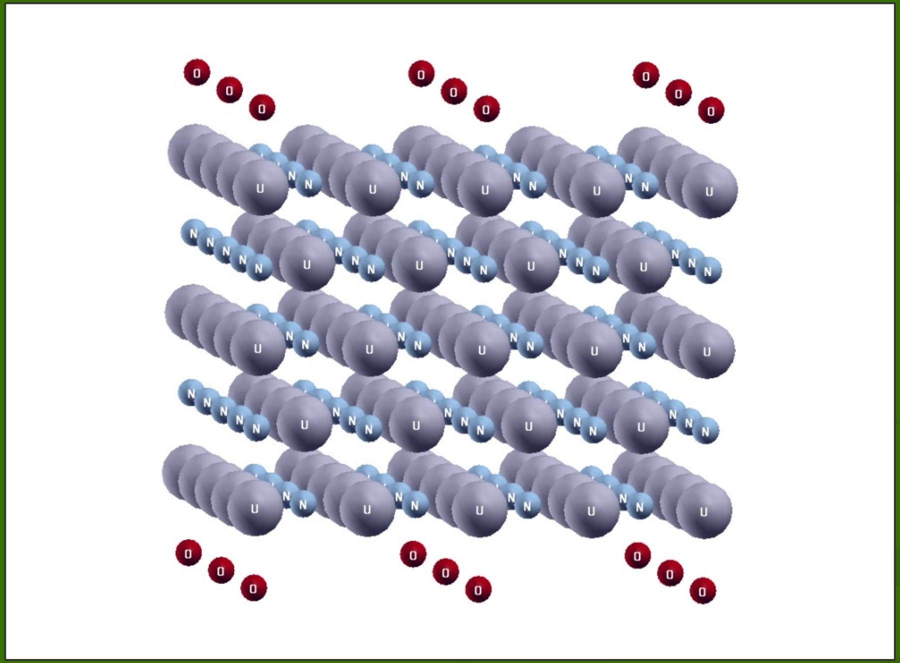
Institute of Solid State Physics, University of Latvia, Riga

Yu.F. Zhukovskii, D. Bocharov,
D. Gryaznov and E.A. Kotomin

FIRST-PRINCIPLES SIMULATIONS ON INITIAL STAGE OF URANIUM MONONITRIDE SURFACE OXIDATION



FMNT, 6 April 2011, ISSP, Riga, Latvia

Motivation 1

Among the actinide compounds, nitrides have received a special interest because of their role of promising advanced fuels and targets for Generation IV fast reactors.

Some advantages:

- high melting point (~2850 C)

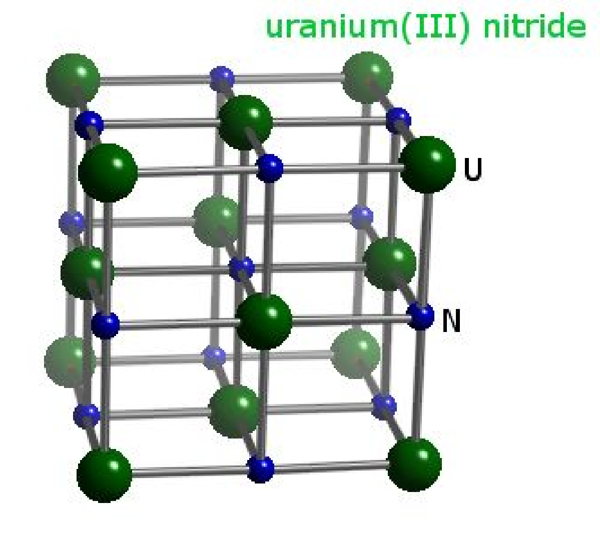
- thermal conductivity

- higher metal density over the oxides

- high solubility in nitric acid (in the case of fuel reprocessing)

Motivation 2

Theoretical simulations on UN bulk and UN(001) substrate, both perfect and defective, have been performed in a close collaboration between the ISSP (University of Latvia), Department of Quantum Chemistry (St. Petersburg State University) and EC Institute for Transuranium Elements (Karlsruhe).



Handling of uranium mononitride fuel require a deeper knowledge of *reactions at the surfaces*. In present study, it is proposed to model at *ab initio* level:

(*i*) perfect and defective UN(001) and UN(110) surfaces with rock-salt structure (the energetically most stable amongst various densely-packed faces of UN single-crystal);

(*ii*) adsorbed species (atomic and molecular oxygen) located on the UN(001) substrate.

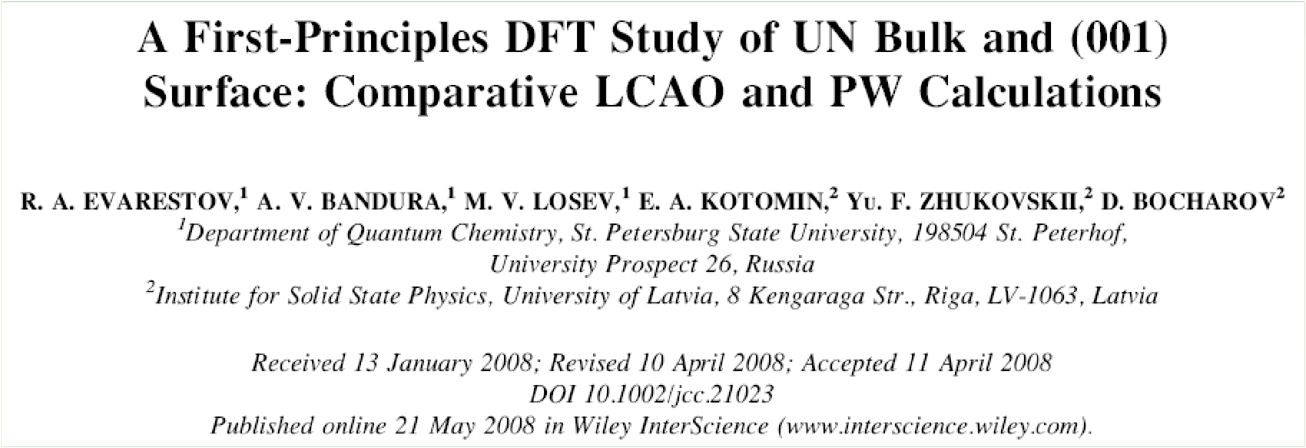
Motivation 3

So far, the atomistic simulations of actinide substrates were performed using the formalism of shell model (long-range Coulomb and short-range Buckingham potentials) focused mainly on the densely-packed surfaces of UO_2 and PuO_2.

The main objective of present study is to acquire reliable information on the atomic and electronic structure of the UN(001) and UN(110) substrates as well as on the early stages of *surface oxidation* beginning with the oxygen adsorption (atomic and molecular). For this aim, a series of large-scale *VASP* calculations have been performed, necessary for understanding of initial stages of nitride fuel oxidation, which are unavoidable during the nuclear fuel fabrication. Moreover, the UN samples contain considerable amounts of oxygen impurities, which affect fuel properties.

What has been done by us so far?

1. J. Comput. Chem.,
29 (2008)
p. 2079-2087.



A First-Principles DFT Study of UN Bulk and (001) Surface: Comparative LCAO and PW Calculations

R. A. EVARESTOV,[1] A. V. BANDURA,[1] M. V. LOSEV,[1] E. A. KOTOMIN,[2] YU. F. ZHUKOVSKII,[2] D. BOCHAROV[2]
[1]*Department of Quantum Chemistry, St. Petersburg State University, 198504 St. Peterhof, University Prospect 26, Russia*
[2]*Institute for Solid State Physics, University of Latvia, 8 Kengaraga Str., Riga, LV-1063, Latvia*

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2. Surf. Sci.,
603 (2009)
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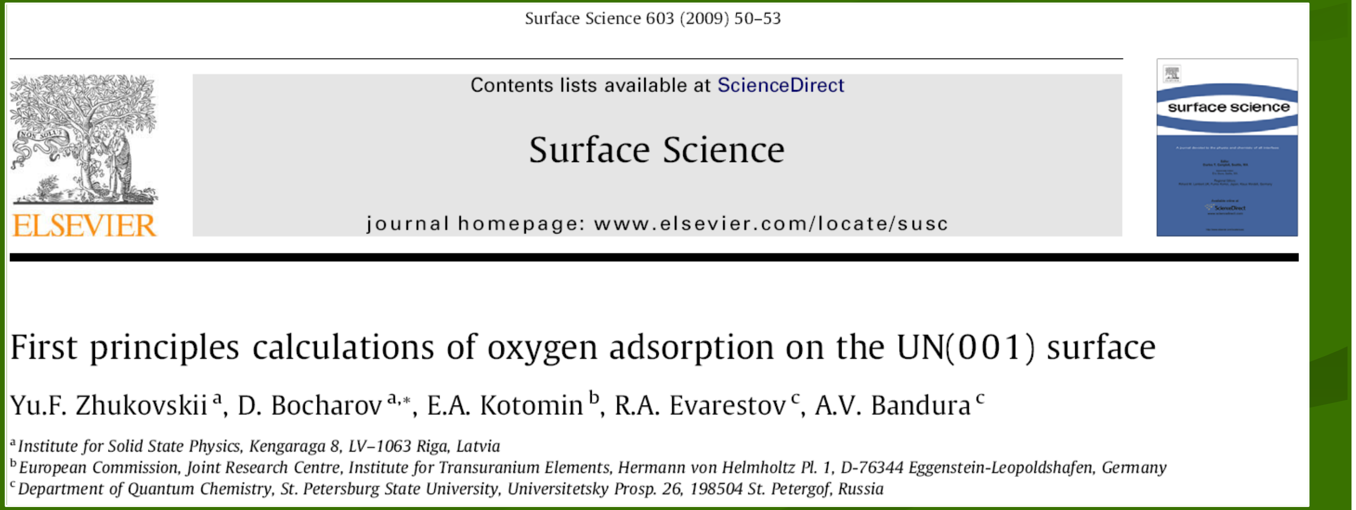


Surface Science 603 (2009) 50–53

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

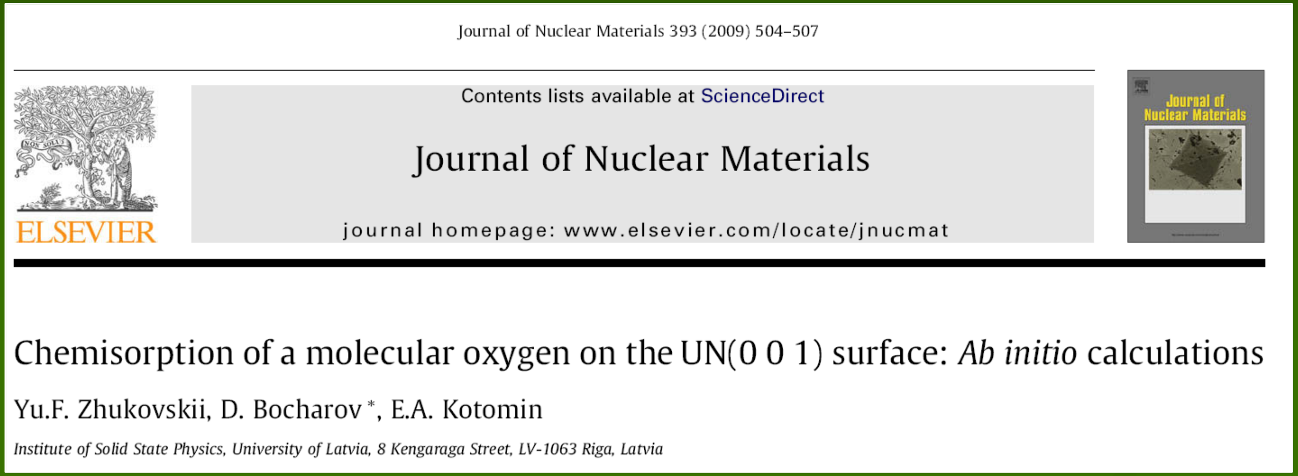
First principles calculations of oxygen adsorption on the UN(001) surface

Yu.F. Zhukovskii[a], D. Bocharov[a,*], E.A. Kotomin[b], R.A. Evarestov[c], A.V. Bandura[c]

[a]*Institute for Solid State Physics, Kengaraga 8, LV–1063 Riga, Latvia*
[b]*European Commission, Joint Research Centre, Institute for Transuranium Elements, Hermann von Helmholtz Pl. 1, D-76344 Eggenstein-Leopoldshafen, Germany*
[c]*Department of Quantum Chemistry, St. Petersburg State University, Universitetsky Prosp. 26, 198504 St. Petergof, Russia*

What has been done by us so far?

3. J. Nucl. Mater., 393 (2009) p. 504-507.



Journal of Nuclear Materials 393 (2009) 504–507

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Journal of Nuclear Materials

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ELSEVIER

Chemisorption of a molecular oxygen on the UN(0 0 1) surface: *Ab initio* calculations

Yu.F. Zhukovskii, D. Bocharov *, E.A. Kotomin

Institute of Solid State Physics, University of Latvia, 8 Kengaraga Street, LV-1063 Riga, Latvia

4. Surf. Sci., 605 (2011) p. 396-400.

Surface Science 605 (2011) 396–400

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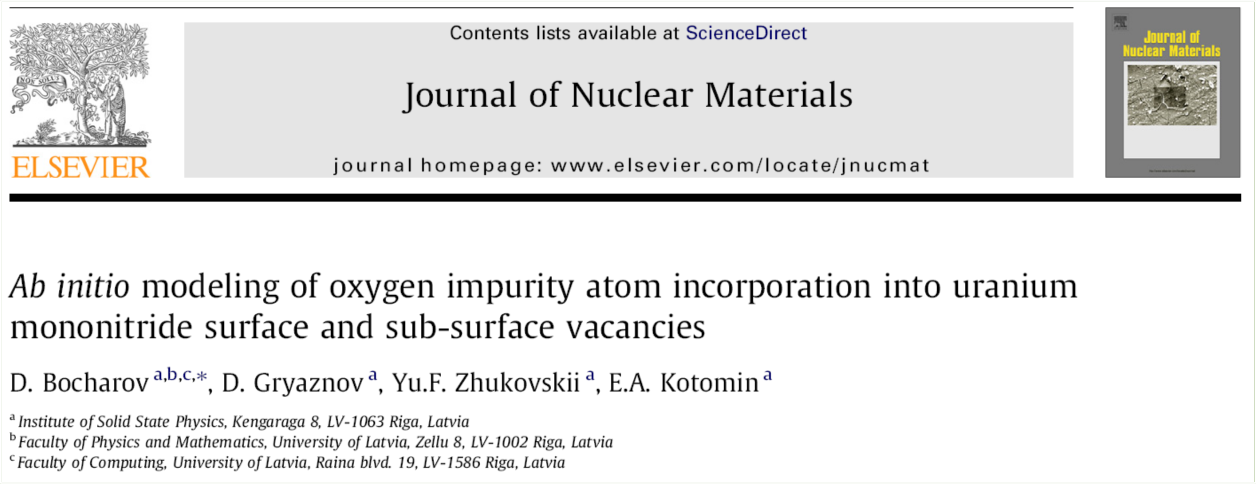
DFT calculations of point defects on UN(001) surface

D. Bocharov [a,b,c,*], D. Gryaznov [a], Yu.F. Zhukovskii [a], E.A. Kotomin [a]

[a] *Institute for Solid State Physics, Kengaraga 8, LV-1063 Riga, Latvia*
[b] *Faculty of Physics and Mathematics, University of Latvia, Zellu 8, LV-1002 Riga, Latvia*
[c] *Faculty of Computing, University of Latvia, Raina blvd 19, LV-1586 Riga, Latvia*

What has been done by us so far and to be done?

