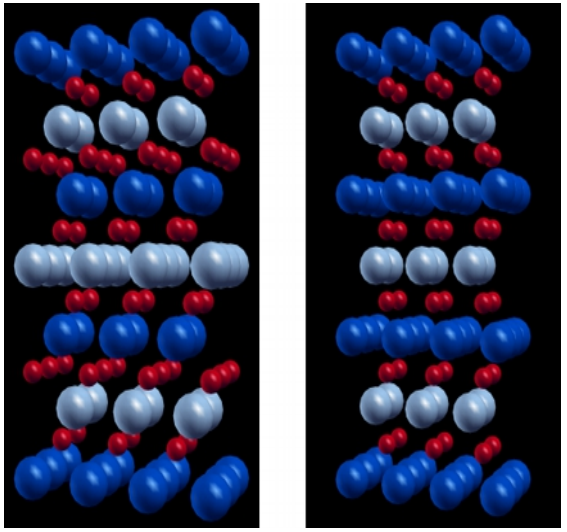
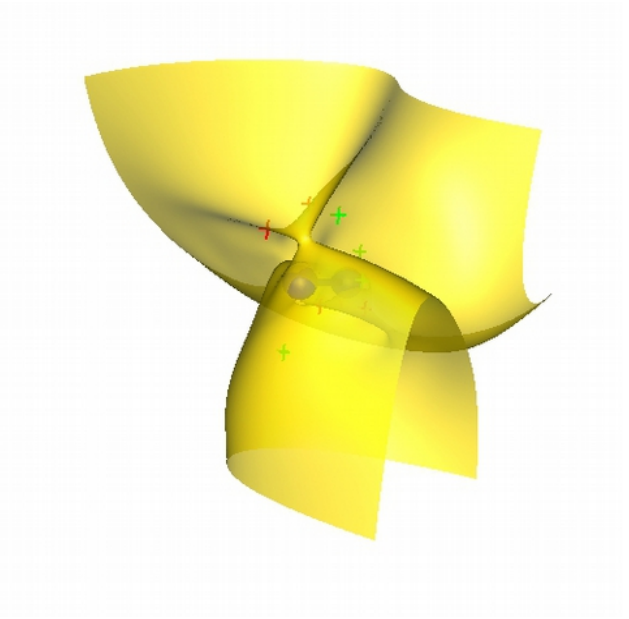
Quantum Monte Carlo: method, applications, impact, relation to quantum computing





Lubos Mitas
North Carolina State University

Sep. 22, 2018

NC STATE UNIVERSITY

Lubos_Mitas@ncsu.edu

The Theory of Everything

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

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

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

* Air	* Steel	* Paper	* Vitamins
* Water	* Plastic	* Dynamite	* Ham Sandwiches
* Fire	* Glass	* Antifreeze	* Ebola Virus
* Rocks	* Wood	* Glue	* Economists
* Cement	* Asphalt	* Dyes	* ...

Robert Laughlin: Nobel Prize Talk, viewgraph #2

Properties of matter: molecules, liquids, solids, ...
→ stationary Schrodinger equation

Hamiltonian of interacting electrons and nuclei

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

Stationary Schrodinger equation

$$H\,\psi_k(\boldsymbol{R}) = E_k\,\psi_k(\boldsymbol{R}) \qquad \boldsymbol{R} = (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$$

Solutions, ie, the spectrum $\{E_k, \psi_k\}_{k=0}^{k=\infty}$ **provides:**

- stability/cohesion, eqs. of state, phase diagrams, magnetic order
- excitations: optical properties, transport, responses, T>0, ...

→ key inputs for subsequent methods (atomistic, etc)

Lubos_Mitas@ncsu.edu

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

Paul Dirac, ~ 1930

Lubos_Mitas@ncsu.edu

challenges

- real systems: many interacting particles ↔ multi-D problem
  since they are indistinguishable:
  H_2O molecule → 30 dimensions
  tiny drop of water → effectively infinite dimensionality

- spatial, spin and other fundamental symmetries, eg, spin, spatial, and

  fermion antisymmetry $\Psi_n(\ldots, \boldsymbol{r}_i^{\uparrow}, \ldots, \boldsymbol{r}_j^{\uparrow}, \ldots) = -\Psi_n(\ldots, \boldsymbol{r}_j^{\uparrow}, \ldots, \boldsymbol{r}_i^{\uparrow}, \ldots)$

- required accuracy for the solutions is astonishingly high:

  total energy per relevant degree of freedom ~ 10^2 - 10^3 eV
  while one needs incredibly high resolution to "read off" the energy →

Lubos_Mitas@ncsu.edu

challenges II

- required accuracy:

~ 0.01 % ↔ 0.1eV ~ 1000K for cohesion, reactions
~ 0.001% ↔ 0.01eV ~ 100K magnetic states
~ 0.0001% ↔ 0.001eV ~ 10K superconductivity
~ 0.00001% ↔ 0.0001eV ~ 1K heavy fermions etc

→ eight, nine, etc … accurate digits !!!

→ this accuracy is inherent here: the most accurate measured constant is e^2/h: 12 exact digits !!! (quantum Hall effect)

Lubos_Mitas@ncsu.edu

traditional methods: Density Functional Theory and (post)-Hartree-Fock

Forget about the wavefunction, that's too difficult ... and reformulate as a functional of one-particle density

$$E_{tot} = \int F[\rho(\boldsymbol{r})]\, d\,\boldsymbol{r} \quad \rightarrow$$ **effectively a one-particle problem**

Troubles: - the exact functional F is unknown → approximations
- systematic accuracy and improvements are problematic

Expand the wave function in one-particle orbitals: Hartree-Fock (HF)

$$\Psi_{HF}(\boldsymbol{r}_1, \boldsymbol{r}_2, ...) = A_{antisymm}[\prod_i \Phi_j(\boldsymbol{r}_i)] = det[\{\Phi_j(\boldsymbol{r}_i)\}]$$

but missing many-body effects → correlation → $E_{corr} = E_{exact} - E_{HF}$

Post-HF improvements $\Psi_{correlated}(\boldsymbol{r}_1, \boldsymbol{r}_2, ...) = \sum_n d_n\, det_n[\{\Phi_i(\boldsymbol{r}_j)\}]$

Troubles: - costly, slow convergence
- can be accurate but inefficient

Lubos_Mitas@ncsu.edu

one idea: project out the ground state → "imaginary time" Schr. eq. (Schroedinger 1930, Fermi 1933)

$$\psi(\boldsymbol{R},t)=\exp(-tH)\psi_T(\boldsymbol{R}) \quad \rightarrow \quad \psi(\boldsymbol{R},t\rightarrow\infty) \propto \phi_0(\boldsymbol{R})$$

projector in parameter t

trial wave function

ground state of of given symm., exponentially fast

Projection equation in a differential form ("imaginary time" Sch. eq.)

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

or in an integral, evolution-like, form

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

Green's function $G(\boldsymbol{R},\boldsymbol{R}',\tau)=\langle \boldsymbol{R}|\exp(-\tau H)|\boldsymbol{R}'\rangle$ **→ transition probability**

Lubos_Mitas@ncsu.edu

quantum Monte Carlo (QMC) in a nutshell

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

but high dimensionality makes ordinary numerical methods useless …

Idea: **map the evolution of the many-body wave function onto an equivalent stochastic process (can be efficiently simulated)**

- **value of the wavefunction ↔ density of sampling points in 3ND-space**

$$\psi(\boldsymbol{R}, t) \longleftrightarrow dens\left[\sum_i^{walkers} \delta(\boldsymbol{R} - \boldsymbol{R}_i(t))\right]$$

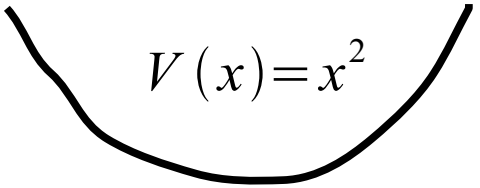
sampling points → "walkers" → eigenstates of position operator

- **find the Green's function G for small τ**
- **iterate in time → propagate the walkers with G as trans. prob.**

