

Functionalization of graphene with 4d and 5d transition metals

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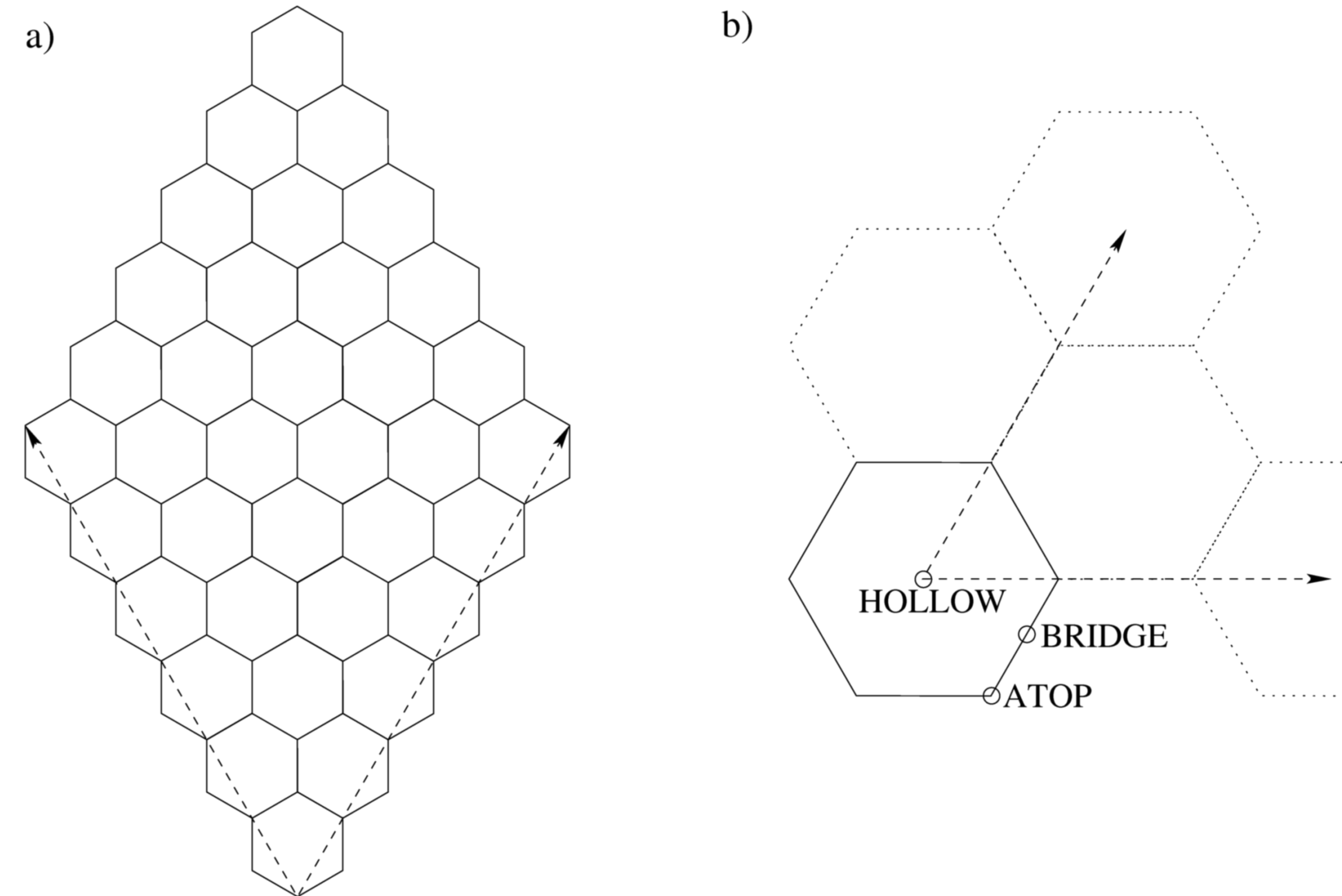
Introduction

Transition metals are widely used as substrates and contacts for graphene and carbon nanotubes. Au contacts are often used but other metals have been used and studied as well, such as Pt and Pd.

As a guide to choosing the optimal contacts in e.g. transport measurements, it is therefore of interest to understand which metals bind most strongly. Furthermore, it has been shown that electronic transport through graphene nanoribbons can be used for single-molecule sensing.

