Linear Scaling in Quantum Monte Carlo

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Quantum Monte Carlo

Diffusion Quantum Monte Carlo (DQMC): the idea (Fermi, 1949, Anderson, 1975)

Schrödinger equation in imaginary time:

$$\frac{\partial \Psi}{\partial \tau} = -\hat{H}\Psi = \frac{1}{2m}\frac{\partial^2 \Psi}{\partial x^2} - V\Psi.$$

formal solution: $\sum_{i=0} a_i \Phi_i e^{-\tau E_i} \qquad \Longrightarrow \qquad \Psi(\tau) \rightarrow \Phi_0$

generalized diffusion equation:

$$\frac{\partial C(x,\tau)}{\partial \tau} = D\frac{\partial^2 C(x,\tau)}{\partial x^2} - V(x)C(x,\tau)$$

Quantum Monte Carlo

generalized diffusion equation:

$$\frac{\partial C(x,\tau)}{\partial \tau} = D\frac{\partial^2 C(x,\tau)}{\partial x^2} - V(x)C(x,\tau)$$

$$\begin{aligned} \frac{\partial C(x,\tau)}{\partial \tau} &= D\frac{\partial^2 C(x,\tau)}{\partial x^2} && \text{Fick's 2nd law} \\ \frac{\partial C(x,\tau)}{\partial \tau} &= -V(x)C(x,\tau) && \text{1st order kinetics} \end{aligned}$$

- simulation like Brownian motion with a *random walk*

Quantum Monte Carlo

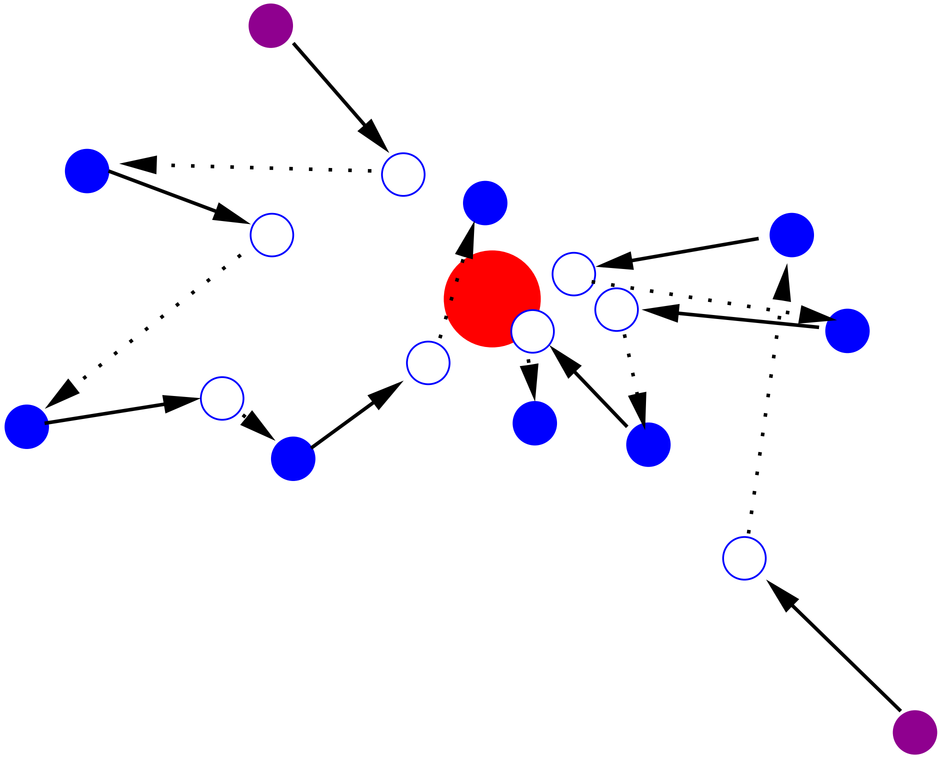
What is diffusing here?

- *random walker* has dimension of Schrödinger equation: $3n$-dim.
- diffusion process describes quantum mechanical kinetic energy
- potential energy as weighting or (better) drift of the random walk Drift

Quantum Monte Carlo

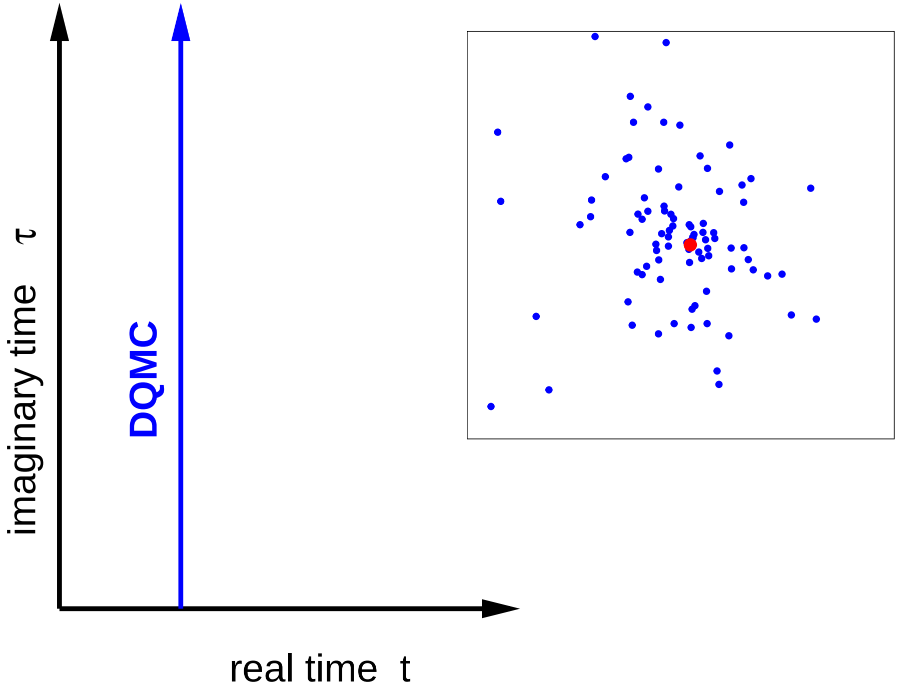
drift-diffusion algorithm: example He atom

random walker is arrangement of *both* electrons



Quantum Monte Carlo

wave function as statistical sample (H atom)



