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Advanced School on Quantum Monte Carlo Methods in Physics and Chemistry

21 January - 1 February, 2008

Pairing wave functions for physics and chemistry.

S. Sorella

DEMOCRITOS, SISSA Trieste

Pairing wave functions for physics and chemistry

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Outline

RVB <u>new physics</u> in Model Hamiltonians:
→ superconductivity in t-J model
→ non conventional spin-liquids, J1-J2,…

→ Realistic Hamiltonian Coulomb, Born-Opp.

→ RVB working well in Chemistry: RVB in benzene molecule and its dimer, C2, water…

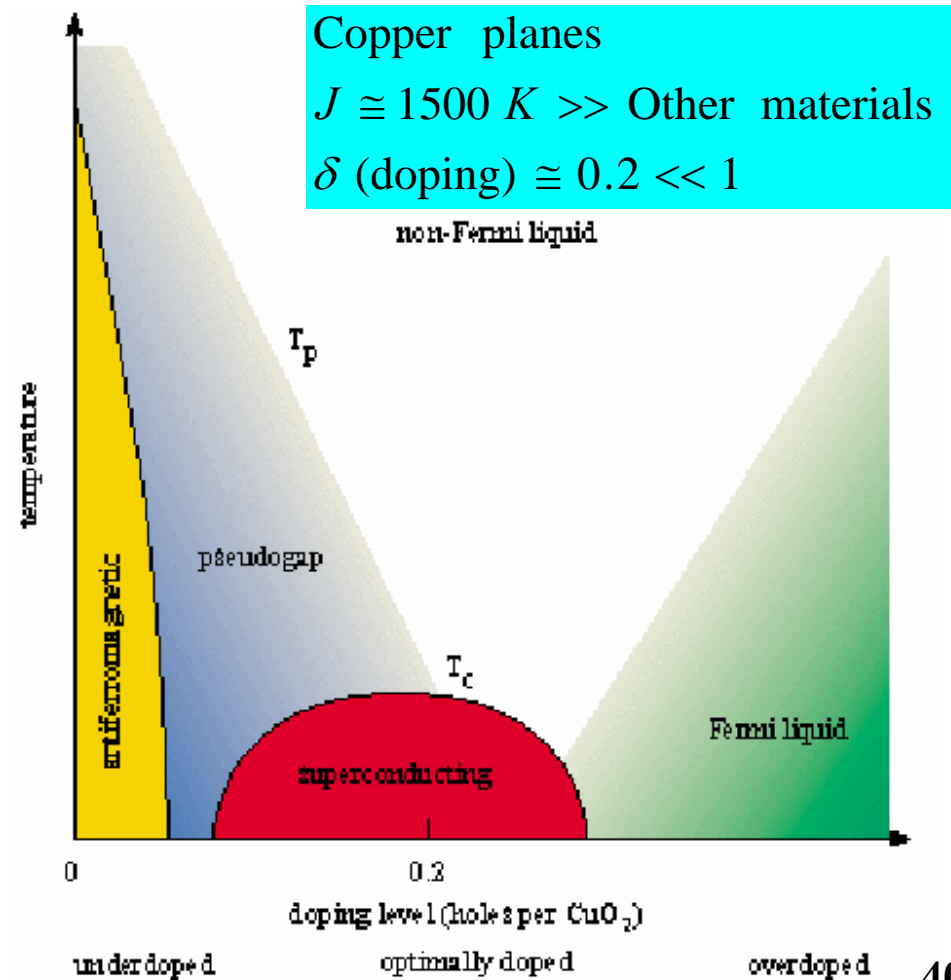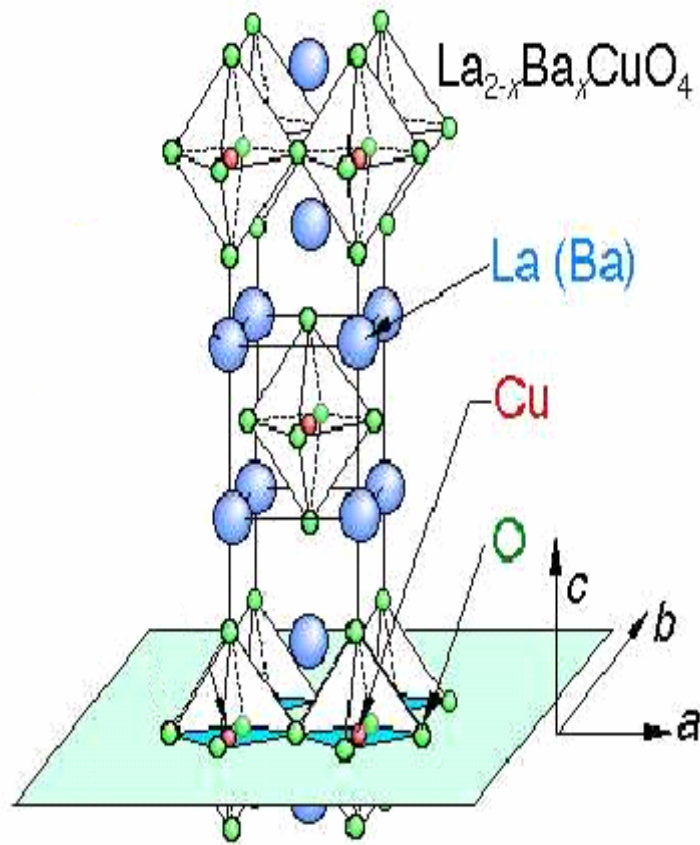Computational advantages (even when it corresponds to Hartree Fock+Jastrow):

→ QMC molecular dynamics with ~100 Hydrogen

→ Solids, Silicon, Hydrogen

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Cuprates

quasi-2D structure

Phase diagram: temperature vs. doping

$La_{2-x}Ba_xCuO_4$

La (Ba)

Cu

O

Copper planes
$J \cong 1500\ K\ >>$ Other materials
δ (doping) $\cong 0.2 << 1$

non-Fermi liquid

T_p

pseudogap

T_c

antiferromagnetic

temperature

superconducting

Fermi liquid

0   0.2

doping level (holes per CuO_2)

underdoped   optimally doped   overdoped

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The Anderson's wavefunction $\delta = 0$

$$H = J \sum_{n.n.Cu} \vec{S}_i \vec{S}_j \quad \text{2D Cu-plane} \quad S = \frac{1}{2} / Cu$$

The most general singlet mean field:

$$H_{BCS} = \sum_{k,\sigma} \varepsilon_k c^+_{k,\sigma} c_{k,\sigma} + \sum_k \Delta_k c^+_{k,\uparrow} c^+_{-k,\downarrow} + h.c.$$

$$e.g. \quad \varepsilon_k = -2t(\cos k_x + \cos k_y) - \mu, \Delta_k = \Delta(\cos k_x - \cos k_y)$$

The GS of H_{BCS} : $H_{BCS} |BCS\rangle = E_{GS} |BCS\rangle$

$$|BCS\rangle = \exp(\sum_k f_k c^+_{k\uparrow} c^+_{-k\downarrow}) |0\rangle$$

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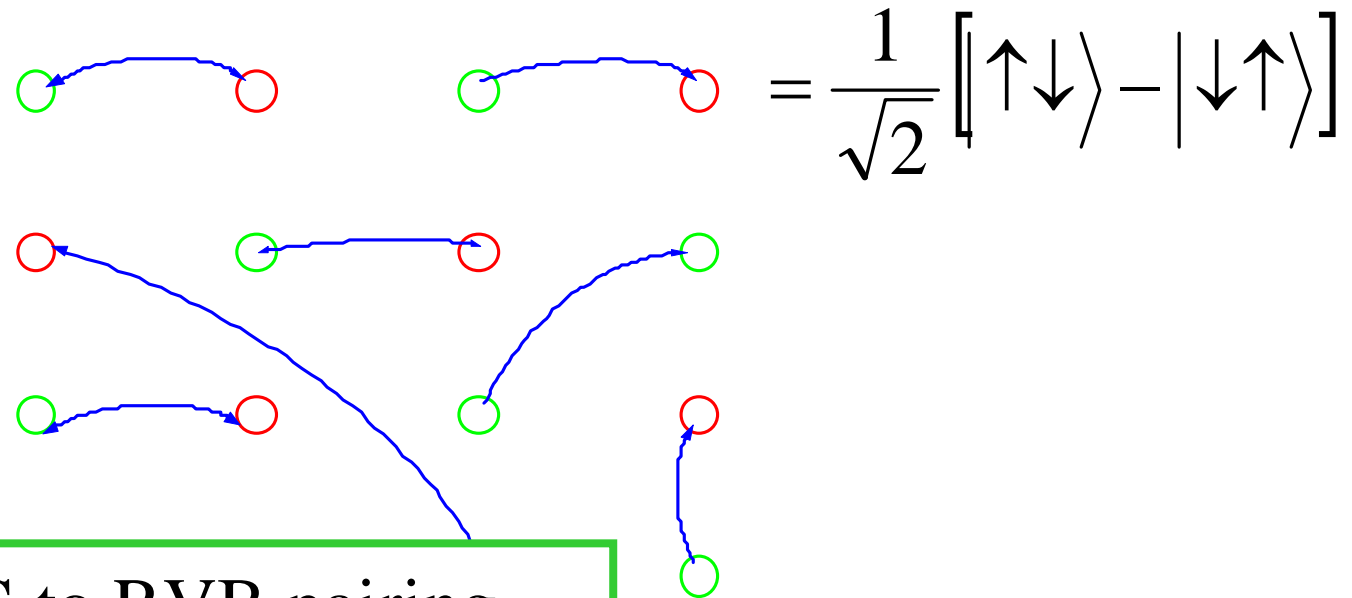January-2007   Diffusion Monte Carlo methods with non-local potentials (Sorella)

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Anderson's variational wavefunction for spin models

$$\psi_{RVB} = \hat{J} \exp\sum_{i,j} f_{i,j} \underbrace{(c^+_{i,\uparrow}c^+_{j,\downarrow} + c^+_{j,\uparrow}c^+_{i,\downarrow})}_{\text{Singlet bond}} |0\rangle$$

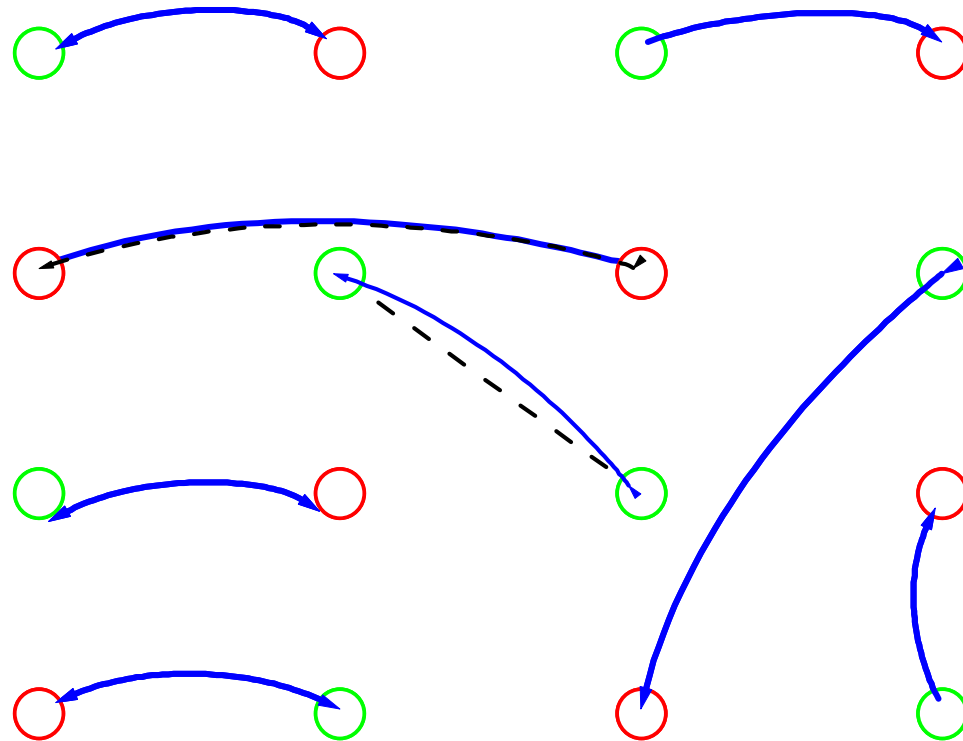$$f_k = \Delta_k \Big/ \left(\varepsilon_k + \sqrt{\varepsilon_k^2 + \Delta_k^2} \right)$$

where Δ_k is the BCS gap function

ε_k the free electron dispersion

But $\hat{J}$ ~~↑↓~~ ⟶ Resonance Valence Bond

$$= \frac{1}{\sqrt{2}}\big[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\big]$$

From BCS to RVB pairing….

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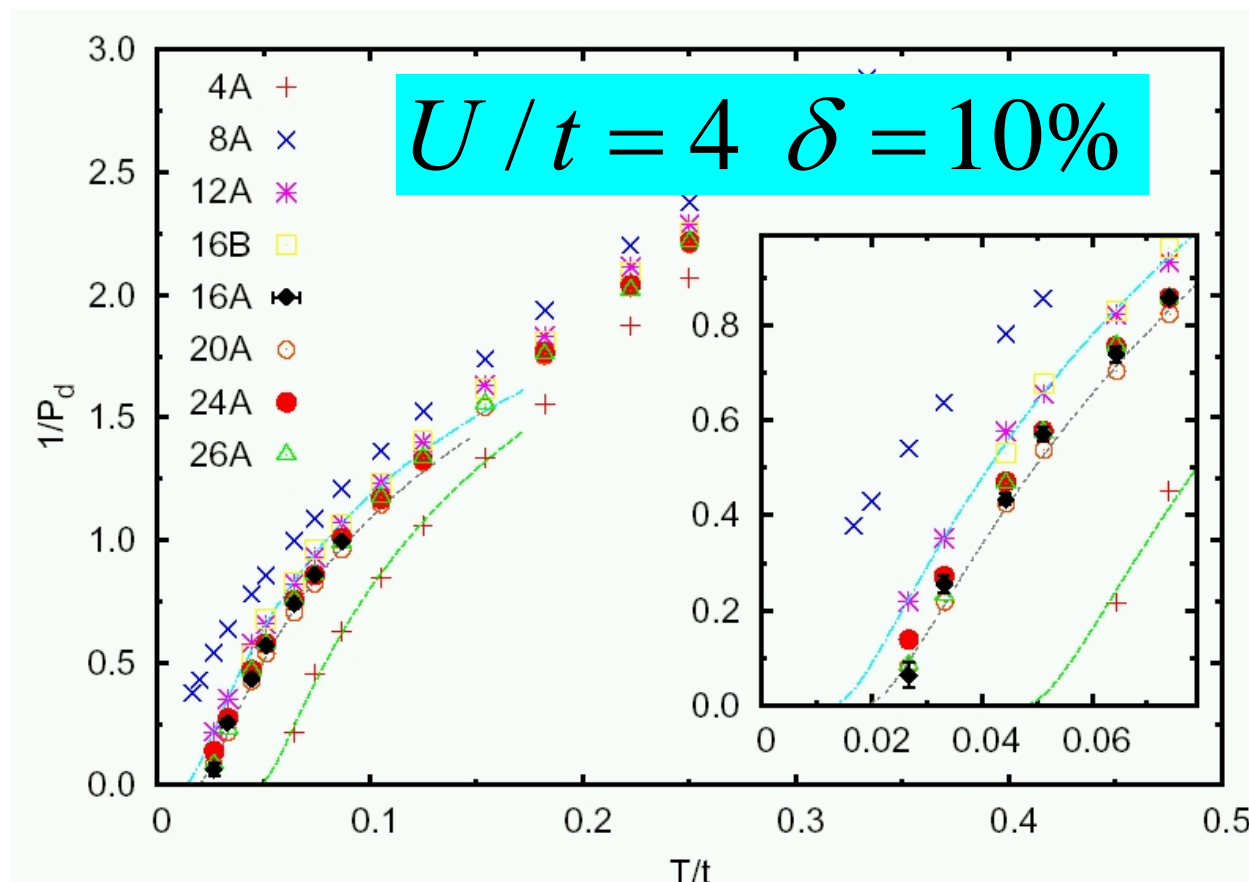
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From RVB insulator to superconductivity

The presence of holes (empty sites) allows charge (super-) current and <u>superconductivity</u>

T. Maier et al. PRL 2005   2D Hubbard model

$$P_d = \text{d-wave susceptibility} \rightarrow 1/P_d = 0 \text{ at } T_c$$
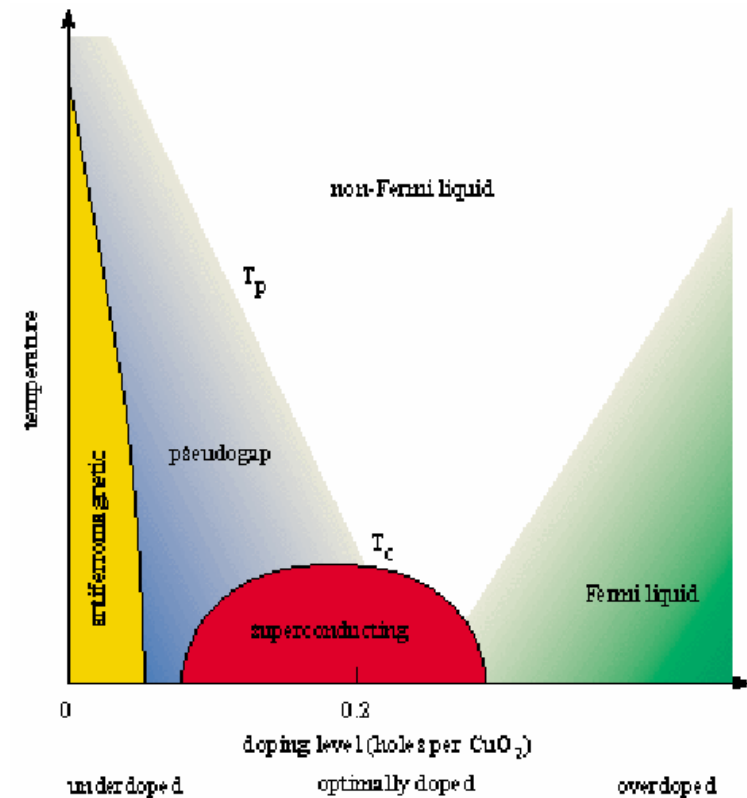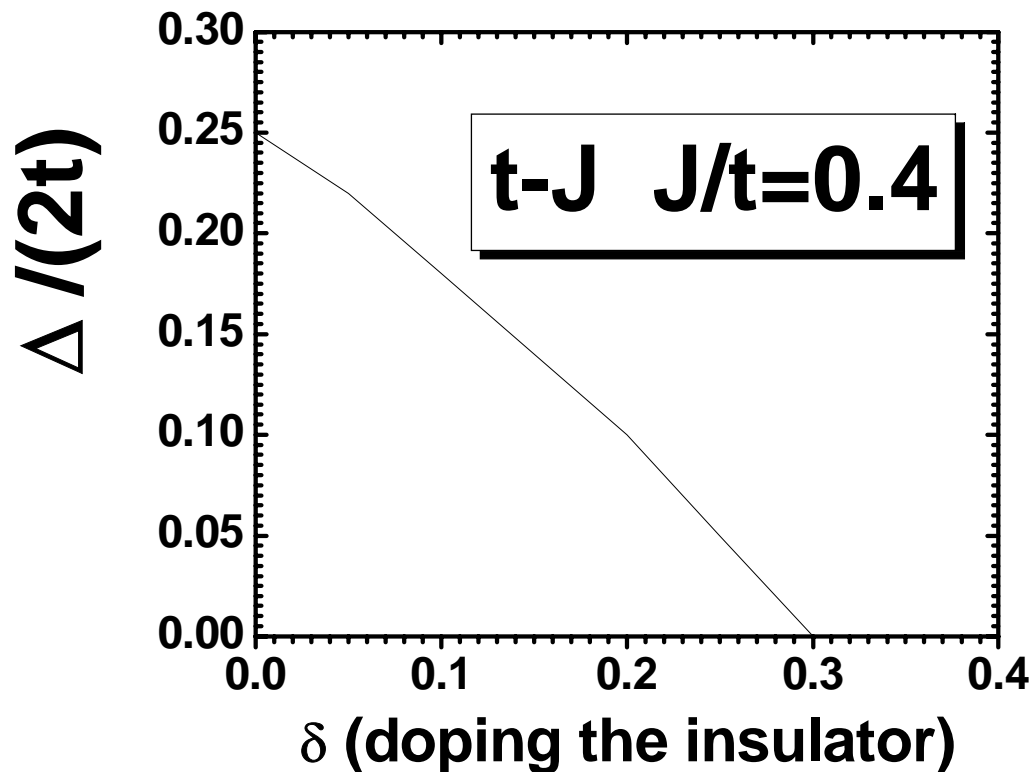

$$U/t = 4 \quad \delta = 10\%$$

Tc about 0.02 t   ~ 100 K, just HTc!!!

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The mean field(+Jastrow) of the t-J model:

$$H_{BCS} = \sum_{k,\sigma} \varepsilon_k c^+_{k,\sigma} c_{k,\sigma} + \sum_{k} \Delta_k c^+_{k,\uparrow} c^+_{-k,\downarrow} + h.c.$$

$$\varepsilon_k = -2t(\cos k_x + \cos k_y) - \mu, \Delta_k = \Delta(\cos k_x - \cos k_y)$$

t-J J/t=0.4

Δ /(2t)

δ (doping the insulator)

non-Fermi liquid

T_p

pseudogap

antiferromagnetic

T_c

superconducting

Fermi liquid

doping level (holes per CuO$_2$)

underdoped   optimally doped   overdoped

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The Cooper pairing in an insulator: 2D Hubbard model N=#electrons=#sites

E. Plehanov F. Becca and S.S. PRB'05

$$F_R = \left\langle N - 2 \left| c_{i\uparrow} c_{i+R\downarrow} + c_{i+R\uparrow} c_{i\downarrow} \right| N \right\rangle$$

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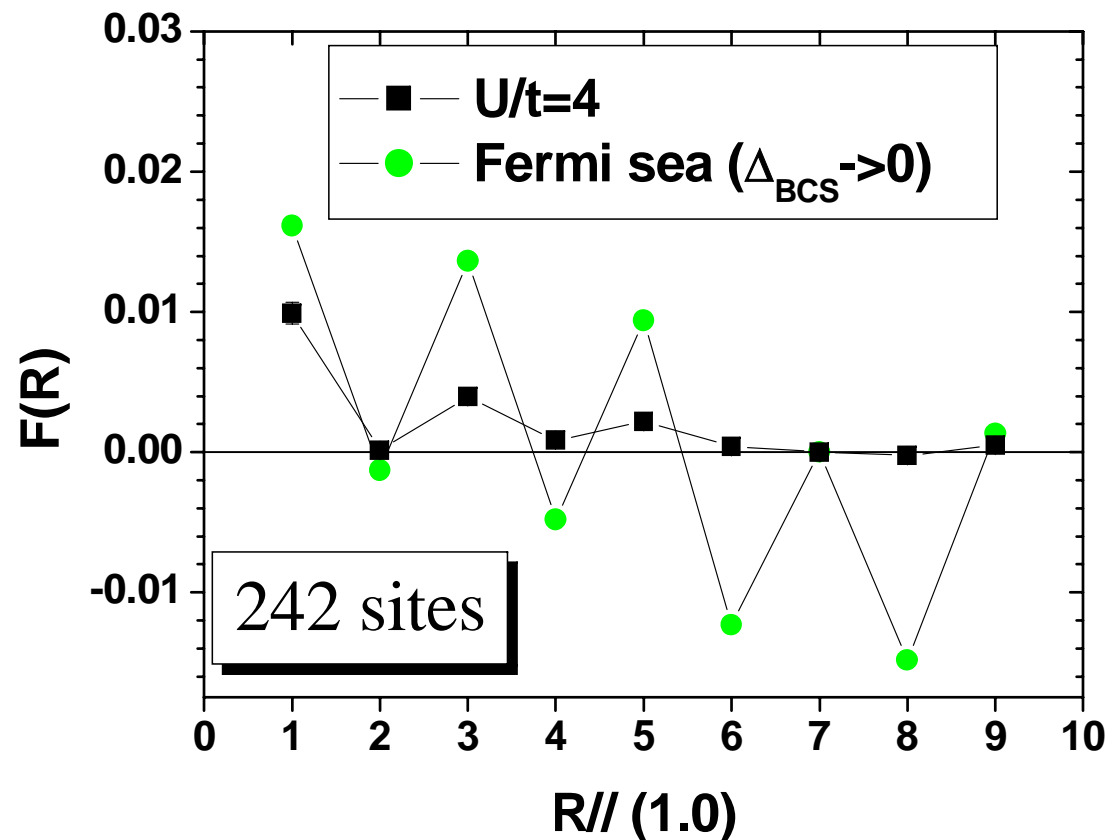
Essential ingredient of RVB theory:
→there may be pairing even in the insulator.

→By means of correlation (by a strong Jastrow)
   a metal can be turned in an insulator (Mott).

The 2D antiferromagnetic Hubbard model is
 a Mott (strong Jastrow) paired (BCS>0) insulator.

→Htc (with or without antiferro) is also
a consequence of RVB i.e. correlation alone
(no phonons, no band effects) push up Tc.

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The variational approach as the simplest tool to detect this new physics induced by correlation

At finite U/t (the physical case) we found that the long range Jastrow is needed for the RVB

$$RVB = \hat{J}\big|BCS + ...\big\rangle$$

$$\hat{J} = \exp(-1/2\sum_q v_q n_q n_{-q}) = \exp\left(-\sum_{i<j} v(r_i - r_j)\right)$$

A new state is obtained after optimization of J and BCS toghether, e.g. without J BCS$\rightarrow$ HF
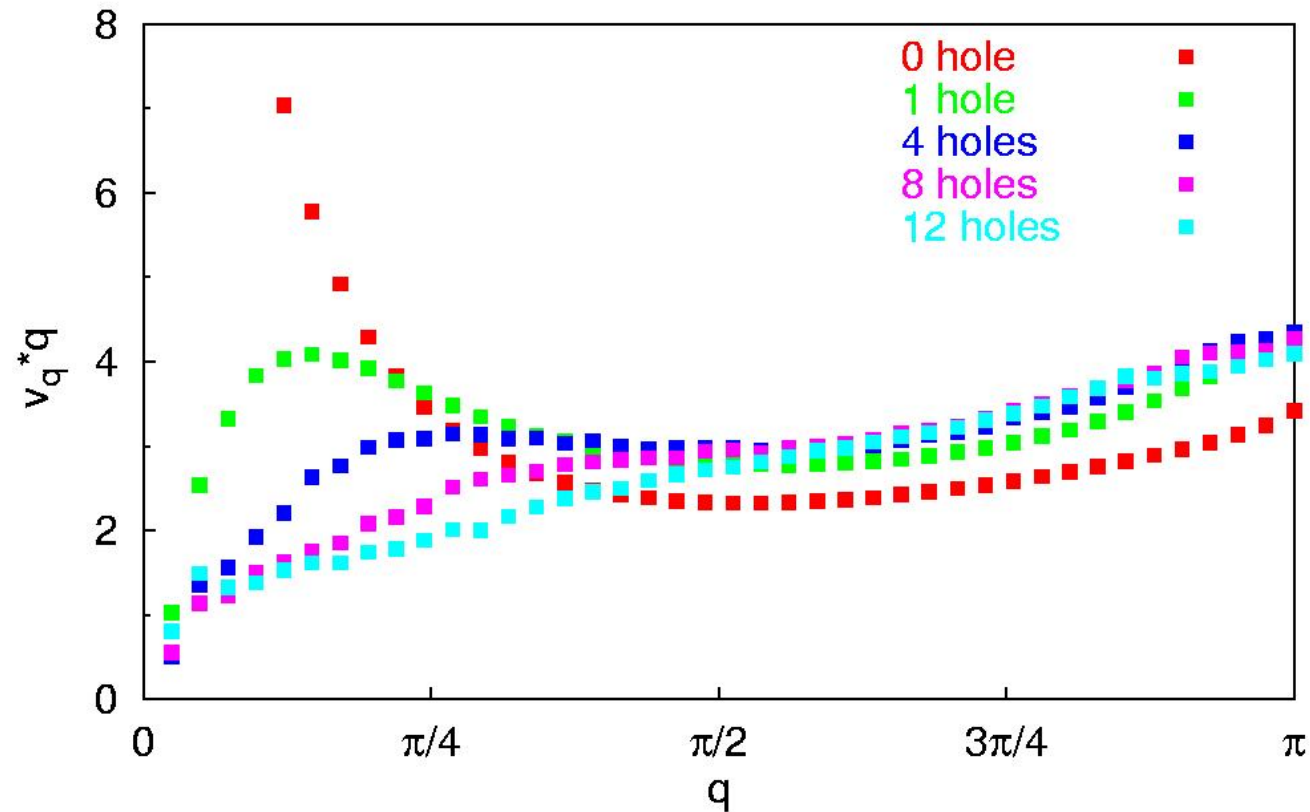
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The 1d numerical solution U/t=4 L=82

Insulator $\rightarrow v_q \sim 1/q^2$

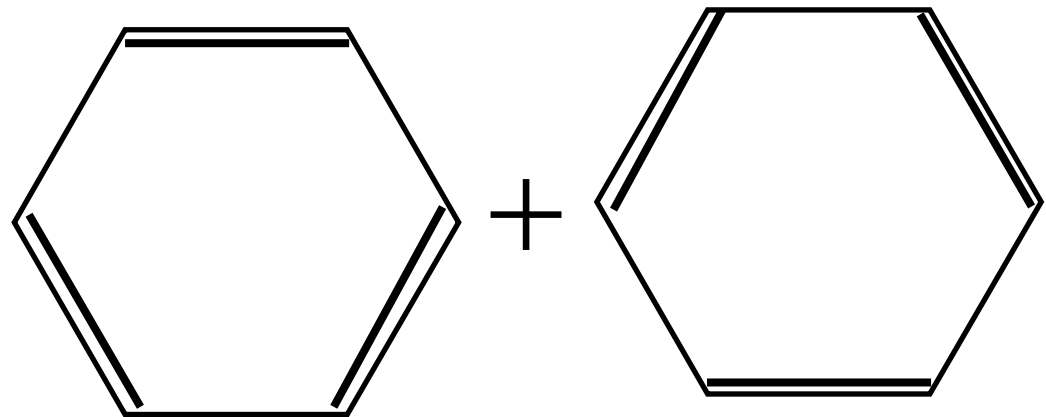Metal $\rightarrow v_q \sim 1/q$

M. Capello et al. PRL 2005

$$J = \exp(-\sum_q v_q n_q n_{-q})$$

Linus Pauling: the concept of resonance is old

Benzene $C_6 H_6$

6 valence electrons occupy the $2p_z$ orbital

then strong correlation $\rightarrow$ $\approx$ Heisenberg model

$$H = J\vec{S}_a \cdot \vec{S}_b$$ a,b nearest Carbon sites

   $= \dfrac{1}{\sqrt{2}}\left[\,|\uparrow\downarrow\rangle - |\uparrow\downarrow\rangle\,\right]\left[\psi^a_{2p_z}(r)\psi^b_{2p_z}(r') + a \leftrightarrow b\right]$

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In the old formulation RVB was expensive

1) Use of non orthogonal configurations
2) The number of VB grows exponentially
 with the number of atoms

The molecular orbital approach won…but

Now (after Htc) we have a better tool

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For QMC on a given electron configuration:

$$|x\rangle = \left\{ r_1^\uparrow, r_2^\uparrow, r_3^\uparrow \quad r_1^\downarrow, r_2^\downarrow, r_3^\downarrow \right\}$$

The wave function should be computed:

$$\langle x | \textbf{\textit{Jastrow}} \times \text{Mean Field} \rangle$$

$$= \textbf{\textit{Jastrow}}(x) \times \langle x | \text{Mean Field} \rangle$$

$\textbf{\textit{e.g. Jastrow}}(x) = 0$ if some pair $\uparrow\downarrow$ occupy the same site

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Small Review Slater determinants SD for QMC

$$Mat_{i,j} = \psi_i(\vec{r}_j^{\sigma_j}) \quad \text{where} \ \sigma_j = \pm 1/2, \ j = 1, 2, \cdots, N$$

$$\text{orbitals} \qquad\qquad i = 1, 2, \cdots, N$$

$$\langle x | SD \rangle = Antisym[\psi_1(r_1^{\sigma_1}), \psi_2(r_2^{\sigma_2}), \psi_3(r_3^{\sigma_3}) \cdots \psi_N(r_N^{\sigma_N})]$$

if $N_\uparrow = N_\downarrow = N/2$ and **singlet**

$$\langle x | SD \rangle = Det \begin{vmatrix} \psi_i(\vec{r}_j^{\uparrow}), & 0 \\ 0 & , & \psi_i(\vec{r}_j^{\downarrow}) \end{vmatrix} = Det \uparrow \times Det \downarrow$$

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How to compute $\langle x|RVB\rangle = J(x)\langle x|AGP\rangle$?[7]

$$AGP = (\sum_{i,j} f_{i,j} c_{i\uparrow}^{+} c_{j\downarrow}^{+})^{N/2}|0\rangle = Antisym(f_{r_1^\uparrow,r_1^\downarrow} \times f_{r_2^\uparrow,r_{21}^\downarrow} \times \cdots f_{r_{N/2}^\uparrow,r_{N/2}^\downarrow})$$

second quantization $\qquad\qquad$ first quantization

$$|x\rangle = \left\{ r_1^\uparrow, r_2^\uparrow, r_3^\uparrow \quad r_1^\downarrow, r_2^\downarrow, r_3^\downarrow \right\}$$

$$\langle x|AGP\rangle = \begin{vmatrix} f_{r_1^\uparrow,r_1^\downarrow} & f_{r_1^\uparrow,r_2^\downarrow} & f_{r_1^\uparrow,r_3^\downarrow} \\ f_{r_2^\uparrow,r_1^\downarrow} & f_{r_2^\uparrow,r_2^\downarrow} & f_{r_2^\uparrow,r_3^\downarrow} \\ f_{r_3^\uparrow,r_1^\downarrow} & f_{r_3^\uparrow,r_2^\downarrow} & f_{r_3^\uparrow,r_3^\downarrow} \end{vmatrix}$$

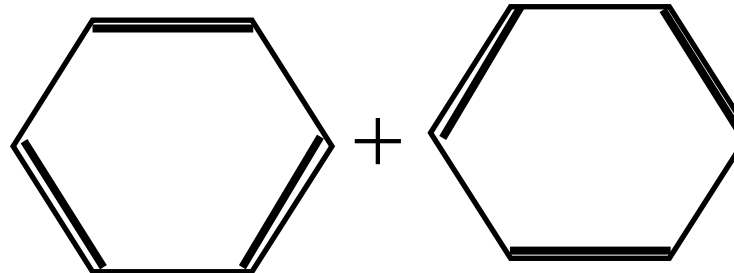## With a single determinant N/2 x N/2, N=# el. even when RVB = many Slater Determinants

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Consider the Heisenberg in 6 sites 1D ring
(a model for Benzene the 1el/2pz orbital)

$$H = J\sum_i \vec{S}_i \vec{S}_{i+1} \quad 1D \quad \vec{S}_{i+6} = \vec{S}_i$$
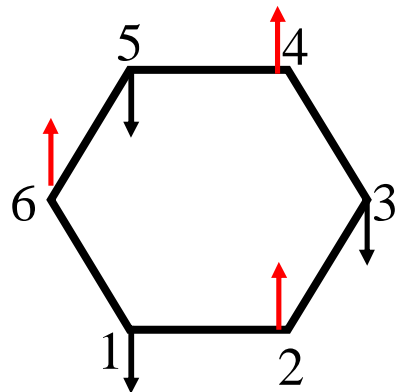
HFNeel state

Kekule'

$$f_{i,i+1} = 1$$

Pairing function:

$$f_{i,i+1} = 1$$

$$f_{i,i+1} = 1 \quad f_{i,i+3} = -0.5$$

Type wf	# Det	Energy	%Corr
HF	1	-1.5J	0
Kekule'	16	-2.7J	92%
Kekule'+Dewar	32	-2.8028	99.8%

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In the thermodynamic limit the accuracy
of the RVB in 1D Heisenberg model
is one part over 10^4!!!

Celebrated Coupled Cluster 5% off
Bishop et al. (PRB'91)

There are good reasons to start with this
RVB-Variational approach for chemistry

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And the wave function for a realistic system?

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Basis set expansion of an atomic orbital

$$\psi_k(r) = p_k(x, y, z) \sum_i C_k \exp(-Z_k\, r) \quad \text{Slater Basis}$$

$$\psi_k(r) = p_k(x, y, z) \sum_i C_k \exp(-Z_k r^2) \quad \text{Gaussian Basis}$$

where $p_k(x, y, z)$ is a suitable polynomial of x, y, z

$e.g.$ for $p-$orbitals $p_k(x, y, z) = x, y, z$

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Wf   for a molecular system

$$\langle x | RVB \rangle = \exp[\sum_{i<j} u_3(r_i, r_j) + u_2(|r_i - r_j|) + \sum_i u_1(r_i)] Det(f_{r_i^\uparrow, r_j^\downarrow})$$

$$f_{r,r'} = \sum_{i,j} \lambda_{i,j}^{a,b} \psi_{a,i}(r) \psi_{b,j}(r') \quad \text{where:}$$

$$\psi_{a,i}(r) \text{ is the } i^{th} (, j^{th}, k^{th}, ...) \text{ orbital on the ion } a(, b, c...)$$

With appropriate $u_1(\vec{r})$ and $u_2(\vec{r})$ <u>all</u> cusp conditions OK

<u>In this way the atomic orbitals are smooth (no cusp)</u>

More general than Hartree-Fock, the most important correlation is included for free

namely with a single determinant

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Wf for a molecular system: Jastrow factors

$$\langle x | RVB \rangle = \exp[\sum_{i<j} u_3(r_i, r_j) + u_2(|r_i - r_j|) + \sum_i u_1(r_i)] Det(f_{r_i^\uparrow, r_j^\downarrow})$$

With appropriate $u_1(\vec{r})$ and $u_2(\vec{r})$ all cusp conditions OK

$$u_1(r) \approx -Z |r - R_j| \text{ for } r \to R_j \text{ and } u_2(r_{i,j}) \approx \frac{r_{i,j}}{2} \text{ for } r_{i,j} \to 0$$

$$u_3(\vec{r}, \vec{r}') = \sum_{i,j} J_{i,j}^{a,b} \psi_{a,i}(\vec{r}) \psi_{b,j}(\vec{r}') \quad \text{where:}$$

$\psi_{a,i}(\vec{r})$ is the ith $(, j^{th}, k^{th}, ...)$ orbital on the ion $a(, b, c...)$

Also for the Jastrow the atomic orbitals have no cusp

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How to get a Slater Determinant from the AGP?

$$f(\boldsymbol{r}_\uparrow, \boldsymbol{r}_\downarrow) = \sum_{i,j} \lambda_{i,j} \phi_i(\boldsymbol{r}_\uparrow) \phi_j(\boldsymbol{r}_\downarrow)$$

Compute the overlap matrix : $S_{i,j} = \langle \phi_i | \phi_j \rangle$

By solving the generalized linear system :

$$\sum_{j} (\lambda S)_{i,j} \, \psi_j^k = \lambda_k^{\mathrm{M}} \psi_i^k$$

We can define molecular orbitals $\langle \psi_i | \psi_j \rangle = \delta_{i,j}$:

$$\psi_k(\mathrm{r}) = \sum_i \psi_i^k \phi_i(\boldsymbol{r}), \; f(\boldsymbol{r}_\uparrow, \boldsymbol{r}_\downarrow) = \sum_k \lambda_k^M \psi_k(\boldsymbol{r}_\uparrow) \psi_k(\boldsymbol{r}_\downarrow)$$

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Now if $\lambda_k^M = 0$ for k > N/2 (half the number of particles)

from $f(r_\uparrow, r_\downarrow) = \sum_k \lambda_k^M \psi_k(r_\uparrow) \psi_k(r_\downarrow)$

and the Pauli principle

$Det[f(r_\uparrow^i, r_\downarrow^j)]$ AGP

$= \text{Antisym}[f(r_\uparrow^1, r_\downarrow^1) f(r_\uparrow^2, r_\downarrow^2)..., f(r_\uparrow^{N/2}, r_\downarrow^{N/2})]$

$= \text{Antisym}[\psi_1(r_\uparrow^1) \psi_1(r_\downarrow^1) \psi_2(r_\uparrow^2) \psi_2(r_\downarrow^2)...\psi_{N/2}(r_\uparrow^{N/2}) \psi_{N/2}(r_\downarrow^{N/2})]$

$= Det[\psi_i(r_\uparrow^j)] \times Det[\psi_i(r_\downarrow^j)]$ Slater Determinants

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More than one Determinant: Berillium atom

$$f(r,r') = 1s_r 1s_{r'} + \varepsilon[2s_r 2s_{r'} + \lambda \sum_{v=x,y,z} 2p_r^v 2p_{r'}^v]$$

$$Antisym(f_{r_1^\uparrow,r_1^\downarrow} \times f_{r_2^\uparrow,r_2^\downarrow}) = \varepsilon[1s_2 2s_2 + \lambda 1s_2 2p_2] + O(\varepsilon^2)$$

For small $\varepsilon \ll 1$ the standard four determinants
see Lab on Monday

Quite generally AGP works for open shells with degenerate or almost degenerate orbitals.

The Berillium atom

Comparison with previous works

Ground state	Energy (Hartree)	reference
4 Det+J (many body)	-14.66662(1)	Huang et al.
AGP+J	-14.66504(4)	Our best VMC
FN 4-Det +J (many body)	-14.66723(1)	Huang et al.
FN AGP+J	-14.66726(1)	Our best DMC

Exp. -14.66736 Hartree

DMC+HF -14.6$\rightarrow$ Wrong

M. Casula and SS JCP '03

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Pseudopotentials and DMC

DMC on the lowest energy JAGP wf.

→Old technique non variational (often unstable) with nonlocal pseudopotential

→New (M.Casula C.Filippi and S.S.) PRL05

LatticeRegularizedDiffusionMonteCarlo
Very stable variational upper bounds
of the pseudo Hamiltonian energy.

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Pfaffian generalization

Let us introduce a pfaffian: signed sum of all distinct pair partitions (Pfaff, Cayley ~ 1850)

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

Example: pfaffian of a skew-symmetric matrix

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

Signs: +   -   +

1 2 3 4   1 2 3 4   1 2 3 4

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From one particle orbitals to general antisymmetrized pairing functions

One-particle orbitals + antisymmetry -> Slater determinant/HF

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

Pair orbital + antisymmetry -> pfaffian !!!

