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Advanced School on Quantum Monte Carlo Methods in Physics and Chemistry

21 January - 1 February, 2008

Diffusion Monte Carlo methods with non local potentials.

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Diffusion Monte Carlo methods with non local potentials

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Outline

- Diffusion Monte Carlo (DMC) methods: the algorithm on a lattice
  - Non local pseudopotentials and locality approximation
  - Lattice regularized Hamiltonians
    - Variational theorem for Lattice regularized Hamiltonians
    - Lattice regularized Diffusion Monte Carlo
- Application to some realistic systems
  - Iron dimer
  - Benzene dimer
  - From Silicon atom to bulk Silicon

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The algorithm on a lattice

e.g. for the 1D Heisenberg $H = J \sum_{i} \vec{S}_i \cdot \vec{S}_{i+1}$

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

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)

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

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The local energy : $e_L(x) = \sum_{x'} \psi_G(x') H_{x',x} / \psi_G(x)$

is decomposed into : $e_L(x) = H_{x,x} + V^+(x) - V^-(x)$

$$V^{\pm}(x) = \pm \sum_{x' | \pm s_{x',x} > 0} \psi_G(x') H_{x',x} / \psi_G(x)$$

$$s_{x',x} = \begin{cases} 0 \ (\text{diagonals do not matter}) & x' = x \\ Sign[\psi_G(x') H_{x',x} \psi_G(x)] & x' \neq x \end{cases}$$

Case I (no sign problem $s_{x',x} \leq 0$) $V^+(x) = 0 \ \forall \ x$

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Sampling the probability :

$$\Pi(\mathrm{x}) \propto \psi_G(\boldsymbol{x}) \langle \boldsymbol{x} | e^{-H\tau} | \psi_G \rangle \to \psi_G(\boldsymbol{x}) e^{-E_0\tau} \psi_0(\boldsymbol{x})$$

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

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

2) $\boldsymbol{t}_T = \boldsymbol{Min}(-\ln z / V^-(\boldsymbol{x}_t), \tau - \boldsymbol{t})$

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

   if $\boldsymbol{t} + \boldsymbol{t}_T < \tau$

     i) for $\boldsymbol{x}' \neq \boldsymbol{x}_t$ $\boldsymbol{p}_{x',x_t} = -H_{x',x_t} \psi_G(\boldsymbol{x}') / \psi_G(\boldsymbol{x}_t) / V^-(\boldsymbol{x}_t)$

     ii) Choose $\boldsymbol{x}_{t+t_T} = \boldsymbol{x}'$ with prob. $\boldsymbol{p}_{x',x_t}$ $(\sum_{x'} \boldsymbol{p}_{x',x_t} = 1)$

     iii) $\boldsymbol{t} = \boldsymbol{t} + \boldsymbol{t}_T$

    go to step 2

   else

   We have done !!!

   endif

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Case II (sign problem, some $s_{x',x} > 0$) $\quad V^+(x) \neq 0$

The local energy : $e_L(x) = \sum_{x'} \psi_G(x') H_{x',x} / \psi_G(x)$

is decomposed into : $e_L(x) = H_{x,x} + V^+(x) - V^-(x)$

$$V^\pm(x) = \pm \sum_{x' | \pm s_{x',x} > 0} \psi_G(x') H_{x',x} / \psi_G(x) = \pm \sum_{x'} \psi_G(x') H^\pm_{x',x} / \psi_G(x)$$

$$s_{x',x} = \begin{cases} 0 \ \ (\text{diagonals do not matter}) & x' = x \\ Sign[\psi_G(x') H_{x',x} \psi_G(x)] & x' \neq x \end{cases}$$

$$H^{eff} = H + (1 + \gamma)O$$

$$O_{x',x} = \delta_{x',x} V^+(x) - H^+_{x',x}$$

$$\forall \ \gamma \geq 0 \ \ H^{eff\,+} = 0 \text{ and we can apply the same!!!}$$

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Sampling the probability:

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

Markov chain : walker $(x_t, w_t) \approx w_t | x_t \rangle$

1) $t = 0$: $x_0 = | x_0 \rangle$ $w_0 = 1$

2) $t_T = Min(-\ln z / (V^-(x_t) + \gamma W^+(x_t)), \tau - t)$

3) $w_{t+t_T} = w_t \exp[-t_T e_L(x_t)]$

if $t + t_T < \tau$

   i) for $x' \neq x_t$ $p_{x',x_t} = \dfrac{-H^-_{x',x_t} + \gamma H^+_{x',x_t}}{V^-(x_t) + \gamma W^+(x_t)} \psi_G(x') / \psi_G(x_t) > 0$

   ii) Choose $x_{t+t_T} = x'$ with prob. p_{x',x_t} $(\sum_{x'} p_{x',x_t} = 1)$

   iii) $t = t + t_T$

  go to step 2

else

We have done !!!

endif

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Upper bound property, **remind** $H = H^{eff} - (1+\gamma)O$

The operator O can be small :

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

$$\rightarrow \mathrm{E}_{MA} = \frac{\langle \psi_G | H^{eff} | \psi_{FN} \rangle}{\langle \psi_G | \psi_{FN} \rangle} = \frac{\langle \psi_{FN} | H^{eff} | \psi_{FN} \rangle}{\langle \psi_{FN} | \psi_{FN} \rangle} \leq \frac{\langle \psi_G | H^{eff} | \psi_G \rangle}{\langle \psi_G | \psi_G \rangle} = \frac{\langle \psi_G | H | \psi_G \rangle}{\langle \psi_G | \psi_G \rangle} = E_{VMC}$$

O is non negative definite, PRB '91...blackboard proof, then :

$$\rightarrow \mathrm{E}_{FN} = \frac{\langle \psi_{FN} | H | \psi_{FN} \rangle}{\langle \psi_{FN} | \psi_{FN} \rangle} = \frac{\langle \psi_{FN} | H^{eff} - (1+\gamma)O | \psi_{FN} \rangle}{\langle \psi_{FN} | \psi_{FN} \rangle} \leq \frac{\langle \psi_{FN} | H^{eff} | \psi_{FN} \rangle}{\langle \psi_{FN} | \psi_{FN} \rangle} = E_{MA}(\gamma)$$

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

Computable for $\gamma \geq 0$

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Why $H^{eff} = H + (1+\gamma)O$?

- for $\gamma = \begin{matrix}-1\end{matrix}$ $H^{eff} = H$ (the physical one)

- for all γ, the ground state energy $E_{MA}(\gamma)$ of H^{eff}

  is monotonic $\dfrac{dE_{MA}(\gamma)}{d\gamma} \geq 0$ and convex $\dfrac{d^2 E_{MA}(\gamma)}{d^2\gamma} \leq 0$

- for $\gamma \geq 0$ H^{eff} has **no sign problem**

  its ground state ψ_0^{FN} is unique and $\psi_0^{FN}(x)\psi_G(x) > 0$

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Pure energy estimate

For the <u>ground state</u> of $\quad H^{eff} = H + (1+\gamma)O$

Hellmann-Feynman theorem $\rightarrow \quad <O>= \dfrac{dE_{MA}(\gamma)}{d\gamma} \geq 0$

$$E_{FN}(\gamma) =\, <H> \text{ and } E_{MA}(\gamma) =\, <H^{eff}>$$

$$E_0 \geq E_{FN}(\gamma) =\, <H^{eff} - (1+\gamma)O> = E_{MA}(\gamma) - (1+\gamma)\dfrac{dE_{MA}(\gamma)}{d\gamma}$$
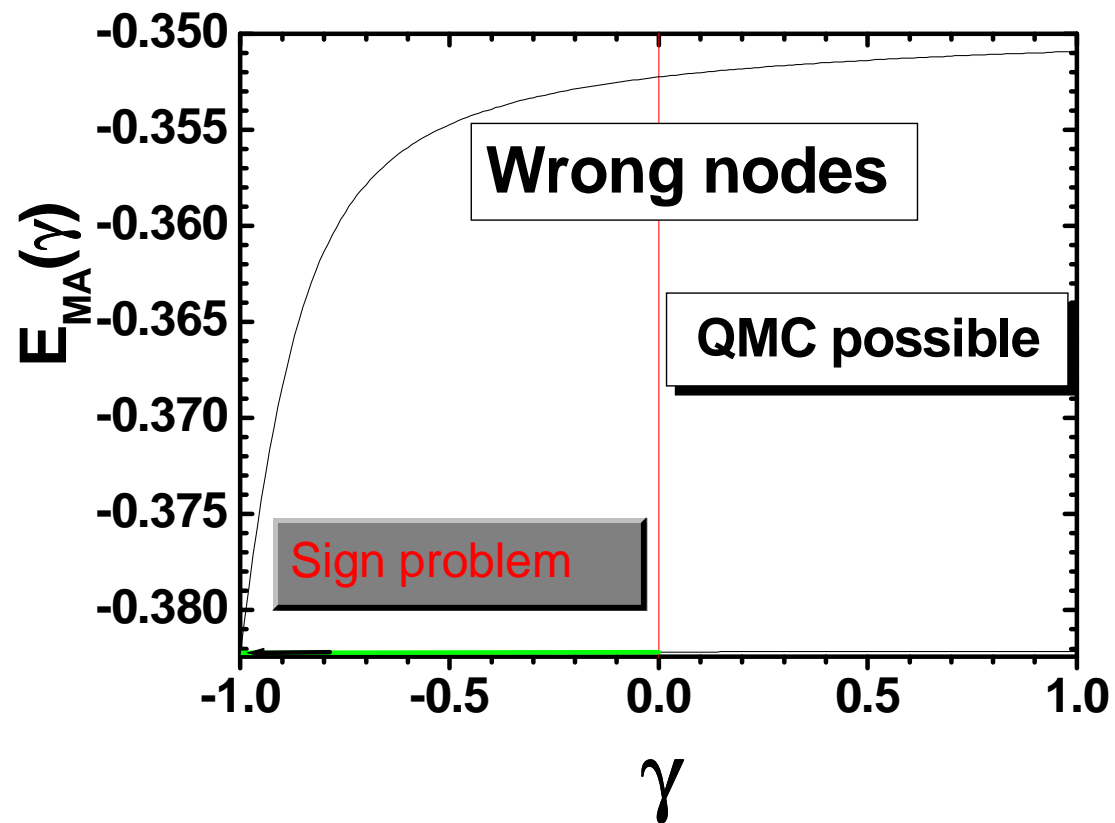
$E_{FN}(\gamma = 0) \qquad$ is the best bound with no sign problem

$$\text{because} \quad \dfrac{dE_{FN}(\gamma)}{d\gamma} = -\dfrac{d^2 E_{MA}(\gamma)}{d^2\gamma} \geq 0$$

