Full configuration interaction quantum Monte Carlo and coupled cluster Monte Carlo: a framework for stochastic quantum chemistry

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Slater determinant space

Expand wavefunction in a basis:

$$|\Psi(\tau)\rangle = \sum_{\boldsymbol{i}} f(\boldsymbol{i}) \, |D_{\boldsymbol{i}}\rangle \tag{1}$$

Slater determinants are a good choice for Fermionic systems:

$$\begin{aligned} |D_{\boldsymbol{i}}\rangle &= |D_{i_1,i_2,\ldots,i_N}\rangle \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{i_1}(1) & \phi_{i_1}(2) & \cdots & \phi_{i_1}(N) \\ \phi_{i_2}(1) & \phi_{i_2}(2) & \cdots & \phi_{i_2}(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{i_N}(1) & \phi_{i_N}(2) & \cdots & \phi_{i_N}(N) \end{vmatrix} \end{aligned} \tag{2}$$

(Sadly the Hilbert space grows factorially…)

Hamiltonian projection

For a given wavefunction ansatz, $f(\boldsymbol{i})$ satisfy:

$$(\hat{H} - E)\,|\Psi\rangle = 0 \tag{3}$$

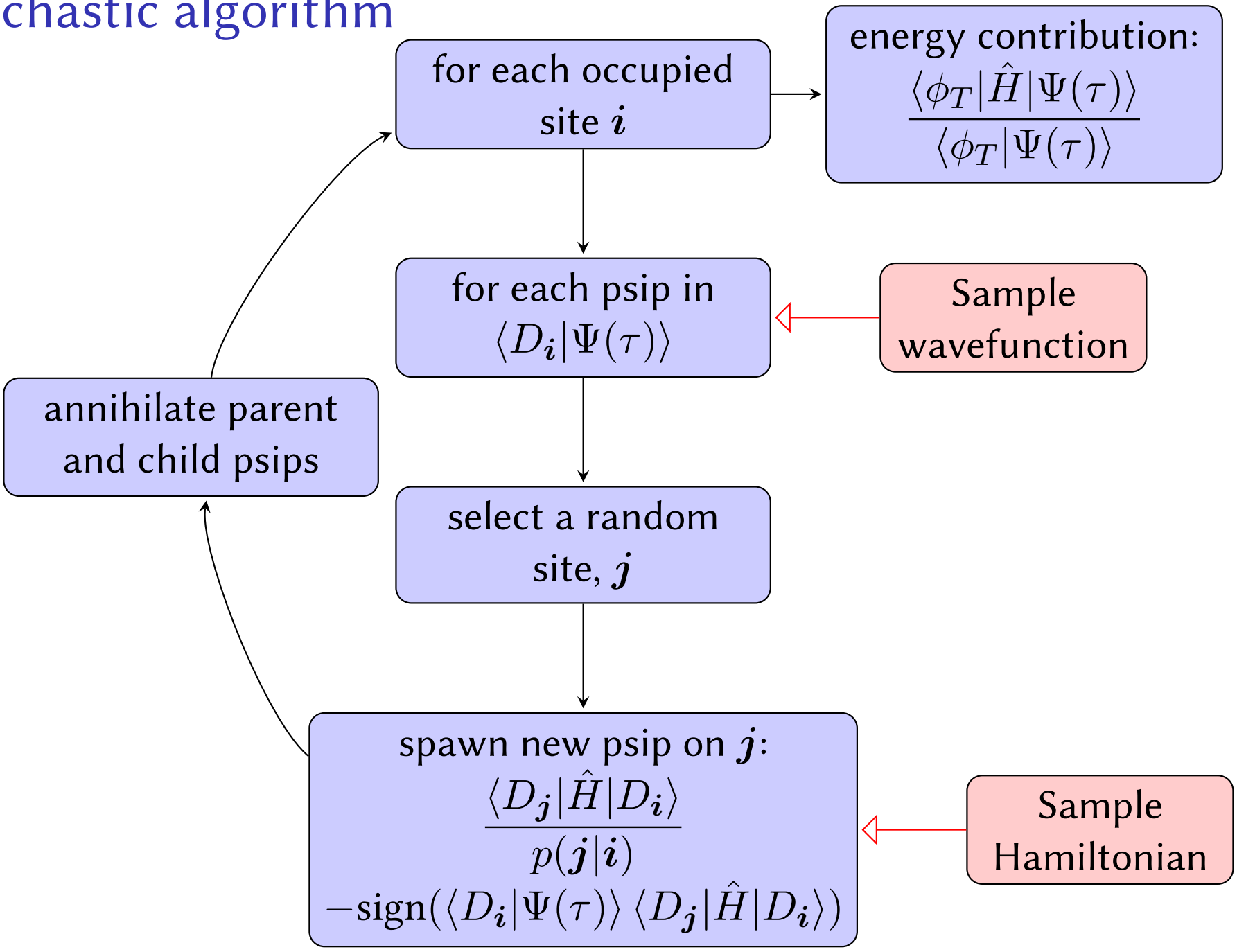
Solve coupled equations:

