1.021, 3.021, 10.333, 22.00 : Introduction to Modeling and Simulation : Spring 2011

Part II – Quantum Mechanical Methods : Lecture 4

From atoms to solids

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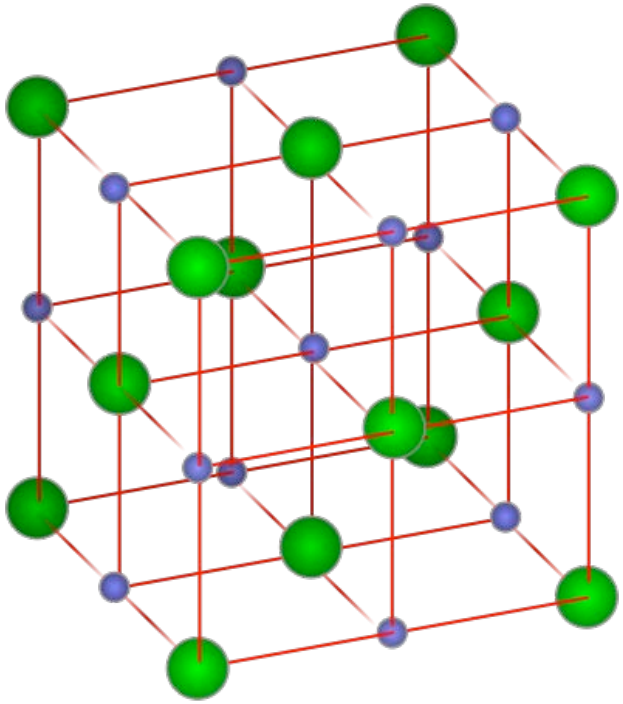
Part II Outline

theory & practice

example applications

1. It's A Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. From Many-Body to Single-Particle; Quantum Modeling of Molecules
4. From Atoms to Solids
5. Quantum Modeling of Solids: Basic Properties
6. Advanced Prop. of Materials: What else can we do?
7. Nanotechnology
8. Solar Photovoltaics: Converting Photons into Electrons
9. Thermoelectrics: Converting Heat into Electricity
10. Solar Fuels: Pushing Electrons up a Hill
11. Hydrogen Storage: the Strength of Weak Interactions
12. Review

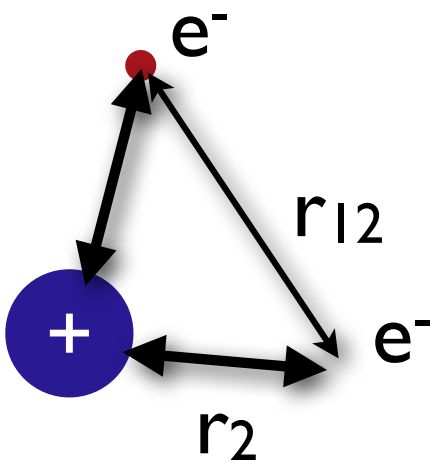
Motivation



Lesson outline

- Review
- Periodic potentials
- Bloch's theorem
- Energy bands

Review: Next? Helium



$$H\psi = E\psi$$

$$\Big[H_1 + H_2 + W\Big]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

$$\Big[T_1 + V_1 + T_2 + V_2 + W\Big]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

$$\Big[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}\Big]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

cannot be solved analytically

problem!

Review: The Multi-Electron Hamiltonian

$$H\psi = E\psi$$

Remember the good old days of the 1-electron H-atom??

They're over!

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right]\psi(\vec{r}) = E\psi(\vec{r})$$

$$H = -\sum_{i=1}^{N}\frac{\hbar^2}{2M_i}\nabla^2_{\mathbf{R}_i} + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ i\neq j}}^{N}\frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} - \frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla^2_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{i=1}^{n}\sum_{\substack{j=1\\ i\neq j}}^{n}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

kinetic energy of ions

potential energy of ions

kinetic energy of electrons

electron-ion interaction

electron-electron interaction

Multi-Atom-Multi-Electron Schrödinger Equation

$$H(\mathbf{R}_1,\ldots,\mathbf{R}_N;\mathbf{r}_1,\ldots,\mathbf{r}_n)\,\Psi(\mathbf{R}_1,\ldots,\mathbf{R}_N;\mathbf{r}_1,\ldots,\mathbf{r}_n) = E\,\Psi(\mathbf{R}_1,\ldots,\mathbf{R}_N;\mathbf{r}_1,\ldots,\mathbf{r}_n)$$

Born-Oppenheimer Approximation

Electrons and nuclei
as "separate" systems

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla_{\mathbf{r}_i}^2 - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_i e^2}{\left|\mathbf{R}_i - \mathbf{r}_j\right|} + \frac{1}{2}\sum_{i=1}^{n}\sum_{\substack{j=1 \\ i\neq j}}^{n}\frac{e^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

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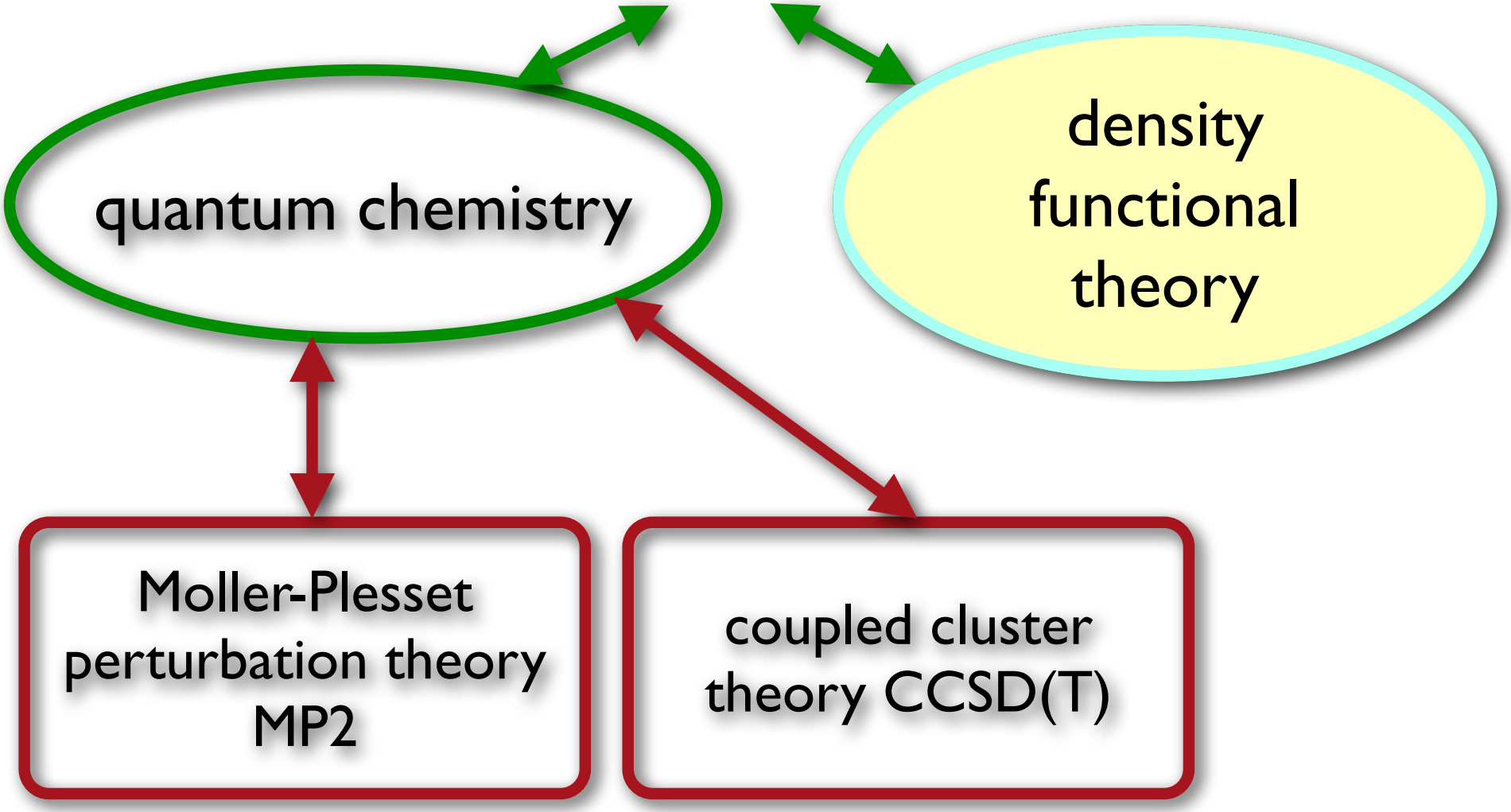
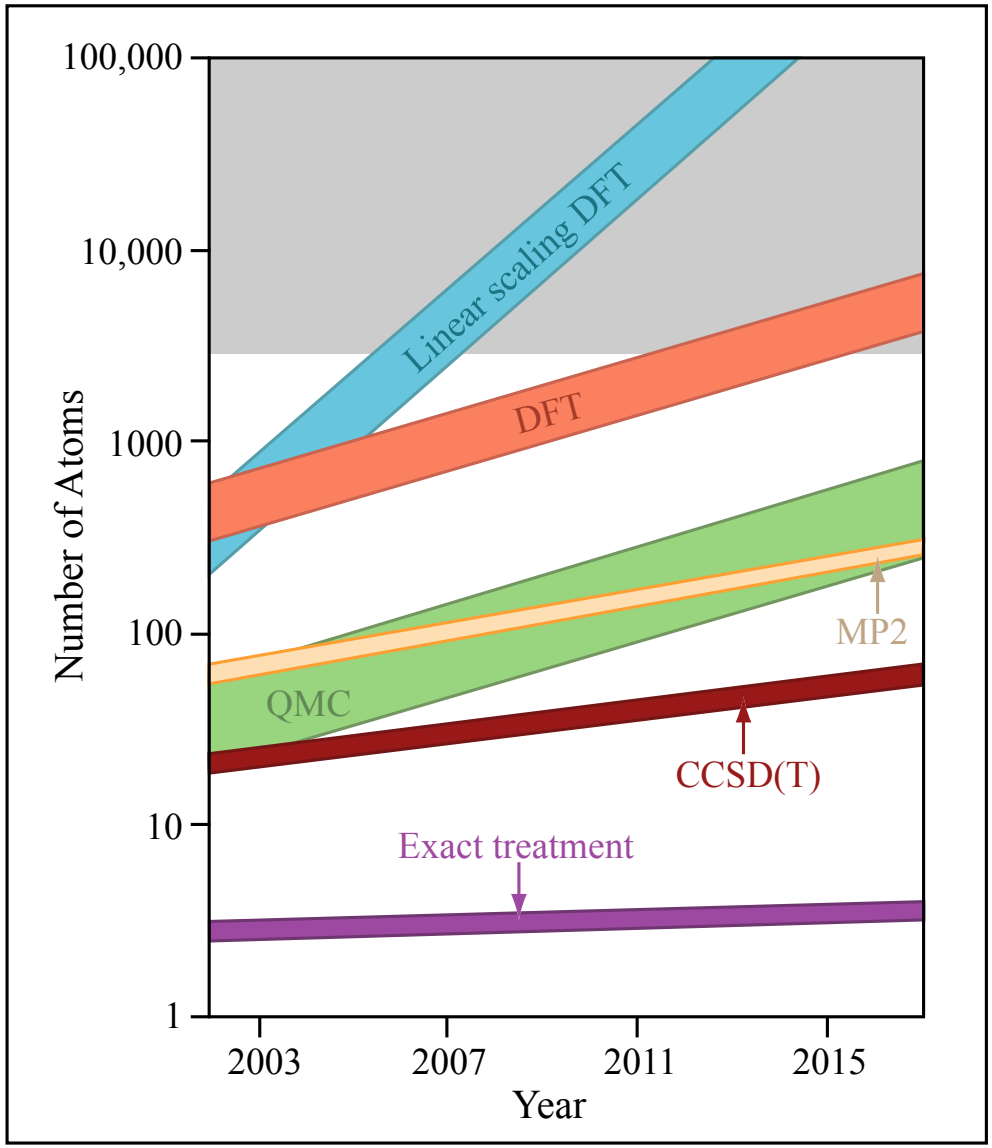
... but this is an
approximation!

