Quantum Monte Carlo methods

Lubos Mitas

North Carolina State University

Urbana, August 2006

Lubos_Mitas@ncsu.edu

NC STATE UNIVERSITY

The Theory of Everything

$$i\hbar \frac{\partial \Phi}{\partial t} = \mathcal{H}\Phi$$

$$\mathcal{H} = -\sum_{j}^{N} \frac{\hbar^2}{2m}\nabla_j^2 - \sum_{\alpha}^{M} \frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 - \sum_{j}^{N}\sum_{\alpha}^{M} \frac{Z_\alpha e^2}{|r_j - R_\alpha|}$$

$$+ \sum_{j<k}^{N} \frac{e^2}{|r_j - r_k|} + \sum_{\alpha<\beta}^{M} \frac{Z_\alpha Z_\beta e^2}{|R_\alpha - R_\beta|}$$

* Air
* Water
* Fire
* Rocks
* Cement

* Steel
* Plastic
* Glass
* Wood
* Asphalt

* Paper
* Dynamite
* Antifreeze
* Glue
* Dyes

* Vitamins
* Ham Sandwiches
* Ebola Virus
* Economists
* . . .

Robert Laughlin: Nobel Prize Talk, viewgraph #2

2.

Electronic structure and properties of materials

Hamiltonian of interacting electrons and ions

$$H = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I}{r_{iI}} + \sum_{i<j} \frac{1}{r_{ij}} + E_{ion-ion}$$

$$H \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ...) = E \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ...)$$

- ground states
- excited states, optical properties
- responses to external fields
- T>0, etc ...

Lubos_Mitas@ncsu.edu

Traditional electronic structure methods

Density Functional Theory :
-based on one-particle density

$$E_{tot} = \int F[\rho(\boldsymbol{r})]d\boldsymbol{r}$$

- exact functional F is unknown

- various approximations for F :
  LDA (local density approx.)
  GGA (generalized grad. approx.)

Problem: efficient but inaccurate
(need accuracy 0.1 eV or higher)

Hartree-Fock : wavefunction as
Slater determinant (antisymmetry)
of one-particle orbitals

$$\psi_{HF}(\boldsymbol{r}_1, \boldsymbol{r}_2, ...) = Det[\{\phi_i(\boldsymbol{r}_j)\}]$$

Post-Hartree-Fock: expansion
in excitations

$$\psi_{corr}(\boldsymbol{r}_1, \boldsymbol{r}_2, ...) = \sum_n d_n Det_n[\{\phi_i(\boldsymbol{r}_j)\}]$$

More advanced: CC, MBPT etc

Problem: accurate but inefficient

Alternatives ?   Quantum Monte Carlo (QMC)

Lubos_Mitas@ncsu.edu

Accuracies which we need

- cohesion, optical excitations, barriers : ~ 0.1 - 0.01eV ~ 1000 -100K

- magnetism, superconductivity, spintronics : ~ 0.001 eV ~ 10K

- QED (important)   : ~ 0.000001 eV

- recent calculations of sixth order QED corrections for He atom:
  12 digit accuracy

Nature employs energy, length, etc scales as a composer employs
various orchestral instruments

NC STATE UNIVERSITY

Accuracies which we need

Density Functional Theory :
-based on one-particle density

$$E_{tot} = \int F[\rho(r)] dr$$

- exact functional F is unknown

- various approximations for F :
  LDA (local density approx.)
  GGA (generalized grad. approx.)

Problem: efficient but inaccurate
(need accuracy 0.1 eV or higher)

Hartree-Fock : wavefunction as Slater determinant (antisymmetry) of one-particle orbitals

$$\psi_{HF}(r_1, r_2, ...) = Det[\{\phi_i(r_j)\}]$$

Post-Hartree-Fock: expansion in excitations

$$\psi_{corr}(r_1, r_2, ...) = \sum_n d_n Det_n[\{\phi_i(r_j)\}]$$

More advanced: CC, MBPT etc

Problem: accurate but inefficient

Alternatives ?   Quantum Monte Carlo (QMC)

Lubos_Mitas@ncsu.edu

Traditional electronic structure methods and quantum Monte Carlo

Post-HF methods:
- convergence in one-particle basis sets is slow, inefficient description of many-body effects
- need to explictly evaluate integrals restricts functional forms which can be used

DFT approaches:
- difficult systematical improvement (the fundamental proof is not constructive)

QMC:
 - use stochastic methods to map the many-body problem onto a sampling/simulation problem
- focus on many-body effects and efficiency of their description
- many ideas applicable to other systems/models: lattices, etc.
- in many ways, complmentary to traditional approaches

Lubos_Mitas@ncsu.edu

Variational Monte Carlo (VMC): Slater-Jastrow wavefunction

"Zero order" wave function: Slater determinant(s)

$$\psi_0(\boldsymbol{R}) = \sum_n d_n Det_n[\phi_\alpha] Det_n[\phi_\beta]$$

one-particle orbitals from - Hartree-Fock, MCSCF

- Density Functional Theory (DFT)

- ...

