Optimization of Jastrow factors for Similarity Transformed quantum chemical methods

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Full CI quantum Monte Carlo

FCIQMC is a CI solver based on imaginary-time projection

FCIQMC master equation

$$\frac{\partial |\Psi(\tau)\rangle}{\partial \tau} = -\hat{H}|\Psi(\tau)\rangle \qquad |\Psi_{\mathrm{CI}}\rangle = \sum_I c_I |D_I\rangle$$

$$-\frac{\partial c_I(\tau)}{\partial \tau} = \left(\langle D_I|\hat{H}|D_I\rangle - S\right) c_I(\tau) + \sum_{J\neq I} \langle D_I|\hat{H}|D_J\rangle\, c_J(\tau)$$

FCIQMC inherits CI's difficulty in describing dynamic correlation

Similarity transformation

Can a Jastrow factor $e^J = e^{\sum_{i<j} u_{ij}}$ be used in FCIQMC?

CI-Jastrow wave function

$$|\Psi\rangle = e^{\hat{J}} \sum_I c_I |D_I\rangle$$

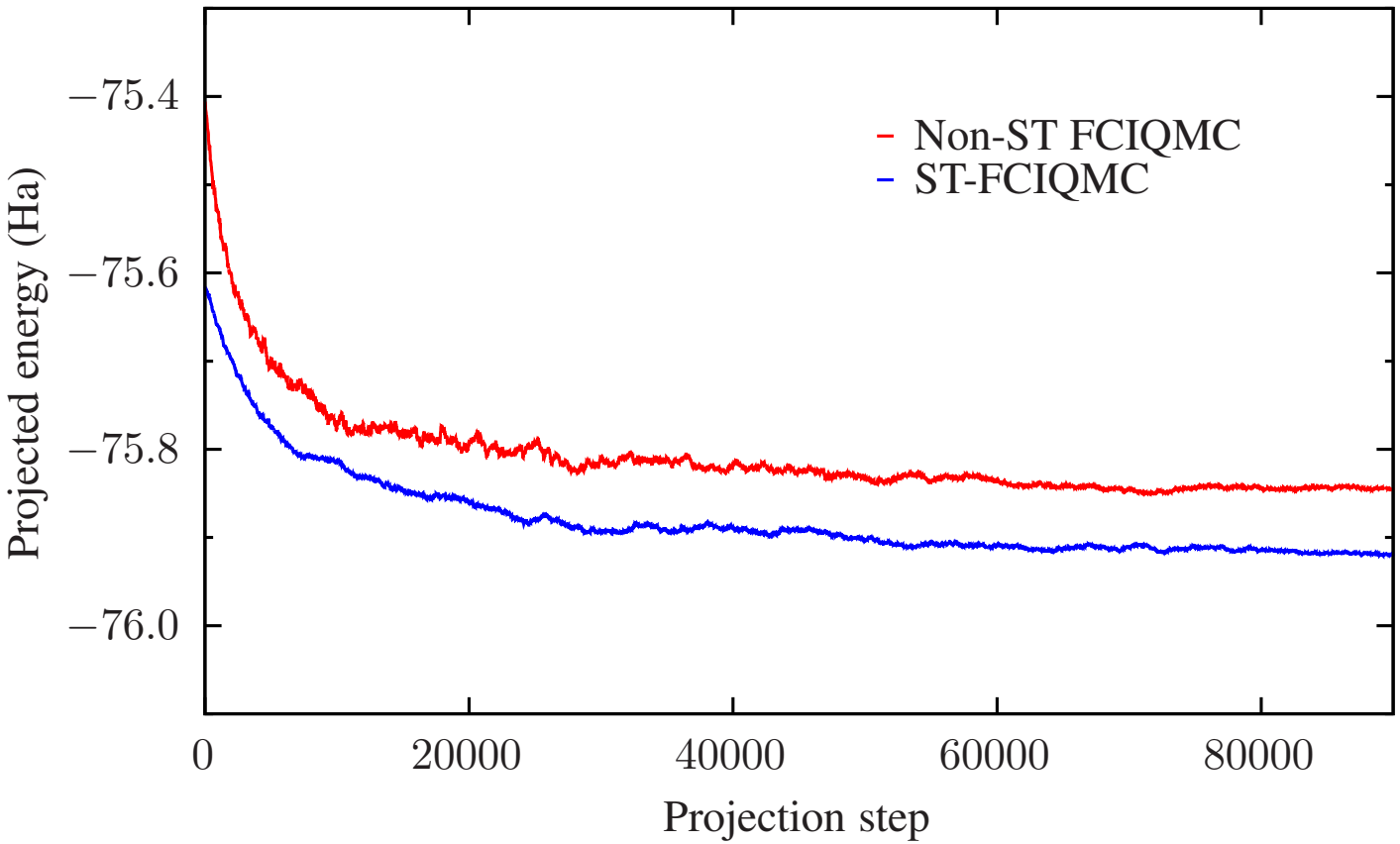
Yes, absorbed into the Hamiltonian [1]

Similarity transformation

$$\tilde{H} = e^{-\hat{J}} \hat{H} e^{\hat{J}} = \hat{H} + [\hat{H}, \hat{J}] + \frac{1}{2}[[\hat{H}, \hat{J}], \hat{J}]$$

[1] A.J. Cohen, H. Luo, K. Guther, W. Dobrautz, D.P. Tew, A. Alavi, J. Chem. Phys. **151**, 061101 (2019)

ST-FCIQMC reference energy



FCIQMC starts at $E_{\mathrm{HF}} = \langle D_0 | \hat{H} | D_0 \rangle$

ST-FCIQMC starts at $E_{\mathrm{ref}} = \langle D_0 | e^{-\hat{J}} \hat{H} e^{\hat{J}} | D_0 \rangle$

(VMC estimate can be used to check for correctness)

Similarity transformed Hamiltonian

$\tilde{H}$ is non-Hermitian, connects triple excitations:

Schrödinger Hamiltonian

$$\hat{H} = \sum_{pq\sigma} h_q^p a_{p\sigma}^\dagger a_{p\sigma} + \frac{1}{2} \sum_{pqrs} V_{rs}^{pq} \sum_{\sigma\tau} a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{s\tau} a_{r\sigma}$$

