UNIVERSITY OF CAMBRIDGE

NOCI Trial Wavefunctions for Diffusion Monte Carlo

$\therefore$ longer acronyms $\Rightarrow$ better methods

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Review of Diffusion Monte Carlo

Time-dependent Schrödinger equation (TDSE) is given by

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \hat{H}\Psi(\mathbf{r},t). \tag{1}$$

We recast TDSE in imaginary time, $\tau = \mathrm{i}t$, and apply an energy offset E_T

$$-\hbar\frac{\partial}{\partial \tau}\Psi(\mathbf{r},\tau) = (\hat{H} - E_T)\Psi(\mathbf{r},\tau). \tag{2}$$

In integral form this can be expressed as

$$\Psi(\mathbf{r},\tau+\delta\tau) = \sum_k \Psi_k(\mathbf{r})\mathrm{e}^{-\delta\tau(E_k-E_T)}\langle\Psi_k|\Psi_{init}\rangle. \tag{3}$$

In the long time limit, Equation 3 projects out lowest eigenstate. By adjusting E_T, a stable simulation can be reached where $E_T = E_0$.

W. M. C. Foulkes, L. Mitas, R. J. Needs and G. Rajagopal, *Rev. Mod. Phys*, **73**, 33–83, (2001)

Review of Diffusion Monte Carlo

Wavefunction is represented by a series of walkers that are propagated through imaginary time with importance sampling using a guide wavefunction $\Psi_T(\mathbf{r})$.

1. **Diffusion:**
   - Each electron is propagated to a new position $\mathbf{r} = \mathbf{r}' + \chi + \tau \mathbf{v}_D(\mathbf{r}')$ where $\mathbf{v}_D(\mathbf{r}')$ is the drift velocity

$$\mathbf{v}_D(\mathbf{r}') = \Psi_T(\mathbf{r}')^{-1} \nabla \Psi_T(\mathbf{r}'). \tag{4}$$

   - Step is accepted using fixed node approximation and with probability

$$\exp\left[\frac{-|\mathbf{r}' - \mathbf{r} - \delta\tau \mathbf{v}_D(\mathbf{r})|^2}{2\delta\tau}\right] \left|\frac{\Psi_T(\mathbf{r})}{\Psi_T(\mathbf{r}')}\right|^2. \tag{5}$$

Review of Diffusion Monte Carlo

2. **Reweighting:**
   - For each diffusion step, walker weight is multiplied by

$$\exp\left[-\delta\tau\left(\frac{E_{loc}(\mathbf{r})+E_{loc}(\mathbf{r}')}{2}-E_T\right)\right], \tag{6}$$

