

Лекция 12

Практическое применение
метода Кона-Шема

Метод псевдопотенциалов

The Kohn-Sham Method – The Kohn-Sham Equations

- Schrödinger-like equations with local potential

$$v_H(\vec{r}) = \frac{\delta U}{\delta \rho} = \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$\frac{\delta E_x[\rho]}{\delta \rho}$$

$$\frac{\delta E_c[\rho]}{\delta \rho}$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\vec{r}) + v_H(\vec{r}) + v_x(\vec{r}) + v_c(\vec{r}) \right] \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

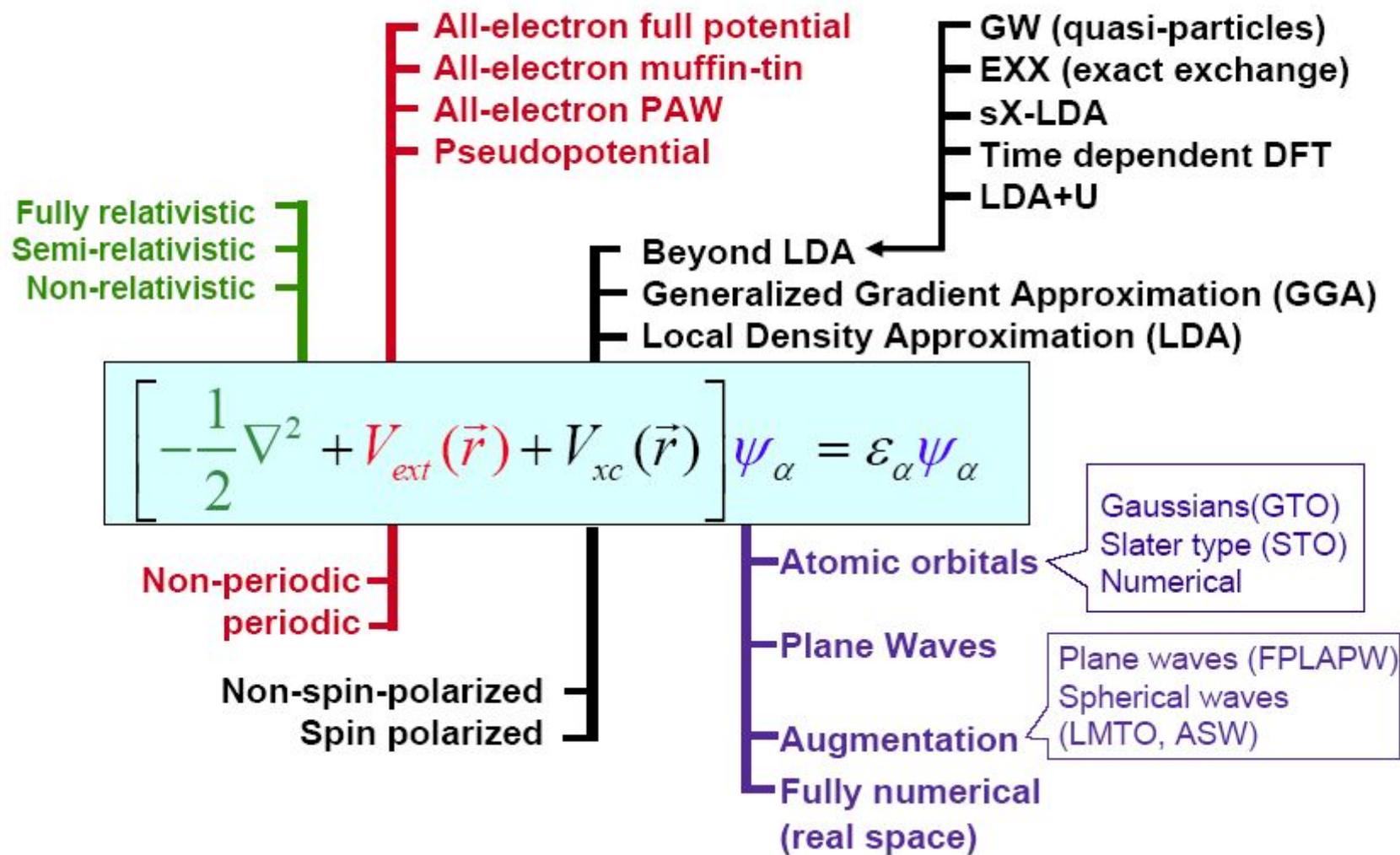
$$v_{ext}(\vec{r}) = -e^2 \sum_{s,n} \frac{Z_s}{|\vec{r} - \vec{r}_s - \vec{R}_n|}$$

$$\rho(\vec{r}) = \sum_{i=1}^N \varphi_i^*(\vec{r}) \varphi_i(\vec{r})$$

- These equations are nonlinear and must be solved iteratively (self-consistently)
- Correlation energy functional $E_c[\rho]$ (also $v_c(\vec{r})$) is *unknown* for *non-homogeneous* systems
 - $E_c[\rho]$ - is known for *homogeneous* electron gas (constant density)



DFT: Implementations of the Kohn-Sham Method



Exchange and Correlation Energy of Homogeneous Electron Gas

- Homogeneous electron gas (free electron gas or “jellium”)

Wave functions: $\psi(\vec{k}, \vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k} \cdot \vec{r}}$ Constant electron density: $\rho = N / \Omega$

Exchange energy per unit volume

$$E_x = -\frac{3}{2} \left(\frac{3}{\pi} \right)^{1/3} e^2 \rho^{4/3} = \varepsilon_x^{\text{hom}} \rho$$

- Dimensionless parameter characterizing density:

$$r_s = \frac{1}{a_B} \left(\frac{3}{4\pi\rho} \right)^{1/3} \quad \rho \text{ in } (a_B)^{-3} \quad \Rightarrow$$

Exchange energy per particle

$$\varepsilon_x^{\text{hom}} = -\frac{3}{2} \left(\frac{3}{\pi} \right)^{1/3} e^2 \rho^{1/3}$$

$$\varepsilon_x^{\text{hom}} = -\frac{3}{2} \left(\frac{9}{4\pi^2} \right)^{1/3} \frac{1}{r_s} \quad \text{in [Ry]}$$

$$\varepsilon_x^{\text{hom}}(r_s) = -0.91633 / r_s \quad \text{[Ry]}$$

- Quantum Monte-Carlo simulations for homogeneous electron gas

D. M. Ceperly & B. J. Alder, Phys. Rev. Lett. 45, 566 (1980)

Parametrization: *J. P. Perdew & A. Zunger, Phys. Rev. B 23, 5048 (1981)*

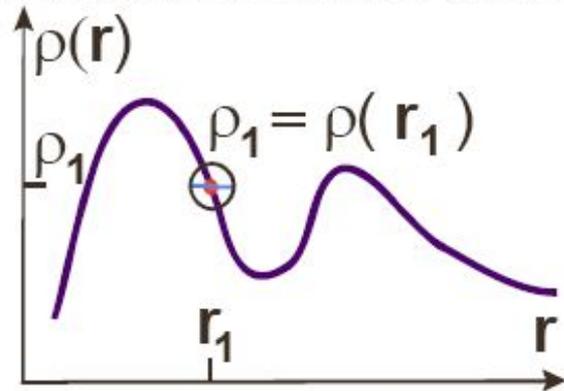
**Correlation
energy
per particle**

$$\varepsilon_c^{\text{hom}}(r_s) = \begin{cases} A \ln r_s + B + C r_s \ln r_s + D r_s & \text{for } r_s < 1 \\ \gamma / (1 + \beta_1 \sqrt{r_s} + \beta_2 r_s) & \text{for } r_s \geq 1 \end{cases} \quad \text{[Ry]}$$

$A, B, C, D, \gamma, \beta_1, \beta_2$ - fitted parameters

Local Density Approximation (LDA) and Gradient Corrections

In atoms, molecules, and solids the electron density is not homogeneous



- The main idea of the **Local Density Approximation**: the density is treated *locally* as constant

$$E_{xc}^{LDA}[\rho] = \int d\vec{r} \rho(\vec{r}) \epsilon_{xc}^{\text{hom}}(\rho(\vec{r}))$$

$$\epsilon_{xc}^{\text{hom}} = \epsilon_x^{\text{hom}} + \epsilon_c^{\text{hom}}$$

Gradient Expansion Approximation

D. C. Langreth & M. J. Mehl, Phys. Rev. B 28, 1809 (1983)

$$E_{xc}^{GEA}[\rho] = E_{xc}^{LDA}[\rho] + \int d\vec{r} \rho(\vec{r}) C_{xc}[\rho] \frac{|\nabla \rho(\vec{r})|^2}{\rho(\vec{r})^{4/3}}$$

Generalized Gradient Approximation

J. P. Perdew & Y. Wang, Phys. Rev. B 33, 8800 (1986)

$$E_{xc}^{GGA}[\rho] = \int d\vec{r} f_{xc}(\rho(\vec{r}), \nabla \rho(\vec{r})) \quad f_{xc} \text{ -constructed to fulfill maximal number of "summation rules"}$$

Exchange-correlation potential can be calculated very easily, $v_{xc} = \frac{\delta E_{xc}}{\delta \rho}$ since explicit dependence of E_{xc} on the density ρ is known.

Exact Exchange Method (EXX)

Exact Exchange for non-homogeneous systems + E_c in LDA or GGA

Main difficulty:

How to calculate the exchange potential $v_x(\vec{r}) = \frac{\delta E_x[\rho]}{\delta \rho(\vec{r})}$?

M. Städele et al., Phys. Rev. B 59, 10031 (1999).

$$E_x[\rho] = -\frac{1}{2} \sum_i \iint d\vec{r} d\vec{r}' \varphi_i^*(\vec{r}) \left(\sum_j \frac{\varphi_j(\vec{r}) \varphi_j^*(\vec{r}')}{|\vec{r} - \vec{r}'|} \right) \varphi_i(\vec{r}')$$

Problem: Explicit dependence of $E_x[\rho]$ (i.e., $\varphi_i[\rho]$) on ρ is unknown

Solution: v_x is the first functional derivative of E_x

→ First order perturbation theory determines exactly $\frac{\delta E_x}{\delta \rho}$

→ Apply chain rule

$$v_x = \frac{\delta E_x}{\delta \rho} = \sum_i \frac{\delta E_x}{\delta \varphi_i} \times \frac{\delta \varphi_i}{\delta v_{KS}} \times \frac{\delta v_{KS}}{\delta \rho}$$

$$(\hat{T} + v_{KS})\varphi_i = \varepsilon_i \varphi_i$$

from E_x

$$\frac{\delta \varphi_i(\vec{r})}{\delta v_{KS}(\vec{r}')} = \sum_{j \neq i} \frac{\varphi_j^*(\vec{r}') \varphi_i(\vec{r}')}{\varepsilon_i - \varepsilon_j} \varphi_i(\vec{r})$$

Perturbation theory

$$\frac{\delta \rho}{\delta v_{KS}} = \frac{\delta \rho}{\delta \varphi_i} \frac{\delta \varphi_i}{\delta v_{KS}} \equiv \mathbf{K} \implies \frac{\delta v_{KS}}{\delta \rho} = \mathbf{K}^{-1}$$

Выводы

Exact Exchange Method (EXX) - CONCLUSIONS

- Systematic improvement in comparison to LDA and GGA 😊
- Numerically very costly in comparison to LDA and GGA 😞
- Very good basis to search for better correlation energy functionals 😊
The work is going on ! (J. Perdew)

➡ **New generation of the energy functionals**

Extensions of the DFT

● Relativistic DFT

A. K. Rajagopal and J. Callaway, Phys. Rev. B 7, 1912 (1973)

- Kinetic energy operator (free Dirac field) $\hat{h} = c\vec{\alpha} \cdot \vec{p} + \beta mc^2$
- The ground-state energy is a functional of the four-vector current density $j_\mu(x)$

● Spin-polarized systems

U. Von Barth & L. Hedin, J. Phys. C 5, 1629 (1972)

- For example, systems with odd number of electrons

$$\rho_\uparrow \neq \rho_\downarrow \quad \rho = \rho_\uparrow + \rho_\downarrow$$

- Energy functional of both spin densities $E_{xc}[\rho_\uparrow, \rho_\downarrow]$
- Exchange-correlation potential $v_{xc\sigma} = \frac{\delta E_{xc}[\rho_\sigma, \rho_{-\sigma}]}{\delta \rho_\sigma} \quad \sigma = (\uparrow, \downarrow)$
- Local Spin Density (LSD) Approximation

● Finite - Temperature ($T \neq 0$)

N. D. Mermin, Phys. Rev. 137, A1441 (1965)

- Grand canonical ensemble, $\Omega = -k_B T \ln \text{Tr}[e^{(\mu\hat{N} - \hat{H})/k_B T}]$
- The **grand potential** of the a system at finite temperature is a functional of the density in the system at that temperature.

