Pulay Nodal Terms in Accurate Diffusion Monte Carlo Forces

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Motivation

Why forces in Diffusion Monte Carlo?

- Equilibrium geometries
- Energy derivatives are very useful!
- Molecular dynamics

Two main problems of forces in DMC are

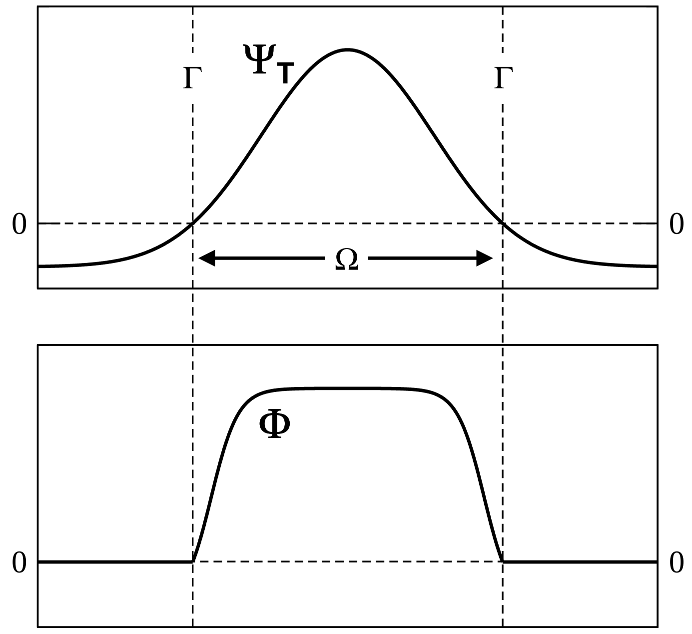
- Infinite variance of force estimator (addressed e.g. with pseudopotentials)[1]
- Discontinuous 1st (higher) derivative in DMC wavefunction at nodal surface

[1]ESDG April 2007; A. Badinski, R.J. Needs PRE **76** 036707 (2007)

Diffusion Monte Carlo

Basics of DMC

- **Project out ground state**
  $|\Phi\rangle = e^{-\tau\hat{H}}|\Psi_T(\tau=0)\rangle$ for $\tau \to \infty, \quad \tau = it$
  using stochastic algorithm
- Φ is DMC wavefunction represented by ensemble of walkers
- Use **fixed node approx.** to eliminate fermionic sign problem
- Ψ_T is a given trial wavefunction
  Γ is nodal surface defined by $\Psi_T = 0$
  Simulate nodal pockets individually



Electron coordinate [arb. units]

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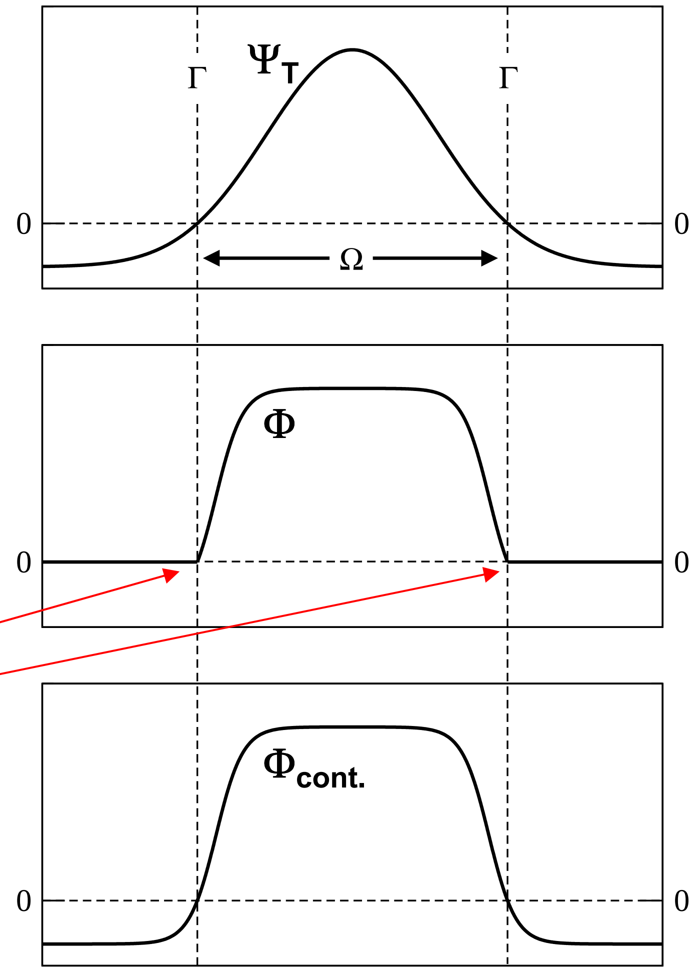
Problem

