Fixed-Node quantum Monte Carlo for Chemistry

Michel Caffarel
Lab. Physique et Chimie Quantiques, CNRS-IRSAMC,
Université de Toulouse
e-mail : caffarel@irsamc.ups-tlse.fr

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The N-body problem of Chemistry

We are essentially interested in the ground-state and low-lying excited states properties ($T = 0$ quantum problem)

Main difficulties :
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- Coulombic potential (nuclear attractions and electronic repulsion)
- Fermions (electrons) in 3D ordinary space.
- N large but finite.
- Very high accuracy on eigensolutions is required.

$\Longrightarrow$ a very difficult (the most difficult ?) N-body quantum problem !

The “chemical” Hamiltonian

$$H = \sum_{i,\sigma} \langle i|h|j\rangle a^{+}_{i\sigma} a_{j\sigma} + \sum_{i,j,k,l\sigma\sigma'} \langle ij|1/r_{12}|kl\rangle a^{+}_{i\sigma} a^{+}_{j\sigma'} a_{k\sigma'} a_{l\sigma}$$

where $|i\rangle$ denotes a set of N orthonormal i one-particle basis functions (molecular orbitals)

with $N \sim 10 n_{electrons}$! !

Chemical accuracy

- Atomization energies : $\Delta E_0/E_0 \lesssim 10^{-4}$
- Energy barriers, electronic affinities, etc. $\Delta E_0/E_0 \lesssim 10^{-5}$
- Weak intermolcular forces (Hydrogen bonds, van der Waals forces) $\Delta E_0/E_0 \lesssim 10^{-6}$

Standard approaches

- Density Functional Theories (DFT)

→ good but ill-controlled

- *Ab initio* wavefunction based approaches (SCF and post-SCF)

→ good but badly-converged

- quantum Monte Carlo (QMC)

→ ?

Essential points of QMC I

- Variational Monte Carlo (VMC) = Markov Chain Monte Carlo with density $\Pi = \psi_T^2$ (standard Metropolis scheme)

ψ_T = known trial wave function (use of the long-term experience of *ab initio* quantum chemistry)

Variational energy : $(\Psi_T, H\Psi_T)/(\Psi_T, \Psi_T)$ is computed as a simple average

$$E_{VMC} = \langle E_L \rangle_\Pi$$

where the local energy is defined as

$$E_L = H\Psi_T/\Psi_T$$

Trial wavefunction ψ_T

$$\psi_T(\vec{r}_1, ..., \vec{r}_{n_{elec}}) =$$

$$\sum_{K=1}^{N_c} c_K \exp\left[\sum_{i,j,\alpha} U_K(r_{i\alpha}, r_{j\alpha}, r_{ij})\right] ||\phi^{(K)}||_\alpha \, ||\phi^{(K)}||_\beta$$

- Spin-free formalism
- N_c= number of determinants
- $\exp U_K$ = Jastrow factors
- $\phi^{\alpha,\beta}_{(K)}(\vec{r})$ = one-electron spatial orbitals
- Without Jastrow factors : standard forms (SCF, DFT, VB, MCSCF, CI, ...)
- No particular constraints on the orbitals (gaussians, slaters, splines, ...)

Jastrow factor

Typical form :

$$\exp \sum_{\alpha} \sum_{<i,j>} U(r_{i\alpha}, r_{j\alpha}, r_{ij}) \tag{1}$$

$$U(r_{i\alpha}, r_{j\alpha}, r_{ij}) = s(x_{ij}) + p^{(\alpha)}(x_{i\alpha}) + c_1 x_{i\alpha}^2 x_{j\alpha}^2 + c_2 (x_{i\alpha}^2 + x_{j\alpha}^2) x_{ij}^2 + c_3 x_{ij}^2 \tag{2}$$

with

$$x_{ij} = \frac{r_{ij}}{1 + b_\sigma r_{ij}}$$

$$x_{i\alpha} = \frac{r_{i\alpha}}{1 + b_\alpha r_{i\alpha}}$$

$$s(x) = s_1 x + s_2 x^2 + s_3 x^3 + s_4 x^4$$

$$p^{(\alpha)}(x) = p_1^{(\alpha)} x + p_2^{(\alpha)} x^2 + p_3^{(\alpha)} x^3 + p_4^{(\alpha)} x^4,$$

