

# Quantum Espresso code



<http://www.quantum-espresso.org/>

# Quantum Espresso code

- Different executables for different tasks in QEDIR/**bin**
- Documentation in QEDIR/**Doc/INPUT\_XX.txt**

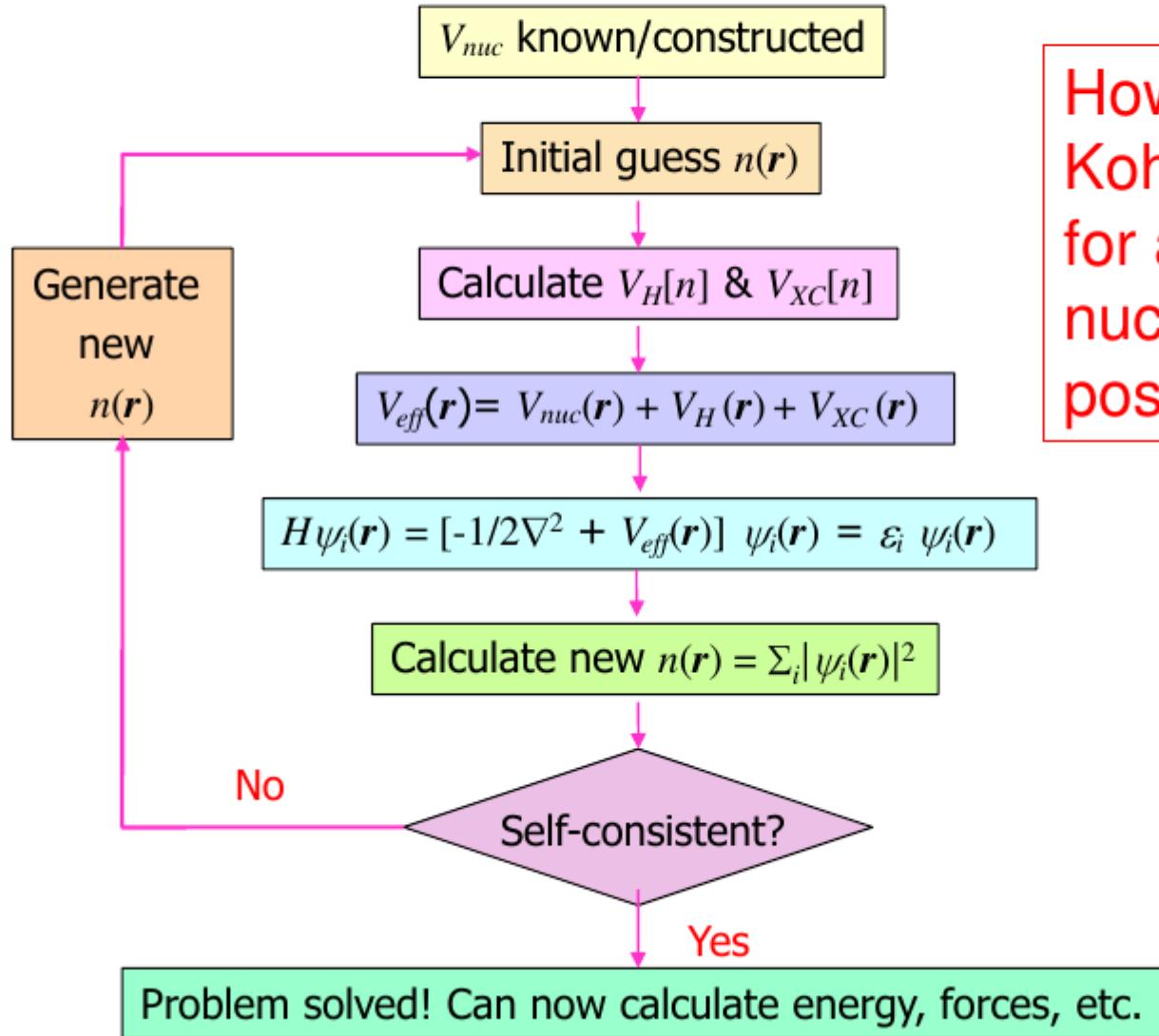
## Code organization

• pw.x	main code
• pp.x	data analysis
• ph.x	phonons/electron-phonon coupling
• dos.x	density of states
• bands.x	plot band structure
• pwcond.x	transmittance
• cp.x	molecular dynamics

more tools available:

*x-ray spectra, optics ,EELS, superconductivity,  
magnetic resonance (NMR) etc..*

# Self-consistent Iterative Solution



How to solve the  
Kohn-Sham eqns.  
for a set of fixed  
nuclear (ionic)  
positions.

The input file for PWscf is structured in a number of **NAMELISTS** and **INPUT\_CARDS**.

&NAMELIST1 ... /

&NAMELIST2 ... /

&NAMELIST3 ... /

INPUT\_CARD1

....

....

INPUT\_CARD2

....

....

**NAMELISTS** are a standard input construct in fortran90.

The use of **NAMELISTS** allows to specify the value of an input variable **only when it is needed** and to define **default values** for most variables that then need not be specified. Variable can be inserted **in any order**.

```
&NAMELIST
```

```
    needed_variable2=XX, needed_variable1=X,  
    character_variable1='a suitable string'
```

```
/
```

**NAMELISTS** are read in a specific order

**NAMELISTS** that are not required are ignored

**INPUT\_CARDS** are specific of QuantumESPRESSO codes and are used to provide input data that are **always needed** and would be boring to specify with the `variable_name=variable_value` syntax used by NAMELIST.

**INPUT\_CARDS** require data in specific order (which may depend on the situation and on the value of a **card\_formatSpecifier** )

For instance:

```
INPUT_CARD    card_format_specifier
data(1,1)  data(1,2)  data(1,3)  ...
data(2,1)  data(2,2)  data(2,3)  ...
data(3,1)  data(3,2)  data(3,3)  ...
...  ...  ...
```

Logically independent **INPUT\_CARDS** can be given in any order

There are **three mandatory** NAMELISTS in PWscf:

**&CONTROL**    input variables that control the flux of the calculation and the amount of I/O on disk and on the screen.

**&SYSTEM**    input variables that specify the system under study.

**&ELECTRONS**    input variables that control the algorithms used to reach the self-consistent solution of KS equations for the electrons.

There are **three mandatory** INPUT\_CARDS in PWscf

ATOMIC\_SPECIES name, mass and pseudopotential used for each atomic species present in the system

ATOMIC\_POSITIONS type and coordinates of each atom in the unit cell

K\_POINTS coordinates and weights of the k-points used for BZ integration

# Typical input file

```
&control
    prefix='silicon',
    pseudo_dir='./'
    outdir = './',
/
&system
    ibrav= 2,
    celldm(1) =10.2,
    nat= 2,
    ntyp= 1,
    ecutwfc = 12.0,
/
&electrons
/
ATOMIC_SPECIES
Si 28.086 Si dojo.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
```

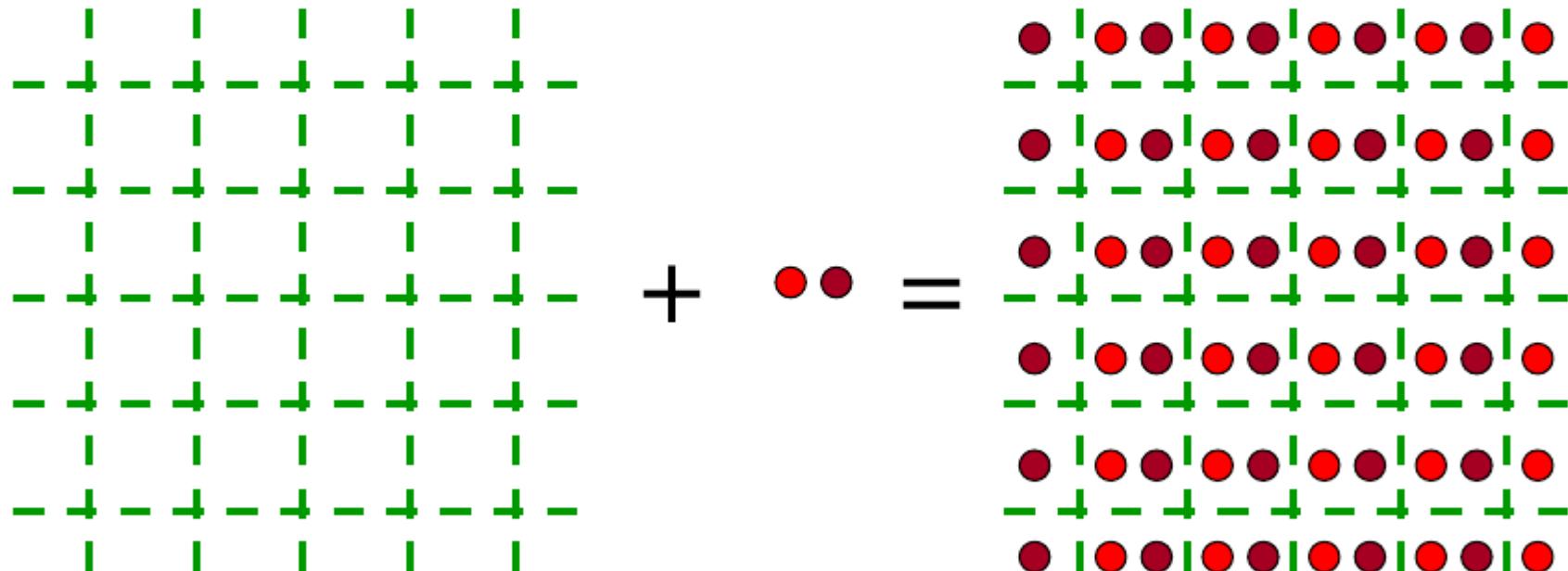
# Step 0: Defining the (periodic) system



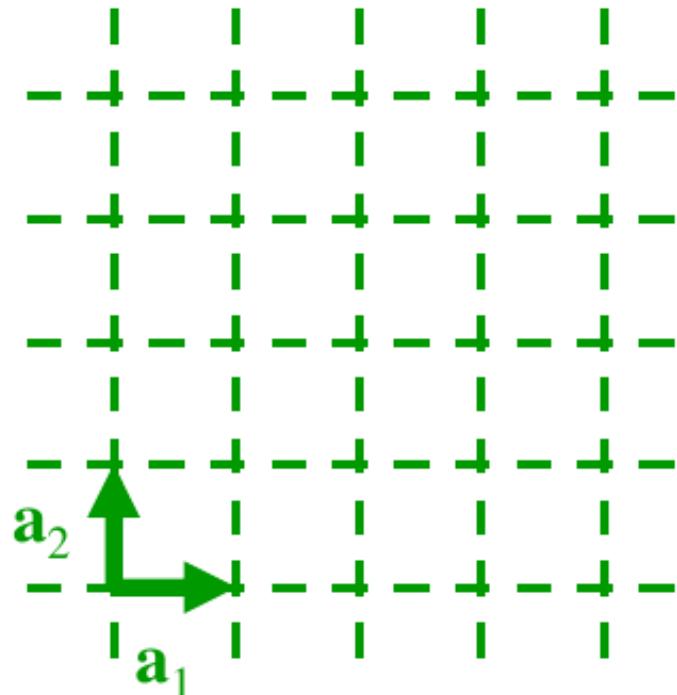
Namelist '**SYSTEM**'

# How to Specify the System

- All periodic systems can be specified by a Bravais Lattice and an atomic basis.