Φ has discontinuous derivatives at Γ

Define $\Phi_{cont.}$ so it has no discontinuities



Electron coordinate [arb. units]

Energy in DMC

Effective Hamiltonian in DMC

After an involved derivation, we obtain

$$\hat{H}\Phi = \Theta(\Psi_T)\hat{H}\Phi_{cont.} - \frac{1}{2}\delta(\Psi_T)\frac{|\nabla\Psi_T|^2}{\Psi_T}\Phi_{cont.}$$

DMC energy

$$E_D = \frac{\int \Psi\hat{H}\Phi \mathbf{d}V}{\int \Psi\Phi \mathbf{d}V}$$

for **mixed DMC** $(\Psi = \Psi_T)$ and **pure DMC** $(\Psi = \Phi)$.
The δ function term (discontinuity in Φ) does not contribute to E_D.
But it may contribute when calculating derivatives of E_D.......

Forces in DMC

Differentiate E_D wrt nucleus coordinate λ

$$\frac{dE_D}{d\lambda} = \underbrace{\frac{\int \Psi \frac{d\hat{H}}{d\lambda} \Phi \, \mathbf{d}V}{\int \Psi\Phi \, \mathbf{d}V}} + \underbrace{\frac{\int \Psi \left(\hat{H} - E_D\right) \frac{d\Phi}{d\lambda} \, \mathbf{d}V}{\int \Psi\Phi \, \mathbf{d}V}} + \underbrace{\frac{\int \frac{d\Psi}{d\lambda} \left(\hat{H} - E_D\right) \Phi \, \mathbf{d}V}{\int \Psi\Phi \, \mathbf{d}V}}$$

$\Psi = \Psi_T$

Hellmann-Feynman force

use Reynolds' approx.[1]

$$\frac{1}{\Phi}\frac{d\Phi}{d\lambda} \approx \frac{1}{\Psi_T}\frac{d\Psi_T}{d\lambda}$$

identify as nodal term **N(mixed)**

$\Psi = \Phi$

Hellmann-Feynman force: F(HFT,pure DMC)

nodal term[2]: **N(pure)**

[1] P. Reynolds, et al. Internat. J. Quant. Chem. **29** 589 (1986)
[2] F. Schautz and H.-J. Flad, J. Chem. Phys. **112**, 4421 (2000)

Nodal Term N

Volume integrals equal **nodal term** (steps omitted)

$$\textbf{N(mixed)} = \frac{\int \frac{d\Psi_T}{d\lambda}\left(\hat{H} - E_D\right)\Phi\,\mathbf{d}V}{\int \Psi_T \Phi\,\mathbf{d}V} = -\frac{1}{2}\frac{\int_\Gamma \Psi_T \Phi \frac{|\nabla \Psi_T|}{\Psi_T}\frac{1}{\Psi_T}\frac{d\Psi_T}{d\lambda}\,\mathbf{d}S}{\int \Psi_T \Phi\,\mathbf{d}V}$$

$$\textbf{N(pure)} = \text{Volume Terms} = -\frac{1}{2}\frac{\int_\Gamma \Phi\Phi \frac{|\nabla \Psi_T|}{\Psi_T}\frac{1}{\Psi_T}\frac{d\Psi_T}{d\lambda}\,\mathbf{d}S}{\int_\Gamma \Phi\Phi\,\mathbf{d}V}$$

1. these are exact expressions!
2. the averaged quantity only depends on Ψ_T
3. the averaged quantities are same in mixed and pure DMC