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1D J1-J2 (toy) model12 sites

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1D J1-J2 (toy) model 12 sites

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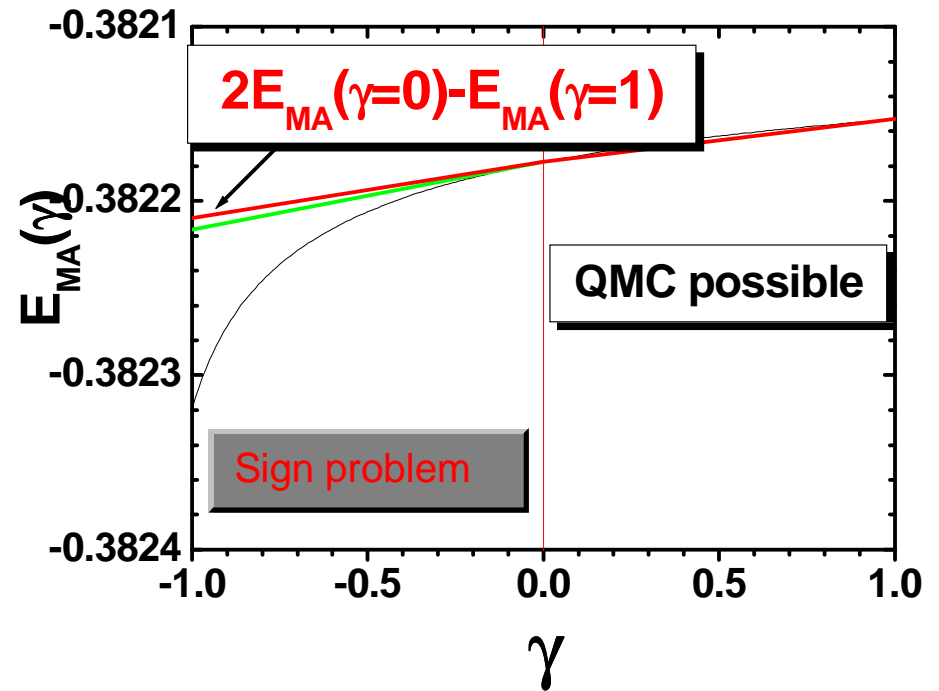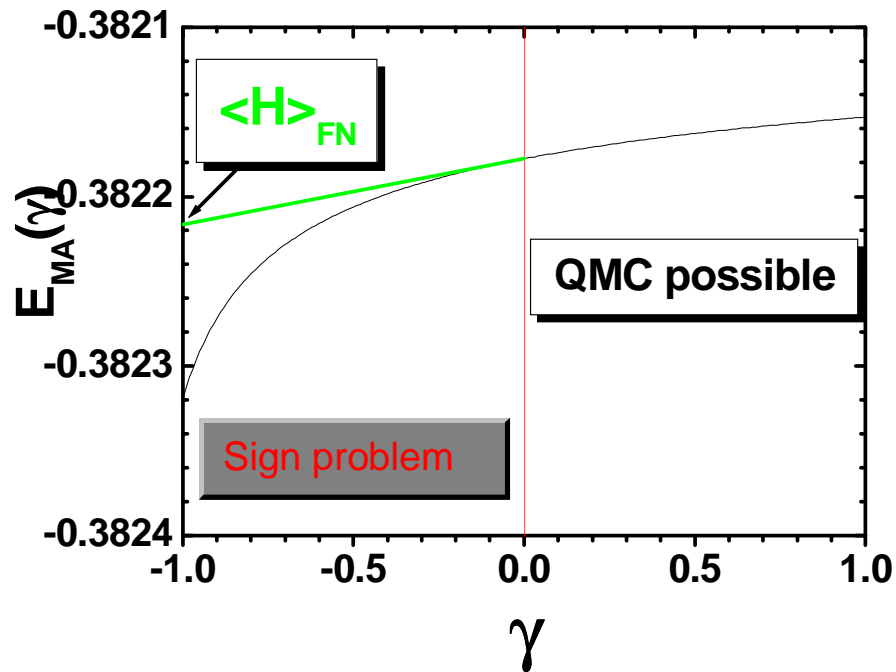
All this approach can be generalized and extended to Hamiltonian defined in the continuous space

All we have used is that for

the number of matrix elements :

$$\langle x' | H | x \rangle \quad \text{can be evaluated, i.e. is } \textbf{finite}$$

But x can belong to the continuous space

We call this type of Hamiltonian:
Lattice Regularized Hamiltonian (LRH)

Important remark, for LRH   the algorithm is ergodic →
The simulation is not restricted to the nodal pocket

$$\forall\, \gamma \neq 0,\, \gamma = 0 \ \text{(the usual approach) is special.}$$

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Can we ''lattice regularize'' the physical Hamiltonian?

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

Namely to find a parameter ''a'' such that:

$$H^a \to H \ \text{for} \ a \to 0 \quad H^a \ \text{is a LRH} \ \forall \, a > 0$$

Motivations:
- The exact Green function can be sampled for LRH hamiltonians:
  no approximations, no particular care to have finite variance algorithms.
- For $\gamma > 0$ everything is rigorous 100%.
- For $\gamma = 0$ the simulation may be restricted to one nodal pocket and we need the tilling theorem, when it applies.
- No restriction to non local operators appearing in H, LRH are always non local by definition.

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Pseudopotentials

❑ For heavy atoms pseudopotentials are **necessary** to re

duce 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→
Lattice regularized Hamiltonian term

$$\langle x'|V_P|x\rangle = V_{x',x}$$

x is given and x' is on a finite mesh around the

pseudo atom $\vec{R}$ such that $|\vec{r}'_k - \vec{R}| = |\vec{r} - \vec{R}|$

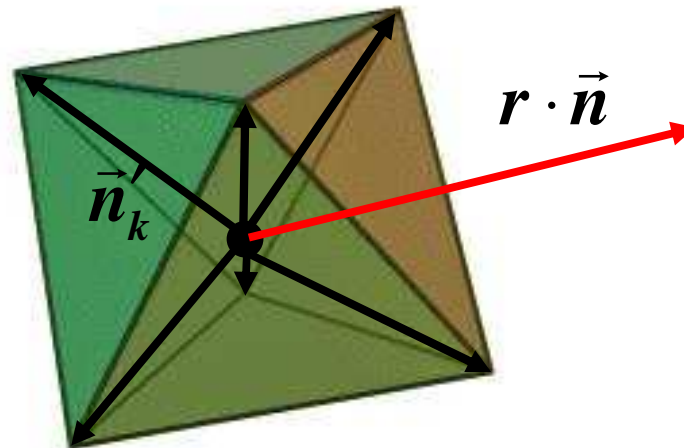for $k = 1,...., p$ (e.g. p = 6 is already good for C, Si,...)

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

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

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

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

$r \cdot \vec{n}$

$\vec{n}'_k$

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Locality approximation

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

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

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

- the mixed estimate is not variational since

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

- in general it will depend on the *shape* of Ψ_G

(locality is exact only if Ψ_G is exact)

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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.

- **dependence**
on the guiding wave function

- **simulations less stable**
when pseudo are included divergencies appear in the localized potential

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Within Lattice Regularized Hamiltonians we can avoid the locality approximation!

But what about the Laplacian?

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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:

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

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

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

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Lattice discretization with two meshes

Double mesh for the discretized laplacian

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

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 $p(\infty) = 0$

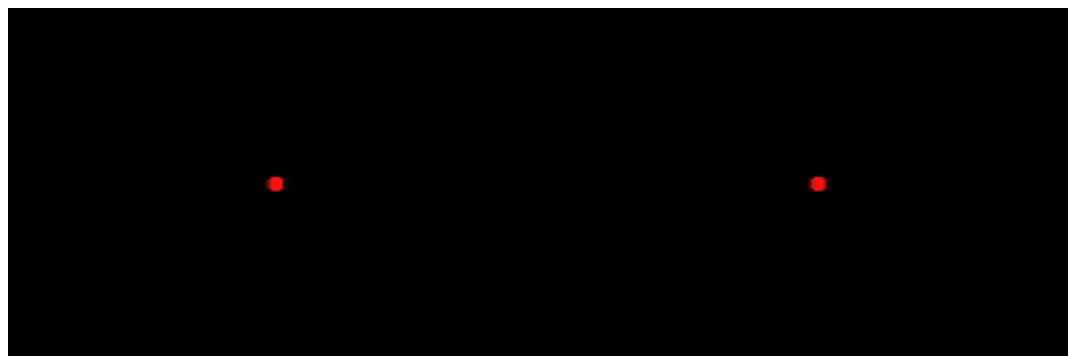Our choice: $p(r) = \dfrac{1}{1 + \gamma r^2}$ $\gamma = Z^2/4$

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! $a'/a = \sqrt{Z^2/4 + 1}$
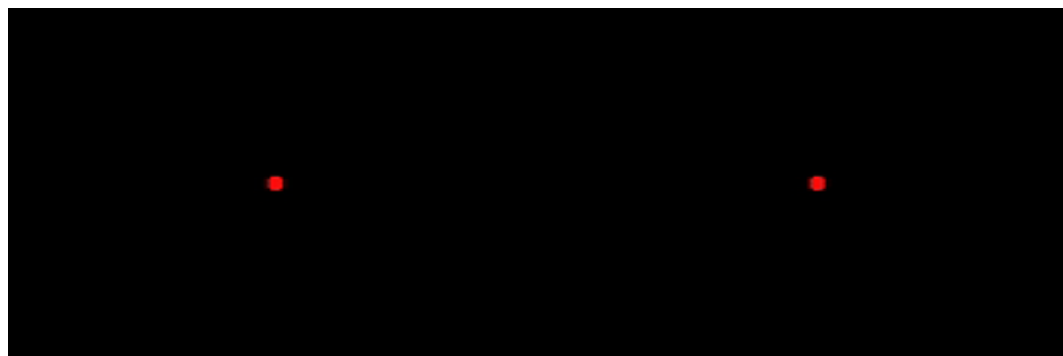
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Two hopping terms

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

$$a' = 2a$$

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

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Lattice regularized Hamiltonian

