A Brief Tutorial on PARSEC
pseudopotential **a**lgorithm for **r**eal-**s**pace **e**lectronic structure **c**alculations

(this tutorial can be found in PARSEC repository on GitLab)

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Outline

PARSEC I

- Kohn–Sham equations are solved in real space
- The Hamiltonian matrix is not stored, only requiring $\hat{H}\psi_i$
- Pseudopotentials are used (solving for valence electrons only)

$$\begin{cases} \left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \\ V_{\text{eff}}(\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \\ \rho(\mathbf{r}) = \sum_{i=1}^{N_s} f_i|\psi_i(\mathbf{r})|^2 \end{cases} \tag{1}$$

$$\{\psi\} = \begin{pmatrix} \psi_1(\mathbf{r}) & \psi_2(\mathbf{r}) & \dots & \psi_{N_s}(\mathbf{r}) \\ & & & \end{pmatrix} = \begin{pmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \dots & \psi_{N_s}(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \dots & \psi_{N_s}(\mathbf{r}_2) \\ . & . & \dots & . \\ . & . & \dots & . \\ \psi_1(\mathbf{r}_N) & \psi_2(\mathbf{r}_N) & \dots & \psi_{N_s}(\mathbf{r}_N) \end{pmatrix}$$

PARSEC II

$$E_{\mathrm{tot}} = \left(\sum_{i=1}^{N_s} \varepsilon_i - E_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}[\rho] - \int v_{xc}\rho(\mathbf{r})d\mathbf{r} \right) + E_{\mathrm{ion-ion}} \quad (2)$$

PARSEC uses "charge-weighted self-consistent residual error" (SRE) as the default convergence criterion.

$$\mathrm{SRE} = \sqrt{\frac{1}{N_{\mathrm{e}}} \int d\mathbf{r}\rho^{(i)}(\mathbf{r}) \left(V_{\mathrm{eff}}^{(i)}(\mathbf{r}) - V_{\mathrm{eff}}^{(i-1)}(\mathbf{r}) \right)^2} \quad (3)$$

PARSEC III

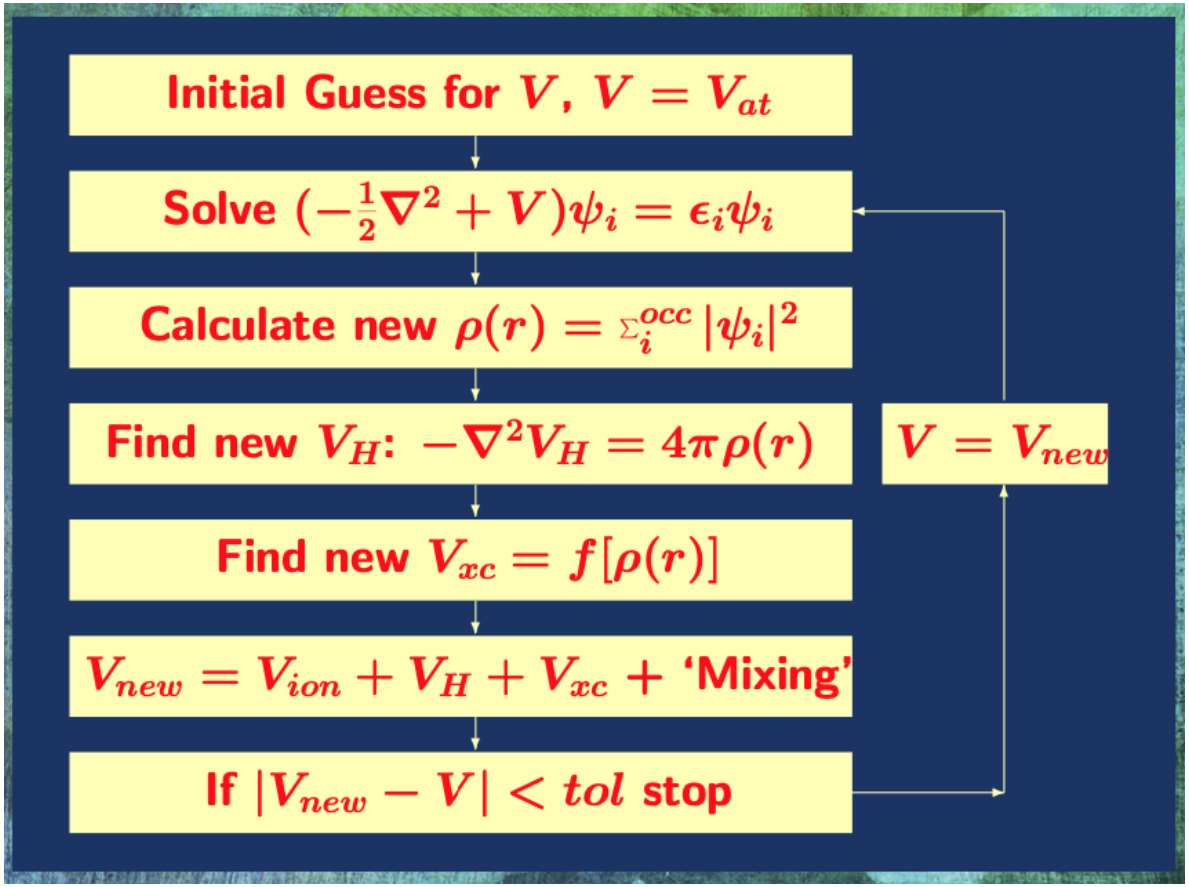


Figure 1: A self-consistent-field calculation

What Can PARSEC Do?