- electrical resistivity
- superconductivity
- ....

Review: Solutions



Review: Why DFT?



Review: DFT

$$\psi = \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

wave function: complicated!

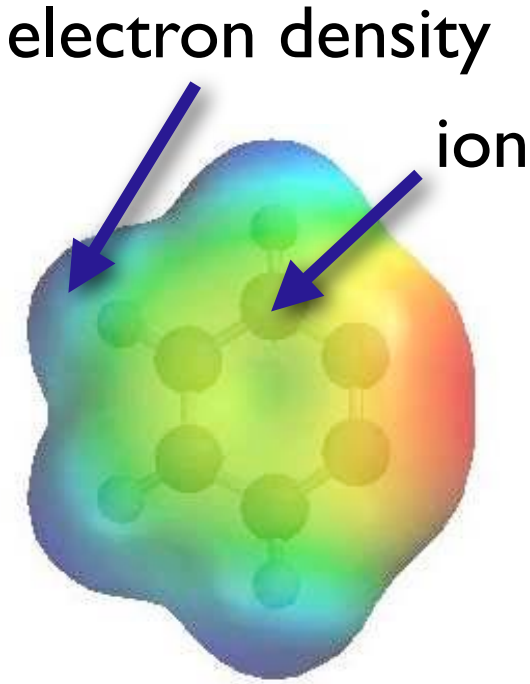
$$n = n(\vec{r})$$

electron density: easy!

Walter Kohn
DFT, 1964

All aspects of the electronic structure of a system of interacting electrons, in the ground state, in an "external" potential, are determined by $n(\mathbf{r})$

Review: DFT



The ground-state energy is a functional of the electron density.

$$E[n] = T[n] + V_{ii} + V_{ie}[n] + V_{ee}[n]$$

kinetic — ion-ion — ion-electron — electron-electron

The functional is minimal at the exact ground-state electron density $n(\mathbf{r})$

The functional exists... but it is unknown!

Review: DFT

$$E[n] = \underbrace{T[n]}_{\text{kinetic}} + \underbrace{V_{ii}}_{\text{ion-ion}} + \underbrace{V_{ie}[n]}_{\text{ion-electron}} + \underbrace{V_{ee}[n]}_{\text{electron-electron}}$$

electron density $n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$

$$E_{\text{ground state}} = \min_{\phi} E[n]$$

Find the wave functions that minimize the energy using a functional derivative.

Review: DFT

Finding the minimum leads to
Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}),$$

$$V_s = V + \int \frac{e^2 n_s(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\mathrm{d}^3r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

ion potential — Hartree potential — exchange-correlation potential

equations for non-interacting electrons

Review: DFT

$$V_s = V + \int \frac{e^2 n_s(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \mathrm{d}^3 r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

Only one problem: v_{xc} not known!

approximations necessary

local density approximation LDA

general gradient approximation GGA

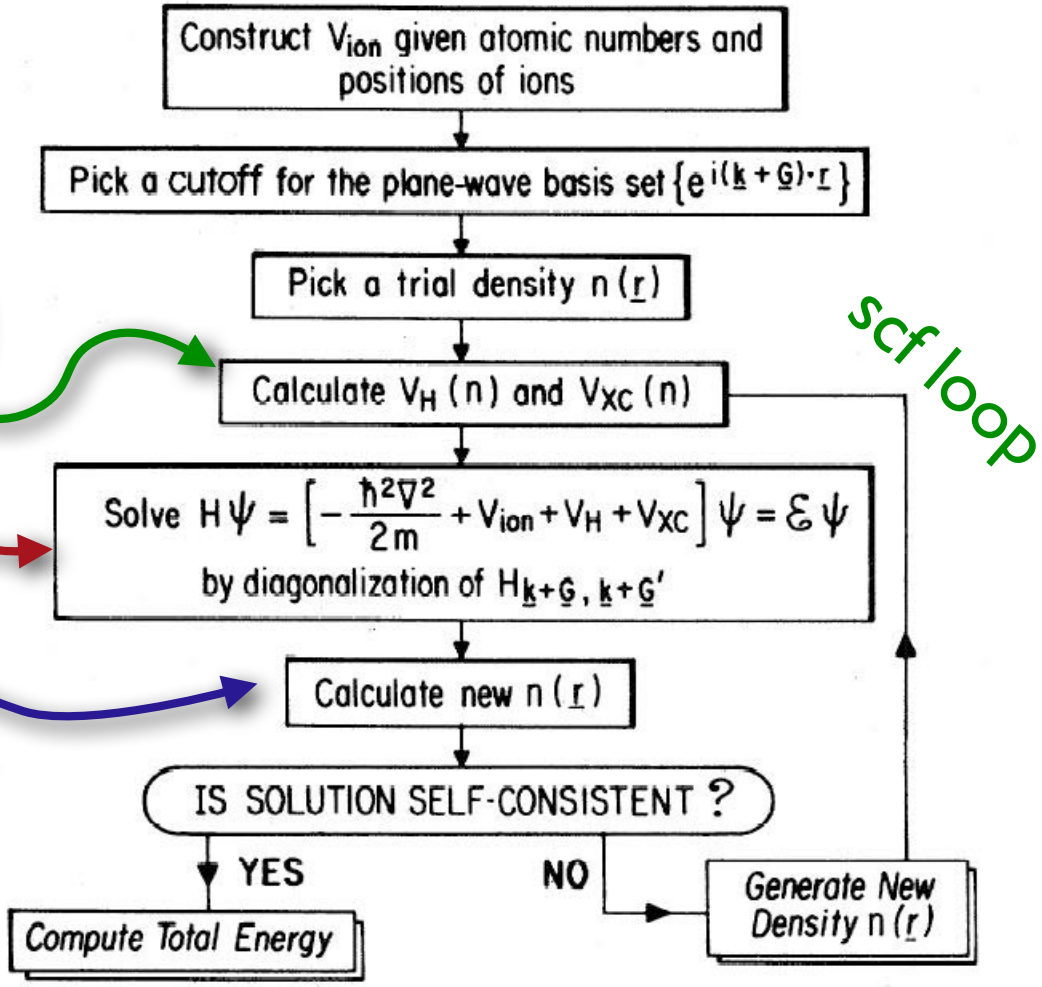
Review: Self-consistent cycle

Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}),$$

$$V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}^3r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$



Review: DFT calculations

scf loop

```
total energy =  -84.80957141 Ry
total energy =  -84.80938034 Ry
total energy =  -84.81157880 Ry
total energy =  -84.81278531 Ry
total energy =  -84.81312816 Ry
total energy =  -84.81322862 Ry
total energy =  -84.81323129 Ry
```

exiting loop;
result precise enough

At the end we get:

1) electronic charge density
2) total energy

Review: DFT calculations

scf loop

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total energy =   -84.80957141 Ry
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```

exiting loop;
result precise enough

At the end we get:

1) electronic charge density
2) total energy

Structure

Elastic constants

Vibrational properties

...