Essential points of QMC II

- Optimization of the parameters entering ψ_T by minimizing energy or variance of energy :

Not so easy but we are able to optimize “relatively well” quite a large number of parameters (main problem : energy computed stochastically). Note that some interesting progress has been made very recently (see, Umrigar *et al.* Phys. Rev. Lett. **98** 110201 (2007))

Essential points of QMC III

DIFFUSION MONTE CARLO (DMC) :

- Markov Chain Monte Carlo of VMC

- + branching process : the configurations are multiplied or killed proportionally to w :

$$w \sim exp[-\tau(E_L - E_T)]$$

It can be shown that the probability density is no longer ψ_T^2, like in VMC, but

$$\Pi_{DMC} \sim \psi_T \phi_0$$

ϕ_0= unknown ground-state and we have :

$$E_0 = \langle E_L \rangle_\Pi$$

Particle Statistics

However, pb. with statistics :

- Bosons : Φ_0 has a constant sign → no problem

- Fermions (e.g., chemistry) : Φ_0 antisymmetric under the exchange of spin-like fermions $\Rightarrow$ Φ_0 has no longer a constant sign.

Essential points of QMC III

The positive density generated by the usual Fixed-Node (FN) DMC for fermions is biased :

$$\Pi_{DMC} = \Psi_T \Phi_{0,FN}$$

where $H\Phi_{0,FN} = E_{0,FN}\Phi_{0,FN}$

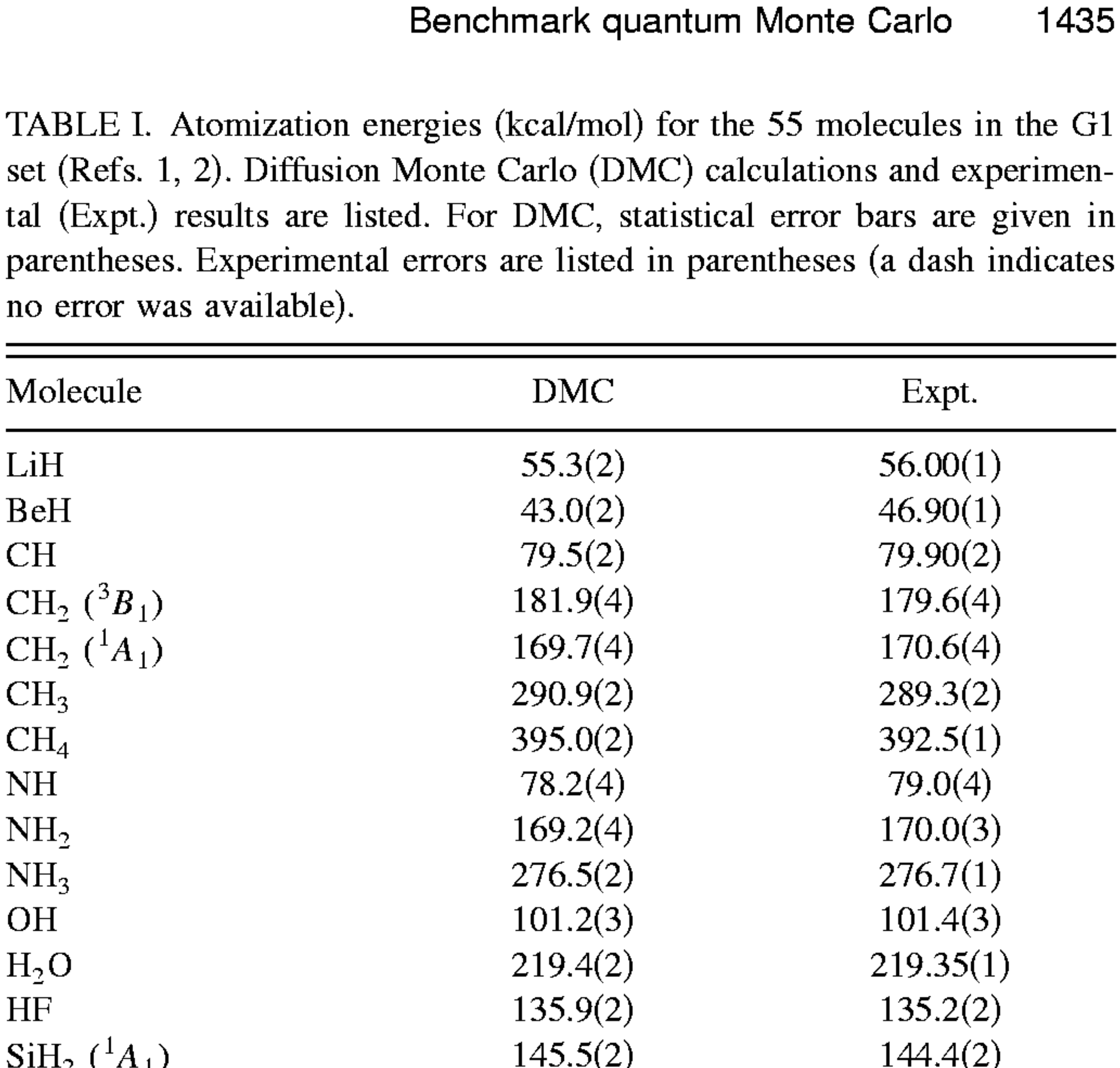
with $\Phi_{0,FN} = 0$ whenener $\Psi_T = 0$

