Surface modelling of UN and other actinides: current state and prospects

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Actinides surface modeling: motivation

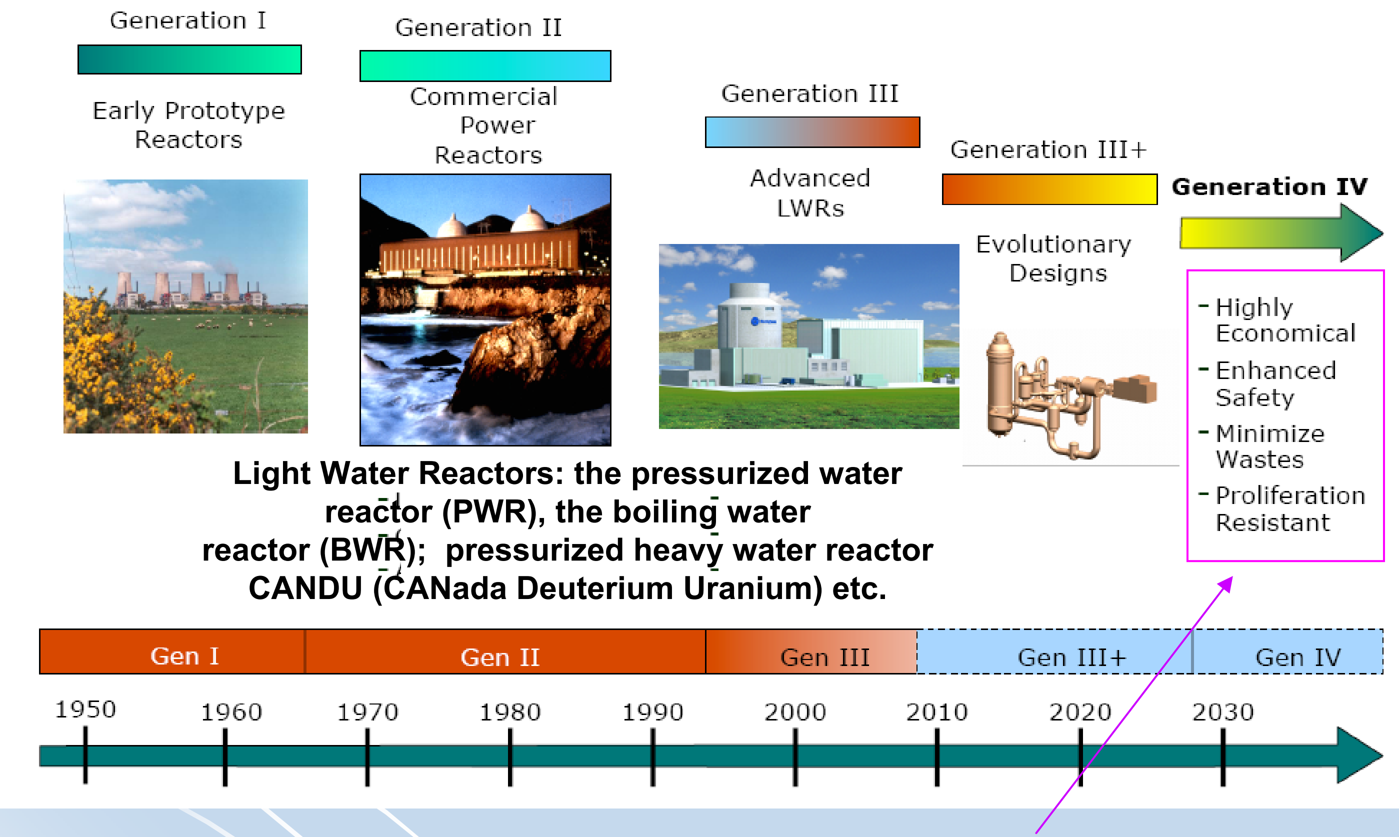
The first-principles modeling of materials promises to revolutionize the way materials are designed, used, and maintained

Calculations of materials are necessary to

- describe actual material properties of compounds
- evaluate how successful are nowadays methods for real materials description

In this presentation we will observe typical problems of actinides surface modeling

Motivation: GEN IV reactors



Light Water Reactors: the pressurized water reactor (PWR), the boiling water reactor (BWR); pressurized heavy water reactor CANDU (CANada Deuterium Uranium) etc.

Picture from [*Tim Abram, Fuel Materials Challenges for Gen-IV Nuclear Systems*]

GEN IV reactors to be in operation in about 20-30 years from now

“GEN IV” name describes general principles of reactor work!

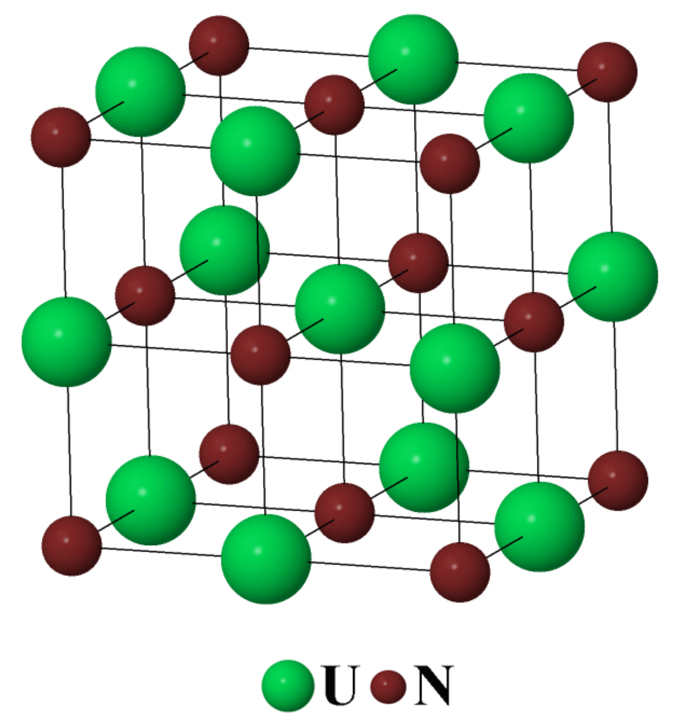
Development of new fuels is very actual: UF in salt, UO_2, UC, MOX.

