Towards ab-initio simulation of high temperature superconductors

Sandro Sorella

SISSA, DEMOCRITOS, Trieste

Santa Barbara 1 September 2009

Motivations

→ Model systems, nice reduction schemes but how much can we trust them?

→ Do they explain or fit the experiments?

→ Variational approach is always approximate and no exact method exists for fermions in 2D /3D strongly correlated systems. Still waiting for PEPS, MERA, Sign problem solution in quantum Monte Carlo…

→ Why do not we try to use the variational scheme for realistic systems with full Coulomb e-e?

Outline

RVB theory, short review on lattice models

Testing RVB theory:

assume RVB wave function is a correct and exhaustive description of correlation → reasonable agreement with experiments

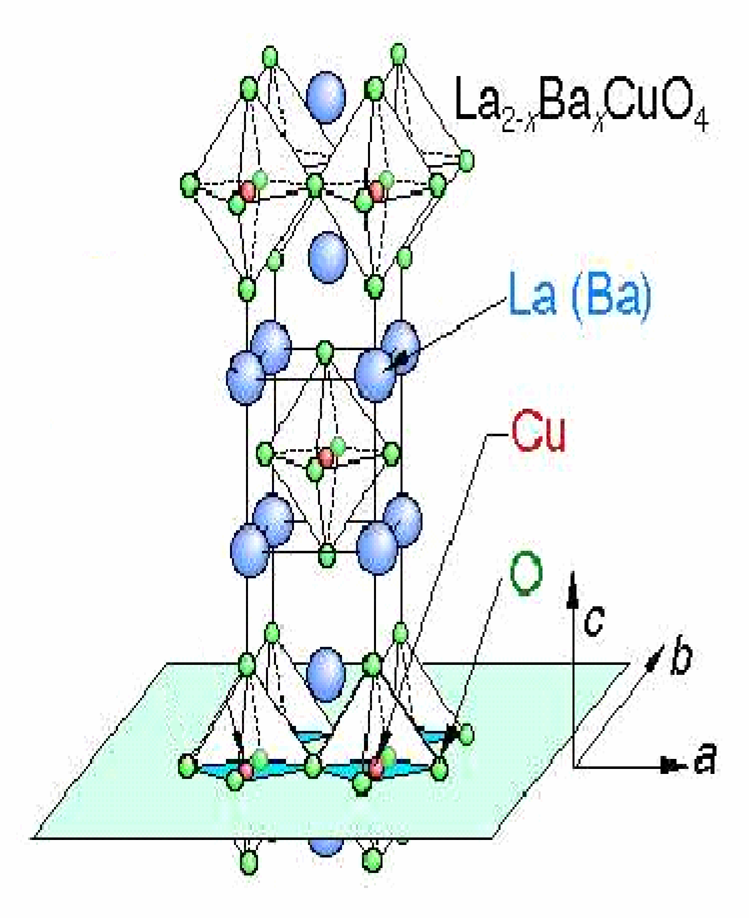
→Starting from 2003 still a lot of work to be done

→ Testing RVB on small molecules, comparison with existing quantum chemistry methods.

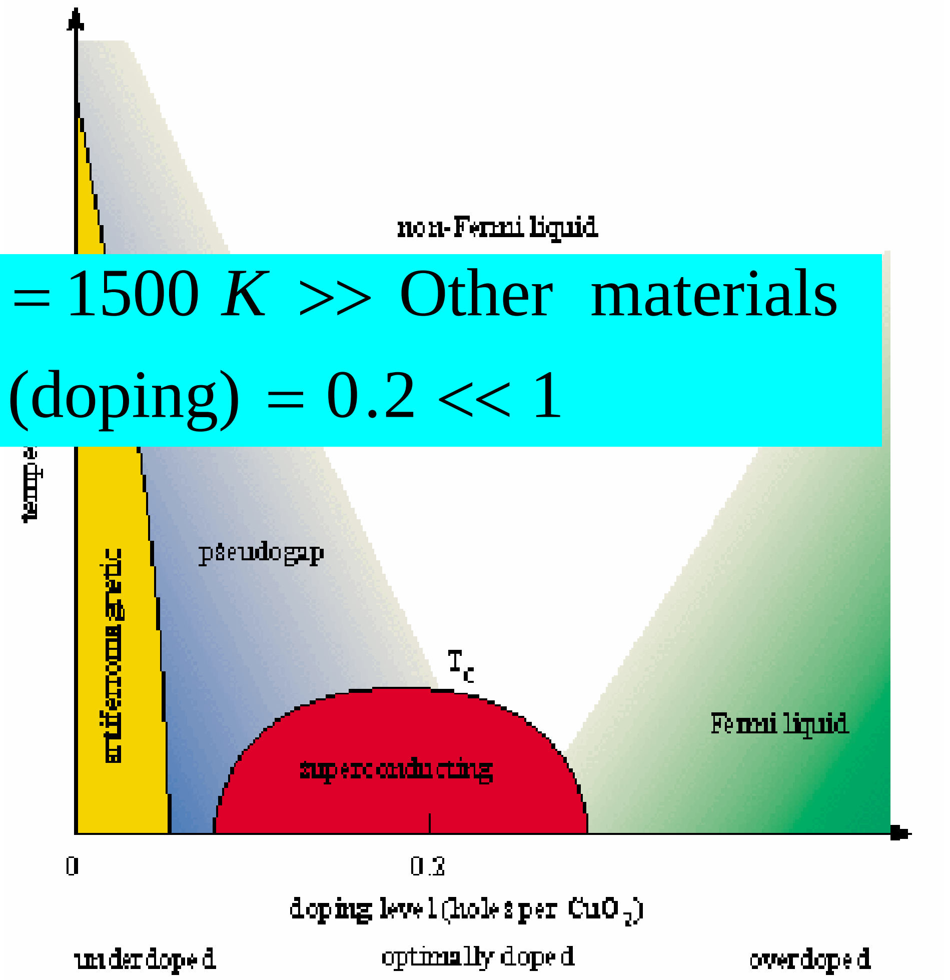
→ HTc: few preliminary results with huge computational resources…

Cuprates

quasi-2D structure



Phase diagram: temperature vs. doping



$J = 1500\ K >>$ Other materials

δ (doping) $= 0.2 << 1$

The Anderson's wavefunction $\delta = 0$

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

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

The pairing function : $f_k = \dfrac{\Delta_k}{\varepsilon_k + \sqrt{\varepsilon_k^2 + \Delta_k^2}}$

$$P\left|BCS\right\rangle = \hat{J} \exp \sum_{i<j} f_{i,j} \underbrace{(c^+_{i,\uparrow} c^+_{j,\downarrow} - c^+_{i,\downarrow} c^+_{j,\uparrow})}_{\text{Singlet bond}} \left|0\right\rangle$$

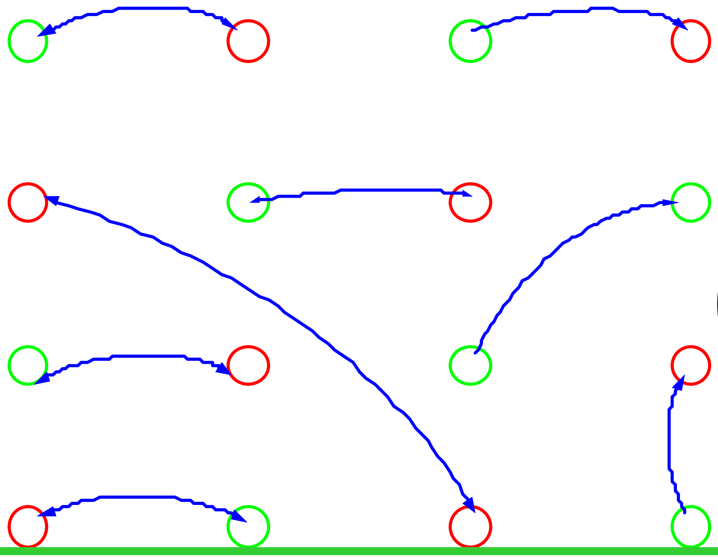
$$\hat{J} = \xcancel{\uparrow\downarrow} = \prod_i (I - n_{i\uparrow} n_{i\downarrow}) = \exp[-\sum_i (g \to \infty) n_i^2]$$

Anderson's variational wavefunction for spin models

$$P\left|BCS\right\rangle = \hat{J}\ \exp\sum_{i<j} f_{i,j}\underbrace{(c^{+}_{i,\uparrow}c^{+}_{j,\downarrow} - c^{+}_{i,\downarrow}c^{+}_{j,\uparrow})}_{\text{Singlet bond}}\ \left|0\right\rangle$$

But J $\cancel{\uparrow\downarrow}$ → Resonance Valence Bond

$$P\left|BCS\right\rangle = \sum_{All}$$



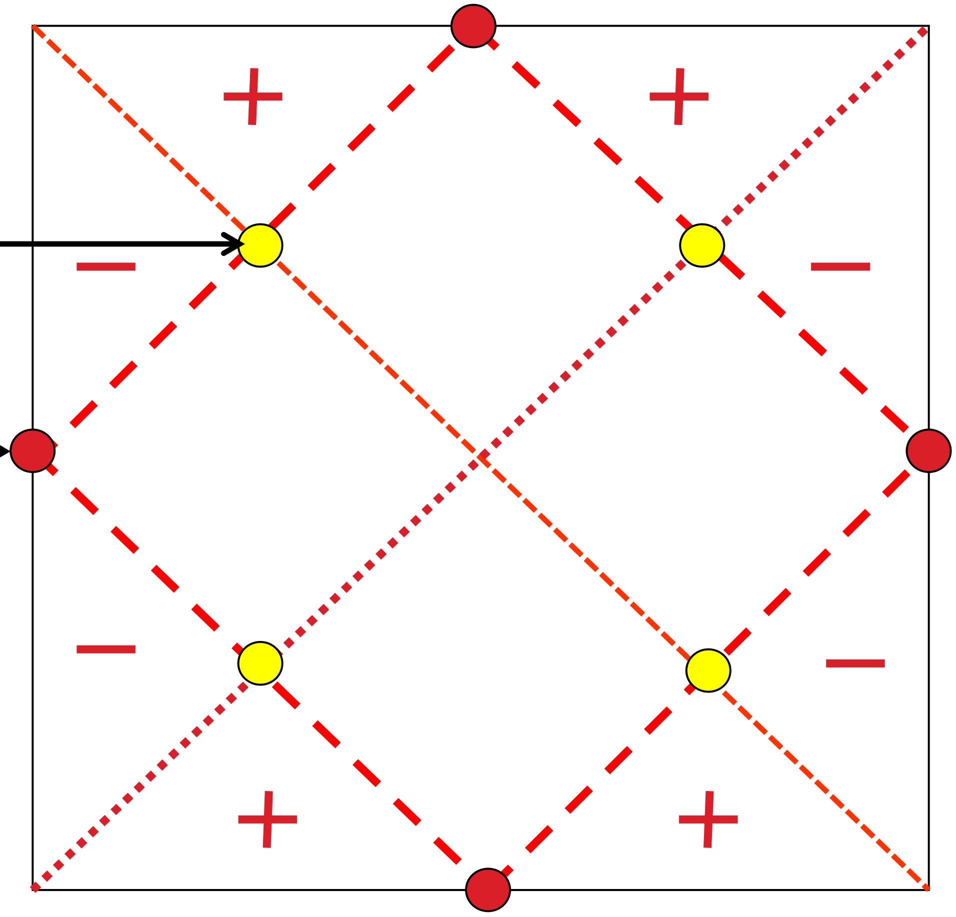
Weight:

$$(-1)^{p}\prod_{k=1}^{\#\text{Sites}/2} f_{i_k,j_k}$$

$(-1)^{p}$ is the sign (+/-) of the permutation of $i_1, j_1, i_2, j_2 \ldots$

Best variational PBCS in Heisenberg model

$$\Delta_k = \frac{\Delta_{BCS}}{2}(\cos k_x - \cos k_y)$$

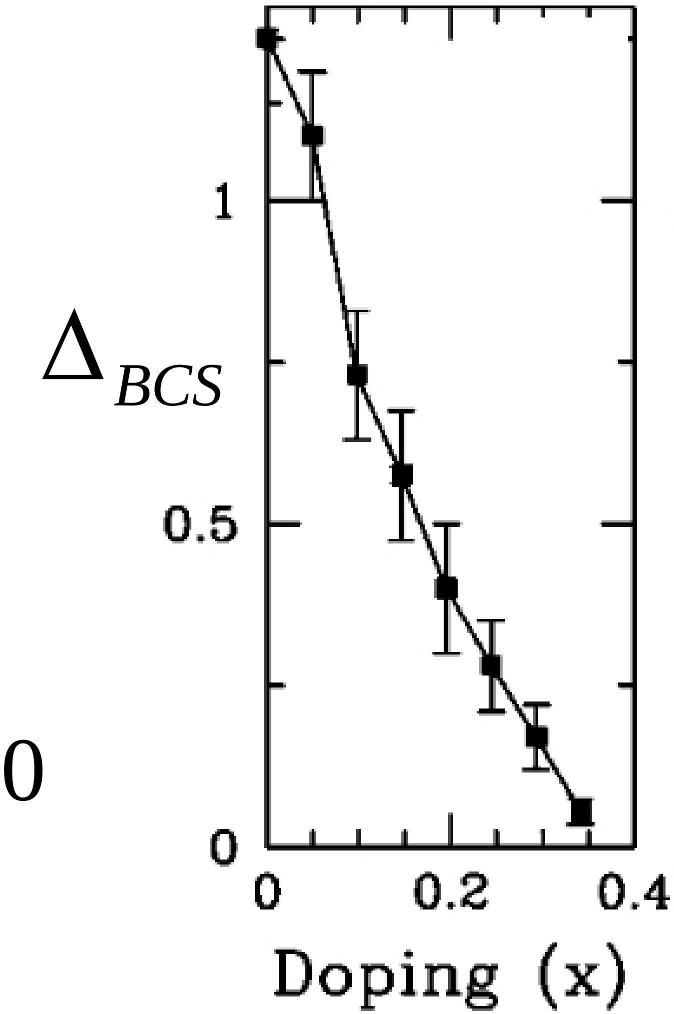


Nodal point gapless

Hot point gap = Δ_{BCS}

Energy of BCS excitations: $E_k = \sqrt{\varepsilon_k^2 + \Delta_k^2}$

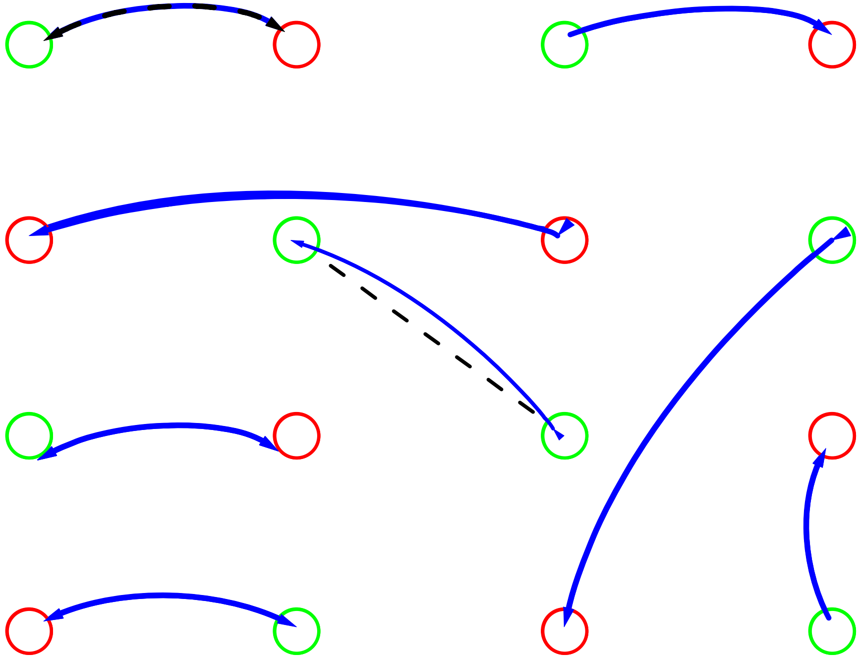
The BCS d-wave variational parameter shows the pseudogap feature observed in experiments



From Pamarekanti,
Randeria, Trivedi, PRB ‘00

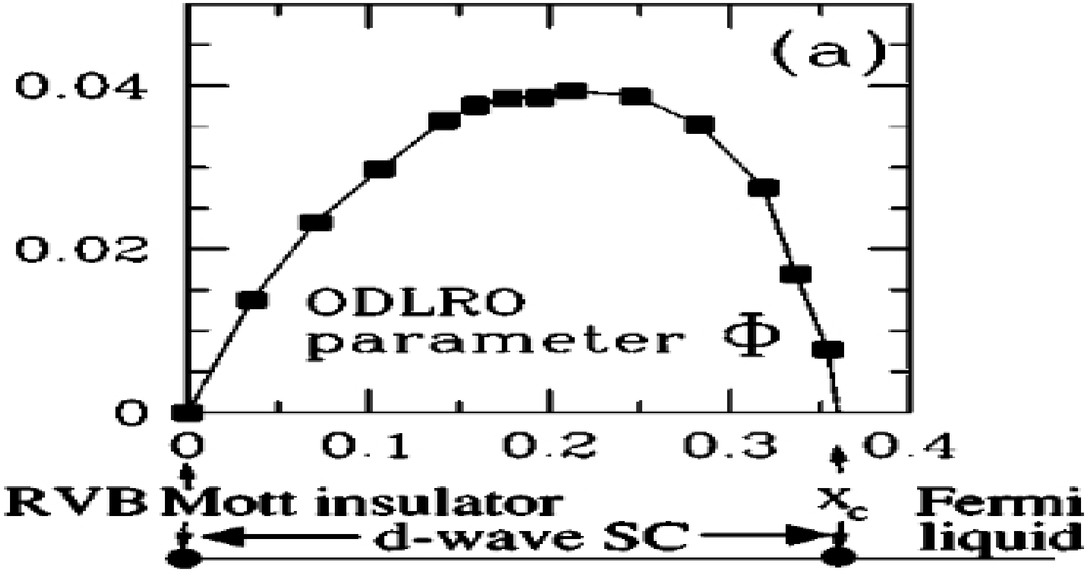
From RVB to superconductivity

$$\left[N(\#\,\mathrm{particles}), \theta(\mathrm{phase\ coherence}) \right] = -i$$



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

Instead the actual order parameter ~ x (doping)



$$\Phi = \left\langle \left(c^{+}c^{+}\right)_{d-wave} \right\rangle \neq 0 \text{ only for } x > 0$$

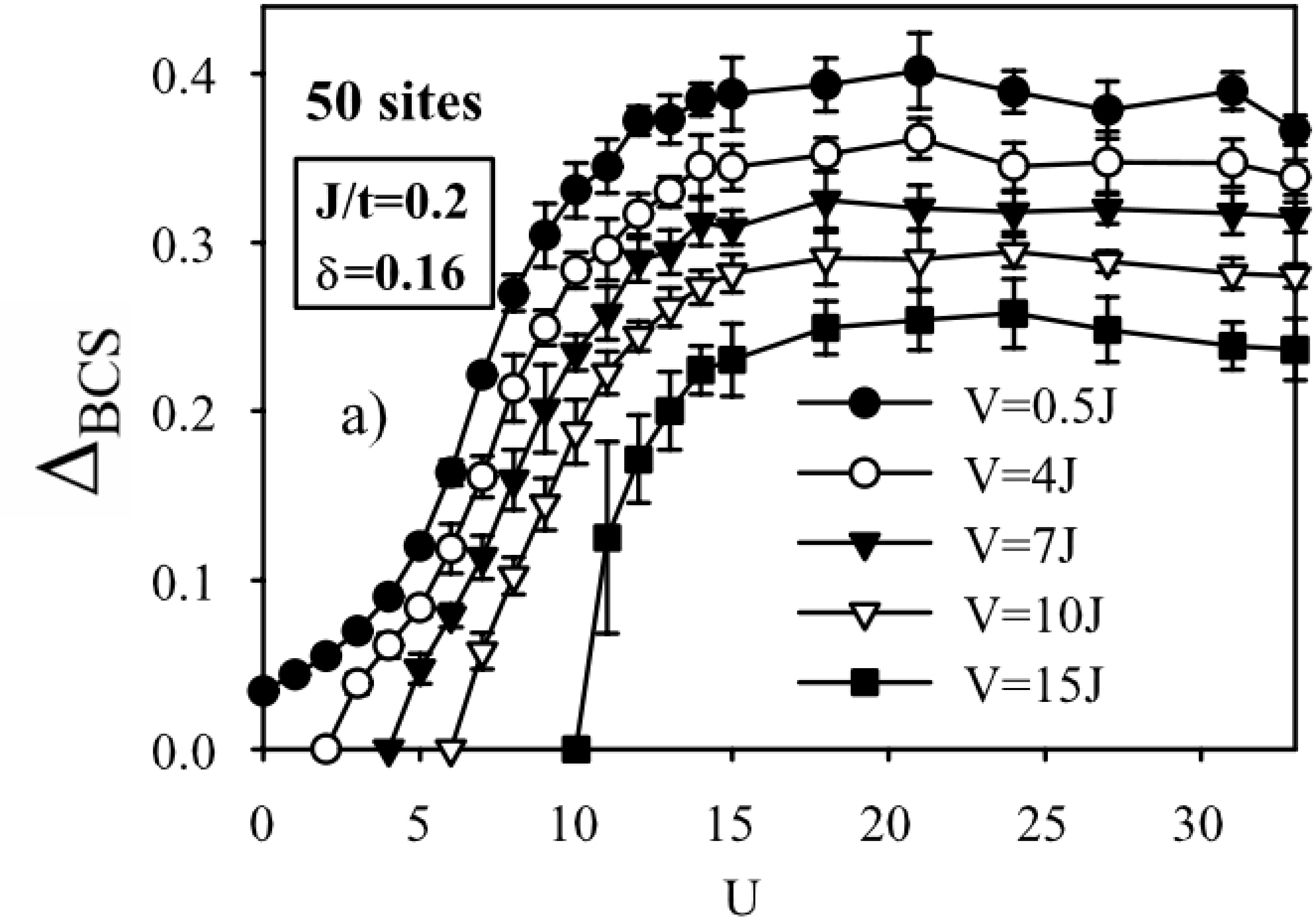
This is the most important feature of an RVB superconductor

Weak coupling theory and RVB are not in conflict

t-J(singlet attraction)-V,U(charge-repulsion):

V (nearest neigbour) U (on site)

Plehanov-Fabrizio-Sorella PRL ‘06



Rational behind High-Tc in Cuprates
M. Capone et al., Science (2002).

We need antiferromagnetic fluctuations J as an electronic attractive channel for supercond.

On the other hand we need a small quasiparticle weight Z (close to a Mott insulator) in order to overscreen the long range Coulomb repulsion:

$$V \rightarrow V\, Z^2$$

$$J \rightarrow J$$

Pnictides, another way to have small Z?

Classification of the possible RVB insulators

Paired RVB, i.e.

$\Delta_{BCS} \neq 0$ gapped

→ with a gap in the mean field, and broken symmetry (e.g. AF)

→ RVB spin liquid, gap but no kind of order(dimer,magnetic,nematic….

