Recent progress in the electronic simulation by ab-initio molecular dynamics and QMC forces

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SISSA, IOM DEMOCRITOS, Trieste

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Outline/Motivations

→ Molecular dynamics has been a dream within QMC until few years ago not only because it is much more expensive than DFT.

→ i) A new paradigm wave function is used to optimize efficiently within QMC: full ab-initio, full many body approach.

→ ii) Forces with finite variance, how to.

→ iii) Efficient calculation of forces, how to.

→ iii) Damped molecular dynamics→ enhance efficiency.

→ Examples: hydrogen and water

RVB as projected BCS


P. W. Anderson

1973: Anderson formulation of RVB theory on the triangular 2D Heisenberg antiferromagnet S=1/2 with **spin frustration**

P. W. Anderson, Mat. Res. Bull **8**, 153 (1973)

The number of bonds grows exponentially with the number of sites, but Anderson found a compact way to represent the RVB wave function.

$$|RVB\rangle = P_G \prod_k (u_k + v_k c^+_{k\uparrow} c^+_{-k\downarrow})|0\rangle$$

Gutzwiller projector forbids double occupancies on the same site

BCS wave function: singlet pairing between electrons

1987: Anderson theory of High temperature superconductivity

P. W. Anderson, Science **235**, 1196 (1987)

Spatial representation of RVB

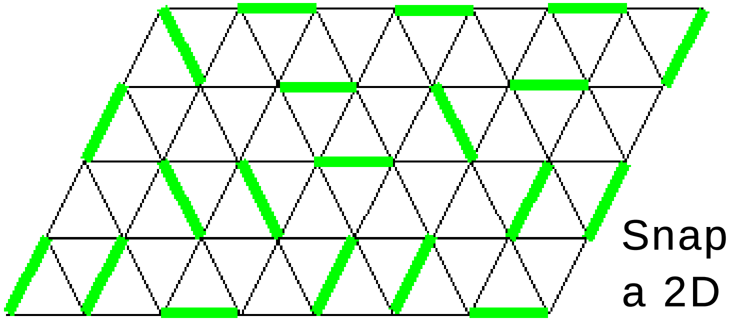
$$\left|RVB\right\langle = P_G \left(\sum_{i,j} f(\vec{R}_i - \vec{R}_j)\left(c^{+}_{i\uparrow}c^{+}_{j\downarrow} + c^{+}_{j\uparrow}c^{+}_{i\downarrow}\right) \right)^{N/2} \left|0\right\rangle$$

We fixed N, the number of particles (canonical ensemble):
N / 2 singlet pairs (valence bonds)

$f(\vec{R}_i - \vec{R}_j)$ Fourier transform of v_k / u_k is the **pairing function**

Pairs do not overlap for the action of the Gutzwiller projector P_G

The RVB wave function includes **all possible combinations** of valence bond configurations



Snapshot (a single configuration) of the RVB state on a 2D triangular lattice introduced by Anderson & Fazekas PM ‘74

TurboRVB : the RVB for real N-electrons

$$R = (\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$$

J

AGP=P_N |BCS>

$$\langle R | RVB \rangle = \exp[\sum_{i<j} u(\vec{r}_i, \vec{r}_j)] Det(f_{\vec{r}_i^{\uparrow}, \vec{r}_j^{\downarrow}})$$

$f_{r,r'} = \sum_{i,j} \lambda_{i,j}\, \phi_i(r)\phi_j(r')$ where:

$\phi_i(r)$ is the i^{th} atomic orbital centered on the ion R_i

$$\phi_i(r) = Y_{l,m}(\theta,\phi)\, |r - R_i|^k \sum_{j=1}^{p} A_j e^{-Z_j |r-R_i|^2}$$

The Jastrow factor is analogously treated, extending the Gutzwiller projection.

Just emphasize the difference with DFT

- In DFT we have to know only the density one function of one particle coordinate

$$n(\mathbf{r})$$

Simple → $\mathrm{Min}_{\{n(\mathbf{r})\}}$ Functional$[n(\mathbf{r})]$

- In this new RVB approach the functional is the energy expectation value and :

$$\mathrm{Min}_{\{f(\mathbf{r},\mathbf{r}'),\, u(\mathbf{r},\mathbf{r}')\}}\ \mathrm{Functional}[f(\mathbf{r},\mathbf{r}'),u(\mathbf{r},\mathbf{r}')]$$

Much more difficult … but not impossible

Most general form for the Jastrow factor

$$u(\vec{r}_i,\vec{r}_{ji}) = u_{2-body}(r_{ij}) + u_{1-body}(|\vec{r}_i - \vec{R}_a|) + u_{3-4body}(\vec{r}_i,\vec{r}_{ji})$$

$$u_{2\,\mathrm{body}} = u(r_{ij}) \quad \text{where} \quad u(r) = \frac{F}{2}\left(1 - e^{-\frac{r}{F}}\right) \approx \frac{r}{2}$$

El.-el. cusp conditions

Electron-ion Jastrow

$$u_{1\,\mathrm{body}} = -\sum_{ia} (2Z_a)^{1/4} u\left((2Z_a)^{3/4} r_{ia}\right) \approx -Z_a r_{ia}$$

El.-ion cusp conditions

Electron-ion-electron-ion Jastrow (4-body)

$$u_{3-4body} = \sum_{i<j}\sum_{lm} u_{lm}\psi_l(\vec{r}_i)\psi_m(\vec{r}_j)$$

M. Casula, C. Attaccalite, and S. Sorella, *J. Chem. Phys.* **2004**

But why we have to be so complicated with J?

Consider two closed shell atoms e.g. He_2 at large distance, then the weak-vdW interactions read:

$$U_{vdW} = -1/R_{AB}^3\left[3\left(\vec{r}_A \cdot \hat{R}_{AB}\right)\left(\vec{r}_B \cdot \hat{R}_{AB}\right) - \vec{r}_A \cdot \vec{r}_B\right]$$

A variational wf allows the second order contribution in U to the energy, namely the vdW, if it is compatible with the first order in U_{vdW}

But $$U_{vdW} = -1/R_{AB}^3 \left[3\left(\vec{r}_A \cdot \hat{R}_{AB}\right)\left(\vec{r}_B \cdot \hat{R}_{AB}\right) - \vec{r}_A \cdot \vec{r}_B \right]$$

$$\exp(-\alpha\ U_{vdW})\left|Det\right\rangle = \exp(u)\left|Det\right\rangle$$

vdW → parametrization of the Jastrow J=exp(u) contains at least p orbitals on the different atoms

A and B

Contained in the general Jastrow factor in TurboRVB

The Berylllium dimer
binding ~0.1ev bond length ~4.6a.u.

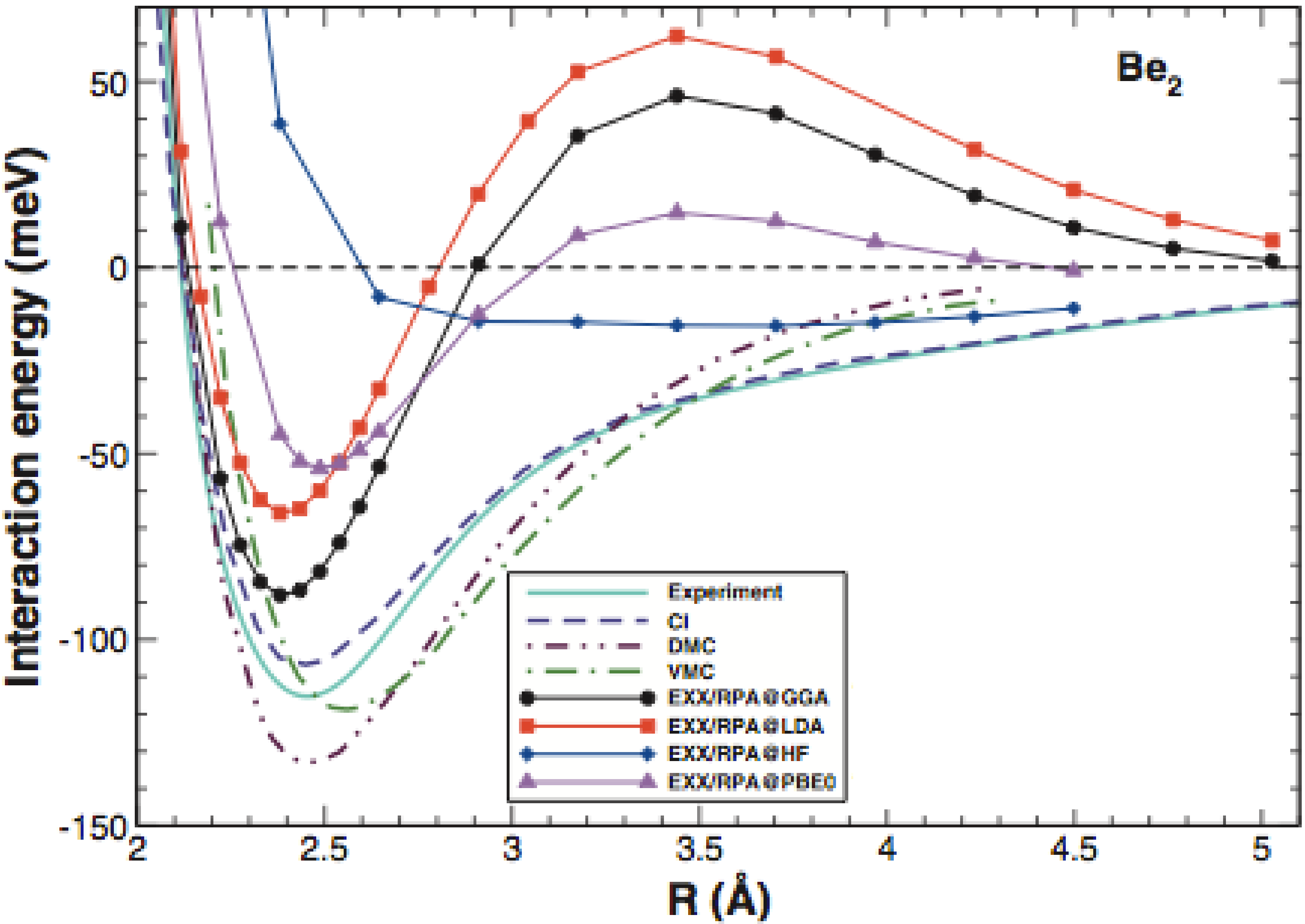
i) Beryllium (Z=4) atom 2s-2p degeneracy→
   Hybridize in the molecule but….

ii) Hartree-Fock is not able to bind (unstable)

iii) Big success of DFT (LDA) but binding energy
     > 0.5 eV !!!

Recent attempts to improve DFT by adding vdW with (or without) consistent methods (RPA...,+…).

No success so far



From H.W. Nguyen and G. Galli JCP 2010

Quantum chemists have succeeded to solve this problem by using several (billions!!!) determinants

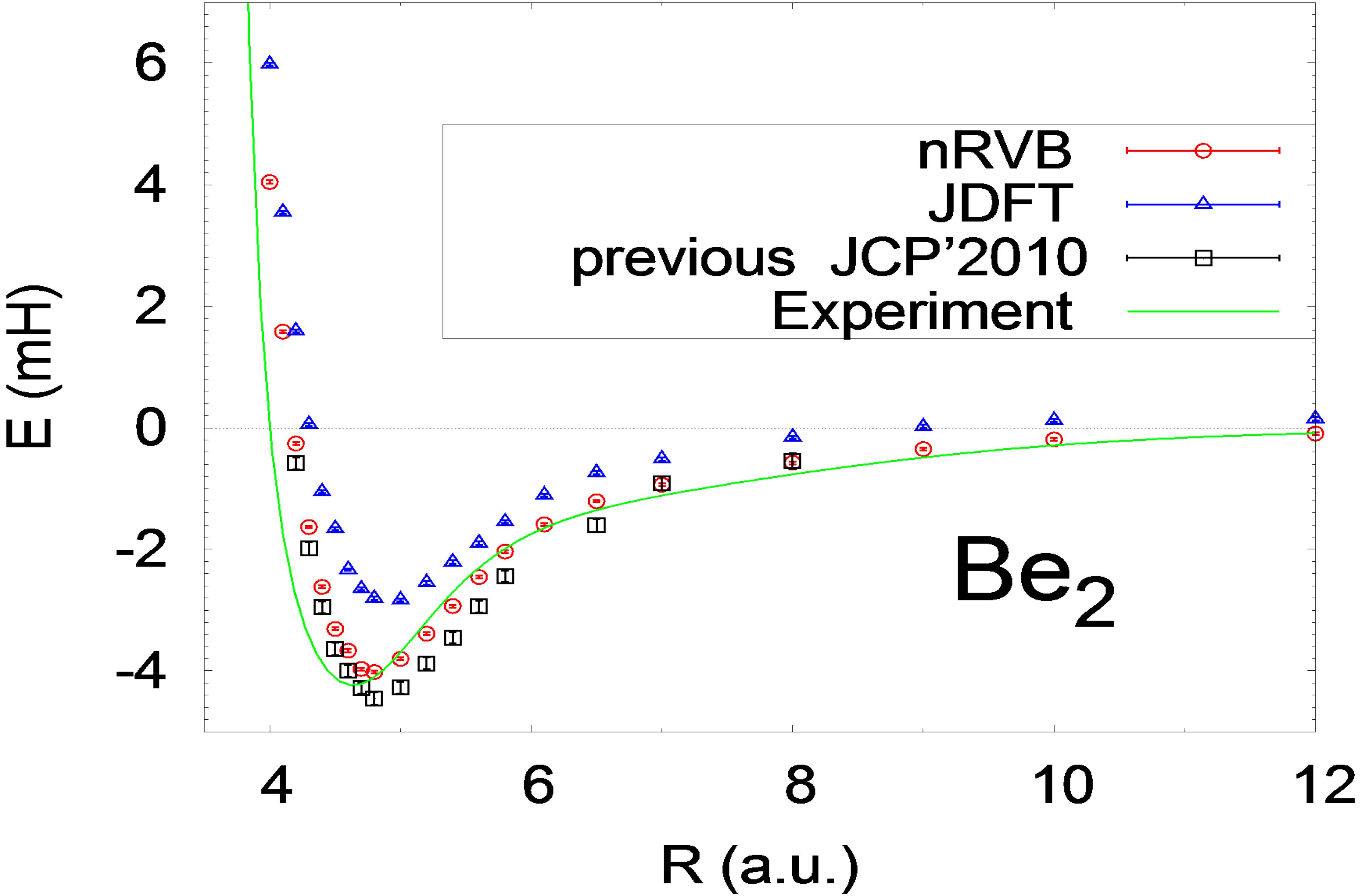
CI- J.M.L. Martin Chem. Phys. Lett. 333,399(1999)

But does it mean they have understood?

In this molecule there exists an accurate balance between hybridization 2s-2p orbitals (uncorrelated) and correlated vdW promotion 2s-2p.

The Beryllium dimer with one determinant and J

Difference now-(2010) Jbasis 4s3p2d-(4s3p)→converged



Remarks

- Without 4-body Jastrow no way to bind the molecule (TurboRVB has this important tool).
- DMC in this case goes in the wrong direction … overbind by 0.04eV:

  i) it may be experiments are wrong.

  ii) DMC does not conserve continuous symmetries (e.g. spin, angular momentum) .
- Ansatz better than JHF also in the wrong direction (do not bind) because the atom is improved much more than the weak bond (JAGP)

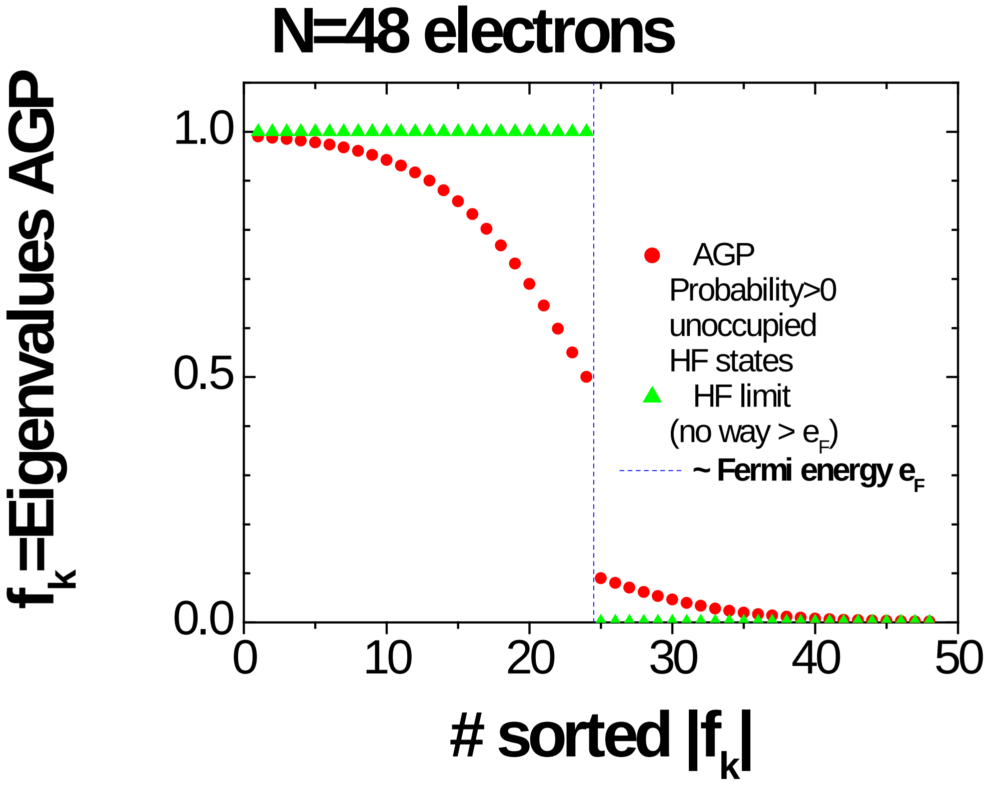
Let us consider now the determinant part of the RVB wavefunction the so called AGP or BCS wf.

$$\langle R | AGP \rangle = Det(f_{\vec{r}_i^{\uparrow}, \vec{r}_j^{\downarrow}})$$

What is its relation with standard HF molecular orbitals?

$$f(r_{\uparrow}, r_{\downarrow}) = \sum_{i,j} \lambda_{i,j} \varphi_i(r_{\uparrow}) \varphi_j(r_{\downarrow}) = \sum_k f_k \, \psi_k(r_{\uparrow}) \psi_k(r_{\downarrow})$$

The eigenvalue spectrum of the AGP is ‘’like’’ a Fermi distribution. Unoccupied HF-DFT- orbitals are ‘’partially’’ occupied to gain RVB energy.



IF $f_k > 0$ for $k > N/2$ in the thermodynamic limit: BCS superconductor or RVB paired insulator.

Thus AGP is a generalization of Slater Det., and certainly improves energy of uncorrelated wf’s.

The matrix » is the density matrix in a clean uncorrelated system and represnts a physical description of a mean-field Slater Determinant or a BCS superconductor:

i) Decays as 1/|el. Distance| in a metal
ii) Exponentially in an insulator or a superconductor with a gap.
iii) in between for a gapless superconductor.

Correlation (Jastrow) can turn a metal into an insulator (Capello .. SS.. PRL 2004)
A paired state is not necessarily a superconductor , rather can be a Mott insulator.

Optimization strategy in TurboRVB: correlated HF

The ansatz: $f(r_\uparrow, r_\downarrow) = \sum_{i,j} \lambda_{i,j}\varphi_i(r_\uparrow)\varphi_j(r_\downarrow) + \sum_{k=1}^{N/2} \psi_k^n(r_\uparrow)\psi_k^n(r_\downarrow)$

Molecular orbitals $\psi_k(r) = \sum_l c_l^k \varphi_l(r)$ defined over all $\{\varphi_l\}$

Start n=0 with $J = 1$ $\lambda_{i,j} = 0$ and

ψ_k^0 taken from TurboRVB-LDA (PRB' 10) in the same basis.

a) At iteration n optimize λ_{ij} and J at fixed ψ_k^n

b) Diagonalize ansatz → $\psi_k^{n+1}, \lambda_{ij} = 0$

c) Go to (a) until convergence.

After many iterations molecular orbitals are obtained and best correlated J+Slater det. ansatz is obtained.

Main advantages:

Easy to use symmetries, e.g. translation invariance in a solid : $\lambda_{i,j} = \lambda(\vec{R}_i - \vec{R}_j)$

Easy to reduce number of variational parameters, e.g. locality, optimize only $\lambda_{i,j}$ with $\left|\vec{R}_i - \vec{R}_j\right| < \xi$ from N^2 variational parameters to N.

Follow up: we can optimize efficiently molecular orbitals of standard J+Slater ansatz. Use of locality (above) possible also in metals.

Test on metallic Hydrogen 54/256 protons rs=1.28

Total energy = -28.849(2)/128.236(4)H   J+LDA error = 0.02/0.08H

Chosen →

R_{max}	**# parameters**	**Err Energyy (H)**
0	330/1542	0.0148(5)/022(6)
2	368/1813	0.0103(5)/0.005(1)
3	596/3003	0.0034(3)/0.001(1)
4	1026/5108	0.0015(3)/0.004(1)
5	1483/8443	0.0010(3)/0.000(1)
•	1761/34181	0/?

With few parameters we improve J+LDA, that is good, but difference in forces may be substantial.

NB DFT favors metallic atomic phase.

Forces: How to deal with M>>1 atoms ?

If we apply finite difference methods we need to compute:

$$F_{\nu a} = -\frac{E(R_a^\nu + \Delta) - E(R_a^\nu)}{\Delta}$$

Thus 3M+1 independent calculation of the energy: a too heavy cost for M large.

Algorithmic differentiation helped much

SS & Luca Capriotti, JCP 133, 234111(2010)

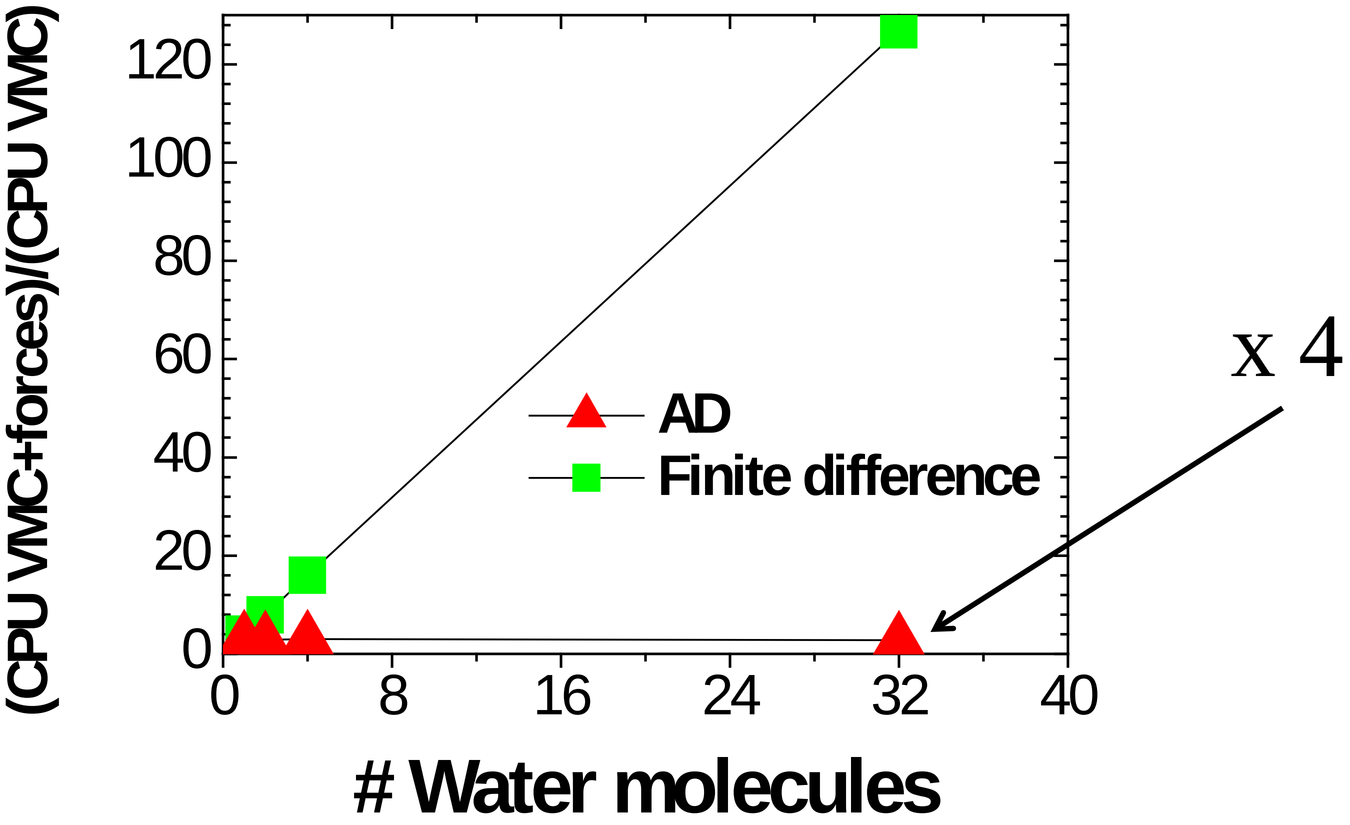
and thanks also to Tapenade:

http://www-sop.inria.fr/tropics/tapenade.html

Automatic derivation of the most boring routines are done automatically.

In practice 10000 lines in few seconds of work.
After that some trivial optimization.

Cpu time referenced to simple VMC (only energy) for computing all 3M force components in water.



x 4

For DMC the overhead to compute all forces is ~0

Use of pseudopotentials & Jastrow possible

Now we have efficient forces. Structural optimization and dynamics possible with QMC?