Lubos_Mitas@ncsu.edu

toy model: 1D harmonic oscillator

$$H = T_{kin} + V(x)$$



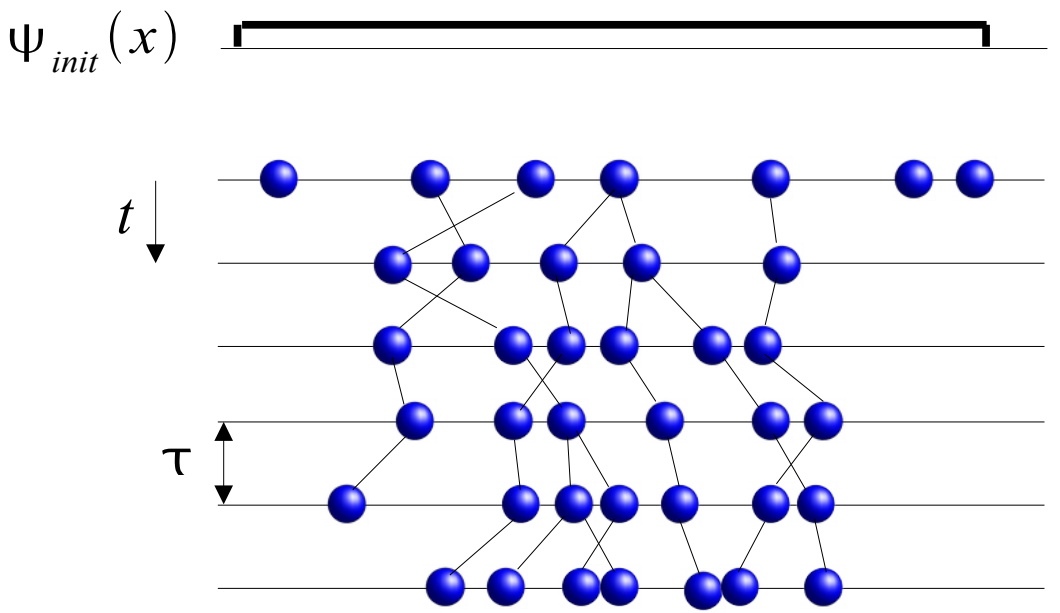
Propagator

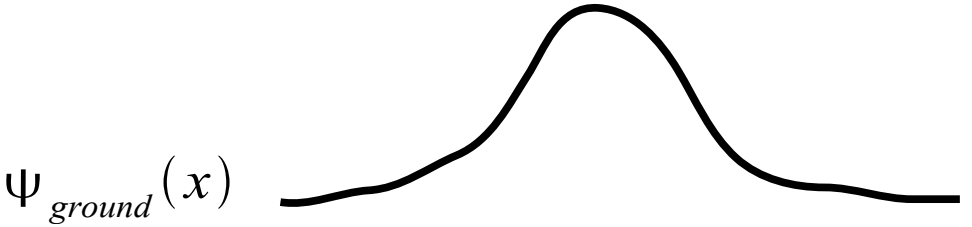
$$G(x, x', \tau)$$

$$\downarrow$$

$$C\, e^{-(x-x')^2/2\tau} \cdot e^{-(V(x)-E_T)\tau}$$

diffusion weight





Lubos_Mitas@ncsu.edu

movie on sampling of H_2 molecule

Lubos_Mitas@ncsu.edu

… but a fundamental problem has been swept under the rug

Lubos_Mitas@ncsu.edu

fermion sign problem

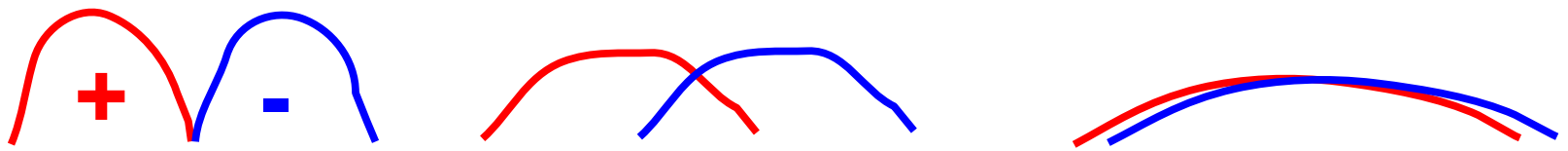
Naïve approach for fermionic wave functions: decompose to + and -

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

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

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

However, + and - components converge independently to the lowest energy solution (which is symmetric/bosonic) because Schr. eq. is linear!



$$lim_{t\to\infty}\,\Psi^+(\boldsymbol{R},t) - lim_{t\to\infty}\,\Psi^-(\boldsymbol{R},t) \;\propto\; \exp\left[-(E_{Fermionic} - E_{Bosonic})\,t\right]$$

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

Lubos_Mitas@ncsu.edu

importance sampling and fixed-node diffusion Monte Carlo (FNQMC)

Consider a product: $f(\boldsymbol{R},t)=\psi_T(\boldsymbol{R})\phi(\boldsymbol{R},t)$

and modify Schr. eq. accordingly $f(\boldsymbol{R},t+\tau)=\int G^*(\boldsymbol{R},\boldsymbol{R}',\tau)f(\boldsymbol{R}',t)d\boldsymbol{R}'$

so that $f(\boldsymbol{R},t\to\infty)\ \propto\ \psi_T(\boldsymbol{R})\phi_{ground}(\boldsymbol{R})$

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

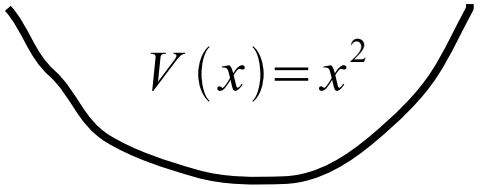
Fixed-node (FN) approximation: $f(\boldsymbol{R},t)>0$

- **antisymmetry (nonlocal) replaced by a boundary (local)**
- **accuracy determined by the nodes of** $\psi_T(\boldsymbol{R})$
- **exact node implies recovering exact energy (in almost polynomial time)**

Lubos_Mitas@ncsu.edu

fermion node toy model: excited state of harmonic oscillator

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



Propagator

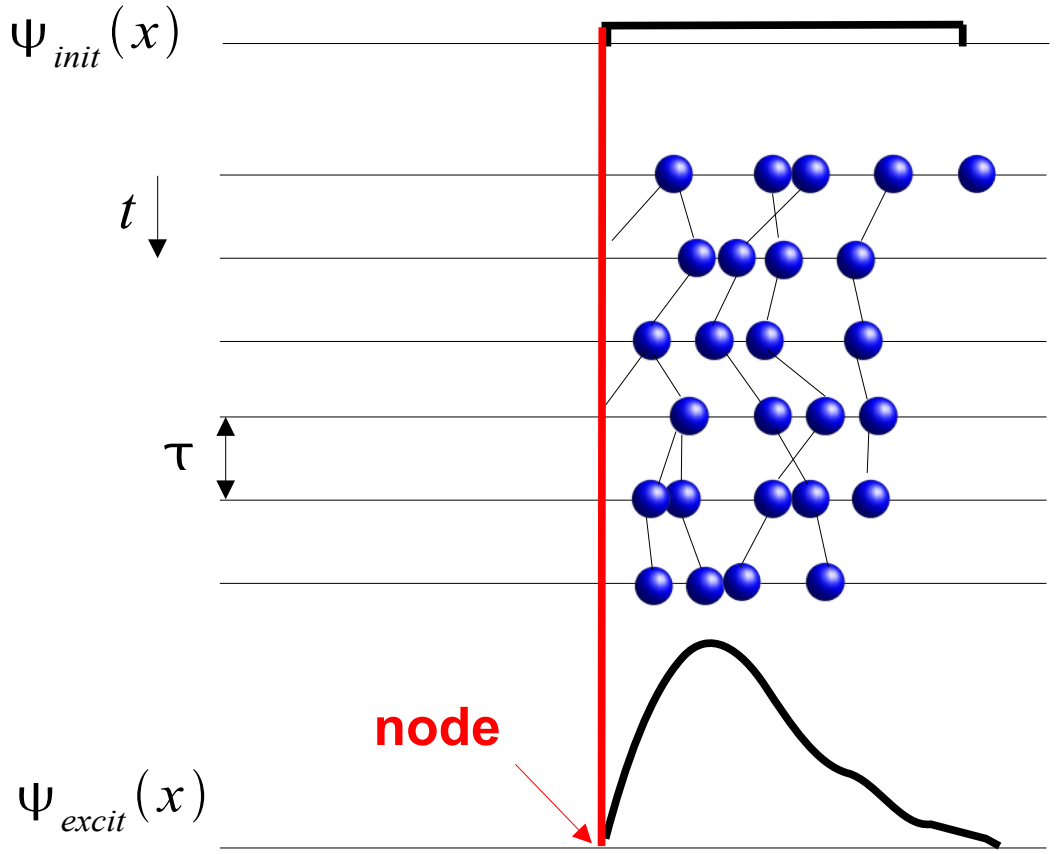
$$G(x, x', \tau)$$

$$\downarrow$$

$$C\, e^{-(x-x')^2/2\tau} \cdot e^{-(V(x)-E_T)\tau}$$

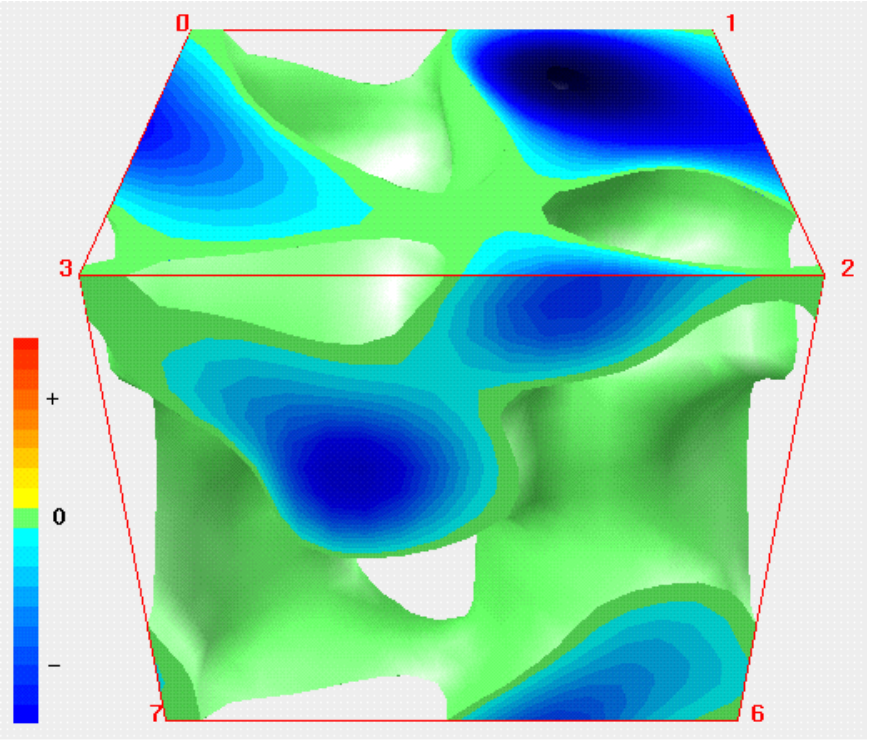
diffusion **renorm**

+ boundary condition (evaluate trial function)



Lubos_Mitas@ncsu.edu

fixed-nodes in reality: complex, impossible to "fully see", ..., but, when done right, unexpectedly effective and accurate!



