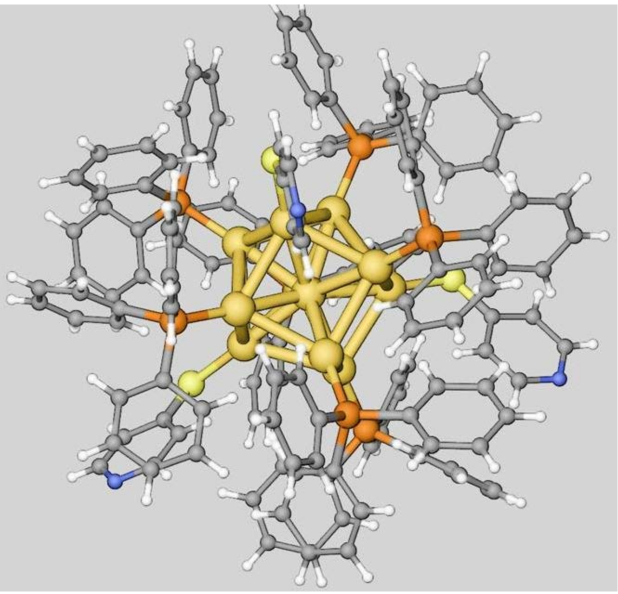
Chimica & Ricerca

Avogadro Colloquia

DFT ON A GOLD NANOCLUSTER[*]

Francesco Muniz-Miranda, Alfonso Pedone, Maria Cristina Menziani
Dipartimento di Scienze Chimiche e Geologiche
Università di Modena e Reggio Emilia
francesco.munizmiranda@unimore.it

There are many computational studies about gold nanoclusters, but a benchmarking of the possible density-functional based approaches on real X-ray resolved particles still lacks. Here we fill the gap and present a series of tests that shall pave the way to future calculations on larger particles.



The undecagold-based nanoparticle investigated here

Noble-metal nanoparticles are of paramount relevance due to their use in catalysis[1], ability to bind biological molecules[2], and their optical properties. In particular, this is true for gold nanoparticles, whose *homo-lumo* gap increases with reduction in size[3], reaching values between about 1 and 2 eV at the sub-nanometer scale[4]. The possibility to manipulate their electronic conduction properties makes them useful for many applications, including, for example, solar cells designed to adsorb a wider range of light frequencies. Moreover, the catalytic activity of Au nanoparticles is a very striking feature because it is not simply an enhancement of a known bulk effect (as in the case of other noble metals, *e.g.* platinum), but rather the emergence of a latent property [5,6].

Because all the physico-chemical properties and potential applications of such particles are deeply affected by their size, the possibility to control their dimensions plays an important role in their

---

[*] *Questo articolo è stato presentato nel corso di "Avogadro Colloquia", Bologna, 27 settembre 2013. L'evento è stato promosso dalla SCI e organizzato in collaborazione con Scuola Normale Superiore di Pisa e il nodo CECAM-IT-SNS e con il supporto della Divisione di Chimica Teorica e Computazionale.*

nanotechnological applications, and, consequently, a deep understanding of the relationship between electronic and structural properties of Au-based nanoparticles is needed.

Density-functional theory (DFT) methods are often employed to study gold at the nanoscale[7,8,9], but a benchmarking of the possible choices of exchange-correlation functionals (XCFs) and combined basis sets/pseudopotentials (BS/PPs) is still lacking on real X-ray resolved nanostructures.

Thus, we investigated a (relatively) small gold-based nanocluster made up of 11 Au atoms coated by aromatic phosphines and thiols[10]. The testing consisted of a series of structural optimizations with the program Gaussian 09[11], with self-consistent field and geometrical optimizations *criteria* set on "verytight" and "tight", respectively. The final structures have been compared with the starting experimental geometry. Accuracy has been checked computing the atom-averaged absolute value of the difference between metal-metal distances of the initial (exp) and final (opt) geometries $<\delta>=<|r_{ij}(opt)-r_{ij}(exp)|>$, where r_{ij} represents the distance between *i* and *j* gold atoms.

