

Accurate Forces in QMC with non-local pseudopotentials

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Outline

1. Motivation
2. The Hellmann-Feynman Theorem (HFT) and its application to Hartree-Fock, VMC and DMC
4. Our Approach to Forces using Nonlocal Pseudopotentials
5. Future Walking Diffusion Monte Carlo
6. Results & Discussion
7. Comparison with other QMC and non-QMC Methods
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Why Forces in QMC

1. Today, QMC calculations are usually performed on geometries previously obtained with DFT or other methods (e.g., over 32 small molecules PBE-DFT overestimates geometries by 0.012 Angstrom¹)
2. Calculating Forces in QMC is a first step to many other interesting properties, like vibrational modes, transition states, Dipol moments, Molecular Dynamics, etc.....
3. “We need forces, dummy!” D. Ceperley private homepage
4. Calculating forces is generally considered to be a hard problem with two general approaches 1) calculating analytic expression for forces, 2) using finite difference

¹ using aug-cc-pVTZ basis, X. Xu and W. Goddard, J. Chem, Phys. 121, 4068 (2004)

Hellmann-Feynman Theorem (HFT)

Total Energy: $E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$ Total Force: $F|_R = -\nabla_R E|_R$

HFT^{1,2}: If the wavefunction Ψ is the exact one, i.e. $\Psi = \Psi_0$, the energy gradient is the average of the expectation value of the gradient of H.

$$\nabla_R E|_R = \frac{\langle \Psi_0 | \nabla_R H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} \Big|_R =: F|_R^{\text{HFT}}$$

Proof: (using that Ψ_0 is real and H is Hermitian and denote ∇ by ‘)

$$\begin{aligned} \nabla_R E &= \frac{\langle \Psi | \nabla_R H | \Psi \rangle}{\langle \Psi | \Psi \rangle} + \frac{\langle \Psi' | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} + \frac{\langle \Psi | H | \Psi' \rangle}{\langle \Psi | \Psi \rangle} \\ &= \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle^2} (\langle \Psi' | \Psi \rangle + \langle \Psi | \Psi' \rangle) + \sum_k \frac{\partial E_v}{\partial c_k} \frac{\partial c_k}{\partial R} \\ &= \underbrace{\frac{\langle \Psi | \nabla_R H | \Psi \rangle}{\langle \Psi | \Psi \rangle} + 2 \frac{\langle \Psi'' | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} - 2 \frac{\langle \Psi' | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}}_{F_R^{\text{HFT}}} + \underbrace{\sum_k \frac{\partial E_v}{\partial c_k} \frac{\partial c_k}{\partial R}}_{F_R^{\text{Pulay}}} \end{aligned} \quad (1)$$

In the limit $\Psi \rightarrow \Phi_0$, all terms cancel except for F_R^{HFT} . QED
Hence, HFT holds when Ψ is exact, with a few exceptions...

¹ H. Hellmann, Einführung in die Quantenchemie, Franz Deuticke, Leipzig (1937)

² R. Feynman Phys. Rev. 41 721 (1939)

HFT in Hartree Fock

The HFT forces is the *exact* force in Hartree Fock in the limit of a complete basis or when the basis fct.s are independent of the nuclear position (*exact* in the sense of Hartree-Fock of course)

Proof: omitted, crucial step though is to assume that the derivatives of the basis fct. w.r.t. nuclear position are zero

This is a quite remarkable result that HFT not only holds for $\Psi = \Phi_0$ but also for $\Psi = \Psi^{\text{SD}}$ in the basis set limit !!!

Note, the same prove holds in DFT (1. if basis is complete or 2. when using plane waves)

HFT in VMC

From Eq. (1): $\nabla_R E_{VMC} = \frac{\langle \Psi_T | \nabla H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} + 2 \frac{\langle \Psi_T' | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} - 2 \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle^2} \langle \Psi_T' | \Psi_T \rangle + \sum_k \frac{\partial E_{VMC}}{\partial c_k} \frac{\partial c_k}{\partial R}$

First, assume: $\sum_k \frac{\partial E_{VMC}}{\partial c_k} \frac{\partial c_k}{\partial R} = 0$ Critical, since variance min is used (Ref.[1])

Can sample: $\nabla_R E_{VMC} = \frac{1}{\langle \Psi_T | \Psi_T \rangle} \langle \Psi_T | \nabla H + 2E_L \frac{\Psi_T'}{\Psi_T} - 2E_{VMC} \frac{\Psi_T'}{\Psi_T} | \Psi_T \rangle$

If one neglects Pulay terms: $\nabla_R E_{VMC} = \frac{\langle \Psi_T | \nabla H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}$ (2)

Problem: Infinite Variance

Variance: $\sigma^2 = \langle (\nabla H)^2 \rangle - \langle \nabla H \rangle^2$ with $\nabla H = \sum_{\alpha,i} Z_\alpha \frac{r_i - R_\alpha}{|r_i - R_\alpha|^3} - \sum_{\alpha,\beta} Z_\alpha Z_\beta \frac{R_\alpha - R_\beta}{|R_\alpha - R_\beta|^3}$

For illustration, consider force on H-atom in x direction; av. must be 0; $\Psi = e^{-\alpha r}$

$$\sigma^2 = \langle \frac{x^2}{r^6} \rangle - \langle \frac{x}{r^3} \rangle^2 = \langle \frac{\hat{x}^2}{r^4} \rangle = \int_{\Omega} (\cos \phi \sin \phi)^2 \sin \phi d\phi \int_0^\infty \frac{1}{r^2} e^{-2\alpha r} dr \rightarrow \infty$$

Previous Solutions: (1) avoid HFT and use finite difference (2) renormalize variance a la Assaraf & Caffarel (3) filter out s-component of wavefct.
Our Solution: use pseudopotentials that take away singularity at origin

¹ M. Lee, M. Mella, A. Rappe, J. Chem. Phys. 122 244103 (2005)

HFT in VMC with Zero Variance

Before, we started derivation from $E_{VMC} = \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}$

Instead, start now from $E_{VMC} = \frac{\langle \Psi_T | E_L | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}$

with the local energy $E_L = \Psi_T^{-1} H \Psi_T$

After some algebra, one gets

$$\nabla E_{VMC} = \frac{1}{\langle \Psi_T | \Psi_T \rangle} \langle \Psi_T | H' + \frac{(H - E_L) \Psi_T'}{\Psi_T} + 2 \frac{\Psi_T'}{\Psi_T} (E_L - E_{VMC}) | \Psi_T \rangle \quad (3)$$

Proof that this is a zero variance estimator

If $\Psi_T = \Phi_0 \Rightarrow E_L = E_{VMC}$

also $H\Phi_0 = E\Phi_0 \Rightarrow H'\Phi_0 + H\Phi_0' = E'\Phi_0 + E\Phi_0' \Leftrightarrow H' = \frac{E'\Phi_0 + (E - H)\Phi_0'}{\Phi_0'}$

hence $\nabla E_{VMC} = \frac{1}{\langle \Psi_T | \Psi_T \rangle} \langle \Psi_T | E' | \Psi_T \rangle \blacksquare$

This idea proposed by Assaraf & Caffarel^{2,3} and even before them by Reynolds¹ Assaraf & Caffarel us finite difference to evaluate Ψ'

¹P. Reynolds, et al. Internat. J. Quant. Chem. 29 589 (1986)

²R. Assaraf, M. Caffarel, Phys. Rev. Lett. 83 4682 (1999)

³R. Assaraf, M. Caffarel, J. Chem. Phys. 119 10536 (2003)

HFT in mixed DMC

Mixed Estimator in DMC $E_{mix} = \frac{\langle \Phi_0 | E_L | \Psi_T \rangle}{\langle \Phi_0 | \Psi_T \rangle}$

$$\nabla E_{mix} = \frac{1}{\langle \Phi_0 | \Psi_T \rangle} \langle \Phi_0 | -\nabla H_T - \frac{(H - E_L)\Psi_T'}{\Psi_T} - (E_L - E_{mix}) \left(\frac{\Psi_T'}{\Psi_T} + \frac{\Phi_0'}{\Phi_0} \right) | \Psi_T \rangle \quad (4)$$

Proposed Solution^{1,2}: $\frac{\Psi_T'}{\Psi_T} = \frac{\Psi_0'}{\Psi_0}$

← Not known!

$$\nabla E_{mix} \approx \frac{1}{\langle \Psi_T | \Phi_0 \rangle} \langle \Psi_T | -\nabla H_T - \frac{(H - E_L)\Psi_T'}{\Psi_T} - 2(E_L - E_{mix}) \frac{\Psi_T'}{\Psi_T} | \Phi_0 \rangle$$

the only difference with the earlier VMC estimator is the value of average energy E_{mix} applied in three studies so far, discussed later

¹P. Reynold et al., Internat. J. Quant. Chem. 19 589 (1986)

²M. Assaraf, R. Caffarel, J. Chem. Phys. 119 10536 (2003)

HFT in pure DMC

Pure Estimator in DMC $E_{pure} := \frac{\langle \Phi_0 | H | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle}$  we can not use E_L here !!!

$$\nabla E_{pure} = \frac{1}{\langle \Phi_0 | \Phi_0 \rangle} \langle \Phi_0 | H | \Phi_0 \rangle + 2 \langle \Phi_0 | \frac{\Phi'}{\Phi} (H - E_{pure}) | \Phi_0 \rangle \quad (5)$$

We use Dirichlet BC on nodal surface when solving for DMC ground state. Therefore

$$H\Phi_0 = E_{pure}\Phi_0 + h(\Phi_0)\delta(\mathbf{r} - \mathbf{r}_{node}[\Phi_0]) \quad (6)$$

where h is fct., δ the Dirac Delta fct. and $\mathbf{r}_{node}[\Phi_0]$ the nodal surface of Φ_0 .

