Ab initio Modelling of Surfaces at Realistic Conditions: Interplay of Adsorbate-Substrate and Adsorbate-Adsorbate Interactions

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Multiscale nature of heterogeneous catalysis h nano meso sintering reactor transport segregation S interparticle transport intraparticle restructuring transport μs



R. Schlögl, Angew. Chem. Int. Ed. 54, 3465 (2015)

Multiscale modeling



Surfaces at realistic conditions

A surface cannot be separated from a gas (or liquid) above it



Development and use of first-principle statistical mechanics approaches

First-principles atomistic thermodynamics $\mu_{\mathsf{O}_2}(T,p_{\mathsf{O}_2})$ equilibrium $G(T, p) = E^{\text{tot}} + F^{\text{vib}} - TS^{\text{conf}} + pV$ DFT Surface free fromation energy: $\gamma_{\text{surf}}(T, p) = \frac{1}{A} \left| G_{\text{sufr}}(\{N_i\}) - \sum_i N_i \mu_i \right|$ **Defect free fromation energy:** $\Delta G(T, p) = \frac{1}{A} \left[G_{def}(\{N_i + \Delta N_i\}) - \sum_i \mu_i \Delta N_i - G_{perf}(\{N_i\}) \right]$

C.M. Weinert and M. Scheffler, Mater. Sci. Forum 10-12, 25 (1986); E. Kaxiras *et al.*, Phys. Rev. B 35, 9625 (1987) Water Adsorption at Alkaline-Earth Metal-Oxide Surfaces

H₂O@CaO(001): Experimental data



STM images of water on CaO(001) surface (10 ML CaO/Mo(001), room temperature)

X. Shao, N. Nilius, M. Sterrer and H.-J. Freund



1) Atomic structure and composition of the 1D structures

2) What breaks the 2D symmetry on the flat surfaces?

3) Is CaO special among other alkaline earth metal oxides?

Computational tools

Structures searching:

 First-principles genetic algorithm (GA) – unbiased search for most stable structures, PBE functional with manybody vdW correction

Total energies and vibrations:

- density-functional theory

FHI-aims -- the workhorse



V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, "Ab Initio Molecular Simulations with Numeric Atom-Centered Orbitals", Computer Physics Communications 180, 2175-2196 (2009)

Main focus:

 Accurate all-electron electronic-structure calculations (DFT and beyond) for both periodic and cluster/ molecular systems

• Massively parallel

Numeric atomic orbital basis sets

Computational tools: which functional?

Benchmark against renormalized second-order perturbation theory (rPT2)



Significant errors with a GGA functional when compared to rPT2

X. Ren *et al.* Phys. Rev. B **88**, 035120, 2013

A. Tkatchenko et al. Phys. Rev. Lett. 108, 236402, 2012

Standard DFT and the self-interaction error

$$E_{\text{tot}} = T[n] - \sum_{I=1}^{M} Z_I \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_I|} d^3r + \frac{1}{2} \sum_{I=1}^{M} \sum_{J=1}^{M} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{\text{XC}}[n]$$

exchange-
(includes self-
interaction) (XC) energy

LDA, GGA, meta-GGA:
$$E_{\rm XC}[n] = E_{\rm X}^{\rm loc}[n] + E_{\rm C}^{\rm loc}[n]$$

Standard DFT: (Semi)local XC operator → low computational cost

Removing self-interaction + preserving fundamental properties (e.g., invariance with respect to subspace rotations) is non-trivial → residual self-interaction (error) in standard DFT

Consequences of self-interaction (no cancellation of errors): localization/delocalization errors, incorrect level alignment (charge transfer, reactivity, etc.)

