PIMC vs DMC

- No wavefunction needed—better black box.
- Non-zero temperature

BUT

- Sampling more complicated
  - Permutations
  - Ergodicity

Is a good application of PIMC disordered condensed-matter systems? e.g. Liquids

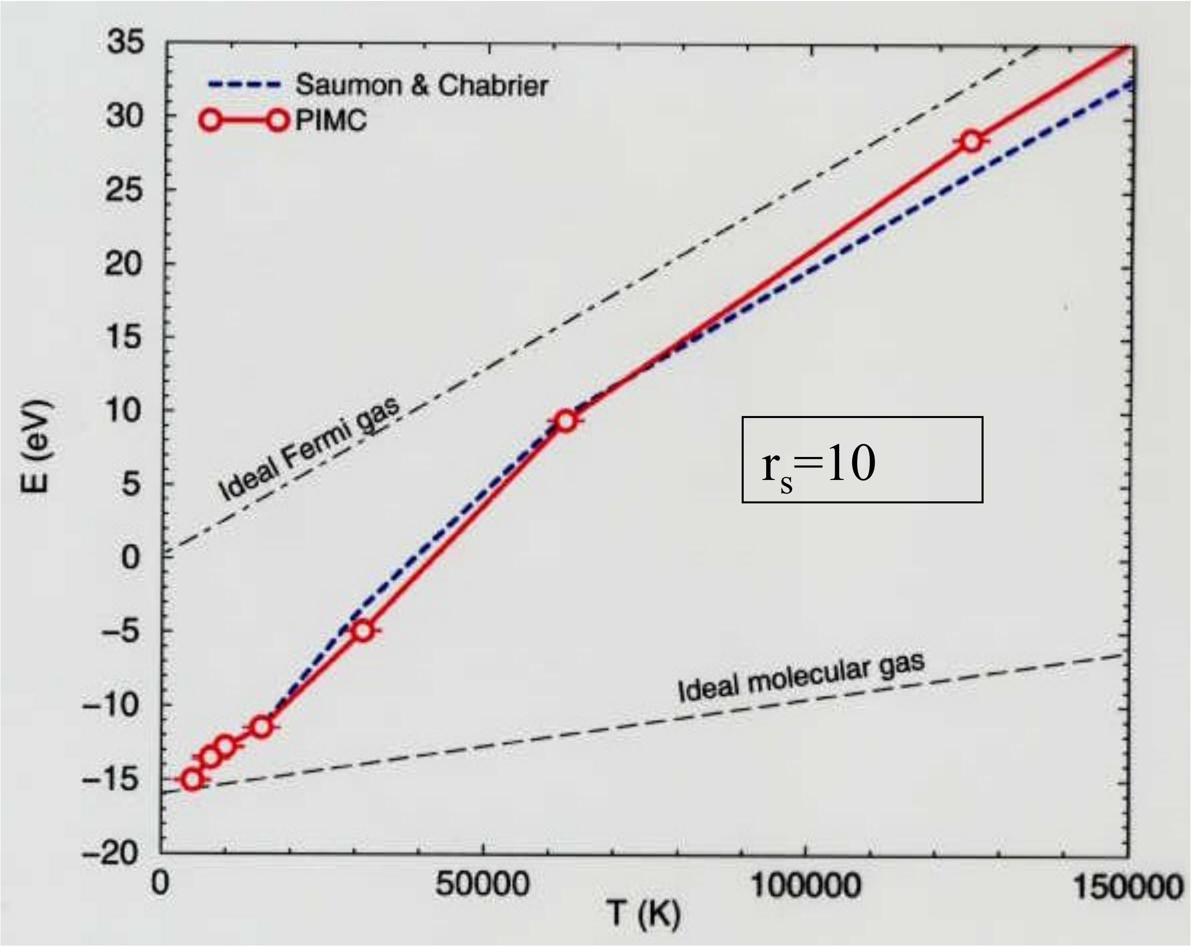
- Wavefunction gives zero variance
- Can optimize the trial function (and nodes)

BUT

- Branching inefficient for large systems
- Population bias
- Mixed estimators a problem

Energy of low density H_2

- Molecules form spontaneously
- Includes vibrational, rotational, translational degrees of freedom.
- Absolute accuracy in energy is 0.1eV.



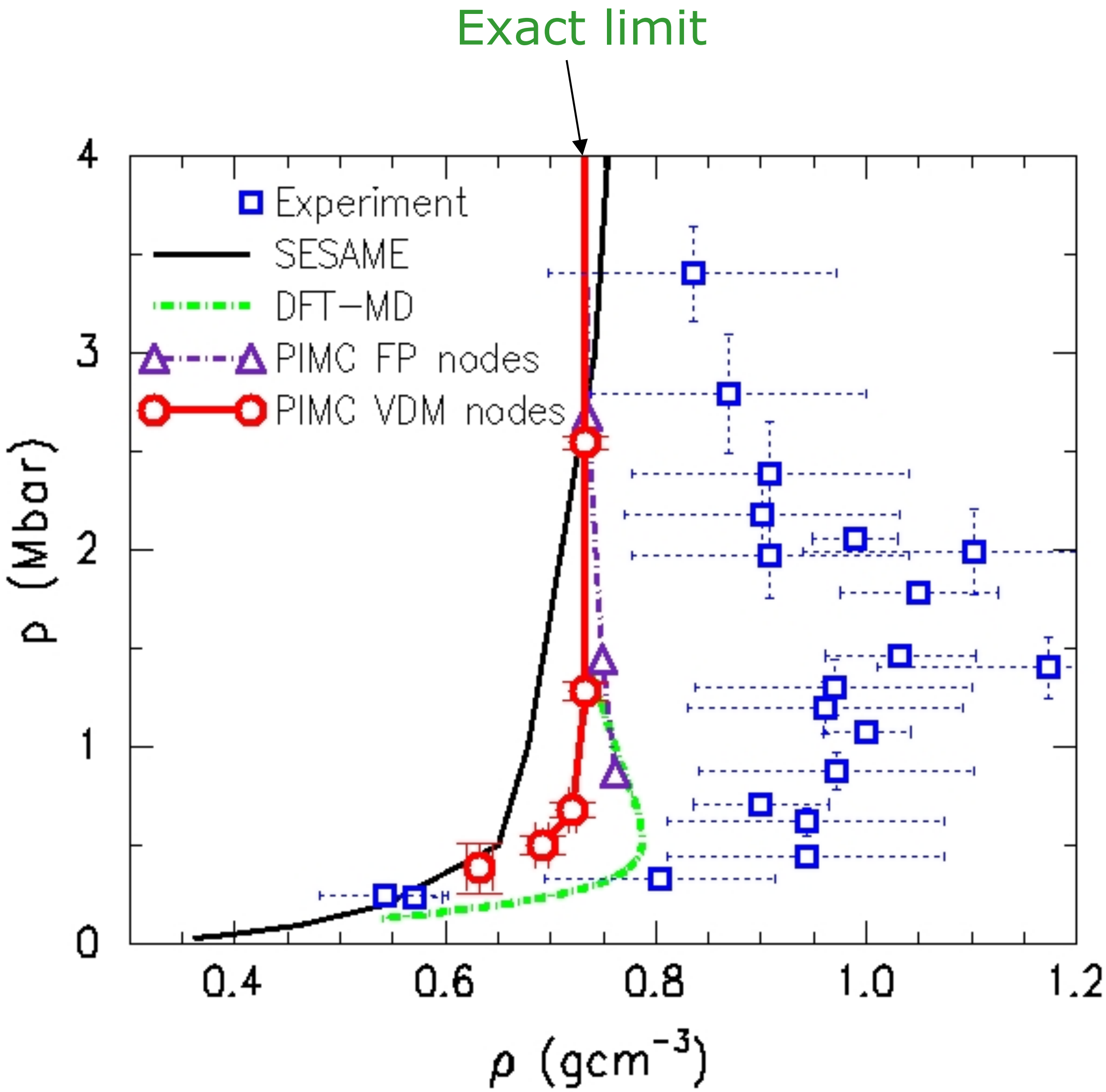
Militzer, Ceperley, Phys Rev. E63, 66404 (2001).