- Self-consistent-field calculation
- Band structure calculation
- Structural optimization
- Molecular dynamics
- Spin-polarization, spin-orbit interaction, external E-field, B-field
- The output of PARSEC can be used as the input for excited-state calculations (e.g., NanoGW and BerkeleyGW)
- ...

Input Files and Parameters I

- pseudopotentials: I usually use Troullier and Martins' norm-conserving pseudopotentials, which can be downloaded from PARSEC website, or generated by yourself (e.g., using atomic programs or APE, etc.).
- `parsec.in`: the input file. Details can be found in PARSEC user's guide.
  - `boundary_conditions` (`cluster`, `bulk`, `slab`, `wire`)
  - `grid_spacing` (h)
  - `boundary_sphere_radius` ($r_{\max}$)
  - `convergence_criterion` (for SRE, see Eq. 3)

Input Files and Parameters II

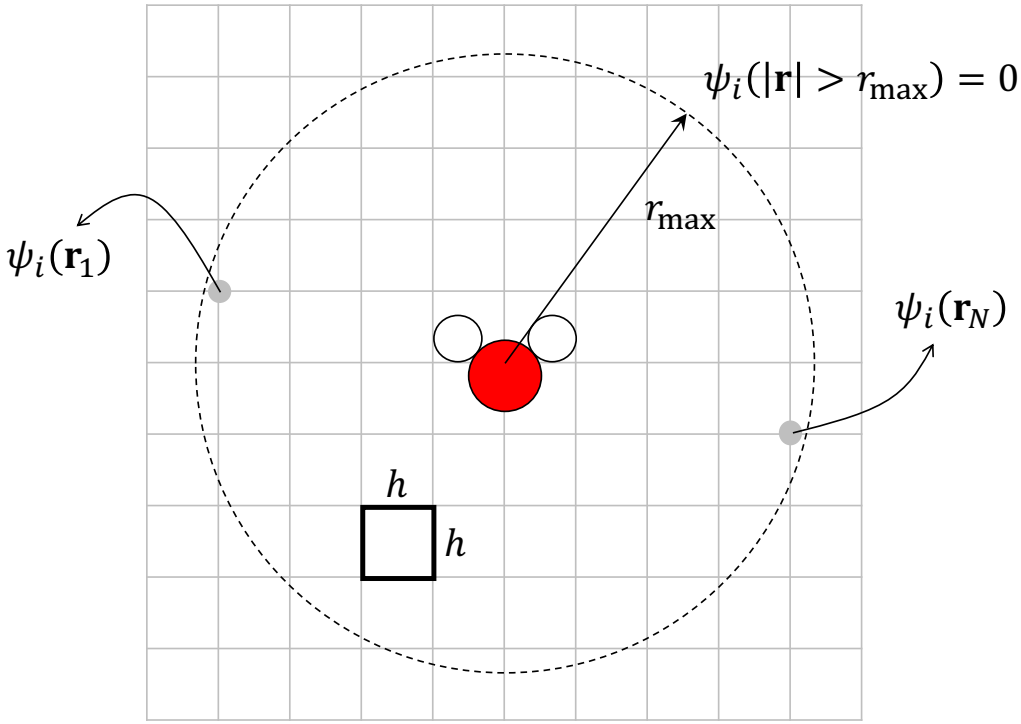


Figure 2: A spherical simulation domain for `cluster` boundary condition

Input Files and Parameters III

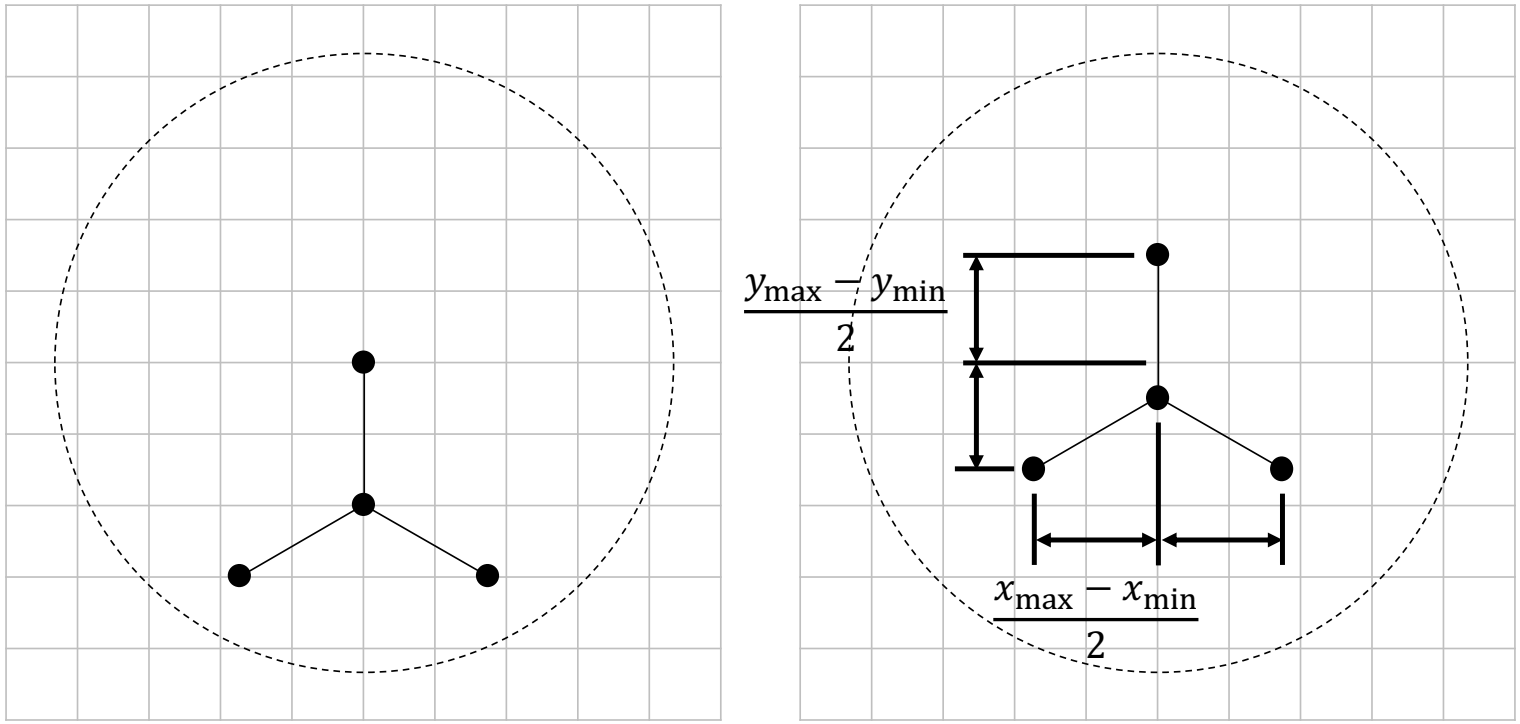


Figure 3: Recentering of a system

Note: As shown in Figure 3, for 0D systems, at the beginning PARSEC will shift "the center of the system" (half way along each dimension. Not necessary of the geometric center) to the origin.

Running PARSEC on NERSC Cori I

We can download the code to our home directory from GitLab by:

```
> cd $HOME && mkdir PARSEC && cd PARSEC
> git clone https://gitlab.com/real-space/parsec.git
```

or copy from Cori:

```
> cd $HOME
> cp -r $CFS/m3034/vESW_2020/PARSEC/ .
```

After getting the code, we go to the source code directory and compile PARSEC (here we show the steps for Haswell):

```
> cd $HOME/PARSEC/parsec/src/
> make MACH=cori_hsw_intel clean
> make MACH=cori_hsw_intel -j8
```

If successful, we should see an executable named "parsec-cori_hsw_intel-ftn-ifort-19.0.3.199.mpi" in the same folder.

Running PARSEC on NERSC Cori II

Now let's copy the examples to Cori scratch

```
> cd $SCRATCH
> cp -r $HOME/PARSEC/parsec/examples/benchmarks/ .
```

Today we will do three examples

- Silicon Nanocrystals (0D)
  `examples/benchmarks/0d_Si29H36`
- Carbon Diamond (3D)
  `examples/benchmarks/3d_C_diamond_bands`
- Monolayer MoS_2 (2D)
  `examples/benchmarks/2d_MoS2_bands`

In general, we put the pseudopotential files and `parsec.in` in a folder, and then run the PARSEC executable.

Silicon Nanocrystals (0D)

