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**INTRODUCTION TO MONTE CARLO**  
**The "Variational Method"**

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*These are preliminary lecture notes, intended only for distribution to participants.*

# The “Variational Method”

The theorem + restrictions

Basis sets

McDonald theorem

Upper and lower bounds: variance

How to do the variation.

# The “Variational Theorem”

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

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

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

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

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

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

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

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

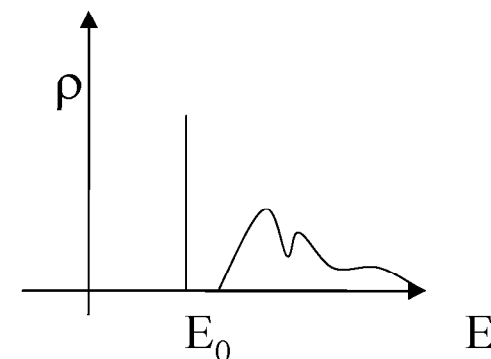
Conditions: matrix elements exist, symmetries and boundary conditions are correct.

Expand trial function in terms of the exact eigenfunctions:

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

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

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



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

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

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

Other properties are first order.

Temple lower bound:

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

# Linear Basis approach

- Assume trial function is a linear combination of known functions: a basis  $f_n(R)$ .

$$\psi(R; \mathbf{a}) = \sum_{n=1}^m a_n f_n(R)$$

$$E_V(\mathbf{a}) = \frac{\sum_{n,m} \mathbf{a}_n^* \mathbf{a}_m H_{nm}}{\sum_{n,m} \mathbf{a}_n^* \mathbf{a}_m S_{nm}}$$

$$S_{nm} = \langle f_n f_m \rangle = \text{overlap matrix}$$

$$H_{nm} = \langle f_n H f_m \rangle = \text{Hamiltonian matrix } H$$

$$S_{nm} = \delta_{nm} \text{ in an orthonormal basis } S$$

$$\frac{dE}{da} = 2[H a - E_V S a]$$

$$H a_\lambda = E_\lambda S a_\lambda \quad \text{generalized eigenvalue problem}$$

Problem that MC solves:

Unless we use 1-particle basis, integrals are too slow to perform.

# Properties of solution to GEP

- For a basis of size  $m$ , there exist “ $m$ ” eigenvalues and orthonormal eigenfunctions:

$$\psi_n(R) = \sum_{k=1}^m a_{k,n} f_k(R)$$

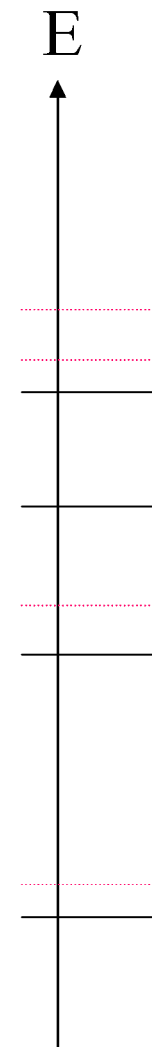
$$\langle \psi_n | \psi_m \rangle = a_n^* S_{nm} a_m = \delta_{nm}$$

- McDonald’s theorem: the  $n^{\text{th}}$  eigenvalue in a basis is an upper bound to the  $n^{\text{th}}$  “exact eigenvalue.

$$E_0 \leq E_1 \leq E_2 \leq \dots \leq E_m$$

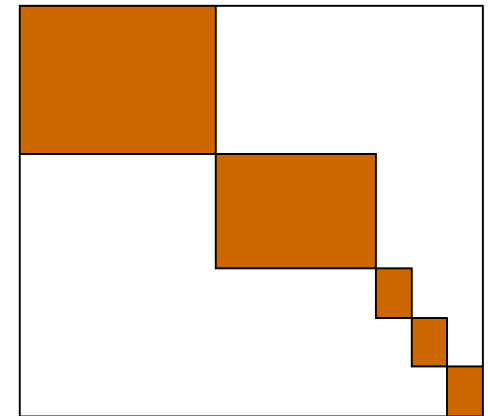
$$E_n^{\text{ex}} \leq E_n$$

- We can always lower all the energies by augmenting the basis
- When basis is complete, we get exact answers!



# Symmetry reduces complexity

- If an operator  $P$  commutes with  $H$ :  $[P,H]=0$  we can reduce complexity by working in a basis with that symmetry.
  - rotational symmetry use  $Y_{lm}$ .
  - Translation symmetry: use plane waves.
  - Inversion symmetry: even/odd functions
- Matrix elements are non-zero only for states within the same “sector”.
- By reordering we can block diagonalize
- Reduces complexity from  $M^3$  to  $k(M/k)^3=M^3/k^2$ .
- McDonald’s theorem applies to each sector individually.



# The Variational Method

- Approximate the solution to an eigenvalue problem with a trial function
- Upper bound guaranteed.
- In a linear basis, problem reduces to the generalized eigenvalue problem for a finite-sized matrix.
- Problems:
  - What goes in, comes out.
  - How do access convergence?
  - Have to do the matrix elements
  - What is the complexity?
    - Eigenvalue problem is  $M^3$
    - Basis needs to scale exponentially with number of particles.