Theory vs. experiment

NOVA (Livermore CA) laser shock experiments

Science **281**, 1178, 1998.

- Liquid is 50% more compressible than thought.
- Important implications for fusion (makes fusion much easier.)
- PIMC is not very accurate. About the same EOS as DFT.



Exact limit

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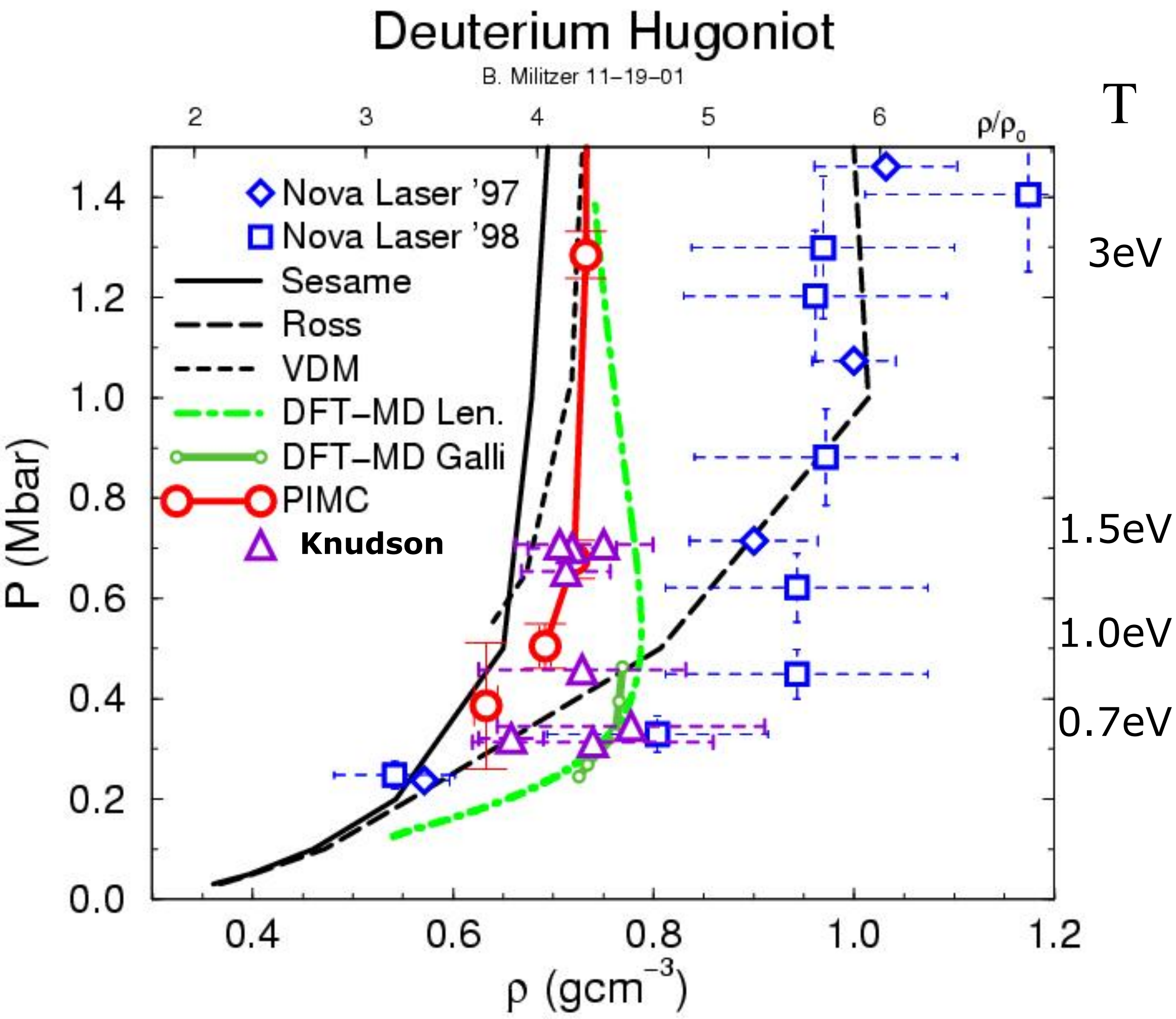
Experiment vs PIMC/DFT simulations

- Older laser (NOVA) shocks are incompatible with microscopic theory.
- Chemical models are not predictive in this regime.
- Z-pinch experiments of *Knudson et al., PRL 87, 225501 (2001)*



"Direct" Fermion Path Integrals

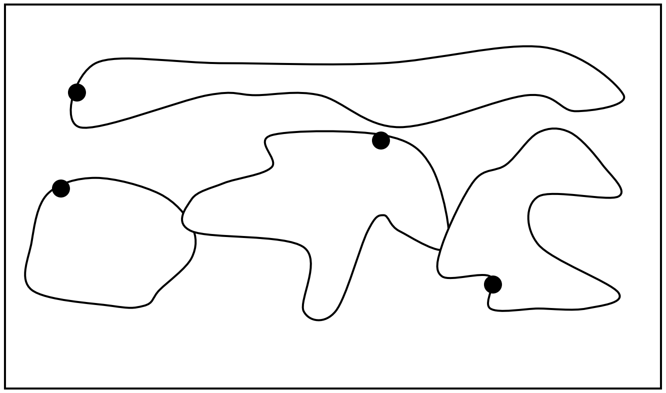
- Path integrals map quantum mechanics into a system of cross-linking closed "polymers."

$$Z = \sum_{p=1}^{N!} \frac{(-1)^P}{N!} \int dR_1 \ldots dR_M e^{-\sum_{i=1}^{M} S(R_i, R_{i+1})}$$

$R_0=PR_M$, **P** permutation,

$S(R_i, R_{i+1})$ is "boltzmannon action"

4 quantum paths



- Bosons are easy: simply sample **P**.
- Fermions: sample the "action" and carry **$(-1)^P$** as a weight.
- Observable is **even P - odd P**. scales exponentially in N and T^{-1}!

$$\text{CPUtime} \propto \varepsilon^{-2} e^{2N[F_F - F_B]/k_B T}$$

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Fixed-Node method with PIMC

- Get rid of negative walks by canceling them with positive walks. We can do this if we know where the density matrix changes sign. Restrict walks to those that stay on the same side of the node.
- Fixed-node identity. Gives exact solution if we know the places where the density matrix changes sign: the nodes.

$$\rho_F(R_\beta, R_*;\beta) = \frac{1}{N!}\sum_P (-1)^P \int_{\rho_F(R_t, R_*;t)>0} dR_t e^{-S(R(t))} \text{ with } R_0 = \mathrm{P}R_*$$