Uranium mononitride (UN) which was studied in ISSP is one of promising fuels for GEN IV. It has several advantages compared with the “traditional” oxide nuclear fuels.

Uranium mononitride (UN)

- *fcc* NaCl structure
- metallic lustre
- low electrical resistivity
- High melting point (~2780±25 K)
- high fissile atom density (14.32 g/cm^2 vs 10.96 g/cm^2 for UO_2)
- high solubility in HNO_3 in the case of fuel reprocessing
- high thermal conductivity (13 W/mK)

Prospective material for Generation IV nuclear reactors



Motivation for UN

One of main problem with UN is their effective oxidation in oxygen-containing atmosphere (even at low partial pressure). Oxygen impurities always presented in UN lead to its unwanted pollution and further degradation in air.

It is important to understand the mechanism of the initial stage of UN oxidation.

- bulk oxidation modelling (other colleagues from ISSP)
- surface oxidation modelling

The study is performed in collaboration frames between ISSP and ITUand as one of tasks included in the EC FP-7 project: Basic Research for Innovative Fuel Design for Generation-IV systems (F-BRIDGE).

Modeling tasks

Modeling of:

- Bulk
- Perfect UN surface
- Single N and U vacancies
- Molecular and atomic oxygen adsorption
- Oxygen migration upon surface
- O adatom incorporation into vacancy

- Comparison of UN (001) and (110) surfaces

- Development of an atomistic model for oxidation of UN surface

Theoretical background: VASP

For UN modeling, we use the VASP-4 computer code, the commercial complex package which elaboration was begun at early 90s.

This package is based on:

- density functional theory (DFT)
- plane-wave basis set

We use:

- Perdew-Wang-91 GGA non-local exchange-correlation functional (PW91)
- Scalar relativistic projector-augmented-wave (PAW) pseudopotentials

Why actinides calculations is so heavy?

- Large numbers of electrons
- U(5*f*) electrons which are found to be intermediate between the highly localized 4*f* electrons of the lanthanides and the strongly delocalized *d* valence electrons in the transition metals.
- Relativistic effects must be taken into account
- Restricted number of experimental data due radioactive nature of actinides

Problems in calculations

1. Necessary *vs* sufficient

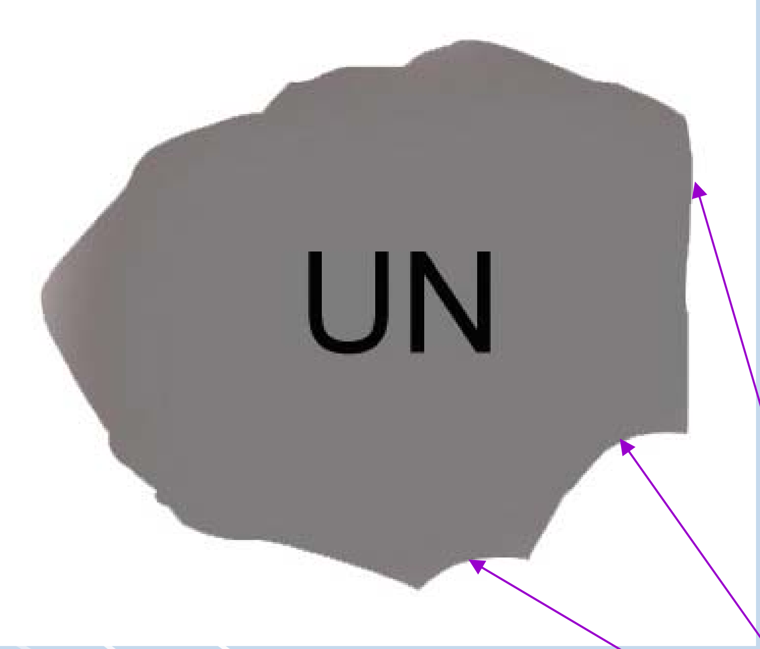
$t \sim n_e^6 \div n_e^8$!!!

symmetry, minimal periodicity, pseudopotentials, elements replacement (for example U → Zr)

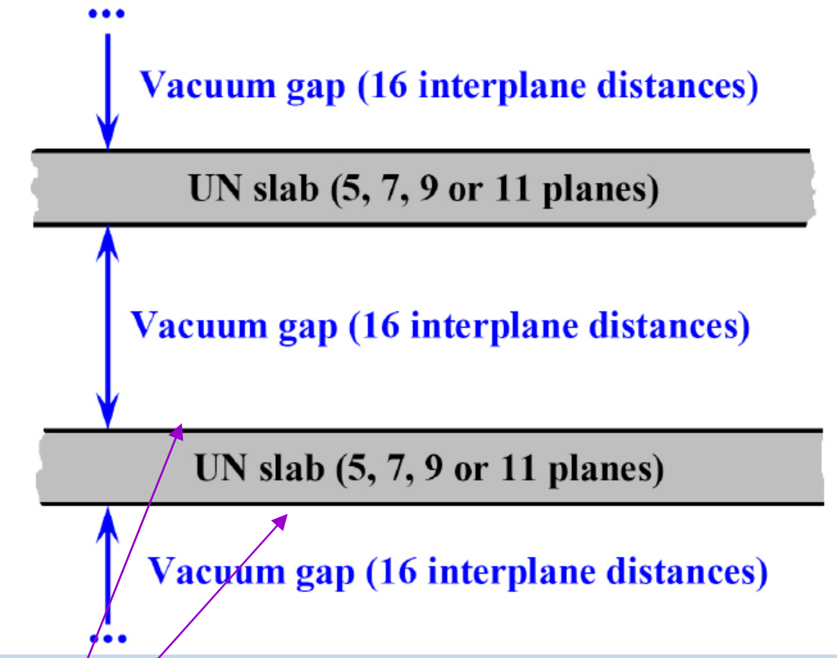
2. GIGO principle: Garbage in – Garbage out.