Review: Basis functions

Matrix eigenvalue equation:

$$\psi = \sum_i c_i \phi_i$$

expansion in orthonormalized basis functions

$$H\psi = E\psi$$

$$H \sum_i c_i \phi_i = E \sum_i c_i \phi_i$$

$$\int d\vec{r}\, \phi_j^* H \sum_i c_i \phi_i = E \int d\vec{r}\, \phi_j^* \sum_i c_i \phi_i$$

$$\sum_i H_{ji} c_i = E c_j$$

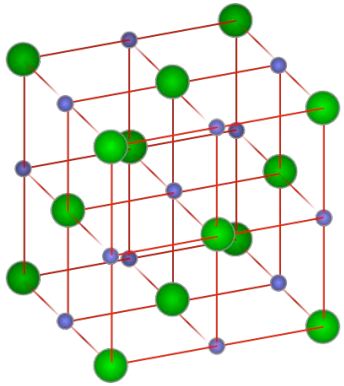
$$\mathcal{H}\vec{c} = E\vec{c}$$

Review: Plane waves as basis functions

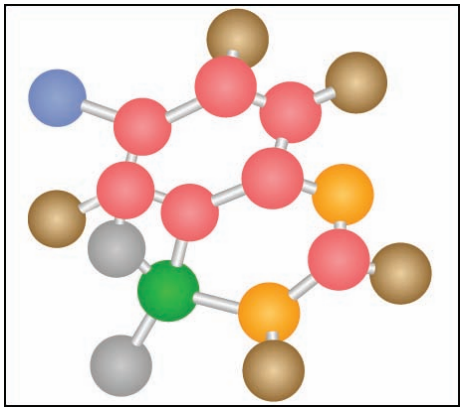
plane wave expansion: $\psi(\vec{r}) = \sum_j c_j e^{i\vec{G}_j \cdot \vec{r}}$

plane wave

Cutoff for a maximum G is necessary and results in a finite basis set.



Plane waves are periodic,
thus the wave function is periodic!



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periodic crystals:
Perfect!!! (next lecture)

atoms, molecules:
be careful!!!

From atoms to solids

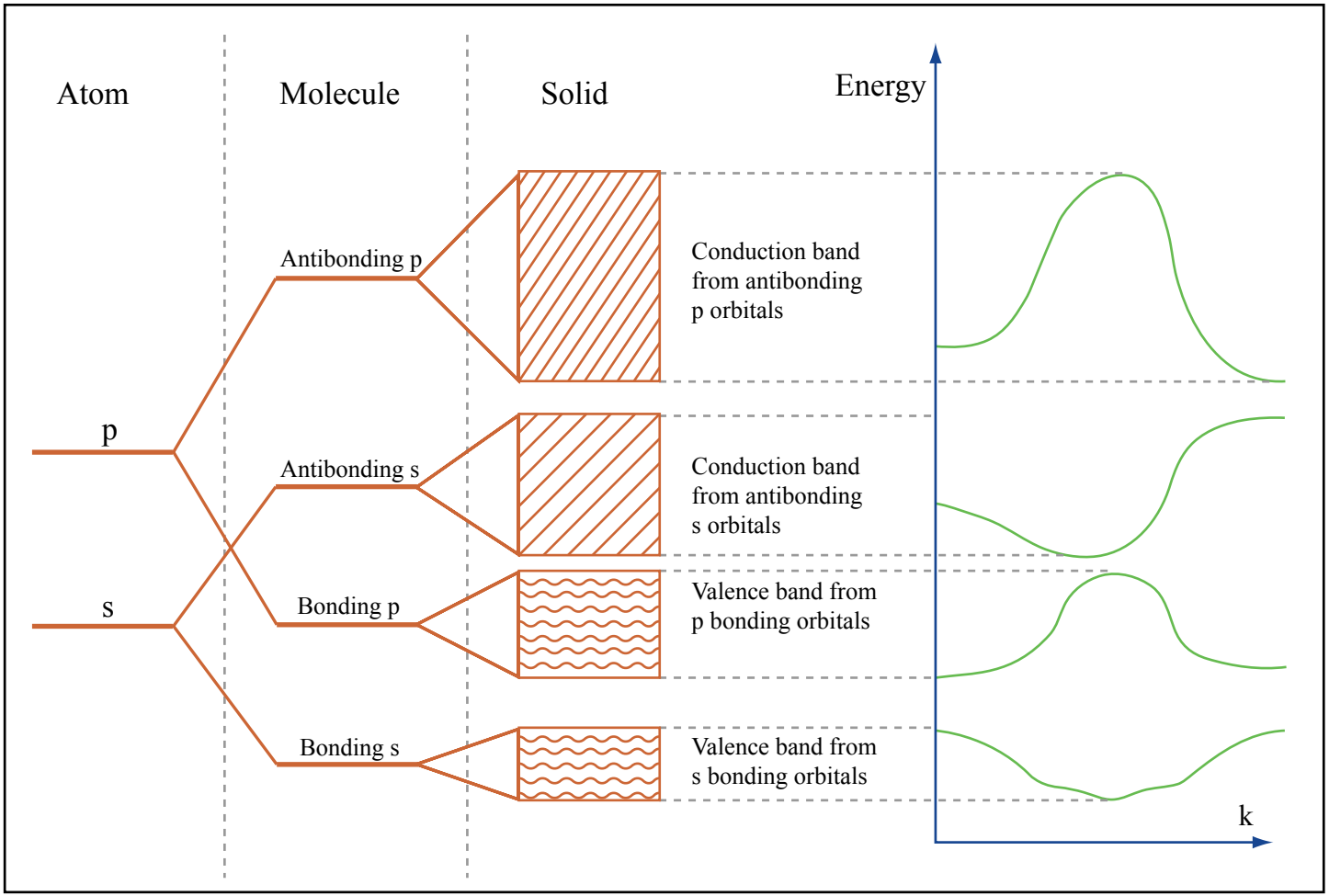
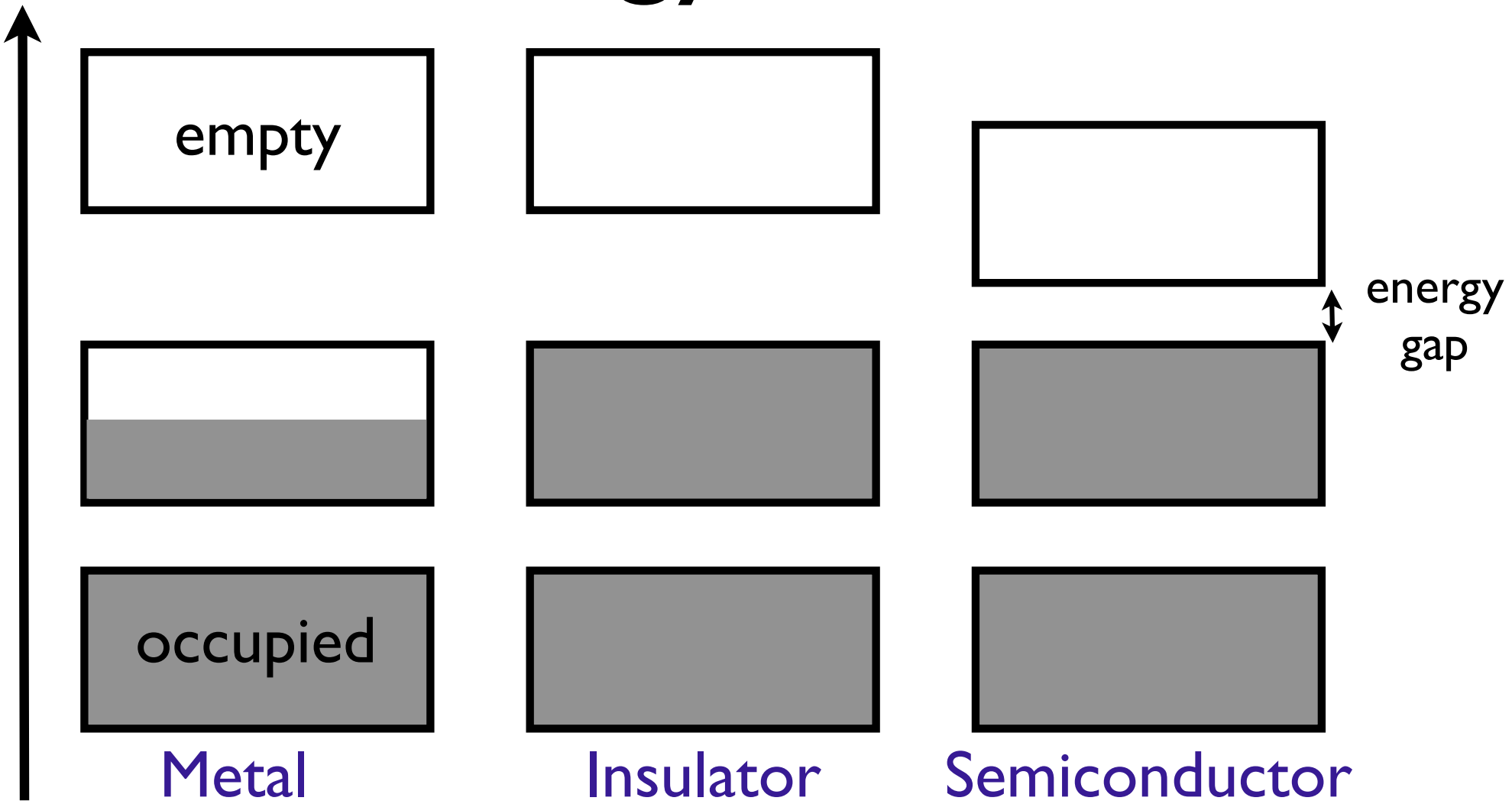


Image by MIT OpenCourseWare.

