

# Understanding bonds and interactions in $\text{Pt}_3(\text{CO})_6$ oligomers and nanowires

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Large-scale electronic structure calculations are today necessary for understanding (and possibly predicting) the properties of supramolecular assemblies. Among the different methods available for these calculations, the density-functional theory (DFT) allows the description of forces acting between atoms, the sampling of relevant atomic configurations (structures, conformations, aggregation states) and the understanding of the dependence of molecular (or phase) properties from collective variables in the ground electronic state.

The level of accuracy of modern DFT calculations in condensed phases allows the simulation of the motion of several hundreds of atoms in the 100-ps time-scale. Depending on the size of the simulated sample, every kind of computer architecture can be accessed, because of the need of relatively simple linear algebra numerical tools that are efficiently implemented on whatever CPU and hardware.

The Quantum-Espresso package [1] collects most of the advantages offered by DFT, developed within a worldwide community of scientists:

1. Ultrasoft pseudopotential (USP) for accurate atomic core-valence electrons interactions.
2. Plane-waves (PW) expansion for condensed phases in periodic boundary conditions.
3. Accurate exchange functionals.
4. Implementation of different types of algorithms for structural relaxation and first principle molecular dynamics.

5. Runs from Intel/Amd PCs to Ibm BlueGene/P.
6. Mixed MPI/OpenMP implementation for parallel tasks.
7. Open source software, highly modular (Fortran 90).

Because of the PW expansion and the lack of atomic tools (atoms enter only via the pseudopotentials), the concept of atoms, retained for instance in most of the quantum chemistry applications relying on density representations based on localized atomic orbitals, is missing in this kind of DFT approach. Therefore, such electronic structure calculations deserve interpretative tools for recovering the concepts of atoms and bonds, useful for understanding chemistry.

After the seminal work of Richard Bader [2], the concept of atoms has been recovered as a result of the observable function on which the DFT approach is based, the electron density. The study of density and its gradient identifies the regions of space in the molecule that can be attributed to the atoms in the molecule. Today, efficient tools exist that allow the extraction of this information from low resolution density representations, like those provided by large-scale DFT calculations [3].

The low resolution of such density maps does not allow the identification of critical points in the Bader's analysis. Nevertheless, the nature of the bonds in the molecule can be investigated by computing the amount of shared electrons between two atoms. This concept, summarized by localization and delocalization indices (DIs) [4], allows the drawing of "bonds" between the atoms identified according to the Bader's analysis of low resolution electron density.

Within the HPC-Europa2 project, I tested, for the first time, this kind of analysis on a supramolecular assembly. I choose the molecule  $\text{Pt}_3(\text{CO})_6^{-2}$  because it forms oligomers and infinite wires in condensed phases by progressive oxidation in selected environments [5,6]. After testing the computation of DIs for simple molecular and crystalline systems, the analysis was applied to the monomeric form of the isolated anion, to several configurations obtained for the dimer and to relaxed configurations obtained for the infinite wire, assuming 8 monomers per unit cell with a total charge of -2 electron units.

The DI shows that during the assembly (*i.e.* when dimeric seeds are formed) there are no bonds between the monomers, because the DI of Pt atoms belonging to different  $\text{Pt}_3$  planes are lower than the sensitivity of the method. The monomers tend to form columns because of dispersive forces. The situation appears similar to the formation of columnar discotic phases, with the further complication that interactions result from the balance between two opposite forces: electrostatic repulsion between charged monomers (decreased by the progressive oxidation during the assembly) and dispersive attractions (increased by the disc-shaped electron density on each monomer).

The electronic structure changes when the wire is formed. This situation is monitored by studying the electronic structure of the configuration obtained, by first principle molecular dynamics at low temperature, in a cell with 8 monomers and with no positively charged counterions. The DI between Pt atoms belonging to different Pt<sub>3</sub> planes (up to 0.6) becomes larger than the maximal DI of Pt-Pt pairs within the same Pt<sub>3</sub> plane (0.5). This effect decreases by increasing the amount of excess electrons, but it is maximal for a neutral wire. This latter observation suggests that the excess electrons have no role in the electron delocalization along the axis of the infinite wire.

The DI between different Pt<sub>3</sub> planes is an effect of the short interplane distances: DIs are larger than 0.4 for Pt-Pt distances larger than 0.31 nm. The extent of formation of any low delocalization within the wire is strongly influenced by the size of the counterion. A small counterion (like sodium) is strongly attracted by the charged wires, forming a defect in the wire preventing any metallic character along its axis. This effect is indeed found by energy minimizing the cell with 8 monomers in the presence of 2 sodium counterions. Therefore, the large size of the N(Bu)<sub>4</sub><sup>+</sup> cation, necessary for the synthesis of the assembly, can be a crucial point for not perturbing the low metallic properties of the assembly.

#### References:

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