Subst. Eq. (6) into Eq. (5) gives

$$\nabla E_{pure} = \frac{1}{\langle \Phi_0 | \Phi_0 \rangle} \left(\langle \Phi_0 | H | \Phi_0 \rangle + 2 \int \Phi' h[\Phi_0] \delta(\mathbf{r} - \mathbf{r}_{nodal}[\Phi_0]) \right)$$

When using pure DMC, the HFT is an unbiased estimator for the negative energy gradient EXCEPT for a ‘‘Pulay nodal term’’

→ Seems favourable to use HFT estimator in pure DMC

Pure Distributions can be obtained by:

- (1) Second-order Extrapolation $\langle F^{HFT} \rangle_{DMC\ pure} \cong 2 \langle F^{HFT} \rangle_{DMC\ mixed} - \langle F^{HFT} \rangle_{VMC}$
- (2) Future Walking
- (3) Reptation MC

Forces via Pseudopotentials (I)

Define the valence Hamiltonian as $H_{\text{val}} = H_{\text{loc}} + W$

where W is non-local psp op. and $H_{\text{loc}} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i < j} \frac{1}{r_{ij}} + \sum_{i,\alpha} V_{\text{loc}}(r_{i\alpha})$

Action of W problematic \rightarrow Pseudopotential Localization Approximation of H_{loc}

using trial wave fct. Ψ_T $H_A = H_{\text{loc}} + \frac{W\Psi_T}{\Psi_T}$

Pure estimator of the HFT Force within the PLA is

$$\langle F \rangle_{\text{HFT}} = -\frac{\langle \Phi_0 | \nabla_R H_A | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} = -\frac{\langle \Phi_0 | \nabla_R \sum V_{\text{loc}} + \nabla \Psi_T^{-1} (W\Psi_T) | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} \quad (7)$$

Get expression for VMC by replacing Φ_0 with Ψ_T

W term from the last equation can be written as

$$\nabla_R \left(\frac{W\Psi_T}{\Psi_T} \right) = \frac{(\nabla_R W)\Psi_T}{\Psi_T} + \frac{W(\nabla \Psi_T)}{\Psi_T} - \frac{(W\Psi_T)(\nabla \Psi_T)}{\Psi_T^2}$$

In VMC, expectation value of last two terms zero (trivial)

$$\text{In DMC: } \int \left(\frac{\Phi_0^2}{\int \Phi_0^2} \frac{W(\nabla \Psi_T) - (\nabla \Psi_T)(W\Psi_T)\Psi_T^{-1}}{\Psi_T} \right) \neq 0 \quad \text{except when } \Psi_T = \Phi_0$$

Classify as additional Pulay terms, are expected to be small \rightarrow neglect later on

Forces via Pseudopotentials (II)

$$\text{Resulting HFT estimator in pure DMC } \langle F \rangle_{HFT} = - \frac{\langle \Phi_0 | \Psi_T^{-1} [(\nabla_R W) \Psi_T] | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} \quad (8)$$

Last expression can be arrived at also differently:

Consider expression for DMC energy without PLA for H_{val} . Then HFT operator is

$$\langle F \rangle_{HFT} = - \frac{\langle \Phi_0 | \nabla_R W | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle}$$

$$\text{Making PLA on HFT operator} \quad \frac{(\nabla_R W) \Phi_0}{\Phi_0} = \frac{(\nabla_R W) \Psi_T}{\Psi_T}$$

Gives same expression for HFT operator as above.

Recall, effective local potential under PLA can be written as

$$\frac{W \Psi_T}{\Psi_T} = \sum_{l,i,\alpha} \frac{2l+1}{4\pi} v_l(r_{i\alpha}) \int d\Omega'_{i\alpha} P_l(\Omega'_{i\alpha}) \frac{\Psi_T(\Gamma_1, \dots, \Gamma'_i, \dots, \Gamma_N)}{\Psi_T(\Gamma_1, \dots, \Gamma_i, \dots, \Gamma_N)} \quad (9)$$

Now, let us derive an expression for $(\nabla W) \Psi_T$, the contribution of W to the HFT force in Eq. (8)

Forces via Pseudopotentials (III)

Let us calculate the force on an atom placed at the origin.

Consider an infinitesimal displacement $\Delta = (x, 0, 0)$ of the nucleus, so that the contribution to the x-component of the HFT force is

$$\frac{dW}{dx} \Big|_{x=0} = \lim_{x \rightarrow 0} \frac{[W(x) - W(0)]\Psi_T(0)}{x}$$

Look at effect of the one-electron non-local operator W on the i^{th} electron at position \mathbf{r}_i

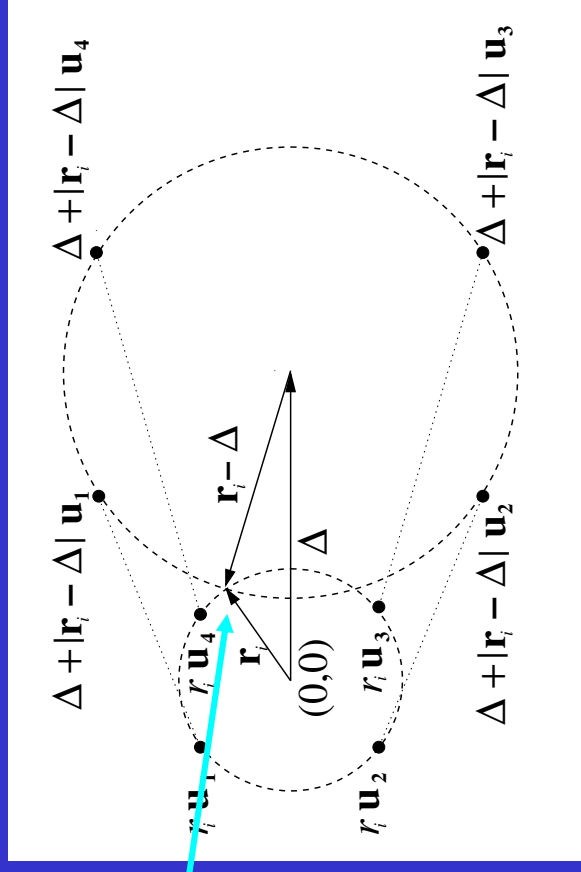
When $\Delta = (0, 0, 0)$, the integration is over a sphere of radius $|\mathbf{r}_i|$ centered at the origin (Eq. (9))

After the displacement, it is over a

sphere of radius $|\Delta - \mathbf{r}_i|$ centered at Δ

Important: need to transform each point of the integration grid

$$\mathbf{r}_i \mathbf{u}_j \rightarrow \Delta + |\Delta - \mathbf{r}_i| \mathbf{u}_j$$



Forces via Pseudopotentials (IV)

Using above analysis, we can straightforwardly obtain the required expressions by

Taylor expanding $[W(\Delta)-W(0)]\Psi_T$ to first order in Δ .