Nodal hypersurfaces of $\Psi_T = 0$ are usually not exact
$\Rightarrow$ fixed-node error

Variational property : $E_{0,FN} \geq E_0$

Benchmark Grossman

Réf : J.C. Grossman J.Chem.Phys. **117**, 1434 (2002).



Benchmark quantum Monte Carlo 1435

TABLE I. Atomization energies (kcal/mol) for the 55 molecules in the G1 set (Refs. 1, 2). Diffusion Monte Carlo (DMC) calculations and experimental (Expt.) results are listed. For DMC, statistical error bars are given in parentheses. Experimental errors are listed in parentheses (a dash indicates no error was available).

Molecule	DMC	Expt.
LiH	55.3(2)	56.00(1)
BeH	43.0(2)	46.90(1)
CH	79.5(2)	79.90(2)
CH_2 ($^3B_1$)	181.9(4)	179.6(4)
CH_2 ($^1A_1$)	169.7(4)	170.6(4)
CH_3	290.9(2)	289.3(2)
CH_4	395.0(2)	392.5(1)
NH	78.2(4)	79.0(4)
NH_2	169.2(4)	170.0(3)
NH_3	276.5(2)	276.7(1)
OH	101.2(3)	101.4(3)
H_2O	219.4(2)	219.35(1)
HF	135.9(2)	135.2(2)
SiH_2 ($^1A_1$)	145.5(2)	144.4(2)