location: `parsec/examples/benchmarks/0d_Si29H36`

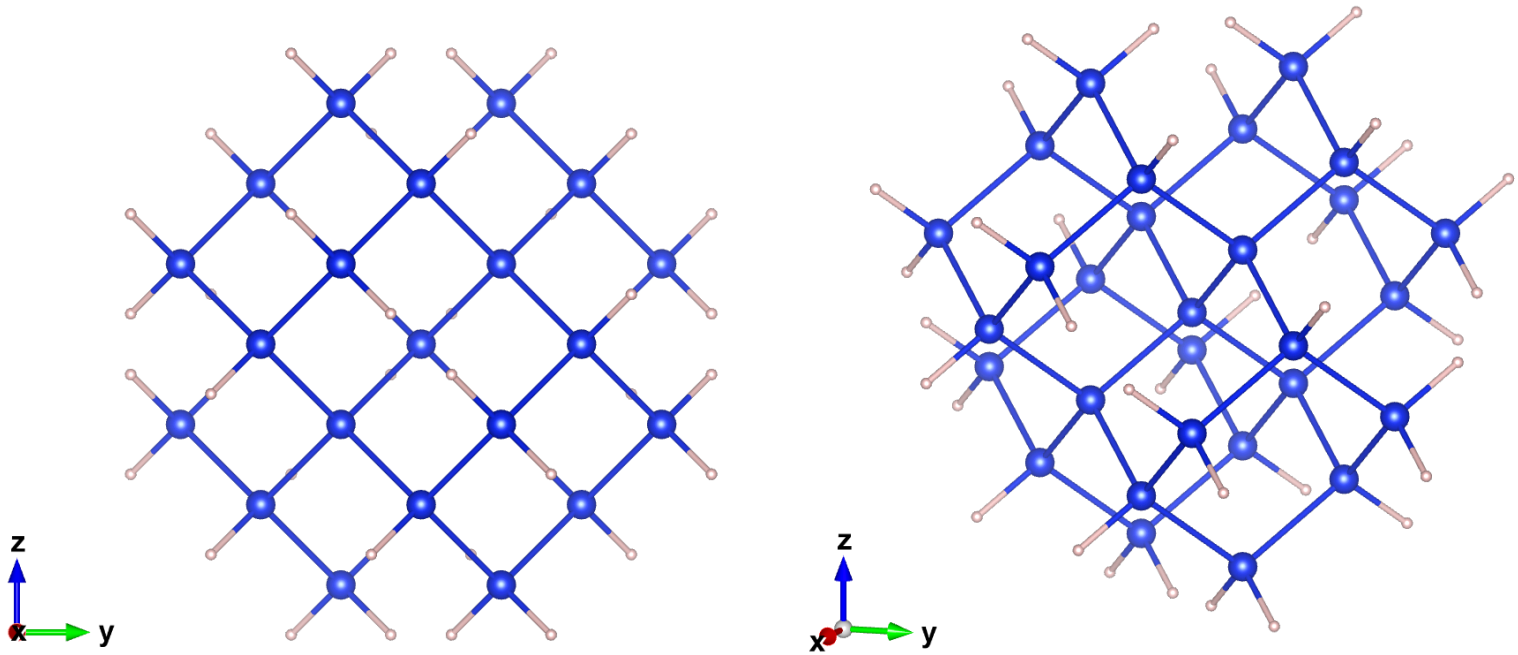


Figure 4: $Si_{29}H_{36}$

Silicon Nanocrystals (0D)–parsec.in I

```
# The real-space grid
boundary_conditions             cluster
boundary_sphere_radius          20 bohr
grid_spacing                    0.7 bohr

# Self-consistency and mixing parameters
max_iter                        50
convergence_criterion           1.d-8 ry

# Electronic parameters
states_num                      104
correlation_type                ca

# Global atom and pseudopotential parameters
atom_types_num                  2
coordinate_unit                 cartesian_bohr

# Parameters specific to each chemical element
# Atom type 1
```

Silicon Nanocrystals (0D)–parsec.in II

```
20 atom_type          Si
21 local_component    p
22
23 begin atom_coord
24 -2.565303 -2.565303 -7.695910
25 ...
26 end atom_coord
27
28 # Atom type 2
29 atom_type          H
30 local_component    s
31
32 begin atom_coord
33 -0.972387 -0.972387 -9.288819
34 ...
35 end atom_coord
```

Listing 1: parsec.in for $Si_{29}H_{36}$

Carbon Diamond (3D)–Direct Lattice

location: `parsec/examples/benchmarks/3d_C_diamond_bands`

lattice: FCC primitive cell

