Extension of the ALMO formalism to metallic systems in CP2K

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With current density functional approximations, charge transfer is usually poorly described, since DFT methods have a tendency to overestimate electron delocalization. This issue can be solved with the use of localized orbitals within the ALMO (also called BLW) formalism, which forces electrons to remain localized on predefined fragments.

This method has already been implemented in the CP2K modeling tool. However, its current development and implementation is not compatible with partially occupied orbitals (i.e. electronic smearing). Therefore, metallic systems cannot be handled with this formalism.

Here we show that the ALMO formalism can be practically extended to metallic systems. We demonstrate that common simplications used in mixed-state theory cannot be applied within the ALMO formalism, which makes the exact approach unpractical, as it is a combinatorial problem with exponential complexity.

However, under a basic mean field approximation, we are able to unify mixed-state theory with ALMO formalism into a simple, practical formulation, that have been implemented in CP2K as S-ALMO.

This formulation is of critical importance for electro-catalysis applications, where we have both metals and electrolytes whose charge must remain localized, for example. Another application of this work is to allow charge transfer analysis for metallic systems, which is illustrated at the example of adsorption of small model molecules such as CO, H_2O and C_6H_6 on Pt(111).

We believe that this tool will provide a deep understanding of charge transfer impact on catalytic processes, especially for alloys where much is yet to be discovered.

This could even represent a first step in the rational design of alloys catalysts, a major challenge for green chemistry development.