# 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 He<sup>4</sup>

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(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
- 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  $R = (r_1, r_2, \dots, r_N)$
- $R$  will also depend on “imaginary time”, “time slice” or “Trotter index” “ $t$ ”
- Total potential energy  $V(R)$
- Kinetic energy  $-\lambda \sum_{i=1}^N \nabla_i^2$  where  $\lambda \equiv \frac{\hbar^2}{2m}$
- Hamiltonian  $\hat{H} = \hat{T} + \hat{V}$

# Variational MC

- 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

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

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

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

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

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

# 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.

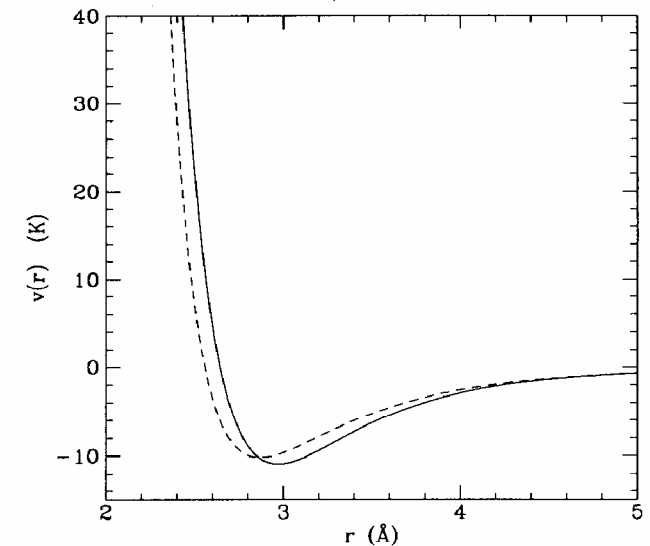


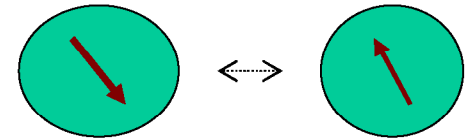
FIG. 1. The semiempirical pair potential between two helium atoms: solid line, Aziz *et al.* (1992); dashed line, Lennard-Jones 6-12 potential with  $\epsilon = 10.22$  K and  $\sigma = 2.556$  Å.

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

# Helium interaction

- Repulsion at short distances because of overlap of atomic cores.
- Attraction at long distance because of the dipole-induced-dipole force. Dispersion interaction is

$$c_6 r^{-6} + c_8 r^{-8} + \dots$$



- He-He interaction is the most accurate. Use all available low density data (virial coefficients, quantum chemistry calculations, transport coefficients, ....) Good to better than 0.1K (work of Aziz over last 20 years).
- Three body interactions are small but not zero.

# 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:

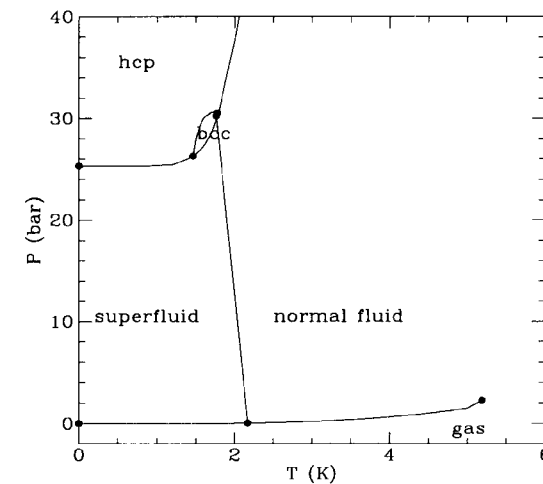


FIG. 2. The phase diagram of  $^4\text{He}$ .

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

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

# 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  $\epsilon r^{-n}$  how should  $u(r)$  diverge? Assume:

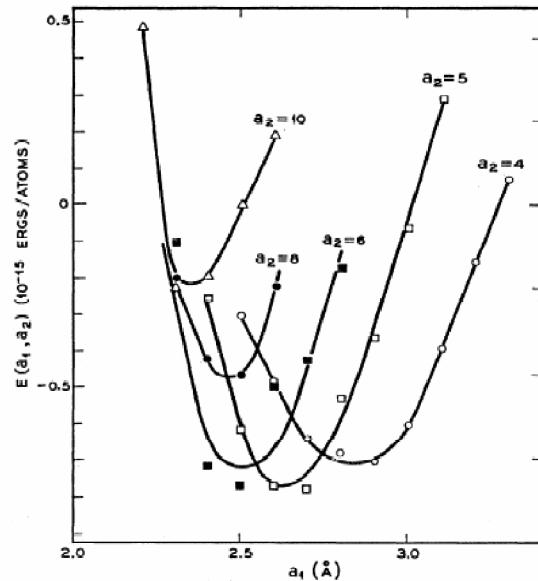
$$U(r) = \alpha r^{-m}$$

Gives a cusp condition on  $u$ .

$$\begin{aligned} -e^2 r^{-1} &= 2\lambda \nabla^2 u(r) = 2\lambda \left( u'' + \frac{D-1}{r} u' \right) \\ u'(0) &= -\frac{e^2}{2\lambda(D-1)} \end{aligned}$$

$$\begin{aligned} \epsilon r^{-n} &= 2\lambda \left( \alpha m r^{-m-1} \right)^2 \quad \text{for } n > 2 \\ m &= \frac{n}{2} - 1 \\ \alpha &= \frac{1}{m} \sqrt{\frac{\epsilon}{2\lambda}} \end{aligned}$$

# 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  $a_0$ .

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

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

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

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

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