



HAL
open science

COBALT DIMER: A DIFFICULT CASE FOR THE DFT, BUT A PRELIMINARY STEP TOWARDS THE STUDY OF REACTIONS CATALYZED BY COBALT CLUSTERS.

Noëllie Tieppo, Emilie-Laure Zins, Mohammad Esmail Alikhani

► **To cite this version:**

Noëllie Tieppo, Emilie-Laure Zins, Mohammad Esmail Alikhani. COBALT DIMER: A DIFFICULT CASE FOR THE DFT, BUT A PRELIMINARY STEP TOWARDS THE STUDY OF REACTIONS CATALYZED BY COBALT CLUSTERS.. International Conference on Density-Functional Theory and its Applications, Jul 2019, Alicante (SPAIN), Spain. hal-03955776

HAL Id: hal-03955776

<https://hal.science/hal-03955776>

Submitted on 25 Jan 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Motivation of the study

Could play a key role in the energy transition if reaction mechanisms would be understood

Versatility of cobalt for homogeneous and heterogeneous catalysis



Co₂: A system with a multi-reference character

One of the last 3d elements for which the electronic structure of the fundamental state remains doubtful

Numerous DFT studies for small cobalt clusters → No consensus emerged neither on the level of calculation to be used nor on the features of the fundamental state

For all these reasons, and using a bottom-up approach, we would like to assess which DFT method would be the most suitable to describe small cobalt clusters.

We start with the smallest cluster, namely Co₂, and we are looking for a rather simple strategy using the user-friendly Gaussian09 software, prior to go towards a study of its catalytic role in collaboration with experimentalists.

Results

| | State | ΔE(kJ/mol) | v(Co-Co) (cm ⁻¹) | Re (Å) |
|---------------------|--|------------|------------------------------|--------|
| PBEPBE/aug-cc-pvtz | ⁵ Δ _g | 0 | 389 | 1,97 |
| | ⁵ Σ _u ⁻ | 28 | 328 | 2,13 |
| | ⁷ Σ _u ⁻ | 60 | 314 | 2,11 |
| | ¹ Σ _g ⁺ | 67 | 239 | 2,26 |
| BLYP/aug-cc-pvtz | ⁵ Δ _g | 0 | 379 | 1,99 |
| | ⁵ Σ _u ⁻ | 24 | 321 | 2,14 |
| | ¹ Σ _g ⁺ | 59 | 231 | 2,28 |
| | ⁷ Σ _u ⁻ | 64 | 302 | 2,14 |
| | 3 | 71 | 315 | 2,10 |
| B3LYP/aug-cc-pvtz | ¹ Σ _g ⁺ | 0 | 221 | 2,36 |
| | ⁵ Σ _u ⁻ | 10 | 225 | 2,44 |
| | ⁵ Σ _u ⁻ | 49 | 349 | 2,10 |
| | 3 | 61 | 222 | 2,30 |
| CCSD(T)/aug-cc-pvtz | ⁷ Σ _u ⁻ | 0 | 204 | 2,24 |
| | ⁵ Δ _g | 75 | 436 | 1,94 |
| PBEPBE/6-311G(3df) | 7 | 0 | 348 | 2,02 |
| | 5 | 2 | 354 | 2,03 |
| | ⁷ Σ _u ⁻ | 5 | 355 | 2,05 |
| | ⁵ Σ _u ⁻ | 7 | 362 | 2,05 |
| | ⁷ Σ _u ⁻ | 28 | 383 | 1,96 |
| | ⁵ Σ _u ⁻ | 29 | 385 | 1,97 |
| | ⁷ Π | 69 | 236 | 2,36 |
| | 5 | 0 | 347 | 2,05 |
| BLYP/6-311G(3df) | ⁵ Σ _u ⁻ | 4 | 353 | 2,07 |
| | 7 | 7 | 339 | 2,04 |
| | ⁷ Σ _u ⁻ | 12 | 344 | 2,07 |
| | ⁵ Σ _u ⁻ | 31 | 376 | 1,99 |
| | ⁷ Σ _g ⁺ | 38 | 372 | 1,98 |
| | ⁷ Σ _u ⁻ | 0 | 349 | 2,02 |
| | ⁵ Σ _u ⁻ | 1 | 355 | 2,03 |
| BPW91/6-311G(3df) | ⁷ Σ _u ⁻ | 5 | 354 | 2,05 |
| | ⁵ Σ _u ⁻ | 6 | 361 | 2,05 |
| | ⁵ Σ _g ⁺ | 31 | 385 | 1,97 |
| | 5 | 0 | 246 | 2,23 |
| | 7 | 0 | 235 | 2,22 |
| B3LYP/6-311G3df | 5 | 43 | 387 | 2,00 |
| | ⁵ Σ _u ⁻ | 45 | 390 | 2,01 |
| | 1 | 48 | 235 | 2,31 |
| | ⁷ Σ _u ⁻ | 49 | 387 | 2,00 |
| | ⁵ Δ _g | 0 | 386 | 1,98 |
| | ⁵ Σ _u ⁻ | 22 | 330 | 2,12 |
| | 5 | 49 | 237 | 2,23 |
| | 1 | 50 | 234 | 2,24 |
| BPW91/6-311+G* | ⁷ Σ _u ⁻ | 52 | 308 | 2,10 |
| | 7 | 58 | 310 | 2,13 |
| | EXPERIMENTAL DATA | | | |
| | 297 | | | |

