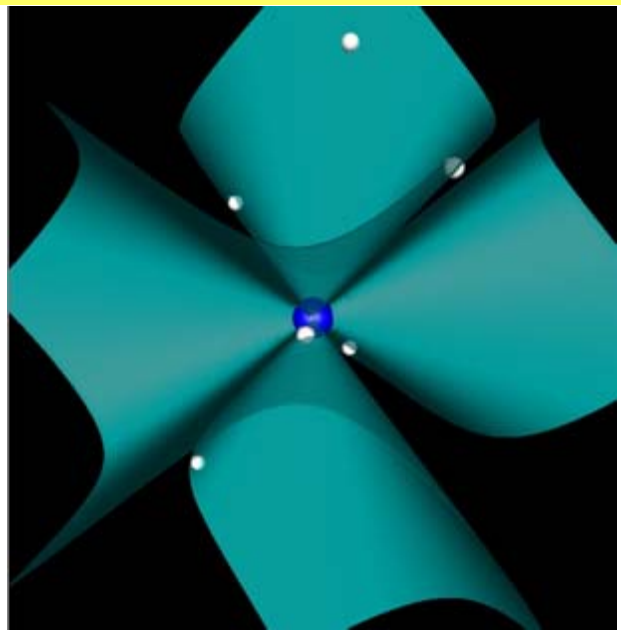
Quantum Monte Carlo advances: pfaffian wave functions, topology of fermion nodes and QMC/MD methods



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PNNL, January 2007

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Talk topics

- QMC intro
- Topology of fermion nodes
- Pfaffians/pairing wave functions
- QMC/MD
- Suggestions to NWChem

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Electronic structure: motivation and challenges

System of interacting electrons and ions in continuous space

$$H\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots)=E\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots)$$

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

- **Fundamental properties of many-body wavefunctions**
- **Development of accurate methods for solving the Schr. eq.**
- **Interesting applications:**
  - **ground states of strongly correlated systems**
  - **excited states, gaps, optical properties**
  - **responses to external fields**
  - **T>0, moleculer dynamics, etc ...**

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Basics of diffusion (projector) Monte Carlo

Construct an approximate trial function and project out the ground state

$$\psi_{ground}(\boldsymbol{R}) = \lim_{t\to\infty} \exp(-tH)\,\psi_T(\boldsymbol{R})$$

or, equivalently, solve the imaginary-time Schr. eq. (Bloch's eq.)

$$\psi(\boldsymbol{R}, t+\tau) = \int G(\boldsymbol{R}, \boldsymbol{R}', \tau)\,\psi(\boldsymbol{R}', t)\,d\boldsymbol{R}', \qquad G(\boldsymbol{R}, \boldsymbol{R}', \tau) = \langle \boldsymbol{R} | e^{-\tau H} | \boldsymbol{R}' \rangle$$

Solved by simulation of an equivalent, diffusion-like stochastic process

- **wavefunction is sampled by points in 3N-dim space ("random walkers")**

wavefunction <=> density of random walkers

- **walkers evolved according to the propagator (transition probability)**

Essentially an exact mapping: statistical method of solution!

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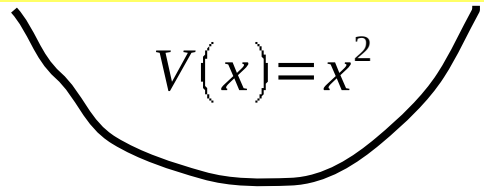
Toy model: 1D harmonic oscillator

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



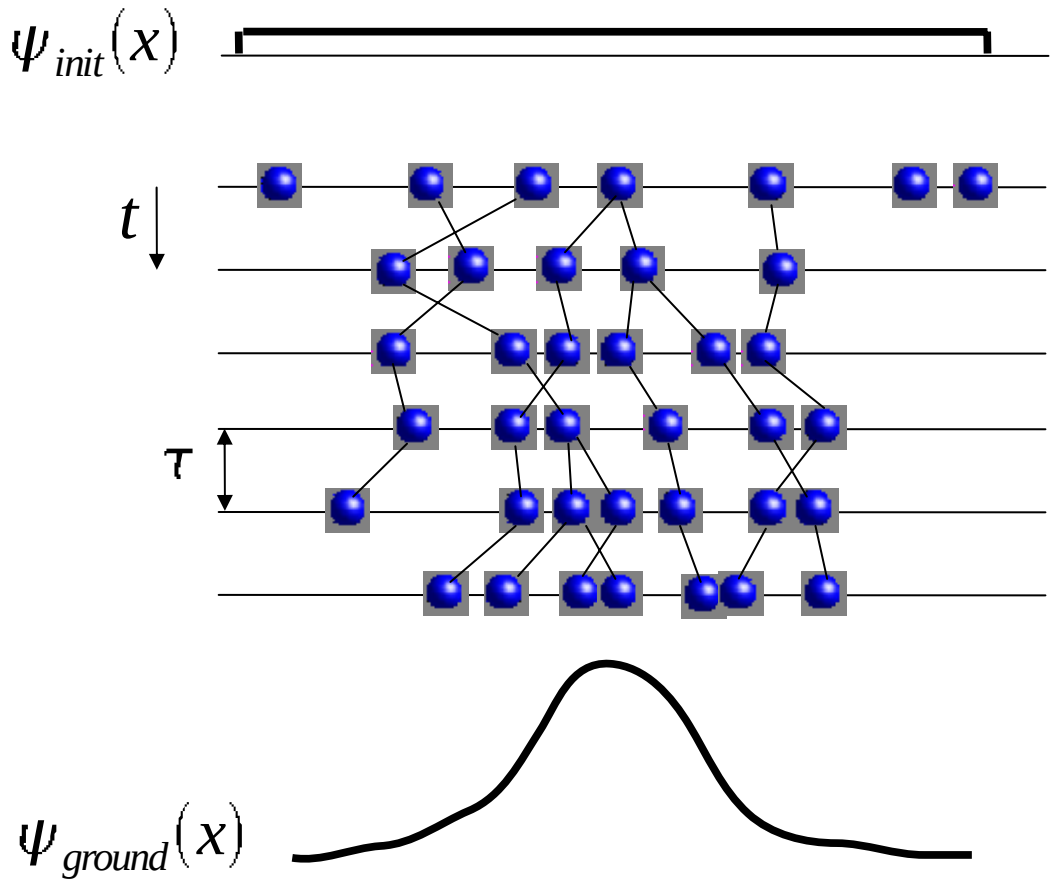
Propagator

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

$$\downarrow$$

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

diffusion **renorm**



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Fermion sign problem

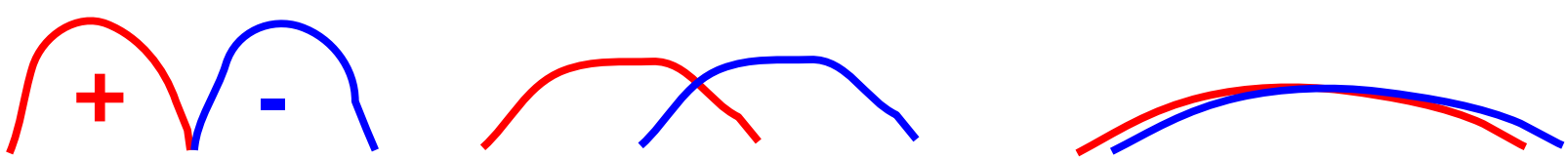
Naïve approach for fermionic wave functions: decompose to + and -

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

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

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

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"

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Efficiency and fermion sign problem: fixed-node diffusion Monte Carlo (FNDMC)

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

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

$$G^*(\boldsymbol{R},\boldsymbol{R}',\tau)=\frac{\langle \boldsymbol{R}|\exp(-\tau H)|\boldsymbol{R}'\rangle}{\psi_T(\boldsymbol{R}')\psi_T^{-1}(\boldsymbol{R})}$$

$$\lim_{\tau\to\infty} f(\boldsymbol{R},\tau)\ \propto\ \psi_T(\boldsymbol{R})\phi_{ground}(\boldsymbol{R})$$

Fermion node: defined as $\phi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)=0$

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

Antisymmetry (nonlocal) replaced by a boundary (local)

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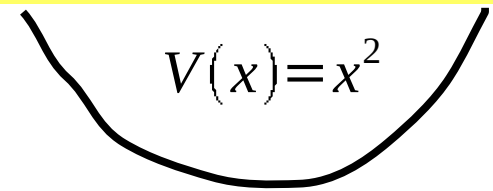
Fermion node toy model: excited state of harmonic oscillator

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



Propagator

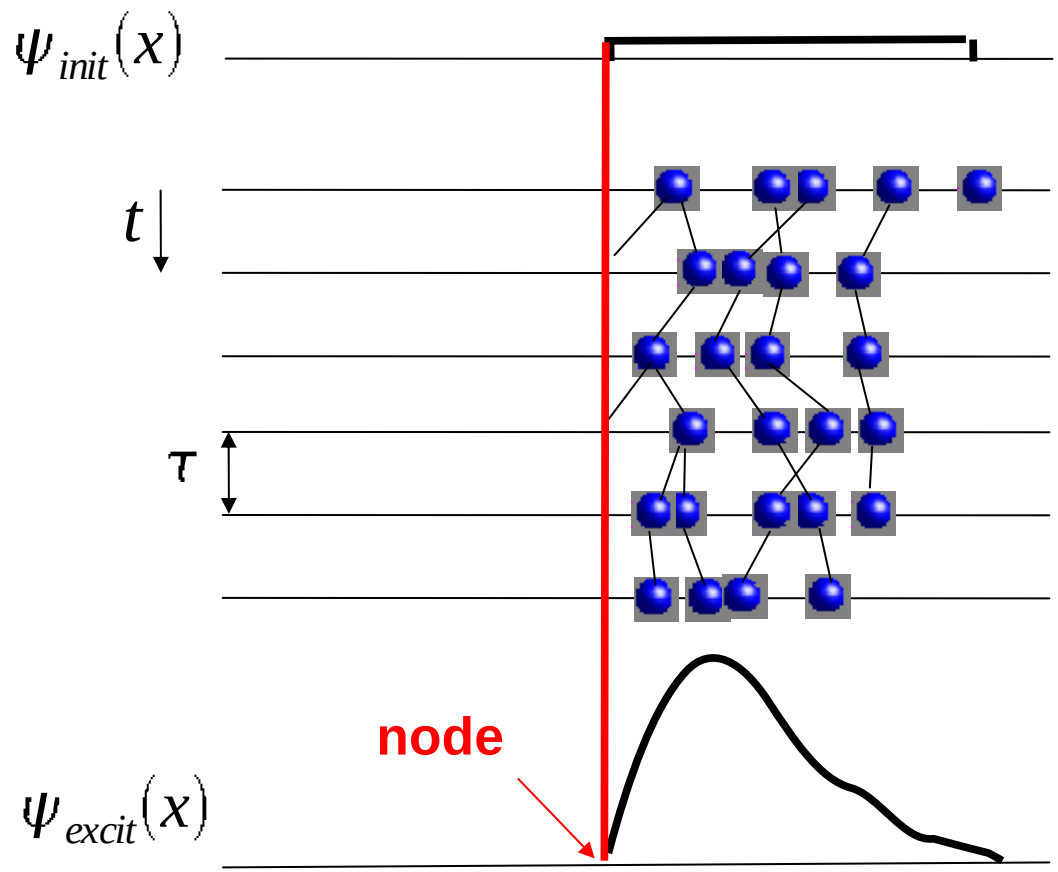
$$G(x, x', \tau)$$

$$\downarrow$$

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

diffusion **renorm**

+ boundary condition (evaluate trial function)



