

*2007 Summer School on Computational Materials Science*

**Quantum Monte Carlo: From Minerals and Materials to Molecules**

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# **New pairing wave functions and methods for non local pseudopotentials**

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# Outline

- Pairing wave functions for realistic systems
  - The concept of the resonating valence bond (RVB)
  - Geminal wave functions
  - Jastrow correlated geminal wave function as RVB ansatz
- Diffusion Monte Carlo (DMC) methods with pseudopotentials
  - Non local pseudopotentials
  - Locality approximation
  - Effective fixed node Hamiltonians
    - Variational theorem
    - Non local Diffusion Monte Carlo
    - Lattice regularized Diffusion Monte Carlo
- Application to some realistic systems
  - Iron dimer
  - Benzene dimer



# Resonating valence bond (RVB)

In this theory the chemical valence bond is described as a **singlet pair** of electrons

$$\frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) [\Psi_a(r)\Psi_b(r') + a \leftrightarrow b]$$

spin up and spin down electrons in a singlet state  
 $a$  and  $b$  are nuclear indexes

The true quantum state of a compound is a **superposition** or **resonance** of many valence bond states. The superposition usually improves the variational energy of the state.

L. Pauling, Phys. Rev. **54**, 899 (1938)

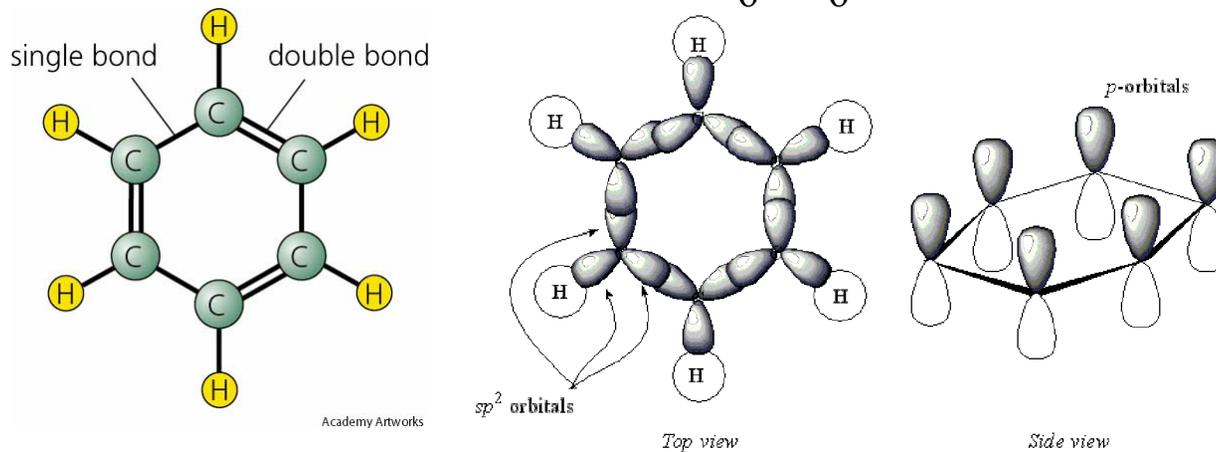


Linus Pauling

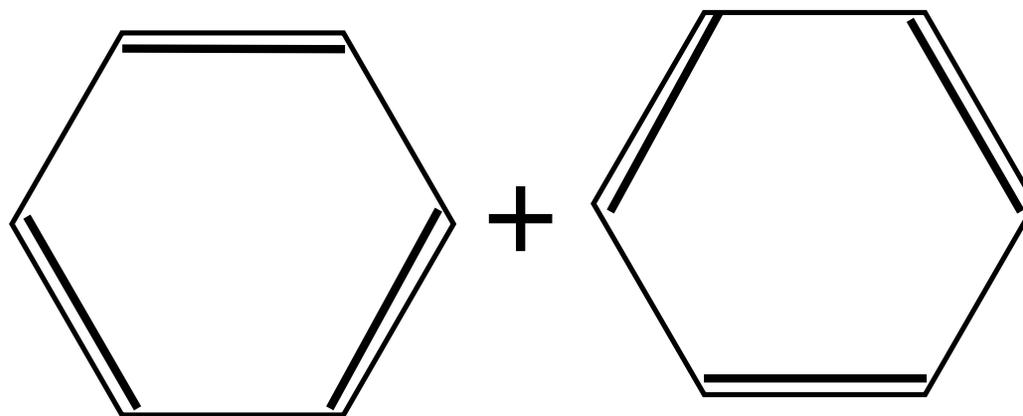


# Example of RVB

Benzene  $C_6H_6$



6 valence electrons in 6 sites ( $2p_z$  type)  
two ways to arrange nearest neighbor bonds (Kekule' states)



# 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)



# Real space representation of RVB

$$|RVB\rangle = P_G \left( \sum_{x,y} \Phi(x-y) (c_{x\uparrow}^+ c_{y\downarrow}^+ + c_{y\uparrow}^+ c_{x\downarrow}^+) \right)^{N/2} |0\rangle$$

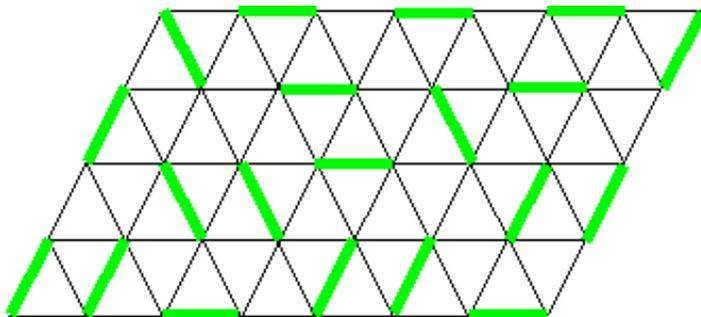
We fixed  $N$ , the number of particles (canonical ensemble):

**$N/2$  singlet pairs (valence bonds)**

$\Phi(x-y)$  Fourier transform of  $\frac{v_k}{u_k}$  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

# Implementation of the RVB concept

## Generalization of the pairing function:

non homogeneous symmetric pairing

$$\Phi(x - y) \rightarrow \Phi(x, y) = \Phi(y, x)$$

In the quantum chemistry community the **pairing function** is called **geminal function**, and the particle conserving version of the **BCS** wave function is called **antisymmetrized geminal product** (or **AGP**)

## Generalization of the Gutzwiller projector:

not only on-site projection, but include also charge-charge (or spin-spin) correlations via a **Jastrow factor J**

$$P_G \rightarrow J[\text{charge } \rho, \text{ spin } \sigma]$$

## Monte Carlo implementation of the Jastrow correlated AGP wave function for realistic systems



# AGP ansatz

$$\langle \mathbf{R} | AGP \rangle = \langle \mathbf{R} | \left( \sum_{x,y} \Phi(x,y) (c_{x\uparrow}^+ c_{y\downarrow}^+ + c_{y\uparrow}^+ c_{x\downarrow}^+) \right)^{N/2} | 0 \rangle = \det(A_{ij})$$

The value of the AGP function on the electron configuration

$$|\mathbf{R}\rangle \equiv \{ \mathbf{r}_1^\uparrow, \dots, \mathbf{r}_{N/2}^\uparrow, \mathbf{r}_1^\downarrow, \dots, \mathbf{r}_{N/2}^\downarrow \}$$

is the determinant of the symmetric  $N/2 \times N/2$  matrix  $A_{ij} = \Phi(\mathbf{r}_i^\uparrow, \mathbf{r}_j^\downarrow)$

## Single particle basis set expansion for the pairing function

$$\Phi(\mathbf{r}, \mathbf{r}') = \sum_{n,m} \lambda_{nm} \varphi_n(\mathbf{r}) \varphi_m(\mathbf{r}')$$

$\lambda_{n,m}$  symmetric matrix       $\varphi_n(\mathbf{r})$  gaussian basis set



# Basis set dependence

The basis set expansion of  $\Phi(\mathbf{r}_i^\uparrow, \mathbf{r}_j^\downarrow)$  will determine the rank (number of non zero eigenvalues) of the matrix  $A_{ij}$

## Minimal basis set:

number of orbitals =  $N/2$

rank of  $A$  =  $N/2$

**AGP = HF** (best wave function written as a single Slater determinant)

## Expansion of the pairing **beyond** the minimal basis set:

a single AGP determinant can be formally written as a **linear combination of many Slater determinants (resonance)**

**correlation is introduced with the computational cost of a single determinant**



# Berillium atom

$1s^2 2s^2$  and  $1s^2 2p^2$  near degeneracy

4 Slater determinants are needed to describe correctly its GS (the number of nodal pockets changes when 2s 2p resonance is included)

The AGP wave function should be expanded to include both 2s and 2p

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

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

**Only one determinant instead of 4!**



# Jastrow correlated AGP wave function

By means of QMC, the **Jastrow correlated AGP (JAGP)** wave function can be sampled just like a Jastrow-Slater determinant. The Jastrow factor reads:

$$\text{Jastrow} = \exp \left[ \sum_{i < j} v(\vec{r}_i, \vec{r}_j) \right]$$
$$v(\vec{r}_i, \vec{r}_j) = u(r_{ij}) + \sum_{i,j} g_{i,j}^{a,b} \phi_{a,i}(\vec{r}_i) \phi_{b,j}(\vec{r}_j)$$

Also the Jastrow factor is expanded using a pairing function. In this case the antisymmetrization is not needed, being the Jastrow a bosonic component of the wave function.

