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Advanced School on Quantum Monte Carlo Methods in Physics and Chemistry

21 January - 1 February, 2008

VMC and trial wave functions.

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Introduction to quantum Monte Carlo methods: VMC and trial wave functions
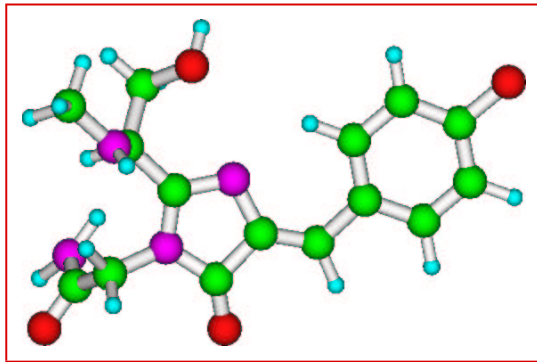
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A quantum mechanical and first-principle approach

$\longrightarrow$ Collection of ions + electrons

$\downarrow$

Only input: Z_α, N_α

Work in the Born-Oppenheimer approximation

Solve the Schrödinger equation for the electrons in the ionic field

$$\mathcal{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_i v_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Solving the many-electron Schrödinger equation

$$\mathcal{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_i v_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

What do we want to compute?

Fermionic ground state and low-lying excited states

Evaluate expectation values $\quad \dfrac{\langle \Psi_n | \mathcal{O} | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle}$

Where is the difficulty?

Electron-electron interaction $\rightarrow$ Non-separable

Is there an optimal theoretical approach?

- Density functional theory methods
  Large systems but approximate exchange/correlation

- Quantum chemistry post-Hartree-Fock methods

  $\downarrow$ $\downarrow$ $\searrow$

  CI   MCSCF   CC ...

  Very accurate on small systems

- Quantum Monte Carlo techniques

  Fully-correlated calculations

  Stochastic solution of Schrödinger equation

  Most accurate benchmarks for medium-large systems

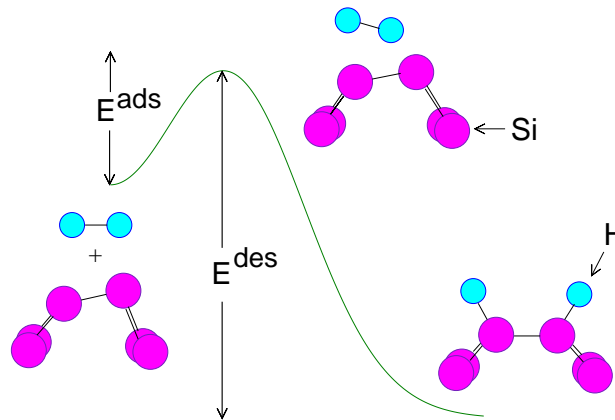If you can, use density functional theory!

HUMAN TIME

Wave function methods

Density functional theory

N^3

Quantum chemistry   Quantum Monte Carlo

$> N^6$ N^4

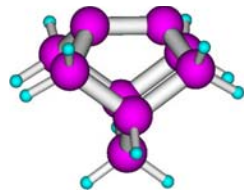COMPUTATIONAL COST
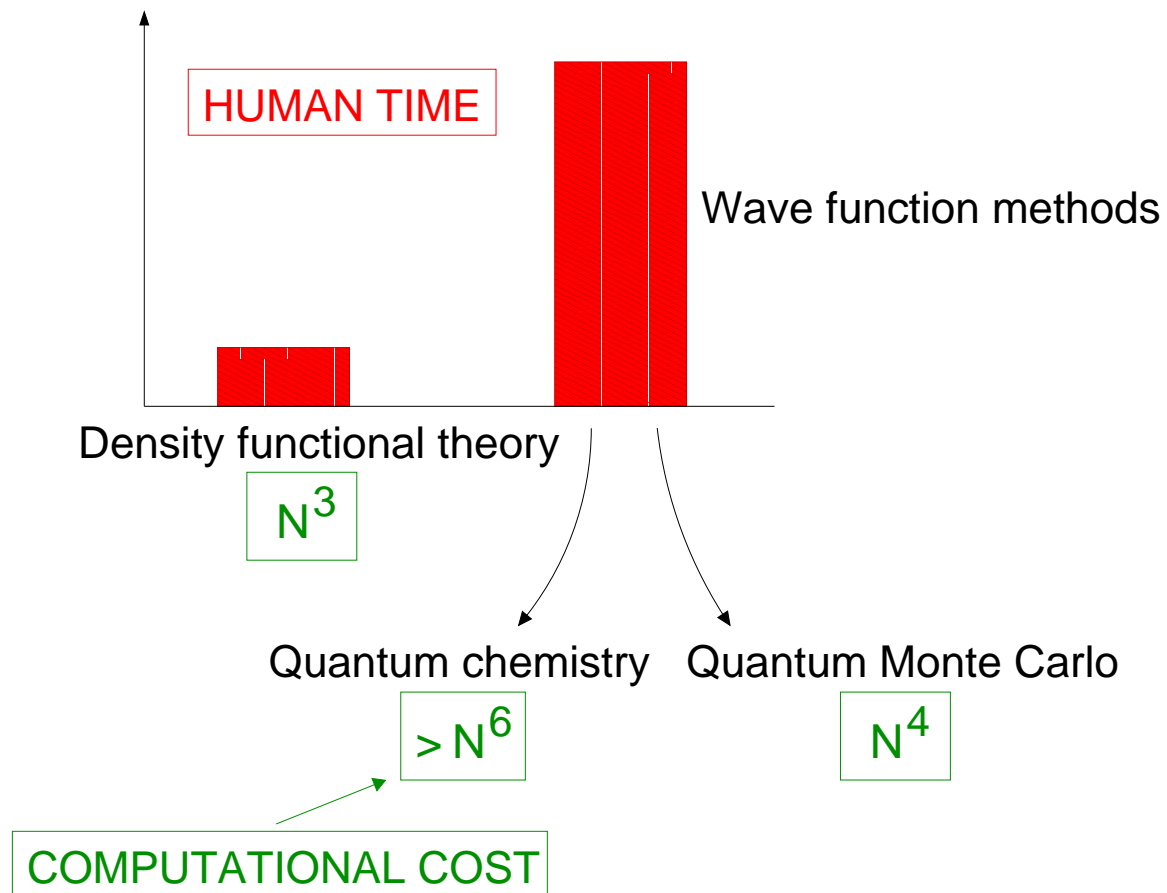
All is relative ...

We think of density functional theory as cheap and painless!

... but density functional theory does not always work

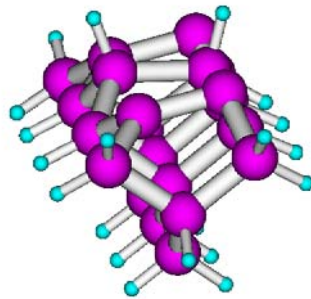A "classical" example: Adsorption/desorption of H_2 on Si(001)

For a small model cluster

DFT error persists for larger models!

	E_a^{ads}	E_a^{des}	E_{rxn}	
DFT	0.69	2.86	2.17	
QMC	1.01(6)	3.65(6)	2.64(6)	eV

Favorable scaling of QMC with system size

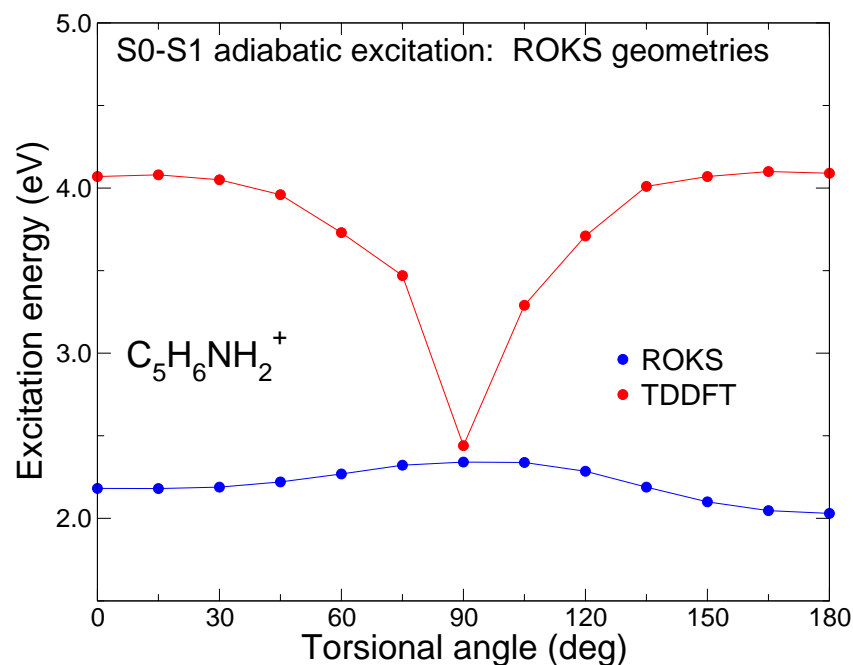QMC possible for realistic clusters with 2, 3, 4 ... surface dimers

Accurate QMC calculations doable from small to large scales

Error of DFT is large $\rightarrow$ 0.8 eV on desorption barrier !
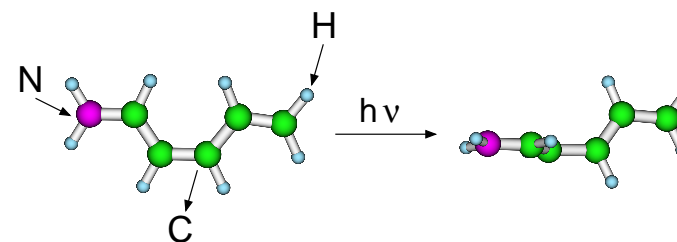
Healy, Filippi *et al.* PRL (2001); Filippi *et al.* PRL (2002)

When DFT has problems $\rightarrow$ Wave function based methods

Wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ where $\mathbf{x} = (\mathbf{r}, \sigma)$ and $\sigma = \pm 1$

How do we compute expectation values?

