ON THE ACCURACY OF DENSITY FUNCTIONALS IN DESCRIBING TRANSITION METAL SURFACE PROPERTIES

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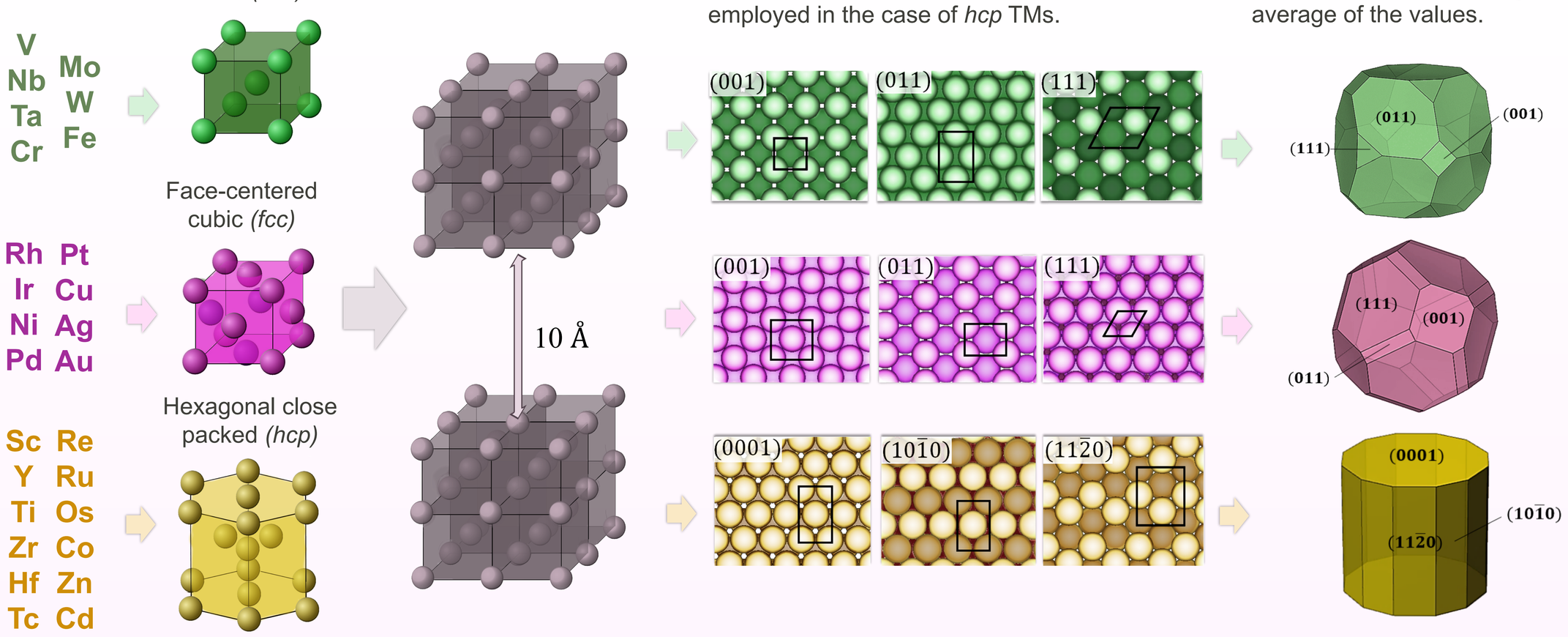
The study evaluates the accuracy of some widespreadly used Density Functional Theory (DFT) functionals in calculating different surface properties, as the surface energy, the work function, and the interlayer distance, following the next workflow.

