

Quantum Monte Carlo for Electronic Structure

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The Electronic Structure Problem

Find the ground state of the time independent Schrodinger equation

$$\hat{H}\psi = E_0\psi$$

For a *many-body* system of electron and (fixed) ions

$$\hat{H} = \sum_i \left(-\frac{\hbar^2}{2m} \nabla_i^2 \right) + \sum_j V(r_i, R_j) + \sum_{j, j \neq i} \frac{1}{|r_i - r_j|}$$

Outline

- Real-world Applications
- Monte Carlo integration
- Variational Monte Carlo
- Diffusion (Greens Function) Monte Carlo
- Improved methods, the Future

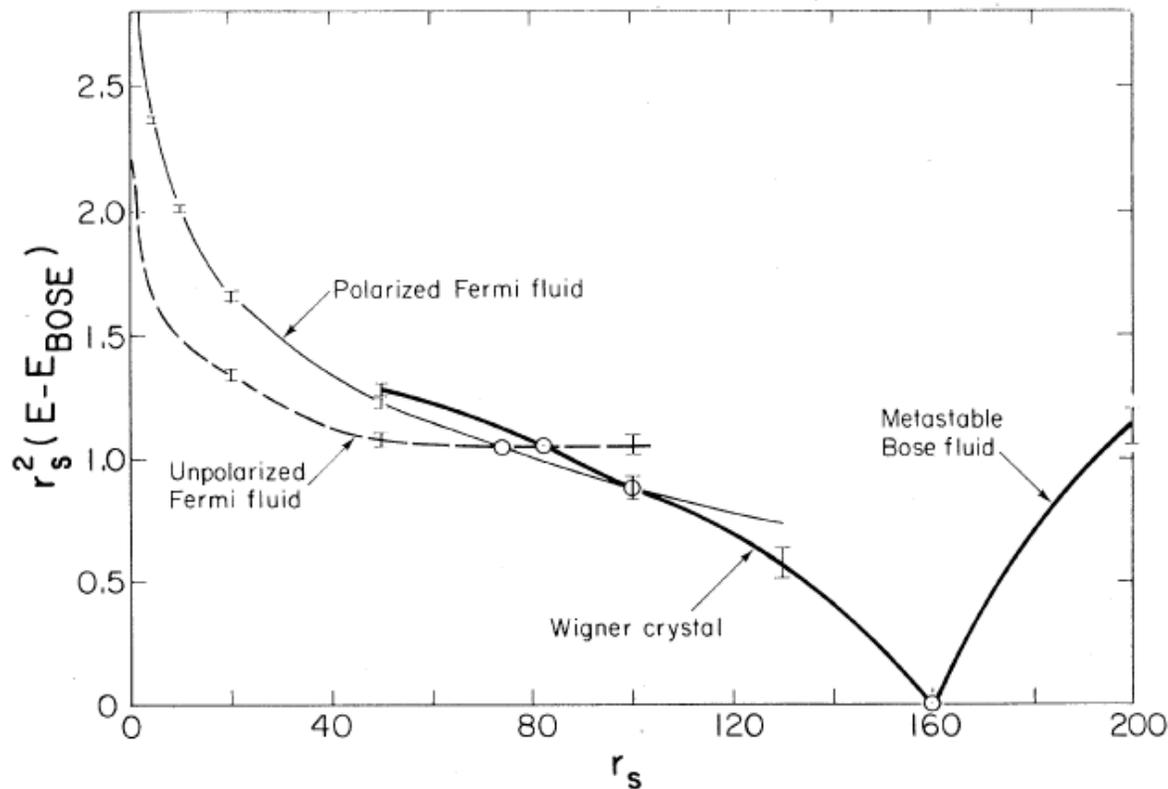
References

Hammond, Lester, and Reynolds. *Monte Carlo Methods in Ab Initio Quantum Chemistry*. World Scientific 1994
(Readable overview, pseudocode)

Foulkes, Mitas, Needs, Rajagopal. *Rev. Mod. Phys.* **73** 33 (2001)
(Recent review article on solid state calculations)