If we define $F_{x,l}^{HFT}$ to be the contribution from angular momentum channel l , we get

$$\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)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} \Big|_{\xi=r_i} \cdot \left[\mathbf{e}_x - \frac{r_{i,x}}{r} \mathbf{u}_k \right] - \frac{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{r_{i,x}}{r_i^3} \right) - \frac{r_{i,x}}{r_i} \frac{dv_1(\xi)}{d\xi} \Big|_{\xi=r_i} \right\} \frac{\mathbf{r}_i \cdot \mathbf{u}_k}{r_i} \right. \\
 &\quad \times \left. \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)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} \Big|_{\xi=r_i} \cdot \left[\mathbf{e}_x - \frac{r_{i,x}}{r_i} \mathbf{u}_k \right] \right) \\
 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{r_{i,x}}{r_i^2} \right\} \right. \\
 &\quad - \left. \frac{dv_2(\xi)}{d\xi} \Big|_{\xi=r_i} \frac{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} - \frac{1}{2} \right\} \right. \\
 &\quad \left. + v_2(r_i) \frac{\nabla_{\xi} \Psi(\mathbf{r}_1, \dots, \xi, \dots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} \Big|_{\xi=r_i} \cdot \left[\mathbf{e}_x - \frac{r_{i,x}}{r_i} \mathbf{u}_k \right] \left\{ 3 \frac{(\mathbf{r}_i \cdot \mathbf{u}_k)^2}{2} - \frac{1}{2} \right\} \right) \\
 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{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{r_{i,x}}{r_i^2} \right] \right. \right. \\
 &\quad \left. \left. + \frac{dv_3(\xi)}{d\xi} \Big|_{\xi=r_i} \left[\frac{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] \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)} \right. \\
 &\quad \left. + v_3(r_i) \frac{\nabla_{\xi} \Psi(\mathbf{r}_1, \dots, \xi, \dots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)} \Big|_{\xi=r_i} \cdot \left[\mathbf{e}_x - \frac{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] \right)
 \end{aligned}$$

Future Walking pure DMC (I)

We want so sample: $\langle A \rangle_{\Phi^2} = \frac{\int \Phi(\mathbf{r}) A(\mathbf{r}) \Phi(\mathbf{r}) d\mathbf{r}}{\int \Phi(\mathbf{r}) \Phi(\mathbf{r}) d\mathbf{r}} = \frac{\int \Phi(\mathbf{r}) A(\mathbf{r}) \frac{\Phi(\mathbf{r})}{\Psi_T(\mathbf{r})} \Psi_T(\mathbf{r}) d\mathbf{r}}{\int \Phi(\mathbf{r}) \frac{\Phi(\mathbf{r})}{\Psi_T(\mathbf{r})} \Psi_T(\mathbf{r}) d\mathbf{r}} = \lim_{k \rightarrow \infty} \frac{\sum_k A(\mathbf{r}_k) w(\mathbf{r}_k)}{\sum_k w(\mathbf{r}_k)}$ (10)

with weights: $w(\mathbf{r}_k) = \frac{\Phi(\mathbf{r}_k)}{\Psi_T(\mathbf{r}_k)}$

Show that $w(\mathbf{r}_k)$ is proportional to the asymptotic pop. of walker \mathbf{r}_k (Ref.[1])

Begin by writing the SE in integral form $\Phi(x,t) = \int G(t,x,z) \Phi(z,t) dz$ (11)

with the Greens fct.

$$G(t,x,z) = \sum_i e^{-(E_i - E_T)t} \Phi_i(x) \Phi_i(z)$$

Get the integral eq. for mixed distribution $f(x,t) = \Psi_T(x) \Phi(x,t)$

Multiply Eq.(11) with Ψ_T $f(x,t) = \int \Psi_T(x) e^{-(E_i - E_T)t} \frac{1}{\Psi_T} \Psi_T(z_0) \Phi(z) dz$ (12)

$$\Phi(z,t) = \sum_i \frac{\Phi_j(z) \Phi_j(z_0)}{\Psi_T(z_0)} \quad (13)$$

Note that identity holds:

Proof: First, assume a single electron, then, associate a delta fct. with it

$$f(z,0) = \Phi(z,0) \Psi_T(z) = \delta(z - z_0) \Leftrightarrow \Phi(z,0) = \frac{\delta(z - z_0)}{\Psi_T(z)} \Leftrightarrow \Phi(z,0) = \frac{\delta(z - z_0)}{\Psi_T(z_0)}$$

then use $\delta(z - z_0) = \sum_i \Phi_i(z) \Phi_i(z_0)$ where Φ_i are eigenfct. of H, Eq. (13) follows ■

Subst. Eq.(13) in (12) gives $f(x,t) = \int \sum_{i,n} \Psi_T(x) e^{-(E_i - E_T)t} \Phi_i(x) \Phi_i(z) \frac{\Phi_n(z) \Phi_n(z_0)}{\Psi_T(z_0)} dz$ (14)

¹K. Liu, M. Kalos *Quantum hard spheres in a channel*, Phys. Rev. A 10, 303 (1974)

Future Walking pure DMC (II)

Last eq. simplifies to $f(x, z_0, t) = \sum_i \Psi_T(x) e^{-(E_i - E_T)t} \Phi_i(x) \frac{\Phi_i(z_0)}{\Psi_T(z_0)}$.

Now, define pop. at time t $q(z_0, t) = \int f(x, z_0, t) dx$,

and the **asymptotic population**, arising from electron z_0 , is defined as

$$q(z_0) = \lim_{t \rightarrow \infty} \int f(x, z_0, t) dx.$$

Therefore, we get $q(z_0) = \lim_{t \rightarrow \infty} \int \sum_i \Psi_T(x) e^{-(E_i - E_T)t} \Phi_i(x) \frac{\Phi_i(z_0)}{\Psi_T(z_0)} dx$
 $= \lim_{t \rightarrow \infty} \sum_i e^{-(E_i - E_T)t} \frac{\Phi_i(z_0)}{\Psi_T(z_0)} \int \Psi_T(x) \Phi_i(x) dx$
 $= \frac{\Phi_i(z_0)}{\Psi_T(z_0)} \int \Psi_T(x) \Phi_0(x) dx = \frac{\Phi_i(z_0)}{\Psi_T(z_0)} \times \text{const.}$

Hence, we can write pure estimator from Eq. (10) as

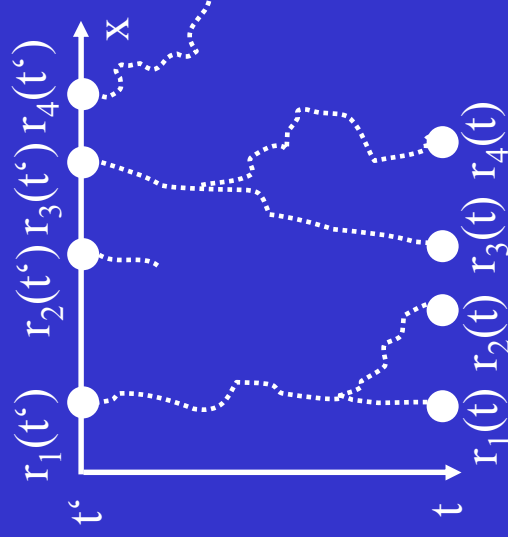
$$\langle A \rangle_{\phi^2} = \frac{\sum_k A(\mathbf{r}_k) \frac{\Psi_T(\mathbf{r})}{\Phi(\mathbf{r})} \sum_k A(\mathbf{r}_k) q(\mathbf{r}_k)}{\sum_k \frac{\Psi_T(\mathbf{r})}{\Phi(\mathbf{r})} \sum_k q(\mathbf{r}_k)}, \quad (15)$$

where the const. cancels in numerator & denominator. Last eq. can be sampled where q is asymptotic population (weights) when $t \rightarrow \infty$ of walker \mathbf{r}_k . Note, sum is over all walkers in one pop & at all time steps.

Future Walking Algorithm (I)

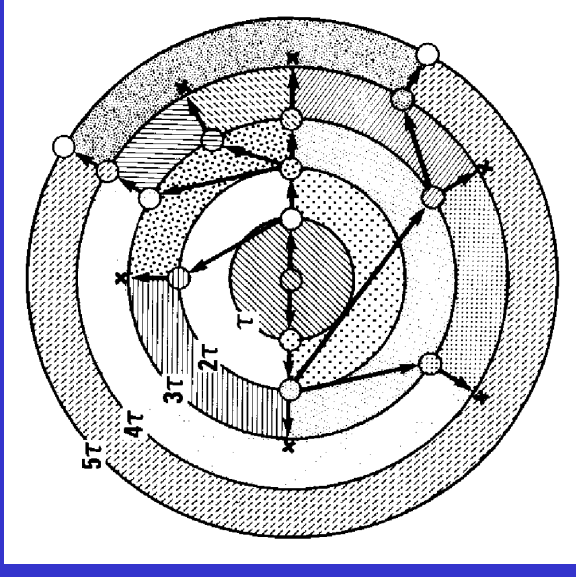
The Tagging Algorithm:

- In the simulation, assign a label to each walker to identify from which parent it is coming from
- Then, at time t , count all descendants that come from $r_k(t')$ with $t > t'$. The total number := $q[r_k(t')]$
- Example



where $q[r_1(t)] = 2$, $q[r_2(t)] = 0$, $q[r_3(t)] = 2$, $q[r_4(t)] = 0$

- evaluate $\langle A \rangle_{\phi^2} \approx \frac{\sum_k A[r_k(t')] q[r_k(t')]}{\sum_k q(r_k)}$ = $\frac{1}{4} (2F(r_1[t']) + 2F(r_3[t']))$



Ref: R. Barnett, et al. J. Chem. Phys. 96, 258 (1991)