Correlate the Slater wave function explicitly: e-e, e-e-I terms, ...

$$\psi_T(\boldsymbol{R}) = \sum_n d_n Det_n[\phi_\alpha] Det_n[\phi_\beta] \exp(U_{corr})$$

$$U_{corr} = \sum_{i,j} \sum_I \sum_{k,l,m} c_{klm} a_k(r_{ij}) b_l(r_{iI}) b_k(r_{jI})$$

electrons   *Ions*   *correlation basis expansion*

Other functional forms: pairing BCS wavefunctions, pfaffians, ...

Variational Monte Carlo (VMC): stochastic methods for multi-D integrals

- **evaluate the expectation values** by **sampling** *3N* **electron coordinates**
  - **no other choice!** **For example, variational energy is given by**

$$E_{VMC} = \frac{\int \psi_T^2 [H\psi_T / \psi_T] d\boldsymbol{R}}{\int \psi^2 d\boldsymbol{R}} = \lim_{M \to \infty} \frac{1}{M} \sum_{sample} \frac{H\psi(\boldsymbol{R}_{sample})}{\psi(\boldsymbol{R}_{sample})}$$

where samples are distributed as $\psi_T^2(\boldsymbol{R})$ **and** $\boldsymbol{R} = (r_1, r_2, ..., r_N)$

- **optimize any variational parameters** $\{c_{klm}\}$ **,**
  eg, minimize the energy or local energy variance (Umrigar et al,'88)

$$\sigma_{VMC}^2 \approx \frac{1}{M} \sum_{sample} \left[\frac{H\psi(\boldsymbol{R}_{sample})}{\psi(\boldsymbol{R}_{sample})} - E_{VMC} \right]^2 = min$$

Beyond VMC

VMC is straightforward, fast, efficient, but not accurace enough:
variational bias

Eliminate the VMC bias by projecting out the (ground) state in imaginary time

$$\psi(\boldsymbol{R}, t) = \exp(-tH)\psi_T(\boldsymbol{R})$$
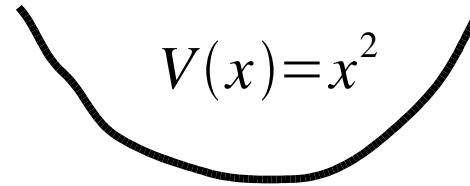
$$-\partial_t \psi(\boldsymbol{R}, t) = H\psi(\boldsymbol{R}, t)$$

$$\psi(\boldsymbol{R}, t+\tau) = \int G(\boldsymbol{R}, \boldsymbol{R}', \tau)\psi(\boldsymbol{R}', t)d\boldsymbol{R}'$$

Wave function can be sampled and the equation solved by interpreting the Green's functions as a transition probability density: simulate by a stochastic process

Lubos_Mitas@ncsu.edu

Toy model: 1D harmonic oscillator

$$V(x)=x^2$$

$$H=T+V(x)$$

$$\psi_{init}(x)$$

Propagator

$$G(x,x',\tau)$$

$\downarrow$

$t \downarrow$

$$C e^{-(x-x')^2/4\tau} \cdot e^{-(V(x)-E_T)t}$$

τ

diffusion   **renorm**

$$\psi_{ground}(x)$$

Lubos_Mitas@ncsu.edu
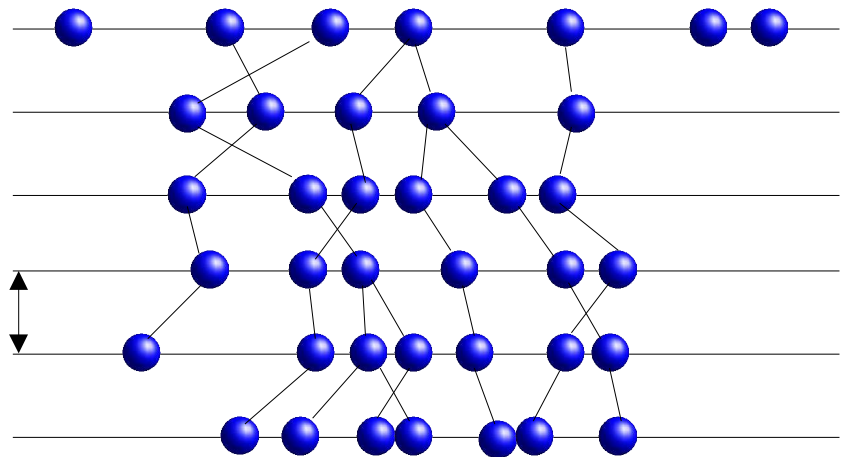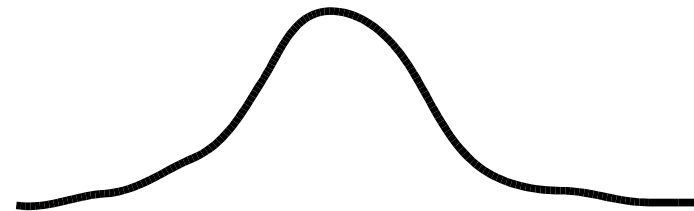
Fermion sign problem

