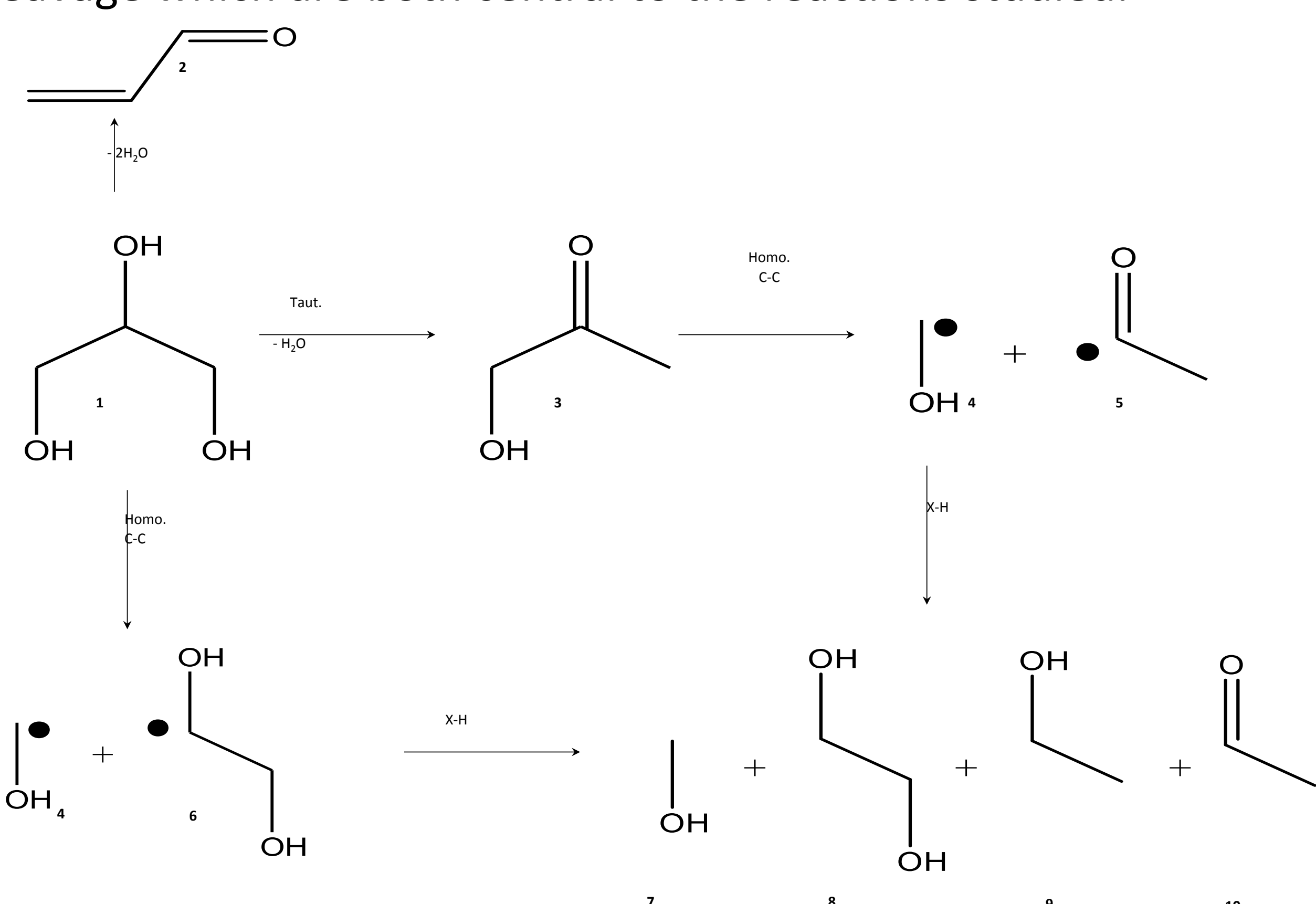


A combined periodic DFT and QM/MM approach to understand the radical mechanism of the catalytic production of methanol from glycerol.

