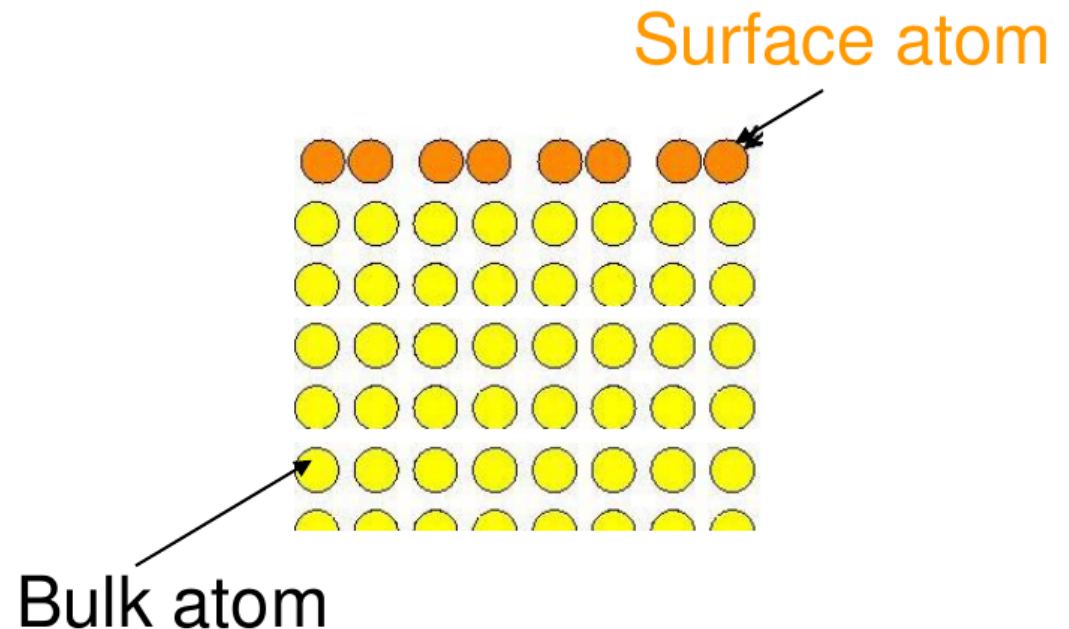


Density functional theory in practice 2/2

- How to simulate non-periodic systems (surfaces, molecules, amorphous, etc..)
- Structural optimization

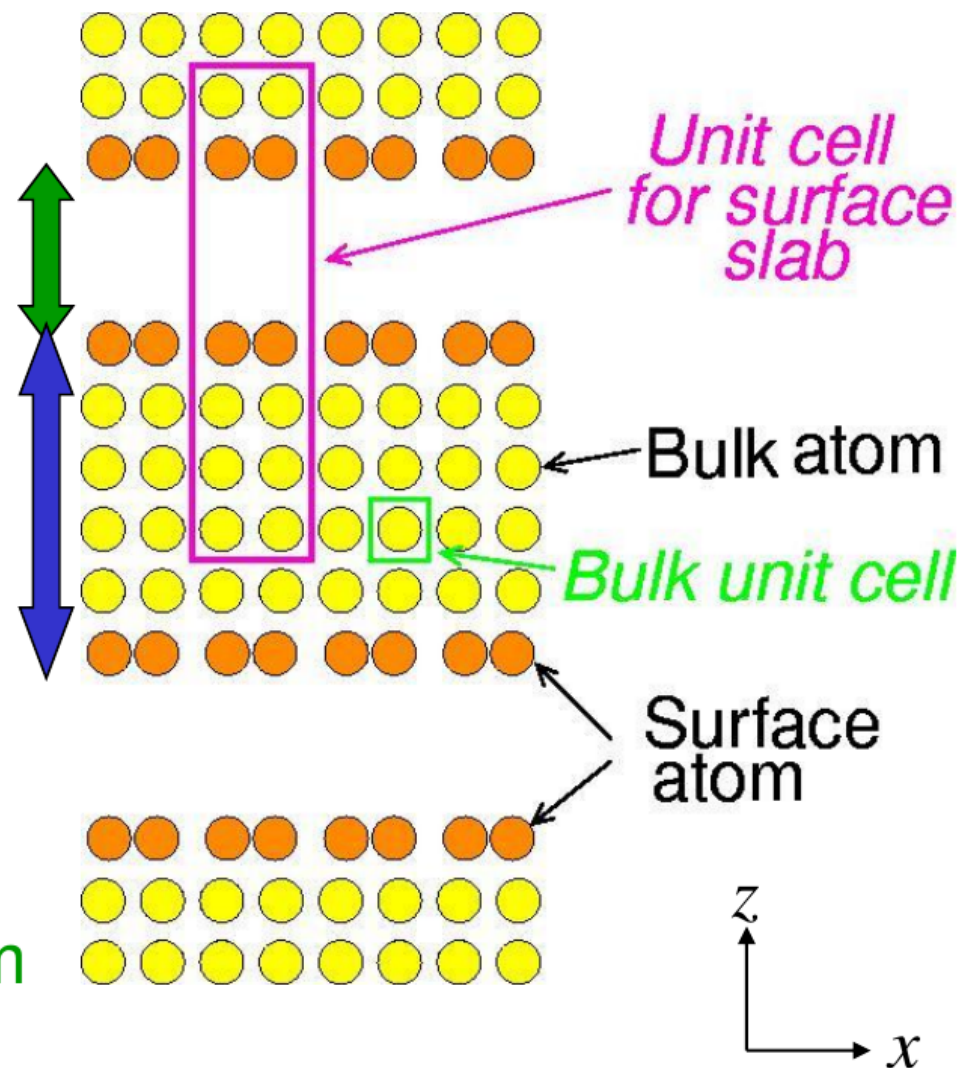
What if the system is not periodic?

