

# Wave functions beyond Slater-Jastrow

Pablo López Ríos

QMC school at S.N.Bose Centre

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# The Slater determinant

- Basic antisymmetric wave function: a Slater determinant

$$\Psi_S(\mathbf{R}) = \begin{vmatrix} \phi_1^\uparrow(\mathbf{r}_1^\uparrow) & \dots & \phi_1^\uparrow(\mathbf{r}_{N_\uparrow}^\uparrow) \\ \vdots & \ddots & \vdots \\ \phi_{N_\uparrow}^\uparrow(\mathbf{r}_1^\uparrow) & \dots & \phi_{N_\uparrow}^\uparrow(\mathbf{r}_{N_\uparrow}^\uparrow) \end{vmatrix} \begin{vmatrix} \phi_1^\downarrow(\mathbf{r}_1^\downarrow) & \dots & \phi_1^\downarrow(\mathbf{r}_{N_\downarrow}^\downarrow) \\ \vdots & \ddots & \vdots \\ \phi_{N_\downarrow}^\downarrow(\mathbf{r}_1^\downarrow) & \dots & \phi_{N_\downarrow}^\downarrow(\mathbf{r}_{N_\downarrow}^\downarrow) \end{vmatrix}$$

- Orbitals  $\{\phi_i^\sigma\}$  can be obtained from HF, DFT, etc.

# The Slater-Jastrow wave function

- Electronic correlation introduced using a multiplicative Jastrow factor,

$$\Psi_{\text{SJ}}(\mathbf{R}) = \exp[J(\mathbf{R})] \Psi_{\text{S}}(\mathbf{R})$$

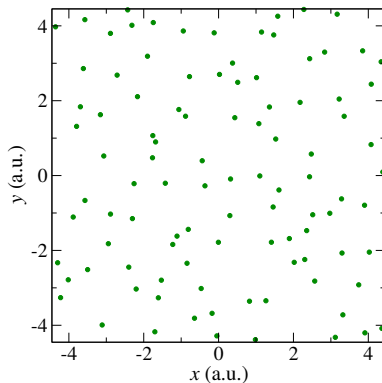
- Advantages of using a Jastrow factor:
  - **Compact** form
  - Fulfills **cusp conditions** → much improved statistics
  - Good description of electronic **correlation** → ability to retrieve 80–90% of the correlation energy in VMC

# Need for better wave functions

Why do we need wave functions other than Slater-Jastrow?

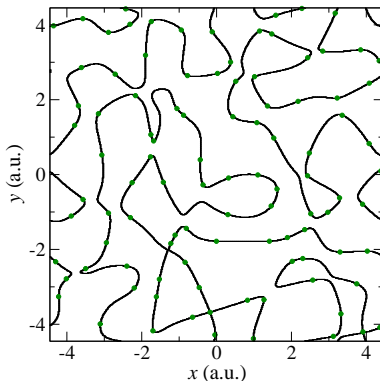
- DMC energies depend on the **nodes** of  $\Psi$ , but Jastrow factors do not modify the nodes of  $\Psi_S$
- Better wave functions **may** help us achieve **chemical accuracy** (error in energy differences  $\leq 1$  kcal mol<sup>-1</sup>)
- **Other expectation values** are far more sensitive to the quality of  $\Psi$  than the energy
- Improving  $\Psi$  and its nodes involves **interesting** Physics/Maths
- A **better description** of certain “exotic” systems may be achieved with wave functions other than  $\Psi_S$

# How complex are nodal surfaces?



HF nodes of a 2D HEG

# How complex are nodal surfaces?



HF nodes of a 2D HEG

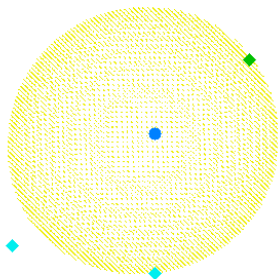
# How complex are nodal surfaces?

