Imperial College London

Stochastic Coupled Cluster Theory

Alex Thom

Quantum Monte Carlo in the Apuan Alps VII, 2012

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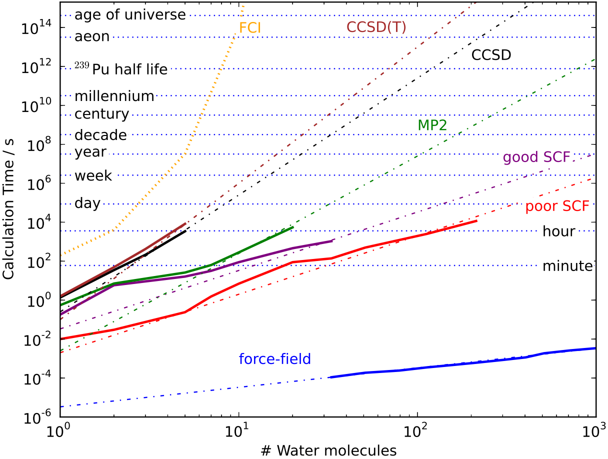
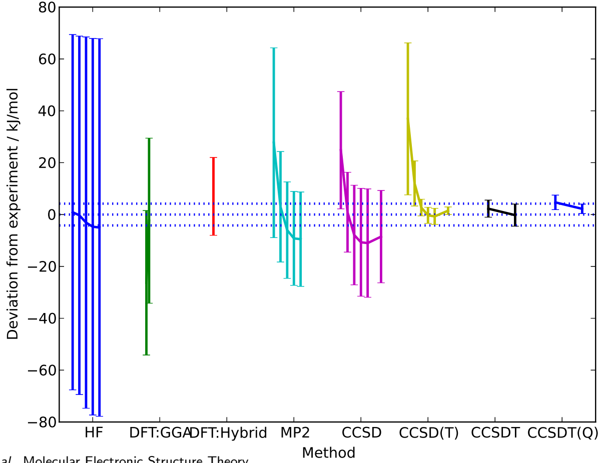
UNIVERSITY OF CAMBRIDGE

Electronic Structure Theory: Scaling



Electronic Structure Theory: Accuracy



Helgaker T. *et al.*, Molecular Electronic Structure Theory
Curtiss L.A., Raghavachari K., Redfern P.C., Pople, J.A. *J. Chem. Phys.* **106**, 1063 (1997)
Klopper W., Helgaker T. *J. Phys. B* **32**, R103 (1999)
Klopper W., Ruscic B., Tew D., Bischoff F., Wolfsegger S. *Chem. Phys.* **356**, 14 (2009)
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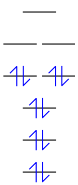
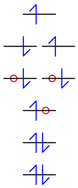
Determinant Space



Hartree-Fock



Triple excitation

- For an N-electron system, N spin-orbitals are chosen out of $2M$ spin-orbitals $\{\phi_1, \phi_2, ..., \phi_{2M}\}$ to form a Slater Determinant, $|D_{\mathbf{i}}\rangle$.

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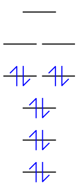

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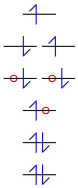

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- For an N-electron system, N spin-orbitals are chosen out of $2M$ spin-orbitals $\{\phi_1, \phi_2, ..., \phi_{2M}\}$ to form a Slater Determinant,$|D_{\mathbf{i}}\rangle$.
- Complete space of determinants is finite, but exponentially growing in N and M as $\binom{2M}{N}$

Full Configuration Interaction

- We can project the many-electron Hamiltonian into the space of Slater Determinants and solve in this space. $H_{\mathbf{ij}} = \langle D_{\mathbf{i}} | \hat{H} | D_{\mathbf{j}} \rangle$.
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- Solve as $|\Psi_{\mathrm{CI}}\rangle = \sum_{\mathbf{i}} c_{\mathbf{i}}|D_{\mathbf{i}}\rangle$
- Exponentially scaling with system size (N or M)

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- Solutions to $\hat{H}|\Psi\rangle = E|\Psi\rangle$ also solve $e^{-\tau\hat{H}}|\Psi\rangle = e^{-\tau E}|\Psi\rangle$.

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- Propagate $\frac{\partial|\Psi\rangle}{\partial\tau} = -\hat{H}|\Psi\rangle$.
- Lowest energy eigenfunction $|\Psi_{\mathrm{CI}}\rangle$ becomes dominant.
- Let $|\Psi_{\mathrm{CI}}\rangle = \sum_{\mathbf{i}} c_{\mathbf{i}}|D_{\mathbf{i}}\rangle$

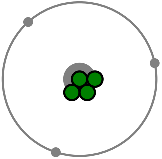
$$\frac{\partial c_{\mathbf{i}}}{\partial\tau} = -\sum_{\mathbf{j}} H_{\mathbf{ij}}c_{\mathbf{j}}.$$

- Represent $c_{\mathbf{i}}$ as populations of signed psips (walkers) propagating through space.

