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Advanced School on Quantum Monte Carlo Methods in Physics and Chemistry

21 January - 1 February, 2008

DMC 2.

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Diffusion Quantum Monte Carlo for Fermions

ICTP Advanced School on Quantum Monte Carlo Methods in Physics and Chemistry

Matthew Foulkes

Condensed Matter Theory Group
Imperial College London

Tuesday 22nd January 2008

Outline

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Introduction

- All (?) fermion QMC methods suffer from sign problems.
  - DMC requires an exponentially difficult cancellation of separately evolving positive and negative walker densities.
  - AFMC requires an exponentially difficult cancellation of contributions from positive and negative Slater determinants.
  - PIMC requires an exponentially difficult cancellation of contributions from positive and negative paths.
- These sign problems look different but have a similar “flavour”.
- Arise when you try to treat something that is not positive as a probability density.

Outline

The DMC Sign Problem

How can we use DMC to study the imaginary-time evolution of a fermionic wavefunction with positive and negative regions?

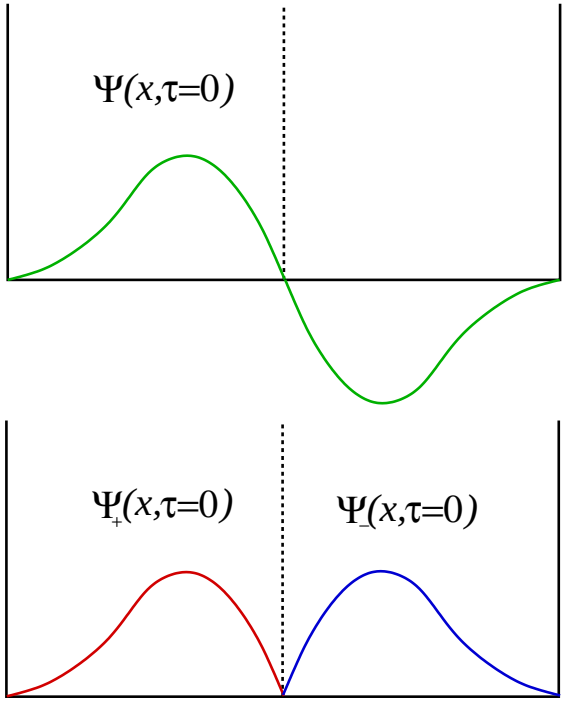
Simple 1D example

$\Psi(x, \tau = 0)$ can be written as the difference of two positive contributions:

$$\Psi = \Psi_+ - \Psi_-$$

where

$$\begin{aligned} \Psi_+ &= \frac{1}{2}(|\Psi| + \Psi) \\ \Psi_- &= \frac{1}{2}(|\Psi| - \Psi) \end{aligned}$$



The imaginary-time Schrödinger equation

$$\frac{\partial \Psi}{\partial \tau} = -\hat{H}\Psi$$

is linear, so solving it with the initial condition

$$\Psi(x, \tau = 0) \quad = \quad \Psi_+(x, \tau = 0) - \Psi_-(x, \tau = 0)$$

is equivalent to solving

$$\frac{\partial \Psi_+}{\partial \tau} = -\hat{H}\Psi_+ \qquad \text{and} \qquad \frac{\partial \Psi_-}{\partial \tau} = -\hat{H}\Psi_-$$

separately and subtracting one solution from the other.

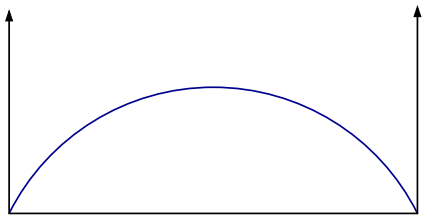
- Expanding $\Psi_+(x, \tau = 0)$ and $\Psi_-(x, \tau = 0)$ in eigenfunctions gives

$$\Psi_\pm(\tau = 0) \quad = \quad c_0^s \psi_0^s \pm c_0^a \psi_0^a + \ldots$$

Hence, as $t \to \infty$,

$$\Psi_\pm \ \to \ c_0^s e^{-E_0^s \tau} \psi_0^s \pm c_0^a e^{-E_0^a \tau} \psi_0^a + \ldots$$

- Since $E_0^s < E_0^a$, both Ψ_+ and Ψ_- evolve to ψ_0^s:



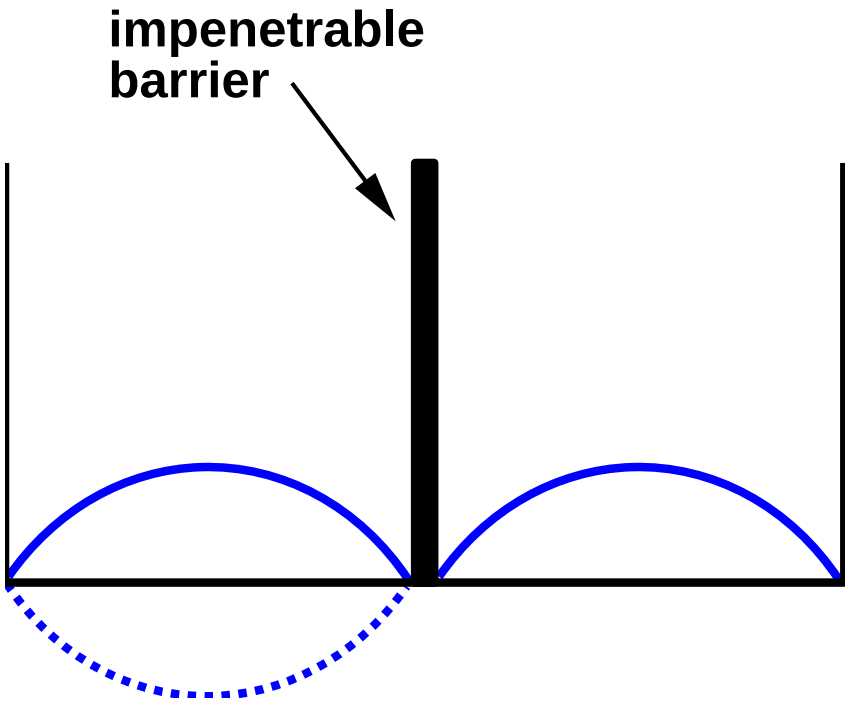
- The antisymmetric component obtained by subtracting one solution from the other becomes exponentially harder to extract

$$\frac{|\Psi_+ - \Psi_-|}{|\Psi_+ + \Psi_-|} \quad \propto \quad \frac{e^{-E_0^a \tau}}{e^{-E_0^s \tau}} \quad \text{as} \quad \tau \to \infty$$

The Fixed-Node Approximation

Problem: The small antisymmetric component is swamped by the random errors

Solution: Fix the nodes! (If you don't know them, guess them.)



Fixed-Node Algorithm

- Distribute walkers according to any positive initial wavefunction.
- Evolve according to imaginary-time Schrödinger equation.
- Walkers that bump into barrier are annihilated (as are walkers that bump in to walls), enforcing $\Psi = 0$ boundary conditions.
- Solution in each nodal pocket evolves independently to ground state in that pocket.

Algorithm is numerically stable (no exponentially growing noise).

