

The Variational Monte Carlo Method

The theorem + restrictions

Upper and lower bounds: variance

How to do the variation.

McMillan's calculation on liquid ^4He

Fermion VMC

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.

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Ground State of Liquid He⁴

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The properties of the ground state of liquid He⁴ 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 -0.78×10^{-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
- Can be generalized to finite temperature by using "trial" density matrix instead of "trial" wavefunction.

The “Variational Theorem”

Assume $\psi(R; a)$ is a trial function where R are the quantum degrees of freedom (positions, spin) “ a ” are “variational “parameters.

$$E_V(a) = \frac{\langle \psi(a) H \psi(a) \rangle}{\langle \psi(a) \psi(a) \rangle} \geq E_0 = \text{exact ground state energy}$$

$$\langle \psi(a) H \psi(a) \rangle \equiv \int dR \psi^*(R; a) H \psi(R; a)$$

$$E_V(a) = E_0 \Leftrightarrow \psi(R; a) = \phi_0(R)$$

$$E_L(R; a) \equiv \frac{1}{\psi(R; a)} H \psi(R; a) = \text{"local energy" of trial function}$$

$$E_V(a) = \left\langle \left\langle E_L(R; a) \right\rangle \right\rangle_{\psi^2} \quad \text{where} \quad \left\langle \left\langle O \right\rangle \right\rangle_{\psi^2} \equiv \frac{\langle \psi(a) O \psi(a) \rangle}{\langle \psi(a) \psi(a) \rangle}$$

$$\sigma^2(a) \equiv \frac{\langle \psi(a) (H - E_V(a))^2 \psi(a) \rangle}{\langle \psi(a) \psi(a) \rangle} = \left\langle \left\langle (E_L(R; a) - E_V(a))^2 \right\rangle \right\rangle_{\psi^2} = \text{variance of the trial function}$$

$$\frac{dE_V(a)}{da} = 2 \left\langle \left\langle \frac{d \ln \psi(R; a)}{da} (E_L(R; a) - E_V(a)) \right\rangle \right\rangle = 0$$

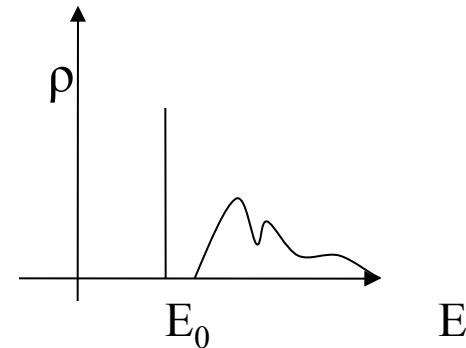
Conditions: matrix elements exist, symmetries and boundary conditions are correct.

Expand trial function in terms of the exact eigenfunctions:

$$\psi(R; a) = \sum_{\alpha} \phi_{\alpha}(R) \langle \alpha | \psi(a) \rangle$$

$$E_V(a) = \frac{\sum_{\alpha} E_{\alpha} \left| \langle \alpha | \psi(a) \rangle \right|^2}{\sum_{\alpha} \left| \langle \alpha | \psi(a) \rangle \right|^2} = \int dE \rho_a(E) E$$

$$\rho_a(E) = \sum_{\alpha} \delta(E - E_{\alpha}) \frac{\left| \langle \alpha | \psi(a) \rangle \right|^2}{\left\langle |\psi(a)|^2 \right\rangle} \geq 0 \quad \int_{-\infty}^{\infty} dE \rho(E) = 1$$



$$\sigma^2(a) = \int dE \rho_a(E) (E - E_V(a))^2$$

$$O(a) \equiv \rho_a(E_0) = 1 - \int_{E_0+}^{\infty} dE \rho_a(E) = \frac{\left| \langle 0 | \psi(a) \rangle \right|^2}{\left\langle |\psi(a)|^2 \right\rangle} = \text{overlap with ground state}$$

Energy and variance are second order in (1-overlap).

Other properties are first order.

Temple lower bound:

$$\boxed{E_v - \frac{\sigma^2}{E_1 - E_0} \leq E_0 \leq E_v}$$

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.

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

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

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

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

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

- Better wavefunction, lower variance!
“Zero variance” principle. (non-classical)

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.