Solution of the Kohn-Sham Equations

- Direct methods on a mesh in r -space
- Expansion of the Kohn-Sham orbitals in a basis $\{\chi_{\alpha\vec{k}}(\vec{r})\}$

$$\varphi_{n\vec{k}}(\vec{r}) = N \sum_{\alpha} c_{\alpha}(n, \vec{k}) \chi_{\alpha\vec{k}}(\vec{r})$$

$$\left[\sum_{\alpha'} \left\langle \chi_{\alpha\vec{k}} \left| -\frac{\hbar^2}{2m} \vec{\nabla}^2 + v_{KS}(\vec{r}) \right| \chi_{\alpha'\vec{k}} \right\rangle - \varepsilon_n(\vec{k}) \left\langle \chi_{\alpha\vec{k}} \left| \chi_{\alpha'\vec{k}} \right\rangle \right] c_{\alpha'}(n, \vec{k}) = 0$$

Hamiltonian
matrix elements

Overlap integrals

$$[H_{\alpha\alpha'}(\vec{k}) - \varepsilon_n(\vec{k}) S_{\alpha\alpha'}(\vec{k})] c_{\alpha'}(n, \vec{k}) = 0$$

Eigenvalueproblem

$$\det[H_{\alpha\alpha'}(\vec{k}) - \varepsilon_n(\vec{k}) S_{\alpha\alpha'}(\vec{k})] = 0$$

→ $\varepsilon_n(\vec{k})$ Bandstructure

Solution of the Kohn-Sham Equations – Survey of Methods

- **LCAO (Linear Combination of Atomic Orbitals)**

 - All electron & pseudopotential

 - Semiempirical Tight-Binding Method**

- **Plane waves and pseudopotential**

 - EMP – Empirical Pseudopotential Method**

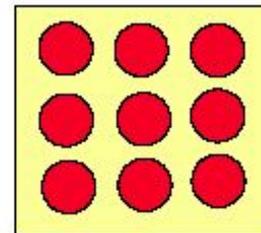
- **OPW (Orthogonalized Plane Waves)**

 - All electron, plane waves orthogonalized to core states

Multi-scattering Methods (All electron)

 - Muffin-tin* form of the potential used to generate basis

 - Basis function* – Numerically obtained wave function inside the muffin-tin sphere + augmented function outside



- **LAPW [FPLAPW] (Full Potential Linearized Augmented Plane Wave)**

 - Plane waves outside muffin-tin spheres

 - Considered to be the most accurate method

- **LMTO (Linearized Muffin-Tin Orbitals)**

 - Hankel functions outside muffin-tin spheres

- **KKR (Kohn – Korringa – Rostoker)**

 - Green's Function Method

Linear Combination of Atomic Orbitals (LCAO) - Method

Kohn-Sham orbitals in periodic systems $\varphi_{n\vec{k}}(\vec{r}) = N \sum_{\alpha} c_{\alpha}(n, \vec{k}) \chi_{\alpha\vec{k}}(\vec{r})$

$$\chi_{\alpha\vec{k}}(\vec{r}) = \sum_{\vec{R}_l} e^{i\vec{k} \cdot \vec{R}_l} \phi_{\alpha}^{at}(\vec{r} - \vec{R}_l - \vec{\tau}_{s(\alpha)})$$

$\{\vec{\tau}_s\}_{\alpha}$ Basis atoms

$\{\vec{R}_l\}$ Primitive translations

ϕ_{α}^{at} - 'Atomic' Kohn-Sham orbitals: $[\frac{\hat{p}^2}{2m} + V_{KS}^{at}] \phi_{\alpha}^{at} = \epsilon_{\alpha}^{at} \phi_{\alpha}^{at}$

$\{\chi_{\alpha\vec{k}}\}$ - fulfill Bloch's theorem $\chi_{\alpha\vec{k}}(\vec{r} + \vec{R}_n) = e^{i\vec{k} \cdot \vec{R}_n} \chi_{\alpha\vec{k}}(\vec{r})$

Problems

- Minimal Basis, i.e., one orbital per electron, is not sufficient
- Results depend on the chosen basis

Semiempirical Tight-Binding Method

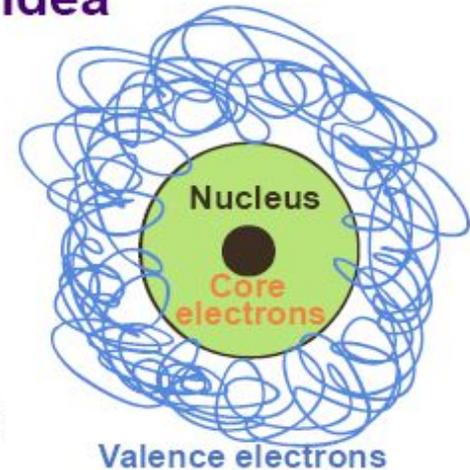
- Hamiltonian matrix elements $\langle \phi_{\alpha} | \hat{H} | \phi_{\alpha'} \rangle \equiv H_{\alpha\alpha'}$, and overlap integrals $\langle \phi_{\alpha} | \phi_{\alpha'} \rangle \equiv S_{\alpha\alpha'}$, are treated as empirical parameters
- Mostly orthonormality of orbitals is assumed, $S_{\alpha\alpha'} = \delta_{\alpha\alpha'}$,
- Qualitative insight into physics and semi-quantitative results

W. A. Harrison, "Electronic Structure and the Properties of Solids The Physics of the Chemical Bond", Freeman & Comp. (1980)

PSEUDOPOTENTIALS - Basic Idea

The basic idea of the pseudopotential theory:

- Core electrons are localized and therefore chemically inactive (inert)
- Valence electrons determine chemical properties of atoms and SOLIDS
- Describe valence states by smooth wavefunctions

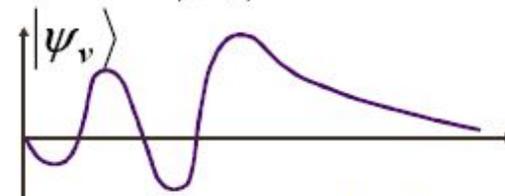


Construction of pseudopotentials from atomic wavefunctions

$$\hat{H}^{at} |\psi_c\rangle = E_c |\psi_c\rangle \quad \text{Philips \& Kleinman, Phys. Rev. 116, 287 (1959)}$$

$$\hat{H}^{at} |\psi_v\rangle = E_v |\psi_v\rangle \quad |\psi_c\rangle \text{ - core states} \quad |\psi_v\rangle \text{ - valence states}$$

- Orthogonality condition $\langle \psi_v | \psi_c \rangle = 0$
leads to oscillations in $|\psi_v\rangle$



- **How to get smooth pseudo-valence-wavefunctions $|\phi_v\rangle$ from atomic valence wavefunctions ?**
- **IDEA:** Project out oscillations from $|\psi_v\rangle$

PSEUDOPOTENTIALS – Philips-Kleinman Method

- First, we define pseudo-wave-function for valence electrons $|\varphi_v\rangle = |\psi_v\rangle + \sum_c |\psi_c\rangle \underbrace{\langle\psi_c|\varphi_v\rangle}_{\alpha_{cv}}$

- Second, we act with atomic Hamiltonian on the pseudo-wavefunction $\hat{H}^{at} |\varphi_v\rangle = E_v |\psi_v\rangle + \sum_c E_c |\psi_c\rangle \alpha_{cv} = E_v |\varphi_v\rangle - E_v \sum_c |\psi_c\rangle \alpha_{cv} + \sum_c E_c |\psi_c\rangle \alpha_{cv} = E_v |\varphi_v\rangle + \sum_c (E_c - E_v) |\psi_c\rangle \alpha_{cv}$

$$\hat{H}^{at} |\varphi_v\rangle - \sum_c (E_c - E_v) |\psi_c\rangle \langle\psi_c|\varphi_v\rangle = E_v |\varphi_v\rangle$$

- $\{\hat{H}^{at} - \sum_c (E_c - E_v) |\psi_c\rangle \langle\psi_c|\} |\varphi_v\rangle = E_v |\varphi_v\rangle$
- The pseudo-wave-function fulfill Schrödinger-like equation with Hamiltonian that is dependent on energy and contains additional repulsive, nonlocal potential.

- $\hat{H}_{ps} = \hat{H}^{at} + \sum_c (E - E_c) |\psi_c\rangle \langle\psi_c|$

PSEUDOPOTENTIALS – Philips-Kleinman Method

$$\hat{H}^{at} |\psi_v\rangle = E_v |\psi_v\rangle$$

Atom

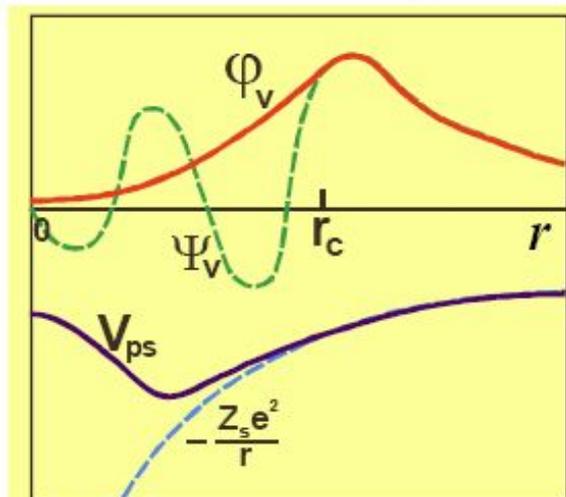
$$\hat{H}_{ps} |\phi_v\rangle = E_v |\phi_v\rangle$$

Pseudoatom

Energies are identical

Effective potential acting on the pseudo-valence electrons

$$\hat{V}_{ps} = \hat{V}^{core} + \sum_c (E - E_c) |\psi_c\rangle \langle \psi_c| \quad \hat{V}_{ps} \text{ is weaker than } \hat{V}^{core}$$



Z_s – No. of valence electrons in neutral atom

- Within the core region ($0 \leq r \leq r_c$)

The potential $V^{core}(r) = \frac{-Z_s e^2}{r}$

and atomic valence wavefunctions are substituted by pseudopotential V_{ps} and knot free pseudowavefunction ϕ_v

- Outside the core region $r > r_c$

$$\phi_v = \psi_v \quad V_{ps} = \frac{-Z_s e^2}{r}$$

- Construction procedure keeps the energies of atomic and pseudoatomic states unchanged.

After paper of Philips & Kleinman, various models of pseudopotentials have been developed. Main weakness: many parameters involved

Parameter Free (Ab-initio) Pseudopotentials – Norm Conserving Pseudopotentials

- Density Functional Theory for Atoms – Kohn-Sham equations for atoms
- Spherical symmetry of atoms is assumed

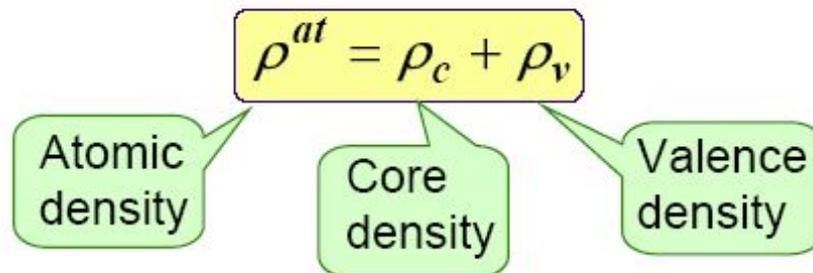
$$\psi^{at}(\mathbf{r}) = \sum_{lm} R_l(r) Y_{lm}(\hat{\Omega}) = \sum_{lm} \frac{u_l(r)}{r} Y_{lm}(\hat{\Omega})$$

- For each “ l ”, one-dimensional Kohn-Sham equation

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + v_{l,KS}^{at}(r) \right] u_l(r) = \varepsilon_l u_l(r) \quad \text{Atomic units: } \hbar = e = m = 1$$

- Effective Kohn-Sham potential contains all electronic interactions

$$v_{l,KS}^{at}(r) = -\frac{Z_s}{r} + \frac{l(l+1)}{2r^2} + v_H([\rho_c + \rho_v]) + v_{xc}([\rho_c + \rho_v])$$



Construction of Norm Conserving Pseudopotentials

- Construction of pseudo-wavefunctions $u_l^{ps}(r)$ from atomic solutions $u_l(r)$

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + v_l^{ps}(r) \right] u_l^{ps}(r) = \varepsilon_l u_l^{ps}(r) \quad u_l(r)$$

The pseudo-wavefunctions $u_l^{ps}(r)$ have to fulfill certain conditions

① $u_l^{ps}(r) = u_l(r) \quad \text{for} \quad r > r_{cl}$

② $\int_0^{r_{cl}} |R_l^{ps}(r)|^2 r^2 dr = \int_0^{r_{cl}} |R_l(r)|^2 r^2 dr$

NORM CONSERVATION

③ $\varepsilon_l^{ps} = \varepsilon_l$

④ $\left. \frac{\frac{d}{dr} R_l^{ps}(r)}{R_l^{ps}(r)} \right|_{r=r_{cl}} = \left. \frac{\frac{d}{dr} R_l(r)}{R_l(r)} \right|_{r=r_{cl}}$

Pseudo-wavefunctions and atomic wavefunctions lead to identical charge in the core region $r \leq r_{cl}$

Identical logarithmic derivatives at cutoff radii

These conditions do not determine the pseudo-wavefunctions uniquely
 \Rightarrow Different types of ab-initio pseudopotentials

Construction of Norm Conserving Pseudopotentials

Older pseudopotentials

BHS pseudopotential *G.B. Bachelet, D.R. Haman, and M. Schlüter, Phys. Rev. B 26, 4199 (1982)*

Kerker pseudopotential *G.P. Kerker, J. Phys. C 13, L189 (1980)*

Troullier-Martins-Pseudopotentials *N. Troullier & J. L. Martins, Phys. Rev. B 43, 8861 (1991)*

The pseudo-wavefunction in the core region ($r < r_{cl}$)

$$u_l^{ps}(r) = r^{l+1} \exp[p_l(r^2)] \quad p_l - \text{polynomial of 6}^{\text{th}} \text{ order}$$

Coefficients of the polynomial are determined from:

- Conditions 1-4
- Continuity of the first, second, third, and fourth derivative of u_l^{ps} in r_{cl}
- Second derivative of ionic pseudopotential should vanish in $r = 0$

Very good convergence properties !

When pseudo-wavefunctions u_l^{ps} are established, then proceed to the next step of pseudopotential construction.

Construction of Norm Conserving Pseudopotentials

- ● Inversion of the Kohn-Sham equations \Rightarrow Atomic pseudopot.

$$v_{l,atom}^{ps}(r) = \epsilon_l - \frac{l(l+1)}{2r^2} + \frac{1}{2} \frac{\frac{d^2}{dr^2} u_l^{ps}(r)}{u_l^{ps}(r)} \quad \text{Note, } u_l^{ps}(r) \text{ are knot free}$$

Atomic pseudopotential contains interaction between valence electrons. This interaction should be subtracted.