The Hartree-Fock (HF) approximation

$$\Psi(\mathbf{r}_{1}\sigma_{1}, \mathbf{K}, \mathbf{r}_{N}\sigma_{N}) = \frac{1}{\sqrt{N!}} \det[\psi_{1}(\mathbf{r}_{1}, \sigma_{1}), \mathbf{K}, \psi_{N}(\mathbf{r}_{N}, \sigma_{N})]$$

one-particle states

$$E_{\text{tot}} = \sum_{n=1}^{N} \left\langle \psi_{n} \left| \hat{h} \right| \psi_{n} \right\rangle + \frac{1}{2} \sum_{I=1}^{M} \sum_{J=1}^{M} \frac{Z_{I} Z_{J}}{\left| \mathbf{R}_{I} - \mathbf{R}_{J} \right|} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{\left| \mathbf{r} - \mathbf{r}' \right|} d^{3}r d^{3}r' - \frac{1}{2} \sum_{m,n=1}^{N} \int \frac{\psi_{m}^{*}(\mathbf{r},\sigma)\psi_{n}^{*}(\mathbf{r}',\sigma')\psi_{n}(\mathbf{r},\sigma)\psi_{m}(\mathbf{r}',\sigma')}{\left| \mathbf{r} - \mathbf{r}' \right|} d^{3}r d^{3}r' d\sigma d\sigma'$$

HF (exact) exchange energy

- No self-interaction
- Coulomb mean-field \rightarrow no dynamic correlation, single determinant \rightarrow no static correlation

Hybrid DFT

$$E_{\rm XC}[\{\psi\}] = \alpha E_{\rm X}^{\rm HF}[\{\psi\}] + (1-\alpha)E_{\rm X}^{\rm loc}[n] + E_{\rm C}^{\rm loc}[n]$$

-- easy in Kohn-Sham formalism ($n = \sum_{n} f_n |\psi_n|^2$)

Perdew, Ernzerhof, Burke (J. Chem. Phys. 105, 9982 (1996)): α = 1/N

MP4 \rightarrow N = 4, but "An ideal hybrid would be sophisticated enough to optimize N for each system and property."

Range-separated functionals: HSE family

 $\frac{1}{r} = \frac{1 - \operatorname{erf}(\omega r)}{r} + \frac{\operatorname{erf}(\omega r)}{r}$ short-range (SR) long-range (LR)

 $E_{\rm XC}^{\rm HSE} = \alpha E_{\rm X}^{\rm HF,SR}(\omega) + (1-\alpha)E_{\rm X}^{\rm PBE,SR}(\omega) + E_{\rm X}^{\rm PBE,LR}(\omega) + E_{\rm C}^{\rm PBE}$

Hartree-Fock exchange – the problem



Lots of integrals, naïve implementation $\rightarrow N^4$ scaling (storage impractical for N > 500 basis functions)

- need fast evaluation
- need efficient use of sparsity (screening)

"Resolution of identity" (RI) (density fitting)



independent auxiliary basis

Basis-pair space is overcomplete, since $\{\varphi_i(\mathbf{r})\}$ approaches completeness \rightarrow size of $\{P_\mu(\mathbf{r})\}$ ~4-5 times size of $\{\varphi_i(\mathbf{r})\}$

Hybrid functionals in FHI-aims

<u>Computational Scaling of Periodic GaAs,</u> <u>HSE06 Hybrid Functional,</u> <u>with Increasing System Size</u>



Levchenko, Ren, Wieferink, Rinke, Johanni, Blum, Scheffler, Comp. Phys. Commun. **192**, 60-69 (2015).

Hybrid functionals in FHI-aims



Levchenko, Ren, Wieferink, Rinke, Johanni, Blum, Scheffler, Comp. Phys. Commun. **192**, 60-69 (2015).

Computational tools: which functional?

