Analysis tools for electronic structure and bonding properties

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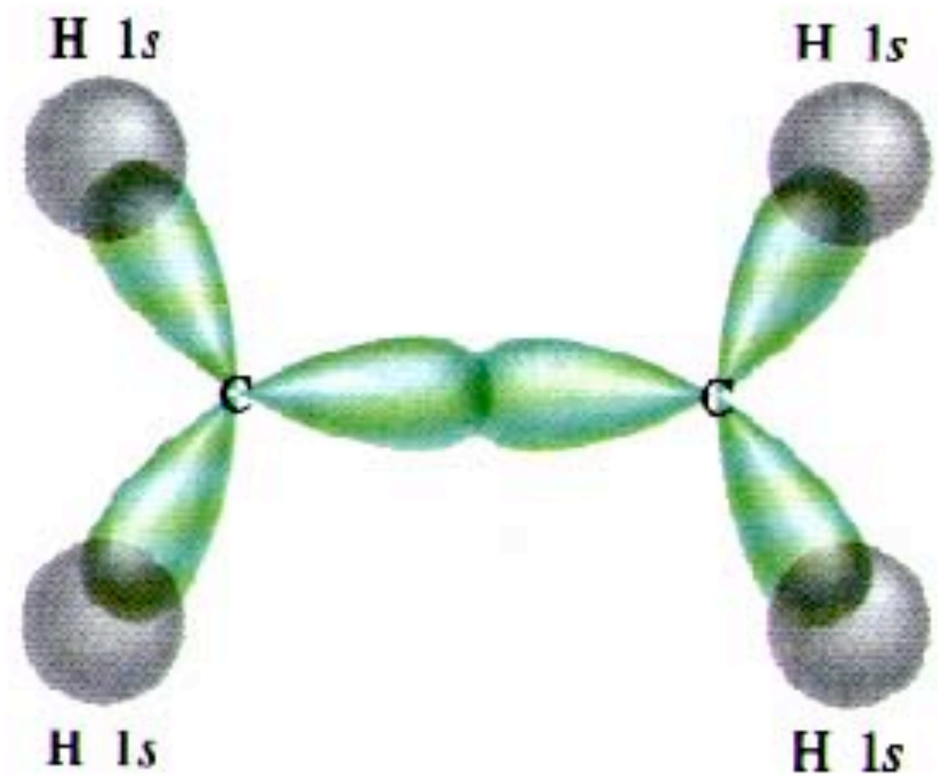
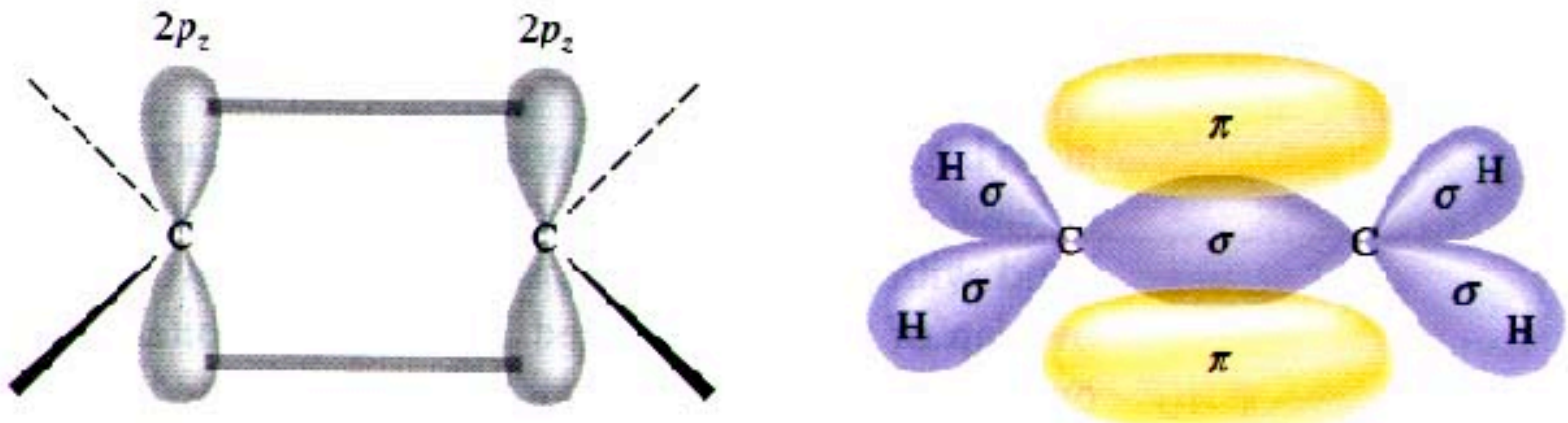
Why atomic orbitals?

- “Atoms” are a very good first approximation.
- The size of the basis is relatively small.
- Most of the language of the chemical bond is based on atomic orbitals.



(a)



$$\psi_i(\boldsymbol{r}) = \sum_{\mu} \phi_\mu(\boldsymbol{r}) c_{\mu i},$$

$$\sum_{\nu\beta} (H^{\alpha\beta}_{\mu\nu} - E_i S_{\mu\nu} \delta^{\alpha\beta}) c^{\beta}_{\nu i} = 0$$

Generalized eigenvalue problem

$$H^{\alpha\beta}_{\mu\nu} = \langle \phi_\mu | \hat{T} + \hat{V}^{KB} + V^{NA}(\boldsymbol{r}) + \delta V^{H}(\boldsymbol{r}) + V^{\alpha\beta}_{XC}(\boldsymbol{r}) | \phi_\nu \rangle$$

$$S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$$

$$\rho(\boldsymbol{r}) = \sum_{\mu\nu} \rho_{\mu\nu} \phi^{*}_{\nu}(\boldsymbol{r}) \phi_\mu(\boldsymbol{r})$$

$$E^{BS} = \sum_i n_i \langle \psi_i | \hat{H} | \psi_i \rangle = \sum_{\mu\nu} H_{\mu\nu} \rho_{\nu\mu} = \mathrm{Tr}(H\rho)$$

$$\rho_{\mu\nu} = \sum_i c_{\mu i} n_i c_{i\nu}$$

Density matrix

$$E^{BS} = \sum_i n_i \langle \psi_i | \hat{H} | \psi_i \rangle = \sum_{\mu\nu} H_{\mu\nu} \rho_{\nu\mu} = \mathrm{Tr}(H\rho)$$

