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PSI

Matthias Krack :: Head of MMM Group :: Paul Scherrer Institut

LSM-MMM Presentation

LSM-Seminar, 22 March 2018, OFLG/402, PSI

Multiscale Materials Modelling (MMM)

Current focus areas of the MMM group

- Modelling of strongly correlated materials especially actinide materials based on Density Functional Theory augmented with a Hubbard U term (DFT+U)
- Irradiation damage in nuclear fuel materials and reactor pressure vessel (RPV) steels using force fields and kinetic Monte Carlo (kMC) methods
- Mechanical behaviour of fluorite-type oxide materials using DFT+U and force fields
- XAFS spectra based on ab initio molecular dynamics (AIMD) simulations using the MD-EXAFS approach
- Chemical processes including rare events using accelerated molecular dynamics (AMD) methods especially metadynamics
- Nuclear fuel behaviour with fuel performance codes

Multiscale Materials Modelling Group

- Monica Kosa (COFUND Postdoc)
  Molecular dynamics simulations using electronic structure (DFT) and force field methods, mechanical properties, dislocations

- Matthias Krack (Group leader)
  Molecular dynamics simulations using electronic structure (DFT) and force field methods, CP2K code development, XAFS spectra simulation, metadynamics, fuel behaviour modelling, HPC

- Raoul A. Ngayam-Happy (Scientist)
  Multiscale simulation of materials aging and degradation (RPV steels and nuclear fuels), kinetic Monte Carlo (aKMC/oKMC), molecular dynamics simulations using force fields and DFT

Multiscale Materials Modelling Group

- Sergii Nichenko (Scientist)
  Molecular dynamics simulations using force field methods, MD code development, thermodynamic modelling using GEMS

- Sriram Venkatesan (PhD student)
  Multiscale simulation of materials aging and degradation (RPV steels), kinetic Monte Carlo (kMC) and MD simulations

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Software Projects

- CP2K: The MMM group contributes to the
  - Development of the open-source CP2K program package
  - Generation and maintenance of the Goedecker-Teter-Hutter (GTH) pseudopotential database
  - Code quality assurance by running several CP2K regression testers on the PSI compute cluster Merlin5
  - Release process of CP2K

- LAKIMOCA: Lattice kinetic Monte Carlo
  - oKMC/aKMC code, especially for reactor pressure vessel (RPV) steel modelling
  - Collaboration with eDF and KTH Stockholm
  - Development of new models

- PERFORM60 platform

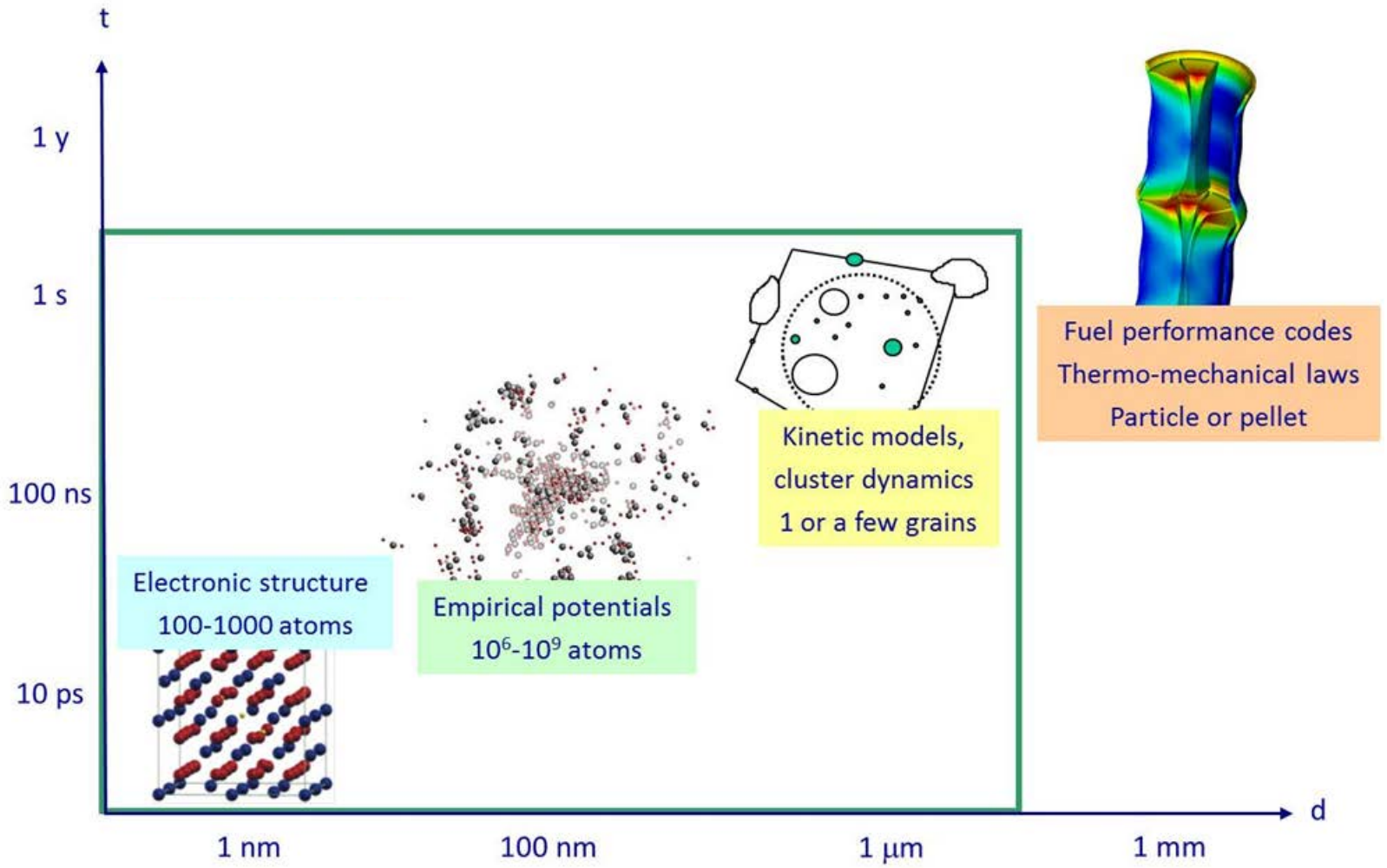
- GEMS: Gibbs Energy Minimization Software for Geochemical Modelling

- ASTRAM: Post-processing tool for defect analysis

H2020 Projects

- INSPYRE: Investigations Supporting MOX Fuel Licensing in ESNII Prototype Reactors
- SOTERIA: Safe long-term operation of light water reactors based on improved understanding of radiation effects
- SAMOFAR: Safety Assessment of the Molten Salt Fast Reactor

Multiscale Modelling Scope



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Electronic structure versus force field methods

Electronic structure methods	Force field methods
Motion of nuclei and electrons	Motion of atoms
No a priori knowledge of the interatomic interactions	pre-defined fitted interaction potentials (empirical potentials)
Dynamic (re)bonding processes	Bonding (topology) pre-defined
Predictive	Only limited predictive

Electronic structure

- Schrödinger equation:

$$\hat{\mathrm{H}} \mid \Psi \rangle = E \mid \Psi \rangle$$

- Wavefunction of a system of N nuclei and n electrons:

$$\Psi \rightarrow \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n; \boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_N)$$