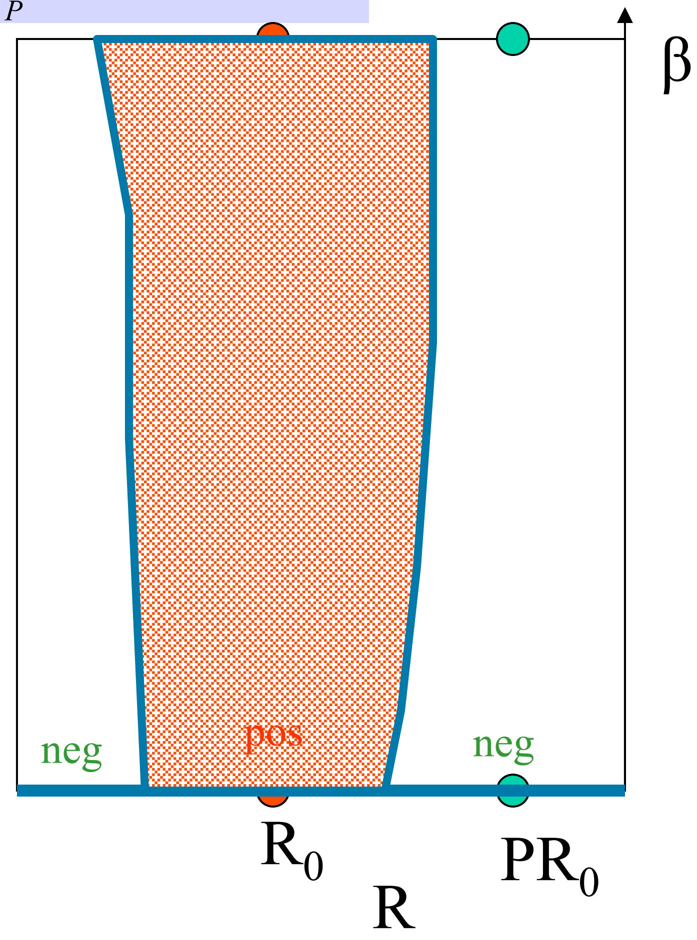
- Classical correspondence exists!!
- Problem: fermion density matrix appears on both sides of the equation. We need nodes to find the density matrix.
- But still useful approach. (In classical world we don't know V(R).)

Proof of the fixed node method

1. The density matrix satisfies the Bloch equation with initial conditions.

$$\frac{\partial\rho(R,t)}{\partial t} = \lambda\nabla^2\rho(R,t) - V(R)\rho(R,t) \quad \rho(R,0) = \frac{1}{N!}\sum_P (-1)^P \delta(R - PR_0)$$

2. One can use more general boundary conditions, not only initial conditions, because solution at the interior is uniquely determined by the exterior-just like the equivalent electrostatic problem.
3. Suppose someone told us the surfaces where the density matrix vanishes (the nodes). Use them as boundary conditions.
4. Putting an infinite repulsive potential at the barrier will enforce the boundary condition.
5. Returning to PI's, any walk trying to cross the nodes will be killed.
6. This means that we just restrict path integrals to stay in one region.



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Ortho-para H_2 example

In many-body systems it is hard to visualize statistics.

- The simplest example of the effect of statistics is the H_2 molecule in electronic ground state.
- Protons are fermions-must be antisymmetric.

1. Spins symmetric (↑↑). spatial wf antisymmetric (ortho) “fermions”
2. Spins antisymmetric (↓↑- ↑↓). spatial wf symmetic (para) “bosons”
3. Non symmetrical case (HD) “boltzmannons”

All 3 cases appear in nature!

- Go to relative coordinates: $r= r_1-r_2$
- Assume the bond length is fixed $|r|=a$. Paths are on surface of sphere of radius a.

PIMC task is to integrate over such paths with given symmetries.

For a single molecule there is no potential term, a “ring polymer” trapped on the surface of a sphere.

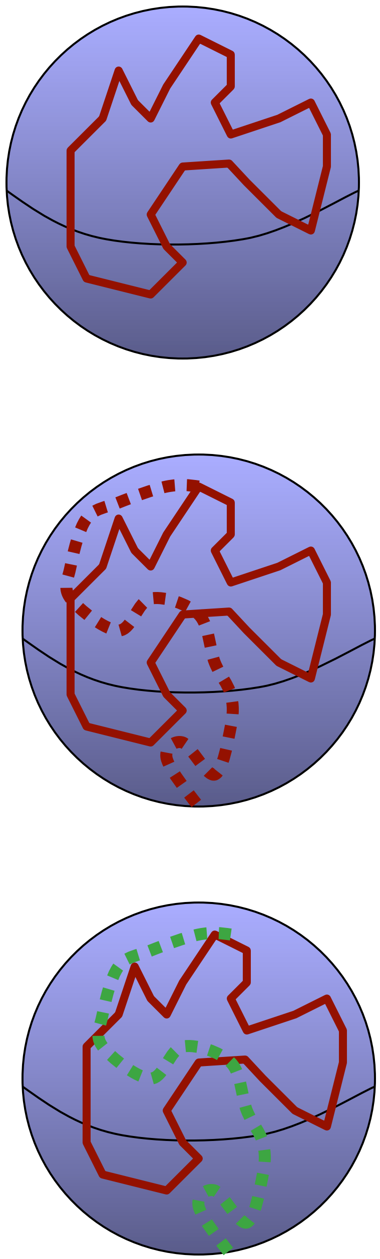
Paths on a sphere

1. “boltzmannons” Ring polymers on sphere O(r → r)

2. “bosons” 2 types of paths allowed. O(r → r) + O(r → -r)

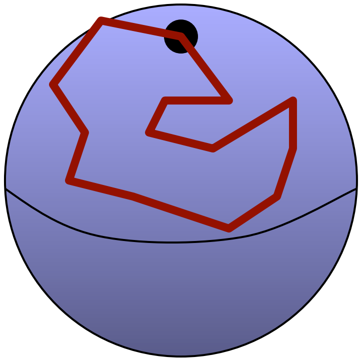
3. ”fermions” 2 types of paths allowed O(r → r) - O(r → -r)
   Low efficiency as

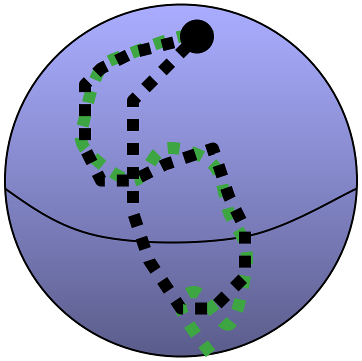
$$\zeta = e^{-\beta(E_1 - E_0)}$$



Restricted paths for ortho H_2

- Fix origin of path: the reference point.
- Only allow points on path with a positive density matrix. paths staying in the northern hemisphere: $r(t)\cdot r(0)>0$
- Clearly negative paths are thrown out.
- They have cancelled against positive paths which went south and then came back north to close.
- The symmetrical rule in "t": $r(t)\cdot r(t')>0$ is incorrect.
- Spherical symmetry is restored by averaging over the reference point: the north pole can be anywhere.
- Can do many H_2 the same way.
- Ortho H_2 is much more orientable than either HD or para H_2.





