Critical reassessment of recent developments in functional theory:
From Hartree-Fock to i-DMFT

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What is i-DMFT

J. Wang, E. Baerends, PRL, 128, 013001 (2022)

- 1RDM ($\gamma = (\mathbf{n}, \{\phi_i\})$) functional theory for $H(h) = h + W$

  $E(\gamma) = \mathrm{Tr}[h\gamma] + \mathscr{F}_W(\gamma) \leftarrow$ **universal functional**

D. Collins, Z. Naturforsch. Teil A 48, 68 (1993)

- Premise - **modified Collin's conjecture**

  $E_{\mathrm{cum}} = \mathscr{F}_W^{\mathrm{HF}} - \mathscr{F}_W \approx \kappa S^{\mathrm{ph}}(\mathbf{n}) + b,$ with

  $S^{\mathrm{ph}}(\mathbf{n}) = -\sum_i n_i \log(n_i) + (1 - n_i)\log(1 - n_i)$

Particle Correlation

⇳

Correlation Energy

- Optimal γ is obtained self-consistently, with (κ, b) pre-fit by two FCI solutions

Capability of i-DMFT

J. Wang, E. Baerends, PRL, 128, 013001 (2022)

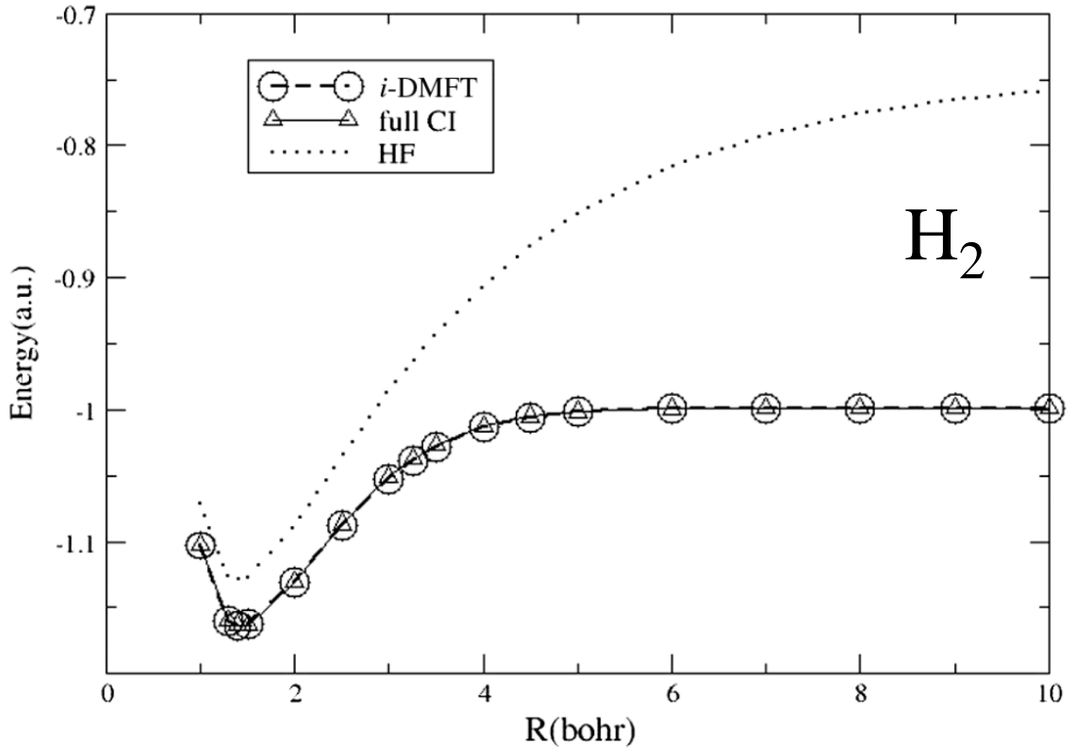

FIG. 1. Total energy curves for HF, full CI, and *i*-DMFT calculations along the dissociation coordinate of H_2. Basis set cc-pVDZ, $\kappa = 0.094681$, and $b = 0.0286186$.