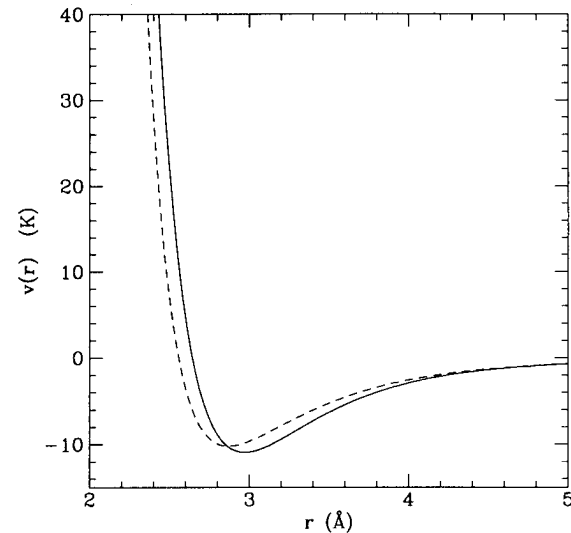


FIG. 1. The semiempirical pair potential between two helium atoms: solid line, Aziz *et al.* (1992); dashed line, Lennard-Jones 6-12 potential with $\epsilon = 10.22$ K and $\sigma = 2.556$ Å.

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

Trial function for helium

- 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:

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

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

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

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

$$U(r) = \alpha r^{-m}$$

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

Gives a cusp condition on u .

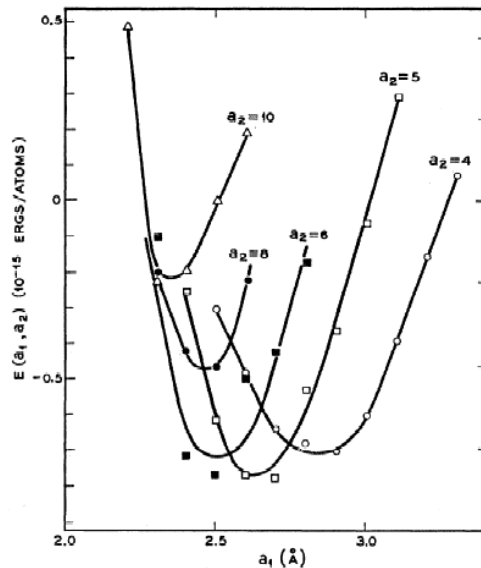
$$-e^2 r^{-1} = 2\lambda \nabla^2 u(r) = 2\lambda \left(u'' + \frac{D-1}{r} u' \right)$$

$$u'(0) = -\frac{e^2}{2\lambda(D-1)}$$

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

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

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 .

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

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

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

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

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

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

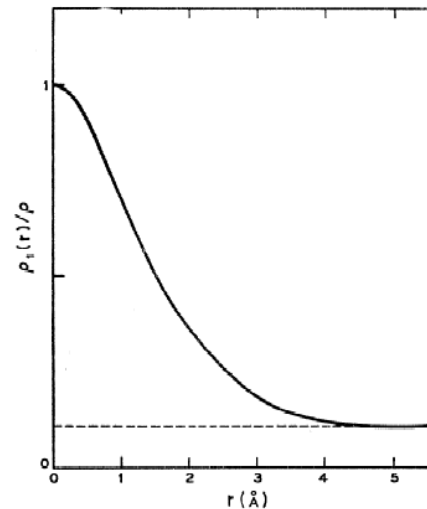
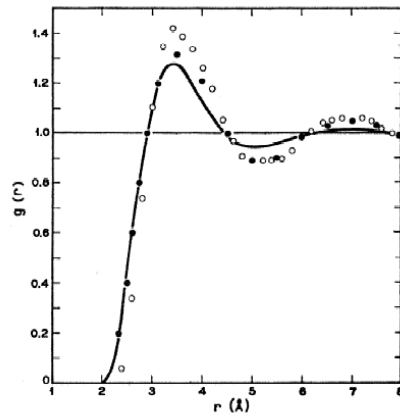


FIG. 7. The single-particle density matrix as a function of separation. The dashed curve indicates the asymptotic limit for large r , $\rho_1(r) \sim \rho_0 = 0.11\rho$.

- 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 $\sim 10\%$

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

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

Ceperley Variational Methods

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 $O(N^2)$.

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

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

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

Slater-Jastrow trial function.

