Update on Force Implementation in QMCPACK

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Summary

Current Status

- Forces in nonlocal pseudopotential calculations work* in both open and periodic boundary conditions with VMC.
- We support reasonable wave functions: Slater-Jastrow with one & two-body Jastrows. Einspline and LCAO type single particle orbitals.
- Scales like $O(N^4)$.

Under Development

- DMC forces.
- $O(N^3)$ evaluation for force components.
- User friendliness.
- More supported wave functions: 3-body Jastrow and multi-determinant wave functions.

*Code exists and is implemented in QMCPACK. However, it's a research code which is currently being validated and requires source tweaks to enable.

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Zero-Variance Zero-Bias Estimator** (VMC)

$$\mathbf{F}_{ZVZB} = \left(-\nabla_I \hat{H}\right) + \frac{(\hat{H} - E_L)(-\nabla_I \Psi_T)}{\Psi_T} + 2(E_L - \langle E_L \rangle)\frac{(-\nabla_I \Psi_T)}{\Psi_T} \quad (1)$$

$$= -\nabla_I E_L + 2(E_L - \langle E_L \rangle)\frac{(-\nabla_I \Psi_T)}{\Psi_T} \quad (2)$$

Why?

- Above expression is derived from $-\nabla_I \langle E_L \rangle$, instead of Hellman-Feynman theorem.
- In the limit that $\Psi_T \to \Phi_0$ and $\nabla_I \Psi_T \to \nabla_I \Phi_0$, we achieve exact answer with zero variance!
- In practice, variance reduction and reduction of error.

**Assaraf & Caffarel, JCP, 119(20), 10536-10552, (2003)

Hamiltonian with Non-Local Pseudopotentials

$$\hat{H} = \hat{T} + \hat{V}_{e-e} + \hat{V}^{L}_{e-I} + \hat{V}^{NL}_{e-I} \tag{3}$$

Only explicit ion dependence is in the "local" electron-ion term $\hat{V}^{L}_{e-I}$ and the nonlocal term $\hat{V}^{NL}_{e-I}$

- $\nabla_I \hat{V}^{L}_{e-I}$ is done for open and periodic boundary conditions. Ewald or optimized breakup used for PBC's.
- Nonlocal term $\hat{V}^{NL}_{e-I}$ done for VMC and DMC within the locality approximation. **No T-moves.**

Badinsky & Needs, PRE, 76(3), 036707, (2007)

Validation of Hellman-Feynman Term

	QMC	HF	Δ	Z
$F^{l}_{0,x}$	0.02472(3)	0.02464	0.00009	2.882
$F^{l}_{0,y}$	0.01943(3)	0.01936	0.00007	2.384
$F^{l}_{0,z}$	0.00773(3)	0.00779	-0.00006	-2.069
$F^{nl}_{0,x}$	-0.01382(5)	-0.01384	0.00003	0.471
$F^{nl}_{0,y}$	-0.00927(5)	-0.00935	0.00008	1.552
$F^{nl}_{0,z}$	-0.00028(5)	-0.00030	-0.00002	0.373

Table: Perturbed BCC unit cell in PBC. 8 Na atoms, BFD 1 electron pseudopotential with s, p, and d channels.

Validated against Quantum Espresso (PBC) and GAMESS (open BC).

ZVZB Force Estimator

$$\mathbf{F}_{ZVZB} = \underbrace{\left(-\nabla_I \hat{H}\right) + \frac{(\hat{H} - E_L)\left(-\nabla_I \Psi_T\right)}{\Psi_T}}_{-\nabla_I E_L} + 2(E_L - \langle E_L \rangle)\frac{\left(-\nabla_I \Psi_T\right)}{\Psi_T} \tag{4}$$

