Chair of Condensed Matter Physics
Institute of Theoretical Physics
Faculty of Physics, Universityof Warsaw

Summer Semester 2013

Lecture

Modeling of Nanostructures and Materials

Jacek A. Majewski

E-mail: Jacek.Majewski@fuw.edu.pl

Modeling of Nanostructures and Materials *Jacek A. Majewski*

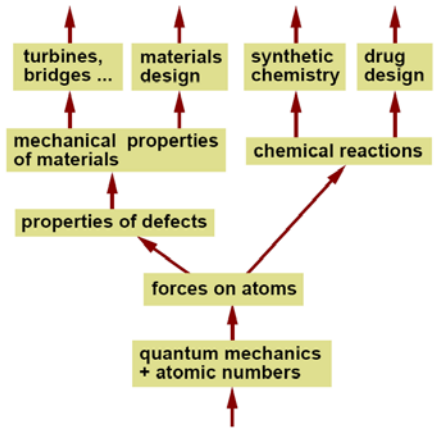
Nevill Gonzalez Szwacki

Lecture 9 – *April 28, 2014*

❖Quantum Monte Carlo Methods

e-mail: Jacek.Majewski@fuw.edu.pl

The Simulation Tree



Materials Science: Examples of Schrödinger Equation?

- Materials are composed of nuclei $\{Z_\alpha, M_\alpha, \vec{R}_\alpha\}$ and electrons $\{\vec{r}_i\}$
  → the interactions are known

$$H = -\sum_\alpha \frac{\hbar^2\nabla_\alpha^2}{2M_\alpha} - \sum_i \frac{\hbar^2\nabla_i^2}{2m} + \frac{1}{2}\sum_{\alpha,\beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{r}_i|} + \frac{1}{2}\sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Kinetic energy of nuclei — Kinetic energy of electrons — Nucleus-Nucleus interaction — Electron-Nucleus interaction — Electron-Electron interaction

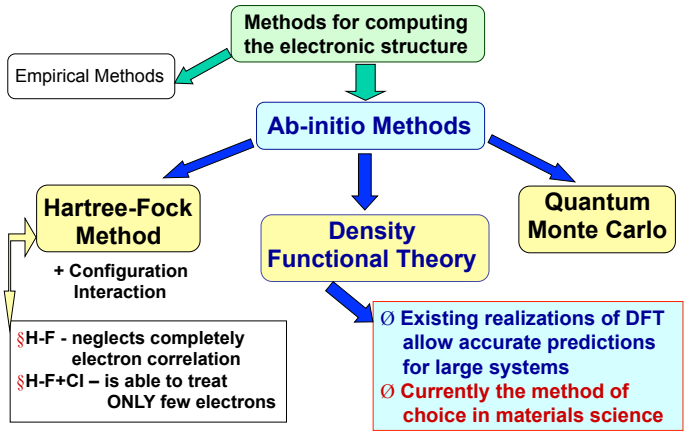
$$H\Psi = E\Psi$$

Ab-initio (first principles) Method –
ONLY Atomic Numbers $\{Z_i\}$ as input parameters

Quantum Monte-Carlo Method

- Efficient (and successful!) approaches to approximate the wave-function are already common in quantum chemistry and physics : **HF, CI, DFT**.
- In these approaches the integration reduces to one and two electron integrals.
- **Here we will present a different approach, namely Quantum Monte Carlo (QMC).**

Spectrum of Electronic Hamiltonian: What ab-initio methods do we have?



Quantum Monte Carlo Methods

Quantum Monte Carlo Methods are methods for solving quantum mechanical problems based on stochastic (or random) processes.

