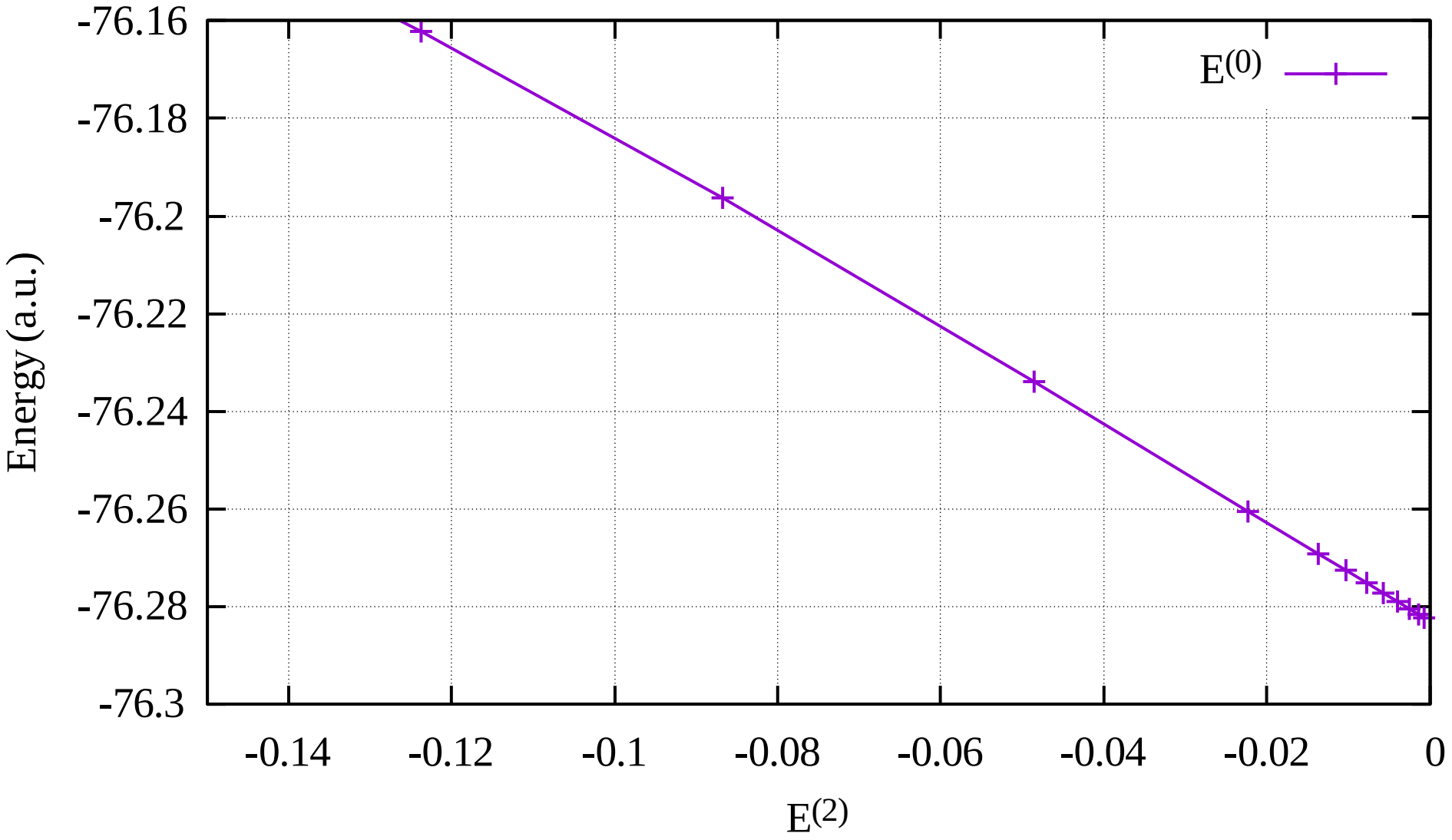


- μ: depth/range of $u(r_{12})$
- Valence μ = 0.87 ?
  - E_{TC} « E_0
  - Not adapted to core
- System dependent μ ?
  - Based on RS-DFT
  - Averaged over n(r)

Convergence of regular SCI



Convergence of regular SCI: extrapolation technique



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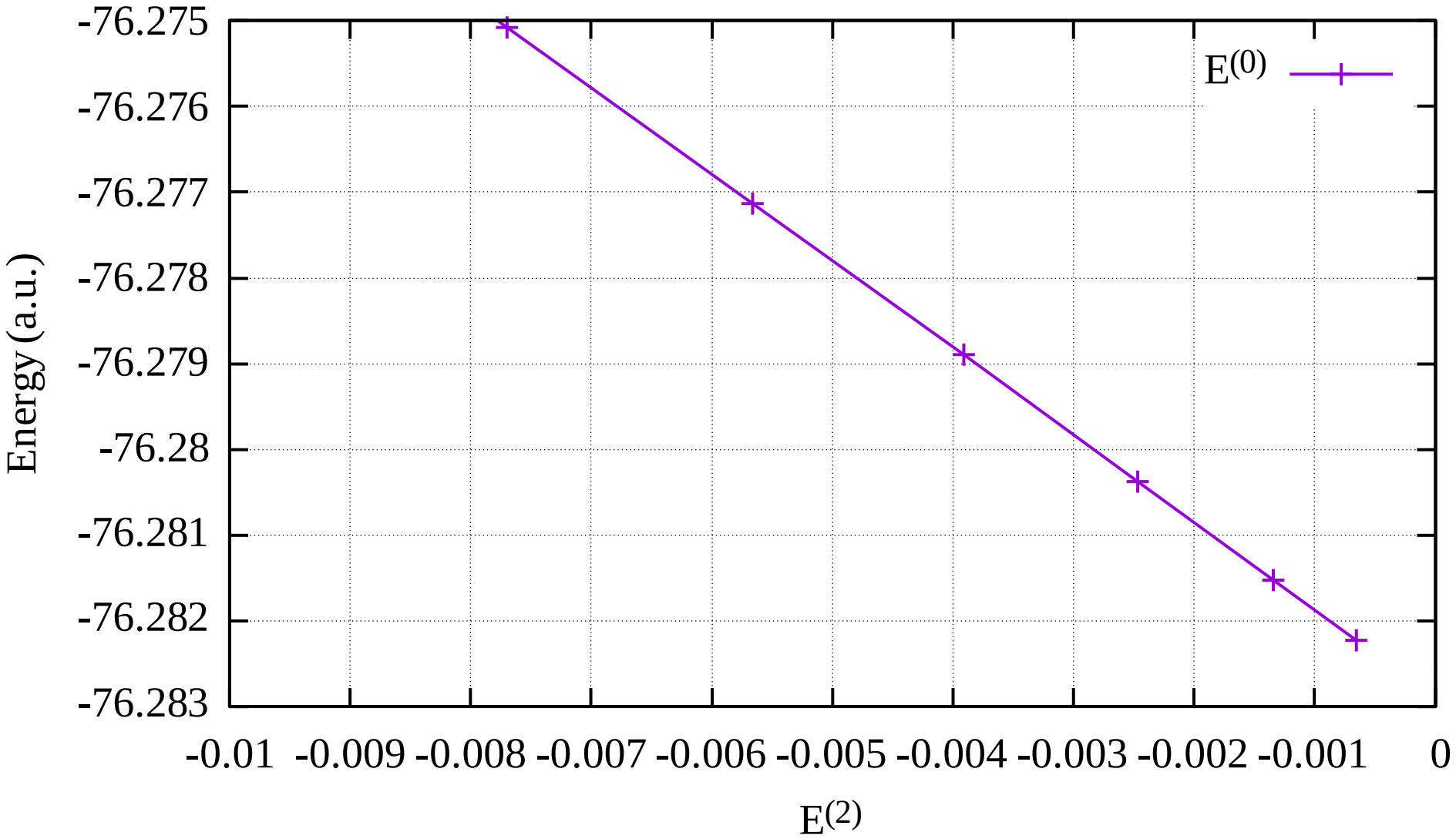