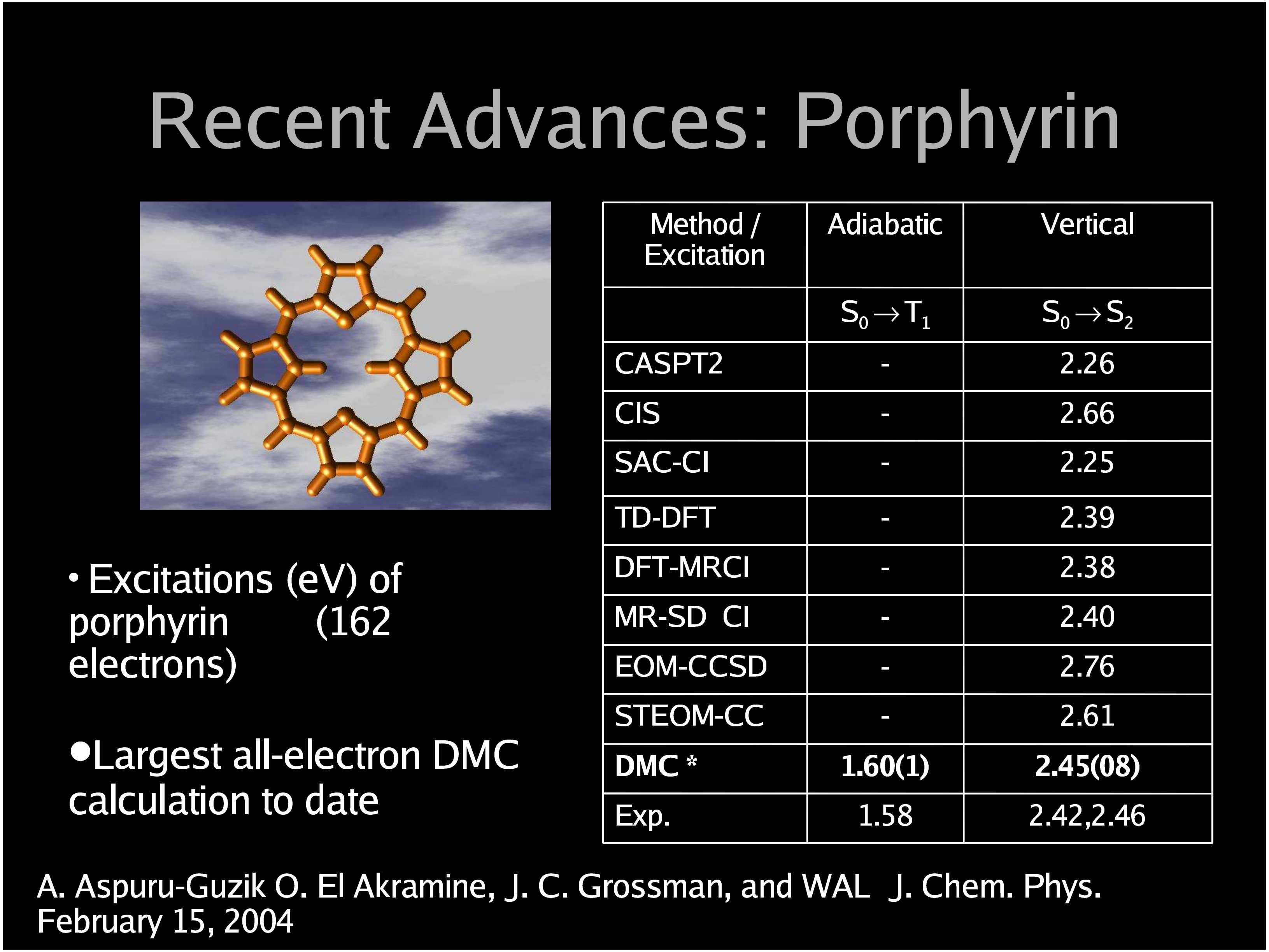
Benchmark Grossman, 2002

G1 set Pople and collab. (1990) = 55 molecules.
Atomisation energies

FN-DMC, pseudo-potential for representing the effect of 1s electrons, mono-configurational wavefunction

Mean absolute deviation : ϵ_{MAD}

- FN-DMC : $\epsilon_{MAD} = 2.9 kcal/mol$
- LDA : $\epsilon_{MAD} \sim 40 kcal/mol$
- GGA : (B3LYP et B3PW91) $\epsilon_{MAD} \sim 2.5 kcal/mol$
- CCSD(T)/aug-cc-pVQZ $\epsilon_{MAD} \sim 2.8 kcal/mol$



Recent Advances: Porphyrin

Method / Excitation	Adiabatic	Vertical
	$S_0 \rightarrow T_1$	$S_0 \rightarrow S_2$
CASPT2	-	2.26
CIS	-	2.66
SAC-CI	-	2.25
TD-DFT	-	2.39
DFT-MRCI	-	2.38
MR-SD CI	-	2.40
EOM-CCSD	-	2.76
STEOM-CC	-	2.61
DMC *	**1.60(1)**	**2.45(08)**
Exp.	1.58	2.42,2.46

- Excitations (eV) of porphyrin (162 electrons)

- Largest all-electron DMC calculation to date

A. Aspuru-Guzik O. El Akramine, J. C. Grossman, and WAL J. Chem. Phys.
February 15, 2004

Reducing errors in FN-DMC for chemistry

Two types of errors :

I. Statistical error like in any Monte Carlo scheme

II.Systematic errors (biases) : mainly the fixed-node error, the other biases can be controlled.