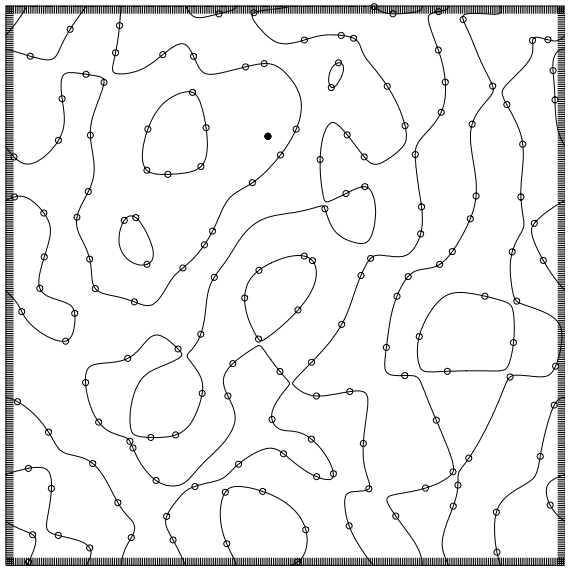
The calculated energy of the antisymmetric ground-state is exact if the nodes are exact and variational if the nodes are approximate.

Outline

What are Nodes?

Definition

The node of an N-electron wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \Psi(\mathbf{R})$ is the surface on which $\Psi = 0$ and across which Ψ changes sign.



A 2D slice through the 321-dimensional nodal surface of a gas of 161 spin-up electrons.

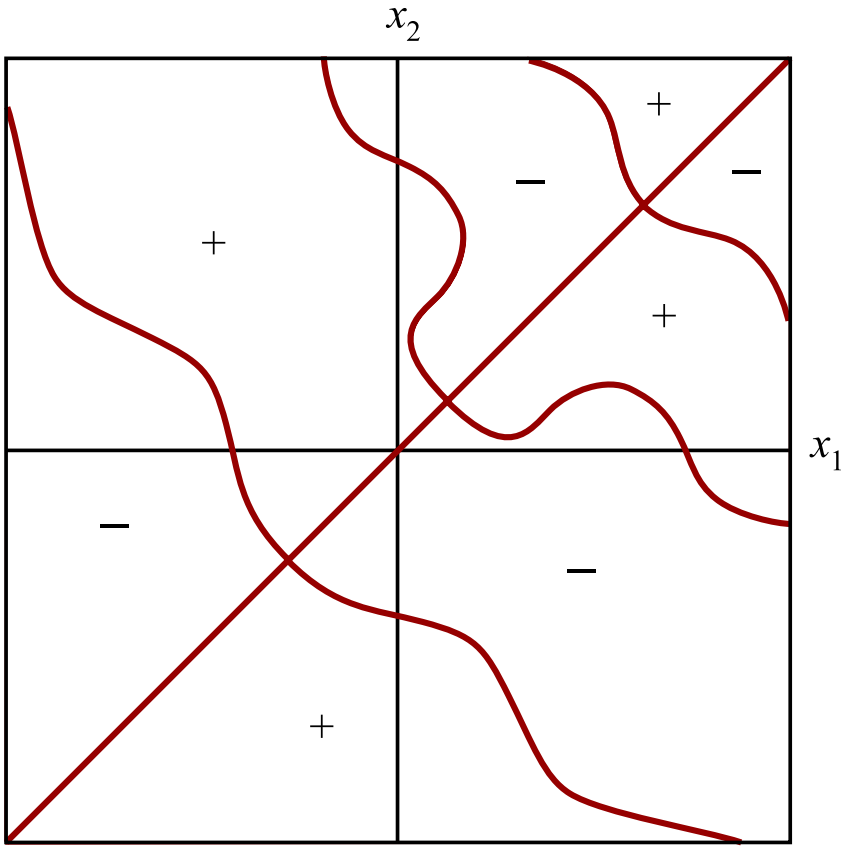
- If the physical space has d (=1,2,3) dimensions, the node is best viewed as a $(dN-1)$-dimensional surface in the dN-dimensional configuration space.

> One constraint ($\Psi = 0$) in a dN-dimensional space implies a $(dN-1)$-dimensional node

- Equations such as $\mathbf{r}_i = \mathbf{r}_j$ define $(dN-d)$-dimensional coincidence surfaces. These provide a framework through which the node must pass but do not define it completely when $d > 1$.
- If $d = 1$, the coincidence points $x_i = x_j$ *do* define the ground-state node completely. One-dimensional problems are easy to simulate and can often be solved exactly (e.g., using the Bethe ansatz).

Nodal Classes

The nodal pockets of a many-electron wavefunction can always be divided up into classes.



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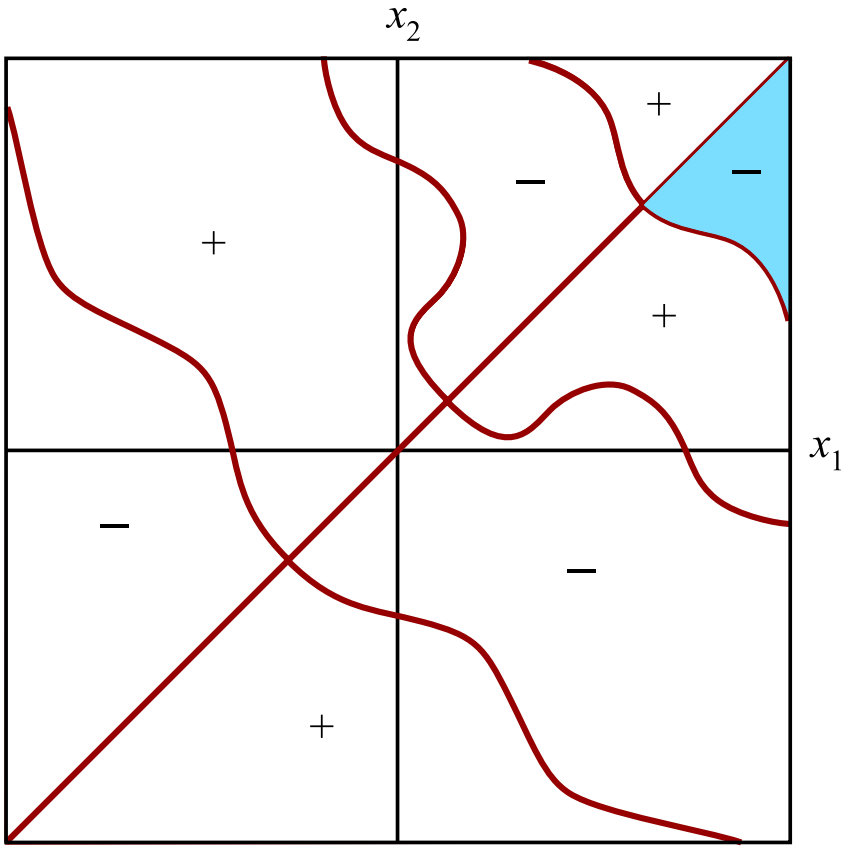