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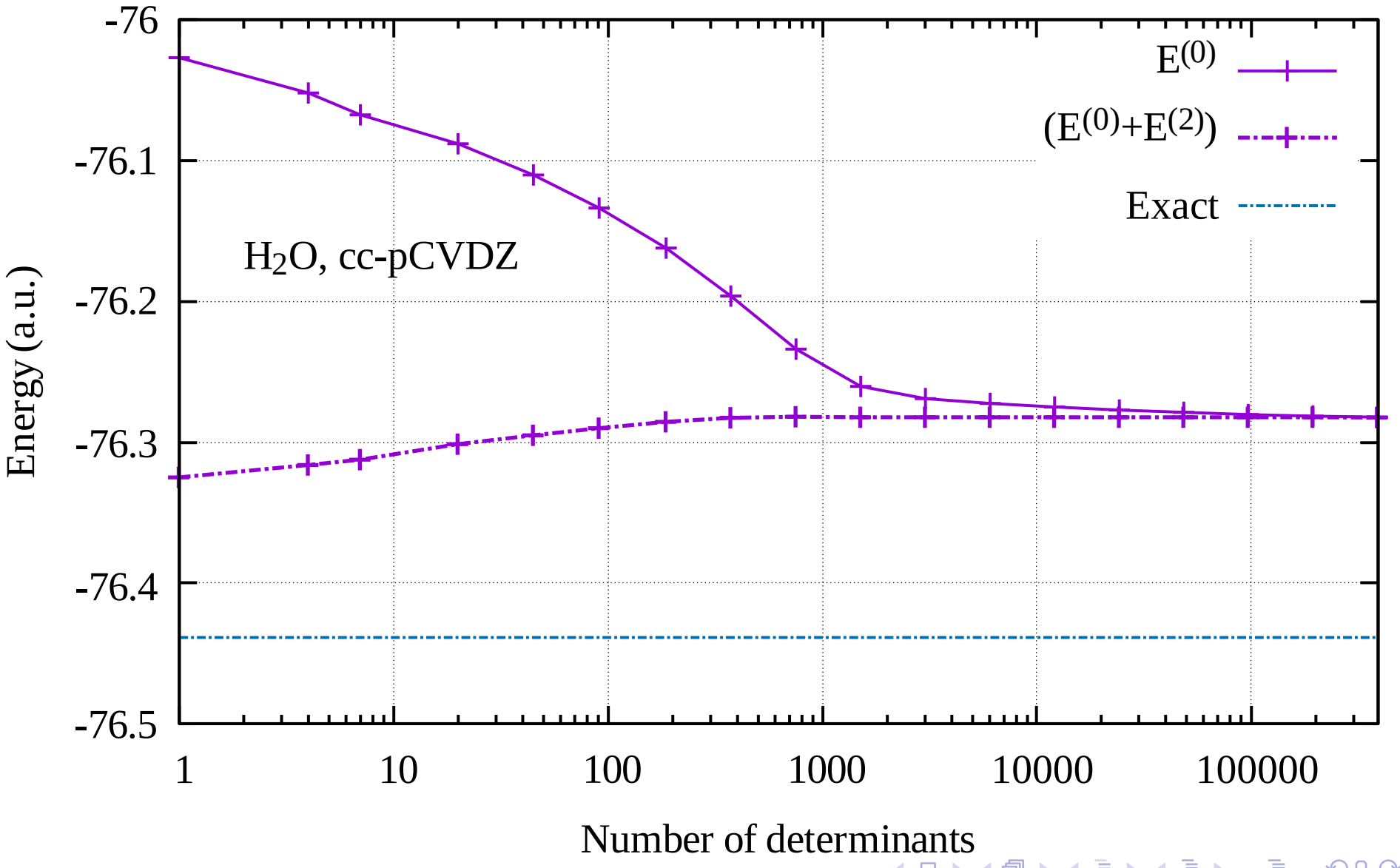
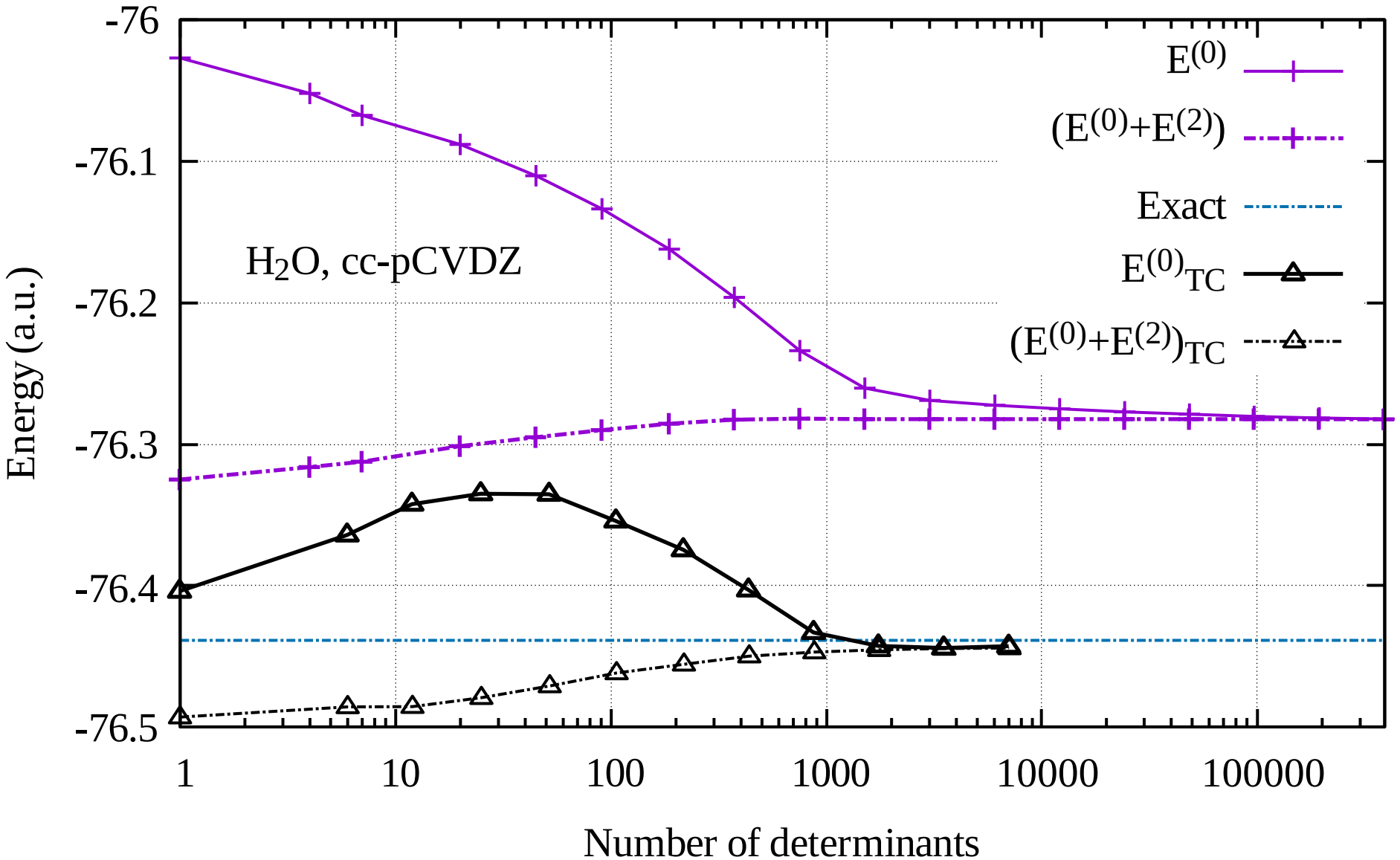
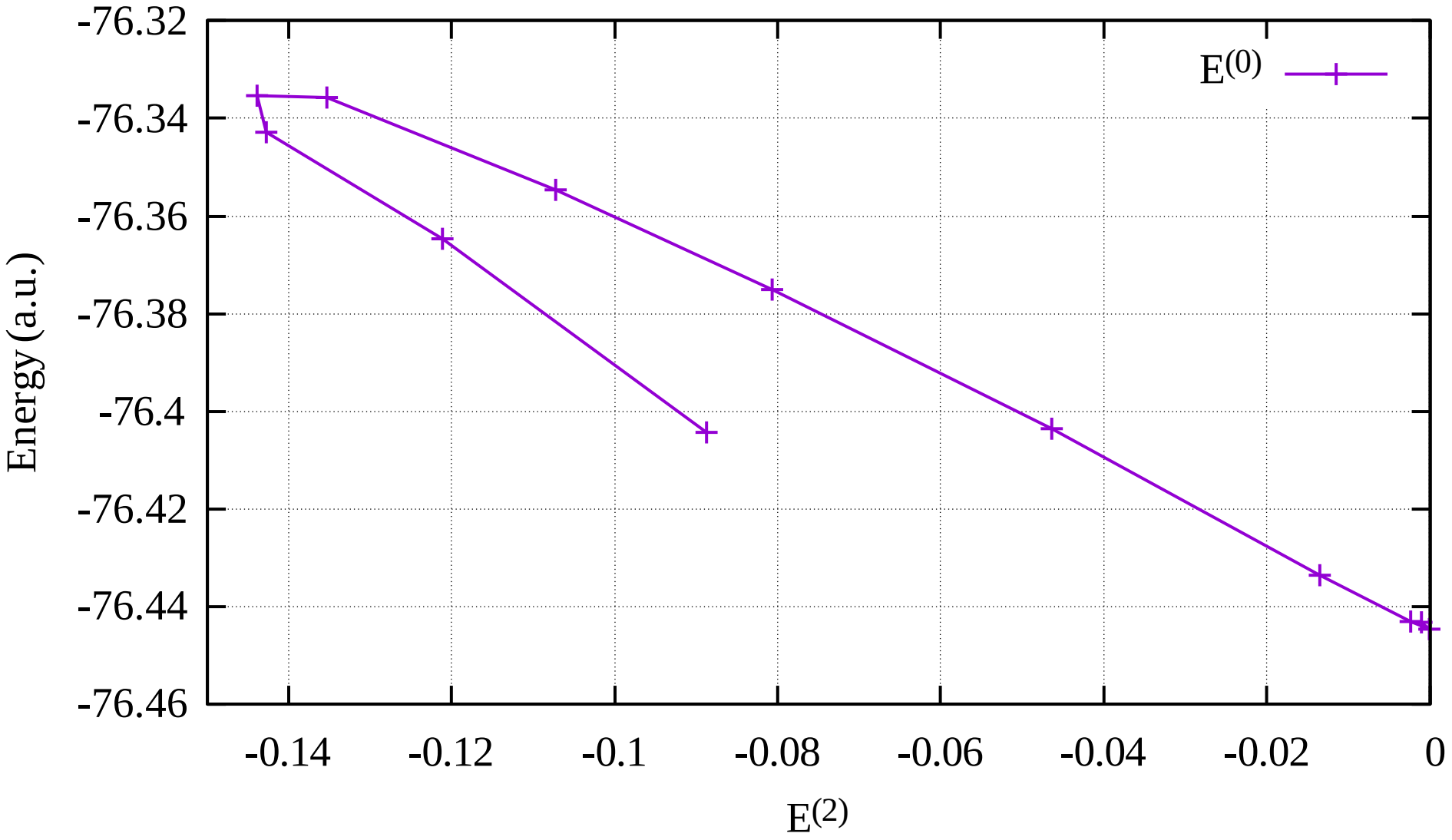


