

Report for the calculation of silicon crystalline

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ABINIT is a software suite to calculate the optical, mechanical, vibrational, and other observable properties of materials based on the density function theory (DFT). In this report, we show the basic application with such software, as a good opportunity of learning to use various tunable variables in the software suite. Specifically, we show the calculation of crystalline silicon in this report, which corresponds to the tutorial Base3 of ABINIT.

I. THEORY AND ALGORITHM

In this report, we will use DFT method to calculation the total energy, the lattice parameter and also the band structure of the crystalline silicon. We first introduce the basic structure of crystalline silicon.

Crystalline silicon is the crystalline forms of silicon, either multi-crystallin consisting of small crystals, or mono-crystalline silicon. Crystalline silicon is in the same pattern as diamond, in a structure which Ashcroft and Mermin call “two interpenetrating face-centered cubic” primitive lattices. The cubic side for silicon is 0.543 nm, which corresponds to 10.18 Bohr in atomic unit. In every lattice point, there are two silicon atoms. In the lattice frame, supposing one of the atom locates at the origin, the other atom locates at $(1/4, 1/4, 1/4)$ in the unit of lattice constant $a = 10.18$ Bohr for silicon crystalline. The primitive vectors are typically defined as $(0, 0.5, 0.5)$, $(0.5, 0, 0.5)$, $(0.5, 0.5, 0)$ in the unit of lattice constant.

Then, let's have a brief review of density function theory, which plays a dominant role in this course. For the interacting electrons, the Hohenberg-Kohn (HK) variational principle takes the forms

$$E_v[\tilde{n}(\mathbf{r})] = \int v(r)\tilde{n}(\mathbf{r}) + T_s(\tilde{n}(\mathbf{r})) + \frac{1}{2} \int \frac{\tilde{n}(\mathbf{r})\tilde{n}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\tilde{n}(\mathbf{r})] \geq E, \quad (1)$$

where $v(r)$ is the potential induced by the external field, $\tilde{n}(r)$ is the trial wave function, $T_s[\tilde{n}(r)]$ is the kinetic energy functional for non-interacting electrons, and E_{xc} is the so-called exchange-correlation energy functional, which accounts for the Fermion property of the electrons, as an additional term compared with classical theory. The corresponding Euler-Lagrange equation for a given number of electrons has the form,

$$\delta E_v[\tilde{n}(\mathbf{r})] = \int \delta \tilde{n}(\mathbf{r}) \left\{ v_{\text{eff}}(\mathbf{r}) + \frac{\delta}{\delta \tilde{n}(\mathbf{r})} T_s[\tilde{n}(\mathbf{r})] \Big|_{\tilde{n}(\mathbf{r})=n(\mathbf{r})} - \epsilon \right\} = 0, \quad (2)$$

where

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \quad (3)$$

is the effective potential felt by the electrons, and

$$v_{xc}(\mathbf{r}) = \frac{\delta}{\delta \tilde{n}(\mathbf{r})} E_{xc}[\tilde{n}(\mathbf{r})] \Big|_{\tilde{n}(\mathbf{r})=n(\mathbf{r})} \quad (4)$$

is the exchange-correlation energy. One can show that such functional minimization density $n(\mathbf{r})$ can be given by solving the single-particle equation

$$\left(-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) - \epsilon_j \right) \varphi_j(\mathbf{r}) = 0, \quad (5)$$

with

$$n(\mathbf{r}) = \sum_{j=1}^N |\varphi_j(\mathbf{r})|^2, \quad (6)$$

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$$v_{\text{eff}} = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}), \quad (7)$$

where $v_{xc}(r)$ is the local exchange-correlation potential, depending functionally on the entire density distribution $n(r)$. Typically, we denote $-\frac{1}{2}\nabla^2 + v_{\text{eff}}$ as the Hamiltonian H_{KS} for KS equation. These self-consistent equations are called Kohn-Sham (KS) equations. Note that if we neglect the property of fermion, and thus neglect the exchange-correlation term, the equation reduces to the self-consistent Hartree equations.