$u(r_{ij})$  **two-body** term to cure electron-electron cusp conditions

Jastrow pairing includes **one-body**, **three-body**, and **four-body** contributions



# Energetics of the Be atom ground state

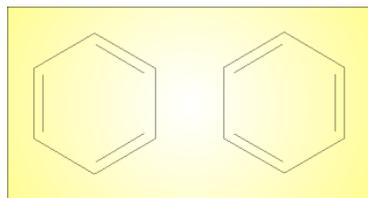
Method	GS Energy (Hartree)
AGP (6s3p2d)	<b>-14.6171</b>
VMC JAGP (2s1p)	<b>-14.66504(4)</b>
Fixed node DMC JAGP (2s1p)	<b>-14.66726(1)</b>
Experiment	<b>-14.66736</b>

Casula, Sorella JCP **119**, 6500 (2003)

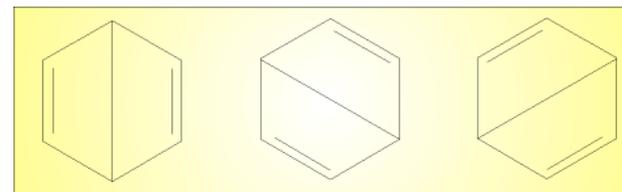
AGP with larger basis **worse** than JAGP



# Benzene with JAGP



Kekule'  
diagrams



Dewar  
diagrams

Terms in the RVB wave function AE calculations	VMC cohesive energy (%)	DMC FN cohesive energy (%)
Kekule + 3 body	83.05(7)	93.75(17)
Resonating Kekule + 3 body	86.65(7)	96.64(15)
Resonating Dewar Kekule + 3 body	88.67(7)	98.60(13)
Resonating Dewar Kekule + 2 body	58.66(8)	95.95(18)

Casula, Attaccalite, Sorella JCP **121**, 7110 (2004)

Jastrow+AGP changes the nodes!



# Interplay Jastrow-AGP

**The AGP wave function** has less variational freedom than the Configuration Interaction (full expansion in the Slater determinant space) but **cures near degeneracy effects**

Effect of the Jastrow factor:

- Cusp conditions fulfilled!
- Faster convergence of the AGP expansion
- Dynamical correlations (charge fluctuations)
- Local conservation of the charge in a molecule



# Spin polarized AGP

Suppose we have a spin unbalance with  $N^\uparrow > N^\downarrow$

then the AGP wave function reads  $|AGP\rangle = \det(A_{ij})$

A is a  $N^\uparrow \times N^\uparrow$  matrix:

$$A_{ij} = \begin{cases} \Phi(r_i^\uparrow, r_j^\downarrow) & \text{for } 1 \leq j \leq N^\downarrow \\ \psi_j(r_i^\uparrow) & \text{for } N^\downarrow + 1 \leq j \leq N^\uparrow \end{cases}$$

where  $\psi_j$  are the unpaired orbitals.

**Notice that for a fully polarized system the AGP reduces to the HF because the AGP does not contain triplet pair correlations!**

**Beyond AGP pairing: multi AGP, pfaffian, multi pfaffian**

See for instance, M. Bajdich, L. Mitas et al. Phys. Rev. Lett. **96**, 130201 (2006)



# Standard DMC

**stochastic method** to find the **ground state (GS) energy**  $E_{GS}$  of  $H$   
In case of fermions, boundary conditions given by the nodes of the guidance wave function  $\Psi_G$  (fixed node approximation)

## DMC algorithm with importance sampling

1. Sample initial walkers from  $|\Psi_G|^2$
2. **Move the walkers** according to the Green's function  $\frac{\Psi_G(x')}{\Psi_G(x)} \langle x' | e^{-\tau H} | x \rangle$ 
  - **Drift and diffuse** (from the kinetic part of  $H$ )
  - **Weight**  $w(x) = e^{-\tau(E_L(x) - \Lambda)}$  **the potential must be local!**
3. **Branching step** (birth-death process according to the weights)  
branching reset the weights to 1.
4. After repeating many times 2. and 3. the walker population will sample the positive mixed distribution  $f(R, t) = \Psi_{FN}(R, t) \Psi_G(R)$



# Mixed estimates

Diffusion Monte Carlo expectation values:

$$\begin{aligned} \langle H \rangle_f &= \int d\mathbf{R} f(\mathbf{R}) E_L(\mathbf{R}) = \int d\mathbf{R} \frac{\Psi_{FN}(\mathbf{R}) \Psi_G(\mathbf{R})}{\int d\mathbf{R} \Psi_{FN}(\mathbf{R}) \Psi_G(\mathbf{R})} \frac{H \Psi_G(\mathbf{R})}{\Psi_G(\mathbf{R})} \\ &= \frac{\int d\mathbf{R} \Psi_{FN}(\mathbf{R}) H \Psi_G(\mathbf{R})}{\int d\mathbf{R} \Psi_{FN}(\mathbf{R}) \Psi_G(\mathbf{R})} = \frac{\langle \Psi_{FN} | H | \Psi_G \rangle}{\langle \Psi_{FN} | \Psi_G \rangle} \end{aligned}$$

As  $\Psi_{FN}$  fixed node GS of H  $\Rightarrow H \Psi_{FN}(\mathbf{R}) = E_{DMC} \Psi_{FN}(\mathbf{R})$

$$E_{DMC} = \frac{\langle \Psi_{FN} | H | \Psi_G \rangle}{\langle \Psi_{FN} | \Psi_G \rangle} = \frac{\langle \Psi_{FN} | H | \Psi_{FN} \rangle}{\langle \Psi_{FN} | \Psi_{FN} \rangle}$$

**MIXED AVERAGE ESTIMATE**  
computed by DMC

**“PURE” EXPECTATION VALUE**

**Important consequence:  $E_{GS} \leq E_{DMC}$  from the variational theorem**  
**UPPER BOUND PROPERTY FOR LOCAL POTENTIALS**



# DMC drawbacks

- **bad scaling** of DMC with the atomic number

cpu time  $\propto Z^{5.5}$  D. M. Ceperley, J. Stat. Phys. 43, 815(1986)  
A. Ma et al., PRE 71, 066704(2005)

- **locality approximation** needed in the presence of non local potentials (pseudopotentials)

**non variational** results

**strong** dependence on the guidance wave function

**simulations less stable** when pseudo are included



# Locality approximation

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

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

$$V^{LA}(x) = \frac{\int dx' V_{x,x'} \Psi_G(x')}{\Psi_G(x)}$$

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

$$\frac{\langle \Psi_G | H | \Psi_{FN}^{LA} \rangle}{\langle \Psi_G | \Psi_{FN}^{LA} \rangle} \neq \frac{\langle \Psi_{FN}^{LA} | H | \Psi_{FN}^{LA} \rangle}{\langle \Psi_{FN}^{LA} | \Psi_{FN}^{LA} \rangle} \quad \Psi_{FN}^{LA} \text{ GS of } H_{FN}^{LA}$$

- in general it will depend on the *shape* of  $\Psi_G$   
(locality is exact only if  $\Psi_G$  is exact)



# Pseudopotentials

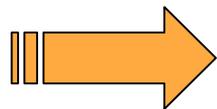
□ For heavy atoms pseudopotentials are **necessary** to reduce the computational time

