An Automated Approach for Developing Graph-Theoretical Cluster Expansions for the Total Energy of Adsorbate Layers

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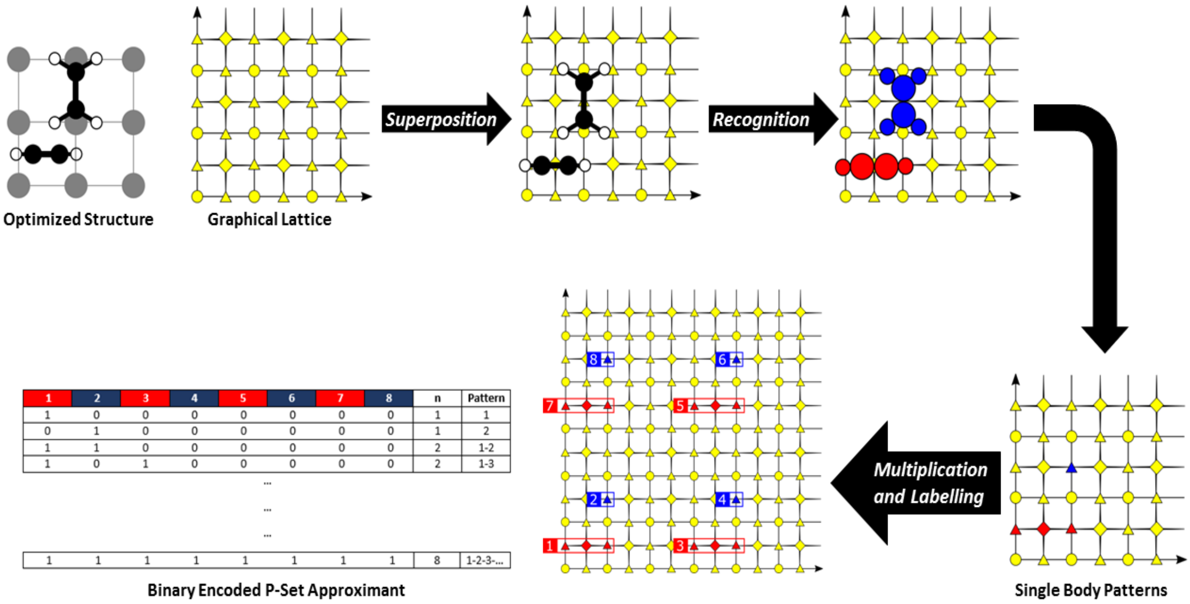
Accurate description of the total energy of adsorbate layers is crucial to understanding chemistry at interfaces. For catalysis applications in particular, adsorbate-adsorbate lateral interactions have been shown to significantly affect activation energies of reactions, thereby shaping experimentally observed trends. Modelling the interactions of atomic adsorbates has traditionally been achieved using effective Ising-type Hamiltonians [1], whereby a set of spin-like values is attributed to the layer's lattice points describing the occupancy of the corresponding catalytic sites (vacant occupied by a species). Pairwise additive adsorbate-adsorbate lateral interactions in this model are captured by appropriate coupling constants.

Such a Hamiltonian is however limited, as it cannot account for adsorbates that bind to more than one sites (bi-dentate or even multi-dentate species), and it cannot capture many-body contributions to the total energy (3-body interactions – triplets). To overcome these limitations one has to adopt a cluster expansion Hamiltonian formalism [2], which has recently been implemented in a graph-theoretical scheme [5] to enable the representation of multi-dentate species. Automating the development of such cluster expansion Hamiltonians for catalytic systems is challenging. Existing approaches for such automation [3] can only tackle monodentate adsorbates and cannot account for the various binding modes molecules exhibit on solid surfaces.

The current work develops a scheme for automating the development of cluster expansions applicable to molecular species on catalytic surfaces. The scheme has been implemented in a FORTRAN 95 program compatible with the graph-theoretical kinetic Monte Carlo code, *Zacros*.



1	2	3	4	5	6	7	8	n	Pattern
1	0	0	0	0	0	0	0	1	1
0	1	0	0	0	0	0	0	1	2
1	1	0	0	0	0	0	0	2	1-2
1	0	1	0	0	0	0	0	2	1-3

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1	1	1	1	1	1	1	1	8	1-2-3-...

Figure 1. Pattern Recognition and Encoding Scheme

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