Knowledge of binding energies could allow such measurements to discriminate between analyte atoms or molecules. In the case of extremely strong binding, novel materials may be produced similar to graphene (fully hydrogenated graphene).

The Geometry



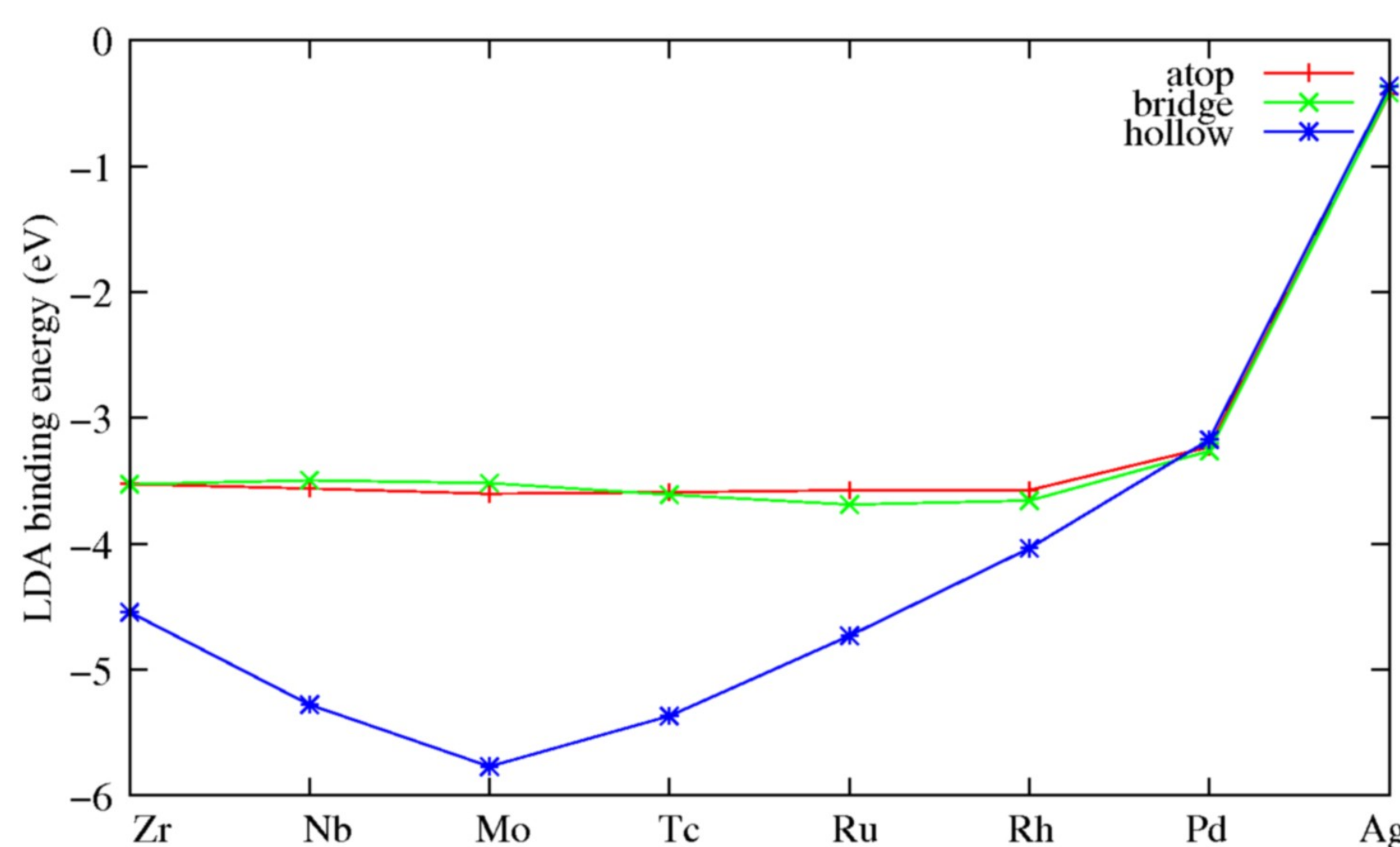
Methods



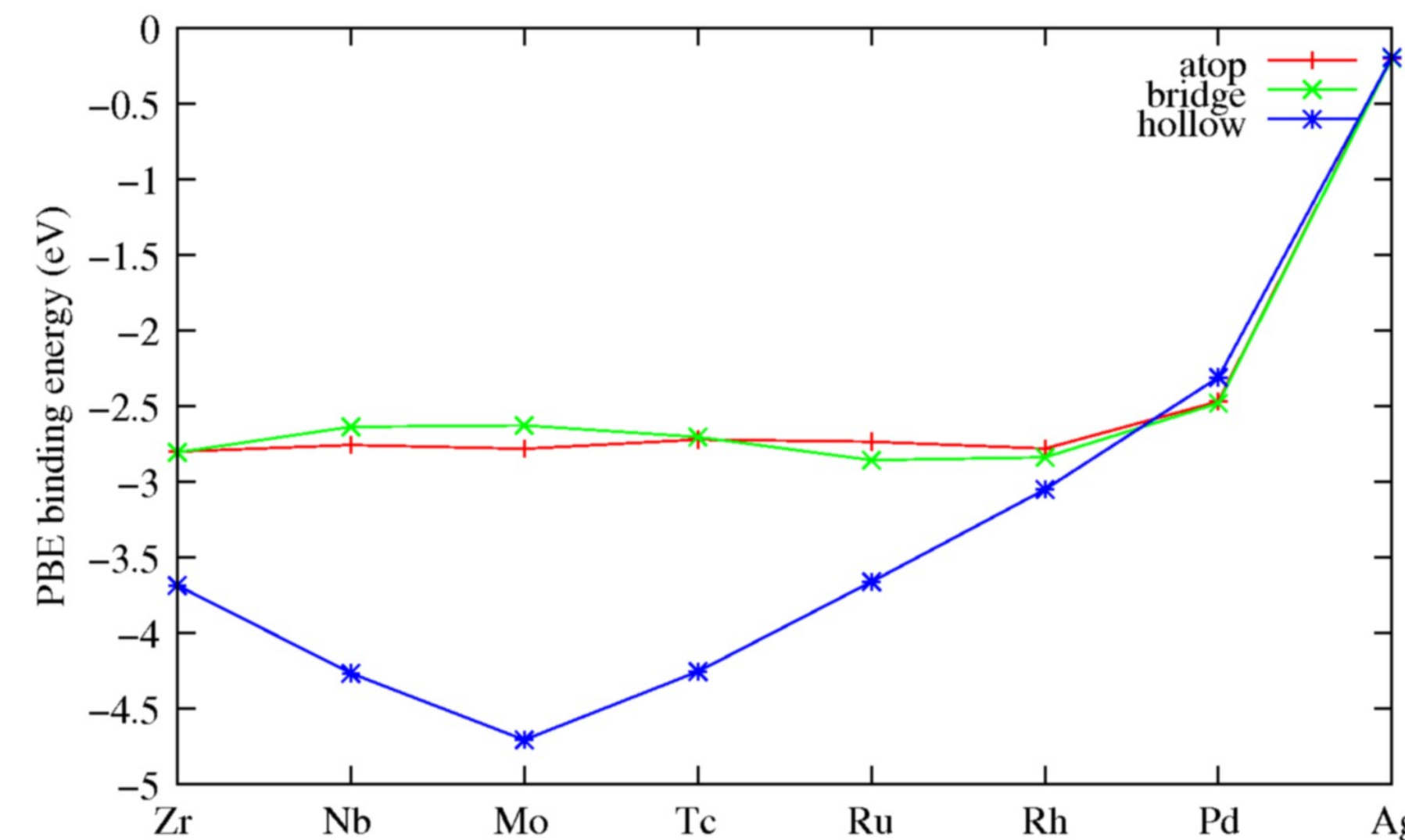
- We use state-of-the-art density functional theory with a plane-wave basis set as implemented in the VASP code (500 eV cutoff, 6×6 k-point grid).
- Low-coverage calculations are performed on a 72 atom supercell (geometry a)
- high coverage calculations are performed on a 6 atom supercell (geometry b) using one adatom per supercell in each case.
- High symmetry sites (atop, bridge, hollow) are examined and bond distances are fully optimized.
- Charge transfer is obtained via Bader charge analysis.
- Perdew-Burke-Ernzerhof functionals (PBE) were used during the calculation, local density approximation (LDA) was applied for comparison calculations.

