

Recent progress with Lattice Regularized Diffusion Monte Carlo

Sandro Sorella

SISSA Democritos Trieste

In collaboration with TurboRVB developers (www.sissa.it/~sorella)

Claudio Attaccalite

University of San Sebastian, Spain

Michele Casula

University of Illinois at Urbana-Champaign, IL, United States

Leonardo Spanu

University of California, Davis, United States

Outline

- Diffusion Monte Carlo (DMC, D.M. Ceperley '82) methods:
the algorithm on a lattice (M.Casula et al. '05)
 - Non local pseudopotentials and locality approximation
 - Lattice regularization
 - Simplification of the algorithm → Improved efficiency.
N.B. Opposite path compared to DMC
(improved algorithm Umrigar '93, quite involved, now standard...).
- Application to some simple test cases (still in progress).
 - Water monomer all electron (no pseudo).
 - Benzene molecule with pseudo Carbon.
 - Bulk Silicon. with pseudo and PBC.

Motivations

- Accurate and efficient methods for Quantum Monte Carlo (peta-scaling).
- Lattice regularization: an approximation that is used in Path integrals.

“Do it with path integrals, they really are discrete” R. Feynmann

My interpretation (extrapolated):

Continuous models are sometimes not well posed mathematically and only the $a \rightarrow 0$ of some lattice regularized theory is well defined: where “a” is the minimum cutoff distance in real space.

e.g. lattice gauge theories or generic field theories.

They make sense when and because the $a \rightarrow 0$ limit exists.

The approximation $a > 0$ is easy to control mathematically.

Here we want to show that :
“ Do it on a lattice, it’s really more efficient ...!!!”

Notations

$|\mathbf{x}\rangle$ Generic configuration of N electrons
determined by $3N$ coordinates : $\{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N\}$

\mathbf{a} Minimum lattice space for LRDMC

τ Minimum diffusion time for DMC

$|\psi_g\rangle$ Guiding function for DMC or LRDMC..

$|\psi_0\rangle$ Ground state of $H = -\Delta + V(\mathbf{x})$

$V(\mathbf{x})$ = el - el , el - ion , ion - ion Coulomb

Δ = full laplacian for the N electrons (\times units e.g. 1/2).

The “DMC” algorithm on a lattice

e.g. for the 1D Heisenberg $H = J \sum_i S_i \cdot S_{i+1}$

$$|x\rangle = |\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\rangle$$

The matrix elements are given and can be computed

e.g. $H_{x',x} = \langle x'|H|x\rangle = J/2$ for $x' \neq x$ (spin - flip)

A guiding function is given (can be computed)

$$\rightarrow \psi_g(\mathbf{x}) \text{ such that } |\psi_g(\mathbf{x})| > 0$$

The local energy :

$$e_L(\mathbf{x}) = \frac{\langle \psi_g | \mathbf{H} | \mathbf{x} \rangle}{\langle \psi_g | \mathbf{x} \rangle} = \sum_{\mathbf{x}'} \psi_g(\mathbf{x}') \mathbf{H}_{\mathbf{x}', \mathbf{x}} / \psi_g(\mathbf{x})$$

$$s_{\mathbf{x}', \mathbf{x}} = \begin{cases} \diamond & \text{(diagonals do not matter) } \mathbf{x}' = \mathbf{x} \\ \psi_g(\mathbf{x}') \mathbf{H}_{\mathbf{x}', \mathbf{x}} / \psi_g(\mathbf{x}) & \mathbf{x}' \neq \mathbf{x} \end{cases}$$

Case I no sign problem $s_{\mathbf{x}', \mathbf{x}} \leq \diamond$

Sampling the probability :

$$\Pi(\mathbf{x}) \propto \psi_{\mathbf{g}}(\mathbf{x}) \langle \mathbf{x} | e^{-H\tau} | \psi_{\mathbf{g}} \rangle \rightarrow \psi_{\mathbf{g}}(\mathbf{x}) e^{-E_0\tau} \psi_0(\mathbf{x})$$

Markov chain : walker $(\mathbf{x}_t, \mathbf{w}_t) \approx \mathbf{w}_t | \mathbf{x}_t \rangle$

1) $t = 0 : \mathbf{x}_0 = | \mathbf{x}_0 \rangle \quad \mathbf{w}_0 = 1$

2) $N = \sum_{x'} -s_{x',x_t} > 0, t_T = \text{Min}(\ln z / N, \tau - t) ; 0 < z \leq 1$ with $p(z) = 1$

3) $\mathbf{w}_{t+t_T} = \mathbf{w}_t \exp[-t_T e_L(\mathbf{x}_t)]$

if $t + t_T < \tau$

i) Choose $\mathbf{x}_{t+t_T} = \mathbf{x}'$ with prob. $p_{x',x_t} = \frac{-s_{x',x_t}}{N}$

ii) $t = t + t_T$

go to step 2

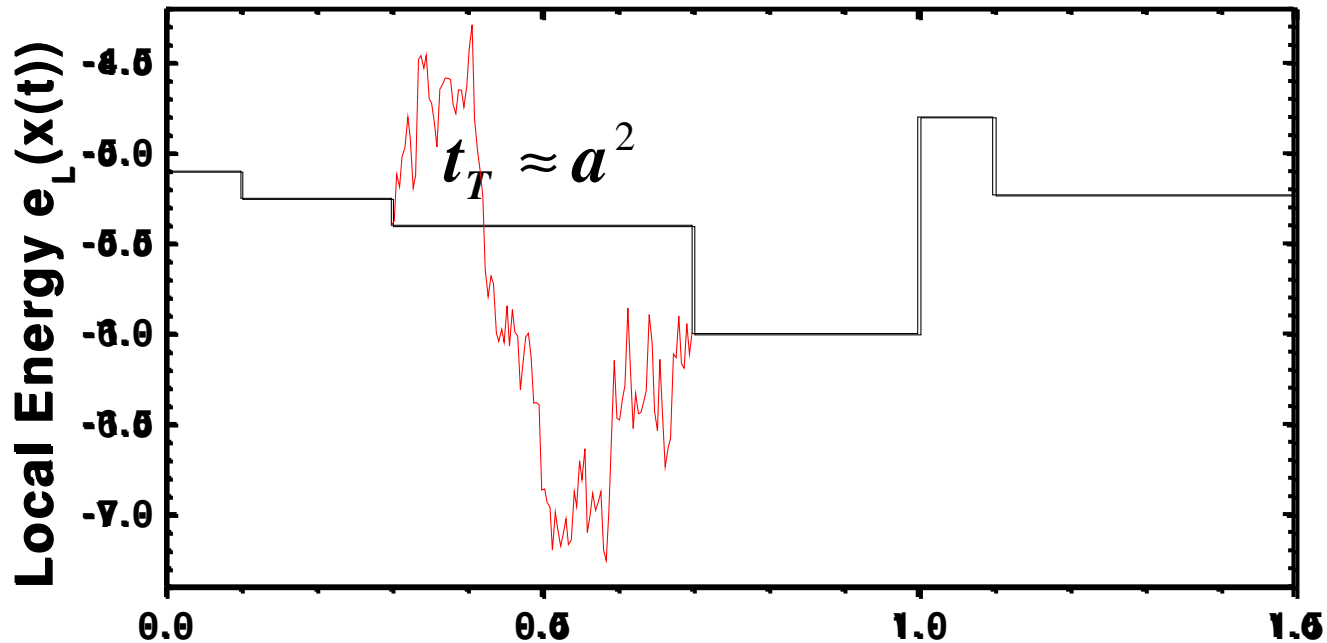
else

We have done !!!

endif

No error in τ

The picture of the DMC on a lattice



In the continuous limit $a \rightarrow 0$ τ

$\langle x' | e^{+\tau\Delta} | x \rangle \rightarrow$ Transition probability for a diffusion process.

From that the name : Diffusion Monte Carlo.

Case II (sign problem, some $s_{x',x} > 0$)

$$s_{x',x} = \begin{cases} 0 & \text{(diagonals do not matter) } x' = x \\ \psi_g(x') \mathbf{H}_{x',x} / \psi_g(x) & x' \neq x \end{cases}$$

$$\mathbf{H}^{eff}_{x',x} = \begin{cases} \mathbf{H}_{x',x} & \text{for } s_{x',x} < 0 \\ 0 & \text{for } s_{x',x} > 0 \\ \mathbf{H}_{x,x} + \sum_{x''(\neq x)} s_{x'',x} > 0 & \text{for } x' = x \end{cases}$$

Fixed node approximation

The ground state ψ_{\cdot}^{eff} of H^{eff} has a better energy of ψ_g :

$$I) E_{FN} = \frac{\langle \psi_{\cdot}^{eff} | H | \psi_{\cdot}^{eff} \rangle}{\langle \psi_{\cdot}^{eff} | \psi_{\cdot}^{eff} \rangle} \leq \frac{\langle \psi_g | H | \psi_g \rangle}{\langle \psi_g | \psi_g \rangle}$$

II) $\psi_g(\mathbf{x})\psi_{\cdot}^{eff}(\mathbf{x}) > \diamond$ That's why Fixed nodes.

III) in the continuous limit $a \rightarrow \diamond$ $\psi_{\cdot}^{eff}(\mathbf{x})$ has the lowest possible energy compatible with II

Sampling the probability :

$$\Pi(\mathbf{x}) \propto \psi_G(\mathbf{x}) \langle \mathbf{x} | e^{-H^{eff} \tau} | \psi_G \rangle \rightarrow \psi_G(\mathbf{x}) e^{-E_{MA} \tau} \psi_{FN}(\mathbf{x})$$

Markov chain : walker $(\mathbf{x}_t, \mathbf{w}_t) \approx \mathbf{w}_t | \mathbf{x}_t \rangle$

$$1) \quad t = 0 : \mathbf{x}_0 = | \mathbf{x} \rangle \quad \mathbf{w}_0 = 1$$

$$2) \quad t_T = \text{Min}(-\ln z / V^-(\mathbf{x}_t), \tau - t)$$

$$3) \quad \mathbf{w}_{t+t_T} = \mathbf{w}_t \exp[-t_T e_L(\mathbf{x}_t)]$$

if $t + t_T < \tau$

$$i) \text{ for } \mathbf{x}' \neq \mathbf{x}_t \quad p_{\mathbf{x}', \mathbf{x}_t} = \frac{-H^-_{\mathbf{x}', \mathbf{x}_t} \psi_G(\mathbf{x}') / \psi_G(\mathbf{x}_t)}{V^-(\mathbf{x}_t)} > \bullet$$

$$ii) \text{ Choose } \mathbf{x}_{t+t_T} = \mathbf{x}' \text{ with prob. } p_{\mathbf{x}', \mathbf{x}_t} \quad \left(\sum_{\mathbf{x}'} p_{\mathbf{x}', \mathbf{x}_t} = 1 \right)$$

$$iii) \quad t = t + t_T$$

go to step 2

else

We have done !!!

endif

Upper bound property, remind $H = H^{eff} - O$

The operator O can be small:

$$\text{Indeed } \langle \psi_G | O | x \rangle = \psi_g(x) V^+(x) - \sum_{x' | \pm s_{x',x} > 0} \psi_g(x') H_{x',x} = 0$$

$$\rightarrow E_{MA} = \frac{\langle \psi_g | H^{eff} | \psi_g^{eff} \rangle}{\langle \psi_g | \psi_g^{eff} \rangle} = \frac{\langle \psi_g^{eff} | H^{eff} | \psi_g^{eff} \rangle}{\langle \psi_g^{eff} | \psi_g^{eff} \rangle} \leq \frac{\langle \psi_g | H^{eff} | \psi_g \rangle}{\langle \psi_g | \psi_g \rangle} = \frac{\langle \psi_g | H | \psi_g \rangle}{\langle \psi_g | \psi_g \rangle} = E_{VMC}$$

O is non negative definite, H. T. Haaf et al. PRB '91, then :

$$\rightarrow E_{FN} = \frac{\langle \psi_g^{eff} | H | \psi_g^{eff} \rangle}{\langle \psi_g^{eff} | \psi_g^{eff} \rangle} = \frac{\langle \psi_g^{eff} | H^{eff} - O | \psi_g^{eff} \rangle}{\langle \psi_g^{eff} | \psi_g^{eff} \rangle} \leq \frac{\langle \psi_g^{eff} | H^{eff} | \psi_g^{eff} \rangle}{\langle \psi_g^{eff} | \psi_g^{eff} \rangle} = E_{MA}$$

$$E_{MA} = \sum_x \Pi(x) e_L(x)$$

Computable

Why O is positive definite?
 Just very simple algebra:

$$\langle \psi | O | \psi \rangle = \sum_{x, x' | s_{x, x'} > 0} s_{x, x'} \left[\psi(x) / \psi_g(x) - \psi(x') / \psi_g(x') \right]^2 \geq 0$$

Remind : $s_{x, x'} = \psi_g(x') H_{x', x} \psi_g(x) \quad x' \neq x$

All this approach can be generalized and extended to Hamiltonian defined in the continuous space

All we have used is that for **a given x**

the number of matrix elements :

$\langle x' | H | x \rangle$ can be evaluated, i.e. is **finite** $\sim \# \text{el.}$

Can we put the physical Hamiltonian on a lattice?