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Introduction:

The production of methanol from glycerol over a basic oxide, such as MgO, using high reaction temperatures (320 °C) is a promising new approach to improving atom efficiency in the production of biofuels. The mechanism of this reaction involves the homolytic cleavage of the C₃ feedstock, or its dehydration product hydroxyacetone, to produce a hydroxymethyl radical species which can then abstract an H atom from other species. Obtaining a detailed reaction mechanism for this type of chemistry is difficult due to the large number of products present when the system is operated at high conversions. In this contribution we show how DFT based modelling studies can provide new insights into likely reaction pathways, in particular the source of H atoms for the final step of converting hydroxymethyl radicals to methanol. We show that water is unlikely to be important in this stage of the process, C-H bonds of C₂ and C₃ species can give an energetically favourable pathway and that the disproportionation of hydroxymethyl radicals to methanol and formaldehyde produces a very favourable route. Experimental analysis of reaction products confirms the presence of formaldehyde. The calculations presented in this work also provides new insight into the role of the catalyst surface in the reaction showing that the base sites of the MgO(100) are able to deprotonate hydroxymethyl radicals but not methanol itself. In carrying out the calculations we also show how periodic DFT and QM/MM approaches can be used together to obtain a rounded picture of molecular adsorption to surfaces and homolytic bond cleavage which are both central to the reactions studied.



Scheme 1: Simplified reaction scheme for the production of methanol from glycerol

Computational Methods:

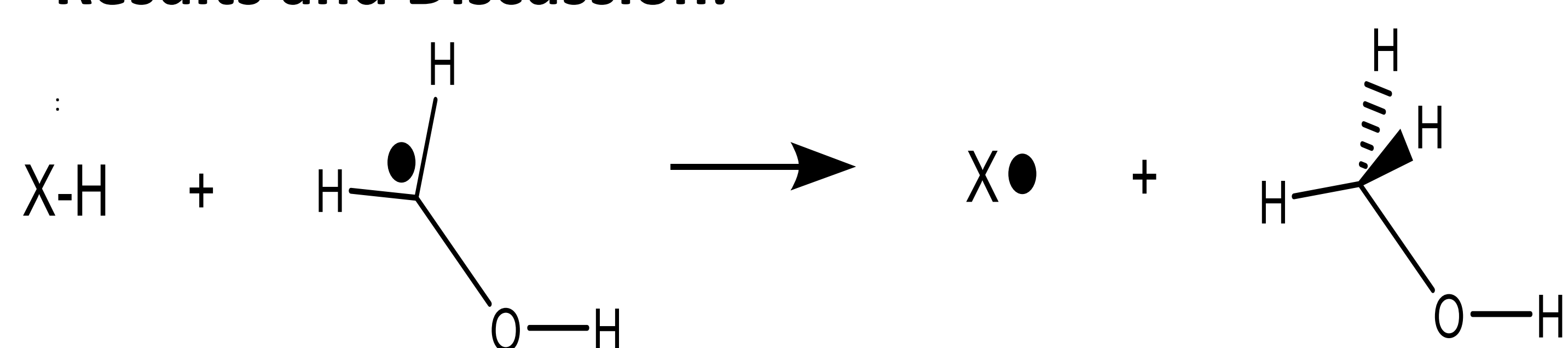
VASP – Vienna Ab-Initio Simulation Package:

- projector augmented-wave (PAW) method reprinted for core states,
- PBESol Functional, with Grimmes D3 Dispersion,
- Forces with a acceptance criterion of 0.01 eV Å⁻¹
- planewave cut off of 800 eV .

QM/MM Technique – Chemshell Interface:

- QM region consisting of 2 Layered 50 ions, FHI-aims implemented,
- PBESol Functional,
- TZVP equivalent Basis sets implemented,
- Non-coulombic repulsion/dispersion interactions are represented with Buckingham potentials,
- MM Region are treated using **GULP** Package software,
- Pseudopotential is positioned on each Mg²⁺ ion in the active MM region,
- CHEMShell** interface is used to link QM and MM calculations.

