

Quantum Monte Carlo for molecules

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Cross talks in the physics of many-body systems, 6-8
December 2006



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Institut de Recherche sur les Systèmes
Atomiques et Moléculaires Complexes

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The many-body problem considered

- **T=0 quantum problem** : we are interested in the ground-state and low-lying excited states properties
- **Coulombic potential** (nuclear attractions and electronic repulsion)
- **Fermions** (electrons) in 3D ordinary space

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

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

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

- Spin-free formalism
- N_c = number of determinants
- $\exp U_K$ = Jastrow factors
- $\phi_{(K)}^{\alpha,\beta}(\vec{r})$ = 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 :

$$\exp \sum_{\alpha} \sum_{\langle i,j \rangle} U(r_{i\alpha}, r_{j\alpha}, r_{ij}) \quad (1)$$

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

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.* arXiv : cond-mat/0611094)

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 \rightarrow no problem
- Fermions (e.g., chemistry) : Φ_0 antisymmetric under the exchange of spin-like fermions $\Rightarrow \Phi_0$ 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 $\Phi_{0,FN} = 0$ whenever $\Psi_T = 0$

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 (³ B ₁)	181.9(4)	179.6(4)
CH ₂ (¹ A 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 ₂ O	219.4(2)	219.35(1)
HF	135.9(2)	135.2(2)
SiH ₂ (¹ A 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 : $\epsilon_{MAD} = 2.9kcal/mol$
- LDA : $\epsilon_{MAD} \sim 40kcal/mol$
- GGA : (B3LYP et B3PW91) $\epsilon_{MAD} \sim 2.5kcal/mol$
- CCSD(T)/aug-cc-pVQZ $\epsilon_{MAD} \sim 2.8kcal/mol$

Recent Advances: Porphyrin



- Excitations (eV) of porphyrin (162 electrons)

- Largest all-electron DMC calculation to date

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

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 :

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

Strategy developed during these last years (R.Assaraf and M.C., PRL(1999), JCP (2000) and (2003))

Reducing statistical errors

Here, very recent application to **one-body densities and properties** (physics/0610132)