5. J. Nucl. Mater., to be published in 2011 (corrected proof)



Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

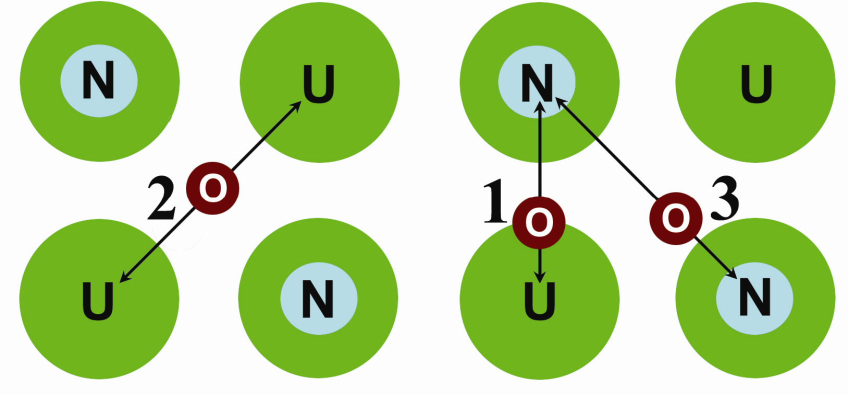
ELSEVIER

Ab initio modeling of oxygen impurity atom incorporation into uranium mononitride surface and sub-surface vacancies

D. Bocharov[a,b,c,*], D. Gryaznov[a], Yu.F. Zhukovskii[a], E.A. Kotomin[a]

[a] *Institute of Solid State Physics, Kengaraga 8, LV-1063 Riga, Latvia*
[b] *Faculty of Physics and Mathematics, University of Latvia, Zellu 8, LV-1002 Riga, Latvia*
[c] *Faculty of Computing, University of Latvia, Raina blvd. 19, LV-1586 Riga, Latvia*

6. Surface diffusion of oxygen adatom and its incorporation within surface nitrogen vacancies (to be submitted to Surf. Sci.)



What has been done by us so far and to be done?

7. Comparison of properties simulated for UN(110) and UN(001) surfaces, possessing smaller and higher atomic densities *per* layer

(FMNT poster PO-76)

8. Influence of the spin-orbit effects on preference of magnetic states (ferro- and antiferromagnetic) as well as vacancy formation energies for perfect and defective UN(001) and UN(110) surfaces

(FMNT poster PO-77)

Ph.D. student D. Bocharov

has to defend PhD Thesis in 2011:

“First principles simulations on

surface properties of uranium mononitride”

Computational method

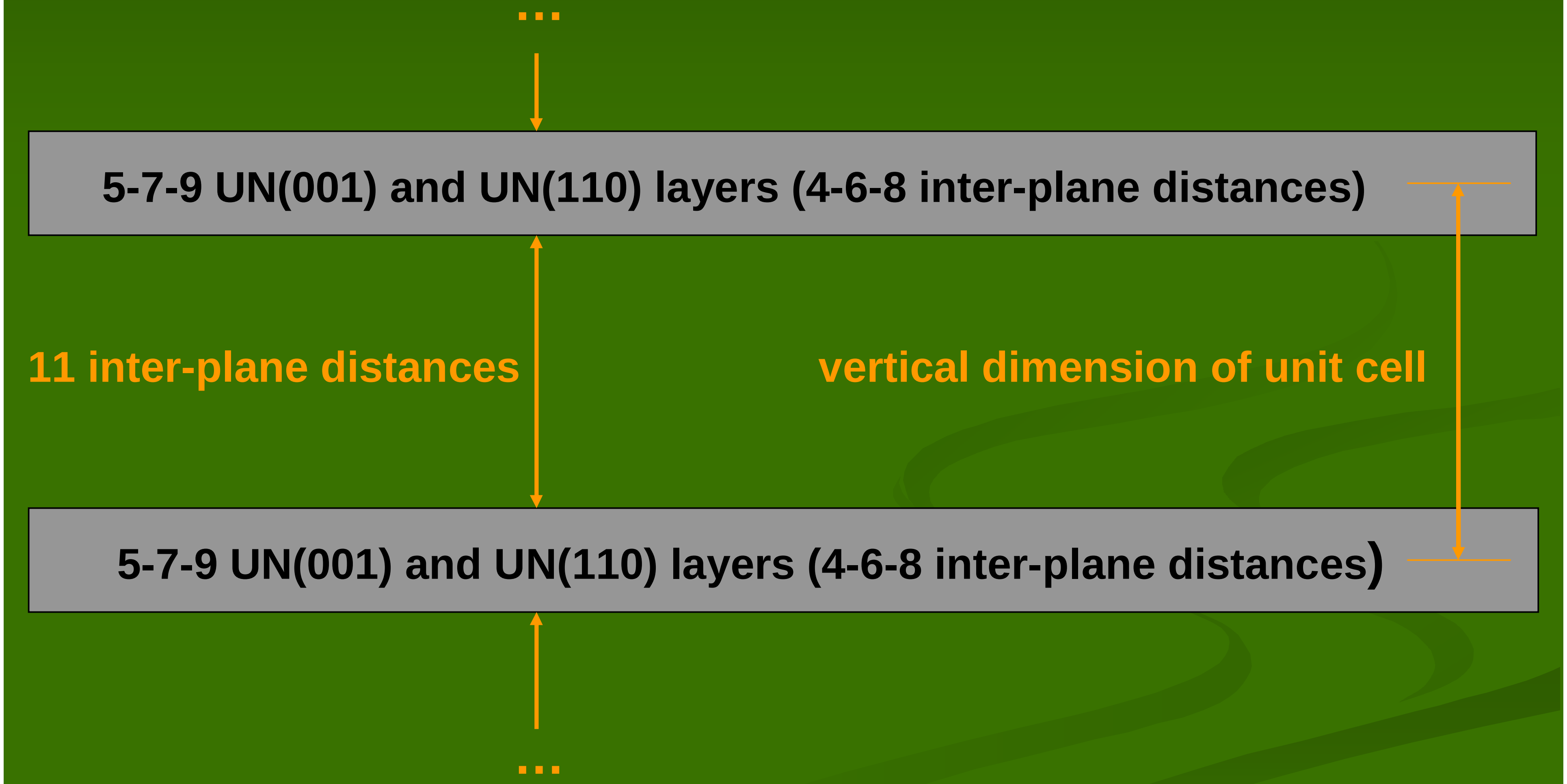
To simulate both perfect and defective UN(001) or UN(110) substrate as well as O/UN(001) or O/UN(110) interface we have mainly employed the DFT computer code *VASP* through the plane-wave basis sets (BSs). We have used the Perdew-Wang-91 GGA non-local exchange-correlation functional (PW91) and the scalar relativistic projector-augmented-wave (PAW) pseudopotentials representing the core electrons of U (with $6s^26p^66d^25f^27s^2$ external shell), N ($2s^22p^3$) and O ($2s^22p^4$) atoms (containing 14, 5 and 6 external electrons, respectively).

The plane wave cut-off energy is chosen to be 500 eV. We have used the Monkhorst-Pack scheme for 4×4×1 and 8×8×1 *k*-point meshes in the Brillouin zone.

There were considered both ferromagnetic (FM) and antiferromagnetic (AFM) states of systems under study. Although the latter were found to be more favorable, they are much more consuming computationally as compared to FM. This is why, detailed calculations on UN(001) and UN(110) were performed mainly for FM since energy parameters were found to be rather similar in both cases.

Periodic 3D model of UN(001) and UN(110) slabs

To set the 3D slab periodicity, we use “vacuum gap” model:



…

5-7-9 UN(001) and UN(110) layers (4-6-8 inter-plane distances)

11 inter-plane distances

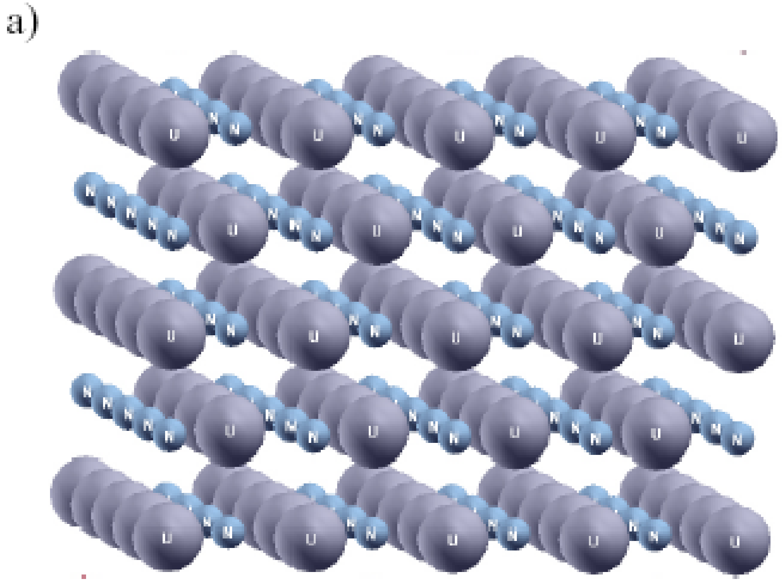
vertical dimension of unit cell

5-7-9 UN(001) and UN(110) layers (4-6-8 inter-plane distances)

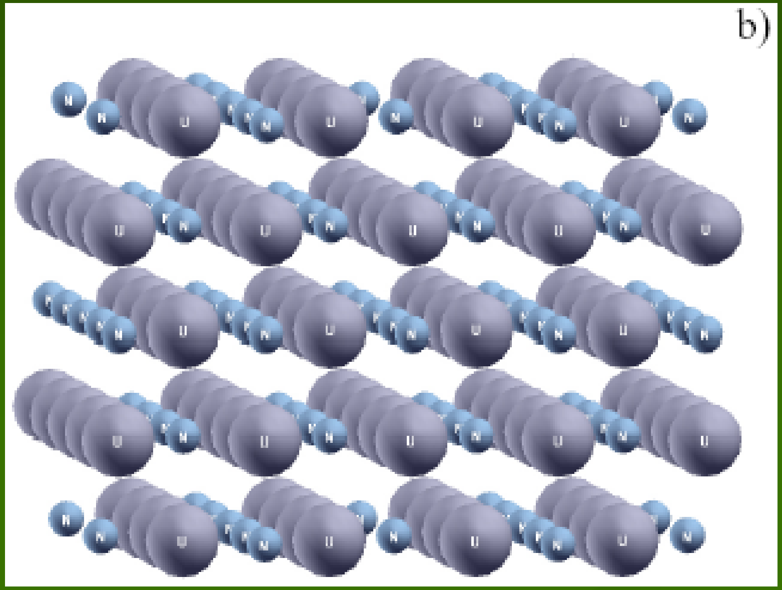
…

There are considered 2×2 and 3×3 surface supercells

Periodic models of perfect and defective UN(001) slab



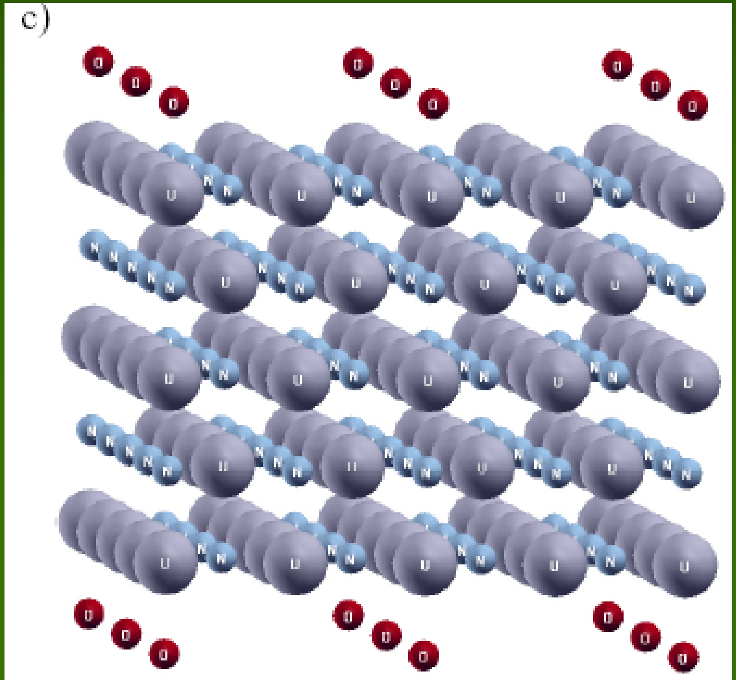
regular 5-layer slab



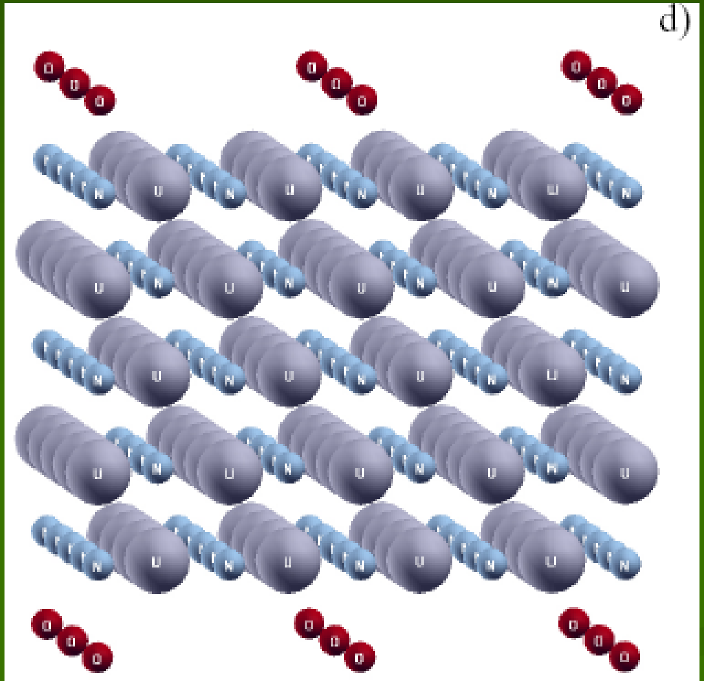
5-layer slab with 2x2
periodicity of surface N vacances

To reduce computational efforts, we have considered symmetric two-sided arrangement of point defects with 2×2 and 3×3 periodicity. For perfect UN slab (Fig. a), we have allowed only atomic relaxation across the slab. For surface models with defects (only N vacancies are shown in Fig. b), we have performed complete structural optimization.