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

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/singlet   antisymmetric/triplet

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DMC correlation energies of atoms and dimers
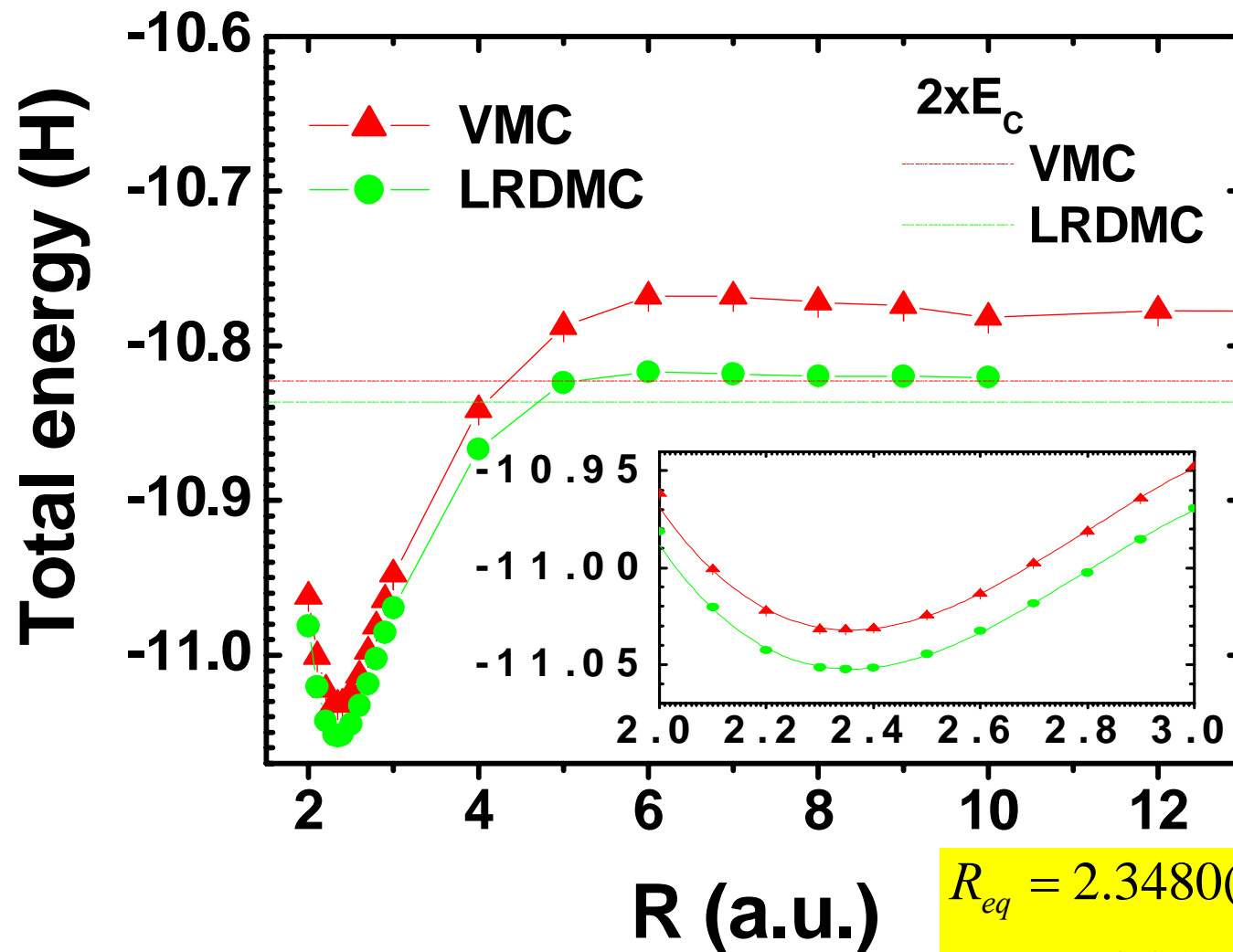## Pairing functions: more accurate and systematic than HF
The improvement of PF nodes on RVB nodes→ marginal
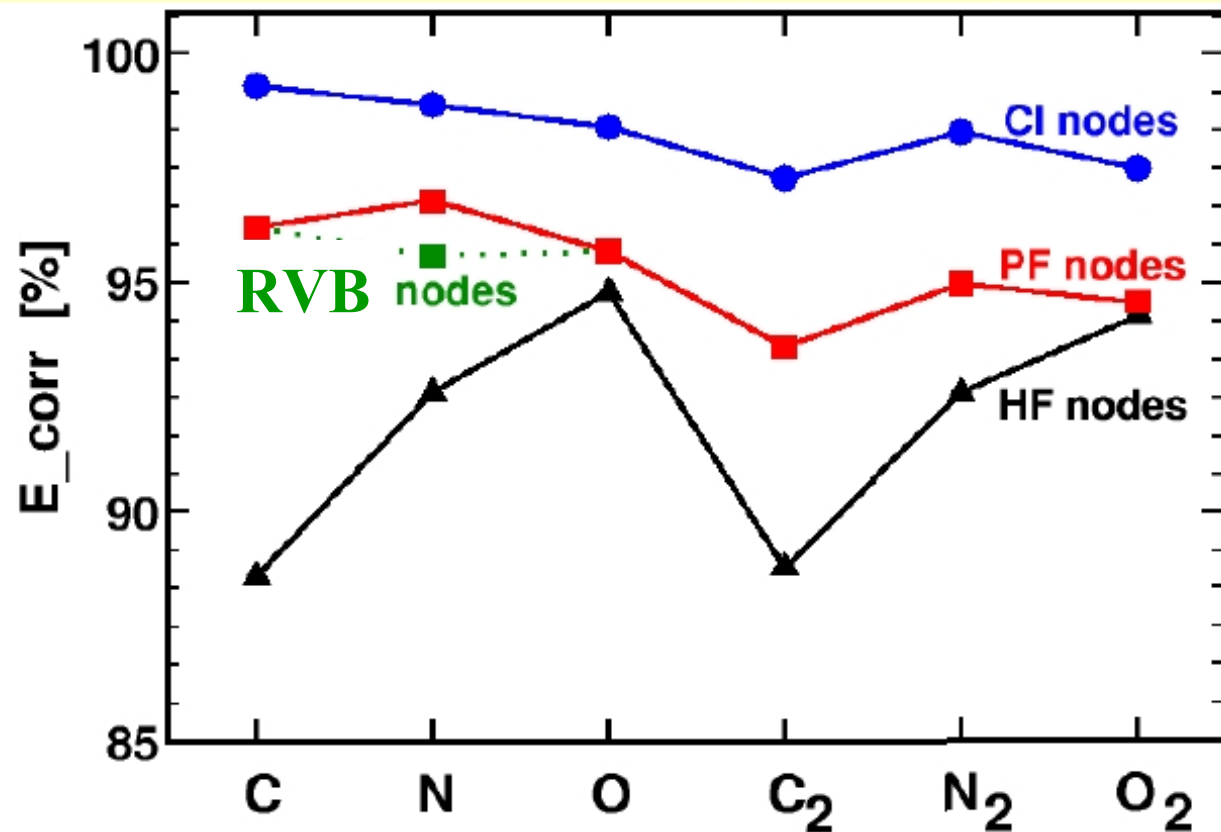
From Bajidic, Mitas,..,and Schmidt, PRL 2006 vol. 96, 130201

Size consistency and energy dispersion in C2
a **singlet** made up of two **triplet**

Aromatic compounds

- Their importance comes from our life

- Hartree-Fock and DFT do not work…

    1) Test the pairing character of the bond

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Binding energy of aromatic molecules

Molecule	Within RVB+LRDMC	Estimated from Exp.
C_2	6.291(7)eV	6.34(14)eV
C_6H_6	59.06(2)eV	59.24(11)eV

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Pairing energy: best HF+J - best RVB

Molecule	Within VMC	Within LRDMC
C	0.205(9)eV	0.169(6)eV
C_2	0.824(11)eV	0.552(6)eV
C_6H_6	0.218(7)eV	0.142(18)eV

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Application to solids and large systems

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Example electron gas

$$f(\vec{r}_\uparrow, \vec{r}_\downarrow) = \sum_{|k|<k_F} exp[i\vec{k} \cdot (\vec{r}_\uparrow - \vec{r}_\downarrow)] = \exp(ik_F |\vec{r}_\uparrow - \vec{r}_\downarrow|) / |\vec{r}_\uparrow - \vec{r}_\downarrow|^2$$
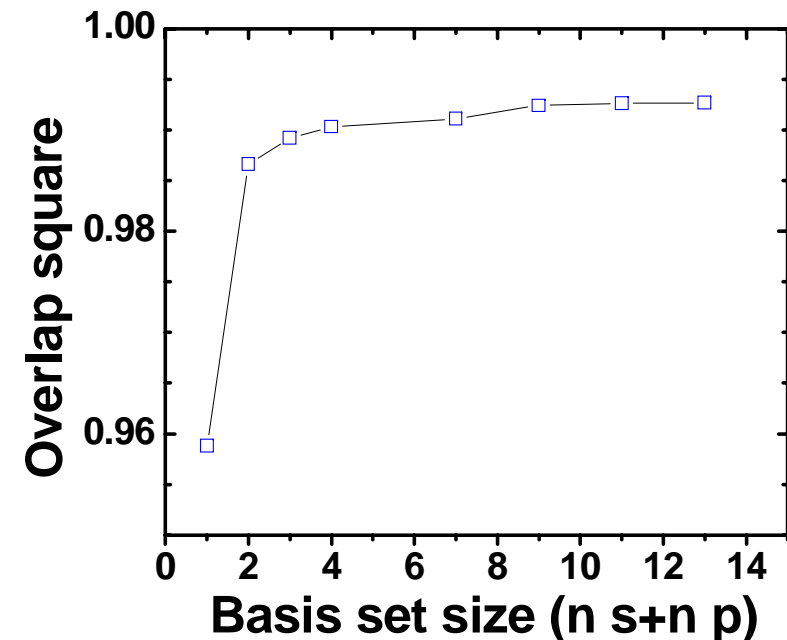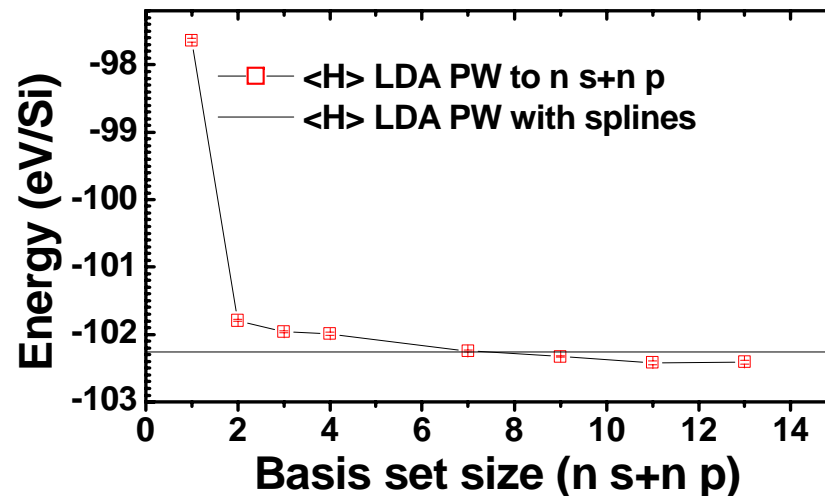
, i.e. Density matrix a physical quantity

Very simple to use symmetries,
e.g. homogeneity and isotropy:

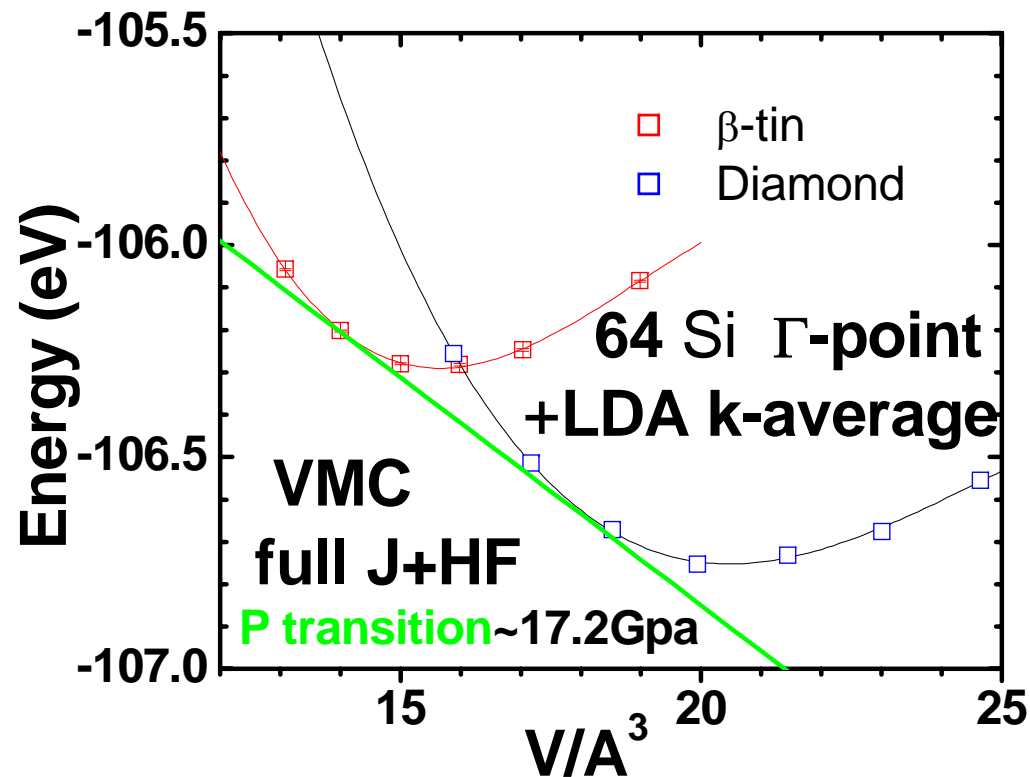$$f(\vec{r}_\uparrow, \vec{r}_\downarrow) = f(|\vec{r}_\uparrow - \vec{r}_\downarrow|)$$

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Using the AGP to represent the LDA wf

Silicon diamond 64 atoms

Left plot: Energy (eV/Si) vs Basis set size (n s+n p)
- □ <H> LDA PW to n s+n p
- — <H> LDA PW with splines

Right plot: Overlap square vs Basis set size (n s+n p)

2s2p+J2s2p (optimized) $\langle H \rangle = -106.339(4)$

DMC ==== $E_{MA} = -106.716(5)$

DMC (spline CASINO) $E_{MA} = -106.695(2)$

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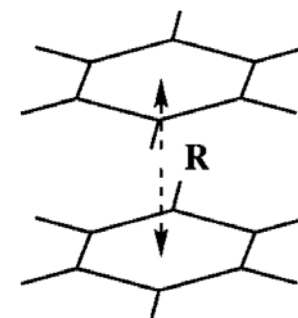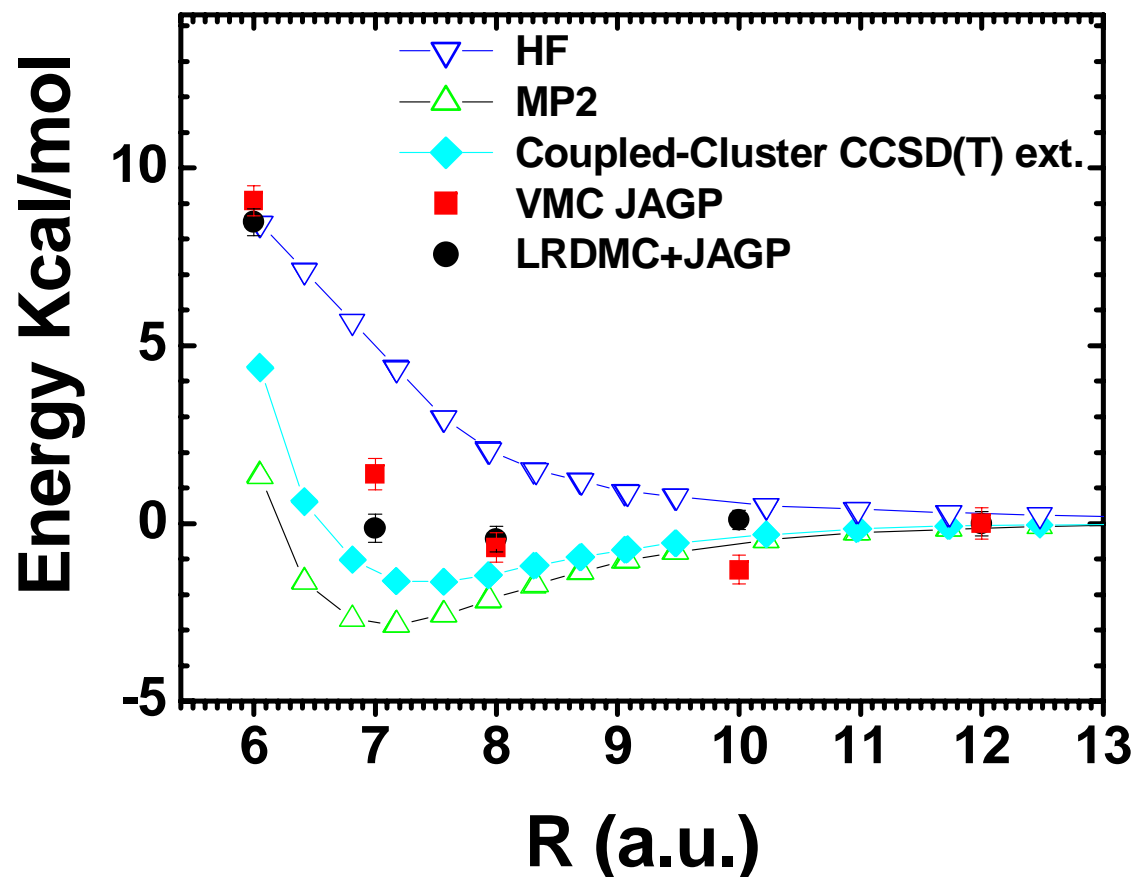
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Metal-Insulator transition in Silicon

This is the **<u>first</u>** J+HF optimization in solids

The plane wave basis ~10^6

Our localized gaussian basis ~10^3

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1 LRDMC run = 20h x 64 on sp5 ~ (VMC +opt)

Fully size consistent after optimization !!!

$|E(C_{12}H_{12})-2E(C_6H_6)|<0.1mH$ for R=12

Binding (kcal/mol:

CC=   1.6
This work   0.5(3)

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Benzene dimer optimization: a challenge

Main problem for large systems: # parameters scales

with # electrons **square**
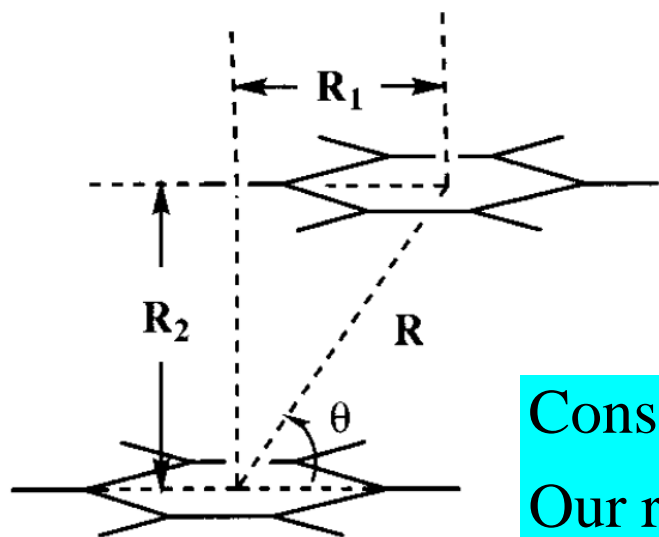
Shifted Parallel → NO simmetry
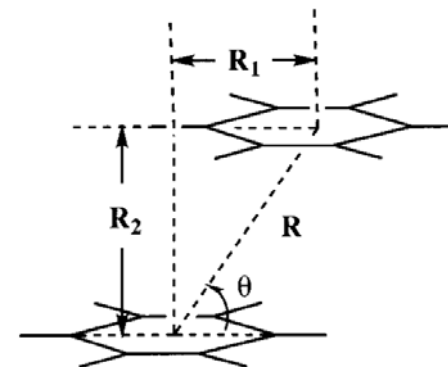
WF	Basis G	Contracted	#Lambda	# Z
Det(AGP)	6s6p	2s 1p	2616	336
Jastrow	3s2p	----	7380	72+1

We optimized all parameters for ~60 iterations with $\sigma_E = \sim 1\mathrm{Kcal/Mol}$

Using the recent Hessian method : S.S. PRB '05, C. Umrigar PRL'05,
C. Umrigar , J. Toulouse, C, Filippi, S.S. and R. Henning PRL '07

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Compared with CCSD(T) (2.8kcal/mol) the binding is sizably weaker

Considering the vibrational contr ~ 0.4 kcal/Mol

Our results agree with experiments 1.6(2) Kcal/Mol

R_1	R_2	F_1	F_2	ΔE_{VMC}	ΔE_{LRDMC}
0	7	0	2.1(2)	-1.4(4)	0.2 (3)
0	8	0	0.1(2)	0.7(3)	0.5(3)
3.4	7	0.20(8)	0.6(1)	1.4(3)	2.2(3)
3.4	8	-0.22(6)	-0.7(1)	2.0 (3)	1.8(3)

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Basis dependence of Coupled Cluster CCSD(T) (the best available post HF method)

Binding energy Kcal/Mol for benzene dimer

Ref.	Parallel	Displaced
2000 C.P.L.	1.02	=
2001 J.C.P.	1.21	2.01
2002 J.C.P.	=	2.59
2006 J.C.P A	1.81	2.78

Exp. 1987: 2.4 (+0.4) (-0.8); 1991: 1.6(+0.2)(-0.2)

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Basis dependence of VMC(optimized)-LRDMC (LRDMC improves by ~10 the correlation energy)

Carbon pseudo atom

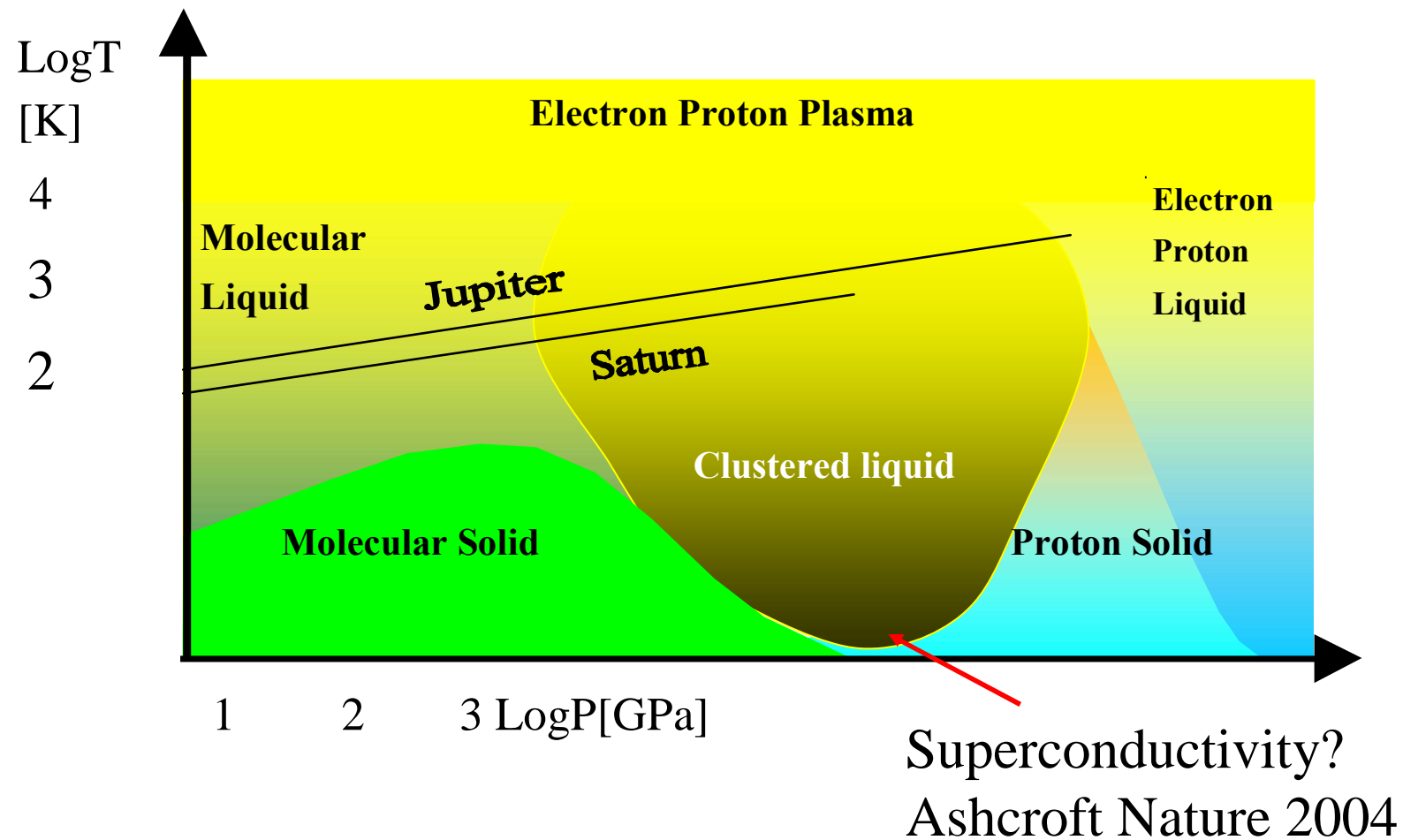| Wave function	Basis Jastrow	Basis AGP	VMC	LRDMC
AGP+2-body	exp	2s2p	-5.266 (1)	-5.397(1)
AGP+2-body	exp	3s3p	-5.392 (1)	-5.416(1)
AGP+2-body	exp	4s4p	-5.4066(4)	-5.4178(3)
AGP+2-body	exp	5s5p	-5.4095(3)	-5.4180(1)
AGP+2-body	exp	6s6p	-5.4096(2)	-5.4181(1)
AGP+2-body	exp	5s5p1d	-5.4096(2)	-5.4182(1)

CCSD(T) + polarization ''d'',JCP'89
→ -63mH in O→ QMC two orders of magn. better !
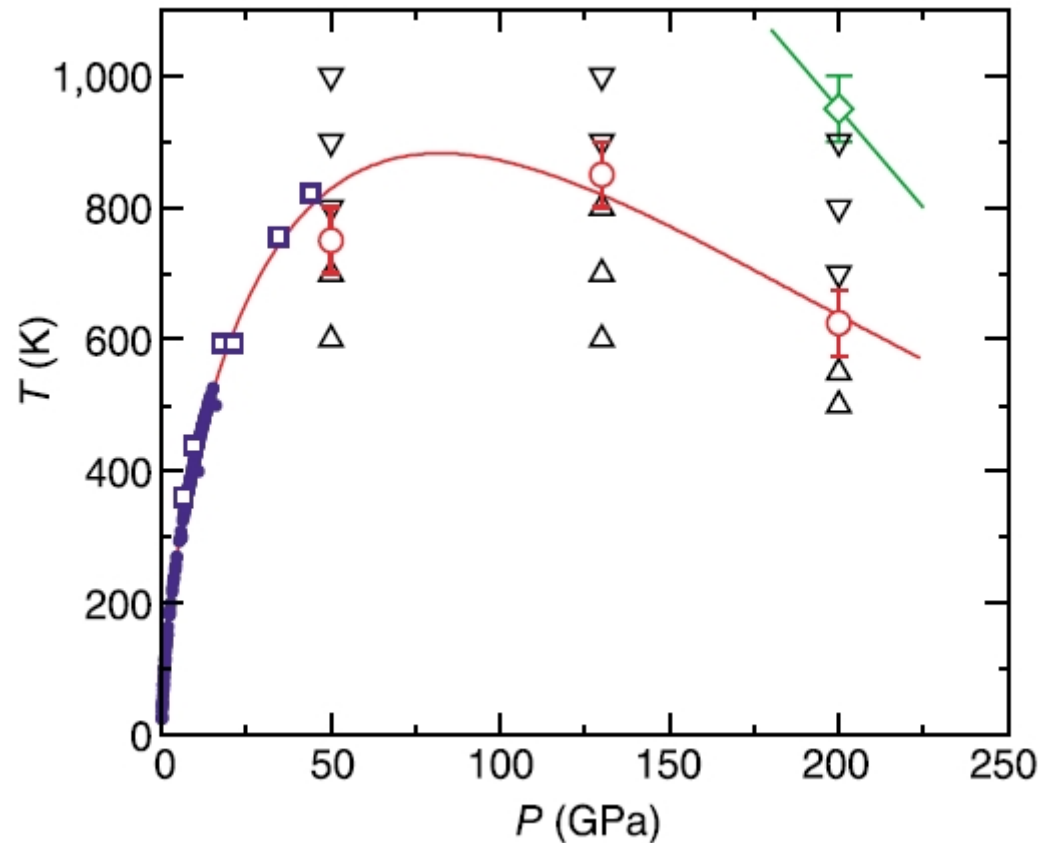
Water molecule
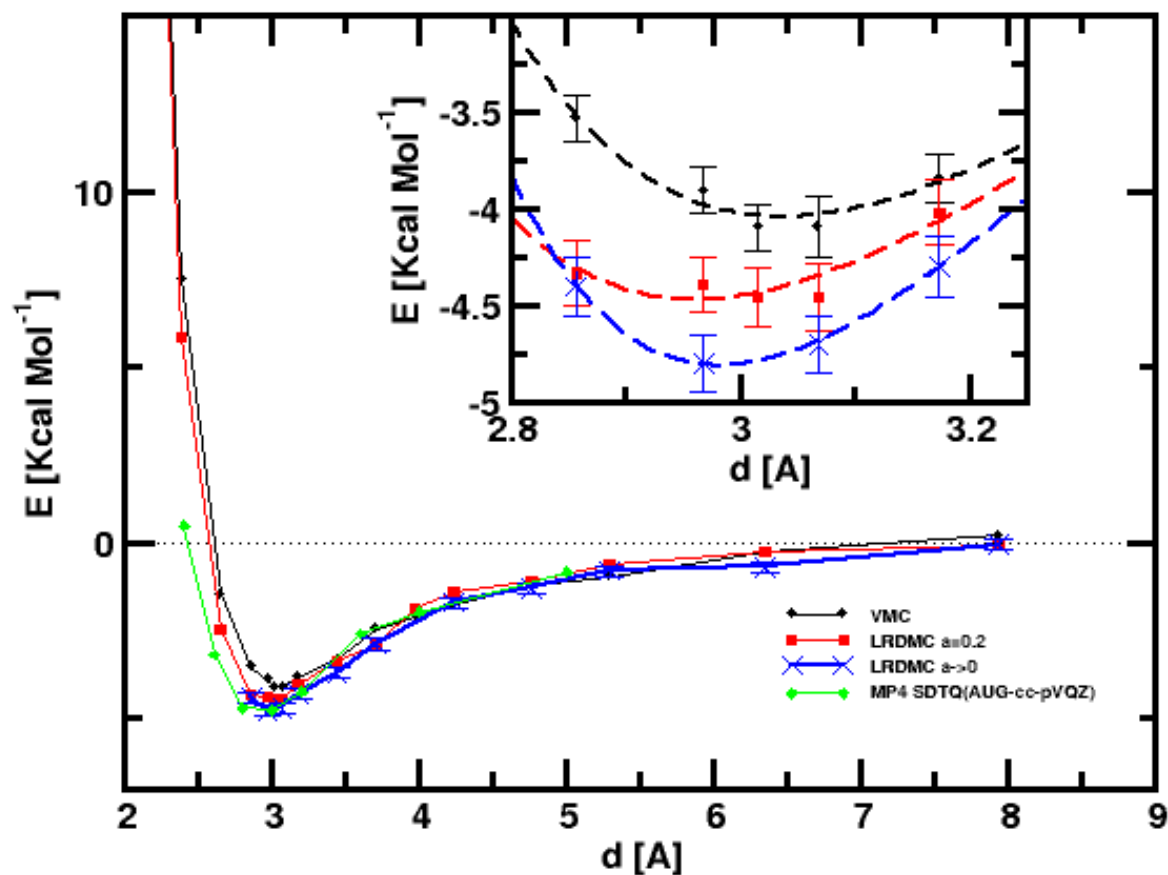
L. Spanu, F. Sterpone, S.S. and L. Guidoni, APS'08

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Phase Diagram of Hydrogen

LogT [K]

Electron Proton Plasma

Molecular Liquid

Jupiter

Saturn

Electron Proton Liquid

Clustered liquid

Molecular Solid

Proton Solid

4

3

2

1   2   3 LogP[GPa]

Superconductivity?
Ashcroft Nature 2004

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Indications of an anomalous melting line
S.A. Bonev, ..,G. Galli Nature 2004

Another quantum T=0 liquid phase?

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Simple test case: solid-metal (bcc) $r_s = 1.31$

$$r_s \approx H_2 \text{ bond length}$$

Energy per H at high-pressure (Hartree)

2 Gaussians per protons (Det)
1 Gaussian   per proton (Jastrow)

Comparison with previous works

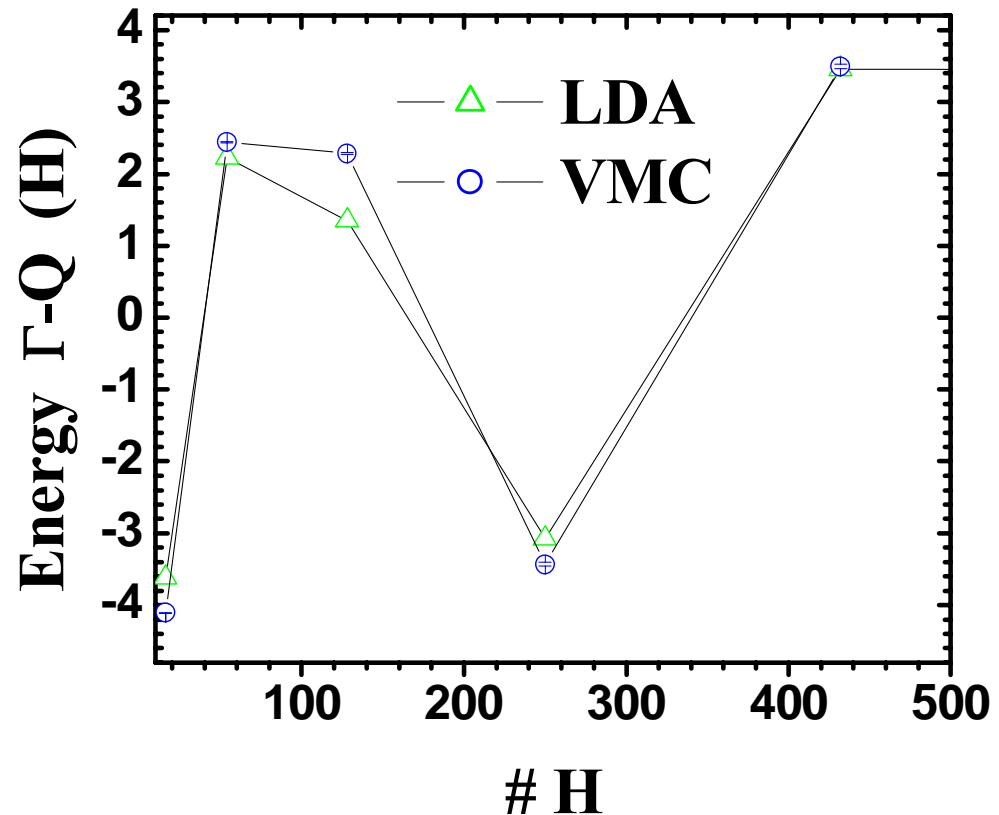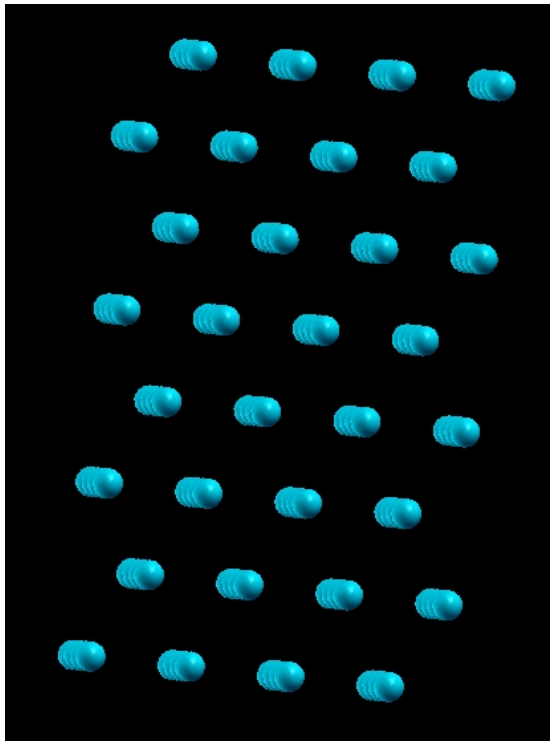| N	$E_{VMC}/N_A{}^a$	$E_{VMC}/N_A{}^b$	$E_{DMC}/N_A{}^a$	$E_{DMC}/N_A{}^b$
16	-0.48875(5)	-0.4878(1)	-0.49164(4)	-0.4905(1)
54	-0.53573(2)	-0.5353(2)	-0.53805(4)	-0.5390(5)
128	-0.49495(1)	-0.4947(2)	-0.49661(3)	-0.4978(4)
250	-0.49740(2)	-	-0.49923(2)	-

(a) This work
(b) C. Pierleoni at al. PRA 2002

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Thermodynamic limit is difficult

QMC Gamma point or Integration BC (TABC)?

Simple Hexagonal c/a=0.6 rs=1.31

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At fixed # H, we simply add the contribution LDA(k-averaged)-LDA(Γ) to QMC(Γ)

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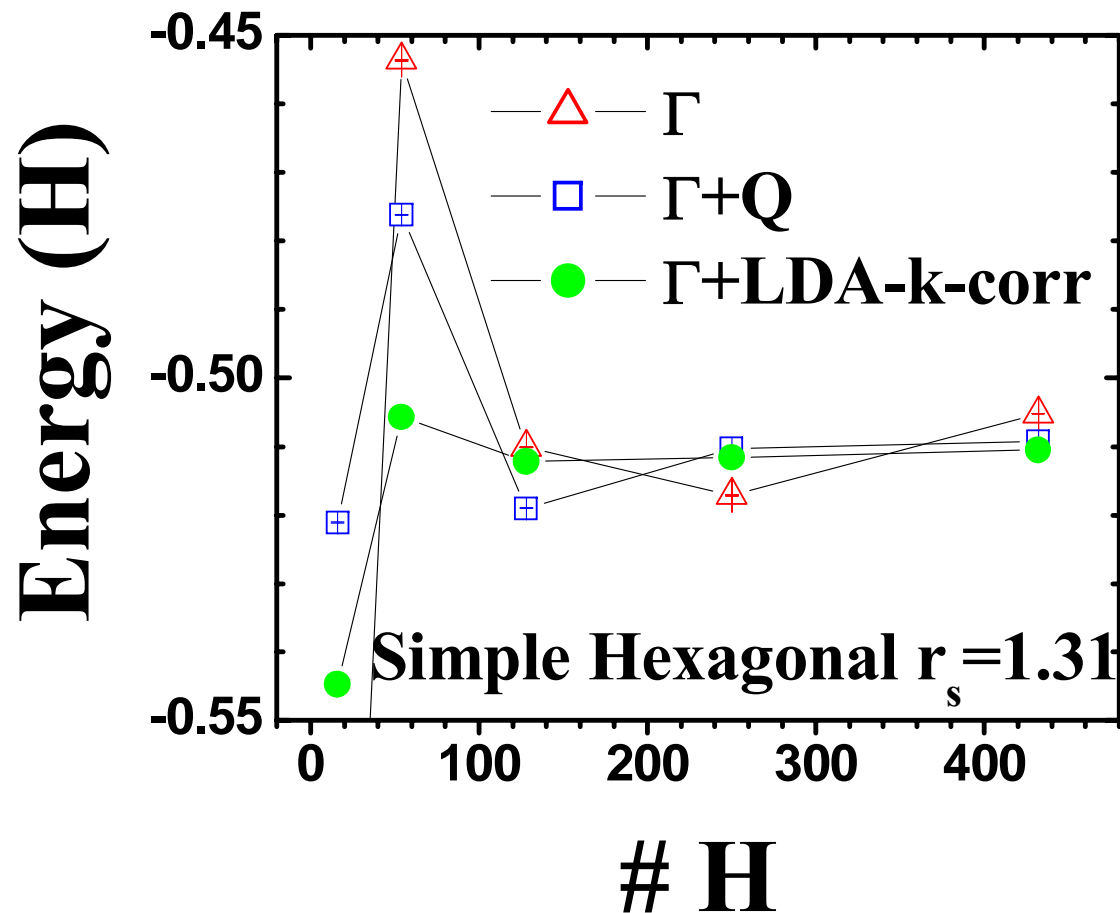
The basic steps for moving atoms

➔ Forces can be computed efficiently with VMC we use Caffarell et al. JCP 2000

➔ Optimization of the electronic VMC parameters:

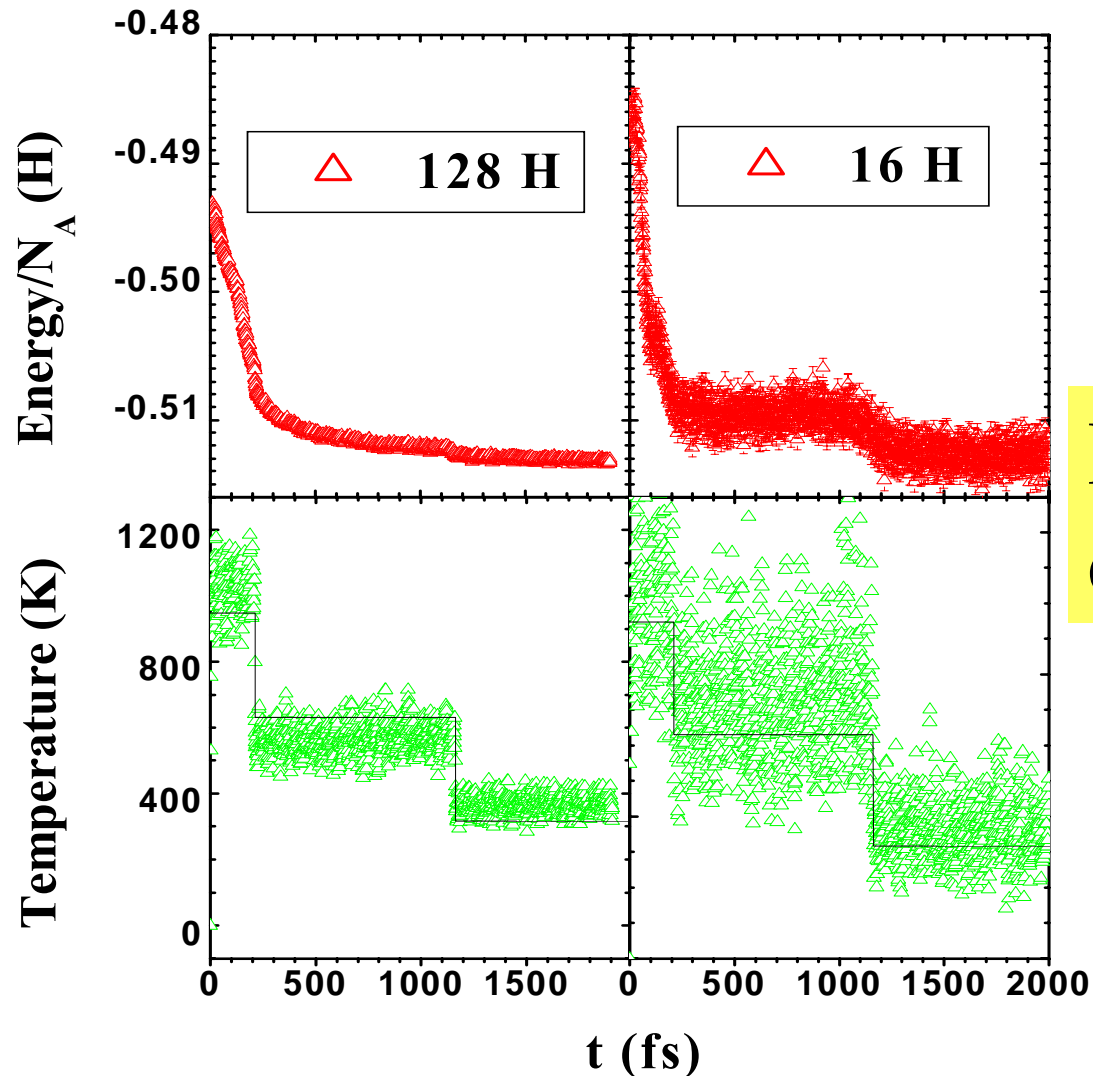1s Gaussian for Geminal and Jastrow

~200 parameters for 16 H

We use Hessian, much progress done in QMC:

C.Umrigar & C. Filippi PRL (2005), S.S. PRB (2005) ,

C. Umrigar et al (also SS) PRL, (2007)

➔ At each step we move ions with MD and VMC parameters (with Hessian), ab initio

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New ab-initio Molecular-dynamics with QMC

Proton → Classical

Internal energy decreases at 1300K!!!

With RVB wf QMC possible for ~100 atoms

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At the end of this simple analysis (repeated for all phases):

Phase	LDA	VMC	DMC
BCC	-0.5079	-0.502(1)	-0.504(1)
Simple Hexagonal	-0.5127	-0.511(1)	-0.514(1)
LIQUID (360K)	-0.5083	-0.512(1)	-0.515(1)

Liquid competes with the most stable solid

Quantum correction and entropy further favors the liquid

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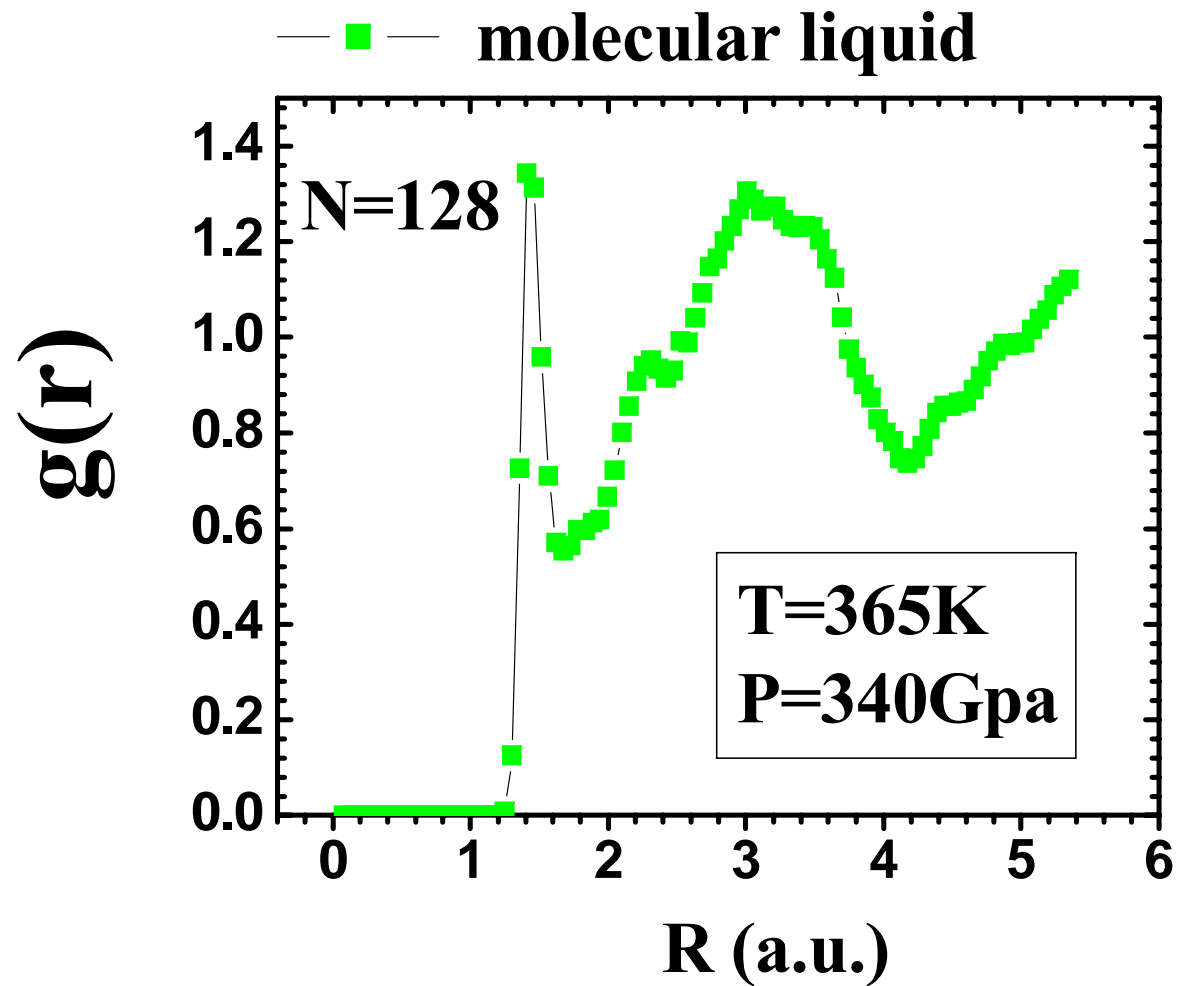January-2007   Diffusion Monte Carlo methods with non-local potentials (Sorella)

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Wigner-Kirkpatrick perturbation theory in $\hbar$
to the internal energy $U = -\partial_\beta \log(Z)$

$$Z_{\text{Quantum}} = Z \left[1 - \hbar^2 \frac{\beta^2}{24M} \, < \left(\vec{\nabla} E \right)^2 >_\beta + O(\hbar^4) \right]$$
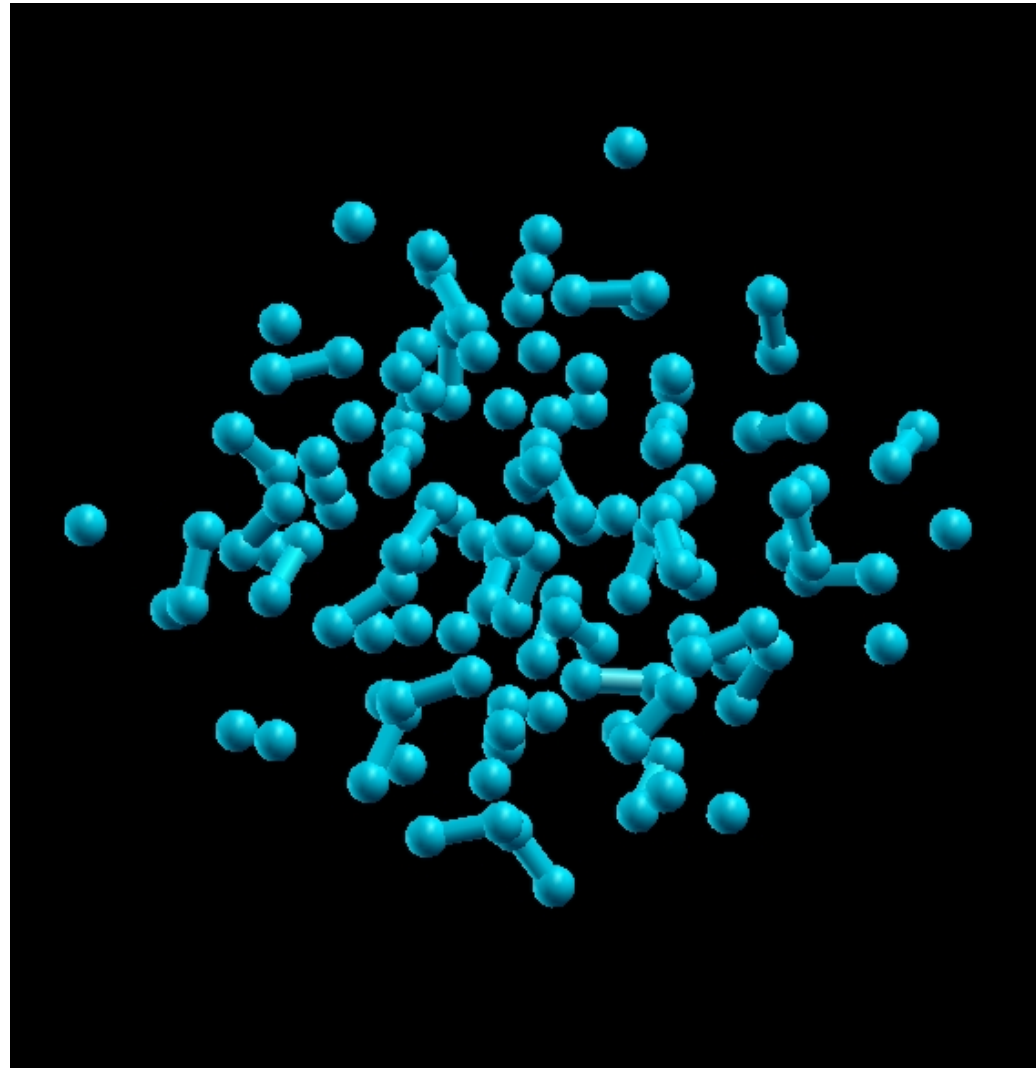
Liquid $\rightarrow$ 0.016(2) H/proton

Simple Hexagonal $\rightarrow$ 0.034(3) H/proton

Consistent with direct evaluation at T=0, Natoli '93

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molecular liquid

N=128

T=365K
P=340Gpa

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Snap-shot of the protons at the last iteration

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Pairing energy: best HF+J - best RVB

Unfortunately pairing energy $<= 10^{-4} \, \boldsymbol{H} \, / \, \text{Proton}$

Difficult to estimate by QMC, too small stat. error

We do not expect that the liquid phase may
be a superconductor driven only by correlation.
It may be a Mott insulator (strong Jastrow+HF)
If SC the mechanism proposed by Aschcroft,
i.e. induced by el-phonon is more likely.

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Conclusion

- RVB wave function considerably improves the HF+J in several cases, not only in lattice models (e.g. Berillium).

- Also the HF+J wavefunction is more physically represented by a particular case of the RVB (J+AGP) wave function.

- More effective simulations can be done by means of this approach (see Lab): effective optimization of HF molecular orbitals in solids.