- Born-Oppenheimer approximation (→ BO-MD)

Kohn-Sham Density Functional Theory (DFT)

- The positive definite electron density of a system is given by

$$\rho(\boldsymbol{r}) = n \int |\Psi(\boldsymbol{r}^n)|^2 \, d\boldsymbol{r}_2 \ldots d\boldsymbol{r}_n = n \int |\Psi(\boldsymbol{r}, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n)|^2 \, d\boldsymbol{r}_2 \ldots d\boldsymbol{r}_n$$

  $\Rightarrow$ reduction of the problem complexity from $3n$ to 3 degrees of freedom

- It provides the key connections

n electron wavefunction	$\Psi(\boldsymbol{r}^n)$	
	$\Updownarrow$	Hohenberg-Kohn (HK)
one-electron density	$\rho(\boldsymbol{r})$	
	$\Updownarrow$	Kohn-Sham (KS)
n one-electron spin orbitals	$\sum_i \lvert\psi_i(\boldsymbol{r})\rvert^2$	

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Major tool: CP2K program package

- Program package to perform primarily
  - Structure optimisations
  - Molecular dynamics (MD) simulations
  - Property calculations
- Developed in the framework of the open source project CP2K
- Fully modular implementation in Fortran 2003 (about 1 Mio code lines)
- Layered module structure with shared basic modules
- Common flexible input structure

http://www.cp2k.org

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CP2K is not CPMD

Please note that there is currently

- **No** plane waves code implemented in CP2K
- **No** Car-Parrinello scheme implemented in CP2K

  (only Born-Oppenheimer molecular dynamics → BOMD)

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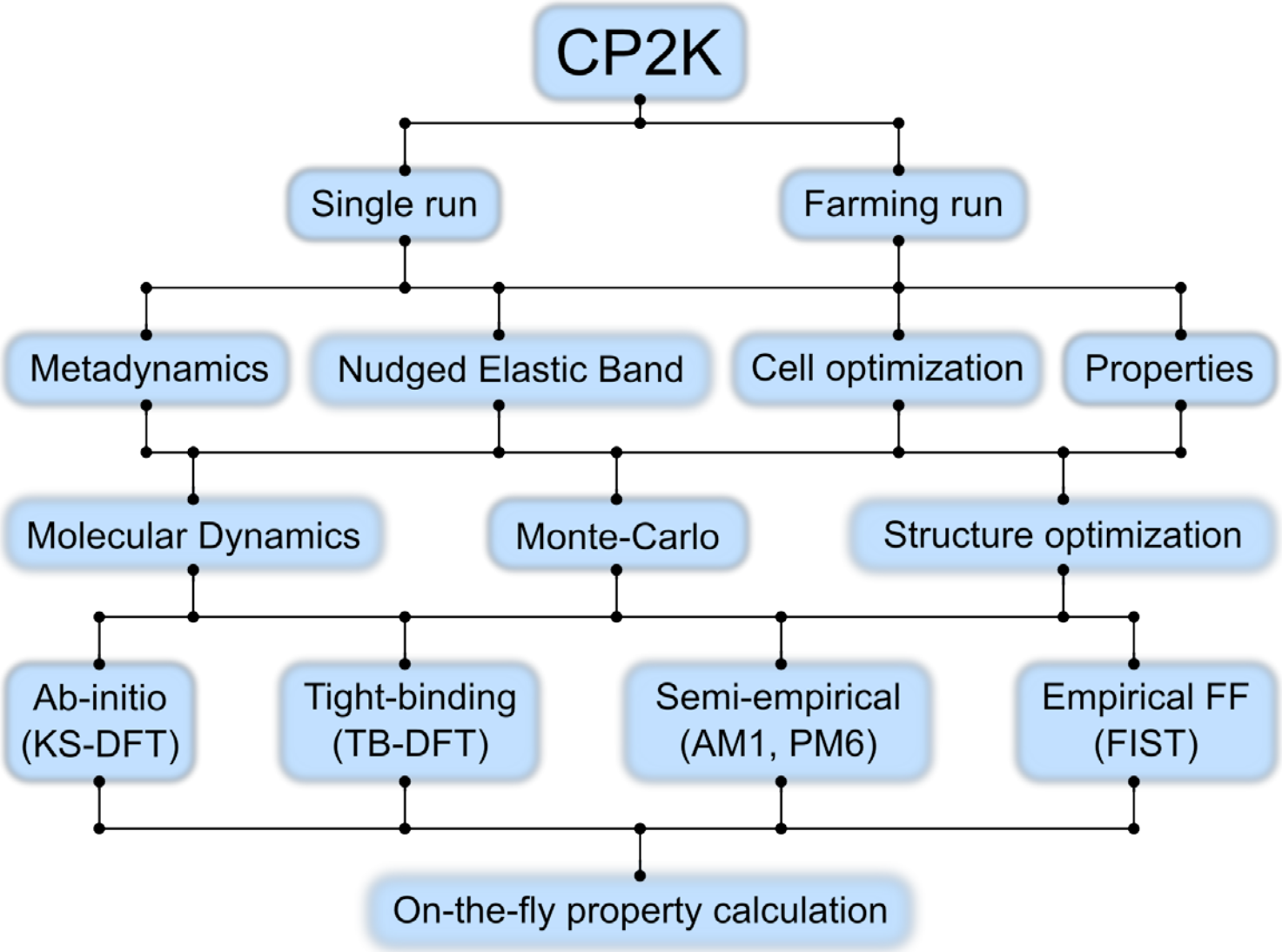
Modules



