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Developments and applications towards realistic and reliable atomistic models in heterogeneous electrocatalysis

LABORATOIRE
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Context

Modelling heterogeneous electrocatalysis:

Gain **atomistic insights** into catalytic reactions that will become large-scale industrial processes:

- ♥ Hydrogen evolution reaction
- ♥ CO₂ electroreduction
- ♥ Biomass electro-oxidation

Despite significant progress over the last two decades,¹ modelling of electrocatalysis remains challenging:

- ♥ Generalized-gradient approximations (GGA) suffer from charge-delocalization²
- ♥ Interfaces with liquids need to be large
- ♥ Diffusion is slow at the solid/liquid interface

Grand-canonical (GC) ensemble: the number of electrons is varied to control the electrochemical potential

Using the **random-phase approximation (RPA)** instead of GGAs³

→ Correct CO site preference

Electrostatic embedding for GC-DFT

→ **Replace the questionable⁴ implicit solvent** by molecular-mechanics/molecular dynamics⁵

Computational details

VASP, PAW for all DFT computations

Implicit solvent (linearized Poisson-Boltzmann equation) via VASPsol

1 M electrolyte

RPA based on PBE electronic structure

Symmetric unit cells (clear definition of workfunction)

SolvHybrid⁶ for MM system setup

Multiple lateral unit cells for larger (10 Å cutoffs)

About 30 Å of solvent/electrolyte (1 M) on top and bottom

TIP3P water model, AMBER force field for Na⁺, Cl⁻

UFF for QM part, except for MoS₂⁷

Amber's sander program for MD simulations (6 ns)

6000 snapshots, numerical grid of 0.25 Å spacing

Grand-potential to account explicitly for the **electrochemical potential**

$$\Omega(\nu, \mu) = E(\nu, \mu) - N \cdot \mu$$

$$G(U) \approx E(q) - \mu(q) \cdot q$$

Grand-canonical RPA³

Validation for metallic surfaces in implicit solvent

The results of RPA provide only the energy, not the electronic structure (no Fermi-level, no work function)

To define the **Fermi energy**:

Use the derivative of the energy (E) with respect to the number of electrons! $\epsilon_F = \frac{\partial E}{\partial n_{\text{electrons}}}$

→ Coherent results are obtained for metallic surfaces (see Fig. 1)