# How to Specify the Bravais Lattice / Unit Cell



Input parameter **ibrav**

- Gives the type of **Bravais lattice** (SC, BCC, Hex, etc.)

Input parameters {**celldm(i)** }

- Give the lengths [& directions, if necessary] of the lattice vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$

- Note that one can choose a non-primitive unit cell (e.g., 4 atom SC cell for FCC structure).

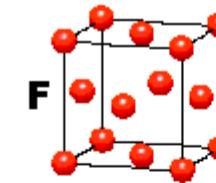
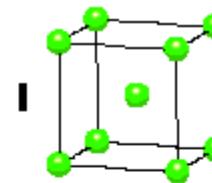
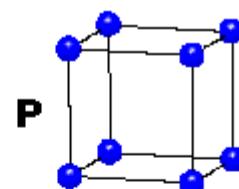
# Bravais Lattices: `ibrav` flag

[https://en.wikipedia.org/wiki/Bravais\\_lattice](https://en.wikipedia.org/wiki/Bravais_lattice)

`ibrav = 1, 3, 2`

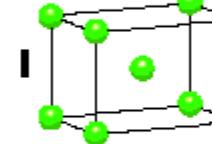
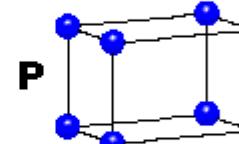
## CUBIC

$a = b = c$   
 $\alpha = \beta = \gamma = 90^\circ$



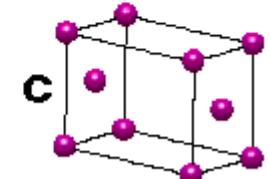
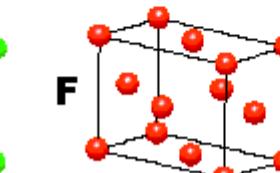
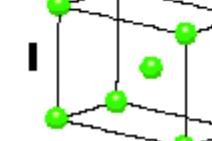
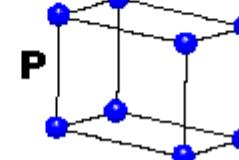
## TETRAGONAL

$a = b \neq c$   
 $\alpha = \beta = \gamma = 90^\circ$



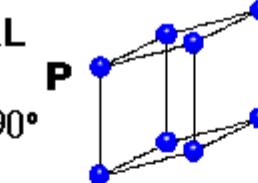
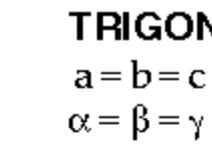
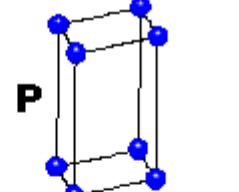
## ORTHORHOMBIC

$a \neq b \neq c$   
 $\alpha = \beta = \gamma = 90^\circ$



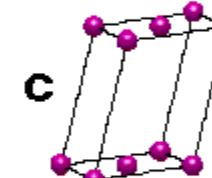
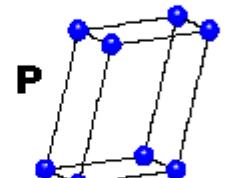
## HEXAGONAL

$a = b \neq c$   
 $\alpha = \beta = 90^\circ$   
 $\gamma = 120^\circ$



## MONOCLINIC

$a \neq b \neq c$   
 $\alpha = \gamma = 90^\circ$   
 $\beta \neq 120^\circ$



## TRICLINIC

$a \neq b \neq c$   
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$



4 Types of Unit Cell

P = Primitive

I = Body-Centred

F = Face-Centred

C = Side-Centred

+

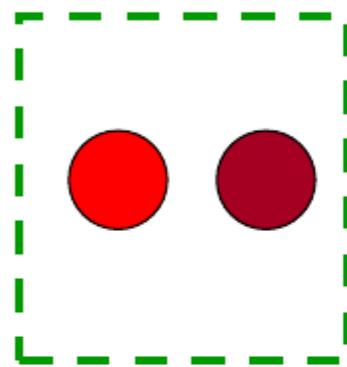
7 Crystal Classes

→ 14 Bravais Lattices

`ibrav = 12, -12, 13`

`ibrav = 14`

# Atoms Within Unit Cell – How many, where?



Input parameter **nat**

- Number of atoms in the unit cell

Input parameter **ntyp**

- Number of types of atoms

## FIELD ATOMIC\_POSITIONS

- Initial positions of atoms (may vary when “**relax**” done).
- Can choose to give in units of lattice vectors (“**crystal**”) or in Cartesian units (“**alat**” or “**bohr**” or “**angstrom**”)

# Typical input file

```
&control
    prefix='silicon',
    pseudo_dir='./'
    outdir = './',
/
&system
    ibrav= 2,
    celldm(1) =10.2,
    nat= 2,
    ntyp= 1,
    ecutwfc = 12.0,
/
&electrons
/
ATOMIC_SPECIES
Si 28.086 Si dojo.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
```

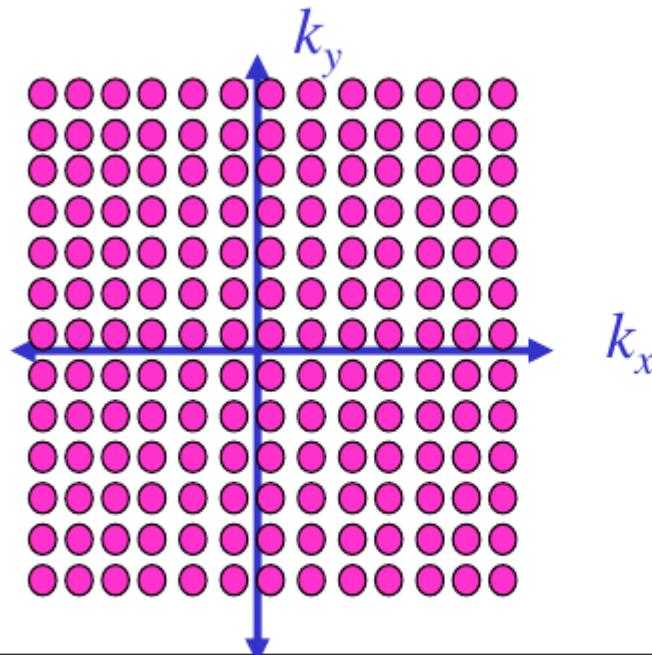
# Plane Waves & Periodic Systems

- For a periodic system:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}$$

where  $\mathbf{G}$  = reciprocal lattice vector

- The **plane waves** that appear in this expansion can be represented as a grid in k-space:



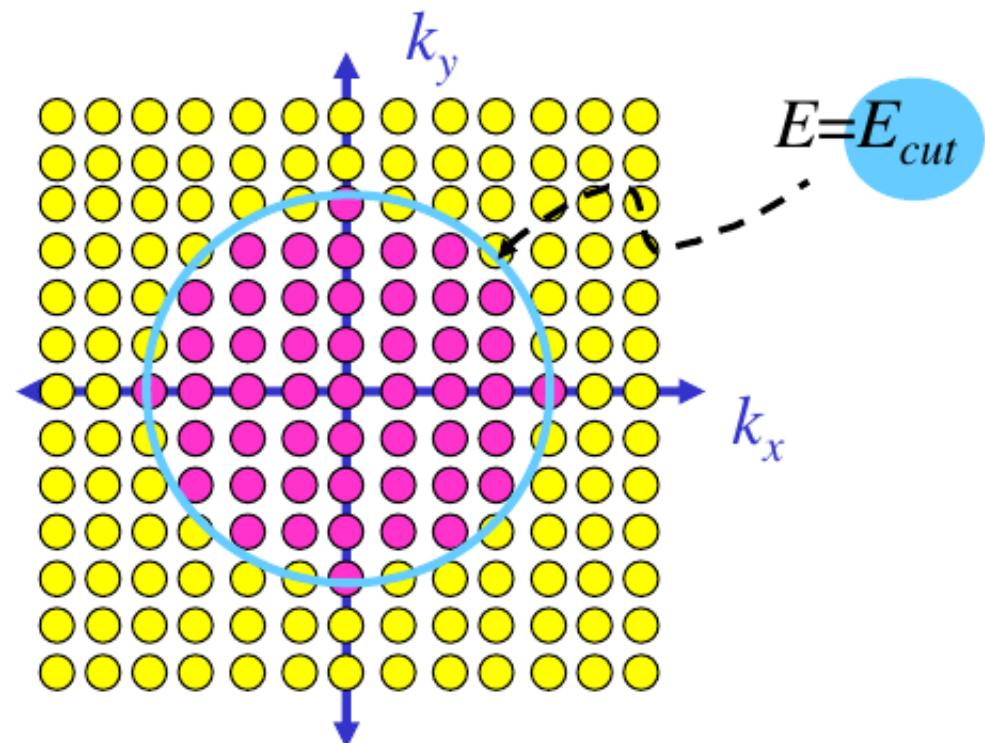
- Only true for periodic systems that grid is discrete.
- In principle, still need infinite number of plane waves.