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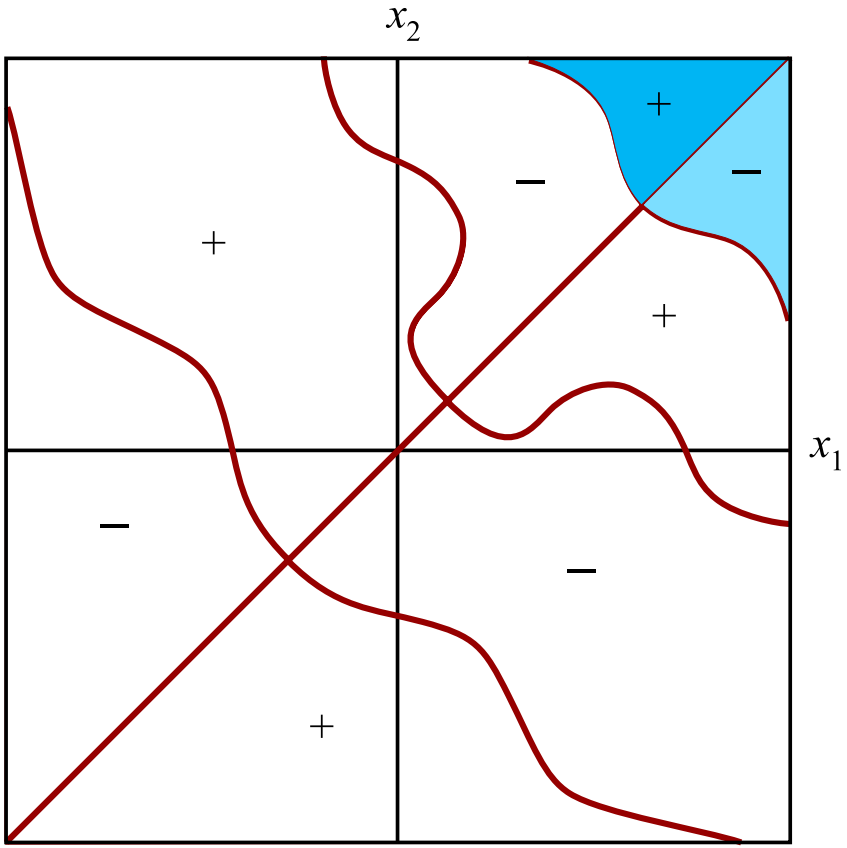

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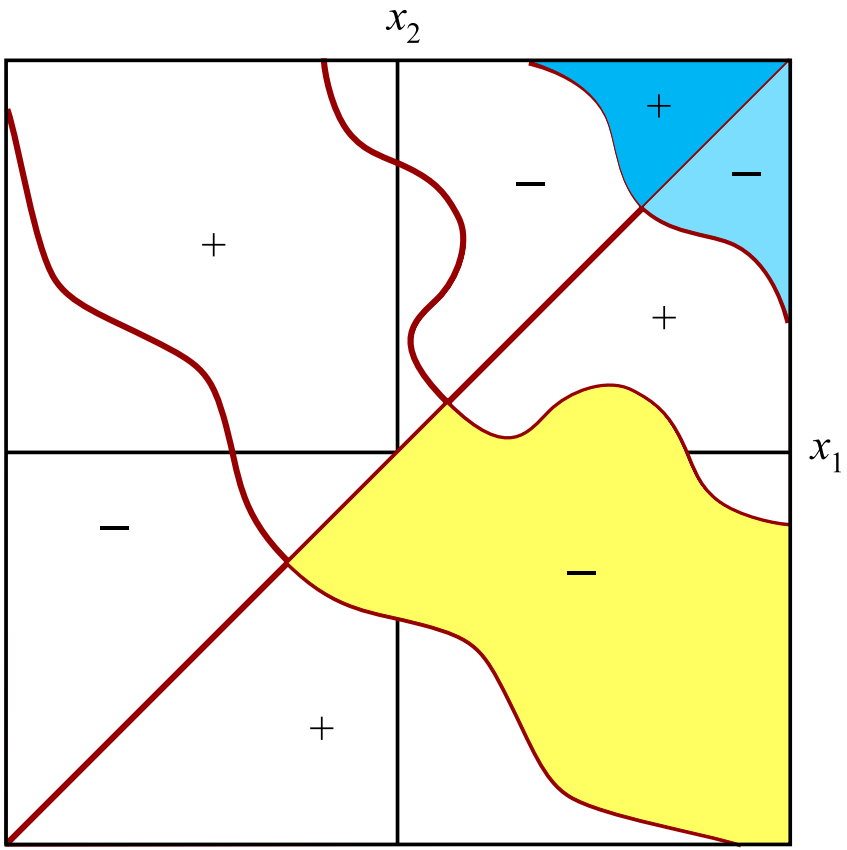

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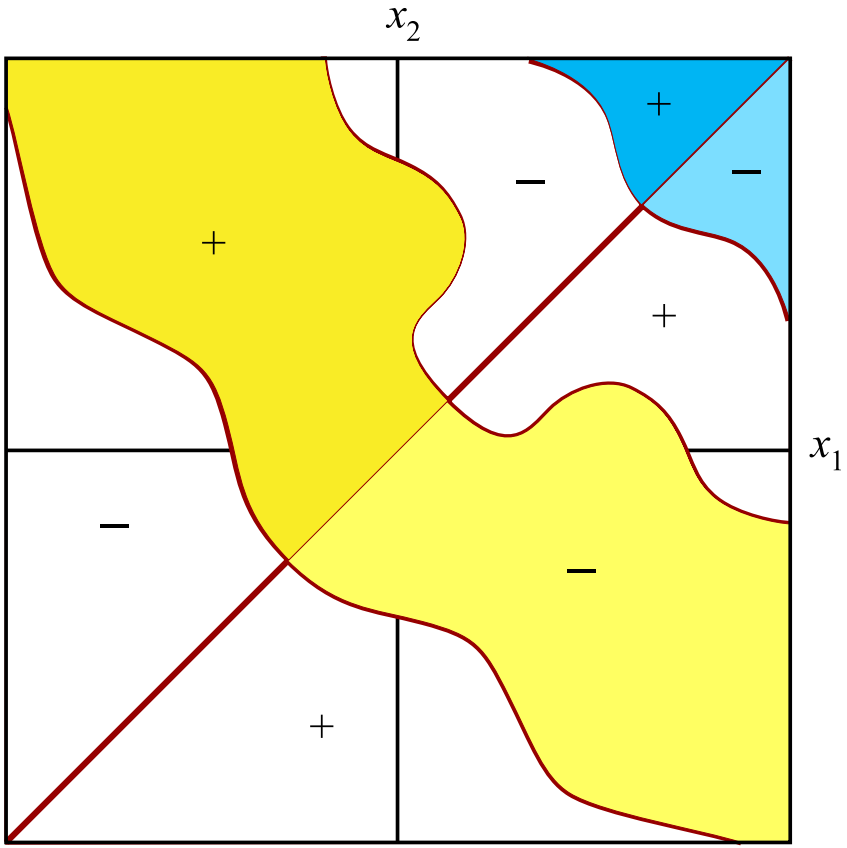

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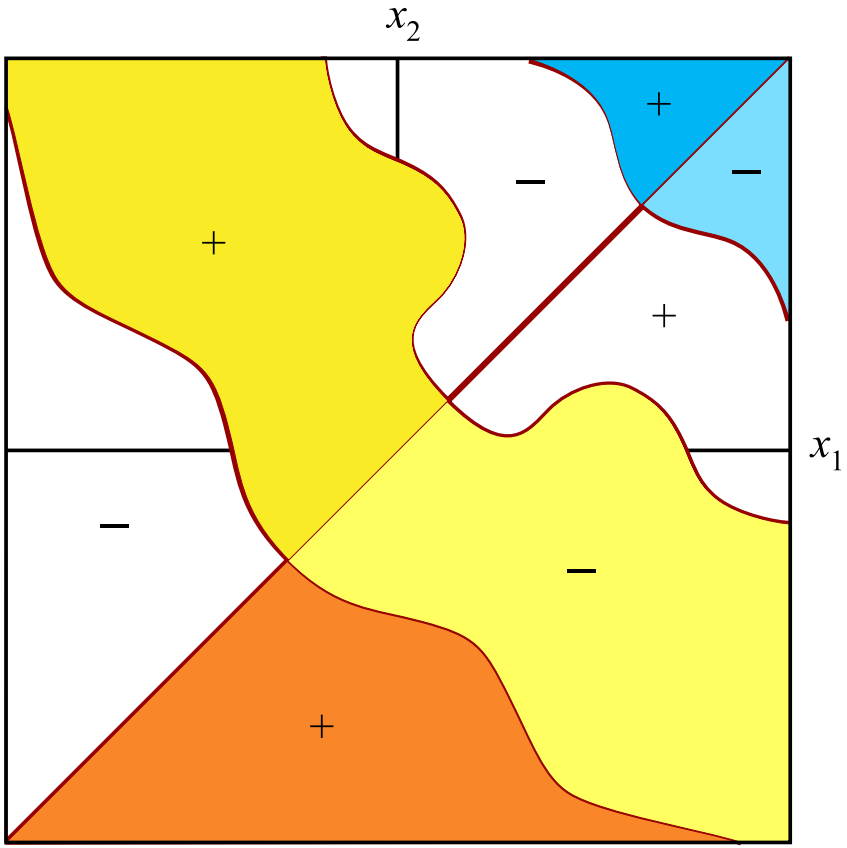

