



# Accurate Forces in Quantum Monte Carlo - a new way to Molecular Dynamics?

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Electronic Structure Discussion Group



# Why do we need Accurate Forces in Quantum Mechanics?

- **Equilibrium geometries** for molecules & solids  
(e.g., DFT overestimates bond lengths for G2 molecules on average by 0.012 Å)
- **Molecular Dynamics**
- **Energy Derivatives** lead to many other interesting properties, such a vibrational modes, dipole moments, etc.....

# Quantum Monte Carlo Methods



Variational ground state energy for many electron system

$$E_T = \langle \Psi_T | H | \Psi_T \rangle \geq E_0$$

with  $\Psi_T(X) = \text{Slater Determinant} \times \text{Jastrow factor}$

Compute  $3N$ -dim. integral using **Monte Carlo Integration**

$$E_T = \int \left( \frac{H\Psi_T}{\Psi_T} \right) |\Psi_T|^2 dR \approx \frac{1}{M} \sum_{j=1}^M \left( \frac{H\Psi_T}{\Psi_T} \right)_{X_j}$$

Iteratively adjust  $\Psi_T$  to minimize energy

**Variational  
Monte  
Carlo**

**Project out ground state**  $|\Phi_0\rangle = e^{-\tau H} |\Phi(\tau=0)\rangle$  for  $\tau \rightarrow \infty$ ,  $\tau = it$

use stochastic algorithm based on “diffusion” & “rate process”

$\Phi(R, \tau)$  is represented by ensemble of walkers

Use **fixed node approx.** to eliminate fermionic sign problem

For efficiency: use **pseudopotentials**  $\rightarrow$  omit core electrons

**Diffusion  
Monte  
Carlo**

# Hellmann-Feynman Theorem

**In VMC** total force on a nucleus at position  $R$  (assume  $\Psi_T$  normalized)

$$F|_R := -\frac{dE}{dR} = \underbrace{-\langle \Psi_T | \frac{\partial H}{\partial R} | \Psi_T \rangle}_{= F^{HFT}|_R} - \underbrace{\langle \frac{\partial \Psi_T}{\partial R} | H | \Psi_T \rangle - \langle \Psi_T | H | \frac{\partial \Psi_T}{\partial R} \rangle - \sum_i \frac{\partial E}{\partial c_i} \frac{\partial c_i}{\partial R}}_{\text{Pulay Terms}}$$

Pulay Terms are zero if  $\Psi_T$  is the exact ground state wave function of  $H$   
 → **Hellmann-Feynman Theorem (HFT)**<sup>1,2</sup>

**In DMC** fixed node ground state  $\Phi_{FN} \dots$

$$F|_R := -\langle \Phi_{FN} | \frac{\partial H}{\partial R} | \Phi_{FN} \rangle + \text{Nodal Term}^3$$

The HFT force is a **pure estimator**

Later on, only calculate  $F^{HFT}|_R$

Note: HFT holds in Hartree-Fock or DFT e.g. if basis set is complete

<sup>1</sup> H. Hellmann, Einführung in die Quantenchemie, Franz Deuticke, Leipzig (1937)

<sup>2</sup> R. Feynman Phys. Rev. 41 721 (1939)

<sup>3</sup> F. Schautz and H.-J. Flad, J. Chem. Phys. 112, 4421 (2000)

# Pseudopotentials in QMC



## In VMC

take Schrödinger Eq.  $\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ps}$

with  $\hat{V}_{ps} = \sum_i \sum_{l=0}^2 \Delta V_l(r_i) \hat{P}_l$  and  $\hat{P}_l \Psi_T = \frac{2l+1}{4\pi} \int P_l(\cos(\theta'_i)) \Psi_T(r_1, \dots, r'_i, \dots, r_N) d\Omega'_i$

evaluate 2-dim integral numerically

## In DMC

**Problem:** not straightforward to act  $\hat{V}_{ps}$  on  $\Phi_{FN}$  (DMC wave function)

$$\text{Solution 1: } \hat{V}_{ps} \approx \frac{\hat{V}_{ps} \Psi_T}{\Psi_T}$$

## Full Localization Approximation (FLA)<sup>1</sup>

$$\text{Solution 2: } \hat{V}_{ps} = \hat{V}_{ps}^+ + \hat{V}_{ps}^- \approx \frac{\hat{V}_{ps}^+ \Psi_T}{\Psi_T} + \hat{V}_{ps}^-$$

$\hat{V}_{ps}^+$  correspond to all positive matrix elements and  $\hat{V}_{ps}^-$  to negative matrix elements

## Semi Localization Approximation (SLA)<sup>2</sup>

<sup>1</sup> M. M. Hurley et. al., J. Chem. Phys. 86, 1069 (1986). L. Mitas, et. al., J. Chem. Phys. 95, 3467 (1991).

