

# All-electron Quantum Monte Carlo using Slater-type orbitals

**Norbert Nemec**

*ESDG*

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# Slater-type orbitals (STO)

- Introduced by J. C. Slater [Phys. Rev. **36**, 57 (1930)]

$$\psi_{\zeta nlm}(r, \theta, \varphi) = R_{\zeta n}(r) \Psi_{lm}(\vartheta, \varphi)$$

$$R_{\zeta n}(r) = r^{n-1} e^{-\zeta r}$$

- inspired by the eigenstates of the hydrogen atom
- nodeless radial function ( $r^{n-1}$  instead of Laguerre polynomials)
- multiple- $\zeta$  basis sets for higher precision (typically up to quadruple- $\zeta$ )  
[typical basis set notation: DZ (“double- $\zeta$ ”)  
TZ2P (“triple- $\zeta$ , doubly polarized”)]



# PROs and CONs of STOs

## PROs

- + localised basis
- + very small basis set  
( $\sim 1/2$  the size of a contracted gaussian basis for similar precision)
- + correct electron-nucleus cusp by simple linear constraint
- + well-behaved asymptotics

## CONs

- no asymptotic basis set completion
- very demanding numerical integration



# ADF

(Amsterdam Density Functional package)



Scientific Computing & Modelling

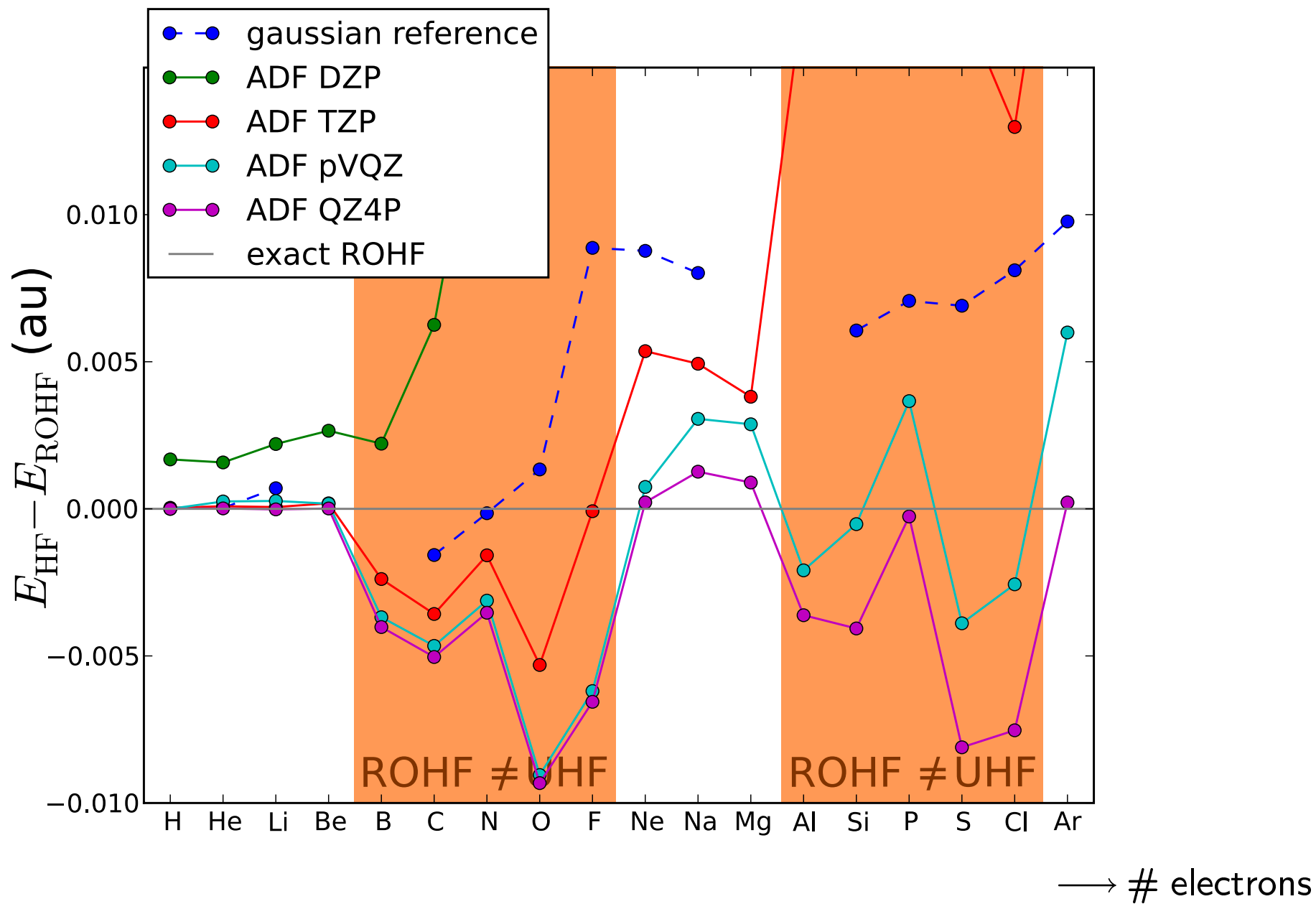
→ The only (?) production-quality electronic structure code based on STOs.

