

Variational Monte Carlo

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

Ceperley Variational Methods

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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(Received 16 November 1964)

The properties of the ground state of liquid He⁴ are studied using a variational wave function of the form $\Psi_{\text{trial}}(\mathbf{r}_N)$. The Lennard-Jones 12-6 potential is used with parameters determined from the gas data by deBoer and Michels. 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^{-38} 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.

Ceperley Variational Methods

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 : $-I \sum_{i=1}^N \nabla_i^2$ where $I \equiv \frac{\hbar^2}{2m}$
- Hamiltonian : $\hat{H} = \hat{T} + \hat{V}$

Ceperley Variational Methods

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.

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

$$s^2 = \frac{\int dR \langle \mathbf{y} | H^2 | \mathbf{y} \rangle}{\int dR \langle \mathbf{y} | \mathbf{y} \rangle} - E_V^2$$

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

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

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

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

Ceperley Variational Methods

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.

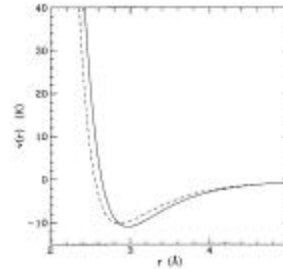


FIG. 1. The semiempirical pair potential between two helium atoms: solid line, Aziz et al. (1992); dashed line, Lennard-Jones 6-12 potential with $\epsilon = 10.22$ K and $\sigma = 2.558$ Å.

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

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

Ceperley Variational Methods

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:

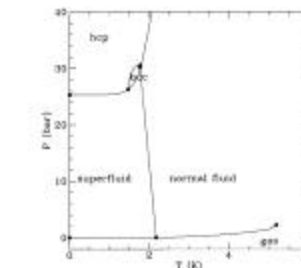


FIG. 2. The phase diagram of ^4He .

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

$$\mathbf{I} \equiv \frac{\hbar^2}{2m_i}$$

Ceperley Variational Methods

Trial function for helium 4

“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:

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

$$E_y(R) = \sum_{i < j} [v(r_{ij}) - 2I \nabla^2 u(r_{ij})] - I \sum_i G_i^2$$

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

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

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

Gives a cusp condition on u .

For Lennard-Jones 6-12 potential,
Jastrow goes as $m=5$

$$e r^{-n} = 2I (a m r^{-m-1})^2 \text{ for } n > 2$$

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

$$a = \frac{1}{m} \sqrt{\frac{e}{2I}}$$

Ceperley Variational Methods

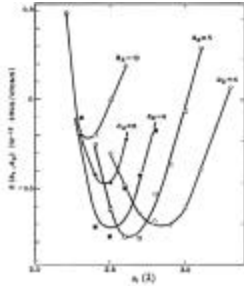
VARIATIONAL MONTE CARLO CODE

```

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
}
    
```

Ceperley Variational Methods

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 .

$$E_v(a) = \frac{\int \mathbf{y}(a) H \mathbf{y}(a)}{\int |\mathbf{y}(a)|^2} = \frac{\sum_k w(R_k, a) E(R_k, a)}{\sum_k w(R_k, a)}$$

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

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

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

Ceperley Variational Methods

Quantum Crystal Trial Function

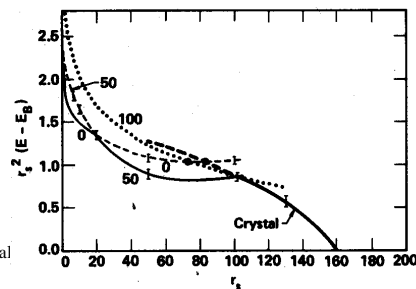
- Jastrow trial function does not “freeze” at appropriate density.
- Solution is to break spatial symmetry “by hand.”
- Introduce a bcc lattice $\{Z_i\}$
- bcc has the lowest Madelung energy, but others may have lower zero point energy.
- Introduce localized one-body terms (Wannier functions).
- Make a Slater determinant possibly with spin ordering.
- More complicated trial functions and methods are also possible.

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

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

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

“C” is a variational parameter to be optimized.