George H. Booth, AJWT, and Ali Alavi, *J. Chem. Phys.* **131**, 054106 (2009)

Dynamics

$$\frac{\partial c_{\mathbf{i}}}{\partial \tau} = -H_{\mathbf{ii}} c_{\mathbf{i}} - \sum_{\mathbf{j} \to \mathbf{i}} H_{\mathbf{ij}} c_{\mathbf{j}}.$$



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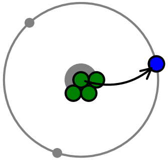

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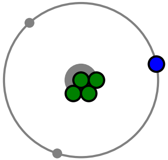

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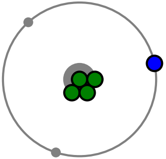

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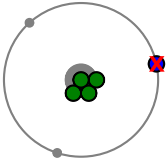

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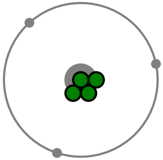

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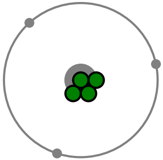

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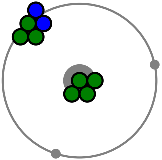

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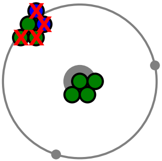

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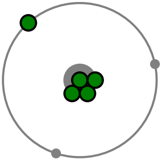

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Example

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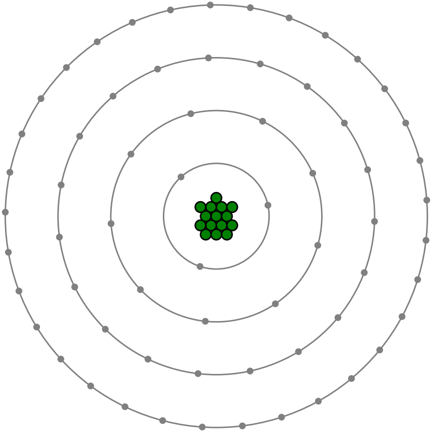
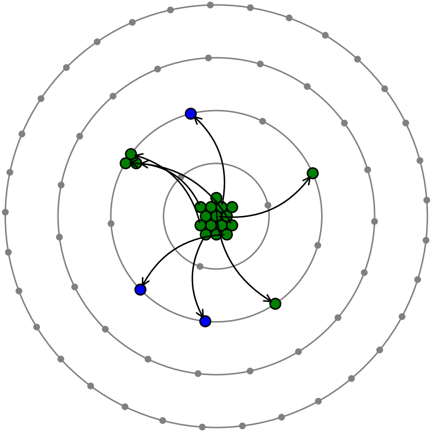


Example

- Initial configuration
- Spawning



Example

- Initial configuration
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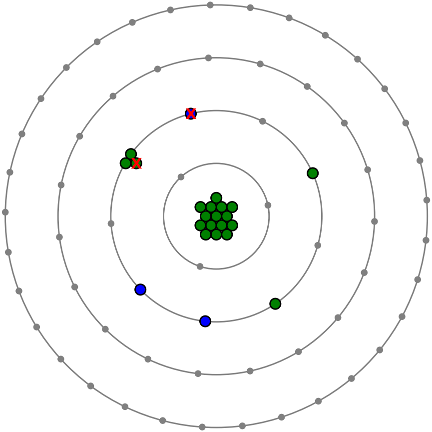
- Death



Example

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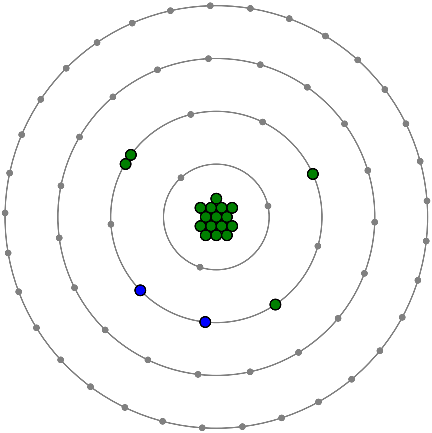

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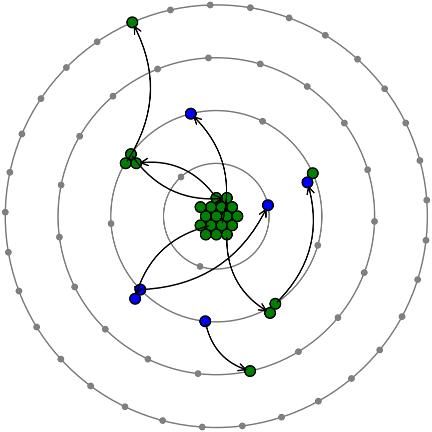

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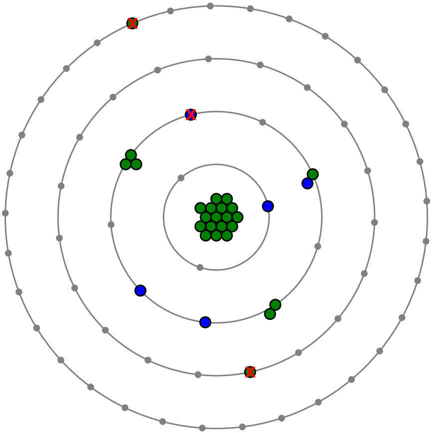

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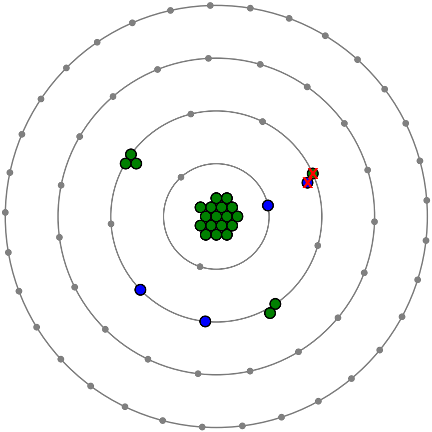