$$N = \sum_{\mu\nu} S_{\mu\nu} \rho_{\nu\mu} = \mathrm{Tr}(S\rho)$$

$$\rho_{\mu\nu} = \sum_i c_{\mu i} n_i c_{i\nu}$$

$$\rho_{\mu\nu} = \sum_i c_{\mu i} n_i c_{i\nu} = \int_0^{\epsilon_F} d\epsilon \sum_i c_{\mu i} c_{i\nu} \delta(\epsilon - \epsilon_i)$$

$$N = \int_0^{\epsilon_F} d\epsilon \sum_i \sum_\mu \sum_\nu c_{\mu i} c_{i\nu} S_{\mu\nu} \delta(\epsilon - \epsilon_i)$$

$$N = \int_0^{\epsilon_F} d\epsilon \sum_i \sum_\mu \sum_\nu c_{\mu i} c_{i\nu} S_{\mu\nu} \delta(\epsilon - \epsilon_i)$$

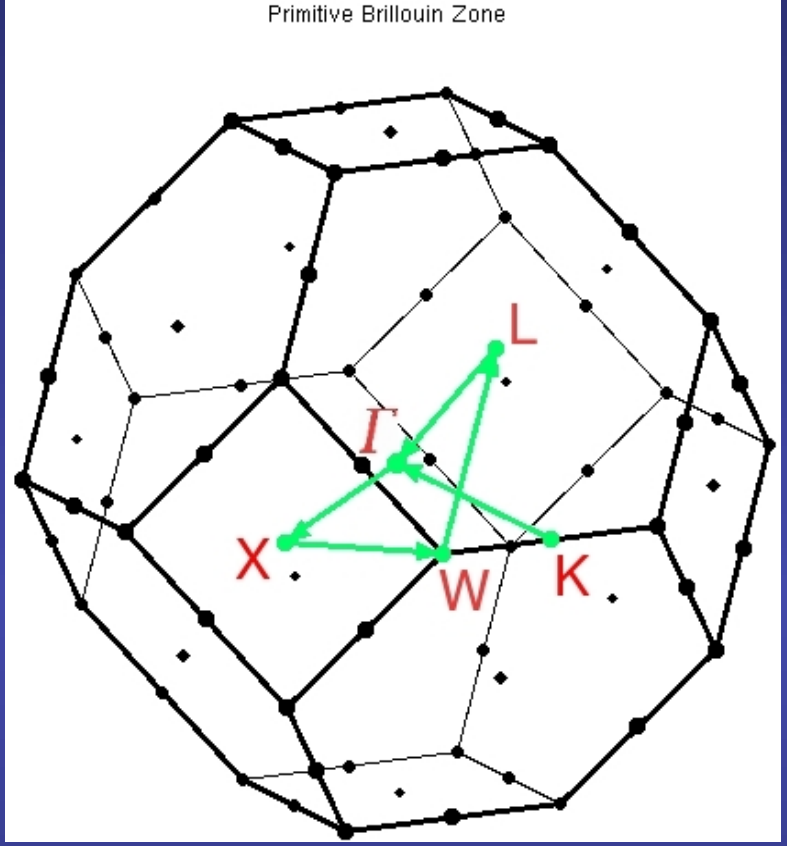
Density of states:

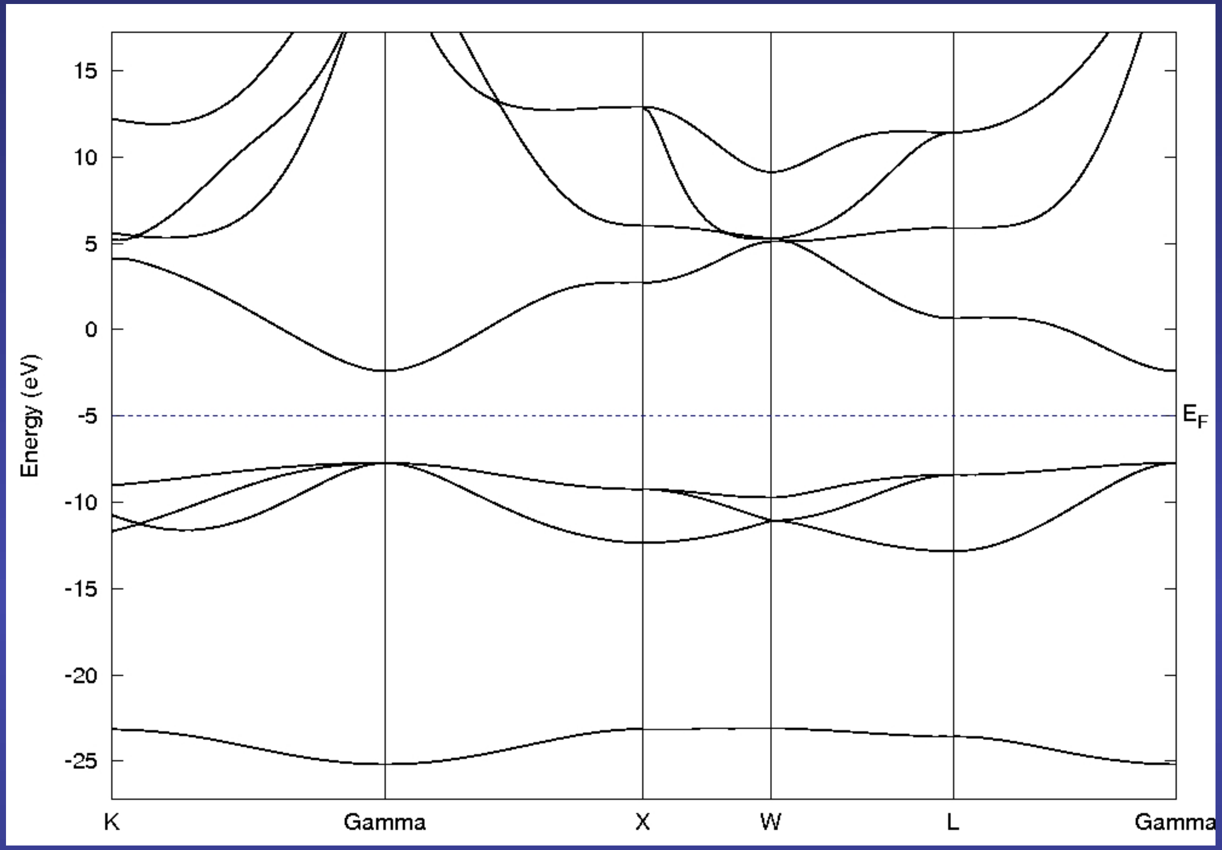
$$DOS(\epsilon) = g(\epsilon) = \sum_i \sum_\mu \sum_\nu c_{\mu i} c_{i\nu} S_{\mu\nu} \delta(\epsilon - \epsilon_i)$$