- Example 1: Want to study properties of a system with a **surface**.
- Presence of surface \Rightarrow No periodicity along z .



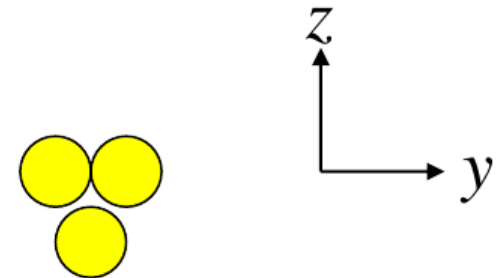
What if the system is not periodic?

- Example 1: Want to study properties of a system with a **surface**.
- Presence of surface \Rightarrow No periodicity along z .
- Use a **supercell**: **artificial periodicity along z** by repeating slabs separated by **vacuum**.
- Have to check convergence w.r.t. **slab thickness** & **vacuum thickness**.



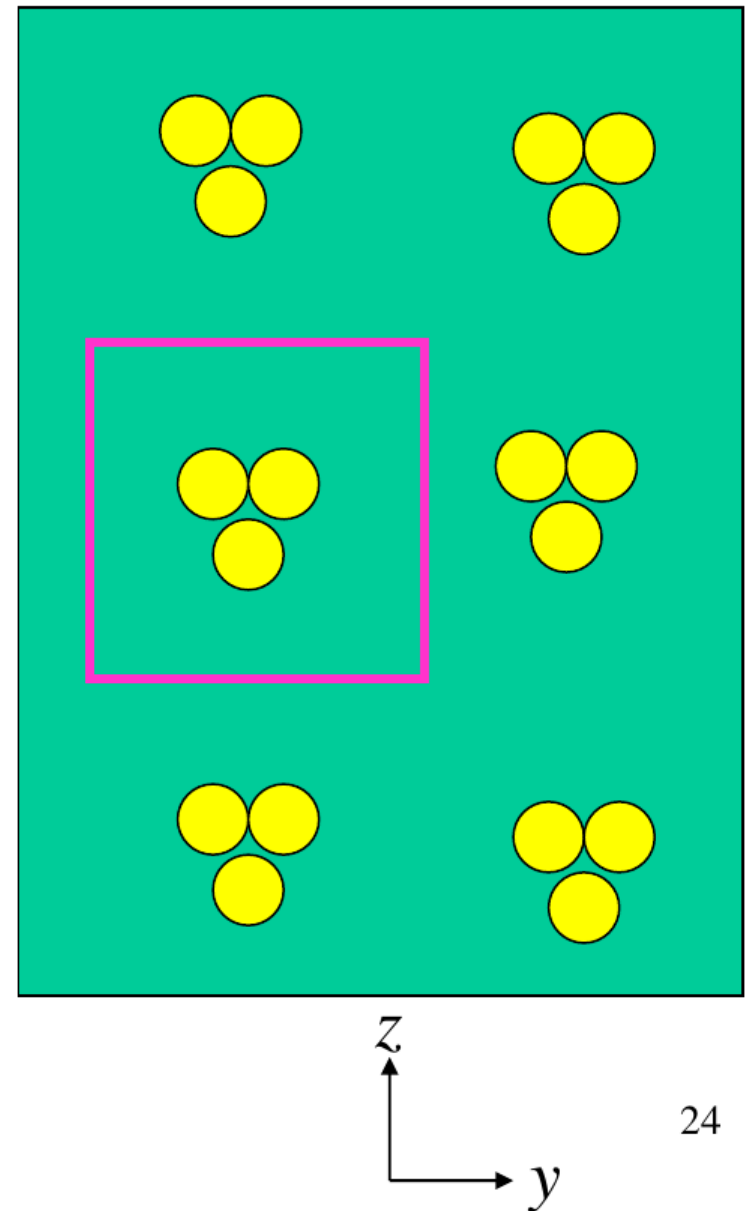
What if the system is not periodic?