3. Simplification of real system: it’s necessary to found our results verification ways

Computational Model: Slab



Real material

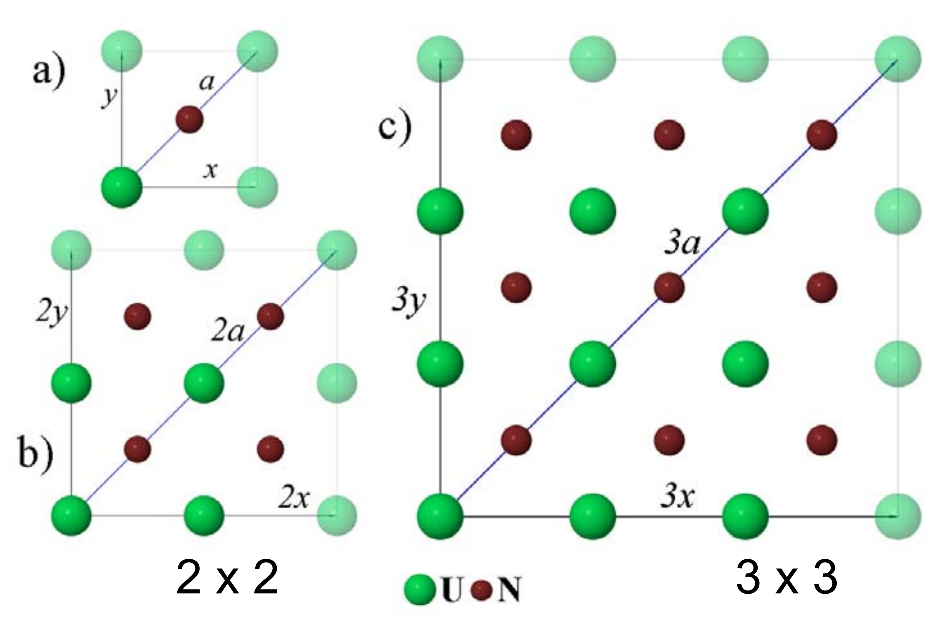


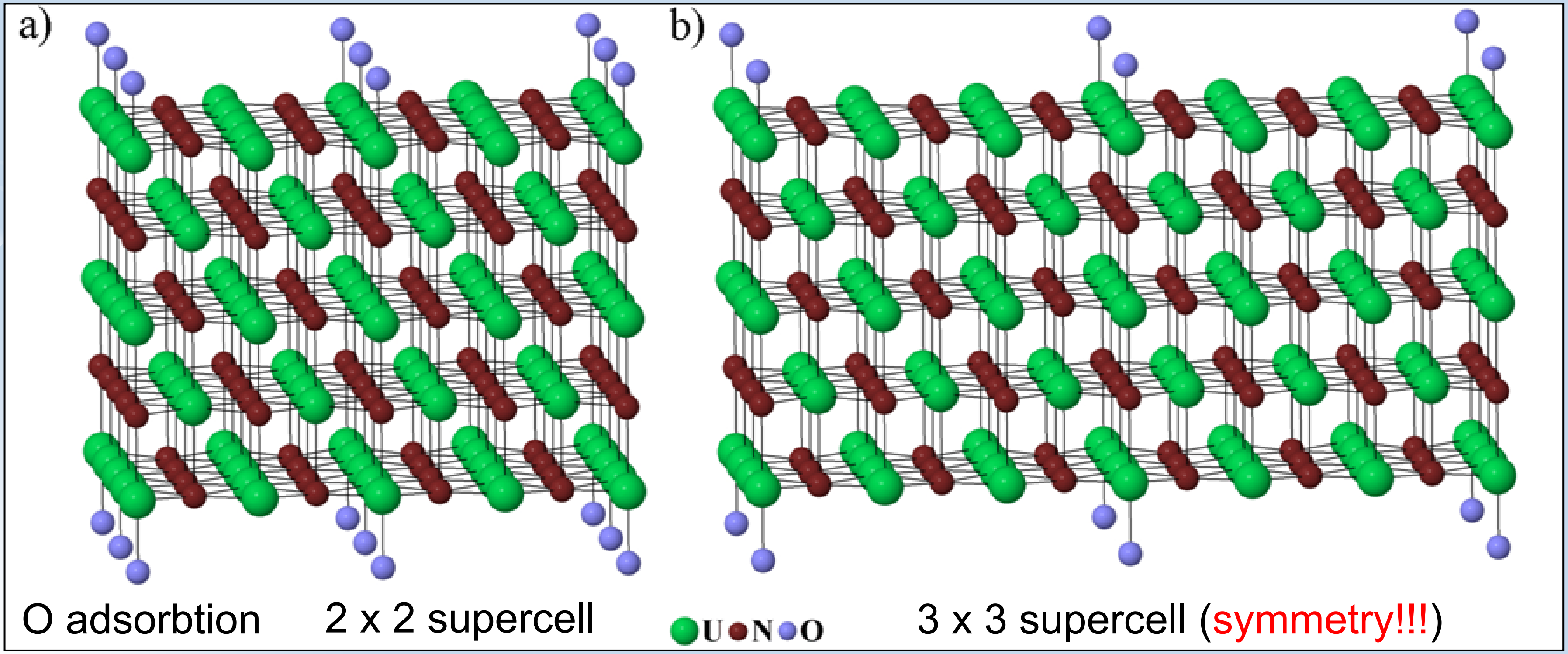
Slab model (with 3D repetition due PW basis)

Surface

Computational model: supercells

To reduce computational efforts, we have often considered the two-sided arrangement of the point defects which is symmetrical with respect to the central (mirror) plane.





O adsorbtion 2 x 2 supercell

3 x 3 supercell (symmetry!!!)

Pseudopotentials

The chemical properties are mostly determined by the valence electrons, the inner shells are chemically rather inert.

It allows us to describe separately only the outer shells' electrons.

Depending on number of included electrons the pseudopotentials can be separated as Large Core (LC) and Small Core (SC) RECP pseudopotentials.