# Truncating the Plane Wave Expansion

- In practice, the contribution from higher Fourier components (large  $|k+G|$ ) is small.
- So truncate the expansion at some value of  $|k+G|$ .
- Traditional to express this cut-off in energy units:

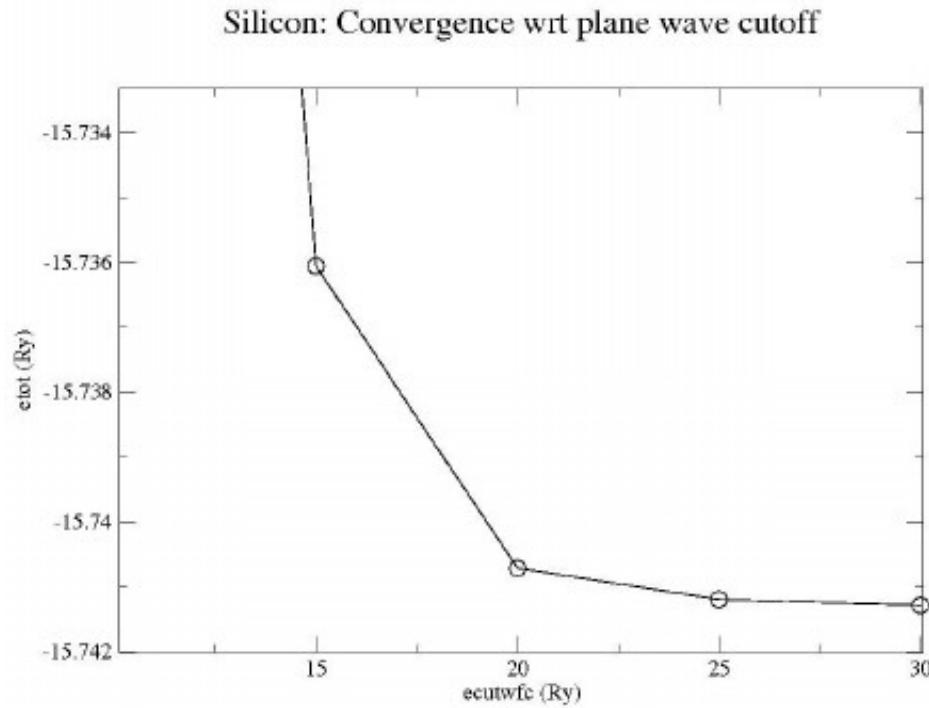
$$\frac{\hbar^2 |k + \mathbf{G}|^2}{2m} \leq E_{cut}$$

Input parameter **ecutwfc**



# Checking Convergence wrt ecutwfc

- Must always check.
- Monotonic (variational).



# Typical input file

```
&control
    prefix='silicon',
    pseudo_dir='./'
    outdir = './',
/
&system
    ibrav= 2,
    celldm(1) =10.2,
    nat= 2,
    ntyp= 1,
    ecutwfc = 12.0,
/
&electrons
/
ATOMIC_SPECIES
Si 28.086 Si dojo.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
```

# Pseudopotentials for Quantum Espresso - 1

- Go to <http://www.quantum-espresso.org>; Click on “PSEUDO”



The screenshot shows the Quantum Espresso homepage. At the top right, there is a navigation bar with links: HOME :: PROJECT :: WHAT CAN QE DO :: DOWNLOAD :: LEARN :: **PSEUDO** :: TOOLS :: QE WIKI :: CONTACTS :: QUOTE :: LOGOS ::. The link for "PSEUDO" is circled in red.

**13 July 2010** A bugfix release, v.4.2.1, of the Quantum ESPRESSO distribution is available for download.

**10 May 2010** A new version, v.4.2, of the Quantum ESPRESSO distribution is available for download.

**12 April 2010** The final bugfix release, v.4.1.3, of a Quantum ESPRESSO distribution is available for download. This supersedes all previous 4.1.x releases.

**20 July 2009** The new release of the Quantum ESPRESSO distribution is available for download (version 4.1).

**21 April 2009** The final bugfix release, v.4.0.5, of the Quantum ESPRESSO distribution, is available for download. This supersedes all previous 4.0.x releases.

Quantum ESPRESSO is an integrated suite of computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials (both norm-conserving and ultrasoft).

What I cannot compute, I do not understand [adapted from Richard P. Feynman]



# Pseudopotentials for Quantum Espresso - 2

- Click on element for which pseudopotential wanted.

The screenshot shows the Quantum Espresso Pseudopotentials website. At the top left is the logo 'QUANTUM ESPRESSO'. Below it is a navigation bar with links: HOME :: PROJECT :: WHAT CAN QE DO :: DOWNLOAD :: LEARN :: **PSEUDO** :: TOOLS :: QE WIKI :: CONTACTS :: QUOTE :: LOGOS ::. On the left, there's a sidebar with 'PSEUDOPOTENTIALS' and two collapsed sections: 'About' and 'Notes'. The main content area features a large periodic table. The element Oxygen (O) is circled in yellow. The table includes elements from Hydrogen (H) to Rutherfordium (Rf), with Lanthanoids (La-Lu) and Actinoids (Ac-Lr) listed below the main body.

1 H	2 He
3 Li	4 Be
5 Na	6 Mg
7 K	8 Ca
9 Rb	10 Sr
11 Cs	12 Ba
13 Fr	14 Ra
15 Sc	16 Ti
17 Y	18 Zr
19 Nb	20 Mo
21 Tc	22 Ru
23 Rh	24 Pd
25 Os	26 Ag
27 Ir	28 Pt
29 Au	30 Hg
31 Tl	32 In
33 Sn	34 Sb
35 Te	36 I
37 La	38 Ce
39 Pr	40 Nd
41 Pm	42 Sm
43 Eu	44 Gd
45 Tb	46 Dy
47 Ho	48 Er
49 Tm	50 Yb
51 Lu	52 Hf
53 Hf	54 W
55 Re	56 Os
57 Ir	58 Pt
59 Au	60 Hg
61 Hg	62 Tl
63 Po	64 Pb
65 At	66 Rn
67 Fr	68 Ra
69 Rf	70 Lr
71 Db	72 Bh
73 Sg	74 Hs
75 Nh	76 Mt
77 Fr	78 Md
79 No	80 Fm
81 Md	82 No
83 Po	84 Fr
85 At	86 Rn
87 Fr	88 Ra
89 Ac	90 Th
91 Pa	92 U
93 Np	94 Pu
95 Am	96 Cm
97 Bk	98 Cf
99 Es	100 Fm
101 Md	102 No

Download the full archive (~30MB)

# Pseudo-potentials of this tutorials

<http://www.pseudo-dojo.org/> (QE format is called UPF)