- Molecular dynamics is possible within the variational approach fully consistent with forces.

- Very simple to distinguish a Mott insulator or a superconductor from a band insulator or a metal: just by computing the resonance energy.

We have a new tool for understanding physics!!!

TurboRVB   see Lab. next week

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The   local approach:
no sign problem for bosons; for fermions
exponential decay $\quad \exp[-t(E_{Fermion} - E_{Boson})]$

The auxiliary field approach :
Exponential instability but much weaker.
But sign problem for bosons with repulsion
difficult to use correlated wavefunctions.

Models without frustration   in a given basis:
e.g. Quantum dimer model on triangular lattice

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The list

Bosons   with repulsion or attraction (t<0)

Hubbard model at half filling   HST

Negative U Hubbard model no magnetic field   =

2D Kondo model at half filling (or depleted)   =

t-V model for V=2t   half filling   Meron

Several quantum dimer models   (bosons)

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Almost all models where sign problem is solved
There exists a ''smart'' basis where:

$$H_{a,b} < 0 \quad \text{if} \quad a \neq b$$

$H_{a,b}$ not necessarily hermitian

the basis $\{a\}$ not necessarily orthonormal

The matrix elements $H_{a,b}$ have to be computable

The ground state writes as: $\psi_0 = \sum_a p(a)|a\rangle$ with $p(a) > 0$

Thus the ground state is non trivial provided
the basis is non trivial

Merons ?

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Different approach, down-top define a state:

$\psi(a)$ and find $H_{a,b}$ such that

$$\sum_b H^{eff}_{a,b} \, \psi(b) = 0$$

See e.g. B. Laughlin (Gossamer superconductivity)

Then we ask whether $H^{eff}_{a,b}$ is physically acceptable (this may depend on the taste…)

This is a P- (not even NP) problem, as long as

$\psi(a)$ is computable: Pfaffians, determinants,...

Can we explore all physical effects with computable states?

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Motivations

DFT fails in describing transition elements compounds

geophysical interest:
- Fe_2SiO_4 Fayalite

biophysical interest:

- cellular respiration (bond between molecular oxygen and hemoglobin)

- catalysis reactions ($N_2 + 3H_2 \Leftrightarrow 2NH_3$: metal center clusters nitrogenase)
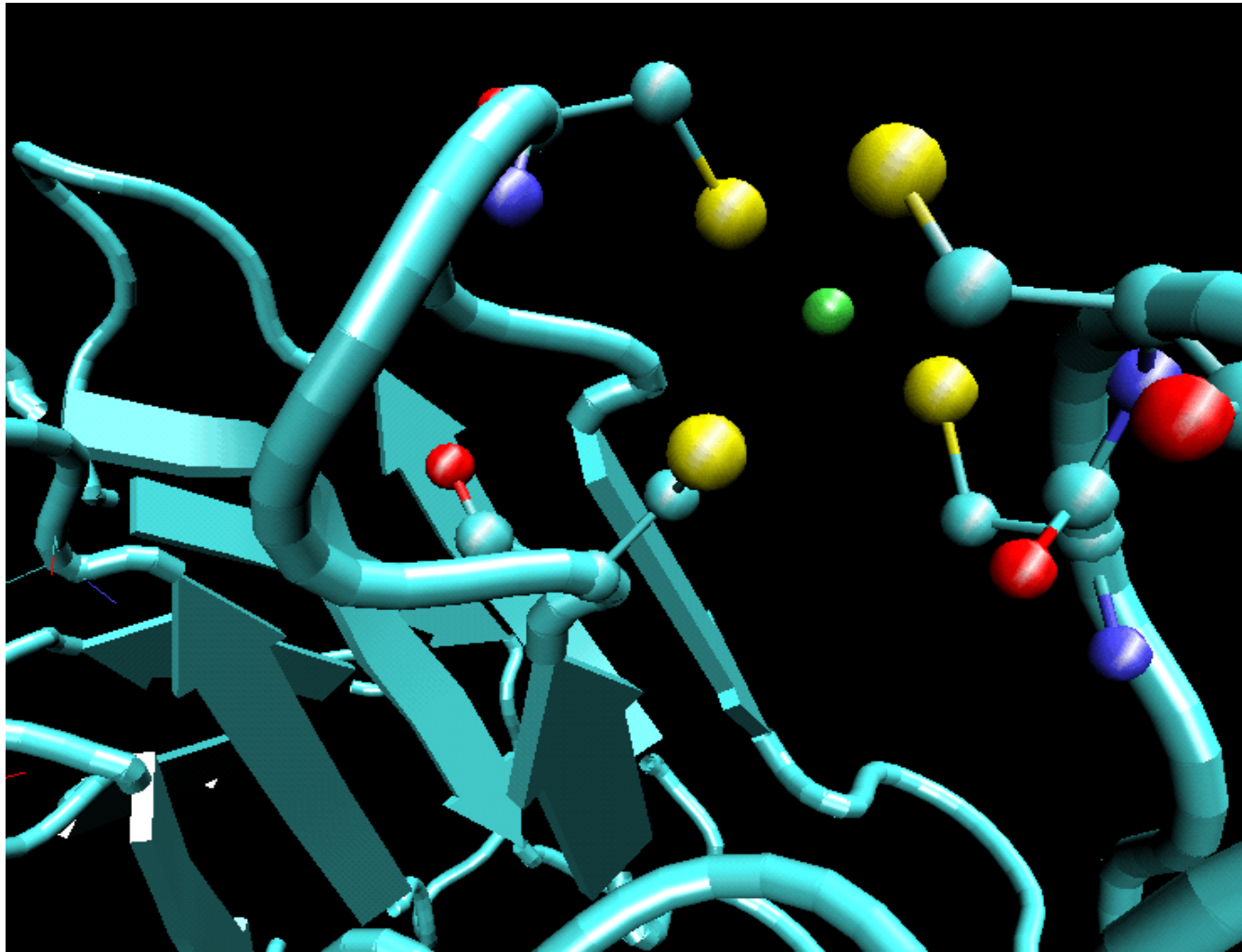
Challenge

dealing with real systems in which the correlation plays a crucial role

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4Fe-4S cluster in Nitrogenase
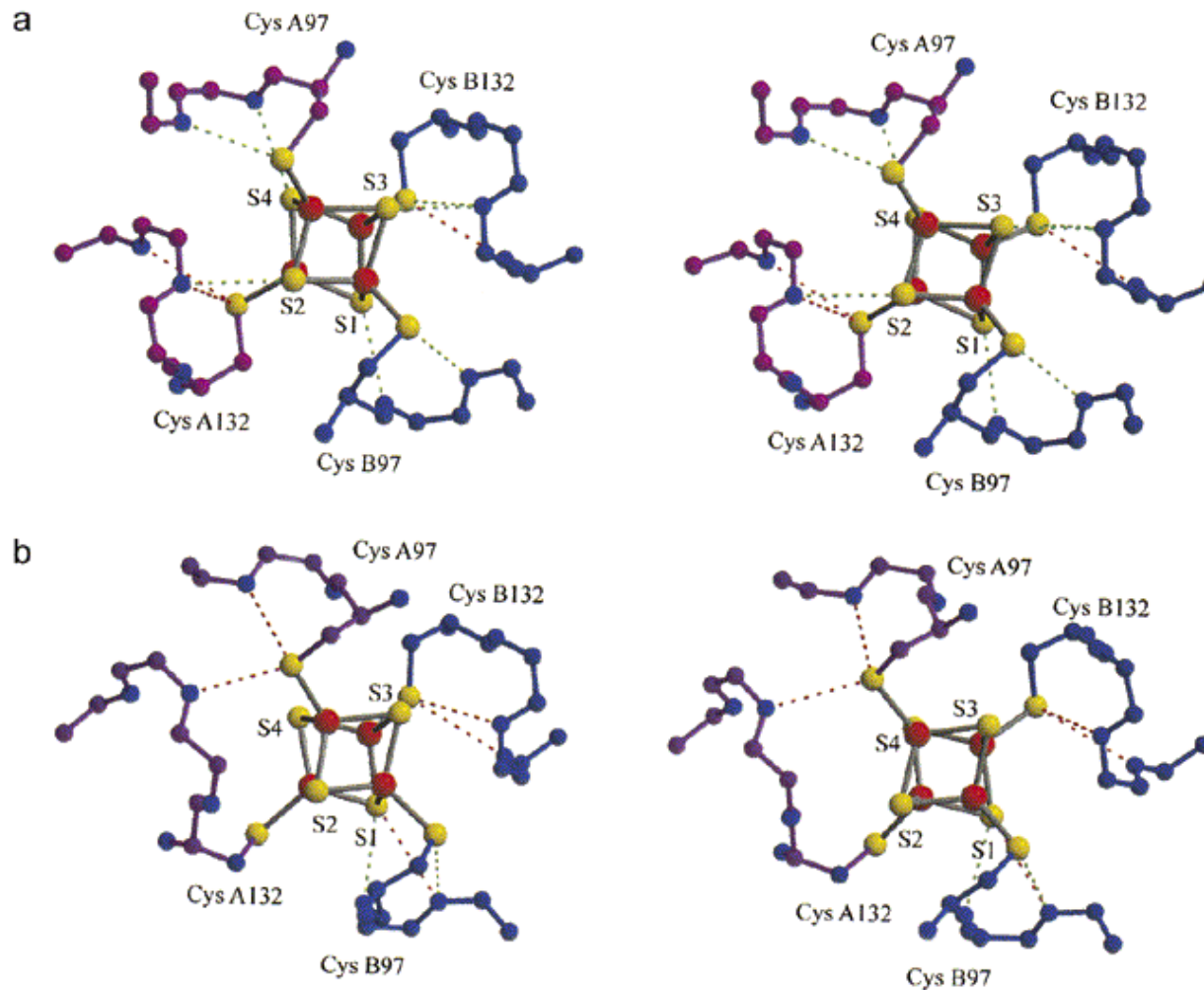
Stereodiagrams form *Biochemistry,* **40**(3), 651, 2001 P.Strop

Fe-4S cluster in Ferrodoxin

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Targets

TOOL

DFT: single particle approach, correlation energy functional obtained in an approximate way

$\Rightarrow$ QMC: many body wave function approach, poor efficiency

AIM

• look for Monte Carlo algorithms that can deal with atoms beyond the first row (all electrons)
• find a "good" trial wave function able to get correlation and to treat molecular bonds: <u>no sign problem</u> within VMC ,
We just want to be more accurate and reliable than DFT.

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Answer :

(M. Capello F.Becca, M. Fabrizio and S.S. PRL'06, PRB in press

Fourier space	Real space
$q \to 0$	$R \to \infty$

$$1D \quad v_q \sim 1/q^2 \qquad\qquad v(R) \propto -|R| + \text{Const}$$

$$2D \quad v_q \sim K/q^2 \quad K > K_c \qquad v(R) \propto -\log(R)$$

$$3D \quad v_q \sim K/q^3 \quad K > K_c \qquad v(R) \propto -\log(R)$$
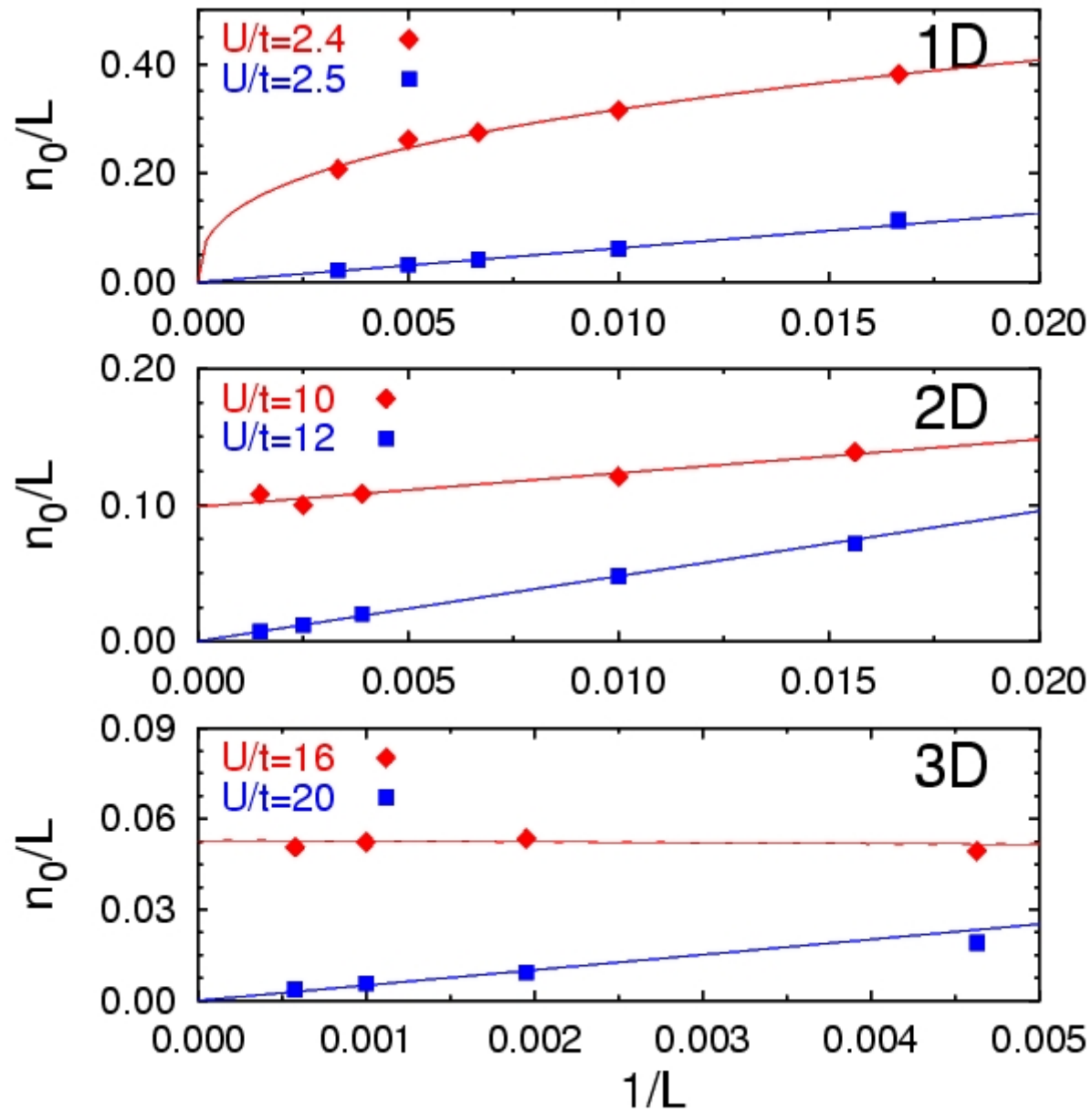
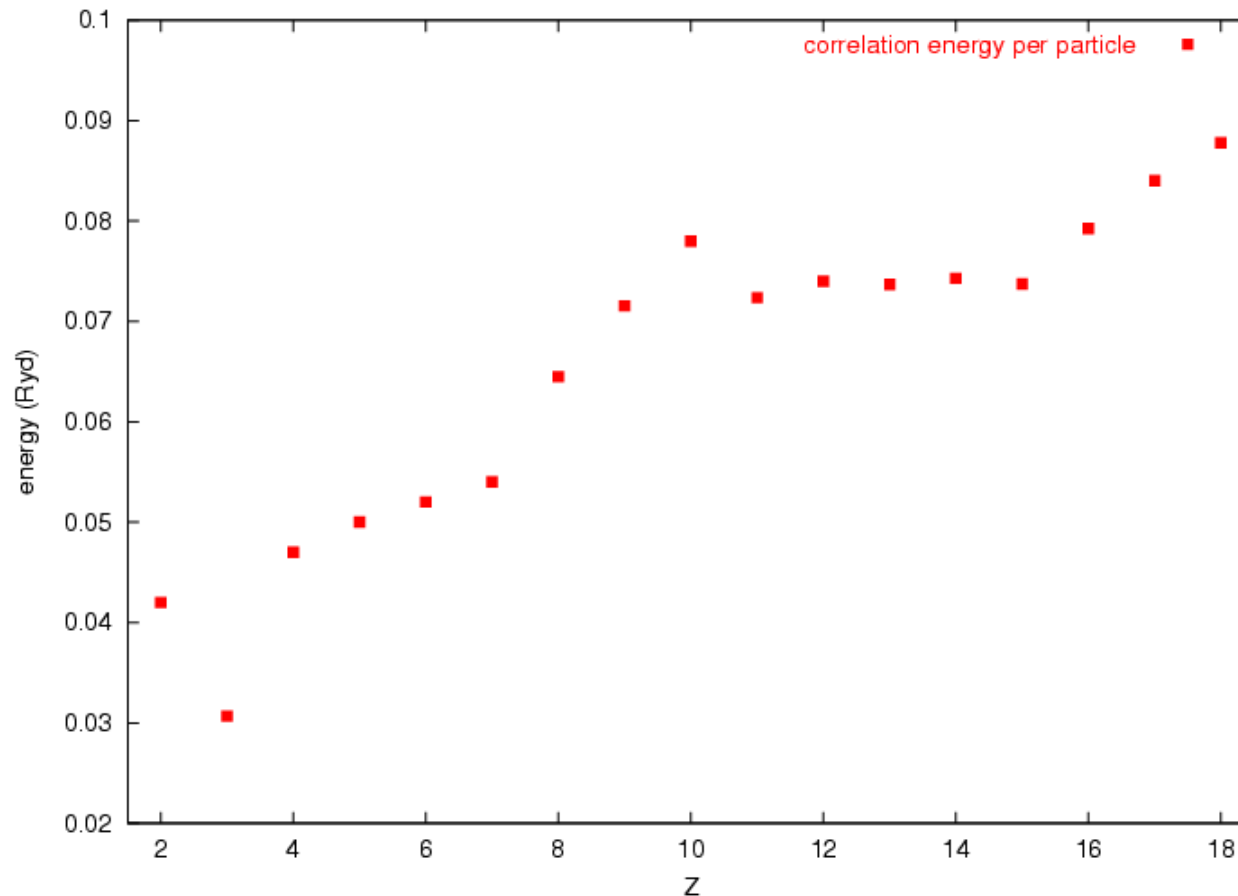Advanced school in quantum Monte Carlo in physics and chemistry
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The metal-insulator with a long-range-Jastrow

Boson Hubbard model one boson/site VMC~Exact

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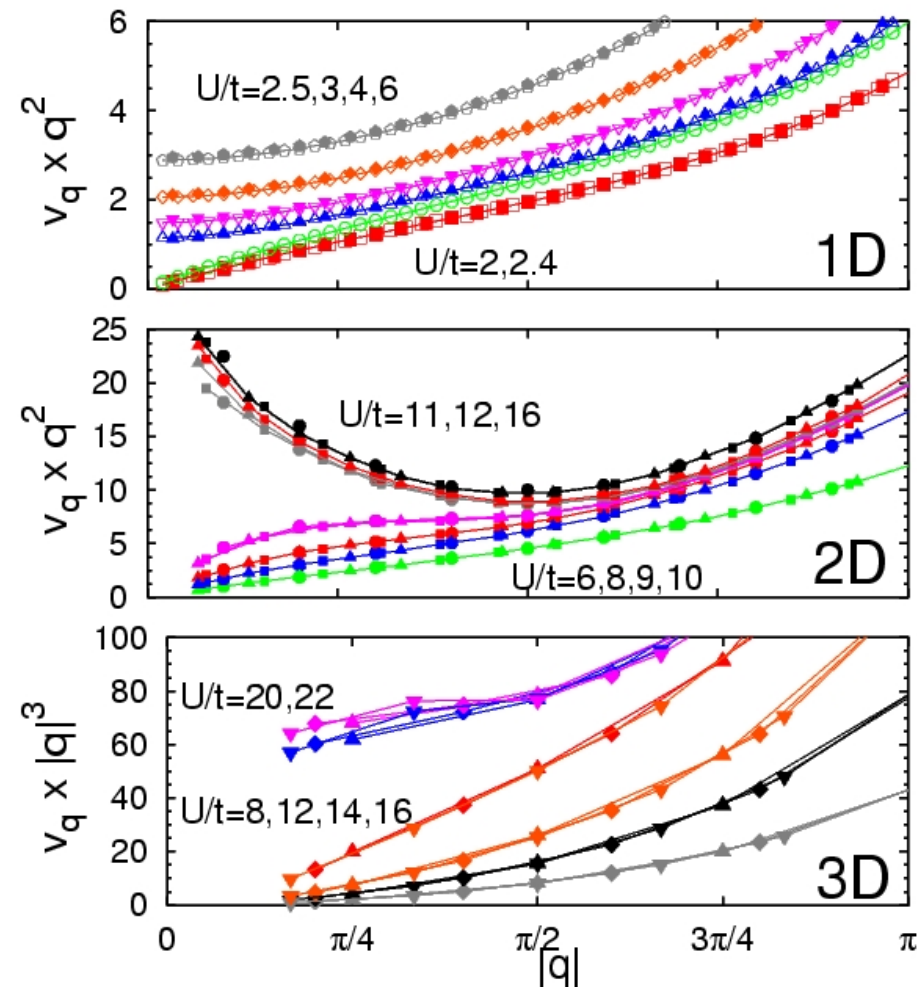
Correlation energy in atoms

- Correlation increases with the atomic number
- It is bigger when two electrons are in the same orbital
  see J. C. Slater, RMP **35**(3), 484(1963)

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VMC approach

Optimized trial wave function Ψ_T

$$\Psi_T = D\,J$$

Slater part $\Rightarrow$ correct antisymmetry for a given spin configuration
Jastrow part $\Rightarrow$ two body correlation (electron-electron)

Expectation value of the hamiltonian

$$\langle E\rangle = \int dR \frac{\left|\Psi_T(R)\right|^2}{\int dR\left|\Psi_T(R)\right|^2} E_L(R)$$

$\dfrac{\left|\Psi_T(R)\right|^2}{\int dR\left|\Psi_T(R)\right|^2}$ Distribution sampled through a Markov chain defined by the Metropolis algorithm

$E_L(R)$ Local energy: electron-electron and nucleus-electron cusp conditions to avoid its divergence (due to the Coulomb potential)

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Double zeta orbitals

Parameterization Slater

double zeta radial orbital * real representation of spherical harmonics
(see Clementi and Roetti, *Atomic data and nuclear data tables, 1974*)

$$r^n \left(a_1 \exp(-Z_1 r) + a_2 \exp(-Z_2 r) + ... \right) \Omega_{lm}$$

Nucleus-electron cusp condition $\Rightarrow$ $Z = \dfrac{a_1 Z_1 + a_2 Z_2 + \cdots}{a_1 + a_2 + \cdots}$ for angular mom. $\; l = n = 0$

Parameterization Jastrow

$$J = \exp\left\{ -\sum_{i<j} u(r_{ij}) + J_3(\vec{r}_i, \vec{r}_j) \right\} \qquad u(r) = \frac{-0.5r}{1+br}$$

$$J_3 = \sum_k \psi_k(\vec{r}_i) \, \psi_k(\vec{r}_j) \quad 3\text{-body} \; (...\text{well convention})$$

Electron-electron cusp condition $\Rightarrow$ satisfied for up-up, **not** for up-down to avoid
the spin contamination

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Why the Jastrow is so useful for correlations?

$$\left|\psi_{\text{VMC}}\right\rangle = \exp(v_q O_q^2)\left|\text{SD}\right\rangle \quad O_q = \sum_R \cos(Rq)\, n_R$$

The minimum energy condition yields:

$$\frac{\left\langle\psi_{\text{VMC}}\middle|O_q^2 H\middle|\psi_{\text{VMC}}\right\rangle}{\left\langle\psi_{\text{VMC}}\middle|H\middle|\psi_{\text{VMC}}\right\rangle} = \frac{\left\langle\psi_{\text{VMC}}\middle|O_q^2\middle|\psi_{\text{VMC}}\right\rangle}{\left\langle\psi_{\text{VMC}}\middle|\psi_{\text{VMC}}\right\rangle} \qquad (1)$$

This is the Euler condition of minimum energy which implies the f - sum rule for $\left|\psi_{\text{VMC}}\right\rangle$:

$$\left\langle O_q\middle|H\middle|O_q\right\rangle =$$

$$\int d\omega\, N(q,\omega)\,\omega = -(1-\gamma_q) < \text{Kinetic energy} > \qquad (2)$$

$$\gamma_q = (\cos q_x + \cos q_y)/2$$

The variational wavefunction with the optimal Jastrow factor, is constrained by (1) to fulfill (2) and provide accurate N(q).

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Sampling the wave function

Sampling driven by the acceptance-rejection procedure of the attempted move

$$p = \min\left[\left|\frac{\Psi_T(R')}{\Psi_T(R)}\right|^2, 1\right]$$

$$R_i' = R_i + \delta$$

Iron 5d HF (Clementi)	Z_1	Z_2
1s	27.03	19.01
2s	13.52	10.13
3s	5.22	3.48
4s	1.93	1.08

different characteristic scale lengths

$\Downarrow$

large energy fluctuations
critical slowing down

Possible improvements: *mapping* of the space or δ depend on R

$$r'(r) = r\frac{1 + \alpha r}{1 + \beta r} \qquad \alpha \propto Z, \beta \propto 1$$

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Then e.g. the steepest descent is possible:

$$\delta\alpha_k = f_k \Delta t \qquad f_k = -\partial E / \partial \alpha_k \qquad \text{Hence}:$$

$$\delta E = \sum_k \delta\alpha_k \, \partial E / \partial \alpha_k = -\Delta t \sum_k f_k^2 \leq 0$$

At equilibrium $\quad f_k = 0 \quad$ for all $\ k$

Then the Euler equation of minimum energy can be always reached for many iterations and Δt small enough

Even when H depends on atomic positions:
Structural optimization & finite temperature!

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Improving the steepest descent

Standard **(Stochastic) reconfiguration SS PRL'98**

$$\delta\alpha_k = f_k \Delta t \qquad\qquad \delta\alpha_k = \Delta t \sum_{k'} s_{k,k'}^{-1} f_{k'}$$

$$\delta E = -\Delta t \sum_k f_k^2 \leq 0 \qquad\qquad \delta E = -\Delta t \sum_{k,k'} f_k\, s_{k,k'}^{-1} f_{k'} \leq 0$$

$$s_{k,k'} = \frac{\langle \Psi_T(\alpha) | (O_k - \langle O_k \rangle)(O_{k'} - \langle O_{k'} \rangle) | \Psi_T(\alpha) \rangle}{\langle \Psi_T(\alpha) | \Psi_T(\alpha) \rangle} \quad \text{is } \mathbf{positive} \text{ definite}$$

where **Filippi,Fahy JCP'00**

$$\langle O_k \rangle = \frac{\langle \Psi_T(\alpha) | O_k | \Psi_T(\alpha) \rangle}{\langle \Psi_T(\alpha) | \Psi_T(\alpha) \rangle}$$

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Each parameter change affects differently the wf

$$\Delta\Psi_T^2 = \sum_{k,k'} s_{k,k'} \delta\alpha_k \delta\alpha_{k'}$$

for given **small** $\Delta\Psi_T^2$ (i.e. Δt) the lowest energy :

$$\text{Min } \delta\mathrm{E} + \mu\Delta\Psi_T^2 \rightarrow \text{SR direction } \delta\alpha_k = -\Delta t\sum_{k'} s_{k,k'}^{-1} f_{k'}$$

$$\left(\text{where } \mu = \frac{1}{2\Delta t} \text{ is a Lagrange multiplier}\right)$$

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To each variational parameter α_k
a physical operator : $\quad O_k = \partial_{\alpha_k} \log \Psi_T^{\alpha}(x)$

X= configuration with given positions and spins

Euler condition of minimum energy :

$$\partial_{\alpha_k} \frac{\sum\limits_{x,x'} \Psi_T(x)\, H_{x,x'}\, \Psi_T(x')}{\sum\limits_{x} \Psi_T(x)^2} = 0$$

$$\rightarrow \quad \langle HO_k \rangle - \langle H \rangle \langle O_k \rangle = 0$$

Satisfied when SR equilibrate: $\quad \left| \Psi_T' \right\rangle = (\Lambda - \langle H \rangle) \left| \Psi_T \right\rangle$

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How the parameters converge?

Be ~20 variational parameters alltoghether

~1 hour run single pc

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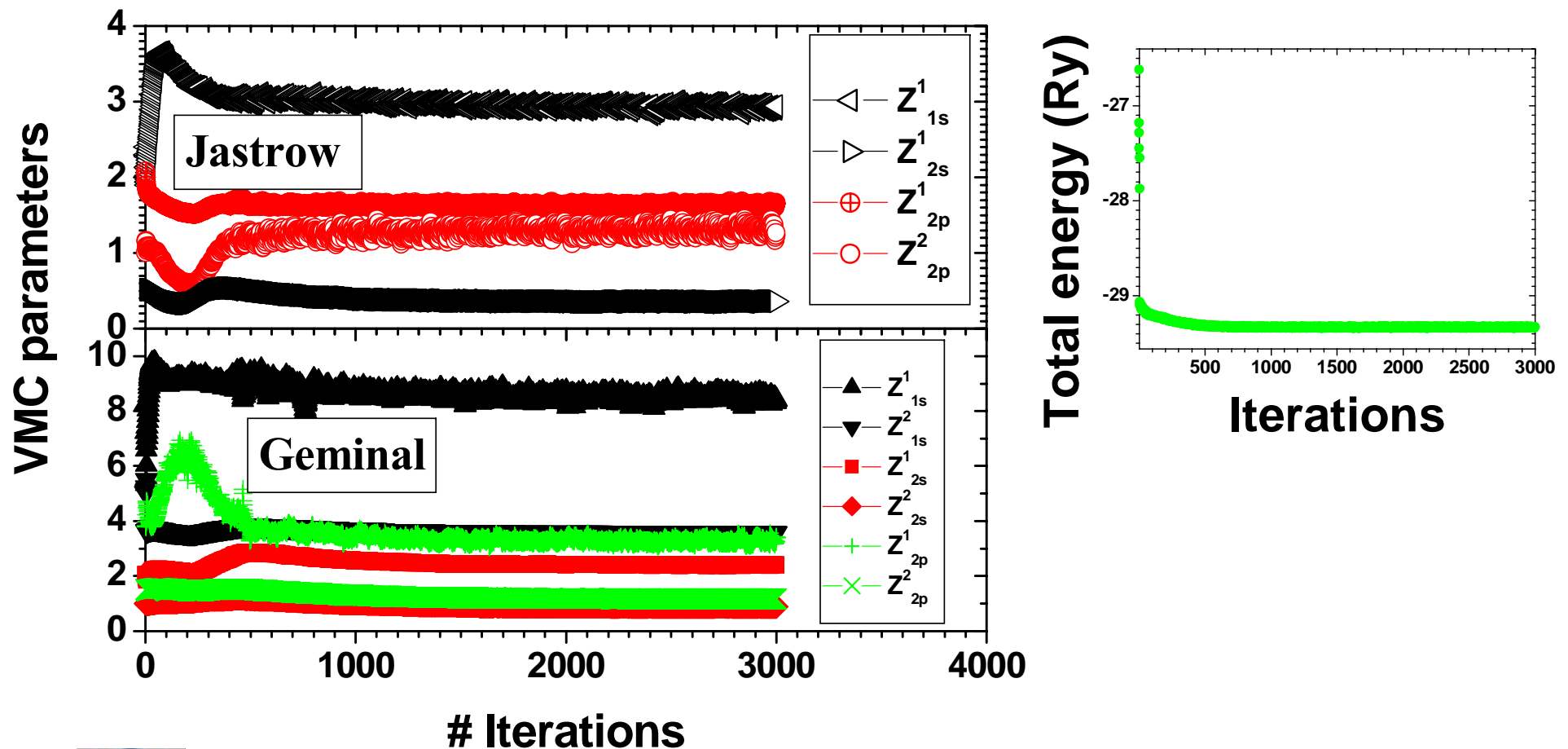
Why stochastic ?

We follow a Langevin dynamic :

$$\dot{\alpha} = (-\frac{\partial E}{\partial \alpha} + \eta)$$

Thus for each stepeest descent (SR) iteration (bin) $\langle \eta^2 \rangle$ is given

$$\alpha_{min} = \langle \alpha \rangle + C \, T^{eff}$$

α_{min} $\langle \alpha \rangle$ E

The temperature : $T^{eff}/2 = \langle \eta^2 \rangle$

can be obviously reduced **at will** :

Thermal fluctuations

$$\langle \eta^2 \rangle \propto 1/\# \, VMC \text{ steps per bin}$$

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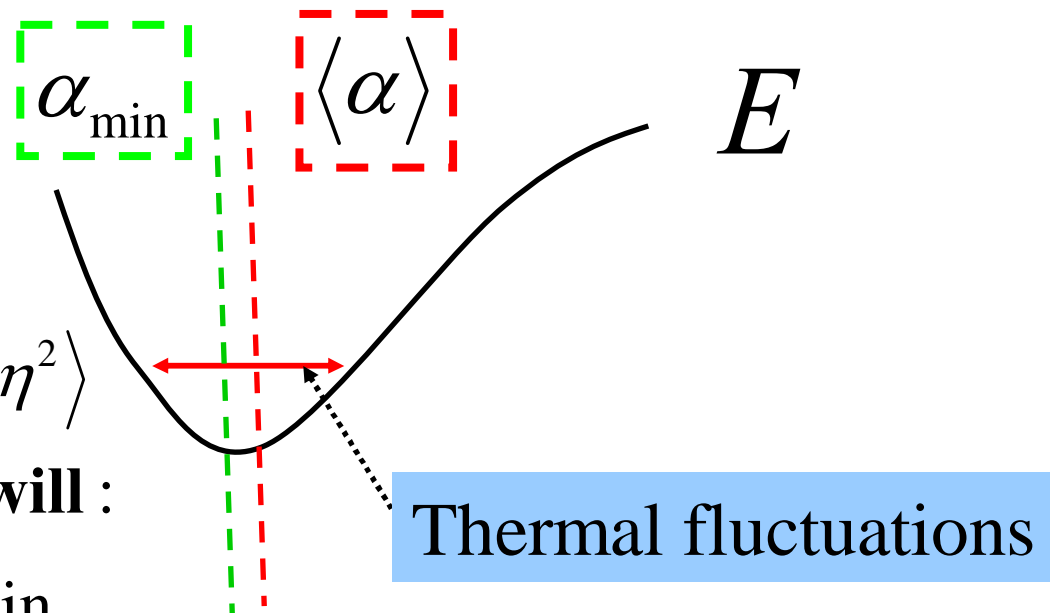
The first (SR) movie on methane CH$_4$ molecule (thanks to L. Guidoni 2004)
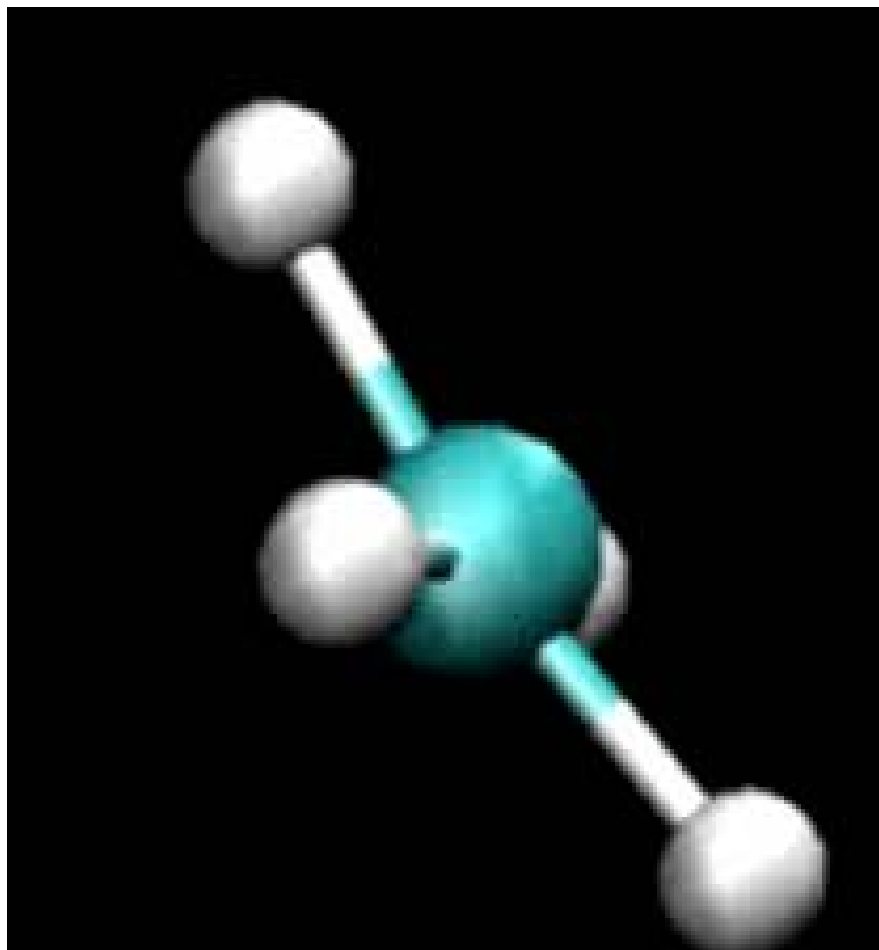
Forces can be computed in O(N^3)

Many atoms (10-100) possible in near future

QMC $\rightarrow$ noisy forces
$\rightarrow$ Finite temperature

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The generalized Langevin dynamics

$$\dot{\vec{v}} = -\bar{\gamma}(\vec{R})\vec{v} + \vec{f}(\vec{R}) + \vec{\eta}(t)$$

$$\dot{\vec{R}} = \vec{v}$$

$$< \vec{\eta}_i(t)\vec{\eta}_j(t') > = \delta(t - t')\bar{\alpha}(\vec{R})$$

$$\boxed{\bar{\gamma}(\vec{R}) = \frac{\beta}{2}\bar{\alpha}(\vec{R})}$$

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Discretization of the Langevin dynamics

$$\vec{v}_{n+1} = e^{-\bar{\gamma}\Delta}\vec{v}_{n-1} + \bar{\Gamma}(\vec{f}(\vec{x}_n) + \vec{\tilde{\eta}})$$

$$\vec{R}_{n+1} = \vec{R}_n + \Delta\vec{v}_n$$

$$\bar{\Gamma} = \bar{\gamma}^{-1}(1 - e^{-\bar{\gamma}\Delta})$$

$$\vec{\tilde{\eta}} = \frac{\bar{\gamma}}{2\sinh(\Delta/2\bar{\gamma})} \int_{t_n-\Delta/2}^{t_n+\Delta/2} dt\, e^{\bar{\gamma}(t-t_n)}\vec{\eta}(t)$$

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$$\bar{\alpha}(\vec{R}) = \bar{\alpha}_0 + \Delta\bar{\alpha}_{QMC}(\vec{R})$$

$$\bar{\gamma}(\vec{R}) = \frac{\beta}{2}\bar{\alpha}(\vec{R})$$

$$< \vec{\bar{\eta}_i}\vec{\bar{\eta}_j} > = \frac{2}{\beta}\bar{\gamma}^2 \frac{\sinh(\Delta\bar{\gamma})}{4\sinh(\Delta\bar{\gamma}/2)^2} = \bar{\alpha}'$$

$$< \vec{\eta}_i^{ext}\vec{\eta}_j^{ext} > = \bar{\alpha}' - \bar{\alpha}_{QMC}$$

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The 16 H case with PBC, MD with friction
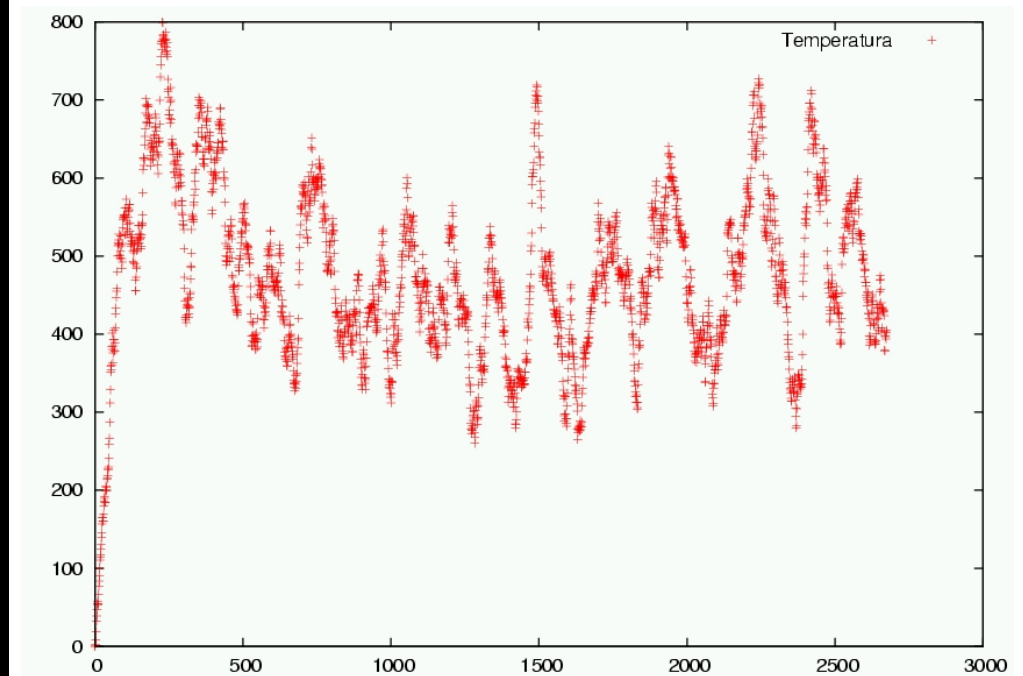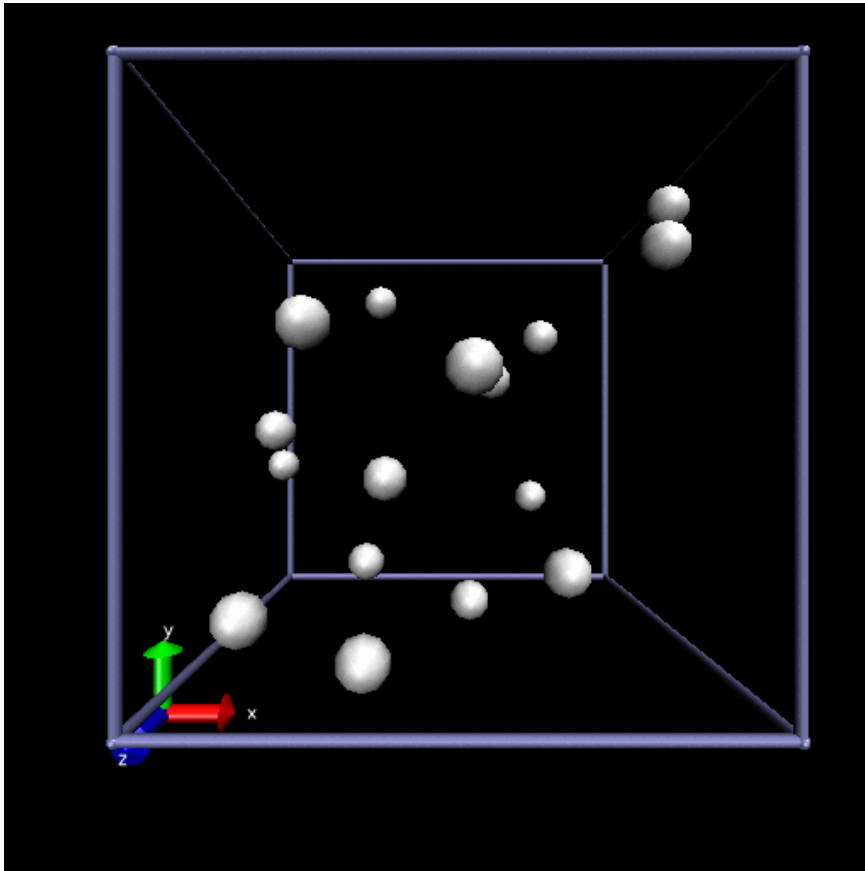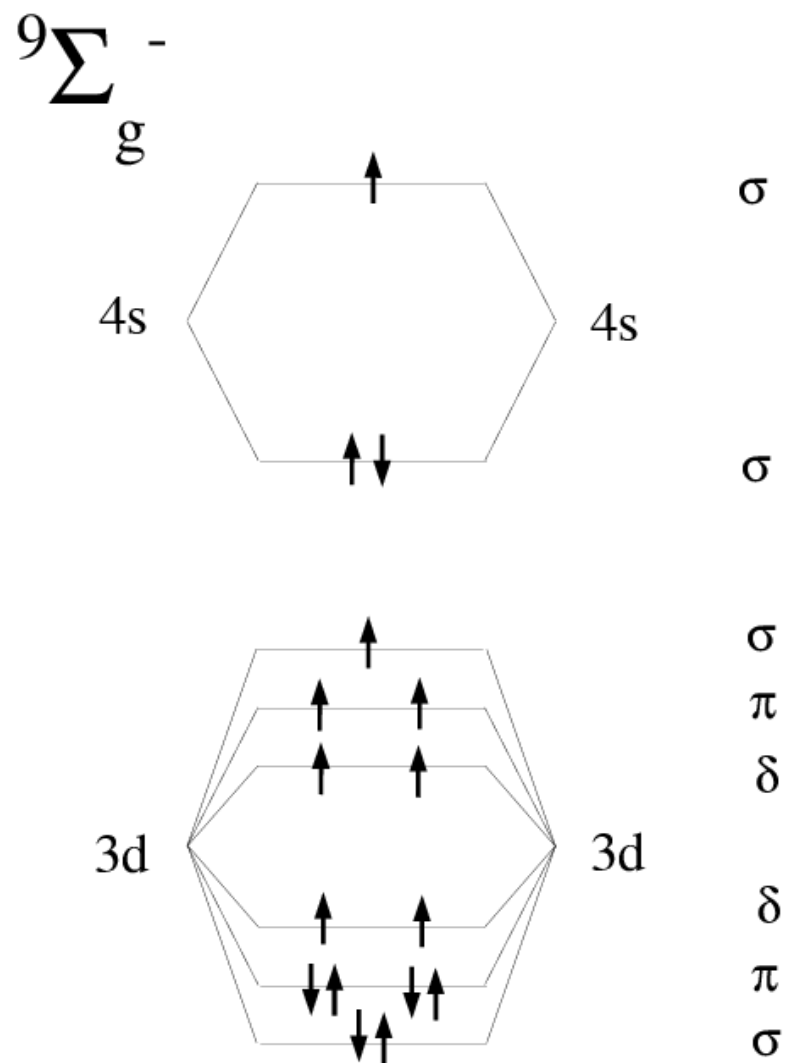

RVB liquid phase possible at high pressure

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For instance the most delocalized orbital 4s the convergence is too slow

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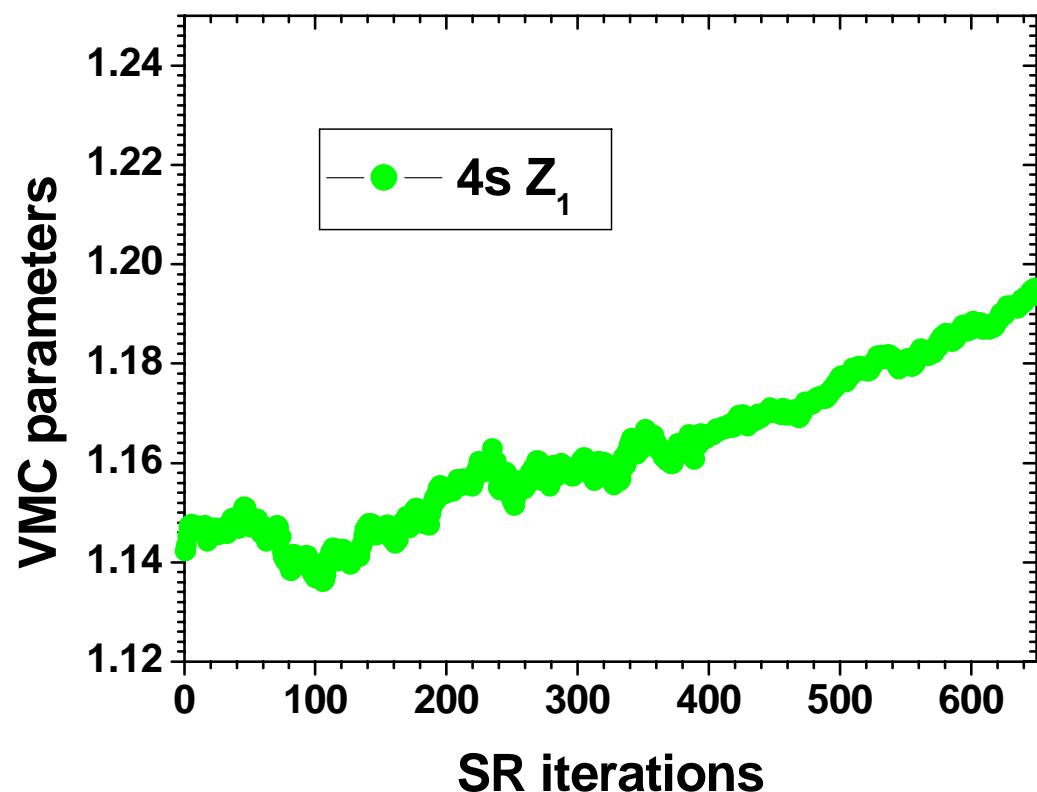
For instance the most delocalized orbital 4s the convergence is too slow
Continuing without core… 2h run 10 param
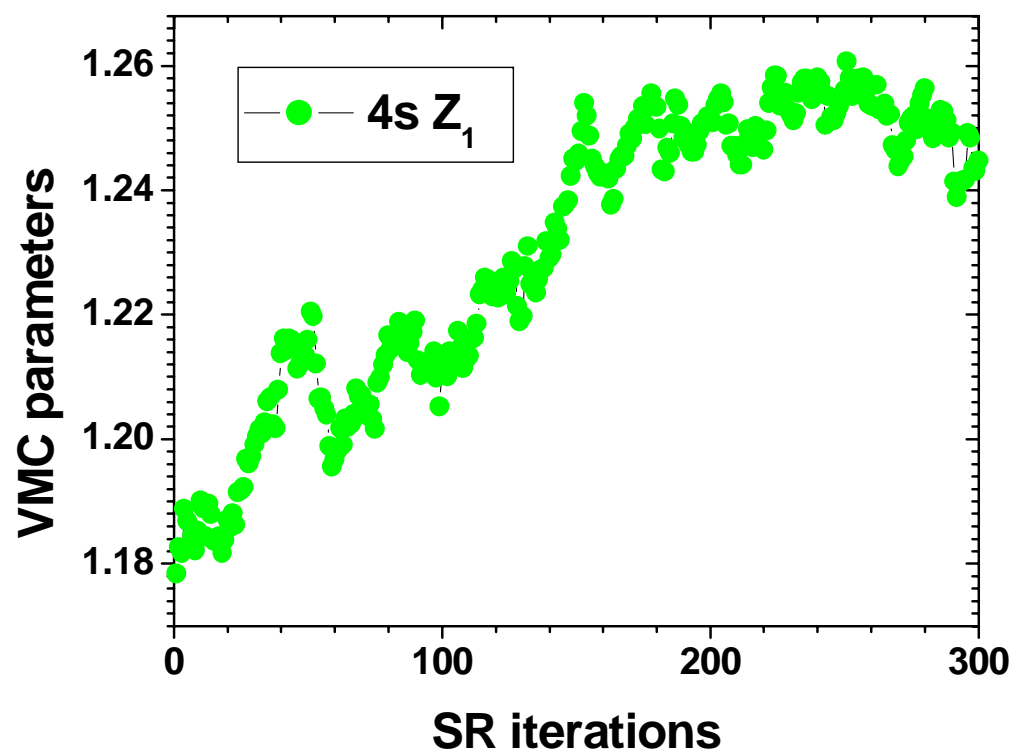
low energy differences ~0.1eV accessible !!!

