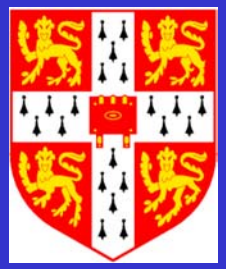


An Introduction to Forces in Quantum Monte Carlo

Literature Review - Problems and Challenges - and what we hope to do about them

Alexander Badinski

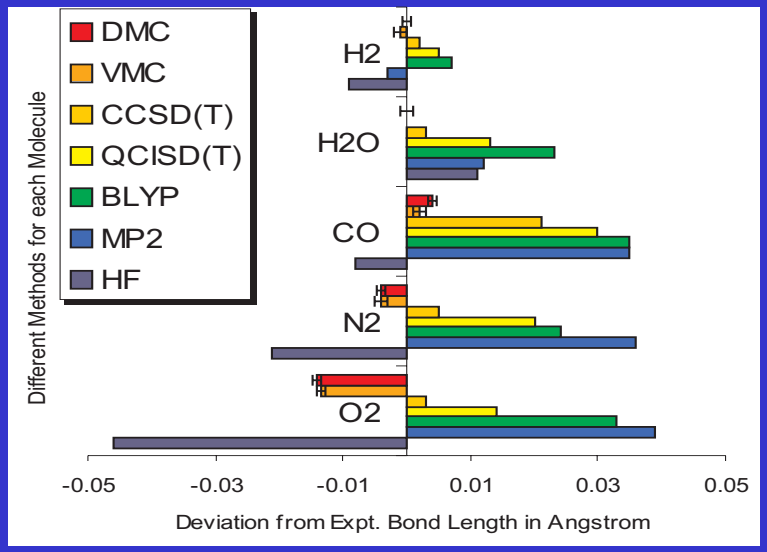
28th of July 2005

Outline

1. Motivation
2. The Hellmann-Feynman Theorem (HFT)
   - HFT and QMC (all electrons, pseudopots)
   - Some First Benchmark Results for H_2
3. Review of Forces and QMC
   - Forces via correlated sampling
   - Forces via renormalization
   - Forces via „smart projections“
4. Our approach: using Pseudopotentials, and a generalized version of previous projection technique

Why Forces with QMC ?

	this work		references				
[in Å]	Δr_{HF}	Δr_{DMC}	$\Delta r_{HF(ref.)}$	Δr_{BLYP}	Δr_{MP2}	Δr_{QCISD}	$\Delta r_{CCSC(T)}$
H_2	-0.009	0.0004(6)	-0.011/-0.007	0.007	-0.003	0.005	0.002
N_2	-0.021	-0.0040(6)	-0.016/-0.017	0.024	0.036	0.020	0.005
O_2	-0.046	-0.0140(4)	-0.039/-0.048	0.033	0.039	0.014	0.003
CO	-0.008	0.0040(8)	-0.001/-0.005	0.035	0.035	0.030	0.021
H_2O	-0.011	0.000(1)	-0.010/-0.011	0.023	0.012	0.013	0.003
[in°]	$\Delta 2\Theta_{HF}$	$\Delta 2\Theta_{DMC}$	$\Delta 2\Theta_{HF(ref.)}$	$\Delta 2\Theta_{BLYP}$	$\Delta 2\Theta_{MP2}$	$\Delta 2\Theta_{QCISD}$	$\Delta 2\Theta_{CCSC(T)}$
H_2O	2.74	0.8(1)	0.99/1.42	-1.81	-0.51	-0.51	-0.91



Accurate Quantum Chemistry Methods are computationally demanding

DFT is often the only option for larger systems

Making QMC a „stand alone“ method

Ref.: Badinski, Dimplomarbeit, Technische Universität Berlin (2003)

Geometries without Forces in QMC

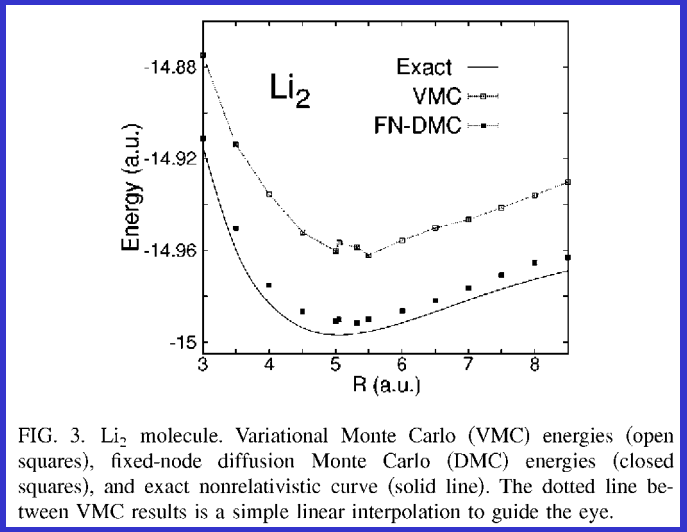
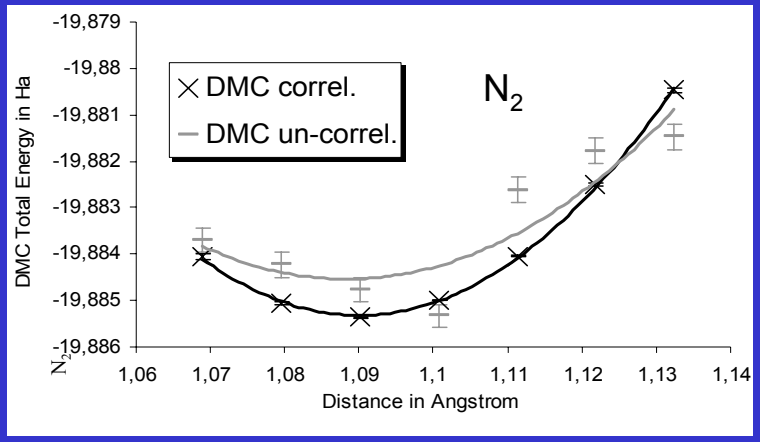


FIG. 3. Li_2 molecule. Variational Monte Carlo (VMC) energies (open squares), fixed-node diffusion Monte Carlo (DMC) energies (closed squares), and exact nonrelativistic curve (solid line). The dotted line between VMC results is a simple linear interpolation to guide the eye.



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

Question: what is meant under equilibrium geometry ? Ambiguous! Why ?

Consider H_2 : $R_e = 0.7417$ Å (Min of Born-Oppenheimer Surface)

$R_0 = 0.7505$ Å (expectation value of bond length in ground state)

$R_0 - R_e \cong 0.01$ Å

Convention in optical spectroscopy: use R_e

Hellmann-Feynman Theorem (HFT)

Total Energy: $E_{VMC} = \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}$ Total Force: $F_{VMC}|_R = -\nabla_R E_{VMC}|_R$

HFT[1,2]: If the wavefunction Ψ_T is the exact one, i.e. $\Psi_T = \Psi_0$, the energy gradient is the average of the expectation value of the gradient of H.

$$-F_R^{HFT} = \nabla_R E_0|_R = \frac{\langle \Psi_0 | \nabla_R H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}|_R$$

Proof: (using that Ψ_0 is real and H is Hermitian)

$$\nabla_R E_T = \frac{\langle \Psi_T | \nabla_R H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} + \frac{\langle \Psi_T' | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} + \frac{\langle \Psi_T | H | \Psi_T' \rangle}{\langle \Psi_T | \Psi_T \rangle}$$

$$- \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle^2} (\langle \Psi_T' | \Psi_T \rangle + \langle \Psi_T | \Psi_T' \rangle) + \sum_k \frac{\partial E_v}{\partial c_k} \frac{\partial c_k}{\partial R}$$

$$= \underbrace{\frac{\langle \Psi_0 | \nabla_R H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}}_{F_R^{HFT}} + \underbrace{2\frac{\langle \Psi_T' | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} - 2\frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle^2} \langle \Psi_T' | \Psi_T \rangle}_{F_R^{Pulay}} + \underbrace{\sum_k \frac{\partial E_v}{\partial c_k} \frac{\partial c_k}{\partial R}}_{F_R^{c}}$$

In the limit $\Psi_T \to \Psi_0$, all terms cancel except for F_R^{HFT}. QED
Hence, using the HFT is only an approximation – with a few exceptions…

[1] H. Hellmann, Einführung in die Quantenchemie, Franz Deuticke, Leipzig (1937)
[2] R. Feynman Phys. Rev. 41 721 (1939)

The HFT in Hartree Fock

The HFT forces is the exact force in Hartree Fock in the limit of a complete basis

Note: - the same is true for DFT

- "exact" in the sense of Hartree-Fock of course

Proof: Start with the total Hartree Fock Energy

$$E^{HF} = <\Psi^{SD}|H|\Psi^{SD}> = \sum_{\nu\mu} P_{\nu\mu} H^{core}_{\nu\mu} + \frac{1}{2}\sum_{\nu\mu\lambda\sigma} P_{\nu\mu}P_{\lambda\sigma}(<\nu\mu|\lambda\sigma> - \frac{1}{2}<\nu\sigma|\lambda\mu>) \qquad (1)$$

with $$H^{core}_{\nu\mu} = \int dr_i \phi_\mu(i)\left(-\frac{1}{2}\Delta - \sum_A \frac{Z_A}{|r_i - R_A|}\right)\phi_\nu(i) \qquad P_{\nu\mu} = 2\sum_{n=1}^{N/2} C_{\mu n}C_{\nu n} \qquad \psi_i = \sum_{\mu=1}^{K} C_{\mu i}\phi_\mu$$

$$<\nu\mu|\lambda\sigma> = \int dr_i dr_j \phi_\nu(i)\phi_\mu(i) r_{ij}^{-1} \phi_\lambda(j)\phi_\sigma(j)$$

Now, get Force from eq.(1),

$$\nabla_R E^{SD} = \sum_{\mu\nu} P_{\mu\nu} \nabla_R H_{\nu\mu}^{core} + O(\text{deriatives of } \phi_\mu \text{ wrt R})$$

with $$\nabla_R H^{core}_{\nu\mu} = \nabla_R <\phi_\nu|H^{core}|\phi_\mu> = <\phi_\nu|\nabla_R H^{core}|\phi_\mu> + <\phi_\nu'|H^{core}|\phi_\mu> + <\phi_\nu|H^{core}|\phi_\mu'>$$