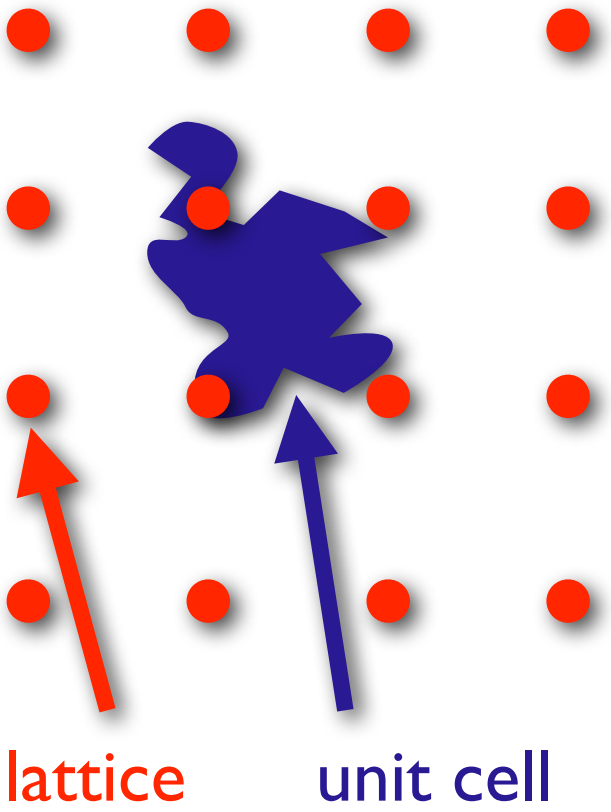
The ground state electron configuration of a system is constructed by putting the available electrons, two at a time (Pauli principle), into the states of lowest energy

Energy bands



NB: boxes = allowed energy regions

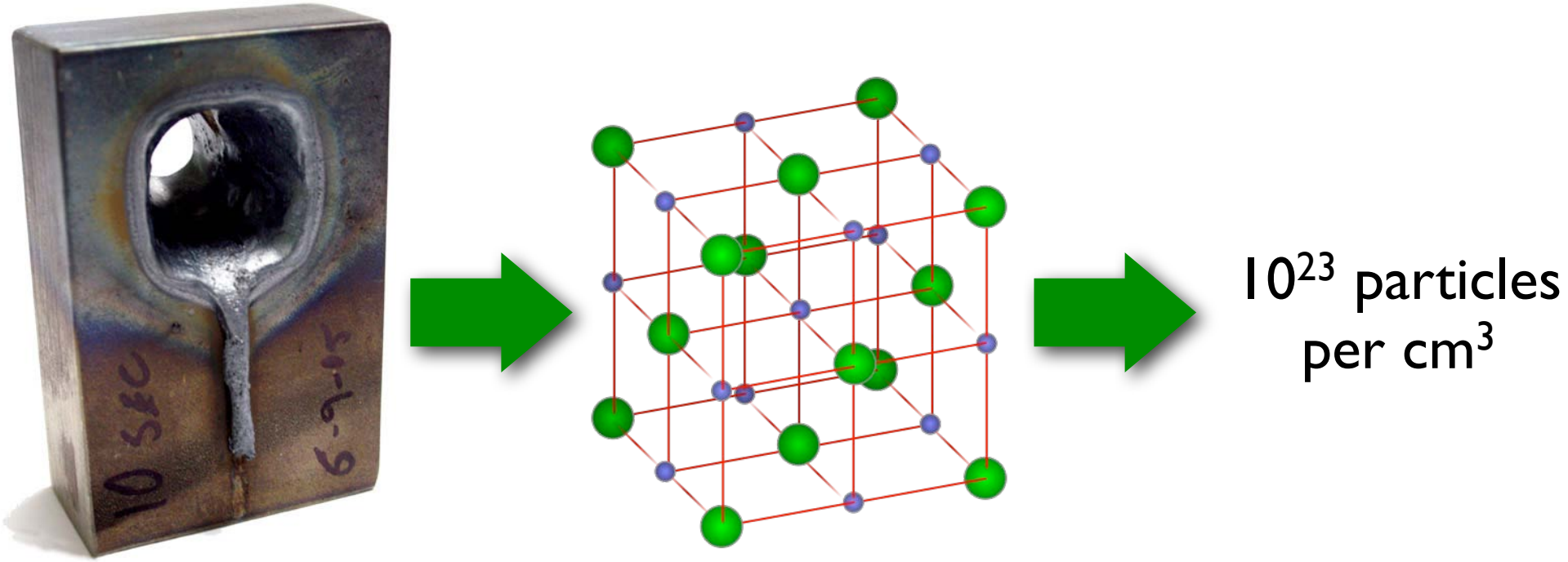
Crystal symmetries



A crystal is built up
of a unit cell and
periodic replicas thereof.

Image of M. C. Escher's "Mobius with Birds" removed due to copyright restrictions.

Crystal symmetries

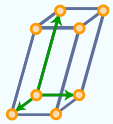
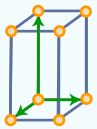
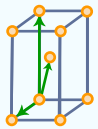
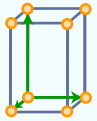
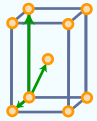
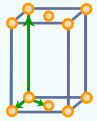
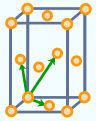
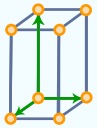
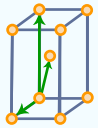
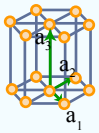


Since a crystal is periodic, maybe we can get away with modeling only the unit cell?

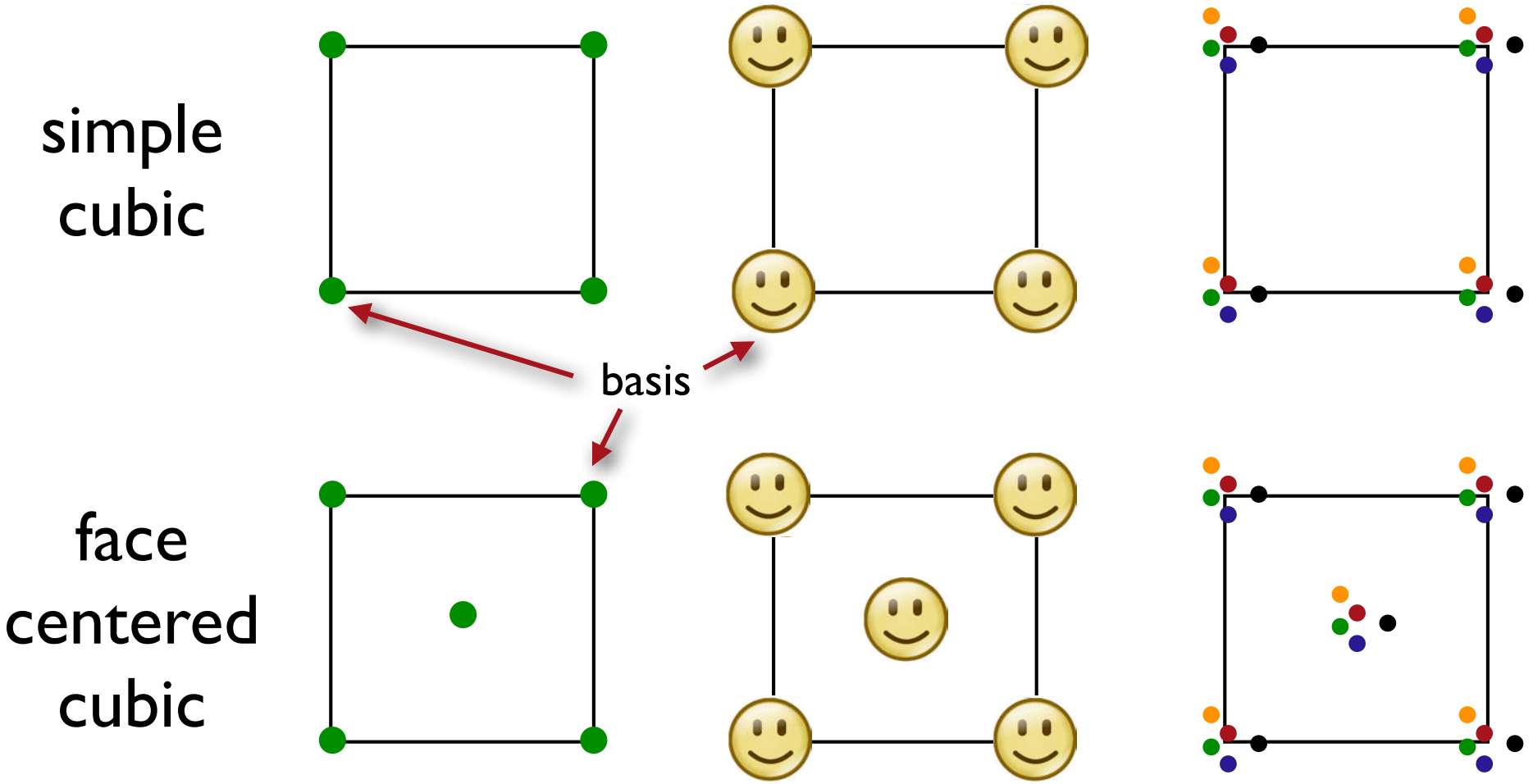
Crystal symmetries

4 Lattice Types

7 Crystal Classes

Bravais Lattice	Parameters	Simple (P)	Volume Centered (I)	Base Centered (C)	Face Centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^0$ $\alpha_{12} \neq 90^0$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^0$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^0$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^0$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^0$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^0$ $\alpha_{23} = \alpha_{31} = 90^0$				

Lattice and basis



The inverse lattice

The real space lattice is described by three basis vectors:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

The inverse lattice is described by three basis vectors:

$$\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$$

$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)} \qquad \mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}$$