<sup>2</sup> M. Casula, Phys. Rev. B 74, 161102 (2006).

# Pseudopotentials and HFT

Now, evaluate HFT force...

**Under FLA**

$$\left\langle \Phi_{FN} \left| \frac{\partial \hat{H}}{\partial R} \right| \Phi_{FN} \right\rangle = \left\langle \Phi_{FN} \left| \frac{1}{\Psi_T} \frac{\partial \hat{V}_{ps}}{\partial R} \Psi_T + \frac{1}{\Psi_T} \frac{\partial \Psi_T}{\partial R} - \frac{1}{\Psi_T^2} \left( \hat{V}_{ps} \Psi_T \right) \frac{\partial \Psi_T}{\partial R} \right| \Phi_{FN} \right\rangle$$

**Pulay Terms**

**Under SLA**

$$\left\langle \Phi_{FN} \left| \frac{\partial \hat{H}}{\partial R} \right| \Phi_{FN} \right\rangle = \left\langle \Phi_{FN} \left| \frac{1}{\Psi_T} \frac{\partial \hat{V}_{ps}^+}{\partial R} \Psi_T + \frac{1}{\Psi_T} \frac{\partial \Psi_T}{\partial R} - \frac{1}{\Psi_T^2} \left( \hat{V}_{ps}^+ \Psi_T \right) \frac{\partial \Psi_T}{\partial R} + \frac{\partial \hat{V}_{ps}^-}{\partial R} \right| \Phi_{FN} \right\rangle$$

**Pulay Terms**

**Pulay Terms** zero in VMC & assumed to be small in DMC → omit

Additional complication under SLA:  $\hat{V}_{ps}^-$  is non-local! Solved by  $\frac{1}{\Phi_{FN}} \frac{\partial \hat{V}_{ps}^- \Phi_{FN}}{\partial R} \cong \frac{1}{\Psi_T} \frac{\partial \hat{V}_{ps}^- \Psi_T}{\partial R}$

Derive expression for  $\frac{1}{\Psi_T} \frac{\partial \hat{V}_{ps}}{\partial R} \Psi_T \dots$