Definition of the lattice regularized Hamiltonian

$$H_a = \eta_a \Delta_a + V_a$$

- Continuous limit: **for a→0, H$_a$→H** $\quad$ if $\eta_a \to 1$
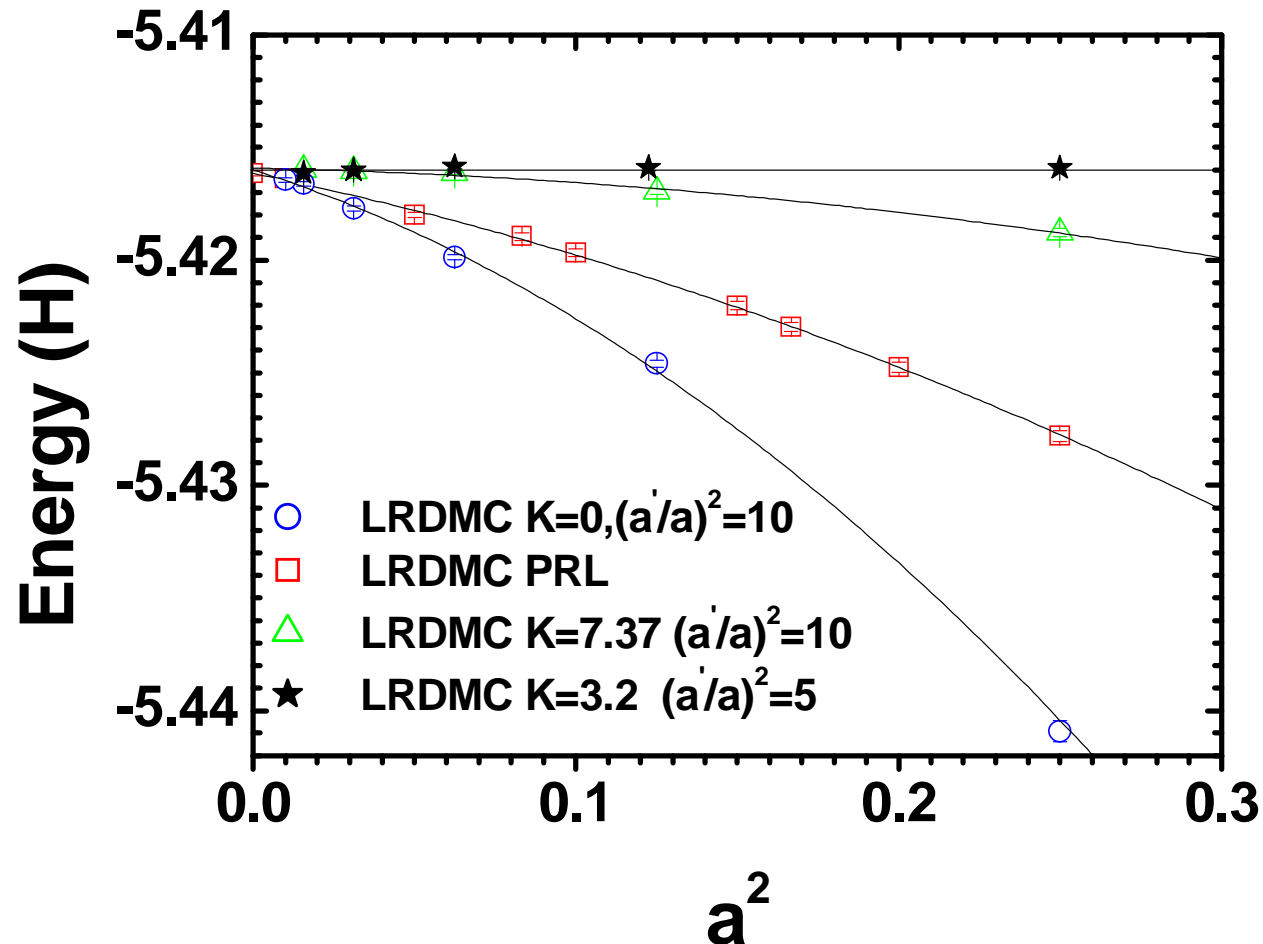
- Local energy of H$_a$ = local energy of H

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

- η_a . rescaling factor of the discretized kinetic energy
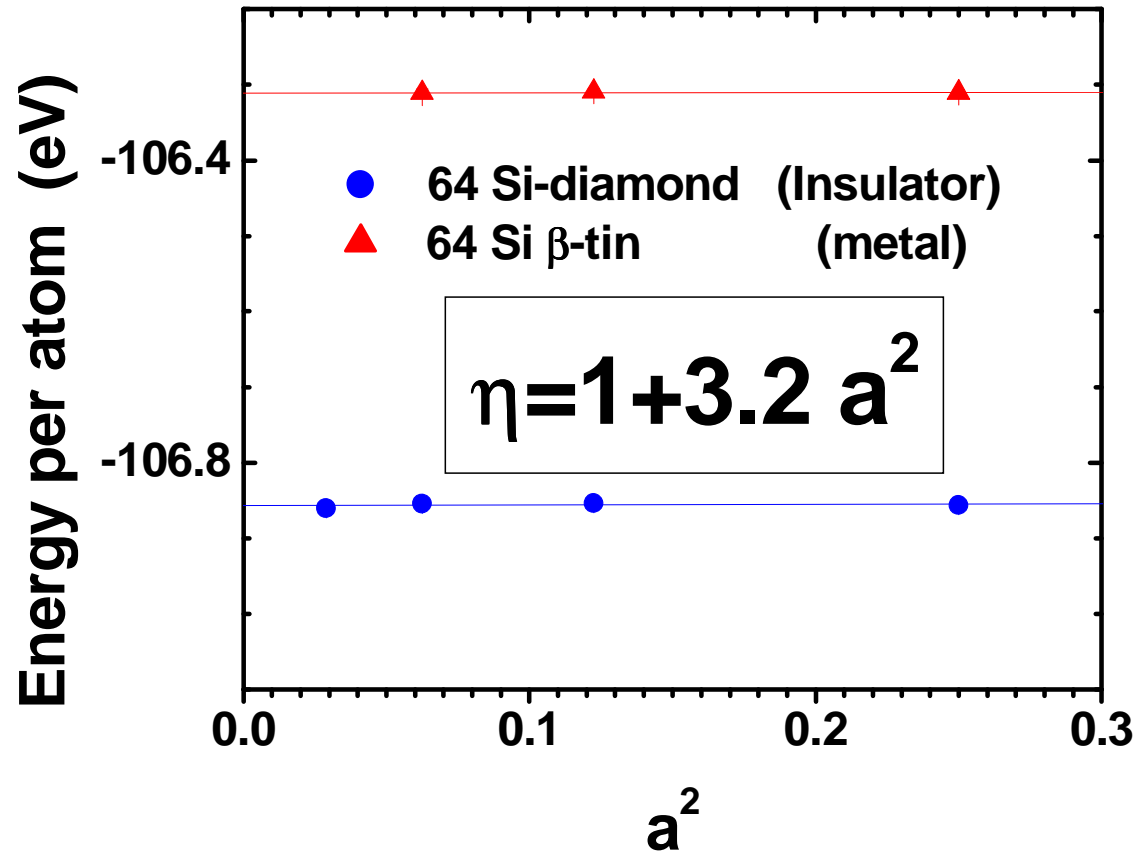
Faster convergence in the lattice space a!

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

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Convergence for C $\eta_a = 1 + Ka^2$

Figure axes — x-axis: a^2, y-axis: Energy (H). Legend:
- LRDMC K=0, $(a'/a)^2 = 10$
- LRDMC PRL
- LRDMC K=7.37 $(a'/a)^2 = 10$
- LRDMC K=3.2 $(a'/a)^2 = 5$

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

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The Silicon metal insulator transition

$$\eta = 1 + 3.2\, a^2$$

Legend:
- 64 Si-diamond (Insulator)
- 64 Si β-tin (metal)

Energy per atom (eV); axes: -106.4, -106.8; a^2 from 0.0 to 0.3

But it depends on the pseudo and on the # pseudoatoms
e.g. K=2 for a single Silicon pseudoatom (Dolg,Filippi)

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Pure energy estimate even for O non positive

For the <u>ground state</u> of $H^{eff} = H + (1+\gamma)O^{\alpha}$

Hellmann-Feynman theorem $\rightarrow$ $<O^{\alpha}> = \dfrac{dE_{MA}(\gamma)}{d\gamma}$

$E_{FN}(\gamma) = <H>$ and $E_{MA}(\gamma) = <H^{eff}>$

$$E_0 \geq E_{FN}(\gamma) = <H^{eff} - (1+\gamma)O^{\alpha}> = E_{MA}(\gamma) - (1+\gamma)\dfrac{dE_{MA}(\gamma)}{d\gamma}$$

$E_{FN}(\gamma = 0)$ is the best bound with no sign problem

because $\dfrac{dE_{FN}(\gamma)}{d\gamma} = -\dfrac{d^2 E_{MA}(\gamma)}{d^2 \gamma} \geq 0$

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From LRDMC back to the locality approximation

The local energy: $e_L(x) = \sum_{x'} \psi_G(x') H_{x',x} / \psi_G(x)$

is decomposed into: $e_L(x) = H_{x,x} + V^+(x) - V^-(x)$

$$V^\pm(x) = \pm \sum_{x' | \pm s_{x',x} > 0} \psi_G(x') H_{x',x} / \psi_G(x) = \pm \sum_{x'} \psi_G(x') H^\pm_{x',x} / \psi_G(x)$$

$$s_{x',x} = \begin{cases} 0 \ \text{(diagonals do not matter)} & x' = x \\ Sign[\psi_G(x') H_{x',x} \psi_G(x)] & x' \neq x \end{cases}$$

$$H^{eff} = H + (1+\gamma)O^\alpha$$

$$O_{x',x}{}^\alpha = \delta_{x',x} V^+(x) - H^+_{x',x} + \alpha\left(\delta_{x',x} V^-{}_{LA}(x) - V^-_{P\,x',x}\right)$$

$$\gamma = 0, \alpha = 1 \rightarrow \text{Locality} \qquad \gamma = \alpha = 0 \rightarrow \text{LRDMC}$$