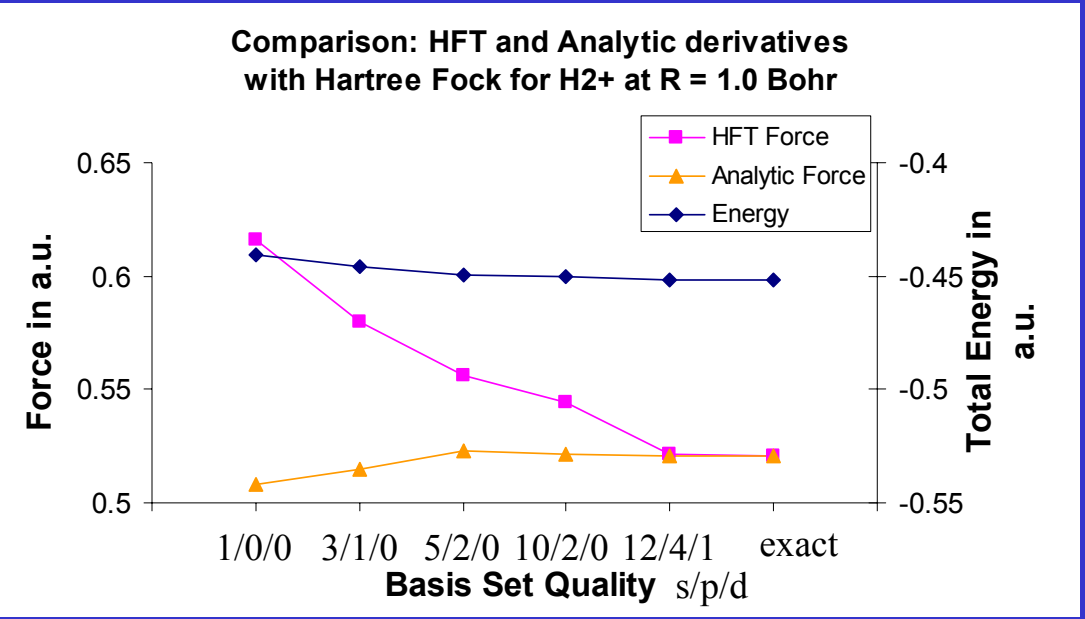
Hence, in the limit of a complet basis set (that e.g. does not depend on the atomic coordinates), the last equation simplifies to

$$\nabla_R E^{SD} = \sum_{\mu\nu} P_{\mu\nu} <\phi_\mu|\nabla H^{core}|\phi_\nu>$$

which is the HFT for Hartree-Fock. QED

This is a quite remarkable result that HFT not only holds for exact $\Psi_T = \Psi_0$ but also for $\Psi_T = \Psi^{SD}$ in the basis set limit !!!

The HFT in Hartree-Fock



Data taken from ref.: B. Hammond, et. al., Monte Carlo Methods, World Scientific (1994)

Total Hartree Fock energy (blue) and consequently its analytic derivative (yellow) converge much faster with the basis set size than the HFT force (purple). (more to say about that in QMC later !!!)

Exact Forces in VMC

From before: $$\nabla_R E_{VMC} = \frac{<\Psi_T|\nabla H|\Psi_T>}{<\Psi_T|\Psi_T>} + 2\frac{<\Psi_T'|H|\Psi_T>}{<\Psi_T|\Psi_T>} - 2\frac{<\Psi_T|H|\Psi_T>}{<\Psi_T|\Psi_T>^2}<\Psi_T'|\Psi_T> + \sum_k \frac{\partial E_{VMC}}{\partial c_k}\frac{\partial c_k}{\partial R}$$

First, assume: $$\sum_k \frac{\partial E_{VMC}}{\partial c_k}\frac{\partial c_k}{\partial R} = 0$$

Critical assumtion, since we generally use variance minimization, Ref.[1]

Using identity: $$<\Psi_T'|H|\Psi_T> = \int \Psi_T' H \Psi_T dr = \int \Psi_T' \frac{\Psi_T}{\Psi_T}(H\Psi_T)\frac{\Psi_T}{\Psi_T} dr = <\Psi_T|\frac{\Psi_T'}{\Psi_T}E_L|\Psi_T>$$

we get: $$\nabla_R E_{VMC} = \frac{1}{<\Psi_T|\Psi_T>}<\Psi_T|\nabla H + 2E_L\frac{\Psi_T'}{\Psi_T} - 2E_{VMC}\frac{\Psi_T'}{\Psi_T}|\Psi_T> \qquad (2)$$

with $$\nabla H = \sum_{\alpha,i}\nabla\frac{-Z_a}{|r_i - R_\alpha|} + \sum_{\alpha,\beta}\nabla\frac{Z_a Z_\beta}{|R_\alpha - R_\beta|} = \sum_{\alpha,i} Z_a \frac{r_i - R_\alpha}{|r_i - R_\alpha|^3} \underbrace{- \sum_{\alpha,\beta} Z_a Z_\beta \frac{R_\alpha - R_\beta}{|R_\alpha - R_\beta|^3}}_{=: \mathrm{II(ion)}}$$

Define local force: $$F_L = F_L^{HFT} + F_L^{Pulay}$$

with the local HFT force $$F_L^{HFT} := -\nabla H$$

and local „Pulay“ correction force: $$F_L^{Pulay} := -2(E_L - E_{VMC})\frac{\Psi_T'}{\Psi_T}$$

Final expression used for MC integration:

$$<F_L>|_{\Psi_T^2} = <-\sum_{i,\alpha} Z_\alpha \frac{r_i - R_\alpha}{|r_i - R_\alpha|^3} - 2(E_L - E_{VMC})\frac{\Psi_T'}{\Psi_T}>|_{\Psi_T^2} + \mathrm{II(ion)} \qquad (3)$$

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

Problem - Infinite Variance in F_L^{HFT}

Relevance ….

Variance: $\sigma(F_{L,i})^2 = <(F_{L,i}^{HFT})^2> - <F_{L,i}^{HFT}>^2$

with $F_{L,i}^{HFT} = (-\nabla H)_i \quad i = 1...3N$ and $\nabla H = \sum_{\alpha,i} Z_a \frac{r_i - R_\alpha}{|r_i - R_\alpha|^3} - \sum_{\alpha,\beta} Z_a Z_\beta \frac{R_\alpha - R_\beta}{|R_\alpha - R_\beta|^3}$

Illustration of the Problem:

consider F_L^{HFT} of H atom in x direction at R = 0 (average must be 0; ✡ = e $^{-♋ r}$)

$$\sigma^2 = <\frac{x^2}{r^6}> - <\frac{x}{r^3}>^2 = <\frac{\hat{x}^2}{r^4}> = \int_\Omega (\cos\varphi \sin\phi)^2 \sin\phi \, d\varphi \, d\phi \int_0^\infty \frac{r^2}{r^4} e^{-2\alpha r} dr \quad \to \infty$$

Possible Solutions:

- Not sample forces with QMC !
- Cut out sampling region around nucleus
- Use pseudopotentials to eliminate $1/r^2$ term close to the nucleus
- Renormalize Variance to finite value
- Projecting out l = 0 component of the charge density at the nucleus

Exact Forces in DMC

For the **Mixed Estimator**:

$$-<F_L>_{\Psi_0\Psi_T} = \nabla \frac{<\Psi_T|H|\Psi_0>}{<\Psi_T|\Psi_0>}$$

$$= \frac{<\Psi_T|\nabla H|\Psi_0>}{<\Psi_T|\Psi_0>} + \frac{<\Psi_T'|H|\Psi_0>}{<\Psi_T|\Psi_0>} + \frac{<\Psi_T|H|\Psi_0'>}{<\Psi_T|\Psi_0>} - E_0\left(\frac{<\Psi_T'|\Psi_0>}{<\Psi_T|\Psi_0>} + \frac{<\Psi_T|\Psi_0'>}{<\Psi_T|\Psi_0>}\right)$$

$$= \frac{<\Psi_T|\nabla H|\Psi_0>}{<\Psi_T|\Psi_0>} + E_0\frac{<\Psi_T'|\Psi_0>}{<\Psi_T|\Psi_0>} + \frac{<\Psi_T|\frac{(H\Psi_T)}{\Psi_T}\frac{\Psi_0'}{\Psi_0}|\Psi_0>}{<\Psi_T|\Psi_0>} - E_0\left(\frac{<\Psi_T'|\Psi_0>}{<\Psi_T|\Psi_0>} + \frac{<\Psi_T|\frac{\Psi_0'}{\Psi_0}|\Psi_0>}{<\Psi_T|\Psi_0>}\right)$$

$$= \left\langle \nabla H + (E_L - E_0)\frac{\Psi_0'}{\Psi_0} \right\rangle_{\Psi_T\Psi_0} \quad \leftarrow \text{Useless Expression since } \Psi_0\text{' unknown} \qquad (4)$$

Unpleasant Solution: Use **Pure Estimator**

In this case however the HFT states that HFT force is the exact force:

$$-<F_L>_{\Psi_0^2} = \frac{<\Psi_0|\nabla H|\Psi_0>}{<\Psi_0|\Psi_0>}$$

Pure Distributions can be obtained by

- Future Walking (considered unstable)
- Reptation QMC (demanding and not much experience)
- Second-order Approximation $<F_L^{HFT}>_{DMC\ pure} \cong 2<F_L^{HFT}>_{DMC\ mixed} - <F_L^{HFT}>_{VMC}$ should give exact force in the limit $\Psi_T = \Psi_0$.