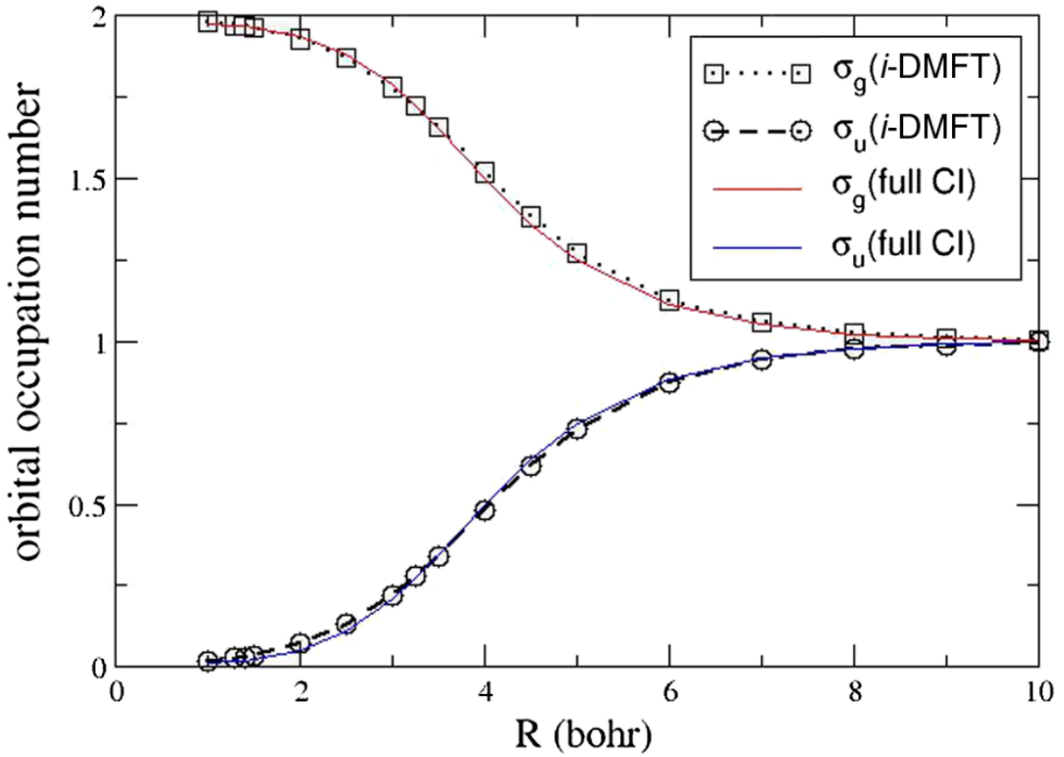

FIG. 2. Occupation numbers of the σ_g and σ_u orbitals in H_2 as a function of the nuclear separation R. The data are calculated with the basis set cc-pVDZ, $\kappa = 0.094681$, and $b = 0.0286186$.

Accurate ground state energy for all geometry (with two data points as input)

Recovering static correlation and NONs at dissociation

How useful/good/accurate is the modified Collin's Conjecture?