Many-body wave functions in traditional quantum chemistry

Interacting $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \leftrightarrow$ Non-interacting one-particle basis

Ψ expanded in determinants of single-particle orbitals $\psi(\mathbf{x})$

Single-particle orbitals expanded on Gaussian basis

$\Rightarrow$ All integrals can be computed analytically

$$\boxed{\text{Many-body wave functions in traditional quantum chemistry}} \quad (1)$$

Starting point $\rightarrow$ Non-interacting Hartree-Fock wave function

$$D_{\mathrm{HF}}(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \begin{vmatrix} \psi_1(\mathbf{x}_1) & \ldots & \psi_1(\mathbf{x}_N) \\ \vdots & & \vdots \\ \psi_N(\mathbf{x}_1) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

Optimal spin-orbitals $\psi_i(\mathbf{x}) = \phi_i(\mathbf{r})\chi_{s_i}(\sigma)$ satisfy HF equations

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\mathbf{r}) + \sum_{j=1}^{N} \int \mathrm{d}\mathbf{r}' \, \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \right] \phi_i(\mathbf{r}) + [\hat{v}_{\mathrm{HF}}\phi_i](\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$\Rightarrow$ $\boxed{\text{occupied}}$ orbitals $(\psi_1 \ldots \psi_N)$ + $\boxed{\text{virtual}}$ orbitals $(\psi_{N+1} \ldots)$

A jungle of acronyms: CI, CASSCF, MRCI, CASPT2 . . .

Expansion in linear combination of determinants

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \longrightarrow D_{\mathrm{HF}} = \begin{vmatrix} \psi_1(\mathbf{x}_1) & \ldots & \psi_1(\mathbf{x}_N) \\ \vdots & & \vdots \\ \psi_N(\mathbf{x}_1) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

$c_0 D_{\mathrm{HF}} + c_1 D_1 + c_2 D_2 + \ldots$ millions of determinants

$$\begin{vmatrix} \psi_1(\mathbf{x}_1) & \ldots & \psi_1(\mathbf{x}_N) \\ \vdots & & \vdots \\ \psi_{N+1}(\mathbf{x}_1) & \ldots & \psi_{N+1}(\mathbf{x}_N) \end{vmatrix}$$

by constructing single, double, . . . up to N-body excitations

$\boxed{\text{Many-body wave functions in traditional quantum chemistry}}$ (3)

$\boxed{\text{Pros and cons}}$ of CI expansion in Slater determinants

$$\Psi_{\mathrm{CI}} = c_0 D_{\mathrm{HF}} + \sum_{ab} c_{a \to b} D^{a \to b} + \sum_{abcd} c_{ab \to cd} D^{ab \to cd} + \dots$$

Optimal CI coefficients by solving generalized eigenvalue equation

$$\Psi_{\mathrm{CI}} = \sum_{i=1}^{K} c_i C_i \quad \Rightarrow \quad \boxed{\sum_{j=1}^{K} \langle C_i | \mathcal{H} | C_j \rangle c_j^{(k)} = E_{\mathrm{CI}}^{(k)} \sum_{j=1}^{K} \langle C_i | C_j \rangle c_j^{(k)}}$$

Orbitals on a Gaussian basis $\to$ $\boxed{\text{Integrals computed analytically}}$

... but $\boxed{\text{slowly converging expansion}}$

Can we use a more compact Ψ?

We want to construct an accurate and more compact Ψ

Explicit dependence on the inter-electronic distances r_{ij}

How do we compute expectation values if no single-electron basis?

Consider the expectation value of the Hamiltonian on Ψ

$$
E_V = \frac{\langle\Psi|\mathcal{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\int \mathrm{d}\mathbf{R}\,\Psi^*(\mathbf{R})\mathcal{H}\Psi(\mathbf{R})}{\int \mathrm{d}\mathbf{R}\,\Psi^*(\mathbf{R})\Psi(\mathbf{R})} \geq E_0
$$

$$
= \int \mathrm{d}\mathbf{R}\,\frac{\mathcal{H}\Psi(\mathbf{R})}{\Psi(\mathbf{R})}\boxed{\frac{|\Psi(\mathbf{R})|^2}{\int \mathrm{d}\mathbf{R}|\Psi(\mathbf{R})|^2}}
$$

$$
= \int \mathrm{d}\mathbf{R}\,E_{\mathrm{L}}(\mathbf{R})\,\rho(\mathbf{R}) = \langle E_{\mathrm{L}}(\mathbf{R})\rangle_\rho
$$

ρ is a distribution function and $E_{\mathrm{L}}(\mathbf{R}) = \dfrac{\mathcal{H}\Psi(\mathbf{R})}{\Psi(\mathbf{R})}$ the local energy

Variational Monte Carlo: a random walk of the electrons

Use Monte Carlo integration to compute expectation values

▷ Sample $\mathbf{R}$ from $\rho(\mathbf{R})$ using Metropolis algorithm

▷ Average local energy $E_{\mathrm{L}}(\mathbf{R}) = \dfrac{\mathcal{H}\Psi(\mathbf{R})}{\Psi(\mathbf{R})}$ to obtain E_V as

$$E_V = \langle E_{\mathrm{L}}(\mathbf{R}) \rangle_\rho \approx \frac{1}{M} \sum_{i=1}^{M} E_{\mathrm{L}}(\mathbf{R}_i)$$

R
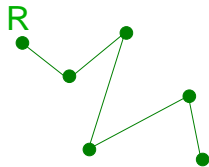
Random walk in 3N dimensions, $\mathbf{R} = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$

Just a trick to evaluate integrals in many dimensions

Is it really "just" a trick?

$Si_{21}H_{22}$
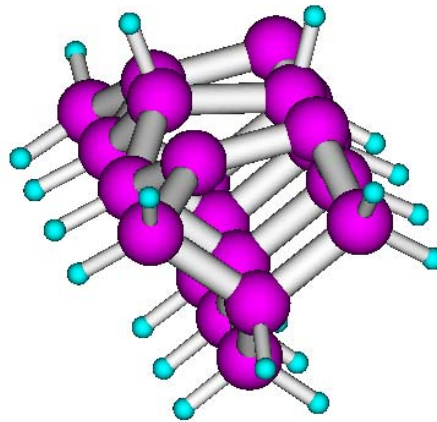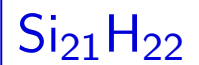
Number of electrons $4 \times 21 + 22 = 106$

Number of dimensions $3 \times 106 = \boxed{318}$

Integral on a grid with 10 points/dimension $\rightarrow 10^{318}$ points!

MC is a powerful trick $\Rightarrow$ Freedom in form of the wave function Ψ

Are there any conditions on many-body Ψ to be used in VMC?

Within VMC, we can use any "computable" wave function if

▷ Continuous, normalizable, proper symmetry

▷ Finite variance

$$\sigma^2 = \frac{\langle \Psi | (\mathcal{H} - E_V)^2 | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle (E_{\mathrm{L}}(\mathbf{R}) - E_V)^2 \rangle_\rho$$

since the Monte Carlo error goes as $\quad \mathrm{err}(E_V) \sim \dfrac{\sigma}{\sqrt{M}}$

Zero variance principle: if $\Psi \to \Psi_0$, $E_{\mathrm{L}}(\mathbf{R})$ does not fluctuate

Variational Monte Carlo and the generalized Metropolis algorithm

How do we sample distribution function $\rho(\mathbf{R}) = \dfrac{|\Psi(\mathbf{R})|^2}{\int d\mathbf{R} |\Psi(\mathbf{R})|^2}$?

Aim $\rightarrow$ Obtain a set of $\{\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_M\}$ distributed as $\rho(\mathbf{R})$

Generate a Markov chain

$\triangleright$ Start from arbitrary initial state $\mathbf{R}_i$

$\triangleright$ Use <u>stochastic</u> transition matrix $P(\mathbf{R}_f | \mathbf{R}_i)$

$$P(\mathbf{R}_f | \mathbf{R}_i) \geq 0 \qquad \sum_{\mathbf{R}_f} P(\mathbf{R}_f | \mathbf{R}_i) = 1.$$

as probability of making transition $\mathbf{R}_i \rightarrow \mathbf{R}_f$

$\triangleright$ Evolve the system by repeated application of P

Stationarity condition

To sample ρ, use P which satisfies stationarity condition :

$$\sum_i P(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i})\,\rho(\mathbf{R}_\mathrm{i}) = \rho(\mathbf{R}_\mathrm{f}) \qquad \forall\ \mathbf{R}_\mathrm{f}$$

Stationarity condition + stochastic property of P + ergodicity

$\Rightarrow$ Any initial distribution will evolve to ρ

More stringent (sufficient but not necessary) condition

In practice, we impose detailed balance condition

$$P(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i})\,\rho(\mathbf{R}_\mathrm{i}) = P(\mathbf{R}_\mathrm{i}|\mathbf{R}_\mathrm{f})\,\rho(\mathbf{R}_\mathrm{f})$$

How do we construct the transition matrix P in practice?