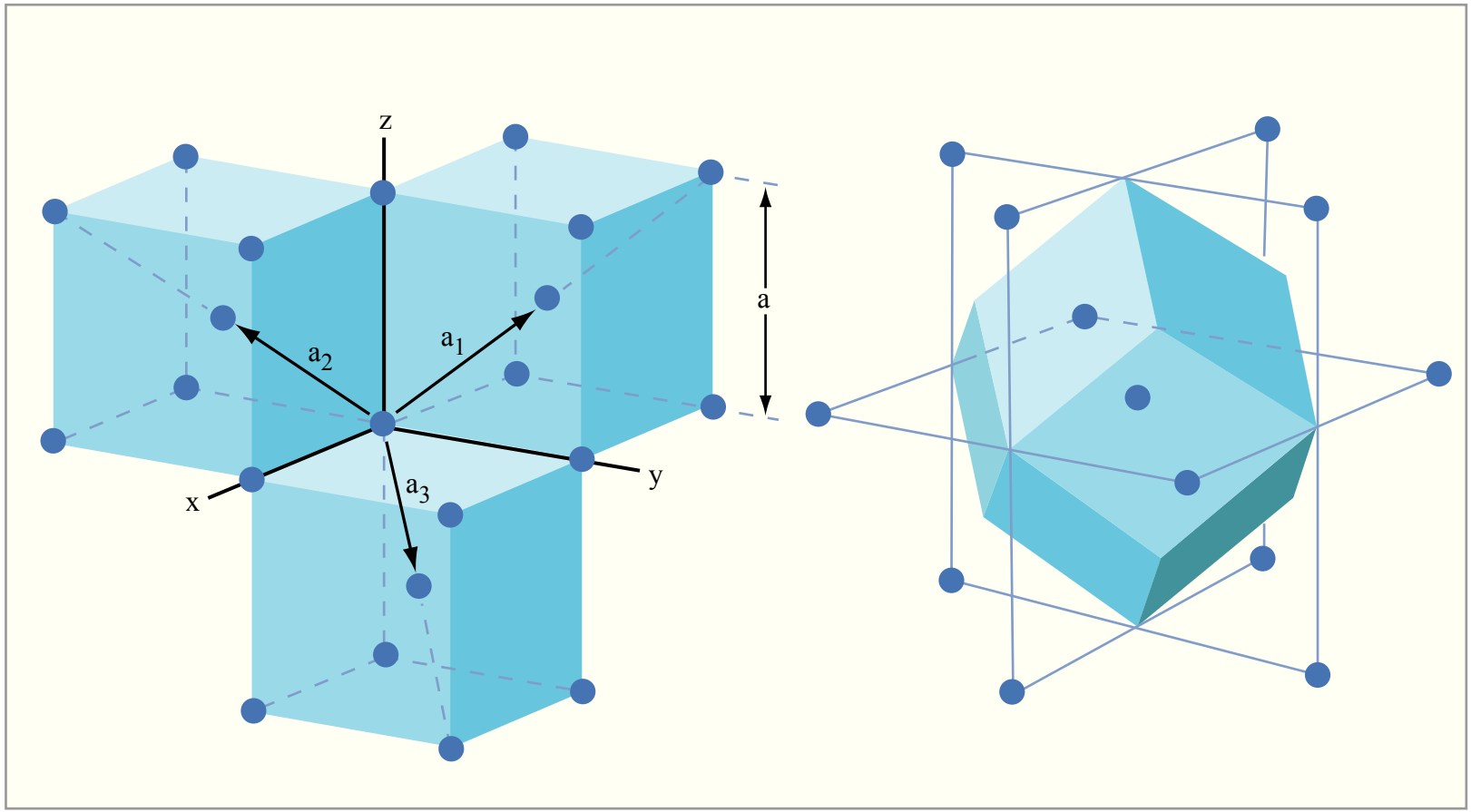
$$e^{i\vec{G}\cdot\vec{R}} = 1 \quad \longrightarrow \quad \psi(\vec{r}) = \sum_j c_j e^{i\vec{G}_j\cdot\vec{r}}$$

automatically periodic in R!

The inverse lattice

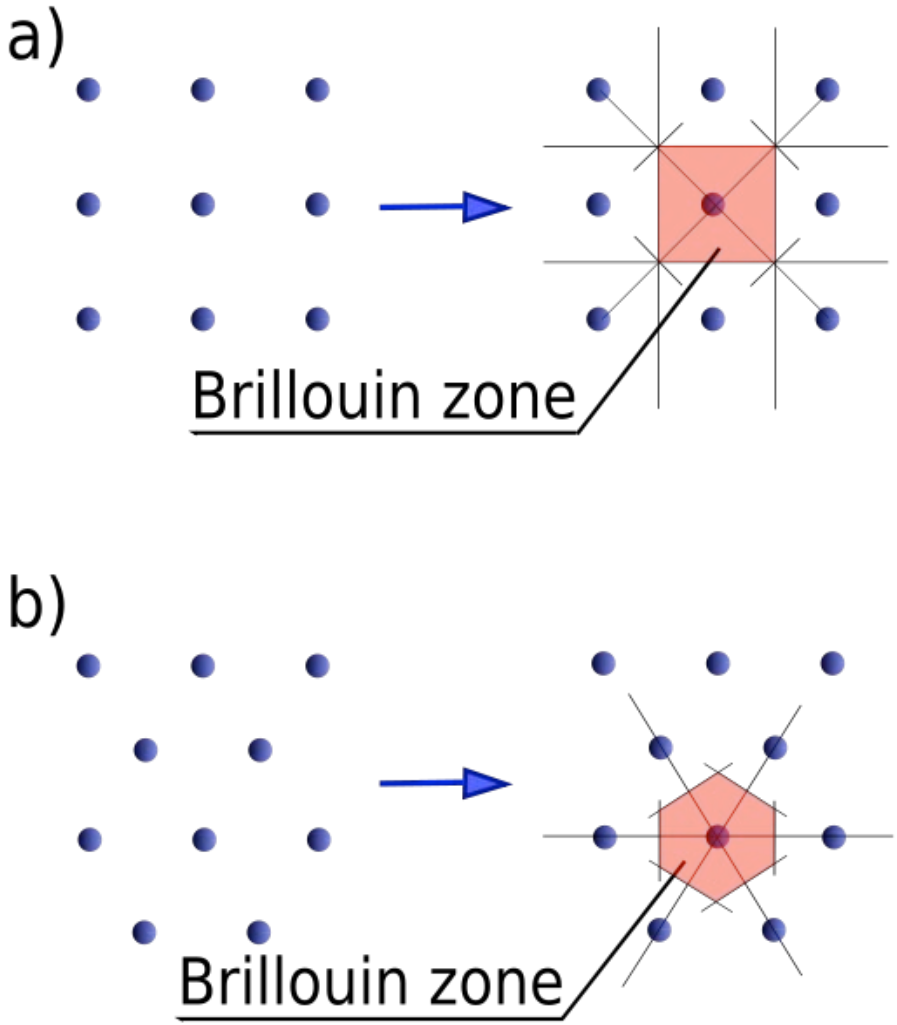
real space lattice (BCC)

inverse lattice (FCC)



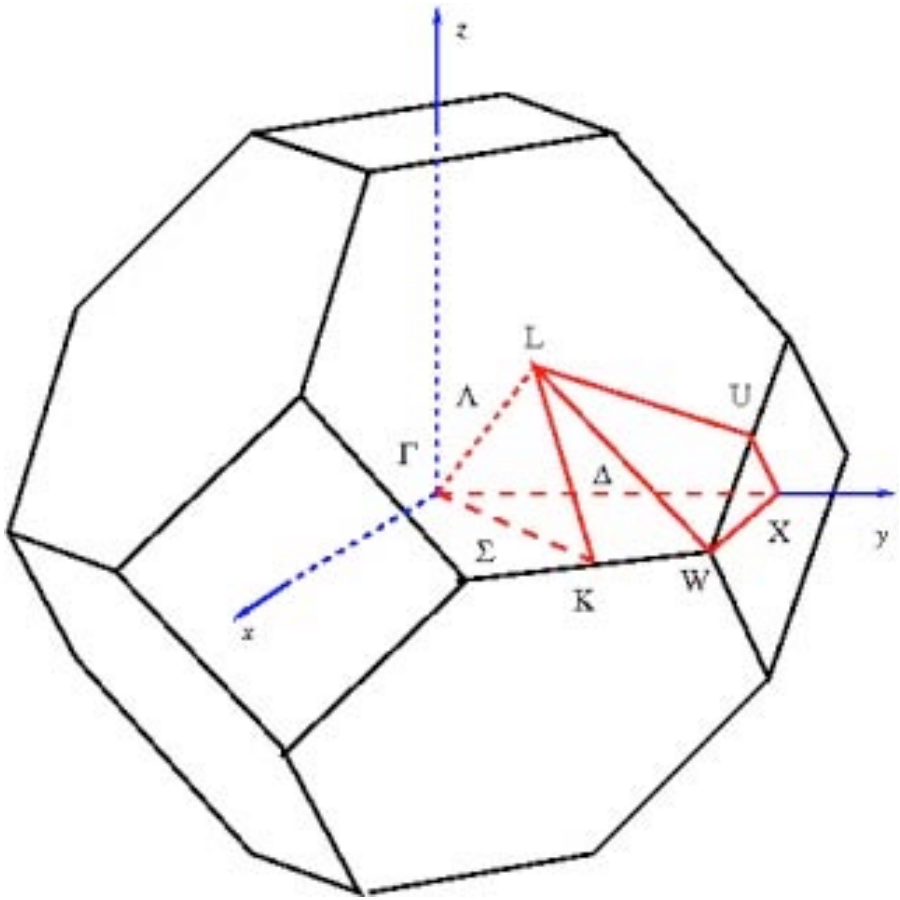
The Brillouin zone

inverse lattice



The Brillouin zone is a special unit cell of the inverse lattice.