$$\langle D_{\boldsymbol{i}}|(\hat{H} - E)|\Psi\rangle = 0 \tag{4}$$

or

$$\langle D_{\boldsymbol{i}}|1 - \delta\tau(\hat{H} - E)|\Psi\rangle = \langle D_{\boldsymbol{i}}|\Psi\rangle \tag{5}$$

Stochastic algorithm



FCIQMC

Use linear expansion of determinants (G.H. Booth, A.J.W. Thom and A. Alavi, JCP 131 054106 (2009)):

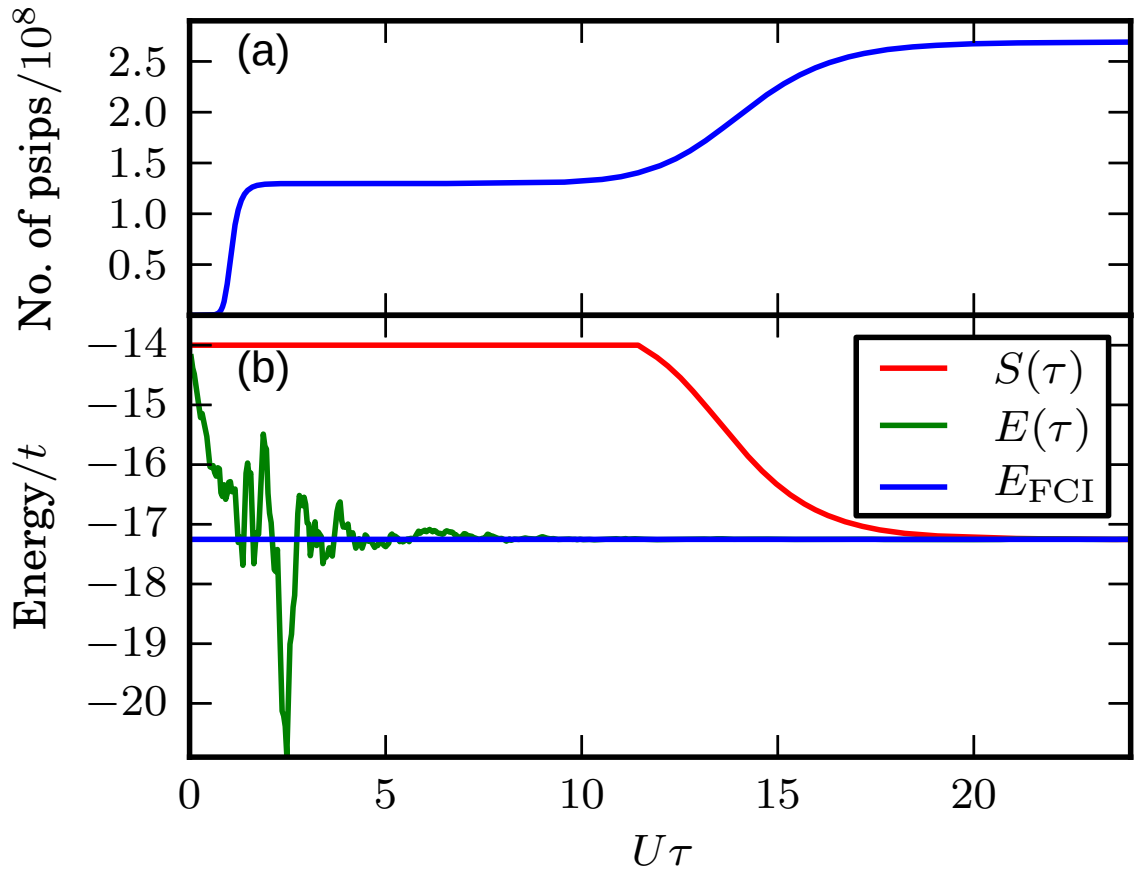
$$|\Psi(\tau)\rangle = \sum_{\boldsymbol{i}} c_{\boldsymbol{i}}(\tau)\,|D_{\boldsymbol{i}}\rangle \tag{6}$$