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

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

The electron gas

D. M. Ceperley, Phys. Rev. B 18, 3126 (1978)

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

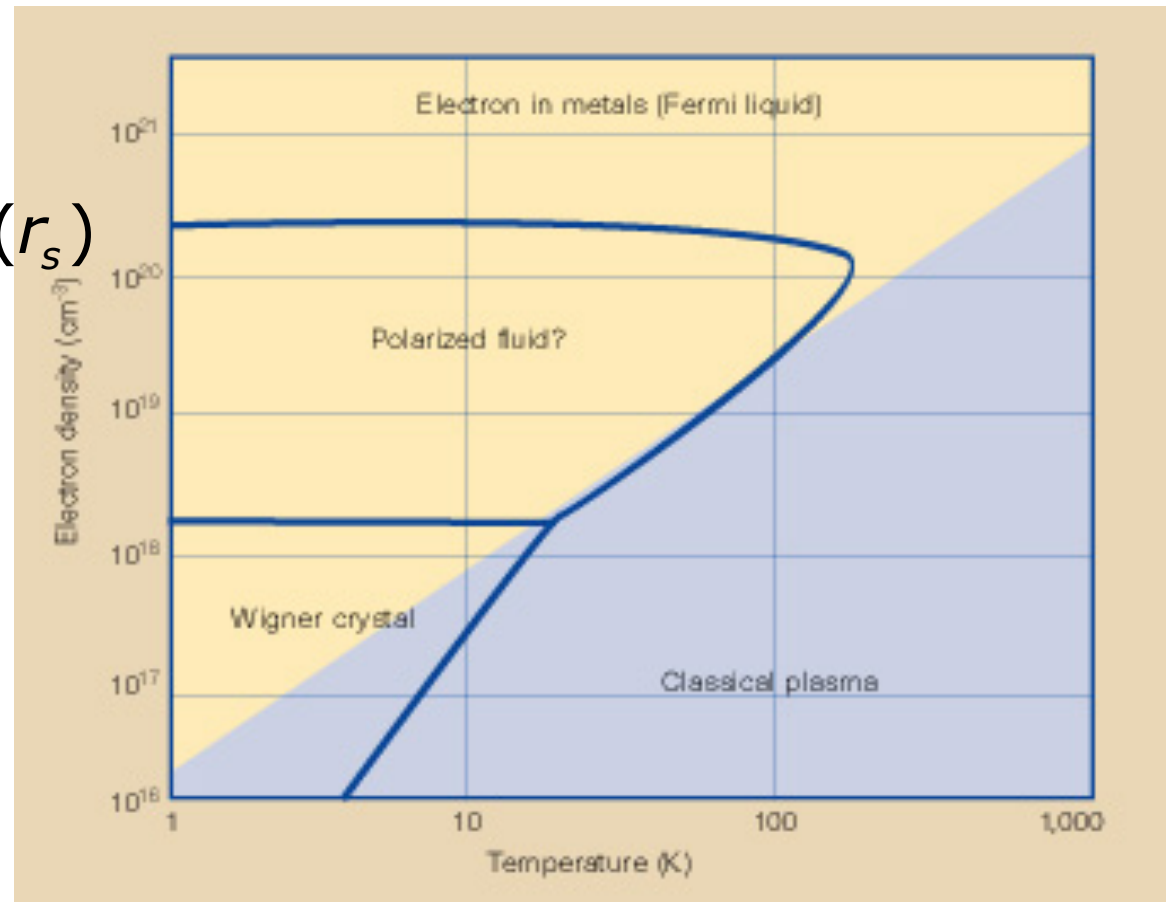
$$r_s = a / a_0$$

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

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

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

$\log(r_s)$



$\Gamma < r_s$ classical OCP

$\Gamma = 175$ classical melting

$\log(\Gamma)$

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
- 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).

$$2\rho u_k = -\frac{1}{S_k} + \sqrt{\frac{1}{S_k^2} + \frac{V_k}{\lambda k^2}}$$

- 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 important

- Gives rise to dielectric properties
- Energy is insensitive to u_k

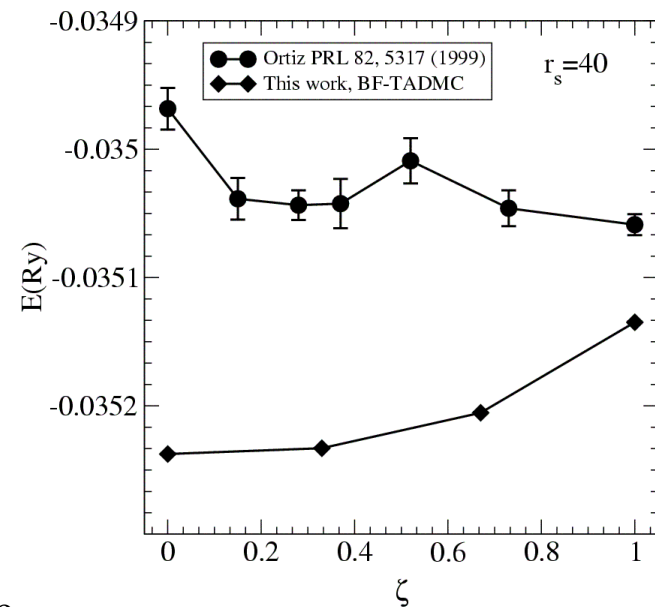
Comparison of Trial functions

- What do we choose for the trial function in VMC and DMC?
- Slater-Jastrow (SJ) with plane wave orbitals :

