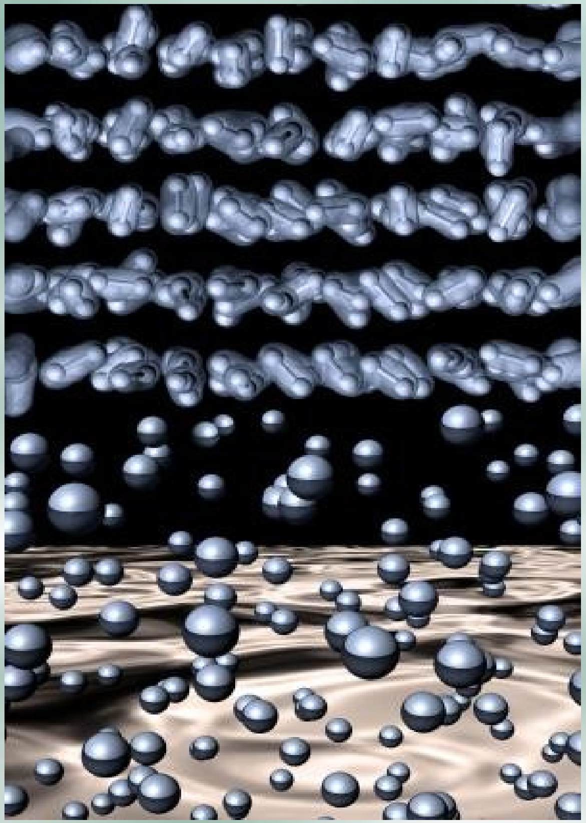
Ab-initio molecular dynamics for High pressure Hydrogen



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Outline

- A brief introduction to Quantum Monte Carlo and the RVB (Resonant Valence Bond) wave-function

- The first *ab-initio* MD with Quantum Monte Carlo forces

- The stability of the liquid Hydrogen phase at P~300Gpa and T~400K

- Looking directly to the new features of the many-body RVB electron correlation

Variational Monte Carlo 1

$$\langle A \rangle_{var} = \frac{\int \Psi_T^*(R)\hat{A}\Psi_T(R)dR}{\int \Psi_T^*(R), \Psi_T(R)dR}$$

Monte Carlo integration is necessary because the wave-function contains explicit particle correlations that leads to non-factoring multi-dimension integrals.

$$\langle A \rangle_{var} = \int P(R)A_L(R)dR$$

$$A_L(R) = \frac{\hat{A}\Psi_T(R)}{\Psi_T(R)}$$

$$P(R) = \frac{|\Psi_T(R)|^2}{\int \Psi_T^*(R)\Psi_T(R)dR}$$

Variational Monte Carlo 2

$$P(R) = \frac{|\Psi_T(R)|^2}{\int \Psi_T^*(R)\Psi_T(R)dR}$$

Density probability sampled using Metropolis algorithm

R_i = electronic configuration

$$\langle A \rangle = \int P(R)A_L(R)dR = \frac{1}{M}\sum_{i=1}^{M} A_L(R_i) + O(\frac{1}{\sqrt{M}})$$

if

$$\int P(R)(\langle A \rangle - A_L(R))^2 dR$$

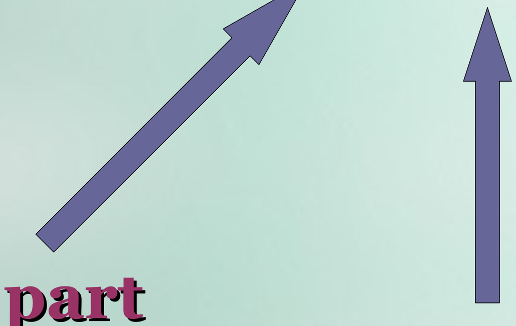
Variance is FINITE

The trial wave-function

The trial-function completely determines quality of the approximation for the physical observables

The wave-function

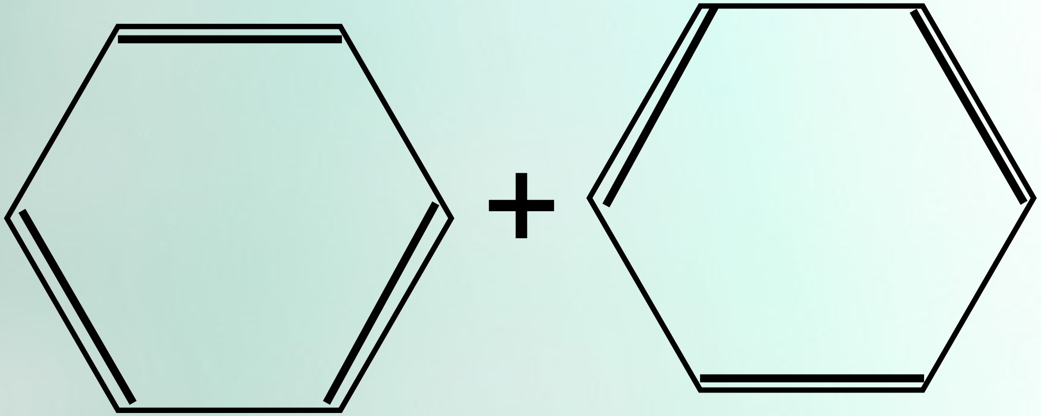
$$\Psi(r_{1,}r_{2,.}..,r_n)=\Phi_{AGP}J$$



Antisymmetric part

Symmetric part (Jastrow)

The Resonant Valence Bond (RVB) wave-function



First application of RVB wave-function
resonance in benzene

On a given electron configuration:

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

The pairing function can be computed:

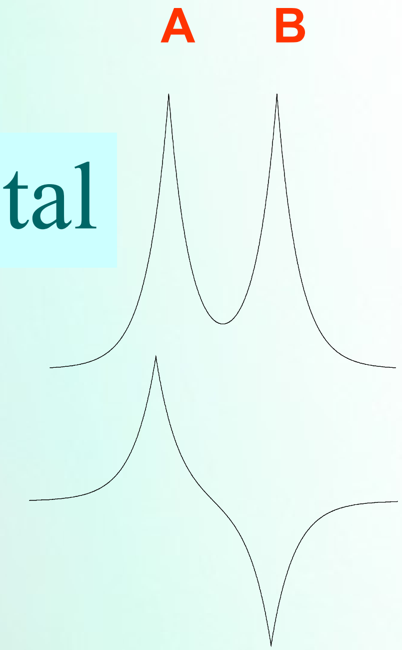
$$\langle x|RVB\rangle = \begin{vmatrix} f_{r_1^{\uparrow},r_1^{\downarrow}} & f_{r_1^{\uparrow},r_2^{\downarrow}} & f_{r_1^{\uparrow},r_3^{\downarrow}} \\ f_{r_2^{\uparrow},r_1^{\downarrow}} & f_{r_2^{\uparrow},r_2^{\downarrow}} & f_{r_2^{\uparrow},r_3^{\downarrow}} \\ f_{r_3^{\uparrow},r_1^{\downarrow}}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

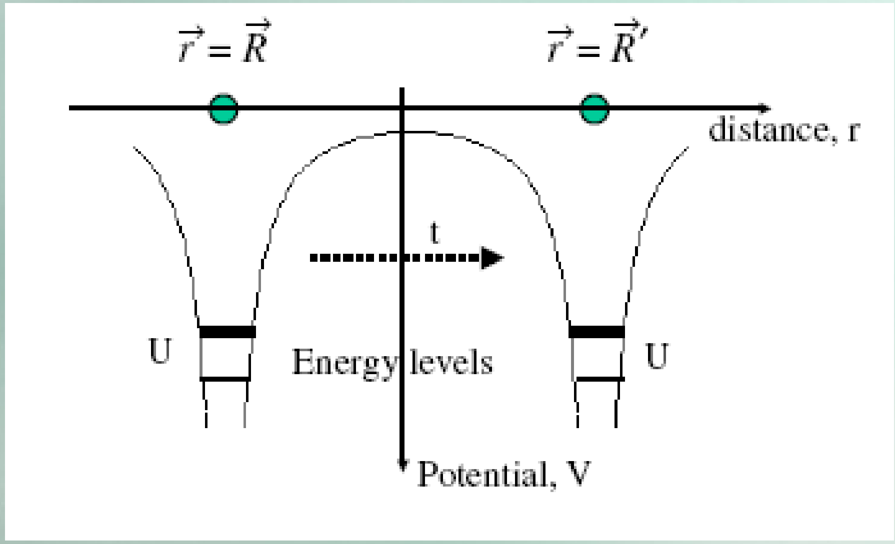
With a single determinant N/2 x N/2, N=# el.
even when RVB = many Slater Determinants

H_2 molecule and RVB

Bonding orbital + Anti-bonding orbital

$$\begin{aligned}\Psi_{H_2} &= \lambda_{11}\phi^A_{1s}(r_1)\phi^A_{1s}(r_2)+\lambda_{22}\phi^B_{1s}(r_1)\phi^B_{1s}(r_2)\\ &+ \lambda_{12}\phi^A_{1s}(r_1)\phi^B_{1s}(r_2)+\lambda_{21}\phi^B_{1s}(r_1)\phi^A_{1s}(r_2)\end{aligned}$$





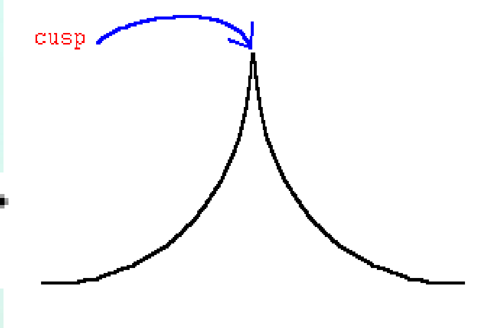
The Jastrow

$$J = J_1 J_2 J_3$$

to describe exact conditions and part of the correlation

J_1 electron-ion cusp condition: e^{-ar}

J_2 electron-electron cusp condition: e^{+br}



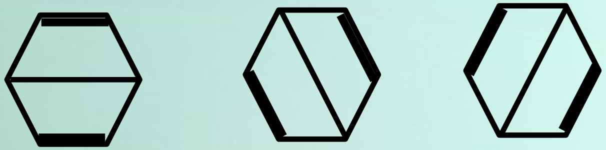
$$J_3(\vec{r}_1, ..., \vec{r}_N) = \exp\left(\sum_{i<j} \Phi_J(\vec{r}_i, \vec{r}_j)\right)$$

$$\Phi_J(\vec{r}_i, \vec{r}_j) = \sum_{l,m,a,b} g^{a,b}_{l,m} \psi_{a,l}(\vec{r}_i) \psi_{b,m}(\vec{r}_j)$$

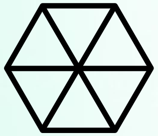
J_3 electron-electron correlation

Binding energy of aromatic molecules

Kekule’