- includes various libraries of basis sets up to QZ4P
- frozen core approximation optional (no pseudopotentials)
- implements Hartree-Fock, DFT and hybrids
- user-friendly interface (also GUI) and excellent documentation  
(including export data formats)
- ADF for molecules, BAND for 1d, 2d and 3d periodic systems

→ <http://www.scm.com>

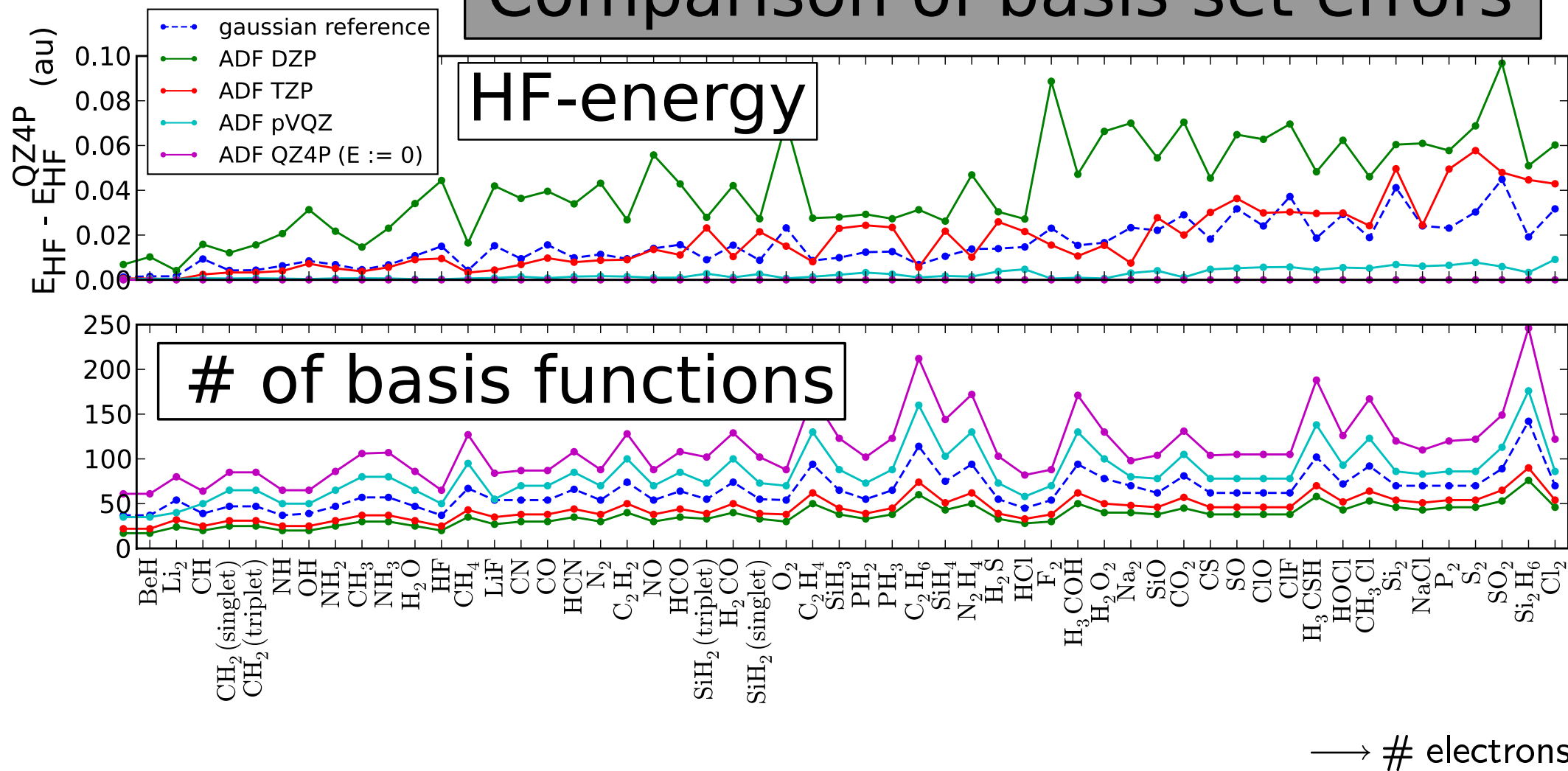


# STO vs. gaussian - atoms



# STO vs. gaussian - molecules

## Comparison of basis set errors



# The electron-nucleus cusp

→ Tosio Kato [Comm. Pure Appl. Math. **10**, 151 (1957)]

