

# Variational and Diffusion Monte Carlo in the Continuum

- Describe VMC and DMC
- Trial functions
- Application to the homogeneous electron gas
- Lab will use QMCPACK to illustrate a simple calculation

David Ceperley lecturer  
Jeremy McMinis Lab instructor

University of Illinois Urbana-Champaign

# Variational Monte Carlo

- Historically first quantum simulation method
- Slater-Jastrow trial function
- Calculations of properties:  $n(k)$ .
- Examples: liquid helium and electron gas.
- Wavefunctions for Quantum solids
- Ewald Sums for Charged systems
- WaveFunctions beyond Slater-Jastrow: back flow and 3-body
- Twist Averaged Boundary Conditions

# First Major QMC Calculation

- PhD thesis of W. McMillan (1964) University of Illinois.
- VMC calculation of ground state of liquid helium 4.
- Applied MC techniques from classical liquid theory.
- Ceperley, Chester and Kalos (1976) generalized to fermions.

PHYSICAL REVIEW

VOLUME 133, NUMBER 2A

12 APRIL 1965

## Ground State of Liquid He<sup>4</sup>

W. L. McMILLAN\*

*Department of Physics, University of Illinois, Urbana, Illinois*

(Received 16 November 1964)

The properties of the ground state of liquid He<sup>4</sup> are studied using a variational wave function of the form  $\prod_{i<j} f(r_{ij})$ . The Lennard-Jones 12-6 potential is used with parameters determined from the gas data by deBoer and Michiels. The configuration space integrals are performed by a Monte Carlo technique for 32 and 108 atoms in a cube with periodic boundary conditions. With  $f(r) = \exp[-(2.6 \text{ \AA}/r)^6]$ , the ground-state energy is found to be  $-0.78 \times 10^{-18}$  ergs/atom, which is 20% above the experimental value. The liquid structure factor and the two-particle correlation function are in reasonably good agreement with the x-ray and neutron scattering experiments.

- Zero temperature (single state) method
- VMC can be generalized to finite temperature by using “trial” density matrix instead of “trial” wavefunction.

Ceperley VMC & DMC

# Notation

- Individual coordinate of a particle  $r_i$
- All  $3N$  coordinates  $\mathbf{R} = (r_1, r_2, \dots, r_N)$
- Total potential energy =  $V(\mathbf{R})$
- Kinetic energy :  $-\lambda \sum_{i=1}^N \nabla_i^2$  where  $\lambda \equiv \frac{\hbar^2}{2m}$
- Hamiltonian :  $\hat{H} = \hat{T} + \hat{V}$

# Liquid helium

## the prototypic quantum fluid

- Interatomic potential is known more accurately than any other atom because electronic excitations are so high.
- A helium atom is an elementary particle. A weakly interacting hard sphere.

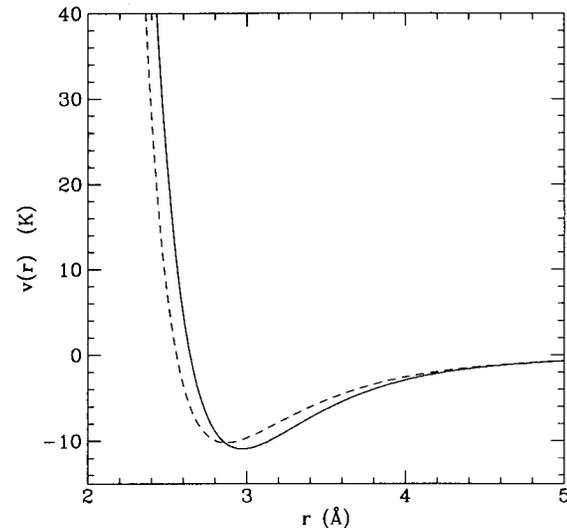


FIG. 1. The semiempirical pair potential between two helium atoms: solid line, Aziz *et al.* (1992); dashed line, Lennard-Jones 6-12 potential with  $\epsilon = 10.22$  K and  $\sigma = 2.556$  Å.

- Two isotopes:
  - $^3\text{He}$  (fermion: antisymmetric trial function, spin 1/2)
  - $^4\text{He}$  (boson: symmetric trial function, spin zero)

$$v_{LJ}(r) = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right)$$

Ceperley VMC & DMC

# Helium phase diagram

- Because interaction is so weak helium does not crystallize at low temperatures. Quantum exchange effects are important
- Both isotopes are quantum fluids and become superfluids below a critical temperature.
- One of the goals of computer simulation is to understand these states, and see how they differ from classical liquids starting from non-relativistic Hamiltonian:

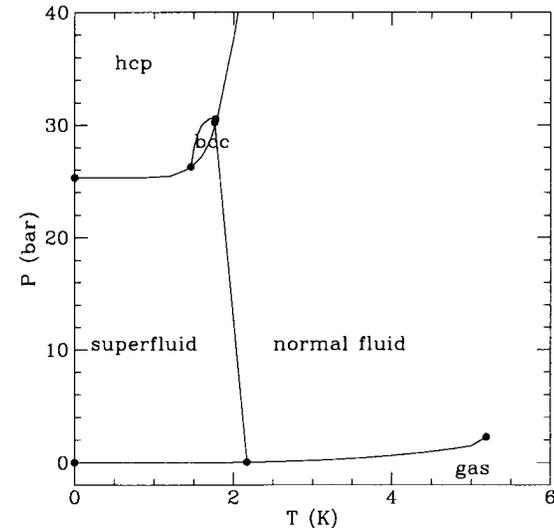


FIG. 2. The phase diagram of  $^4\text{He}$ .

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + V(R)$$

$$\lambda \equiv \frac{\hbar^2}{2m_i}$$

# Variational Monte Carlo (VMC)

- Variational Principle. Given an appropriate trial function:
  - Continuous
  - Proper symmetry
  - Normalizable
  - **Finite variance**
- Quantum chemistry uses a product of single particle functions
- With MC we can use any “computable” function.

- Sample  $R$  from  $|\Psi|^2$  using MCMC.
  - Take average of local energy:
  - Optimize  $\Psi$  to get the best upper bound

- Error in energy is 2<sup>nd</sup> order
- Better wavefunction, lower variance!
- **(non-classical) “zero variance” principle.**

$$E_V = \frac{\int dR \langle \psi | H | \psi \rangle}{\int dR \langle \psi \psi \rangle} \geq E_0$$

$$\sigma^2 = \frac{\int dR \langle \psi | H^2 | \psi \rangle}{\int dR \langle \psi \psi \rangle} - E_V^2$$

$$E_L(R) = \Re \left[ \psi^{-1}(R) H \psi(R) \right]$$

$$E_V = \langle E_L(R) \rangle_{\psi^2} \geq E_0$$

# Spin & real vs. complex

- How do we treat spin in QMC?
- For extended systems we use the  $S_z$  representation.
- We have a fixed number of up and down electrons and we antisymmetrize among electrons with the same spin.
- This leads to 2 Slater determinants.
- For a given trial function, its real part is also a trial function (but it may have different symmetries)

$$\left( e^{ikr}, e^{-ikr} \right) \quad \text{or} \quad \left( \cos(kr), \sin(kr) \right)$$

- For the ground state, without magnetic fields or spin-orbit interaction, we can always work with real functions.
- However, it may be better to work with complex functions.

## Trial function for $^4\text{He}$ : “Jastrow” or pair product

- We want finite variance of the local energy.
- Whenever 2 atoms get close together wavefunction should vanish.
- The pseudopotential  $u(r)$  is similar to classical potential
- Local energy has the form:  
G is the pseudoforce:

$$\psi(R) = \prod_{i < j} e^{-u(r_{ij})}$$

$$E_\psi(R) = \sum_{i < j} \left[ v(r_{ij}) - 2\lambda \nabla^2 u(r_{ij}) \right] - \lambda \sum_i G_i^2$$

$$G_i = \sum_j \nabla_i u(r_{ij})$$

If  $v(r)$  diverges as  $r^{-n}$  how should  $u(r)$  diverge? Assume:

$$u(r) = r^{-m}$$

Keep  $N-1$  atoms fixed and let 1 atom approach another and analyze the singular parts of the local energy.

Gives a condition on  $u$  at small  $r$ .

For Lennard-Jones 6-12 potential,  
Jastrow,  $u \sim r^{-5}$

$$\epsilon r^{-n} = 2\lambda (\alpha m r^{-m-1})^2 \quad \text{for } n > 2$$

$$m = \frac{n}{2} - 1$$

$$\alpha = \frac{1}{m} \sqrt{\frac{\epsilon}{2\lambda}}$$

# Fermions: antisymmetric trial function

- At mean field level the wavefunction is a Slater determinant. Orbitals for homogenous systems are a filled set of plane waves.
- We can compute this energy analytically (HF).
- To include correlation we multiply by a pseudopotential. We need MC to evaluate properties.
- New feature: how to compute the derivatives of a determinant and sample the determinant. Use tricks from linear algebra.
- Reduces complexity to  $O(N^2)$ .

$$\Psi_s(R) = \text{Det} \left\{ e^{ik_i r_j} \eta_i(\sigma_j) \right\}$$

$$\text{PBC: } k \cdot L = 2\pi n + \{\theta\}$$

$$\Psi_{SJ}(R) = \text{Det} \left\{ e^{ik_i r_j} \right\} e^{-\sum_{i < j} u(r_{ij})}$$

*Slater-Jastrow trial function.*

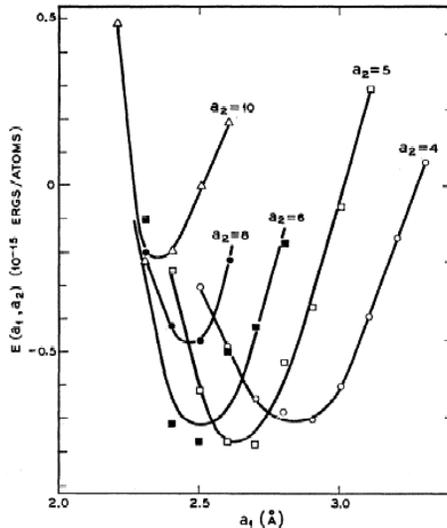
$$\det(\phi_k(r_j^T)) = \det(\phi_k(r_j)) \sum_k \phi_k(r_j^T) M_{k,i}^{-1}$$

$$\frac{1}{\det(M)} \frac{\partial \det(M)}{\partial a} = \text{Tr} \left\{ M^{-1} \frac{\partial M}{\partial a} \right\}$$

# VARIATIONAL MONTE CARLO CODE

```
call initstate (s_old) ← Initialize the state
p_old = psi2 (s_old) ← Evaluate psi_trial
LOOP {
  call sample (s_old,s_new,T_new,1) ← Sample new state
  p_new = psi2 (s_new) ← Evaluate psi_trial
  call sample (s_new,s_old,T_old,0) ← Find transition prob.
  A = (p_new/T_new)/(p_old/T_old) ← for going backward
  if(A > rand () ) { ← Acceptance prob.
    s_old=s_new
    p_old=p_new
    naccept = naccept +1} ← Accept the move
  call averages (s_old) ← Collect statistics
}
```

# Optimization of trial function



Try to optimize  $u(r)$  using reweighting (correlated sampling)

- Sample  $R$  using  $P(R)=\Psi^2(R,a_0)$
- Now find minima of the analytic function  $E_V(a)$
- Or minimize the variance (more stable but wavefunctions less accurate).
- Statistical accuracy declines away from  $a_0$ .
- New methods allow many more parameters

$$E_V(a) = \frac{\int \psi(a) H \psi(a)}{\int |\psi(a)|^2}$$

$$= \frac{\sum_k w(R_i, a) E(R_i, a)}{\sum_k w(R_i, a)}$$

$$w(R_i, a) = \frac{|\psi(R, a)|^2}{P(R)}$$

$$E(R, a) = \psi^{-1}(R, a) H \psi(R, a)$$

$$N_{eff} = \frac{\left[ \sum_i w_i \right]^2}{\sum_i w_i^2}$$

## “modern” optimization

- With more computer time, we do a MC rw in both R and a (parameter space).
- Do usual VMC for a “block” and collect statistics on  $E$ ,  $dE/da$ ,  $d^2E/(da_i da_j)$ .
- Special estimators for these quantities.
- Then make a change in a:  $a_{\text{new}} = a_{\text{old}} + c dE/da + \dots$
- Iterate until convergence.
- Lots more tricks to make it stable.
- Can do hundreds of parameters.

# Scalar Properties, Static Correlations and Order Parameters

What do we get out of a simulation? Energy by itself doesn't tell you very much.