Ceperley Variational

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

Ceperley Variational Methods

Pair Correlation Function, $g(r)$

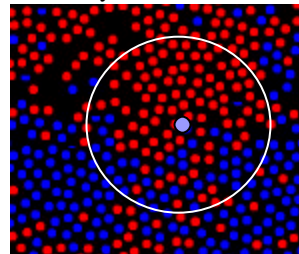
Primary quantity in a liquid is the probability distribution of pairs of particles. Given a particle at the origin what is the density of surrounding particles

$$g(r) = \langle \sum_{i < j} \delta(r_i - r_j - r) \rangle (2 \Omega / N^2)$$

Density-density correlation function

From $g(r)$ you can calculate all pair quantities (potential, pressure, ...)

$$V = \sum_{i < j} v(r_{ij}) = \frac{N \mathbf{r}}{2} \int d^3 r v(r) g(r)$$

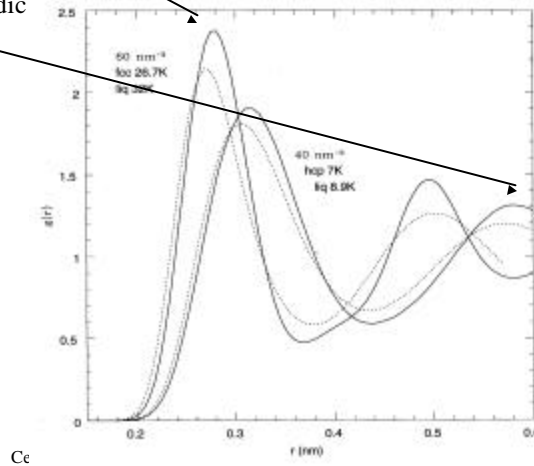


A function gives more information than a number!

Ceperley Variational Methods

$g(r)$ in liquid and solid helium

- First peak is at inter-particle spacing. (shell around the particle)
- goes out to $r < L/2$ in periodic boundary conditions.



(The static) structure factor $S(k)$

- The Fourier transform of the pair correlation function is the structure factor

$$S(k) = \langle |\rho_k|^2 \rangle / N \quad (1) \text{ "direct"}$$

$$S(k) = 1 + \rho \int dr \exp(ikr) (g(r) - 1) \quad (2) \text{ "FT"}$$

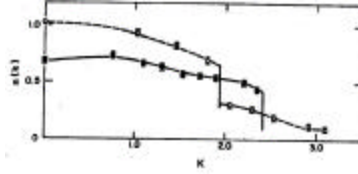
- problem with (2) is to extend $g(r)$ to infinity
- $S(K)$ is measured in neutron and X-Ray scattering experiments.
- Can provide a direct test of the assumed potential.
- Used to see the state of a system:

liquid, solid, glass, gas? (much better than $g(r)$)

- Order parameter in solid is ρ_G where G is a particular wavevector (reciprocal lattice vector).

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.



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

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

Ceperley Variational Methods

Derivation of momentum formula

- Suppose we want the probability n_k 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

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

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

- 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:

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

(states occupied with the Boltzmann distribution.)

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

Ceperley Variational Methods

Calculation of n(r)

Naïve procedure

- Generate sample with VMC
- Take one particle at random and displace by a distance r.
- Find ratio of trial function for old and new position.
- O(1) work/1 distance

McMillan procedure

- Generate sample with VMC
- Determine change of trial function if each particle is destroyed. a_k
- Insert a new particle at a random position in the box and determine trial function for the insertion "b"
- For each k perform the average b/a_k and add to $n(|r-r_k|)$.
- Repeat for O(N) insertions.
- O(N) work/O(N²) distances

$$n(r, r') = \int dr_2 \dots dr_N \frac{\Psi^*(r, r_2, \dots) \Psi(r', r_2, \dots)}{\langle \Psi^*(r, r_2, \dots) \Psi(r, r_2, \dots) \rangle}$$

Ceperley Variational Methods

The electron gas

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

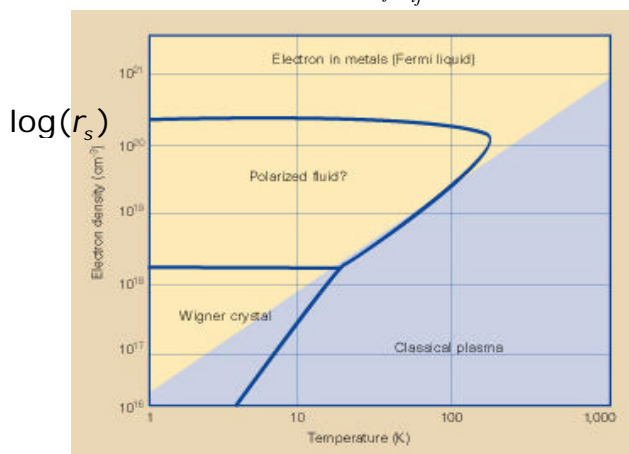
- Standard model for electrons in metals
- Basis of DFT.
- Characterized by 2 dimensionless parameters:

$$r_s = a/a_0$$

$$\Gamma = e^2 / T a$$

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

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



$$\Gamma < r_s \text{ classical OCP}$$

$$\Gamma = 175 \text{ classical melting}$$

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 $O(N^2)$.