# Pseudopotentials and HFT

Contributions for different angular momentum channels  $l$

$$\begin{aligned}
 F_{x,l=0}^{HFT} &= \frac{1}{4\pi} \sum_k \left( v_0(r) \frac{\nabla_{\xi} \Psi(\mathbf{r}_1, \dots, \xi, \dots, \mathbf{r}_N) |_{\xi=r_i \mathbf{u}_k}}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} \cdot \left[ \mathbf{e}_x - \frac{\mathbf{r}_{i,x}}{r} \mathbf{u}_k \right] - \frac{\mathbf{r}_{i,x}}{r_i} \frac{dv_0(\xi)}{d\xi} \Big|_{\xi=r_i} \frac{\Psi(\mathbf{r}_1, \dots, r_i \mathbf{u}_k, \dots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} \right) \\
 F_{x,l=1}^{HFT} &= \frac{3}{4\pi} \sum_k \left( \left\{ -v_1(r_i) \mathbf{e}_x \cdot \frac{\mathbf{u}_k}{r_i} + v_1(r_i) \left( \mathbf{r}_i \cdot \mathbf{u}_k \frac{\mathbf{r}_{i,x}}{r_i^3} \right) - \frac{\mathbf{r}_{i,x}}{r_i} \frac{dv_1(\xi)}{d\xi} \Big|_{\xi=r_i} \frac{\mathbf{r}_i \cdot \mathbf{u}_k}{r_i} \right\} \right. \\
 &\quad \times \frac{\Psi(\mathbf{r}_1, \dots, r_i \mathbf{u}_k, \dots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} + v_1(r_i) \frac{\mathbf{r}_i \cdot \mathbf{u}_k}{r_i} \frac{\nabla_y \Psi(\mathbf{r}_1, \dots, \xi, \dots, \mathbf{r}_N) |_{\xi=r_i \mathbf{u}_k}}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} \cdot \left[ \mathbf{e}_x - \frac{\mathbf{r}_{i,x}}{r_i} \mathbf{u}_k \right] \Bigg) \\
 F_{x,l=2}^{HFT} &= \frac{5}{4\pi} \sum_k \left( v_2(r_i) \frac{\Psi(\mathbf{r}_1, \dots, r_i \mathbf{u}_k, \dots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} \left\{ -3 \frac{(\mathbf{r}_i \cdot \mathbf{u}_k)}{r_i^2} \mathbf{u}_k + 3 \frac{(\mathbf{r}_i \cdot \mathbf{u}_k)^2}{r_i^2} \frac{\mathbf{r}_{i,x}}{r_i} \right\} \right. \\
 &\quad - \frac{dv_2(\xi)}{d\xi} \Big|_{\xi=r_i} \frac{\mathbf{r}_i}{r_i} \frac{\Psi(\mathbf{r}_1, \dots, r_i \mathbf{u}_k, \dots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} \left\{ 3 \frac{(\mathbf{r}_i \cdot \mathbf{u}_k)^2}{2 r_i^2} - \frac{1}{2} \right\} \\
 &\quad + v_2(r_i) \frac{\nabla_{\xi} \Psi(\mathbf{r}_1, \dots, \xi, \dots, \mathbf{r}_N) |_{\xi=r_i \mathbf{u}_k}}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} \cdot \left[ \mathbf{e}_x - \frac{\mathbf{r}_{i,x}}{r_i} \mathbf{u}_k \right] \left\{ \frac{3}{2} \frac{(\mathbf{r}_i \cdot \mathbf{u}_k)^2}{r_i^2} - \frac{1}{2} \right\} \Bigg) \\
 F_{x,l=3}^{HFT} &= \frac{7}{4\pi} \sum_k \left( \left\{ v_3(r_i) \left[ \frac{5}{r_i^3} (\mathbf{r}_i \cdot \mathbf{u}_k)^3 \frac{\mathbf{r}_{i,x}}{r_i^2} - \frac{5}{r_i^3} (\mathbf{r}_i \cdot \mathbf{u}_k)^2 \mathbf{u}_{k,x} + \frac{3}{2 r_i} \mathbf{u}_{k,x} - \frac{3}{2 r_i} \mathbf{r}_i \cdot \mathbf{u}_k \frac{\mathbf{r}_{i,x}}{r_i^2} \right] \right. \right. \\
 &\quad + \frac{dv_3(\xi)}{d\xi} \Big|_{\xi=r_i} \left[ \frac{\mathbf{r}_{i,x}}{r_i} \frac{3}{2 r_i} (\mathbf{r}_i \cdot \mathbf{u}_k) - \frac{5}{2 r_i^3} (\mathbf{r}_i \cdot \mathbf{u}_k)^3 \right] \left. \right\} \frac{\Psi(\mathbf{r}_1, \dots, r_i \mathbf{u}_k, \dots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} \\
 &\quad + v_3(r_i) \frac{\nabla_{\xi} \Psi(\mathbf{r}_1, \dots, \xi, \dots, \mathbf{r}_N) |_{\xi=r_i \mathbf{u}_k}}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} \cdot \left[ \mathbf{e}_x - \frac{\mathbf{r}_{i,x}}{r_i} \mathbf{u}_k \right] \left[ \frac{5}{2 r_i^3} (\mathbf{r}_i \cdot \mathbf{u}_k)^3 - \frac{3}{2 r_i} (\mathbf{r}_i \cdot \mathbf{u}_k) \right] \Bigg)
 \end{aligned}$$