There are several QMC methods:

- ***Variational Monte Carlo (VMC)***
- ***Diffusion Monte Carlo (DMC)***
- Auxiliary-field Monte Carlo
- Path-integral Monte Carlo

W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal Rev. Mod. Phys. **73**, 33 (2001)

Variational Monte Carlo Method

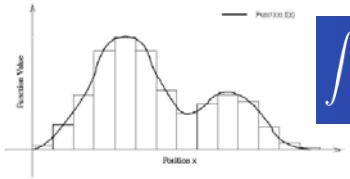
- In VMC one assumes a variational form of the trial wave-function, Ψ_T
- and evaluates the expectation value of the Hamiltonian in this state as the variational ground-state energy.

$$\langle E_\alpha \rangle = \frac{\int \Psi_T^* \hat{H} \Psi_T d\tau}{\int \Psi_T^* \Psi_T d\tau} \qquad \langle E_\alpha \rangle \geq E_0$$

- VMC thus provides an upper bound to the exact ground state energy.

Monte Carlo Integration

'Traditional' one-dimensional integration



$$\int f(x)dx \approx \sum_{i=1}^{m} \omega_i f(x_i)$$

- Traditional numerical integration techniques are virtually impossible for high-dimensional integration:

  The computational time scales as m^d **!!!**

$$d = 3N$$

(3 x number of particles)

Monte Carlo Integration (2)

- We now introduce a normalized function $g(x)$
- and may rewrite the integral as

$$\int \frac{f(x)}{g(x)} g(x)dx \approx \sum_{i=1}^{n} \omega_i' \frac{f(x_i)}{g(x_i)}$$

- Metropolis (1949) introduced a means to sample the points randomly from the distribution $g(x)$

  ➡ **the *Metropolis algorithm***

$$\int f(x)dx \approx \sum_{X \in g(x)} \frac{f(X)}{g(X)}$$

- where the points X are taken from the distribution $g(x)$

Monte Carlo Integration (3)

The Metropolis algorithm

1. *Given a starting point* X_n.
2. *Propose a random trial move* $X_t = X_n + \xi$.
3. *Acceptance ratio given by:* $r = min(1, \frac{g(X_t)}{g(X_n)})$
4. *Generate a random number* x *between* 0 *and* 1
5. *If* $x \leq r$ *accept move, else reject move.*

For integration *Sample the integrand* $I_{n+1} = \frac{f(X_{n+1})}{g(X_{n+1})}$.

Monte Carlo Integration (4)

- Steps 1-5 in the Metropolis algorithm creates a sequence of points $\underbrace{\{X_0, \ldots, X_n, \ldots\}}_{\text{called a } \textbf{\textit{walker}}}$
- Metropolis showed that a population of walkers will evolve according to the function $g(x)$, when n becomes large.

Monte Carlo integration scheme

1. *Randomize the starting position of walkers.*
2. *Move every walker by the Metropolis algorithm (steps1-5) a* **sufficient** *number of times.*
3. Sample *the integrand, and move walkers (steps 1-6).*
4. *Quit when the standard deviation is below a given level.*

Variational Monte Carlo Method

- The variational Monte Carlo simulation for a quantum many-particle system can be performed by an importance sampling with respect to the square of the normalized trial wavefunctions

$$g(R) = |\Psi_T(R)|^2 / \int dR\, |\Psi_T(R)|^2$$

a point in 3N-dimensional space

probability distribution function

- Since $\hat{H}$ is an operator the quantity that is averaged is the ***local energy*** $E_T(R) = \hat{H}(R)\Psi_T(R)/\Psi_T(R)$
- Ideally, if $\Psi_T(R)$ is the exact ground-state wavefunction the local energy $E_T(R)$ should be a constant.

Variational Monte Carlo Method

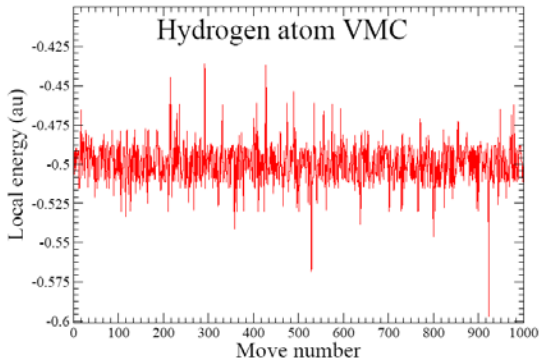
Local energy $E_T(R)$

$$E_{\mathrm{VMC}} = \frac{\int \Psi \hat{H} \Psi \, d\mathbf{R}}{\int \Psi^2 \, d\mathbf{R}} = \frac{\int \Psi^2 \left(\frac{\hat{H}\Psi}{\Psi} \right) d\mathbf{R}}{\int \Psi^2 \, d\mathbf{R}}$$

Average local energies $E_T(R)$ over the walk → $\mathbf{E_{VMC}}$.