$$\Psi_s(R) = \text{Det} \left\{ e^{i k_j r_j} \mathbf{h}_i(\mathbf{s}_j) \right\}$$

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

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

Slater-Jastrow trial function.

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

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

Ceperley Variational Methods

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.

$$2ru_k = \sqrt{\frac{V_k}{Ik^2}} \propto \frac{1}{k^2}$$

- Can combine 2 exact properties in the Gaskell form. Write E_v in terms structure factor making "random phase approximation." (RPA).

$$2ru_k = -\frac{1}{S_k} + \sqrt{\frac{1}{S_k^2} + \frac{V_k}{Ik^2}} \quad S_k = \text{ideal structure factor}$$

- 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 important

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

Ceperley Variational Methods

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
- Even a problem with dipolar forces.
- 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.

Ceperley Variational Methods

Ewald summation method

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

$$V = \sum_{i < j, L} f(r_i - r_j + nL)$$

$$V = \sum_k f_k (|\mathbf{r}_k|^2 - N) \quad \text{where } \mathbf{r}_k = \sum_i e^{i\mathbf{k} \cdot \mathbf{r}_i}$$

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

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

- Hence converges slowly at large r (in r-space)
- And at large k (in k-space)

Ceperley Variational Methods

Classic Ewald

- Split up using Gaussian charge distribution

$$f(r) = \frac{\text{erfc}(kr)}{r} \text{ decays fast at large } r$$

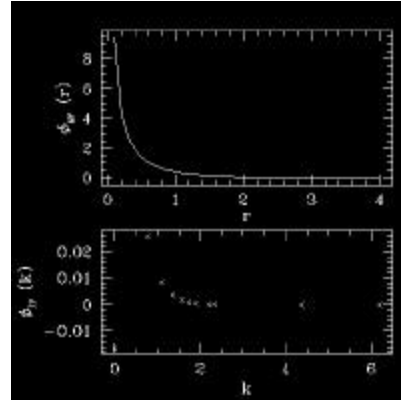
$$f_k = \frac{4pe^{-(k/2k)^2}}{k^2} \text{ decays fast at large } k$$

k = convergence parameter

- If we make it large enough we can use the minimum image potential in r -space.

- Extra term for insulators:

$$V_{dipole} = \frac{2p}{(2e+1)\Omega} \left| \sum_i m_i \right|^2$$



Ceperley Variational Methods

How to do it

- r -space part same as short-ranged potential $O(N^{3/2})$
- k -space part:
 1. Compute $\exp(ik_0 x_i) = (\cos(ik_0 x_i), \sin(ik_0 x_i))$, $k_0 = 2\pi/L \forall i$ $O(N)$
 2. Compute powers $\exp(i2k_0 x_i) = \exp(ik_0 x_i) * \exp(ik_0 x_i)$ etc.
This way we get all values of $\exp(ik \cdot r_i)$ with just multiplications. $O(N^{3/2})$
 3. Sum over particles to get ρ_k all k . $O(N^{3/2})$
 4. Sum over k to get the potentials. $O(N^{1/2})$
 5. Forces can also be done by taking gradients. $O(N^{3/2})$
- Constant terms to be added. $O(1)$
- Checks: perfect lattice: $V = -1.4186487/a$ (cubic lattice).