Mathematical Formalism

wave function propagation in imaginary time

$$|\Psi(\tau)\rangle = \mathsf{e}^{-\tau\hat{\mathsf{H}}}|\Psi(0)\rangle$$

in position space:

$$\Psi(\mathbf{r},\tau) = \int d\mathbf{r}' \mathsf{G}(\mathbf{r},\mathbf{r}',\tau)\Psi(\mathbf{r}',0) \qquad \text{with } \mathsf{G}(\mathbf{r},\mathbf{r}',\tau) = \langle\mathbf{r}|\mathsf{e}^{-\tau\hat{\mathsf{H}}}|\mathbf{r}'\rangle$$

short time approximation (Trotter):

$$\mathsf{e}^{-\tau\hat{\mathsf{H}}} = \mathsf{e}^{-\tau(\hat{\mathsf{T}}+\mathsf{V})} = \lim_{n\to\infty}\left(\mathsf{e}^{-\frac{\tau}{n}\hat{\mathsf{T}}}\mathsf{e}^{-\frac{\tau}{n}\mathsf{V}}\right)^{n}.$$

$$\mathsf{G}_{\mathrm{exact}}(\mathbf{r}_n,\mathbf{r}_0;\tau) = \lim_{n\to\infty}\int d\mathbf{r}_{n-1}\cdots\int d\mathbf{r}_1 \prod_{i=1}^{n}\mathsf{G}_{\mathrm{diff}}(\mathbf{r}_i,\mathbf{r}_{i-1};\Delta\tau)\mathsf{e}^{-\Delta\tau\mathsf{V}(\mathbf{r}_{i-1})}$$

in path integral form (Feynman-Kac):

$$\mathsf{G}_{\mathrm{exact}}(x,x';\tau) = \int_{(x',0)\to(x,\tau)} \exp\left\{-\int_0^{\tau}\mathsf{V}[x(t)]\,dt\right\}\mathcal{D}^{W}x$$

Quantum Monte Carlo

Properties

- direct quantum simulation of (almost) arbitrary Schrödinger equations
- quantum mechanical properties as statistical expectation
- statistical error like $1/\sqrt{M}$ (sample size M)
- possibly great computational effort

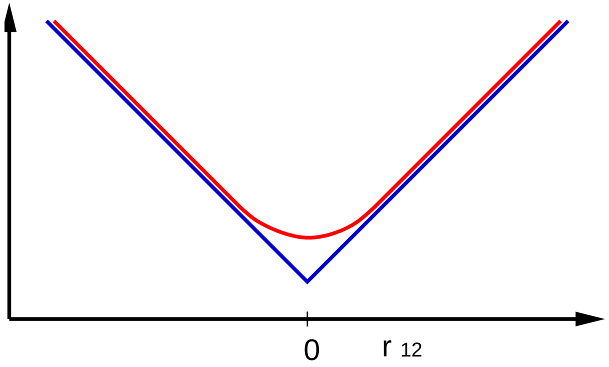
Applications

- high-dimensional coupled quantum systems
- correlation of electrons in molecules, solids (electronic Schrödinger equation
- coupled vibrations (Schrödinger equation for nuclear motion)

Quantum Monte Carlo for Electron Structure

Why QMC for electron structure?

- electron correlation: binding energy
- electron cusp: requires large basis sets
- or: $\Psi \propto r_{ij}$ for $r_{ij} \to 0$
- R12 methods (Kutzelnigg, Klopper), basis set extrapolation
- or: quantum Monte Carlo



QMC: Guidance Function

guidance function $\Phi_G(\mathbf{r})$ forces space and spin symmetry

$$f(\mathbf{r},\tau) := \Psi(\mathbf{r},\tau)\Phi_G(\mathbf{r})$$

Importance sampled DQMC algorithm:

- *diffusion step*
- *drift step* towards large $|\Phi_G(\mathbf{r})|$
- *weight step* with $e^{-(E_L(\mathbf{r})-E_T)\tau}$

with *local energy*: $E_L(\mathbf{r}) = \dfrac{\hat{H}\Phi_G(\mathbf{r})}{\Phi_G(\mathbf{r})}$

Asymptotic probability density $f(\mathbf{r}) \to \Phi_G(\mathbf{r})\Phi_0(\mathbf{r})$

QMC: Energy Estimator

Exact lowest eigenvalue E_0:

$$E_0 = \frac{\langle \Phi_G | \hat{H} \Phi_0 \rangle}{\langle \Phi_G | \Phi_0 \rangle} = \frac{\langle \Phi_0 | \hat{H} \Phi_G \rangle}{\langle \Phi_0 | \Phi_G \rangle} = \frac{\int \frac{\hat{H}\Phi_G}{\Phi_G} \Phi_0 \Phi_G \, dx}{\int \Phi_0 \Phi_G \, dx}$$

mixed estimator $E_0 = \lim_{N\to\infty} \frac{\sum_{i=1}^{N} w_i \, E_L(i)}{\sum_{i=1}^{N} w_i}$

This estimator has the *zero-variance property*, giving *exact eigenvalue without statistical error* when the guidance function is an exact eigenfunction

QMC: Guidance and Trial Functions

- good guidance functions: approximations to exact wavefunction
- Electron-electron cusp condition (Kato):

$$\Psi \propto e^{\frac{1}{2} r_{ij}} \qquad \text{for } r_{ij} \longrightarrow 0$$