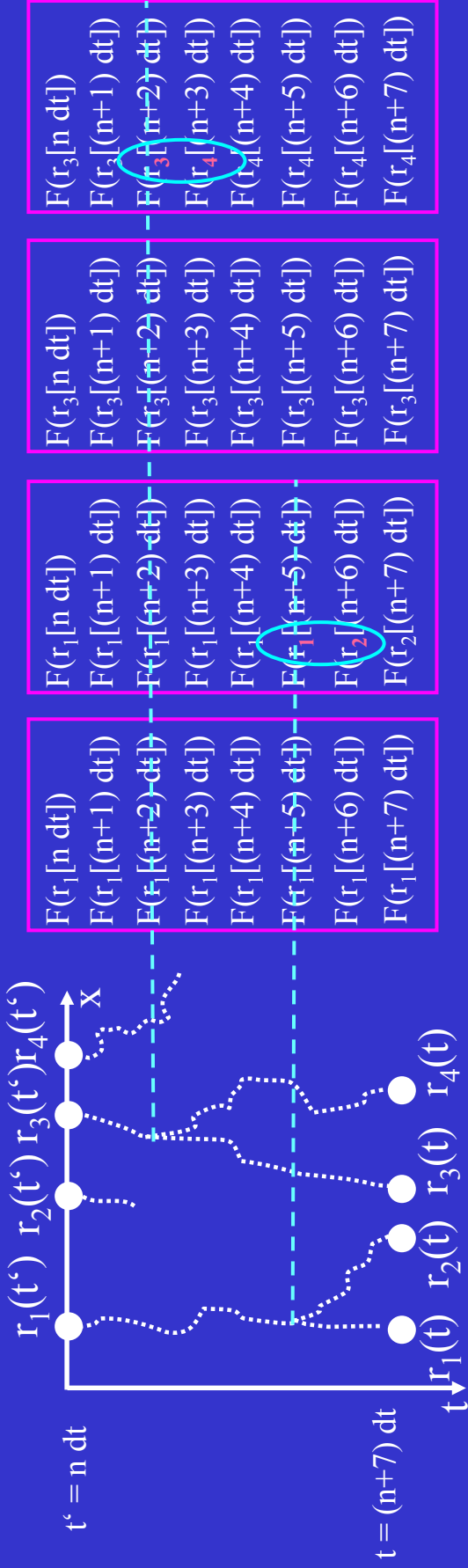
Future Walking Algorithm (II)

History vector of walker r at

time $t = (n+7) dt$ for local force

F and no branching

- A no-Tagging Algorithm:
 - Store all sampled past items (e.g., local forces) in a **“history vector”** for each walker
 - Branch/Delete walker as usual; at the same time branch/delete history vector
 - Example of history vectors at time $t = (n+7) dt$



- evaluate estimator at time t by averaging over all F at time t'

$$\langle A \rangle_{\phi^2} \approx \frac{1}{N} \sum_k A[R_k(t')] = \frac{1}{4} (2F(r_1[ndt]) + 2F(r_3[ndt]))$$

which is same as before!

QMC Calculations

Use trial wave fct. of single-determinant Slater Jastrow form

Basis set: Orbitals forming SD from HF calculations using CRYSTAL with Gaussian basis set of sixtuple-zeta quality (no f and g fct.) Zeta coefficients are carefully re-optimized (line-minimization)

Jastrow factor: with e-e, e-n and e-e-n interaction terms with expansion orders of 6,6 and 3, respectively. Consider spin-dependency. Use unweighted variance minimization to optimize values

Pseudopotentials: use Dirac-Fock Average Relativistic Effective Potential (AREP). The derivatives of componentas are evaluated numerically using extended from of Neville's algorithm

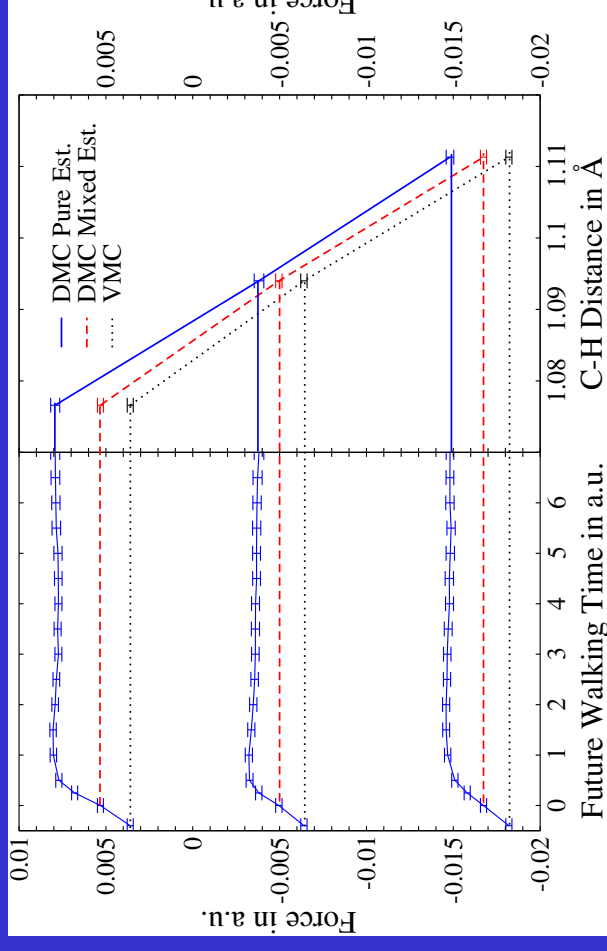
Used CASINO code (future walking is now standard in CASINO2.0 !!)

Quality of our Wave fct.s

	E_{HF} [Ha]	E_{VMC} [Ha]	E_{DMC} [Ha]	E_{corr} [%]
H ₂ J(660)	-1.13368	-1.17240(0)	-1.17441(1)	95.1
H ₂ J(663)	-1.13368	-1.17391(0)	-1.17439(1)	98.8
LiH	-0.75060	-0.78780(1)	-0.78811(0)	99.2
CH ₄	-7.84247	-8.06684(3)	-8.07840(7)	95.1
SiH ₄	-6.08890	-6.27142(3)	-6.27906(5)	96.0
H ₂ O	-16.91977	-17.19972(6)	-17.21482(5)	94.9

→ overall very good trial wave fct.s

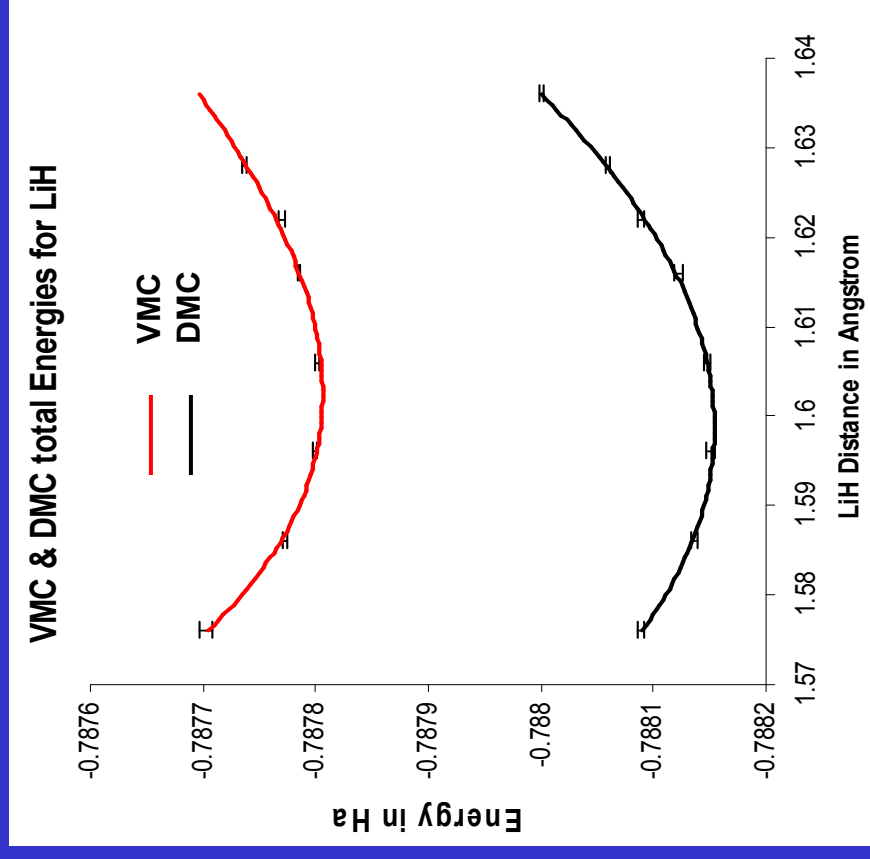
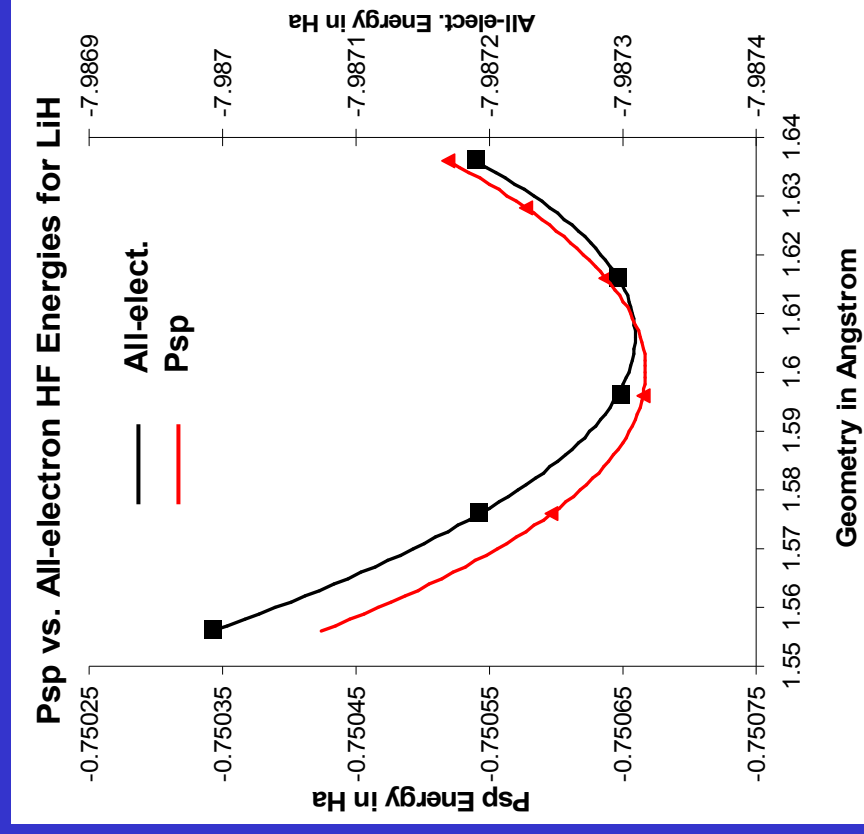
Some Technicalities



