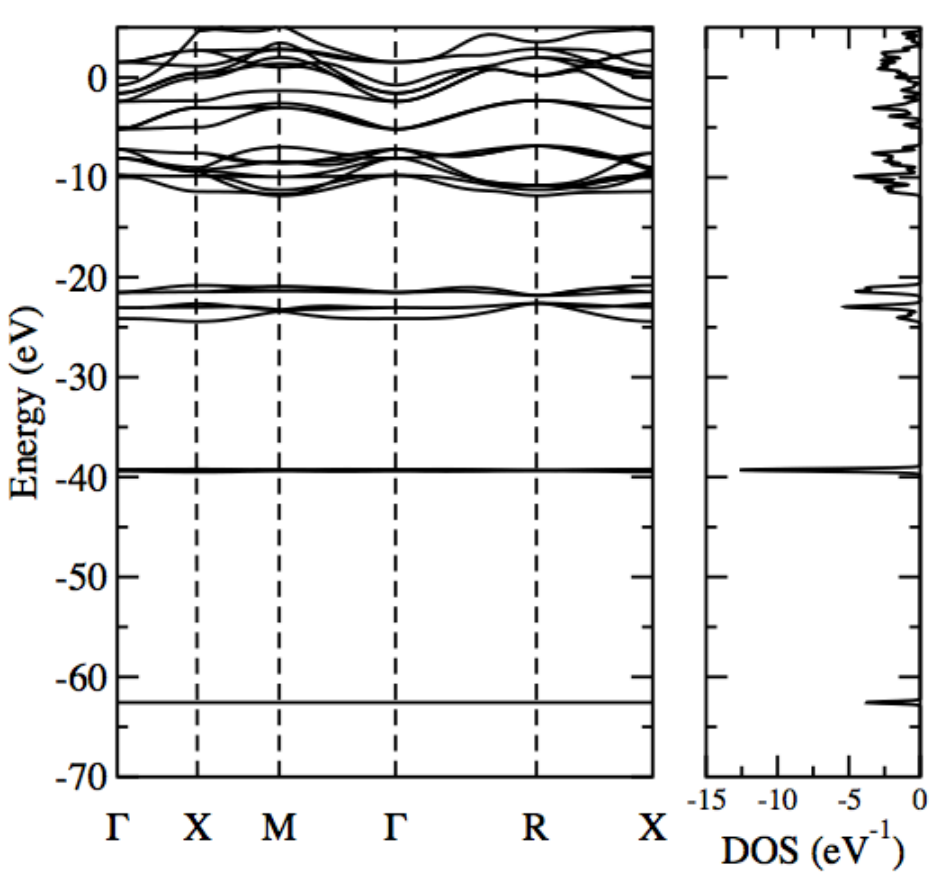
How to compute the projected density of states (PDOS)



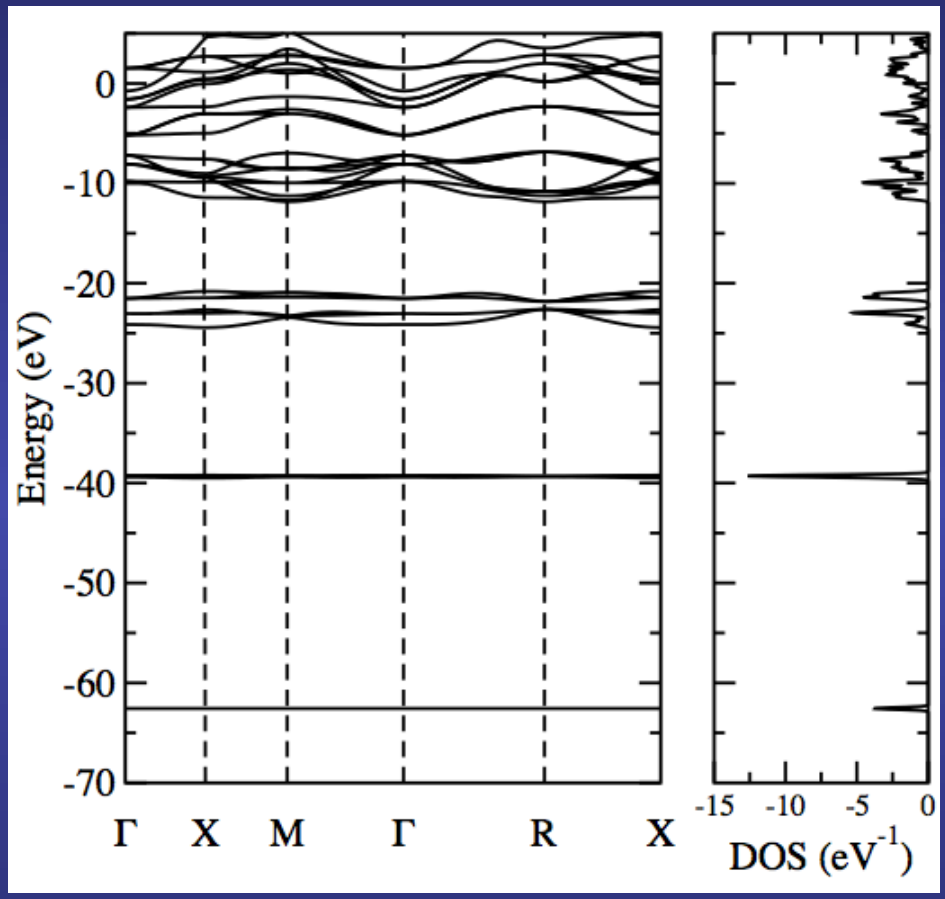
Javier Junquera

UNIVERSIDAD DE CANTABRIA

Density Of States (DOS)

