Bonding in WAu_{12}

Mikael P. Johansson, Michael Patzschke, and Pekka Pyykkö

Department of Chemistry, P.O. Box 55 (A.I. Virtanens plats 1), FIN-00014 University of Helsinki, Finland. *e-mail: mikael.johansson@helsinki.fi*

Introduction

- **Metal clusters** are of great current interest, not least due to their possible application in nano-technology and catalysis.

- Pyykkö and Runeberg [1] recently predicted the existence of **the WAu_{12} cluster**.

- Here, **the bonding** in the molecule is investigated in more detail, using various methods.

Computational methods

- The quantum chemical calculations were performed using the **TURBOMOLE** and **Amsterdam Density Functional, ADF**, program suites. ELF calculations were done with `dgrid`.

Level

- **Density functional theory** was used in most calculations. Both hybrid **B3LYP** and pure **BP86** was employed.

- Electron densities were calculated with DFT and the approximate singles and doubles **coupled cluster** method, **CC2**.

- Augmented triple-zeta and quadruple-zeta basis sets were used.

- With TURBOMOLE, the **Stuttgart Effective Core Potentials** with 60 core electrons were used,
- With ADF, the **Zeroth Order Regular Approximation (ZORA)** was used, with a frozen core of 60 electrons.
- Both methods leave the 5*s*, 5*p*, 5*d*, and 6*s* shells free.

- The **density fitting resolution of the identity** (RI) approximation was used, when applicable, at both DFT [2] and CC2 [3] levels.

- The RI-DFT and RI-CC2 methods reduce the computational cost significantly, without noticeable loss off accuracy.

Electron density calculations

- The electron densities were studied by evaluating them in equidistant Cartesian grid points.
- Direct numerical integrations of the electron densities were performed.

The accumulated electron density inside a sphere of radius r is defined by:

$$\rho_{el}(r) = \frac{1}{N(r)} \frac{4}{3} \pi r^3 \sum_{i}^{N(r)} \rho_{el,i}$$

where $N(r)$ is the number of integration points and i runs over all three Cartesian coordinates.

- In addition to the core, the **5*s* orbitals of Au were left out** of the integrations. This improves the numerical accuracy.

Electron Localisation Function

- The **ELF** is a useful tool developed by Becke and Edgecombe.
- The elf is constructed from the total electron density, its gradient and the kinetic energy density.
- Plots of the ELF reveal **regions of highly localised electrons**, as in covalent bonds or lone pairs.