However, we note that $E_{xc}[\tilde{n}(r)]$, which is in a very complicated dependence of $\tilde{n}(r)$, is difficult to calculate, and typically we apply some approximations to simplify the calculation. Local-density approximation (LDA) is the simple but powerful approximation, which says

$$E_{xc}^{LDA} = \int e_{xc}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}, \quad (8)$$

where $e_{xc}(n)$ is the exchange-correlation energy per particle of a uniform electron gas of density n , which is further given by

$$e_{xc}(n) = e_x(n) + e_c(n) = -\frac{0.458}{r_s} - \frac{0.44}{r_s + 7.8}. \quad (9)$$

With LDA, we can simplify the calculation of DFT. Start with a trial wave function, we can solve the self-consistent KS equation to find the ground state of the system, which is the energy minimum point.

Practically, we can write the potential in the plane wave basis of momentum space, i.e.

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{eff}}(\mathbf{r} + \mathbf{R}) = \sum_{\mathbf{G}} V_{\text{eff}}(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}, \quad \mathbf{G} \cdot \mathbf{R} = 2\pi n, \quad (10)$$

therefore,

$$H_{KS} = \sum_{\mathbf{k}} \frac{1}{2}k^2 c_{\mathbf{k}}^\dagger c_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\text{eff}}(\mathbf{G})c_{\mathbf{k}+\mathbf{G}}^\dagger c_{\mathbf{k}} + h.c. \quad (11)$$

In the momentum space, from the trial density function $n(\mathbf{r})$, one can calculate the exchange-correlation potential v_{xc} , and combine it with the potential of lattice, and obtain the KS Hamiltonian H_{KS} . Then one can diagonalize the Hamiltonian to calculate the eigenfunction. Note that people typically set a cut off value for the momentum G to further simplify the calculation. With the new eigenfunction, one can get the new electron density $n(r)$, combined which with the old trial density function we can get the new trial function. One can conduct several iterations until the program reach convergence, i.e. with the exchange-correlation potential given by the trial electron density, one can calculate the ground state electron density that matches exactly with the trial electron density (in a given accuracy).

Note that due to the rapid oscillation of valence electrons in core region and the tightly-bound core orbitals, the cut-off value for the plane wave basis is reasonably high. In this case, people usually replace the ionic potential with a pseudopotential, which is smoother in the core region compared with the real potential. Based on the fact that the scattering from the two potentials is indistinguishable outside the core region, which dominates most of the electronic property people are interested in.

II. NUMERICAL CALCULATION

To calculate the electronic property of silicon crystalline, we identify the following input parameters:

Information about silicon crystalline

```
#Definition of the unit cell
acell 3*10.18          # This is equivalent to 10.18 10.18 10.18
rprim 0.0 0.5 0.5      # In tutorials 1 and 2, these primitive vectors
          0.5 0.0 0.5    # (to be scaled by acell) were 1 0 0 0 1 0 0 0 1
          0.5 0.5 0.0    # that is, the default.

#Definition of the atom types
ntypat 1               # There is only one type of atom
```

```

znucl 14          # The keyword "znucl" refers to the atomic number of the
                  # possible type(s) of atom. The pseudopotential(s)
                  # mentioned in the "files" file must correspond
                  # to the type(s) of atom. Here, the only type is Silicon.

#Definition of the atoms
natom 2           # There are two atoms
typat 1 1         # They both are of type 1, that is, Silicon.
xred              # This keyword indicate that the location of the atoms
                  # will follow, one triplet of number for each atom
                  # Triplet giving the REDUCED coordinate of atom 1.
0.0 0.0 0.0      # Triplet giving the REDUCED coordinate of atom 2.
1/4 1/4 1/4      # Note the use of fractions (remember the limited
                  # interpreter capabilities of ABINIT)

```

The lattice constant is given by **acell**, i.e. 10.18 Bohr. Then, the primitive vector is given by **rprim**. The number of the element species is **ntypat**. The species of the atom type is given by **znucl**, i.e. the atomic number of the element, for silicon crystalline, is 14. In a single lattice point, the number of atoms is **natom**, the type and position of which is determined by **typat** and **xred** in the unit of lattice constant.