Homogeneous Electron Gas

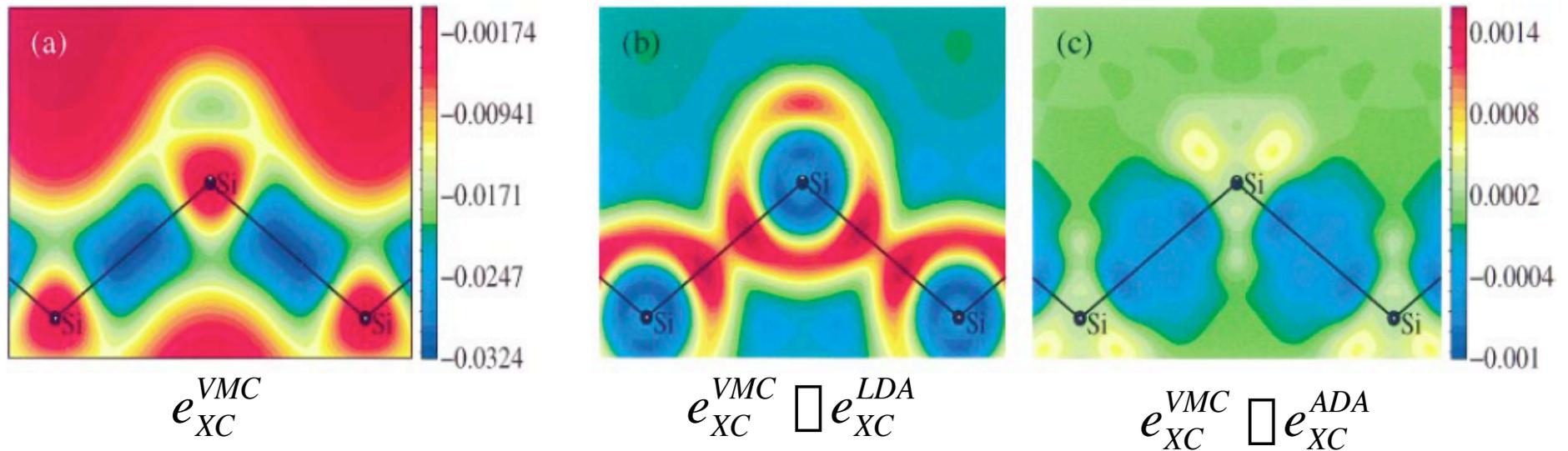
Ceperley and Alder. Phys. Rev. Lett. **45** 566 (1980)



- “Release node” QMC calculation of up to 246 electrons
- *Still* the most important QMC calculation:
 - Parameterised in the Local Density Approximation (LDA)

Exchange-Correlation in Real Materials

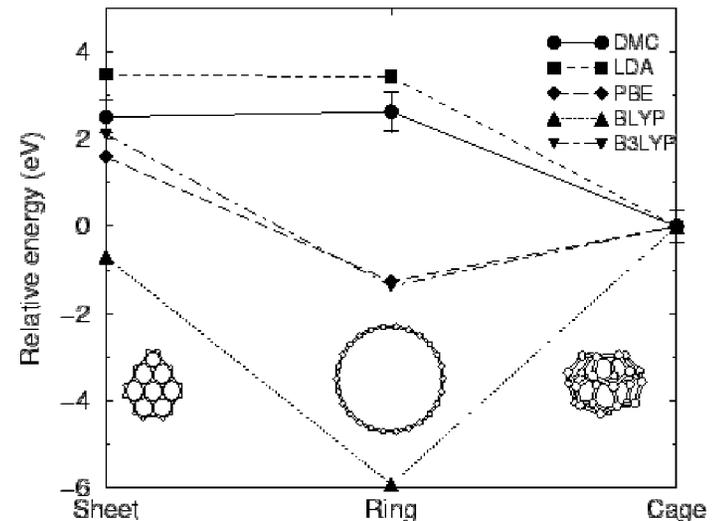
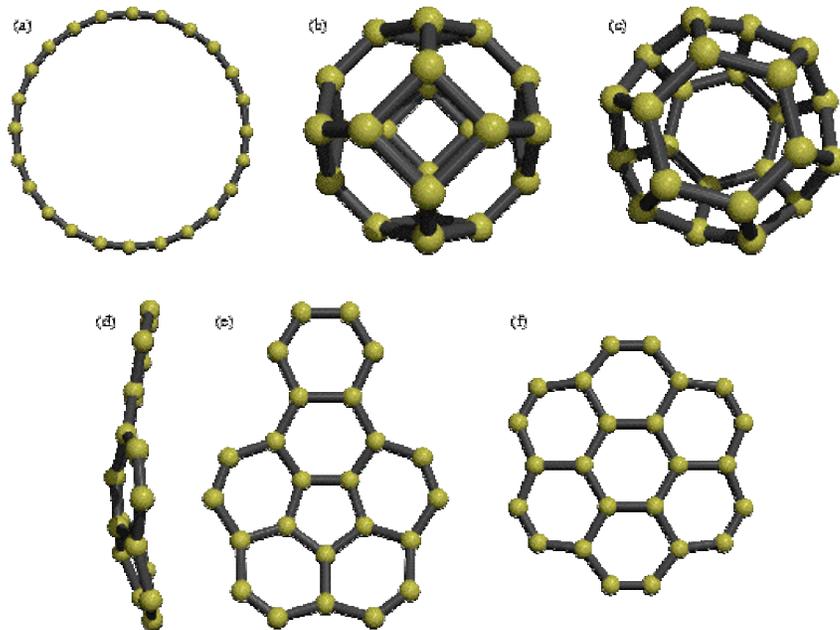
Hood et al. Phys. Rev. Lett. **78** 3350 (1997)