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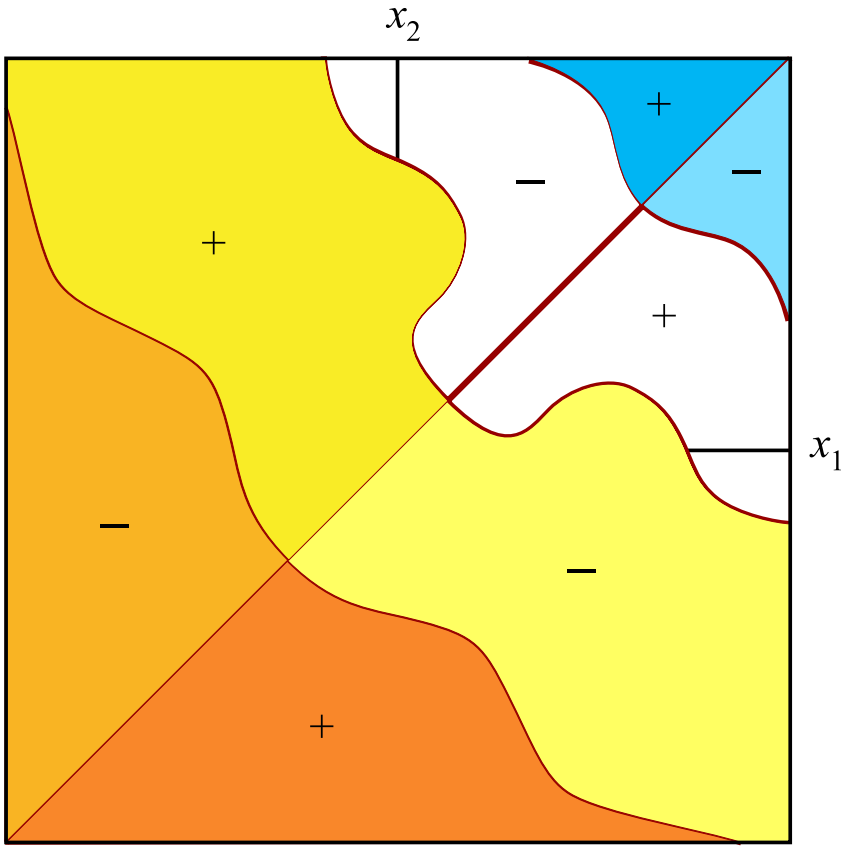

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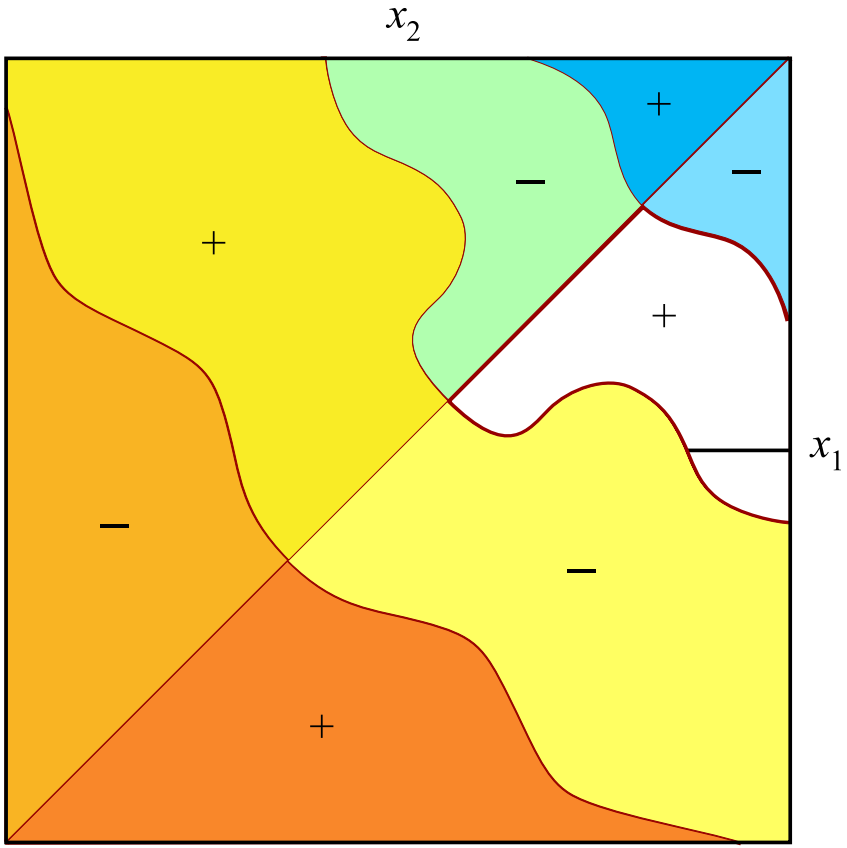