Restricted Path Integral Applications

- Homogenous electrons/plasma (Ethan to discuss)
- High Temperature hydrogen/helium (interior of planets)(Pierleoni, Bernu, Militzer, Magro,…)
- Carbon (Militzer & Driver)
- Liquid/solid ^{3}He (Jonathon?)
- Electron-hole liquid (Shumway)
- BEC of fermions (Akkineni)

Nodal Properties

If we know the sign of the exact density matrix(the nodes), we can solve the fermion problem with the fixed-node method.

- If $\rho(R)$ is real, nodes are $\rho(R)=0$ where **R** is the **3N** dimensional vector.
- Nodes are a **3N-1** dimensional surface. (Do not confuse with single particle orbital nodes!)
- Coincidence points $\mathbf{r}_i = \mathbf{r}_j$ are **3N-3** dimensional hyper-planes
- In **1** spatial dimension these "points" exhaust the nodes. *fermion problem is easy to solve in 1D* with the "no crossing rule."
- Coincidence points (and other symmetries) only constrain nodes in higher dimensions, they do not determine them.
- The nodal surfaces define nodal volumes. How many nodal volumes are there? **Conjecture**: <u>there are typically *only* 2 different volumes</u> (+ and -) except in 1D. (but only demonstrated for free particles.)
- At high T, nodes are free particle-like, Vornoi polyhedra.

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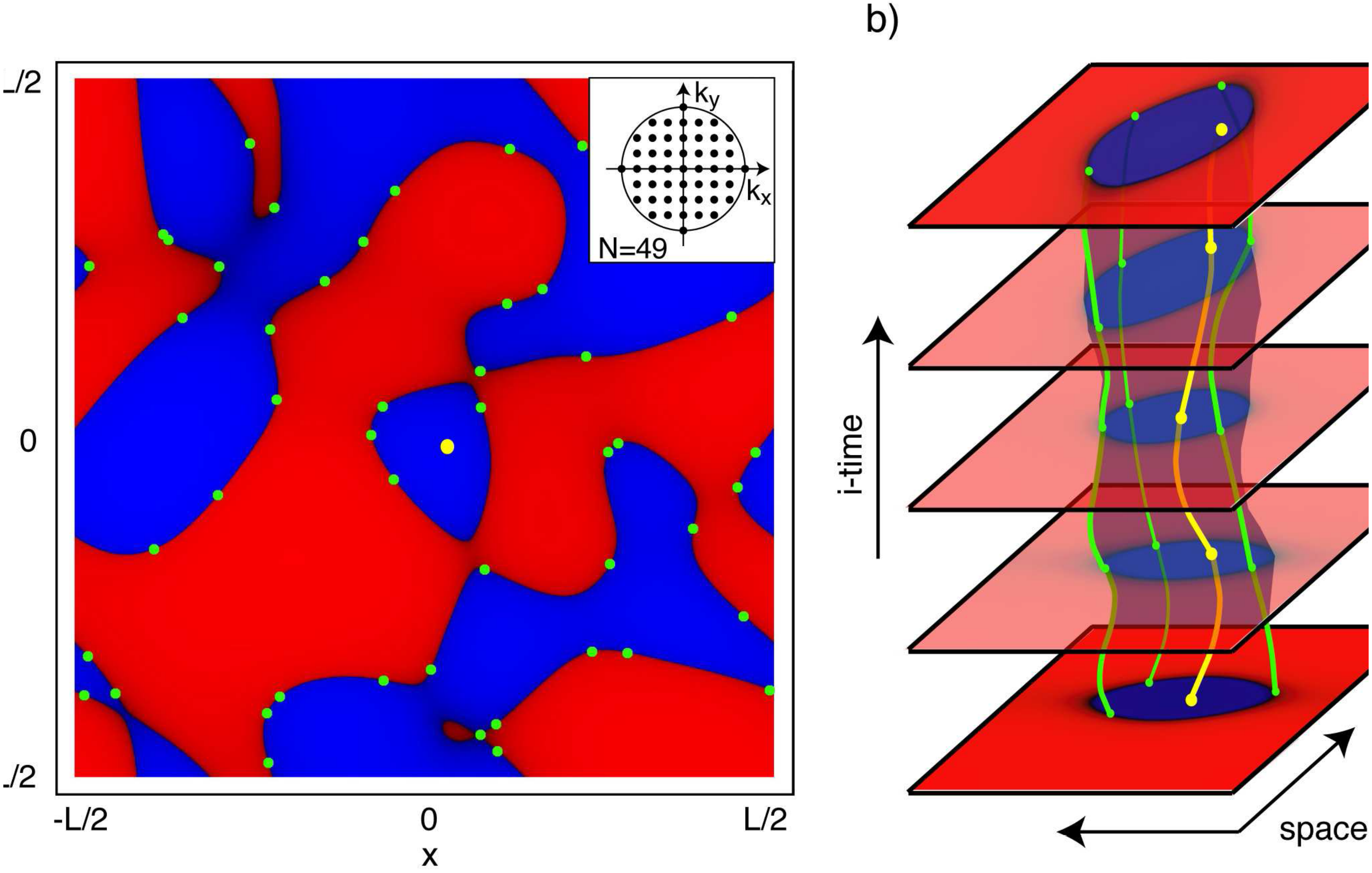
For a density matrix



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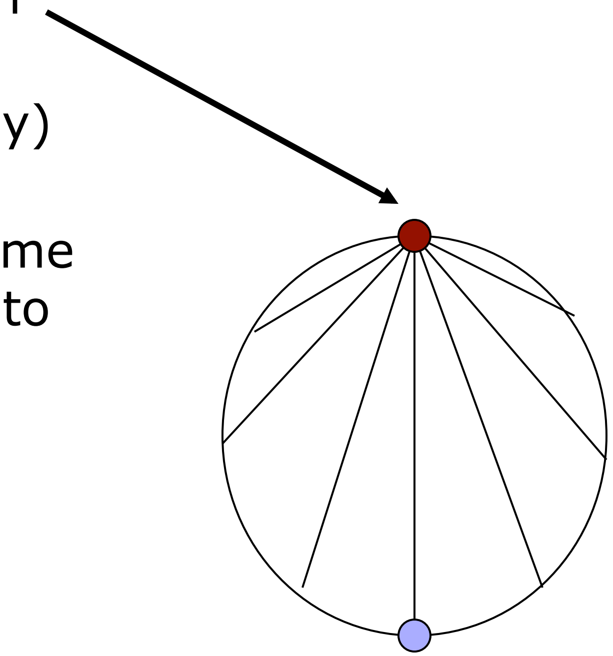
Reference Point



- Scalar averages can only be taken at the reference point. New feature compared with boson path integrals.
- Partition function and all derivatives (energy) use information from the whole path.
- We lose time slice symmetry if nodes are time dependent. But this is probably necessary to fix phase of density matrix.
- Reference point moves are expensive and ultimately cause RPIMC to get "stuck" for $T<E_F/10$.
- One can use a 2 reference points. This restores time-reversal symmetry and means we only need nodes for $t<\beta/2$.
- More than 2 reference points will bring back the "sign" problem.
- Shumway tried a "wagon-wheel"; correct?