Periodic models of oxygen adatoms on UN(001) slab



5-layer slab with 2x2 periodicity of O adatoms atop U

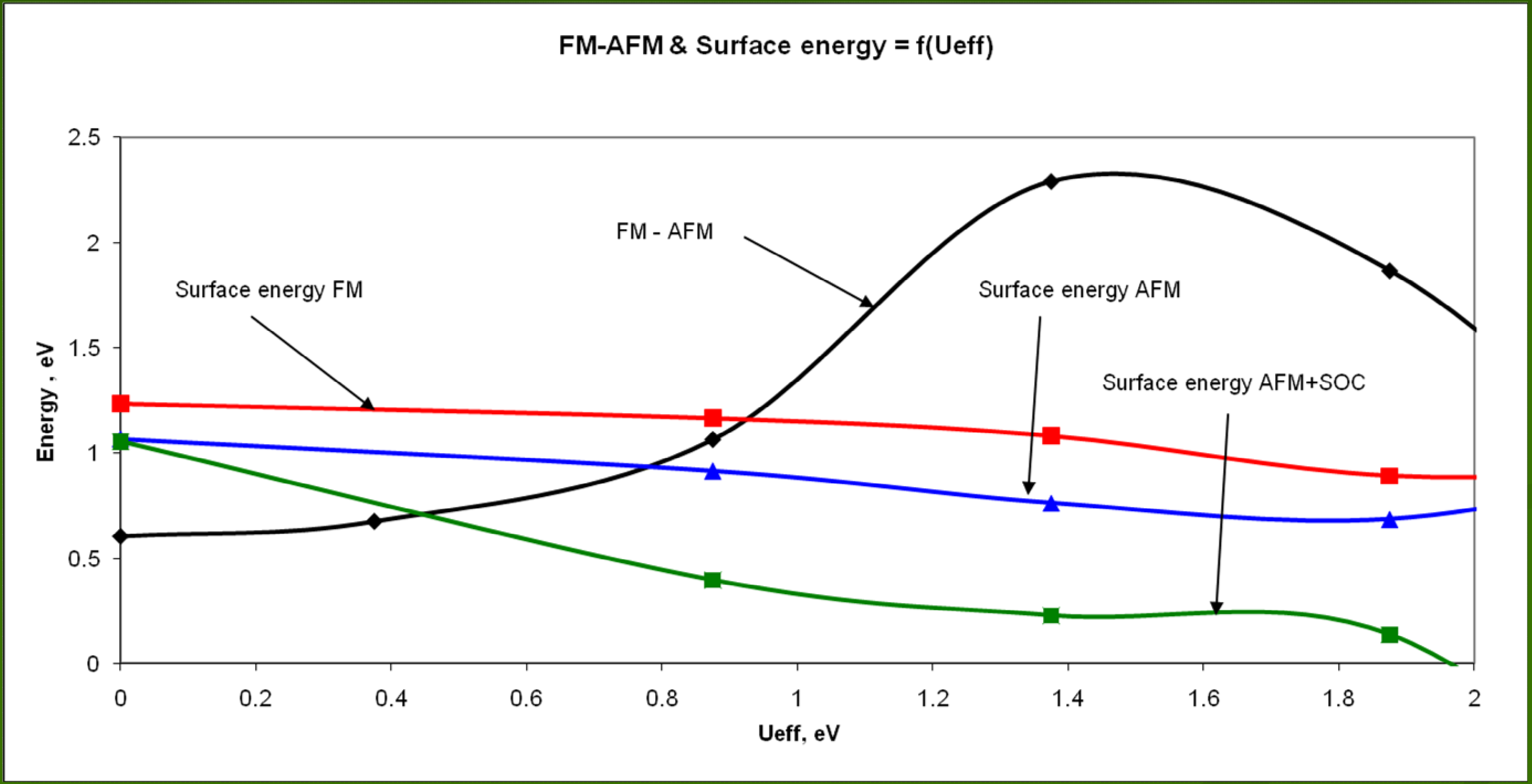


5-layer slab with 2x2 periodicity of O adatoms atop N

For models of oxygen adatoms atop the surface U and N atoms (Figs. c and d, respectively) we have performed complete structural optimization including O.

Ferromagnetic (FM) *vs.* antiferromagnetic (AFM) states for UN(001)

DFT+U_{eff} calculations



The best known examples of spin-orbit coupling (SOC) are shifts in an electron's atomic energy levels, due to electromagnetic interaction between the electron's spin and the nucleus's magnetic field.

Results for regular UN(001) surface

For the defect-less UN(001) substrate, we observe rather small vertical displacement of surface atoms, perpendicular to the slab, from their unrelaxed atomic sites in UN bulk: 0.34 a_0 *per cent* inward U displacement and 0.38 a_0 *per cent* outward N displacement, whereas subsurface atoms relax in the same directions but their displacements are as 1.4-1.5 times as smaller. The topological (Bader) atomic charges in UN bulk (±1.6 *e* for U and N respectively) considerably deviate from the formal charges, due to U and N atomic function hybridization. In our calculations, surface and subsurface U atoms possess reduced charges (1.65 and 1.62 *e*, respectively), the same we observe for surface and subsurface N atoms (-1.61 and –1.60 *e*, respectively). Asymmetric electron charge redistribution on both U and N atoms is caused by deviation of atomic layers from 2D planes. An additional redistribution indicates an increase in the surface U-N bond covalency. This is in a line with recent theoretical and experimental studies suggesting the mixed metallic-covalent chemical bonding in UN.

Verification of results for UN bulk and UN(001) surface

Comparison of DFT LCAO and Plane Wave approaches for periodic models

1. Proper choice of relativistic effective core pseudopotentials (RECP) is important for reliable DFT calculations. The small-core and large-core pseudopotentials of U atom (60 and 78 core electrons, respectively) with $5s^2 5p^6 5d^{10} 6s^2 6p^6 6d^1 5f^3 7s^2$ and $6s^2 6p^6 5f^3 6d^1 7s^2$ electrons referred to the valence shell were generated for LCAO and PW calculations, respectively.
2. Reliable LCAO calculations of the surface properties needs introduction of an extra layer of the ghost functions simulating correct electronic density decay into vacuum from the surface.
3. Results obtained by means of two substantially different DFT methods, LCAO and PW, using PW91 Hamiltonian, demonstrate good agreement. There was observed onsiderable relaxation of surface atoms which affects the surface energy. These results have been used in study of surface defects and processes, first of all, UN surface oxidation.
4. As a result, the first detailed study on properties of the densely packed UN(001) surface has been performed

Comparison of properties for UN bulk calculated within LCAO and PW DFT formalisms

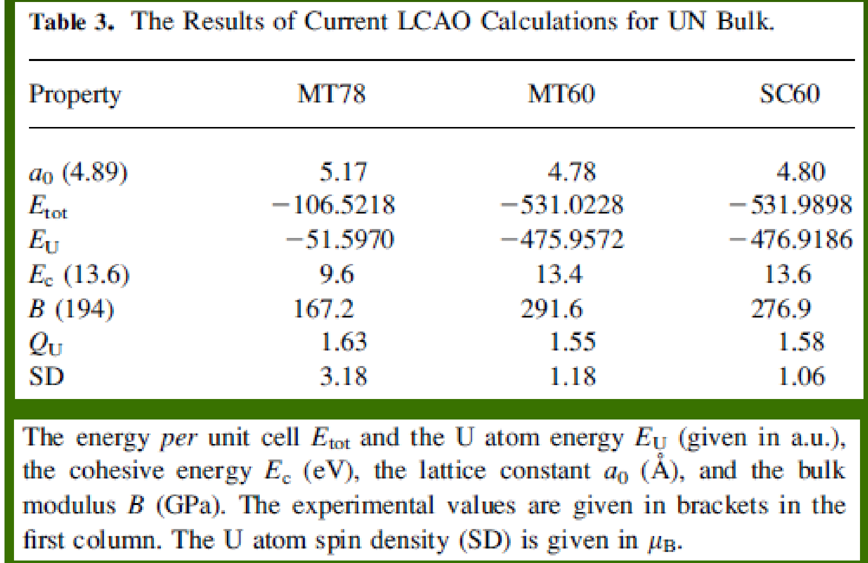


Table 3. The Results of Current LCAO Calculations for UN Bulk.

Property	MT78	MT60	SC60
a_0 (4.89)	5.17	4.78	4.80
E_{tot}	−106.5218	−531.0228	−531.9898
E_U	−51.5970	−475.9572	−476.9186
E_c (13.6)	9.6	13.4	13.6
B (194)	167.2	291.6	276.9
Q_U	1.63	1.55	1.58
SD	3.18	1.18	1.06

The energy *per* unit cell E_{tot} and the U atom energy E_U (given in a.u.), the cohesive energy E_c (eV), the lattice constant a_0 (Å), and the bulk modulus B (GPa). The experimental values are given in brackets in the first column. The U atom spin density (SD) is given in μ_B.

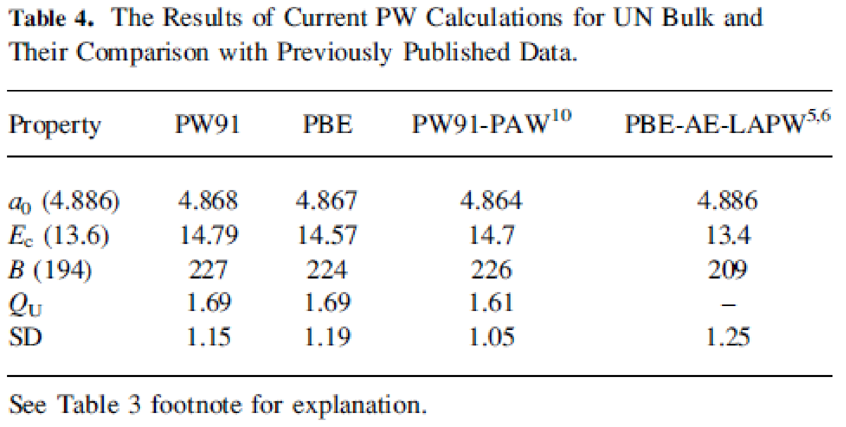


Table 4. The Results of Current PW Calculations for UN Bulk and Their Comparison with Previously Published Data.

Property	PW91	PBE	PW91-PAW[10]	PBE-AE-LAPW[5,6]
a_0 (4.886)	4.868	4.867	4.864	4.886
E_c (13.6)	14.79	14.57	14.7	13.4
B (194)	227	224	226	209
Q_U	1.69	1.69	1.61	–
SD	1.15	1.19	1.05	1.25

See Table 3 footnote for explanation.

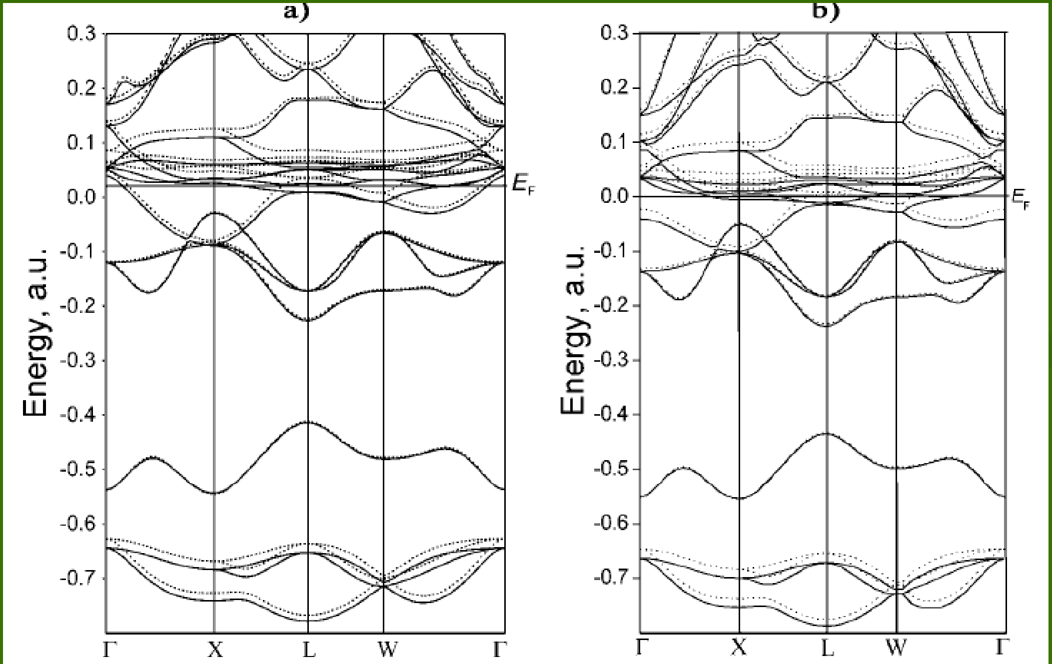


Figure 1. The energy bands of UN crystal constructed for: (a) LCAO PW91 (RECP 60) and (b) PW PW91 (RECP 78) Hamiltonians. The energies are given in a.u., solid and dotted lines correspond to the states with spin up and spin down, respectively.

Comparison of surface properties for UN (001) calculated within LCAO and PW DFT formalisms

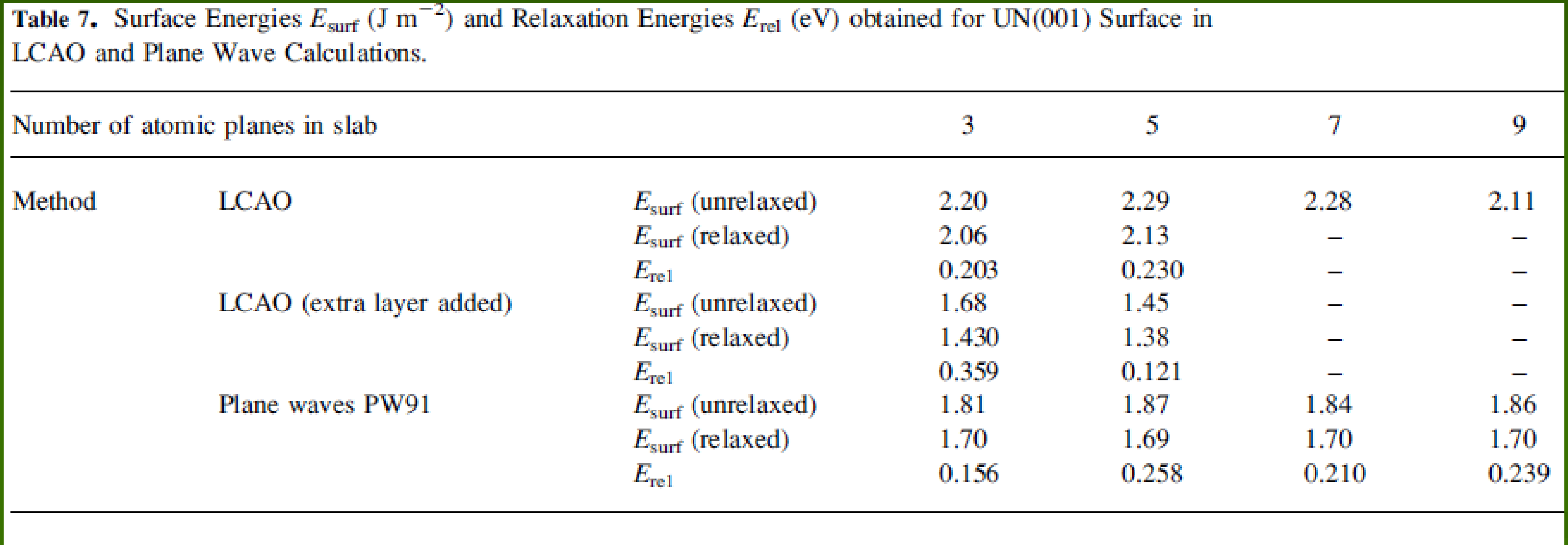
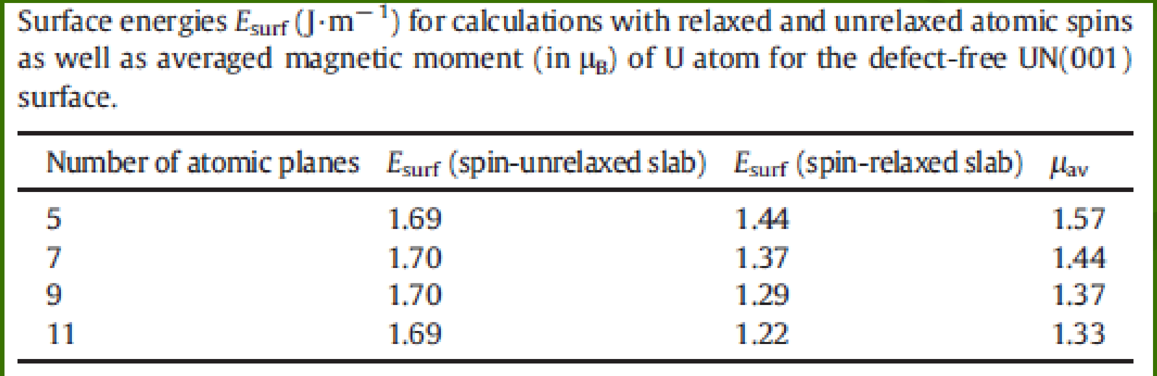


Table 7. Surface Energies E_{surf} (J m^{-2}) and Relaxation Energies E_{rel} (eV) obtained for UN(001) Surface in LCAO and Plane Wave Calculations.

