Efficient Quantum Monte Carlo Simulations with Large Atomic Numbers

GDR NBODY Meeting

Jonas Feldt

12.01.2022

Quantum Monte Carlo

- real space & zero-temperature
  - variational Monte Carlo
  - diffusion Monte Carlo

$$E_{\mathrm{v}} = \frac{\int \Psi(\mathbf{R})^* \hat{H} \Psi(\mathbf{R}) \mathrm{d}\mathbf{R}}{\int |\Psi(\mathbf{R})|^2 \mathrm{d}\mathbf{R}}$$

$$\rho = \frac{|\Psi(R)|^2}{\int |\Psi(R)|^2 \mathrm{d}\mathbf{R}} \qquad E_{\mathrm{L}} = \frac{\hat{H}\Psi(\mathbf{R})}{\Psi(\mathbf{R})}$$

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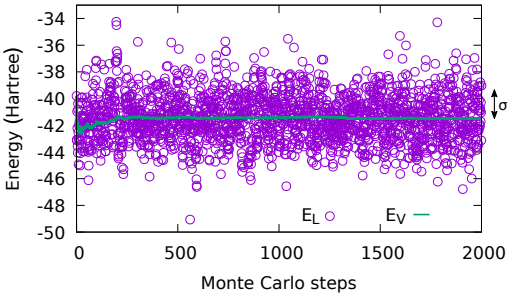

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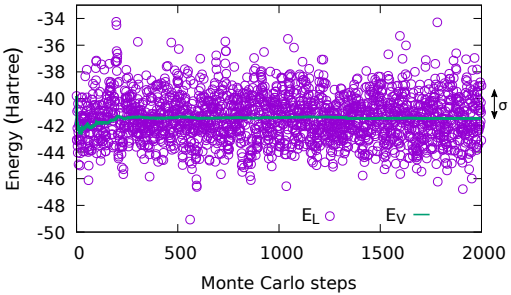

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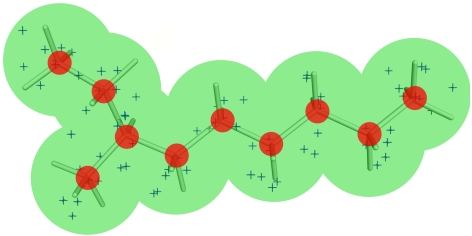
$$\sigma = \sqrt{\frac{V(E_L)}{M}}$$

Electrons in Molecular Systems

- valence electrons
- core electrons
  - distance to the core $\mathcal{O}(1/Z)$
  - contribution to energy $\mathcal{O}(Z^2)$
- DMC cost $\sim \mathcal{O}(Z^6)$



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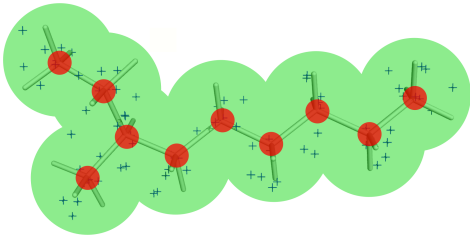

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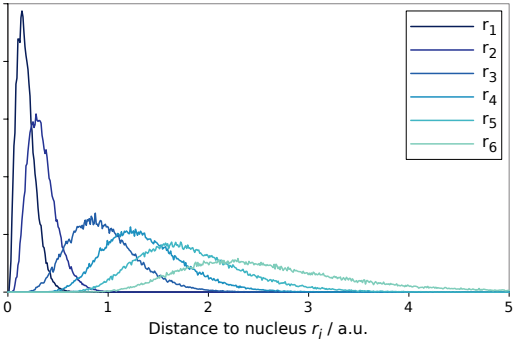

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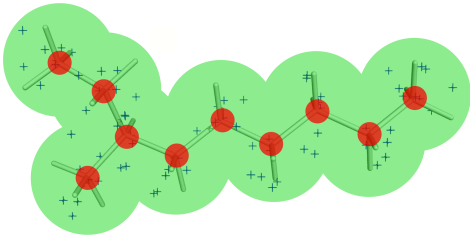

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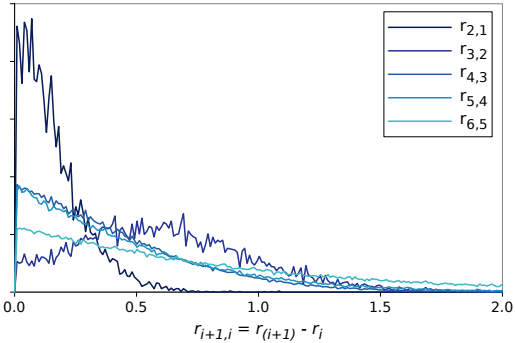