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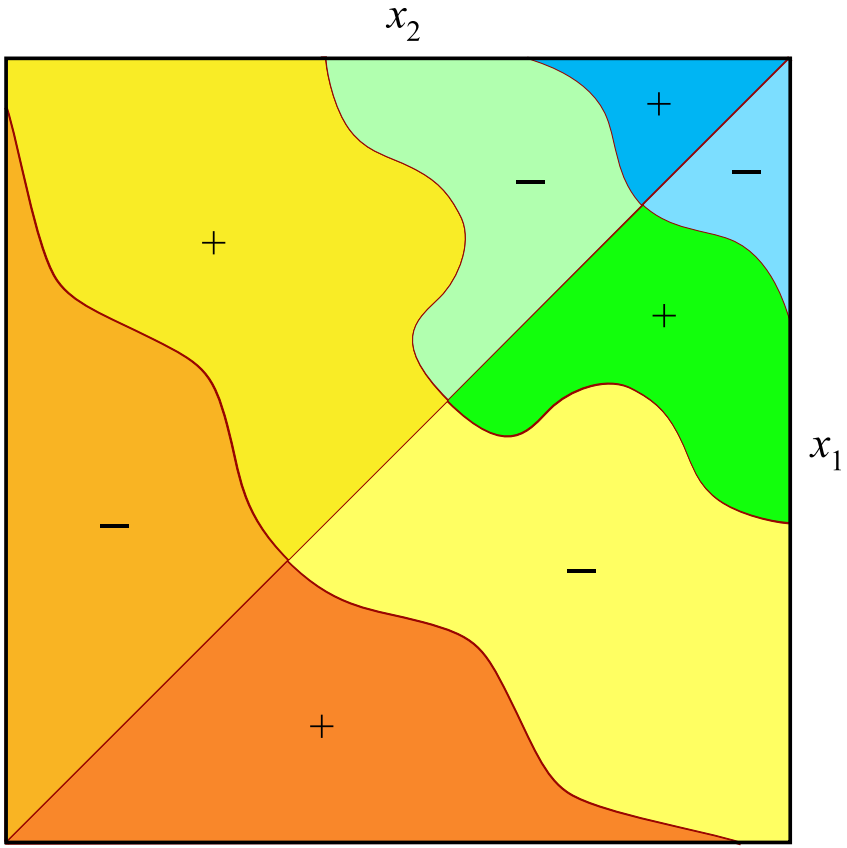
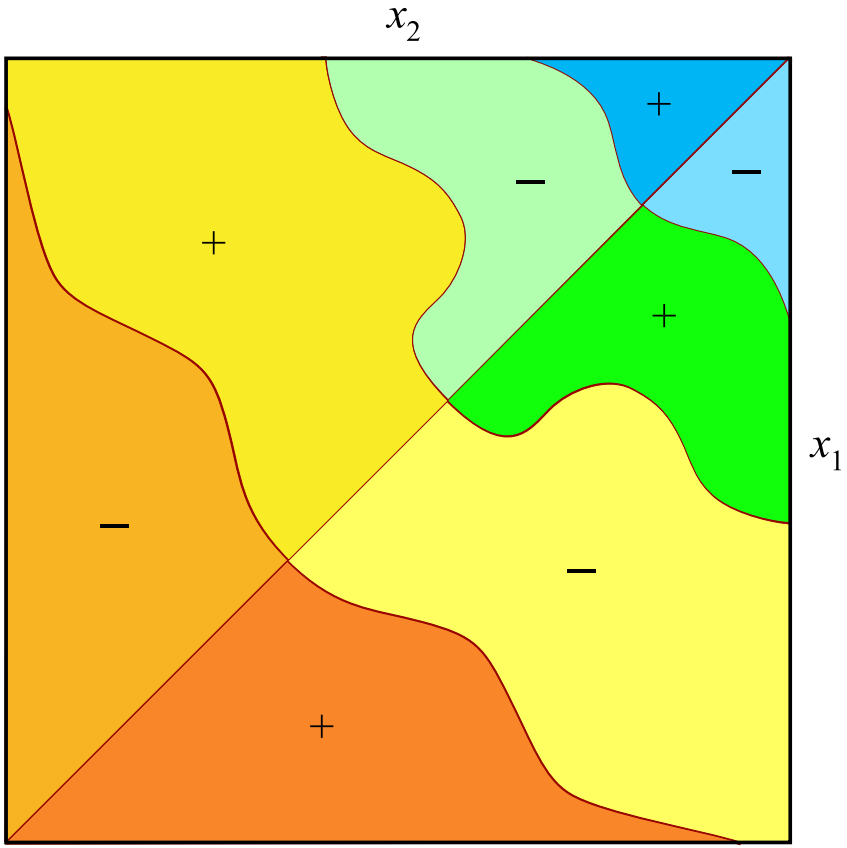


The Tiling Theorem

If the wavefunction is the ground state of a Hamiltonian with a local potential, all pockets must be in the same class.



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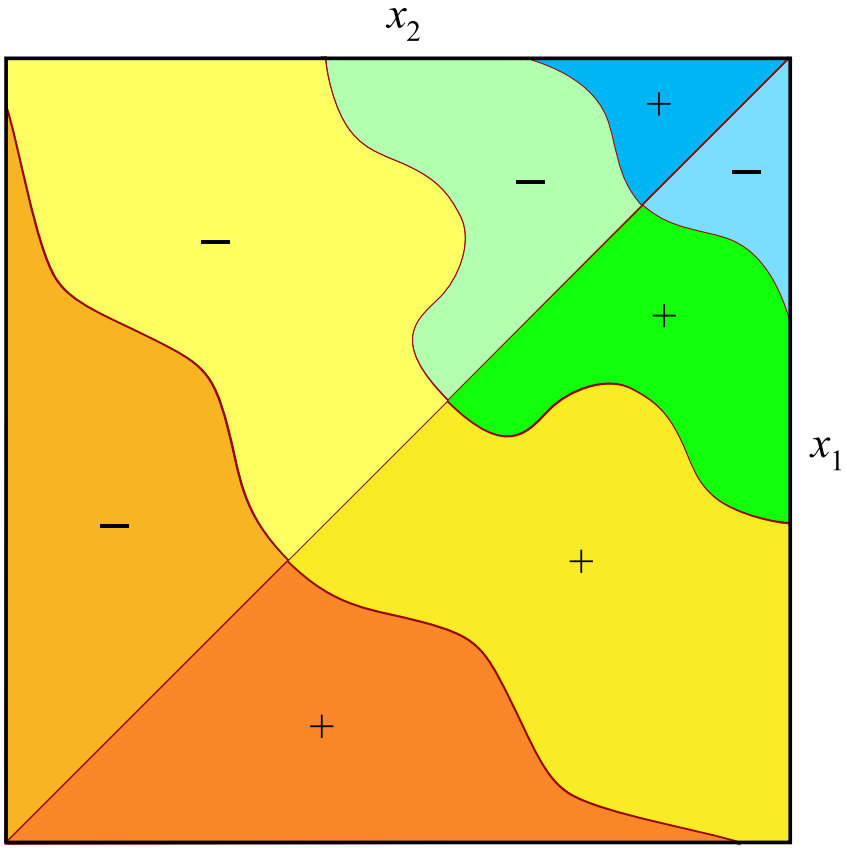

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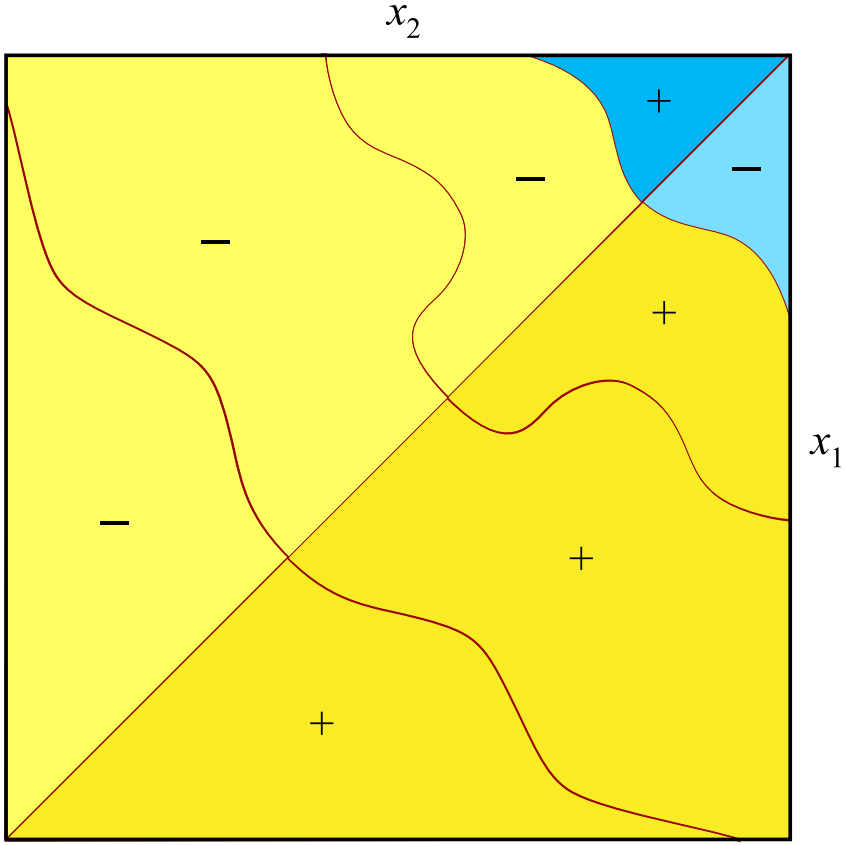