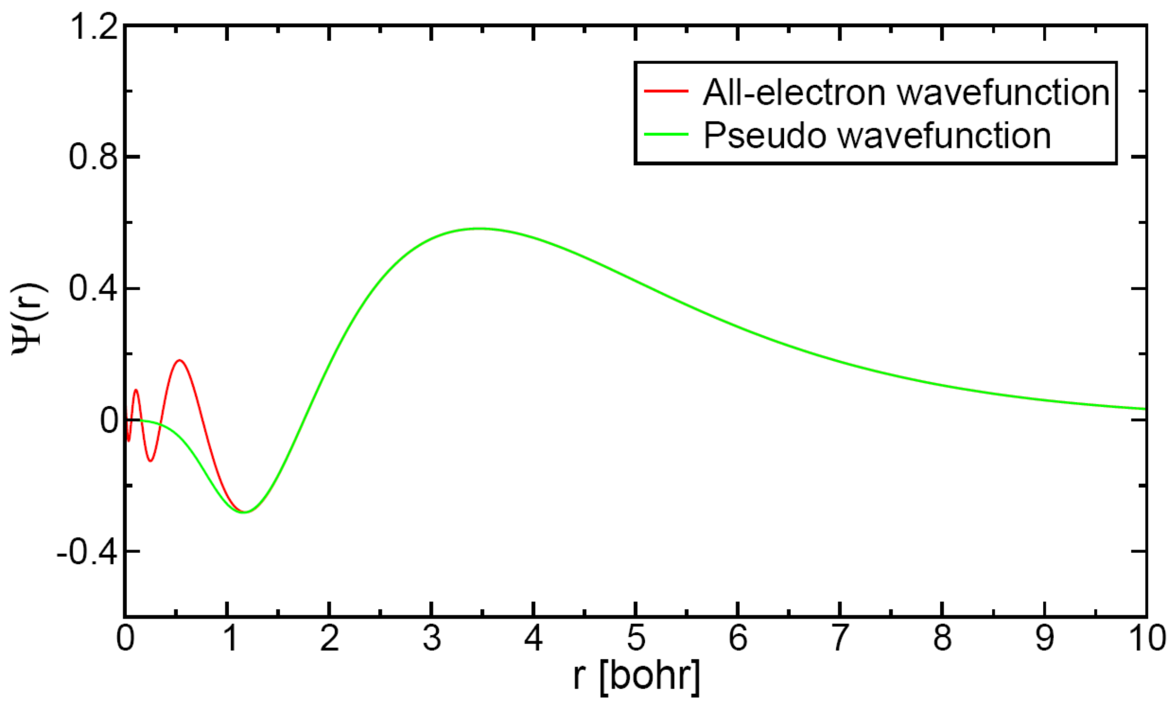
$1s^2 2s^2 2p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^2 5f^3 6d^1$

Atom configuration with Large Core pseudopotential: 78 + 14 electrons

$[\mathrm{Xe}\ 4f^{14} 5s^2 5p^6 5d^{10}] 6s^2 6p^6 7s^2 5f^3 6d^1$

For calculations performed within the current PhD study, we have applied RECP pseudopotential for 78 U internal electrons as well as 2 core electrons for both N and O atoms

Large-core pseudopotential for uranium (14 valence electrons)



From: Matthias Krack, Electronic Structure Calculations

$t \sim n_e^6 \div n_e^8$!!!

For 3 x 3 supercell and 7-layer slab in UN full-electron calculations number of atoms is equal to 126, but number of electrons is equal to (92+7)*63 = 6237 electrons

For REPC potentials we calculated system with 126 cores as well as (14+5)*63 = 1197 electrons

$6237^6 = 2.94147E+18$, $1197^6 = 5.88646E+22$, $T_{fe}/T_{pc} \approx 20000$

1 day vs 54 years

Calculated results verifications

Due to a restricted number of theoretical and experimental data available in literature so far, very important question was a proper verification of the calculated results. My PhD Thesis considers the following verification methods:

- Comparison of obtained results with existing experimental or theoretical data.
- Simultaneous application and comparison of different theoretical methods: The results of our PW calculations on UN bulk and perfect (001) surface as well as atomic oxygen adsorption on this substrate were compared with the corresponding LCAO results calculated by group of Prof. R.A. Evarestov
- Comparison of different crystallographic orientation surfaces

Calculated results verifications

- Comparison of results obtained for the same system with varied computational parameters. For example, we compared vacancy formation energy for the same defect periodicity (2 x 2 or 3 x 3) but for different number of atomic layers
- Finding of internal criteria for convergence (For example, in calculations on vacancy-containing UN slab, the control of spin distribution is very important. Averaged magnetic moment μ_{av} per U atom in spin-relaxed calculations must be larger than 1 μ_B, otherwise we cannot achieve a convergence of formation energies for defects depending on thickness of UN slab).

Previous theoretical data

- The first electronic structure simulations on actinide surfaces and their reactivity towards the molecular and atomic oxygen were performed only recently, due to a large number of electrons per unit cell. Nevertheless, some results of simulations performed for α-U, δ-Pu and UO_2 surfaces are available in the literature.

- The PW91 functional has been used for simulations on (111), (110), and (100) surfaces of UO_2. The calculations showed that the (111) surface has the lowest surface energy (0.461 J/m^2), followed by the (110) surface (0.846 J/m^2), and the (100) surface (1.194 J/m^2).

[N. Skomurski, R.C. Ewing, A.L. Rohl, J.D. Gale, and U. Becker, Quantum mechanical vs. empirical potential modeling of uranium dioxide (UO2) surfaces: (111), (110), and (100). - Amer. Mineral., 2006, ***91,*** *p. 1761-1772].*

Previous theoretical data

- The calculations were performed using the GGA PBE exchange-correlation functional. Only a 50% δ-Pu surface coverage by O, C and N adatoms was considered.
- Calculations were performed at two levels: with and without spin-orbit coupling. Inclusion of spin-orbit coupling lowers the chemisorption energy by 0.05–0.27 eV, on the other hand, it negligibly influences on chemisorption geometries.
- Analysis of effective charges for each atom indicates that chemisorption primarily occurs on the surface layer. Pu-adatom hybridizations is dominated by Pu(6*d*) and adatom 2*p* states, with a significant reduction in the first peak of the projected Pu(5*f*) DOS, indicating the delocalization of some Pu(5*f*) electrons.