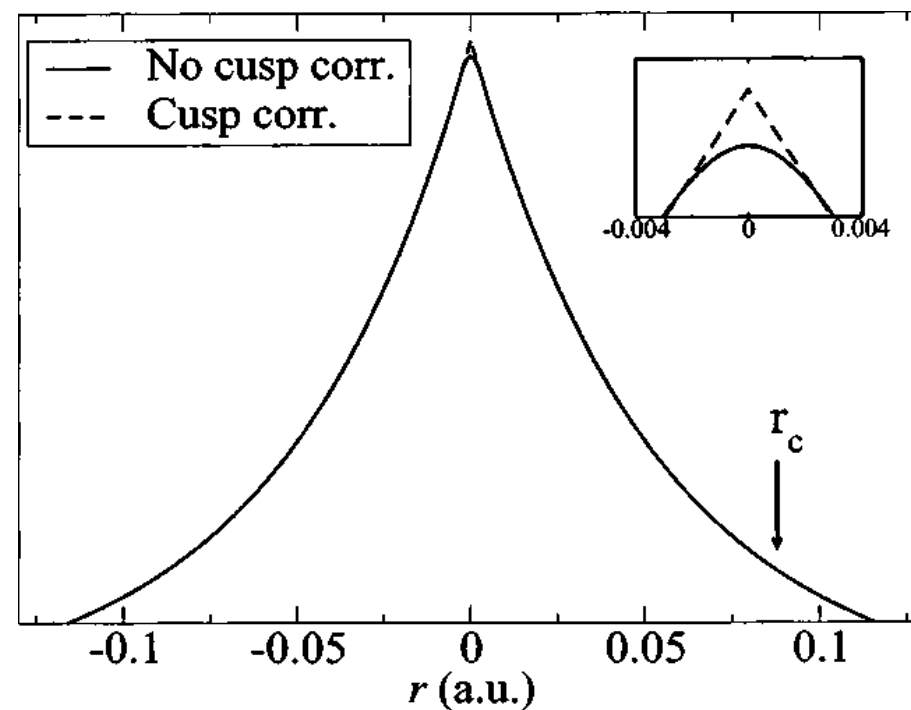
Kato cusp condition for electronic wavefunction near nucleus (point charge):

$$\left( \frac{\partial \langle \Psi \rangle}{\partial r} \right)_{r \rightarrow 0} = -Z \langle \Psi \rangle_{r=0}$$

[ $\langle \Psi \rangle$ : spherical average of wfn at distance  $r$  from nucleus]

**HF/DFT** — appropriate basis set necessary to represent wave function near nucleus  
(e.g. contracted gaussians)

**QMC** — cusp condition has to be exactly satisfied to prevent divergent local energy

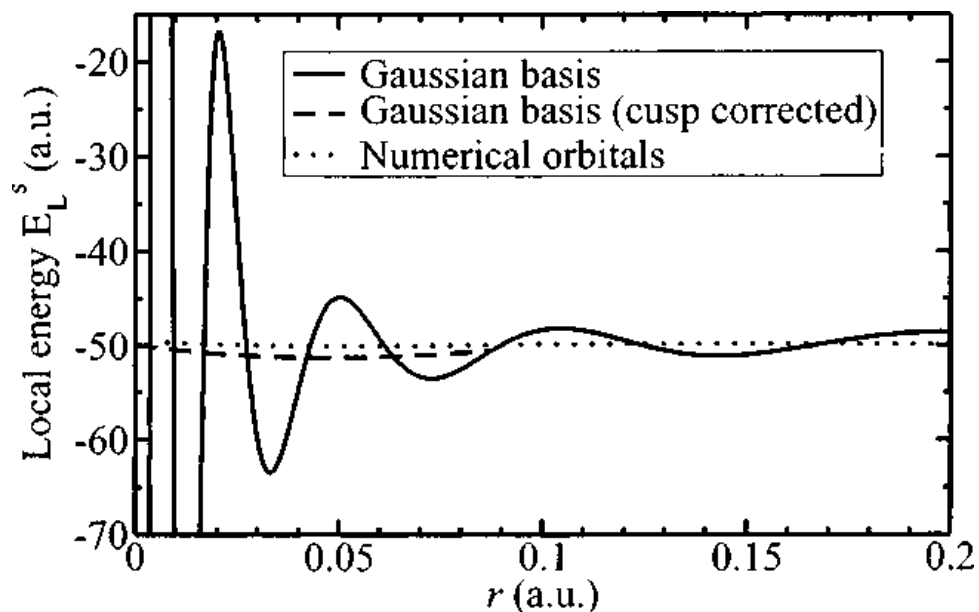
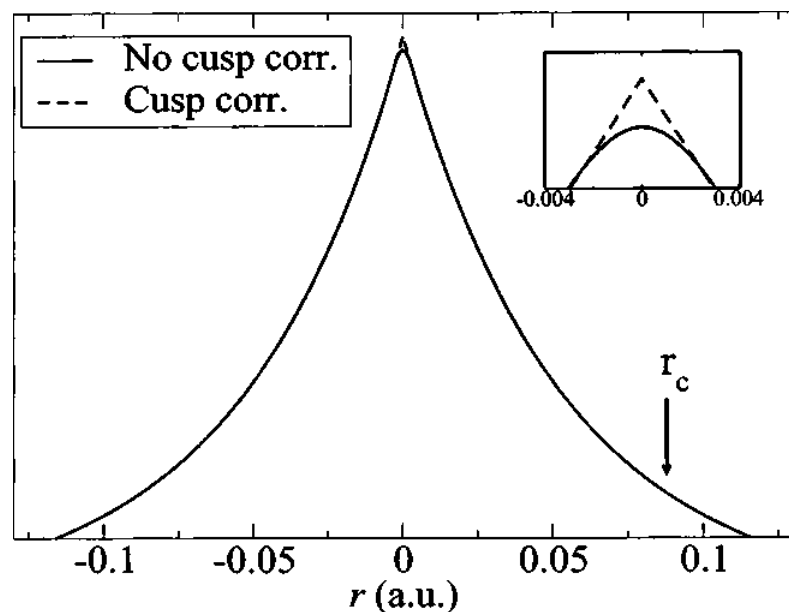