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A benchmark correlated dimer Fe_2

Method	HF	DFT	RVB	Exp.
R_0 (a.u.)	?	3.721	4.1 (1)	3.82(20)
ω_0 (cm^{-1})	?	468	285(18)	299.7
Type	?	$^7\Delta_u$	$^9\Sigma_g^-$	$^9\Sigma_g^-$

It is possible to explain the photoemission spectrum in the anion Fe_2^-

Leopold JPC (1988)

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DFT occupation molecular orbitals

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$^9\Sigma_g^-$
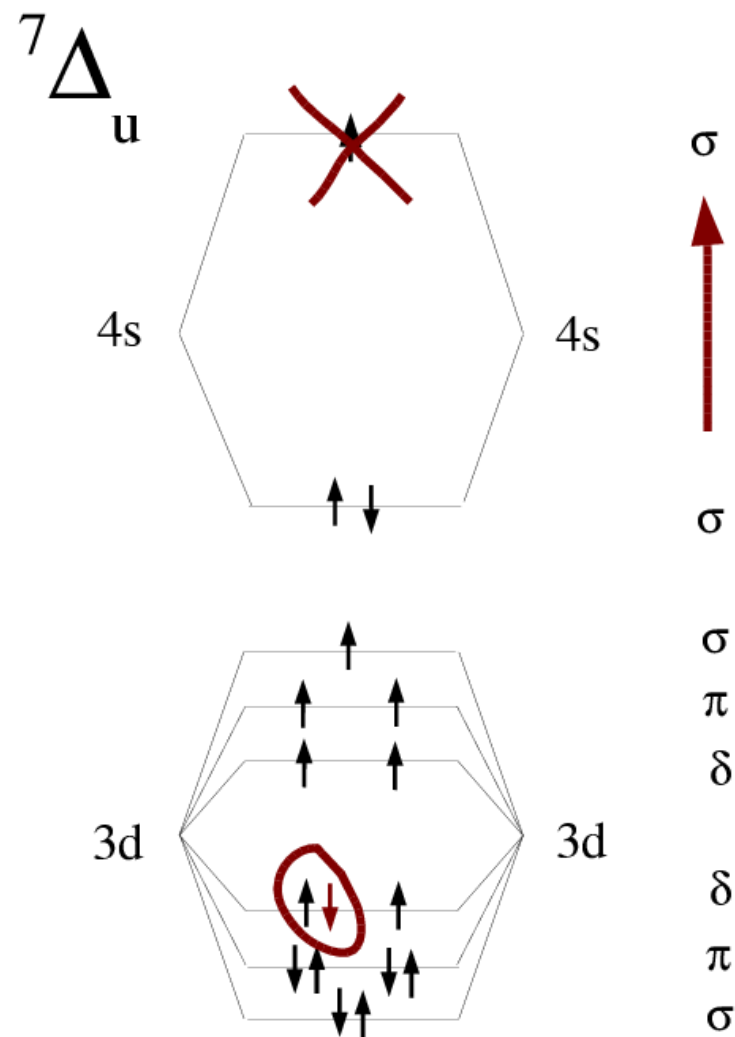
The right occupation is due to correlation

Explains the Fe_2^- exp.

$^8\Sigma_u^-$

4s   4s   σ

           σ

4s   4s   σ

           σ
           π
           δ

3d   3d   δ
           π
           σ
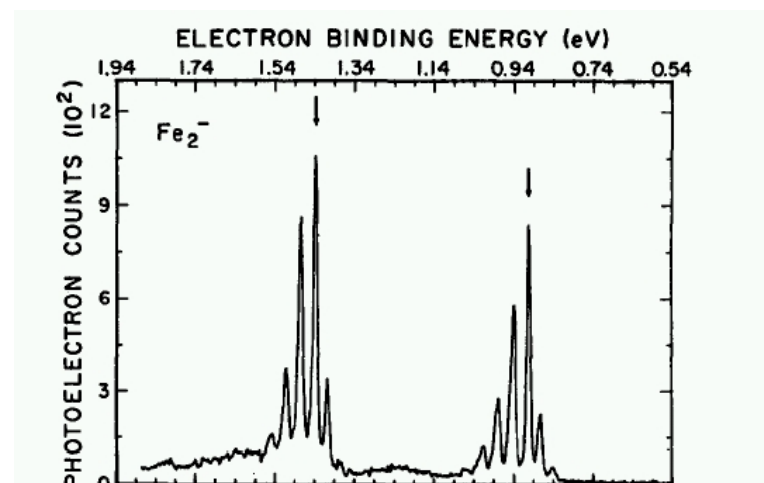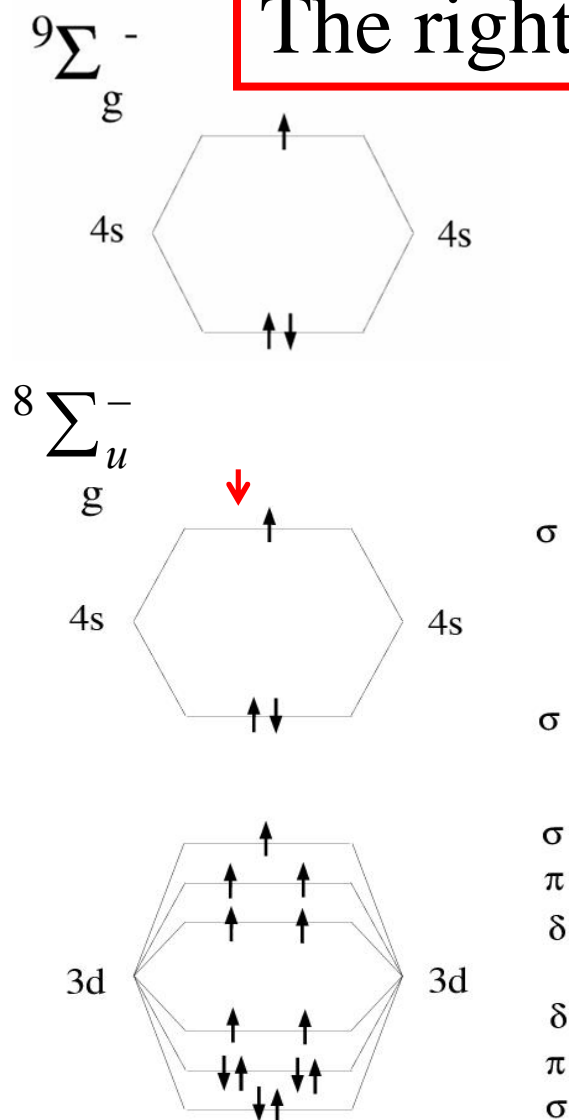
Within our RVB wf

$^7\Delta_u$ is 0.7 eV higher

Confirmed also by recent CI, Hubner JPC'02

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Iron dimer (II)

$$^9\Sigma_g^-$$

Harmonic frequency: 284 (24) cm^{-1}
Experimental value: ~ 300 (15) cm^{-1}

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93
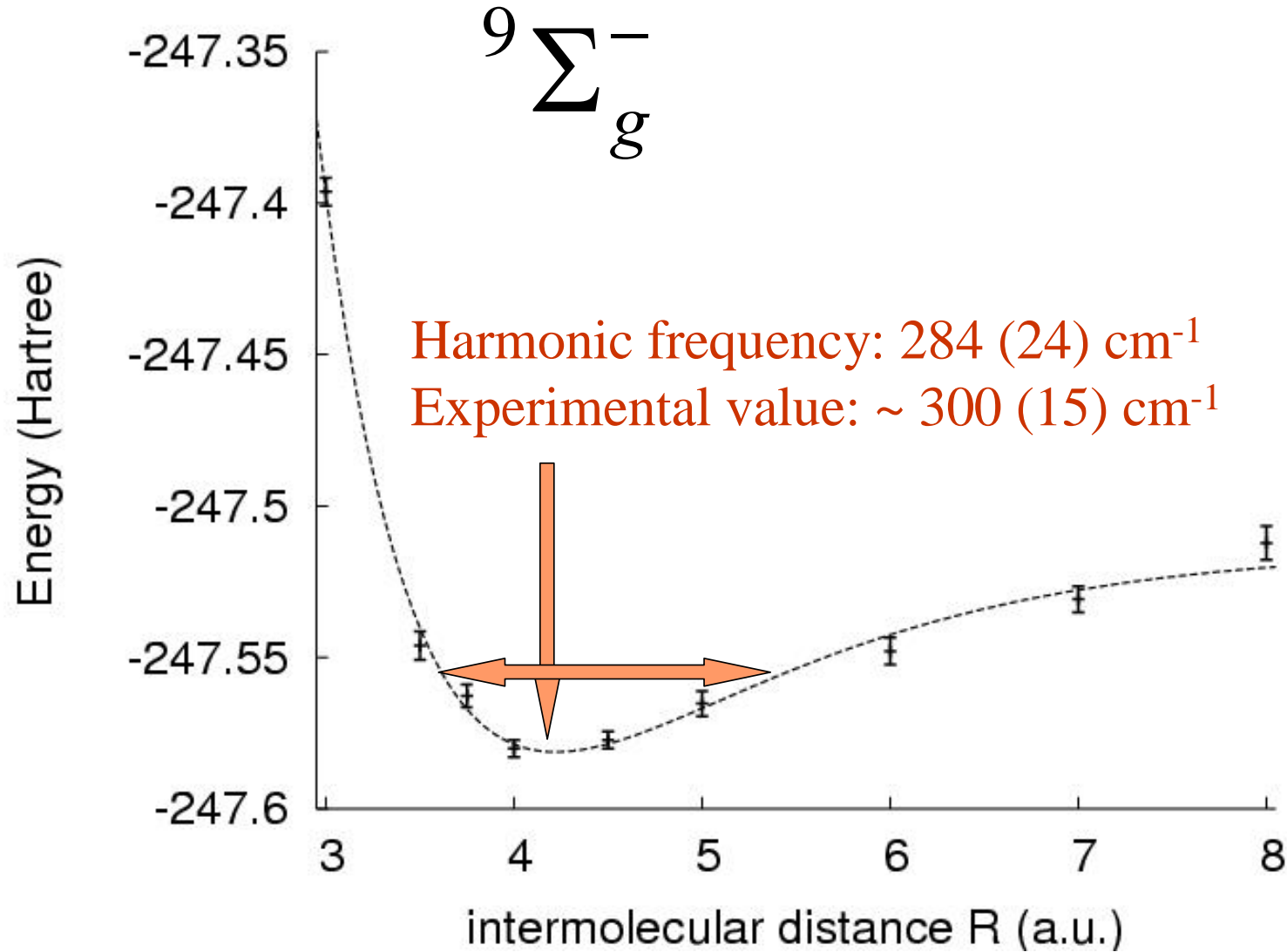
Iron

Data without relativistic corrections

Ground state (D^5)	Energy (Ryd)	references
HF	-2524.8864	*Clementi and Roetti, Atomic data and nuclear data table, 1974*
HF+J	-2526.254(7)	
HF+J (3-body)	-2526.675(7)	**Our best VMC**
CSD	-2526.0578	*C. W. Bauschlicher, J. Chem. Phys. 86 (10), 5591 (1987)*
GFMC FN	-2526.98(2)	

CPU time (pentium IV, serial code)

VMC 250 hours to compute the iron energy with 10^{-3} Ryd of error

FN 4000 hours to get 10^{-3} Ryd of error

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Optimization is <u>important</u> Jastrow+Slater
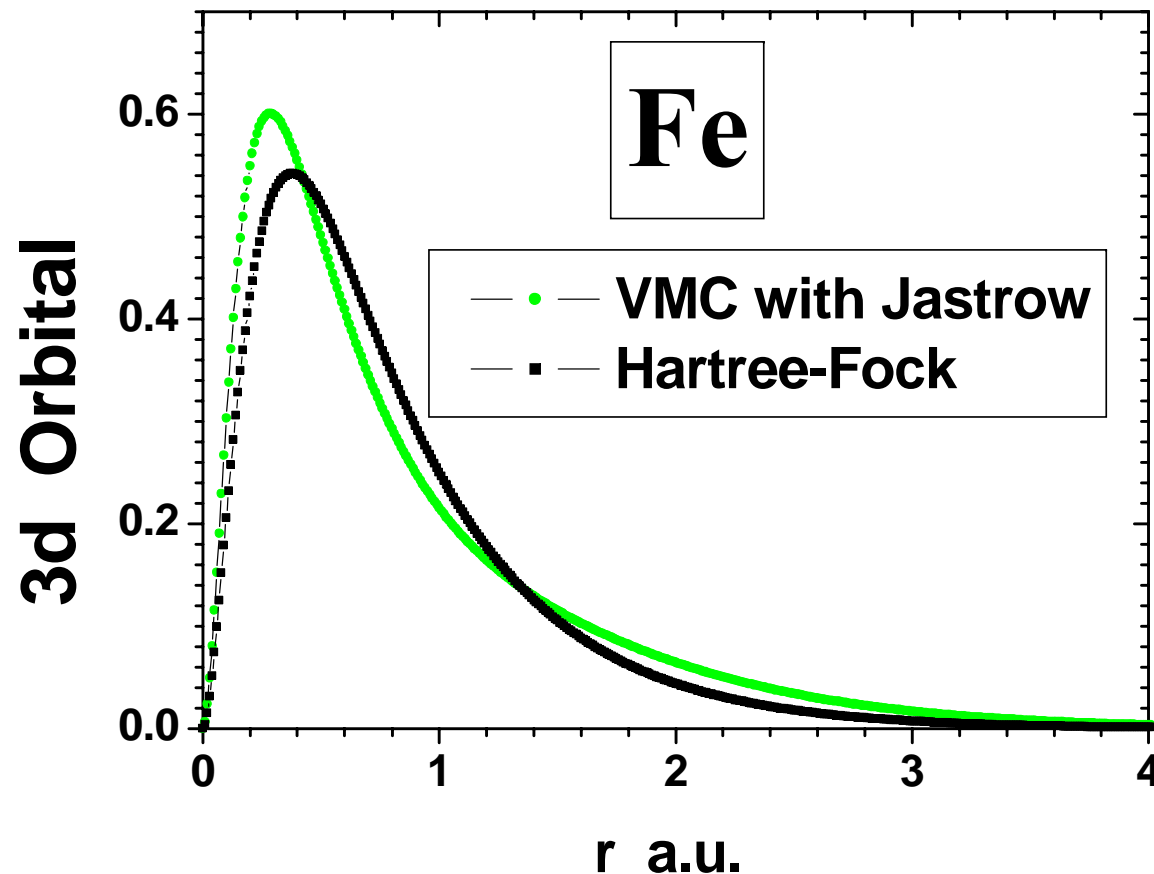
The 3d orbitals crucially depend upon Jastrow correlation factor

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AGP wave function

Antisymmetrized Geminal Product
(N particle component of a BCS state, pair correlated system)

$$\Phi(r_i^\uparrow, r_j^\downarrow) = \sum_{l=1}^{\overline{N}} \lambda_l \varphi_l(r_i^\uparrow) \varphi_l(r_j^\downarrow) \qquad \text{singlet } L = 0, S = 0$$

$$\Psi = \det A_{ij} \qquad\qquad A_{ij} = \Phi(r_i^\uparrow, r_j^\downarrow)$$

- Earliest works with AGP in quantum chemistry:

*Hurley et all, Proc. R. Soc. London, Ser. A **220**, 446 (1953)*

- 60's first numerical calculations (Be, C_6H_6, ...)
- Extension to polarized systems (GAGP), Li with 87,7% of correlation energy:

*H. A. Kurtz and all, Int. J. Quant. Chem. Symp. **16**, 605 (1982)*

- Latest work (application to diatomic molecules):

*V. A. Rassolov, J. Chem. Phys. **117**, 5978 (2002)*

AGP + J (QMC) $\Rightarrow$ faster convergence with the Jastrow
main advantage: beyond the HF nodes computing only one determinant (exact for two particles interacting system)

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Results for HF+J (no 3-body)
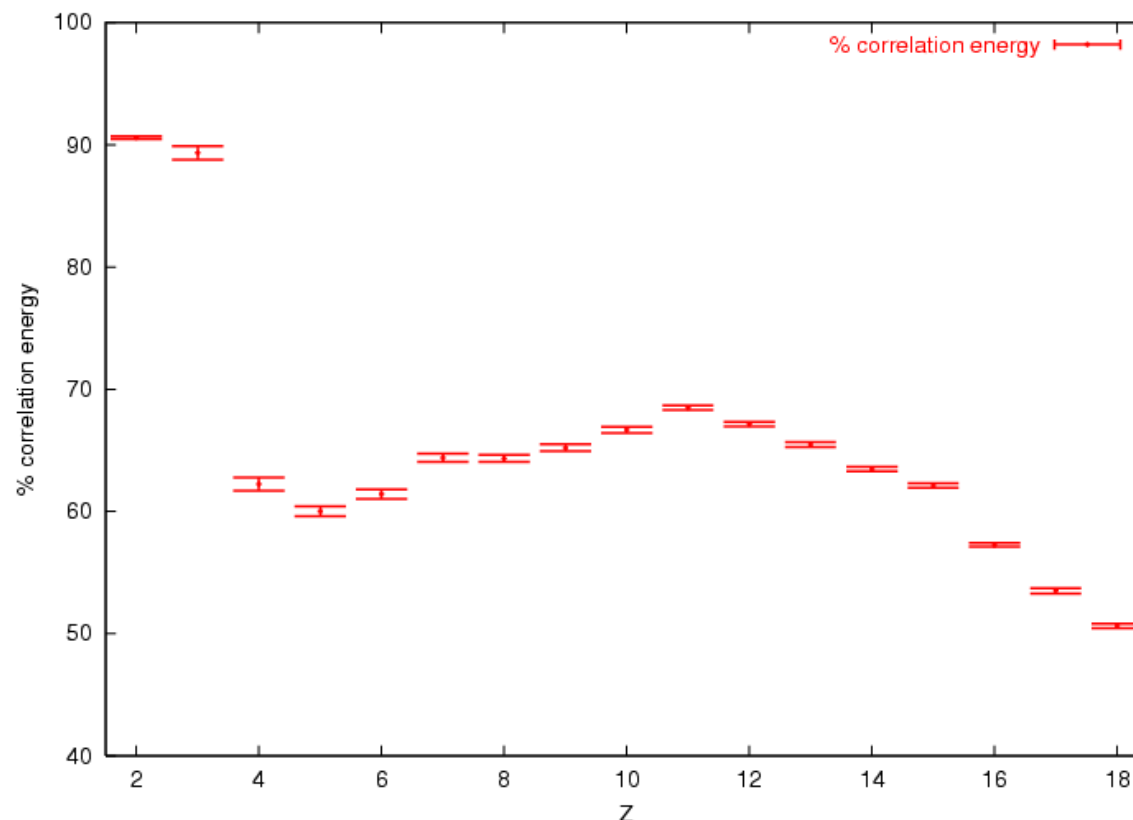
• Lack of correlation energy for Be, B, C

•The gain decreases when Z increases

$\Rightarrow$ **Jastrow factor too simple**

$\Rightarrow$ **One Slater determinant is not enough?**

(see D.Bressanini et al., JCP 97(12), 9200 (1992))

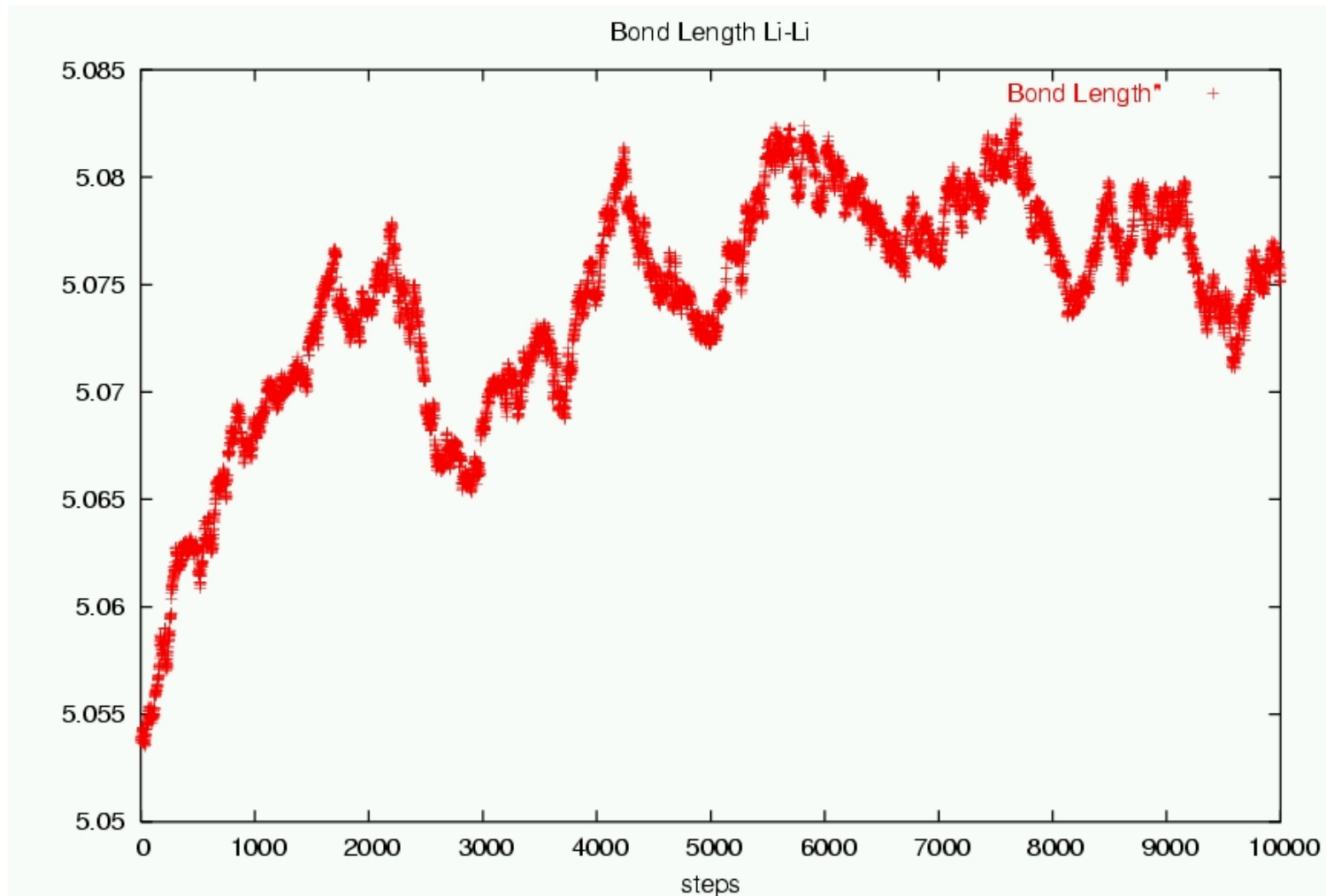Advanced school in quantum Monte Carlo in physics and chemistry
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Li$_2$ molecule, 34 variational parameters and R

Use of the warp algorithm (Filippi-Umrigar) for force

R

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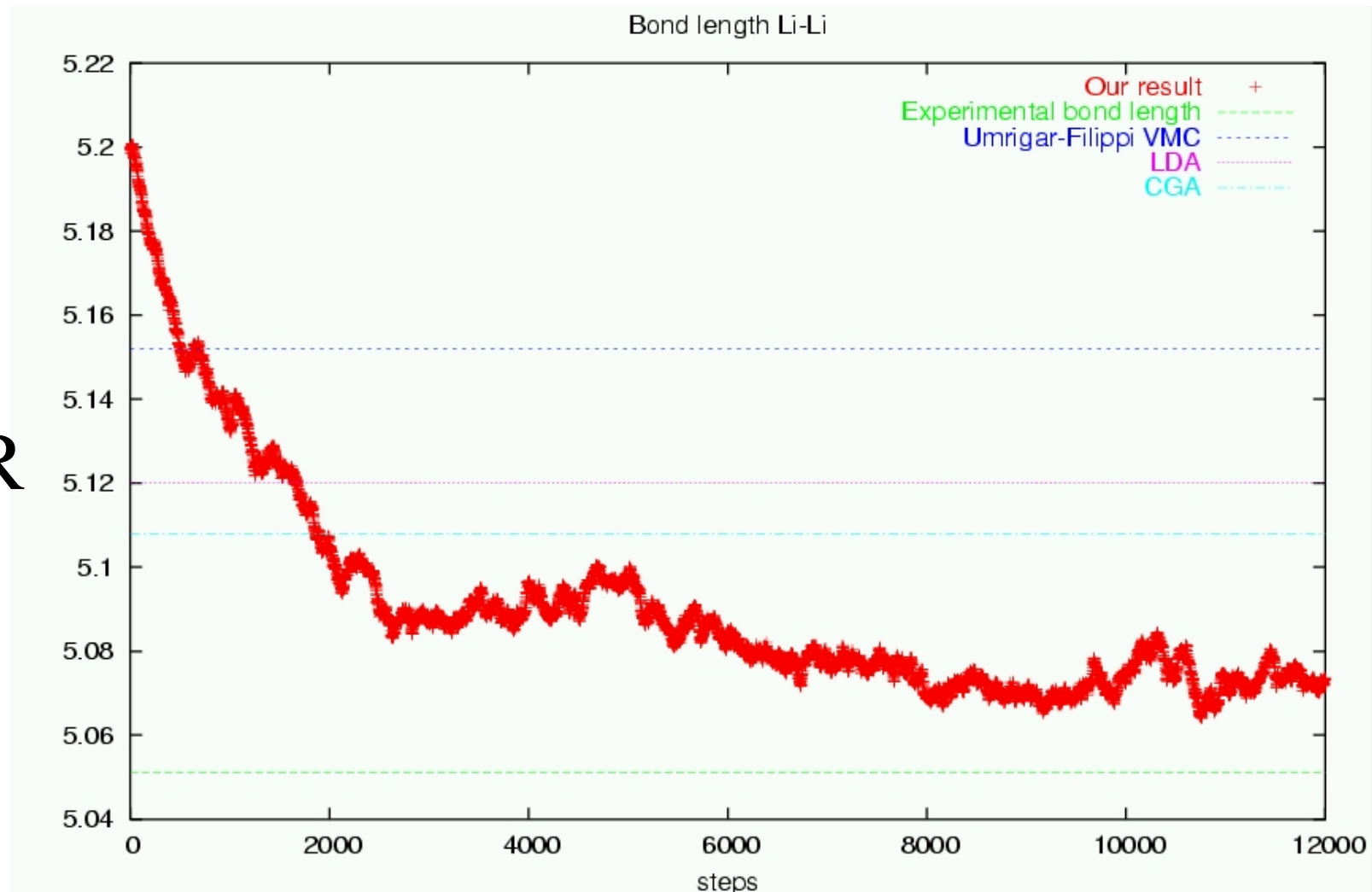
The same can be done starting from below

Bond Length Li-Li

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A typical parameter (from 34)

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100
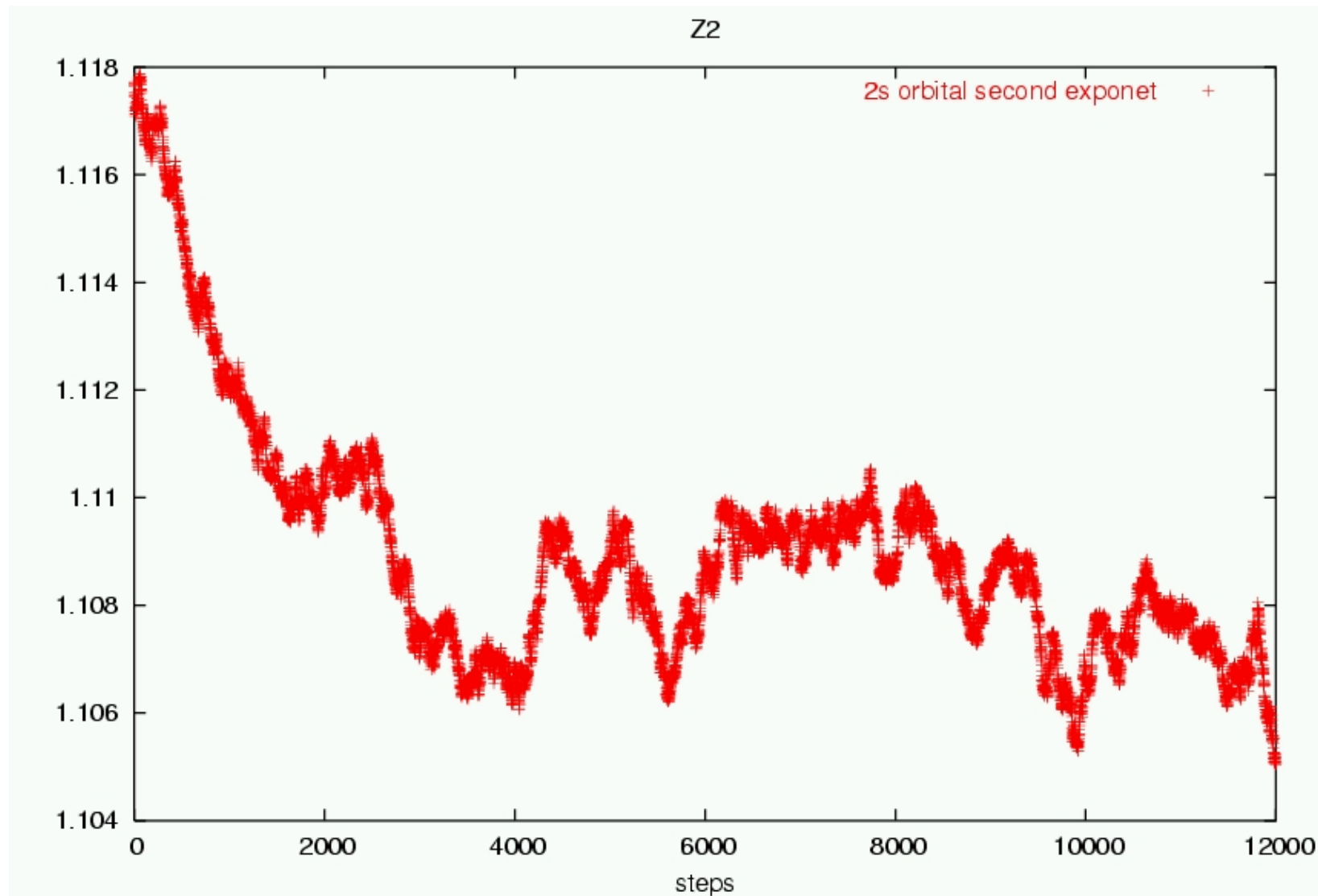
Systematic control of the thermal bias
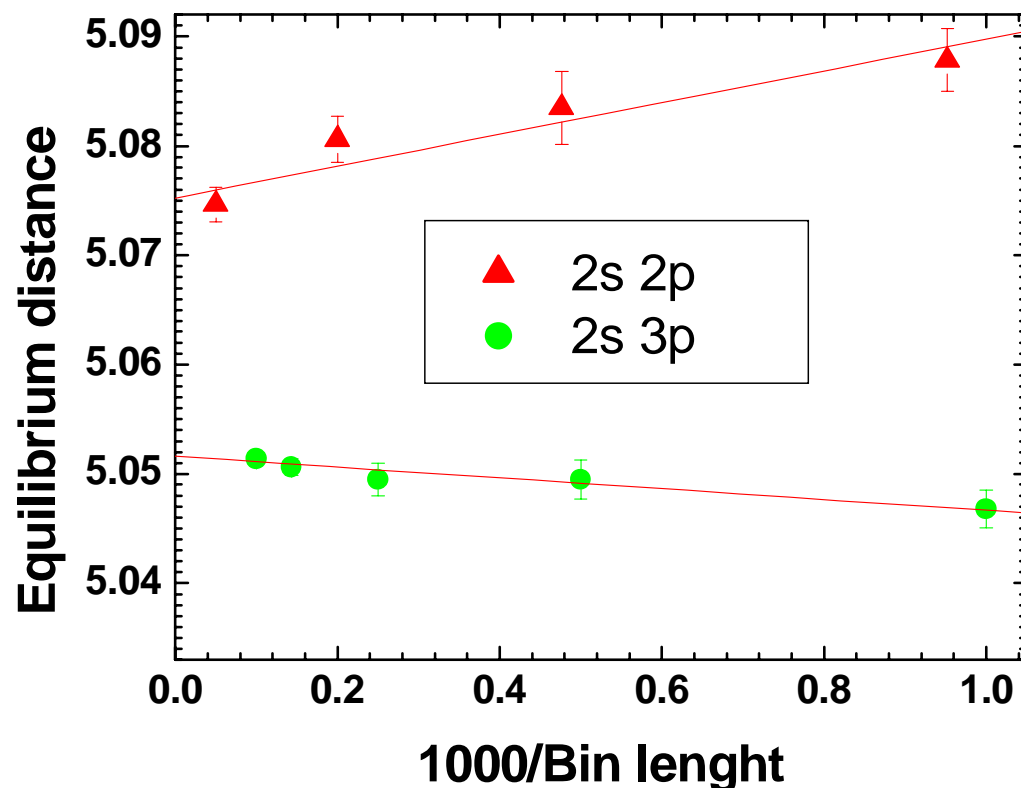
In the limit of infinite bin length the Euler conditions are satisfied exactly.

even for the remaining 34 parameters

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The stochastic approach is in general superior for high enough statistical accuracy calculations

Suppose a statistical accuracy 10 times better is required on the Li-Li bond length

➔ by QMC 100 times longer run

1) The thermal bias can be reduced by 10 by increasing the bin length by 10

2) The statistical fluctuations by further increasing the number of iterations by 10 after equilibration

Then the equilibration time is 10 times less important!

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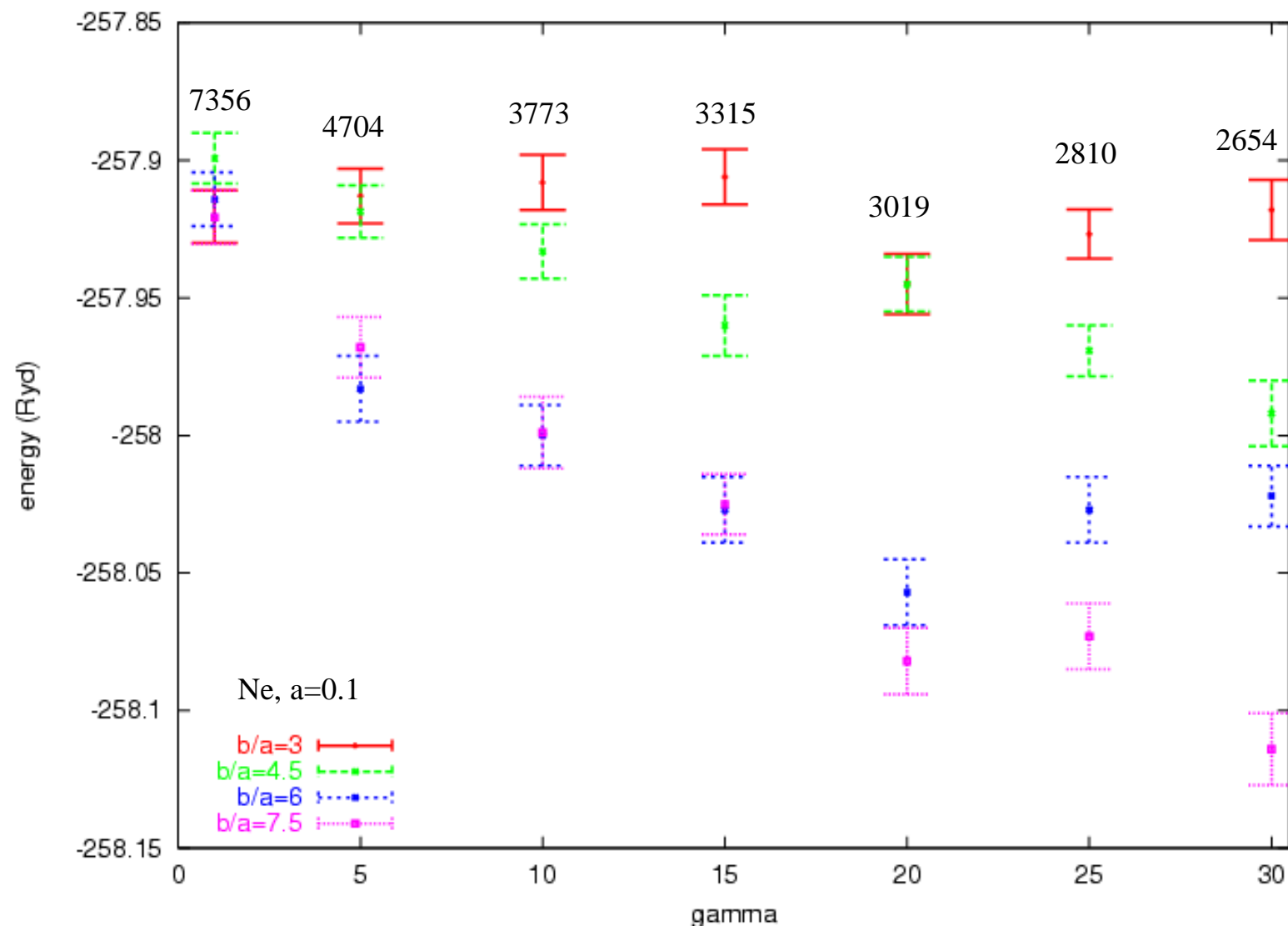
Fixed nodes results
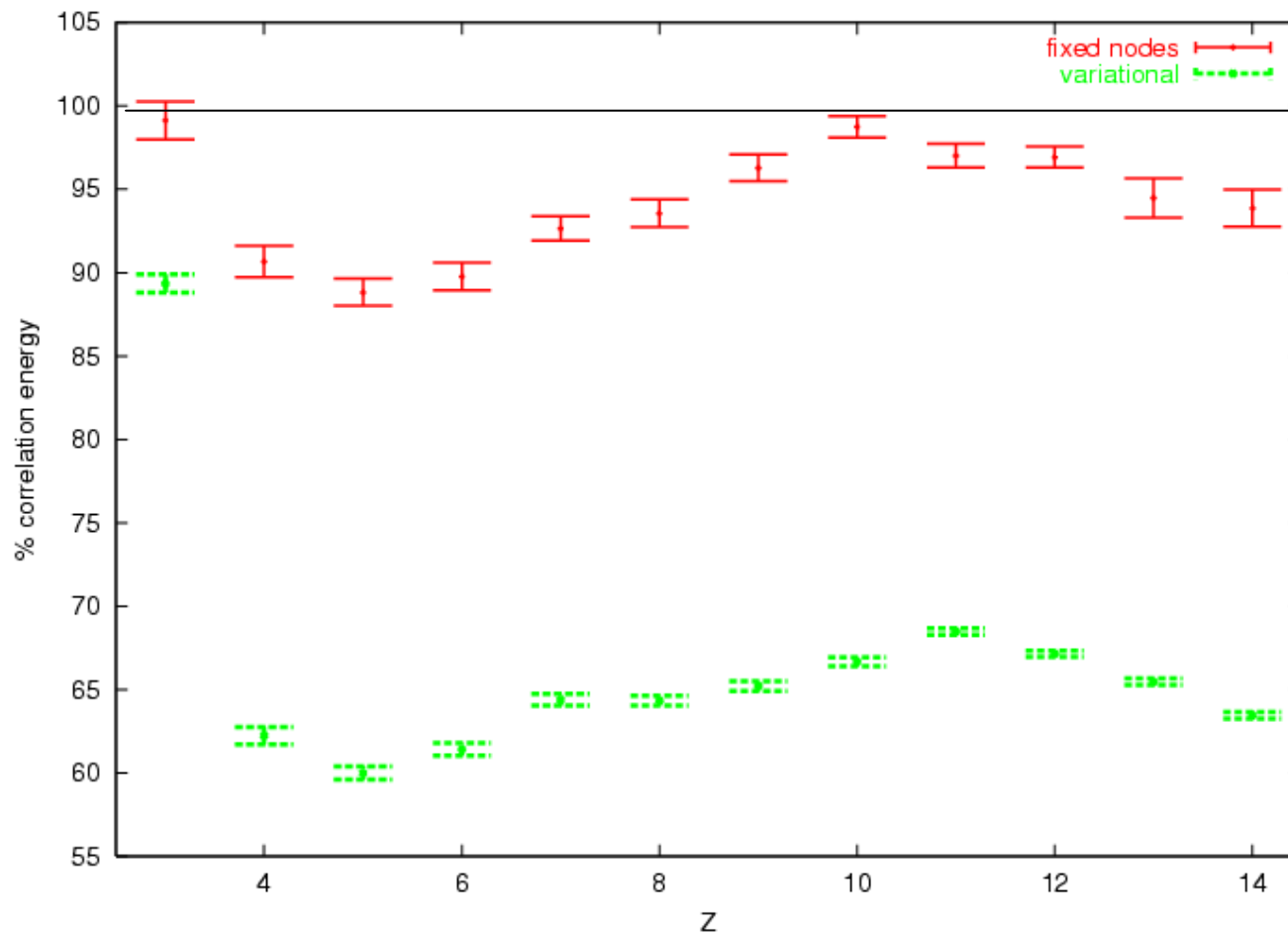
- Exact energy for closed shells atoms
- Relevant part of correlation missing for Be, B and C

⇒ **nodes have to be improved**

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Results for AGP + J (VMC)

Improvement for Be, B, C (Mg, Al, Si) adding a 2p (3p) component to the geminal

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Improvement for Be, B, C (Mg, Al, Si) adding a 2p (3p) component to the geminal

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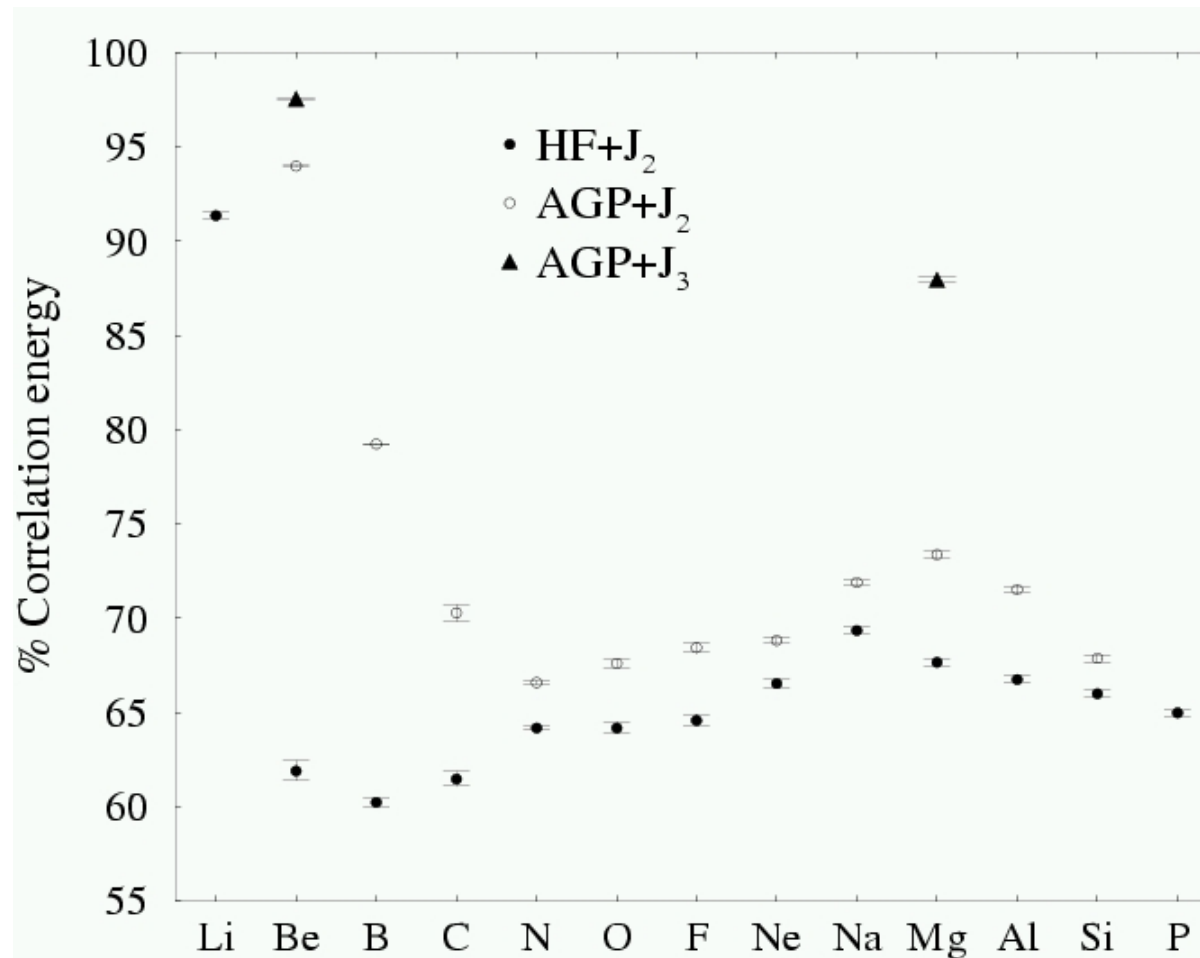
Results for AGP + J (GFMC)
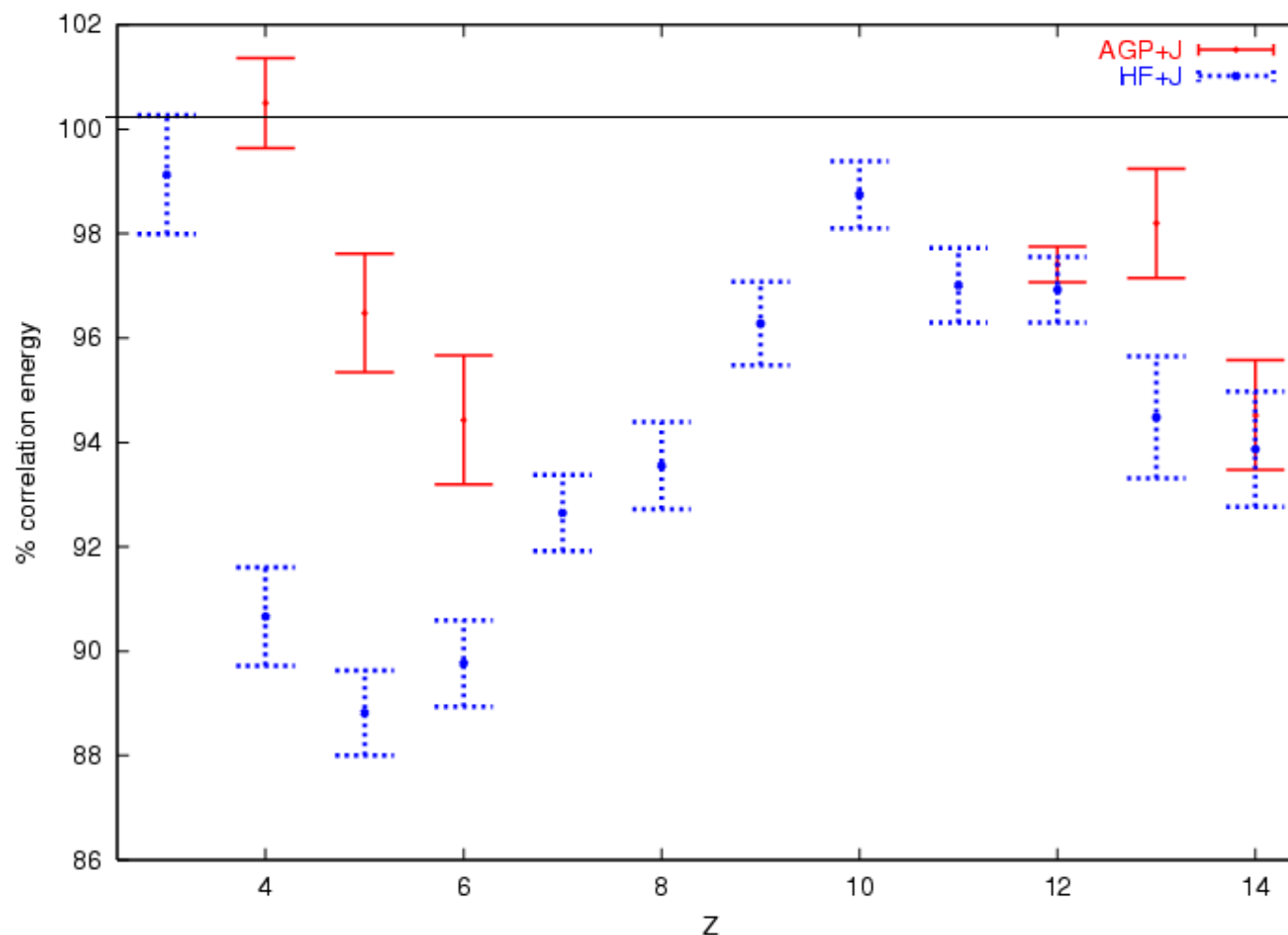
Be is exact within the error bars, the other atoms treated by AGP require further orbitals on the geminal to get the exact energy.