Results

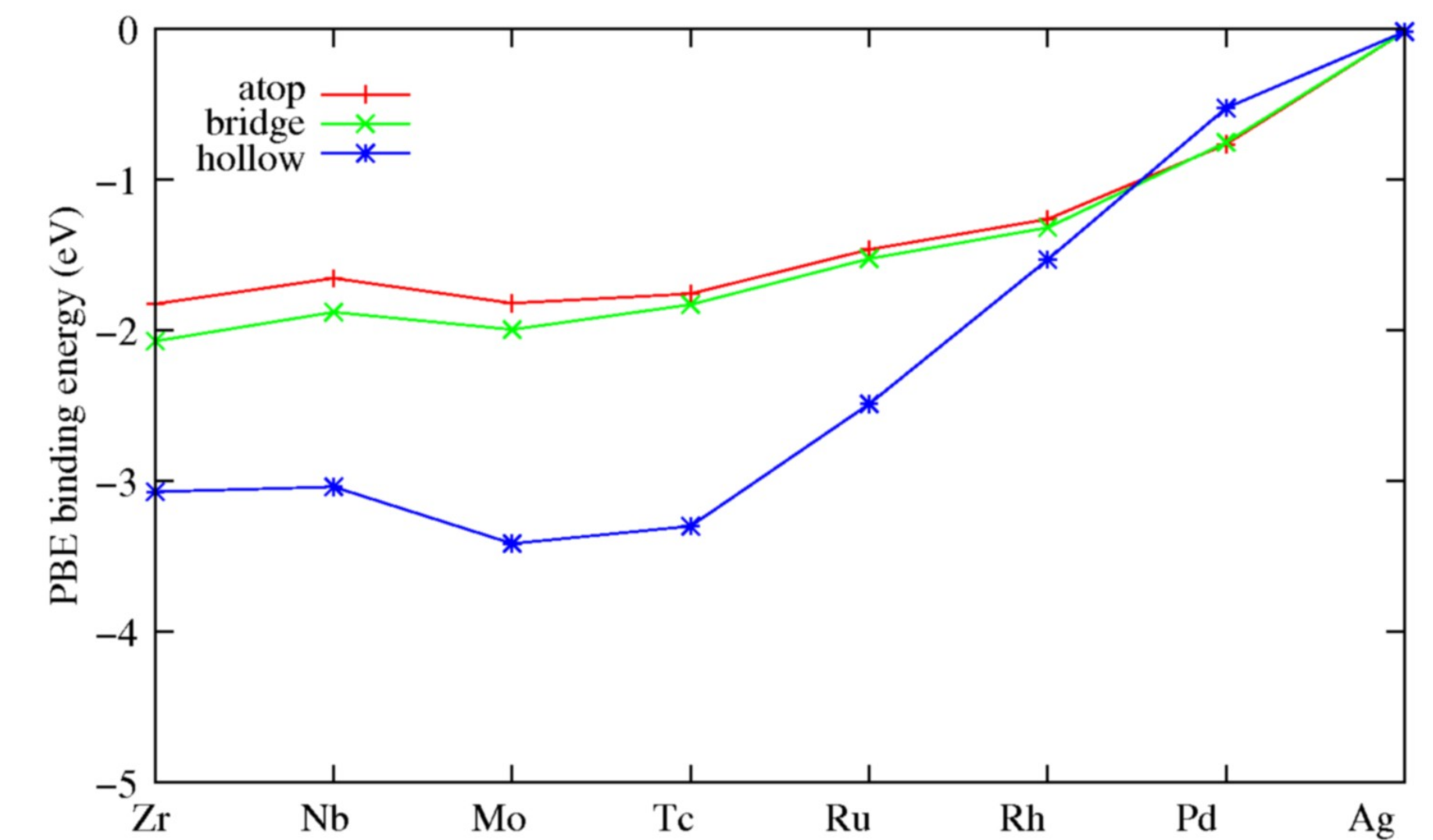
LDA 4d metals – low coverage



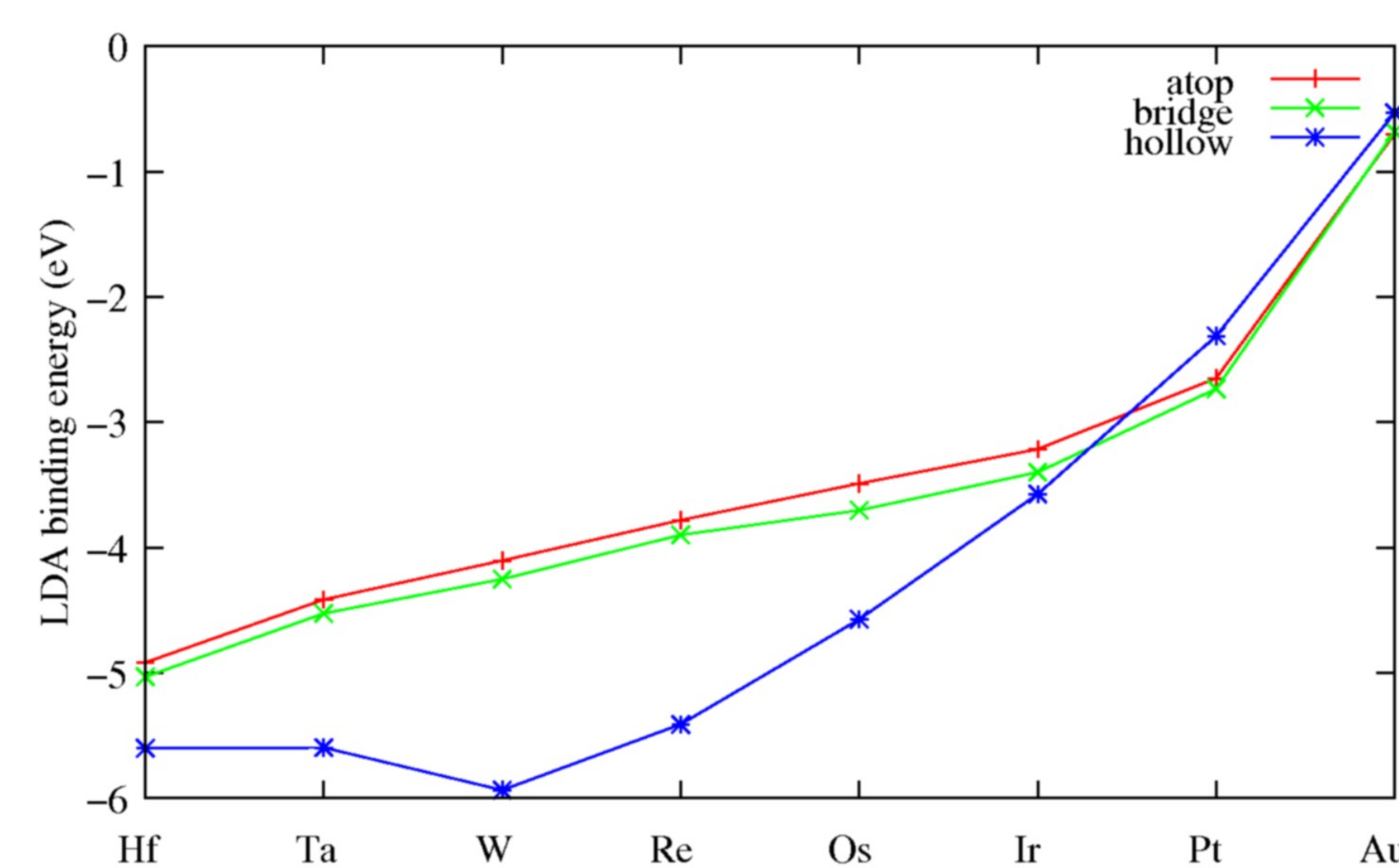
PBE 4d metals – low coverage



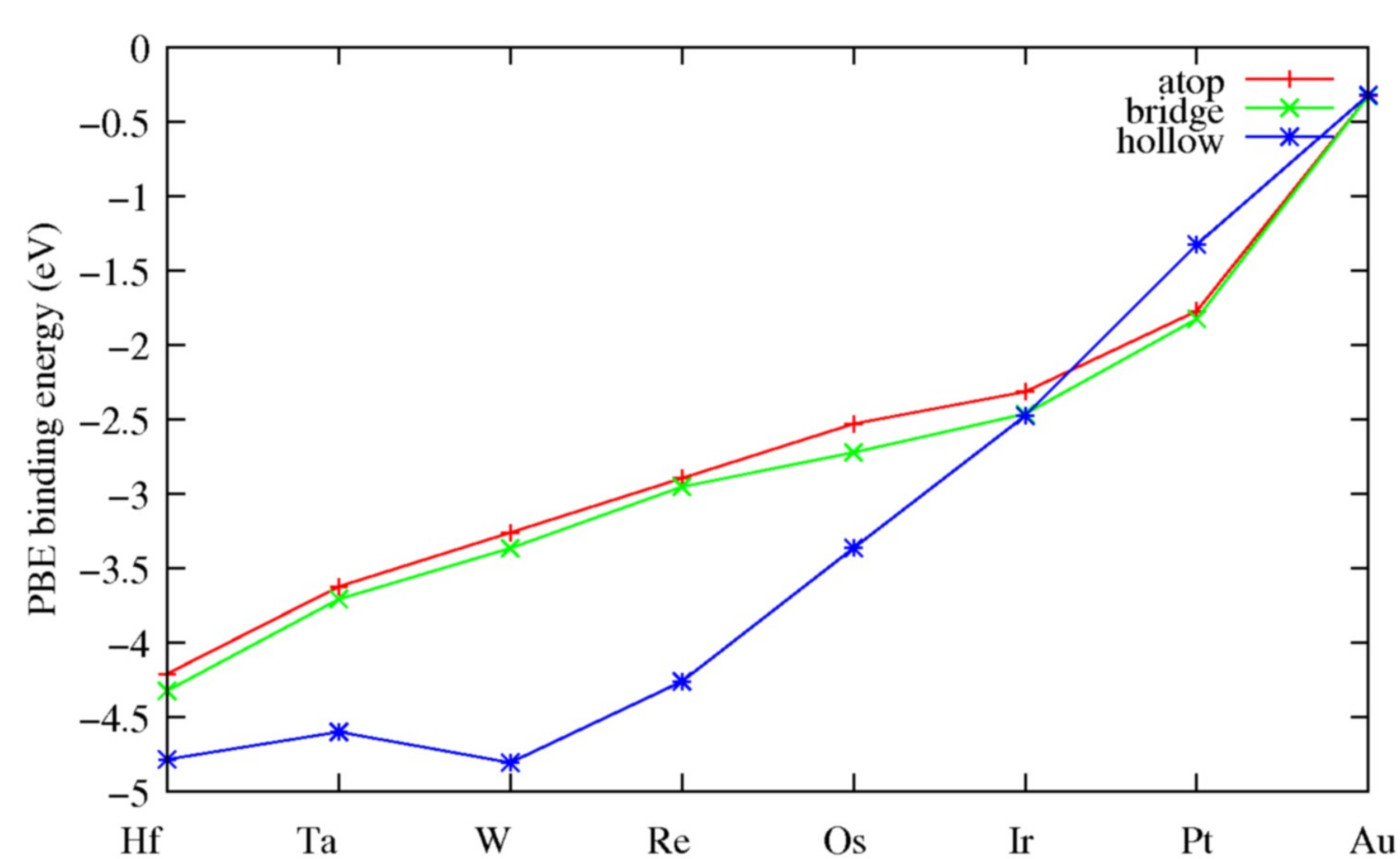
PBE 4d metals – high coverage



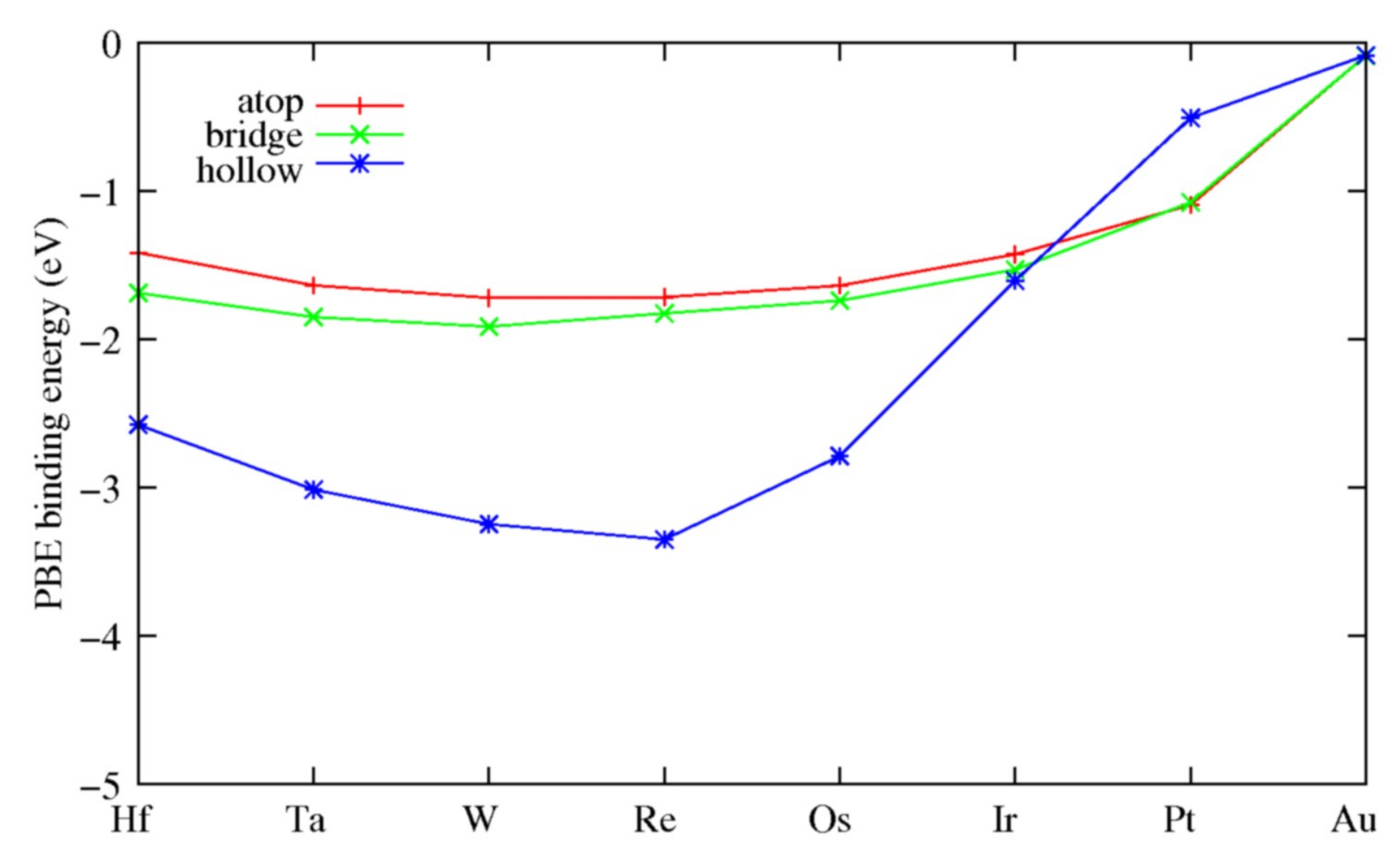
LDA 5d metals – low coverage



PBE 5d metals – low coverage



PBE 5d metals – high coverage



Discussion

A smooth increasing trend can be observed in the strength of the binding as the number of d valence electrons decreases. In some cases (e.g. Hf) the binding is very strong, suggesting that there is strong orbital hybridization for some of these metals.