Similarity-transformed Hamiltonian

$$\tilde{H} = \sum_{pq\sigma} h_q^p a_{p\sigma}^\dagger a_{p\sigma} + \frac{1}{2} \sum_{pqrs} (V_{rs}^{pq} - K_{rs}^{pq}) \sum_{\sigma\tau} a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{s\tau} a_{r\sigma}$$
$$- \frac{1}{6} \sum_{pqrstu} L_{stu}^{pqr} \sum_{\sigma\tau\lambda} a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{r\lambda}^\dagger a_{u\lambda} a_{t\tau} a_{s\sigma}$$

Matrix elements

Matrix elements involving u to be obtained by grid integration:

Matrix elements

$$
\begin{aligned}
h_q^p &= \langle \phi_p | h | \phi_q \rangle \\
V_{rs}^{pq} &= \langle \phi_p \phi_q | r_{12}^{-1} | \phi_r \phi_s \rangle \\
K_{rs}^{pq} &= \langle \phi_p \phi_q | \frac{1}{2} \left(\nabla_1^2 u_{12} + \nabla_2^2 u_{12} + (\nabla_1 u_{12})^2 + (\nabla_2 u_{12})^2 \right) \\
&\quad + (\nabla_1 u_{12} \cdot \nabla_1) + (\nabla_2 u_{12} \cdot \nabla_2) | \phi_r \phi_s \rangle \\
L_{stu}^{pqr} &= \langle \phi_p \phi_q \phi_r | \nabla_1 u_{12} \cdot \nabla_1 u_{13} + \nabla_2 u_{21} \cdot \nabla_2 u_{23} \\
&\quad + \nabla_3 u_{31} \cdot \nabla_3 u_{32} | \phi_s \phi_t \phi_u \rangle
\end{aligned}
$$

Storage for L_{stu}^{pqr}: $\sim$ 170-orbital basis needs 2TiB memory

Embarrassing parallelizability of L_{stu}^{pqr} evaluation

TCHInt library

- The TCHInt library [2] precomputes K_{rs}^{pq} and provides precomputed/on-the-fly/hybrid access to L_{stu}^{pqr}

```
matel = tc_matel(det, excit)
```

- TCHInt uses the Jastrow evaluator from **CASINO** and orbital evaluator from **PySCF**

- TCHInt currently works with **NECI** (as library) and **MolPRO** (via FCIDUMP); trivial to use from other ST-capable packages; TREXIO supported

[2] K. Guther, A.J. Cohen, P. López Ríos, K. Ghanem, *to be released*

Choice of VMC optimization method

Variational Monte Carlo is a real-space method:

- Slater-Jastrow trial wave function:
  $\Psi_{\mathrm{SJ}}(\mathbf{R}) = e^{J(\mathbf{R})} D_0(\mathbf{R})$
  using J of Drummond-Towler-Needs form [3,4]
- VMC generates $\{\mathbf{R}\}$ distributed according to Ψ^2

VMC-based optimization methods:

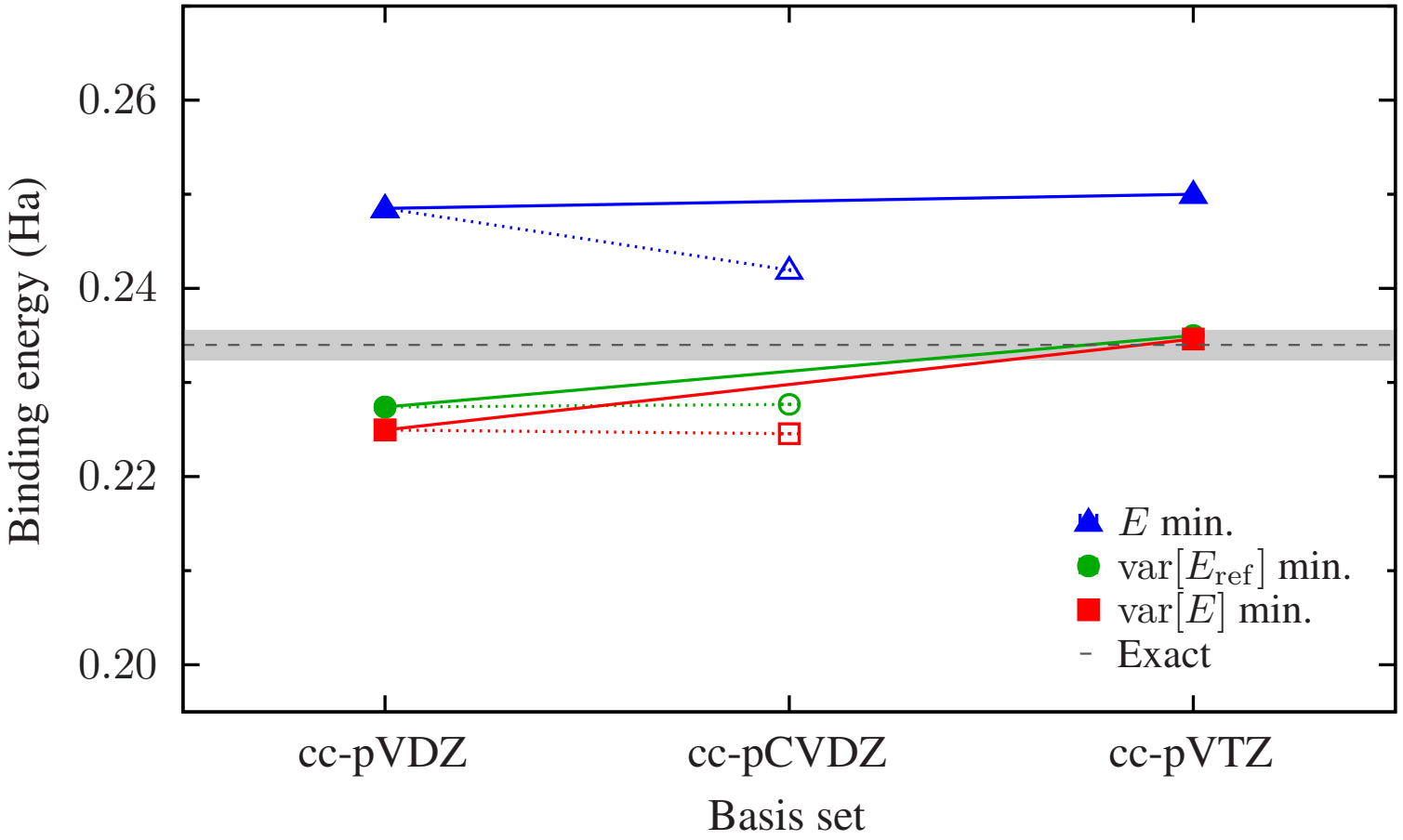
- Minimize the energy
- Minimize $\mathrm{var}[E]$
- Minimize $\mathrm{var}[E_{\mathrm{SJ}}]_{D_0^2} \equiv \mathrm{var}[E_{\mathrm{ref}}]$