The nodes of  $\Psi_S$ :

- Are the  $3N - 1$  dimensional region  $\{\mathbf{R} \mid \Psi_S(\mathbf{R}) = 0\}$
- Have **no** connection with the nodes of the orbitals
- Are **rarely sampled**  $\rightarrow$  are **hard to optimize** within standard schemes  $\rightarrow$  but are **the source of error** anyway
- Tend to divide config space into too many regions (nodal pockets)  $\rightarrow$  tend to have the **wrong topology**
- Do satisfy the **tiling theorem**: all nodal pockets are equivalent
- Are not too far off the true answer

# How complex are nodal surfaces?

HF nodes vs. exact nodes



Beryllium atom (see separate animation)



## Possible wave function modifications

- Optimize the **orbitals** in  $\Psi_S$
- Explicitly include inter-particle distances in  $\Psi_S$  via coordinate transformations  $\rightarrow$  **backflow**
- Explicitly include inter-particle distances in  $\Psi_S$  via orbital prefactor  $\rightarrow$  **orbital-dependent Jastrow factor**

## Orbital parametrization

- In atomic systems, modify the radial function,

$$\phi_{nlm}(\mathbf{r}) = [\rho_{nl}^{\text{HF}}(r) + \Delta\rho_{nl}(r)] r^l Y_{lm}(\theta, \phi)$$

with

$$\Delta\rho_{nl}(r) = \left( \sum_{j=0}^{N_p} c_{jnl} r^j \right) \exp\left( \frac{-A_{nl} r^2}{1 + B_{nl} r} \right)$$

N. D. Drummond *et. al.*, J. Chem. Phys. **124**, 224104 (2006)

- In small molecules one can expand the orbitals in a Slater basis  
 C. Filippi and C. J. Umrigar, J. Chem. Phys. **105**, 213 (1996)
- For orbitals expanded in Gaussians, one could optimize expansion coefficients and exponents directly

# How well does orbital optimization work?

- Varying degree of success in different studies
- In general the improvements are rather modest, e.g.,
  - All-electron Ne and Ne<sup>+</sup>:
    - **VMC**:  $E_{\text{unopt}} - E_{\text{opt}} \approx 12\% (E_{\text{unopt}} - E_0)$
    - **DMC**:  $E_{\text{unopt}} - E_{\text{opt}} \approx 3\% (E_{\text{unopt}} - E_0)$   
→ little nodal improvement
  - Pseudo-Ne and pseudo-Ne<sup>+</sup>:
    - **VMC**:  $E_{\text{unopt}} - E_{\text{opt}} \approx 2\% (E_{\text{unopt}} - E_0)$
    - **DMC**:  $E_{\text{unopt}} - E_{\text{opt}} \approx 2\% (E_{\text{unopt}} - E_0)$   
→ little overall improvement

## The Slater-Jastrow-backflow wave function

The backflow transformation applied to  $\Psi_S$  is

$$\Psi_S^{\text{BF}}(\mathbf{R}) = \Psi_S[\mathbf{X}(\mathbf{R})]$$

where  $\mathbf{X}$  is a vector of *quasi-particle* coordinates,

$$\mathbf{x}_i(\mathbf{R}) = \mathbf{r}_i + \boldsymbol{\xi}_i(\mathbf{R})$$

i.e.,

$$\Psi_S^{\text{BF}}(\mathbf{R}) = \begin{vmatrix} \phi_1[\mathbf{x}_1(\mathbf{R})] & \phi_1[\mathbf{x}_2(\mathbf{R})] & \dots & \phi_1[\mathbf{x}_N(\mathbf{R})] \\ \phi_2[\mathbf{x}_1(\mathbf{R})] & \phi_2[\mathbf{x}_2(\mathbf{R})] & \dots & \phi_2[\mathbf{x}_N(\mathbf{R})] \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N[\mathbf{x}_1(\mathbf{R})] & \phi_N[\mathbf{x}_2(\mathbf{R})] & \dots & \phi_N[\mathbf{x}_N(\mathbf{R})] \end{vmatrix}$$

## Interpreting backflow

- Backflow originally derived to account for the **momentum dependence of correlations** between He<sub>3</sub> impurity and He<sub>4</sub> gas

R.P. Feynman and M. Cohen, Phys.Rev. **102**, 1189 (1956)

- Backflow can also be derived as a **second order correction** to  $\Psi_S$  within “many-body perturbation theory”, based on the Feynman-Kacs formula