Naïve approach for fermionic wave functions: decompose to + and -

$$\psi_T(\boldsymbol{R}) = \psi_T^+(\boldsymbol{R}) - \psi_T^-(\boldsymbol{R})$$

$$-\partial_t \psi^+(\boldsymbol{R}, t) = H \psi^+(\boldsymbol{R}, t)$$

$$-\partial_t \psi^-(\boldsymbol{R}, t) = H \psi^-(\boldsymbol{R}, t)$$

Unfortunately, + and - components converge independently to the lowest energy solution (which is bosonic) because Schr. eq. is linear!
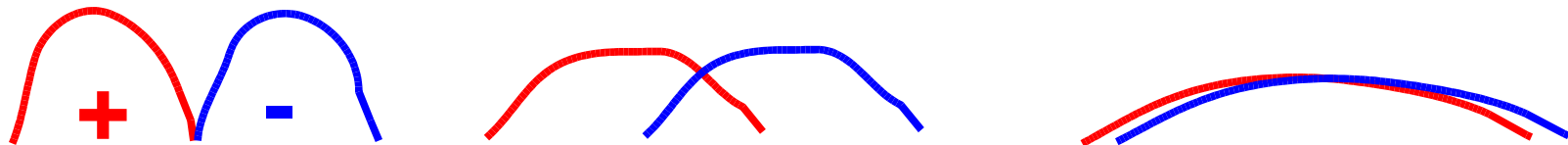
$$\lim_{t \to \infty} \psi^+(\boldsymbol{R}, t) - \lim_{t \to \infty} \psi^-(\boldsymbol{R}, t) \propto \exp\left[-(E_{Fermi} - E_{Boson})t\right]$$

Fermion "signal" decays exponentially quickly into a bosonic "noise"

Lubos_Mitas@ncsu.edu

Importance sampling and fixed-node diffusion Monte Carlo (FNDMC)

$$f(\mathbf{R}, t+\tau) = \int G^*(\mathbf{R}, \mathbf{R}', \tau) f(\mathbf{R}', t) d\mathbf{R}'$$

$$f(\mathbf{R}, t) = \psi_T(\mathbf{R}) \phi(\mathbf{R}, t), \qquad \psi_T = \psi_{HF} e^{U_{corr}} = det\{\phi_\alpha\} det\{\phi_\beta\} e^{U_{corr}}$$

$$f(\mathbf{R}, t \rightarrow \infty) \propto \psi_T(\mathbf{R}) \phi_{ground}(\mathbf{R}) \qquad G^*(\mathbf{R}, \mathbf{R}', \tau) = \frac{\langle \mathbf{R} | \exp(-\tau H) | \mathbf{R}' \rangle}{\psi_T(\mathbf{R}') \psi_T^{-1}(\mathbf{R})}$$

Fermion node: (3N-1)-dimen. hypersurface defined as $\phi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = 0$

Fixed-node approximation: $f(\mathbf{R}, t) > 0$

- antisymmetry (nonlocal) replaced by a boundary (local)
- exact node implies recovering exact energy (in polynomial time)