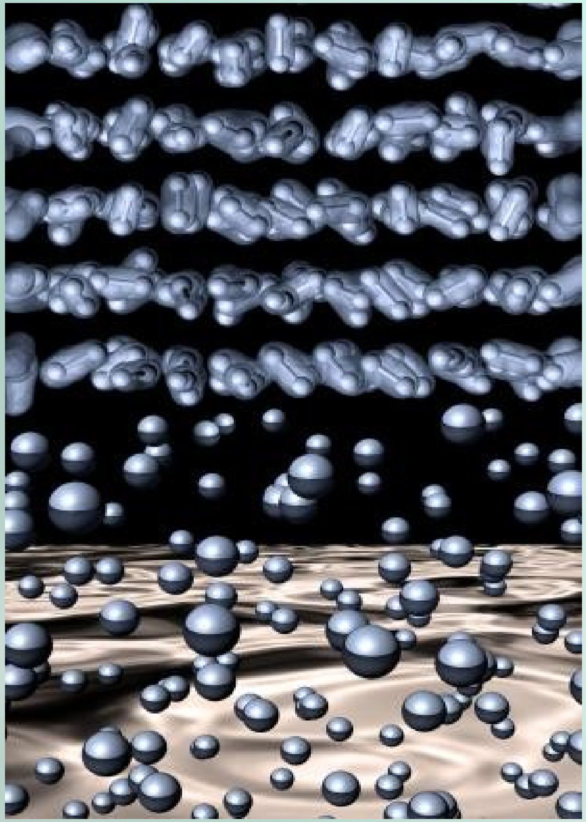
Dewar



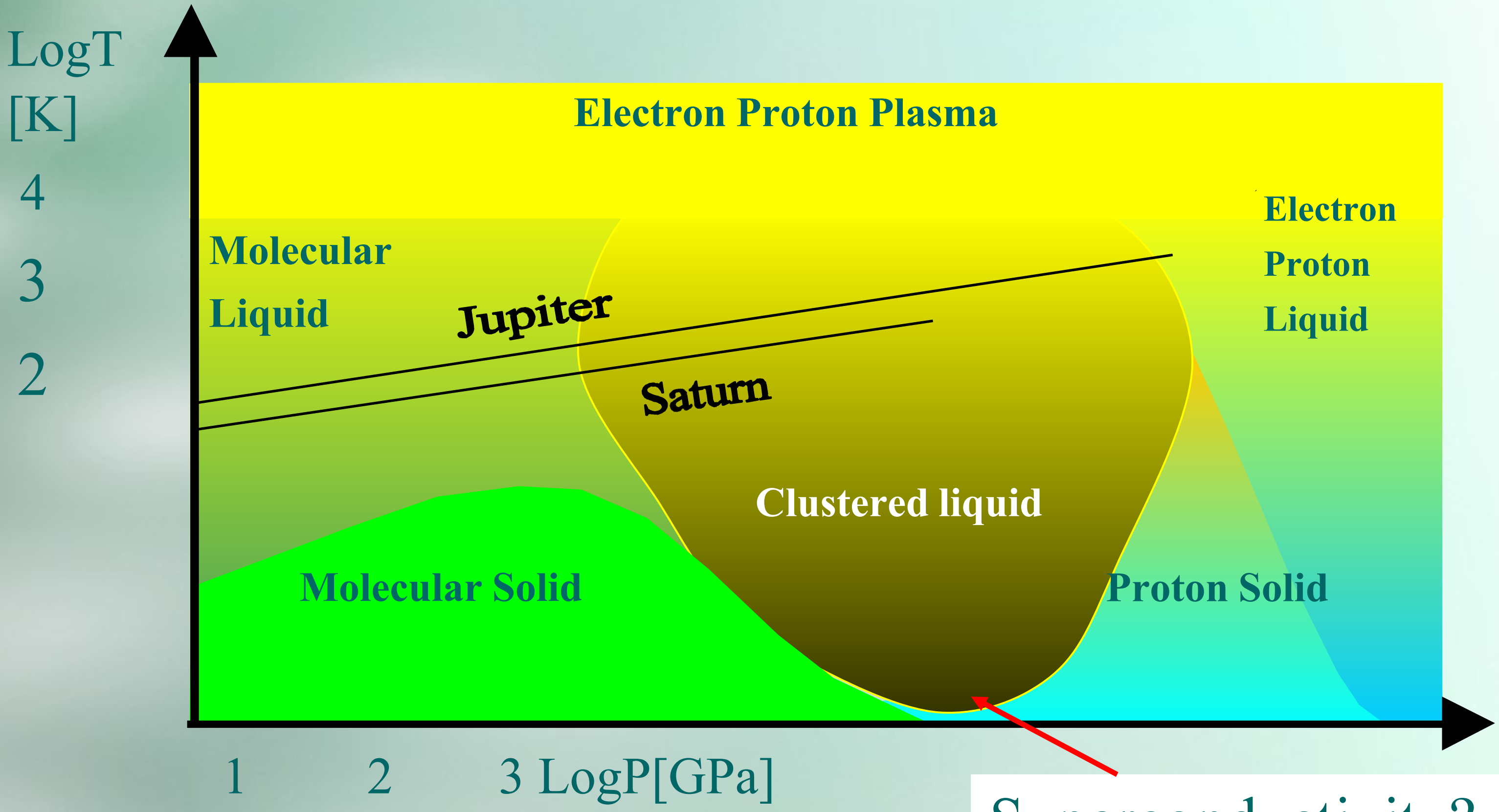
Claus-Armstrong
Baeyer

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

Phase Diagram of Hydrogen



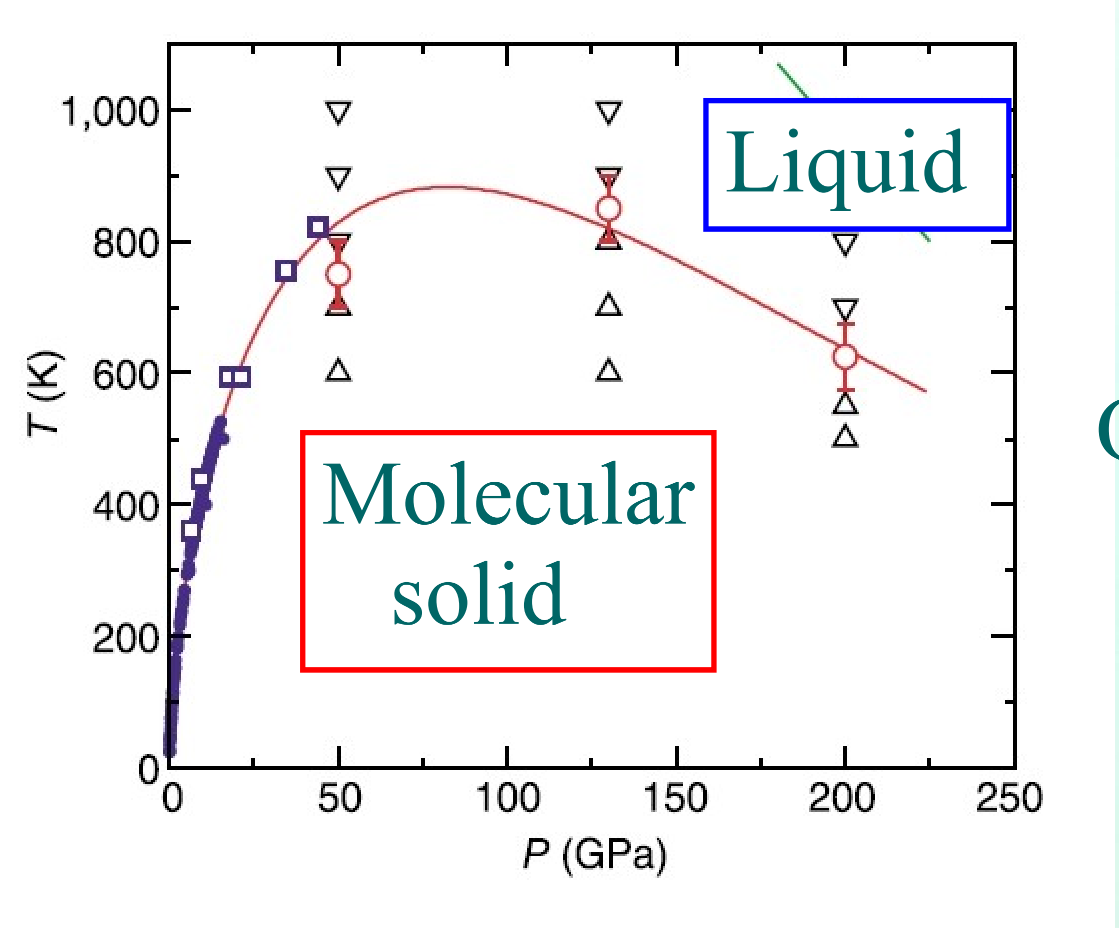
Phase Diagram of Hydrogen



Superconductivity?
Ashcroft Nature 2004

Indications of an anomalous melting line

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



QMC

●

Another quantum T=0 liquid phase?

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

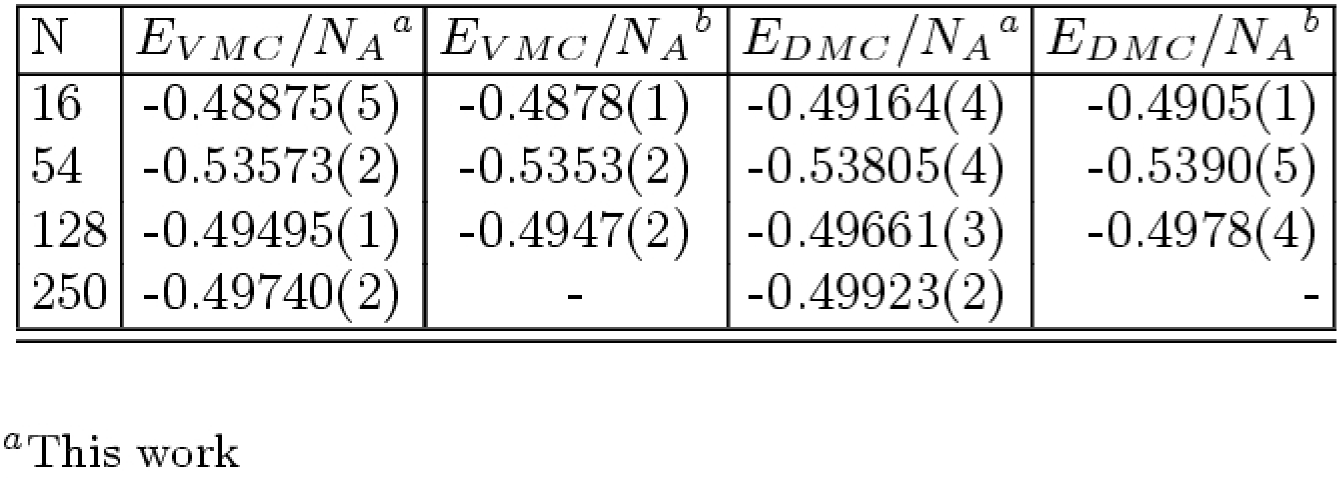
$r_s \approx H_2$ bonding lenght

Energy per H at high-pressure (Hartree)