We tested 13 XCFs and 6 BS/PPs on a simplified structure composed by the metal core and the atoms directly bonded to it (*viz*. P and S), with added hydrogen atoms to complete the connectivity of the latter, as shown in Fig. 1. In particular, we employed 3 GGA (PBE, BPBE, BLYP), 1 meta-GGA (TPSS), 5 hybrid (B3LYP, PBE0, mPw1Pw91, M06, M06HF) and 4 long-range corrected hybrid (HSE06, cam-B3LYP, LC-BLYP, LC-PBE) functionals. All atoms have been set free to relax during the optimizations.

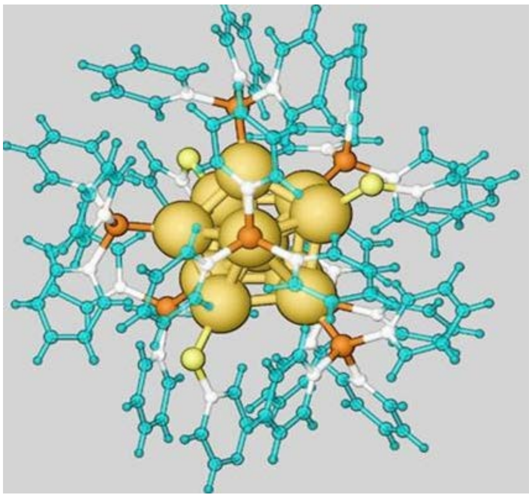


Fig. 1 - The undecagold cluster. Cyan atoms are not included into calculations on the bare metal core. Hydrogen atoms (white) are added to complete the connectivity of S and P atoms, and are put in place of C atoms of the complete nanoparticle

The BS/PPs adopted here are the large core Lanl1-DZ, small core Lanl2-DZ, a modified version of the latter with added (n+1) optimized |p> orbitals (modLanl2-DZ[12]), Lanl2-TZ[13], as well as relativistic corrected mWB60 and mDF60. modLanl2-DZ and Lanl2-TZ have been imported into the calculations via Basis Set Exchange website[14], while for other BS/PPs we adopted the implementation included in Gaussian09. For S, P, and H atoms the 6-311G** basis set has been used. Results of this testing are summarized in Fig. 2, but data for Lanl1-DZ are omitted since this BS/PP proved inadequate for the benchmarking (*i.e.* led to optimized structures very distorted with respect to the experimental one, with <δ> values exceeding 0.3 Å).

As can be appreciated, the structural accuracy depends on both the XCF and BS/PP adopted. Apart from the Lanl1-DZ, the widely employed Lanl2-DZ BS/PP (blue bars) provides the worst results with most XCFs. Both modLanl2-DZ (cyan bars) and Lanl2-TZ (red bars) yield significantly better results, with just a slightly greater computational cost. Also semi-relativistic mWB60 (yellow bars) often gives satisfying results, but at the price of much more demanding computations. The full relativistic

Dirac-Fock mDF60 (green bars), on the contrary, proves demanding as mWB60 but often provides inaccurate structures as Lanl2-DZ.

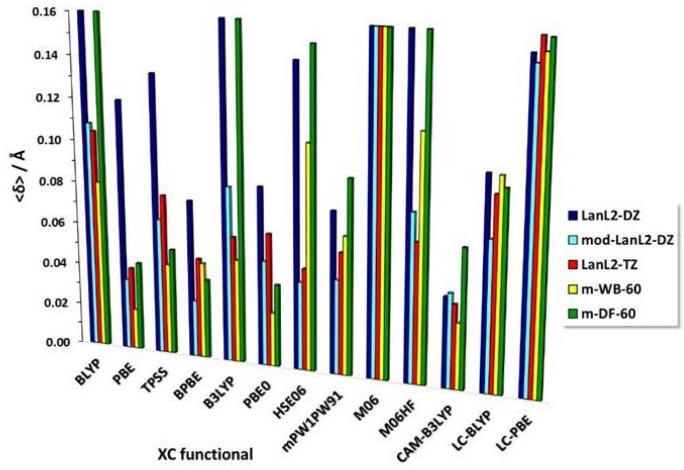


Fig. 2 - Structural errors reported as a function of the XCF and BS/PP adopted. Errors bars are cut above the 0.16 Å threshold