Ma et al., J. Chem. Phys. 122, 224322 (2005)

# Cusp corrections for gaussian orbitals

→ Ma, Towler, Drummond and Needs [J. Chem. Phys. **122**, 224322 (2005)]

- Replace wfn near nucleus by polynomial that exactly satisfied cusp





# Linear cusp constraints for STOs

Basis set (unnormalized):

$$\psi_i(\mathbf{r}) = Y_{l_i, m_i}(\vartheta(\mathbf{r} - \mathbf{R}_i), \varphi(\mathbf{r} - \mathbf{R}_i)) \times |\mathbf{r} - \mathbf{R}_i|^{n_i} \times \exp(-\zeta_i |\mathbf{r} - \mathbf{R}_i|)$$

One molecular orbital:  $\Psi(\mathbf{r}) = \sum_i c_i \psi_i(\mathbf{r} - \mathbf{R}_i)$

One linear constraint per nucleus  $I$  at position  $\mathbf{R}_I$ :

$$\left\langle \frac{d}{dr} \Psi(\mathbf{r}) \right\rangle \Big|_{\mathbf{r}=\mathbf{R}_I} = -Z_I \Psi(\mathbf{R}_I)$$

→ LHS depends only on local  $1s$  and  $2s$  basis functions:

$$\langle \partial_r \Psi \rangle_{R_I} = - \sum_{i \in (1s, I)} \zeta_i c_i + \sum_{i \in (2s, I)} c_i$$

→ RHS depends only on local  $1s$  and all nonlocal basis functions:

$$\Psi(\mathbf{R}_I) = \sum_{i \in (1s, I)} c_i + \sum_{i \notin (I)} c_i \psi_i(\mathbf{R}_I - \mathbf{R}_i)$$



# Linear cusp constraints for STOs

Linear constraint for nucleus  $I$ :

$$-\sum_{i \in (1s, I)} \zeta_i c_i + \sum_{i \in (2s, I)} c_i = -Z_I \left( \sum_{i \in (1s, I)} c_i + \sum_{i \notin (I)} c_i \psi_i(\mathbf{R}_I - \mathbf{R}_i) \right)$$

Cusp constraint vector  $\chi^I$  for nucleus  $I$  (depends on basis set only):