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

Namely to find a minimum length cutoff "a" such that:

$$H^a \rightarrow H \text{ for } a \rightarrow 0 \text{ and}$$

$$H^a \text{ for reasonable } a \sim a.u. \text{ is "close" to } H$$

Motivations:

- The exact Green function can be sampled for lattice hamiltonians:
no approximations, no time discretization.
- **No restriction to non local operators appearing in H.**

Non local pseudopotentials

□ For heavy atoms pseudopotentials are **necessary** to reduce the computational time

□ Usually they are **non local** $V_P(\mathbf{r}_i - \mathbf{R}_j) = \sum_l v_l(\mathbf{r}_{i,j}) \sum_m |lm\rangle\langle lm|$

In QMC angular momentum projection is calculated by using a **quadrature rule** for the integration

S. Fahy, X. W. Wang and Steven G. Louie, PRB **42**, 3503 (1990)



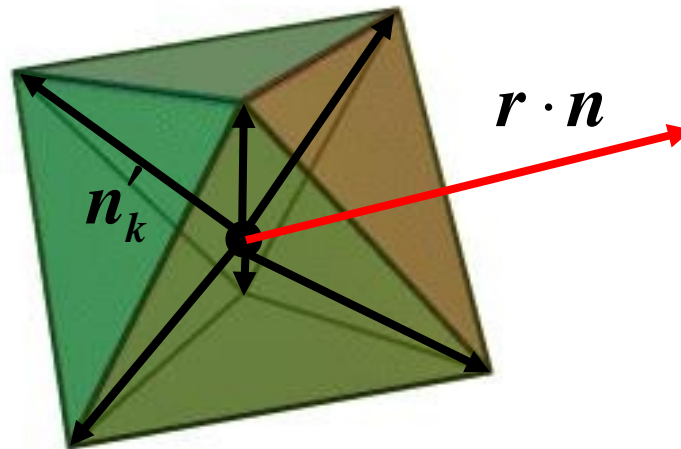
Discretization of the projection →
Lattice Hamiltonian term

The pseudo potential acts on single particle wavefunctions with a reference centered on the pseudoatom we have:

$$V_P = v_{loc}(\mathbf{r}) + \sum_l V^l$$

$$V^l \psi(\mathbf{r}, \vec{\mathbf{n}}) = v^l(\mathbf{r}) \int d\vec{\mathbf{n}}' \sum_{m=-l}^l Y_{lm}(\vec{\mathbf{n}}) Y_{l,-m}(\vec{\mathbf{n}}') \psi(\mathbf{r}, \vec{\mathbf{n}}')$$

$$= \frac{4\pi}{l+1} \int d\vec{\mathbf{n}}' P_l(\vec{\mathbf{n}} \cdot \vec{\mathbf{n}}') \psi(\mathbf{r}, \vec{\mathbf{n}}') \cong \frac{4\pi}{l+1} \sum_{\vec{\mathbf{n}}'_k} P_l(\vec{\mathbf{n}} \cdot \vec{\mathbf{n}}'_k) \psi(\mathbf{r}, \vec{\mathbf{n}}'_k)$$



Directions are randomized and discretized :

6 "lattice" points are usually enough great idea !!! Borrowed

Locality approximation

Locality approximation in DMC
Mitas et al. J. Chem. Phys. **95**, 3467 (1991)

Effective Hamiltonian H^{LA} containing the localized potential:

$$V^{LA}(\mathbf{x}) = \frac{\sum_{x'} V_{x',x}^P \psi_g(\mathbf{x}')}{\psi_g(\mathbf{x})}$$

- the mixed estimate is **not variational** since

$$\frac{\langle \psi_g | \mathbf{H} | \psi_\tau \rangle}{\langle \psi_g | \psi_\tau \rangle} \neq \frac{\langle \psi_\tau | \mathbf{H} | \psi_\tau \rangle}{\langle \psi_\tau | \psi_\tau \rangle} \quad \psi_\tau = \text{GS of } \mathbf{H}^{LA} \text{ for } \tau \rightarrow 0$$
$$\mathbf{H}^{LA} = -\Delta + V + V^{LA}$$

- (locality is exact only if ψ_g is exact)
- $\psi_g(\mathbf{x}) = 0 \rightarrow$ Divergences in V^{LA}

Locality approximation drawbacks

- **non variational** results:

The energy may be good but we do not really know if it corresponds to a good wavefunction close to the ground state.

- **simulations less stable**

when pseudo are included divergencies appear in the localized potential close

to the nodal surface: $\psi_g(\mathbf{x}) = 0$

Within Lattice Regularized Hamiltonians
we can avoid the locality approximation!

But what about the Laplacian?

Lattice regularization

Kinetic term: discretization of the laplacian

Laplacian with finite differences in the 1D case:

$$\frac{d^2}{dx^2} f(x) = \frac{f(x+a) + f(x-a) - 2f(x)}{a^2} + O(a^2)$$

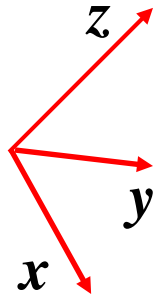
3 dimensional case:

$$\Delta \rightarrow \Delta^a = \frac{1}{a^2} \sum_{v=x,y,z} [f(\vec{r} + a\vec{v}) + f(\vec{r} - a\vec{v}) - 2f(\vec{r})]$$

hopping term $t \rightarrow 1/a^2$ where a is the discretization mesh

The simplification: the simple LRDMC

In order to sample the continuous space we use randomized reference frames for the three orthogonal directions.



This is exactly the same trick to compute angular integrals with pseudopotentials and allows to sample the continuous space in a very simple and efficient way.

Use of randomized directions (no real lattice) necessary for Coulomb potential: for a real lattice there is a **finite** probability that two electrons occupy the same site. We simply do not know what to do in this case (yet).

Further simplification?

Previous approach: Lattice discretization with two meshes

Double mesh for the discretized laplacian

$$\Delta \Psi(\mathbf{x}) \approx p \Delta_a \Psi(\mathbf{x}) + (1-p) \Delta_{a'} \Psi(\mathbf{x}) + \mathcal{O}(a^2, a'^2)$$

a finest mesh, a' largest

p is a function which sets the relative weight of the two meshes.

It can depend on the distance from the nucleus:

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

Our choice:
$$p(r) = \frac{1}{1 + \gamma r^2} \quad \gamma = Z^2 / 4$$

Separation of core and valence dynamics for heavy nuclei
by means of **two hopping terms in the kinetic part**

Moreover, if a' is not a multiple of a , the random walk can sample the space more densely!

$$a' / a = \sqrt{Z^2 / 4 + 1}$$

Lattice regularization (main idea): how to work with $a \sim 1$ (a.u.)?

Definition of the lattice regularized Hamiltonian

$$H_a = -\Delta_a + V_a = -\Delta + V + \mathcal{O}(a^2)$$

➤ For a better continuous limit: **for $a \rightarrow 0$, $H_a \rightarrow H$ choose:**

➤ **Local energy of $H_a =$ local energy of H**

$$\longrightarrow V^a = V(\mathbf{x}) + \frac{(\Delta^a - \Delta)\psi_g(\mathbf{x})}{\psi_g(\mathbf{x})}$$

$$= V(\mathbf{x}) + \mathcal{O}(a^2)$$

Much faster convergence in the lattice space a !

M. Casula, C. Filippi, S. Sorella, PRL **95**, 100201 (2005)

Why this is a much better choice?

For any $a > 0$ we compute the ground state energy :

E_a of $H^a = H + a^2 \Delta H$ with corresponding GS $|\psi_a\rangle$

with $\Delta H |\psi_g\rangle = 0$ (I)

coming from the LRDMC condition :

$$\langle x | H^a | \psi_g \rangle = \langle x | H | \psi_g \rangle \quad \text{for all } x$$

Then by simple perturbation theory :

$$E_a = E_0 + a^2 \langle \psi_0 | \Delta H | \psi_0 \rangle + \dots$$

But using (I): $\langle \psi_0 | \Delta H | \psi_0 \rangle = \langle \psi_0 - \psi_g | \Delta H | \psi_0 - \psi_g \rangle = \mathcal{O}(|\psi_0 - \psi_g|^2)$

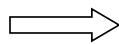
Thus LRDMC error $|E_a - E_0| = \mathcal{O}(a^2 |\psi_0 - \psi_g|^2)$

DMC vs LRDMC

extrapolation properties

DMC	LRDMC
Trotter approximation	For each a well defined Hamiltonian
Efficiency $\sim 1/\tau$	Efficiency $\sim 1/a^2$
Error (my guess) $\tau \psi_g - \psi $	Error $a^2 \psi_g - \psi_0 ^2$

$$\tau \approx a^2$$



Same Error with same efficiency
but different prefactor...

But there is a subtle point....

For fermions there exists the nodal surface

$$\psi_g(\mathbf{x}) = 0$$

Let's look back to the potential:

$$V^a = V(\mathbf{x}) + \frac{(\Delta^a - \Delta)\psi_g(\mathbf{x})}{\psi_g(\mathbf{x})} = e_L(\mathbf{x}) - \frac{\Delta^a \psi_g(\mathbf{x})}{\psi_g(\mathbf{x})}$$

Namely V^a can be $-\infty$ on the nodal surface

But $|\Delta^a| < \frac{12\#el}{a^2} \rightarrow$ GS energy of $H^a = -\Delta^a + V^a = -\infty$

H^a was not defined correctly in the original LRDMC
 only H^a_{eff} the fixed node was OK.

$$V^a = V(\mathbf{x}) + \frac{(\Delta^a - \Delta)\psi_g(\mathbf{x})}{\psi_g(\mathbf{x})} = e_L(\mathbf{x}) - \frac{\Delta^a\psi_g(\mathbf{x})}{\psi_g(\mathbf{x})}$$

By satisfying all the cusp conditions $e_L(\mathbf{x})$

can be finite for el-el and el-ion distance $\rightarrow 0$

$$V^a = \begin{cases} \text{Max} \left[V(\mathbf{x}), e_L(\mathbf{x}) - \frac{\Delta^a\psi_g(\mathbf{x})}{\psi_g(\mathbf{x})} \right] & \text{if } s_{x,x'} > \bullet \text{ for some } \mathbf{x}' \\ e_L(\mathbf{x}) - \frac{\Delta^a\psi_g(\mathbf{x})}{\psi_g(\mathbf{x})} & \text{otherwise} \end{cases}$$

N.B. No ad hoc parameter has been used
 in this simple LRDMC.

Estimation of the error due to the nodal surface

The nodal surface has area S .

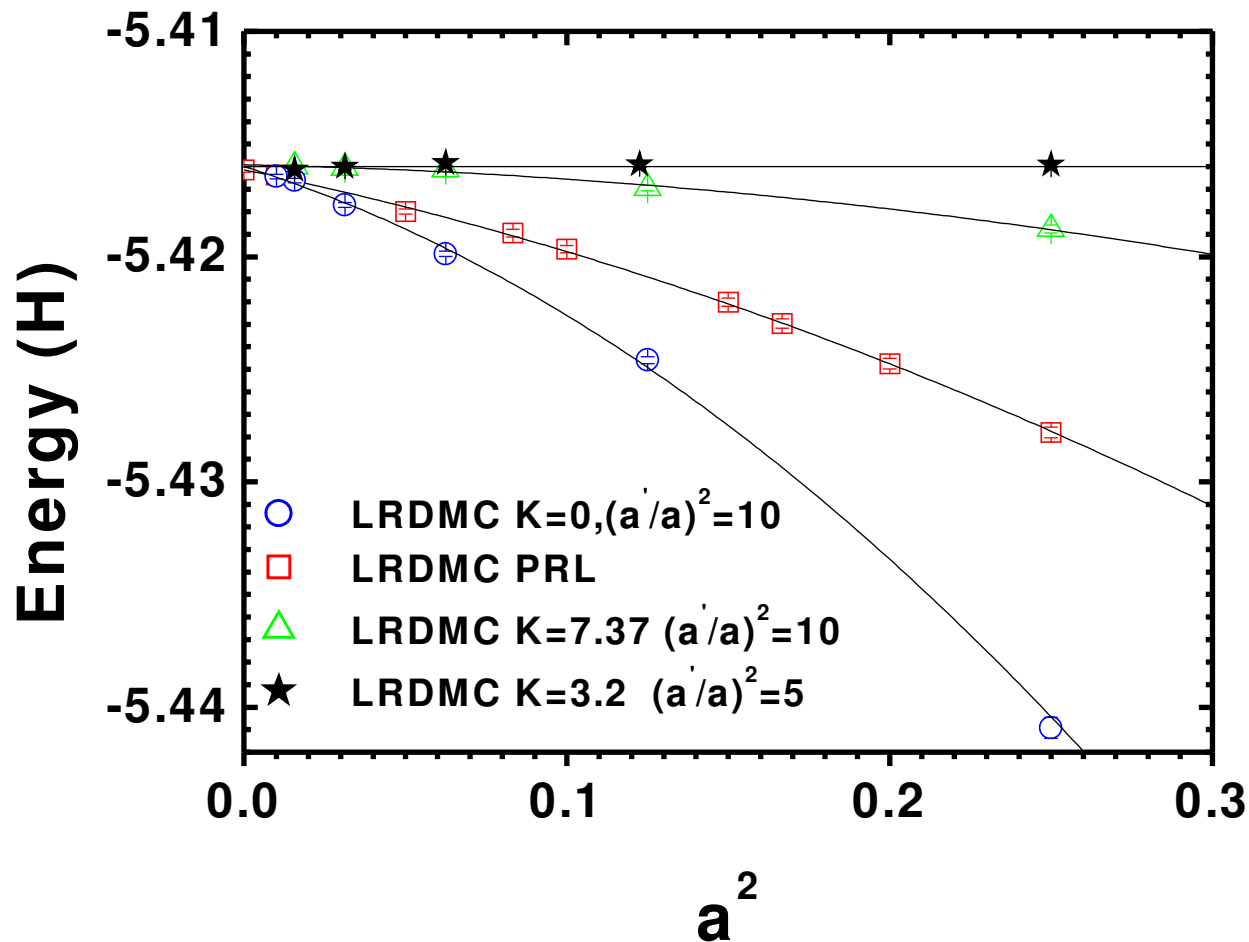
The volume around the nodal region $\sim a S$

In this region the wavefunction vanishes $\sim a$

if Fixed node approximation is employed.