- ● ● Unscrening procedure

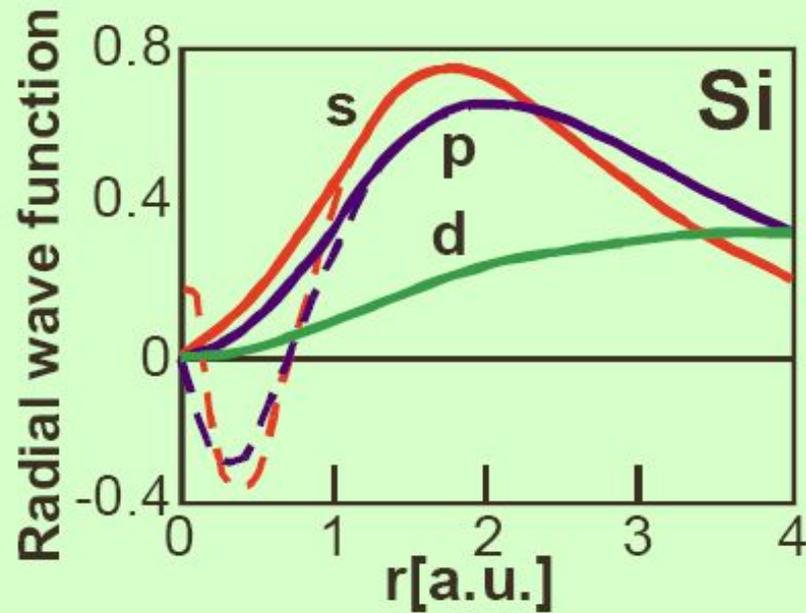
$$v_{l,atom}^{ps}(r) \Rightarrow V_{l,ion}^{ps}(r) \quad \text{IONIC PSEUDOPOTENTIAL}$$

$$V_{l,ion}^{ps}(r) = v_{l,atom}^{ps}(r) - v_H([\rho_{val}^{ps}]; r) - v_{xc}([\rho_{val}^{ps}]; r)$$

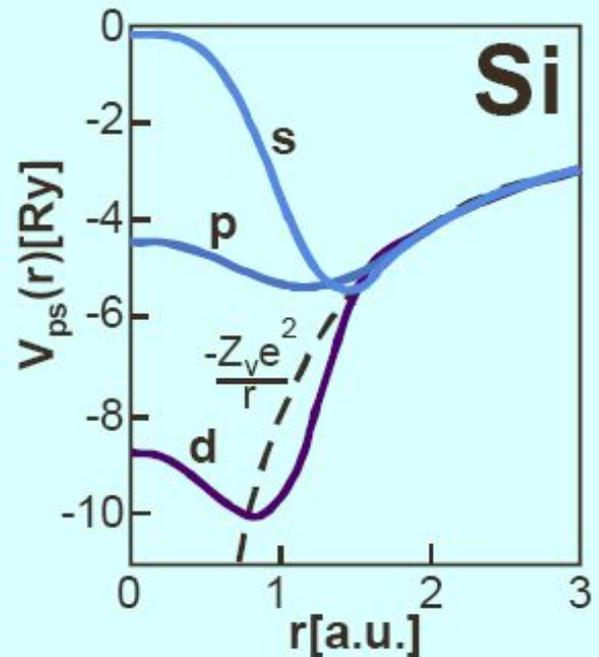
$V_{l,ion}^{ps}(r)$ - For each angular momentum quantum number “ l ”

Norm Concerning Pseudopotentials

Comparison of the **pseudo-wavefunction** (solid lines) and the corresponding all-electron wavefunctions (dashed lines)



Components of the ionic pseudo-potential for angular momentum $l = 0, 1, 2$



Norm Conserving Pseudopotentials

$V_{l,ion}^{ps}(\mathbf{r})$ - different component
for each "l"

Non-local pseudopotential

$$\hat{V}_{ion}^{ps} = \sum_l V_{l,ion}^{ps}(\mathbf{r}) \hat{P}_l = \sum_l V_{l,ion}^{ps}(\mathbf{r}) |l\rangle \langle l|$$

$$\langle \vec{r} | \hat{V}_{ion}^{ps} | \vec{r}' \rangle = V_{ion}^{ps}(\vec{r}, \vec{r}')$$

Projection operator

$$\langle \vec{r} | l \rangle = Y_{lm}(\hat{\mathbf{r}})$$

In Solids:

$$\hat{V}_{ion}^{ps} = \sum_{n,s} \sum_l V_{l,ion}^{ps,(s)}(|\vec{r} - \vec{R}_n - \vec{\tau}_s|) \hat{P}_l$$

Extensions

- **Relativistic effects are extremely important for core electrons**
 - Dirac equation for atoms
 - Schrödinger-like equation for pseudo-valence wavefunctions
 - "l" component of the ionic pseudopotential is obtained through the averaging over "j +" and "j -" components

- **Exchange-correlation functional is nonlinear in $\rho = \rho_c + \rho_v$**

$$E_{xc}[\rho_c + \rho_v] \neq E_{xc}[\rho_c] + E_{xc}[\rho_v]$$

Equality was assumed, for simplicity,
by the unscreening procedure

⇒ Nonlinear core correction

Plane Waves Formalism

Kohn-Sham equations in momentum space

Basis – plane waves

$$\chi_{\vec{k}}^{\vec{G}}(\vec{r}) = e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}$$

$$\varphi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k} \cdot \vec{r}} u_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} c_{n\vec{k}}(\vec{G}) e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}$$

Expansion with respect to basis = Fourier series

Expansion coefficients

$\{\vec{G}\}$ - reciprocal lattice vectors $\vec{G}_n = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3$

In practical calculations $\{\vec{G} : \frac{1}{2}(\vec{k} + \vec{G})^2 \leq E_{cutoff}\}$

$$\left[-\frac{\hbar^2}{2m} \vec{\nabla}^2 + v_H(\vec{r}) + v_{xc}(\vec{r}) + \hat{V}_{ion}^{ps} \right] \varphi_{n\vec{k}}(\vec{r}) = \varepsilon_{n\vec{k}} \varphi_{n\vec{k}}(\vec{r}) \quad (\text{KS-Eq.})$$

↓ Fourier transformation

$$\sum_{\vec{G}'} \left[\frac{\hbar^2}{2m} (\vec{k} + \vec{G})^2 \delta_{\vec{G}, \vec{G}'} + v_H(\vec{G} - \vec{G}') + v_{xc}(\vec{G} - \vec{G}') + V^{ps}(\vec{k} + \vec{G}, \vec{k} + \vec{G}') \right] c_{n\vec{k}}(\vec{G}') = \varepsilon_{n\vec{k}} c_{n\vec{k}}(\vec{G})$$

Eigenvalue problem – system of equations for expansion coefficients $c_{n\vec{k}}(\vec{G})$

Plane Waves Formalism

Fourier coefficients of the electronic (pseudoelectronic) density

$$\rho_{val}(\vec{r}) = \frac{\Omega_0}{(2\pi)^3} \sum_v \int_{BZ}^{occ} |\varphi_{n\vec{k}}(\vec{r})|^2 d^3\vec{k} = \sum_{v,\vec{k}} |\varphi_{n\vec{k}}(\vec{r})|^2$$

$$\rho_{val}(\vec{r}) = \sum_{\vec{G}} \rho_{val}(\vec{G}) e^{i\vec{G}\cdot\vec{r}} \quad \rho_{val}(\vec{G}) = \frac{1}{\Omega_0} \sum_{v\vec{k}\vec{G}'} c_{v\vec{k}}(\vec{G} + \vec{G}') c_{v\vec{k}}^*(\vec{G})$$

Methods to solve eigenvalue problem for expansion coefficients

- For small number of expansion coefficients $c_{n\vec{k}}(\vec{G})$
say ~ 2000 , standard diagonalization procedure is used.
- For larger number of coefficients, the modern iterative techniques based on direct minimization of the total energy are used.

Commercial or open source (GNU-license) codes available

VASP (Univ. Vienna, com.), CASTEP (Accelrys, com.)

ABINIT (Univ. de Louvain, GNU), SPINOR (UCSB, GNU)

Empirical Pseudopotential Method

$$\sum_{\vec{G}'} \left[\frac{\hbar^2}{2m} (\vec{k} + \vec{G})^2 \delta_{\vec{G}, \vec{G}'} + V_{EMP}^{ps}(\vec{k} + \vec{G}, \vec{k} + \vec{G}') \right] c_{n\vec{k}}(\vec{G}) = \varepsilon_n(\vec{k}) c_{n\vec{k}}(\vec{G})$$

Non-local empirical pseudopotential

Fourier components are treated as empirical parameters

Very accurate band structure description of elemental (diamond), zinc-blende, wurtzite, and chalcopyrite structure semiconductors.

Particularly simple model

$$\sum_{\vec{G}'} \left[\frac{\hbar^2}{2m} (\vec{k} + \vec{G})^2 \delta_{\vec{G}, \vec{G}'} + V_{EMP,loc}^{ps}(\vec{G} - \vec{G}') \right] c_{n\vec{k}}(\vec{G}) = \varepsilon_n(\vec{k}) c_{n\vec{k}}(\vec{G})$$

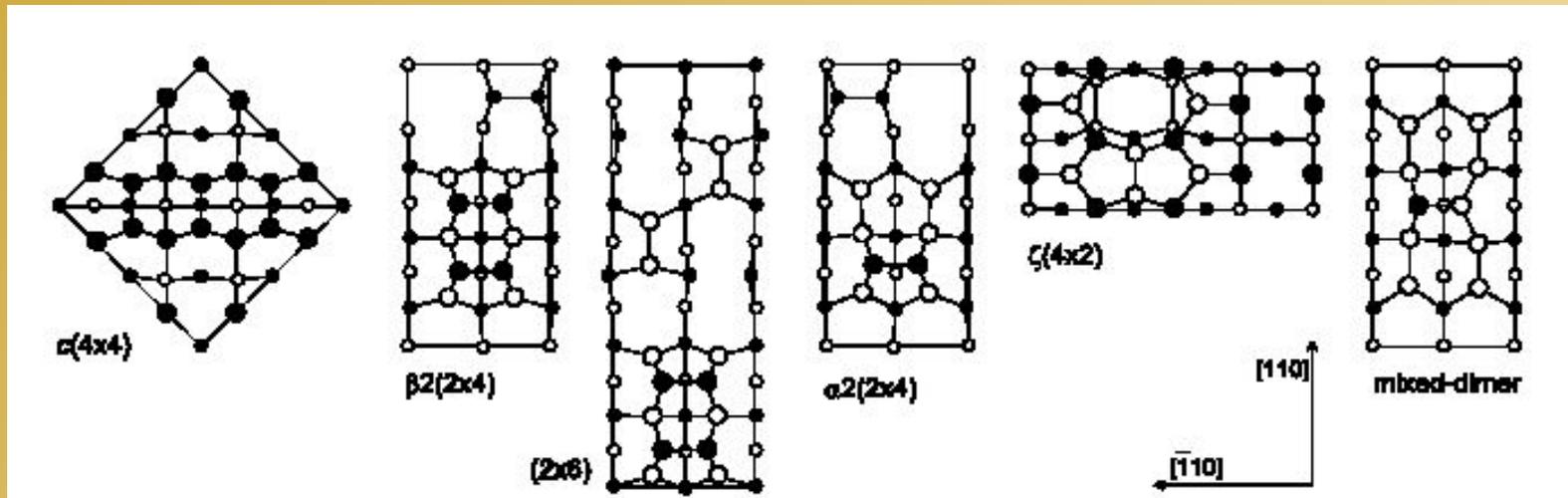
Local empirical pseudopotentials

Ten parameters give very reasonable description of the band structure

J. Chelikovsky & M. Cohen, "Electronic Structure and Optical Properties of Semiconductors", (Springer, Heidelberg, 1988)

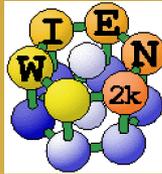
INTRODUCTION

Apart from the application aspect, much interest in the structure and stability of the polar (001) surface has also been caused by the rich variety of surface reconstructions which can be observed depending on the surface preparation. The GaAs(001) surface shows a $c(4\times 4)$ structure for As-rich conditions but changes its periodicity to $(2\times 4)/c(2\times 8)$ and finally $(4\times 2)/c(8\times 2)$ as the surface gets more cation rich.



The large number of surface structures observed on III-V (001) surfaces have early on prompted attempts to classify and understand them from a more general point of view. The determination of most stable reconstruction depending on element concentration in the surface layers needs for understanding of its interaction with adsorbates (metals, gases and complex hydrides systems).

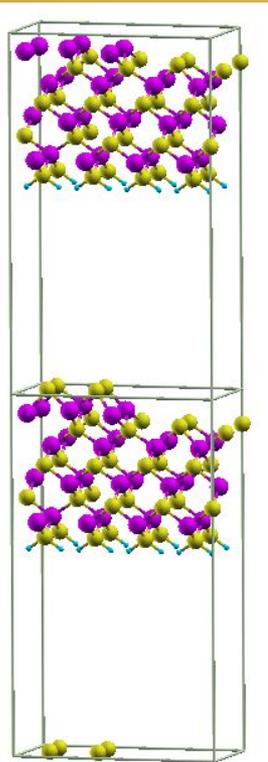
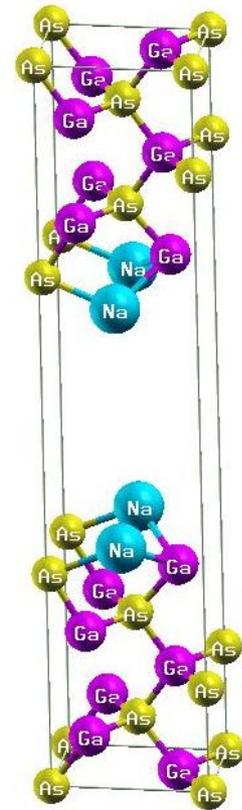
Computational details



WIEN2k

P. Blaha, K. Schwarz et al.
An augmented Plane Wave +
Local Orbitals Program for
Calculating Crystal Properties
<http://www.wien2k.at>

full-potential method

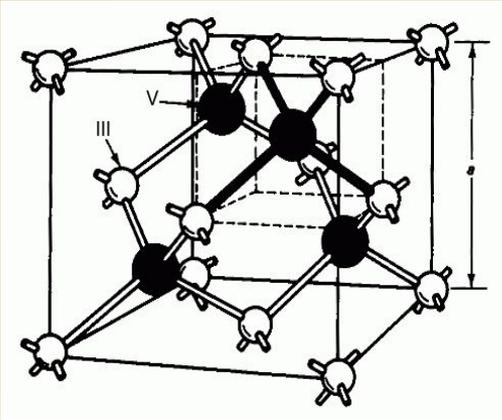


G. Kresse, J. Hafner et al.
Vienna Ab-initio Simulation
Package (VASP)
<http://cms.mpi.univie.ac.at>

pseudopotential approach

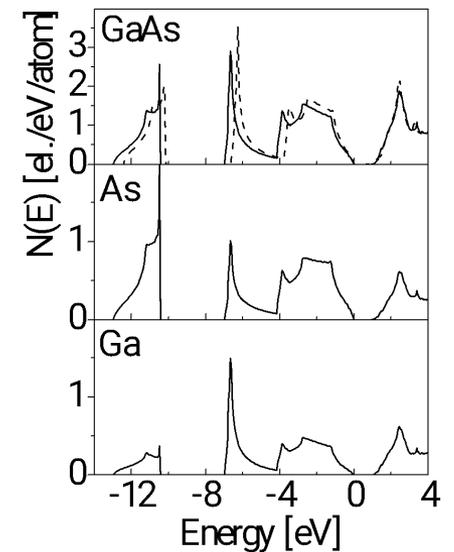
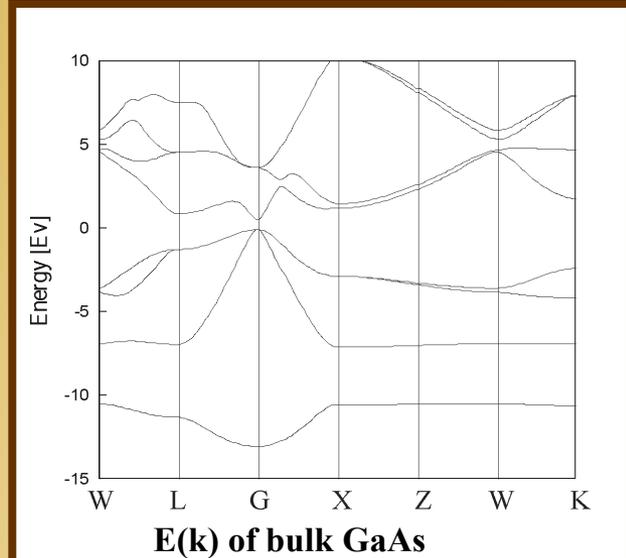


PSEUDOPOTENTIAL APPROACH (VASP)



The values of lattice parameters for different approximation of exchange-correlation effects