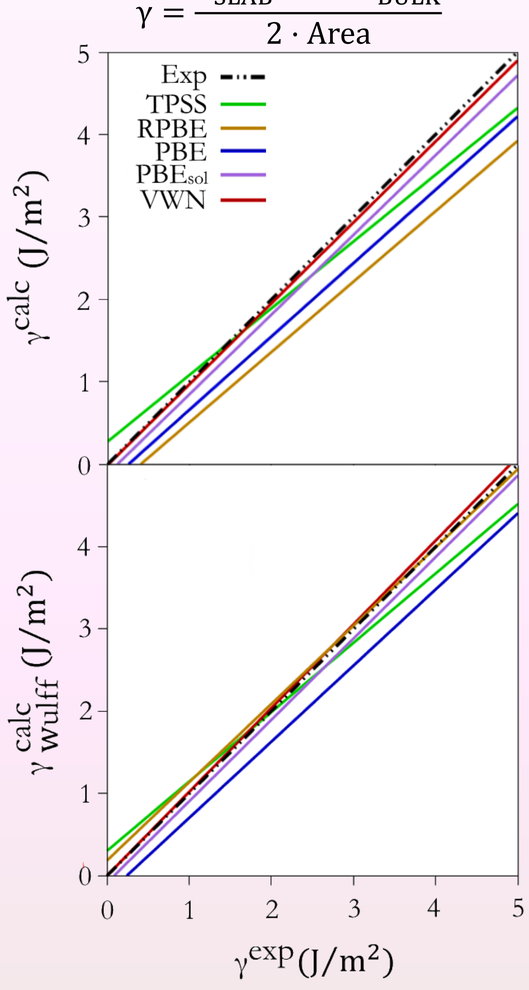
Object	Structure	Simulation	**3** Surfaces	Wulff Constructions[1]	**5** Functionals
27 Transition Metals (TMs).	Body-centered cubic *(bcc)*	Slab model with boundary conditions in $\vec{x}$, $\vec{y}$, i $\vec{z}$.	Most stable lowest Miller indexes surfaces with a maximum index order of 1 are considered. Miller−Bravais indexes are employed in the case of *hcp* TMs.	Obtained by the stability of the studied surfaces. They are used to make a weighted average of the values.	Exchange and correlation (*xc*) DFT functionals.



Surface Energy (γ):

Necessary energy to create a surface.

$$\gamma = \frac{E_{SLAB} - N \cdot E_{BULK}}{2 \cdot Area}$$

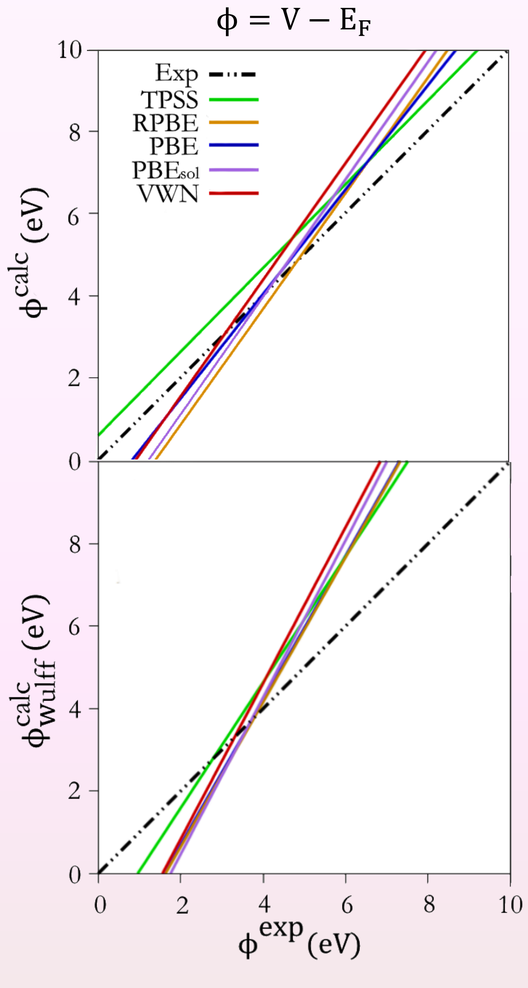


Comparison of the linear fits between calculated (calc) and experimental (exp) surface energies for the different explored *xc* functionals. The top panel considers only the most stable surface, γ^{calc}, whereas the bottom panel compares Wulff-shape-averaged values, γ^{calc}_{Wulff}.

Work Function (ϕ):

Necessary energy to bring an electron from the last occupied level (Fermi energy, E_F) to the vacuum (V).