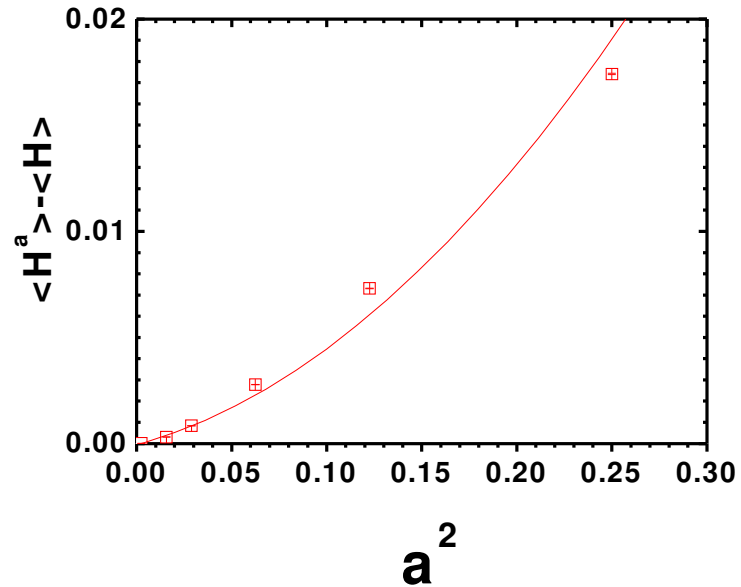
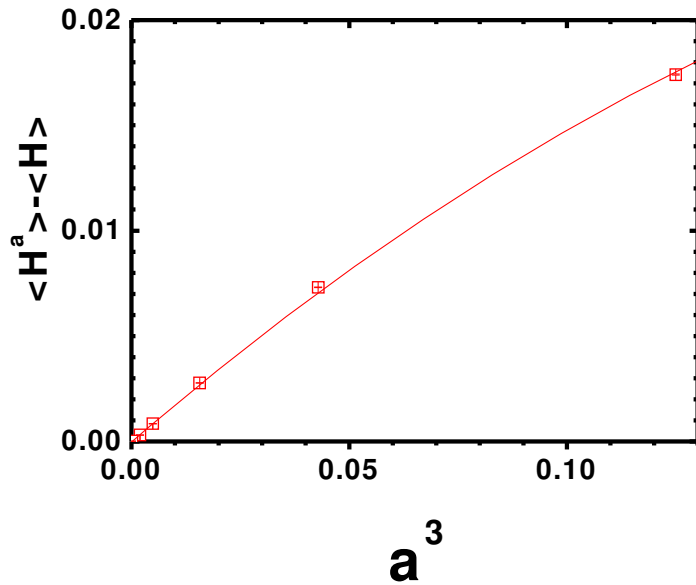
$$\text{Thus } |\Delta E_a|_{NODAL} \approx a S \langle \psi^2(\mathbf{x}) \rangle \approx a^3$$

Convergence for $C \eta_a = 1 + K a^2$



S. Sorella, M. Casula, D. Rocca, J. Chem. Phys. **127**, 014105 (2007)

Nodal error contr. in LRDMC $\sim a^3$



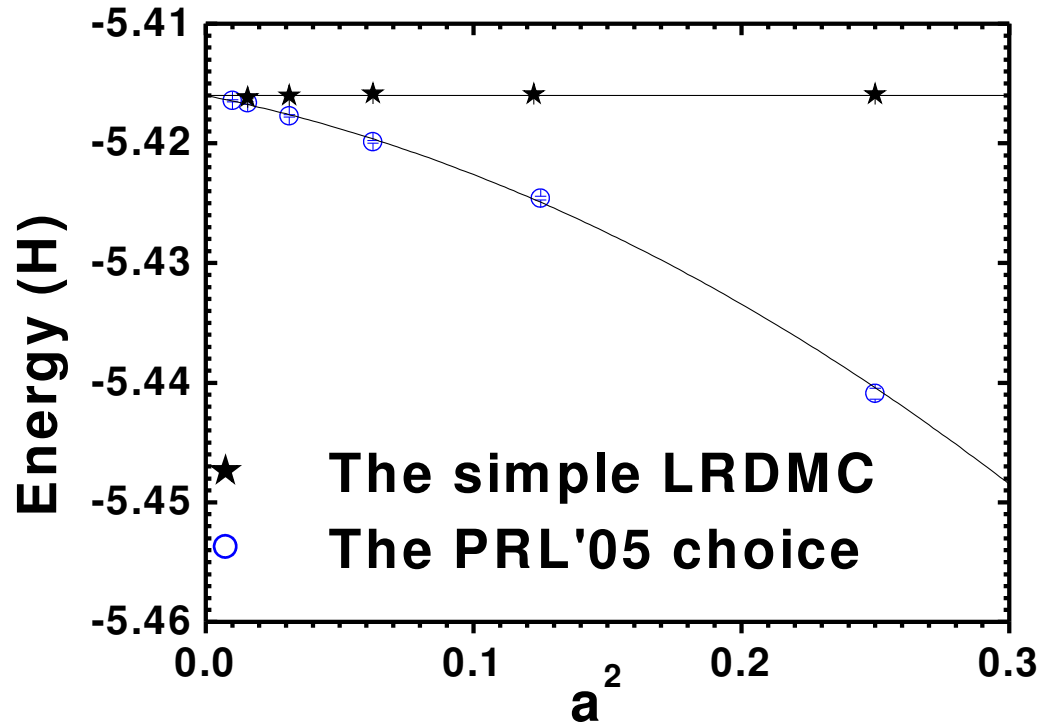
$$\langle H^a \rangle = \frac{\langle \psi_g | H^a | \psi_a \rangle}{\langle \psi_g | \psi_a \rangle}$$

$$\langle H \rangle = \frac{\langle \psi_g | H | \psi_a \rangle}{\langle \psi_g | \psi_a \rangle}$$

$$H^a | \psi_a \rangle = \langle H^a \rangle | \psi_a \rangle$$

The new approach

Carbon pseudoatom



The problem was the a^3 term coming from the nodal surface. It was antivariational because $V(\mathbf{x}) \rightarrow -\infty$.

What about locality approximation?

$$V^{LA}(\mathbf{x}) = \frac{\sum_{\mathbf{x}'} V_{\mathbf{x}', \mathbf{x}}^P \psi_g(\mathbf{x}')}{\psi_g(\mathbf{x})}$$

Again $V^{LA}(\mathbf{x}_0)$ can be $-\infty$ when $\psi_g(\mathbf{x}_0) \rightarrow 0$

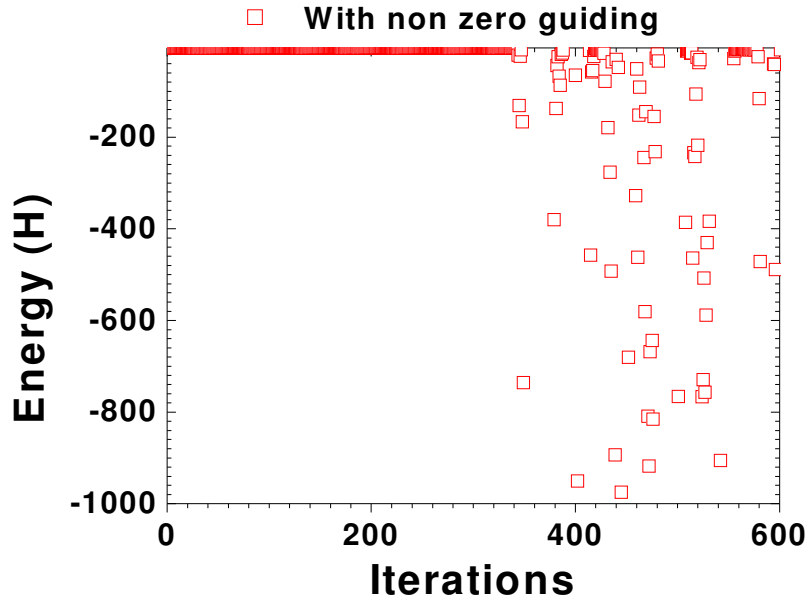
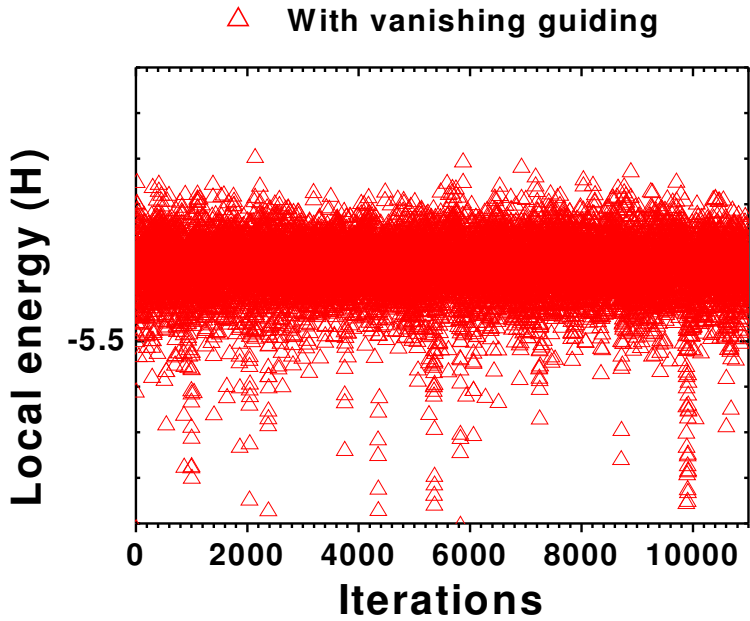
The locality approximation is simply **not defined** in LRDMC as:

$$H^a = -\Delta^a + V^a(\mathbf{x}) + V^{LA}(\mathbf{x})$$

$$E^a = V^{LA}(\mathbf{x}_0) = -\infty \quad \text{UNBOUNDED}$$

The problem of UNBOUNDED ground state energy was overlooked

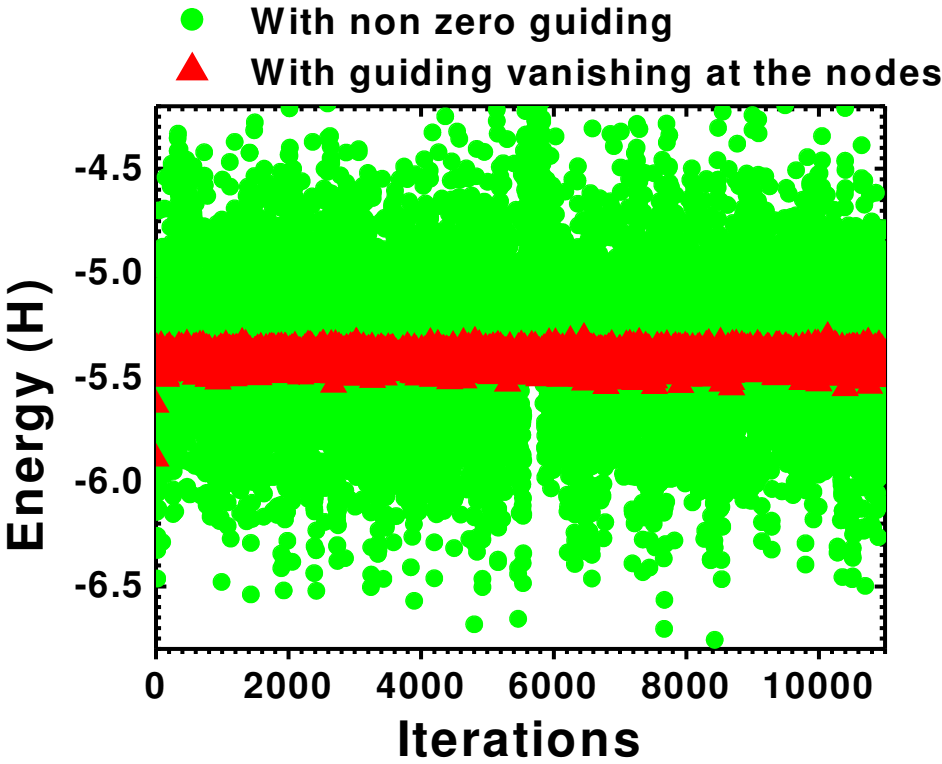
The exact LRDMC energy with locality approx. should be $-\infty$!!!



