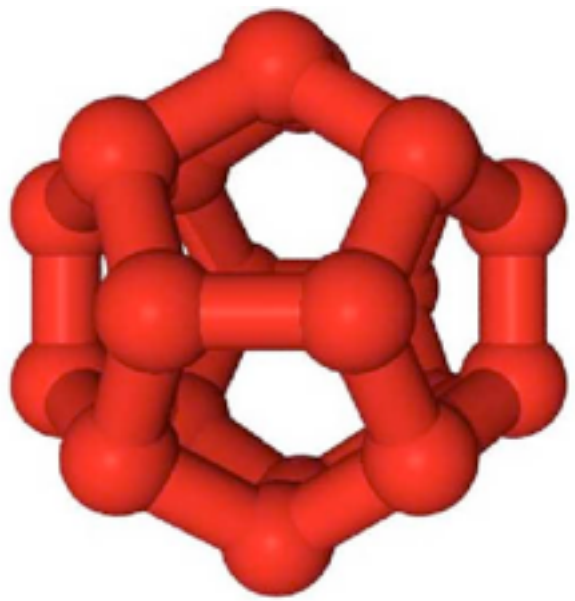
Systematic reduction of sign errors in many-body calculations of atoms and molecules



C_{20}^{2+} / 78 electrons

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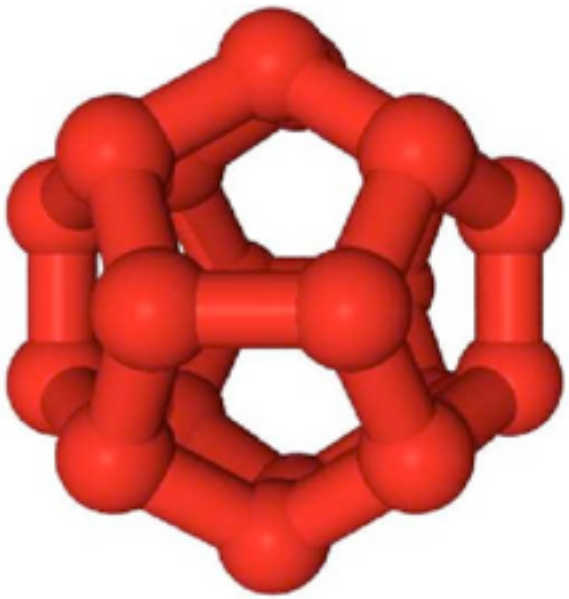
Codes: Qwalk, CASINO

Support: DOE Computers: NERSC, NCCS

OAK RIDGE National Laboratory

“Self-healing DMC for real systems”



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Self-healing Diffusion Monte Carlo