- Example 2: Want to study properties of a nanowire.
- Example 3: Want to study properties of a cluster



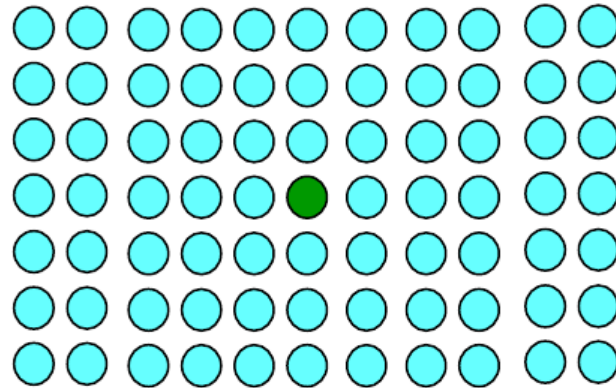
What if the system is not periodic?

- Example 2: Want to study properties of a nanowire \Rightarrow introduce **artificial periodicity along y & z** .
- Example 3: Want to study properties of a cluster \Rightarrow introduce **artificial periodicity along x , y & z** .



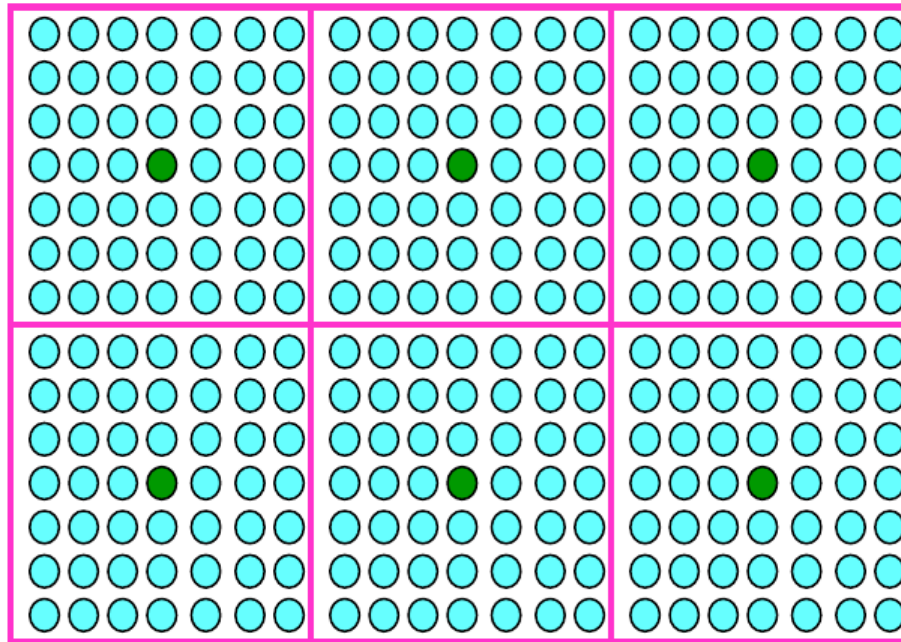
What if the system is not periodic?

- Example 4: Want to study a system with a defect, e.g., a **vacancy or impurity**:



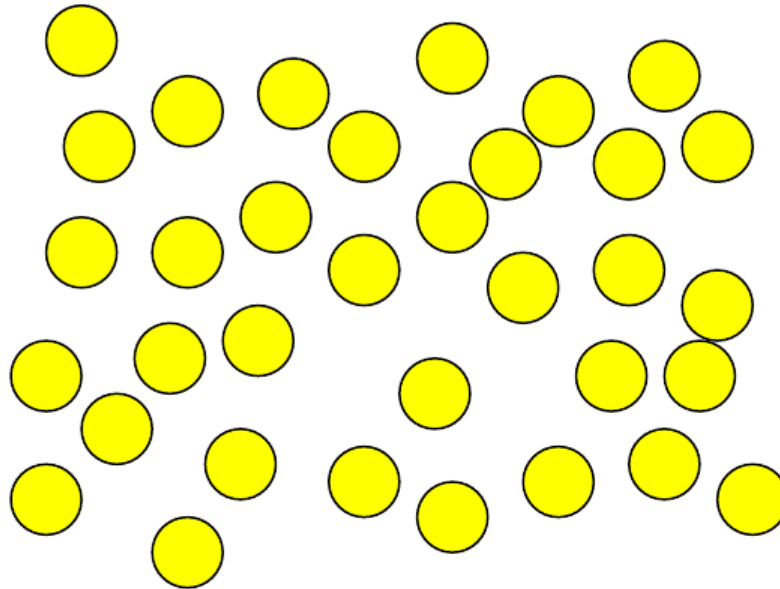
What if the system is not periodic?