NB: need gradients of  $\Psi_T$  w.r.t. electron positions

# QMC Calculations



**Slater Determinant** from Hartree-Fock calculations using CRYSTAL & GAMESS

**Jastrow factor** with e-e, e-n and e-e-n interaction terms

**Pseudopotentials** use Dirac-Fock Average Relativistic Effective Potential

Use CASINO code

Calculate: HFT **forces** and **energies** at 5 geometries,

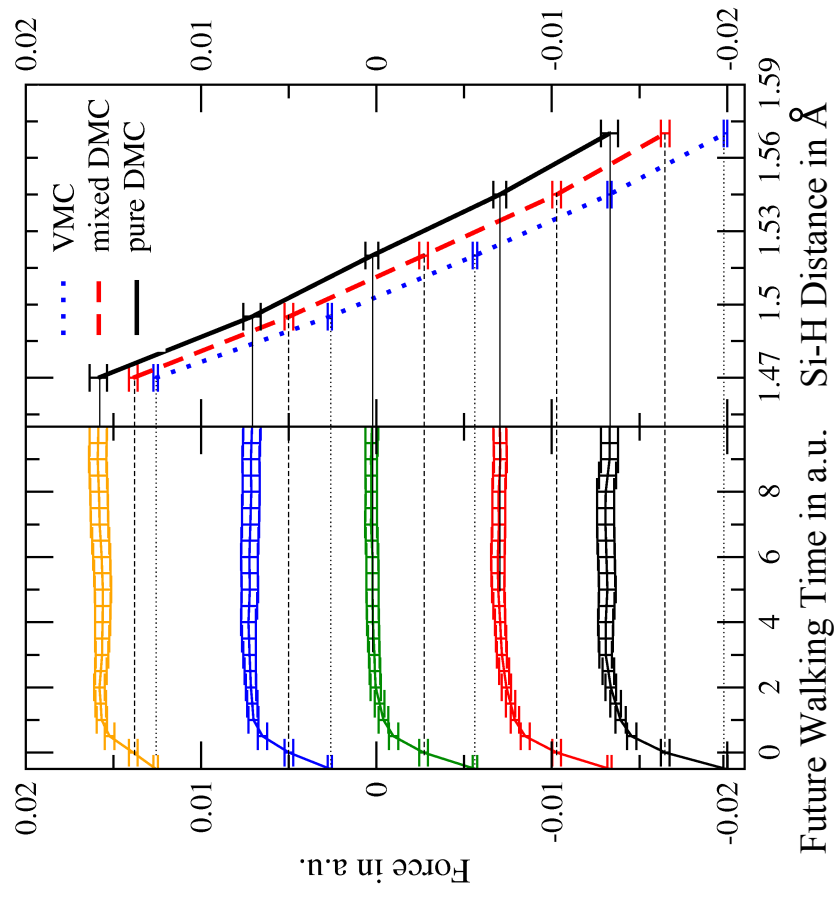
→ do fit → locate bond lengths & harmonic vibrational frequencies