Convergence of TC-SCI



Convergence of TC-SCI: extrapolation breaks down



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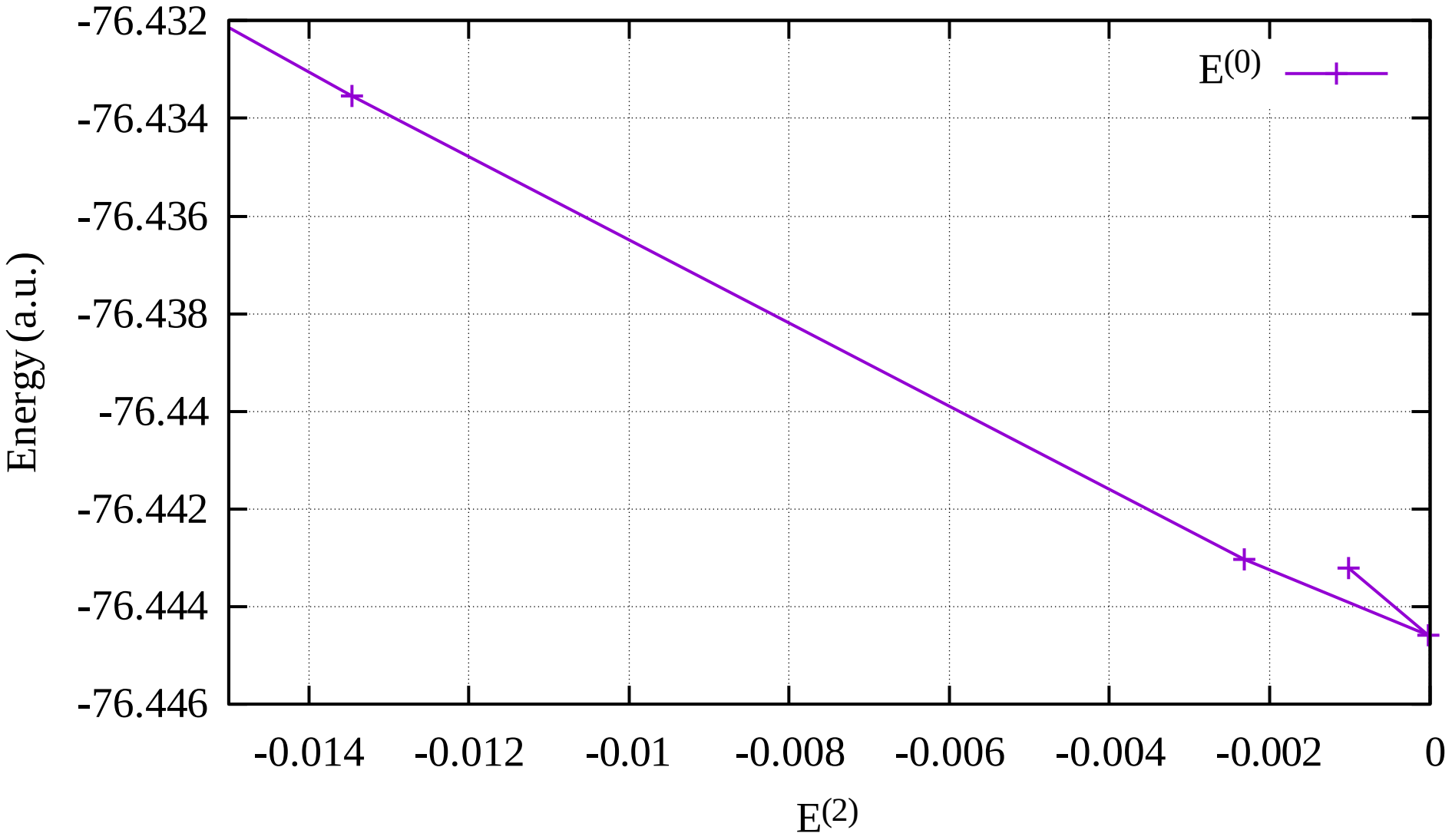
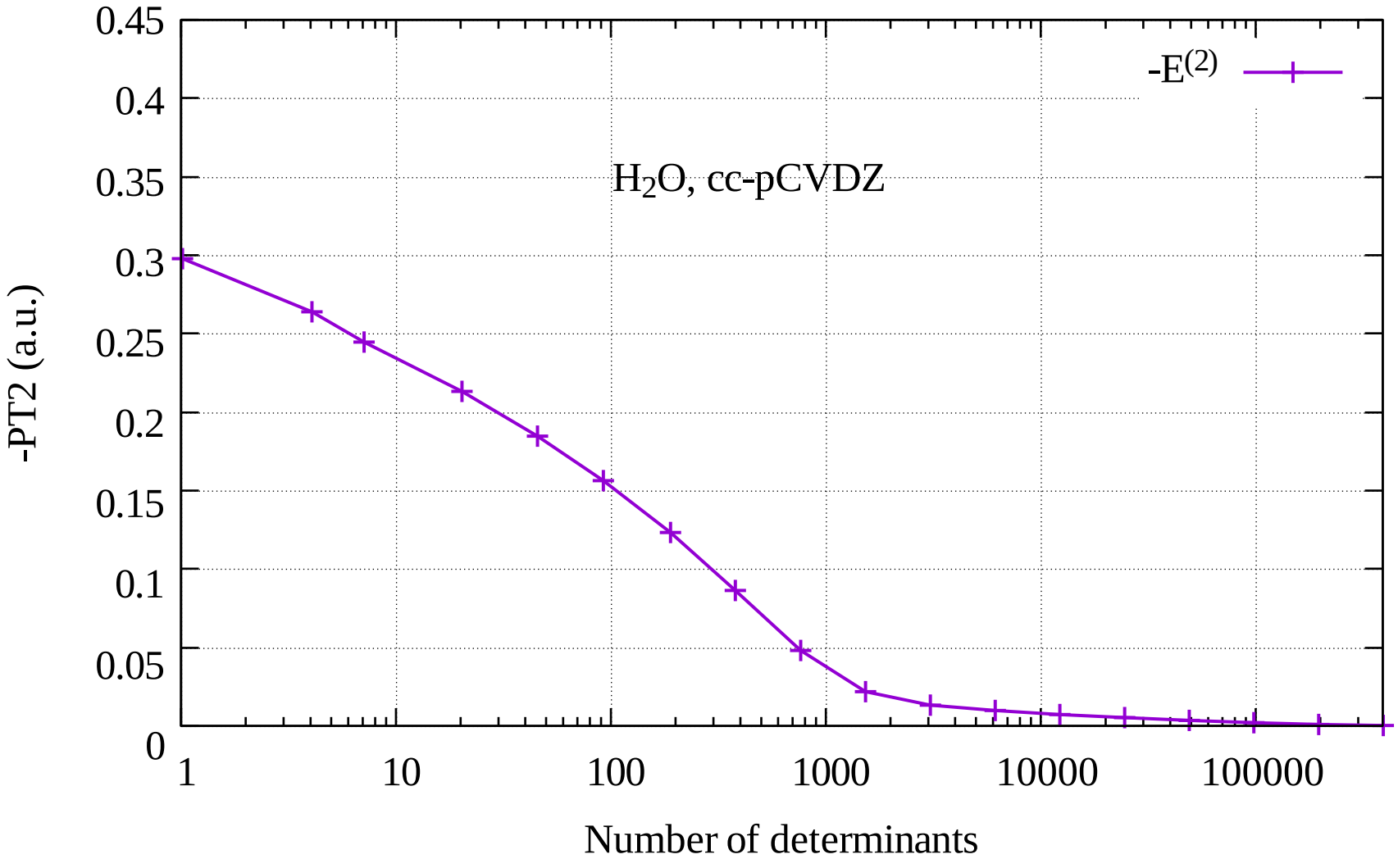


Deeper analysis: convergence of PT2



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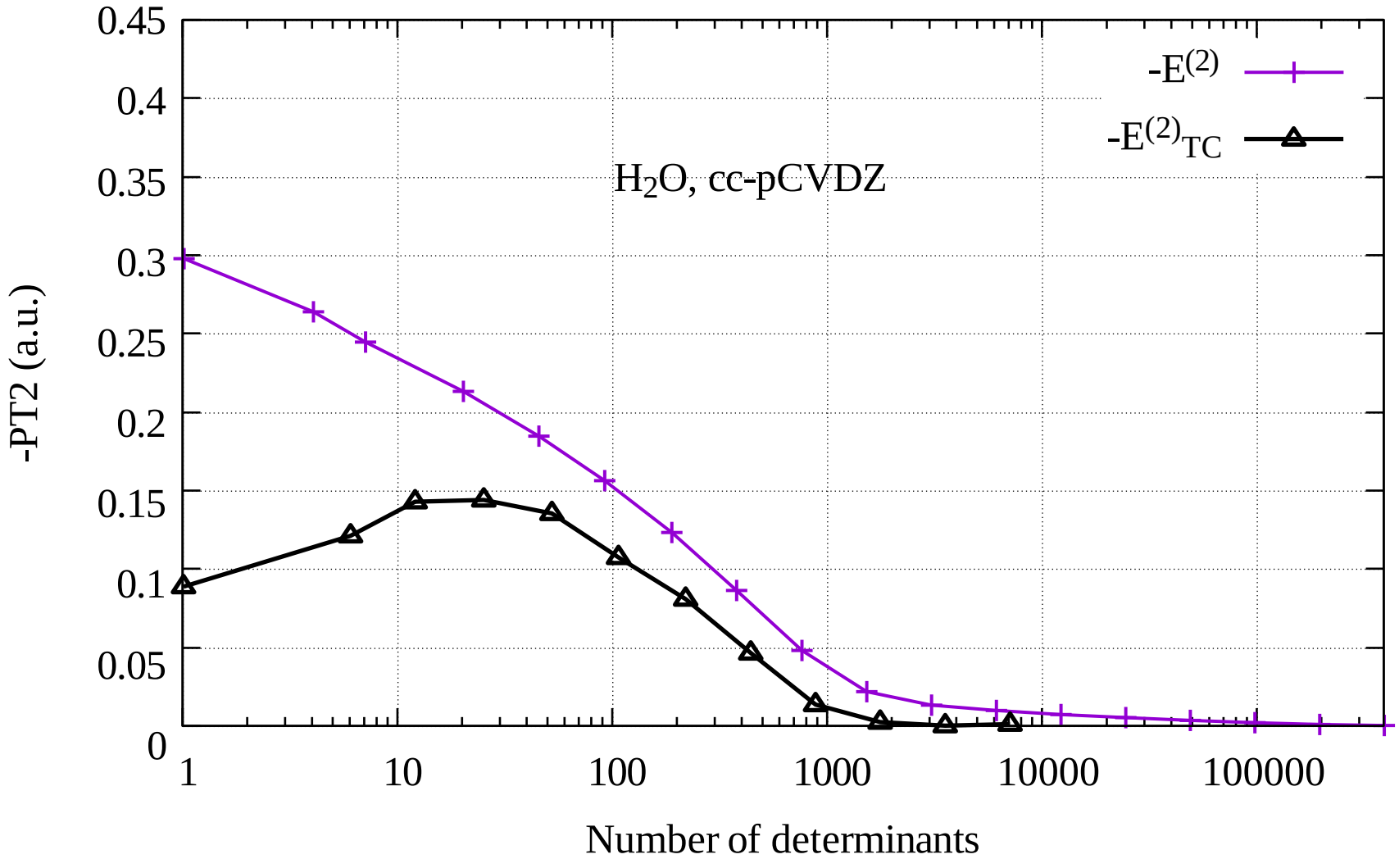

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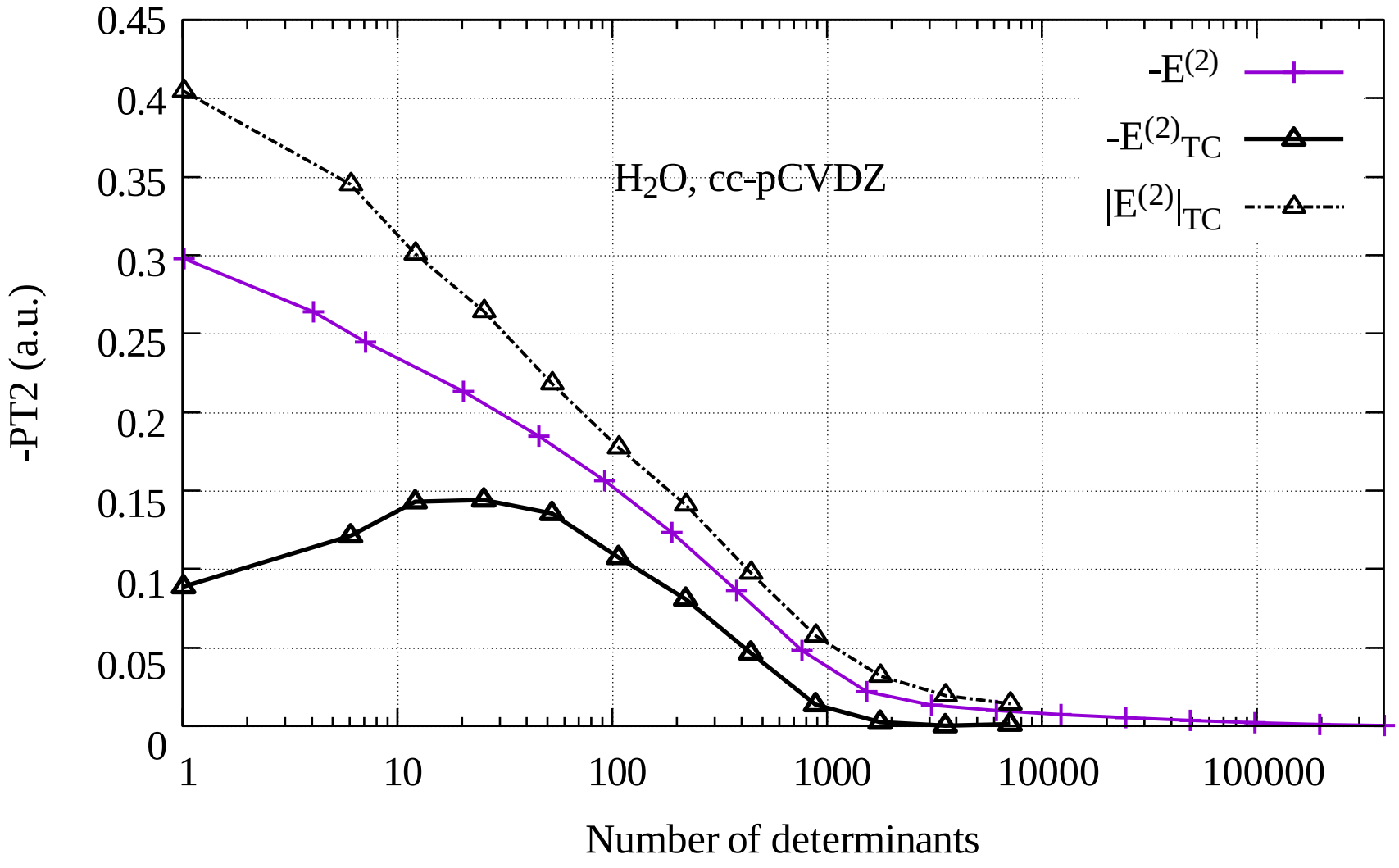

$E_{TC}^{(2)}$ is not a good measure !