- Example 4: Want to study a system with a defect, e.g., a **vacancy or impurity**:



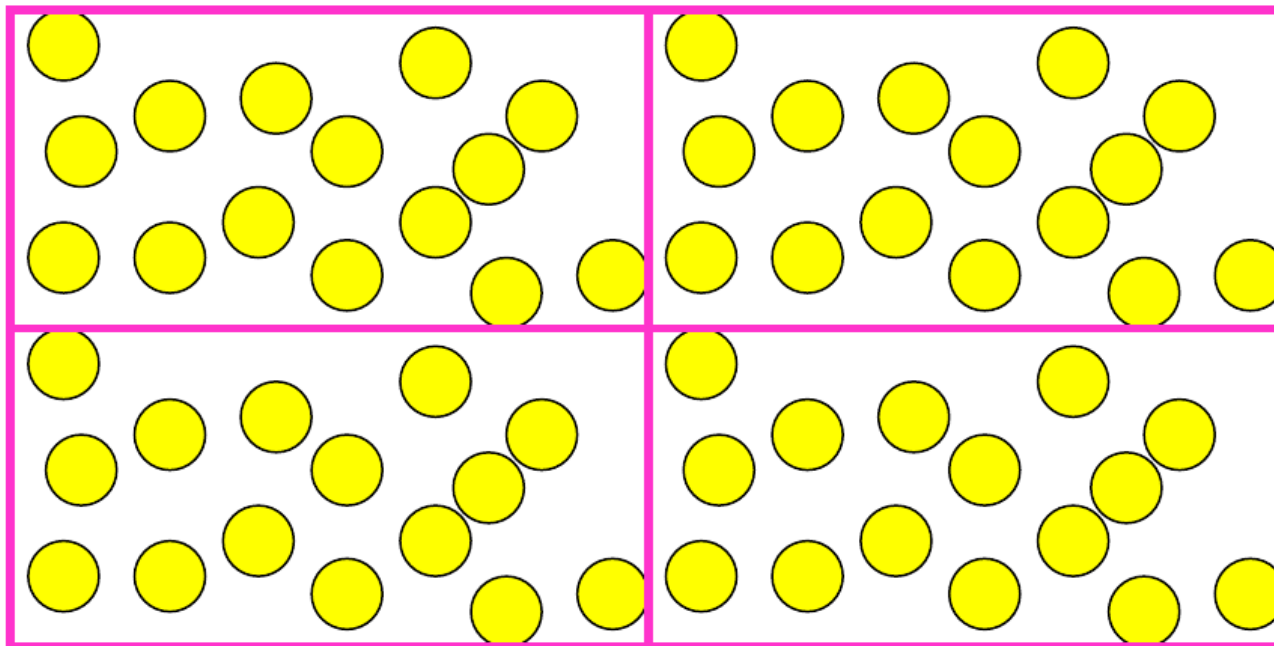
What if the system is not periodic?

- Example 5: Want to study an amorphous or quasicrystalline system.



What if the system is not periodic?

- Example 5: Want to study an amorphous or quasicrystalline system: approximate by a periodic system (with large **unit cell**).



Artificially Periodic Systems \Rightarrow Large Unit Cells

- Note: In all these cases, to minimize the effects of the artificially introduced periodicity, need a large unit cell.