$g(E)dE$ **the number of one-electron levels between E and $E + dE$**

$SrTiO_3$ bulk



$$g(E) = \frac{1}{N_{\vec{k}}} \sum_{i}^{bands} \sum_{\vec{k}} \delta\left(E - E_i(\vec{k})\right)$$

Units: (Energy)$^{-1}$

Projected Density Of States (PDOS)

$g_\mu(E)dE$ **the number of one-electron levels with weight on orbital μ between E and $E + dE$**

$$g_\mu(E) = \frac{1}{N_{\vec{k}}} \sum_{i}^{bands} \sum_{\vec{k}} \sum_{\nu} c^*_{\nu i}(\vec{k}) c_{\mu i}(\vec{k}) S_{\nu\mu}(\vec{k}) \delta\left(E - E_i(\vec{k})\right)$$

Coefficients of the eigenvector $\psi_i(\vec{k})$ with eigenvalue $E_i(\vec{k})$

Overlap matrix of the atomic basis

Units: (Energy)$^{-1}$

Relation between the DOS and PDOS:

$$g(E) = \sum_{\mu} g_\mu(E)$$

Normalization of the DOS and PDOS

$$\int_{-\infty}^{+\infty} g(E)\,dE = \text{Number of bands per k-point} = \text{Number of atomic orbitals in the unit cell}$$

$$\int_{-\infty}^{+\infty} g(E)n(E)\,dE = \text{Number of electrons in the unit cell}$$

Occupation factor at energy E

Important labels to compute the density of states and the projected density of states

```
%block ProjectedDensityOfStates
  -70.00  5.00  0.150 3000  eV
%endblock ProjectedDensityOfStates

%PDOS.kgrid_Monkhorst_Pack
   60  0  0  0.5
    0 60  0  0.5
    0  0 60  0.5
%end PDOS.kgrid_Monkhorst_Pack
```

A separate set of k-points, usually on a finer grid than the one used to achieve self-consistency. Same format as the Monkhorst-Pack grid.