Green surface: 3D subset of 59-dimensional fermion node hypersurface

- difficult to parametrize with arbitrary accuracy but systematically improvable

- rather simple wave functions lead to remarkably high accuracy (sometimes beyond expectations)

- easy to enforce, eg, evaluate the sign of a determinant

Lubos_Mitas@ncsu.edu

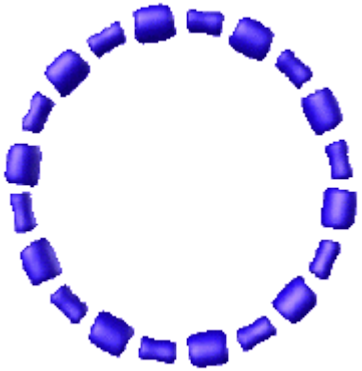
how does it work ?

let us look at some applications

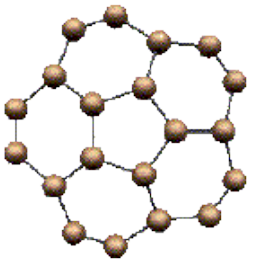
Lubos_Mitas@ncsu.edu

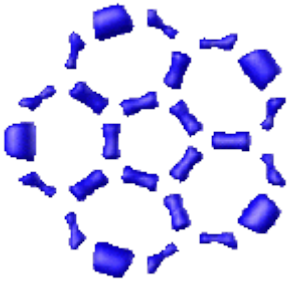
application example: which is the lowest energy isomer of C_{20} ???

ring

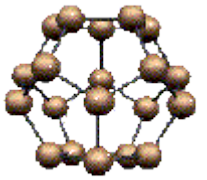


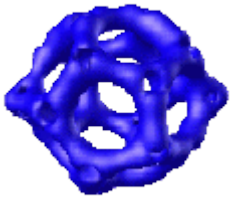
bowl





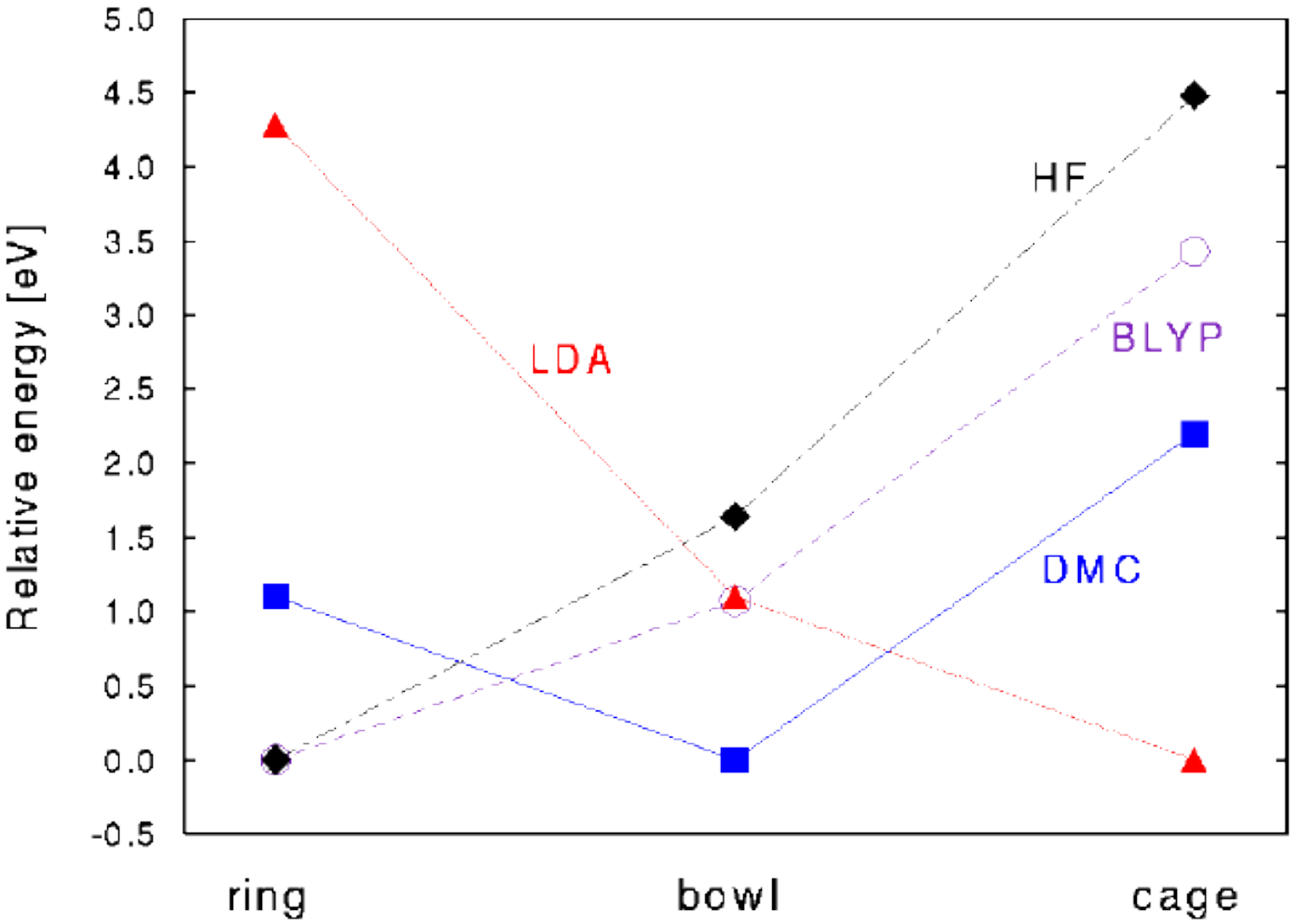
cage





Lubos_Mitas@ncsu.edu

QMC: the lowest is the bowl isomer!
(later confirmed by independent methods & exp.)



J.C. Grossman, L. M., K. Raghavachari, Phys. Rev. Lett. '95

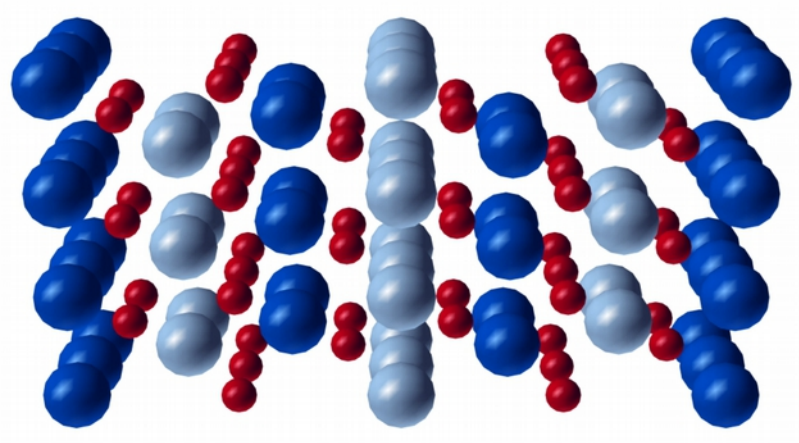
Lubos_Mitas@ncsu.edu

more recent project: FeO solid at high pressures

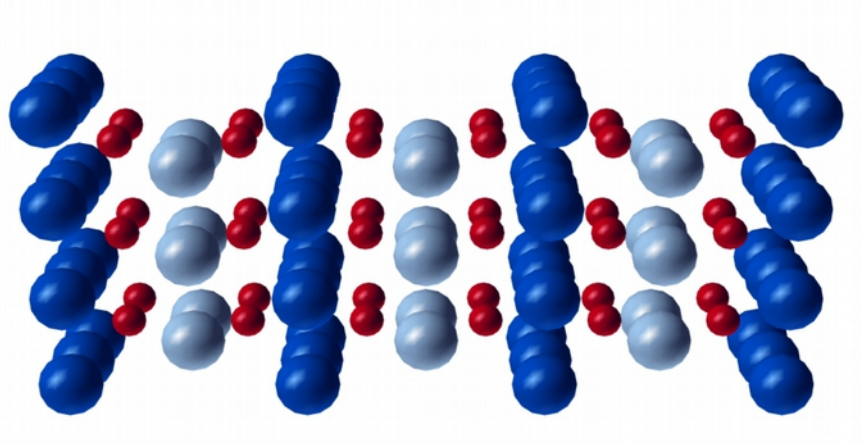
- large e-e correlations, difficult: competition of Coulomb, exchange, correlation and crystal-field effects; important high-pressure physics (Earth interior, for example)