- Long $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ (primitive lattice vectors)



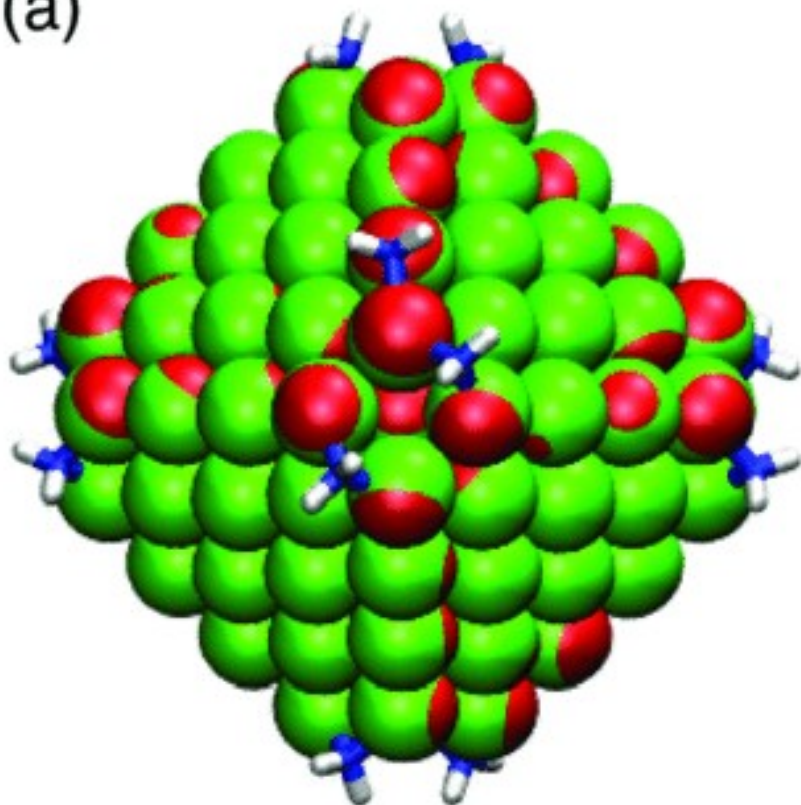
- Short $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ (primitive reciprocal lattice vectors)



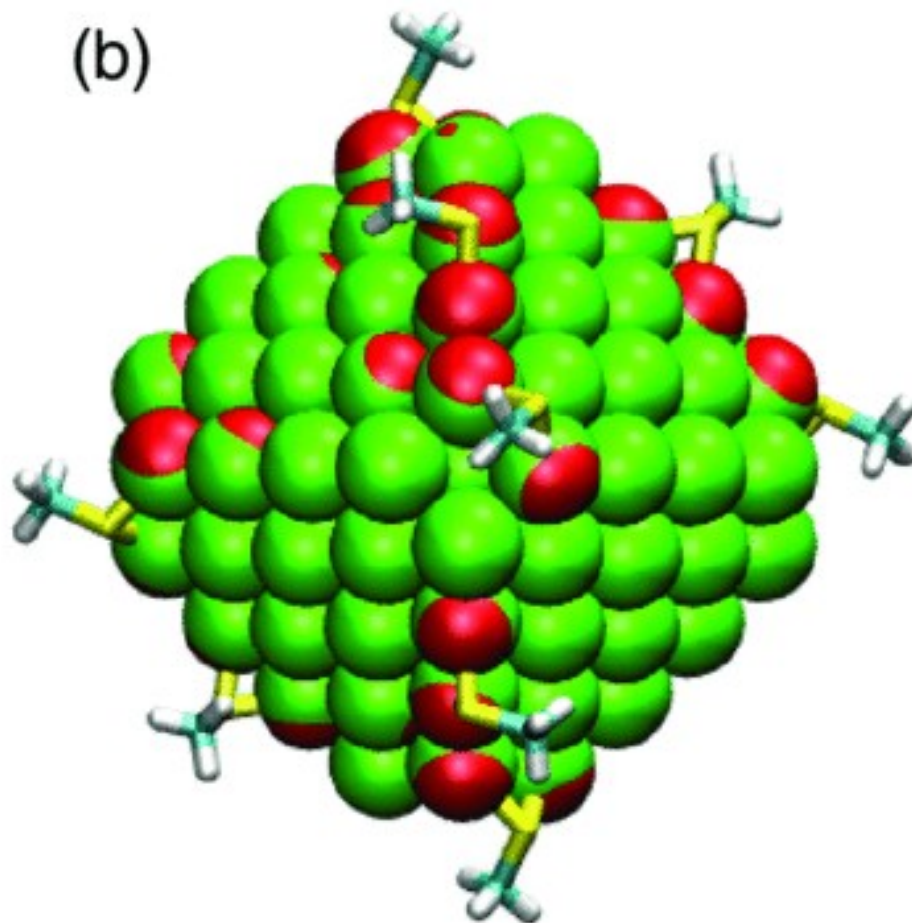
- Many \mathbf{G} 's will fall within E_{cut} sphere!