$$\mathbf{a} = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$$

$$\mathbf{a}_1 = \frac{a_0}{2}\begin{pmatrix}0\\1\\1\end{pmatrix}$$

$$\mathbf{a}_2 = \frac{a_0}{2}\begin{pmatrix}1\\0\\1\end{pmatrix}$$

$$\mathbf{a}_3 = \frac{a_0}{2}\begin{pmatrix}1\\1\\0\end{pmatrix}$$

basis:

$$\mathbf{r} = f_1\mathbf{a}_1 + f_2\mathbf{a}_2 + f_3\mathbf{a}_3$$

$$\begin{cases}\mathbf{r}_1 = (f_1, f_2, f_3) = (0,0,0)\\ \mathbf{r}_2 = (0.25, 0.25, 0.25)\end{cases}$$

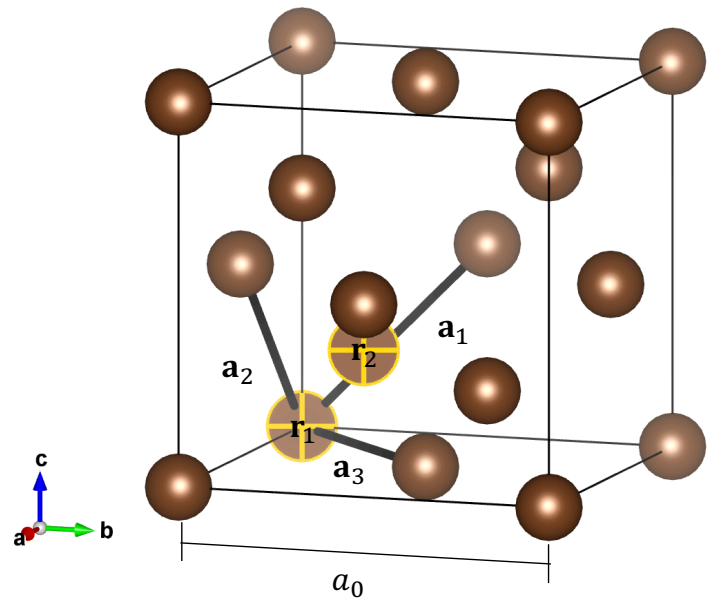


Figure 5: FCC diamond structure

Carbon Diamond (3D)–Reciprocal Lattice

reciprocal lattice:

$$\mathbf{b} = k_x\hat{\mathbf{k}}_x + k_y\hat{\mathbf{k}}_y + k_z\hat{\mathbf{k}}_z$$

$$\mathbf{b}_1 = \frac{2\pi}{a_0}\begin{pmatrix}-1\\1\\1\end{pmatrix}$$

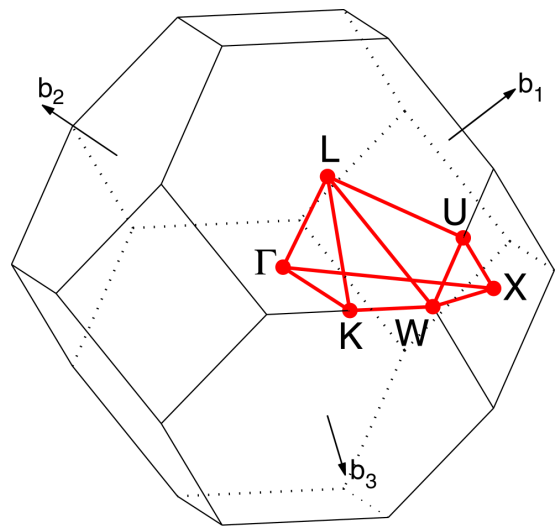
$$\mathbf{b}_2 = \frac{2\pi}{a_0}\begin{pmatrix}1\\-1\\1\end{pmatrix}$$

$$\mathbf{b}_3 = \frac{2\pi}{a_0}\begin{pmatrix}1\\1\\-1\end{pmatrix}$$

high-symmetry points:

$$\mathbf{X} \equiv \frac{2\pi}{a_0}\begin{pmatrix}0\\1\\0\end{pmatrix} = 0.5\mathbf{b}_1 + 0.5\mathbf{b}_3$$

$$\mathbf{W} \equiv \frac{2\pi}{a_0}\begin{pmatrix}0.5\\1\\0\end{pmatrix} = 0.5\mathbf{b}_1 + 0.25\mathbf{b}_2 + 0.75\mathbf{b}_3$$



