

# The Reaction of Water with Iron: Surface Science by Random Phase Approximation

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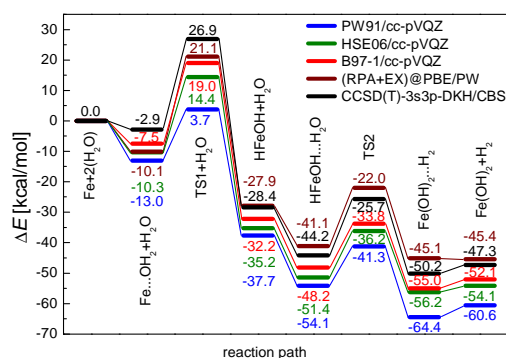
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The critical processes in surface science such as adsorption, diffusion, and chemical reaction involve many-body quantum effects which reach beyond standard semilocal approximations to the exchange-correlation energy in the density functional theory (DFT). The random phase approximation (RPA) for the electron correlation energy is fully nonlocal, and in combination with the exact exchange energy represents one of the most promising methods for first-principles total energy calculations in periodic boundary conditions.

We investigate the reaction of water with zero-valent iron, which plays the key role in processes such as anaerobic corrosion and water remediation by nanoscale zero-valent iron (nZVI) particles. The reaction involves physisorption and chemisorption events in interplay with localized d-states of iron. We decipher mechanism and kinetics of the reaction of water molecule with an iron atom [1,2] and Fe(100) surface [3] and evaluate various computational methods for both models [4]. In addition, we present the reaction kinetics of nZVI nanoparticles as monitored by  $^{57}\text{Fe}$  Mossbauer spectroscopy [5].

We show that RPA improves the description of the reaction on the Fe(100) surface with respect to gradient corrected and hybrid DFT functionals, owing to the reduction of electron self-interaction and to non-local correlation effects. The reaction of water with iron atom enables to gauge RPA against coupled-cluster theory (up to perturbative triples in complete basis set limit; CCSD(T)-3s3p-DKH/CBS). Reaction profiles demonstrate that common DFT methods significantly underestimate reaction barriers, while the reaction kinetics and thermodynamics from RPA method agree with the reference data.



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