Criticism of a system-dependent μ (JCP, 2021, JCP, 2022)

- Fast convergence cand **be fortuite ... 8**
- Unable to **extrapolate ... 8**
- Positive correlation energy !
  - Positive contributions come from the core !
  - Correlation hole too big for core electrons
  - μ must increase in core regions
- Average μ: Size-consistency ?
  - Dissociation of $A \cdots B$ molecule
  - $\mu \approx (\mu_A + \mu_B)/2$
  - $E \neq E_A + E_B$!
- Potential solution:
  - **Fixed valence** $\mu = 0.87$ (based on FROGG of Ten No)
  - **Remove core electrons from Jastrow !**

A potential solution: cheap 3-body Jastrow (JCTC, 2023)

- **Valence** μ: $\mu = 0.87 \approx$ FROGG
- Multiply $u(\mu, r_{12})$ by an **atom-centered gaussian envelope**

$$u(r_1, r_2) = u(\mu, r_{12}) \left(1 - \sum_A \exp(\alpha_A (r_1 - R_A))^2\right)\left(1 - \sum_A \exp(\alpha_A (r_2 - R_A))^2\right)$$

- **Kills** the correlation factor when $r \to R_A$
- **Integrals** can be computed **analytically**
- **Optimize** the α parameter in **VMC**
- Obtain **atomic parameters**: is it transferables to molecules ?
- Use a single **Slater determinant** anzats $e^U \Phi$
  - How to optimize the orbitals of Φ ?
  - **TC in a bi orthonormal** framework !

Bi-orthonormal framework

- General case of $\hat{H}\Phi = E\Phi$ **projected** on B^L and B^R

  $\hat{H}|\Phi\rangle = E\hat{S}|\Phi\rangle$, with $|\Phi\rangle = \sum_i c_i^r |\varphi_i\rangle$ and $H_{ij} = \langle\chi_i|\hat{H}|\varphi_j\rangle$, $S_{ij} = \langle\chi_i|\varphi_j\rangle$

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$$O_{ij}^{kl} = (\chi_k\chi_l|\hat{O}|\varphi_i\varphi_j\rangle$$

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$$X_I(r_1, r_2, \cdots, r_N) \neq \Phi_I(r_1, r_2, \cdots, r_N)$$

- But **bi-orthogonality relation** (as for orthonormal basis)

$$(X_I|\Phi_J\rangle = \delta_{IJ}$$

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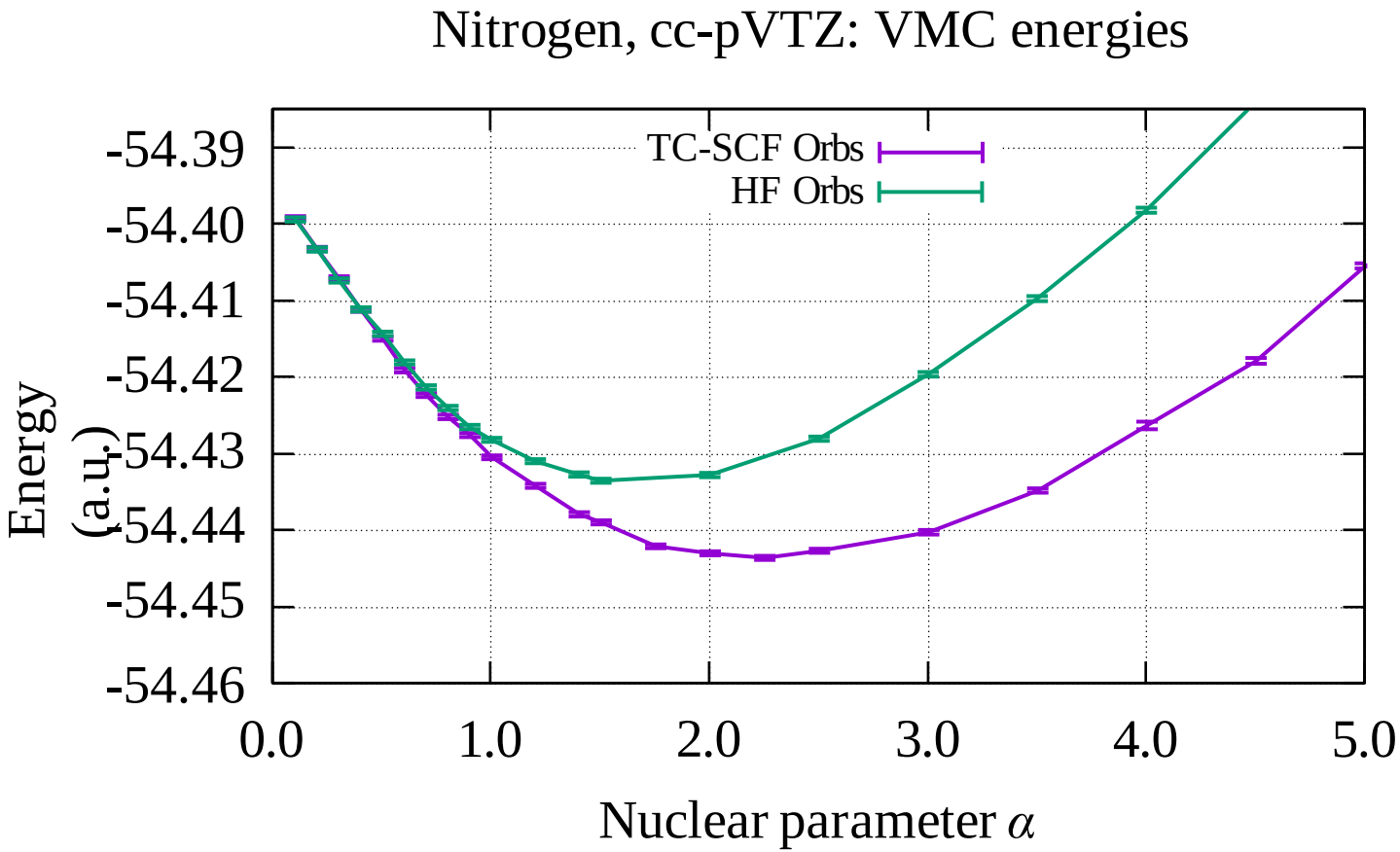

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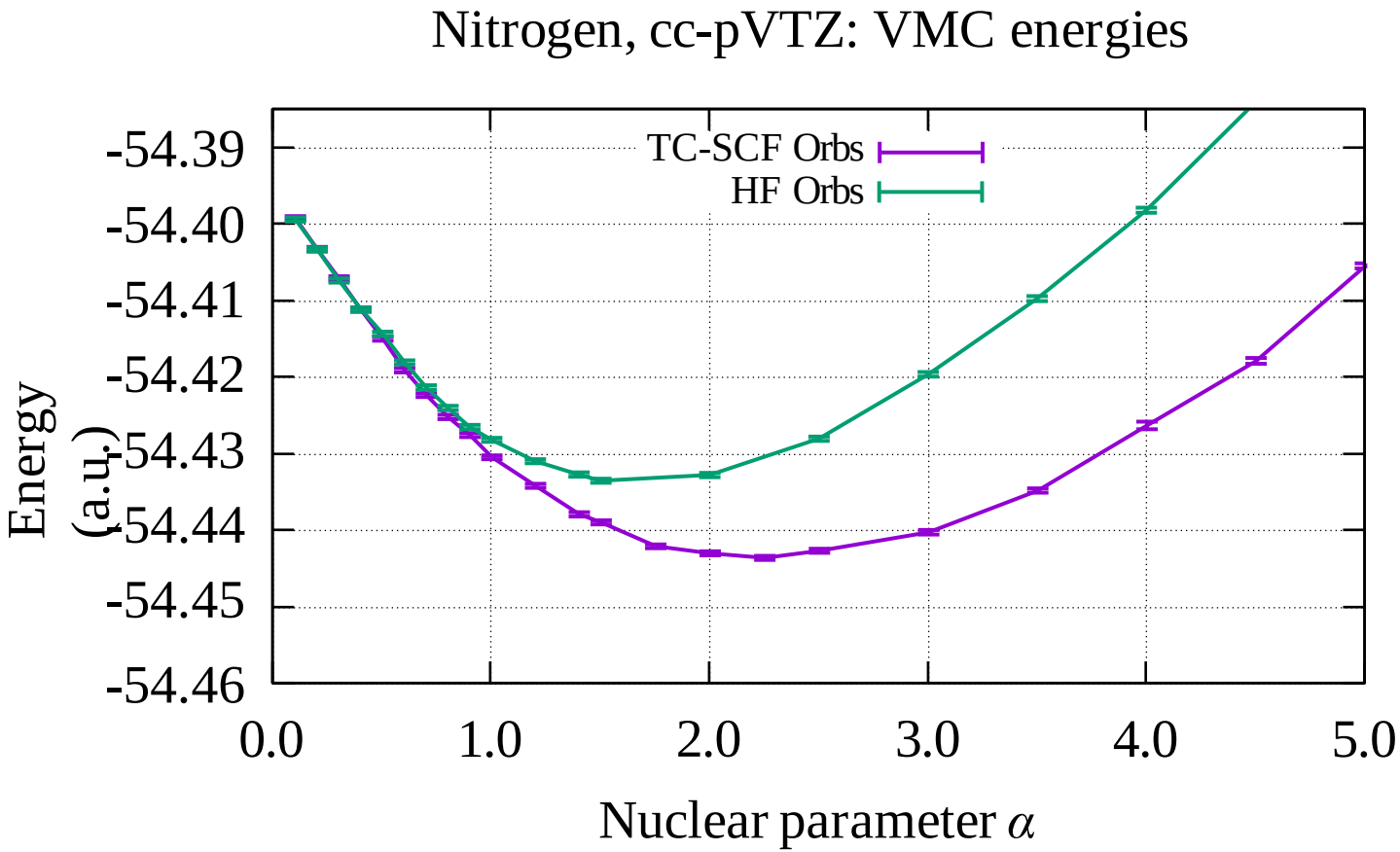