The first attempt of MD+QMC(DMC):
J. C. Grossman and L. Mitas PRL ’05
But here we want to use QMC forces…

With QMC each MD iteration can be done with a short and noisy evaluation of forces (much faster…)
C. Attaccalite and S. S. PRL’08

$$\boxed{\begin{array}{l} \dot{v} = -\gamma(R)v + f(R) + \eta \\ \dot{R} = v \qquad < \eta\eta > = 2T\gamma(R) \end{array}}$$

In QMC $< f f > = \alpha(R)$ Covariance matrix

So we have the noise for free if $\gamma \propto \alpha$

Discretization of the damped Langevin equation

The most important thing is to choose the largest possible time step ” without too much error

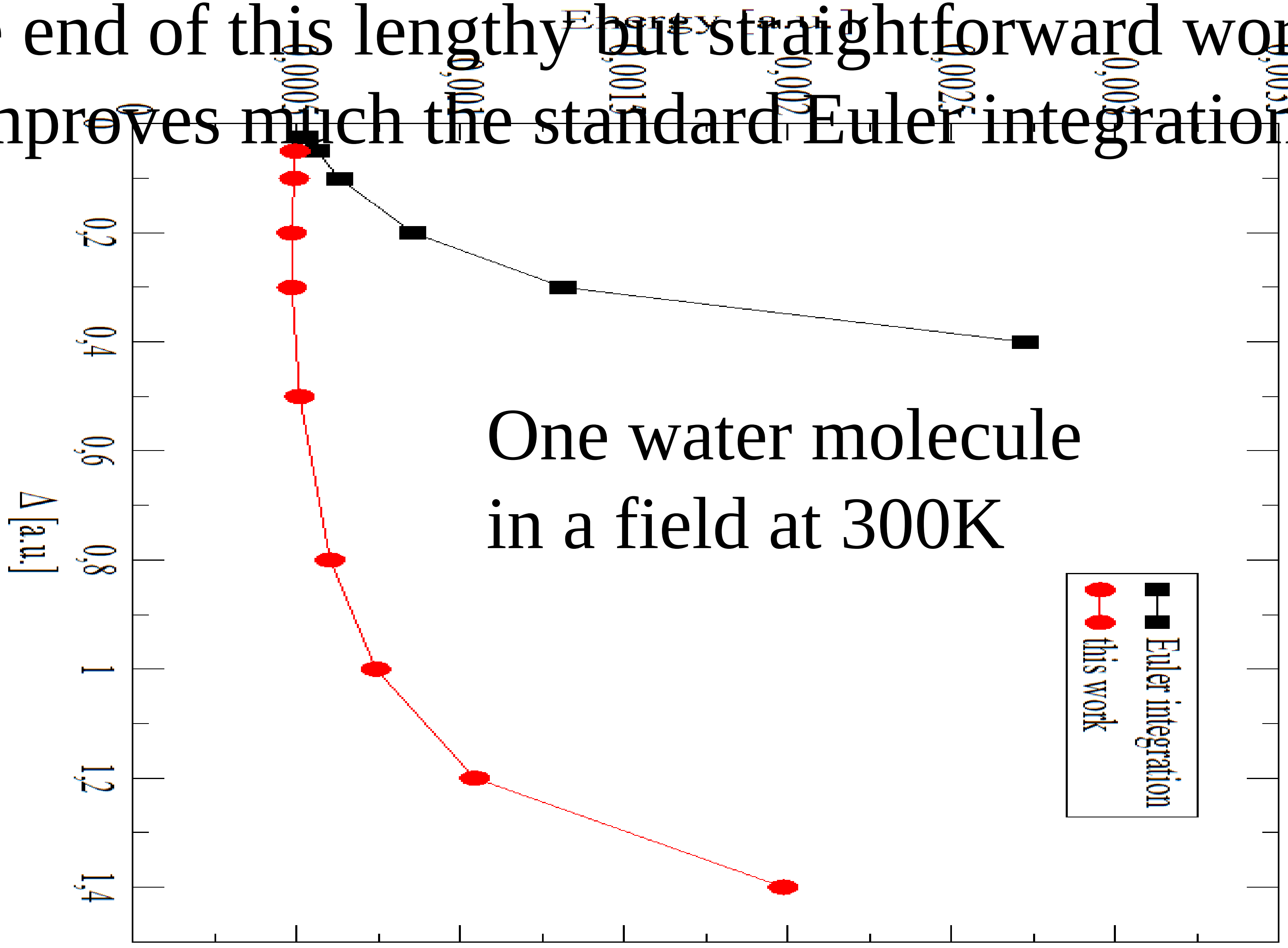
Since the equation at fixed x are linear in v we can integrate exactly the equation assuming x does not change much in the interval t,t+” no matter how large is the value of the friction ³(x)

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

and….

$$
\begin{aligned}
< \tilde{\eta}_i \tilde{\eta}_j > &= \bar{\alpha}'_{1,1} \\
&= \bar{\alpha}\bar{\gamma}\frac{\sinh(\Delta\bar{\gamma})}{4\sinh(\Delta\bar{\gamma}/2)^2} \\
< \tilde{\tilde{\eta}}_i \tilde{\tilde{\eta}}_j > &= \bar{\alpha}'_{2,2} \\
&= \bar{\alpha}\bar{\Theta}^{-2}\left[\frac{\Delta}{\bar{\gamma}^2}\right. \\
&+ \left.\frac{1}{2\bar{\gamma}^3}\left(-2 + e^{-\Delta\bar{\gamma}} + 2e^{-2\bar{\gamma}\Delta} - e^{-3\bar{\gamma}\Delta}\right)\right] \\
< \tilde{\tilde{\eta}}_i \tilde{\eta}_j > &= \bar{\alpha}'_{2,1} = \bar{\alpha}'_{1,2} \\
&= \frac{\bar{\alpha}\bar{\Theta}^{-1}}{4\bar{\gamma}\sinh(\frac{\Delta\bar{\gamma}}{2})} \\
&\quad \left(2e^{\frac{\bar{\gamma}\Delta}{2}} - 2 - e^{-\bar{\gamma}\Delta} + e^{-2\bar{\gamma}\Delta}\right)
\end{aligned}
$$

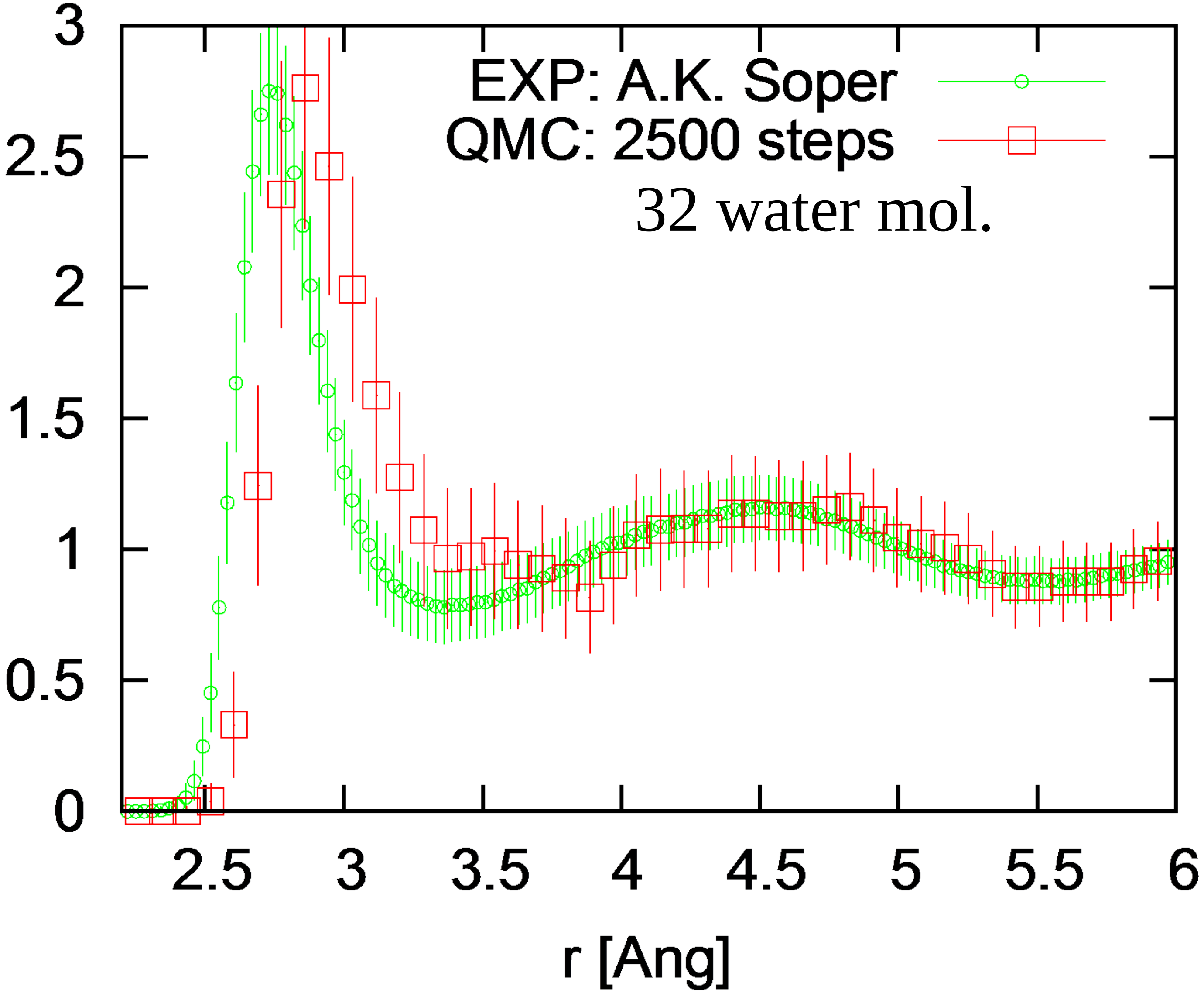
At the end of this lengthy but straightforward work one improves much the standard Euler integration…



One water molecule in a field at 300K

Radial distribution OO

Langevin dyn. - dt=1fs



This is like a dream in Monte Carlo so far…
A molecular dynamics with a variational wf.

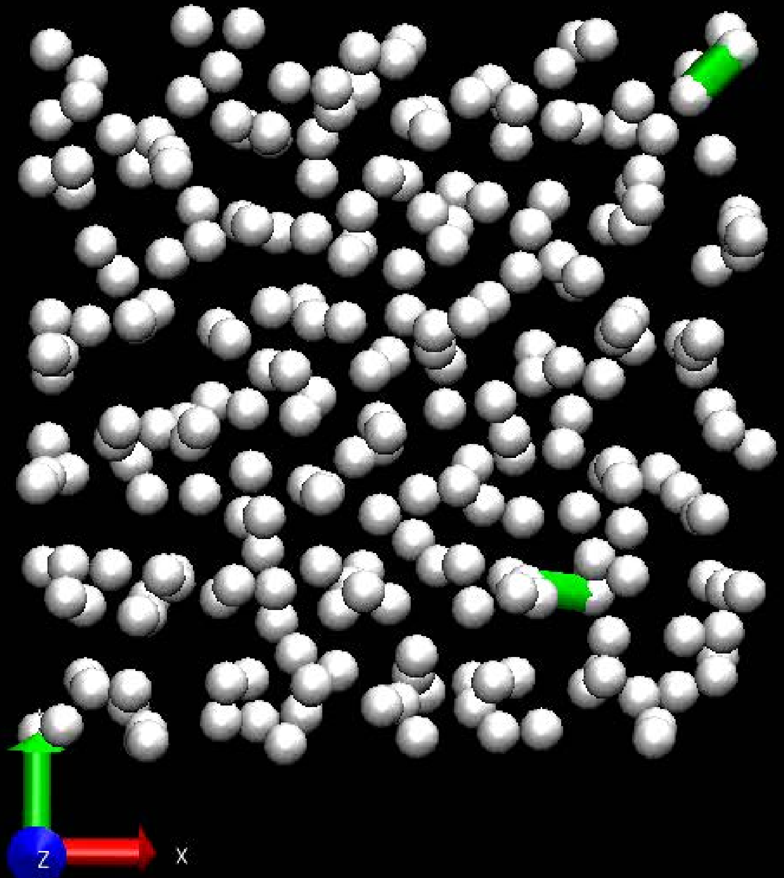
Forces are computed at each step at the optimal minimum of variational parameters,i.e. to enforce the Borh-Oppenheimer constraint, namely
6 optimization steps each iteration.

But it took 3-5 years to understand that….
i) Large time steps are necessary to equilibrate.
ii) Compact (few parameters) and well parametrized wf in a local basis for an efficient optimization.

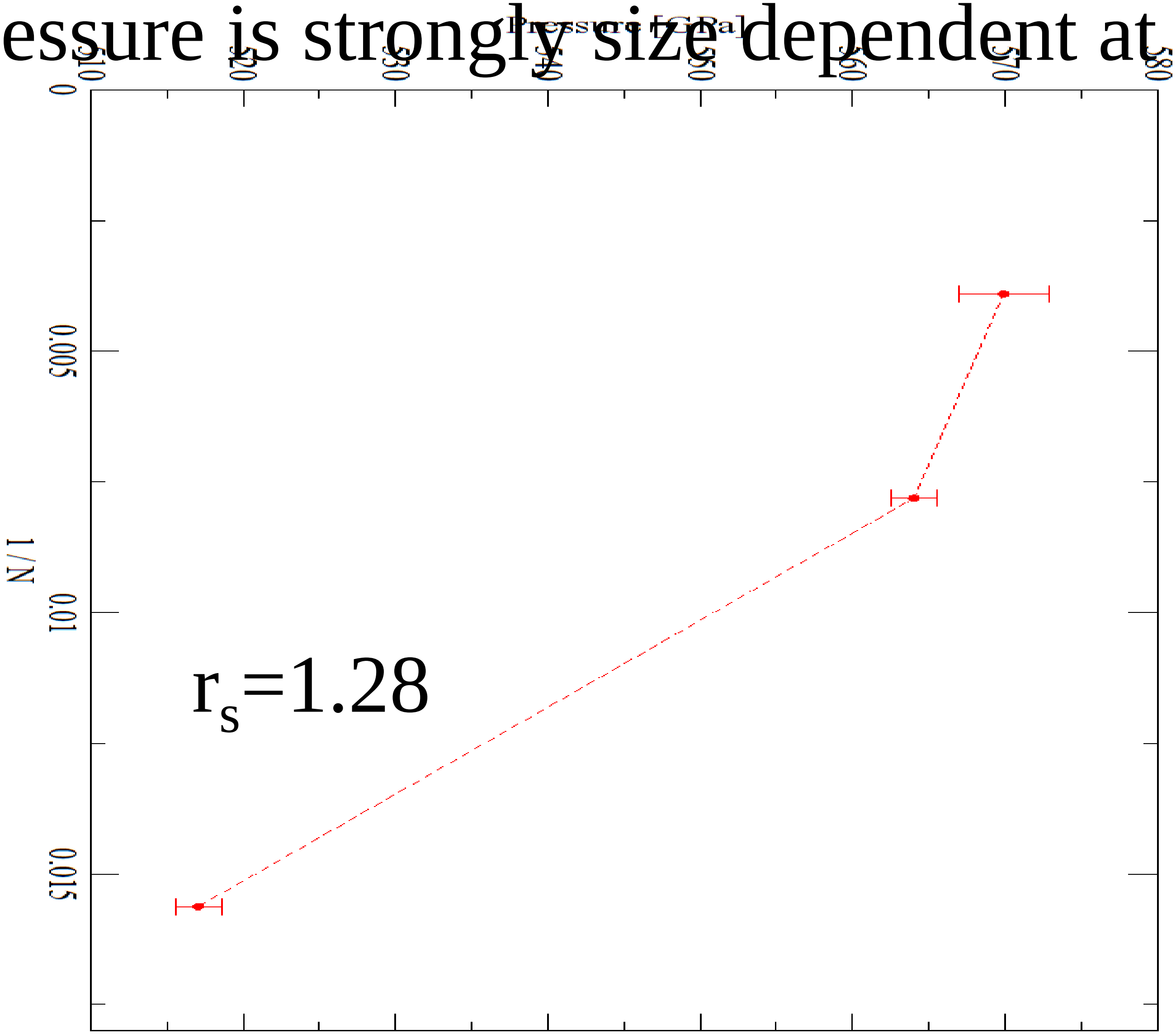
And now let’s talk about Hydrogen.

A metallic liquid phase is difficult to simulate without a sample system containing several atoms.

In this film we want to show 256 Hydrogen even at 425 Gpa and 600K, molecular bonds are clearly formed during the simulation.
Notice we start with the expected atomic liquid DFT solution.

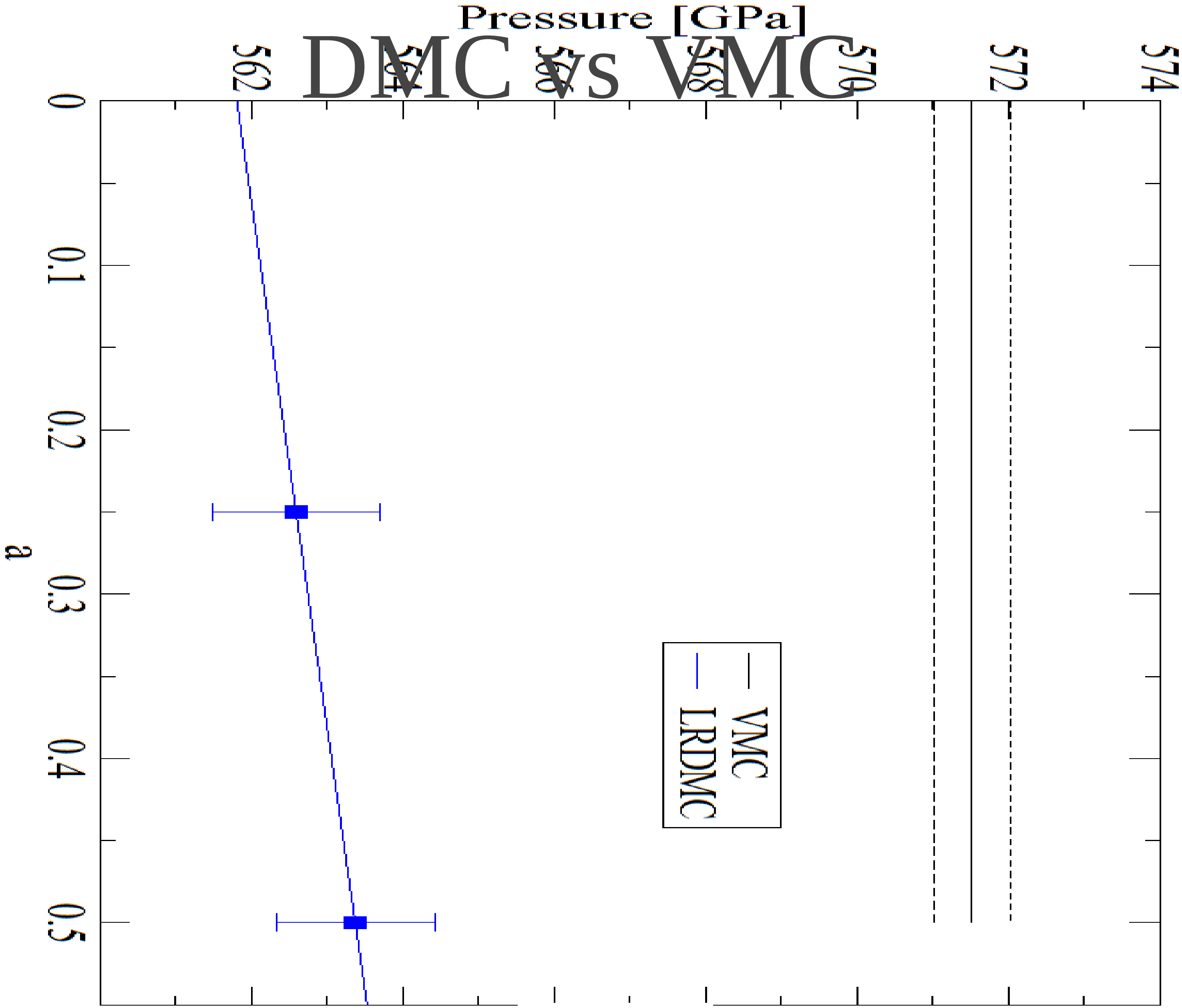

Z
X

The pressure is strongly size dependent at 600K



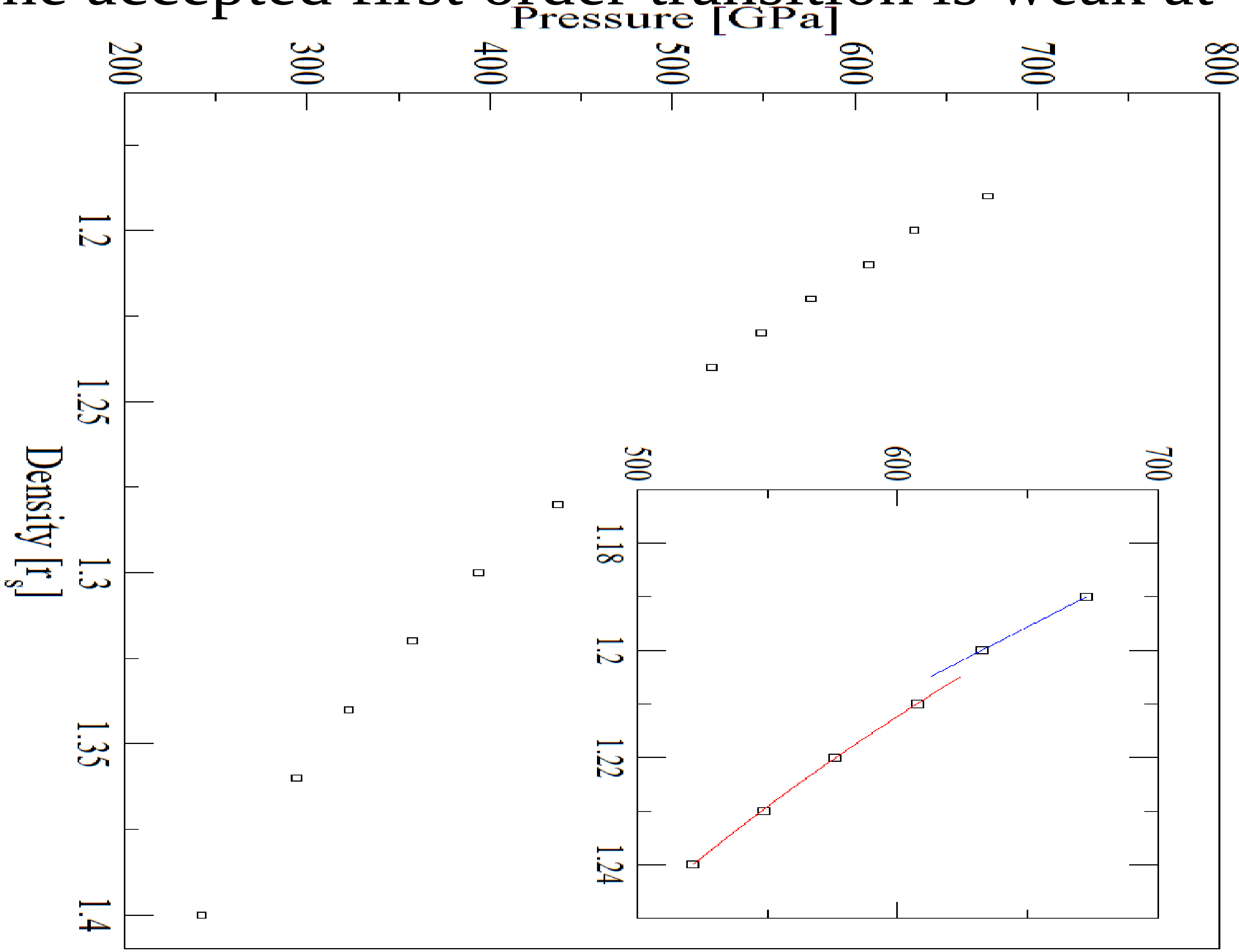
r_s=1.28

DMC vs VMC

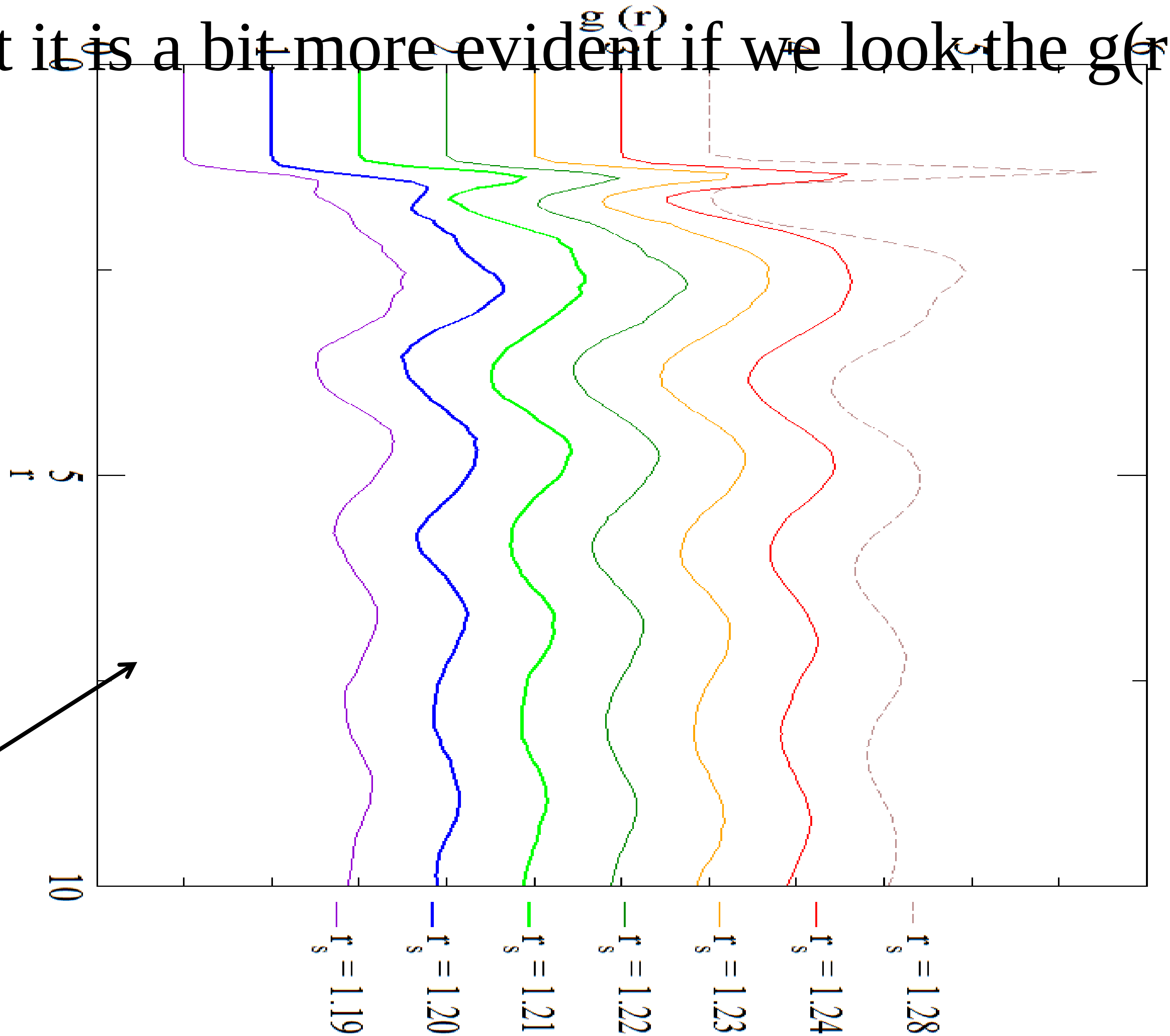


10 ” Ä

The accepted first order transition is weak at 600K

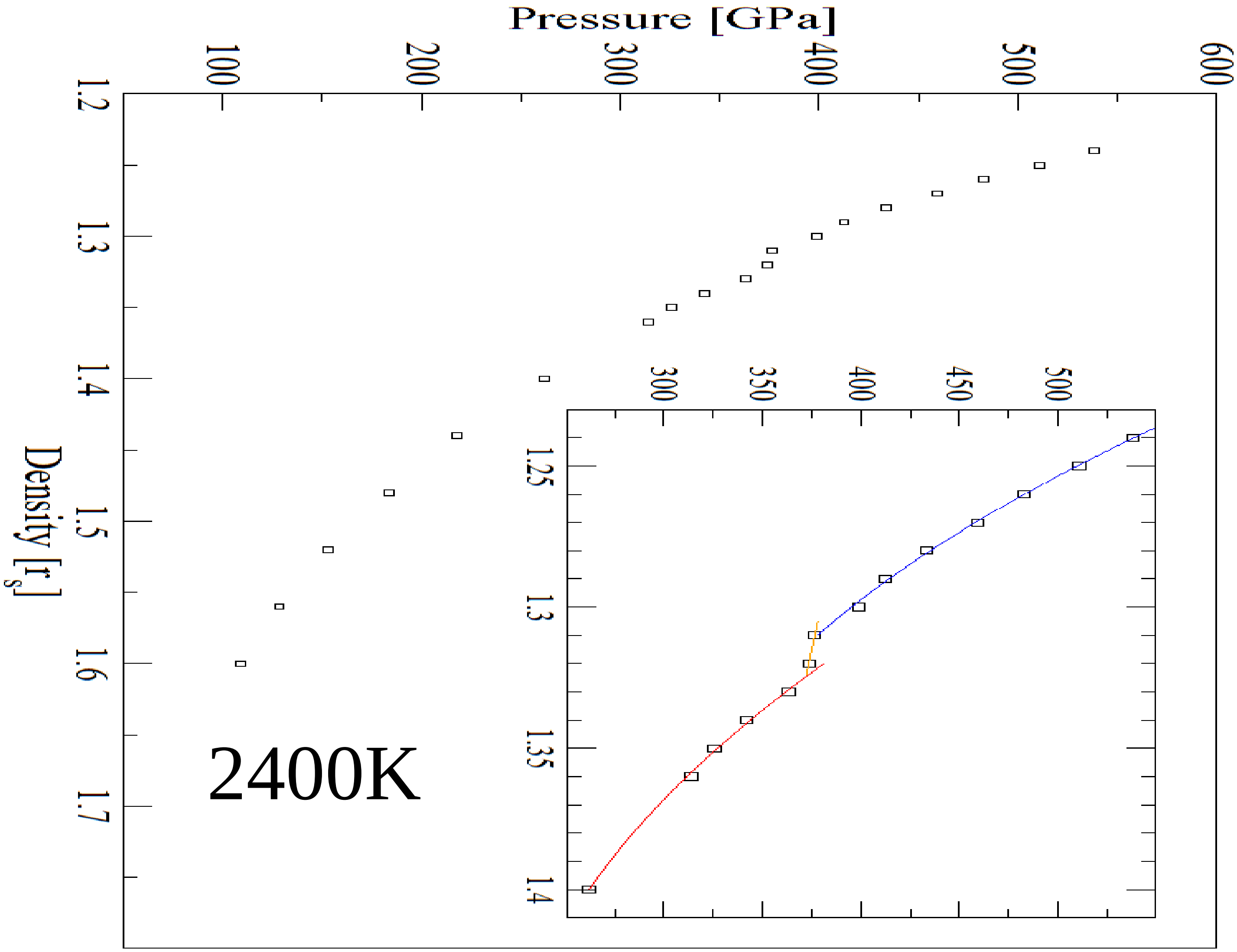


But it is a bit more evident if we look the g(r)