RPIMC with approximate nodes

- In almost all cases, we do not know the “nodal” surfaces.
- We must make an an ansatz.
- This means we get a fermion density matrix (function with the right symmetry) which satisfies the Bloch equation at all points except at the node.
- That is, it has all the exact “bosonic” correlation
- There will be a derivative mismatch across the nodal surface unless nodes are correct.
- In many cases, there is a free energy bound. Proved at high temperature and at zero temperature and when energy is always lower.
- Maybe one can find the best nodes using the variational principle. (variational density matrix approach)

Free particle nodes

- For non-interacting (NI) particles the nodes are the finite temperature version of a Slater determinant:

$$\rho_F^{NI}(R',R;t) = \frac{1}{N!}\det\left[g\left(r'_i,r_j;t\right)\right]$$

where $g\left(r'_i,r_j;t\right)$ is the single particle density matrix.

$$g\left(r',r;t\right)=\left(4\pi\lambda\tau\right)^{-3/2} e^{-\frac{(r-r')^2}{4\lambda\tau}} + \text{periodic images}$$

At high T, nodes are hyperplanes.

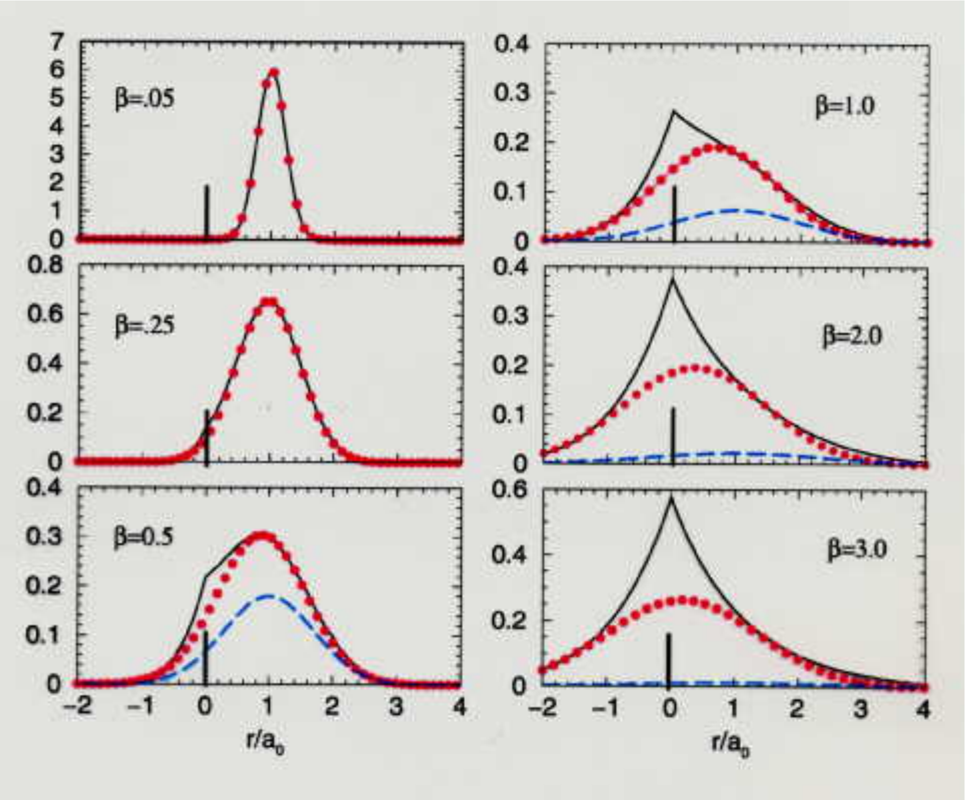
At low T, nodes minimize the kinetic energy.

Nodes have "time dependence".

- Problems: no spin-coupling in nodes, no formation of electronic bound states.
- Militzer-Pollock compute g(r,r' ;t) with Hartree eqs. (VDM or variational density matrix)

Variational Density Matrix

- Approximate density matrix by a determinant of single particle Gaussians.
- Follow evolution of center and width in imaginary time using a variational ansatz.
- Introduces electron-proton coupling in density matrix.
- Exact at high temperature.
- Goes to SCF at zero temperature.
- *Only used for restriction not for the action.*



H atom example

Militzer and Pollock, PRE 61, 3470 (2000).

Nodal optimization

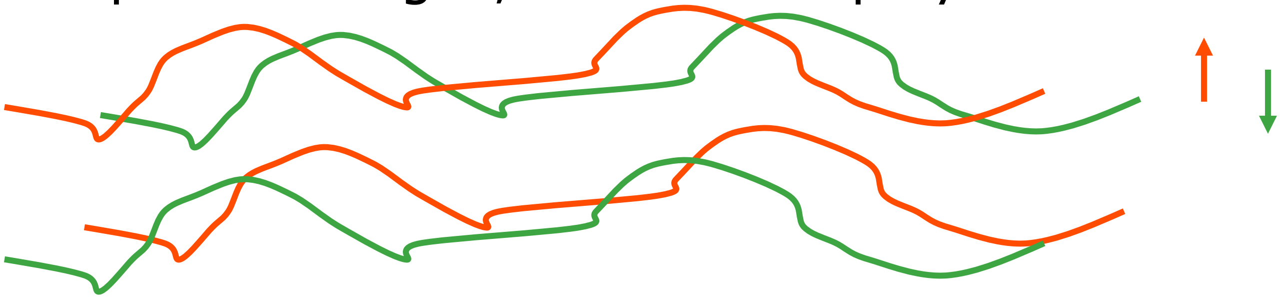
- General scheme: work with a determinant(s) with parameters.
- Minimize RPIMC energy (or overlap) wrt nodal parameters (use the gradients)
- Compute forces on these parameters and update. What estimator to use?

Momentum distribution

- For bosons the momentum distribution shows evidence of BEC.
  - Long exchange cycles n(r) long range $n_0 > 0$
- What is effect for fermions? Run logic in reverse.
  - For NI fermions, n(k) has discontinuity at k_F.
  - Hence $n(r) \propto \cos(k_F r) / \left(k_F r\right)^2$
  - We must have cancellation of long-range positive and negative exchanges!
  - Negative permutations allowed/required off-diagonal.
- Algorithm : *cond-mat/0310401*
- Exchanges are needed to get a Fermi-liquid.
- In contrast to boson Pis, long exchanges do not lead to a phase transition or superfluidity.

Fermion superfluidity

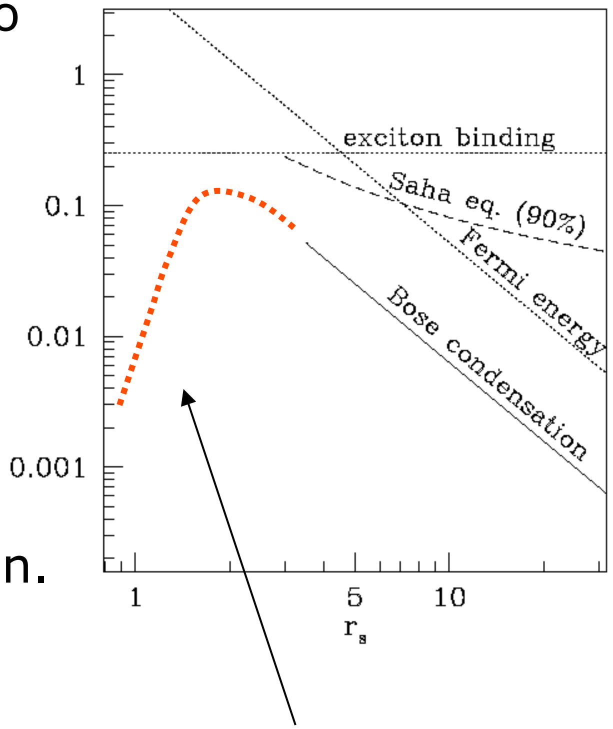
- Liquid ^{3}He becomes superfluid at very low temperatures ($T_c \sim 1$mK).
- With the exact nodal restriction this must also happen within RPIMC, because we can calculate the free energy.
- What happens to the paths at this phase transition?
- SPECULATION: there is a “Cooper” pairing of up and down spin exchanges, similar to a polymer blend



- Not tried in ^{3}He because of difficulties of length, temperature and knowledge of nodes.