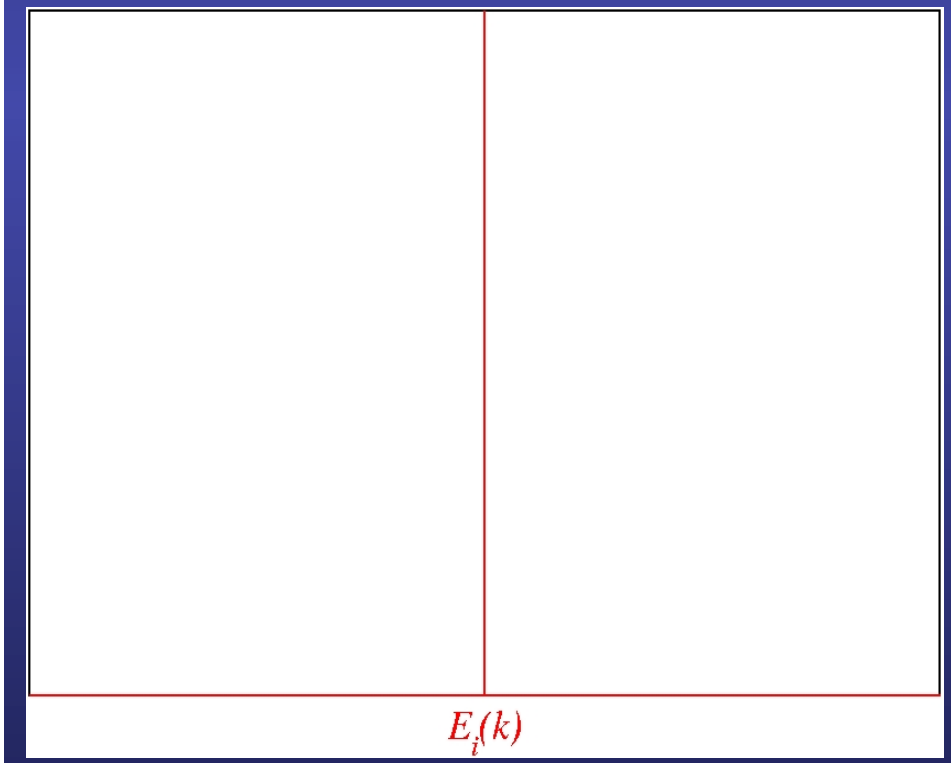
How to compute the DOS and PDOS

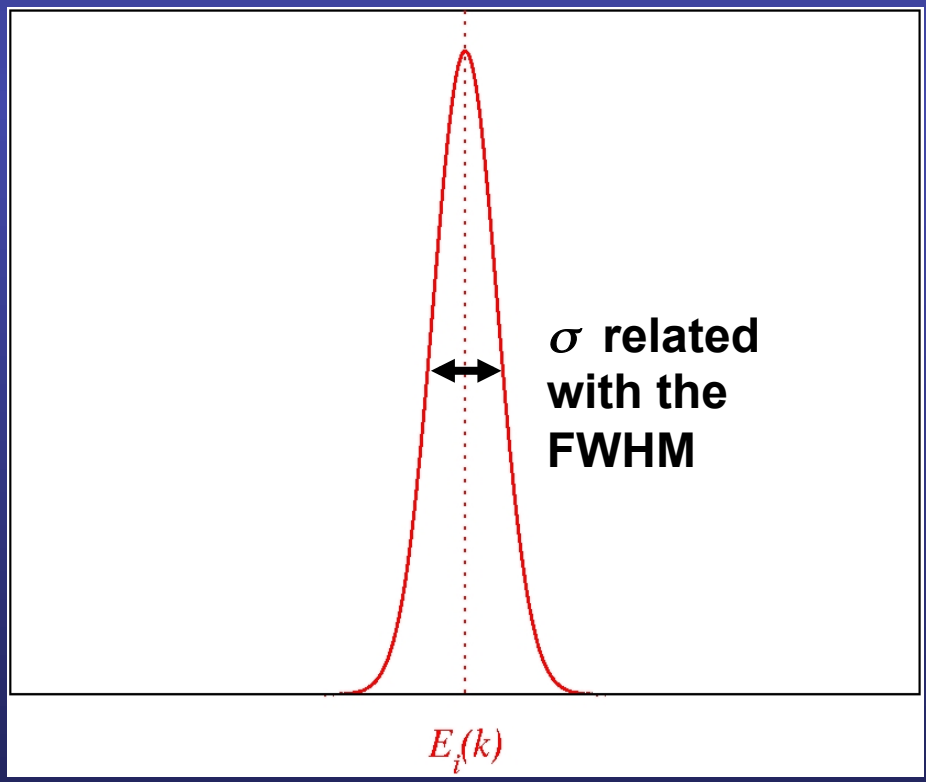
```
%block ProjectedDensityOfStates
     -70.0  5.0  0.150 3000 eV
%endblock ProjectedDensityOfStates
```

-70.0 5.0 : Energy window where the DOS and PDOS will be computed (relative to the program's zero, i.e. the same as the eigenvalues printed by the program)

The eigenvalues are broadening by a gaussian to smooth the shape of the DOS and PDOS

$$\delta\left(E - E_i(\vec{k})\right) \rightarrow \frac{1}{\sigma\sqrt{\pi}} e^{-\frac{\left(E - E_i(\vec{k})\right)^2}{\sigma^2}}$$





How to compute the DOS and PDOS

```
%block ProjectedDensityOfStates
     -70.0  5.0  0.150 3000 eV
%endblock ProjectedDensityOfStates
```

-70.0 5.0 : Energy window where the DOS and PDOS will be computed (relative to the program's zero, i.e. the same as the eigenvalues printed by the program)

0.150 : Peak width of the gaussian used to broad the eigenvalues (energy)

It should be twice as large as the fictitious electronic temperature used during self-consistency.

In this example:

ElectronicTemperature 0.075 eV

(see Appendix B of M. Stengel et al. Phys. Rev. B 83, 235112 (2011)

How to compute the DOS and PDOS

```
%block ProjectedDensityOfStates
     -70.0  5.0  0.150 3000 eV
%endblock ProjectedDensityOfStates
```

-70.0 5.0 : Energy window where the DOS and PDOS will be computed (relative to the program's zero, i.e. the same as the eigenvalues printed by the program)

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(see Appendix B of M. Stengel et al. Phys. Rev. B 83, 235112 (2011)

3000 : Number of points in the histogram

How to compute the DOS and PDOS

```
%block ProjectedDensityOfStates
     -70.0  5.0  0.150 3000 eV
%endblock ProjectedDensityOfStates
```

-70.0 5.0 : Energy window where the DOS and PDOS will be computed (relative to the program's zero, i.e. the same as the eigenvalues printed by the program)

0.150 : Peak width of the gaussian used to broad the eigenvalues (energy)

It should be twice as large as the fictitious electronic temperature used during self-consistency

(see Appendix B of M. Stengel et al. Phys. Rev. B 83, 235112 (2011)

3000 : Number of points in the histogram

eV : Units in which the previous energies are introduced

Output for the Density Of States

SystemLabel.DOS

Format

Energy (eV)	DOS Spin Up (eV^{-1})	DOS Spin Down (eV^{-1})
-69.99993	0.00000	0.00000
-69.97492	0.00000	0.00000
-69.94991	0.00000	0.00000
.	.	.
.	.	.
.	.	.

Output for the Projected Density Of States

SystemLabel.PDOS

Written in XML

```
<pdos>
<nspin>1</nspin>
<norbitals>  72</norbitals>
<energy_values units="eV">
           -69.99993
           -69.97492
           -69.94991
           .
           .
           .
</energy_values>
<orbital
 index="                          1"
 atom_index="                         1"
 species="Sr"
 position="  -0.000000  -0.000000   0.000000"
 n="                          4"
 l="                          0"
 m="                          0"
 z="                          1"
>
<data>
   0.00000
   0.00000
   0.00000
   .
   .
   .
</data>
</orbital>
</pdos>
```

Energy Window

One element <orbital> for every atomic orbital in the basis set

How to digest the SystemLabel.PDOS file

fmpdos (by Andrei Postnikov)

Go to the directory Util/Contrib/Apostnikov, or download from

http://www.home.uni-osnabrueck.de/apostnik/download.html

Compile the code (in the Util directory, simply type $ make)

Execute fmpdos and follow the instructions at run-time

```
$ <your_siesta_directory_path>/Util/Contrib/APostnikov/fmpdos
  Input file name (PDOS):
SrTiO3.PDOS
  Output file name :
Sr.PDOS.dat
  Extract data for atom index (enter atom NUMBER, or 0 to select all),
  or for all atoms of given species (enter its chemical LABEL):
1
  Extract data for n= ... (0 for all n ):
0
```

