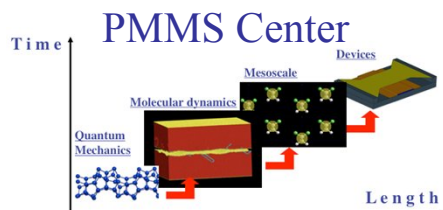# nanoHUB.org learning module: Bonding and band structure in Si

Ravi Vedula, Janam Javerhi, Alejandro Strachan

Center for Predictive Materials Modeling and Simulation,

School of Materials Engineering, Purdue University

strachan@purdue.edu

Based on Purdue MSE270 lectures by Alejandro Strachan

Learning module on: Bonding and band structure in Si

Learning Objectives:
•Understand how the band structure of a semiconductor develops from the electronic states of the atoms
•Understand cohesion energy in the crystal

Approach:
•This is hand-on learning module where students will run online electronic structure calculations in nanoHUB.org at the DFT level to explore bonding and band structures
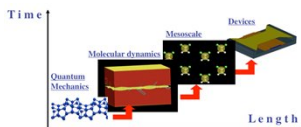
Outline

- A quantum mechanics refresher
    - Quantum mechanics in 5 postulates
- Electronic structure of atoms
    - Orbitals and their energies
- Di-atomic molecules
    - Bonding and anti-bonding states
    - Cohesion
- Crystals
    - The formation of electronic bands
    - Cohesion
- Links to hands-on activities
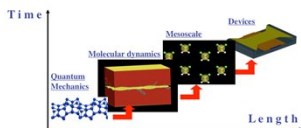
Quantum mechanics in 5 postulates

1. The state of electrons is determined by their wave function

$$\Psi(r,t)$$

We will focus on equilibrium properties:
WF does not depend on time $\longrightarrow$ $\Psi(r)$

2. Physical observables ↔ linear operators

Mathematical objects that act on functions

Position: $\vec{r}$

Momentum: $\vec{p} = \dfrac{\hbar}{i}\vec{\nabla} = \dfrac{\hbar}{i}\left(\dfrac{\partial}{\partial x}, \dfrac{\partial}{\partial y}, \dfrac{\partial}{\partial z}\right)$
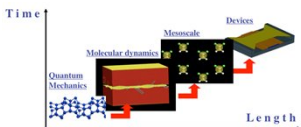
Quantum mechanics in 5 postulates
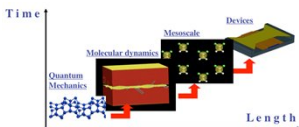
3. Average results of measurements is given by

$$\langle O \rangle = \int \Psi(r) O \Psi(r) d^3 r$$

Example:

$$\langle \vec{r} \rangle = \int \Psi(\vec{r}) \vec{r} \Psi(\vec{r}) d^3 r = \int \vec{r} \left| \Psi(\vec{r}) \right|^2 d^3 r$$

$$\left| \Psi(\vec{r}) \right|^2 \qquad \text{Probability density of electron being in volume } d^3r \text{ around } r$$

Quantum mechanics in 5 postulates

4. The equilibrium wave function can be obtained from the Schrödinger equation:

Hamiltonian operator
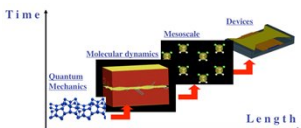
$$H\psi(\vec{r}) = E\psi(\vec{r})$$

Energy (scalar)