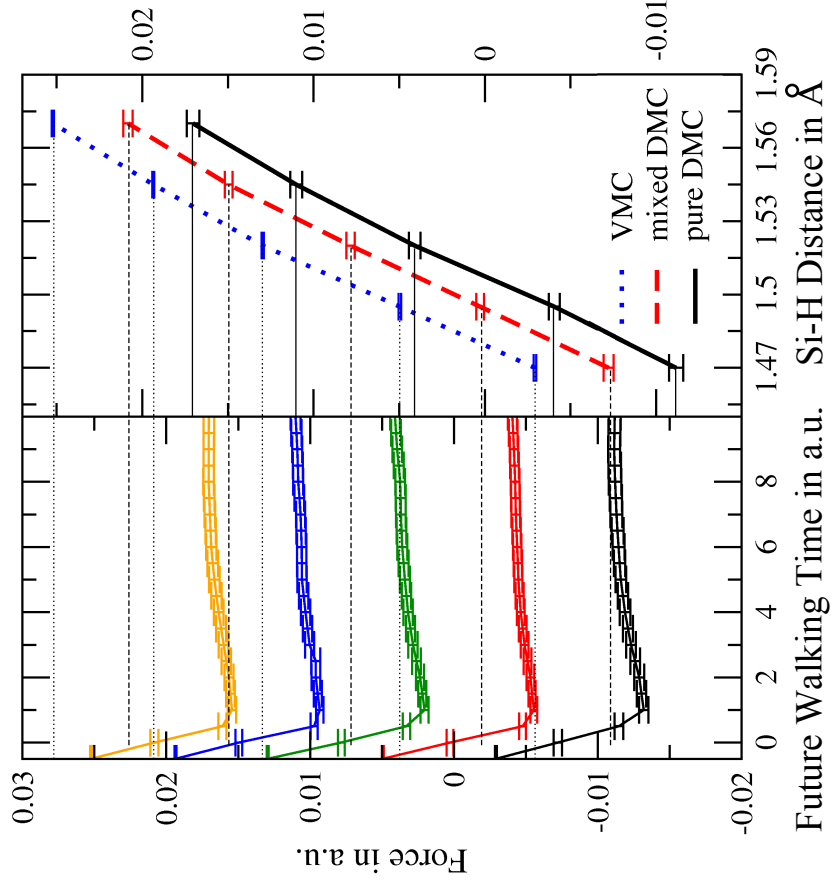


# Example: HFT Forces for SiH

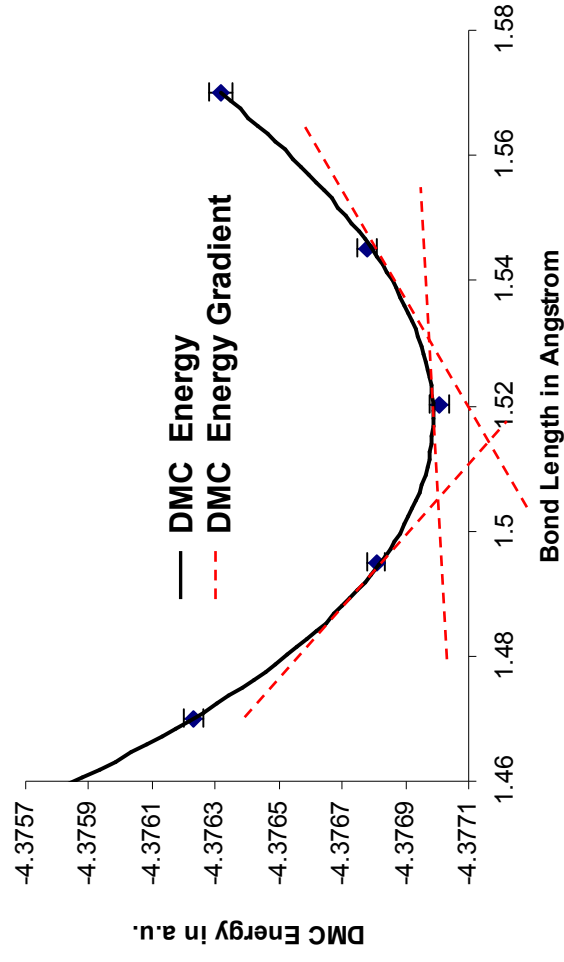
Force on the H atom



Force on the Si atom

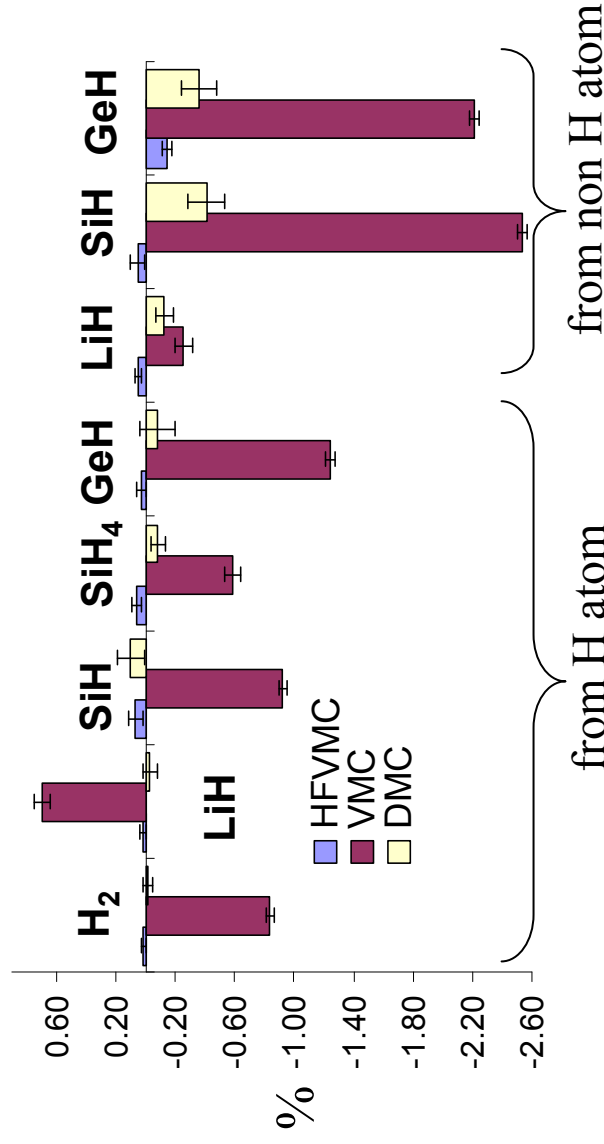


# Example: DMC Energy for SiH



# Bond Lengths in QMC (I)

Bond lengths from **force** minus bond lengths from **energy**



**HFVMC**

Deviation less than 2 standard errors (except for GeH)

