Surface relaxation and band structures

Atomic Geometry , Energetics & Electronic Structure of GaAs (110) surface

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Workshop on
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Motivation

God made solids…..

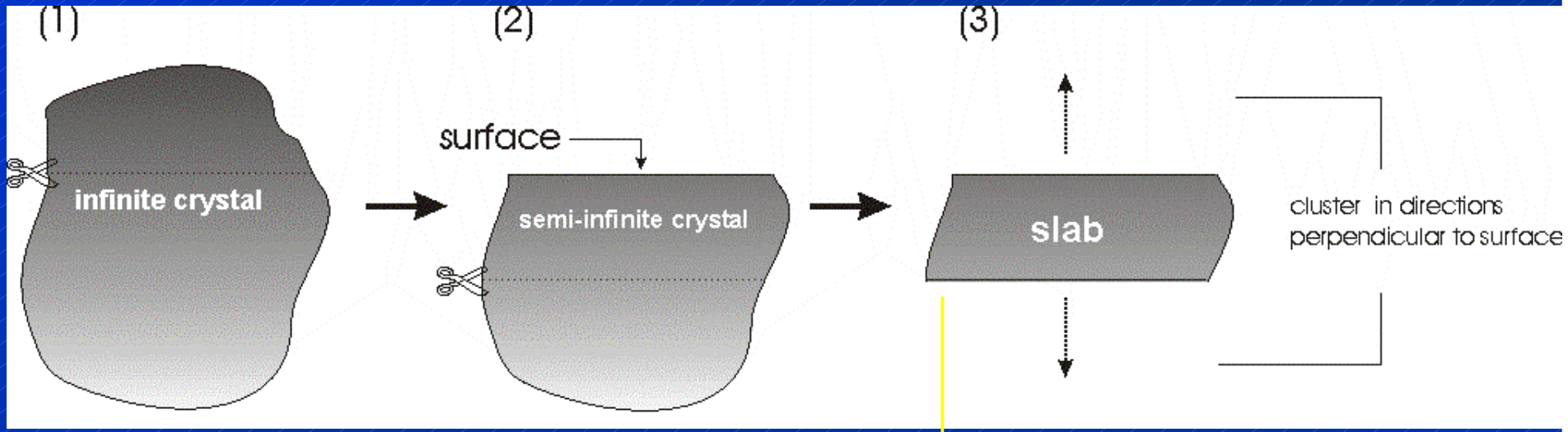
…….but surfaces were the work of the devil.

W. Pauli

Why surfaces?

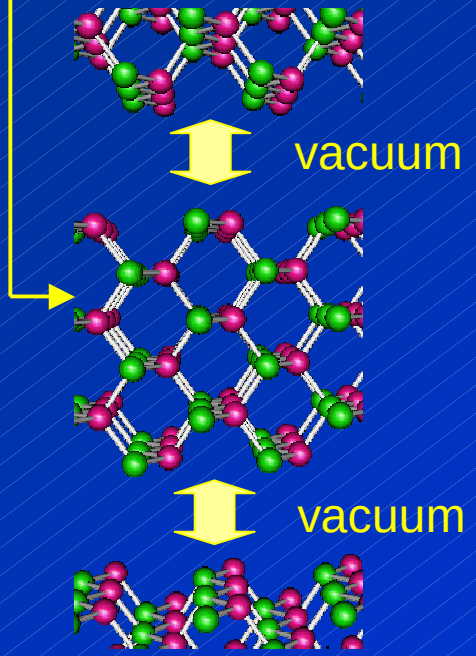
Why GaAs(110)?

Slab approach

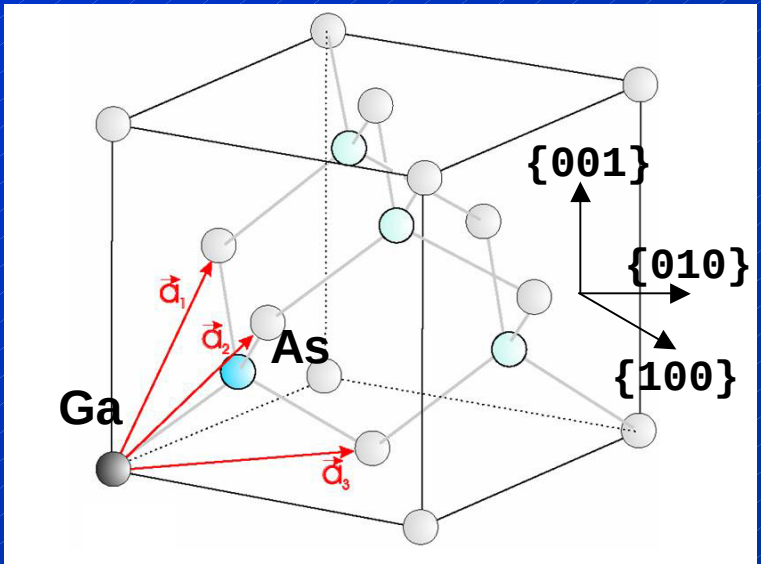


Explore:

- surface energy
- atomic geometry
- electronic structure

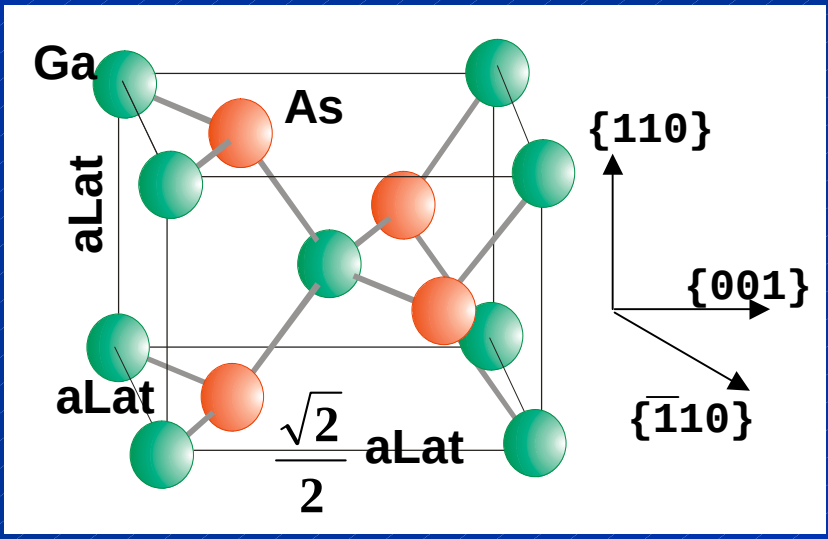


GaAs (110) surface unit cell



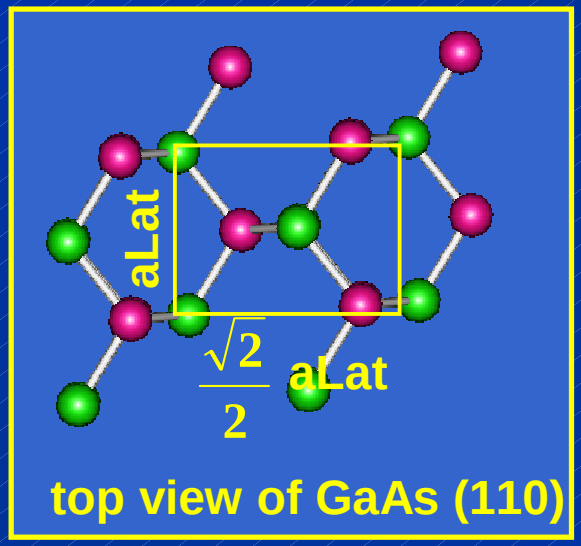
Primitive fcc cell

- 2 atoms per cell



tetragonal cell

- 4 atoms per unit cell
- building (110) surface




```
cell = [ aLat * [ 1, 0          , 0 ],
         aLat * [ 0, sqrt(2)/2  , 0 ],
         aLat * [ 0, 0          , 1 ] ];
```