Accuracy quite high: energy differences within a few % of experiment

Lubos_Mitas@ncsu.edu

Fermion node toy model: excited state of harmonic oscillator

$$V(x)=x^2$$

$$H=T+V(x)$$

$$\psi_{init}(x)$$

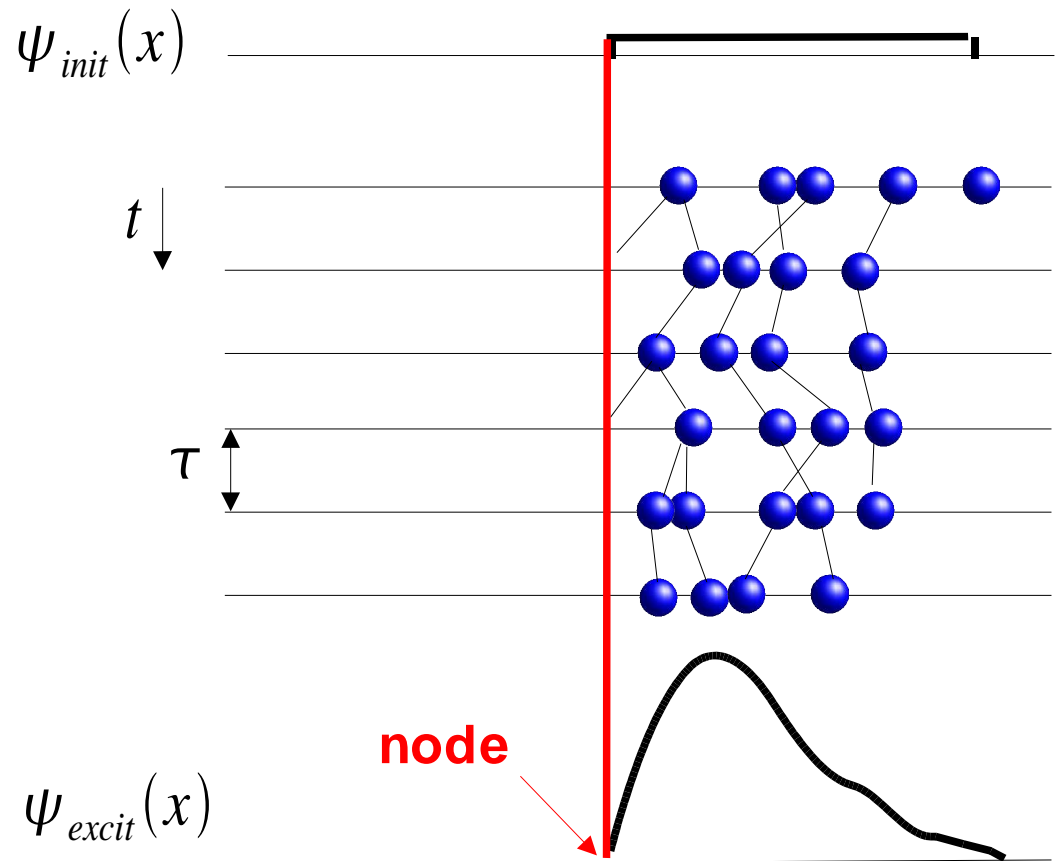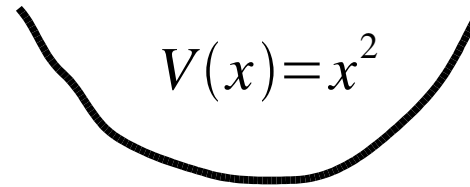**Propagator**

$$G(x,x',\tau)$$

$\downarrow$

$t\downarrow$

$$Ce^{-(x-x')^2/4\tau}\cdot e^{-(V(x)-E_T)t}$$

τ

diffusion   **renorm**

**+ boundary condition
(evaluate trial function)**

node

$$\psi_{excit}(x)$$

Lubos_Mitas@ncsu.edu

Fixed-node approximation

- bosonization of the fermionic problem

- important shift (and a leap of faith):

  antisymmetry   ->   boundary condition
     (nonlocal)   (local)

- fermion node is (3N-1)-dim hyper - surface:

  - easy to enforce (check the sign of the determinant)

  - difficult to parametrize with arbitrary accuracy
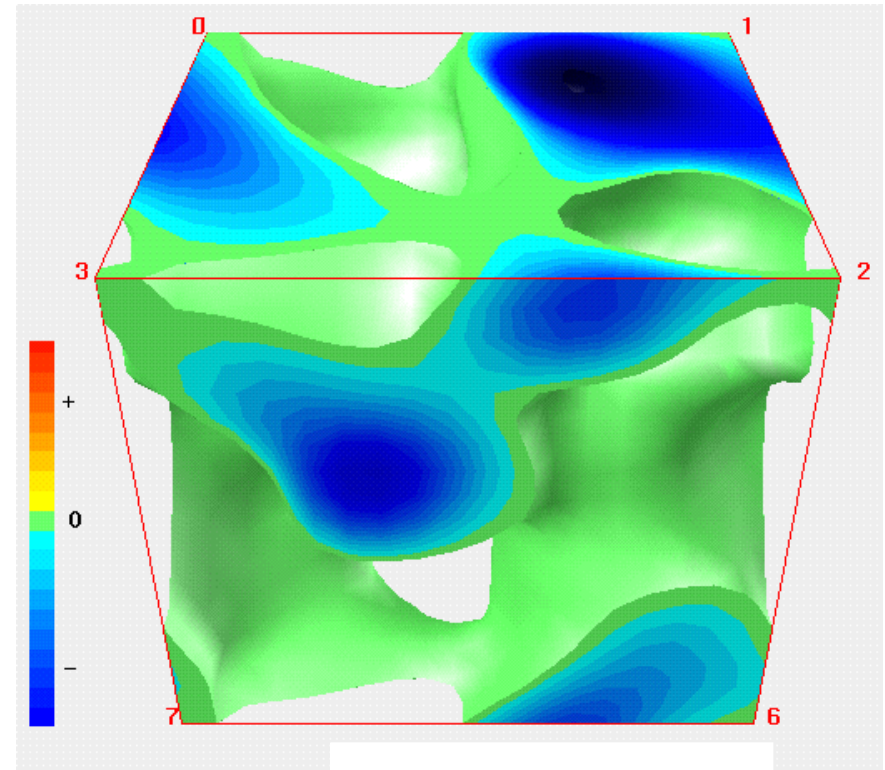
Green surface: 3D cut of 59-dimensional fermion node hypersurface