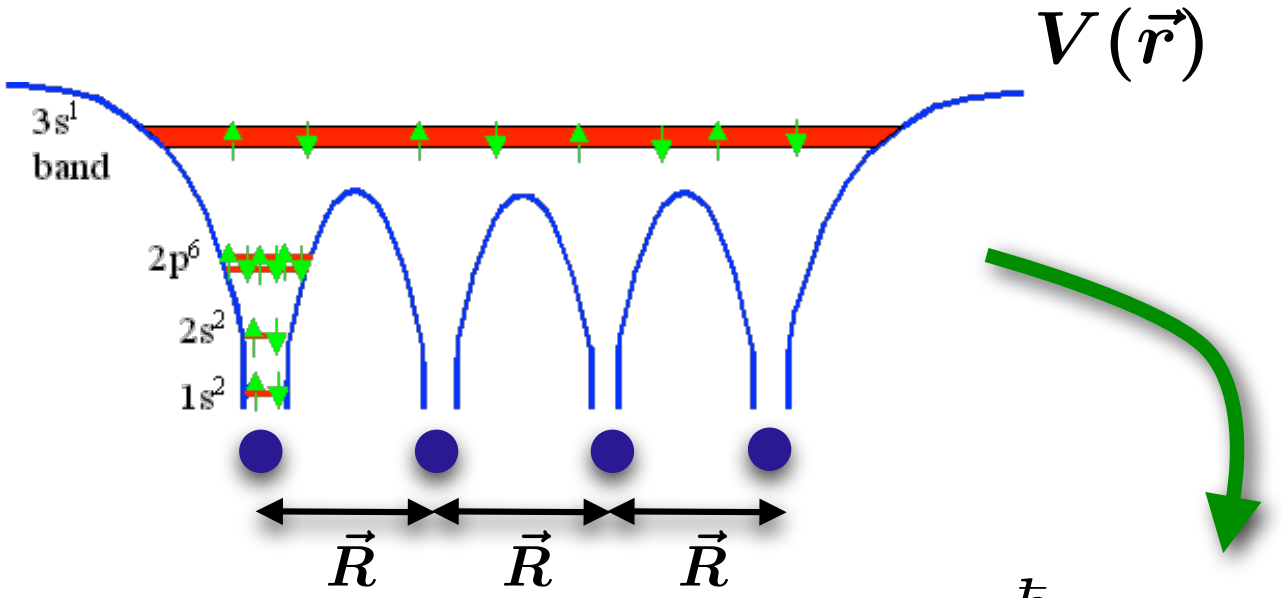
The Brillouin zone



Brillouin zone of the FCC lattice

Periodic potentials

metallic sodium



$$\left[-\frac{\hbar}{2m}\nabla^2 + V(\vec{r}) \right] \psi = E\psi$$

Periodic potentials

It becomes much easier if you use the periodicity of the potential!

attice vector

$$V(\vec{r}) = V(\vec{r} + \vec{R})$$

NEW quantum number k that lives in the inverse lattice!

Bloch's theorem $\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$$

Periodic potentials

Bloch's theorem

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$$

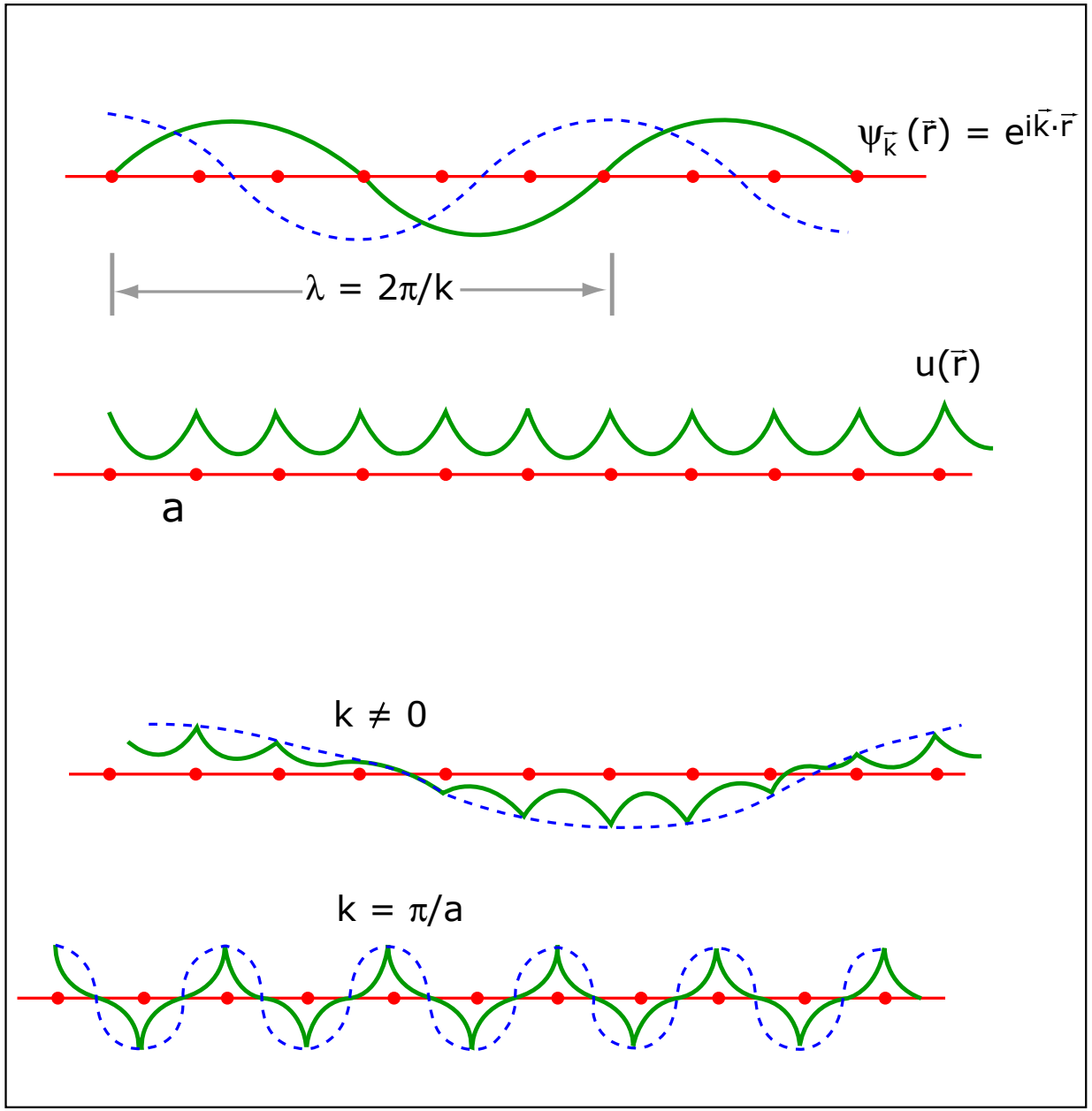


Image by MIT OpenCourseWare.

Periodic potentials

Results of the Bloch theorem:

$$\psi_{\vec{k}}(\vec{r}+\vec{R}) = \psi_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$$

$$|\psi_{\vec{k}}(\vec{r}+\vec{R})|^2 = |\psi_{\vec{k}}(\vec{r})|^2$$

charge density is lattice periodic

if solution $\psi_{\vec{k}}(\vec{r}) \longrightarrow \psi_{\vec{k}+\vec{G}}(\vec{r})$ also solution

with $E_{\vec{k}} = E_{\vec{k}+\vec{G}}$

Periodic potentials

Schrödinger equation	certain symmetry	quantum number
hydrogen atom	spherical symmetry $[H, L^2] = HL^2 - L^2H = 0$ $[H, L_z] = 0$	$\psi_{n,l,m}(\vec{r})$
periodic solid	translational symmetry $[H, T] = 0$	$\psi_{n,\vec{k}}(\vec{r})$

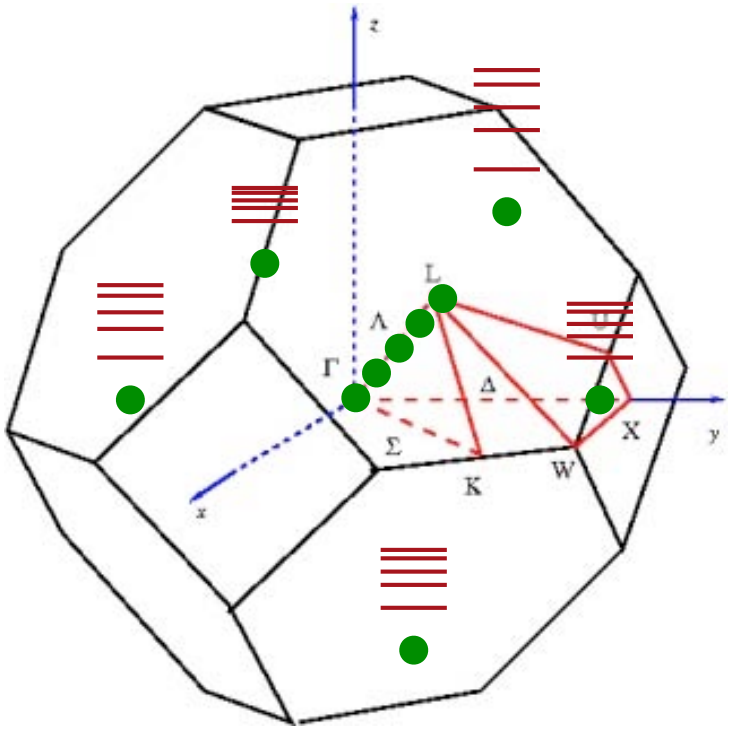
The band structure

Different wave functions can satisfy the Bloch theorem for the same ***k***: eigenfunctions and eigenvalues labelled with ***k*** and the index n

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}}\psi_{\vec{k}}(\vec{r}) \longrightarrow \begin{matrix}\psi_{n,\vec{k}}(\vec{r}) \\ \epsilon_{n,\vec{k}}\end{matrix}$$