The AGP+J wave function improves significantly the nodal structure.

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TABLE III: Bond lengths (R) in atomic units; the subscript 0 refers to the "exact" results. For the water molecule R is the distance between O and H and θ is the angle HOH (in deg), for CH_4 R is the distance between C and H and θ is the HCH angle.

	R_0	R	θ_0	θ
Li_2	5.051	5.0516(2)		
O_2	2.282	2.3425(18)		
C_2	2.348	2.366(2)		
H_2O	1.809	1.8071(23)	104.52	104.74(17)
CH_4	2.041	2.049(1)	109.47	109.55(6)
	R_0^{CC}	R^{CC}	R_0^{CH}	R^{CH}
C_6H_6	2.640	2.662(4)	2.028	1.992(2)

But for Be dimer ….does not work (basis small?)

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Benzene radical cation

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Benzene molecule

TABLE IV: Binding energies in eV obtained by variational (Δ_{VMC}) and diffusion (Δ_{DMC}) Monte Carlo calculations with different trial wave functions for benzene. In order to calculate the binding energies yielded by the 2-body Jastrow we used the atomic energies reported in Ref. 10. The percentages ($\Delta_{VMC}(\%)$ and $\Delta_{DMC}(\%)$) of the total binding energies are also reported.

	Δ_{VMC}	$\Delta_{VMC}(\%)$	Δ_{DMC}	$\Delta_{DMC}(\%)$
Kekule + 2body	−30.57(5)	51.60(8)	−	−
resonating Kekule + 2body	−32.78(5)	55.33(8)	−	−
resonating Dewar Kekule + 2body	−34.75(5)	58.66(8)	−56.84(11)	95.95(18)
Kekule + 3body	−49.20(4)	83.05(7)	−55.54(10)	93.75(17)
resonating Kekule + 3body	−51.33(4)	86.65(7)	−57.25(9)	96.64(15)
resonating Dewar Kekule + 3body	−52.53(4)	88.67(7)	−58.41(8)	98.60(13)
full resonating + 3body	−52.65(4)	88.869(7)	−58.30(8)	98.40(13)

Jastrow+AGP changes the nodes!

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Size consistency:
for large distance the wavefunction factorizes

$$\psi_{ja,\sigma}^+ = \int dR\, \varphi_{j,a}(R)\, \psi_\sigma^+(R) \qquad \text{where } \varphi_{j,a}(R) \text{ atomic orbitals}$$

$a = $ atomic index $\qquad j = $ atomic orbidal index (s, p, d...).

$$\left| AGP \right\rangle = \left[\sum_{j,k,a,b} \lambda_{a,b}^{j,k} \psi_{ja,\uparrow}^+ \psi_{kb,\downarrow}^+ \right]^{N/2} \left| 0 \right\rangle$$

where $\left[\psi_{ja,\sigma}^+ \right]^2 = 0$ due to Pauli and $\lambda_{a,b}^{j,k} = \lambda_{b,a}^{k,j}$

In the expansion of $\left| AGP \right\rangle$ each term :

$\lambda_{a,b}^{j,k}\, \lambda_{c,d}^{l,m}\, \psi_{ja,\uparrow}^+ \psi_{k,b\downarrow}^+ \psi_{lc,\uparrow}^+ \psi_{m,d\downarrow}^+ \cdots \left| 0 \right\rangle$ is a Slater determinant

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For H_2 molecule we obtain at large a,b distance:

We can go smoothly from

Heitler - London $\lambda_{a,b} = \lambda_{b,b} = \lambda_{a,a} = \lambda$ to the singlet

$$|AGP\rangle = \left[\psi^+_{1s,a,\uparrow}\psi^+_{1s,b,\downarrow} + \psi^+_{1s,b,\uparrow}\psi^+_{1s,a,\downarrow}\right]|0\rangle$$

when   only $\lambda_{a,b} \neq 0$

Thus size consistency is recovered.

What happens for large number (>2) of H?

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In the expansion of the geminal we get Slater det. as:

$$\lambda_{a,b}\lambda_{b,c}\ \psi^{+}_{a,\uparrow}\psi^{+}_{b,\downarrow}\psi^{+}_{b,\uparrow}\psi^{+}_{c,\downarrow}\cdots|0\rangle$$

i.e. no matter how we choose the matrix $\lambda_{a,b}$
we have Slater determinants with large
Coulomb energy, <u>no size consistency</u>.

That's why we need the Jastrow term:
AGP+J is easily size consistent as the ''bad''
Slater determinants are suppressed by J.

This is the RVB   wavefunction with 1 Det. !!!

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Conclusions and Perspectives

-d-wave superconductivity in strongly correlated models

-exploiting the RVB=BCS+J for molecular calculations
M. Casula and S. Sorella JCP '01
M. Casula C. Attaccalite and S.S. JCP '04
The Iron dimer a successful test case relevant for biophysics

-Possible stable low-temperature high-pressure liquid phase for hydrogen

Final goal:
simulation of complex correlated electron systems by Monte Carlo calculation and beyond DFT

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Lattice GFMC

Lattice hamiltonian: $H = -t \sum_{i,a} (c_{i+a}^\dagger c_i + h.c.) + \frac{1}{2} \sum_{i,j} V_{ij} n_i n_j$

Green function: $G_{x,x'} = (\Lambda \delta_{x,x'} - H_{x,x'}) \dfrac{\Psi_T(x')}{\Psi_T(x)}$ $\Rightarrow$ importance sampling

Markov chain
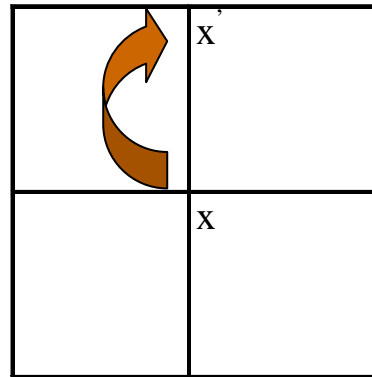
transition probability

$$p_{x,x'} = \frac{G_{x,x'}}{\sum_{x'} G_{x,x'}} = \frac{G_{x,x'}}{\Lambda - e_L(x)}$$

weight $w^{i+1} = w^i (\Lambda - e_L(x))$

Transition probability well defined? NO, for the fermionic sign problem
$\Rightarrow$ **FN approximation**
(see D.M.Ceperley et al. PRB **51**, 13039 (1995))

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From continuous to lattice

Kinetic term

$$\Delta \to \Delta_a = \sum_{i=1}^{d} \frac{T_{a_i} + T_{-a_i} - 2I}{a_i^2} + O(a^2) \qquad T_{\hat{a}} \Psi_T(\bar{x}) = \Psi_T(\bar{x} + \hat{a})$$

hopping term $t \to 1/a^2$

Potential term

For a faster convergence $a \to 0 \Rightarrow$ **regularisation Potential energy** $V \to V^a + O(a^2)$

$$e_L(x) = \sum_{x'} G_{x,x'} = \frac{H\Psi_T(x)}{\Psi_T(x)} = E_L(x)$$

$$\Longrightarrow \qquad V(x) \to V^a(x) = V(x) + \left(\frac{\Delta_a \Psi_T(x)}{\Psi_T(x)} - \frac{\Delta \Psi_T(x)}{\Psi_T(x)} \right)$$

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From lattice to pseudo lattice (dense continuum)

Separation of core and valence dynamics for heavier atoms
and molecules $\Rightarrow$ **two hopping terms in the kinetic part**

$$\Delta \Psi(x) \approx p \Delta_a \Psi(x) + (1-p) \Delta_b \Psi(x) + O(a^2)$$

p can depend on the distance from the nucleus

if $a < b,$ $\quad p(0) = 1$ and $\quad p(\infty) = 0$

Our choice: $\quad p(r) = \dfrac{1}{1 + \gamma \, r^2}$

Moreover, if b is not a multiple of a, the random walk can
sample all over the space!

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Comparison with the ''best'' DMC (Umrigar,Nightingale,Runge '93)

C atom all electrons

$$\sqrt{\Delta\tau} \ (a)$$

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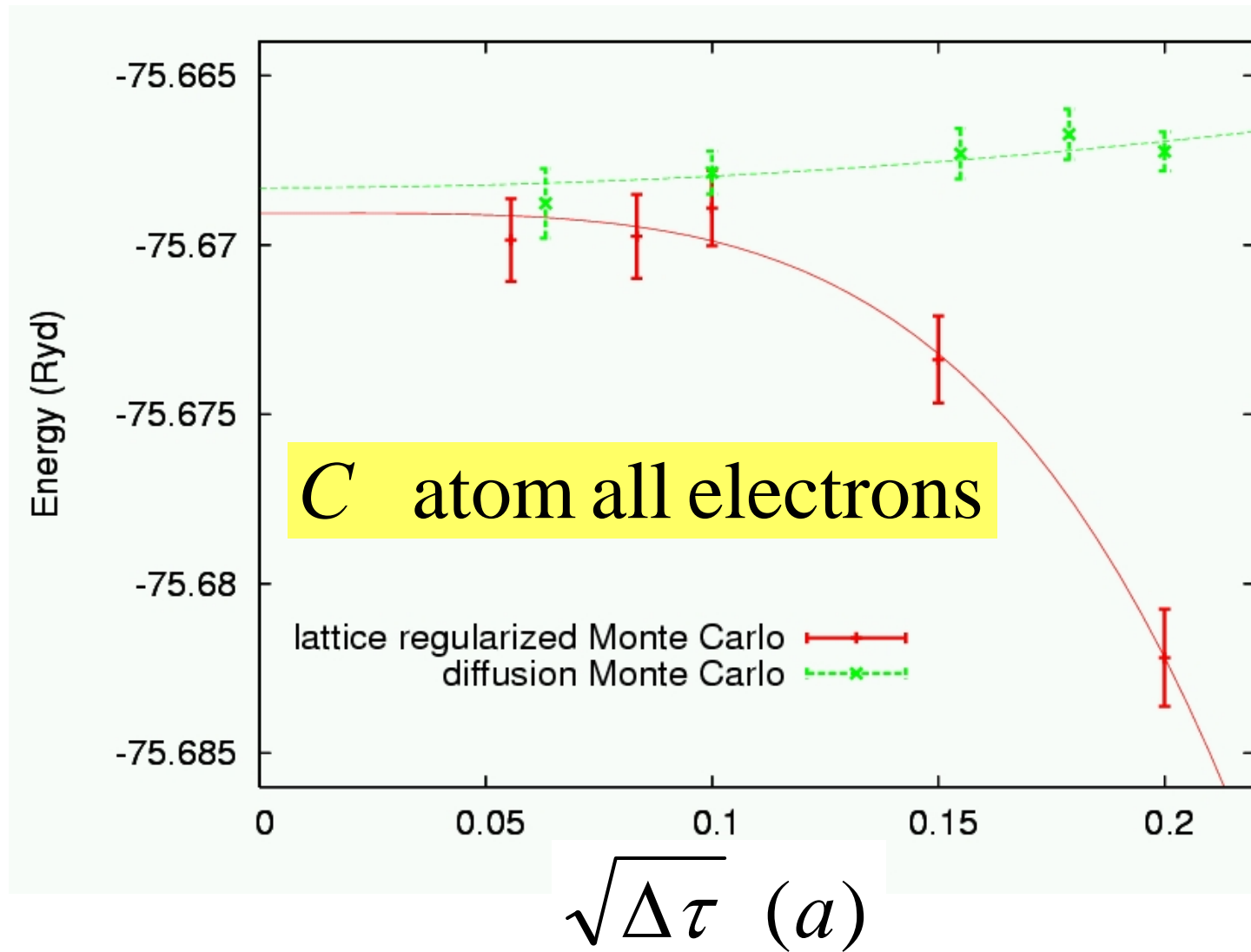
Non local pseudo possible!!!

For heavy atoms Z>20 it is impossible to avoid them
(see L.Mitas PRB **49**(6), 4411 (1994))

1) No localization approximation employed
2) Still variational upper bound theorem holds
   exactly as in the lattice fixed node
3) It works also without Jastrow optimization
4) The fixed node energy depends only on the
nodal structure and weakly on the amplitudes

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The disease of the localization approximation

C pseudoatom with 4 electrons (2 core)

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Why is that?

Nodal surface

$+$

$-$

$+$
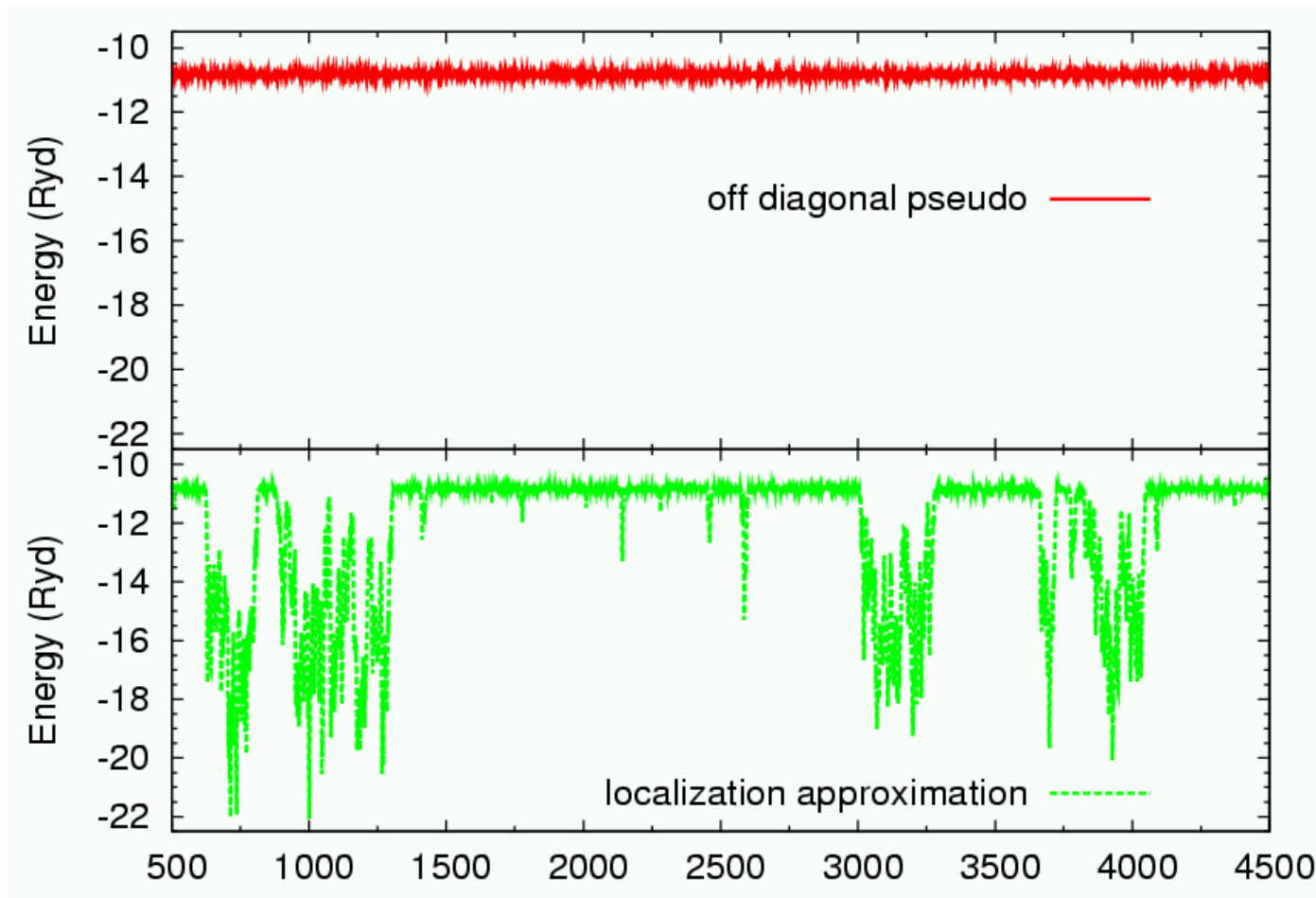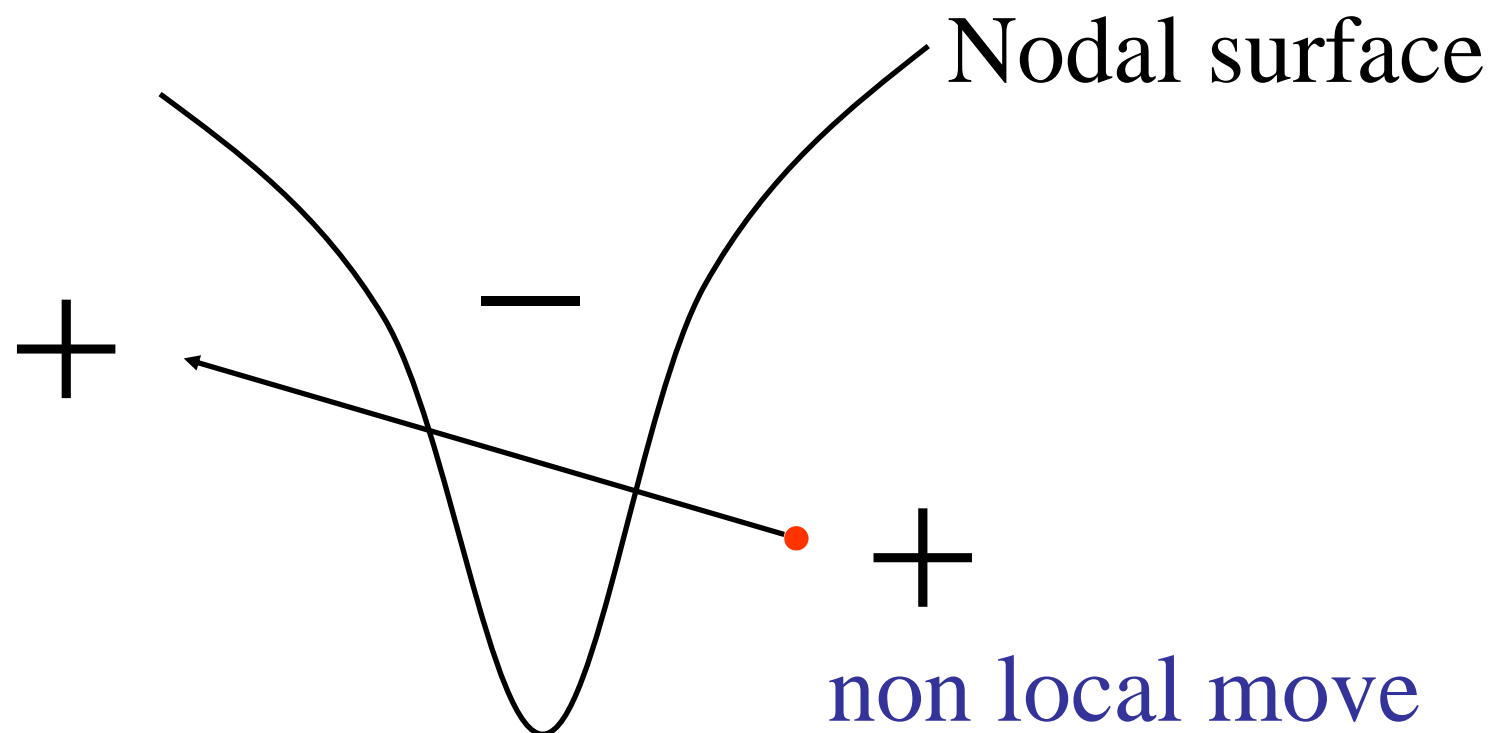
non local move

By neglecting the allowed non local moves the localization approximation → infinitely negative attractive potential close to the nodal surface.
It works only for very good trial function.

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Standard DMC and lattice GFMC

extrapolation properties

DMC	GFMC
Trotter approximation	For each a well defined effective H
τ extrapolation	a extrapolation
$\tau^{1/2}$ behaviour	a^2 behaviour (it can be smoother)

dependence on N for the atomic problem

	DMC	GFMC
Determinant	N^2	N^2
Decorrelation	N	N
Diffusion	$Z^2\tau \approx 1 \Rightarrow N^2$	$Za \approx 1 \Rightarrow N^2$
Total	N^5	N^5

acceptance rate for off-diagonal moves

$$\frac{1}{a^2} \propto N^2$$

but using two different hops

$$\frac{1}{a^2} \propto N_{core}^2$$

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Setting the kinetic parameters
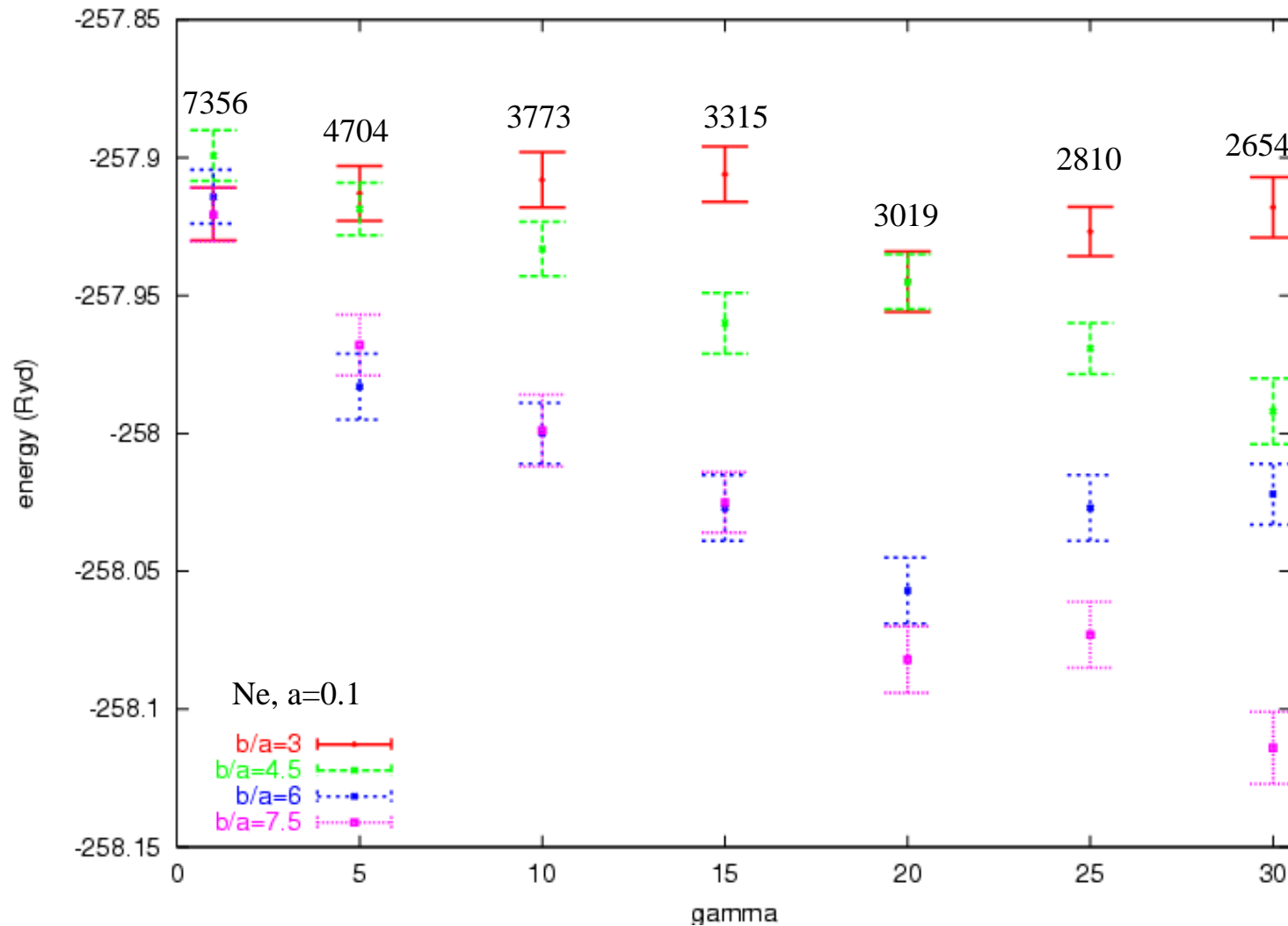
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Targets

- look for Monte Carlo algorithms that can deal with atoms beyond the first row (all electrons)
- find a "good" trial wave function able to get correlation and to treat molecular bonds

The pseudo-lattice approach can improve the efficiency?
Possible use of pseudopotentials within fully variational DMC calculations even for heavier atoms?

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Accuracy in the total energy (~76Ry) of C as compared with the ionization energy 11.26eV

HF	38%
HF+J	14%
AGP+J	6.5%
DMC+AGP+J	1%

For poor accuracy also the HF is enough

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1) For given energy accuracy per ion a simple algorithm (N^3) is enough: no (sign) problem

2) For correlation functions we need an accuracy ~1/N (below the gap) unfortunately

3) I do not see any hope for this, so far any improvement (like DMC) reduces the energy accuracy by a factor at most.

4) The realistic hope is the effective Hamiltonian

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A short review of fixed node approximation

1) It works in configuration space x: electrons and spins given

$$H = -\frac{\hbar^2}{2m}\Delta + V(x)$$

2) Given <u>any</u> wave function $\psi_G(x)$ an Hamiltonian is found

$$H_G\psi_G = 0 \quad \text{choice: } H_G = H + \delta V(x) \implies \delta V(x) = -\frac{\langle x | H | \psi \rangle}{\langle x | \psi \rangle}$$

3) An effective hamiltonian is studied "closer" to H:

$$H^{eff} = H_G - \delta V(x) \quad \text{with constraint } \langle x | \psi_G \rangle > 0$$

Note: exact for bosons and in the classical limit $\hbar \to 0$
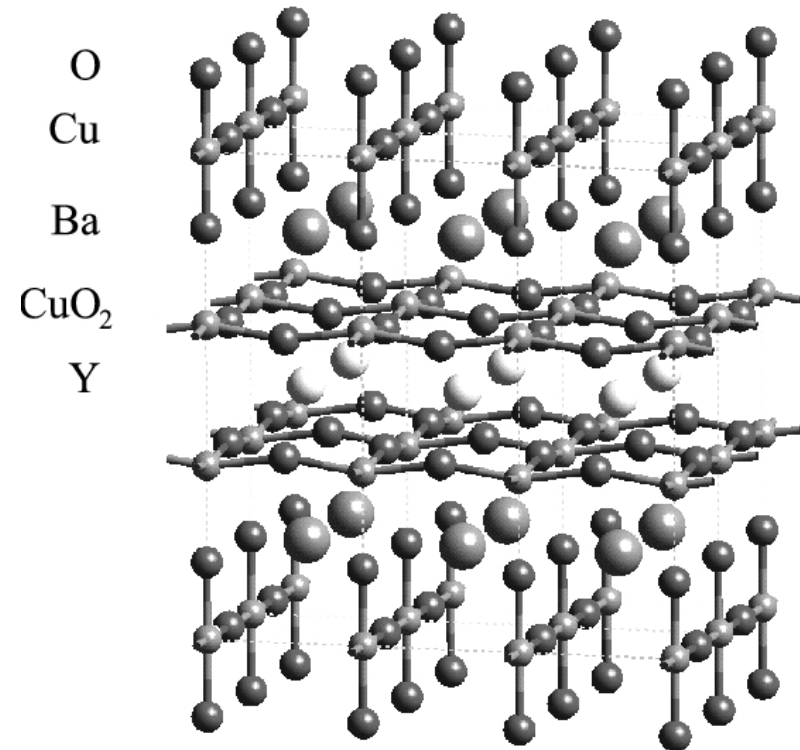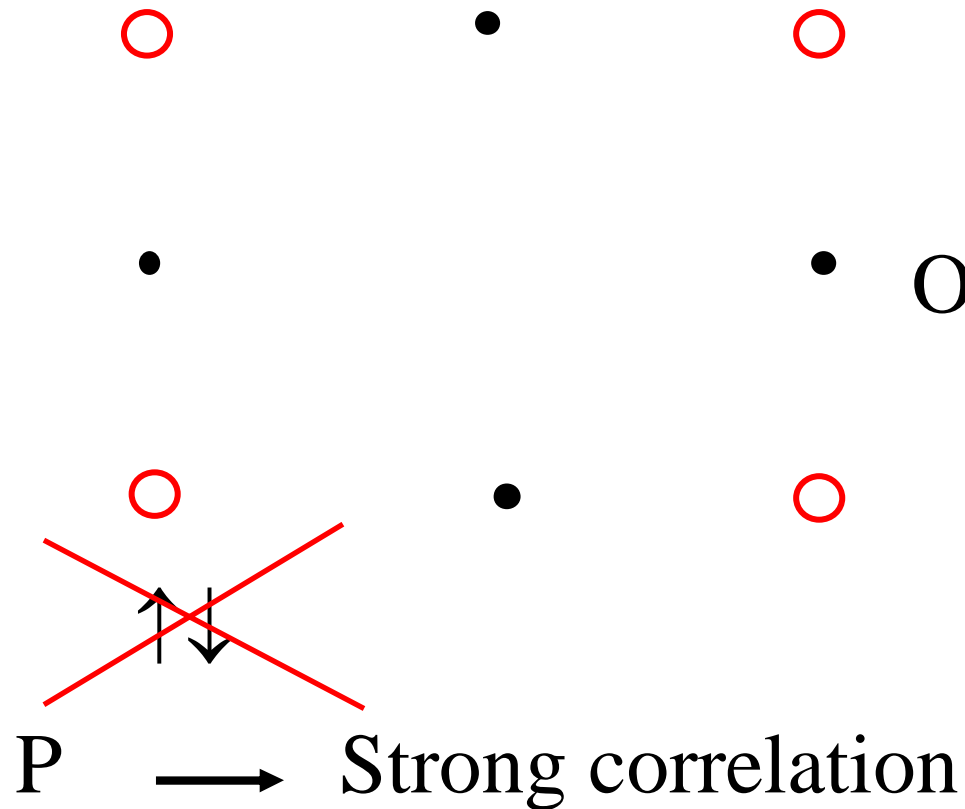
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Effective Hamiltonian on a lattice

Given *any* Hamiltonian H and *any* guiding ψ_G, $H_G\psi_G = 0$ (**easy**) and:

$$H^{eff} = H_G + \delta V(x) = \begin{cases} H_{x',x} & \text{if } x \neq x' \text{ and } \psi_G(x')H_{x',x}/\psi_G(x) \leq 0 \\ -\gamma\, H_{x',x} & \text{if } x \neq x' \text{ and } \psi_G(x')H_{x',x}/\psi_G(x) > 0 \\ H_{x,x} + (1+\gamma)\, V^{sf}(x) & \text{if } x = x' \end{cases}$$

where: **sign-flip** $\quad V^{sf}(x) = \displaystyle\sum_{x' \neq x\ \&\ \psi_G(x')H_{x',x}/\psi_G(x)>0} \psi_G(x')H_{x',x}/\psi_G(x)$

for $\gamma \geq 0$ the ground state of H^{eff} has the same signs of $\psi_G(x)$

$\gamma = 0 \quad$ for best energy fixed node Hamiltonian

$\gamma = -1 \quad H^{eff} = H$

From D. ten Haaf et al. PRB'95, L. Capriotti & SS PRB'00

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"Philosophy" of the approach

Assume there are physical Hamiltonian that describe
a phase and are therefore stable away from critical points:

$$H \rightarrow H + \delta V$$

The phase remains stable for physical perturbation δV

With lattice fixed node we can simulate H with several δV :

If $|\psi_G\rangle$ is stable than we can say that $|\psi_G\rangle$ may represent
a ground state of some stable hamiltonian (not necessarily H)

For practical purposes $|\psi_G\rangle$ is taken by minimizing the energy of H

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Solution of model Hamiltonians

??? ???
Ground state Properties
of stable Hamiltonians

???

??? ???

???

Properties of "reasonable"
wave functions

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Effective hamiltonian approach for strongly correlated lattice models

References

M. Calandra & S. Sorella Phys. Rev. B. '98

S. Sorella PRL '98

S. Sorella & L. Capriotti Phys. Rev. B 2000

S. Sorella Phys. Rev. B 2001

Outline of the lecture:

- The Lanczos algorithm and variance extrapolation

- Beyond the variational approach: the fixed node approximation

- Generalized Lanczos by Stochastic Reconfiguration

- Application to the t - J model: $\begin{cases} \text{d - wave superconductivity for J/t} >\sim 0.2 \\ \text{effective t - J model for } La_2CuO_4 \end{cases}$

Kerkrade 24/2-1/3-2002

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The Lanczos algorithm in QMC:
From lattice model to continuous models?

O

Cu

Ba

CuO$_2$

Y

O

P $\longrightarrow$ Strong correlation

$$H = \sum -t \, P \, c^+_{i\sigma} c_{j\sigma} P + h.c. + J \left(\vec{S}_i \vec{S}_j - \frac{1}{4} n_i n_j\right)$$

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Lanczos with QMC on lattice models (L sites):

For p>1 Lanczos steps   #operation /MC ~ L^{p+1}

Always polynomial at fixed p.
Probably improvement to p! # operations

The question is how much computer effort is required for prescribed accuracy at given L.

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Variational energy for various QMC vs. variance by VMC wavefunction with p=0,1,2 Lanczos iterations
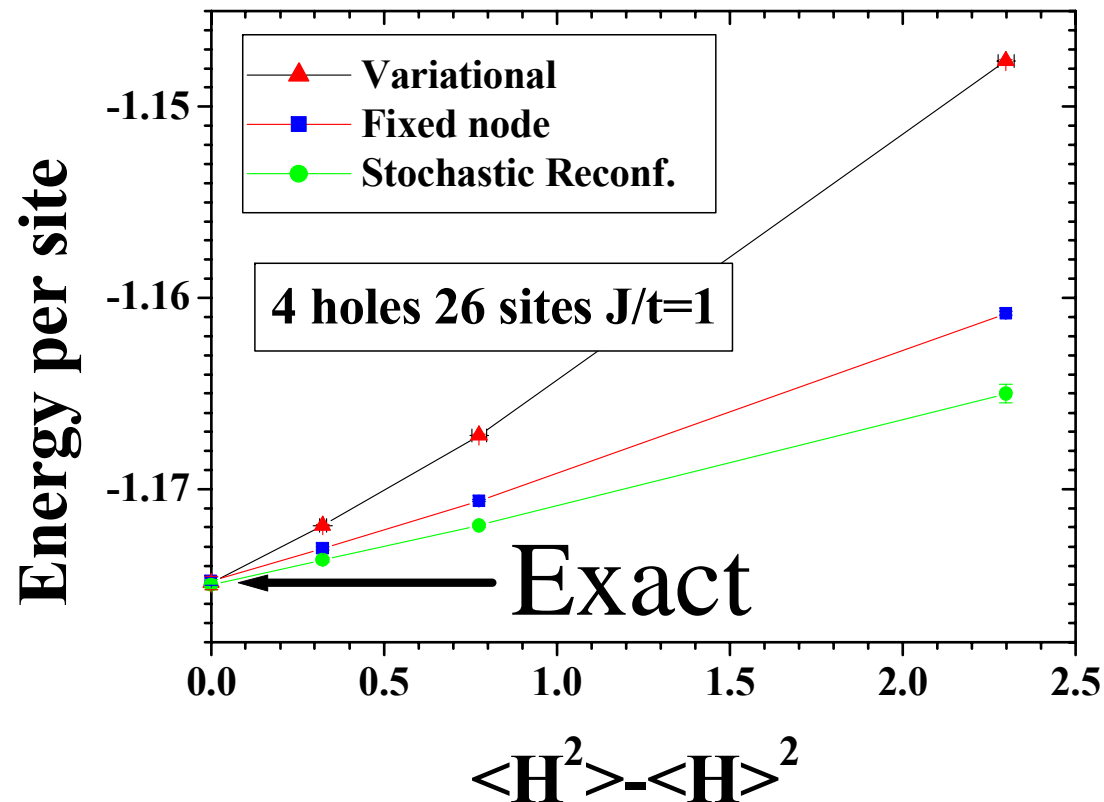
The improvement in energy for both fixed node and present method (best) is irrelevant as far as energy ....

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On a **6x6** (not possible exactly) SR convergence is evident for p=2

▲ VMC   ■ p=1   ● p=2   ▼ p=3

From optimal Δ_{BCS} From Δ_{BCS}-->0
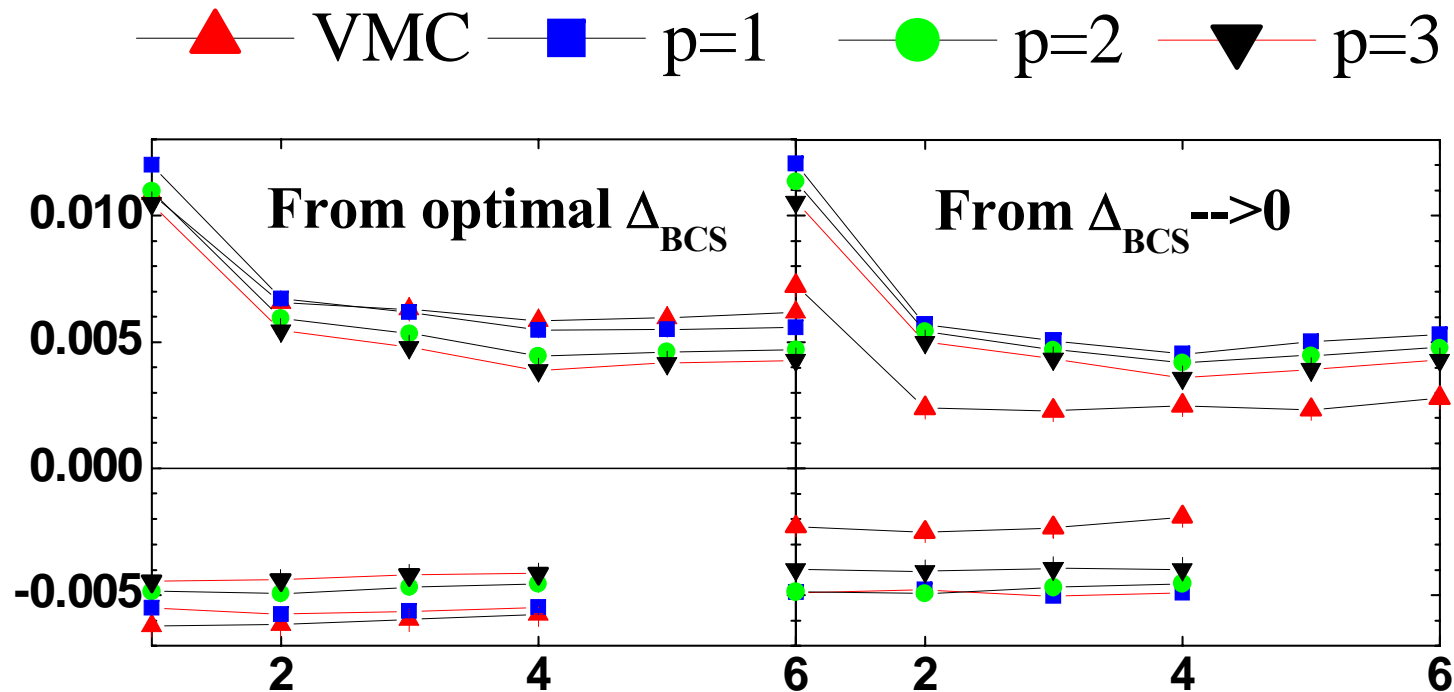
Manhattan Distance=|x|+|y|

SR p=3 pairing   consistent within 3% (error bars)

FN+2LS   ============   20%

VMC + 2LS   =========   70%

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Lanczos method for continuous models?

Unfortunately for the first Lanczos step:

$$\frac{\langle \Psi_T | (1 + \alpha H) H (1 + \alpha H) | \Psi_T \rangle}{\langle \Psi_T | (1 + \alpha H)(1 + \alpha H) | \Psi_T \rangle}$$

and $\quad \langle \Psi_T | H^3 | \Psi \rangle \rightarrow +\infty \Rightarrow \alpha \rightarrow 0$

Only a statistical method known with $e^{-\Delta t H}$
Caffarel & Ceperley … or
''backflow wavefunctions'' (poor scaling)

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Projected BCS wave function on triangular lattice

$$\left|\text{P-BCS}\right\rangle = \widehat{P}_{\text{G}}\left|\text{BCS}\right\rangle \quad : \text{projected BCS state}$$

$$\left|\text{BCS}\right\rangle = \left[\sum_{\vec{k}} f_{\vec{k}}\, C^{\dagger}_{\vec{k},\uparrow} C^{\dagger}_{-\vec{k},\downarrow}\right]^{L/2} \left|0\right\rangle \quad : \text{ground state of BCS Hamiltonian}$$

$$H_{\text{BCS}} = -t \sum_{\langle \vec{r},\vec{r}'\rangle,\sigma} \left(C^{\dagger}_{\vec{r},\sigma} C_{\vec{r},\sigma} + \text{h.c.}\right) - \boxed{\mu} \sum_{\vec{r},\sigma} C^{\dagger}_{\vec{r},\sigma} C_{\vec{r},\sigma}$$

$$+ \sum_{\vec{r}=1}^{L}\left[\sum_{\vec{l}} \boxed{\Delta_{\vec{l}}}\left(C^{\dagger}_{\vec{r},\uparrow} C^{\dagger}_{\vec{r}+\vec{l},\downarrow} - C^{\dagger}_{\vec{r},\downarrow} C^{\dagger}_{\vec{r}+\vec{l},\uparrow}\right) + \text{h.c.}\right]$$

$$f_{\vec{k}} = \Delta_{\vec{k}} \Big/ \left[\left(\varepsilon_{\vec{k}} - \mu\right) + \sqrt{\left(\varepsilon_{\vec{k}} - \mu\right)^2 + \Delta_{\vec{k}}^2}\right] \propto \Delta_{\vec{k}} \quad \left(\mu \to -\infty\right)$$

$$\left|\text{BCS}\right\rangle \propto \sum_{\vec{r}}\left[\sum_{\vec{l}} \Delta_{\vec{l}}\left(C^{\dagger}_{\vec{r},\uparrow} C^{\dagger}_{\vec{r}+\vec{l},\downarrow} - C^{\dagger}_{\vec{r},\downarrow} C^{\dagger}_{\vec{r}+\vec{l},\uparrow}\right)\right]^{L/2} \left|0\right\rangle$$

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➤ **Marshall sign rule**

$$\widehat{H} = \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

$J_{ij} \geq 0$: if i and j on the same sub-lattice
$J_{ij} \leq 0$: if i and j on the different sub-lattice

$$|x\rangle = \prod_i |m_i\rangle \quad \text{: bases}$$

$$\begin{cases} \vec{S}_i^2 |m_i\rangle = s(s+1)|m_i\rangle \\ \widehat{S}_i^Z |m_i\rangle = m_i |m_i\rangle \end{cases}$$

$$\widehat{U}^\dagger = \exp\left[-i\pi \sum_{i\in B}\left(s + \widehat{S}_i^Z\right)\right]$$

$$\widetilde{H} \equiv \widehat{U}^\dagger \widehat{H}\widehat{U} = \widehat{H}_{dig} + \widehat{H}_{off}$$

$$\widehat{H}_{dig} = \sum_{i,j} J_{ij} \widehat{S}_i^Z \cdot \widehat{S}_j^Z$$

$$\widehat{H}_{off} = -\frac{1}{2}\sum_{i,j}|J_{ij}|\left(\widehat{S}_i^+ \cdot \widehat{S}_j^- + \widehat{S}_i^- \cdot \widehat{S}_j^+\right)$$

Ground state of $\widetilde{H}$: $\left|\widetilde{\Psi}_0^{(M)}\right\rangle = \sum_x f_x |x\rangle \text{ with } f_x > 0$ ⟹ k=0 A₁

$$\left|\Psi_0^{(M)}\right\rangle = \widehat{U}^\dagger \left|\widetilde{\Psi}_0^{(M)}\right\rangle = \sum_x (-1)^{N(x)} f_x |x\rangle$$

: Marshall sign rule

$$N(x) = \sum_{i\in B}(s + m_i)$$

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➤ Fixed node approximation

✓ Effective Hamiltonian with no negative sign problem

$$\overline{H}^{\text{eff}}_{x'x} = \begin{cases} \overline{H}_{x'x} & \text{if } \overline{H}_{x'x} < 0 \text{ and } |x'\rangle \neq |x\rangle \\ -\gamma \overline{H}_{x'x} & \text{if } \overline{H}_{x'x} > 0 \text{ and } |x'\rangle \neq |x\rangle \\ \overline{H}_{xx} + (1+\gamma)v_{\text{sf}}(x) & \text{if } |x'\rangle = |x\rangle \end{cases}$$

$$\overline{H}_{x'x} \equiv \Psi_{\text{G}}(x')H_{x'x}/\Psi_{\text{G}}(x) \qquad \gamma : \text{positive constant}$$

$|x\rangle$: spin configurations $\quad H_{x'x} \equiv \langle x'|\widehat{H}|x\rangle$: matrix elements

$\Psi_{\text{G}}(x) \equiv \langle x|\Psi_{\text{G}}\rangle$: variational (guiding) wave function

✓ A standard Green function MC for effective Hamiltonian

$$\langle x|\left(\overline{G}^{\text{eff}}\right)^n|\varphi_{\text{init}}\rangle \xrightarrow{n \to \infty} \Psi_{\text{G}}(x)\Phi_0^{\text{eff}}(x)$$

$|\Phi_0^{\text{eff}}\rangle$: ground state of H^{eff}

$$\overline{G}^{\text{eff}}_{x'x} = \Lambda\delta_{x'x} - \overline{H}^{\text{eff}}_{x'x}$$

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➢ <u>Fixed node approximation</u> (II)

1. $\Phi_0^{\text{eff}}(x)$ same phase as $\Psi_G(x)$

2. $\Phi_0^{\text{eff}}(x)$ variational state for $\widehat{H}$ better than $\Psi_G(x)$

$$\langle \Psi_G | \widehat{H} | \Psi_G \rangle \geq E_0^{\text{eff}} \geq \langle \Phi_0^{\text{eff}} | \widehat{H} | \Phi_0^{\text{eff}} \rangle \geq E_0$$

$$\widehat{H}^{\text{eff}} | \Phi_0^{\text{eff}} \rangle = E_0^{\text{eff}} | \Phi_0^{\text{eff}} \rangle$$

$$\widehat{H} | \Phi_0 \rangle = E_0 | \Phi_0 \rangle$$

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➢ 1D limit (J'=0)

- ✓ Projected BCS wave function: $\left|\text{P-BCS}\right\rangle = \widehat{P_{\text{G}}}\left|\text{BCS}\right\rangle$
- ✓ |BCS>: ground state of BCS Hamiltonian

$$H_{\text{BCS}} = -t \sum_{\langle i,j\rangle,\sigma}\left(C^{\dagger}_{i,\sigma}C_{j,\sigma} + \text{h.c.}\right)$$

$$+ \sum_{i=1}^{L}\left[\sum_{l}\Delta_{l}\left(C^{\dagger}_{i,\uparrow}C^{\dagger}_{i+l,\downarrow} - C^{\dagger}_{i,\downarrow}C^{\dagger}_{i+l,\uparrow}\right) + \text{h.c.}\right]$$

- ✓ Δ_{l} up to 3rd neighbors, $l \leq 3$
- ✓ Ground state properties well described (Gros et.al.)
- ✓ Low-lying excited states (spinon): $\left|\text{k}\right\rangle = \widehat{P_{\text{G}}}\,\gamma^{\dagger}_{k,\uparrow}\left|\text{BCS}\right\rangle$

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Benzene molecule

TABLE IV: Binding energies in eV obtained by variational (Δ_{VMC}) and diffusion (Δ_{DMC}) Monte Carlo calculations with different trial wave functions for benzene. In order to calculate the binding energies yielded by the 2-body Jastrow we used the atomic energies reported in Ref. 10. The percentages ($\Delta_{VMC}(\%)$ and $\Delta_{DMC}(\%)$) of the total binding energies are also reported.