□ Usually they are **non local**

$$V_P(x_i) = \sum_l v_l(x_i) \sum_m |lm\rangle\langle lm|$$

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

# Non locality in DMC

$$H = K + V_{loc} + V_{non\ loc} \quad \text{Hamiltonian with local and non local potentials}$$

$$e^{-\tau H} = e^{-\tau K} e^{-\tau V_{loc}} e^{-\tau V_{non\ loc}} + O(\tau^2) \quad \text{Trotter breakup}$$

$$G(x \rightarrow x', \tau) = \frac{\psi_T(x')}{\psi_T(x)} \langle x' | e^{-\tau H} | x \rangle \quad \begin{array}{l} \text{Importance sampling} \\ \text{Green function} \end{array}$$

$$= \frac{\psi_T(x')}{\psi_T(x)} \int dx'' \langle x' | e^{-\tau(K+V_{loc})} | x'' \rangle \langle x'' | e^{-\tau V_{non\ loc}} | x \rangle + O(\tau^2)$$

$$= \int dx'' G_{DMC}(x \rightarrow x'') \underbrace{T(x'', x)}_{\text{Non local matrix T}} + O(\tau^2)$$



# Non local T matrix

$$T(x', x) = \frac{\psi_T(x')}{\psi_T(x)} \langle x' | e^{-\tau V_{non\ loc}} | x \rangle$$

**linear form** from expansion up to order  $\tau$

$$T(x', x) = \delta_{x,x'} - \tau V(x', x) + O(\tau^2)$$

same matrix elements for non local  $V$  as computed in the locality approximation

$$V(y, x) = \left( \sum_l \frac{2l+1}{4\pi} v_l(x) P_l [\cos \vartheta_{xy}] \right) \frac{\psi_T(y)}{\psi_T(x)}$$

$V(y, x)$  **is not positive definite**, we have to impose the FN approximation to interpret  $T(y, x)$  as a **transition probability**



# Non local T with fixed node approximation

$$T^{FN}(y, x) = \begin{cases} 1 & y = x \\ -\tau V^-(y, x) & V^-(y, x) \leq 0 \\ 0 & V^+(y, x) > 0 \end{cases}$$

In order to interpret the T matrix as a **transition probability**, we should normalized it, by integrating over all possible final positions, whose number is **finite** (heat bath move). The normalization factor is:

$$w_T(x) = \sum_y T^{FN}(y, x) = \exp \left[ -\tau \sum_y V^-(y, x) \right] + O(\tau^2)$$

**IMPORTANT STEP:** add the discarded  $V^+$  terms to the local potential

$$V_{loc}^{eff}(x) = V_{loc}(x) + \sum_y V^+(y, x)$$

**Sign flip term in local V**  **Upper bound property!!!**



# Sign flip and upper bound property

True Hamiltonian

$$H_{x,x'} = \begin{cases} K + V_{loc}(x) & \text{for } V(x',x) \leq 0 \\ \langle x' | V_{non\ loc} | x \rangle & \text{for } V(x',x) > 0 \end{cases}$$

Effective Hamiltonian

$$H_{x,x'}^{eff} = \begin{cases} K + V_{loc}(x) + V_{sign\ flip}(x) & \text{for } V(x',x) \leq 0 \\ \langle x' | V_{non\ loc} | x \rangle & \text{for } V(x',x) > 0 \\ 0 & \text{for } V(x',x) > 0 \end{cases}$$

$$V_{sign\ flip}(x) = \sum_y V^+(y,x)$$

Sign flip term: sum over all the positive  $V(y,x)$  discarded in the effective H

**Only positive terms are localized in  $V_{loc}(x)$**

$$\Delta E = \langle \Psi | H^{eff} - H | \Psi \rangle = \langle \Psi | V_{sign\ flip} - V^+ | \Psi \rangle$$

$$= \int_D dx' dx \left| H_{x,x'} \right| \left| \Psi(x) \sqrt{\frac{\Psi_T(x')}{\Psi_T(x)}} - sign(H_{x,x'}) \Psi(x') \sqrt{\frac{\Psi_T(x)}{\Psi_T(x')}} \right|^2 \geq 0$$

The integration domain  $D$  is given by those pairs  $(x',x)$  s.t.  $V(x',x) > 0$ , taken only once.

Straightforward extension of the proof given by D.F.B. ten Haaf et al. (PRB **51**, 13039 (1995)) for lattice Hamiltonians.



# Final scheme: non local DMC

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

$$G_{DMC}(x \rightarrow y, \tau) \quad \text{diffusion + drift (with rejection)}$$
$$w_{DMC}(x) = \exp \left\{ -\tau \left[ K + V_{loc}(x) + \sum_y V^+(y, x) - \Lambda \right] \right\}$$

$$p(x \rightarrow y) = T^{FN}(y, x) / w_T(x) \quad \text{non local move (heat bath)}$$
$$w_T(x) = \exp \left[ -\tau \sum_y V^-(y, x) \right]$$

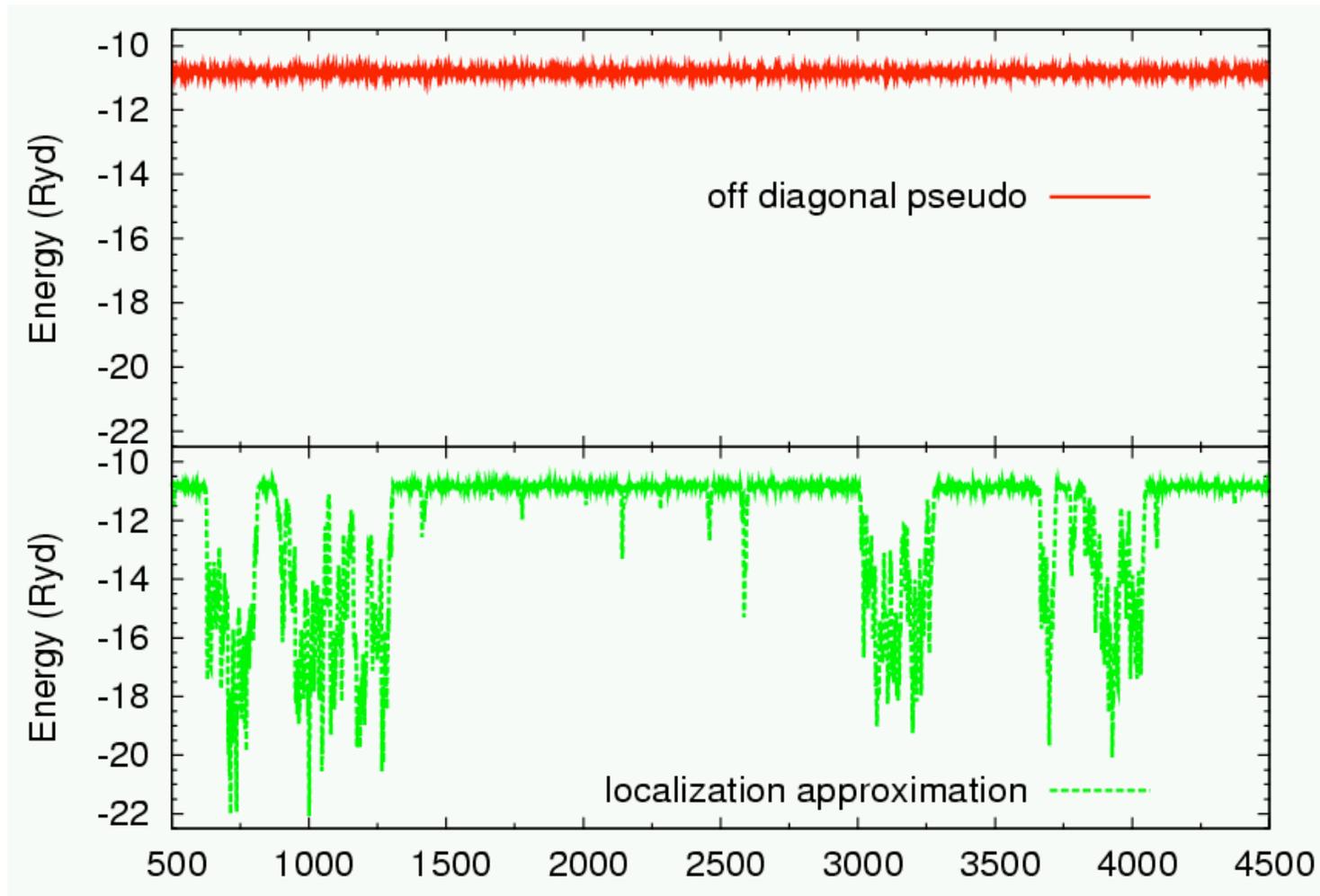
$$w(x) = e^{-\tau(E_L(x) - \Lambda)} \quad \text{weight with local energy}$$