HFT and Pseudopotentials in QMC

Let us re-express the HFT force for pseudopotentials

$$-\langle F_L^{HFT} \rangle = \langle \Psi_0 | \nabla_R H_{loc} + \nabla_R V_{nloc} | \Psi_0 \rangle$$

with $\nabla_R H_{loc} = \sum_i \nabla_R v_{loc,l_{max},i} + II(ion)$ $\qquad \nabla_R V_{nloc} = \sum_i \nabla_R v_{nloc,i}$

$$= \underbrace{\int \Psi_0^2 \sum_i \nabla_R v_{loc,l_{max}+1,i} dr}_{=: -\langle F_{loc} \rangle} + II + \underbrace{\int \Psi_0(r_1,..r_i,..r_N) \sum_i \langle r_i | \nabla_R v_{nloc} | r_i' \rangle \Psi_0(r_1,..r_i',..r_N) dr}_{=: -\langle F_{nloc} \rangle}$$

Local Part $\langle F_{loc} \rangle$

$$\langle F_{loc} \rangle = -\left\langle \sum_{i=1}^{N} \sum_{\alpha=1}^{M} \left(\frac{d}{dr_{i\alpha}} v_{loc,l_{max}+1}(r_{i\alpha}) \frac{R_\alpha - r_i}{|R_\alpha - r_i|} \right) \right\rangle_{|\Psi|^2} + II(ion)$$

with $\nabla v_{loc,l_{max}+1}(r_{i\alpha}) = \sum_{i=1}^{N} \sum_{\alpha}^{M} \frac{d}{dr_{i\alpha}} v_{loc,l_{max}+1}(r_{i\alpha}) \frac{R_\alpha - r_i}{|R_\alpha - r_i|}$ and $r_{i\alpha} := |R_\alpha - r_i|$

To get non-local Part $\langle F_{nloc} \rangle$ we first need to calculate

$$\langle r_i | \nabla_R v_{nloc} | r_i' \rangle = \nabla_R \langle r_i | v_{nloc} | r_i' \rangle = \nabla_R \sum_{l=0}^{l_{max}} \frac{\delta(r_{i\alpha} - r_{i\alpha}')}{r_{i\alpha}^2} v_{l,nloc}(r_{i\alpha}) \frac{2l+1}{4\pi} P_l(\gamma_i)$$

…… (See Overhead)

HFT and Pseudopotentials in QMC

Some Technicalities:

In general (in Casino), $V_{loc,lmax+1}$ is give on a grid. Therefore,

$$\frac{d}{dr_{i\alpha}} V_{loc,l_{max}+1}(r_{i\alpha})$$

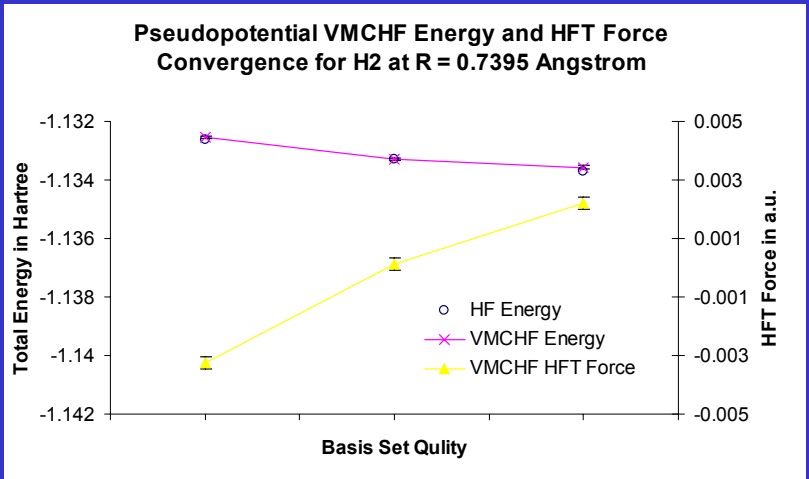
can be obtained by polynomial interpolation: extend Neville's Algorithm[1] to include derivative (thanks to John)

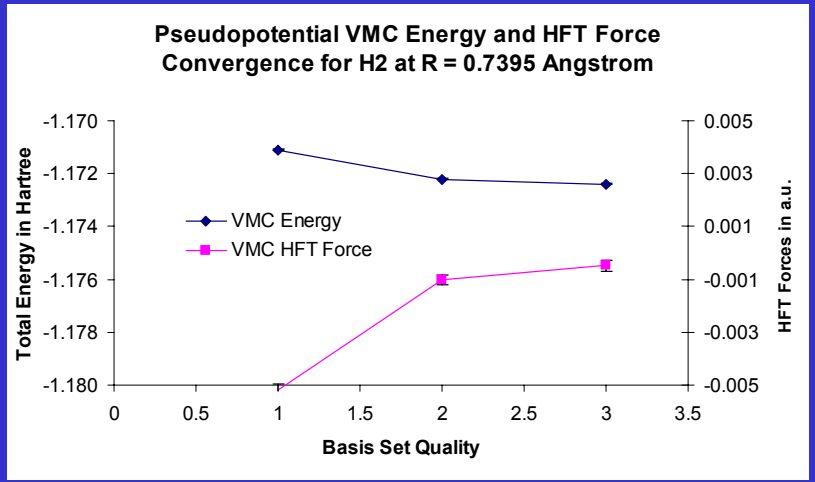
Questions:

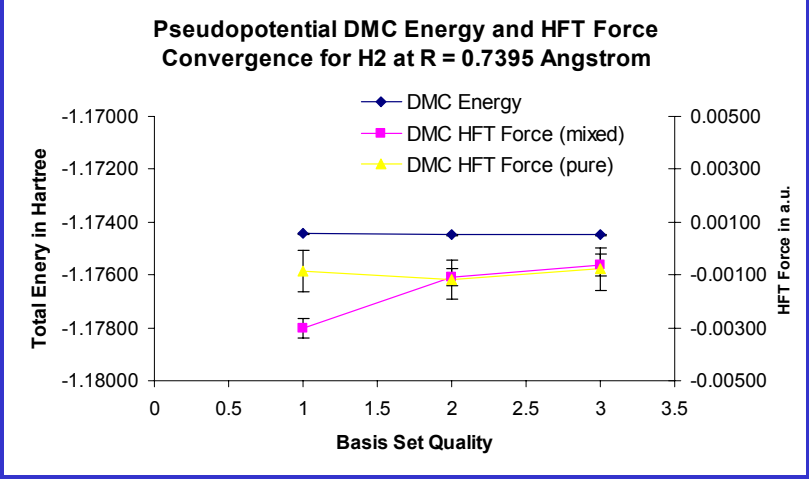
1. Which degree of Interpolation to choose ?
2. How good is the numerical interpolation of the derivatives compared to the analytic once ?

[1] Numerical Recipes, p. 99-107

Calculated Pseudopotential Forces for H_2



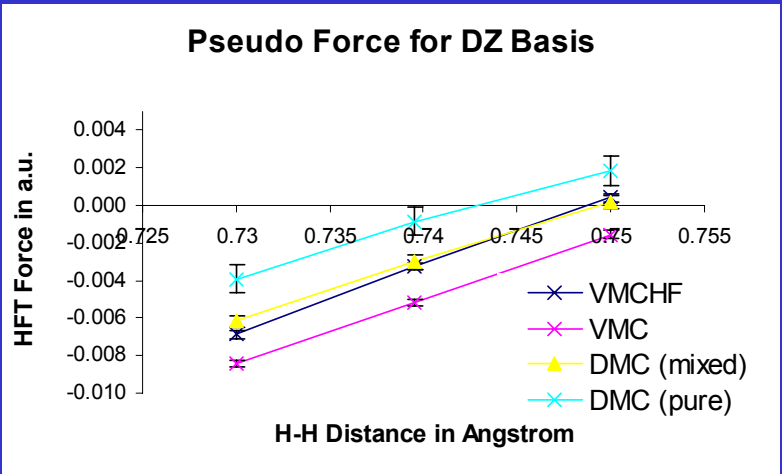


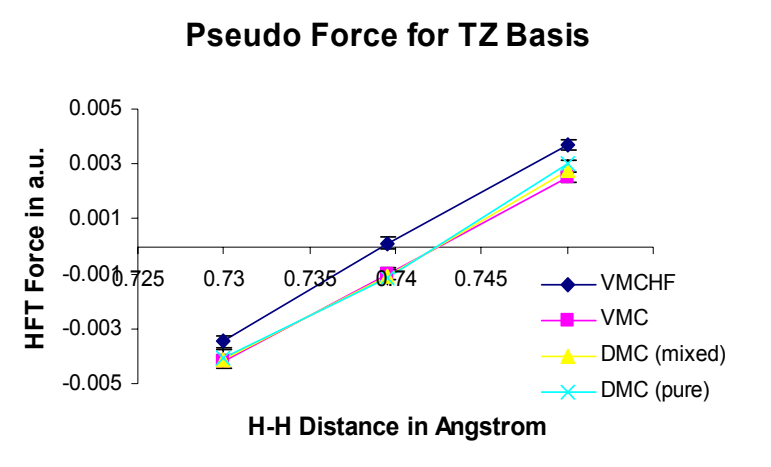


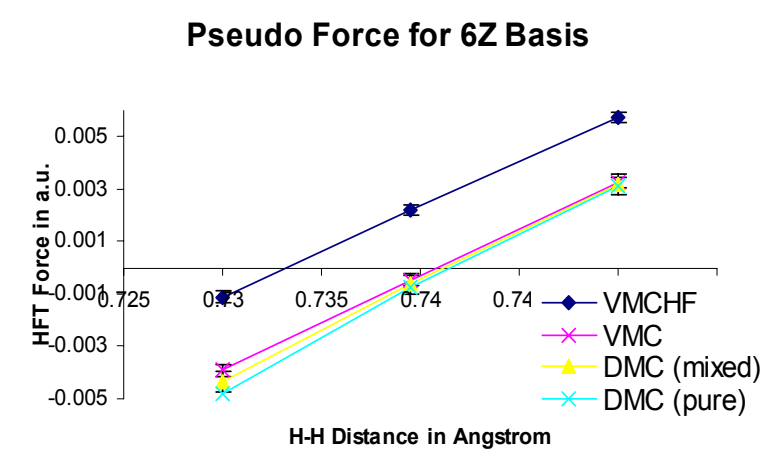
- In VMCHF, force „overshoots“ as basis set quality increases
- in VMC, Jastrow factor corrects „overshooting of the force“
- DMC pure estimate seems to improve results over mixed one

Different HF basis sets used: cc-pCVDZ (4s,1p), cc-pCVTZ (5s,2p,1d), cc-pCV6Z (10s,5p,4d)