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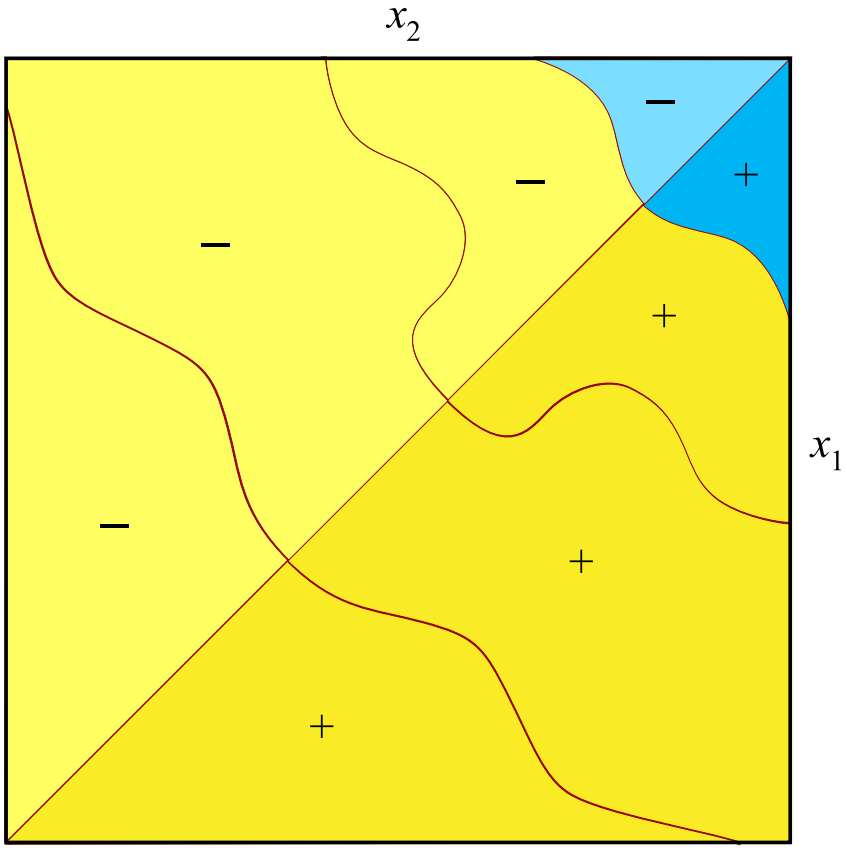

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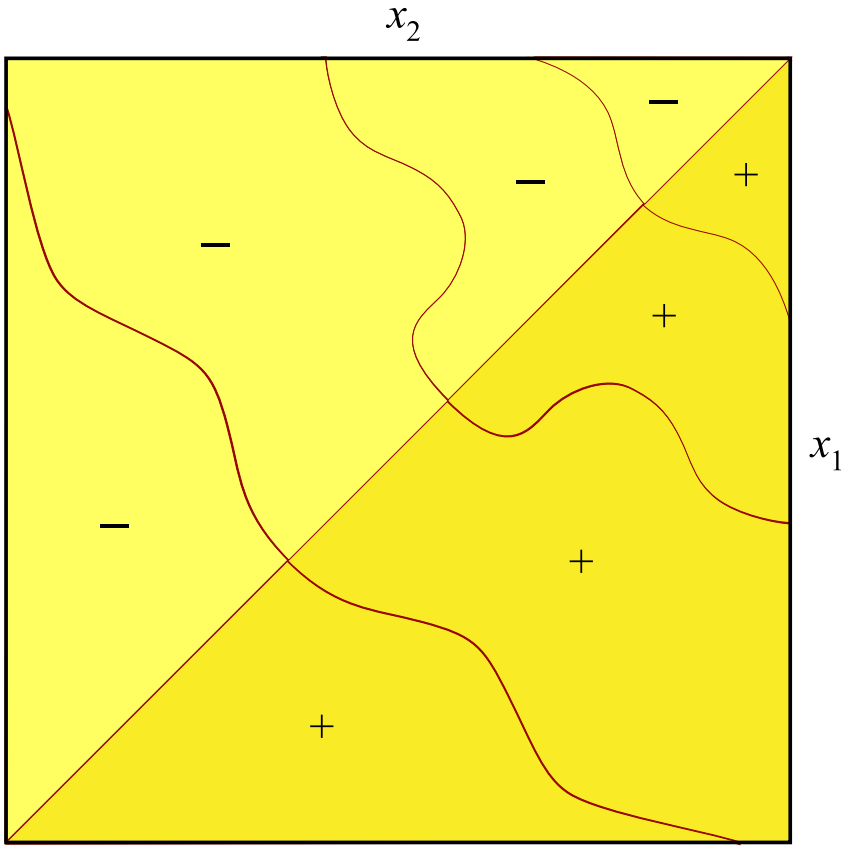
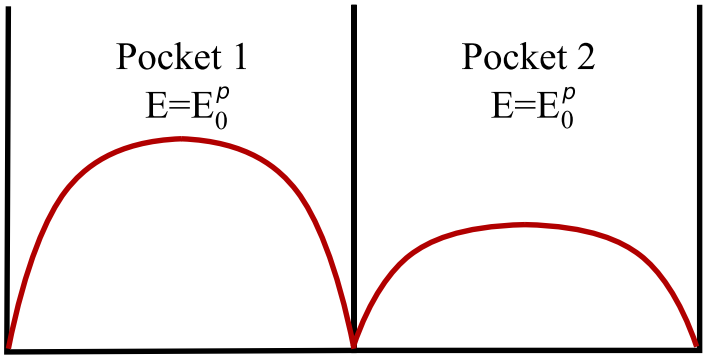


The Fixed-Node Variational Principle

- FN DMC solves the imaginary-time Schrödinger equation *separately* in each nodal pocket.
- Random fluctuations cause some pockets to contain more walkers than others, but all ground-state pockets are equivalent.
  (In *excited-state* DMC simulations, all the walkers end up in pockets of the lowest energy class.)
- The $\tau \rightarrow \infty$ walker distribution in each pocket samples the corresponding pocket ground state.



- Consider the pocket ground state ϕ_0^i in pocket p_i. Within p_i, ϕ_0^i satisfies

$$\left(-\frac{1}{2}\nabla^2 + V\right)\phi_0^i = E_0^p \phi_0^i$$

- The fixed-node variational principle states that

$$E_0^p \geq E_0$$

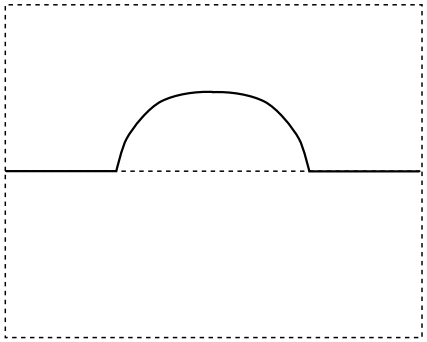
with the equality holding if the imposed nodal surface is exact.

- If the imposed nodal surface is wrong, the error in the energy is proportional to the error in the nodal surface squared.