Number of atomic planes in slab			3	5	7	9
Method	LCAO	E_{surf} (unrelaxed)	2.20	2.29	2.28	2.11
		E_{surf} (relaxed)	2.06	2.13	–	–
		E_{rel}	0.203	0.230	–	–
	LCAO (extra layer added)	E_{surf} (unrelaxed)	1.68	1.45	–	–
		E_{surf} (relaxed)	1.430	1.38	–	–
		E_{rel}	0.359	0.121	–	–
	Plane waves PW91	E_{surf} (unrelaxed)	1.81	1.87	1.84	1.86
		E_{surf} (relaxed)	1.70	1.69	1.70	1.70
		E_{rel}	0.156	0.258	0.210	0.239

$$E_{surf}(n) = \frac{1}{2S}(E_n - nE_b)$$



Surface energies E_{surf} ($\mathrm{J\cdot m^{-1}}$) for calculations with relaxed and unrelaxed atomic spins as well as averaged magnetic moment (in μ_B) of U atom for the defect-free UN(001) surface.

Number of atomic planes	E_{surf} (spin-unrelaxed slab)	E_{surf} (spin-relaxed slab)	μ_{av}
5	1.69	1.44	1.57
7	1.70	1.37	1.44
9	1.70	1.29	1.37
11	1.69	1.22	1.33

VASP results for oxygen adatoms on UN(001) surface

Binding energy of O:

1) **6.9 eV for O adatom atop U** 2) **5.0 eV for O adatom atop N**

Values of both energies point out on metallic behavior of UN substrate.
However, nature of both bonds is different:

1) O atop U:

Δq_O = - 0.92 *e* (O ion in triplet state)
Δq_U = 1.92 *e* (*vs.* 1.65 *e* on surface)

$d_{O\text{-}U}$ = 1.92 Å and U atom is displaced *outward* the substrate by 0.17 Å

2) O atop N:

Δq_O = - 1.2 e (O ion **in** triplet state)
Δq_N = -1.44 *e* (*vs.* -1.61 on surface)

$d_{O\text{-}N}$ = 2.19 Å and N atom is displaced *inward* the substrate by 0.61 Å

Thus, although the O-U bond is stronger than O-N one, the former adsorption configuration can be considered as localized one-center complex whereas atop the surface N atom oxygen adatom is attracted towards the substrate and this configuration can be defined as pseudo multi-center complex (N is the nearest neighbor whereas four U atoms are the next-nearest neighbors).

Verification of results for adsorption of O atoms upon UN(001) surface

Comparison of DFT LCAO and Plane Wave approaches for periodic models

1. For *VASP* calculations, $6s^2 6p^6 5f^3 6d^1 7s^2$, $2s^2 2p^3$ and $2s^2 2p^4$ valence shells have been considered for U, N and O atoms, respectively, while for *CRYSTAL* calculations, $5s^2 5p^6 5d^{10} 6s^2 6p^6 6d^1 5f^3 7s^2$ valence shell with relativistic SC RECP pseudopotential has been used for U atom as well as the all-electron basis sets 6-311G(2d) and 8-411G(1d) have been used for N and O atoms, respectively.
2. The excellent agreement of the results obtained using two very different first principles methods used for calculations supports their reliability

$$E_{\text{bind}} = \frac{1}{2}\left(E_{\text{tot}}^{\text{UN}} + 2E_{\text{tot}}^{\text{O}_{\text{triplet}}} - E_{\text{tot}}^{\text{O/UN}}\right)$$

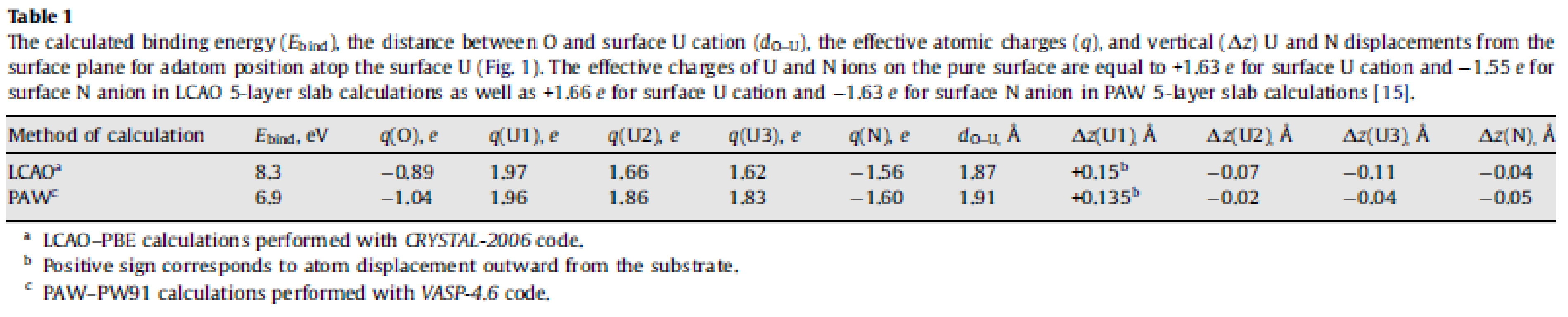


Table 1

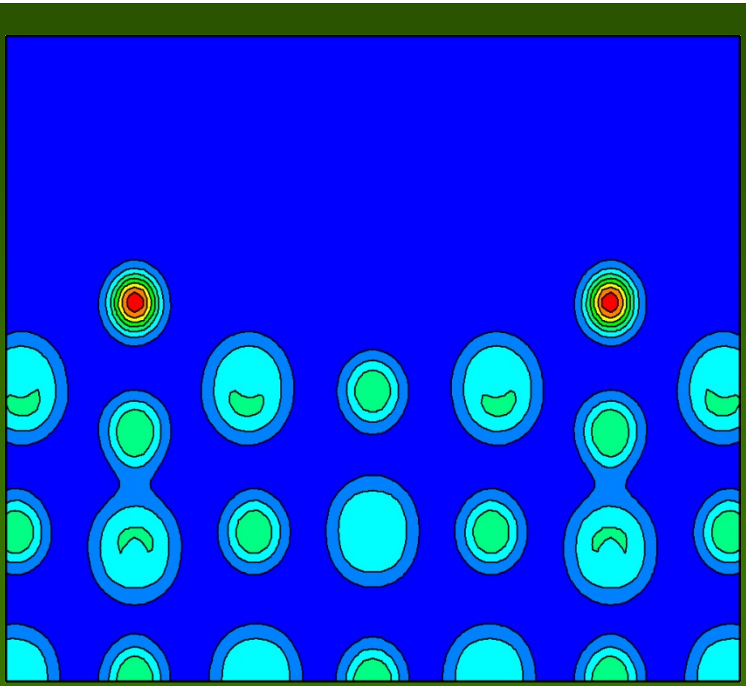
The calculated binding energy (E_{bind}), the distance between O and surface U cation ($d_{\text{O-U}}$), the effective atomic charges (q), and vertical (Δz) U and N displacements from the surface plane for adatom position atop the surface U (Fig. 1). The effective charges of U and N ions on the pure surface are equal to +1.63 *e* for surface U cation and −1.55 *e* for surface N anion in LCAO 5-layer slab calculations as well as +1.66 *e* for surface U cation and −1.63 *e* for surface N anion in PAW 5-layer slab calculations [15].

Method of calculation	E_{bind}, eV	q(O), *e*	q(U1), *e*	q(U2), *e*	q(U3), *e*	q(N), *e*	$d_{\text{O-U}}$, Å	Δz(U1), Å	Δz(U2), Å	Δz(U3), Å	Δz(N), Å
LCAO[a]	8.3	−0.89	1.97	1.66	1.62	−1.56	1.87	+0.15[b]	−0.07	−0.11	−0.04
PAW[c]	6.9	−1.04	1.96	1.86	1.83	−1.60	1.91	+0.135[b]	−0.02	−0.04	−0.05

[a] LCAO–PBE calculations performed with *CRYSTAL-2006* code.

[b] Positive sign corresponds to atom displacement outward from the substrate.

[c] PAW–PW91 calculations performed with *VASP-4.6* code.



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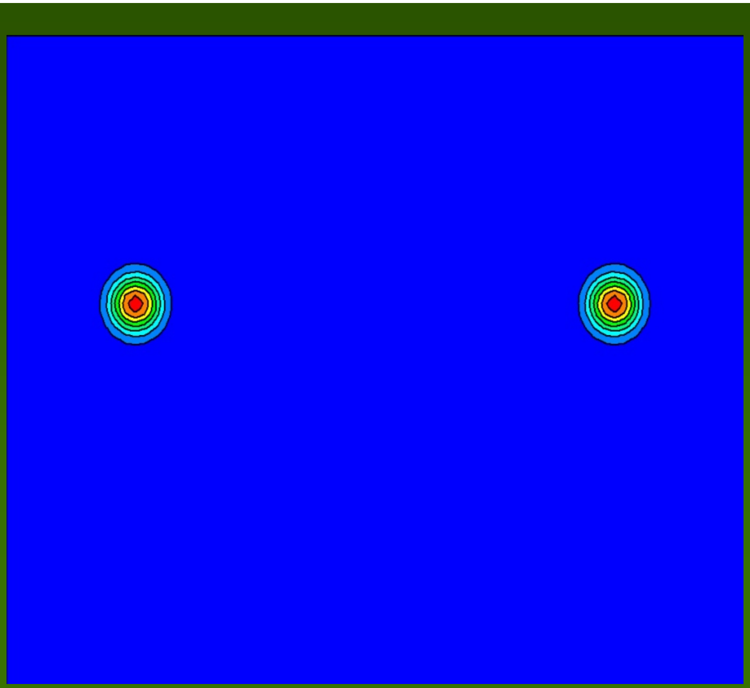

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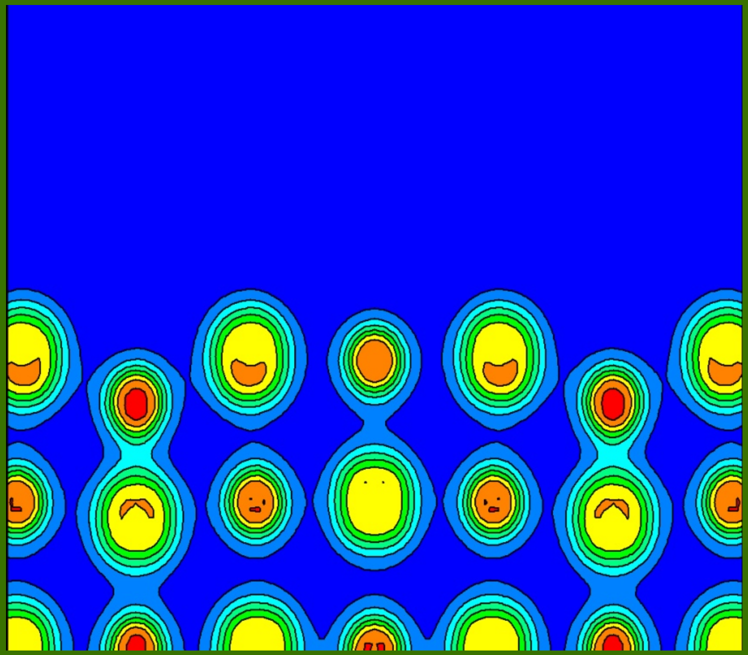


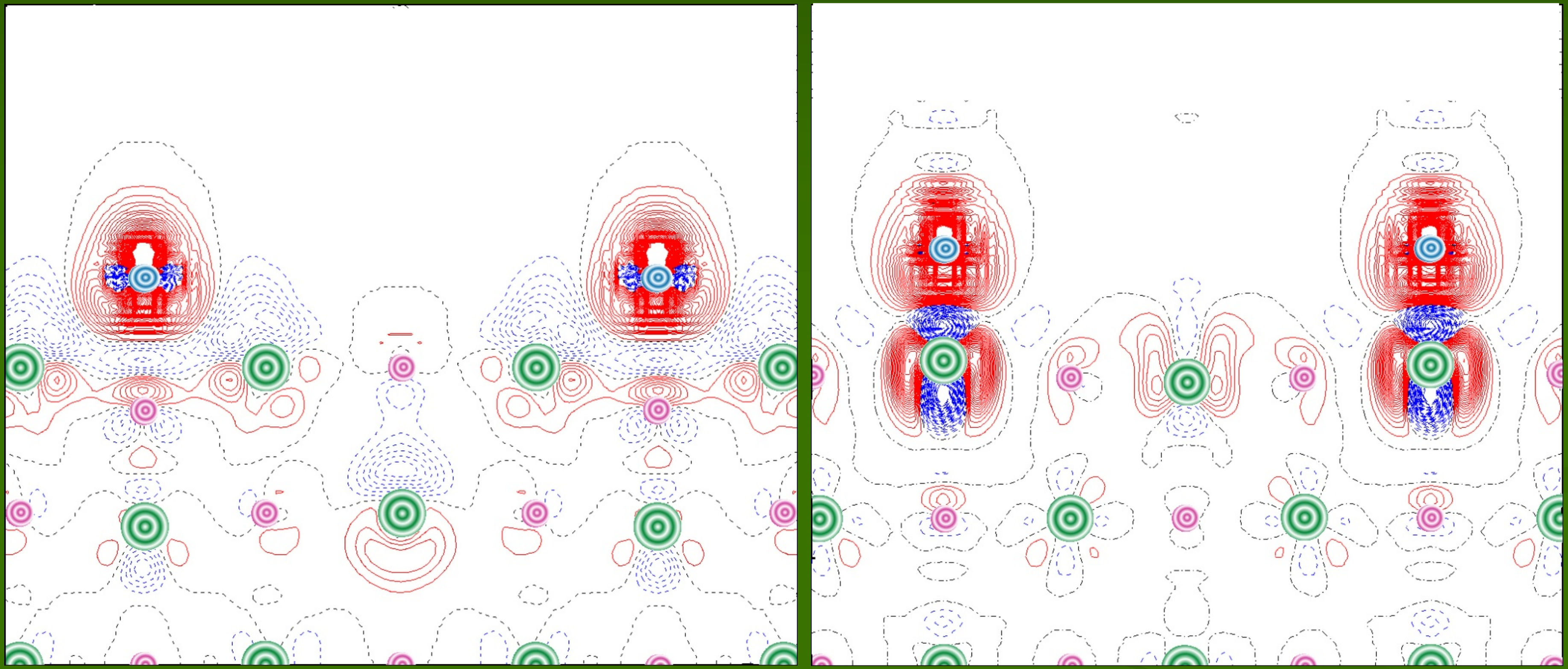
Difference charge distribution

optimized adsorption system
– relaxed atoms
– relaxed substrate

Binding energy

$$E_{bind} = -\frac{1}{2}\left(E_{tot}^{O/UN} - 2E_{tot}^{O_{triplet}} - E_{tot}^{UN}\right)$$