Particularly efficient for (some) quantum systems.

- Applications to atoms, molecules and solids.
- Allowed access to FCI energies for Hilbert spaces orders of magnitude greater than conventional diagonalisation.
- Recent developments:
  - Semi-stochastic: Petruzielo *et al*, PRL 109, 230201 (2012).
  - Approximations: Roggero *et al*, arXiv:1304.1549.
  - Properties via Hellmann–Feynman: JSS, WMC Foulkes (in preparation).
  - Density Matrix Quantum Monte Carlo: N. Blunt, T. Rogers, JSS, WMC Foulkes, arXiv:1303.5007.

Example: 2D Hubbard model

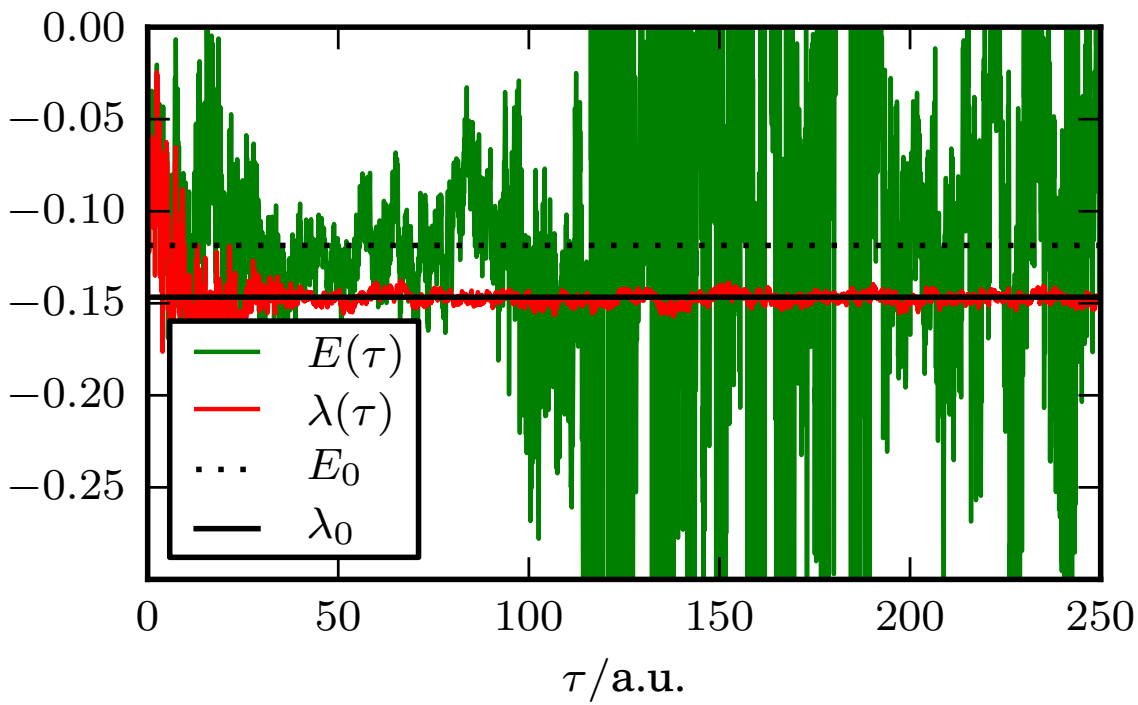
18 sites, half filling, $U/t = 4$.