- mainstream Density Functional Theories (DFT) predict: wrong equilibrium structure; and for the correct structure predict a metal instead of a large-gap insulator

B1/AFII (equil.)



iB8/AFII



Lubos_Mitas@ncsu.edu

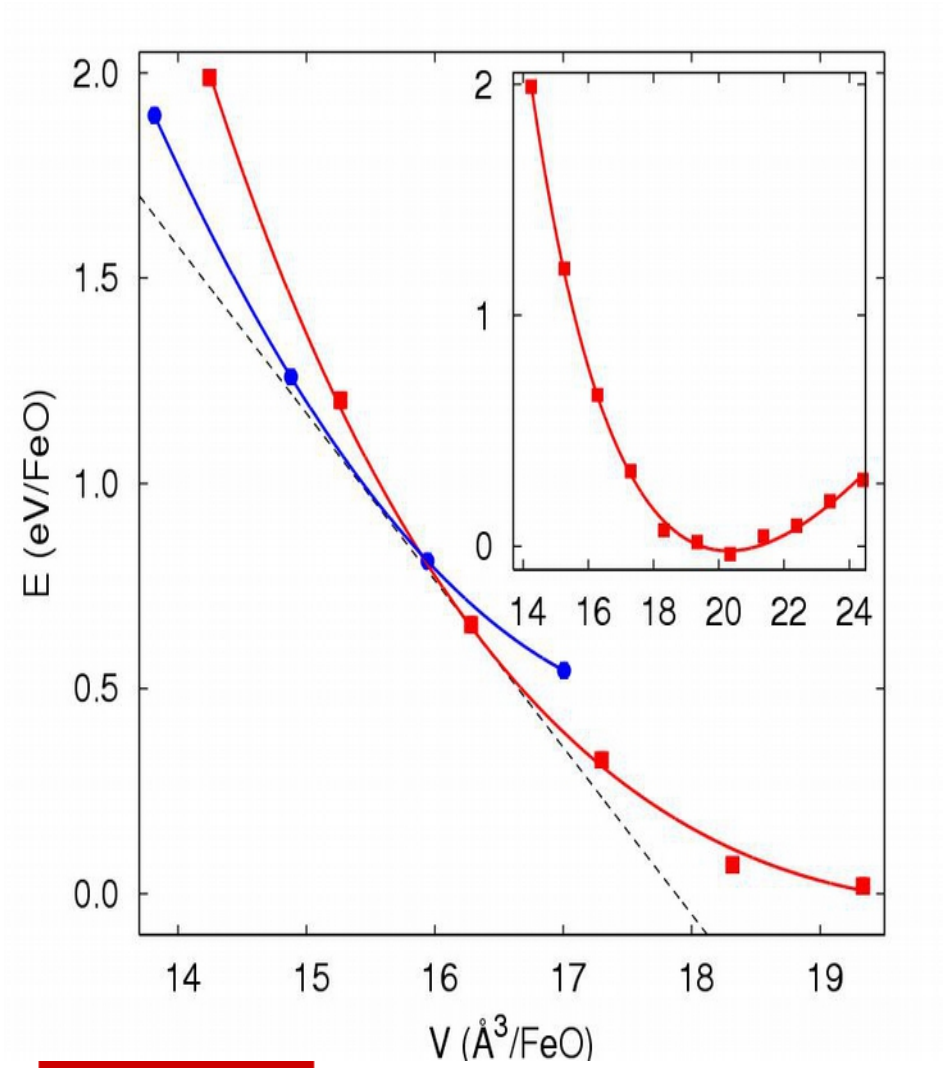
comparisons of the FeO solid equilibrium parameters

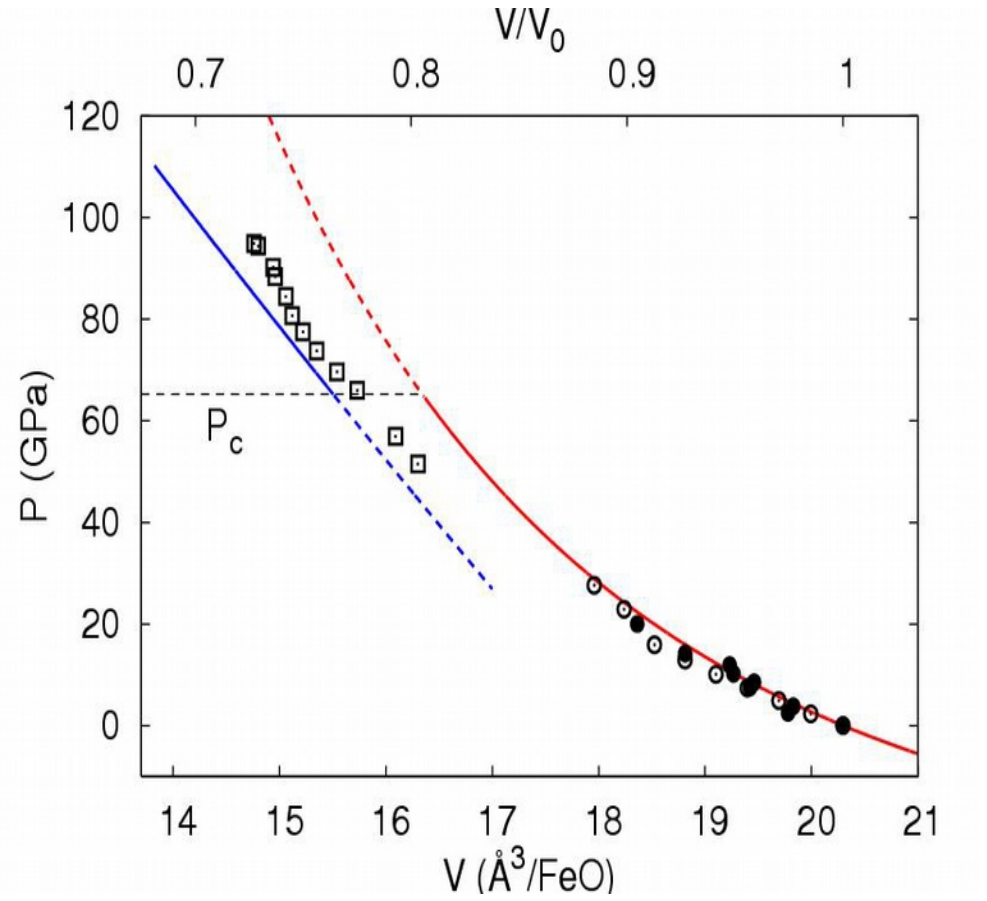
	DFT/PBE	QMC	Exp.(FeO_{1-x})
iB8-B1/AFMII [eV]	-0.2	0.5 (1)	>0
Cohesion [eV]	~ 11	9.7 (1)	9.7(2)
a_0 [A]	4.28	4.32	4.33
K_0 [GPa]	180	170(10)	152(10)
Opt. gap [eV]	~ 0 (metal)	2.8(3)	~2.4

J. Kolorenc & LM, Phys. Rev. Lett. '08

Lubos_Mitas@ncsu.edu

FeO solid at high pressures
QMC shows transition at ~ 65 GPa (Exper. 70-100)



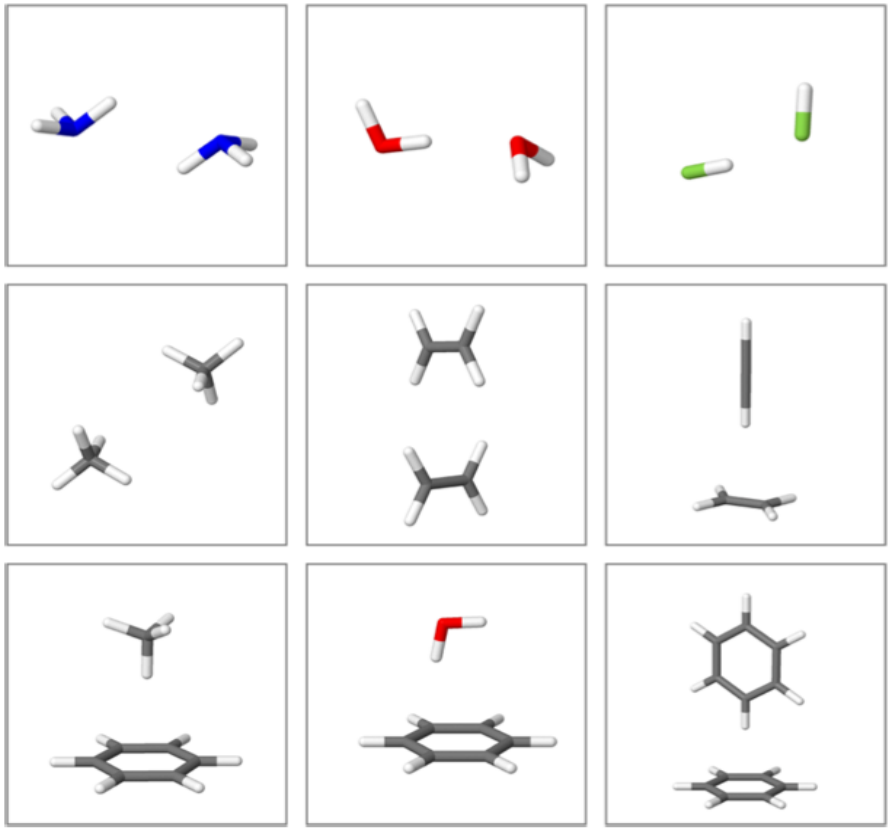


Lubos_Mitas@ncsu.edu

NC STATE UNIVERSITY

JK & LM, Phys. Rev. Lett. '08

when the fixed-node DMC works amazingly well: non-covalently bonded complexes



FNDMC agrees with CBS extrapolated CCSD(T) within 0.1 kcal/mol (0.005 eV)