FCC path: Γ-X-W-K-Γ-L-U-W-L-K|U-X

[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

Carbon Diamond (3D)–parsec.in I

```
# The real-space grid
boundary_conditions          bulk

begin cell_shape
 0.0     0.5     0.5
 0.5     0.0     0.5
 0.5     0.5     0.0
end cell_shape

lattice_vector_scale         3.57 ang
grid_spacing                 0.3 bohr

# Self-consistency and mixing parameters
max_iter                     100
convergence_criterion        1d-6 ry

# Electronic parameters
states_num                   10
correlation_type             ca
```

Carbon Diamond (3D)–parsec.in II

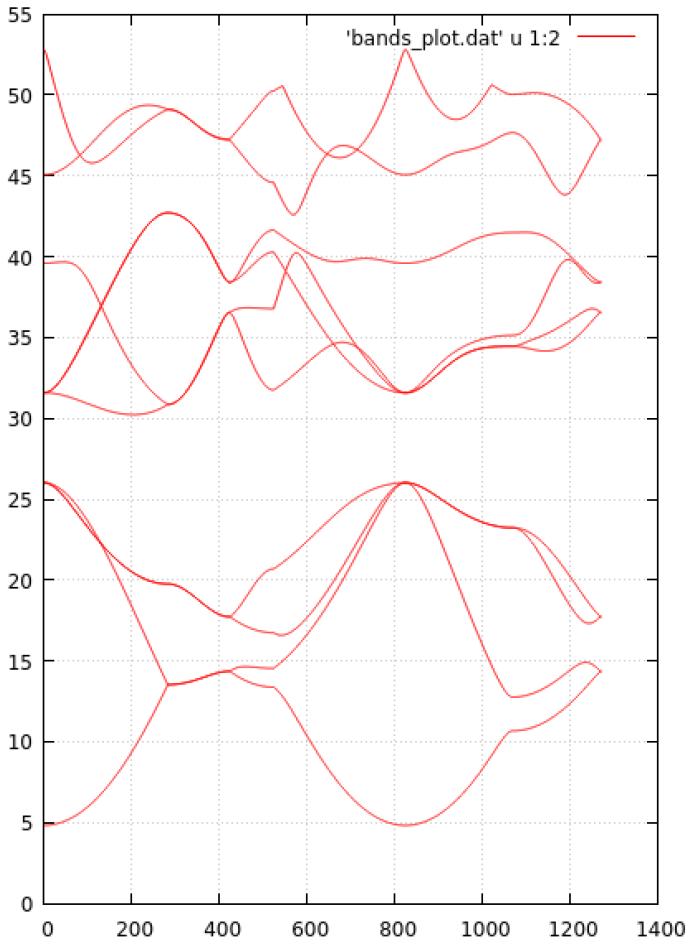
```
20
21 # Wave functions and k-points
22 kpoint_method                  mp
23
24 begin monkhorst_pack_grid
25  5     5     5
26 end monkhorst_pack_grid
27
28 begin monkhorst_pack_shift
29  0.5     0.5     0.5
30 end monkhorst_pack_shift
31
32 # Band structure and density of states calculation
33 begin bandstruc
34  1 0.00   0.00   0.00    0.50   0.00   0.50    gamma-X
35  2 0.50   0.00   0.50    0.50   0.25   0.75    X-W
36  3 0.50   0.25   0.75    0.375 0.375 0.75    W-K
37  4 0.375 0.375 0.75    0.00   0.00   0.00    K-gamma
38  5 0.00   0.00   0.00    0.50   0.50   0.50    gamma-L
39  6 0.50   0.50   0.50    0.50   0.25   0.75    L-W
```

Carbon Diamond (3D)–parsec.in III

```
40 end bandstruc
41
42 # Global atom parameters
43 atom_types_num                 1
44 coordinate_unit                lattice_vectors
45
46 # For each atom type
47
48 atom_type                      C
49 pseudopotential_format         martins_new
50 local_component                p
51
52 begin atom_coord
53 0           0           0
54 0.25        0.25        0.25
55 end atom_coord
```