2 Gaussian per protons (Det)

1 Gaussian per proton (Jastrow)

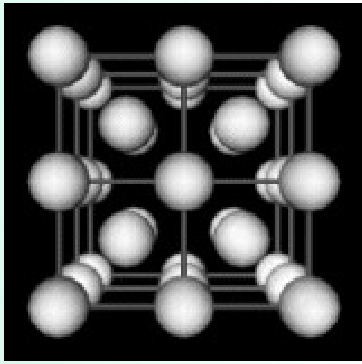
Comparison with previous works



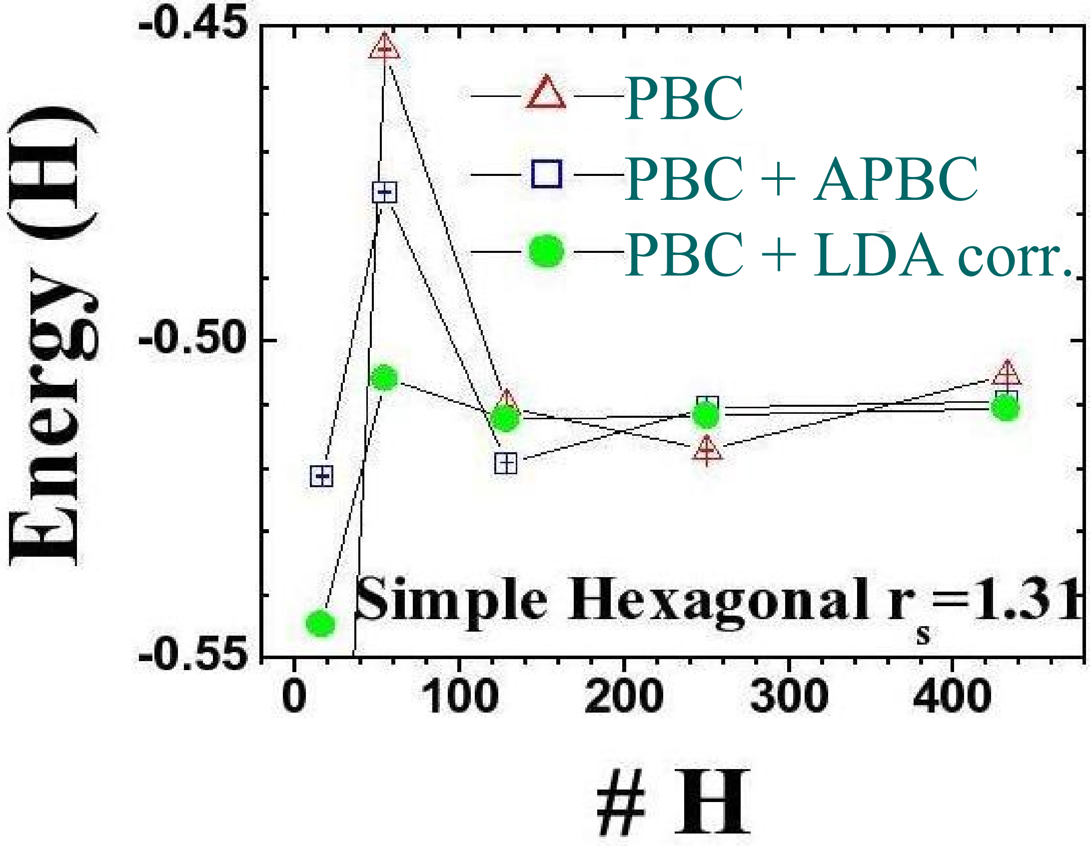
N	E_{VMC}/N_A [a]	E_{VMC}/N_A [b]	E_{DMC}/N_A [a]	E_{DMC}/N_A [b]
16	-0.48875(5)	-0.4878(1)	-0.49164(4)	-0.4905(1)
54	-0.53573(2)	-0.5353(2)	-0.53805(4)	-0.5390(5)
128	-0.49495(1)	-0.4947(2)	-0.49661(3)	-0.4978(4)
250	-0.49740(2)	-	-0.49923(2)	-

[a] This work

(b) C. Pierleoni , D.M. Ceperley at al. PRA 2002



At fixed number of H, we simply add the contribution LDA(averaged on k-points)-LDA(gamma) to QMC data



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

Phase	LDA	VMC	DMC
BCC	-0.5079	-0.502(1)	-0.504(1)
Simple Hexagonal(a)	-0.5127	-0.511(1)	-0.514(1)

Simple Hexagonal is
the lowest energy structure at high pressure
but how it compares with the liquid phase?

(a) T.W.Barbee III and M. L. Choen Phys. Rev B (44) 11563, 1991
V.Natoli R.M. Martin and D.M. Ceperley PRL(70) 1952, 1993

Finite Temperature Simulation how to do it?

Problem: the forces!!

The Forces problem in QMC

$$F_i = \langle \frac{\partial H}{\partial R_i} \rangle + 2 \left(\langle \frac{H\Psi}{\Psi} \frac{\partial \Psi}{\partial R_i} \frac{1}{\Psi} \rangle - \langle \frac{H\Psi}{\Psi} \rangle \langle \frac{\partial \Psi}{\partial R_i} \frac{1}{\Psi} \rangle \right)$$

Hellman-Feynman force **Pulay force**

Both of them have not finite variance!!!

For the first one the problem was solved using a “renormalized” operator such that

$\langle \tilde{O} \rangle = \langle O \rangle$ but $\langle \tilde{O}^2 \rangle - \langle \tilde{O} \rangle^2$ is finite!

Assaraf
and Caffarel 2000

Typical problem in MC for computing forces

Assume |x| is the distance from a node where $\Psi(0) = 0$

$$A(x) \approx 1/x^2 \text{ and } P(0) \propto \Psi(0)^2 \approx 0$$

and so close to a node

$$\langle A \rangle = \int 1/x^2 P(x) \text{ is finite but the variance } \ldots .$$

$$\int dx P(x)(1/x^2)^2 = \int dx 1/x^2 \to \infty!!!!$$

Solution → Reweighting method

$$\langle A \rangle = \int A(x)R(x)\frac{P(x)}{R(x)}dx$$ with $R(x) \propto x^2$

in such a way the new operator

$$A'(x) = A(x)R(x)$$

does not diverge anymore on the nodes and

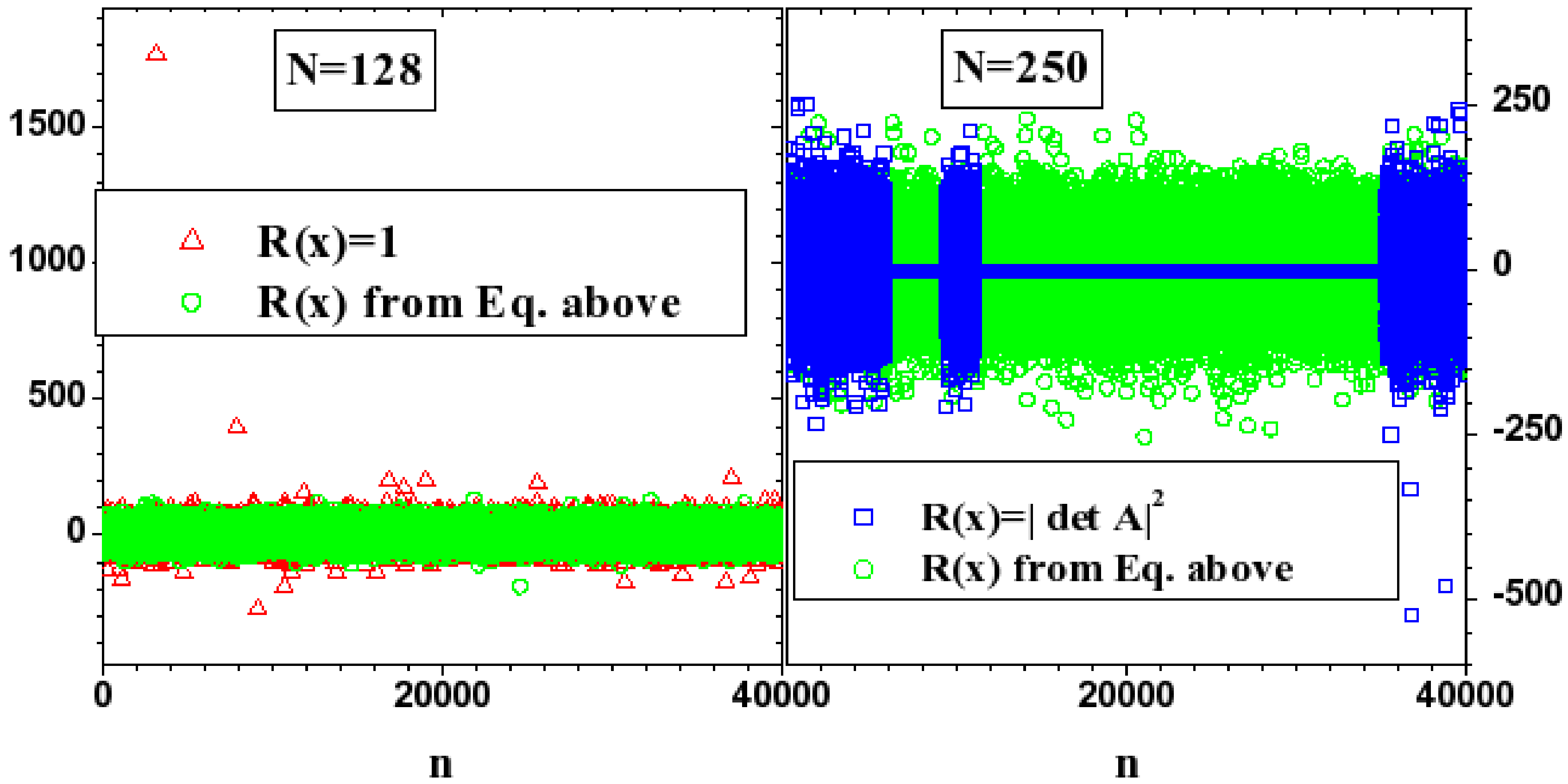
$$\langle A \rangle = \frac{\sum R(x_i)A(x_i)}{\sum R(x_i)} + O(1/\sqrt(M))$$

Umbrella sampling

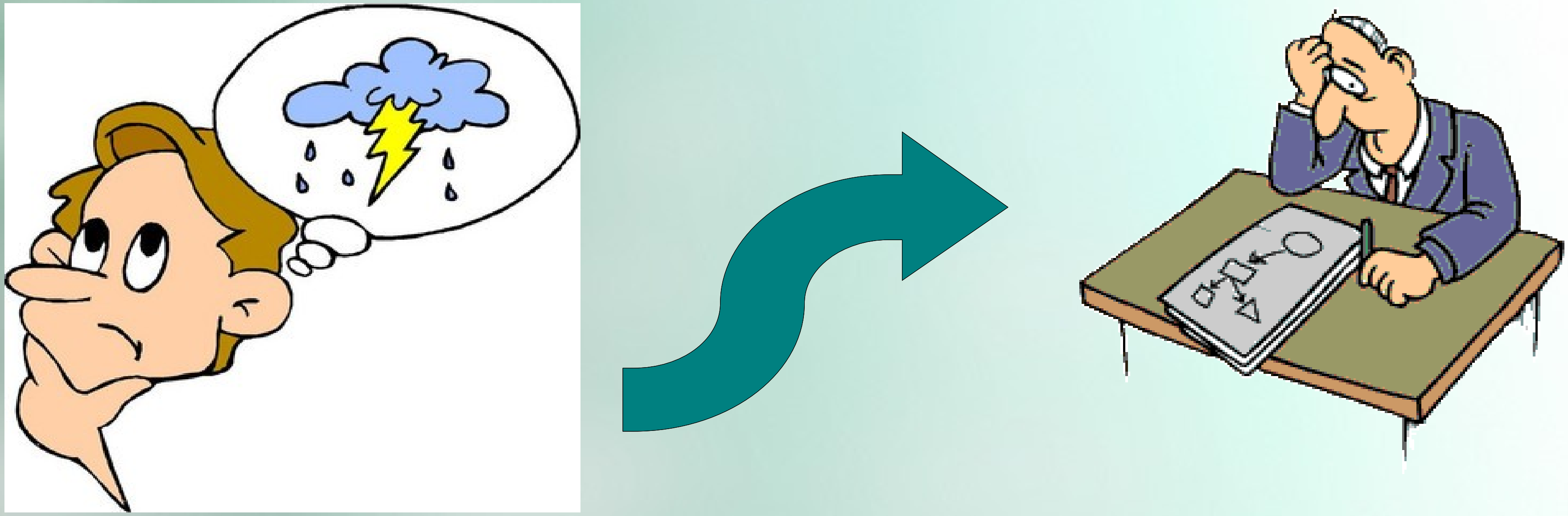
Different choices of R(x)

$$\Psi(x) = det D(x)$$

$$R(x) = 1/\sum_{i,j} |D^{-1}_{i,j}|^2$$



Now we solved half of the problem we have forces with finite variance



Second problem: the noise !!