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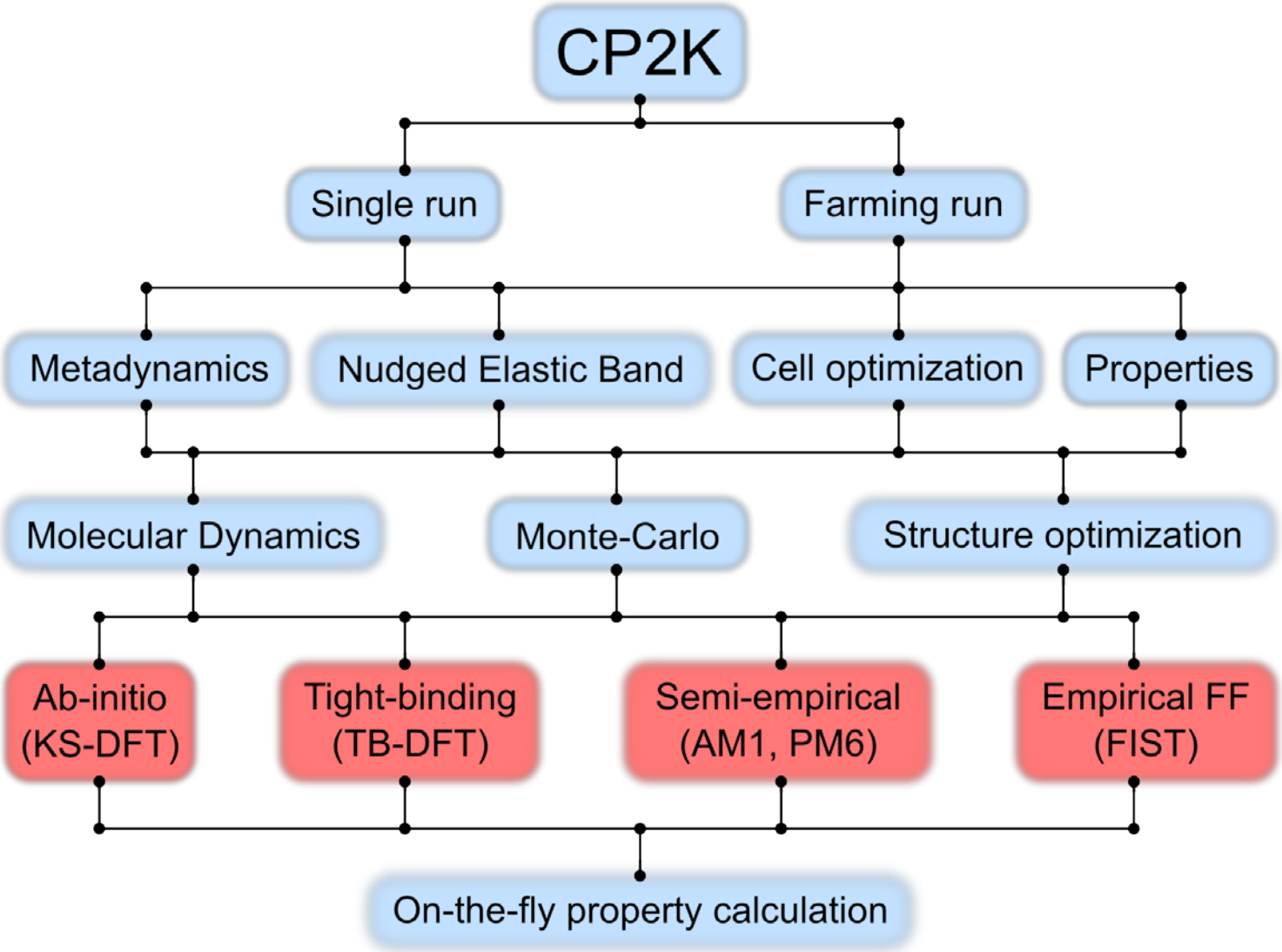
Computational methods: Energy and forces



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QUICKSTEP module

- Electronic structure method based on Kohn-Sham DFT

- Implementation of Gaussian Plane Waves (GPW) basis sets:
  - Linear combination of Gaussian-type orbitals (LC-GTOs) for the Kohn-Sham orbitals
  - Auxiliary plane waves basis set for the expansion of the electronic charge density

- Gaussian Augmented Plane Waves (GAPW) method allows for all-electron calculations

- Due to the hybrid basis set approach:
  - Kohn-Sham matrix construction scales **quasi linearly** with system size
  - Large and accurate Gaussian basis sets can be employed

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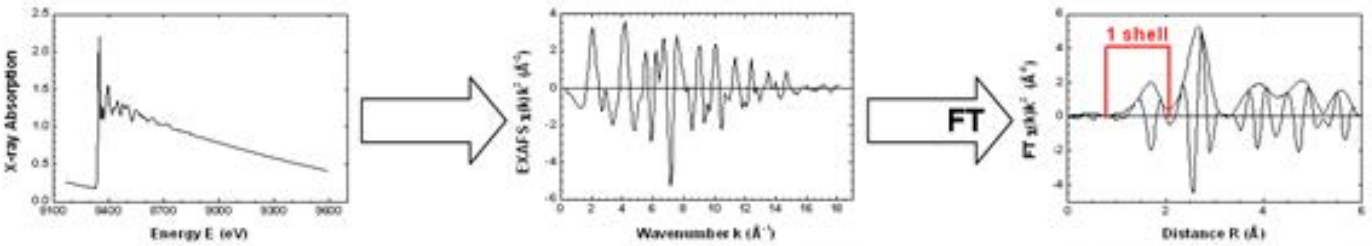
Merit of a hybrid basis set

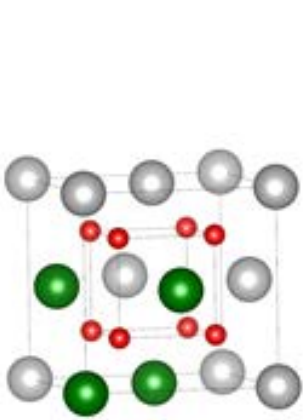
- Multiple representations of the electronic charge density are *concurrently* available:
  - $\mathbf{P}$: density matrix (atom-centred Gaussian-type orbital basis set)
  - $\tilde{\rho}(\boldsymbol{r})$: real-space density (auxiliary plane wave basis set)
  - $\tilde{\rho}(\boldsymbol{g})$: g-space density (auxiliary plane wave basis set)
- Efficient solution of the Coulomb problem is enabled:

$$\mathbf{P} \xrightarrow{\text{collocate}} \tilde{\rho}(\boldsymbol{r}) \underbrace{\xrightarrow{\text{FFT}} \tilde{\rho}(\boldsymbol{g}) \rightarrow V_{\text{H}}(\boldsymbol{g}) = \frac{\tilde{\rho}(\boldsymbol{g})}{g^2} \xrightarrow{\text{FFT}^{-1}}}_{O(n \log n)} V_{\text{H}}(\boldsymbol{r}) \xrightarrow{\text{integrate}} \mathbf{V}_{\text{H}}$$

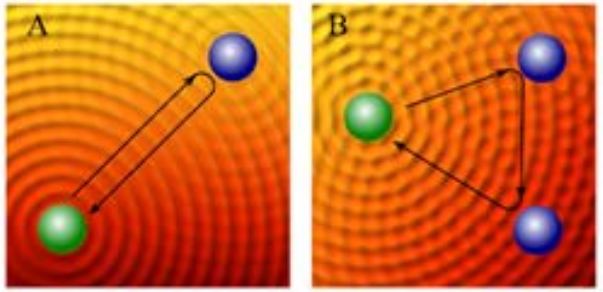
- Hartree potential build scales (quasi) linearly
- Attempts to combine the best of two worlds