Other properties

- do NOT have an upper bound property
- Only first order in accuracy

EXAMPLES

- Static properties: pressure, specific heat etc.
- Density
- Pair correlation in real space and fourier space.
- Order parameters and broken symmetry: How to tell a liquid from a solid
- Specifically quantum: the momentum distribution

# Other quantum properties

- Kinetic energy
- Potential energy
- Pair correlation function
- Structure function
- Pressure (virial relation)

Like properties from classical simulations

No upper bound property

Only first order in accuracy

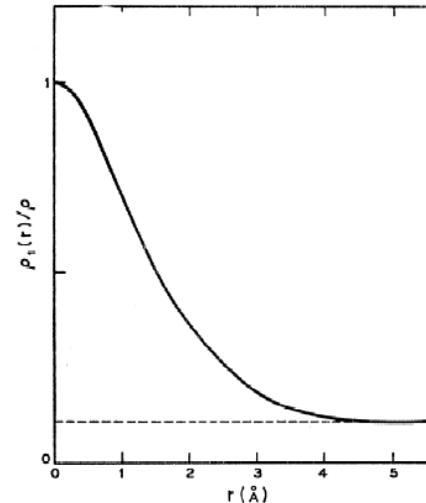
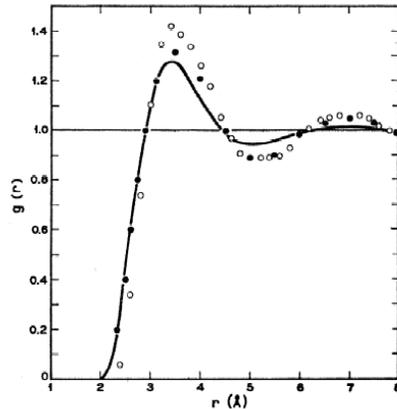


FIG. 7. The single-particle density matrix as a function of separation. The dashed curve indicates the asymptotic limit for large  $r$ ,  $\rho_1(r) \sim \rho_0 = 0.11\rho$ .

- Momentum distribution
  - Non-classical showing effects of bose or fermi statistics
  - Fourier transform is the single particle off-diagonal density matrix
- Compute with McMillan Method.
- Condensate fraction  $\sim 10\%$

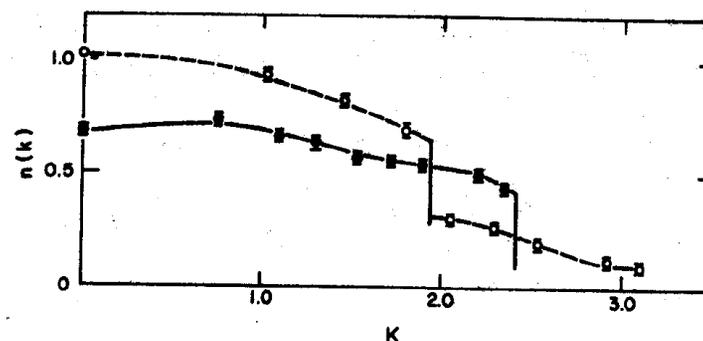
Ceperley VMC & DMC

$$n(r, r') = \int dr_2 \dots dr_N \psi^*(r, r_2 \dots) \psi(r', r_2 \dots)$$

$$= \left\langle \frac{\psi^*(r', r_2, \dots)}{\psi(r, r_2, \dots)} \right\rangle$$

# Momentum Distribution

- Momentum distribution
  - Classically momentum distribution is always a Gaussian
  - Non-classical showing effects of bose or fermi statistics
  - Fourier transform is the single particle off-diagonal density matrix
- Compute with McMillan Method.
- For fermions we need to use the determinant update formulas to find the effect of the movement of 1 electron.



$$n(r, r') = \frac{1}{Z} \int dr_2 \dots dr_N \psi^*(r, r_2 \dots) \psi(r', r_2 \dots)$$
$$= \left\langle \frac{\psi^*(r, r_2 \dots)}{\psi(r', r_2 \dots)} \right\rangle$$

# Derivation of momentum formula

- Want probability that a given atom has momentum  $\hbar k$ .
- Find wavefunction in momentum space by FT wrt all the coordinates and integrating out all but one electron

$$\text{Pr}(k_1, \dots, k_N) = \left| \int dR e^{-i(k_1 r_1 + \dots + k_N r_N)} \Psi(R) \right|^2$$

$$n_k = \int dk_2 \dots dk_N \text{Pr}(k, k_2, \dots, k_N)$$

- Expanding out the square and performing the integrals we get.

$$n_k = \int \frac{d^3 r d^3 s}{(2\pi)^3 V} \exp(-ik(r-s)) n(r, s) = \int \frac{d^3 r}{(2\pi)^3} e^{-ikr} n(r)$$

Where:  $n(r, s) = \frac{V}{Q} \int dr_2 \dots dr_N \psi^*(r, r_2 \dots r_N) \psi(s, r_2 \dots r_N)$

For a homogeneous system,  $n(r, s) = n(|r-s|)$

# The electron gas

- Standard model for electrons in metals
- Basis of DFT.
- Characterized by 2 dimensionless parameters:
  - Density
  - Temperature

$$r_s = a / a_0$$

$$\Gamma = e^2 / Ta$$

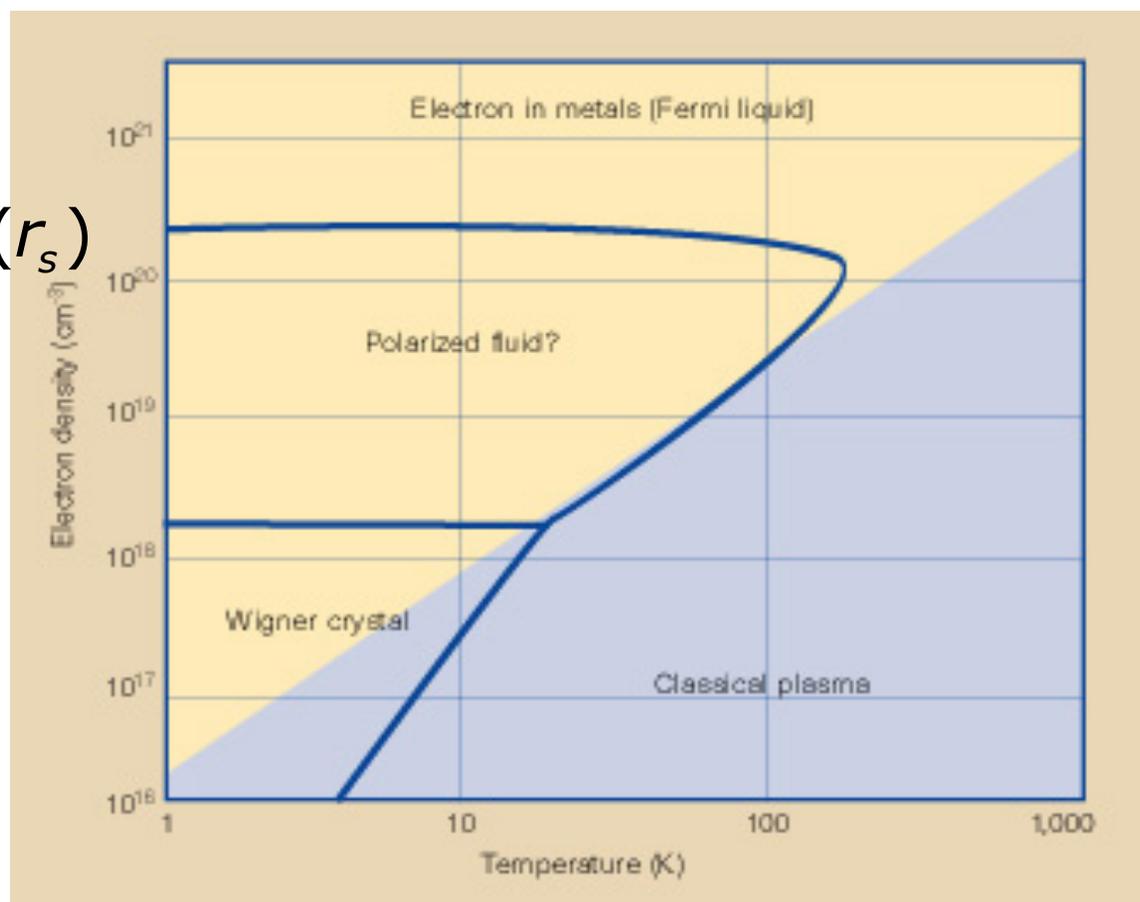
- What is energy?
- When does it freeze?
- What is spin polarization?
- What are properties?

$\Gamma < r_s$  classical OCP

$\Gamma = 175$  classical melting

$$H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i<j} \frac{1}{r_{ij}}$$

$\log(r_s)$



Ceperley VMC & DMC

$\log(\Gamma)$

# Charged systems

How can we handle charged systems?

- Just treat like short-ranged potential: cutoff potential at  $r > L/2$ .

Problems:

- Effect of discontinuity never disappears:  $(1/r)$  ( $r^2$ ) gets bigger.
- Will violate Stillinger-Lovett conditions because Poisson equation is not satisfied
- Image potential solves this:

$$V_I = \sum v(r_i - r_j + nL)$$

- But summation diverges. We need to resum. This gives the ewald image potential.
- For one component system we have to add a background to make it neutral.
- Even the trial function is long ranged and needs to be resummed.

# Ewald summation method

- Key idea is to split potential into k-space part and real-space part. We can do since FT is linear.

$$V = \sum_{i < j, L} \phi(\mathbf{r}_i - \mathbf{r}_j + n\mathbf{L})$$

$$V = \sum_{\mathbf{k}} \phi_{\mathbf{k}} \left( |\rho_{\mathbf{k}}|^2 - N \right) \quad \text{where } \rho_{\mathbf{k}} = \sum_i e^{i\mathbf{k} \cdot \mathbf{g}_i}$$

$$\text{and } \phi_{\mathbf{k}} = \frac{1}{\Omega} \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \phi(\mathbf{r})$$

$$\text{For } \phi(\mathbf{r}) = e^2/r \Rightarrow \phi_{\mathbf{k}} = \frac{4\pi e^2}{k^2}$$

- Bare potential converges slowly at large  $r$  (in  $r$ -space) and at large  $k$  (in  $k$ -space)

# Classic Ewald

- Split up using Gaussian charge distribution

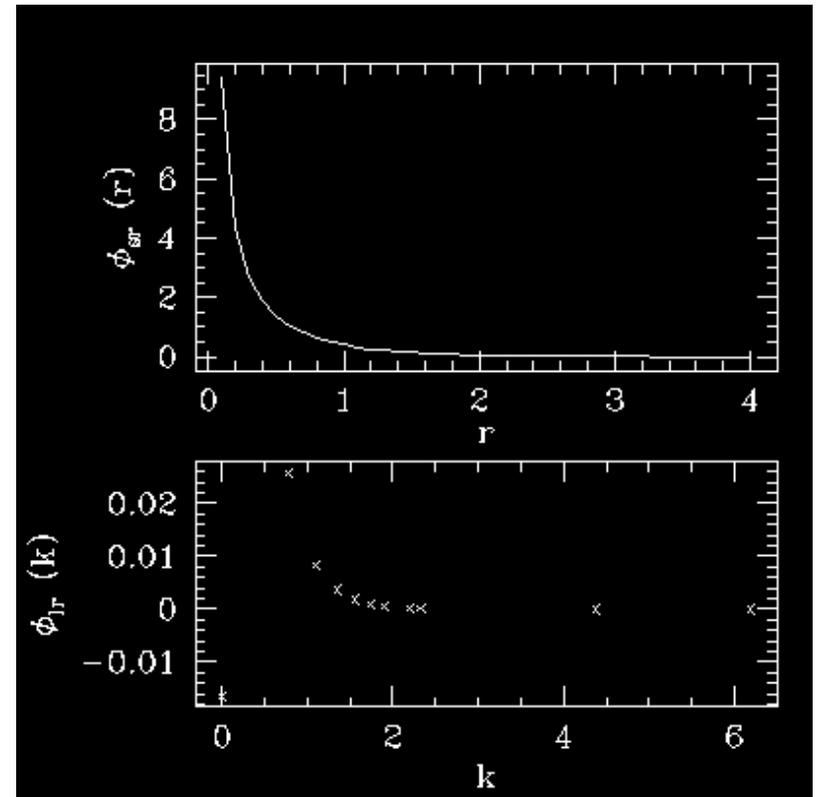
$$\phi(r) = \frac{\text{erfc}(\kappa r)}{r} \text{ decays fast at large } r$$

$$\phi_k = \frac{4\pi e^{-(k/2\kappa)^2}}{k^2} \text{ decays fast at large } k$$

$\kappa$  = convergence parameter

- If we make it large enough we can use the minimum image potential in r-space.
- Extra term for insulators:

$$V_{dipole} = \frac{2\pi}{(2\epsilon + 1)\Omega} \left| \sum_i \mu_i \right|^2$$



# Jastrow factor for the e-gas

- Look at local energy either in r space or k-space:
- r-space: as 2 electrons get close gives cusp condition:  $du/dr|_0 = -1$
- k-space, charge-sloshing or plasmon modes.

$$2\rho u_k = \sqrt{\frac{V_k}{\lambda k^2}} \propto \frac{1}{k^2}$$

- Can combine 2 exact properties in the Gaskell form. Write  $E_V$  in terms structure factor making “random phase approximation.” (RPA).

$$2\rho u_k = -\frac{1}{S_k} + \sqrt{\frac{1}{S_k^2} + \frac{V_k}{\lambda k^2}} \quad S_k = \text{ideal structure factor}$$

- Optimization can hardly improve this form for the e-gas in either 2 or 3 dimensions. **RPA works better for trial function than for the energy.**
- NEED EWALD SUMS because potential trial function is long range, it also decays as  $1/r$ , but it is not a simple power.

$$\lim_{r \rightarrow \infty} u(r) = \begin{cases} r^{-1} & 3D \\ r^{-1/2} & 2D \\ \log(r) & 1D \end{cases}$$

## Long range properties

- Give rise to dielectric properties
- Energy is insensitive to  $u_k$  at small  $k$
- Those modes converge  $t \sim 1/k^2$

# Spline Jastrow factor

- For the HEG, the most general Jastrow factor has the form:

$$u(\vec{r}) = u_{sr}(r) + \sum_{\vec{k}} u_k e^{i\vec{k}\vec{r}}$$

$$u_{sr}(r) = 0 \quad \text{for } r > L/2$$

- $u(r)$  must be continuous, with a continuous derivative.
- We can impose the cusp condition at  $r=0$ , and BC at  $r=L/2$ .
- It is a smooth function: represent it as piecewise cubic polynomial in the region  $0 < r < L/2$ .
- $M$  “Knots” at  $b_n$ . Total number of unknowns is  $2M-1$
- Also  $u_k$   $k$ -space Jastrows. Do we use RPA values?