$$E_{\mathrm{cum}} \approx \kappa S^{\mathrm{ph}}(\mathbf{n}) + b$$

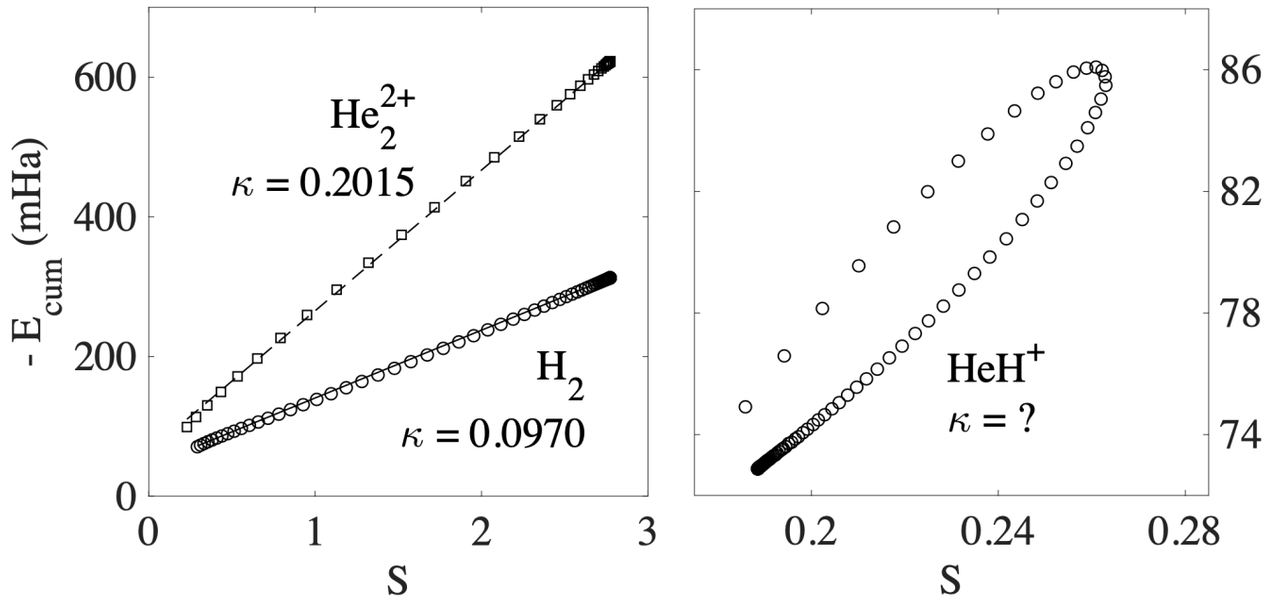

FIG. 1. Cumulant energy $E_{\mathrm{cum}}(R)$ versus particle-hole symmetric entropy $S(\boldsymbol{n}(R))$ for the ground states of H_2, He_2^{2+} (left) and HeH^+ (right) for different internuclear separations R. The basis set cc-pVDZ was used.

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- For fixed N_e and nuclear charge, sometimes it is extremely good! Why?
- Different (κ, b) for same N_e but different nuclear charge
  $\Rightarrow$ give up universality entirely
- (κ, b) depends on data points chosen for fitting
- $E_{\mathrm{cum}}(S)$ is not always a function

Errors swept under the rug... why do they almost "cancel"?