Ab-initio molecular dynamics with noisy forces

Using a generalized Langevin dynamics

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

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

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

→

Boltzman distribution!!

$$\boxed{W_{eq}(x,v) = e^{\frac{-\sum_i \frac{m_i v_i^2}{2} - V(x)}{KT}}}$$

The basic steps for moving atoms

(1) Forces can be computed efficiently with VMC

(2) Optimization of the electronic VMC parameters

(3) At each step we move ions with MD

Why MD can be so efficient for QMC?

(1) The simulation at finite T requires some external noise to the forces But the noise is given for free within QMC!!!

(2) 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

SR optimization with Hessian acceleration

Using Hessian matrix information
to accelerate the convergence

$$\vec{\gamma} = B^{-1}\vec{f}$$

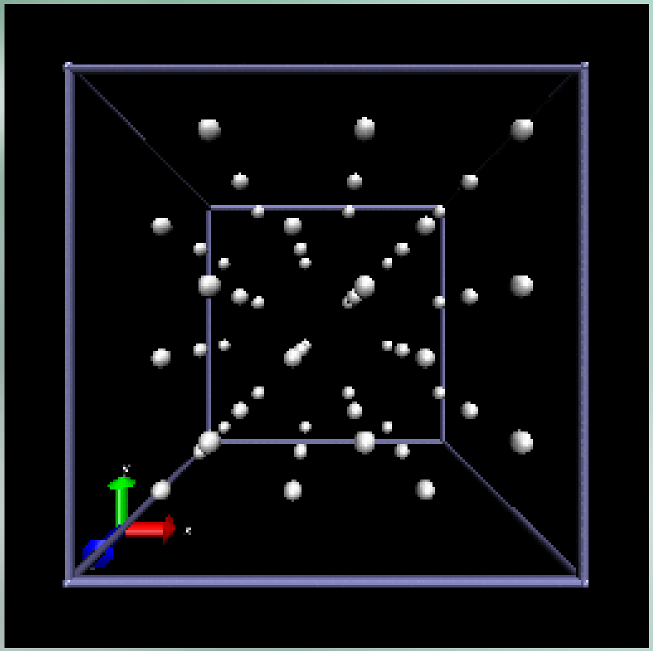
$$B = H + \mu S$$

in order to have a stable optimization
the variation of the WF has to be small

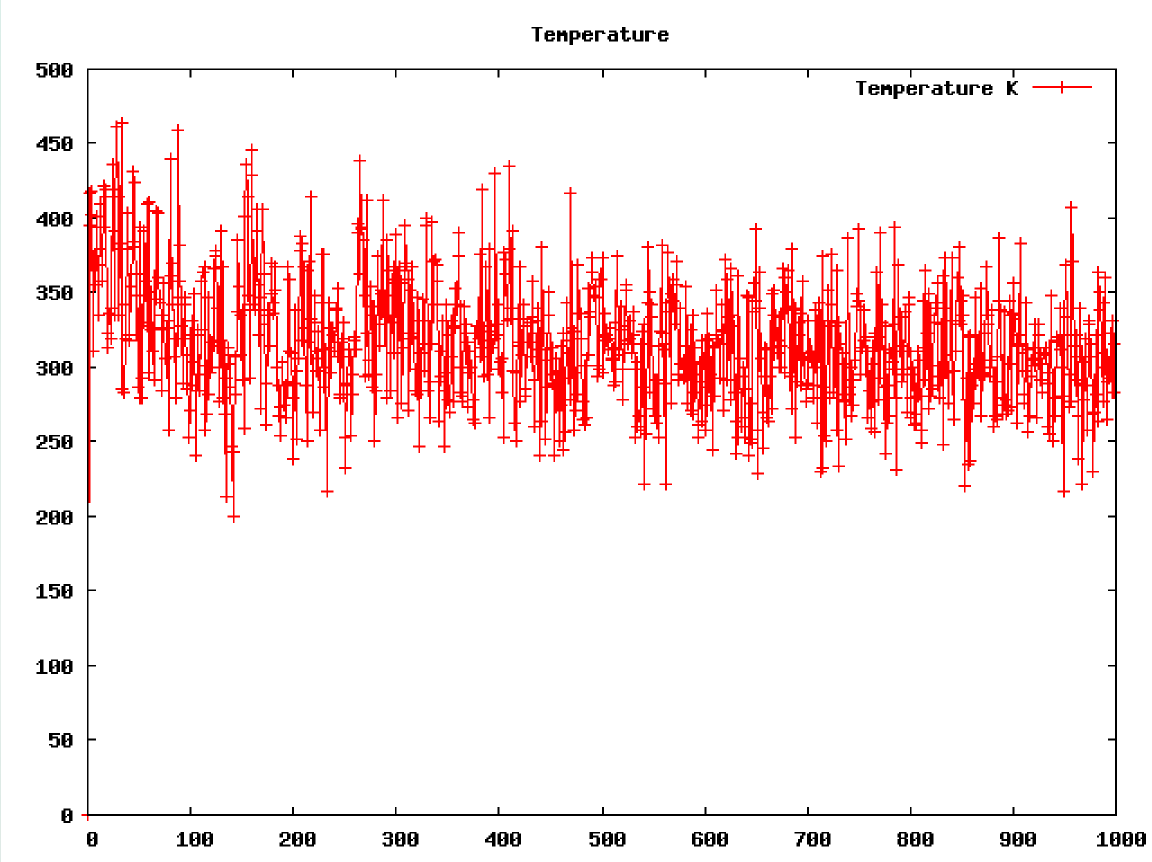
$$|\Delta WF|^2 = \langle \phi_\alpha | \phi_{\alpha+\gamma} \rangle = \sum_{k,k'} \gamma_k \gamma_{k'} S^{k,k'}$$

It works !!!

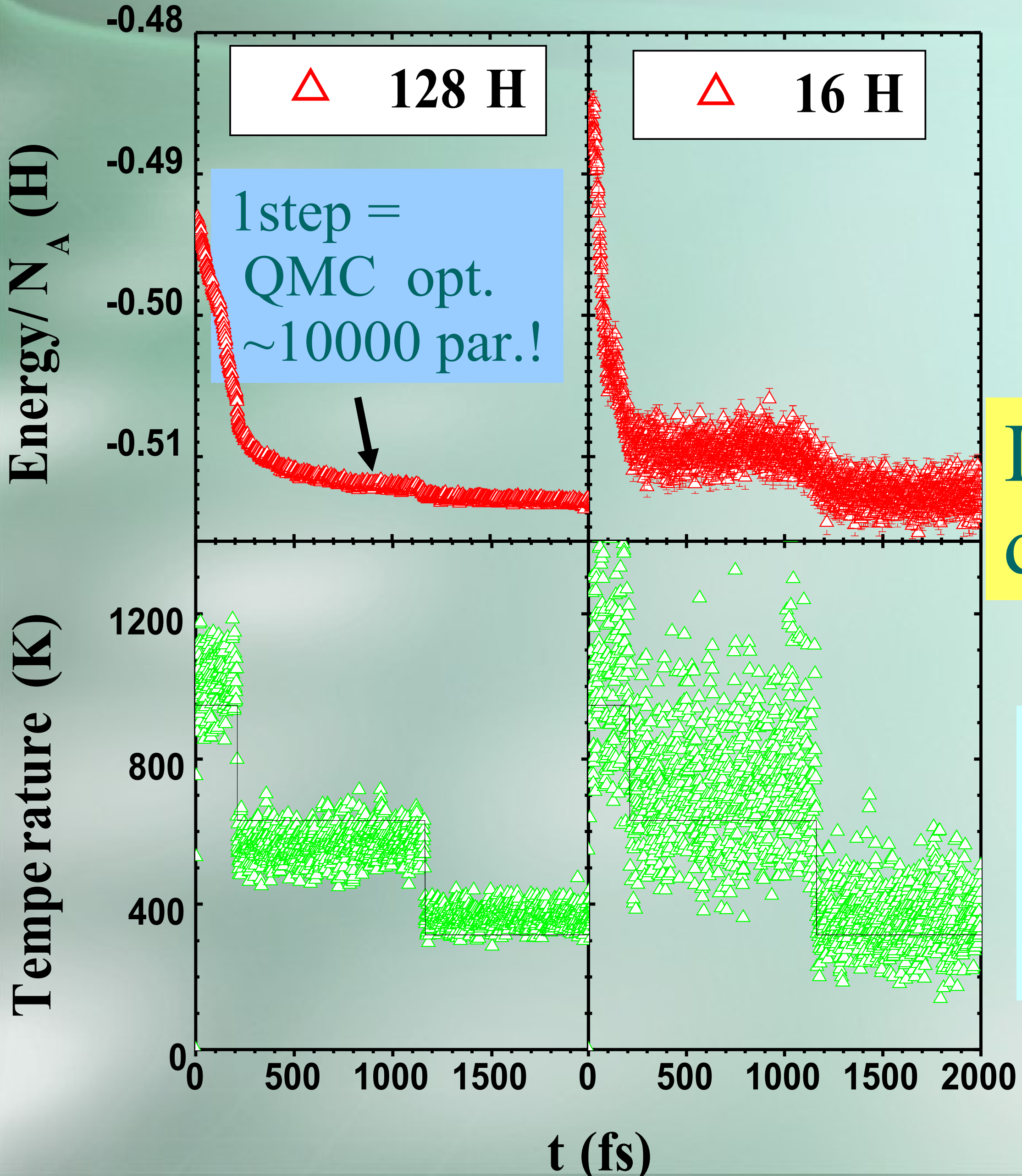
Melting of 54 hydrogens in a BCC lattice



54 hydrogens at 300K



New ab-initio Molecular-dynamics with QMC



$\Delta t = 1 fs$

Proton → Classical

Internal energy decreases at 1300K!!!

With RVB wf QMC possible for ~100 atoms

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

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

(Hartree per atom)

Liquid competes with the most stable solid

And quantum corrections?