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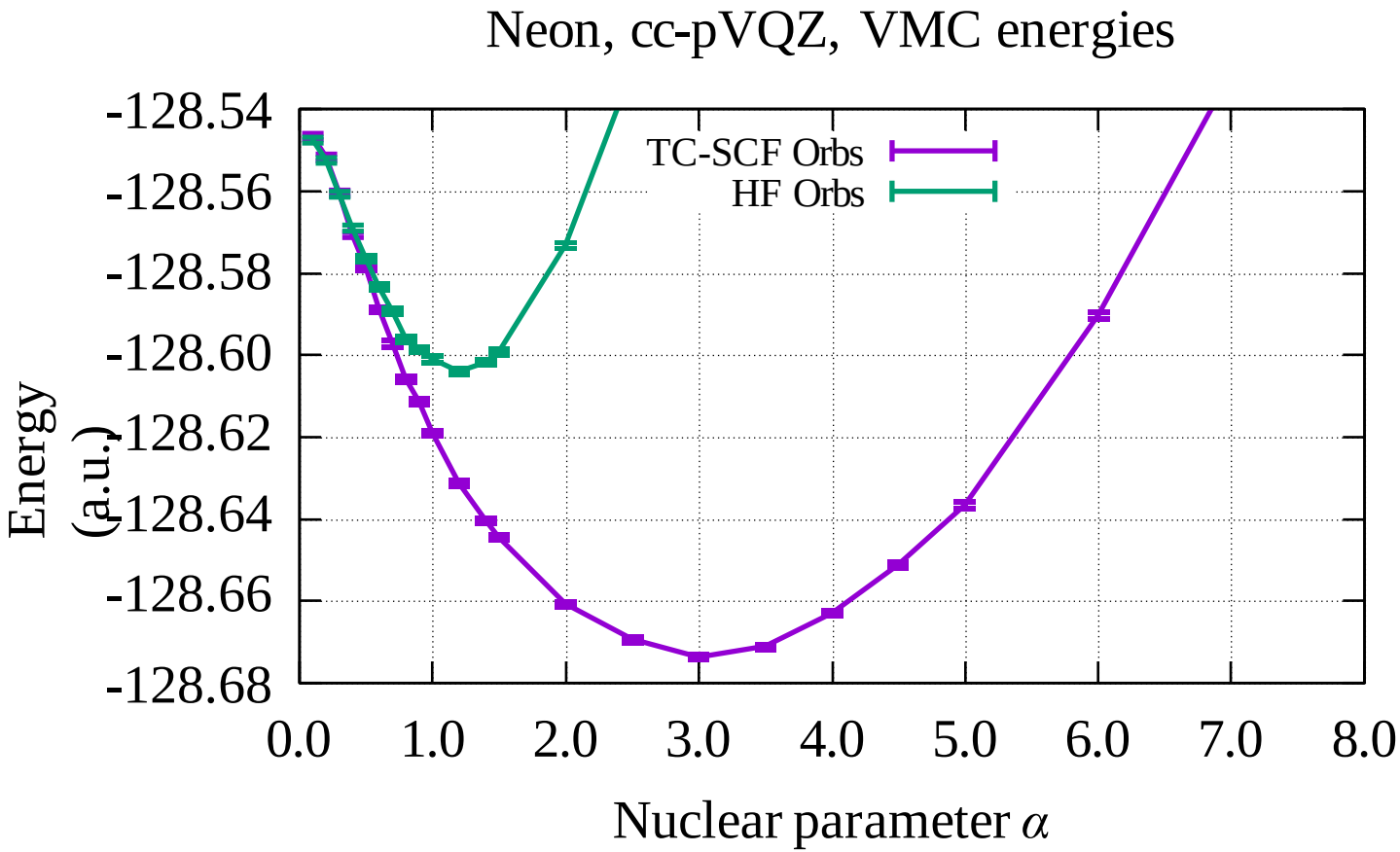

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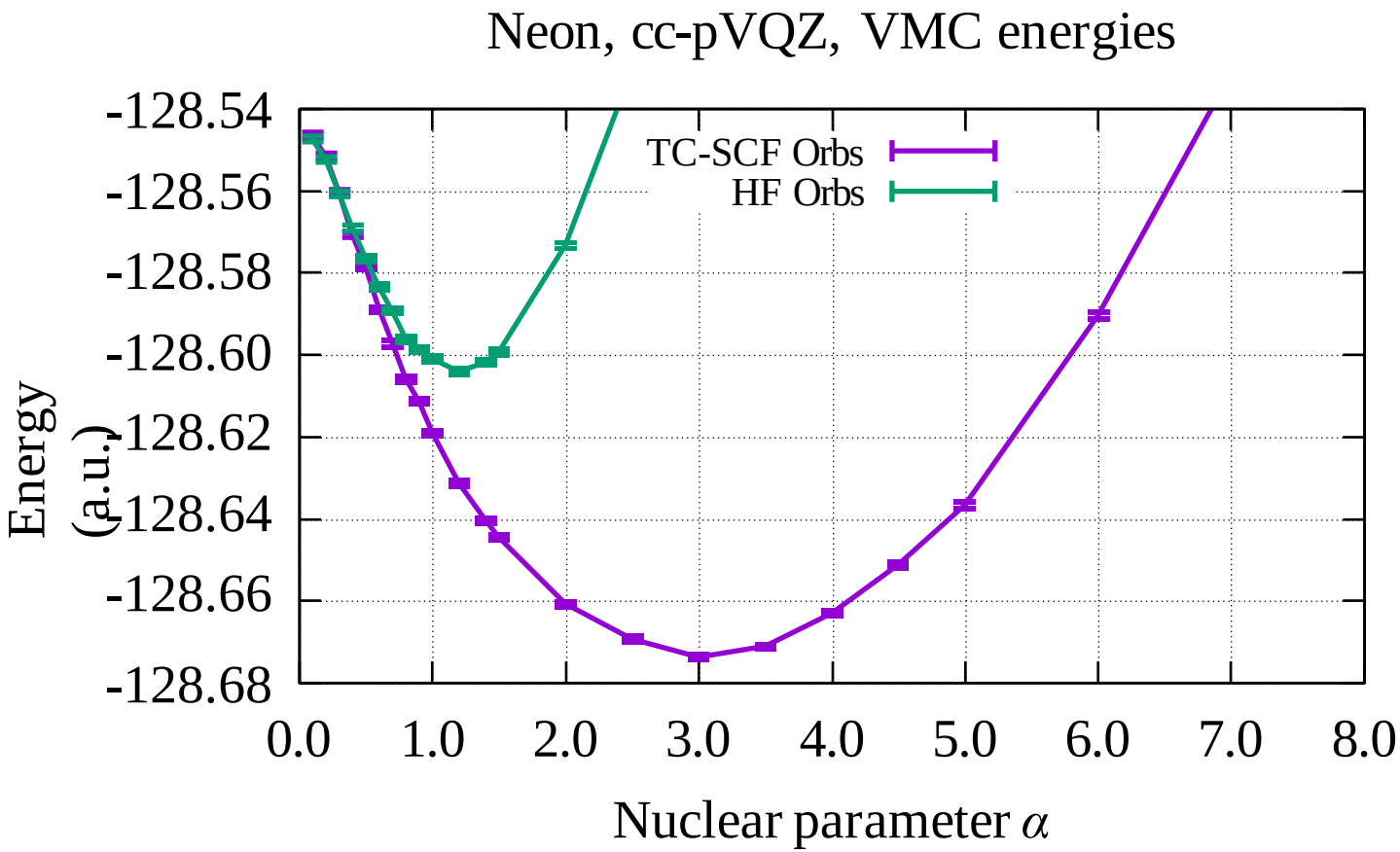