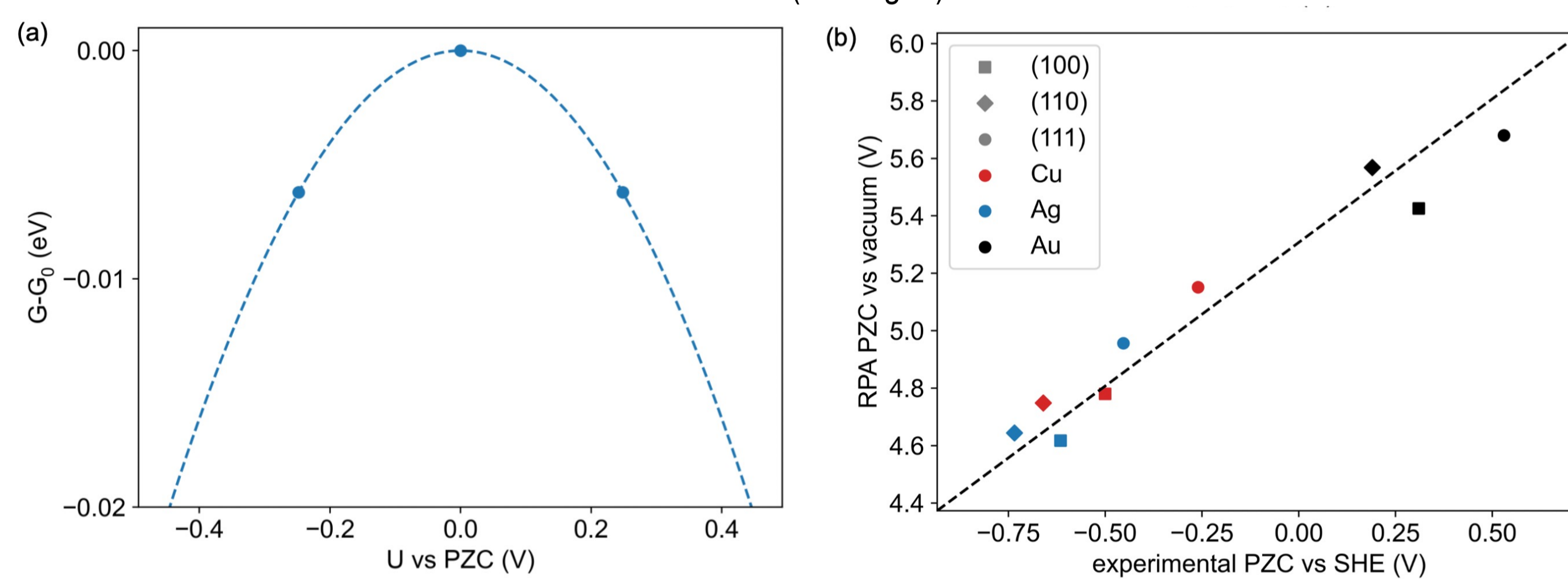


Figure 1 Grand-potential as a function of the electrochemical potential (a) and the potential of zero charge for selected surface facets and metals (b) as obtained by GC-RPA in the implicit solvent based on the linearized Poisson-Boltzmann equation.

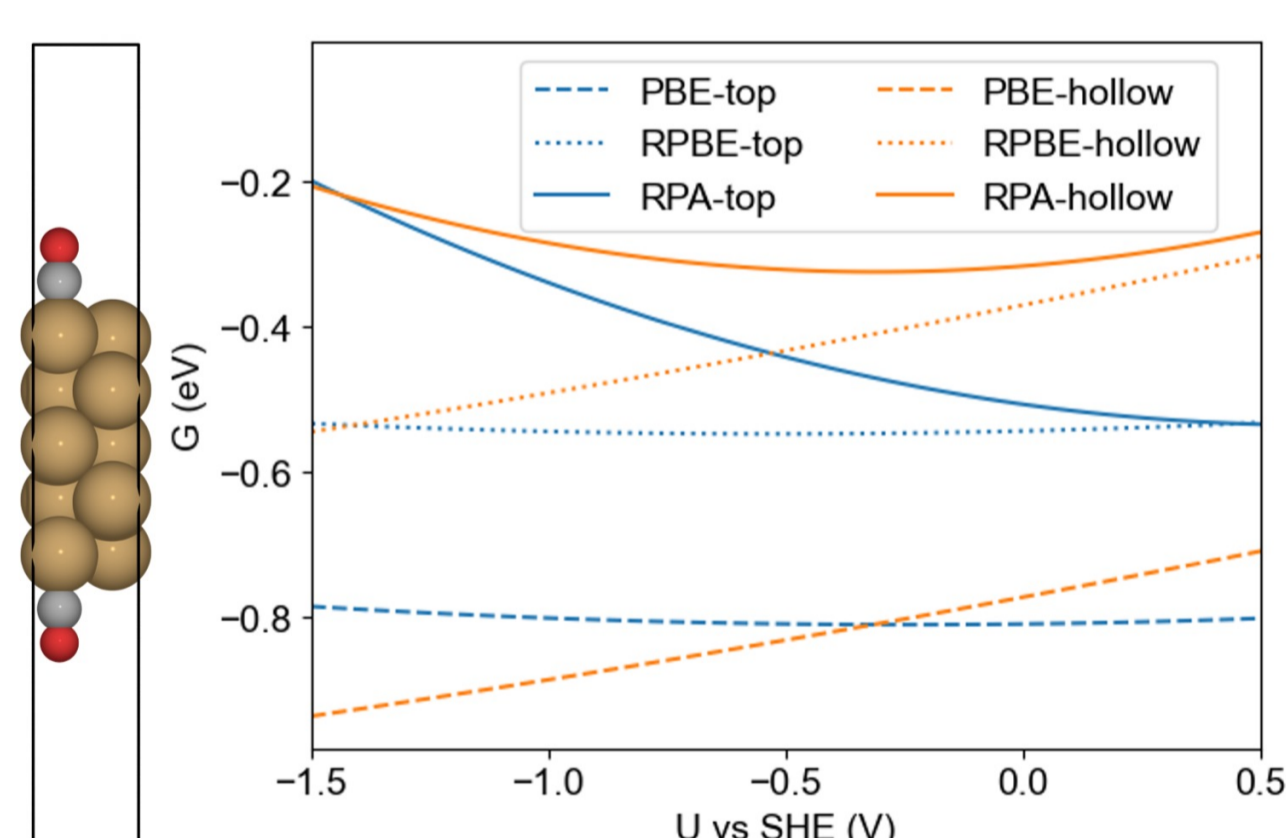
Application to CO adsorption on Cu(100)