Density of states projected on orbital μ:

$$g_\mu(\epsilon) = \sum_i \sum_\nu c_{\mu i} c_{i\nu} S_{\mu\nu} \delta(\epsilon - \epsilon_i)$$

Band structure of an ionic solid: The case of MgO





```
%block kgrid_Monkhorst_Pack
  6  0  0  0.5
  0  6  0  0.5
  0  0  6  0.5
%endblock kgrid_Monkhorst_Pack
...
MeshCutoff                   200 Ry
...
COOP.write T          # NOTE
```

New H,S, and wavefunction files produced

```
-rw-r-----  1 ag  ag  397564 Jun 10 17:59 MgO.HSX
-rw-r-----  1 ag  ag  358248 Jun 10 17:59 MgO.fullBZ.WFSX
```

Input file for (P)DOS processing by mprop

```
MgO                             SystemLabel
DOS                             Keyword
PDOS_Mg            Curve Label
Mg                 Orbital spec
PDOS_O                ...
O
PDOS_O_2s          Curve Label
O_2s               Orbital spec
PDOS_O_2p             ...
O_2p
PDOS_Mg_3s
Mg_3s
```

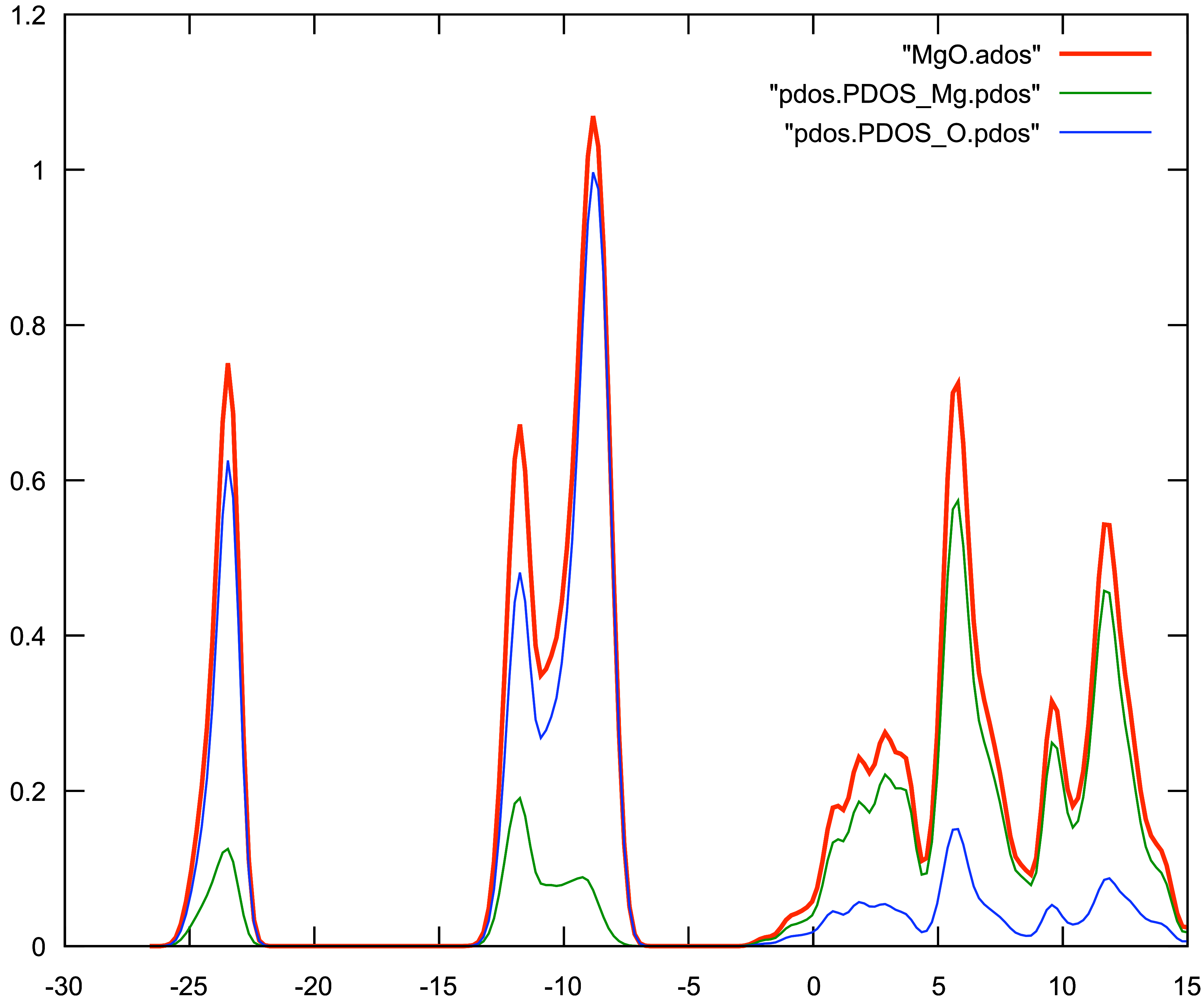
pdos.mpr

```
mprop -m Min_Energy -M Max_Energy  input_label

mprop -m -26.0 -M 15.0  pdos
```