Results and Discussion:



Scheme 2. Hydrogen transfer to produce methanol from hydroxymethyl radical

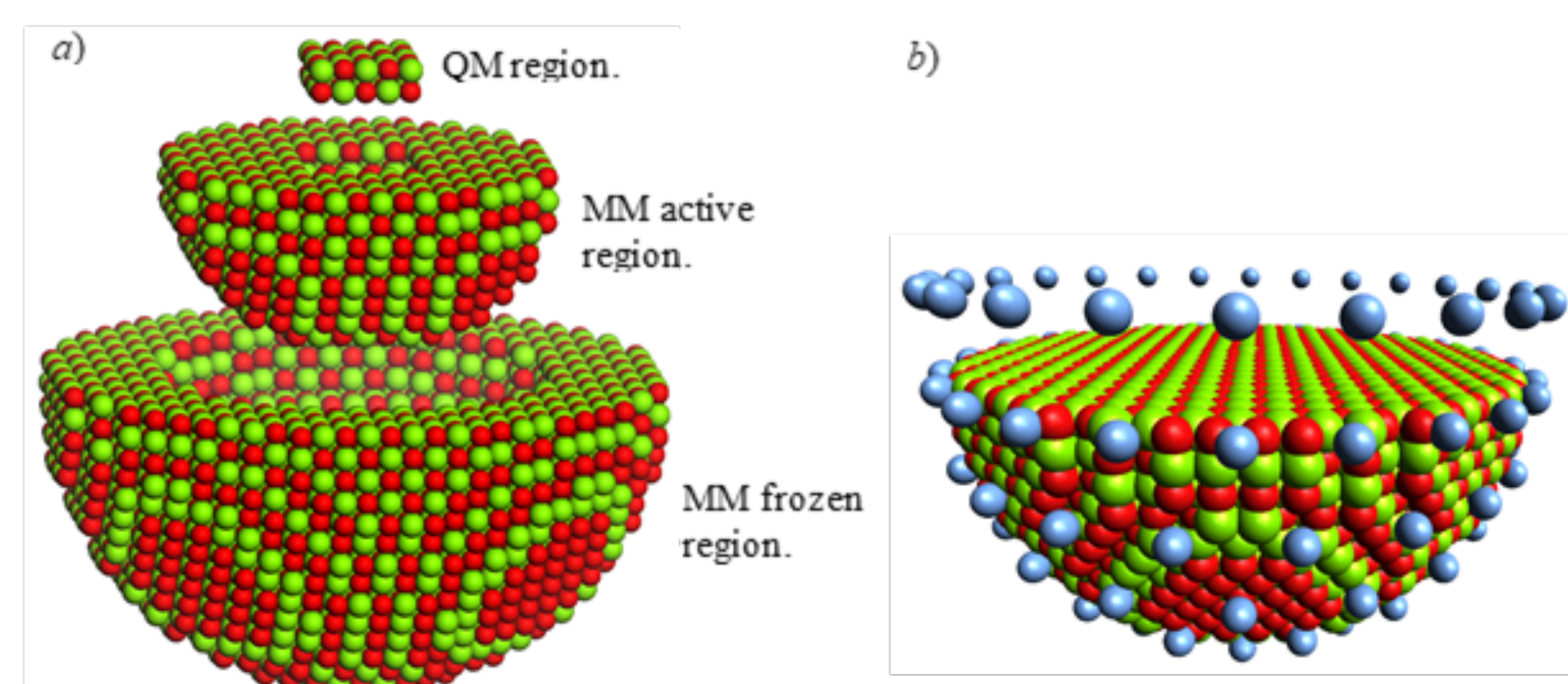
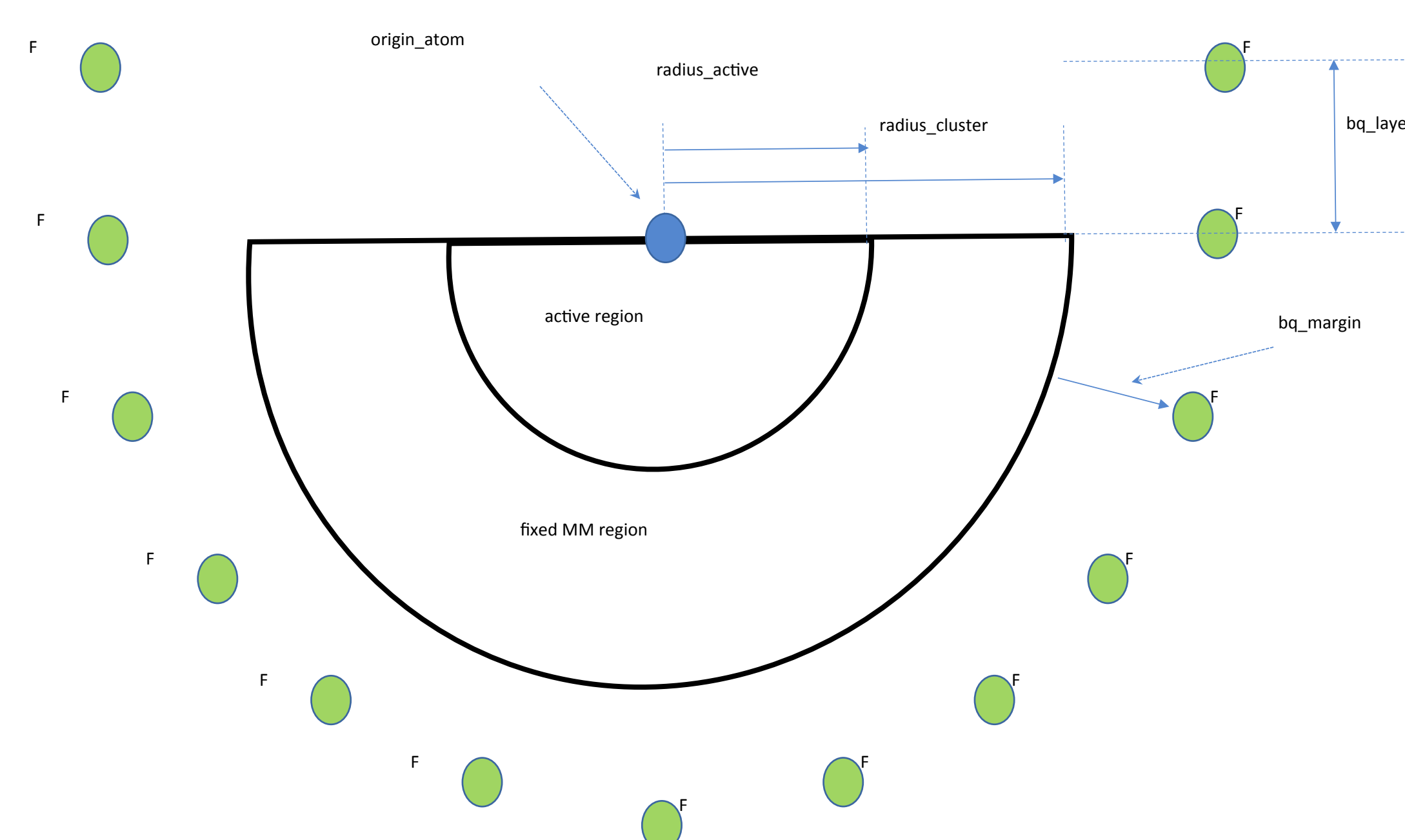
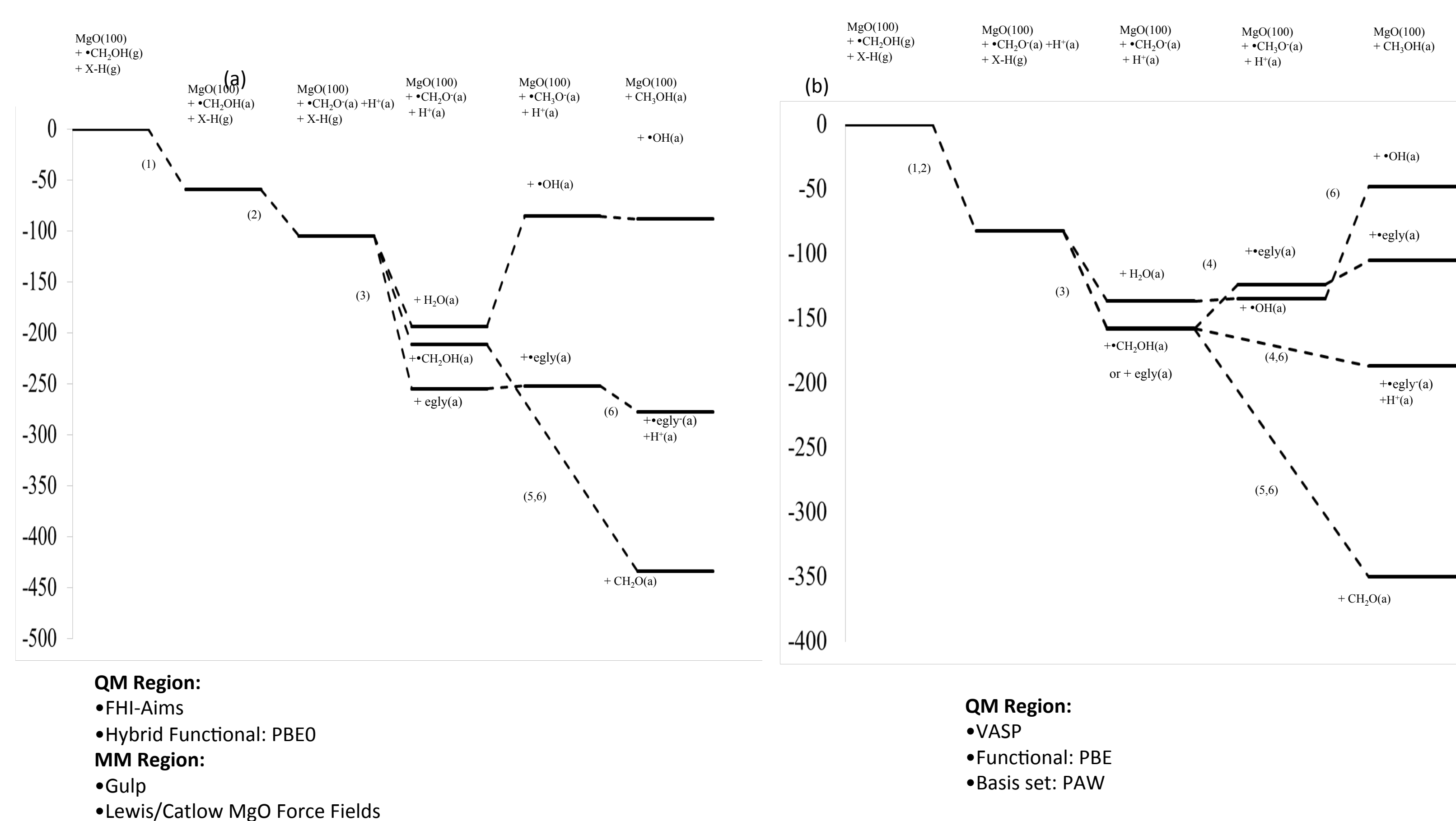


Figure 1: An expanded view of the QM/MM simulation regions used



Conclusion:

- we have used DFT calculations both with periodic boundary and with an embedded QM/MM approach ,
- We find that alcohol groups at C-centred radicals are deprotonated by the weak O_{5c} base sites on the surface, whereas alcohol groups of normal alcohols are not,
- we have shown how periodic and QM/MM approaches can be used in unison to arrive at a consistent model of surface processes,

Reference:

Sainna, MA; *et al. Faraday Discuss.* 229, 108 (2020),