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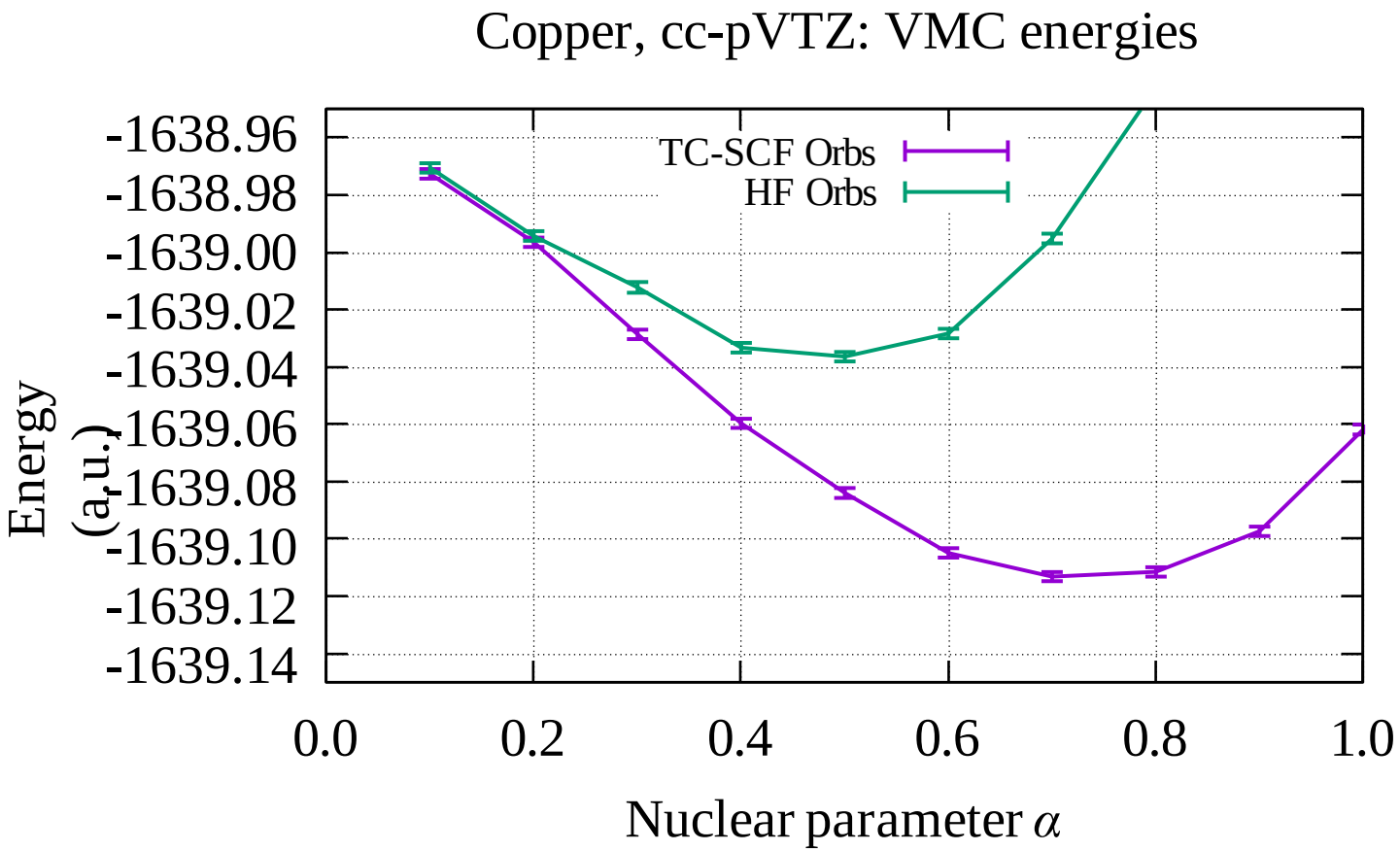
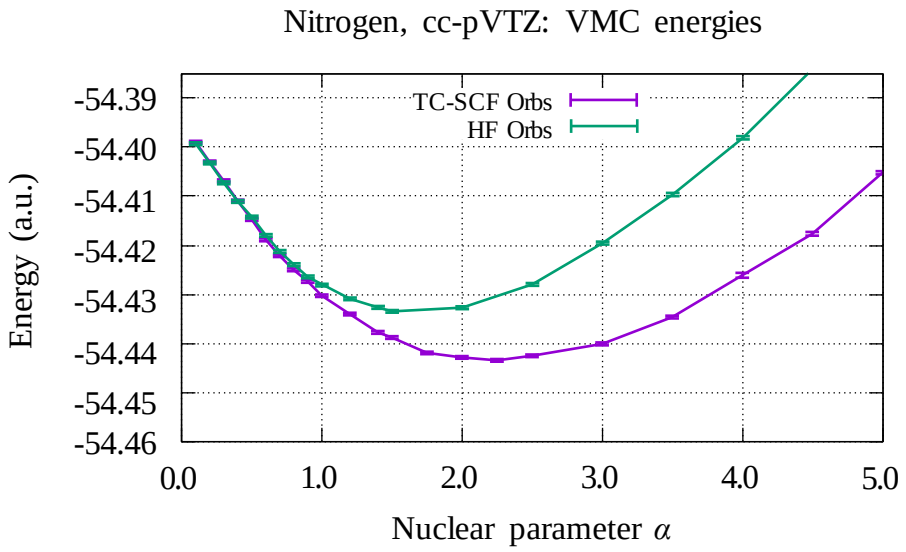
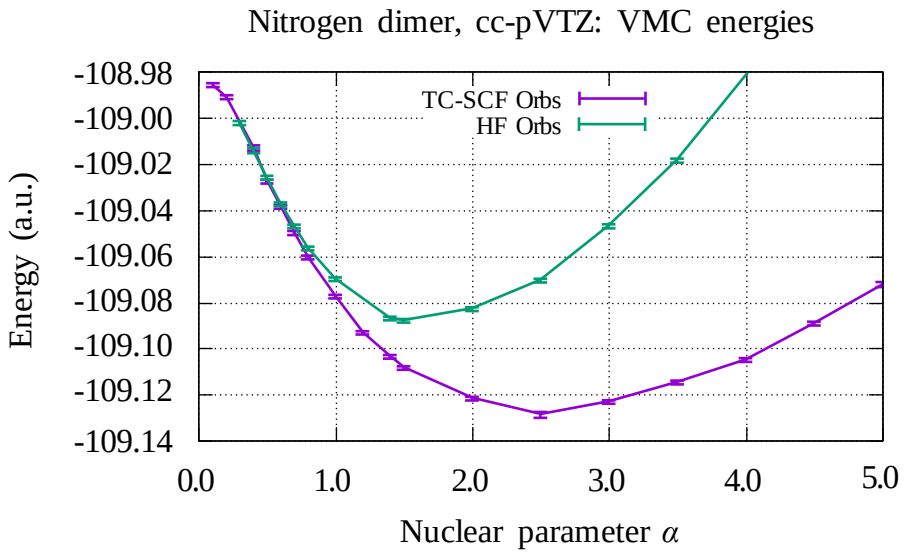
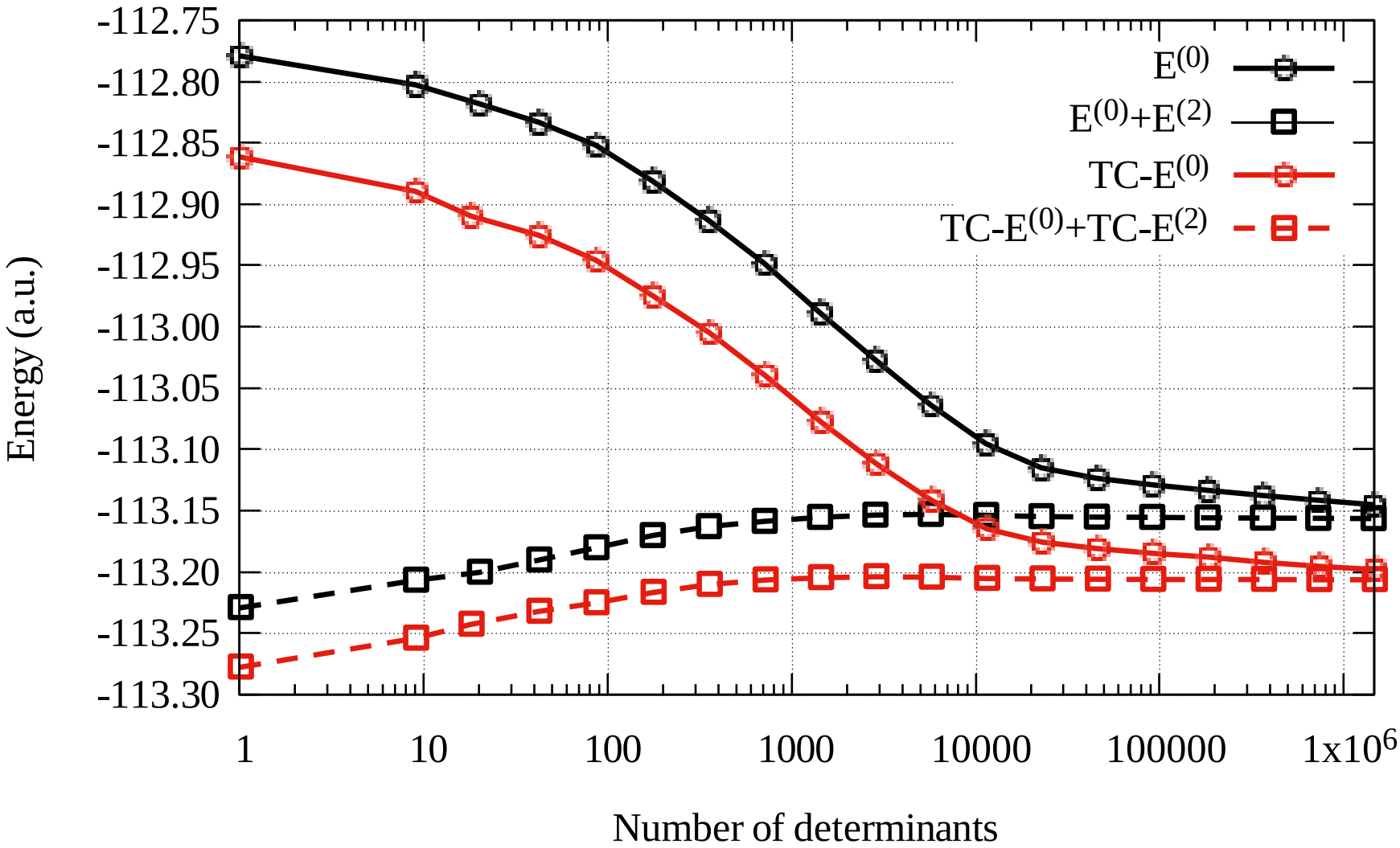


Transferable from atoms to molecules





Numerical example: CO, cc-pVTZ, frozen core



Similar stability than the usual selected CI

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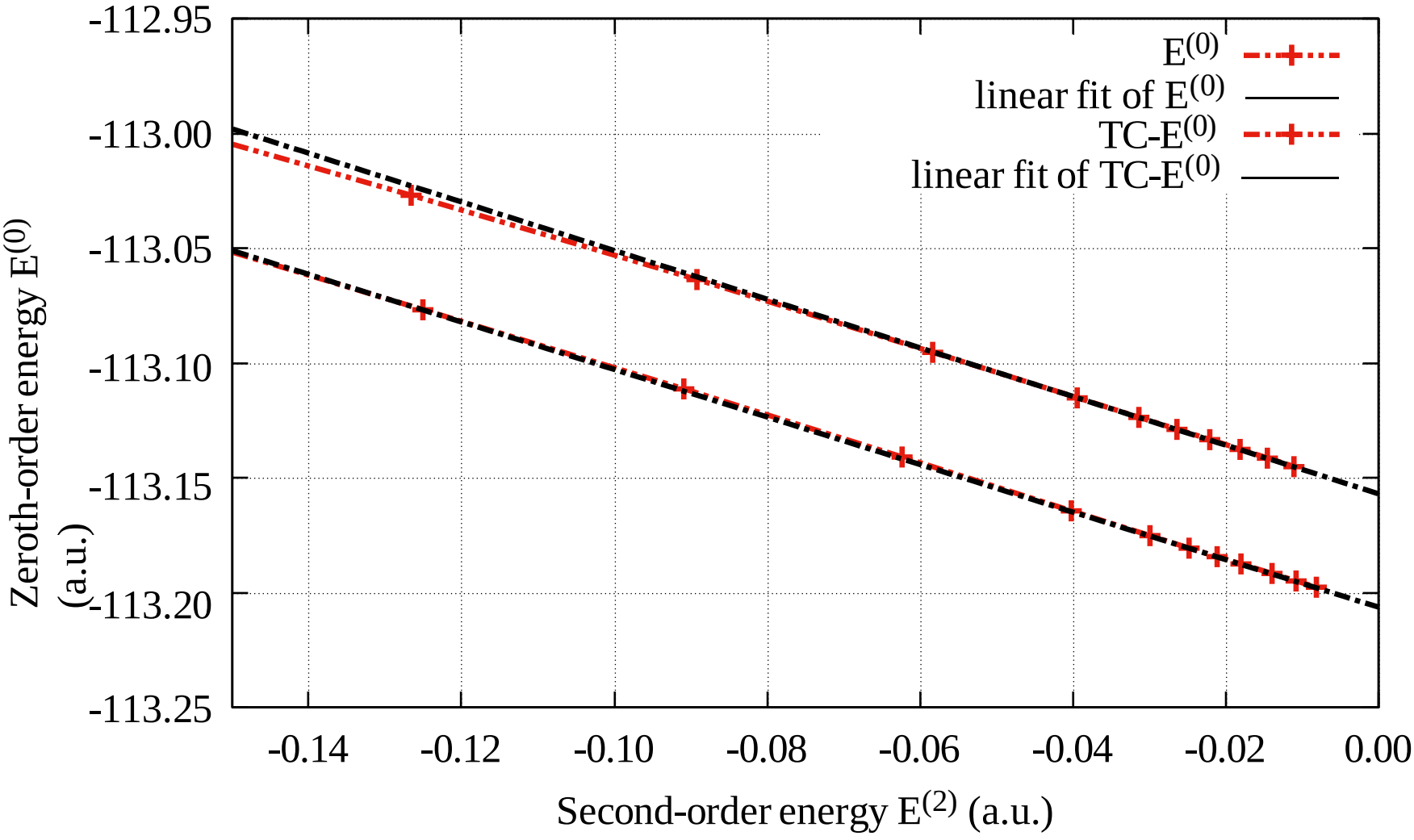