Repeat this for all the atoms you might be interested in

How to digest the SystemLabel.PDOS file

Plot the layer by layer Projected Density of States

```
$ gnuplot

G N U P L O T
Version 4.2 patchlevel 5
last modified Mar 2009
System: Darwin 11.4.2

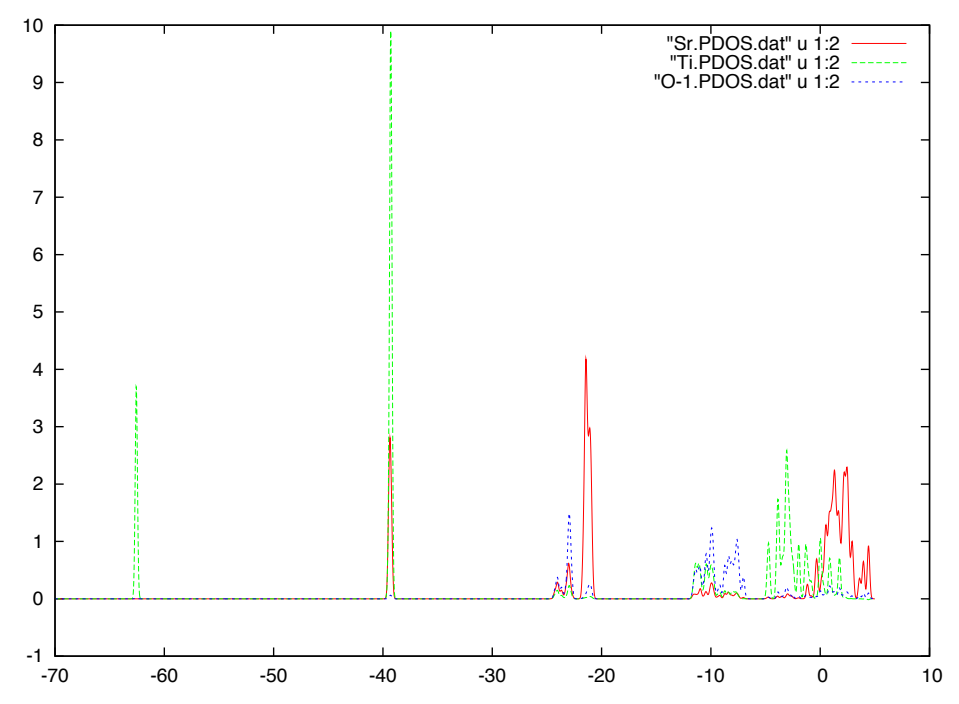
Copyright (C) 1986 - 1993, 1998, 2004, 2007 - 2009
Thomas Williams, Colin Kelley and many others

Type ‘help‘ to access the on-line reference manual.
The gnuplot FAQ is available from http://www.gnuplot.info/faq/

Send bug reports and suggestions to <http://sourceforge.net/projects/gnuplot>


Terminal type set to ’aqua’
gnuplot> plot "Sr.PDOS.dat" u 1:2 w l, "Ti.PDOS.dat" u 1:2 w l, "O-1.PDOS.dat" u 1:2 w l
```

The PDOS for the three O atoms are equivalent by symmetry



How to digest the SystemLabel.PDOS file

Plot the layer by layer Projected Density of States

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$ gnuplot

G N U P L O T
Version 4.2 patchlevel 5
last modified Mar 2009
System: Darwin 11.4.2

Copyright (C) 1986 - 1993, 1998, 2004, 2007 - 2009
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Type ‘help‘ to access the on-line reference manual.
The gnuplot FAQ is available from http://www.gnuplot.info/faq/