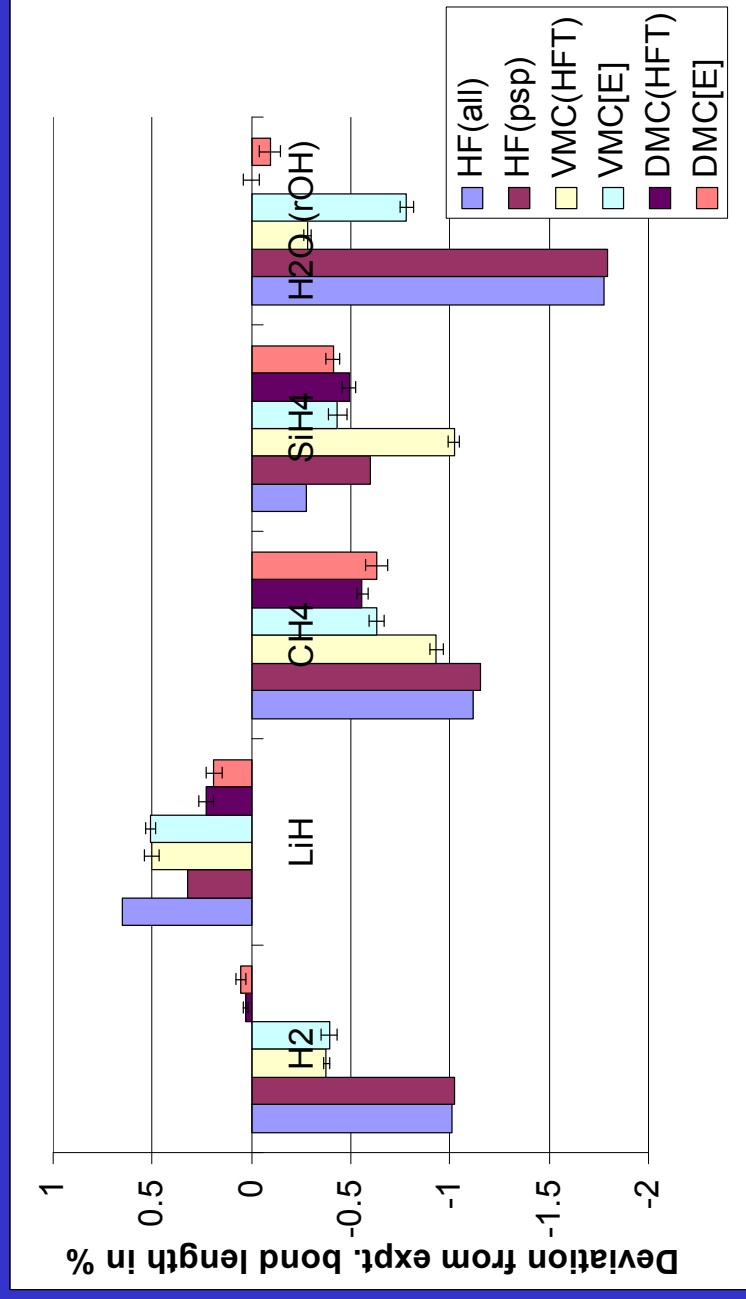
- Sufficient to use future walking projection time of 5 a.u. (for all systems)
- Future walking (pure) DMC estimates correspond to extrapolated estimates (2DMC-VMC) – true for all our calculations !!
- To extract forces & vibrational frequencies, we evaluate HFT force at 5 different geometries around equilibrium geometry, then do quadratic fit
- As ref. data, we also obtain geometries & frequency from total energies

Extracting Geometries

What do we mean by “equilibrium geometries“ ? Geometries where the potential energy surface has a minimum \Leftrightarrow geometries where the interatomic forces are zero



Equilibrium Geometries in DMC



Define error in VMC $\epsilon_{VMC}^{Pulay} = a_{VMC}^{HFT} - a_{VMC}^E$

and in DMC $\epsilon_{DMC}^{Pulay+PLA} = a_{DMC}^{HFT} - a_{DMC}^E$

Note: even if wave fct. (hence the nodes) are exact, still deviation from experiment

Seems plausible to correct disagreement $a_{DMC}^{HFT} - a_{expt}$ by adding difference

$a_{HF(all)}^E - a_{HF(pp)}^E$ to a_{DMC}^{HFT}

→ improves disagreement for some molecules, but not for all

Geometries in DMC & VMC

	$a_{\text{HF}}^{\text{E}}(\text{all})$	$a_{\text{HF}}^{\text{E}}(\text{pp})$	$a_{\text{VMCHF}}^{\text{HFT}}$	$a_{\text{VMC}}^{\text{HFT}}$	$a_{\text{VMC}}^{\text{E}}$	$\epsilon_{\text{VMC}}^{\text{Pulay}}$	$a_{\text{DMC}}^{\text{HFT}}$	$a_{\text{DMC}}^{\text{E}}$	$\epsilon_{\text{DMC}}^{\text{Pulay+PLA}}$	$a_{\text{expt.}}$
H ₂ J(660)	0.7335	0.7334	0.7335(1)	0.7382(1)	0.7381(3)	0.0001(3)	0.7412(1)	0.7414(2)	-0.0002(2)	0.741
H ₂ J(663)	0.7335	0.7334	0.7335(1)	0.7332(1)	0.7394(2)	-0.0062(2)	0.7412(1)	0.7413(2)	-0.0001(2)	0.741
LiH	1.6061	1.6008	1.6007(6)	1.6037(6)	1.6038(4)	-0.0001(7)	1.5993(6)	1.5987(3)	0.0006(7)	1.5957
CH ₄ (<i>r</i> CH)	1.0818	1.0814	1.0823(4)	1.0838(4)	1.0871(4)	-0.0033(6)	1.0879(3)	1.0871(6)	0.0008(7)	1.094
SiH ₄ (<i>r</i> SiH)	1.4759	1.4711	1.4721(5)	1.4649(4)	1.4736(7)	-0.0087(8)	1.4727(5)	1.4739(5)	-0.0012(7)	1.480
H ₂ O (<i>r</i> HO)	0.9408	0.9406	0.9417(2)	0.9551(2)	0.9503(3)	0.0048(4)	0.9578(4)	0.9569(5)	0.0009(6)	0.9578
H ₂ O (α HO)	105.72	105.73	105.68(9)	109.42(19)	106.06(45)	3.36(49)	105.48(34)	104.66(48)	0.82(59)	104.51

- On DMC level, $\epsilon_{\text{DMC}}^{\text{Pulay+PLA}}$ is rather small for all bond lengths, is largest for SiH₄ → good agreement between $a_{\text{DMC}}^{\text{HFT}}$ and $a_{\text{DMC}}^{\text{E}}$
- Agreement with expt., i.e., between $a_{\text{DMC}}^{\text{HFT}}$ and $a_{\text{expt.}}$, is a bit worse; it is worst for SiH₄ (0.0073(7)Å); this discrepancy is possibly due to Pulay nodal term or PLA
- On VMC level, $\epsilon_{\text{VMC}}^{\text{Pulay}}$ is larger than in DMC → wave fct. very good, but probably not good enough ... also, we used variance minimization
- Agreement with experiment is much worse than in DMC with the largest deviation of 0.0149(4) Å for SiH₄. This is plausible...

