First Principles Calculation Hands on Session (II)

Silicon
Outline

• First-principles calculation with periodic boundary condition (crystal)
  • Bravais lattice
  • Periodic boundary condition
  • Bloch theory and reciprocal space
  • Brillouin zone

• Si crystal
  • SCF calculation
  • Band structure
  • Density of states
Density Functional Theory

• Time-independent Schrödinger equation of multiple nuclei and electrons

\[ \hat{H}\Psi(\{R\}, \{r\}) = E\Psi(\{R\}, \{r\}) \]

• Kohn-Sham equations of single electron:

\[ (\hat{T} + \hat{V}_{ext} + \hat{V}_{Hartree} + \hat{V}_{xc})\psi_i(r) = \varepsilon_i\psi_i(r) \]
We can solve a small molecule but…

• $10^{23}$ atoms in 1 cm$^3$ solid material
• Impossible to calculate directly!
• Crystal: solid material arranged in a ordered structure
• Utilize this condition to simplify the problem?
Bravais Lattice

• A system a potential with translation symmetry
• $T = n_1 a_1 + n_2 a_2 + n_3 a_3$
• $n_i$ : integers
• $a_i$ : lattice vector
• Subscript $i$ for dimensions
• $V(T + r) = V(r)$
Bravais Lattice

- Classified in 7 lattice systems and 14 lattices according to symmetry
- Centered cell can be further reduced to smaller primitive cell

<table>
<thead>
<tr>
<th>Crystal Family</th>
<th>Lattice System</th>
<th>Schönflies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>$C_i$</td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$C_{2h}$</td>
<td>$\beta \neq 90^\circ$ $a \neq c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta \neq 90^\circ$ $a \neq c$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$D_{2h}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$a \neq b \neq c$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$D_{4h}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$a \neq c$</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>$D_{3d}$</td>
<td>$\alpha \neq 90^\circ$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$D_{6h}$</td>
<td>$\gamma = 120^\circ$</td>
</tr>
<tr>
<td>Cubic</td>
<td>$O_h$</td>
<td></td>
</tr>
</tbody>
</table>

Convention cell (FCC)  Primitive cell (FCC)

https://en.wikipedia.org/wiki/Bravais_lattice
Reciprocal lattice

• Fourier transform: \( V(r) = \sum_G V(G) \exp(iG \cdot r) \)
• For a periodic \( V(r) \), \( V(G) \) is nonzero only at

\[
G = n_1 b_1 + n_2 b_2 + n_3 b_3
\]

• \( b_i = 2\pi \frac{a_m \times a_n}{\Omega} \) where \( i, m, n = (1,2,3)/(2,3,1)/(3,1,2) \)
• \( \Omega \) : volume of the unit cell
Born-von Karman boundary condition

• The partial differential equation must be solved with boundary condition
  • Molecule: $\psi(r) \to 0$ when $r \to \infty$
• The wavefunction must be periodic:

$$\psi(r + N_i a_i) = \psi(r)$$

• $a_i$: length of repeat unit
• $N_i$: a (very large) integer
Reciprocal vector

• \( \psi(r + N_i a_i) = \psi(r) \), \( a_i b_i = 2\pi \), \( a_i b_{j \neq i} = 0 \)

• For a planewave
  \[
  \phi(r) = \exp(ik \cdot r - \omega t) = \phi(r + N_i a_i) \\
  \exp(iN_i a_i k) = 1
  \]

\[
  k = \sum_i \frac{m_i}{N_i} b_i
  \]

• From linear algebra view:
  • \( N_1 N_2 N_3 \) wavefunctions (one per unit cell)
  • \( N_1 N_2 N_3 \) k-points, each with one wavefunctions
    • Correspond to same physics and can be transformed each other

• As \( N_i \to \infty \), \( k \) is dense on real axis ( can be any value )
Bloch theorem

• All wavefunctions in above conditions can be written as
  \[ \psi(r) = \exp(ik \cdot r)u(r) \]
  where \( u(r) \) is a periodic function with period \( a_i \)

• Proof:
  \[
  \psi(r) = \sum_{k'} C_{k'} \exp(ik' \cdot r) = \sum_{k,G} C_{k,G} \exp(i(k + G) \cdot r)
  \]
  