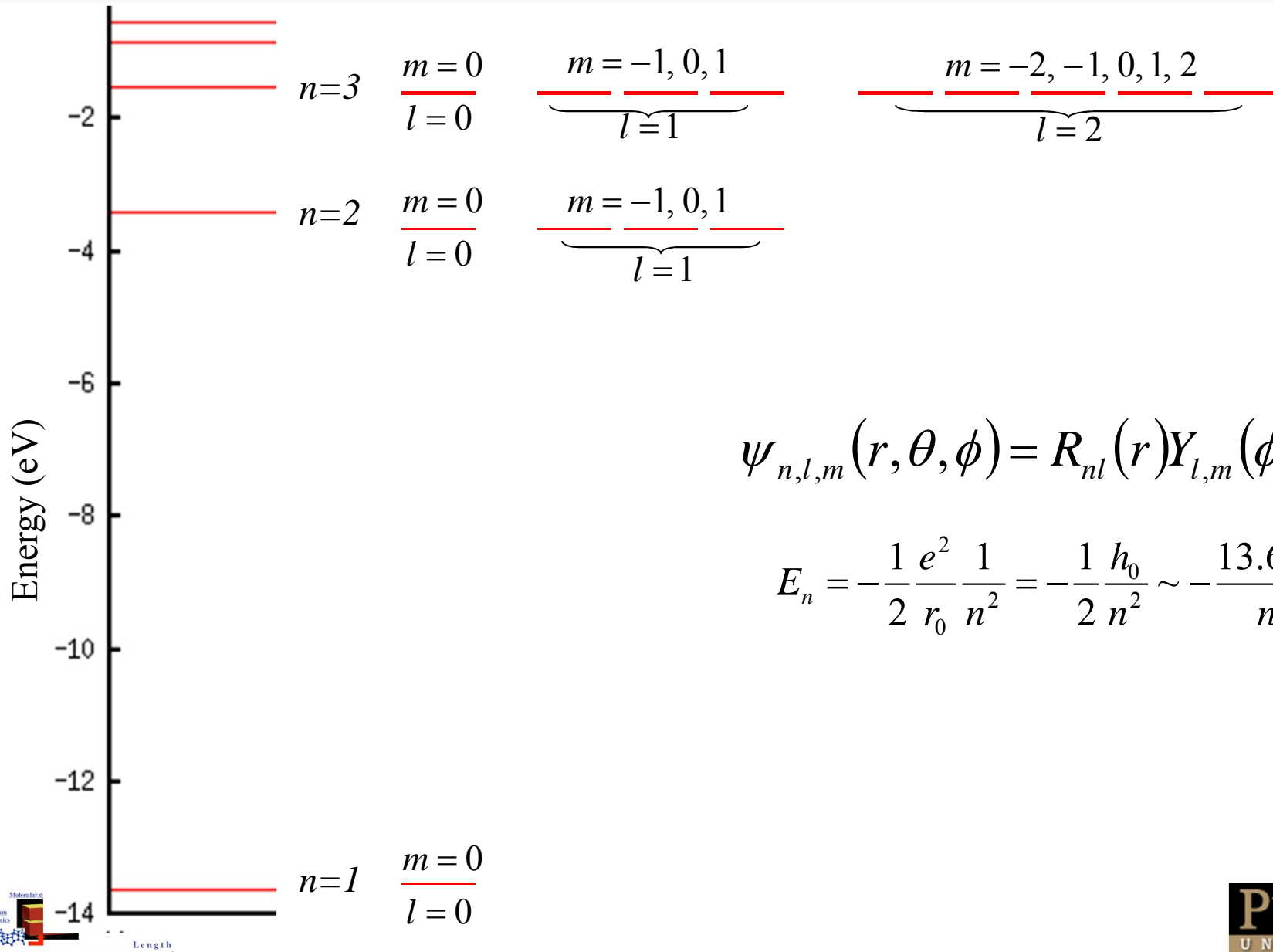Solution: family of wavefunctions ψ_n each with its own energy: E_n