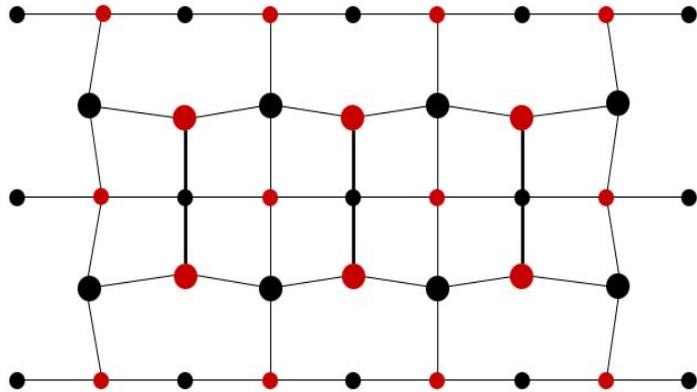
	a (Å)
Experiment	5.654
PAW-GGA	5.756
PAW-PBE	5.76
	5.78*
PAW-LDA	5.626
GGA-91	5.722
LDA	5.591
	5.52**
	5.56***



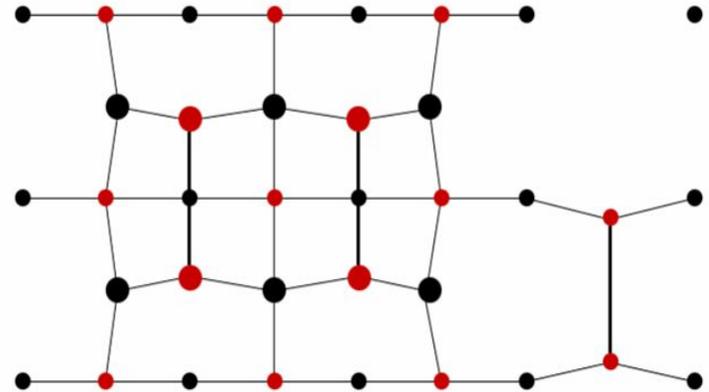
Total and local DOS of GaAs

- * - S.Lee, S. Lee, M. Scheffler. PRB 69, 125317 (2004) (FHI)
- ** - G. Qian, M. Martin, D.Chadi. PRB 37, 1303 (1988)
- *** - N. Moll, A.Kley, M. Scheffler. PRB. 54, 8844 (1996) (FHI)

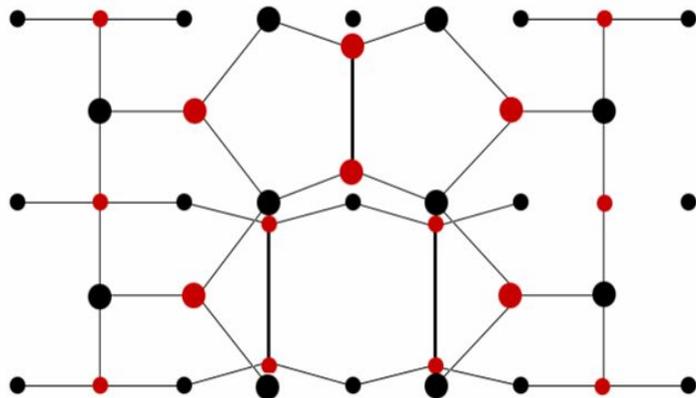
Models of Ga-terminated GaAs(001)-(4x2) surface



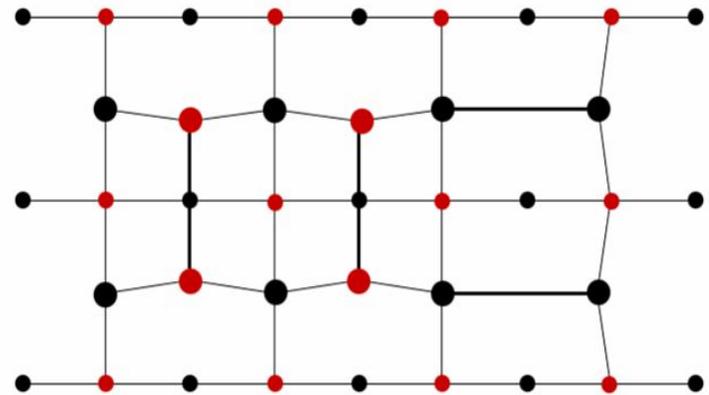
GaAs(001) β (4x2)



**GaAs(001)
 β_2 (4x2)**

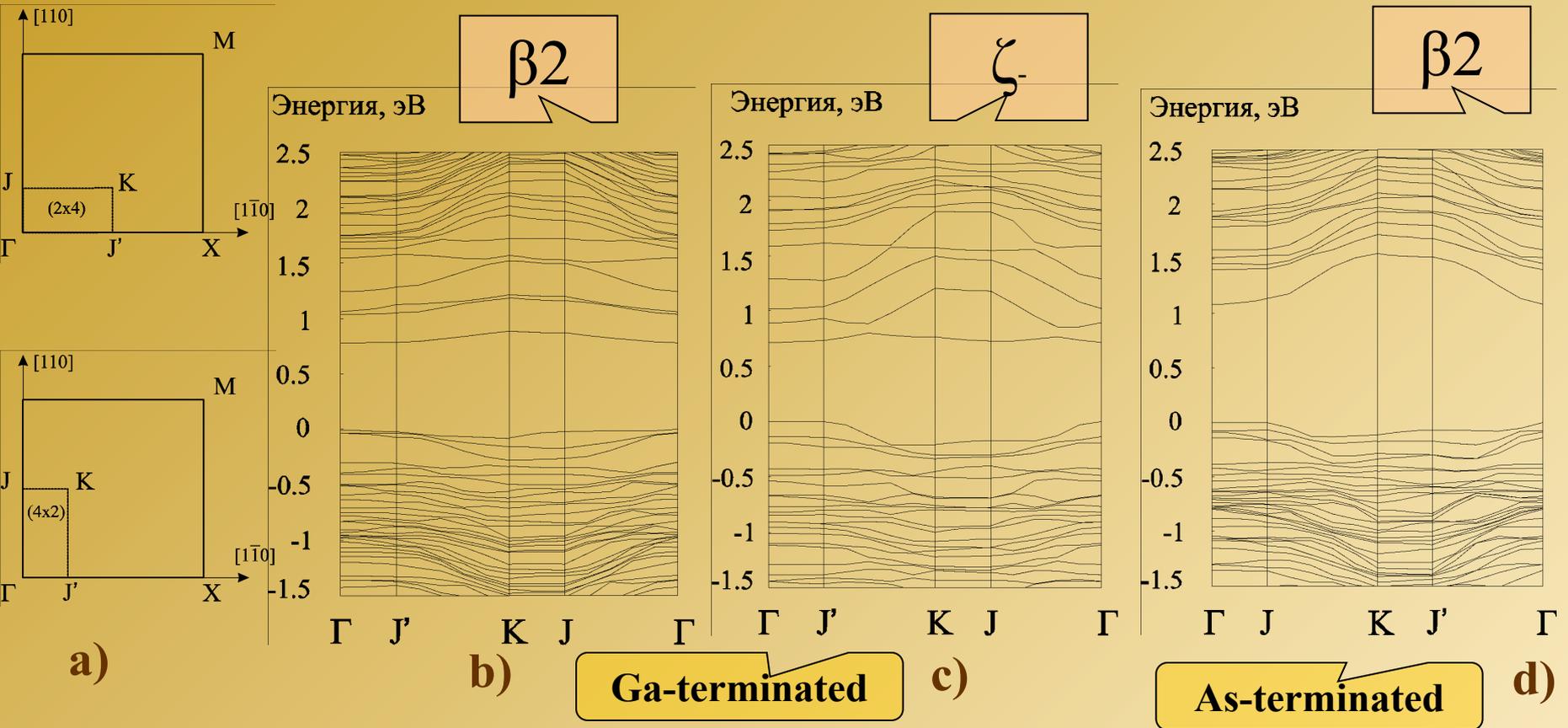


GaAs(001) ζ (4x2)



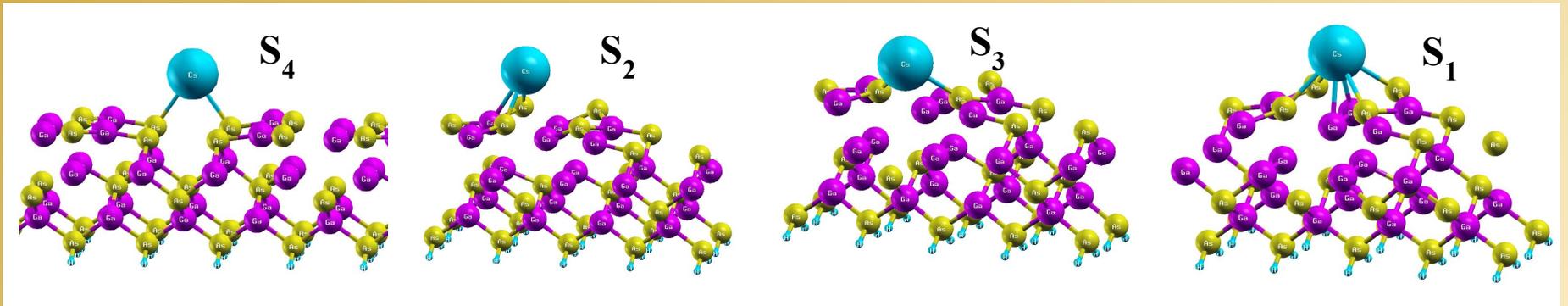
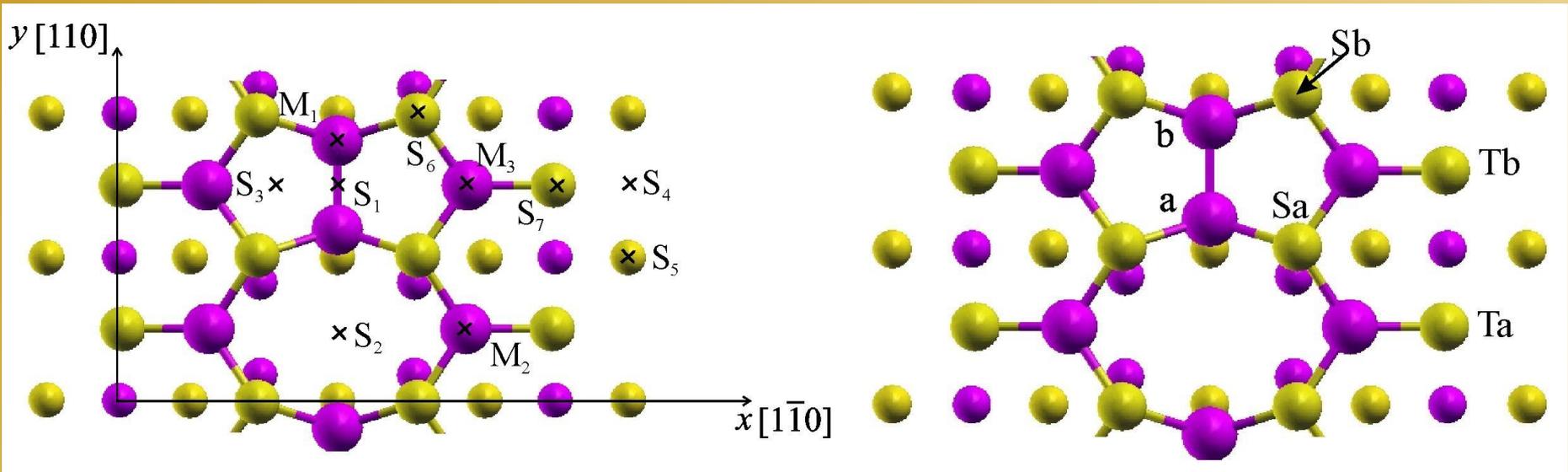
GaAs(001) α (4x2)

ELECTRONIC STRUCTURE



Two dimensional Brillouin zone (a) and $E(k)$ for Ga-terminated $\beta 2$ - (b) and ζ -GaAs(001)-(4x2) (c), in comparison with As-terminated $\beta 2$ -GaAs(001)-(2x4) (d).

Adsorption on ζ -GaAs(001)-(4 \times 2)



The position of adsorbates (cesium and chlorine) on surface ζ -GaAs(001)-(4 \times 2) after relaxation

Adsorption energies of Cs and Cl on ζ -GaAs(001)-(4 \times 2) surface

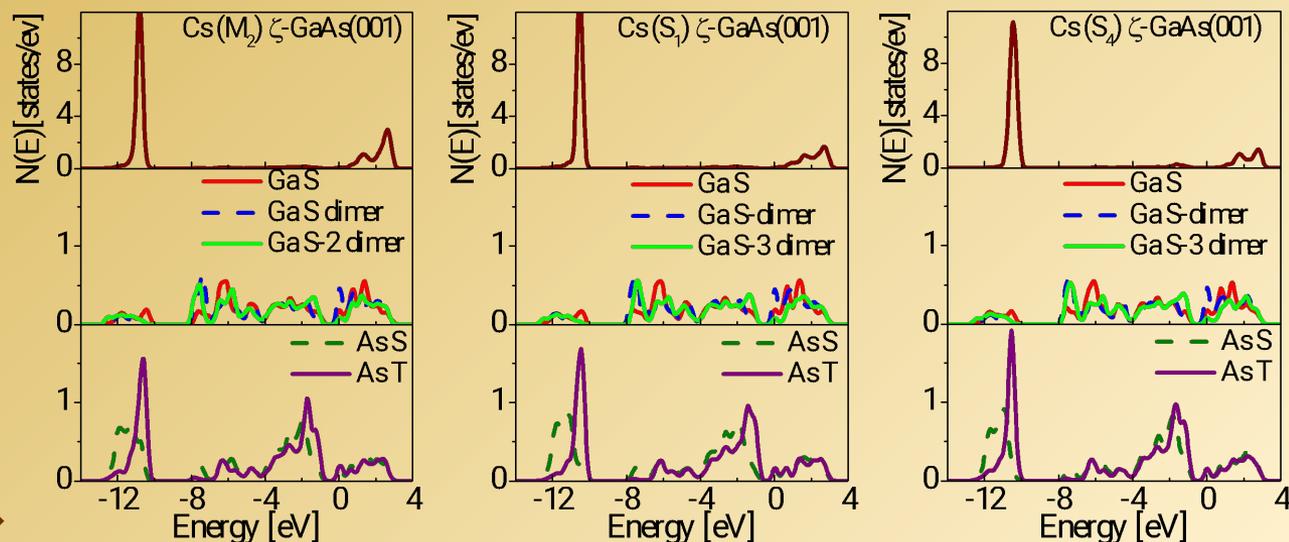
More preferable site

Cs (Cl)	M_1	M_2	M_3	S_1	S_2	S_3	S_4	S_5	S_6	S_7
E_{ads} (Cs) VASP	-1.81	-1.79	-1.77	-1.91	-2.13	-1.80	-2.33	-2.57	-1.60	-1.93
E_{ads} (Cs) SIESTA		-1.33	-1.68	-1.38	-1.94	-1.32	-	-2.10	-1.76	-
E_{ads} (Cl) VASP	-2.86	-2.84	-2.56	-2.64	-2.06	-1.70	-1.80	-	-	-
FHI *	-2.87	-2.74	-2.48	-2.41	-2.01	-2.02	-1.89	-	-	-

