

## Abstracts

### A few aspect of QMC for molecules

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(joint work with R. Assaraf, A. Khelif, A. Scemama, A. Ramírez-Solís)

In this talk a number of recent works aimed at improving quantum Monte Carlo (QMC) approaches for molecular structure are reported.

#### 1. IMPROVED ONE-PARTICLE PROPERTIES

First, a recent proposal to greatly increase the efficiency of Monte Carlo calculations of one-body properties (*e.g.* charge and spin densities) is presented. The general idea is to construct an “improved” estimator whose average is identical to the desired average but with a much smaller variance.[1, 2, 3]

In the case of the charge density,  $\rho(\mathbf{r})$ , the standard estimator has the following form

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

where  $N$  is the number of particles (here, electrons) and  $\Pi$  the underlying probability density sampled by Monte Carlo. Our proposed improved estimator is

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

where the two functions  $f$  and  $g$  play the role of auxiliary quantities. They are introduced to decrease as much as possible the variance of the density estimator. As with any optimization problem, there is no universal strategy for choosing  $f$  and  $g$ . However, the guiding principle is to identify the leading sources of fluctuations and, then, to adjust the auxiliary functions to remove most of them.

Let us emphasize that this approach is not limited to QMC calculations; our estimator can be readily used in any type of Monte Carlo simulation (*e.g.* Monte Carlo for classical thermodynamics). Furthermore and in sharp contrast with the usual estimator based on the regularization of the delta-function on a grid, our expression leads to accurate estimates of the density at any point in space, even in the regions never visited during the Monte Carlo simulation (*e.g.*, in the large-distance regime). This property is particularly interesting when a global knowledge of the density map is searched for.

Here, we present an application to the water dimer for which we have been able to compute a smooth and accurate map of the charge density for a large number of grid points ( $51 \times 51 \times 51 = 132651$  points). Remark that such a calculation would be vastly more difficult with the standard approach. Details of the method can be found in Ref.[4].

## 2. THE FERMION MONTE CARLO METHOD REVISITED

A second work presented here concerns a detailed mathematical study of a recent proposal by Kalos *et al.*[6] -the Fermion Monte Carlo (FMC) method- to solve the “Fermion-sign” problem. This problem is presently considered as one of the most important challenge in computational physics. In short, the FMC method is based on the use of two types of walkers simulating the positive and negative parts of the signed wavefunction. The “positive” and “negative” walkers are correlated so that to meet with a high probability and, whenever they meet, a cancellation step is done. We have performed a careful mathematical analysis of the various aspects of the method. We have shown that FMC is indeed *exact*. However, the method is still *unstable* but with a weaker instability. We have proved that the statistical error  $\delta E$  on the energy behaves as  $\delta E \sim \frac{e^{(E_F - \tilde{E}_B)N}}{\sqrt{N}}$  where  $E_F$  is the fermi ground-state energy,  $E_B$  the bose ground-state energy, and  $\tilde{E}_B$  some effective bose energy verifying  $E_F \geq \tilde{E}_B > E_B$ . Note that the exact QMC methods proposed so far can be viewed as unstable approaches with  $\tilde{E}_B = E_B$  (no change of the Bose state). To summarize, FMC is as an exact fermion method having an attenuate exponential blow up of statistical fluctuations at large simulation times. However, the pathological behavior of the error as a function of the number of fermions (rapid increase of the Bose-Fermi gap) is still present. Details about this study can be found in Ref.[5].

## 3. FIXED-NODE ERROR IN CHEMISTRY

A last work presented here concerns the role played by the “fixed-node” error in the chemistry of real systems. It is usually said that the fixed-node approximation is very good. For total energies it is certainly true since, in general, the fixed-node error represents only a few percents of the total correlation energy (defined as the difference between the exact and the Hartree-Fock energies), a result which is considered as very good in computational chemistry. However, we emphasize that such impressive result does not necessarily extend to the calculations of the *very small differences* of energies involved in chemistry. In other words, the small errors in total energies can lead to large uncontrolled errors in the very small energy differences we are interested in. When computing differences of energies with standard *ab initio* wavefunction-based and DFT methods a large cancellation of systematic errors is at work (use of a common basis set and common molecular orbitals not involved in the chemical process). This is not the case in QMC simulations. Let us present two applications illustrating this important point.

### A. Dissociation barrier of $O_4$

We are interested in the process:  $O_4$  (singlet metastable state)  $\Leftrightarrow O_4$  [singlet transition state (TS)]  $\Leftrightarrow 2 O_2$  (stable triplet state). Experimental results indicate that the dissociation barrier associated with  $O_4 \Rightarrow O_4(\text{TS})$  is probably greater than 10 kcal. Sophisticated *ab initio* calculations [CCSD(T), ACPF, etc.] lead to a barrier of about 8-9 kcal. Our fixed-Node DMC calculations give a barrier of  $26.2 \pm 2.9$  kcal with SCF nodes, and  $12.7 \pm 3.7$  kcal with MCSCF nodes. As seen,

the value of the dissociation barrier is very dependent on the nature of the nodes (“monoconfigurational” or “multiconfigurational”).

### B. Fixed-Node DMC for Cr<sub>2</sub>.

The chromium dimer is known to be a very difficult problem for all computational chemistry approaches. The experimental binding energy of this molecule is  $\sim -0.056$  a.u. The SCF binding energy (basis set= [20s12p9d5f]) is about  $+0.795$  a.u. In other words the “SCF molecule” does not exist (unbound by a large amount). Our fixed-node DMC calculation obtained with SCF nodes leads to:  $E_0(\text{Cr}_2) - 2E_0(\text{Cr}) = +0.01(3)$ . Cr<sub>2</sub> is therefore found to be unbound (or slightly bound) at the fixed-node DMC level with “monoconfigurational” nodes, although a large part of the correlation energy is recovered. Clearly, in this case, multiconfigurational trial wavefunctions are called for. This result illustrates the importance of correctly describing the nodal structure of the exact wavefunctions when applying FN-DMC. Details about fixed-node simulations for “difficult” systems of quantum chemistry can be found in [7, 8].

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### Numerical analysis for electronic structure calculations: an overview

ERIC CANCE`S

The first part of my talk will be devoted to the numerical simulation of the Hartree-Fock model for molecular systems of moderate size (up to a few hundreds of electrons). After recalling the structure and the main mathematical properties of the Hartree-Fock model, I will present some theoretical results on Self-Consistent Field (SCF) algorithms [1]. In particular, I will analyze the failures of the Roothaan algorithm [2], and introduce the Optimal Damping Algorithm [3, 4]