Equivalent to eigenvalue problem in algebra

5. Pauli's exclusion principle

- Two electrons maximum per orbital
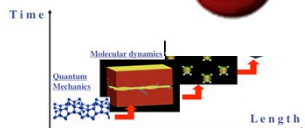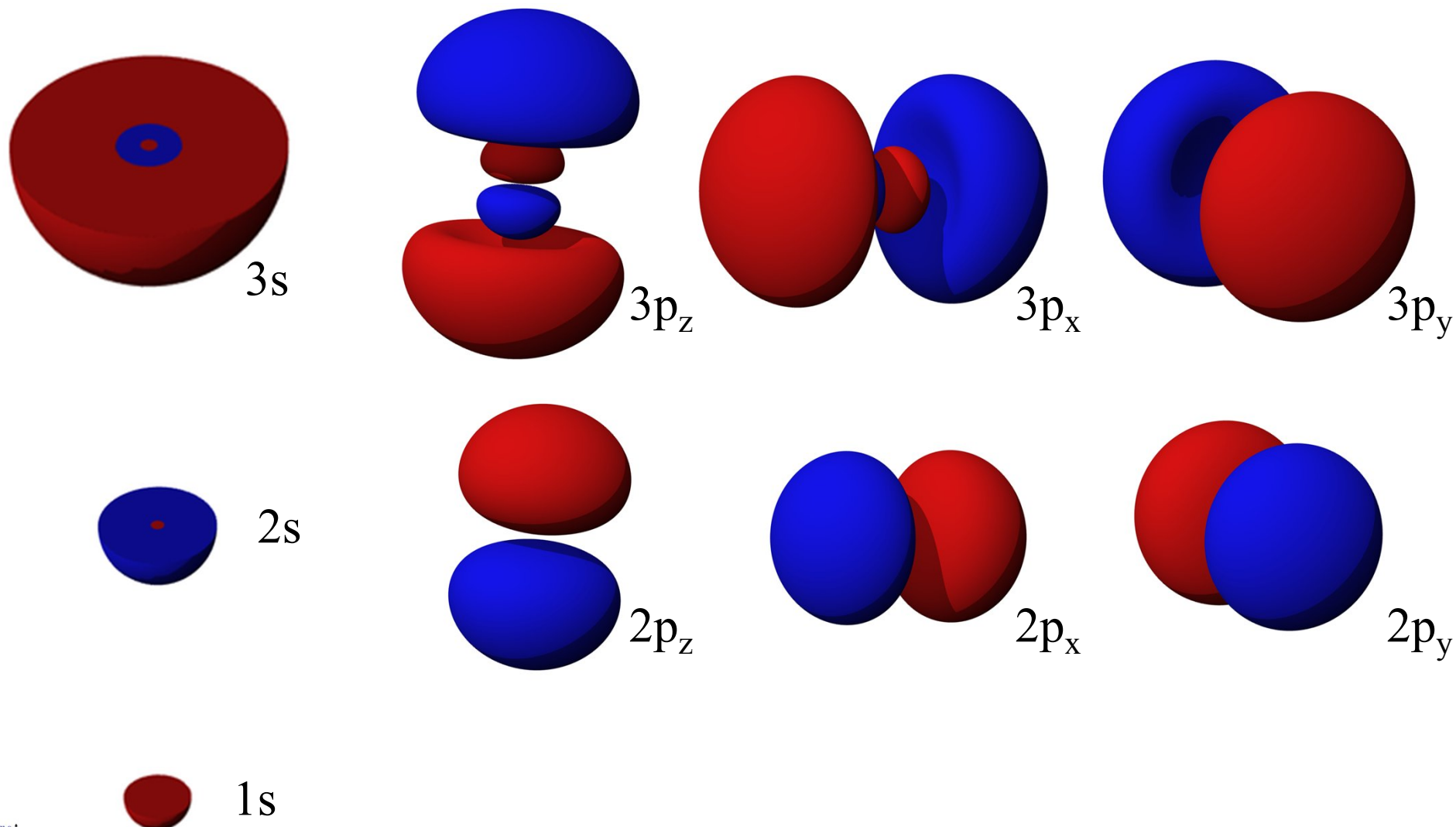- Electrons in one orbital must have different spin

Energy levels of the hydrogen atom

$n=3$

$m = 0$ $l = 0$

$m = -1, 0, 1$ $l = 1$

$m = -2, -1, 0, 1, 2$ $l = 2$

$n=2$

$m = 0$ $l = 0$

$m = -1, 0, 1$ $l = 1$

$n=1$

$m = 0$ $l = 0$

Energy (eV): -2, -4, -6, -8, -10, -12, -14

$$\psi_{n,l,m}(r,\theta,\phi) = R_{nl}(r) Y_{l,m}(\phi,\theta)$$

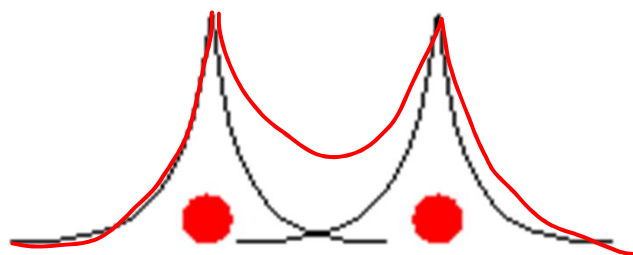$$E_n = -\frac{1}{2}\frac{e^2}{r_0}\frac{1}{n^2} = -\frac{1}{2}\frac{h_0}{n^2} \sim -\frac{13.6 eV}{n^2}$$