The key paradigm shift in QMC

- the many-body (Schrodinger) differential equation mapped onto
  equivalent stochastic process which is easy to simulate

density of walkers in 3N-dim space <=> value of the wavefunction

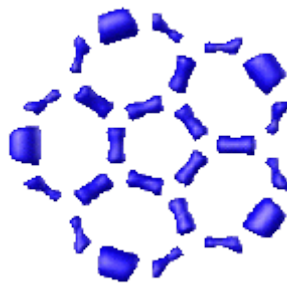NC STATE UNIVERSITY
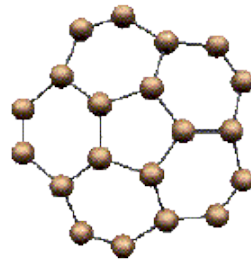
The key directions of (my) QMC research

- applications of QMC to challenging materials and to materials design: **strongly correlated systems, competing many-body effects, new materials**

- development of fundamental understanding of quantum many-body systems and methods capable of solving such challenging problems: **fermion nodes, treatment of magnetic effects, etc**

- coupling of QMC with other approaches for multi-scale application: **coupling of QMC with molecular dynamics, T>0, etc**

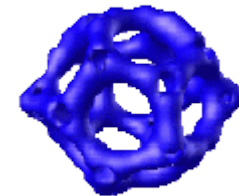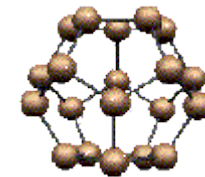# Example of application: which is the lowest energy isomer???
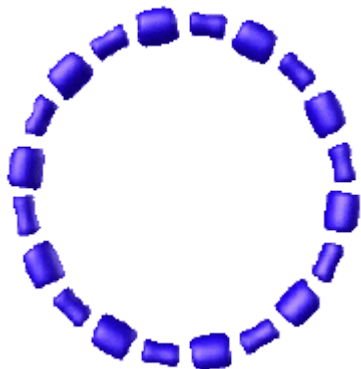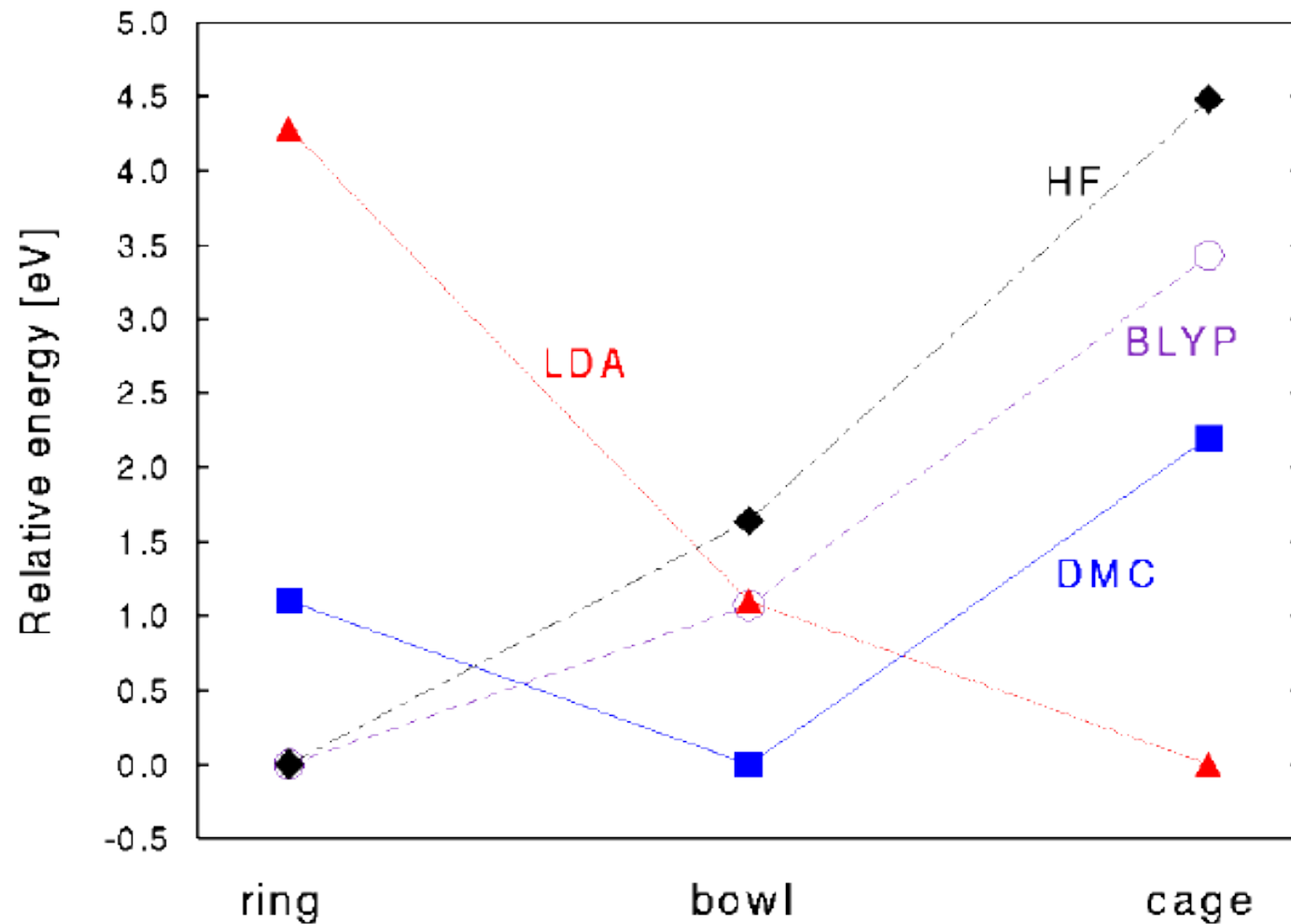
C20 challenge: ring   **bowl**   **cage**