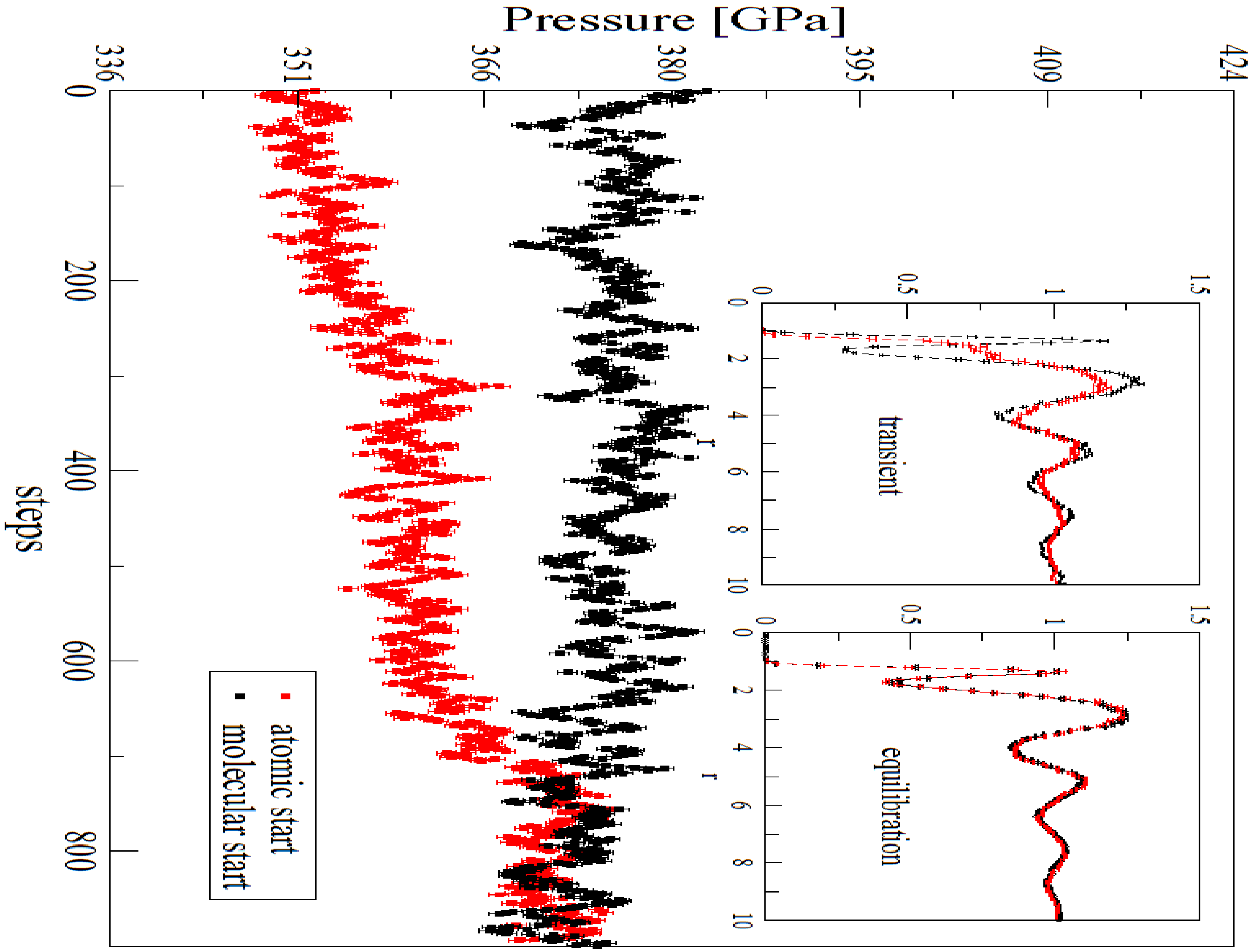


Jump

At large temperature is instead clear



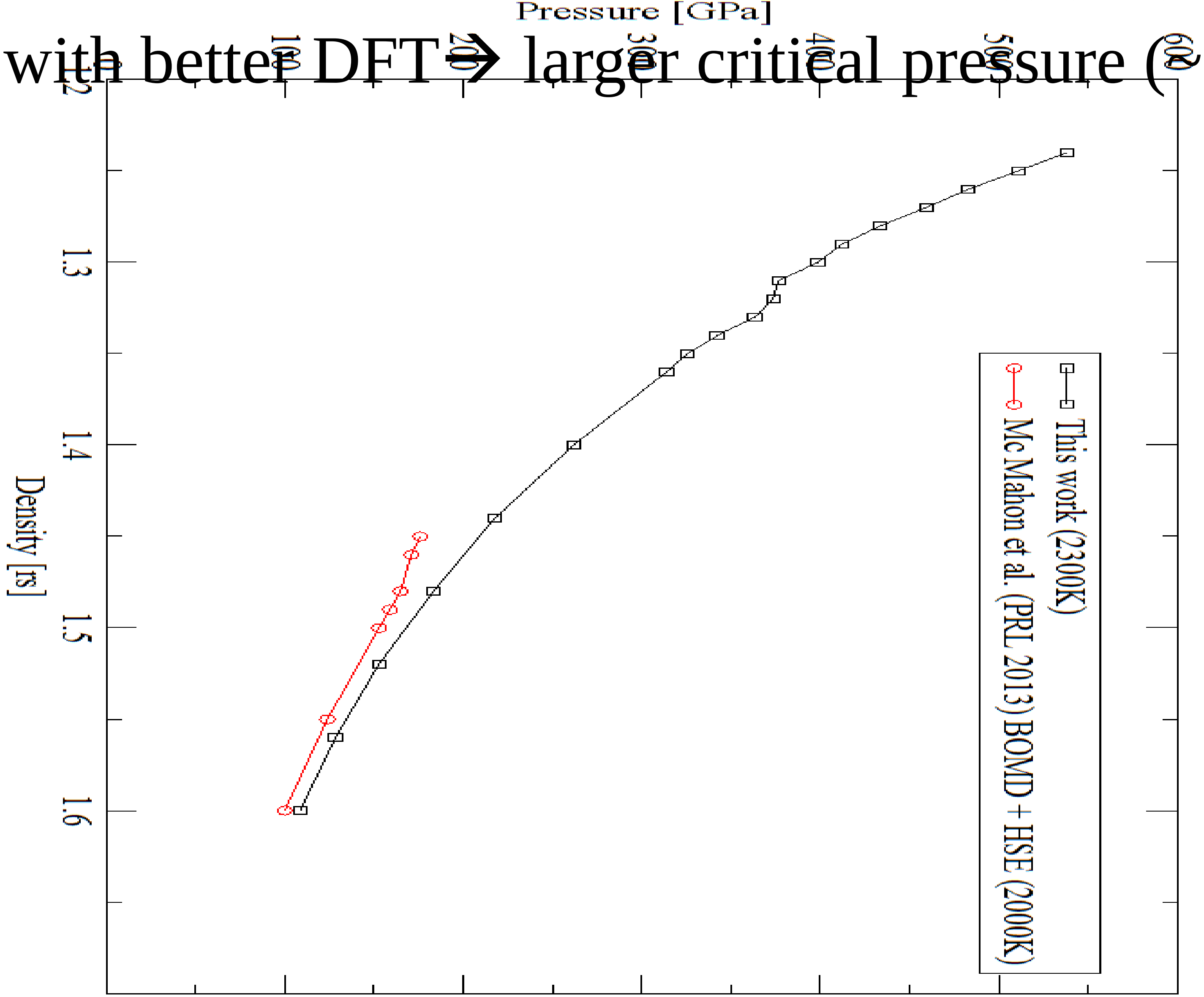
To show the power of QMCMD we take atomic liquid at r_s=1.31 and start MD at r_s=1.32



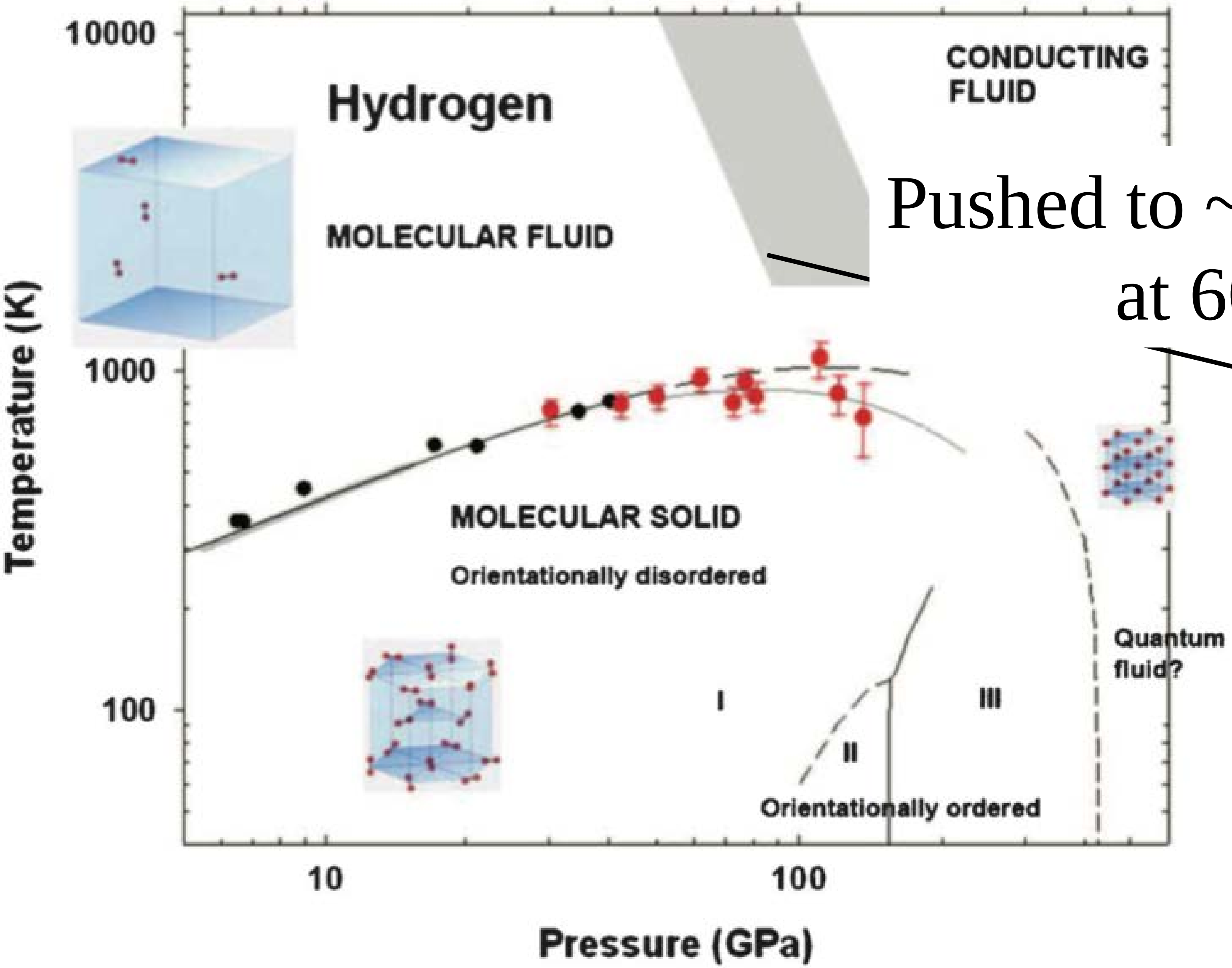
Comparison with previous work

Old claim same authors CEIMC → no first order

Now with better DFT → larger critical pressure (~200Gpa)

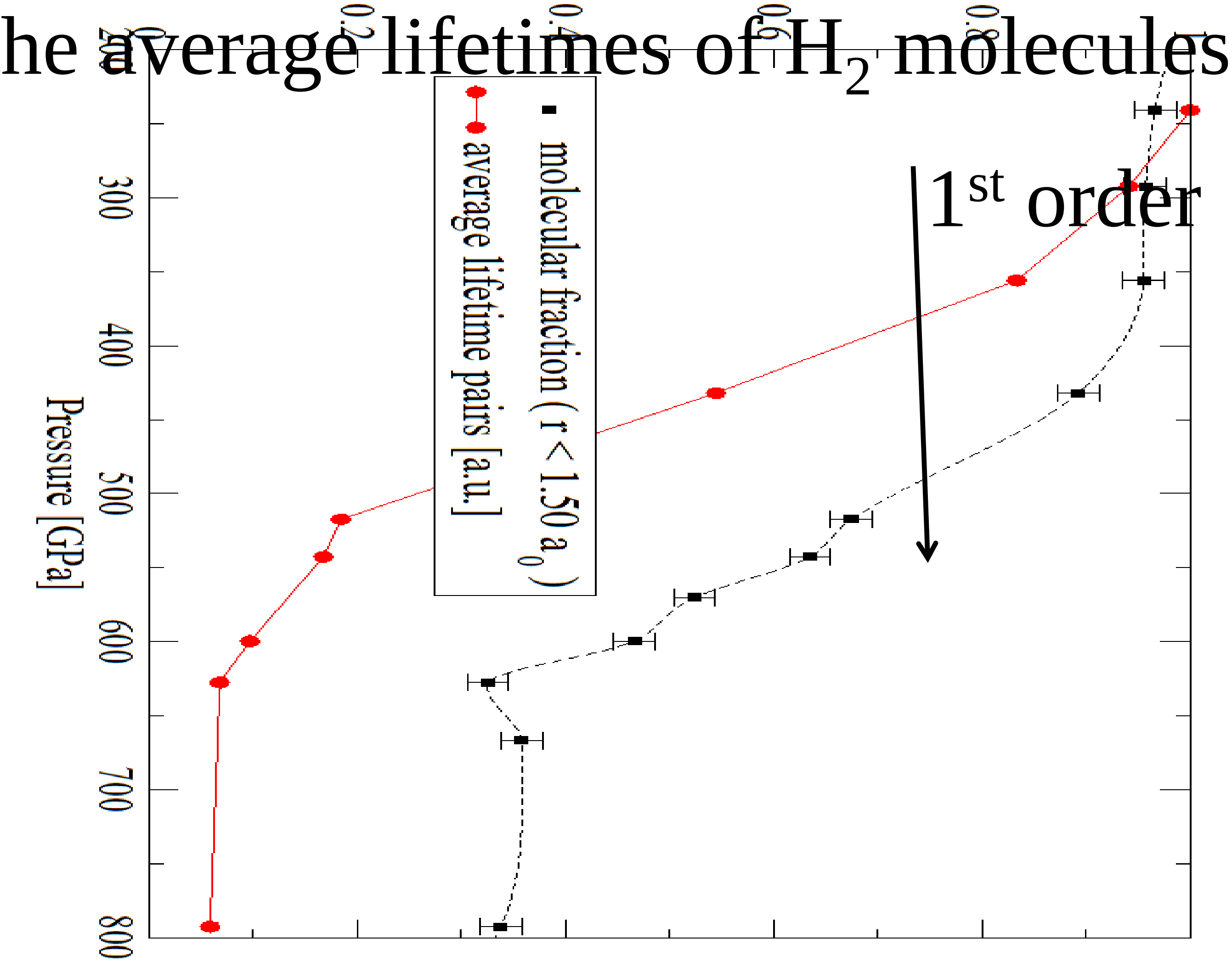


First order transition at very large P



Pushed to ~500Gpa
at 600K

We have found a sharp crossover around 400Gpa of the average lifetimes of H_2 molecules.



1st order

Thus experiments may have just seen the crossover not the real metallic phase, still out of reach.

Conclusions

Realistic simulation of liquids are now possible also within QMC, at least VMC. 256 ions are not so far from what has been done within DFT (432H).

Long range interactions-so difficult for DFT-are very accurately described by the Jastrow factor:

the Be_2 molecule is successfully described.

By using locality (local basis, short range couplings) the number of variational parameters becomes affordable even for large number of atoms and efficient MD QMC is possible.

- **TurboRVB Quantum Monte Carlo package**

http://turborvb.qe-forge.org/index.html

main developers:

Sandro Sorella
Michele Casula
Claudio Attaccalite
Leonardo Spanu

- **Funding:**

MIUR-CNR, Riken-Tokio, PRACE…

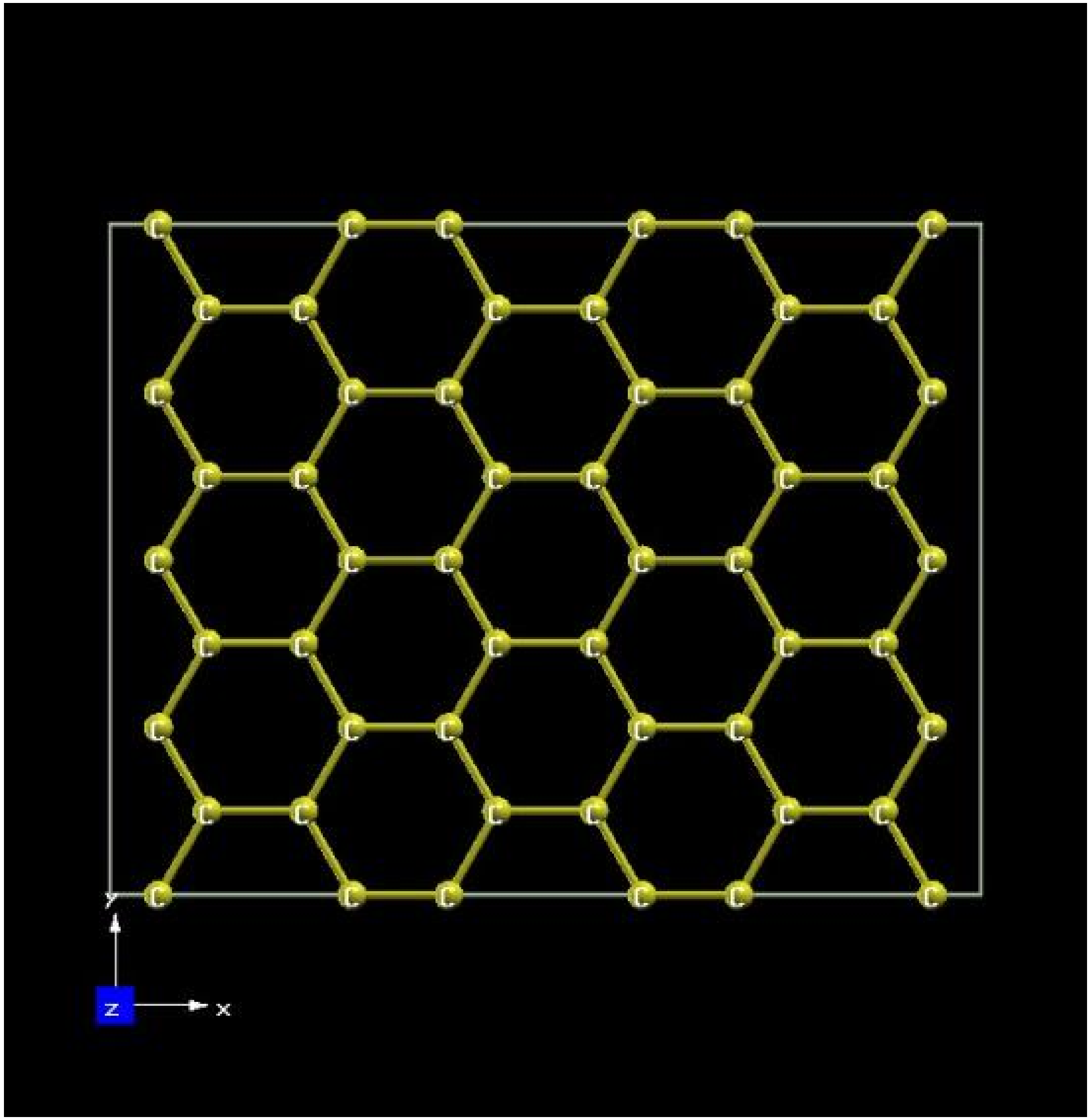
- **Computational support**

CINECA Bologna
CCRT at CEA
SISSA

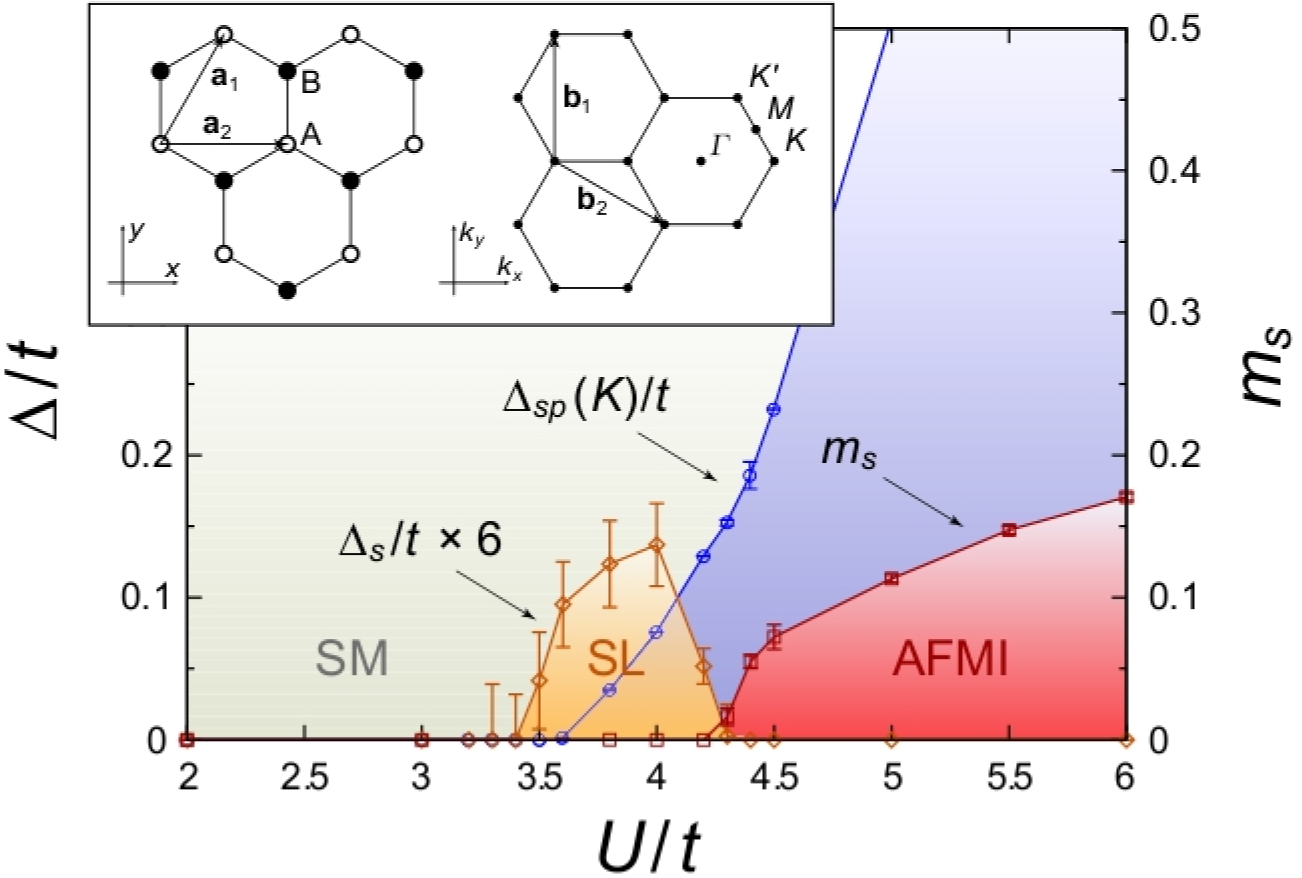
And now let us discuss about graphene the solid state version of benzene.

Is the RVB energy gain completely irrelevant?

Graphene layers can be experimentally prepared



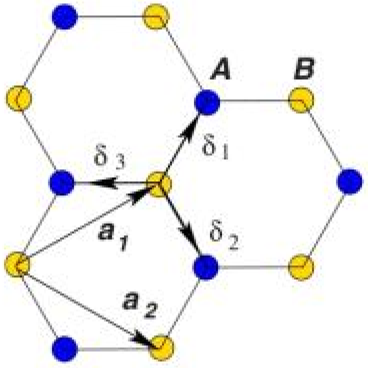
Recent exciting result on the Hubbard model… Muramatsu group, Nature 2010.