- Variational Monte Carlo study of exchange-correlation in bulk silicon
- LDA (centre) successful due to significant cancellation of errors
- ADA appears better - at least for silicon

Molecular Applications

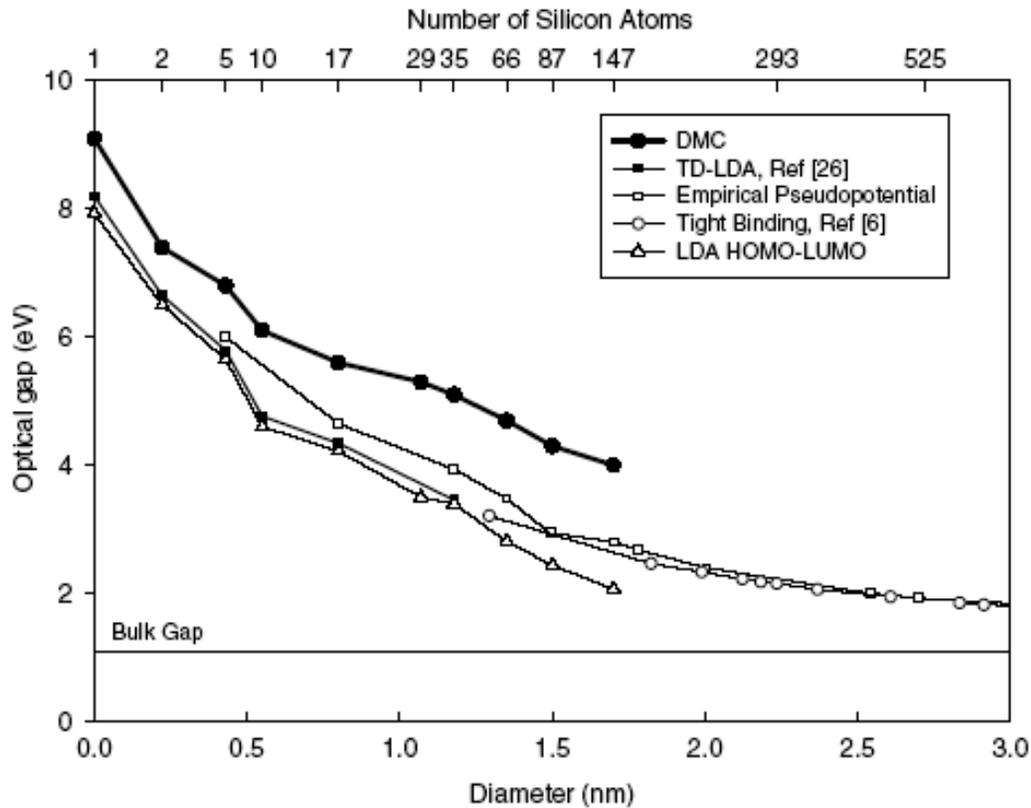
High precision total energy calculations of molecules, reactions