Difference electron density re-distribution for adsorption of O atoms upon UN(001) surface

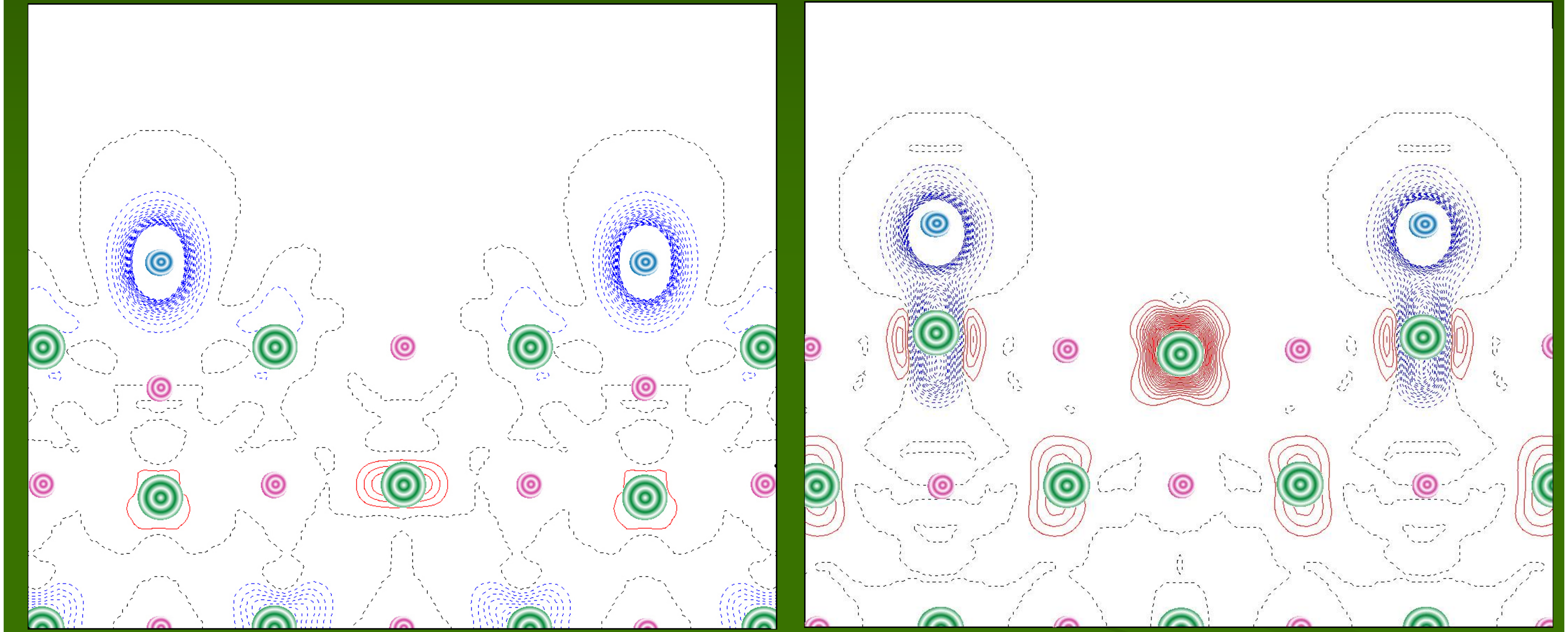


O adatoms atop surface N

O adatoms atop surface U

(110) cross-section ⊥ (001) surface, 2x2 supercell

Difference spin density re-distribution for adsorption of O atoms upon UN(001) surface



O adatoms atop surface N

O adatoms atop surface U

(110) cross-section ⊥ (001) surface, 2x2 supercell

Chemisorption of a molecular oxygen on the UN(001) surface

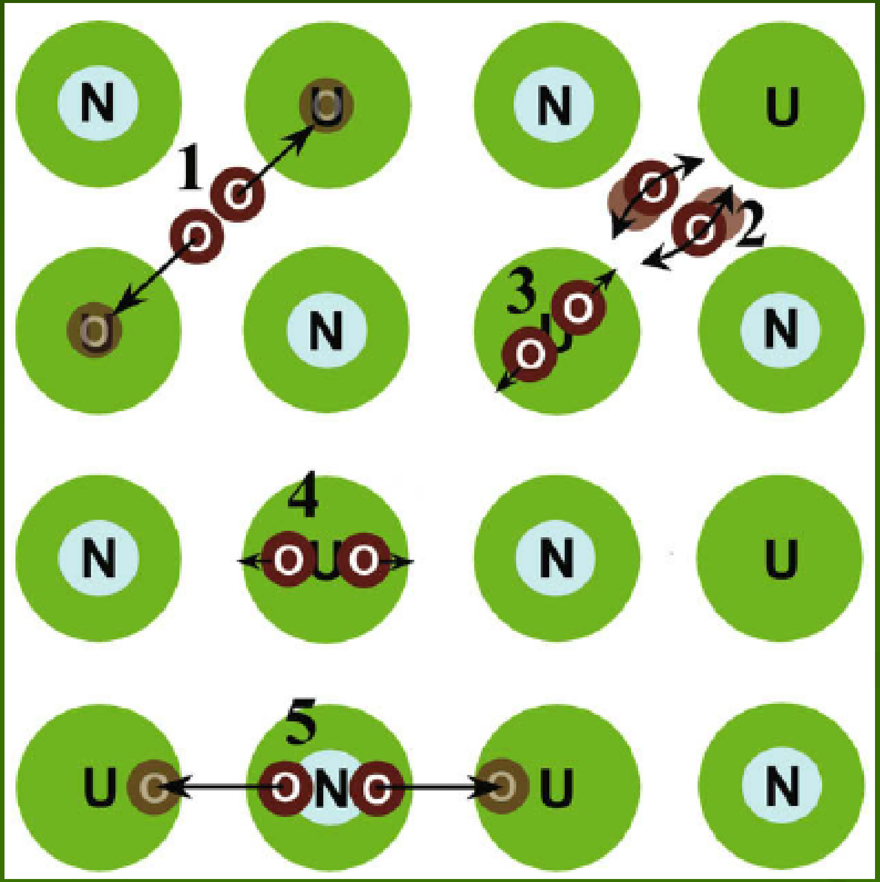


Fig. 1. Schematic view of five different horizontal configurations for the O_2 molecule adsorption on UN surface: (1) atop the hollow site oriented towards the nearest surface U ions, (2) atop the hollow site oriented towards the nearest surface N ions, (3) atop the surface U ions oriented towards the next-nearest surface U ions, (4) atop the surface U ions oriented towards the nearest surface N ions, (5) atop the surface N ions oriented towards the nearest surface U ions. We show, using arrows,that molecule spontaneous dissociation can occur when O2 is located either atop the hollow site (1) or atop ion N (5).

Molecular oxygen on the UN(001) surface

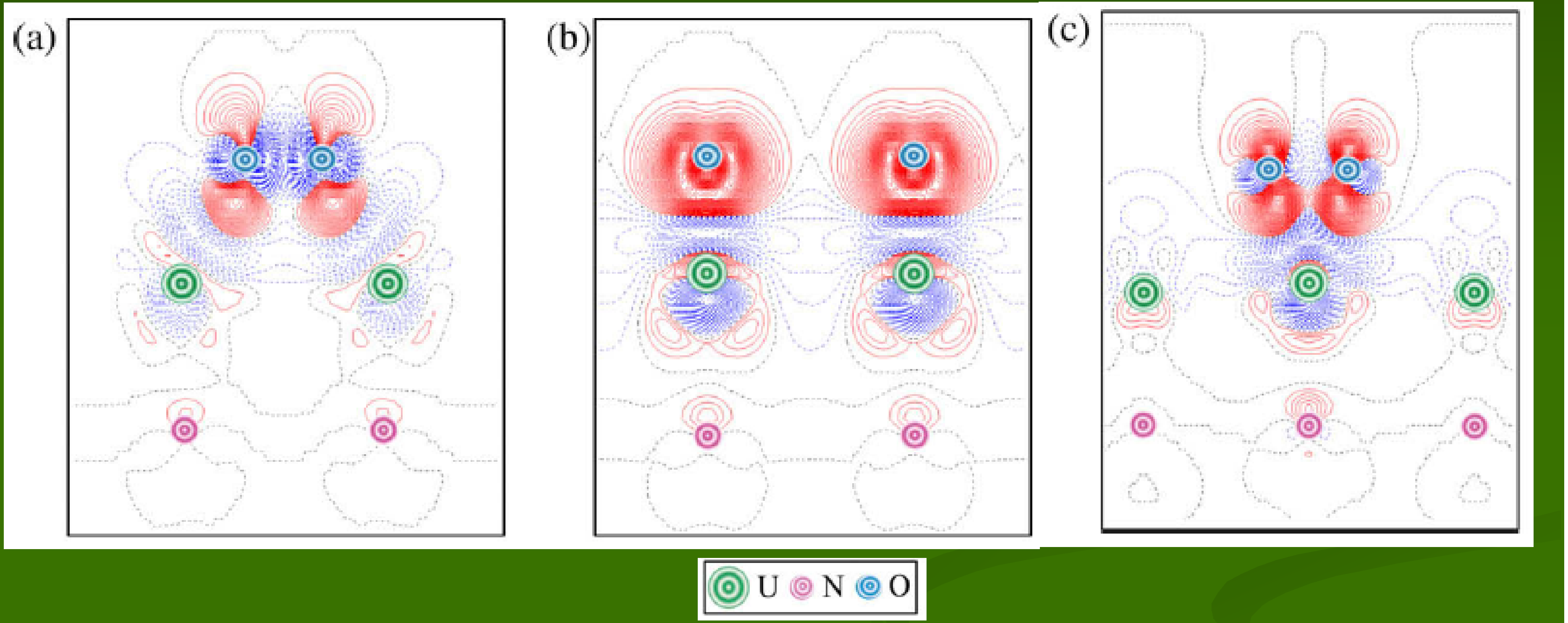
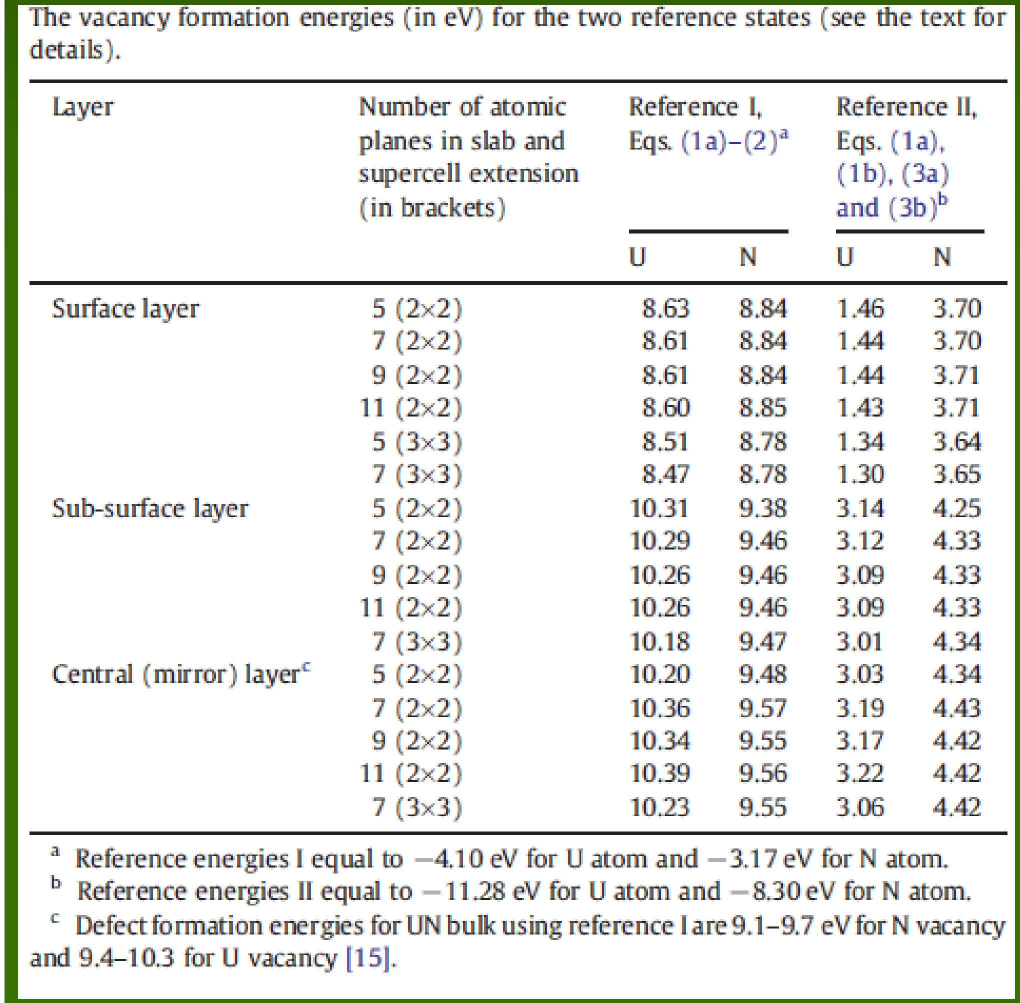


Fig. 2. The difference electron density maps $Dr(\mathbf{r})$ (the total density of the interface minus the sum of densities of substrate and adsorbate with optimized interfacial geometry) for (a) the O_2 molecule upon the hollow position oriented to the nearest surface U ions, (b) after its dissociation in the configuration 1 (Fig. 1) with O atoms atop the surface U ions and (c) for the O_2 molecule atop the surface U ion in the configuration 3 (Fig. 1). Solid (red) and dashed (blue) isolines correspond to positive (excess) and negative (deficiency) electron density, respectively. Isodensity increment is 0.003 e Å^{-3}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Calculations on defective UN(001) surface

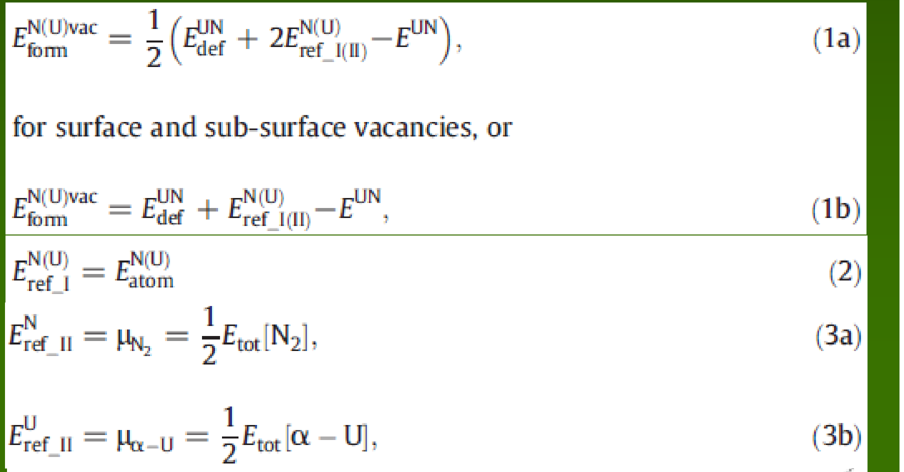

The vacancy formation energies (in eV) for the two reference states (see the text for details).

