

Electronic Supplementary Information

How to Determine Accurate Chemical Ordering in Several Nanometer Large Bimetallic Crystallites from Electronic Structure Calculations

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1. Relation between topological energy expression and model Hamiltonians

For nanoparticles (NPs) with a *fcc* lattice and extended {111} facets exposed, there is a relation between the topological energy expression

$$E_{TOP} = E_0 + \varepsilon_{BOND}^{A-B} N_{BOND}^{A-B} + \varepsilon_{CORNER}^A N_{CORNER}^A + \varepsilon_{EDGE}^A N_{EDGE}^A + \varepsilon_{TERRACE}^A N_{TERRACE}^A \quad (1)$$

and a model Hamiltonian \hat{H}_{TOP} acting on local degrees of freedom of the system. Namely, let $\hat{\sigma}_i$ be a *fictitious atomic spin* operator that upon acting on the wave function of the system returns value 1, if the lattice site i is occupied by atom A and -1, if the site i is occupied by atom B. Then, one can express the number of heteroatomic bonds A-B in the system as

$$\hat{N}_{BOND}^{A-B} = \frac{1}{4} \sum_{i,j} (1 - \hat{\sigma}_i \hat{\sigma}_j) \quad (2),$$

where the sum is taken over adjacent pairs of atoms. In turn, the coordination number of an atom in the nanoparticle is

$$\hat{N}_i^{COR} = \sum_j \hat{\sigma}_j^2 \quad (3),$$

where the sum is taken over sites adjacent to the site i . In the nanoparticle with *fcc* structure corner atoms have coordination number 6, edge atoms – 7, atoms on {111} terraces – 9 and interior atoms – 12. (Atoms on {100} terraces with coordination number 8 are not considered here for simplicity.) Hence, one can express the quantities in (1) as operators in the following way:

$$\hat{N}_{CORNER}^A = - \sum_i (\hat{\sigma}_i + 1) (\hat{N}_i^{COR} - 7) (\hat{N}_i^{COR} - 9) (\hat{N}_i^{COR} - 12) / 36 \quad (4),$$

$$\hat{N}_{EDGE}^A = \sum_i (\hat{\sigma}_i + 1) (\hat{N}_i^{COR} - 6) (\hat{N}_i^{COR} - 9) (\hat{N}_i^{COR} - 12) / 20 \quad (5),$$

$$\hat{N}_{TERRACE}^A = - \sum_i (\hat{\sigma}_i + 1) (\hat{N}_i^{COR} - 6) (\hat{N}_i^{COR} - 7) (\hat{N}_i^{COR} - 12) / 36 \quad (6),$$

where sums are taken over all atoms. Consequently, the topological energy expression E_{TOP} can be obtained by applying the following Hamiltonian to the system's wave function:

$$\hat{H}_{TOP} = E_0 + \varepsilon_{BOND}^{A-B} \hat{N}_{BOND}^{A-B} + \varepsilon_{CORNER}^A \hat{N}_{CORNER}^A + \varepsilon_{EDGE}^A \hat{N}_{EDGE}^A + \varepsilon_{TERRACE}^A \hat{N}_{TERRACE}^A \quad (7).$$

Presently we do not see a practical advantage of the topological Hamiltonian in eq. (7) over the topological energy expression in eq. (1).

2. Dependence of calculated mixing energies on the basis set size

Smaller cut-off energies, ϵ_{CUT} , were used in the electronic structure (DFT) calculations to construct topological energy expressions and to assess their accuracy, whereas the bigger cut-off energies of 415 eV could be recommended for VASP calculations involving C and O atoms (*i.e.* in studies of organic reactions catalyzed by transition metals). The differences between the mixing energies calculated with the two cut-off values are less than 1 meV per atom, which justifies the employment of the smaller cut-off in the present study.

Table S1. Comparison of the mixing energies per atom E_{ES}^{MIX} of the most stable Pd₇₀X₇₀ NPs (X = Au, Ag, Cu, Zn), obtained from density functional plane-wave calculations performed with the common (415 eV) and reduced cut-off energy values ϵ_{CUT} .

X	E_{ES}^{MIX} , meV	ϵ_{CUT} , eV
Au	-108.99	250.9
	-109.35	415
Ag	-107.94	250.9
	-108.67	415
Cu	-119.47	273.2
	-118.85	415
Zn	-498.05	276.7
	-498.52	415

3. Chemical ordering in Au₆₁Pd₆₁ crystallite:

Evaluation of method performance for less symmetric nanoparticles

In the present work we determine the chemical ordering in highly symmetric truncated octahedral NPs. In order to demonstrate that our method is not limited by any means to such “magic” particle shapes we also calculated the chemical ordering in Au₆₁Pd₆₁ NP of only C_{3v} symmetry. The NP shape is derived from a Pd NP supported on MgO(100), the structure of which was optimized by some of us in Ref. 28 [S. M. Kozlov, H. A. Aleksandrov, J. Goniakowski and K. M. Neyman, *J. Chem. Phys.*, 2013, **139**, 084701].