J.C. Grossman, L. Mitas, K. Raghavachari, Phys. Rev. Lett. 75, 3870 (1995)

Lubos_Mitas@ncsu.edu

J.C. Grossman, L. Mitas, K. Raghavachari, Phys. Rev. Lett. 75, 3870 (1995)

Silicon clusters
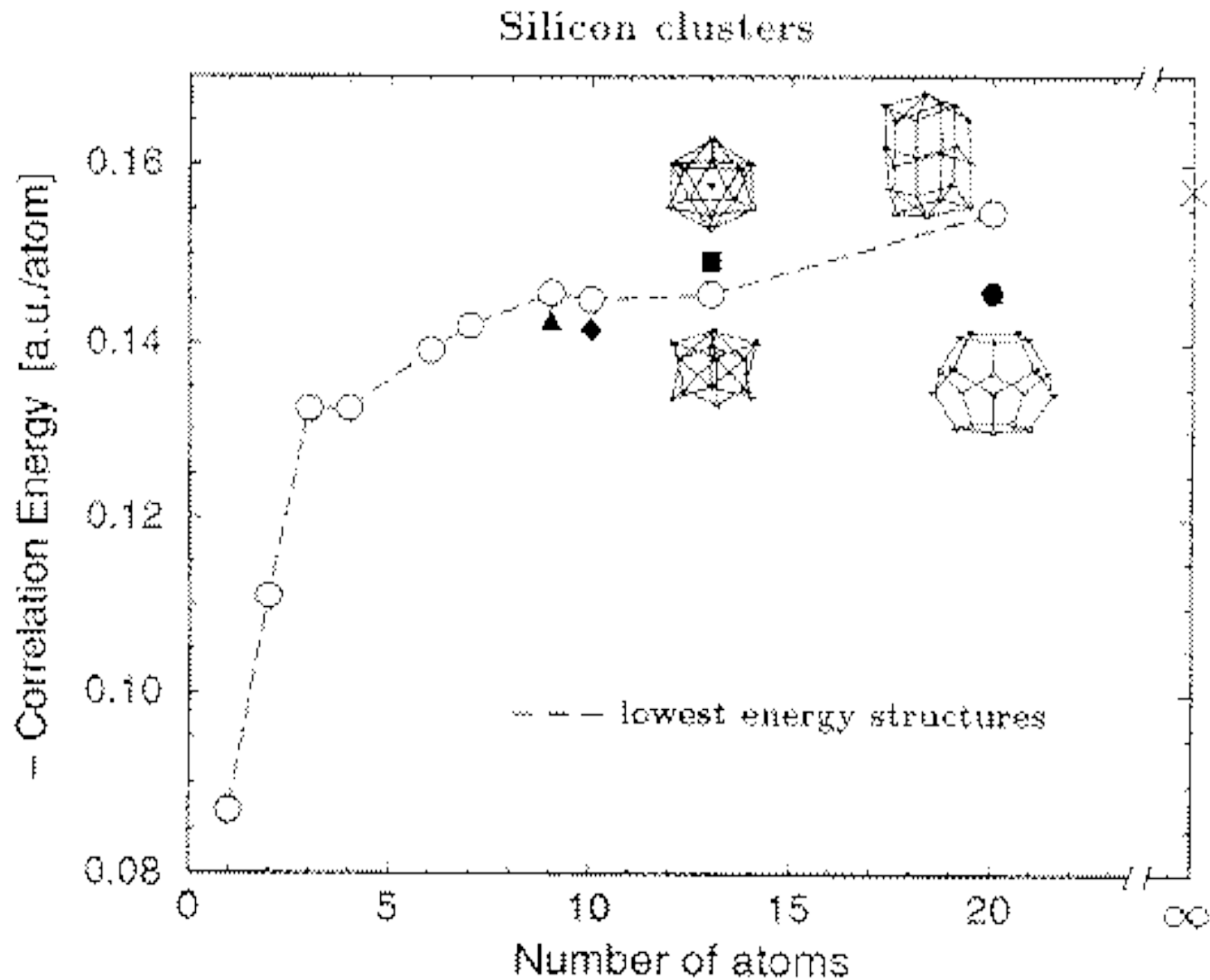
Performance of the fixed-node DMC method using a few-determinant trial functions