Write transition matrix P as proposal T $\times$ acceptance A

$$P(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i}) = A(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i})\ T(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i})$$

P and T are stochastic matrices but A is not

Rewriting detailed balance condition

$$P(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i})\ \rho(\mathbf{R}_\mathrm{i}) = P(\mathbf{R}_\mathrm{i}|\mathbf{R}_\mathrm{f})\ \rho(\mathbf{R}_\mathrm{f})$$

$$A(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i})\ T(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i})\ \rho(\mathbf{R}_\mathrm{i}) = A(\mathbf{R}_\mathrm{i}|\mathbf{R}_\mathrm{f})\ T(\mathbf{R}_\mathrm{i}|\mathbf{R}_\mathrm{f})\ \rho(\mathbf{R}_\mathrm{f})$$

$$\text{or}\quad \frac{A(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i})}{A(\mathbf{R}_\mathrm{i}|\mathbf{R}_\mathrm{f})} = \frac{T(\mathbf{R}_\mathrm{i}|\mathbf{R}_\mathrm{f})\ \rho(\mathbf{R}_\mathrm{f})}{T(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i})\ \rho(\mathbf{R}_\mathrm{i})}$$

Choice of acceptance matrix A

Detailed balance condition is

$$\frac{A(\mathbf{R}_f|\mathbf{R}_i)}{A(\mathbf{R}_i|\mathbf{R}_f)} = \frac{T(\mathbf{R}_i|\mathbf{R}_f)\,\rho(\mathbf{R}_f)}{T(\mathbf{R}_f|\mathbf{R}_i)\,\rho(\mathbf{R}_i)}$$

For a given choice of T, $\boxed{\text{infinite}}$ choices of A satisfy this equation

Any function $A(\mathbf{R}_f|\mathbf{R}_i) = F\left(\frac{T(\mathbf{R}_i|\mathbf{R}_f)\,\rho(\mathbf{R}_f)}{T(\mathbf{R}_f|\mathbf{R}_i)\,\rho(\mathbf{R}_i)}\right)$ with

$$\frac{F(x)}{F(1/x)} = x$$

will do the job!

Choice of acceptance matrix A (2)

Original choice by Metropolis *et al.* maximizes the acceptance

$$A(\mathbf{R}_f|\mathbf{R}_i) = \min\left\{1, \frac{T(\mathbf{R}_i|\mathbf{R}_f)\,\rho(\mathbf{R}_f)}{T(\mathbf{R}_f|\mathbf{R}_i)\,\rho(\mathbf{R}_i)}\right\}$$

Note: $\rho(\mathbf{R})$ does not have to be normalized

Original Metropolis method

Symmetric $T(\mathbf{R}_f|\mathbf{R}_i) = 1/\Delta^{3N} \;\Rightarrow\; A(\mathbf{R}_f|\mathbf{R}_i) = \min\left\{1, \frac{\rho(\mathbf{R}_f)}{\rho(\mathbf{R}_i)}\right\}$

Is the original choice of T by Metropolis the best possible choice ?

The configurations M of the walk are sequentially correlated

$\Rightarrow$ Smaller number $M_{\text{eff}} < M$ of independent observations

$$M_{\text{eff}} = \frac{M}{T_{\text{corr}}}$$

with T_{corr} is the autocorrelation time of desired observable

Choice of proposal matrix T

Aim is to achieve fast evolution of the system and reduce T_{corr}

Use freedom in choice of T to have high acceptance

$$\frac{T(\mathbf{R}_{\mathrm{i}}|\mathbf{R}_{\mathrm{f}})\,\rho(\mathbf{R}_{\mathrm{f}})}{T(\mathbf{R}_{\mathrm{f}}|\mathbf{R}_{\mathrm{i}})\,\rho(\mathbf{R}_{\mathrm{i}})} \approx 1 \;\Rightarrow\; A(\mathbf{R}_{\mathrm{f}}|\mathbf{R}_{\mathrm{i}}) \approx 1$$

and small T_{corr} of desired observable

Limitation: we need to be able to sample T directly!

Choice of proposal matrix T

If Δ is the linear dimension of domain around $\mathbf{R}_i$

$$\frac{A(\mathbf{R}_f|\mathbf{R}_i)}{A(\mathbf{R}_i|\mathbf{R}_f)} = \frac{T(\mathbf{R}_i|\mathbf{R}_f)}{T(\mathbf{R}_f|\mathbf{R}_i)}\frac{\rho(\mathbf{R}_f)}{\rho(\mathbf{R}_i)} \approx 1 - \mathcal{O}(\Delta^m)$$

▷ T symmetric as in original Metropolis algorithm gives $\boxed{m = 1}$

▷ A choice motivated by diffusion Monte Carlo with $\boxed{m = 2}$ is

$$T(\mathbf{R}_f|\mathbf{R}_i) = \mathcal{N}\exp\left[-\frac{(\mathbf{R}_f - \mathbf{R}_i - \mathbf{V}(\mathbf{R}_i)\tau)^2}{2\tau}\right] \quad \text{with } \mathbf{V}(\mathbf{R}_i) = \frac{\nabla\Psi(\mathbf{R}_i)}{\Psi(\mathbf{R}_i)}$$

▷ Other (better) choices of T are possible

Example: All-electron Be atom with simple wave function

Simple Metropolis

Δ	$T_{\rm corr}$	$\bar{A}$
1.00	41	0.17
0.75	21	0.28
0.50	17	0.46
0.20	45	0.75

Drift-diffusion transition

τ	$T_{\rm corr}$	$\bar{A}$
0.100	13	0.42
0.050	7	0.66
0.020	8	0.87
0.010	14	0.94

Generalized Metropolis algorithm

1. Choose distribution $\rho(\mathbf{R})$ and proposal matrix $T(\mathbf{R}_{\mathrm{f}}|\mathbf{R}_{\mathrm{i}})$

2. Initialize the configuration $\mathbf{R}_i$

3. Advance the configuration from $\mathbf{R}_i$ to $\mathbf{R}'$

   a) Sample $\mathbf{R}'$ from $T(\mathbf{R}'|\mathbf{R}_{\mathrm{i}})$.

   b) Calculate the ratio $p = \dfrac{T(\mathbf{R}_{\mathrm{i}}|\mathbf{R}')}{T(\mathbf{R}'|\mathbf{R}_{\mathrm{i}})} \dfrac{\rho(\mathbf{R}')}{\rho(\mathbf{R}_{\mathrm{i}})}$

   c) Accept or reject with probability p

   Pick a uniformly distributed random number $\chi \in [0, 1]$

   if $\chi < p$, move accepted $\rightarrow$ set $\mathbf{R}_{\mathrm{f}} = \mathbf{R}'$

   if $\chi > p$, move rejected $\rightarrow$ set $\mathbf{R}_{\mathrm{f}} = \mathbf{R}$

4. Throw away first κ configurations of equilibration time

5. Collect the averages and block them to obtain the error bars

Improvements on simple and drift-diffusion algorithms

▷ For all-electron and pseudopotential systems:

  Move one electron at the time $\rightarrow$ Decorrelate faster

  Does total matrix $P = \prod_{i=1}^{N} P_i$ satisfy stationarity condition?

  Yes if matrices $P_1, P_2, \ldots, P_n$ satisfy stationarity condition

▷ For all-electron systems (Umrigar PRL 1993)

  $-$ Core electrons set the length scales

    $\rightarrow T$ must distinguish between core and valance electrons

  $-$ Do not use cartesian coordinates

    $\rightarrow$ Derivative discontinuity of Ψ at nuclei

Better algorithms can achieve $T_{\mathrm{corr}} = 1 - 2$

Expectation values in variational Monte Carlo

We compute the expectation value of the Hamiltonian $\mathcal{H}$ as

$$
\begin{aligned}
E_V \; &= \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \\
&= \int \mathrm{d}\mathbf{R} \, \frac{\mathcal{H}\Psi(\mathbf{R})}{\Psi(\mathbf{R})} \, \frac{|\Psi(\mathbf{R})|^2}{\int \mathrm{d}\mathbf{R} |\Psi(\mathbf{R})|^2} \\
&= \int \mathrm{d}\mathbf{R} \, E_{\mathrm{L}}(\mathbf{R}) \, \rho(\mathbf{R}) \\
&= \langle E_{\mathrm{L}}(\mathbf{R}) \rangle_\rho \approx \frac{1}{M} \sum_{i=1}^{M} E_{\mathrm{L}}(\mathbf{R}_i)
\end{aligned}
$$

<u>Note</u>: a) Metropolis method: ρ does not have to be normalized

$\rightarrow$ For complex Ψ we do not know the normalization!