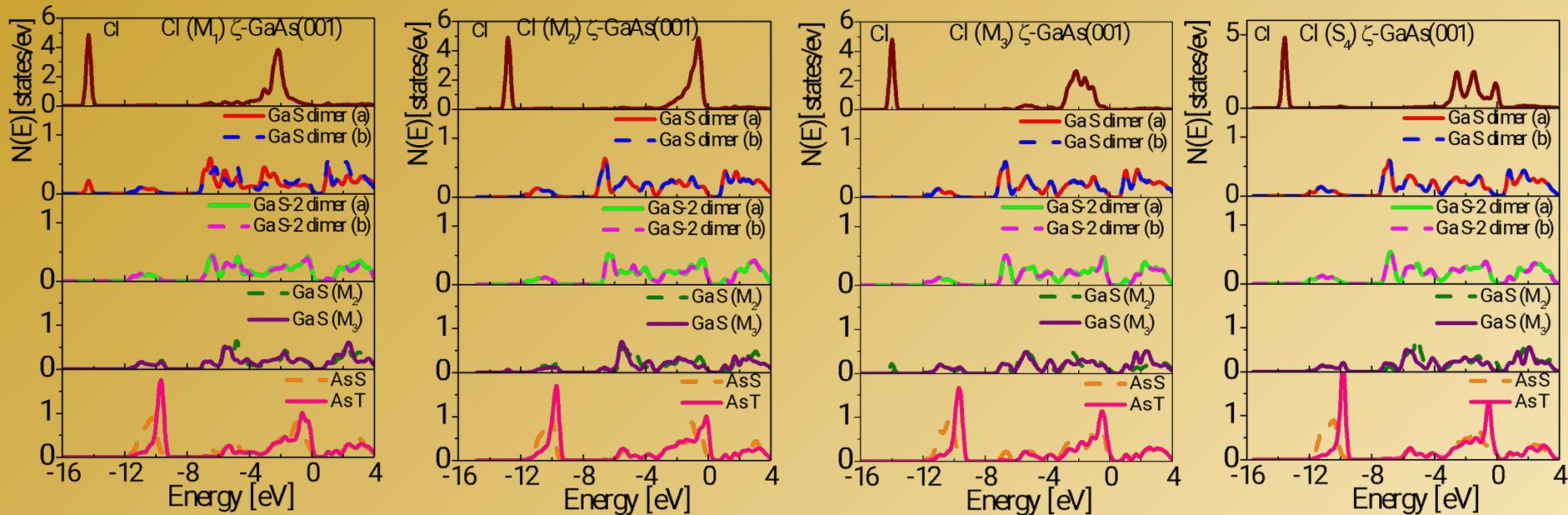
* S.M. Lee, S.H. Lee, M. Scheffler. Phys.Rev., B69, 125317 (2004).

Adsorption of cesium is due to the energy gain for different adsorbates sites and their number on the structural unit cell

Локальные ПЭС для Cs на ζ -GaAs(001)-(4 \times 2)

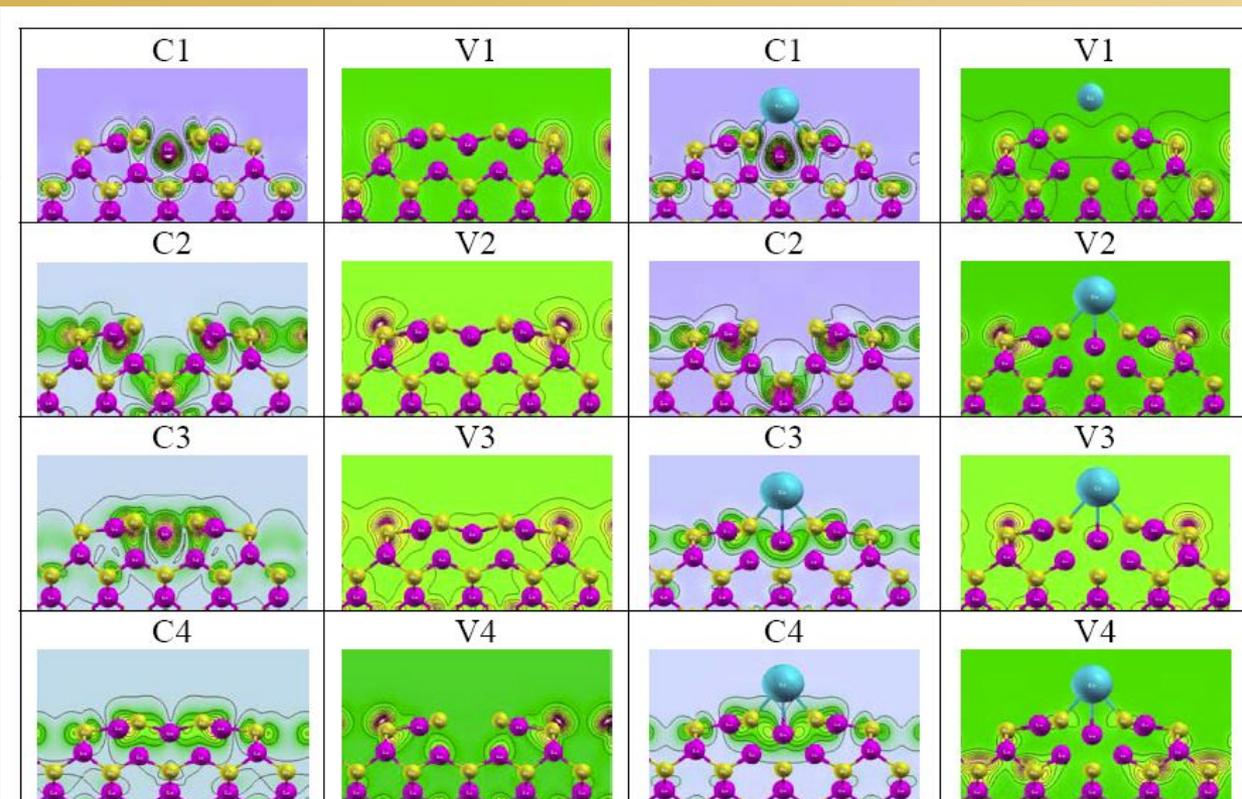
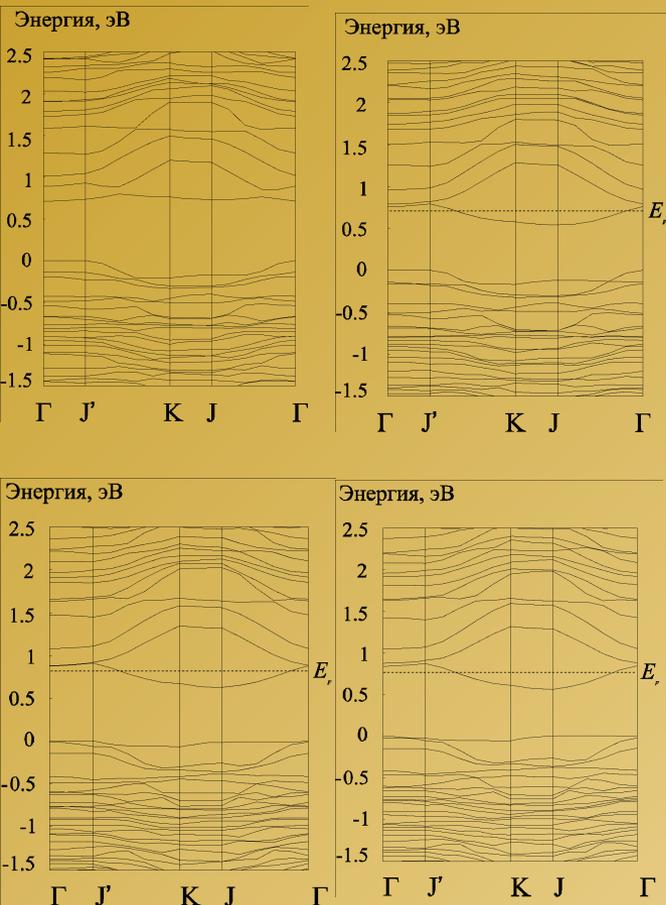


Chlorine adsorption- local DOS for Cl - ζ -GaAs(001)-(4 \times 2)



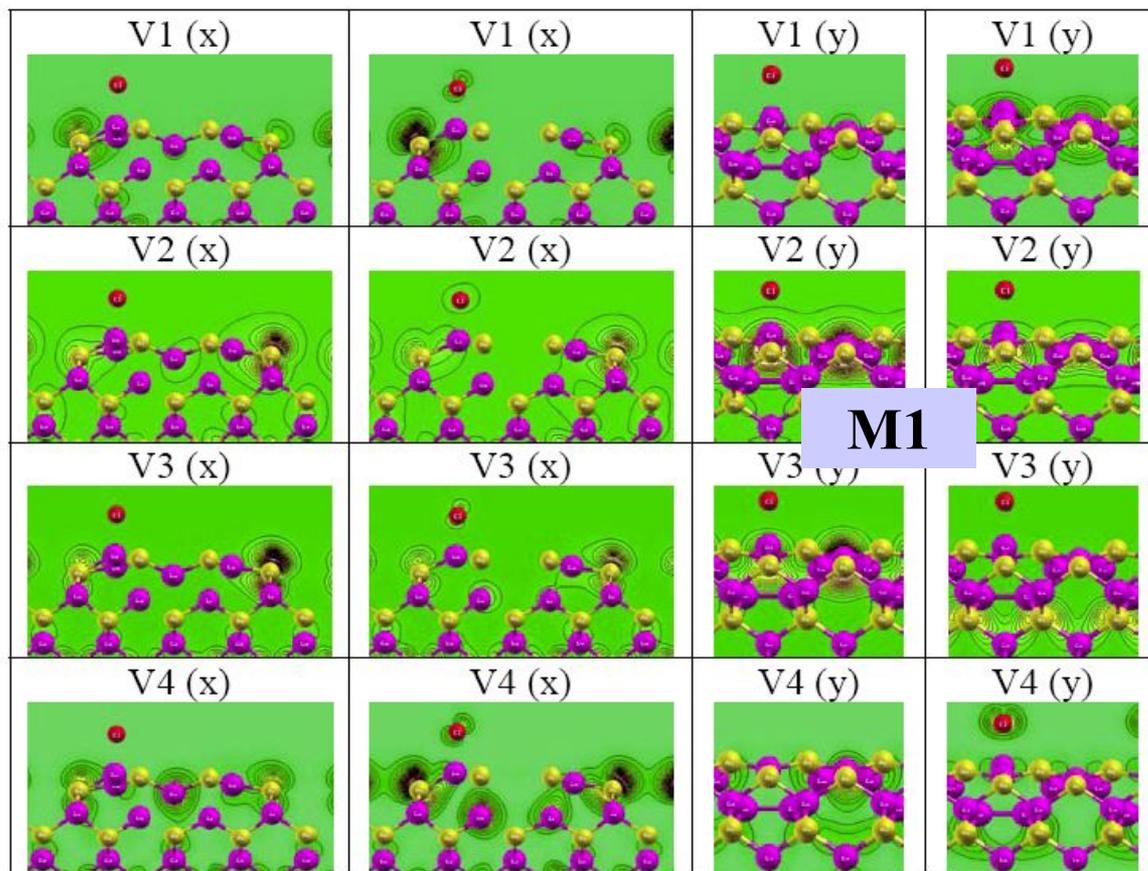
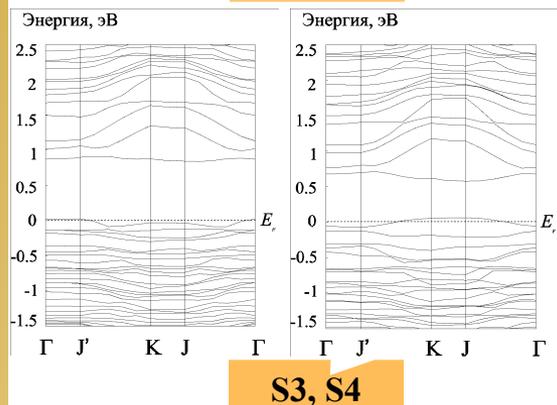
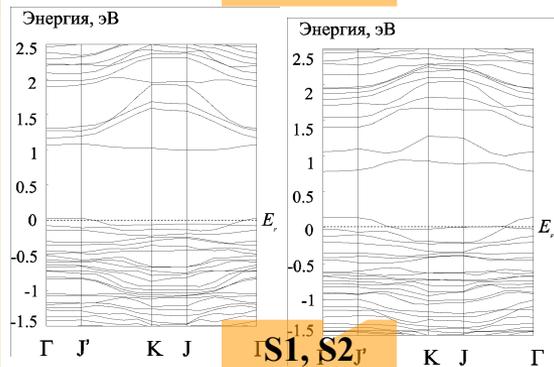
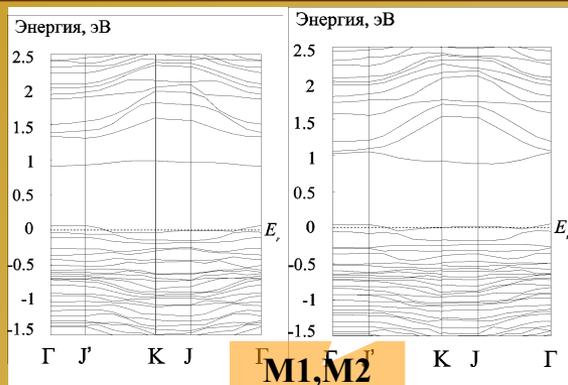
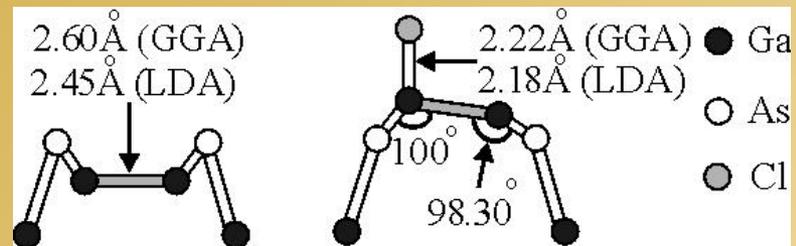
Strong hybridization of As and Ga p-states with Cl p-orbitals together with weak s-s hybridization is observed. Local DOS of chlorine depend strongly on its positions on surface. The ionic contribution increases in the interaction of Cl with substrate.