Example

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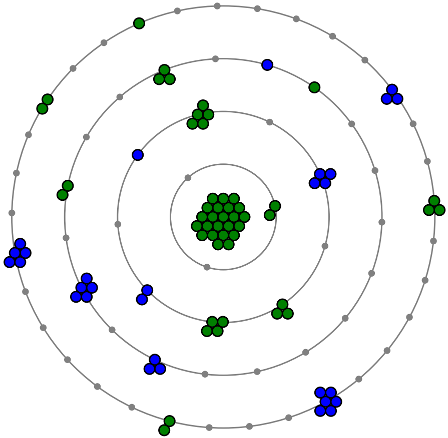
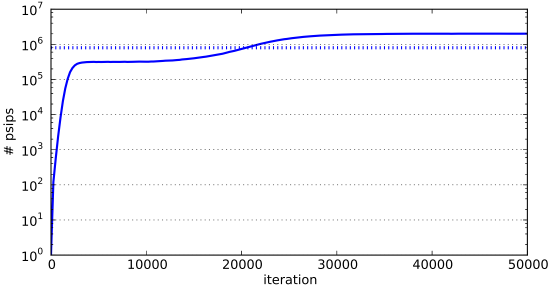
- Many steps later



Performance

- With a system-dependent critical number of psips, FCIQMC reproduces CI energy essentially exactly.
- Critical psip number, N_c, needed to allow the correct sign structure of the wavefunction to develop.
- Below this, energy is wrong. Plateau shows what N_c is.



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- Only allow psips on determinants with a significant population (3+) to spawn to unoccupied determinants.
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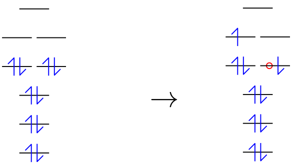
- Vastly reduces N_c. Introduces systematic, but controllable error.
- Scaling exponential with increasing system size — even with initiators.
- Able to calculate energies for previously insoluble systems (larger by many orders of magnitude).

Deidre Cleland, George H. Booth, and Ali Alavi, *J. Chem. Phys.* **132**, 041103 (2010)

George H. Booth, and Ali Alavi, *J. Chem. Phys.* **132**, 174104 (2010)

Deidre Cleland, George Booth, and Ali Alavi, *J. Chem. Phys.* **134**, 024112 (2011)

Excitors



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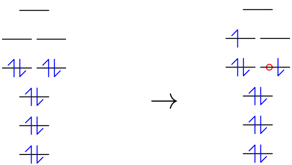

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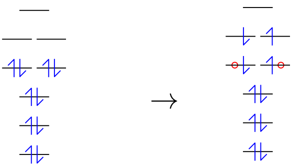

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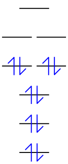

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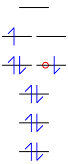

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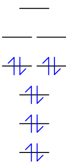

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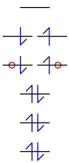

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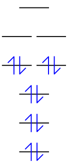

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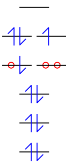

$$\hat{a}_i^a\hat{a}_{jk}^{bc}|D_{\mathbf{0}}\rangle = \hat{a}_{ijk}^{abc}|D_{\mathbf{0}}\rangle$$

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$$\hat{T}_1 = \sum_{\substack{i\\a}} t_i^a \hat{a}_i^a \qquad \hat{T}_2 = \sum_{\substack{i<j\\a<b}} t_{ij}^{ab} \hat{a}_{ij}^{ab} \qquad \cdots$$

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- Use an exponential to generate the wavefunction

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}} |D_0\rangle$$

- Exponential generates products of excitors $e^{\hat{T}} = \hat{1} + \hat{T}_1 + \hat{T}_2 + \dots + \frac{1}{2}\hat{T}_1^2 + \frac{1}{2}\hat{T}_1\hat{T}_2 + \cdots$

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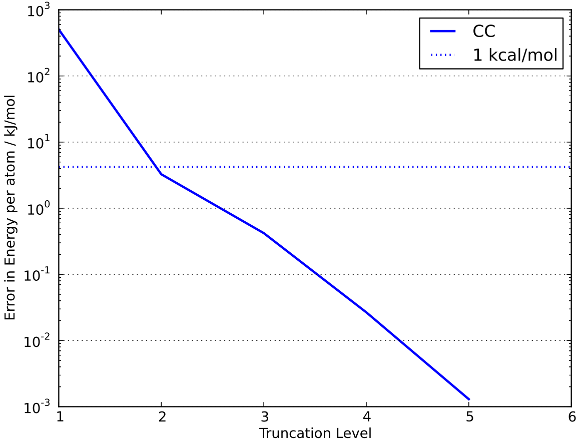
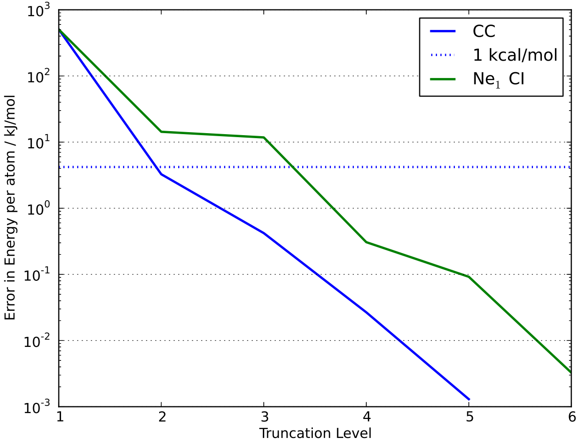
- As number of electrons increases, truncated CI rapidly worsens.