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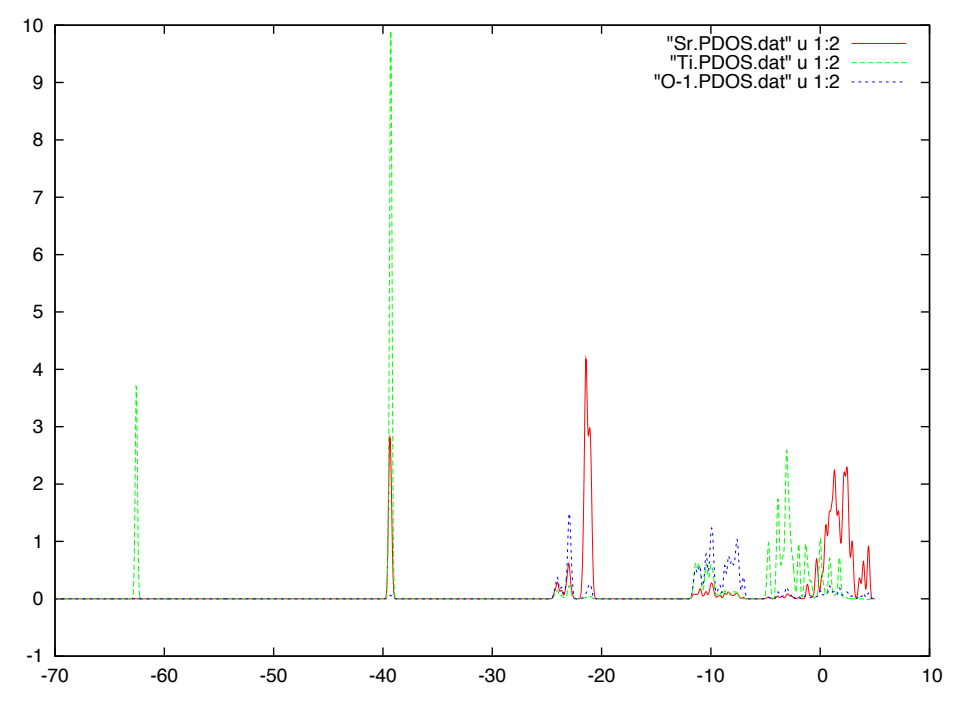
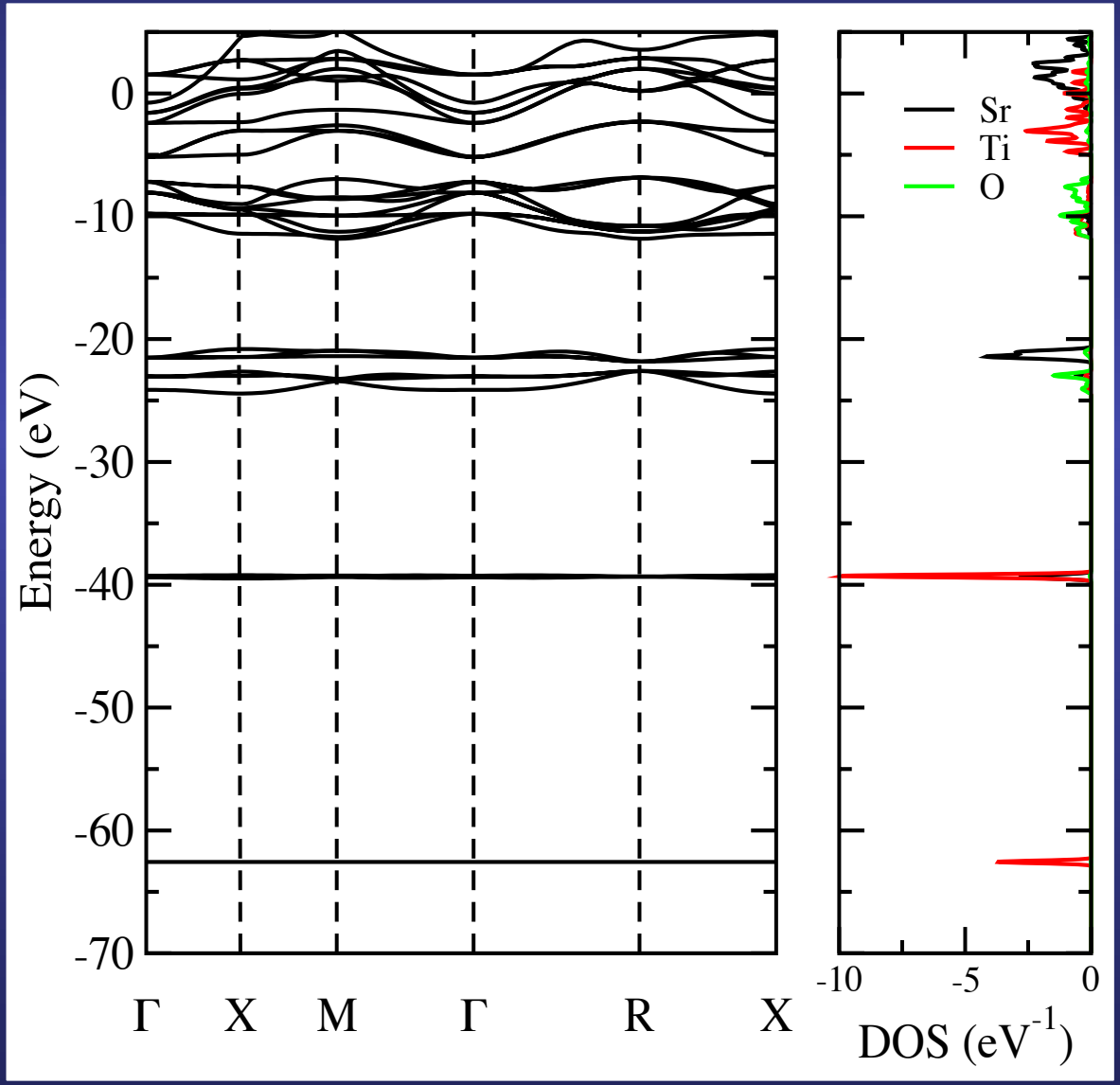
Terminal type set to ’aqua’
gnuplot> plot "Sr.PDOS.dat" u 1:2 w l, "Ti.PDOS.dat" u 1:2 w l, "O-1.PDOS.dat" u 1:2 w l
```

The PDOS for the three O atoms are equivalent by symmetry



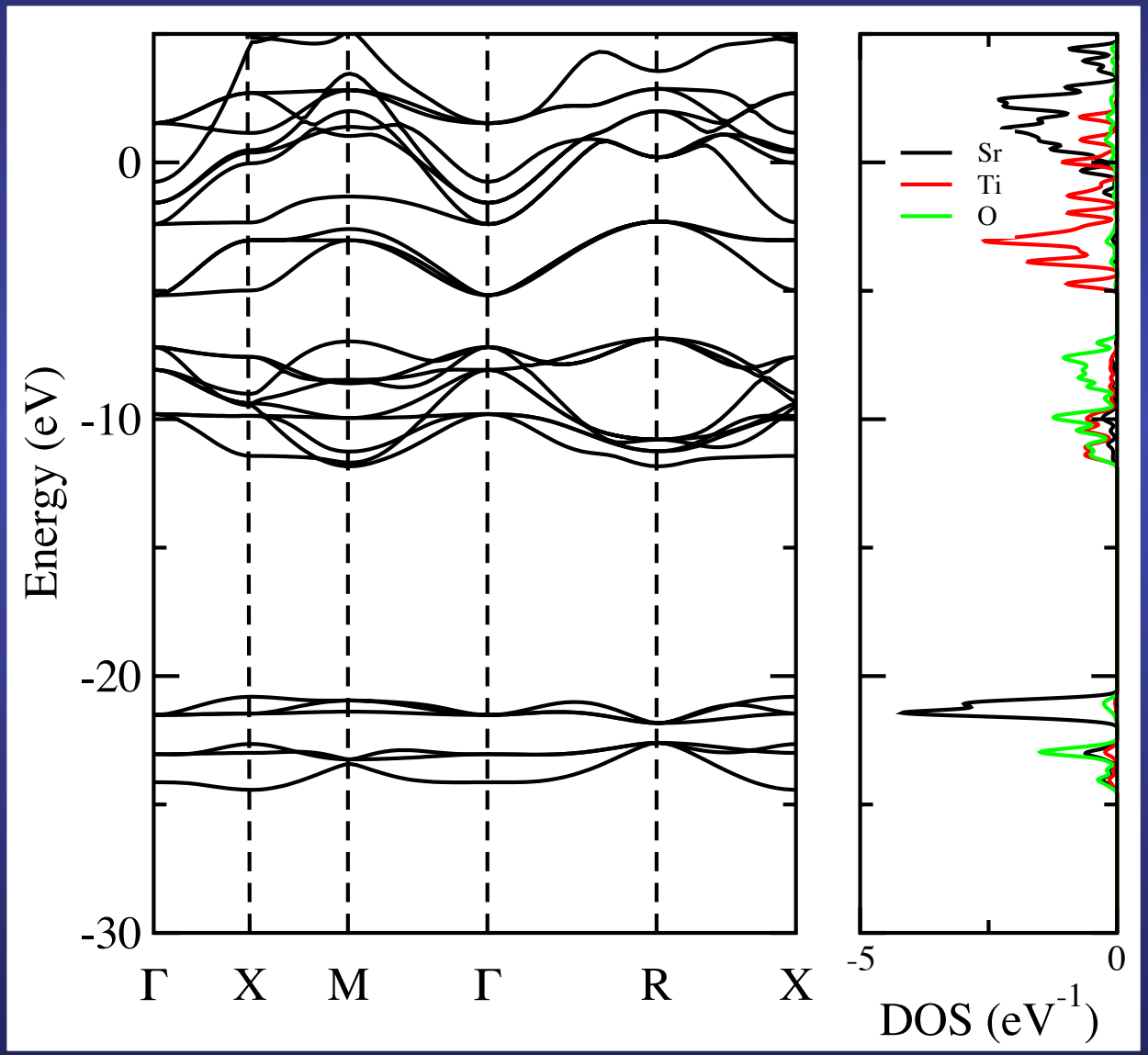
We can analyze the character of the different bands

Which atoms contribute more to the bands at a particular energy window



We can analyze the character of the different bands

Which atoms contribute more to the bands at a particular energy window
Zoom around the top of the valence bands and bottom of conduction bands



Bottom of conduction bands: mostly Ti character

Top of valence bands: mostly O character

We can project on particular atomic orbitals within an atom to further define the charcter.

To know the order of the orbitals, explore the SystemLabel.ORB_INDX file

