

DISCRETE CALCULATION OF POLARIZABILITY AND ENERGIES

Nancy-Université
Université
Henri Poincaré

Bastien Mussard, János G. Ángyán, Sébastien Lebègue
CRM², Faculté des Sciences, Université Henry Poincaré, Nancy

CRM²
Cristallographie, Résonance Magnétique et Modélisations

bastien.mussard@crm2.uhp-nancy.fr

Background

The expression of the *correlation energy* when using an adiabatic-connection fluctuation-dissipation DFT based on range separation is :

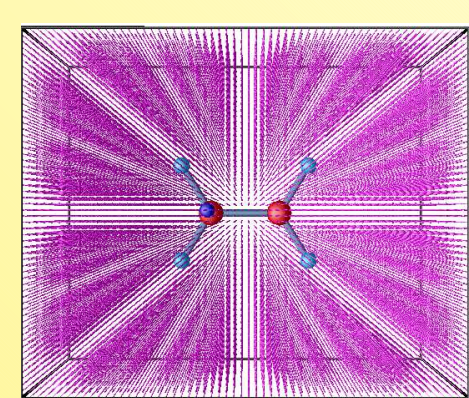
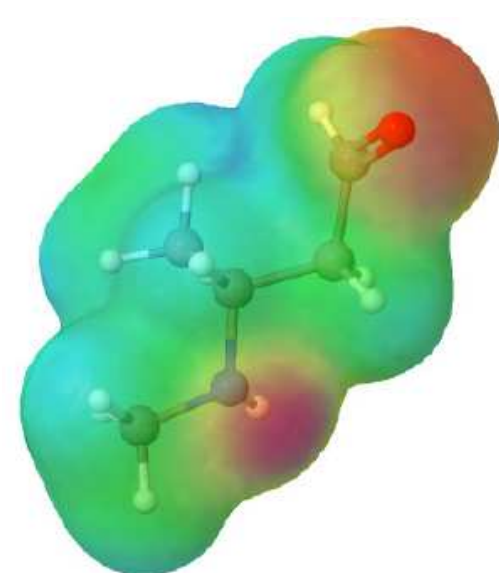
$$E_c = \frac{1}{2} \int_0^1 d\alpha \int_{r_1, r_2} w(r_1, r_2) \cdot P_{c,\alpha}(r_1, r_2)$$

$$P_{c,\alpha}(r_1, r_2) = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} (\chi_{\alpha}(r_1, r_2) - \chi_0(r_1, r_2))$$

χ : the density response function, as in linear response theory

$$\Delta\rho(r_1; \omega) = \int dr_2 \chi(r_1, r_2; \omega) V(r_2; \omega)$$

detailed ref : [1]



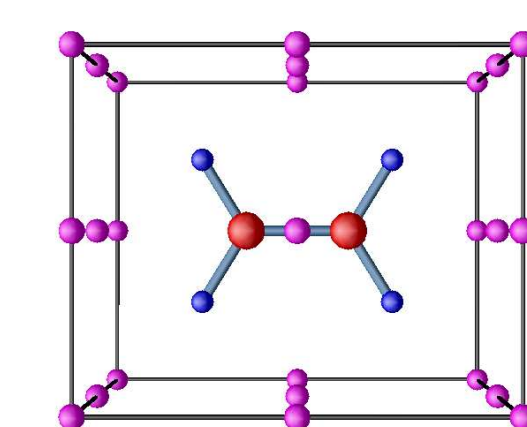
Starting point

The idea : use a spatial grid to calculate χ .

Lehmann representation formula :

$$\chi(A, B; i\omega) = \sum_{i \in occ} \sum_{a \in vir} \phi_i(A) \phi_a^*(A) \phi_a^*(B) \phi_i(B) \frac{2\epsilon_{ai}}{\omega^2 + \epsilon_{ai}^2}$$

The point being : χ is a central object in this field. The whole idea here is to calculate χ on each point of a grid, as a matrix of the grid points.