Holzmann *et al*, Phys.Rev. E **68**, 046707 (2003)

- The Jastrow factor and the backflow transformation can be seen as **complementary tools** to improve  $\Psi_S$ :
  - Jastrow factor **modulates**  $\Psi_S$  in the “vertical” direction
  - Backflow **deforms**  $\Psi_S$  in the “horizontal” direction

## Parametrization of backflow

We construct  $\xi_i(\mathbf{R})$  as a sum of e-e, e-n and e-e-n functions:

$$\xi_i^{e-e} = \sum_{j \neq i}^{N_e} \eta_{ij} \mathbf{r}_{ij} \quad , \quad \eta_{ij} = \eta(r_{ij})$$

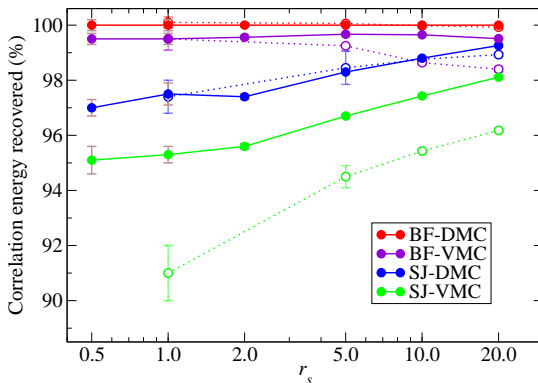
$$\xi_i^{e-n} = \sum_I^{N_n} \mu_{iI} \mathbf{r}_{iI} \quad , \quad \mu_{iI} = \mu(r_{iI})$$

$$\xi_i^{e-e-n} = \sum_{j \neq i}^{N_e} \sum_I^{N_n} (\Phi_i^{jI} \mathbf{r}_{ij} + \Theta_i^{jI} \mathbf{r}_{iI}) \quad , \quad \Phi_i^{jI} = \Phi_I(r_{ij}, r_{iI}, r_{jI})$$

$$\Theta_i^{jI} = \Theta_I(r_{ij}, r_{iI}, r_{jI})$$

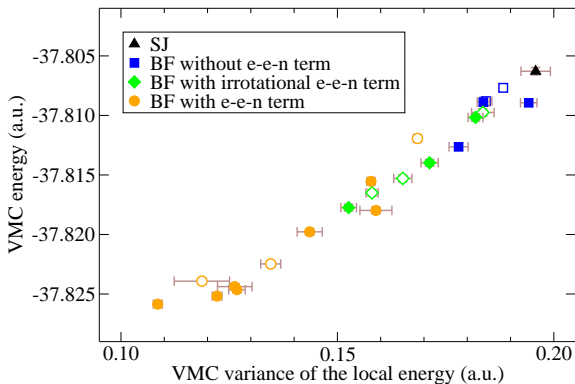
$$\text{Total } \xi_i = \xi_i^{e-e} + \xi_i^{e-n} + \xi_i^{e-e-n}$$

# Backflow results



3D 54-electron HEG

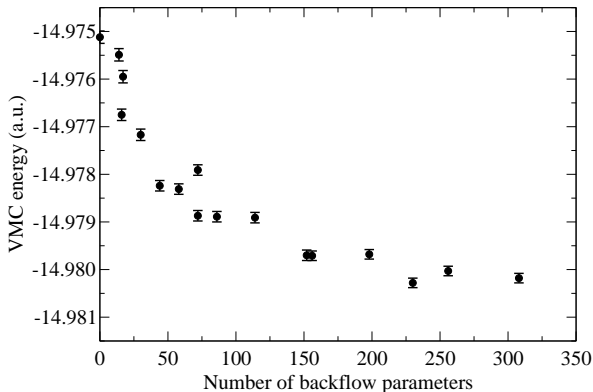
# Backflow results



All-electron carbon atom



## Backflow results



All-electron  $\text{Li}_2$  molecule

## Backflow results

Practicalities of backflow:

- Variance of the local energy **reduced** → need fewer data for fixed target uncertainty
- Wave function update algorithms are a **factor of  $N$  more costly** (CBCS simpler but EBES still favourable)