Sketch of Proof

ϕ_0^i satisfies the Schrödinger equation inside and outside p_i but not on the enclosing nodal surface:

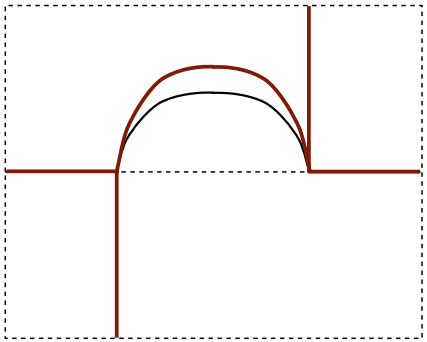
$$\left(-\tfrac{1}{2}\nabla^2 + V\right)\phi_0^i = E_0^p \phi_0^i$$



Sketch of Proof

ϕ_0^i satisfies the Schrödinger equation inside and outside p_i but not on the enclosing nodal surface:

$$\left(-\tfrac{1}{2}\nabla^2 + V\right)\phi_0^i = E_0^p\phi_0^i + \delta^i$$



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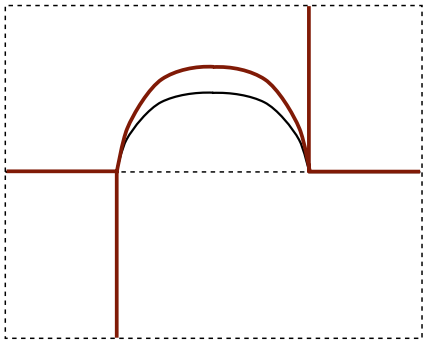


Note, however, that the δ-functions do not affect the expected energy

$$\int \phi_0^i \hat{H}\phi_0^i = \int \phi_0^i(E_0^p\phi_0^i + \delta^i) = \int \phi_0^i E_0^p\phi_0^i = E_0^p$$

Now consider the normalised *antisymmetrised* pocket eigenstate

$$\Psi_0^i = \hat{A}\phi_0^i$$

This is a valid fermionic trial wave function and satisfies

$$\int \Psi_0^i \hat{H} \Psi_0^i = E_0^p$$

for the same reasons ϕ_0^i does.
Hence, by the ordinary variational principle of QM,

$$E_0^p \geq E_0$$

Outline

Reminder

The practical utility of DMC relies on importance sampling.

- Rewrite the imaginary-time Schrödinger equation

$$\frac{1}{2}\nabla^2\Psi - V\Psi = \frac{\partial\Psi}{\partial\tau}$$

as an equation for $f(\mathbf{R},\tau) = \Psi(\mathbf{R},\tau)\Psi_T(\mathbf{R})$:

$$\frac{1}{2}\nabla^2 f - \boldsymbol{\nabla}\cdot(\mathbf{v}f) - E_L f = \frac{\partial f}{\partial\tau}$$

where

$$\mathbf{v}(\mathbf{R}) = \frac{\boldsymbol{\nabla}\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} \quad \text{and} \quad E_L(\mathbf{R}) = \frac{(-\frac{1}{2}\nabla^2 + V(\mathbf{R}))\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}$$

A Happy Surprise

- As $\tau \to \infty$, expect

$$f(\mathbf{R}, \tau) \propto e^{-E_0 \tau} \Psi_0(\mathbf{R}) \Psi_T(\mathbf{R})$$

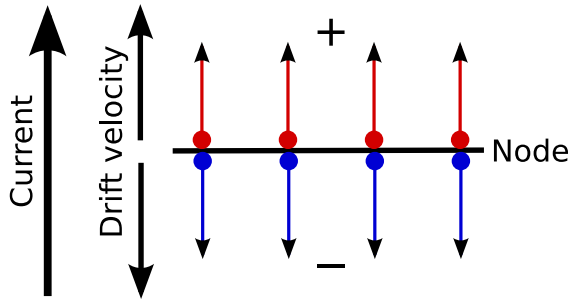
  where $\Psi_0(\mathbf{R})$ is the overall (bosonic) ground state.
- Could impose FN approximation by deleting walkers that cross nodes of Ψ_T. (This is easy to check: evaluate $\Psi_T(\mathbf{R})$ and look for sign changes.)
- In practice, we find that walkers *never* cross nodes (if the time step is small enough). The fixed-node boundary conditions are imposed automatically.

$$f(\mathbf{R}, \tau) \propto e^{-E_0^{\mathrm{FN}} \tau} \Psi_0^{\mathrm{FN}}(\mathbf{R}) \Psi_T(\mathbf{R}) \quad \text{as} \quad \tau \to \infty$$

What Happened to the Bosonic Solution?

Question: How can this be? Isn't the importance-sampled Schrödinger equation mathematically equivalent to the original version?

Answer: The many-boson ground state is still a mathematical solution, but its description in terms of walkers is peculiar at the nodes (where the importance-sampled equation is singular).



The finite walker current across the nodal surface is sustained by the creation of pairs of positive and negative walkers on either side. The positive walkers are swept off into the positive pocket and the negative walkers into the negative pocket.

- Since our FN-DMC algorithm does not create walker-antiwalker pairs (i.e. since it doesn't take proper account of the singularities in the transformation) we cannot access the many-boson solution.
- Only solutions for which $\Psi = 0$ on the nodes of Ψ_T are within reach.
- This is a *good thing*.

(In practice, because $\Delta t \neq 0$, some walkers do occasionally try to cross nodes. Rejecting these moves gives smaller time-step errors than killing the walkers involved.)

Accuracy of the Fixed Node Approximation

- How long is a piece of string?
- Atomization energies of G1 set of 55 molecules (Grossman):
$$\langle \Delta E \rangle \approx 0.13\,\text{eV/molecule}.$$
- Cohesive energies of solids to < 0.1 eV per atom.
- Surface energies (Wood et al.):
$$\Delta E_{\text{surface}} - \Delta E_{\text{bulk}} \approx 0.03\,\text{eV/electron when } r_s = 2.07 a_0.$$
- Electron gas release-node calculations (Ceperley and Alder):
$$\Delta E \approx 0.007\,\text{eV/electron when } r_s = 10 a_0.$$
- Electron gas backflow corrections (Kwon et al.):

r_s (a_0)	ΔE (eV/electron)
1	0.0250
5	0.0087
10	0.0045

Outline

Backflow

Replace $\mathbf{r}_i$ in Slater determinant(s) by

$$\mathbf{x}_i = \mathbf{r}_i + \sum_{j\,(\neq i)} \eta(r_{ij})(\mathbf{r}_i - \mathbf{r}_j)$$

(Kwon et al.)

or inhomogeneous generalisation (Lopez-Rios et al.)

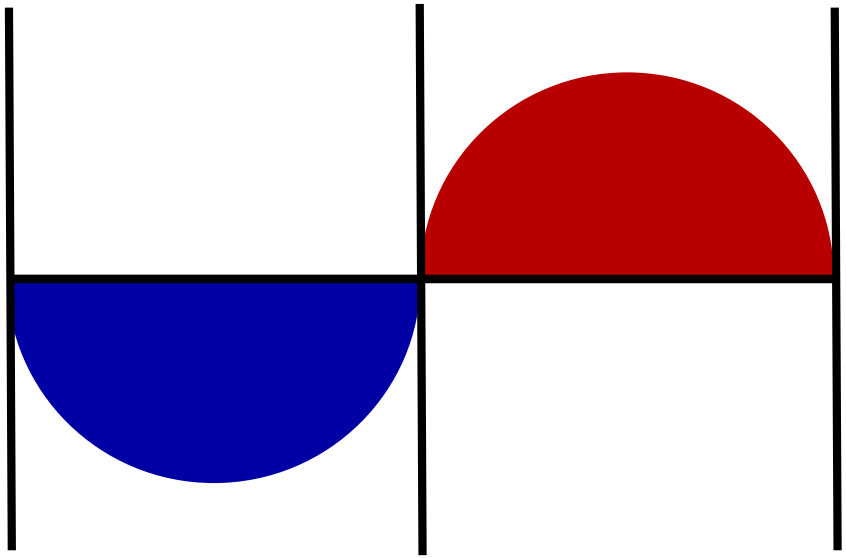
- *Substantially* improves VMC trial functions in electron-gas like systems.
- Fraction of fixed-node error recovered is hard to estimate in solids. Not very large in atoms and molecules (20% for all-electron C).
- Backflow VMC energies are surprisingly close to DMC energies when the nodes are good.