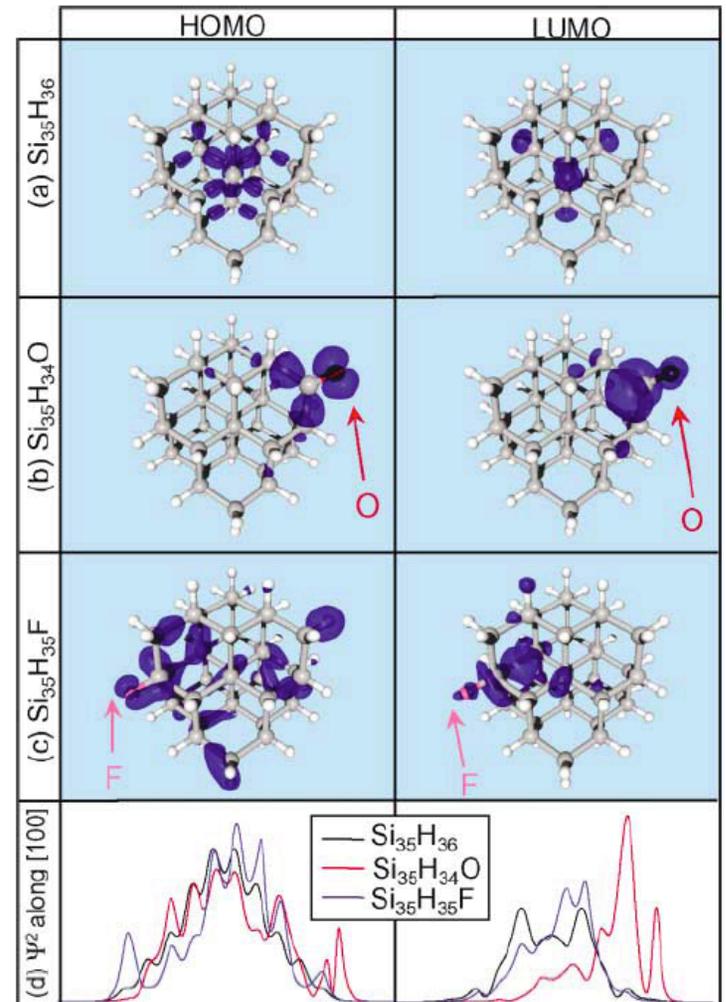
- 0.05 eV (0.0018 Ha, 1.2 kcal mol⁻¹) accuracy even for large systems
- Competitive with coupled cluster (CC) techniques
- Advantageous scaling (N^3 compared to CC - N^6), although linear methods may change this

Optical properties of Quantum Dots

Williamson et al. Phys. Rev. Lett. **89** 196803 (2002)



Phys. Rev. Lett. **88** 09741 (2002)



Variational Monte Carlo

A direct application of the variational principle:

$$E_0 \approx \int \psi_T^* \hat{H} \psi_T$$

1. How to perform the integration? (3N dimensions)
2. How to choose the trial wavefunction?

Monte Carlo Integration

$$F = \int_a^b f(x) dx$$

Approximate with N uniform samples: $F_N = \frac{b-a}{N} \sum_{i=1}^N f(\mathbf{X}_i)$

More efficient to sample non-uniformly if we can guess where f is large:

$$p(x) = \frac{w(x)}{\int_a^b w(x) dx} \quad F = \int_a^b g(x) p(x) dx = \frac{1}{M} \sum_{i=1}^M g(\mathbf{X}_i) \quad g=f/p$$

Better than numeric integration if we have many dimensions &/or we have good intelligence where f is large. Use the Metropolis algorithm (or variant) to generate the distribution $p(x)$.

Variational Monte Carlo

Form suitable for MC sampling:

$$E_0 \approx E_{VMC} = \frac{\int |\psi(\mathbf{X})|^2 \hat{H} \psi(\mathbf{X}) d\mathbf{X}}{\int |\psi(\mathbf{X})|^2 d\mathbf{X}}$$

$$E_{VMC} = \frac{1}{M} \sum_{i=1}^M \hat{H} \psi(\mathbf{R}_i) / \psi(\mathbf{R}_i) = \frac{1}{M} \sum_{i=1}^M E_L(\mathbf{R}_i)$$

where the points \mathbf{R} are sampled from $|\psi(\mathbf{R})|^2 / \int |\psi(\mathbf{R})|^2 d\mathbf{R}$

Note: for an exact eigenfunction E_L is a constant
Use fluctuations in E_L as guide to accuracy “intrinsic variance”

Trial Wavefunctions

Mean-field Hartree Fock determinants and correlated quantum chemistry wavefunctions provide a controlled starting point:

Slater-Jastrow wavefunction:
(explicitly antisymmetric/fermionic) $\Psi = \left[\Psi a_i D \right] e^J$