Nodal RVB

$\Delta_{BCS} \neq 0$ gapless

→ Spin liquid (algebraic)
Nodal fermions quasiparticles

Fermi RVB

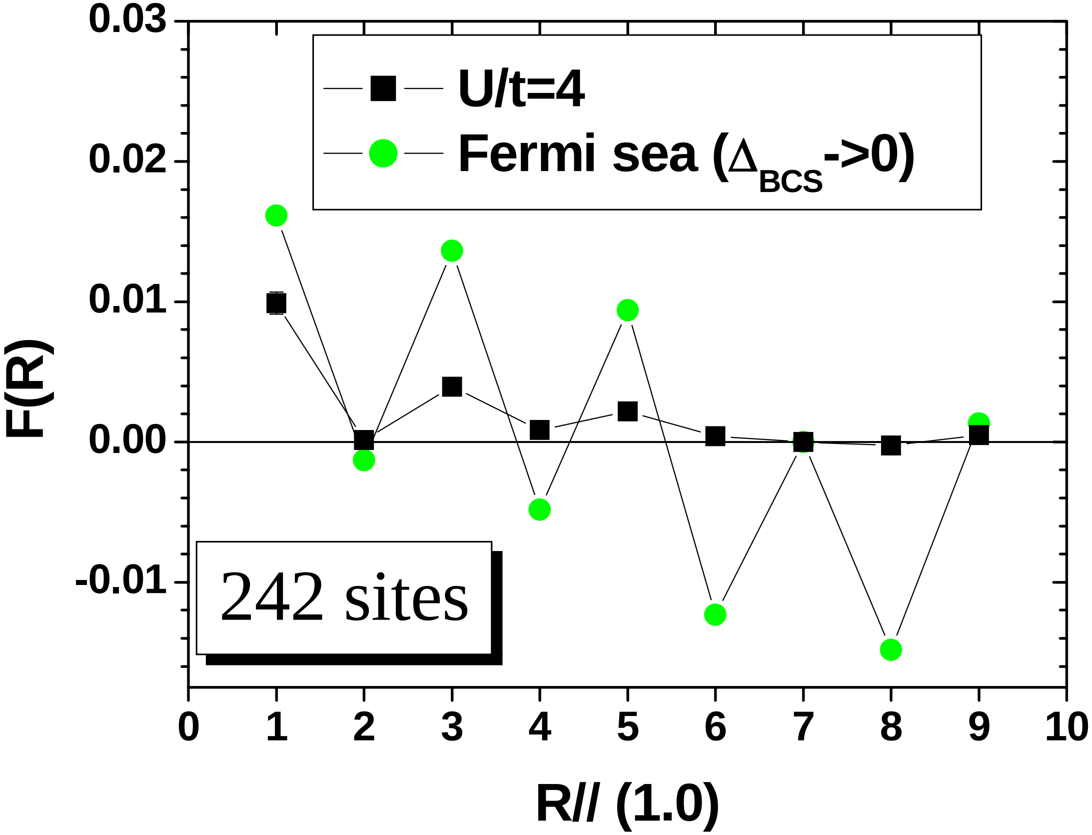
$\Delta_{BCS} = 0$ gapless on a Fermi surface

→ Fermi gas spin properties:
e.g. finite susceptibility

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

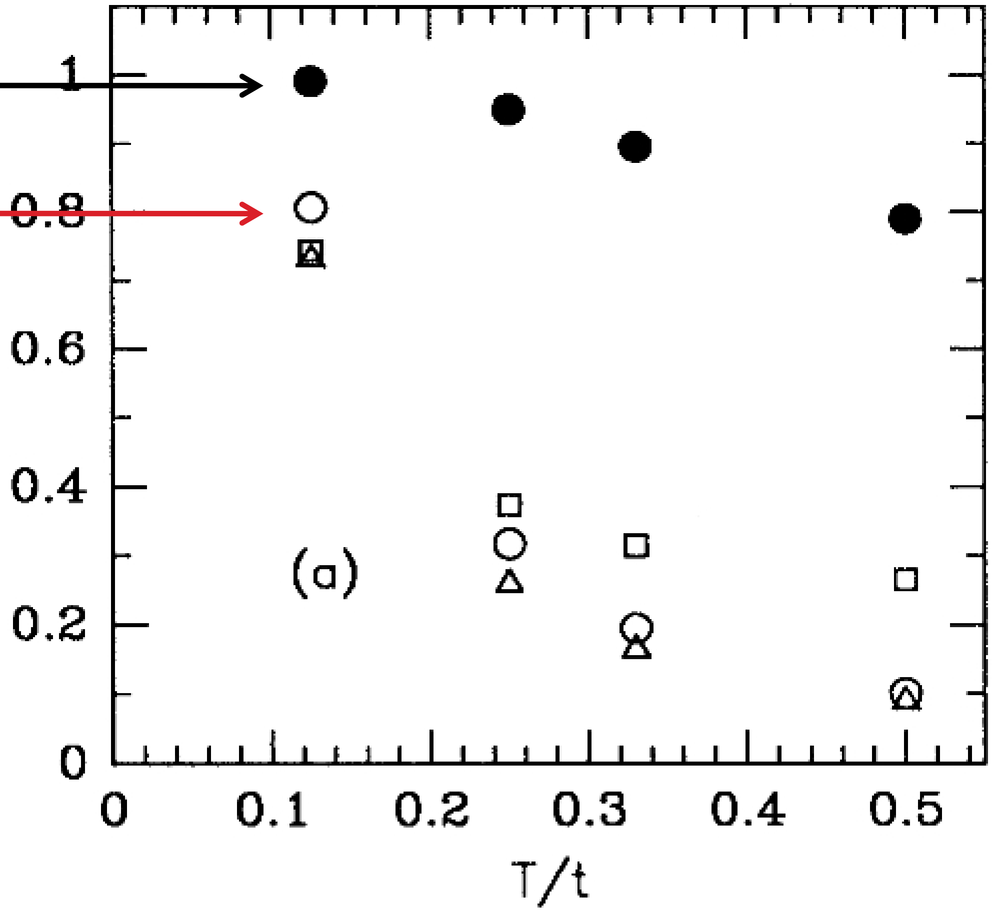
E. Plehanov F. Becca and S.S. PRB’05

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



Similar conclusions in Bulut, Scalapino, White, PRB’93

Half filled Hubbard model testing instabilities $\lambda \sim 1$ of the quasiparticles interactions



AF

D-wave singlet

For a lattice model

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

TurboRVB : the RVB for real electrons (see qeforge web page)

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

$$\boldsymbol{f}_{\boldsymbol{r},\boldsymbol{r}'}(\upsilon_{\boldsymbol{r},\boldsymbol{r}'}) = \sum_{\boldsymbol{i},\boldsymbol{j}} \lambda_{\boldsymbol{i},\boldsymbol{j}}^{\boldsymbol{a},\boldsymbol{b}} (\boldsymbol{g}_{\boldsymbol{i},\boldsymbol{j}}^{\boldsymbol{a},\boldsymbol{b}}) \psi_{\boldsymbol{a},\boldsymbol{i}}(\boldsymbol{r}) \psi_{\boldsymbol{b},\boldsymbol{j}}(\boldsymbol{r}') \quad \text{where :}$$

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

$$\psi(\boldsymbol{r}) = \boldsymbol{Y}_{\boldsymbol{l},\boldsymbol{m}}(\theta, \phi) \boldsymbol{r}^{\boldsymbol{k}} \sum_{\boldsymbol{j}=1}^{\boldsymbol{p}} \boldsymbol{A}_{\boldsymbol{j}} \boldsymbol{e}^{-\boldsymbol{Z}_{\boldsymbol{j}} \boldsymbol{r}^2} \quad \text{p contracted}$$

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

with a single determinant

Technical achievements used for TurboRVB

I) Optimization of several ~10000 Variational parameters now possible

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
S. Sorella, M. Casula and D. Rocca JCP '07

II) DMC: the lowest energy state with the same nodes of the Variational wf with pseudo: Old i) often unstable, ii) non variational energy upper bound

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

→LatticeRegularizedDiffusionMonteCarlo

Very stable variational upper bounds of the pseudo Hamiltonian energy.

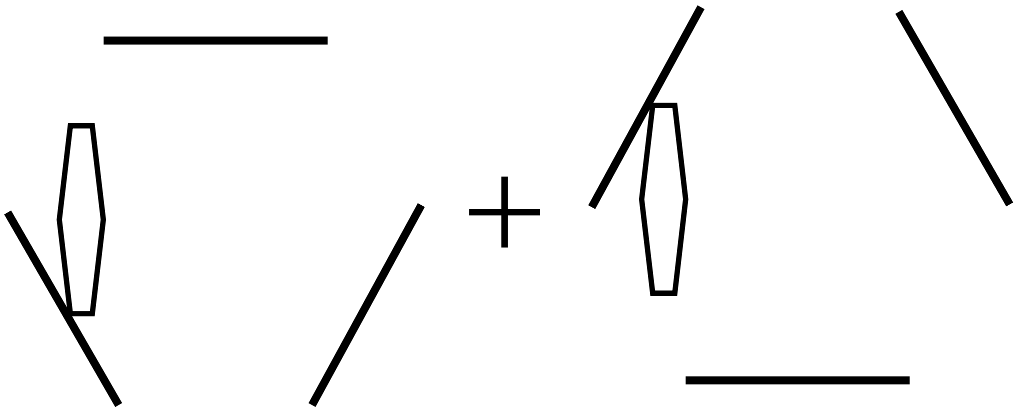
Key idea: on a lattice all interactions are nonlocal

III) Very general parametrization of the Jastrow factor, in principle complete (so vdW correct)

‘’Small’’ systems where electron correlation is very important and TurboRVB was successful

- Hydrogen and benzene (JCP’08)
- Benzene dimer (JCP ‘05)
- Beryllium dimer (Archive)
- Iron dimer (CPL ‘09)

Binding energy of aromatic molecules

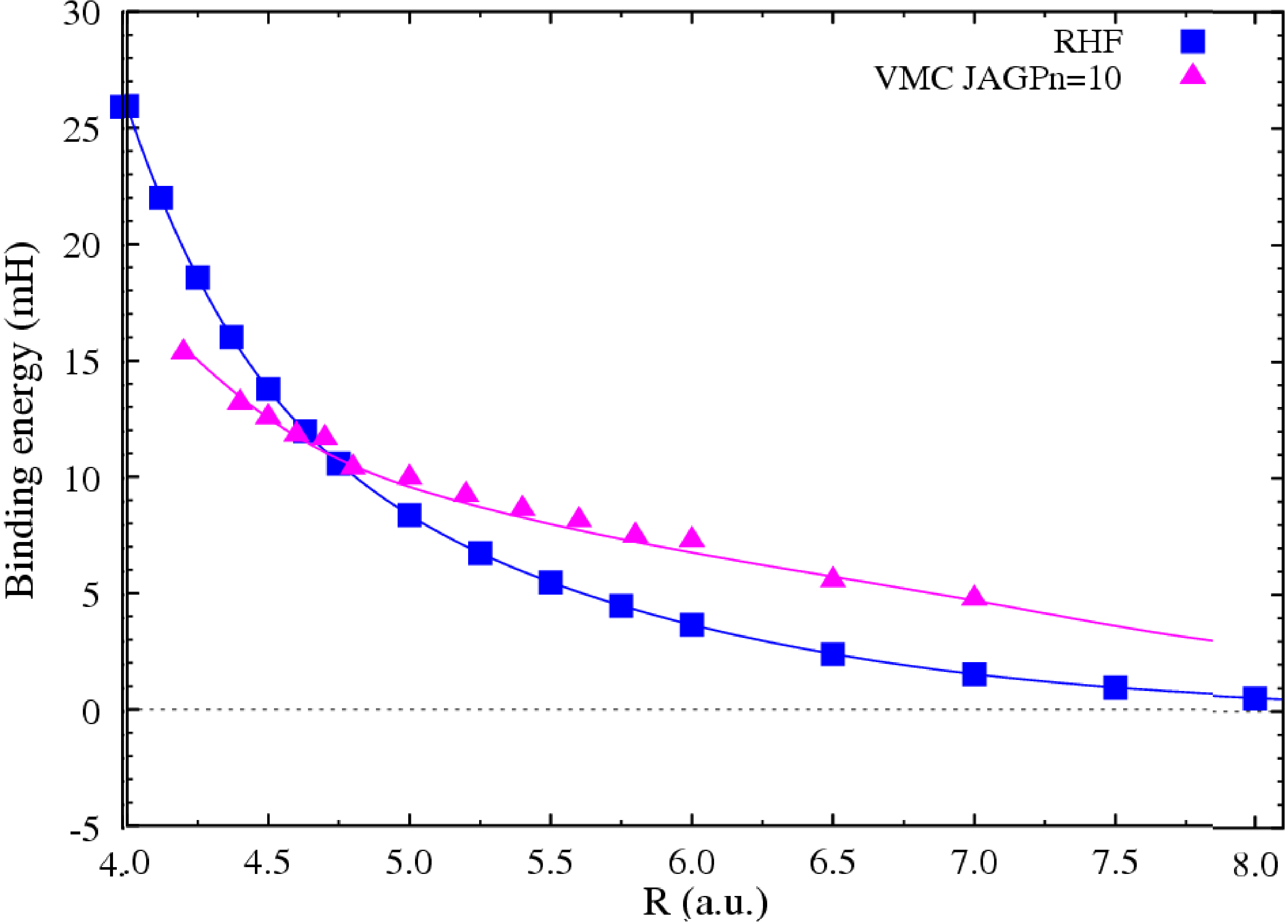


Molecule		Within RVB+LRDMC	Estimated from Exp.
C_2		6.291(7)eV	6.34(14)eV
C_6H_6		59.06(2)eV	59.24(11)eV

The Beryllium dimer

- The weakest bounded dimer (~0.1eV).
- Without vdW unbounded (HF)
- LDA binds (it is a luck?…)

Beryllium dimer: a challenging molecule



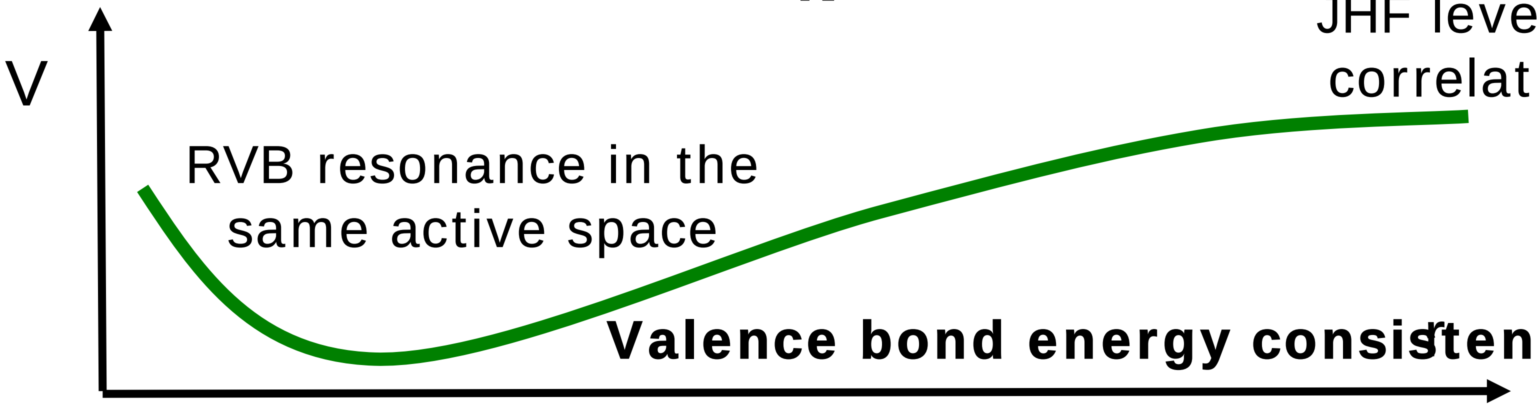
The solution:
a constrained energy minimization

Realize that the chemical bond ~eV << Atomic energy ~10H

To have an accurate description of the chemical bond **inter-atomic correlations** are more important than **intra-atomic correlations**

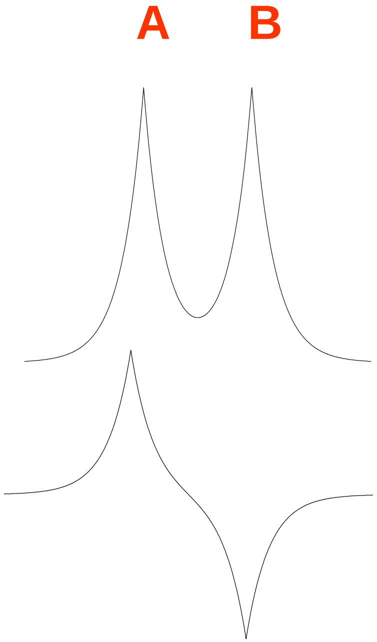
We constrain the energy minimization to have a number n* of molecular orbitals

$$n^* = \sum_A n_{HF}(A) \geq N/2$$



Valence bond energy consistent RVB

Start with a simple case: the H dimer



$1\sigma_g$

Bonding orbital

$$e^{-|\vec{r}-\vec{r}_A|}+e^{-|\vec{r}-\vec{r}_B|}$$

$1\sigma_u$

Antibonding orbital

$$e^{-|\vec{r}-\vec{r}_A|}-e^{-|\vec{r}-\vec{r}_B|}$$

$$\boldsymbol{n}^{*}=2\ \ (\text{RHF}\ \boldsymbol{n}_{\boldsymbol{HF}}=1)$$

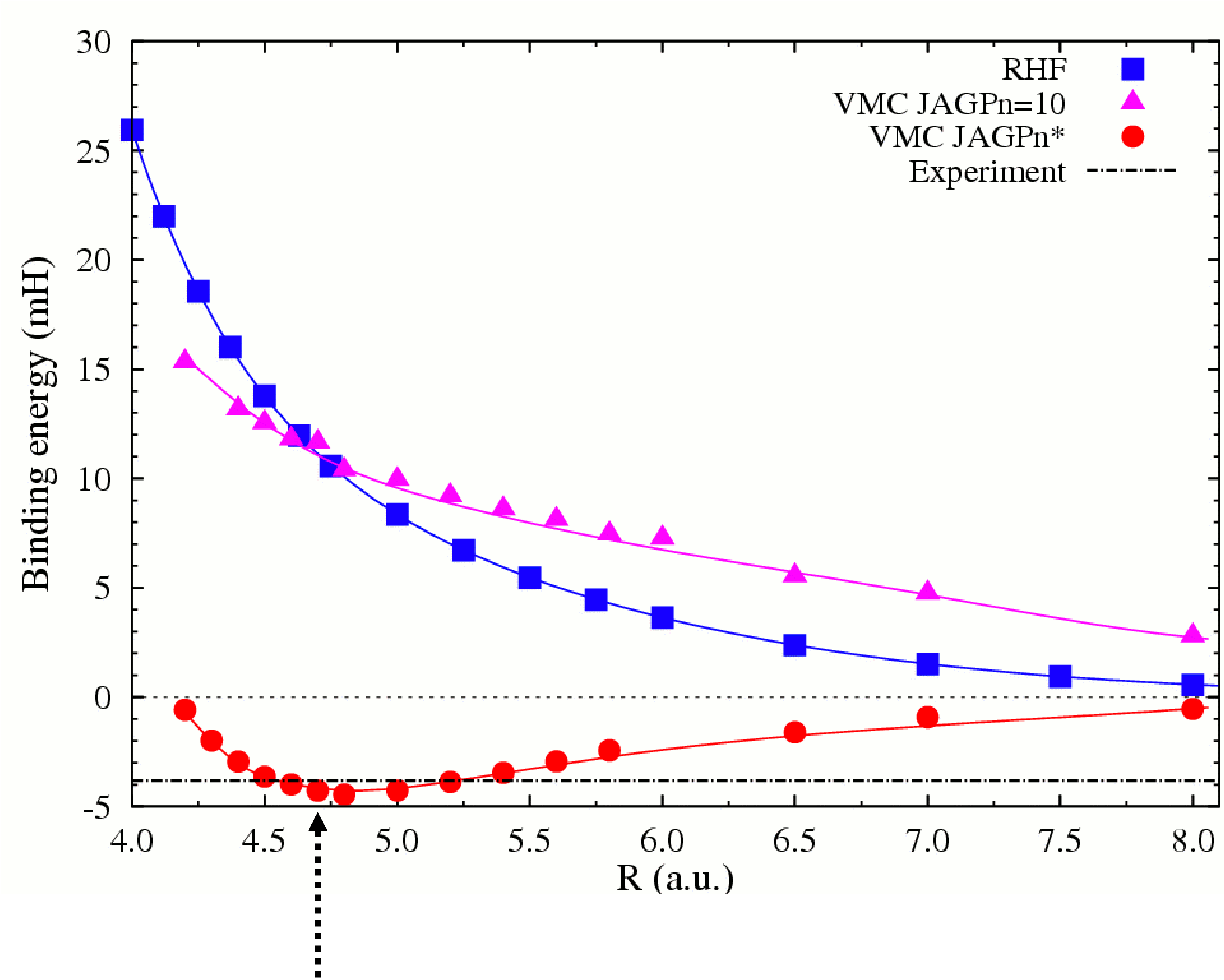
$$\boldsymbol{f}_{\vec{r},\vec{r}'}=1\sigma_{\boldsymbol{g}}(\vec{\boldsymbol{r}})1\sigma_{\boldsymbol{g}}(\vec{\boldsymbol{r}}')+\lambda 1\sigma_{\boldsymbol{u}}(\vec{\boldsymbol{r}})1\sigma_{\boldsymbol{u}}(\vec{\boldsymbol{r}}')$$

At equilibrium $\lambda = 0.25$, at large distance (strong correlation) $\lambda \to 1:$

Heitler-London:

$$=\frac{1}{\sqrt{2}}\left[\left|\overset{A}{\uparrow}\ \ \overset{B}{\downarrow}\right\rangle-\left|\overset{A}{\downarrow}\ \ \overset{B}{\uparrow}\right\rangle\right]$$

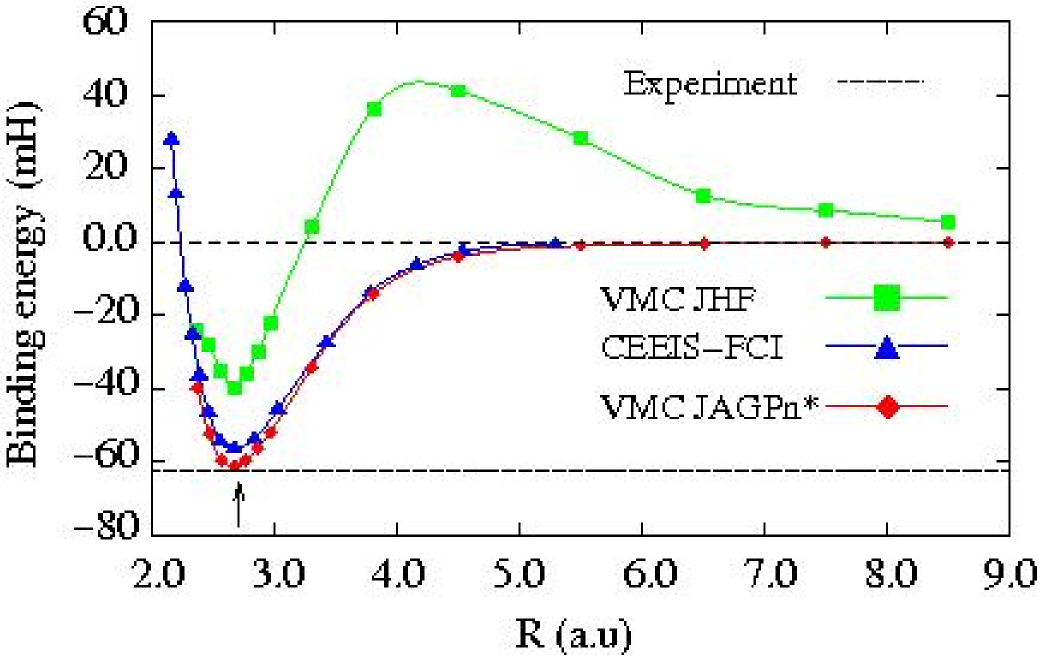
Beryllium dimer



Fluorine dimer

F_2 molecule S=0
F atom S=1/2

JAGPn* size consistent!
(bonding-antibonding resonance)



CEEIS-FCI: correlation energy extrapolation by intrinsic scaling - full CI
L. Bytautas, T. Nagata, M. S. Gordon, K. Ruedenberg, J. Chem. Phys. ***127**, 164317 (2007)*

Systematic tests on simple molecules

In several important molecules: all the first raw dimers and the most difficult ones of the G1 set: CN, LiH, SO and others (calculation in progress) the accuracy in the binding energy and bond length is from 4 to 10 times better than the previous best DMC results on single Slater determinant (J. Grossman, JCP 2002, Toulouse, Umrigar, 2008) Often the JRVB improves the accuracy of the chemical bond by an order of magnitude (e.g. F2):

The resonance valence bond really works!

Consistent description of the spectrum of the Iron dimer

Configuration (quantum numbers)	Charge	JAGPn* (eV)	EXP (eV)
$^{8}\Sigma_{u}^{-}$	+e (Anion)	**-0.89(12)**	**-0.902(8)**
$^{9}\Sigma_{g}^{-}$	0 (Neutral)	**0** **(Reference JAGPn*)**	**0** **(Reference photoemission)**
$^{7}\Sigma_{g}^{-}$	0 (Neutral)	**+0.64(7)**	**+0.534(4)**
$^{7}\Delta_{u}$	0 (Neutral)	**-0.44(9)**	**no accessible from photoemission**

$$\text{Equilibrium distance } ({}^{7}\Delta_{u}) : 3.89(2) \quad \text{Exp.} : 3.82(2)$$

From chemistry to solid state physics &HTc

Problems (NB sign problem is not in the list):

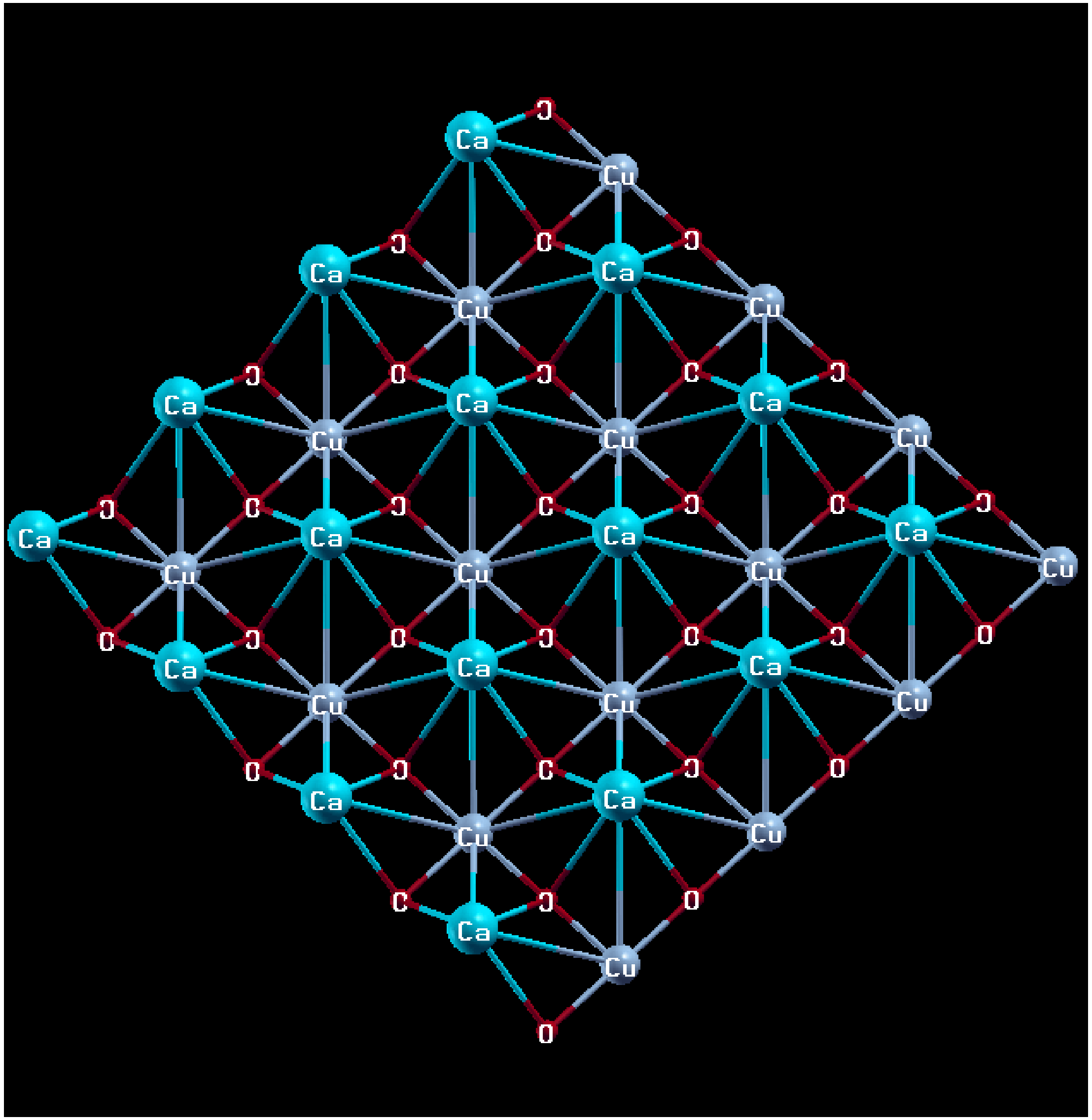
1)Pseudopotential for QMC are often not available
  e.g. La is a problem.

2) Correlated periodic systems:
  difficult to reach thermodynamic properties.
  DFT simple→ Average over k vectors (linear).
  QMC→ system large enough. #el^2 complexity

3) Error bar small enough for large systems…
  e.g. condensation energy is ~10K/Cu
  Error bar so far reached is 100K/Cu.

QMC→ huge computer time, next 5 years?