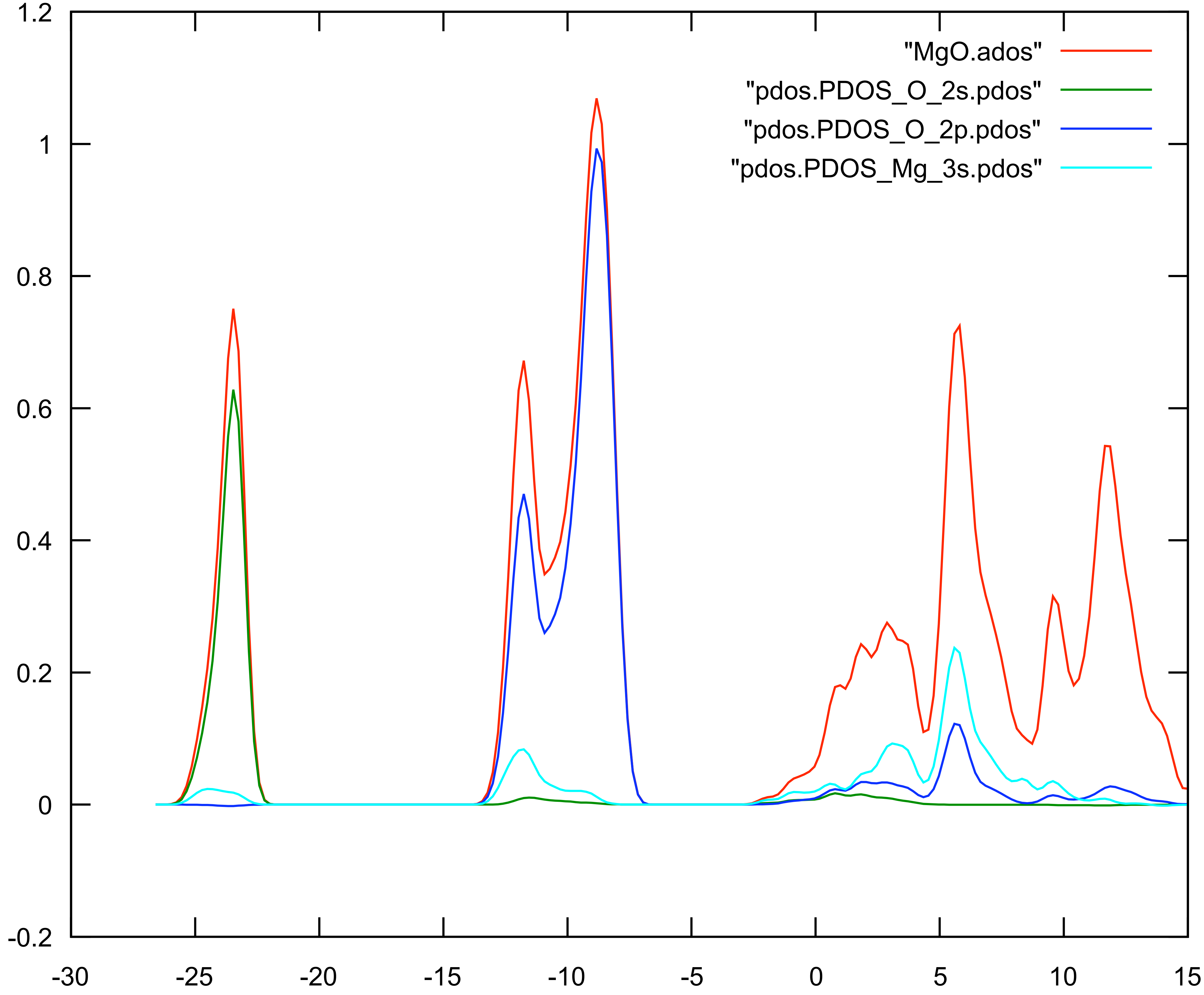
```
-rw-r-----  1 ag  ag  10624 Jun 11 23:00 MgO.ados
-rw-r-----  1 ag  ag   6840 Jun 11 23:00 pdos.PDOS_Mg.pdos
-rw-r-----  1 ag  ag   6840 Jun 11 23:00 pdos.PDOS_Mg_3s.pdos
-rw-r-----  1 ag  ag   6840 Jun 11 23:00 pdos.PDOS_O.pdos
-rw-r-----  1 ag  ag   6840 Jun 11 23:00 pdos.PDOS_O_2p.pdos
-rw-r-----  1 ag  ag   6840 Jun 11 23:00 pdos.PDOS_O_2s.pdos
```

Total DOS (in specified range): SystemLabel.ados

Projected DOS: InputLabel.CurveLabel.pdos



"MgO.ados"
"pdos.PDOS_Mg.pdos"
"pdos.PDOS_O.pdos"
1.2
1
0.8
0.6
0.4
0.2
0
-30
-25
-20
-15
-10
-5
0
5
10
15



"MgO.ados"
"pdos.PDOS_O_2s.pdos"
"pdos.PDOS_O_2p.pdos"
"pdos.PDOS_Mg_3s.pdos"
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-30
-25
-20
-15
-10
-5
0
5
10
15

Density of states projected on orbital μ:

$$g_\mu(\epsilon) = \sum_i \sum_\nu c_{\mu i} c_{i\nu} S_{\mu\nu} \delta(\epsilon - \epsilon_i)$$

Crystal Orbital Overlap Population (COOP)

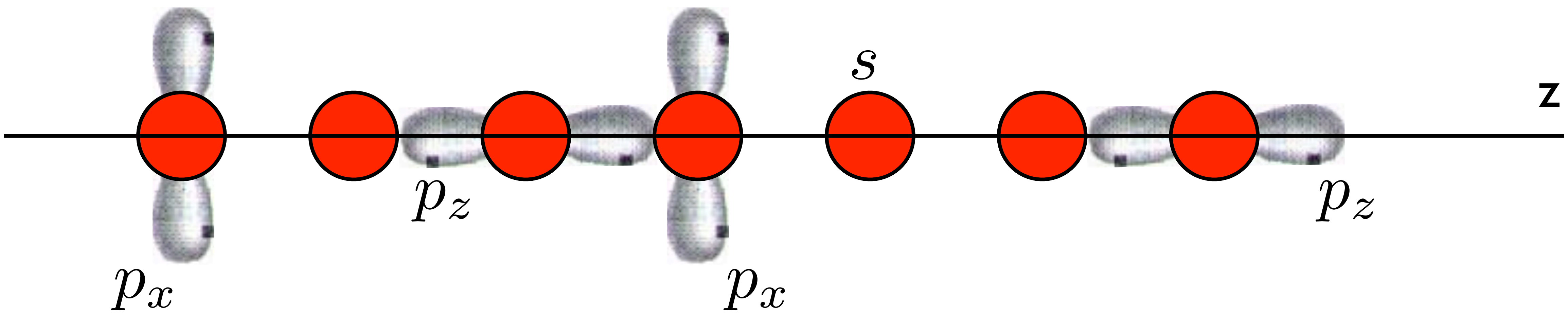
$$g_{\mu\nu}(\epsilon) = \sum_i c_{\mu i} c_{i\nu} S_{\mu\nu} \delta(\epsilon - \epsilon_i)$$