Model reaction for CO₂ electroreduction: CO electroreduction on Cu(100)

CO adsorption is tricky for GGA functionals:

PBE is qualitatively wrong (hollow site is not observed experimentally)

RPBE is shifted in terms of energy (Fig. 2), is this correct?



RPA: capacitance and relative adsorption energies are corrected with respect to GGA

→ **Agreement with experiment**

Figure 2 Adsorption energy of CO on Cu(100) as a function of the electrochemical potential at the top (blue) and hollow (orange) adsorption site. RPA predicts CO to be adsorbed at the top site across the whole range of potentials.

Electrostatic embedding⁵

Coupling VASP and molecular mechanics (point charges)

Implementation of coupling between point charges from MM and DFT in VASP

Averaged distributions for solvent and electrolyte (see Fig. 3)

Charge balance via discrete numbers of excess cations or anions

→ Replacement of implicit solvent for GC-DFT

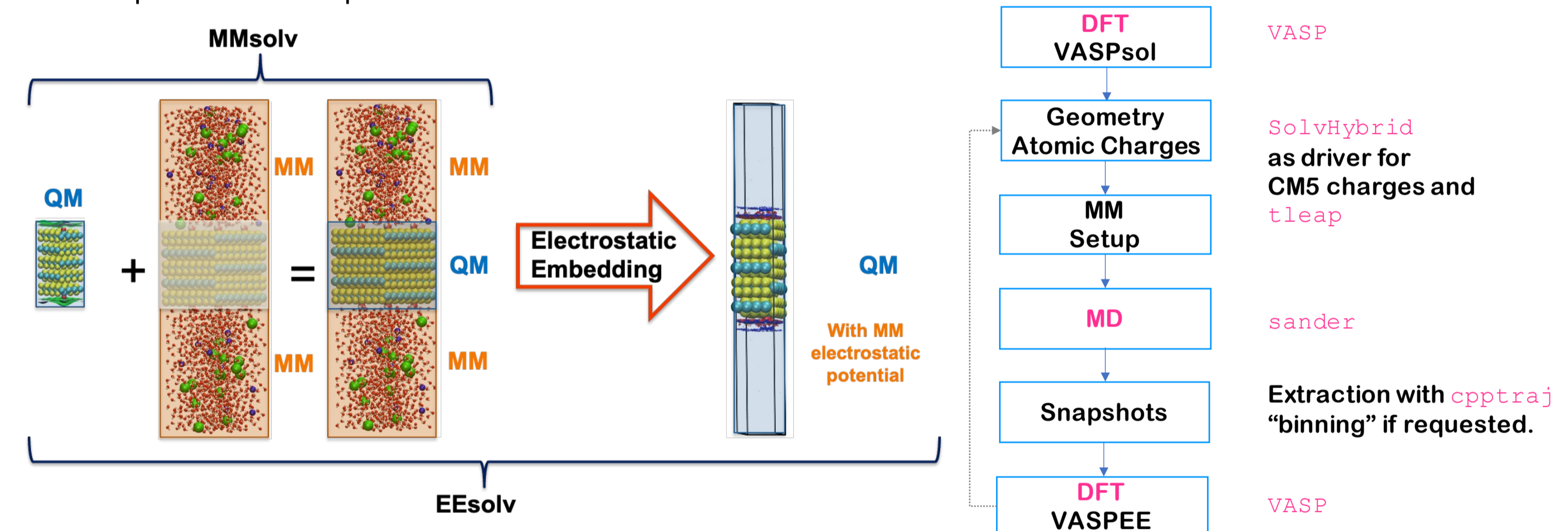


Figure 3 Scheme (left) and workflow (right) for electrostatic embedding in VASP. Repeating the procedure at different numbers of electrons leads to GC-DFT with VASPEE.