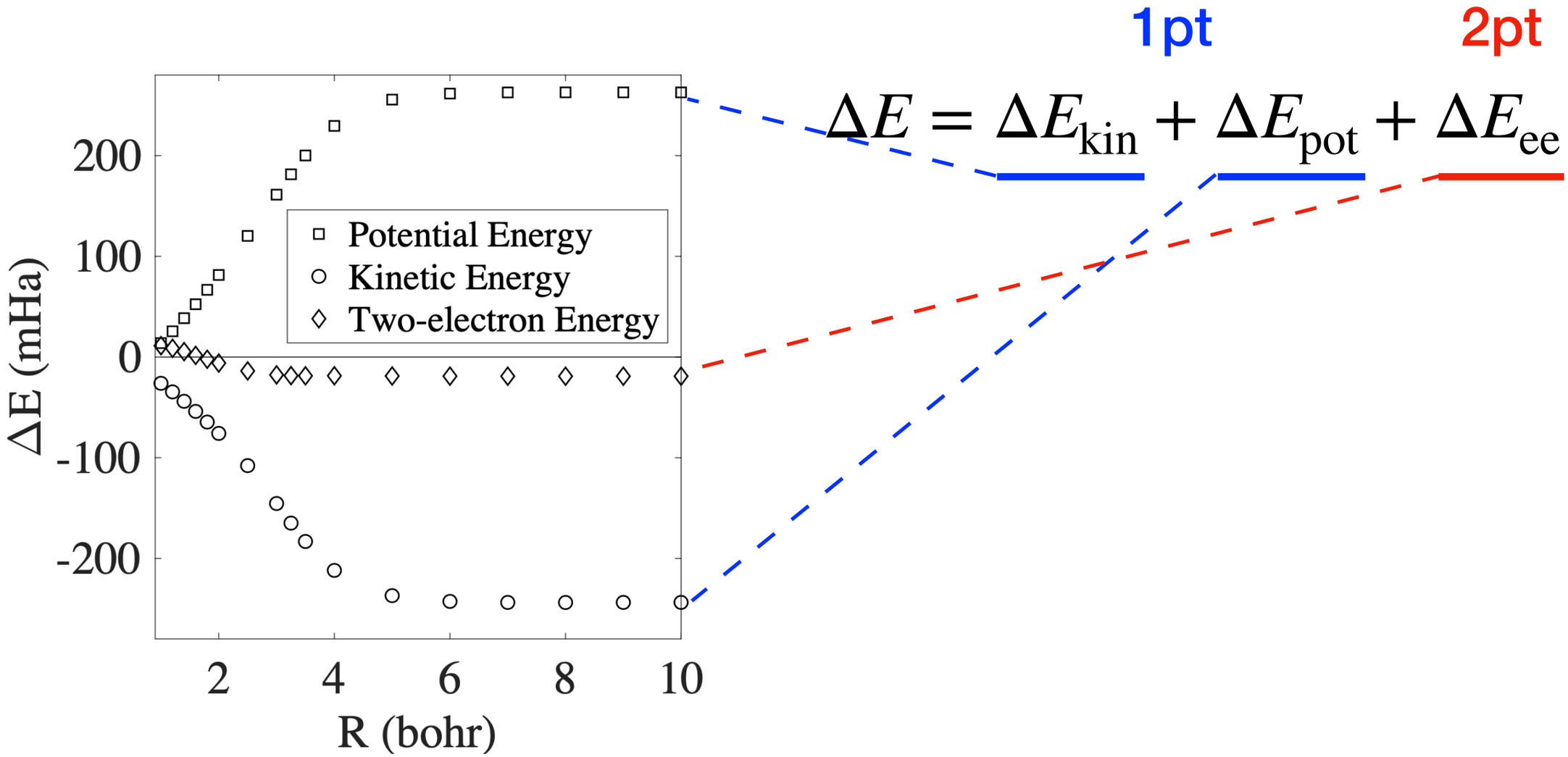

FIG. 3. i-DMFT (with basis set cc-pVDZ) applied to H_2 at different internuclear separation R: Error in the 1RDM γ_i measured by the Frobenius norm $\sqrt{\text{Tr}[(\gamma_i - \gamma)^2]}$ with γ the exact/FCI 1RDM (left), error ΔE in the kinetic energy, potential energy and interaction energy (right).