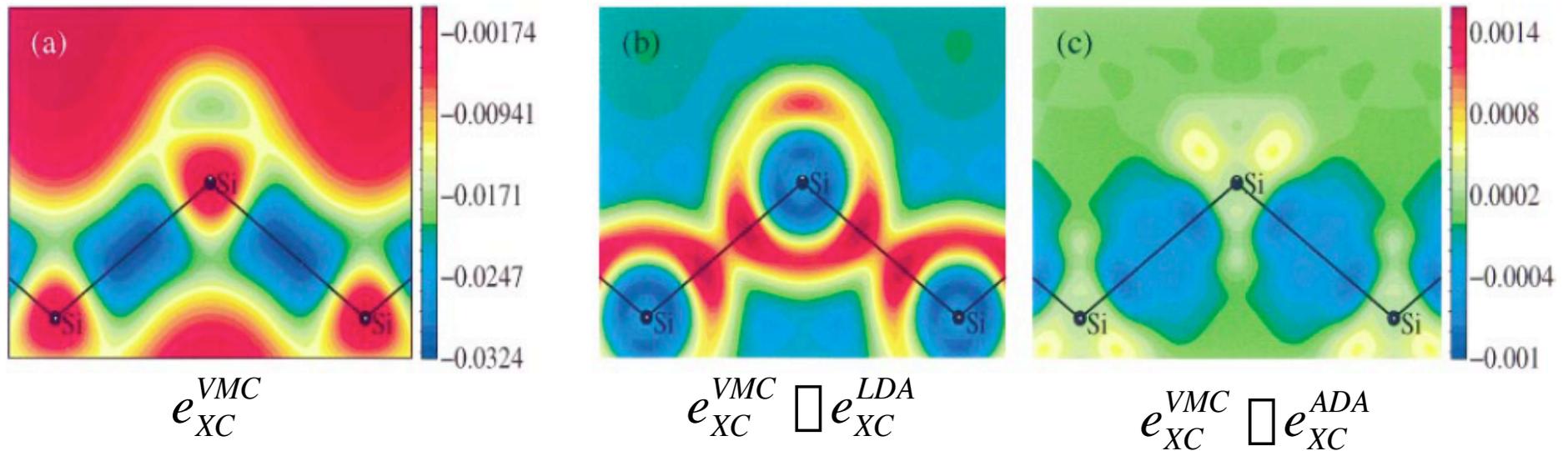
Jastrow factor: a polynomial parameterised in inter-particle distances.

Jastrow factor coefficients (typically 10-50) are determined via an iterative optimization procedure

e.g. variance minimization, energy minimization

Exchange-Correlation in Real Materials

Hood et al. Phys. Rev. Lett. **78** 3350 (1997)



- Variational Monte Carlo study of exchange-correlation in bulk silicon
- Many-body quantities computed from VMC wavefunction

Pair correlation function

$$g(\mathbf{r}, \mathbf{r}') = \frac{N(N-1)}{n(\mathbf{r})n(\mathbf{r}')} \int |\Psi(\mathbf{r}, \mathbf{r}', \mathbf{x}_3, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_3 \dots d\mathbf{x}_N$$

VMC Advantages

- Simple
- Reliably obtains 85% (solids) to 85-95% (atoms/molecules) of correlation energy
- Intrinsic error bars: statistical error and intrinsic variance.
Unique amongst electronic structure methods
- Easy to evaluate most QM operators

VMC Disadvantages

- “What you put in is what you get out”
 - Limited flexibility in current trial function forms
 - Don't expect to find new physics by accident
- Size scaling is N^3 , but Z scaling is $\sim Z^6$ (argued!)
- Unclear how to systematically improve current trial function forms - determinant expansions from quantum chemistry are too inefficient
- Computationally costly
- No reliable forces - yet
- You have to be a DFT/Q. Chemistry expert *and* a QMC expert

Diffusion Monte Carlo

Solve time dependent Schrodinger equation in imaginary time.

Projects out the exact many-body ground state from an initial trial wavefunction with few approximations. Variational (in principle).

Given $\psi = \sum_{i=0} c_i |\psi_i\rangle$ and $\hat{H} |\psi_i\rangle = \epsilon_i |\psi_i\rangle$ $\epsilon_{i+1} > \epsilon_i$

$$\frac{\partial \psi}{\partial \tau} = -\hat{H} \psi$$

Then

$$|\psi(\tau)\rangle = \sum_{i=0} c_i e^{-\epsilon_i \tau} |\psi_i\rangle$$

At large times, we are left with the ground state:

$$\lim_{\tau \rightarrow \infty} |\psi(\tau)\rangle = c_0 e^{-\epsilon_0 \tau} |\psi_0\rangle$$

Diffusion Process

Interpret ρ as density of diffusing particles: potential terms are rate terms increasing or decreasing the particle density.

$$\rho \frac{\partial \rho(\mathbf{R}, \Delta)}{\partial \Delta} = \sum_{i=1}^N \rho \frac{1}{2} \nabla_i^2 \rho(\mathbf{R}, \Delta) + (V(\mathbf{R}) - E_T) \rho(\mathbf{R}, \Delta)$$

Importance sampling

Introduce importance sampling for efficiency:

$$f(\mathbf{R}, \Delta) = \psi_T(\mathbf{R}) \rho(\mathbf{R}, \Delta)$$

A VMC optimized wavefunction is ideal.