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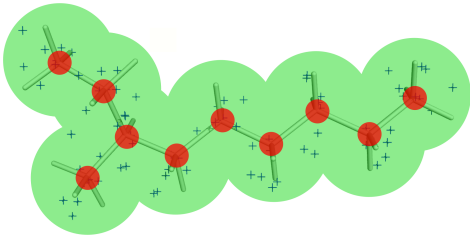

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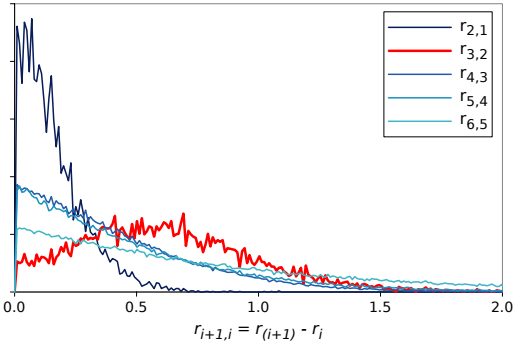

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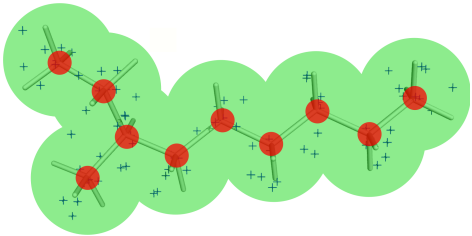

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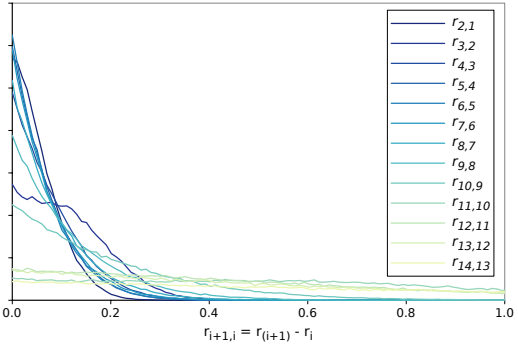

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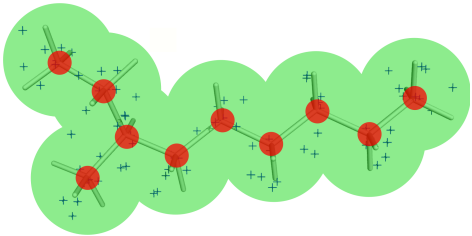

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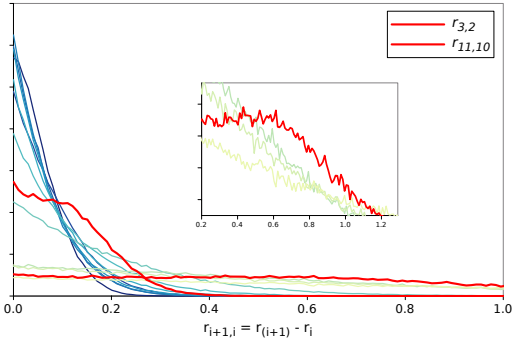

Electrons in Molecular Systems

Different Scales

- **core electrons**:
  Many high-energy electrons moving within small but well separated volumes
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How to simulate molecular systems efficiently?

$\Rightarrow$ usually: empirical effective core potentials $\rightarrow$ unknown bias

$\Rightarrow$ exact contribution of the core electrons

$\Rightarrow$ treat core and valence electrons differently

$\Rightarrow$ treat different cores independently

Efficiency of Stochastic Algorithms

Computational Cost f

$$f = Vct = \sigma^2 T$$

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- improved sampling $\rightarrow$ reduces serial correlation c
  - VMC: spherical coordinates (Umrigar, *Physical Review Letters*. 1993)
  - DMC: different timesteps (Nakano, Maezono, and Sorella, *Physical Review B*. 2020)
- Subsampling of the Core Regions $\rightarrow$ reduces all three: V, c, t (Feldt and Assaraf, *Journal of Chemical Theory and Computation*. 2021)

Variance Reduction

- Law of Total Variance: $V(X) = \mathbb{E}(V(X|\Omega)) + V(\mathbb{E}(X|\Omega))$

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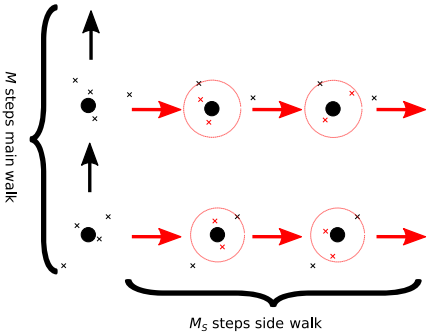
- Improved Estimator

$$\tilde{X} = X + (\mathbb{E}(X|\Omega) - X)$$
$$\tilde{X} = X + \lambda \underbrace{\sum_i \left(\mathbb{E}(X^i|\Omega_i) - X^i\right)}_{\text{sum over cores}}$$