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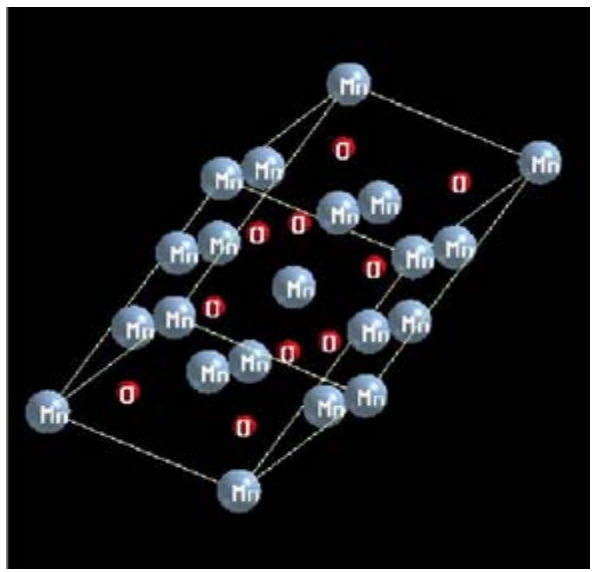
MnO solid calculations: paradigmatic TMO antiferromagnet



- large correlation effects, difficult to treat by traditional methods: competition of Coulomb, exchange, correlation and crystal-field effects

- supercells with 8, 16, 20 and 24 atoms: up to ~ 250 valence electrons

- gap estimations using promotion from valence -> to conduction band

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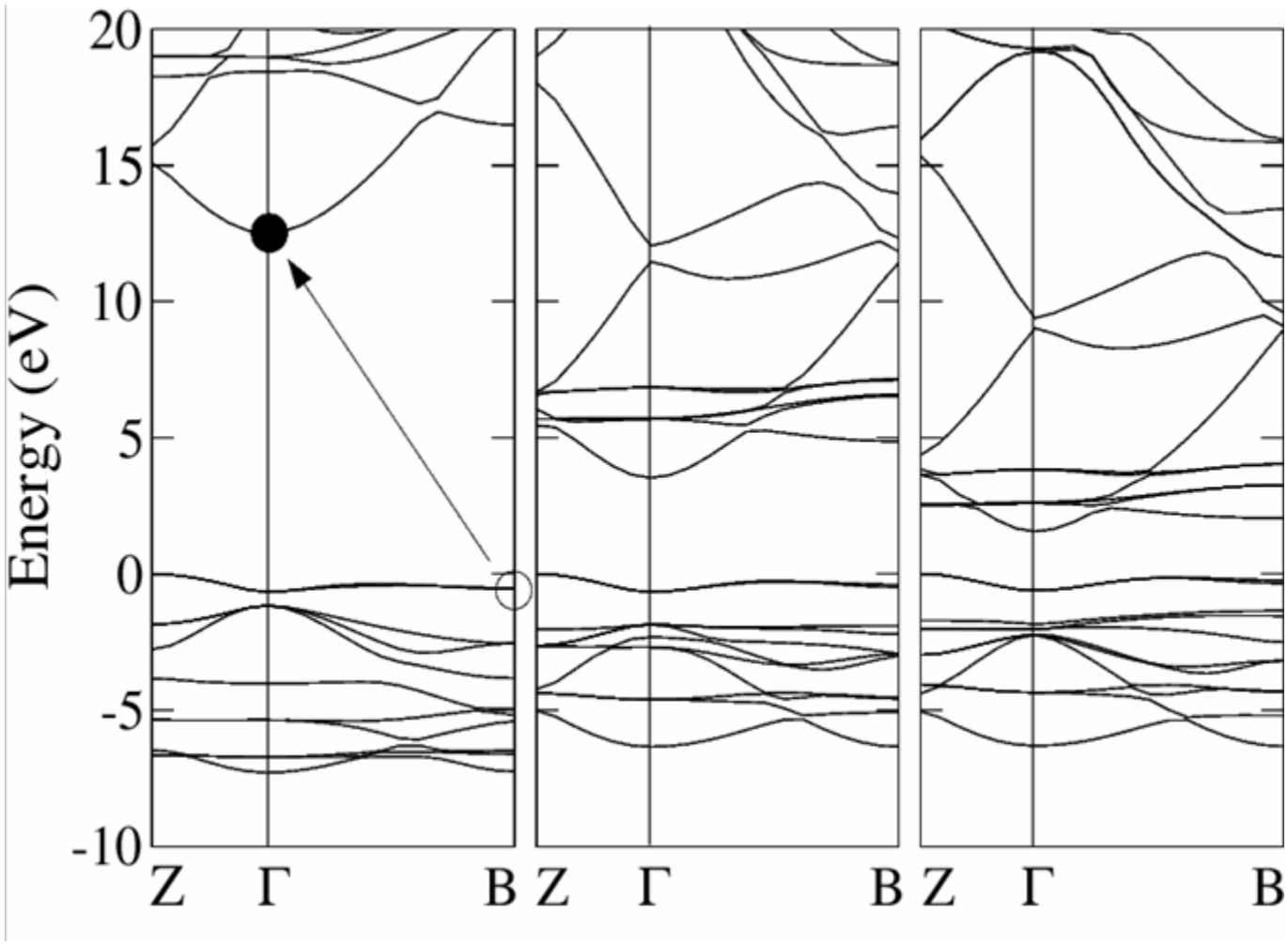
Band structure of MnO by HF and DFT:
UHF B3LYP PW91



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MnO cohesion and band gap

Cohesive energy [eV]

HF	B3LYP	DMC	Exp.
6.0	10.2	9.40(5)	9.5

Band gap: B -> Γαμμα excitation

HF	B3LYP	DMC	Exp.
14.2	4.0	4.6(3)	4.2

Small bias towards higher energy for the excited state (we need better virtuals for solids!!!)

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BaTiO3 cohesion

Cohesive energy [eV]

DFT/PW91	DMC/HF	DMC/DFT	Exp.
38.0	30.9(4)	31.2(4)	31.56

Note: cohesion comes very close to experiment from a straightforward application of QMC

Current effort: ferroelectric distortion

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FeO solid ground state and structure (DFT results plain wrong, also for FeO molecule)

	DFT/PW91	DMC/DFT	Exp.
iB8-B1/AFMII	- 0.2 eV	0.5 eV	>0
cohesion	~ 11 eV	9.6 (1) eV	9.7 eV
gap	0 (metal)	~ 5 eV	~ 4 eV

Current effort: MnO high pressures, collapse of magnetic moments (experiments at LLNL)

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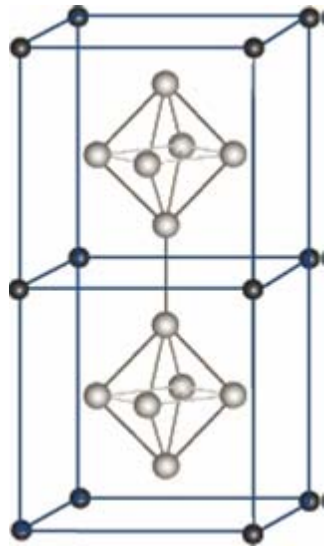
Electronic structure of hexaborides CaB_6, $La_xCa_{1-x}B_6$, ...

3% La-doped CaB_6 is a weak magnet up to 600-900K (!)



No *d* or *f* electrons: - genuine itinerant magnetism ?

Undoped CaB_6 : insulator ? exitonic insulator ? metal ?

Experiments contardictory:
both metallic and insulating behavior observed

Calculations inconclusive:
semimetal or insulator

Can we calculate the gap before the experiment ?

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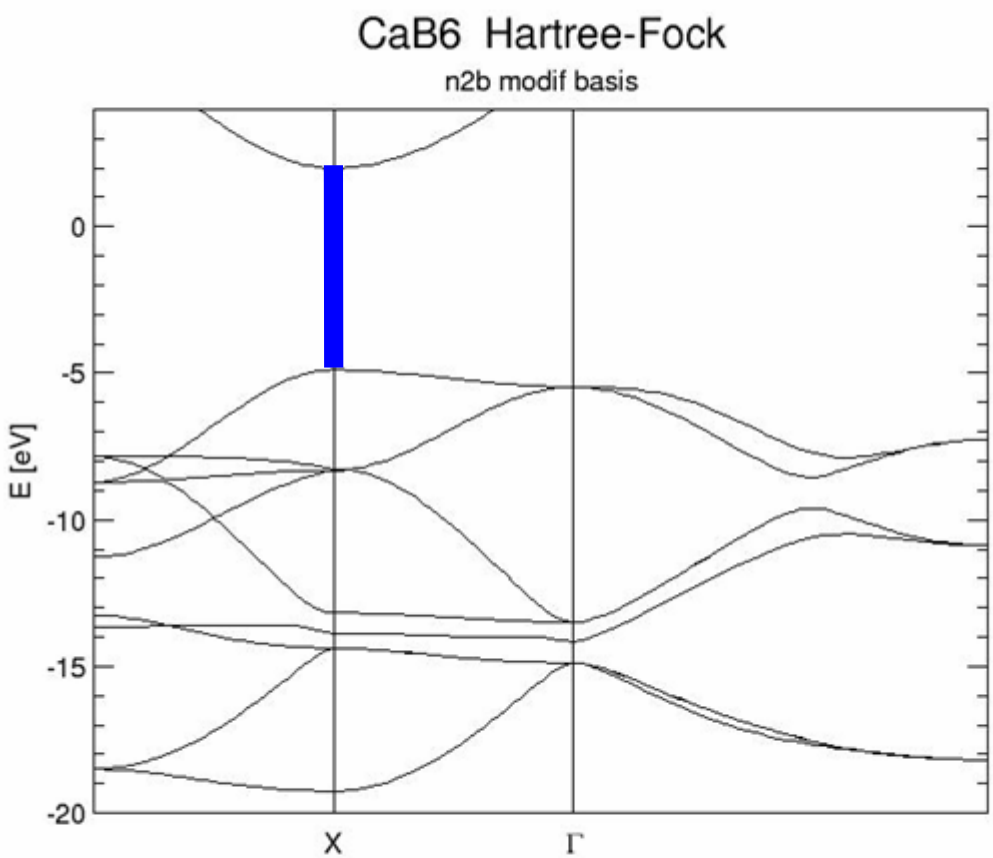
CaB_6 band structure in Hartree-Fock