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

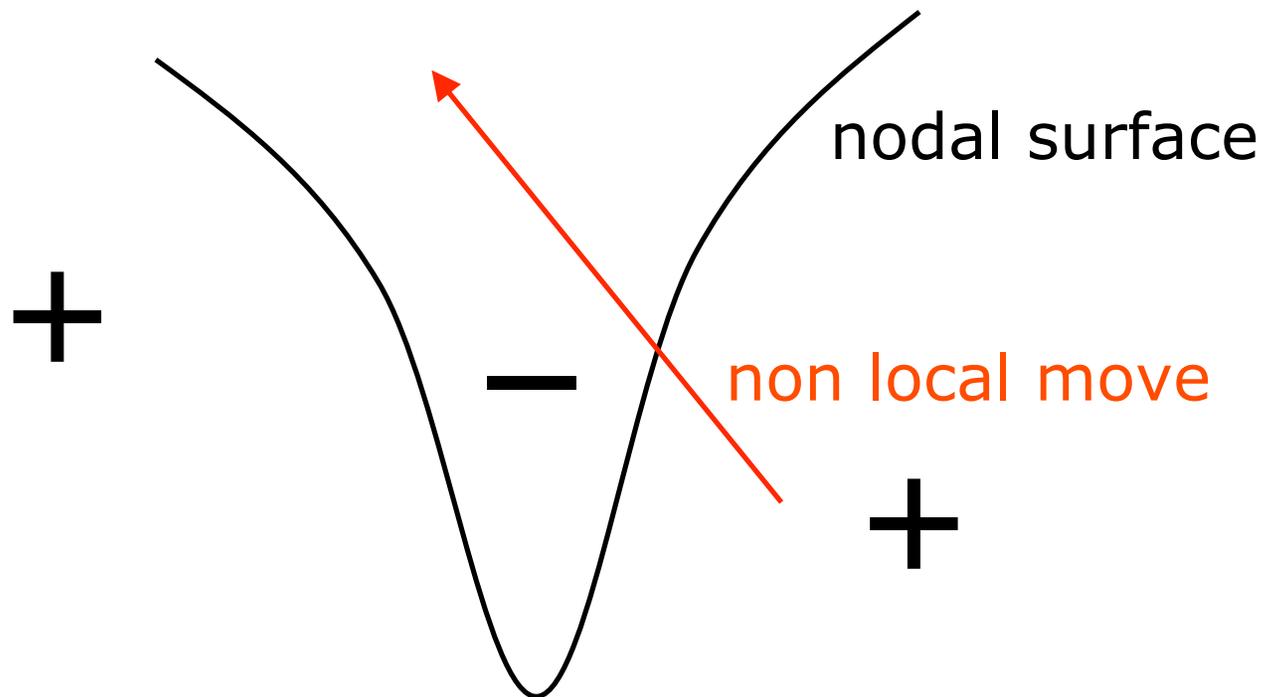


# Stability

Carbon pseudoatom (He core, SBK pseudo)



# Stability



- locality approximation  $\rightarrow$  large and negative attractive potential close to the nodal surface  
(it works for good trial functions / small time steps)
- non local move  $\rightarrow$  jumps the divergence and crosses the node  
(the nasty negative contributions in the locality approximation are good non local matrix elements in the non local DMC scheme)

# Non local DMC: summary

- **robust**  
(stable even for “poor” wave functions or “hard” pseudopotentials)
- **upper bound of the energy**  
(sign flip term included)
- **pure expectation value of the FN Hamiltonian**  
(but an extra cost is required, and usually the mixed estimate error cancels out in the energy differences)
- **easy to implement**  
(only one extra step in the propagation of the standard DMC algorithm)
- **time step error only slightly larger than standard DMC**  
(due to the linearization of the T matrix)

M. Casula, PRB **74**, 161102(R) (2006)



# From non local DMC to lattice regularized DMC (LRDMC)

$$H = \boxed{K} + V_{loc} + \textcircled{V_{non\ loc}}$$

Lattice regularized DMC  
discretization of the laplacian  
+ discretization of the non local potential

Non local DMC  
discretization of the  
non local potential



# Lattice regularization

Kinetic term: discretization of the laplacian

Laplacian with finite differences in the 1D case:

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

General  $d$  dimensional case:

$$\Delta \rightarrow \Delta_a = \sum_{i=1}^d \frac{T_{a_i} + T_{-a_i} - 2I}{a_i^2} + O(a^2)$$

where  $T_{\hat{a}} \Psi_T(\bar{x}) = \Psi_T(\bar{x} + \hat{a})$  are **translation operators**.

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

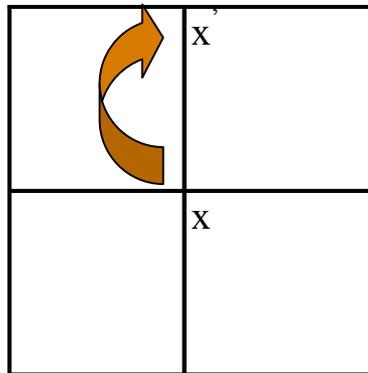


# Projection Monte Carlo on a lattice

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

Propagator: 
$$G_{x,x'} = (\Lambda \delta_{x,x'} - H_{x,x'}) \frac{\Psi_G(x')}{\Psi_G(x)} \Rightarrow \text{Importance sampling}$$

For  $\Lambda$  large enough, **G will project  $\Psi_G$  to the lowest energy state**  
 Projection implemented by the following Markov process:



hopping given by the transition probability

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

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

For fermions, **fixed node approximation**  
 to have a well defined transition probability

# Fixed node with sign flip contribution

$$G_{x,y} = \Lambda \delta_{x,y} - H_{x,y} \Psi_G(x) / \Psi_G(y) \quad \text{Green's function}$$

$$H_{x,y}^{eff} = \begin{cases} V(x) + v_{sf}(x) & \text{DIAGONAL TERM} \\ H_{x,y} & \text{if } G_{x,y} \geq 0 \quad \text{OFF DIAGONAL TERM} \\ 0 & \text{otherwise} \end{cases}$$

$$v_{sf}(x) = - \sum_y G_{x,y} \quad \text{with } G_{x,y} < 0 \quad \text{SIGN FLIP TERM}$$

**Hop with sign change replaced by a positive diagonal potential**

## UPPER BOUND THEOREM !

$$\langle \Psi_0^{eff} | H | \Psi_0^{eff} \rangle \leq \langle \Psi_0^{eff} | H^{eff} | \Psi_0^{eff} \rangle \quad \Psi_0^{eff} \text{ GS of } H^{eff}$$

D.F.B. ten Haaf et al. PRB **51**, 13039 (1995)



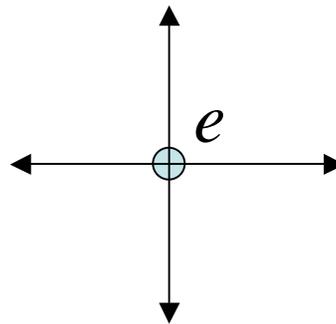
# LRDMC with pseudo

$$G_{x y} = \Lambda \delta_{x y} - H_{x y} \Psi_G(x) / \Psi_G(y) \quad \text{propagator}$$

Two types of off diagonal matrix elements

## Discretized Laplacian

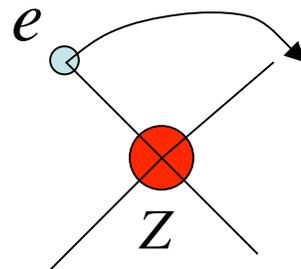
translations



$$\bar{x} = \bar{y} \pm \bar{a}$$

## Discretized non local pseudopotential

rotations around  
a nucleus



$$G_{x y} = - \sum_l v_l(\bar{y}) a_l \frac{\Psi_G(\bar{x})}{\Psi_G(\bar{y})}$$

$$\bar{x} = \bar{y} + \bar{c}$$



# DMC vs LRDMC

## extrapolation properties

DMC	LRDMC
Trotter approximation	For each $a$ well defined Hamiltonian
Time step $\tau$ extrapolation	Lattice space $a$ extrapolation
$\tau$ ( $\tau^2$ ) dependence	$a^2$ ( $a^4$ ) dependence

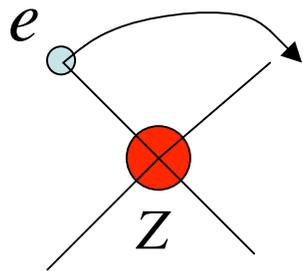
$$\sqrt{\tau} = a \quad \Longrightarrow \quad \text{same diffusion constant}$$

Efficiency (CPU time to have the same statistical error)  $\propto \tau^{-1} (a^{-2})$