primitive vectors of the tetragonal cell

GaAs (110) surface unit cell

primitive vectors
+
high symmetry k-points

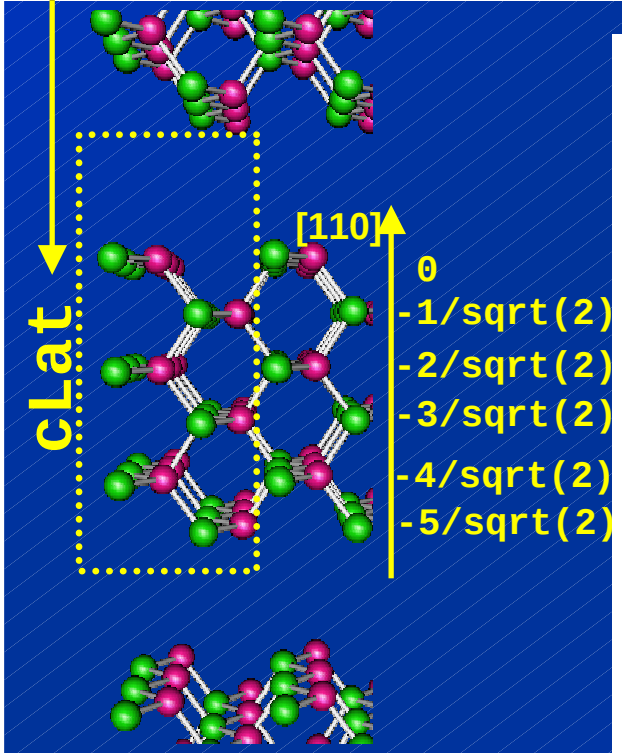
input.sx

```
aLat = 10.47;
cLat = 37.017; \\ 6L slab + 4L vacuum

structure {
    include "../structures/GaAs110.sx";
    include "../structures/GaAs_110noH.sx";
}
```

GaAs110.sx

```
cell = [ aLat * [ 1, 0           , 0 ],
         aLat * [ 0, 1/sqrt(2)   , 0 ],
         cLat * [ 0, 0           , 1 ] ];
```

atomic coordinates



GaAs_110noH.sx

```
species {
  include species_1;
  atom { coords = aLat/2 * [ 0, 0         ,  0          ]; }
  atom { coords = aLat/2 * [ 1, 1/sqrt(2), -1/sqrt(2) ]; }
  atom { coords = aLat/2 * [ 0, 0         , -2/sqrt(2) ]; }
  atom { coords = aLat/2 * [ 1, 1/sqrt(2), -3/sqrt(2) ]; }
  atom { coords = aLat/2 * [ 0, 0         , -4/sqrt(2) ]; }
  atom { coords = aLat/2 * [ 1, 1/sqrt(2), -5/sqrt(2) ]; }
  }
species {
  include species_2;
  atom { coords = aLat/2 * [ 1/2, 1/sqrt(2),  0          ]; }
  atom { coords = aLat/2 * [ 3/2, 2/sqrt(2), -1/sqrt(2) ]; }
  atom { coords = aLat/2 * [ 1/2, 1/sqrt(2), -2/sqrt(2) ]; }
  atom { coords = aLat/2 * [ 3/2, 2/sqrt(2), -3/sqrt(2) ]; }
  atom { coords = aLat/2 * [ 1/2, 1/sqrt(2), -4/sqrt(2) ]; }
  atom { coords = aLat/2 * [ 3/2, 2/sqrt(2), -5/sqrt(2) ]; }
}
```

GaAs (110) input file

```
basis {
    eCut    = 10.;
    kPoint { coords = [1/2 ,1/2 , 0];
             weight = 1;
             relative;
    }
    folding = [2, 2, 1];

}

Hamiltonian  {
    xc              = LDA;
    ekt             = 0.;
    nEmptyStates = 0;
                  }

main  {
        CCG { maxSteps      = 1000;
              dEnergy       = 1.e-6;
              printSteps    = 25;
              }
          }
```

input.sx

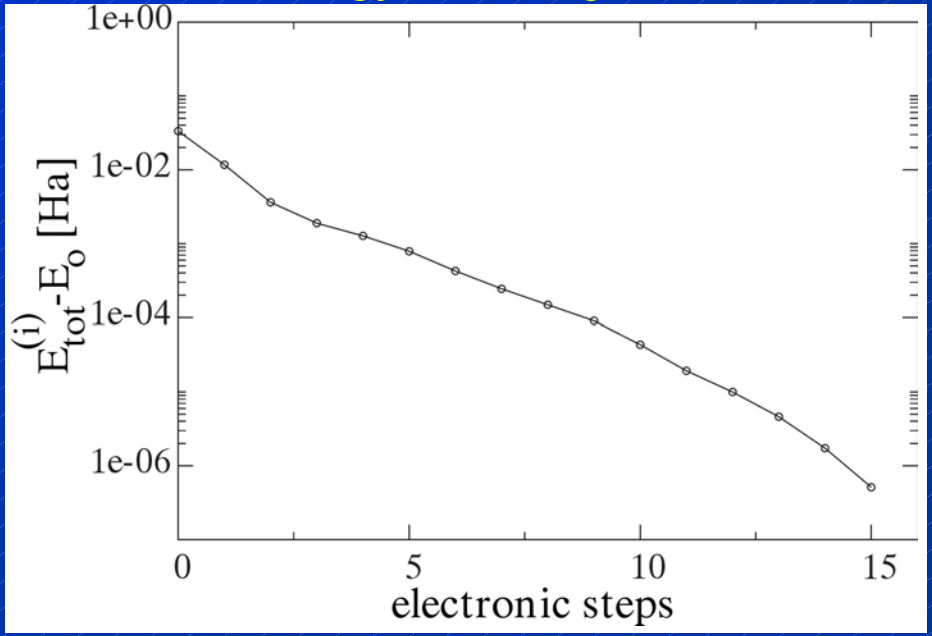
ideally no dispersion of the band structure along z direction