➔ Basis set nearly complete in Hartree-Fock

**VMC**

Including Jastrow factor (correlation): deviation several standard errors

➔ Jastrow factor yet not good enough

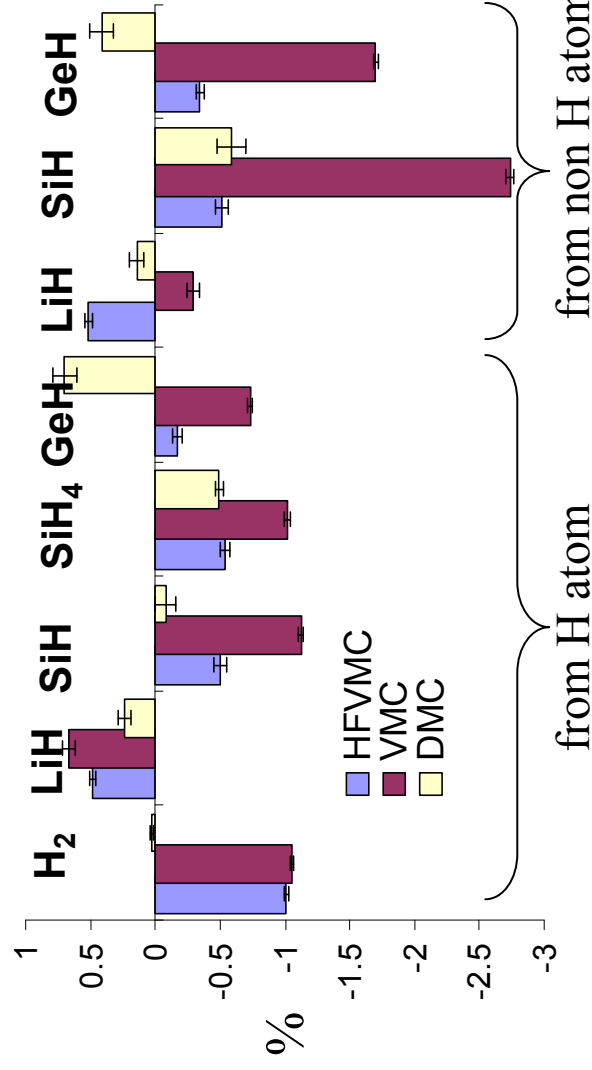
**DMC**

Deviations smaller than 3 standard errors

➔ **nodal & gradient terms negligible for light atoms and small for heavier atoms**

# Bond Lengths in QMC (II)

Bond lengths from force minus bond lengths from experiment



**VMC**

Including Jastrow factor does not improve bond lengths

➔ Jastrow factor yet not good enough

**DMC**

Deviations from expt. on average 0.33(3) % or 0.0051(4) Å

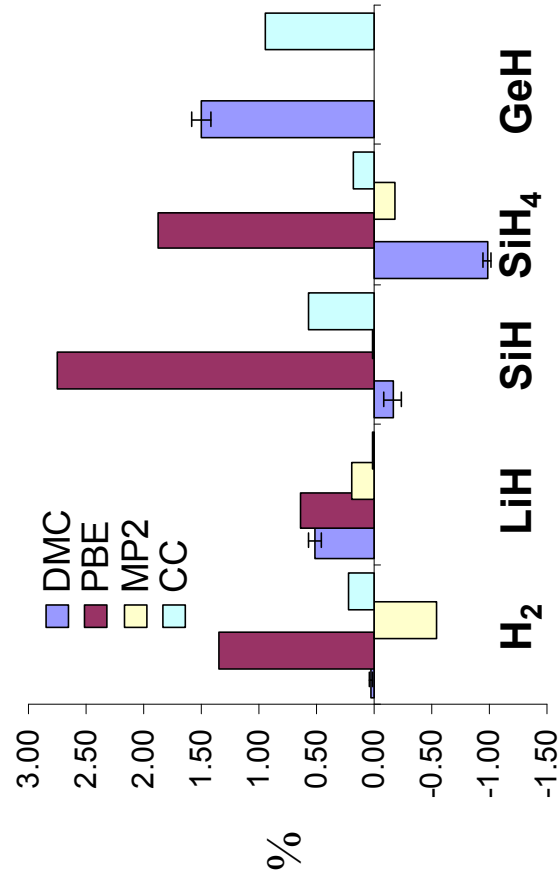
Deviations for light atoms not due to Nodal or Pulay errors

**Possible reasons:**

- pseudopotentials are approx. to all-electron problems • FLA.