Application to hydrogen evolution on MoS₂ edges

VASPEE: qualitatively similar to VASPsol for MoS₂ defective basal plane (see Fig 4)

Subtle differences when polarity of the surface changes due to explicit solvent distributions.

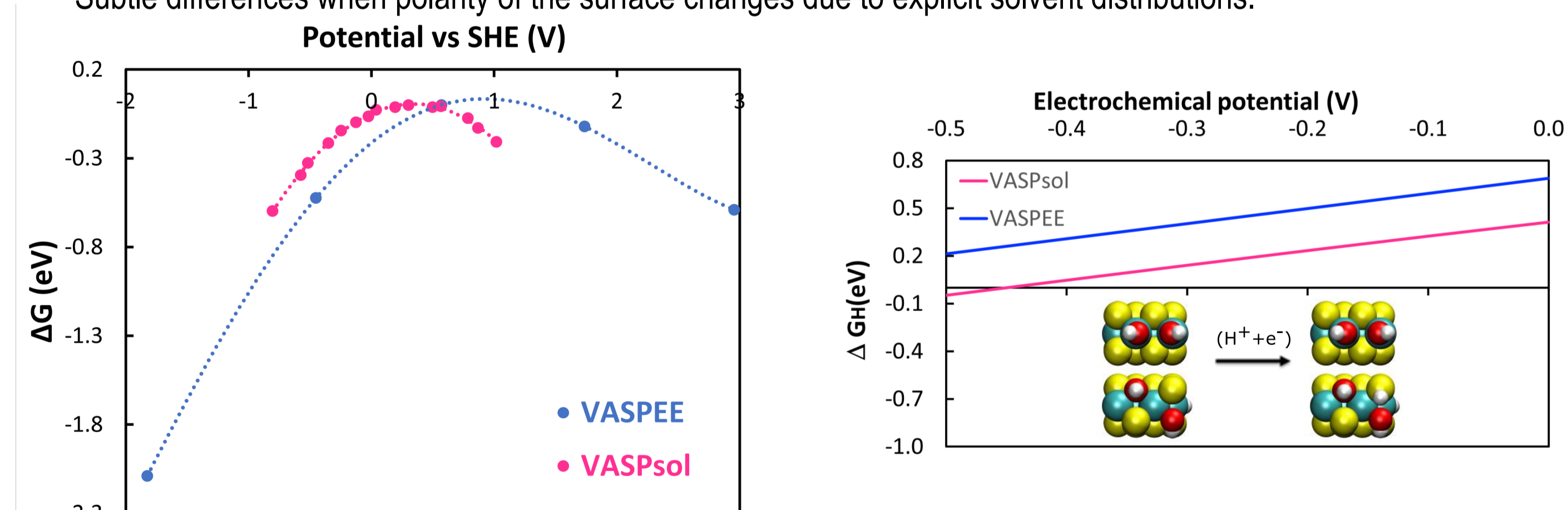


Figure 4 Example of GC-DFT energy with implicit solvent (VASPsol) and electrostatic embedding (VASPEE) (left) and example of H⁺ + e⁻ adsorption (Volmer step) on a reconstructed MoS₂ edge (right).

Conclusions

- ♥ GC-RPA is very expensive for metallic systems
- ♥ GC-RPA leads to significant changes compared to GC-GGA
- ♥ **Electrostatic embedding is a practical tool overcome limitations of implicit solvents**
- ♥ Solvent effects are crucial in electrocatalysis: "small" variations can lead to changes in interpretations

Perspectives

- ♥ Streamline the workflow, interface to CP2K
- ♥ Coupling of electrostatic embedding to accurate metal/water force fields (GAL17/GAL21)
- ♥ Application of electrostatic embedding to experimentally well characterized model systems
- ♥ Investigation of oxide catalysts and pH effects

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