The Nuts and Bolts of First-Principles Simulation

6: Plane waves, unit cells, $k$-points and all that...

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CASTEP Developers’ Group
with support from the ESF $\psi_k$ Network
Overview

☐ Start here
☐ Basis set – plane waves, the discerning choice!
☐ Grids, grids everywhere...
☐ Unit cells – when is a crystal not a crystal...?
☐ K-points and symmetry
The Starting Point

- The object is to find the single particle solutions to the Kohn-Sham equation.

\[
\left( \nabla^2 + V_{\text{eff}} \right) |\psi_i\rangle = \varepsilon_i |\psi_i\rangle
\]

- The single particle orbitals (bands) can be represented in any complete basis set.
Basis Sets – Some Choices

- Linear combination of atomic orbitals (LCAO)
  - STO-xG
  - 6-31G
  - 6-311G*
  - 6-311G**
- Real space grid
- Wavelets
- Plane Waves
Plane Waves

Represent the orbital in Fourier space

$$\psi (\mathbf{r}) = \int \tilde{\psi} (\mathbf{g}) e^{i \mathbf{g} \cdot \mathbf{r}} d^3 \mathbf{g}$$

For a periodic system (Bloch’s Theorem)

$$\psi_k (\mathbf{r}) = \sum_G c_{k,G} e^{i (\mathbf{G} + \mathbf{k}) \cdot \mathbf{r}}$$

Where the $\mathbf{G}$s are reciprocal lattice vectors and $\mathbf{k}$ is a symmetry label in the 1$^{\text{st}}$ Brillouin zone.
Reciprocal Space
The Cut-off Energy

Limit the number of plane wave components to those such that

\[
\frac{(G + k)^2}{2} \leq E_{cut}
\]

This defines a length scale

\[
\lambda = \frac{\pi}{\sqrt{E_{cut}}}
\]
How to Choose a Cut-off Energy

- The minimum length scale depends on the elements in the system
- Variational principle $\Rightarrow$ energy monotonically decreases to ground state energy as $E_{cut}$ increases
- Converge required property with respect to cut-off energy
Convergence with $E_{cut}$ (Si8)
The Reciprocal Space Sphere
The FFT Grid

grid_scale

* $2k_{\text{cut}}$

$\approx 4k_{\text{cut}}$

$2k_{\text{cut}}$
The Charge Density Grid
Periodic Systems
SiC beta 8-atom unit cell
SiC beta Crystal
Defects – H defect in Si Bond Centre Site (64 Si cell)

001 direction

111 direction
Defects – H defect in Si
Tetrahedral Site (64 Si cell)

001 direction

111 direction
Surfaces – SiC (110)
SiC (110) Surface Slabs
Reducing interactions –
H termination
Molecules (Aflatoxin B1)
Aflatoxin B1 "Crystal"
Convergence with Supercell Size (NH$_3$)
Now, Where Were We...?

\[ \psi_k (r) = \sum_{G} c_{k,G} e^{i(G+k).r} \]

For all \( \frac{(G + k)^2}{2} \leq E_{cut} \)

And \( k \) within the first Brillouin zone.
Integrating over the 1\textsuperscript{st} Brillouin Zone

Observables are calculated as an integral over all $k$-points within the 1\textsuperscript{st} Brillouin zone. For example:

\[
E_{tot} = \frac{1}{V_{BZ \ 1stBZ}} \int E(k) d^3k
\]

\[
n(r) = \frac{1}{V_{BZ \ 1stBZ}} \int n_k(r) d^3k
\]
Example Integration

\[ \frac{-\pi}{L} \quad \frac{0}{L} \quad \frac{\pi}{L} \]
K-points and Metals

\[ \frac{-\pi}{L} \quad 0 \quad \frac{\pi}{L} \]
Defining the k-point Grid

- Standard method is the Monkhorst-Pack grid. A regular grid in k-space.


- The symmetry of the cell may be used to reduce the number of k-points which are needed.