# Other Methods

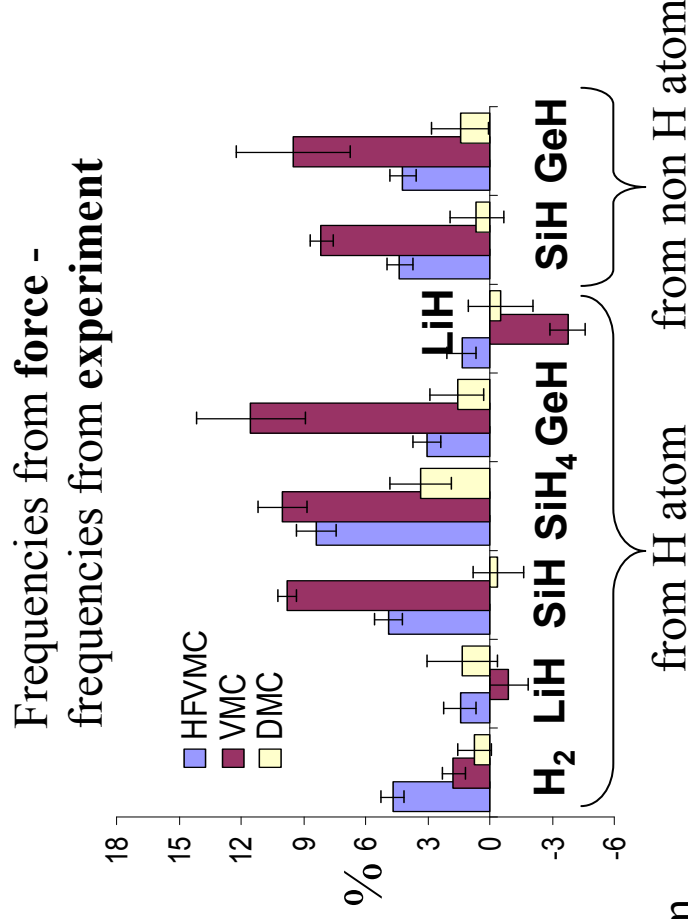
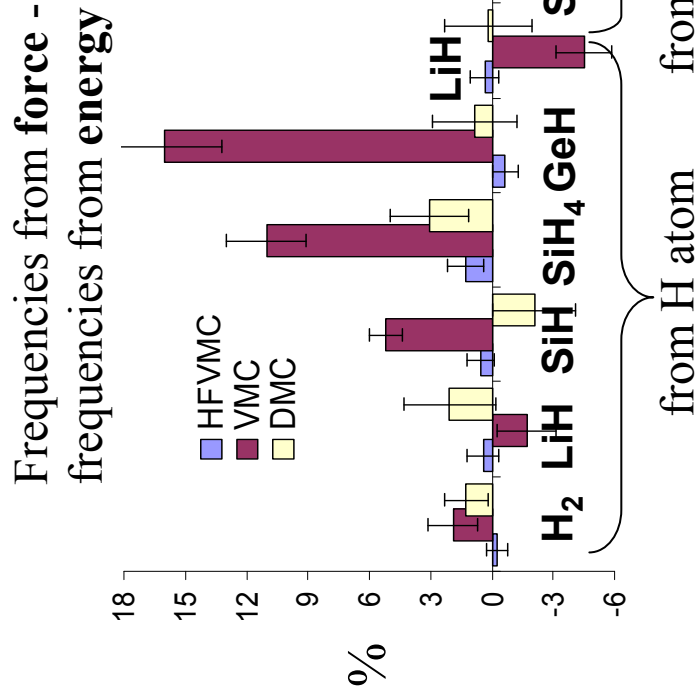
Deviation of bond lengths from  
expt. value for reference methods\*



Deviations on average:  
 0.0051(3) Å in DMC  
 0.0225 Å in PBE-DFT  
 0.0025 Å in MP2  
 0.0056 Å in CC

