Calculation of the polarizability on a grid

Bastien Mussard, János G. Ángyán, Sébastien Lebègue
CRM^2, Faculté des Sciences, Université Henry Poincaré, Nancy

bastien.mussard@crm2.uhp-nancy.fr

Background

detailled ref : [1]

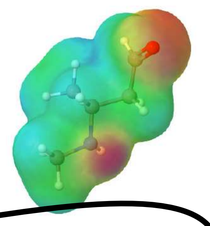
The expression of the *correlation energy* when using an adiabatic-connection fluctuation-dissipation DFT based on range separation is :

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

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

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

$$\boxed{\Delta\rho(r_1;\omega) = \int dr_2\ \chi(r_1,r_2;\omega)V(r_2;\omega)} \quad (3)$$

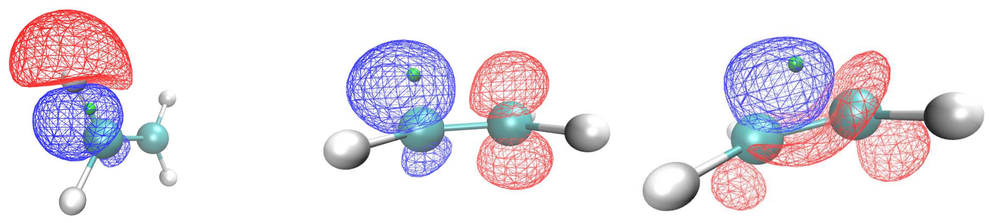


the integral vanishes

First steps

On a grid, with a local Kronecker potential $V(r,\omega) = \delta_{r,r_{perturb}}$

$$\Delta\rho(A;\omega) = \chi(A,B_{perturb};\omega) \quad (5)$$



C_2H_4 *(vdz, 60.60.60)*

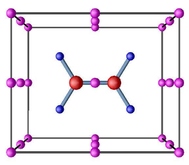
Starting point

The idea : use a spatial grid to calculate χ.

Lehmann representation formula :

$$\boxed{\chi(A,B;i\omega) = \sum_{i\in occ}\sum_{a\in vir}\phi_i(A)\phi_a^*(A)\phi_a^*(B)\phi_i(B)\frac{2\epsilon_{ai}}{\omega^2+\epsilon_{ai}^2}} \quad (4)$$

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.



This is already good !

- a functionable program has been written (takes the output of a Molpro calculation)
- good insight is provided

What need's to be done :
- find a way to **shorten the time cost** ($o(n_{grid}^2)$) !

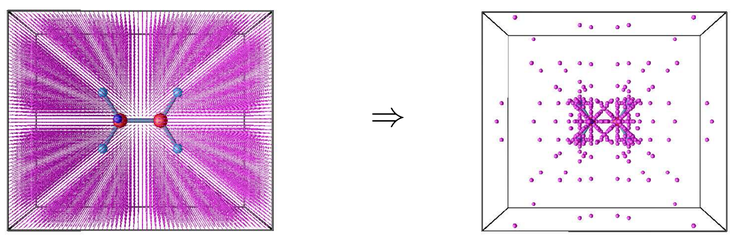
To go further...

Lowering the number of grid points might do the job.

The idea : use a DFT integration grid.

A DFT integration grid is a grid that fits/is built on parameters that **depend on the system** (grid points coordinates are polar, different densities around different atoms, etc).

all the points are not equally important

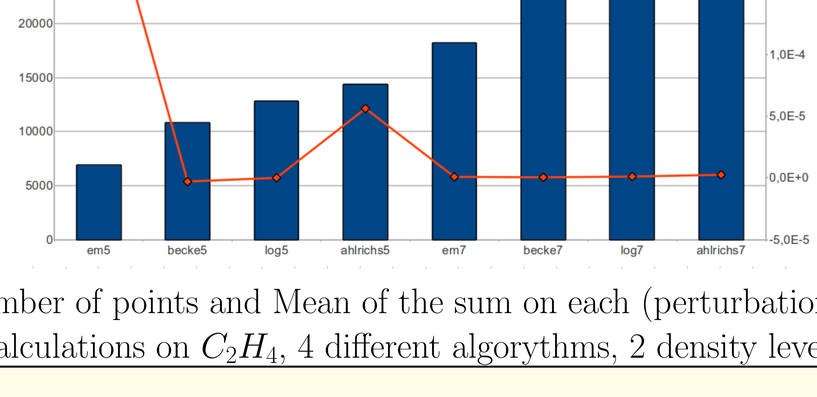


As always with an approximation : **we need to monitor it**

The perturbation $V(r_2,\omega)$ must not create a charge, that is to say :

$$\int dr_1\ \Delta\rho(r_1;\omega) = \int dr_1 dr_2\ \chi(r_1,r_2;\omega)V(r_2;\omega) = 0 \quad (6)$$

$$\sum_A \Delta\rho(A;\omega) = \sum_A \chi(A,B_{perturb};\omega) = 0 \quad (7)$$



Total number of points and Mean of the sum on each (perturbation) points. Calculations on C_2H_4, 4 different algorythms, 2 density levels.

Acknowledgement

The author wants to thank János G. Ángyán

References

1. J. Toulouse, W. Zhu, J. G. Ángyán, A. Savin, Physical Review A, 82, 032502 1-15 (2010)
2. Molpro, version 2010.1, H.-J. Werner, P. J. Knowles, F. R. Manby, M. Schütz