Help me



**PSEUDŌ  
Dōjō**

Download

Type: NC SR (ONCVPSP v0.4.1) XC: PBE Accuracy: stringent Format: upf

Element	Z	Name	Symbol	Atomic Mass	Electron Configuration	Ionization Energy (eV)	Electronegativity	Molar Volume (cm³/mol)	Density (g/cm³)	Boiling Point (°C)	Melting Point (°C)	Electron Affinity (eV)	Pauli Exclusion Principle	Period	Group	Block	Category	Notes
Hydrogen	1	Hydrogen	H	1.008	1s <sup>1</sup>	13.6	2.2	10.0	0.07	-259	-259	-1.4	1	1	1	s	Alkali metals	None
Lithium	3	Lithium	Li	6.94	1s <sup>2</sup> 2s <sup>1</sup>	5.39	1.0	14.3	0.53	-180	-180	-3.4	2	1	2	s	Alkali metals	None
Beryllium	4	Beryllium	Be	9.01	1s <sup>2</sup> 2s <sup>2</sup>	9.32	1.5	15.7	0.8	-170	-170	-5.3	2	2	2	s	Alkaline earth metals	None
Sodium	11	Sodium	Na	22.99	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>1</sup>	10.89	0.4	10.8	0.9	-149	-149	-7.0	3	1	3	s	Alkali metals	None
Magnesium	12	Magnesium	Mg	24.31	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup>	12.31	0.4	12.3	1.5	-145	-145	-7.8	3	2	2	s	Alkaline earth metals	None
Potassium	19	Potassium	K	39.09	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>1</sup>	18.38	0.2	18.3	0.3	-132	-132	-8.8	3	1	3	s	Alkali metals	None
Calcium	20	Calcium	Ca	40.08	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>2</sup>	19.87	0.1	19.8	0.3	-128	-128	-9.6	3	2	2	s	Alkaline earth metals	None
Scandium	21	Scandium	Sc	45.0	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>1</sup> 4s <sup>2</sup>	21.88	1.3	21.8	1.3	-120	-120	-10.6	4	3	3	d	Transition metals	None
Titanium	22	Titanium	Ti	47.87	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>2</sup> 4s <sup>2</sup>	24.40	0.9	24.4	1.3	-115	-115	-11.2	4	4	4	d	Transition metals	None
Vanadium	23	Vanadium	V	50.94	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>3</sup> 4s <sup>2</sup>	26.70	1.3	26.7	1.7	-110	-110	-11.8	4	5	5	d	Transition metals	None
Chromium	24	Chromium	Cr	51.99	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>5</sup> 4s <sup>1</sup>	27.60	1.1	27.6	2.3	-105	-105	-12.4	4	6	6	d	Transition metals	None
Manganese	25	Manganese	Mn	54.94	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>5</sup> 4s <sup>2</sup>	29.50	1.1	29.5	2.3	-100	-100	-13.0	4	7	7	d	Transition metals	None
Iron	26	Iron	Fe	55.85	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>6</sup> 4s <sup>2</sup>	30.45	2.1	30.4	3.1	-95	-95	-13.6	4	8	8	d	Transition metals	None
Cobalt	27	Cobalt	Co	58.93	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>7</sup> 4s <sup>1</sup>	32.25	0.5	32.2	0.7	-90	-90	-14.2	4	9	9	d	Transition metals	None
Nickel	28	Nickel	Ni	58.69	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>8</sup> 4s <sup>1</sup>	33.50	1.0	33.5	1.5	-85	-85	-14.8	4	10	10	d	Transition metals	None
Copper	29	Copper	Cu	63.55	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>1</sup>	35.45	0.5	35.4	0.9	-80	-80	-15.4	4	11	11	d	Transition metals	None
Zinc	30	Zinc	Zn	65.39	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup>	37.00	0.3	37.0	0.8	-75	-75	-16.0	4	12	12	d	Transition metals	None
Gallium	31	Gallium	Ga	69.72	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>1</sup>	38.95	0.3	38.9	0.9	-70	-70	-16.6	5	13	13	p	Post-transition metals	None
Germanium	32	Germanium	Ge	72.61	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>2</sup>	40.08	0.1	40.0	0.1	-65	-65	-17.2	5	14	14	p	Post-transition metals	None
Arsenic	33	Arsenic	As	75.00	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup>	41.90	0.1	41.9	0.2	-60	-60	-17.8	5	15	15	p	Post-transition metals	None
Selenium	34	Selenium	Se	78.96	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup>	43.80	0.1	43.8	0.1	-55	-55	-18.4	5	16	16	p	Post-transition metals	None
Bromine	35	Bromine	Br	80.00	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>5</sup>	45.53	0.0	45.5	0.1	-50	-50	-19.0	3	17	17	p	Halogen	None
Krypton	36	Krypton	Kr	83.80	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup>	47.87	0.0	47.8	0.2	-45	-45	-19.6	2	18	18	p	Noble gases	None
Rubidium	37	Rubidium	Rb	84.75	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>1</sup>	49.90	0.2	49.9	0.4	-40	-40	-20.2	3	19	19	p	Alkali metals	None
Sr	38	Sr	Sr	87.67	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>2</sup>	51.90	0.2	51.9	0.4	-35	-35	-20.8	3	20	20	p	Alkaline earth metals	None
Yttrium	39	Yttrium	Y	88.91	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup>	54.45	0.1	54.4	0.3	-30	-30	-21.4	4	21	21	p	Transition metals	None
Zirconium	40	Zirconium	Zr	91.22	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup>	56.45	0.1	56.4	0.5	-25	-25	-22.0	4	22	22	p	Transition metals	None
Niobium	41	Niobium	Nb	92.91	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>5</sup>	58.70	0.1	58.7	0.8	-20	-20	-22.6	4	23	23	p	Transition metals	None
Molybdenum	42	Molybdenum	Mo	95.94	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup>	60.70	1.4	60.7	1.5	-15	-15	-23.2	4	24	24	p	Transition metals	None
Ruthenium	43	Ruthenium	Tc	98.00	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>7</sup>	62.60	1.6	62.6	1.7	-10	-10	-23.8	4	25	25	p	Transition metals	None
Rhodium	44	Rhodium	Ru	101.09	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>8</sup>	64.40	2.1	64.4	1.5	-5	-5	-24.4	4	26	26	p	Transition metals	None
Palladium	45	Palladium	Pd	102.90	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>9</sup>	66.50	1.1	66.5	1.3	0	-10	-25.0	4	27	27	p	Transition metals	None
Silver	46	Silver	Ag	106.45	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>10</sup>	68.60	0.6	68.6	0.8	-5	-10	-25.6	4	28	28	p	Post-transition metals	None
Cadmium	47	Cadmium	Cd	112.41	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>11</sup>	70.70	0.3	70.7	0.5	-5	-10	-26.2	4	29	29	p	Post-transition metals	None
Indium	48	Indium	In	114.81	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>12</sup>	72.90	0.4	72.9	1.4	0	-10	-26.8	5	30	30	p	Post-transition metals	None
Tin	49	Tin	Tl	115.48	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>13</sup>	75.00	0.6	75.0	1.2	0	-10	-27.4	5	31	31	p	Post-transition metals	None
Antimony	50	Antimony	Sb	116.86	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>14</sup>	77.40	0.7	77.4	1.1	0	-10	-28.0	5	32	32	p	Post-transition metals	None
Te	51	Te	Te	117.50	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>15</sup>	79.00	0.6	79.0	1.2	0	-10	-28.6	5	33	33	p	Post-transition metals	None
Iodine	52	Iodine	I	118.85	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>16</sup>	80.90	0.9	80.9	2.9	0	-10	-29.2	5	34	34	p	Post-transition metals	None
Cs	55	Cs	Cs	122.90	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>17</sup>	82.00	0.1	82.0	0.6	0	-10	-29.8	3	35	35	p	Noble gases	None
Ba	56	Ba	Ba	125.40	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>18</sup>	83.70	0.9	83.7	4.8	0	-10	-30.4	3	36	36	p	Noble gases	None
Hf	72	Hafnium	Hf	144.24	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>19</sup>	91.70	0.3	91.7	0.4	0	-10	-31.0	4	37	37	p	Transition metals	None
Ta	73	Tantalum	Ta	145.00	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>20</sup>	93.80	1.0	93.8	0.9	0	-10	-31.6	4	38	38	p	Transition metals	None
W	74	Wolfram	W	149.00	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>21</sup>	95.50	0.4	95.5	1.0	0	-10	-32.2	4	39	39	p	Transition metals	None
Os	75	Osmium	Os	151.90	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>22</sup>	97.40	0.7	97.4	1.5	0	-10	-32.8	4	40	40	p	Transition metals	None
Ir	77	Iridium	Ir	153.80	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>23</sup>	99.50	0.9	99.5	1.6	0	-10	-33.4	4	41	41	p	Transition metals	None
Pt	78	Platinum	Pt	157.80	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>24</sup>	101.40	0.6	101.4	1.6	0	-10	-34.0	4	42	42	p	Transition metals	None
Au	79	Gold	Au	160.90	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>25</sup>	103.40	1.3	103.4	1.6	0	-10	-34.6	4	43	43	p	Post-transition metals	None
Hg	80	Mercury	Hg	161.40	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>26</sup>	105.40	0.6	105.4	1.6	0	-10	-35.2	4	44	44	p	Post-transition metals	None
Tl	81	Thallium	Tl	162.40	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>27</sup>	107.40	0.2	107.4	0.8	0	-10	-35.8	5	45	45	p	Post-transition metals	None
Pb	82	Lead	Pb	164.90	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>28</sup>	112.40	0.6	112.4	0.8	0	-10	-36.4	5	46	46	p	Post-transition metals	None
Bi	83	Bismuth	Bi	168.00	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>29</sup>	119.70	0.6</td											

## Element & $V_{ion}$ for Quantum-ESPRESSO

- Should have same exchange-correlation functional for all pseudopotentials.

input

```
mixing_alpha = 0.8, mixing_beta  
mixing_beta = 0.7, conv_thr = 1.0  
/  
ATOMIC_SPECIES  
Fe 55.85 Fe pzfnd-rrkjus.UPF  
Co 58.93 Co pbe-nd-rrkjus.UPF  
ATOMIC_POSITIONS (crystal)  
Fe 0.00 0.00 0.00
```

oops!

output

```
Max angular momentum in pseudopotentials  
from readpp : error # 2  
inconsistent DFT read  
stopping ..■
```

# Typical input file

```
&control
    prefix='silicon',
    pseudo_dir='./'
    outdir = './',
/
&system
    ibrav= 2,
    celldm(1) =10.2,
    nat= 2,
    ntyp= 1,
    ecutwfc = 12.0,
/
&electrons
/
ATOMIC_SPECIES
Si 28.086 Si dojo.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
```

# First calculation: Self-consistent calculation for Silicon in the diamond structure

**Espace de Travail:** tutorials/Si\_bulk/  
or download from [http://attaccaelite.com/QE\\_tutorial/](http://attaccaelite.com/QE_tutorial/)

**Unpack files:** tar zxvf Si\_bulk.tgz

**Look the input file:**

```
cd Si_bulk/  
gedit/xed/nano/vi/emacs Si.scf.in
```

**Run calculations!!**

```
pw.x -inp Si.scf.in > output_scf
```

## Look the output file: check electrons, convergence, etc...

run pw.x code

```
prompt> espresso_dir/bin/pw.x < si.scf.in > si.scf.out
```

look at outdir and its content

```
prompt> ls /scratch/my_name/espresso
```

```
silicon.save    silicon.wfc
```

examine output file and look how convergence proceeds

```
prompt> grep -e 'total energy' -e estimate si.scf.out
```

```
total energy          = -15.78885161 ryd
```

```
estimated scf accuracy < 0.06378063 ryd
```

```
total energy          = -15.79407709 ryd
```

```
estimated scf accuracy < 0.00231243 ryd
```

```
total energy          = -15.79448017 ryd
```

```
estimated scf accuracy < 0.00006733 ryd
```

```
total energy          = -15.79449452 ryd
```

```
estimated scf accuracy < 0.00000619 ryd
```

```
! total energy          = -15.79449556 ryd
```

