# Improving the efficiency of embedded cluster approach with the aid of the Fast Multipole algorithm

**COLINET Pauline**;[A] **NEESE Frank**;[A] **HELMICH-PARIS Benjamin**[A]

*A)Molecular Theory and Spectroscopy Group, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, D-45470, Germany*

colinet@kofo.mpg.de

Over time, electrostatic embedded cluster approaches (cf. Figure1) have proven very efficient for studying semi-conductors and insulators. The strategy is to put most of the computational effort on the area of interest, the cluster, using accurate but demanding quantum mechanical (QM) methods to describe it. The cluster is then electrosatically embedded into point charges (PCs) to take into account the effect of the environment, in an approximate fashion. A thin isolating shell of effective-core potentials (ECPs) surrounds the QM cluster to prevent over-polarization in the QM region. In particular, this approach has been used in theoretical spectroscopy studies of oxide surfaces under catalytic oxidation conditions, in combination with accurate QM methods, to properly model the antiferromagnetic properties.
In order to go beyond and reach real-surface electro-catalysis with accurate atomistic structure description under *operando* conditions, it is necessary to increase the cluster size. today, it appears that the necessary number of point charges to reach convergence, depending on the property of interest, can go up to $N_{PC} = 10^4$ if not $10^6$ for QM clusters made of 200-300 atoms. However, for more than $10^5$ point charges, the evaluation of the point-charge electrostatic energy becomes one of the most demanding step of the whole SCF calculation (scaling in $O(N_{PC} \times N_{BF}^2)$, with $N_{BF}$ the number of basis functions). Among existing solutions, the well established Fast Multipole Method (FMM) algorithm[1] provides a way to reduce the scaling to $O(N_{PC} + N_{BF}^2)$.

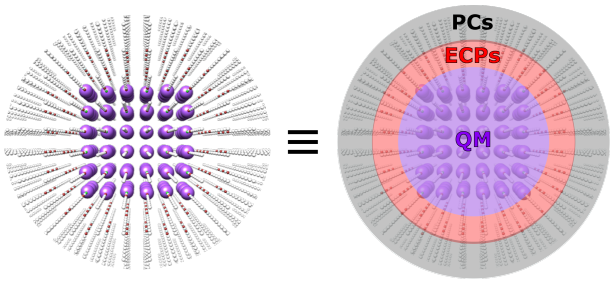


Figure 1: ECM scheme.

The aim of this work is to implement the FMM algorithm to make these QM/MM calculations faster which should allow us to investigate surface environment effects on active catalytic sites. This implementation is done in ORCA[2].
We first implemented the algorithm for interactions between point charges only (PCs/PCs). The calculation of the total Coulomb energy is then accelerated by more than ten times compared with a calculation without algorithm, with an accuracy in the order of micro Hartree. This first step enabled us to validate the implementation and to better measure the impact of the various model parameters on calculation time and accuracy.
Adapting the algorithm to QM/PCs calculations require the evaluation of multipole expansion of an electronic distribution. These integrals are currently evaluated using the McMurchie Davidson scheme for each pair of orbitals in the quantum system. The evaluation of the distant interactions with the point charges using the FMM method, then alllows a drastic acceleration of the evaluation of the one-electron integrals during the formation of the Fock matrix, which leads to a decrease in the total calculation time of the sytem. With the evaluation of the multipole moments becoming the limiting element in the evalution of the one-electron integrals, another way of calculating them is currently being investigated.

**Keywords**: ECM, Coulomb interactions, FMM, ORCA.

[1] L. Greengard and V. Rokhlin, *J. Comp. Phys*, **1987**, *73(2)*, 325-348
[2] Neese F., *WIREs Computational Molecular Science*, **2022**, 12, e1606