Size Consistency



1 kcal/mol = 10 meV

Size Consistency



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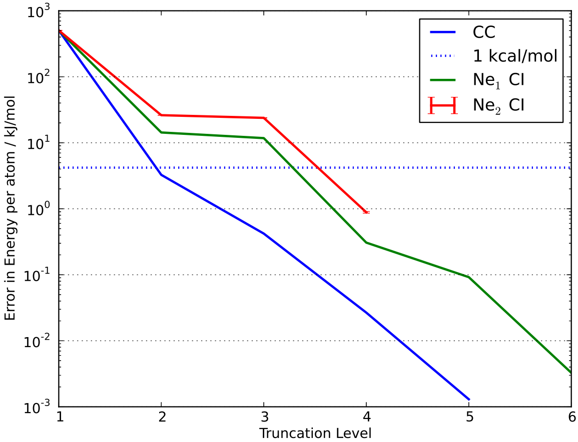

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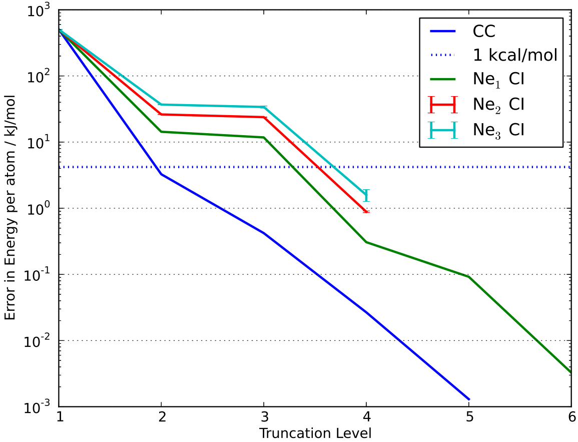
Size Consistency



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Naïve Coupled Cluster Theory

- Solve $\hat{H}|\Psi_{\rm CC}\rangle = E|\Psi_{\rm CC}\rangle$.

Naïve Coupled Cluster Theory

- Solve $\hat{H}|\Psi_{\mathrm{CC}}\rangle = E|\Psi_{\mathrm{CC}}\rangle$.
- Could solve projected equations like
  $\langle D_0|\hat{H} - E|e^{\hat{T}} D_0\rangle = 0$
  $\langle D_i^a|\hat{H} - E|e^{\hat{T}} D_0\rangle = 0$
  $\langle D_{ij}^{ab}|\hat{H} - E|e^{\hat{T}} D_0\rangle = 0$, etc.

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  $\langle D_{ij}^{ab}|\hat{H} - E|e^{\hat{T}} D_0\rangle = 0$, etc.
- Complicated and non-linear, so solve iteratively.
- Not variational.
- Full CI and Full CC are equivalent. $\hat{C} = e^{\hat{T}}$.
- Normally easier to solve $\langle D_{\mathbf{i}}|e^{-\hat{T}}(\hat{H} - E)e^{\hat{T}}|D_0\rangle = 0$.

CI vs. CC Theory

$$\langle D_{\mathbf{i}}|(\hat{H} - E)|\Psi_{\mathrm{CI}}\rangle \quad = \quad 0$$

CI vs. CC Theory

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\begin{aligned}
\langle D_{\mathbf{i}} | (\hat{H} - E) | \Psi_{\mathrm{CI}} \rangle &= 0 \\
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e.g. $D_{\mathbf{i}} = D_{ij}^{ab}$. $\langle D_{\mathbf{i}}|\Psi_{\mathrm{CC}}\rangle = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a = t_{\mathbf{i}} + \mathcal{O}[T^2]$.

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Sampling the CC equations

$$t_{\mathbf{i}}(\tau) - \delta\tau \sum_{\mathbf{j}} (H_{\mathbf{ij}} - E\delta_{\mathbf{ij}}) \langle D_{\mathbf{j}} | \Psi_{\mathrm{CC}}(\tau) \rangle = t_{\mathbf{i}}(\tau + \delta\tau)$$

.

- $\forall \mathbf{i}, \forall \mathbf{j}$, calculate $\langle D_{\mathbf{j}} | \Psi_{\mathrm{CC}}(\tau) \rangle$ and update $t_{\mathbf{i}}$.

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- $\forall \mathbf{j}$, calculate $\langle D_{\mathbf{j}} | \Psi_{\mathrm{CC}}(\tau) \rangle$. Now randomly pick $\mathbf{i}$, and update $t_{\mathbf{i}}$.

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$$e^{\hat{T}} = 1 + \sum_{\mathbf{i}} t_{\mathbf{i}} \hat{a}_{\mathbf{i}} + \frac{1}{2!} \sum_{\mathbf{i},\mathbf{j}} t_{\mathbf{i}} t_{\mathbf{j}} \hat{a}_{\mathbf{i}} \hat{a}_{\mathbf{j}} + \frac{1}{3!} \sum_{\mathbf{i},\mathbf{j},\mathbf{k}} t_{\mathbf{i}} t_{\mathbf{j}} t_{\mathbf{k}} \hat{a}_{\mathbf{i}} \hat{a}_{\mathbf{j}} \hat{a}_{\mathbf{k}} + \ldots$$

.

Sampling the CC equations

$$t_{\mathbf{i}}(\tau) - \delta\tau \sum_{\mathbf{j}} (H_{\mathbf{ij}} - E\delta_{\mathbf{ij}}) \langle D_{\mathbf{j}} | \Psi_{\mathrm{CC}}(\tau) \rangle = t_{\mathbf{i}}(\tau + \delta\tau)$$

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.