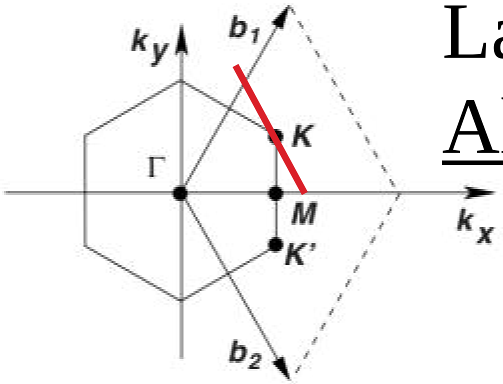


No broken symmetry but a full gap at U/t~4…

this is an RVB phase…

Graphene

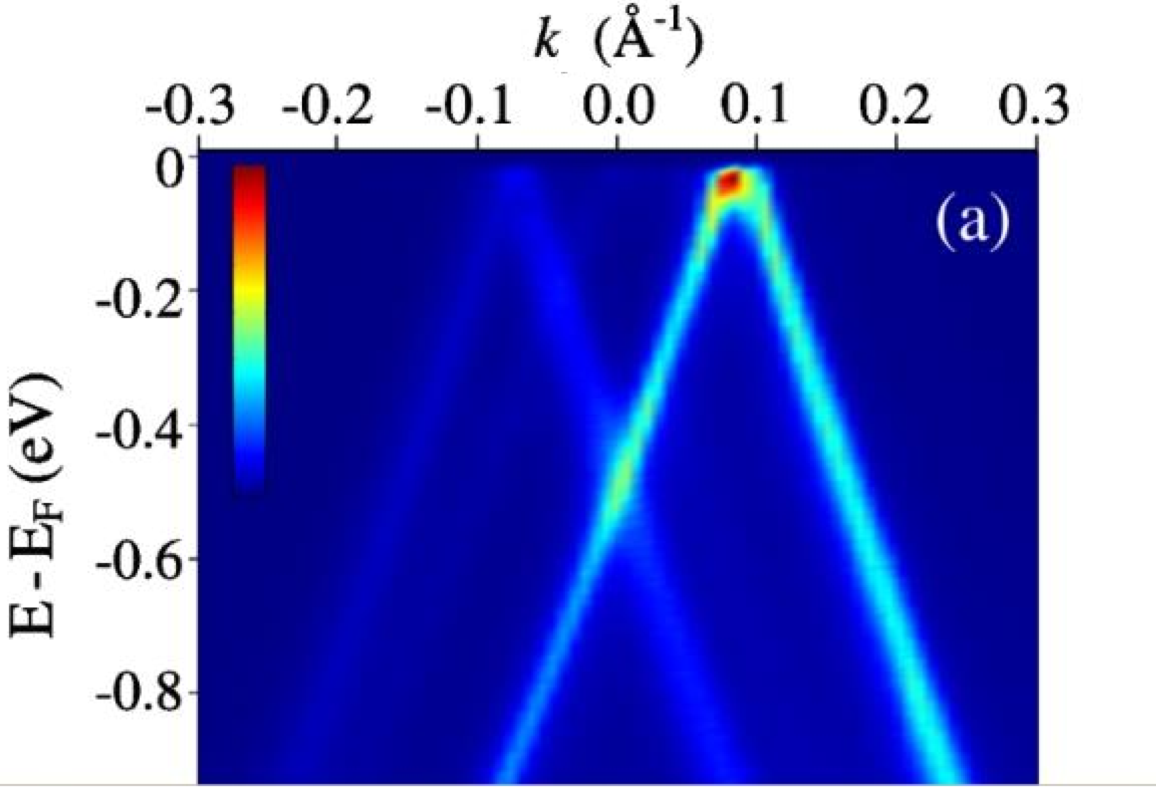




Lanzara group, PRL’10

<u>Almost</u> perfect Dirac spectrum:

$$E(\vec{k}+\vec{K}) = \pm v_F\, |\, k\, |$$



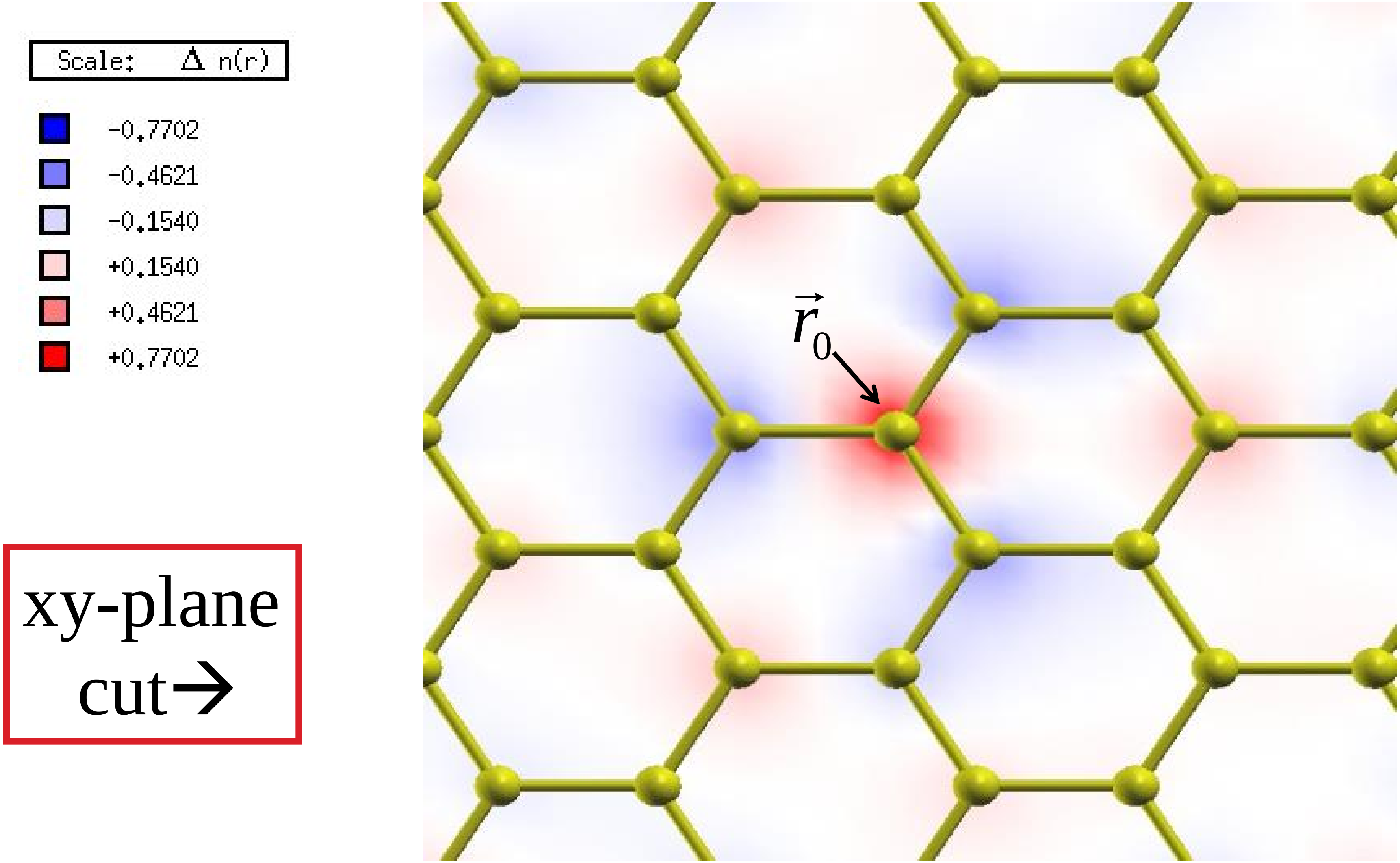
We have minimized the energy in a large
Basis 11s7p5d2f/atom for up to 112 C atoms
Within Periodic Boundary conditions.

~2000 variational parameters
Several iterations of state of the art QMC
Optimization Jastrow + AGP with fixed number
n^* of molecular orbitals $n^* >$ #el/2.

Huge cpu time ~100000 core hours.

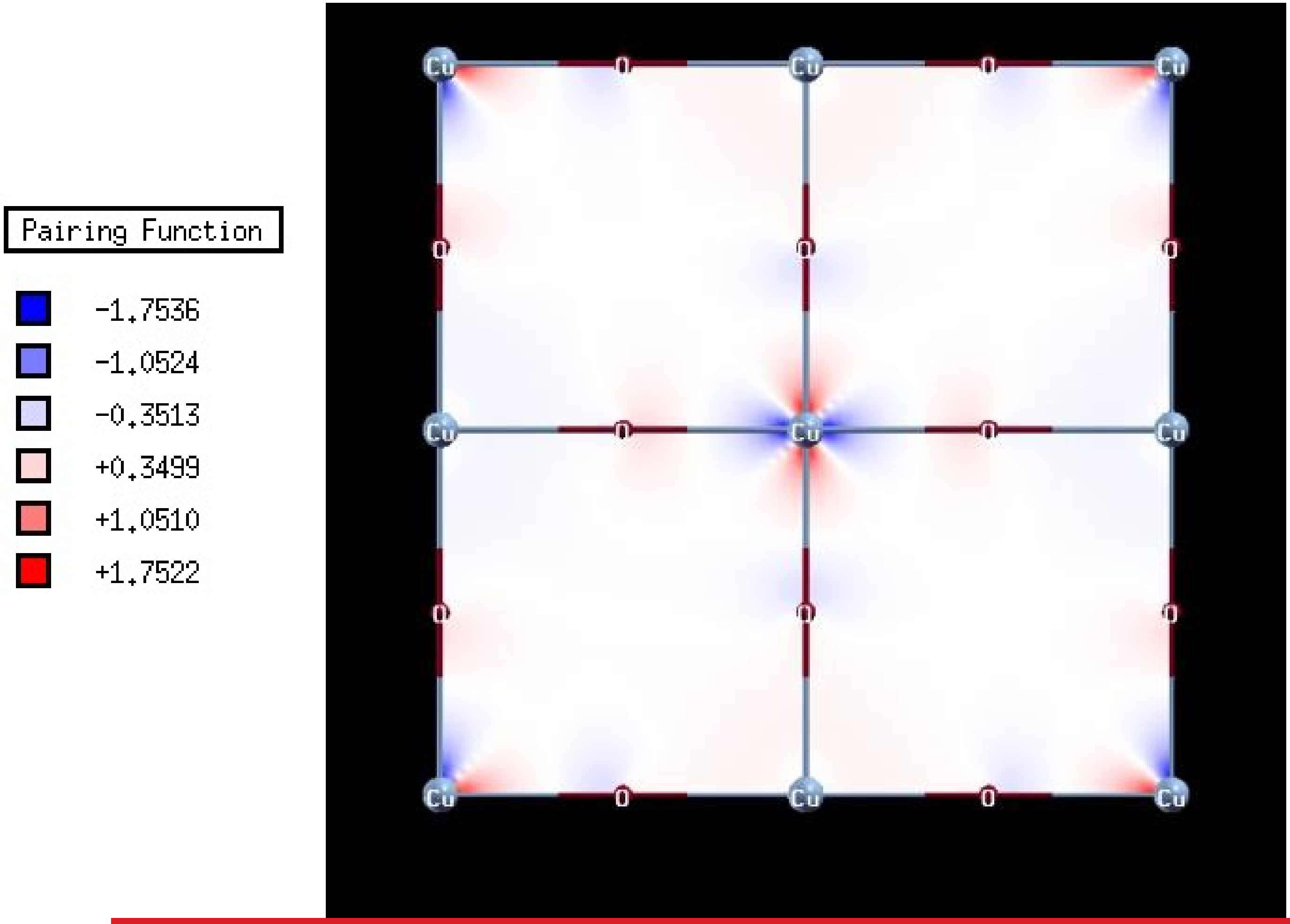
The projected pairing function $\pi - \text{band}$

$$f(\vec{r}, \vec{r}_0) \quad \text{vs} \quad \vec{r} \quad \text{at} \quad \vec{r}_0 \text{ fixed on an atom}$$



xy-plane cut→

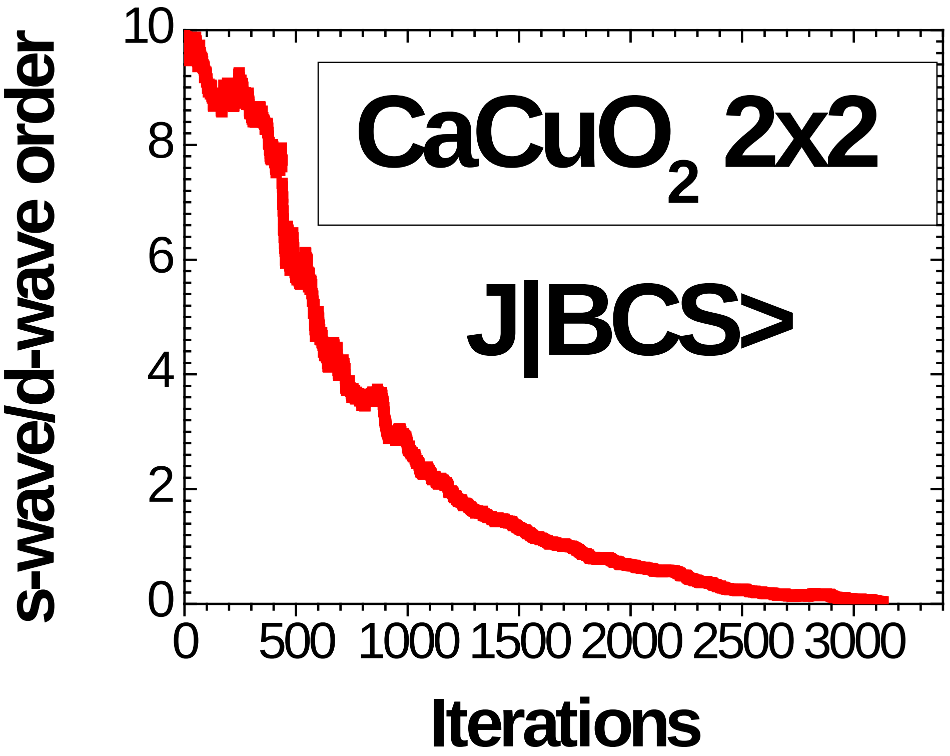
Instead for the valence projected pairing function in the HTc-parent-compound $CaCuO_2$



Huge energy gain 1 eV/Cu atom !!!

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

We started with a mixed s-wave/d-wave 10/1 pairing and …



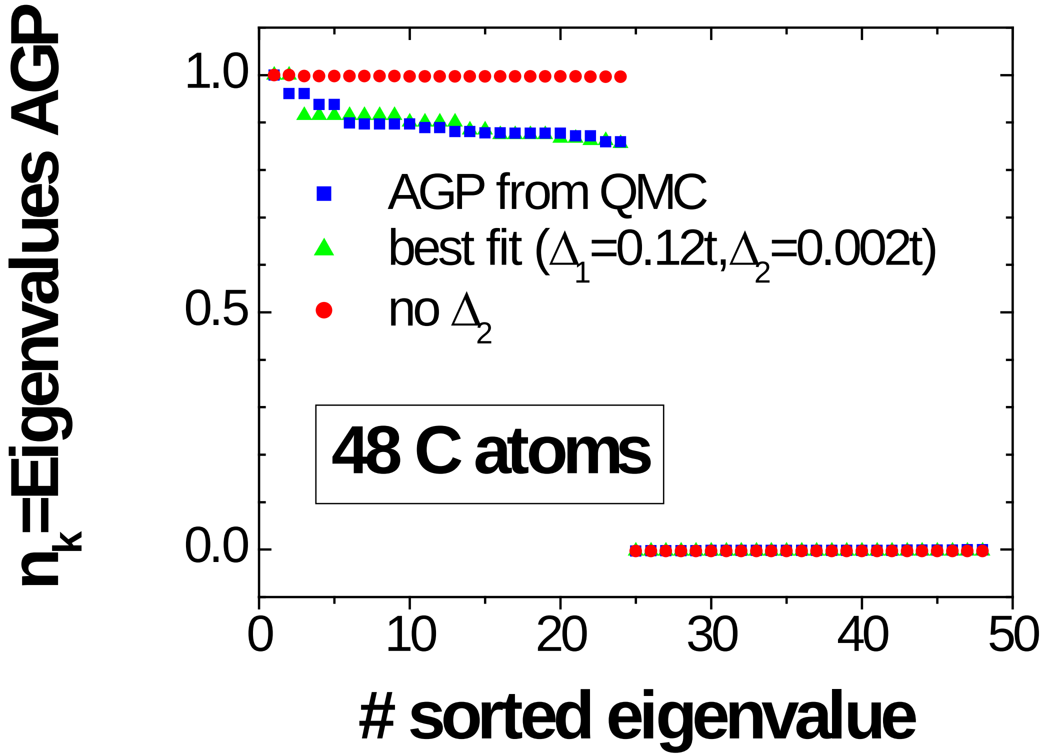
After ~2000 iterations the s-wave is gone and d-wave is definitively the right pairing in cuprates

Back to graphene

How can we determine a BCS effective low energy Hamiltonian for our pairing function that we have obtained by energy minimization?

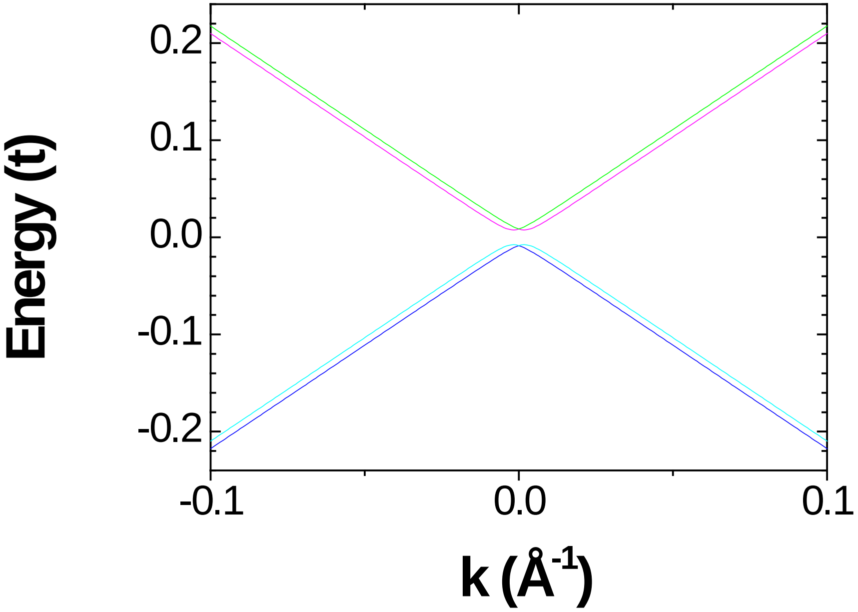
Remind, after the minimization we have direct access to the eigenvalues f_k of the pairing function

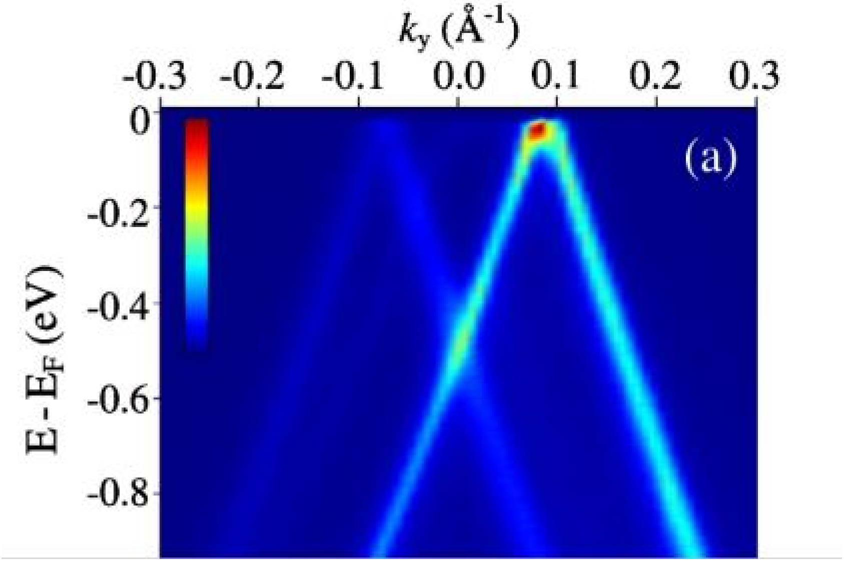
$$H_{BCS} = \sum_{<i,j>,\sigma} -t c^{+}_{i\sigma} c_{j\sigma} - \mu \sum_{i,\sigma} c^{+}_{i\sigma} c_{j\sigma} + \sum_{i,j} \Delta(|\vec{r}_i - \vec{r}_j|) c^{+}_{i\uparrow} c^{+}_{j\uparrow} + h.c.$$



#Carbon	Δ_1	Δ_2	μ
16	0.16t	0.0012t	-0.0041t
48	0.12t	0.0020t	0.0017t
∞	0.10t	0.0024t	0.0045t

Due to the presence of next-neighbor s-wave pairing, a small gap ~0.01eV (t=2.8eV) is found.





No broken A-B symmetry no time-reversal,
Just an RVB spin-liquid makes the effect.

Conclusions

The RVB wave function has been tested on several compounds up to graphene (112 C supercell)

Contrary to lattice simulation (Baskaran PRB’ 10) the Coulomb repulsion favors s-wave pairing.

The energy gain is tiny (<0.01ev/C) much smaller than in cuprates (~1eV/Cu), thermodynamic limit?.

In graphene we have evidence of an s-wave RVB, Marginally gapped due to second neighbor BCS.

Back to RVB theory for graphene?

Acknowledgments

Thanks for the new ideas and intuitions

that will be always alive…

Acknowledgments

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  Leonardo Spanu (UC Davis)

- H_2 @ benzene

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  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

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

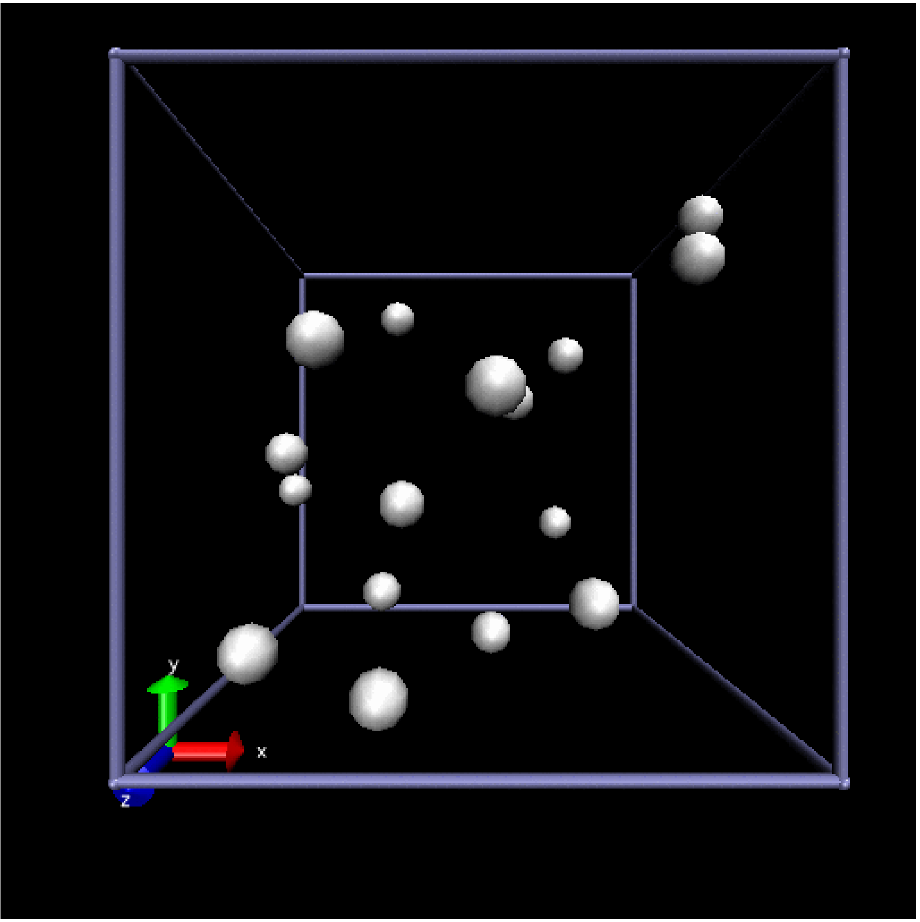
$$\bar{\alpha}(\vec{R}) = \bar{\alpha}_0 + \Delta\bar{\alpha}_{QMC}(\vec{R})$$

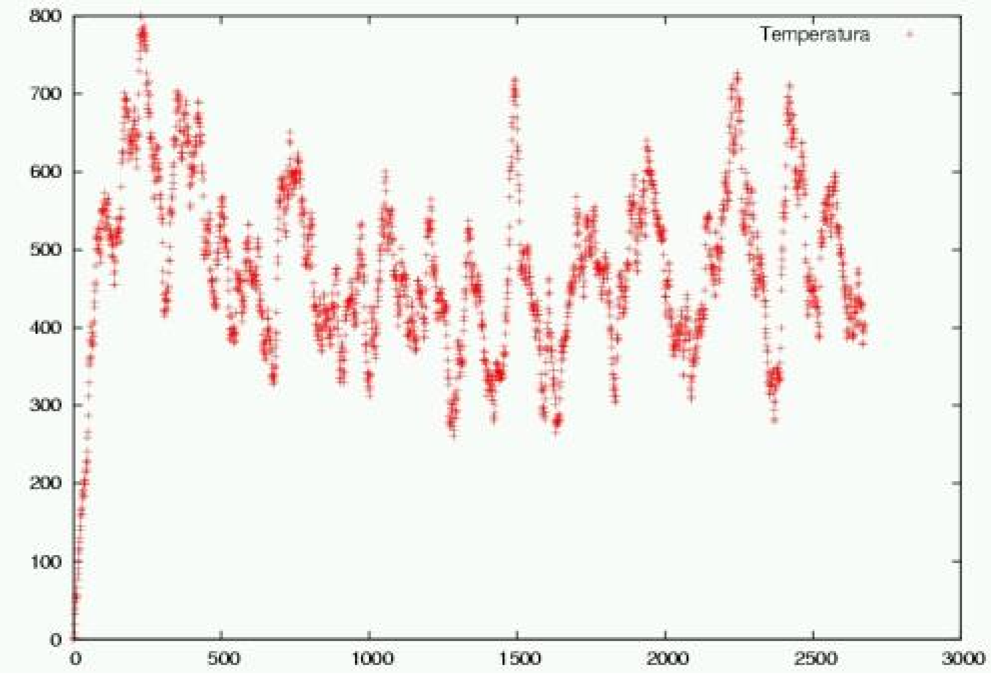
$$\boxed{\bar{\gamma}(\vec{R}) = \frac{\beta}{2}\bar{\alpha}(\vec{R})}$$

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

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

The 16 H case with PBC, MD with friction





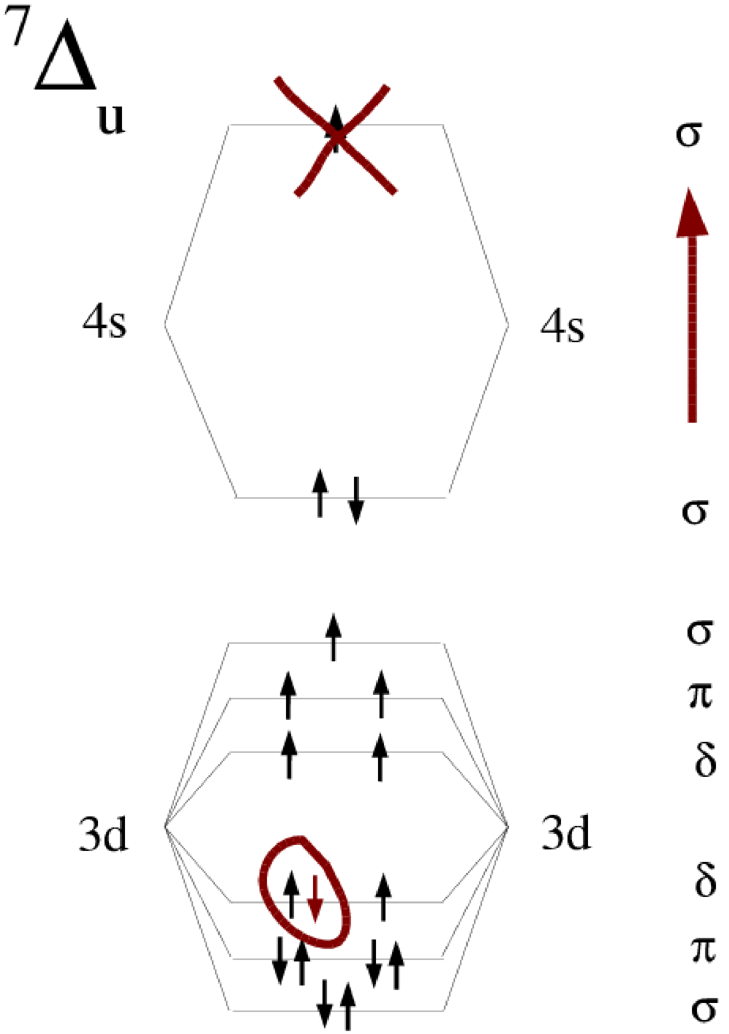
RVB liquid phase possible at high pressure

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

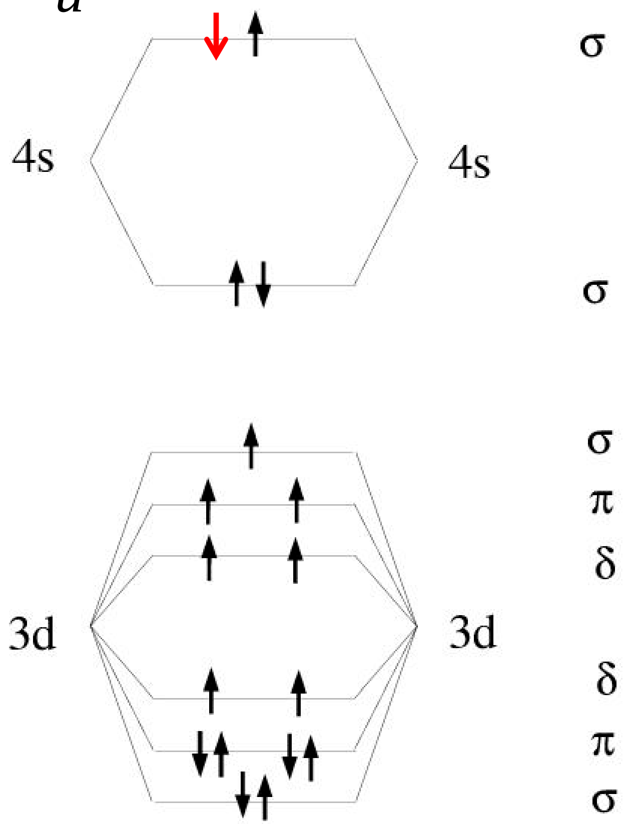
It is possible to explain the photoemission spectrum in the anion Fe_2^-
Leopold JPC (1988)

DFT occupation molecular orbitals

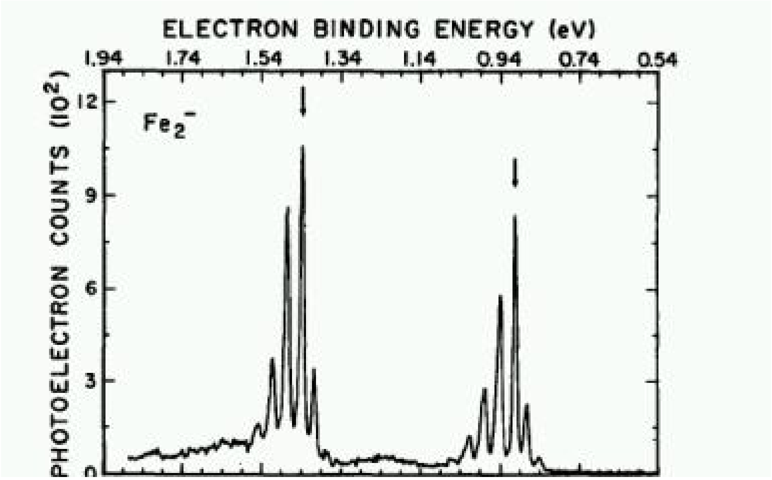


The right occupation is due to correlation

$^8\Sigma_u^-$



Explains the Fe_2^- exp.