$CaCuO_2$ the parent compund of HTc superconductors



4x4 unit cell 64 atoms and 544electrons by QMC

Calculation details

Dolg-Filippi pseudopotentials

neon core

spd non local components

scalar relativistic corrections included

Gaussian basis set for orbitals wave function

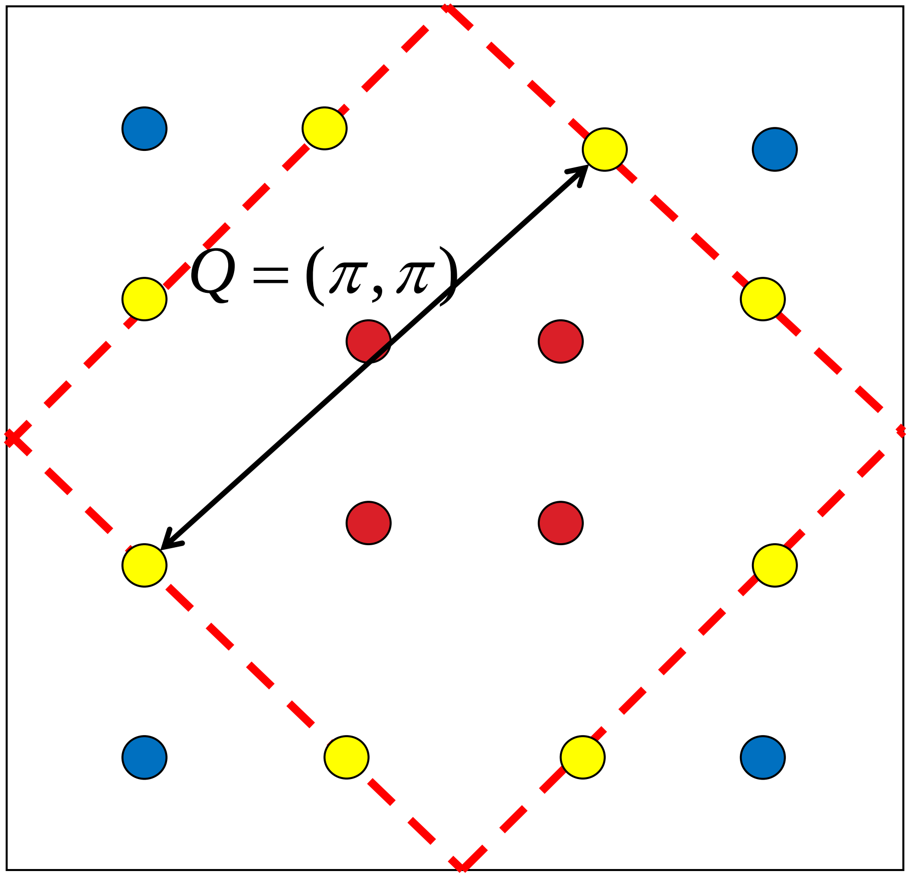
Cu (8s7p5d2f)

O (4s5p2d2f)

Ca (6s6p2d1f)

Total one particle basis: ~5000 gaussians.

4x4 supercell with antiperiodic boundary cond.



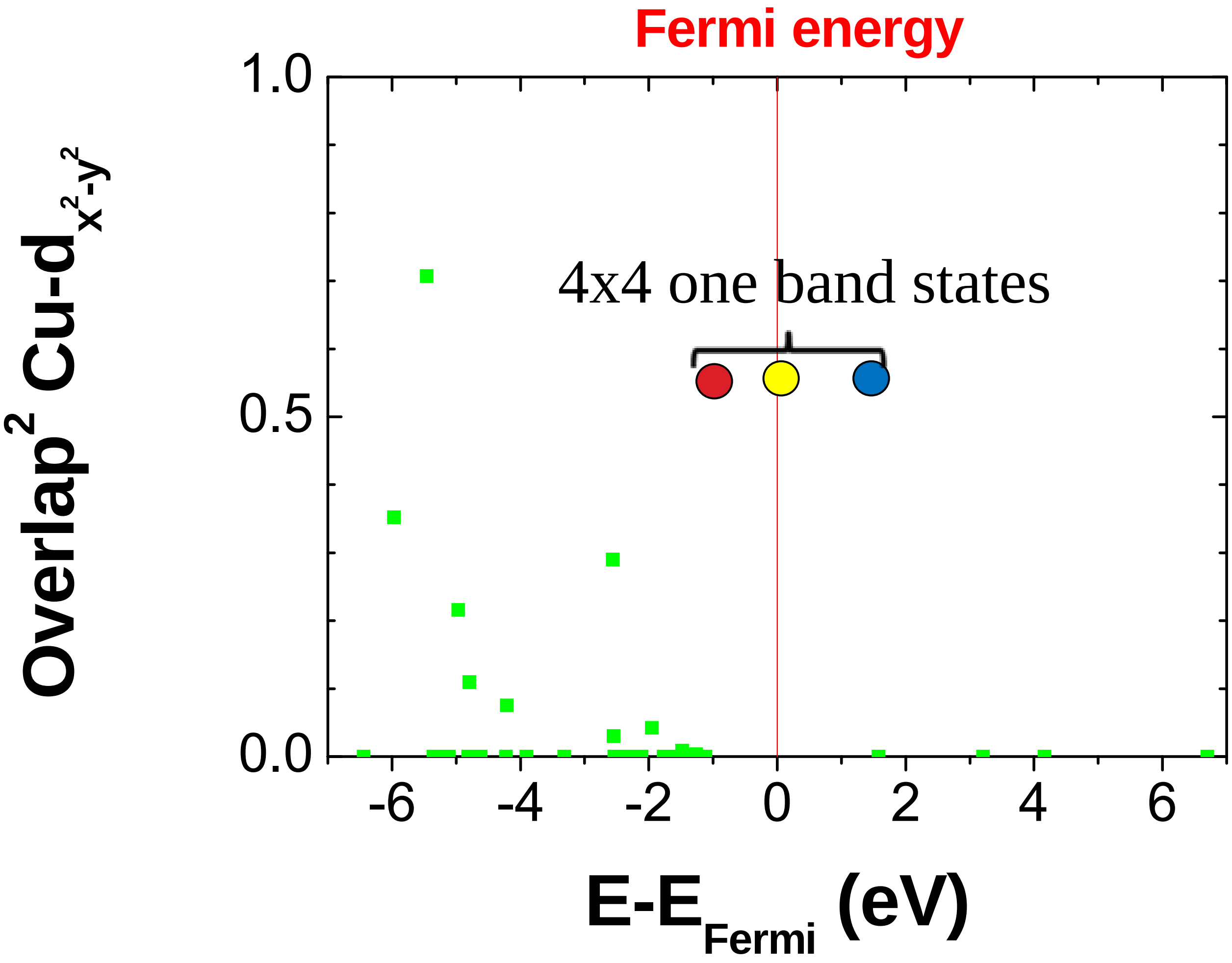
🔴 $(\pm\frac{\pi}{4},\pm\frac{\pi}{4})$

🟡 $(\pm\frac{3\pi}{4},\pm\frac{\pi}{4}),(\pm\frac{\pi}{4},\pm\frac{3\pi}{4})$

🔵 $(\pm\frac{3\pi}{4},\pm\frac{3\pi}{4})$

There are 16 states occupied 4x2(spin) 🔴 so the 8 🟡 degenerate → half occupied for each spin→ AF

Characterizing the DFT orbitals



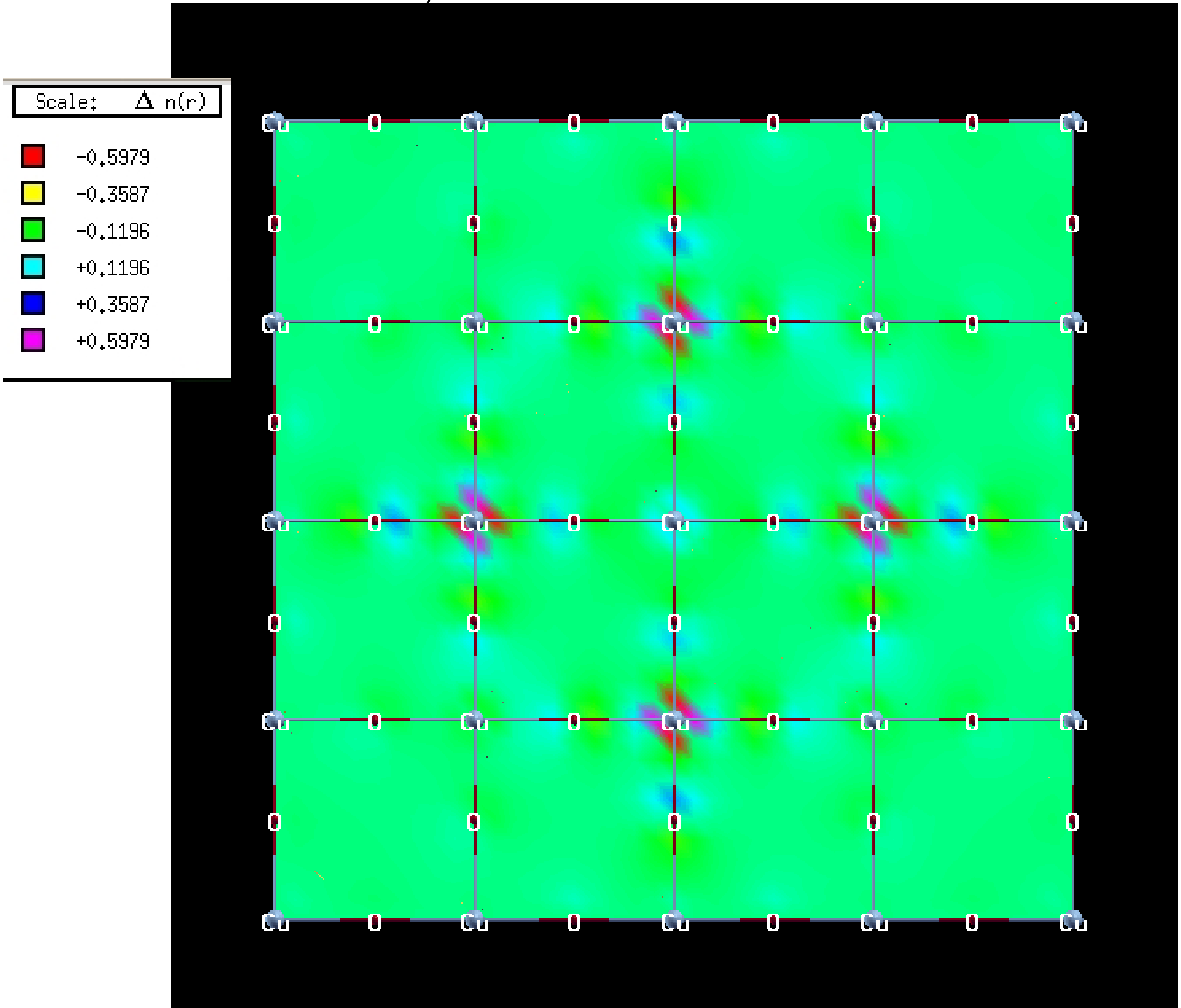
One can classify the 8 ● degenerate DFT orbitals in terms of point spatial group symmetries

1 s (x^2+y^2)	defined on	A sublattice	
1s (odd x<->y)	=	B	=
1d (xy)	=	B	
1d (x^2-y^2)	=	A	=
2E (x+iy p-wave)	linear combination in A or B		

Thus 4 molecular orbitals are in the A and 4 in B

→ Easy to build AF (4 up in A and 4 down in B)

A typical molecular orbital at the Fermi energy: localized $d_{x^2-y^2}$ character on the Copper.



We use DFT orbitals and combine them in an AF fashion to gain energy:

$$\text{Lattice model} \rightarrow u_k e^{ikR} \pm v_k e^{i(k+Q)R}$$

$$\text{Real electrons} \rightarrow u_k \left| k \right\rangle_{DFT} \pm v_k \left| k+Q \right\rangle_{DFT}$$

We optimize all possible u_k v_k and include a Jastrow factor fully optimized and local (analogous to Gutzwiller wavefunction). Total of ~200 variational parameters.

By considering the LDA molecular orbitals and optimizing the energy with AF order and Jastrow correlation we obtain (4x4 unit cell point):

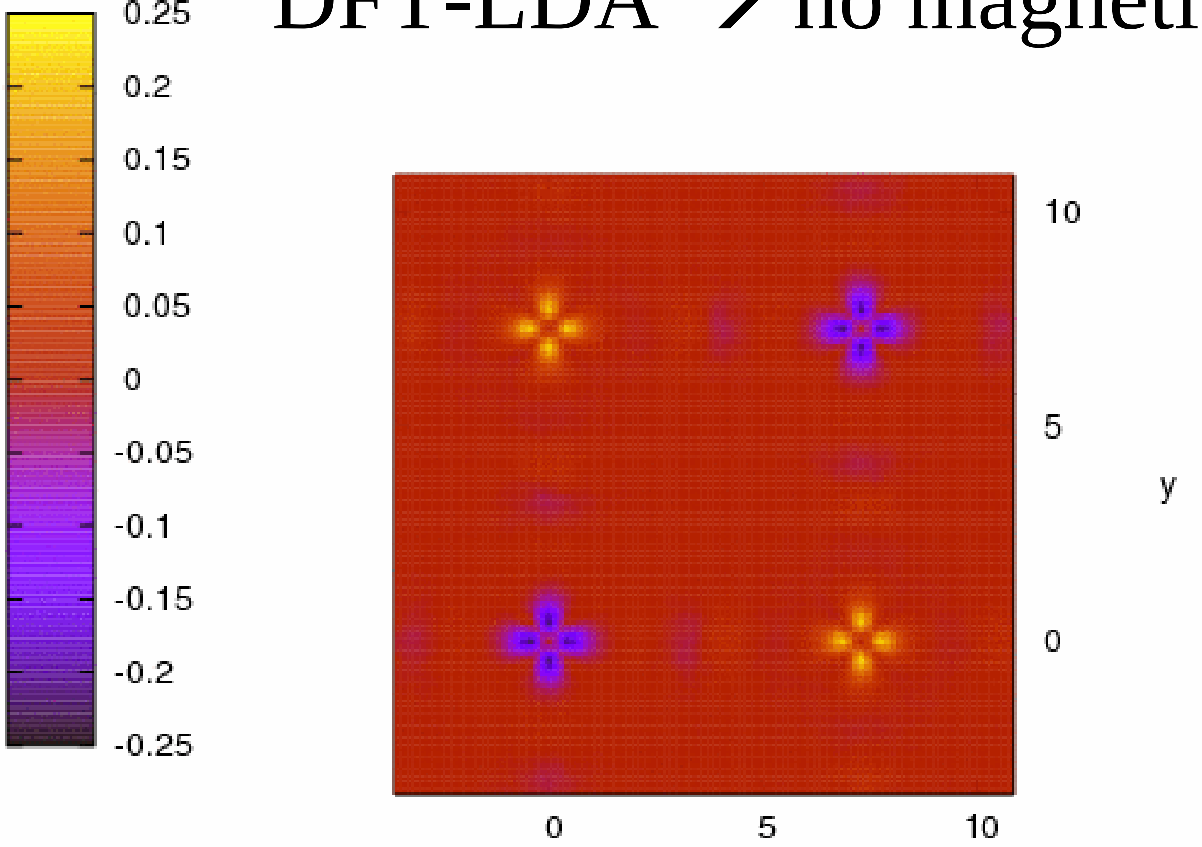
Magnetic moment $CaCuO_2$ (μ_B)

LSDA	HF	LDA+U	B3Lyp	VMC RVB	Exp
0.0	0.89	0.66	0.51	0.572±0.003	0.51±0.05

It is clear that the missing ingredient of LSDA is the correct exchange energy.

4x4 unit cell 64 atoms and 544electrons by QMC
The spin density in CaCuO2 parent compound HTc

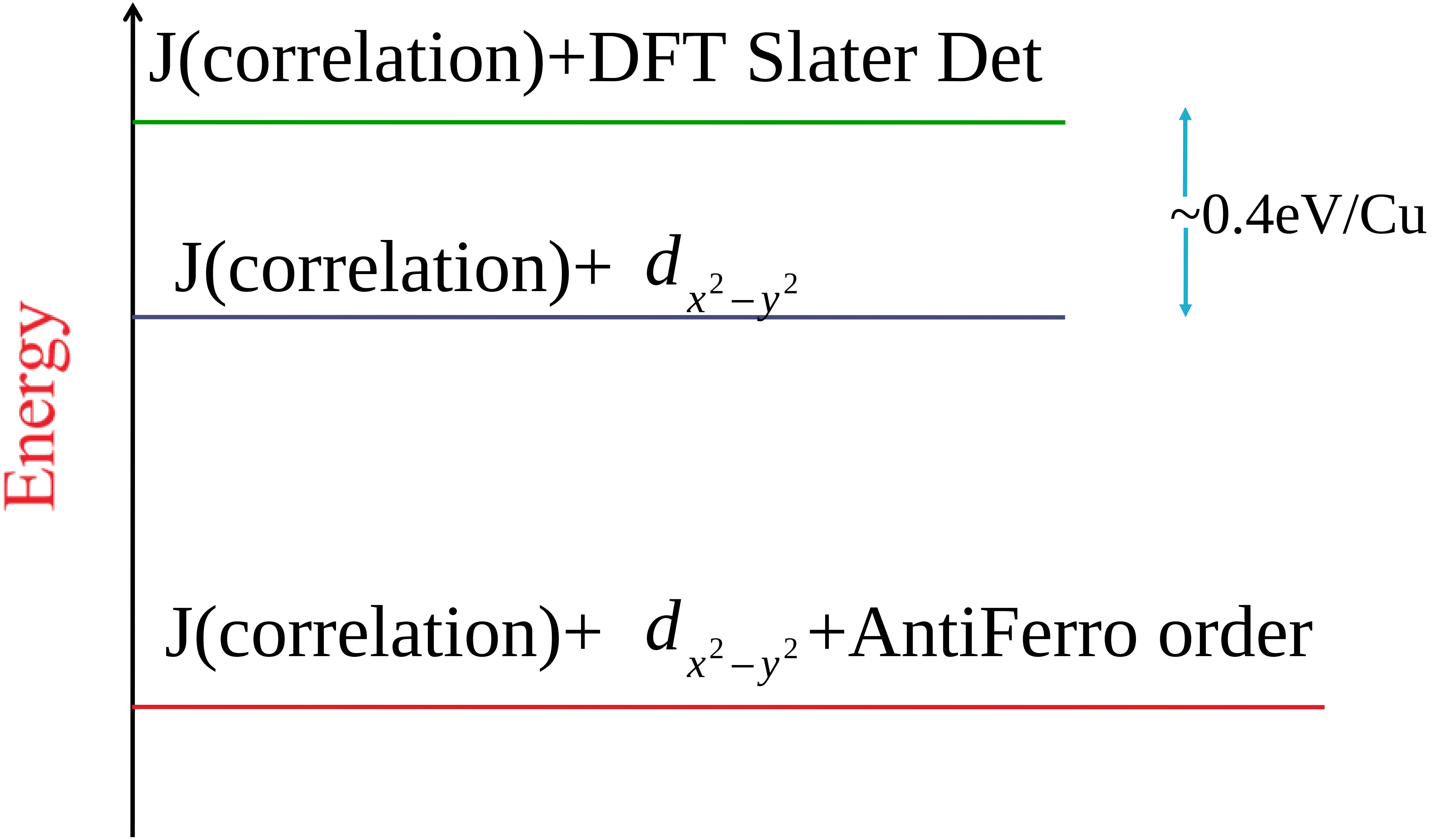
DFT-LDA → no magnetic moment



QMC takes into account electron correlation and
leads to AF order compatible with exp. ~0.51±0.05

This is a promising result, probably the initial step
to understand HTc-superconductivity by simulation

As in the one band HM can we gain energy in the insulator by allowing $d_{x^2-y^2}$ pairing?



J(correlation)+DFT Slater Det

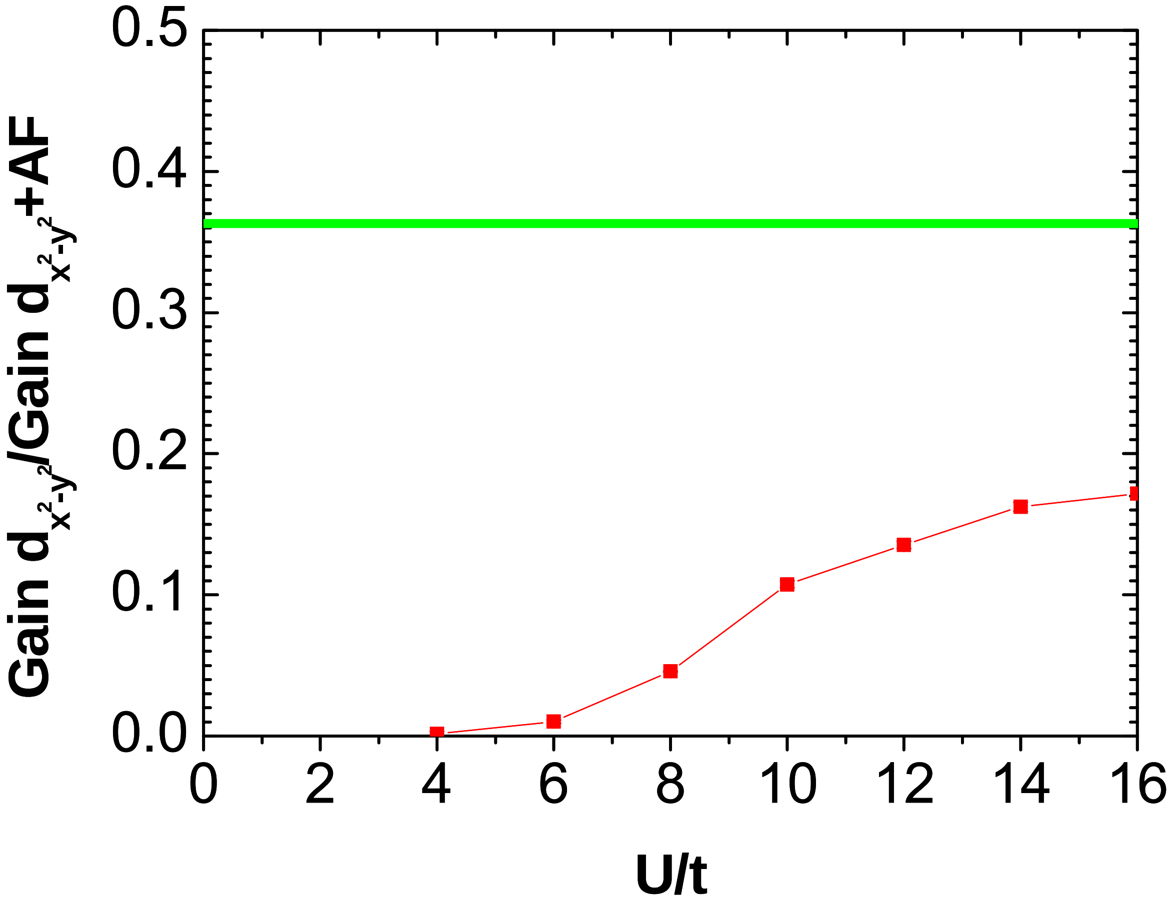
~0.4eV/Cu

J(correlation)+ $d_{x^2-y^2}$

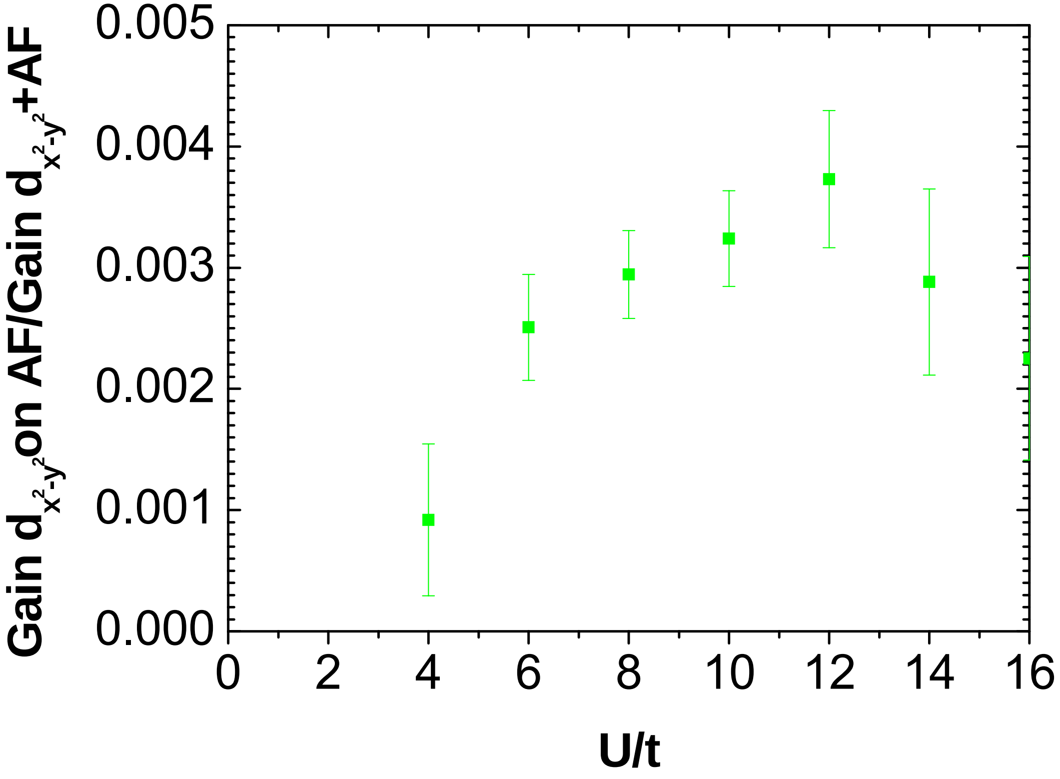
Energy

J(correlation)+ $d_{x^2-y^2}$+AntiFerro order

Comparison with the Hubbard model

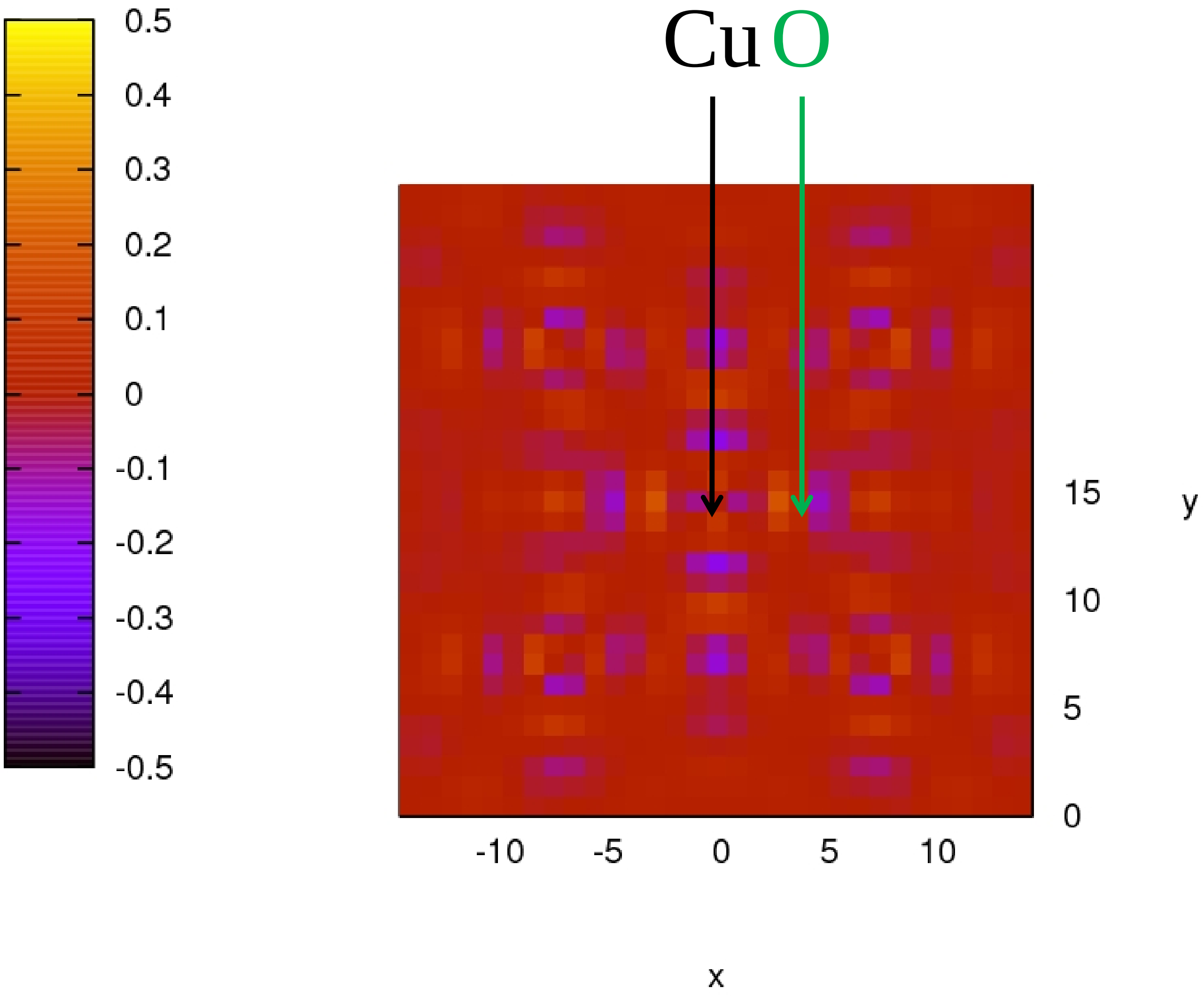


The true ‘’pairing’’ condensation energy is the BCS gain in energy with respect to the AF state



Not accessible in realistic simulation → too small error bars. Probably with correlated sampling.

