# Effect of graphene support on large Pt nanoparticles

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## Supplementary Information

The following table summarises the main quantities analysed, aiming to show that the results obtained with RPBE-D2 and rVV10 functionals are qualitatively similar, resulting in comparable overall trends for the geometric and electronic effects of the graphene support over the Pt nanoparticles.

**Table 1: Comparison between results obtained with RPBE-D2 and rVV10 XC functionals.**

| | **RPBE-D2** | | | **rVV10** | | |
|---|---|---|---|---|---|---|
| | **Pt-Pt bond length Expansion (%)** | **Δq (e/atom)** | **d-band centre shift** | **Pt-Pt bond length Expansion (%)** | **Δq (e/atom)** | **d-band centre shift** |
| **$Pt_{13}$ (100)** | 7.84 | 0.32 | -0.5 | 8.98 | 0.27 | -0.31 |
| **$Pt_{55}$ (100)** | 1.88 | 0.12 | -0.06 | 4.24 | 0.11 | -0.03 |
| **$Pt_{147}$ (100)** | 0.99 | 0.05 | -0.10 | 1.82 | 0.05 | -0.03 |
| **$Pt_{13}$ (111)** | 3.81 | 035 | -0.51 | 15.03 | 0.30 | -0.33 |
| **$Pt_{55}$ (111)** | 3.14 | 0.23 | -0.33 | 4.77 | 0.21 | -0.22 |
| **$Pt_{147}$ (111)** | 1.42 | 0.07 | -0.06 | 2.30 | 0.10 | -0.03 |

The results compared in this table are: (i) the Pt-Pt bond length expansion in the closest facet of Pt cuboctahedral nanoparticles interacting with the graphene support; (ii) The charge difference per Pt atom in contact with the graphene support obtained via Mulliken population analysis, where positive values indicate charge transfer from the Pt cluster to the graphene support; and (iii) the difference between the d-band centre obtained by the closest Pt facet before and after the contact, where negative values indicate a downshift in the d-band centre.

Meanwhile, the next two tables present the average Pt-Pt bond length for cuboctactahedral Pt nanoparticles interacting with a graphene support. The data is given from the closest to the

farthest Pt facet from the graphene support. Table 2, presents the results for nanoparticles with the (100) facet interacting with the graphene, while in Table 3 the (111) facet is the one in contact with the support.

The results presented in brackets were obtained for the same facets in isolated Pt nanoparticles. In both cases, we observe Pt-Pt bond length expansions (contractions) in the closest (farthest) facets from the graphene support, strengthening the discussion from the main text. In smaller clusters this effect is more pronounced, while almost no change can be observed in the farthest facets of larger nanoparticles.

**Table 2: Average Pt-Pt bond length for cuboctahedral Pt nanoparticles with the (100) facet interacting with a graphene support. The results are presented for all the (100) planes, where the first one is the closest to the graphene support. Results in brackets were obtained for the same facets in an isolated nanoparticle.**

| | **$Pt_{13}$** (Å) | **$Pt_{55}$** (Å) | **$Pt_{147}$** (Å) | **$Pt_{309}$** (Å) |
|---|---|---|---|---|
| **Plane1** | 2.94 [ 2.70 ] | 2.83 [ 2.71 ] | 2.8 [ 2.75 ] | 2.78 [ 2.75 ] |
| **Plane2** | 2.69 [ 2.70 ] | 2.83 [ 2.79 ] | 2.83 [ 2.79 ] | 2.82 [ 2.78 ] |
| **Plane3** | 2.67 [ 2.70 ] | 2.82 [ 2.79 ] | 2.82 [ 2.79 ] | 2.81 [ 2.79 ] |
| **Plane4** | | 2.79 [ 2.79 ] | 2.82 [ 2.79 ] | 2.80 [ 2.79 ] |
| **Plane5** | | 2.71 [ 2.71 ] | 2.80 [ 2.79 ] | 2.80 [ 2.79 ] |
| **Plane6** | | | 2.79 [ 2.79 ] | 2.79 [ 2.79 ] |
| **Plane7** | | | 2.75 [ 2.75 ] | 2.79 [ 2.79 ] |
| **Plane8** | | | | 2.79 [ 2.78 ] |
| **Plane9** | | | | 2.76 [ 2.75 ] |

**Table 3: Average Pt-Pt bond length for cuboctahedral Pt nanoparticles with the (111) facet interacting with a graphene support. The results are presented for all the (111) planes, where the first one is the closest to the graphene support. Results in brackets were obtained for the same facets in an isolated nanoparticle.**

| | **$Pt_{13}$** | **$Pt_{55}$** | **$Pt_{147}$** | **$Pt_{309}$** |
|---|---|---|---|---|
| **Plane1** | 3.11 [ 2.70 ] | 2.88 [ 2.75 ] | 2.81 [ 2.75 ] | 2.87 [ 2.76 ] |
| **Plane2** | 2.72 [ 2.70 ] | 2.84 [ 2.80 ] | 2.83 [ 2.81 ] | 2.87 [ 2.80 ] |
| **Plane3** | 2.68 [ 2.70 ] | 2.73 [ 2.73 ] | 2.80 [ 2.80 ] | 2.83 [ 2.81 ] |
| **Plane4** | | 2.80 [ 2.80 ] | 2.75 [ 2.75 ] | 2.82 [ 2.80 ] |
| **Plane5** | | 2.74 [ 2.75 ] | 2.80 [ 2.80 ] | 2.77 [ 2.76 ] |
| **Plane6** | | | 2.81 [ 2.81 ] | 2.81 [ 2.80 ] |
| **Plane7** | | | 2.75 [ 2.75 ] | 2.81 [ 2.81 ] |
| **Plane8** | | | | 2.80 [ 2.80 ] |
| **Plane9** | | | | 2.76 [ 2.76 ] |