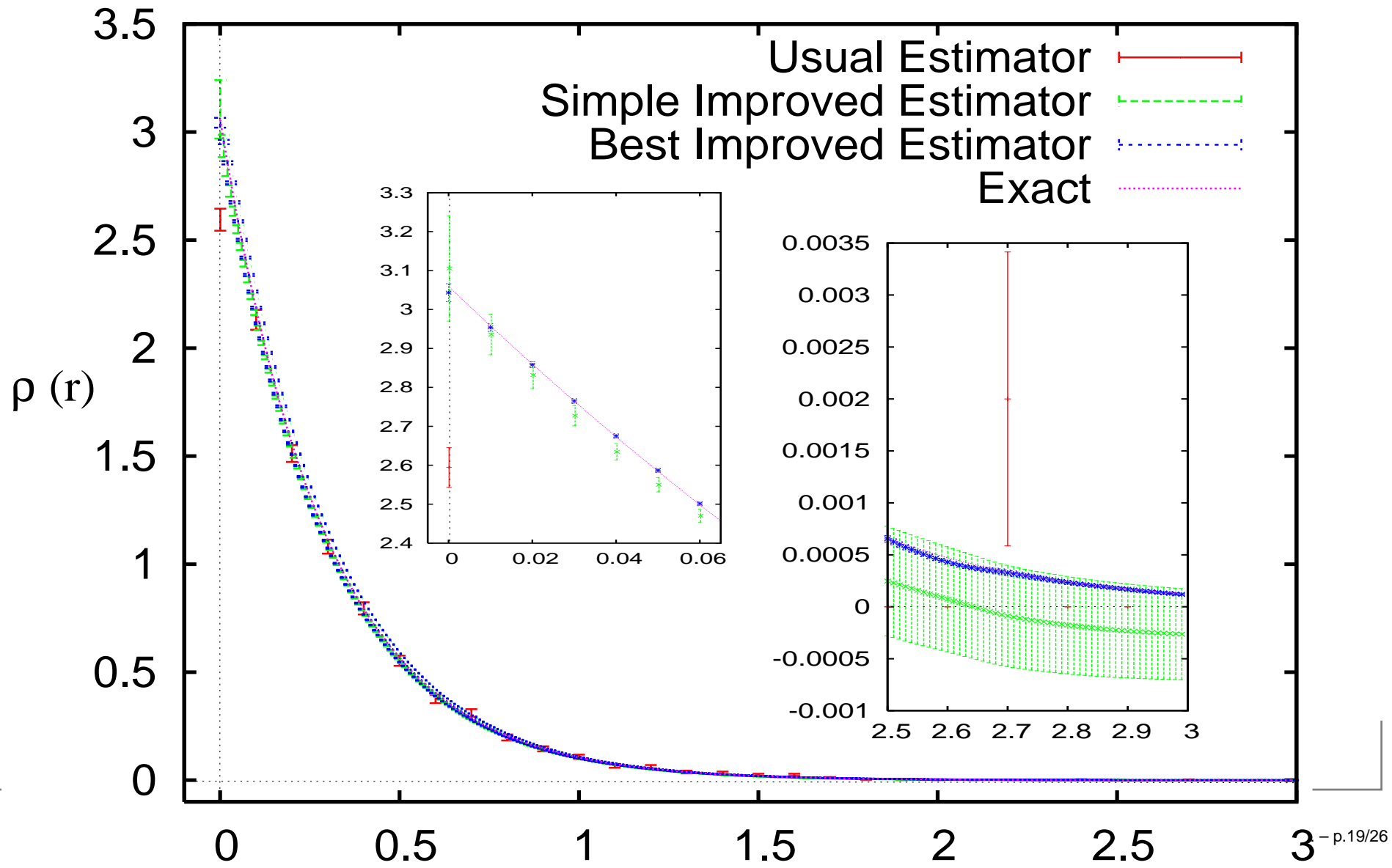
$$\rho(\mathbf{r}) = \left\langle \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle_{\Pi} \quad (4)$$

Improved estimator :