Negative sign problem

Without annihilation, both positive and negative psips can exist on the same determinant

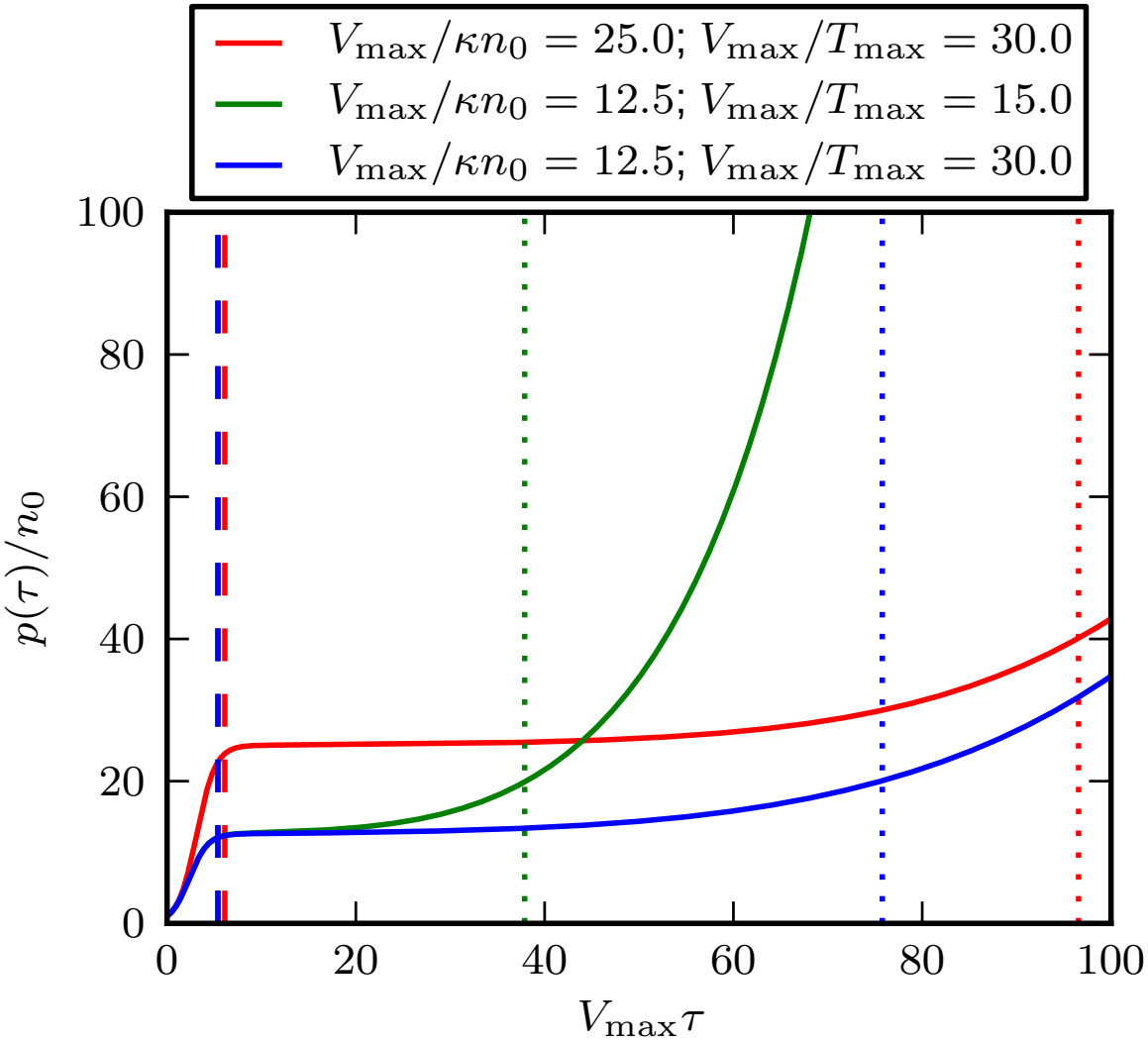
In-phase combination evolves according to $-|\boldsymbol{H}|$. Out-of-phase combination evolves according to $\boldsymbol{H}$.



JSS, N Blunt, WMC Foulkes, JCP 136, 054110 (2012)

Population dynamics: 1−component analogue

Analytic solution. Captures key features of FCIQMC simulations:



But...