Most of the XCFs including PBE-like correlation (*viz.* PBE itself, BPBE, PBE0, HSE06, mPw1Pw91) provided the best results, with structural errors consistently below the 0.05 Å threshold when adopted in conjunction with modLanl2-DZ or Lanl2TZ BS/PPs. This is particularly remarkable for BPBE, which yields <δ> values less than 0.03 Å. Long-range corrected CAM-B3LYP also leads to accurate optimizations, while other long-range hybrids like LC-BLYP/PBE yield larger errors. M06 hybrid provides distorted geometries regardless of the BS/PP employed, while BLYP, B3LYP, M05, and M06HF seem very sensible to the BS/PP choice, at least for this specific system.

On these premises, we performed calculations on the complete nanocluster, including the organic coating. Due to the size of the particle (more than 280 atoms), we had to scale the level of theory of the inner and outer regions, following a rationale widely employed in computational chemistry[15,16]. We employed the STO-3G and 6-31G basis sets to describe atoms belonging to the organic ligands, with the exception of the S and P atoms that retained their 6-311G** basis sets, as in the benchmark calculations on the bare metal core. As XCF, we used BPBE and CAM-B3LYP, since they belong to different "families" but, at the same time, both yielded good optimized geometries for the bare metal core benchmarks. modLanl2-DZ has been used as BS/PP for gold atoms. Geometrical optimizations have been performed both fixing the atoms of the outer layer (*viz.* C, H, and N) to their positions and leaving all the system free to relax.

The constrained calculations gave excellent results with both BPBE and CAM-B3LYP, yielding errors of ~0.05 Å when STO-3G basis set is used for the organic ligands, and ~0.03 Å when is adopted the larger 6-31G. However, the all-free-to-relax calculations gave larger errors, of ~0.11 Å and ~0.13 Å with STO-3G and 6-31G basis sets, respectively. Both XCFs, despite being very different and requiring different computational efforts (CAM-B3LYP is much more demanding), provided similar structures (differences in <δ> values less than 0.01 Å).

In conclusion, with these calculations we show that some GGA functionals (in particular, BPBE) can provide the same structural accuracy obtained with much more complex XCFs for the hybrid organic-gold nanoparticle. modLanl2-DZ improves the accuracy with respect to the widely employed Lanl2-DZ without increasing the computational burden. These combinations of XCFs and PS/BBs can be used to simulate both the metal core and the whole nanocluster, thus representing a good choice for investigations on larger particles and their excited states.

References

[1] A. Grirrane *et al., Science,* 2008, **322**, 1661.
[2] J.R. Heath, *et al.*, *Annual Review of Medicine,* 2008, **59**, 251.
[3] D.M. Schaadt, *et al.*, *Applied Physics Letters,* 2005, **86**, 063106.
[4] M. Walter *et al.,* Proc. of the National Academy of Sciences, 2008, **105**, 9157.
[5] T.G. Schaaff *et al.*, *The Journal of Physical Chemistry B,* 2000, **104**, 2630.
[6] Z. Deng *et al.*, *ACS Applied Materials & Interfaces,* 2012, **4**, 5625.
[7] M. Walter *et al.,* Proc. of the National Academy of Sciences, 2008, **105**, 9157.
[8] H. Häkkinen *et al.*, *Phys. Rev. Lett.,* 1999, **82**, 3264.
[9] C.M. Aikens, *Molecular Simulation,* 2012, **38**, 607.
[10] A. Das *et al.*, *J. Am. Chem. Soc.,* 2012, **134**, 20286.
[11] M.J. Frisch *et al*. Gaussian 09. Gaussian, Inc., Wallingford CT, 2010.
[12] M. Couty *et al.*, *J. Comput. Chem.,* 1996, **17**, 1359.
[13] L.E. Roy *et al.*, *Journal of Chemical Theory and Computation,* 2008, **4**, 1029.
[14] K. Schuchardt *et al.*, *Journal of Chemical Information and Modeling,* 2007, **47**, 1045.
[15] S. Dapprich *et al.*, *J. Mol. Struct.* {THEOCHEM} 1999, **461-462**, 1.
[16] T. Vreven *et al.*, *Comput. Chem.,* 2003, **24**, 760.