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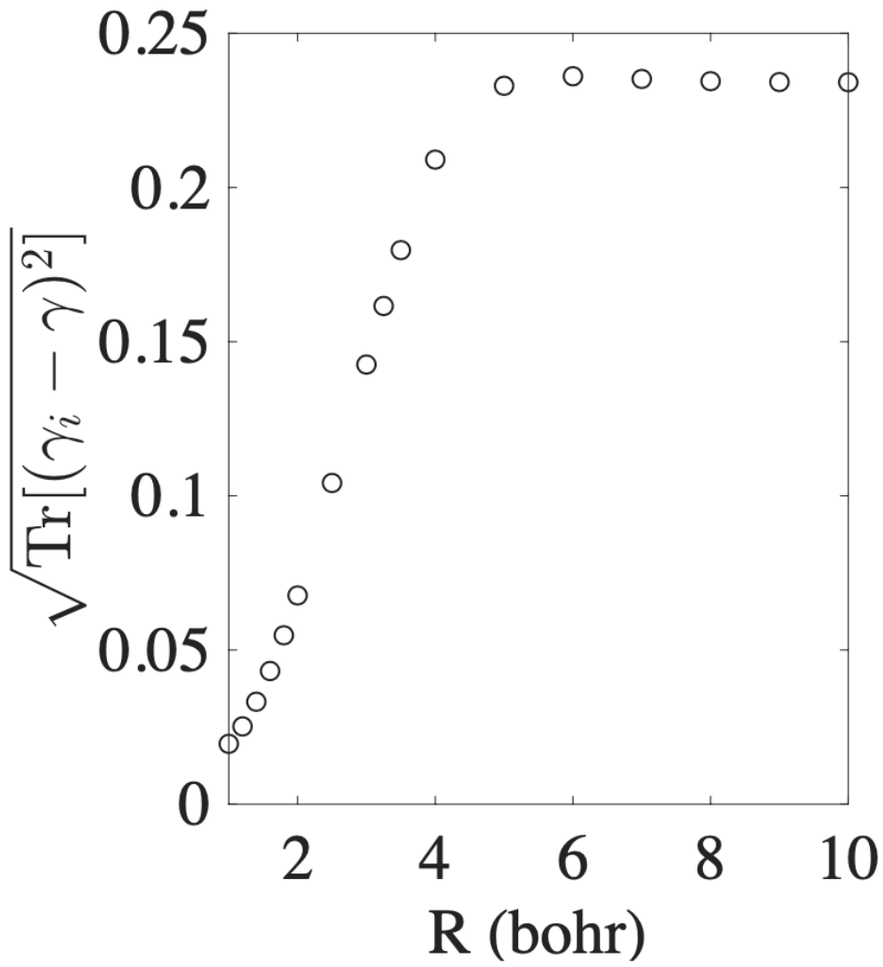
Does i-DMFT recover the correct 1RDM?



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Similarity between matrices

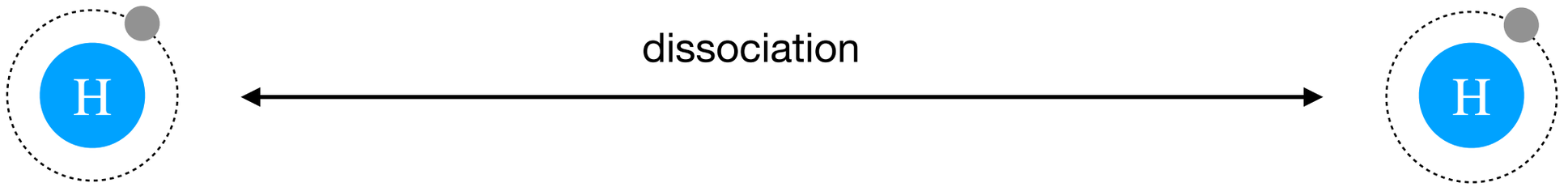
$$\|\rho-\sigma\|_F=\sqrt{(\mathrm{Tr}(\rho-\sigma)^\dagger(\rho-\sigma))}$$

Bounds discrepancy in observables

$$\|(\rho-\sigma)O\|_F\leq\|O\|_{\mathrm{op}}\|\rho-\sigma\|_F$$

Bad orbitals ⟶ Bad 1pt quantities

From Hartree-Fock to i-DMFT: conceptual flaw



Suppose at dissociation limit for H_2, i-DMFT obtained the correct 1RDM

$$\bar{\gamma} = \frac{1}{2} \sum_{i=L/R,\tau=\uparrow,\downarrow} |1s_i\tau\rangle\langle 1s_i\tau|$$