Cs on Ga-terminated ζ -GaAs(001)-(4 \times 2)



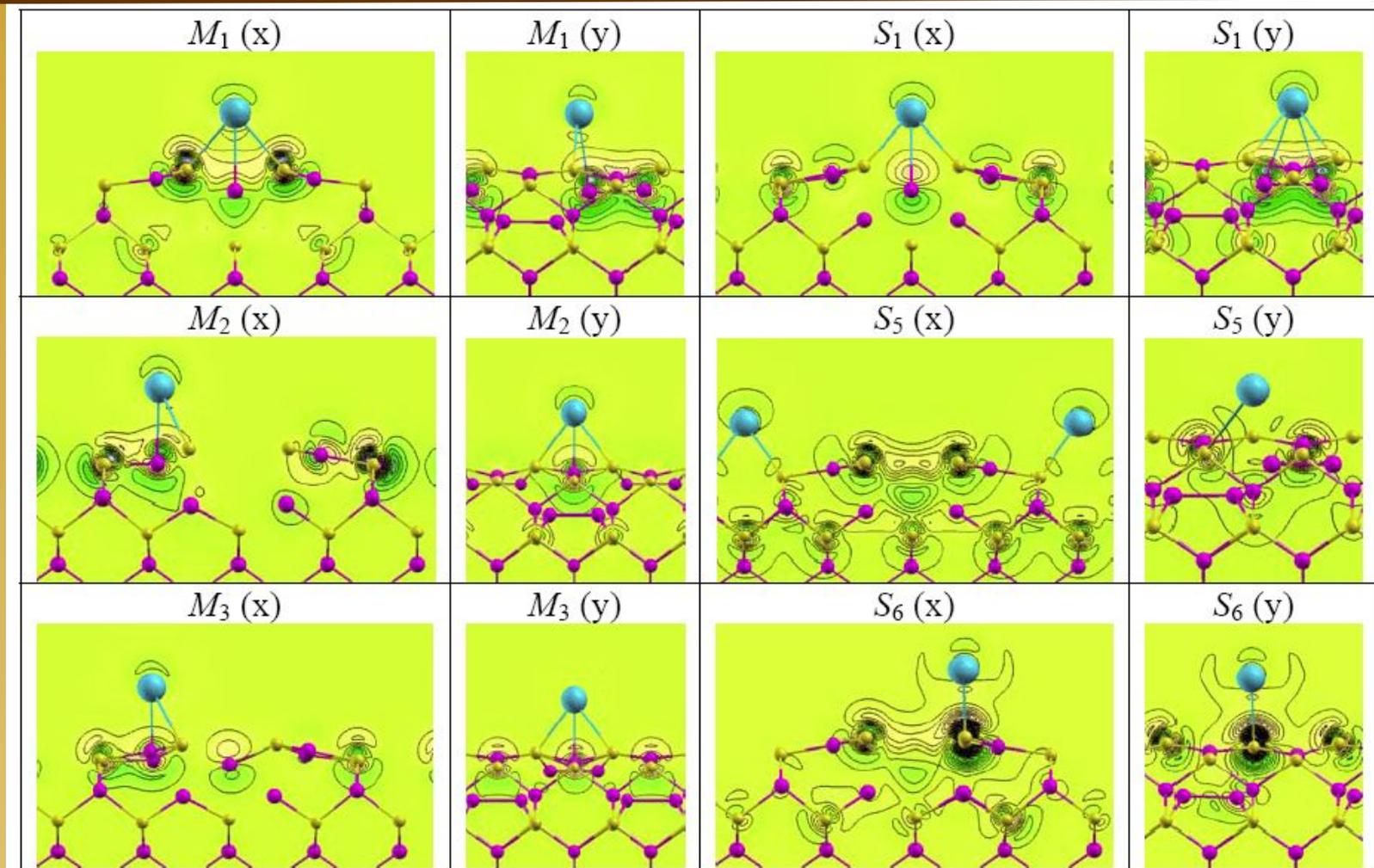
$E(k)$ for clean surface and Cs in M_1 , S_4 , S_5 sites and orbital composition of surface states for clean surface and Cs in M_1

Cl on Ga-terminated ζ -GaAs(001)-(4×2)



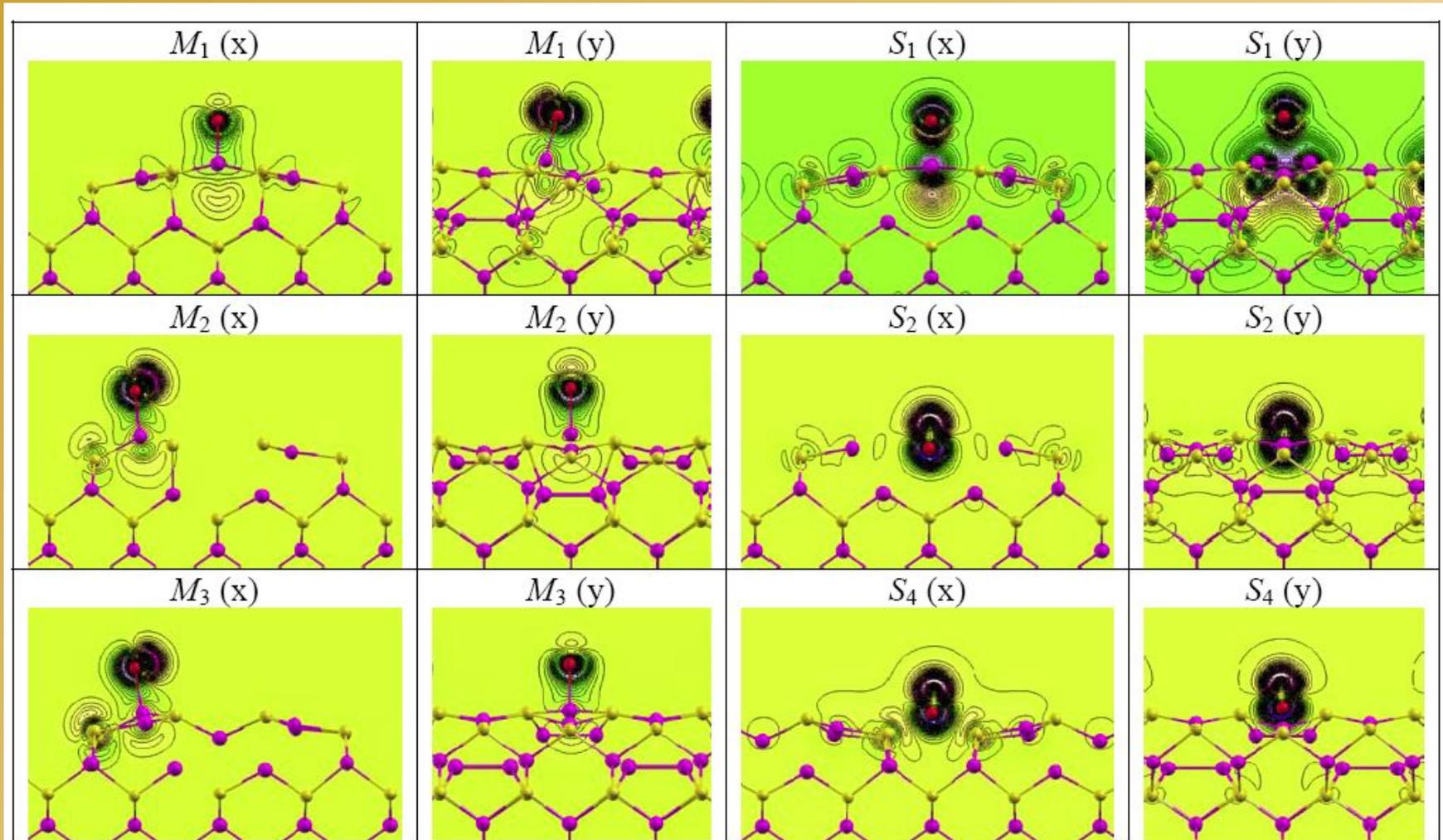
The orbital composition of wave function and their localization on atoms for M1 position

The charge difference for Cs in $M1 - M3$, $S1$, $S5$, $S6$ positions on Ga-terminated ζ -GaAs(001)-(4 \times 2). X corresponds the cross section in (110) plane, Y -(1-10) plane. Yellow and green colors mean the region with depletion and accumulation of electrons, respectively



$$\Delta\rho(r) = \rho_{GaAs}(r) + \rho_{Cs}(r) - \rho_{Cs/GaAs}(r)$$

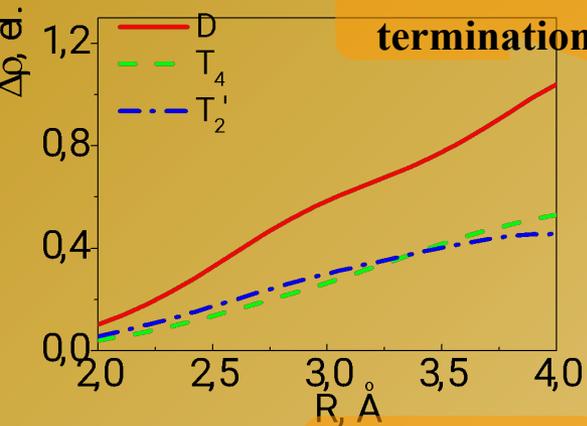
The charge difference for Cl in $M1 - M3$, $S1$, $S5$, $S6$ positions on Ga-terminated ζ -GaAs(001)-(4 \times 2). X corresponds the cross section in (110) plane, Y -(1-10) plane. Yellow and green colors mean the region with depletion and accumulation of electrons, respectively



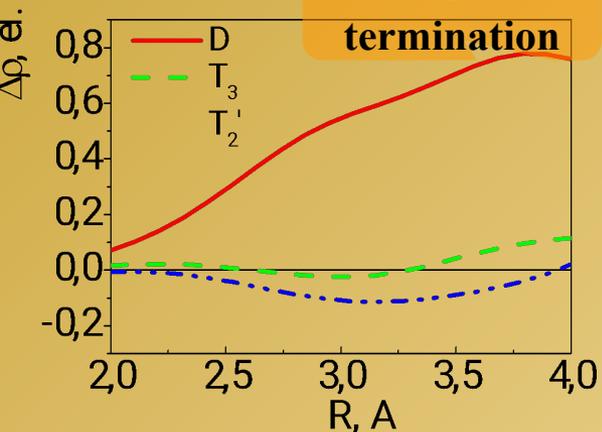
$$\Delta\rho(r) = \rho_{GaAs}(r) + \rho_{Cs}(r) - \rho_{Cs/GaAs}(r)$$

Charge transfer

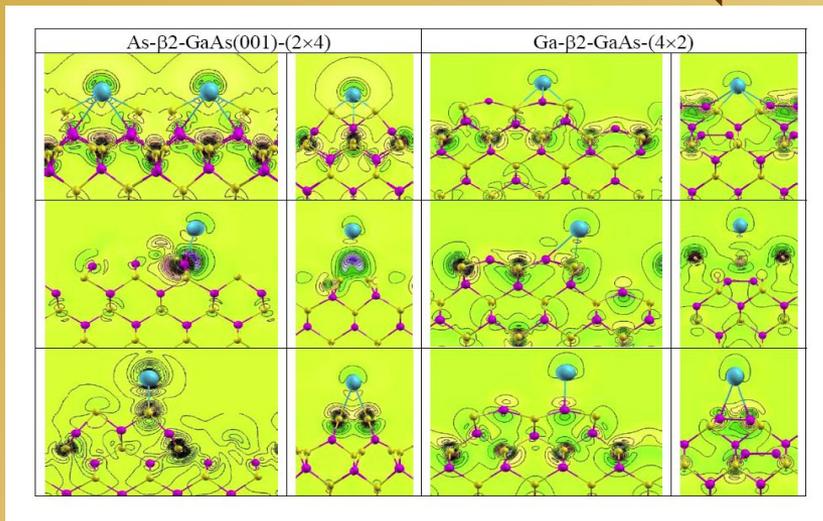
Ga-termination



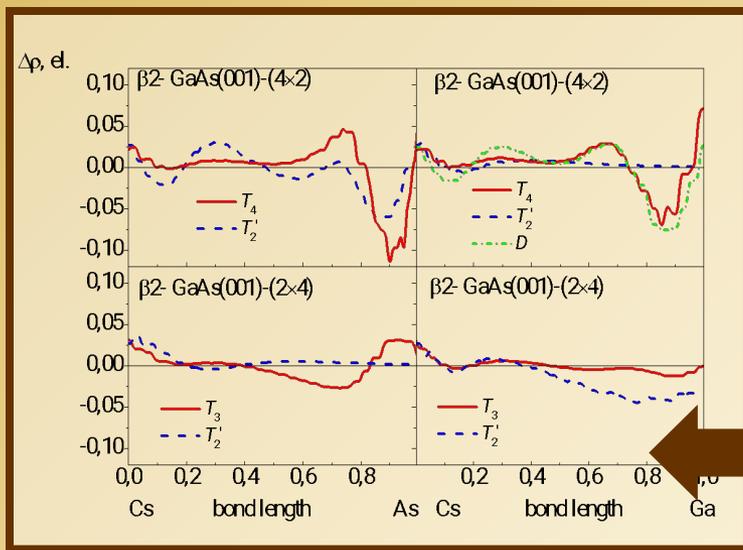
As termination



Integrated Cs valence charge difference as function of integration radius for different adsorption sites



The valence charge difference shows the charge redistribution in the surface layers with dipole formation



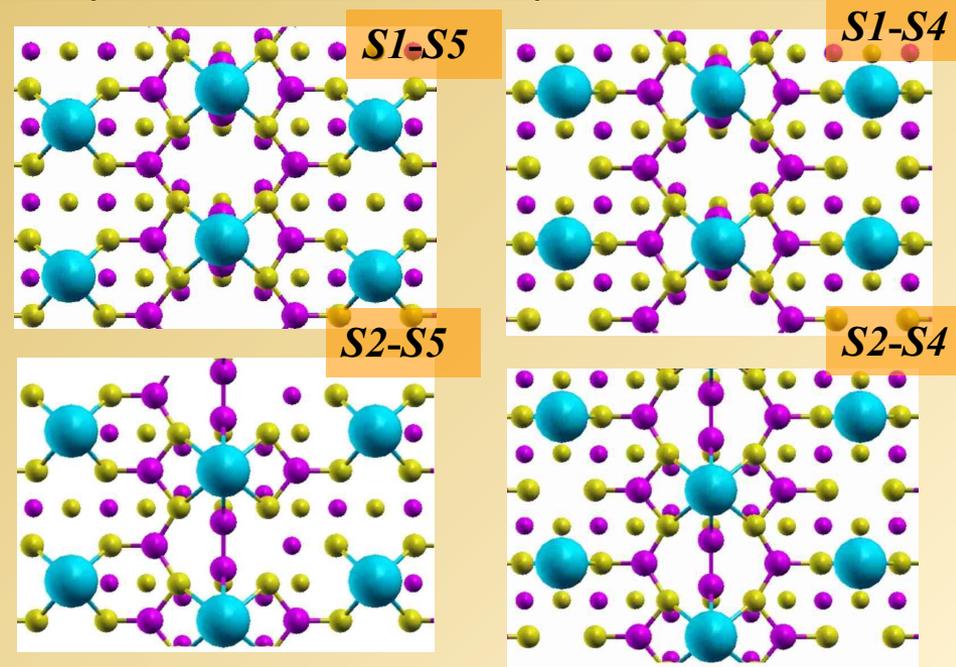
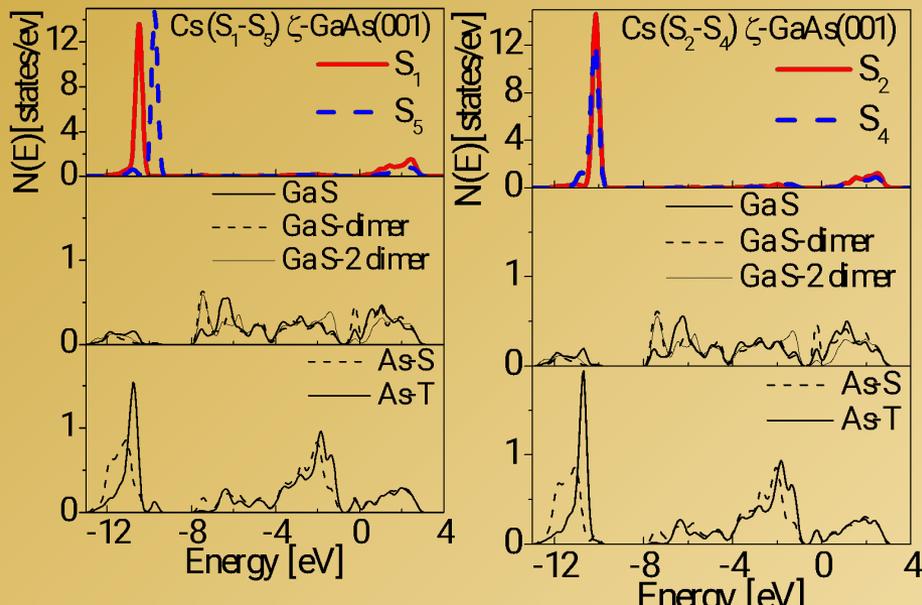
Electrons accumulation region along Cs-Ga bonding in T_2' site expresses more pronounced in comparison with T_3 -site.