- Pick a random term in $e^{\hat{T}}$ and work out $\mathbf{j}$ and $\langle D_{\mathbf{j}} | \Psi_{\mathrm{CC}}(\tau) \rangle$ **from just this term**. Now randomly pick $\mathbf{i}$, and update $t_{\mathbf{i}}$.

Discretization

- Represent $\hat{T} = \sum_{\mathbf{i}} t_{\mathbf{i}} \hat{a}_{\mathbf{i}}$ as a population of excips for each excitation.
- Need to sample

$$e^{\hat{T}} = 1 + \sum_{\mathbf{i}} t_{\mathbf{i}} \hat{a}_{\mathbf{i}} + \frac{1}{2!} \sum_{\mathbf{i},\mathbf{j}} t_{\mathbf{i}} t_{\mathbf{j}} \hat{a}_{\mathbf{i}} \hat{a}_{\mathbf{j}} + \frac{1}{3!} \sum_{\mathbf{i},\mathbf{j},\mathbf{k}} t_{\mathbf{i}} t_{\mathbf{j}} t_{\mathbf{k}} \hat{a}_{\mathbf{i}} \hat{a}_{\mathbf{j}} \hat{a}_{\mathbf{k}} + \dots$$

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- From list of excips randomly select a number of them (remembering signs). Need normalized probabilities.

$$+_i^a \quad +_i^b \quad +_i^b \quad -_j^a \quad -_j^b \quad +_j^c \quad +_j^c \quad +_j^c \quad -_{ij}^{ab} \quad +_{ik}^{ac} \quad -_{ijk}^{abc}$$

AJWT *Phys. Rev. Lett.* **105**, 263004 (2010)

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AJWT *Phys. Rev. Lett.* **105**, 263004 (2010)

Discretization

$$+^{ac}_{ik} \qquad -^{b}_{j}$$

Discretization

$$+^{ac}_{ik} \quad -^{b}_{j} \rightarrow -\hat{a}^{abc}_{ijk}$$

- Collapse this into a single excitor and apply to the reference, resulting in a determinant.

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- Death: Die according to $\delta\tau(\langle D_{ijk}^{abc}|\hat{H}|D_{ijk}^{abc}\rangle - S)$.

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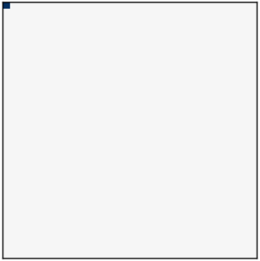
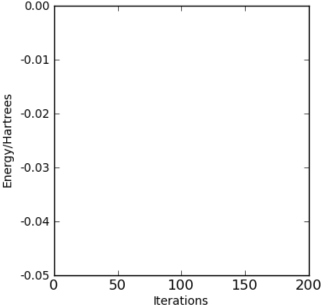
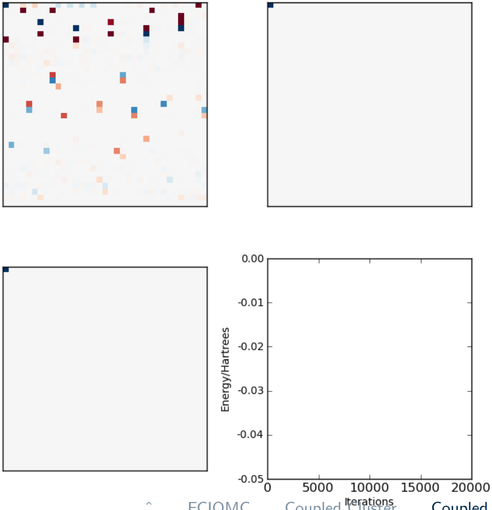
- Death: Die according to $\delta\tau(\langle D^{abc}_{ijk}|\hat{H}|D^{abc}_{ijk}\rangle - S)$. …Create new $+^{abc}_{ijk}$ excip.
- Annihilate as in FCIQMC.

Coupled Cluster






0.00
-0.01
-0.02
-0.03
-0.04
-0.05
Energy/Hartrees
0
5000
10000
15000
20000
Iterations

Performance

- Initial excip growth much faster than FCIQMC.
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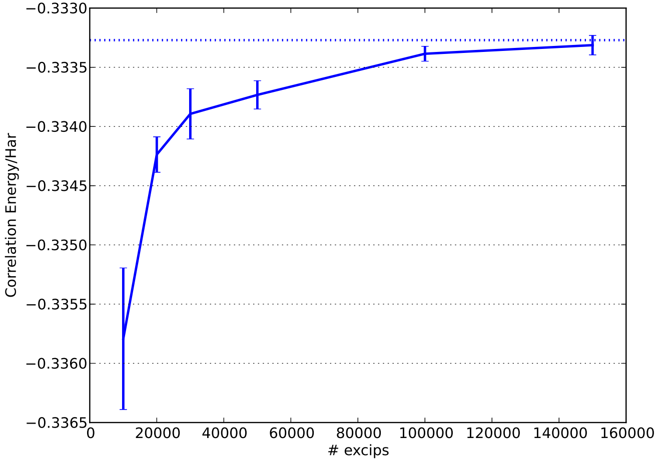
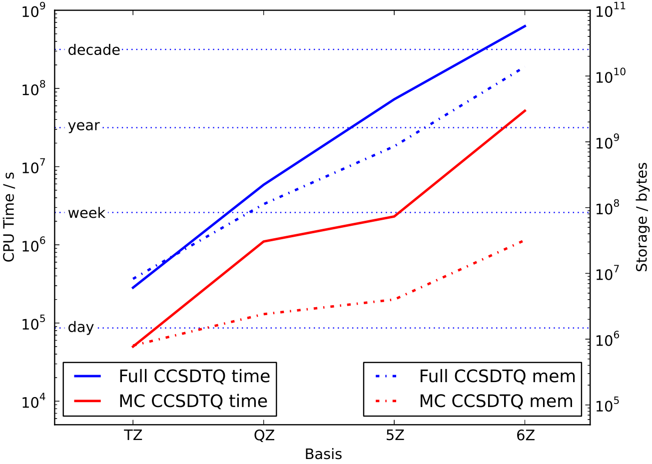
- Critical number of excips seems to scale with size of space. e.g. CCSD $N_c \sim N^4$.
- Able to reproduce large coupled cluster calculations in less time.
- Initiator approximation also applicable.
- Cluster is initiator iff all component excips have sufficient amplitude.
- Much fewer excips, so much faster.