Orbital shapes

3s

$3p_z$

$3p_x$

$3p_y$

2s

$2p_z$

$2p_x$

$2p_y$

1s

Ref: From wikipedia(http://en.wikipedia.org/wiki/Atomic_orbital)

PURDUE
UNIVERSITY

Molecular orbitals as combinations of atomic orbitals

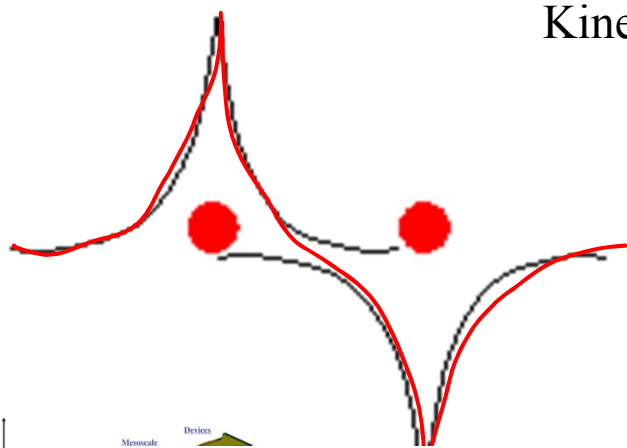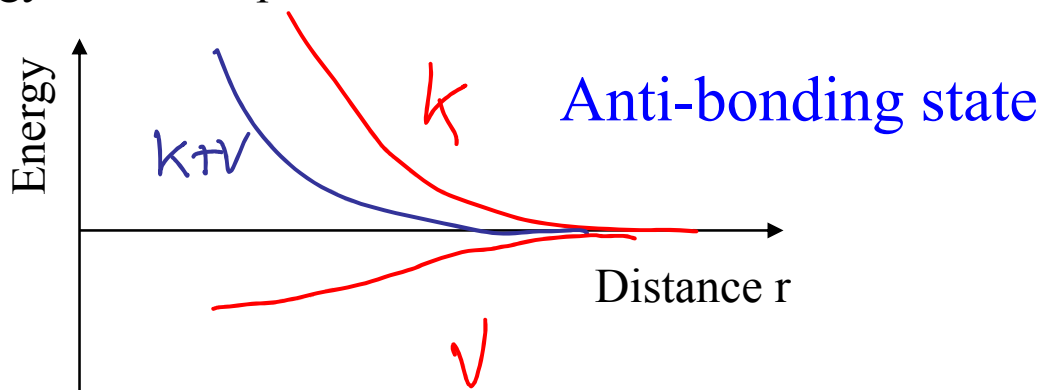Symmetric:

Potential energy: more electron density between atoms → less density near protons → potential energy increases