k–point mesh → in xy plane

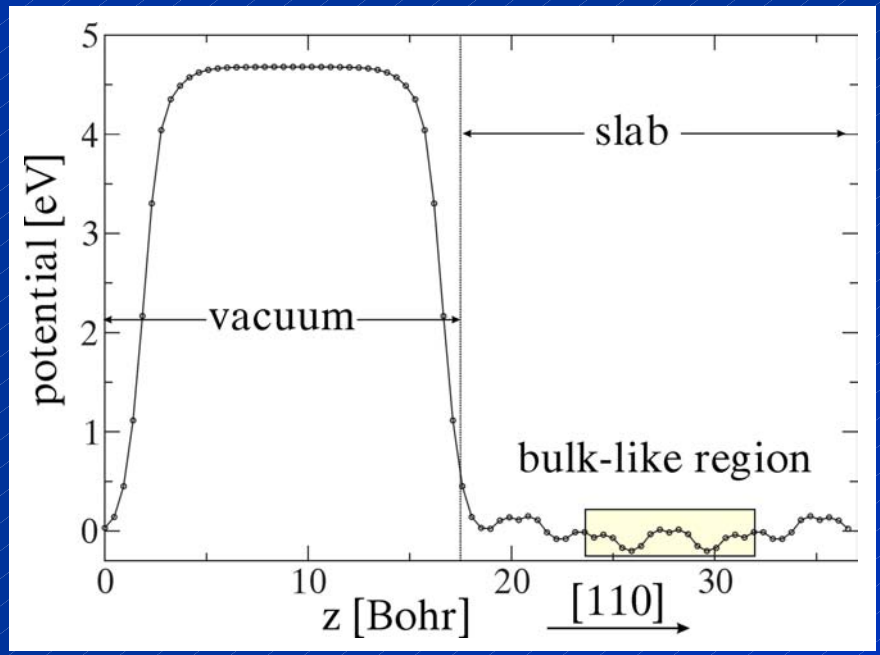
all state CCG scheme doesn't allow empty states

GaAs (110) unPassivated – output files

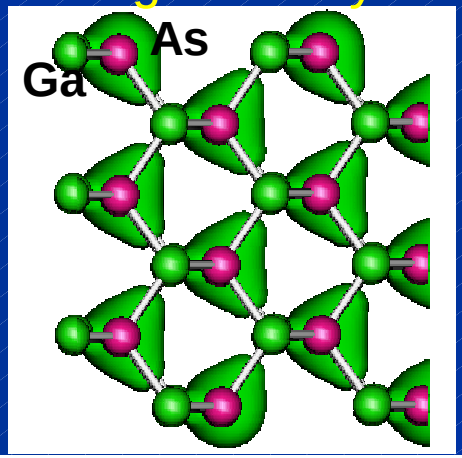
energy convergence



electrostatic potential

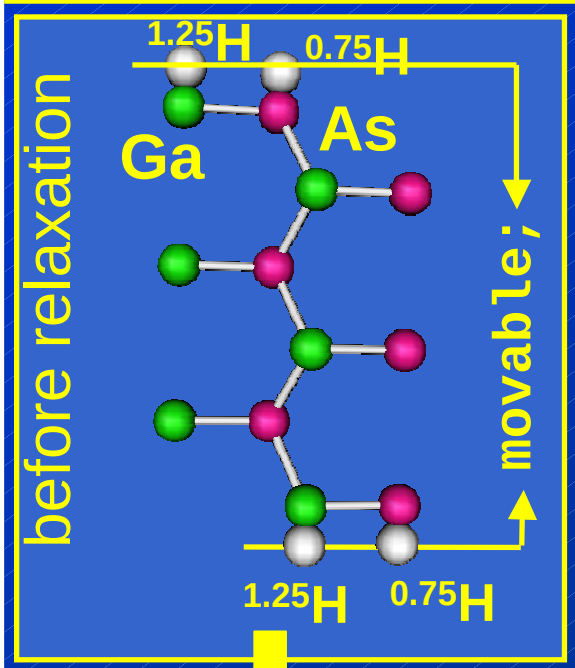


charge density



- **GaAs is ionic to a certain extend**
- **Charge–density maximum → towards the anion**

passivation with Hydrogen

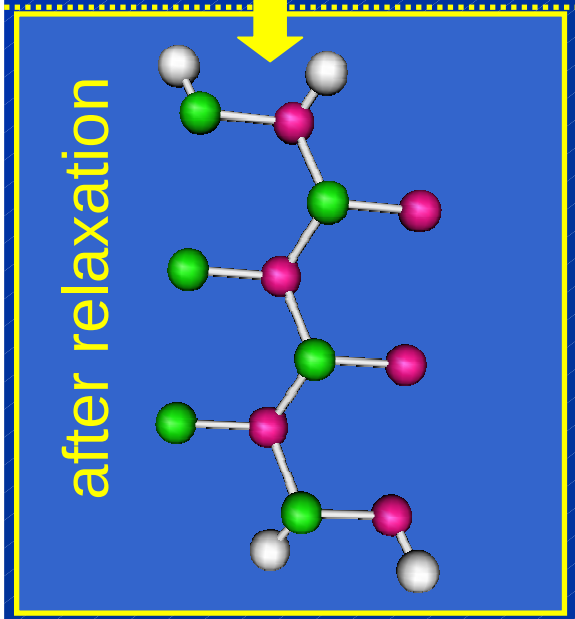


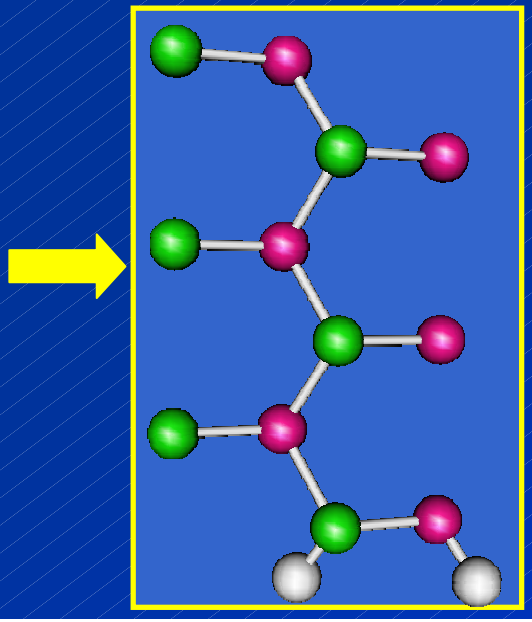
electron counting rule

Ga : $-\frac{3}{4}e^-$ to a bond ⟶ passivated by $-\frac{5}{4}e^-$

As : $-\frac{5}{4}e^-$ to a bond ⟶ passivated by $-\frac{3}{4}e^-$

- **no charge transfer**
- **use of thinner slab**
- **treatment of slabs with no equivalent sides (i.e. GaN(000**