Orders of magnitude improvement equates to only a handful more electrons.

Coupled Cluster Monte Carlo

Sample coupled cluster wavefunction instead of CI wavefunction:

$$|\Psi(\tau)\rangle = e^{\hat{T}} |D_{\mathrm{HF}}\rangle \tag{7}$$

$$\hat{T} = \sum_{ia} t_i^a \hat{a}_i^a + \sum_{ijab} t_{ij}^{ab} \hat{a}_{ij}^{ab} + \cdots \tag{8}$$

Highly parallel.

Keeps advantanges of traditional CC: fast convergence with truncation and size consistency.

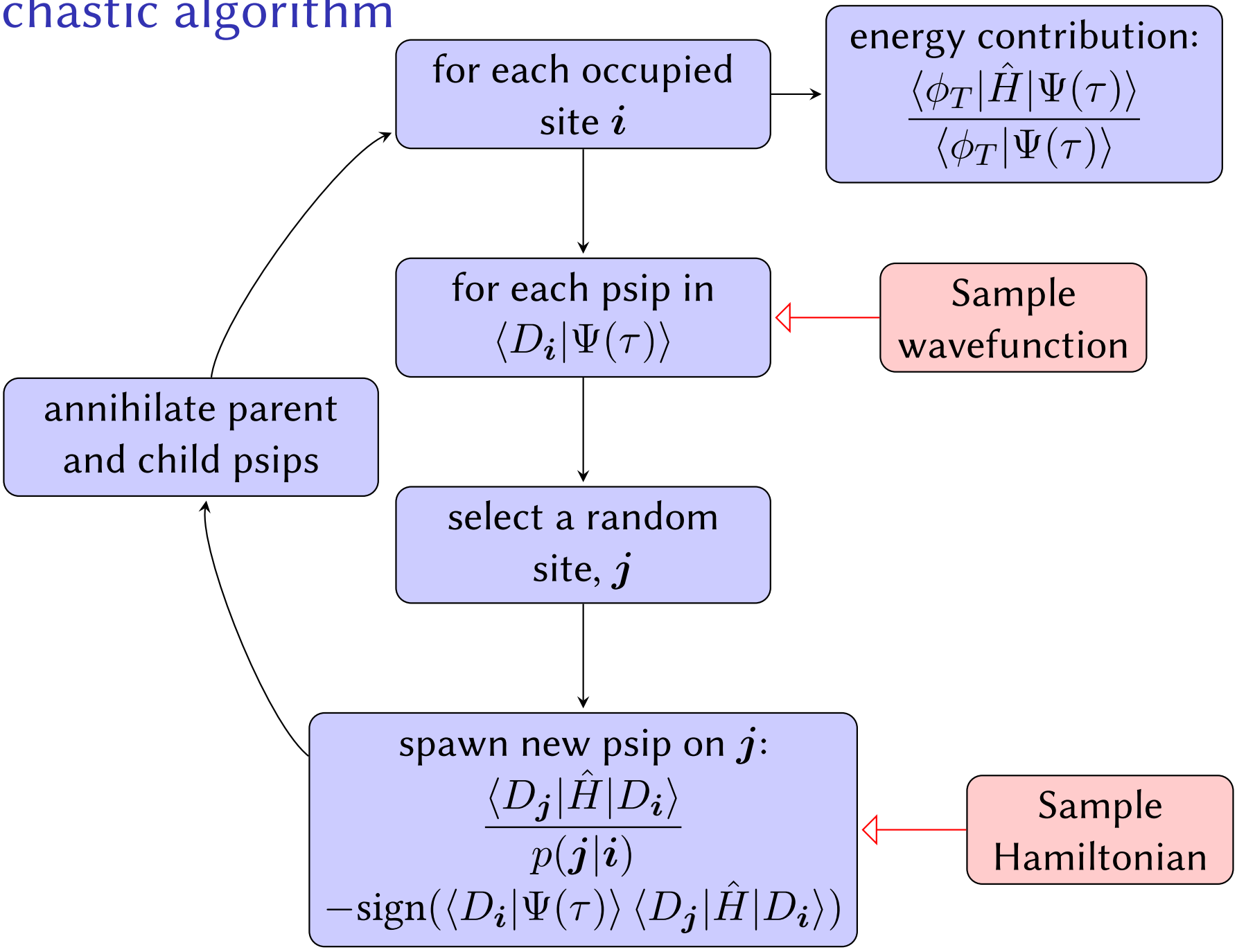
Alex Thom, PRL 105, 263004, (2010).