Can be extrapolated as usual selected CI

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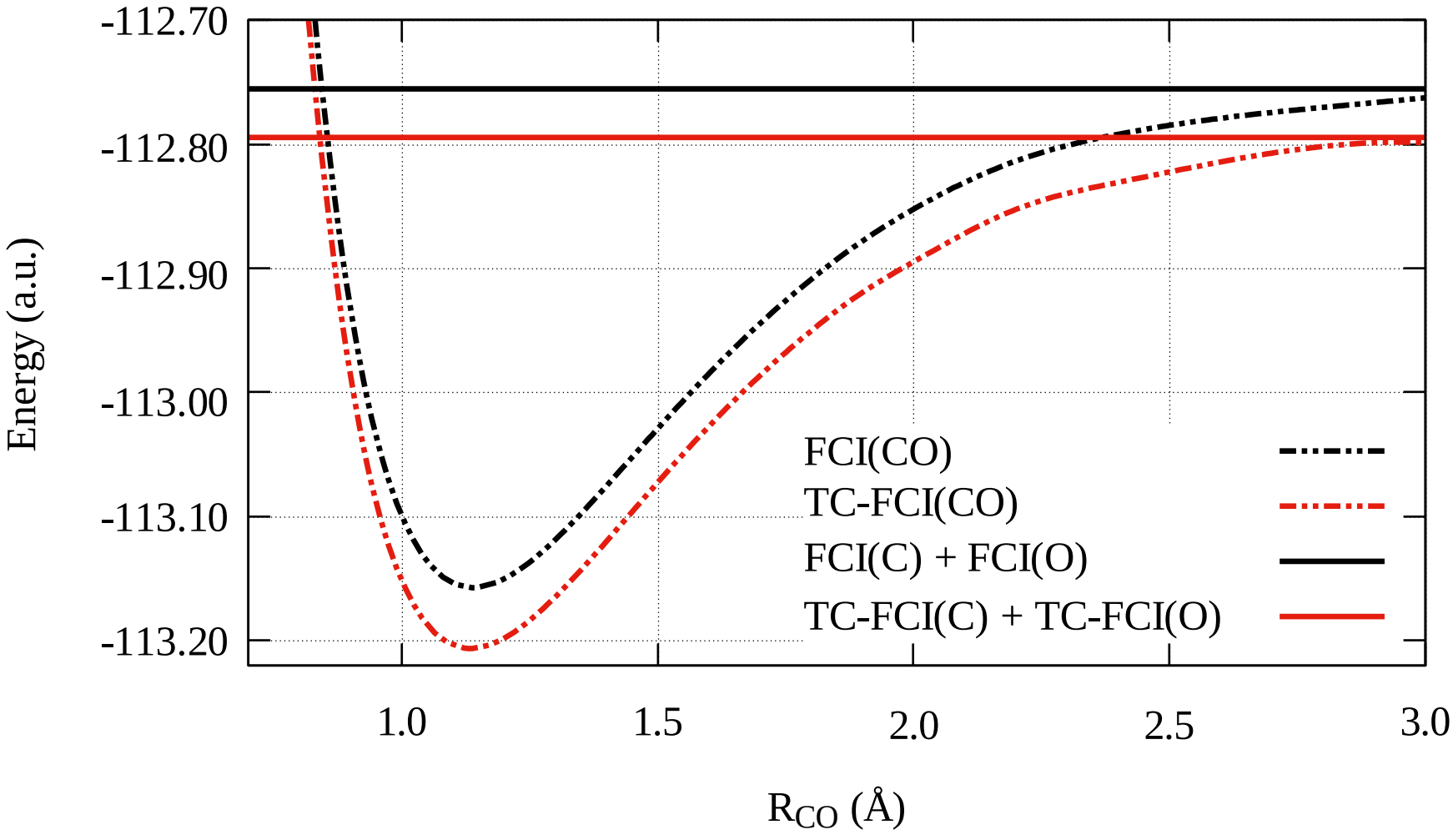
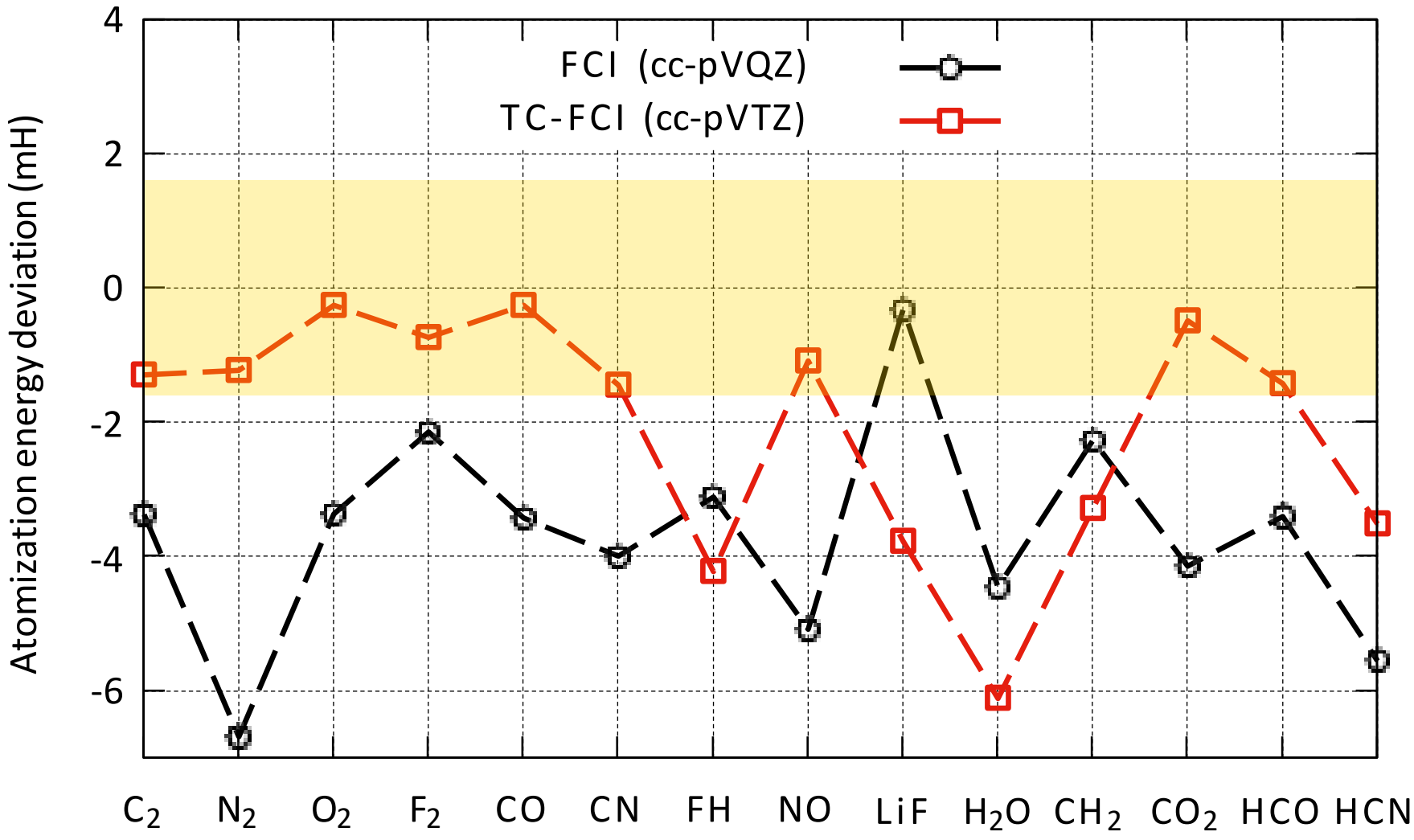


Size-consistent correlation factors

Numerical example: Atomization energies, cc-pVTZ



Improves the quality of ΔE

Frozen core TC ?

Difference between the **all-electron** and **frozen core** energy differences (mH)

	SCI	TC-SCI	
		RHF orbs	TC-SCF orbs
IP of F	-0.2	-2.2	-0.1
IP of Ne	-0.3	-3.2	-0.2
AE of F_2	-0.4	-2.3	-0.2

- Significative error on ΔE with RHF orbs
- Better core-valence splitting with TC-SCF orbs
- Make frozen core calculations possible
- Open to CASSCF calculations

How to go towards larger systems ? 3-e terms

- L_{ijm}^{kln} tensor: N^6 **to store !**
- Makes $\langle X_J|\tilde{H}|\Phi_I\rangle$ much **more complex**
- Approximation: **normal-ordering**
  - Contract the 3-e op. on a reference $|\Phi\rangle$
  - Yield effective 0, 1, 2, and 3-e operator
  - Discard the 3-e operator
  - General formulation by Kutzelnigg/Mukherjee
  - Intense use in nuclear physics
  - Used also in TC (Alavi *et. al.*)
  - **We extended it to a bi-orthonormal framework**

C_6H_6 frozen core atomization energy (Hartree):

	CCSD(T)	CCSD(T)-F12	TC-SCI
VDZ	2.0222	2.1526	2.1558
VTZ	2.1229	2.1660	-

Conclusion

- **Determinisitc TC** can be used to optimize Φ
- **VMC** can be used to optimize e^U
- **Bi-orthonormal** for TC has many advantages
  - Optimize both left- and right-eigenvectors
  - Allow for frozen core approximations
  - Normal ordering of the 3-e terms
- Simple 3-body Jastrow
  - Parametrized only for atoms
  - No need to reoptimize !
  - Size-consistent
- **On going work**
  - Compare TC with QMC orbital optimization
  - Implementation of TC-BiO-CASSCF
  - Improve the correlation factor (1-e term)
  - Investigate $\mu(r)$

Advertisement zone

- TC has been implemented in
  - **Quantum Package** (V3 coming soon !)
  - **QMCKL** was used for Jastrow factors
- QMC calculations
  - **QMC=Chem**
  - Thanks to **TREXIO** interface
- **post-doc/PhD position available in Paris ! 8**

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Some technicalities about integrals

- Integrals can be computed as

$$K_{ij}^{kl} = \int \mathrm{d}\mathbf{r}_1 \varphi_k(\mathbf{r}_1)\varphi_i(\mathbf{r}_1)(g_{jl}^1(\mathbf{r}_1) + g_{jl}^2(\mathbf{r}_1)) \qquad \text{numerical grid on } \mathbb{R}^3$$

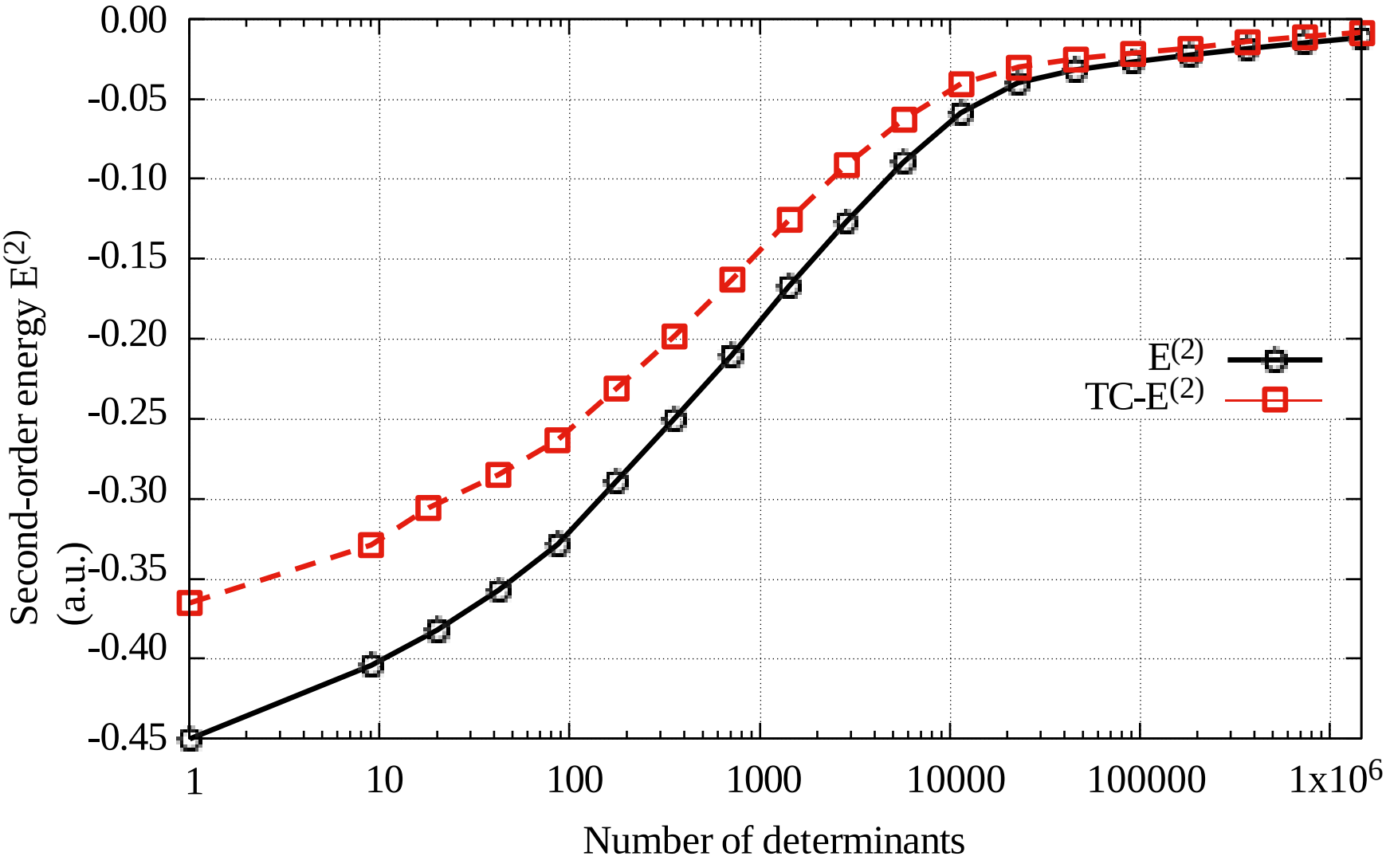
$$L_{ijm}^{kln} = \int \mathrm{d}\mathbf{r}_1 \varphi_k(\mathbf{r}_1)\varphi_i(\mathbf{r}_1) g_{jl}^1(\mathbf{r}_1) g_{mn}^1(\mathbf{r}_1) \qquad \text{numerical grid on } \mathbb{R}^3$$