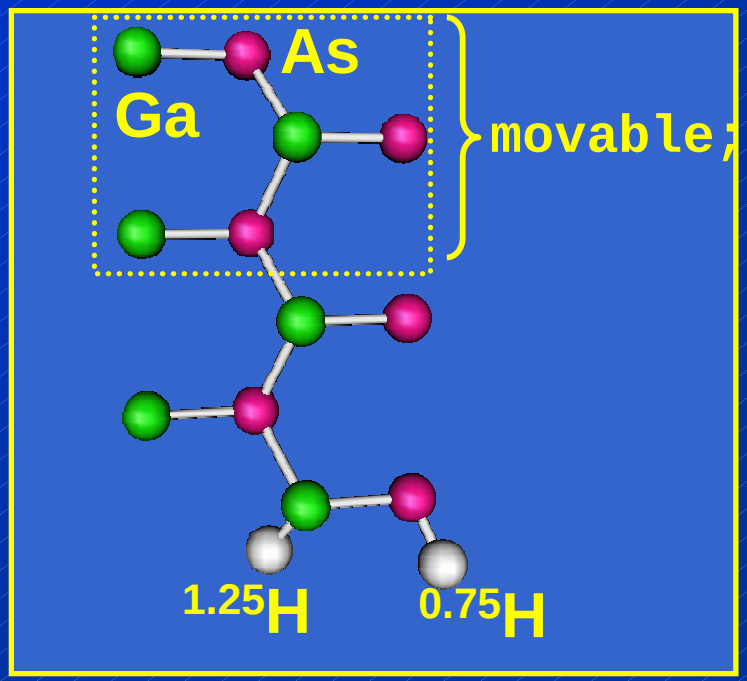


ideal GaAs(110) surface

calculate:

- **total energy**
- **electrostatic potential**
- **charge density**

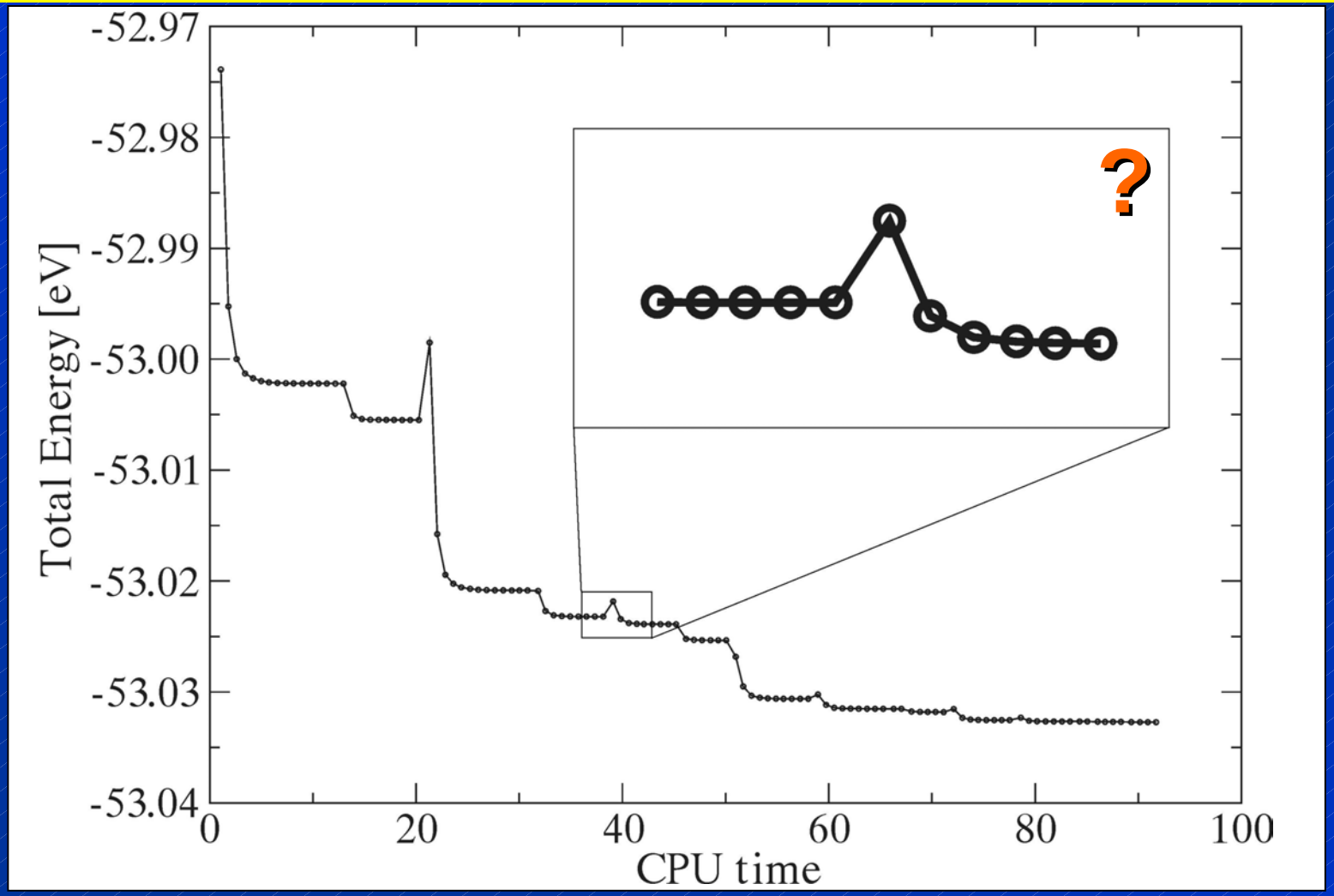
structure relaxation with quasi Newton scheme



input.sx

```
main  {
……
    quasiNewton {
……
        convergence {
            dEnergyStruct = 1.e-4;
        }

        CCG {
            maxSteps      = 1000;
            dEnergy       = 1.e-6;
            printSteps    = 25;
        }

        output {
            saveWaves = 1;
        }
    }
}
```