b) If $\Psi \rightarrow$ eigenfunction, $E_L(\mathbf{R})$ does not fluctuate

The energy is computed by averaging the local energy

$$E_V = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle E_L(\mathbf{R}) \rangle_\rho$$
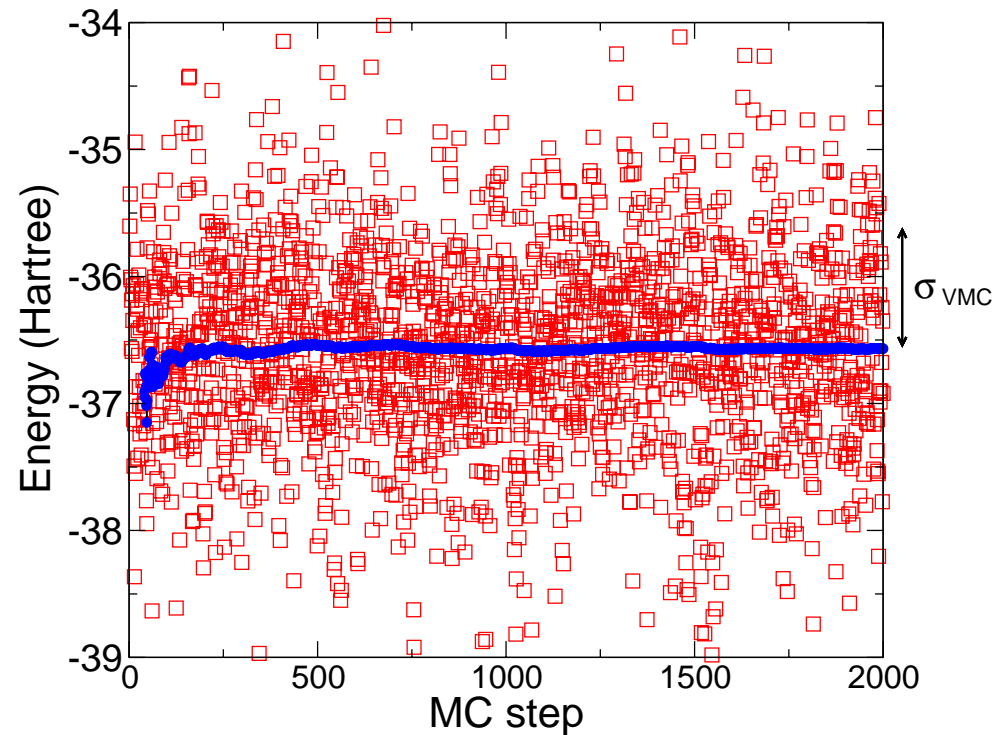
The variance of the local energy is given by

$$\sigma^2 = \frac{\langle \Psi | (\mathcal{H} - E_V)^2 | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle (E_L(\mathbf{R}) - E_V)^2 \rangle_\rho$$

The statistical Monte Carlo error goes as $\mathrm{err}(E_V) \sim \dfrac{\sigma}{\sqrt{M}}$

Note: For other operators, substitute $\mathcal{H}$ with $\mathcal{X}$

Typical VMC run

Example: Local energy and average energy of acetone (C_3H_6O)

$$E_{\mathrm{VMC}} = \langle E_{\mathrm{L}}(\mathbf{R}) \rangle_\rho = -36.542 \pm 0.001 \text{ Hartree } (40 \times 20000 \text{ steps})$$

$$\sigma_{\mathrm{VMC}} = \langle (E_{\mathrm{L}}(\mathbf{R}) - E_{\mathrm{VMC}})^2 \rangle_\rho = 0.90 \text{ Hartree}$$

Variational Monte Carlo → Freedom in choice of Ψ

Monte Carlo integration allows the use of complex and accurate Ψ

⇒ More compact representation of Ψ than in quantum chemistry

⇒ Beyond $c_0 D_{\mathrm{HF}} + c_1 D_1 + c_2 D_2 + \dots$ millions of determinants

$$\boxed{\text{Jastrow-Slater wave function}} \tag{1}$$

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \mathcal{J}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \sum_k d_k D_k^{\uparrow}(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) D_k^{\downarrow}(\mathbf{r}_{N_\uparrow+1}, \ldots, \mathbf{r}_N)$$

$\boxed{\mathcal{J}} \longrightarrow$ Jastrow correlation factor

- Positive function of inter-particle distances

- Explicit dependence on electron-electron distances r_{ij}

- Takes care of divergences in potential

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \mathcal{J}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \sum_k d_k D_k^{\uparrow}(\mathbf{r}_1, \ldots, \mathbf{r}_{N_{\uparrow}}) D_k^{\downarrow}(\mathbf{r}_{N_{\uparrow}+1}, \ldots, \mathbf{r}_N)$$

$$\boxed{\sum_k d_k\, D_k^{\uparrow} D_k^{\downarrow}} \longrightarrow \text{Determinants of single-particle orbitals}$$

- $\boxed{\text{Few}}$ and not millions of determinants as in quantum chemistry

- Slater basis to expand orbitals in all-electron calculations

$$\phi(\mathbf{r}) = \sum_{\alpha}^{\text{Nuclei}} \sum_{k_\alpha} c_{k_\alpha}\, r_\alpha^{n_{k_\alpha}-1}\, \exp(-\zeta_{k_\alpha} r_\alpha)\, \mathrm{Y}_{l_{k_\alpha} m_{k_\alpha}}(\widehat{r}_\alpha)$$

  Gaussian atomic basis used in pseudopotential calculations

- Slater component determines the nodal surface

What is strange with the Jastrow-Slater wave function?

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \mathcal{J}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \sum_k d_k D_k^{\uparrow}(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) \, D_k^{\downarrow}(\mathbf{r}_{N_\uparrow+1}, \ldots, \mathbf{r}_N)$$

▷ Why is Ψ not depending on the spin variables σ?

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \Psi(\mathbf{r}_1, \sigma_1, \ldots, \mathbf{r}_N, \sigma_N) \quad \text{with} \quad \sigma_i = \pm 1$$

▷ Why is Ψ not totally antisymmetric?

Why can we factorize $D_k^\uparrow D_k^\downarrow$?

Consider N electrons with $N = N_\uparrow + N_\downarrow$ and $S_z = (N_\uparrow - N_\downarrow)/2$

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \Psi(\mathbf{r}_1, \sigma_1, \ldots, \mathbf{r}_N, \sigma_N) \quad \text{with} \quad \sigma_i = \pm 1$$

Define a spin function ζ_1

$$\zeta_1(\sigma_1, \ldots, \sigma_N) = \chi_\uparrow(\sigma_1) \ldots \chi_\uparrow(\sigma_{N_\uparrow}) \chi_\downarrow(\sigma_{N_\uparrow + 1}) \ldots \chi_\downarrow(\sigma_N)$$

Generate $\boxed{K = N!/N_\uparrow! N_\downarrow! \text{ functions } \zeta_i}$ by permuting indices in ζ_1

The functions ζ_i form a complete, orthonormal set in spin space

$$\sum_{\sigma_1 \ldots \sigma_N} \zeta_i(\sigma_1, \ldots, \sigma_N) \zeta_j(\sigma_1, \ldots, \sigma_N) = \delta_{ij}$$

Expand the wave function Ψ in terms of its spin components

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \sum_{i=1}^{K} F_i(\mathbf{r}_1, \ldots, \mathbf{r}_N)\, \zeta_i(\sigma_1, \ldots, \sigma_N)$$

Ψ is totally antisymmetric $\Rightarrow$

▷ $F_i = -F_i$ for interchange of like-spin

▷ $F_i = \pm$ permutation of F_1

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \mathcal{A}\left\{ F_1(\mathbf{r}_1, \ldots, \mathbf{r}_N)\, \zeta_1(\sigma_1, \ldots, \sigma_N) \right\}$$

Note that if $\mathcal{O}$ is a spin-independent operator

$$\langle \Psi | \mathcal{O} | \Psi \rangle = \langle F_1 | \mathcal{O} | F_1 \rangle$$

since the functions ζ_i form an orthonormal set

More convenient to use F_1 instead of full wave function Ψ

To obtain F_1, assign the spin-variables of particles:

Particle	1	2	...	$N_\uparrow$	$N_{\uparrow+1}$	...	N
σ	1	1	...	1	-1	...	-1

$$F_1(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \Psi(\mathbf{r}_1, 1, \ldots, \mathbf{r}_{N_\uparrow}, 1, \mathbf{r}_{N_\uparrow+1}, -1, \ldots, \mathbf{r}_N, -1)$$

Be atom, $1s^2\, 2s^2 \Rightarrow N_\uparrow = N_\downarrow = 2,\ S_z = 0$

Determinant of spin-orbitals $\phi_{1s}\,\chi_\uparrow$, $\phi_{2s}\,\chi_\uparrow$, $\phi_{1s}\,\chi_\downarrow$, $\phi_{2s}\,\chi_\downarrow$

$$
D = \frac{1}{\sqrt{4!}}
\begin{vmatrix}
\phi_{1s}(\mathbf{r_1})\chi_\uparrow(\sigma_1) & \cdots & \phi_{1s}(\mathbf{r_4})\chi_\uparrow(\sigma_4) \\
\phi_{2s}(\mathbf{r_1})\chi_\uparrow(\sigma_1) & \cdots & \phi_{2s}(\mathbf{r_4})\chi_\uparrow(\sigma_4) \\
\phi_{1s}(\mathbf{r_1})\chi_\downarrow(\sigma_1) & \cdots & \phi_{1s}(\mathbf{r_4})\chi_\downarrow(\sigma_4) \\
\phi_{2s}(\mathbf{r_1})\chi_\downarrow(\sigma_1) & \cdots & \phi_{2s}(\mathbf{r_4})\chi_\downarrow(\sigma_4)
\end{vmatrix}
$$

