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## Computational electrocatalysis: methods and fundamental applications on CO<sub>2</sub> reduction and formic acid oxidation

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**Propositions**  
accompanying the thesis  
**Computational Electrocatalysis: Methods and Fundamental Applications on CO<sub>2</sub>  
Reduction and Formic Acid Oxidation**

- 1) Over-binding functionals (PBE, PW91) and under-binding functionals (RPBE, PBE+D3, RPBE+D3 BEEF-vdW, optPBE) provide different magnitudes of solvation energy of \*OH on different near-surface alloys of Pt. The average difference between the two groups is ~0.15 eV, therefore extrapolation of solvation energies from one group to the other should be avoided.  
Chapter 2
- 2) Using tabulated half-cell standard equilibrium potentials provides a simple and accurate method to calculate free energies of solution-phase charged species which are otherwise challenging to perform with DFT.  
Chapter 3
- 3) Errors in the calculated formation energies of gas-phase molecules using DFT-GGA functionals can be corrected following an algorithm based on group additivity. By using this scheme, the mean absolute errors (MAEs) of calculated formation energies of CO<sub>2</sub> and CO reduction reactions are reduced by one order of magnitude.  
Chapter 4
- 4) Pd<sub>ML</sub>Pt(111) is a promising bimetallic surface for formic acid oxidation to CO<sub>2</sub> and CO<sub>2</sub> reduction to formic acid. This material catalyzes these reactions almost reversibly at low overpotentials, and combines the robustness of Pt and the tolerance toward CO poisoning of Pd.  
Chapter 5 and 6
- 5) Plotting the DFT-calculated adsorption free energy as a function of coverage and electrochemical potential enables a direct comparison with experimentally measured cyclic voltammograms by providing information on the identity and the relevant coverage of the species adsorbed on the surface at a particular potential.  
Chapter 5
- 6) High coverage of strongly adsorbed formate helps prevent CO poisoning on Pd<sub>ML</sub>Pt(111) at oxidizing potentials by blocking the ensemble sites needed for its formation.  
Chapter 6
- 7) The opening of the poisoning path during CO<sub>2</sub> reduction is related to the adsorption of \*COOH at less negative potentials on Pt(111) than on Pd<sub>ML</sub>Pt(111).  
Chapter 6
- 8) Humans are a time machine that only moves forward.
- 9) To err is human; to edit, divine.  
(Grammatically adaptation of Alexander Pope's quote)