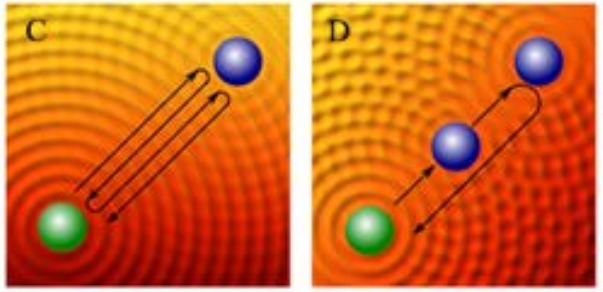
XAFS spectra simulation





Compare
$\chi(k)$
phase





Crystal structure model

atoms.inp

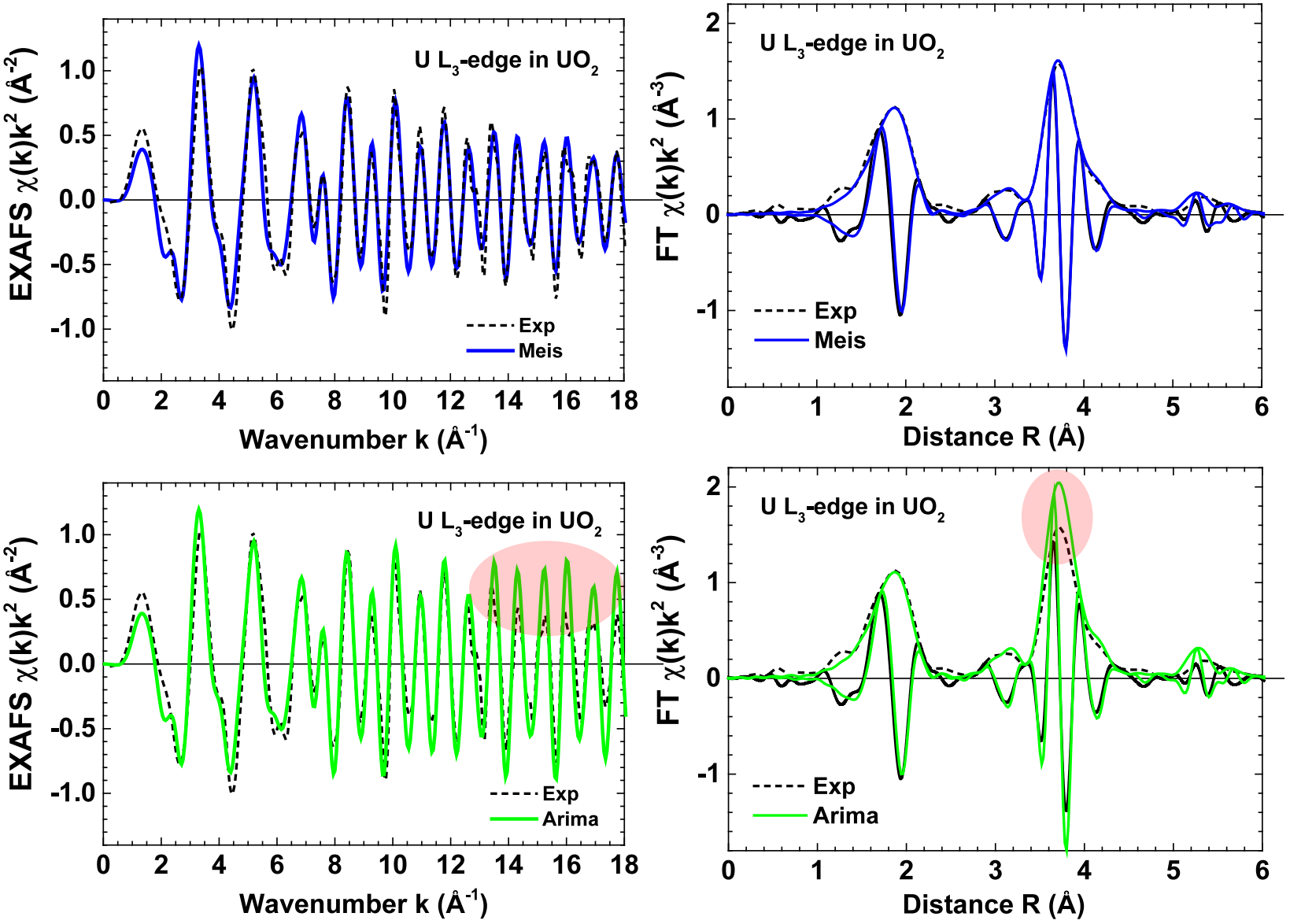
ATOM

feff.inp

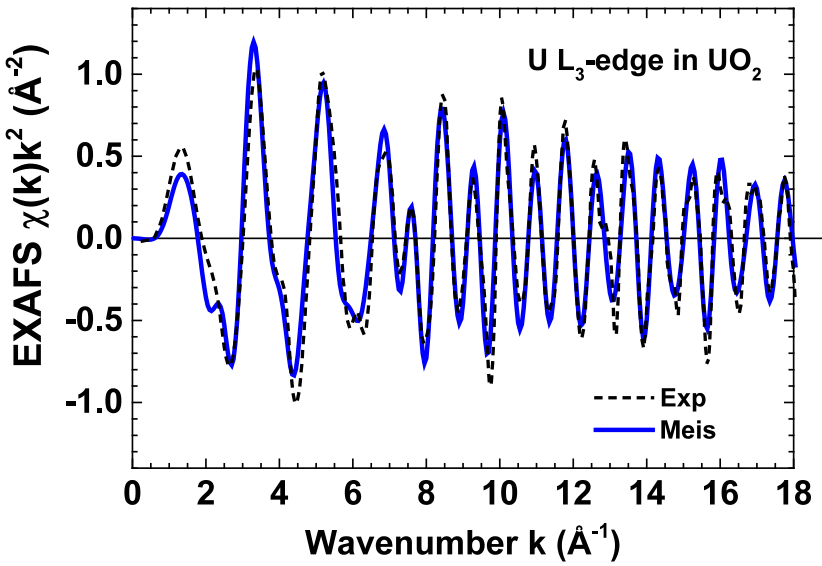
FEFF8

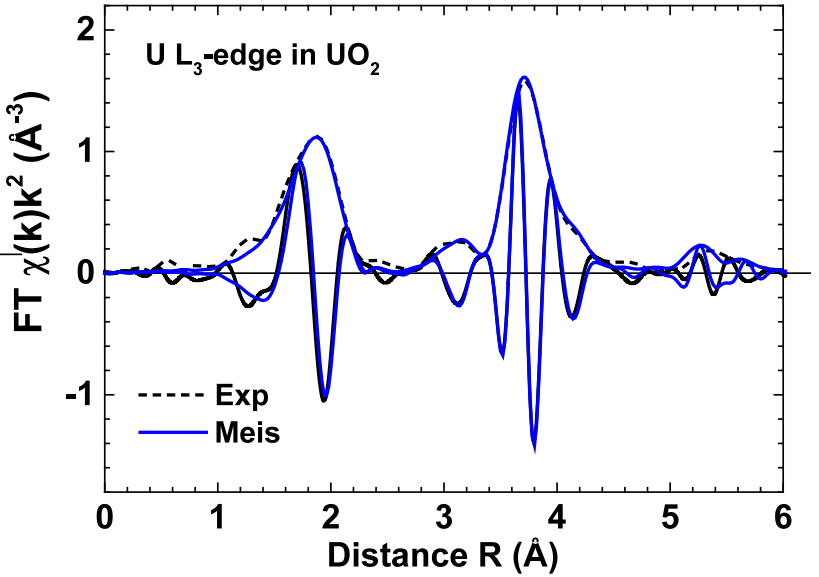
$\chi_{FEFF}(k)$

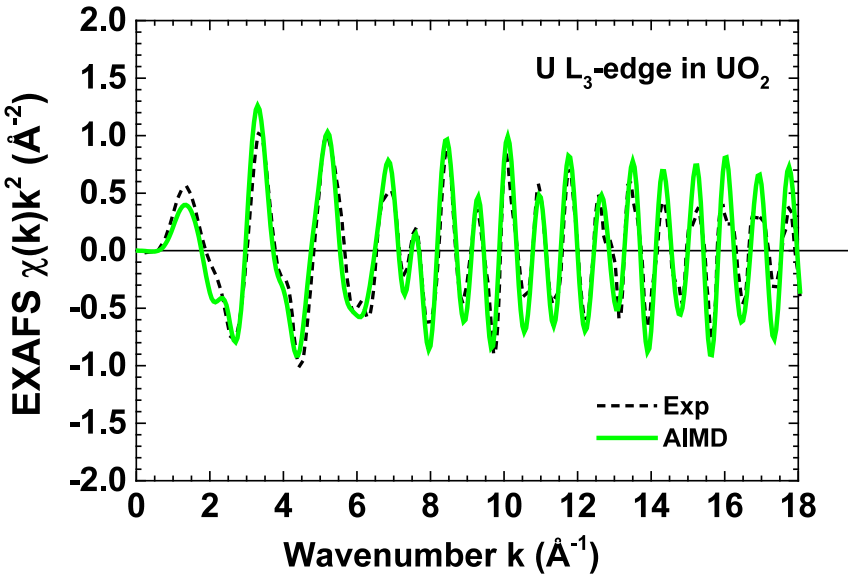
Force field vs Experiment for pristine UO_2