surface relaxation – total energy convergence

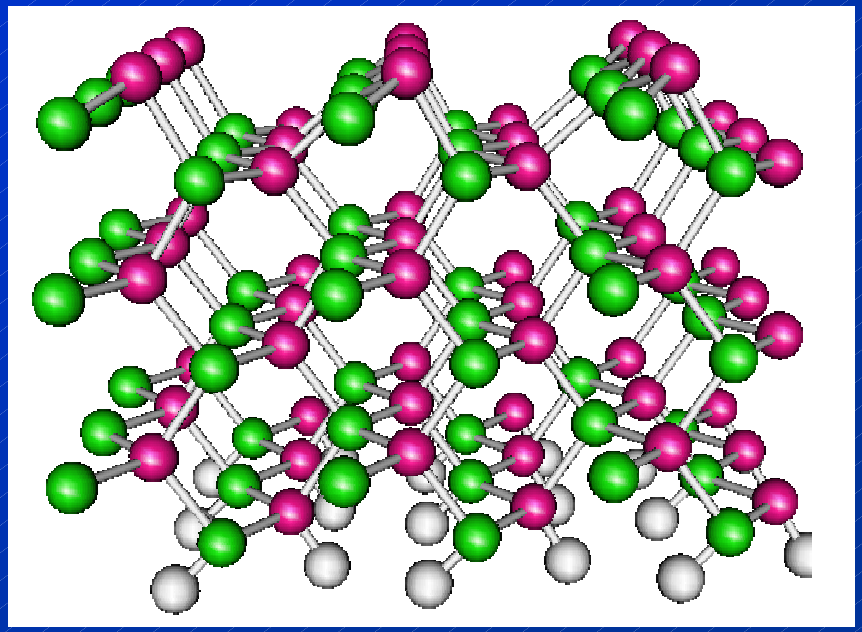


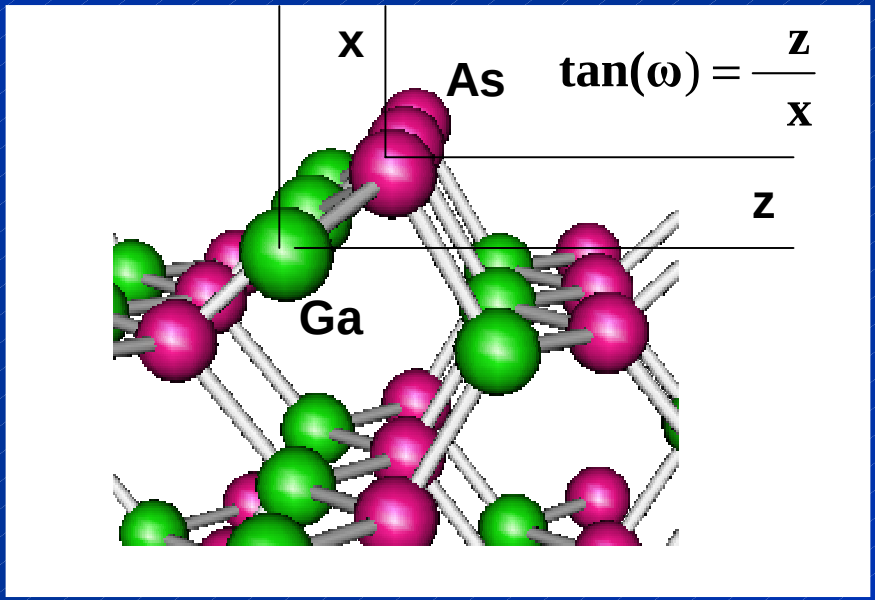
- After an ionic step → charge density doesn't correspond to the new atomic geometry

?

- Born–Oppenheimer surface has to be approximated after each ionic step

surface relaxation – atomic geometry



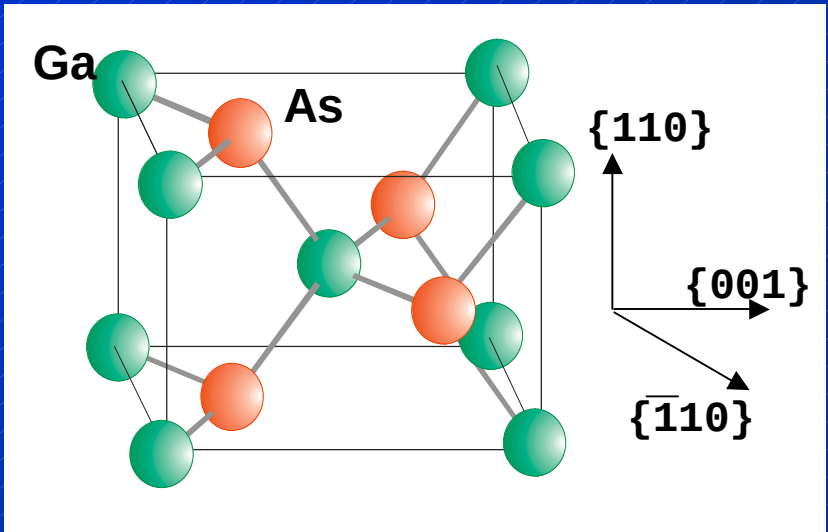


- Check the displacement of atoms in each layer.
- Compare your calculated structural parameters:

	aLat [Bohr]	x [Bohr]	z [Bohr]	ω
DFT-LDA ($E_{\not\propto}$=8Ry) [1]	10.39	1.19	2.17	28.6
Experiment [2]	10.69	1.30	2.48	31.1

[1] J. L. A. Alves, J. Hebenstreit, and M. Scheffler, Phys. Rev. B 44, 6188 (1991).
[2] C. B. Duke, S. L. Richardson, A. Paton, and A. Kahn, Surf. Sci. 127, L135 (1983).

bulk calculation



energetics

- Total energy of the bulk GaAs is needed
- The same special k-points and cut off energy with the slab is needed

projected band structure

- projection of the bulk bands onto the first surface BZ

Same lateral unit cell (x-y) as for the surfa

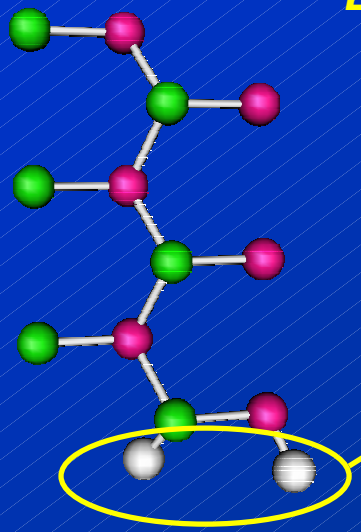
```
aLat = 10.47;

structure  {
   include "../structures/bulk.sx";
}

basis {
     eCut   = 10.;
     kPoint { coords = [1/2 ,1/2 , 1/2];
              weight = 1;
              relative;
            }
     folding = [2, 2, 5];
       }
```

input.sx

```
cell=[aLat*[ 1, 0          , 0 ],
      aLat*[ 0, sqrt(2)/2  , 0 ],
      aLat*[ 0, 0          , 1 ]];
```

bulk.sx

Surface energies



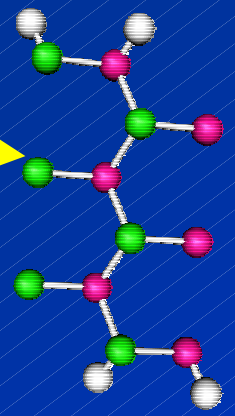
Energy necessary to cut the crystal at some plane

$$E_{SURF} = \left(E_{SLAB} - E_{BULK}\right) / 2$$

→ the slab has 2 surfaces

$$E_{hydrogens} = \left(E_{SLABbothH} - 3 \cdot E_{BULK}\right) / 2$$

energy of the hydrogen saturated surface



$$E_{SURF} = E_{SLAB} - 3 \cdot E_{BULK} - E_{hydrogens}$$

	Formation energy $[eV/1\times1]$
DFT [1]	1.13
DFT [2]	1.12
Experiment [3]	1.17 ± 0.2
Your calculations relaxed	
Your calculations unrelaxed	

[1] N. Moll, A. Kley, E. Pehlke, and M. Scheffler, Phys. Rev. B 54, 8844 (1996).
[2] G. Qian, R.M. Martin, and D.J. Chadi, Phys. Rev. B. 37, 1303 (1988).
[3] C. Messmer and J.C. Billelo, J. Appl. Phys. 52, 4623 (1981).

