Selective hybridization, a path for DFT evolution.

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Introduction

Density Functional Theory (DFT) is one of the most utilized methodologies in modern quantum and computational chemistry. Nevertheless, the exact functional for the $E_{xc}[\rho]$ component is not known and the failures arising from current approximations to it are known and well documented[1]. Here, we have built new DFT $E_{xc}[\rho]$ functionals (built from B3LYP functional) to face two problems:

1. Get an accurate description of the two- and three-electron Harmonium Atom (HA) systems using DFT. The HA model systems are systems where the Coulomb electron-nucleus potential is replaced by a parabolic confinement ($-\frac{Z}{r_i} \rightarrow \frac{1}{2}\omega^2 r_i^2$, where ω is known as the confinement strength; which plays a crucial role in correlation) and where the actual Coulomb electron-electron potential is kept unchanged ($1/r_{ij}$). It has been used previously for benchmarking and calibrating DFT functionals but some ω regions represent a real challenge for standard DFT functionals since HA-systems allow stronger correlation regimes than Z-isoelectronic series making these model systems excellent for testing and building new DFT functionals[2].
2. Overcome the pitfalls of DFT to describe non-linear optical properties (NLOP) for H_2 dissociation. A new hybrid functional is constructed to face this problem and give accurate results for properties like polarizabilities and hyperpolarizabilities.

These new functionals were built from reparameterizing B3LYP functional:

$$\begin{aligned} E_{xc}^{\text{B3LYP}} =& E_{xc}^{\text{LDA}} + a(E_x^{\text{HF}} - E_x^{\text{LDA}}) + b(E_x^{\text{B88}} - E_x^{\text{LDA}}) \\ &+ c(E_c^{\text{LYP}} - E_c^{\text{LDA}}) \end{aligned} \tag{1}$$

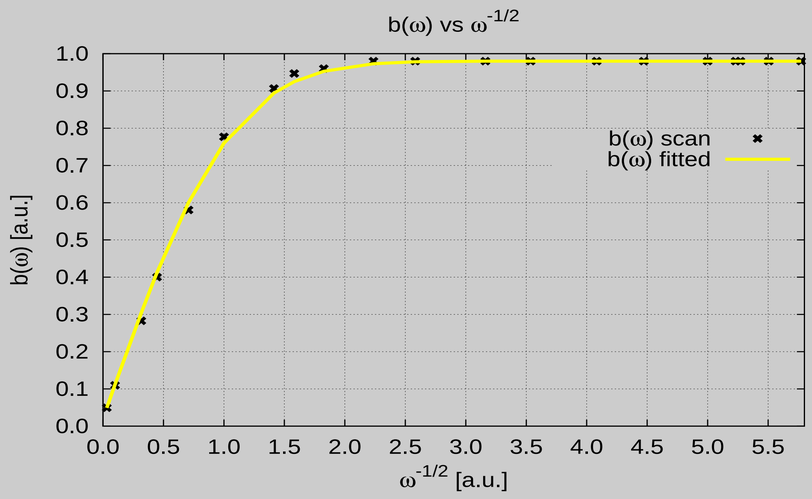
but taking the a parameter to be $a = 1 - b$, which allows us to have only two degrees of freedom, making simpler the physical interpretation of the values obtained for these parameters.

Computational details

All calculations were performed using gaussian03 and gaussian09 packages. We took the optimized parameters for the basis set obtained by E. Matito et al[3] for the two-electron-HA and by Cioslowski et al[4] for the three-electron HA. For the NLOP we worked with cc-pVTZ basis set and generalized Romberg scheme for the numerical derivatives.

Two-electron harmonium atom

For the two-electron HA we looked for the best parameters of B3LYP functional to reproduce FCI energies[3] for a large set of ω values and fitted those parameters to an equation. The c parameter was found to be constant ($c = 0.82$) while for b we obtained:



whose fitted equation reads

$$b(\omega) = 0.96\ \text{erf}(0.85\ \omega^{-1/2}) + 0.02 \qquad \text{RMS} = 0.01 \tag{2}$$

Table 1: Absolute errors in Kcal/mol for the energies obtained with HF, B3LYP functional and fitted-B3LYP functional for a large set of ω values.

ω	$\lvert E_{\text{FCI}} - E_{\text{Fitted}}\rvert$	$\lvert E_{\text{FCI}} - E_{\text{B3LYP}}\rvert$	$\lvert E_{\text{FCI}} - E_{\text{HF}}\rvert$
0.03	0.04	0.16	12.93
0.04	0.01	0.13	14.20
0.05	0.08	0.09	15.19
0.10	0.36	0.06	18.23
0.15	0.48	0.04	19.90
0.20	0.49	0.08	21.03
0.30	0.41	0.49	22.49
0.40	**0.29**	1.01	23.44
0.50	**0.18**	1.57	24.12
1.00	**0.14**	4.44	25.94
2.00	**0.36**	9.52	27.35
5.00	**0.57**	20.88	28.69
10.0	**0.68**	34.30	29.40
100.0	**0.24**	135.03	30.62
1000.0	**0.25**	456.89	31.00

Acknowledgments

M.R.M and E.M. acknowledge the financial support from the Spanish Ministry of Economy and Competitiveness (MINECO) for the project CTQ2014-52525-P. M.R.M. thanks the Spanish Ministry of Education, Culture and Sports for the FPU 13/00176 fellowship. E.M. thanks the IKERBASQUE science foundation.