No big sign of instability seen



Instead without Locality everything is well defined within LRDMC



Summary

The LRDMC $a \rightarrow 0$ is well defined with :

$$H^a = -\Delta^a + V^a(\mathbf{x})$$

if $V^a(\mathbf{x})$ is bounded from below.

This is possible if:

- 3) The guiding function satisfies the cusp conditions.
- 4) No type of locality approximation is employed or use a “bosonized” guiding function that never vanishes for fermions with large $a \rightarrow 0$ error.

Standard DMC is based on the discretization in time
e.g. Trotter approximation.

Even in this formalism the problem of
infinitely negative potentials exists.

The Green function matrix :

$$\mathbf{G}_{x,x'} = \langle \mathbf{x}' | e^{-H\tau} | \mathbf{x} \rangle, \quad \mathbf{H} = -\Delta + V(\mathbf{x})$$

has bounded eigenvalues $< +\infty$ if \mathbf{H} makes sense
even when $V(\mathbf{x}_0) = -\infty$.

A naive discretization in time (Trotter) :

$$\mathbf{G}_{x,x'} = \langle \mathbf{x}' | e^{-V(\mathbf{x}')\tau/2} e^{+\Delta\tau/2} e^{-V(\mathbf{x})\tau/2} | \mathbf{x} \rangle$$
$$\rightarrow \mathbf{G}_{x_0,x_0} = e^{-V(x_0)\tau} \langle \mathbf{x}_0 | e^{+\Delta\tau/2} | \mathbf{x}_0 \rangle \rightarrow +\infty$$

I just note here that:

- 1) There is no proof in the literature that the Green function used with the locality approximation has a bounded spectrum once the discretization in time is employed.

By simple inspection it should be like that in the Umrigar '93 DMC because there is a cutoff

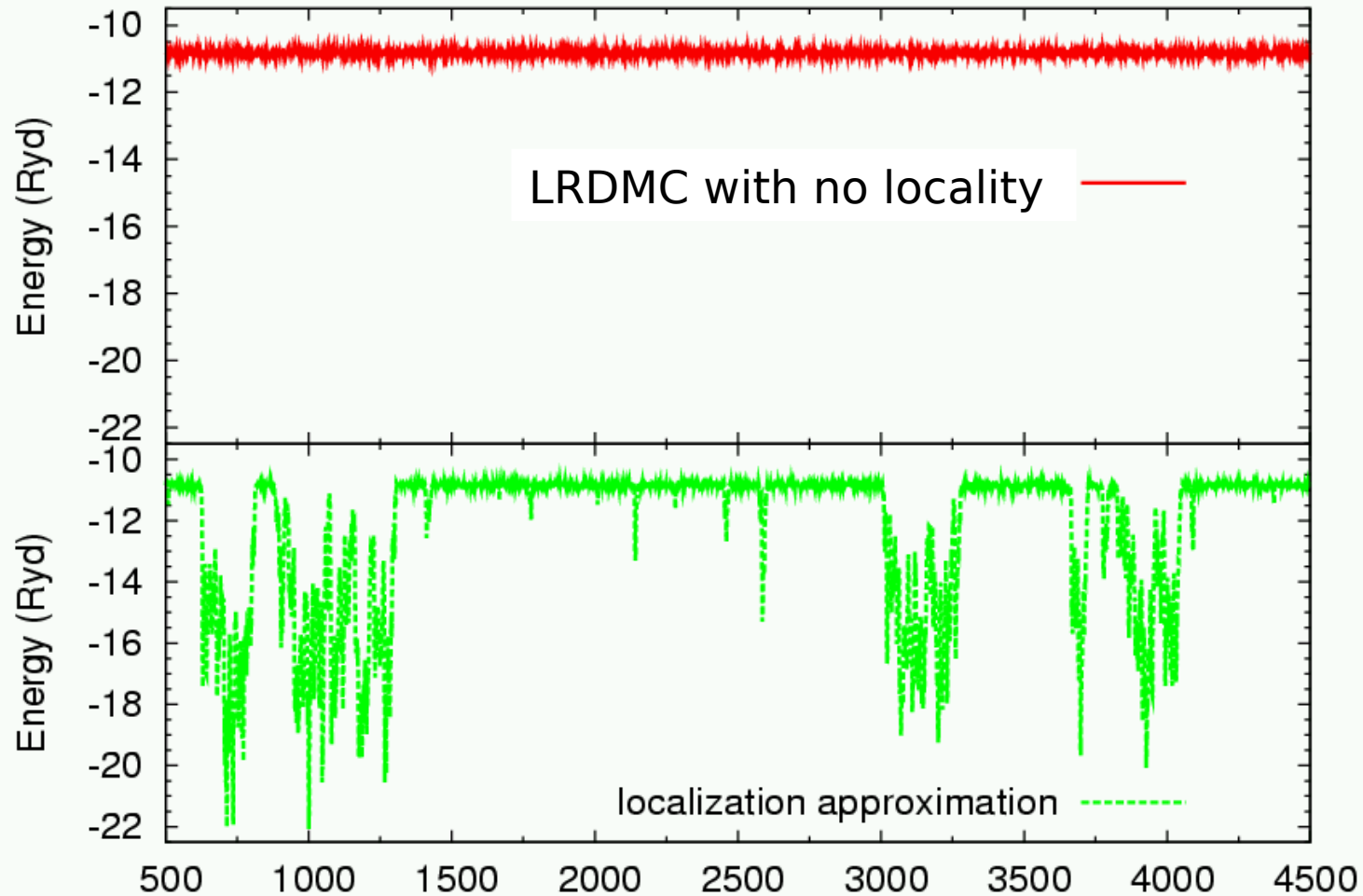
$$\approx \frac{1}{\sqrt{\tau}}$$

in the local energy

- 2) Even if the simulation is stable, this does not mean that the numbers make sense (see LRDMC example). So some care should be used before trusting a DMC energy if you do not know what the algorithm does to avoid divergences close to the nodal surface.

Nevertheless even Umrigar '93 may fail

Carbon pseudoatom (He core, SBK pseudo)



This is easily understood

$$V^{LA}(\mathbf{x}) = \frac{\sum_{\mathbf{x}'} V_{\mathbf{x}', \mathbf{x}}^P \psi_g(\mathbf{x}')}{\psi_g(\mathbf{x})}$$

$$V_P = v_{loc}(\mathbf{r}) + \sum_l V^l$$

$$V^l = v^l(\mathbf{r}) \int d\mathbf{n}' \sum_{m=-l}^l Y_{lm}(\vec{\mathbf{n}}) Y_{l,-m}(\vec{\mathbf{n}}')$$

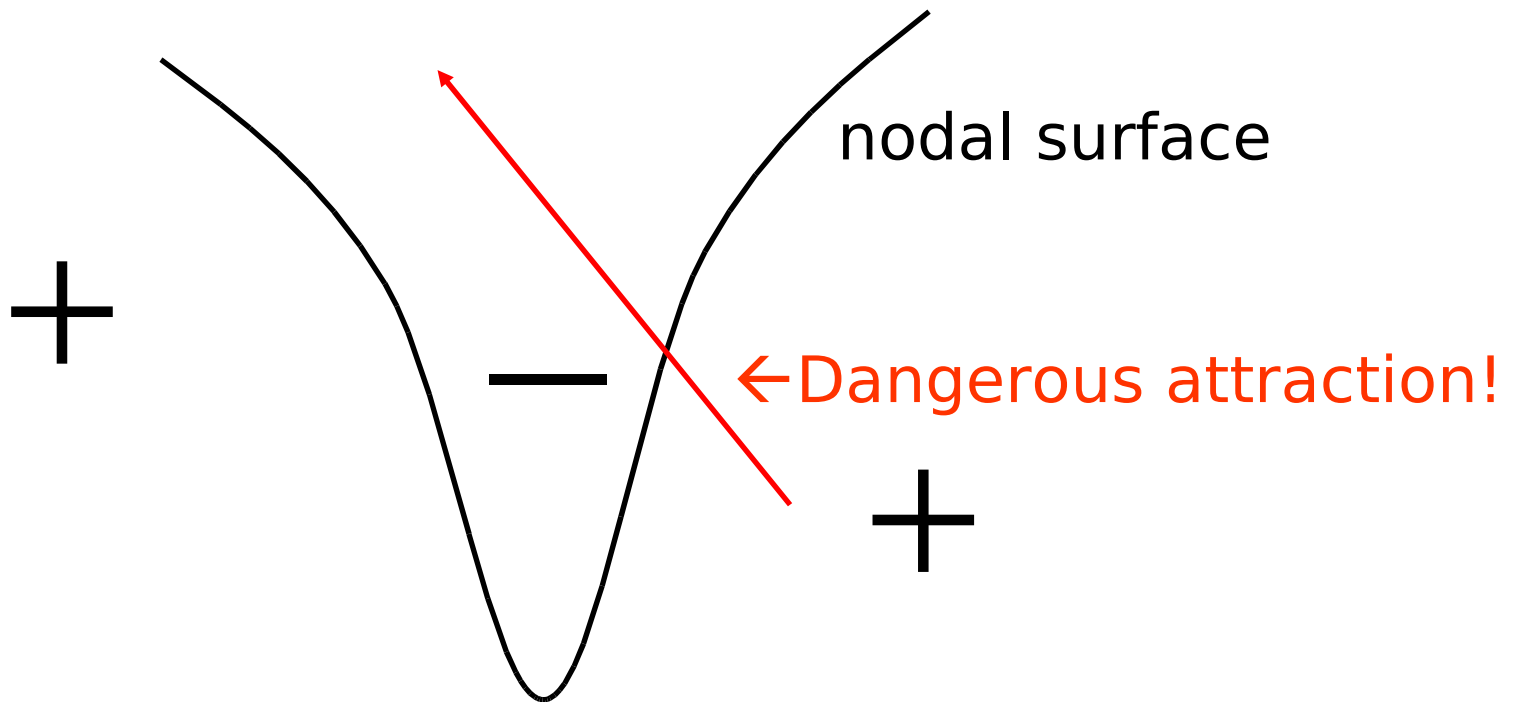
But the SBK $v^l(\mathbf{r}) \sim +1/r^l$

Thus close to the nodes $|\psi_g(\mathbf{x})| \sim |s|$ $V^{LA}(s) \sim \pm 1/|s|^3$

$$H^{LA} = -\Delta + V + V^{LA} \approx -\partial_s^2 - V/s^3$$

NO calculation needed the GS energy of H^{LA} is simply $-\infty$
See e.g. Landau, "collapse of a particle in an attractive centre"

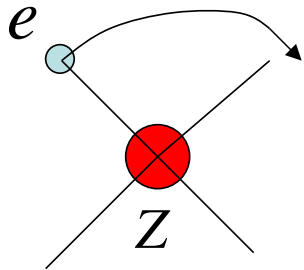
Stability



- locality approximation → large and negative attractive potential close to the nodal surface.
It works for **finite** non local pseudo but depends strongly on the way the algorithm allow (or not) the crossing of the nodal surface.
- LRDMC → works **always** as long as the non local pseudo has a bounded spectrum from below (no matter if it is infinitely positive).