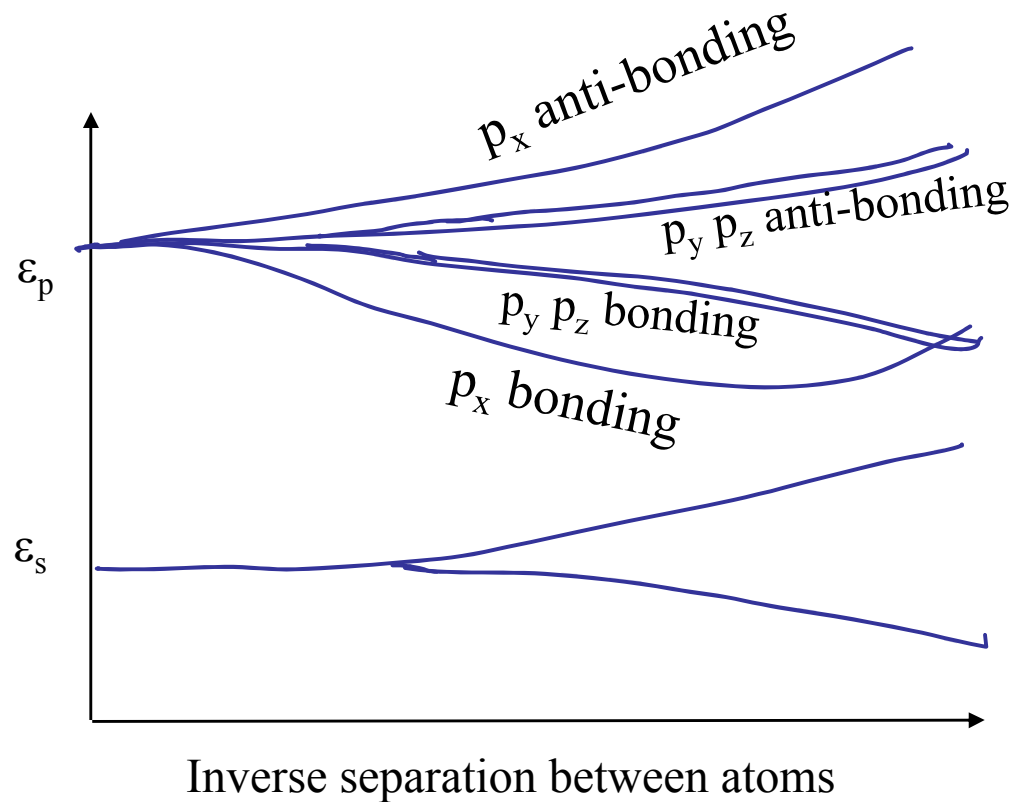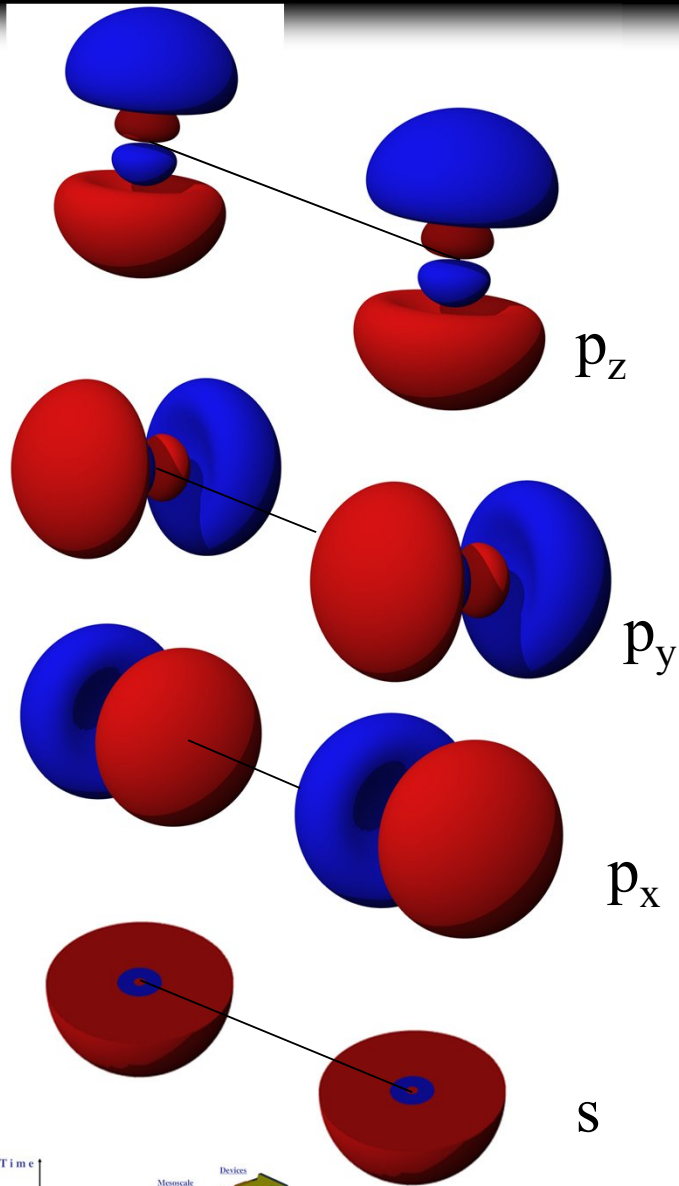Kinetic energy: smaller gradients → K.E. decreases