Layer	Number of atomic planes in slab and supercell extension (in brackets)	Reference I, Eqs. (1a)–(2)[a]		Reference II, Eqs. (1a), (1b), (3a) and (3b)[b]	
		U	N	U	N
Surface layer	5 (2×2)	8.63	8.84	1.46	3.70
	7 (2×2)	8.61	8.84	1.44	3.70
	9 (2×2)	8.61	8.84	1.44	3.71
	11 (2×2)	8.60	8.85	1.43	3.71
	5 (3×3)	8.51	8.78	1.34	3.64
	7 (3×3)	8.47	8.78	1.30	3.65
Sub-surface layer	5 (2×2)	10.31	9.38	3.14	4.25
	7 (2×2)	10.29	9.46	3.12	4.33
	9 (2×2)	10.26	9.46	3.09	4.33
	11 (2×2)	10.26	9.46	3.09	4.33
	7 (3×3)	10.18	9.47	3.01	4.34
Central (mirror) layer[c]	5 (2×2)	10.20	9.48	3.03	4.34
	7 (2×2)	10.36	9.57	3.19	4.43
	9 (2×2)	10.34	9.55	3.17	4.42
	11 (2×2)	10.39	9.56	3.22	4.42
	7 (3×3)	10.23	9.55	3.06	4.42

[a] Reference energies I equal to −4.10 eV for U atom and −3.17 eV for N atom.

[b] Reference energies II equal to −11.28 eV for U atom and −8.30 eV for N atom.

[c] Defect formation energies for UN bulk using reference I are 9.1–9.7 eV for N vacancy and 9.4–10.3 for U vacancy [15].


$$E^{N(U)vac}_{form} = \frac{1}{2}\left(E^{UN}_{def} + 2E^{N(U)}_{ref\_I(II)} - E^{UN}\right), \quad (1a)$$

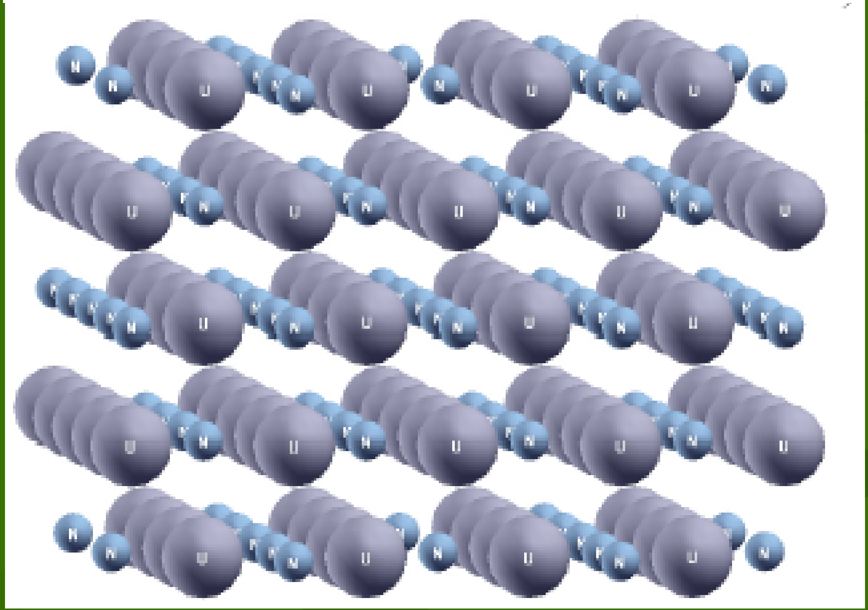
for surface and sub-surface vacancies, or

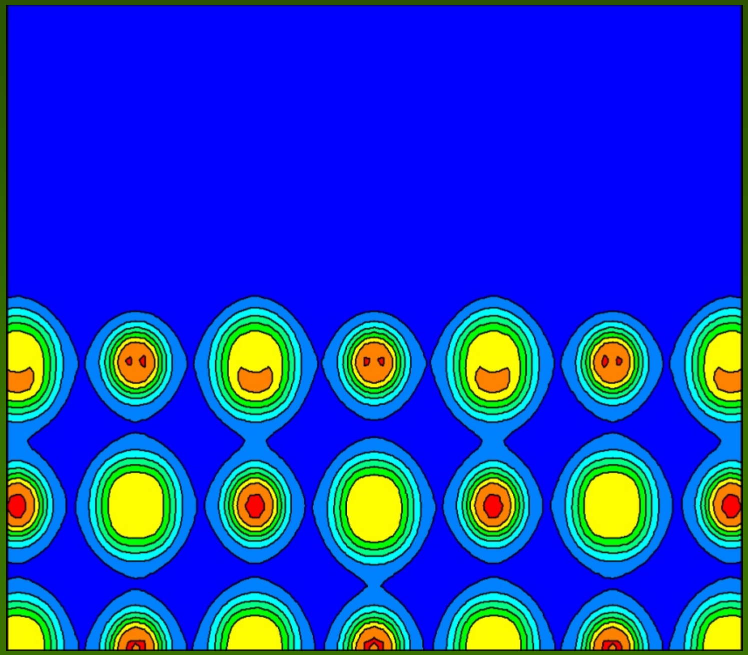
$$E^{N(U)vac}_{form} = E^{UN}_{def} + E^{N(U)}_{ref\_I(II)} - E^{UN}, \quad (1b)$$

$$E^{N(U)}_{ref\_I} = E^{N(U)}_{atom} \quad (2)$$

$$E^{N}_{ref\_II} = \mu_{N_2} = \frac{1}{2}E_{tot}[N_2], \quad (3a)$$

$$E^{U}_{ref\_II} = \mu_{\alpha-U} = \frac{1}{2}E_{tot}[\alpha-U], \quad (3b)$$





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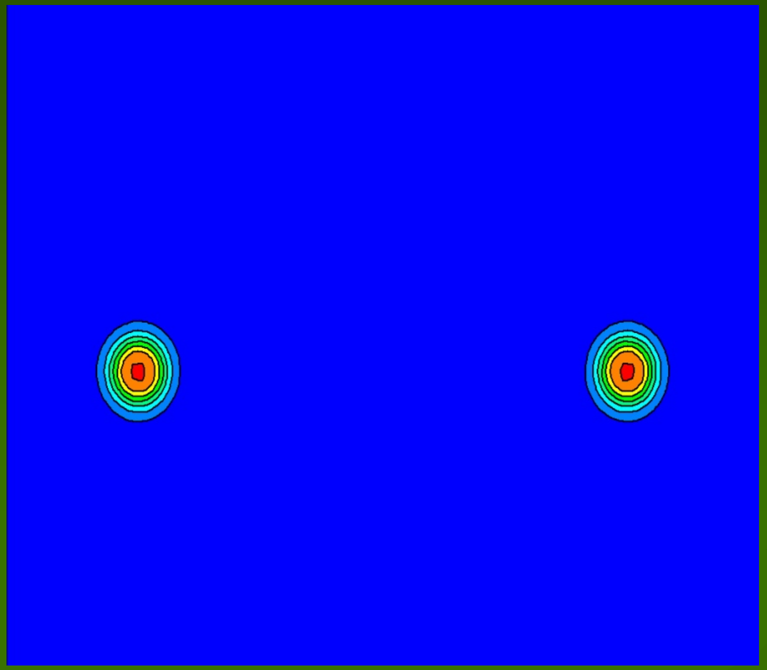

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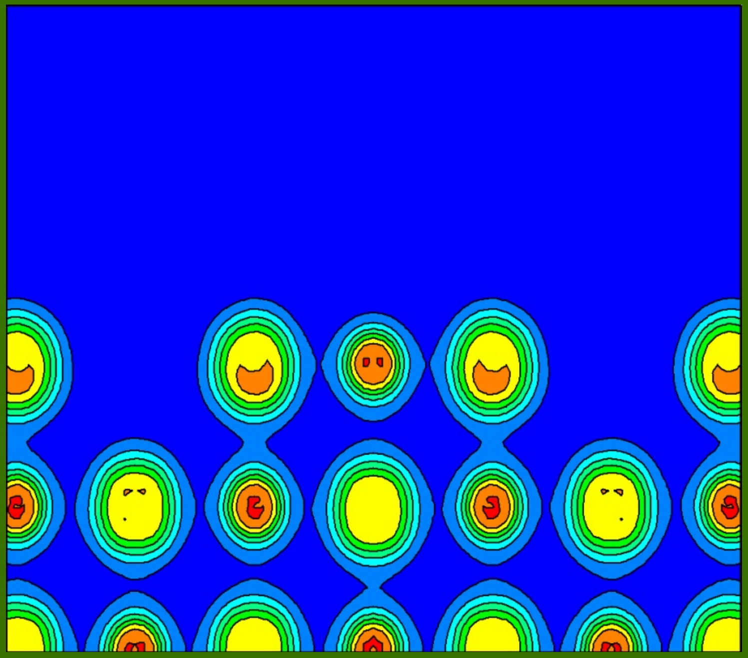


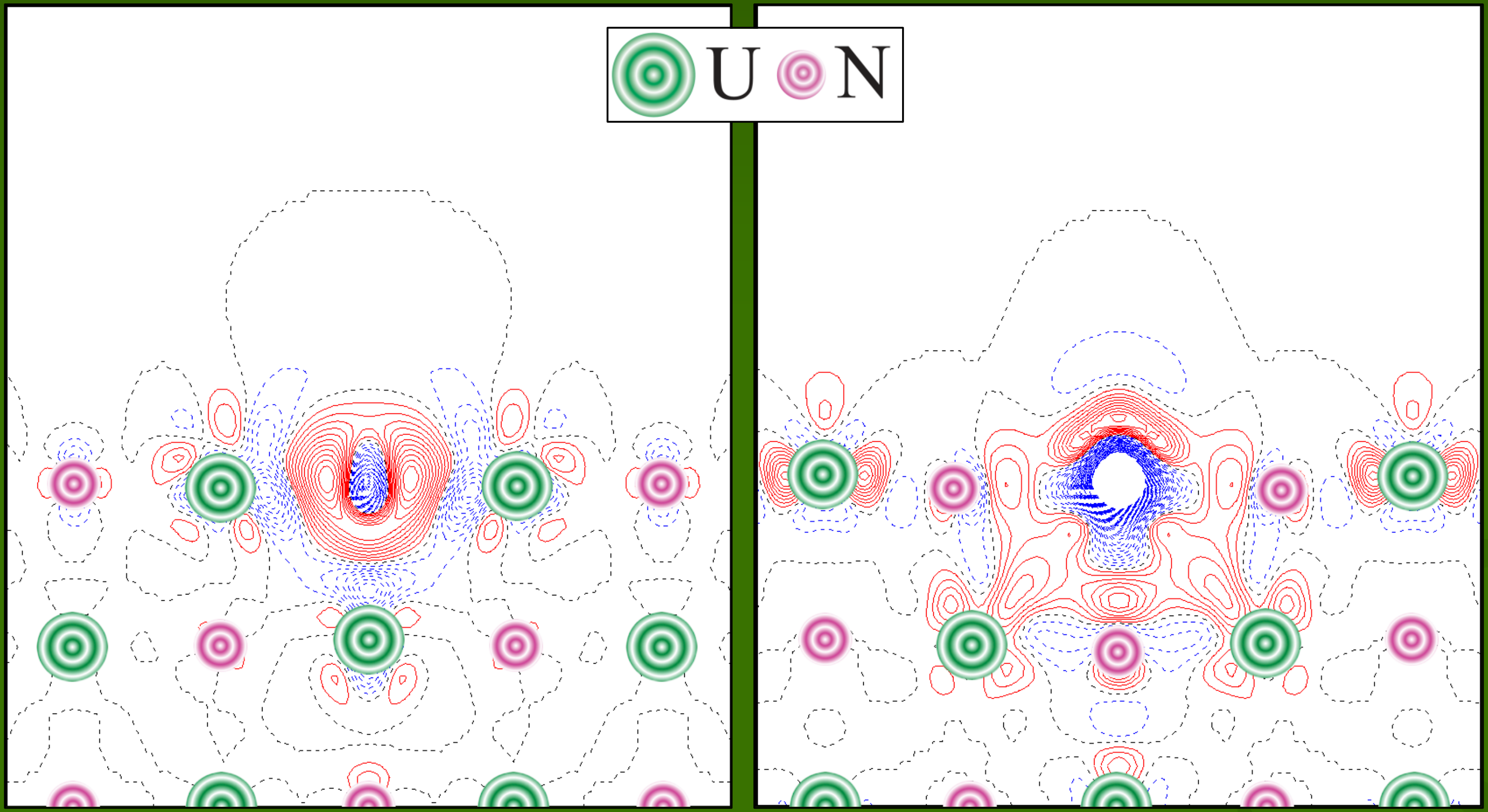
Main results: Electron density re-distributions

System without vacancies –

– vacancy atoms -

– Slab with vacancies

Defective UN(001): Electron density re-distributions



2D difference electron density maps projected onto the (100) section plane for N vacancies (left) and U vacancies (right). Solid (red) and dash (blue) isolines describe positive and negative values of electron density, respectively.