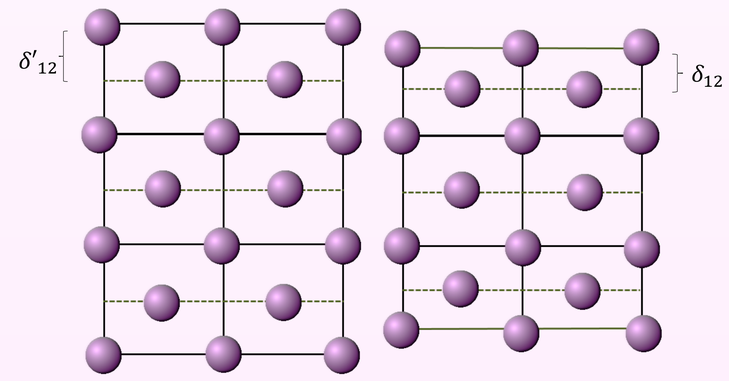
$$\phi = V - E_F$$



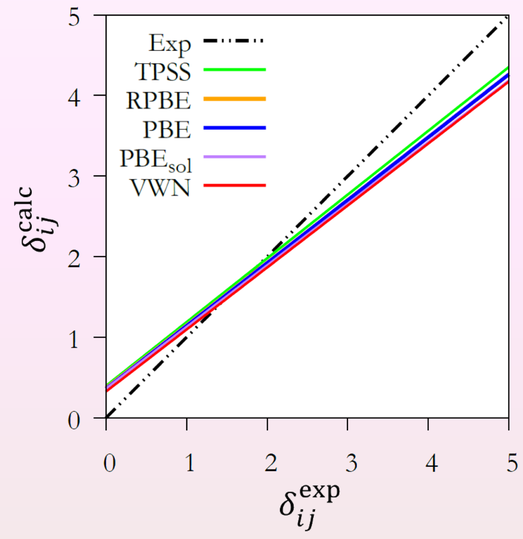
Comparison of the linear fits between calculated (calc) and experimental (exp) work functions for the different explored *xc* functionals. The top panel considers only single-crystal data, ϕ^{calc}, whereas the bottom panel compares polycrystal data with Wulff-shape-averaged values, ϕ^{calc}_{Wulff}.

Interlayer Distance (δ_{ij}):

Distance between layers after the surface is created and relaxed.



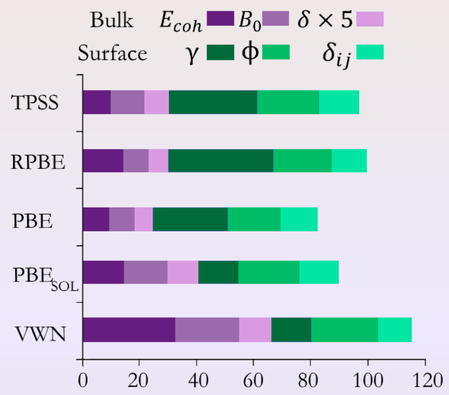
6 layers slab model before relaxation (δ'_{ij}) and after relaxation (δ_{ij}), respectively.



Comparison of the calculated interlayer distances, δ^{calc}_{ij}, to experimental data, δ^{exp}_{ij}, as calculated and adjusted to linear regression for each functional.

Conclusions[2]

Summary of *xc* functional accuracy in describing bulk and surface related properties according to the sum of Mean Absolute Percentage Error (MAPE) values.



- Wulff shapes provides better results for surface energies and although not for the work functions, the polycrystal data is more representative than the single values due to the small amount of data.
- Jacob's ladder is not followed by TM surface properties. See in the table below the best functional, according to MAPE average values, for each surface property.

γ	ϕ	δ_{ij}
VWN	PBE	PBE

- Taking into account bulk[3] and surface properties, the best functional is PBE closely followed by PBE$_{SOL}$. For pure surfaces properties PBE$_{SOL}$ is advised.

[1] Viñes, F., Gomes, J.R.B., Illas, F., *Chem. Soc. Rev.*, **43**, 4922 (2014).
[2] Vega, L., Ruvireta, J., Viñes, F., Illas, F., *J. Chem. Theory Comput.*, **14**, 395 (2018).
[3] Janthon, P., Lao, S., Kozlov, S.M., Viñes, F., Limtrakul, J., Truhlar, D.G., Illas, F., *J. Chem. Theory Comput.,* **10**, 3832 (2014).