Bonding state
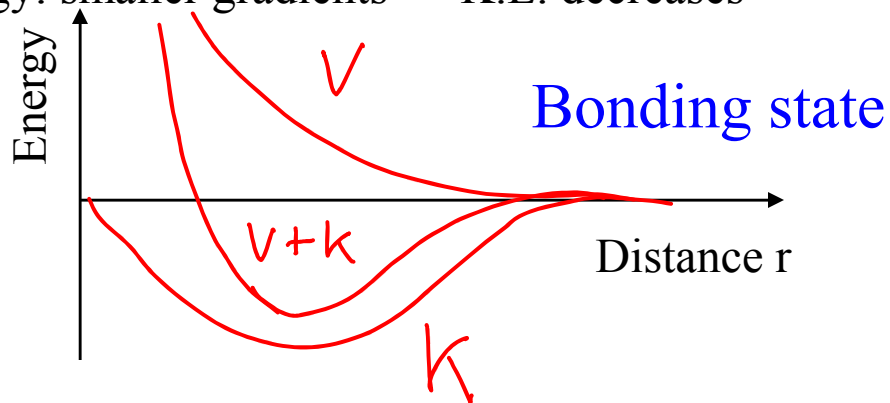
Anti-symmetric:

Potential energy: less electron density between atoms → more density near protons → potential energy decreases

Kinetic energy: more steep between atoms → K.E. increases

Anti-bonding state

Bonding is governed by K.E.: delocalization leads to lower K.E.

p_z

p_y

p_x

s

ε_p

ε_s

p_x anti-bonding

p_y p_z anti-bonding

p_y p_z bonding

p_x bonding

Inverse separation between atoms

Ref: Atomic Orbitals from wikipedia
(http://en.wikipedia.org/wiki/Atomic_orbital)

Adapted from Harrison, "Electronic
structure and the properties of solids"
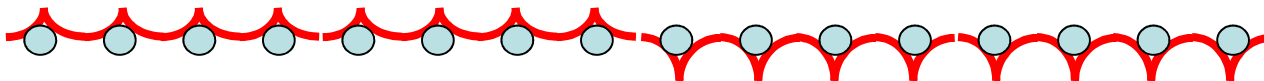
PURDUE
UNIVERSITY
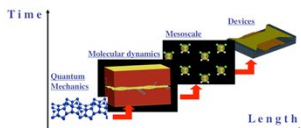
Wave functions of solids

Bloch Theorem: If the solid is periodic, then the wave-function at any point is described by plane wave times wave-function at a unit cell site, where the wavenumber k of the plane wave determines the coupling between the two wave-functions. Mathematically,
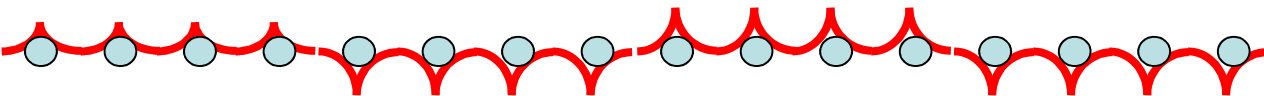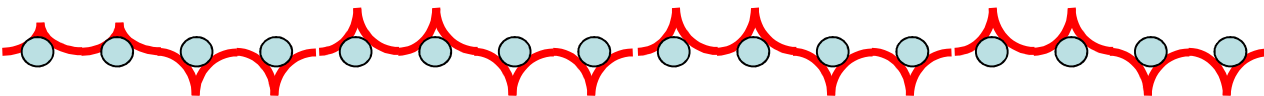
$$\psi(r + R) = e^{iK.R}\psi(r)$$
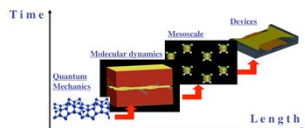