Stochastic quantum chemistry

Many other quantum chemistry methods exist. Specific methods can be highly accurate for specific systems.

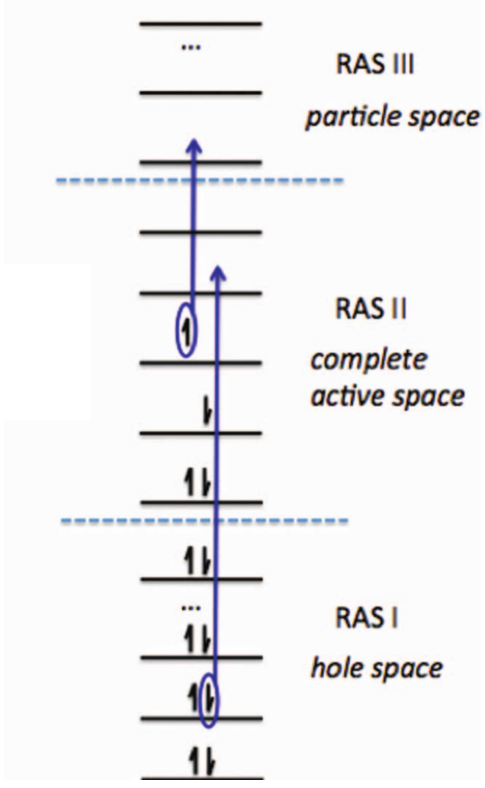
Can we exploit the infrastructure required for FCIQMC and CCMC to sample these theories as well?

Stochastic algorithm



Restricted active space configuration interaction

Restrict space in which excitations are allowed to regions of (chemical) interest.

