Advanced School on
QUANTUM MODELLING
of Materials with CRYSTAL

One-Electron Properties

Hands-On Session

UNIVERSITÀ DI TORINO

COMPUTATIONAL TOOL FOR SOLID STATE CHEMISTRY AND PHYSICS
CRYSTAL

Tutorial Outline

- ✓ Band structure
- ✓ Density of states
- ✓ Additional/advanced keywords
- ✓ Visualization tools (CRYSPLOT, CRYSTALClear)
- ✓ 3D electrostatic potential maps

Computing One-Electron Properties

One-electron properties and wave function analysis can be computed from the SCF wave function by running properties. Data stored in "wavefunction file" (*file.f9*):

- geometry, symmetry, crystal structure;
- basis set;
- reciprocal lattice k-point sampling information;
- irreducible Fock/KS matrix in direct space;
- irreducible density matrix in the direct space

Note that Hamiltonian eigenvectors are not stored; they must be recomputed when necessary (keyword **NEWK**)

PROPERTIES is the binary taking care of the post-processing

```
runPROP23 input_file wavefunction_file
```

(without `.d3` and `.f9` extensions)

Band Structure

Calculation of the band structure from density matrix is key describe the electronic structure of a material, since it tells us if it acts like a conductor, an insulator, a semiconductor.

PROPERTIES input for band structure calculation: *filename.d3*

```
BAND
Path:  G-X-W-L-G
4  8  60  7  14  1  0
 0  0  0   4  0  4
 4  0  4   4  2  6
 4  2  6   4  4  4
 4  4  4   0  0  0
END
```

keyword

title/note

parameters

path in reciprocal space

- `4`: number of segments in the reciprocal space to explore;
- `8`: shrinking factor in term of which the coordinates of the extreme of the segments are expressed;
- `60`: total number of **k** points along the path;
- `1`: first band to be saved;
- `18`: last band to be saved;
- `1`: plotting option (if `1`, write data on filename.25);
- `0`: no printing option are activated

Exercise

1. Compute the band structure for MgO (path: Gamma-X-W-L-Gamma) and plot it with CRYSPLOT. Perform the same operation on a different path.
2. Compute the band structure for urea (path: Gamma-M-X-R-A-Z-Gamma)
3. Compute the band structure for silicon (Gamma-X-W-L-Gamma-K-X)
4. Compute the band structure for Beryllium (Gamma-X-W-L-Gamma-K-X)
5. Compare the results:
   - Which system shows the flattest bands and which the most dispersive ones?
   - Classify each system as insulator, semiconductor or metal based on the band structure

Remember to run a single-point calculation with CRYSTAL to get the wavefunction file (.f9) before computing the band structure!

Density of States

Calculation of density of states allows to obtain a chemical insight into the band structure. This allows to identify which atomic species and even which atomic orbitals contribute the most to valence and conduction bands.

```
NEWK
8  8
1  0
DOSS
2  200  7  14  1  12  0
-1  1
-1  2
END
```

compute Hamiltonian eigenvectors

parameters

- 8: shrinking factor for reciprocal space Pack-Monkhorst net;
- 8: shrinking factor for reciprocal Gilat net;
- 1: evaluation of the Fermi level with the new k-points net;
- 0: no printing options

keyword

parameters

- 2 : number of projections (total DOS is always computed);
- 200: number of points along the energy axis in which DOSS is calcul
- 7: first band;
- 14: last band;
- 1: plot option (if 1, data are saved in `filename.25`);
- 12: degree of the polynomial used for DOSS expansion;
- 0: no printing options

projection onto all AOs

- -1 1: projection onto all AOs (-1) of Mg (1, first atom);
- -1 2: projection onto all AOs (-1) of O (2, second atom)

Density of States

Projection onto a set of AOs

```
NEWK
8 8
1 0
DOSS
8 200 7 14 1 12 0
4 1 2 6 10          4 AOs of Mg (S shell)
3 3 7 11            3 AOs of Mg (SP shell, PX)
3 4 8 12            3 AOs of Mg (SP shell, PY)
3 5 9 13            3 AOs of Mg (SP shell, PZ)
4 14 15 19 23       4 AOs of O  (S shell)
3 16 20 24          3 AOs of O  (SP shell, PX)
3 17 21 25          3 AOs of O  (SP shell, PY)
3 18 22 26          3 AOs of O  (SP shell, PZ)
END
```