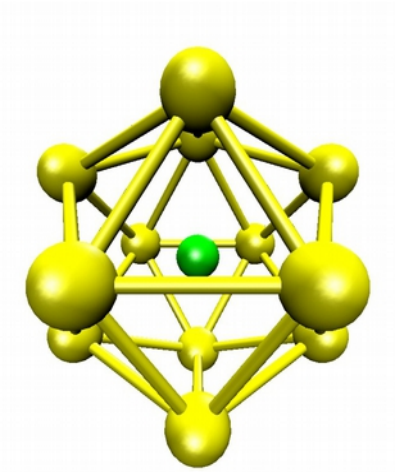
that's subchemical accuracy, as needed for these systems

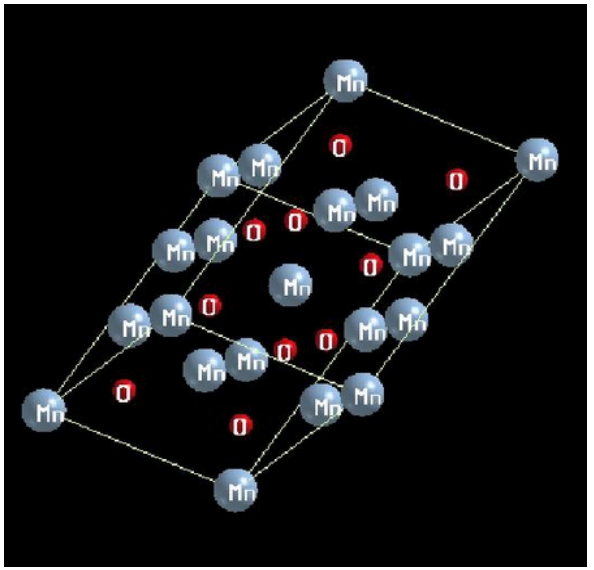
recent calcs included also DNA base pairs → 0.2 kcal/mol agreement

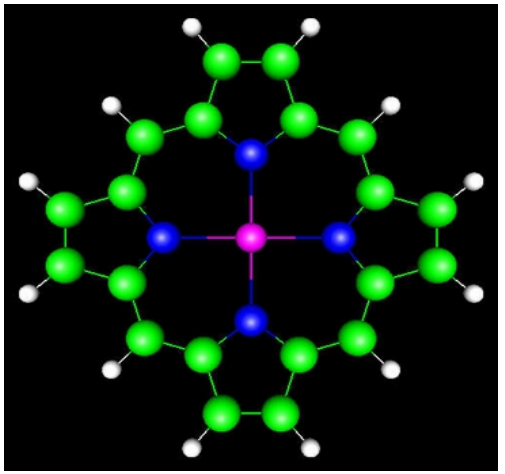
NH_3-NH_3, H_2O-H_2O, etc

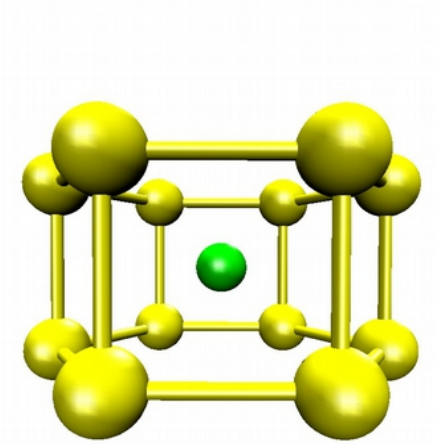
M. Dubecky, P. Jurecka, M. Otyepka, P. Hobza, LM, JCTC, 9, 4287 (2013); PCCP 16, 20915 (2014)

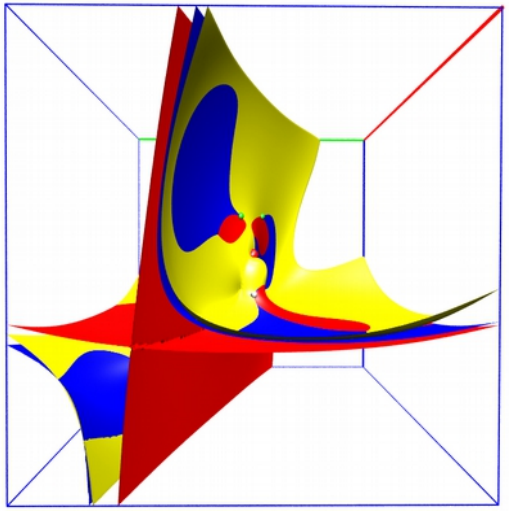
QMC can study quantum effects and properties of nanosystems, clusters, solids, biomolecules → tons of other possible applications ...

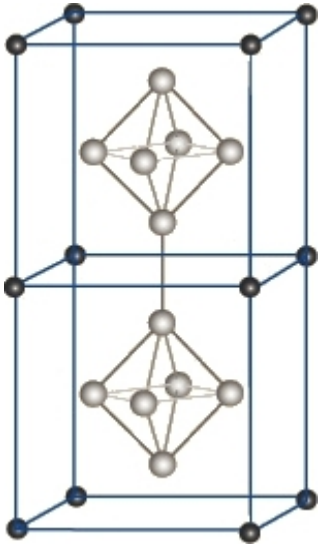












Lubos_Mitas@ncsu.edu

QMC calculations: basic steps

Hamiltonian: - often valence e- only, using pseudopots/ECPs
- explicit e-e interactions, fully many-many body

trial wave functions:

- correct symmetries
- sampling efficiency
- capture the physics

explicitly correlated Slater-Jastrow type, self-consistent orbitals:

$$\psi_{Trial} = \sum_k c_k \, det_k^{\uparrow}[\{\phi_\alpha\}] \, det_k^{\downarrow}[\{\phi_\beta\}] \exp[U_{corr}]$$

typical code/package: 100,000 lines → from laptop to 1M cores

Lubos_Mitas@ncsu.edu

impact of QMC methods

breakthroughs and benchmark calculations:

- homogeneous electron gas in '80 (Ceperley & Alder)
  → 4th most cited paper over 110 years of APS journals
- quantum liquids and solids (4He, 3He, Ceperley, others)
- barrier of H+H2 → H2+H with 0.001 eV accuracy (J. B. Anderson)
- calculations of solids, clusters, etc (last 25 years), up to 1000 e-, predictions

relative accuracy for variety of systems (molecules, solids, etc) → captures 95 % of the quantum many-body effects

- energy differences typically within 1-3% of experiment, for large systems better than anything else

sizes of systems and resources/timing

- 100-200 valence electron systems becoming routine; (1000 or more doable at the current level of development)
- typical run: 1000 processors for a day (exaflop after 2020, ~ $1.3B)

Lubos_Mitas@ncsu.edu

Ceperley and Alder

VOLUME 45, NUMBER 7 PHYSICAL REVIEW LETTERS 18 AUGUST 1980

Ground State of the Electron Gas by a Stochastic Method

D. M. Ceperley
National Resource for Computation in Chemistry, Lawrence Berkeley Laboratory, Berkeley, California 94720

and

B. J. Alder
Lawrence Livermore Laboratory, University of California, Livermore, California 94550

(Received 16 April 1980)

An exact stochastic simulation of the Schroedinger equation for charged bosons and fermions has been used to calculate the correlation energies, to locate the transitions to their respective crystal phases at zero temperature within 10%, and to establish the stability at intermediate densities of a ferromagnetic fluid of electrons.

The key quantum Monte Carlo paper (used Cray machine at LLNL)

Google Scholar:

[PDF] The ground state of the electron gas by a stochastic method esch
DM Ceperley - 2010 - escholarship.org
ABSTRACT: We have used an exact stochastic simulation of the Scbroedinger equation for charged Bosons and Fermions to calculate the correlation energies, to locate the transitions to their respective crystal phases at zero temperature within 10%, and to establish the ...
Cited by 10042 Related articles All 14 versions Import into BibTeX More

2018 ~ 14,000 cits

Ceperley and Alder work:

- calculation of correlation energies of homogeneous electron gas (the simplest quantum condensed many-body interacting system)

- these accurate exact energies of paradigmatic model used as an input into the Density Functional Theory:
  → used in physics, chemistry, materials research, etc

- huge impact: 4th most cited physics paper over 100 years of APS journals

TABLE II: Top-10 cited PR articles. The asterisks denote citation undercount due to citations with missing prepended A/B page numbers – 123 out of 3227 total for item 1 and 120 out of 2640 for item 2.