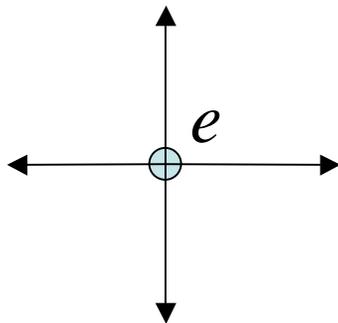
# Error in the discretization

## 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**



# Lattice discretization with two meshes

Double mesh for the discretized laplacian

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

$a$  finest mesh,  $b$  largest

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

**It can depend on the distance from the nucleus:**

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

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

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

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

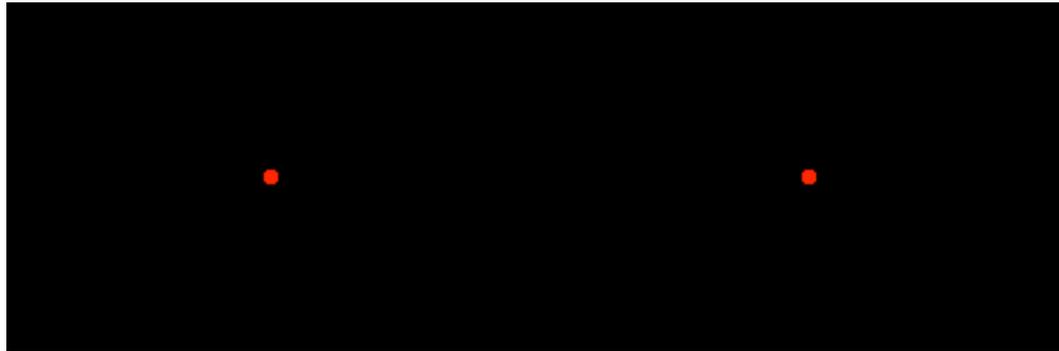
$$b/a = \sqrt{Z^2 + 1}$$



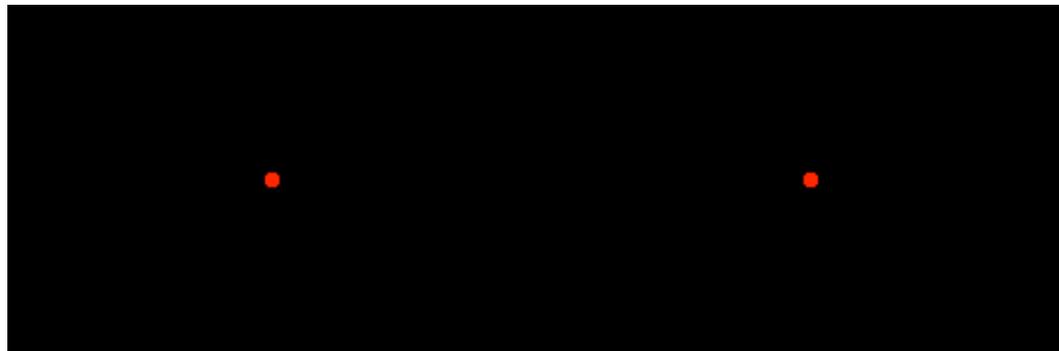
# Two hopping terms

Example: **1D system** with **2 electrons** (1 up, 1 down) and **PBC**

$$b = 2a$$



$$b = \sqrt{5}a$$



# Lattice regularized Hamiltonian

## Definition of lattice regularized Hamiltonian

$$H_a = \eta \Delta_a + V_a$$

- Continuous limit: **for  $a \rightarrow 0$ ,  $H_a \rightarrow H$**
- Local energy of  $H_a$  = local energy of  $H$

➔  $V(x) \rightarrow V^a(x) = V(x) + \left( \frac{\Delta_a \Psi_G(x)}{\Psi_G(x)} - \frac{\Delta \Psi_G(x)}{\Psi_G(x)} \right)$

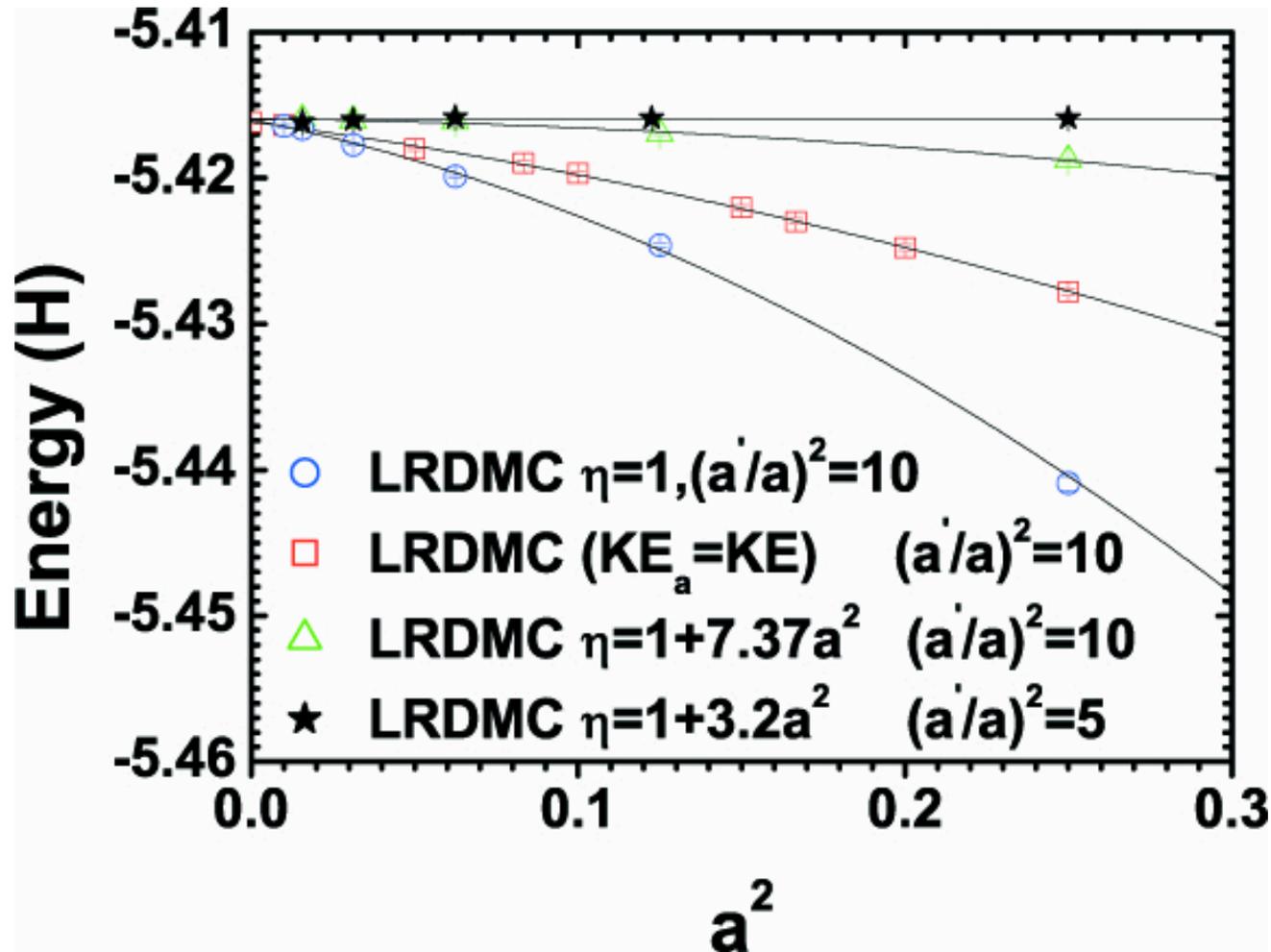
- $\eta$  rescaling factor of the discretized kinetic energy