Wigner-Kirkpatrick perturbation theory in $\hbar$ to the internal energy

$$U = -\partial_\beta log(Z)$$

$$Z_{quantum} = Z\left[1 - \hbar^2 \frac{\beta^2}{24M}\langle(\Delta E)^2\rangle_\beta + O(\hbar^4)\right]$$

Liquid → 0.016(2) H/proton

Simple Hexagonal → 0.034(3) H/proton

Consistent with direct evaluation at T=0, Natoli ‘93

Conclutions

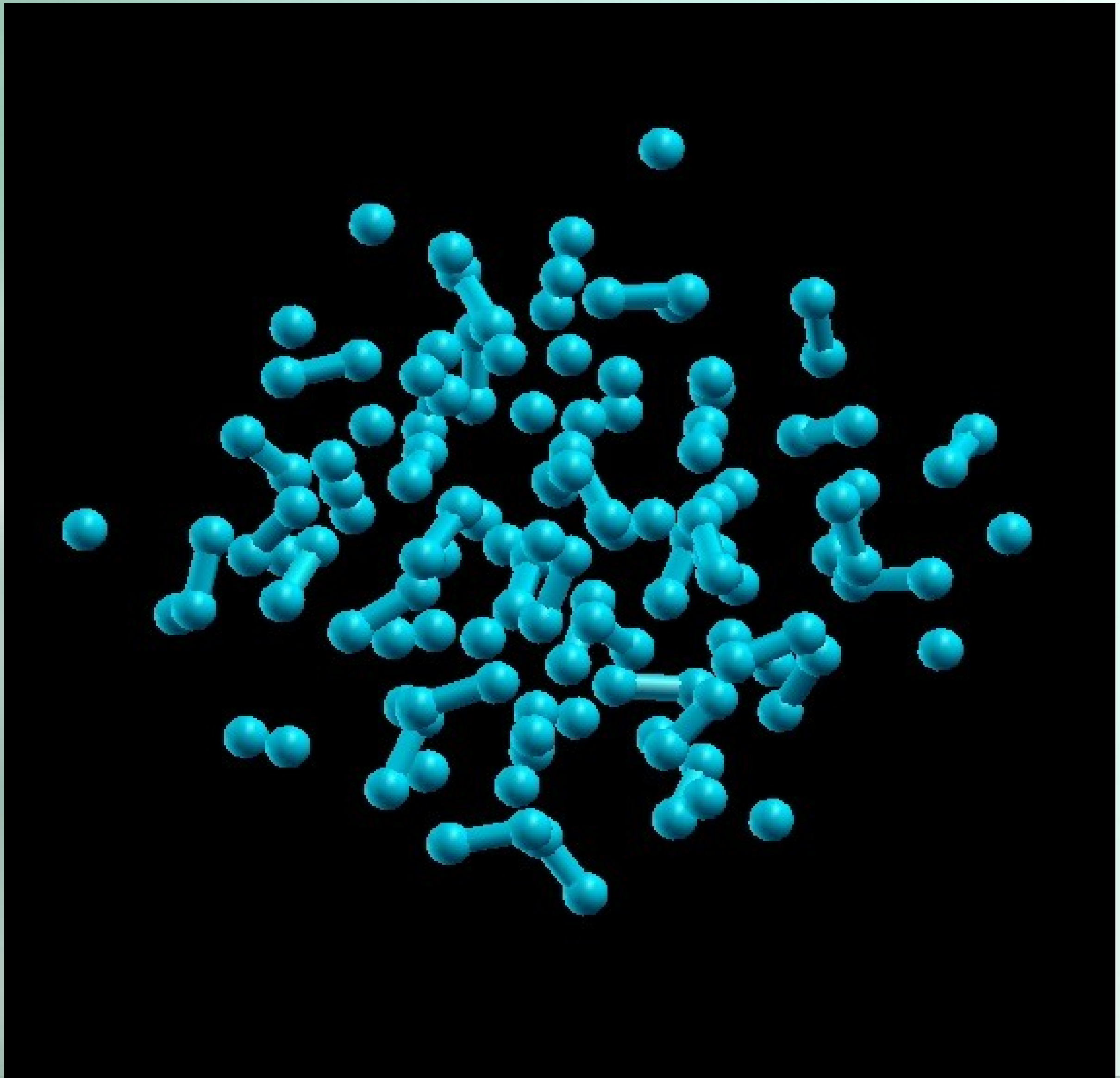
1) Forces with finite variance

2) Ab-initio molecular dynamics with noisy forces

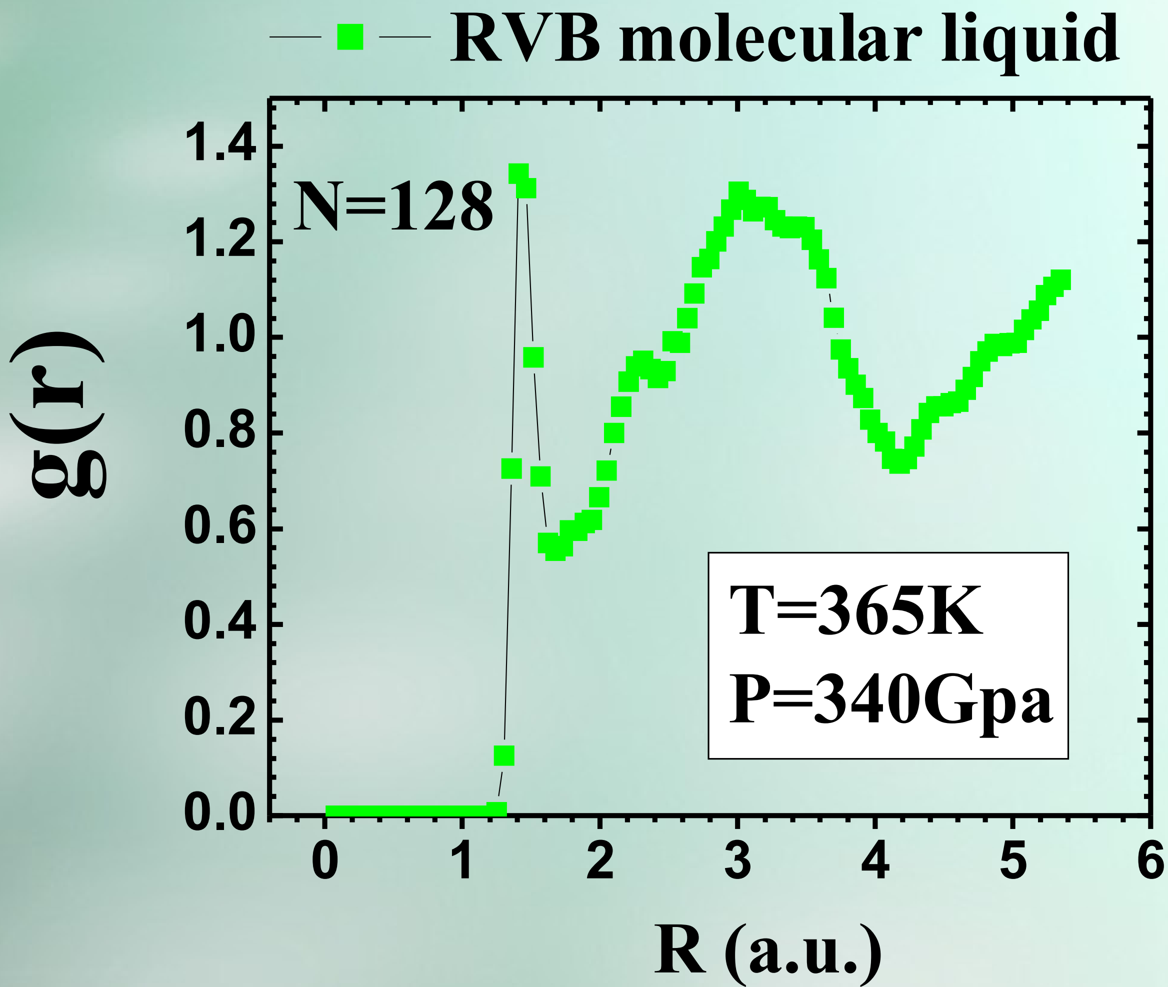
3) Stable liquid phase in high pressure hydrogen

….. but this is not the end …..

Snap-shot of the protons at the last iteration



Proton-proton pair correlation function

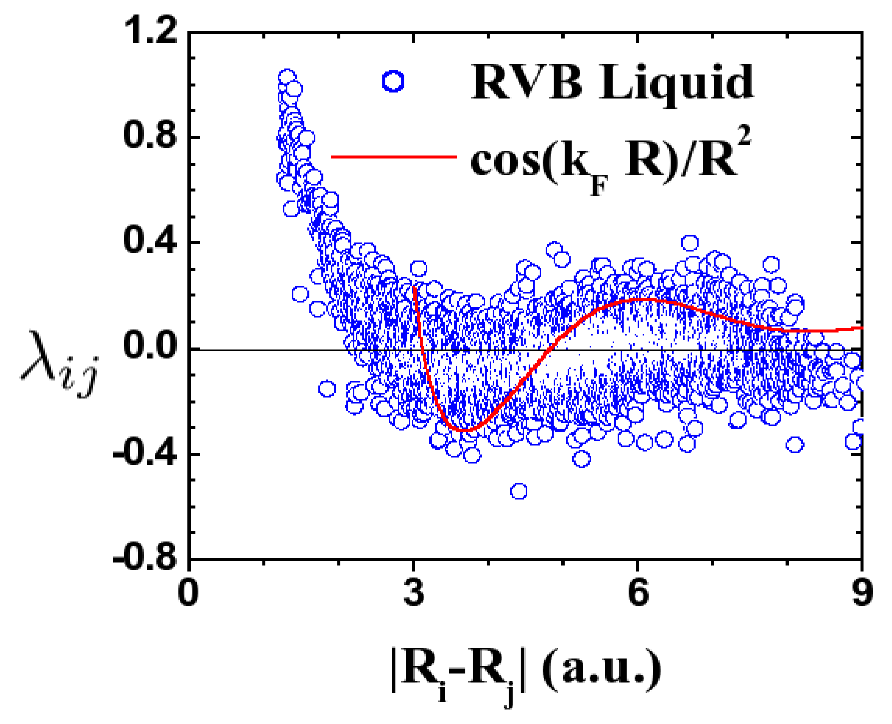


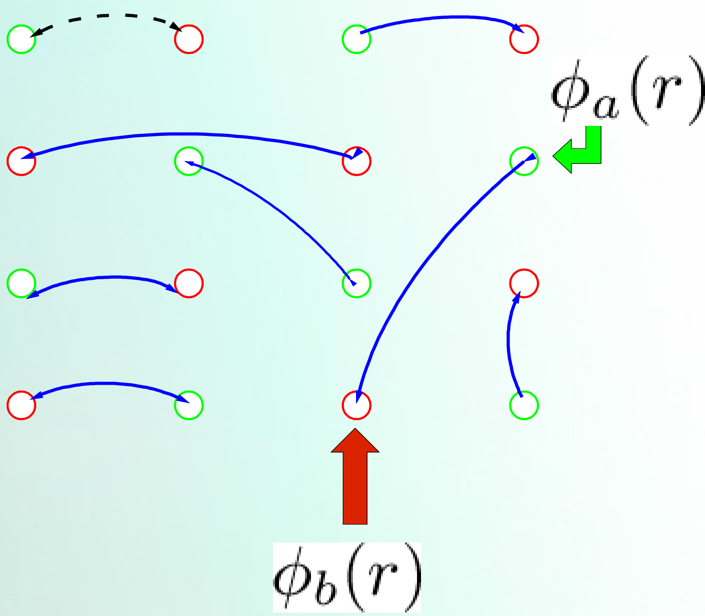
The variational approach as the simplest tool to detect this new physics induced by correlation