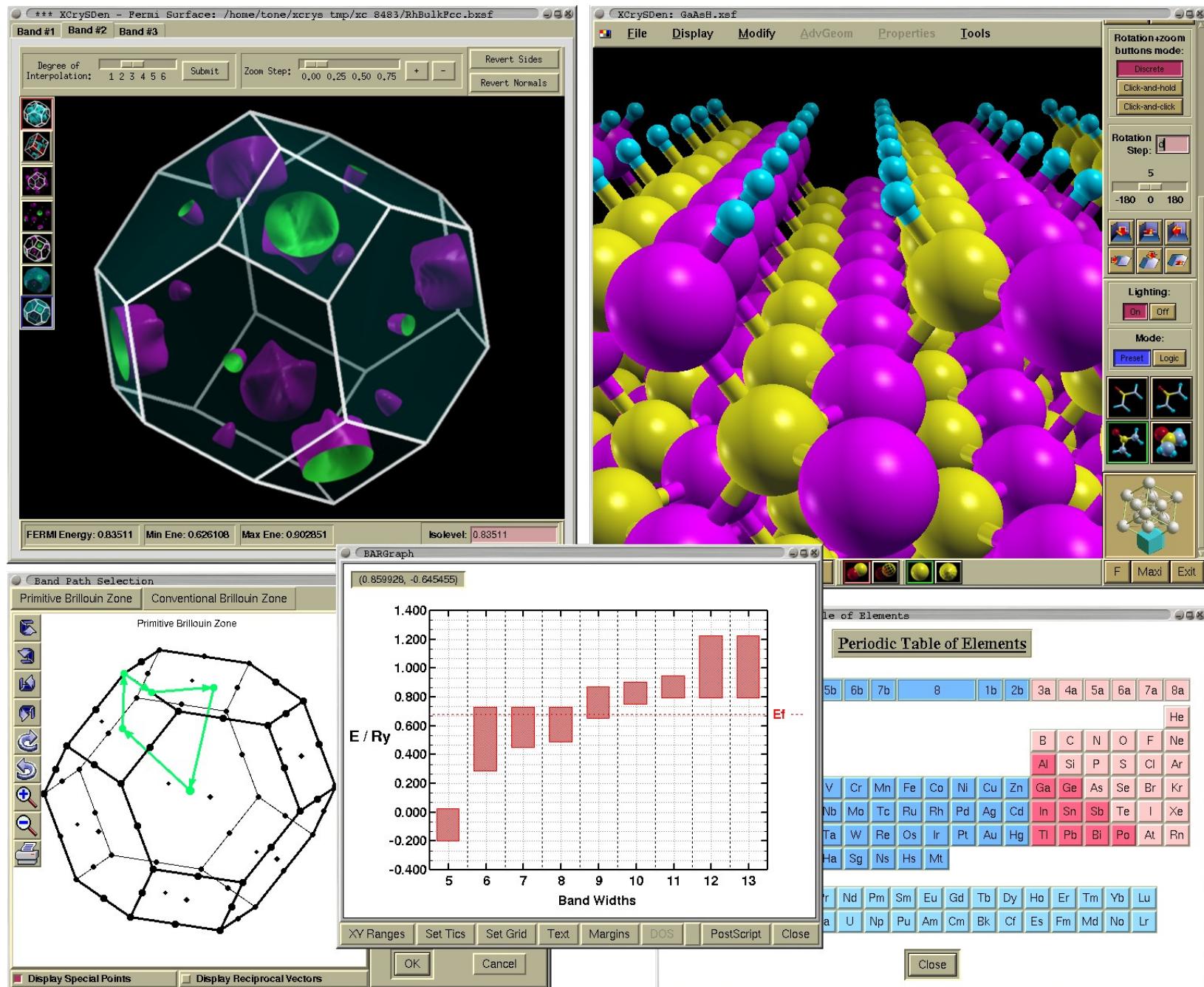
```
estimated scf accuracy < 0.00000006 ryd
```

First calculation:  
Converge the total energy  
with respect  
to G-vectors and K-points

You can use ‘gnuplot’ or  
‘xmgrace’

```
&control
  prefix='silicon',
  pseudo_dir='./'
  outdir = './',
/
&system
  ibrav= 2,
  celldm(1) =10.2,
  nat= 2,
  ntyp= 1,
  ecutwfc = 12.0,
/
&electrons
/
ATOMIC_SPECIES
Si 28.086 Si dojo.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
```

# Using XCrySDen to verify input/output



# Using Xcrysden to verify input/output

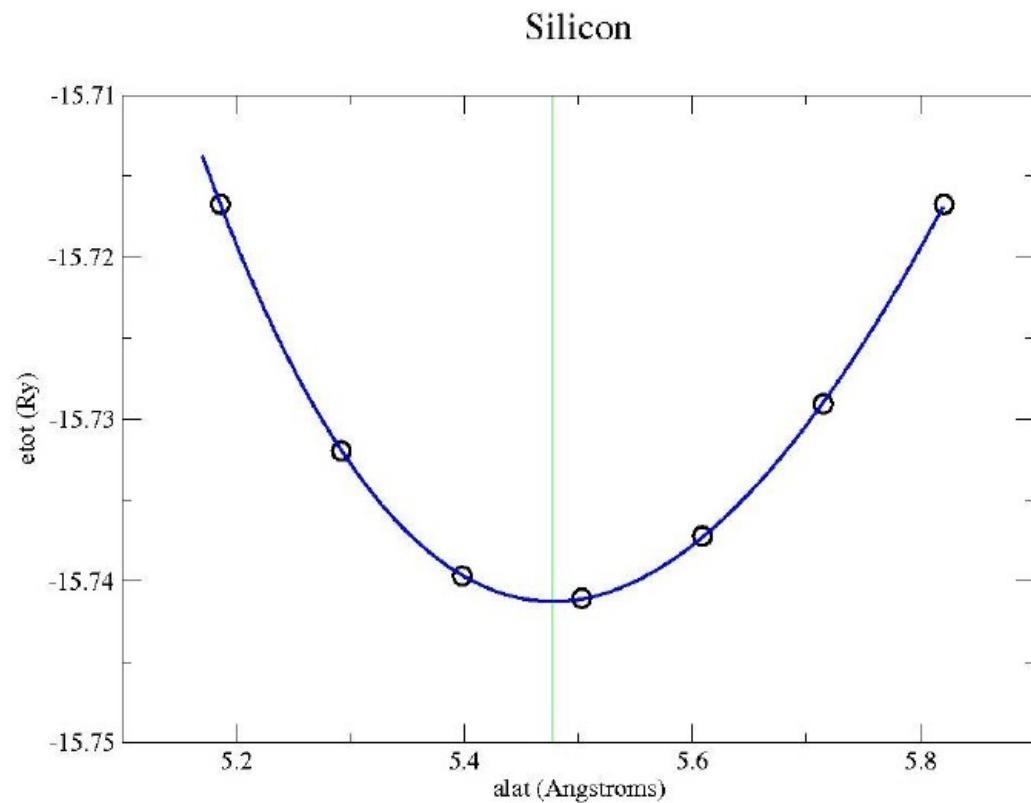
- Visualization of structures from PW.X **input** file:
  - `xcrysden --pwi input.file`
- Visualization of structures from PW.X **output** file:
  - `xcrysden --pwo output.file`

# What can we do with the total energy?

Structure optimization, phonons,  
compressibility, phase transitions, binding  
energy, etc...

## Second calculation: Optimal lattice parameter for Silicon

- Perhaps the most important output quantity is the TOTAL ENERGY
- Can use, e.g., to optimize structure
- e.g., for a cubic crystal, where the structure can be specified by a single parameter (side of cube):



# Third calculation: Silicon band structure (Si.nscf.in)

```
&control
  calculation='nscf',
  prefix='silicon',
  pseudo_dir='./'
  outdir = './',
/
&system
  ibrav= 2,
  celldm(1) =10.2,
  nat= 2,
  ntyp= 1,
  ecutwfc = 12.0,
  nbnd=8
/
&electrons
/
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 crystal_b
3
0.5 0.5 0.5 20
0.0 0.0 0.0 20
0.5 0.5 10
```

New calculation type

Number of bands

k-points list using crystal b  
(generate a path in *k*-space)

# Bands plot

```
&bands
  prefix = 'silicon'
  outdir= './'
  filband = 'bands.dat'
/

```

**bands.in** file

## Run bands.x

```
bands.x < bands.in > output_scf
```

## Plot with gnuplot

```
gnuplot
gnuplot> plot 'bands.dat.gnu' u 1:2 w l
```

# 4th calculation: data analysis

## Charge density

```
&inputpp
prefix = 'silicon'
outdir='./'
filplot = 'sicharge'
plot_num= 0
/
&plot
iflag = 3
output_format = 5
fileout = 'si.rho.xsf'
/
```