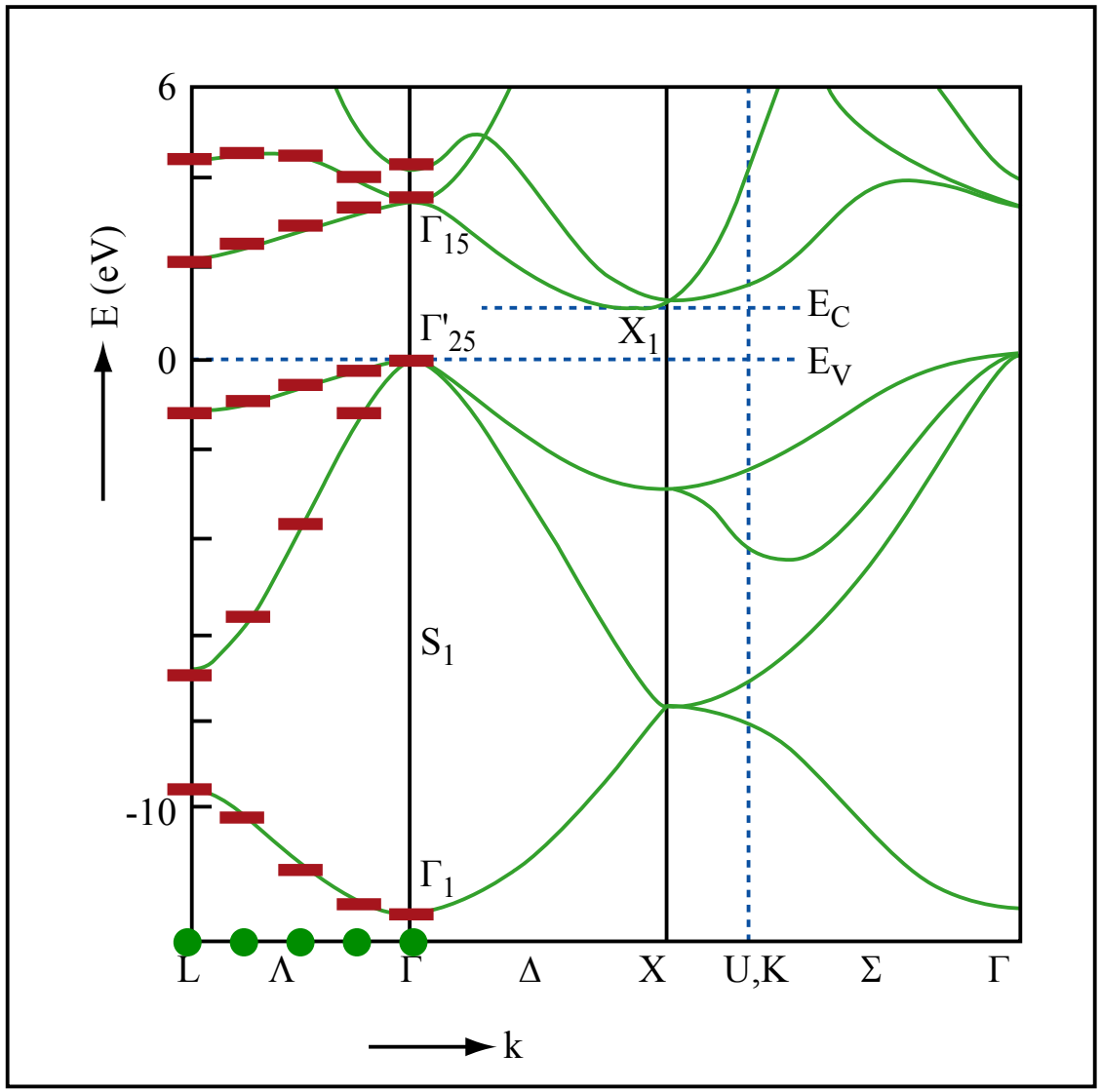
energy bands

The band structure

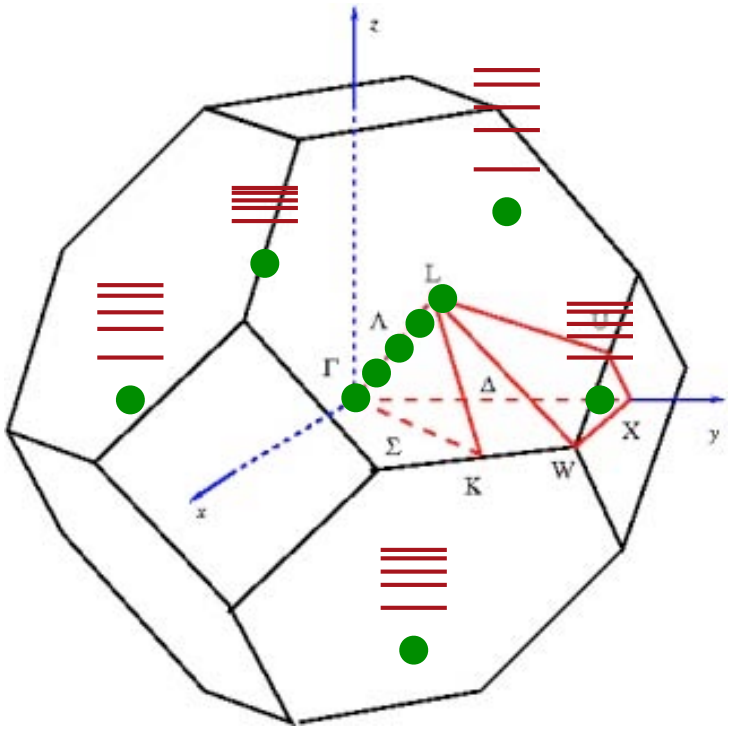


energy levels
in the Brillouin zone

Silicon

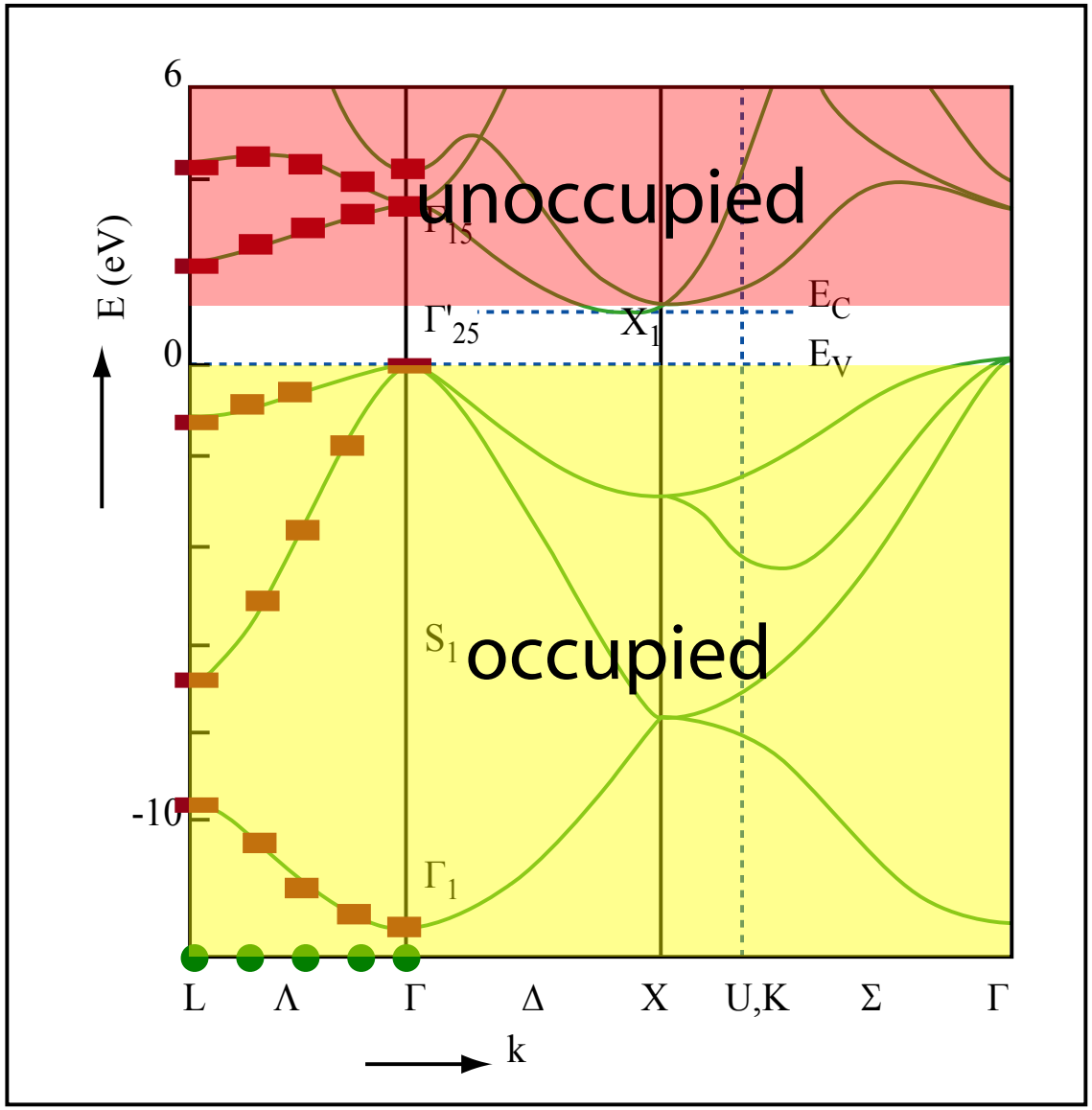


The band structure



energy levels
in the Brillouin zone

Silicon



Energy bands

simple example: infinitesimal small potential
solutions: plane waves with quadratic energies