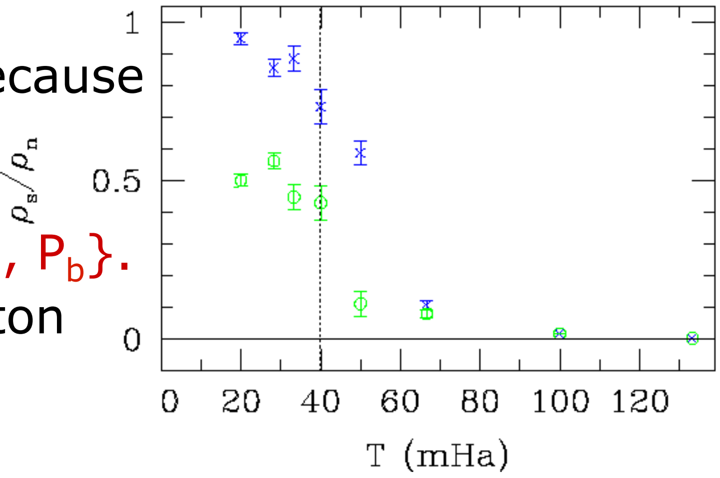
Exciton superfluidity

- What system is the most appropriate to observe superfluidity of fermions? (strongest pairing)
- Consider the simplest 1-band model of particles and holes in a semiconductor.
- Assume masses are isotropic and the same; only the charge is different.
- At low temperature a particle and hole can bind together to form an *exciton* (like a hydrogen atom) which is a boson.
- If the exciton density is high enough, they can bose condense.: $T\rho^{3/2}<2.7$
- Shumway-Ceperley (1999) observed this transition for excitons.
- What do the paths look like?
- Observed in Oct 2003 in atom traps!
- However, RPIMC has problems with nodes: can we find a single determinant continuous from high T to low T?



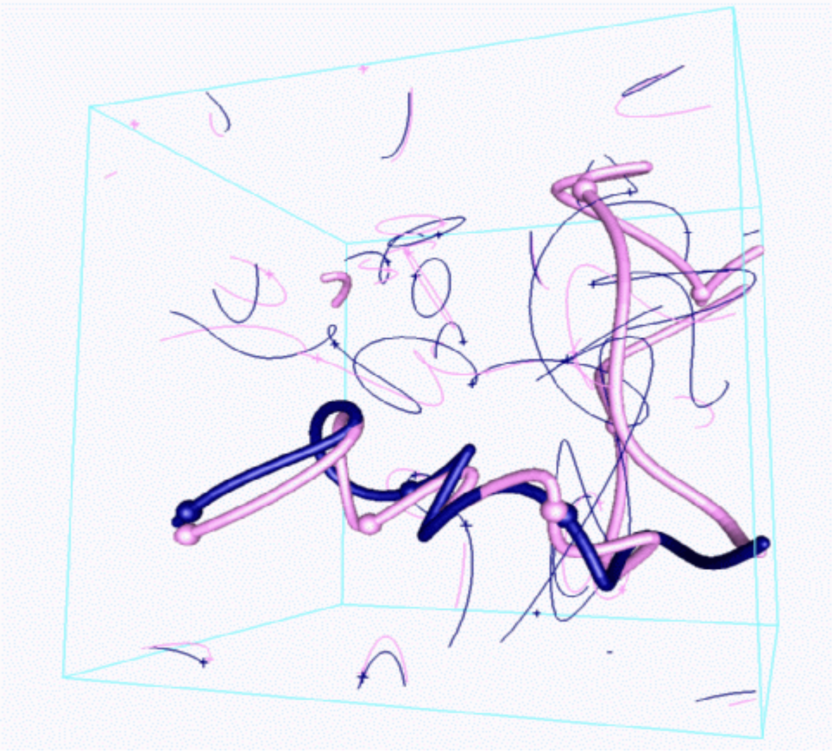
BCS region

Pairing Nodes

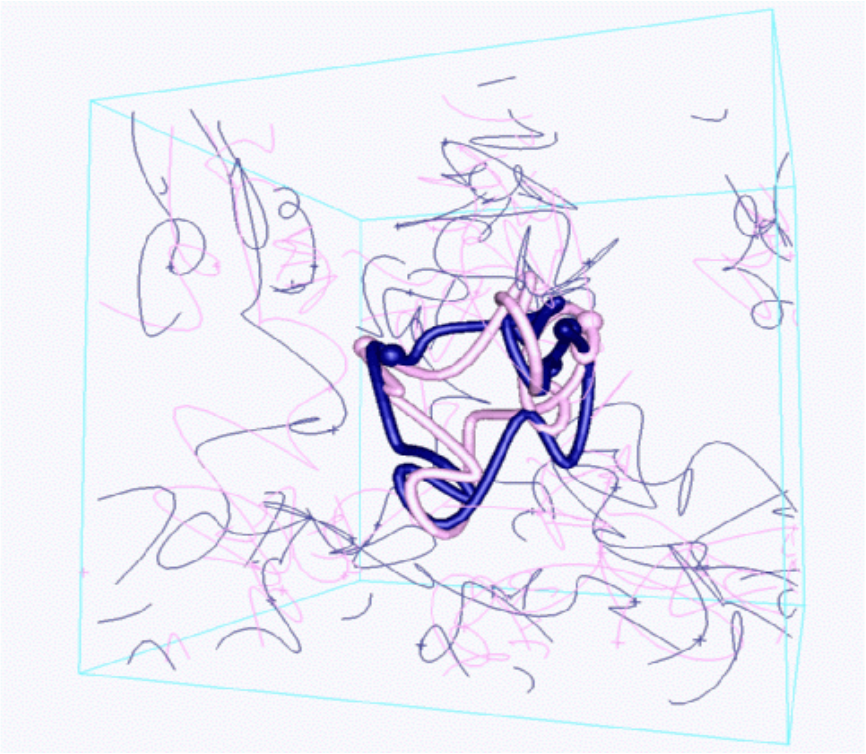


- Free fermion nodes does not allow pairing because nodes of two species are independent.
    - Consider two types of fermions, a&b.
    - Possible exchanges are $\{I, P_a P_b\}$ and $\{P_a , P_b\}$.
    - The permutation $P_a P_b$ represents an exciton exchange but it is forbidden if nodes are independent since the path will cross "a" nodes or "b" nodes first.
- Instead we used paired nodes: $\boldsymbol{A}\{ \Pi_k g(a_k - b_k)\}$ where g(r) is a pairing function (we used a Gaussian).
- Nodes are time-independent ➔ winding number formula for superfluid response.
- We can define 2 different responses. Let W_x be winding number of species x.
    - movement of walls: $<(W_a+W_b)^2>$
    - magnetic field: $<(W_a-W_b)^2>$

BEC of excitons $[r_s=6 \ \ T<T_c]$



Winding exchange (3,6)



Pair exchange (2,2)

Blue=electron   lavendar=hole

Superconductivity is (cooper pairing) of paths.