- compact, physically motivated wavefunctions

Typical guidance functions $\Phi_G(\mathbf{r})$ are products of HF-SCF or small MCSCF functions with *correlation functions*

$$\Phi_G = \Phi_{det}\, e^U$$

QMC: Correlation functions

Many-body decomposition of the *correlation function* U:

$$U = U_1 + U_2 + U_3 + \ldots$$

with

$$U_1 = \sum_i U_1(\mathbf{x}_i)$$

$$U_2 = \sum_{i<j} U_2(\mathbf{x}_i, \mathbf{x}_j)$$

$$U_3 = \sum_{i<j<k} U_3(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k)$$

Schmidt/Moskowitz ansatz, based on transcorrelated wavefunctions of Boys/Handy:

$$U_{aij} = \sum_k^{N_a} c_k(\bar{r}_{ai}^{l_k}\bar{r}_{aj}^{m_k} + \bar{r}_{aj}^{l_k}\bar{r}_{ai}^{m_k})\bar{r}_{ij}^{n_k}$$

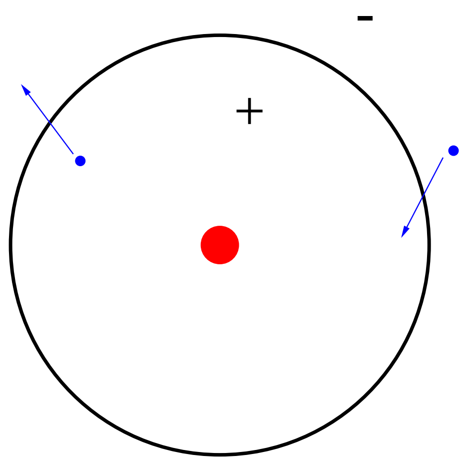
with electrons i,j and nuclei a, and $\bar{r} := \dfrac{br}{1+br}$

(satisfies electron-electron cusp for $b = 1/2$)

Quantum Monte Carlo for Electron Structure

Pauli principle causes nodes in wave function

example: exact nodes for ^{3}S He: $r_1 = r_2$



- fixed node approximation: use nodes from known functions (here: ab initio)
- → *node location error*

Quantum Monte Carlo for Electron Structure

method: DQMC/HF

- coupling of DQMC with ab initio HF/SCF wave functions
- accuracy of DQMC/HF depends on the nodes of the ab initio function
- error cancellation is necessary if "chemical accuracy" is to be achieved
- use standard ab initio basis sets in DQMC
- all electrons, no pseudo potentials

scaling with system size

- computer time grows like n^{3-4} with the number of electrons n
- cf. CCSD(T) like n^7

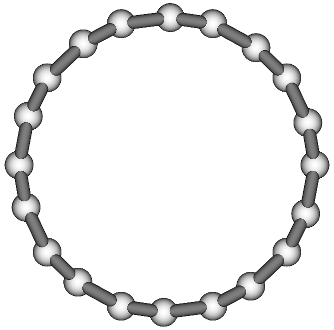
Quantum Monte Carlo for Electron Structure

reaction energies (0 K) in kJ/mol calculated with DQMC/HF/cc-pVTZ and MP2/cc-pVTZ geometries

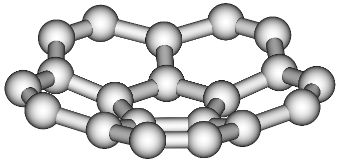
reaction	exp	DQMC		cc-pVTZ		cc-pVDZ	
	ΔH_e	ΔH_e	$\Delta\Delta H_e$	ΔH_e	$\Delta\Delta H_e$	ΔH_e	$\Delta\Delta H_e$
$CH_2 + H_2 \rightarrow CH_4$	−544(2)	−552(2)	−8	−537	7	−529	15
$C_2H_2 + H_2 \rightarrow C_2H_4$	−203(2)	−209(2)	−6	−207	−4	−215	−12
$C_2H_2 + 3\ H_2 \rightarrow 2\ CH_4$	−446(2)	−442(2)	4	−451	−5	−457	−11
$N_2H_2 \rightarrow N_2 + H_2$	−174	−192(2)	−18	−179	−5	−188	−14
$CO + H_2 \rightarrow H_2CO$	−21(1)	−32(2)	−11	−16	5	−1	20
$N_2 + 3\ H_2 \rightarrow 2\ NH_3$	−164(1)	−186(2)	−22	−146	18	−101	63
$F_2 + H_2 \rightarrow 2\ HF$	−563(1)	−618(2)	−55	−545	18	−510	53
$O_3 + 3\ H_2 \rightarrow 3\ H_2O$	−933(2)	−1050(2)	−117	−912	21	−850	83
$H_2CO + 2\ H_2 \rightarrow CH_4 + H_2O$	−251(1)	−262(2)	−11	−241	10	−217	34
$H_2O_2 + H_2 \rightarrow 2\ H_2O$	−365(2)	−384(2)	−19	−351	14	−328	37
$CO + 3\ H_2 \rightarrow CH_4 + H_2O$	−272(1)	−294(2)	−22	−257	15	−218	54
$HCN + 3\ H_2 \rightarrow CH_4 + NH_3$	−320(3)	−338(2)	−18	−313	7	−289	31
$HNO + 2\ H_2 \rightarrow H_2O + NH_3$	−444(1)	−485(2)	−41	−427	17	−381	63
$HNC \rightarrow HCN$	−64	−66(2)	−2	−63	1	−66	−2
$H_2O + F_2 \rightarrow HOF + HF$	−129(4)	−141(2)	−12	−115	14	−107	22
$CO_2 + 4\ H_2 \rightarrow 2\ H_2O + CH_4$	−244(1)	−272(2)	−28	−226	18	−178	66
$2\ CH_2 \rightarrow C_2H_4$	−844(3)	−871(2)	−27	−830	14	−815	29