How the d-wave pairing looks like in a realistic calculation?



Remark:

There is a clear energy gain to have a pairing function with d-wave symmetry.

This is clearly not a direct evidence of RVB HTc

But at least does not exclude this theory, as if no d-wave energy gain→ RVB death.

Conclusions

The RVB wavefunction is a new paradigm for Mott insulators: paired, gapless, Fermi…

From lattice model to realistic simulations:
A new accurate and ‘’cheap’’ method for physics/chemistry
RVB=JAGP with constrained number of molecular orbitals:

Accurate description of dispersive forces by means of a more accurately parametrized Jastrow

First consistent description of Iron dimer spectrum (Chem. Phys. Lett.)

It looks in all cases studied accurate <0.1eV/Atom and is ‘’cheap’’ because requires 1Det + QMC

Application to HTc materials in progress, promising

Acknowledgments

- Main developers of the TurboRVB, the QMC code used in this work:

Michele Casula (Ecole Polytechnique, Palaiseau, France),

Claudio Attaccalite (San Sebastian, Spain)

Leonardo Spanu (UC Davis)

- H_2 @ benzene

Todd Beaudet (UIUC)

Jeongnim Kim (UIUC)

Richard Martin (UIUC)

- benzene dimer

Dario Rocca (UC Davis)

- first row dimers

Mariapia Marchi (SISSA)

Sam Azadi (SISSA)

- iron dimer

Leonardo Guidoni (Universita' dell'Aquila)

- **Lattice models**

Federico Becca, Luca Tocchio, Evgeny Plehanov, M. Lugas (SISSA).

Grants: Cineca INFM, Cineca SISSA, QMCHTC DEISA (2009), 266000hours on sp6.

The generalized Langevin dynamics

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

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

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

Discretization of the Langevin dynamics

$$
\begin{aligned}
\vec{v}_{n+1} &= e^{-\bar{\gamma}\Delta}\vec{v}_{n-1} + \bar{\Gamma}(\vec{f}(\vec{x}_n) + \tilde{\vec{\eta}}) \\
\vec{R}_{n+1} &= \vec{R}_n + \Delta\vec{v}_n \\
\bar{\Gamma} &= \bar{\gamma}^{-1}(1 - e^{-\bar{\gamma}\Delta}) \\
\tilde{\vec{\eta}} &= \frac{\bar{\gamma}}{2\sinh(\Delta/2\bar{\gamma})} \int\limits_{t_n-\Delta/2}^{t_n+\Delta/2} dt e^{\bar{\gamma}(t-t_n)}\vec{\eta}(t)
\end{aligned}
$$

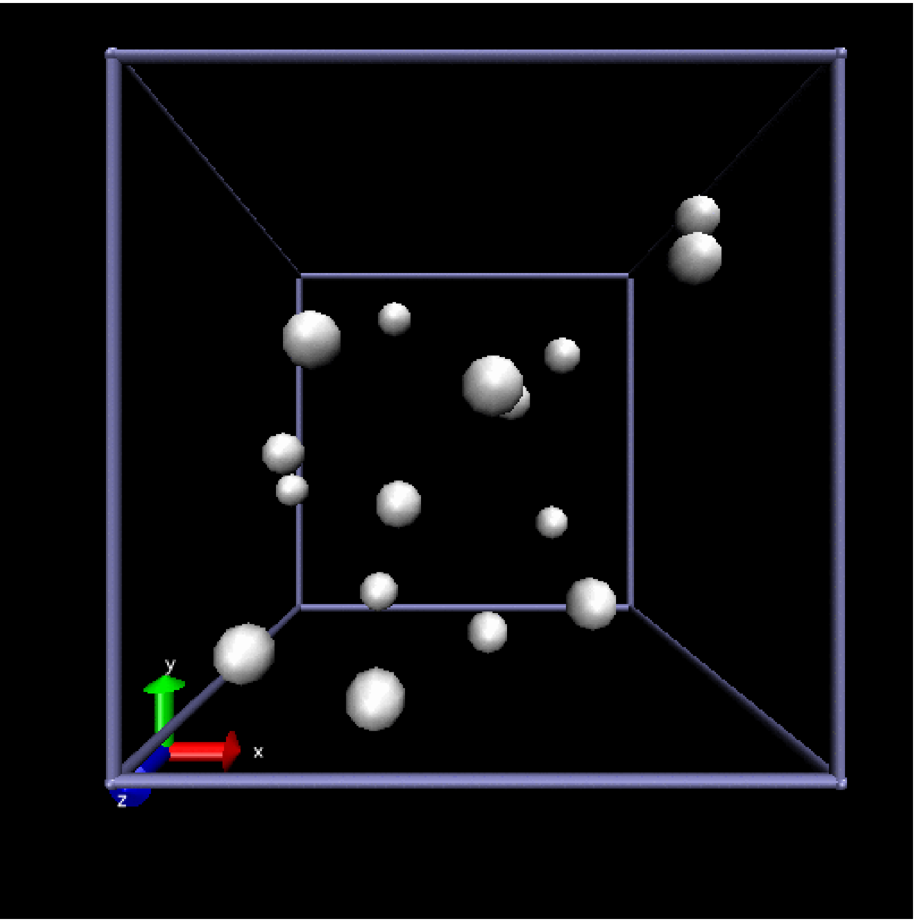
$$\bar{\alpha}(\vec{R}) = \bar{\alpha}_0 + \Delta\bar{\alpha}_{QMC}(\vec{R})$$

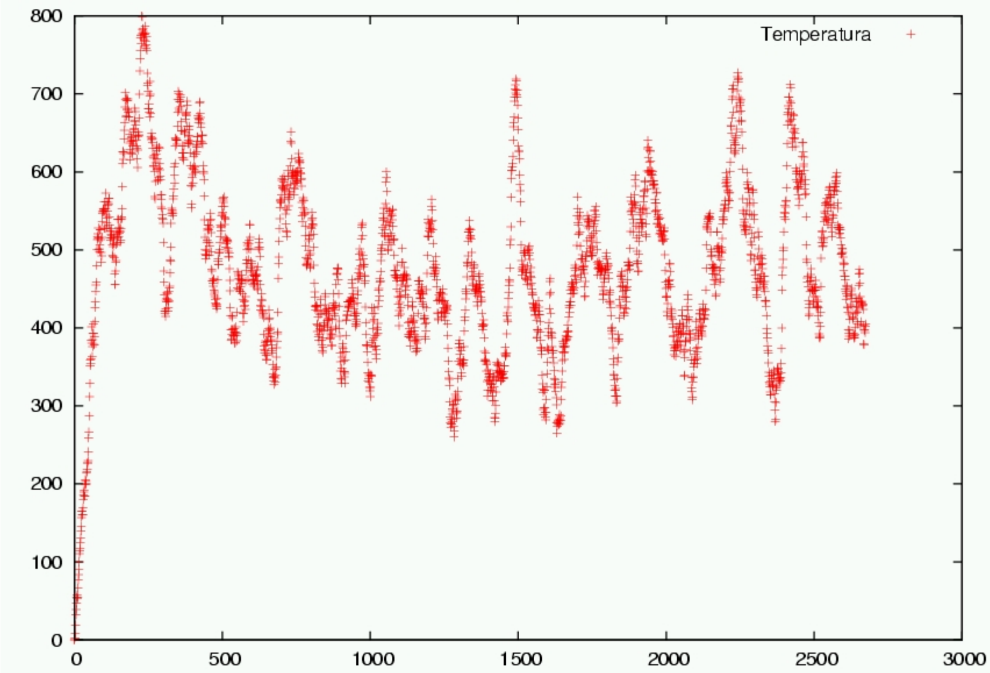
$$\boxed{\bar{\gamma}(\vec{R}) = \frac{\beta}{2}\bar{\alpha}(\vec{R})}$$

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

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

The 16 H case with PBC, MD with friction





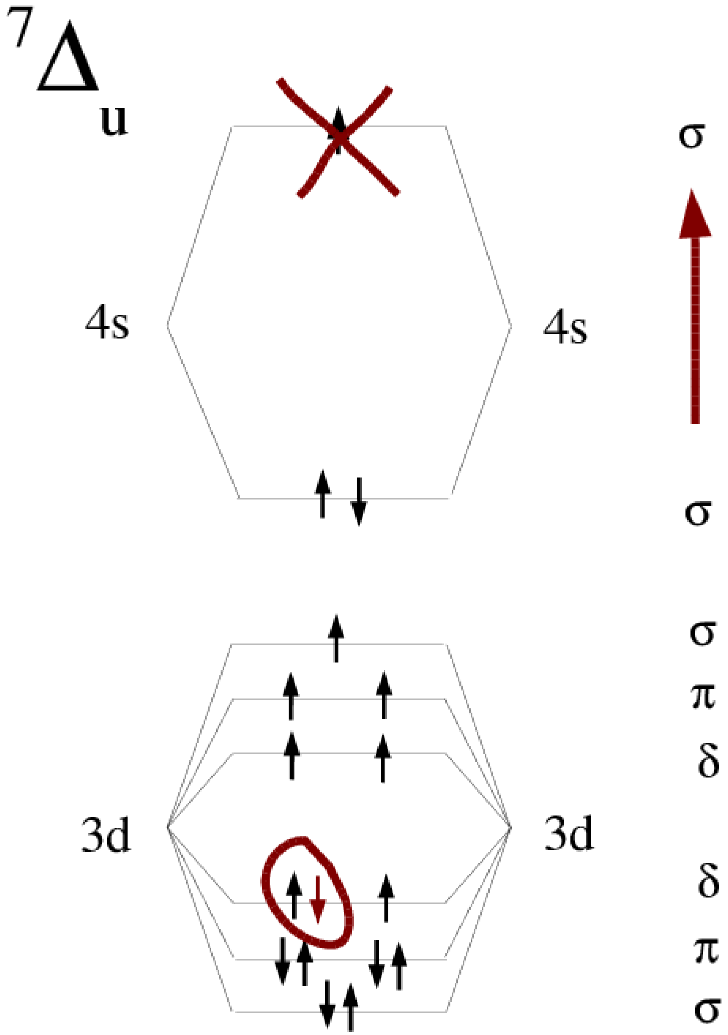
RVB liquid phase possible at high pressure

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	?	$^7\Delta_u$	$^9\Sigma_g^-$	$^9\Sigma_g^-$

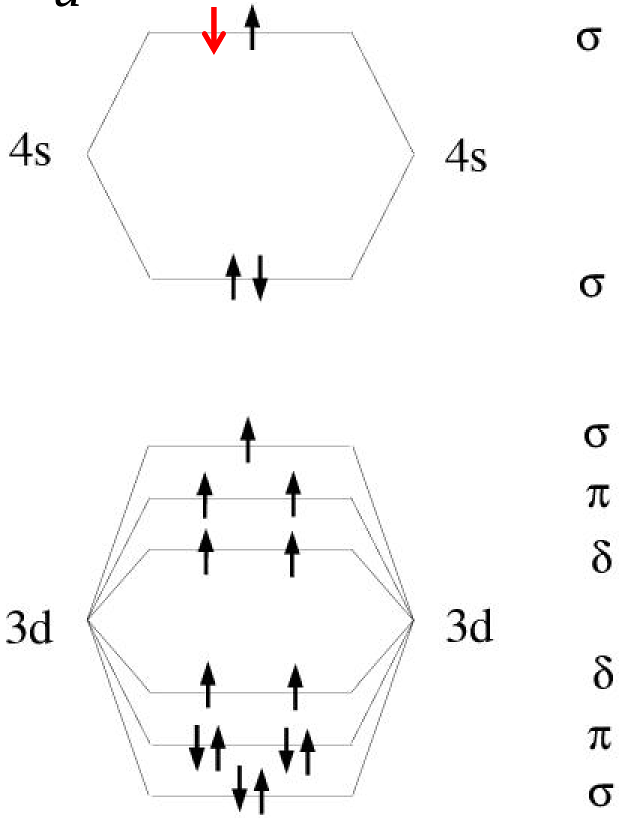
It is possible to explain the photoemission spectrum in the anion Fe_2^-
<u>Leopold</u> JPC (1988)

DFT occupation molecular orbitals

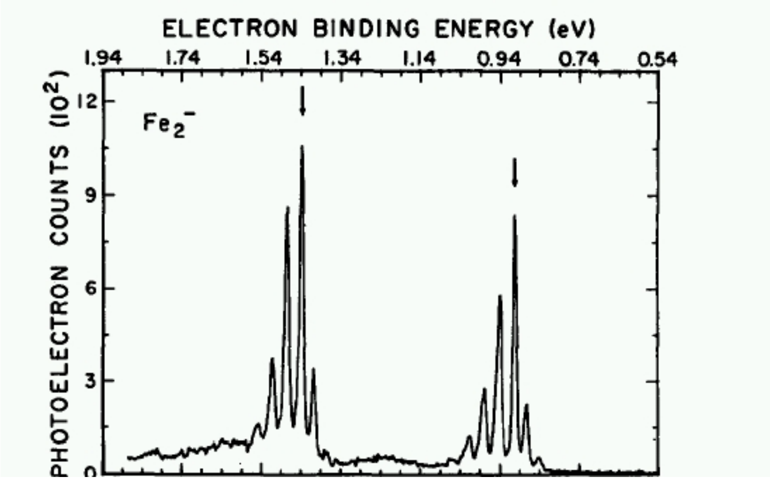


The right occupation is due to correlation

$^8\Sigma_u^-$



Explains the Fe_2^- exp



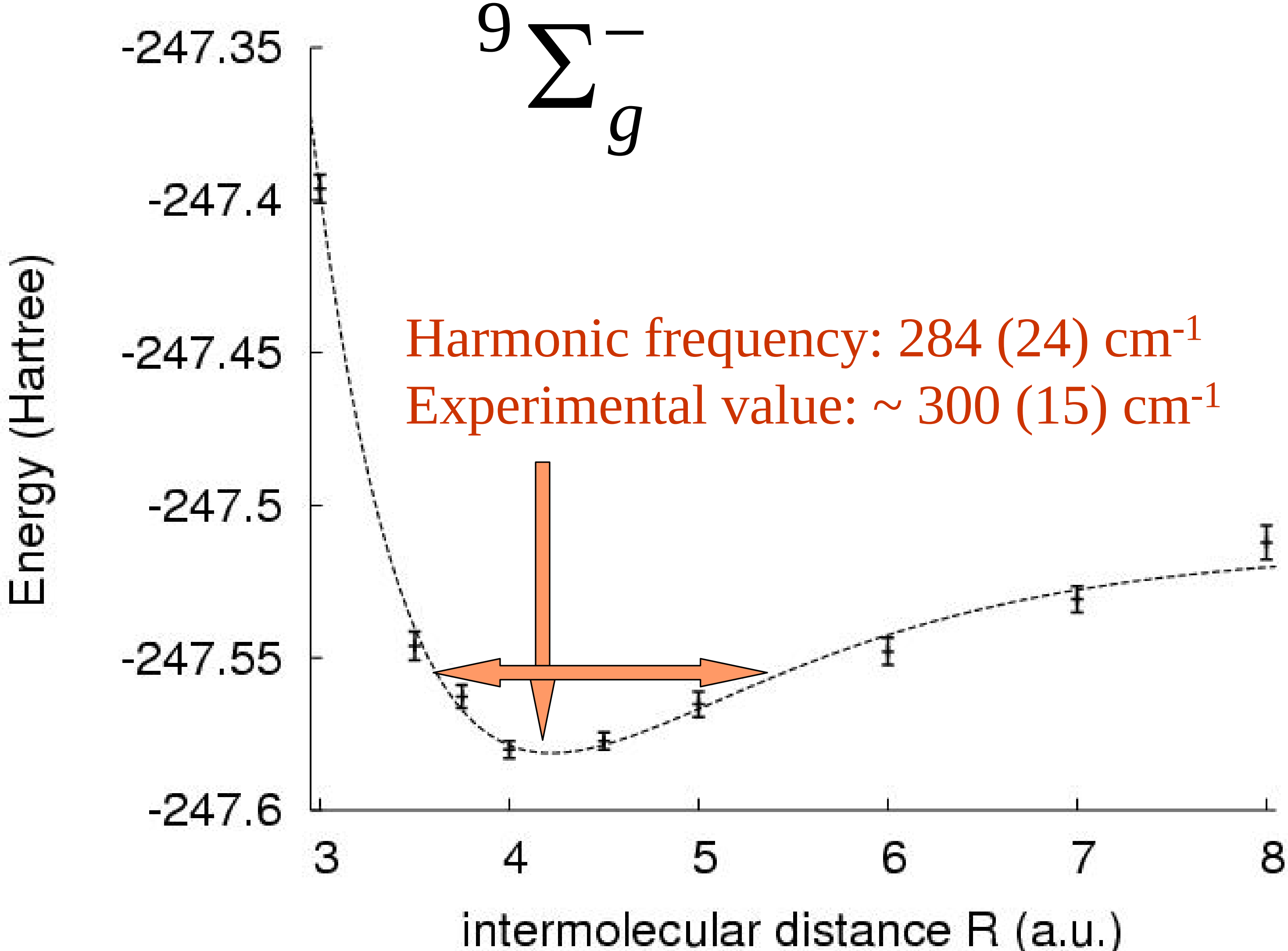
Within our RVB wf

$^7\Delta_u$ is 0.7 eV higher

Confirmed also by recent CI, Hubner JPC'02

Iron dimer (II)

$$^{9}\Sigma_{g}^{-}$$



Harmonic frequency: 284 (24) cm^{-1}

Experimental value: ~ 300 (15) cm^{-1}

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

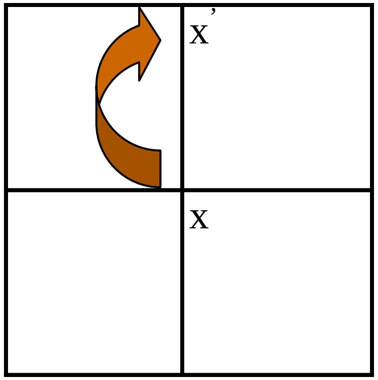
Final goal:
simulation of complex correlated electron systems by Monte Carlo calculation and beyond DFT

Lattice GFMC

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

Green function: $G_{x,x'} = (\Lambda\delta_{x,x'} - H_{x,x'})\frac{\Psi_T(x')}{\Psi_T(x)}$ ⇒ 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

⇒ **FN approximation**

(see D.M.Ceperley et al. PRB **51**, 13039 (1995))

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** $V \to V^a + O(a^2)$

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

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

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**

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

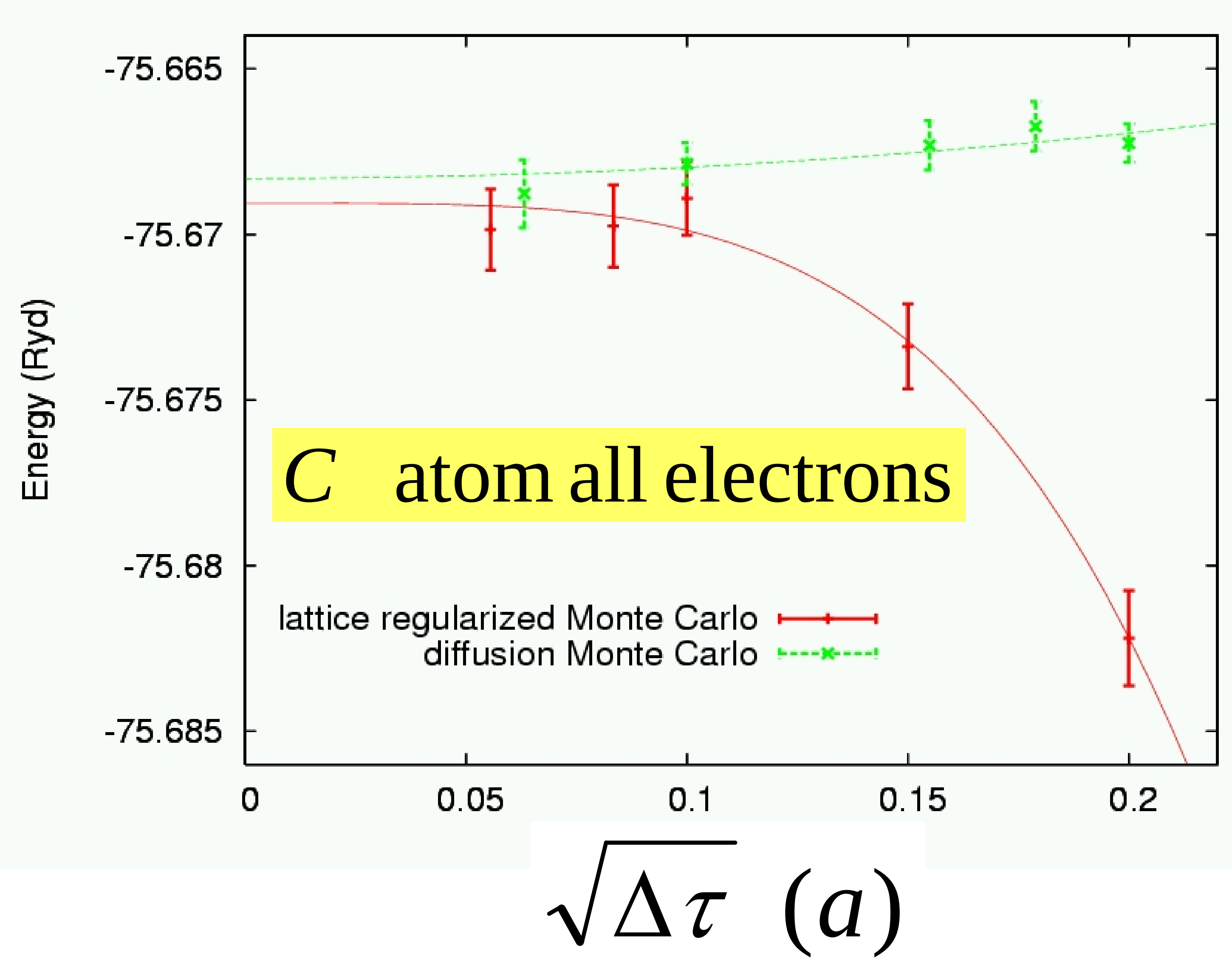
p can depend on the distance from the nucleus

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

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

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

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



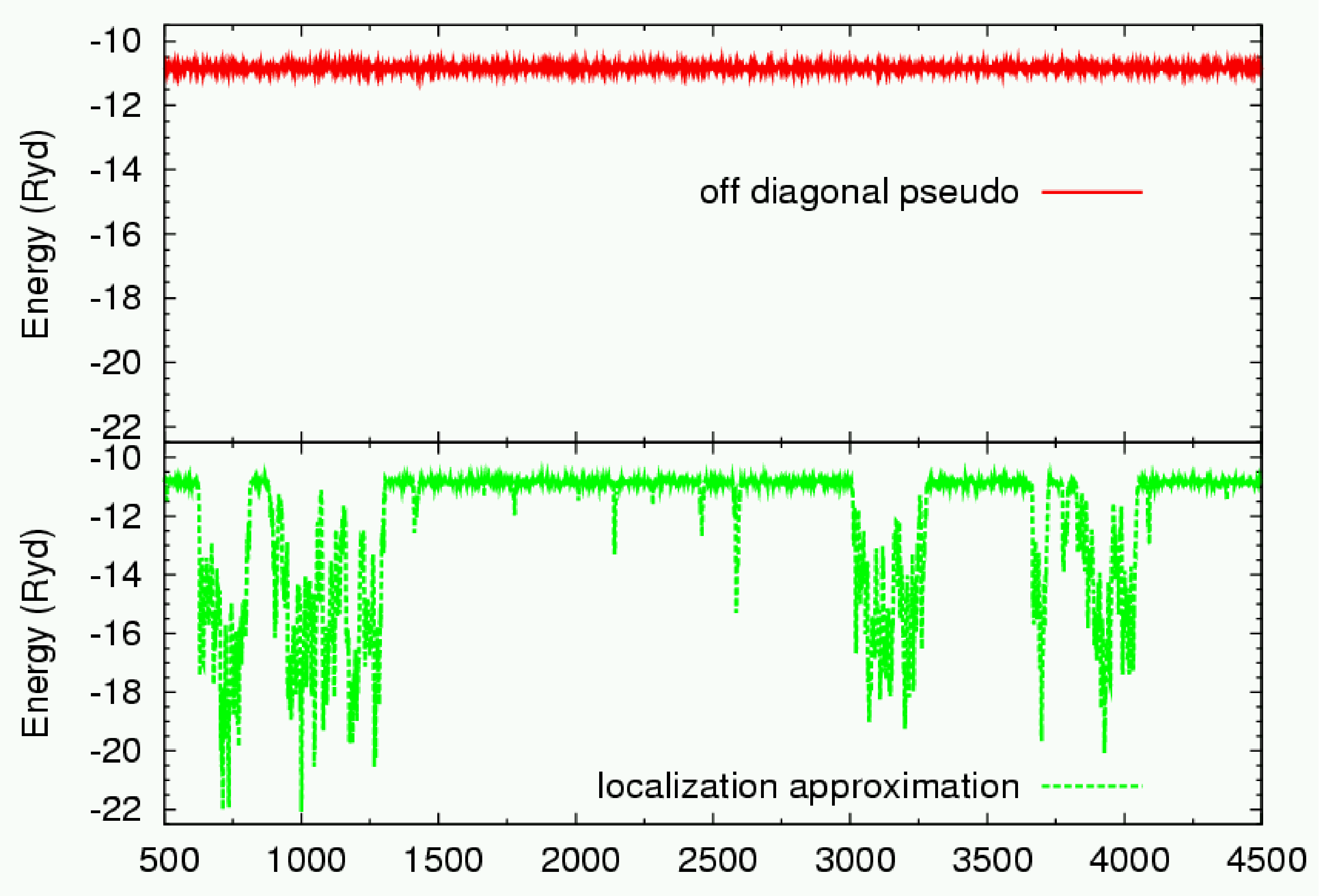
Non local pseudo possible!!!