Problem with pairing nodes

Generalization for complex actions

How does the the real machinery generalize to complex action?

Can we generalize the concept of nodal surfaces?

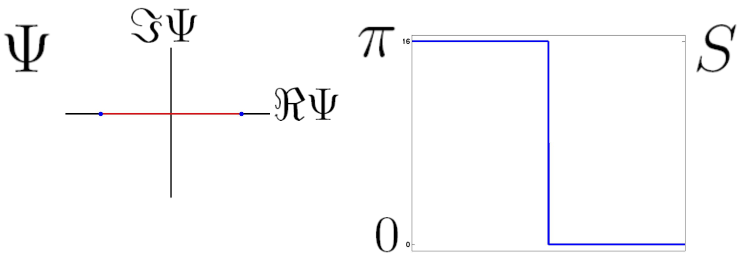
For insulators we expect that electrons are localized (quantum mechanics is “nearsighted”) so boundary conditions should not matter.

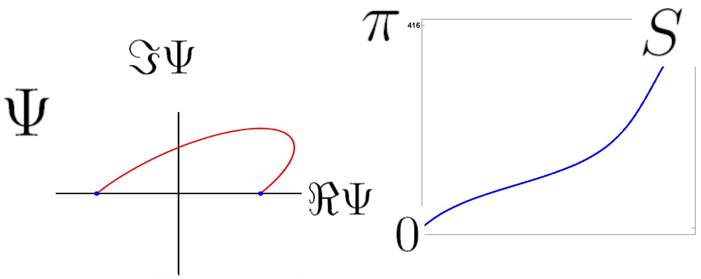
How about metals?

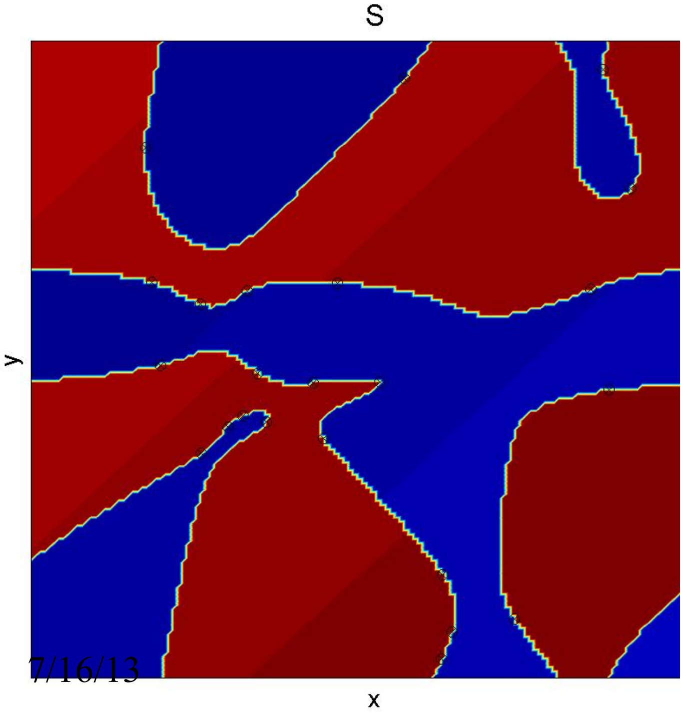
The nodes and phases under interchange

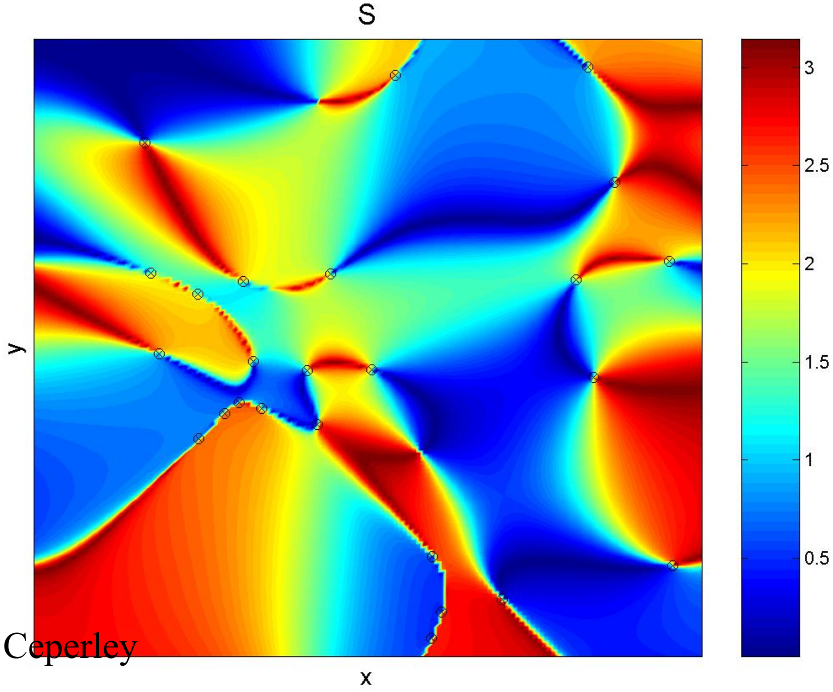
Real or Real-like Wavefunction

Complex Wavefunction



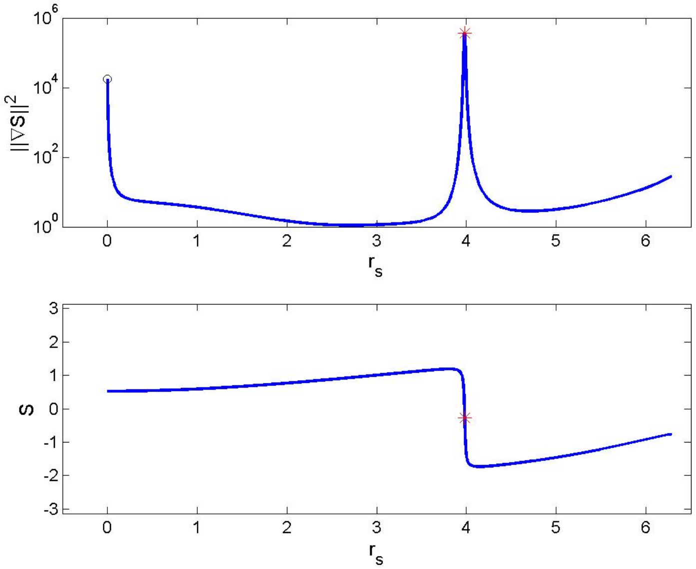






Phase of density matrix

Step structure reappears in the thermo-dynamic limit! Lin thesis (2001)