### Run pp.x

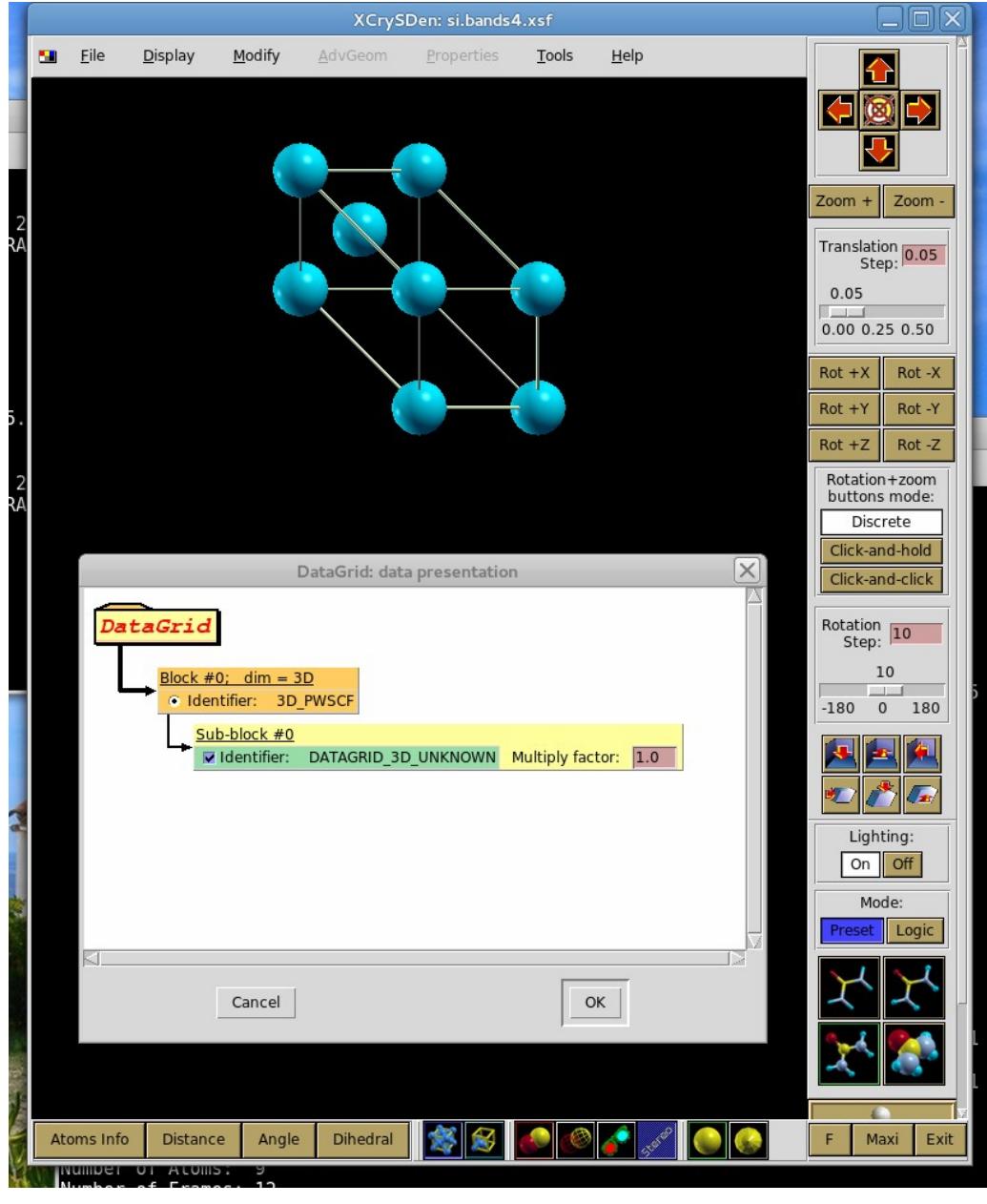
```
pp.x < si.pp_rho.in > output_pp
```

### Visualize with Xcrysden

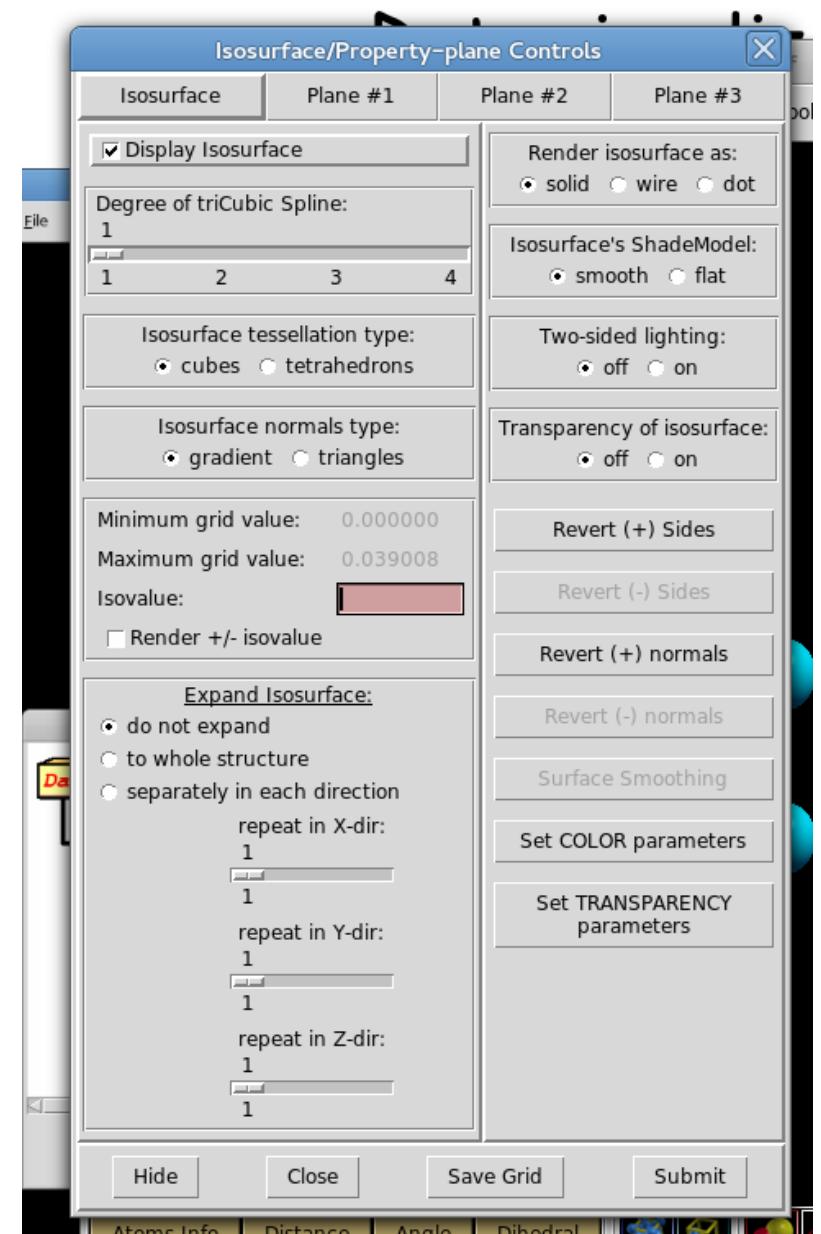
```
xcrysden --xsf si.rho.xsf
```

# Data Visualization with XCrySDen

Tools → Data grid

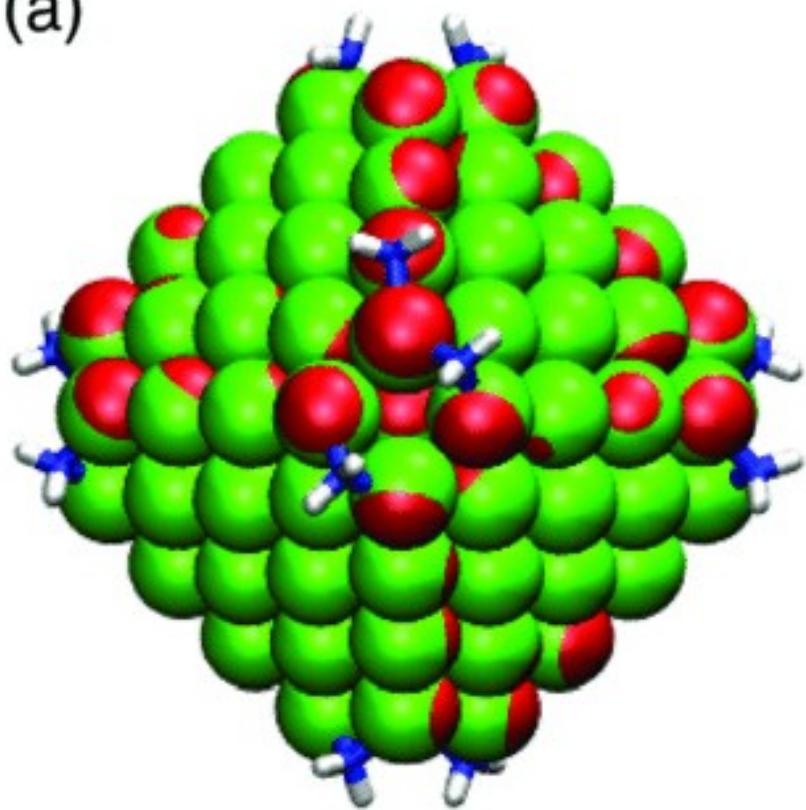


Set Isolevel

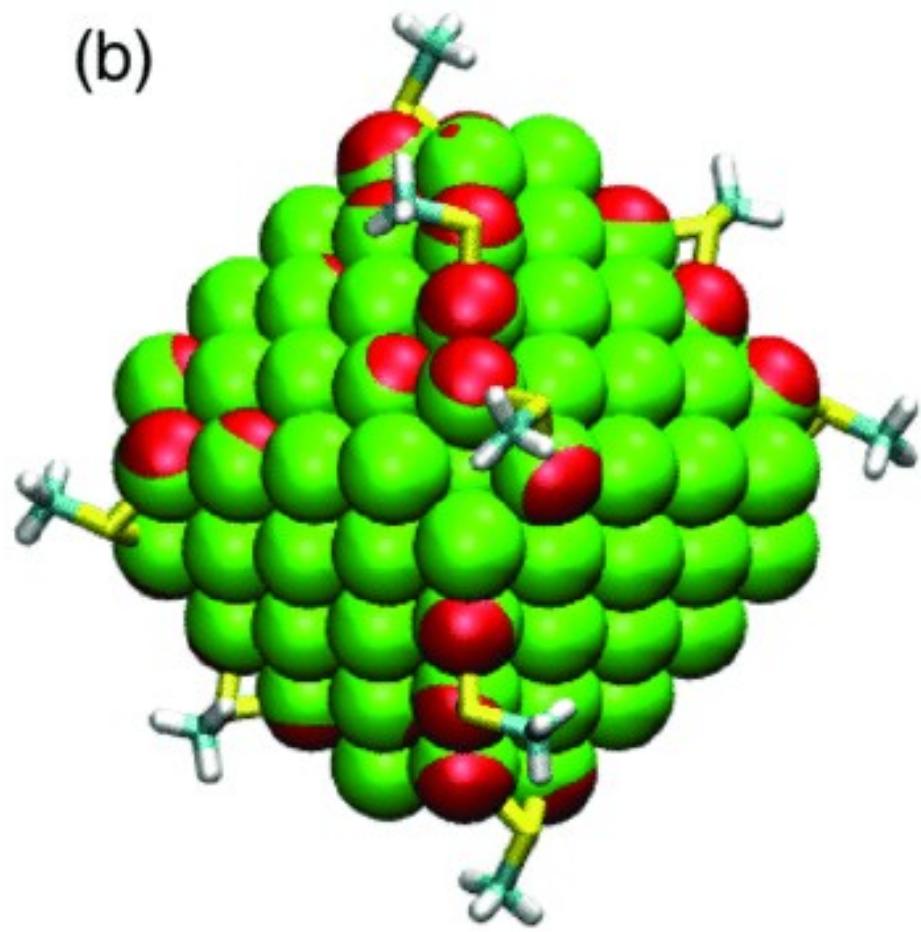


# Structure optimization

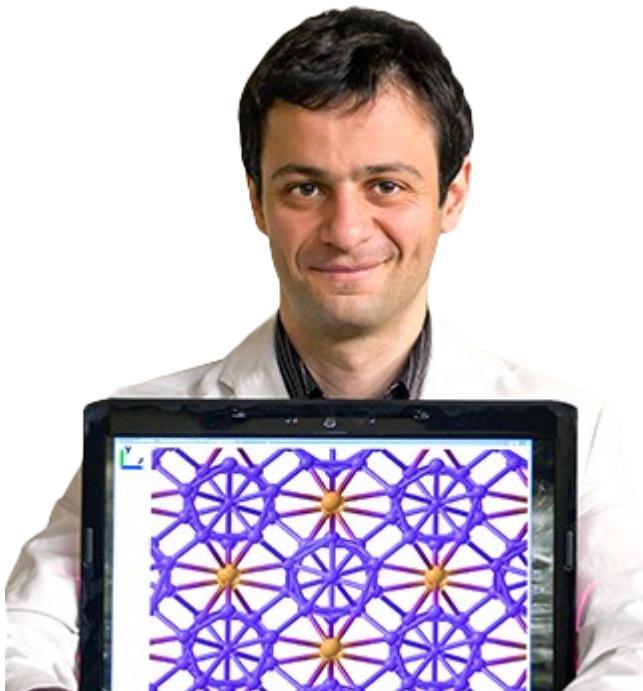
(a)