[3] N. D. Drummond, M. D. Towler, and R. J. Needs, Phys. Rev. B **70**, 235119 (2004)

[4] P. López Ríos, P. Seth, N. D. Drummond, and R. J. Needs, Phys. Rev. E **86**, 036703 (2012)

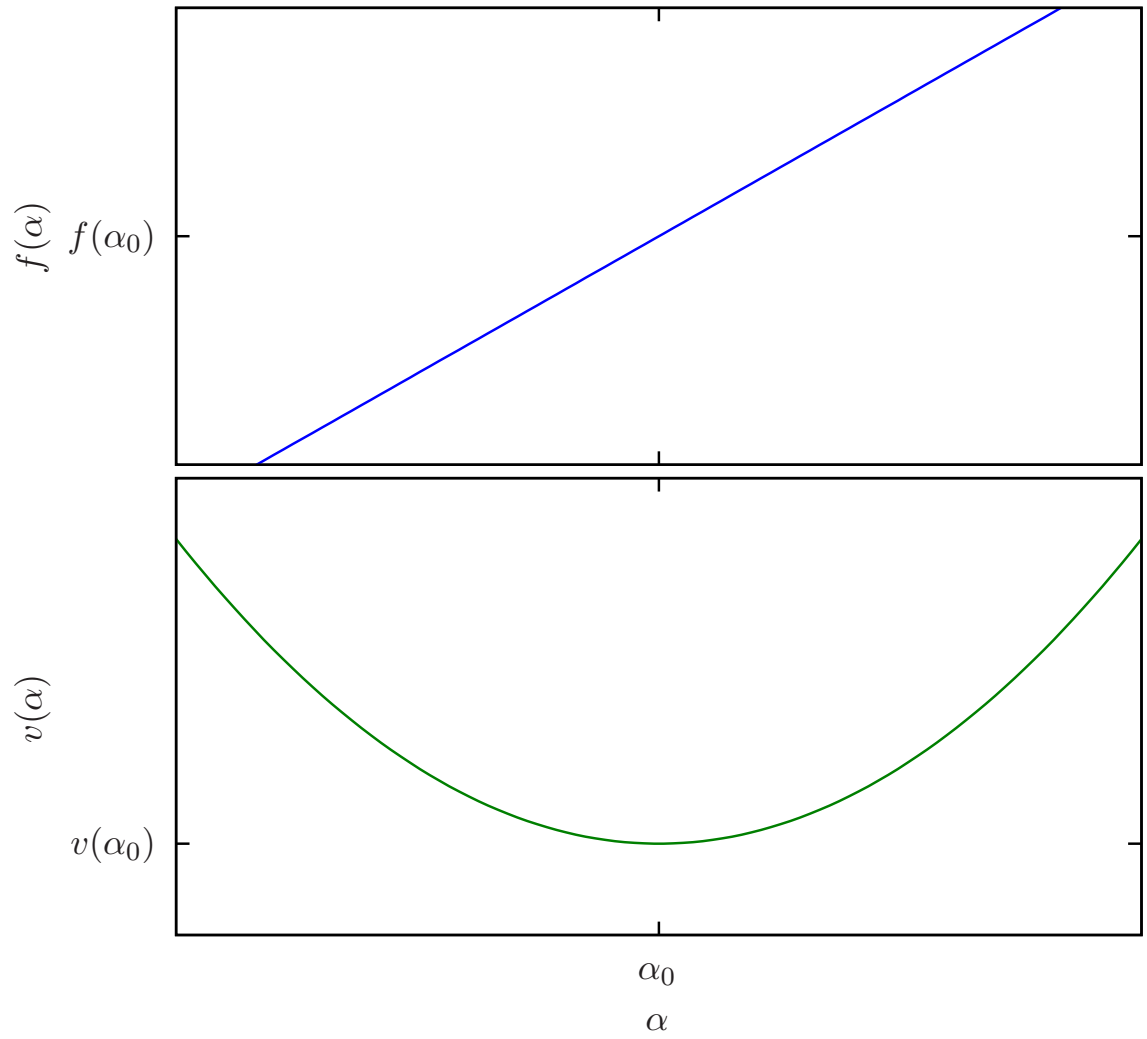
Choice of VMC optimization method

Binding energy of C_2 demonstrates need for variance minimization:



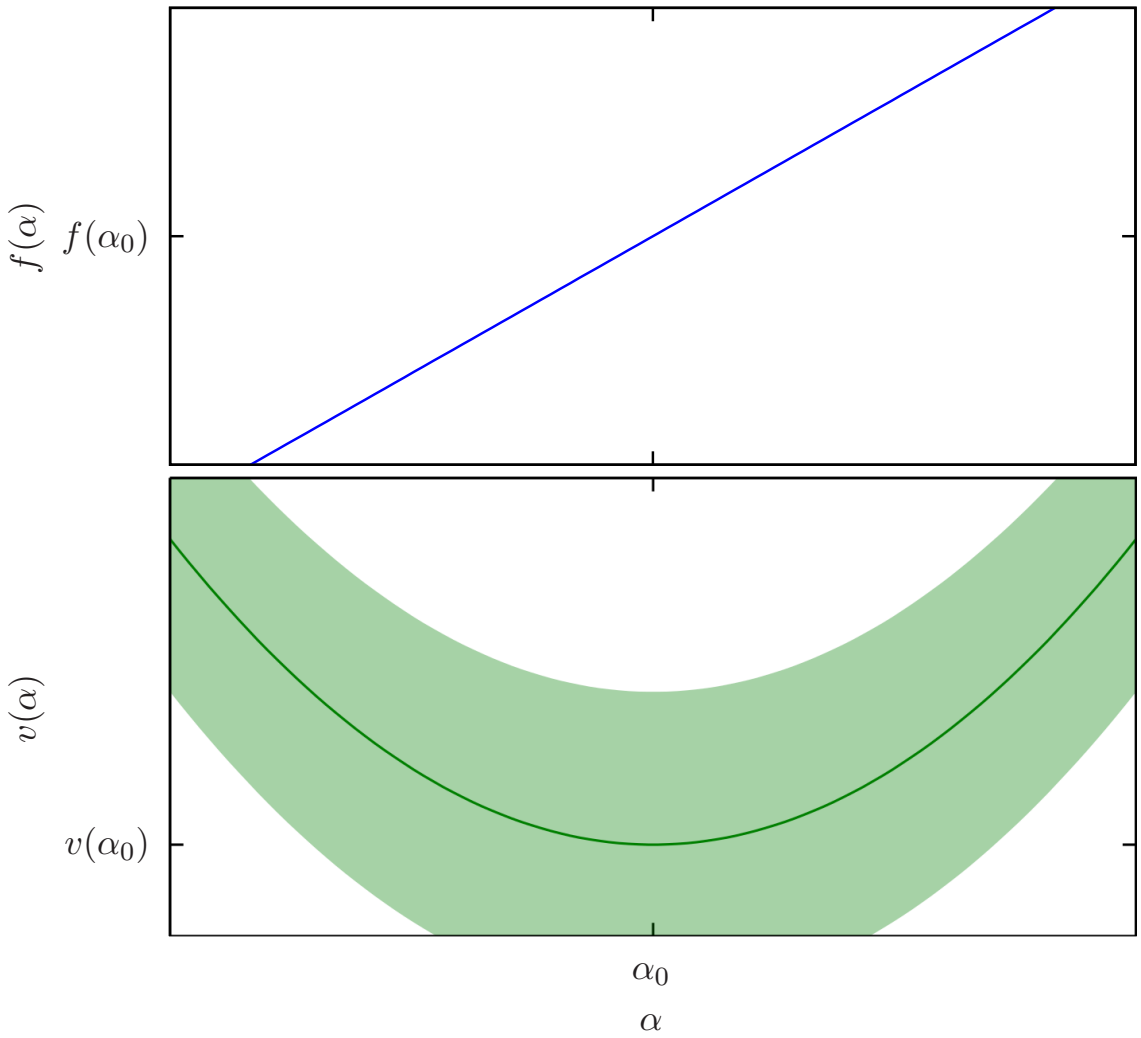
Handling optimization noise

Wave function parameters α optimized by minimizing $v(\alpha)$:



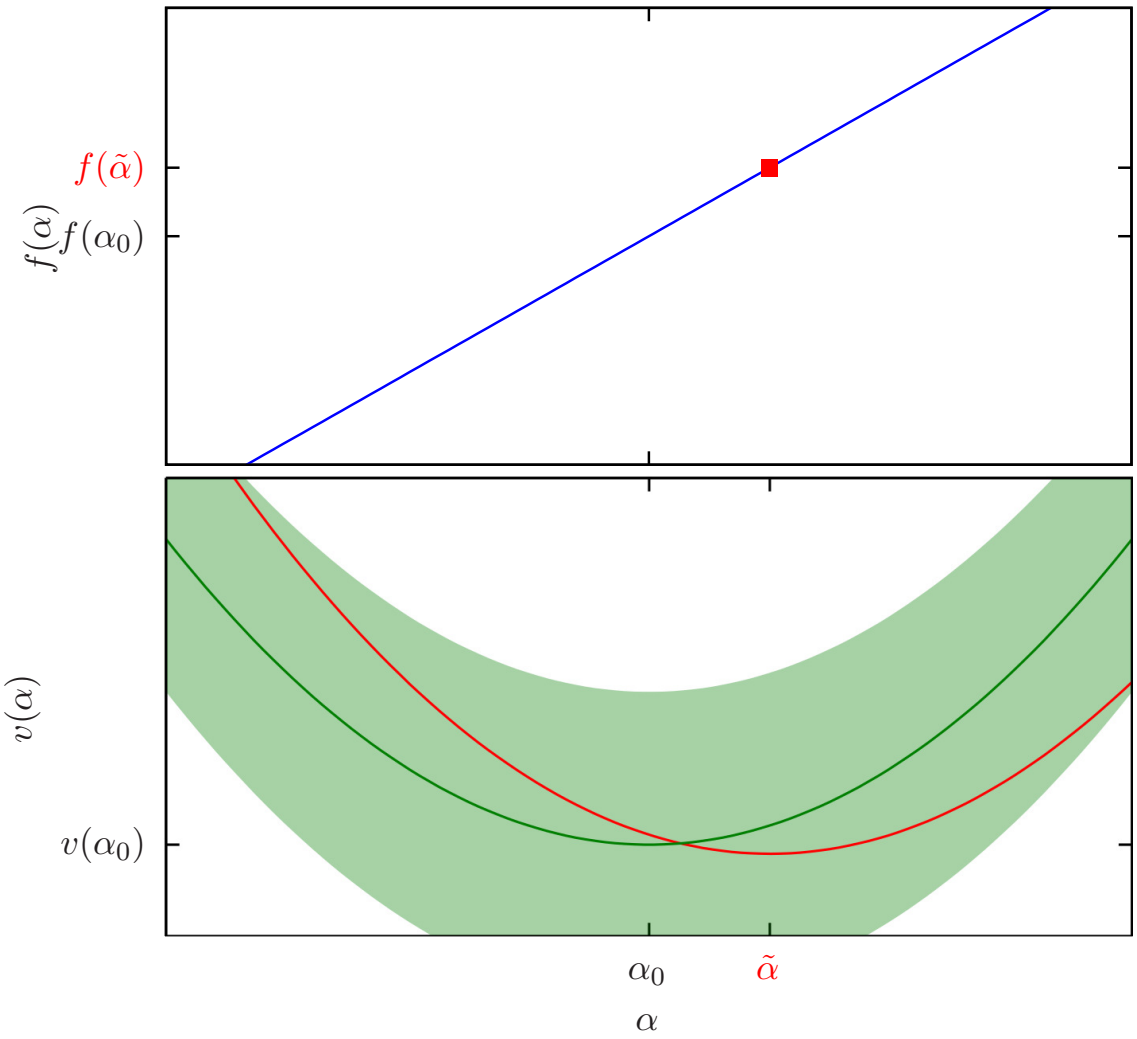
Handling optimization noise

Finite random sampling adds noise:



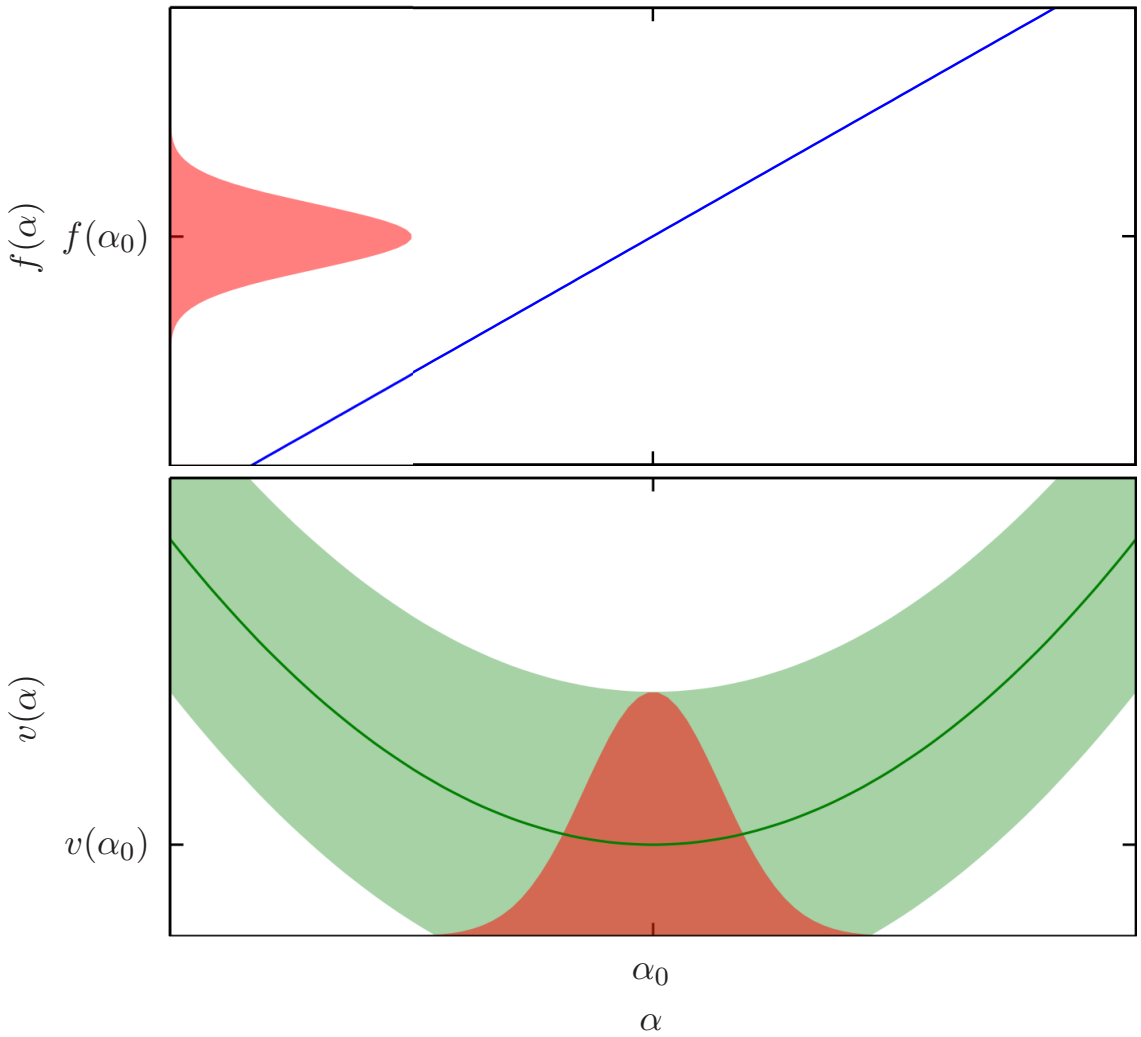
Handling optimization noise

Correlated sampling with M real-space configurations:



Handling optimization noise

$\mathrm{stddev}[\tilde{\alpha}] \propto \mathrm{stddev}[f(\tilde{\alpha})] \propto M^{-1/2}$:



Handling optimization noise

Observations:

- Correlated-sampling optimization yields more accurate energy than the random sample resolves:

$$\mathrm{stddev}[E_{\mathrm{ref}}] < \mathrm{stderr}[E_{\mathrm{ref}}]$$

- ST-FCIQMC energy is relatively insensitive to fluctuations in the reference energy:

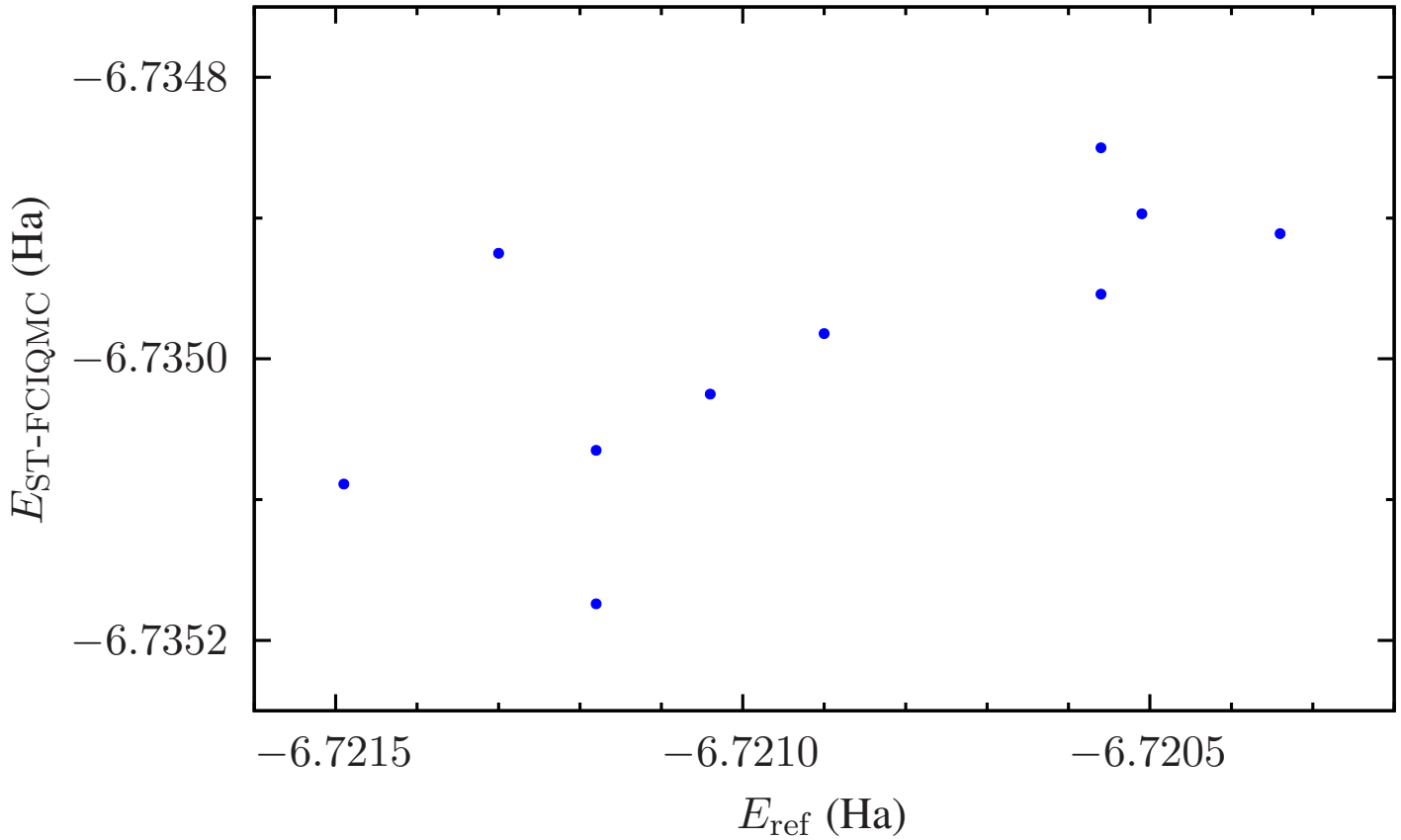
$$\mathrm{stddev}[E_{\text{ST-FCIQMC}}] < \mathrm{stddev}[E_{\mathrm{ref}}]$$

So we choose M assuming there is a universal constant r such that:

$$\mathrm{stddev}[E_{\text{ST-FCIQMC}}] \approx \frac{1}{r}\mathrm{stderr}[E_{\mathrm{ref}}]$$

Handling optimization noise

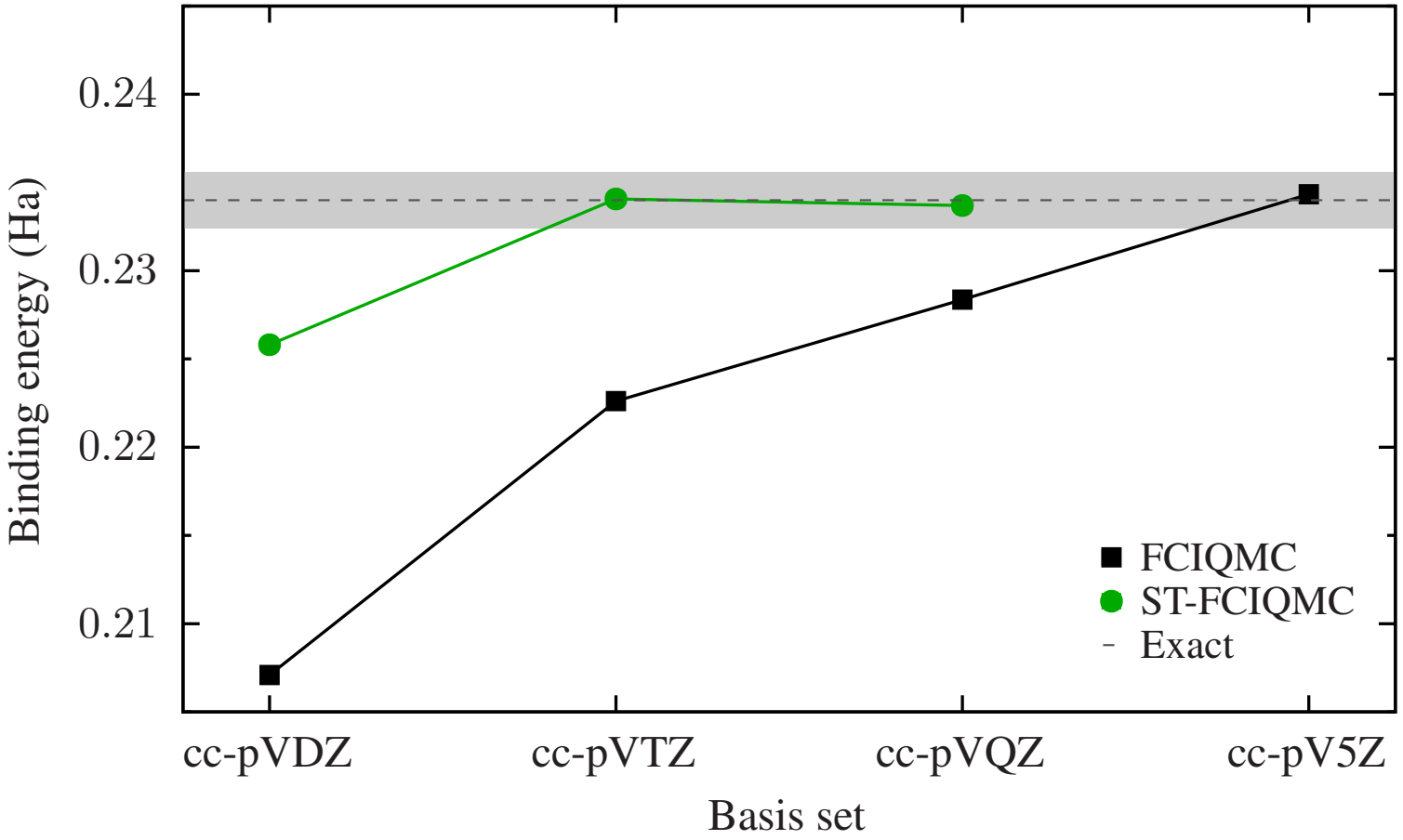
Typical scatter plot: (this is for an assembly of He_2 H_2)