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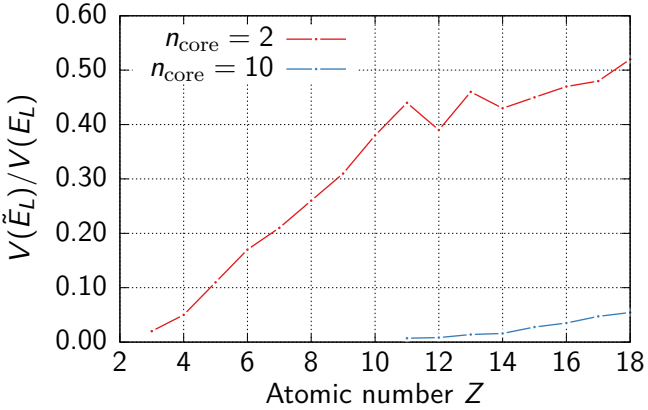
Subsampling: Atoms



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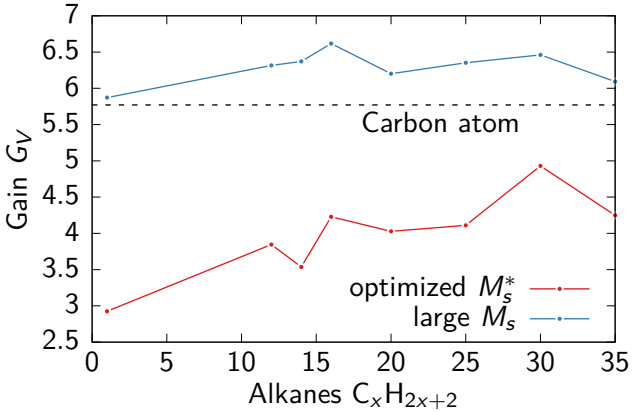
Subsampling: Independence of Cores



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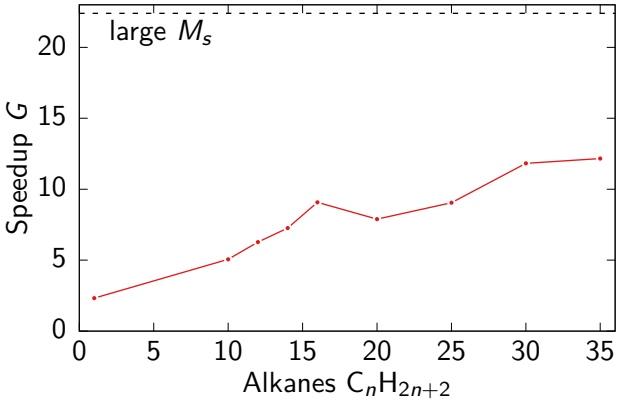
Subsampling: Efficiency



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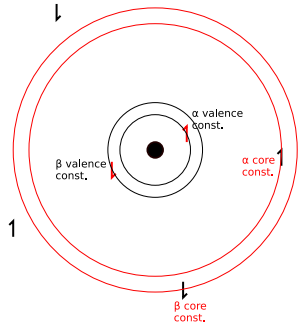
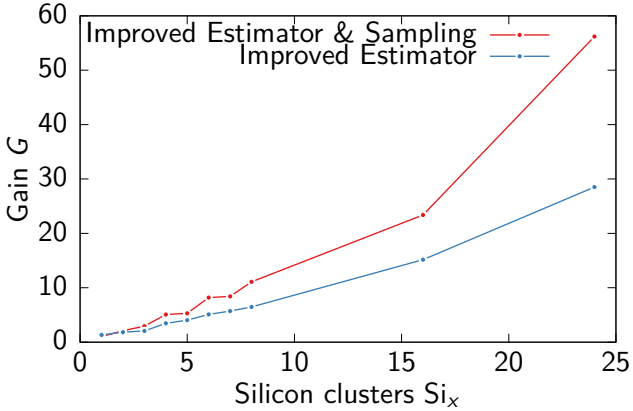
Subsampling: Efficiency

- spin-dependent core





Summary & Outlook

Subsampling

- exact on-the-fly construction of effective core potentials
- adapting the simulation for different regions
  - variance
  - correlation & time step
- results suggest reduced scaling with Z

Perspective

- Derivatives/Forces for Optimization of the Wavefunction/Geometry
  $\rightarrow V(\tilde{O})$ less sensitive to quality of Ψ
- Projector Monte Carlo

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  ($\rightarrow$ *Tuesday, Partition Monte Carlo*)

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