Impact Rank	Publication			# cites	Av. Age	Impact	Title	Author(s)
1	PR	140	A1133	1965	3227*	26.64	85972	Self-Consistent Equations...	W. Kohn & L. J. Sham
2	PR	136	B864	1964	2460*	28.70	70604	Inhomogeneous Electron Gas	P. Hohenberg & W. Kohn
3	PRB	23	5048	1981	2079	14.38	29896	Self-Interaction Correction to	J. P. Perdew & A. Zunger
4	PRL	45	566	1980	1781	15.42	27463	Ground State of the Electron ...	D. M. Ceperley & B. J. Alder
5	PR	108	1175	1957	1364	20.18	27526	Theory of Superconductivity	J. Bardeen, L. N. Cooper, & J. R. Schrieffer
6	PRL	19	1264	1967	1306	15.46	20191	A Model of Leptons	S. Weinberg
7	PRB	12	3060	1975	1259	18.35	23103	Linear Methods in Band Theory	O. K. Andersen
8	PR	124	1866	1961	1178	27.97	32949	Effects of Configuration...	U. Fano
8	RMP	57	287	1985	1055	9.17	9674	Disordered Electronic Systems	P. A. Lee & T. V. Ramakrishnan
9	RMP	54	437	1982	1045	10.82	11307	Electronic Properties of...	T. Ando, A. B. Fowler, & F. Stern
10	PRB	13	5188	1976	1023	20.75	21227	Special Points for Brillouin-...	H. J. Monkhorst & J. D. Pack

quantum Monte Carlo and quantum many-body systems in general

- "hot" area (and will stay that way for a long time :-))
- quantum engineering – one of the key areas for future (both fundamental science and applications)
- QMC: perhaps the most promising approach to tackle the problem computationally
- combination of analytical insights + stochastic techniques + algorithms + ever faster machines
- permeates now all scales, from macro to meso to micro to QCD
- perhaps, it also naturally couples with quantum computers ...

Lubos_Mitas@ncsu.edu

QMC vs quantum computing (= real time quantum dynamics)

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

- works in imaginary time (just a rigorous math transform)
  → parabolic diff. eq. that gives one state, eg, $\psi_{0,\,ground\ state}$

- we need more → spectrum $\{E_k, \psi_k\}_{k=0}^{k=k_{max}}$
  → repeat the same process for another state, $\psi_1, \ldots$
  we are doing that but it is an exascale (and beyond) problem

Quantum computing = real-time quantum dynamics

$$i\partial_t \psi(\boldsymbol{R},t) = H\,\psi(\boldsymbol{R},t) \quad \rightarrow \quad \psi(\boldsymbol{R},t) = \sum_k c_k \exp(-iE_k t)\psi_k(\boldsymbol{R})$$

solution ? well-known, fundamentally difficult problem

→ hyperbolic diff. eq. that keeps all engaged states present at all times → can produce the spectrum!

Lubos_Mitas@ncsu.edu

existing quantum computers: basis states are qubits

- basis states of one qubit = 0,1 (essentially, 2 discrete points)

  any state $\psi(t)=\alpha(t)|0\rangle+\beta(t)|1\rangle;\quad \alpha(t)=\langle 0|\psi(t)\rangle, etc$

- N qubits → (0,1)^N corners of hypercube in N dimensions → 2^N

  exponentially big, discrete basis

$$\psi(t)=\sum_k^{2^N} c_k(t)|k\rangle;\quad |k\rangle=\{(0\vee 1;\ 0\vee 1;\ \ldots,\ 0\vee 1)\}$$

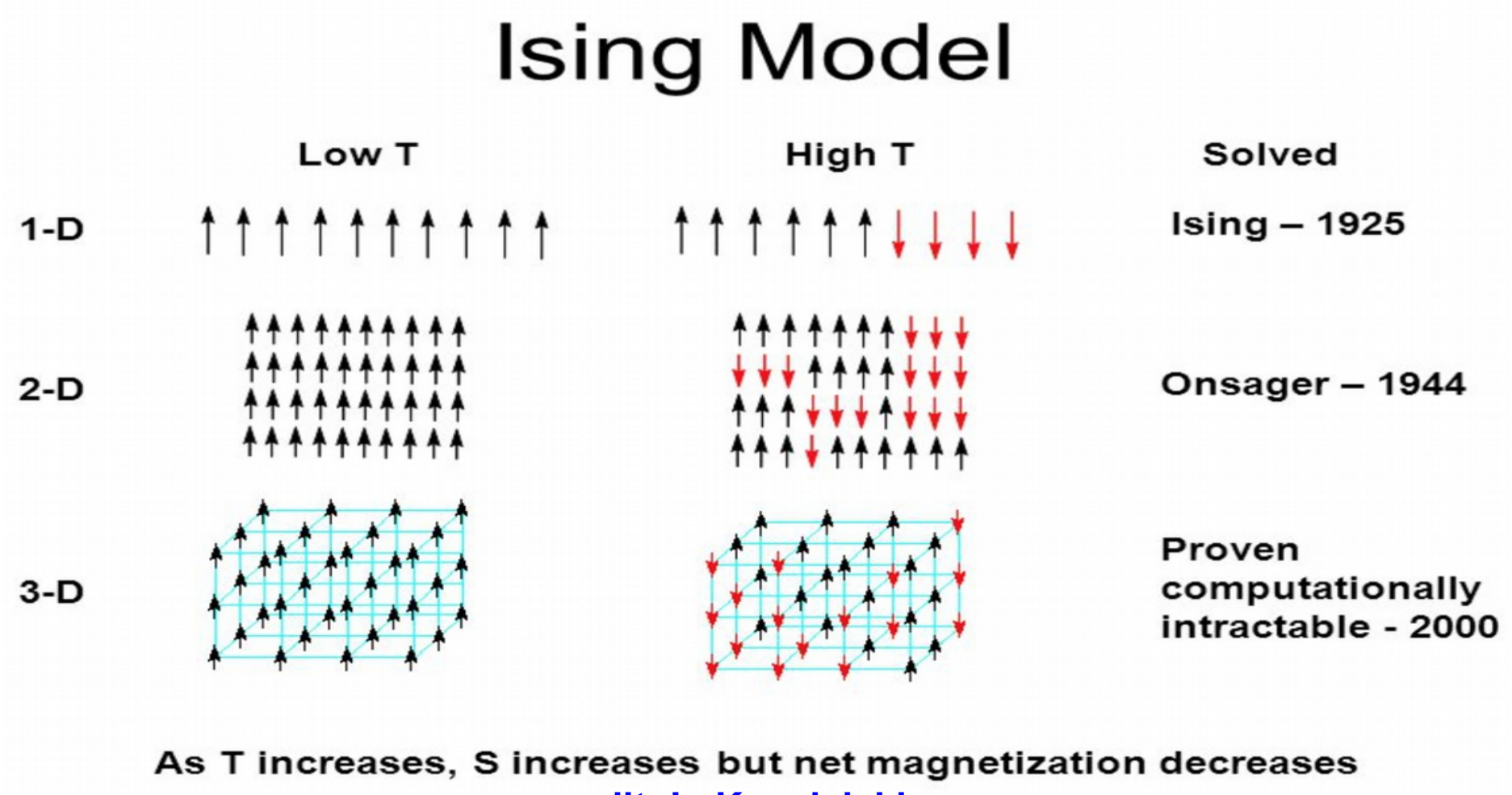
$$i\partial_t\psi(t)=H_{your\,code}(t)\psi_{initial}(t=0)$$

- H_{your code} is whatever you make it (ie, map your problem on H)

Lubos_Mitas@ncsu.edu

building an analogy: Ising model of ferromagnet classical physics problem (can be made quantum, too)

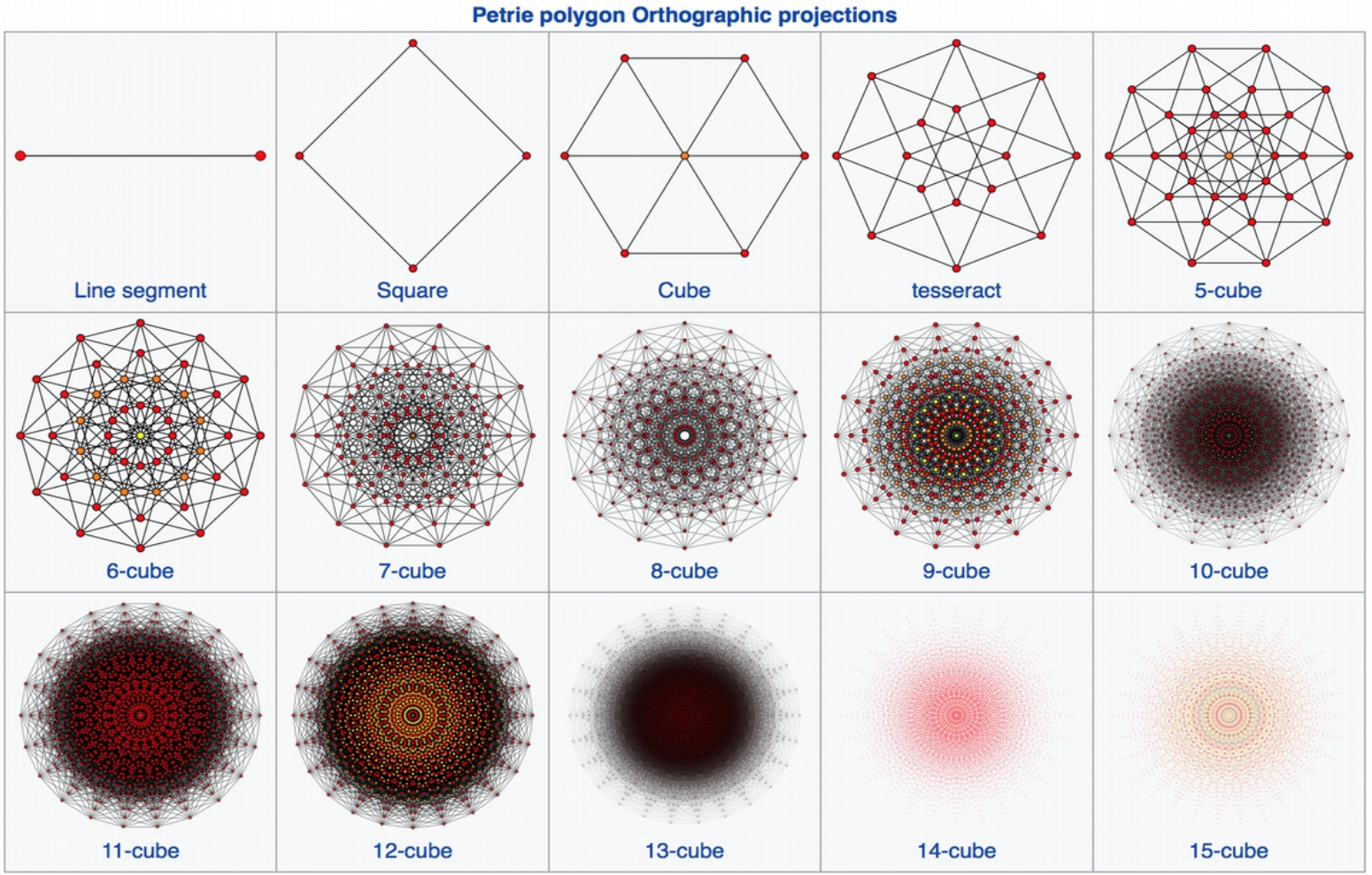
Ising model : $H = -J \sum_{i,j}^{\text{nearest neigh.}} s_i s_j, \quad s_i = \pm 1$