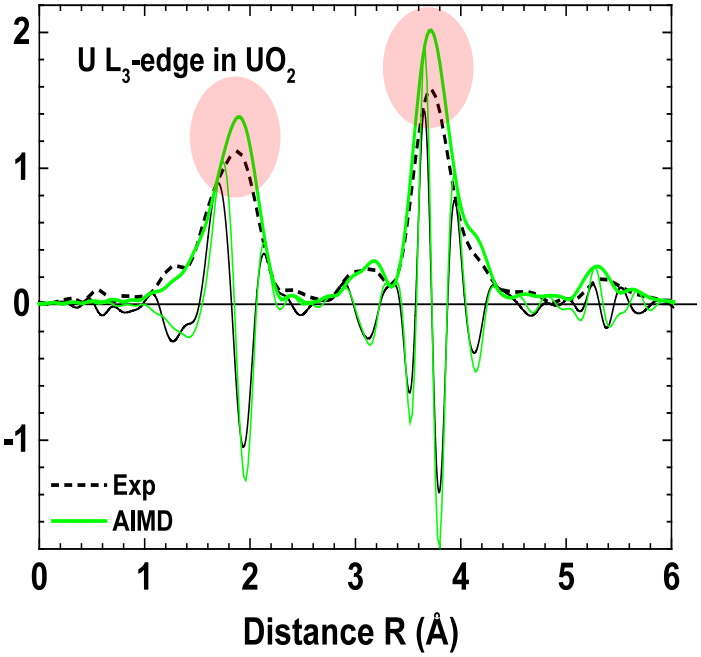


Ab initio vs Experiment for pristine UO_2



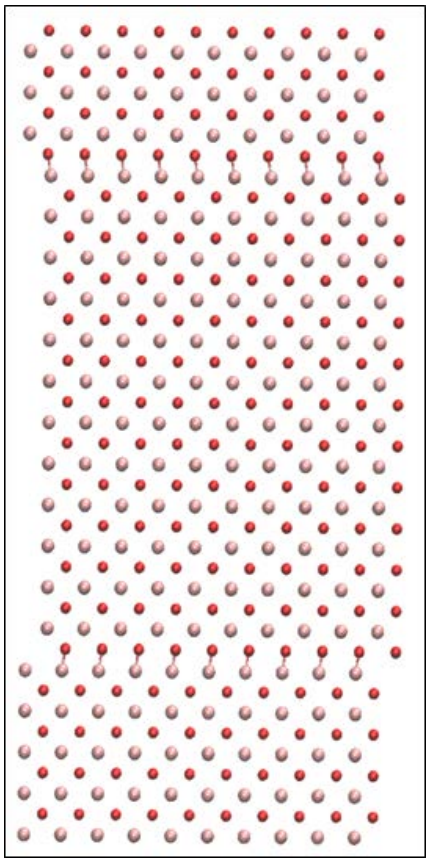






Computational study of dislocations in UO_2

γ-surface or the Generalised Stacking Fault Energy Surface



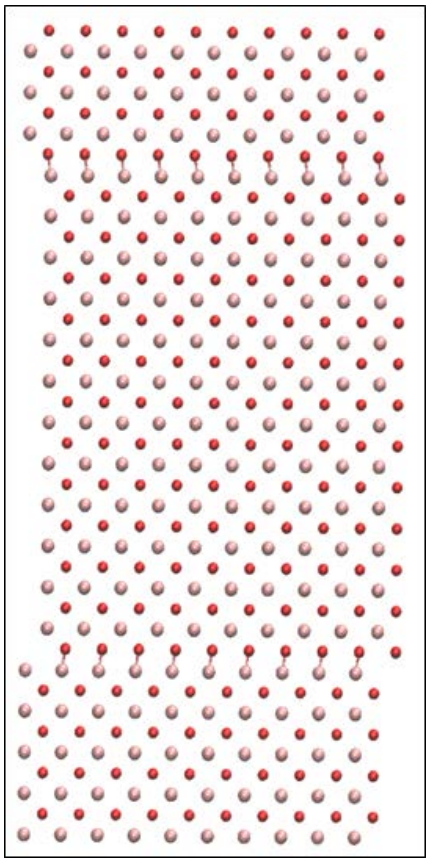
1) Choose a surface gliding plane, e.g. {001} *according to experimentally known glide planes*

2) Displace part of the crystal while keeping the other steady

V. Vitek, Philos. Mag. **40**, 903 (1968)
V. Vitek, *Prog. Mater. Sci.* **36**, 1 (1992)

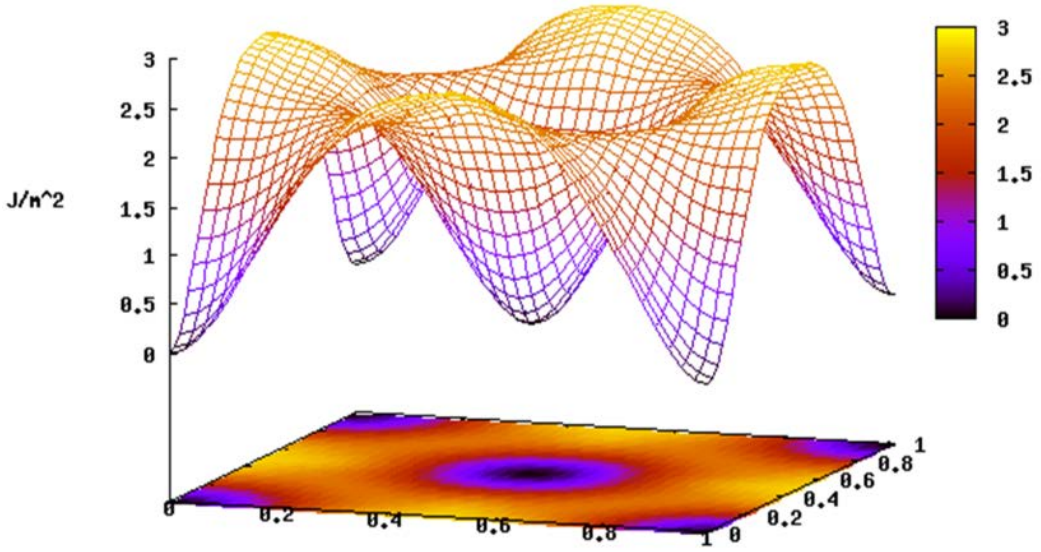
Computational study of dislocations in UO_2