```
$ more SrTiO3.ORB_INDX
     72   15552 = orbitals in unit cell and supercell. See end of file.

    io    ia is   spec iao  n  l  m  z  p          sym      rc     isc      iuo
     1     1  1     Sr   1  4  0  0  1  F            s   6.602  0  0  0     1
     2     1  1     Sr   2  5  0  0  1  F            s   7.116  0  0  0     2
     3     1  1     Sr   3  5  0  0  2  F            s   5.542  0  0  0     3
     4     1  1     Sr   4  4  1 -1  1  F           py   6.769  0  0  0     4
     5     1  1     Sr   5  4  1  0  1  F           pz   6.769  0  0  0     5
     6     1  1     Sr   6  4  1  1  1  F           px   6.769  0  0  0     6
     7     1  1     Sr   7  5  1 -1  1  F           py   4.004  0  0  0     7
     8     1  1     Sr   8  5  1  0  1  F           pz   4.004  0  0  0     8
     9     1  1     Sr   9  5  1  1  1  F           px   4.004  0  0  0     9
    10     1  1     Sr  10  4  2 -2  1  F          dxy   6.602  0  0  0    10
    11     1  1     Sr  11  4  2 -1  1  F          dyz   6.602  0  0  0    11
    12     1  1     Sr  12  4  2  0  1  F          dz2   6.602  0  0  0    12
    13     1  1     Sr  13  4  2  1  1  F          dxz   6.602  0  0  0    13
    14     1  1     Sr  14  4  2  2  1  F       dx2-y2   6.602  0  0  0    14
    15     2  2     Ti   1  3  0  0  1  F            s   5.806  0  0  0    15
    16     2  2     Ti   2  4  0  0  1  F            s   6.104  0  0  0    16
    17     2  2     Ti   3  4  0  0  2  F            s   5.124  0  0  0    17
    18     2  2     Ti   4  3  1 -1  1  F           py   5.806  0  0  0    18
    19     2  2     Ti   5  3  1  0  1  F           pz   5.806  0  0  0    19
    20     2  2     Ti   6  3  1  1  1  F           px   5.806  0  0  0    20
    21     2  2     Ti   7  4  1 -1  1  F           py   3.108  0  0  0    21
    22     2  2     Ti   8  4  1  0  1  F           pz   3.108  0  0  0    22
    23     2  2     Ti   9  4  1  1  1  F           px   3.108  0  0  0    23
    24     2  2     Ti  10  3  2 -2  1  F          dxy   5.953  0  0  0    24
    25     2  2     Ti  11  3  2 -1  1  F          dyz   5.953  0  0  0    25
    26     2  2     Ti  12  3  2  0  1  F          dz2   5.953  0  0  0    26
    27     2  2     Ti  13  3  2  1  1  F          dxz   5.953  0  0  0    27
    28     2  2     Ti  14  3  2  2  1  F       dx2-y2   5.953  0  0  0    28
    29     2  2     Ti  15  3  2 -2  2  F          dxy   4.754  0  0  0    29
    30     2  2     Ti  16  3  2 -1  2  F          dyz   4.754  0  0  0    30
    31     2  2     Ti  17  3  2  0  2  F          dz2   4.754  0  0  0    31
    32     2  2     Ti  18  3  2  1  2  F          dxz   4.754  0  0  0    32
    33     2  2     Ti  19  3  2  2  2  F       dx2-y2   4.754  0  0  0    33
    34     3  3      O   1  2  0  0  1  F            s   4.931  0  0  0    34
    35     3  3      O   2  2  0  0  2  F            s   3.653  0  0  0    35
    36     3  3      O   3  2  1 -1  1  F           py   5.056  0  0  0    36
    37     3  3      O   4  2  1  0  1  F           pz   5.056  0  0  0    37
    38     3  3      O   5  2  1  1  1  F           px   5.056  0  0  0    38
     .
     .
     .
```

Ti 3d

O 2p

Projections on the Ti 3d t_{2g} orbitals