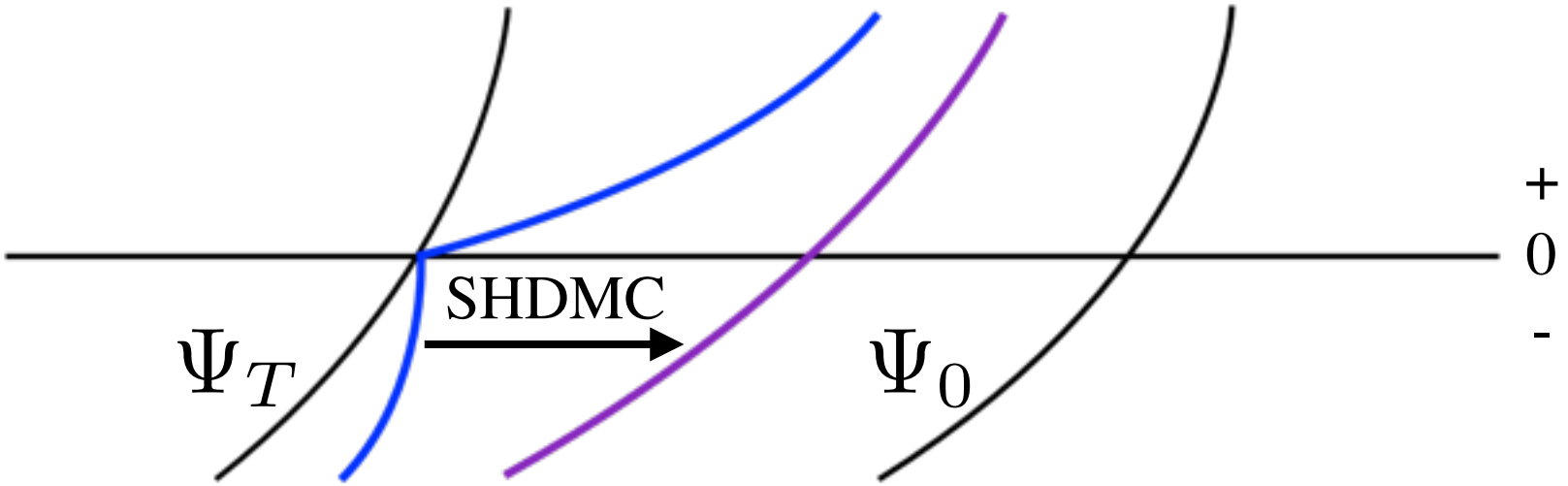
arXiv:0912.3826

1. Achieves chemical accuracy for the ground state in small systems where benchmarks are possible

2. Can start from very poor wavefunctions, potentially avoiding the need for quantum chemical calculations

3. Successfully reduces the fixed-node error in large systems

SHDMC smooths the discontinuities in the fixed node wavefunction



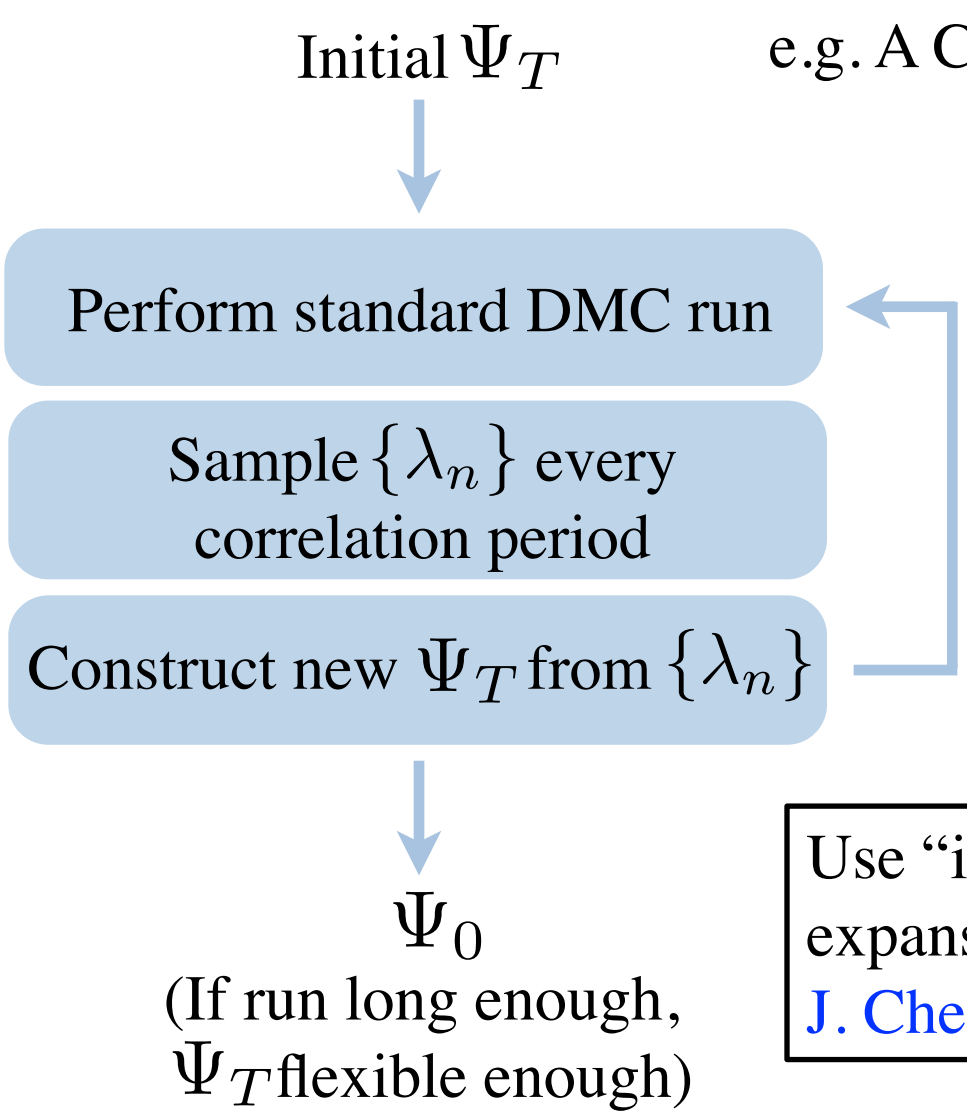
PRB 79 195117 (2009)