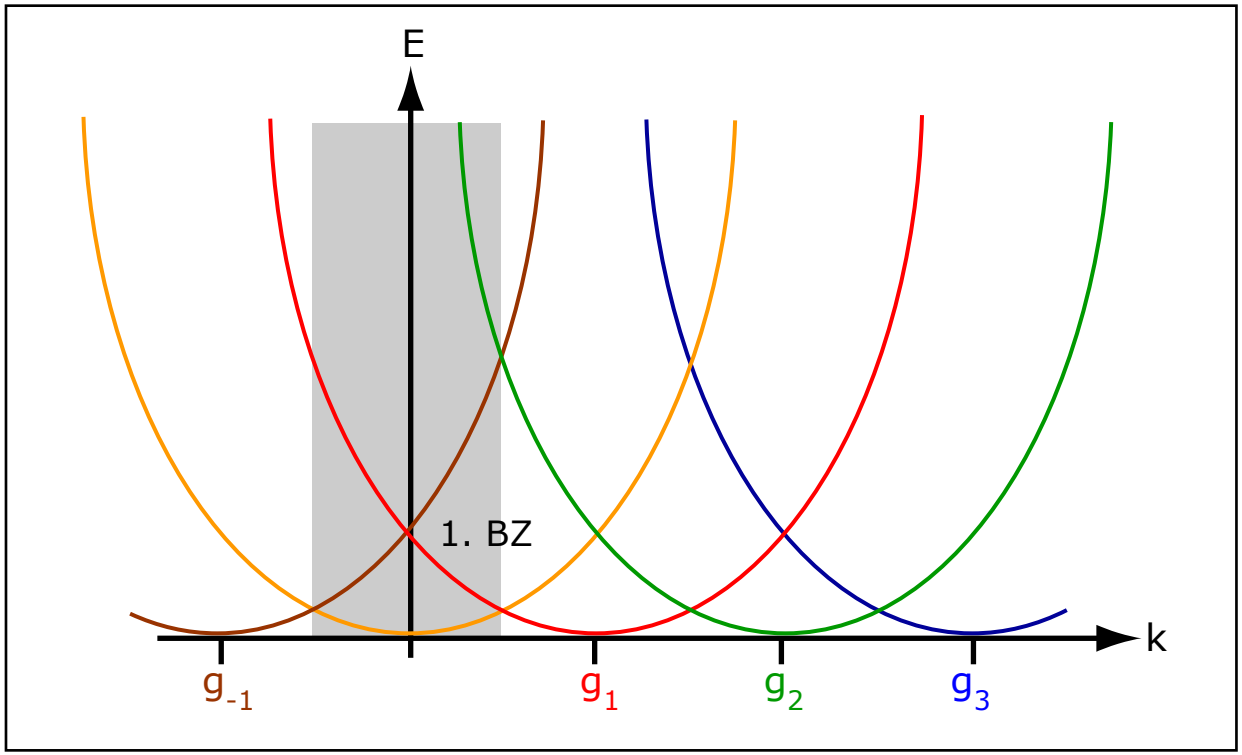
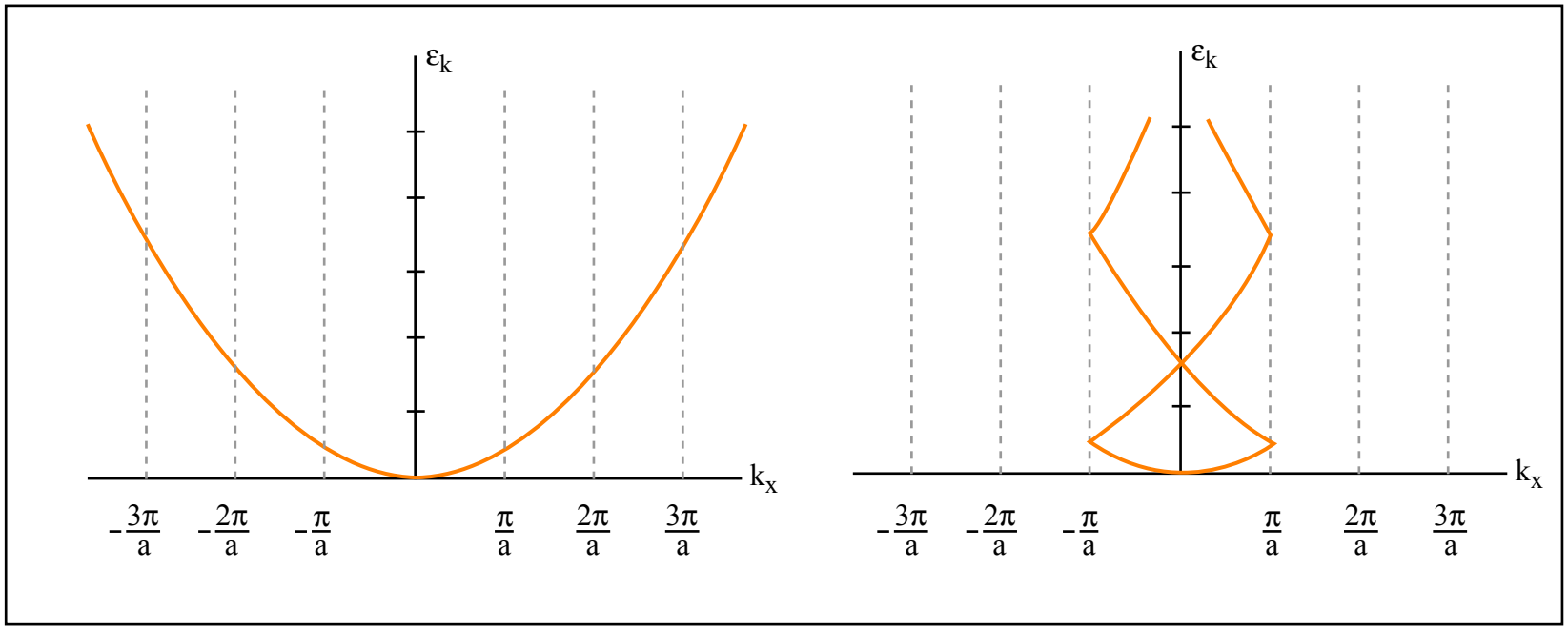


Image by MIT OpenCourseWare.

$$E_{\vec{k}} = E_{\vec{k}+\vec{G}}$$

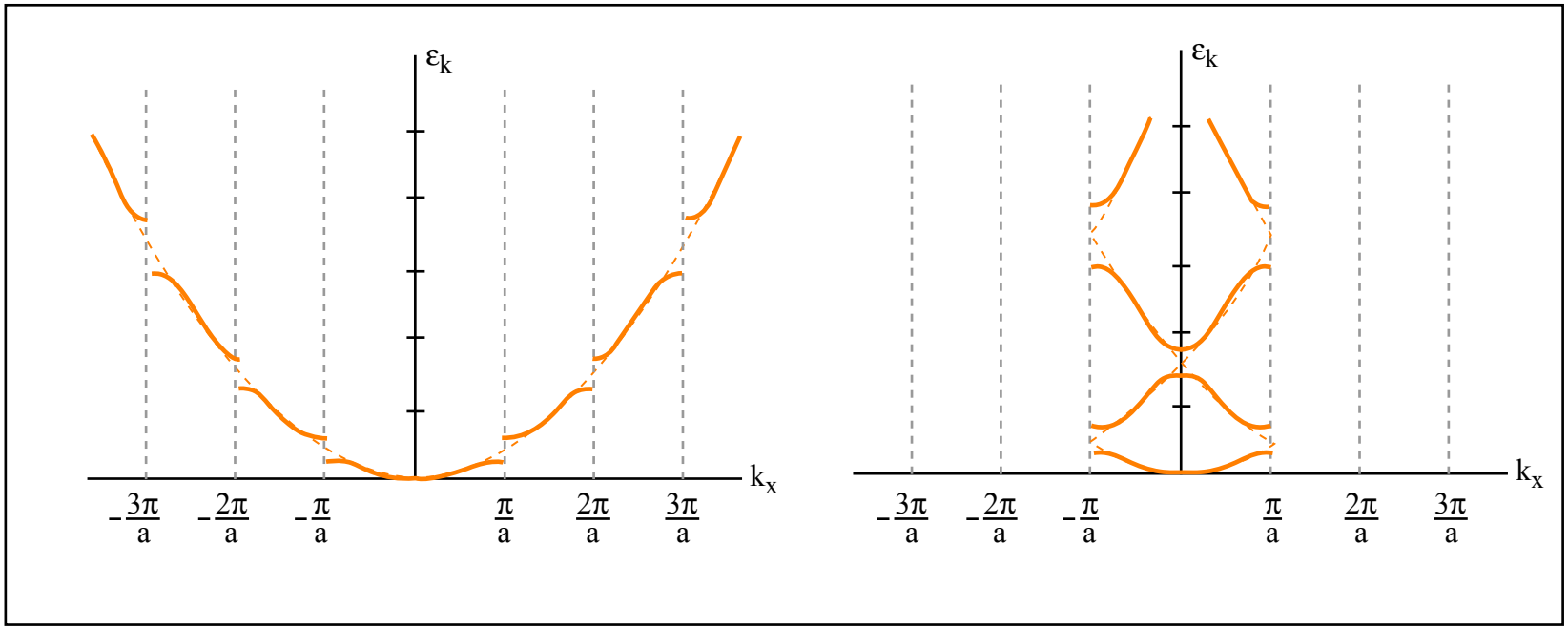
The band structure

folding of the band structure



The band structure

real band structure



Review

- Review
- Periodic potentials
- Bloch's theorem
- Energy bands

Literature

- Charles Kittel, Introduction to Solid State Physics
- Richard M. Martin, Electronic Structure
- wikipedia, “solid state physics”, “condensed matter physics”, ...
- Simple band structure simulations: http://phet.colorado.edu/simulations/sims.php?sim=Band_Structure

3.021J / 1.021J / 10.333J / 18.361J / 22.00J Introduction to Modeling and Simulation
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