# Generalized Feynman-Kacs formula

gives relation between trial function and exact wavefunction!

average “population” starting from a single point  $R_0$  after a imaginary time “t”:

$$P(R_0; t) = \int dR \frac{\psi(R)}{\psi(R_0)} \langle R | e^{-t(H-E_T)} | R_0 \rangle = \left\langle \left\langle e^{-\int_0^t dt E_L(t)} \right\rangle \right\rangle_{|\psi\rangle}$$

expand the density matrix in terms of exact eigenstates

$$P(R_0; t) = \int dR \frac{\psi(R)}{\psi(R_0)} \sum_{\alpha} \phi_{\alpha}^*(R) \phi_{\alpha}(R_0) e^{-t(E_{\alpha}-E_T)}$$

$$\lim_{t \rightarrow \infty} P(R_0; t) = \frac{\phi_0(R_0)}{\psi(R_0)} \langle \psi \phi_0 \rangle$$

$$\frac{\phi_0(R_0)}{\psi(R_0)} \sim e^{-\int_0^t dt \langle \langle E_L(t) \rangle \rangle_{|\psi\rangle}}$$

# Wavefunctions beyond Jastrow

- Use method of residuals construct a sequence of increasingly better trial wave functions. Justify from the Importance sampled DMC.
- Zeroth order is Hartree-Fock wavefunction
- First order is Slater-Jastrow pair wavefunction (RPA for electrons gives an analytic formula)
- Second order is **3-body backflow** wavefunction
- Three-body form is like a squared force. It is a bosonic term that does not change the nodes.

$$\phi_{n+1}(R) \approx \phi_n(R) e^{-\tau \langle \phi_n^{-1} H \phi_n \rangle}$$

smoothing

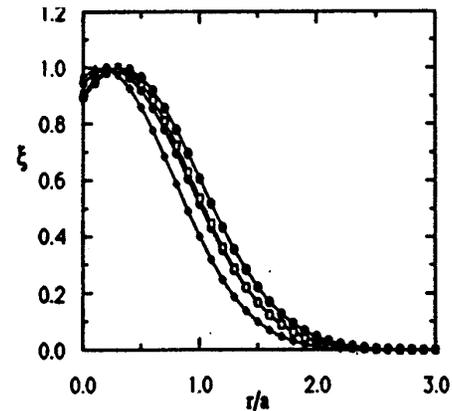
$$\phi_0 = e^{i \sum_j \mathbf{k}_j \cdot \mathbf{r}_j}$$

$$E_0 = V(R)$$

$$\phi_1 = \phi_0 e^{-U(R)}$$

$$E_1 = U(R) - [\nabla W(R)]^2 + i \sum_j \mathbf{k}_j \cdot (\mathbf{r}_j - \nabla_j Y(R))$$

$$\exp\left\{ \sum_i \left[ \sum_j \xi_{ij}(r_{ij}) (\mathbf{r}_i - \mathbf{r}_j) \right]^2 \right\}$$



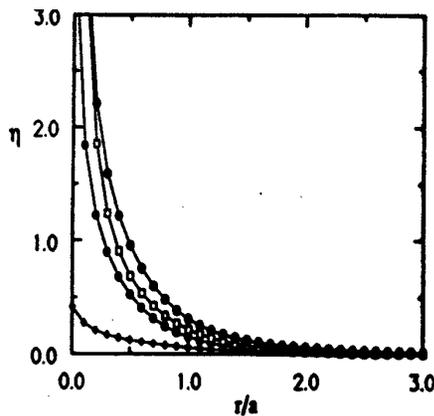
# Backflow wave function

- Backflow means change the coordinates to quasi- coordinates.
- Leads to a much improved energy and to improvement in nodal surfaces. Couples nodal surfaces together.

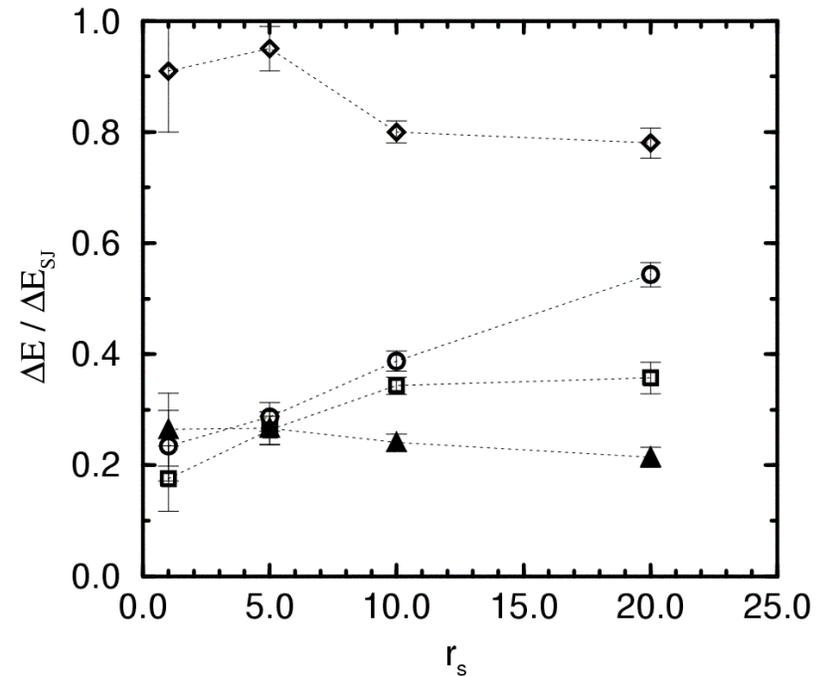
$$\text{Det}\{e^{i\mathbf{k}_i \mathbf{r}_j}\} \Rightarrow \text{Det}\{e^{i\mathbf{k}_i \mathbf{x}_j}\}$$

$$\mathbf{x}_i = \mathbf{r}_i + \sum_j \eta_{ij}(r_{ij})(\mathbf{r}_i - \mathbf{r}_j)$$

*Kwon PRB 58, 6800 (1998).*



## 3DEG

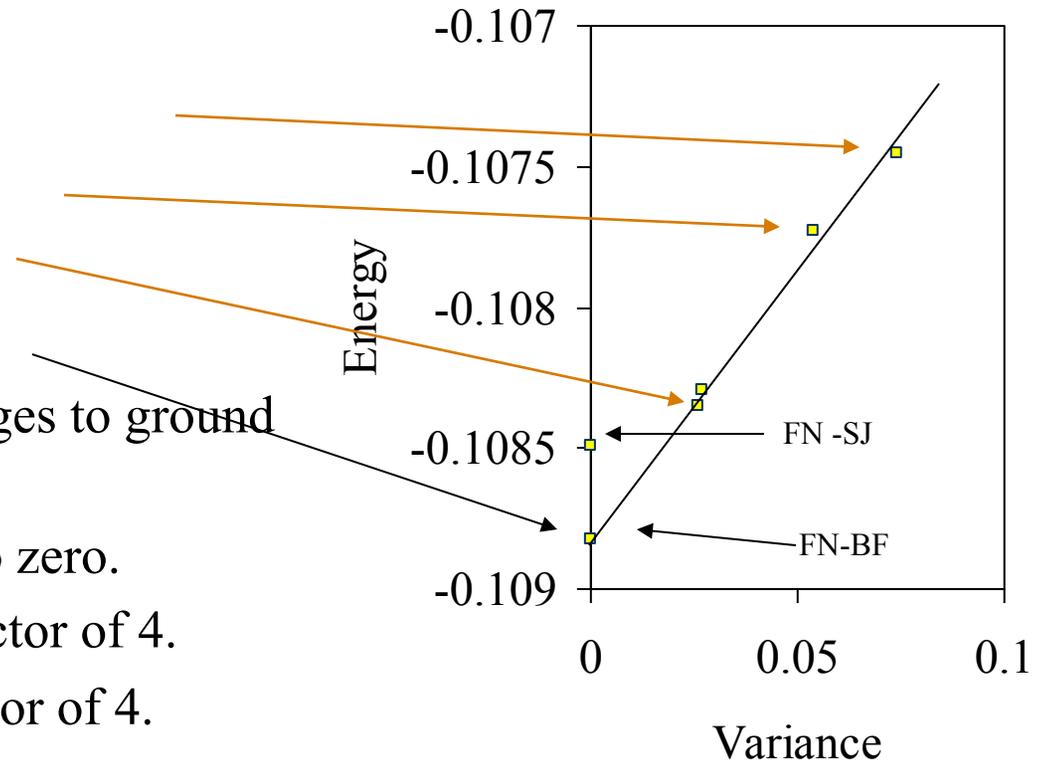


# Dependence of energy on wavefunction

3d Electron fluid at a density  $r_s=10$

*Kwon, Ceperley, Martin, Phys. Rev. B58,6800, 1998*

- Wavefunctions
  - Slater-Jastrow (SJ)
  - three-body (3)
  - backflow (BF)
  - fixed-node (FN)
- Energy  $\langle f | H | f \rangle$  converges to ground state
- Variance  $\langle f | [H-E]^2 | f \rangle$  to zero.
- Using 3B-BF gains a factor of 4.
- Using DMC gains a factor of 4.