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

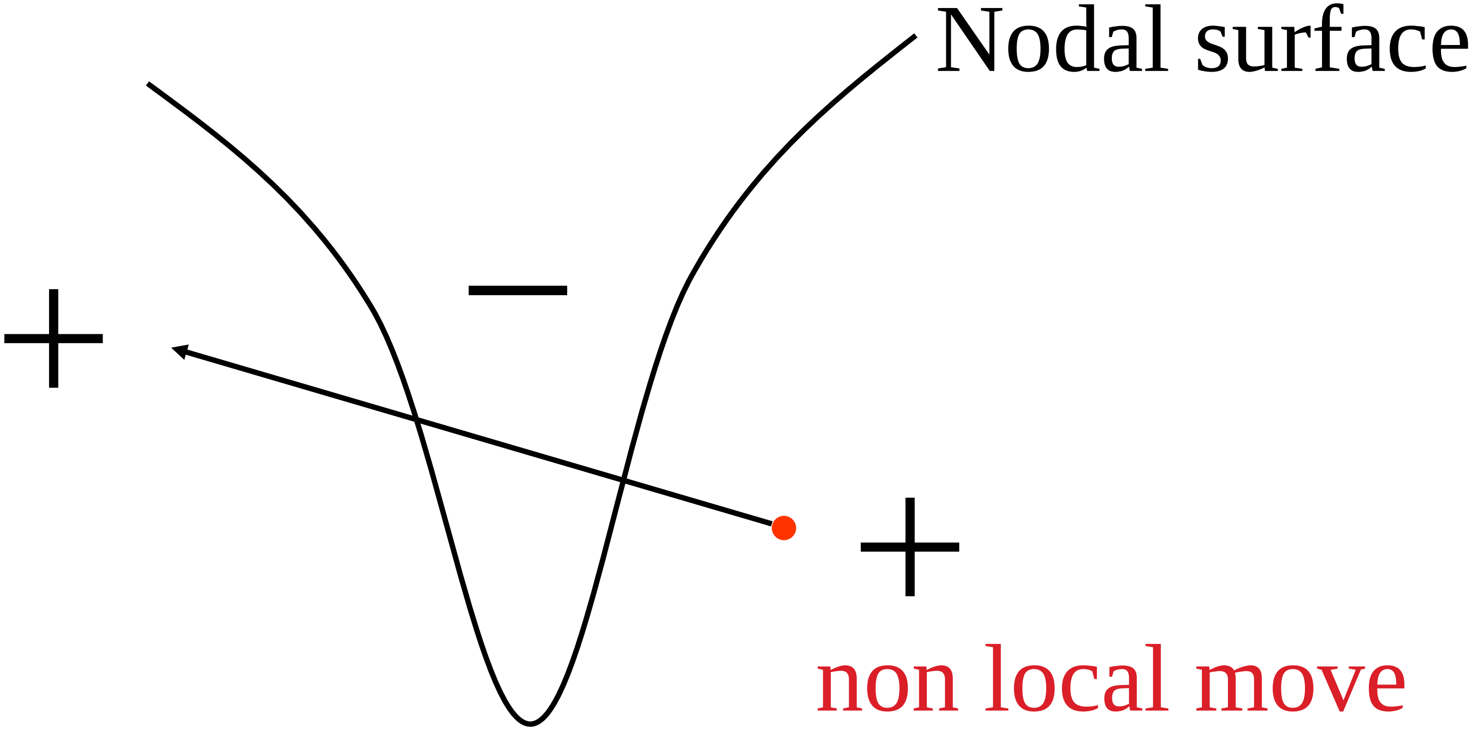
1) No localization approximation employed
2) Still variational upper bound theorem holds exactly as in the lattice fixed node
3) It works also without Jastrow optimization
4) The fixed node energy depends only on the nodal structure and weakly on the amplitudes

The disease of the localization approximation

C pseudoatom with **4** electrons (**2** core)



Why is that?



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.

Targets

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

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

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

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

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

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

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

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

Note: exact for bosons and in the classical limit $\hbar \to 0$

‘’Philosophy’’ of the approach

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

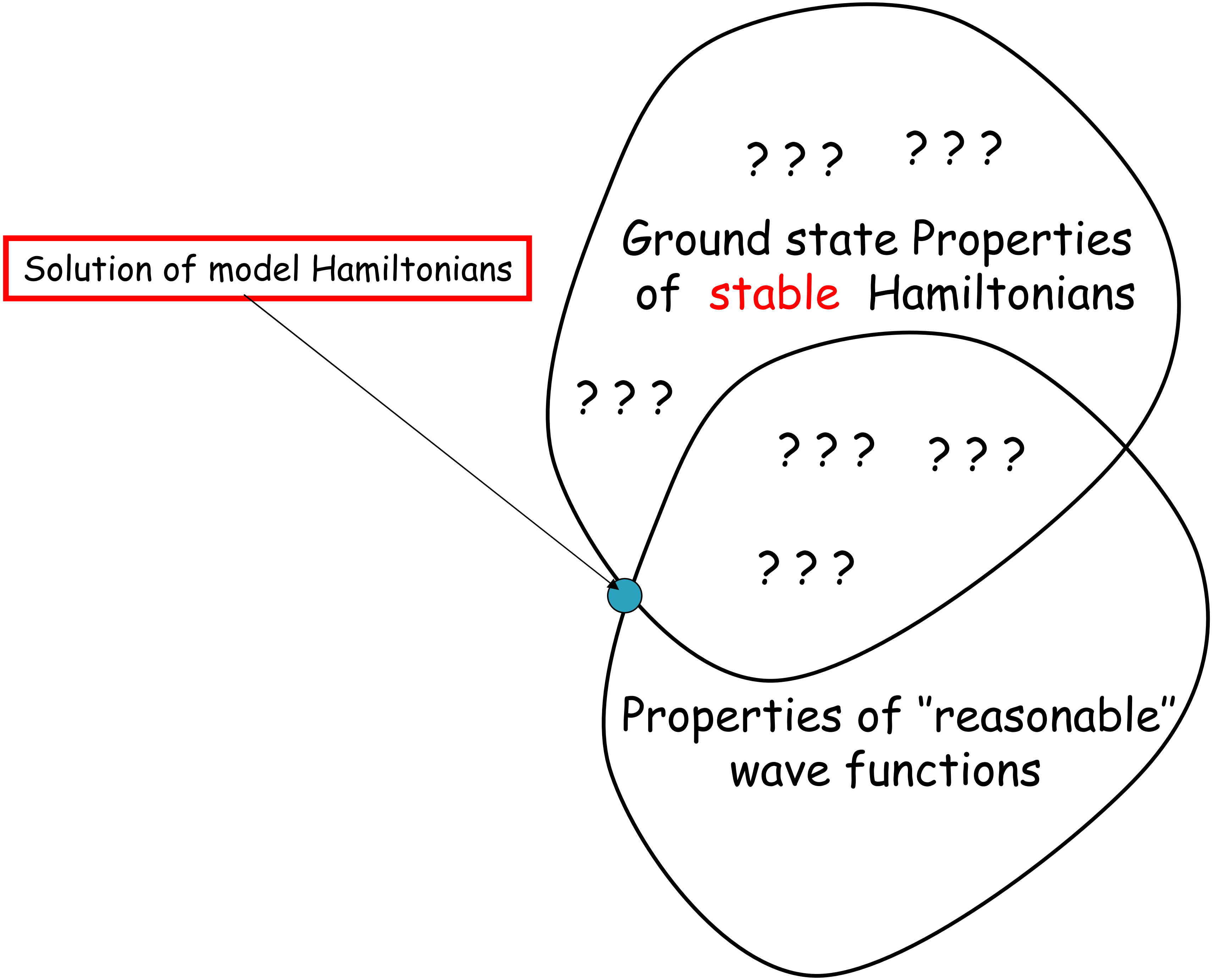
$$H \to H + \delta V$$

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



Solution of model Hamiltonians

? ? ?   ? ? ?

Ground state Properties
of stable Hamiltonians

? ? ?

? ? ?   ? ? ?

? ? ?

Properties of "reasonable"
wave functions

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

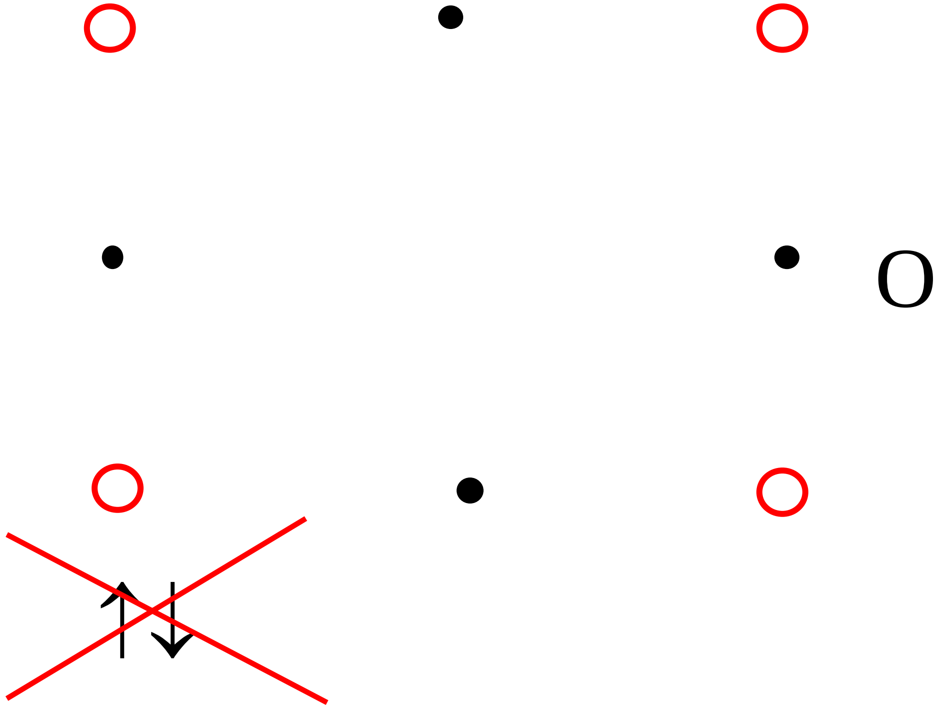
S. Sorella Phys. Rev. B 2001

Outline of the lecture:

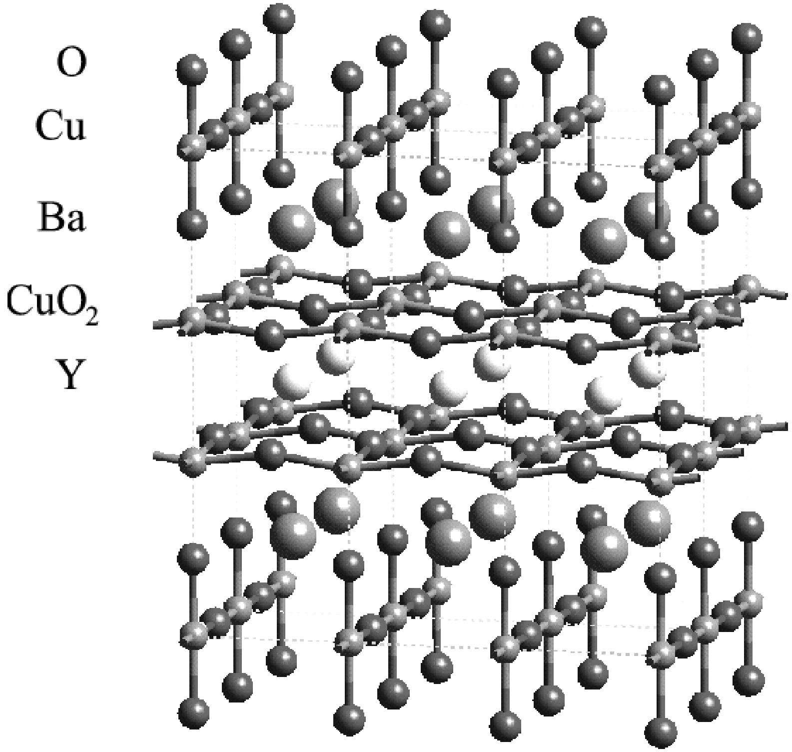
- The Lanczos algorithm and variance extrapolation
- Beyond the variational approach: the fixed node approximation
- Generalized Lanczos by Stochastic Reconfiguration
- Application to the t - J model: $\begin{cases} \text{d - wave superconductivity for J/t >~ 0.2} \\ \text{effective t - J model for } La_2CuO_4 \end{cases}$

Kerkrade 24/2-1/3-2002

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



P → Strong correlation



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

Lanczos with QMC on lattice models (L sites):

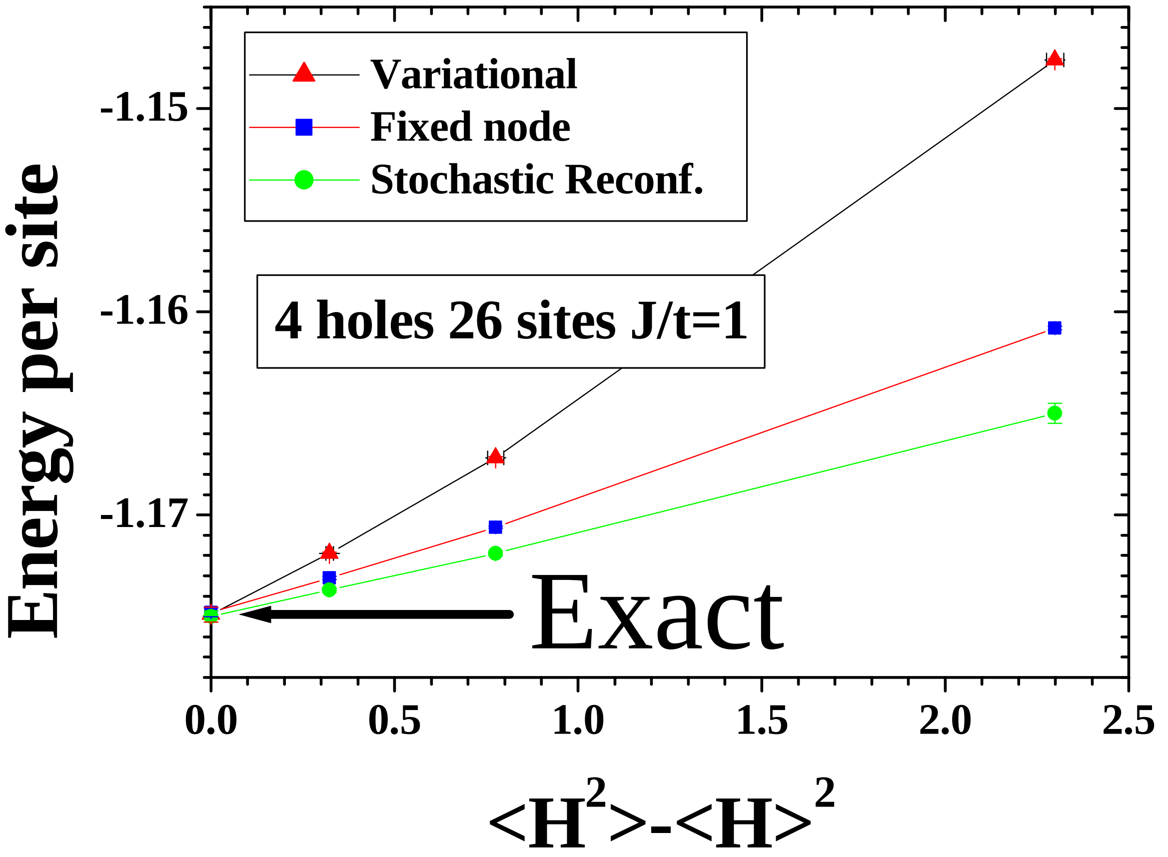
For p>1 Lanczos steps #operation /MC $\sim L^{p+1}$

Always polynomial at fixed p.

Probably improvement to p! # operations

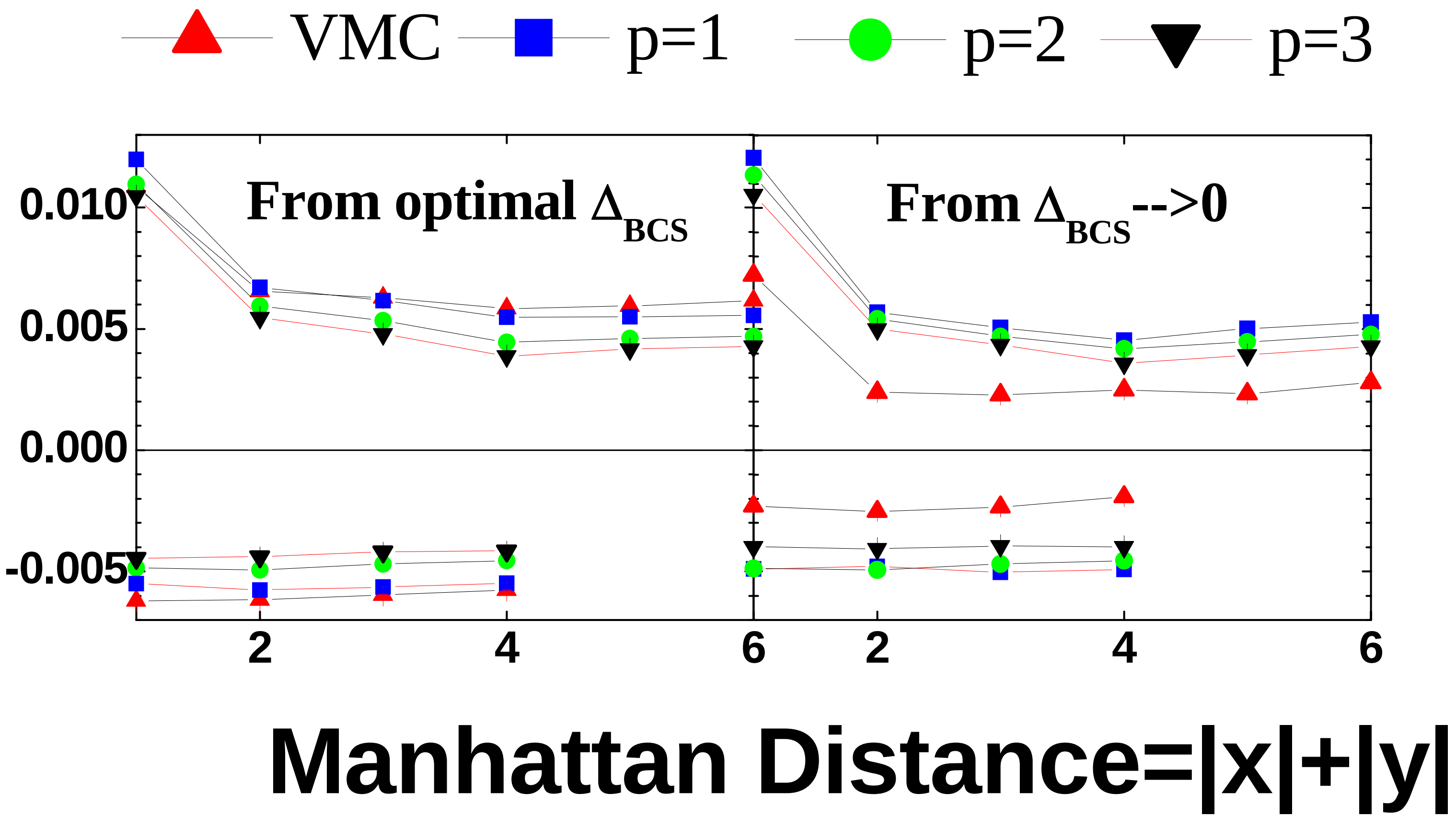
The question is how much computer effort is required for prescribed accuracy at given L.

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 ….

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



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

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

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

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 $\langle \Psi_\mathrm{T} | H^3 | \Psi \rangle \to +\infty \Rightarrow \alpha \to 0$

Only a statistical method known with $e^{-\Delta t H}$

Caffarel & Ceperley … or

‘’backflow wavefunctions’’ (poor scaling)

➢ Projected BCS wave function on triangular lattice

$$\boxed{\left|\text{P-BCS}\right\rangle = P_{\mathrm{G}}\left|\text{BCS}\right\rangle}$$: projected BCS state

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

$$\boxed{\begin{aligned} H_{\mathrm{BCS}} &= -t \sum_{\langle \vec{r},\vec{r}'\rangle,\sigma} \left(C^{\dagger}_{\vec{r},\sigma} C_{\vec{r},\sigma} + \text{h.c.}\right) - \boxed{\mu} \sum_{\vec{r},\sigma} C^{\dagger}_{\vec{r},\sigma} C_{\vec{r},\sigma} \\ &+ \sum_{\vec{r}=1}^{L} \left[\sum_{\vec{l}} \boxed{\Delta_{\vec{l}}} \left(C^{\dagger}_{\vec{r},\uparrow} C^{\dagger}_{\vec{r}+\vec{l},\downarrow} - C^{\dagger}_{\vec{r},\downarrow} C^{\dagger}_{\vec{r}+\vec{l},\uparrow}\right) + \text{h.c.}\right] \end{aligned}}$$

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

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

➢ Marshall sign rule

(W.Marshall, Proc.R.Soc.London Ser. A **232**,48 (1955))

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

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

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

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

$$|x\rangle=\prod_i|m_i\rangle$$: bases

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

$$\overset{\square}{H}\equiv\overset{\square}{U}^{\dagger}\overset{\square}{H}\overset{\square}{U}=\overset{\square}{H}_{dig}+\overset{\square}{H}_{off}$$

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

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

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

$$\boxed{\begin{gathered}\left|\Psi_0^{(M)}\right\rangle=\overset{\square}{U}^{\dagger}\left|\overset{\square}{\Psi}{}_0^{(M)}\right\rangle=\sum_x(-1)^{N(x)}f_x|x\rangle\\ N(x)=\sum_{i\in B}(s+m_i)\end{gathered}}$$

: Marshall sign rule

➢ Fixed node approximation

(D.F.B.ten Haaf et al., PRB **51**, 13039 ('95))

✓ Effective Hamiltonian with no negative sign problem

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

$\overline{H}_{x'x} \equiv \Psi_{\mathrm{G}}(x') H_{x'x} / \Psi_{\mathrm{G}}(x)$ γ : positive constant

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

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

✓ A standard Green function MC for effective Hamiltonian

$$\boxed{\langle x | \left(\overline{G}^{\mathrm{eff}} \right)^{n} | \varphi_{\mathrm{init}} \rangle \xrightarrow{n \to \infty} \Psi_{\mathrm{G}}(x) \Phi^{\mathrm{eff}}_{0}(x)}$$

$|\Phi^{\mathrm{eff}}_{0}\rangle$: ground state of H^{eff}

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

Fixed node approximation (II)

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

2. $\Phi_0^{\text{eff}}(x)$ variational state for $\hat{H}$ better than $\Psi_{\text{G}}(x)$

$$\langle \Psi_{\text{G}} | \hat{H} | \Psi_{\text{G}} \rangle \geq E_0^{\text{eff}} \geq \langle \Phi_0^{\text{eff}} | \hat{H} | \Phi_0^{\text{eff}} \rangle \geq E_0$$

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

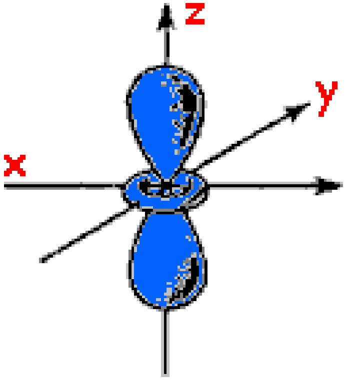
$$\hat{H} | \Phi_0 \rangle = E_0 | \Phi_0 \rangle$$

➢1D limit (J'=0)

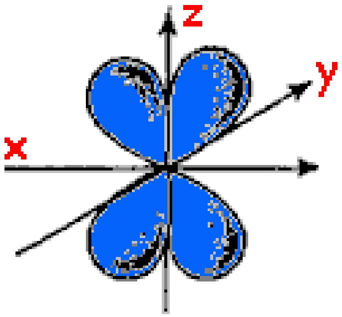
- ✓ Projected BCS wave function: $\boxed{\left|\text{P-BCS}\right\rangle = P_{\mathrm{G}}\left|\mathrm{BCS}\right\rangle}$
- ✓ $|\mathrm{BCS}>$: ground state of BCS Hamiltonian

$$\boxed{\begin{aligned} H_{\mathrm{BCS}} &= -t\sum_{\langle i,j\rangle,\sigma}\left(C_{i,\sigma}^{\dagger}C_{j,\sigma}+\mathrm{h.c.}\right)\\ &\quad+\sum_{i=1}^{L}\left[\sum_{l}\boxed{\Delta_l}\left(C_{i,\uparrow}^{\dagger}C_{i+l,\downarrow}^{\dagger}-C_{i,\downarrow}^{\dagger}C_{i+l,\uparrow}^{\dagger}\right)+\mathrm{h.c.}\right]\end{aligned}}$$

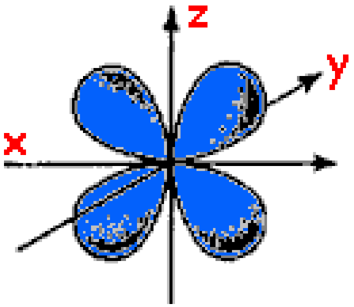
- ✓ Δ_l up to 3rd neighbors, $l \le 3$
- ✓Ground state properties well described (Gros et.al.)
- ✓Low-lying excited states (spinon): $\boxed{\left|\mathrm{k}\right\rangle = P_{\mathrm{G}}\boxed{\gamma_{k,\uparrow}^{\dagger}}\left|\mathrm{BCS}\right\rangle}$