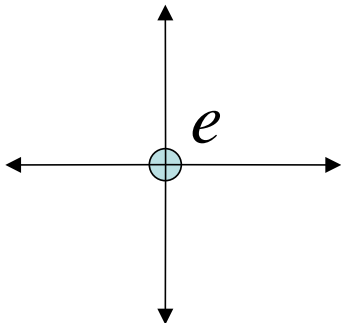
Error in the discretization

Discretized non local pseudopotential



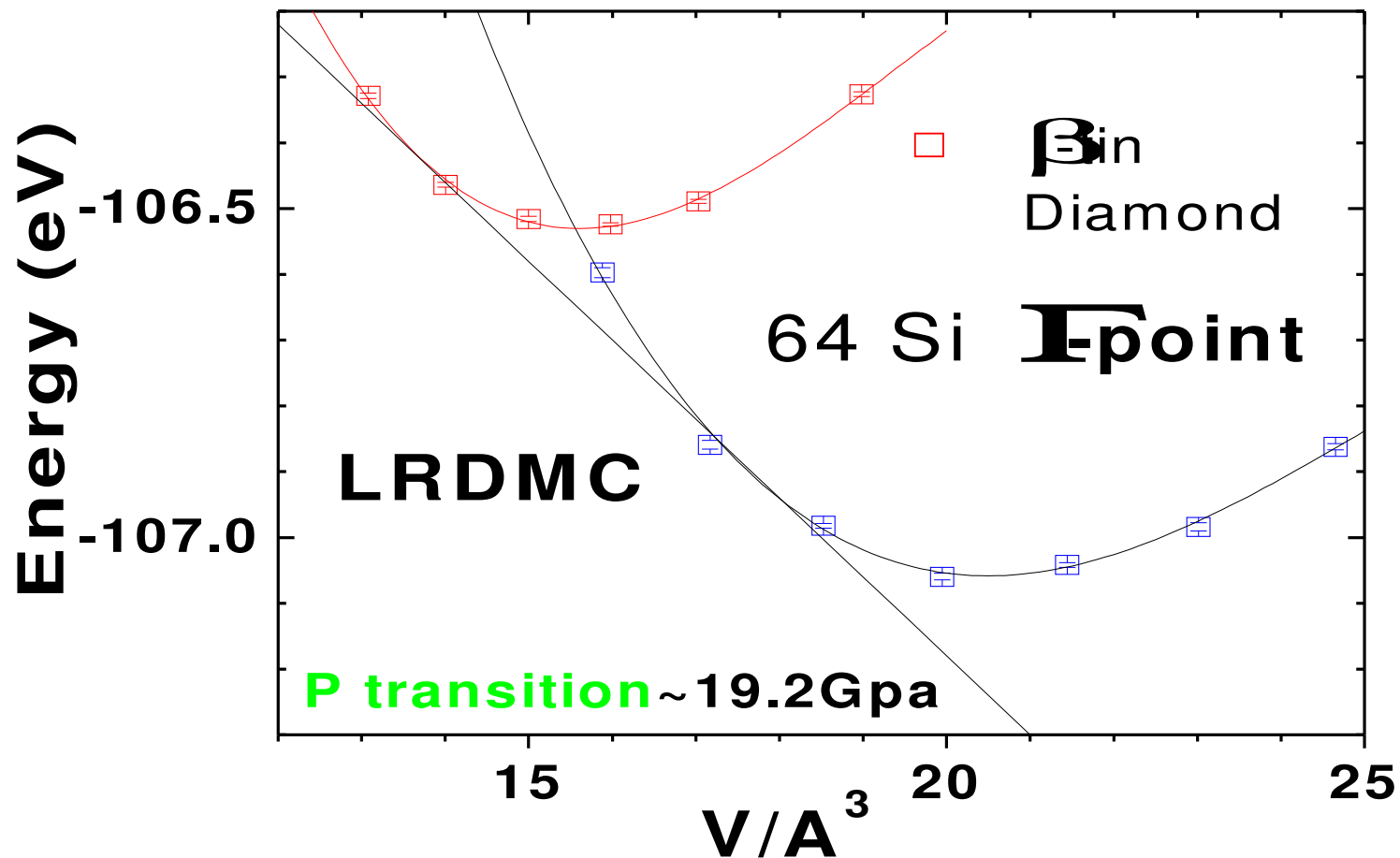
discretization error reduced
by the **randomization** of the quadrature mesh

Discretized Laplacian



discretization error reduced
by the introduction of a **double mesh**

The metal insulator transition within LRDMC



Relative efficiency for carbon atom with SBK pseudopotentials

$$\eta \propto \frac{1}{\sigma^2 T}$$

Variance σ^2
CPU time T

Z effective = 4

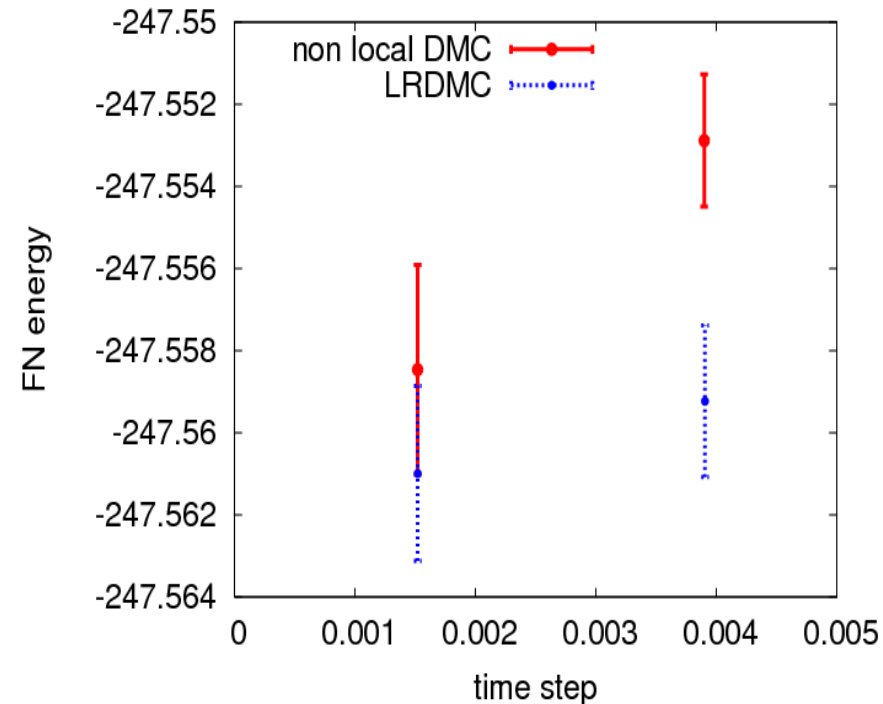
Time step	Non local DMC	LRDMC	Lattice space
0.0068	1.0	0.8	0.083
0.0120	1.5	1.3	0.11
0.0256	3.4	2.0	0.16

LRDMC is slightly less efficient than the non local DMC

Relative efficiency for **iron dimer** with Dolg pseudopotentials

Z effective = 16

Time step	Non local DMC	LRDMC	Lattice space
0.0008	1.0	5.2	0.0284
0.0015	1.8	7.0	0.0390
0.0039	5.2	15.0	0.0625



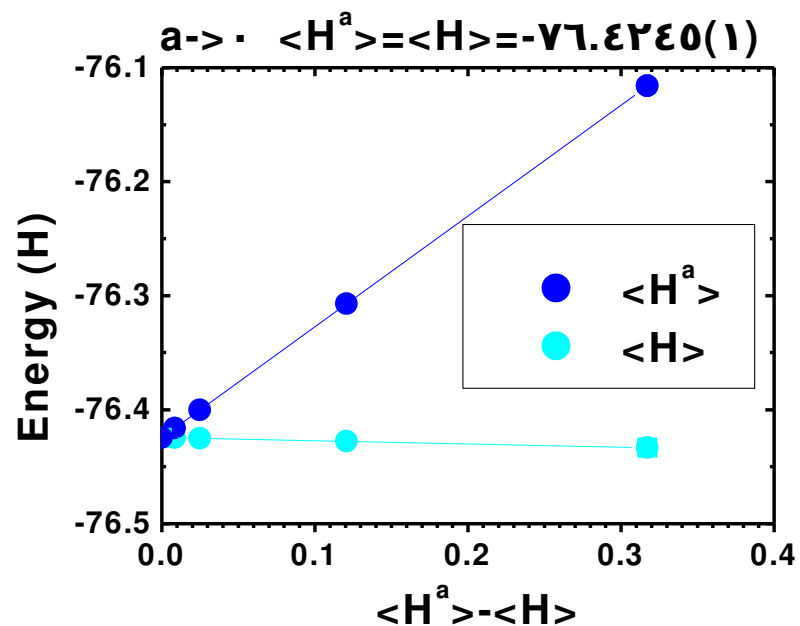
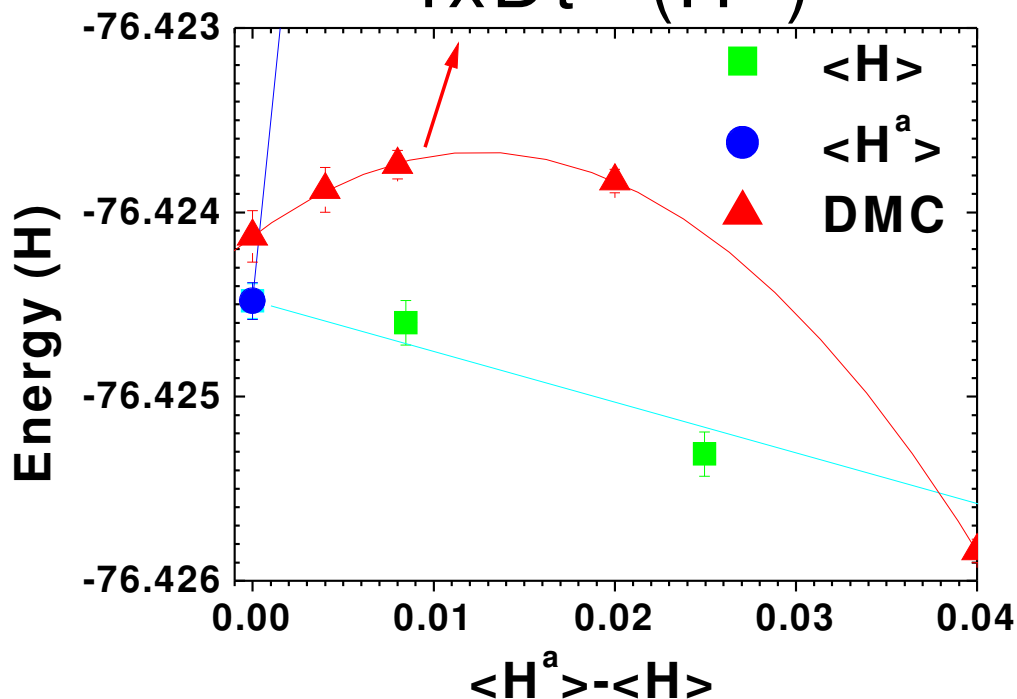
LRDMC is 3-5 times faster than the non local DMC

When stable, the standard DMC is 1.25 faster than the non local DMC

Water monomer (no pseudo)

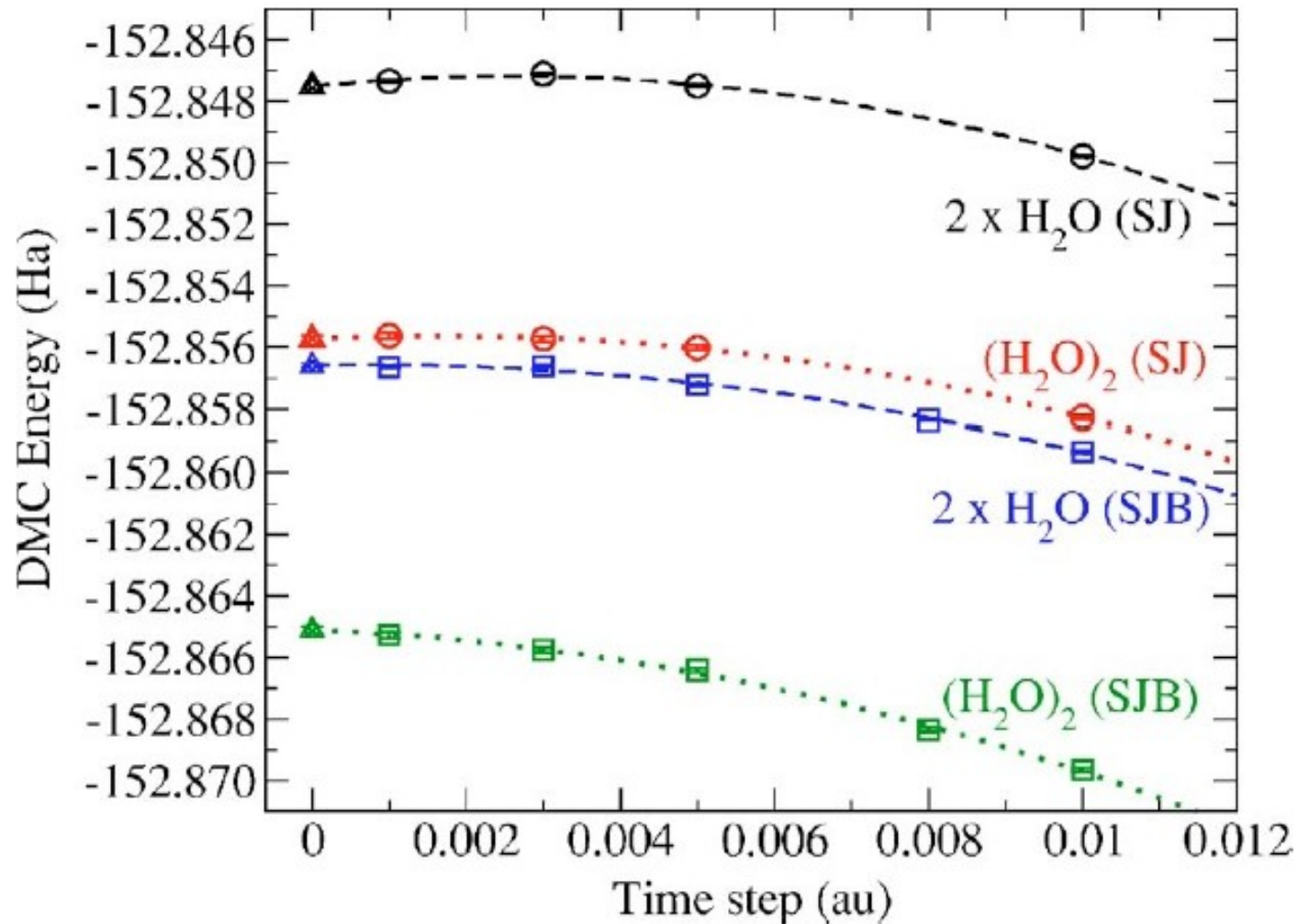
$$E_{DMC}(\Delta t) = E_{DMC} + a \Delta t + b (\Delta t)^{\gamma}$$