Two-electron harmonium atom improved densities

For small-ω values ($\omega \leq 0.042$) there is a displacement of the maximum of the density from the origin (called the "cusp catastrophe") due to the strong electronic correlation effects. With our new functional we have also improved the densities as we observe in Table 2 (notice that the position that the maximum for the small-ω values for HF and B3LYP is the origin):

Table 2: Radial position of the maximum of the density for small-ω values in Å. The "Exact" value was calculated taking Eq. 81 from ref. [5].

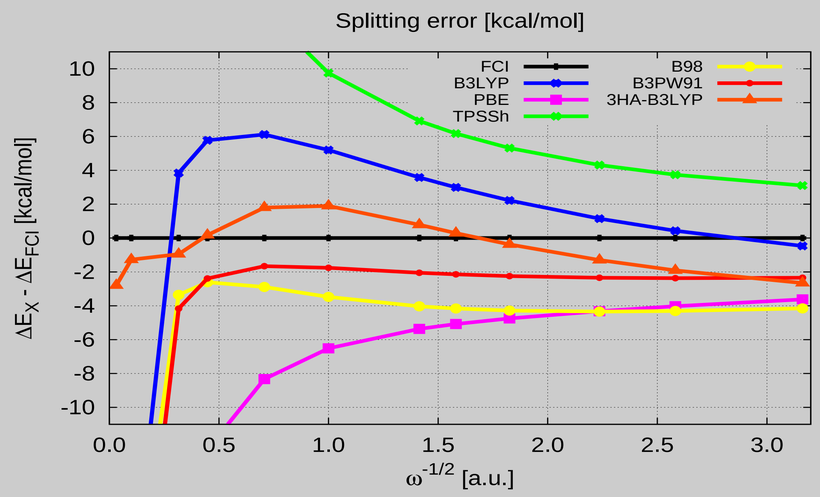
ω	"Exact"	Fitted-B3LYP	B3LYP	HF
0.030	4.52	3.81	0.00	0.00
0.033	4.18	3.01	0.00	0.00
0.036	3.89	2.30	0.00	0.00
0.037	3.84	2.20	0.00	0.00
0.040	3.56	1.40	0.00	0.00
0.050	0.00	0.00	0.00	0.00

Three-electron harmonium atom

For three-electron HA, we scanned for several ω values the best B3LYP parameters to reproduce the FCI doublet-quartet splitting energies. We obtained the following equation for the b parameter:

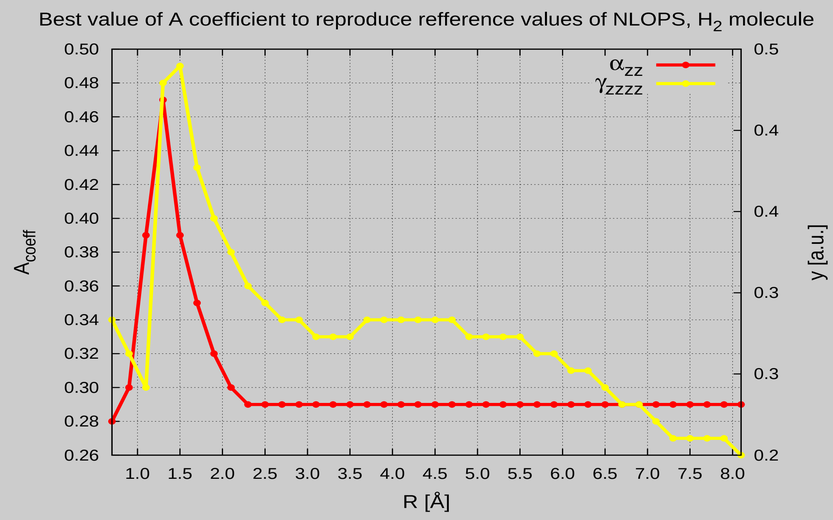
$$b(\omega, S) = 0.83\ \text{erf}\left[\left(\frac{4.00 + 0.39[2S+1]}{2S+1}\right)\omega^{-1/2}\right] + 0.07 \tag{3}$$

where S is the total spin (1/2 or 3/2). For c we obtained two values: $c = 0.84$ for $S = 1/2$ and $c = 0.80$ for $S = 3/2$. The errors obtained in the splitting energy with this new fitted functional (3HA-B3LYP) are plotted below where we observe the goodness of our new functional against standard functionals.



H_2 dissociation NLOP

We applied the same strategy to solve the pitfalls of DFT for NLOP for H_2 dissociation. To do so, we scanned for the best b and c parameters to reproduce FCI polarizabilities and hyperpolarizabilities during the dissociation. The scan at different interatomic distances shown that c parameter was not playing and important role and keeping it constant, as it is in standard B3LYP, gives enough accuracy. Nevertheless, for a parameter (recall that we worked with $a = 1 - b$) we obtained:



where we have a dependency of the a parameter with the interatomic distance. We need to find some property (probably based on the density) to link between our system and the parameters to make a functional which does not depend on interatomic distances.

Conclusions

We have followed the same strategy to face two different problems: get an accurate description of HA systems and avoid the problems encountered when calculating NLOP for H_2 dissociation. Nonethless, we found that there is no universal amount of exchange required neither for the energies of HA nor for NLOP (the need for a non-fixed amount of exchange to obtain a more "universal" hybrid functionals was also found previously by Perdew et al[6]). Our results suggest that the amount of exchange is crucial for both systems but there must be a smart way to self-adjust the amount of exchange in DFT functionals to get a more "universal" functional.

References

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