The distribution of valence charge difference along binding with Cs nearest atoms: As (left) and Ga (right) for two interface.

Cs adsorption on ζ -GaAs(001)-(4 \times 2) (coverage increase)

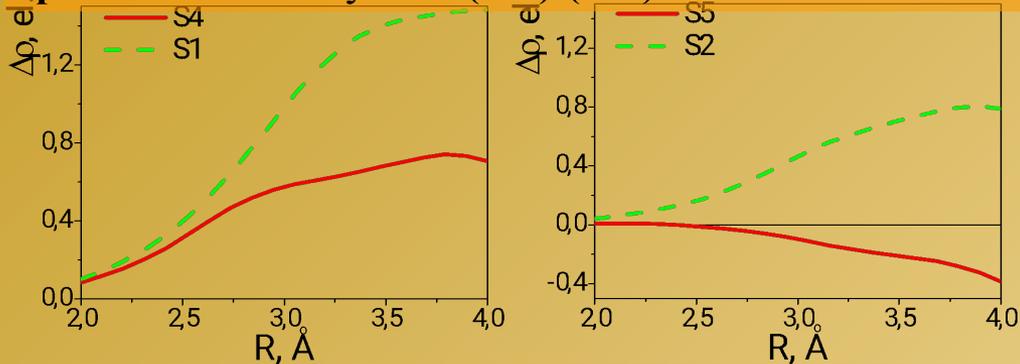
The adsorption energies of Cs for S_1 and S_2 sites on ζ -GaAs(001)-(4 \times 2) with adsorbed Cs in S_4 and S_5

S_1 - S_5		S_2 - S_5		S_1 - S_4		S_2 - S_4	
-1.71		-1.96		-1.66		-1.93	
S_1	-1.97	S_2	-2.13	S_1	-1.91	S_2	-2.13
S_5	-2.57	S_5	-2.57	S_4	-2.33	S_4	-2.33



Charge transfer

Integrated valence charge difference as a function of spheres radius for ζ -GaAs(001)-(4 \times 2) with two Cs atoms



The values of work function (eV) for S_4 - S_1 , S_4 - S_2 , S_5 - S_1 and S_5 - S_2 geometries in comparison with Cs adsorption in S_4 and S_5 sites and their changes in respect to clean surface

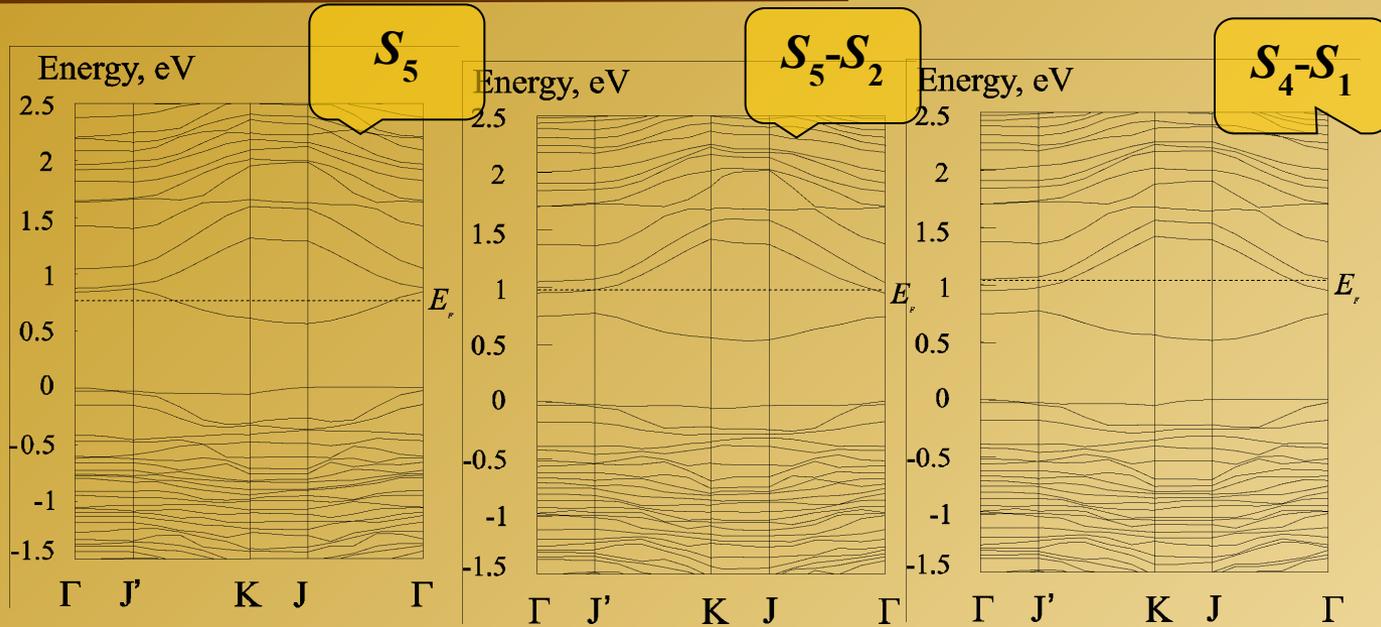
	ϕ	$\Delta\phi$		ϕ	$\Delta\phi$
S_4 - S_1	3.04	-1.50	S_4	3.57	-0.97
S_4 - S_2	3.13	-1.40			
S_5 - S_1	3.14	-1.40	S_5	3.66	-0.88
S_5 - S_2	3.22	-1.32			

Sites dependent changes in the work function is shown in our calculations

The increase of Cs coverage up to 0.25 ML on ζ -surface leads to increase of charge transfer from Cs to substrate. Apart the factors mentioned for one atoms adsorption the role of lateral Cs-Cs interaction can influence adsorption energies.

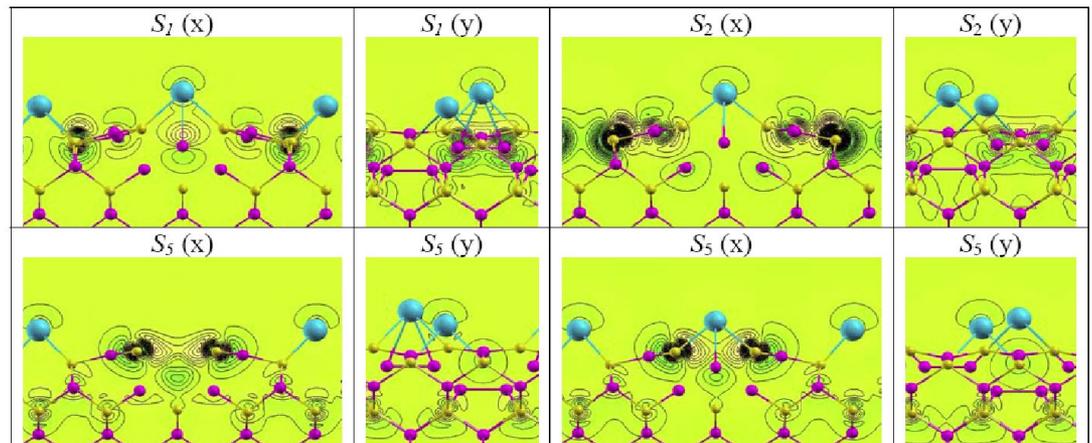
The energy of ionization (I) for β 2-GaAs(001) is 4.86 eV for Ga-terminated surface and 5.38 eV (5.43, 5.61 –other calculation, 5.5 eV –experiment) for As-terminated surface. $I \approx 4.9$ eV for ζ -GaAs(001)-(4 \times 2)

Cs on ζ -GaAs(001)-(4×2)

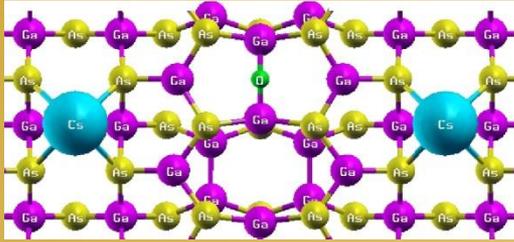
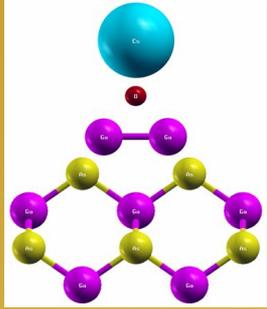


E(k) for ζ -GaAs(001)-(4×2) with Cs adsorbed in S_5 site (a), with two Cs atoms in S_5 and S_2 (b) as well as in S_4-S_1 (c)

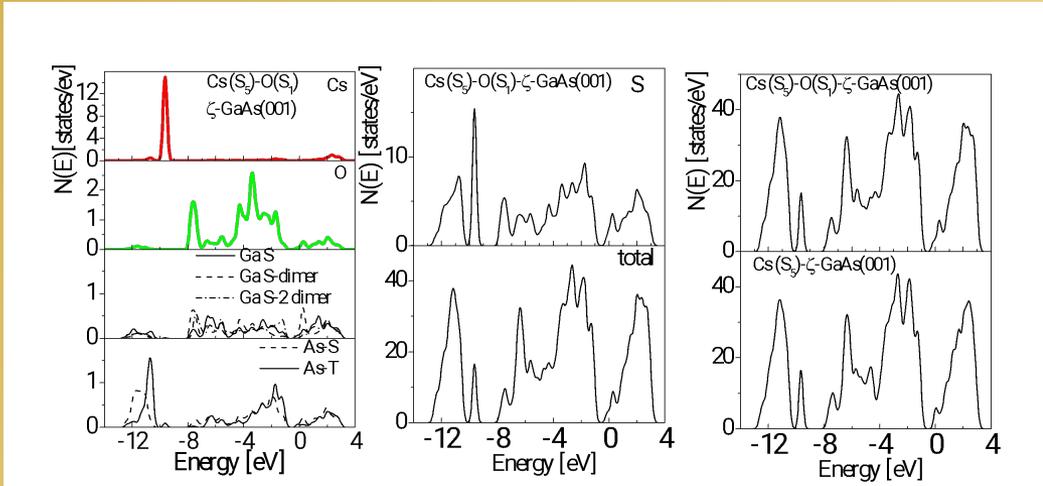
The decrease of work function at higher Cs concentration is due to filling of the conduction band edge at the addition of the second atom



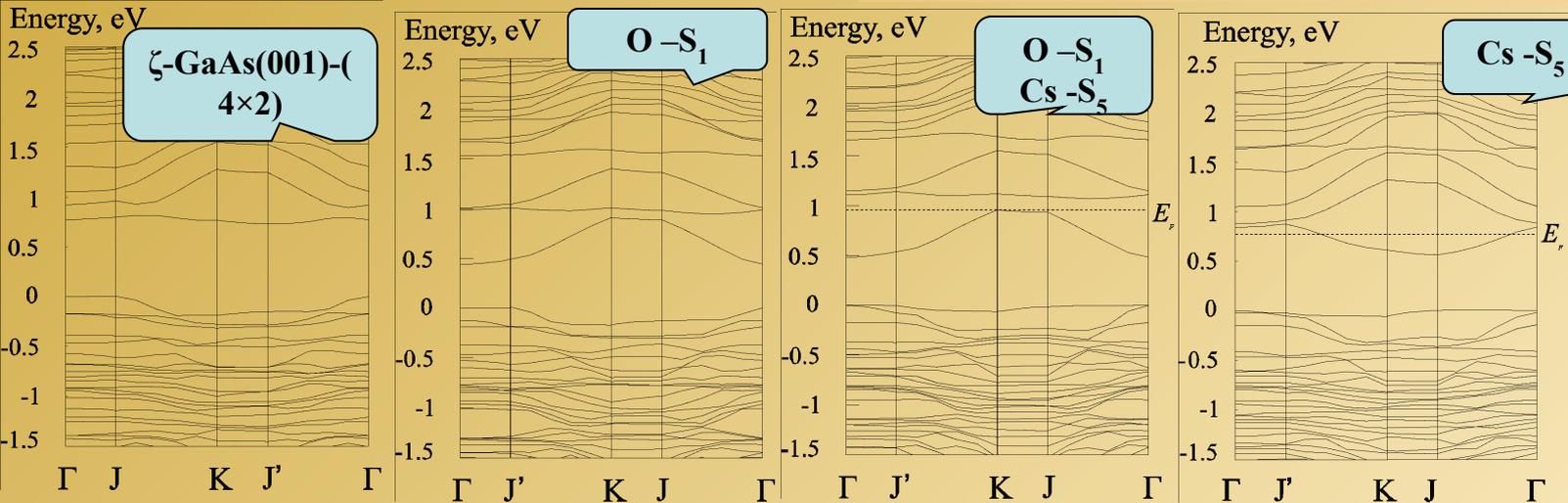
Electronic structure of (Cs-O)/GaAs(001) interface



Models of (Cs-O)/GaAs(001) interface



Total, local surface DOS of ζ -GaAs(001)-(4x2) with adsorbed oxygen and cesium

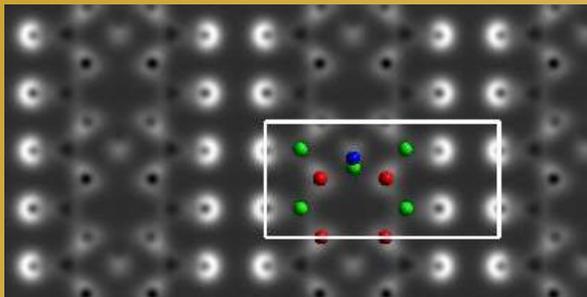


The change of $E(k)$ upon adsorption

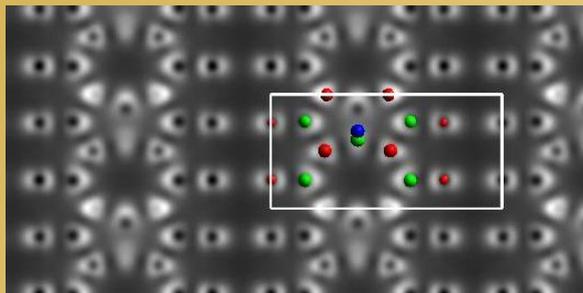
S_1 - S_5 geometry does not influence significantly the work function. The adsorption of Cs and O in dimer bridge S_1 position decreases the value of the work function by ~ 0.3 eV. So the formation of dipole oriented perpendicular to surface at thin coverage leads to better quantum effect.