Variational Monte Carlo Method

Local energy



Variational Monte Carlo Method

- Regarding the importance sampling, the trial ground-state energy is given by

$$E_T = \frac{1}{N_P} \sum_{i=1}^{N_P} E_T(R_i)$$

where N_P points R_i are sampled according to the square of the trial wavefunction (probability distribution function).

- In this way, provided enough points are taken to sample the distribution function, the resulting total energy converges to the exact trial energy with the standard deviation proportional to $1/\sqrt{N_P}$

Variational Monte Carlo Method

The trial wave-function

- So far, there has been no limitations on the trial wave-function, $\Psi_T(R)$
- However, for practical applications we need a good starting point
- The difficulty in the VMC method is the appropriate choice of the trial function $\Psi_T(R)$

It must have the proper symmetry

- antisymmetric for Fermions (symmetric for Bosons)
- must be an eigenstate of all operators that commute with Hamiltonian

Variational Monte Carlo Method

Jastrow function

R. Jastrow, Phys. Rev. **98**, 1479 (1955).

$$\Psi_T = D(R)\, exp\left[-\frac{1}{2}\sum_{i<j} u(r_{ij})\right]$$

Slater-determinant part (HF or DFT)

Jastrow factor

The ***Jastrow factor*** is introduced to build in correlation effects

Contains two-body or three-body terms and up to 30 parameters that could be varied to minimize the ground state energy

Variational Monte Carlo Method

Problems and challenges:

1. Creating accurate trial wave-functions that are fast to evaluate. (fermion calculations take much more CPU time and memory than boson calculations)
2. Efficient energy (or variance) minimization schemes.
3. Sample the whole state space.
4. Auto-correlation effects.
5. Creating the correct nodal structure.

- **The accuracy of VMC is rather limited.**
- **VMC is most efficiently used in conjunction with DMC.**

Diffusion Monte Carlo (DMC) Method

- The DMC method is based on rewriting the Schrödinger equation in imaginary time, $\tau = it$

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

- This equation looks like a diffusion equation, and its effect is to converge the initial wavefunction to the ground state

Diffusion Monte Carlo Method

- Diffusion Monte Carlo (DMC) is a stochastic projector method for solving the imaginary-time many-body Schrödinger equation,

$$-\partial_t \Phi(\mathbf{R},t) = (\hat{H} - E_T)\Phi(\mathbf{R},t)$$

$$\Phi(\mathbf{R},t+\tau) = \int G(\mathbf{R}\leftarrow\mathbf{R}',\tau)\Phi(\mathbf{R}',t)d\mathbf{R}'$$

where $G(\mathbf{R}\leftarrow\mathbf{R}',\tau) = \langle\mathbf{R}|\exp[-\tau(\hat{H}-E_T)]|\mathbf{R}'\rangle$

is a Green's function that obeys the same equation as the wave function

$$-\partial_t G(\mathbf{R}\leftarrow\mathbf{R}',t) = (\hat{H}(\mathbf{R}) - E_T)G(\mathbf{R}\leftarrow\mathbf{R}',t)$$

with the initial condition $G(\mathbf{R}\leftarrow\mathbf{R}',0) = \delta(\mathbf{R}-\mathbf{R}')$

Diffusion Monte Carlo Method

Using the spectral expansion

$$\exp(-\tau\hat{H}) = \sum_i |\Psi_i\rangle\exp(-\tau E_i)\langle\Psi_i|$$

one can express the Green's function as

$$G(\mathbf{R}\leftarrow\mathbf{R}',\tau) = \sum_i \Psi_i(\mathbf{R})\, e^{-\tau(E_i-E_T)}\, \Psi_i^*(\mathbf{R}')$$

where $\{\Psi_i\}$ and $\{E_i\}$ denote the complete sets of eigenfunctions and eigenvalues of $\hat{H}$, respectively.