$4xDt \text{ (H}^{-1}\text{)}$



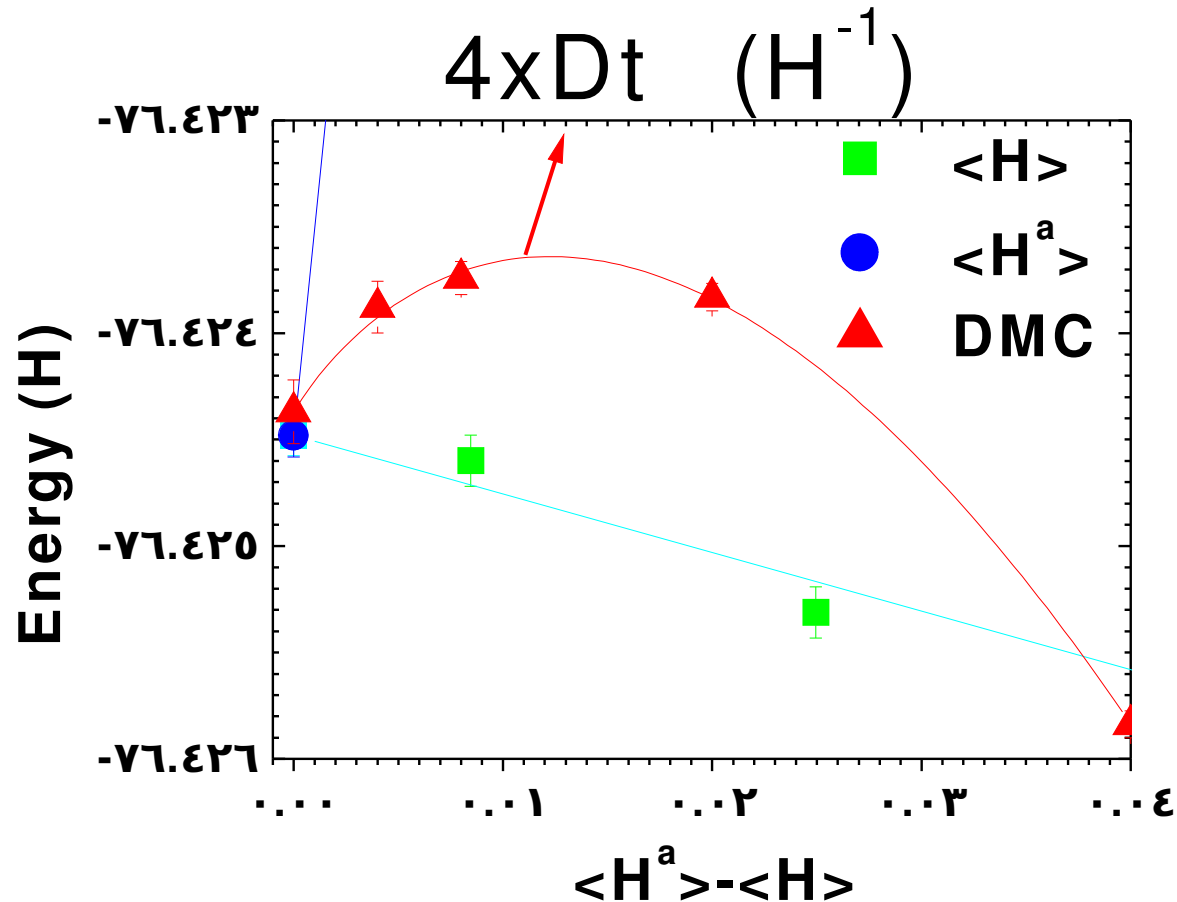
Similar non linear DMC extrapolation in a recent paper

(*) I. G. Gurtubay and R. Needs JCP, 127, 124306 (2007).



Water monomer

$$E_{DMC}(\Delta t) = E_{DMC} + a \Delta t + b (\Delta t)^{3/2}$$



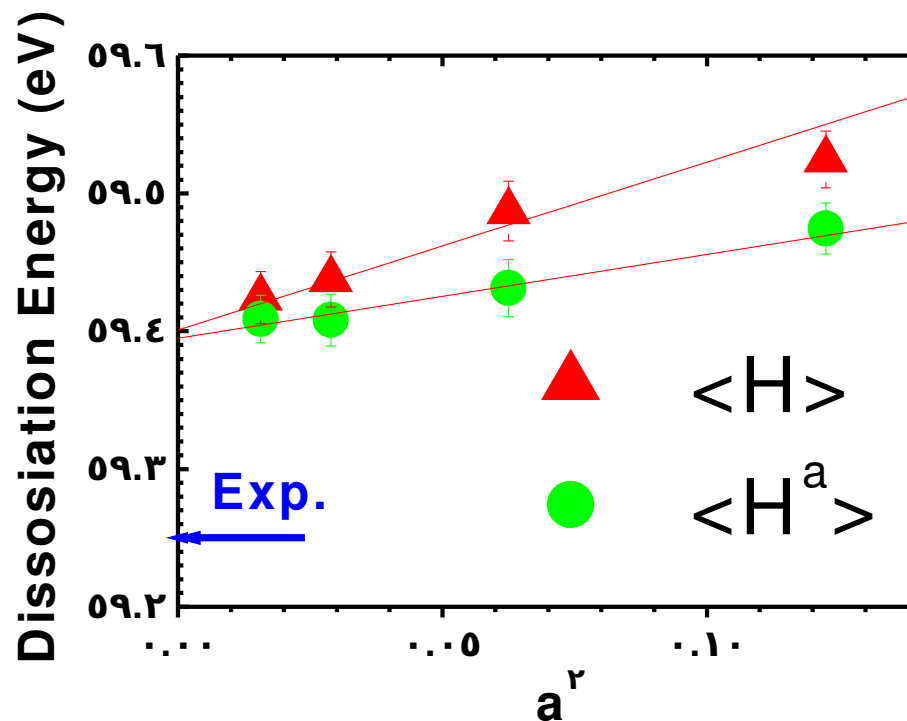
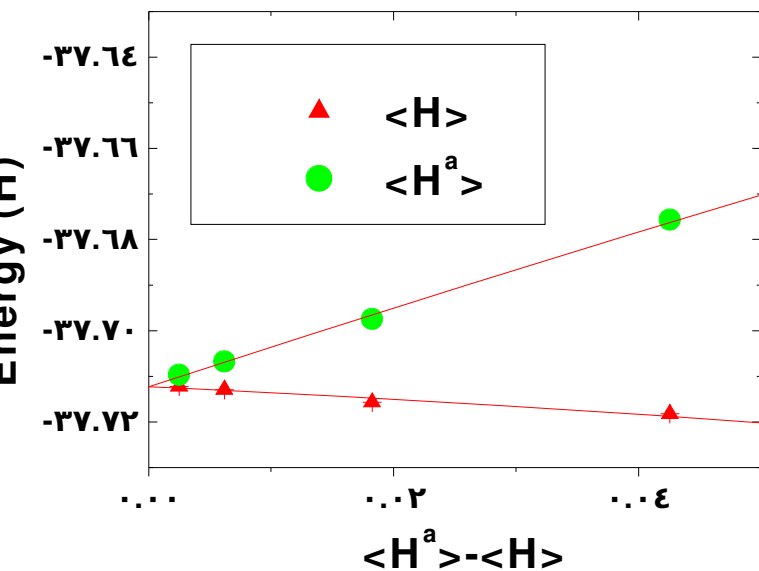
Water monomer

Wavefunction nodes	Optimization method	DMC energy (Hartree)
Hartree-Fock	GAUSSIAN No QMC	-76.4219(1)
Hartree-Fock	HF+J2+J3 (2-and 3-bodies)	-76.4230(2)
Hartree-Fock	DMC with few parameters(*)	-76.42376(5)
Hartree-Fock	HF+J2+J3+J4 (2-3-4 bodies)	-76.4245(1)
AGP (+)	AGP+J2+J3+J4	-76.4257(1)
HF+ Backflow	DMC with few par.(*)	-76.42830(5)
EXACT	CCSDT....	-76.438(1)

(*) I. G. Gurtubay and R. Needs JCP, 127, 124306 (2007).

(+) M. Casula et al. JCP, 121, ...(2004), with small basis -76.4175(4).

The benzene molecule



Non local DMC (Casula '06)

Three steps in the evolution of the walkers: the non local move is the new one introduced in the non local DMC scheme

$G_{DMC}(x \rightarrow y, \tau)$ **diffusion + drift (with rejection)**

$$w_{DMC}(x) = \exp \left[-\frac{1}{\tau} \int_0^\tau \left(\sum_y V^+(y, x) - \Lambda \right) dt \right] + V_{loc}(x)$$

$p(x \rightarrow y) \propto T^{FN}(y, x) / w_T(x)$ **non local move (heat bath)**

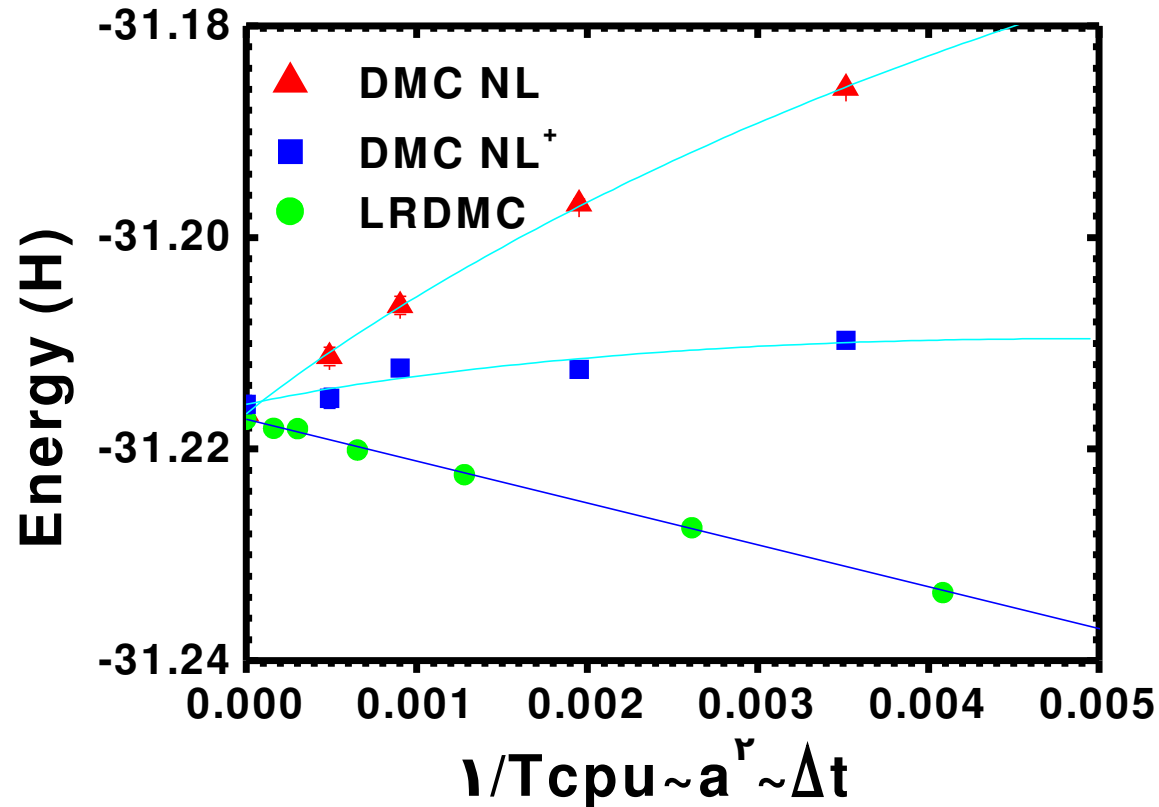
$$w_T(x) = \exp \left[-\frac{1}{\tau} \int_0^\tau \sum_y V^-(y, x) dt \right]$$

$$w(x) = e^{-\tau(E_L(x) - \Lambda)}$$

weight with local energy

(it includes the contribution from both diffusion and non local move)

8 Silicon diamond

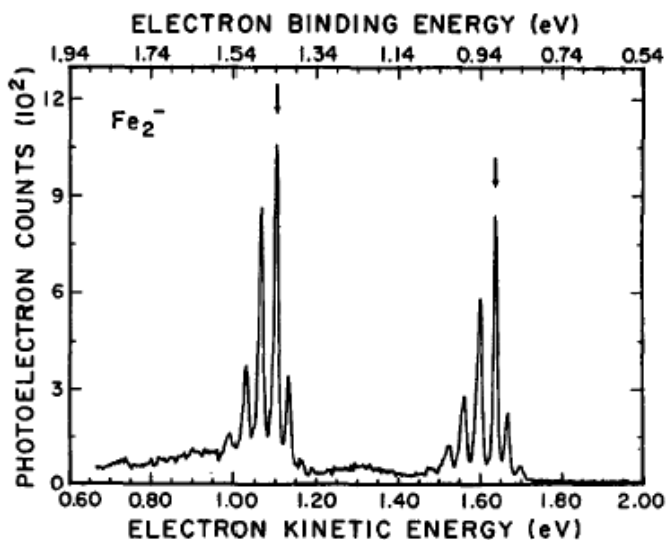


The CPU time to have a given error bar is proportional to T_{cpu} : the number of accepted single electron moves per unit time.