Benchmark against renormalized second-order perturbation theory (rPT2)



HSE06+vdW gives better adsorption energy than PBE+vdW when compared with rPT2

X. Ren *et al.* Phys. Rev. B **88**, 035120, 2013 A. Tkatchenko *et al.* Phys. Rev. Lett. **108**, 236402, 2012

Computational tools

Structures searching:

- Genetic algorithm (GA) unbiased search for most stable structures
- **Total energies:**
- HSE06 hybrid functional with many-body vdW correction^b

Ab initio atomistic thermodynamics

$$\Delta G^{\rm ad}(T, p_{\rm H_2O}, p_{\rm O_2}) = -\frac{1}{A} (E_{\rm H_mO_n/slab} + F^{\rm vib}(T) - E_{\rm slab} - \frac{m}{2} \mu_{\rm H_2O}(T, p_{\rm H_2O})) - (\frac{n}{2} - \frac{m}{4}) \mu_{\rm O_2}(T, p_{\rm O_2})$$

^b A. Tkatchenko, et al., Phys. Rev. Lett. **108**, 236402,2012

Results for CaO(001) and MgO(001)



1e-25
100 200 300 400 500 600 700 800 100 200 300 400 500 600 700 800
Temperature(K)
H₂O/CaO(001)
H₂O/MgO(001)

Experimental conditions: Temperature: ~ 300K Pressure of water (dosing): ~3×10⁻¹⁰ atm

Pressure of water(atm.)

Including $\Delta F^{vib}(T)$ calculated with PBE

The adsorbed water structures on CaO(001) – 1D



- 5H₂O/CaO(001) is slightly more stable

IR spectrum for D₂O on CaO(001)



Y. Fujimori, M. Sterrer, and H.-J. Freund

Theoretical XPS spectra for D₂O on CaO(001)



Trends in water adsorption on MgO, CaO and SrO



As water-substrate interaction becomes stronger, water-water interaction becomes weaker



Interaction within the adsorbed water layer is reduced due to the "lattice" mismatch with the oxide

Conclusions

 Accurate treatment of exchange-correlation and long-range dispersion interaction is necessary for a predictive modelling of H₂O@alkaline-earth metal oxide surfaces thermodynamics

• 1D structures are thermodynamically stable on CaO(001), but not MgO(001) or SrO(001)

• The 2D symmetry is broken due to the asymmetric structure of the "magic" tetramer

• The thermodynamic stability of the 1D adsorbed water structures on CaO(001) is due to the balance between adsorbate adsorbate surface interactions



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Ab Initio Atomistic Thermodynamics of Adsorbed Atomic H at ZnO(1010)

Maria E. Stournara, Sergey V. Levchenko, Santiago Rigamonti, Maria Troppenz, Oliver T. Hofmann, Patrick Rinke, Claudia Draxl, and Matthias Scheffler



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How does H affect the electronic properties? What phases are thermodynamically stable at realistic conditions of (T, p)?

Low production cost Large direct band gap (~3.4 eV) High electron mobility

Top candidate for hybrid electronics



Methodology combining ...

All-electron full-potential density-functional theory (DFT)

PBE+vdW [1] Selected structures with HSE*+vdW $\omega = 0.2 \text{ }^{\text{A}^{-1}}$, $\alpha = 0.375$



Cluster-expansion technique: CELL [2]

based on 106 DFT calculations

Monte-Carlo simulations

Wang-Landau method for configurational density of states

DFT calculations with 32-site surface unit cell Surface phase diagram for a 2048-site surface unit cell

 [1] G. X. Zhang, A. Tkatchenko, J. Paier, H. Appel, and M. Scheffler, PRL 107, 245501
[2] M. Troppenz, S. Rigamonti, and C. Draxl, Chem. Mater., in print, DOI: http://dx.doi.org/10.1021/acs.chemmater.6b05027 Hyrdogen adsorption on ZnO

32-site surface unit cell



$m{L}$	— <i>E</i>	$m{E}$	
^L ads	$= L_{surf+H}$	- <i>L</i> surf	$-\frac{1}{2}L_{H_2}$