Crystal Orbital Hamilton Population (COHP)

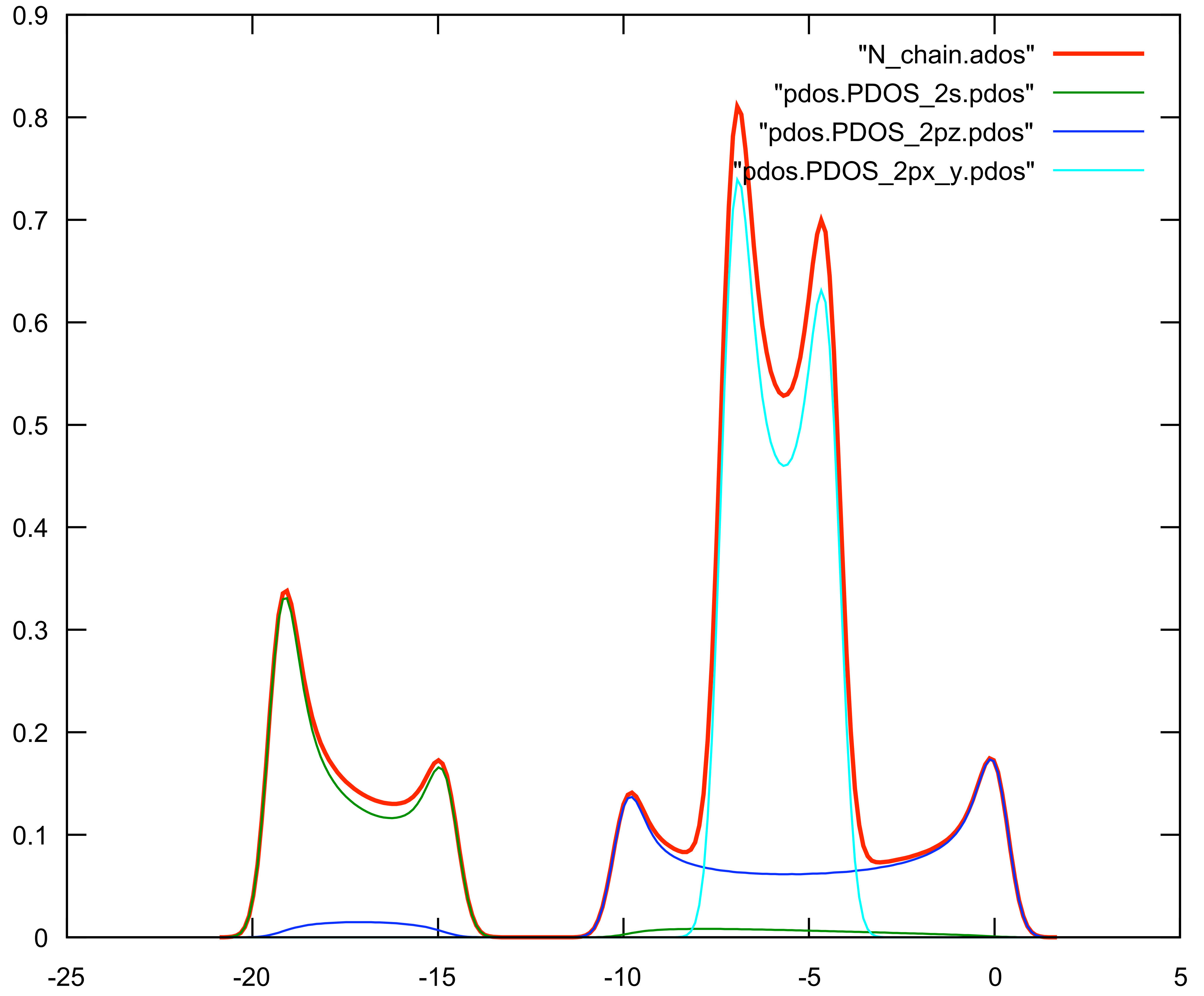
$$h_{\mu\nu}(\epsilon) = \sum_i c_{\mu i} c_{i\nu} H_{\mu\nu} \delta(\epsilon - \epsilon_i)$$

$$\psi_i(\boldsymbol{r}) = \sum_\mu \phi_\mu(\boldsymbol{r}) c_{\mu i},$$

A chain of nitrogen atoms



(lattice constant: 2 Ang)


"N_chain.ados"
"pdos.PDOS_2s.pdos"
"pdos.PDOS_2pz.pdos"
"pdos.PDOS_2px_y.pdos"
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-25
-20
-15
-10
-5
0
5

```
n_chain
COOP
N2s-N2px
N_2s
1.95 2.05
N_2px
N2px-N2px
N_2px
1.95 2.05
N_2px
N2s-N2pz
N_2s
1.95 2.05
N_2pz
N2s-N2s
N_2s
1.95 2.05
N_2s
N2pz-N2pz
N_2pz
1.95 2.05
N_2pz
```

Curve Label, orb1 spec, distance range, orb2 spec.

....

....