Large gap
of the order of 7 eV

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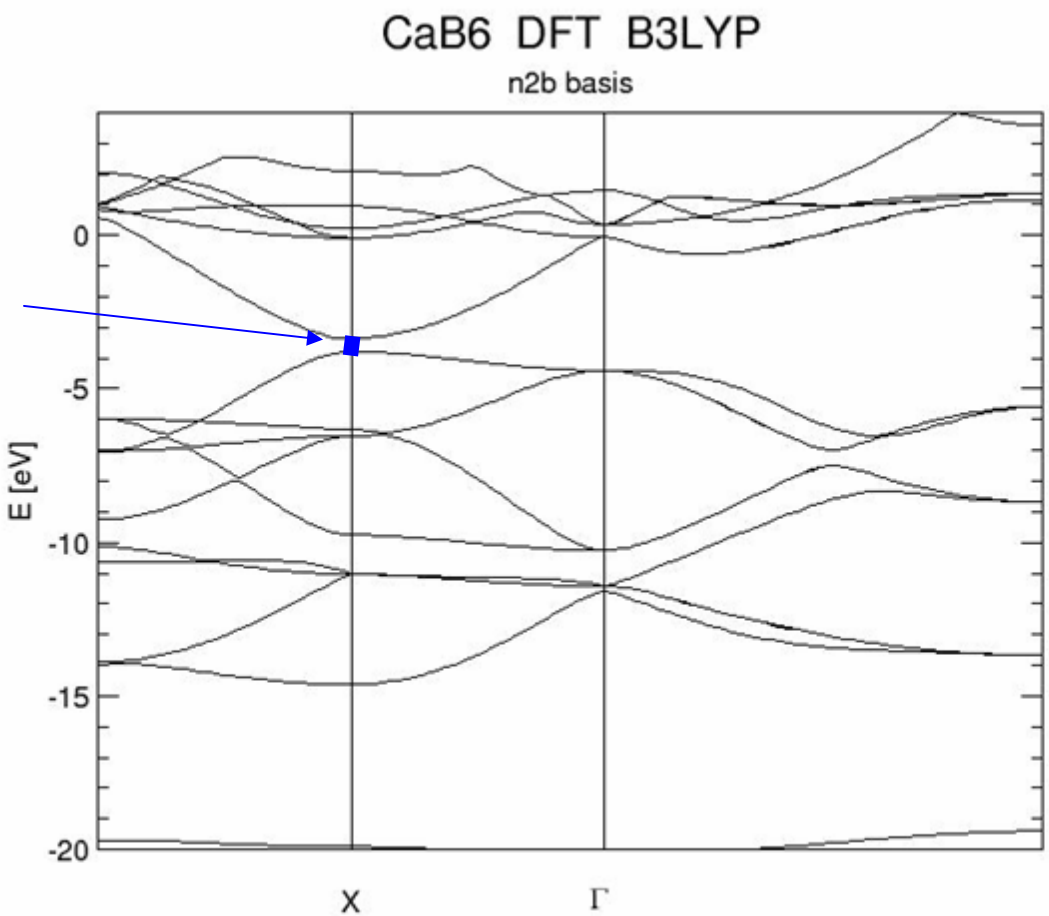
CaB_6 band structure in DFT - B3LYP



Gap is now only about 0.5 eV

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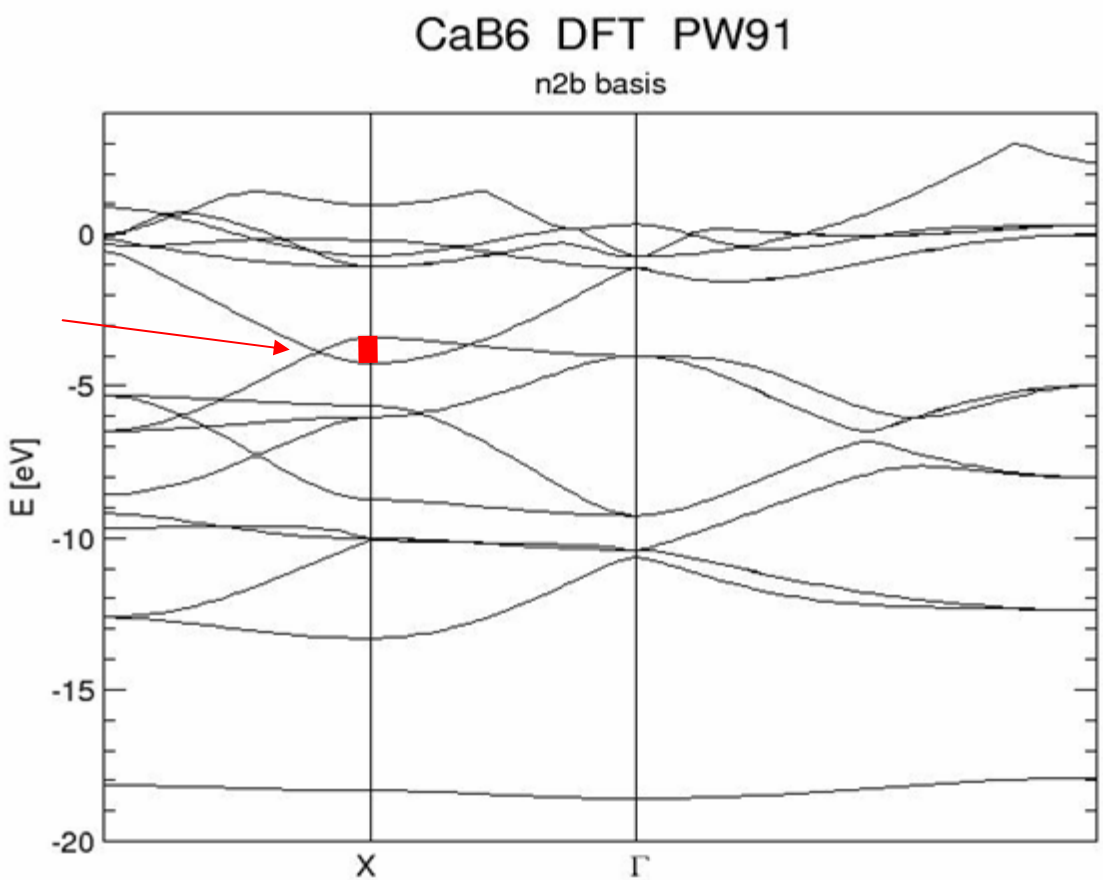
CaB_6 band structure in DFT - PW91



1 eV overlap at the X point:
d-states on Ca

Fixed-node DMC gap:

1.2(2) eV

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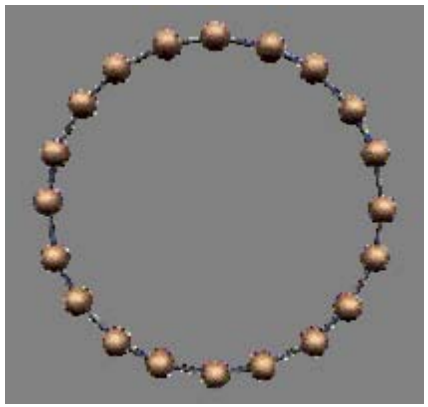
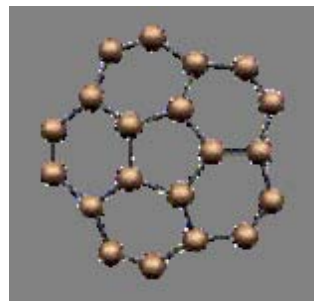
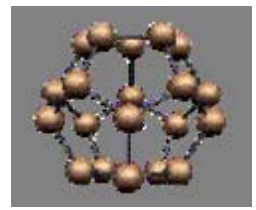
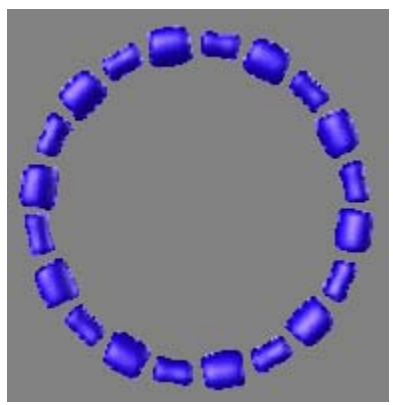
Example of application: which is the lowest energy isomer of C20 ???

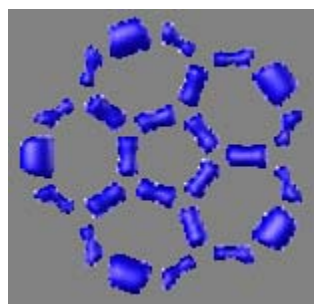
ring **bowl** **cage**

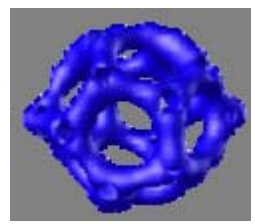












J.C. Grossman, L. Mitas, K. Raghavachari, Phys. Rev. Lett. 75, 3870 (1995)

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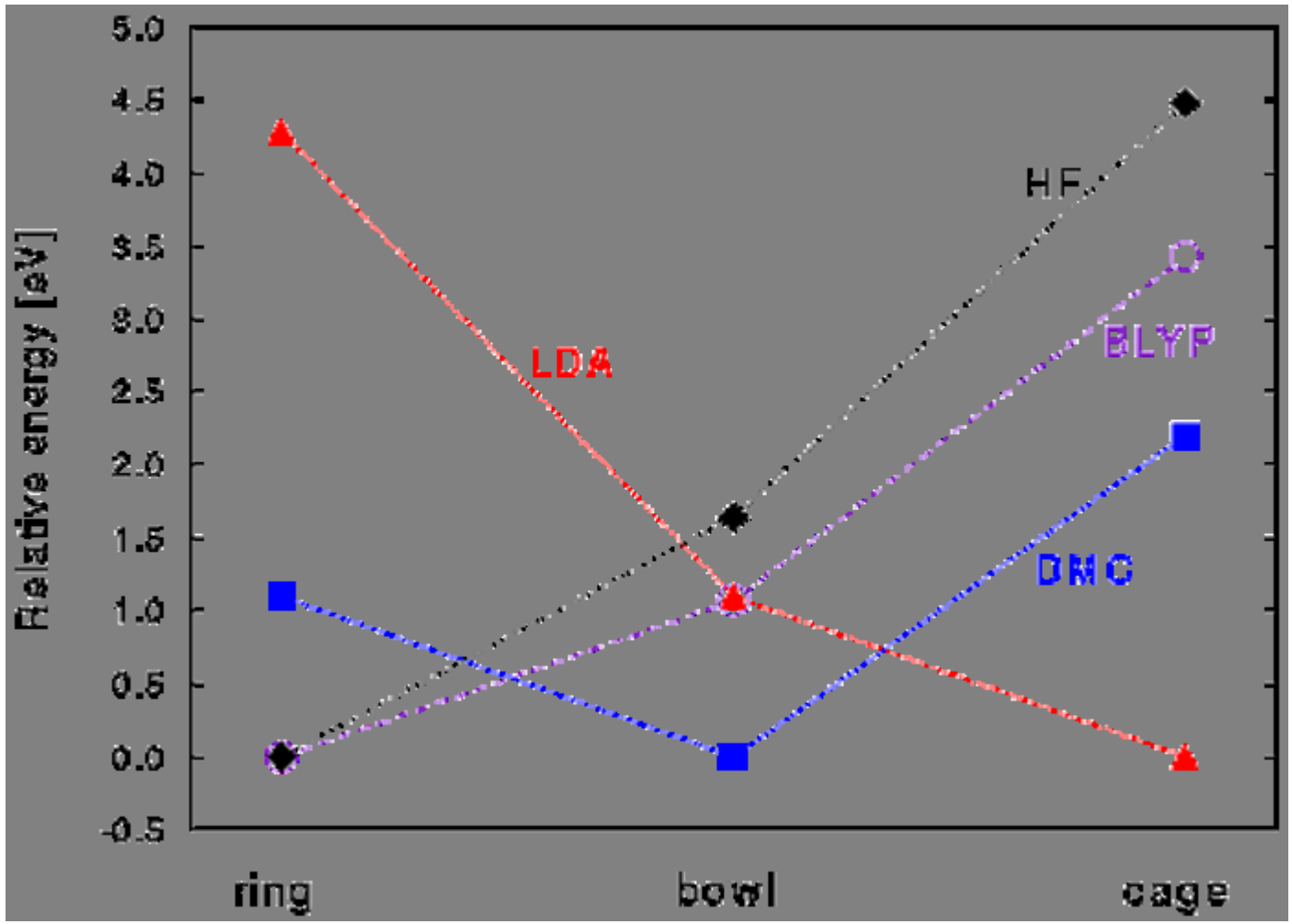
QMC was the first method to predict this (later confirmed by independent methods)