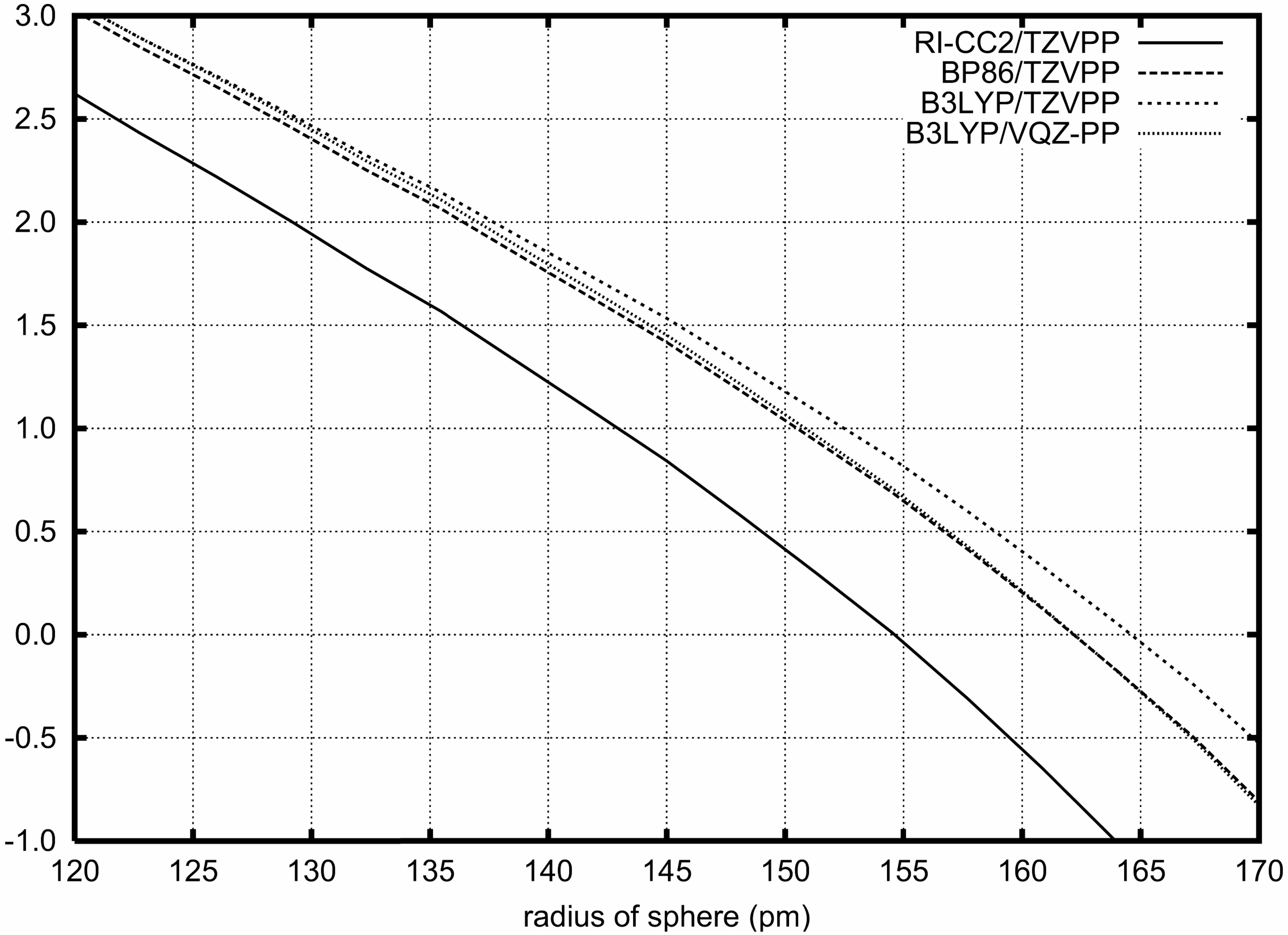
Results

Atomic charges

- No **definition of partial charges** can be considered perfect.
- The concept is, nevertheless, chemically very useful, as is the related concept of **oxidation state**.

- Here, none of the usual schemes of partial charge calculations are employed, due to their unreliability; the Mulliken charge for W, for example, was found to be –78 (B3LYP/VQZPP).

- For a highly symmetrical species as WAu_{12}, a **more direct** method for extracting the charge of the central atom exists.
- A direct integration of the electron density around W, assuming a spherical atom, yields a good picture of the charge localisation:

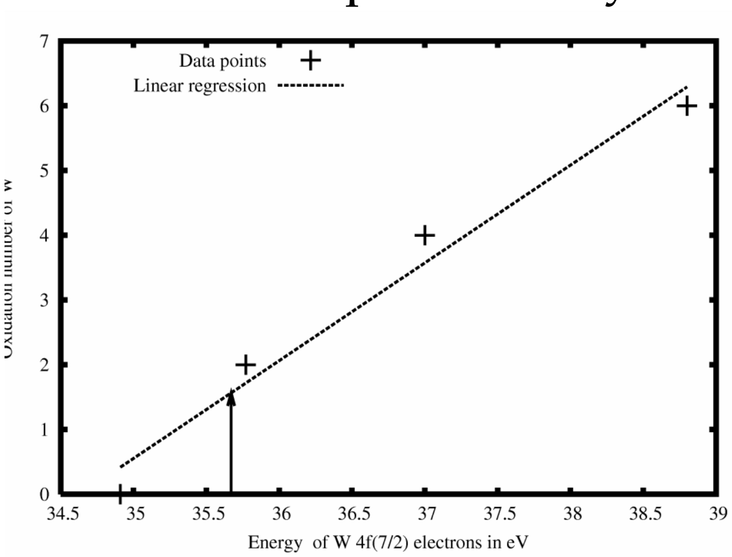


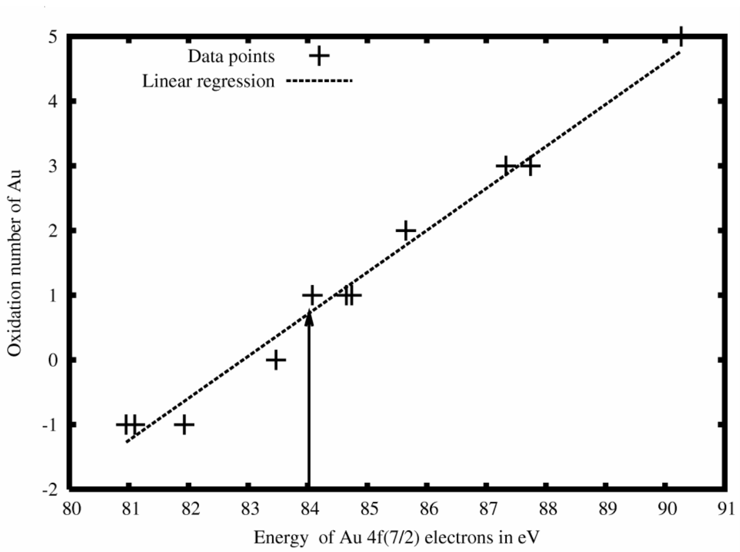
RI-CC2/TZVPP
BP86/TZVPP
B3LYP/TZVPP
B3LYP/VQZ-PP
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
120
125
130
135
140
145
150
155
160
165
170
radius of sphere (pm)

- **The charge of W is clearly positive**, even if the definition of the radius is not unambiguous.
- To get a negative tungsten, a very large radius would have to be used.
- Correcting for the assumption of a spherical W atom, using a dodecahedral charge distribution, does not change the conclusion.

Oxidation states

- The energy of the $4f_{7/2}$ orbital, obtained by **Electron Spectroscopy for Chemical Analysis, ESCA**, has been used for determination of the **oxidation state** of gold.
- Here, we employed this method computationally:





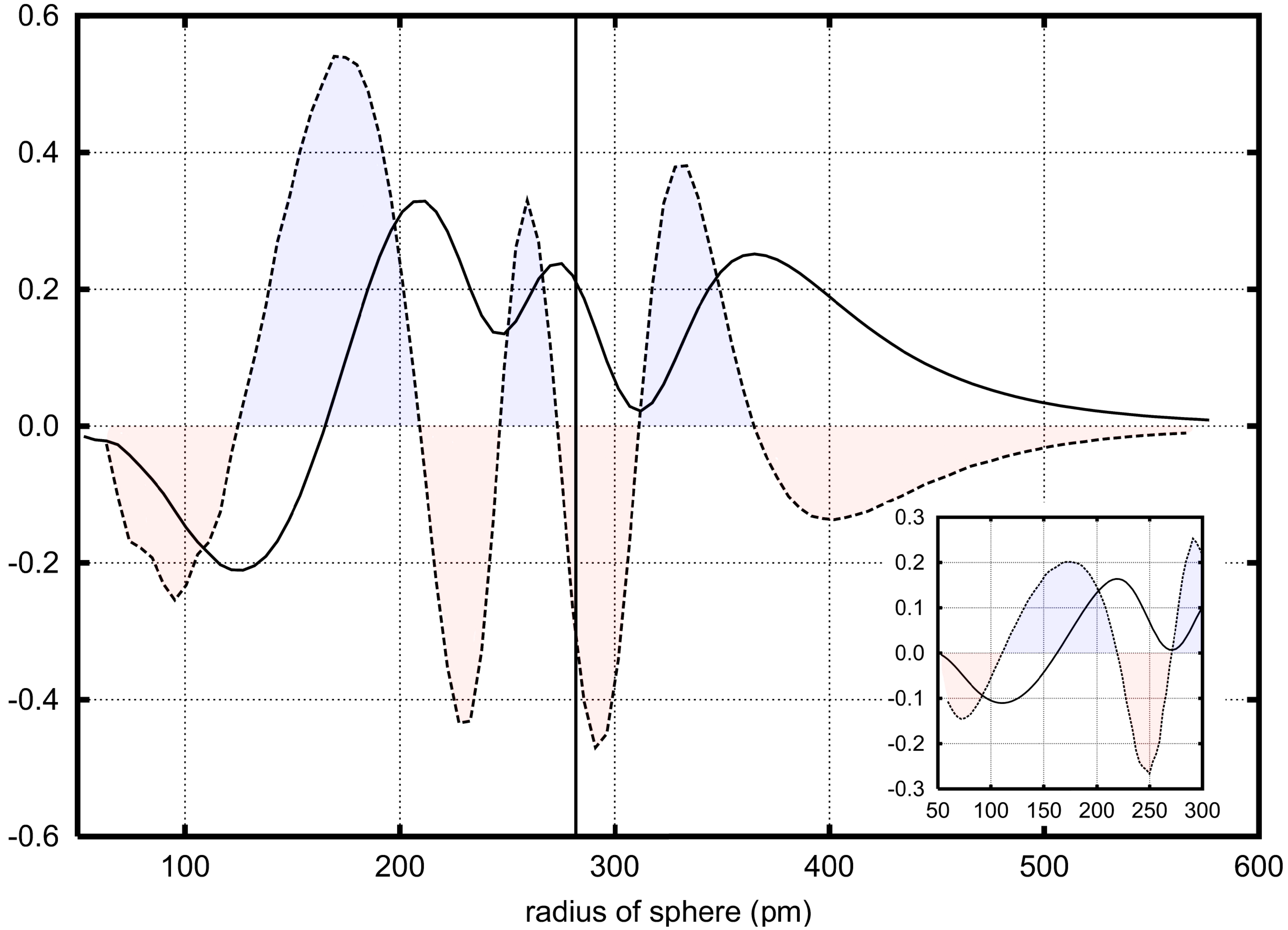
- All atoms get positive oxidation states:

  W: +2

  Au: +1

Bonding

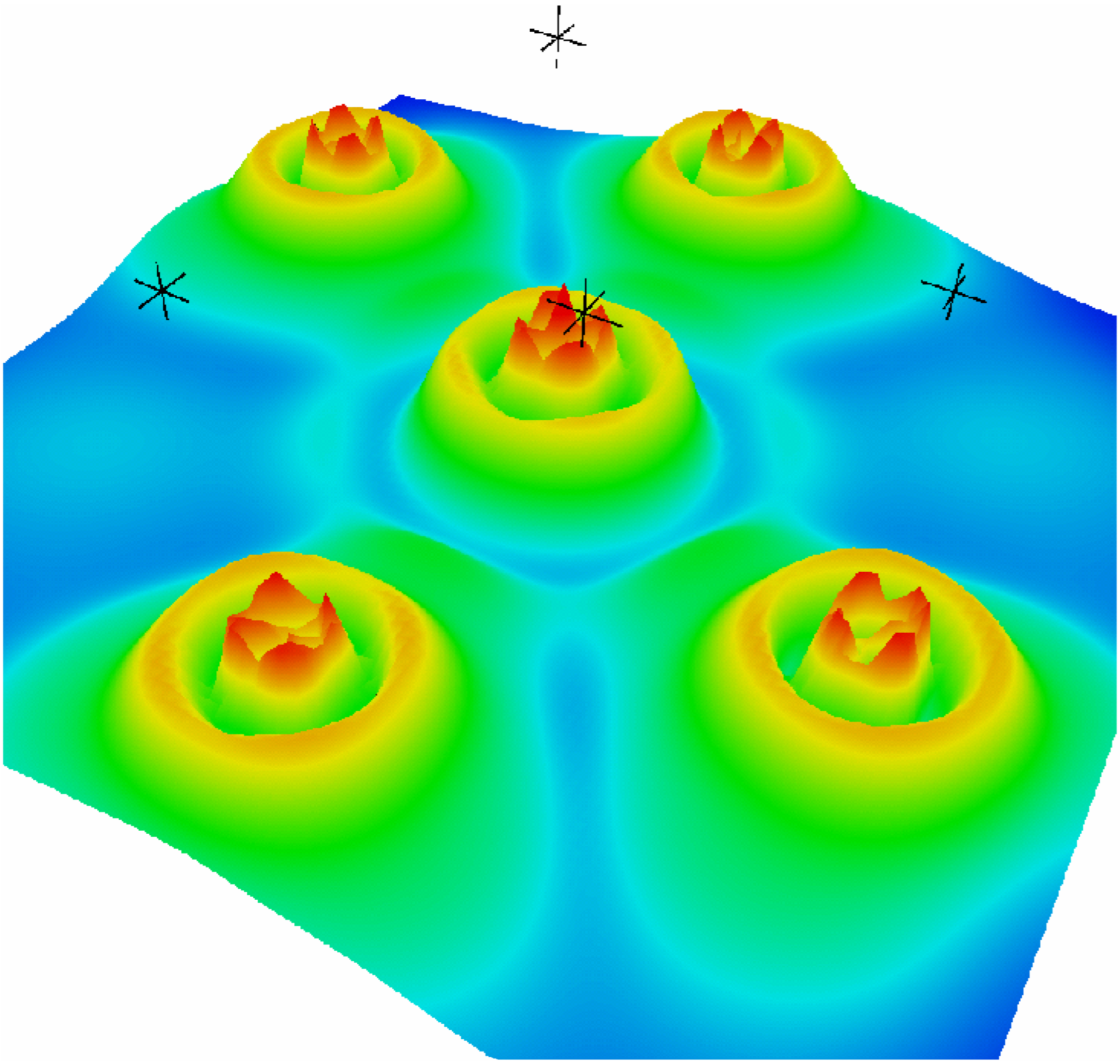
- The **electron density difference** between WAu_{12} and its constituent atoms show how the electrons move upon formation of the cluster.
- The integrated electron density difference within spheres around W and Au gives an explanation to how all atoms have positive oxidation states.
- The electron density difference near the atoms (whole lines) is negative; **both W and Au in WAu_{12} are more positively charged than the neutral atoms**.


0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
100
200
300
400
500
600
radius of sphere (pm)
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
50
100
150
200
250
300

