

# Multiconfigurational study of dissociation of water molecule on the surfaces of ionic oxides

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The electron correlation is important for describing chemistry. The correlation effects can be treated in an approximate way using the density functional theory (DFT), or time-dependent DFT. The results obtained by DFT depend on the choice of the functional, and often fail for the description of the systems with localized electron density: charge transfer, bond creation, etc.

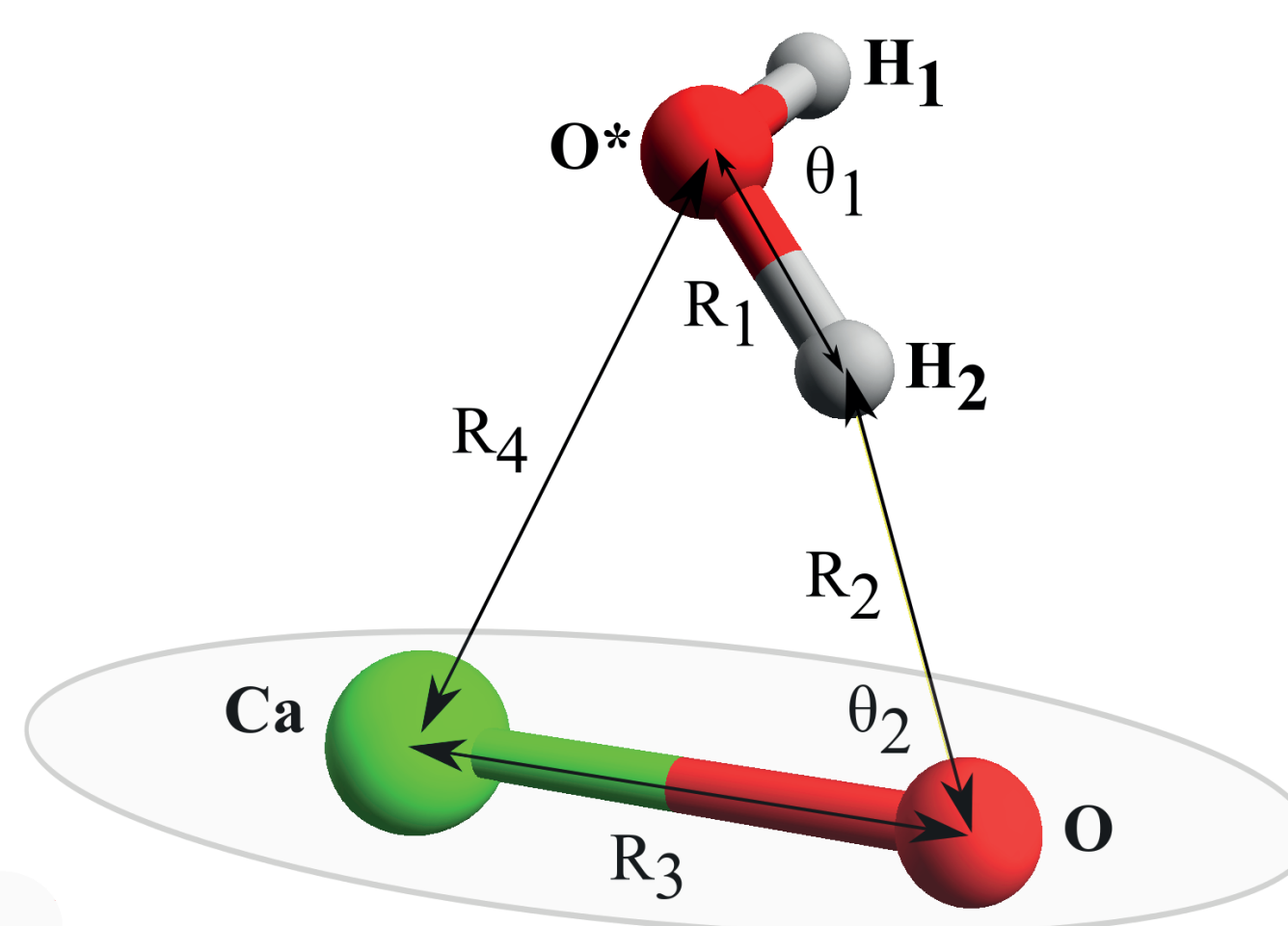
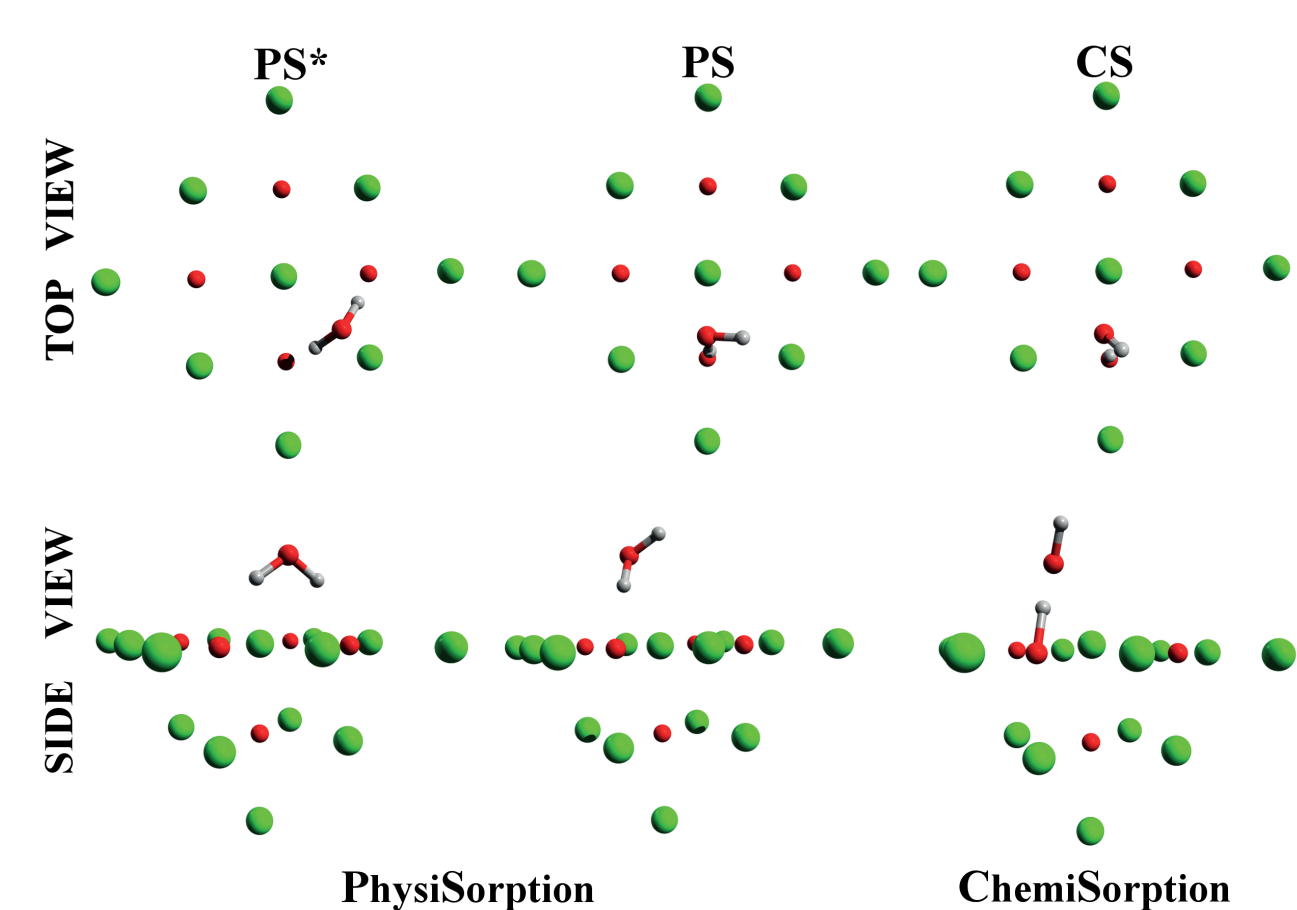
Multiconfigurational methods, in particular, complete active space CASSCF/RASSCF followed by second order perturbation theory correction CASPT2/RASPT2, are known to be very accurate and reliable ab initio technique. The selection of the active space, where all possible excitations are treated explicitly, requires a manual set up for each calculation. Also, the computational costs can become prohibitively large especially when applied to large systems.