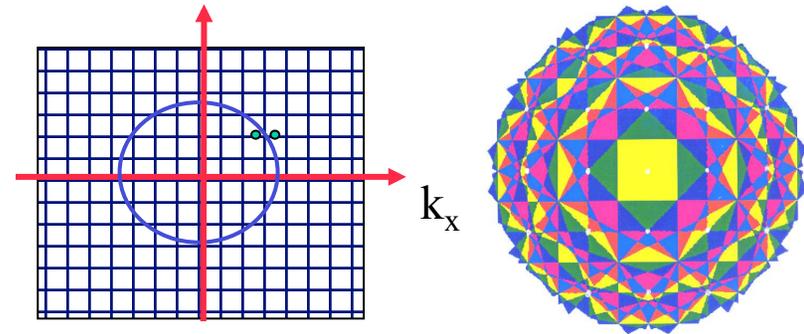


# Twist averaged boundary conditions

$$\varphi = e^{ikr}$$

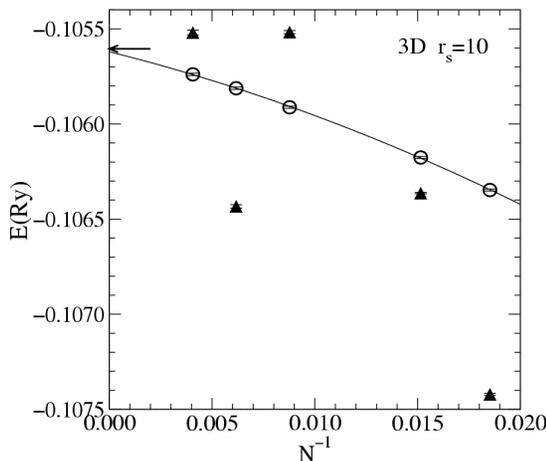
$$kL = 2\pi n + \theta$$

- In periodic boundary conditions ( $\Gamma$  point), the wavefunction is periodic  $\rightarrow$  **Large finite size effects for metals because of shell effects.**
- Fermi liquid theory can be used to correct the properties.
- In twist averaged BC we use an arbitrary phase as  $r \rightarrow r+L$
- If one integrates over all phases the momentum distribution changes from a lattice of k-vectors to a fermi sea.
- Smaller finite size effects

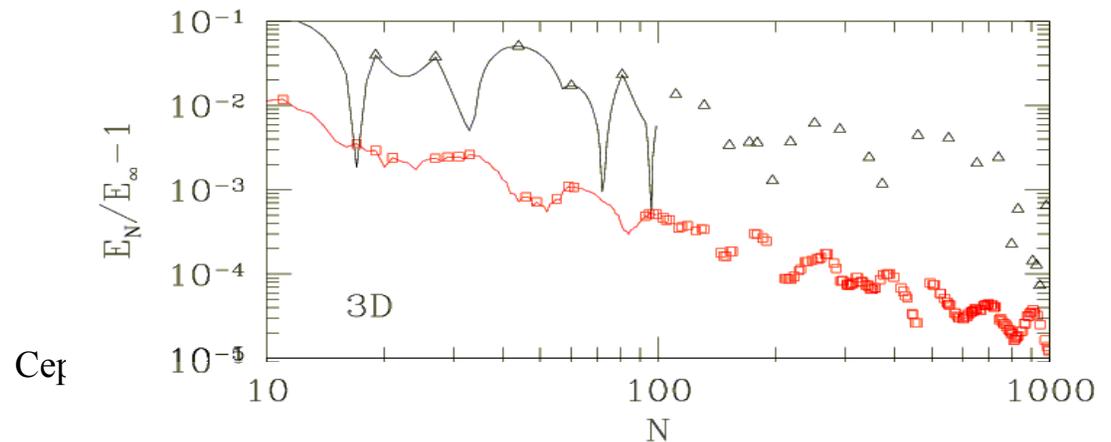


$$\Psi(x + L) = e^{i\theta}\Psi(x)$$

$$\bar{A} = \frac{1}{(2\pi)^3} \int_{-\pi}^{\pi} d^3\theta \langle \Psi_{\theta} A \Psi_{\theta} \rangle$$



PBC  
TABC



Ce $\uparrow$

# Twist averaged MC

- Make twist vector dynamical by changing during the random walk.

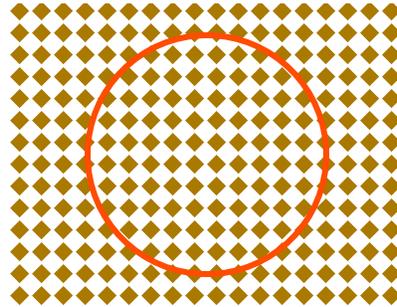
$$-\pi < \theta_i \leq \pi \quad i=(1,2,3)$$

- Within GCE, change the number of electrons
- Within TA-VMC
  - Initialize twist vector.
  - Run usual VMC (with warmup)
  - Resample twist angle within cube
  - (iterate)
- Or do in parallel.

# Grand Canonical Ensemble QMC

- GCE at T=0K: choose N such that  $E(N) - \mu N$  is minimized.
- According to Fermi liquid theory, interacting states are related to non-interacting states and described by  $\mathbf{k}$ .
- Instead of N, we input the fermi wavevector(s)  $\mathbf{k}_F$ . Choose all states with  $k < k_F$  (assuming spherical symmetry)
- N will depend on the twist angle = number of points inside a randomly placed sphere.

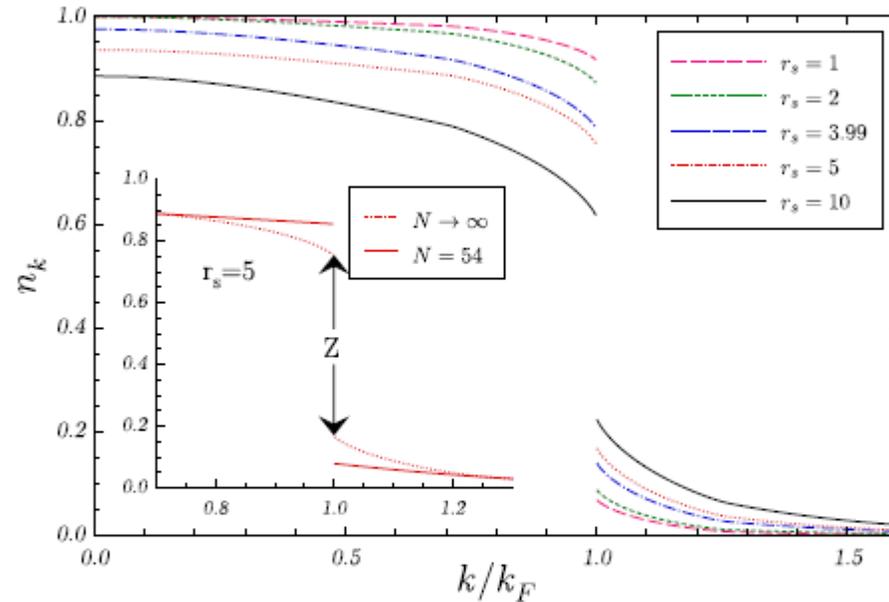
$$\vec{k}_n = \frac{2\pi}{L} \vec{n} + \frac{\vec{\theta}}{L}$$
$$k_n \leq k_F$$



- After we average over twist we get a sphere of filled states.
- **Is there a problem with Ewald sums as the number of electrons varies?**  
No! average density is exactly that of the background. We only work with averaged quantities.

# Single particle size effects

- Exact single particle properties with TA within HF
- Implies momentum distribution is a continuous curve with a sharp feature at  $k_F$ .
- With PBC only 5 k points for  $k < k_F$



- Holzmann et al. PRL 107,110402 (2011)
- No size effect within single particle theory!
- Kinetic energy will have much smaller size effects.

$$T = \int d^3k \frac{\hbar^2}{2m} k^2 n(k)$$

Ceperley VMC & DMC

# Potential energy

- Write potential as integral over structure function:

$$V = \int d^3k \frac{4\pi}{k^2} S(k) \quad S(k) = \langle \rho_{-k} \rho_k \rangle = 1 + (N-1) \langle e^{i(r_1 - r_2)k} \rangle$$

- Error comes from 2 effects.

- Approximating integral by sum
- Finite size effects in  $S(k)$  at a given  $k$ .

$$S_{HF}(k) = 1 - \frac{2}{N} \sum_{q, q'} \delta_{q - q' + k}$$

- Within HF we get exact  $S(k)$  with TABC.

- Discretization errors come only from non-analytic points of  $S(k)$ .

- the absence of the  $k=0$  term in sum. We can put it in by hand since we know the limit  $S(k)$  at small  $k$  (plasmon regime)

- Remaining size effects are smaller, coming from the non-analytic behavior of  $S(k)$  at  $2k_F$ .

$$S(k) = \frac{k^2}{2m\omega_p} \Rightarrow \Delta E = \frac{\omega_p}{N}$$

# Brief History of Ferromagnetism in electron gas

What is polarization state of fermi liquid at low density?

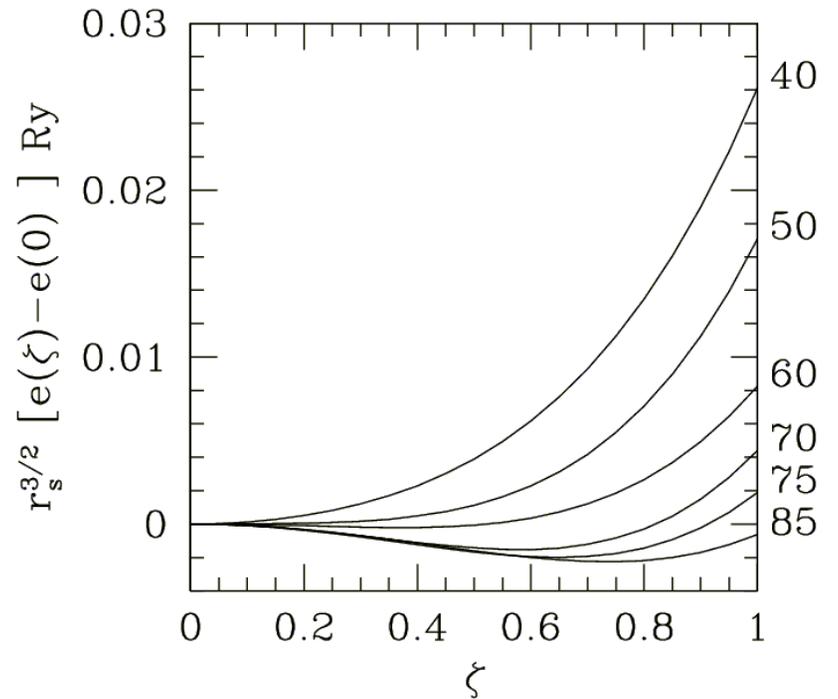
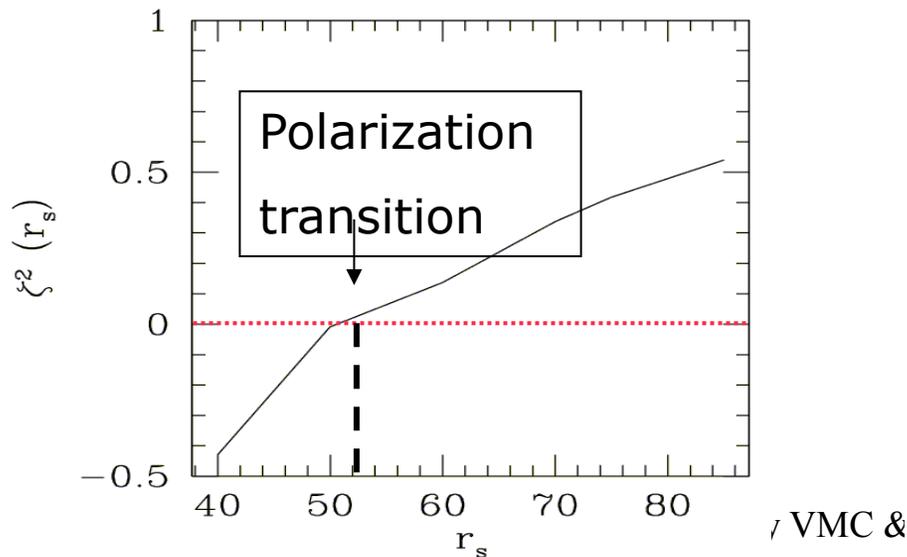
$$\zeta = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}}$$

- Bloch 1929 got polarization from exchange interaction:
  - $r_s > 5.4$  3D
  - $r_s > 2.0$  2D
- Stoner 1939: include electron screening: contact interaction
- Herring 1960
- Ceperley-Alder 1980  $r_s > 20$  is partially polarized
- **Young-Fisk experiment on doped  $\text{CaB}_6$  1999  $r_s \sim 25$ .**
- Ortiz-Balone 1999 : ferromagnetism of e gas at  $r_s > 20$ .
- Zong et al Redo QMC with backflow nodes and TABC.