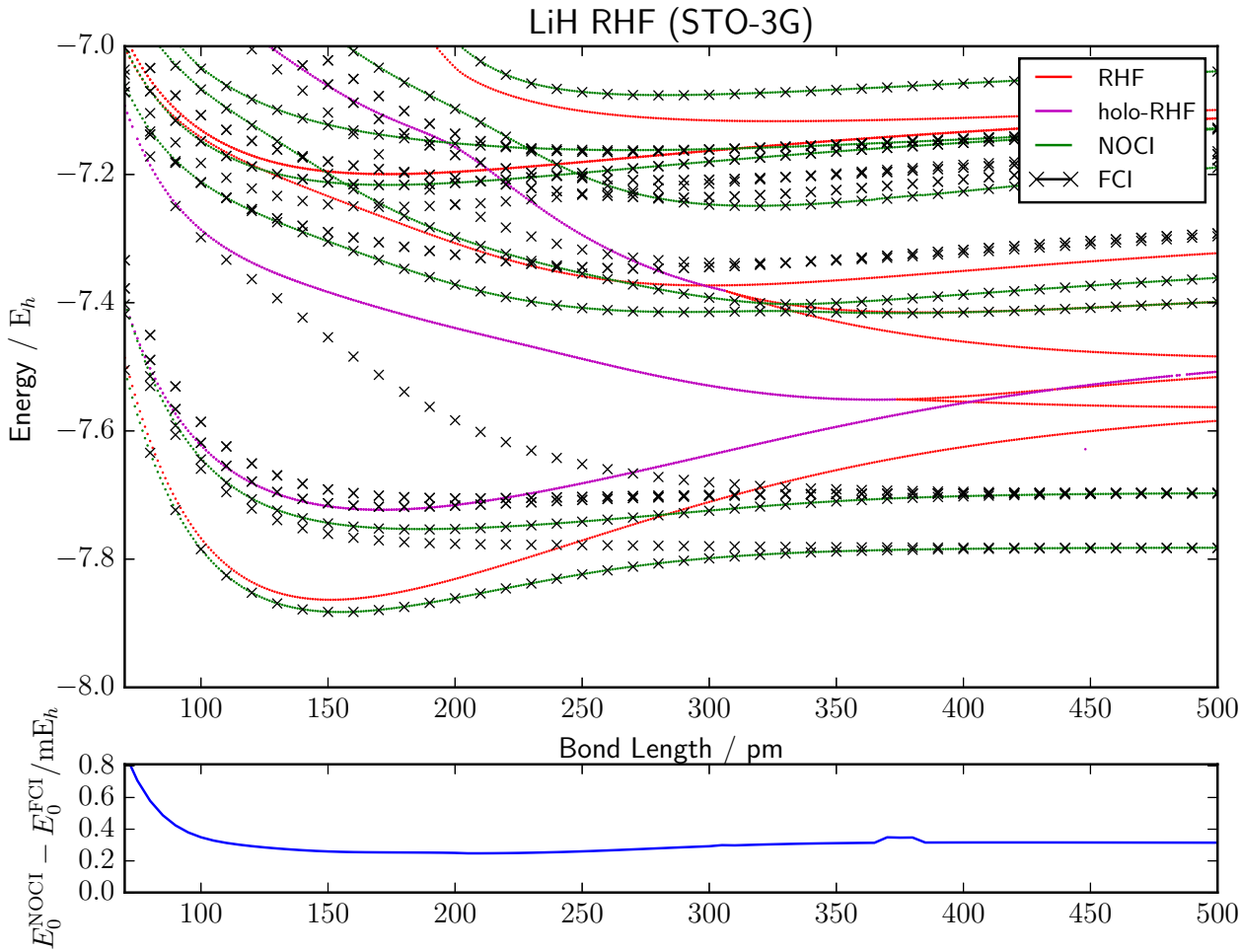
   where E_{loc} is the local energy given by $E_{loc}(\mathbf{r}) = \Psi_T(\mathbf{r})^{-1}\hat{H}\Psi_T(\mathbf{r})$.
3. **Branching:**
   - Walkers with low weights below a certain threshold are killed, whilst those above a certain threshold are copied.
4. **Sampling:**
   - Energy is sampled from weighted sum of individual walker local energies

$$E_D \approx \frac{1}{M}\sum_M E_L(\mathbf{r}_M). \tag{7}$$

So what's the problem?

- Quality of trial wavefunction controls statistical efficiency and limits final accuracy of simulation.
- Fixed node approximation yields lowest energy for a given nodal surface.
- **Only** when the nodal surface is exactly correct can this give the exact answer.

Could NOCI provide improved trial wavefunctions?



Could NOCI provide improved trial wavefunctions?

NOCI states are constructed from a linear combination of determinants containing holomorphic HF solutions.

- Wavefunction is constructed from multiple determinants, each based on a different set of molecular orbitals.
- Wavefunction is complex valued in general.

Exploiting NOCI trial wavefunctions requires a multi-determinantal method and the fixed phase approximation.

Using a multi-determinantal trial wavefunction

Trial wavefunction is given by

$$\Psi_T = \sum_k^{n_{dets}} a_k \det M^{\uparrow k} \det M^{\downarrow k}. \tag{8}$$

For most of the DMC algorithm we just loop over each reference determinant, but we must be careful when computing $\nabla \Psi_T$ and $\nabla^2 \Psi_T$...

$$\frac{\nabla_{\mathbf{r}_i} \Psi_T}{\Psi_T} = \frac{\sum_k^{n_{dets}} a_k \left[\nabla_{\mathbf{r}_i} \det M^{\uparrow k}\right] \det M^{\downarrow k}}{\sum_k^{n_{dets}} a_k \det M^{\uparrow k} \det M^{\downarrow k}} \tag{9}$$

In the standard case ($n_{dets} = 1$) this reduces to

$$\frac{\nabla_{\mathbf{r}_i} \Psi_T}{\Psi_T} = \frac{\nabla_{\mathbf{r}_i} \det M^{\uparrow}}{\det M^{\uparrow}} = \sum_\mu \left[\nabla_{\mathbf{r}_i} M^{\uparrow}_{i\mu}(\mathbf{r})\right] M^{\uparrow}(\mathbf{r})^{-1}_{\mu i}. \tag{10}$$