$\rightarrow$ we assume $r \approx 5$

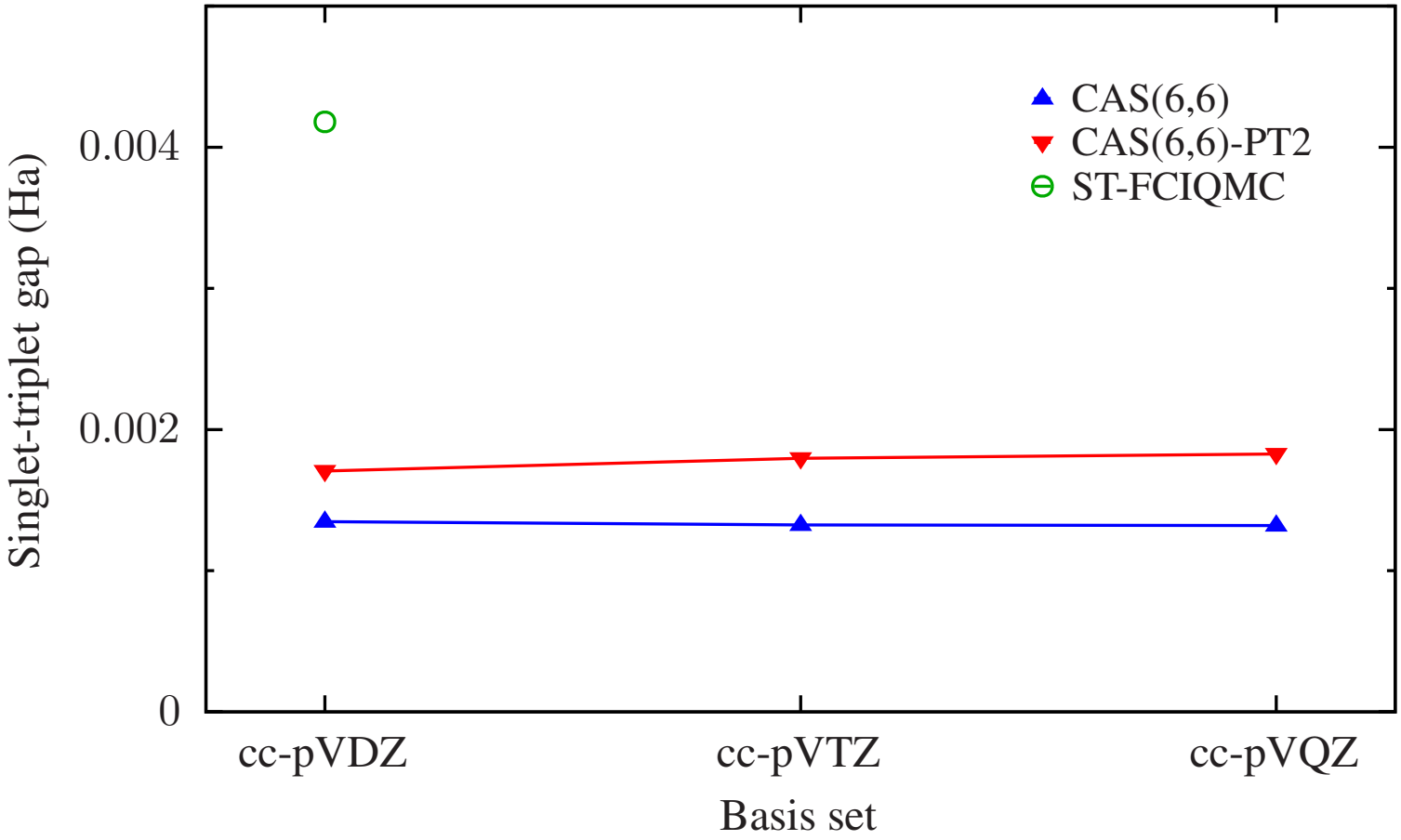
Benchmarking ST-FCIQMC

Binding energy of C_2:



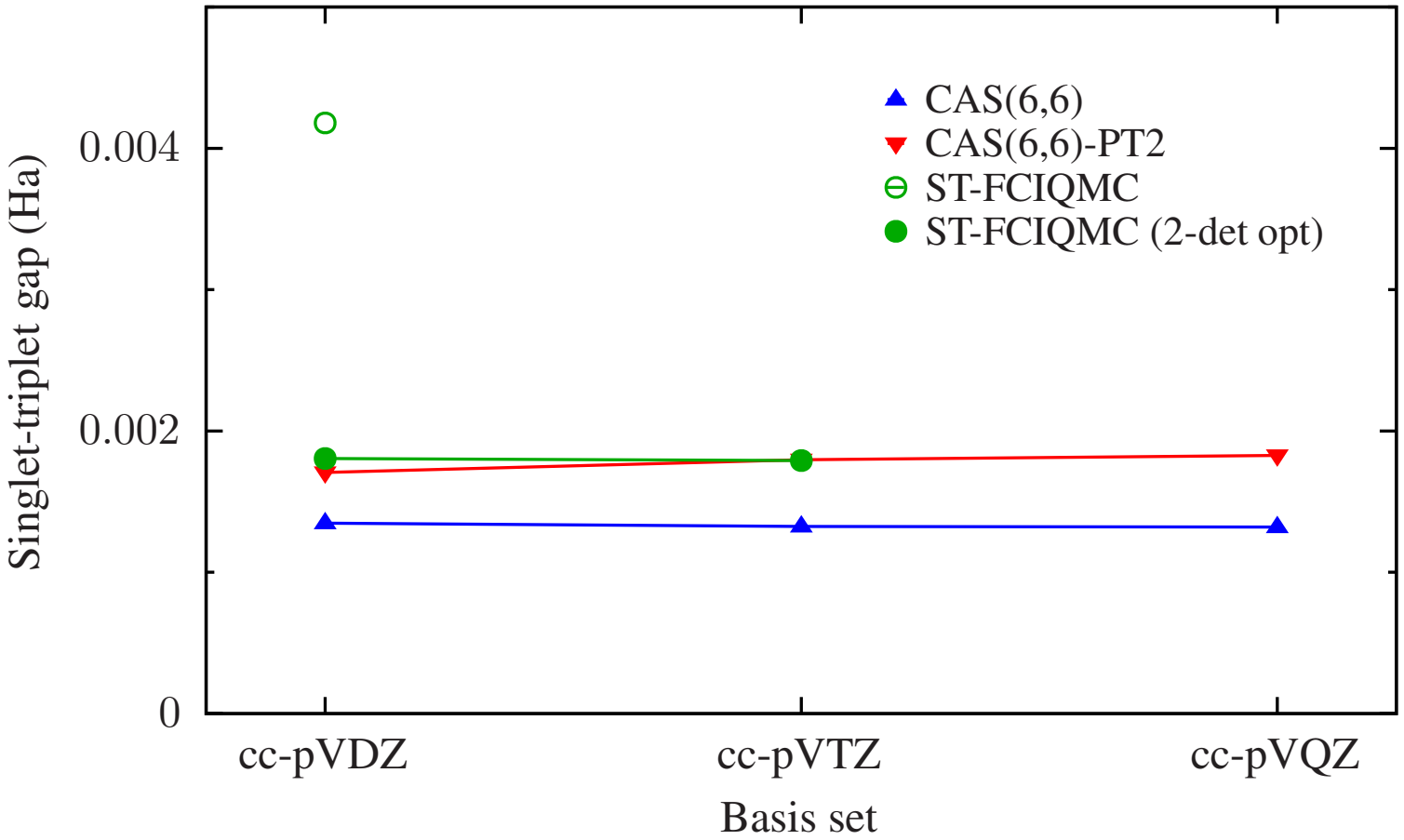
Multireference character

Spin gap in assembly of He_2 H_2:



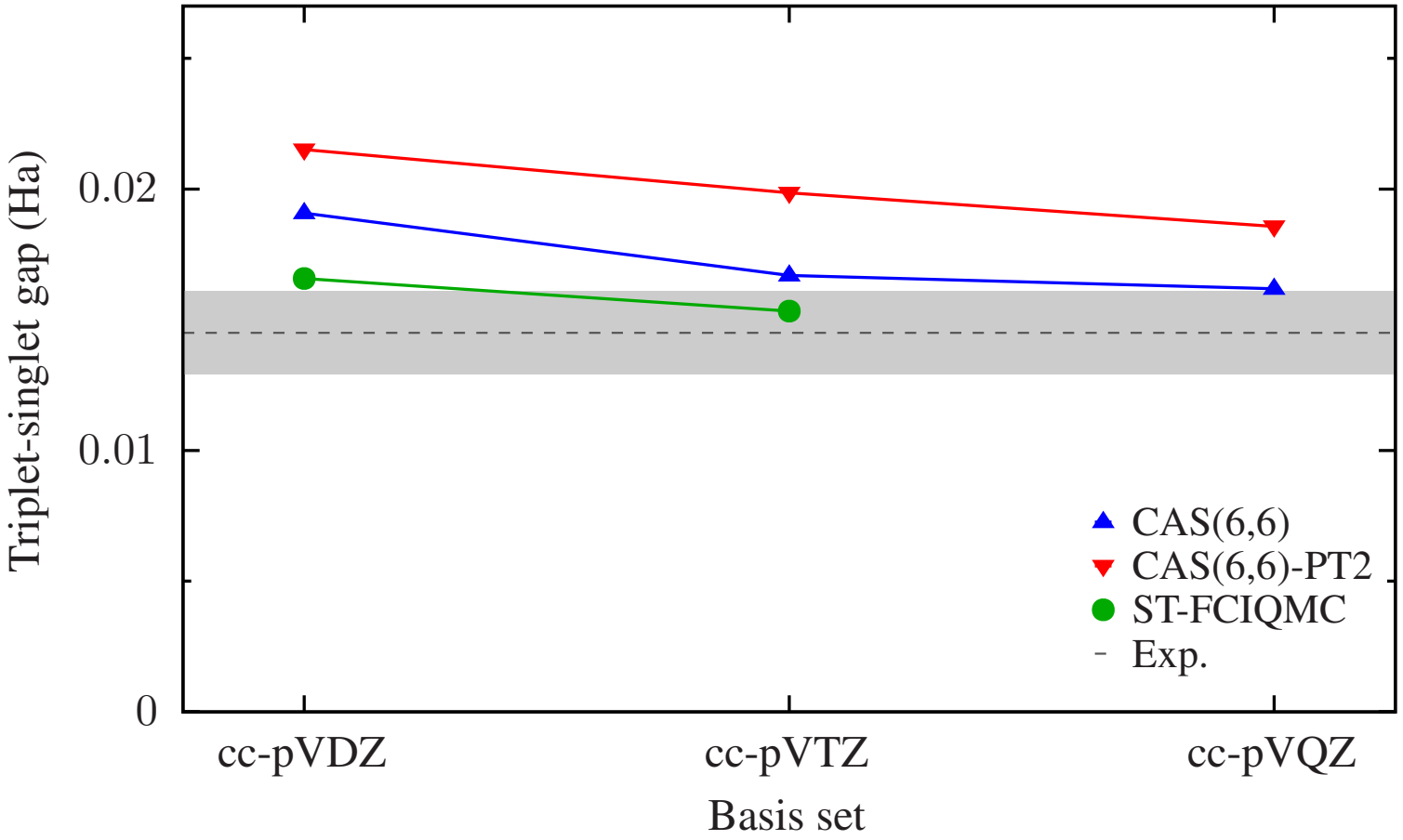
Multireference character

Singlet needs $\Psi = e^J (c_0 D_0 + c_1 D_1)$



Benchmarking ST-FCIQMC

Spin gap of CH_2:



Conclusions

More things to do

- Periodic systems
- Spin-dependent Jastrow factors
- Get VMC optimizer into TCHInt?
- Explore other Jastrow factor forms
- Work with other codes

Outlook

- Extremely promising methodology!