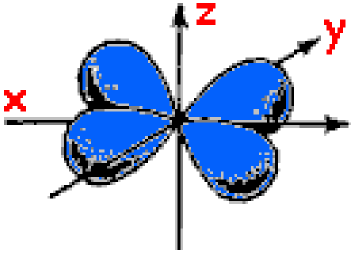
d_{z^2}



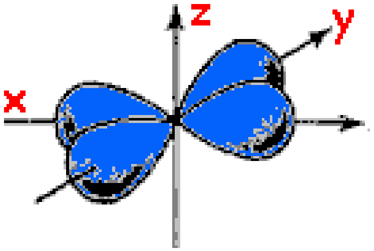
d_{yz}



d_{xz}



d_{xy}



$d_{x^2-y^2}$

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: ε_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

$$f_k \neq 0 \quad \varepsilon_{\mathrm{k}} \sim \varepsilon_F$$

New phase

JAGP = J x AGP → RVB

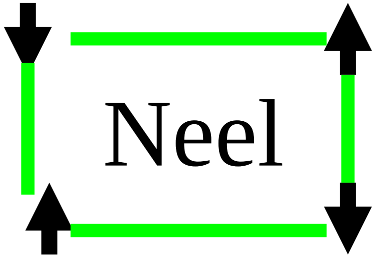
$$J = \exp\left(\sum_{i<j} v(r_i, r_j)\right)$$

$$f_k \neq 0 \quad \varepsilon_{\mathrm{k}} \sim \varepsilon_F$$

But insulator

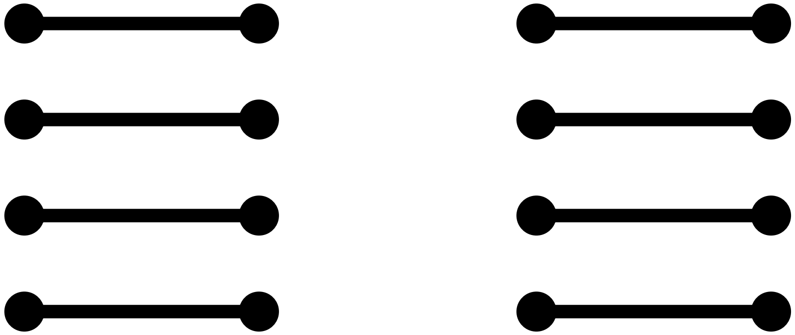
Definition of spin liquid

A spin state with



no magnetic order (classical trivial)

no broken translation symmetry (less trivial):



no Dimer state

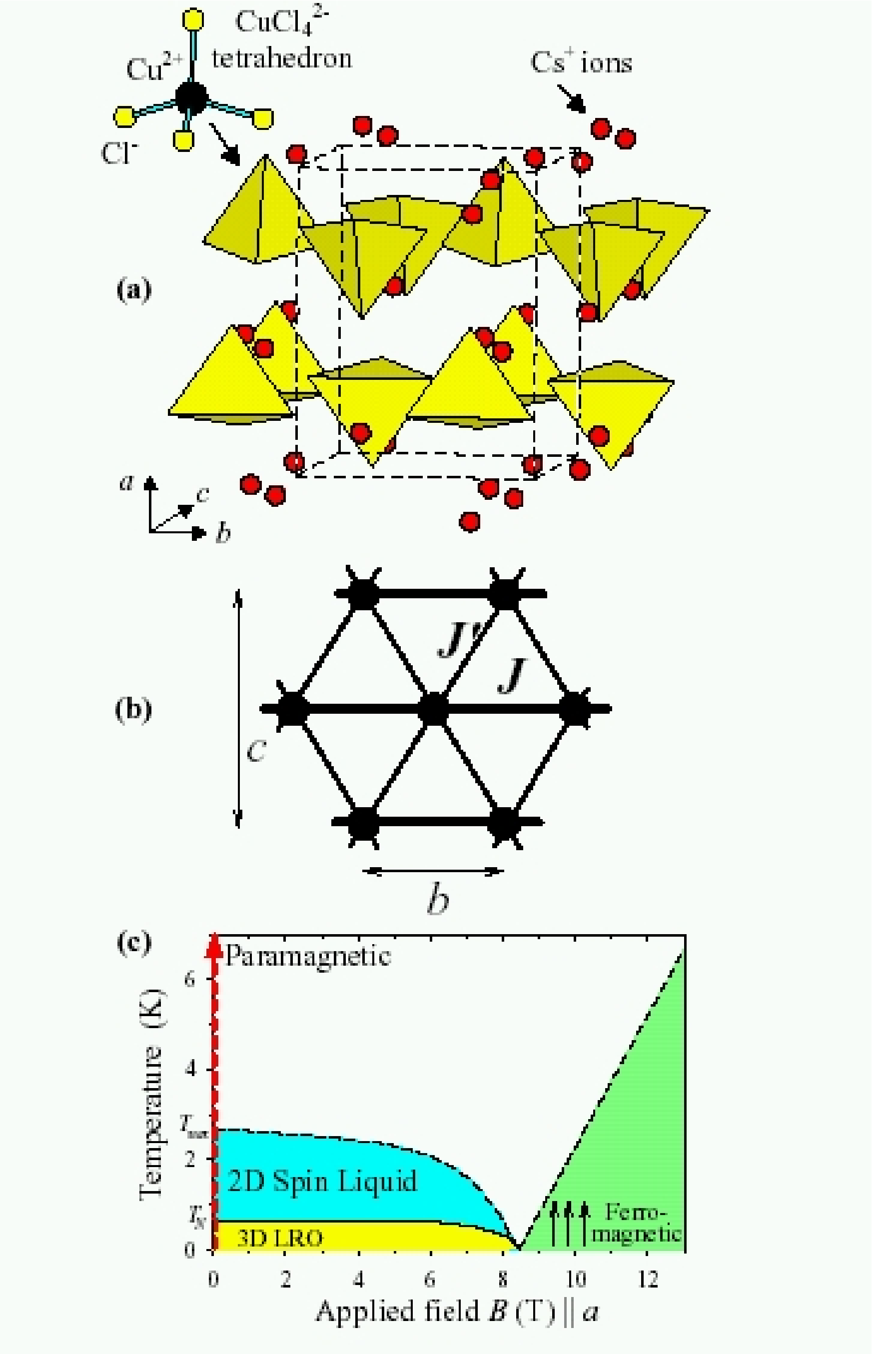
(Read,Sachdev)

is a spin liquid

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

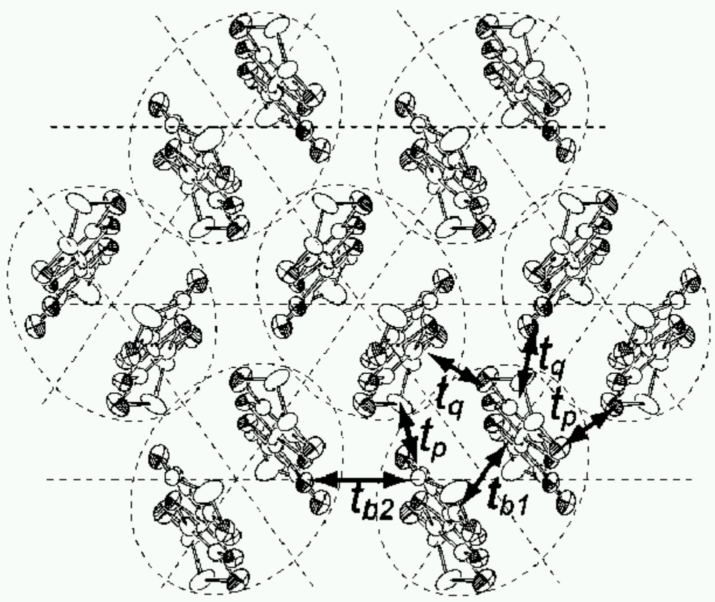
J’/J=1/3
J=0.375meV

“J” between planes ~1K



$\kappa-(\mathrm{ET})_2\mathrm{Cu}_2(\mathrm{CN})_3$

Spin Liquid ?



J=250K !!!

Shimizu et al. PRL '03

$J'/J\approx0.9$ $J'/J\approx1.8$

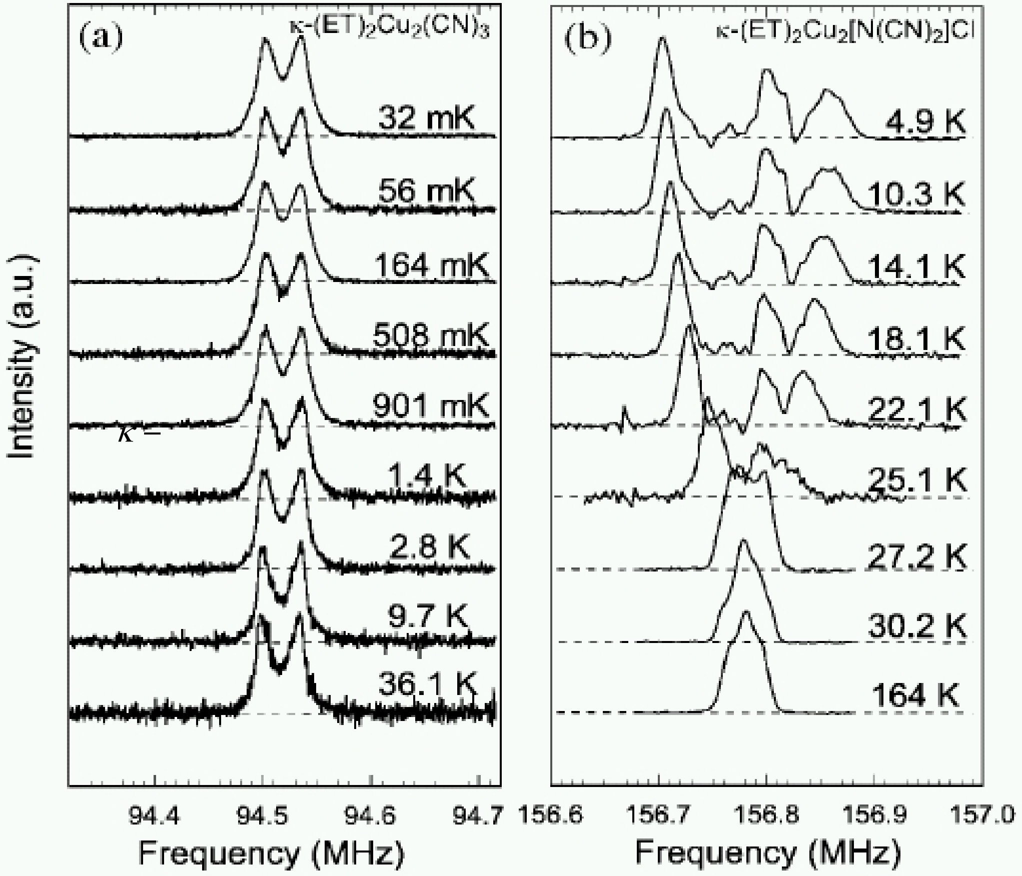


FIG. 3. (a) ^{1}H NMR absorption spectra for single crystals of κ-$(\mathrm{ET})_2\mathrm{Cu}_2(\mathrm{CN})_3$ and κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N(CN)}_2]\mathrm{Cl}$ [9] under the magnetic field perpendicular to the conducting planes.

➢ Methods (S. Sorella, PRB **64**, '01)

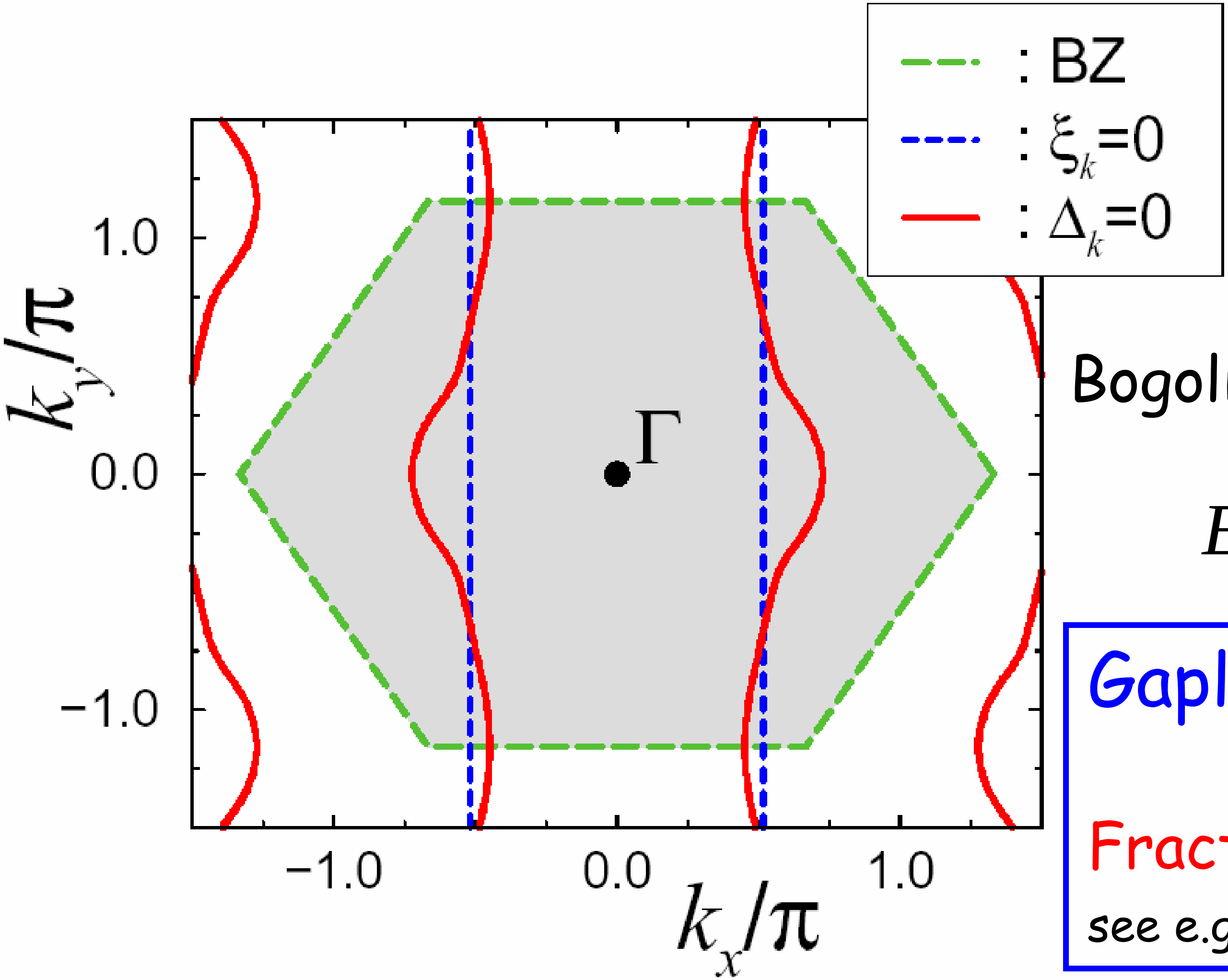
- ✓ Variational quantum Monte Carlo (QMC) method
- ✓ Projected BCS wave function: $|\text{P-BCS}\rangle = P_{\text{G}}\,|\text{BCS}\rangle$
- ✓ $|BCS\rangle = e^{\sum_{i,j} f_{i,j} C^{+}_{i,\uparrow} C^{+}_{j,\downarrow}} |0\rangle$: GS of BCS Hamiltonian

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

Notice : $t_{i,i} = \mu$ 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.

➢ 2D with J'/J=0.33



$$\xi_k = \varepsilon_k - \mu$$

Bogoliubov QP spectrum:

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

Gapless excitations

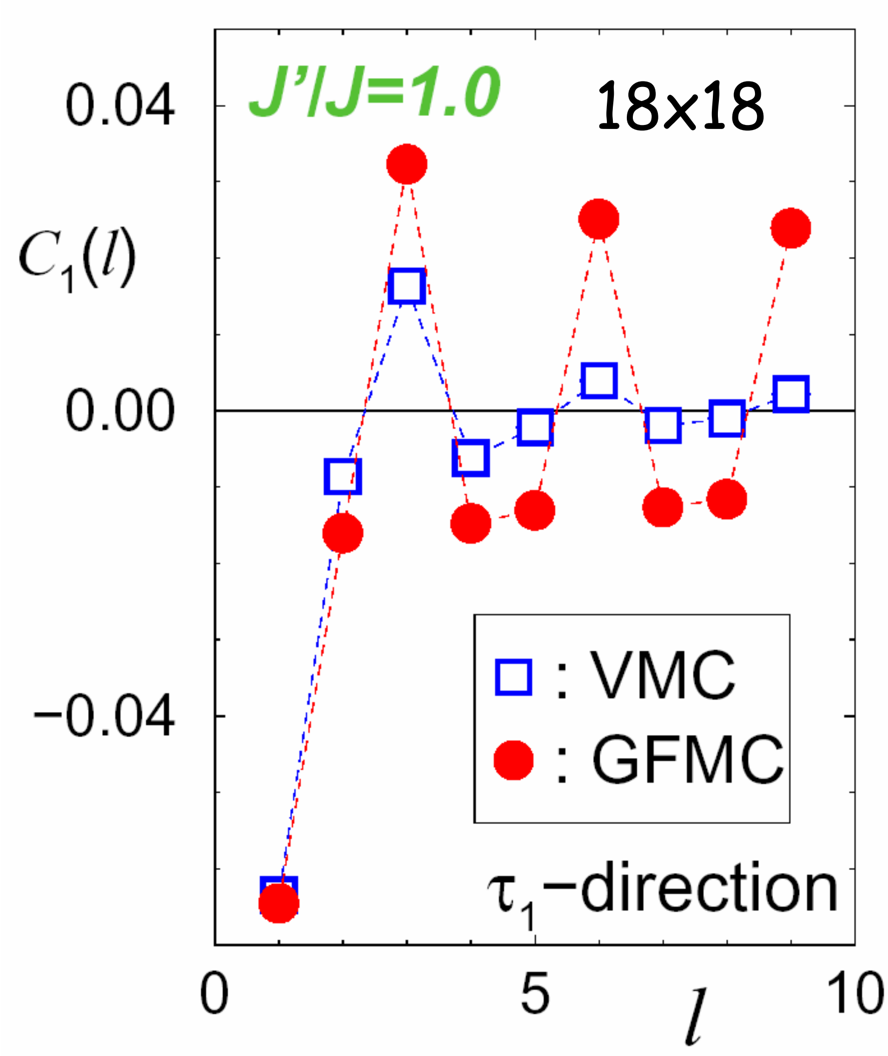
S=1/2 →

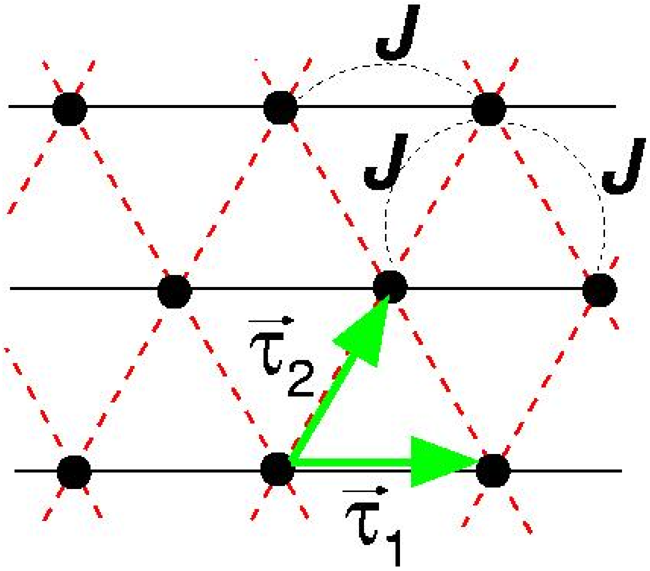
Fractionalization in 2D!

see e.g. X.G. Wen or M. Fisher

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

➢ Isotropic triangular lattice with J'/J=1.0



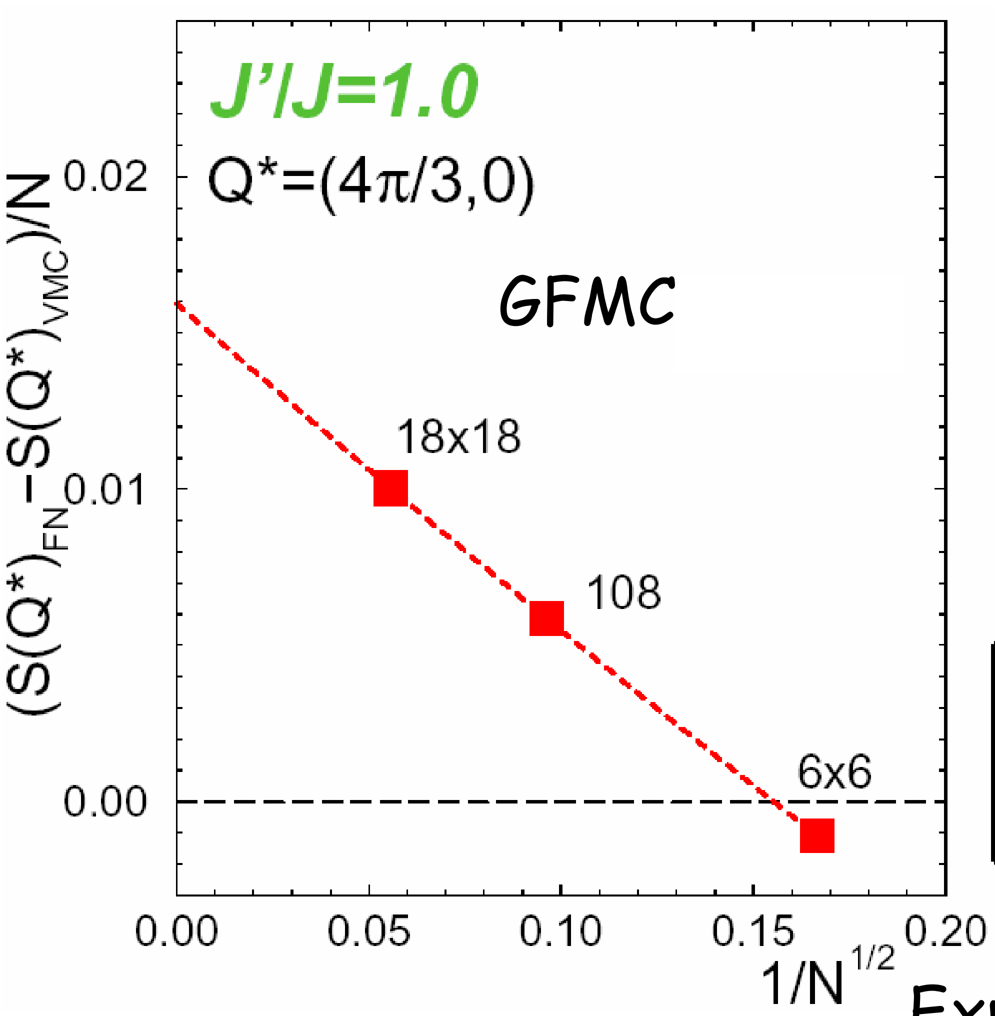


- ✓ Green function Monte Carlo
- ✓ Spin correlation function:

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

- ✓ Spin liquid state unstable toward classical Neel state

➢ Spin structure factor for J'/J=1.0



Order parameter:

- ✓ Starting from a spin liquid :

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

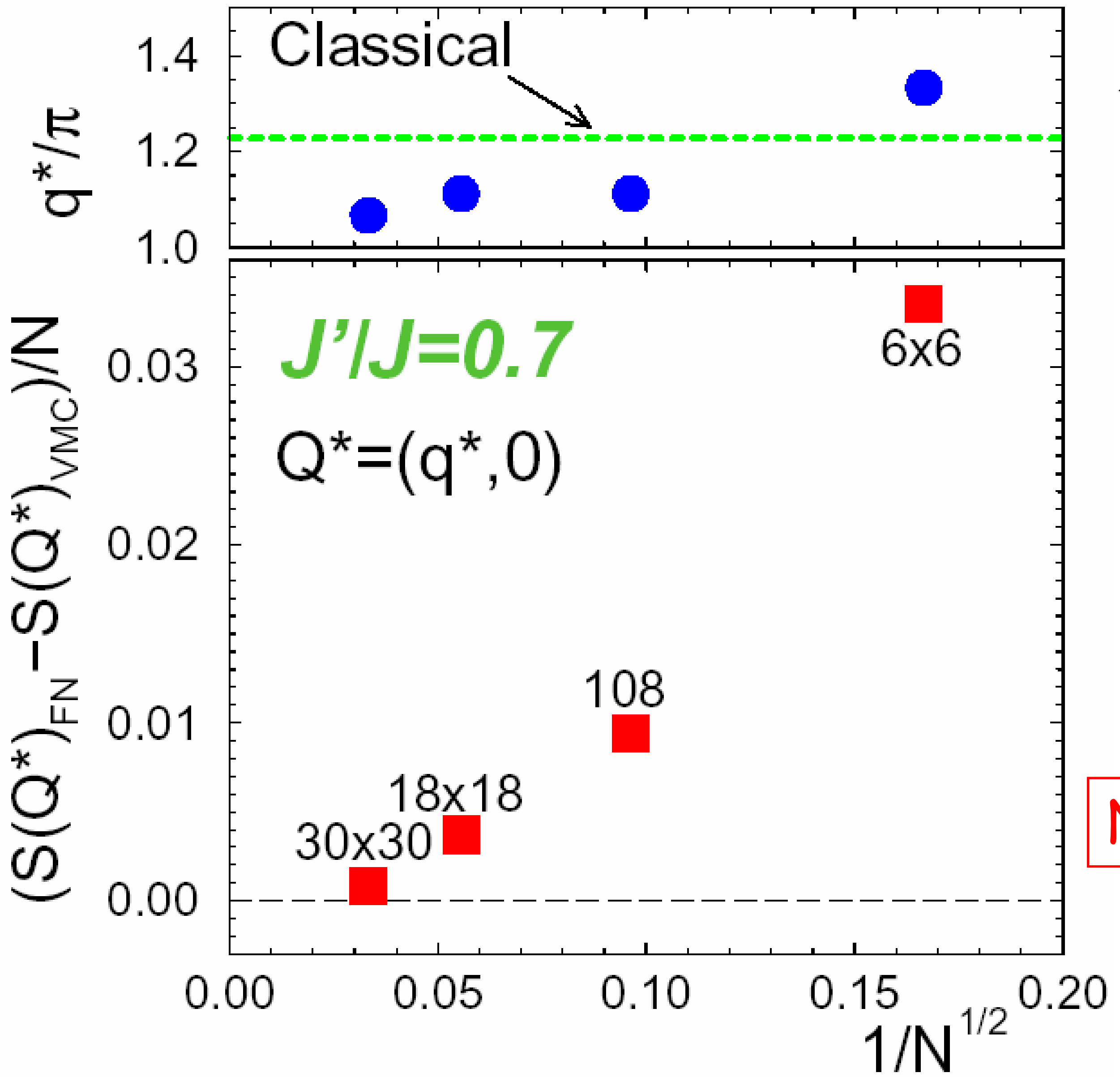
- ✓ Starting from ordered state :