Calculated Pseudopotential Forces for H_2



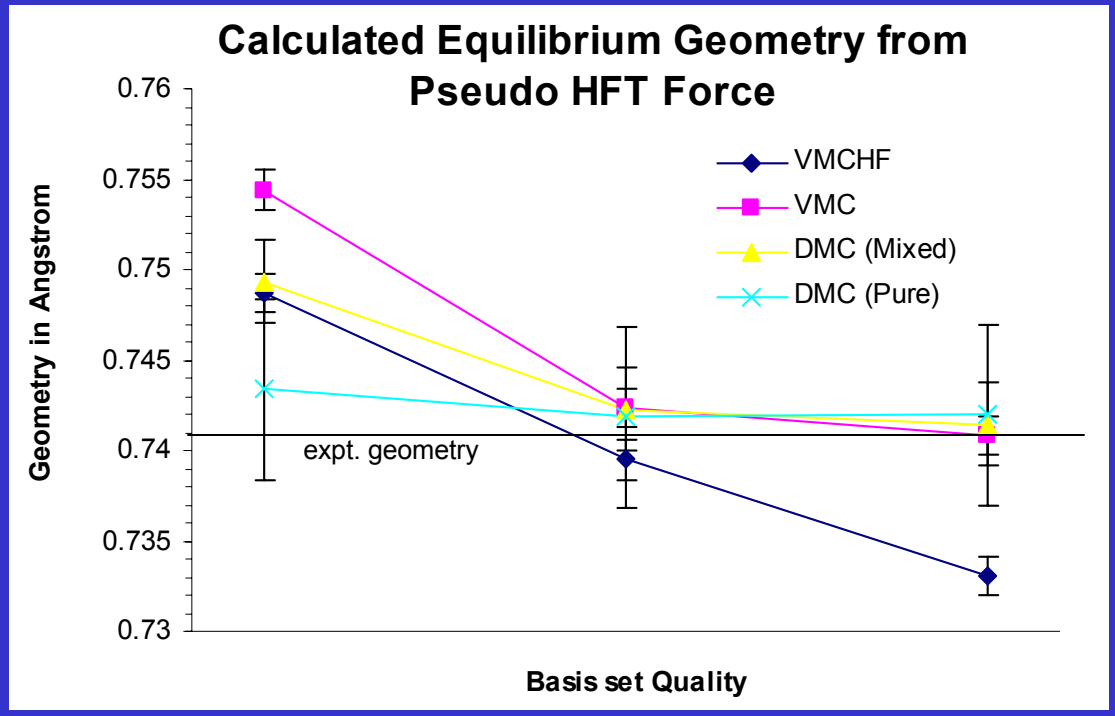




- For DZ basis, including Jastorw factor might worsen force ....
- For TZ VMC and DMC agree with each other (same for 6Z basis)
- 6Z basis set force seems to have a closer zero to the experimental value of 0.741 Angstrom

Different HF basis sets used: cc-pCVDZ (4s,1p), cc-pCVTZ (5s,2p,1d), cc-pCV6Z (10s,5p,4d)

Calculated Pseudopotential Forces for H_2



Hartree Fock Geometry optained from quadartic fit to the (pseudo) total Energy:

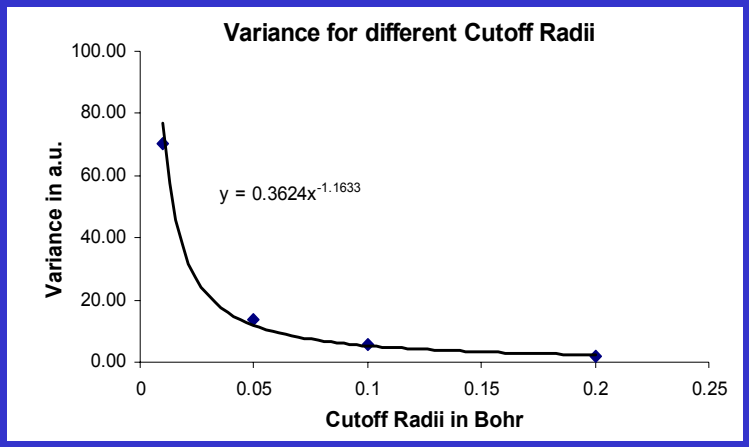
Basis Set	Opt. Geometry [A]
cc-pCVDZ	0.7332
cc-pCVTZ	0.7338
cc-pCV6Z	0.7335

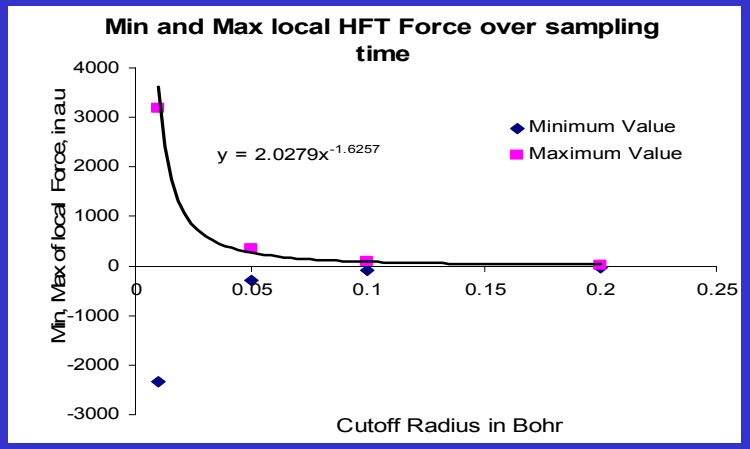
Seems converged !

- The VMCHF equilibrium geometry from HFT reproduces the equilibrium Geometry from energy minimization ☙ HFT seems to reproduce exact force for largest cc-pCVQZ basis set
- For smaller basis set, adding Jastrow may worsens geometry
- For larger basis set, good agreement with experimental geometry

The same for all Electron….

Look at different cutoff radii:
calculate HFT force in VMC for H_2 with 1m moves, 1 block, at 0.7395 Å





The same for all Electron….

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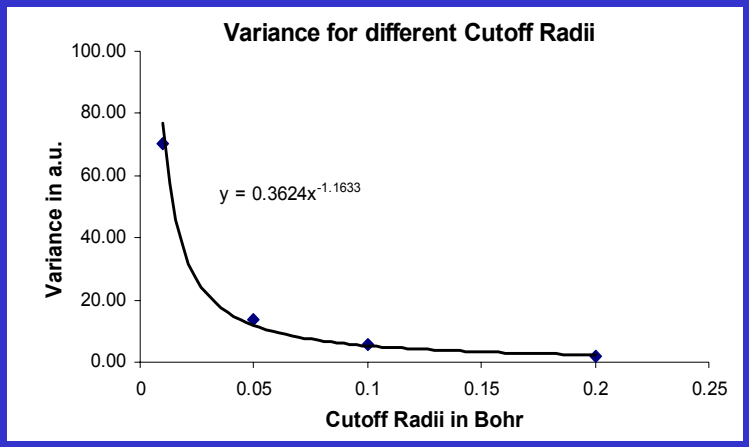
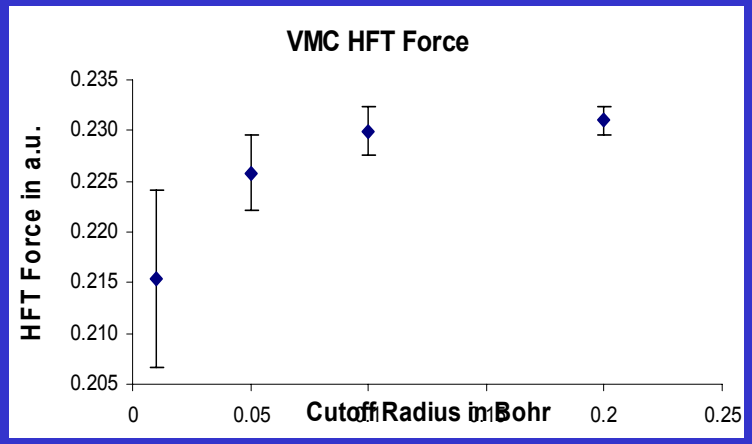
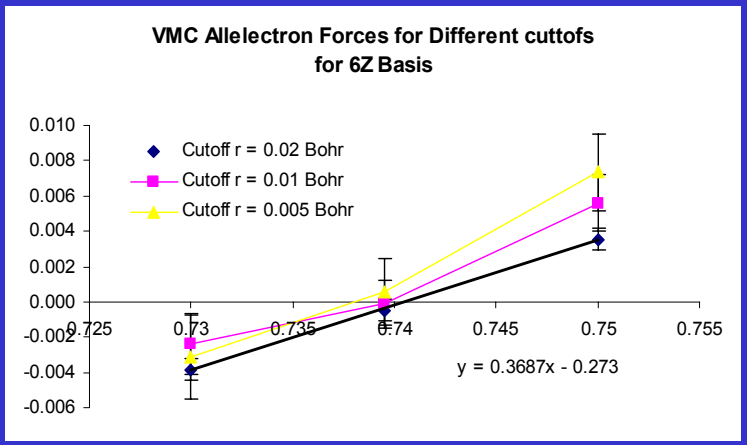
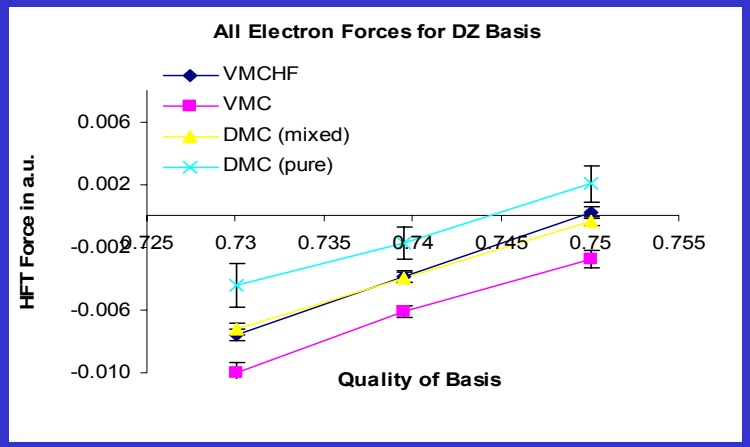