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Si pseudoatom

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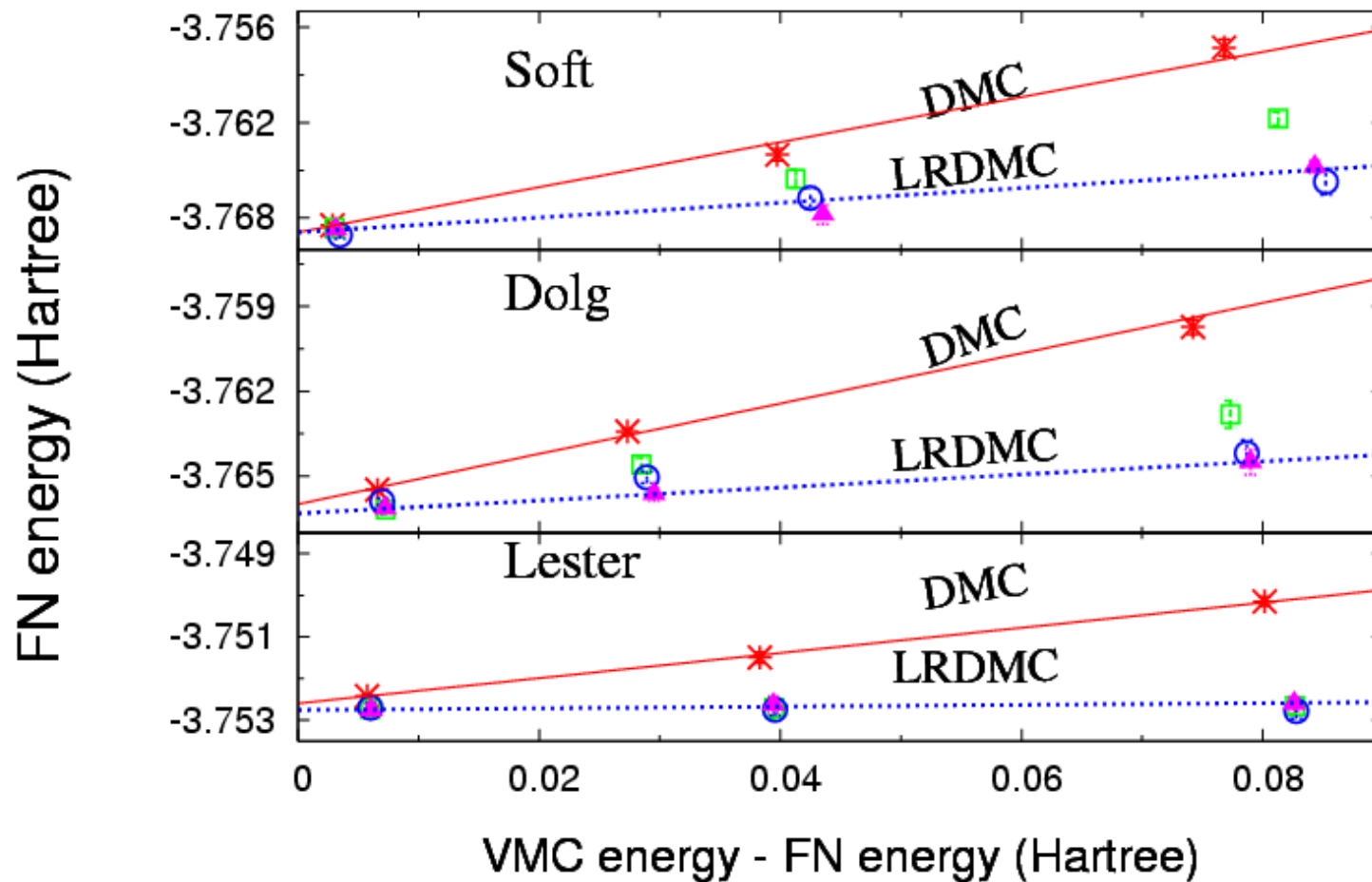
Silicon N=64 diamond V/N (A^3)=19

α	E_{FN} / N
0 (LRDMC)	-106.894 +/- 0.01
0.5	-106.858+/- 0.015
1 (**LOCALITY**)	-106.831+/- 0.01

Quite generally we expect that for systems
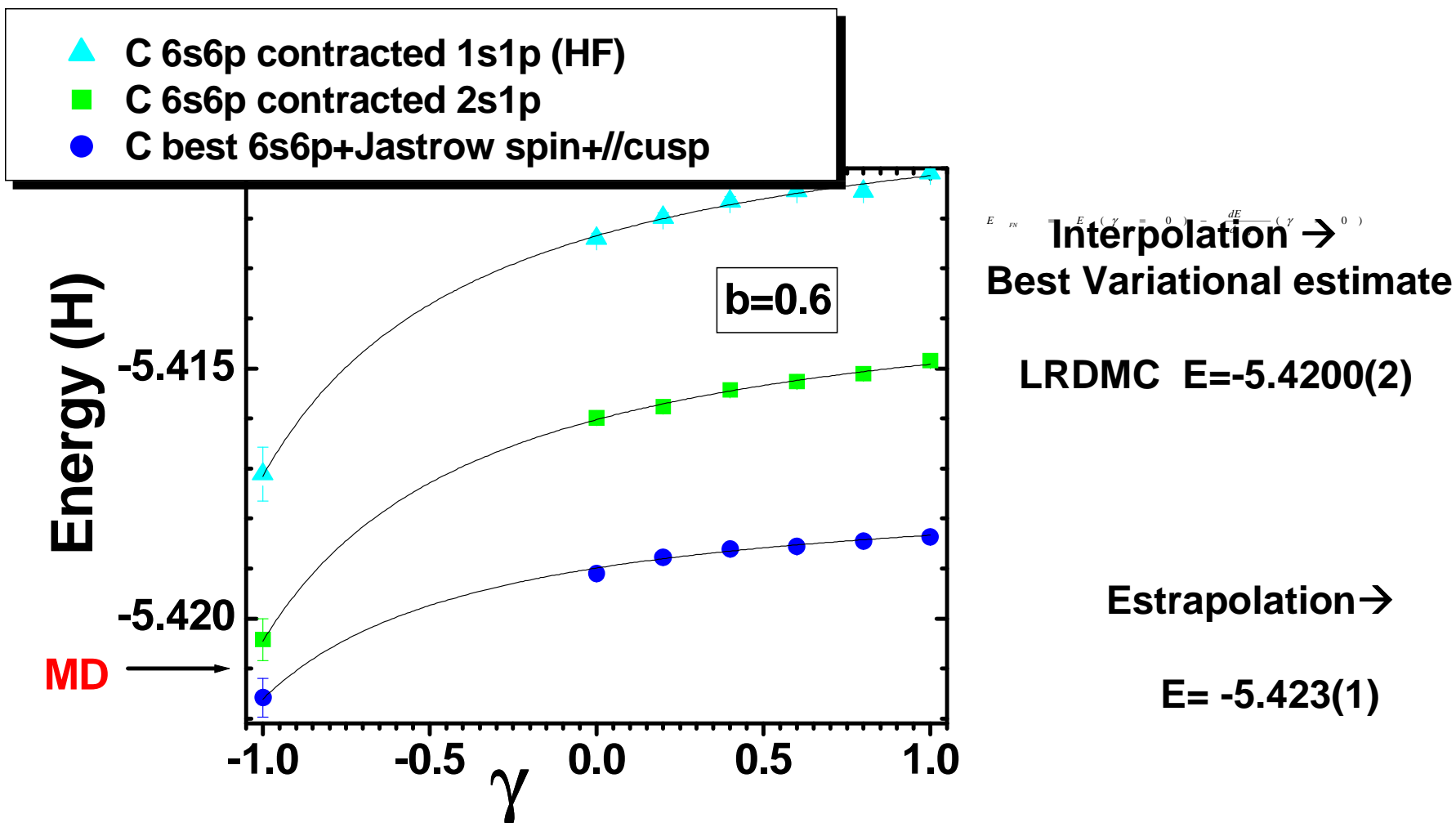 with no rotational symmetry $\alpha = 0$ best

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Scandium

$4s^2 3d^n \rightarrow 4s^1 3d^{n+1}$ excitation energies

eV	VMC	DMC	LRDMC
2 body	1.099(30)	1.381(15)	1.441(25)
3 body	1.303(29)	1.436(22)	1.478(22)

Experimental value: 1.43 eV

LRDMC: two simulations with $\gamma = 0$ and $\gamma = 1$

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Estimating the nodal error

Legend:
- ▲ C 6s6p contracted 1s1p (HF)
- ■ C 6s6p contracted 2s1p
- ● C best 6s6p+Jastrow spin+//cusp

b=0.6

Interpolation →
Best Variational estimate

LRDMC E=-5.4200(2)

Estrapolation→

E= -5.423(1)

Similar things were done by Koonin PRL'94 g>0 possible by QMC g→-1 by extrap.

For large systems we choose the simplest LRDMC with 6s6pc2s1p $\gamma = 0$

What the meaning of η ?

LRDMC has perfect importance sampling without rejection:

Sampling the probability:

$$\Pi(x) \propto \psi_G(x)\langle x|e^{-H\tau}|\psi_G\rangle = \int [dx(t)]\exp(-\int_0^\tau dt\, e_L(x_t))$$

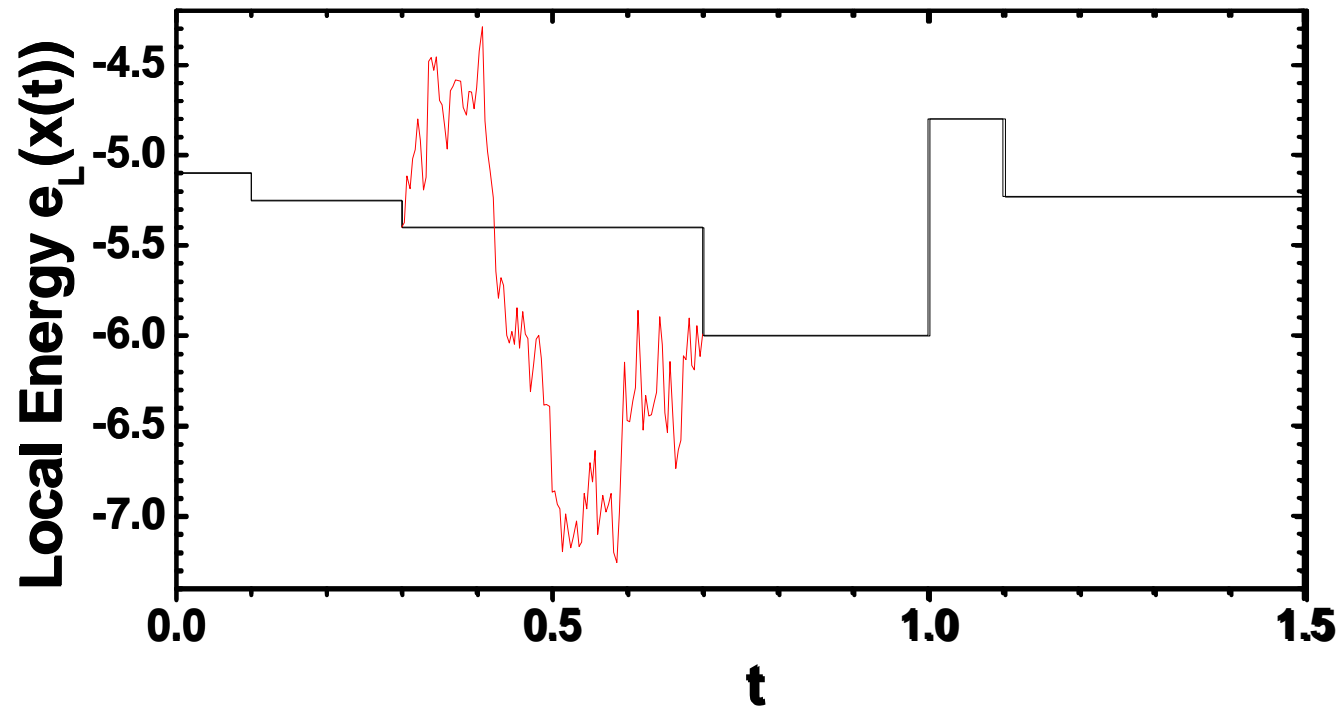The integration over the paths $x(t), 0 < t < \tau$ is **exact**
but continuous generic paths are replaced by
piecewise constant (in time) paths with steps $\Delta x \approx a$ for $\Delta\tau \approx a^2$.