- **Wavefunction is smoothed towards the exact ground state**
- **We sample a normalized weighted ratio**

$$\lambda_n(\tau'+\tau) = \lim_{N_c\to\infty} \frac{1}{\mathcal{N}} \sum_i^{N_c} W_i^j(k) e^{-2J(\mathbf{R}_i^j)} \frac{\Phi_n^*(\mathbf{R}_i^j)}{\Phi_T^*(\mathbf{R}_i^j,\tau')}$$

- **Excited states: Reboredo PRB 80 125110 (2009)**

SHDMC procedure



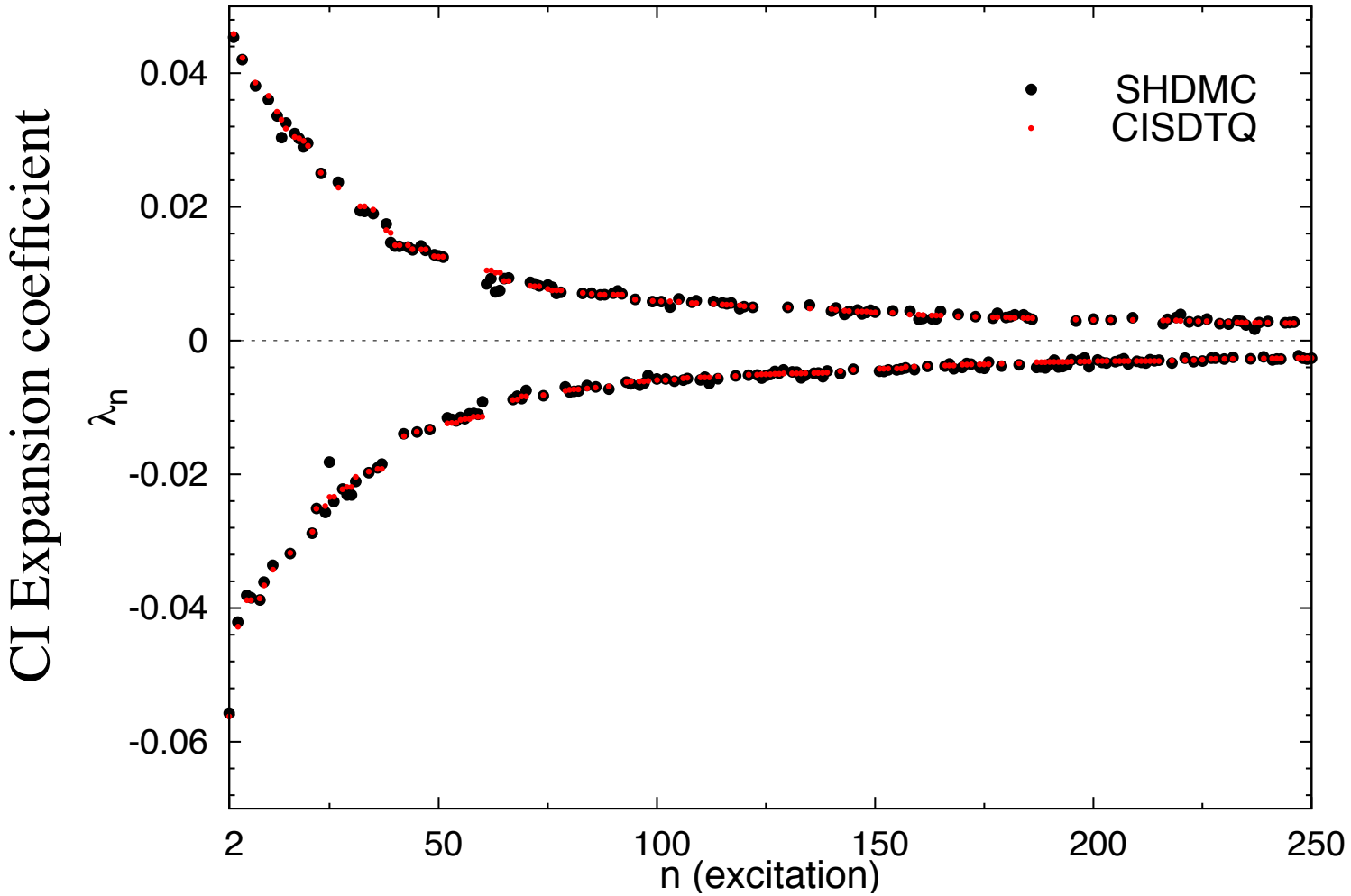
Use "iterative updates" for large CI expansions/systems Nukala & Kent J. Chem. Phys. 130 204105 (2009)