Diffusion Monte Carlo Method

- It is straightforward to show that as $\tau\to\infty$

the operator $\exp[-\tau(\hat{H}-E_T)]$

projects out the lowest eigenstate $|\Psi_0\rangle$

that has nonzero overlap with the chosen initial state

$$|\Phi(t=0)\rangle = |\Phi_{\text{init}}\rangle$$

- The imaginary-time development is just a mathematical trick used to convert an arbitrary starting state into the ground state without assuming any particular functional form.

Diffusion Monte Carlo Method

$$\lim_{\tau\to\infty}\langle\mathbf{R}|\exp[-\tau(\hat{H}-E_T)]|\Phi_{\text{init}}\rangle$$

$$= \lim_{\tau\to\infty}\int G(\mathbf{R}\leftarrow\mathbf{R}',\tau)\Phi_{\text{init}}(\mathbf{R}')d\mathbf{R}'$$

$$= \lim_{\tau\to\infty}\sum_i \Psi_i(\mathbf{R})\exp[-\tau(E_i-E_T)]\langle\Psi_i|\Phi_{\text{init}}\rangle$$

$$= \lim_{\tau\to\infty}\Psi_0(\mathbf{R})\exp[-\tau(E_0-E_T)]\langle\Psi_0|\Phi_{\text{init}}\rangle.$$

Diffusion Monte Carlo Method

- By adjusting E_T to equal E_0, one can make the exponential factor in the last line constant, while the higher states in the previous line are all exponentially damped because their energies are higher than E_0

- This fundamental property of the projector

$$\exp[-\tau(\hat{H}-E_T)]$$

is the basis of the diffusion Monte Carlo method and similar projector-based approaches.

Diffusion Monte Carlo Methods

Possible choice of the Green's function

$$G(\mathbf{R}',\mathbf{R},\delta\tau) = (2\pi\delta\tau)^{-\frac{3N}{2}}\exp\left[-\left(\frac{\mathbf{R}'-\mathbf{R}-\delta\tau\mathbf{F}(\mathbf{R})}{2\delta\tau}\right)^2\right]$$
$$\times\exp\left[-\delta\tau\left(\frac{E_{\rm L}(\mathbf{R})+E_{\rm L}(\mathbf{R}')}{2}-E_{\rm T}\right)\right]$$

Quantum Monte Carlo Simulations

CASINÒ

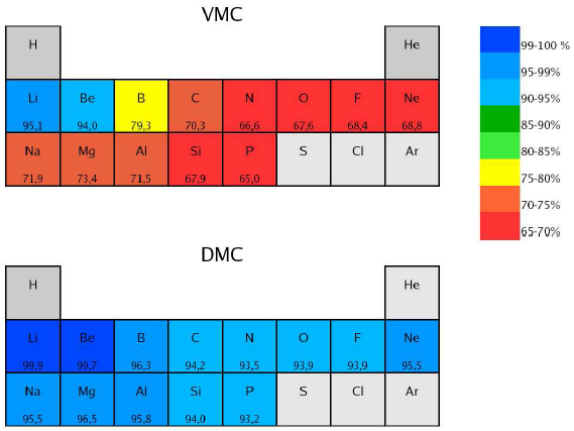
The Cambridge Quantum Monte Carlo Code

R.J Needs, M.D. Towler, N.D. Drummond, P.R.C. Kent

Can treat atoms, molecules, polymers, slabs, solids, 2D/3D electron phases and 2D/3D electron-hole phases.

www.tcm.phy.cam.ac.uk/~mdt26/casino.html

QMC – Atomic Results: Correlation Energy



QMC – Atomic Results: Correlation Energy

VMC

Jastrow-factor	Be	Mg
Two-body	94.00(1)	73.4(2)
Three-Body	97.54(5)	88.0(1)

DMC

Jastrow-factor	Be	Mg
Two-body	99.73(3)	96.5(2)
Three-Body	99.89(1)	96.8(1)