$k = 0$

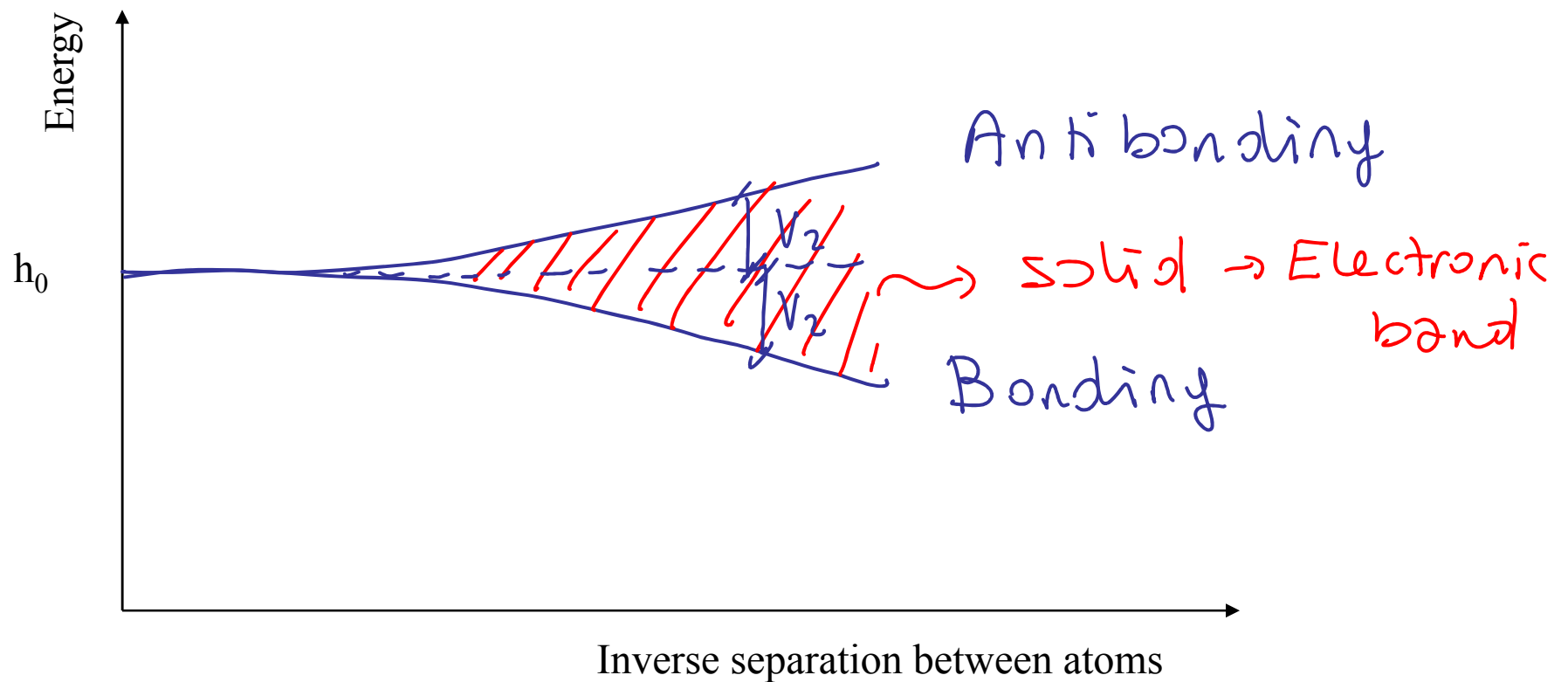$k = \dfrac{2\pi}{L}$

$k = 2 \cdot \dfrac{2\pi}{L}$

$k = 4 \cdot \dfrac{2\pi}{L}$

$k = \dfrac{2\pi}{2a} \approx \dfrac{\pi}{a}$

Energy

h_0

Antibonding

solid → Electronic band

Bonding

V_2

V_2

Inverse separation between atoms
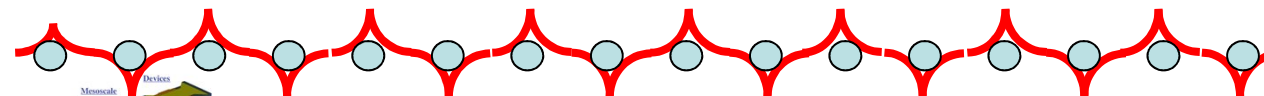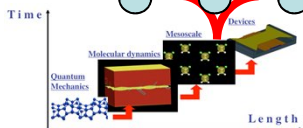
Column IV bonding and band structure