$$\sum_i \chi_i^I c_i = 0$$



# Enforcing cusp constraints (c-c)

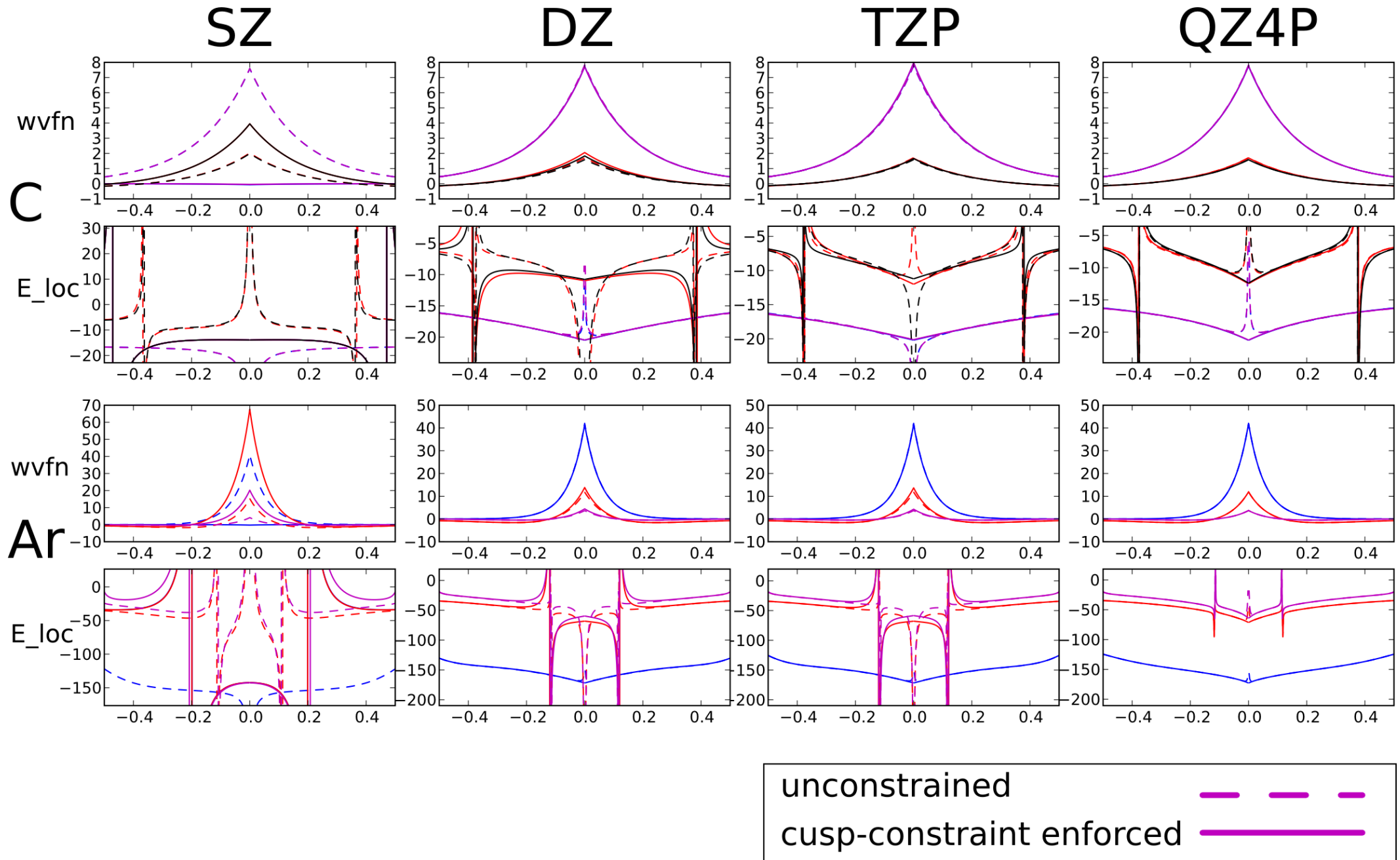
- unconstrained molecular orbital  $C \in \text{Vec}(N_{\text{bas}})$
- c-c-matrix  $\chi \in \text{Mat}(N_{\text{nuc}} \times N_{\text{bas}})$
- find constrained orbitals  $C'$  satisfying cusp condition:  $\chi C' = 0$
- select  $N_{\text{nuc}}$  c-c-orbitals (the narrowest  $s$ -type orbital of each nucleus)  
→  $\zeta_{\text{cc}}$  should be larger than  $Z + 1$  to prevent long-ranged effects
- assume coefficients ordered as  $\begin{pmatrix} C_{\text{cc}} \\ C_{\text{non-cc}} \end{pmatrix}$
- split  $\chi$  into blocks  $\begin{pmatrix} \chi_{\text{cc}} & \chi_{\text{non-cc}} \end{pmatrix}$   
→ cusp condition:  $\chi_{\text{cc}} C'_{\text{cc}} + \chi_{\text{non-cc}} C'_{\text{non-cc}} = 0$

$$C'_{\text{cc}} := -\chi_{\text{cc}}^{-1} \chi_{\text{non-cc}} C_{\text{non-cc}} \qquad C'_{\text{non-cc}} = C_{\text{non-cc}}$$

( $\chi_{\text{cc}}^{-1}$  ill-conditioned only if  $\zeta_{\text{cc}}$  close to  $Z$ )