# Polarization of 3DEG

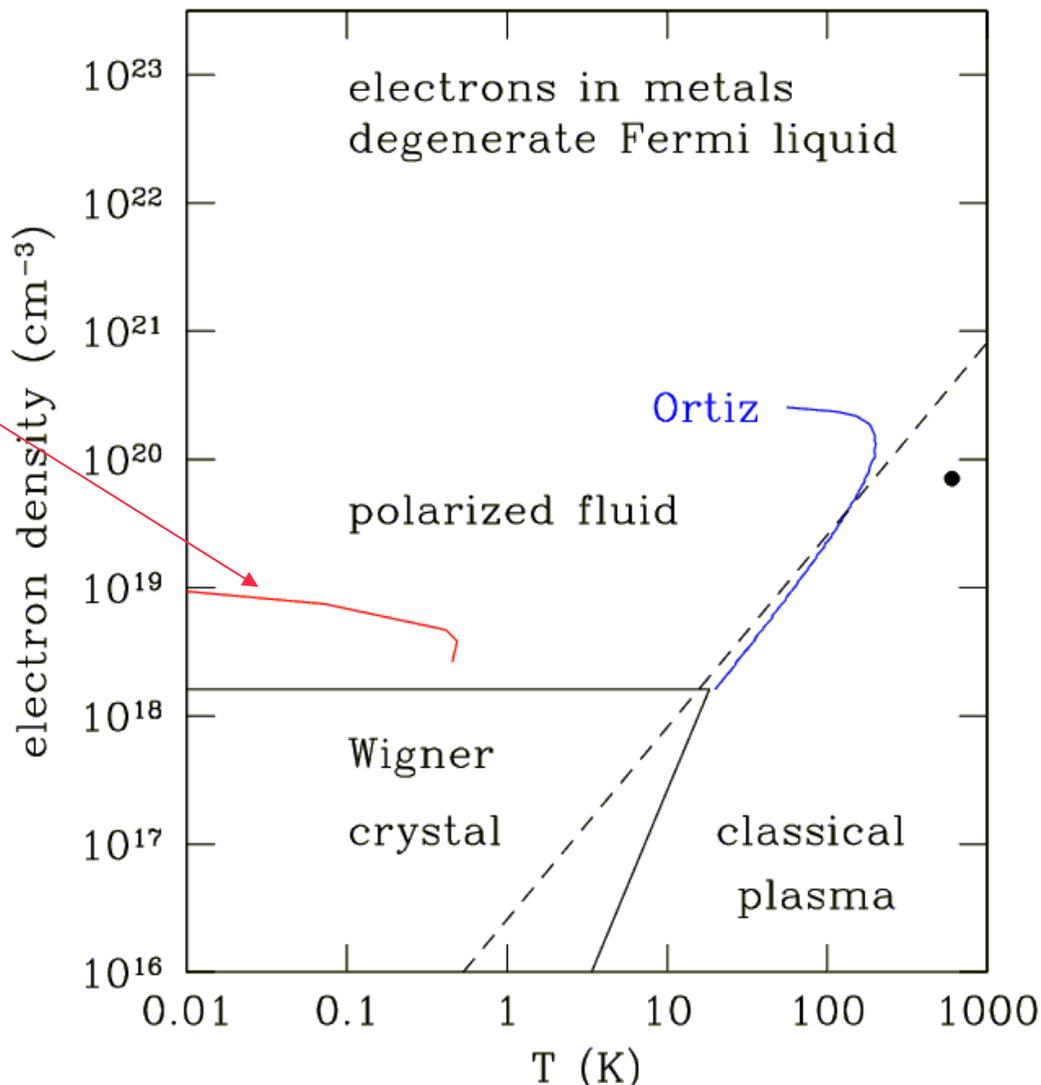
- We see second order partially polarized transition at  $r_s=52$
- Is the Stoner model (replace interaction with a contact potential) appropriate? Screening kills long range interaction.
- Wigner Crystal at  $r_s=105$

- Twist averaging makes calculation possible--much smaller size effects.
- Jastrow wavefunctions favor the ferromagnetic phase.
- Backflow 3-body wavefunctions more paramagnetic

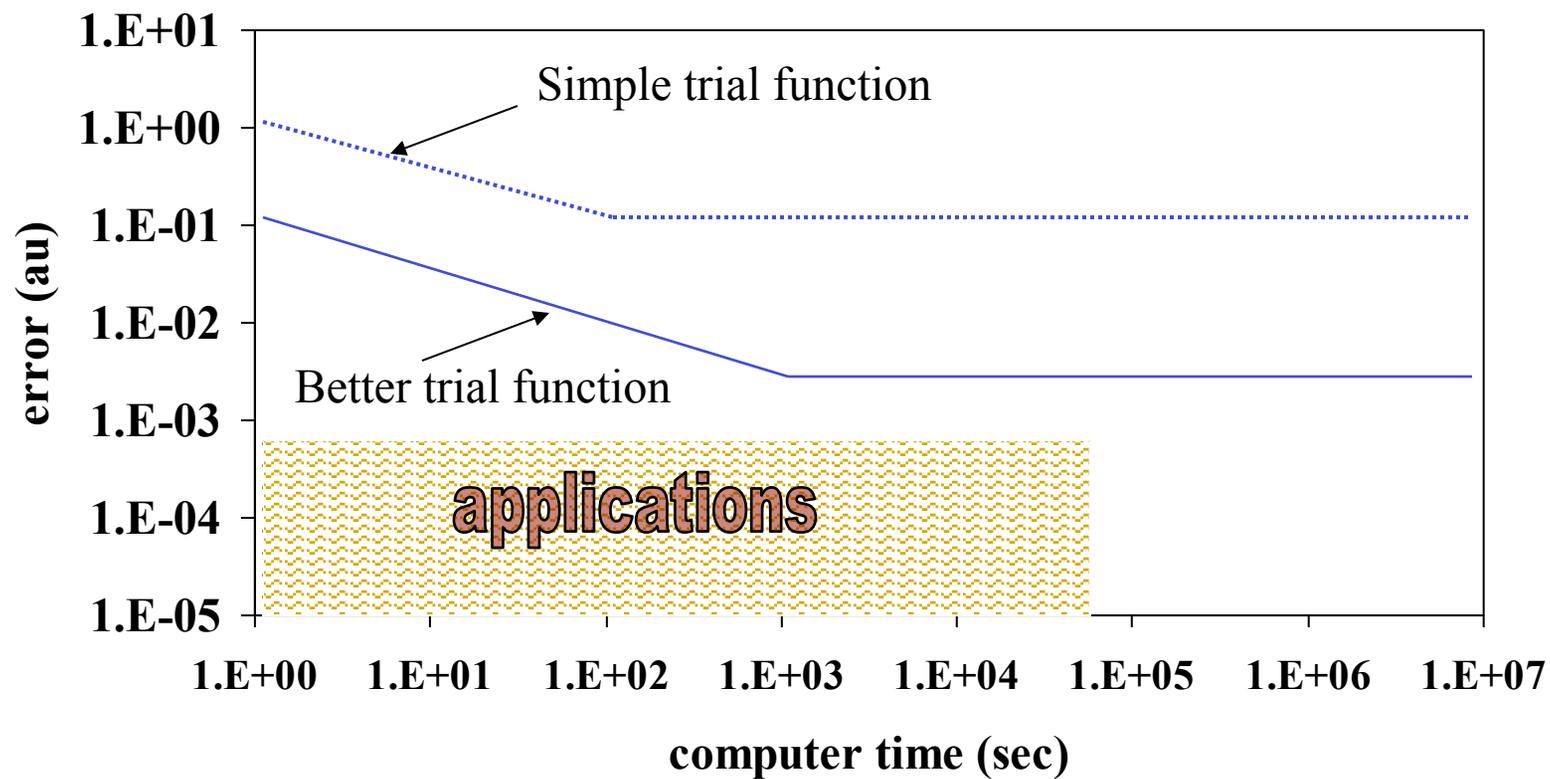


# Phase Diagram

- Partially polarized phase at low density.
- But at lower energy and density than before.
- As accuracy gets higher, polarized phase shrinks
- Real systems have different units.



# Summary of Variational (VMC)



# Summary and problems with variational methods

- Powerful method since you can use any trial function
- Scaling (computational effort vs. size) is almost classical
- Learn directly about what works in wavefunctions
- No sign problem
- Optimization is time consuming
- Energy is insensitive to order parameter
- Non-energetic properties are less accurate.  $O(1)$  vs.  $O(2)$  for energy.
- Difficult to find out how accurate results are.
- Favors simple states over more complicated states, e.g.
  - Solid over liquid
  - Polarized over unpolarized

What goes into the trial wave function comes out! “GIGO”

We need a more automatic method! Projector Monte Carlo

# Projector Monte Carlo

- Originally suggested by Fermi and implemented in 1950 by Donsker and Kac for H atom.
- Practical methods and application developed by Kalos:

PHYSICAL REVIEW A

VOLUME 9, NUMBER 5

MAY 1974

## Helium at zero temperature with hard-sphere and other forces

M. H. Kalos\*

*Courant Institute of Mathematical Sciences, New York University, New York, New York 10012*

D. Levesque and L. Verlet

*Laboratoire de Physique Théorique et Hautes Energies, Orsay, France* †

(Received 22 August 1973)

Various theoretical and numerical problems relating to heliumlike systems in their ground states are treated. New developments in the numerical solution of the Schrödinger equation permit the solution of 256-body systems with hard-sphere forces. Using periodic boundary conditions, fluid and crystal states can be described; results for the energy and radial-distribution functions are given. A new method of correcting for low-lying phonon excitations

# Diffusion Monte Carlo

- How do we analyze this operator?

$$\psi(R, t) = e^{-(H-E_T)t} \psi(R, 0)$$

- Expand into exact eigenstates of H.

$$H\phi_\alpha = E_\alpha\phi_\alpha$$

$$\psi(R, 0) = \sum_\alpha \phi_\alpha(R) \langle \phi_\alpha | \psi(0) \rangle$$

- Then the evolution is simple in this basis.

$$\psi(R, t) = \sum_\alpha \phi_\alpha(R) e^{-t(E_\alpha - E_T)} \langle \phi_\alpha | \psi(0) \rangle$$

- Long time limit is lowest energy state that overlaps with the initial state, usually the ground state.

$$\lim_{t \rightarrow \infty} \psi(R, t) = \phi_0(R) e^{-t(E_0 - E_T)} \langle \phi_0 | \psi(0) \rangle$$

$$E_0 \approx E_T \Rightarrow \textit{normalization fixed}$$

- How to carry out on the computer?

# Monte Carlo process

- Now consider the variable “t” as a continuous time (*it is really imaginary time*).
- Take derivative with respect to time to get evolution.
- This is a diffusion + branching process.
- Justify in terms of Trotter’s formula.

$$-\frac{\partial \psi(R,t)}{\partial t} = (H - E_T)\psi(R,t)$$

$$H = -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + V(R)$$

Requires interpretation of the wavefunction as a probability density.

$$\left\{ \begin{array}{l} -\frac{\partial \psi(R,t)}{\partial t} = -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 \psi(R,t) \\ -\frac{\partial \psi(R,t)}{\partial t} = (V(R) - E_T)\psi(R,t) \end{array} \right.$$

But is it? Only in the boson ground state. Otherwise there are nodes. Come back to later.

# Trotter's formula

- How do we find the solution of:  $\frac{d\hat{\rho}}{dt} = (A+B)\hat{\rho}$

- The operator solution is:  $\hat{\rho} = e^{(A+B)t}$

- Trotter's formula (1959):**  $\hat{\rho} = \lim_{n \rightarrow \infty} \left[ e^{\frac{t}{n}\hat{A}} e^{\frac{t}{n}\hat{B}} \right]^n$

- Assumes that A,B and A+B are reasonable operators.

$$\left\langle R_0 \left| \left[ e^{\frac{t}{n}\hat{A}} e^{\frac{t}{n}\hat{B}} \right]^n \right| R_n \right\rangle = \left\langle R_0 \left| e^{\frac{t}{n}\hat{A}} \right| R'_1 \right\rangle \left\langle R'_1 \left| e^{\frac{t}{n}\hat{B}} \right| R_1 \right\rangle \dots \left\langle R_{n-1} \left| e^{\frac{t}{n}\hat{A}} \right| R'_n \right\rangle \left\langle R'_n \left| e^{\frac{t}{n}\hat{B}} \right| R_n \right\rangle$$

- This means we just have to figure out what each operator does independently and then alternate their effect. This is rigorous in the limit as  $n \rightarrow \infty$ .
- In the DMC case A is diffusion operator, B is a branching operator.
- Just like “molecular dynamics”: at small time we evaluate each operator separately.

# Evaluation of kinetic density matrix

$$\langle r | e^{-\tau \hat{T}} | r' \rangle = \sum_{\alpha} \phi_{\alpha}^*(r) \phi_{\alpha}(r') e^{-\tau T_{\alpha}}$$

In PBC eigenfunctions of  $\hat{T} = \frac{1}{\sqrt{\Omega}} e^{-i\vec{k}\vec{r}}$

and eigenvalues are  $\lambda k^2$

$$\langle r | e^{-\tau \hat{T}} | r' \rangle = \sum_k \frac{1}{\Omega} e^{-i\vec{k}\vec{r}} e^{i\vec{k}\vec{r}'} e^{-\tau \lambda k^2}$$

convert to an integral

$$\langle r | e^{-\tau \hat{T}} | r' \rangle = \frac{1}{(2\pi)^3} \int d\vec{k} e^{i\vec{k}(\vec{r}' - \vec{r}) - \tau \lambda k^2} = (4\pi\lambda\tau)^{-3/2} e^{-(r-r')^2/4\lambda\tau}$$

**Danger:** makes assumption about boundaries and statistics.

This is a diffusion process.

# Putting this together

$$\hat{\rho} = e^{-\beta(\hat{T}+\hat{V})}$$

- n is number of time slices.
- $\tau$  is the “time-step”

$$\hat{\rho} = \lim_{n \rightarrow \infty} \left[ e^{-\tau \hat{T}} e^{-\tau \hat{V}} \right]^n$$

$$\tau = \beta / n$$

- V is “diagonal”

$$\langle r | e^{-\tau \hat{T}} | r' \rangle = (4\pi\lambda\tau)^{-3/2} e^{-(r-r')^2/4\lambda\tau}$$

$$\langle r | e^{-\tau \hat{V}} | r' \rangle = \delta(r - r') e^{-\tau V(r)}$$

$$\langle R_0 e^{-n\tau \hat{H}} R_n \rangle \sim \langle R_0 | e^{-\tau \hat{T}} | R_1 \rangle e^{-\tau V(R_1)} \dots \langle R_{n-1} | e^{-\tau \hat{T}} | R_n \rangle e^{-\tau V(R_n)}$$

- Error at finite n comes from commutator is roughly:

$$e^{-\frac{\tau^2}{2} [\hat{T}, \hat{V}]}$$

- Diffusion preserves normalization but potential does not!