Ceperley Variational Methods

Wavefunctions beyond Jastrow

- Use method of residuals construct a sequence of increasingly better trial wave functions. Justify from the Importance sampled DMC.

$$f_{n+1}(R) \approx f_n(R) e^{-t \langle f_n^{-1} H f_n \rangle} \quad \text{smoothing}$$

$$f_0 = e^{i \sum_j \mathbf{k}_j \cdot \mathbf{r}_j}$$

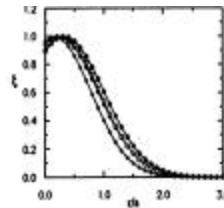
- Zeroth order is Hartree-Fock wavefunction
- First order is Slater-Jastrow pair wavefunction (RPA for electrons gives an analytic formula)
- Second order is **3-body backflow** wavefunction
- Three-body form is like a squared force. It is a bosonic term that does not change the nodes.

$$E_0 = V(R)$$

$$f_1 = f_0 e^{-U(R)}$$

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

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



Ceperley Variational Methods

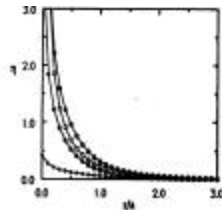
Backflow wave function

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

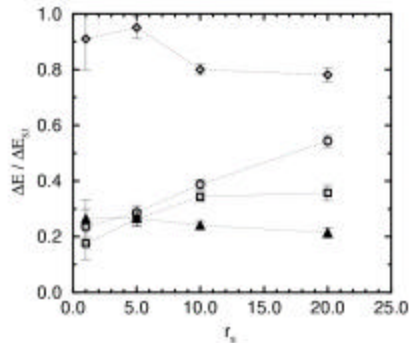
$$\text{Det}\{e^{i\mathbf{k} \cdot \mathbf{r}_j}\} \Rightarrow \text{Det}\{e^{i\mathbf{k} \cdot \mathbf{x}_j}\}$$

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

Kwon PRB 58, 6800 (1998).



3DEG



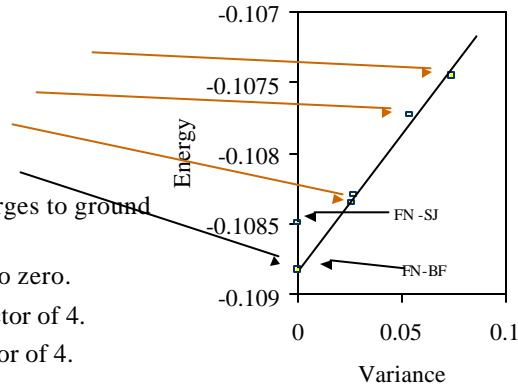
Ceperley Variational Methods

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



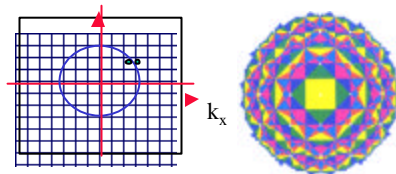
Ceperley Variational Methods

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

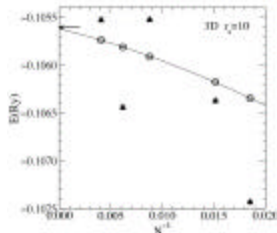
$$\mathbf{j} = e^{i\mathbf{k}\mathbf{r}}$$

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



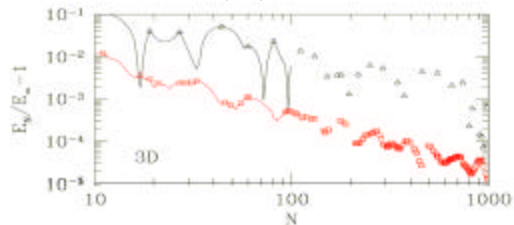
$$\Psi(x+L) = e^{i\theta} \Psi(x)$$

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



PBC
TABC

Ceperl



Brief History of Ferromagnetism in electron gas

What is polarization state of fermi liquid at low density?

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

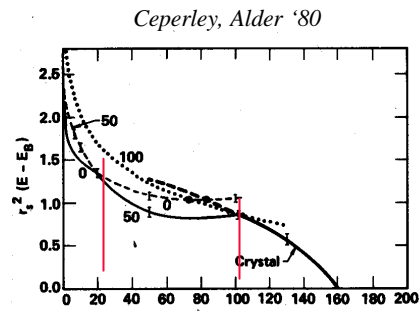
- Bloch 1929 got polarization from exchange interaction:
 - $r_s > 5.4$ 3D
 - $r_s > 2.0$ 2D
- Stoner 1939: include electron screening: contact interaction
- Herring 1960
- Ceperley-Alder 1980 $r_s > 20$ is partially polarized
- **Young-Fisk experiment on doped CaB_6 1999 $r_s \sim 25$.**
- Ortiz-Balone 1999 : ferromagnetism of e gas at $r_s > 20$.
- Zong et al Redo QMC with backflow nodes and TABC.