	Δ_{VMC}	$\Delta_{VMC}(\%)$	Δ_{DMC}	$\Delta_{DMC}(\%)$
Kekule + 2body	−30.57(5)	51.60(8)	−	−
resonating Kekule + 2body	−32.78(5)	55.33(8)	−	−
resonating Dewar Kekule + 2body	−34.75(5)	58.66(8)	−56.84(11)	95.95(18)
Kekule + 3body	−49.20(4)	83.05(7)	−55.54(10)	93.75(17)
resonating Kekule + 3body	−51.33(4)	86.65(7)	−57.25(9)	96.64(15)
resonating Dewar Kekule + 3body	−52.53(4)	88.67(7)	−58.41(8)	98.60(13)
full resonating + 3body	−52.65(4)	88.869(7)	−58.30(8)	98.40(13)

Jastrow+AGP changes the nodes!

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The Cooper problem in an insulator

$$F_R = \langle N - 2 | c_{i\uparrow} c_{i+R\downarrow} + c_{i+R\uparrow} c_{i\downarrow} | N \rangle$$

242 sites U/t=4

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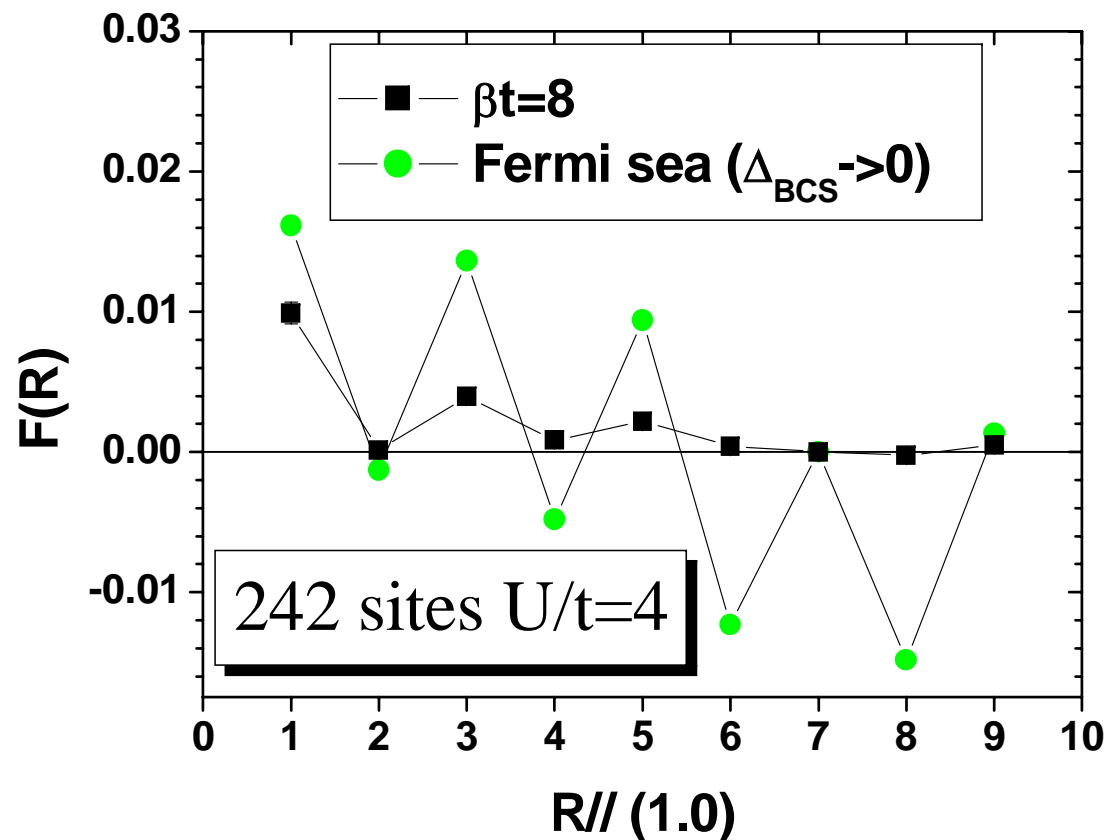
Definition of RVB insulator: pairing strenght

$$Z_c = |F(\text{shortest distance})| / \sqrt{\sum_{\text{all distances}} F_R^2}$$

Legend:
- - - - $\Delta = 0$ (metal)
- ■ $\Delta_{AF} = 0.1$ (band insulator)
- —— $\Delta = 0.05$ (superconductor)
- ●   **Projected**   **(RVB insulator)**

Y-axis: Z_c (pairing strength)

X-axis: 1/l (side length in a lxl cluster)
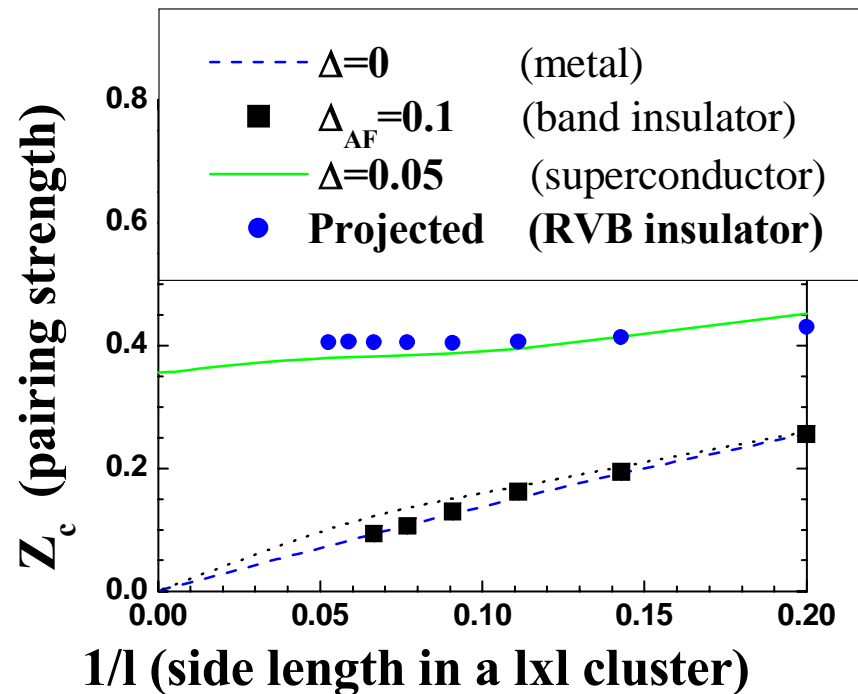
1) The anomalous averages F vanish for all R in all insulators (no supercond.)
2) The pairing strength is finite in the RVB state obtained by projecting out doubly occupied sites in a BCS wf.

Qualitative new physics from strong correlation

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Recent results on the Hubbard model:

E. Plehanov, F. Becca and S.S. cond-mat/0404206

Exact results ($\tau \to \infty$) from auxiliary fields
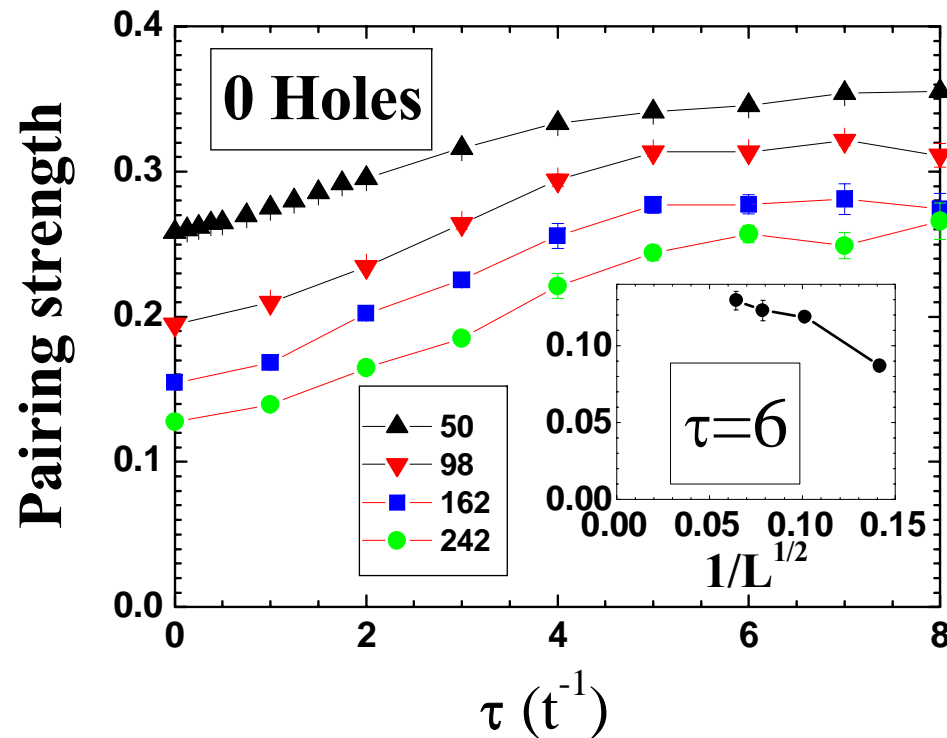
Even in the antiferromagnetic phase
the insulator is highly non trivial (RVB)

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The Berry phase R. Resta and S. Sorella, Phys. Rev. Lett. (1999)

It is possible to discriminate between a metal and an insulator by a direct inspection of the ground state

Difference in the electron organization W. Khon, Phys. Rev. (1964)

- Metal: delocalized states

- Insulator: localized states

$$Z_c = \langle \Psi | e^{\frac{2\pi i}{L} \sum_j j\, n_j} | \Psi \rangle / \langle \Psi | \Psi \rangle$$

$|Z_c| = 1$ if the system is localized, i.e., insulating

$|Z_c| = 0$ if the system is delocalized, i.e., metallic

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A Jastrow long range correlation (GWF+J) can drive a metallic Fermi sea to a Mott insulator!!
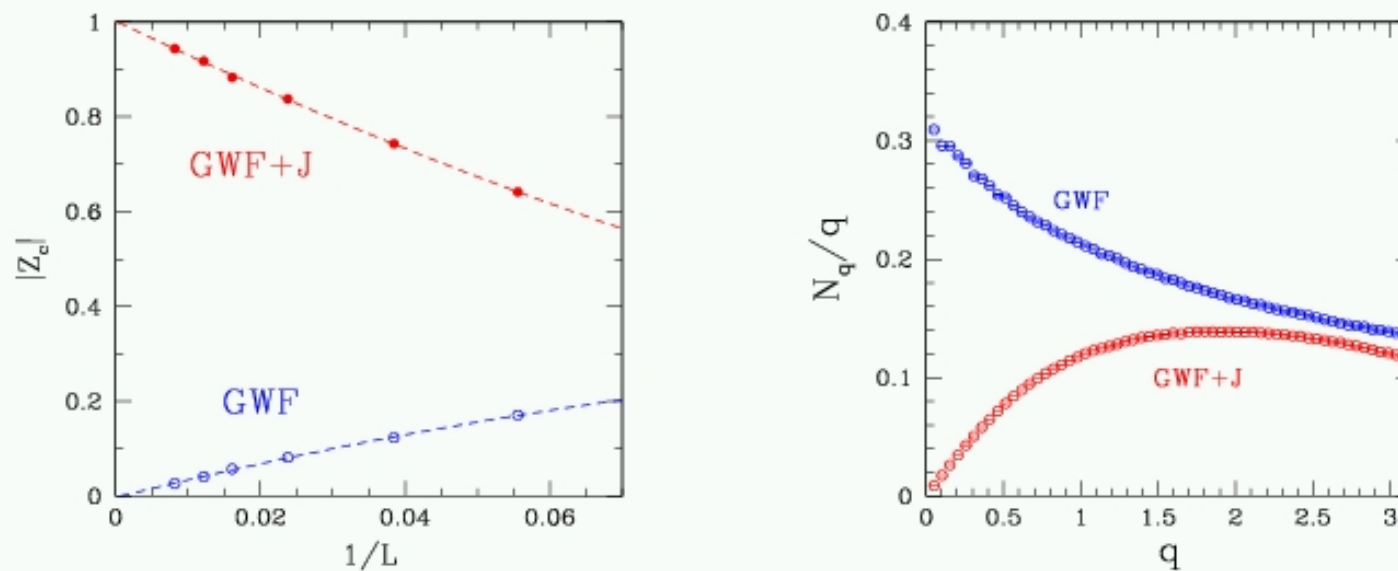
The GWF+J describes an insulator

- $|Z_c| \rightarrow 1$ in the thermodynamic limit
- $N(q) \sim q^2$

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➤ Projected BCS WF on triangular lattice
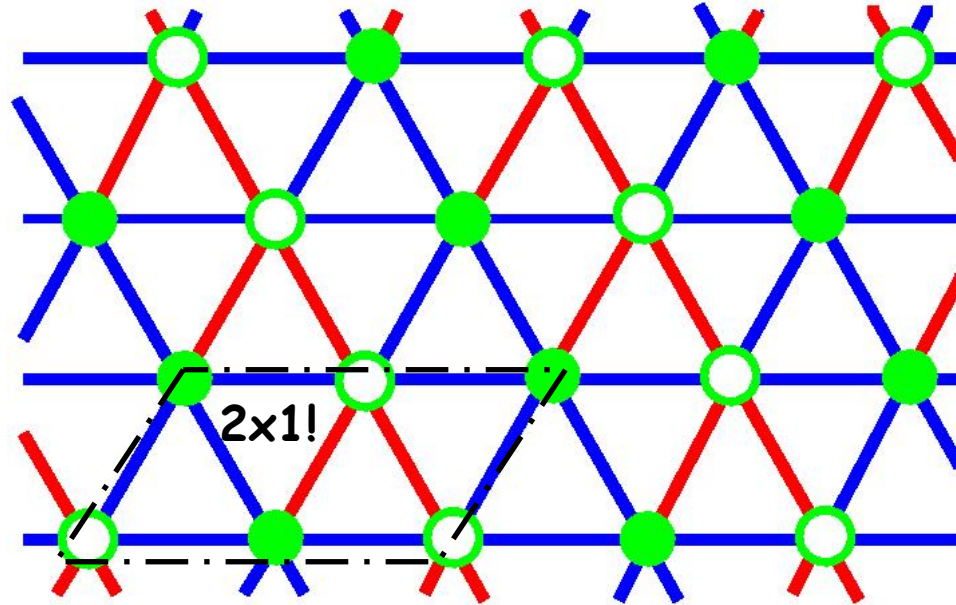
(P.Fendley,et al., PRB **66**,214513 ('02))

____ : positive $\Delta_{i,j}$

____ : negative $\Delta_{i,j}$

2x1!

The wave function is translation invariant after projection!

$$\exp(-1/2\sum_{i,j} v_{i,j}\ S_i^z S_j^z)P\big|\Delta_{BCS}\big\rangle$$

$v_{i,j}$

- short-range spin Jastrow factors (up to 4-th nearest neighbors)

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➢ Projected BCS WF on triangular lattice

(P.Fendley,et al., PRB **66**,214513 ('02))

2x1!
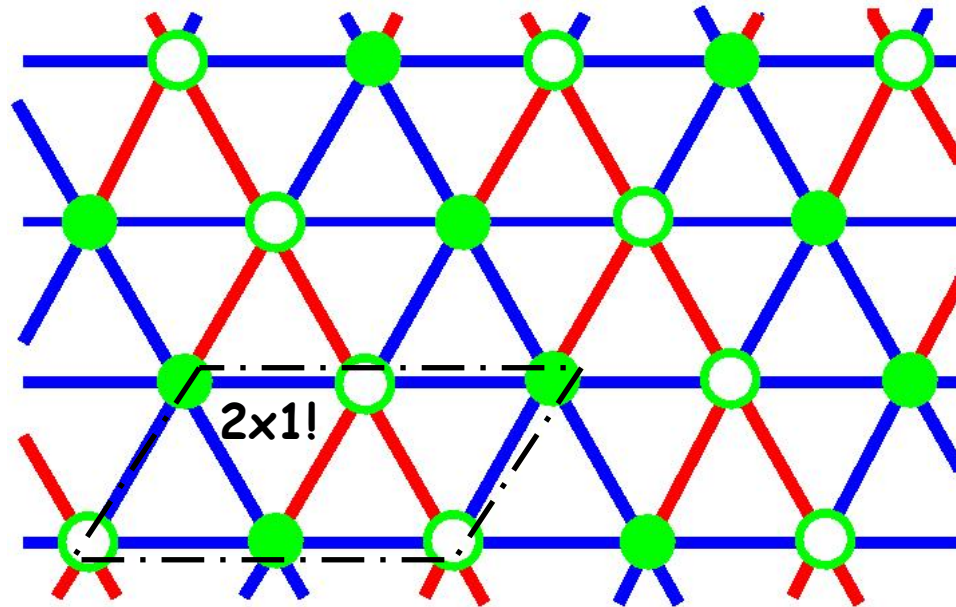
—— : positive

—— : negative

$\Delta_{i,j}$

The wave function is translation invariant after projection!

According to Wen (PRB'02) the physical translation can be recovered after a gauge transformation:

$$c^{+}_{R,\sigma} \rightarrow (-1)^{y} c^{+}_{R,\sigma} \quad R = (x, y)$$

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$$\left|\psi_0\right\rangle = P\exp\left(\sum_{i,j} f_{i,j} c^{+}_{i,\uparrow} c^{+}_{j,\downarrow}\right)\left|0\right\rangle \qquad f_{i,j} = f_{j,i}$$

$$H_{BCS} = \sum_{k,\sigma} \varepsilon_k \, c^{+}_{k,\sigma} c_{k,\sigma} + \sum_{i,j} \Delta_{i,j} c^{+}_{i,\uparrow} c^{+}_{j,\uparrow} + \text{h.c.}$$

$$\varepsilon_k = -2\cos(k_x) - \mu$$

for $\mu \to -\infty$

the corresponding pairing function:

$$f_{i,j} \approx \Delta_{i,j} / \left|\mu\right|$$

The signs of f are such to cancel the fermion sign
(the permutation of the pfaffian) and the short range RVB
is obtained, i.e. the spin liquid wf of the QDM!

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Comparison of variational energy (J'/J=1.0)
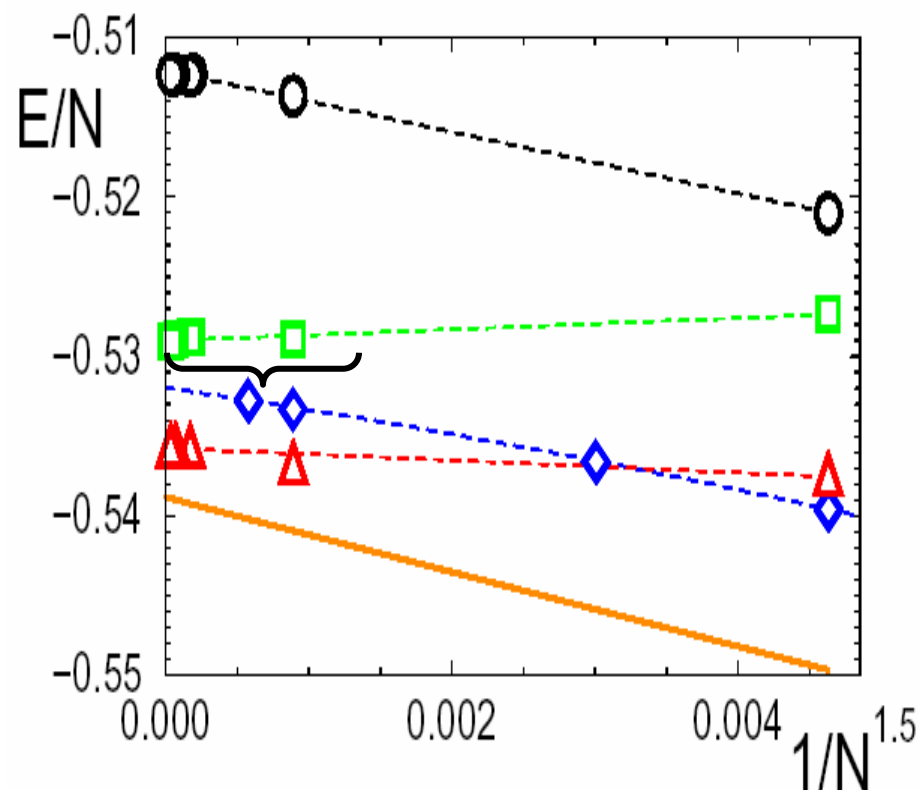
□ Variational energy in the thermodynamic limit

short range RVB	-0.51219(5)
Long range RVB with $\mu = 0$	-0.52892(4)
Neel ordered [1]	-0.53191(9)
Present (gapped)	-0.53563(4)

[1] Huse & Elser, PRL **60**, 2531 ('88)
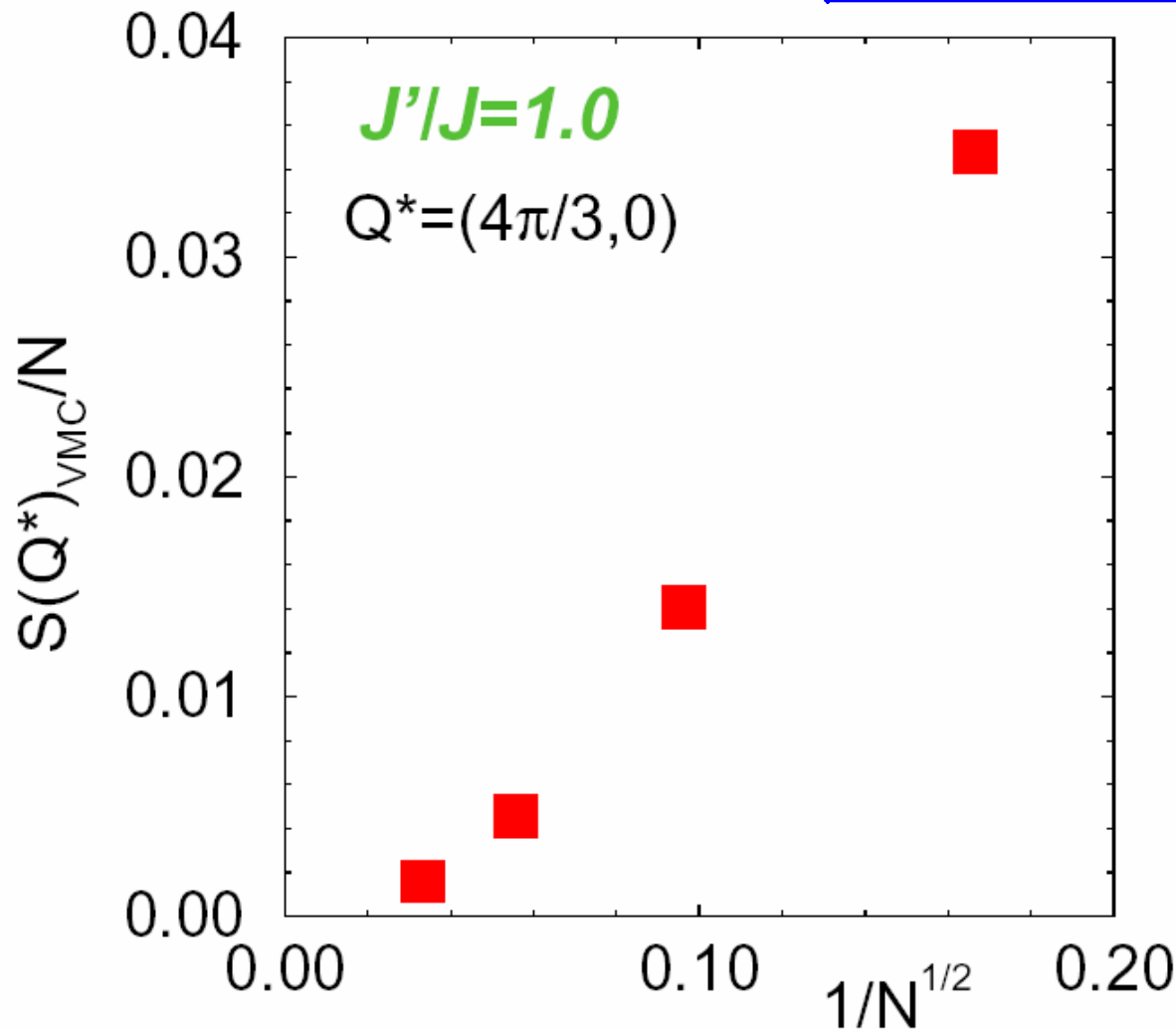
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> ## Property of the wave function

- Spin structure factor: $S(\mathbf{q}) = \sum_{\mathbf{l}} e^{i\mathbf{q}\cdot\mathbf{l}} \langle S_z(\mathbf{r}) S_z(\mathbf{r}+\mathbf{l}) \rangle$

Short-ranged spin Jastrow factor is not enough to induce magnetic ordering

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➤ Isotropic triangular lattice with J'/J=1.0

$J'/J=1.0$

$C_1(l)$

0.04

0.00

−0.04

□ : VMC

● : GFMC

τ_1-direction

0   5   10
l

J

J J J

$\vec{\tau}_2$

$\vec{\tau}_1$

✓ **Green function Monte Carlo**
✓ Spin correlation function:

$$C_i(l) = \langle S_z(\vec{r}) S_z(\vec{r} + l\vec{\tau}_i) \rangle$$

✓ Spin liquid state unstable toward classical Neel state

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Spin structure factor for J'/J=1.0

$J'/J=1.0$

$Q^*=(4\pi/3,0)$

30x30 ?

18x18

108

6x6

$(S(Q^*)_{FN}-S(Q^*)_{VMC})/N$

$1/N^{1/2}$
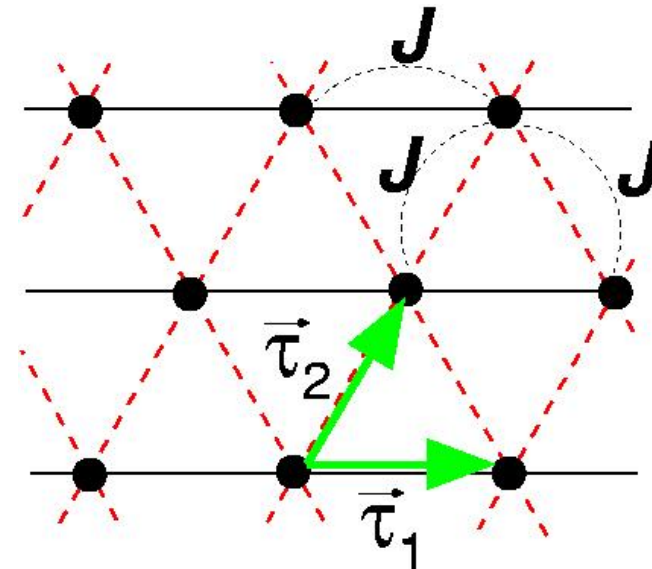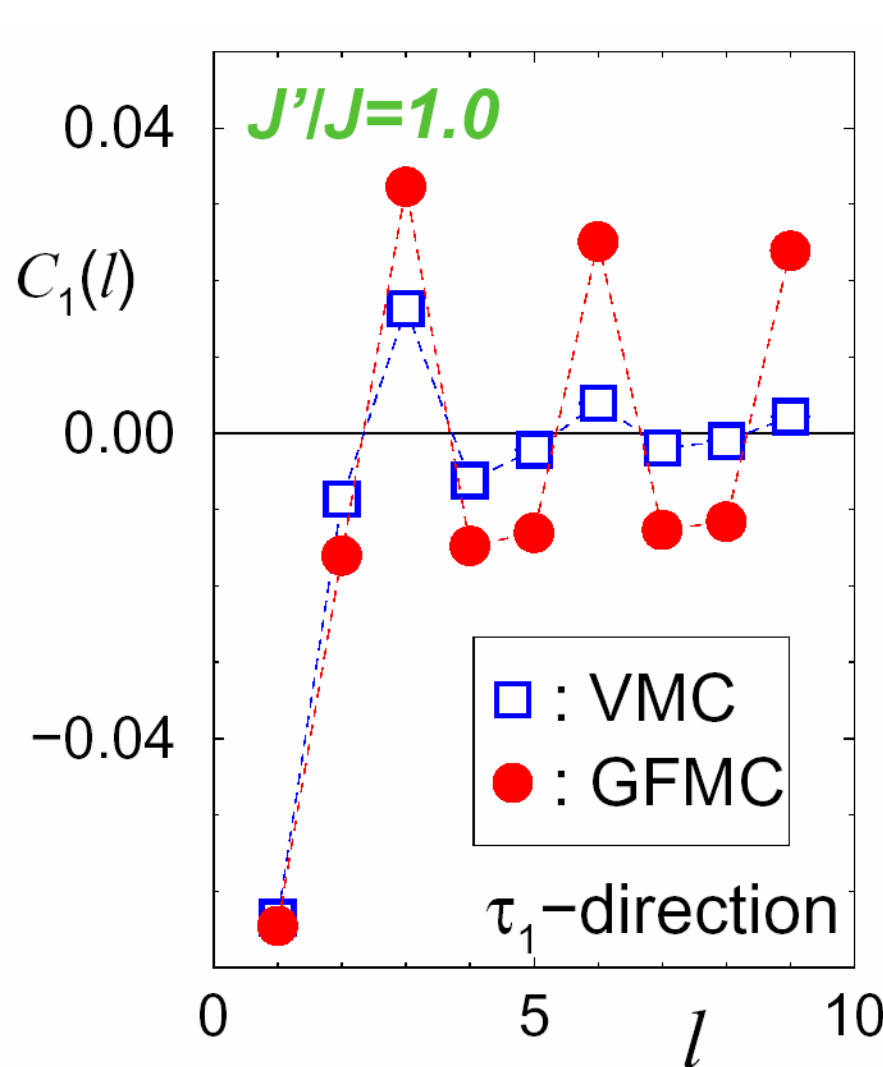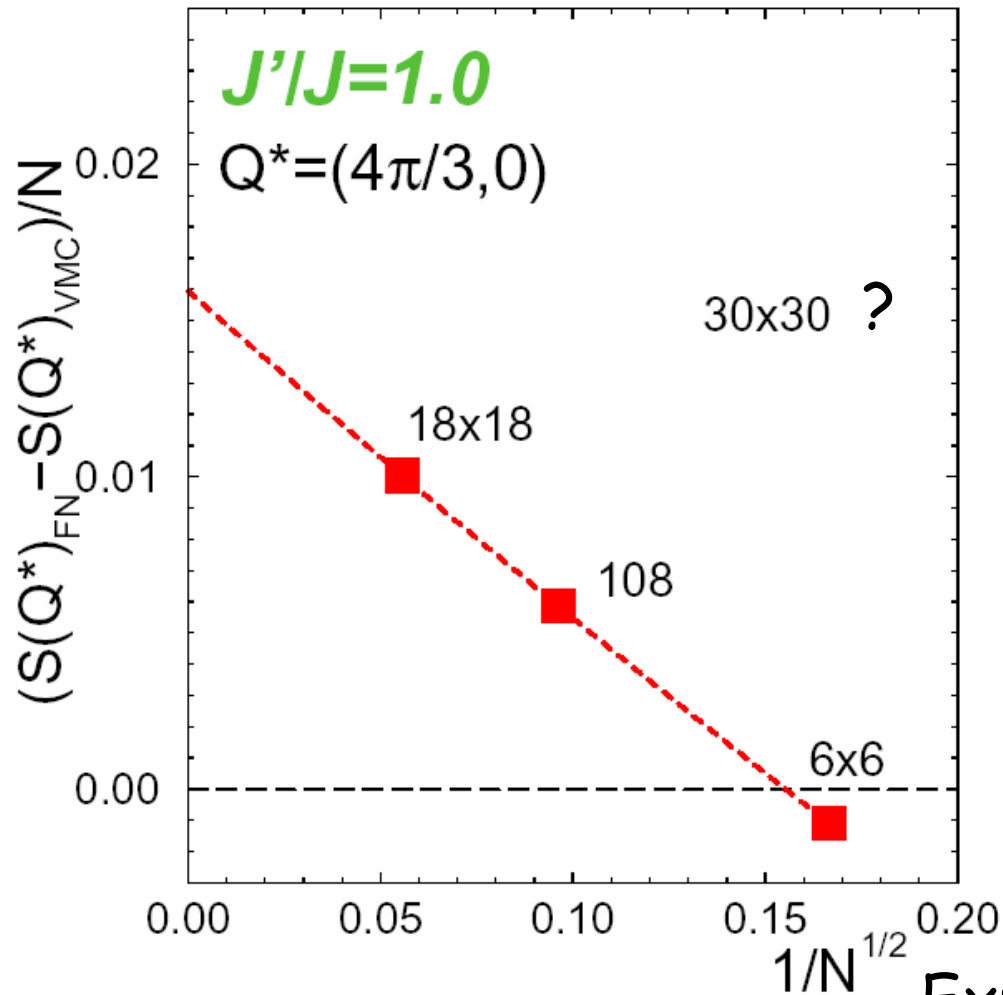
Order parameter:

$$m/m_{max} = 0.351 \pm 0.003$$

✓ Starting from a spin liquid
✓ a reasonable lower bound

FN (Neel) [1]	0.529??
Linear spin wave	0.4773(1)
Stochastic reconfiguration [1]	0.41(2)

Exp. ~0.45 (organic) at J'/J=1.8

[1] Capriotti, Trumper, SS, PRL **82**, 3899 ('99)

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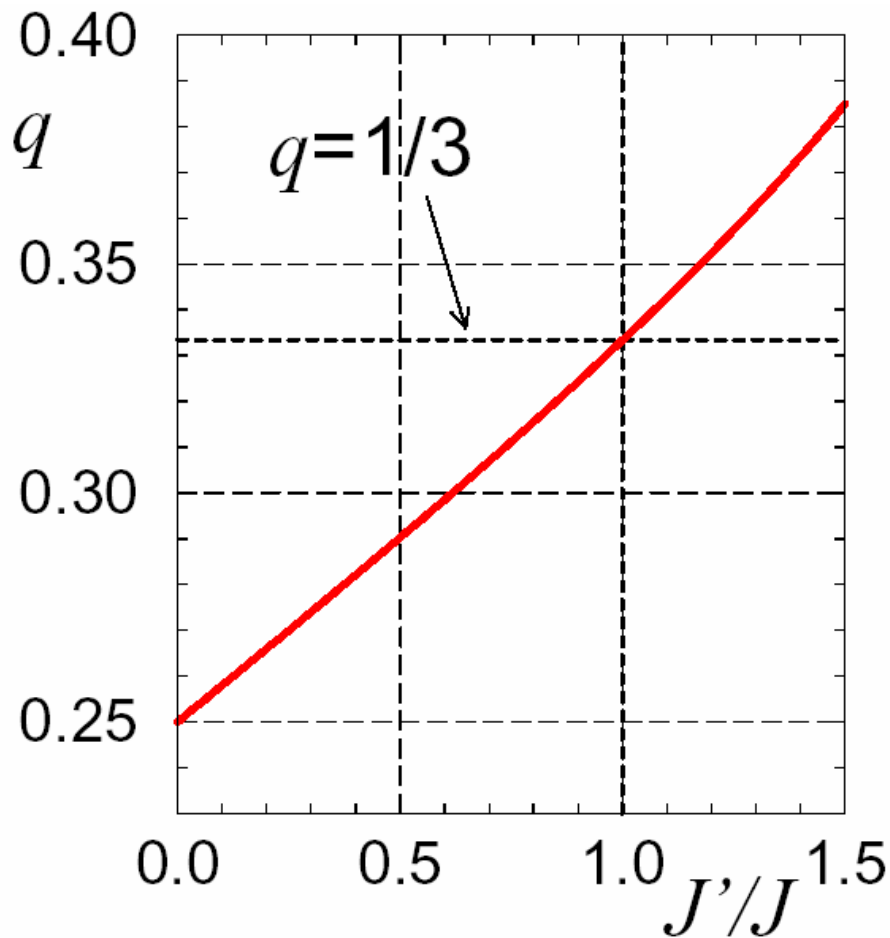
$$H = \sum_{\vec{q}} J(q)\, \vec{S}_{\vec{q}} \cdot \vec{S}_{-\vec{q}}$$

Find $\vec{Q}$ where $\dfrac{\partial J(\vec{q})}{\partial q_i} = 0$

$$\boxed{\vec{Q} = 4\pi q\,(1,0)}$$

where $\cos(2\pi q) = -J'/2J$
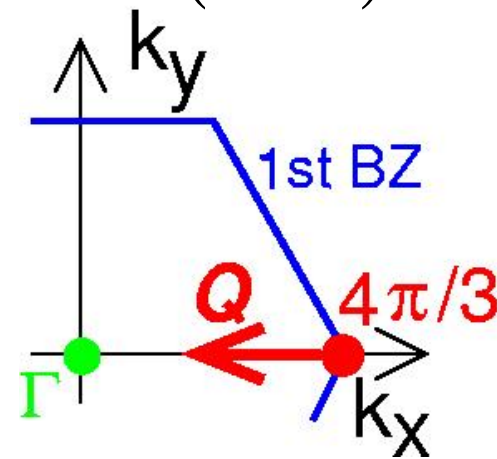
Spin configuration: $\boxed{\vec{S}(\vec{r}) = S\big(\sin \vec{Q}\cdot\vec{r},\, \cos\vec{Q}\cdot\vec{r},\, 0\big)}$

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Spin structure factor for J'/J=0.7

✓ Incommensurate peaks at $Q^*=(q^*,0)$

No long range order

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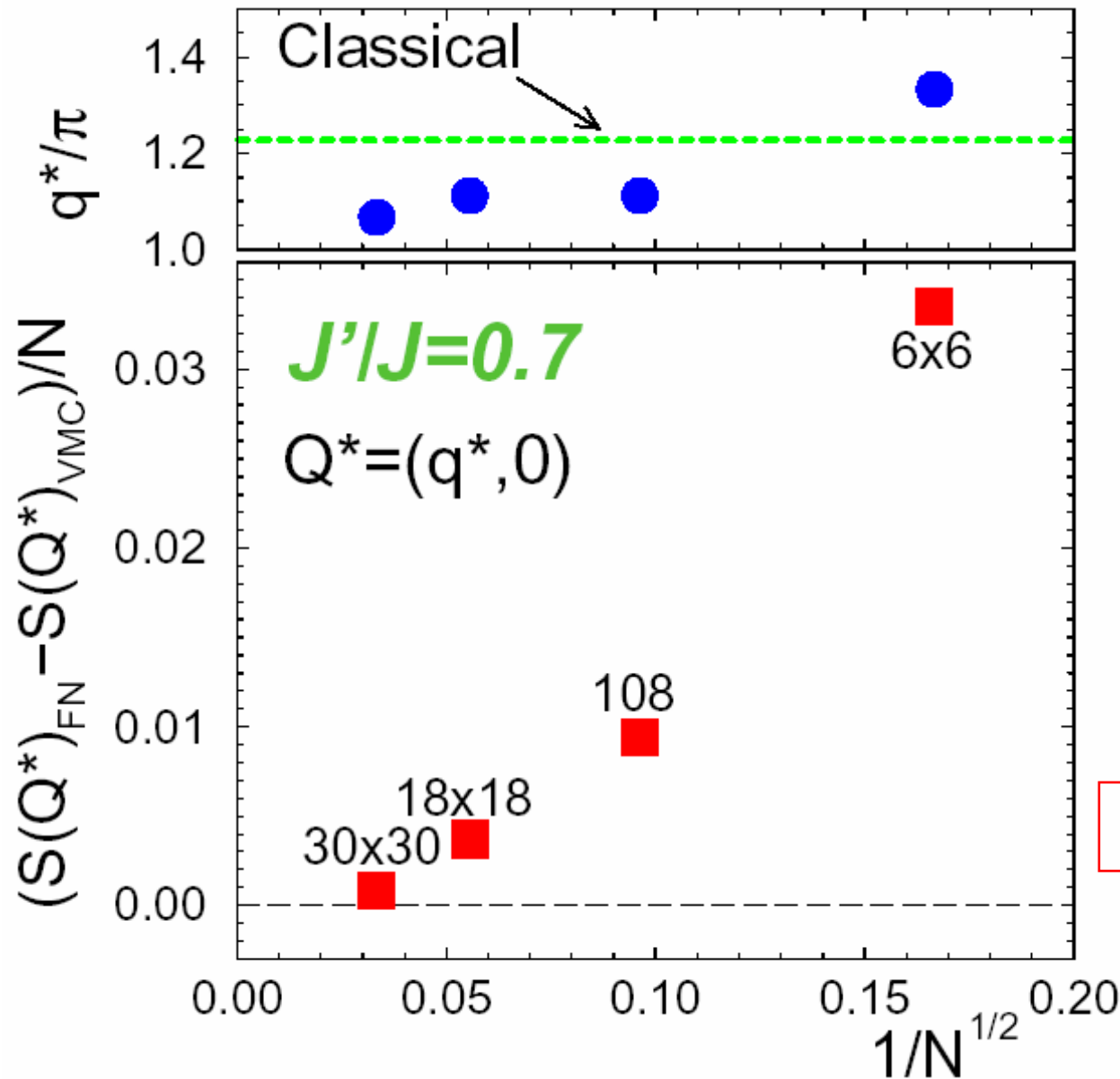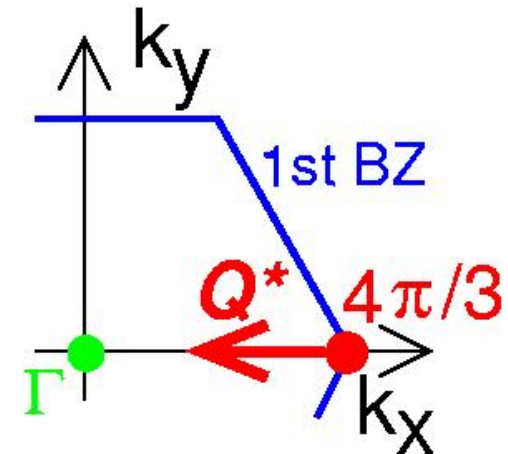
➤ "Boundary" of the two spin liquid states

● Variational and FN energies
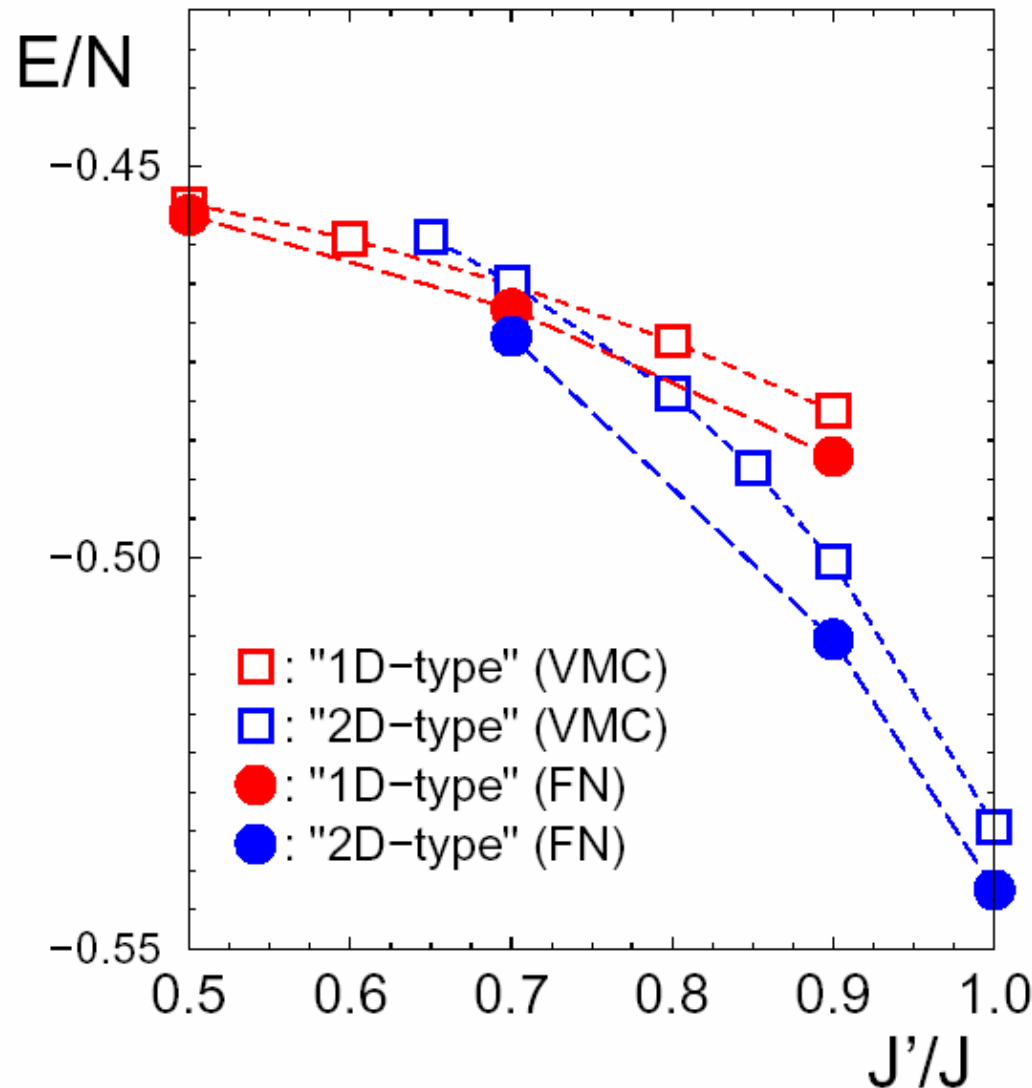
● Boundary is at about

$$J_C' / J \approx 0.6 - 0.7$$

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Dimer-dimer correlations for J'/J=0.7

$$D(l) = \left\langle S^z(\mathbf{r}) S^z(\mathbf{r+x}) \cdot S^z(\mathbf{r}+l\mathbf{x}) S^z(\mathbf{r+x}+l\mathbf{x}) \right\rangle - \left\langle S^z(\mathbf{r}) S^z(\mathbf{r+x}) \right\rangle^2$$