Introducing the fixed-phase approximation

- Take wavefunction as a combination of amplitude and phase

$$\Psi(\mathbf{r},\tau) = \rho(\mathbf{r},\tau)\exp\left[\mathrm{i}\Phi(\mathbf{r},\tau)\right]. \tag{11}$$

- Substituting into imaginary time Schrödinger equation gives two coupled differential equations

$$-\frac{\partial\rho(\mathbf{r},\tau)}{\partial\tau} = \left[-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + \frac{1}{2}|\nabla\Phi(\mathbf{r},\tau)|^2\right]\rho(\mathbf{r},\tau) \tag{12}$$

$$-\frac{\partial\Phi(\mathbf{r},\tau)}{\partial\tau} = \left[-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + \frac{\nabla\rho(\mathbf{r},\tau)\cdot\nabla}{\rho(\mathbf{r},\tau)}\right]\Phi(\mathbf{r},\tau). \tag{13}$$

- Fixed phase approximation sets $\frac{\partial\Phi(\mathbf{r},\tau)}{\partial\tau} = 0$, giving $\Phi(\mathbf{r},\tau) = \Phi_T(\mathbf{r})$.

G. Oritz, D. M Ceperley and R. M. Martin, *Phys. Rev. Lett.*, **71**, 2777, (1993)
C. A. Melton, M. C. Bennett and L. Mitas, *J. Chem. Phys.*, **144**, 244113, (2016)

Implementing FPDMC

FPDMC proceeds in same manner as FNDMC with a few modifications:

- Drift velocity calculated from trial amplitude $\rho_T(\mathbf{r})$

$$\mathbf{v}_D(\mathbf{r}) = \rho_T^{-1}\nabla\rho_T(\mathbf{r}). \tag{14}$$

- Local energy includes phase dependent repulsive term

$$E_L(\mathbf{r}) = \rho_T^{-1}(\mathbf{r})\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + \frac{1}{2}|\nabla\Phi_T(\mathbf{r})|^2\right]\rho_T(\mathbf{r}). \tag{15}$$

Straightforward expressions for Equations 14 and 15 can be derived from $\nabla\Psi_T$ and $\nabla^2\Psi_T$

$$\rho_T^{-1}(\mathbf{r})\nabla\rho_T(\mathbf{r}) = \Re\left(\Psi_T^*\nabla\Psi_T\right)/\rho_T^2, \tag{16}$$

$$E_L(\mathbf{r}) = -\frac{1}{2}\Re\left(\Psi_T^*\nabla^2\Psi_T\right)/\rho_T^2 + V(\mathbf{r}). \tag{17}$$

Fixed-node as a special case of fixed-phase

Construct a complex trial function from real and imaginary part

$$\Psi_T = \Psi_R + \mathrm{i}\epsilon\Psi_B \tag{18}$$

Potential generate by phase of $\Phi_T(\mathbf{r})$ is

$$V_{ph} = \frac{1}{2}\left|\frac{\epsilon\left(\Psi_R\nabla\Psi_B - \Psi_B\nabla\Psi_R\right)}{\Psi_R^2 + \epsilon^2\Psi_B^2}\right|^2. \tag{19}$$

- Away from nodal surface ($\Psi_R \neq 0$), limit $\epsilon \to 0$ yields $V_{ph} = 0$.
- At the nodal surface ($\Psi_R = 0$), generally $|\nabla\Psi_R|^2 \geq 0$ so limit $\epsilon \to 0$ yields $V_{ph} = \infty$.

Putting it all together

Combining multi-determinantal DMC and FPDMC should require minimal alterations to the DMC algorithm.

- Implement multi-determinantal algorithm and test for real wavefunctions.
- Back compatibility achieved by setting $n_{det} = 1$.
- Independent of Jastrow factor implementation.
- Code up the FPDMC and test using NOCI states constructed from holomorphic solutions.

Method is being written into the group `simpleDMC` code.

Questions to investigate

Beyond implementation, the interesting technical questions include

- Do NOCI trial functions give more efficient convergence?
- If an excited NOCI state is used, do we converge onto the related FCI state?
- What result would we obtain for 'dormant' holomorphic solutions that are complex everywhere?

Using the new framework we will hopefully be able to use NOCI trial wavefunctions for wider applications!