Statistical error

- For a stable calculation (bosons or fermions treated with FN approximation) :

$$\langle F \rangle_{\Pi} + \delta F$$

with

$$\delta F = \frac{\sigma(F)}{\sqrt{N/N_c}}$$

where $\sigma(F) = \sqrt{\langle F^2 \rangle - \langle F \rangle^2}$

N = number of Monte Carlo steps

N_c = correlation time in unit of time step

Sign problem

- For an unstable calculation where fermions are treated exactly (nodal release-type approaches) :

$$\delta E \sim \frac{e^{(E_F - E_B)N}}{\sqrt{N}}$$

where :

$E_F =$ fermion ground-state energy, $E_F \sim O(N)$

$E_B =$ boson ground-state energy, $E_B \sim O(N^\gamma)$ with $\gamma > 1$

→ famous "sign problem"

Reducing statistical errors

$$\delta F = \frac{\sigma(F)}{\sqrt{N/N_c}}$$

where $\sigma(F) = \sqrt{\langle F^2 \rangle - \langle F \rangle^2}$

An efficient way of decreasing ϵ is to reduce σ :

“Improved” or “renormalized” estimators :

$$\langle \tilde{F} \rangle_{\Pi} = \langle F \rangle_{\Pi} \quad \text{and} \quad \sigma^2(\tilde{F}) << \sigma^2(F). \tag{3}$$

Strategy developed during these last years [R.Assaraf and MC, PRL **83** (1999), , JCP **113** (2000) and JCP **119** (2003)]

Reducing statistical errors

Here, recent application to one-body densities and properties (R.Assaraf et al. Phys.Rev.E **75** 035701 (2007))

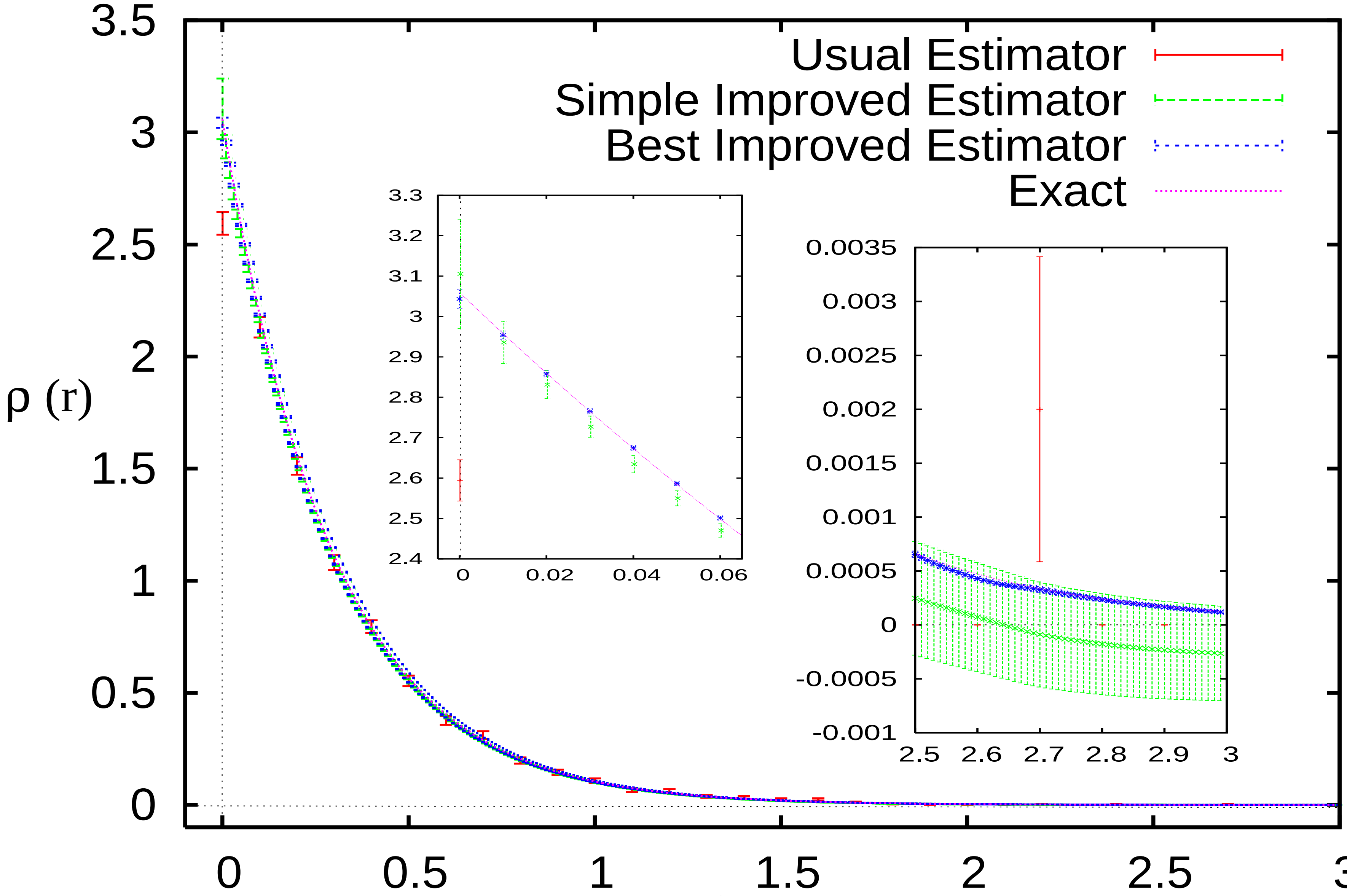
$$\rho(\mathbf{r}) = \langle \sum_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{r}) \rangle_\Pi \tag{4}$$