Calculations on defective UN(001) surface

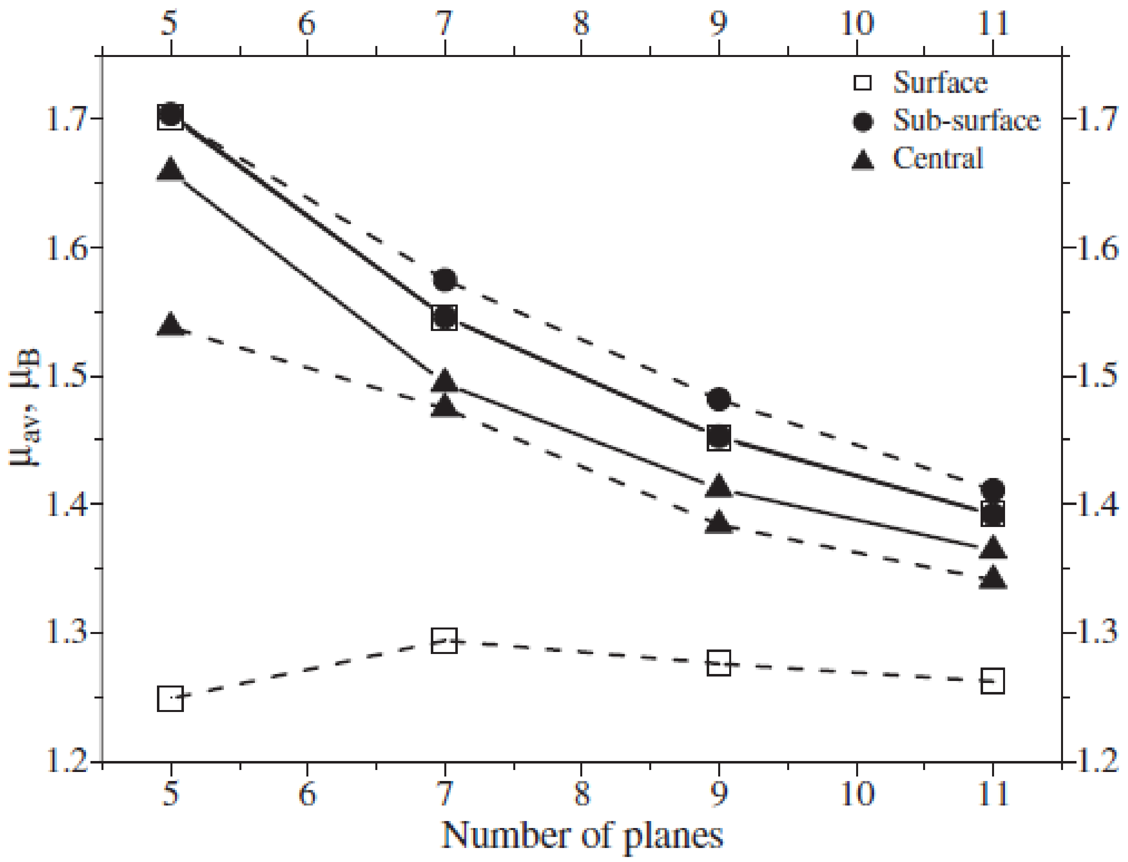


Fig. 5. The average U magnetic moment μ_{av} (in μ_B) in the slab as a function of a number of planes. The dashed curves correspond to U vacancy, whereas the solid curves describe the N vacancy.

Defective UN(001): Electron density re-distributions

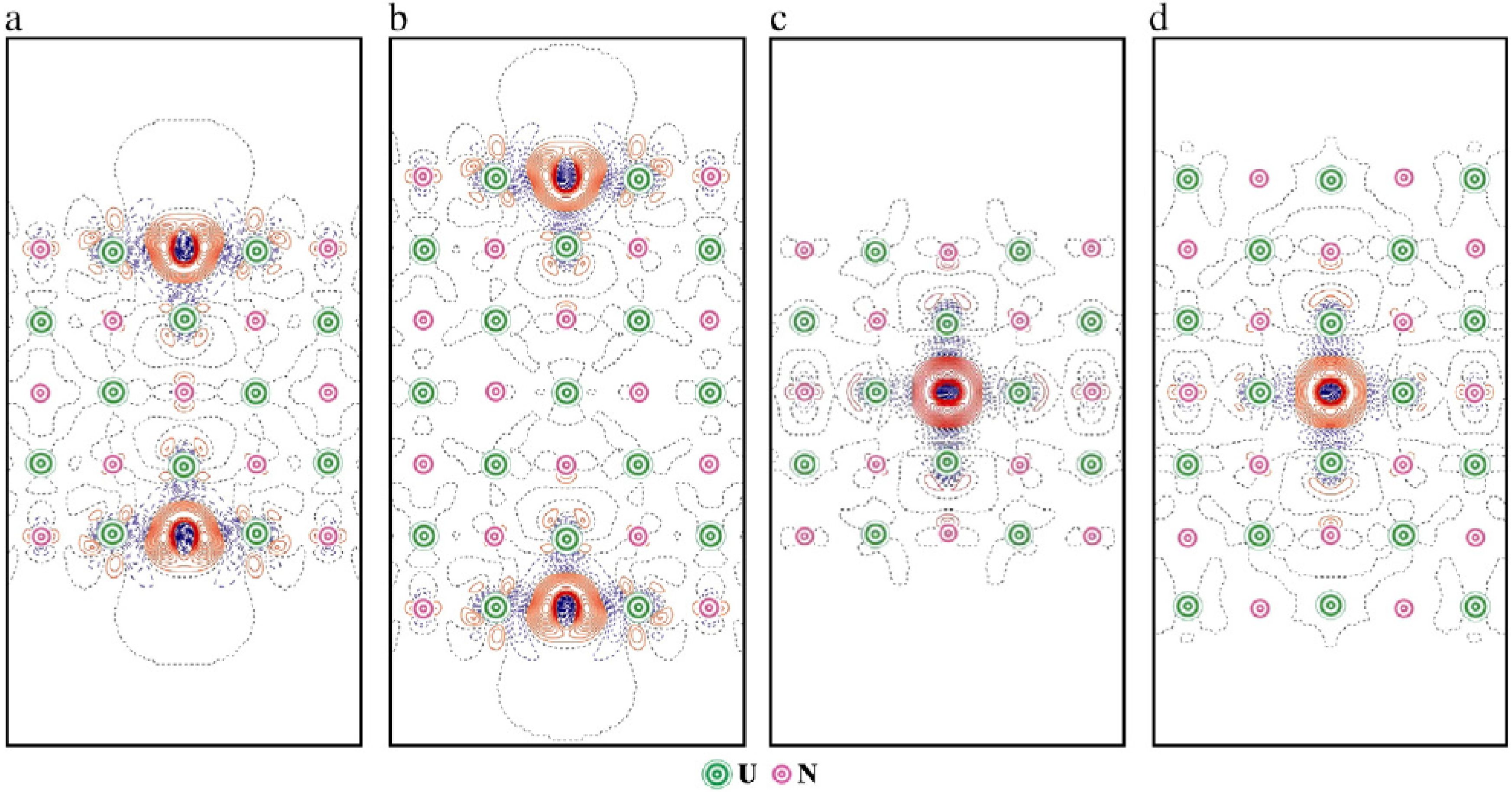
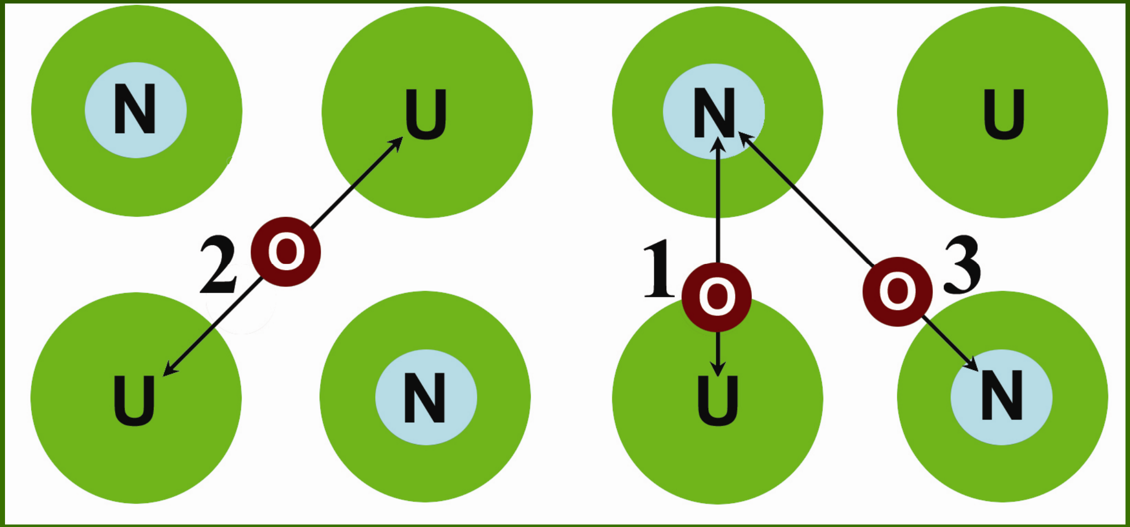
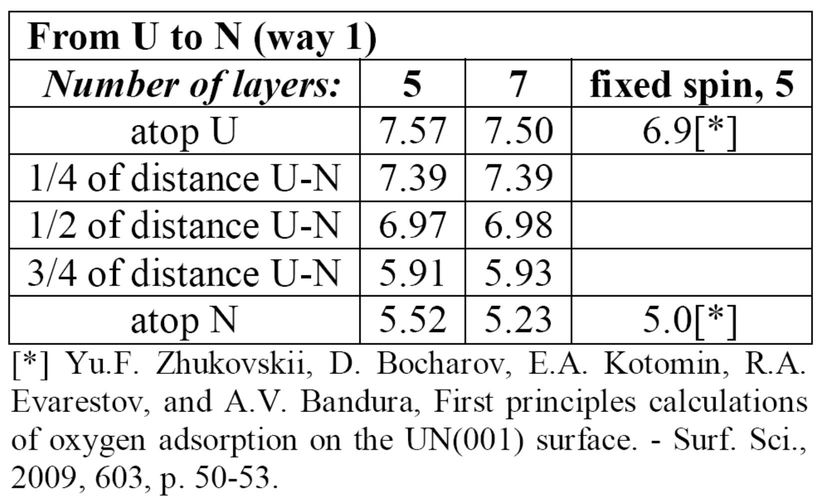


Fig. 3. 2D sections of the electron density redistributions around the nitrogen vacancies in five- and seven-layer UN(001) slabs with 2 × 2 supercell extension defined as the total electron density of defected surface minus a superposition of the electron densities for both perfect surface and isolated atom in the regular position on the surface: a) N vacancy in a surface plane, five-layer slab, b) the same, 7-layer slab, c) N vacancy in a central plane, five-layer slab, d) the same, 7-layer slab. Solid (red) and dashed (blue) isolines correspond to positive and negative electron density, respectively. Isodensity increment is 0.25 e a.u.$^{-3}$.

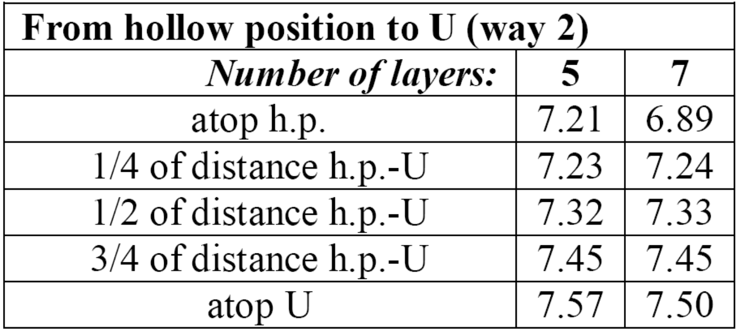
Surface migration of oxygen adatom upon perfect substrate



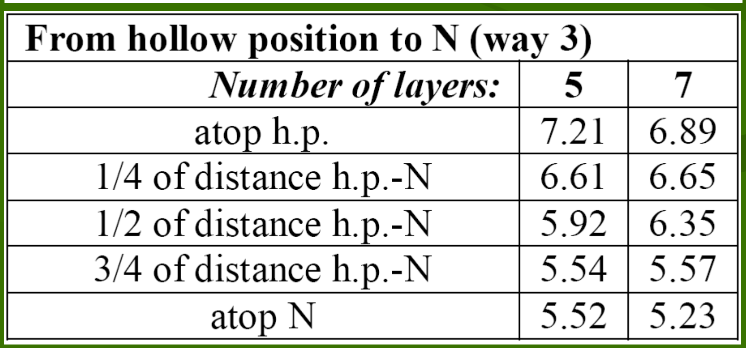


From U to N (way 1)			
Number of layers:	**5**	**7**	**fixed spin, 5**
atop U	7.57	7.50	6.9[*]
1/4 of distance U-N	7.39	7.39	
1/2 of distance U-N	6.97	6.98	
3/4 of distance U-N	5.91	5.93	
atop N	5.52	5.23	5.0[*]

[*] 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.



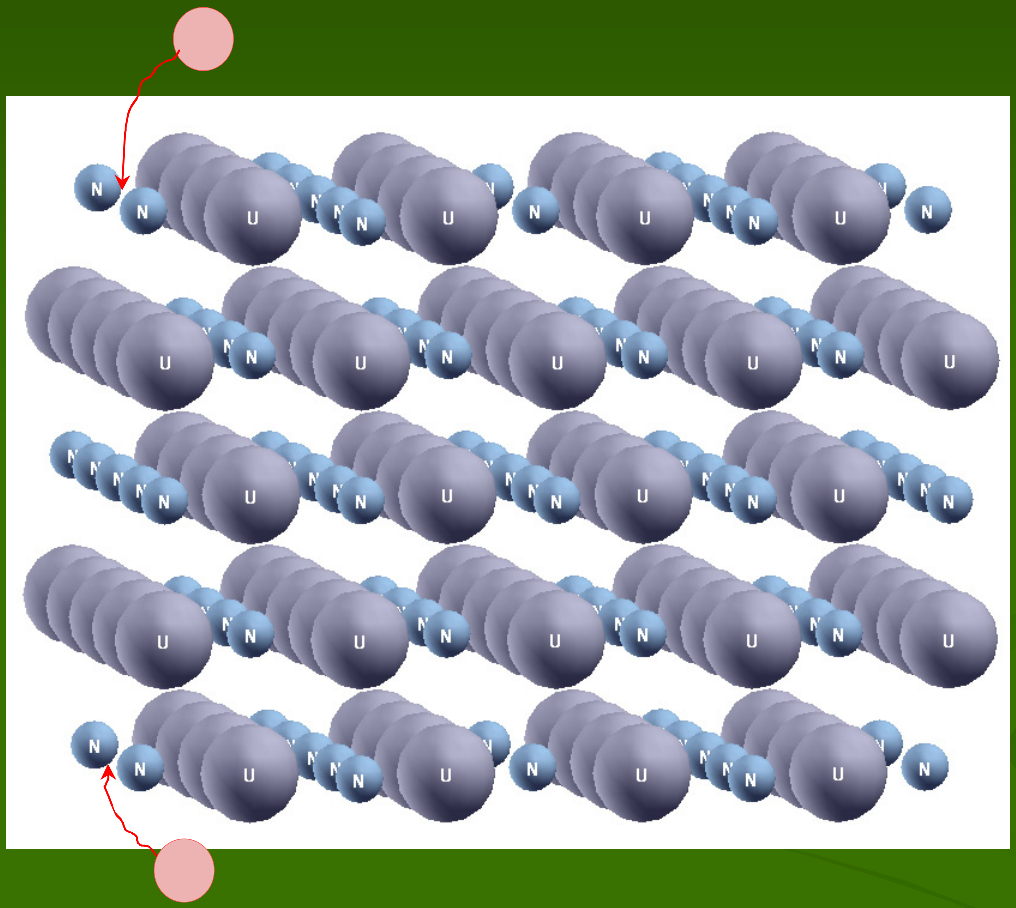
From hollow position to U (way 2)		
Number of layers:	**5**	**7**
atop h.p.	7.21	6.89
1/4 of distance h.p.-U	7.23	7.24
1/2 of distance h.p.-U	7.32	7.33
3/4 of distance h.p.-U	7.45	7.45
atop U	7.57	7.50