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

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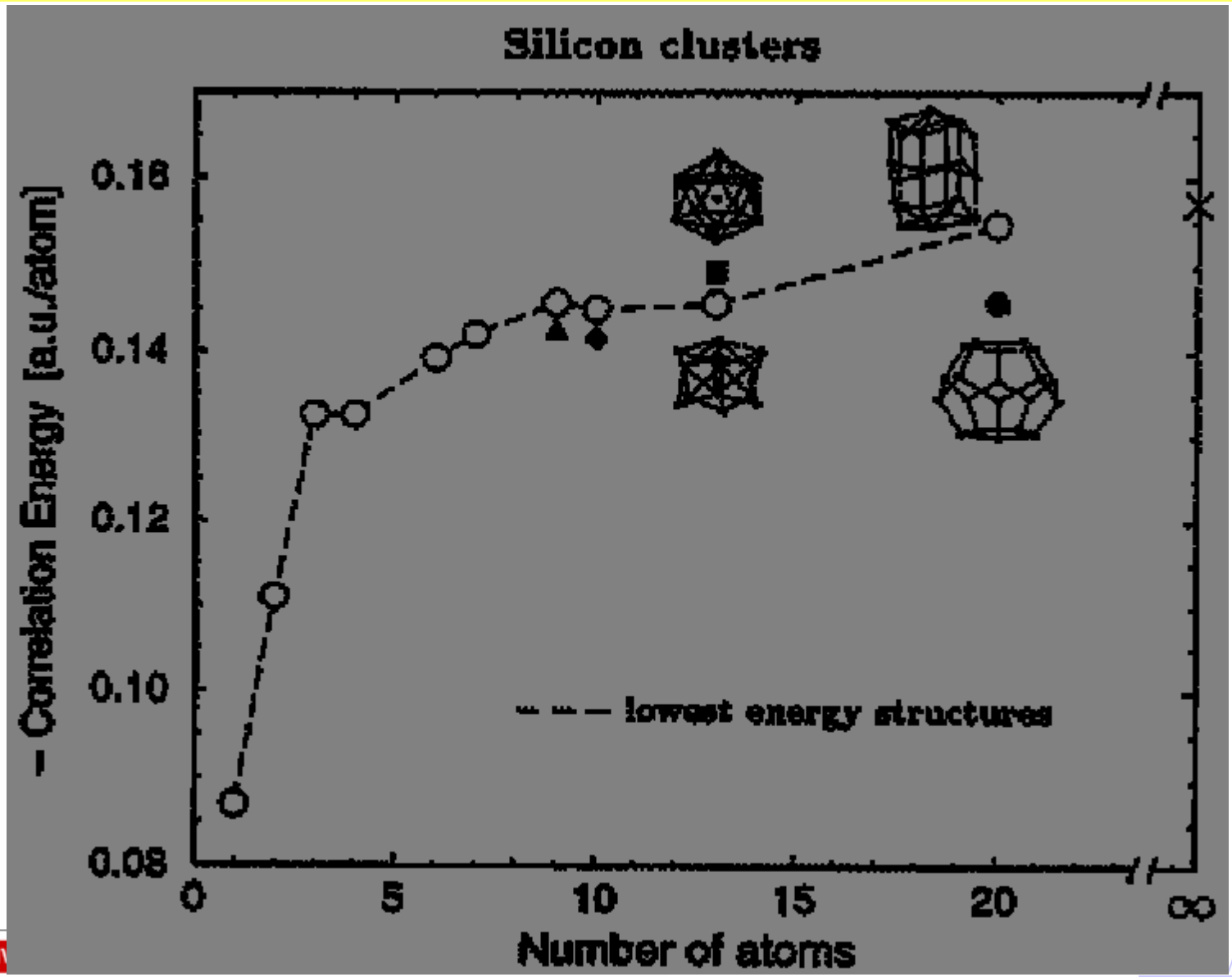
Another example: evaluate correlation energy from a single atom to molecule to clusters, all the way to the solid



Summary on performance of fixed-node DMC ("plain vanilla" method)

- fixed-node DMC typically recovers about 95% of the valence correlation energy (done for up to ~ 1000 electrons)

- energy differences agree with experiments within a few %

- 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

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Computational advantages of QMC: flagship application for each newgeneration of the largest parallel machines

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

- sampling walkers (almost) independent -> flexibility
  current developments to scale to 100,000 compute cores!!!

- cycle intensive, less memory intensive

- can accommodate any basis, any type of trial function

- enable to focus on interesting physics: type of many-body effects which are important, symmetries, phases, processes

- correlation problem "cornered" into the last 5% of E_corr!

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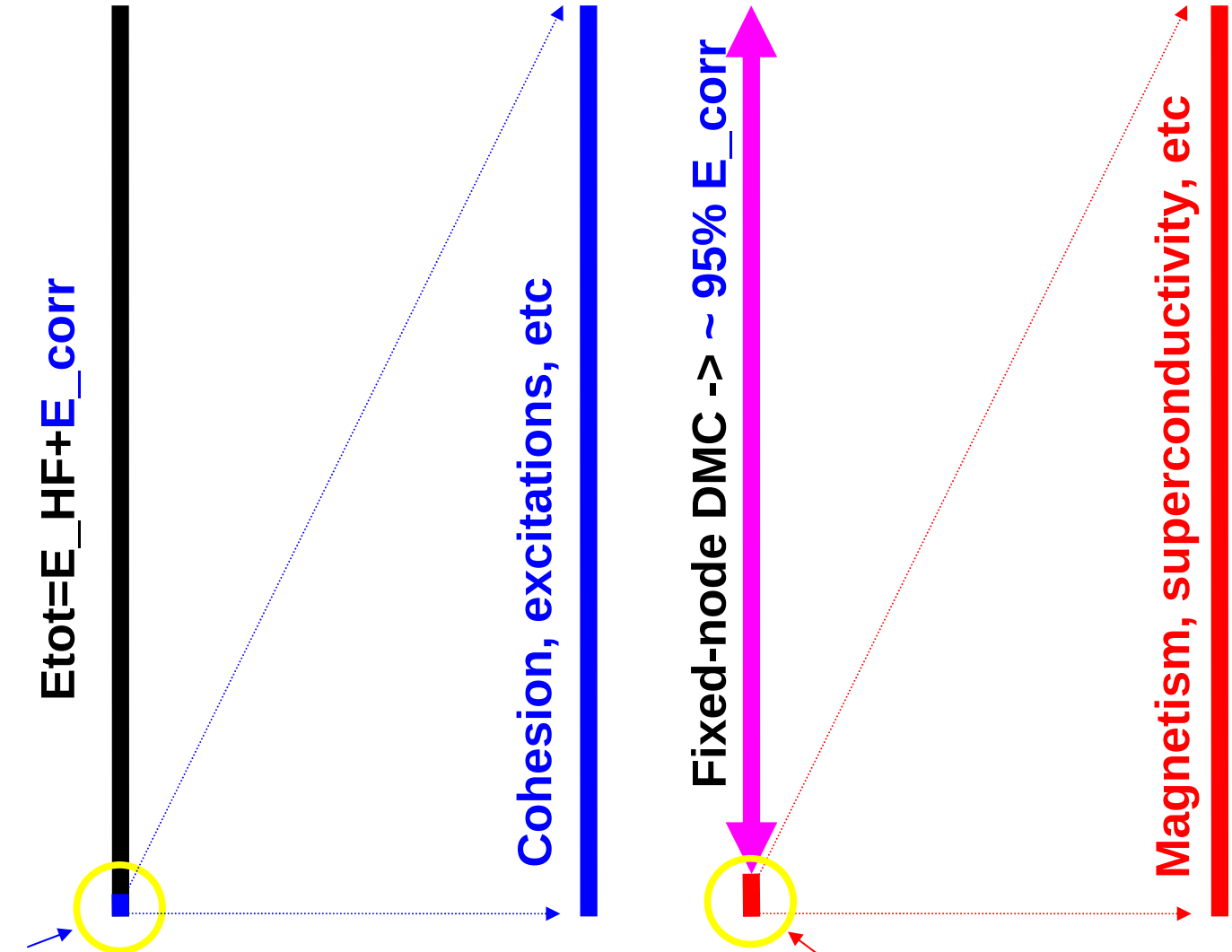
Beyond the fixed-node DMC: magnetism, superconductivity, etc



E_corr = ~3% Etot

-FN error: ~5% Ecorr
- agree with exper: ~ 1-2%

Methods which work here ??? (beyond the fixed-node ...)

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Fixed-node approximation

- bosonization of the fermionic problem

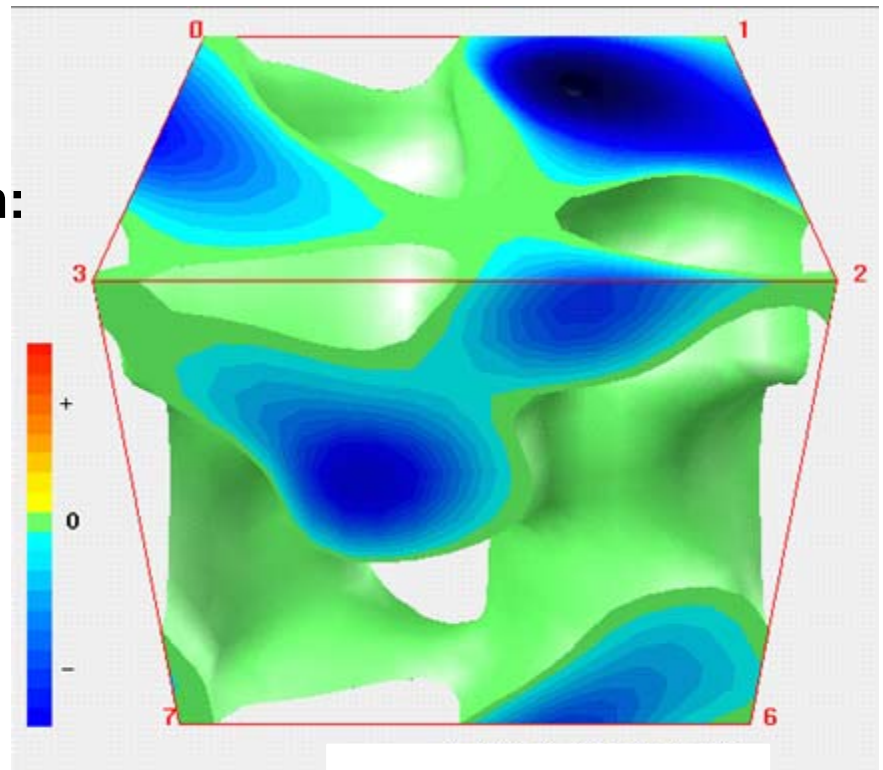
- important (funadmental) approximation:

  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 (more on that later)



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

Fermion node: manifold of configurations for which the wave function vanishes

The (only) approximation in quantum Monte Carlo

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

Fixed-node approximation: $f(\boldsymbol{R}, t) > 0$ **(boundary replaces antisymmetry)**

The Schrodinger eq.