# The orbital-dependent Jastrow factor

- Functional form:

$$\Psi_S^{\text{ODJ}}(\mathbf{R}) = \begin{vmatrix} e^{J_1(\mathbf{R})} \phi_1[\mathbf{r}_1] & e^{J_1(\mathbf{R})} \phi_1[\mathbf{r}_2] & \dots & e^{J_1(\mathbf{R})} \phi_1[\mathbf{r}_N] \\ e^{J_2(\mathbf{R})} \phi_2[\mathbf{r}_1] & e^{J_2(\mathbf{R})} \phi_2[\mathbf{r}_2] & \dots & e^{J_2(\mathbf{R})} \phi_2[\mathbf{r}_N] \\ \vdots & \vdots & \ddots & \vdots \\ e^{J_N(\mathbf{R})} \phi_N[\mathbf{r}_1] & e^{J_N(\mathbf{R})} \phi_N[\mathbf{r}_2] & \dots & e^{J_N(\mathbf{R})} \phi_N[\mathbf{r}_N] \end{vmatrix}$$

- **Modulates** the individual orbitals instead of modulating/deforming the entire wave function (normal Jastrow factor/backflow)
- Has the ability to **modify the nodes** of  $\Psi_S$
- In practice results in a **very small improvement**

T. Bouabça *et al*, J.Chem.Phys. **133**, 044111 (2010).

# Alternative wave functions

- **Multi-determinant** expansions
- **(Multi-)geminal/(multi-)Pfaffian** (pairing) wave functions
- **Tailor-made** wave functions for specific problems

# Multi-determinant expansions

- Eigenstates  $\psi_n(\mathbf{r})$  of a single-particle Hamiltonian  $\equiv$  **basis** for functions of  $\mathbf{r}$
- Hence, determinants of  $N$  orbitals for  $N$  particles  $\equiv$  **basis** for **antisymmetric** functions of  $\mathbf{R}$
- Hence, the **exact wave** function is

$$\Phi_0(\mathbf{R}) = \sum_{k=0}^{\infty} c_k D_k^{\uparrow}(\mathbf{R}^{\uparrow}) D_k^{\downarrow}(\mathbf{R}^{\downarrow})$$

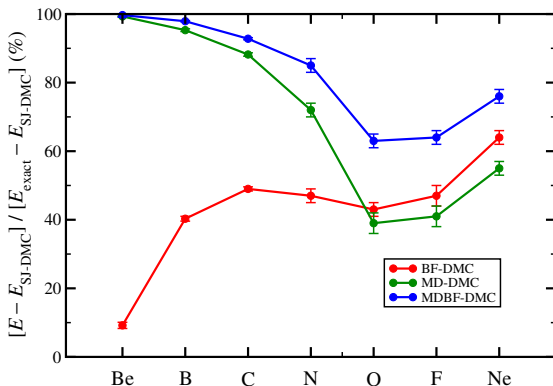
- Truncated expansion is an **approximation** to  $\Phi_0$
- First term of expansion = Hartree-Fock wave function
- Relatively **small** expansions in QMC thanks to **exact cusps**

# Applicability

- Small atoms and molecules → **excellent** results
- Medium-sized systems → **expensive** and/or **mediocre** results
- Large/crystalline systems → **infeasible**

Multi-determinant expansions are **not size-consistent**

# Multi-determinants vs. backflow



Backflow catches up with fixed-size multi-determinants by  $Z = 8$

\* M.D. Brown *et al*, *J.Chem.Phys.* **126**, 224110 (2007); see also: P. Seth *et al*, *J.Chem.Phys.* **134**, 084105 (2011)

# Antisymmetrized Geminal Power (AGP) wave function

The **geminal** or **AGP** wave function is

$$\Psi_{\text{AGP}}(\mathbf{R}) = \begin{vmatrix} \Phi(\mathbf{r}_1^\uparrow, \mathbf{r}_1^\downarrow) & \Phi(\mathbf{r}_1^\uparrow, \mathbf{r}_2^\downarrow) & \dots & \Phi(\mathbf{r}_1^\uparrow, \mathbf{r}_N^\downarrow) \\ \Phi(\mathbf{r}_2^\uparrow, \mathbf{r}_1^\downarrow) & \Phi(\mathbf{r}_2^\uparrow, \mathbf{r}_2^\downarrow) & \dots & \Phi(\mathbf{r}_2^\uparrow, \mathbf{r}_N^\downarrow) \\ \vdots & \vdots & \ddots & \vdots \\ \Phi(\mathbf{r}_N^\uparrow, \mathbf{r}_1^\downarrow) & \Phi(\mathbf{r}_N^\uparrow, \mathbf{r}_2^\downarrow) & \dots & \Phi(\mathbf{r}_N^\uparrow, \mathbf{r}_N^\downarrow) \end{vmatrix}$$