Optimizing the Nodes

- Optimization of weights in linear combinations of Slater determinants is standard in molecular calculations.
- Direct optimization of the orbitals within each Slater determinant was considered impractical until recently. Fahy, Umrigar, Filippi and others have begun to show that this was an overly pessimistic assessment.

Releasing the Nodes

First do a fixed-node DMC simulation:



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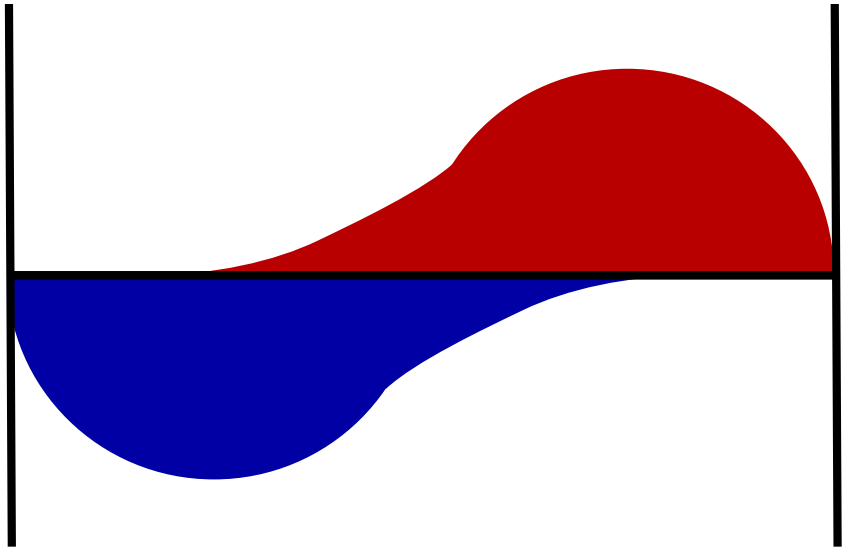

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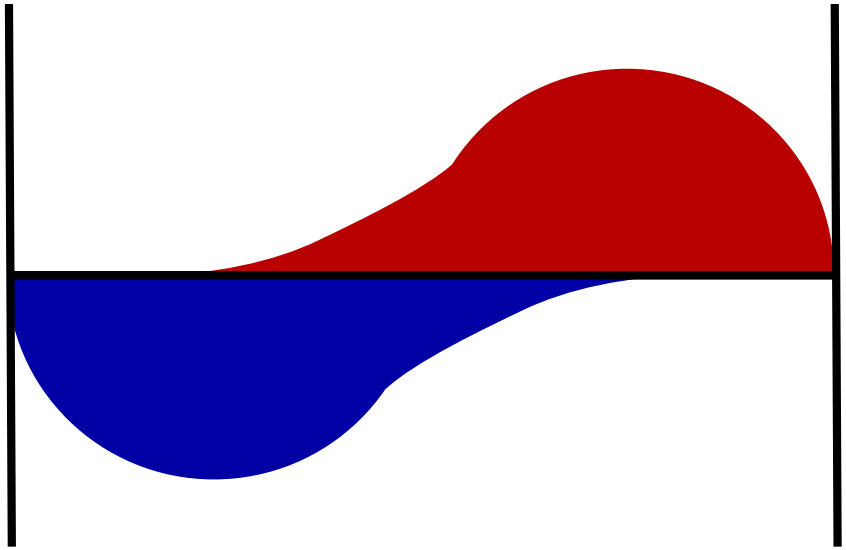


- Red and blue solutions collapse to boson ground state, but their difference approaches the fermion ground state.
- Back to the sign problem: exponentially growing noise.

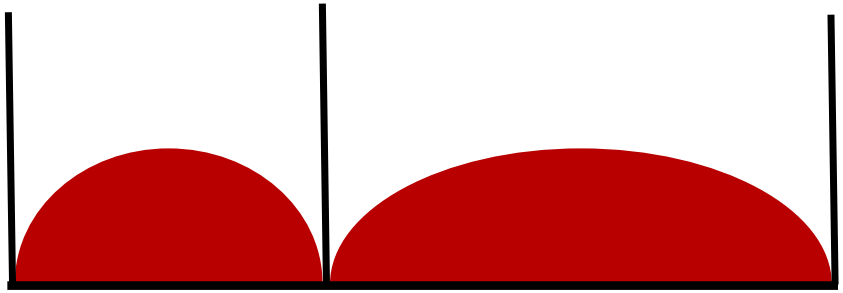
The Fixed Phase Approximation

- The fixed node approximation only works when the Hamiltonian is real (has time-reversal symmetry); the ground state can then also be chosen to be real.
- A generalisation called the fixed-phase approximation (Ortiz et al.) exists for cases with broken time-reversal symmetry.
- Particularly useful for studying systems with applied magnetic fields.

Excited States

There is no general fixed-node variational principle for excited states.

$\tau = \mathbf{0}$:



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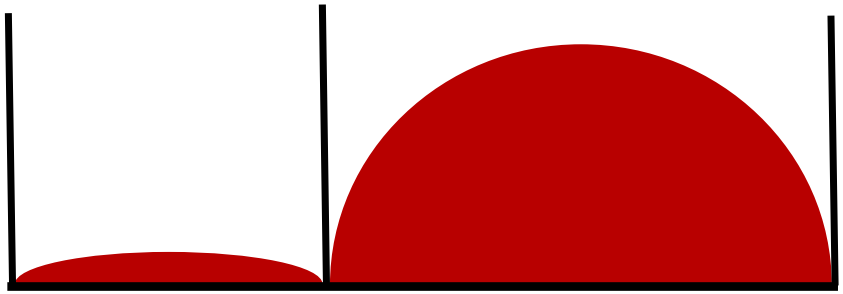

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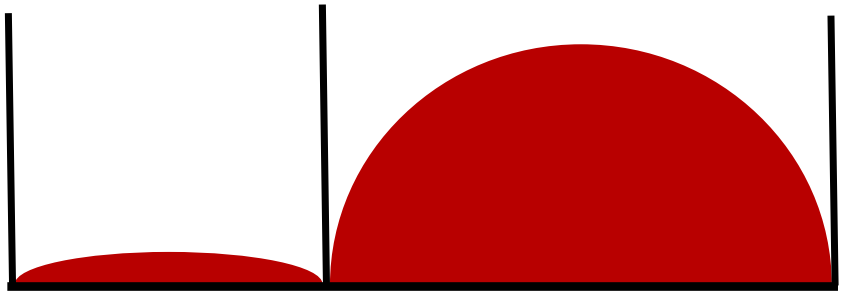

- In $\tau \rightarrow \infty$ limit, only pockets of the lowest energy class are occupied.

$$E_0^{\mathrm{FN}} < E_0$$

- Error in energy is *linear* in nodal error.

The Fixed-Node Variational Principle for Excited States

The fixed-node variational principle and tiling theorem generalise to the lowest state of a given symmetry only if that state is non-degenerate.

- The state in question must transform according to a 1D irreducible representation of the symmetry group of $\hat{H}$
- . . . or according to a 1D irreducible representation of any *subgroup* of the symmetry group of $\hat{H}$.
- In practice, FN DMC calculations for excited states often work well even when this condition is *not* satisfied.

Outline

Conclusions

The fixed-node DMC method is:

- Easy to do.
- Stable.
- Accurate enough for quantum chemistry, especially in large systems.
- Not accurate enough for subtle correlation physics (superconductivity, Kondo, FQHE, . . .) with full Hamiltonian.