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

$$f(\boldsymbol{R}, t \to \infty) = \psi_{Trial}(\boldsymbol{R})\, \phi_{Ground}(\boldsymbol{R})$$

Exact node -> exact energy in polynomial time

Exact nodes:
- **in 1D, particle concidence points**
- **in 3D known for a few 2e and 3e states**

In general, high-dimensional problem influenced by many-body effects and interactions

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Exciting new developments in antisymmetry/fermion sign problem: ideas and key focal points

~~"Sample-them-out": - nodal realease (Ceperley '80s)~~
~~- walker pairing (Kalos '90s), etc~~

"Understand the nodes": - general properties, new insights
- more fundamental issues (?)

↓

Key questions: - correct topology, ie, number of nodal cells
- correct shape

"Capture the physics (the nodes will follow)":

Key effort: - more accurate wavefunctions
- better physics, better math

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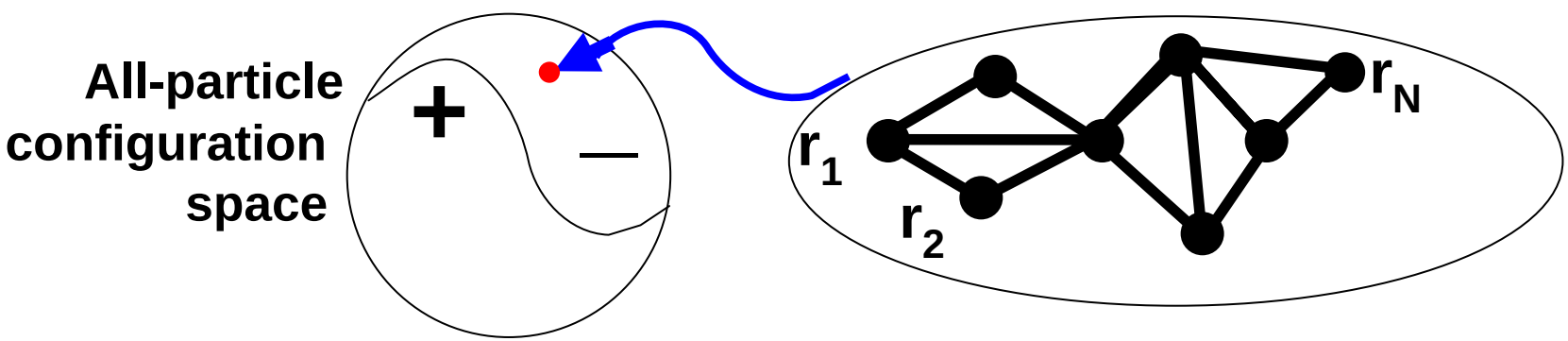
From a few-electron exact nodes, numerical studies -> Conjecture: for d >1 ground states have only two nodal cells, one "+" and one "-"

So far unproven even for noninteracting systems !

How to prove that some $\psi(R)$ has only two cells (Ceperley '92, numerical proof for 200 noninteracting fermions):

Find a point such that triple exchanges connect all the particles into a single cluster: then there are only two nodal cells



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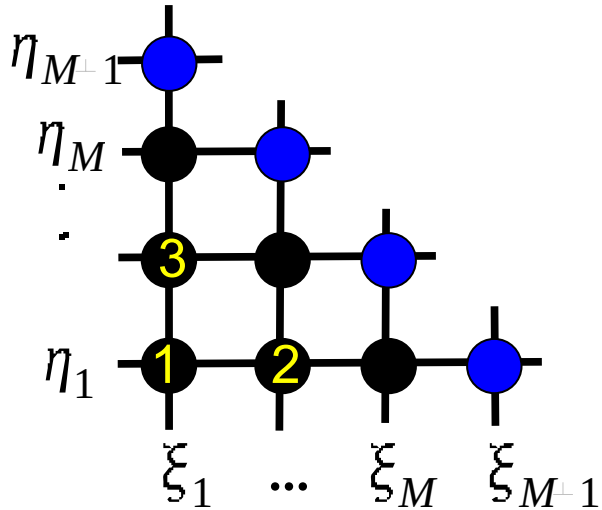
Explicit proof of two nodal cells for spin-polarized noninteracting system for any size (Idea illustrated for 2D harmonic fermions)

Place fermions in a Pascal-like triangle



M **lines ->** $N_M=(M+1)(M+2)/2$ **particles**

The wavefunction:

$$\psi_M(1,..,N_M)=C_{gauss}\,det[1,x,y,x^2,xy,y^2,...]$$

Evaluated explicitly by recursion:
factorizing out "lines of particles"

$$\psi_M(1,...,N_M)=\psi_{M-1}(1,...,N_M/I_{\xi_1})\prod_{i<j}^{i,j\in I_{\xi_1}}(y_j-y_i)\prod_{1<k\le M}(\xi_k-\xi_1)^{n_k}$$

By induction: if N_M **particles are connected, then also** N_{M+1} **. QED.**

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Two nodal cells theorem: generic (and fundamental) property of fermionic ground states of many models

Two nodal cells theorem. Consider a spin-polarized system with a closed-shell ground state given by a Slater determinant times an arbitrary prefactor (which does not affect the nodes)

$$\Psi_{exact} = C(1,\ldots,N)\, det\{\phi_i(j)\}$$

Let the Slater matrix elements be monomials $x_i^n y_i^m z_i^l \ldots$ of positions or their homeomorphic maps.

Then the wavefunction has only two nodal cells.

With some effort can be generalized to some open shells. (Mitas 2006)

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For noninteracting/HF systems adding another spin channel or imposing additional symmetries generate more nodal cells

Unpolarized nonintenracting/HF systems: 2*2=4 nodal cells!!!

-> product of two independent Slater determinants

$$\psi_{HF} = det^{\uparrow}\{\phi_{\alpha}\}\, det^{\downarrow}\{\phi_{\beta}\}$$

- in general, imposing symmetries generates more nodal cells: the lowest quartet of S symmetry ^{4}S(1s2s3s) has six nodal cells

What happens when interactions are switched on ?

"Nodal/topological degeneracy" is lifted and multiple nodal cells fuse into the minimal two again!

First time showed on Be atom, Bressanini etal '03

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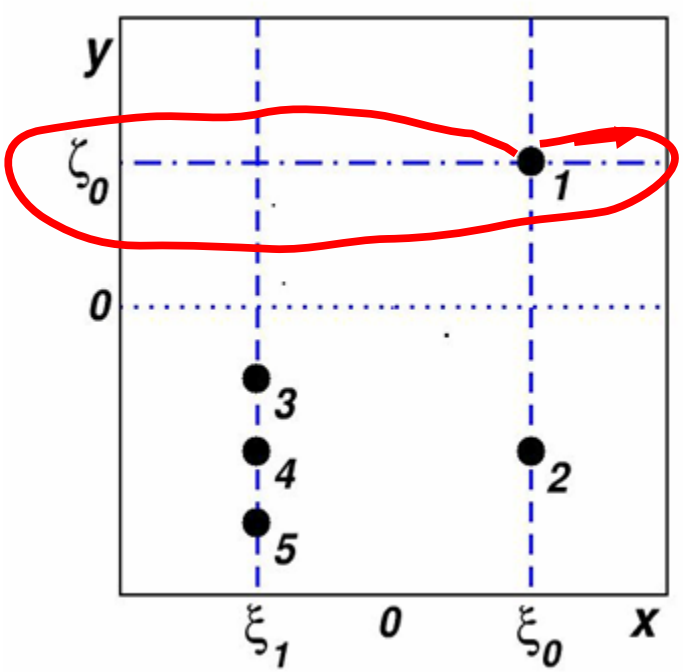
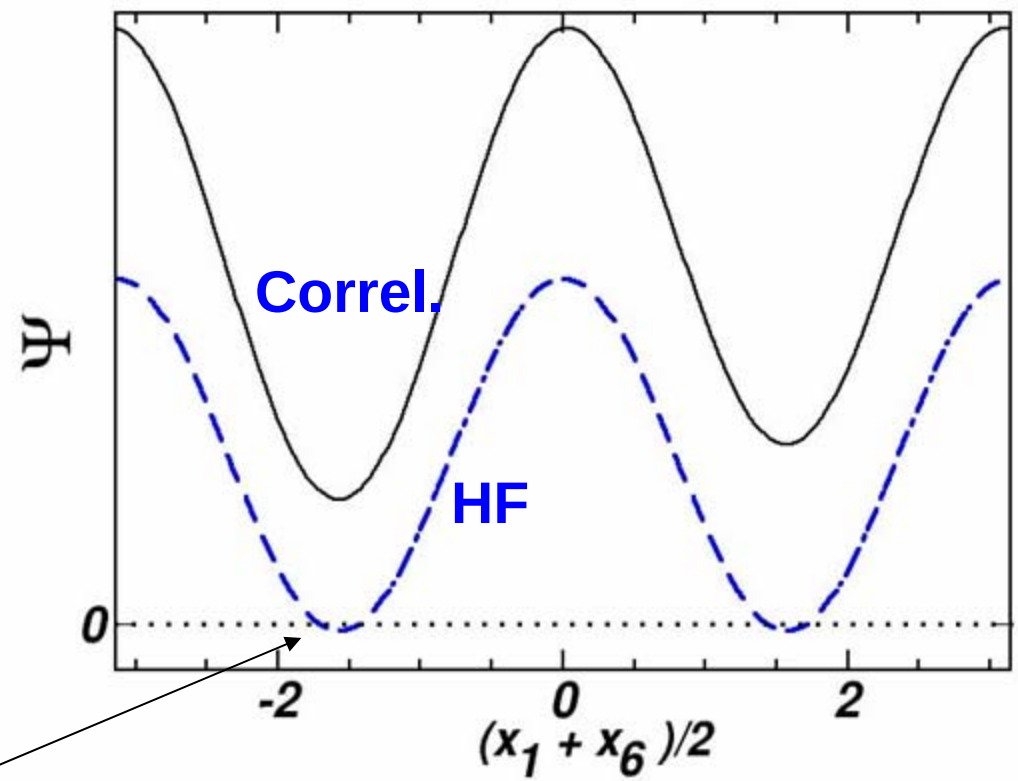
Correlation in homogeneous electron gas: singlet pair of e- winds around the box without crossing the node

$$r_i\uparrow = r_{i+5}\downarrow + offset, \quad i=1,\ldots,5$$



Wavefunction along the winding path



HF crosses the node multiple times, BCS does not (supercond.)

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The same applies to the nodes of temperature/imaginary time density matrix

Analogous argument applies to temperature density matrix

$$\rho(R,R',\beta)=\sum_{\alpha}\exp[-\beta E_{\alpha}]\psi*_{\alpha}(R)\psi_{\alpha}(R')$$

fix R',β -> nodes/cells in the R subspace

At high (classical) temperatures

$$\rho(R,R',\beta)=C_N det\{\exp[-(r_i-r'_j)^2/2\beta]\}$$

It is not too difficult to prove that at classical temperatures R and R' subspaces have only two nodal cells: it is stunning since there is a summation over the whole spectrum!