Listing 2: parsec.in for carbon diamond

Carbon Diamond (3D)–Band Structure



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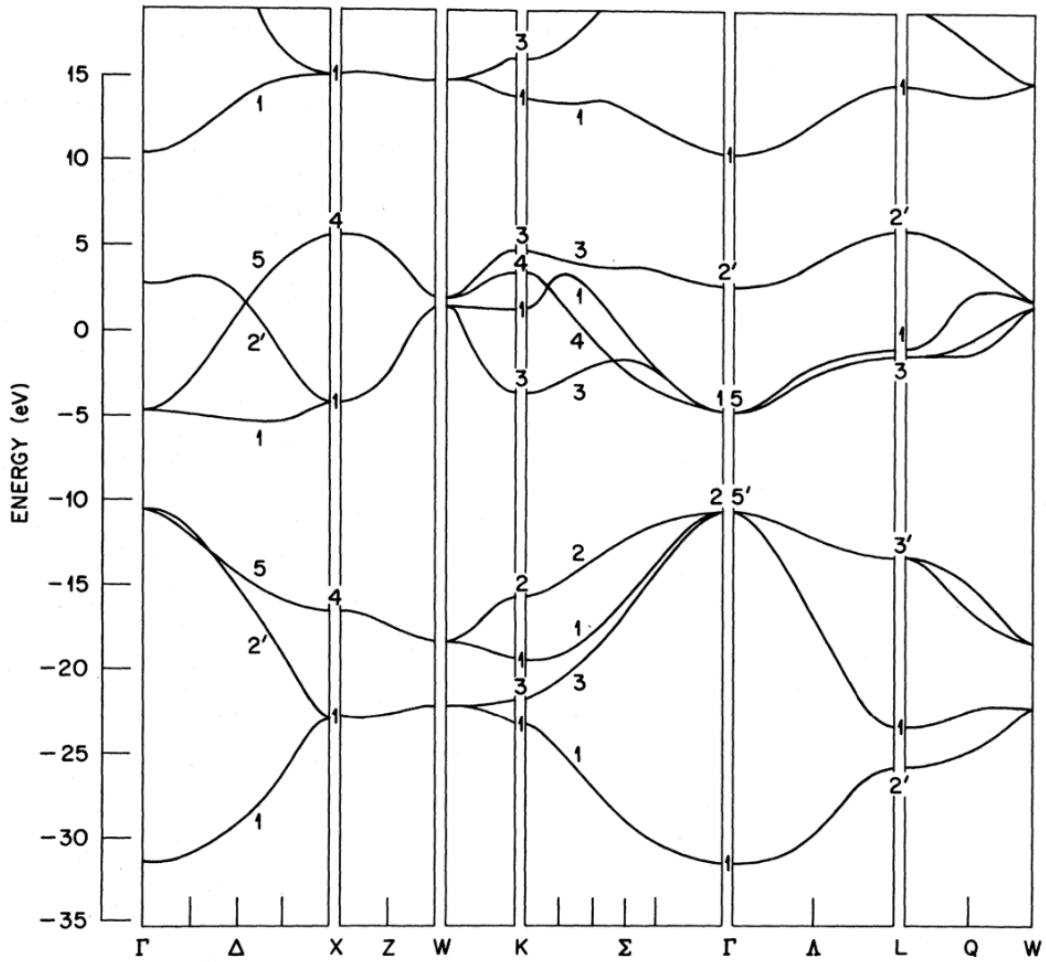
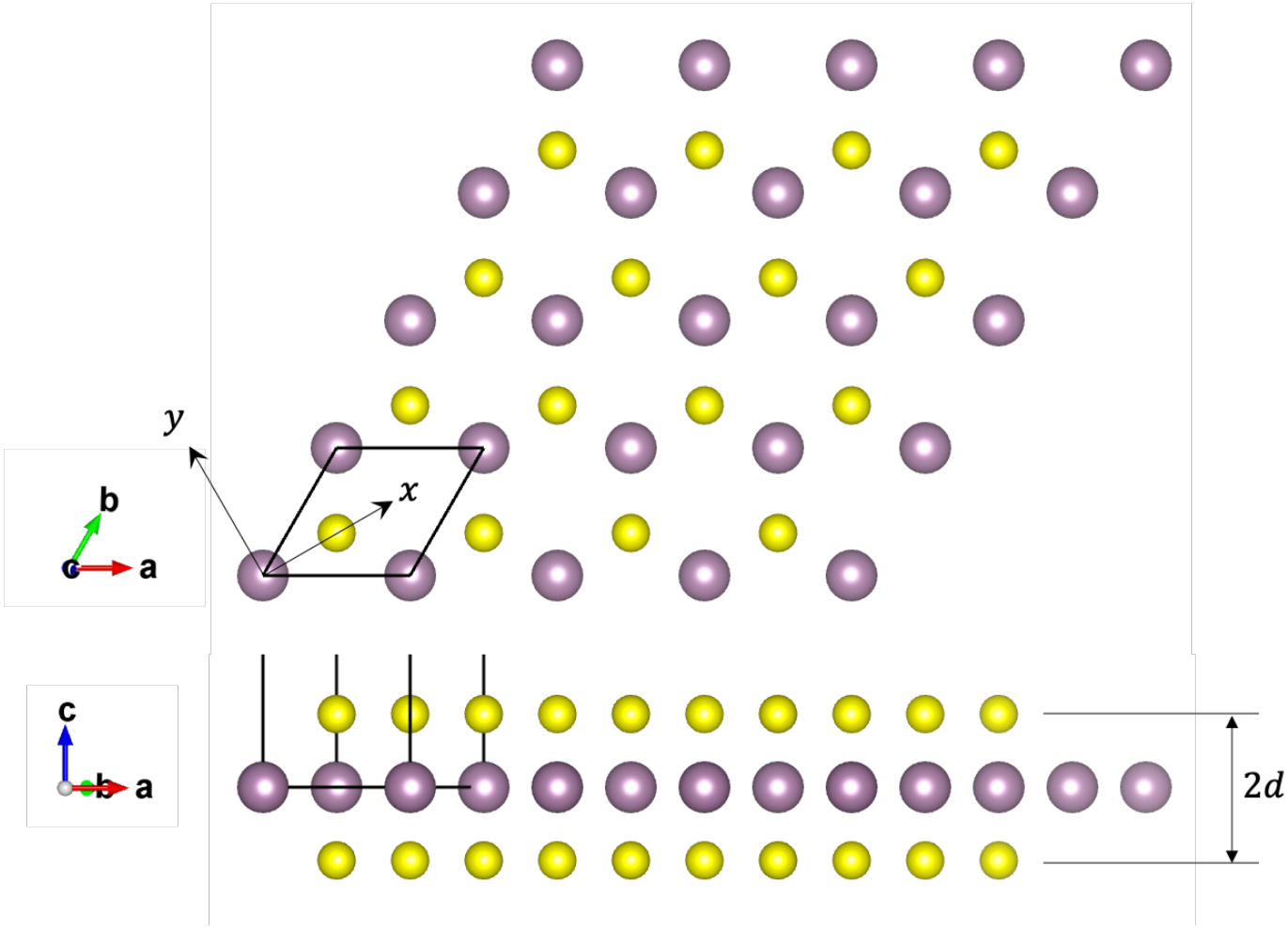