Etot=E_HF+E_corr

Cohesion, excitations, barriers, ...

Fixed-node DMC gets about 95 % of E_corr

~3% Etot -> E_corr ->

-Fixed-node error ~5% Ecorr
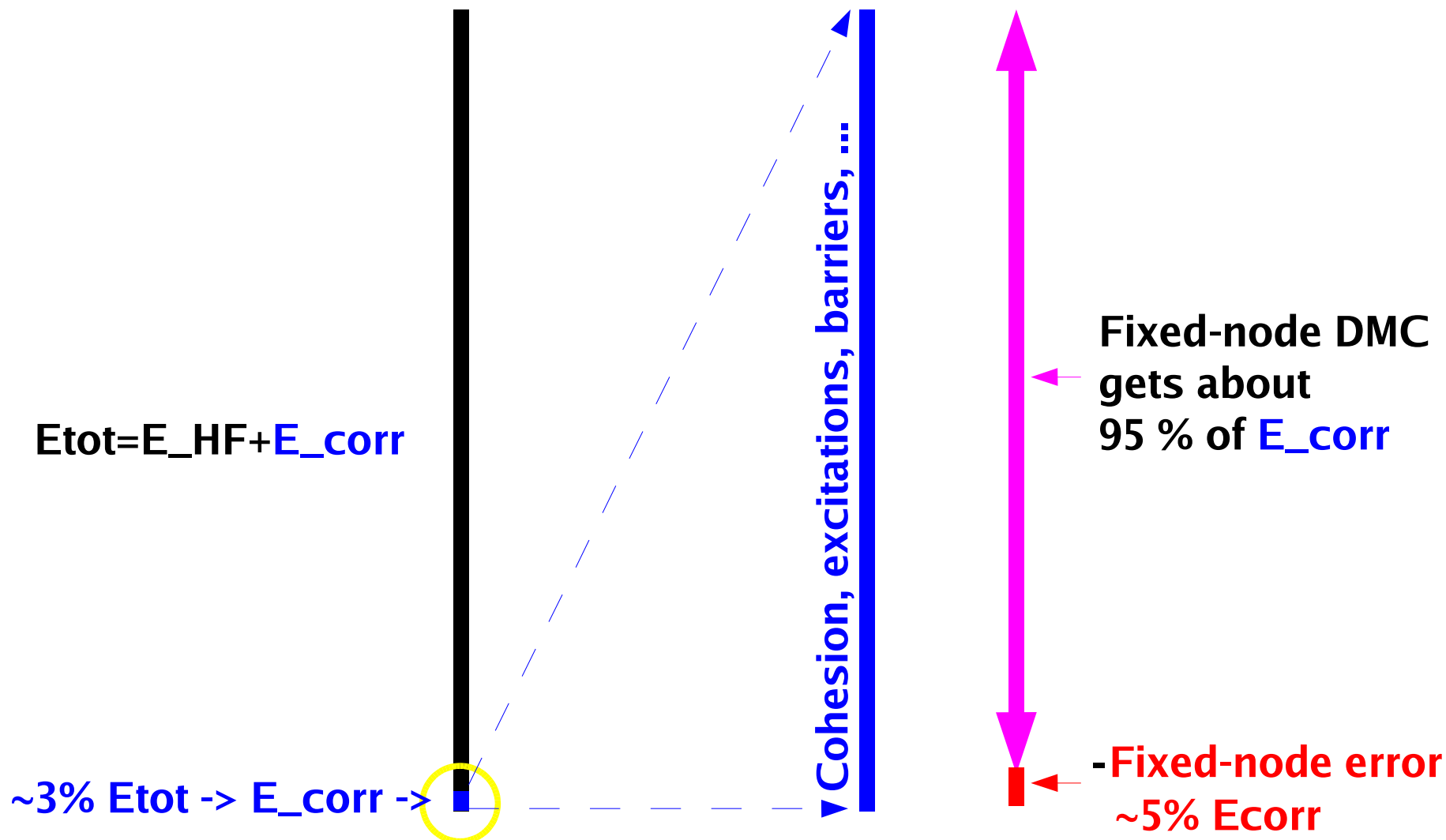
Solving the stationary Schrödinger equation: key ingredients