LRDMC: summary

- Simple and robust method to make reliable calculations.
- Simplification of the approach makes possible:
to have a very good extrapolation of the energy for $a \rightarrow 0$.
In all cases studied very accurate numbers even compared with the standard state of the art DMC methods.
- double mesh in the laplacian can help to decorrelate faster the electrons (core-valence separation). Not treated here.
- Locality approximation can be avoided and variational and more stable results can be obtained with QMC.
- It is simple to control the $a \rightarrow 0$ limit and compute energy Derivatives (e.g. forces) or energy differences.

Iron dimer



PHOTOELECTRON SPECTROSCOPY

GS anion: $(3d)^{13} (4s)^2 (4s^*)^2 \quad 8 \Sigma_u^-$

GS neutral: $(3d)^{13} (4s)^2 (4s^*)^1 \quad 9 \Sigma_g^-$

Leopold and Lineberger, J. Chem. Phys. 85, 51(1986)

previous NUMERICAL STUDIES on the neutral iron dimer

❑ DFT methods: $7 \Delta_u$

❑ more correlated methods (CC, MRCI, DFT+U): $9 \Sigma_g^-$

❑ electron affinity very hard to compute

Calculation details

Dolg pseudopotentials

neon core

spd non local components

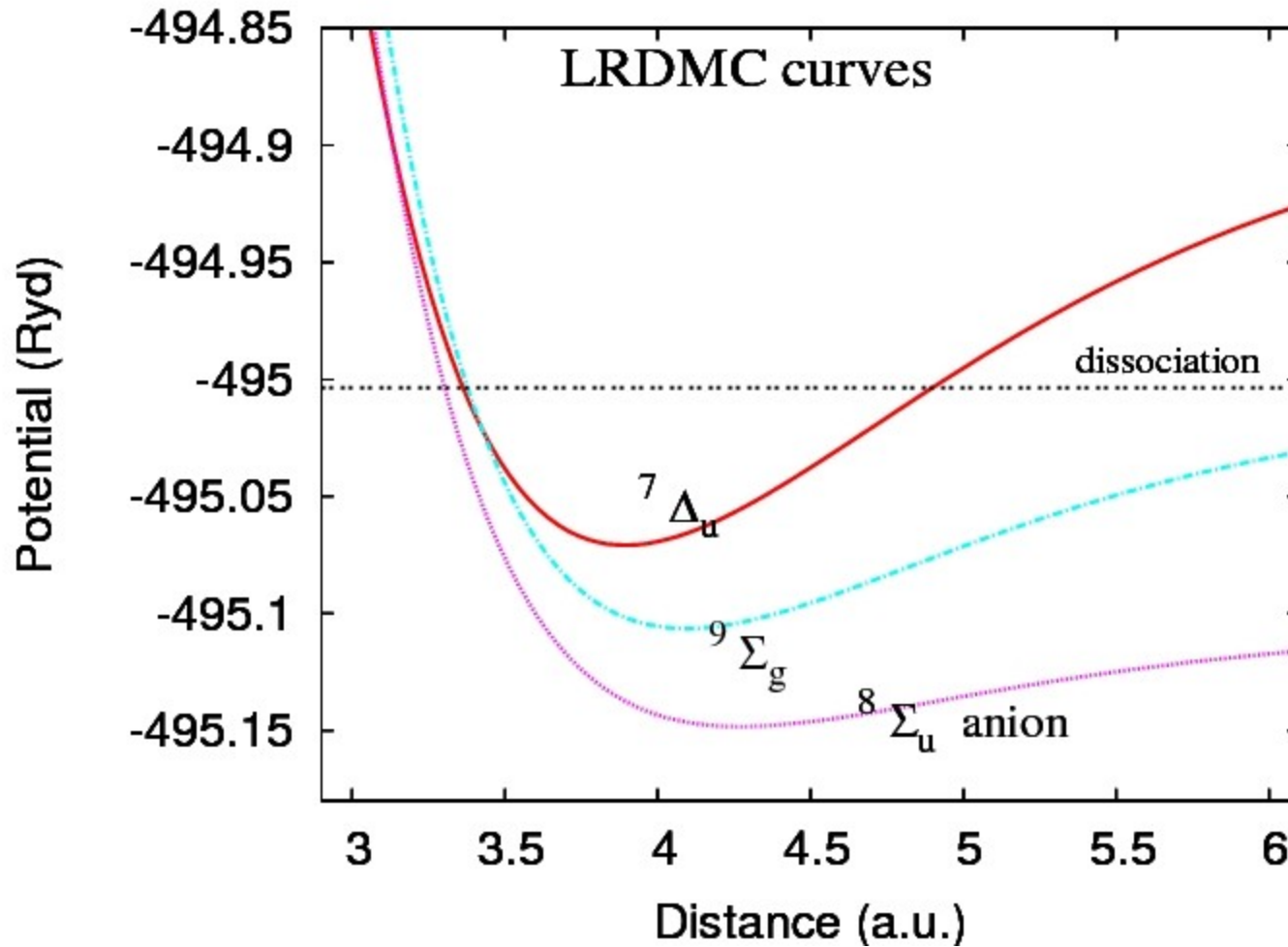
scalar relativistic corrections included

Gaussian basis set for JAGP wave function

(8s5p6d)/[2s1p1d] contracted for AGP

Total independent parameters: 227

Dispersion curves



Neutral ground state

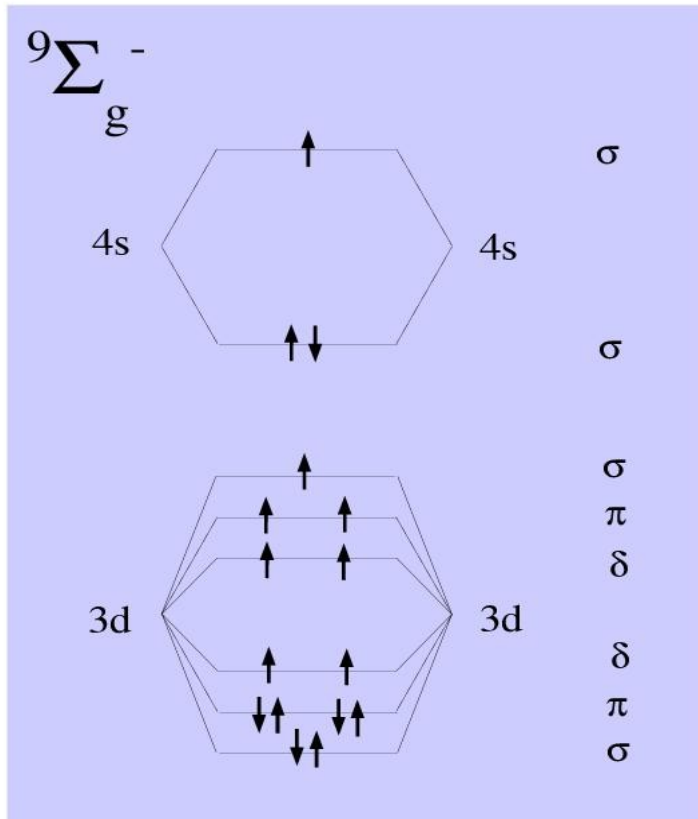
LRDMC gives for neutral dimer

$${}^9\Sigma_g^-$$

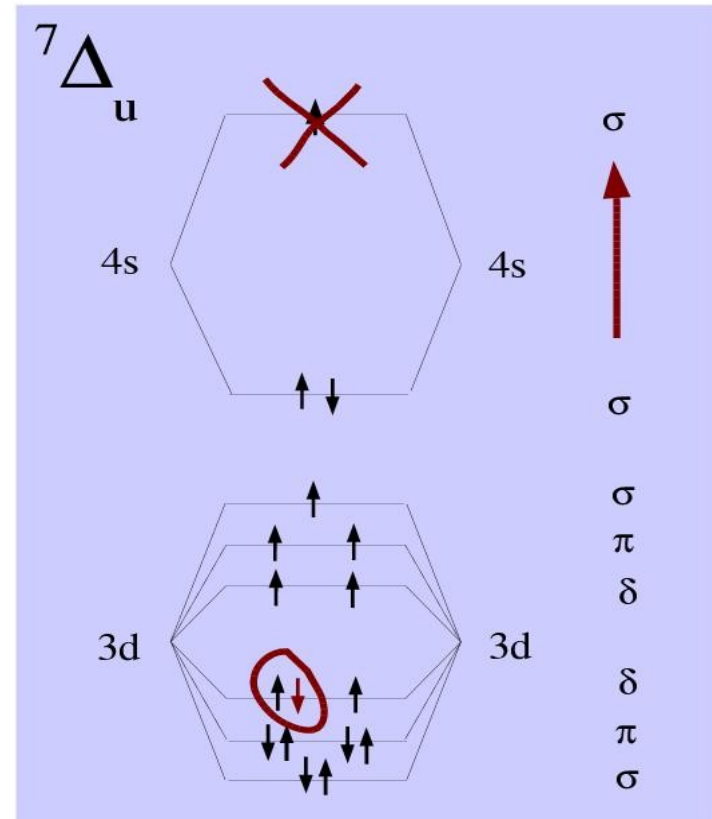
$$E({}^7\Delta_u) - E({}^9\Sigma_g^-) = 0.52 \text{ (10) eV}$$

Neutral ground state

The lack of correlation leads to underestimate the “on-site” repulsion in the d orbitals, and overestimate the 4σ splitting.