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

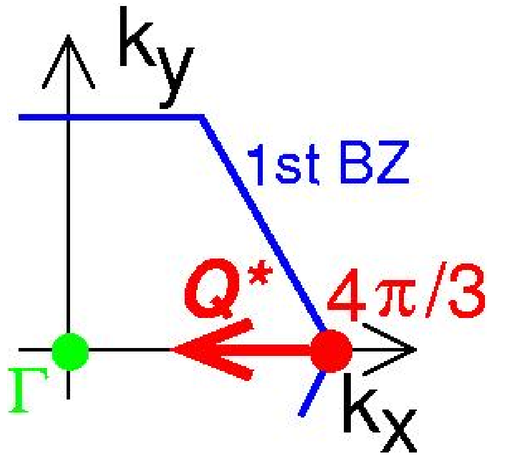
Exp. ~0.45 (organic) at J'/J=1.8

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

➢ Spin structure factor for J'/J=0.7



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

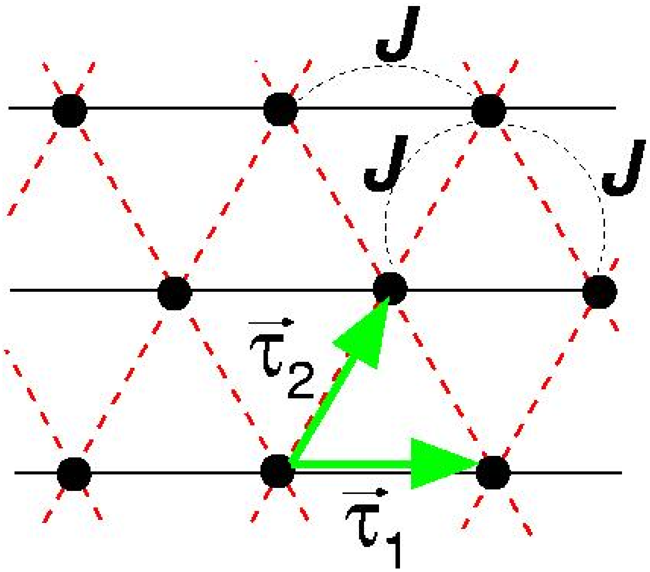


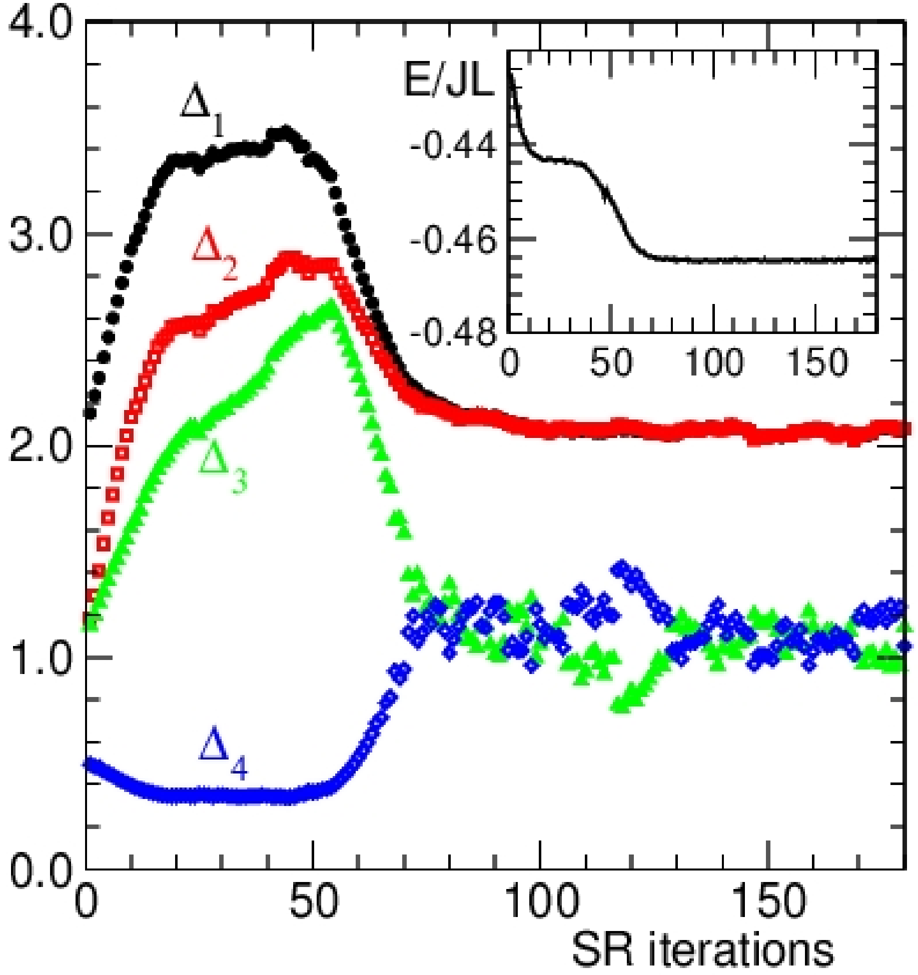
No long range order

Stability against dimerization

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

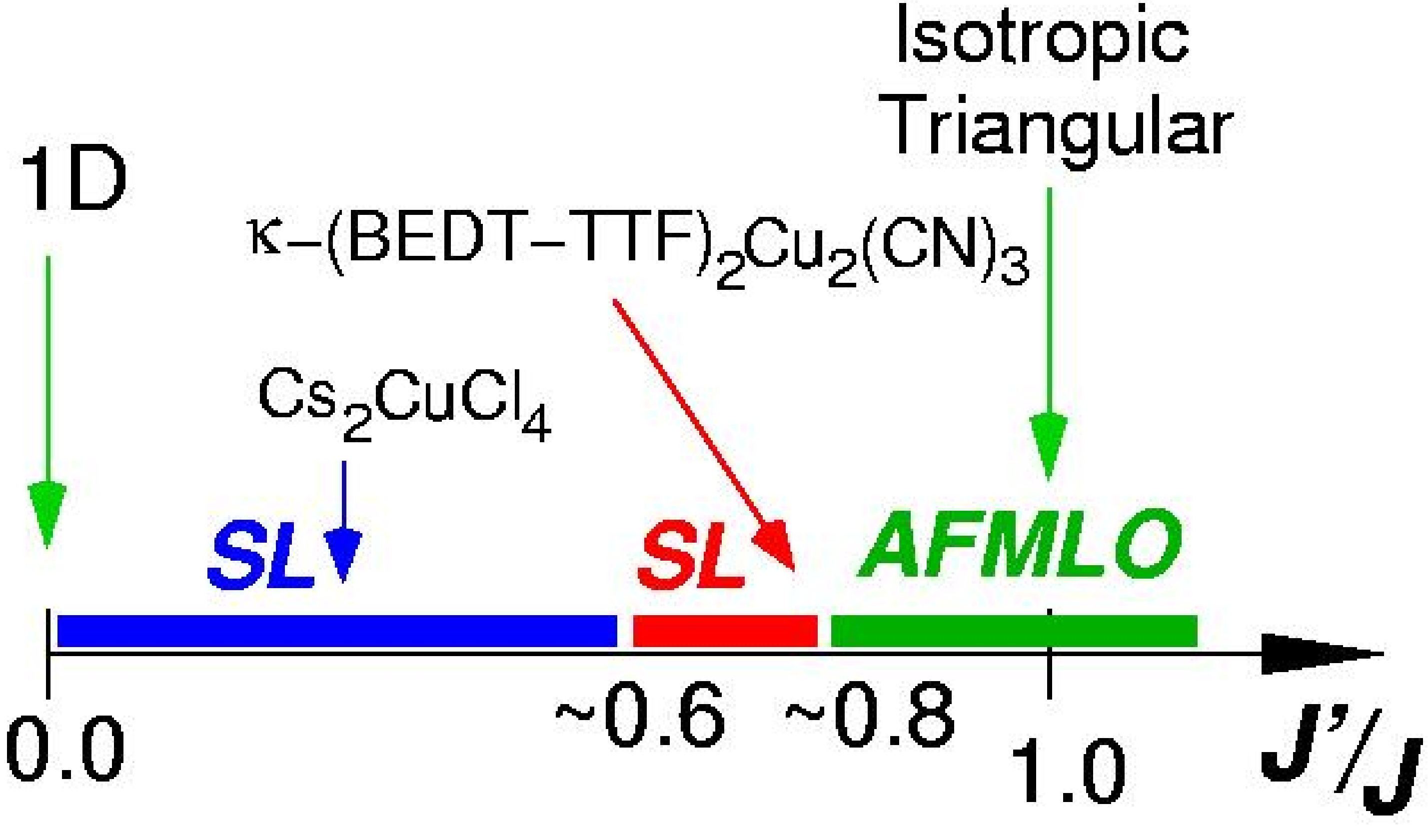
$$\begin{cases} \Delta_1 = \Delta_{0,\vec{\tau}_1}, \\ \Delta_2 = \Delta_{\tau_1,\vec{2}\tau_1}, \\ \Delta_3 = \Delta_{0,\vec{\tau}_2}, \text{ and} \\ \Delta_4 = -\Delta_{\tau_1,\tau_1+\vec{\tau}_2}, \end{cases}$$





Summary

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



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

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

Computational complexity now N^4

In QMC for given accuracy (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 :

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

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

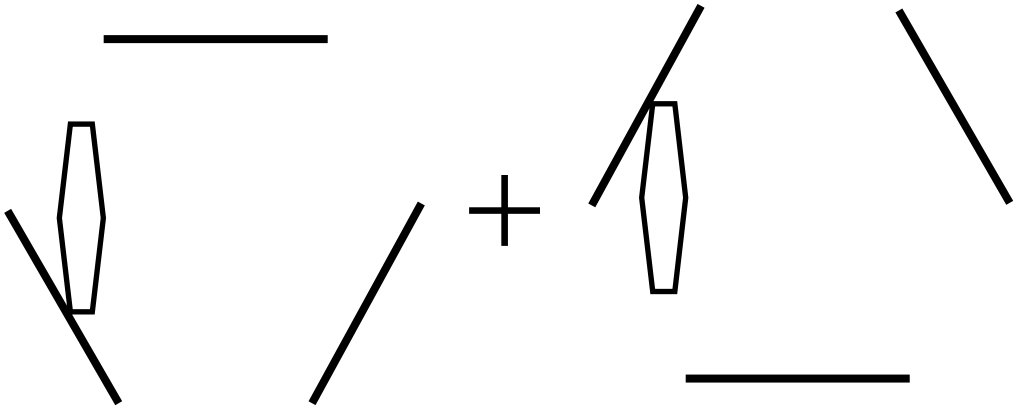
LatticeRegularizedDiffusionMonteCarlo

Very stable variational upper bounds of the pseudo Hamiltonian energy.

Key idea: on a lattice all interactions are nonlocal

Linus Pauling: the concept of resonance is old

Benzene C_6H_6



6 valence electrons occupy the $2p_z$ orbital

then strong correlation → $\approx$ Heisenberg model

$$H = J\vec{S}_a \cdot \vec{S}_b$$

a,b nearest Carbon sites

$$= \frac{1}{\sqrt{2}}\Big[\big|\uparrow\downarrow\big\rangle - \big|\uparrow\downarrow\big\rangle\Big]\Big[\psi^{a}_{2p_z}(r)\psi^{b}_{2p_z}(r') + a \leftrightarrow b\Big]$$

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

On a given electron configuration:

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

The pairing function can be computed:

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

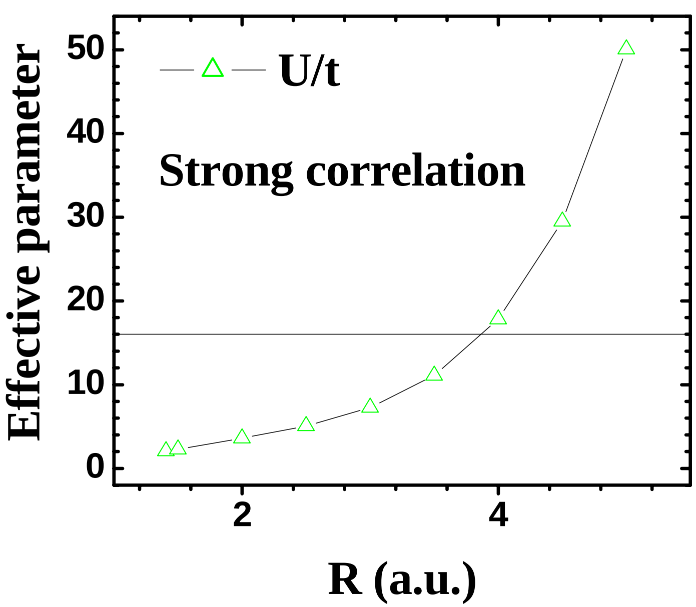
With a single determinant N/2 x N/2, N=# el.
even when RVB = many Slater Determinants

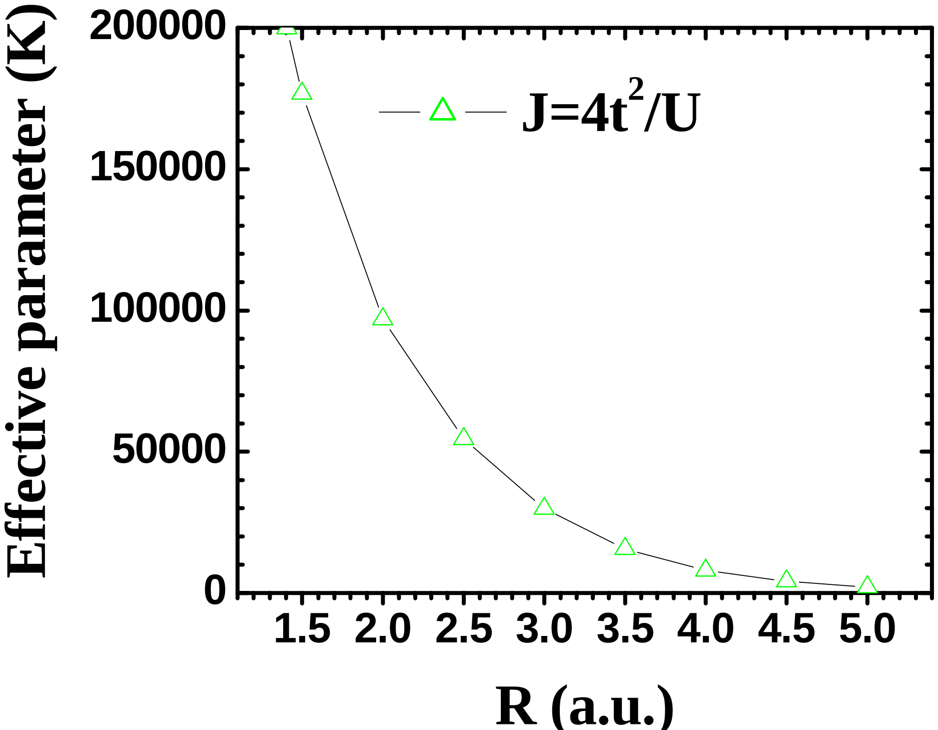
Mapping to a simple model: the 2-site Hubbard U

$$H = -t(R)\sum_{\sigma} c^{+}_{A,\sigma} c_{B,\sigma} + U(R) c^{+}_{A,\uparrow} c_{A,\uparrow} c^{+}_{A,\downarrow} c_{A,\downarrow} + A \leftrightarrow B$$

We use the Singlet-Triplet gap and the optimized

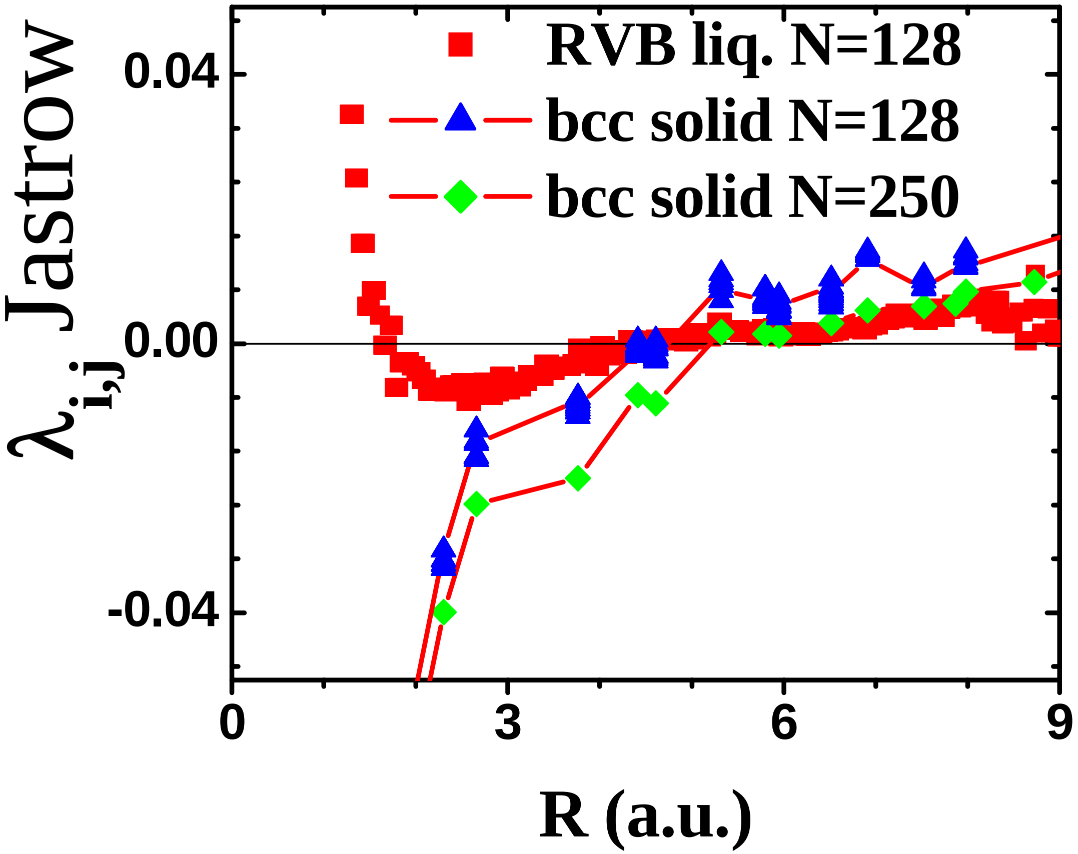
pairing function $1\sigma_g(r)1\sigma_g(r') - \lambda \ \ 1\sigma_u(r)1\sigma_u(r')$



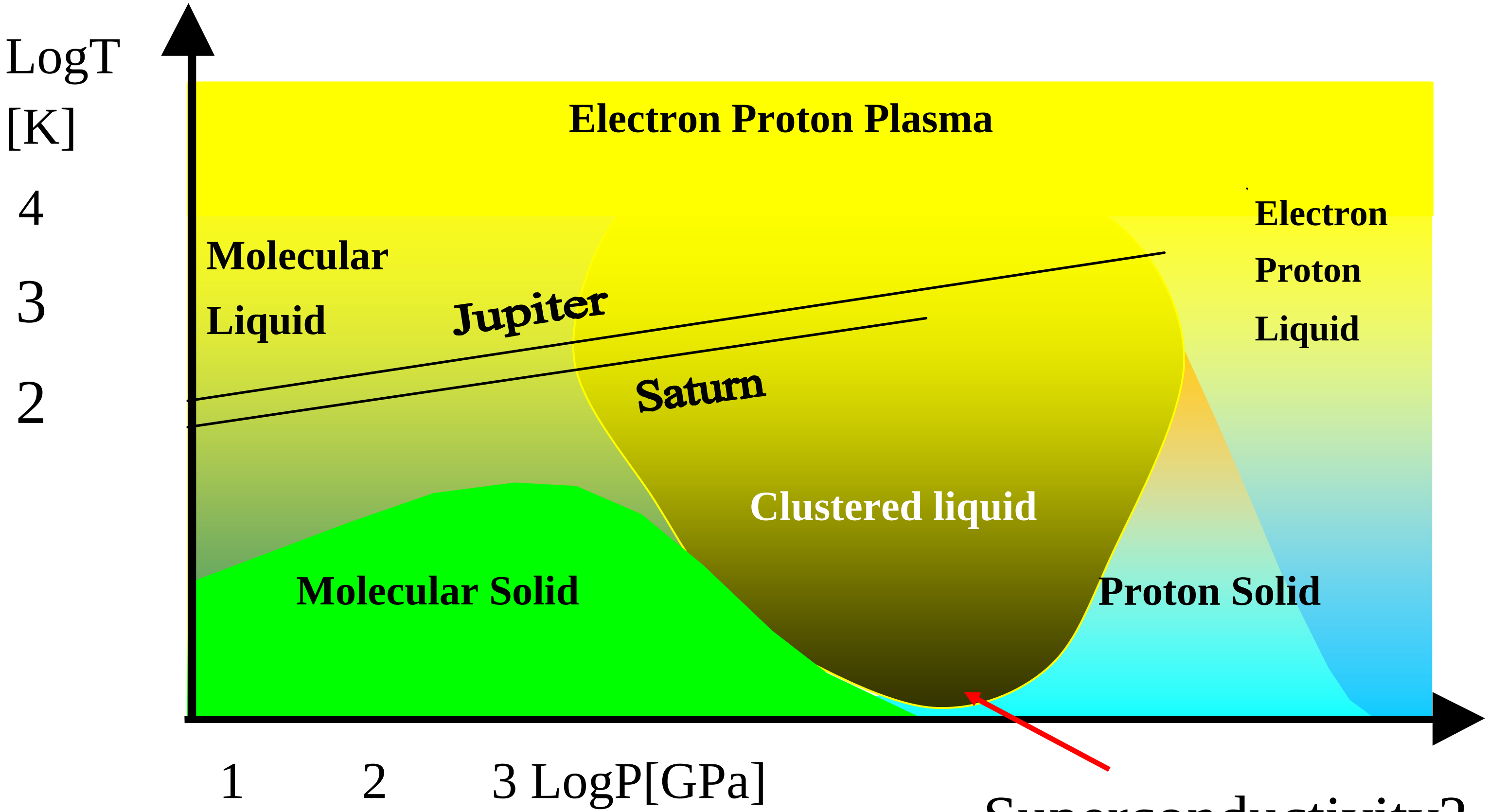


The crucial difference between an Htc superconductor and a RVB insulator is:

The long distance Jastrow factor 1/R or log(R)



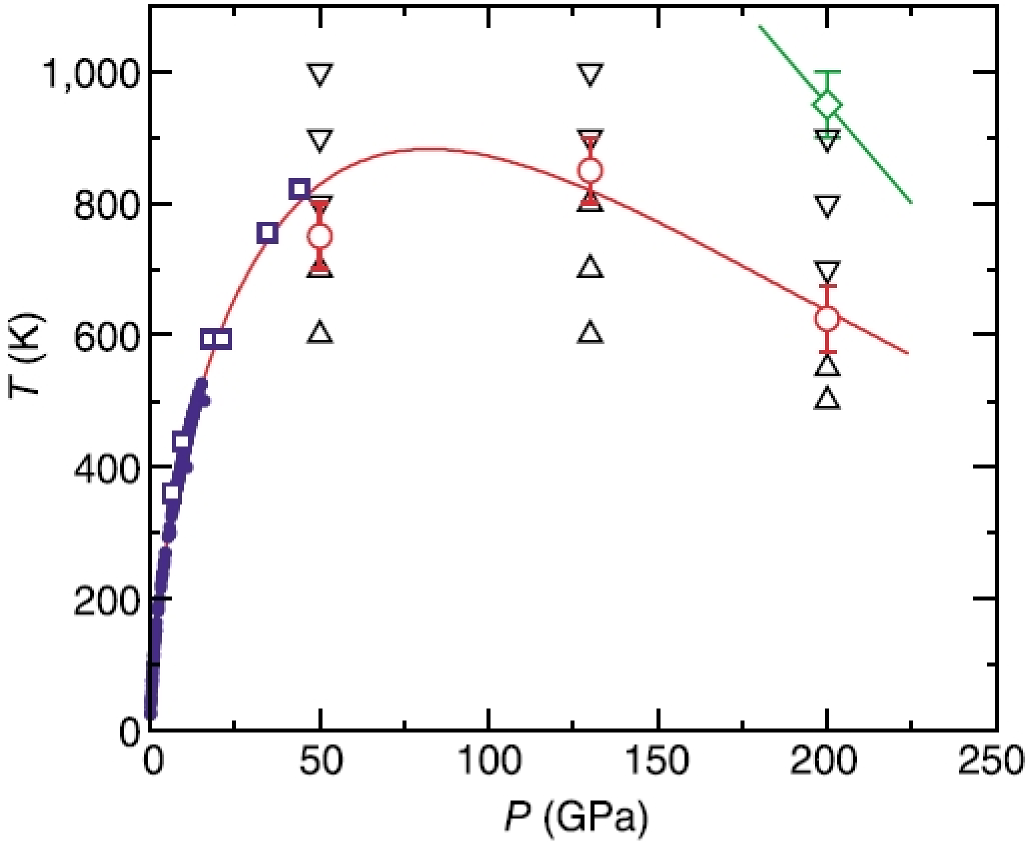
Phase Diagram of Hydrogen



Superconductivity?
Ashcroft Nature 2004

Indications of an anomalous melting line

S.A. Bonev, ..,G. Galli Nature 2004



Another quantum T=0 liquid phase?