Spin liquid is stable

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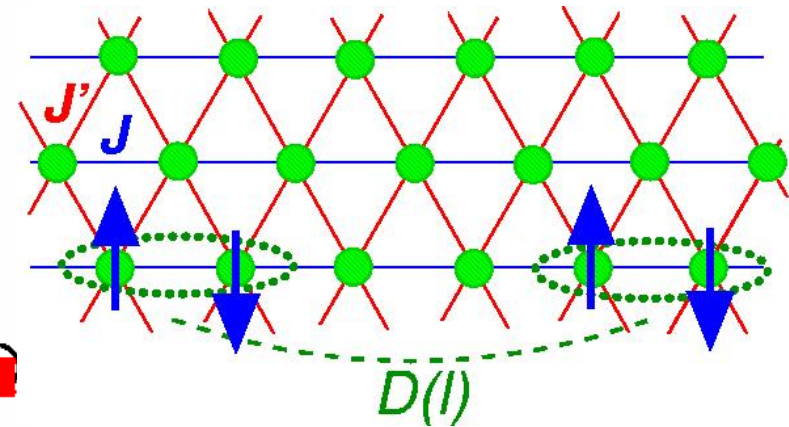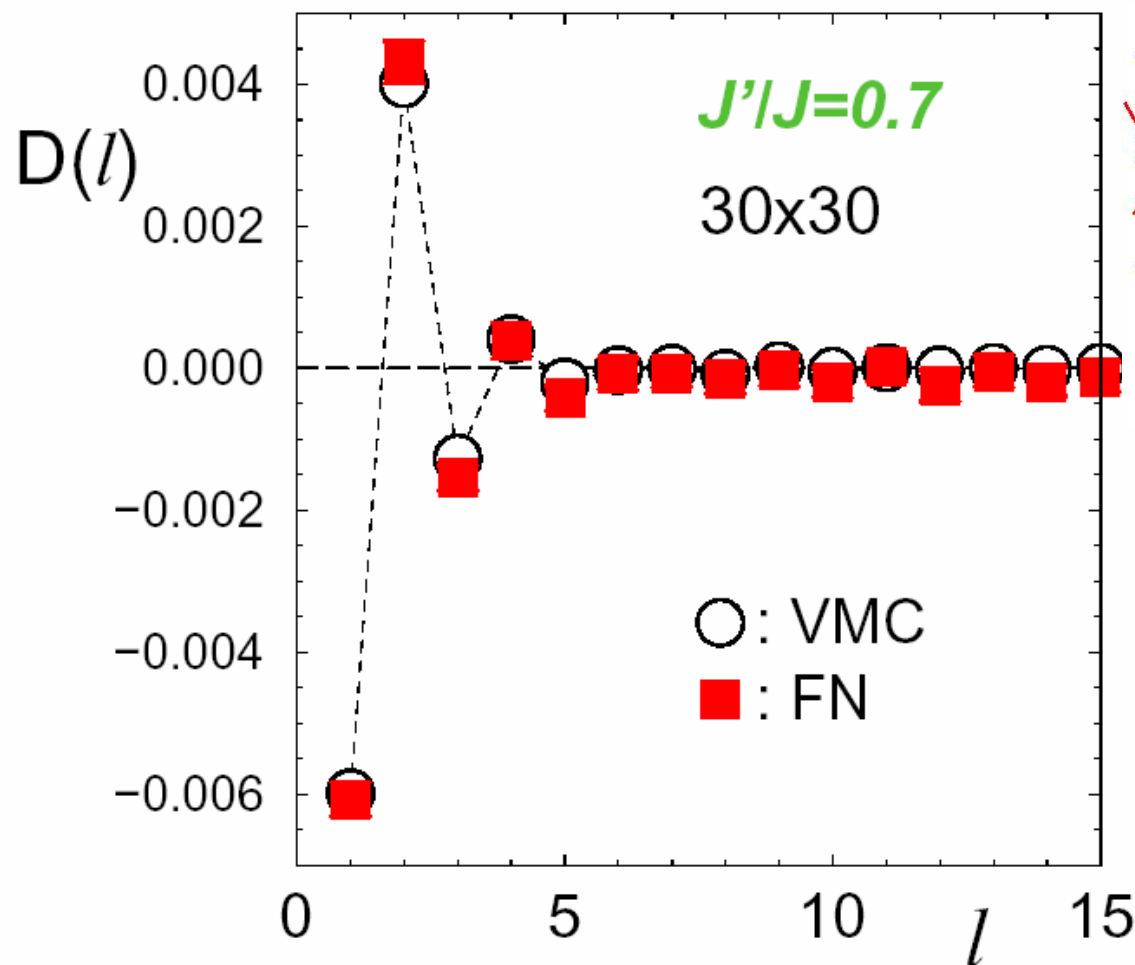
Numerical methods for 2D t-J model

I) Lanczos: Given a good ansatz $\left| RVB \right\rangle$

p Lanczos steps→
Minimize the energy in the Krilov basis:

$$\left| p \right\rangle = (1 + \alpha_1 H + ... + \alpha_p H^p) \left| RVB \right\rangle$$

II) FN (fixed node): minimize the energy
with the same nodes of |p>→ Exact for p>>1

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What about the RVB when doping ?
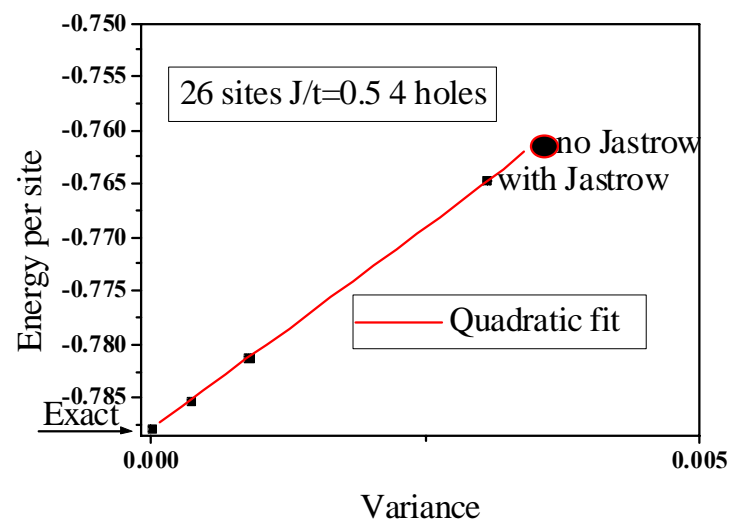
Hole-hole correlation function

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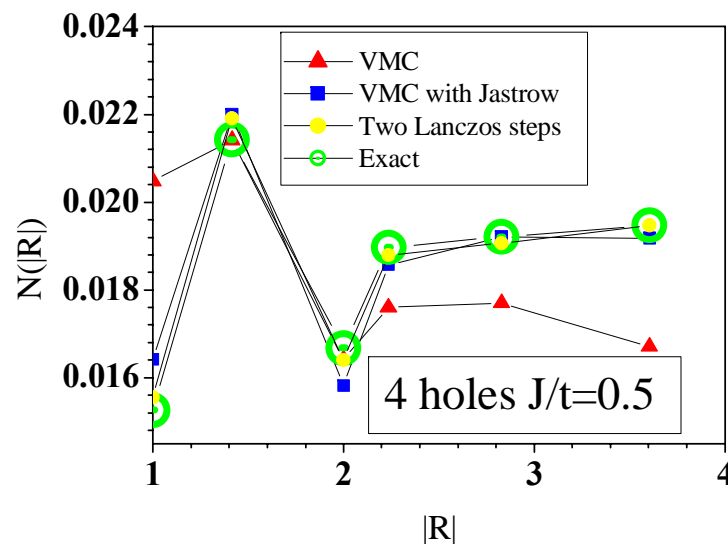
Pairing ?

$$\langle \psi_0 | \Delta_{i,j}^+ \, \Delta_{k,l} | \psi_0 \rangle$$

$$\Delta_{k,l} = c_{k\uparrow} \, c_{l\downarrow} + c_{l\uparrow} \, c_{k\downarrow}$$

26 sites 4 holes J/t=0.5

Legend:
- △ VMC
- □ = +1 LS
- ○ =+ 2 LS
- ● Extrapolated
- ○ Exact
- ▲ VMC no pairing

Pairing vs Distance

i   k
j   l

j   k   l
j

d-wave <0

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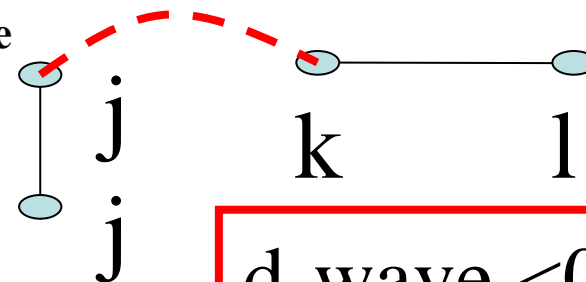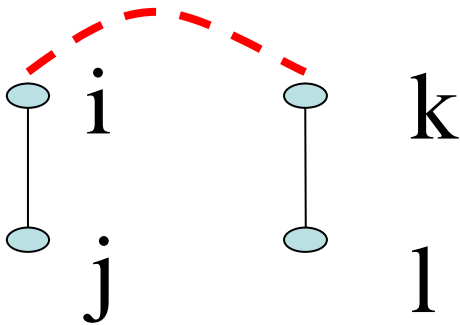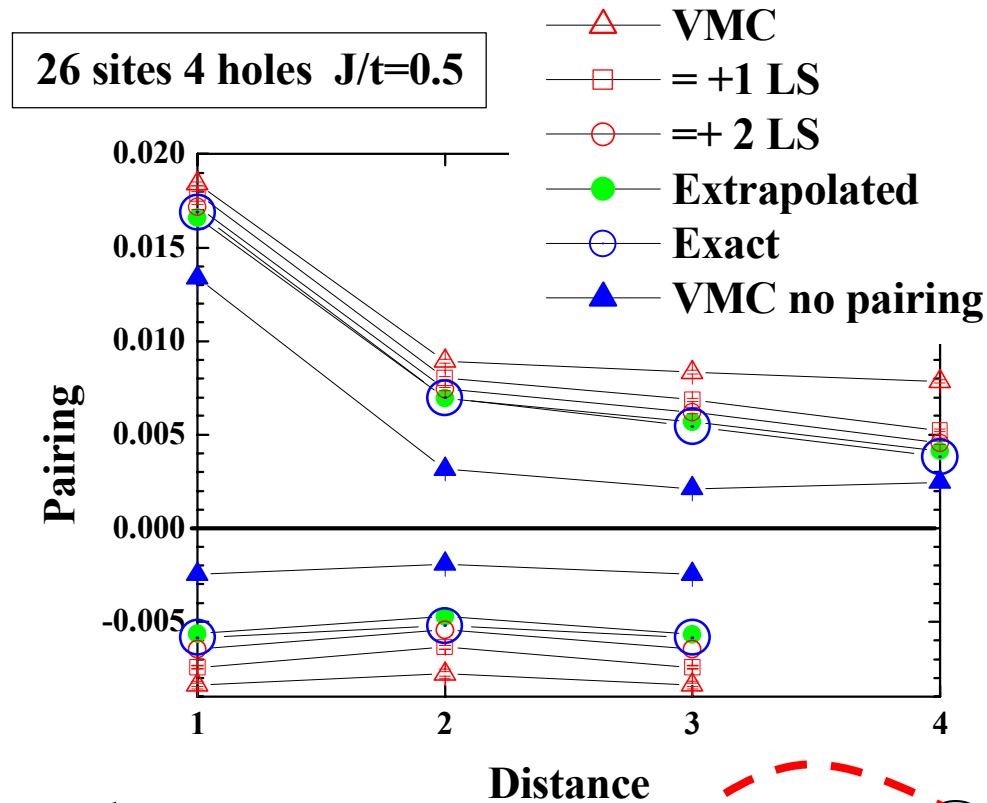
This reduction looks irrelevant

$$P_d = 2\sqrt{\left|\langle\psi_0|\Delta^+_{i,j}\,\Delta_{k,l}|\psi_0\rangle\right|}$$

at the   largest   distance
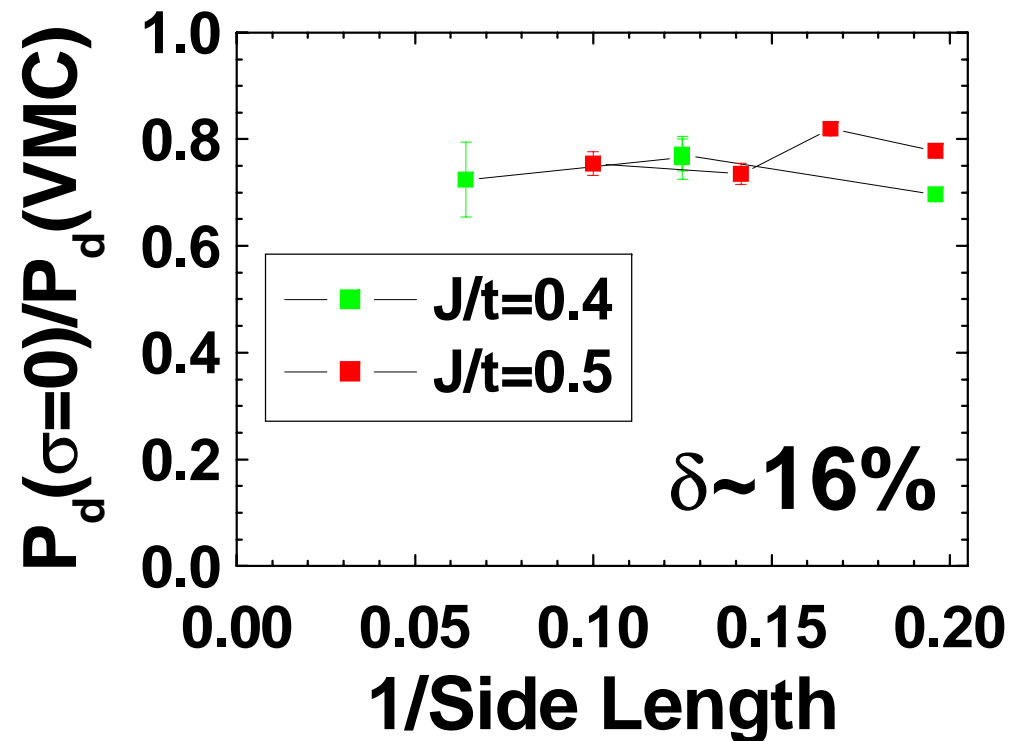
S. Sorella et al. PRL 2002

Superconductivity from strong correlation t-J model

$$P_d = 2 \sqrt{\left| \langle \psi_0 | \Delta_{i,j}^+ \, \Delta_{k,l} | \psi_0 \rangle \right|}$$

at the   largest   distance
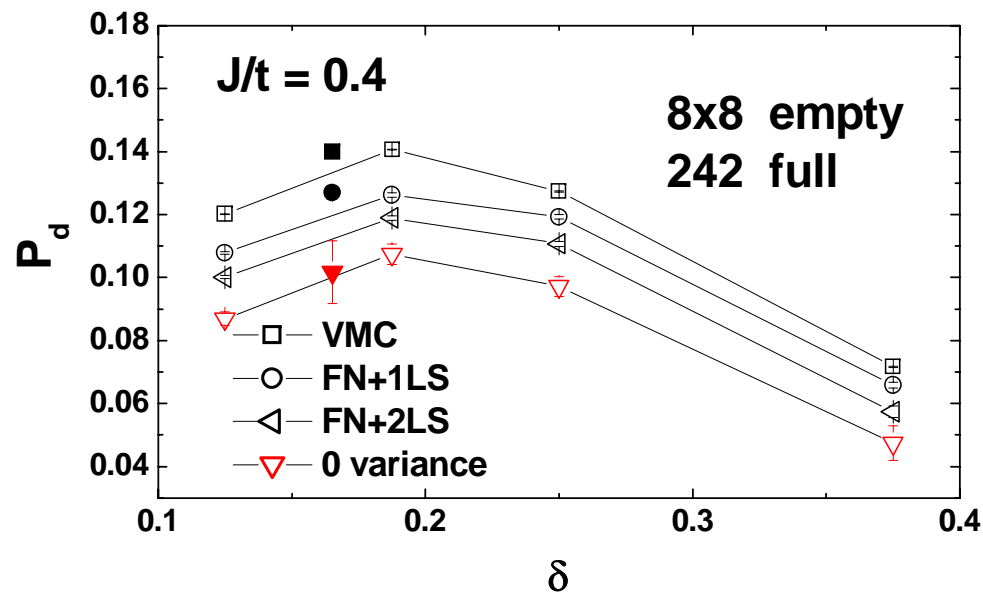
S. Sorella et al. PRL '02
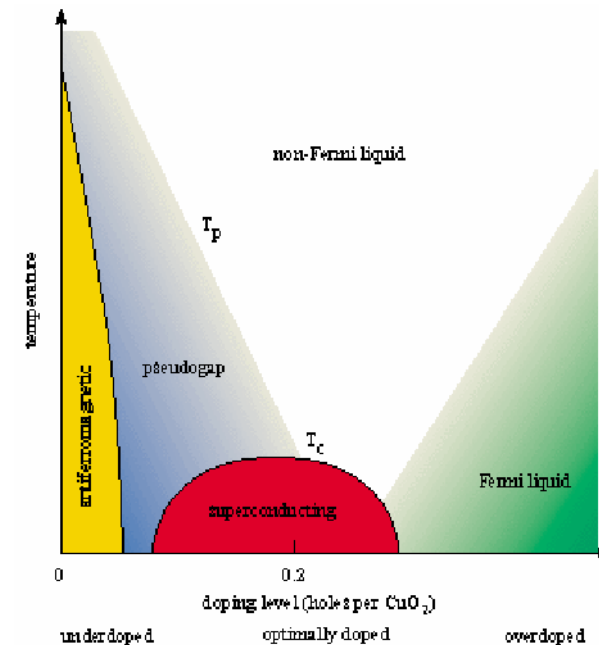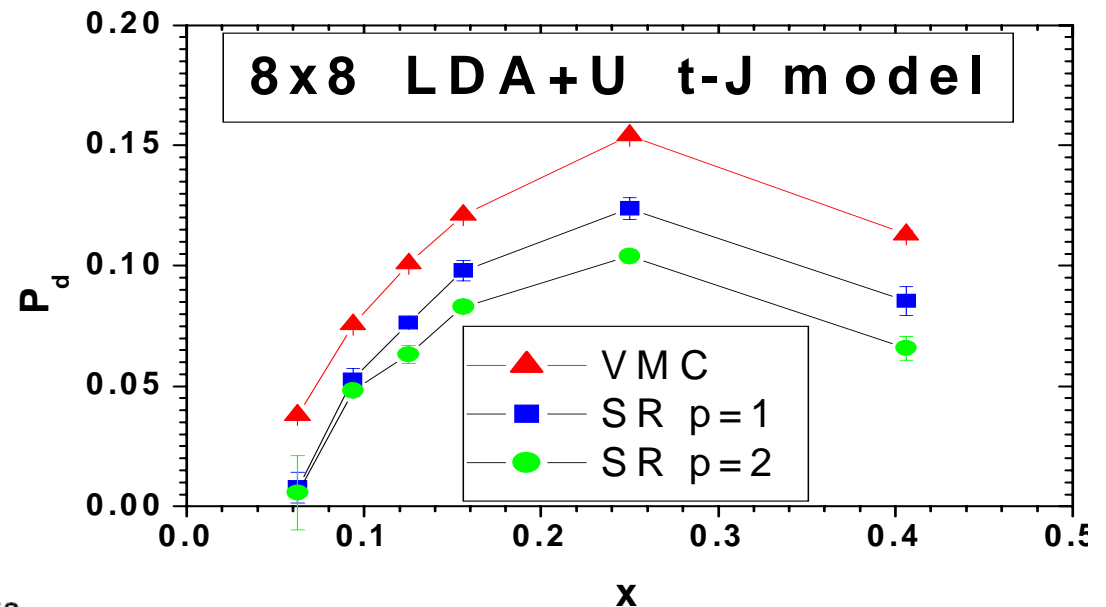
But t-J alone overestimate pairing at small δ

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The famous $La_{2-x}Sr_xCuO_4$
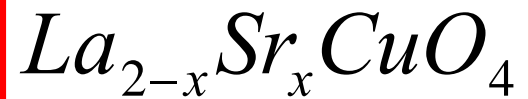
experiment   vs.   ab initio calculated t-t'-J…
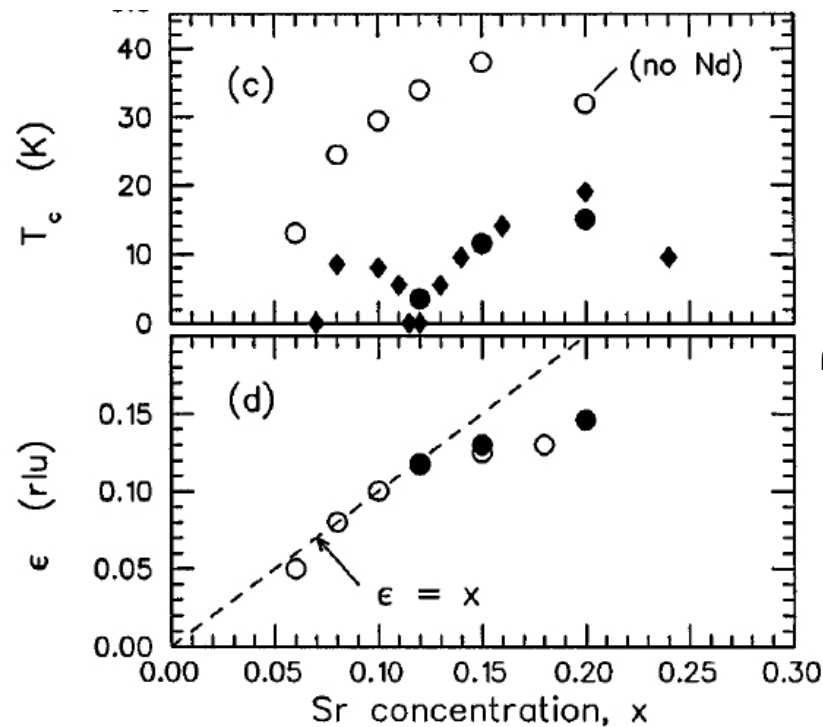
From Tranquada et al. PRL '97

V. Anisimov S.S. et al. PRB'02

In the right direction...

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The variational parameter :

$$\Delta_k = \Delta_{var}(\cos k_x - \cos k_y)$$

increases for x (doping)➔ 0
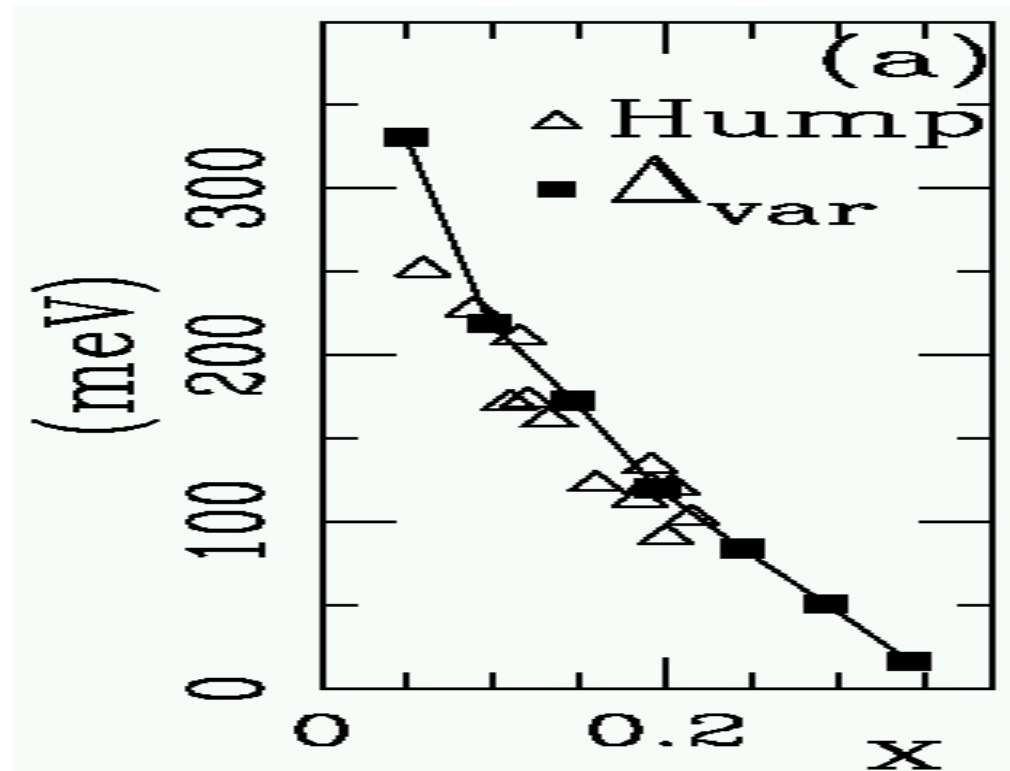
Thus explaining photoemission pseudogap

(Paramekanti, Randeria, Trivedi, PRL '01)

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Check on low dimensional systems where ''exact'' solution known

1 Chain J/t=0.4 8 holes

- VMC no Jastrow
- VMC |Anderson RVB> + Jastrow
- Exact (QMC)

2 Chain Ladder J/t=1 16 holes
The VMC |Anderson RVB> + **Jastrow** is "OK"

- Exact   (DMRG (m=500))
- VMC
- FN
- FN+1LS

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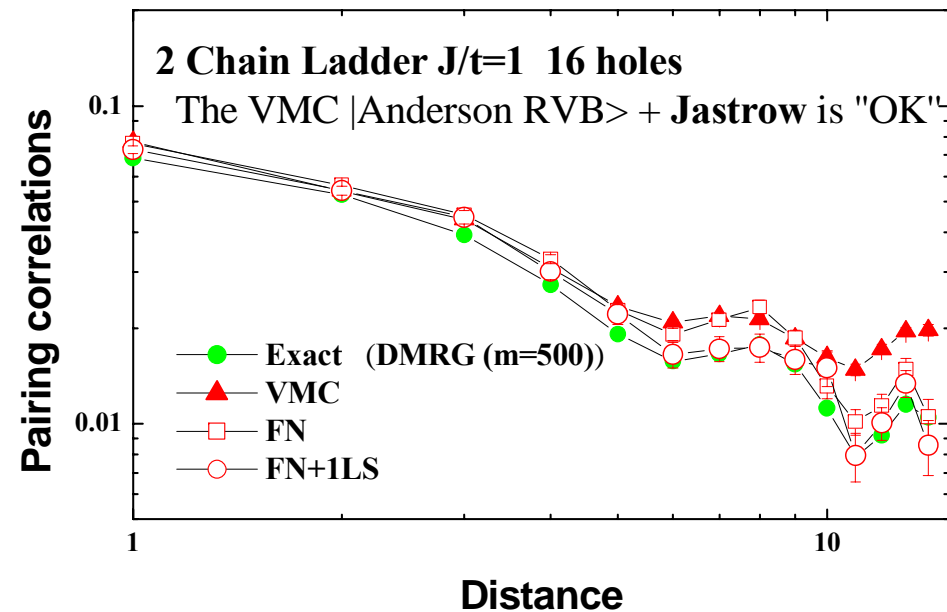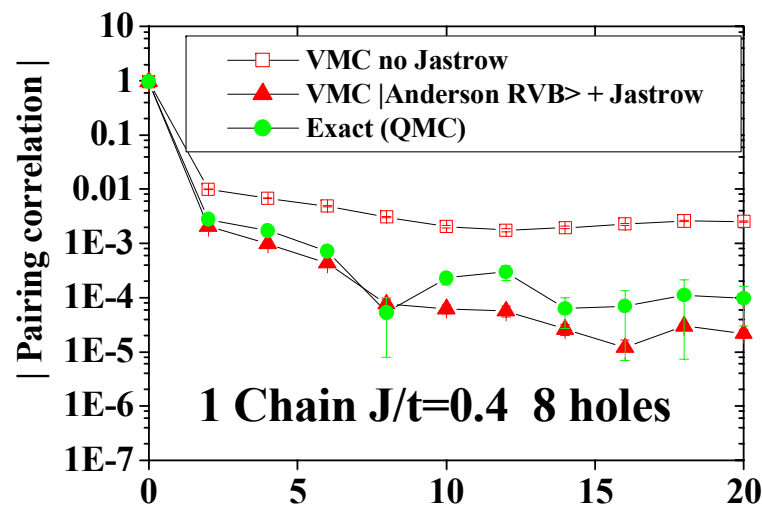
By QMC, the wavefunction can be sampled
Just like a Jastrow-Slater determinant, where:

$$\text{Jastrow} = \exp\left[\sum_{i<j} v(r_i, r_j)\right] \quad v(r,r) = -\infty \text{ (no double occupancy)}$$

If we have to use the Jastrow, it is just more
accurate to use the J+AGP

More correlation for free!!!

Natural question, is it enough AGP ? If so:
Everything with little more than GAUSSIAN

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RVB variational wavefunction for lattice models

$$\psi_{BCS} = \exp \sum_{i,j} f_{i,j} \underbrace{(c_{i,\uparrow}^+ c_{j,\downarrow}^+ + c_{j,\uparrow}^+ c_{i,\downarrow}^+)}_{\text{Singlet bond}} |0\rangle$$

$$f_k = \Delta_k \Big/ \left(\varepsilon_k + \sqrt{\varepsilon_k^2 + \Delta_k^2} \right)$$

where Δ_k is the BCS gap function

ε_k the free electron dispersion

$$P_N \, BCS = AGP = A \prod_{Pairs} f(r_{i\uparrow}, r_{i\downarrow})$$

General: $\varepsilon_k = $ Single particle dispersion

→ metal (no pairing) $f_k = \Theta(\varepsilon_k < \varepsilon_F)$

→ Band Insulator

→ Superconductor $f_k \neq 0 \quad \varepsilon_k \sim \varepsilon_F$

$$P_N \, BCS = AGP = A \prod_{Pairs} f(r_{i\uparrow}, r_{i\downarrow})$$

General: $\varepsilon_k = $ Single particle dispersion

→ metal (no pairing)

→ Band Insulator

$$f_k = \Theta(\varepsilon_k < \varepsilon_F)$$

→ Superconductor

$$f_k \neq 0 \quad \varepsilon_k \sim \varepsilon_F$$

New phase

JAGP = J x AGP → RVB

$$f_k \neq 0 \quad \varepsilon_k \sim \varepsilon_F$$

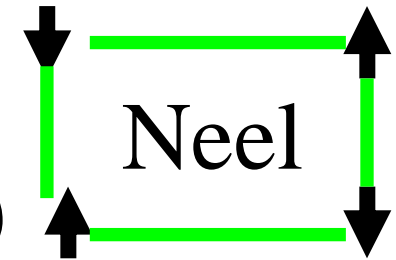$$J = \exp\left(\sum_{i<j} v(r_i, r_j)\right)$$

But insulator

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Definition of spin liquid

A spin state with

no magnetic order (classical trivial)
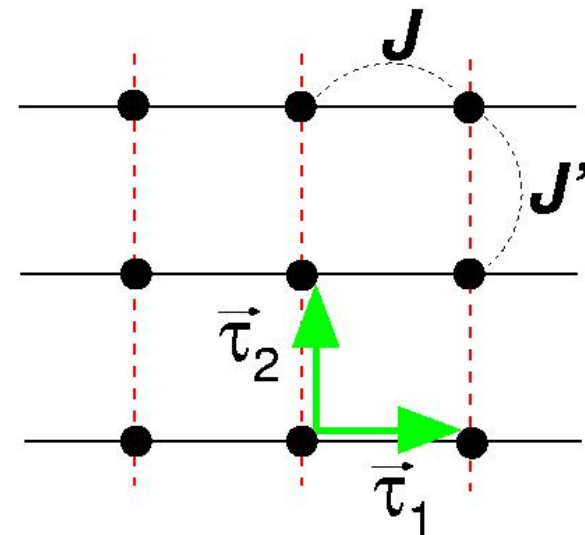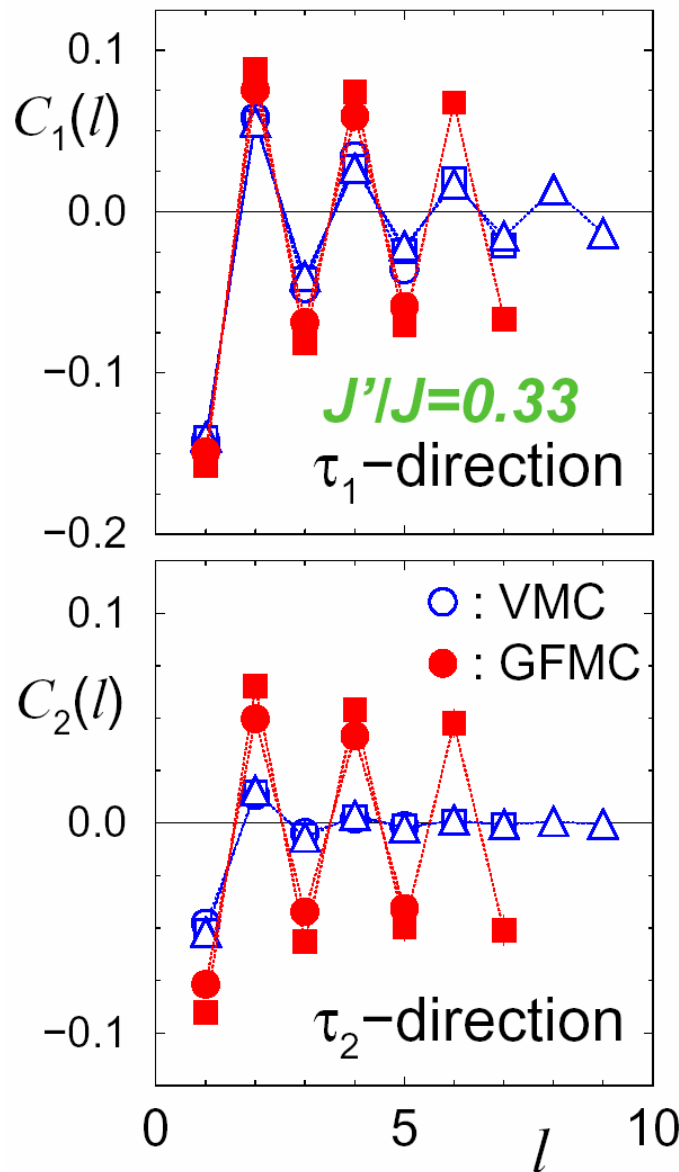
no broken translation symmetry (less trivial):

no Dimer state
(Read,Sachdev)

is a spin liquid

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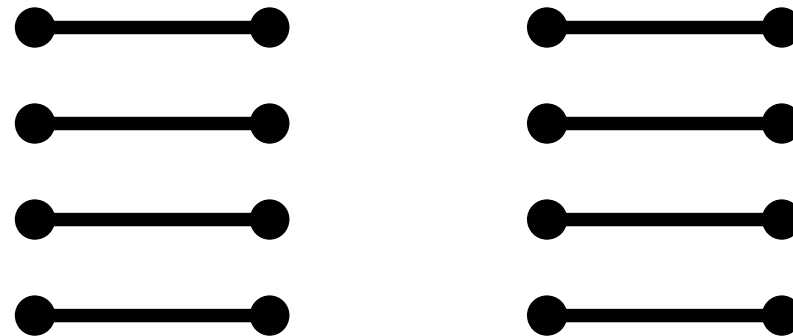
Square lattice with J'/J=0.33

$J'/J=0.33$
τ_1-direction

○ : VMC
● : GFMC

τ_2-direction

✓ Stability of the spin liquid
✓ Spin correlation function:

$$C_i\left(l\right)=\left\langle S_z\left(\vec{r}\right)S_z\left(\vec{r}+l\vec{\tau}_i\right)\right\rangle$$

✓ Spin liquid unstable toward AFM long range ordering !!
(A.W.Sandvik, PRL **83**, 3069, '99)

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Experiments from:
Coldea et al (PRL '01)
         PRB '03

J'/J=1/3
J=0.375meV

"J" between planes ~1K

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$$\kappa - (ET)_2 Cu_2 (CN)_3$$
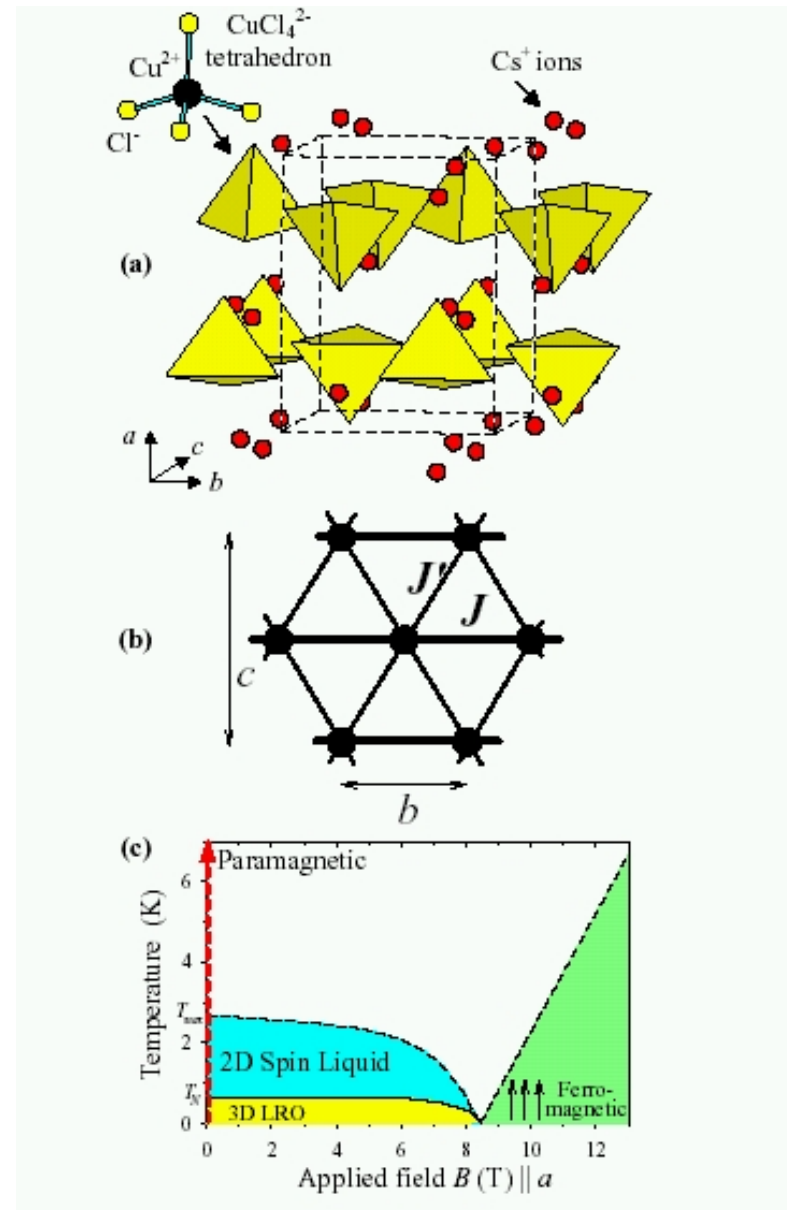
Spin Liquid ?

J=250K !!!

Shimizu et al. PRL '03
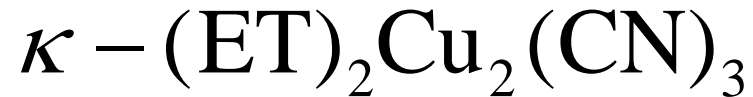
$$J'/J \approx 0.9 \qquad J'/J \approx 1.8$$
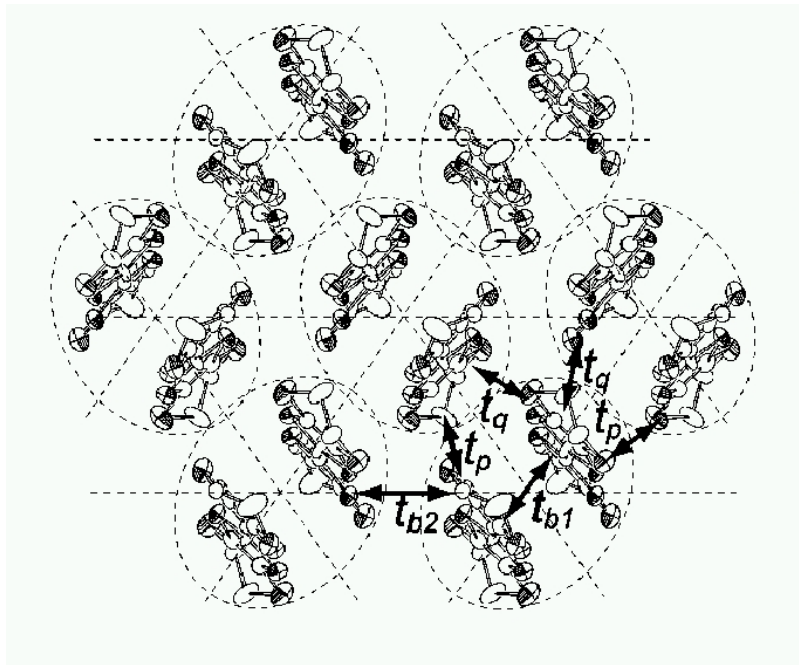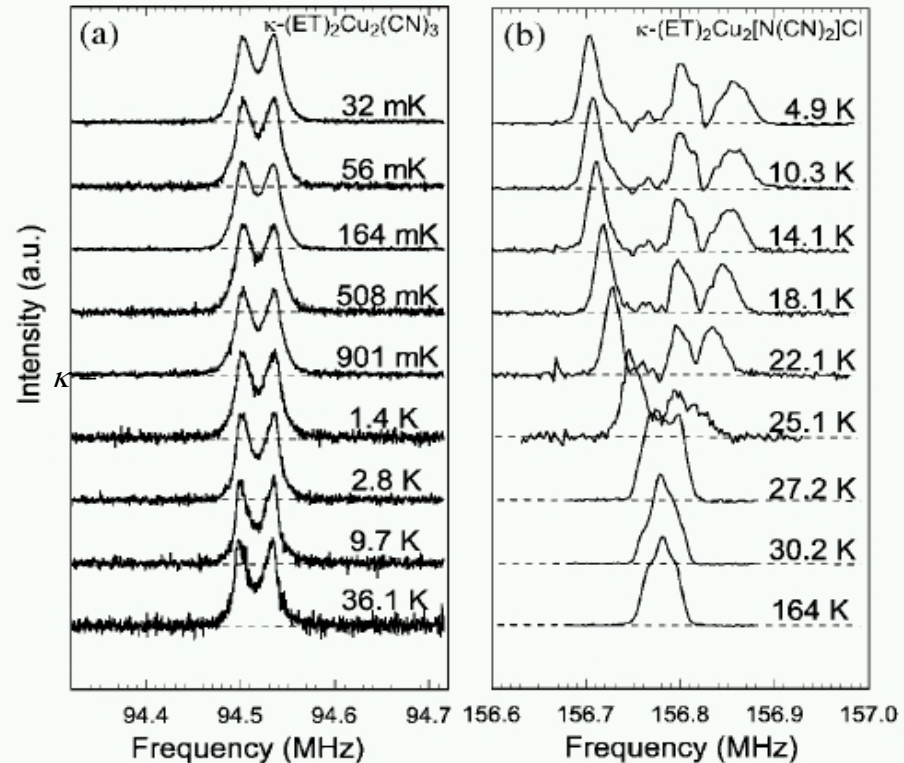
FIG. 3. (a) ^{1}H NMR absorption spectra for single crystals of κ-(ET)$_2$Cu$_2$(CN)$_3$ and κ-(ET)$_2$Cu[N(CN)$_2$]Cl [9] under the magnetic field perpendicular to the conducting planes.

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➢ <u>Methods</u>   (S. Sorella, PRB **64**, '01)

✓ **Variational** quantum Monte Carlo (QMC) method

✓ Projected BCS wave function: $\left| \text{P-BCS} \right\rangle = \hat{P}_{\text{G}} \left| \text{BCS} \right\rangle$

✓ $\left| BCS \right\rangle = e^{\sum\limits_{i,j} f_{i,j} C^{+}_{i,\uparrow} C^{+}_{j,\downarrow}} \left| 0 \right\rangle$: GS of BCS Hamiltonian

$$H_{BCS} = -\sum_{i,j,\sigma} t_{i,j} C^{+}_{i,\sigma} C_{i,\sigma} + \sum_{i,j} (\Delta_{i,j} C^{+}_{i,\uparrow} C^{+}_{i,\downarrow} + \text{h.c.})$$

$$\text{Notice}: \qquad t_{i,i} = \mu \quad \text{Chemical potential}$$

✓ Resonating valence bond states from PBCS
✓ **QMC** with Fixed node appr., (D. ten Haaf et al. PRB'95)
  to study the stability of the spin liquid state.

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2D with J'/J=0.33

Legend:
- --- : BZ
- --- : $\xi_k = 0$
- — : $\Delta_k = 0$
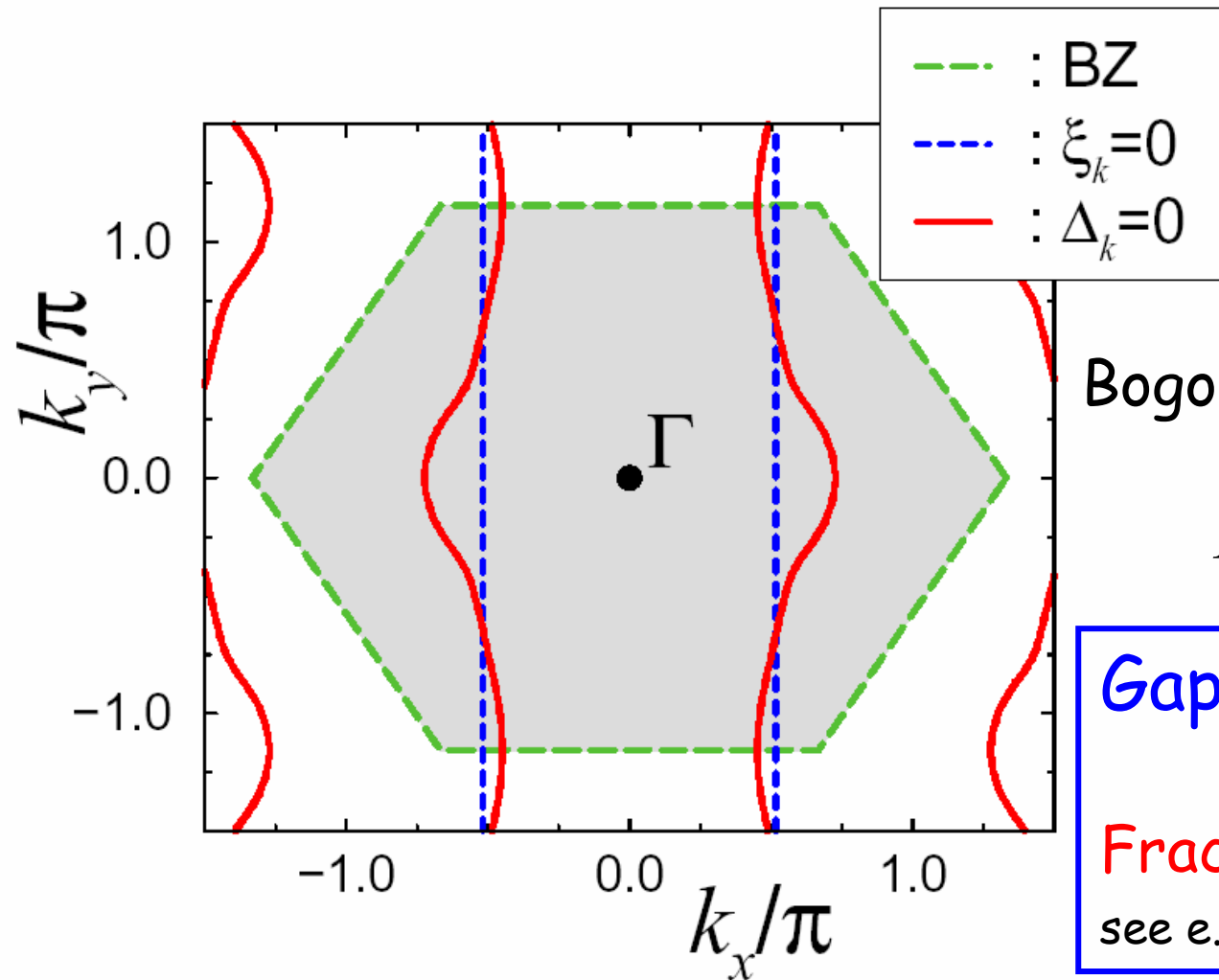
$$\xi_k = \varepsilon_k - \mu$$

Bogoliubov QP spectrum:

$$E_k = \sqrt{\xi_k^2 + \Delta_k^2}$$

Gapless excitations
S=1/2 →
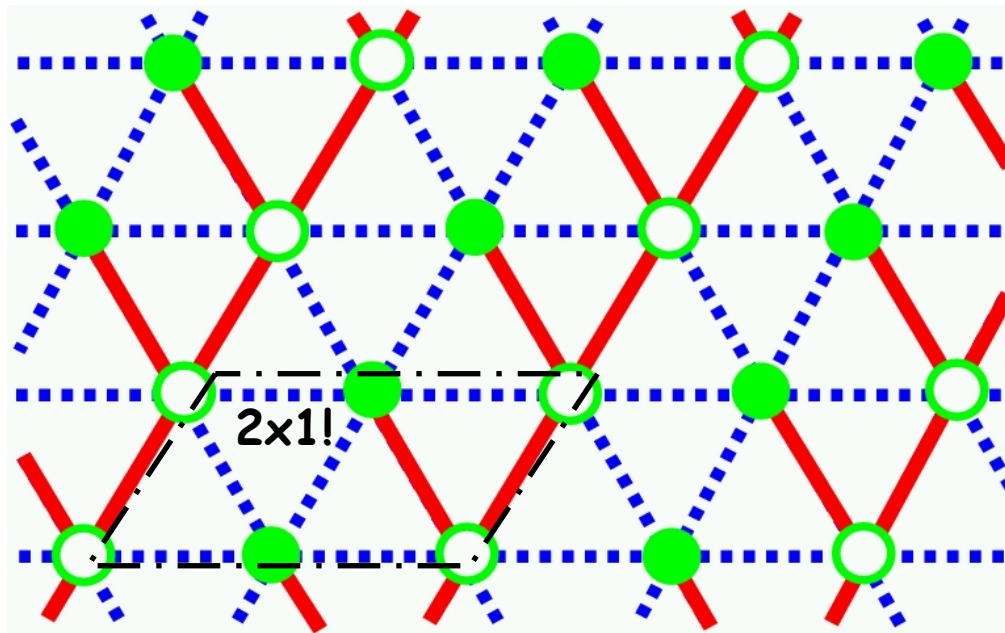**Fractionalization in 2D!**
see e.g. X.G. Wen or M. Fisher

No particular d-wave or s-wave symmetry due to anisotropy

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(P.Fendley,et al., PRB **66**,214513 ('02))

∙∙∙∙∙∙ : positive

—— : negative $\Delta_{i,j}$

2x1!

