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In silico study of reaction mechanisms and design principles for water oxidation catalysts

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and design principles for water oxidation
catalysts**

José Luis Vallés Pardo

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Ph.D. Thesis, Leiden University, December 2012

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***In silico* study of reaction mechanisms and design principles for water oxidation catalysts**

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List of abbreviations

ADF	Amsterdam Density Functional program
AIMD	Ab-initio molecular dynamics
B3LYP	Becke 3-Parameter, Lee-Yang-Parr exchange-correlation functional
BLYP	Becke-Lee-Yang-Parr exchange-correlation functional
BOMD	Born-Oppenheimer Molecular Dynamics
CHARMM	Chemistry at HARvard Molecular Mechanics force field
CMD	Constrained molecular dynamics
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
CP2K	Open Source Molecular Dynamics software package
CPMD	Car-Parrinello Molecular Dynamics
CV	Collective Variable
DFT	Density functional theory
DZVP	Double Zeta Valence Plus basis set with one set of Polarization functions
EXAFS	Extended X-ray absorption fine structure
FES	Free-energy surface
GGA	Generalized Gradient Approximation
GPW	Gaussian and plane waves method
GTH	Goedecker-Teter-Hutter pseudopotential
GTO	Gaussian type orbitals
KS	Kohn-Sham
LDA	Local Density Approximation
MD	Molecular Dynamics
MM	Molecular Mechanics
MTD	Metadynamics
OEC	Oxygen evolving complex
OPBE	Perdew-Burke-Ernzerhof exchange-correlation functional
PBC	Periodic Boundary Conditions
PCET	Proton-Coupled Electron Transfer
PSII	Photosystem II

PWs	Plane Waves
QM	Quantum Mechanics
QM/MM	Quantum Mechanics/Molecular Mechanics
QS	QuickStep
TZP	Triple-Zeta basis set with one set of Polarization functions
TZVP	Triple Zeta Valence Plus basis set with one set of Polarization functions
WOR	Water oxidation reaction

Notation

$\hat{A}$	Operator A
χ, χ_s	Response function
χ_μ	Basis set function
χ_p	Primitive basis function
Δ	Laplacian
∇	Nabla
ϵ_0	Permittivity of vacuum
e	Electron charge, exponent
E	Energy
E_{xc}	Exchange-correlation functional
$\hbar$	Planck constant
$\hat{H}$	Hamiltonian
J	Coulomb electron-electron repulsion
m	Electron mass
M	Nuclear mass
n	In a summation, the number of electrons
N	In a summation, the number of nuclei
Ψ	Wavefunction of a system
ϕ	Kohn-Sham orbital
ρ	Electron density
$\mathbf{r}$	Vector position of electrons in space.

$\mathbf{r}_i$	Position of electron i
r_{ij}	Distance between electrons i and j
$\mathbf{R}$	Position of the nuclei
$\mathbf{R}_I$	Position of nucleus I
R_{IJ}	Distance between nuclei I and J
$\dot{\mathbf{R}}$	First time derivative of $\mathbf{R}$
$\ddot{\mathbf{R}}$	Second time derivative of $\mathbf{R}$
t	Time
T	Kinetic energy
V	Potential energy
Z	Atomic number
E_{eff}	Effective potential
v_{ext}	External potential
$P_{\mu\nu}$	Density matrix
Ω	Volume of the unit cell
$\mathbf{G}$	Reciprocal lattice vectors
$s(x)$	Collective variable
h	Height of the bias potential
w	Width of the bias potential
τ_g^{-1}	Deposition rate of the bias potential

Preface

Fossil fuel is among the most important valuables for the developed and the developing world. Since the industrial revolution its use and demand has been growing exponentially, arriving to the point where limitations to its availability can be expected within less than three decades, in the most optimistic analyses.

Even more worrying than this possible lack of primary energy supply are the environmental consequences of society moved by carbon-based fuels. The biosphere is not able to assimilate the vast amount of CO₂ released into the atmosphere by burning fuel.

For these reasons a transition to carbon-free or carbon-neutral primary energy carriers is urgent. What could be the best solution? Probably there is not a universal solution. It is not a competition for the best, first or quickest scientific development. The society has a problem and the scientific community should do its best in order to solve it.

In this framework one interesting direction is the development of an efficient device to perform the water splitting process in order to use hydrogen as a clean fuel, an “artificial leaf”, by which the conversion of solar energy into chemical energy on a large scale may become reality.