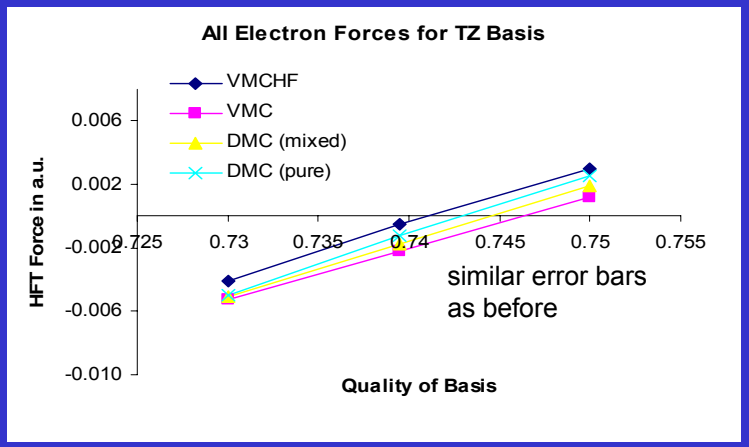


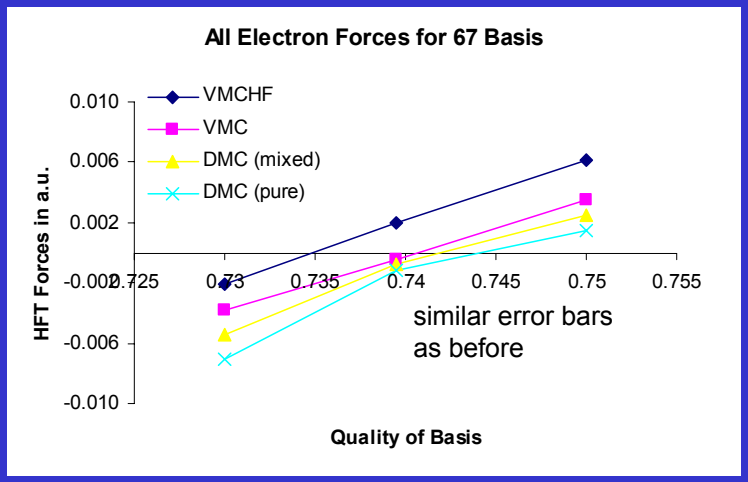


- Diverging variance for r ☙ 0, hence, the errorbar of my calculated force would diverge
- But force seems to agree within the error bar for all cutoff radii
- Tradeoff of r = 0.05 Bohr seems ok, my expectation: similar in DMC

The same for all Electron….

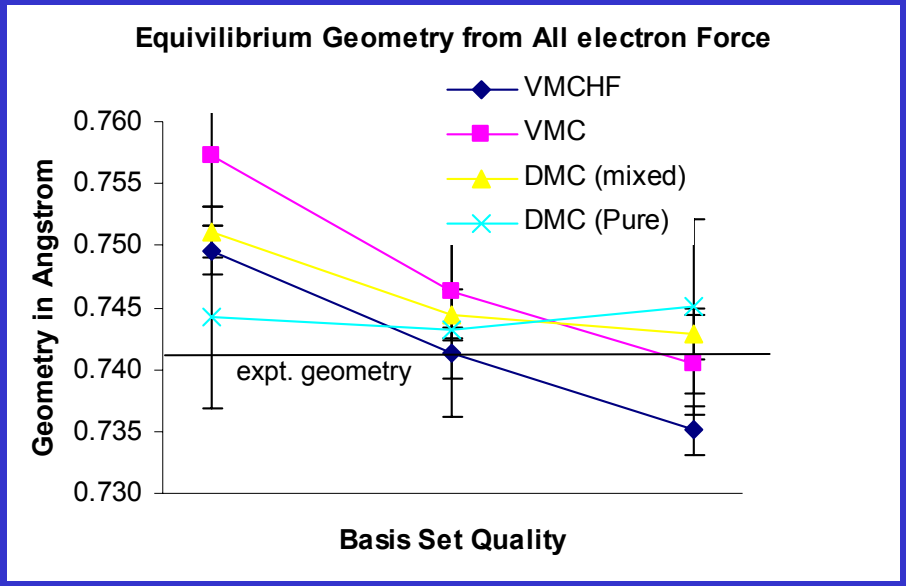






- Again, for DZ basis including Jastrow seems to worsen force
- VMCHF estimate for geometry seems to be converged again for largest basis
- For VMC and DMC not clear …

The same for all Electron….



- For VMC and DMC (mixed, pure) equilibrium geometry corresponds with expt. For largest basis set
- For VMCHF same results as previously with pseudos
- Again, including Jastrow might worsen force (and hence geometry)
- VMC results seem to be already very good for largest basis set
- DMC (mixed and pure) geometry is less good then VMC (probably due to the still large error bares)

Summary so far

- **Basis set** seems to be crucial for HFT estimator in VMC and mixed and 2nd order approx. pure DMC

- Our **initial hope** to only look at HFT estimator and to neglect the Pulay terms is difficult to justify

- All equilibrium geometries in agreement with experiment for largest basis in their error bars (0.01 Å for 2nd order approx pure DMC).

- **Forces with Pseudopotentials** in QMC seem promosing: optained equilibrium geometry for QMC pseudopotential calculations seem to be in excellent agreement with experiment, and closer to experiment than all electron calculations. Next step (1) include nonlocal components, (2) try other systems.

- Already for H_2, obtaining forces this way is **quite exensive** !!! And other methods will appear to be necessary.

Forces via Correlated Sampling (CS)

Idea of CS: use same configurations to sample different Ψ_T's

In VMC: Start from $\Psi_T[\alpha]$ and generate $\Psi_T[\beta]$ by looking at small differences in the objective function

Variance Minimzation (α represents a set of parameters)

$$\sigma^2[\alpha] = \frac{\int |\Psi_T[\alpha]|^2 (E_L[\alpha] - E_{VMC})^2 \, dr}{\int |\Psi_T[\alpha]|^2 \, dr} \approx \frac{1}{M_{conf}} \sum_{i=1}^{M_{conf}} (E_L[\alpha, r_i] - E_{VMC})^2$$

Use CS to express

$$\sigma^2[\beta] = \frac{\int |\Psi_T[\beta]|^2 (E_L[\beta] - E_{VMC})^2 \, dr}{\int |\Psi_T[\beta]|^2 \, dr} =$$

$$= \frac{\int |\Psi_T[\alpha]|^2 (E_L[\beta] - E_{VMC})^2 \, \omega[\alpha,\beta] dr}{\int |\Psi_T[\alpha]|^2 \, \omega[\alpha,\beta] dr} \approx \frac{\frac{1}{M} \sum_{i=1}^{M} (E_L[\beta, r_i] - E_{VMC})^2 \, \omega[\alpha,\beta]}{\sum_{i=1}^{M} \omega[\alpha,\beta]}$$

with $\omega[\alpha,\beta] = \frac{\Psi[\beta]^2}{\Psi[\alpha]^2}$, using the same set of configurations $\{r_i\}$.

Forces via CS in VMC

Geometry Optimization[1] (α represents set of nuclear coordinates $\{R_n\}$)

For the reference geometry $\{R_n^{ref}\} = \alpha$

$$E_{VMC}[\alpha] = \frac{\int |\Psi_T[r,\alpha]|^2 E_L[r,\alpha] dr}{\int |\Psi_T[r,\alpha]|^2 \, dr} \approx \frac{1}{M_{conf}} \sum_{i=1}^{M_{conf}} E_L[r_i,\alpha]$$

For the secondary geometry $\{R_n^{sec}\} = \beta$

(Notice: $\{R_n^{sec}\}$ enters $\hat{H}_T$ and H)

$$E_{VMC}[\beta] = \frac{\int |\Psi_T[\alpha,r]|^2 E_L[\beta,r]\, \omega[\alpha,\beta,r] dr}{\int |\Psi_T[\alpha,r]|^2 \, \omega[\alpha,\beta,r] dr} \approx \frac{\frac{1}{M}\sum_{i=1}^{M} (E_L[\beta,r_i]\omega[\alpha,\beta,r_i]}{\sum_{i=1}^{M} \omega[\alpha,\beta,r_i]}$$

with $\omega[\alpha,\beta,r_i] = \frac{\Psi[\beta,r_i]^2}{\Psi[\alpha,r_i]^2}$

[1] C. Filippi, C, Umrigar, *Interatomic Forces and Correlated Samplin in QMC*, World Scientific, (6/2001)

Forces via CS in VMC

Further Improvements:

Space-Warp Transformation

Idea: improve the set of reference configs $\{r_i^{ref}\}$ via a smart trafo to a secondary set of configs $\{r_i^{sec}\}$

Choose: $r_i^{sec}[r_i] = r_i + \sum_n^{N_{atom}} (R_n^{sec} - R_n^{ref}) \cdot W_n[r_i, \{R_m\}]$

with $W_n[r_i, \{R_m\}] := \frac{(r_i - R_n)^{-4}}{\sum_{m=1}^{N_{atom}} (r_i - R_n)^{-4}}$

a) replace r_i by r_i^{sec} and

b) write $r_i^{sec}[r_i]$ in terms of r_i using space warp trafo

$$E_{VMC}[\beta] = \frac{\int |\Psi_T[\alpha, r^{sec}(r^{ref})]|^2 E_L[\beta, r^{sec}(r^{ref})]\, \omega[\alpha, \beta, r^{sec}(r^{ref})] \cdot |J(r^{ref})|\, dr^{ref}}{\int |\Psi_T[\alpha, r^{sec}(r^{ref})]|^2\, \omega[\alpha, \beta, r^{sec}(r^{ref})] \cdot |J(r^{ref})|\, dr^{ref}}$$

Reoptimize HF Orbitals for $\Psi_T(R^{sec})$

Forces via CS in DMC

CS in DMC

1. drift/diffuse/branch primary walker $\{\mathbf{r}\}$
2. Get secondary walker $\{\mathbf{r}^s\}$ via space-warp trafo
   Notice: $\{\mathbf{r}^s\}$ is effectively proposed by wrong dynamics by using $G_{drift/diff}(R,R',\tau)$ and p instead of $G^s_{drift/diff}(R^s,R'^s,\tau^s)$ and p^s
3. Correct wrong dynamics by multiplying weights of $\{\mathbf{r}^s\}$ by