```
$ <your_siesta_path>/Util/Contrib/APostnikov/fmpdos
  Input file name (PDOS):
SrTiO3.PDOS
  Output file name :
Ti-dxy.PDOS.dat
  Extract data for atom index (enter atom NUMBER, or 0 to select all),
  or for all atoms of given species (enter its chemical LABEL):
2
  Extract data for n= ... (0 for all n ):
3
  Extract data for l= ... (-1 for all l ):
2
  Extract data for m= ... (9 for all m ):
-2


$ <your_siesta_path>/Util/Contrib/APostnikov/fmpdos
  Input file name (PDOS):
SrTiO3.PDOS
  Output file name :
Ti-dyz.PDOS.dat
  Extract data for atom index (enter atom NUMBER, or 0 to select all),
  or for all atoms of given species (enter its chemical LABEL):
2
  Extract data for n= ... (0 for all n ):
3
  Extract data for l= ... (-1 for all l ):
2
  Extract data for m= ... (9 for all m ):
-1


$ <your_siesta_path>/Util/Contrib/APostnikov/fmpdos
  Input file name (PDOS):
SrTiO3.PDOS
  Output file name :
Ti-dxz.PDOS.dat
  Extract data for atom index (enter atom NUMBER, or 0 to select all),
  or for all atoms of given species (enter its chemical LABEL):
2
  Extract data for n= ... (0 for all n ):
3
  Extract data for l= ... (-1 for all l ):
2
  Extract data for m= ... (9 for all m ):
1
```

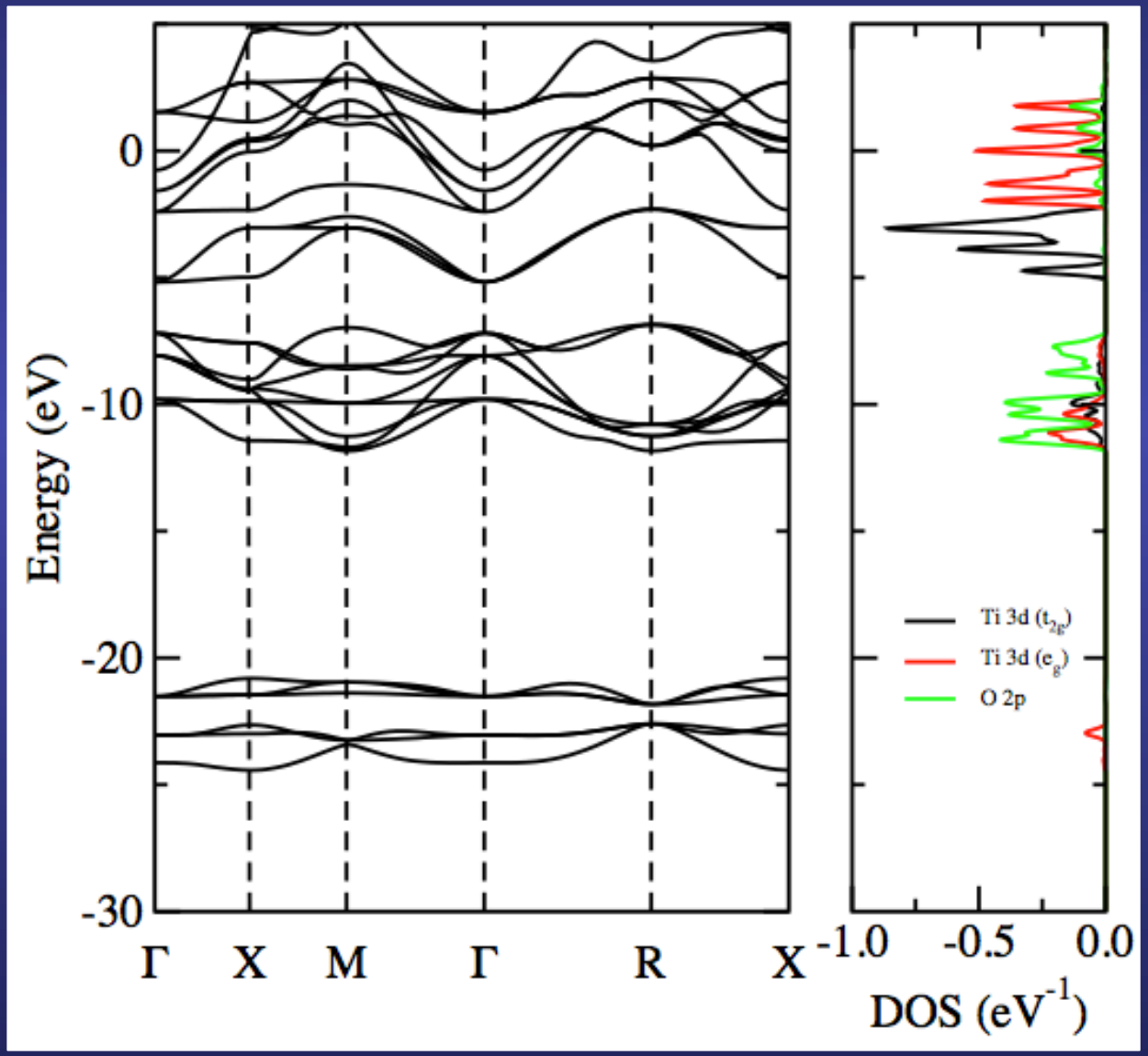
Projections on the Ti 3d e_g orbitals