# The effects of cusp-constraints



# Comparison of timing

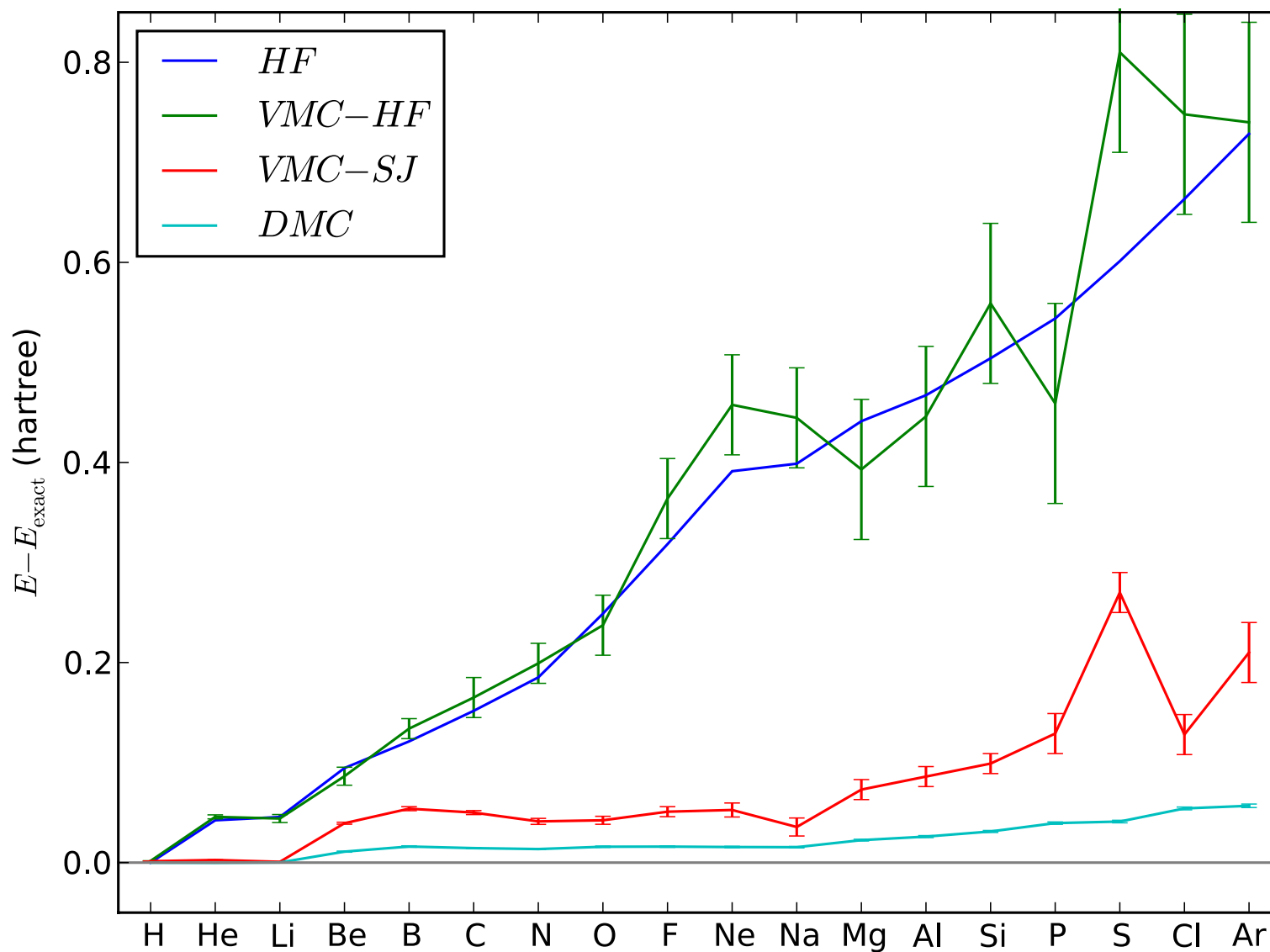
all runs: NaCl molecule (28 electrons), 500000 VMC steps/proc

	# of basis functions	WFDET total (sec)
gaussian (no CC)	70	40.6
gaussian (gauss. CC)	70	41.3
gaussian (gen. purp)	70	40.6
STO (TZP)	51	37.3
STO (pVQZ)	83	46.4
STO (QZ4P)	110	62.0