$$\Psi_2(R) = \text{Det}\{\phi_k(r_j)\} e^{-\sum_{i<j} u_{ij}(r_{ij})}$$

- For higher accuracy we need to go beyond this form.
- Include backflow-three body.

Example of incorrect physics within SJ



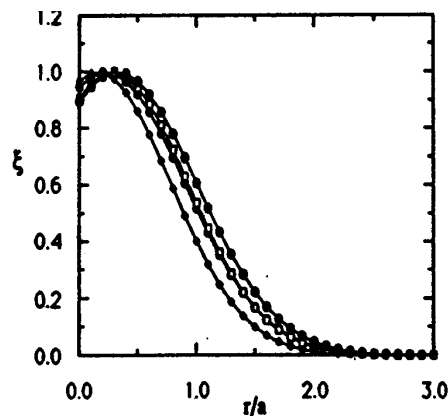
Ceperley Variational Metho

Wavefunctions beyond Jastrow

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

↑
smoothing

- Use method of residuals construct a sequence of increasingly better trial wave functions.
- 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.



$$\Psi_2(R) \exp \left\{ \sum_i \left[\sum_j \xi_{ij}(r_{ij}) (\mathbf{r}_i - \mathbf{r}_j) \right]^2 \right\}$$

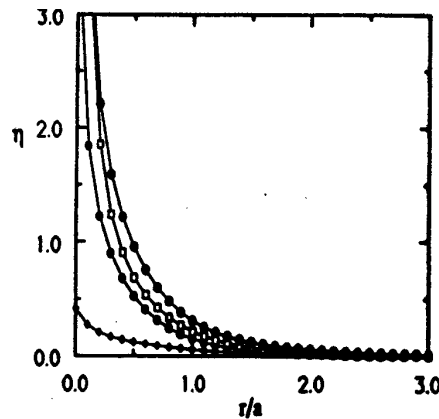
Backflow- 3B Wave functions

- Backflow means change the coordinates to quasi- coordinates.
- Leads to a much improved energy

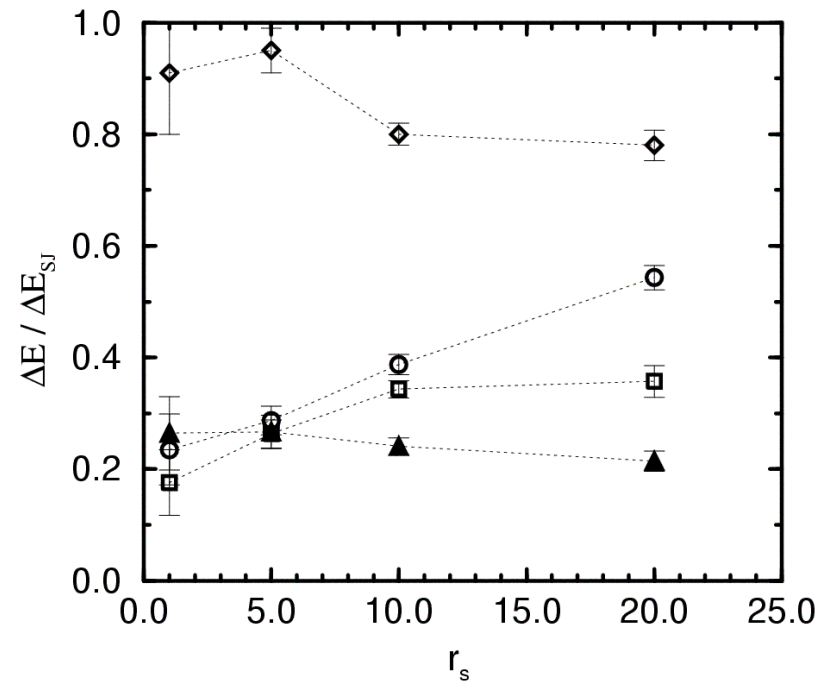
$$\text{Det}\{e^{i\mathbf{k}_i\mathbf{r}_j}\} \Rightarrow \text{Det}\{e^{i\mathbf{k}_i\mathbf{x}_j}\}$$

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

Kwon PRB 58, 6800 (1998).