PRL, 96, 240402 /cond-mat/0601485 (the basic ideas)
cond-mat/0605550 (all the models, density matrix)

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Two nodal cells: generic property, possible exceptions
The next problem: the exact shape of the node

Topology of the nodes closed-shell ground states is surprisingly simple:

The ground state node bisects the configuration space (the most economic way to satisfy the antisymmetry)

Possible exceptions:

- nonlocal interactions, strong interactions
- impose more symmetries or boundaries
- large degeneracies

The next problem: the exact nodal shape is difficult to get!
The key: better wavefunctions, better math, better physics

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More general wave function form -> object called pfaffian: signed sum of all distinct pair partitions

$$pf[a_{ij}] = \sum_P (-1)^P a_{i_1 j_1} \ldots a_{i_N j_N}, \quad i_k < j_k, \quad k = 1, \ldots, N$$

The elements form a skew-symmetric matrix, eg, for 2N=4

$$pf \begin{bmatrix} 0 & a_{12} & a_{13} & a_{14} \\ -a_{12} & 0 & a_{23} & a_{24} \\ -a_{13} & -a_{23} & 0 & a_{34} \\ -a_{14} & -a_{24} & -a_{34} & 0 \end{bmatrix} = a_{12}a_{34} - a_{13}a_{24} + a_{14}a_{23}$$

Signs: **+** **-** **+**

Relations of determinants and pfaffians

- For any square matrix B

$$det(B) = (-1)^{n(n-1)/2} pf \begin{bmatrix} 0 & B \\ -B^T & 0 \end{bmatrix}$$

- For any skew-symmetric matrix A (2nx2n)

$$det(A) = [pf(A)]^2$$

- Any determinant can be written as pfaffian but not vica versa: pfaffian is more general, determinant is a special case

More identities exist, pfaffian can be expanded in minors, etc, pfaffian can be calculated by a Gaussian-like “elimination” directly

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The simplest antisymmetric wavefunctions built from one-particle vs. pair orbitals

One-particle (spin)orbitals wavefunction: Slater determinant

$$\psi_{HF} = A[h_1(x_1)h_2(x_2)\ldots] = det[h_k(x_i)] \qquad x_i = (r_i, \sigma_i) \qquad i,k = 1,\ldots,N$$

Pair orbital wavefunction: pfaffian

$$\psi_{PF} = A[\phi(x_1,x_2)\phi(x_3,x_4)\ldots] = pf[\phi(x_i,x_j)] \qquad i,j = 1,\ldots,2N$$

Note: in the simplest case only one pair (spin)orbital!

$$\phi(x_i,x_j) = \phi^{\uparrow\downarrow}(r_i,r_j)(\uparrow\downarrow - \downarrow\uparrow) + \chi^{\uparrow\uparrow}(r_i,r_j)(\uparrow\uparrow) + \chi^{\downarrow\downarrow}(r_i,r_j)(\downarrow\downarrow) + \chi^{\uparrow\downarrow}(r_i,r_j)(\uparrow\downarrow + \downarrow\uparrow)$$

symmetric **antisymmetric**

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Bardeen-Cooper-Schrieffer (BCS): a special case of the pfaffian wavefunction

Antisymmetized product of singlet pair orbitals $\phi^{\uparrow\downarrow}(i,j)$

$$\Psi_{BCS}=A[\phi(i,j)]=det[\phi(i,j)]$$

- used to describe supeconductivity or BEC, Sorella et al for electronic structure, '04

Problem with spin-polarized case: $N^{\downarrow}=n$ **while** $N^{\uparrow}=n+o$

$$\Psi_{BCS}=A[\phi(1,n)\ldots\phi(n,2n)\times h_1(2n+1)\ldots h_o(2n+o)]$$

where $h_k(i)$ **are one-particle orbitals (usually HF)**

- fully spin-polarized state trivially recovers Hartree-Fock :-(

$$\Psi_{BCS}=A[h_k(i)]=det[h_k(i)]=\Psi_{HF}$$

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Beyond BCS: pfaffian wavefunctions with both singlet and triplet pairs -> all spin states treated consistently

$$\Psi_{PF} = pf\begin{bmatrix} \chi^{\uparrow\uparrow} & \phi^{\uparrow\downarrow} & \psi^{\uparrow} \\ -\phi^{\uparrow\downarrow T} & \chi^{\downarrow\downarrow} & \psi^{\downarrow} \\ -\psi^{\uparrow T} & -\psi^{\downarrow T} & 0 \end{bmatrix} \times \exp[U_{corr}]$$

- **pairing orbitals expanded in one-particle basis**

$$\phi(i,j) = \sum_{\alpha \geq \beta} a_{\alpha\beta}[h_\alpha(i)h_\beta(j) + h_\beta(i)h_\alpha(j)]$$
$$\chi(i,j) = \sum_{\alpha > \beta} b_{\alpha\beta}[h_\alpha(i)h_\beta(j) - h_\beta(i)h_\alpha(j)]$$

- unpaired $\psi(i) = \sum_\alpha c_\alpha h_\alpha(i)$

- expansion coefficients and the Jastrow correlation optimized (M.Bajdich, L.M., etal, PRL, 2006)

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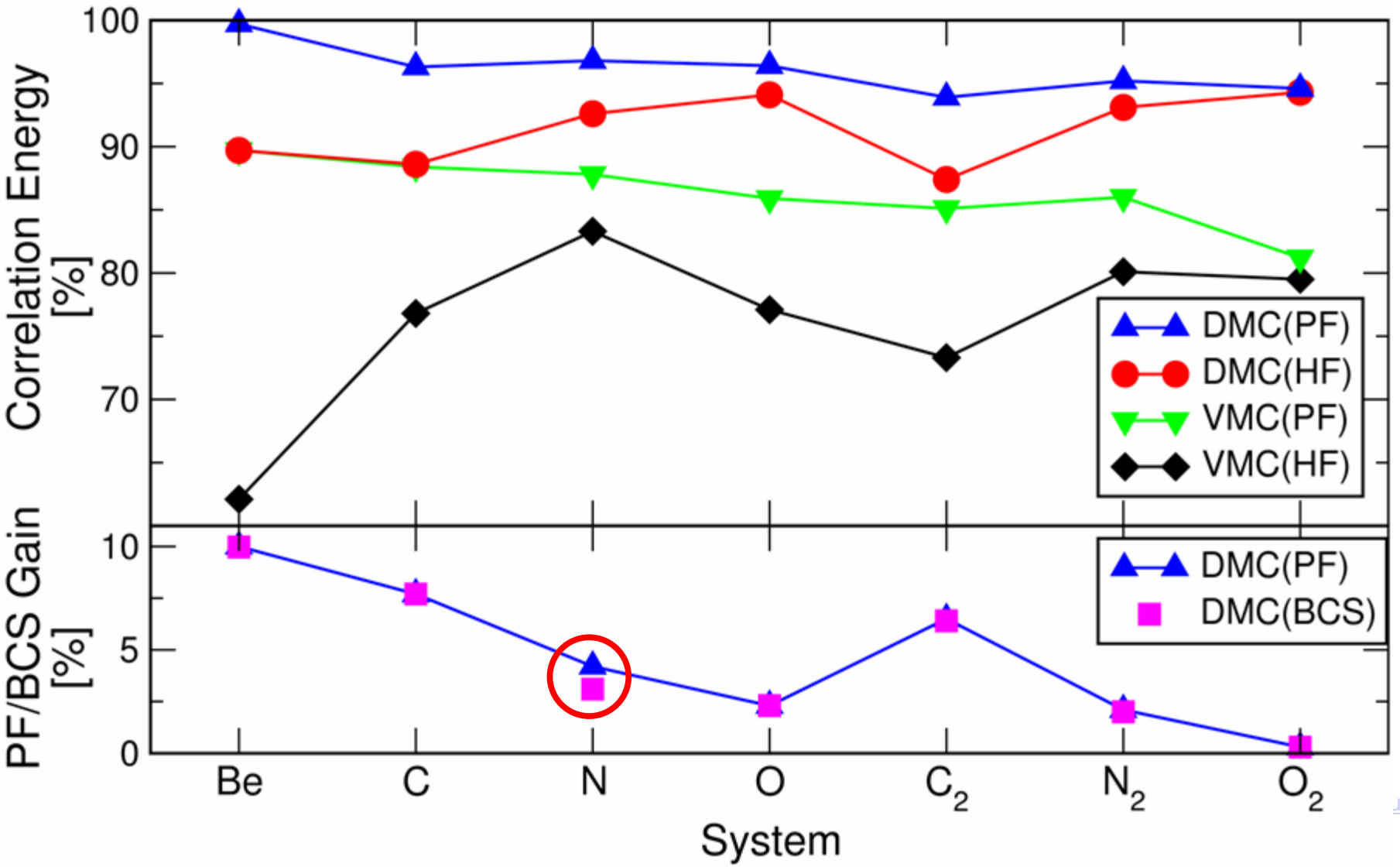
Results: correlation energies of atoms, dimers
Correlation gain from singlet vs triplet pairing



Multi-pfaffian wavefunctions for first row atoms: FNDMC ~98-99 % of correlation with a few pfaffians!

Table of % of correlation energies recovered for CI vs MPF w.f.
- n denotes the number of dets/pfs in the expansion

WF	n	C	n	N	n	O
VMC(MPF)	3	92.3(1)	5	90.6(1)	11	92.6(3)
VMC(CI)	98	89.7(4)	85	91.9(2)	136	89.7(4)
DMC(MPF)	3	98.9(2)	5	98.4(1)	11	97.2(1)
DMC(CI)	98	99.3(3)	85	98.9(2)	136	98.4(2)

- number of pfaffians n
- subject to symmetry constraints
- in principle all distinct pairs could be included