AOs are identified by their sequence number within basis set

Exercise

1. Compute the projected DOS of MgO: i) on the whole set of AOs for both Mg and O, and ii) on the S, PX, PY and PZ subsets of AOs, including only the valence bands.
2. Compute the projected DOS of urea on the whole set of AOs of each of the constituent atoms (C, O, N, H); can you find evidence of a hydrogen bond between atoms?
3. Calculate the projected DOS of beryllium on the S, PZ and PX+PY subsets of AOs, including only the valence bands. For metals, denser sampling nets may be needed for revealing details in the total and projected DOSs, so a high shrinking factor for both the Pack-Monkhorst and Gilat nets is recommended.
4. Compute the projected DOS of silicon onto the S and P subsets of AOs, including only the valence bands. Please, note that: i) there are two Si in the unit cell so the total amount of AOs is 26, and ii) the 1st and the 14th AO are the 1S of the first and second Si atom, respectively, the 2nd and the 15th are the *2S* of the first and second Si atom, respectively, the 3rd-6th and the 16th-19th are the 2P of the first and second Si atom, respectively, and so on…

Exercise

1. Compute the band structure of MgO (path: Gamma-X-W-L-Gamma) by making using of a hybrid functional. Generate a single plot showing the comparison with CRYSTALClear. What happens to the band gap? Do band shapes change?
2. Generate a unified plot of band structure and DOSS and export it in high resolution.

CRYSTALClear

Electron Charge Density

The ground-state electron charge density is an observable of primary importance. The **total electron** density maps provide a pictorial representation of the total electronic distribution. However, more useful information is obtained by considering **difference maps:** difference between the crystal electron density and a "reference" electron density. The "reference" density is a superposition of atomic (or ionic) charge distributions.

```
ECHG
0
65
COORDINA
-4.0 -4.0 0.0
 4.0 -4.0 0.0
 4.0  4.0 0.0
MARGINS
1.5 1.5 1.5 1.5
END
```

keyword

parameters
- `0`: order of the derivatives: if not `0`, charge density gradients are computed;
- `65`: number of point along the AB segment (see manual)

plane definition
- Cartesian coordinates of points A, B and C defining the window in a plane

margins
- Margins are added in the order AB, CD, AD, BC; widths are specified below

Exercise

1. Compute the total electron density map of MgO and plot it with CRYSPLOT.
2. Add the definition of a new density matrix (using the keyword **PATO)** to the input**,** as superposition of isolated atoms (or ions) densities (according to the electron charge you attributed to the atoms when defining the basis set). Repeat the **ECHG** block. Plot the difference with CRYSPLOT.
3. Repeat these procedure for each system. Tip: both total and difference maps are saved in the .f25 file when the **PATO** keyword is used.
4. Try to correlate the electron charge density with the nature of bonds in these crystals.

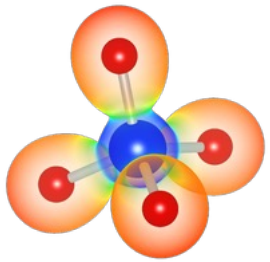
3D Plots of Electron Density and Electrostatic Potential

With CRYSTAL, generating cube files to be plotted with VESTA or VMD is quite easy.

ECH3: This keyword allows the calculation of **the electronic charge density** (electron/bohr^3) at a regular 3-dimensional grid of points. The first line after the keyword indicates the number of points to be sampled along the first lattice vector of the primitive unit (equally spacing is,used along the other dimensions).

POT3: This keyword allows the calculation of the **electrostatic potential** at a regular 3-dimensional grid of points. The input is almost equal to that of the ECH3 keyword. Just remember to add an addition line in which a penetration tolerance is indicated, after the line containing the number of points along the first direction.

Exercise

Generate an isodensity surface colorcoded with the electrostatic potential for MgO, urea, beryllium and silicon:

1. Run a PROPERTIES calculation for each system. Tip: **ECH3** and **POT3** can be inserted in the same input file
2. Open VESTA and import the cube file generated by **ECH3**. Adjust the level of the isosurface in Style > Properties > Isosurfaces > Isosurface Level.
3. Color the surface according to the electrostatic potential: Edit > Edit Data > Volumetric Data > Surface Coloring > Import (load the cube file generated by **POT3**)