$$g_{jl}^1(\mathbf{r}_1) = \int \mathrm{d}\mathbf{r}_2 \nabla_1 u(\mathbf{r}_1, \mathbf{r}_2)\varphi_l(\mathbf{r}_2)\varphi_j(\mathbf{r}_2) \qquad \text{numerical or analytical}$$

$$g_{jl}^2(\mathbf{r}_1) = \int \mathrm{d}\mathbf{r}_2 |\nabla_1 u(\mathbf{r}_1, \mathbf{r}_2)|^2 \varphi_l(\mathbf{r}_2)\varphi_j(\mathbf{r}_2) \qquad \text{numerical or analytical}$$

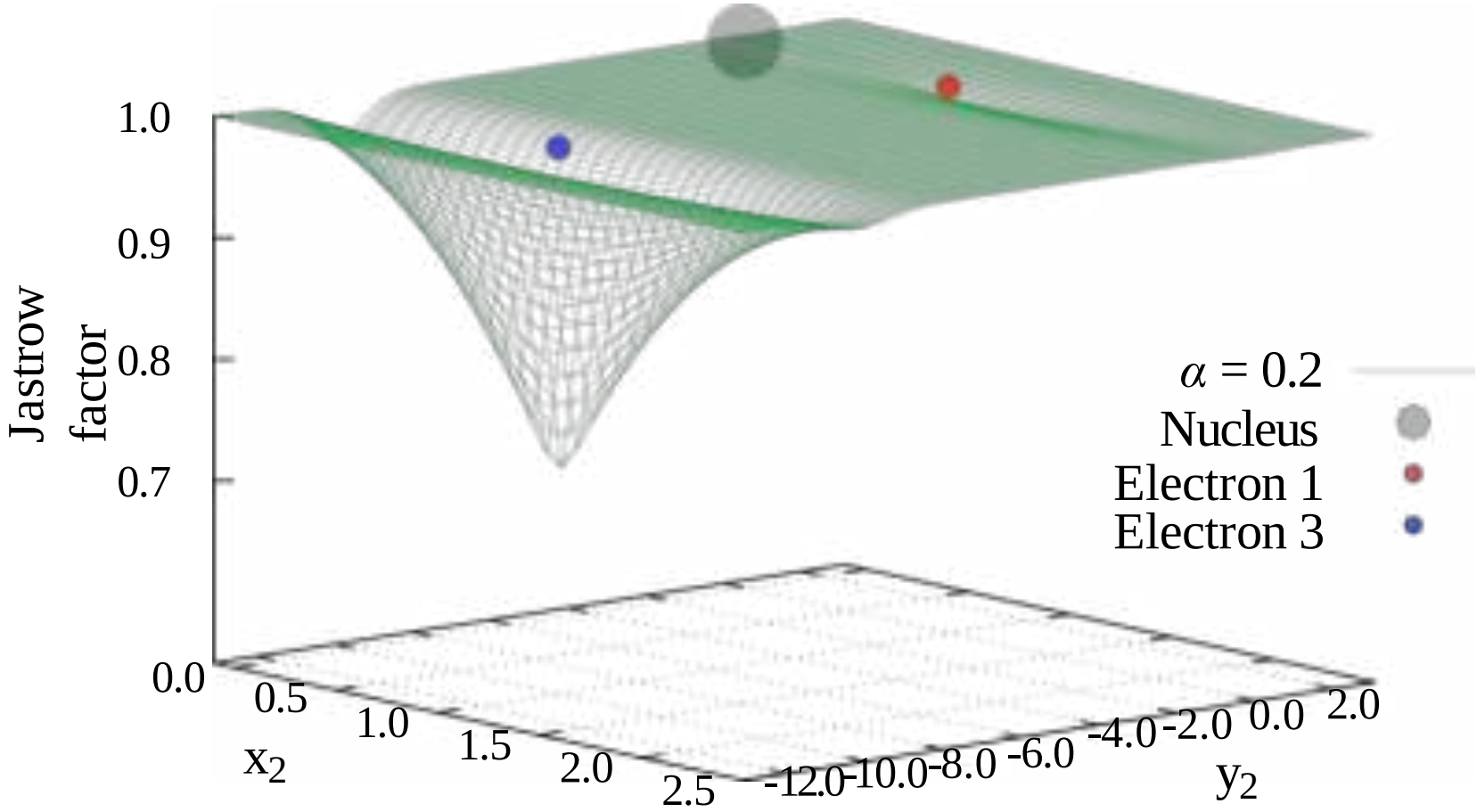
- If simple enough $u(\mathbf{r}_1, \mathbf{r}_2)$ then $g_{jl}^1(\mathbf{r}_1)$ and $g_{jl}^2(\mathbf{r}_1)$ are analytical
- Storage of intermediate $\propto N^2 \times N_g$
- Storage of $L_{ijm}^{kln} \propto N^6 \rightarrow$ Normal ordering approximations for L_{ijm}^{kln} (Nuclear physics, CC community)
  - Contract L_{ijm}^{kln} with HF one-, two- and three-rdm
  - End up with effective zero, one-, two- and three-operators
  - discard the three-body

Numerical example: CO, cc-pVTZ, frozen core

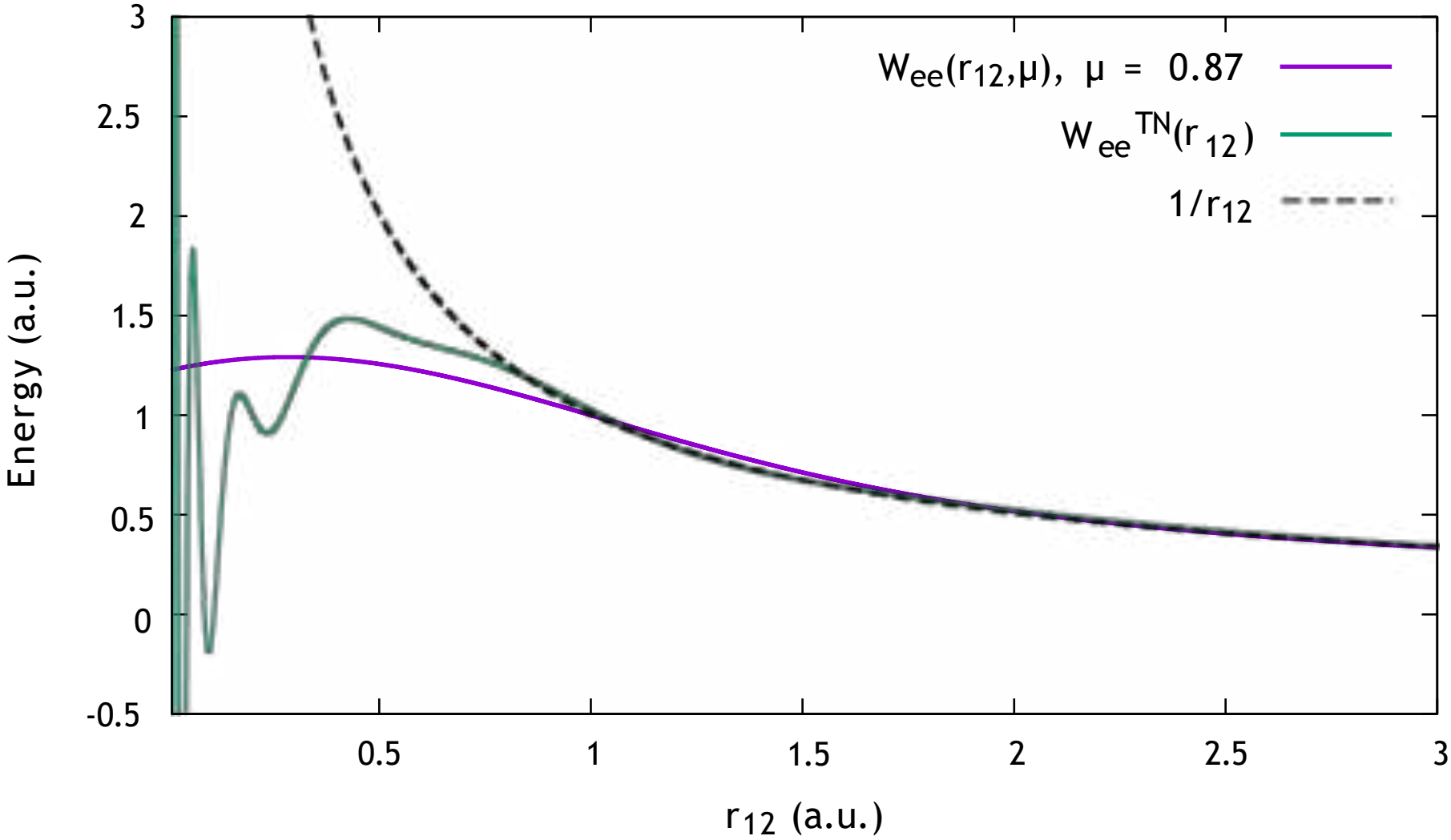


Smaller PT2 than the usual selected CI

Graphical example



What is the shape of scalar e–e potential with μ



Adapting SCI to TC: PT for non hermitian

- Split the Hamiltonian in $\tilde{H} = H_0 + \lambda V$

$$H_0|\Phi_0\rangle = E^{(0)}|\Phi^{(0)}\rangle, \qquad H_0| \qquad {}^{(0)}_{\mathrm{I}}$$

Main results

- For the wave function at first-order

$$c_I^{(l)} = ($$

Taylor expansion in terms of left-function

- Here Φ is kept fixed

$$|\chi_0\rangle = \sum_{l=0}^{\infty} \lambda^l |\chi^{(l)}\rangle, \qquad |\chi^{(l)}\rangle = \sum_{I} C_{I}^{(l)} |$$