surface band structure

```
global G , X , XPrime , M , aLat1 , aLat2;
aLat1 = aLat;
aLat2 = aLat/sqrt(2);                    GaAs110.sx

G =      [0.0      , 0.0      , 0.0];
X =      [0.0      , pi/aLat2 , 0.0];
M =      [pi/aLat1 , pi/aLat2 , 0.0];
XPrime = [pi/aLat1 , 0.0      , 0.0];
```

primitive vectors
+
high symmetry k-points

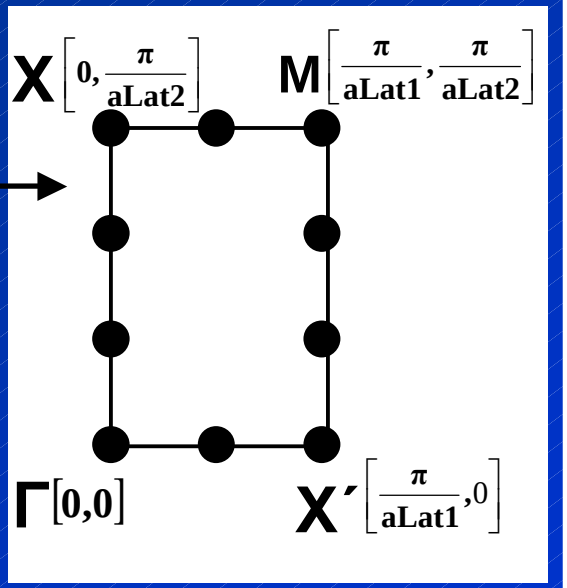
```
structure  {
   include "../structures/GaAs110.sx";
   include "../04_relSurf/relSlab.sx";
}
```

```
basis  {
   eCut    = 10;
   kPoints {
      from { coords = G;      label="G";}
      to   { coords = XPrime; label="XPrime"; nPoints=3;}
      to   { coords = M;      label="M";      nPoints=4;}
      to   { coords = X;      label="X";      nPoints=3;}
      to   { coords = G;      label="G";      nPoints=4;}
   }
}
```

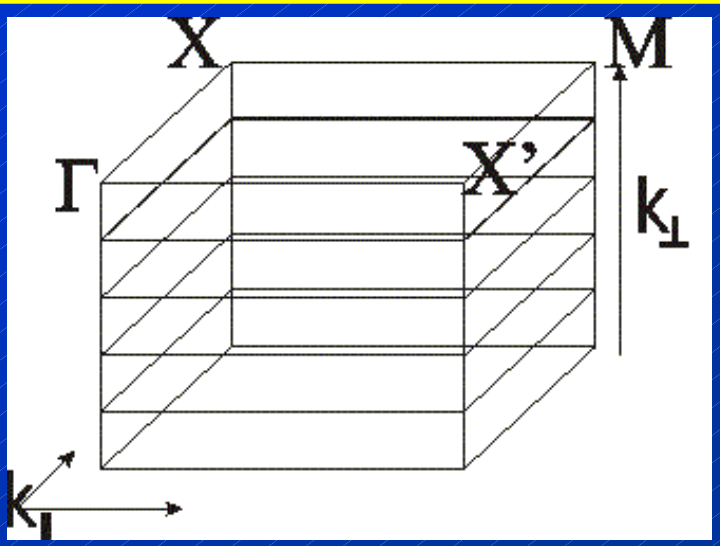
```
initialGuess  {
   waves { lcao { maxSteps = 1; rhoMixing = 0.05; } }
   rho   { file = "../04_relSurf/rho.sxb"; }
}
```

```
main  {
   DIIS_CCG {
      … … …
      keepRhoFixed;
      … … …
   }
}
```

input.sx



projected bulk band structure



- Same set of k⌨ as for the surface
- Several k❍=k_z in [-π/$α_❍$,π/$α_❍$]

Mirror symmetry

↓

k❍: [0,π/$α_❍$]

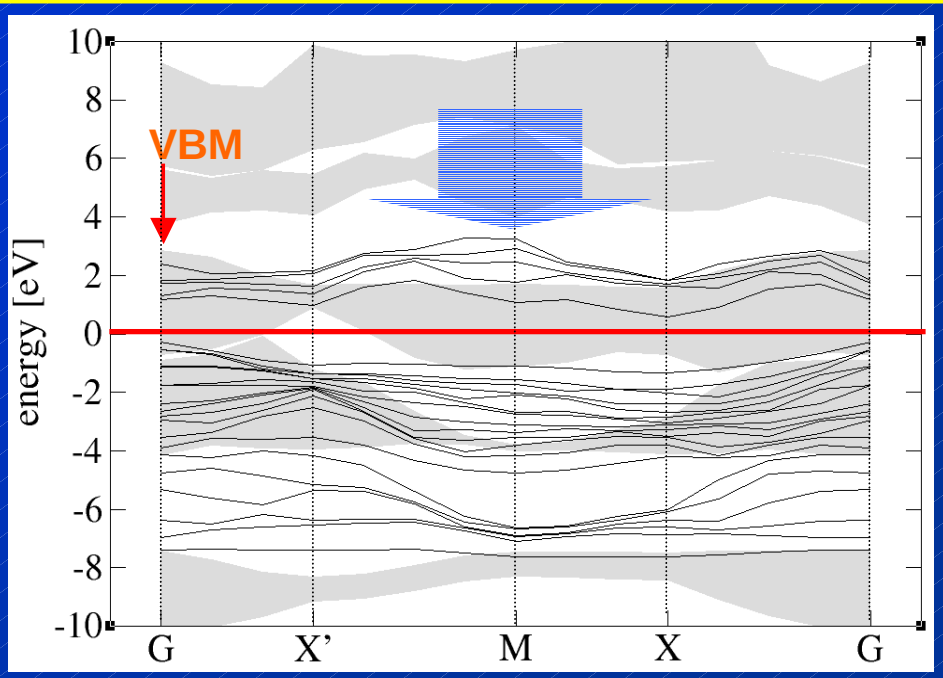
```
global Gx , Gy … … …
… … … …
aLat1 = aLat;
aLat2 = aLat/sqrt(2);
aLat3 = aLat/sqrt(2);

Gx  = 0;
Gy  = 0;
Xx  = 0;
Xy  = pi/aLat2;
Mx  = pi/aLat1;
My  = pi/aLat2;
XPx = pi/aLat1;
XPy = 0;

Z1=0.0*pi/aLat3;
Z2=0.1*pi/aLat3;
.. .. ..
.. .. ..
```