3DEG



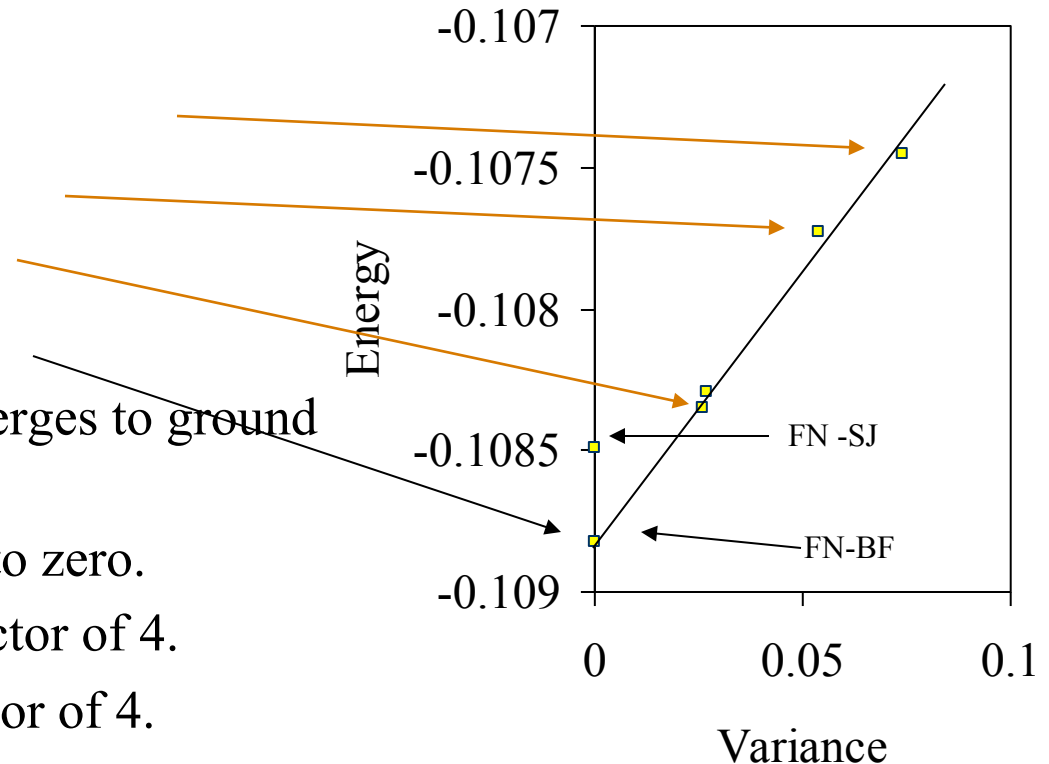
Ceperley Variational methods

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 $\langle \psi | H | \psi \rangle$ converges to ground state
- Variance $\langle \psi | [H-E]^2 | \psi \rangle$ to zero.
- Using 3B-BF gains a factor of 4.
- Using DMC gains a factor of 4.



Wigner Crystal Trial Function

- Jastrow trial function does not “freeze” at appropriate density.
- Solution is to break spatial symmetry “by hand.”
- Introduce a bcc lattice
 $\{Z_i\}$
- bcc has the lowest Madelung energy, but others may have lower zero point energy.
- Introduce localized one-body terms (Wannier functions).
- Non-symmetric but provides a very good description of a quantum crystal.
- More complicated trial functions and methods are also possible.

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

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

$$\phi(r) = e^{-Cr^2}$$

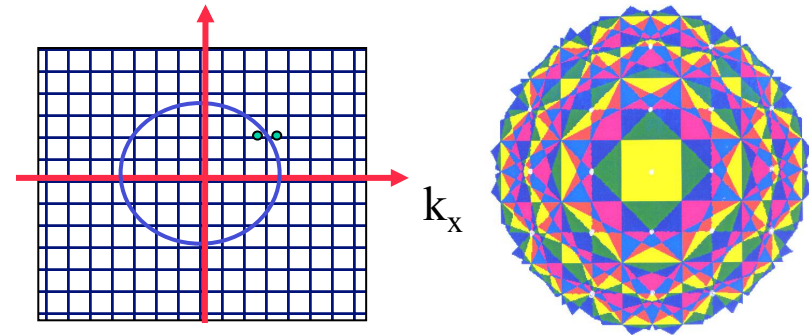
“C” is a variational parameter to be optimized.

