Variational Monte Carlo

- Historically first quantum simulation method
- Slater-Jastrow trial function
- Calculations of properties: g(r) S(k) n(k).
- Examples: electron gas.
- Wavefunctions for Quantum solids
- Ewald Sums for Charged systems

First Major QMC Calculation

- VMC calculation of ground state of liquid helium 4.
- Applied MC techniques from classical liquid theory.
- Ceperley, Chester and Kalos (1976) generalized to fermions.

**Ground State of Liquid He**

W. L. McMillan
Department of Physics, University of Illinois, Urbana, Illinois
(Received 16 November 1964)

The properties of the ground state of liquid He are studied using a variational wave function of the form \( \Pi_{\text{eff}}(\rho) \). The Lennard Jones 12-6 potential is used with parameters determined from the gas data by de Heer and McMillan. The configuration space integrals are performed by a Monte Carlo technique for 32 and 108 atoms in a cube with periodic boundary conditions. With \( \langle \rho \rangle = 0.64 \text{ atoms} / \text{cubic nm}^3 \), the ground-state energy is found to be \( -0.88 \times 10^{-2} \text{ ergs/atom} \), which is 3% 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.
Notation

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

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.
- Sample \( R \) from \( |\psi|^2 \) using MCMC.
- Take average of local energy:
  - Error in energy is 2nd order
- Better wavefunction, lower variance!
  “Zero variance” principle. (non-classical)
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), for example momentum
  \[
  (e^{i\mathbf{k}\mathbf{r}}, e^{-i\mathbf{k}\mathbf{r}}) \text{ or } (\cos(k\mathbf{r}), \sin(k\mathbf{r}))
  \]
- 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, in some cases.

Two electron (bose) ground state.

- Assume spin $\frac{1}{2}$ fermions (or bosons).
- Total wf is antisymmetric.
- Assume spin function is a singlet ($\uparrow\downarrow - \downarrow\uparrow$)
- Then spatial wavefunction is symmetric.
  \[
  \Psi(r_1, r_2) = \Psi(r_2, r_1)
  \]
- If ground state is non-degenerate (true if space is “ergodic” or connected).
- Then we can assume $\psi(r_1, r_2)$ is real, positive and symmetric by fixing the “gauge.”
- Why? Otherwise we could always lower the energy.
  \[
  \therefore \Psi = e^{-u(r_1, r_2)} \quad u(r_1, r_2) = u(r_2, r_1)
  \]

Ceperley Variational Methods
H2 molecule:

\[ f(r) = \exp(-r) \]

\[ \Psi_{RHF} = \phi(r_1)\phi(r_2) \quad \phi(r) = f_a(r) + f_b(r) \]

\[ \Psi_{HL} = f_a(r_1)f_b(r_2) + f_b(r_1)f_a(r_2) \]

\[ \Psi_e = \Psi_{HL}e^{-u(r_1,r_2)} \]

\[ \lim_{r_1 \to r_2} u(r_1,r_2) = u_0 - \frac{1}{2}|r_1 - r_2| \]

Cusp condition gives derivative of \( u(r_1,r_2) \) whenever two electrons approach each other.

Trial function for bosons: “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:

\[
\psi(R) = \prod_{i<j} e^{-u(r_{ij})} \\
E_\psi(R) = \sum_{i<j} [v(r_{ij}) - 2\lambda \nabla^2 u(r_{ij})] - \lambda \sum_i G_i^2 \\
G_i = \sum_j \nabla_j u(r_{ij})
\]

If \( v(r) \) diverges as \( \varepsilon r^m \) how should \( u(r) \) diverge? Assume:
\( u(r) = \alpha r^{m-1} \)

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 goes as \( m=5 \)

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 $O(N^2)$.

\[
\Psi_s(R) = \text{Det}\left\{e^{ik_i r_i}\eta_i(\sigma_j)\right\}
\]

\[
PBC: \quad k \cdot L = 2\pi n + \{\theta\}
\]

\[
\Psi_{SJ}(R) = \text{Det}\left\{e^{ik_r r_i}e^{-\sum_{ij} u(r_{ij})}\right\}
\]

**Slater-Jastrow trial function.**

\[
\text{det}\left\{\phi_i(r_j')\right\} = \text{det}\left\{\phi_i(r_j)\right\}\sum_i \phi_i(r_j') M_{ij}
\]

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

Ceperley Variational Methods

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**VARIATIONAL MONTE CARLO CODE**