Spin-assigned $F_1(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \mathbf{r_4}) = D(\mathbf{r_1}, +1, \mathbf{r_2}, +1, \mathbf{r_3}, -1, \mathbf{r_4}, -1)$

$$
F_1 = \frac{1}{\sqrt{4!}}
\begin{vmatrix}
\phi_{1s}(\mathbf{r_1}) & \phi_{1s}(\mathbf{r_2}) & 0 & 0 \\
\phi_{2s}(\mathbf{r_1}) & \phi_{2s}(\mathbf{r_2}) & 0 & 0 \\
0 & 0 & \phi_{1s}(\mathbf{r_3}) & \phi_{1s}(\mathbf{r_4}) \\
0 & 0 & \phi_{2s}(\mathbf{r_3}) & \phi_{2s}(\mathbf{r_4})
\end{vmatrix}
$$

Be atom, $1s^2\, 2s^2 \Rightarrow N_\uparrow = N_\downarrow = 2$, $S_z = 0$

$$F_1 = \frac{1}{\sqrt{4!}} \begin{vmatrix} \phi_{1s}(\mathbf{r_1}) & \phi_{1s}(\mathbf{r_2}) & 0 & 0 \\ \phi_{2s}(\mathbf{r_1}) & \phi_{2s}(\mathbf{r_2}) & 0 & 0 \\ 0 & 0 & \phi_{1s}(\mathbf{r_3}) & \phi_{1s}(\mathbf{r_4}) \\ 0 & 0 & \phi_{2s}(\mathbf{r_3}) & \phi_{2s}(\mathbf{r_4}) \end{vmatrix}$$

$$= \frac{1}{\sqrt{4!}} \begin{vmatrix} \phi_{1s}(\mathbf{r_1}) & \phi_{1s}(\mathbf{r_2}) \\ \phi_{2s}(\mathbf{r_1}) & \phi_{2s}(\mathbf{r_2}) \end{vmatrix} \times \begin{vmatrix} \phi_{1s}(\mathbf{r_3}) & \phi_{1s}(\mathbf{r_4}) \\ \phi_{2s}(\mathbf{r_3}) & \phi_{2s}(\mathbf{r_4}) \end{vmatrix}$$

$$\boxed{D(\mathbf{x_1}, \mathbf{x_2}, \mathbf{x_3}, \mathbf{x_4}) \rightarrow D^{\uparrow}(\mathbf{r_1}, \mathbf{r_2}) \times D^{\downarrow}(\mathbf{r_3}, \mathbf{r_4})}$$

Spin assignment: $\Psi = \sum_k d_k D_k$ (1)

Care with order of spin-orbitals in determinants

$\Rightarrow$ First all $\uparrow$ spin-orbitals and then all $\downarrow$ spin-orbitals

Example: He atom, two-determinant singlet excited state $1s^1 2s^1$

$(1s^\uparrow, 2s^\downarrow) - (1s^\downarrow, 2s^\uparrow)$ with orbitals $\phi_{1s}\chi_\uparrow$, $\phi_{1s}\chi_\downarrow$, $\phi_{2s}\chi_\uparrow$, $\phi_{2s}\chi_\downarrow$

$$
\Psi = \begin{vmatrix} \phi_{1s}(\mathbf{r_1})\chi_\uparrow(\sigma_1) & \phi_{1s}(\mathbf{r_2})\chi_\uparrow(\sigma_2) \\ \phi_{2s}(\mathbf{r_1})\chi_\downarrow(\sigma_1) & \phi_{2s}(\mathbf{r_2})\chi_\downarrow(\sigma_2) \end{vmatrix}
$$

$$
- \begin{vmatrix} \phi_{1s}(\mathbf{r_1})\chi_\downarrow(\sigma_1) & \phi_{1s}(\mathbf{r_2})\chi_\downarrow(\sigma_2) \\ \phi_{2s}(\mathbf{r_1})\chi_\uparrow(\sigma_1) & \phi_{2s}(\mathbf{r_2})\chi_\uparrow(\sigma_2) \end{vmatrix}
$$

Spin assignment: $\Psi = \sum_k d_k D_k$

First all $\uparrow$ spin-orbitals and then all $\downarrow$ spin-orbitals

$$
\Psi = \begin{vmatrix} \phi_{1s}(\mathbf{r_1})\chi_\uparrow(\sigma_1) & \phi_{1s}(\mathbf{r_2})\chi_\uparrow(\sigma_2) \\ \phi_{2s}(\mathbf{r_1})\chi_\downarrow(\sigma_1) & \phi_{2s}(\mathbf{r_2})\chi_\downarrow(\sigma_2) \end{vmatrix}
$$

$$
+ \begin{vmatrix} \phi_{2s}(\mathbf{r_1})\chi_\uparrow(\sigma_1) & \phi_{2s}(\mathbf{r_2})\chi_\uparrow(\sigma_2) \\ \phi_{1s}(\mathbf{r_1})\chi_\downarrow(\sigma_1) & \phi_{1s}(\mathbf{r_2})\chi_\downarrow(\sigma_2) \end{vmatrix}
$$

Assign spins:

	Particle	1	2
	σ	1	-1

$$
F_1(\mathbf{r_1}, \mathbf{r_2}) = \phi_{1s}(\mathbf{r_1})\phi_{2s}(\mathbf{r_2}) + \phi_{2s}(\mathbf{r_1})\phi_{1s}(\mathbf{r_2})
$$

See example of excited state of CH_2NH tomorrow afternoon

To obtain spin-assigned Jastrow-Slater wave functions, impose

Particle	1	2	...	$N_\uparrow$	$N_{\uparrow+1}$	...	N
σ	1	1	...	1	-1	...	-1

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = F_1(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

$$= \mathcal{J}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \sum_k d_k D_k^\uparrow(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) \, D_k^\downarrow(\mathbf{r}_{N_\uparrow+1}, \ldots, \mathbf{r}_N)$$

How do we impose space and spin symmetry on Jastrow-Slater Ψ?

$\sum_k d_k D_k$ is constructed to have the proper space/spin symmetry

▷ Spacial symmetry

Often, $\mathcal{J} = \mathcal{J}(\{r_{ij}\}, \{r_{i\alpha}\})$ with i, j electrons and α nuclei

$\Rightarrow \mathcal{J}$ invariant under rotations, no effect on spacial symmetry of Ψ

▷ Spin symmetry

If $\mathcal{J}$ is symmetric

$\rightarrow$ for interchange of like-spin electrons $\Rightarrow \Psi$ eigenstate of S_z

$\rightarrow$ for interchange of spacial variables $\Rightarrow \Psi$ eigenstate of S^2

Jastrow factor and divergences in the potential

At interparticle coalescence points, the potential diverges as

$$-\frac{Z}{r_{i\alpha}} \quad \text{for the electron-nucleus potential}$$

$$\frac{1}{r_{ij}} \quad \text{for the electron-electron potential}$$

Local energy $\boxed{\dfrac{\mathcal{H}\Psi}{\Psi} = -\dfrac{1}{2}\sum_i \dfrac{\nabla_i^2 \Psi}{\Psi} + \mathcal{V}}$ must be $\boxed{\text{finite}}$

$\Rightarrow$ Kinetic energy must have opposite divergence to the potential $\mathcal{V}$

Consider two particles of masses m_i, m_j and charges q_i, q_j

Assume $r_{ij} \to 0$ while all other particles are well separated

Keep only diverging terms in $\dfrac{\mathcal{H}\Psi}{\Psi}$ and go to relative coordinates

close to $\mathbf{r} = \mathbf{r}_{ij} = 0$

$$-\frac{1}{2\mu_{ij}}\frac{\nabla^2\Psi}{\Psi} + \mathcal{V}(r) \sim -\frac{1}{2\mu_{ij}}\frac{\Psi''}{\Psi} - \frac{1}{\mu_{ij}}\frac{1}{r}\frac{\Psi'}{\Psi} + \mathcal{V}(r)$$

$$\sim \boxed{-\frac{1}{\mu_{ij}}\frac{1}{r}\frac{\Psi'}{\Psi} + \mathcal{V}(r)}$$

where $\mu_{ij} = m_i\, m_j / (m_i + m_j)$

Diverging terms in the local energy

$$-\frac{1}{\mu_{ij}}\frac{1}{r}\frac{\Psi'}{\Psi} + \mathcal{V}(r) = -\frac{1}{\mu_{ij}}\frac{1}{r}\frac{\Psi'}{\Psi} + \frac{q_i q_j}{r} = \text{finite}$$

$\Rightarrow \Psi$ must satisfy Kato's cusp conditions:

$$\left.\frac{\partial\hat{\Psi}}{\partial r_{ij}}\right|_{r_{ij}=0} = \mu_{ij} q_i\, q_j \Psi(r_{ij}=0)$$

where $\hat{\Psi}$ is a spherical average

Note: We assumed $\Psi(r_{ij}=0) \neq 0$

$\boxed{\text{Cusp conditions: example}}$

The condition for the local energy to be finite at $r = 0$ is

$$\frac{\Psi'}{\Psi} = \mu_{ij} q_i \, q_j$$

- Electron-nucleus: $\mu = 1,\ q_i = 1,\ q_j = -Z \ \Rightarrow \ \boxed{\left.\dfrac{\Psi'}{\Psi}\right|_{r=0} = -Z}$

- Electron-electron: $\mu = \dfrac{1}{2},\ q_i = 1,\ q_j = 1 \ \Rightarrow \ \boxed{\left.\dfrac{\Psi'}{\Psi}\right|_{r=0} = 1/2}$

Generalized cusp conditions

What about two electrons in a triplet state?