where

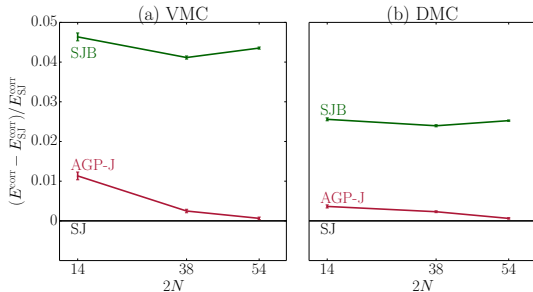
$$\Phi(\mathbf{r}^\uparrow, \mathbf{r}^\downarrow) = \sum_{i,j}^{N_{\text{orb}}} g_{ij} \phi_i(\mathbf{r}^\uparrow) \phi_j(\mathbf{r}^\downarrow)$$

with  $g_{ij} \equiv$  optimizable parameters, and  $N_{\text{orb}} \geq N$ .



# Antisymmetrized Geminal Power (AGP) wave function

- $\Psi_{\text{AGP}}$  introduces **correlations** between opposite-spin electrons
- When  $g_{ij} = \delta_{ij}$  and  $N_{\text{orb}} = N$ ,  $\Psi_{\text{AGP}}$  reduces to  $\Psi_{\text{S}}$

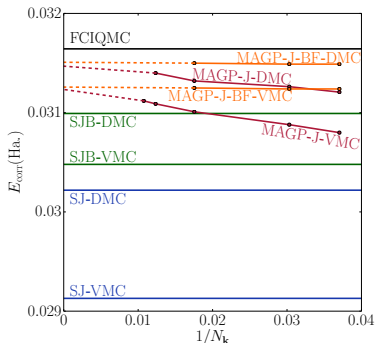


- $\Psi_{\text{AGP}}$  is equivalent to a multi-determinant expansion – but **not a particularly good one**

\* figure from P. Bugnion, *PhD Thesis*, University of Cambridge (2014)

## Multi-AGP (MAGP) wave function

- However, the **multi-geminal expansion**  $\Psi_{\text{MAGP}}$  is **very successful** for the HEG, although **expensive**



- The MAGP wave function is the subject of current research

\* figure from P. Bugnion, *PhD Thesis*, University of Cambridge (2014)

## Pfaffian and multi-Pfaffian wave functions

- Pfaffians are similar to geminals, but allow correlations between **same-spin** electrons
- (Multi-)Pfaffians have been tested on small systems with **good results**

M. Bajdich *et al*, Phys.Rev. B **77**, 115112 (2008)

- (Multi-)Pfaffians suffer from similar **size-consistency problems** as multi-determinants and (multi-)geminals

## Pairing determinants

- Simple wave function suitable for electron-hole systems
- Functional form:

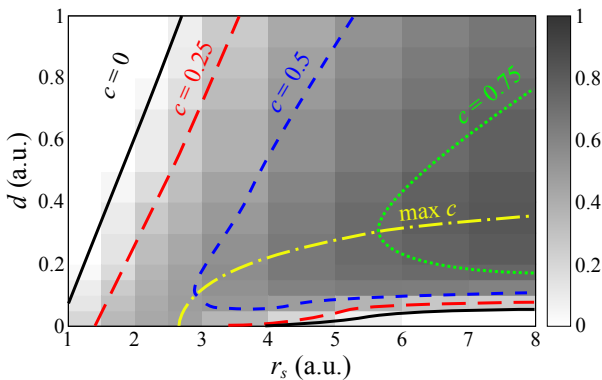
$$\Psi_P(\mathbf{R}) = \begin{vmatrix} \phi(\mathbf{e}_1 - \mathbf{h}_1) & \phi(\mathbf{e}_1 - \mathbf{h}_2) & \dots & \phi(\mathbf{e}_1 - \mathbf{h}_N) \\ \phi(\mathbf{e}_2 - \mathbf{h}_1) & \phi(\mathbf{e}_2 - \mathbf{h}_2) & \dots & \phi(\mathbf{e}_2 - \mathbf{h}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi(\mathbf{e}_N - \mathbf{h}_1) & \phi(\mathbf{e}_N - \mathbf{h}_2) & \dots & \phi(\mathbf{e}_N - \mathbf{h}_N) \end{vmatrix}$$