<table>
<thead>
<tr>
<th>Call</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><code>initstate</code> (s_old)</td>
<td>Initialize the state</td>
</tr>
<tr>
<td><code>psil2</code> (s_old)</td>
<td>Evaluate psi_trial</td>
</tr>
<tr>
<td><code>sample</code> (s_old, s_new, T_new, 1)</td>
<td>Sample new state</td>
</tr>
<tr>
<td><code>psil2</code> (s_new)</td>
<td>Evaluate psi_trial</td>
</tr>
<tr>
<td><code>sample</code> (s_new, s_old, T_old, 0)</td>
<td>Find transition prob. for going backward</td>
</tr>
<tr>
<td><code>A = (p_new/T_new)/(p_old/T_old)</code></td>
<td>Acceptance prob.</td>
</tr>
<tr>
<td><code>if (A &gt; rand (i))</code></td>
<td>Accept the move</td>
</tr>
<tr>
<td><code>{</code></td>
<td>Collect statistics</td>
</tr>
<tr>
<td><code>s_old=s_new</code></td>
<td></td>
</tr>
<tr>
<td><code>p_old=p_new</code></td>
<td></td>
</tr>
<tr>
<td><code>naccept = naccept +1</code></td>
<td></td>
</tr>
<tr>
<td><code>call averages (s_old) {</code></td>
<td></td>
</tr>
</tbody>
</table>

Ceperley Variational Methods
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

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
\[ g(r) = \langle \sum_{i<j} \delta (r_i - r_j - r) \rangle \]
Density-density correlation function

From g(r) you can calculate all pair quantities (potential, pressure, …)
\[ V = \sum_{i<j} v(r_{ij}) = \frac{N\rho}{2} \int d^3r v(r)g(r) \]

A function gives more information than a number!
g(r) in liquid and solid helium

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

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

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

\[
S(k) = \frac{1}{N} \left\langle |\rho_k|^2 \right\rangle \quad \text{where} \quad \rho_k = \sum_{i=1}^{N} e^{ik \cdot r_i} \\
S(k) = 1 + \rho \int dr e^{ik \cdot r} \left( g(r) - 1 \right)
\]

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 \( \rho_G \) where \( G \) is a particular wavevector (reciprocal lattice vector).

Ceperley Variational Methods
Momentum Distribution

- Momentum distribution
  - Classically momentum distribution is always a Gaussian
  - Non-classically 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.

\[
n(r,r') = \frac{1}{2^N} \int dr_2 ... dr_N \psi^*(r,r_2...)\psi(r',r_2...)
\]

\[
= \begin{pmatrix}
\psi^*(r,r_2...)
\end{pmatrix}
\begin{pmatrix}
\psi(r',r_2...)
\end{pmatrix}
\]

Derivation of momentum formula

- Suppose we want the probability \( n_k \) that a given atom has momentum \( hk \).
- Find wavefunction in momentum space by FT wrt all the coordinates and integrating out all but one electron

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

\[
n_k = \int dk_2 ... dk_N \ Pr(k, k_2, ..., k_N)
\]

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

\[
n_k = \int \frac{d^3rd^3s}{(2\pi)^3} \exp(-i(k-r))n(r,s) = \int \frac{d^3r}{(2\pi)^3} e^{-ikr}n(r)
\]

Where:

\[
n(r,s) = \frac{V}{Q} \int dr_2 ... dr_N \psi^*(r,r_2...r_N)\psi(s,r_2...r_N)
\]

(states occupied with the Boltzmann distribution.)

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

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

\[ \log(r_s) \]

\[ \Gamma < r_s \text{ classical OCP} \]
\[ \Gamma = 175 \text{ classical melting} \]

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:

\[ V_i = \Sigma v(r_i - r_j + nL) \]

- 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.

\[ V = \sum_{r \neq L} \phi(r_i - r_j + nL) \]

\[ V = \sum_k \phi_k \left( |\rho_k|^2 - N \right) \text{ where } \rho_k = \sum_i e^{ikr_i} \]

and \( \phi_k = \frac{1}{\Omega} \int dr e^{ikr} \phi(r) \)

For \( \phi(r) = e^2/\tau \Rightarrow \phi_k = \frac{4\pi e^2}{k^2} \)

- 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

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

\( \phi_k = \frac{4\pi e^{-ik/2\epsilon^2}}{k^2} \) 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: \( du/dr |_{r_0} = -1 \)
- K-space, charge-sloshing or plasmon modes.

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

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

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

- 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.

\[
\lim_{r \to \infty} u(r) = \begin{cases} r^{-1} & \text{3D} \\ r^{-1/2} & \text{2D} \\ \log(r) & \text{1D} \end{cases}
\]

Long range properties important
- Give rise to dielectric properties
- Energy is insensitive to \( u_k \) at small \( k \)
- Those modes converge \( t \sim 1/k^2 \)

Summary of Variational (VMC)

![Summary of Variational (VMC)](image)
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

Ceperley Variational Methods