Or more generally two like-spin electrons ($D^{\uparrow}$ or $D^{\downarrow} \to 0$)?

$$\boxed{\Psi(r = r_{ij} = 0) = 0} \ ?!?$$

Near $\mathbf{r} = \mathbf{r}_{ij} = 0$, $\qquad \Psi = \sum_{l=l_0}^{\infty} \sum_{m=-l}^{l} f_{lm}(r) \, r^l \, Y_{lm}(\theta, \phi)$

Local energy is finite if

$$\boxed{f_{lm}(r) = f_{lm}^{(0)} \left[1 + \frac{\gamma}{(l+1)} \, r + O(r^2) \right]}$$

where $\gamma = q_i \, q_j \, \mu_{ij}$

R. T. Pack and W. Byers Brown, JCP **45**, 556 (1966)

- Electron-electron singlet: $l_0 = 0 \Rightarrow \boxed{\Psi \sim \left(1 + \frac{1}{2}\, r\right)} \Rightarrow \frac{\Psi'}{\Psi} = \frac{1}{2}$

- Electron-electron triplet: $l_0 = 1 \Rightarrow \boxed{\Psi \sim \left(1 + \frac{1}{4}\, r\right) r}$

$$\boxed{\text{Cusp conditions and QMC wave functions}}$$

$\sigma = +1$ for first $N_\uparrow$ electrons, $\sigma = -1$ for the others

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \mathcal{J}(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) \sum_k d_k \, D_k^\uparrow(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) D_k^\downarrow(\mathbf{r}_{N_\uparrow+1}, \ldots, \mathbf{r}_N)$$

▷ Anti-parallel spins: $r_{ij} \to 0$ for $i \leq N_\uparrow$, $j \geq N_\uparrow + 1$

   Usually, determinantal part $\neq 0$

$$l_0 = 0 \quad \Rightarrow \quad \boxed{\Psi \sim \left(1 + \frac{1}{2}\, r_{ij}\right)}$$

$$\Rightarrow \quad \mathcal{J}(r_{ij}) \sim \left(1 + \frac{1}{2}\, r_{ij}\right) \quad \Leftrightarrow \quad \boxed{\left.\frac{\mathcal{J}'}{\mathcal{J}}\right|_{r_{ij}=0} = \frac{1}{2}}$$

$\sigma = +1$ for first $N_\uparrow$ electrons, $\sigma = -1$ for the others

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \mathcal{J}(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) \sum_k d_k \, D_k^\uparrow(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) D_k^\downarrow(\mathbf{r}_{N_\uparrow+1}, \ldots, \mathbf{r}_N)$$

▷ Parallel spins: $r_{ij} \to 0$ for $i, j \leq N_\uparrow$ or $i, j \geq N_\uparrow + 1$

Determinantal part $\to 0$

$$l_0 = 1 \quad \Rightarrow \quad \boxed{\Psi \sim \left(1 + \frac{1}{4} r_{ij}\right) r_{ij}}$$

$$\Rightarrow \quad \mathcal{J}(r_{ij}) \sim \left(1 + \frac{1}{4} r_{ij}\right) \quad \Leftrightarrow \quad \boxed{\left.\frac{\mathcal{J}'}{\mathcal{J}}\right|_{r_{ij}=0} = \frac{1}{4}}$$
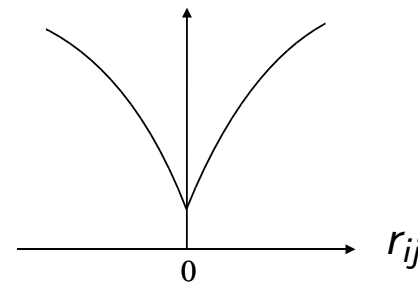
▷ Electron-electron cusps imposed through the Jastrow factor

Example: Simple Jastrow factor

$$\mathcal{J}(r_{ij}) = \prod_{i<j} \exp\left\{ b_0 \, \frac{r_{ij}}{1 + b \, r_{ij}} \right\}$$
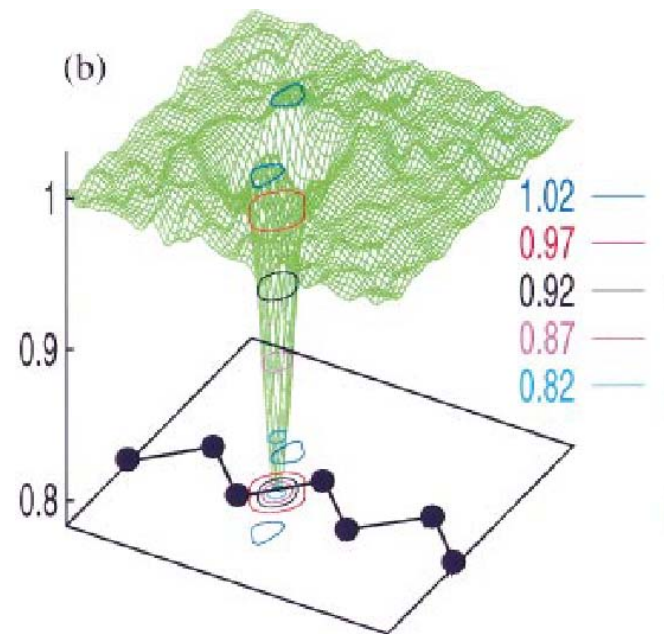
with $b_0^{\uparrow\downarrow} = \dfrac{1}{2}$ or $b_0^{\uparrow\uparrow} = b_0^{\downarrow\downarrow} = \dfrac{1}{4}$

Imposes cusp conditions
+
keeps electrons apart

Pair correlation function for ↑↓ electrons in the (110) plane of Si

$g_{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}')$ with one electron is at the bond center

Hood *et al.* Phys. Rev. Lett. **78**, 3350 (1997)

▷ Electron-nucleus cusps imposed through the determinantal part

Assume that the nucleus is at the origin and $\Psi(r_i = 0) \neq 0$

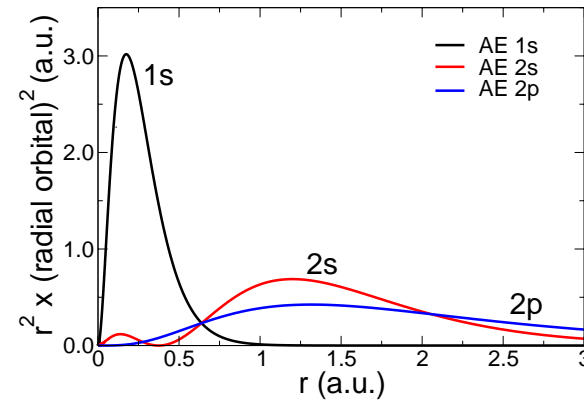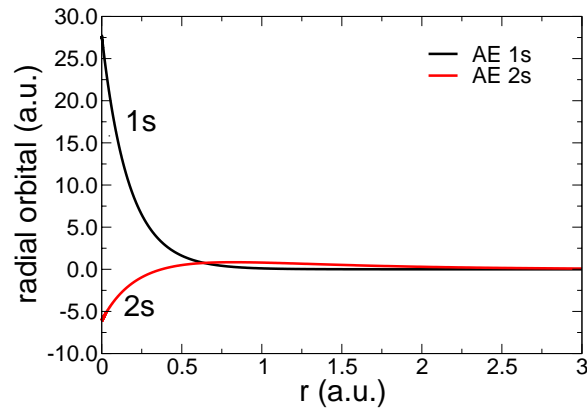If each orbital satisfies the cusp conditions

$$\left. \frac{\partial \hat{\phi}_j}{\partial r} \right|_{r=0} = -Z \hat{\phi}_j(r = 0)$$

$$\Rightarrow \left. \frac{\partial \sum_k d_k \hat{D}_k}{\partial r} \right|_{r=0} = -Z \sum_k d_k \hat{D}_k(r = 0)$$

Note: Slater basis best suited for all-electron systems
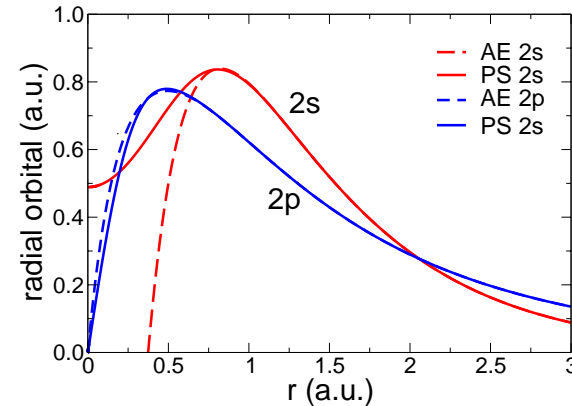
No electron-nucleus cusp with pseudopotential