(Painter, 1971)

Monolayer MoS_2 (2D)–Structure

location: `parsec/examples/benchmarks/2d_MoS2_bands`



PARSEC

Monolayer MoS_2 (2D)–Direct Lattice

lattice: hexagonal lattice

$$\mathbf{a} = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$$

$$\mathbf{a}_1 = a_0 \begin{pmatrix} \frac{\sqrt{3}}{2} \\ -\frac{1}{2} \\ 0 \end{pmatrix}$$

$$\mathbf{a}_2 = a_0 \begin{pmatrix} \frac{\sqrt{3}}{2} \\ \frac{1}{2} \\ 0 \end{pmatrix}$$

basis:

Mo:

$$\mathbf{r}_1 = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

S:

$$\mathbf{r}_2 = \begin{pmatrix} \frac{\sqrt{3}}{3} a_0 \\ 0 \\ -d \end{pmatrix}$$

$$\mathbf{r}_3 = \begin{pmatrix} \frac{\sqrt{3}}{3} a_0 \\ 0 \\ d \end{pmatrix}$$

Monolayer MoS_2 (2D)–Direct and Reciprocal Lattice

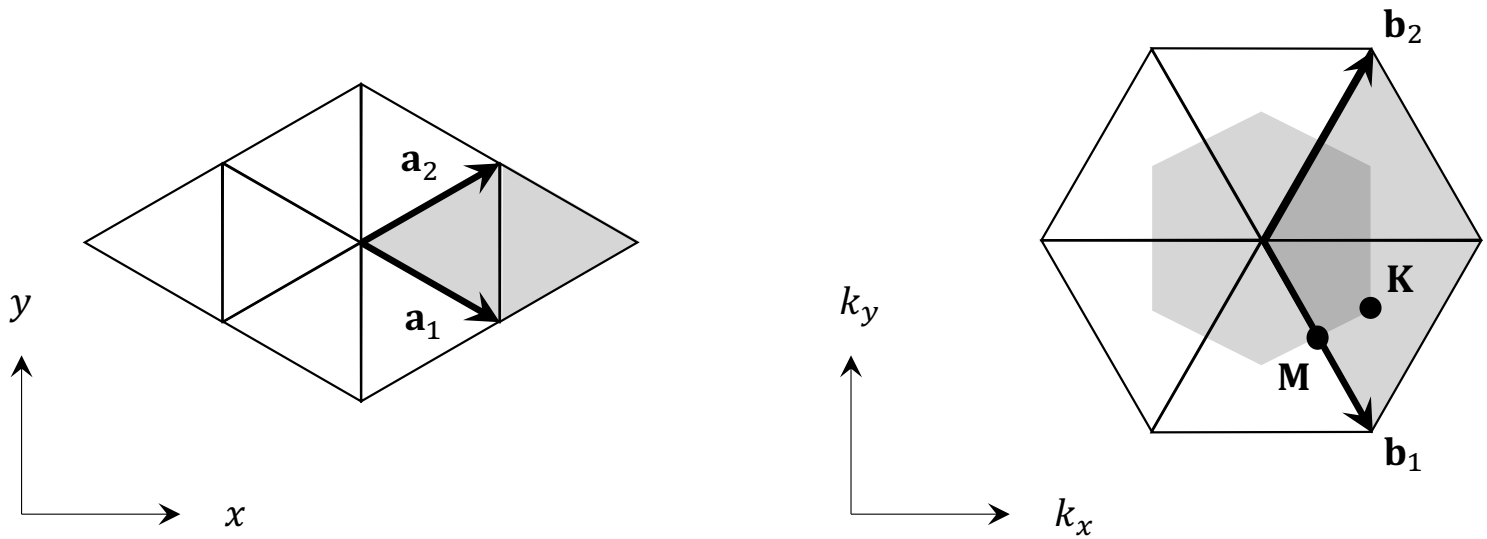


Figure 6: The direct and reciprocal lattice of monolayer MoS_2. The shaded regions are unit cells.