Table 1: Influence of the level of theory on the description of Co₂

Computational approach

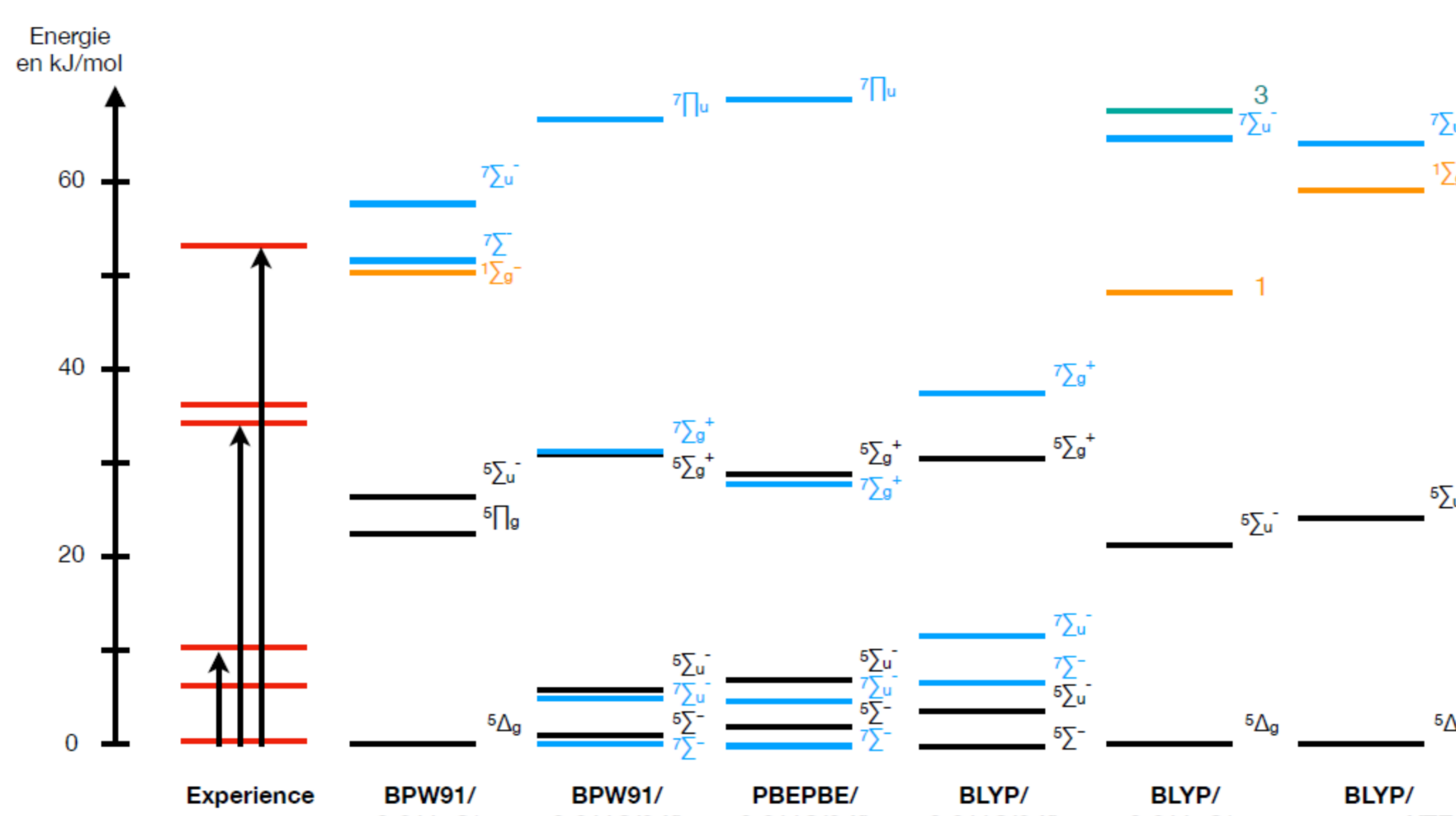
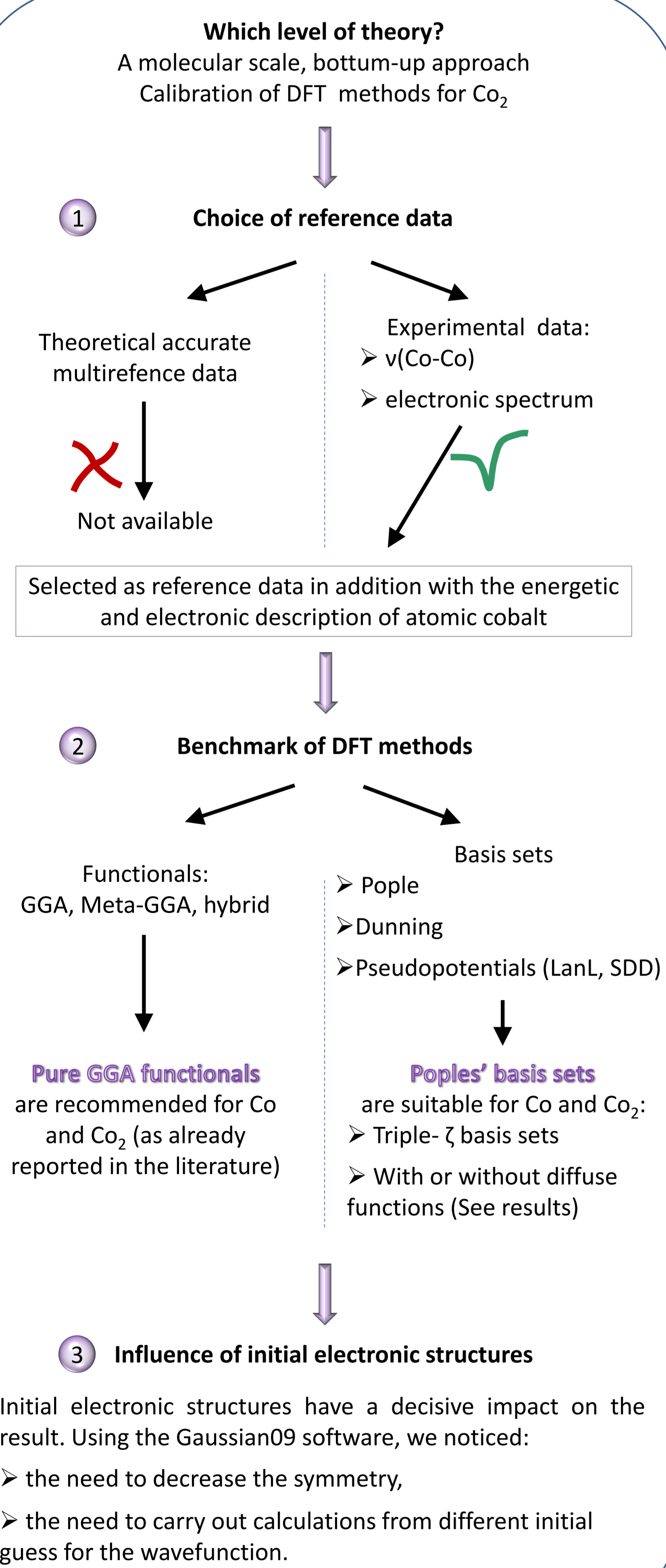