The many-body problem splits into two parts

- **fermion nodes**, ie, boundary conditions

- often one or few determinants are very reasonable

- "non-dynamical" correlation, multi-reference wavefunctions

- can be obtained within mean-field/basis set methods

- **"bosonic" correlations** within the **fermion node domains**

- e-e cusps, multiple collision points, etc

- "dynamical" correlation, very difficult for other methods

- easy within QMC

The combined strategy "corners" the error in the treatment of many-body effects into the last few percent of correlation energy
The methods are complementary: together best of both, productive

Lubos_Mitas@ncsu.edu

NC STATE UNIVERSITY

Summary on application and performance of QMC methods

- fixed-node DMC typically recovers about 95% of the valence correlation energy for up to hundreds of electrons

- energy differences agree with experiments within a few percent

- method scales like a N^3 where N is the number of valence electrons (core electrons eliminated by pseudopotentials)

- applied to a number of systems, eg, electron gas and quantum liquids, atoms, molecules, solids etc; often the results became benchmarks for other methods

- about two orders of magnitude slower than mean-field methods but very efficient (perfectly scalable) on parallel architectures

Lubos_Mitas@ncsu.edu

Computational advantages

- scaling in the number of particles: N^a, $a = 1 \sim 3$

- sampling walkers independent -> natural parallelism and scalability, slow networks OK, heterogeneous clusters, ...

- cycle intensive, less memory intensive

- robust

- enable to focus in interesting physics

Lubos_Mitas@ncsu.edu

Impact of QMC methods

Breakthroughs and benchmark calculations:

- homogeneous electron gas in '80 (Ceperley & Alder)
- quantum liquids and solids
- barrier of H+H2 -> H2+H with **0.001 eV** accuracy (J. B. Anderson)
- calculations of solids, clusters, etc (last 15 years)

Relative accuracy for s-p systems
- energy differences typically within 1-3% of experiment

Sizes of systems and timing
- 100-200 valence electron systems becoming routine;
  (1000 or more doable at the current level of development)
- typical run: 32 processors for a day
- about 100 times slower than mean-field approaches

Current limitations of QMC methods

Fundamentally, fixed-node approximation is still present:
- sometimes the physical effect of interest is in the last few percent of the correlation

Quantities beyond energies:
- we need better methods for getting correlation functions, forces, responses to external fields, etc
- small energy scales (ie, magnetism) is burried in the error bars

Need inputs (orbitals) from other approaches:
- often that is the most time consuming part :-(
- many of currently available DFT/HF codes are not built for the purpose to provide the best possible inputs to QMC

NC STATE UNIVERSITY

Lubos_Mitas@ncsu.edu

One- and two-particle quantities   vs many-particle wave functions

Traditional approaches are based on one- or two-particle quantities:
   - one-particle density (matrix), orbitals
   - one-particle Green's function
   - pair-correlation functions, etc
 since these contain just the right amount of information necessary
 to describe the physics.
 We think and "understand" in terms of reduced quantities.

QMC, however, is based on wave functions: ... despite that
  - in general, wave functions are intractable and contain too much
    of information most of which is irrelevant
  - limited to small number of particles, otherwise intractable
  - difficult to understand the physics

**QMC shows that maybe the traditional reductionism might have
reached its limits ...**

Lubos_Mitas@ncsu.edu

NC STATE UNIVERSITY

QMC and wavefunctions: only an accurate method or a paradigm shift ?

- in many cases it is more efficient to carry out the many-particle calculations rather than to (re)build a better mean-field

- let the machine to worry about reducing the unnecessary information

- combination of analytical insights and stochastic techniques a key for getting high accuracy solutions of Schr. eq.

- in working with wave functions one is closiest to the many-body physics and understanding (perhaps even the most efficient way how to capture the correlation effects)

- history of high accuracy benchmark/reference calculations

Lubos_Mitas@ncsu.edu