We need the following terms

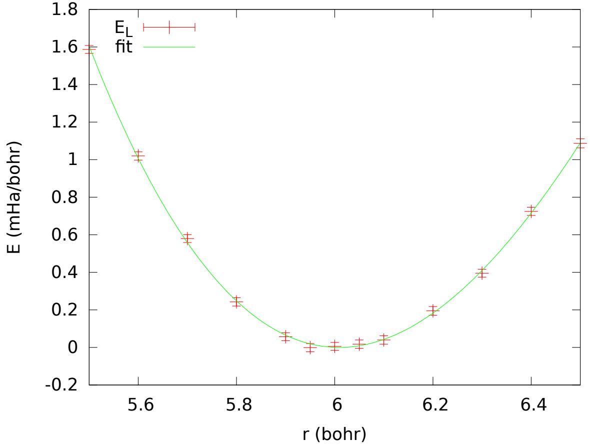
$$\frac{\nabla_i^2(\nabla_I \Psi_T)}{\Psi_T}, \ \frac{\hat{V}_{NL}(\nabla_I \Psi_T)}{\Psi_T}, \ \frac{\nabla_I \Psi_T}{\Psi_T}$$

- Above terms implemented Slater-Jastrow wave functions.
- Support einspline and LCAO orbitals, one and two body Jastrows.
- Forces from determinants are slow $O(N^4)$. No 3-body Jastrow.

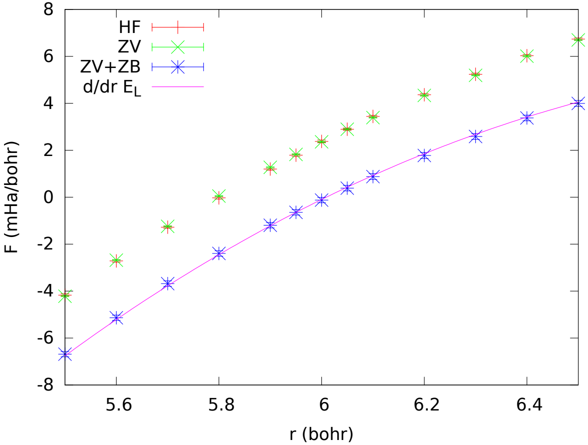
Testing ZV and ZB Terms: Nodeless Case

- Consider a sodium dimer in periodic boundary conditions.
- BFD pseudopotential with 1 electron valence.
- Cubic box with $L = 20a_0$.
- Considered Jastrow only (1-bdy & 2-bdy) wave function, optimized at $r = 6.05a_0$ and frozen.

Local Energy "Reference" For Jastrow Wave Function



Force Comparison For Jastrow Wave Function



Conclusions for Jastrow Wave Function

- The full ZVZB estimator matches differentiation of the local energy to within error bars.
- Large bias which the ZB term corrects.
- Error bar on HF+ZV term is 2-3x lower than the bare HF term.

VMC with Guiding Function

$$\langle \hat{O}_L \rangle = \frac{\int d\mathbf{r} |\Psi_T|^2 O_L(\mathbf{r})}{\int d\mathbf{r} |\Psi_T|^2} = \frac{\int d\mathbf{r} |\Psi_G|^2 \left(w^{VMC}(\mathbf{r}) O_L(\mathbf{r}) \right)}{\int d\mathbf{r} |\Psi_G|^2 w^{VMC}(\mathbf{r})} = \frac{\langle w^{vmc} \hat{O}_L \rangle}{\langle w^{vmc} \rangle} \tag{5}$$

$$w^{VMC}(\mathbf{r}) = \left| \frac{\Psi_T(\mathbf{r})}{\Psi_G(\mathbf{r})} \right|^2 \tag{6}$$

Why?

- ZVZB estimators diverge like $1/d^2$ with distance to node d.
- We can cancel this divergence in the estimator $w\hat{O}_L$ by use of a guiding function.
- Finite variance estimate of $w\hat{O}_L$!

