

## Constrained DFT and its applications in electrochemistry

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### ABSTRACT

Traditional DFT functionals, *e.g.* those from the PBE and BLYP families, have been widely adopted to model electrochemical systems, but they all suffer from varying degrees of self-interaction error. This error leads to spurious charge delocalization, which can manifest, for instance, as inaccuracies in calculated reaction barriers. [1] A prototypical example of a pathological system is the inconspicuous looking  $\text{H}_2^+$  dimer, where traditional functionals fail to localize the excess positive charge on one of the hydrogen atoms when the atoms are pulled apart.

Constrained DFT (CDFT) is one possible tool for overcoming these issues [1, 2]. Charge and spin localized states are conveniently created in CDFT by augmenting the standard Kohn-Sham energy functional with additional density dependent external potentials, which enforce the desired localization criteria. These so-called diabatic states are central in different charge transfer theories, such as Marcus theory, and they also form the basis for performing CDFT-based multireference calculations.

Recent years have seen a renewed interest in CDFT simulations as measured by the number of new CDFT implementations. In this contribution, we will discuss the constrained DFT implementation of the CP2K computational code [3, 4] and highlight some applications that are ideally suited for this implementation. We will also present preliminary data for the extension of the Soudackov–Hammes-Schiffer model [5] of diabatic proton-coupled electron transfer to investigate the initial steps of the electrochemical hydrogen evolution reaction on carbon nanostructures.

### REFERENCES

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