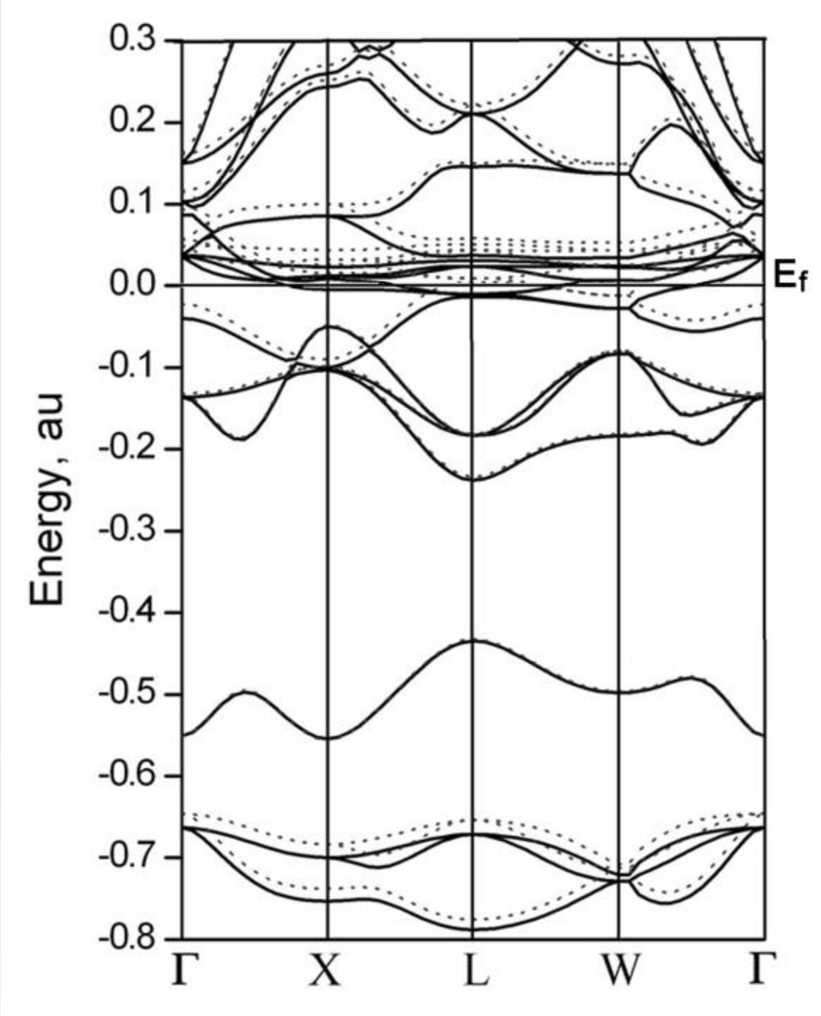
[R. Atta-Fynn and A. K. Ray, Ab initio full-potential fully relativistic study of atomic carbon, nitrogen, and oxygen chemisorption on the (111) surface of δ-Pu. - Phys. Rev. B, 2007, ***75****, 195112 (p. 1-13).]*

UN calculations. FM or AFM?

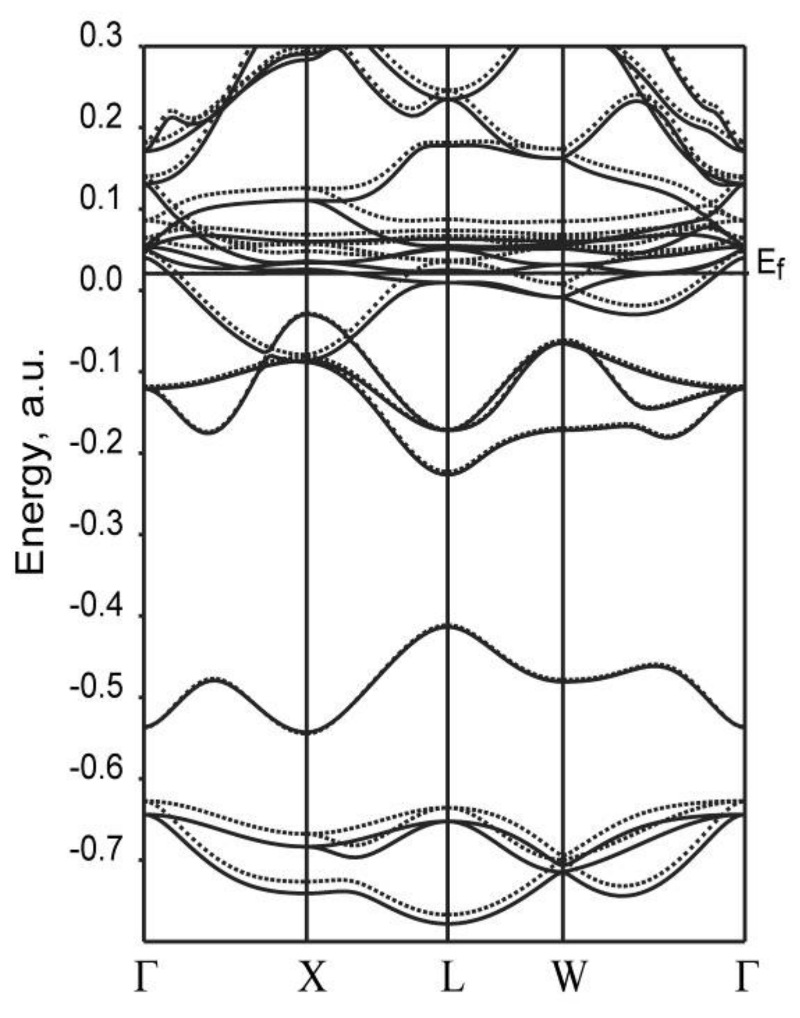
- In experiment the UN bulk was found to be AFM at temperatures lower than a Neel temperature (~ 53 K, 0.75 μ_B)
- We have performed the calculations on both FM and AFM states. Our PAW test calculations on UN bulk have shown that the FM phase is energetically slightly more favorable than AFM phase. Analogous results were obtained using LCAO method as applied by group of Prof. R.A. Evarestov.
- Ferromagnetic nature of UN surface was described in *D. Rafaja, L. Havela, R. Kuel, F. Wastin, E. Colineau, and T. Gouder, Real structure and magnetic properties of UN thin films. – 2005, 386, p. 87-95.*
- Due to a small diference between the energies in FM and AFM states (~0.001-0.01 eV) and due to a complicated magnetic structure of UN surface, only FM state has been considered in our UN surface calculations.