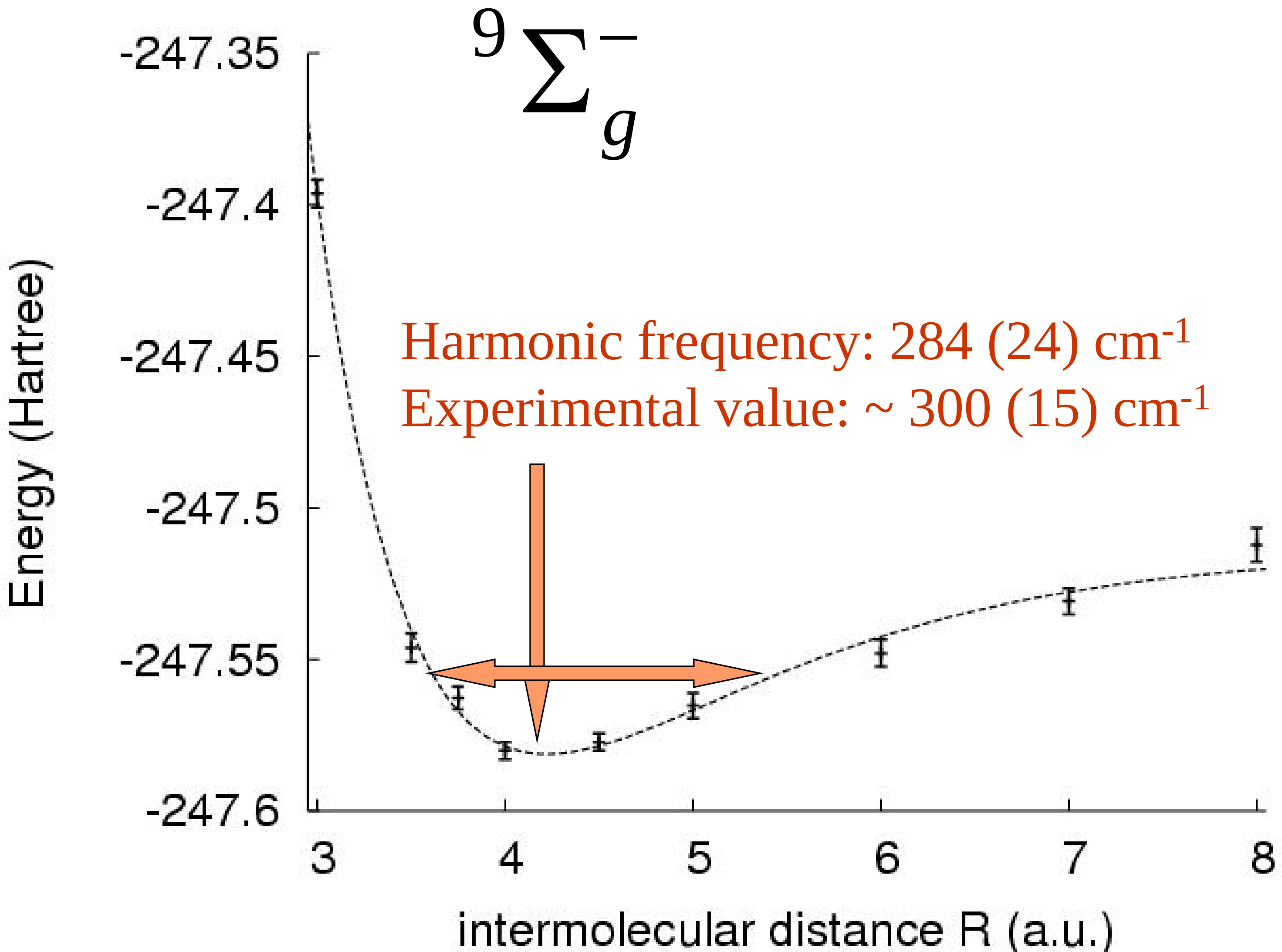


Within our RVB wf

$^7\Delta_u$ 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:

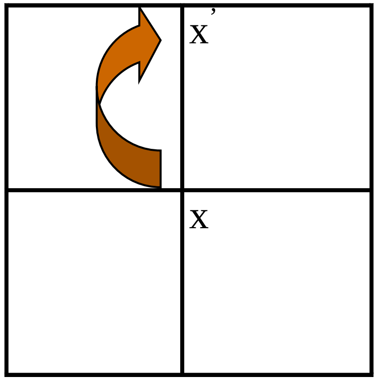
simulation of complex correlated electron systems by Monte Carlo calculation and beyond DFT

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→$1/a^2$

Potential term

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

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

⇒

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

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**

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

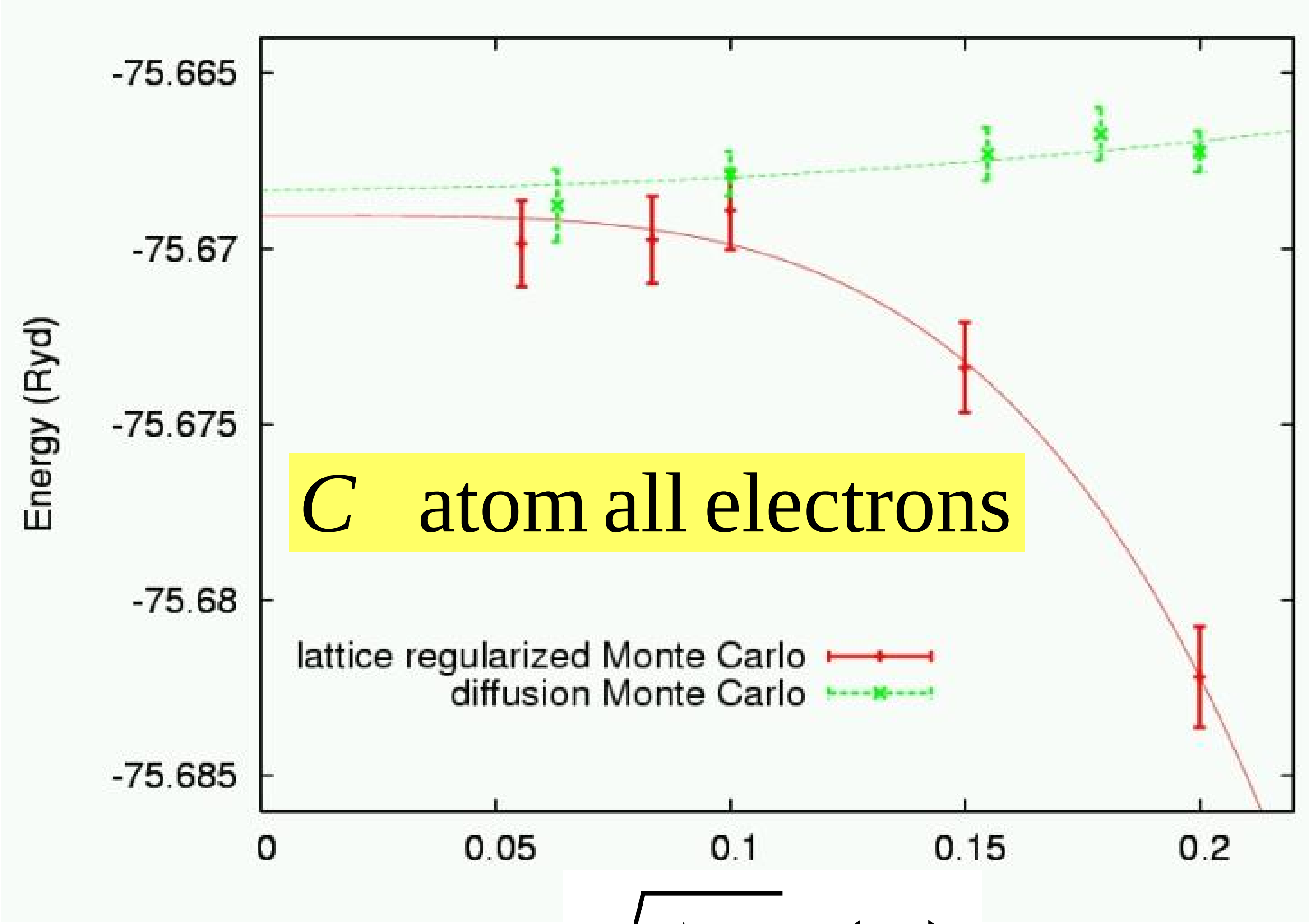
p can depend on the distance from the nucleus

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

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



C atom all electrons

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

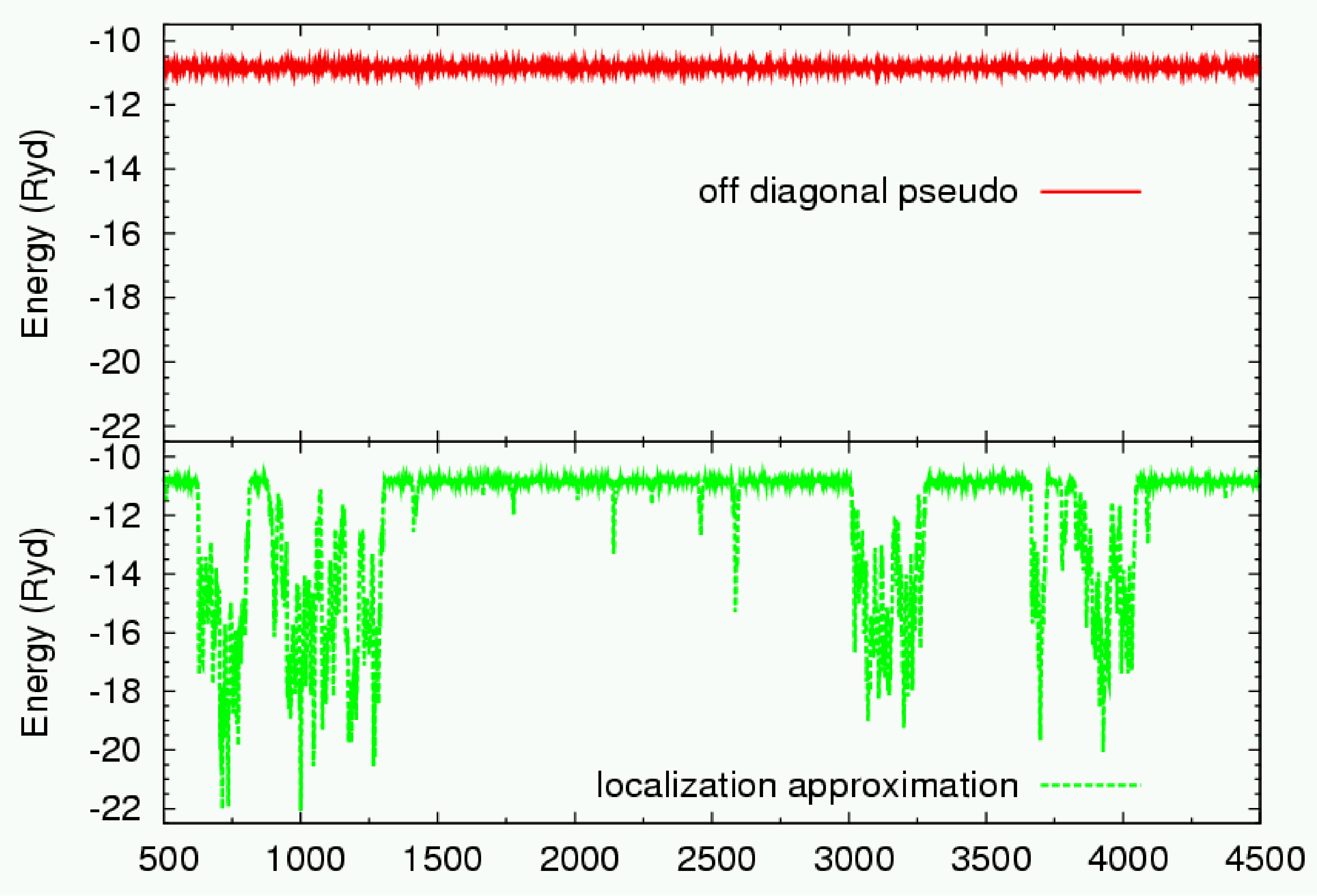
Non local pseudo possible!!!

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

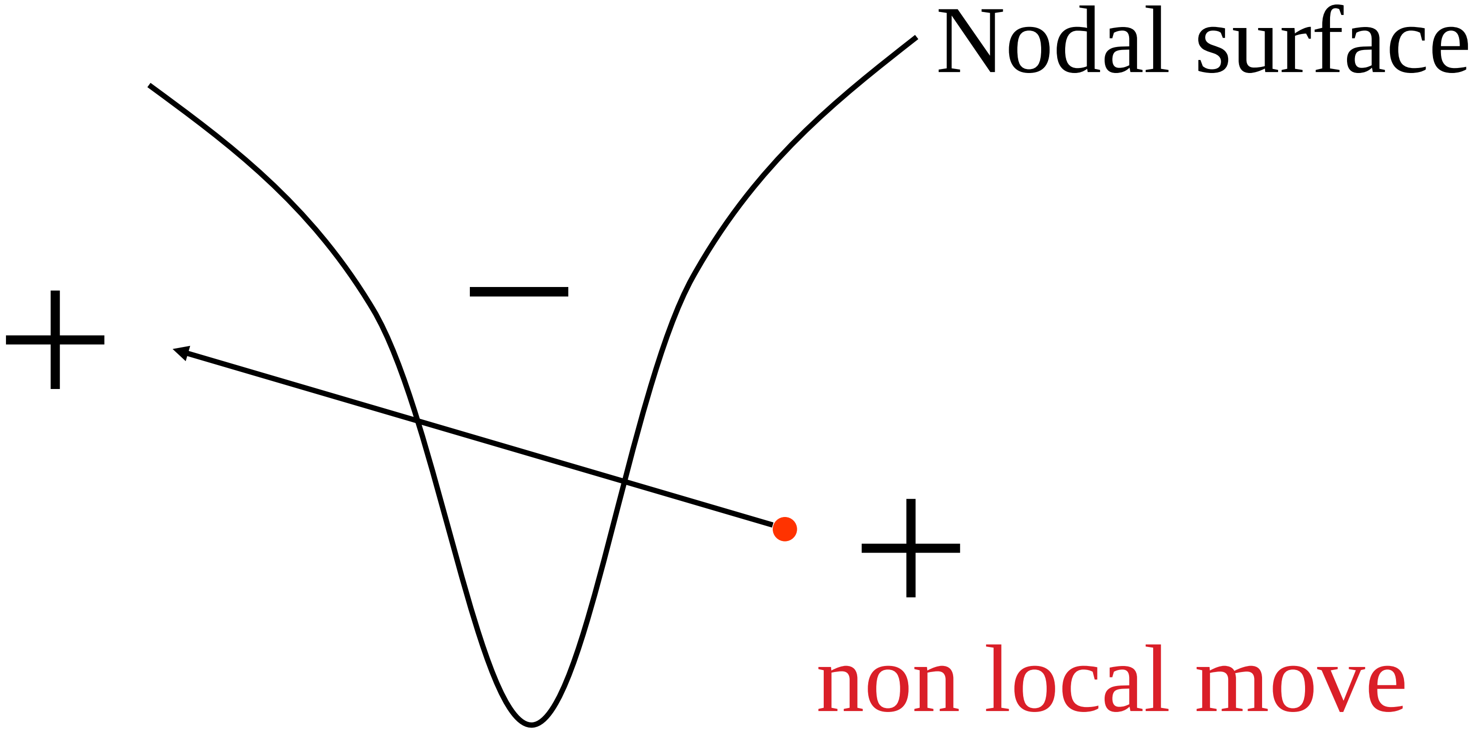
1) No localization approximation employed
2) Still variational upper bound theorem holds exactly as in the lattice fixed node
3) It works also without Jastrow optimization
4) The fixed node energy depends only on the nodal structure and weakly on the amplitudes

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

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

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:

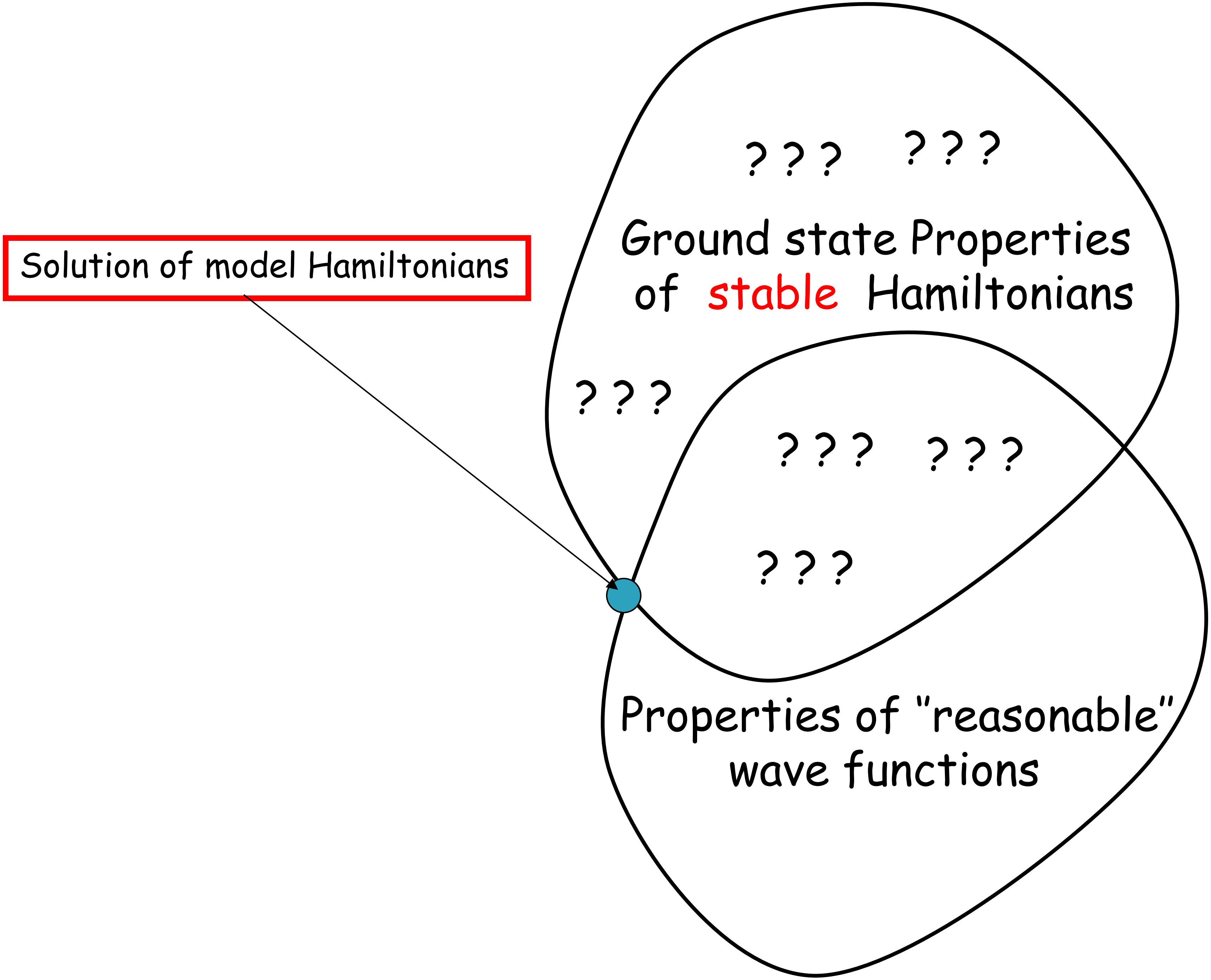
$$H \rightarrow H + \delta V$$

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



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

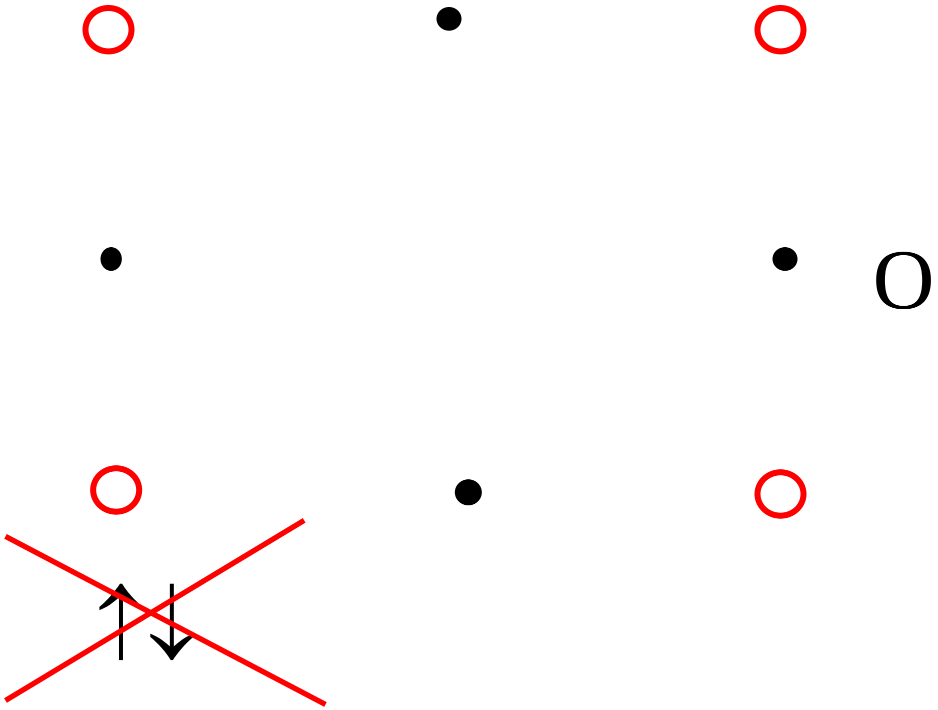
S. Sorella Phys. Rev. B 2001

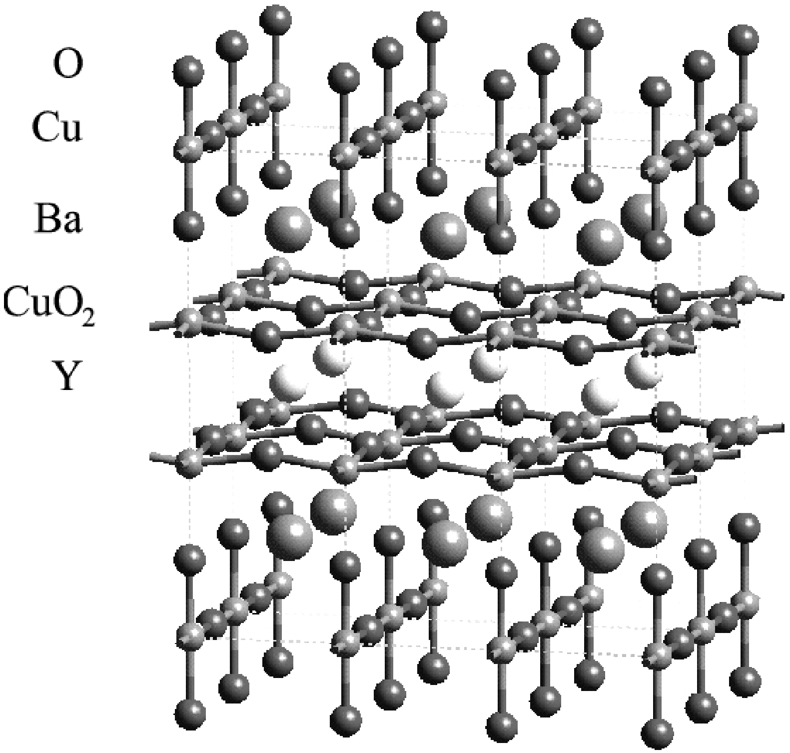
Outline of the lecture:

- 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

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

Lanczos with QMC on lattice models (L sites):

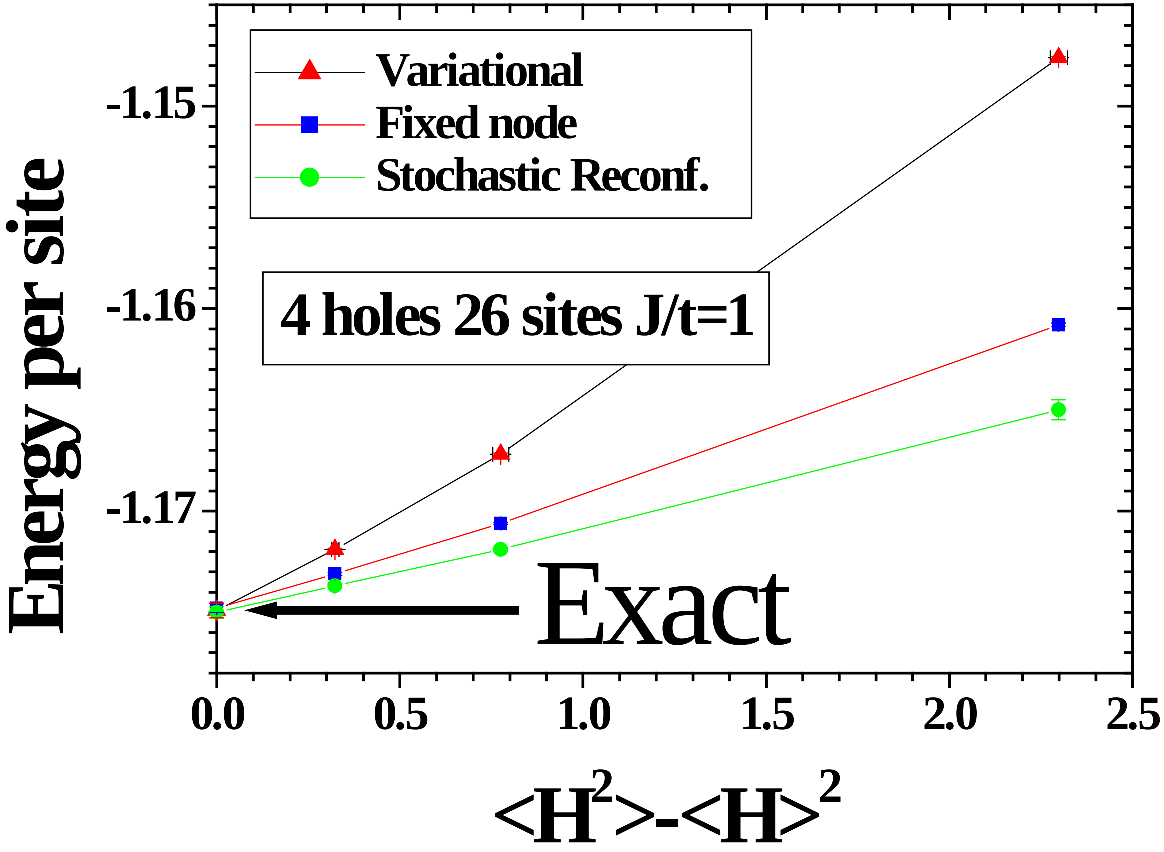
For p>1 Lanczos steps #operation /MC ~ L^{p+1}

Always polynomial at fixed p.