By choosing $\eta > 1$ one is considering the same paths:

$$\Pi^\eta(x) \propto \psi_G(x)\langle x|e^{-H\tau}|\psi_G\rangle = \int [dx(t)]\exp(-\frac{1}{\eta}\int_0^\tau dt\, e_L(x_t))$$

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This overcomes the smaller diffusion rate due to the discretization in time and space

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Diffusion rate in LRDMC

$$\left\langle \dot{\vec{R}}^2 \right\rangle = D = <[\vec{R},[H,\vec{R}] >= 3\#\boldsymbol{el}.$$

But on a lattice :

$$D^a = <[\vec{R},[H^a,\vec{R}] >= \left\langle \frac{1}{2} \sum_{\mu=x,y,z,i} (T^a_{\mu,i} + T^{-a}_{\mu,i}) \right\rangle < 3\#\boldsymbol{el}.$$

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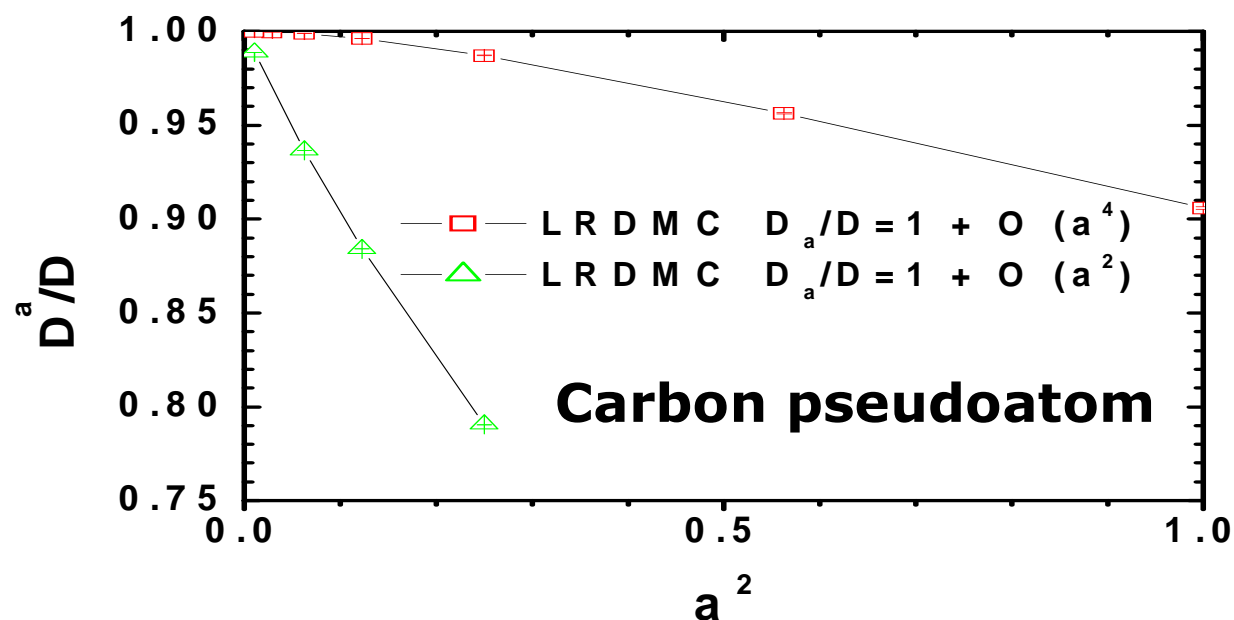
Stability

Carbon pseudoatom (He core, SBK pseudo)

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Stability

+

−

nodal surface

non local move

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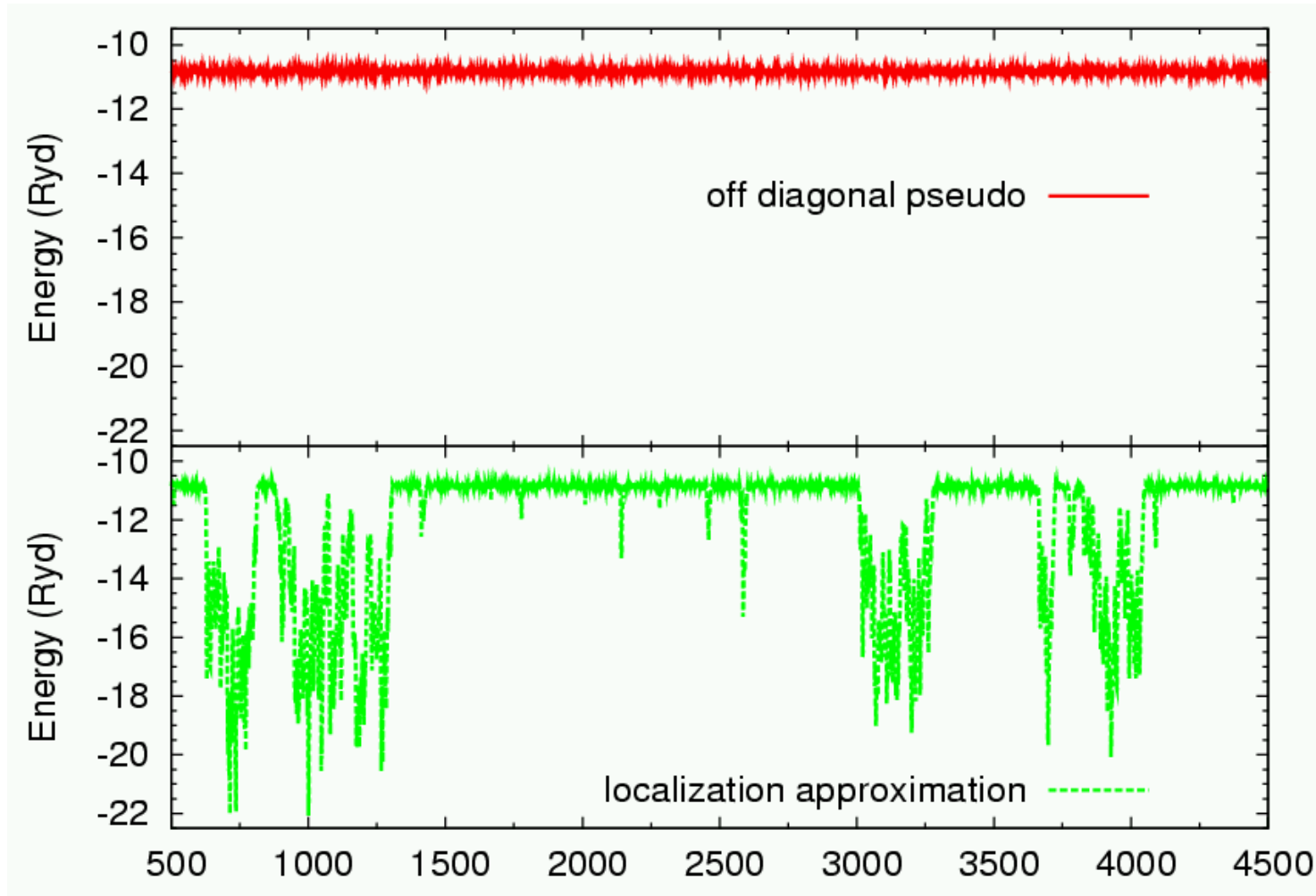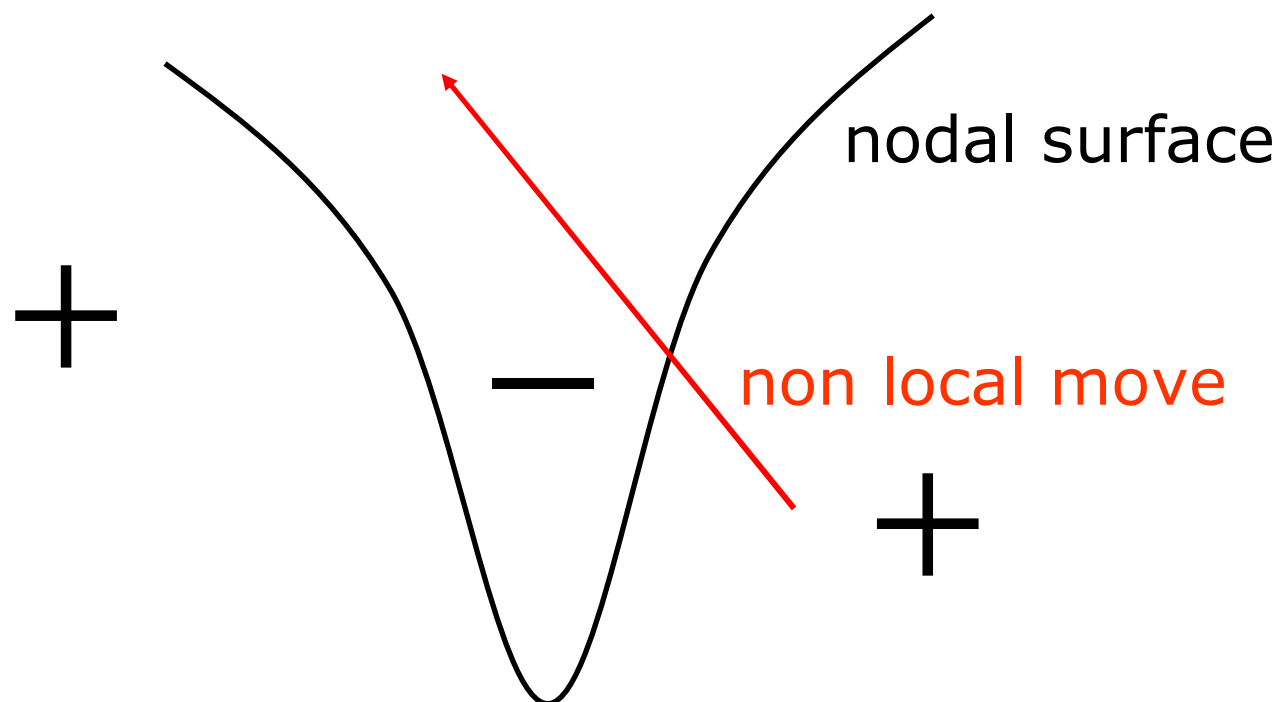
❑ locality approximation → large and negative attractive potential close to the nodal surface
(it works for good trial functions / small time steps)
❑ non local move → jumps the divergence and crosses the node
(the nasty negative contributions in the locality approximation are good non local matrix elements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