Using the extrapolation formula

$$\langle Q\rangle_{pure} \approx 2\langle Q\rangle_{mixed} - \langle Q\rangle_{VMC} \quad \text{with} \quad Q = \frac{|\nabla \Psi_T|}{\Psi_T}\frac{1}{\Psi_T}\frac{d\Psi_T}{d\lambda}$$

and $\langle Q\rangle_{VMC} = 0$ (proof omitted)

we find **N (pure) ≈ 2 N (mixed)**

Summary

mixed DMC

$$\frac{dE_D}{d\lambda} = \frac{\int \Psi_T \frac{d\hat{H}}{d\lambda} \Phi \mathbf{d}V}{\int \Psi_T \Phi \mathbf{d}V} + \frac{\int \Psi_T \Phi \left[\frac{1}{\Psi_T} \frac{d\Psi_T}{d\lambda} \frac{1}{\Psi_T} \left(\hat{H} - E_D \right) \Psi_T \right] \mathbf{d}V}{\int \Psi_T \Phi \mathbf{d}V} + \frac{\int \Psi_T \Phi \frac{1}{\Psi_T} \left(\hat{H} - E_D \right) \frac{d\Psi_T}{d\lambda} \mathbf{d}V}{\int \Psi_T \Phi \mathbf{d}V} + O(\Delta \Psi_T)$$

pure DMC

$$\frac{dE_D}{d\lambda} = \frac{\int \Phi \frac{d\hat{H}}{d\lambda} \Phi \mathbf{d}V}{\int \Phi \Phi \mathbf{d}V} + 2 \frac{\int \Psi_T \Phi \frac{1}{\Psi_T} \left(\hat{H} - E_D \right) \frac{d\Psi_T}{d\lambda} \mathbf{d}V}{\int \Psi_T \Phi \mathbf{d}V} + O(\Delta \Psi_T^2)$$

Computational Details

GeH:

- **no electron-electron interaction** (nodal terms from kinetic energy!)
- trial wavefunction: **single determinant** with 4 basis sets
- **local pseudopotentials** (to avoid infinite variance!)

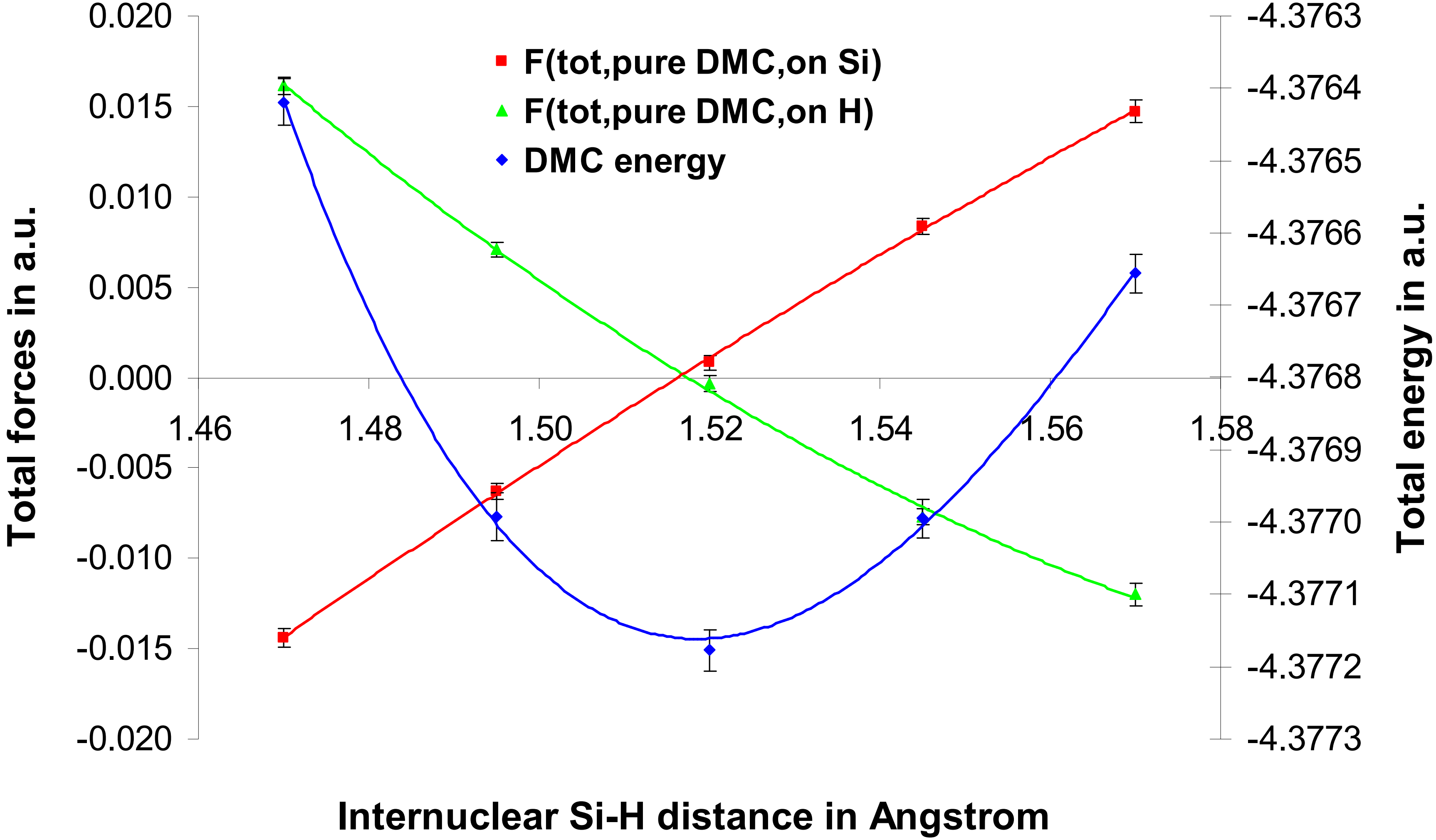
GeH,SiH,SiH_4:

- **full electron-electron interaction**
- trial wavefunction: **single determinant** x Correlation function
- **nonlocal pseudopotentials**[1]

- calculate $\frac{\partial \Psi_T}{\partial \lambda}$ rather than $\frac{d\Psi_T}{d\lambda}$
- use **future walking** method to calculate pure estimates
- for reference also calculate energy gradient from potential energy curves

[1] A. Badinski, R.J. Needs PRE **76** 036707 (2007)

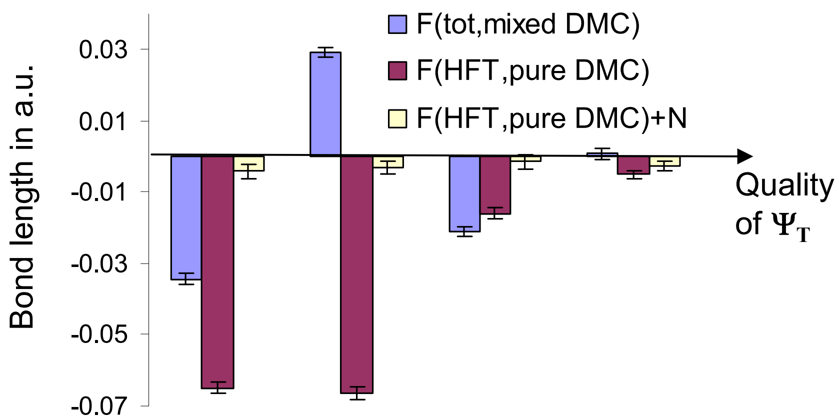
How to get geometries? (e.g. SiH)