credit: L. Koscielski

configuration space of the Ising model: 2^N, where N is # of spins, $(\pm 1, \pm 1, \ldots, \pm 1)$

- configuration space: vertices of hypercube in N-dim space

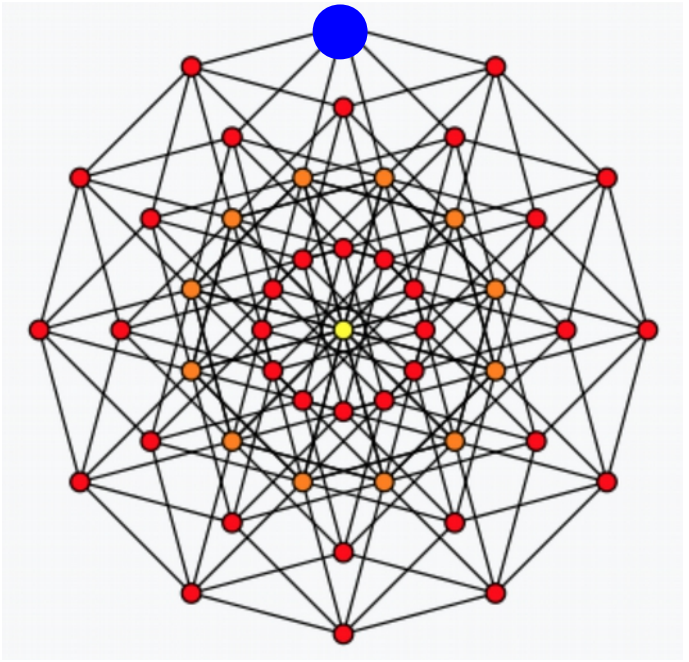


credit: Wikipedia

Lubos_Mitas@ncsu.edu

sampling of such space classically

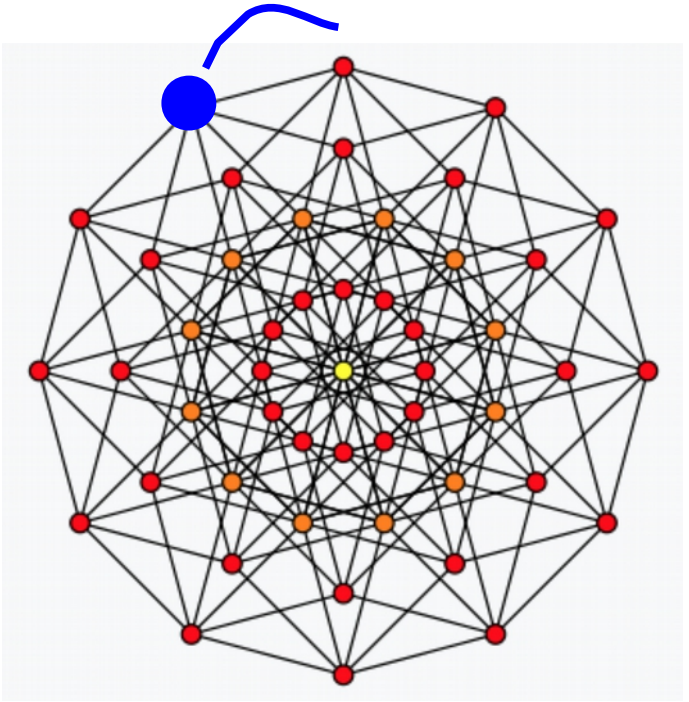
- classical random walk: random move to any of N-neighbors, prob=1/N



Lubos_Mitas@ncsu.edu

sampling of such space classically

- classical random walk: random move to any of N-neighbors, prob=1/N

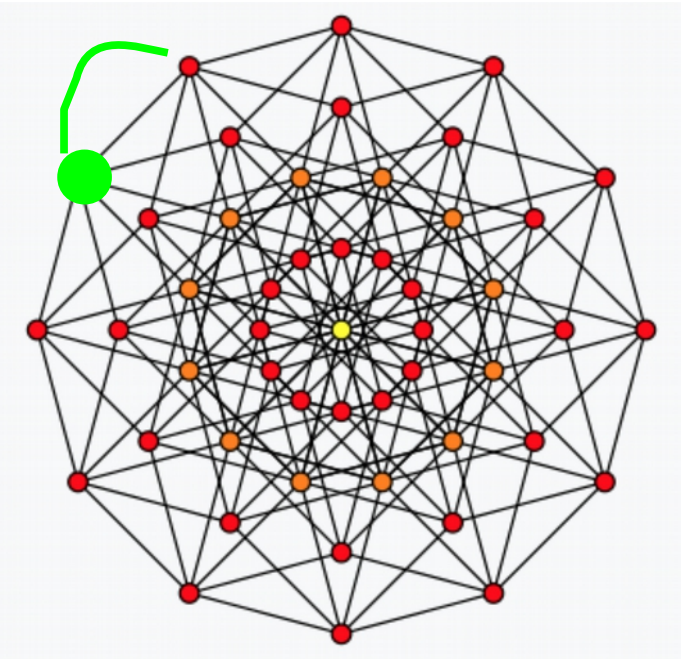


Lubos_Mitas@ncsu.edu

sampling of such space classically

- classical random walk: random move to any of N-neighbors, prob=1/N

2nd step

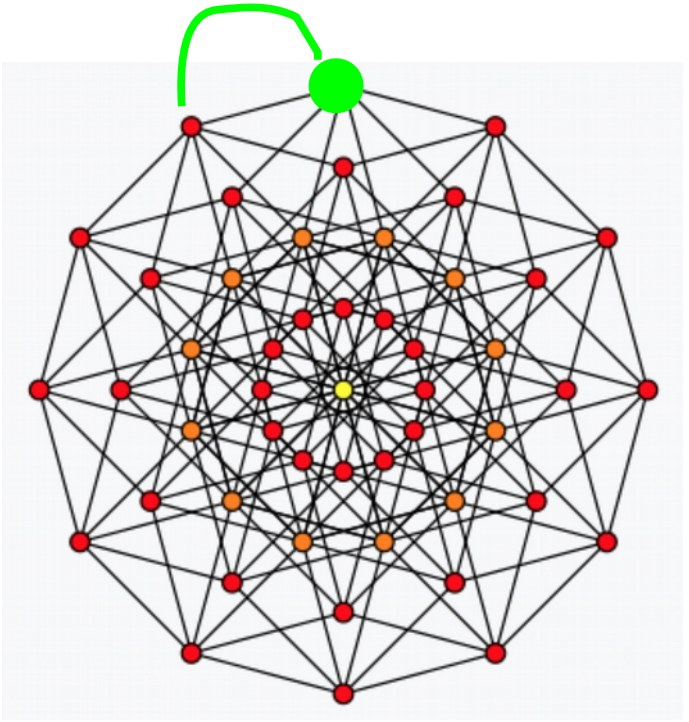


Lubos_Mitas@ncsu.edu

sampling of such space classically

- classical random walk: random move to any of N-neighbors, prob=1/N

2nd step

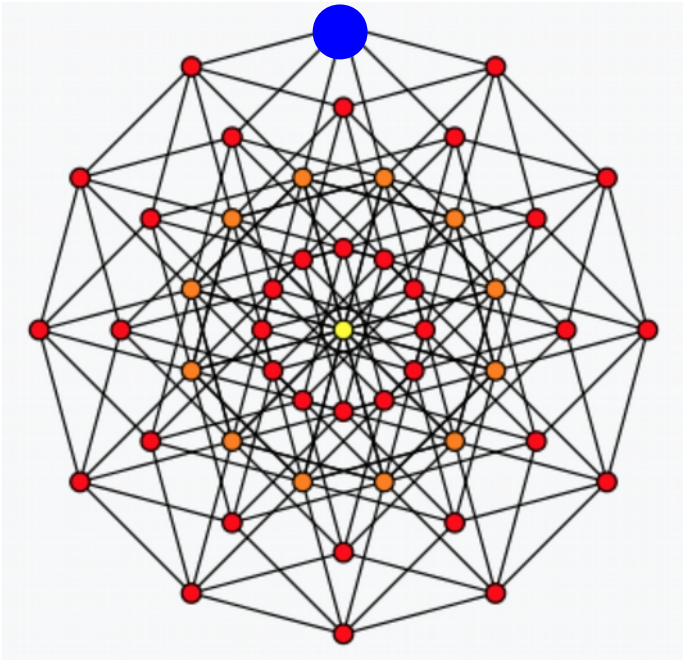


→ can go even back, ie, evolves very slowly !
needs ~ exp(aN) steps to visit the antipodal point (body diagonal)