```
$ <your_siesta_path>/Util/Contrib/APostnikov/fmpdos
  Input file name (PDOS):
SrTiO3.PDOS
  Output file name :
Ti-dz2.PDOS.dat
  Extract data for atom index (enter atom NUMBER, or 0 to select all),
  or for all atoms of given species (enter its chemical LABEL):
2
  Extract data for n= ... (0 for all n ):
3
  Extract data for l= ... (-1 for all l ):
2
  Extract data for m= ... (9 for all m ):
0


$ <your_siesta_path>/Util/Contrib/APostnikov/fmpdos
  Input file name (PDOS):
SrTiO3.PDOS
  Output file name :
Ti-dx2-y2.PDOS.dat
  Extract data for atom index (enter atom NUMBER, or 0 to select all),
  or for all atoms of given species (enter its chemical LABEL):
2
  Extract data for n= ... (0 for all n ):
3
  Extract data for l= ... (-1 for all l ):
2
  Extract data for m= ... (9 for all m ):
2
```

We can analyze the character of the different bands

Which atoms contribute more to the bands at a particular energy window
Zoom around the top of the valence bands and bottom of conduction bands



Bottom of conduction bands: mostly Ti character
The crsytal field splits the t_{2g} and e_g bands

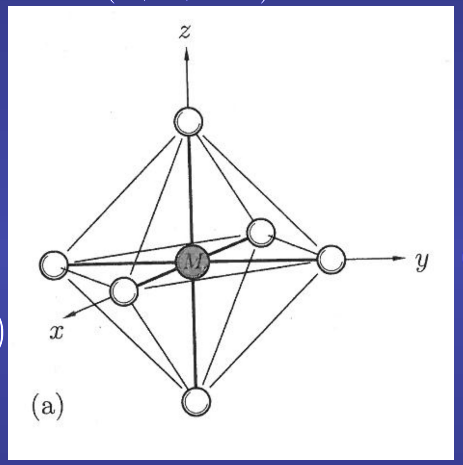
Top of valence bands: mostly O character (O 2p)

We can project on particular atomic orbitals within an atom to further define the charcter.

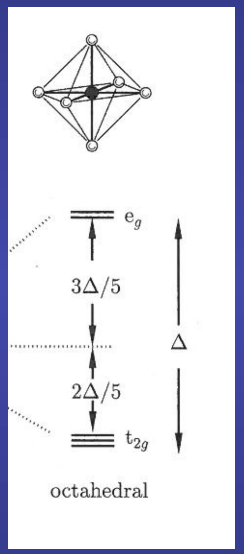
The environment affect the orbitals in different ways

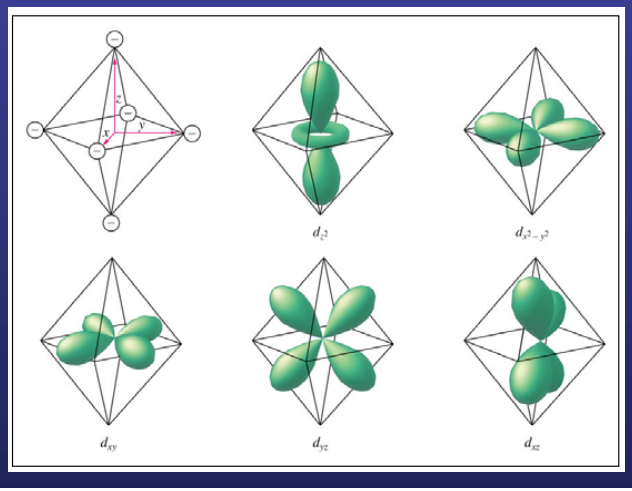
In an octahedral environment the ligands (considered negative point charges) congregate at six points

$(0, 0, \pm r)$



$(\pm r, 0, 0)$ $(0, \pm r, 0)$





$d_{z^2}, d_{x^2-y^2}$ **point along the x, y, z axis will be raised in energy**

d_{xy}, d_{yz}, d_{xz} **point between the x, y, z axis will be lowered in energy**