Calculated STM images of filled and empty states: I adsorbed in the M_1 position on ζ -GaAs(001)-(4x2)

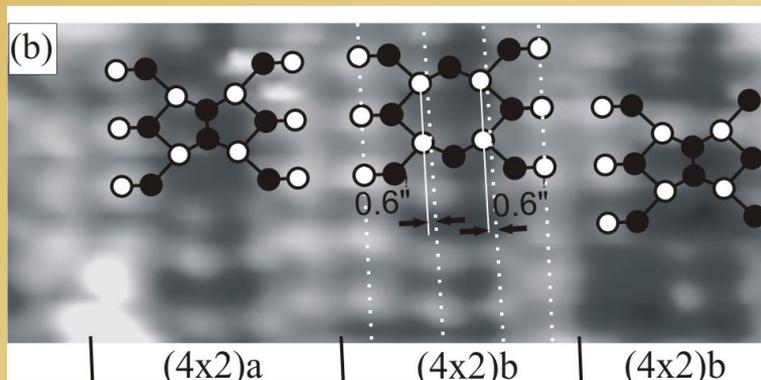
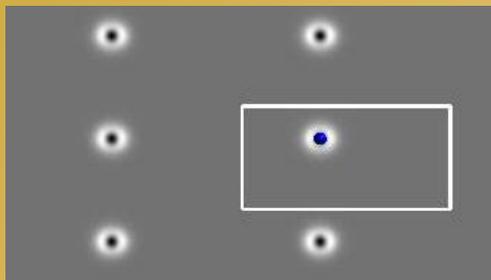
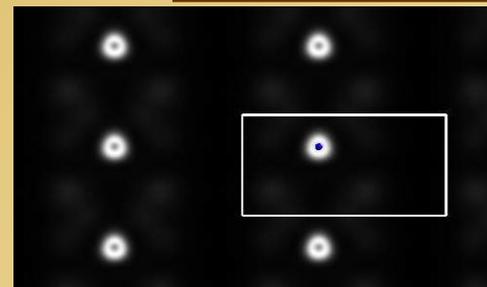
$U = -1.5$ V (filled)



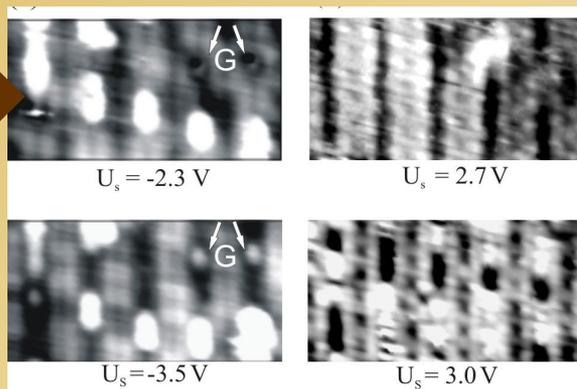
$U = 1.8$ V (empty)



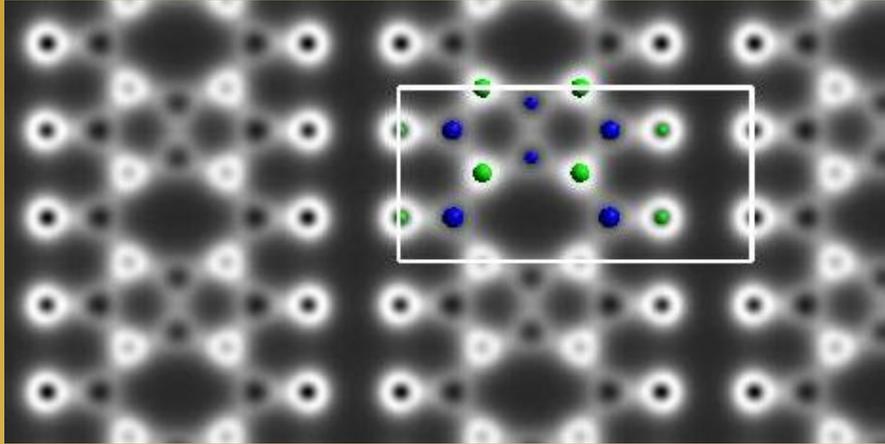
← calculation



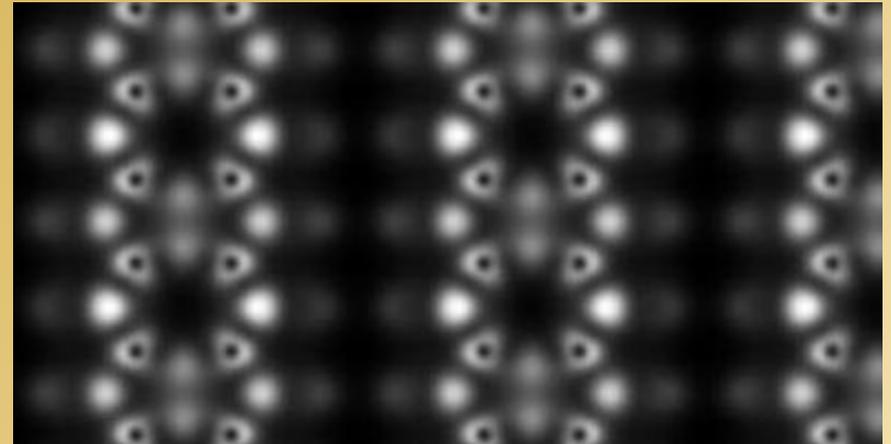
Experiment by Vedeev A.A. and
Eltsov K.H. JETP Letters, 2005.
– V.82. – P.46 –51.



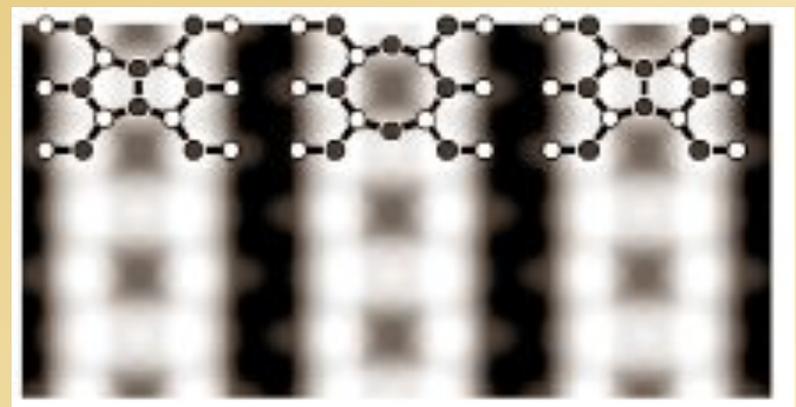
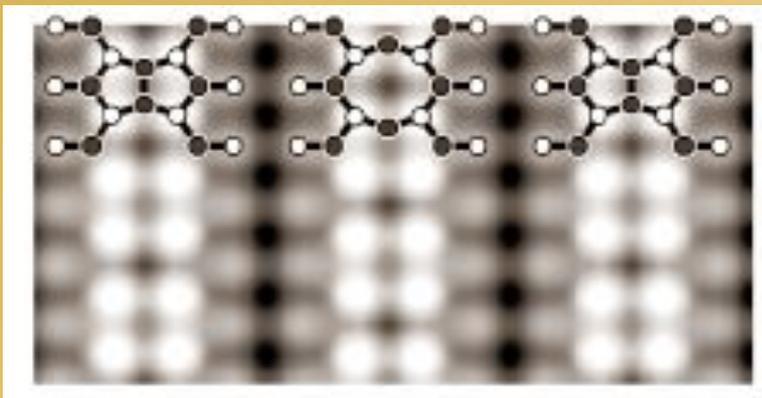
Calculated STM images: clean ζ -GaAs(001)-(4 \times 2)



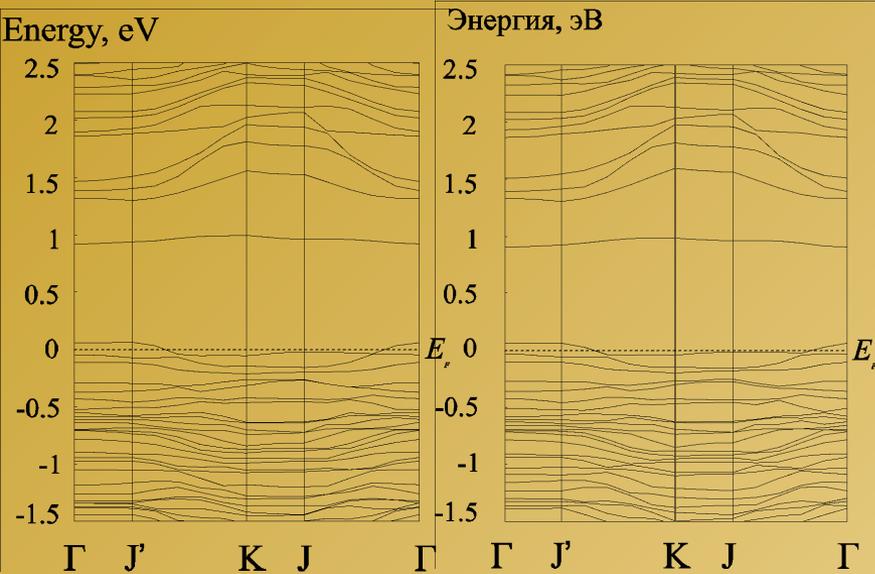
U = -1.5 V (filled)



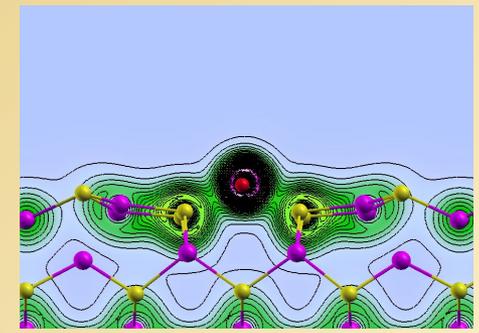
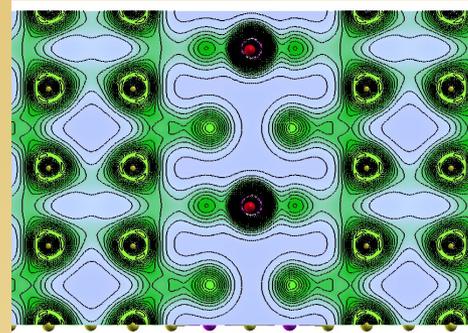
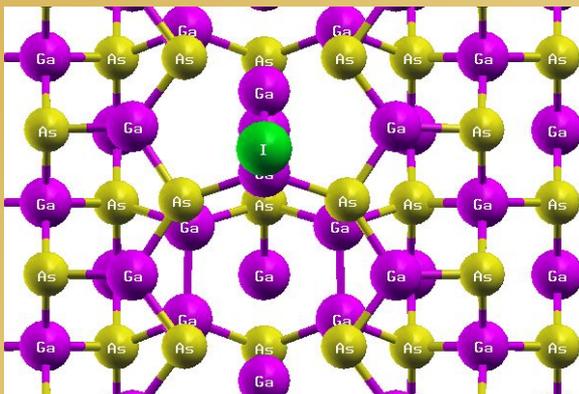
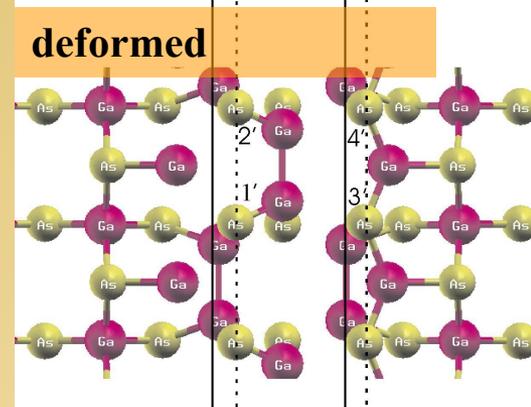
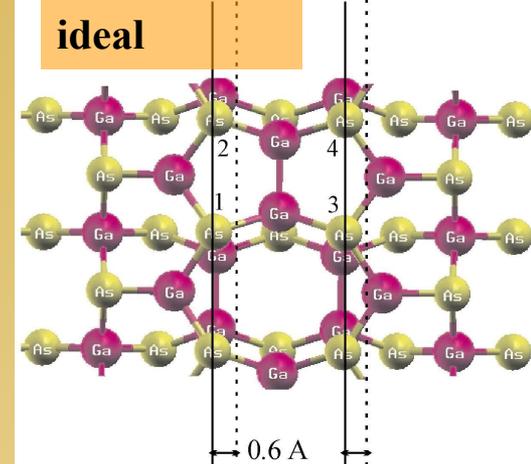
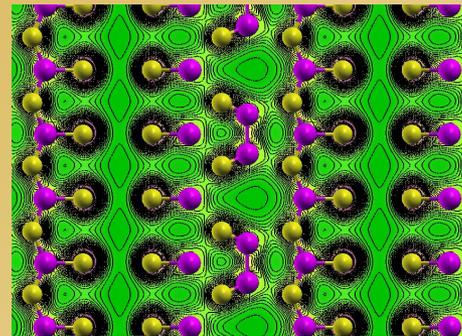
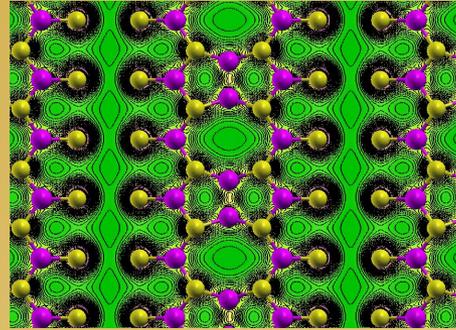
U = 1.8 V (empty)



I adsorption on ζ -GaAs(001)-(4×2)



$E(k)$ of I/GaAs(001) (left) and Cl/GaAs(001) (right) in M_1



S_4 position can be occupied at increased concentration of halogens