**Faster convergence in the lattice space  $a$ !**

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



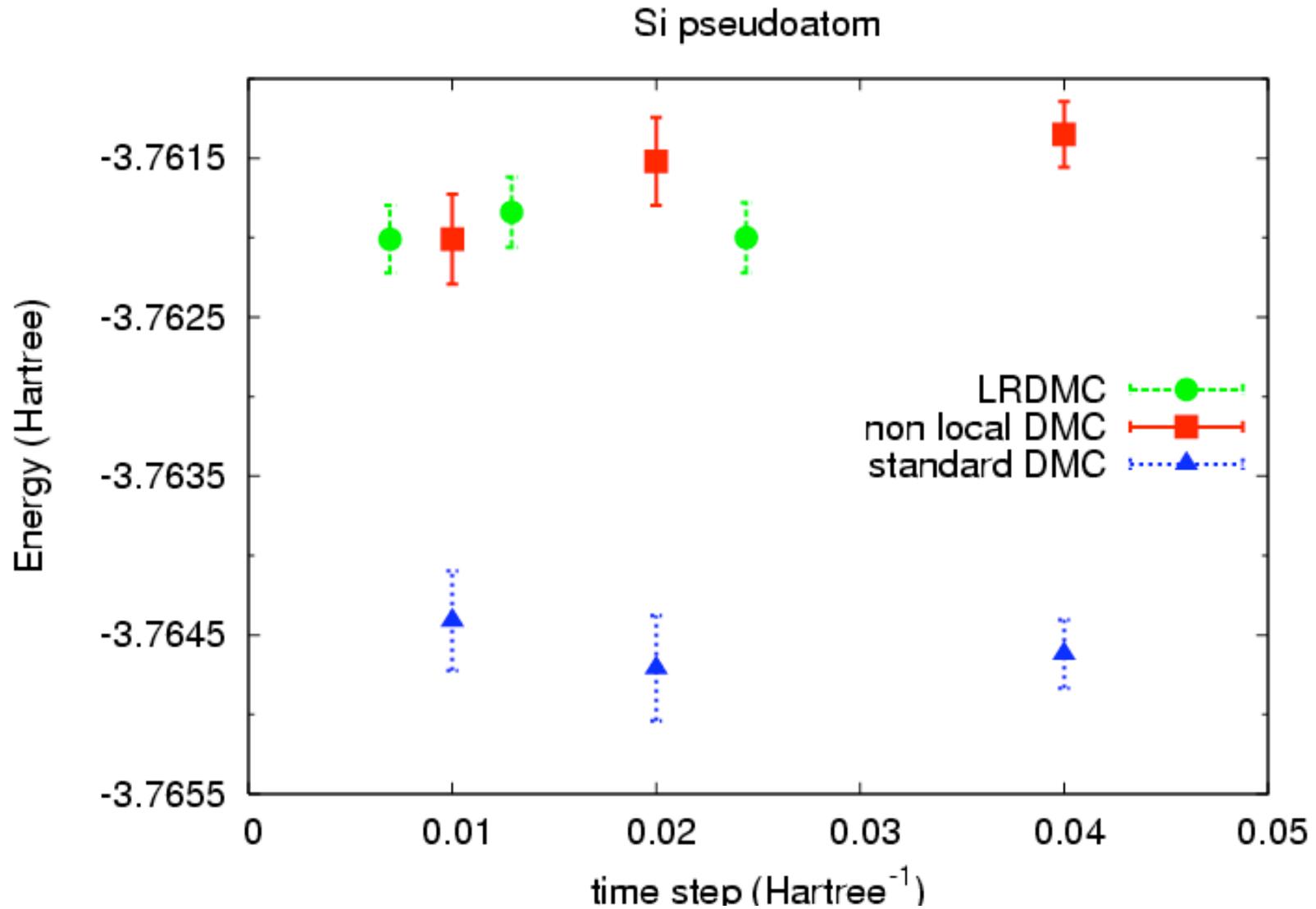
# Convergence for C



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



# Silicon



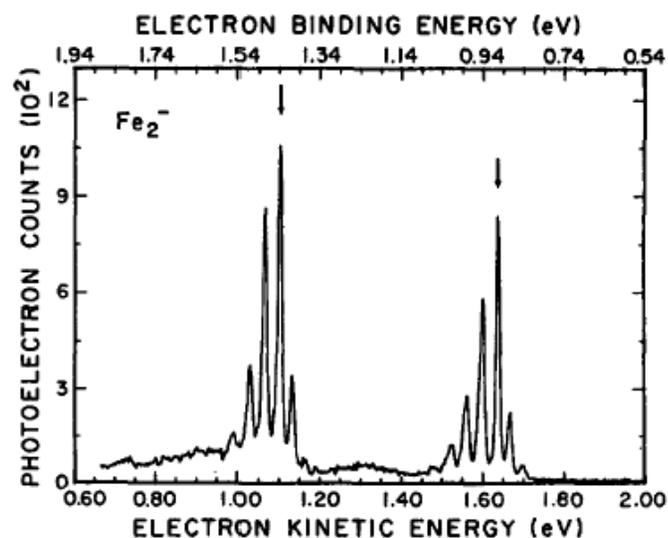
# LRDMC: summary

- same properties of the non local DMC in terms of stability and variational upper bound  
(also the LRDMC effective Hamiltonian includes the sign flip term)
- more difficult to implement in the available codes  
(LRDMC is based more upon the lattice Green function Monte Carlo, than the standard Diffusion Monte Carlo)
- double mesh in the laplacian can help to decorrelate faster the electrons  
(core-valence separation)
- freedom in the kinetic part of the effective Hamiltonian allows to reduce a lot the lattice space error, and improve the efficiency  
(by “fitting” the lattice space dependence for the heaviest element in the compound)

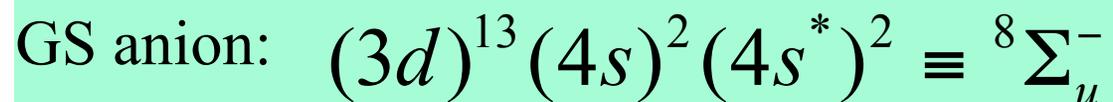
See also <http://www.sissa.it/cm/thesis/2005/casula.pdf>



# Iron dimer



## PHOTOELECTRON SPECTROSCOPY



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

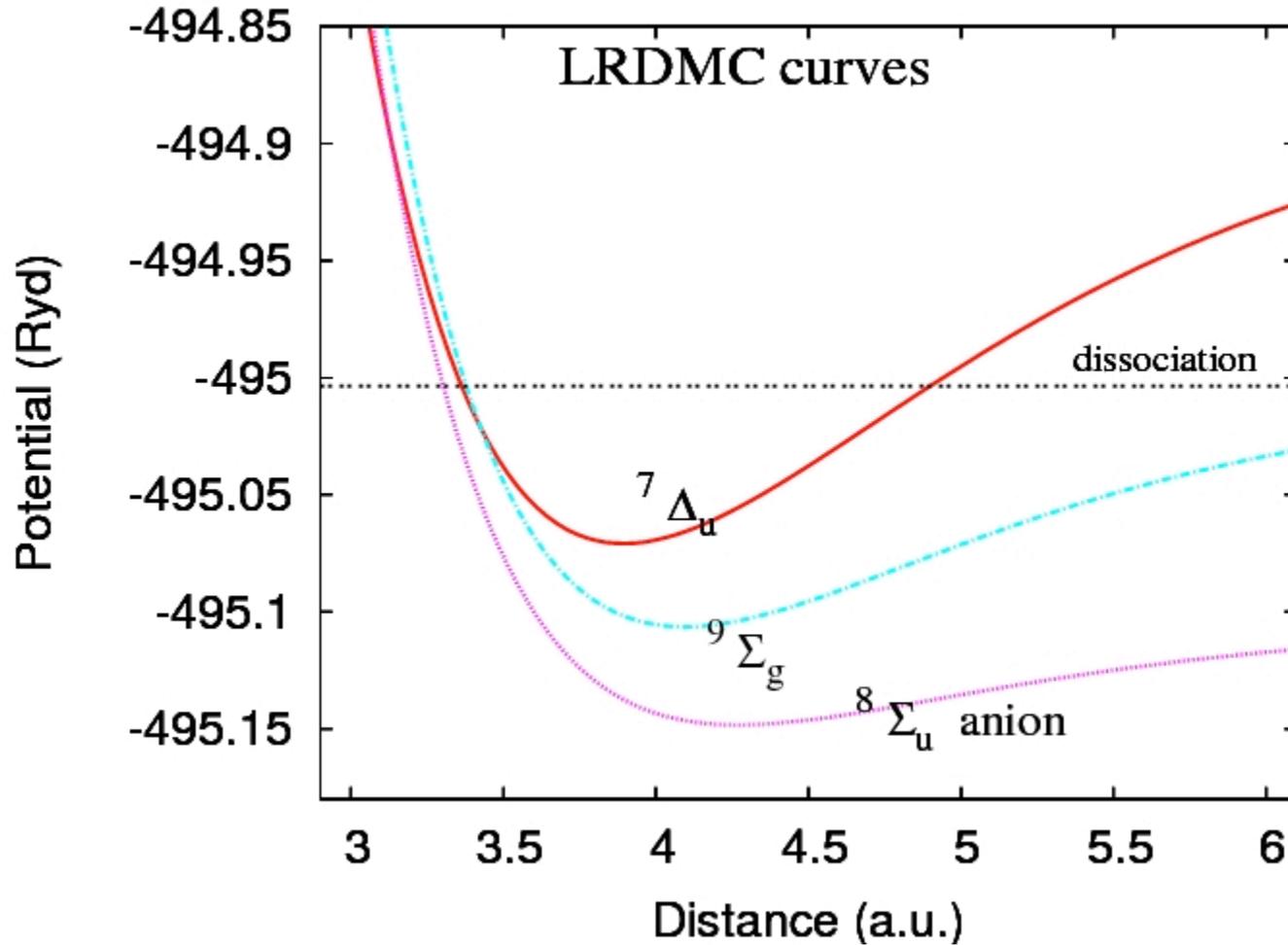
## *Gaussian basis set for JAGP wave function*