γ-surface or the Generalised Stacking Fault Energy Surface



3) Compute the energy difference between the unperturbed crystal and the perturbed crystal

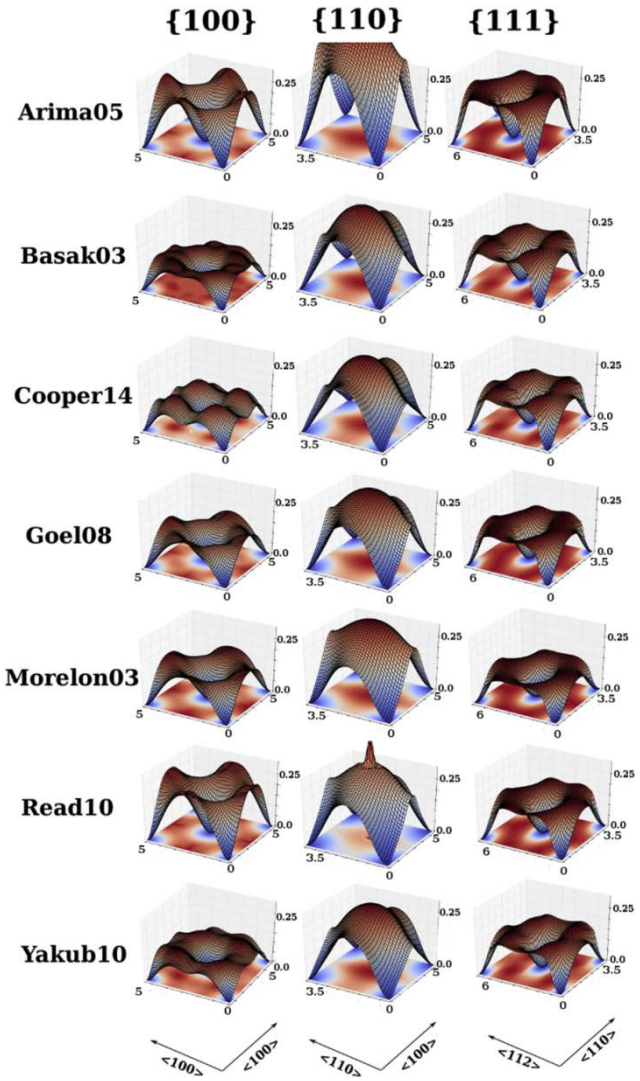
4) Repeat 2) and 3) to sample the chosen {001} plane



γ-surface (Energy in J/m^2 as function of the displacement)

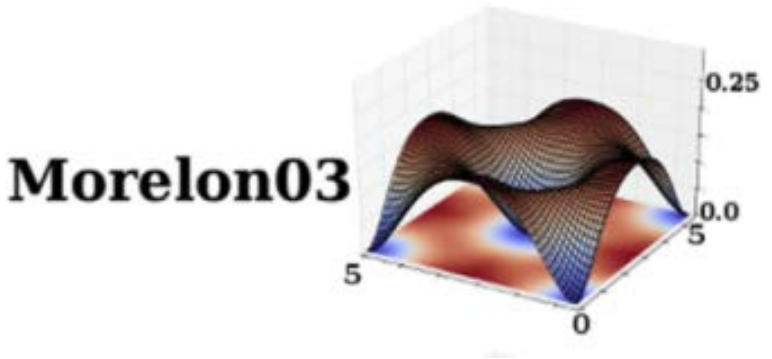
V. Vitek, Philos. Mag. **40**, 903 (1968)
V. Vitek, *Prog. Mater. Sci.* **36**, 1 (1992)

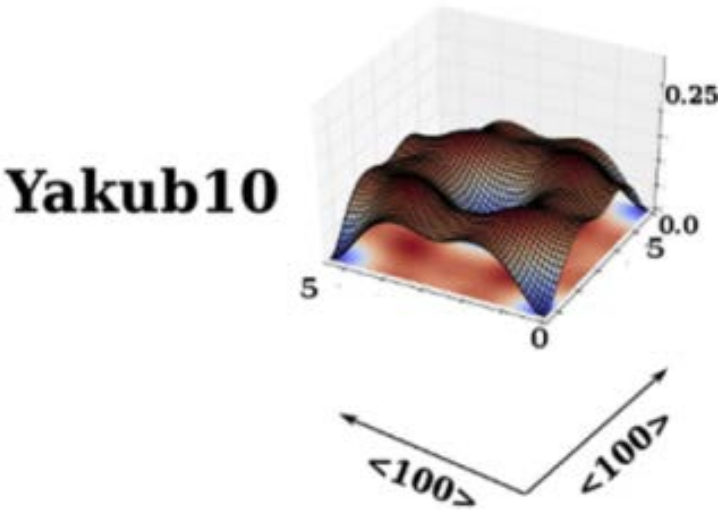
γ-surface modelling of UO_2



R. Skelton, A.M. Walker, J. Nucl. Mater. **495,** 202 (2017)

Recent literature shows qualitative and quantitative differences among different empirical potentials:

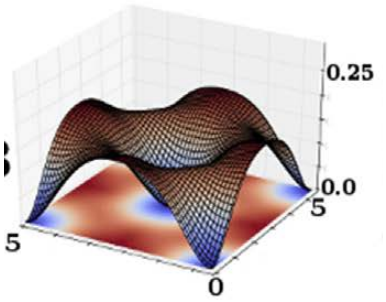


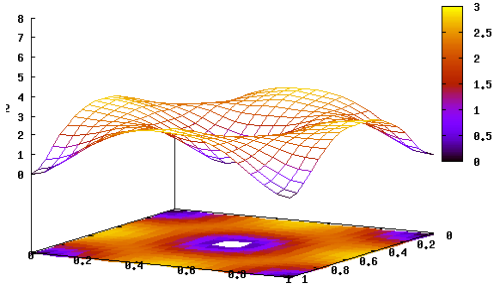


Modelling the slip systems on three planes

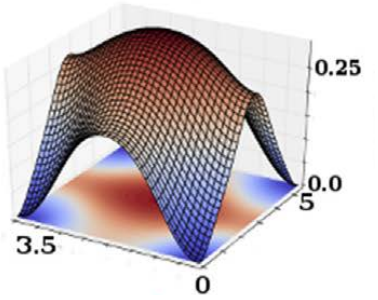
Validation of the theoretical procedure

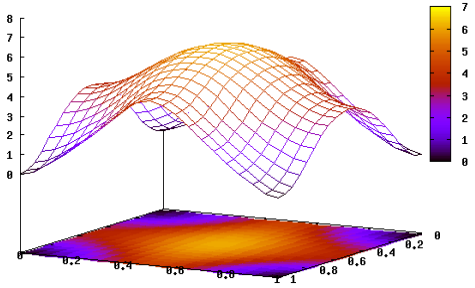
{001}



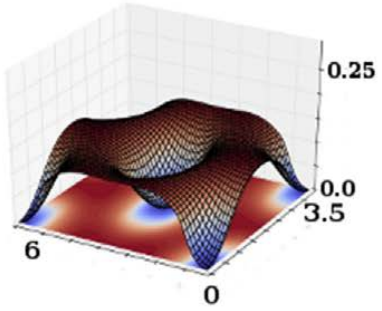


{110}

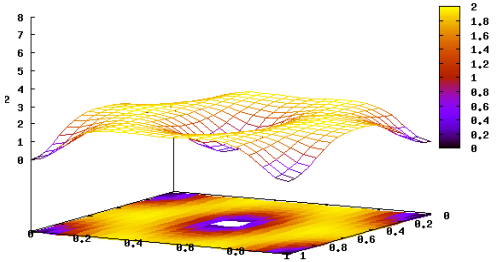




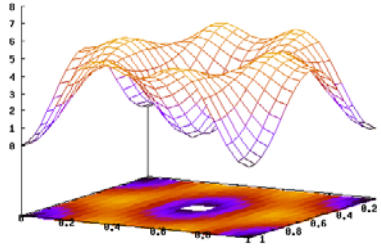
{111}



Displacing adjacent O-O planes



Displacing adjacent U-O planes



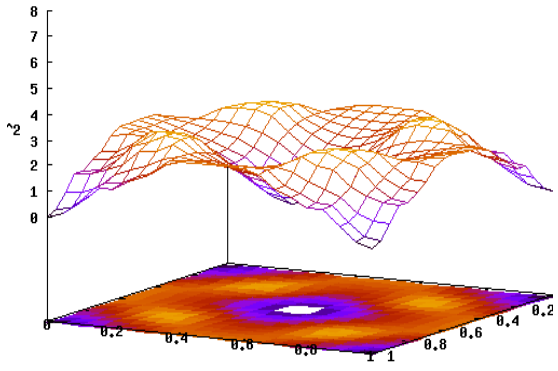
R. Skelton, A.M. Walker, J. Nucl. Mater. **495,** 202 (2017)

M. Kosa, M. Krack, preliminary results (Morelon EP, Energies in J/m^2)

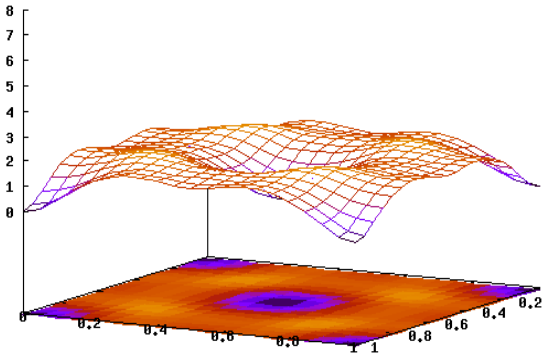
Validating Empirical Potentials with DFT+U

{001} glide plane:

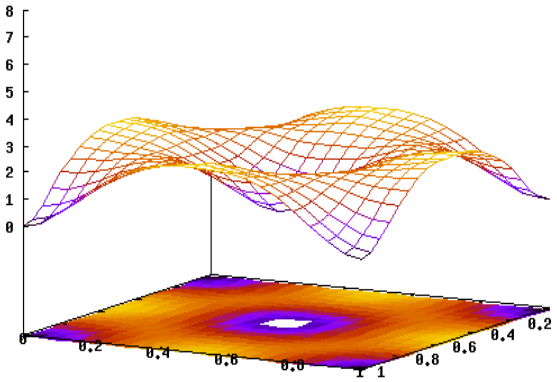
DFT+U



Yakub10



Morelon03



(3x3x8 cell, 864 atoms)

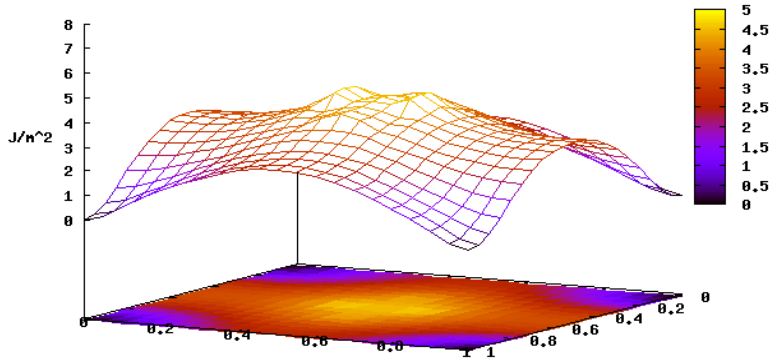
- DFT+U results in a surface with shape similar to Yakub10 EP and a more corrugated γ-surface
- Electrons have the freedom to rearrange around the displaced ions
  Will be demonstrated for the {110} surface

M. Kosa, M. Krack (preliminary results, DFT+U (U = 2 eV), Energies in J/m^2, {001}, FOP: -3,-1,+1,+3)

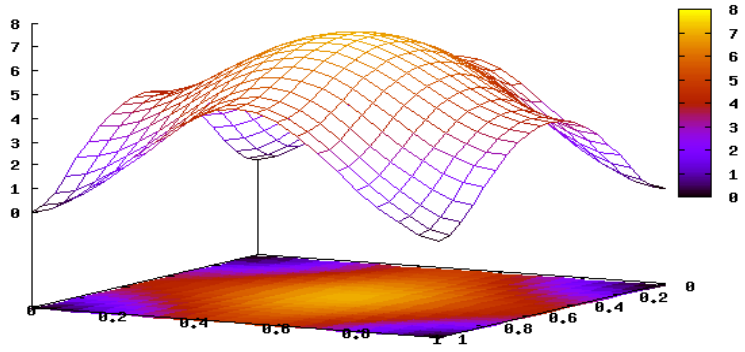
Validating Empirical Potentials with DFT+U

{110} glide plane:

DFT+U



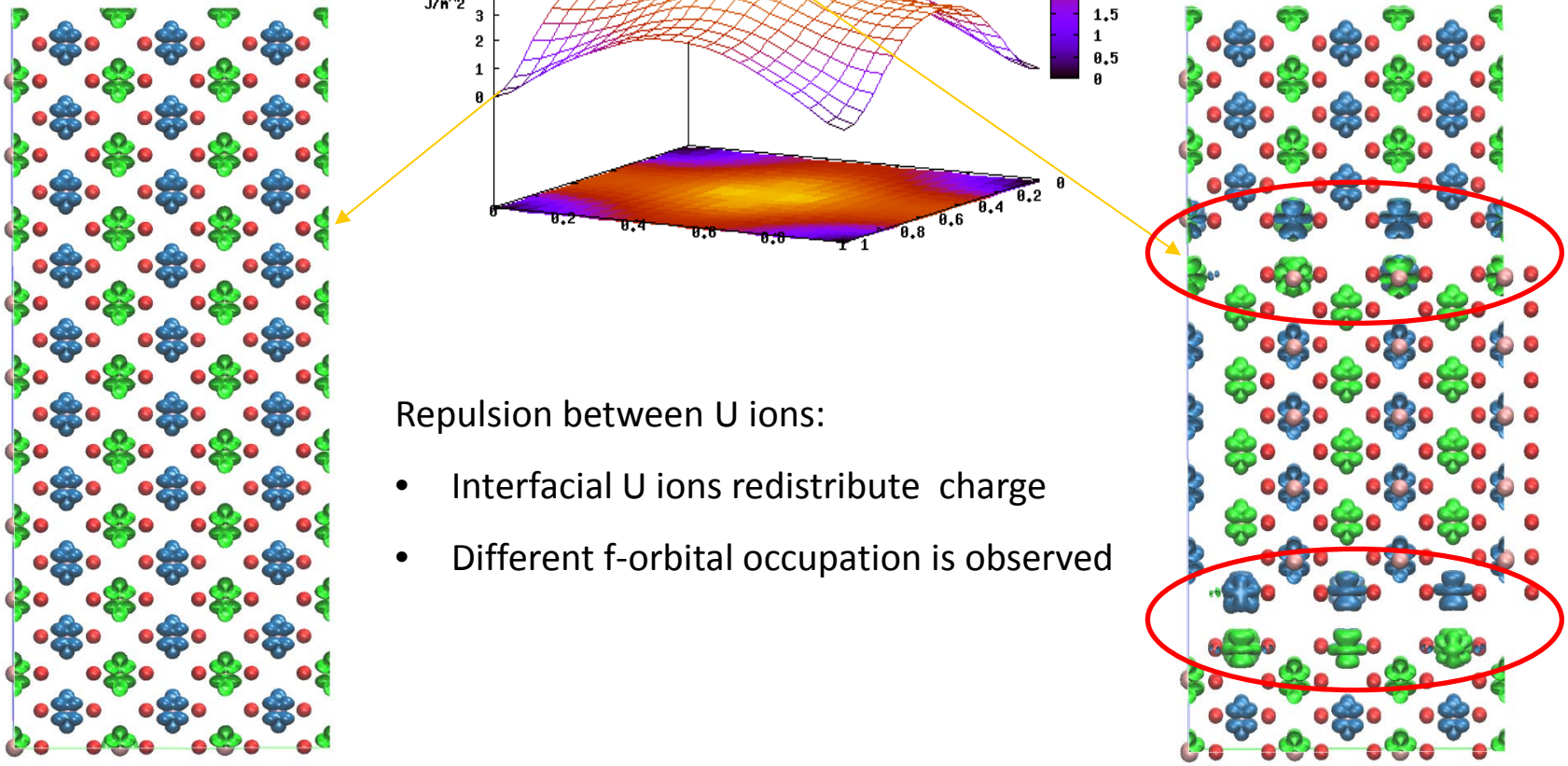
Yakub10



- The DFT+U {110} γ-surface is qualitatively different from any of the considered EP
- Local minimum at the top of the cap, a metastable state

M. Kosa, M. Krack (preliminary results, DFT+U (U = 2 eV), Energies in J/m^2, {001}, FOP: -3,-1,+1,+3)

Electronic effects during {110} sampling



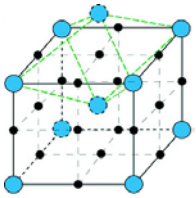
Repulsion between U ions:

- Interfacial U ions redistribute charge
- Different f-orbital occupation is observed

M. Kosa, M. Krack (preliminary results, DFT+U (U = 2 eV), Energies in J/m^2, {110}, FOP: -2,0,-2,0)

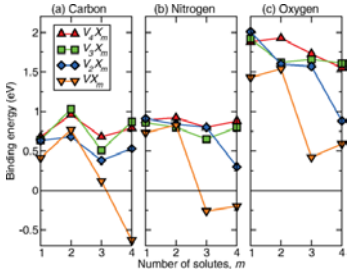
Microstructural evolution in Ferritic steels

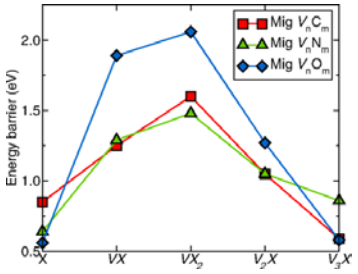
- Framework: H2020 EU-project SOTERIA
- PhD in collaboration with KTH Sweden (P. Olsson): Started in Feb 2018
- Our contribution: Modelling carbides and their effects on radiation-induced microstructure changes
  - Carbon sits on a different lattice than Fe



→ Multi-lattice model

  - Carbon has specific interactions with solute atoms and point defects





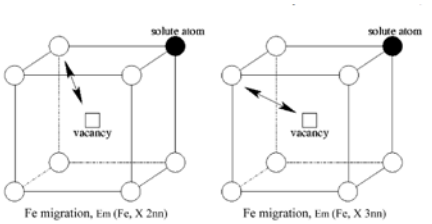
→ Development of an interaction and migration model

- DFT-based Kinetic Monte Carlo method: LAKIMOCA code (developed at EDF R&D, France)

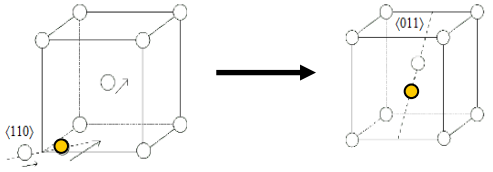
Microstructural evolution in Ferritic steels

+ Carbon

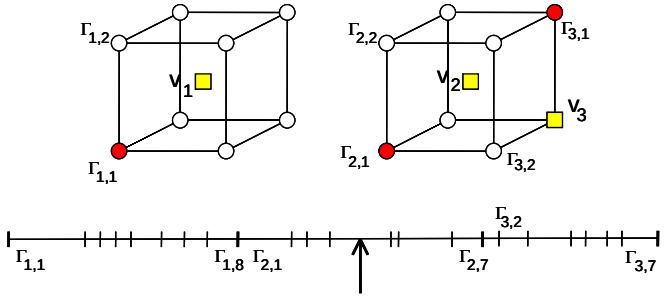
- Treatment of multi-component Fe alloys on a 3D rigid lattice with PBC or absorbing surfaces:
  - Elements on substitutional sites: Cu, Mn, Ni, Si, P
  - Self-interstitial atoms (SIA): Fe, Cu, Mn, Ni, Si, P



- Diffusion by 1st nearest neighbour (1nn) jump:
  - Via vacancy
  - Via self-interstitial
  - Jump probability

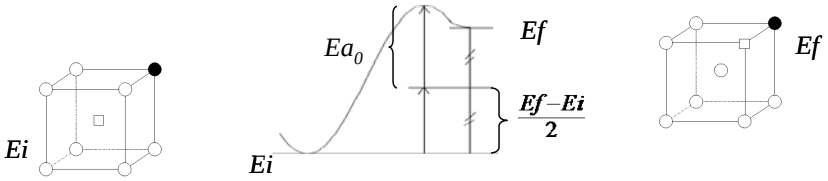


- Residence time algorithm applied to all events
  - Point defect jumps
  - Point defect fluxes
  - Average time step: $\Delta t = \frac{1}{\sum_{j,k} \Gamma_{jk}}$



- Environment-dependent form for the jump activation energy

$$E_a = E_{a_0}(X_i) + \frac{E_f - E_i}{2}$$



Outlook on Future Activities and Projects

- Modelling of Silicon anodes for high energy density Li-ion batteries
  - Partners: PSI/LEC, EMPA, BIU (Sinergia)
  - Mechanical behaviour of organic coating materials
  - Modelling of the Li-ion diffusion and lithiation process
  - Reactivity of the solid electrolyte interface (SEI)

- Crystal structure prediction
  - Partner: Novartis
  - Relative phase stability
  - Co-crystal formation
  - Salt stability

- Development of ab initio based Monte Carlo models for predicting thermodynamic and transport properties of fluorite-type functional oxides
  - Partner: Uni Zurich (SNSF)

- Follow-up to SAMOFAR
  - Viscosity of the salt melt derived from MD simulations
  - Thermo-dynamical modelling (GEMS)

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