Structure optimization

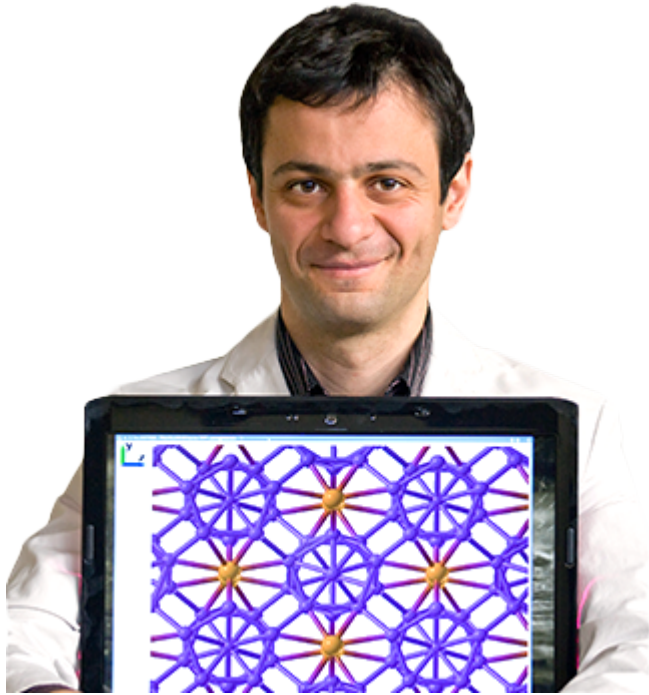
(a)



(b)



The king of structure optimization



Artem Oganov

https://en.wikipedia.org/wiki/Artem_R._Oganov

Among the highlights are the discovery of the structure of a **superhard phase of boron**, **gamma-B**, **transparent phase of sodium**, **new carbon allotrope**, **stability of MgSiO₃ post-perovskite in the Earth's mantle**, **prediction and synthesis of "forbidden" compounds (e.g., Na₃Cl)**, **discovery of helium chemistry**, and **creation of borophene - a 2D-monolayer of boron atoms**, with great promises for future technologies

see wiki for references.

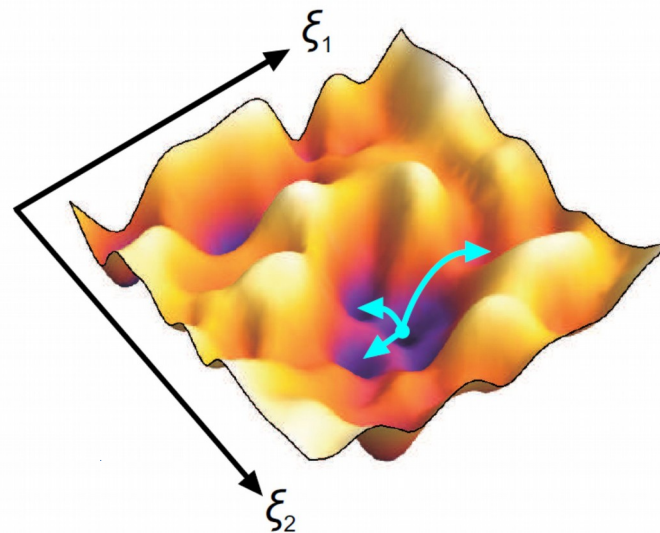
Why you will not be as successful as Artem Oganov



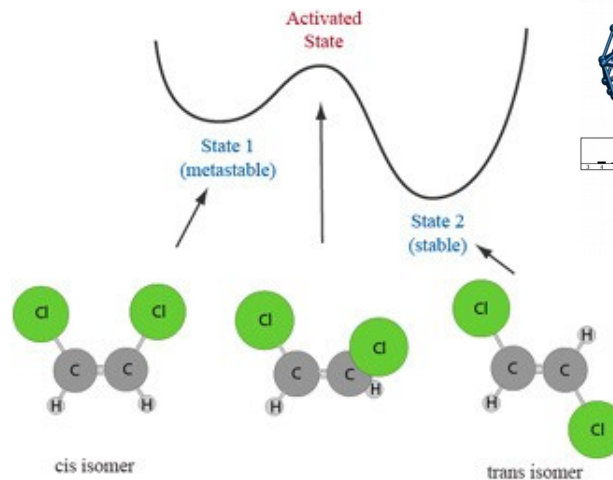
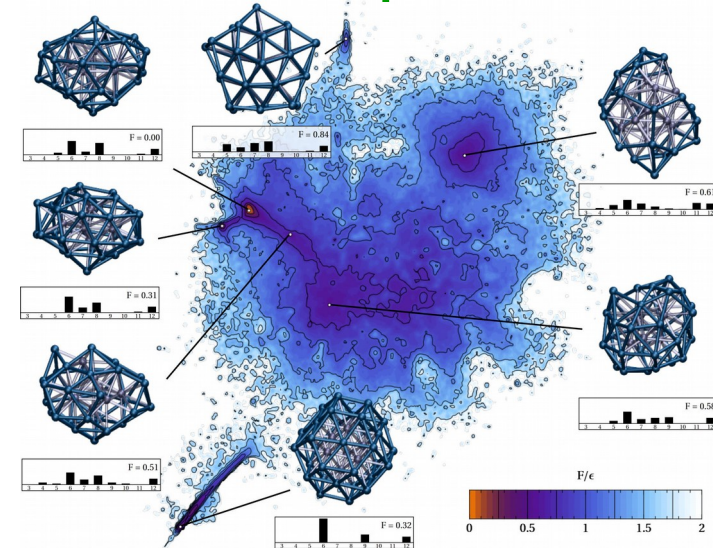
Artem Oganov