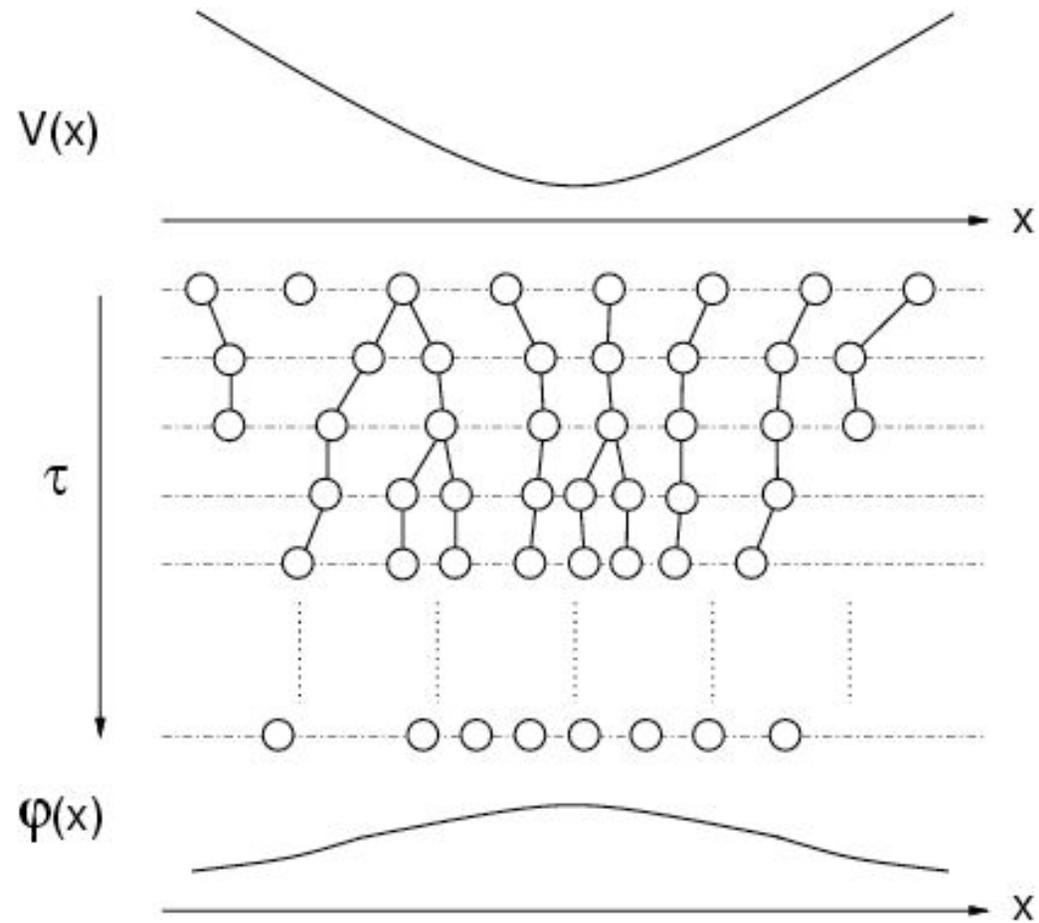
Fixed node approximation

Problem: Without constraints, ground state solution will not be fermionic

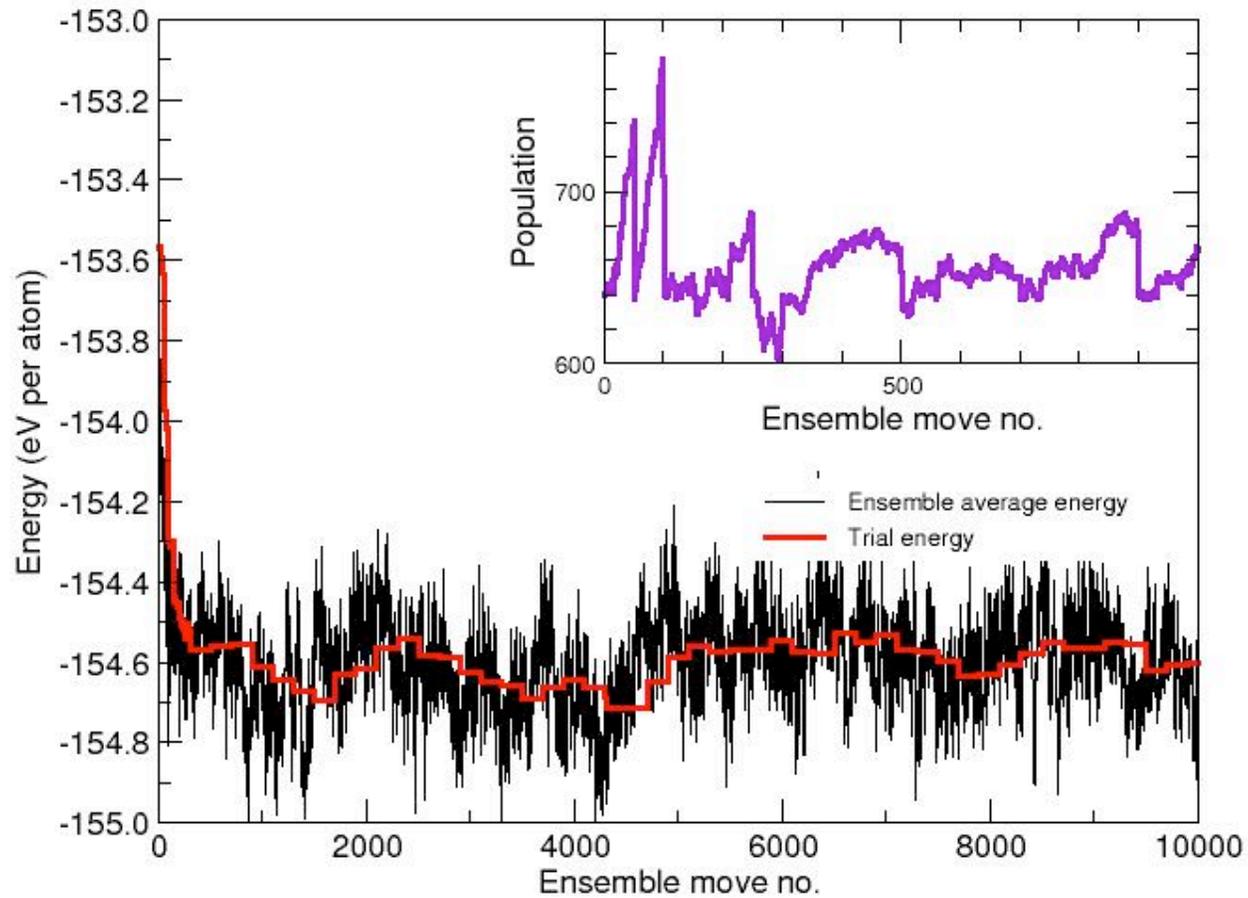
Solution: Impose “fixed nodes” (Anderson). Restrict solution to nodes of a trial function. Variational.

In practice: Use optimized VMC wavefunction (usually with DFT nodes) for importance sampling and fixed node approximation.

“Walker” Evolution