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

Total independent parameters: 227



# Dispersion curves



# Neutral ground state

LRDMC gives for neutral dimer

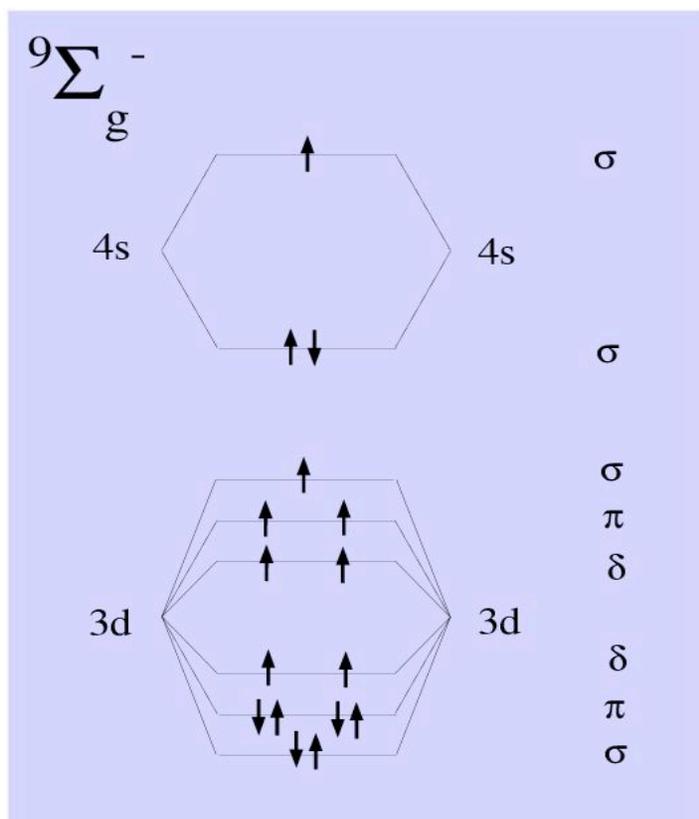


$$E({}^7\Delta_u) - E({}^9\Sigma_g^-) = 0.52 \text{ (10) eV}$$

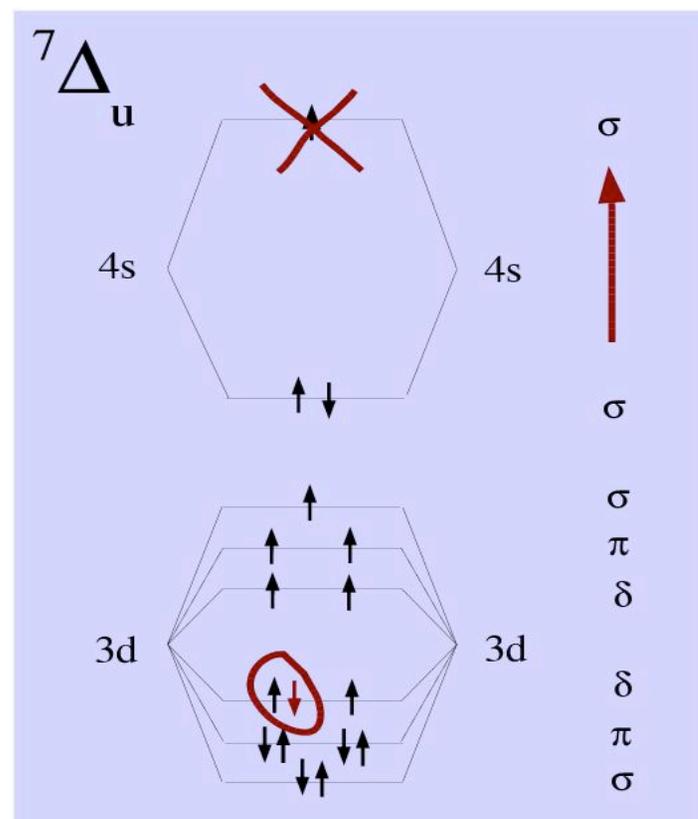


# Neutral ground state

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



LRDMC

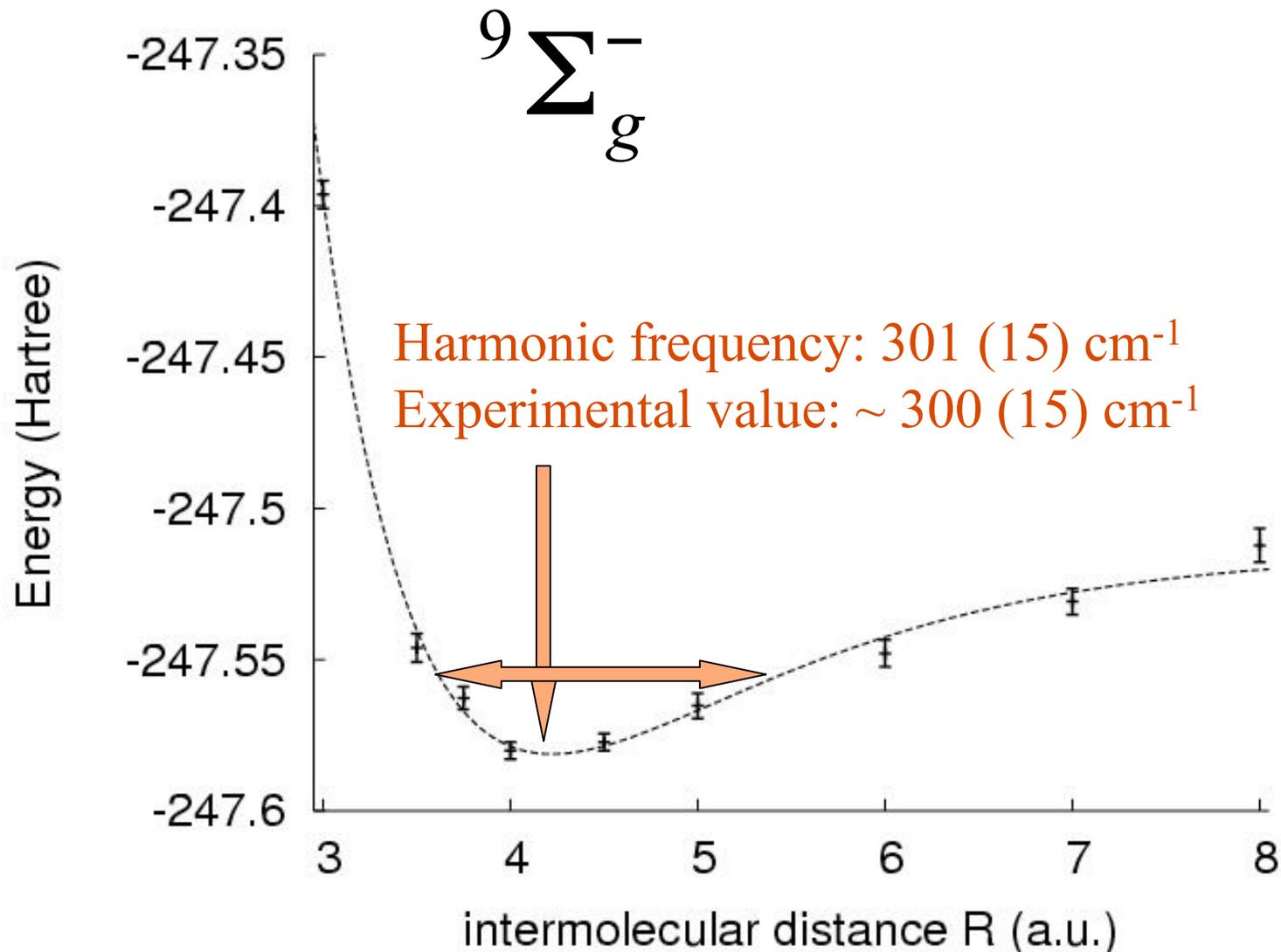


DFT-PP86

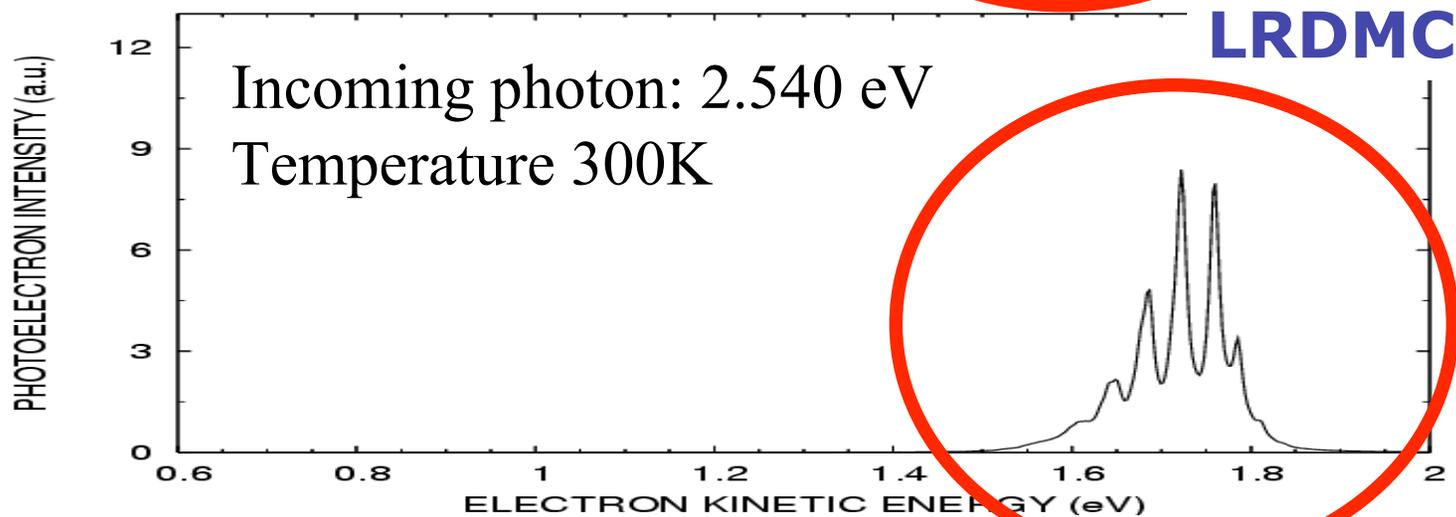
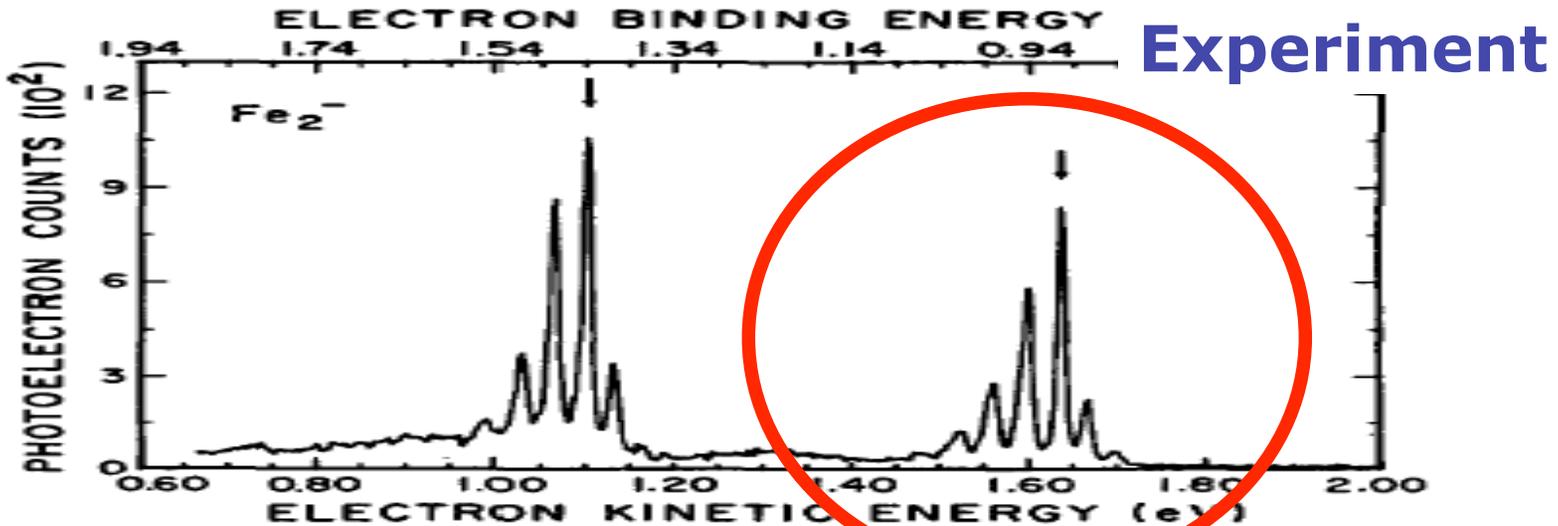
Physical Review B, 66 (2002) 155425



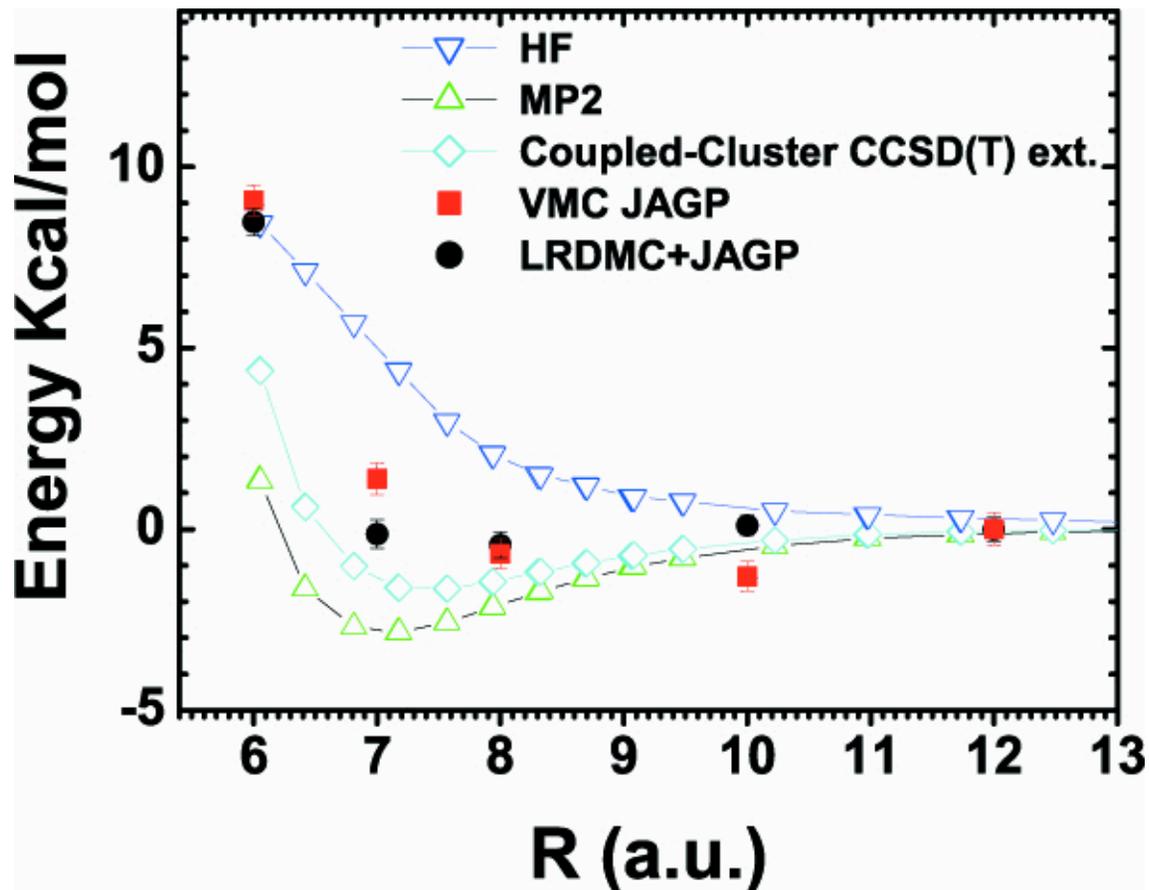
# Iron dimer: structural properties



# Iron dimer: photoelectron spectrum



# Benzene dimer



Van der Waals +  
p/p 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)



# Conclusion and perspectives about the DMC method

- 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 flexibility in the **new correlated trial wave functions** (like geminals, pfaffians, backflow transformations) can partially alleviate the fixed node error, which is very small for very good trial wave functions.
- However we need **efficient optimization methods** to optimize complex wave functions with many parameters and within a stochastic framework (see C. Umrigar’s lecture on the variational optimization)