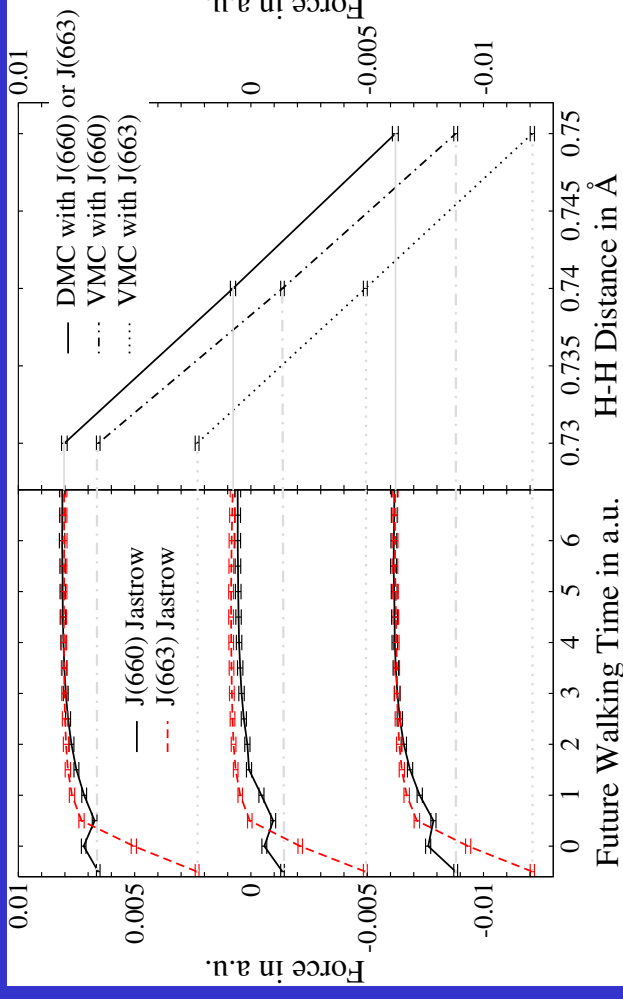
Geometries in VMC

	$E_{\text{HF}}^{\text{(all)}}$	$E_{\text{HF}}^{\text{(pp)}}$	$\alpha_{\text{VMCHF}}^{\text{HFT}}$	$\alpha_{\text{VMC}}^{\text{HFT}}$	E_{VMC}	$\epsilon_{\text{VMC}}^{\text{Pulay}}$	$\alpha_{\text{DMC}}^{\text{HFT}}$	E_{DMC}	$\epsilon_{\text{DMC}}^{\text{Pulay+PLA}}$	$a_{\text{expt.}}$
H ₂ J(660)	0.7335	0.7334	0.7335(1)	0.7382(1)	0.7381(3)	0.0001(3)	0.7412(1)	0.7414(2)	-0.0002(2)	0.741
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H ₂ O (α HO)	105.72	105.73	105.68(9)	109.42(19)	106.06(45)	3.36(49)	105.48(34)	104.66(48)	0.82(59)	104.51

	E_{HF} [Ha]	E_{VMC} [Ha]	E_{DMC} [Ha]	E_{corr} [%]
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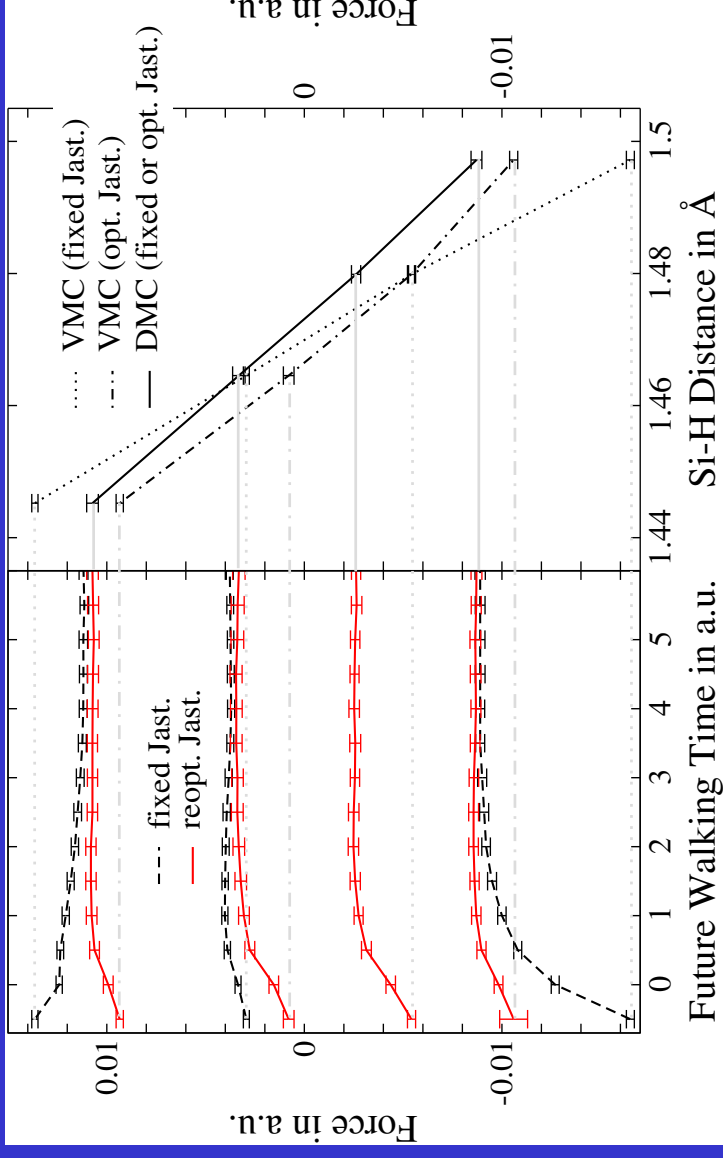
- Note, we also do not find correlation between magnitude of Pulay error and %age of correlation energy, in particular, compare results H₂ using Jastrow factors J(660) and J(663)

Influence of Jastrow factor for H_2



- VMC forces for H_2 is closer to DMC forces with the J(660) Jastrow factor than with the J(663) one

Influence of Jastrow factor for SiH₄



- VMC forces for SiH₄ very different for unopt. Jastrow than for re-opt. one
- DMC forces seem independent of slightly different Jastrow factors

Geometries in HFVMC

	$a_{\text{HF(all)}}^{\text{E}}$	$a_{\text{HF(pp)}}^{\text{E}}$	$a_{\text{VMCHF}}^{\text{HFT}}$	$a_{\text{VMC}}^{\text{HFT}}$	$a_{\text{VMC}}^{\text{E}}$	$\epsilon_{\text{VMC}}^{\text{Pulay}}$	$a_{\text{DMC}}^{\text{HFT}}$	$a_{\text{DMC}}^{\text{E}}$	$\epsilon_{\text{DMC}}^{\text{Pulay+PLA}}$	$a_{\text{expt.}}$
H ₂ J(660)	0.7335	0.7334	0.7335(1)	0.7382(1)	0.7381(3)	0.0001(3)	0.7412(1)	0.7414(2)	-0.0002(2)	0.741
H ₂ J(663)	0.7335	0.7334	0.7335(1)	0.7332(1)	0.7394(2)	-0.0062(2)	0.7412(1)	0.7413(2)	-0.0001(2)	0.741
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H ₂ O (α HO)	105.72	105.73	105.68(9)	109.42(19)	106.06(45)	3.36(49)	105.48(34)	104.66(48)	0.82(59)	104.51

- Recall that HFT holds on HF level if basis set is complete!
- On the HFVMC level, $a_{\text{HF(pp)}}^{\text{E}}$ and $a_{\text{VMCHF}}^{\text{HFT}}$ agree within error bars for H₂ and LiH indicating that basis sets are nearly complete
- For other molecules, deviation about 2-5 times statistical error bar with the largest deviation for H₂O (*r*OH) of 0.0011(2) Å. This indicates that basis sets are of good quality