Bulk Diamond DMC



DMC In Practice

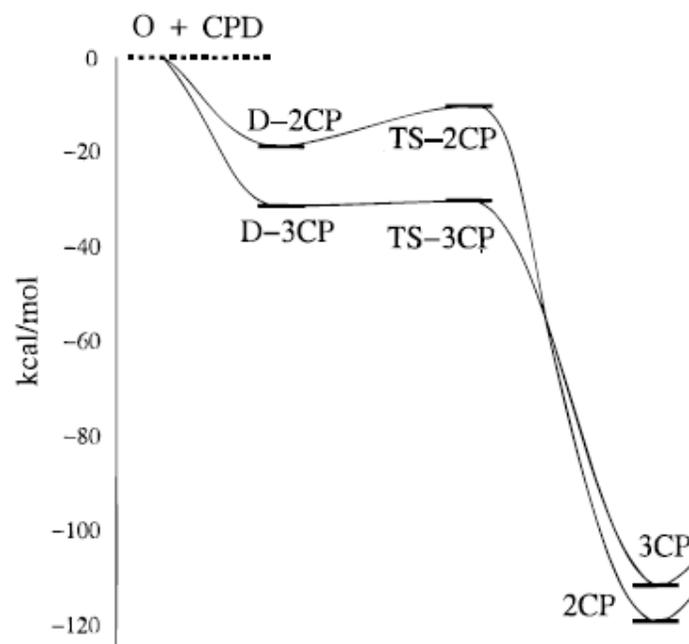
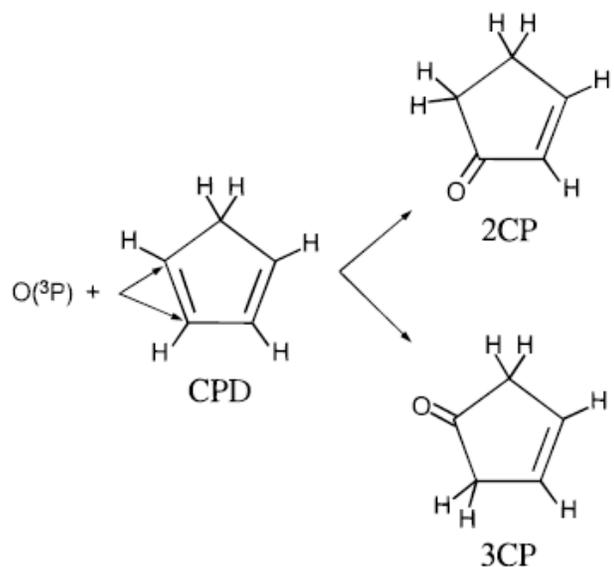
- In molecules, 95-98% of correlation energy obtained
- Similar? fraction of correlation energy in solids
- Properties hard to evaluate: density obtained is $\rho_0 \rho_T$
- Order of magnitude more expensive than VMC (depends)
- Finite size effects in supercell calculations add to computational cost
- Same scaling as VMC