(b)



# The king of structure optimization



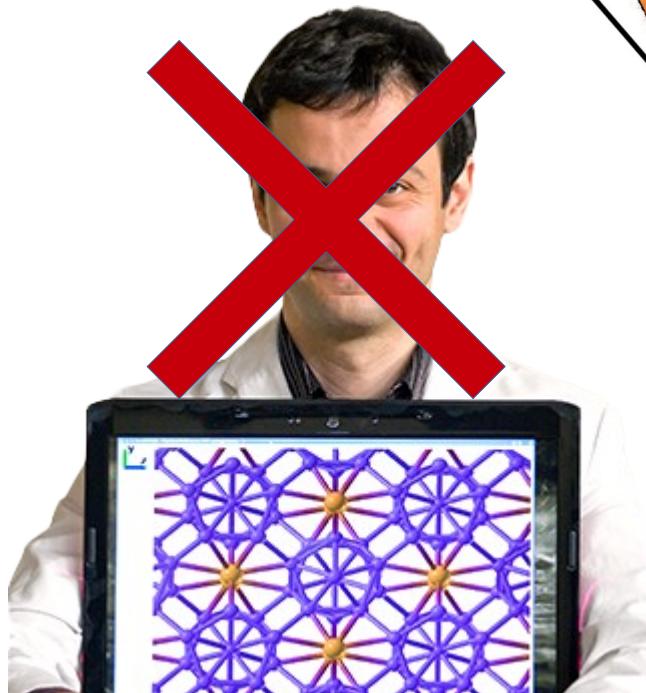
Artem Oganov

[https://en.wikipedia.org/wiki/Artem\\_R.\\_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 MgSiO<sub>3</sub> post-perovskite** in the Earth's mantle, prediction and synthesis of "forbidden" compounds (e.g., Na<sub>3</sub>Cl), discovery of helium chemistry, and creation of **borophene** - a **2D-monolayer of boron atoms**, with great promises for future technologies

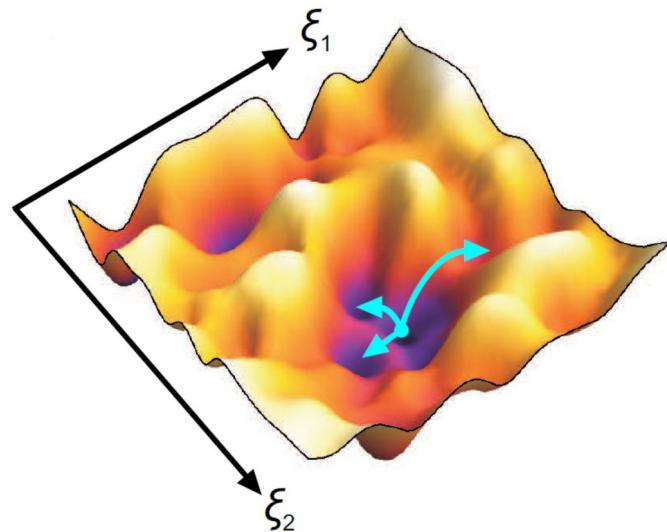
see wiki for references.

# Why you will not be as successful as Artem Oganov

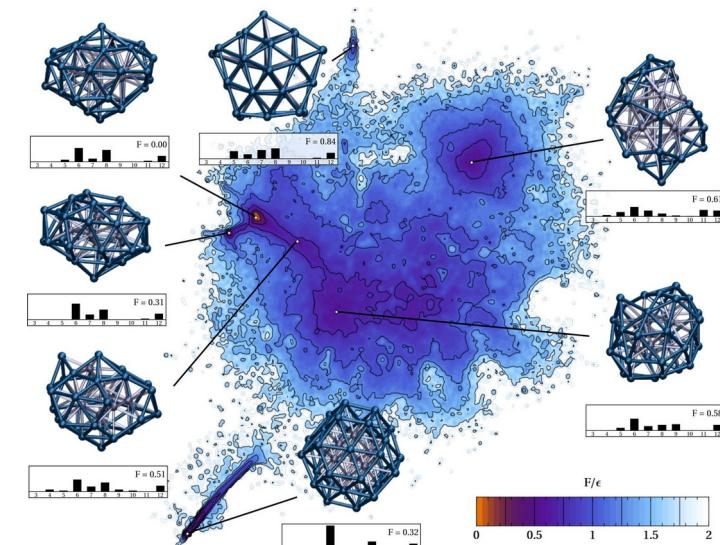
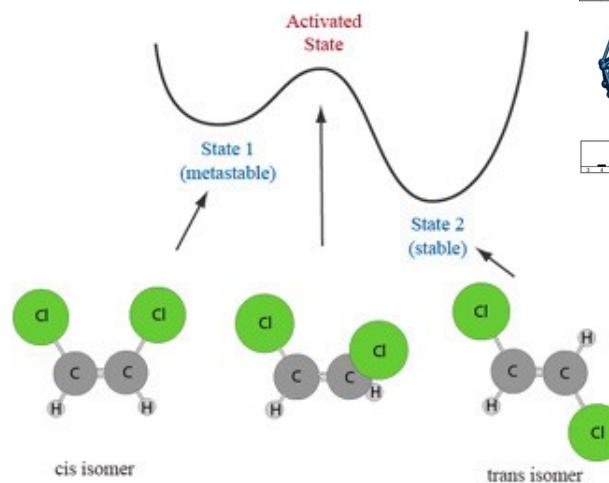


Artem Oganov

[https://en.wikipedia.org/wiki/Artem\\_R.\\_Oganov](https://en.wikipedia.org/wiki/Artem_R._Oganov)



Energy landscape  
too complex



Use UPEX!!

# 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.)

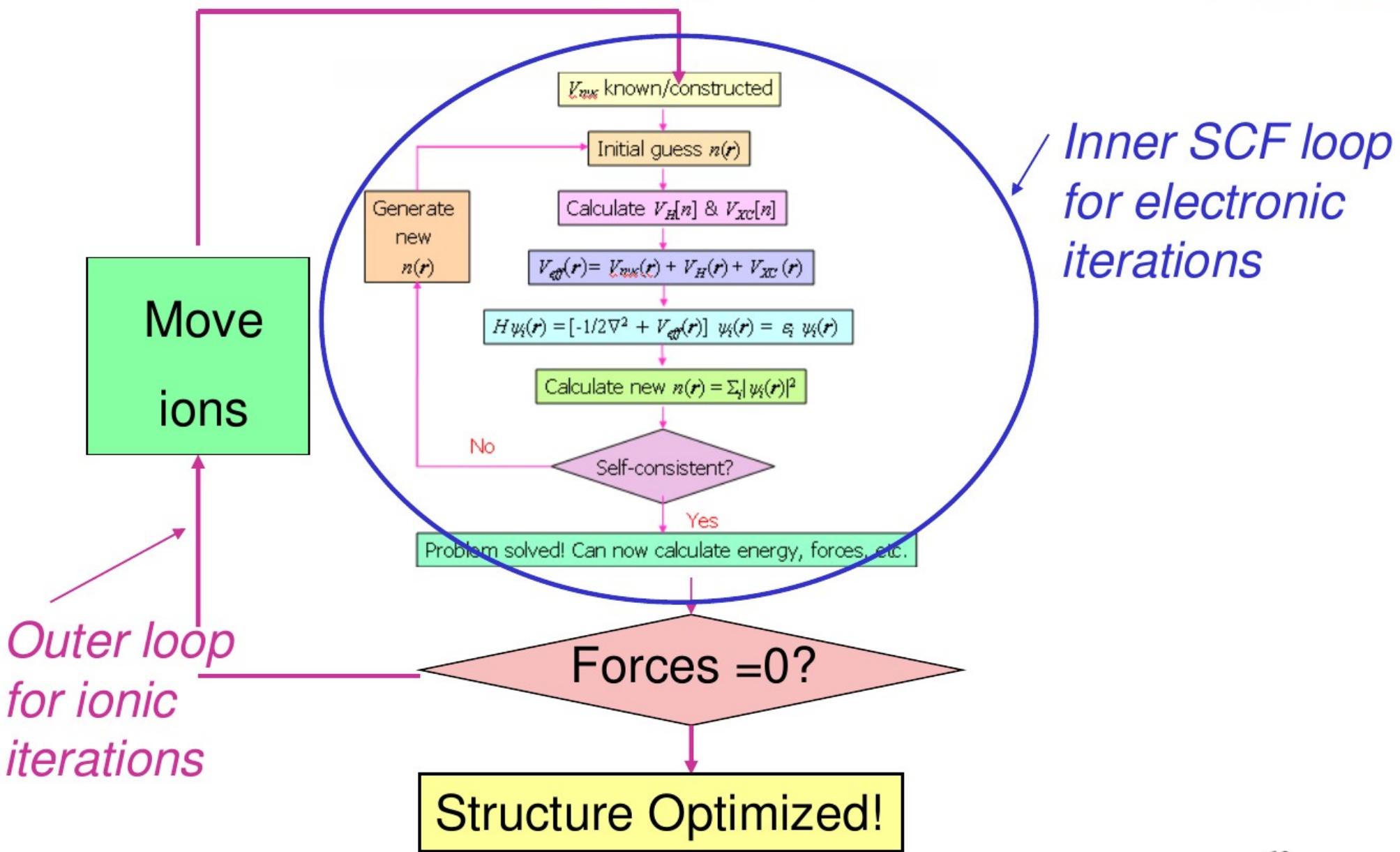
- The force is now given by

$$\begin{aligned}\mathbf{F}_I &= -\langle \Psi | \frac{\partial H}{\partial \mathbf{R}_I} | \Psi \rangle - E \langle \frac{\partial \Psi}{\partial \mathbf{R}_I} | \Psi \rangle - E \langle \Psi | \frac{\partial \Psi}{\partial \mathbf{R}_I} \rangle \\ &= -\langle \Psi | \frac{\partial H}{\partial \mathbf{R}_I} | \Psi \rangle - E \frac{\partial}{\partial \mathbf{R}_I} \langle \Psi | \Psi \rangle \xrightarrow{0}\end{aligned}$$