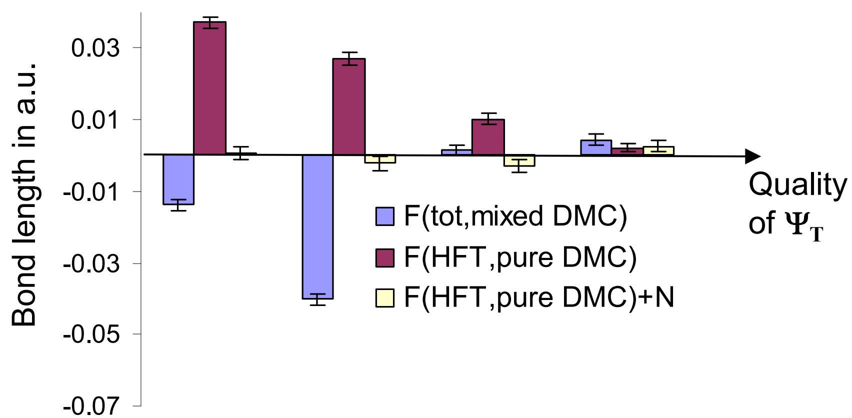
GeH (no e-e interaction)

Difference between force & exact energy gradient (within basis set)

Forces on Ge



Forces on H



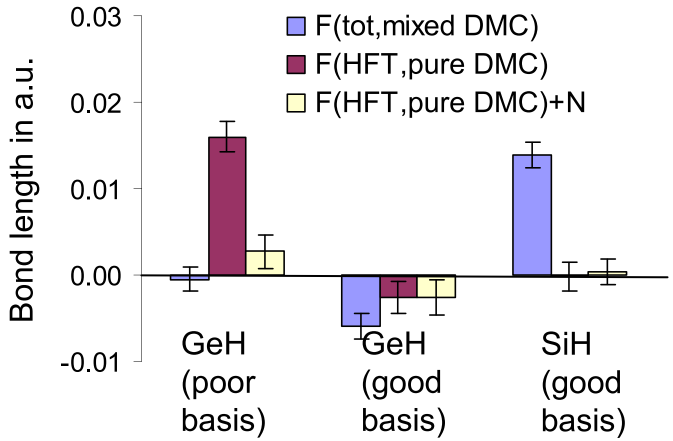
- F(tot,mixed DMC) is slightly better than F(HFT,pure DMC)
- Adding nodal term N to F(HFT,pure DMC) improves forces significantly
- F(tot,pure DMC) always better than F(tot,mixed DMC)

Nodal terms may be significant, should be included!

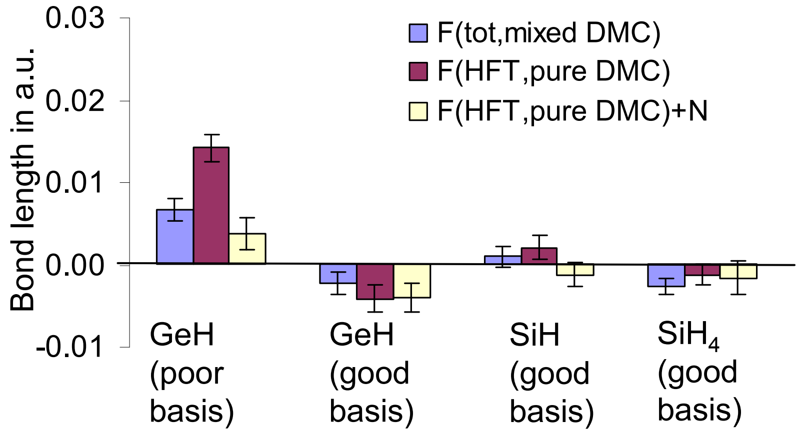
GeH,SiH,SiH_4 (with e-e interaction)

Difference between forces & exact energy gradient

Forces on Ge or Si



Forces on H



For poor basis:

- F(HFT,pure DMC) worse than F(tot,mixed DMC)
- Adding nodal term N to F(HFT,pure DMC) significantly improves forces

For good basis:

- F(HFT,pure DMC) equal or better than F(tot,mixed DMC)
- Adding nodal term N to F(HFT,pure DMC) has no significant effect

Nodal terms seem less important if basis set is good!

Conclusions

- We derived **exact expressions for forces** within mixed and pure DMC
- The nodal term in mixed DMC can be calculated straightforwardly
  In pure DMC, it may be approximated as twice the mixed nodal term
- Tests for small molecules indicate that **nodal terms may be significant** and including them can significantly improve forces!
- Pure DMC forces including nodal terms seem more accurate than mixed DMC forces

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