Corresponding HF 2RDM $\quad \Gamma_{\mathrm{HF}} = \frac{1}{2}(1 - \mathrm{Ex})\gamma \otimes \gamma$

$$Y = \mathrm{Tr}[W\Gamma_{\mathrm{HF}}] = \frac{1}{4} \sum_{\tau,\tau'=\uparrow,\downarrow} \langle 1s_L\tau, 1s_R\tau' | W | 1s_L\tau, 1s_R\tau' \rangle \qquad \textbf{Inter-nuclear}$$

$$+\frac{1}{4} \sum_{i=L/R} \langle 1s_i\uparrow, 1s_i\downarrow | W | 1s_i\uparrow, 1s_i\downarrow \rangle \qquad \textbf{Intra-nuclear}$$

From Hartree-Fock to i-DMFT: conceptual flaw

$$\frac{1}{4}\sum_{i=L/R}\langle 1s_i\uparrow, 1s_i\downarrow | W | 1s_i\uparrow, 1s_i\downarrow\rangle$$

This intra-nulcear energy is unlikely to be accommodated by 1pt quantities such as $S(\mathbf{n})$

J. Wang, E. Baerends, arxiv:2207.02616v1 (2022)

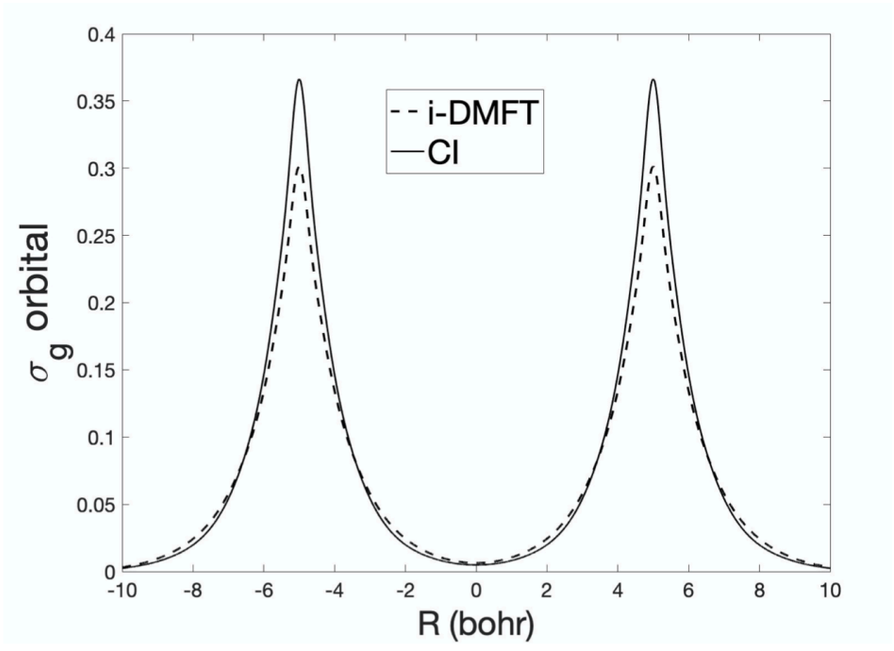


FIG. 1. The σ_g orbital from the *i*-DMFT calculation and the σ_g NO from a CI calculation at R=10 bohr with the basis set cc-pVDZ. The *i*-DMFT parameters are κ=0.094681 and b=0.0286189 (in a.u.).