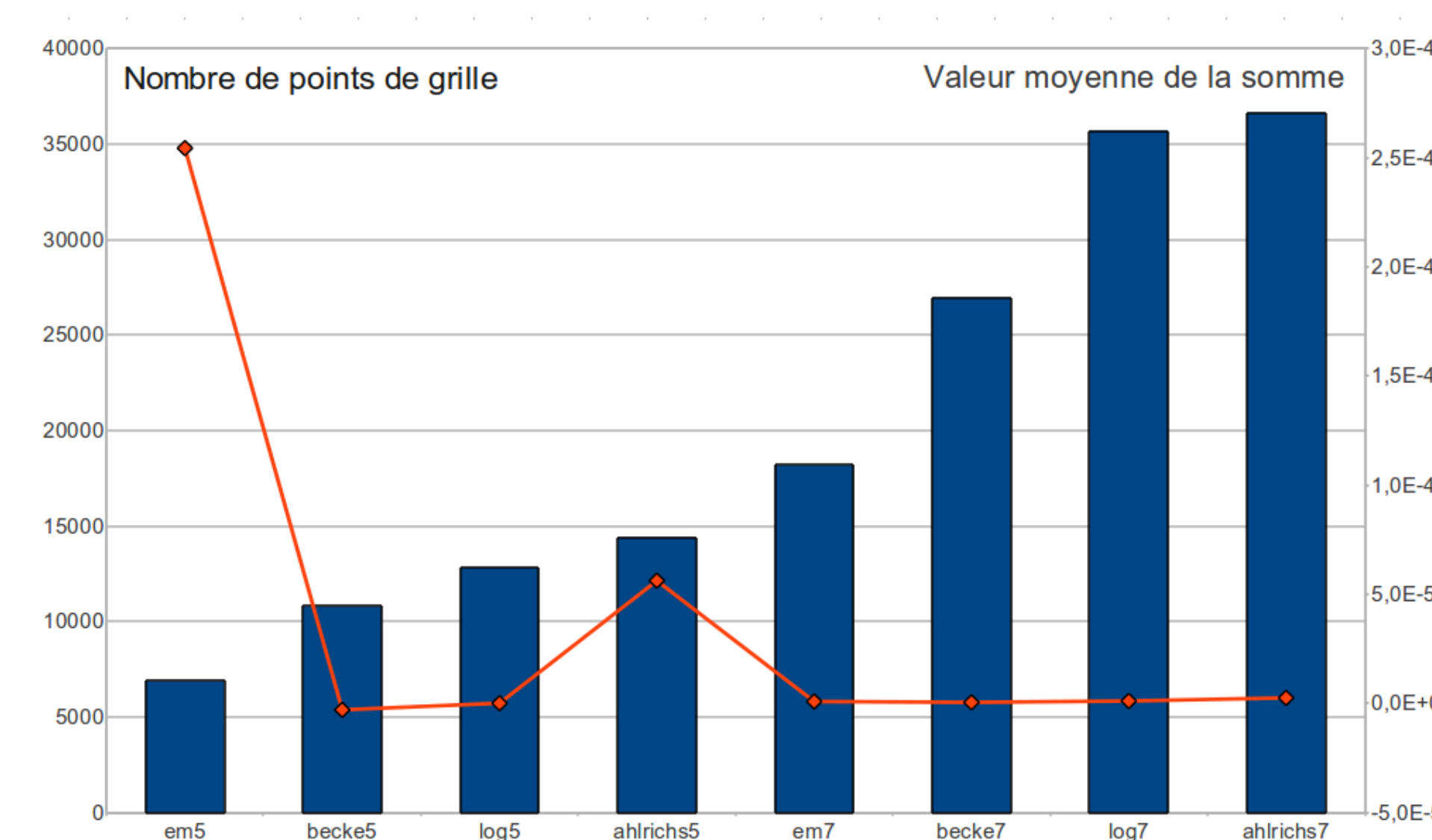
First steps

A careful attention must be put into the time cost ($O(n_{grid}^2)$) i.e. into **the choice of the grid points**. One can use a :

- ▷ regular grid : points are homogenely placed (lots of points to cover the whole space around a molecule)
- ▷ DFT grid : points are placed where the density is expected to be large. (points around atoms, depending on the nature of the atom)

We need to choose a proper algorithm to select meaningful grid points (that gives good insight)