Lubos_Mitas@ncsu.edu

quantum sampling of such space

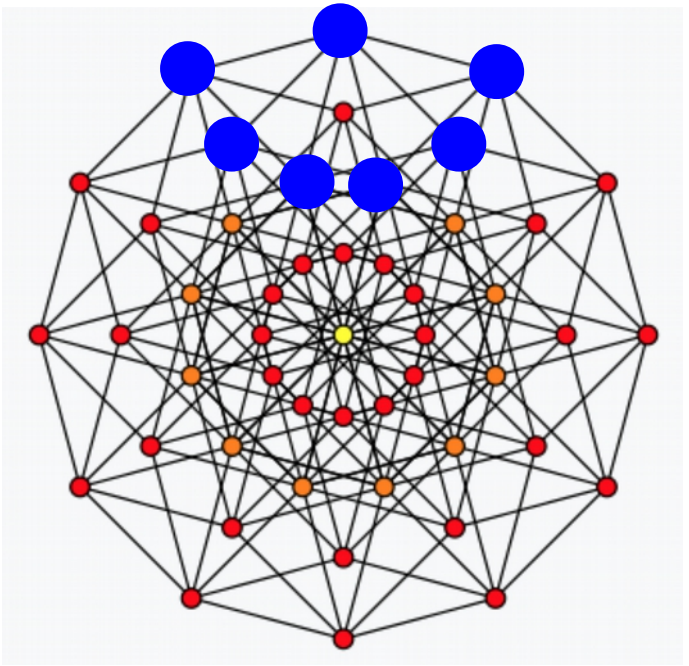
- quantum random walk: one step → amplitude= ~1/N to all nearest points



Lubos_Mitas@ncsu.edu

quantum sampling of such space

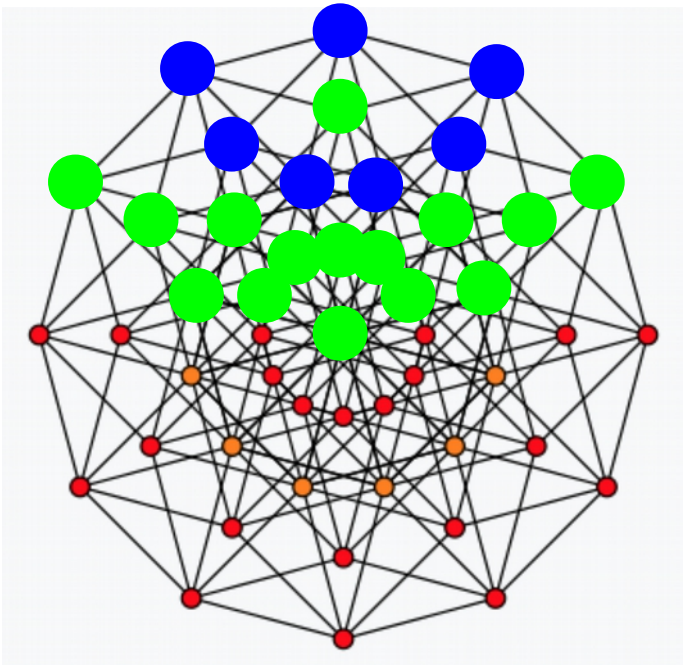
- quantum random walk: one step → ~ 1/N amplitude to all nearest points



Lubos_Mitas@ncsu.edu

quantum sampling of such space

- quantum random walk: one step → ~ 1/N amplitude to all nearest points



→ needs ~ N steps to visit the antipodal point !!! (J. Kempe, 2003)

Lubos_Mitas@ncsu.edu

hypercube and quantum processes

PHYSICAL REVIEW A **71**, 012306 (2005)

Scattering model for quantum random walks on a hypercube

Jozef Košík[1] and Vladimír Bužek[1,2]
[1]*Research Center for Quantum Information, Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovakia*
[2]*Faculty of Informatics, Masaryk University, Botanická 68a, 602 00 Brno, Czech Republic*
(Received 22 March 2004; published 4 January 2005)

Following a recent work by Hillery *et al*. [Phys. Rev. A **68**, 032314 (2003)], we introduce a scattering model of a quantum random walk (SQRW) on a hybercube. We show that this type of quantum random walk can be reduced to the quantum random walk on the line and we derive the corresponding hitting amplitudes. We investigate the scattering properties of the hypercube, connected to the semi-infinite tails. We prove that the SQRW is a generalized version of the coined quantum random walk. We show how to implement the SQRW efficiently using a quantum circuit with standard gates. We discuss one possible version of a quantum search algorithm using the SQRW. Finally, we analyze symmetries that underlie the SQRW and may simplify its solution considerably.

DOI: 10.1103/PhysRevA.71.012306 PACS number(s): 03.67.Lx, 05.40.Fb

Lubos_Mitas@ncsu.edu

hypercube and quantum processes

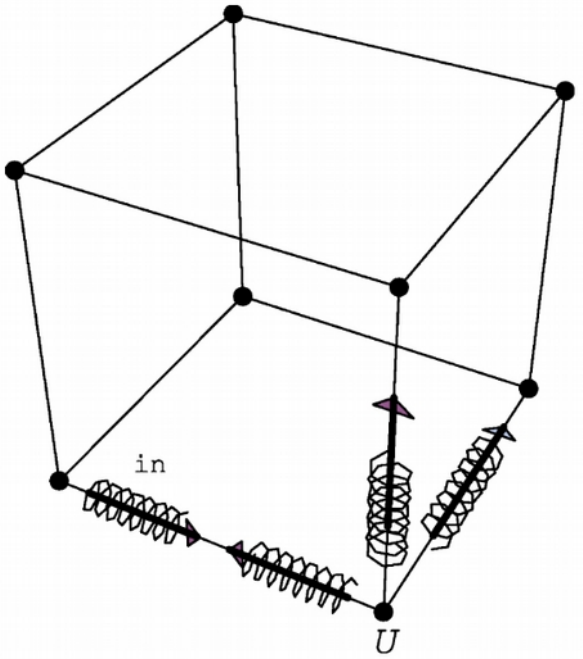


FIG. 1. Action of the multiport (U) on the ingoing photon (in) on the dim 3 hypercube. Coherent superposition of three photonic excitations is created.

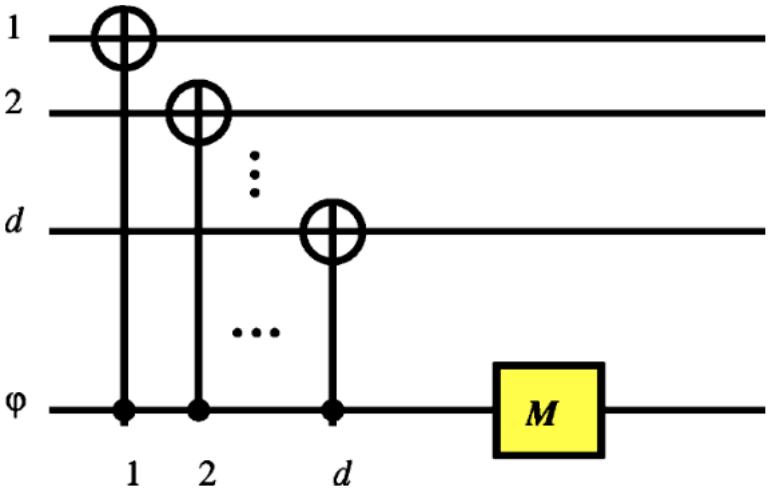


FIG. 10. The gate which implements the SQRW on the d-dimensional hypercube. The input state is the position register (d qubits labeled as $1,\ldots,d$) and the direction register $|\varphi\rangle$. There are d ϕ_{CNOT} gates stacked together, with accepting states $|1\rangle,\ldots,|d\rangle$, which change the position register, and the gate M which changes the direction register.

Lubos_Mitas@ncsu.edu

classical algorithms that almost knock down the exponential scalings

- TSP (self-organizing neuron maps)

- Ising-like models (cluster algorithms)

- electronic structure by QMC

- calculation of (some) permanents in O(N^a) within a given error

- ...

Lubos_Mitas@ncsu.edu