- Regardless of FM state is preferable for UN surface the reason why bulk in calculations undergoes FM ordering in bulk calculations still isn't clear. This situation is similar with [*R. Atta-Fynn and A.K. Ray, Density functional study of the actinide nitrides. - Phys. Rev. B, 2007, 76, 115101 (p. 1-12)*] results where LAPW formalism within the GGA approximation was used. Although lattice constants were calculated in a good agreement with the experiment (within ~0.4%), the UN, AmN, PuN, and NpN were found to be ferromagnetic (FM) that contradict to experimental AFM results.

Bulk modelling: band structure



PW PW91 (RECP SC78) Riga



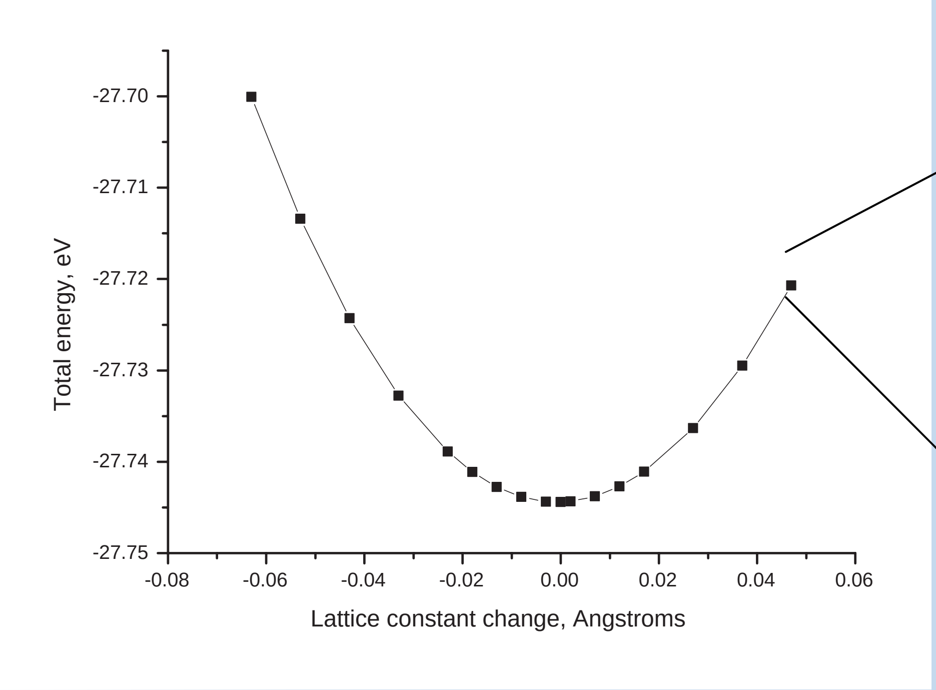
LCAO PW91 (RECP SC60) SPb

Band structure demonstrate a good qualitative agreement with experiment:
T. Ito, H. Kumigashira, S. Souma, T. Tahakashi, and T. Suzuki, High-resolution angle-resolved photoemission study of UN and USb; Dual character of 5f electrons. - J. Magn. Magn. Mater., 2001, ***226-230****, p. 68-69.*

Bulk modulus (I)

The bulk modulus in our calculations is equal to 224 GPa in PBE calculation and 227 GPa in PW91 calculation. Experimental value taken from [*Hj. Matzke, Science of Advanced LMFBR Fuel, North Holland, Amsterdam, 1986*] is equal to 194 GPa. Why appears this difference?

- The 194 GPa is not the only experimental value. In [*Hj. Matzke, Science of Advanced LMFBR Fuel, North Holland, Amsterdam, 1986*] bulk modulus from different experiments ranges between 184 till 206 GPa.
- The approximation also introduce error.



The simplest plausible dependence of energy on volume would be a harmonic solid

$$E = E_0 + \frac{1}{2} B_0 \frac{(V - V_0)^2}{V_0}.$$

227 GPa

Murnaghan sophisticated equation of state

$$E(V) = E_0 + \frac{B_0 V}{B_0'} \left(\frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1 \right) - \frac{B_0 V_0}{B_0' - 1}.$$

219 GPa

Bulk modulus (II)

Bulk modulus strongly depends of porosity, temperature, stoichiometry (UN have tendence to be in non-stoichiometric UN_{1-x} state) etc.