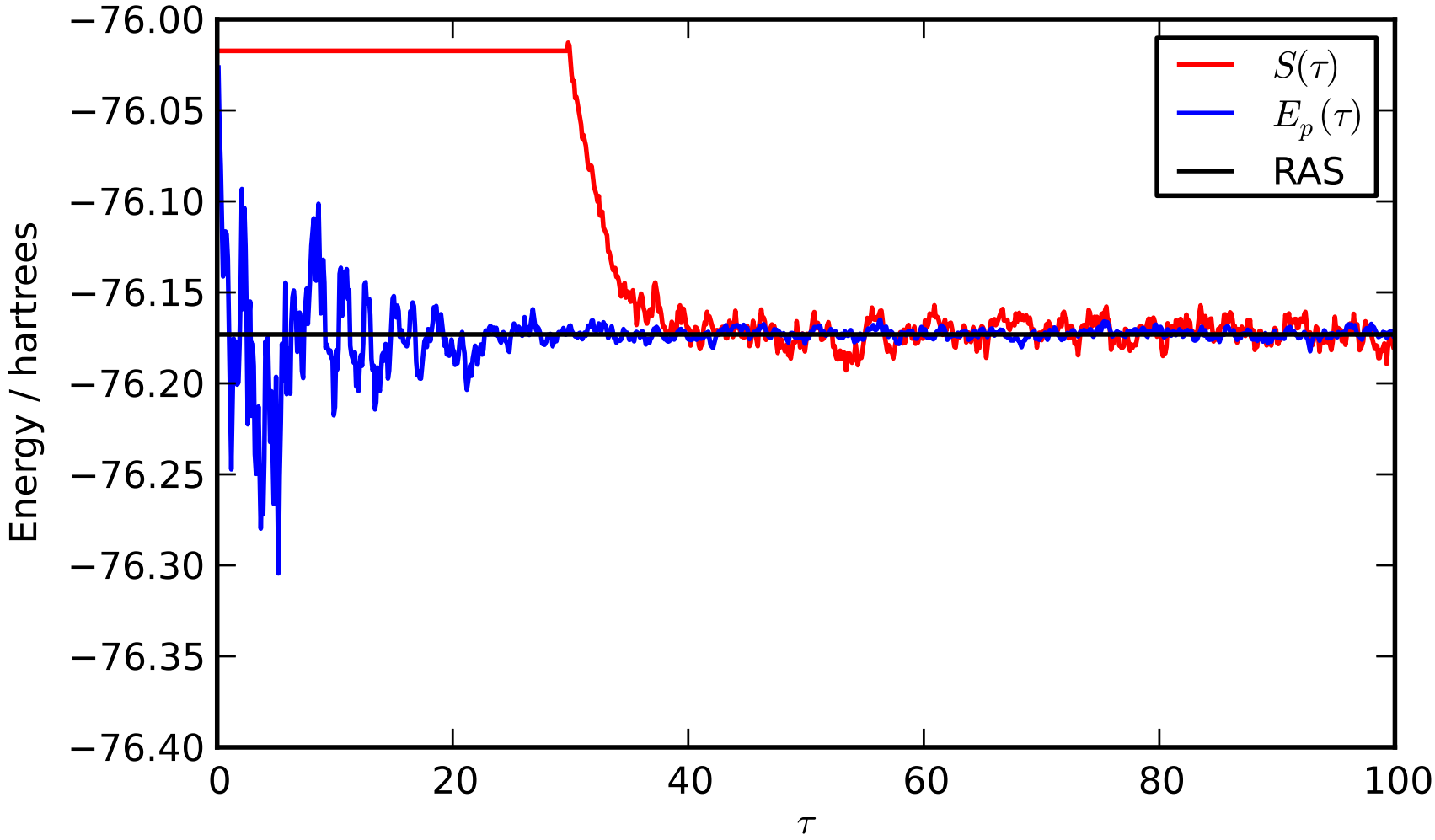


Reduces the size of the Hilbert space without (hopefully) removing the important physics of the system of interest.

Zimmerman *et al*, JCP 137 164110 (2012)

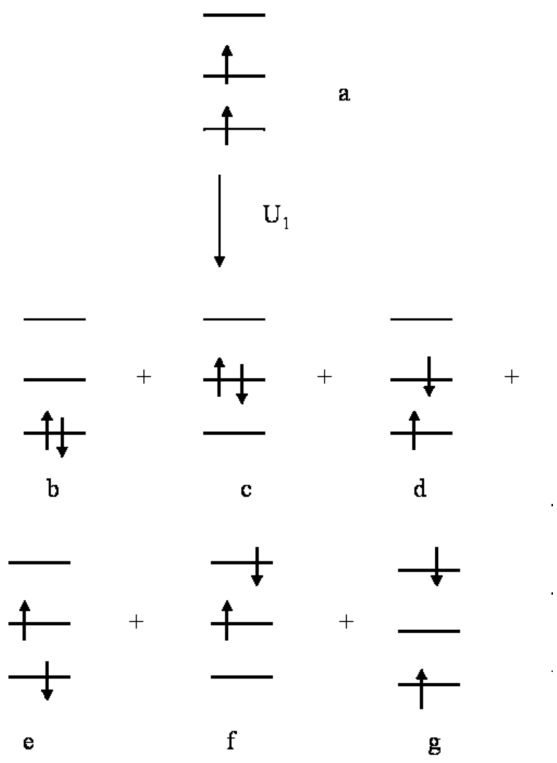
RAS CI

H_2O; 6-31G** basis set; CISDTQ; RAS=(4,3,8); RAS III ≤ 2.



Spin-flip configuration interaction

Truncate the configuration interaction expansion based upon a high spin reference determinant:



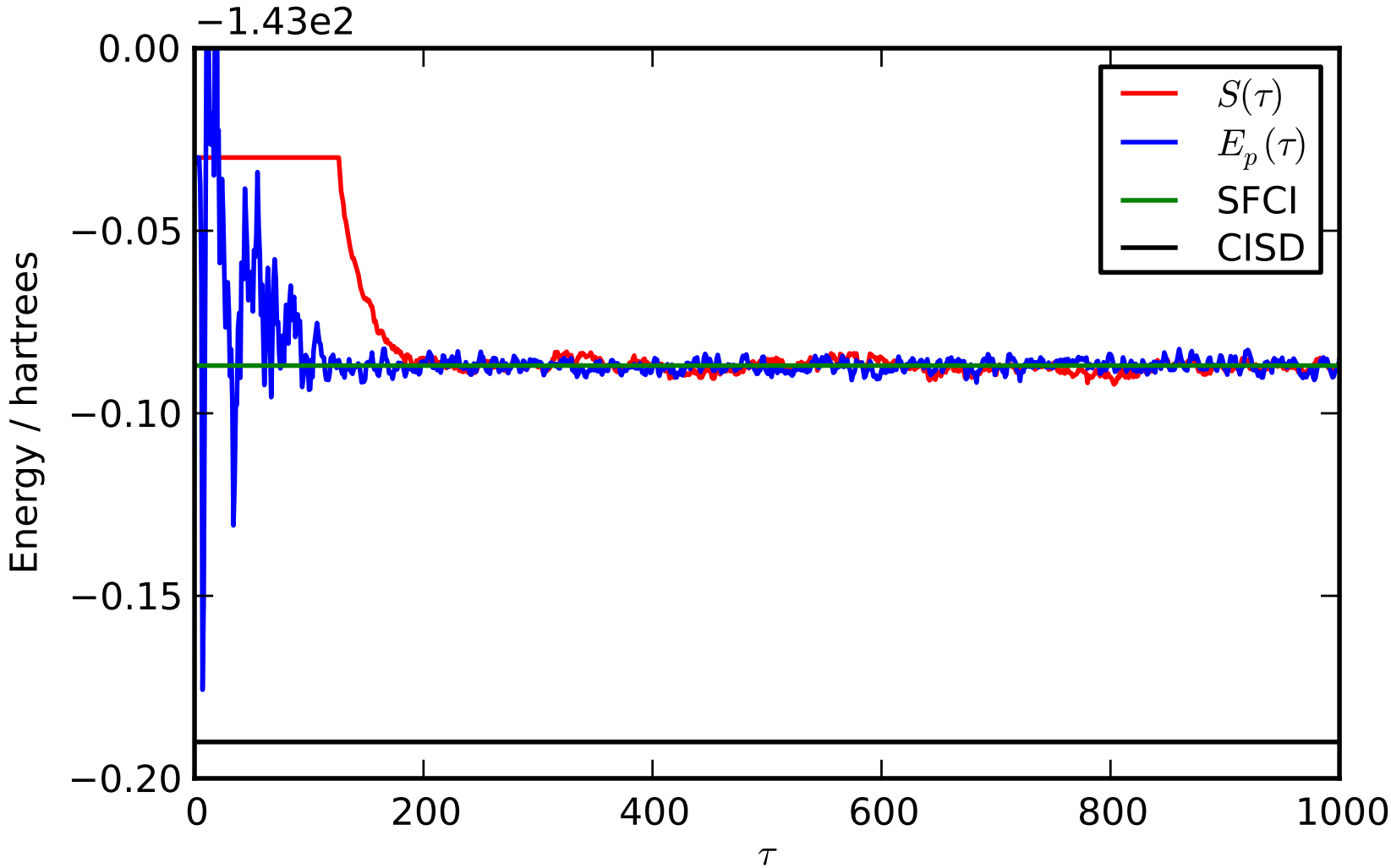
Useful for studying radicals, high-spin complexes…

"Size consistent" if unpaired electrons in reference are localized.

Anna Krylov, CPL 338 375 (2001); CPL 350 522 (2001)

SF CI

Be–Ne; 100A; 6-31G basis set; $M_s = 1$ spin-flip reference.



Work in progress: random phase approximation

Direct RPA is exactly equivalent to direct ring coupled cluster doubles[1].

Ansatz: $|\Psi\rangle = e^{\hat{T}_2} |D_{\mathrm{HF}}\rangle$.

Include only ring diagrams in action of Hamiltonian—must modify the generation of random excitations to exclude ladder and mosiac diagrams.

[1] Scuseria, Henderson, Sorenson, JCP 129 231101 (2008)

Conclusions

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But much, much more:

- General framework for stochastic quantum chemistry methods.
- Simple to develop and test new theories.
- "Batteries included":
  - parallelization
  - lower memory demands
  - faster
  - initiator approximation
  - ...

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PSI4 (http://www.psicode.org).