- 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 tprnfor

# 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)

# Structural optimisation of an acetylene ( $C_2H_2$ ) molecule

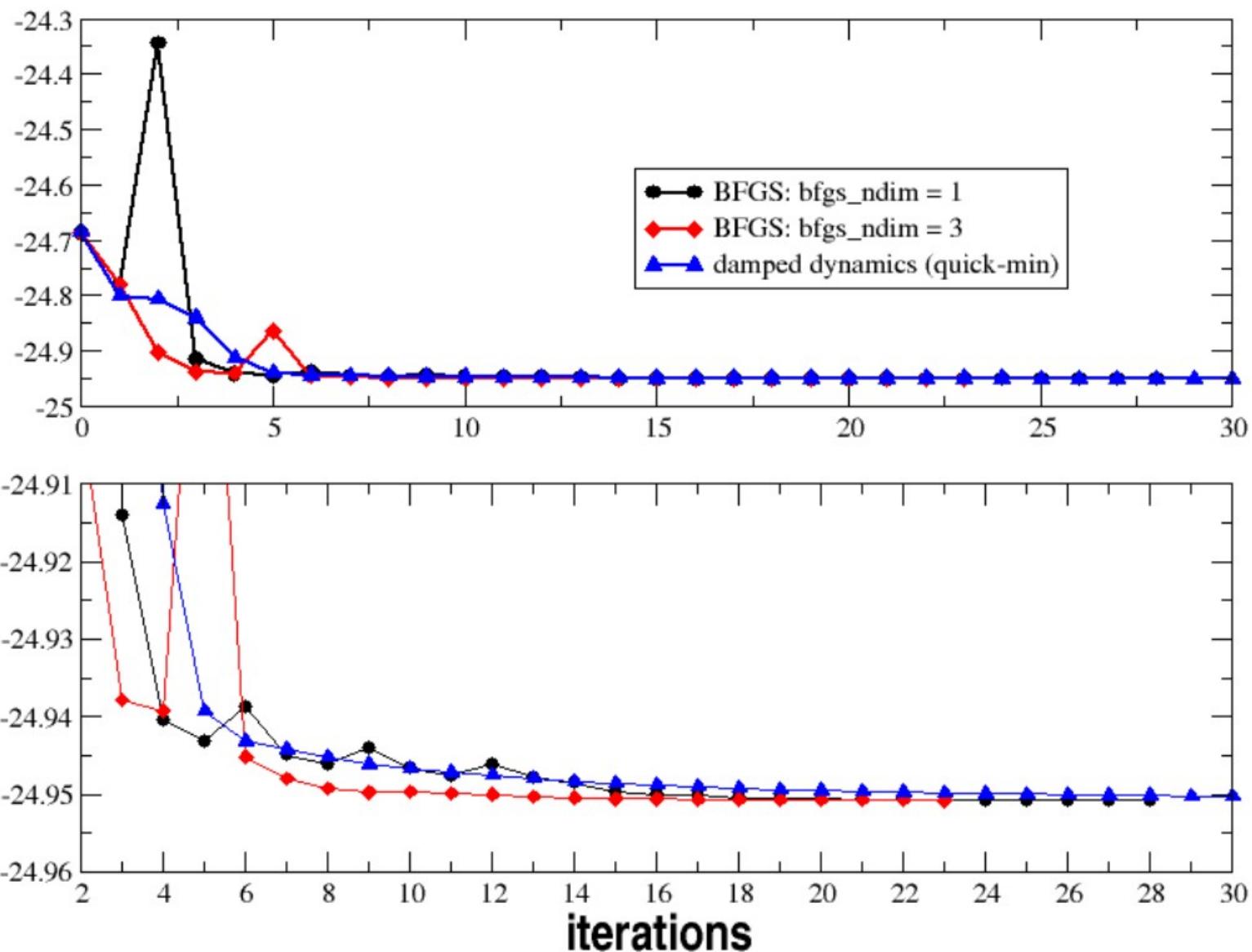
- ✓ Run a fourth simulation to identify, with the BFGS algorithm, the equilibrium geometry of the acetylene molecule:

```
prompt> pw.x < acetylene-BFGS.in > acetylene-BFGS.out
```

- ✓ Visualize the movie of the relaxation with xcrysden:

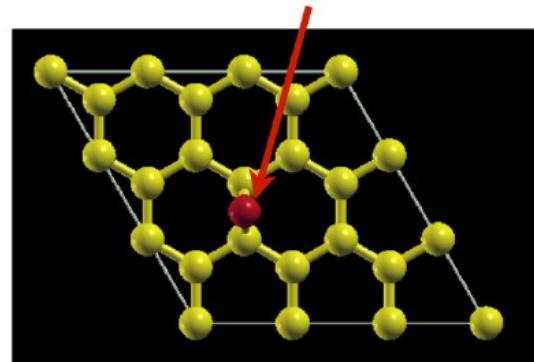
```
prompt> xcrysden --pwo acetylene-BFGS.out
```

# Structural optimisation: convergence



# Graphene Oxide

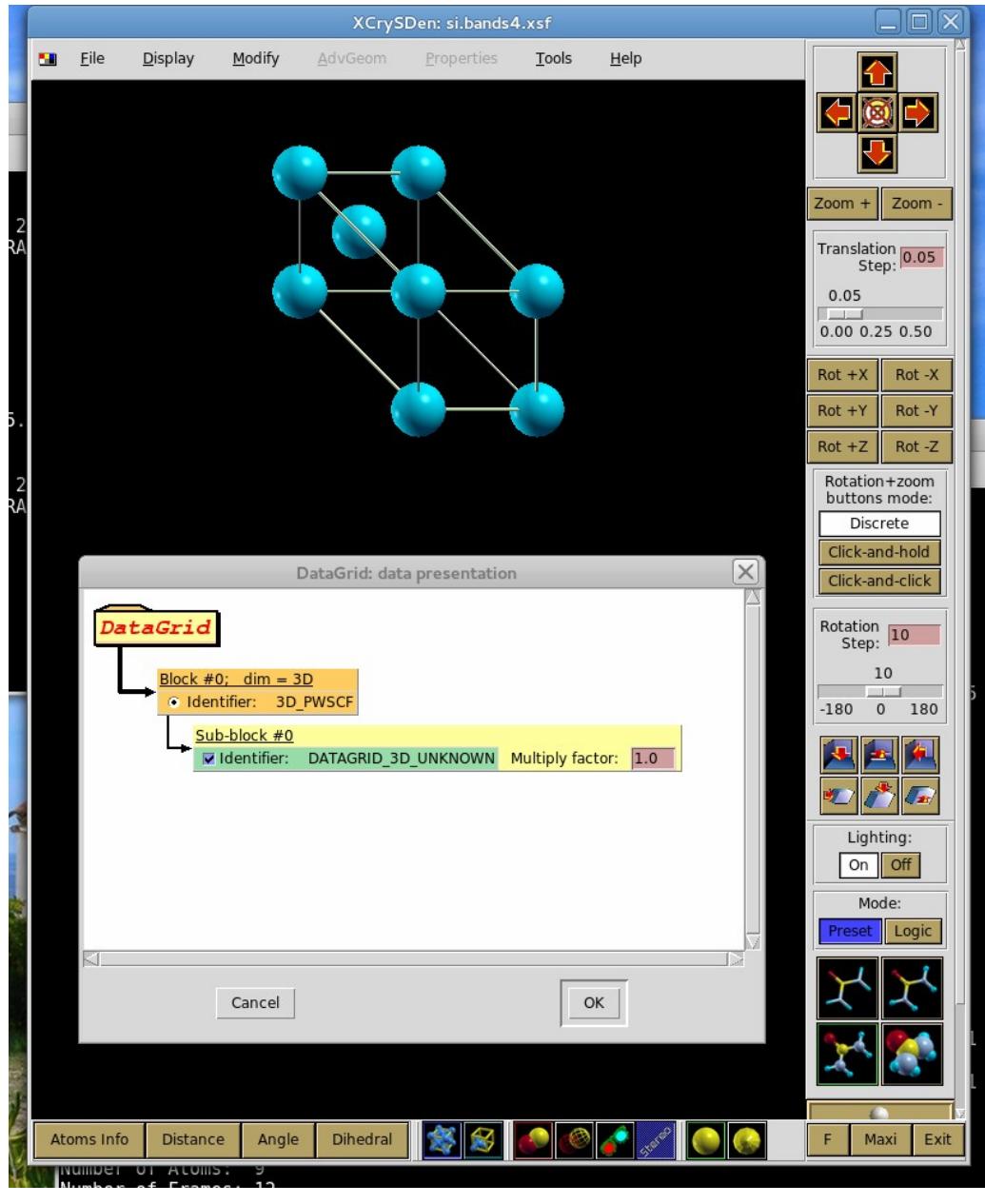
- The first stage of graphene oxidation is the formation of an epoxy bridge. Let us add an O atom on a  $3 \times 3$  supercell of graphene



- Input file for the 3x3 graphene: graphene3x3.in
- Input file for the oxygen: oxygen.in
- Put the oxygen on the graphene and relax the structure
  - `calculation='relax'` for structural optimization, new namelist IONS
  - `ntyp=2` (2 types of atoms), `nat=19` (19 atoms in the cell)
  - `ATOMIC_POSITION` card with 19 initial positions (C-O distance  $\sim 1.5 \text{ \AA}$ )
  - `ATOMIC_SPECIES` card with 2 species of atoms and pseudopotentials
- Calculate the absorption energy  
 $E_{\text{abs}} = E_{\text{tot}} - E_{\text{graphene}} - E_{\text{O}}$

# Data Visualization with XCrySDen

Tools → Data grid



Set Isolevel