Applications

Chemistry: Reaction paths, thermodynamics etc.

“roughly CCSD(T)/aug-cc-pVQZ” accuracy with
single Determinant

Grossman J. Chem Phys. **117** 1434 (2002)

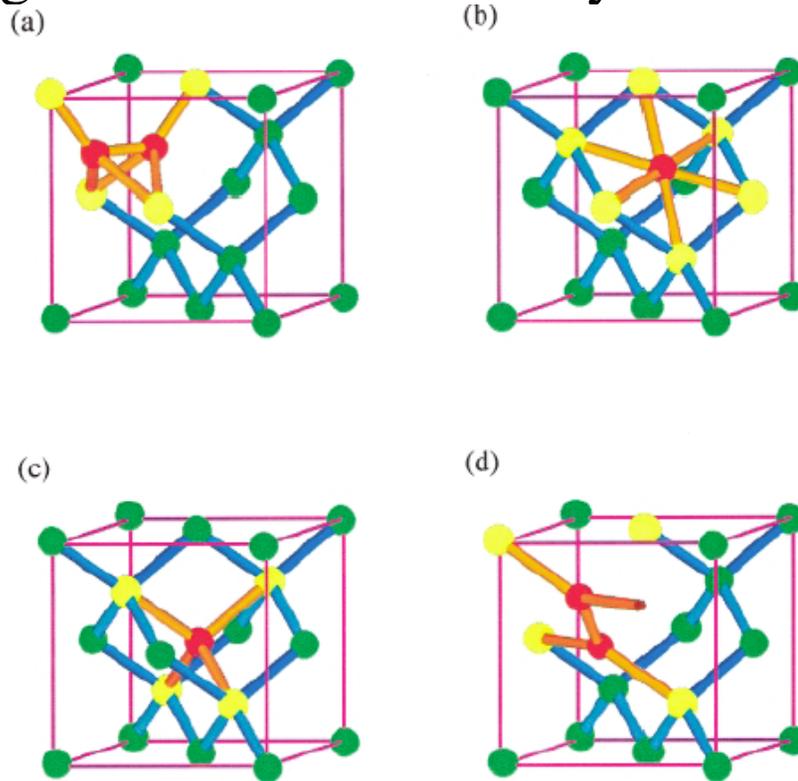


J. Am. Chem. Soc. **122** 705(2000)

Applications

Solid state: Defects calculations becoming tractable

e.g. Si self-interstitial Phys. Rev. Lett. **83** 2351 (1999)



54+1 atoms DMC

Obtained formation+migration energy in agreement with experiment

Improved DMC algorithms

Release node calculations

Only useful with excellent trial/guiding functions

Label “+” and “-” walkers and allow to cross nodes

Release node energy determined from *difference* in energies of “+” and “-” populations

H₂O in 1984

An exact fermion algorithm?

M. H. Kalos and F. Pederiva Phys. Rev. Lett. **85** 3547 (2000)

Still too costly

Others, e.g. AFMC

The Future

- Expect more “first row” and “simple semiconductor” results
- For real progress, need better wavefunctions: must optimize orbitals, their nodes, and functional form of trial functions.
- Well suited to grid computing, parasitic computing, PC hardware