The RVB wave-function can describe metals, insulators and superconductors depending by the pairing function and the Jastrow factor

$$RVB = J|BCS + ...\rangle$$

The pairing function in the liquid phase



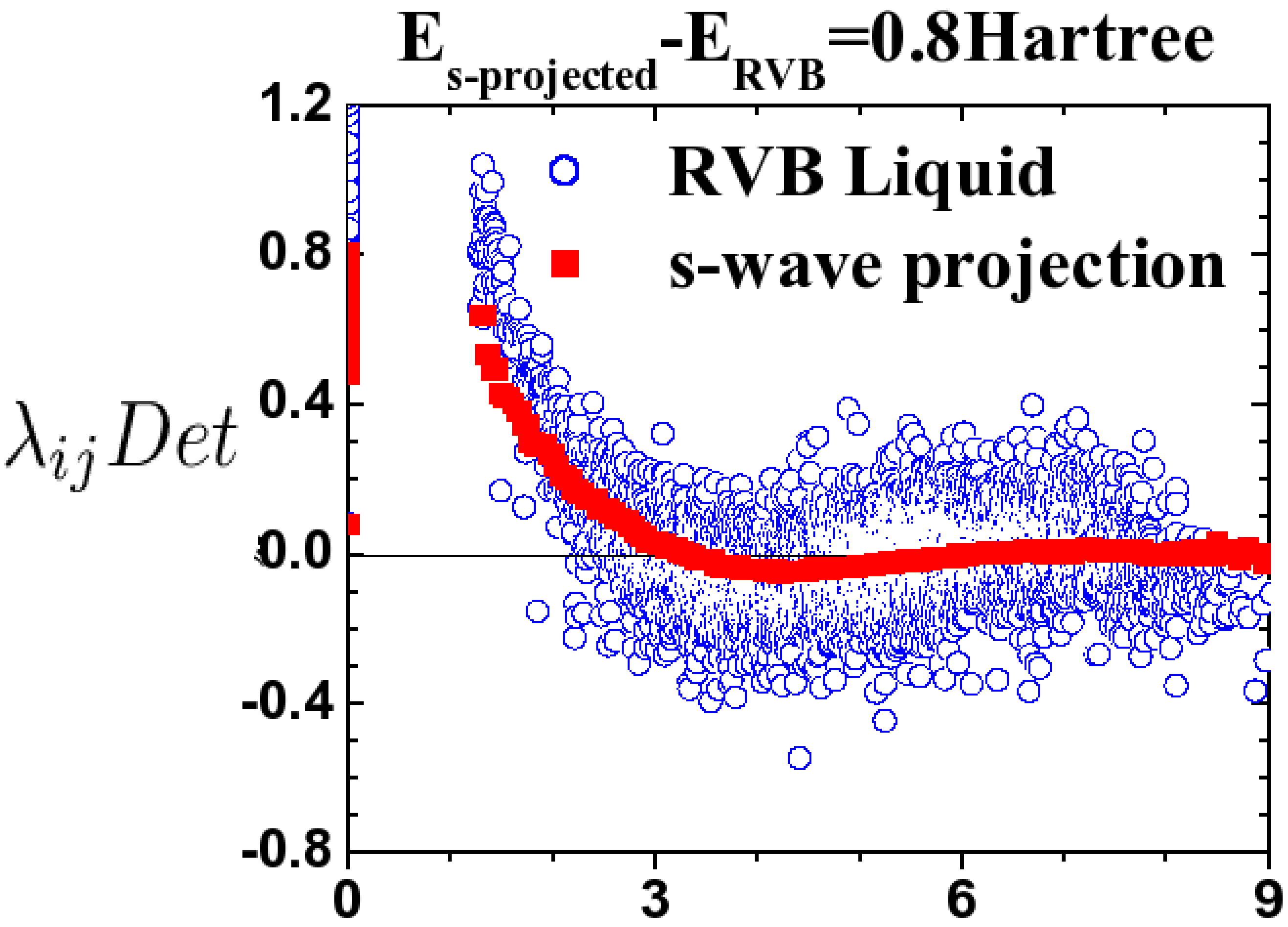


$$\Phi_{RVB}(r^{\uparrow}, r^{\downarrow}) = \sum_{a,b} \lambda_{a,b} \phi_a(r^{\uparrow}) \phi_b(r^{\downarrow})$$

Remind: in a bcc-metal we expect occupied all: $|k| \leq k_F$

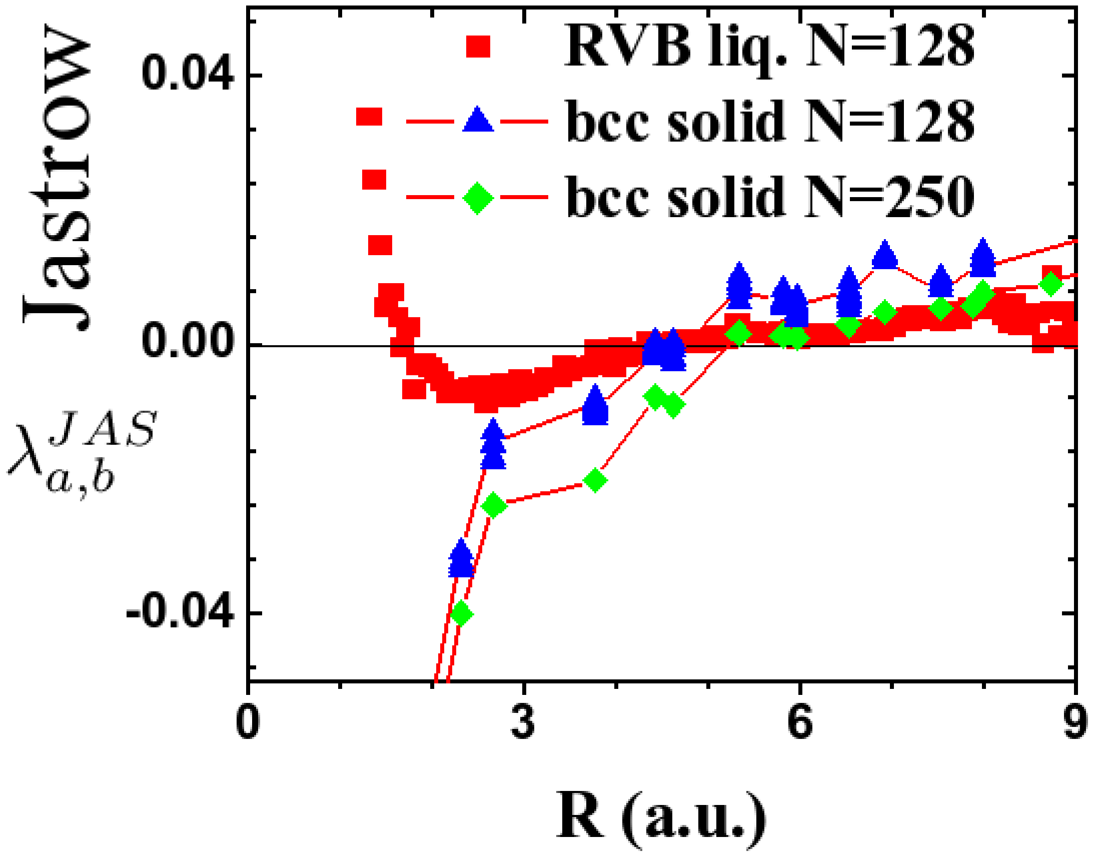
$$\lambda_{ij} = \sum_{|k|<k_F} e^{ik(R_i - R_j)} \propto cos(k_F |R_i - R_j|)/|R_i - R_j|^2$$

Optimization with the s-wave constraint



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

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



$$\Phi_J(r_i,r_j)=\sum_{a,b}\lambda^{JAS}_{a,b}\phi_a(r_i)\phi_b(r_j)$$

(a) Capello et al. condmat/0611306

A new possibility

HTc or Insultor 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 ?

Conclutions

1) Forces with finite variance

2) Ab-initio molecular dynamics with noisy forces

3) Stable liquid phase in high pressure hydrogen

4) A new possible superconductive phase
at high pressure?

Acknowledgement

Sandro Sorella

Michele Casula

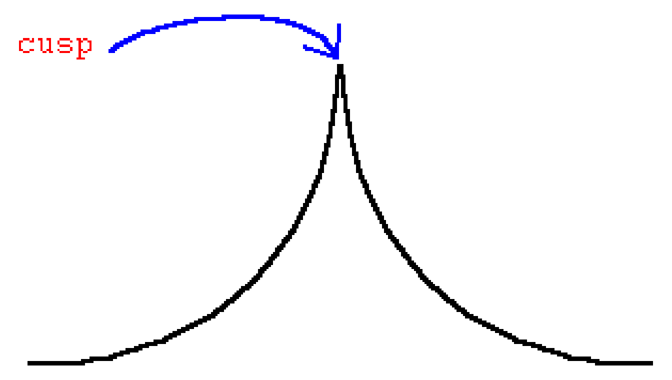
The Jastrow $J = J_1 J_2 J_3$

nuclear and electron cusp conditions

$$-\psi'' - \frac{1}{r}\left(Ze^2\psi + \psi'\right) = E\psi \quad \Longrightarrow \quad \frac{1}{\psi}\psi' = -Ze^2$$

$$J_1(\vec{r}_1, \ldots, \vec{r}_N) = \exp\left[\sum_{i,a}^{N} \left(\xi_a(\vec{r}_i) + \Xi_a(\vec{r}_{ia})\right)\right], \quad \Longrightarrow \quad \xi_a(r) = \frac{-Z_a r}{(1 + br)}$$

$$J_2(\vec{r}_1, \ldots, \vec{r}_N) = \exp\left(\sum_{i<j}^{N} u(r_{ij})\right)$$



The Three-body Jastrow

$$J_3(\vec{r}_1, ..., \vec{r}_N) = \exp\left(\sum_{i<j} \Phi_J(\vec{r}_i, \vec{r}_j)\right)$$

$$\Phi_J(\vec{r}_i, \vec{r}_j) = \sum_{l,m,a,b} g_{l,m}^{a,b} \psi_{a,l}(\vec{r}_i) \psi_{b,m}(\vec{r}_j)$$

The three-body Jastrow factor:

- describes Van Der Waals forces
- suppress superconductivity
- describes Mott insulators
- keeps charge constant on atoms or molecules (not fixed by AGP)

Discretization of the Langevin dynamics

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

Noise Correction

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

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

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

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

Noise Correction 1

ideal beautifull noise: $\langle \eta_i \eta_j \rangle = \alpha_i \delta_{ij}$

QMC noise: $\langle \tilde{\eta}_i^{QMC} \tilde{\eta}_j^{QMC} \rangle = \alpha_{ij}^{QMC}(R)$

SOLUTION

We add external noise
to sample the Boltzman distribution!

$$\langle \tilde{\eta}_i^{ext} \tilde{\eta}_j^{ext} \rangle = \alpha - \alpha^{QMC}$$