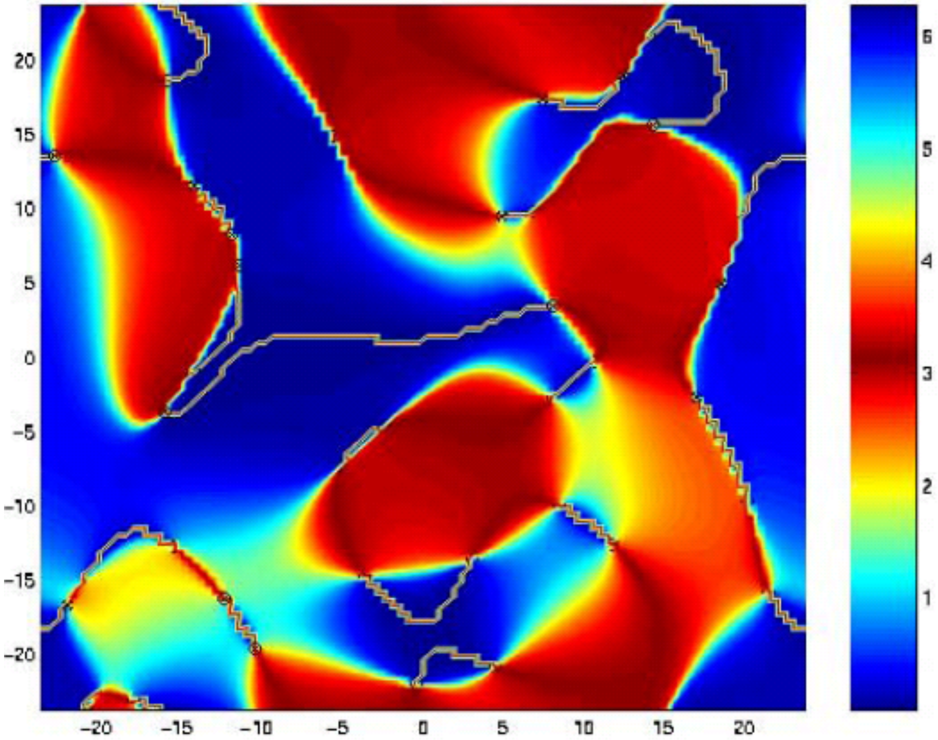
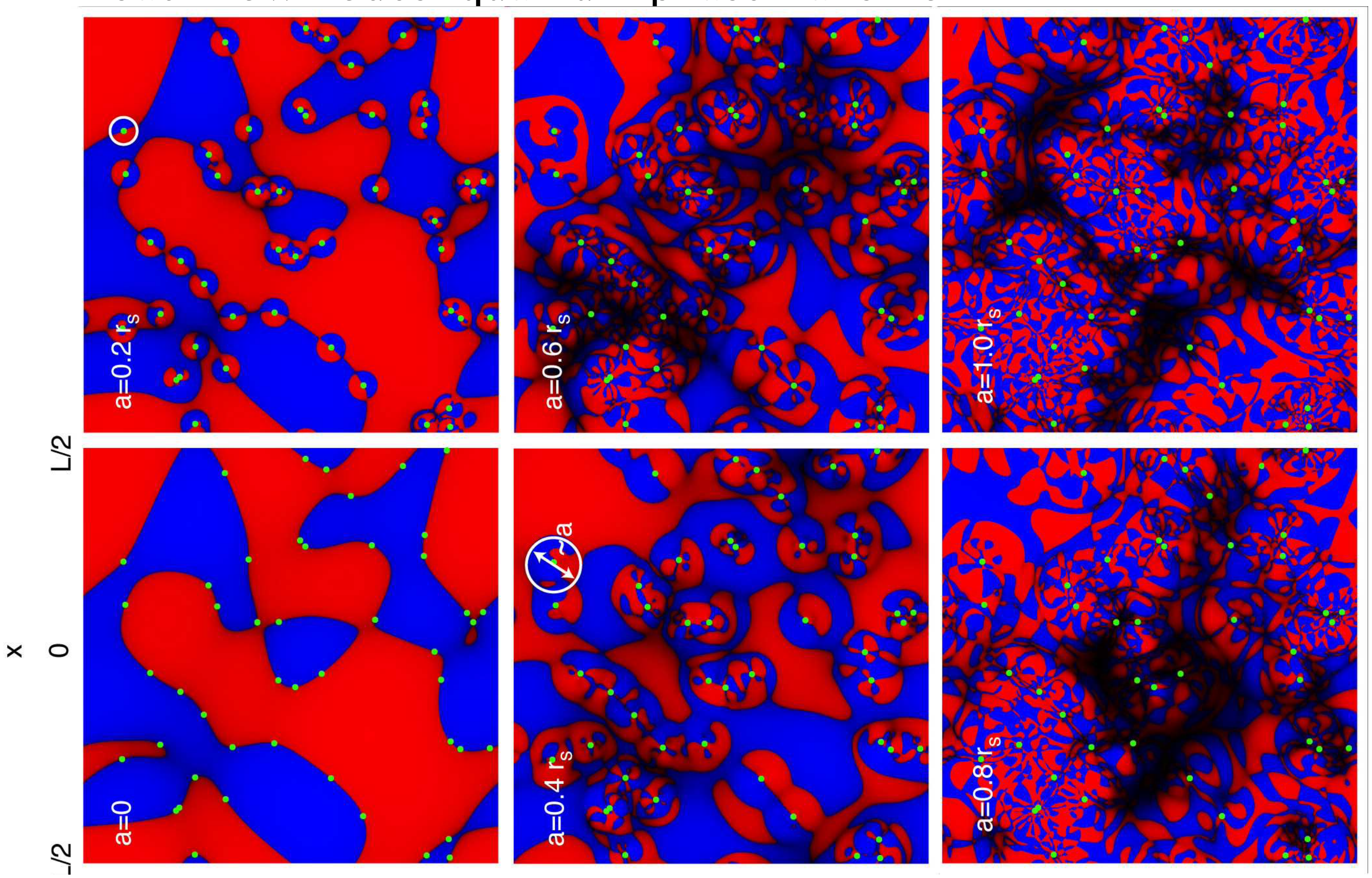


Figure 2.3: 2D phase contour of the density matrix of 21 free spinless fermion in a periodic box. The phase here is represented by colors, with blue corresponding to 0 or 2π and red corresponding to π, respectively. The plot is generated by moving one of the particles while keeping the other 20 fixed. The open circles are the fixed positions of 20 fermions; The contour lines are places where $\mathcal{S}$ changes by 2π, and have no significance. The temperature is $T = 0.2K$ (the Fermi temperature for this system is $T_K \simeq 7K$).

Kruger and Zaanen PRB 2008

backflow nodes=quantum phase transition



“The collapse of the Fermi liquid at a quantum critical point as observed in the heavy fermion metals is necessarily associated with a qualitative change of the nodal surface from a smooth to a fractal geometry.”

Dictionary of the Quantum-Classical Isomorphism

Attention: *some words have opposite meanings.*

We need to enlarge this dictionary

"fermion dictionary"?

Quantum	**Classical**
Bose condensation	Delocalization of ends
Boson statistics	Joining of polymers
Exchange frequency	Free energy to link polymers
Free energy	Free energy
Imaginary velocity	Bond vector
Kinetic energy	Negative spring energy
Momentum distribution	FT of end-end distribution
Particle	Ring polymer
Potential energy	Iso-time potential
Superfluid state	Macroscopic polymer
Temperature	Polymer length
Pauli Principle	Restricted Paths
Cooper Pairing	Paired Fermion Paths
Fermi Liquid	Winding restricted paths
Insulator	Nonexchanging paths

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