Quantum Monte Carlo for Electron Structure

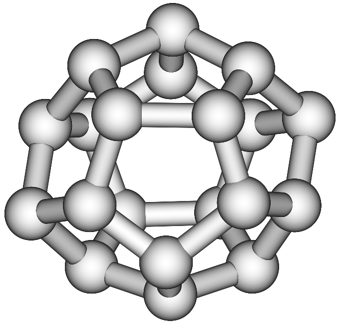
DQMC/HF calculations for carbon clusters C_{20}



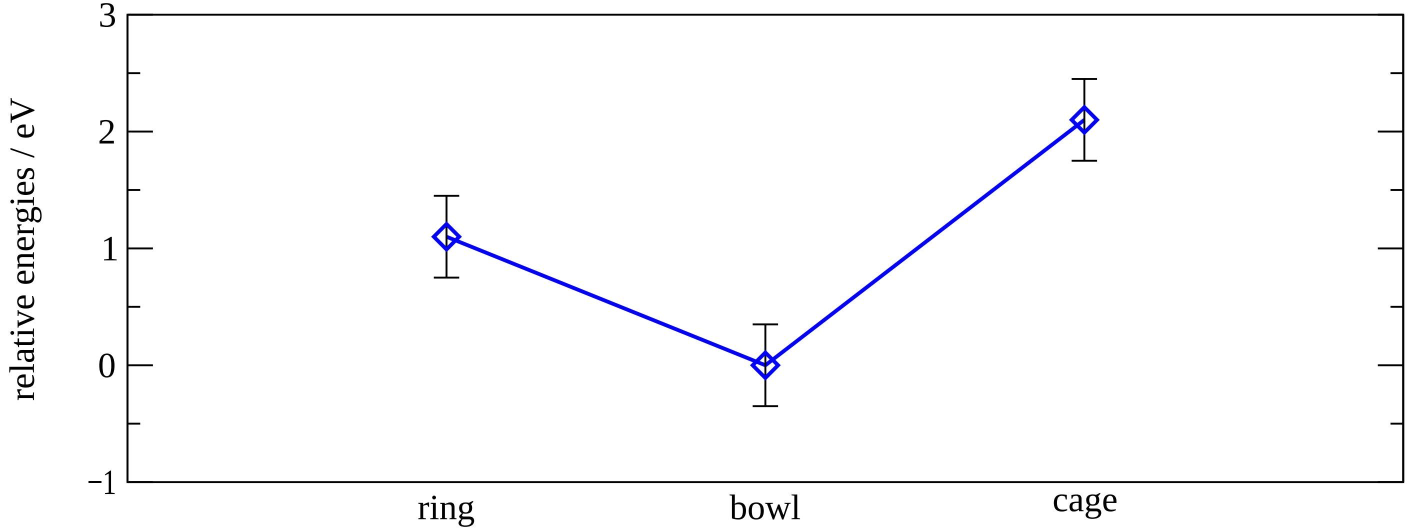
ring



bowl



cage



Quantum Monte Carlo for Electron Structure

methods: DQMC/MCSCF and DQMC/PNOCI

- coupling of DQMC with correlated *ab initio* wave functions
- analysis of node location error: dynamical node error and non-dynamical node error analogously to electron correlation
- use DQMC/MCSCF (DQMC/CASSCF) when non-dynamical correlation important
- use DQMC/PNOCI for *systematical reduction of node error*

Quantum Monte Carlo for Electron Structure

DQMC/PNOCI results in comparison to other methods

method	reference	E_0
variational results:		
DQMC/MCSCF	(this work)	–109.506(2)
ICMRCI/cc-pCV5Z	Peterson 1997	–109.5095
DQMC/PNOCI	(this work)	–109.520(3)
nonvariational results:		
ICMRCI+Q/CBS	Peterson 1997	–109.5346
CCSD(T)/cc-pCV5Z	Peterson 1997	–109.5359
r_{12}-MR-ACPF	Gdanitz 1998	–109.5370
“experimental”	–	–109.5424

Quantum Monte Carlo for Electron Structure

Local DQMC

- electron correlation is a short-range effect (dispersion like r^{-6})
- localized MOs *and* short-range correlation functions
- improvement of scaling from n$^{3-4}$ to n$^{2-3}$
- sparse matrix algorithms
- approach similar to current local *ab initio* methods

Electron QMC: Scaling

cpu time $\propto N_{\mathrm{steps}} \times t_{\mathrm{localenergy}}$

$\mathsf{t}_{\mathrm{localenergy}}$: $E_{\mathrm{local}} = \frac{\hat{H}\Psi}{\Psi}$ with $\Psi = \Phi_{\mathrm{Det}} e^{U}$

for the current electron *positions* calculate:

1. atomic orbitals (AOs)
2. molecular orbitals (MOs) from AOs
3. Slater determinant(s) from MOs
4. electron correlation function U
5. coulomb energy

Electron QMC: Scaling

Scaling of standard implementation using canonical MOs:

1. AOs: n^2, each AO for each electron
2. MOs: n^3, each MO is LCAO for each electron
3. Determinants: n^3, via LU decomposition
4. correlation: n^2 for electron pair function
5. coulomb: n^2

(*scaling with number of electrons* n *assumed* $\propto$ *number of basis functions* N)

scaling of local energy calculation: n^3
overall scaling of DQMC: $n^3 - n^4$

Electron QMC: Improved Scaling

Improved scaling for calculation of AOs:

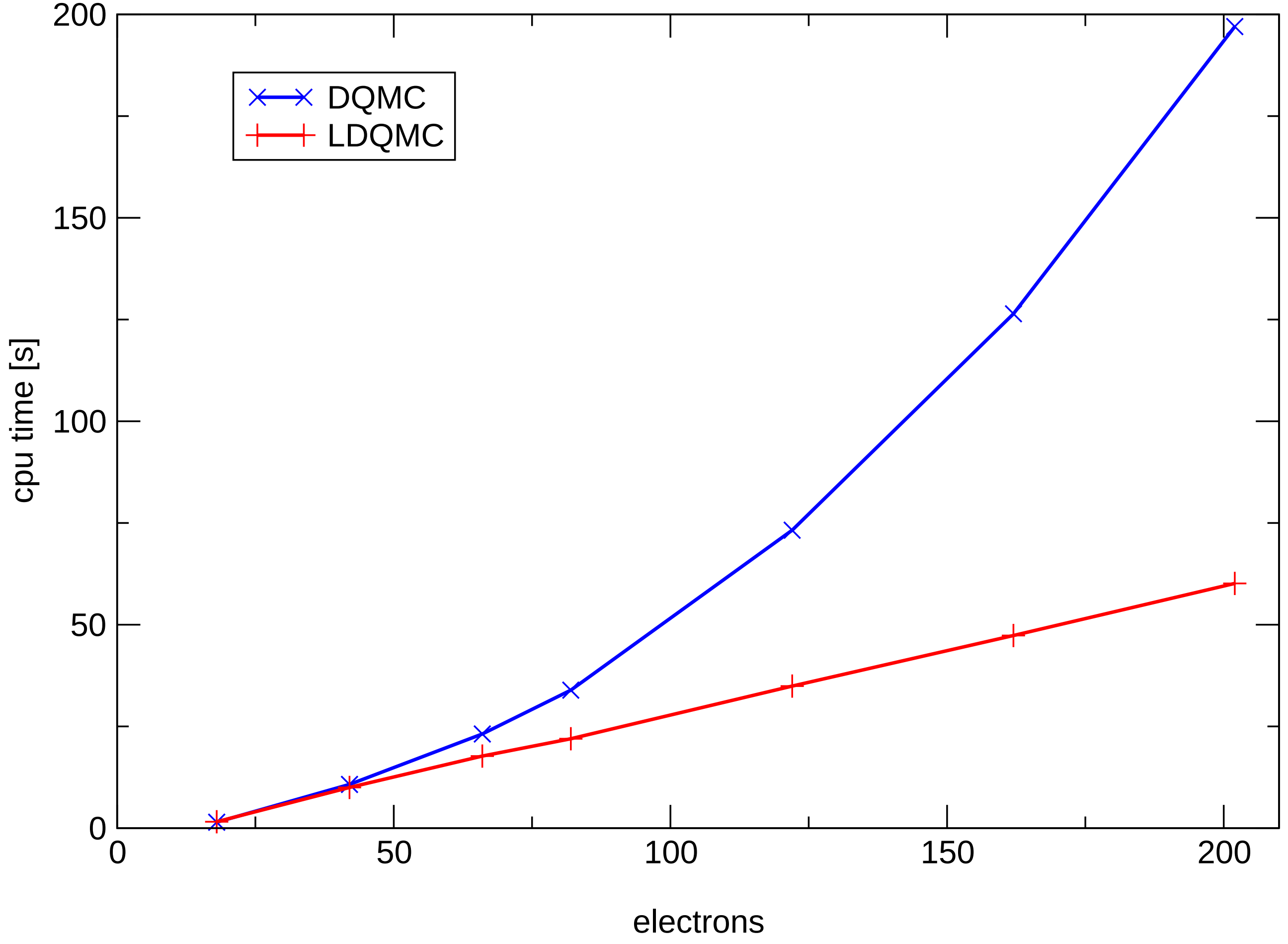
AOs decay exponentially:

- calculate AO only for electrons within cutoff radius
- constant number of electrons per AO

improved scaling: $O(n^2) \rightarrow O(n)$ (*linear*)

Electron QMC: Improved Scaling

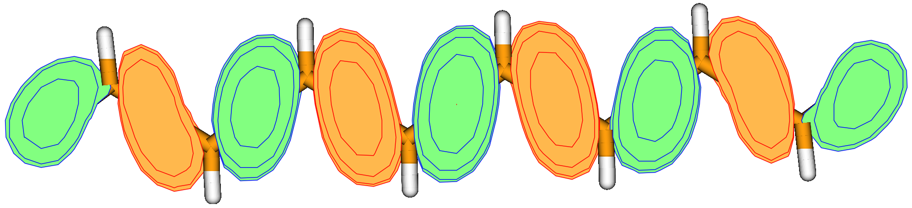
AO contribution: old vs. new DQMC calculation for C_nH_{2n+2}



Electron QMC: Improved Scaling

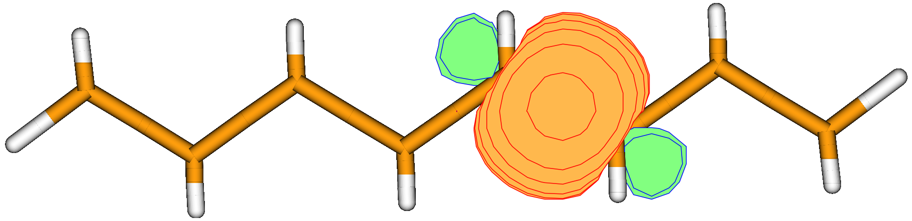
Localized MOs instead of canonical MOs

canonical HOMO for C_8H_{18}:



unitary transformation:

localized C-C valence MO C_8H_{18}:



Electron QMC: Improved Scaling

improved scaling for calculation of MOs

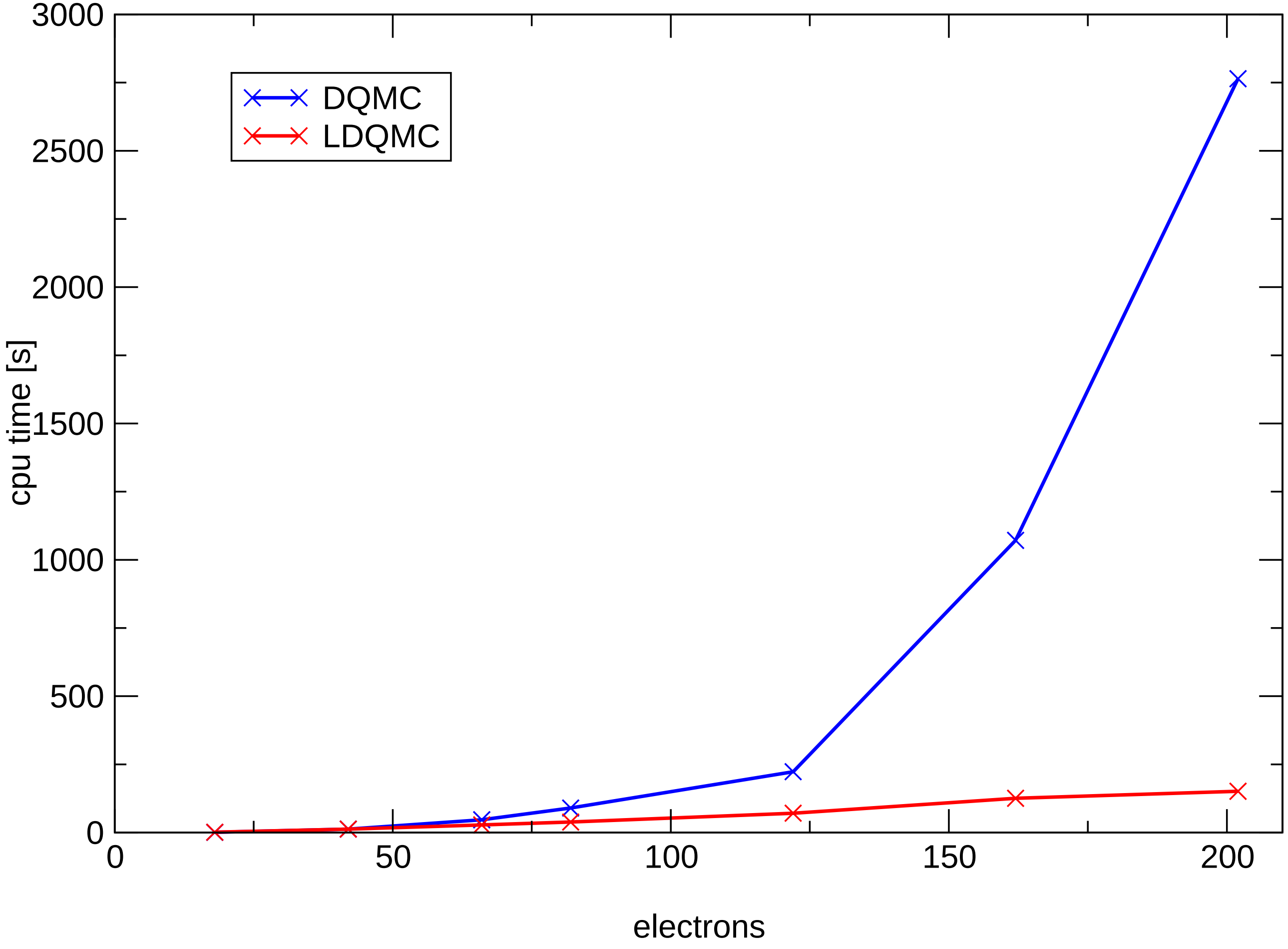
Local MOs decay exponentially:

- calculate Local MO only from AOs within a cutoff radius
- calculate Local MO only for electrons within a cutoff radius
- constant number of electrons and AOs per Local MO

improved scaling: $O(n^3) \rightarrow O(n)$ *(linear)*

Electron QMC: Improved Scaling

MO contribution: old vs. new DQMC calculation for C_nH_{2n+2}



Electron QMC: Improved Scaling

improved scaling for calculation of Slater determinants

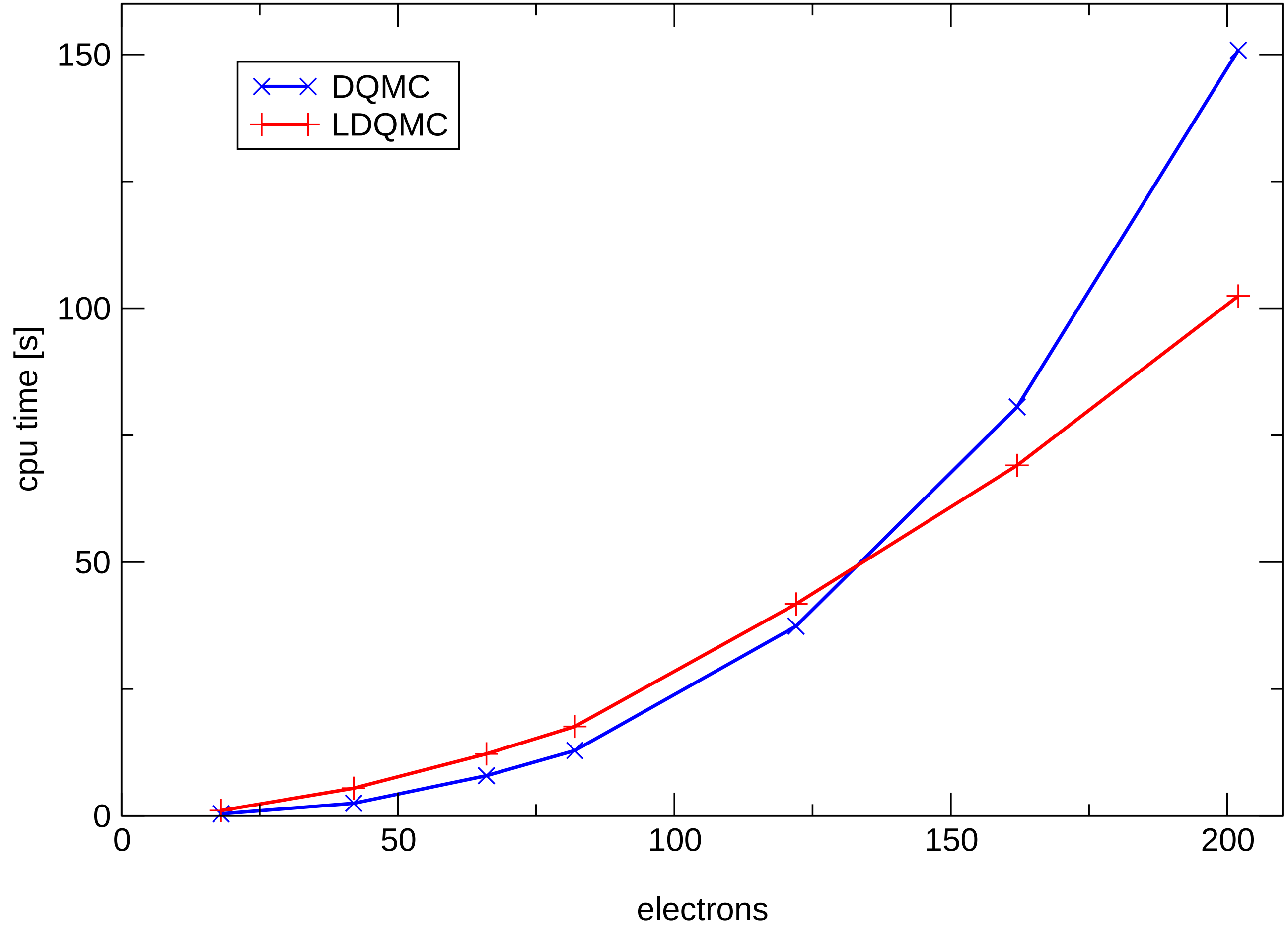
With Local MOs, Slater determinants are sparse:

- use sparse matrix algorithm for LU decomposition
- → linear time $O(n)$ per determinant
- But: n determinants required for $\nabla^2\Psi$
- Either: sparse matrix algorithm for inverse matrix ($O(n^2)$) and updates
- Or: direct calculation of n determinants each in linear time

improved scaling: $O(n^3) \rightarrow O(n^2)$

Electron QMC: Improved Scaling

determinant contribution: old vs. new DQMC calculation for C_nH_{2n+2}



Electron QMC: Improved Scaling

improved scaling for calculation of electron correlation

The electron correlation term e^U is:

$$\mathrm{U} = \sum_a \sum_{i<j} U_{aij} \text{ with } U_{aij} = \sum_k^{N_a} c_{ka}\left(\bar{r}_{ai}^{\,l_{ka}} \bar{r}_{aj}^{\,m_{ka}} + \bar{r}_{aj}^{\,l_{ka}} \bar{r}_{ai}^{\,m_{ka}}\right) \bar{r}_{ij}^{\,n_{ka}},$$

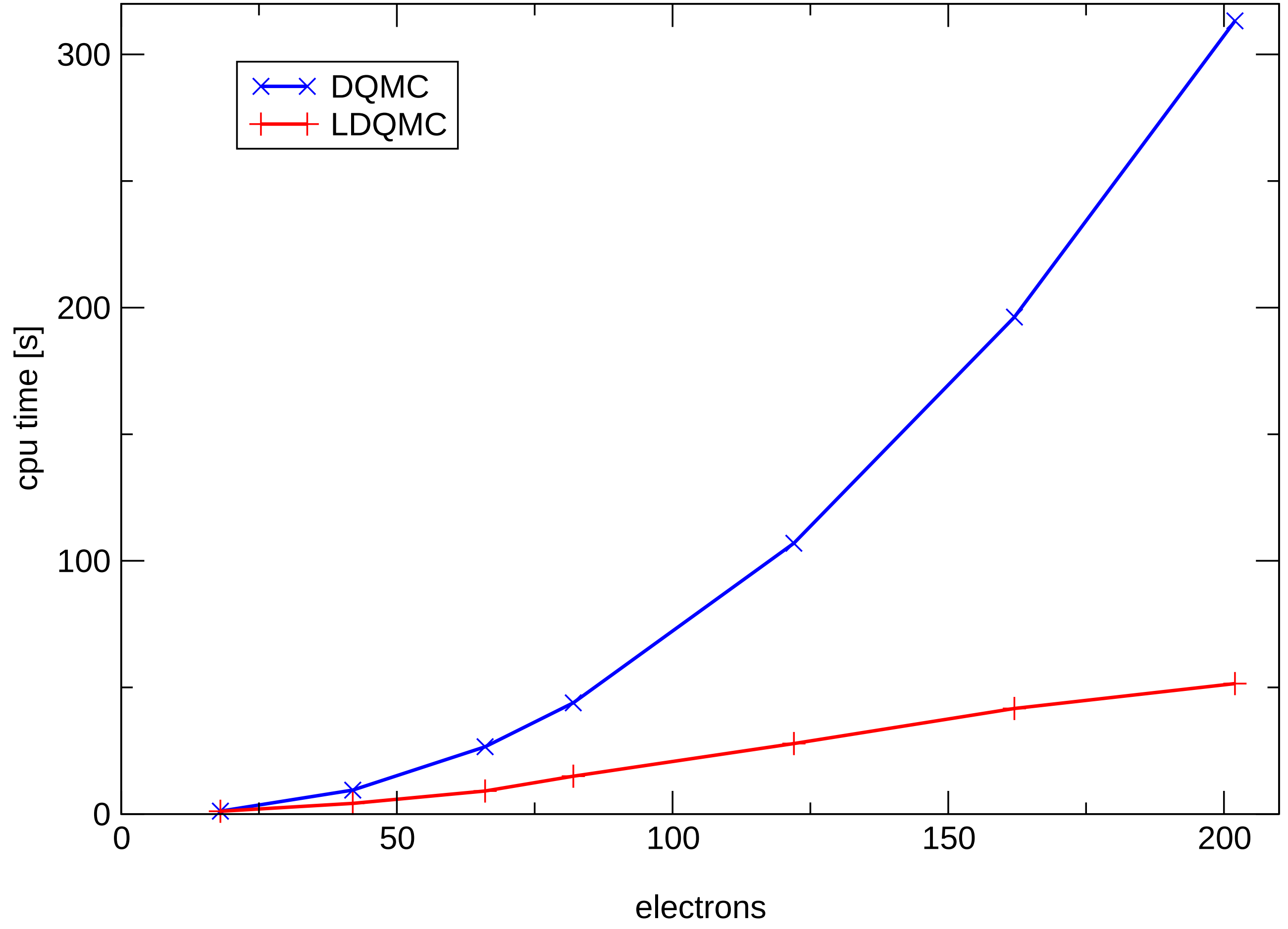
(nuclei a, electrons i, j, Schmidt/Moskowitz, 1993)