https://en.wikipedia.org/wiki/Artem_R._Oganov

Use UPEX!!



Energy landscape too complex



Forces

- Need for geometry optimization and molecular dynamics.
- Could get as finite differences of total energy - too expensive!
- Use force (Hellmann-Feynman) theorem:
 - Want to calculate the force on ion I :

$$\mathbf{F}_I = -\frac{d}{d\mathbf{R}_I} \langle \Psi | H | \Psi \rangle$$

- Get three terms:

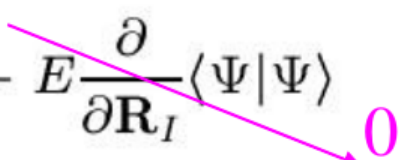
$$\mathbf{F}_I = -\langle \Psi | \frac{\partial H}{\partial \mathbf{R}_I} | \Psi \rangle - \langle \frac{\partial \Psi}{\partial \mathbf{R}_I} | H | \Psi \rangle - \langle \Psi | H | \frac{\partial \Psi}{\partial \mathbf{R}_I} \rangle$$

When $|\Psi\rangle$ is an eigenstate, $H|\Psi\rangle = E|\Psi\rangle$

-Substitute this...

Forces (contd.)

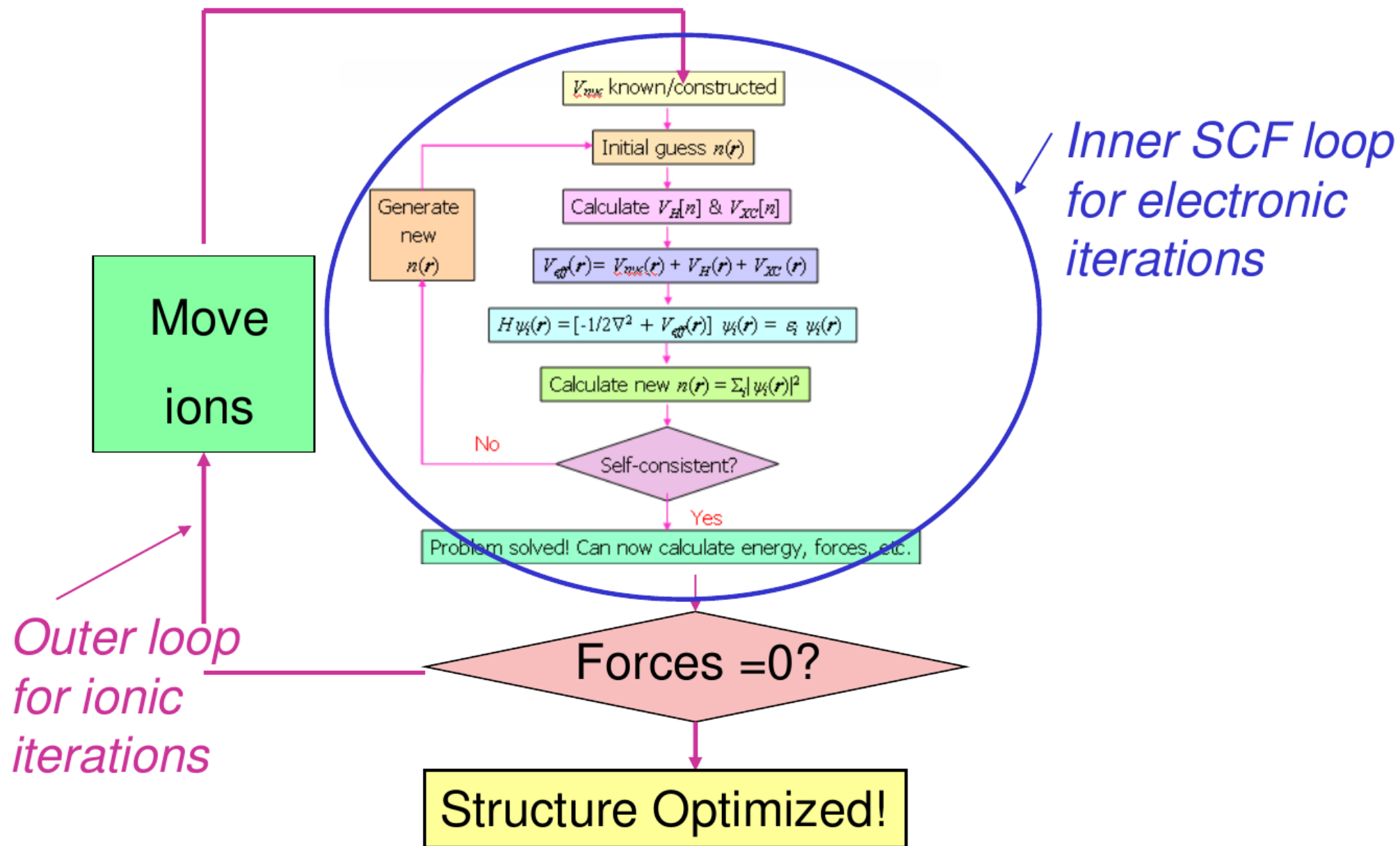
- The **force** is now given by

$$\begin{aligned}\mathbf{F}_I &= -\langle \Psi | \frac{\partial H}{\partial \mathbf{R}_I} | \Psi \rangle - E \langle \frac{\partial \Psi}{\partial \mathbf{R}_I} | \Psi \rangle - E \langle \Psi | \frac{\partial \Psi}{\partial \mathbf{R}_I} \rangle \\ &= -\langle \Psi | \frac{\partial H}{\partial \mathbf{R}_I} | \Psi \rangle - E \frac{\partial}{\partial \mathbf{R}_I} \langle \Psi | \Psi \rangle\end{aligned}$$


- Note that we can now **calculate the force** from a calculation at **ONE configuration alone** – huge savings in time.
- If the basis depends upon ionic positions (not true for plane waves), would have extra terms = **Pulay forces**.
- $|\Psi\rangle$ should be exact eigenstate, i.e., scf well-converged!

Input parameter `tpnfor`