with  $\phi(\mathbf{r})$  an appropriate pairing function

- These wave functions have been widely used to study electron-hole systems.

## Pairing determinants

Phase diagram of the 2D equal-mass electron-hole bilayer using flexible  $\phi$  designed to describe both fluid and excitonic phases.



# The “EXMOL” wave function

- Wave function designed for “excitonic molecules” (small assemblies of positive and negative particles in general)
- Inspired by a very accurate wave function for  $\text{Ps}_2$  (2 electrons + 2 positrons) based on:

$$\begin{aligned} \Psi_{\text{Ps}_2} = & \phi_1(\mathbf{e}_\uparrow - \mathbf{h}_\uparrow)\phi_1(\mathbf{e}_\downarrow - \mathbf{h}_\downarrow)\phi_2(\mathbf{e}_\uparrow - \mathbf{h}_\downarrow)\phi_2(\mathbf{e}_\downarrow - \mathbf{h}_\uparrow) \\ & + \phi_2(\mathbf{e}_\uparrow - \mathbf{h}_\uparrow)\phi_2(\mathbf{e}_\downarrow - \mathbf{h}_\downarrow)\phi_1(\mathbf{e}_\uparrow - \mathbf{h}_\downarrow)\phi_1(\mathbf{e}_\downarrow - \mathbf{h}_\uparrow) \end{aligned}$$

which favours “indirect” pairing between Ps “atoms”

# The “EXMOL” wave function

- Functional form:

$$\Psi_{\text{EXMOL}}(\mathbf{R}) = \sum_k^n c_k \prod_i^{N_e} \prod_j^{N_h} \phi_{\lambda_{ijk}}(\mathbf{e}_i - \mathbf{h}_j)$$

where

- $n$  = n. of terms,  $N_e$  = n. of electrons,  $N_h$  = n. of holes
- $\mathbf{e}_i$  and  $\mathbf{h}_j$  are electron and hole coordinates
- $\phi_\lambda$  is the  $\lambda$ th pairing function (e.g., “cusplless exponential”)
- $\lambda_{ijk}$  is a function chooser
- $c_k$  is the coefficient of the  $k$ th term
- $\{c_k\}$  and  $\{\lambda_{ijk}\}$  must obey certain rules to ensure the relevant symmetries and antisymmetries

## The “EXMOL” wave function

- This is an example of the **flexibility** offered by QMC in choosing a wave function form — tailor-made wave function form for a specific problem
- The EXMOL wave function was implemented in CASINO to study stability of  $Ps_3$ ,  $Ps_4$ , etc
- These turned out to be **unstable**, so EXMOL remains an **undocumented** feature awaiting use in publication (we will soon publish results for e-e-h “ions”)
- The implementation is reliable and well tested, with automatic symmetry, backflow support, etc — sample input available on request



# What should be combined with what?

- **Orbital optimization + backflow:**  
orbital optimization largely **overlaps** with backflow
- **Orbital optimization + multi-determinants:**  
orbital optimization largely **overlaps** with multi-determinants  
multi-determinants
- **Multi-determinants/MAGP/...** and **backflow:**  
**excellent** results where multi-determinants/MAGP/... are  
feasible to use

# Summary

- There are many **alternatives** to  $\Psi_S$ , but have **restricted applicability** and/or **greater cost**
- There are several **modifications** to a given base wave function, the most successful and widely applicable of which is **backflow**, which provide **better accuracy** but come at an **increased cost**
- The **system** you study and the available computational **resources** will determine which wave function you can use