Probably improvement to p! # operations

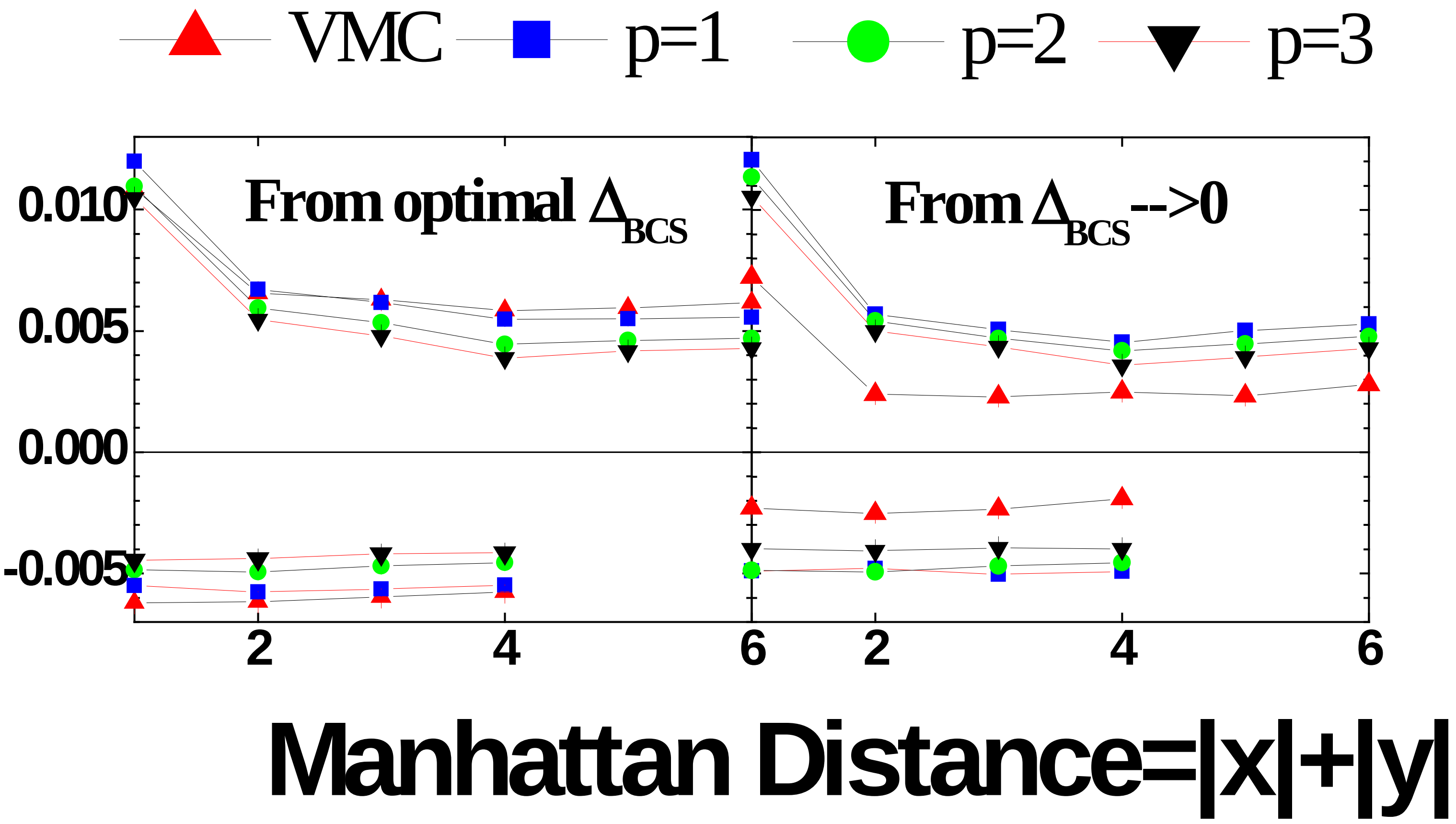
The question is how much computer effort is required for prescribed accuracy at given L.

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

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

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

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

➢ Marshall sign rule

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

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

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

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

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

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

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

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

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

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

Ground state of $\hat{H}$: $\left|\hat{\Psi}_0^{(M)}\right\rangle=\sum_x f_x|x\rangle$ with $f_x>0$ $\Longrightarrow$ k=0 A_1

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

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

: 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 $H_{x'x} \equiv \langle x' | \hat{H} | x \rangle$: 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

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

$|\Phi_0^{\mathrm{eff}}\rangle$: 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 $\Psi_G(x)$
2. $\Phi_0^{\text{eff}}(x)$ variational state for $\hat{H}$ better than $\Psi_G(x)$

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

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

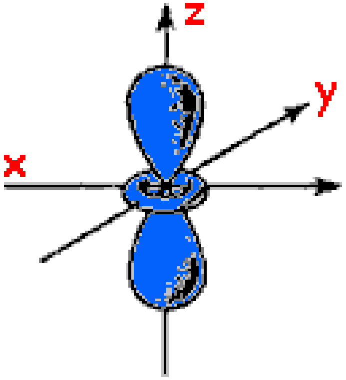
$$\hat{H} | \Phi_0 \rangle = E_0 | \Phi_0 \rangle$$

➢1D limit (J'=0)

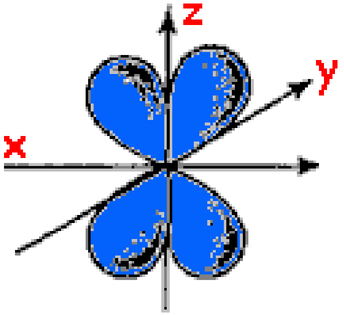
- ✓ Projected BCS wave function: $\boxed{\left|\text{P-BCS}\right\rangle = P_{\mathrm{G}}\left|\mathrm{BCS}\right\rangle}$
- ✓ |BCS>: ground state of BCS Hamiltonian

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

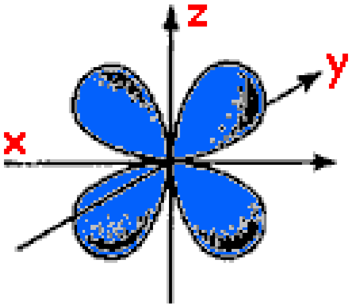
- ✓ Δ_l up to 3rd neighbors, $l \le 3$
- ✓Ground state properties well described (Gros et.al.)
- ✓Low-lying excited states (spinon): $\boxed{\left|\mathrm{k}\right\rangle = P_{\mathrm{G}}\boxed{\gamma_{k,\uparrow}^{\dagger}}\left|\mathrm{BCS}\right\rangle}$



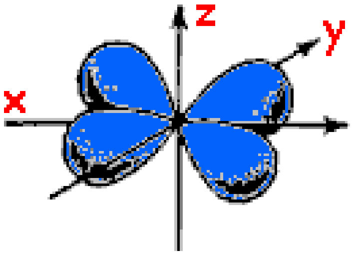
d_{z^2}



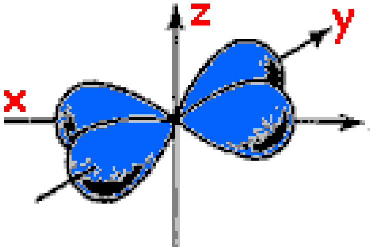
d_{yz}



d_{xz}



d_{xy}



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

RVB variational wavefunction for lattice models

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

$$f_k = \Delta_k \Big/ \varepsilon_k + \sqrt{\varepsilon_k^2 + \Delta_k^2}$$

where Δ_k is the BCS gap functio

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

→ Band Insulator

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

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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

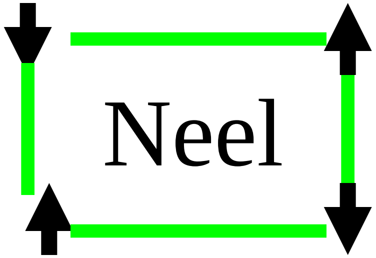
$$J = \exp\left(\sum_{i<j} v(r_i, r_j)\right)$$

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

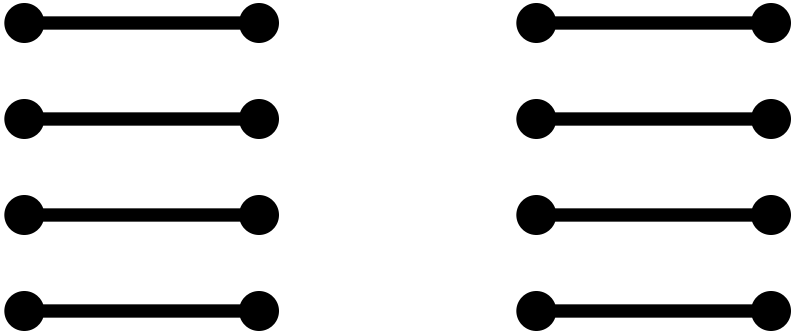
But insulator

Definition of spin liquid

A spin state with



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



- no Dimer state

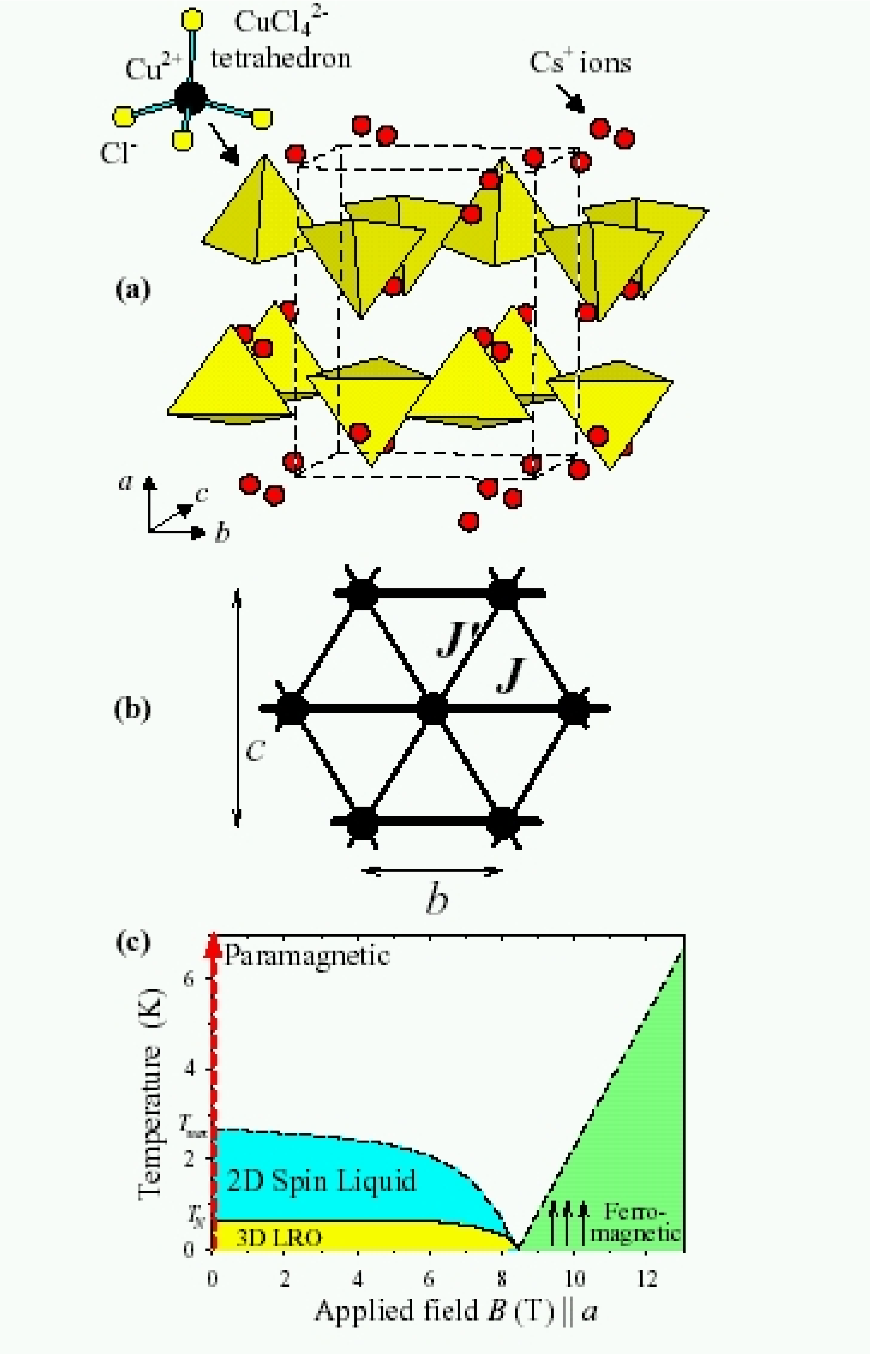
(Read,Sachdev)

is a spin liquid

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

J’/J=1/3
J=0.375meV

“J” between planes ~1K



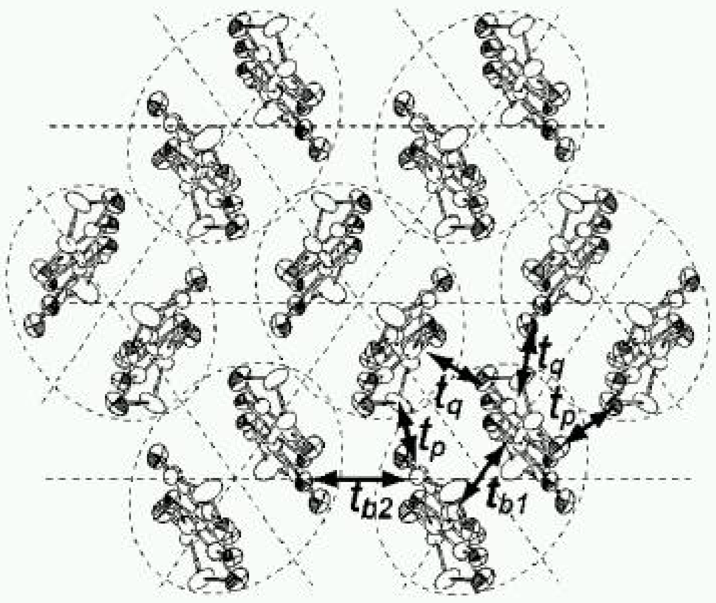
$\kappa-(\mathrm{ET})_2\mathrm{Cu}_2(\mathrm{CN})_3$

Shimizu et al. PRL '03

$J'/J \approx 0.9$

$J'/J \approx 1.8$

Spin Liquid ?



J=250K !!!

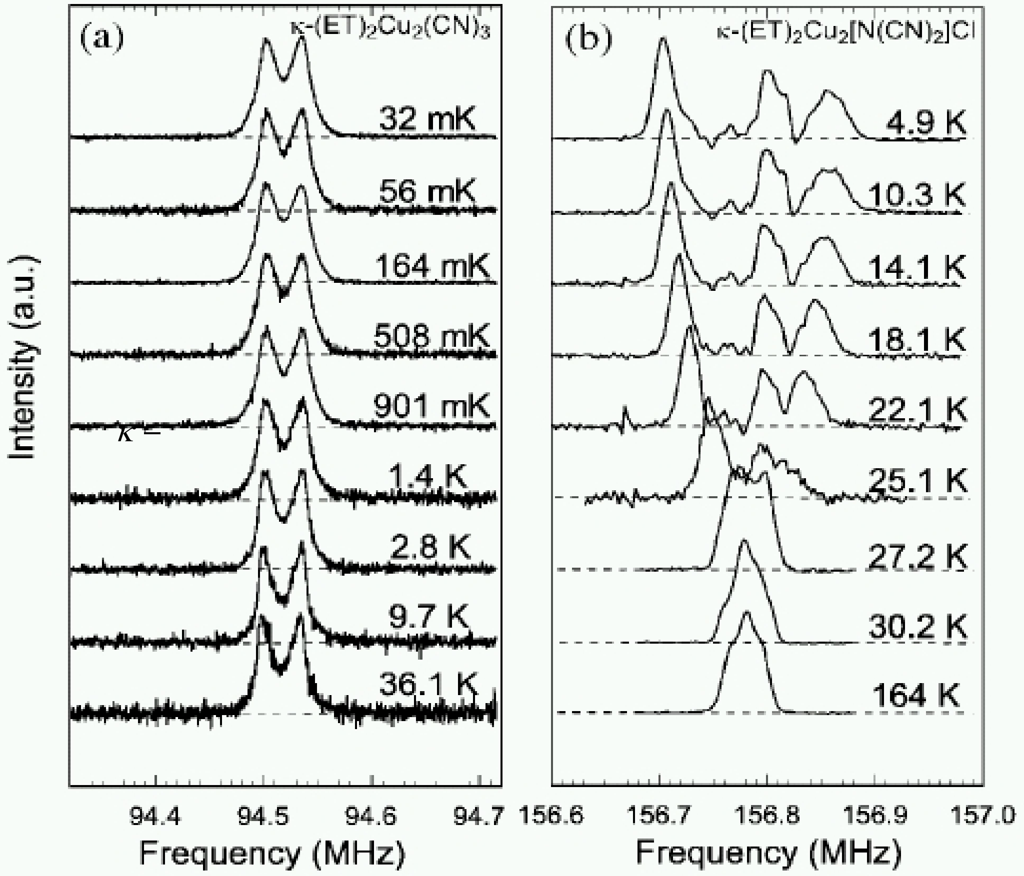


FIG. 3. (a) ^{1}H NMR absorption spectra for single crystals of κ-$(\mathrm{ET})_2\mathrm{Cu}_2(\mathrm{CN})_3$ and κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Cl}$ [9] under the magnetic field perpendicular to the conducting planes.

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

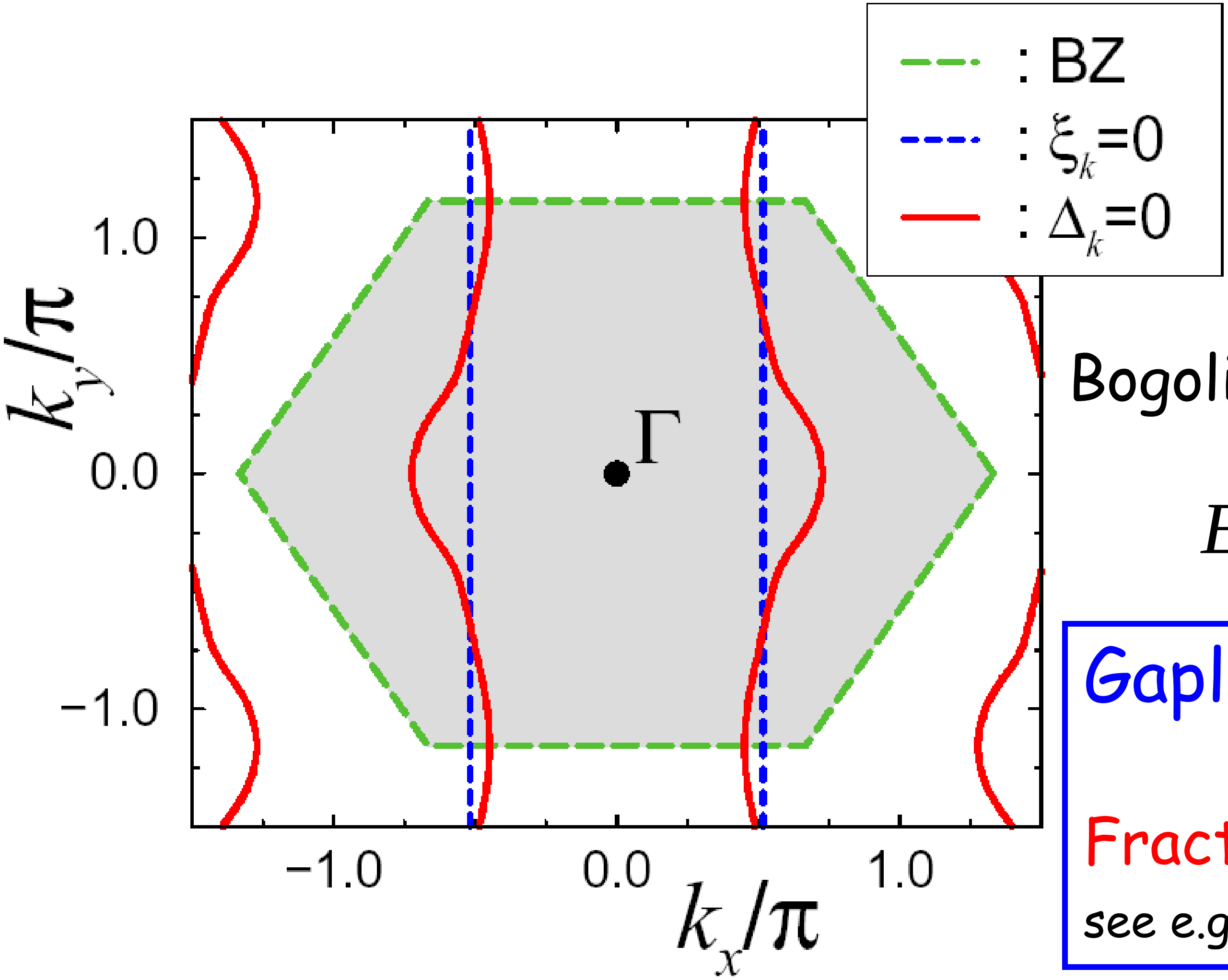
- ✓ Variational quantum Monte Carlo (QMC) method
- ✓ Projected BCS wave function: $|\text{P-BCS}\rangle = P_G\,|\text{BCS}\rangle$
- ✓ $|BCS\rangle = e^{\sum_{i,j} f_{i,j} C^+_{i,\uparrow} C^+_{j,\downarrow}} |0\rangle$: GS of BCS Hamiltonian

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

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

- ✓ 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.

➢ 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

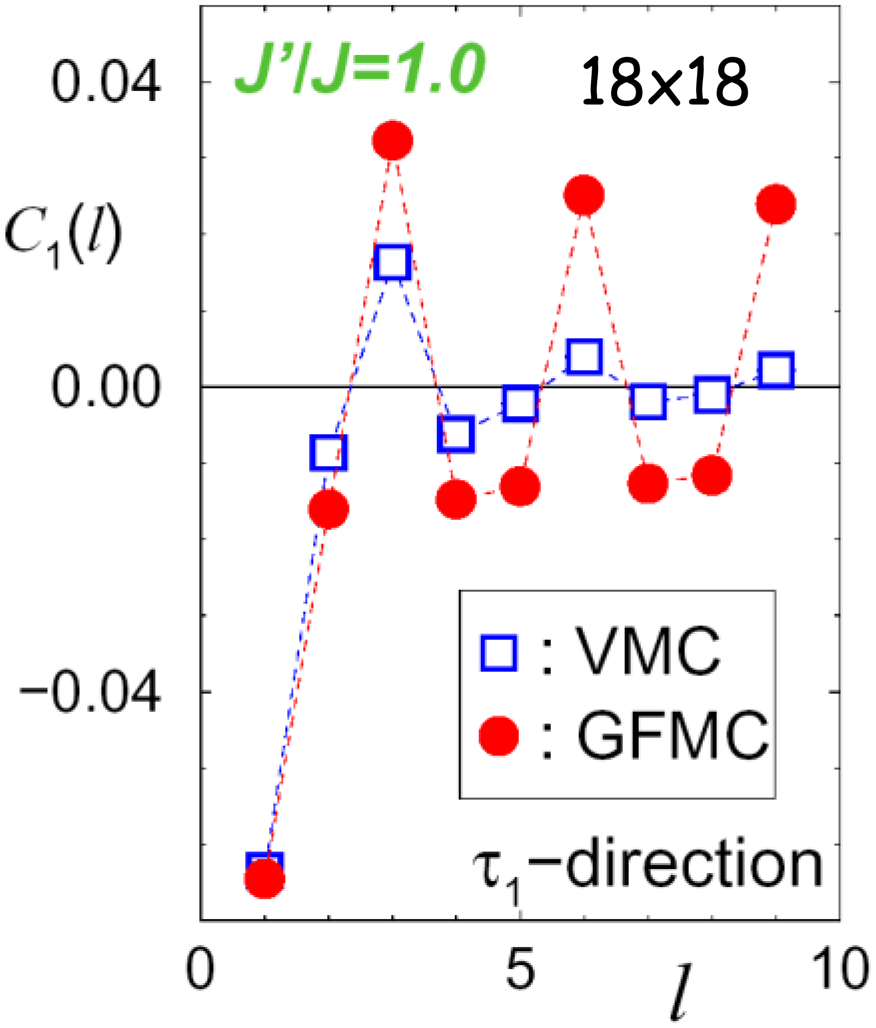
S=1/2 →

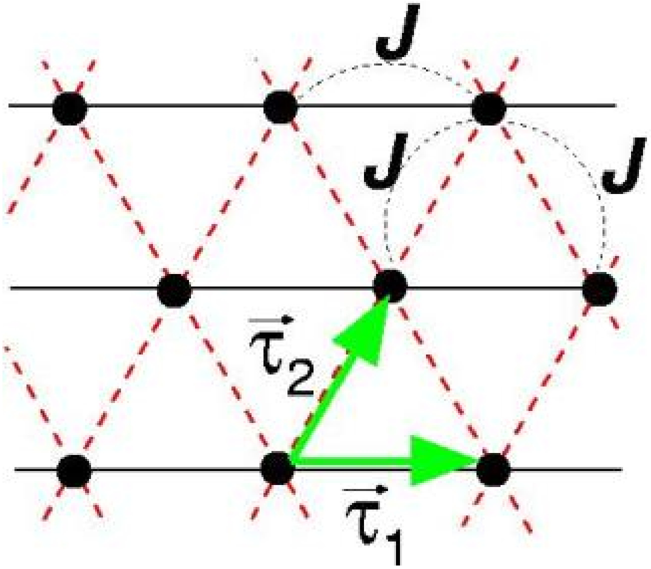
Fractionalization in 2D!