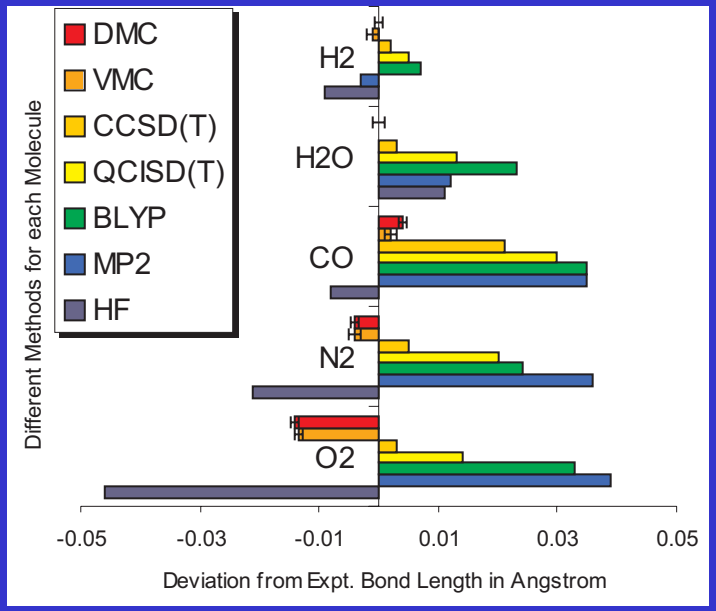
$$\frac{G^s_{drift/diff}(R'^s,R^s,\tau^s)}{G(R',R,\tau)}\cdot\frac{p^s}{p}\cdot e^{S^s(R'^s,R^s,\tau^s)} \quad \text{with} \quad S(R',R,\tau) = -1/2(E_L(R) - E_L(R') - 2E_T)\tau$$

4. Step 3 introduces large fluctuations
   Instead of Step 3: approximate secondary weights by

$$w^S = w\prod_{N_{project}}\frac{e^{S^s(R^s',R^s,\tau^s)}}{e^{S(R',R,\tau)}}$$

   In theory: $N_{project}$ as large as possible
   In practice: $N_{project}$ ~ 50 to minimize fluctuations

Some Results and Critique



A. Badinski, Dimplomarbeit, TU Berlin (2003)

Pros:

-Agreement with experimant relatively good

- error bars small

Cons:

- Limited to very small systems

Forces via Renormalization (VMC)

Idea: renormalize HFT force to reduce infinite variance

Recall: $F_L = -\nabla H - 2(H - E_{VMC})\frac{\Psi_T'}{\Psi_T}$

Redue derivation of last eq. by substituting $H \to \frac{H\Psi_T}{\Psi_T}$

Similar as before, one gets

$$\tilde{F}_L = -\nabla H_T - \frac{(H - E_L)\Psi_T'}{\Psi_T} - 2(E_L - E_{VMC})\frac{\Psi_T'}{\Psi_T} \qquad (6)$$

Assaraf eq.(19) with $\tilde{O} = -\tilde{F}_L$, $O = \nabla H = -F_L^{HFT}$

Hence $\tilde{F}_L = F_L - \frac{(H - E_L)\Psi_T'}{\Psi_T}$

The last eq. can be interpreted as a trafo of the local force F_L.
It can actually be shown that this trafo can be generalized to

$$\tilde{F}_L = F_L - \frac{(H - E_L)\alpha}{\Psi_T}$$

with α being any (reasonable) fct.

Note: $< \tilde{F}_L >_{|\Psi|^2} = < F_L >_{|\Psi|^2}$ holds (F_L is "renormalized")

Proof: $< F_T > - < \tilde{F}_T > = < \Psi_T | \left(\frac{(H - E_L)\alpha}{\Psi_T} \right) | \Psi_T > = \int \Psi_T \frac{(H\alpha) - E_L\alpha}{\Psi_T} \Psi_T = \int \frac{\Psi_T}{\Psi_T}(H\Psi_T)\alpha + \Psi_T \frac{(H\Psi_T)}{\Psi_T}\alpha = 0$

QED.

Now, see that proposed trafo $\tilde{F}_L$ reduces variance (to zero in the limit of $\alpha = \Psi_T' = \Psi_0'$) . . . . . .

[1] R. Assaraf, M. Caffarel, Phys. Rev. Lett. 23 4682 (1999)

Forces via Renormalization (VMC)

Recall: Ψ is exact (satisfies the Schrödinger equation) $\Leftrightarrow$ the local energy has zero variance (with $E_L = E_0$)

Theorem: $\Psi(\lambda)$ and $\Psi'(\lambda)$ are exact (the Schrödinger eq. and its first derivative with respect to a parameter hold) $\Leftrightarrow$ the local energy and transformed local force have zero variance and the **zero-variance equations** hold

$$E_L = \quad < E_L >_{|\Psi|^2} \tag{7}$$

$$\widetilde{F}_L = \quad < \widetilde{F}_L >_{|\Psi|^2} \tag{8}$$

Assaraf eq.(33)

Further, Ψ_0, Ψ_0', E_0, $\widetilde{F}_L$ are a unique solution if H is non-degenerate.

Eq.(7) is ordinary Schrödinger equation.
Eq.(8) is obtained by taking the derivative of the Schrödinger eq. wrt λ.

Forces via Renormalization (VMC)

Proof: $\nabla\left([H-E_{VMC}]\Psi_T\right)=0 \quad \Leftrightarrow (\nabla H-\nabla E_{VMC})\Psi_T+(H-E_{VMC})\Psi'_T=0$

eq.(2)

$$\Leftrightarrow (-F_L-2\frac{(E_L-E_{VMC})\Psi'_T}{\Psi_T}+<F_L>)\Psi_T+(H-E_{VMC})\Psi'_T=0$$

Now, in the limit of $\Psi_T=\Psi_0$:

$$\Leftrightarrow (-F_L+<F_L>)\Psi_T+(H-E_{VMC})\Psi'_T=0 \qquad \text{Assaraf eq.(34)}$$

$$\Leftrightarrow F_L=<F_L>+\frac{(H-E_{VMC})\Psi'_T}{\Psi_T} \qquad (9)$$

from which it follows: $F_L \neq <F_L>_{|\Psi|^2}$ (even if $\Psi_T = \Psi_0$!!!)

Now, to see that $\tilde{F}_L$ has zero variance, just plug $\tilde{F}_L$ from eq.(6) in eq.(9) for $\alpha = \Psi$'

$$\Leftrightarrow \tilde{F}_L+\frac{(H-E_L)\Psi'_T}{\Psi_T}=<F_L>+\frac{(H-E_{VMC})\Psi'_T}{\Psi_T}$$

$$\Leftrightarrow \tilde{F}_L=<\tilde{F}_L>+\frac{(E_L-E_{VMC})\Psi'_T}{\Psi_T}$$

which means that $\tilde{F}_L$ has zero variance in the limit of $\Psi_T=\Psi_0$. QED

Conclusion: Ψ_0 and Ψ_0 ' are exact $\Leftrightarrow$ eq.(7) and eq.(8) are satisfied. Hence, the zero-variance equations determine a unique solution Ψ_0, Ψ_0', E_0, $\tilde{F}_L$.

Forces via Renormalization (VMC)

Back to VMC, in theory one would then sample

$$\tilde{F}_L = F_L^{HFT} - \frac{(H - E_L)\Psi'_T}{\Psi_T} - \frac{(E_L - < E_L >)\Psi'_T}{\Psi_T}$$

← Problem: Derivative of Ψ_T

Possible Solutions:

1. Make a good ansatz for α rather than choosing the exact Ψ_T'

   $$\alpha := Q\,\Psi_T \qquad \text{with} \qquad Q = Z_A \sum_{i=1}^{n_{ele}} \frac{r_i - R}{|r_i - R|}$$

   It follows that $$\frac{(H - E_L)\alpha}{\Psi_T} = Z_A \sum_{i=1}^{n_{ele}} \frac{r_i - R}{|r_i - R|^3} - \frac{\nabla Q \cdot \nabla \Psi_T}{\Psi_T}$$

   Clearly, this would then remove the singular part responsible for the infinite variance

2. Approximating Ψ_L' with a finite-difference form of Ψ_L

   $$\alpha := \frac{\Psi_T[R + \Delta R, \{c_k[R + \Delta R]\}] - \Psi_T[R, \{c_k[R]\}]}{\Delta R}$$

   Thereby, $\{c_k\}$ denotes a set of parameters entering Ψ_T. And ΔR can be interpreted as an additional parameter to minimize the fluctuation!

3. Derive an analytic expression for Ψ_L'

Forces via Renormalization (VMC)

Solution 1

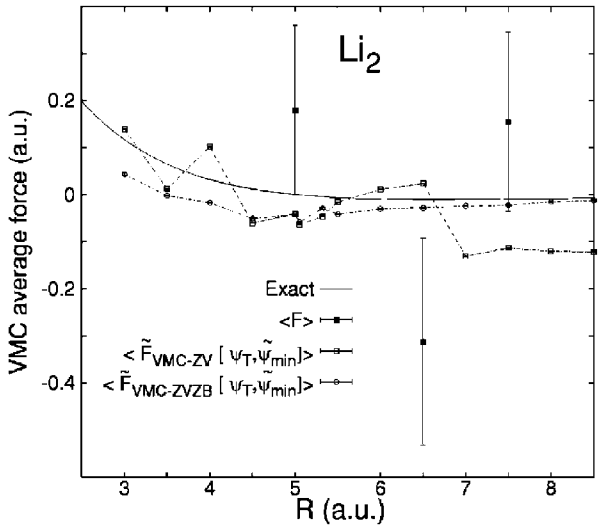


FIG. 4. Various VMC average forces for Li_2. Closed squares with large error bars: $\langle F \rangle$, Eq. (67). Open squares joined by the dashed line: $\langle \tilde{F}_{\text{VMC-ZV}}[\psi_T, \tilde{\psi}_{\text{min}}] \rangle$, Eq. (72). Circles joined with the dotted line: $\langle \tilde{F}_{\text{VMC-ZVZB}}[\psi_T, \tilde{\psi}_{\text{min}}] \rangle$, Eq. (73). Solid line: exact nonrelativistic force curve.