  • \( k \) limited to \(-\frac{b_i}{2} < k_i < \frac{b_i}{2}\) (first Brillouin zone; see later discussion)
  
  • With \( V(r) = \sum_G V(G) \exp(iG \cdot r) \), \( C_{k,G} \) is non zero only for same \( k \)
  
  \[
  \psi(r) = \exp(ik \cdot r) \sum_{k,G} C_{k,G} \exp(iG \cdot r) = \exp(ik \cdot r)u(r)
  \]
Bloch theorem and DFT

- Single particle wavefunction $\psi(r)$
  - Only wavefunctions with same $k$ are coupled with each other!

- DFT Kohn–Sham equations:
  - For single particle wavefunction
  - Block diagonal Hamiltonian
  - Can be solved for each $k$ individually

K-point sampling

\[ \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \] wavefunctions in real space

\[ \mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3 \] \( N_1N_2N_3 \) k-points in reciprocal space

Continuous in reciprocal space

A few k-points in reciprocal space

- Only a few k-points (10^1~10^3) are necessary to get most properties of a bulk!
Brillouin zone in reciprocal space

• Only one point in \( \{ \mathbf{k} + G_0, \mathbf{k} + G_1, \cdots \} \) is necessary to represent the whole group
• Pick one from each group can form different Brillouin zones
• First Brillouin zone: The Wigner–Seitz cell around the original point


https://en.wikipedia.org/wiki/Brillouin_zone
Self consistent field (SCF)

Finish! -> Yes

ρ_{j+1} = ρ_j?

No

ρ_j

V_H, V_{xc}

ψ_i, ε_i

Atomic Density

External potential
Self consistent field (SCF) with k-points

Finish!

$\rho_{j+1} = \rho_j$?

No

Sum

$\psi_i, \epsilon_i (k_1)$

$\psi_i, \epsilon_i (k_2)$

$V_H, V_{xc}$

Atomic Density

External potential
Example: Si bulk

- FCC lattice
- 2 atoms in primitive cell
- Each Si bonded with 4 Si

- Band structures: eigenvalues at each k-points
  - Band gap (direct or indirect)
- Density of states: number of states at given energy
Practice in terminal

• Top left : Applications – System Tools – Terminal

• Type commands and press enter to run commands in terminal

• Run following commands one by one to start:
  • cp –r /home/chem263/si ./
  • cd si/input
  • xcrysden –pwi scf.in
Tasks

• Run a scf calculation to get charge density
  \texttt{pw.x < scf.in > scf.out}

• Run a nscf calculation to get eigenvalues on special k-points
  \texttt{pw.x < nscf.in > nscf.out}
  • Run \texttt{bands.x} and \texttt{plotband.x} to generate data files to plot
    \texttt{bands.x < bands.in > bands.out}
    \texttt{plotband.x < plotband.in > plotband.out}

• Run a nscf calculation for better density of states plot
  \texttt{pw.x < nscf-dos.in > nscf-dos.out}
  • Run \texttt{dos.x} to generate data files to plot
    \texttt{dos.x < dos.in > dos.out}

• Plot bandstructure and DOS
  \texttt{gnuplot –persist plot.v4.gnu}
Run SCF

- 'scf' for self-consistent-field
- Set files/folder to read and write and what to write
- 10.26 Bohr (5Å) FCC cell
- 2 atoms and 1 types of atoms (Si)
- Basis set size of wavefunction
- Species: Pseudo potentials filename
- Position of 2 atoms
- 6x6x6 K-points
Run NSCF for band structure

Non-self consistent field: compute eigenvalues and wavefunctions from fixed charge density (no update)

Including more bands to plot

A list of special k-points
5 points along each line
Run NSCF for density of states

Non-self consistent field: compute eigenvalues and wavefunctions from fixed charge density (no update)

Specific to make DOS looks better

More k-points for better looking DOS and preserve fine DOS structures (In this example only 6x6x6 for speed)
FCC band structure

- Special k-points
- Xcrysden: Menu-Tools-k-path

https://en.wikipedia.org/wiki/Brillouin_zone
Band structure and DOS

- Experimental band gap: 1.1eV, indirect

- DFT band gap problem: always underestimate gap, 40% to no gap