\*reference methods use cc-pVTZ basis set

# Vibrational Frequencies in QMC



**VMC**

Deviation several standard errors → trial wave function yet not good enough

**DMC**

Deviations within standard error → nodal & gradient terms small

**DMC**

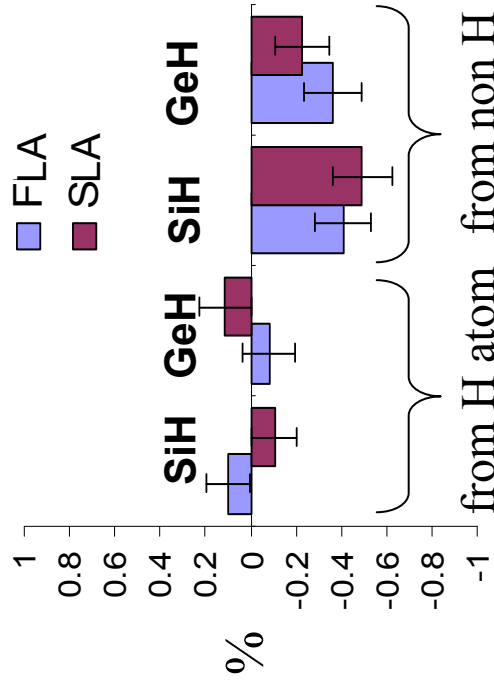
Agreement with experiment on average 1.24(48) % or 26(9) cm<sup>-1</sup>

# Comparing Localization Schemes

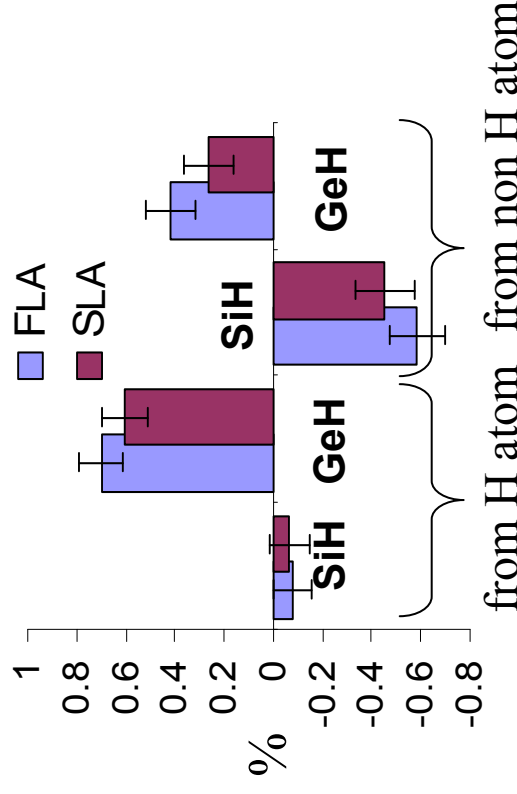


Compare bond lengths for SiH and GeH obtained under the FLA and SLA in DMC

Bond lengths from **force** - bond lengths from **energy**



Bond lengths from **force** - bond lengths from **experiment**



➔ No significant difference in results between FLA and SLA schemes

# Confirm Correctness of Formulae



Consider 3 estimators by choosing s,p or d angular momentum channel of the HFT estimator local. Can evaluate them all in a single run  $\rightarrow$  correlated sampling .....

Calculate forces for SiH

	local channel	$F^{\text{HFT}}$ on H atom	$F^{\text{HFT}}$ on Si atom
HFVMC	<i>s</i>	-0.00256330(17995)	0.00355527(10006)
	<i>p</i>	-0.00256327(17995)	0.003467232(9982)
	<i>d</i>	-0.00256325(17995)	0.002518533(9945)
VMC	<i>s</i>	-0.00561230(12888)	0.01277395(16857)
	<i>p</i>	-0.00561228(12888)	0.01286839(16822)
	<i>d</i>	-0.00561227(12887)	0.01296538(16752)
DMC	<i>s</i>	0.00025314(42964)	0.00153481(44006)
	<i>p</i>	0.00025312(42964)	0.00172872(44006)
	<i>d</i>	0.00025310(42964)	0.00193854(44006)

The 3 estimators in excellent agreement for force on H atom and good on Si atom

- $\rightarrow$  formulae seem correct
- $\rightarrow$  contribution from higher angular momentum channels treated equally well by different local channels  $\rightarrow$  higher channels for HFT operator not necessary





# Conclusions

- Derived expressions for the contribution of non-local pseudopotentials to the **Hellmann-Feynman force in VMC and DMC**
- Calculated **bond lengths & vibrational frequencies** in excellent agreement with those from energies and in good agreement with experiment
- Results **comparable to or better than** those from standard quantum chemistry methods
- **Outlook:** include Pulay terms, improve wave function, larger systems ...

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