Then, we should give the parameters related to the DFT calculation, which select calculation techniques and options.

Information about the DFT method

```

#Definition of the planewave basis set
ecut 8.0          # Maximal kinetic energy cut-off, in Hartree

#Definition of the k-point grid
kptopt 1          # Option for the automatic generation of k points, taking
                  # into account the symmetry
ngkpt 2 2 2       # This is a 2x2x2 grid based on the primitive vectors
nshftk 4          # of the reciprocal space (that form a BCC lattice !),
                  # repeated four times, with different shifts :
shftk 0.5 0.5 0.5
                0.5 0.0 0.0
                0.0 0.5 0.0
                0.0 0.0 0.5
                  # In cartesian coordinates, this grid is simple cubic, and
                  # actually corresponds to the
                  # so-called 4x4x4 Monkhorst-Pack grid

#Definition of the SCF procedure
nstep 10          # Maximal number of SCF cycles
toldfe 1.0d-6     # Will stop when, twice in a row, the difference
                  # between two consecutive evaluations of total energy
                  # differ by less than toldfe (in Hartree)
                  # This value is way too large for most realistic
                  # studies of materials
diemac 12.0       # Although this is not mandatory, it is worth to
                  # precondition the SCF cycle. The model dielectric
                  # function used as the standard preconditioner
                  # is described in the "dielng" input variable section.
                  # Here, we follow the prescription for bulk silicon.

```

ecut gives the maximal cut-off kinetic energy in the unit of Hartree. Typically, one can obtain better accuracy with larger cut-off energy with large consumption of computation resource. **kptopt** controls the set up of the k-points list. Here, we select the mode in which the program take the symmetry full into consideration to generate k points in the irreducible Brillouin Zone only. Often, the k points will form a lattice in reciprocal space. In this case, one will also aim at initializing input variables that give the reciprocal of this k-point lattice, as well as its shift with

respect to the origin: **ngkpt** or **kptrlatt**, as well as on **nshiftk** and **shiftk**. In the calculation of silicon crystalline, we specify the parameters related to k points generation by Monkhorst-Pack sampling, which is a efficient and usual sampling method used in the case of FCC lattice. Further more, **nstep** gives the maximal number of iterations in a self-consistent field (SCF) or non-SCF run. Here, 10 is adequate for the program to reach the designed accuracy. **toldfe** shows the designed accuracy of the total energy of system.

Before we conduct the formal run, we should confirm that the parameters related to the computation method is adequate for our study. First, we will test **ngkpt**, and set it as 2 2 2, 4 4 4, 6 6 6 and 8 8 8. We find that the energy difference for the latter two dataset is rather small, say 0.000004 Hartree. Here, we get the converged value at fixed **acell** and **ecut** is -8.8726 Ha. In the following calculation, we focus on the former two datasets, i.e. **ngkpt** is 2 2 2 or 4 4 4, for simplicity.

Then, we test whether the lattice constant **acell** given in the former text is precise or not. We use the following code to finish the automatic optimization of cell shape and volume.

Determination of the lattice parameters

```
optcell 1
ionmov 2
ntime 10
dilatomx 1.05
ecutsm 0.5
```

And the result is

Result of lattice parameters Determination

acell1	1.0233363682E+01	1.0233363682E+01	1.0233363682E+01	Bohr
acell2	1.0216447241E+01	1.0216447241E+01	1.0216447241E+01	Bohr

for **ngkpt** is 2 2 2 or 4 4 4. The difference of the lattice constant computed with different k points is only 0.1%. We can believe that the converged lattice constant for silicon crystalline in LDA approximation with the specific pseudopotential (14si.pspnc) is 10.216 Bohr, which corresponds to 5.406 Angstrom. We mention that the experiment value is 5.431 Angstrom at 25 degree Celsius. Therefore, we can fix **acell** as 10.216 Ha, and the grid of k-points **ngkpt** as 4 4 4 in the following calculation.