Improved estimator :

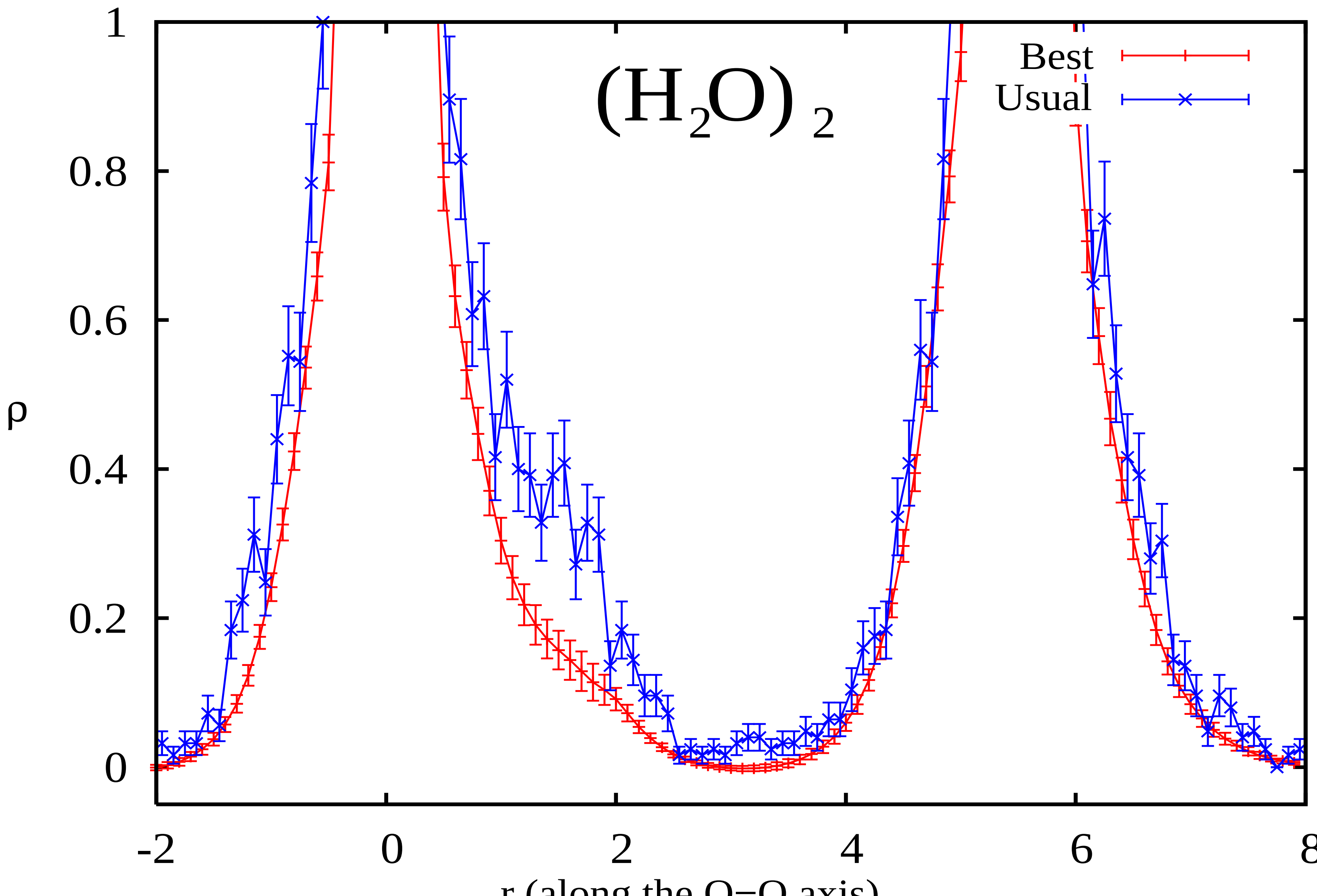
$$\rho(\mathbf{r}) = -\frac{1}{4\pi} \sum_{i=1}^{N} \langle [\frac{1}{|\mathbf{r}_i - \mathbf{r}|} - g] \frac{\nabla_i^2 (f\Pi)}{\Pi} \rangle_\Pi, \tag{5}$$

