

# Periodic Subsystem Density-Functional Theory

*Alessandro Genova<sup>1</sup>, Davide Ceresoli<sup>1,2</sup>, Michele Pavanello<sup>1</sup>*

1. Department of Chemistry, Rutgers University, Newark, NJ 07102, USA
2. CNR-ISTM: Institute of Molecular Sciences and Technologies, Milano, Italy

By partitioning the electron density into subsystem contributions, the Frozen Density Embedding (FDE) formulation of subsystem DFT has recently emerged as a powerful tool for reducing the computational scaling of Kohn-Sham DFT. To date, however, FDE has been employed to molecular systems only. Periodic systems, such as metals, semiconductors, and other crystalline solids have been outside the applicability of FDE, mostly because of the lack of a periodic FDE implementation.

To fill this gap, in this work we aim at extending FDE to treat subsystems of molecular and periodic character. This goal is achieved by a dual approach. On one side, the development of a theoretical framework for periodic subsystem DFT. On the other, the realization of the method into a parallel computer code (QUANTUM-ESPRESSO). We find that periodic FDE is capable of reproducing total electron densities and (to a lesser extent) also interaction energies of molecular systems weakly interacting with metallic surfaces.

In the pilot calculations considered, we find that FDE fails in those cases where there is appreciable density overlap between the subsystems. Conversely, we find FDE to be in semi-quantitative agreement (but still within chemical accuracy) with Kohn-Sham DFT when the inter-subsystem density overlap is low. We also conclude that to make FDE a suitable method for describing molecular adsorption at surfaces, kinetic energy density functionals that go beyond the GGA level must be employed.