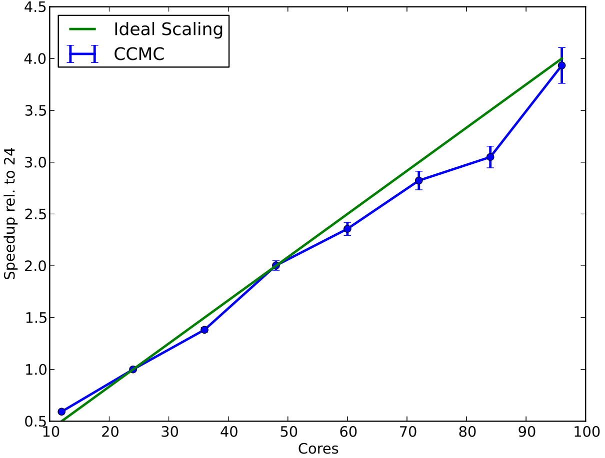
Ne cc-pVQZ initiator



Scaling

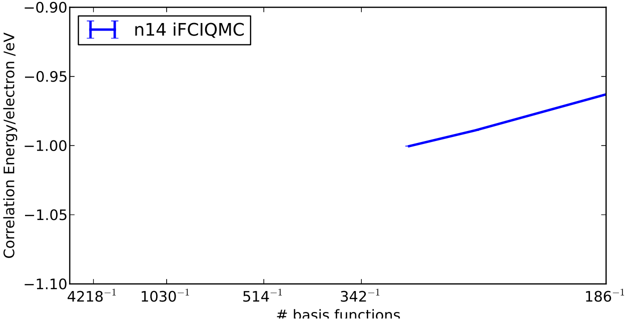

10^9
10^8
10^7
10^6
10^5
10^4
10^{11}
10^{10}
10^9
10^8
10^7
10^6
10^5
decade
year
week
day
CPU Time / s
Storage / bytes
Full CCSDTQ time
MC CCSDTQ time
Full CCSDTQ mem
MC CCSDTQ mem
TZ
QZ
5Z
6Z
Basis

Parallel Scaling



The Uniform Electron Gas

$r_s = 1$



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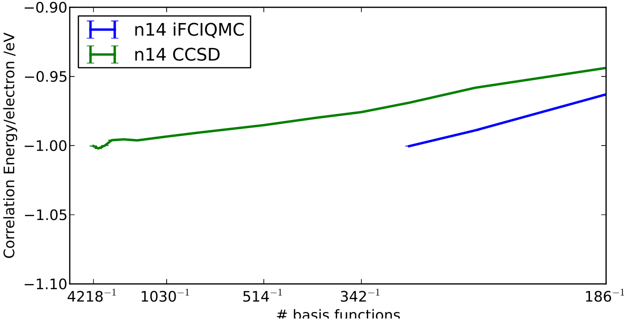

The Uniform Electron Gas

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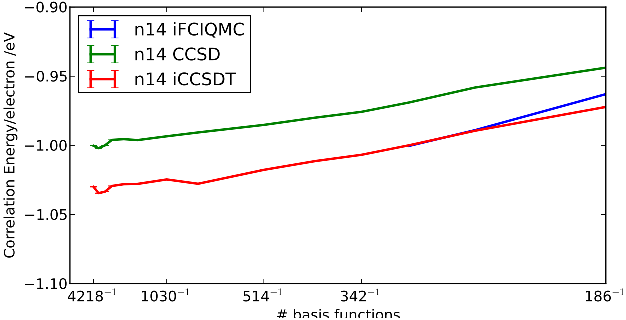

$n = 14$ Cutoff 64Ry, $M = 4218$, triples: 3×10^8, full 10^{34}

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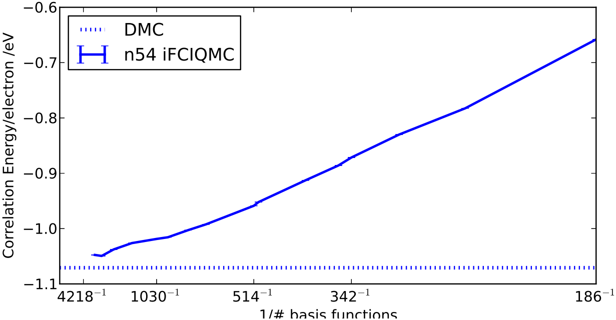

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$n = 54$ Cutoff 64Ry, $M = 4218$, triples: 2×10^{10}, full 10^{117}