An Outer Loop: Ionic Relaxation



Geometry Optimization With Forces

- Especially useful for optimizing internal degrees of freedom, surface relaxation, etc.

```
calculation = 'relax'
```

- Choice of algorithms for ionic relaxation, e.g., steepest descent, BFGS.

```
NAMELIST &IONS
```

```
Input parameter ion_dynamics
```

Structural relaxation

&control

calculation= 'relax', ←

prefix='silicon',

pseudo_dir='./'

outdir = './',

/

&system

ibrav= 2,

celldm(1) =10.2,

nat= 2,

ntyp= 1,

ecutwfc = 12.0,

/

&electrons

/

&ions ←

ions_dynamics='damp' or 'BFGS'

/

ATOMIC_SPECIES

Si 28.086 Si.vbc.UPF

ATOMIC_POSITIONS {crystal}

Si 0.00 0.00 0.00

Si 0.25 0.25 0.25

K_POINTS automatic

2 2 2 0 0 0

New calculation type

New namelist

Optimization methods for finding minimum energy paths
J. Chem. Phys. 128, 134106 (2008)

CO molecule tutorial

Structure optimization of CO molecule

Tutorial files: on [Dropbox](#)

[didatticaSdM \(1\)/EsercitazioneDFT_2017-2018/DFT-2017-2018/](#)

Go to the CO/CO_relax folder

Run `pw.x < co.optimize> output_optimize &`

Visualize output with

`xcrysden -pwo output_optimize`

Extract energies from output

`grep “! total energy” > tot_energy`

Bond length and HOMO-LUMO

Bond length vs Ecut: CO/CO_relax/run_ecut

Bond length vs cell-size: CO/CO_cellsize/run_cellsize

- 1) Extract bond-length from output
- 2) Plot bond length vs Ecut and cell-size

HOMO and LUMO: CO/CO_HomoLumo

- 3) Which atom is positive charged?

Binding Energy of CO

Binding energy folder: CO/CO_binding

**Calculate the energy of CO then subtract
the C and O energy**

1) Is the CO molecule stable?