Twist averaged boundary conditions

- In periodic boundary conditions (Γ 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 θ 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

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

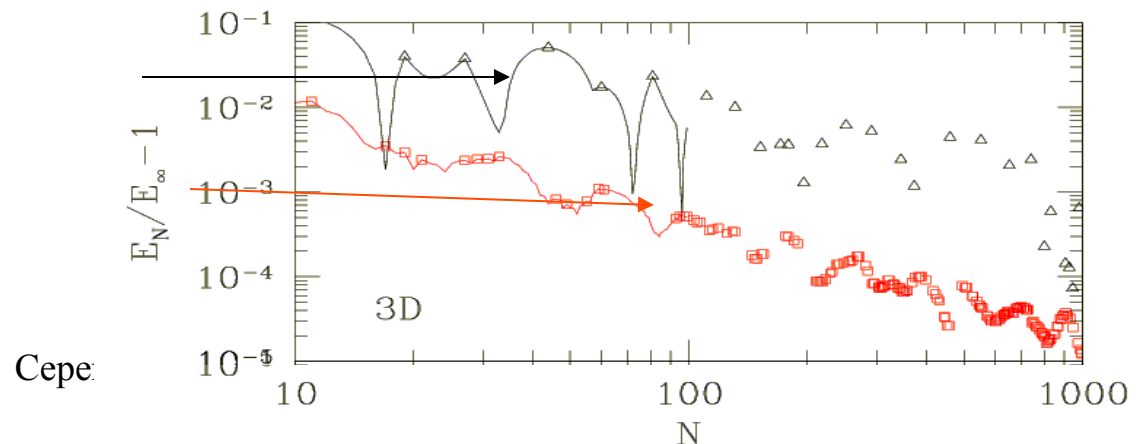
$$kL = 2\pi n + \theta$$



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

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

Error with PBC
Error with TABC



Twist averaged MC

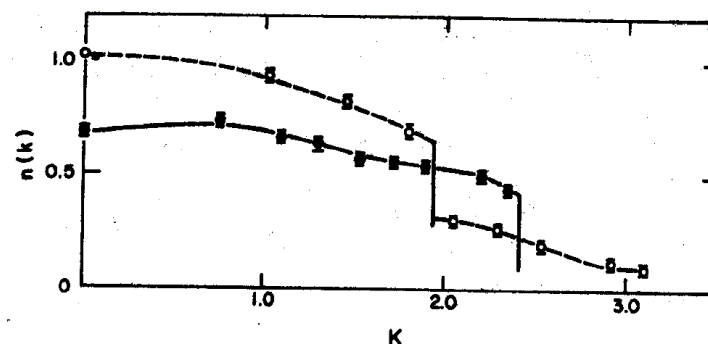
- Make twist vector dynamical by changing during the random walk.

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

- 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.

Momentum Distribution

- 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.



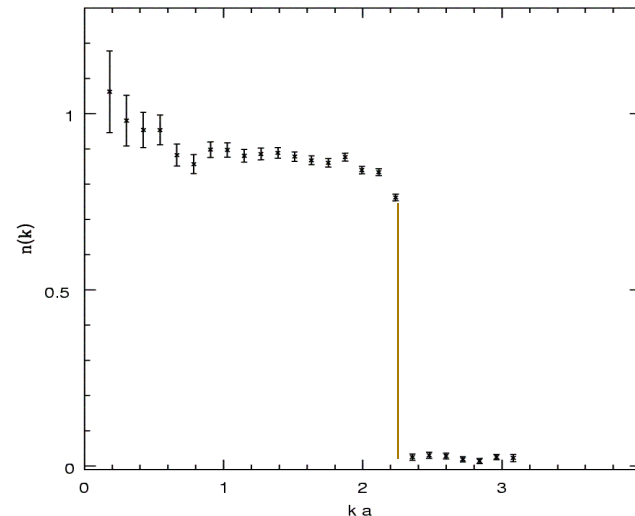
$$n(r, r') = \frac{1}{Z} \int dr_2 \dots dr_N \psi^*(r, r_2 \dots) \psi(r', r_2 \dots)$$

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

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 points on curve

$r_s=4$ $N=33$ polarized



- No size effect within single particle theory!
- Kinetic energy will have much smaller size effects.

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

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 $2k_F$.

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

Summary of T=0 methods:

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