Figure 1: Comparison experimental electronic spectra with DFT calculations of the firsts electronic states for cobalt dimer

It has been pointed out in the literature that the theoretical characterization of cobalt dimer strongly depends on the functional used. There is also a considerable influence of the base, for the same functional. Quintet states ⁵Δ_g seem to be strongly stabilized with bases containing diffuse functions, whereas they are not found when the diffuse functions are removed (Table 1).

The use of a pure GGA functional in combination with a base that has no diffuse function makes it possible to better reproduce the experimental electronic spectrum (Figure 1). It also leads to the identification of three states that are quasi-degenerated with the fundamental state, which is consistent with the multi-reference nature of the system (Table 1, Figure 1).

The topological analysis QTAIM (Quantum Theory of Atoms in Molecules) reveals that the Co-Co chemical bond is calculated as being similar in the most stable quintet and septet at the BPW91/6-311G(3df) level of theory (Table 2).

On the other hand, when the 6-311+G* basis set is used with the same functional, the most stable quintet is calculated as having a stronger chemical bond than the most stable septet (Table 2).

It is noted that, for this septet calculated as the most stable at BPW91/6-311G(3df), the 6-311+G* base leads to a vibration frequency fully consistent with the experimental data (Table 2).

| Method | Co ₂ septet | | Co ₂ quintet | | Comparison with Exp. |
|--------------------|------------------------|---|-------------------------|---|--|
| | ΔE kJ/mol | Features | ΔE kJ/mol | Features | |
| BPW91 6-311 G(3df) | 0 | ρ = 0.11 ∇ ² ρ = 0.4 r _c = 2.02 Å ω _c = 348 | 2 | ρ = 0.11 ∇ ² ρ = 0.4 r _c = 2.03 Å ω _c = 354 | Consistent with the exp. electronic spectrum |
| BPW91 6-311+G* | 52 | ρ = 0.09 ∇ ² ρ = 0.3 r _c = 2.10 Å ω _c = 308 | 0 | ρ = 0.11 ∇ ² ρ = 0.5 r _c = 1.98 Å ω _c = 386 | |

Table 2: Comparison of the QTAIM features of the most stable quintet and septet states calculated at the BPW91/6-311G(3df) and BPW91/6-311+G* levels of theory. Bond critical points are shown in green, and the variation of the Laplacian of the electron density is plotted in the plane of the molecule.

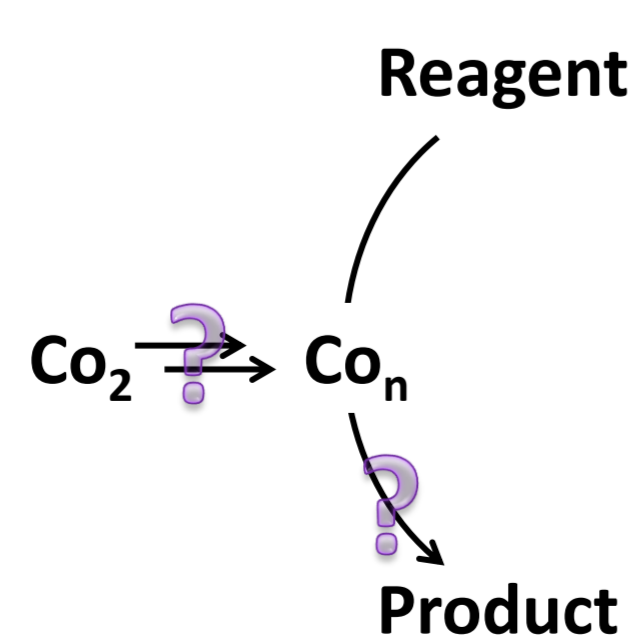
Conclusions and perspectives

Cobalt dimer: a challenge for quantum-chemistry calculation

In the case of DFT calculations, the influence of the functional is supplemented by the influence of the base on the theoretical description of the cobalt dimer:

As far as the functional are concerned, pure-GGAs clearly appear as the most adequate for the description of Co₂,

As far as the choice of the base is concerned, the situation is more complex... and more disappointing. No common basis set implemented in the Gaussian09 software and that correctly reproduces all the experimental data was found.



For more complex systems (Co_{n>2} and/or reactivity study), there is a lack of experimental data.

To achieve an explanatory and predictive approach to the catalytic activity of small cobalt clusters, we need to overcome a twofold challenge:

- a lack of experimental and theoretical benchmark data,
- the unavailability of a simple and common method for a precise and correct description of the cobalt dimer.

At this stage of our study, we could suggest to study a panel representation of cobalt clusters and similar systems with pure GGA functionals such as PBEPBE and BPW91, with two complementary triple-ζ Pople basis sets:

- the 6-311G(3df) basis set, which would better reproduce the quasi-degenerated states that are responsible for the multi-reference character of the cobalt dimer,
- the 6-311+G* basis set, which would better reproduce the experimental vibration frequency of the fundamental electronic state identified using the 6-311G(3df) basis set.

References:

Ai, W. et al. (2018). *Chem. Rev.*, 119, 2876

Sauer, J. et al. (2015). *Catalysis Letters*, 145, 109

Hammes-Schiffer, S. (2017). *Acc. Chem. Res.*, 50, 561

Hübner, O. & Himmel, H. J. (2018). *Chem. Eur. J.*, 24, 8941

Dong, J. G. et al. (1994). *J. Chem. Phys.*, 101, 9280

Danset, D. & Manceron, L. (2004). *Phys. Chem. Chem. Phys.*, 6, 3928

Gutsev, G. L. et al. (2001). *Chem. Phys. Lett.*, 345, 481

Calaminici, P. et al. (2007). *J. Chem. Phys.*, 126, 044108

Jamorski, C. et al. (1997) *Physical Review B*, 55(16), 10905

Schultz, N. E. et al. (2005). *The Journal of Physical Chemistry A*, 109(49), 11127-11143.

Frisch, M. J. (2009). Gaussian09. <http://www.gaussian.com/>.

AIMAll (Version 19.02.13), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, 2019 (aim.tkgristmill.com)