We present 3 SHDMC examples:

1. **Oxygen atom**
   - **No jastrow, to compare with CI**
2. **Nitrogen dimer**
   - **To demonstrate chemical accuracy**
3. **Carbon 20 fullerene**
   - **To demonstrate robustness, scaling, applicability**

Oxygen atom

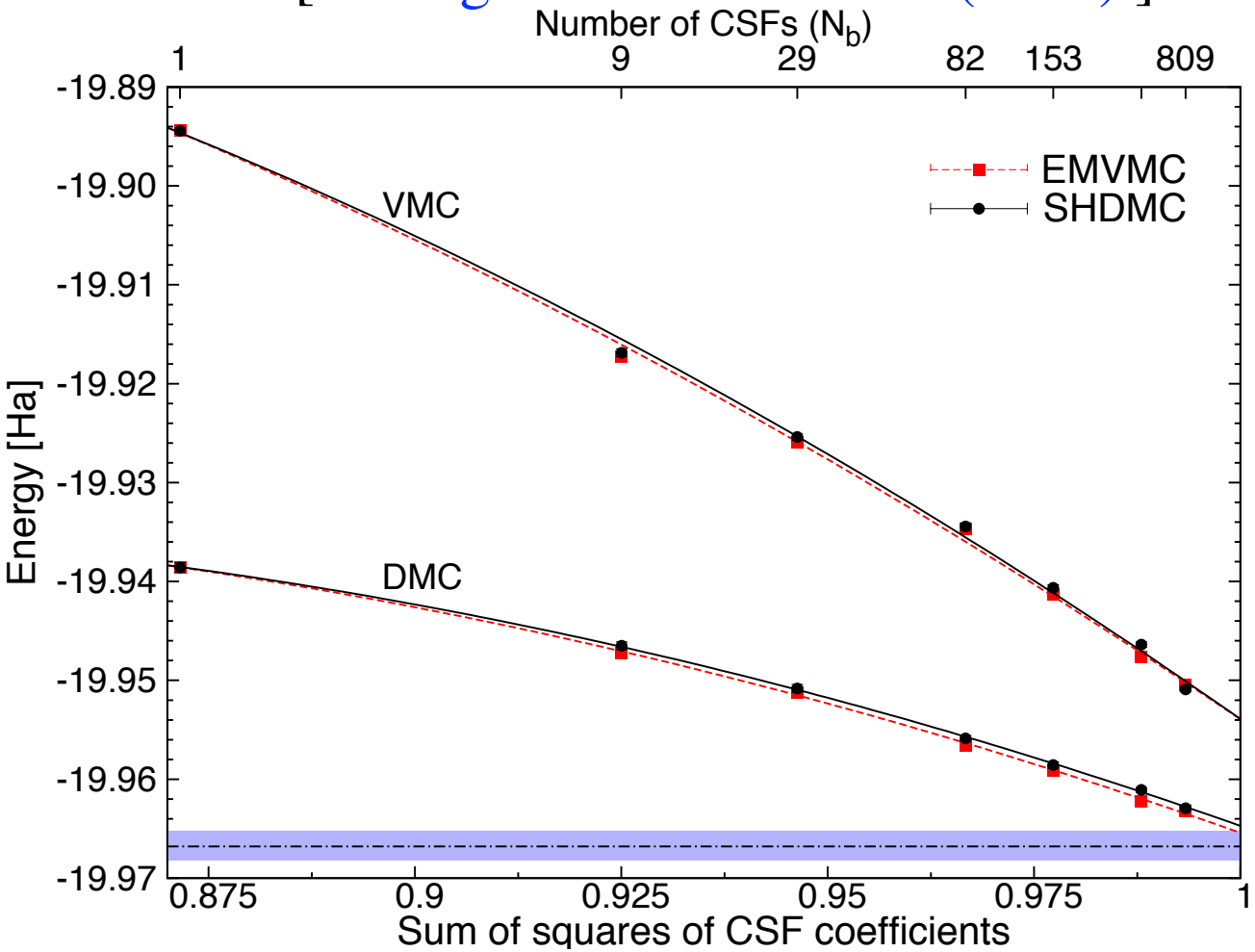
SHDMC optimized multideterminant wavefunctions (no jastrow) accurately reproduce quantum chemical results.