# Basic DMC algorithm

- Construct an ensemble (population  $P(0)$ ) sampled from the trial wavefunction.  $\{R_1, R_2, \dots, R_P\}$
- Go through ensemble and diffuse each one (timestep  $\tau$ )

$$R'_k = R_k + \sqrt{2\lambda\tau}\zeta(t) \leftarrow \text{ndrn}$$

- number of copies =  $\frac{e^{-\tau(V(R)-E_T)} + u}{\text{floor function}}$   $\leftarrow \text{uprn}$
- Trial energy  $E_T$  adjusted to keep population fixed.

$$E_0 = \lim_{t \rightarrow \infty} \frac{\int dR H \phi(R, t)}{\int dR \phi(R, t)} \approx \langle V(R) \rangle_{\phi(\infty)}$$

- Problems:
  1. Branching is uncontrolled
  2. Population unstable
  3. What do we do about fermi statistics?

# Population Bias

- Having the right trial energy guarantees that population will on the average be stable, but fluctuations will always cause the population to either grow too large or too small.
- Various ways to control the population
- Suppose  $P_0$  is the desired population and  $P(t)$  is the current population. How much do we have to adjust  $E_T$  to make  $P(t+T)=P_0$ ?  $P(t+T) = e^{-T(-\delta E_T)} P(t) = P_0$

$$\delta E_T = \frac{\ln(P(t)/P_0)}{T}$$

- Feedback procedure:  $E_T = E_{T0} + \kappa \ln(P/P_0)$
- There will still be a (much smaller) bias in the energy caused by a limited population.

# Importance Sampling

- Why should we sample the wavefunction? The physically correct pdf is  $|\phi|^2$ .
- Importance sample (multiply) by trial wave function.

$$f(R,t) \equiv \psi_T(R)\phi(R,t) \quad \lim_{t \rightarrow \infty} f(R,t) \equiv \psi_T(R)\phi_0(R)$$

$$-\frac{\partial f(R,t)}{\partial t} = \psi_T(R)H[f(R,t)/\psi_T(R)] \quad \text{Commute } \Psi \text{ through } H$$

$$-\frac{\partial f(R,t)}{\partial t} = -\lambda \nabla^2 f - \lambda \nabla (2f \nabla \ln \psi_T(R)) + (\psi_T^{-1} H \psi_T) f(R,t)$$

**Evolution = diffusion + drift + branching**

- We have three terms in the evolution equation. Trotter's formula still applies.

- To the pure diffusion algorithm we have added a drift step that pushes the random walk in directions of increasing trial function:

$$R' = R + 2\lambda\tau\nabla \ln \psi_T(R)$$

- Branching is now controlled by the local energy

$$E_L(R) - E_T = \psi^{-1}(R) \hat{H} \psi(R) - E_T$$

- Because of zero variance principle, fluctuations are controlled.
- Cusp condition can limit infinities coming from singular potentials.
- We still determine  $E_T$  by keeping asymptotic population stable.

$$E_0 = \lim_{t \rightarrow \infty} \frac{\int dR \phi(R, t) H \psi_T(R)}{\int dR f(R, t)} \approx \langle E_\psi(R) \rangle_{f(\infty)}$$

- Must have accurate “time” evolution. Adding accept/reject step is a major improvement.

- Importance sampled Green's function:

$$G(R \rightarrow R') = \frac{\psi(R')}{\psi(R)} \langle R | e^{-\tau H} | R' \rangle$$

- Exact property of DMC Green's function

$$|\Psi(R)|^2 G(R \rightarrow R') = |\Psi(R')|^2 G(R' \rightarrow R)$$

- We enforce detailed balance to decrease time step errors.

$$A(s \rightarrow s') = \min \left[ 1, \frac{G(s' \rightarrow s) |\psi(s')|^2}{G(s \rightarrow s') |\psi(s)|^2} \right]$$

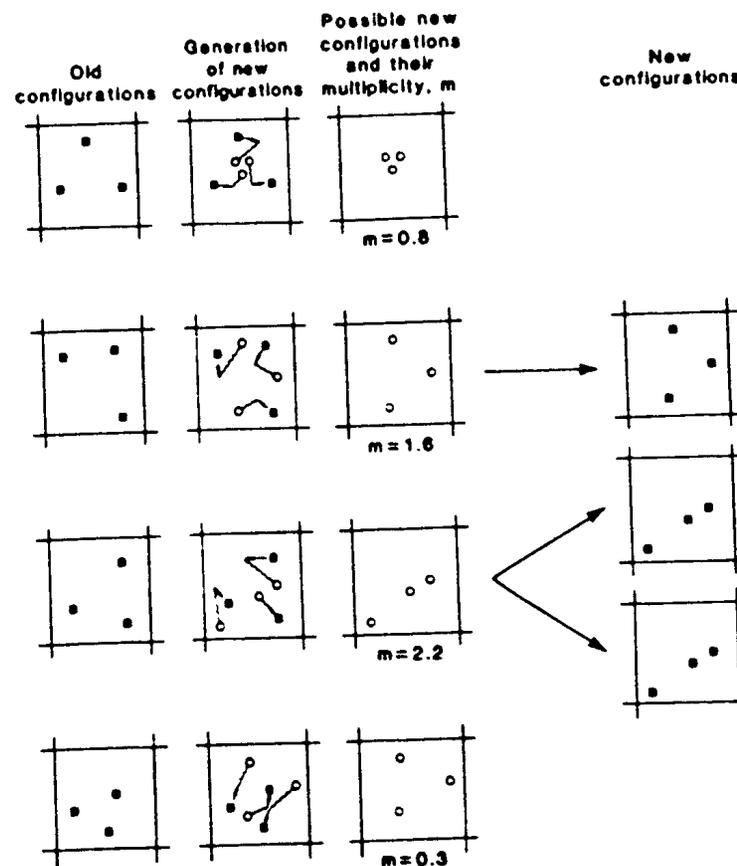
- VMC satisfies detailed balance.
- Typically we choose time step to have 99% acceptance ratio.
- Method gives exact result if either time step is zero or trial function is exact.

# Schematic of DMC

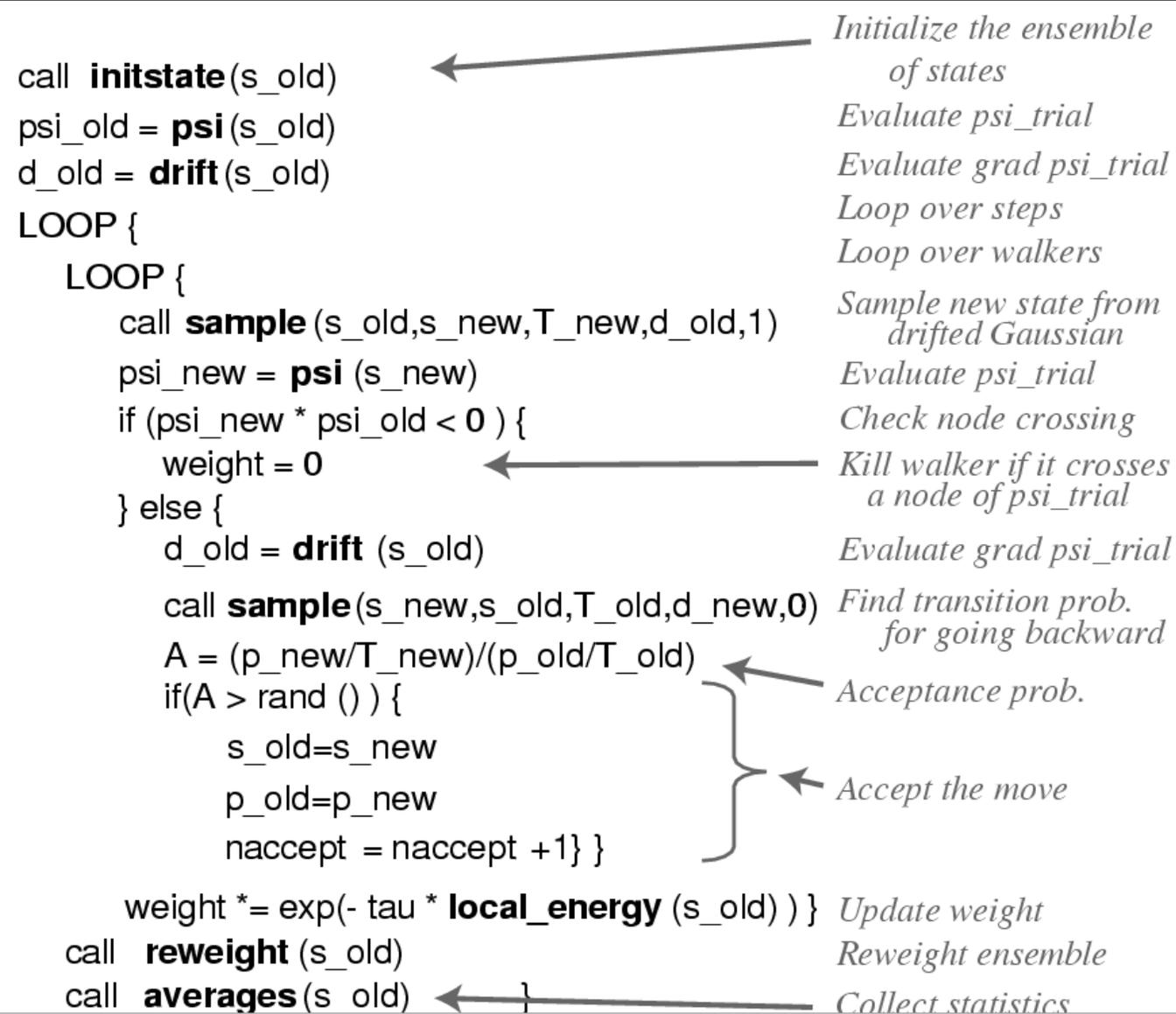
Ensemble evolves according to

- Diffusion
- Drift
- branching

**ensemble**



# DIFFUSION MONTE CARLO CODE



# Mixed estimators

- Problem is that PMC samples the wrong distribution.
- OK for the energy
- Linear extrapolation helps correct this systematic error

$$\langle A \rangle_M \equiv \frac{\int dR \psi^*(R) A \phi(R)}{\int dR \psi^*(R) \phi(R)}$$

$$\langle A \rangle_o \equiv \frac{\int dR \phi^*(R) A \phi(R)}{\int dR \phi^*(R) \phi(R)}$$

$$\langle A \rangle_V \equiv \frac{\int dR \psi^*(R) A \psi(R)}{\int dR \psi^*(R) \psi(R)}$$

- Other solutions:
  - Maximum overlap
  - Forward walking
  - Reptation/path integrals

$$\langle A \rangle_o ; 2\langle A \rangle_M - \langle A \rangle_V + O((\phi - \psi)^2)$$

$$\langle A \rangle_o ; \frac{\langle A \rangle_M^2}{\langle A \rangle_V} + O((\phi - \psi)^2) \text{ for the density}$$

$$\langle A \rangle_M = \langle A \rangle_V \Rightarrow \int dR (\phi - \psi)^2 \text{ minimized wrt } A$$

# Forward Walking

- Let's calculate the average population resulting from DMC starting from a single point  $R_0$  after a time 't'.

$$P(R_0; t) = \int dR \frac{\psi(R)}{\psi(R_0)} \left\langle R \left| e^{-t(H-E_T)} \right| R_0 \right\rangle$$

expand the density matrix in terms of exact eigenstates

$$P(R_0; t) = \int dR \frac{\psi(R)}{\psi(R_0)} \sum_{\alpha} \phi_{\alpha}(R) \phi_{\alpha}(R_0) e^{-t(H-E_T)}$$

$$\lim_{t \rightarrow \infty} P(R_0; t) = \frac{\phi_0(R_0)}{\psi(R_0)} \langle \psi \phi_0 \rangle$$

- We can estimate the correction to the mixed estimator by weighting with the number of descendants of a given configuration.

$$\langle A \rangle_0 = \lim_{t \rightarrow \infty} \frac{1}{M} \sum_i P(R_i; t) A(R_i)$$

- Problem: the fluctuations in the weights eventually diverge. Don't make 't' too large.

# Fusion sticking coefficient

*Phys. Rev. A* **31**, 1999 (1985).