## MOLCAS computational package [1] (<http://www.molcas.org>)

Recent improvements include:

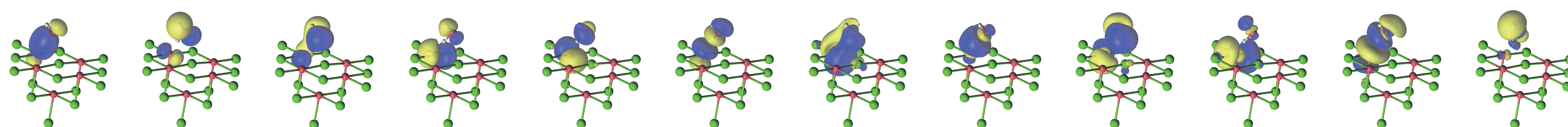
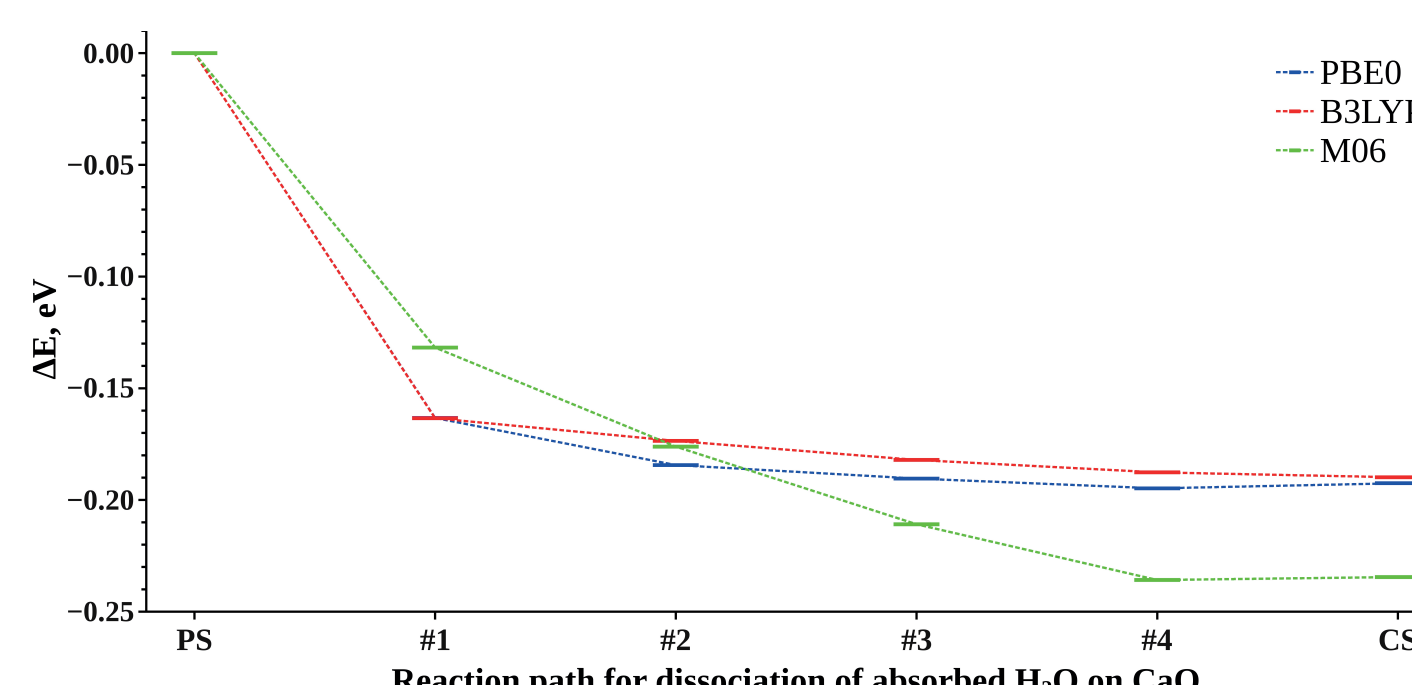
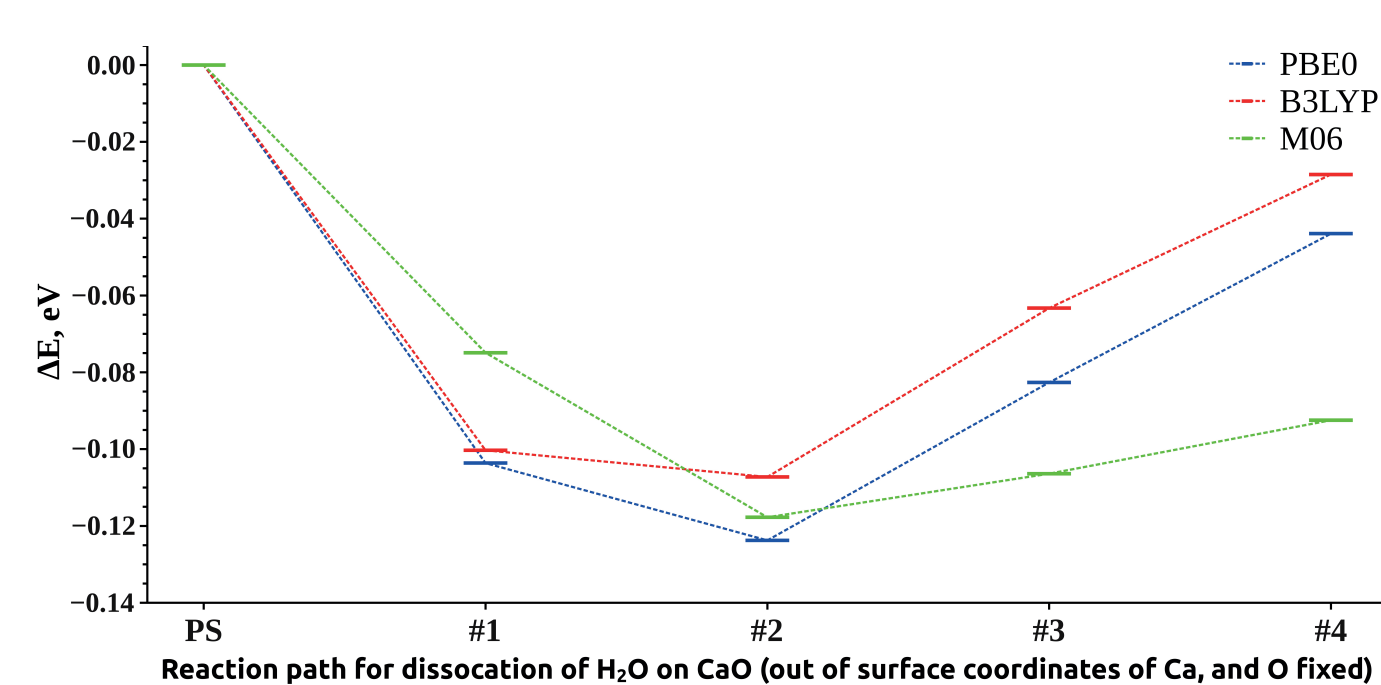
1. development of new computational methods (e.g. multiconfigurational method RASPT2)
2. better handling of two-electron integrals (Resolution of Identity, Cholesky Decomposition)
3. new embedding technique: EMBQ code (P.Sushko), AIMP basis sets (L.Seijo)
4. adjustment to modern hardware (parallelization, efficient memory use) [2]
5. new geometry optimization algorithms for large fragments [3]