Method	O-H	Zn-H
PBE+vdW	-1.10 eV	+0.74 eV
HSE*+vdW	-1.14 eV	+0.83 eV

Hyrdogen adsorption on ZnO





pristine surface



Adsorption on O ⇒ H+ + e- in CB ⇒ band bending







Adsorption on Zn ⇒ H states near VBM ⇒ VBM^{δ+} + H^{δ-}





Adjacent O-H/Zn-H ⇒ Zn-H- /O-H ⇒ no band bending



Cluster Expansion with CELL

$$\hat{E_s} = \sum_{\alpha}^{N_{\alpha}} m_{\alpha} J_{\alpha} X_{s\alpha}$$

Evaluate coefficients J:

$$S^{2} = \frac{1}{N_{s}} \sum_{s=1}^{N_{s}} (E_{s} - \hat{E}_{s})^{2} + \sum_{\alpha \in \beta'}^{N_{\alpha}} \lambda_{\alpha} (J_{\alpha} - J_{\alpha}^{o})^{2}$$

Verify with I_1 norm:

$$\min_{J} \left[\frac{1}{2} (||E - XJ||_2)^2] + \mu ||J||_1 \right]$$

✓ Use a <u>32-site ZnO surface</u> model

✓ 106 DFT structures

✓ 19 clusters

CELL: Cluster Expansion package for large parent cells

Cluster Expansion with CELL

- ✓ Use a <u>32-site ZnO surface</u> model
- ✓ 106 DFT structures
- ✓ 19 clusters

From 32 to 2048 surface sites

Adsorption on Zn becomes favorable above 0.06 ML

Realistic conditions

Distinct phases characterized by constant difference in O-H/Zn-H surface concentration

$$\Delta \eta = \frac{N_{\rm O-H} - N_{\rm Zn-H}}{\text{surface area}}$$

Ensemble-averaged coverage: $\langle \theta \rangle(T, p_{\mathrm{H}_2}) = \int_0^1 \theta' P(\theta', T, p_{\mathrm{H}_2}) d\theta'$ \int Local coverage fluctuations

Coverage as function of T

Pronounced fluctuations since

 $\mu_{\rm H}$ is high enough to stabilize coverages above 0.5 ML

where the Gibbs free energy of adsorption is low

 $\mu_{\rm H}$ is low enough to keep sufficient number of sites free and preserve configurational freedom

$$P(\theta, T, p_{\mathrm{H}_2}) = \frac{e^{-\Delta G(\theta, T, p_{\mathrm{H}_2})/k_B T}}{\int_0^1 e^{-\Delta G(\theta', T, p_{\mathrm{H}_2})/k_B T}} d\theta'$$

Work function

Coverage fluctuates → ensemble average at experimental *T* Work function reduction by about 0.8 eV upon band bending (exp. 0.7 eV) J. C. Deinert, O. T. Hofmann, D. Meyer, P. Rinke, J. Staehler, PRB 91 (2015)

Conclusions

- At coverages <6%, H adsorbs exclusively on O
- At higher coverages, H starts to adsorb also on Zn
- Adsorbed H forms randomly arranged O-H terminated Zn-H/O-H chains along the [0001] direction
- The arrangement is due to the long-range repulsion between the O-H terminated chains, so that any possible relative ordering of the chains is destroyed at T > 60 K.
- There are well-defined regions on the phase diagram characterized by a constant excess of O-H over Zn-H
- There are significant fluctuations of the adsorbed H coverage.

Our machine learning/data mining studies

1) Train a machine learning model to sample potential-energy surfaces (collaboration with A. Oganov and A. Shapeev)

2) Use machine learning/data mining to find *descriptors* (for high-throughput screening of catalytic materials)

Descriptors

Simple(r) properties (bulk d-band center position and CO dissociation energy) are correlated to more complex properties (adsorption energy and reaction barrier)

The simpler quantities are called descriptive parameters (a descriptor)

J. K. Nørskov, T. Bligaard, J. Rossmeisl and C. H. Christensen, Nature Chemistry 1, 37 (2009)

Descriptors

A simple physical model (Newns-Anderson) motivates the *d*-band center descriptor

What if we don't know such a model, or we need a more accurate and more widely applicable model?

We develop compressed sensing approaches to search for physically interpretable descriptors

Work Function Prediction

Photoemission spectroscopy measurements

J. C. Deinert, O. T. Hofmann, D. Meyer, P. Rinke, J. Staehler, PRB 91 (2015)