- Consider the 3 body system ( $\mu$  d t)
- For the sticking coefficient, we need the exact wavefunction at the point where 2 nuclei are at the same position. (this is a singular point)  
 $\Psi(r_1 = r_2, r_3)$

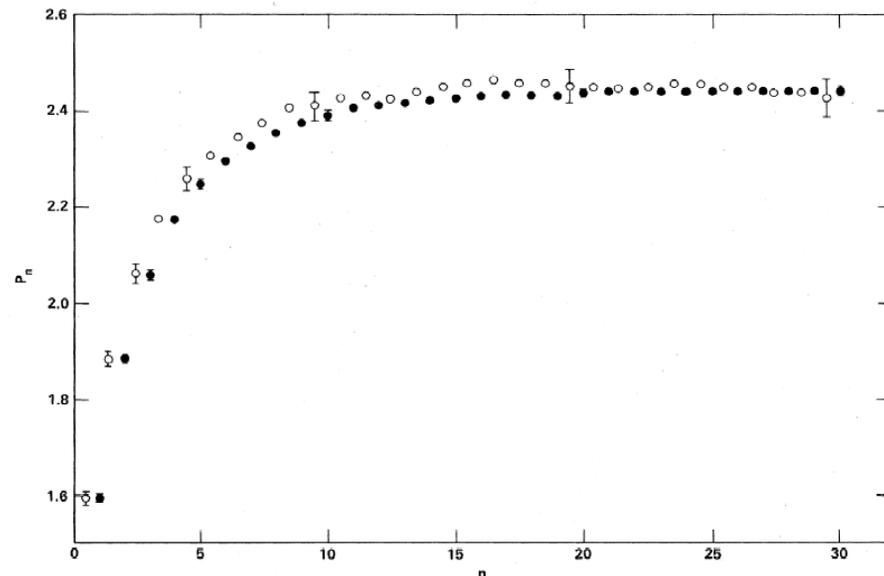
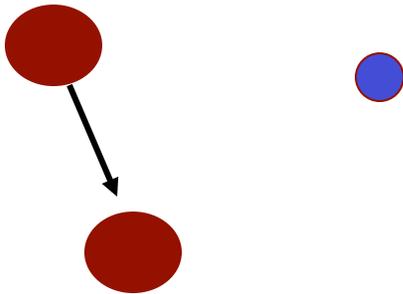
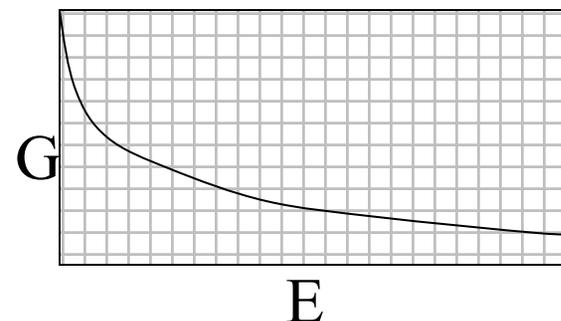


FIG. 1. The growth of the population vs the number of Monte Carlo generations using the population estimator (○) and the local energy estimator (●) at the triplet coalescence point (all three particles starting at the origin). The ○'s are shifted one-half generation to the left for clarity.

# Other projector functions can be used

$$G(E) = \begin{cases} e^{-\tau(E-E_T)} & \text{Diffusion MC} \\ [1 + \tau(E - E_T)]^{-1} & \text{Green's Function MC} \\ [1 - \tau(E - E_T)] & \text{Power MC} \end{cases}$$



$G(E_T) = 1 \Rightarrow$  ground state remains after many iterations

$$\tau = - \left. \frac{dG}{dE} \right|_0 = \text{time step}$$

for all 3 cases:  $\lim_{n \rightarrow \infty} G(E)^n = e^{-n\tau(E-E_T)}$

- Common effect on long-time (iteration) limit.
- 3<sup>rd</sup> choice generates a Krylov sequence. Only works for bounded spectra such as a lattice model.

# Green's Function Monte Carlo

*Kalos, Levesque, Verlet Phys. Rev. A9, 2178 (1974).*

- It is possible to make a zero time-step-error method
- Works with the integral formulation of DMC

$$G(R, R') = \left\langle R \left| \left[ 1 + \tau (H - E_T) \right]^{-1} \right| R' \right\rangle = \int_0^\infty \frac{d\beta}{\tau} e^{-\beta \left( \frac{1}{\tau} + H - E_T \right)}$$

- Sample time-step from Poisson distribution
- Express operator in a series expansion and sample the terms stochastically.

$$G(R, R') = H(R, R') + \int dR'' G(R, R'') K(R'', R')$$

- Recent Revival: “Continuous time Monte Carlo” for lattice models.

# Fermions?

- How can we do fermion simulations? The initial condition can be made real but not positive (for more than 1 electron in the same spin state)
- In *transient estimate* or *released-node* methods one carries along the sign as a weight and samples the modulus.

$$\phi(t) = e^{-(\hat{H}-E_T)t} \text{sign}(\phi(R,0)) |\phi(R,0)|$$

- Do not forbid crossing of the nodes, but carry along sign when walks cross.
- What's wrong with node release:
  - Because walks don't die at the nodes, the computational effort increases (bosonic noise)
  - The signal is in the cancellation which dominates

Monte Carlo can add but not subtract

# Transient Estimate Approach

$$\Psi(\beta) = e^{-\frac{\beta}{2}H} \Psi$$

$$Z(\beta) = \langle \Psi(\beta) \Psi(\beta) \rangle = \langle \Psi e^{-\beta H} \Psi \rangle = \int dR_0 \dots dR_p \Psi(R_0) \langle R_0 e^{-\tau H} R_1 \rangle \dots \langle R_{p-1} e^{-\tau H} R_p \rangle \Psi(R_p)$$

$$E(\beta) = \frac{\langle \Psi(\beta) H \Psi(\beta) \rangle}{\langle \Psi(\beta) \Psi(\beta) \rangle} = \langle E_L(R_0) \rangle_\beta \quad \tau = \frac{\beta}{p}$$

- $\psi(\beta)$  converges to the exact ground state
- $E$  is an upper bound converging to the exact answer monotonically

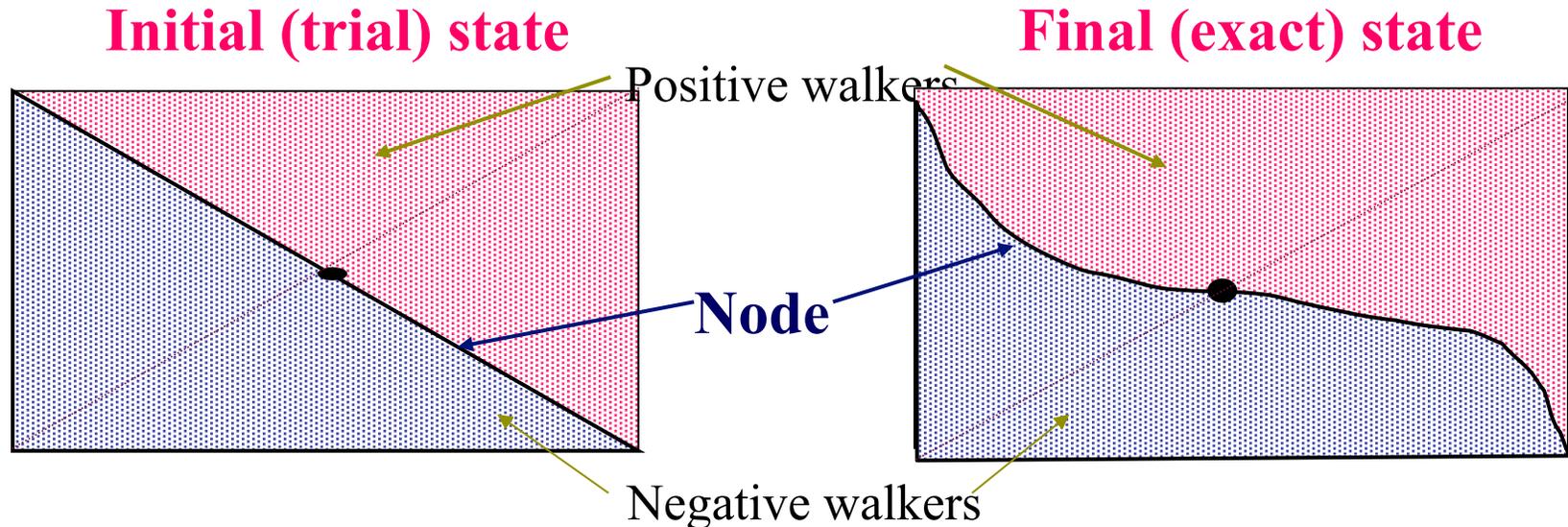
$$Z(\beta) = \int dR_0 \dots dR_p |\Psi(R_0)| \langle R_0 e^{-\tau H} R_1 \rangle \dots \langle R_{p-1} e^{-\tau H} R_p \rangle |\Psi(R_p)| \sigma(R_0) \sigma(R_p)$$

$$\frac{Z_{\text{fermi}}}{Z_{\text{bose}}} = \langle \sigma(R_0) \sigma(R_p) \rangle$$

## Model fermion problem: Particle in a box

Symmetric potential:  $V(\mathbf{r}) = V(-\mathbf{r})$

Antisymmetric state:  $f(\mathbf{r}) = -f(-\mathbf{r})$

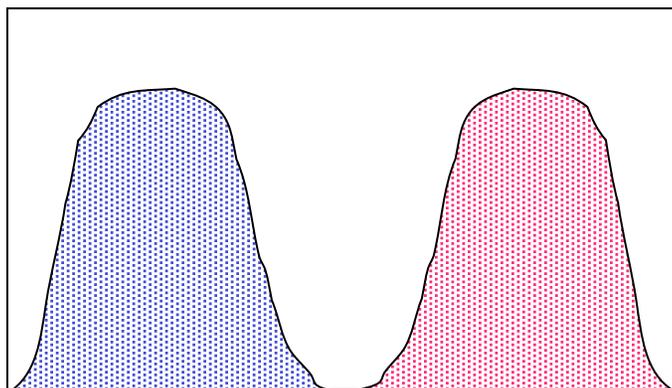


Sign of walkers fixed by initial position. They are allowed to diffuse freely.  
 $f(r)$  = number of positive-negative walkers. Node is dynamically established by diffusion process. (cancellation of positive and negative walkers.)

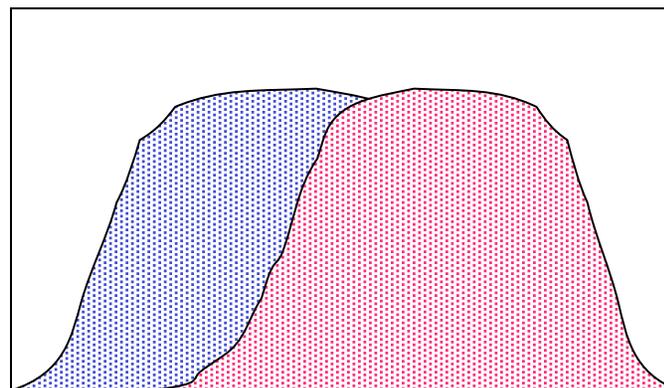
$$\langle E(t) \rangle = \frac{\sum \sigma(0)\sigma(t)E(t)}{\sum \sigma(0)\sigma(t)}$$

# Scaling in Released-Node

**Initial distribution**



**Later distribution**

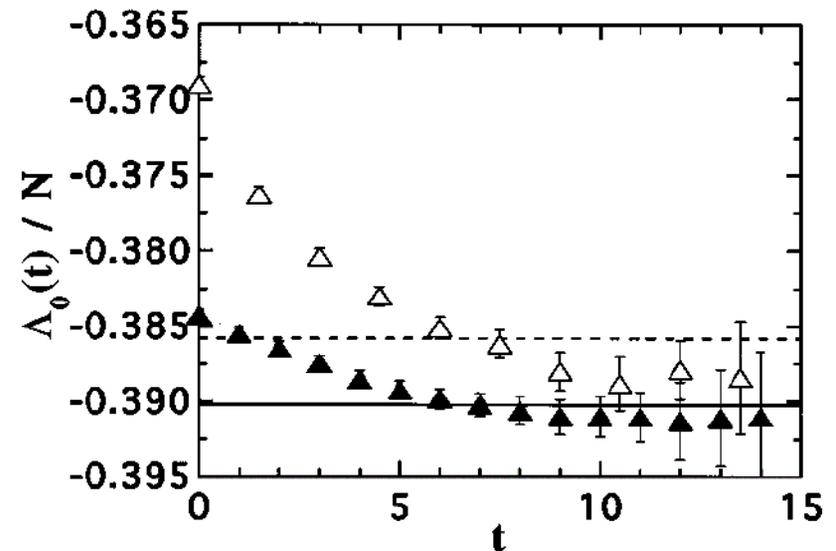


- At any point, positive and negative walkers will tend to cancel so the signal is drown out by the fluctuations.
- Signal/noise ratio is :  $e^{-t[E_F - E_B]}$  **t**=projection time  
 **$E_F$**  and  **$E_B$**  are Fermion, Bose energy (proportional to **N**)
- Converges but at a slower rate. Higher accuracy, larger **t**.
- For general excited states:  
**Exponential complexity!**  $\text{CPUtime} \propto \mathcal{E}^{-2(1+\frac{E_F}{E_g})} \approx \mathcal{E}^{-2N\frac{e_F}{E_g}}$
- Not a fermion problem but an excited state problem.
- Cancellation is difficult in high dimensions.