Monolayer MoS_2 (2D)–parsec.in I

```
# The real-space grid
boundary_conditions          slab

begin cell_shape
 5.20423371392659 -3.004665735661225  0
 5.20423371392659  3.004665735661225  0
end cell_shape

lattice_vector_scale         1
boundary_sphere_radius       20
grid_spacing                 0.45

# Diagonalization parameters
eigensolver                  chebdav
diag_tolerance               1d-7

# Self-consistency and mixing parameters
max_iter                     20
convergence_criterion        1d-4
```

Monolayer MoS_2 (2D)–parsec.in II

```
20
21 # Electronic parameters
22 states_num                    30
23 correlation_type               pb
24
25 # Wave functions and k-points
26 kpoint_method                  mp
27
28 begin monkhorst_pack_grid
29  8    8
30 end monkhorst_pack_grid
31
32 begin monkhorst_pack_shift
33  0.0  0.0  0.0
34 end monkhorst_pack_shift
35
36 # Band structure and density of states calculation
37 begin bandstruc
38  1 0.0       0.0       0.0 0.5       0.0       0.0 gamma-M
39  2 0.5       0.0       0.0 0.666666 0.333333 0.0 M-K
```

Monolayer MoS_2 (2D)–parsec.in III

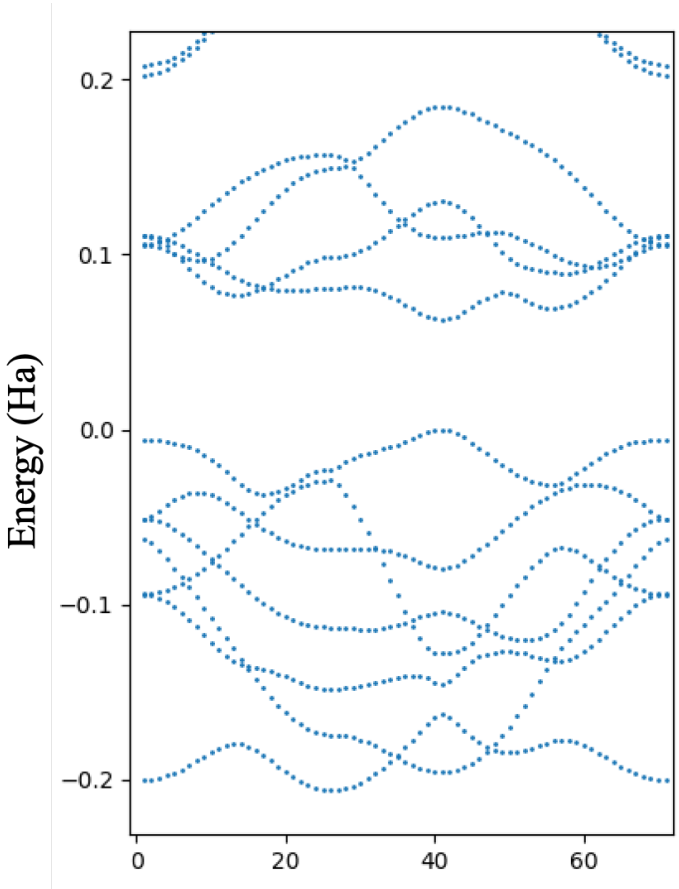
```
 3 0.666666 0.333333 0.0 0.0        0.0        0.0 K-gamma
end bandstruc

bandstruc_points                15

# Global atom parameters
atom_types_num                  2
coordinate_unit                 cartesian_bohr

#------------ new atom type -----------------
atom_type                       Mo
local_component                 s

begin atom_coord
 0.0 0.0 0.0
end atom_coord

atom_type                       S
local_component                 s

```

Monolayer MoS_2 (2D)–parsec.in IV

```
60 begin atom_coord
61  3.46948914261767   0.00000000000000   -2.98576846688340
62  3.46948914261767   0.00000000000000    2.98576846688340
63 end atom_coord
64 #------------ end of atom type -------------
```

Listing 3: parsec.in for MoS_2

Monolayer MoS_2 (2D)–Band Structure



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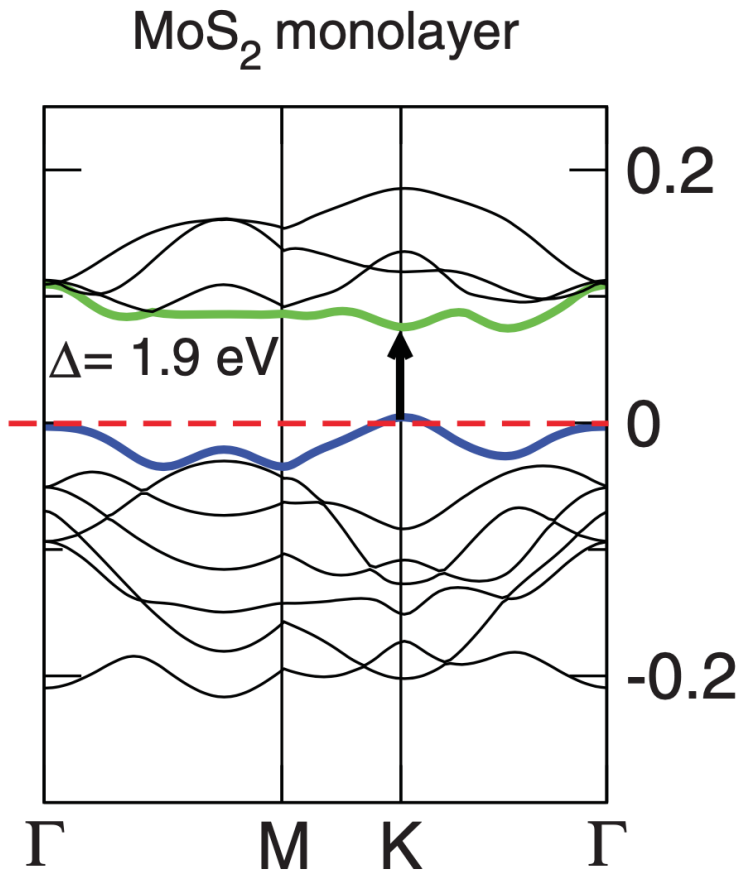

Crystal09 (Kuc, 2011)