To model CaO surface we constructed several clusters, the smallest one:  $\text{Ca}_{14}\text{O}_6$  has been used for all calculations, including DFT, CASSCF/CASPT2, CCSD and CCSD(T). The remaining crystal has been modelled by 3354 atomic charges. Ca atoms on the border of the cluster have AIMP basis set. For all other atoms SVP basis set has been used.



Parameter	PS	#2	CS
R <sub>1</sub>	0.960	1.101	1.378
R <sub>2</sub>	1.629	1.350	1.062
R <sub>3</sub>	2.399	2.445	2.505
R <sub>4</sub>	2.679	2.522	2.398
θ <sub>1</sub>	109.5	109.9	123.0
θ <sub>2</sub>	71.06	68.97	68.02
Z <sub>Ca</sub>	0.000	+0.112	+0.182
Z <sub>O</sub>	0.000	-0.023	-0.024

\*distances and out-of-plane-positions in Å, angles in degrees



Method	PS		PS*
	Physi/Chemi-sorption E, eV		
B3LYP//B3LYP	-0.907	-1.097	-1.018
CCSD//B3LYP	-0.936	-1.066	-1.034
CCSD(T)//B3LYP	-0.971	-1.109	-1.082
CASPT2//B3LYP	-0.963	-1.319	

[1] F. Aquilante, L. D. Vico, N. Ferré, G. Ghigo, P.-Å. Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitoňák, M. Reiher, B. O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov, R. Lindh, MOLCAS-7: The next generation, *J. Comput. Chem.* 31, 224-247 (2010).

[2] S. Vancoillie, M. G. Delcey, R. Lindh, V. Vysotskiy, P.-Å. Malmqvist, V. Veryazov, Parallelization of a multiconfigurational perturbation theory, *J. Comp. Chem.* 34, 1937-1948 (2013)

[3] V. P. Vysotskiy, J. Boström, V. Veryazov "A new module for constrained multi-fragment geometry optimization in internal coordinates implemented in the Molcas package", *J. Comp. Chem.*, 34, 2657-2665 (2013).

Game-changing development

CaO surface

Physical and Chemical sorption of water

Dissociation of water molecule on CaO surface