Results on molecules 1

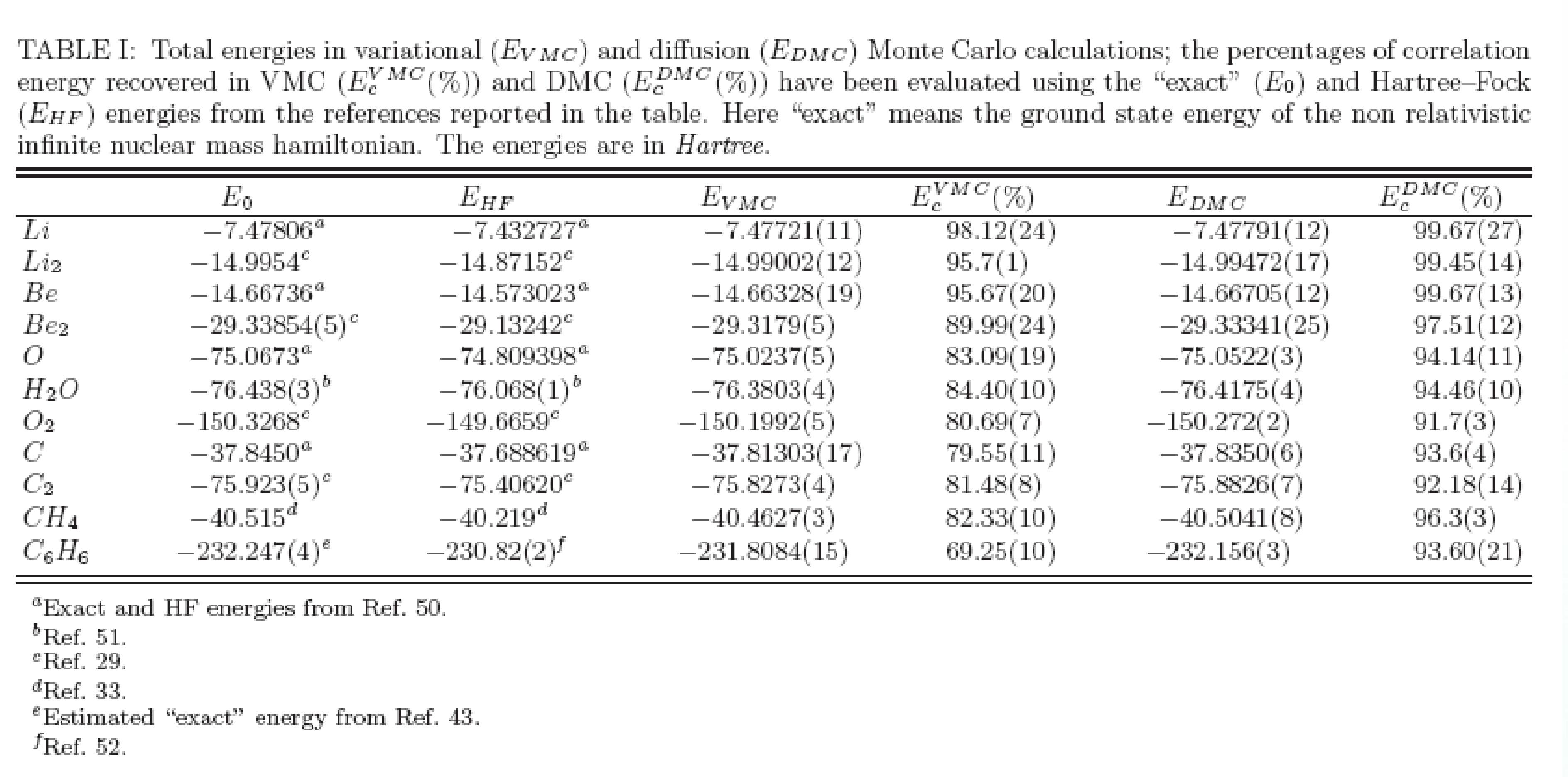


TABLE I: Total energies in variational (E_{VMC}) and diffusion (E_{DMC}) Monte Carlo calculations; the percentages of correlation energy recovered in VMC ($E_c^{VMC}(\%)$) and DMC ($E_c^{DMC}(\%)$) have been evaluated using the “exact” (E_0) and Hartree–Fock (E_{HF}) energies from the references reported in the table. Here “exact” means the ground state energy of the non relativistic infinite nuclear mass hamiltonian. The energies are in *Hartree*.

	E_0	E_{HF}	E_{VMC}	$E_c^{VMC}(\%)$	E_{DMC}	$E_c^{DMC}(\%)$
Li	−7.47806[a]	−7.432727[a]	−7.47721(11)	98.12(24)	−7.47791(12)	99.67(27)
Li_2	−14.9954[c]	−14.87152[c]	−14.99002(12)	95.7(1)	−14.99472(17)	99.45(14)
Be	−14.66736[a]	−14.573023[a]	−14.66328(19)	95.67(20)	−14.66705(12)	99.67(13)
Be_2	−29.33854(5)[c]	−29.13242[c]	−29.3179(5)	89.99(24)	−29.33341(25)	97.51(12)
O	−75.0673[a]	−74.809398[a]	−75.0237(5)	83.09(19)	−75.0522(3)	94.14(11)
H_2O	−76.438(3)[b]	−76.068(1)[b]	−76.3803(4)	84.40(10)	−76.4175(4)	94.46(10)
O_2	−150.3268[c]	−149.6659[c]	−150.1992(5)	80.69(7)	−150.272(2)	91.7(3)
C	−37.8450[a]	−37.688619[a]	−37.81303(17)	79.55(11)	−37.8350(6)	93.6(4)
C_2	−75.923(5)[c]	−75.40620[c]	−75.8273(4)	81.48(8)	−75.8826(7)	92.18(14)
CH_4	−40.515[d]	−40.219[d]	−40.4627(3)	82.33(10)	−40.5041(8)	96.3(3)
C_6H_6	−232.247(4)[e]	−230.82(2)[f]	−231.8084(15)	69.25(10)	−232.156(3)	93.60(21)

[a] Exact and HF energies from Ref. 50.

[b] Ref. 51.

[c] Ref. 29.

[d] Ref. 33.

[e] Estimated “exact” energy from Ref. 43.

[f] Ref. 52.

Results on molecules 2

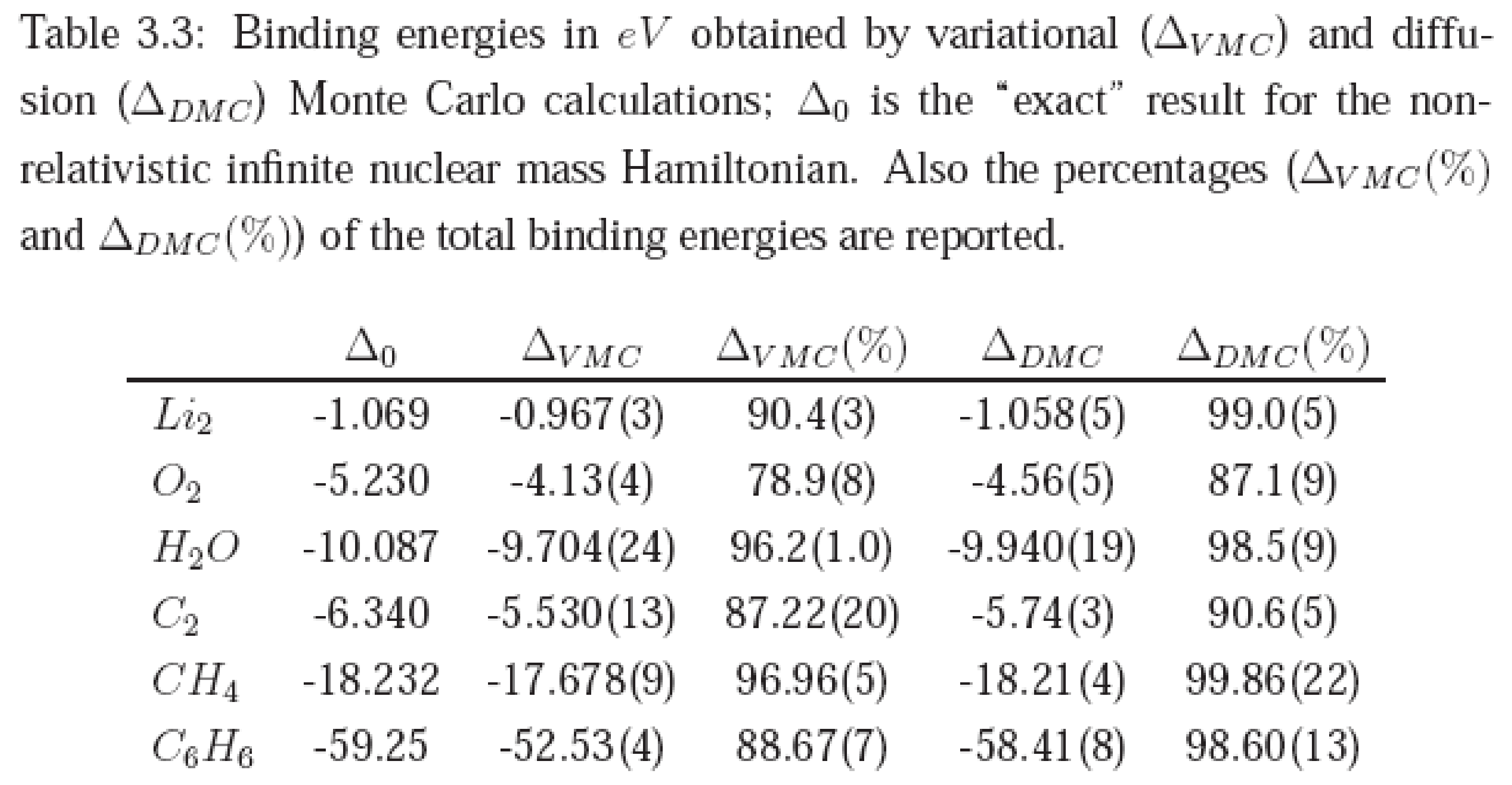


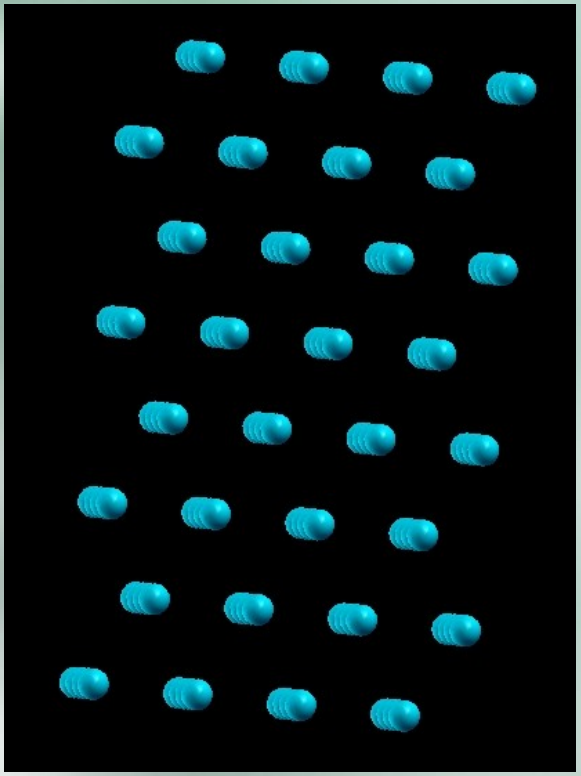
Table 3.3: Binding energies in eV obtained by variational (Δ_{VMC}) and diffusion (Δ_{DMC}) Monte Carlo calculations; Δ_0 is the "exact" result for the non-relativistic infinite nuclear mass Hamiltonian. Also the percentages ($\Delta_{VMC}(\%)$ and $\Delta_{DMC}(\%)$) of the total binding energies are reported.