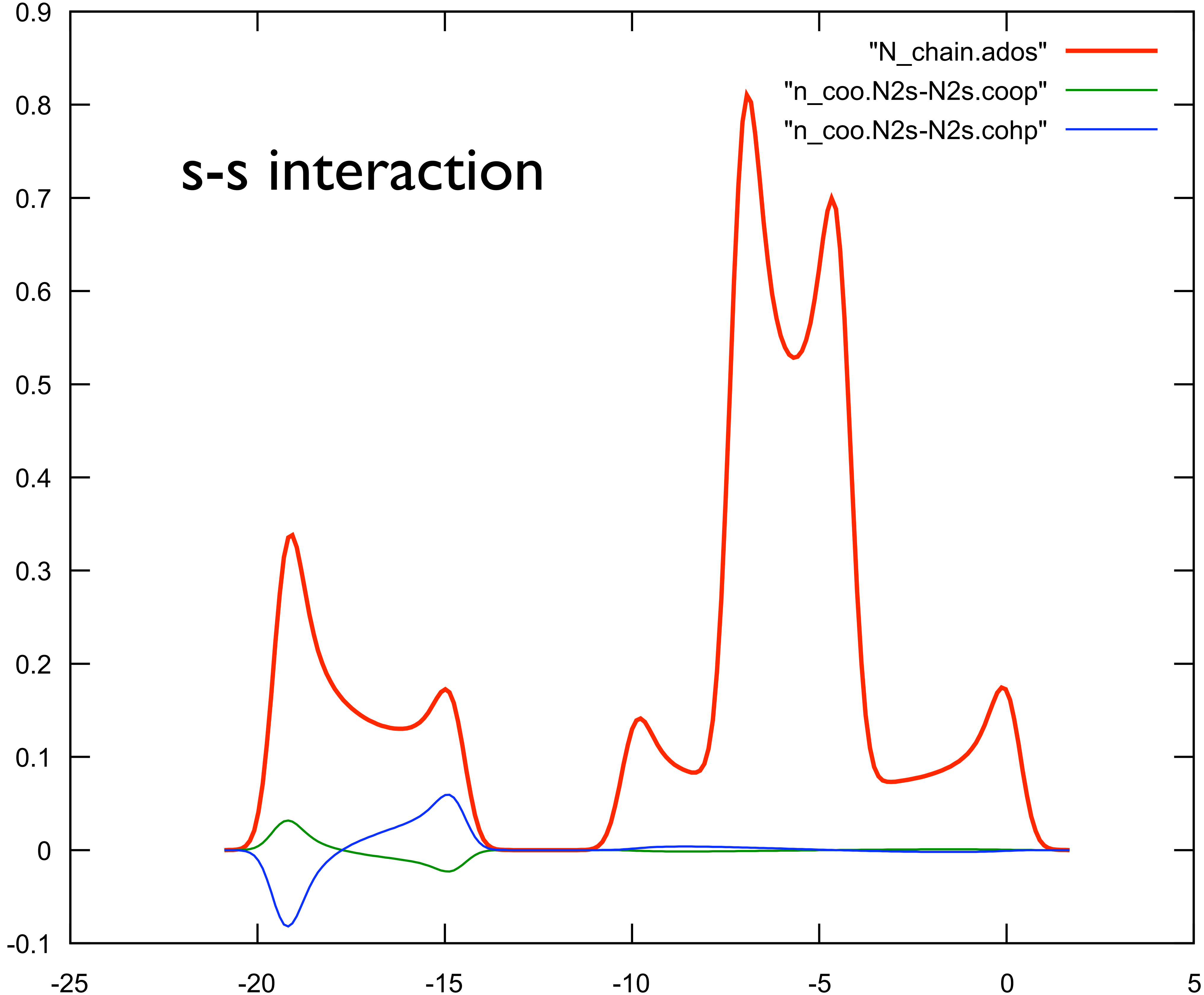
n_coo.mpr

Distance ranges select nearest neighbors

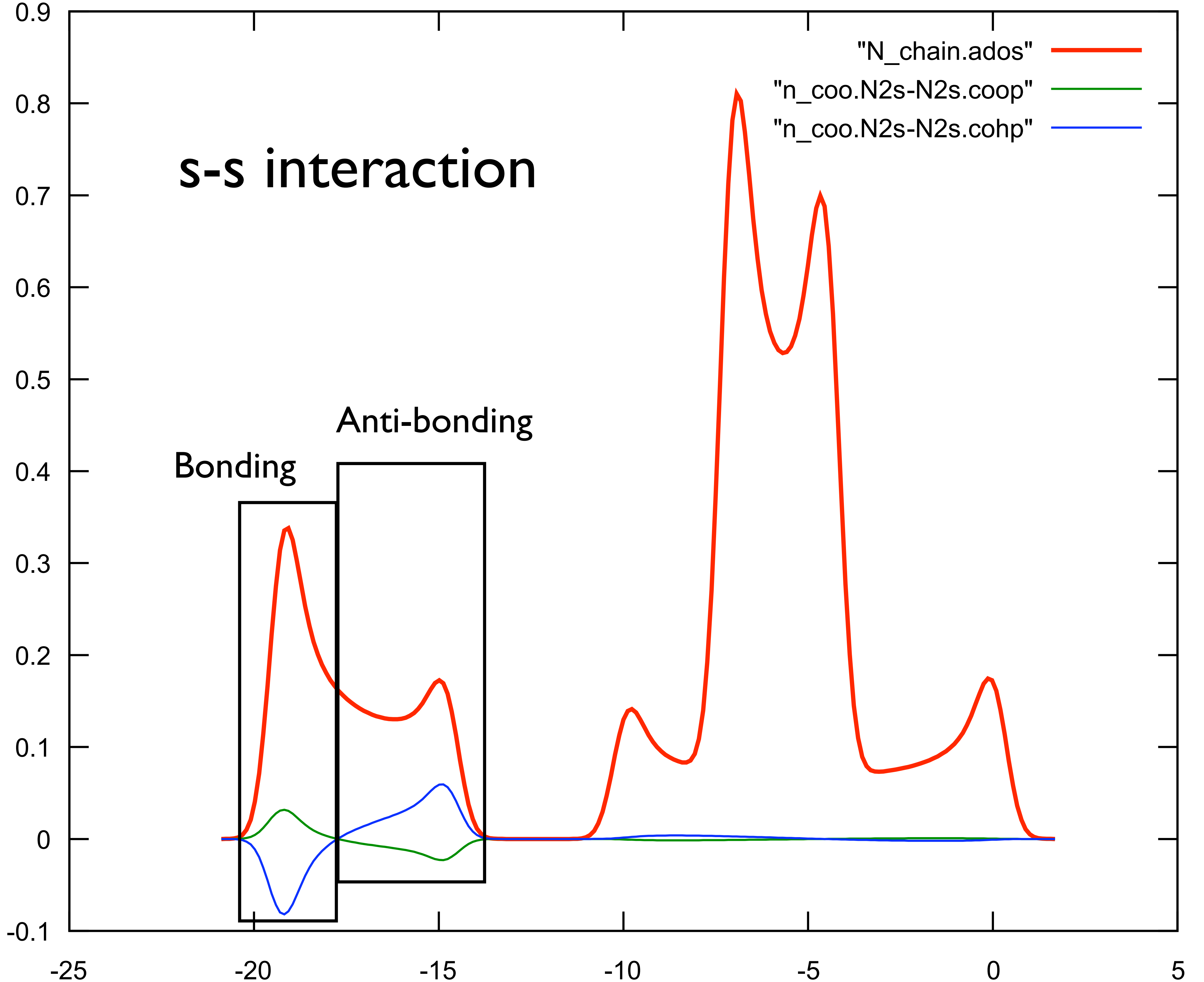
```
mprop n_coo

-rw-r-----  1 ag  ag  6840 Jun 12 00:10 n_coo.N2px-N2px.coop
-rw-r-----  1 ag  ag  6840 Jun 12 00:10 n_coo.N2pz-N2pz.coop
-rw-r-----  1 ag  ag  6840 Jun 12 00:10 n_coo.N2s-N2px.coop
-rw-r-----  1 ag  ag  6840 Jun 12 00:10 n_coo.N2s-N2pz.coop
-rw-r-----  1 ag  ag  6840 Jun 12 00:10 n_coo.N2s-N2s.coop
```