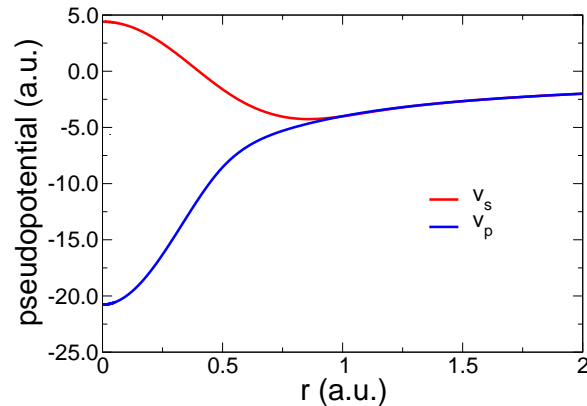Example: Carbon atom $\rightarrow Z = N_{\text{elec}} = 6$ with $[1s^2]2s^2 2p_x^{\uparrow} 2p_y^{\uparrow}$

QMC computational cost scales as N^4 but as $Z^{5.5-6.5}$

Remove the $1s^2$ core electrons with pseudopotential with $Z_{\text{eff}} = 4$

Simple wave function for the Be atom

Be atom, $1s^2\, 2s^2 \Rightarrow N_\uparrow = N_\downarrow = 2,\ S_z = 0$

Spin-assigned $\Psi(\mathbf{r}_1, +1, \mathbf{r}_2, +1, \mathbf{r}_3, -1, \mathbf{r}_4, -1) = \mathcal{J}\, D$

▷ Factorized determinant

$$D = D^\uparrow \times D^\downarrow = \begin{vmatrix} \phi_{1s}(\mathbf{r}_1) & \phi_{1s}(\mathbf{r}_2) \\ \phi_{2s}(\mathbf{r}_1) & \phi_{2s}(\mathbf{r}_2) \end{vmatrix} \times \begin{vmatrix} \phi_{1s}(\mathbf{r}_3) & \phi_{1s}(\mathbf{r}_4) \\ \phi_{2s}(\mathbf{r}_3) & \phi_{2s}(\mathbf{r}_4) \end{vmatrix}$$

▷ Simple Jastrow factor

$$\mathcal{J} = \prod_{ij=13,14,23,24} \exp\left\{ \frac{1}{2} \frac{r_{ij}}{1 + b\, r_{ij}} \right\} \times \prod_{ij=12,34} \exp\left\{ \frac{1}{4} \frac{r_{ij}}{1 + b\, r_{ij}} \right\}$$

Boys and Handy's form

$$\mathcal{J}(r_i, r_j, r_{ij}) = \prod_{\alpha, i<j} \exp\left\{\sum c_{mnk}^{\alpha}\left(\bar{r}_{i\alpha}^m\,\bar{r}_{j\alpha}^n + \bar{r}_{i\alpha}^n\,\bar{r}_{j\alpha}^m\right)\bar{r}_{ij}^k\right\}$$

with $\quad \bar{r}_{i\alpha} = \dfrac{a\,r_{i\alpha}}{1 + a\,r_{i\alpha}}\quad$ and $\quad \bar{r}_{ij} = \dfrac{d\,r_{ij}}{1 + d\,r_{ij}}$

Cusp conditions imposed by requiring:

For electron-electron cusps: $m = n = 0$ if $k = 1$

For electron-nucleus cusps: No $n = 1$ or $m = 1$, D satisfies cusps

More general form: Lift constraints and allow all values of n, m, k

Impose the cusp conditions via linear dependencies among c_{mnk}^{α}

Other scaling functions are possible, e.g. $(1 - e^{-a\,r})/a$

More general Jastrow form with e-n, e-e and e-e-n terms

$$\prod_{\alpha,i} \exp\left\{A(r_{i\alpha})\right\} \prod_{i<j} \exp\left\{B(r_{ij})\right\} \prod_{\alpha,i<j} \exp\left\{C(r_{i\alpha}, r_{j\alpha}, r_{ij})\right\}$$
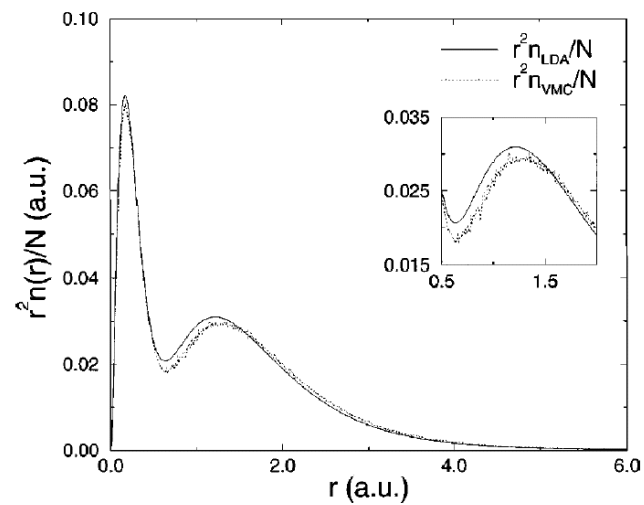
▷ Polynomials of scaled variables, e.g. $\bar{r} = r/(1 + ar)$

▷ $\mathcal{J} > 0$ and becomes constant for large r_i, r_j and r_{ij}

▷ Electron-electron terms B

- Imposes the cusp conditions and keeps electrons apart

- More general than simple $\mathcal{J}(r_{ij})$ gives small improvements

▷ Electron-nucleus terms A

Should be included if determinantal part (DFT or HF) is not reoptimized: e-e terms alter the single-particle density
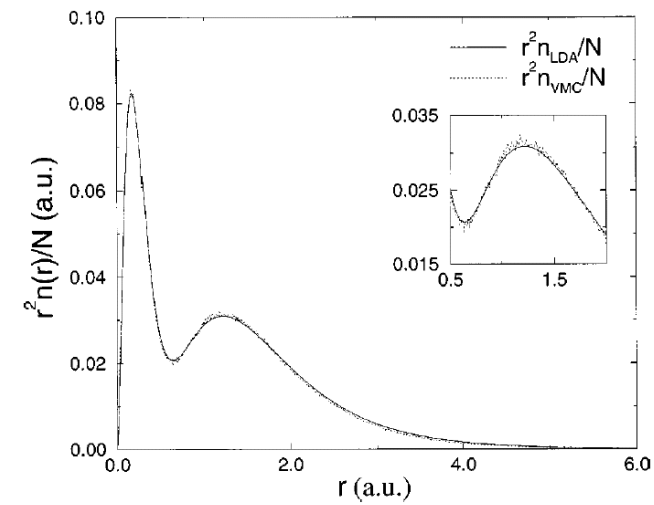
Role of the electron-nucleus terms

Example: Density of all-electron Carbon atom

DFT determinant + e-e $\mathcal{J}$ + e-n $\mathcal{J}$

Foulkes *et al.* Rev. Mod. Phys. **73**, 33 (2001)

▷ Electron-electron-nucleus terms C

If the order of the polynomial in the e-e-n terms is infinite, Ψ can exactly describe a two-electron atom or ion in an S state

For these systems, a 5th-order polynomial recovers more than 99.99% of the correlation energy, $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$

▷ Is this Jastrow factor adequate for multi-electron systems?

The e-e-n terms are the most important: due to the exclusion principle, it is rare for 3 or more electrons to be close, since at least 2 electrons must necessarily have the same spin

Jastrow factor with e-e, e-e-n and e-e-e-n terms

	$\mathcal{J}$		E_{VMC}	$E_{\mathrm{VMC}}^{\mathrm{corr}}$ (%)	σ_{VMC}
Li	E_{HF}		-7.43273	0	
		e-e	-7.47427(4)	91.6	0.240
		$+$ e-e-n	-7.47788(1)	99.6	0.037
		$+$ e-e-e-n	-7.47797(1)	99.8	0.028
	E_{exact}		-7.47806	100	0
Ne	E_{HF}		-128.5471	0	
		e-e	-128.713(2)	42.5	1.90
		$+$ e-e-n	-128.9008(1)	90.6	0.90
		$+$ e-e-e-n	-128.9029(3)	91.1	0.88
	E_{exact}		-128.9376	100	0

Huang, Umrigar, Nightingale, J. Chem. Phys. **107**, 3007 (1997)