where f, g two arbit. funct. adjusted to lower statistical errors

Reducing statistical errors



Reducing statistical errors



Reducing statistical errors

Advantages :

- Errors can be greatly reduced (orders of magnitude)
- Can be used for any type of Monte Carlo simulation
- Compute density everywhere in space
- The density is much smoother over a larget set of grid points (132651 for the water dimer, below)

Fixed-Node Error and Chemistry

Correlation energy : CE $\equiv$ E$_0$(exact) - E$_0$[mean-field(SCF)]

CE/E$_0$(exact) $\sim$ 1/1000

The fixed-node is “small” $\sim$ a few percent of the correlation energy (relative error on E$_0$ of about a few 1/100000 ! !) ....

However :

Dissociation barrier of O_4

[Collaboration with A. Ramírez-Solís, R. Hernández-Lamoneda (Cuernavaca, Mexique) and A. Scemama (Paris, LCT)].

O_4 (metastable) $\rightarrow$ O_4 (transition state, TS) $\rightarrow$ 2 O_2 (triplet)

Expt : some indications that the barrier between O_4 $\rightarrow$ and O_4(TS) is greater than 10 kcal.

FN-DMC calculations : O_4 $\rightarrow$ O_4 (TS) = 26.2 +/- 2.9 kcal with SCF nodes

O_4 $\rightarrow$ O_4 (TS) = 12. +/- 1.6 kcal with MCSCF nodes

Most sophisticated *ab initio* calculations (CCSD(T),ACPF) : 8-9 kcal

Fixed-Node DMC for Cr_2

Experimental binding energy $\sim$ -0.056 a.u.

SCF Binding energy (basis set= [20s12p9d5f])

E(Cr_2)-2 E(Cr) = + 0.795 a.u. unbound (by far !) molecule

Fixed-node DMC calculation :

SCF nodes : E(Cr_2)-2 E(Cr) = + 0.01(3)

Cr_2 is not bound (or slightly bound) at the Fixed-SCF Node DMC level ! !

Fixed-Node DMC for Cr_2

Very interesting comparison with Scuseria's calculation (1991) :

Scuseria : (10s8p3d2f1g) $E_{SCF}(R_{opt} = 2.76)$=-2085.952 a.u.

Here : (20s12p9d5f) $E_{SCF}(R = 3.2)$=-2085.917 a.u.

Correlated calculations for E_0 :

E_0[CCSD(T) ;$R_{opt} = 3.03$]= -2087.516 a.u.

E_0[FN-DMC ;$R = 3.2$]= -2088.612(24) a.u. (about 1.1 a.u. lower ! !)

Binding energies :

Scuseria : -0.018

Here : +0.01(3)

⇒ "monoconfigurational nodes" is the problem...

Some conclusions

We need either :

to improve the trial wave functions with the hope that nodal hypersurfaces are improved (e.g., Umrigar and coll.)

or :

to get some physical insight into fermionic nodes for coulombic systems (e.g., Bressanini et coll., Mitas et coll.)

or :

to solve the sign problem (e.g., almost everyone in QMC..)

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