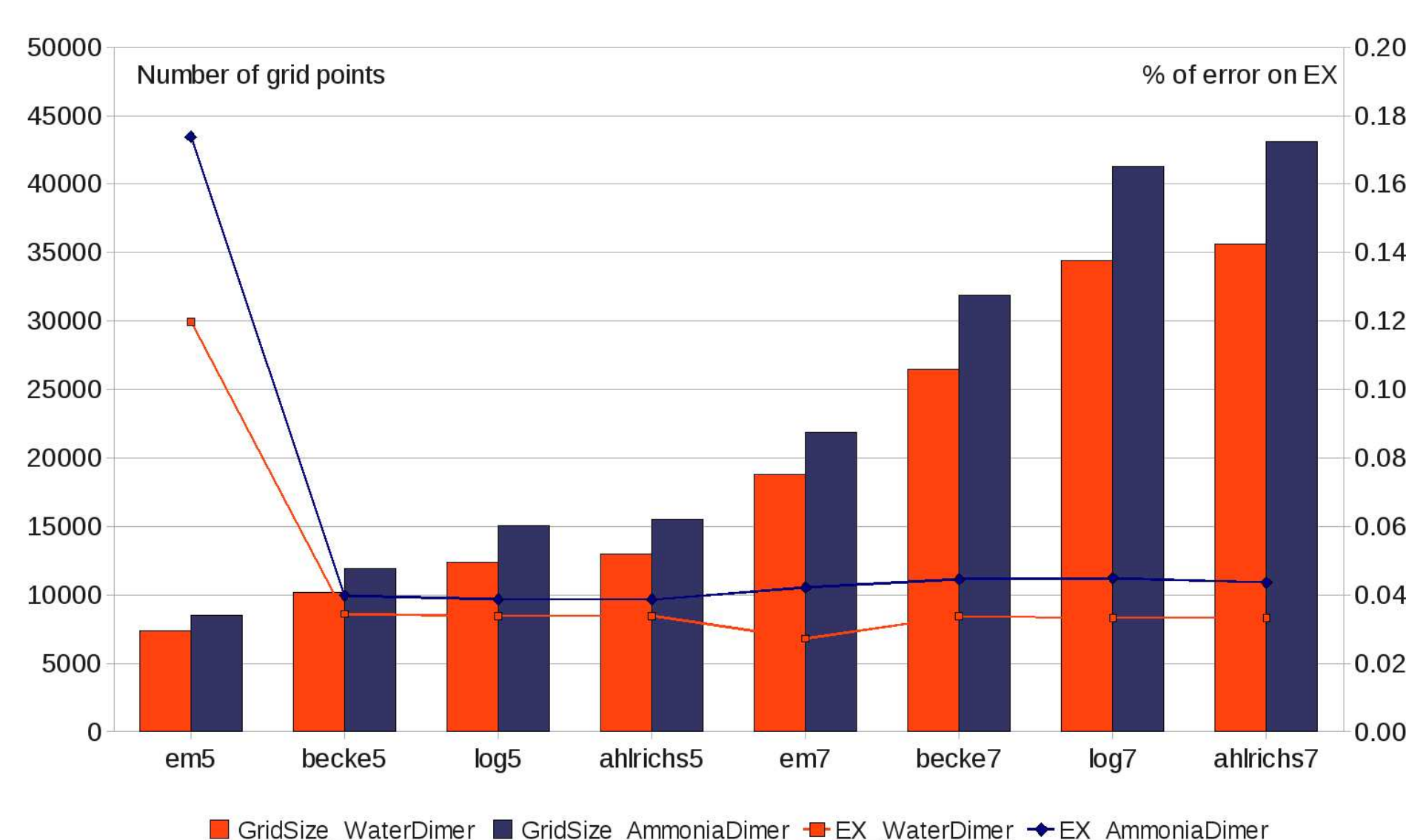
We monitor known properties of χ (here its Sum Rule) for different combinations of different algorithms, density levels, and numerical zeros :



Total number of points and Mean of the sum on each (perturbation) points. Calculations on C₂H₄, 4 different algorithms, 2 density levels.

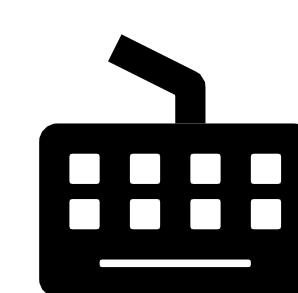
To go further...

It can be interesting to see if we can access E_H and E_X via the same method. Calculations have been done for the S22 benchmark^[2] of molecules.



The overall conclusion : as before, we can choose the less dense DFT grids

THIS IS ALREADY GOOD !



- ▷ a functionable **parallelized** program has been written (takes the output of a Molpro^[3] calculation)
- ▷ efficient ways to choose between algorithms have been found : we can choose among the less dense algorithms.
- ▷ good insight is provided for both the polarizability and the energies using these algorithms.

What needs to be done :

- ▷ systematic calculations for all molecules of S22 (so far : errors of less than 1% for the exchange energy on 10 molecules).

Acknowledgement

The author wants to thank János G. Ángyán and Sébastien Lebègue for fruitful discussions.

References

1. J. Toulouse, W. Zhu, J. G. Ángyán, A. Savin, Physical Review A, 82 (032502), 1-15 (2010)
2. P. Jurecka, J. Sponer, J. Cerny, P. Hobza, Phys Chem Chem Phys, 8 (17), 1985-1993 (2006)
3. Molpro, version 2010.1, H.-J. Werner, P. J. Knowles, F. R. Manby, M. Schütz