QMC – Atomic Results: Correlation Energy

Atom	Method	Orb. type	Total energy (a.u.)	E_c
	HF	G	−2.86165214	0 %
	HF	N	−2.86168000	0 %
	VMC	G	−2.903499(8)	99.5 %
He	VMC	N	−2.903527(9)	99.5 %
	DMC	G	−2.903732(5)	100 %
	DMC	N	−2.903719(2)	100 %
	"Exact"[27]	-	−2.903724	100 %

G – Gaussians, N – numerial orbitals

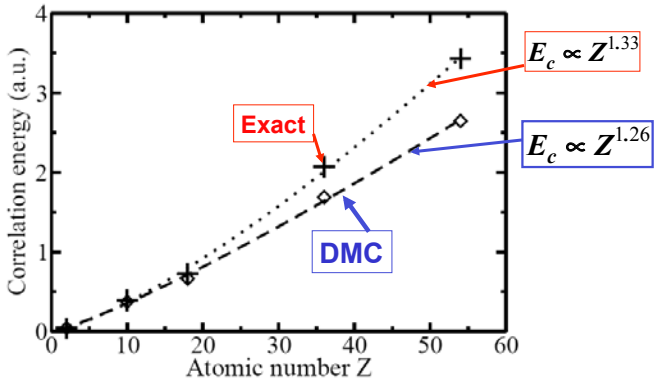
QMC – Atomic Results: Correlation Energy

	HF	G	−128.53832860	0 %
	HF	N	−128.54709811	0 %
	VMC	G	−128.8794(4)	85 %
Ne	VMC	N	−128.891(5)	88 %
	DMC	G	−128.9232(5)	96 %
	DMC	N	−128.9231(1)	96 %
	"Exact"[28]	-	−128.939	100 %

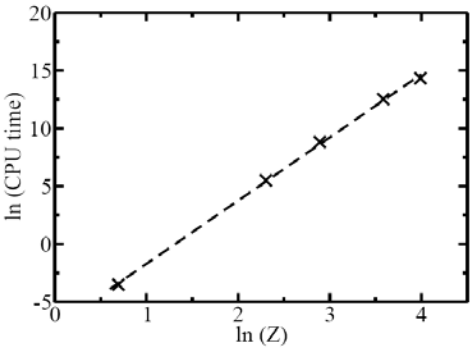
QMC – Atomic Results: Correlation Energy

	HF	N	−2752.05497715	0 %
Kr	VMC	N	−2753.2436(6)	57 %
	DMC	N	−2753.7427(6)	82 %
	"Exact"[30]	-	−2754.13	100 %
	HF	N	−7232.13836331	0 %
Xe	VMC	N	−7233.700(2)	46 %
	DMC	N	−7234.785(1)	77 %
	"Exact"[30]	-	−7235.57	100 %

Correlation Energy for Atoms as a Function of Atomic Number Z



Computational Burden of DMC for Atoms



- The dashed line shows the fitted scaling of $Z^{5.47}$
- The CPU times are measured in seconds.

The logarithm of the CPU time required to obtain a fixed error bar in the energy versus ***ln(Z)*** for **DMC** calculations.

Cohesive Energy of Solids

Possible calculations involving up to 2000 electrons

Table 1. The Cohesive Energy of Ge Obtained Using Three Different Methods

Method Used	Cohesive Energy (eV/atom)
LDA Calculation	4.59
Diffusion QMC Calculation	3.85
Experiment	3.85

W. M. C. Foulkes, M. Nekovee, R. L. Gaudoin, M. L. Stedman, R. J. Needs, R. Q. Hood, G. Rajagopal, M. D. Towler, P. R. C. Kent, Y. Lee, W.-K. Leung, A. R. Porter, and S. J. Breuer