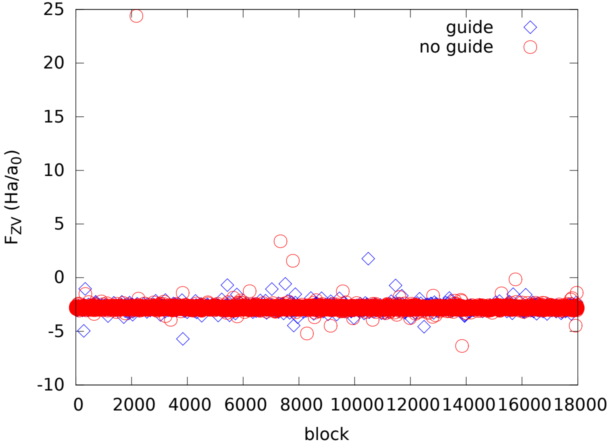
Guiding Function

$$G(\mathbf{R}) = \frac{1}{\| M^{-1} \|_F} \tag{7}$$

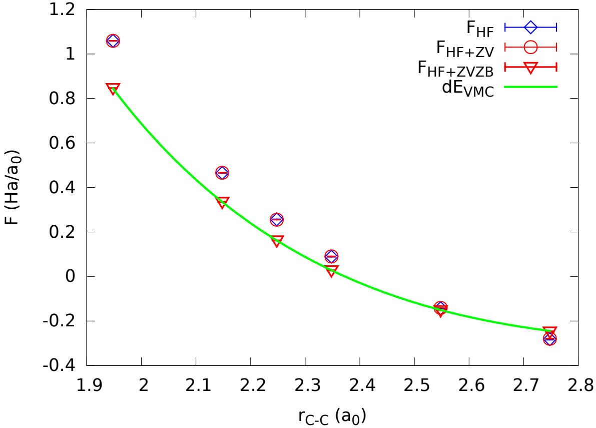
$$\Psi_G(\mathbf{R}) = \begin{cases} |\Psi_T(\mathbf{R})| & G \geq \epsilon \\ |\Psi_T(\mathbf{R})| \left[\frac{G(\mathbf{R})}{\epsilon}\right]^{\frac{G(\mathbf{R})}{\epsilon}-1} & G \leq \epsilon \end{cases} \tag{8}$$

- Above guiding function from Attaccalite & Sorella, PRL, 100(11), 114501, (2008).
- Carbon dimer with BFD pseudopotential (4e valence). Open BC's.
- Slater-Jastrow with optimized 1 and 2 body terms. LCAO orbitals from Hartree-Fock (ccVTZ).
- $\epsilon = 1 \times 10^{-4}$

ZV Force using Guiding Function



C_2 Force Comparison for Slater-Jastrow Wave Function



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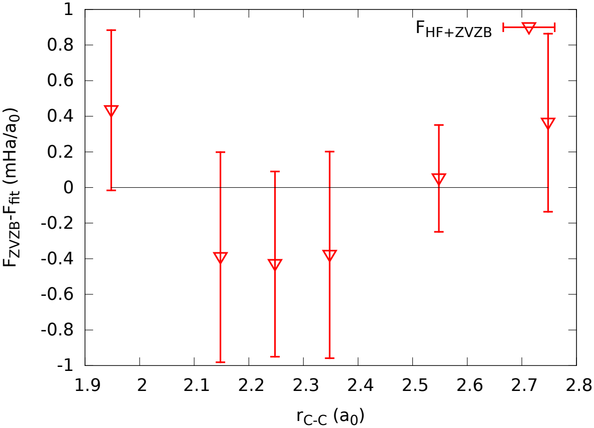

- Reference is a 6th order polynomial fit to energy.
- ZVZB forces agree very well with total energy differentiation.
- Consistently show 2-3x reduction in **error bar** from HF term alone.