M. Bajdich et al, PRL 96, 130201 (2006)

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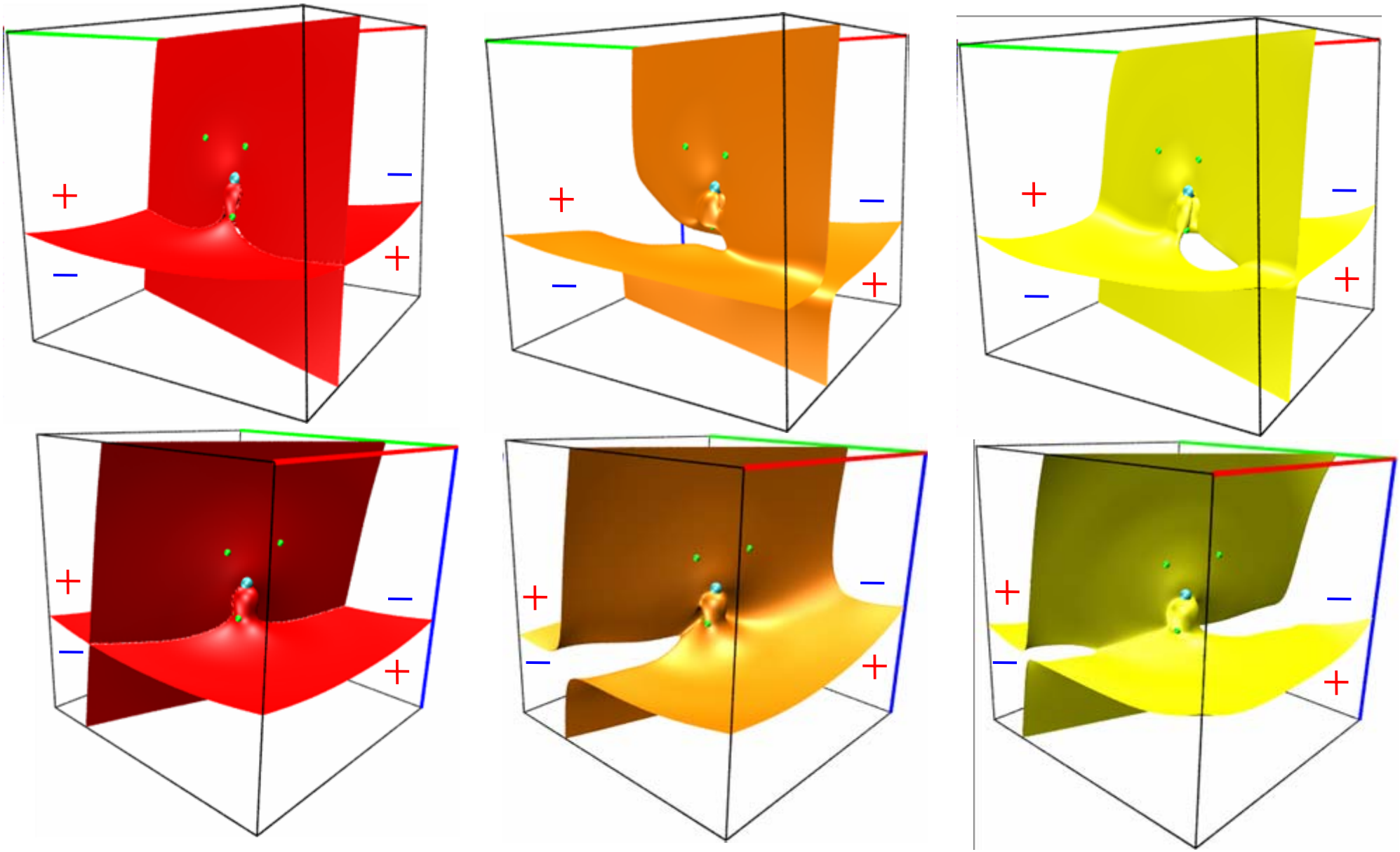
3D scan of the oxygen atom node by 2e- singlet: Topologies of different wfs (fixed-node DMC Ecorr)

HF (94.0(2)%) **MPF** (97.4(1)%) **CI** (99.8(3)%)



Observations from comparison of HF and "exact" nodes

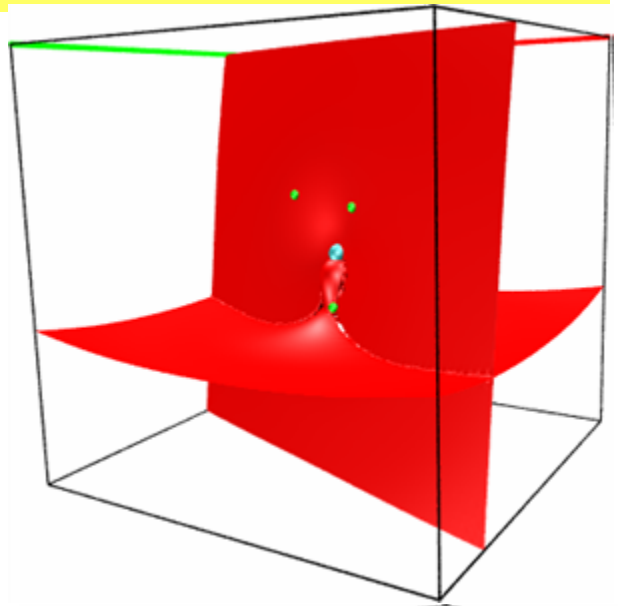
- the two nodal cells for Coulomb interactions as well

- the nodal openings have rather fine structure

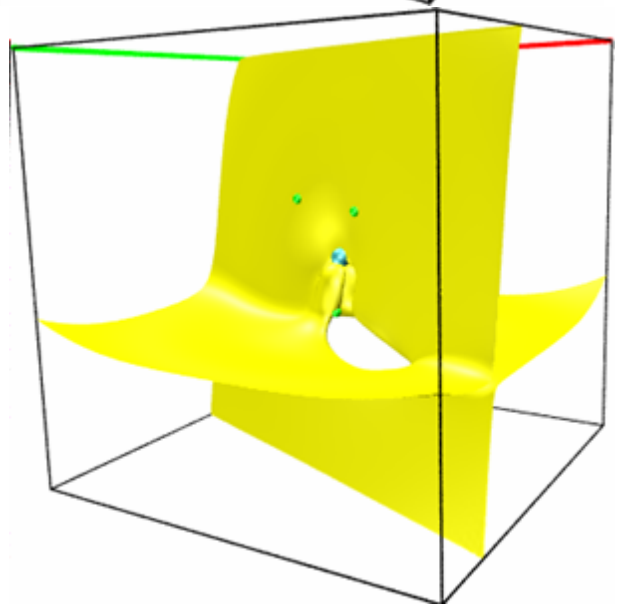
- openings are important -> ~ 5% of the correlation energy

- although topologically incorrect, away from openings the HF nodes unexpectedly close to exact

HF



CI



Summary on topology of nodes and pairing wave functions

- explicit proof that, in general, fermionic ground states and density matrices have two nodal cells for d>1 and for any size - fundamental property of fermionic systems

- overall mean-field nodes excellent (that's why fixed-node works) but nodal openings in correlated wave functions and exact nodal shape important: 5 % of correlation energy; better physics and better math: pfaffian pairing wavefunctions look promising

- non-perturbative character of pfaffians (certain diagrams summed to infinity) - long-range/macroscopic correlations in supercond.

- fermion nodes: another example of importance of quantum geometry (field theory) and topology for electronic structure

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More developments: coupling of QMC with ab initio molecular dynamics -> QMC/MD !

- so far QMC used only for static, state-by-state calculations

- Car-Parrinello MD: - ions evolve according to classic EOM
  - electrons with Density Functional Theory

Typical displacement of an ion in one MD step

10^{-3} to 10^{-4} a.u.

Typical displacement of an e- in one DMC step

10^{-1} to 10^{-2} a.u.

Key idea: QMC walkers are fast, couple the evolution of ions with the evolution of the wavefunction (factor 50 in efficiency!)

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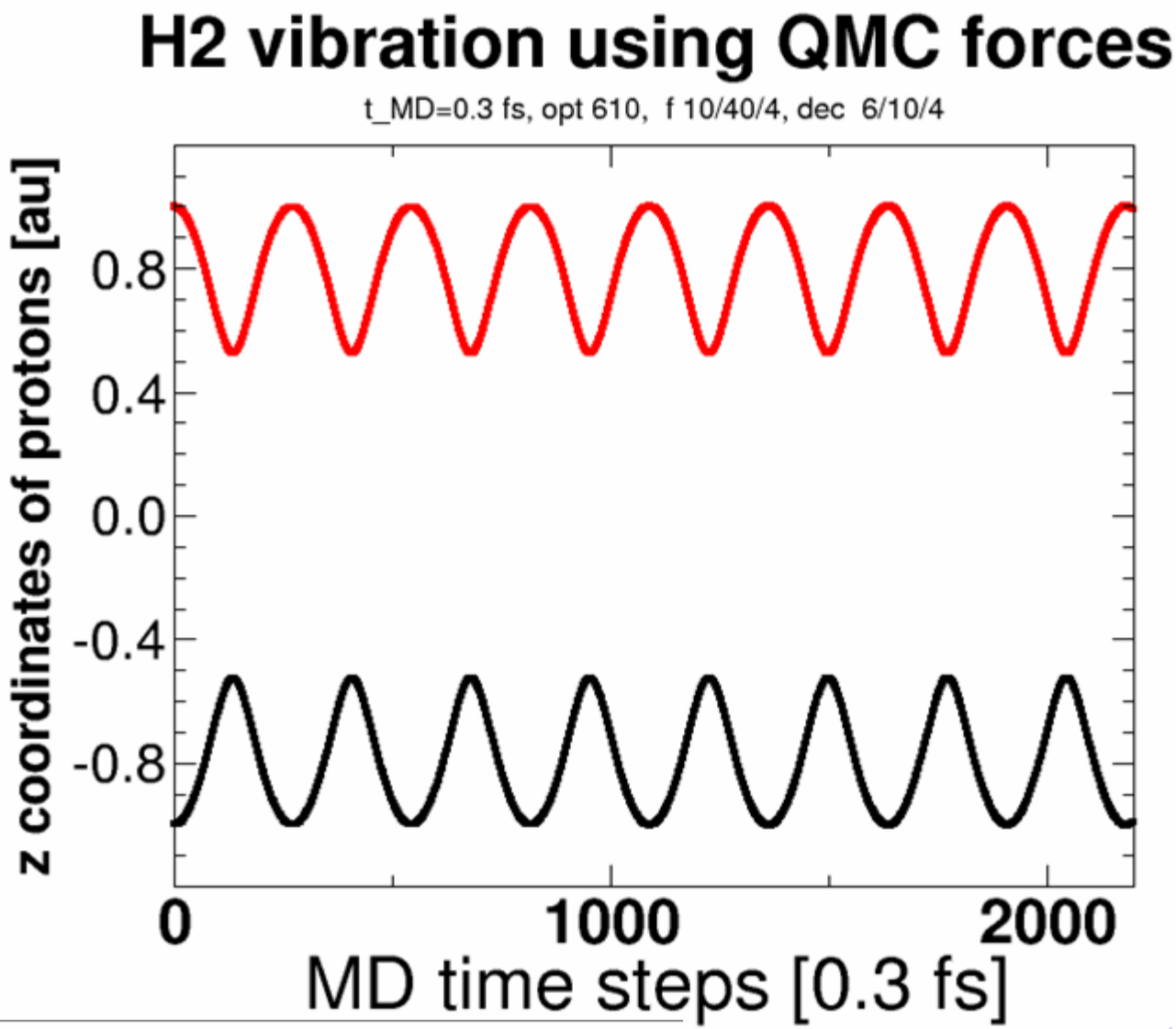
First calculations with QMC/MD method