Adjustment by Wang & Baerands

$$E_{cum} = AE_xS - b \qquad E_x = -\tfrac{1}{2}\sum_{ij} n_i n_j \langle ij|ji\rangle$$

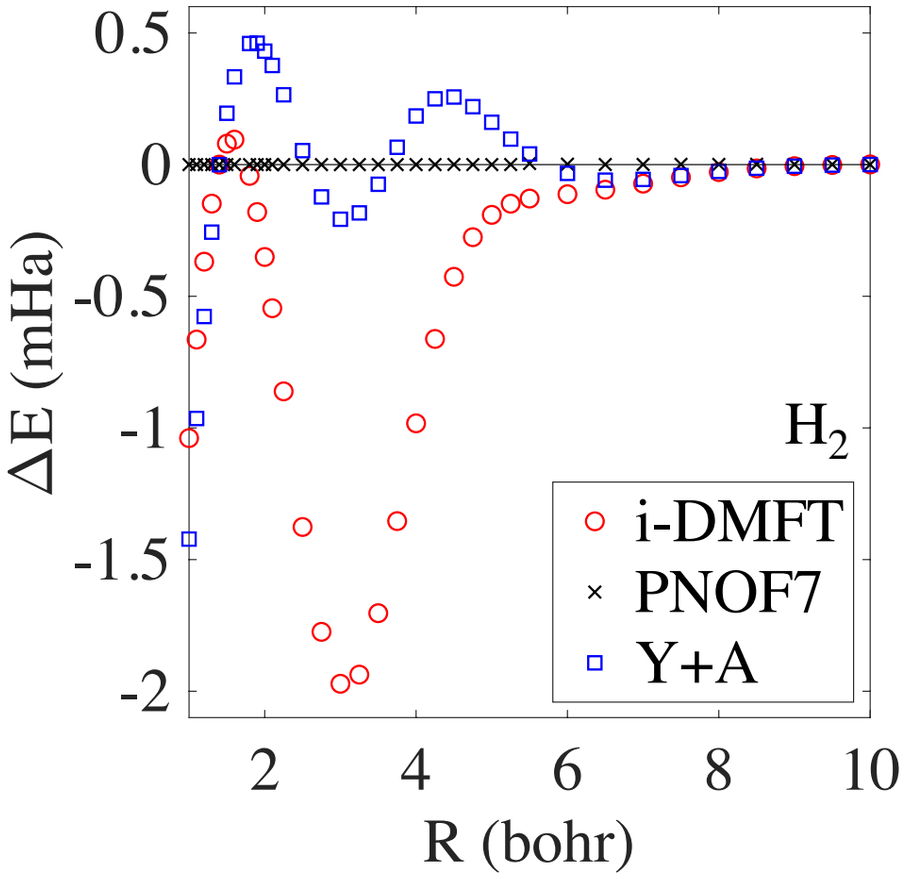
Collin's conjecture is perfect for H_2

$$E_{\text{cum}} \approx \kappa\, S^{\text{ph}}(\mathbf{n}) + b$$

Open questions

- When and why is the Collin's conjecture correct?
- Is convergence of i-DMFT guaranteed?
- How to do fitting for (κ, b)? Two-point? Linear regression? Not conclusive!
- Is the von Neumann entropy the only relevant/ useful QI quantity? Renyi entropy? Other Schul convex functions?
- 2RDM instead of 1RDM as optimization variable?

$$A(\mathbf{n}) = -\sum_i n_i^{0.8}\log(n_i^{0.8}) + (1-n_i)^{0.8}\log((1-n_i)^{0.8})$$



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What people look for in a good RDMFT?

- correct static correlation in dissociation limit
- correct scaling at boundary, exchange force