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DMC vs LRDMC

extrapolation properties

DMC	LRDMC
Trotter approximation	For each a well defined Hamiltonian
Time step τ extrapolation	Lattice space a extrapolation
τ (τ^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) $\propto \tau^{-1}(a^{-2})$

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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

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

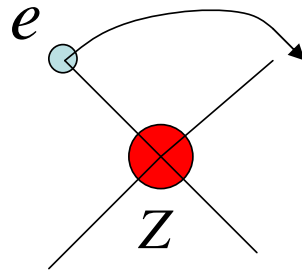$$w_{DMC}(x) = \exp\left\{-\tau\left[K + V_{loc}(x) + \sum_y V^+(y,x) - \Lambda\right]\right\}$$

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

$$w_T(x) = \exp\left[-\tau\sum_y V^-(y,x)\right]$$

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

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

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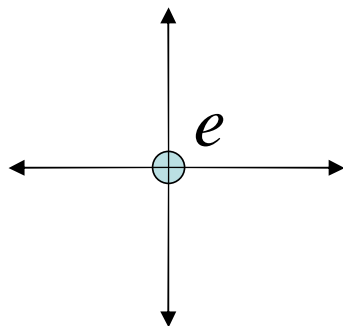
38

Error in the discretization
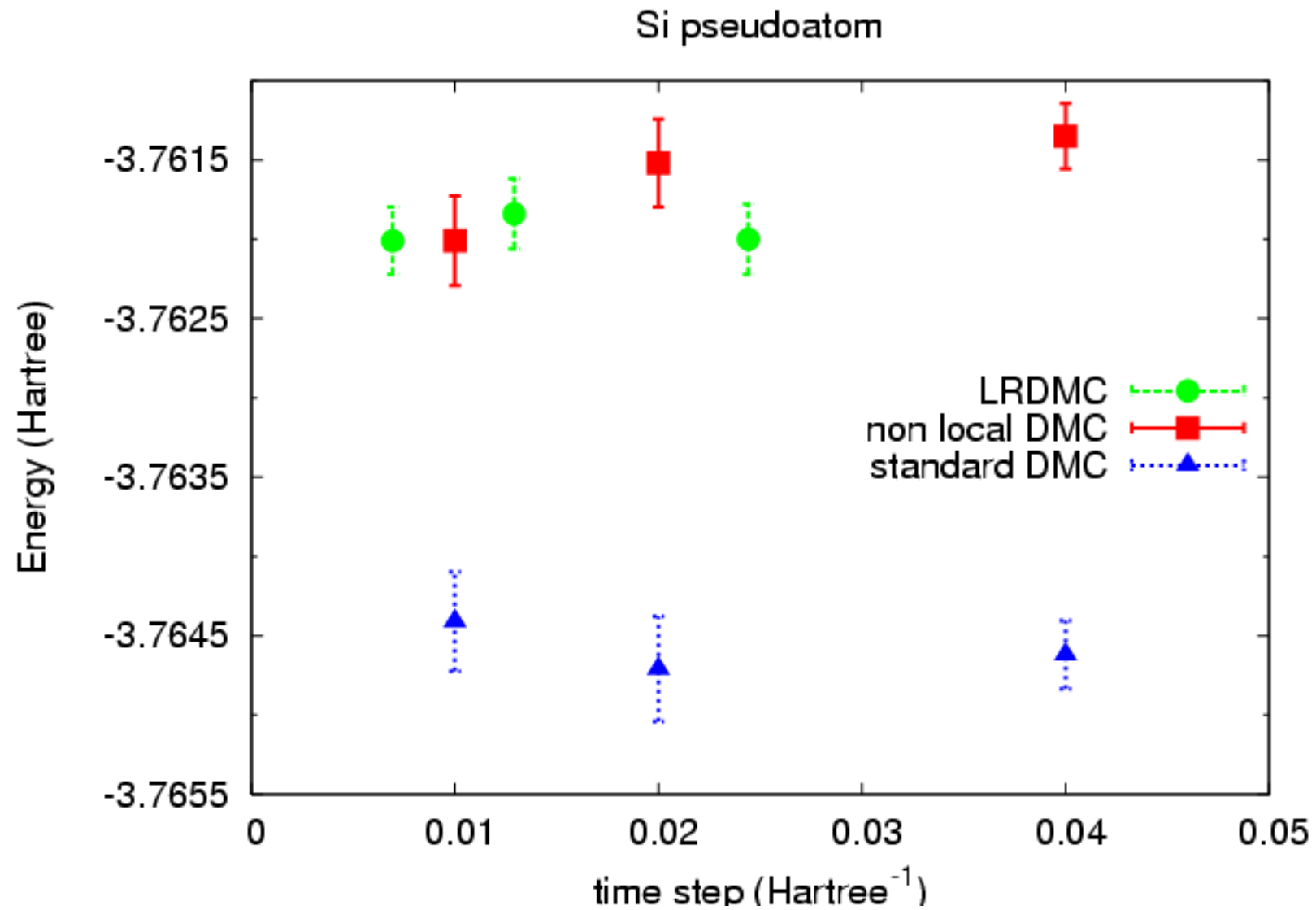
Discretized non local pseudopotential

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

Discretized Laplacian

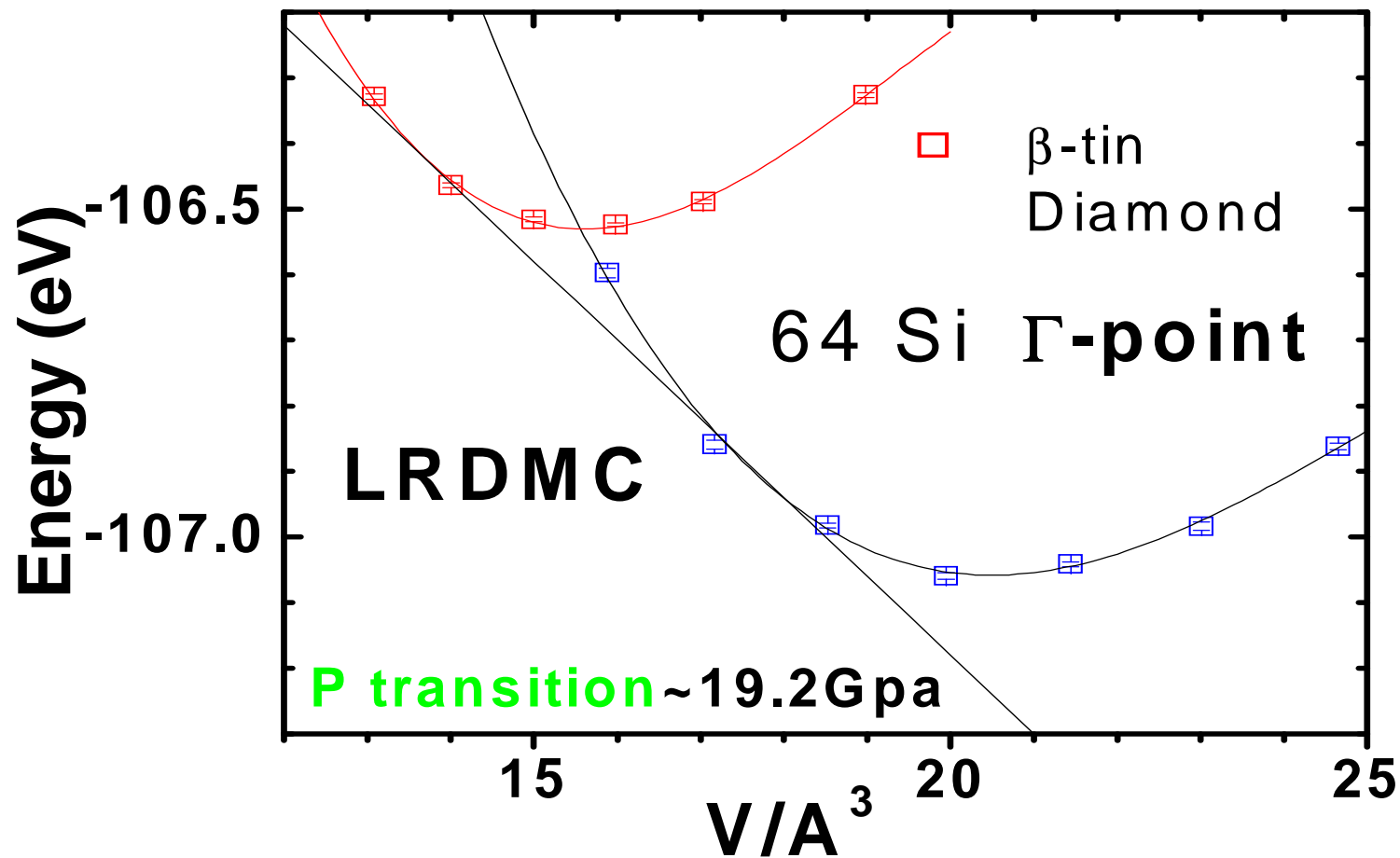discretization error reduced
by the introduction of a **double mesh**

Silicon

Si pseudoatom

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The metal insulator transition within LRDMC

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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