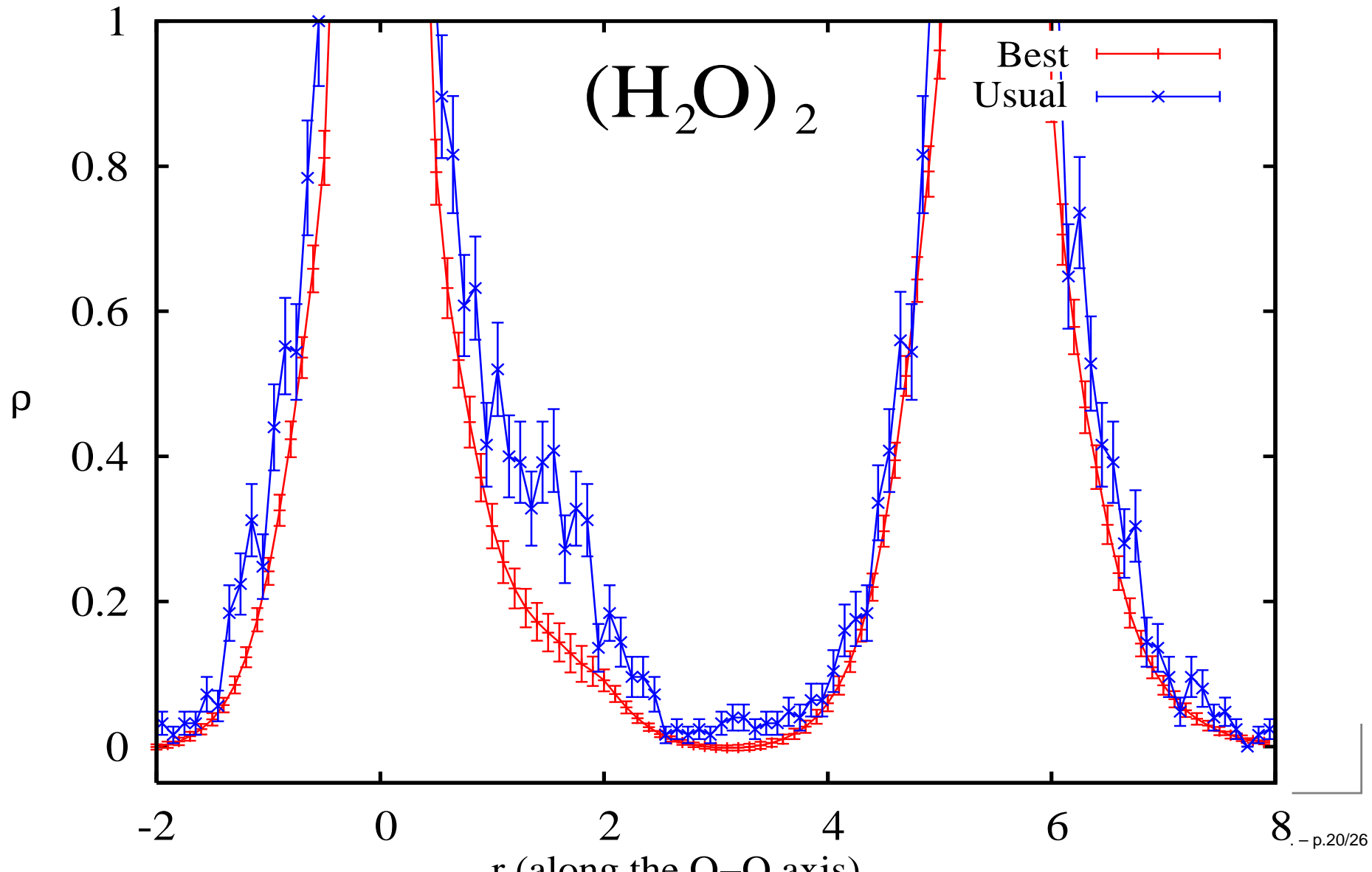
$$\rho(\mathbf{r}) = -\frac{1}{4\pi} \sum_{i=1}^N \left\langle \left[\frac{1}{|\mathbf{r}_i - \mathbf{r}|} - g \right] \frac{\nabla_i^2 (f\Pi)}{\Pi} \right\rangle_{\Pi}, \quad (5)$$

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 target set of grid points (132651 for the water dimer, below)

Fixed-Node Error and Chemistry

Correlation energy : $CE \equiv E_0(\text{exact}) - E_0[\text{mean-field(SCF)}]$

$CE/E_0(\text{exact}) \sim 1/1000$

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 O₄

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

O₄ (metastable) → O₄ (transition state, TS) → 2 O₂ (triplet)

Expt : some indications that the barrier between O₄ → and O₄(TS) is **greater than 10 kcal**.

FN-DMC calculations : O₄ → O₄ (TS) = **26.2 +/- 2.9 kcal**
with SCF nodes

O₄ → O₄ (TS) = **12. +/- 1.6 kcal** with MCSCF nodes

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

Fixed-Node DMC for Cr₂

Experimental binding energy ~ -0.056 a.u.

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

$E(\text{Cr}_2) - 2 E(\text{Cr}) = + 0.795$ a.u. unbound (by far!) molecule

Fixed-node DMC calculation :

SCF nodes : $E(\text{Cr}_2) - 2 E(\text{Cr}) = + 0.01(3)$

**Cr₂ is not bound (or slightly bound) at the Fixed-SCF Node
DMC level!!**

Fixed-Node DMC for Cr₂

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 :

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

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

Binding energies :

Scuseria : -0.018

Here : +0.01(3)

⇒ “monoconfigurational nodes” is the problem...

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