6 electrons, pseudopotential, multi-determinants

Nitrogen dimer

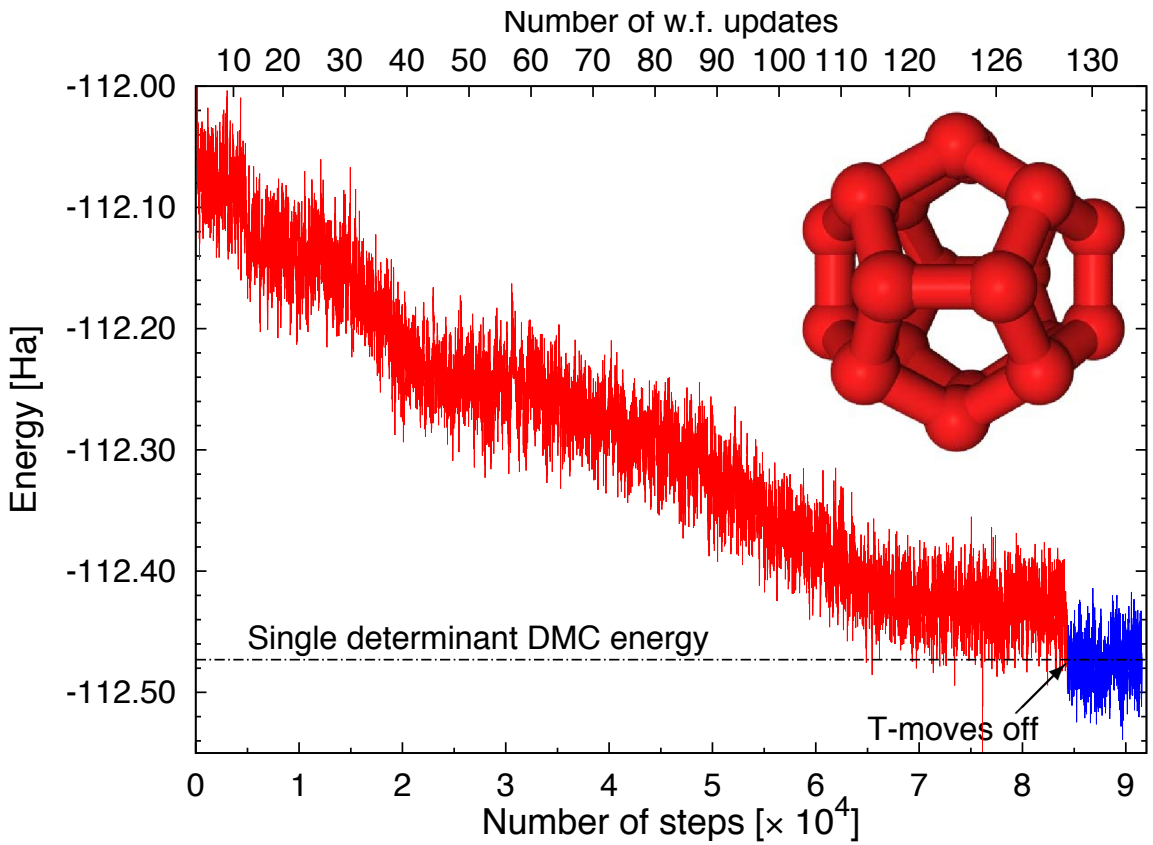
Near chemical accuracy achieved by both SHDMC and Energy Minimization VMC [Umrigar PRL 98 110201 (2007)]



10 electrons, pseudopotential, multi-determinants+jastrow

$C20^{2+}$

- 5.53eV DFT gap indicates single determinant dominant
- 694 determinants
- We improve single determinant energy by ~0.4 eV
- Converges from either random or mean field start



Contrast with Energy Minimization VMC

- We like both EMVMC and SHDMC 
- EMVMC optimizes the energy of a trial wavefunction within VMC and concomitantly reduces the nodal error.
- SHDMC is a direct optimization of the nodes within DMC
- EMVMC requires diagonalization of a noisy matrix, SHDMC does not
- SHDMC must pay the DMC time step penalty
- SHDMC currently slower than EMVMC for small systems. Competitive by ~ C20 / 80 electrons
- We expect both methods to be improved in future
  - e.g. Simple iterative optimization currently in SHDMC does not exploit optimization history. Can beat current algorithm by eye!

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