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

Z effective = 16

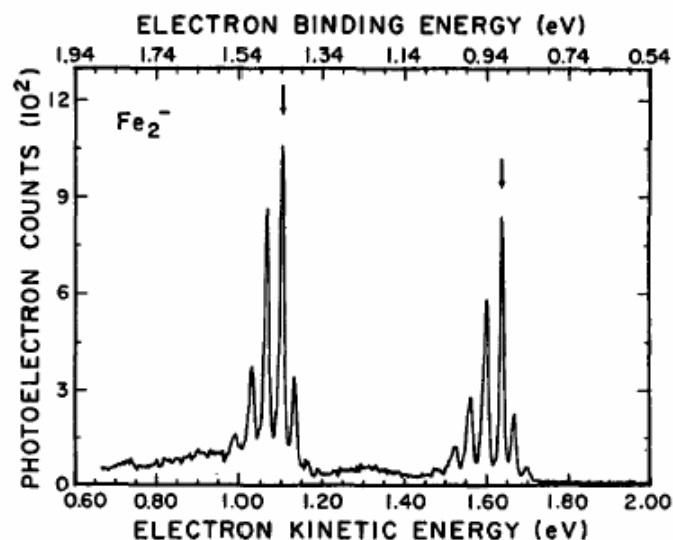| Time step	Non local DMC	LRDMC	Lattice space
0.0008	**1.0**	5.2	0.0284
0.0015	1.8	7.0	0.0390
0.0039	5.2	15.0	0.0625
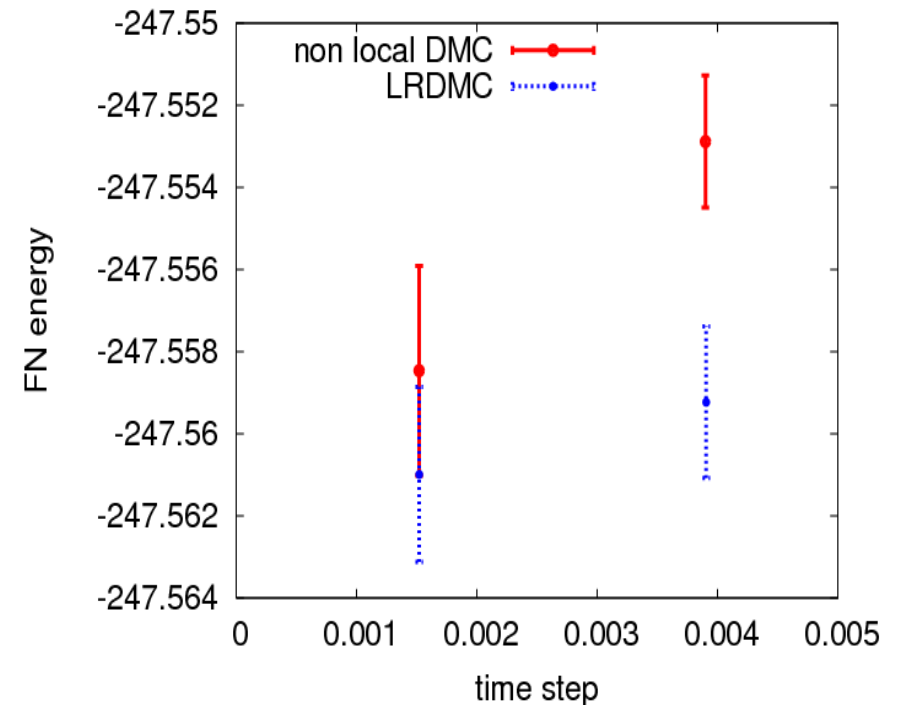
LRDMC is 3-5 times faster than the non local DMC

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

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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) but it is easier if you have to begin by scratch…
- 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).