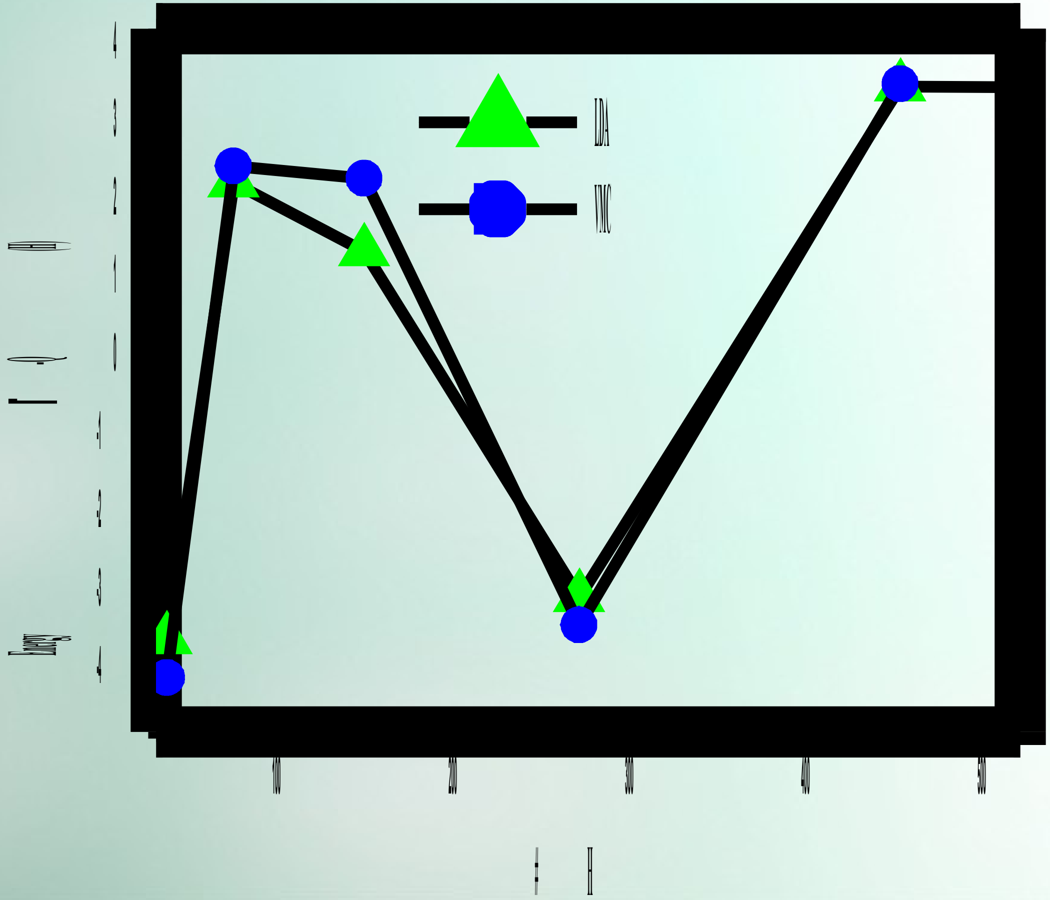
	Δ_0	Δ_{VMC}	$\Delta_{VMC}(\%)$	Δ_{DMC}	$\Delta_{DMC}(\%)$
Li_2	-1.069	-0.967(3)	90.4(3)	-1.058(5)	99.0(5)
O_2	-5.230	-4.13(4)	78.9(8)	-4.56(5)	87.1(9)
H_2O	-10.087	-9.704(24)	96.2(1.0)	-9.940(19)	98.5(9)
C_2	-6.340	-5.530(13)	87.22(20)	-5.74(3)	90.6(5)
CH_4	-18.232	-17.678(9)	96.96(5)	-18.21(4)	99.86(22)
C_6H_6	-59.25	-52.53(4)	88.67(7)	-58.41(8)	98.60(13)

Thermodynamic limit is difficult

QMC Gamma point or Integration BC (TABC)?

Simple Hexagonal c/a=0.6 rs=1.31





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 S. Sorella) PRL, (2007)

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

Why MD can be so efficient for QMC?

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

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

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

The AGP wave-function

$$\Psi_{AGP}(\vec{r}_1, ..., \vec{r}_N) = \det\left(\Phi_{AGP}(\vec{r}_i, \vec{r}_{j+N/2})\right).$$

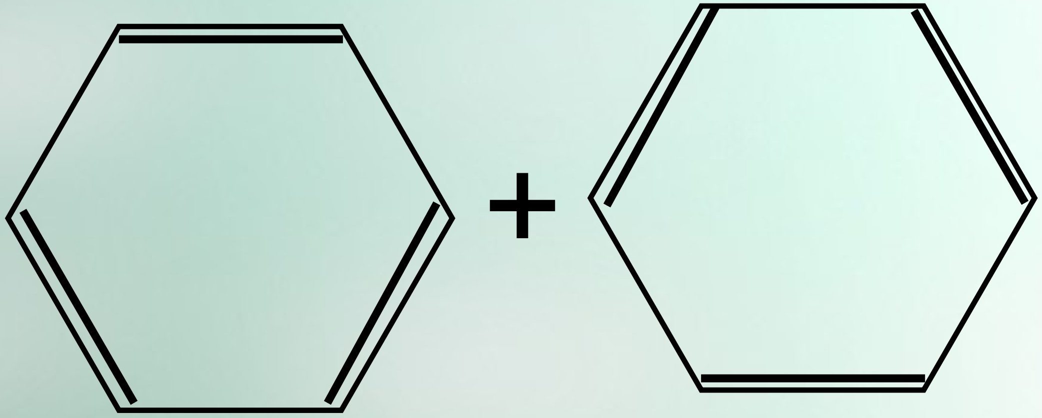
$$\Phi_{AGP}(\vec{r}^{\uparrow}, \vec{r}^{\downarrow}) = \sum_{l,m,a,b} \lambda_{a,b}^{l,m} \phi_{a,l}(\vec{r}^{\uparrow}) \phi_{b,m}(\vec{r}^{\downarrow})$$

where

i,j are spin up and down electrons

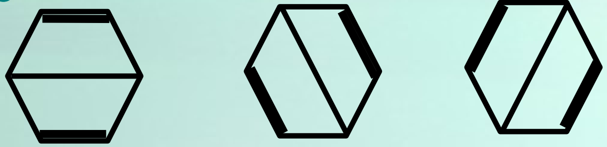
a,b are different atoms

l,m different orbitals

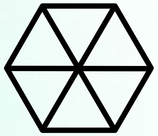


Binding energy of aromatic molecules

Kekule’



Dewar



Claus-Armstrong

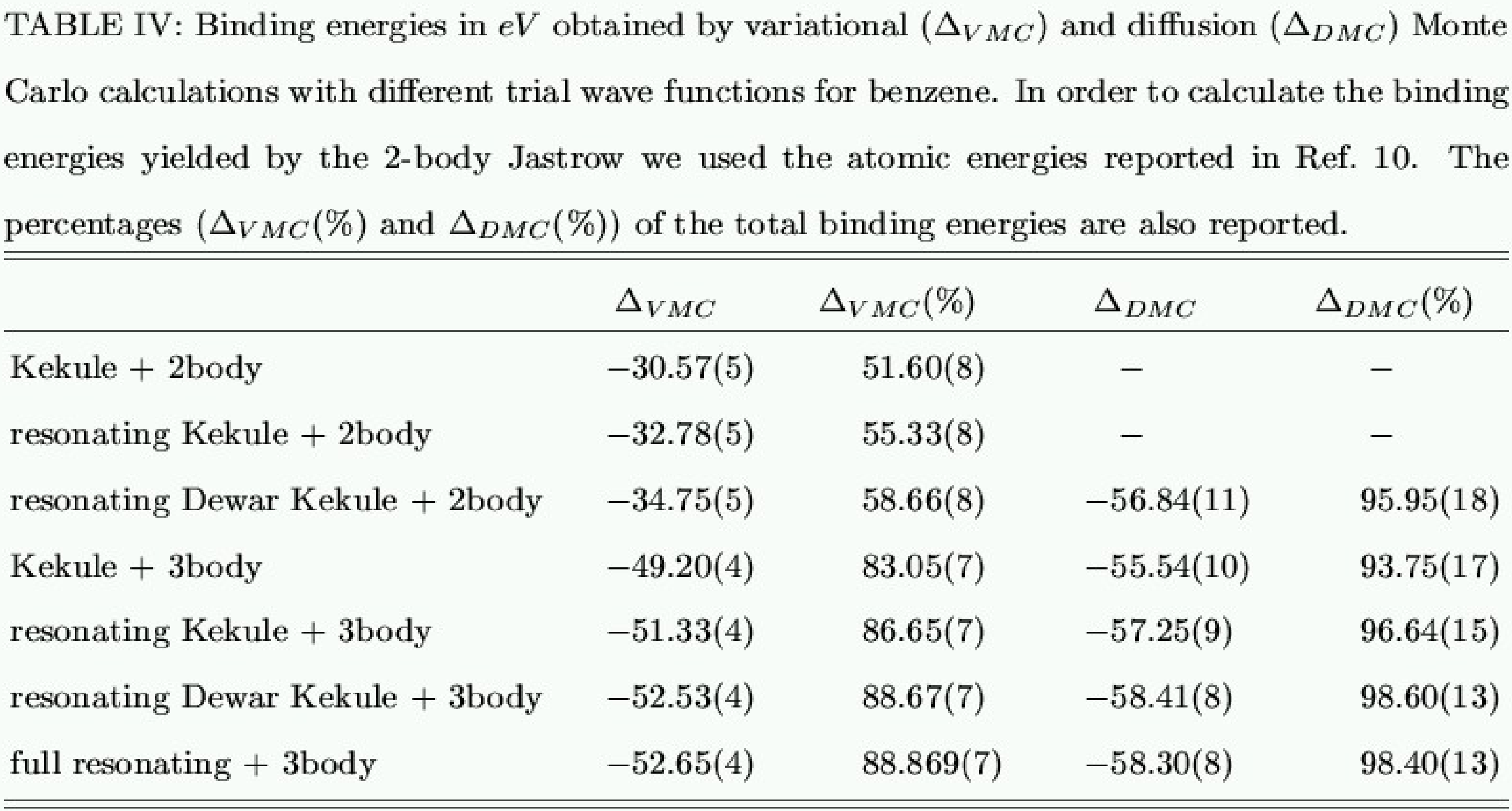


TABLE IV: Binding energies in *eV* obtained by variational (Δ_{VMC}) and diffusion (Δ_{DMC}) Monte Carlo calculations with different trial wave functions for benzene. In order to calculate the binding energies yielded by the 2-body Jastrow we used the atomic energies reported in Ref. 10. The percentages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

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