From hollow position to N (way 3)		
Number of layers:	**5**	**7**
atop h.p.	7.21	6.89
1/4 of distance h.p.-N	6.61	6.65
1/2 of distance h.p.-N	5.92	6.35
3/4 of distance h.p.-N	5.54	5.57
atop N	5.52	5.23

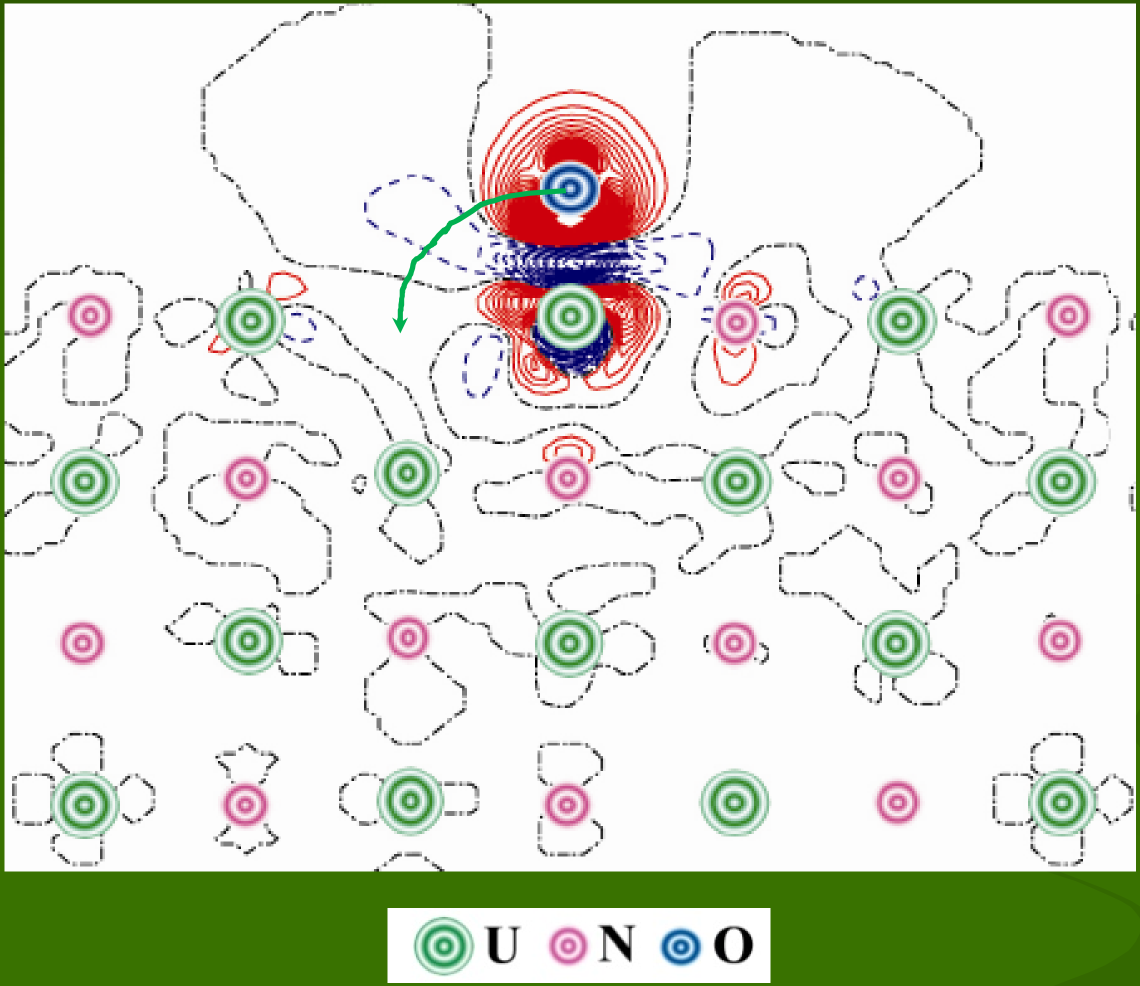
Migration barriers: 1 (1.05-1.27 eV), 2 (0.38-0.61 eV), 3 (1.66-1.69 eV)

Surface migration of oxygen adatom on defective substrate



Spontaneous barrier-less adatom migration from the equilibrium position atop the outer U atom towards the nearest N vacancy. Energy gain for this jump has been found to be 1.94 eV and 2.00 eV *per* O_{ads} for 2x2 and 3x3 supercell models, respectively.

Surface diffusion of oxygen adatom on defective substrate



The 2D section of the electron charge density re-distribution around the O adatom upon surface U atom nearest to the surface N vacancy. The green rrow shows the most probable trajectory of adatom migration towards the vacancy.

Oxygen impurity atom incorporation into uranium mononitride surface and subsurface vacancies

The energy balance for the incorporation of an O atom into a vacancy can be characterized by the incorporation energy E_I suggested by Grimes and Catlow in the shell model calculations on fission products in UO_2:

$$E_I = E^{\mathrm{N(U)}}_{\mathrm{O}\_inc} - E^{\mathrm{N(U)}}_{vac} - E_{\mathrm{O}}$$

for the O atom incorporated into the N- and U-vacancy disposed in the central atomic layer and

$$E_I = \frac{1}{2}(E^{\mathrm{N(U)}}_{\mathrm{O}\_inc} - E^{\mathrm{N(U)}}_{vac} - 2E_{\mathrm{O}})$$

for the same incorporation in the surface or sub-surface layers. Here $E^{\mathrm{N(U)}}_{\mathrm{O}\_inc}$ is the total energy of the supercell containing the O atom at either the N- or U-vacancy ($E^{\mathrm{N(U)}}_{\mathrm{O}\_inc} < 0$), $E^{\mathrm{N(U)}}_{vac}$ the energy of the supercell containing an unoccupied (empty) vacancy, and E_{O} a half of the total energy of isolated O_2 molecule in the triplet state. It is defined by the chemical potential of O at 0 K. Since the value of E_{I} describes the energy balance for the incorporation into pre-existing vacancies, it has to be negative for energetically favorable incorporation processes.

To take into account the total energy balance, including the vacancy formation energy E_{form} in the defect-free slab, the solution energy was defined as:

$$E_S = E_I + E_{form}$$

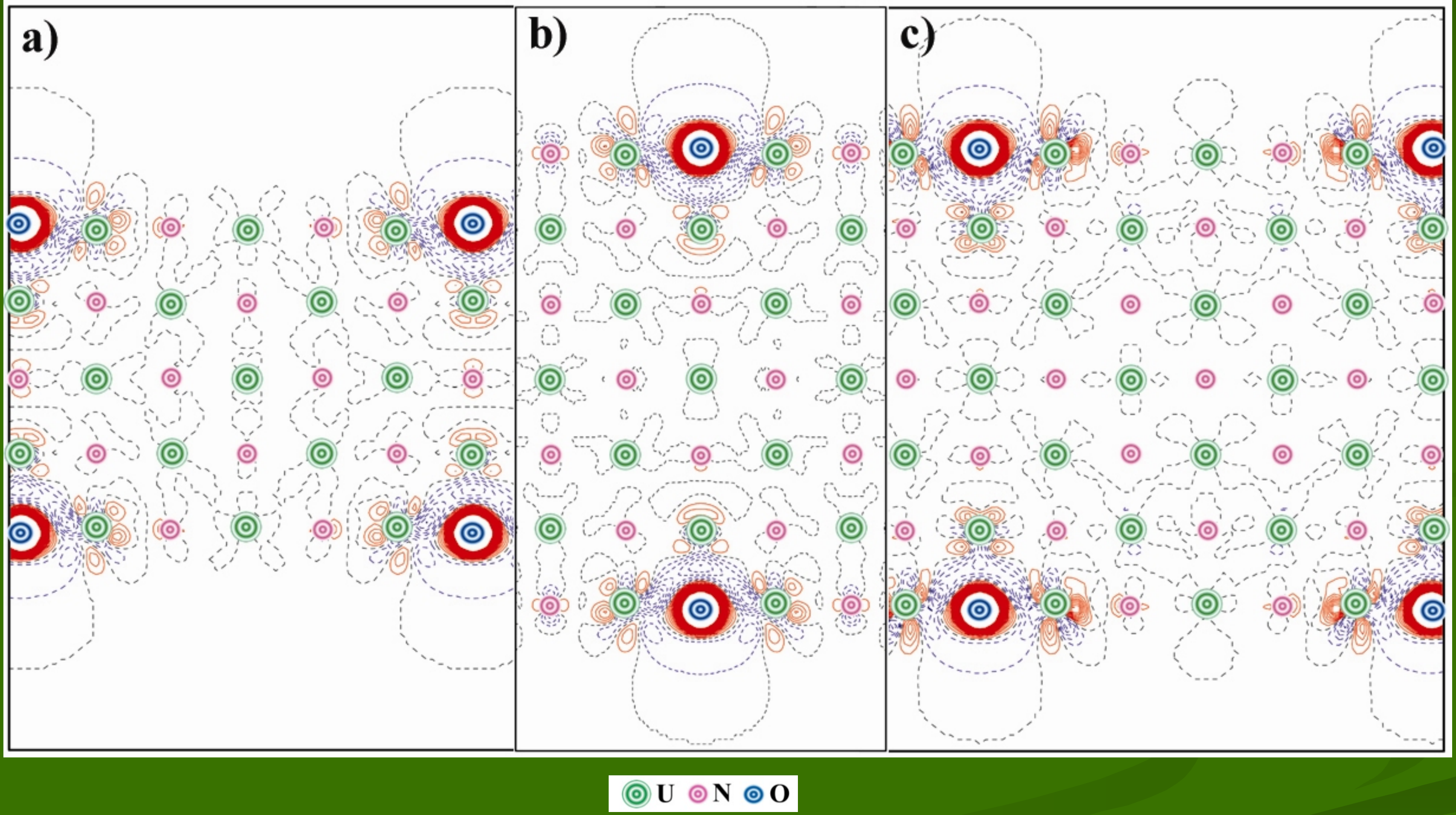
where *S* describes the energetic preference for impurity atom incorporation into the defectless slab while E_{form} the formation energy of N- or U- vacancy in the slab.

Oxygen impurity atom incorporation into uranium mononitride surface and subsurface vacancies

Incorporation (E_I), solution (E_S) energies in eV, average spin magnetic moments of U atoms m_{av}^{U} in μ_B and effective charge of O atoms in e^- for O incorporation into the UN(001) surface. The reference states for calculating the incorporation and solution energies are the chemical potentials of O, N and U calculated for O_2, N_2 molecules and α-U, respectively.

Layer	Supercell size	Number of atomic layers in slab	N vacancy				U vacancy			
			E_I (eV)	E_S (eV)	(μ_B)	$q_{eff}(e^-)$	E_I (eV)	E_S (eV)	(μ_B)	$q_{eff}(e^-)$
Surface	2x2	5	-6.173	-2.473	1.65	-1.36	-0.339	1.120	1.16	-0.98
		7	-6.181	-2.476	1.49	-1.36	-0.855	0.583	1.36	-1.03
		9	-6.188	-2.479	1.41	-1.36	-0.943	0.493	1.31	-1.06
	3x3	5	-6.122	-2.481	1.60	-1.37	-0.683	0.654	1.48	-1.05
		7	-6.126	-2.480	1.46	-1.36	-1.073	0.230	1.38	-1.08
Subsurface	2x2	5	-6.314	-2.068	1.64	-1.42	-1.856	1.284	1.66	-1.10
		7	-6.419	-2.090	1.49	-1.40	-1.823	1.297	1.45	-1.10
		9	-6.417	-2.091	1.41	-1.40	-1.823	1.271	1.38	-1.10
	3x3	7	-6.428	-2.093	1.46	-1.39	-2.012	1.000	1.43	-1.10
Central (mirror)	2x2	7	-6.611	-2.180	1.47	-1.42	0.736	3.923	1.44	-0.89
		9	-6.608	-2.192	1.39	-1.38	0.669	3.838	1.38	-0.90
	3x3	7	-6.599	-2.182	1.45	-1.42	0.317	3.378	1.47	-0.94

Oxygen impurity atom incorporation into uranium mononitride surface and subsurface vacancies



The 2D sections of the electron charge density re-distributions around the O atoms incorporated into the surface N-vacancies of the five- and seven-layer UN(001) slabs with 2×2 and 3×3 supercell extensions.

Comparison of properties for UN(001) and UN(110) surfaces

(FMNT poster PO-76)

1. Comparison of both UN(001) [4] and UN(110) surfaces shows that the former is energetically more favorable. Depending on slab thickness, the surface energies equal to 1.22-1.44 $J \cdot m^{-1}$ for UN(001) *vs.* 1.83-1.98 $J \cdot m^{-1}$ for UN(110) surface.

2. Energies of the nitrogen vacancy formation on the uranium mononitride surface are also larger for (110) surfaces, by ~0.7 eV, irrespectively of slab thickness.

3. Effective charges on N and U atoms of both perfect and defective UN(110) surface are slightly smaller than those for UN(001) surface.

4. Averaged magnetic moment μ_{av} is slightly larger on both regular and defective UN(110) surface as compared to UN(001).

Conclusions

1. The atomic scale DFT-GGA PW calculations with scalar relativistic pseudopotentials as implemented in the standard *VASP-4.6* code (combined with a supercell approach) can be applied for simulations of oxygen adsorption and surface diffusion upon perfect UN(001) substrate as well as incorporation of O adatom within the N vacancy. Both “frozen spin” and spin-polarized calculations have been performed.

2. To verify DFT-PW calculations, the DFT-LCAO method has been applied.

3. Results obtained within this study provides us with the necessary information for better understanding of surface processes on uranium nitride surfaces, including effects of point defects (U and N vacancies) on oxygen adsorption and initial step of the O_{ads} penetration into the UN substrate. This should be aimed at understanding a role of *grain boundaries* in a real UN powdered fuel and its oxidation mechanism.

Acknowledgements

Authors acknowledge Theoretical Research Unit of EC JRC ITU for collaboration between the ITU (Karlsruhe) and ISSP (Riga). Authors sincerely acknowledge R. A. Evarestov, A. V. Bandura and M. V. Losev for performed LCAO calculations and stimulating discussions.

Large-scale *VASP* calculations on perfect, defective and O-containing UN(001) and UN(110) surfaces with total geometry optimization have been performed in parallel regime using computer clusters at Garching Forschungzetrum and at ISSP (Riga).

This study was partly supported by the EC FP7 F-BRIDGE project and ESF project No.2009/0216/1DP/1.1.1.2.0/09/APIA/VIAA/044.

Thanks for your attention!

Announcement

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