Ceperley Variational Methods

T=0 calculations with FN-DMC

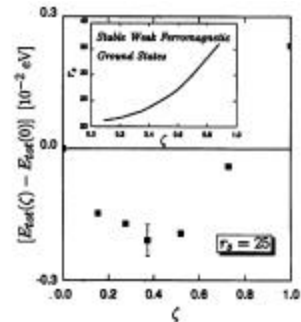
3d electron gas

- $r_s < 20$ unpolarized
- $20 < r_s < 100$ partial
- $100 < r_s$ Wigner crystal



Energies are very close together at low density!

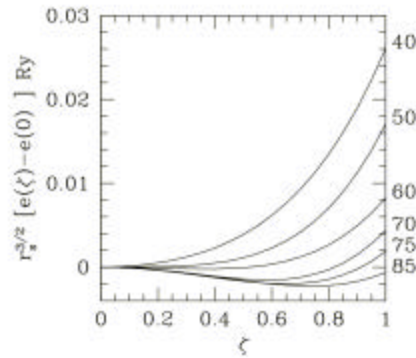
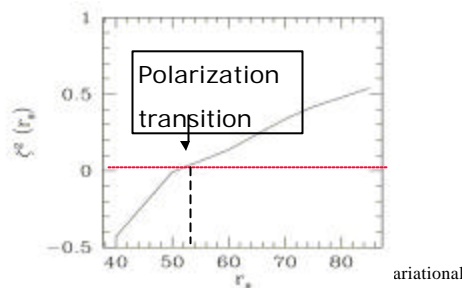
More recent calculations of *Ortiz, Harris and Balone PRL 82, 5317 (99)* confirm this result but get transition to crystal at $r_s = 65$.



Ceperley Variational Method

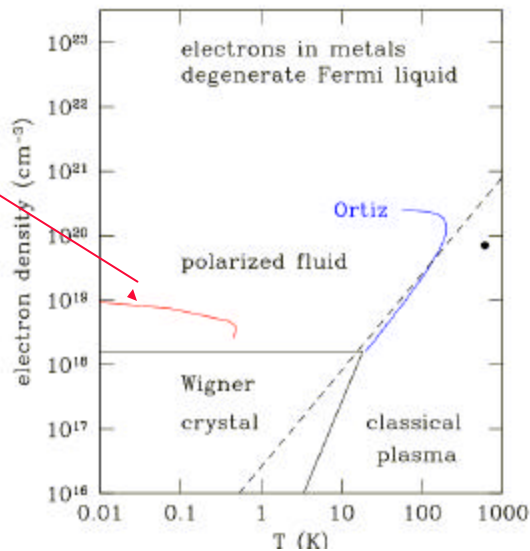
Polarization of 3DEG

- 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

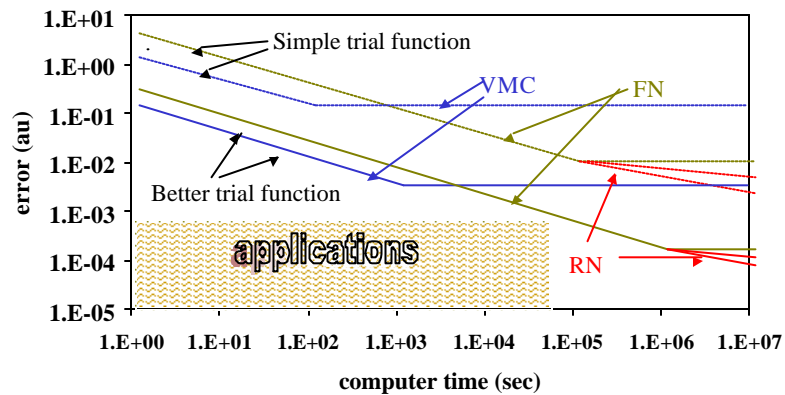
- Partially polarized phase at low density.
- But at lower energy and density than before.
- As accuracy gets higher, polarized phase shrinks
- Real systems have different units.



Ceperley Variational Methods

Summary of T=0 methods:

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



Ceperley Variational Methods

The Variational Method

- Approximate the solution to an eigenvalue problem with a trial function
- Upper bound guaranteed.
- Complexity (scaling vs computer time) reasonable
- You learn how important terms in the trial function are
- Problems:
 - What goes in, comes out.
 - How do access convergence?
 - Bias to simple states versus complex states
 - crystal vs liquid
 - Polarized vs unpolarized
 - Energy is accurate, other properties less so

Ceperley Variational Methods