- replace scaled distance $\bar{r} = r/(1 + ar)$
  with exponentially decaying $\bar{r} = 1 - \exp(-ar)$
- use cutoff distance
- no loss in variance of trial function!

improved scaling: $O(n^3)$ or $O(n^2) \rightarrow O(n)$ (*linear*)

Electron QMC: Improved Scaling

correlation contribution: old vs. new DQMC calculation for C_nH_{2n+2}



Electron QMC: Scaling

Scaling of new Local DQMC (LDQMC) version:

1. AOs: *linear* (cutoff)
2. MOs: *linear* (cutoff, Local MOs)
3. determinants: n^2, (sparse matrix algorithm)
4. correlation: *linear* (special form, cutoff)
5. coulomb: n^2 (linear possible)

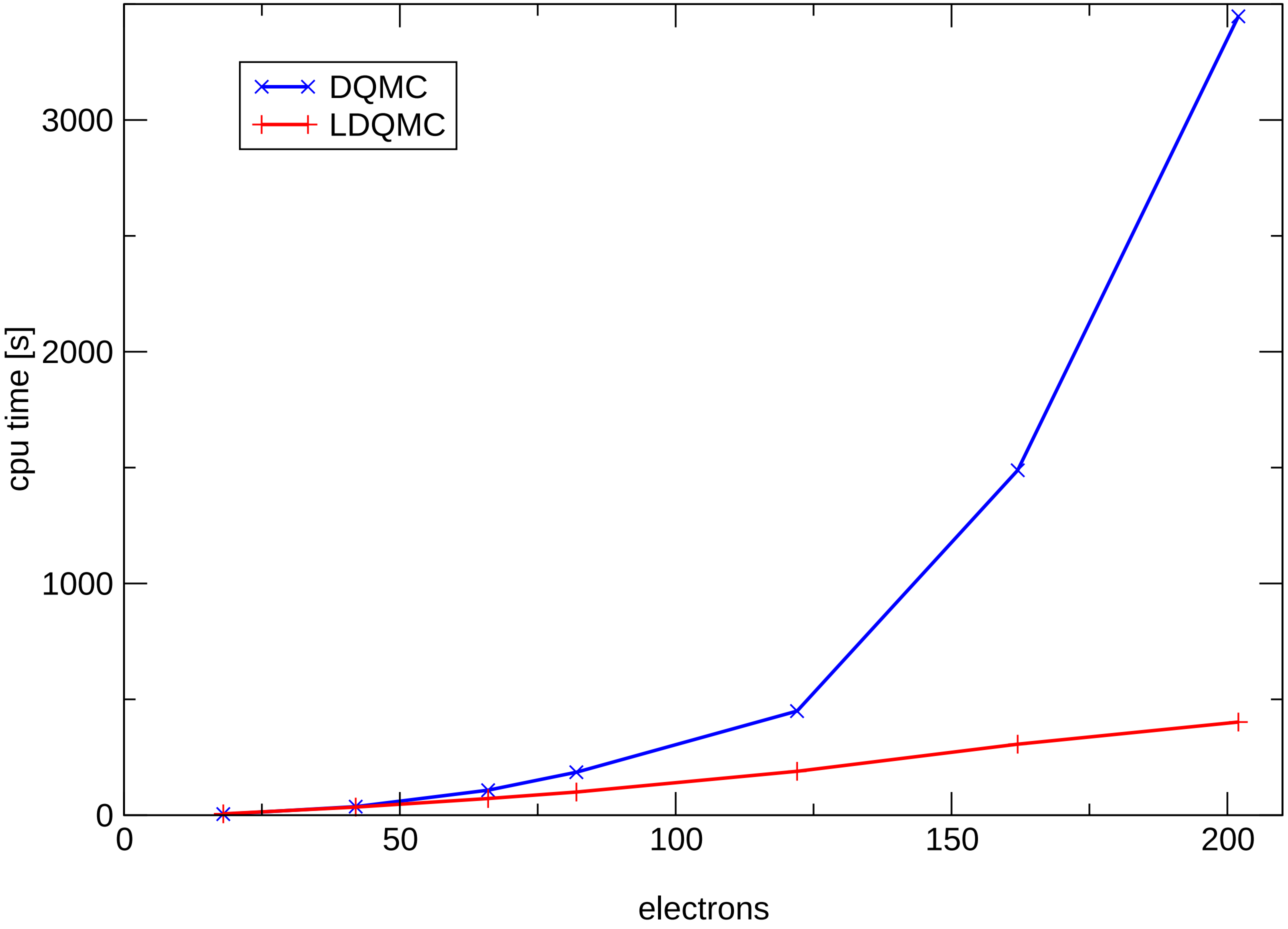
(*scaling with number of electrons* n *assumed* $\propto$ *number of basis functions* N)

scaling of local energy calculation: n^2

overall scaling of DQMC: $n^2 - n^3$

Electron QMC: Improved Scaling

total cpu time: old vs. new DQMC calculation for C_nH_{2n+2}



Electron QMC: Improved Scaling