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Prospects for DMC

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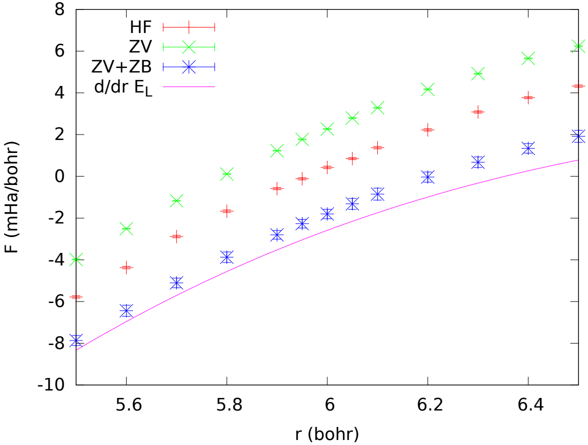
$$\frac{d}{dc}E_{FN} = \left\langle \frac{\langle \mathbf{R}|\frac{d}{dc}\hat{H}|\Psi_T\rangle}{\Psi_T(\mathbf{R})} + \frac{\langle \mathbf{R}|\hat{H} - E_L|\frac{d}{dc}\Psi_T\rangle}{\Psi_T(\mathbf{R})} + \left(\underbrace{\frac{\frac{d}{dc}\Phi_0(\mathbf{R})}{\Phi_0(\mathbf{R})}}_{\approx \partial\Psi_T/\Psi_T} + \frac{\frac{d}{dc}\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} \right) [E_L - \langle E_L \rangle] \right\rangle_{FN} \tag{9}$$

- Depending how good derivative approximation is, the estimator should be usable.
- There are ways to reduce/eliminate this approximation based on extrapolation and forward-walking. We are looking into these.*
- Guiding function/post-processing required. In progress.

*Moroni, Saccani, Filippi, JCTC, 10(11), 4823-4829 (2014).

Na_2 in PBC's: DMC Forces



- ZV term reduces variance within DMC. Doesn't average out to zero any more!
- ZB term corrects most of the discrepancy between the HF force and differentiation of DMC total energy.
- However, the error introduced by the approximation $\nabla\Phi_{FN} \approx \nabla\Psi_T$ is measurable.

VMC with Guiding Function

$$\langle \hat{O}_L \rangle = \frac{\int d\mathbf{r} \Phi_{FN} |\Psi_T| O_L(\mathbf{r})}{\int d\mathbf{r} \Phi_{FN} |\Psi_T|} = \frac{\int d\mathbf{r} \Phi_{FN} |\Psi_G| \left(w^{DMC}(\mathbf{r}) O_L(\mathbf{r}) \right)}{\int d\mathbf{r} \Phi_{FN} |\Psi_G| w^{DMC}(\mathbf{r})} = \frac{\langle w^{DMC} \hat{O}_L \rangle}{\langle w^{DMC} \rangle} \quad (10)$$

$$w^{DMC}(\mathbf{r}) = \left| \frac{\Psi_T(\mathbf{r})}{\Psi_G(\mathbf{r})} \right| \quad (11)$$

Advantages

- Still fixes infinite-variance problem of ZVZB estimators.
- Branching must be done with $E_L = |\Psi_G|^{-1} \hat{H} |\Psi_G|$.

Using QMCPACK Forces

Hamiltonian Block

```
 <hamiltonian ...>
...
 <estimator name="ac" type="Force" mode="acforce" source="ion0"
target="e"/>
 </hamiltonian>
```

QMC Block

```
 <qmc ...>
...
 <parameter name="useGuide"> yes </parameter>
 </qmc>
```

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*Assaraf, Moroni, Filippi, JCP, 144, 194105 (2016)

References

Generic QMC, ZVZB estimators, and Guiding Functions

1. Assaraf & Caffarel, JCP, 119(20), 10536-10552, (2003)
2. Attaccalite & Sorella, PRL, 100(11), 114501, (2008)
3. Moroni, Saccani, Filippi, JCTC, 10(11), 4823-4829 (2014)
4. Assaraf, Moroni, Filippi, JCP, 144, 194105 (2016)

Nonlocal Pseudopotentials in QMC

1. Badinsky & Needs, PRE, 76(3), 036707, (2007)