The band structure is computed by solving the KS equation for different k points along different lines of Brillouin zone. As an example, we can make a L- Γ -X-(U)- Γ circuit, with 10, 12 and 17 divisions for each line. We can use the following code to set the lines in the Brillouin zone

Information of band structure calculation

```
iscf2 -2
getden2 -1
kptopt2 -3
nband2 8
ndivk2 10 12 17 # 10, 12 and 17 divisions of the 3 segments, delimited
# by 4 points.
kptbounds2 0.5 0.0 0.0 # L point
0.0 0.0 0.0 # Gamma point
0.0 0.5 0.5 # X point
1.0 1.0 1.0 # Gamma point in another cell.
tolwfr2 1.0d-12
enunit2 1 # Will output the eigenenergies in eV
```

We set **iscf** as -2 to conduct a non-self-consistent calculation, and **getden** as -1 to print the result of electron density. **nband** gives number of bands, occupied or unoccupied, for which wave functions are being computed along with eigenvalues. Meanwhile, we set **kptopt** to -3 to define three segments in the Brillouin Zone, and **ndivk** to 10 12 17 to specify the divisions for each line. The parameter **kptbounds** gives the point which determine the line we are interested in, and **eunit** sets the unit of eigenenergies as eV. The only tolerance criterion admitted for non-self-consistent calculation is **tolwfr**, which also suppresses **toldfe**.

After the calculation, we can use AbiPy to visualize the result. The band structure of silicon crystalline is shown in Fig.1. According to the division given in **ndivk** and the points given in **kptbounds**, there are three region separated

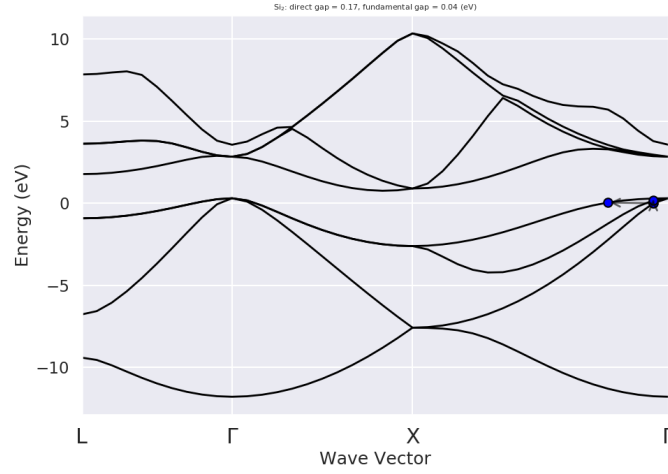


FIG. 1. Band structure of silicon crystalline

by four points. From the figure, we can see that some of the bands are degenerate in some specific region. Only in the region for X to Γ , we can see all of the eight non-degenerate bands. In the other region, there are six different bands, two of which are two-fold degenerate. Also, the Γ and X point have high symmetry, where there are only four distinct energy values for eight bands. In X point, there are four two-fold degenerate bands; while in Γ points, there are two non-degenerate bands and two three-fold degenerate bands. The position of X, L and Γ is visualized in Fig.2.

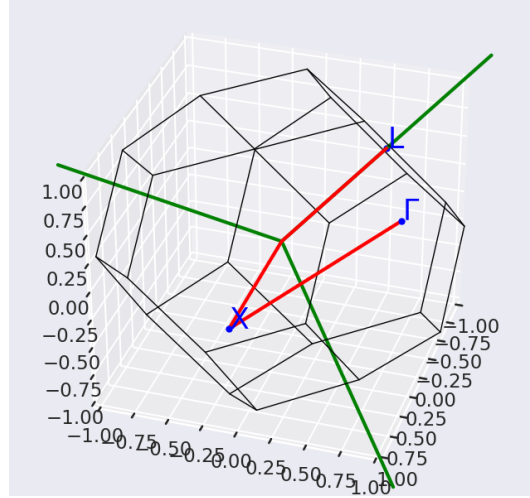


FIG. 2. The line corresponding to the band structure

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