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CONTINUUM QUANTUM MONTE CARLO METHODS
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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.

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

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

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

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

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

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

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

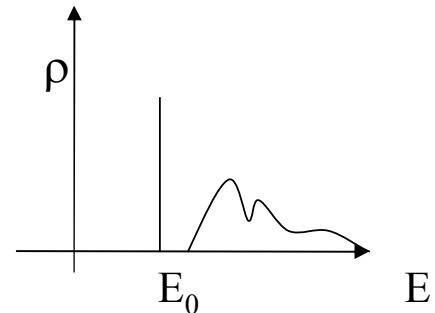
Conditions: matrix elements exist, symmetries and boundary conditions are correct.

Expand trial function in terms of the exact eigenfunctions:

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

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

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



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

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

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 $f_n(\mathbf{R})$.

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

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

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

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

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

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

$$H\mathbf{a}_\lambda = E_\lambda S\mathbf{a}_\lambda \quad \text{generalized eigenvalue problem}$$

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:

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

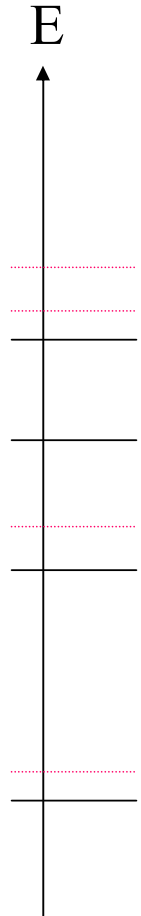
$$\langle \psi_n | \psi_m \rangle = a_n^* S_{nm} a_m = \delta_{nm}$$

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

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

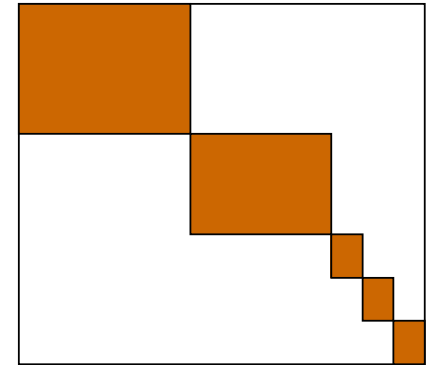
$$E_n^{ex} \leq E_n$$

- 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.

Ground State of Liquid He⁴

W. L. McMILLAN*

Department of Physics, University of Illinois, Urbana, Illinois

(Received 16 November 1964)

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.

Notation

- Individual coordinate of a particle r_i
- All $3N$ coordinates $\mathbf{R} = (r_1, r_2, \dots, r_N)$
- \mathbf{R} will also depend on “imaginary time”, “time slice” or “Trotter index” “ t ”

- Total potential energy $V(\mathbf{R})$
- Kinetic energy $-\lambda \sum_{i=1}^N \nabla_i^2$ where $\lambda \equiv \frac{\hbar^2}{2m}$

- Hamiltonian $\hat{H} = \hat{T} + \hat{V}$

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 ψ 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.

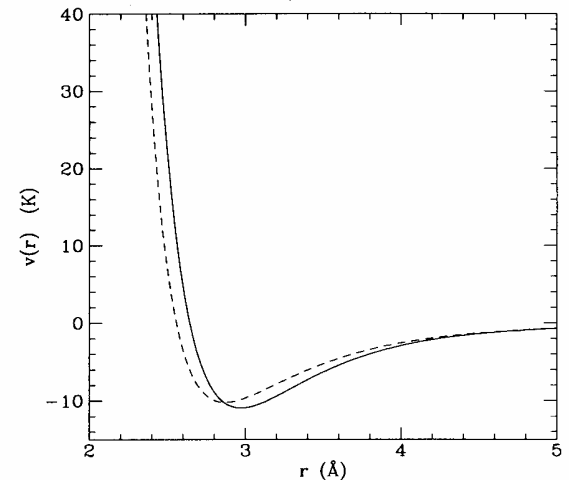
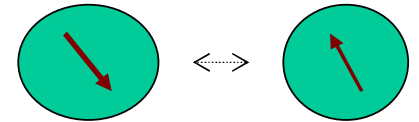


FIG. 1. The semiempirical pair potential between two helium atoms: solid line, Aziz *et al.* (1992); dashed line, Lennard-Jones 6-12 potential with $\epsilon = 10.22$ K and $\sigma = 2.556$ Å.

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

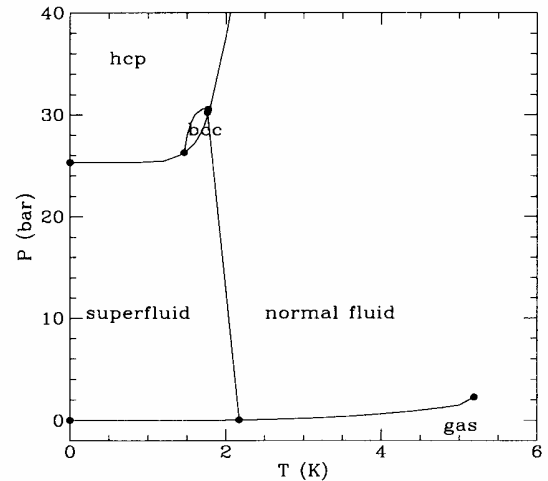


FIG. 2. The phase diagram of ^4He .

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

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

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

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

Gives a cusp condition on u .

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

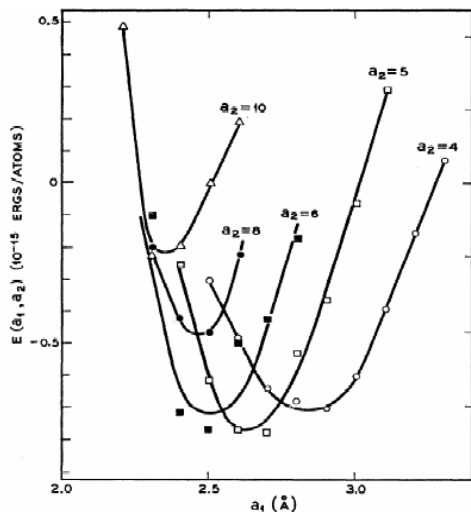
$$u'(0) = -\frac{e^2}{2\lambda(D-1)}$$

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

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

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

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 .

$$E_V(a) = \frac{\int \psi(a) H \psi(a)}{\int |\psi(a)|^2} = \frac{\sum w(R_i, a) E(R_i, a)}{\sum_k w(R_i, a)}$$

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

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

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