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

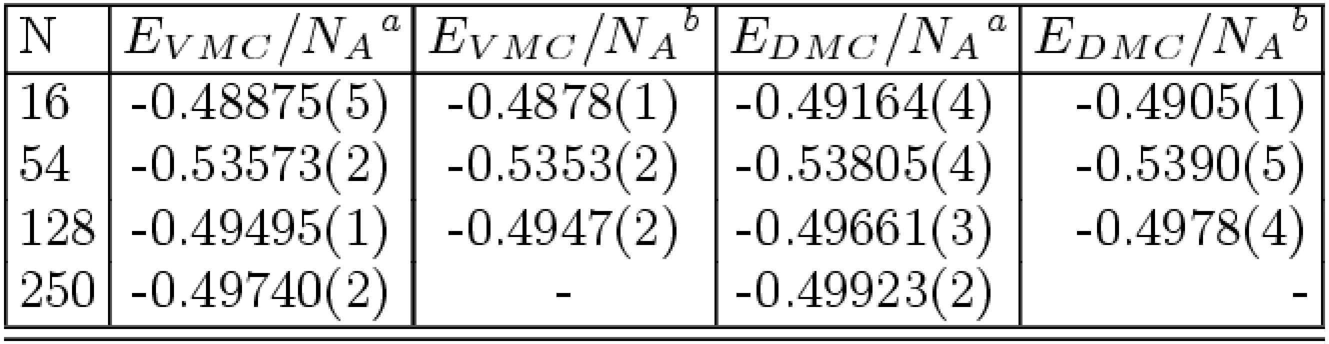
$r_s \approx H_2$ bond length

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

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

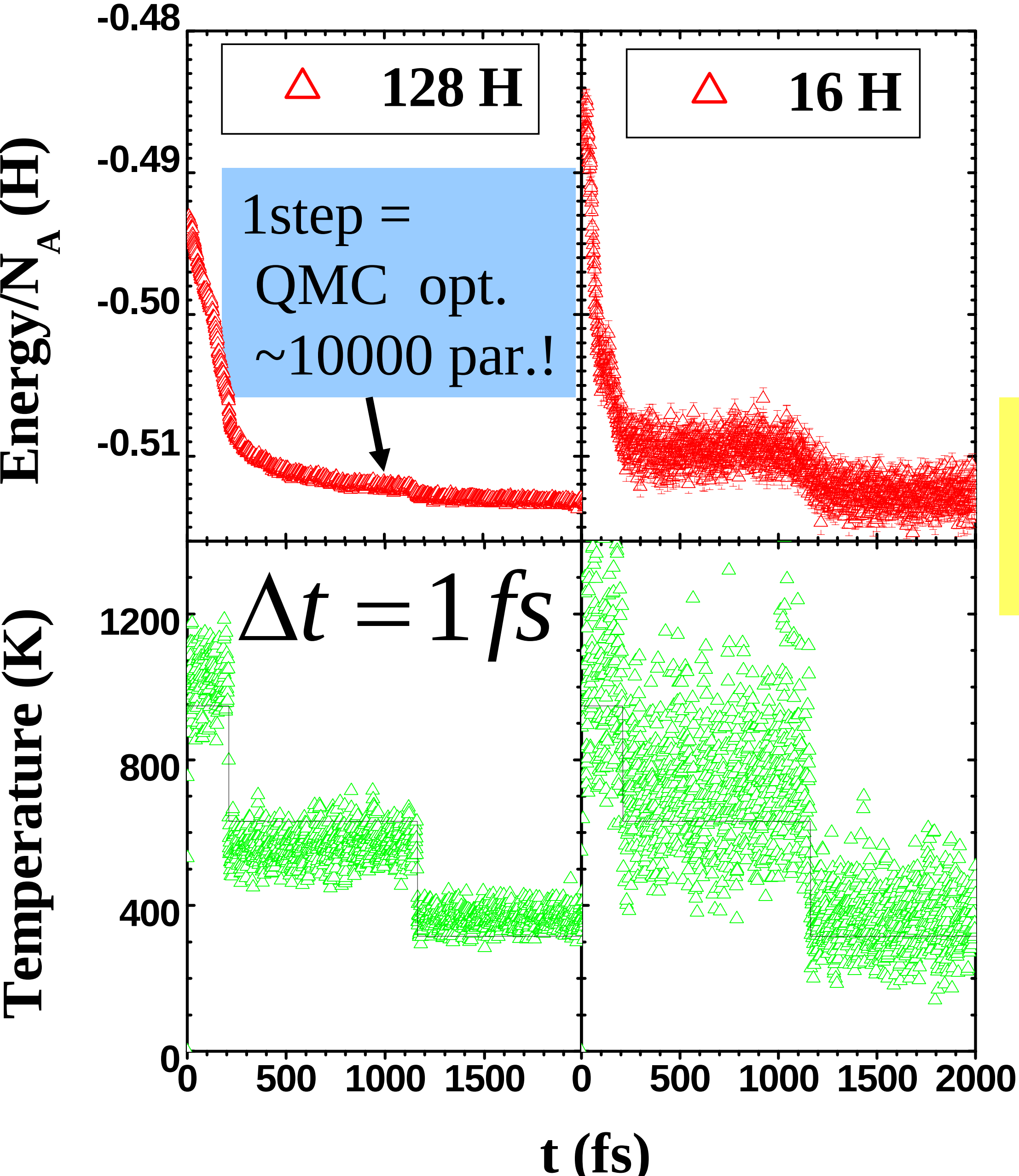
We use Hessian, much progress done in QMC:

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

New ab-initio Molecular-dynamics with QMC



Proton → Classical

Internal energy decreases at 1300K!!!

With RVB wf QMC possible for ~100 atoms

Why MD can be so efficient for QMC?

→The simulation at finite T requires some external noise to the forces e.g. Langevin dynamics

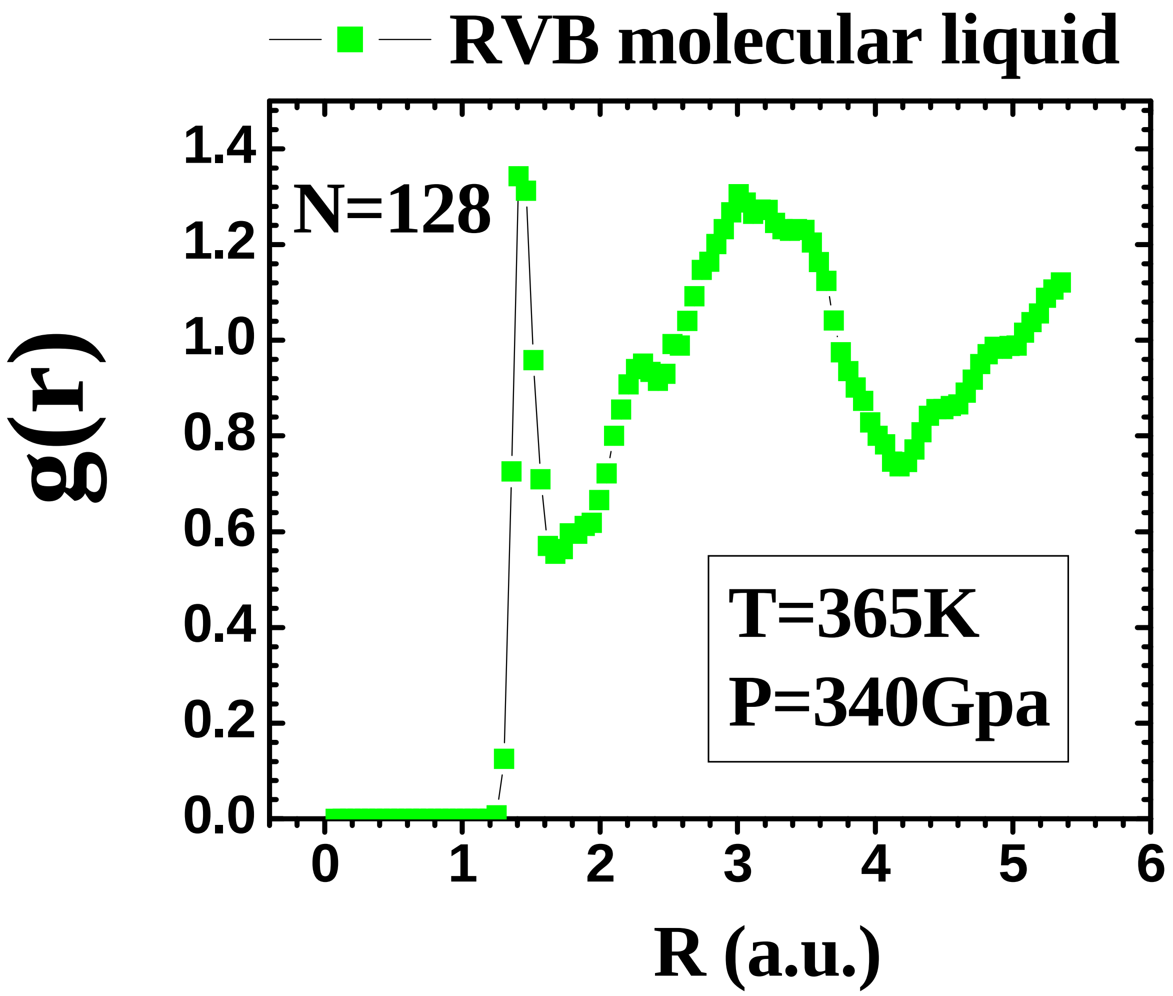
$$\dot{\vec{R}} = \vec{f} + \vec{\eta} \ \text{ with } \ < \vec{\eta}(t)\vec{\eta}(t^{'}) >= 2T\delta(t - t^{'})$$

But the noise is given for free within QMC!!!

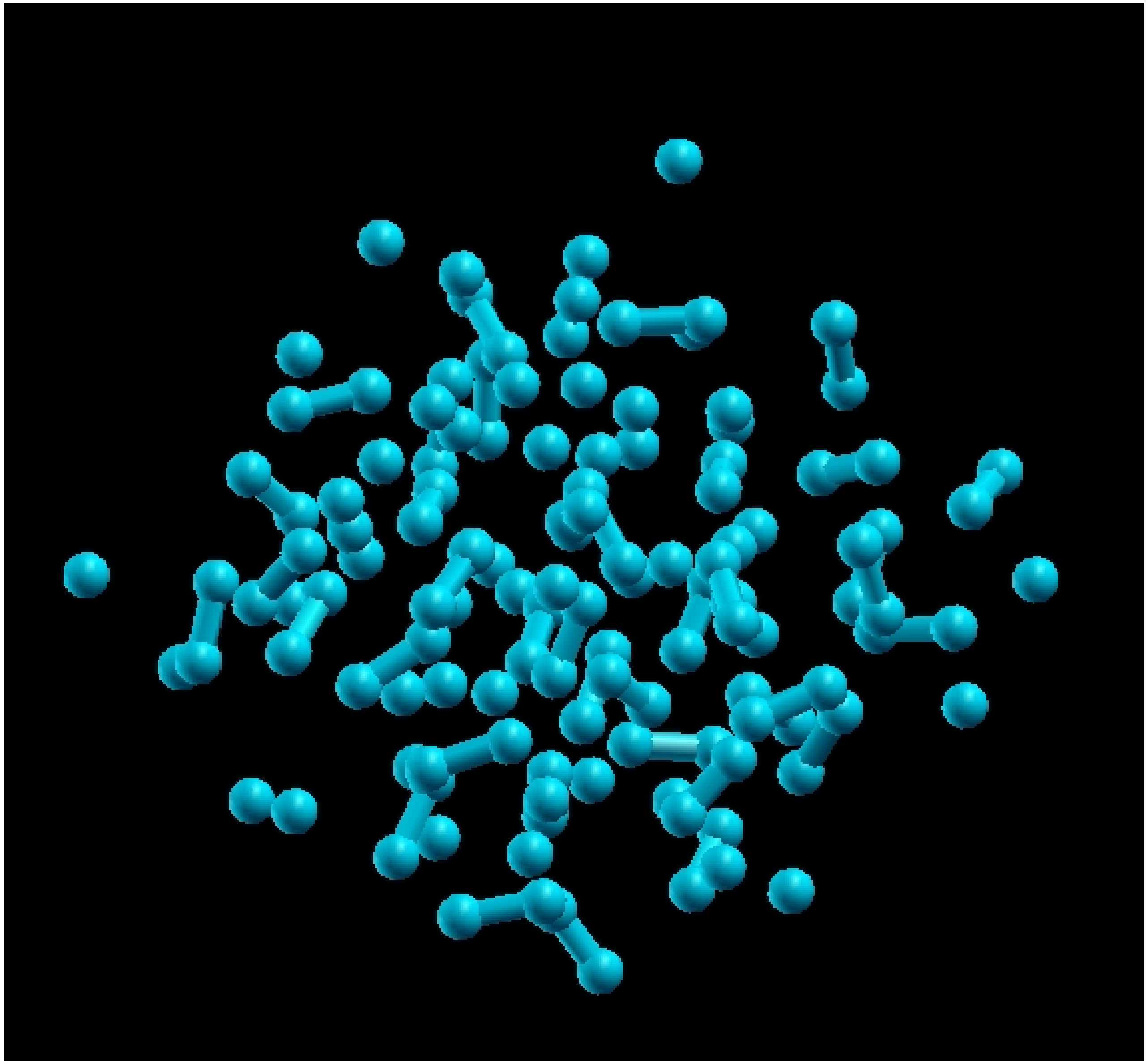
→ Compared with methods based only on energy we use 3N entries (forces) with the same cost.

Expected at least a factor N speed-up improvement

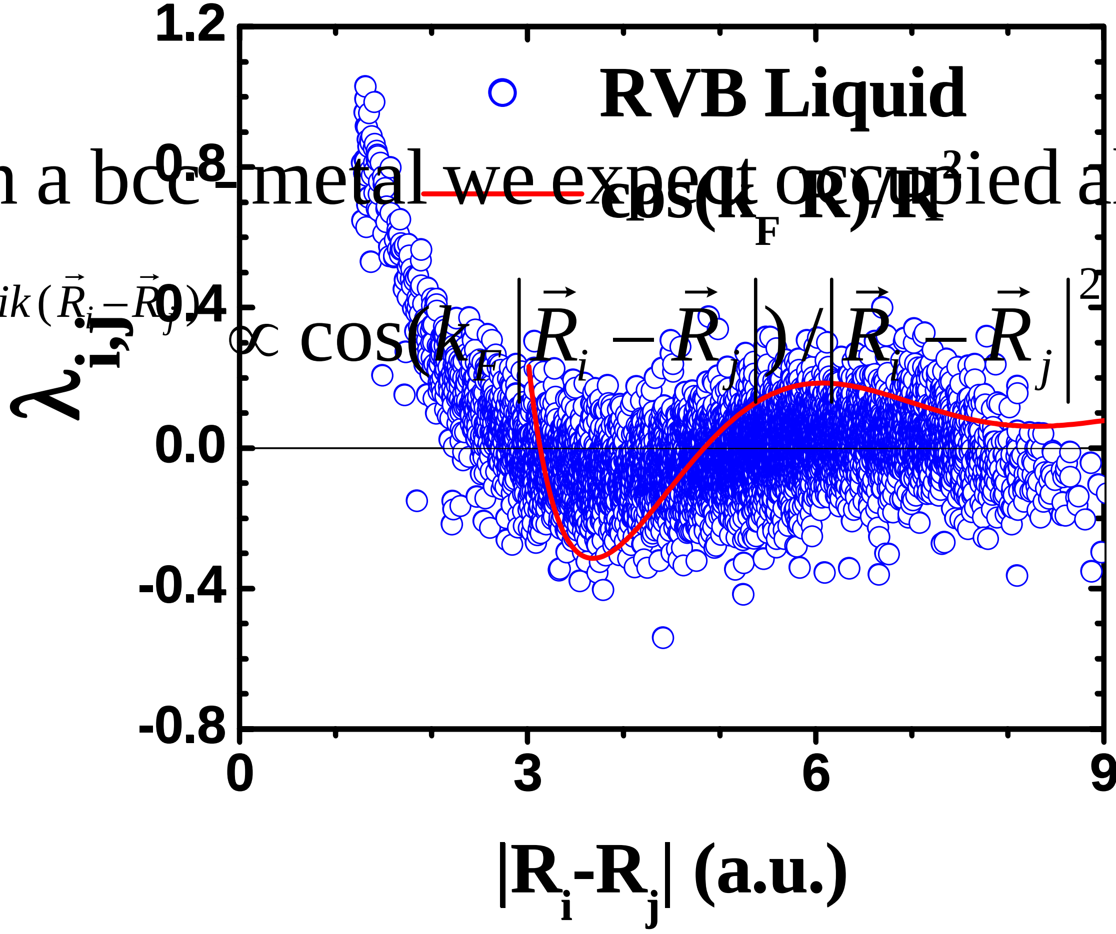
Proton-proton pair correlation function



Snap-shot of the protons at the last iteration



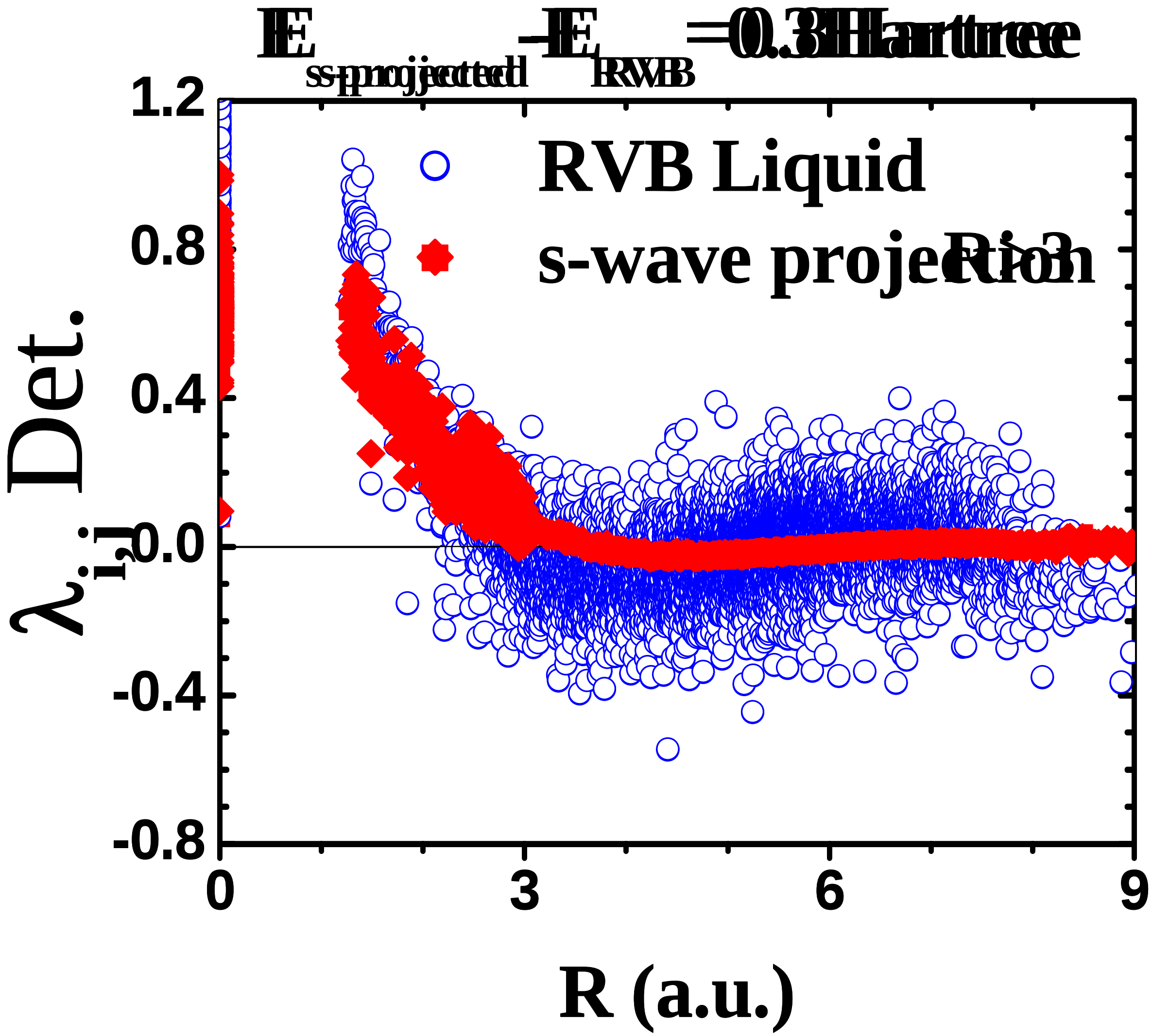
The pairing function in the liquid phase



Remind: in a bcc metal we expect occupied all $|k| \le k_F$, i.e.:

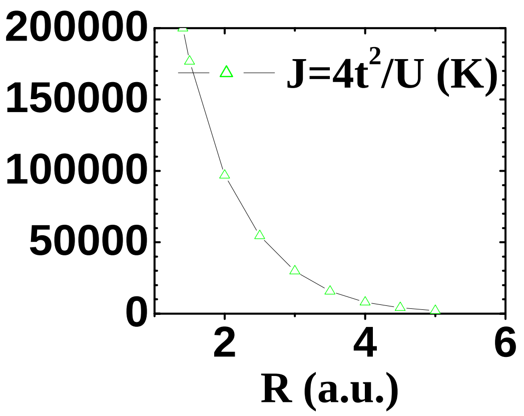
$$\lambda_{i,j} = \sum_{|k|\le k_F} e^{ik(\vec{R}_i - \vec{R}_j)} \propto \cos(k_F|\vec{R}_i - \vec{R}_j|)/|\vec{R}_i - \vec{R}_j|^2$$

Optimization with the s-wave constraint



Our energy is below any published one for the solid

A new possibility



HTc in Hydrogen at 300Gpa ?

J at the broad peak of g(R) is about 10000K
In Copper Oxide J is 1500K, Tc~100K

Tc > Room temperature ?

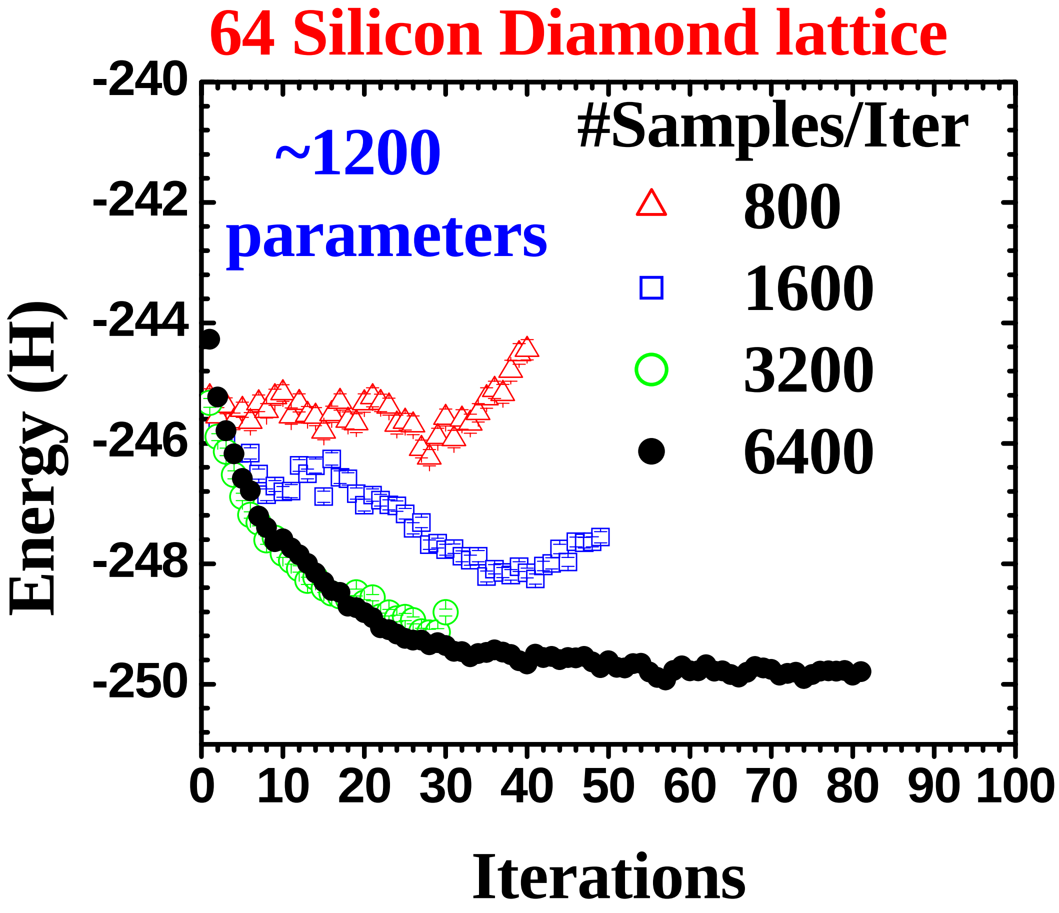
At rs=1.31 the solid phase simple hexagonal is competing in energy (Natoli et al. PRL ’93)
…under current investigation.

Conclusions

- ✓ The Jastrow+RVB (AGP) gives an accuate description of the chemical bond.
- ✓ It is described by a single determinant and is computationally convenient for QMC.
- ✓Reproduced several experiments on simple molecules, benzene and its dimer, water, C2….
- ✓Due to important achievements in the energy optimization. Realistic MD with most of the correlation

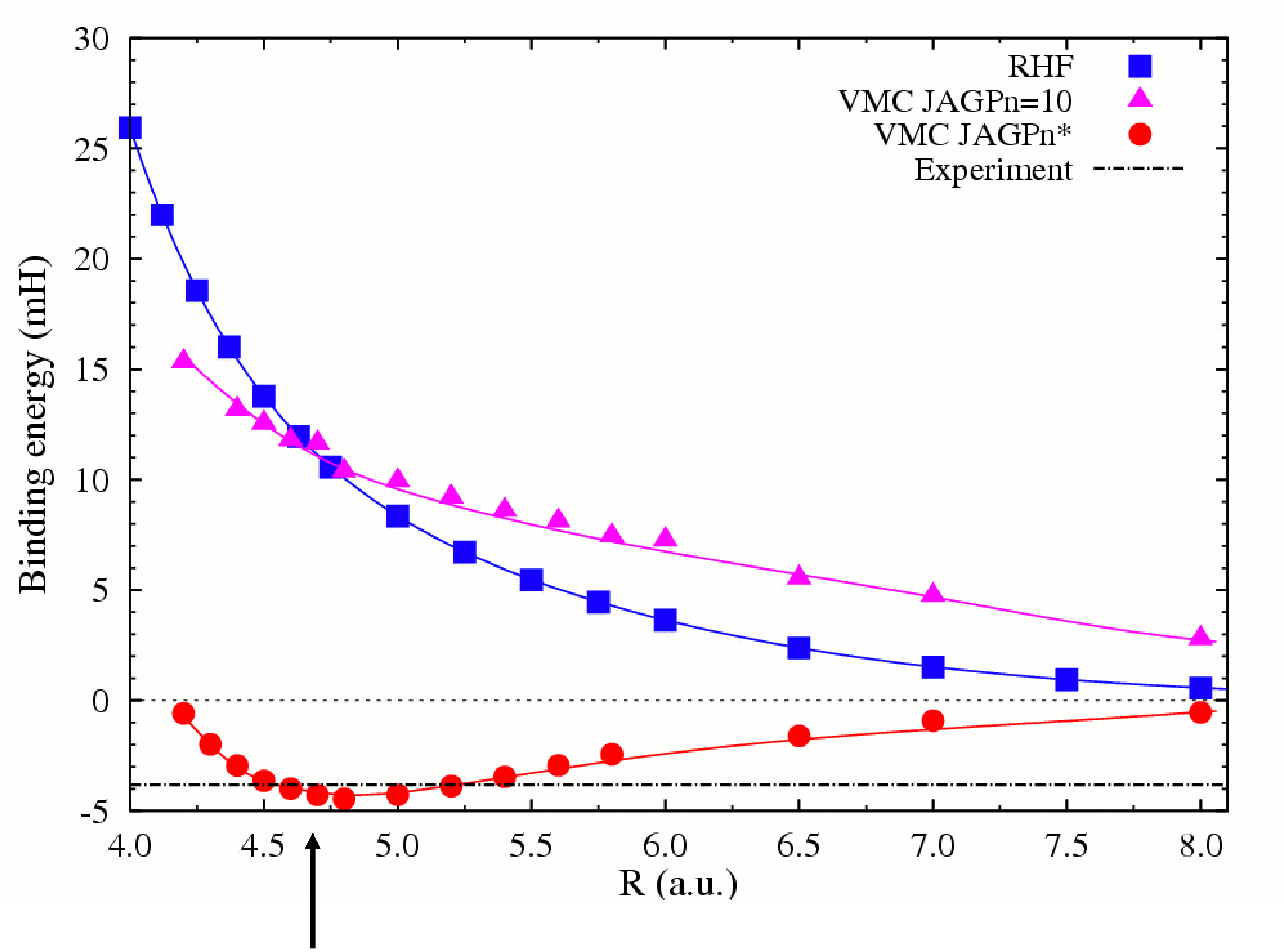
HTc physics in hydrogen at 300Gpa?

The drawback of many VMC parameters….



‘’Sick’’ when #parameters > # QMC Samples

The Berillium dimer: a challenging molecule



The F2 molecule and the problem of size-consistent results