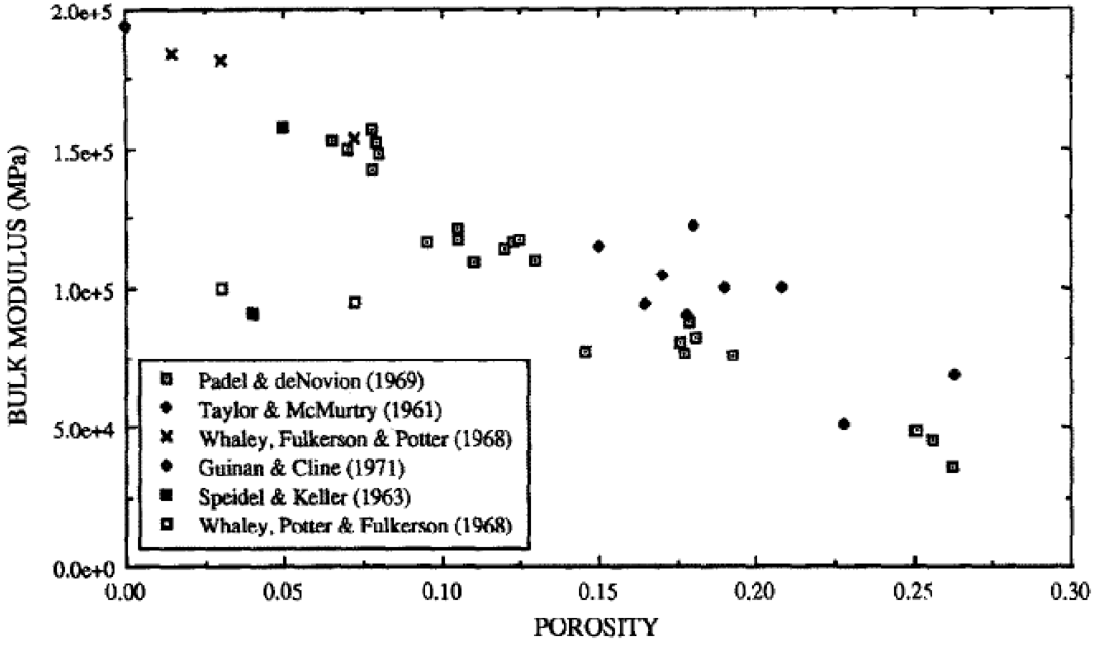


Fig. 4. Experimental data for bulk modulus of UN at room temperature.

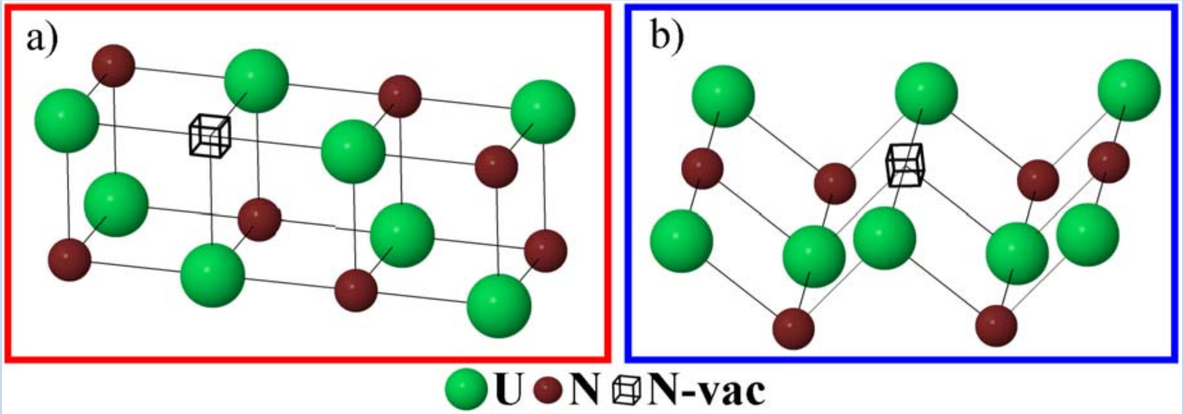
[S.L. Hayes, J.K. Thomas, and K.L. Peddicord, Material property correlations for uranium mononitride: II. Mechanical properties Journal of Nuclear Materials Volume 171, Issues 2–3, May 1990, Pages 271–288].

The bulk modulus measurements was performed in room temperatures.

Quantum chemistry observe system at T = 0 K.

Finally, number of measurement still is limited.

Modeling of single N vacancies: (001) surface vs (110) surface



(001) surface has the lowest surface energy according to Tasker analysis *[P.W. Tasker, The stability of ionic crystal surfaces. - J. Phys. C: Solid State Phys., 1979, **12**, p. 4977-4984]*.

$$E_{form}^{\mathrm{N(U)}vac} = \frac{1}{2}\left(E^{\mathrm{UN(N\_vac)}} + 2E^{\mathrm{N(U)}} - E^{\mathrm{UN}}\right)$$

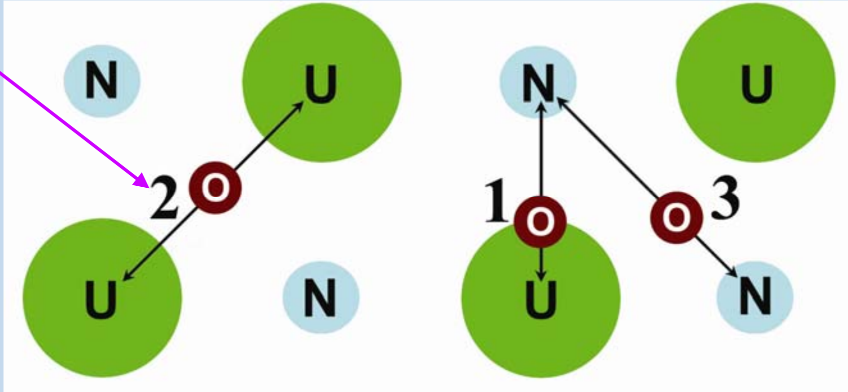
Number of layers and supercell size	N vacancy E_{form} on (001) surface	$\mu_{av}(\mu_B)$ (001)	N vacancy E_{form} on (110) surface	$\mu_{av}(\mu_B)$ (110)
5, 2×2	3.700	1.702	3.075	1.818
7, 2×2	3.706	1.548	3.028	1.585
9, 2×2	3.708	1.452	3.036	1.512
11, 2×2	3.712	1.392	3.026	1.453
7, 3×3	3.646	1.487	2.966	1.498