J. J. Shepherd, G. H. Booth and A. Alavi *J. Chem. Phys.* **136**, 244101 (2012)

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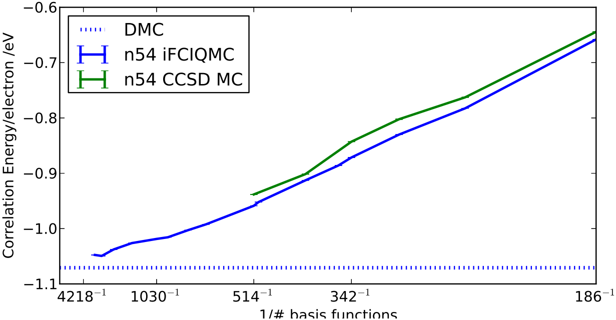

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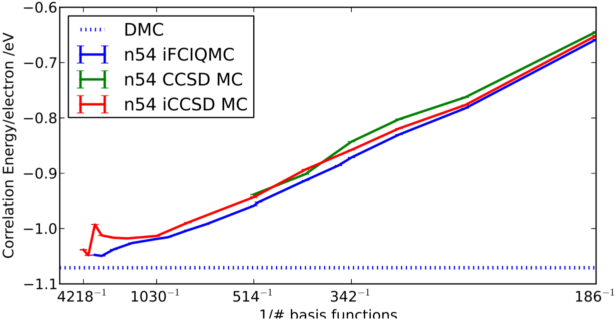

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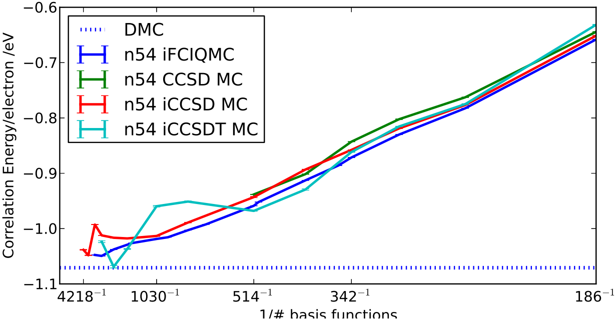

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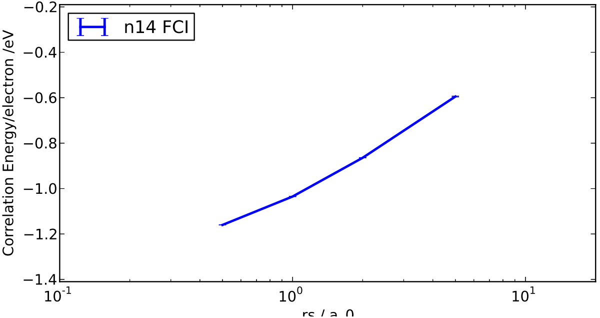

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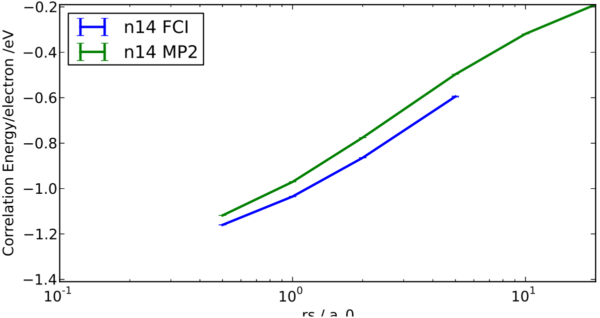

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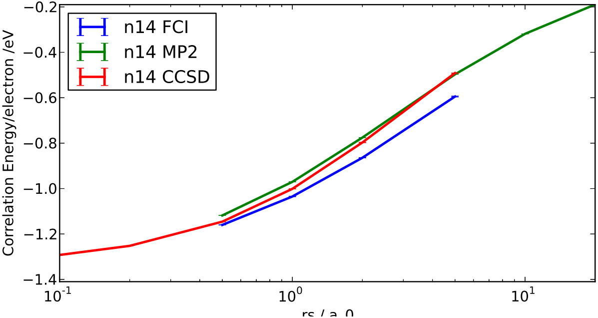

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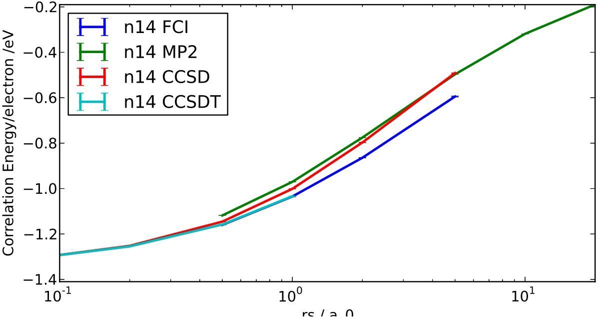

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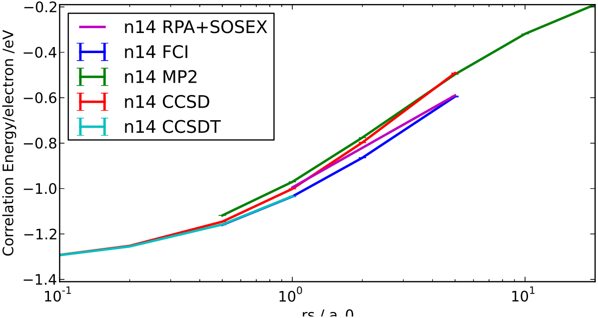

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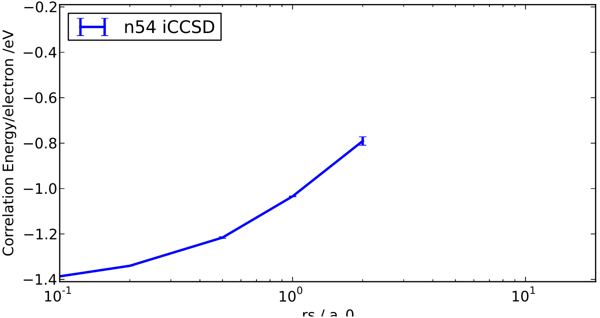