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Iron dimer

PHOTOELECTRON SPECTROSCOPY

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

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

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

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Calculation details

Dolg pseudopotentials
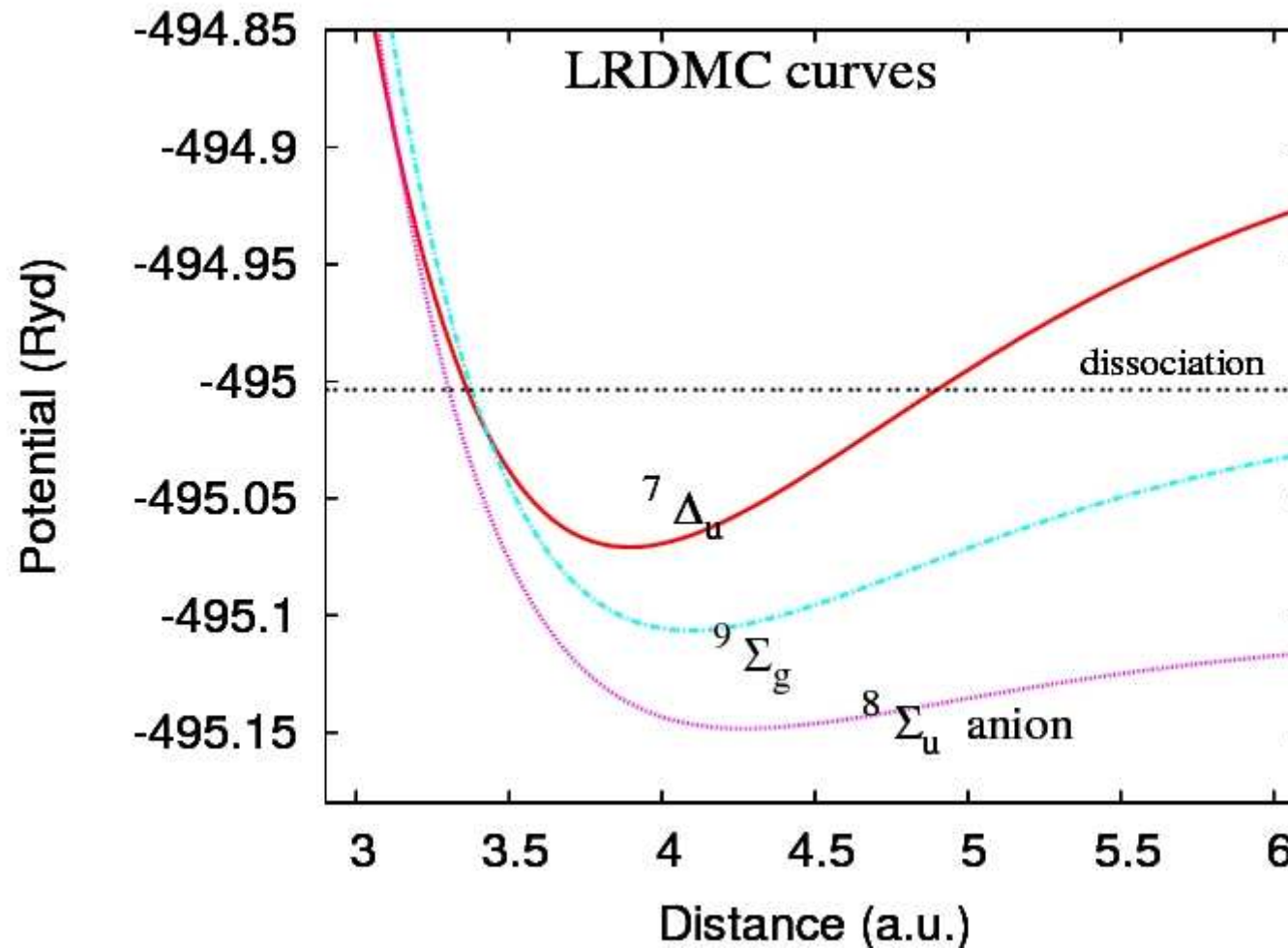
neon core

spd non local components

scalar relativistic corrections included

Gaussian basis set for JAGP wave function

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

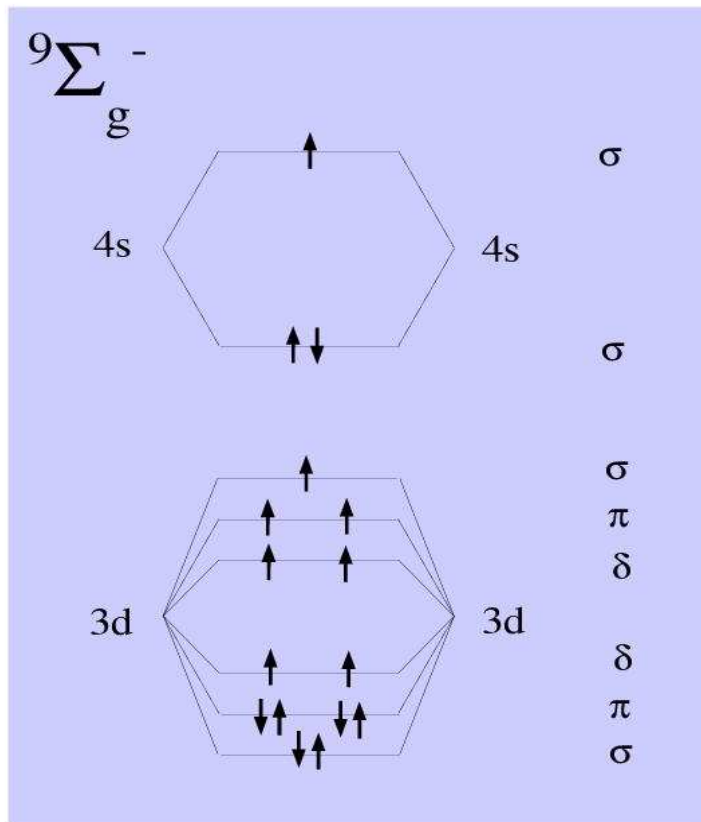Total independent parameters: 227

Dispersion curves

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Neutral ground state

LRDMC gives for neutral dimer

$$^9\Sigma_g^-$$

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

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Neutral ground state

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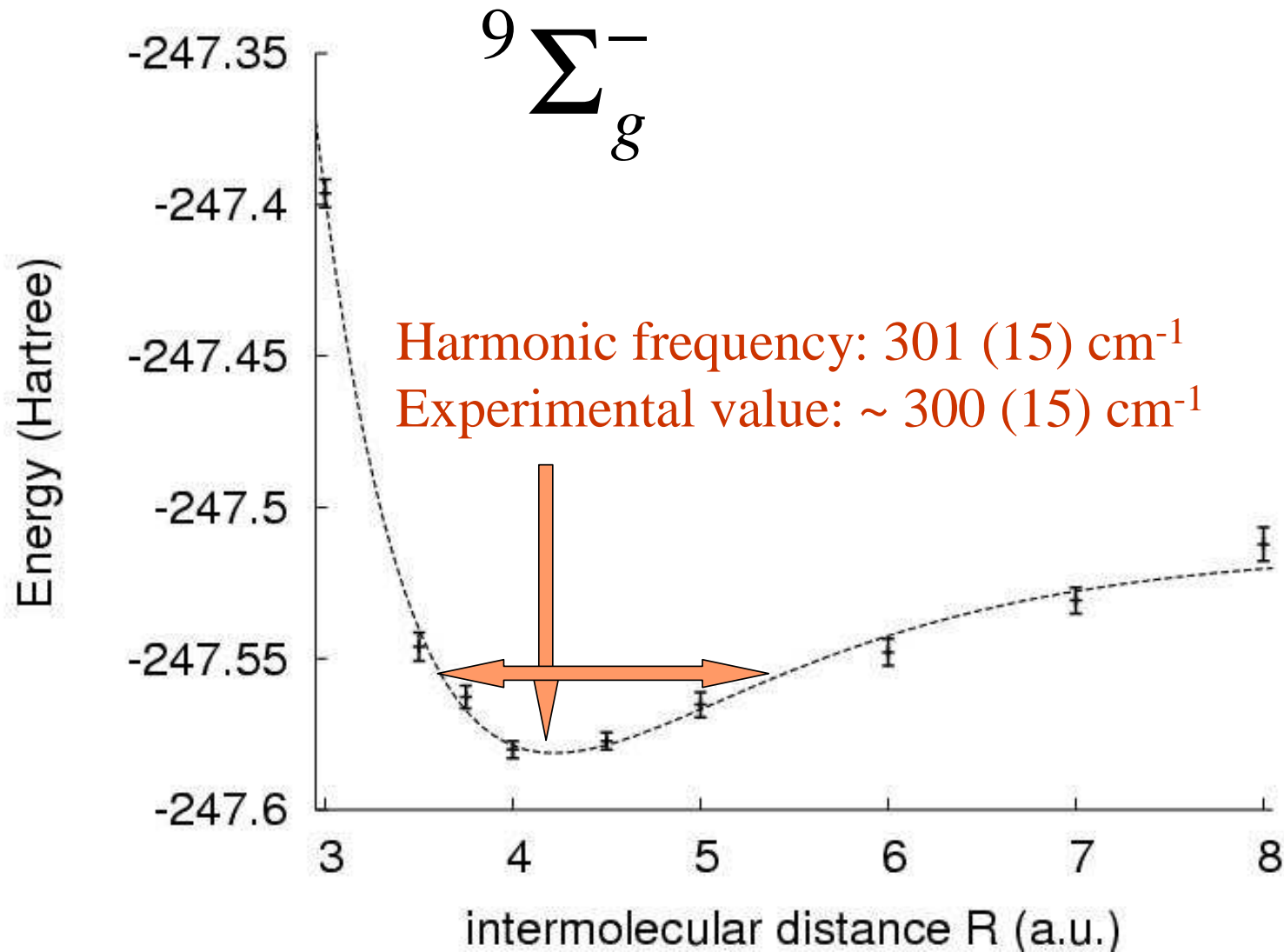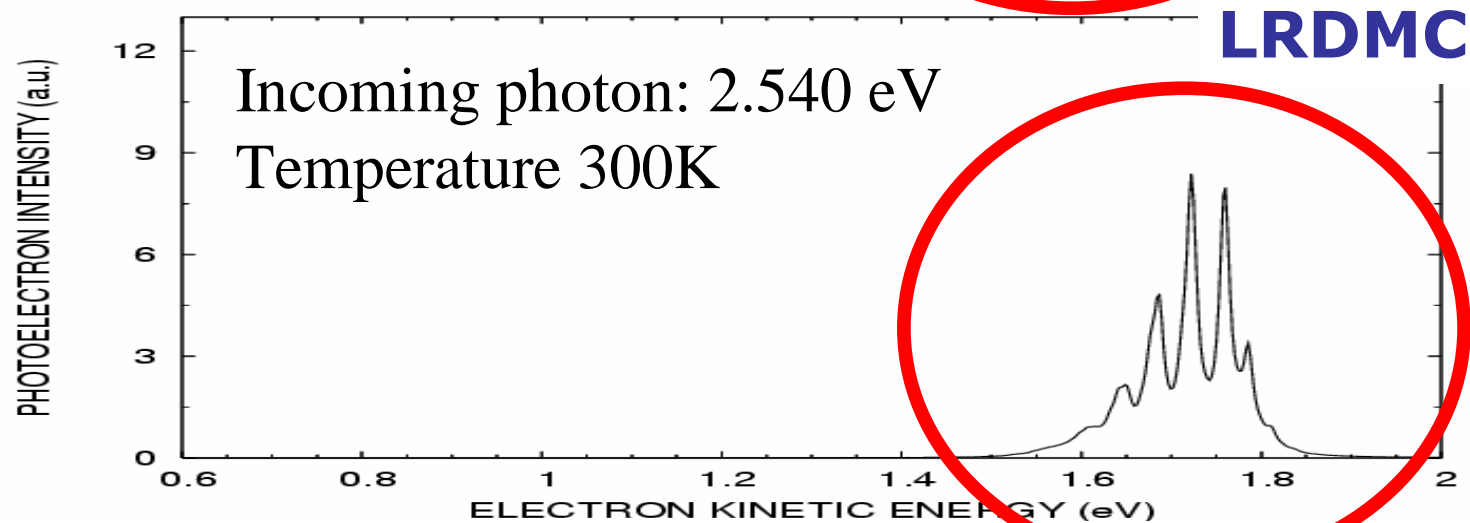

LRDMC
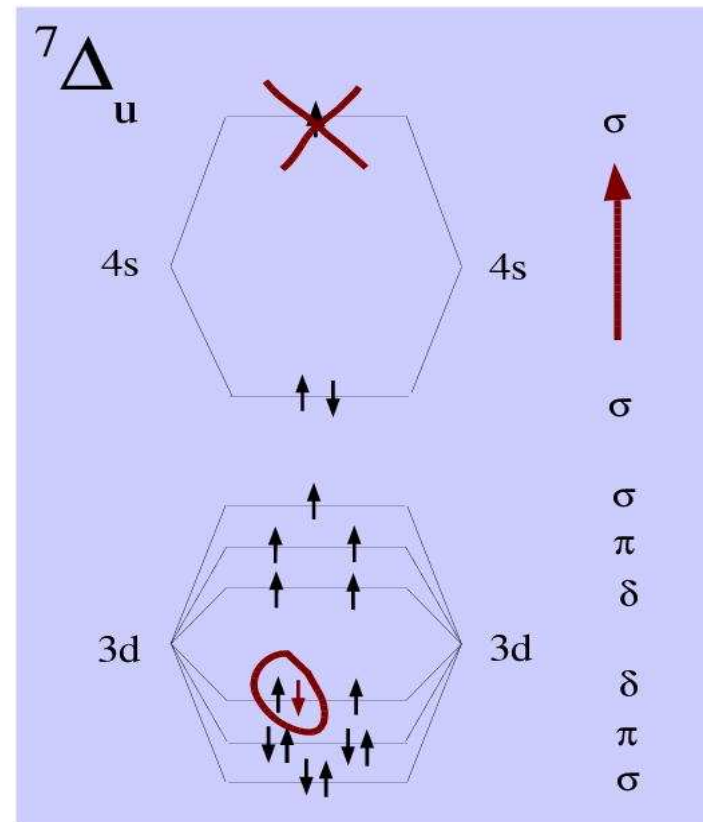
DFT-PP86

Physical Review B, 66 (2002) 155425

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Iron dimer: structural properties

$$^9\Sigma_g^-$$

Harmonic frequency: 301 (15) cm^{-1}
Experimental value: ~ 300 (15) cm^{-1}

Energy (Hartree) vs intermolecular distance R (a.u.)

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Iron dimer: photoelectron spectrum

Experiment

LRDMC

Incoming photon: 2.540 eV
Temperature 300K

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Benzene dimer

Van der Waals +
$\tilde{S} \tilde{S}$ interactions

Important for DNA
and protein structures

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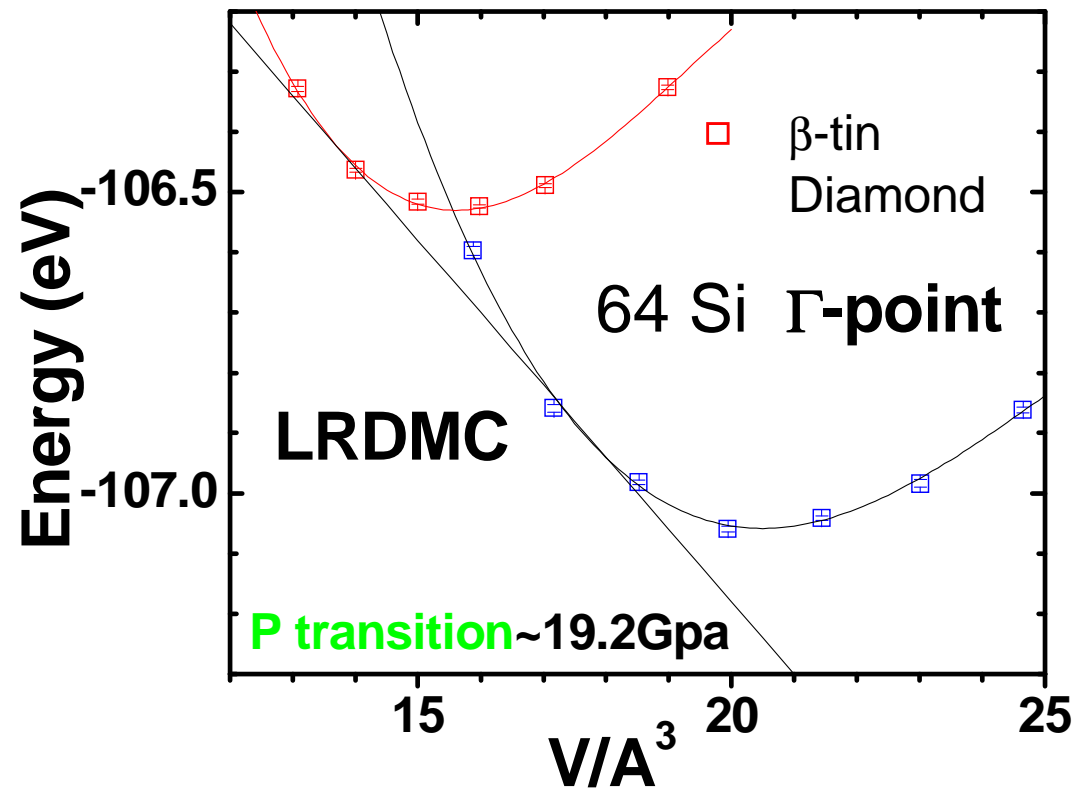**0.5(3) parallel**
2.2(3) slipped parallel
0.37   ZPE
1.6(2) experiment

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

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Conclusions

• The **pseudopotentials** can be "safely" included in the DMC, with the possibility to perform <u>accurate simulations for large or extended systems</u>, in solid state physics or quantum chemistry.

• The **fixed node approximation** is still the <u>major problem</u> for this zero temperature technique.

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The LRDMC upper bound theorem

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