# Exact fermion calculations

- Possible for the electron gas for up to 60 electrons.
- 2DEG at  $r_s=1$   $N=26$
- Transient estimate calculation with SJ and BF-3B trial functions.

$$\left\langle \Psi_T \left| e^{-tH} \right| \Psi_T \right\rangle$$



# General statement of the “fermion problem”

- Given a system with **N** fermions and a known Hamiltonian and a property **O**. (usually the energy).
- How much time **T** will it take to estimate **O** to an accuracy  $\epsilon$ ? How does **T** scale with **N** and  $\epsilon$ ?
- If you can map the quantum system onto an equivalent problem in classical statistical mechanics then:

$$T \propto N^a \epsilon^{-2} \quad \text{With } 0 < a < 4$$

This would be a “solved” quantum problem!

- All approximations must be controlled!
- Algebraic scaling in N!

e.g. properties of Boltzmann or Bose systems in equilibrium.

# Fixed-node method

- Initial distribution is a pdf. It comes from a VMC simulation.  $f(R,0) = |\psi_T(R)|^2$
- Drift term pushes walks away from the nodes.  $\phi(R) = 0$  when  $\psi_T(R) = 0$ .
- Impose the condition:
- This is the fixed-node BC
- Will give an upper bound to the exact energy, the best upper bound consistent with the FNBC.  $E_{FN} \geq E_0$   
 $E_{FN} = E_0$  if  $\phi_0(R)\psi(R) \geq 0$  all  $R$
- $f(R,t)$  has a discontinuous gradient at the nodal location.
- Accurate method because Bose correlations are done exactly.
- Scales well, like the VMC method, as  $N^3$ . Classical complexity.
- Can be generalized from the continuum to lattice finite temperature, magnetic fields, ...
- One needs trial functions with accurate nodes.

# Proof of fixed-node theorem

- Suppose we solve S.E. in a subvolume  $V$  determined by the nodes of an antisymmetric trial function.

$$\hat{H}\phi_{FN} = E_{FN}\phi_{FN} \quad \text{inside } V$$

Extend the solution to all space with the permutation operator.

$$\hat{\phi}_{FN}(R) \equiv \frac{1}{N!} \sum_P (-1)^P \phi_{FN}(PR)$$

Inside a given sub-volume only permutations of a given sign ( $\pm$ ) contribute.

Hence the extended solution is non-zero.

Evaluate the variational energy the extended trial function.

$$E_0 \leq \frac{\sum_{PP'} (-1)^{P+P'} \int dR \phi_{FN}^*(PR) \hat{H} \phi_{FN}(P'R)}{\sum_{PP'} (-1)^{P+P'} \int dR \phi_{FN}^*(PR) \phi_{FN}(P'R)} = E_{FN} \leq E_{VMC}$$

Edges of volumes do not contribute to the integral since the solution vanishes

## Nodal Properties

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

- If  $f(\mathbf{R})$  is real, nodes are  $f(\mathbf{R})=0$  where  $\mathbf{R}$  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:** there are typically only 2 different volumes (+ and -) except in 1D. (but only demonstrated for free particles.)

# Nodal Picture: 2d slice thru 322d space

- Free electron
- Other electrons
- Nodes pass thru their positions
- Divides space into 2 regions
- Wavelength given by interparticle spacing

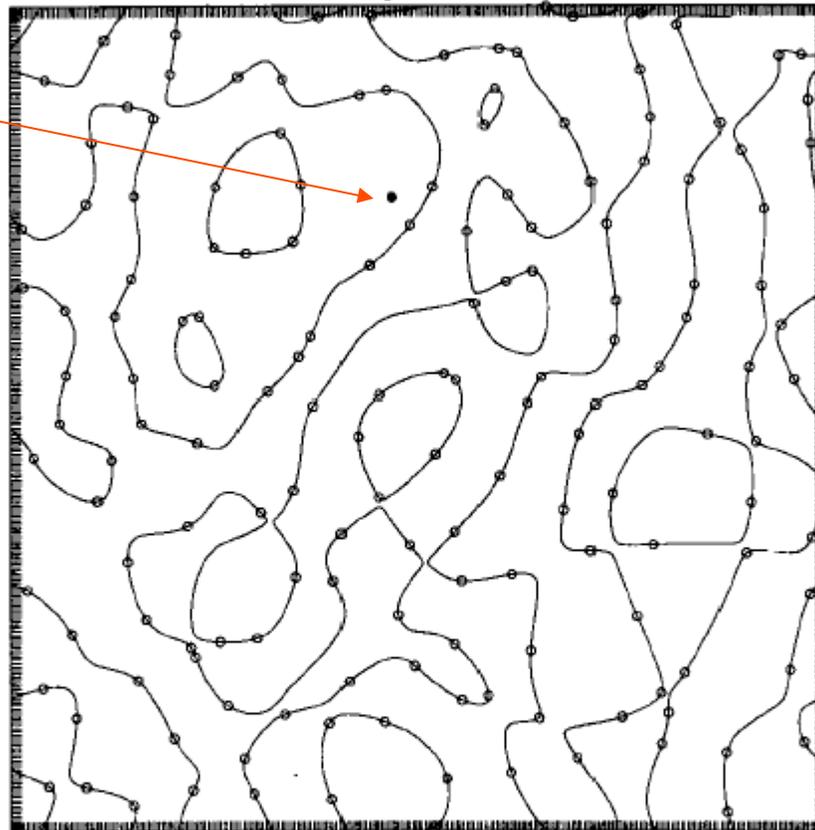


Fig. 3. A 2D cross section of the ground-state wave function of 161 free (polarized) fermions in a periodic square. All 161 particle positions were sampled using variational Monte Carlo from  $\phi(R)^2$ . The filled circle indicates the original position of the first particle. The other 160 particles are fixed at positions indicated by the open circles, and nodes of the wave function as a function of the position of the first particle are plotted. The resolution of the contouring program is approximately half of the fine scale shown around the border of the plot.

# Fixed-Phase method

- Generalize the FN method to complex trial functions:  $\Psi(R) = e^{-U(R)}$
- Since the Hamiltonian is Hermitian, the variational energy is real:

$$E_V = \frac{\int dR e^{-2\Re U(R)} \left[ V(R) + \lambda \nabla^2 U(R) - \lambda [\Re \nabla U(R)]^2 + \lambda [\Im \nabla U(R)]^2 \right]}{\int dR e^{-2\Re U(R)}}$$

- We see only one place where the energy depends on the phase of the wavefunction.
- If we **fix the phase**, then we add this term to the potential energy. In a magnetic field we get also the vector potential.

$$\text{effective potential} = V(R) + \sum_i \lambda_i \left[ A(r_i) + \Im \nabla_i U(R) \right]^2$$

- We can now do VMC or DMC and get upper bounds as before.
- The imaginary part of the local energy will not be zero unless the right phase is used.
- Used for twisted boundary conditions, magnetic fields, vortices, phonons, spin states, ...

# Problem with core electrons

- Bad scaling in both VMC and DMC
- In VMC, energy fluctuations from core dominate the calculation
- In DMC, time step will be controlled by core dynamics
- Solution is to eliminate core states by a pseudopotential

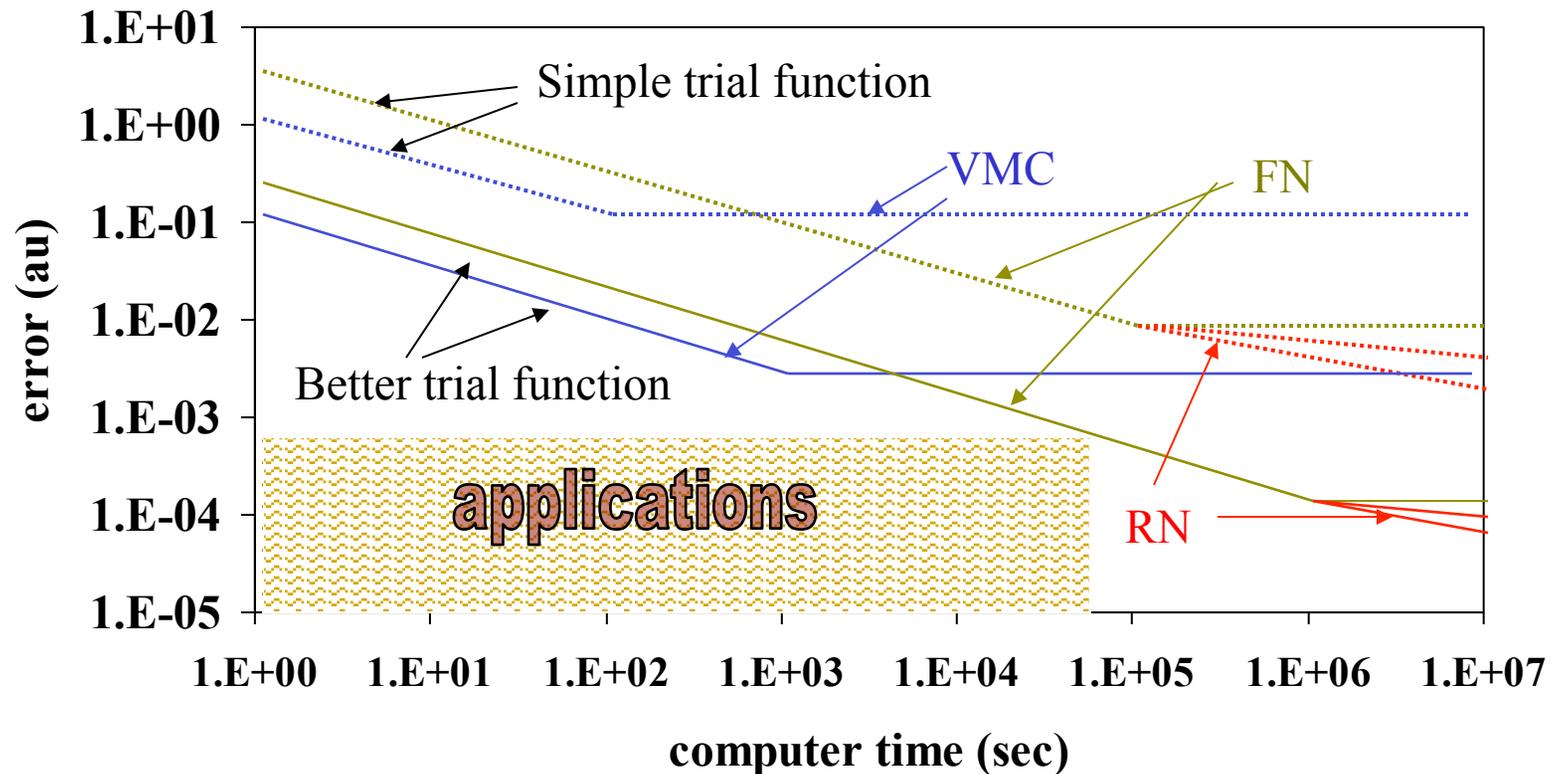
- Conventional solution: semi-local form

$$\langle r | \hat{v}_{e-core} | r' \rangle = v_{local}(r) \delta(r - r') + \sum_l v_l(r) P_l(\cos(r \cdot r'))$$

- Ensures that valence electrons go into well defined valence states with the wavefunction and energy for each angular momentum state prescribed.
- PP is non-local: OK for VMC. Leads to an extra MC integral. But DMC uses a locality approximation and good trial functions. **Extra approximation.**

# Summary of $T=0$ methods:

Variational(VMC), **Fixed-node(FN)**, **Released-node(RN)**



# Problems with projector methods

- Fixed-node is a super-variational method
- DMC dynamics is determined by Hamiltonian
- Zero-variance principle allows very accurate calculation of ground state energy if trial function is good.
- Projector methods need a trial wavefunction for accuracy. They are essentially methods that perturb from the trial function to the exact function. (Note: if you don't use a trial function, you are perturbing from the ideal gas)
- Difficulty calculating properties other than energy. We must use “extrapolated estimators” or “forward walking”.

$$f(R, \infty) = \phi_0(R)\psi_T(R) \text{ not } |\phi_0(R)|^2$$

- Bad for phase transitions and finite temperature, complex systems.
- Path Integral MC (reptation MC) solves some of these problems.