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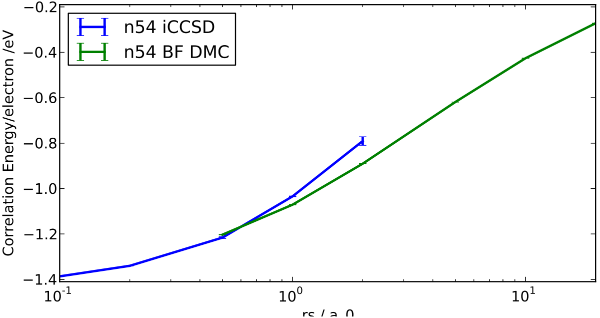

P. López Ríos, A. Ma, N. D. Drummond, M. D. Towler, and R. J. Needs *Phys. Rev. E* **74**, 066701 (2006)

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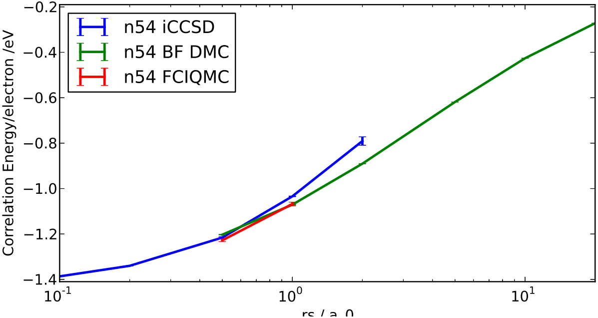

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Conclusions

- Stochastic Coupled Cluster (CCMC) behaves very similar to FCIQMC
- Truncated CC allows polynomial scaling spaces to be used.
- Much simpler to implement than deterministic CC.
- Required number of excips appears to scale with size of space.
- Initiator approximation very successful at reducing critical number of excips.
- Feasible on workstations, and very parallelizable.

Directions

- Benchmarking.
- Solids. Complex excips.
- Large-scale parallelization.
- f12-CCMC.
- CASCC.
- Soon to be available in MOLPRO
- Applications...

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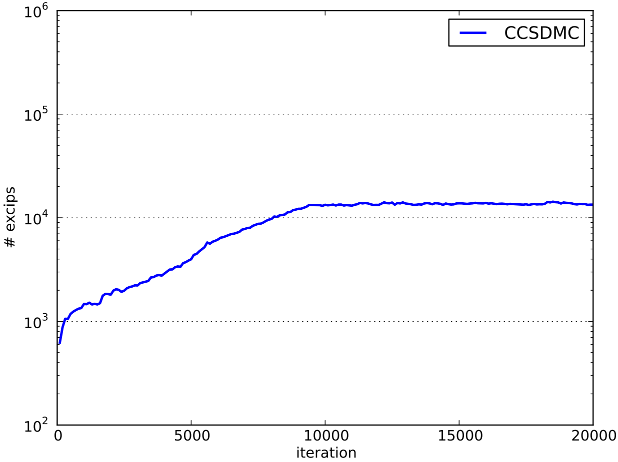
- Churchill College Cambridge
- Imperial College London
- Ali Alavi
- George Booth — FCIQMC
- Deirdre Cleland — Initiators
- James Shepherd — FCIQMC UEG
- James Spencer, Andreas Grüneis — VASP integration

Ne cc-pVQZ growth



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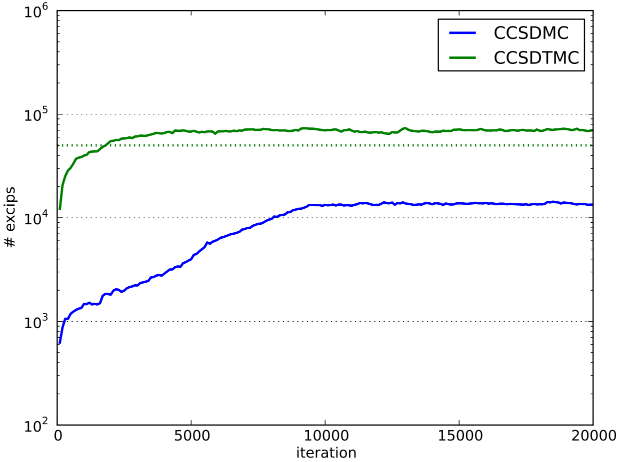

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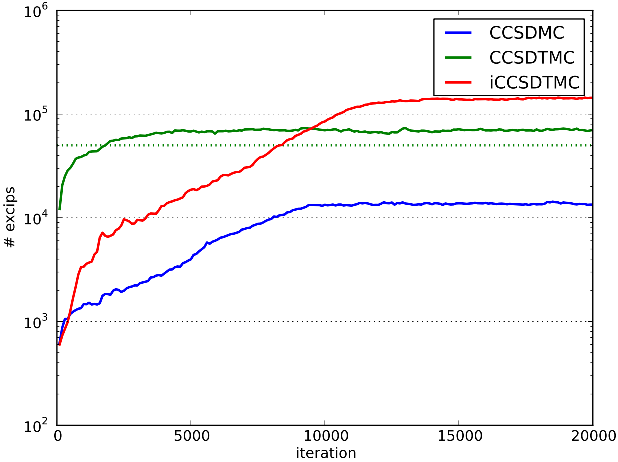

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