Vibrational Frequencies

	$\omega_{\text{HF(ae)}}^{\text{E}}$	$\omega_{\text{HF(pp)}}^{\text{E}}$	$\omega_{\text{VMCHF}}^{\text{HFT}}$	$\omega_{\text{VMC}}^{\text{HFT}}$	$\omega_{\text{VMC}}^{\text{E}}$	$\epsilon_{\text{VMC}}^{\text{Pulay}}$	$\omega_{\text{DMC}}^{\text{HFT}}$	$\omega_{\text{DMC}}^{\text{E}}$	$\epsilon_{\text{DMC}}^{\text{Pulay+PLA}}$	ω_{expt}
H ₂	4580	4621	4608(24)	4478(25)	4394(48)	84(54)	4434(35)	4379(30)	55(46)	4401
LiH	1488	1413	1418(20)	1381(13)	1424(24)	-43(27)	1387(20)	1409(17)	-22(26)	1405
CH ₄ (<i>r</i> CH)	3147	3175	3141(22)	3123(31)	2925(20)	198(37)	3045(24)	2959(53)	86(58)	2917
SiH ₄ (<i>r</i> SiH)	2336	2340	2370(21)	2405(26)	2166(33)	239(42)	2260(23)	2193(27)	67(35)	2187

- Define error terms as before
- On the DMC level, Pulay error $\epsilon_{\text{DMC}}^{\text{Pulay+PLA}}$ is smaller than two standard deviations \rightarrow good agreement between $\omega_{\text{DMC}}^{\text{HFT}}$ and $\omega_{\text{DMC}}^{\text{E}}$
- Agreement with experiment a bit less good, largest for CH₄ (128(24) cm⁻¹)
- On the VMC level, Pulay error $\epsilon_{\text{VMC}}^{\text{Pulay}}$ largest for SiH₄ (239(42) cm⁻¹) and similar for CH₄
- On HFVMC level, same good agreement between frequencies from HFT force and from energy \rightarrow good basis sets

Confirm Correctness of Formulae

- Consider 3 estimators by choosing s,p or d angular moment. channel of the HFT estimator local. Can evaluate them all in a single run → correlated sampling
- Calculate forces for SiH₄ and H₂O for each level of theory

	local channel	F _{HFT}	
		SiH ₄ (<i>r</i> SiH)	H ₂ O (<i>a</i> HO)
VMCHF	<i>s</i>	-0.00303498(21578)	-0.00201223(17723)
	<i>p</i>	-0.00303499(21577)	-0.00201253(17723)
	<i>d</i>	-0.00303499(21577)	-0.00201272(17722)
VMC	<i>s</i>	-0.00542549(20553)	-0.00993357(28437)
	<i>p</i>	-0.00542543(20554)	-0.00993423(28438)
	<i>d</i>	-0.00542539(20554)	-0.00993456(28439)
DMC	<i>s</i>	-0.00427329(14329)	-0.00261773(22800)
	<i>p</i>	-0.00427319(14329)	-0.00261743(22801)
	<i>d</i>	-0.00427315(14329)	-0.00261727(22802)

- The three estimators are in excellent agreement at each level of theory. Also, agreement does not even change when going from HFVMC to VMC and DMC
- ➡ - That means our formulae and their implementation seem correct
- ➡ - Also, contribution from f and higher angular momentum channels are treated equally well using each of the different local channels → higher non-local channels for HFT operator seem not necessary

Different Contributions to HFT forces

- Evaluate HFT force for same molecules using HFVMC and break down different contributions

	SiH ₄ (r_{SiH})	H ₂ O (a_{HO})
$\langle F \rangle_{s(\text{local})}^{\text{VMCHF}} (> r_c)$	-0.57147(7)	0.06804(6)
$\langle F \rangle_{s(\text{local})}^{\text{VMCHF}} (< r_c)$	-0.04267(8)	0.00335(8)
$\langle F \rangle_{\text{VMCHF}}^{\text{VMCHF}}$	-0.01814(15)	0.00139(12)
$\langle F \rangle_{p-s(\text{non-local})}^{\text{VMCHF}}$	0.00032(1)	-0.00002(1)
$\langle F \rangle_{d-s(\text{non-local})}^{\text{VMCHF}}$	0.6289213	0.0747658
$F_{\text{Ion- Ion}}$		
$\langle F \rangle_{\text{total}}^{\text{VMCHF}}$	-0.0030(2)	-0.0020(2)
$-\nabla E_{\text{HF}}$	-0.003475	-0.001958

- Largest contribution from outside the local cutoff radius
- Contribution from second non-local channel generally two orders of magnitude smaller

Error Analysis (I)

Non-local pseudopotentials introduce two separate errors in the evaluate of HFT forces within DMC:

a) One error is due to PLA for valence Hamiltonian (replacing H_{val} by H_A)
→ changes dynamics in diffusion equation → alters mixed distribution
(error is quadratic when evaluating energy¹)

b) One error is due to PLA of HFT operator

To derive expressions for these errors, make splitting

$$\Phi_A = \alpha_A \Phi_0 + \beta_A \delta_A \quad \text{and} \quad \Psi_T = \alpha_T \Phi_0 + \beta_T \delta_T$$

where Φ_0 is exact ground state of H_{val} , and $\delta_{A/T}$ components orthogonal to it.

Define exact pure estimator of Hermitian op. O as $\langle O \rangle_{0,pure} := \frac{\langle \Phi_0 | O | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle}$

Define VMC estimator and effective pure DMC estimator as

$$\langle O \rangle_{VMC} := \frac{\langle \Psi_T | O | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} \quad \text{and} \quad \langle O \rangle_{A,pure}^{loc} := \frac{\langle \Phi_A | \Psi_T^{-1}(O \Psi_T) | \Phi_A \rangle}{\langle \Phi_A | \Phi_A \rangle}.$$

¹ L. Mitas, E. Shirley, D. Ceperley, J. Chem. Phys. 95 3467 (1991)

Error Analysis (II)

Inserte expansions for Ψ_T and Φ_A into estimators and Taylor approximate:

$$\begin{aligned} \langle O \rangle_{VMC} - \langle O \rangle_{0,pure} &= 2 \frac{\beta_T \langle \Phi_0 | O | \delta_T \rangle}{\alpha_T \langle \Phi_0 | \Phi_0 \rangle} + \frac{\beta_T^2 \langle \delta_T | O - \langle O \rangle_0 | \delta_T \rangle}{\alpha_T^2 \langle \Phi_0 | \Phi_0 \rangle} + O\left(\frac{\beta_T^3}{\alpha_T^3}\right) \\ \langle O \rangle_{A,pure}^{loc} - \langle O \rangle_{0,pure} &= \frac{\beta_A \langle \Phi_0 | O | \delta_A \rangle}{\alpha_A \langle \Phi_0 | \Phi_0 \rangle} + \frac{\beta_A^2 \langle \delta_A | \Phi_0^{-1}(O\Phi_0) - \langle O \rangle_{0,pure} | \delta_A \rangle}{\alpha_A^2 \langle \Phi_0 | \Phi_0 \rangle} \\ &+ \frac{\beta_T^2 \langle \delta_T | \Phi_0^{-1}(O\Phi_0) - \langle O \rangle_{0,pure} | \delta_A \rangle}{\alpha_T^2 \langle \Phi_0 | \Phi_0 \rangle} - \frac{\beta_A \beta_T \langle \delta_A | \Phi_0^{-1}(O\Phi_0) - \langle O \rangle_{0,pure} | \delta_T \rangle}{\alpha_A \alpha_T \langle \Phi_0 | \Phi_0 \rangle} + O\left(\frac{\beta^3}{\alpha^3}\right) \end{aligned}$$

- Error in VMC estimator is linear in β_T/α_T
- **!!!** In DMC estimator, 1st&2nd term result from PLA(H), 1st is linear in β_A/α_A unless...
- 3rd term arises from PLA(F) and is quadratic in β_T/α_T
- PLA(H) & PLA(F) can principally be done independently. 4th term arises only when these two approximations are made together and is quadratic
- Note, all error terms vanish if $\Psi_T = \Phi_0$
- Recall, $\varepsilon_{VMC}^{Pulay} > \varepsilon_{DMC}^{Pulay+PLA}$, this can be explained by $|\beta_A/\alpha_A| \ll |\beta_T/\alpha_T|$ since Φ_A is likely to be much more accurate than Ψ_T

Comparison with Ref. Methods

Look at deviations of geometries & frequencies from experimental data

	Δa_{DMC}	Δa_{PBE}	Δa_{MP2}	Δa_{CC}	$a_{\text{expt.}}$
H ₂	0.0002(1)	0.010	-0.004	0.0016	0.741
LiH	0.0036(7)	0.0103	0.0030	0.0002	1.5957
CH ₄ (<i>r</i> CH)	0.0061(3)	0.002	0.0055	0.0096	1.094
SiH ₄ (<i>r</i> SiH)	-0.0073(6)	0.0277	-0.0026	0.0026	1.480
H ₂ O (<i>r</i> HO)	0.0000(4)	0.0132	0.0012	0.0017	0.9578
H ₂ O (<i>a</i> HO)	0.97(34)	-0.44	-0.99	-0.92	104.51

TABLE VI: Equilibrium geometries in Å calculated using various all-electron reference methods and given as deviations from the experimental geometries are compared with those obtained from calculated DMC HFT forces. The PBE results are obtained using the aug-cc-pVTZ basis set,³² except for SiH₄, where the cc-pVDZ basis set is used.²⁶ The MP2 results are obtained using the cc-pVTZ basis set, except for LiH, where the 6-311G** basis set is used.²⁶ The CC results are obtained with the cc-pVTZ basis and the CCSD(T) method,²⁶ except for LiH, where the CCD method is used with a basis set of a quality better than sixtuple-zeta.³³ All experimental values are taken from Ref. 26 except for H₂O which is from Ref. 31.