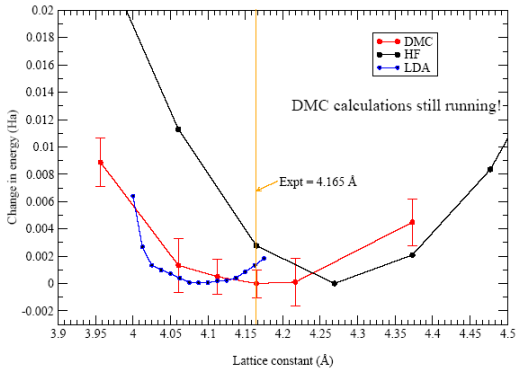
Blackett Laboratory, Imperial College
Cavendish Laboratory, Cambridge University

Cohesive Energy of Solids

Method	Si	Ge	C	BN	NiO
LDA	5.28	4.59	8.61	15.07	10.96
VMC	4.48±0.01	3.80±0.02	7.36±0.01	12.85±0.09	8.57±0.01
	4.38±0.04		7.27±0.07		
	4.82±0.07				
DMC	4.63±0.02	3.85±0.02	7.346±0.006	-	9.44±0.01
Exp.	4.62±0.08	3.85	7.37	12.9	9.45

Units: eV per atom Si/Ge/C and eV per 2 atoms BN/NiO

NiO lattice constant



Mike Towler, Theory of Condensed Matter Group, Cavendish Laboratory
University of Cambridge

Silicon Defect Formation Energies

Defect	LDA	GGA	DMC
Split–⟨110⟩	3.31	3.84	4.96(28)
Hexagonal	3.31	3.80	4.82(28)
Tetrahedral	3.43	4.07	5.40(28)

LDA, GGA and DMC formation energies in eV of the self-interstitial defects

Quantum Monte Carlo

- **VMC** using Slater-Jastrow wave functions with ~30 variational parameters can recover between 75 and 85% of the valence correlation energy, and **DMC** calculations can recover roughly 95% plus.
- In solids, **QMC is the *only* practical method** based on many-body correlated wave functions, the variational principle, and the many-electron Schrödinger equation. It is now the method of choice for tackling large quantum many-body problems.

Quantum Monte Carlo

- Efficient implentations of VMC and DMC for finite and periodic systems have been made in the computer program CASINO (and few other codes). Much remains to be done to make QMC as flexible and easy to use as traditional methods.
- With its emphasis on many-electron wave functions and probabilities, QMC has shown that it is possible to study interacting electrons in real solids using very direct computational techniques.
  There is no need to resort to perturbation theory or mean-field approximations.

Quantum Monte Carlo & Molecular Dynamics

PRL 94, 056403 (2005) PHYSICAL REVIEW LETTERS week ending 11 FEBRUARY 2005

Efficient Quantum Monte Carlo Energies for Molecular Dynamics Simulations

Jeffrey C. Grossman
Lawrence Livermore National Laboratory, 7000 East Avenue L-415, Livermore, California 94550, USA

Lubos Mitas
Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202, USA
(Received 27 August 2004; published 10 February 2005)

A method is presented to treat electrons within the many-body quantum Monte Carlo (QMC) approach "on-the-fly" throughout a molecular dynamics (MD) simulation. Our approach leverages the large (10–100) ratio of the QMC electron to MD ion motion to couple the stochastic, imaginary-time electronic and real-time ionic trajectories. This continuous evolution of the QMC electrons results in highly accurate total energies for the full dynamical trajectory at a fraction of the cost of conventional, discrete sampling. We show that this can be achieved efficiently for both ground and excited states with only a modest overhead to an *ab initio* MD method. The accuracy of this dynamical QMC approach is demonstrated for a variety of systems, phases, and properties, including optical gaps of hot silicon quantum dots, dissociation energy of a single water molecule, and heat of vaporization of liquid water.

DOI: 10.1103/PhysRevLett.94.056403 PACS numbers: 71.15.Pd, 31.25.–v, 71.15.Nc, 71.15.Mb

A (QMC) song …

He deals the cards to find the answers
the secret geometry of chance
the hidden law of a probable outcome
the numbers lead a dance

Sting: Shape of my heart

Dario Bressanini
Universita' dell'Insubria, Como, Italy
http://www.unico.it/~dario

Thank you !