We have performed a full optimization of the functionalized graphene in the low-coverage limit for the four most strongly bound metals and have found that the distortion of the graphene is relatively small, atoms move out of plane by less than 0.1Å. While this will have important effects on the electronic structure, the binding energies seem to be only slightly influenced by the distortion.

Rigid vs. distorted graphene

	ΔE_1 (eV)	ΔE_2 (eV)	d_1 (Å)	d_2 (Å)	CT_1 (-e)	CT_2 (-e)
Mo	-4.710	-4.831	1.696	1.655	1.25	1.25
Hf	-4.787	-4.832	2.008	1.968	1.34	1.34
Ta	-4.604	-4.689	1.836	1.734	1.38	1.38
W	-4.810	-4.960	1.682	1.639	1.48	1.48

The binding energies of Mo, Hf, Ta, and W on graphene at low-coverage (at hollow sites). ΔE_i : binding energy per transition metal atom. d_i : distance of the transition metal atom from the sheet. CT_i : charge transfer, i.e. number of electrons removed from the transition metal and transferred to graphene. $i=1$ in these parameters corresponds to the case of the approximation of a rigid graphene sheet, while $i=2$ corresponds to the results obtained after the full optimization of the graphene sheet.

Conclusions

- A smooth increasing trend can be observed in the strength of the binding as the number of d valence electrons decreases.
- For a few metals, binding is very strong, possibly creating a new material similar to graphane.
- The graphene sheet distorts slightly but its effects upon the binding energy are negligible.
- Charge is transferred from the adatoms to the graphene on the order of 1-2 electrons per adatom.