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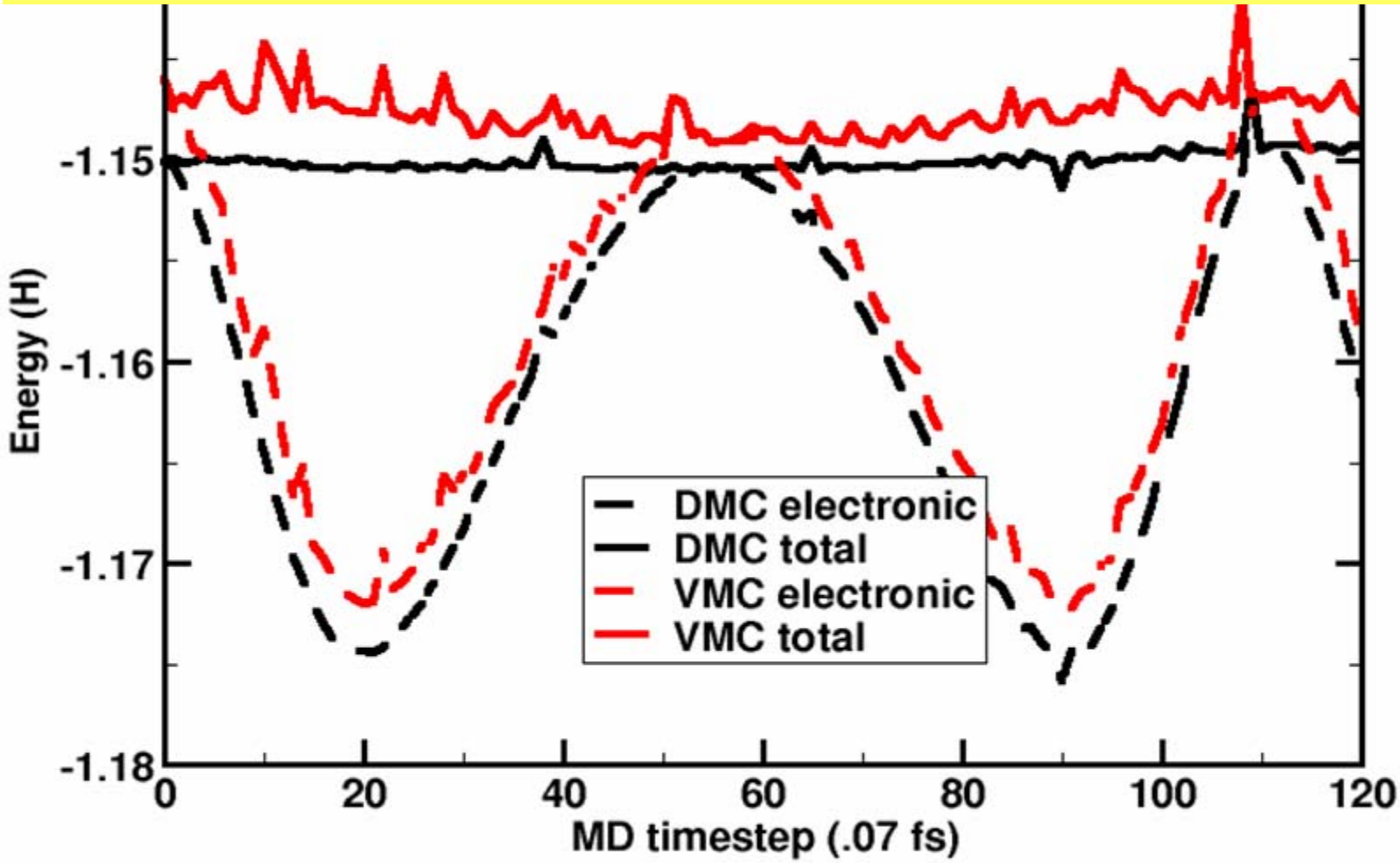
H2 vibration: total and electronic energies in VMC and DMC



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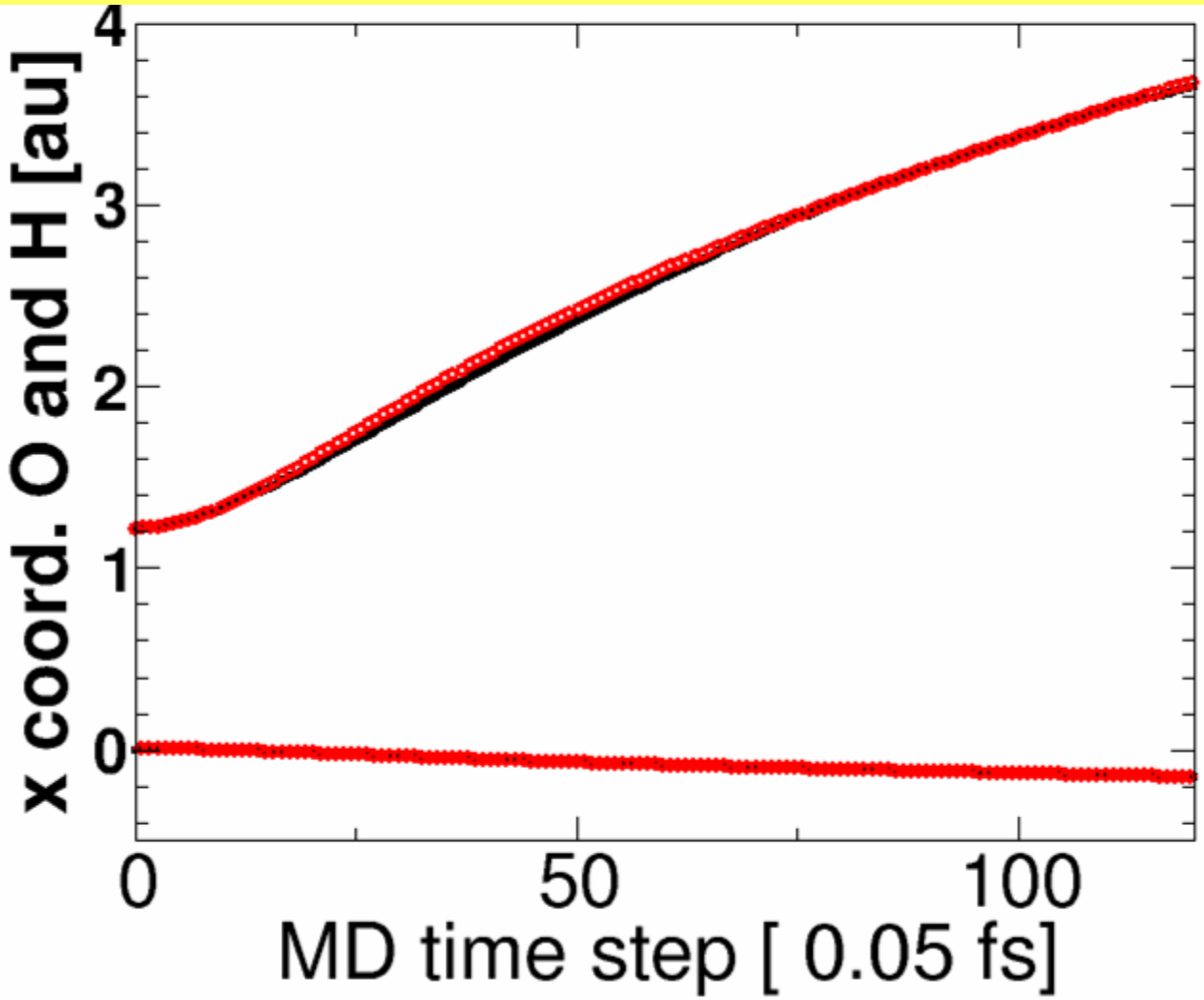
Dynamical dissociation of H_2O molecule: QMC/MD vs Car-Parrinello AIMD



Grossman & Mitas, PRL, 94, 056403 ('05)

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QMC as an alternative for electronic structure

- focus on efficient description many-body effects, put the many-body effects where they belongs: to the wavefunction (new wave function was/is always a milestone: Hartree-Fock, BCS, Laughlin...)

- input from other (CI,CC, ect) correlated wave function methods very important: efficiency!!!

- one still has to do the physics/chemistry: which types of correlations, symmetries, phases, . . ., the fundamental and fun part!

- but: tedious integrals, averaging, etc, left to machines, gives a good use of parallelism, scales N^(1-3), robust, flexible

- often the most accurate method available: benchmarks

- opens new perspectives and science on many-body quantum phenomena

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QMC: only an accurate method or a paradigm shift ?

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

- let the machine to worry about integrals etc ($/cycle decreasing exponentially in time)

- combination of analytical insights, reliable mean-fields 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 (fundamental point), the most efficient in capturing correlation effects

- history of high accuracy benchmark/reference calculations and the only correlated wave function method which works also for solids

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Current status of our QMC code Qwalk ("Quantum Walk")

- molecules and solids (3D periodicity), 1D rings other systems (effective interactions etc, model systems etc)

- any basis (gaussian, Slater, PW, numerical, etc) or combination

- plethora of correlated wavefunctions (CI, development of pfaffian libraries)

- variety of methods (variational, fixed-node DMC, optimizations, etc)

- current, new version of the code, C++, 50,000 lines: main author Lucas K. Wagner, soon to be GPL released

- interfaces and converters to GAMESS, CRYSTAL (ABINIT, Gaussian in progress, NWChem ...)

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Suggestions to NWChem developers: collaborate with us on groundbreaking and win-win projects!

- QMC needs complete info about wave functions: beyond MOs, determinants, CI coefficients, CSF determinants and coeffs, ...

- we need very nimble tools for both design and analysis of various correlated wavefunctions (eg, only these excitations into these particular states while keeping the density constant); nonorthogonal basis, each CSF with different orbitals: could lead to several breakthroughs in compactness of wave functions;

- CI-like calculations of solids nonexistent: would be a breakthrough! with QMC even modest size CI wave functions could be extermely important (eg, key excitations in high-Tc compounds)

- new direction: optimization of pairing wave functions and beyond

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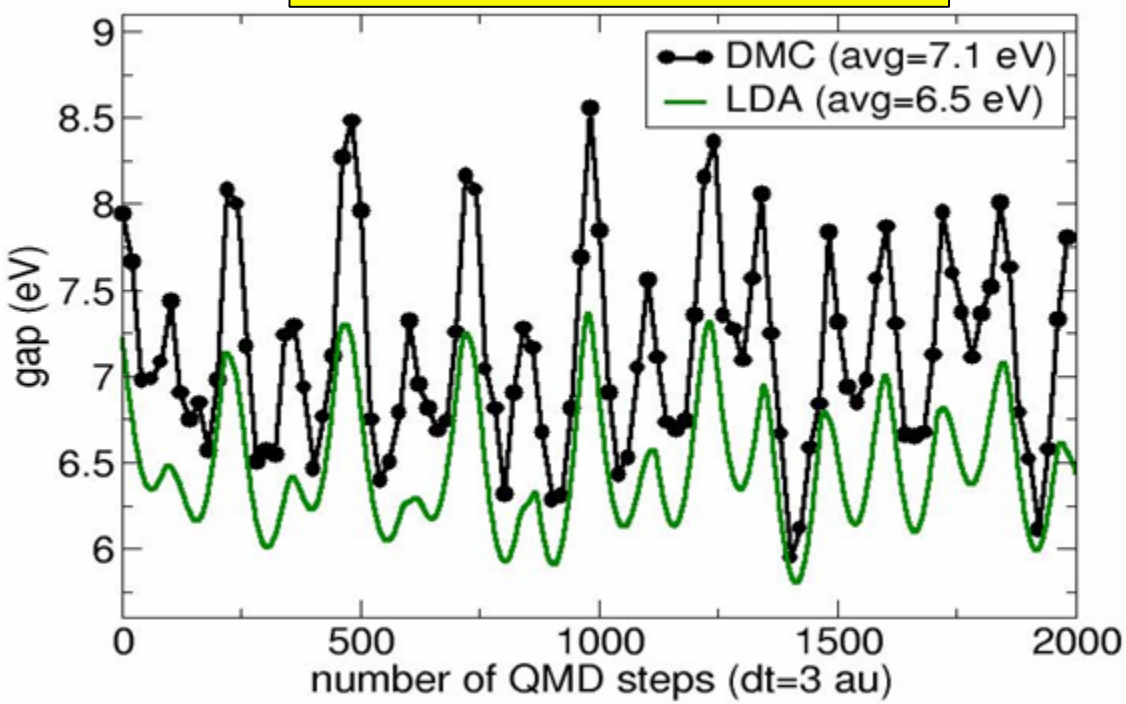
Merci. C'est fini ...

First try: MD/DFT trajectories, energies from DMC
Excited state evolution for hot silane molecule, water heat of vaporization

Optical Gap vs Time



Done also for larger systems, up to 32 water molecules: heat of vaporization of 6.1 kcal/mol vs. DFT of 9 kcal/mol, dynamical and T>0 quantity!

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