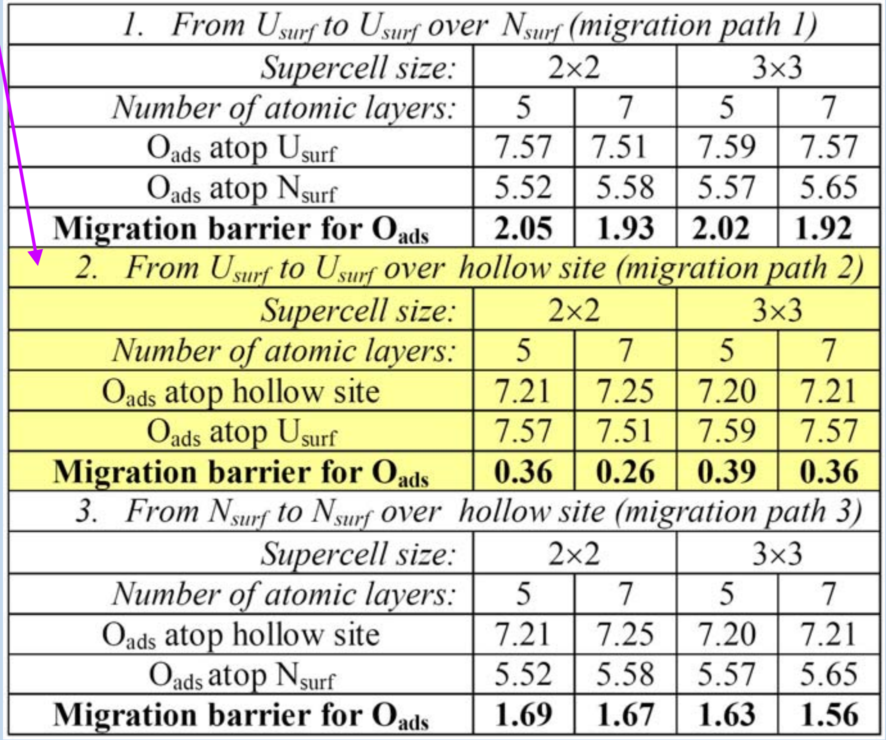
All (001) surface basic tendencies remain similar for vacancies on (110) surface. Vacancy formation energies are by ~0.7 eV smaller for UN(110) surface. This distinction is easy explainable due to a larger friability of the (110) surface as compared to the (001) surface.

Simulation of migration path for O adatom along the UN(001) surface

The most favorable migration trajectory has been optimized to be the line joining the sites atop the nearest surface U atoms and the hollow sites between them (trajectory 2). The corresponding energy barriers found to be 0.36 eV (5-layer slab) and 0.26 eV (7-layer slab) indicates on a high mobility of O_{ads} atoms upon UN. The energy barriers along other two migration trajectories are substantially larger (1.93-2.05 eV and 1.31-1.69 eV) for trajectories 1 and 3.

NB: To obtain more precise results for oxygen diffusion along the UN(001) surface, the Nudged Elastic Band method must be applied which allows one to obtain more realistic trajectories of atom migration. In our study this not performed due restricted computer resources.





1. From U_{surf} to U_{surf} over N_{surf} (migration path 1)				
Supercell size:	2×2		3×3	
Number of atomic layers:	5	7	5	7
O_{ads} atop U_{surf}	7.57	7.51	7.59	7.57
O_{ads} atop N_{surf}	5.52	5.58	5.57	5.65
Migration barrier for O_{ads}	**2.05**	**1.93**	**2.02**	**1.92**
2. From U_{surf} to U_{surf} over hollow site (migration path 2)				
Supercell size:	2×2		3×3	
Number of atomic layers:	5	7	5	7
O_{ads} atop hollow site	7.21	7.25	7.20	7.21
O_{ads} atop U_{surf}	7.57	7.51	7.59	7.57
Migration barrier for O_{ads}	**0.36**	**0.26**	**0.39**	**0.36**
3. From N_{surf} to N_{surf} over hollow site (migration path 3)				
Supercell size:	2×2		3×3	
Number of atomic layers:	5	7	5	7
O_{ads} atop hollow site	7.21	7.25	7.20	7.21
O_{ads} atop N_{surf}	5.52	5.58	5.57	5.65
Migration barrier for O_{ads}	**1.69**	**1.67**	**1.63**	**1.56**

Summary

- Evaluations of formation energies for U vacancies performed so far demand additional verifications of these results using other theoretical methods as well as further development of uranium atom pseudopotentials.
- To obtain more precise results for oxygen diffusion along the UN(001) surface, the Nudged Elastic Band method must be applied.
- The new experimental measurements on UN surface (for example, EXAFS measurements, which allow one to observe atomic environment around separate atoms or UPS spectra for identification of oxynitride-like structures) will be also significant for versatile picture construction of UN oxidation process.

Conclusion

- We have performed the first detailed study of UN surfaces and their interaction with oxygen using the slab model.

- The prospects and typical problems of actinide surface modeling are observed in this presentation systematizing results obtained by us and other researchers.

Publications related to this work

[1] R.A. Evarestov, A.V. Bandura, M.V. Losev, E.A. Kotomin, Yu.F. Zhukovskii, and D. Bocharov, A first principles DFT study in UN bulk and (001) surface: comparative LCAO and PW calculations. - J. Comput. Chem., 2008, **29**, p. 2079-2087.

[2] Yu.F. Zhukovskii, D. Bocharov, E.A. Kotomin, R.A. Evarestov, and A.V. Bandura, First principles calculations of oxygen adsorption on the UN(001) surface. - Surf. Sci., 2009, **603**, p. 50-53.

[3] Yu.F. Zhukovskii, D. Bocharov, and E.A. Kotomin, Chemisorption of a molecular oxygen on the UN (001) surface: *ab initio* calculations. - J. Nucl. Mater., 2009, **393**, p. 504-507.

[4] D. Bocharov, D. Gryaznov, Yu.F. Zhukovskii, and E.A. Kotomin, DFT calculations of point defects on UN(001) surface. - Surf. Sci., 2011, **605**, p. 396-400.

[5] D. Bocharov, D. Gryaznov, Yu.F. Zhukovskii, E.A. Kotomin, J. Nucl. Mater. (2011), - Surf. Sci., 2011, **416,** p. 200-204.

[6] D. Bocharov, Yu.F. Zhukovskii, D. Gryaznov, and E.A. Kotomin, Oxygen diffusion processes on UN (001) surface - Surf. Sci., 2012, *to be submitted*.

[7] Yu.F. Zhukovskii, D. Bocharov, D. Gryaznov, and E.A. Kotomin, First principles simulations on oxidation of nitride nuclear fuels. – Chapter in book “Nuclear Fuel”, 2012, InTech Publishing, *in press.*

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