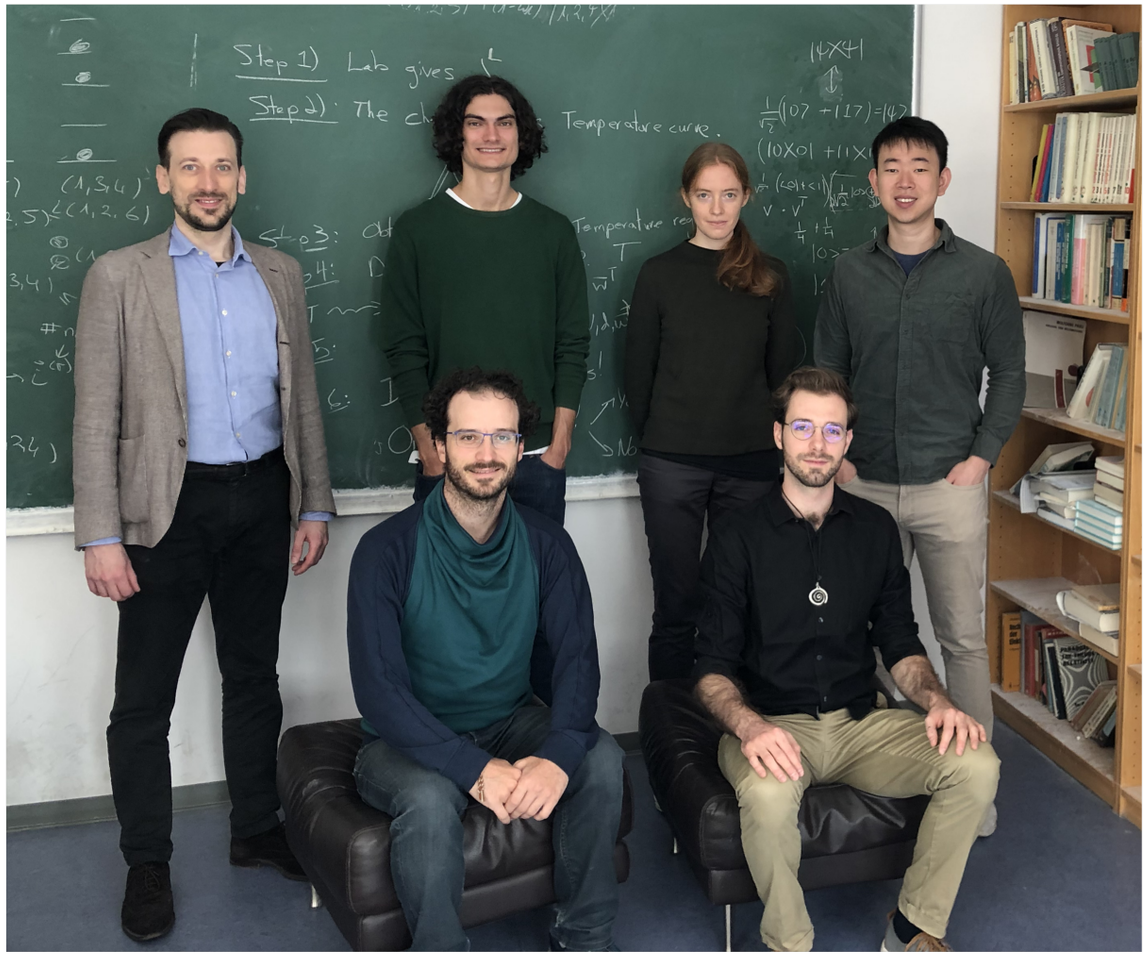
  J. Liebert, C. Schilling Phys. Rev. Research 3, 013282 (2021)

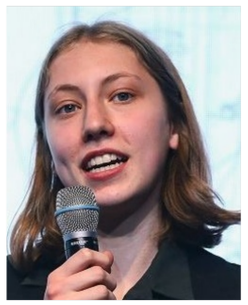
  C. Schilling, R. Schilling Phys. Rev. Lett. 122, 013001 (2019)
- size versus volume extensivity

  J. Cioslowsky J. Chem. Phys. 120, 10364 (2004)
- accuracy of other 1-pt quantities other than energy, dipole moments, polarisability, kinetic energies...

  C. A. Coulson, Rev. Mod. Phys. 32, 170, (1960)
- …

Schilling group: Theoretical Quantum Physics





Thank you!