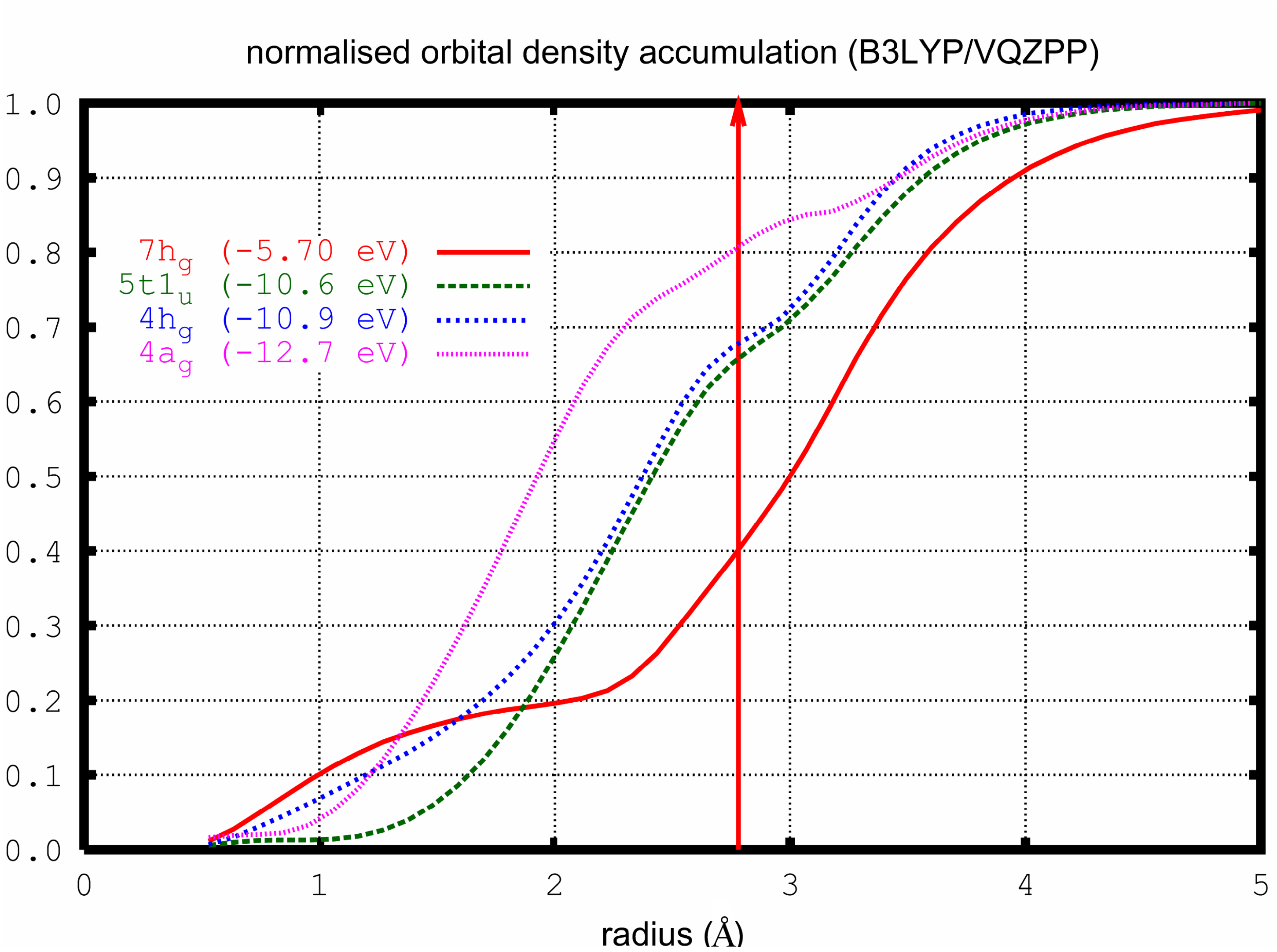
- The dashed lines show the **differentiated change in electron density**.
- Areas with a negative derivative suffer a loss of electrons upon molecule formation, positive areas gain electrons.
- Large gathering of electrons between W and the Au's are seen: **a bond is formed**.

- Other interesting features are also revealed.

- **The ELF** also shows where the electrons of W went:



- The **proposed 18-electron bonding** is corroborated by the quantum chemical calculations.
- Contributions of the 5*d*, 6*s* and 6*p* orbitals of W to the MO's of WAu_{12} were found.
- Also, a look at the radial distributions of selected orbitals of a_g, $t1_u$, and h_g symmetry (corresponding to the *s*, *p*, and *d* symmetries of W) shows their participation in bonding:



- The **Shared Electron Number analysis** shows the **strong multicentre character** of the bonding in the molecule:

"participants"	*SEN*
W–Au	4.1
Au–Au	2.2
W–Au–Au	1.8
Au–Au–Au	1.3
W– Au–Au–Au	1.2

- The **SEN analysis also supports the 18-electron binding**; the only positive contributors to the shared 4.1 electrons between W and the Au's are the a_g, $t1_u$, and h_g orbitals.

Conclusions

- W is positive.
- WAu_{12} exhibits clear multicentre bonding behaviour, even if it is very flexible [4].
- The notion of $W@Au_{12}$ is thus not motivated.

Acknowledgements

The ELF plot was made using the **gOpenMol** package [5], while the curves where obtained with **gnuplot**. CSC – Scientific Computing Ltd. is acknowledged for continuous extension of computational quota. A travel grant from Acta Chemica Scandinavica resulted in new insight to the problem at hand.

References

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[5] Laaksonen, *http://www.csc.fi/gopenmol/*