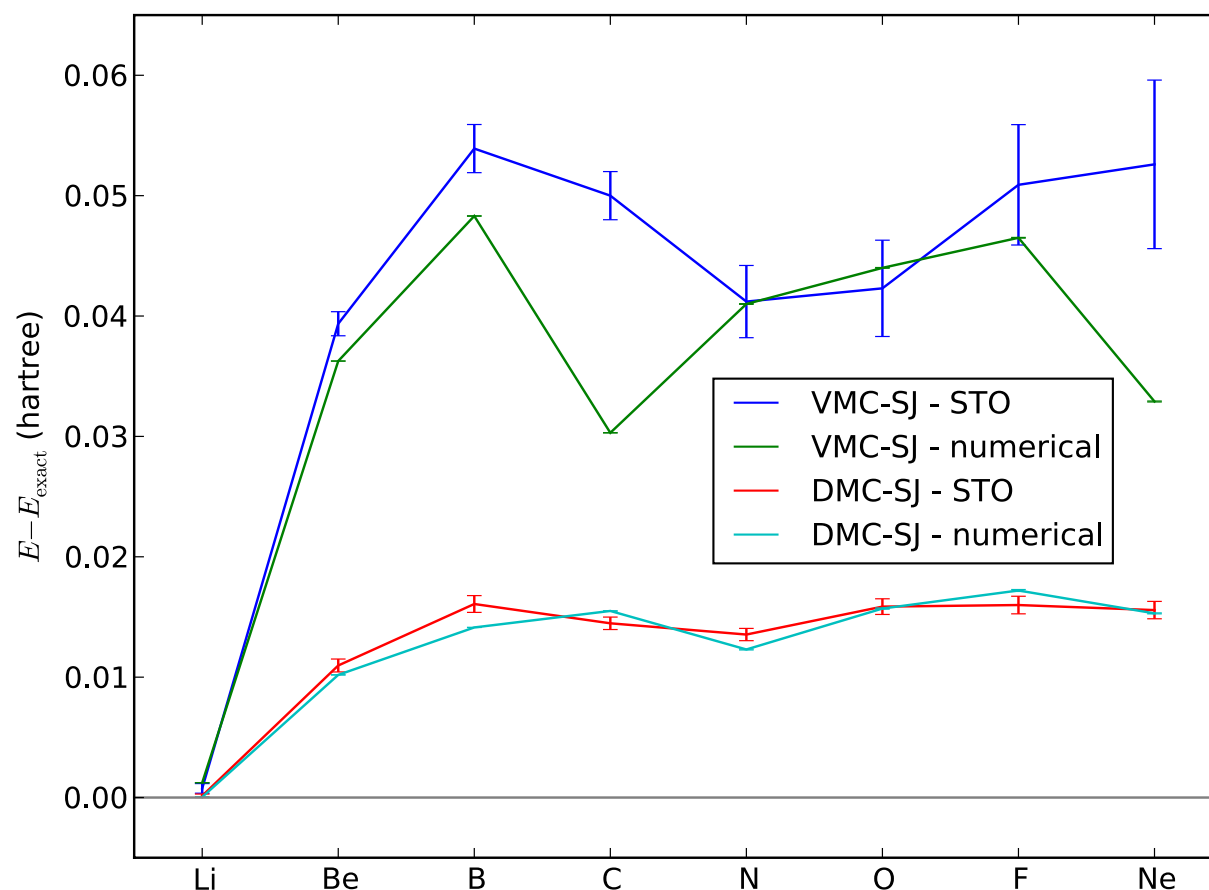
→ performance of STO in QMC similar to that of gaussians