## Monkhorst-Pack Grids for SC Cell

<table>
<thead>
<tr>
<th>q</th>
<th>Number of Points (full grid)</th>
<th>Number of Points (Symmetrised)</th>
<th>$R^2$</th>
<th>Offset</th>
<th>Number of Points (Symmetrised Offset)</th>
<th>$R^2$ (Offset)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1.0</td>
<td>1/4,1/4,1/4</td>
<td>1</td>
<td>4.0</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>1</td>
<td>4.0</td>
<td>1/8,1/8,1/8</td>
<td>3</td>
<td>16.0</td>
</tr>
<tr>
<td>3</td>
<td>27</td>
<td>4</td>
<td>9.0</td>
<td>1/4,0,1/2</td>
<td>8</td>
<td>18.0</td>
</tr>
<tr>
<td>4</td>
<td>64</td>
<td>4</td>
<td>16.0</td>
<td>1/16,1/16,1/16</td>
<td>20</td>
<td>64.0</td>
</tr>
</tbody>
</table>
# Monkhorst-Pack Grids for BCC Cell

<table>
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<tr>
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<th>Number of Points (full grid)</th>
<th>Number of Points (Symmetrised)</th>
<th>$R^2$</th>
<th>Offset</th>
<th>Number of Points (Symmetrised Offset)</th>
<th>$R^2$ (Offset)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>1</td>
<td>0.75</td>
<td>0,1/4,1/2</td>
<td>1</td>
<td>2.0</td>
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<tr>
<td>2</td>
<td>8</td>
<td>2</td>
<td>3.0</td>
<td>1/4,1/4,1/4</td>
<td>2</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>27</td>
<td>4</td>
<td>6.75</td>
<td>1/2,1/2,1/2</td>
<td>5</td>
<td>9.0</td>
</tr>
<tr>
<td>4</td>
<td>64</td>
<td>6</td>
<td>12.0</td>
<td>1/8,1/8,1/8</td>
<td>8</td>
<td>16.0</td>
</tr>
</tbody>
</table>

Nuts and Bolts 2001 Lecture 6: Plane waves etc.
# Monkhorst-Pack Grids for FCC Cell

<table>
<thead>
<tr>
<th>q</th>
<th>Number of Points (full grid)</th>
<th>Number of Points (Symmetrised)</th>
<th>$R^2$</th>
<th>Offset</th>
<th>Number of Points (Symmetrised Offset)</th>
<th>$R^2$ (Offset)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>0,1/2,1/2</td>
<td>1</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>2</td>
<td>4.0</td>
<td>0,0,0</td>
<td>2</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>27</td>
<td>4</td>
<td>4.5</td>
<td>1/2,1/2,1/2</td>
<td>6</td>
<td>9.0</td>
</tr>
<tr>
<td>4</td>
<td>64</td>
<td>10</td>
<td>16.0</td>
<td>0,0,0</td>
<td>10</td>
<td>16.0</td>
</tr>
</tbody>
</table>
Why Plane Waves?

- Systematic convergence with respect to single parameter $E_{cut}$
- Non-local. Cover all space equally
  - Cheap forces (No Pulay term)
  - No basis-set superposition error
- Numerically efficient
  - Use FFTs to transform between real and reciprocal space
  - Calculation scales as $N_{pw} \ln N_{pw}$
- The obvious choice for periodic and works well for aperiodic systems
Disadvantages of Plane Waves

☐ Need lots of basis functions/atom
  • ‘Waste’ basis functions in vacuum regions
  • **But**, rapidly becomes more efficient than localised basis set due to better scaling

☐ Need pseudopotentials for tractability
  • To represent core features would require **huge** cut-off energy
  • **But**, Core features can be reconstructed

☐ Does not encode ‘local’ properties
  • **But**, can overcome this using projection analysis
Summary

- **Bands** – single particle solutions to Kohn-Sham equation
- **Plane wave basis set** – bands represented on reciprocal space grid within cut-off
- **Supercells** – approximating aperiodic system with a periodic one
- **K-points** – integration grid in 1st Brillouin zone