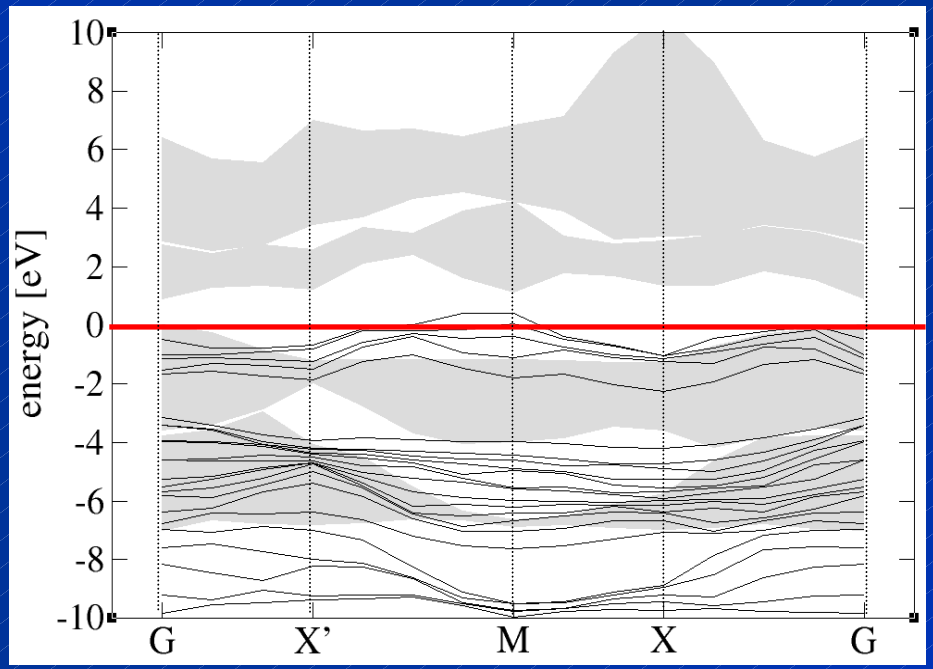
bulk.sx

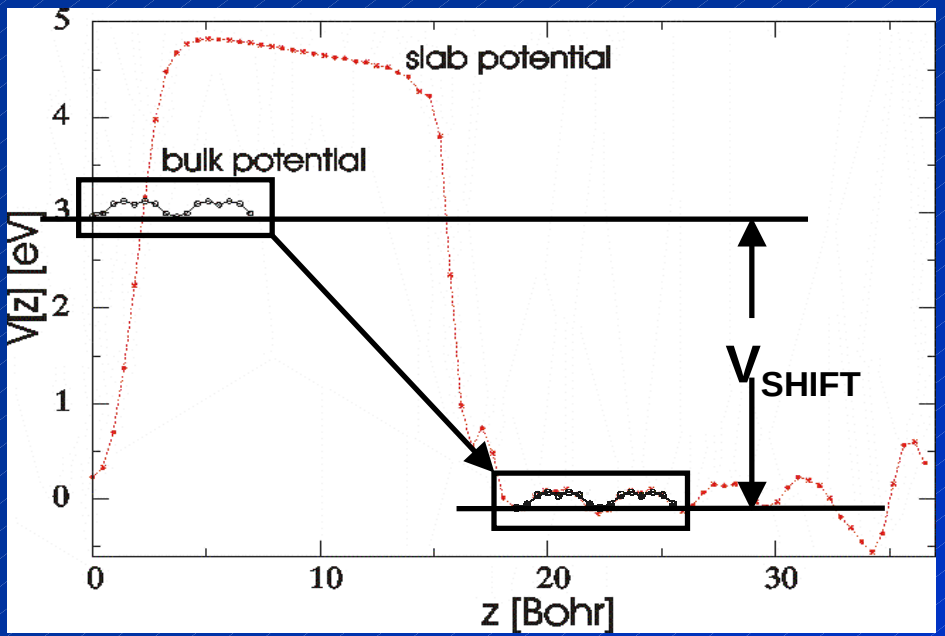
```
structure  {
   include "../structures/bulk.sx";
}
… … …
… … …
kPoints {
  from { coords = [Gx ,Gy ,Z1]; label="G";}
  to   { coords = [XPx,XPy,Z1]; label="XP"; nPoints=3;}
  to   { coords = [Mx ,My ,Z1]; label="M“;  nPoints=4;}
  to   { coords = [Xx ,Xy ,Z1]; label="X“;  nPoints=3;}
  to   { coords = [Gx ,Gy ,Z1]; label="G";  nPoints=4;}

  to   { coords = [Gx ,Gy ,Z2]; label="G";  nPoints=0;}
   ...
}
```