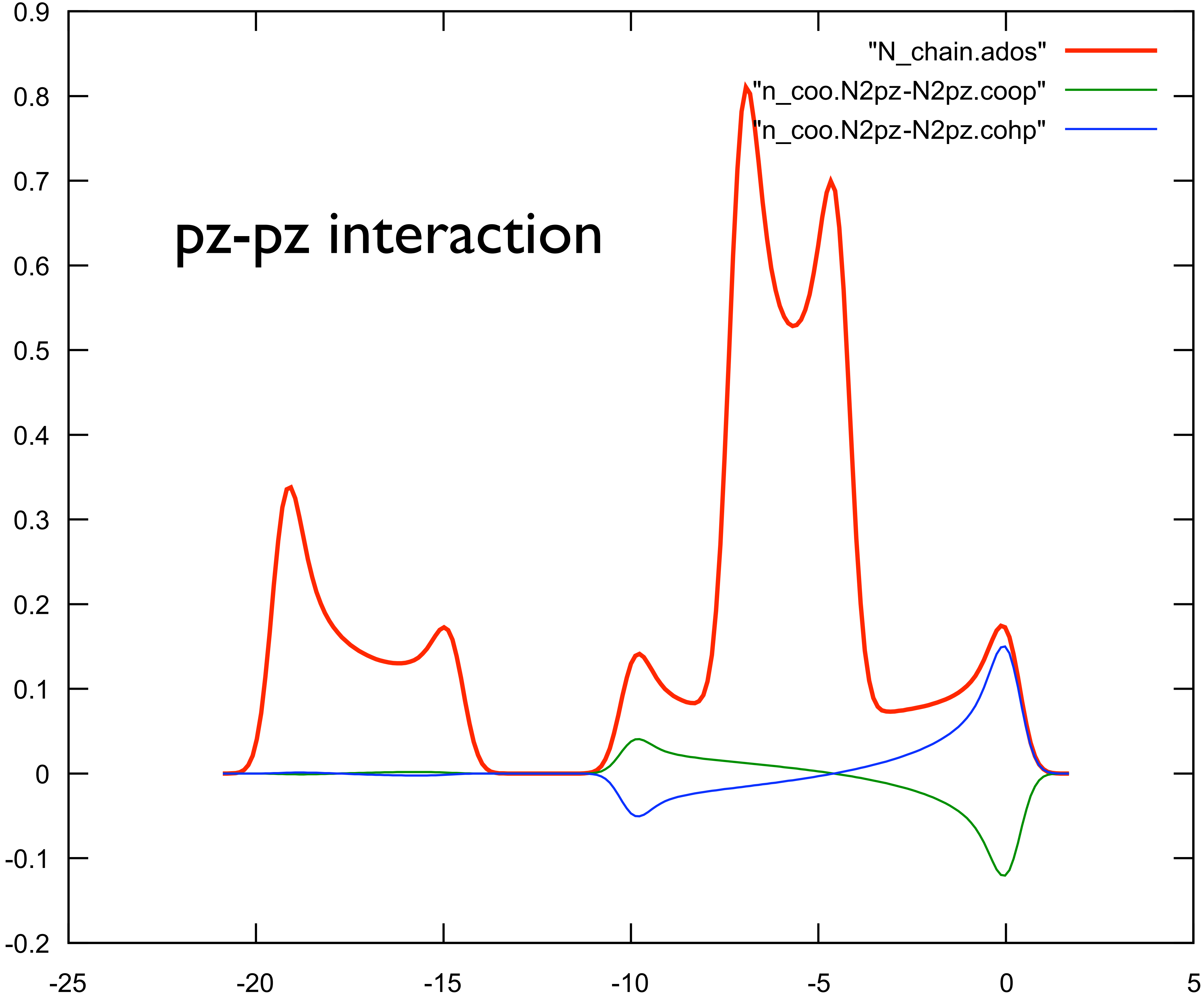
COOP file: InputLabel.CurveLabel.coop

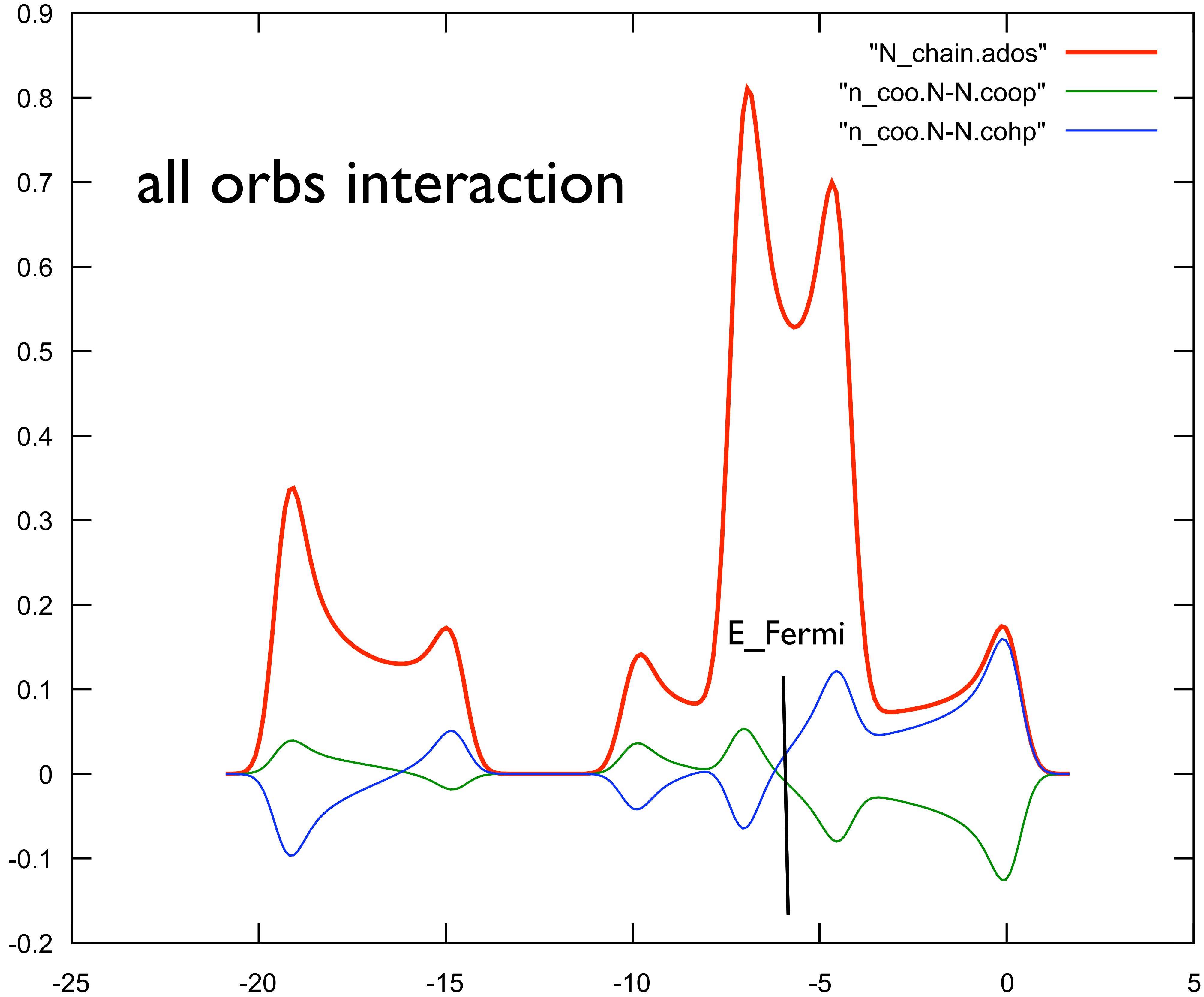
COHP file: InputLabel.CurveLabel.cohp



s-s interaction
"N_chain.ados"
"n_coo.N2s-N2s.coop"
"n_coo.N2s-N2s.cohp"
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-25
-20
-15
-10
-5
0
5


s-s interaction
Bonding
Anti-bonding
"N_chain.ados"
"n_coo.N2s-N2s.coop"
"n_coo.N2s-N2s.cohp"
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-25
-20
-15
-10
-5
0
5


pz-pz interaction
"N_chain.ados"
"n_coo.N2pz-N2pz.coop"
"n_coo.N2pz-N2pz.cohp"
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-25
-20
-15
-10
-5
0
5



"N_chain.ados"
"n_coo.N-N.coop"
"n_coo.N-N.cohp"
all orbs interaction
E_Fermi
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-25
-20
-15
-10
-5
0
5

mprop lives in Util/COOP in the Siesta distribution

mprop -h   Built-in help

```
* MPROP PROGRAM
  Miquel Llunell, Universitat de Barcelona, 2005
  Alberto Garcia, ICMAB-CSIC, 2007

    MPROP calculates both DOS projections and COOP curves
    using output files obtained with SIESTA. The atomic orbital (AO)
    sets are defined in an input file (MLabel.mpr).

 Usage: mprop [ options ] MPROP_FILE_BASENAME
 Options:
           -h:  print manual
           -d:  debug
           -l:  print summary of energy information
    -s SMEAR  :  set value of smearing parameter (default 0.5 eV)
    -m Min_e  :  set lower bound of energy range
    -M Max_e  :  set upper bound of energy range
```

```
* .mpr FILE STRUCTURE
         SLabel                       # Name of the siesta output files
         DOS/COOP                     # Define the curve type to be calculated
     /-[ If DOS selected; as many blocks as projections wanted ]