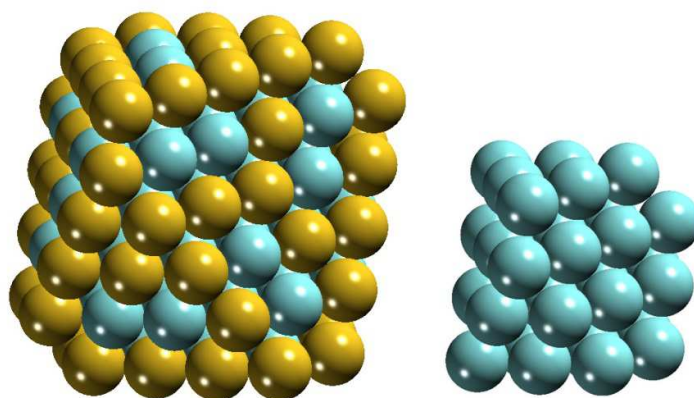


Figure S1. Surface (left) and interior (right) shells of the lowest-energy Pd₆₁Au₆₁ homotop according to density functional calculations. Pd atoms are displayed as cyan spheres, Au atoms – gold spheres.

Table S2. Comparison of descriptors ε_i^a in the topological expressions E_{TOP} for Pd₆₁Au₆₁ and Pd₇₀Au₇₀ NPs with the precision and accuracy values (in meV) and the number of structures used for the fitting, N_{FIT} .

	Pd ₆₁ Au ₆₁	Pd ₇₀ Au ₇₀
$\varepsilon_{BOND}^{Pd-Au}$	-16_{-3}^{+2}	-13_{-6}^{+4}
$\varepsilon_{CORNER}^{Au}$	-409_{-38}^{+27}	-404_{-72}^{+76}
ε_{EDGE}^{Au}	-421_{-35}^{+51}	-301_{-77}^{+52}
$\varepsilon_{TERRACE}^{Au}$	-320_{-45}^{+65}	-200_{-64}^{+52}
ε_{LAYER}	–	–
N_{FIT}	27	32
precision, δ	106	115
accuracy, ΔE	64	26

^a 95% confidence intervals of ε_i (${}_{-1}^{+k}$) are also given.

As shown in Tables S2, S3 and Figure 1, the individual topological descriptors, the overall picture of interactions as well as the chemical ordering in the Pd₆₁Au₆₁ NP are very similar to those obtained for the highly symmetric truncated octahedral Pd₇₀Au₇₀ NP. The accuracy ΔE and precision δ values of the E_{TOP} expressions for Pd₆₁Au₆₁ and Pd₇₀Au₇₀ are also very close. These findings strongly suggest that the method is applicable to reliably describe chemical ordering also in nanocrystallites with less symmetrical shapes. Notably, there are two different types of corner atoms with coordination numbers 5 and 6 in Pd₆₁Au₆₁. One may account for this difference by substituting $\varepsilon_{CORNER}^{Au} N_{CORNER}^{Au}$ by two separate terms $\varepsilon_{CORNER-5}^{Au} N_{CORNER-5}^{Au}$ and $\varepsilon_{CORNER-6}^{Au} N_{CORNER-6}^{Au}$. However, in this case the fitted values of $\varepsilon_{CORNER-5}^{Au}$ and $\varepsilon_{CORNER-6}^{Au}$ would be within 15 meV from each other, which is notably lower than the statistical inaccuracy of these parameters.

Table S3. Structural data of Pd₆₁Au₆₁ and Pd₇₀Au₇₀ homotops with the lowest energies E_{ES} . N_{BOND}^{Pd-Au} – the number of Pd–Au bonds; N_{CORNER}^{Au} , N_{EDGE}^{Au} , $N_{TERRACE}^{Au}$, $N_{SURFACE}^{Au}$, $N_{INTERIOR}^{Au}$ - the numbers of Au atoms in corner, edge, terrace, surface and interior positions, respectively. The first row for each NP shows the absolute numbers and the percentage of the possible maximum values is in the second row.

NP	N_{BOND}^{Pd-Au} ^a	N_{CORNER}^{Au} ^b	N_{EDGE}^{Au}	$N_{TERRACE}^{Au}$	$N_{SURFACE}^{Au}$ ^c	$N_{INTERIOR}^{Au}$ ^d
Pd ₆₁ Au ₆₁	225/543 41%	18/18 100%	27/27 100%	16/43 37%	61/88 69%	0/34 0%
Pd ₇₀ Au ₇₀	260/636 41%	24/24 100%	24/24 100%	22/48 46%	70/96 73%	0/44 0%

^a The percentage of Pd–Au bonds is given with respect to the total number of bonds in the NP;

^b N_{CORNER}^{Au} is the sum of Au atoms in 5- and 6-coordinated corner positions;

^c $N_{SURFACE}^{Au} = N_{CORNER}^{Au} + N_{EDGE}^{Au} + N_{TERRACE}^{Au}$ is the total number of Au atoms on the surface;

^d $N_{INTERIOR}^{Au}$ is the number of Au atoms not exposed on the NP surface.