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



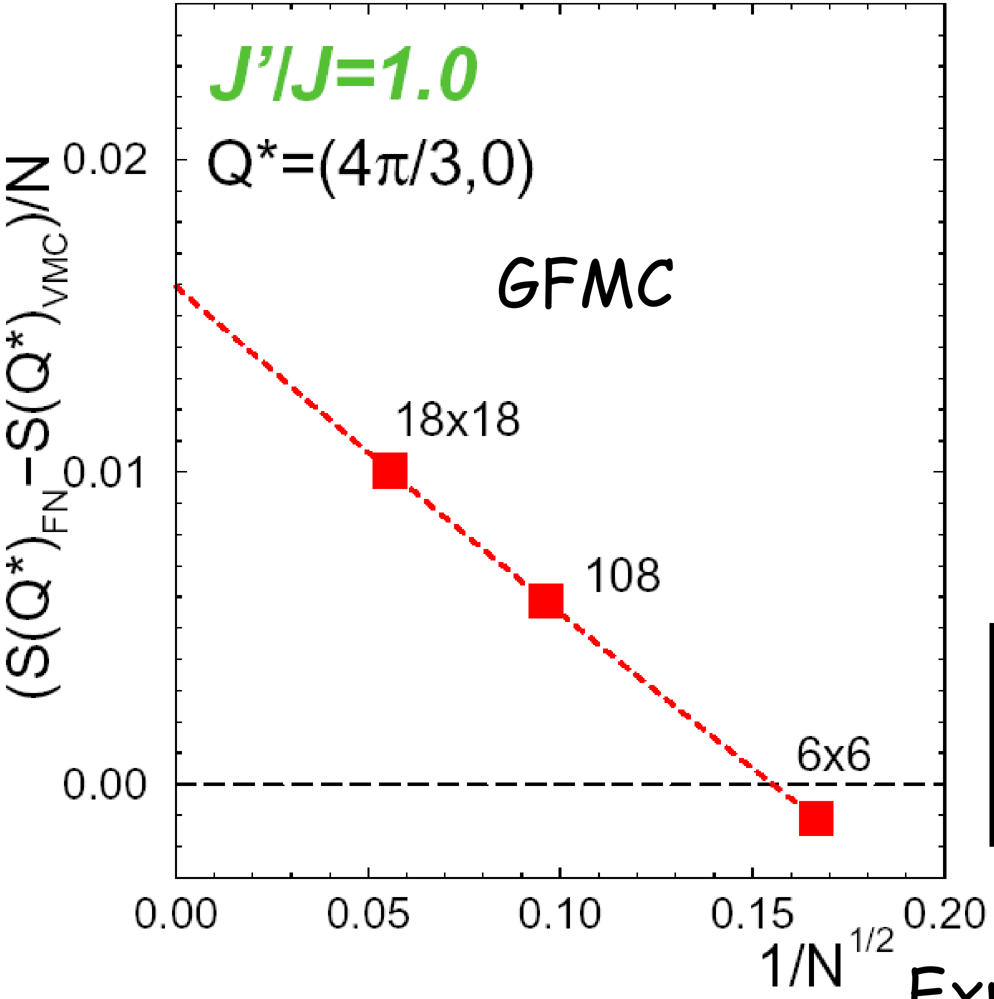


- ✓ Green function Monte Carlo
- ✓ Spin correlation function:

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

- ✓ Spin liquid state unstable toward classical Neel state

➢ Spin structure factor for J'/J=1.0



Order parameter:

- ✓ Starting from a spin liquid :

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

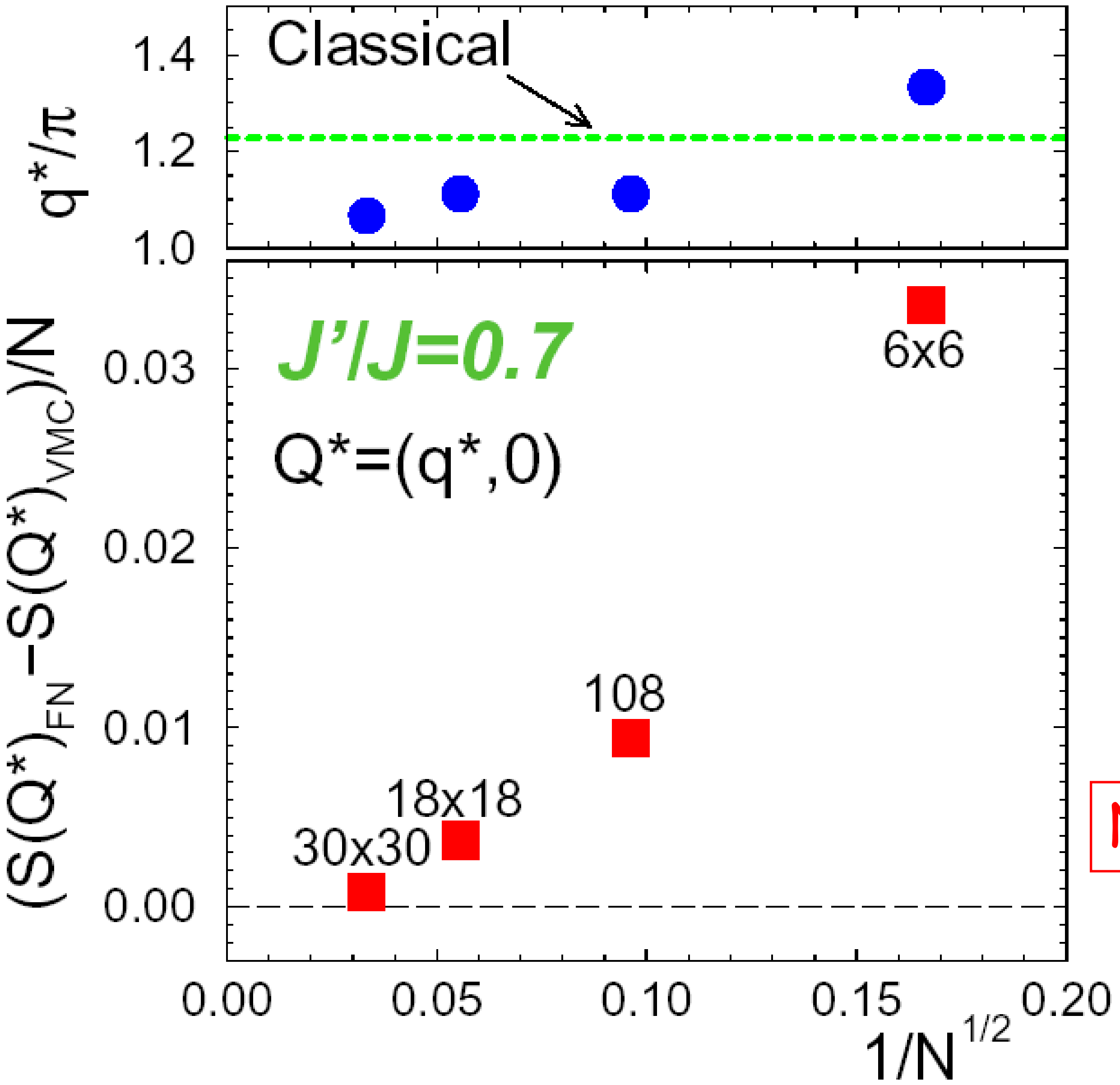
- ✓ Starting from ordered state :

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

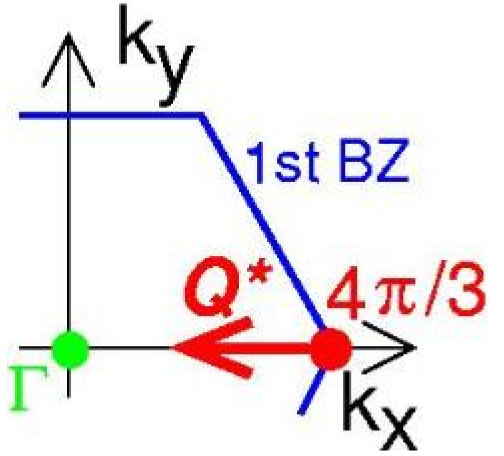
Exp. ~0.45 (organic) at J'/J=1.8

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

➢ Spin structure factor for J'/J=0.7



✓ Incommensurate peaks at Q*=(q*,0)

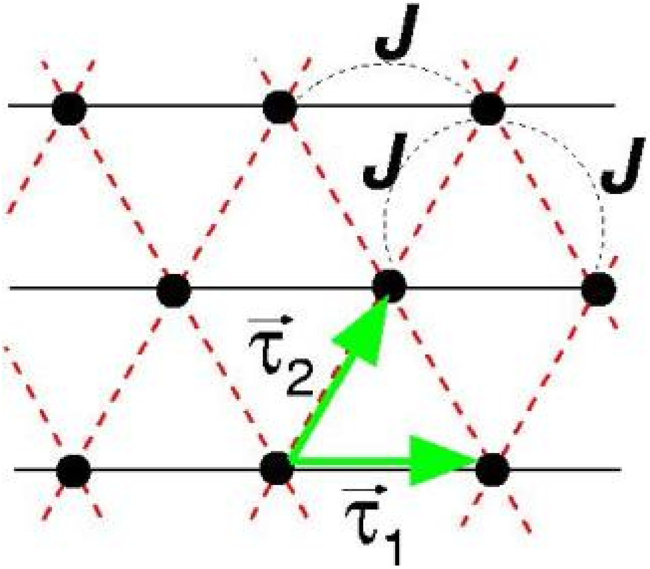


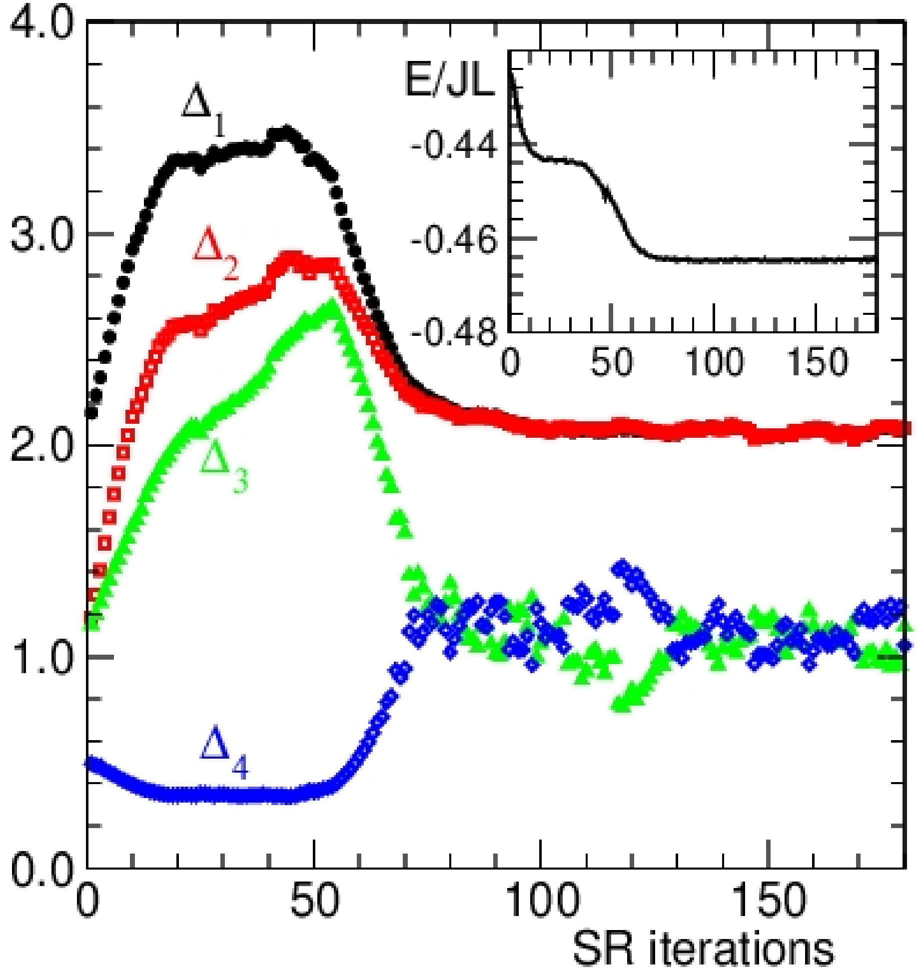
No long range order

Stability against dimerization

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

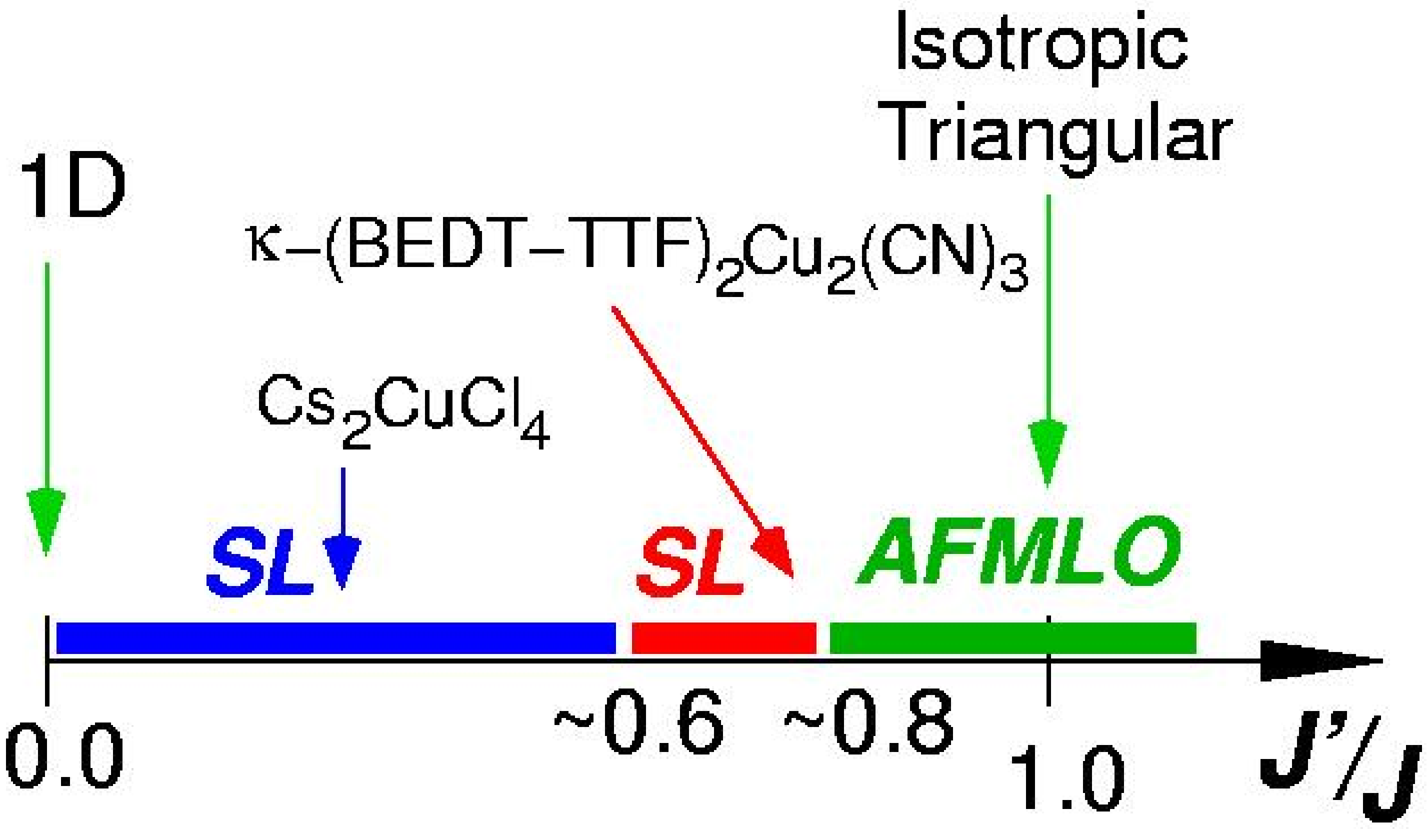
$$\begin{cases} \Delta_1 = \Delta_{0,\vec{\tau}_1}, \\ \Delta_2 = \Delta_{\tau_1,\vec{2}\tau_1}, \\ \Delta_3 = \Delta_{0,\vec{\tau}_2}, \text{ and} \\ \Delta_4 = -\Delta_{\tau_1,\tau_1+\vec{\tau}_2}, \end{cases}$$





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

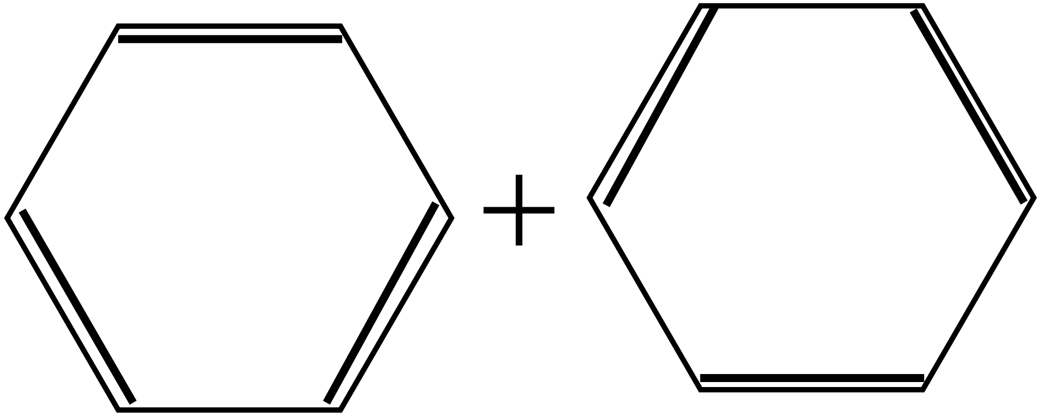
LatticeRegularizedDiffusionMonteCarlo

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:

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

The pairing function can be computed:

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

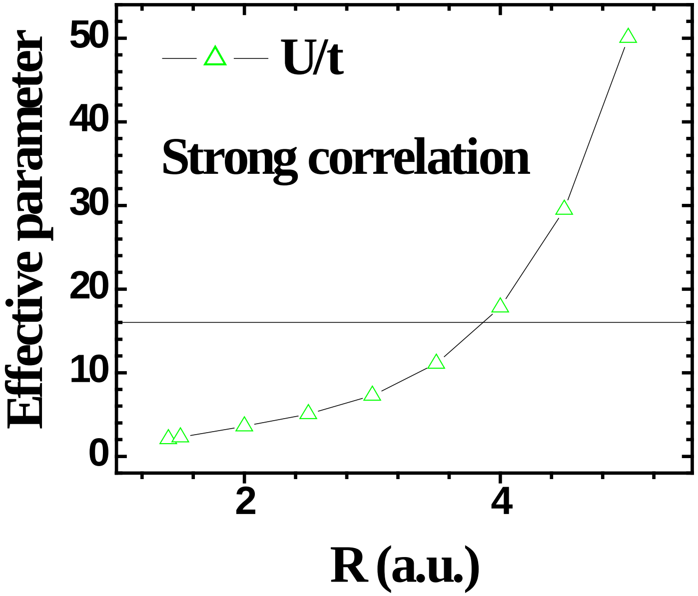
With a single determinant N/2 x N/2, N=# el.
even when RVB = many Slater Determinants

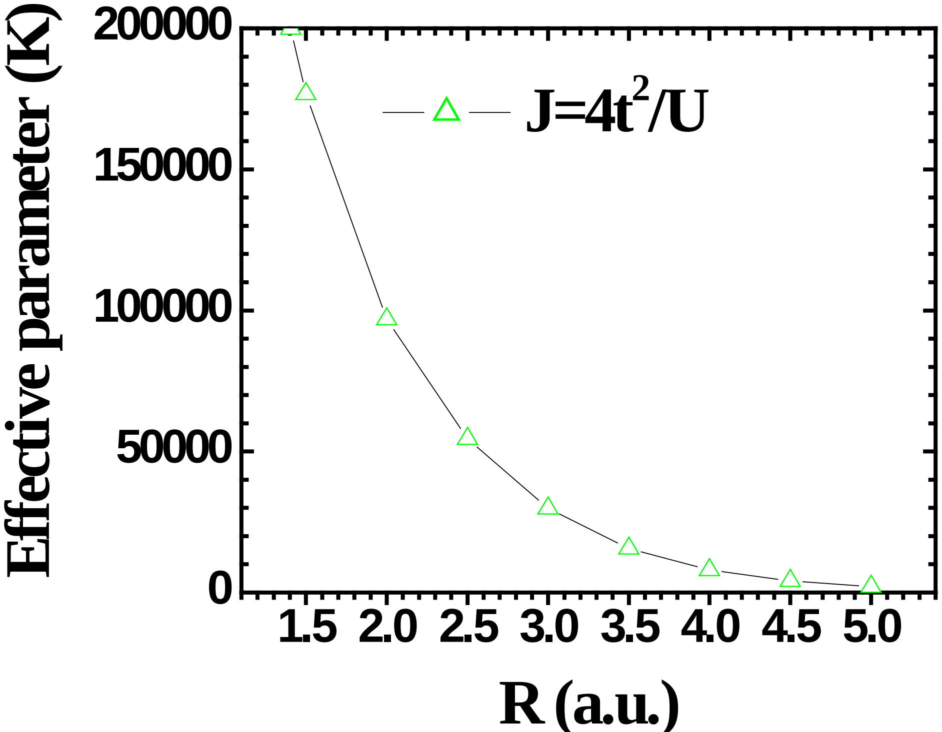
Mapping to a simple model: the 2-site Hubbard U

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

We use the Singlet-Triplet gap and the optimized

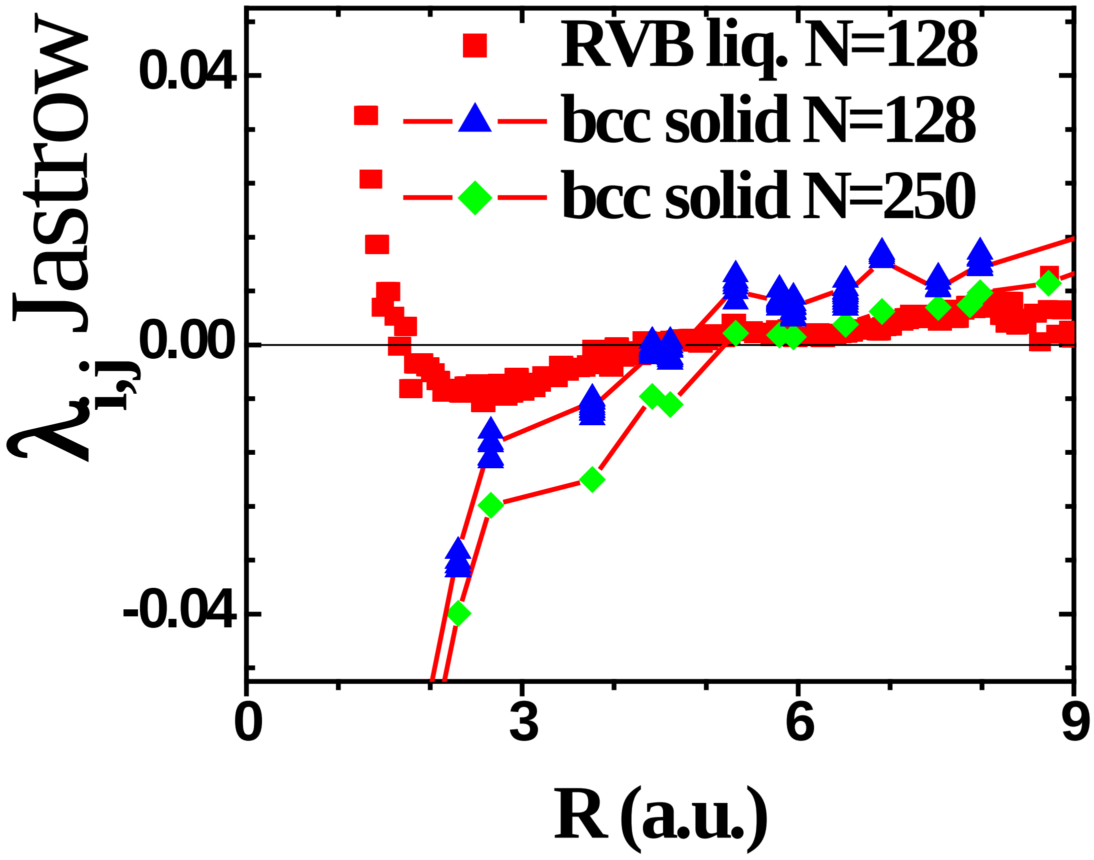
pairing function $1\sigma_g(r)1\sigma_g(r') - \lambda \;\; 1\sigma_u(r)1\sigma_u(r')$



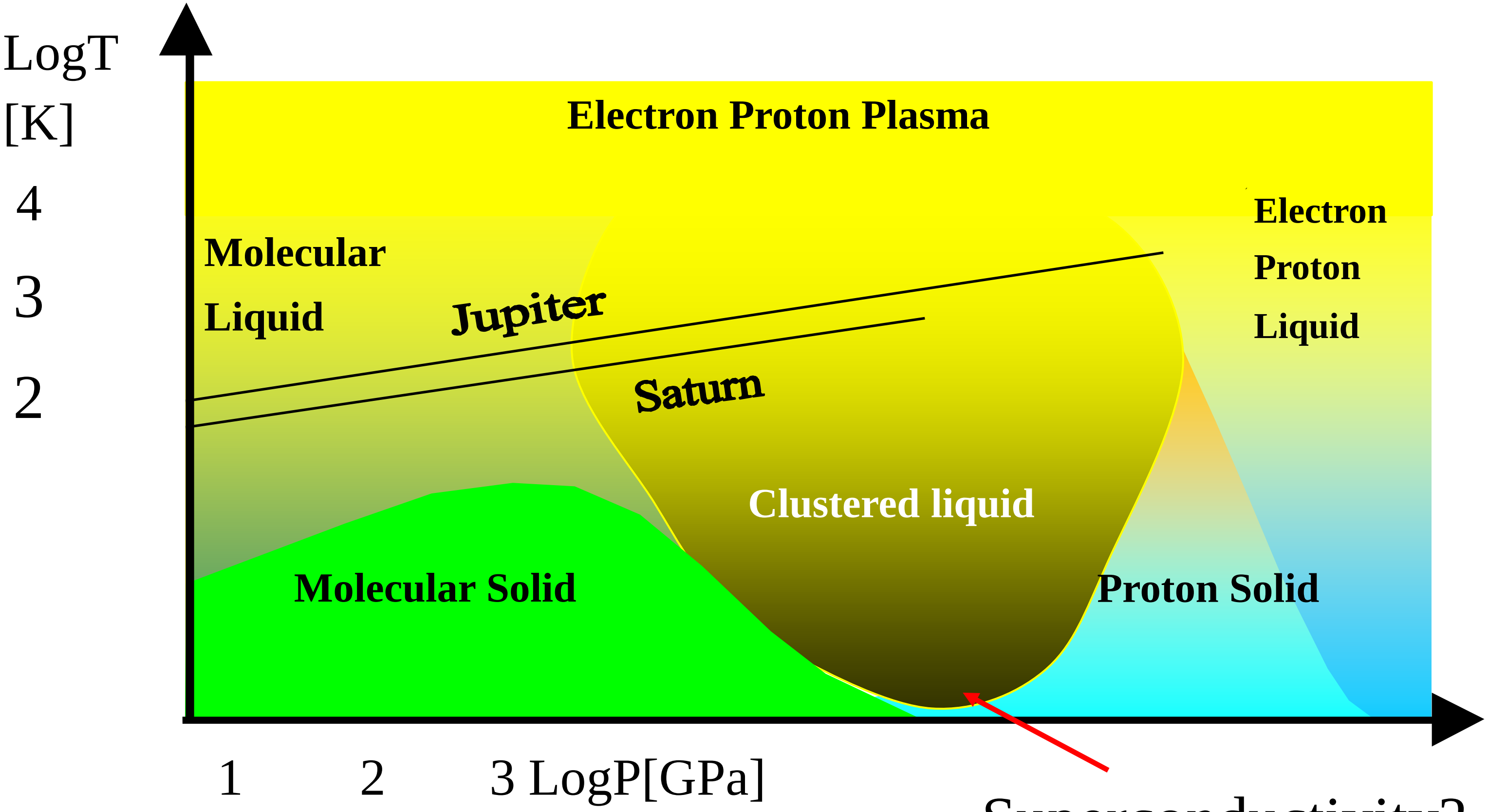


The crucial difference between
an Htc superconductor and a RVB insulator is:

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

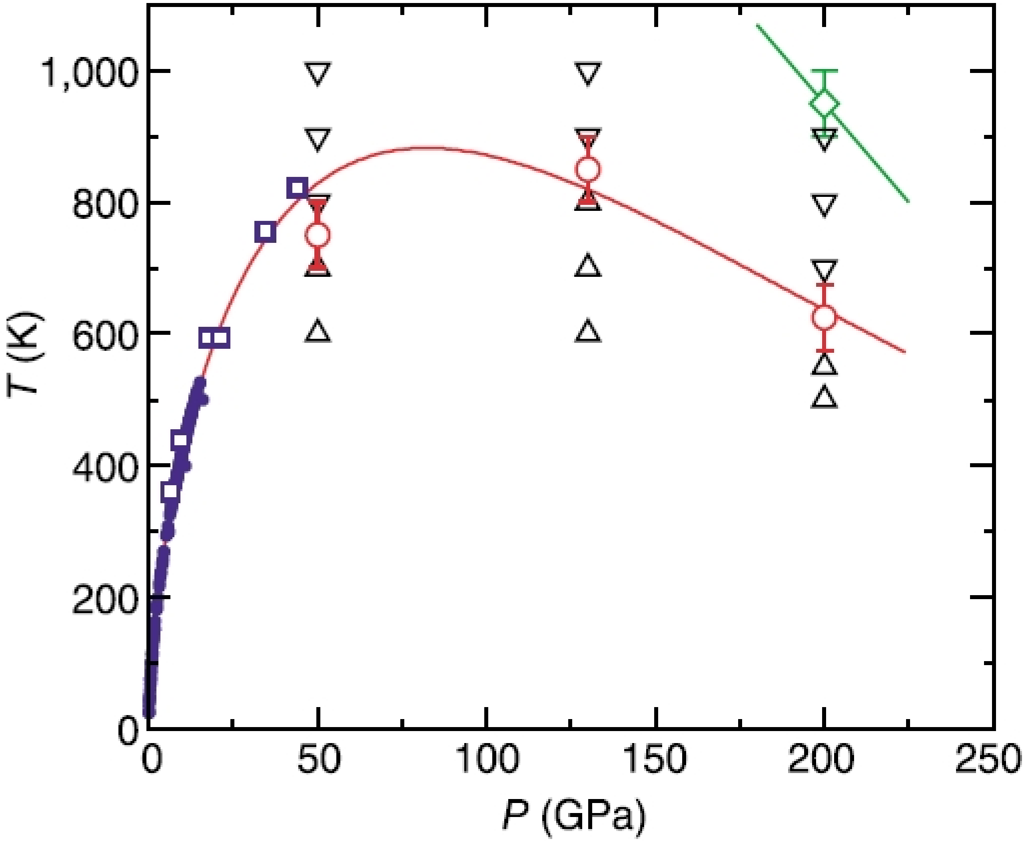


Phase Diagram of Hydrogen



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) $r_s = 1.31$

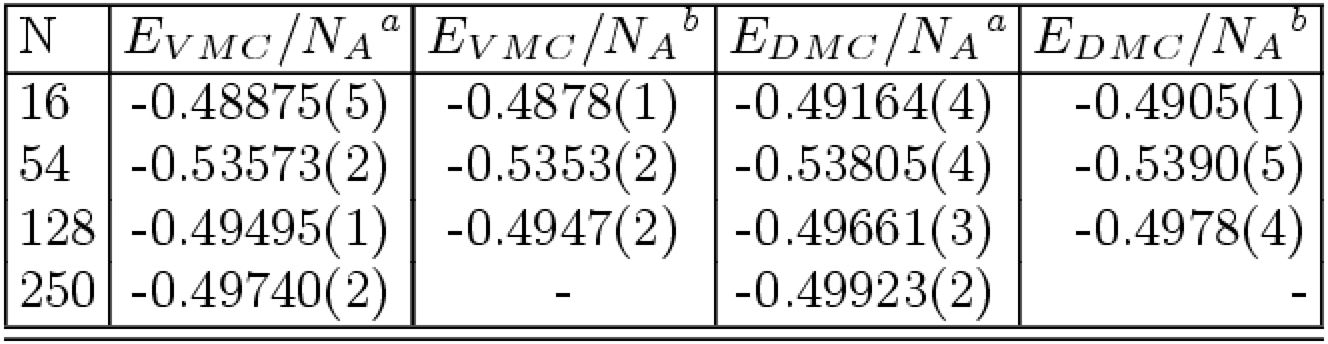
$r_s \approx H_2$ bond length

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

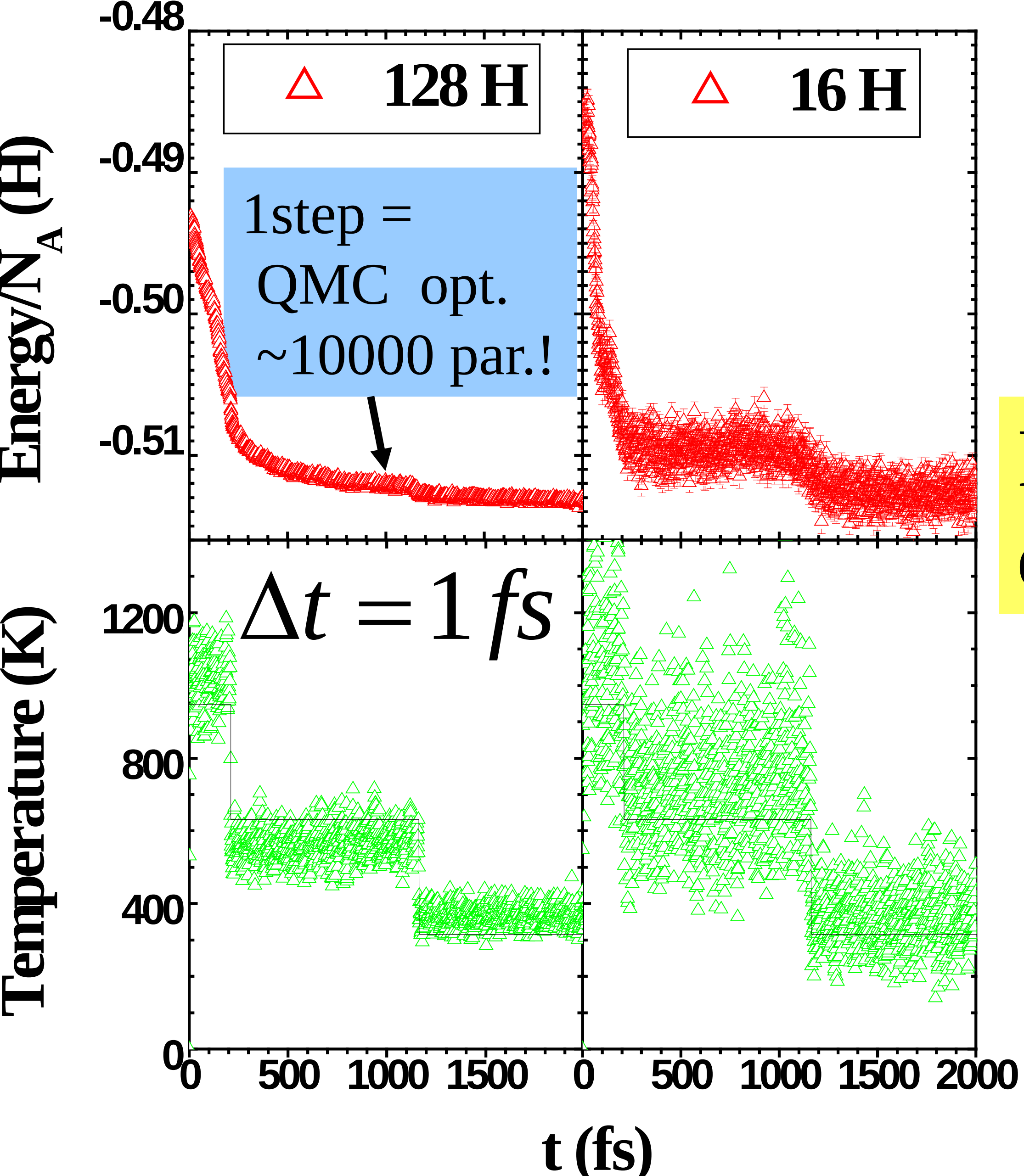
We use Hessian, much progress done in QMC:

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



1step =
QMC opt.
~10000 par.!

$\Delta t = 1 fs$

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

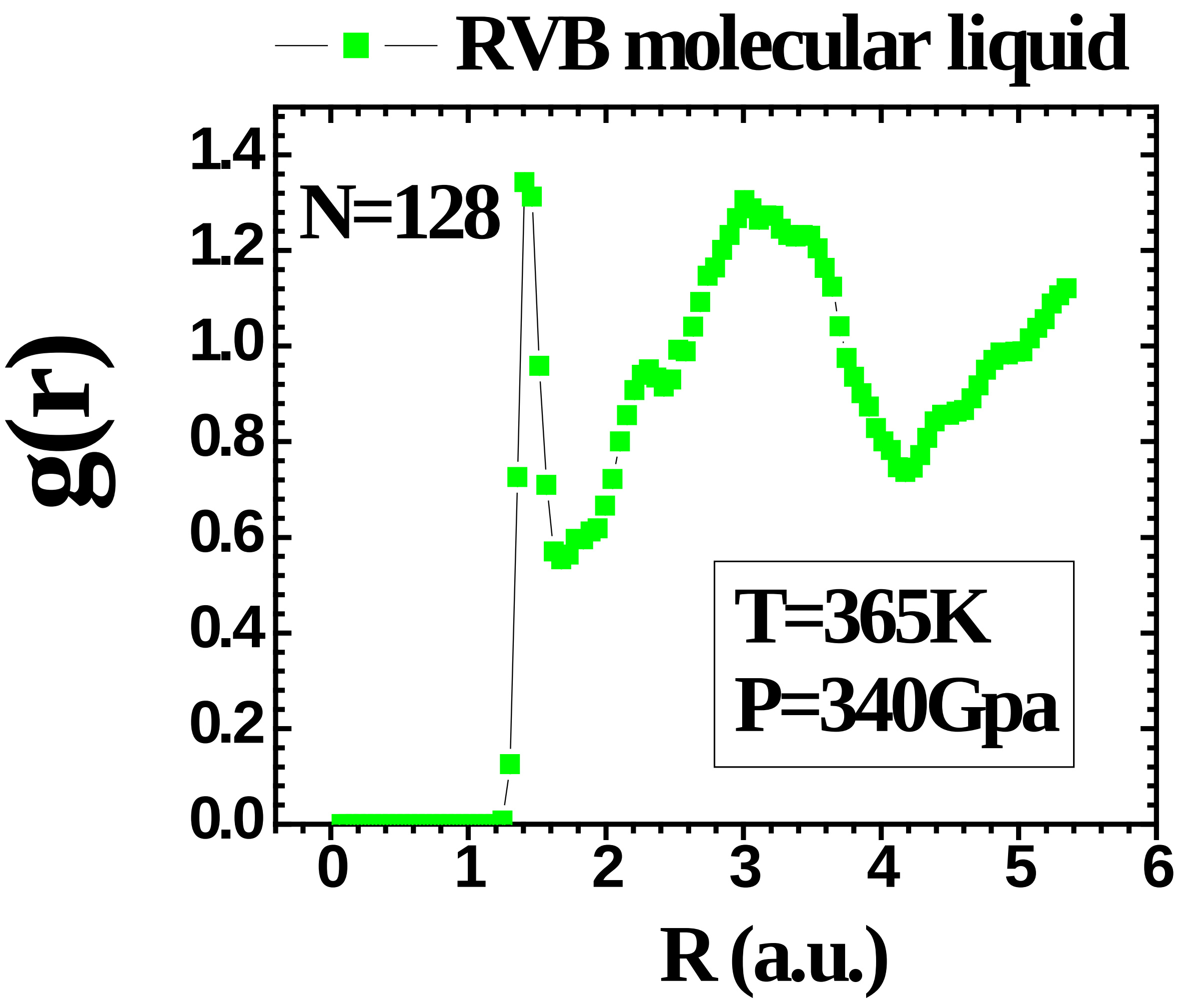
$$\dot{\vec{R}} = \vec{f} + \vec{\eta} \quad \text{with} \quad < \vec{\eta}(t)\vec{\eta}(t') >= 2T\delta(t-t')$$

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

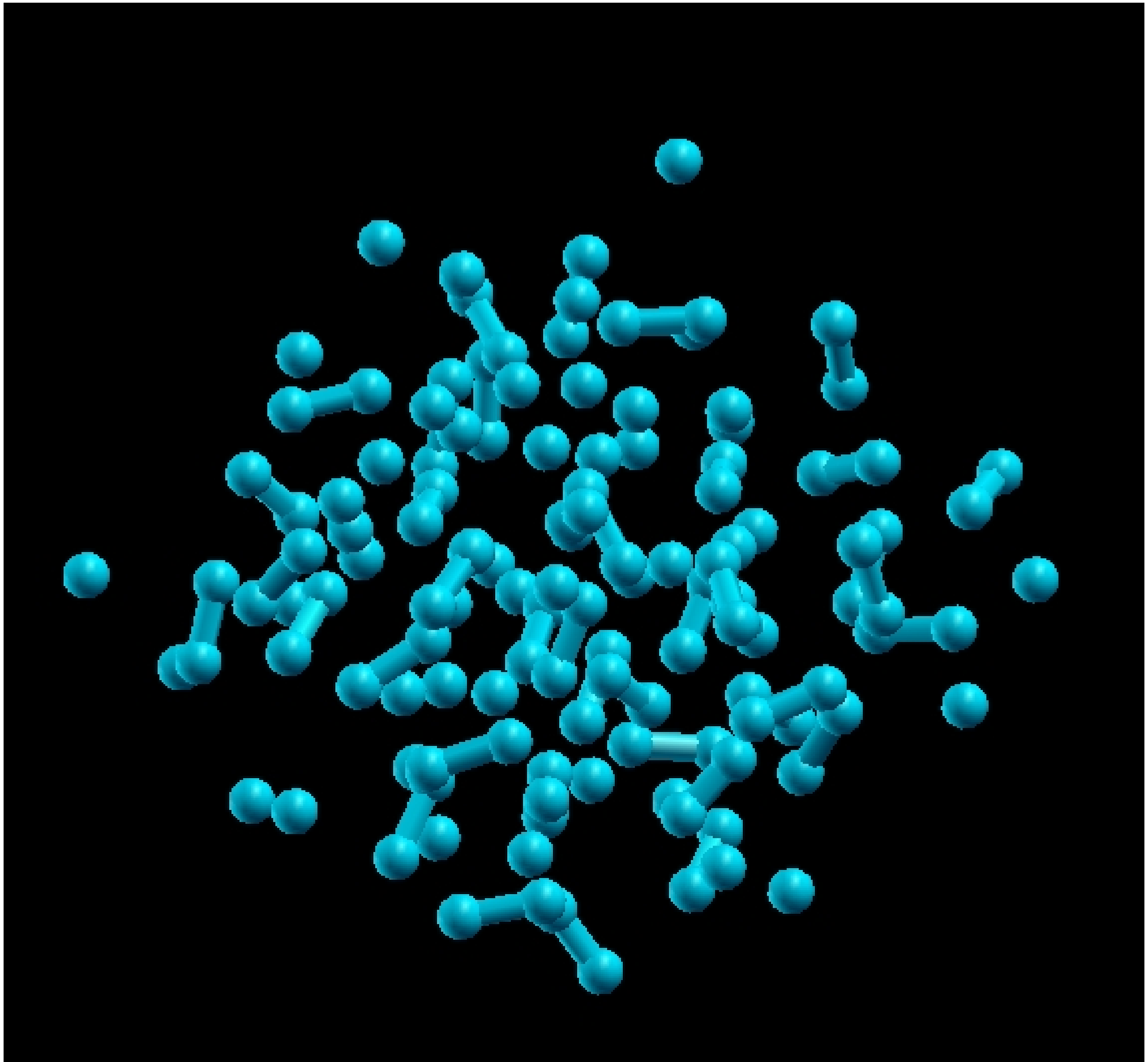
→ Compared with methods based only on energy we use 3N entries (forces) with the same cost.

Expected at least a factor N speed-up improvement

Proton-proton pair correlation function



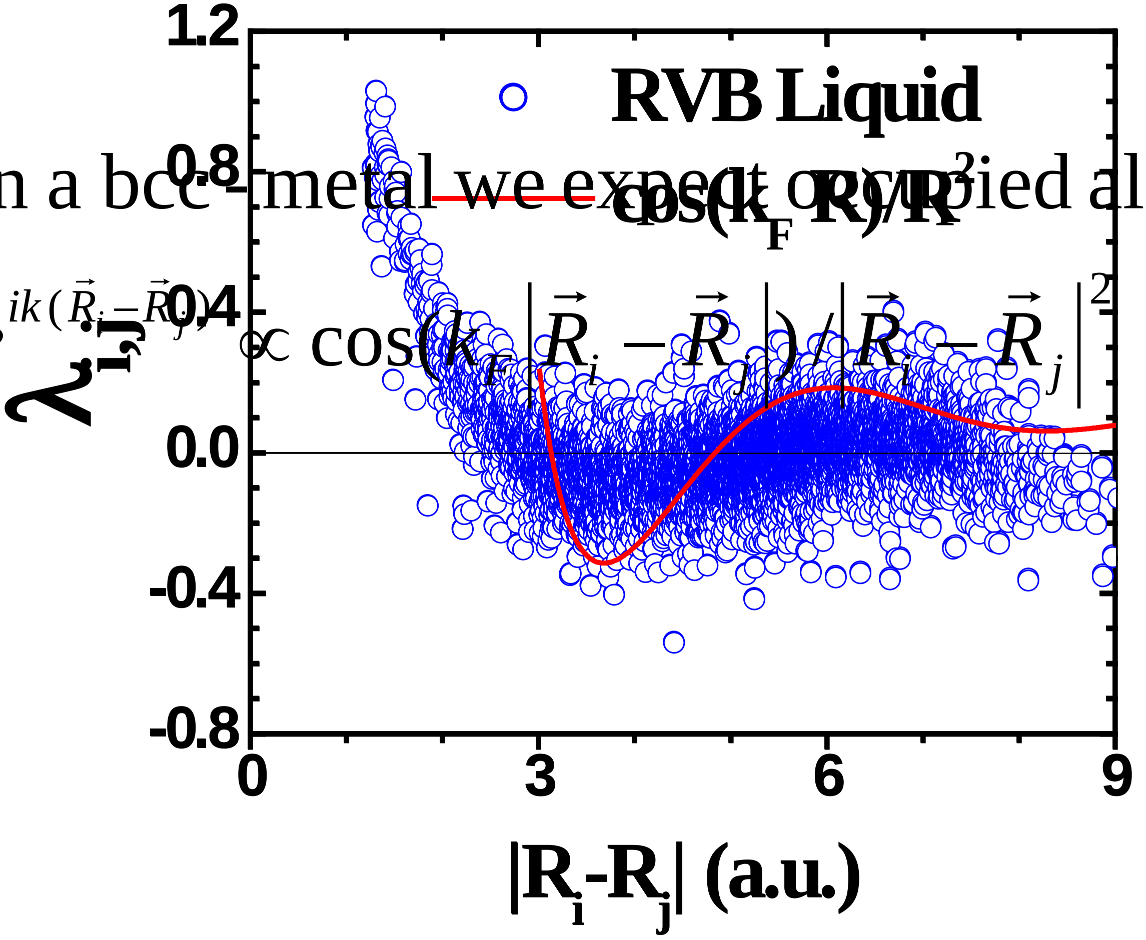
Snap-shot of the protons at the last iteration



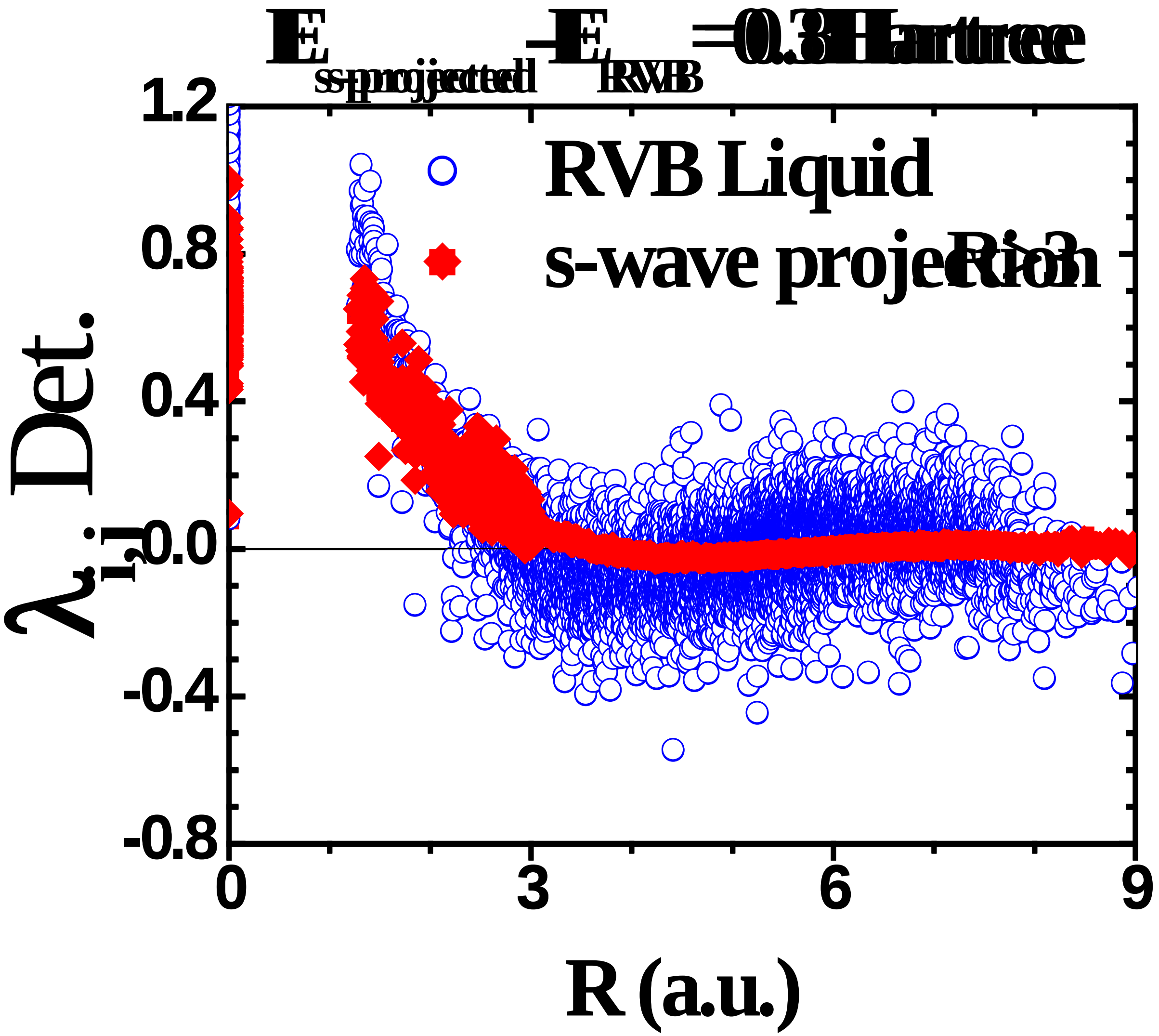
The pairing function in the liquid phase

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

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

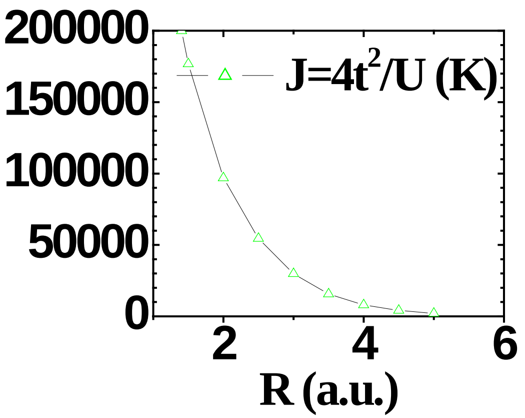


Optimization with the s-wave constraint



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.

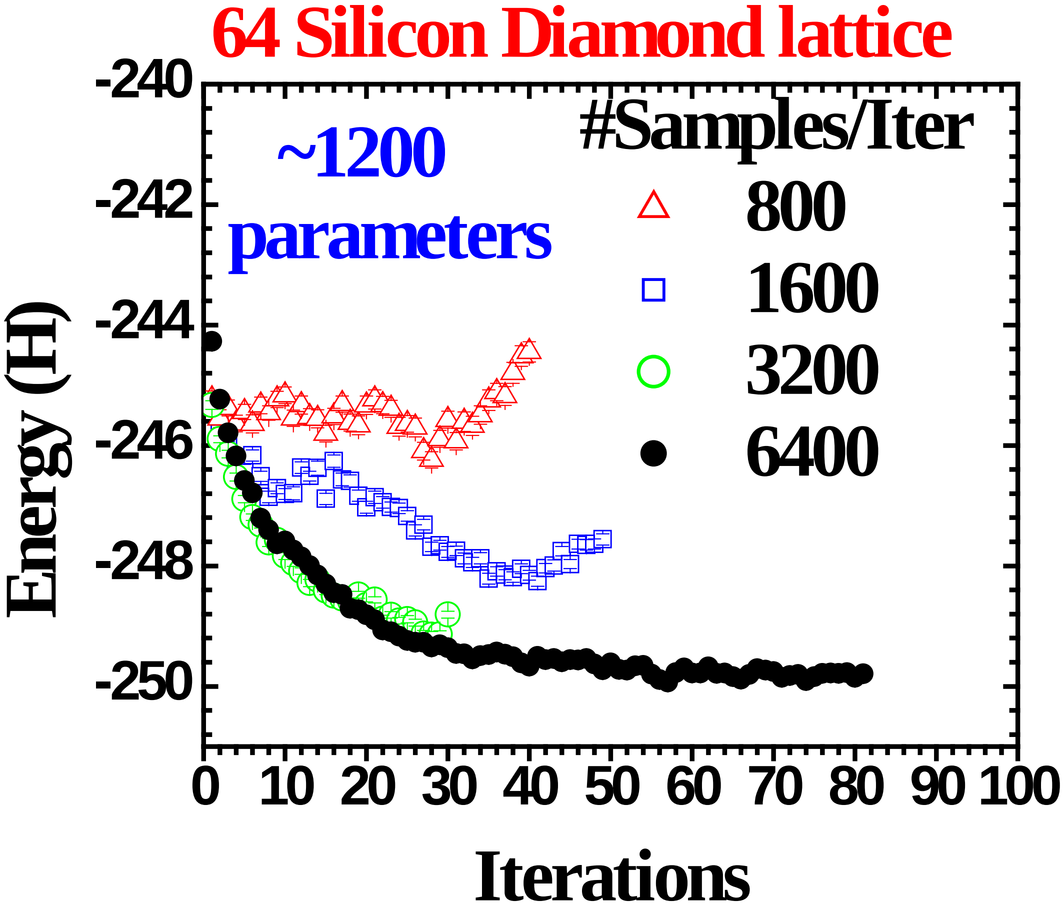
✓ It is described by a single determinant and is computationally convenient for QMC.

✓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

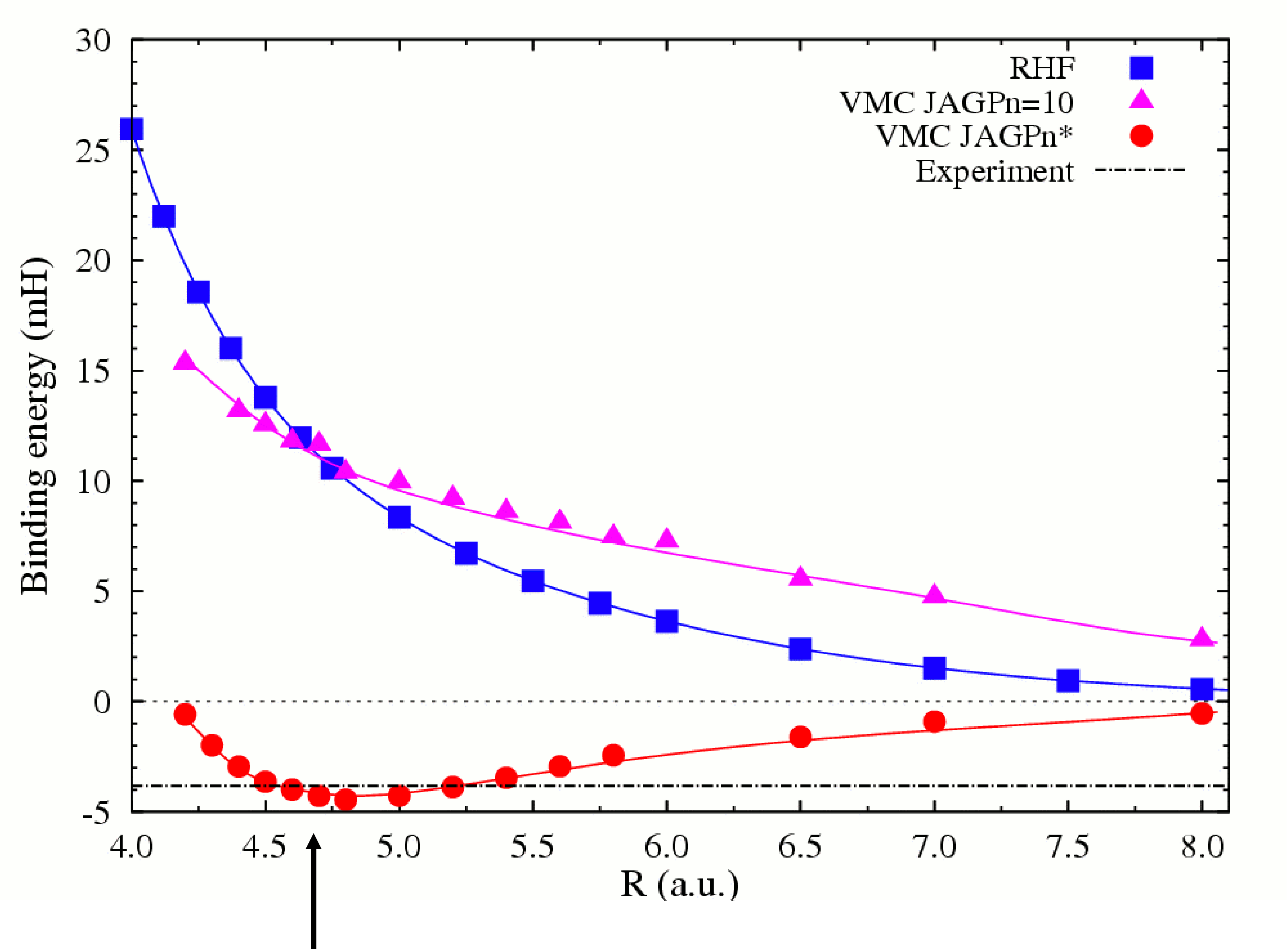
HTc physics in hydrogen at 300Gpa?

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