     |   projection_name              # DOS projection name
     \-  Subset of AO (*)             # Subset of orbitals included
     /-[ If COOP selected; as many blocks as projections wanted ]
     |   curve_name                   # COOP curve name
     |   Subset I of AO (*)           # Reference atoms or orbitals
     |   d1 d2                        # Distance range
     \-  Subset II of AO (*)          # Neighbour atoms or orbitals
      (*) See below how to define subsets of AO
      A final line with leading chars  ----  can signal the end of the input
```

```
* SUBSET OF AO USING ATOM_SHELL NOTATION
    List of atoms and shell groups of AO
    General notation: ATOM_SHELL
     > ATOM:  Atomic symbol refers to all the atoms of that type
              Integer number refers to the N-th atom in unit cell
     > SHELL: Integer1+Letter+Integer2
               > Integer1 refers to the n quantum number
               > Letter   refers to the l quantum number (s,p,d,f,g,h)
               > Integer2 refers to a single AO into the n-l shell
                   Alternatively, alphanumerical strings can be used
                     p-shells   1  y    d-shells   1  xy   4  xz
                                2  z               2  yz   5  x2-y2
                                3  x               3  z2
    Particular cases:
     > Just ATOM is indicated: all the AO of the atom will be included
     > No value for Integer2:  all the AO of the shell will be included
    Example: Ca_3p Al 4_4d3 5 O_2py
```

- mprop can be used off-line to analyze as many curves and energy ranges as needed.
- It can replace the PDOS functionality within Siesta.
- It has a flexible orbital specification syntax.

Useful reference with examples of the use of COOP and COHP curves