Solution 2

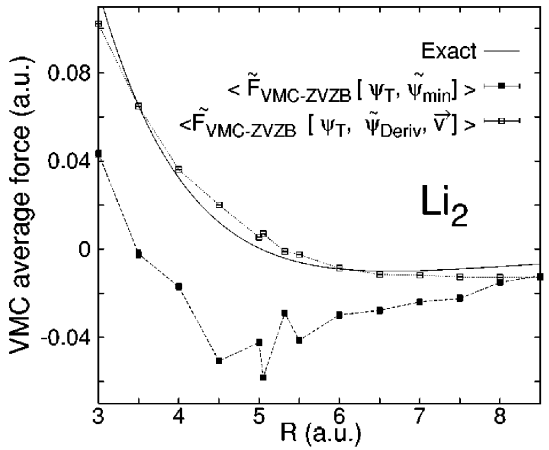


FIG. 6. VMC force for Li_2. Lowest irregular curve with closed squares: $\langle \tilde{F}_{\text{VMC-ZV}}[\psi_T, \tilde{\psi}_{\text{min}}] \rangle$, Eq. (72). Upper curve with open squares: $\langle \tilde{F}_{\text{VMC-ZV}}[\psi_T, \tilde{\psi}_{\text{deriv}}, \vec{v}] \rangle$, Eq. (79). Solid line: exact nonrelativistic force curve.

Solution 1: $\alpha = Q\ \Psi_T$ is still not good enough

Solution 2: the finite difference method seems already better

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

Forces via Renormalization (DMC)

Mixed Estimator in DMC

In a similar derivation as previously in VMC, one gets for the mixed estimator

$$\tilde{F}_L = -\nabla H_T - \frac{(H - E_L)\Psi_T'}{\Psi_T} - (E_L - E_0)\left(\frac{\Psi_T'}{\Psi_T} + \frac{\Psi_0'}{\Psi_0}\right)$$

← Same Problem as before in DMC !

Assaraf eq.(52)

Proposed Solution: make the following approximation

$$\frac{\Psi_T'}{\Psi_T} = \frac{\Psi_0'}{\Psi_0}$$

whence

$$\tilde{F}_L = -\nabla H_T - \frac{(H - E_L)\Psi_T'}{\Psi_T} - 2(E_L - E_0)\frac{\Psi_T'}{\Psi_T} \qquad (10)$$

Note: the only difference with the earlier VMC estimator lies in the value of the average energy $E_0 = < E_L >$.

"Residual systematic error": in the limit of exact nodes the mixed estimator is not exact in eq.(10) - as it is in the case of the energy - since H acts on Ψ_T'.
Solution: it can be shown that the **pure estimator** partially reduces that error.
"Error" here means that the reduction of the variance is not optimally!

Forces via Renormalization (DMC)

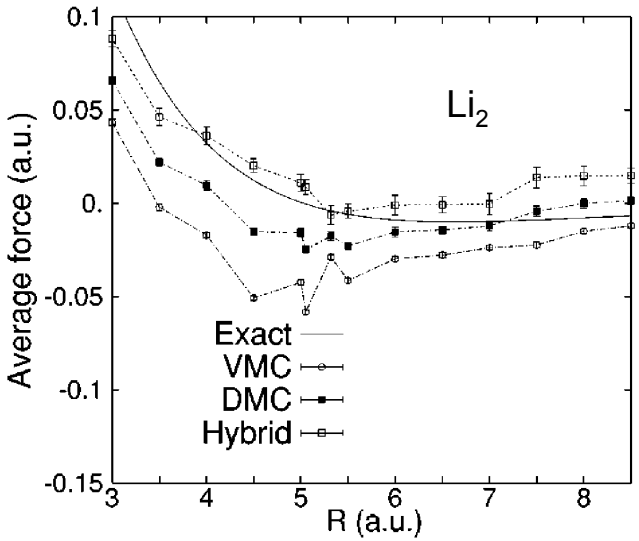


FIG. 5. Li_2 molecule. Average forces using $\tilde{F}_{\mathrm{ZVZB}}(\tilde{\psi}_T, \tilde{\psi}_{\mathrm{min}})$, Eqs. (73)–(75). VMC average: lowest curve with open circles. DMC average: intermediate curve with closed squares. Hybrid average: highest curve with open squares. Solid line: exact nonrelativistic force curve. Dashed lines between QMC results are a simple linear interpolation to guide the eye.

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

Forces via Renormalization (DMC)

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 ^{1}H and 7.016 003 0 amu for ^{7}Li.

	H_2	LiH	Li_2
R_e (VMC)	1.463(12)	3.111(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)

In both Ref. date, the forces are extracted by a leased square fit of the Morse potential (and its derivative)

$$V(r) = D_e[1 - e^{-\beta(r-r_e)}]^2$$

to binding energy (and its forces) ?

Question: How general is this approach if we are interested in forces in larger systems ?

Using energy minimization

TABLE I. E_0, r_e, ω_e, and $\omega_e x_e$ for LiH–HF and CO obtained from VMC and DMC calculations and experimental data.

		E_0(hartree)	r_e(bohr)	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})
LiH	VMC	-8.063	3.038(1)	1402(4)	25.7(1)
	DMC	-8.070	3.020(1)	1417(4)	24.8(1)
	Exp	-8.070	3.015	1406	23.2
BeH	VMC	-15.235	2.519(1)	2141(4)	56.6(2)
	DMC	-15.246	2.515(1)	2134(4)	58.5(2)
	Exp	-15.248	2.537	2061	36.3
BH	VMC	-25.254	2.370(1)	2332(5)	47.0(2)
	DMC	-25.275	2.386(1)	2369(5)	47.3(2)
	Exp	-25.289	2.329	2367	49.4
CH	VMC	-38.438	2.097(1)	2961(6)	77.2(3)
	DMC	-38.463	2.112(1)	2898(6)	71.8(3)
	Exp	-38.490	2.116	2858	63.0
NH	VMC	-55.178	1.941(1)	3415(7)	104.3(4)
	DMC	-55.206	1.962(1)	3253(7)	92.0(4)
	Exp	-55.247	1.958	3282	78.4
OH	VMC	-75.687	1.820(1)	3854(7)	101.2(4)
	DMC	-75.720	1.843(1)	3690(7)	91.4(4)
	Exp	-75.778	1.832	3738	84.9
HF	VMC	-100.407	1.729(1)	4206(9)	89.9(4)
	DMC	-100.442	1.755(1)	4040(9)	82.4(4)
	Exp	-100.531	1.733	4138	89.9
CO	VMC	-113.176	2.095(1)	2539(16)	21.1(3)
	DMC	-113.286	2.116(2)	2251(26)	14.2(3)
	Exp	-113.377	2.132	2170	13.3

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

Side Note: Density Matrix in QMC

General Definition

$$\rho(\mathrm{r_i},\mathrm{r_i}') = \int \Psi(\mathrm{r_1},..\mathrm{r}_i,..\mathrm{r}_N)\Psi(\mathrm{r_1},..\mathrm{r}_i,..\mathrm{r}_N)d\mathrm{r_1}...d\mathrm{r}_{i-1}d\mathrm{r}_{i+1}...d\mathrm{r}_N$$

Expand it

$$\rho(\mathrm{r}_n,\mathrm{r}'_n) = \sum_{i,j}\rho_{ij}\phi_i(\mathrm{r}_n)\phi_j{}^*(\mathrm{r}'_n)$$

with $$\rho_{ij} = N\int \phi_i{}^*(\mathrm{r_n})\phi_j(\mathrm{r'_n})\frac{\Psi(...,\mathrm{r'_n},...)}{\Psi(...,\mathrm{r_n},...)}|\Psi(...,\mathrm{r_n},...)|^2\, d\mathrm{r'_n}\, d\mathrm{r}$$

or sampled in QMC[1] using pure distribution

$$\rho_{ij} = \left\langle \sum_{n=i} \int \phi_i{}^*(\mathrm{r}_n)\phi_j(\mathrm{r}'_n)\frac{\Psi(...,\mathrm{r}'_n,...)}{\Psi(...,\mathrm{r}_n,...)}d\mathrm{r_n}' \right\rangle_{|\Psi|^2}$$

Proof: $$\chi^2 = \int d\mathrm{r}_n d\mathrm{r}_n'[\rho(\mathrm{r}_n,\mathrm{r}_n') - \sum_{i,j}\rho_{ij}\phi_i(\mathrm{r}_n)\phi_j(\mathrm{r}_n)]^2 \qquad \frac{d\chi^2}{d\rho_{ij}} = 0 \quad .....$$

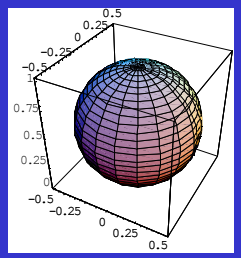
Generalization to non-orthogonal basis sets possible and necessary for Gaussian basis set !!!

P. Kent, R. Hood, M. Towler, R. Needs, G. Rajagopal, Phys. Rev. B, Vol.57, 15293 (1998)

Forces via Projection

Idea: Projecting out the s component of the charge density reduces the variance of the HFT estimator

s-component of charge density



Motivation: The force from the s component of the charge averages out to zero due to its spherical symmetry, e.g. the previous hydrogen atom

$$F^{HFT}(R=0) = \int_0^\infty dr \frac{1}{r^2} e^{-2\alpha r} \times \int_\Omega d\Omega \frac{\mathrm{r}}{|\mathrm{r}|^3} = const \times 0 = 0$$

Derivation: Differentiate between electrons that are closer to the nucleus than R and those that are further away, R ~ 1 Bohr

$$F^{HFT} = F^{>R} + F^{<R}$$

$F^{<R}$ will be calculated ordinarily using the HFT estimator.

To rewrite $F^{<R}$, introduce a force density f

$$f(r) = Z\int d\Omega \rho(r,\phi,\varphi)\nabla H \qquad \text{with} \qquad F^{<R} = \int_0^R f(r)dr$$

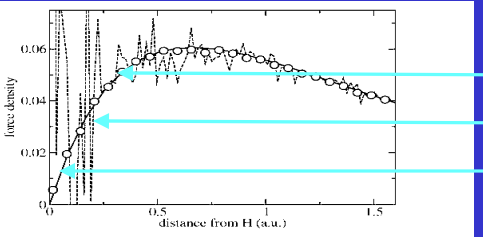
1st Crucial Step: Require *f(r)* to be a smooth fct. of r that tends to 0 linearly as r ∝ 0. Therefore, expand it in the interval (0,R) with a polynomial

$$f^{\mathrm{fit}}(r) = \sum_{k=1}^{M} a_k r^k$$

[1] S. Chiesa, S. Zhang Phys. Rev. Lett. 94 36404-1 (2005)

Forces via Projection

Look at the force density for H in the LiH molecule



DMC using antithetic variates

DMC using bare estimator

Hartree Fock

FIG. 1. Force density along the z direction for the H atom in LiH. The bond is along the z axis, with a length of 3.316 bohrs. The continuous black curve is calculated from the Hartree-Fock orbitals. The dashed line is the estimate of f_z using the bare estimator. Circles are obtained in an identical QMC simulation using the antithetic sampling technique outlined in the text.