	$\Delta \omega_{\text{DMC}}$	$\Delta \omega_{\text{PBE}}$	$\Delta \omega_{\text{MP2}}$	$\Delta \omega_{\text{CC}}$	$\omega_{\text{expt.}}$
H ₂	33(35)	-84	125	9	4401
LiH	-18(20)	-31	31	-1	1405
CH ₄ (<i>r</i> CH)	128(24)	57	159	119	2917
SiH ₄ (<i>r</i> SiH)	73(23)	-27	109	64	2187

TABLE VII: Harmonic vibrational frequencies in cm⁻¹ calculated using various methods and given as deviations from the experimental frequencies are compared with those obtained from calculated DMC HFT forces. The PBE and MP2 data are obtained using the cc-pVTZ basis set, except for LiH, where the 6-311G** basis set is used for MP2.²⁶ The CC results are obtained with the cc-pVTZ basis and the CCSD(T) method,²⁶ except for LiH, where a basis set of quality better than sixtuple-zeta with the CCD method is used.³³ The experimental values are taken from Ref. 26.

In summary, consider average over all deviations

0.002(0) Å for DMC, 0.012 Å for PBE-DFT, 0.003 Å for MP2, 0.003 for CC
63(26) cm⁻¹ for DMC, 50 cm⁻¹ for PBE-DFT, 106 cm⁻¹ for MP2, 48 cm⁻¹ for CC

Comp. with other QMC methods

1. (2003) Assaraf & Caffarel¹ obtain with their variance reduction scheme and variance minimization optimization method geometries that differ for DMC on average by 0.007(4) Å from expt. data for H₂, LiH and LiI₂.
2. (2003) Casalegno et al.² used same method in addition with an energy minimization scheme and include the Pulay error terms. Their geometries for H₂ and LiH deviate from expt. by 0.002(1) Å and 0.006(3) Å, respectively.
3. (2005) Using the same method, Lee et al.³ present bond lengths for eight diatomic molecules with an average deviation of 0.0097(5) Å from experimental data.
Note: all geometries so far are extracted from Morse Potential fit !!!
4. (2005) Chiesa & Ceperley⁴ obtain with their filtering technique geometries that differ for DMC on average by 0.002(1) Å from expt. data for 6 molecules.

¹Assaraf, M. Caffarel, J. Chem. Phys. 119 10536 (2003)

²M. Casalegno, M. Mella, A. Rappe J. Chem. Phys. 118 7193 (2003)

³M. Lee et al., J. Chem. Phys. 122 244103 (2005)

⁴S. Chiesa and D. Ceperley, S. Zhang, PRL 94 036404 (2005)

Conclusion

- We derived expression for the contribution of a non-local pseudopotential to the HFT force in VMC and DMC.
- Expressions for the components of the HFT force arising from non-local pseudopotentials involve gradients of Ψ_T w.r.t. electron position.
- Derived equilibrium geometries and harmonic vibrational frequencies are in excellent agreement with those obtained from energies as well as in good agreement with experimental data.
- The Jastrow factor seems to be very important on the VMC level but seems much less important on the DMC level.
- In future studies, our approach can be used in connection with other methods previously conceived to improve the HFT estimator, e.g., using energy minimization, using better trial wave fct.s such as multi-ref. or backflow fct.s and adding Pulay terms.
- Also, our expressions can straight forwardly be applied to larger systems, in particular, systems with periodic boundary conditions.

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Comp. with other QMC methods (I)

Using variance minimization

TABLE I. VMC, DMC, and hybrid estimates of the equilibrium geometry R_e (a.u.) and harmonic frequency ω_e (cm^{-1}). The atomic isotopic masses taken^a are 1.007 825 035 amu for ¹H and 7.016 003 0 amu for ⁷Li.

	H ₂	LiH	Li ₂
R_e (VMC)	1.463(12)	3.11(17)	5.346(27)
R_e (DMC)	1.426(13)	3.056(6)	5.200(16)
R_e (hybrid)	1.395(15)	3.001(15)	5.068(27)
R_e (Expt.) ^b	1.401	3.015	5.051
ω_e (VMC)	4194(130)	1559(40)	366(9)
ω_e (DMC)	4432(165)	1549(22)	373(5)
ω_e (hybrid)	4662(205)	1519(31)	387(8)
ω_e (Expt.) ^b	4395.2	1405.65	351.4

Ref.: Assaraf, M. Caffarel, J. Chem. Phys. 119 10536 (2003)

Consider DMC only:

Assaraf & Caffarel obtain geometries that differ on average by 0.006(10) Å from expt. data for 3 molecules

Lee et al. obtain average deviation of 0.0097(5) Å from expt. Data for 8 molecules

Note: Both extract geometries from Morse Potential fit!!!

Using energy minimization + Pulay

TABLE I. E_0 , γ_e , ω_e , and $\omega_e \gamma_e$ for LiH-HF and CO obtained from VMC and DMC calculations and experimental data.

	E_0 (hartree)	γ_e (ohr)	ω_e (cm^{-1})	$\omega_e \gamma_e$ (cm^{-1})
LiH	VMC	-8.063	3.038(1)	1402(4)
	DMC	-8.070	3.030(1)	1417(4)
	Exp	-8.070	3.015	1406
BeH	VMC	-15.235	2.519(1)	2141(4)
	DMC	-15.246	2.515(1)	2134(4)
	Exp	-15.248	2.537	2061
BH	VMC	-25.254	2.370(1)	2332(5)
	DMC	-25.275	2.386(1)	2369(5)
	Exp	-25.289	2.329	2367
CH	VMC	-38.438	2.037(1)	2861(6)
	DMC	-38.463	2.112(1)	2898(6)
	Exp	-38.490	2.116	2858
NH	VMC	-55.178	1.941(1)	3415(7)
	DMC	-55.206	1.952(1)	3253(7)
	Exp	-55.247	1.958	3282
OH	VMC	-75.687	1.830(1)	3854(7)
	DMC	-75.720	1.843(1)	3690(7)
	Exp	-75.778	1.832	3738
HF	VMC	-100.407	1.729(1)	4206(9)
	DMC	-100.442	1.755(1)	4040(9)
	Exp	-100.531	1.733	4138
CO	VMC	-113.176	2.035(1)	2339(16)
	DMC	-113.286	2.116(2)	2251(26)
	Exp	-113.377	2.132	2170

Ref.: M. Lee et al., J. Chem. Phys. 122 244103 (2005)

Comp. with other QMC methods (II)

Use filtering technique from Chiesa & Ceperley

TABLE I. Equilibrium distances in Å. Experimental, CCSD(T), and B3LYP values were taken from Ref. [10]. The CCSD(T) and the B3LYP results were obtained using the cc-pVTZ basis set with the exception of LiH where the 6-311G* set was used. PBE results [11] were all obtained using the aug-cc-pVTZ basis set.

	QMC	Exp.	CCSD(T)	B3LYP	PBE
H ₂	0.7419(4)	0.741	0.743	0.743	0.751
LiH	1.592(4)	1.596	1.618	1.595	1.606
CH ₄	1.091(1)	1.094	1.089	1.088	1.096
NH ₃ (N-H)	1.009(2)	1.012	1.014	1.014	1.023
NH ₃ (H-H)	1.624(2)	1.624	1.616	1.624	1.634
H ₂ O (O-H)	0.959(2)	0.956	0.959	0.961	0.971
H ₂ O (H-H)	1.519(3)	1.517	1.508	1.520	1.531
HF	0.919(1)	0.918	0.917	0.923	0.932

Difference of 1st
and 2nd column :

0.001(1)
0.004(4)
0.003(1)
0.003(2)
0.000(2)
0.003(2)
0.002(3)
0.001(1)

Ref.: S. Chiesa, S. Zhang Phys. Rev. Lett. 94 36404-1 (2005)

Average deviation of calculated geometries from expt. data is 0.002(2) Å