input.sx

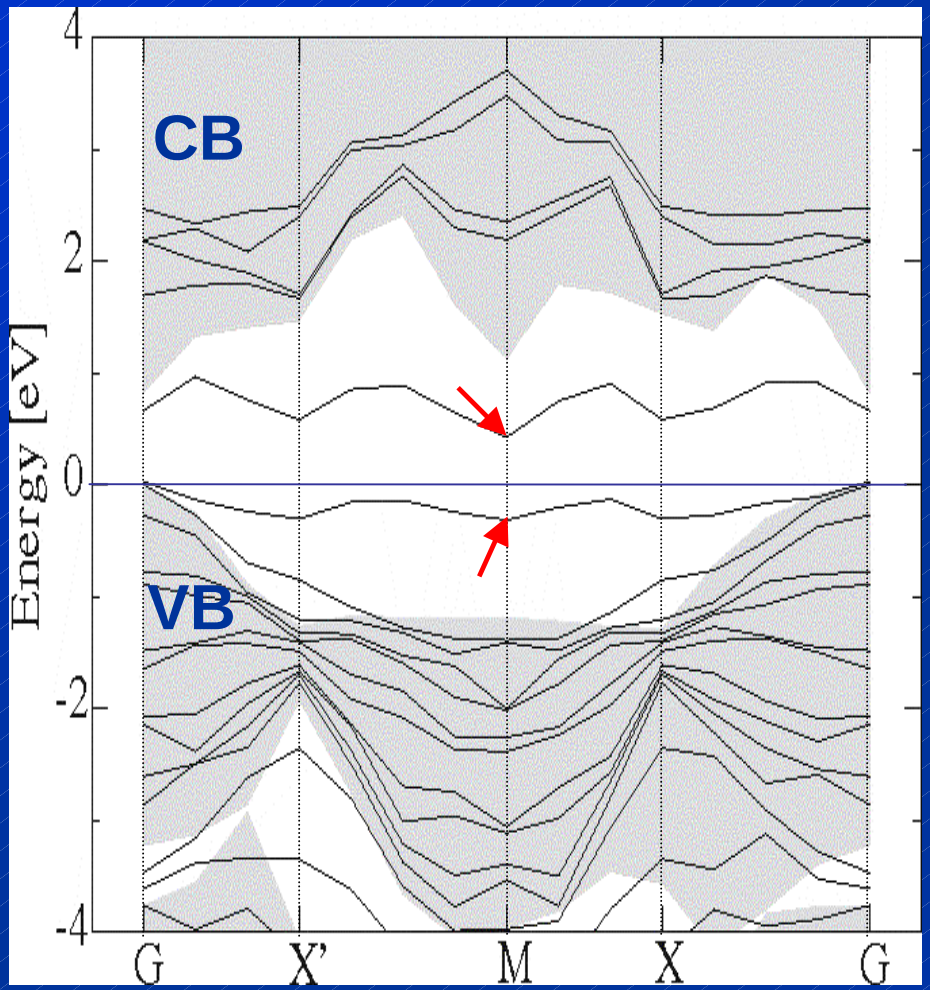
band structure alignment



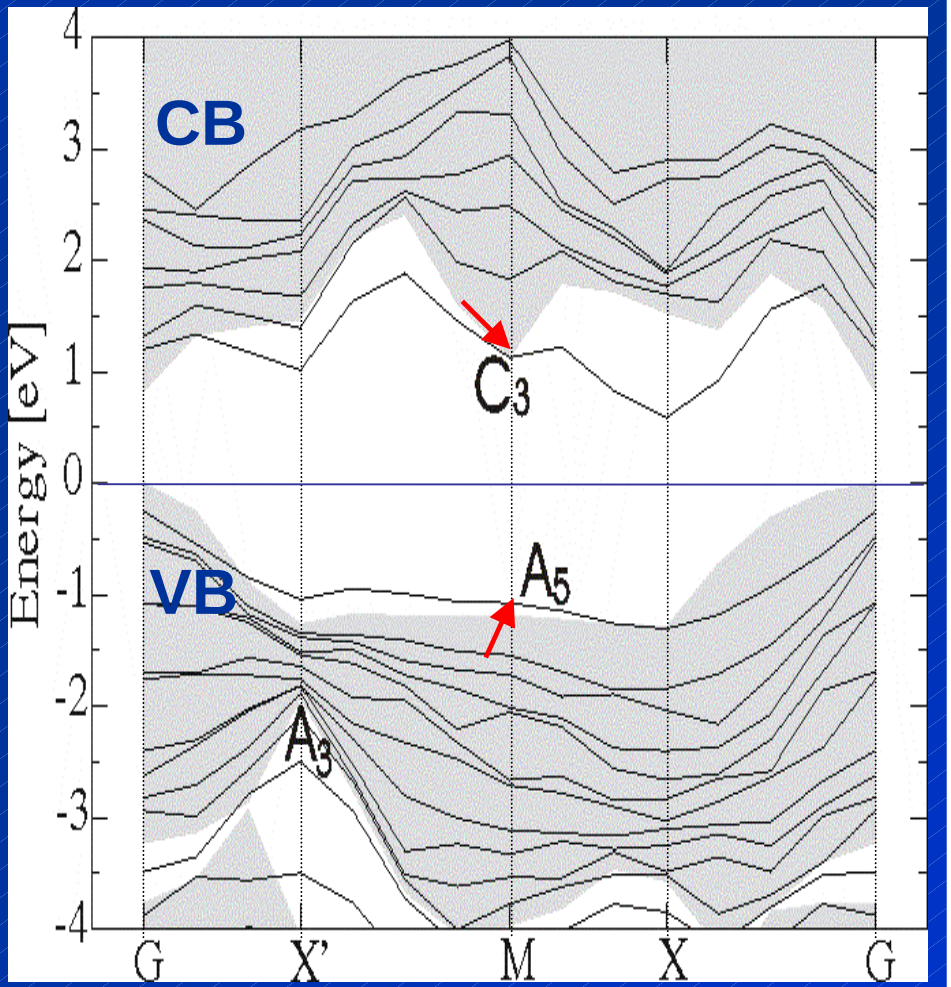




band structure alignment

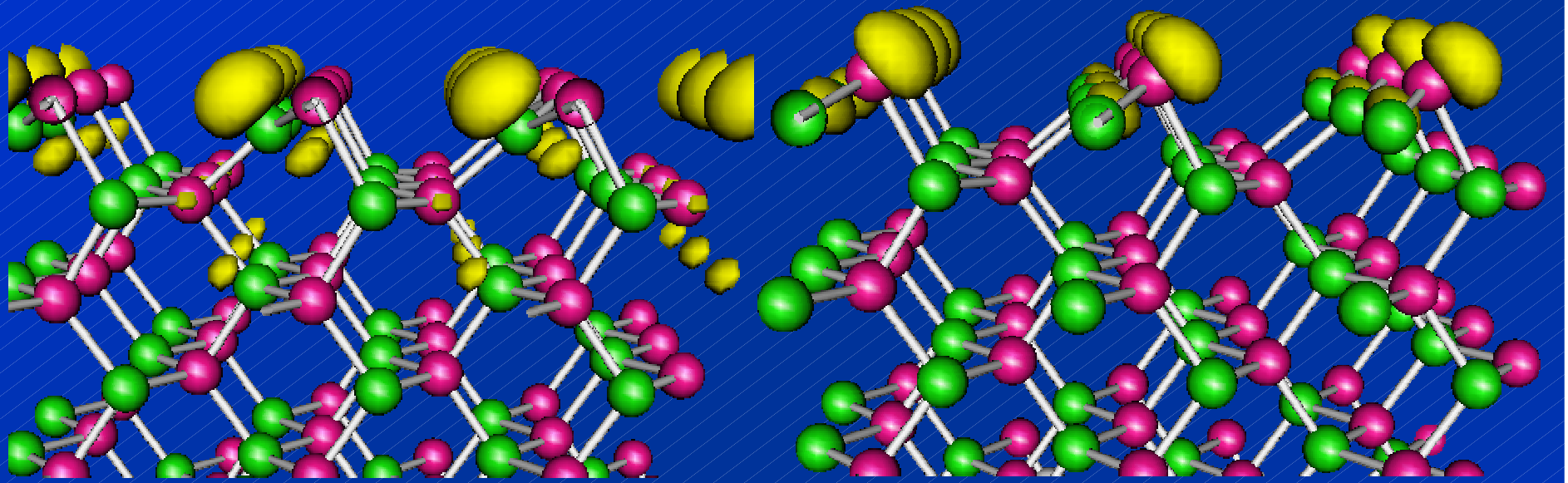


band structure of the unrelaxed surface



band structure of the relaxed surface

Charge densities of the C_3 and A_5 states at M point



Ga-derived empty surface state C_3 As-derived filled surface state A_5

Localized surface states

Optional Exercise

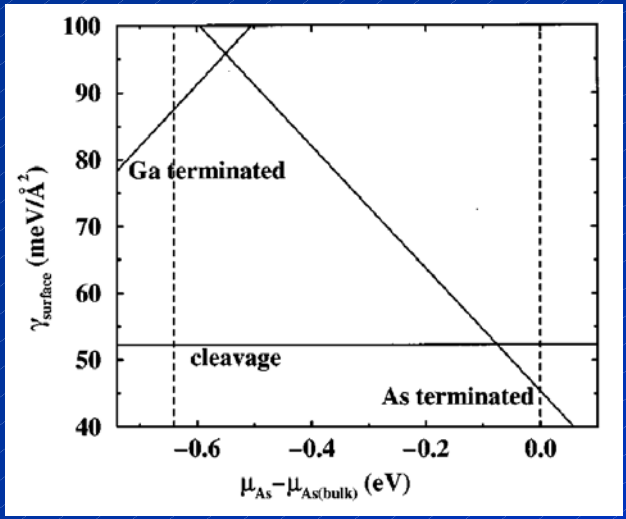
- **Explore the nature of other surface states (for example the A3 state in the pocket in the valence band)**
- **Explore the nature of surface states in the ideal GaAs(110) surface**

Optional Exercises

- **Optimization of surface relaxation**
- **Explore the origin of other surface states**
- **Photoelectric threshold (or ionization potential)**

Minimum energy to knock one electron out from the valence band

- **Study the Ga- and As- terminated GaAs(110) surfaces**



N. Moll, A. Kley, E. Pehlke, and M. Scheffler, Phys. Rev. B 54, 8844 (1996)