# Atomic energies



# Atomic energies - compare STO with numerical

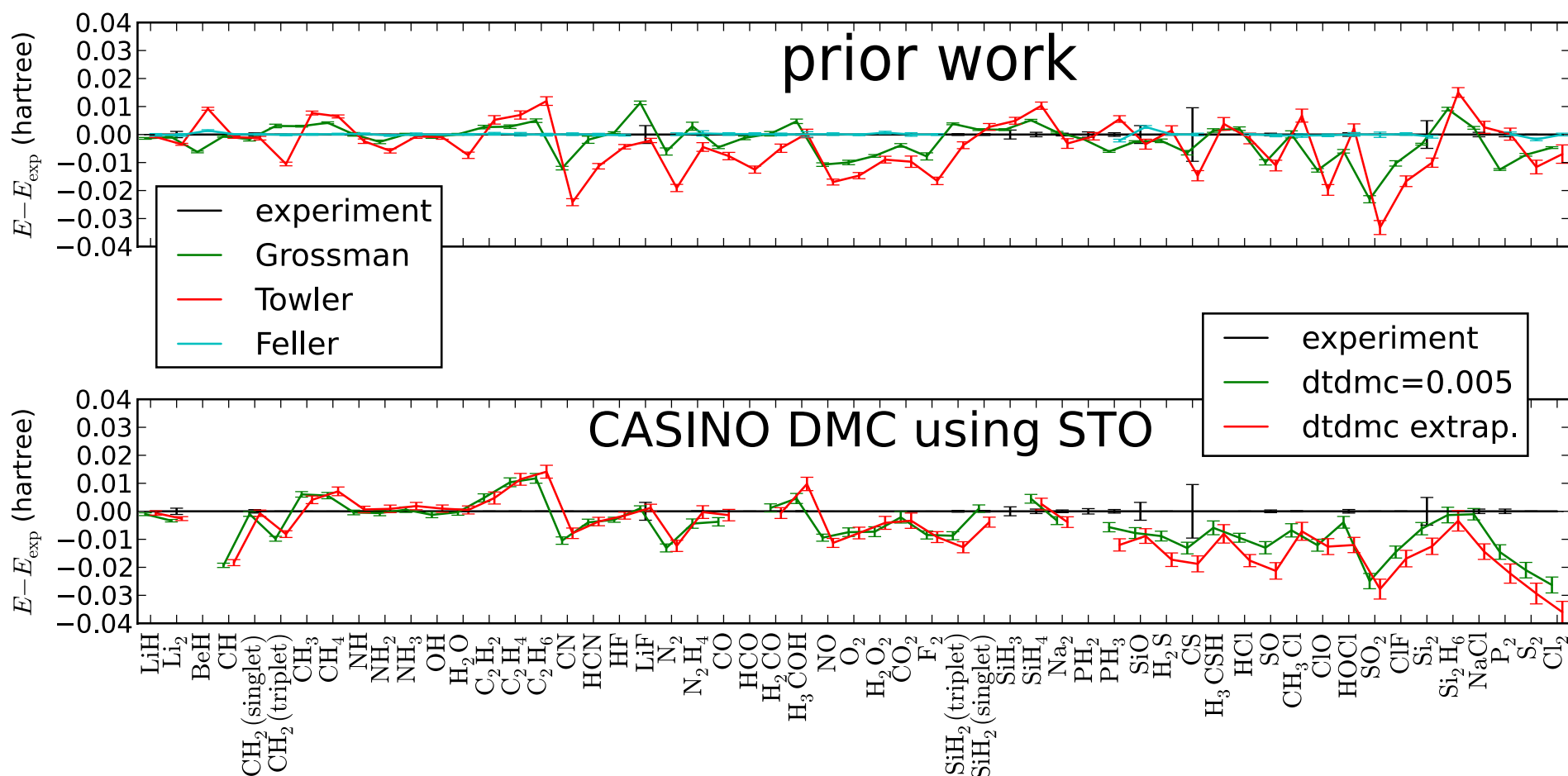


→ numerical basis set data by M.D.Brown et al [J. Chem. Phys. **126**, 224110 (2007)]

STO (pVQZ basis) allow same precision as numerical orbitals

→ basis set limit reached within target precision

# Molecules - atomization energies (G2 set)



- J. C. Grossman [J. Chem. Phys. 117, 1434 (2002)]: pseudopotential DMC
- M.D. Towler [unpublished]: CASINO DMC using gaussian orbitals
- Feller et al. [J. Chem. Phys. 129, 204105 (2008)]: CCSDT+corrections





# Technical details for DMC calculations

- STO/pVQZ basis set, LDA trial wavefunction
- optimized Slater-Jastrow term:  $C = 3$ ,  $N_u = N_\chi = 10$ ,  $N_F = 3$
- using MADMIN  $\rightarrow$  recovering avg. 75% of correlation energy
- DMC computing time:  $\sim 1$  CPU hour / electron (at  $dtdmc=0.005$ )
- target population: 100 walkers, using weighted DMC (lwdmc)
- using automatic reblocking (thanks, Pablo!)



# Overall quality of G2 energies

			mean abs dev
J.C.Grossman	2002	pseudopotential DMC	2.9 kcal/mol
M.D.Towler	200?	CASINO AE-DMC (Gaussians)	4.7 kcal/mol
D.Feller et al.	2008	CCSD(T) + corrections	0.2 kcal/mol
my attempt	2009	CASINO AE-DMC (STO)	4.6 kcal/mol
		experimental precision	0.3 kcal/mol

## Error sources:

- timestep error  $< 1.9$  kcal/mol ( $< \langle |E_{dt=0.01} - E_{dt=0.005}| \rangle$ )
- statistical error  $< 0.46$  kcal/mol
- population control error  $< 0.3$  kcal/mol
- fixed node error: in total energy  $\sim 9.5$  per atom (Be...F)  
 $\Rightarrow$  hoping for cancellation...



# Conclusions

- STO wavefunctions in CASINO and ADF import filter implemented and tested for atoms and G2 molecules
- e-n cusp condition exactly satisfied by linear constraint
- constraint can be safely applied to existing wave functions  
if basis set is large enough
- performance of STO in QMC comparable to Gaussians (same basis size)
- STO basis sets smaller for same precision ( $\sim$  factor 1/2)
- basis set limit reached with pVQZ basis set  
for atomic calculations using DMC-SJ
- G2 energies reproduced with same precision as previous attempt based on Gaussian orbitals
- G2 energies not quite as good as pseudopotential-based QMC