Dynamic and static correlation

$\Psi = $ Jastrow $\times$ Determinants $\rightarrow$ Two types of correlation

   ▷ Dynamic correlation

      Described by Jastrow factor

      Due to inter-electron repulsion

      Always present

   ▷ Static correlation

      Described by a linear combination of determinants

      Due to near-degeneracy of occupied and unoccupied orbitals

      Not always present

Static correlation

Example: Be atom and $2s$-$2p$ near-degeneracy

HF ground state configuration $\qquad$ $1s^2 2s^2$

Additional important configuration $\qquad$ $1s^2 2p^2$

Ground state has ^1S symmetry $\Rightarrow$ 4 determinants

$$
\begin{aligned}
D = (1s^\uparrow, 2s^\uparrow, 1s^\downarrow, 2s^\downarrow) + c \Big[&(1s^\uparrow, 2p_x^\uparrow, 1s^\downarrow, 2p_x^\downarrow) \\
&+ (1s^\uparrow, 2p_y^\uparrow, 1s^\downarrow, 2p_y^\downarrow) \\
&+ (1s^\uparrow, 2p_z^\uparrow, 1s^\downarrow, 2p_z^\downarrow) \Big]
\end{aligned}
$$

$$
\begin{aligned}
1s^2 2s^2 \qquad\qquad &\times \mathcal{J}(r_{ij}) \quad \rightarrow E_{\text{VMC}}^{\text{corr}} = 61\% \\
1s^2 2s^2 \oplus 1s^2 2p^2 \quad &\times \mathcal{J}(r_{ij}) \quad \rightarrow E_{\text{VMC}}^{\text{corr}} = 93\%
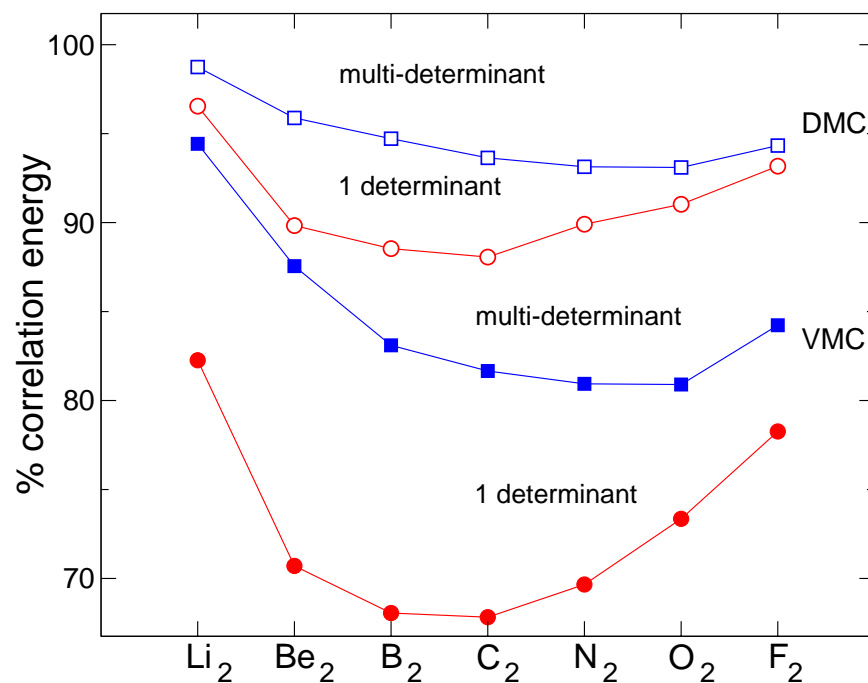\end{aligned}
$$

Static correlation

Example: $E_{\mathrm{VMC}}^{\mathrm{corr}}$ and $E_{\mathrm{DMC}}^{\mathrm{corr}}$ for 1st-row dimers

MO orbitals with atomic s-p Slater basis (all-electron)

Active MO orbitals are $2\sigma_g, 2\sigma_u, 3\sigma_g, 3\sigma_u, 1\pi_u, 1\pi_g$

5th-order polynomial $\mathcal{J}$ (e-n, e-e, e-e-n)

Filippi and Umrigar, J. Chem. Phys. **105**, 213 (1996)

Determinant versus Jastrow factor

Determinantal part yields the nodes (zeros) of wave function
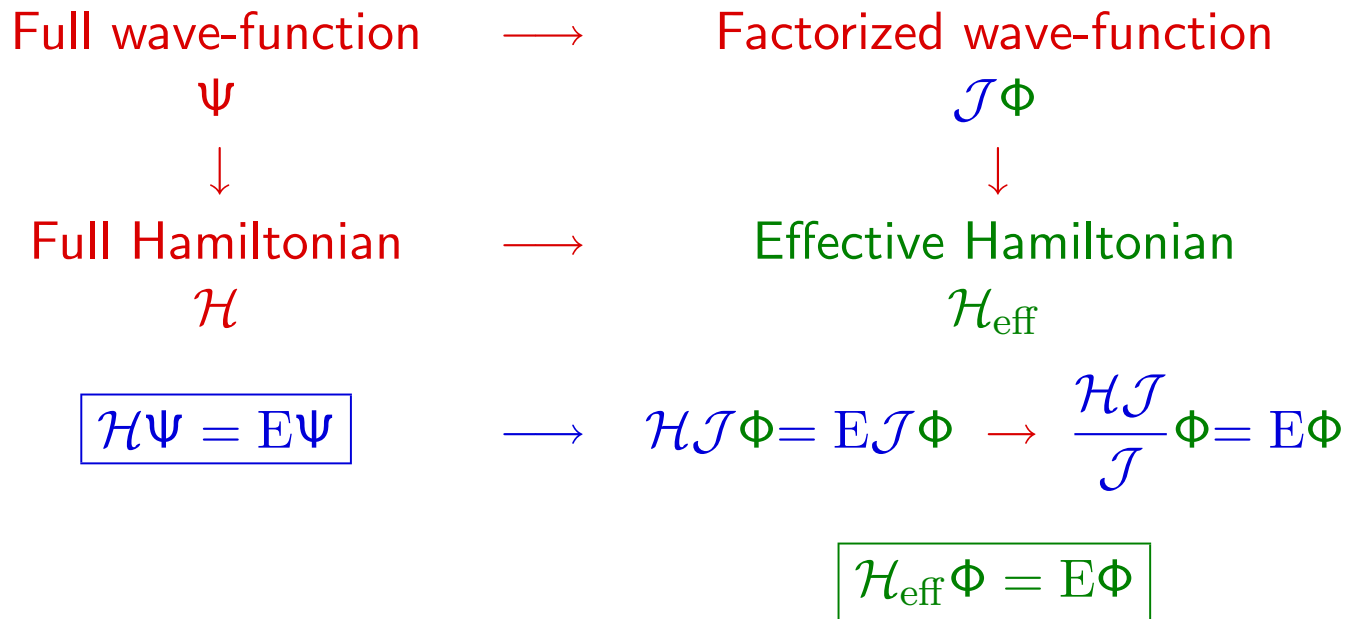
$\Rightarrow$ Quality of the fixed-node DMC solution

Why bother with the Jastrow factor?

Implications of using a good Jastrow factor for DMC:

▷ Efficiency: Smaller σ and time-step error $\Rightarrow$ Gain in CPU time

▷ Expectation values other than energy $\Rightarrow$ Mixed estimator

▷ Non-local pseudopotentials and localization error

$\quad \Rightarrow$ Jastrow factor does affect fixed-node energy

Why should $\Psi_{\mathrm{QMC}} = \mathcal{J}D$ work?

Full wave-function $\longrightarrow$ Factorized wave-function

Ψ $\qquad\qquad\qquad\qquad$ $\mathcal{J}\Phi$

$\downarrow$ $\qquad\qquad\qquad\qquad\qquad$ $\downarrow$

Full Hamiltonian $\longrightarrow$ Effective Hamiltonian

$\mathcal{H}$ $\qquad\qquad\qquad\qquad$ $\mathcal{H}_{\mathrm{eff}}$

$\mathcal{H}\Psi = \mathrm{E}\Psi$ $\qquad\longrightarrow\qquad$ $\mathcal{H}\mathcal{J}\Phi = \mathrm{E}\mathcal{J}\Phi$ $\;\rightarrow\;$ $\dfrac{\mathcal{H}\mathcal{J}}{\mathcal{J}}\Phi = \mathrm{E}\Phi$

$\mathcal{H}_{\mathrm{eff}}\Phi = \mathrm{E}\Phi$

$\mathcal{H}_{\mathrm{eff}}$ weaker Hamiltonian than $\mathcal{H}$

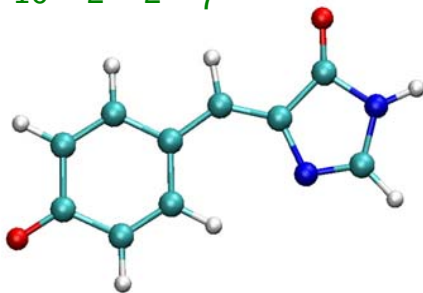$\Rightarrow \Phi \approx$ non-interacting wave function D

$\Rightarrow$ Quantum Monte Carlo wave function $\Psi = \mathcal{J}D$

Construction of the wave function

How do we obtain the parameters in the wave function?

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \mathcal{J} \sum_k d_k D_k^\uparrow D_k^\downarrow$$

$C_{10}N_2O_2H_7^-$

70 electrons and 21 atoms

VTZ s-p basis $+$ 1 polarization

$3\,s + 3\,p + 1\,d$ functions for C, N, O

$2\,s + 1\,p$ for H

▷ Parameters in the Jastrow factor $\mathcal{J}$ (≈ 100)

▷ CI coefficients d_k (< 10)

▷ Linear coefficients in expansion of the orbitals (5540 !)

Jastrow-Slater wave function

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \mathcal{J} \sum_k d_k D_k^\uparrow D_k^\downarrow$$

▷ Jastrow factor optimized in variance/energy minimization

▷ Orbitals and d_k coefficients in determinantal part are from

○ Hartree-Fock or DFT (LDA, GGA, B3LYP ...)

○ CI or multi-configuration self-consistent-field calculation

○ Optimized in energy minimization (very simple for d_k)

See lecture by Umrigar tomorrow

Beyond VMC?

Removing or reducing wave function bias?

$\Rightarrow$ Projection Monte Carlo methods

See lecture on DMC by Filippi/Foulkes tomorrow