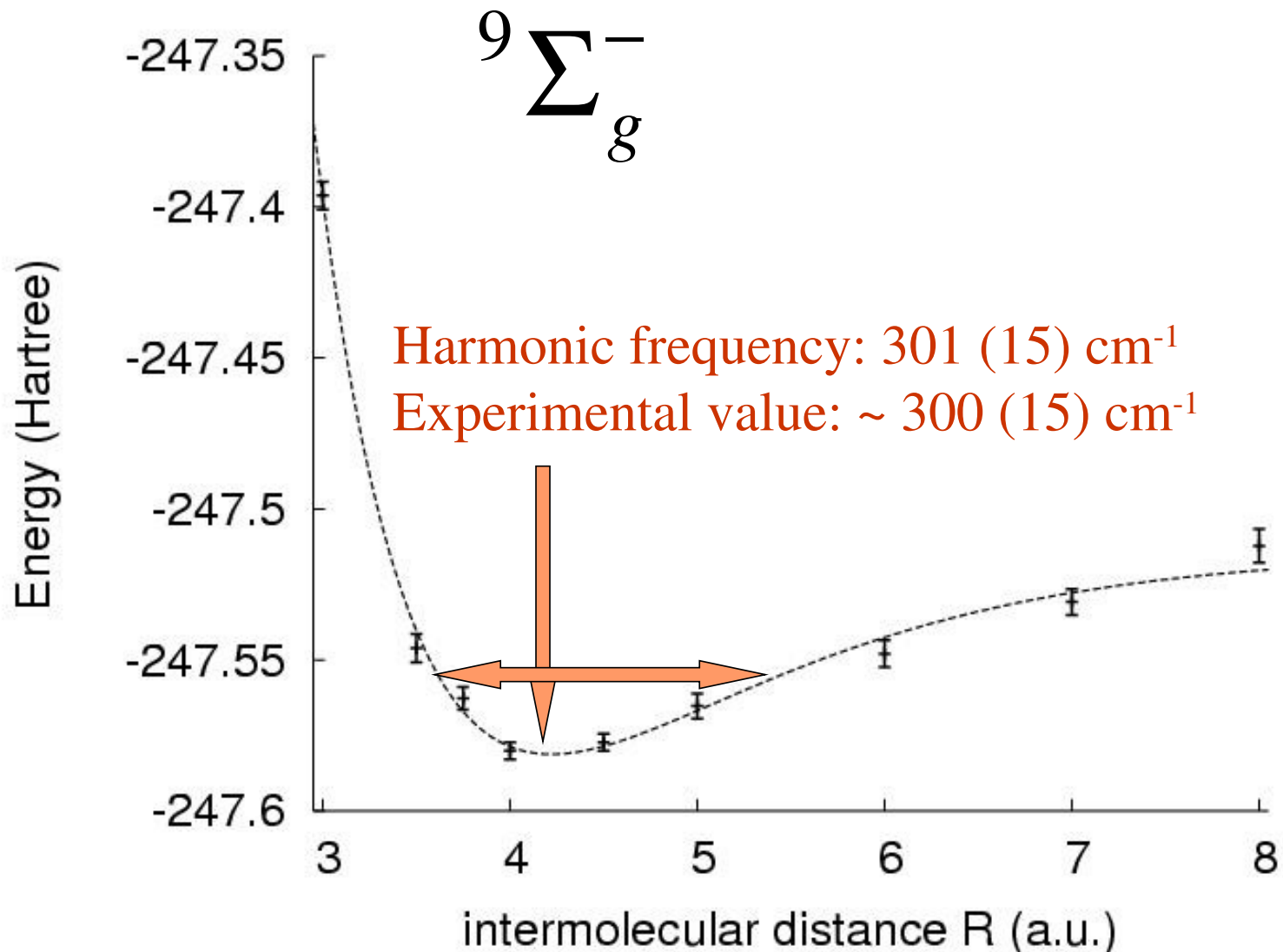
LRDMC



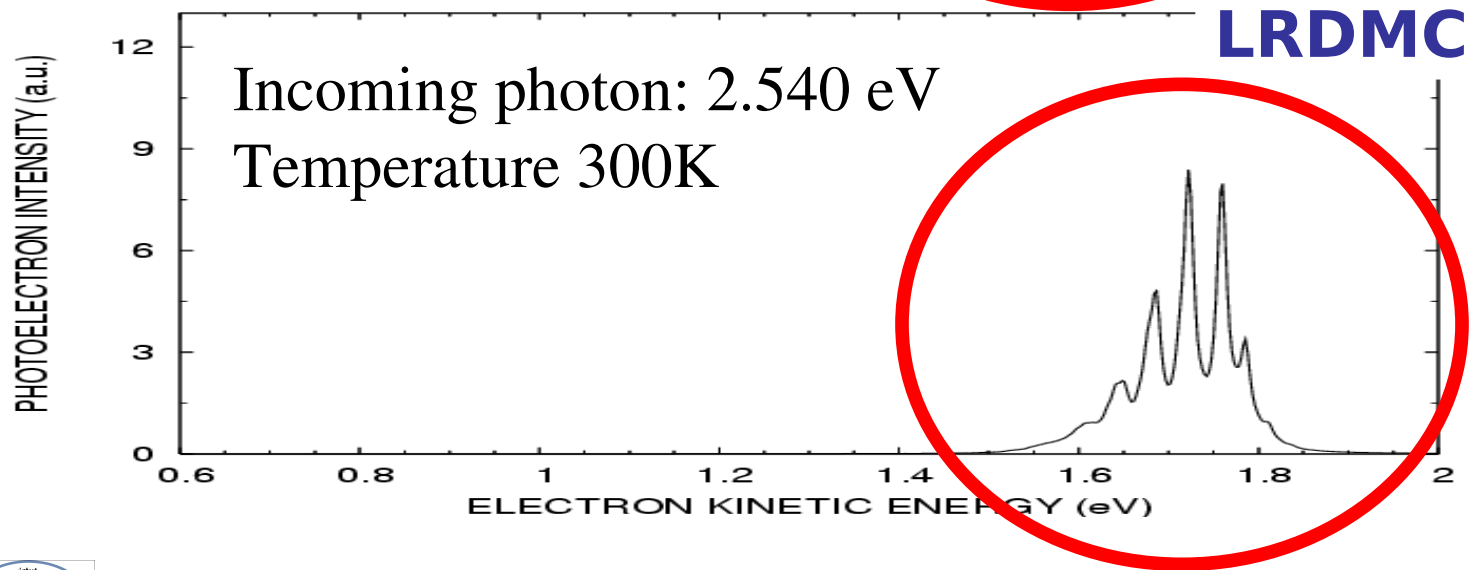
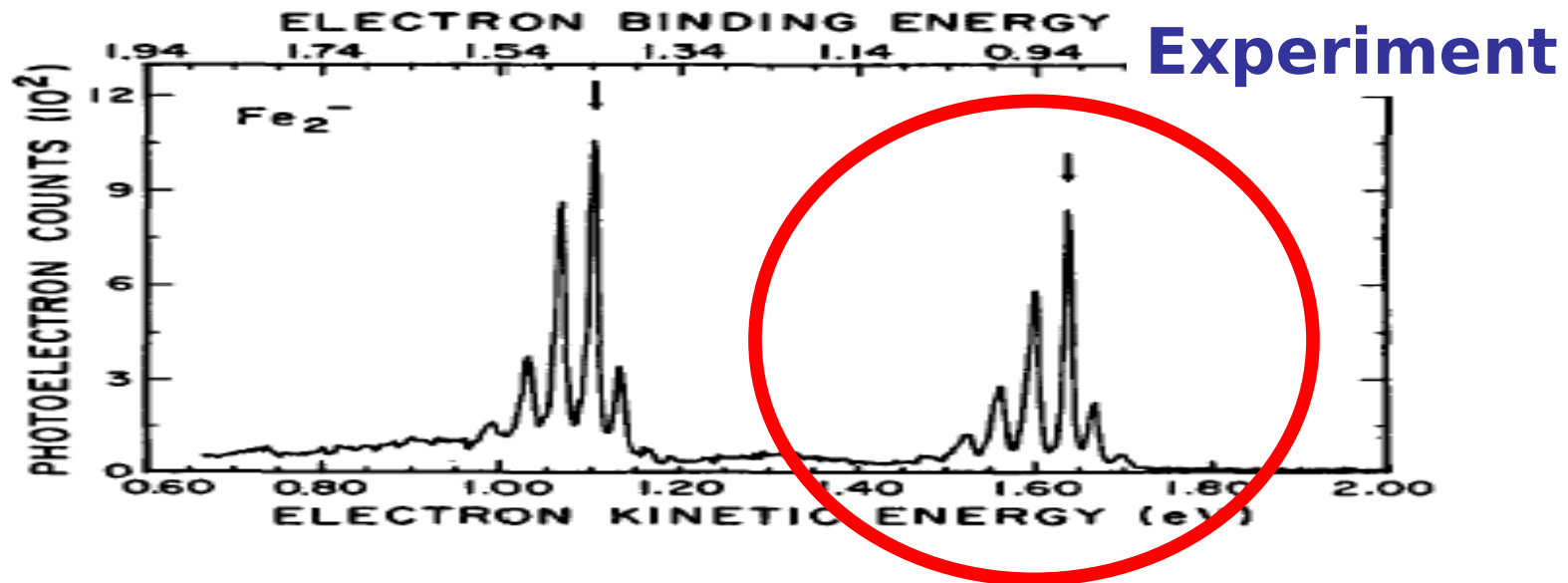
DFT-PP86

Physical Review B, 66 (2002) 155425

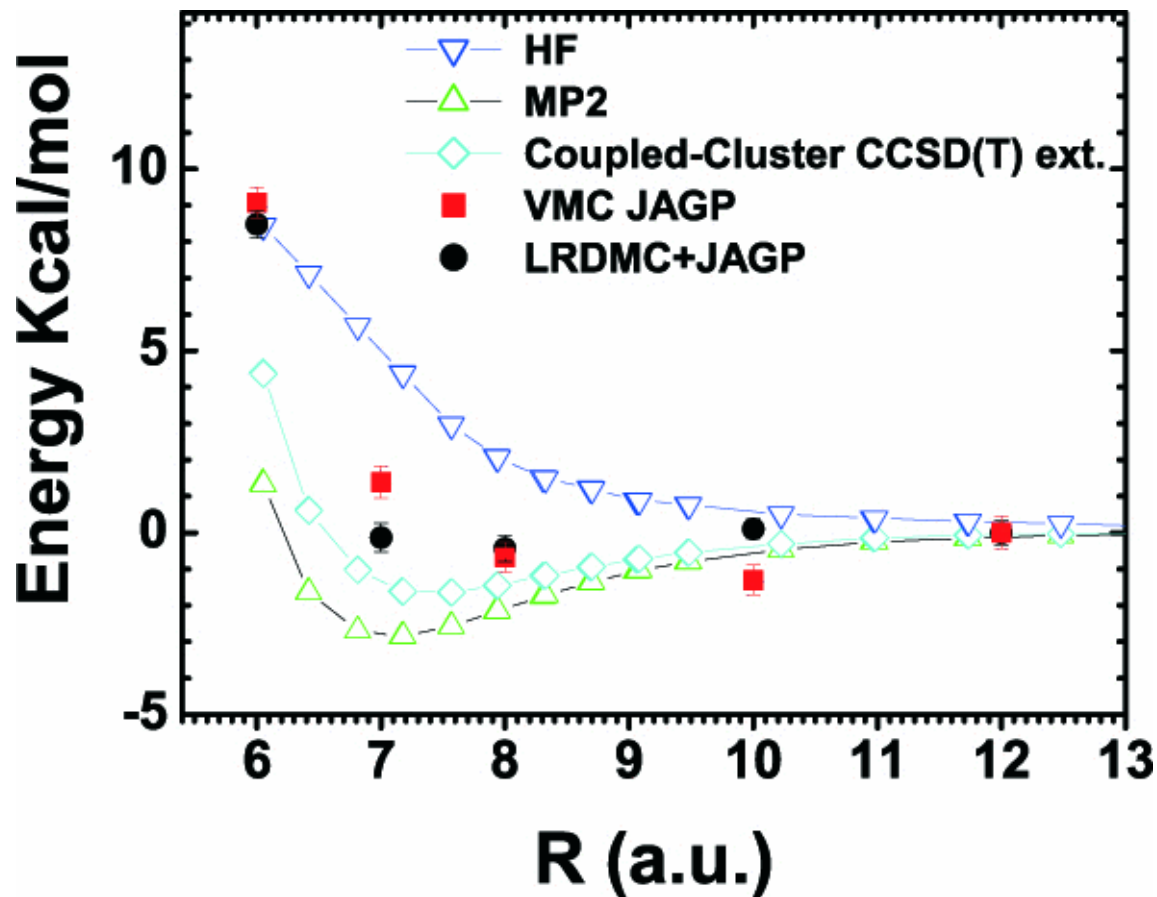
Iron dimer: structural properties



Iron dimer: photoelectron spectrum



Benzene dimer



Van der Waals +
interactions

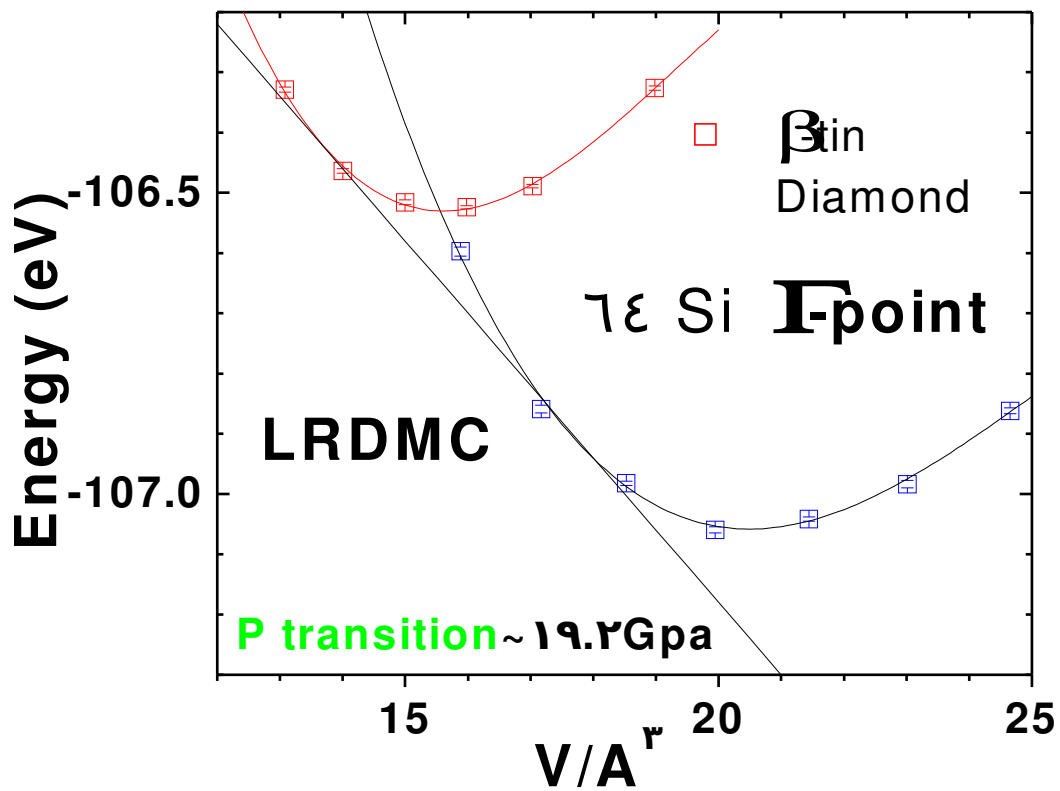
Important for DNA
and protein structures

Binding energy (kcal/mol)
0.5(3) parallel
2.2(3) slipped parallel
0.37 ZPE
1.6(2) experiment

S. Sorella, M. Casula, D. Rocca, J. Chem. Phys. **127**, 014105 (2007)

Conclusions

- The **pseudopotentials** can be “safely” included in the DMC, with the possibility to perform accurate simulations for large or extended systems, in solid state physics or quantum chemistry.
- The **fixed node approximation** is still the major problem for this zero temperature technique.



The LRDMC upper bound theorem