The wave function is translation invariant after projection!
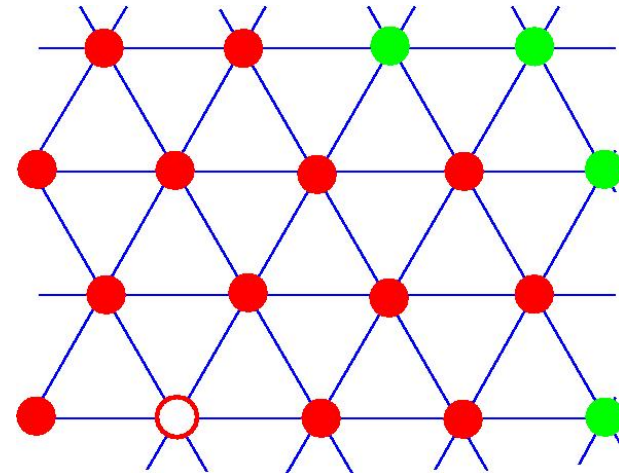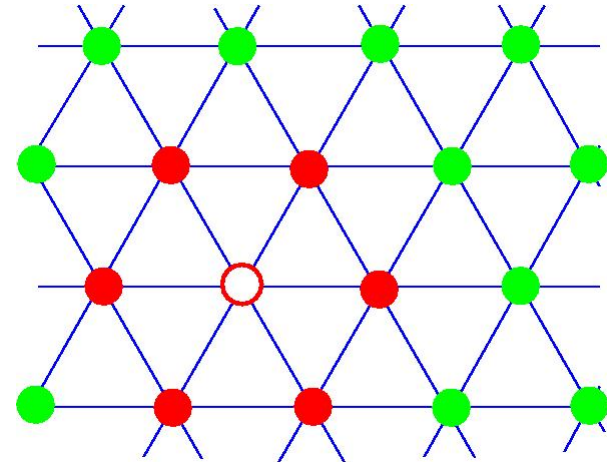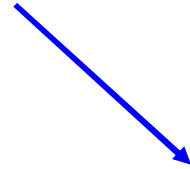The physical translation can be recovered after:

$$c^{+}_{R,\sigma} \rightarrow (-1)^{y}\, c^{+}_{R,\sigma} \qquad R = (x, y)$$

A new description of this spin liquid (i.e. translation invariant)
with a BCS hamiltonian that is generally gapped, as:

2 spin ½ per unit cell

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➢ Projected BCS WF on triangular lattice (II)

● WF consisting of

- nearest neighbor hoppings →

- up to 4-th nearest neighbor pairing functions (15 independent pairing functions in total)

- chemical potential μ

- short-range spin Jastrow factors (up to 4-th nearest neighbors)

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$$|\psi_0\rangle = P\exp(\sum_{i,j} f_{i,j} c^+_{i,\uparrow} c^+_{j,\downarrow})|0\rangle \qquad f_{i,j} = f_{j,i}$$

$$H_{BCS} = \sum_{k,\sigma} \varepsilon_k \, c^+_{k,\sigma} c_{k,\sigma} + \sum_{i,j} \Delta_{i,j} c^+_{i,\uparrow} c^+_{j,\uparrow} + \text{h.c.}$$

$$\varepsilon_k = -2\cos(k_x) - \mu$$
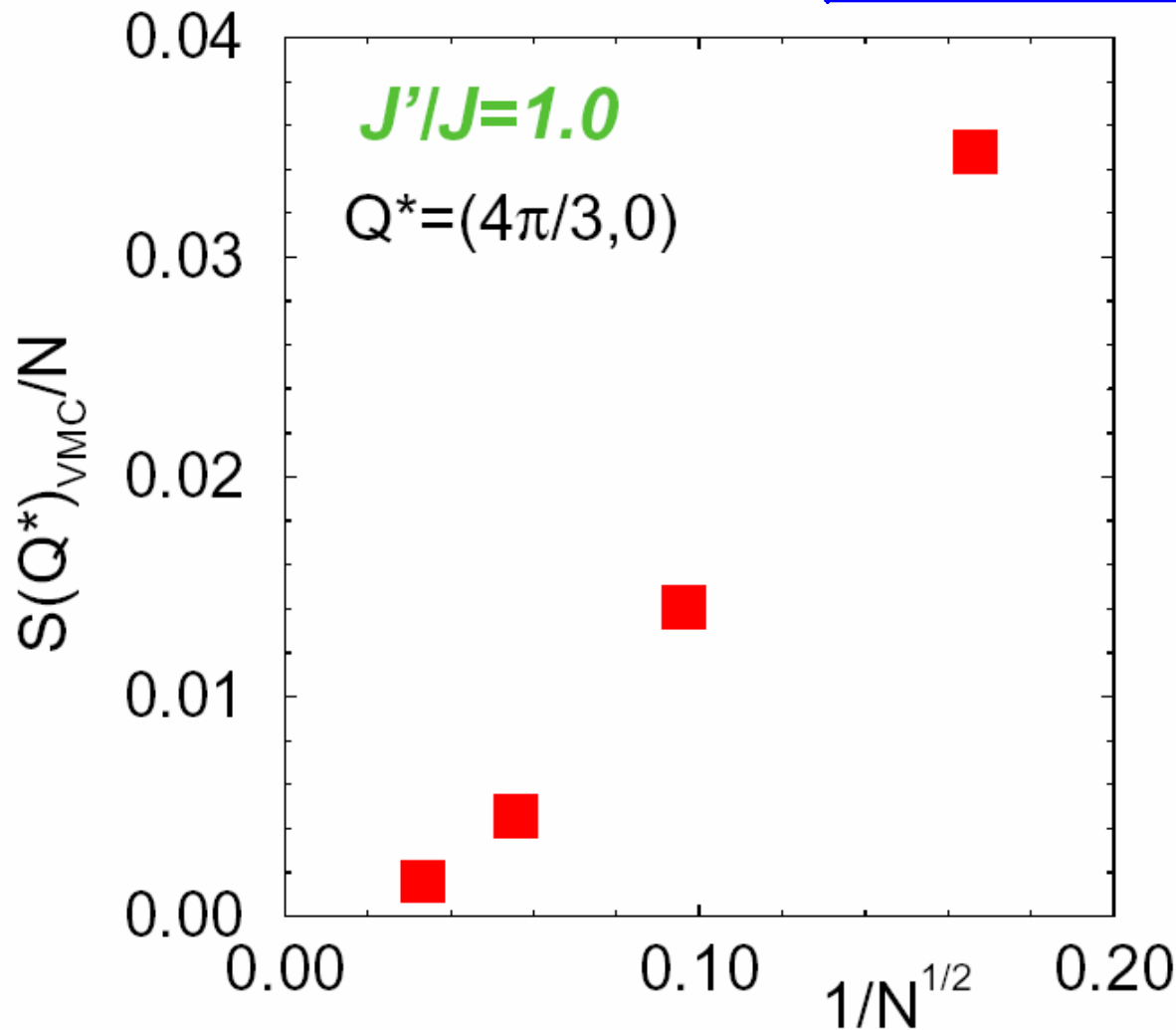
for $\mu \to -\infty$

the corresponding pairing function:

$$f_{i,j} \approx \Delta_{i,j} / |\mu|$$

The signs of f are such to cancel the fermion sign (the permutation of the pfaffian) and the short range RVB is obtained, i.e. the spin liquid wave function of the Quantum Dimer Model with a correlation length very short. (Fendley, Sondhi et al. PRB '02).

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Property of the wave function
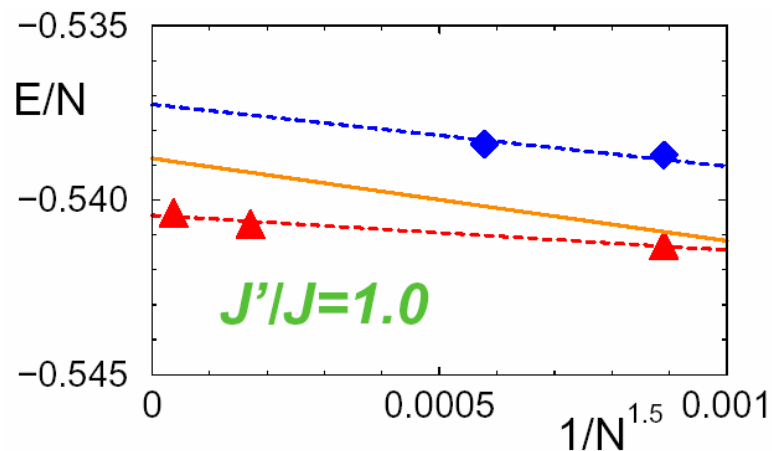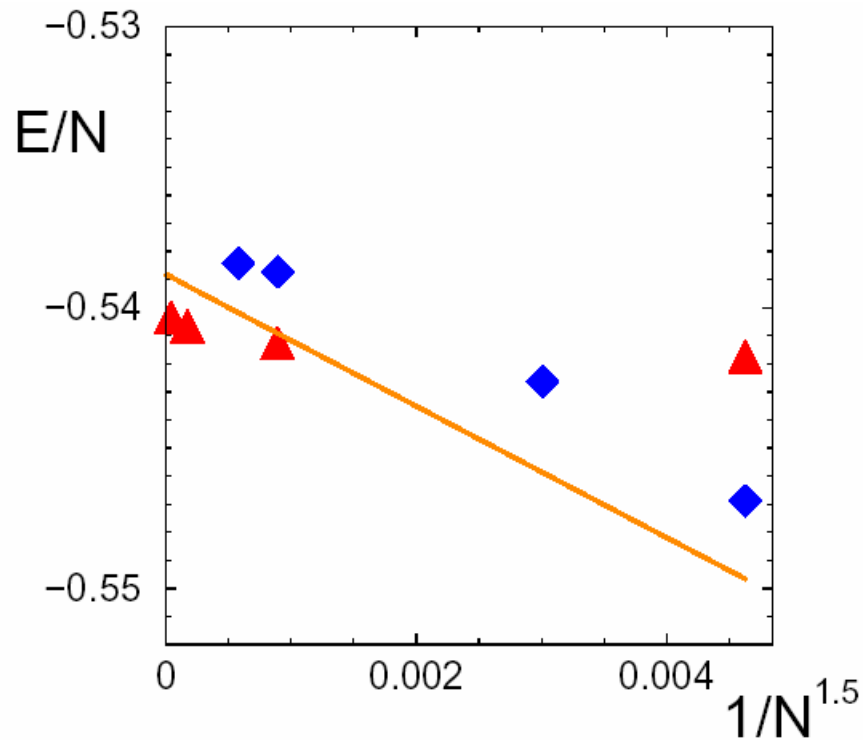
- Spin structure factor: $S(\mathbf{q}) = \sum_{\mathbf{l}} e^{i\mathbf{q}\cdot\mathbf{l}} \langle S_z(\mathbf{r}) S_z(\mathbf{r}+\mathbf{l}) \rangle$

Short-ranged spin Jastrow factor is not enough to induce magnetic ordering

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Comparison of FN (GFMC) energy (J'/J=1.0)

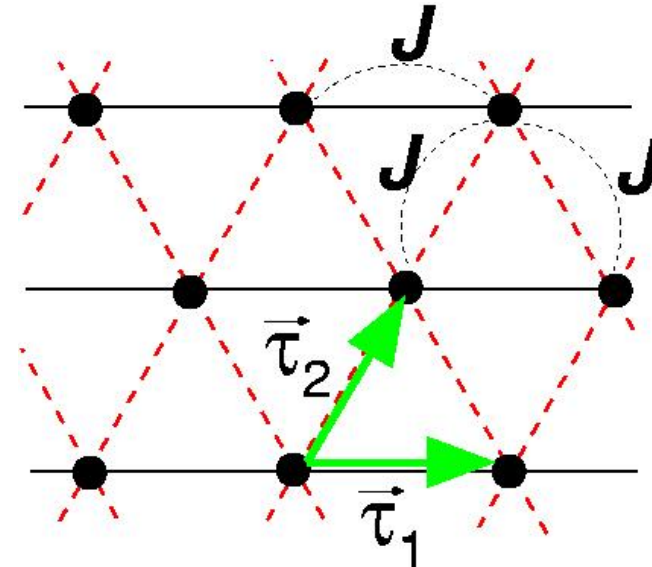□ FN energy in the thermodynamic limit

Neel ordered [1]	-0.53726(5)
linear spin wave theory	-0.5388090
present	-0.54044(5)
stochastic reconfiguration [1]	-0.5458(1)

[1] Capriotti, Trumper, SS, PRL **82**, 3899 ('99)
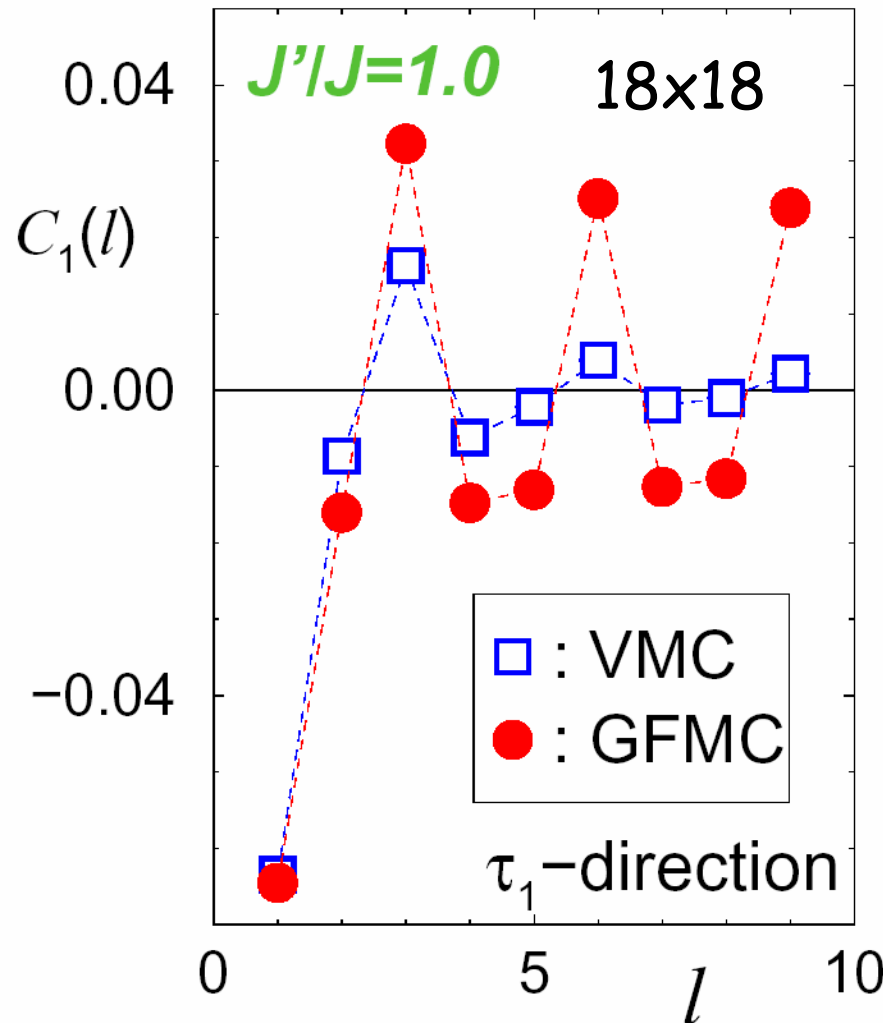
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➢ Isotropic triangular lattice with J'/J=1.0

$J'/J=1.0$ 18×18

$C_1(l)$

□ : VMC
● : GFMC

τ_1-direction

✓ Green function Monte Carlo
✓ Spin correlation function:

$$C_i(l) = \left\langle S_z(\vec{r}) S_z(\vec{r} + l\vec{\tau}_i) \right\rangle$$

✓ Spin liquid state unstable toward classical Neel state

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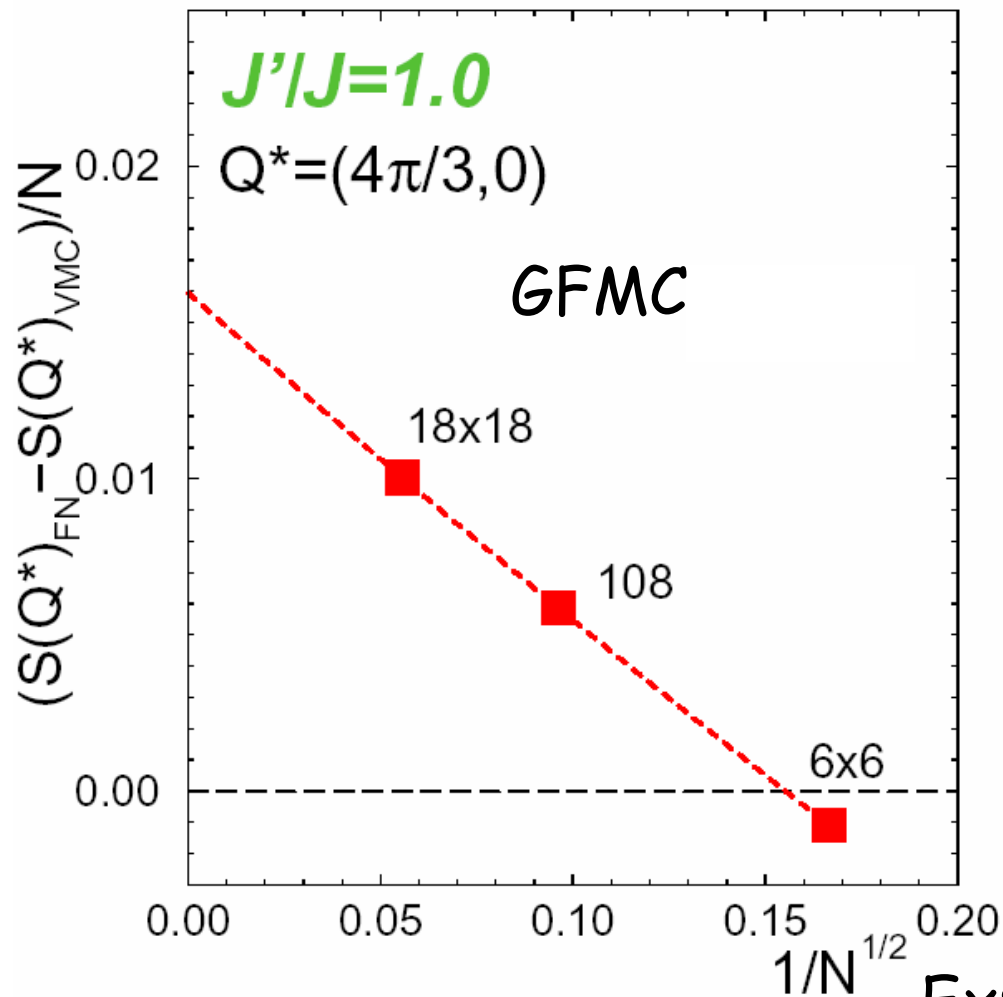# ➢ Spin structure factor for J'/J=1.0

$J'/J=1.0$

$Q^*=(4\pi/3,0)$

GFMC

18x18

108

6x6

$(S(Q^*)_{FN}-S(Q^*)_{VMC})/N$

$1/N^{1/2}$

Order parameter:

✓ Starting from a spin liquid :

$$m/m_{max} = 0.351 \pm 0.003$$

✓ Starting from ordered state :

Linear spin wave	0.4773
GFMC [1]	0.41(2)

Exp. ~0.45 (organic) at J'/J=1.8

[1] Capriotti, Trumper, SS, PRL **82**, 3899 ('99)

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Spin structure factor for J'/J=0.7

✓ Incommensurate peaks at $Q^*=(q^*,0)$

No long range order

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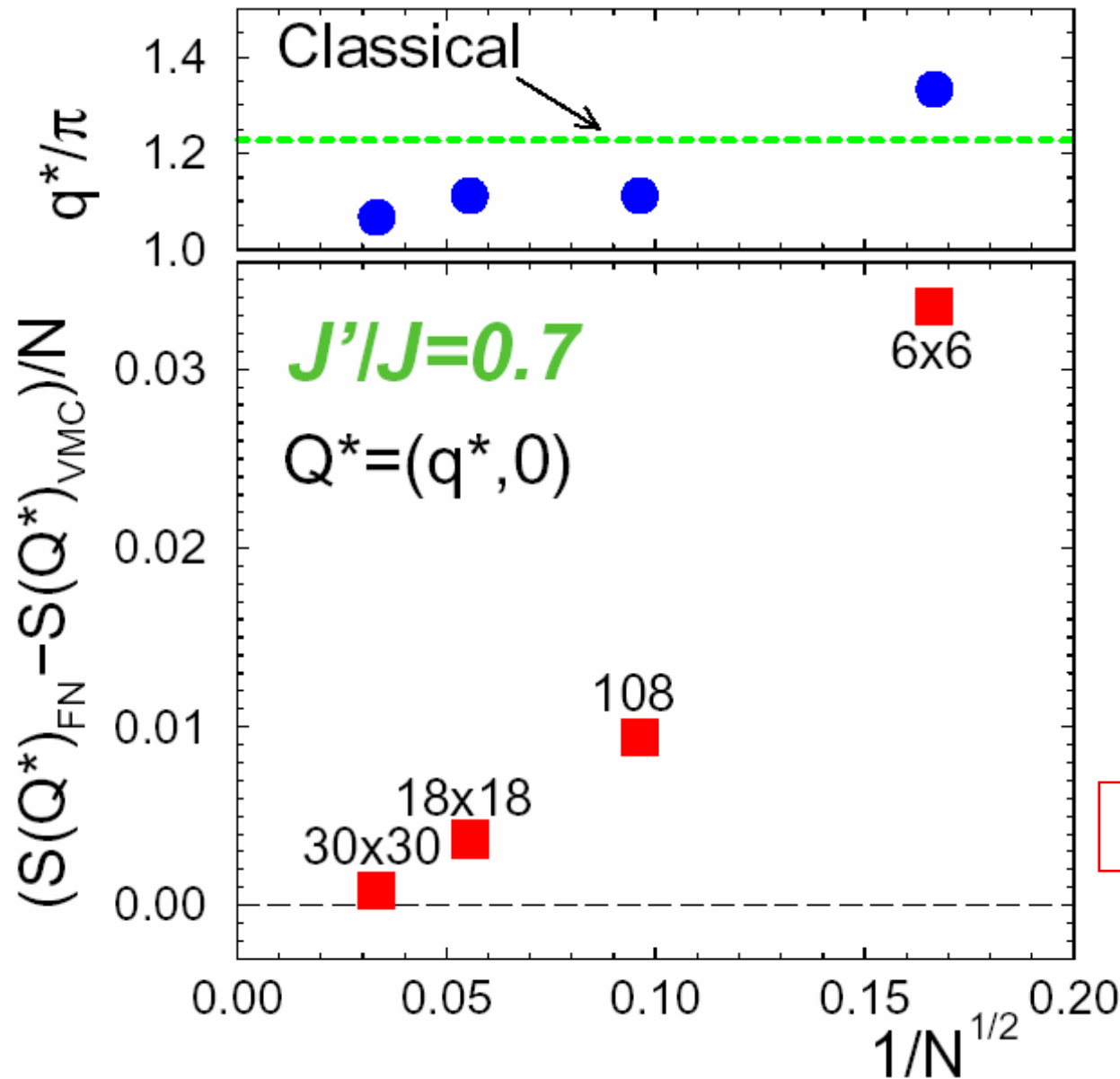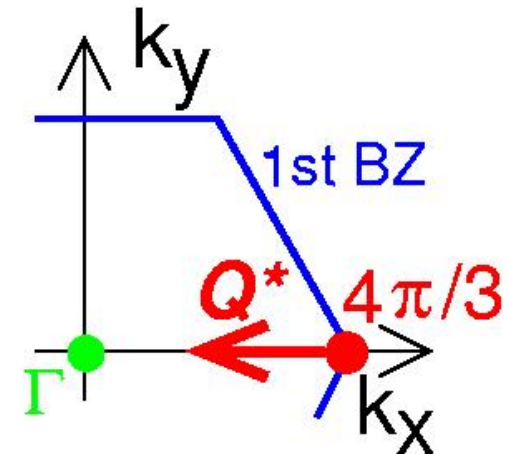
Stability against dimerization

the first four $\Delta_{i,j}$'s at the shortest distances:

$$
\begin{cases}
\Delta_1 = \Delta_{0,\vec{\tau}_1}, \\
\Delta_2 = \Delta_{\tau_1, 2\vec{\tau}_1}, \\
\Delta_3 = \Delta_{0,\vec{\tau}_2}, \text{ and} \\
\Delta_4 = -\Delta_{\tau_1, \tau_1 + \vec{\tau}_2},
\end{cases}
$$

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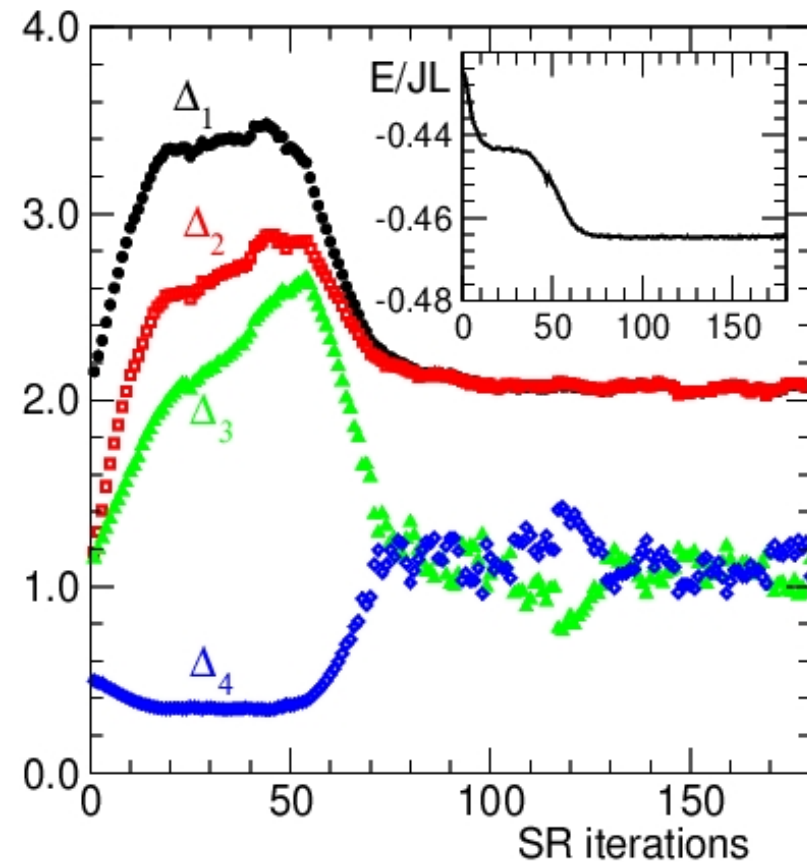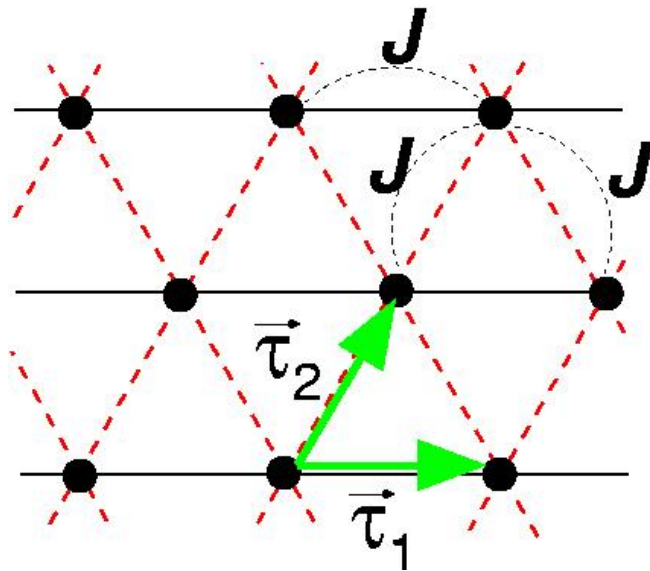
➢ Summary

- Possible spin liquid (SL) state in 2D
- Two different SL?
- Gapless vs. gaped?

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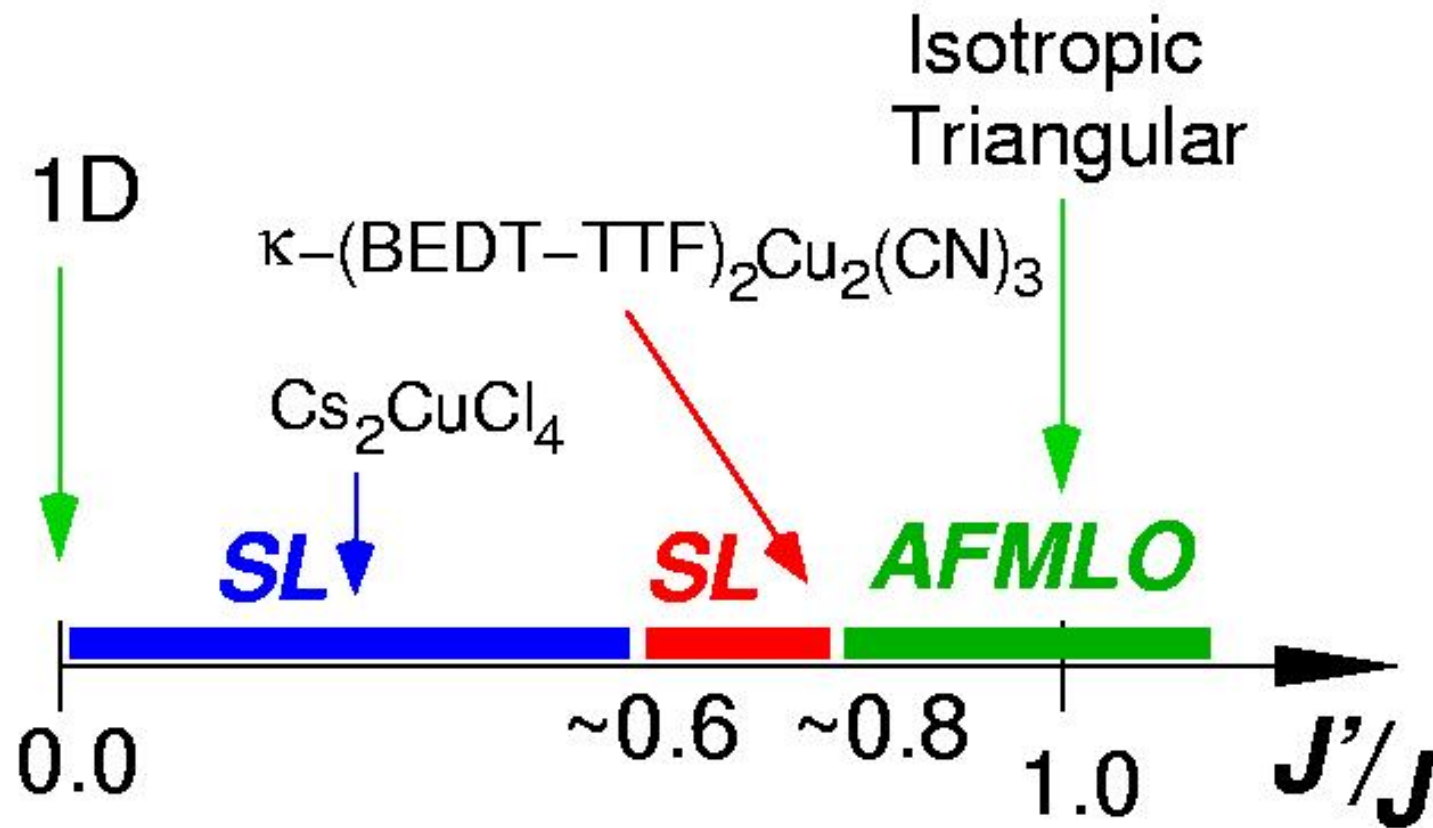
Correlation plays a crucial role:

1) No way to have superconductivity in a model with repulsive interaction.
 HTc not explained, HeIII, spin liquid (organic)

2) No way to obtain insulating behavior with a model with 1el/unit cell (Mott Insulator).
This is instead possible with correlated Jastrow

→We should optimize the RVB wavefunction in presence of its Jastrow.
 QMC only for correcting the HF is meaningless

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Why RVB wavefunction should work for molecules?

A molecule has a gap → ''insulator''
Why not RVB insulator ?

Van der Waals forces are included by Jastrow

In a complex system the molecular orbitals are often nearly degenerate →
Resonance Valence Bond approach OK

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Computational complexity now N^4

In QMC for <u>given accuracy</u> (e.g. Kcal/Mol)
Cost= N^4 , as sampling length=M~N.

One has to solve :

$sx = f$ where s has linear dimension N^2

N^6 ???

No!!! One can exploit conj. grad. and that :

$$s = M^{+} M \text{ where } M = (M \sim N, N^2)$$

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The Beryllium atom

$1s_2 2s_2$ and $1s_2 2p_2$ similar energy

Thus it is better to have 4 Slater determinants

Instead with the AGP wavefunction:

$$f(r_i^\uparrow, r_j^\downarrow) = \varphi_{1s}(r_i^\uparrow)\, \varphi_{1s}(r_j^\downarrow) + \lambda_{2s}\varphi_{2s}(r_i^\uparrow)\, \varphi_{2s}(r_j^\downarrow) + \lambda_{2p} \sum_{\mu=x,y,z} \varphi_{2p_\mu}(r_i^\uparrow)\, \varphi_{2p_\mu}(r_j^\downarrow)$$

Only one 2x2 determinant instead of 4 !!!
(M. Casula & S.S JCP '03)

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Size consistency (for complete Jastrow)

- A far from B   E = energy , S= spin

$$E_{A+B} = E_A + E_B$$

$$S_{A+B} = S_A + S_B \qquad \text{(as Hartree-Fock)}$$

$$S_{A+B} = 0 \text{ and } S_{A,B} = 1/2 \text{ (more than HF)}$$

AGP is not size consistent but JAGP in most cases

The wavefunction is <u>always</u> size extensive for a macroscopic system (join small pieces)

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$e.g.$ in the H_2 gas with N/2 nuclear pairs (a_i, b_i)

$$J = \exp(1/2 \sum_{i,j} v(r_i, r_j)) = \exp\left(-g \sum_{(a_k, b_k)} (\sum_j \phi_{a_k, b_k}(r_j) - 2)^2\right)$$

where $\phi_{a,b}(r) \cong 1$ in the dimer region (a,b) and $g \gg 1$

Gutzwiller projection term !!!

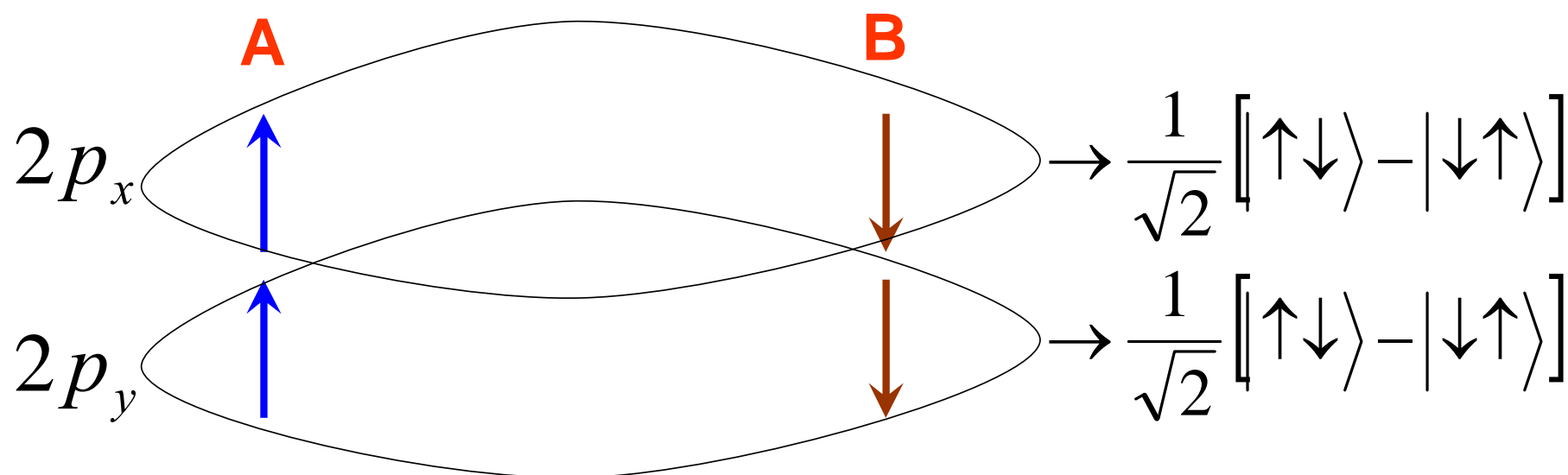$$\langle x | RVB \rangle = \exp(\sum_{i<j} v(r_i, r_j)) Det(f_{r_i^{\uparrow}, r_j^{\downarrow}})$$

in general $\qquad v_{r,r'} = \sum_{i,j} g_{i,j}^{a,b} \phi_{a,i}(r) \phi_{b,j}(r') + u(|r - r'|)$

Many variational parameters….

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Size consistency with J+BCS (RVB)

- C is a triplet   and $2p_x$ with the same spin $2p_y$

A   **B**

$$2p_x \qquad \to \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]$$

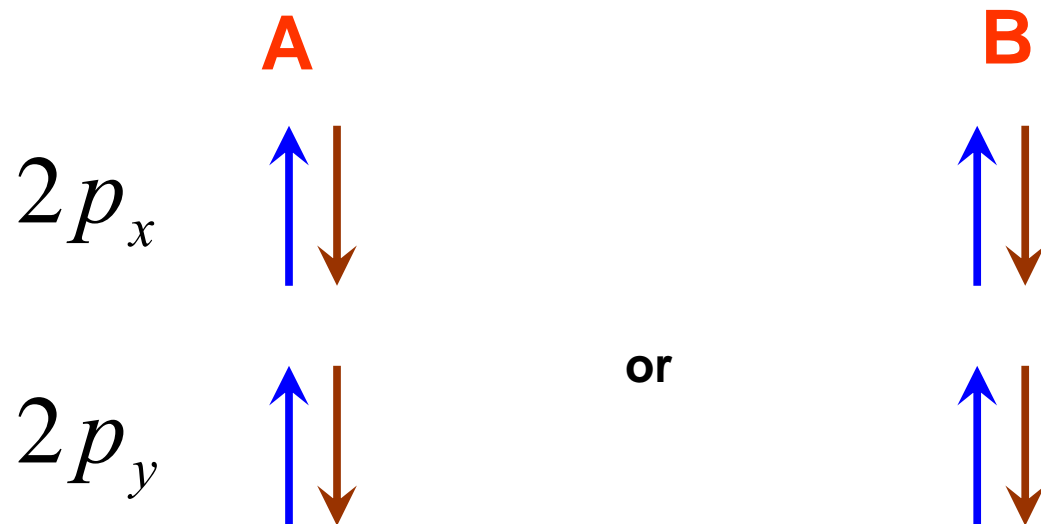$$2p_y \qquad \to \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]$$

To have a singlet out of two triplet → 6 determinants (no doubly occupied)
or use JAGP (all det) and pay something in size consistency

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However:

With J+BCS we can have 2 spurious terms such:

A   **B**

$2p_x$

or

$2p_y$

That can be substantially eliminated by the Jastrow, suppressing double-occup.

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DMC on the lowest energy JAGP wf.

→ Old technique non variational (often unstable) with nonlocal pseudopotential

→ New (M.Casula C.Filippi and S.S.) PRL05

LatticeRegularizedDiffusionMonteCarlo

Very stable variational upper bounds of the pseudo Hamiltonian energy.

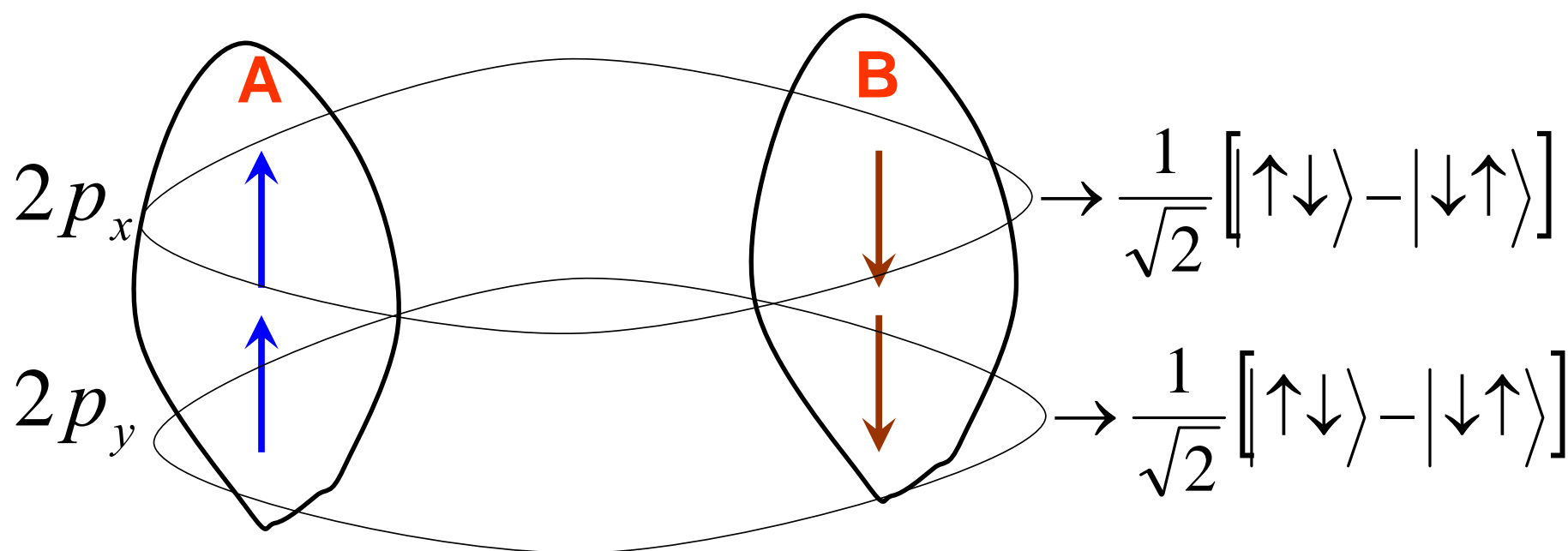Key idea: on a lattice all interactions are nonlocal

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Size consistency with J+BCS (RVB)

- C is a triplet   and $2p_x$ with the same spin $2p_y$

$$2p_x \qquad \rightarrow \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]$$

$$2p_y \qquad \rightarrow \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]$$

To have a singlet out of two triplet → 6 determinants (no doubly occupied)
or use JAGP (all det) and pay something in size consistency

The challenge of hydrogen-bonded systems...

-76.438 h

Weakness of the interaction

$$\theta = 104.52^0$$

Variety of source:
Electrostatic, covalent bond, VdW

0.9572 A
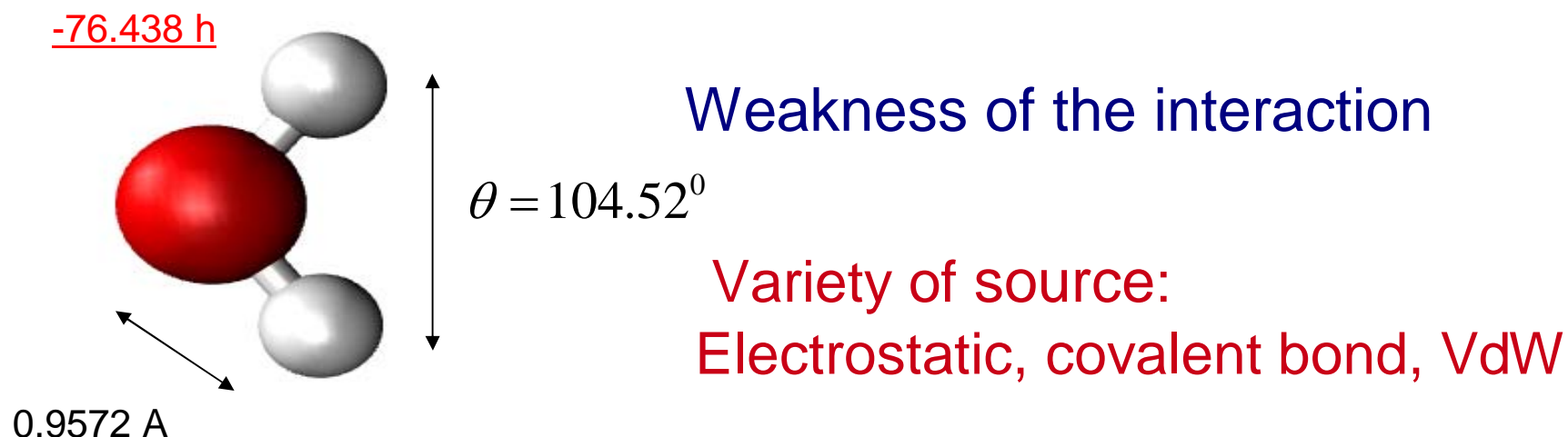
All electrons calculation

HF	-76.063
B3LYP	-76.469
VMC-HF	-76.327(5)
VMC-B3LYP	-76.334(5)

DMC	-76.4211(3)
DMC B3LYP	-76.4230(1)
CCSD(T)-R12	-76.4373

VMC 1pTVZ	-76.3746(2)
VMC (2s3p)	-76.3646(4)

←From scratch

Bendel et al. J.Chem.Phys. 125 104302 (2006); W.Ermler J.Chem. Phys. 61,5362(2001);H.Muller et al. Mol.Phys. 92,535 (1997)

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Accurate description of the molecule at any R

ZPE=0.187(3) eV
R eq.= 1.400(3) a.u.

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