Ref.: Chiesa, et. al. (see before)

2nd Crucial Move: determine the coefficients a_k by minimizing

$$\chi^2 = \int_0^R dr[f_i(r) - f^{\text{fit}}{}_i(r)]^2 r^2$$

in particular after optimization w.r.t. all a_k, we get

$$a_k = \sum_{j=1}^{M} S_{jk}^{-1} A_j \quad \text{with} \quad S_{jk} = \frac{R^{m+j+k+1}}{m+j+k+1} \qquad A_j = Z \sum_{i=1}^{N} \int r_i^{2+j} \rho(\mathrm{r}_i) \frac{\mathrm{r}_i}{|\mathrm{r}_i|^3}$$

Since A_j can be sampled using a pure distribution,

$$A_j = Z \left\langle \sum_{i=1}^{N} r_i^{m+j} \frac{\mathrm{r}_i}{|\mathrm{r}_i|^3} \Theta(R - r_i) \right\rangle_{|\Psi|^2}$$

we get the final expression

$$F^{<R} = \int_0^R f(r)dr \cong \int_0^R f^{\text{fit}}(r)dr = \sum_{k=1}^{M} a_k \int_0^R r^k dr \quad \Leftrightarrow \quad F^{<R} = Z \sum_{k=1}^{M} \sum_{j=1}^{M} S_{jk}^{-1} \left\langle \sum_{i=1}^{N} r_i^{2+j} \frac{\mathrm{r}_i}{|\mathrm{r}_i|^3} \Theta(R - r_i) \right\rangle_{|\Psi|^2} \frac{R^{k+1}}{k+1}$$

Forces via Projection

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_2O (O-H)	0.959(2)	0.956	0.959	0.961	0.971
H_2O (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

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

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)

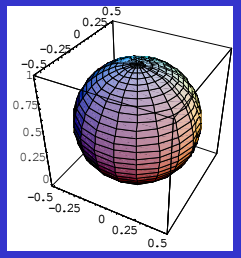
Geometries calculated with QMC agree well with the experimental bond length !

Note: pure sampling has been used (i.e. future walking)

Our Idea (for all electron)

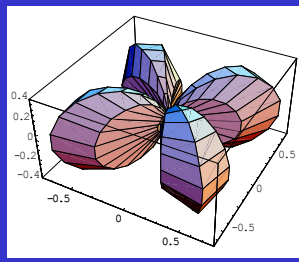
Similar Motivation: Project out parts of the Density which is not relevant (disturbing)

Start with All Electron case: (consider nucleus R=(0,0,0))



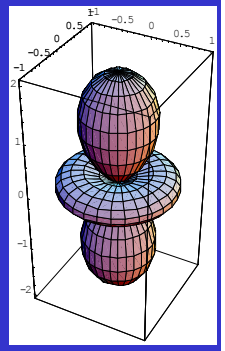
$$-F^{HFT} = <\Psi|\nabla_R H|\Psi> \quad \text{with} \quad \nabla_R H = \sum_i \left(\nabla_R v_i^{e-ion}(\mathrm{r_i})\right) + II(ion-ion)$$

$$= \int \sum_i \Psi^2(\mathrm{r_1},...\mathrm{r_N})(\nabla_R \mathrm{v_i^{e-ion}}(\mathrm{r_i}))\mathrm{dr} + II$$



$$= \frac{1}{N}\int \sum_i \rho(\mathrm{r_i},\mathrm{r_i})(\nabla_R \mathrm{v_i^{e-ion}}(\mathrm{r_i}))\mathrm{dr_i} + II$$

Now, expand ρ in Spherical Harmonics:



$$F^{HFT} = \frac{1}{N}\sum_i \int \sum_{l=0}^{\infty} \sum_{m=-l}^{l} R_{lm}(r_i)Y_{lm}(\Omega_i)(\nabla_R \mathrm{v_i^{e-ion}}(\mathrm{r_i}))\mathrm{dr_i} + II$$

$$\text{with} \quad R_{lm}(r_i) = \int \rho(r_i,\Omega_i)Y_{lm}{}^*(\Omega_i)d\Omega_i \qquad (11)$$

$$= \frac{Z_0}{N}\sum_i \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \int dr_i \frac{1}{|r_i|^2} R_{lm}(r_i) \int d\Omega_i \frac{\mathrm{r_i}}{|r_i|} Y_{lm}(\Omega_i) + II \qquad (12)$$

$$\text{with} \quad \nabla_R \mathrm{v_i^{e-ion}}(\mathrm{r_i}) = Z_0 \frac{\mathrm{r_i}}{|\mathrm{r_i}|^3}$$

Our Idea (for all electrons)

From the Identity: $$\int \frac{r_i}{|r_i|} Y_{lm}(\Omega_i) d\Omega_i = \begin{pmatrix} \sqrt{2\pi/3}(-\delta_{1l}\delta_{1m} + \delta_{1l}\delta_{-1m}) \\ i\sqrt{2\pi/3}(-\delta_{1l}\delta_{1m} - \delta_{1l}\delta_{-1m}) \\ 2\sqrt{\pi/3}\,\delta_{1l}\delta_{0m} \end{pmatrix}$$

Hence, only three R_{lm}-terms need to be evaluated: $R_{1\pm1}$ and R_{10}

$$R_{lm}(r_i) = \int \rho(r_i, \Omega_i) Y_{lm}(\Omega_i) d\Omega_i$$

And since ρ is expanded in Gaussians

$$\chi_{\xi nlm}(r, \varphi, \phi) = N Y_{lm}(\varphi, \phi) r^{(2n-2-l)} e^{-\zeta r^2}$$

the spherical Integral in eq.(11) is just a product of three Spherical Harmonics and can be evaluated analytically

Finally, the radial integration over r_i needs to be performed to get F^{HFT} in eq.(12), should analytically be possible

Our Idea (for Pseudopotentials)

Recall from before :

$$-<F_L^{HFT}>=<\Psi_0|\nabla_R H_{loc}+\nabla_R V_{nloc}|\Psi_0>$$

$$=\underbrace{\int \Psi_0^2 \nabla_R \sum_i v_{loc,l_{max}+1,i}\,d\mathrm{r}}_{=: -<F_{loc}>} + II + \underbrace{\int \Psi_0(\mathrm{r}_1,..\mathrm{r}_i,..\mathrm{r}_N)\sum_i <\mathrm{r}_i|\nabla_R v_{nloc}|\mathrm{r}_i'>\Psi_0(\mathrm{r}_1,..\mathrm{r}_i',..\mathrm{r}_N)\,d\mathrm{r}}_{=: -<F_{nloc}>}$$

Recall local Part $<F_{loc}>$ via direct sampling

$$-<F_{loc}>=\left\langle \sum_{i=1}^{N}\sum_{\alpha=1}^{M}\left(\frac{d}{dr_{i\alpha}}v_{loc,l_{max}+1}(r_{i\alpha})\frac{\mathrm{R}_\alpha-\mathrm{r}_i}{\mathrm{R}_\alpha-\mathrm{r}_i}\right)\right\rangle_{|\Psi|^2} + II(ion)$$

Now, get **local Part $<F_{loc}>$ via Density Matrices**

Recall, $v_{loc,lmax,i}$ is a single-electron operator; therefore rewrite

$$-<F_{loc}>=\sum_{i=1}^{N}\int \rho(\mathrm{r}_i,\mathrm{r}_i)\left(\frac{d}{dr_{i\alpha}}v_{loc,l_{max}+1}(r_{i\alpha})\frac{\mathrm{R}_\alpha-\mathrm{r}_i}{|\mathrm{R}_\alpha-\mathrm{r}_i|}\right)d\mathrm{r}_i + II(ion)$$

The further steps are in analogy to the previous all electron case: expand ρ sin Spherical Harmonics and reduce the infinit expansion to the same three R_{lm} – terms R_{11}, R_{1-1} and R_{10}.

Our Idea (for Pseudopotentials)

Now, get **non-local Part $<F_{loc}>$ via Density Matrices**

Similar as for the local component

$$-<F_{nloc}>=\int \Psi_0(r_1,..r_i,..r_N)\sum_i <r_i|\nabla_R v_{nloc}|r_i'>\Psi_0(r_1,..r_i',..r_N)dr$$

$$=\sum_i \int \rho(r_i,r_i')<r_i|\nabla_R v_{nloc}|r_i'>dr_i dr_i'$$

Only difference is that ρ is now depending on r_i and r_i‘

Now, follow similar procedure as before, i.e. expand ρ AND $<r_i|\nabla_R\ v_{noc}|r_i'>$ in Spherical Harmonics.

For the l components in the pseudopotential, we get the following number of $R_{lml'm'}$ terms when simplifying the integrals over Spherical Harmonic
for l = 1: additional 21 terms
for l = 2: additional 19 terms
for l = 3: additional 19 terms
for l = 3: additional 91 terms

See my notes for excessive expressions

Conclusions

- Forces in QMC are very **challenging** and are by far not a routine tool yet
- Forces is QMC is quite an **interdisciplinary field** requiring new ways of sampling (e.g. Reptation MC) and better ways of optimizing trial wavefunctions
- Pseudopotentials seem to be one way of removing the infinit variance, however, it appears to be computationally still rather demanding. Therefore, there is a need for alternative ways….
- Different Approaches exist but it is not clear yet which one is the most promising one; the projection technique suggested for all electrons seems to produce results closest to the experiment.
- *Study questions and next things to do:*

  - Will our good results for local pseudopotentials (H_2) generalize for bigger systems using non-local pseudopotentials ?

  - How good/reliable/expensive will Reptation MC be to sample pure distributions ?

  - Is our proposed generalization of removing higher angular momenta via projection doable and how good will it be ?