empty states

ε_{3p}

6AP

ε_{3s}

filled states

Inverse separation between Si atoms

s-p splitting larger than bonding anti-bonding splitting
Metals

Bonding/anti-bonding splitting larger than s-p splitting:
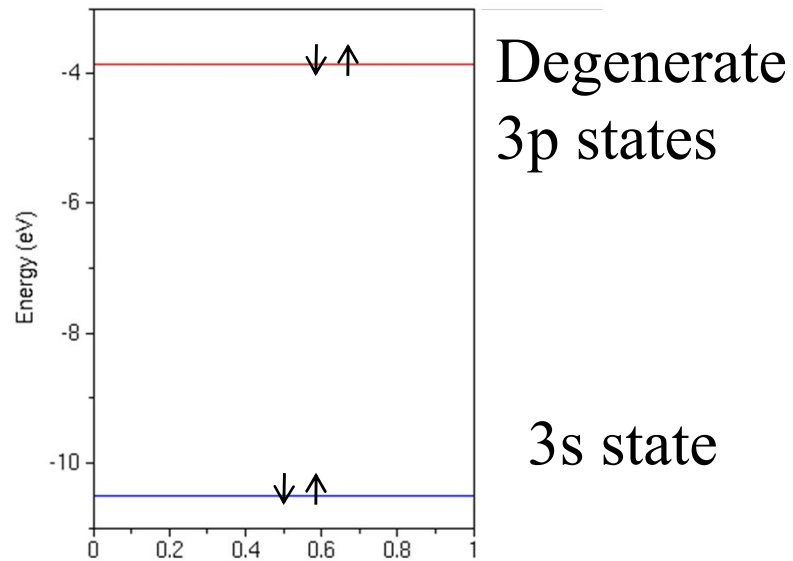Semiconductors and insulators (covalent bonding)
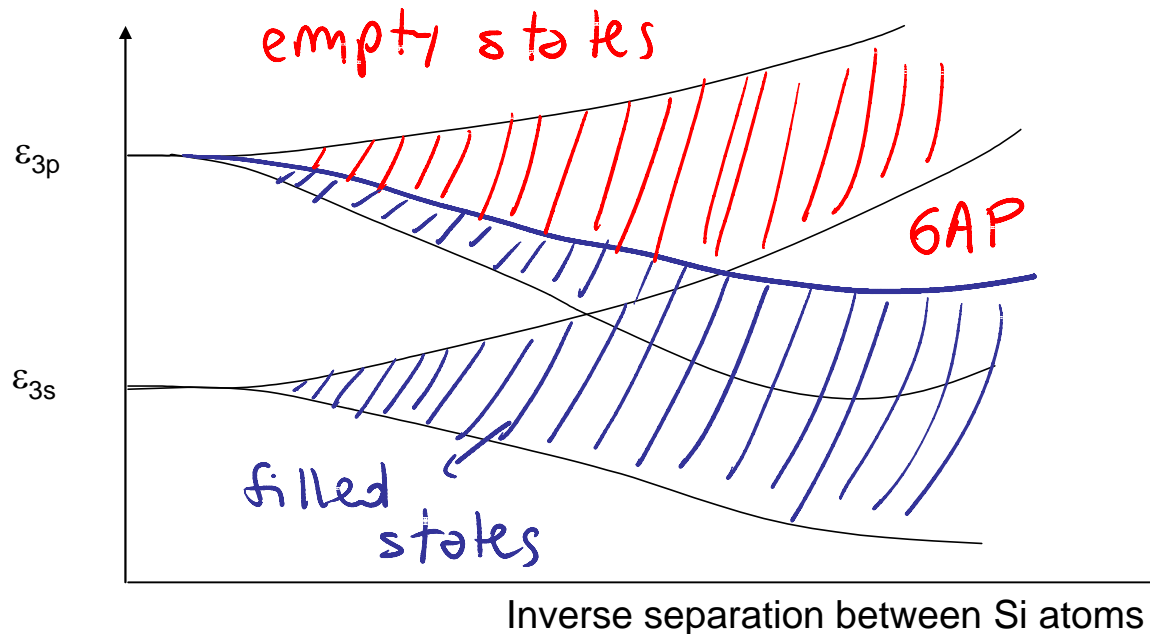
Band gaps

C   5.5 eV

Si   1.11 eV

Ge   0.67 eV

Sn   0.0 eV

Low temp:
α-Sn (diam)
High temp:
β-Sn (tetra)
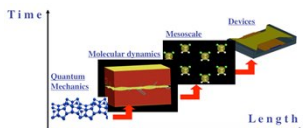
Let's explore bonding and band structure in Si

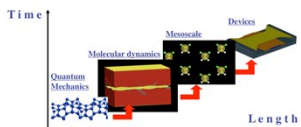• Calculations are performed with nanoHUB.org quantum ESPRESSO tool
• See tutorial in this Lecture to run your own simulations online free!

Degenerate
3p states

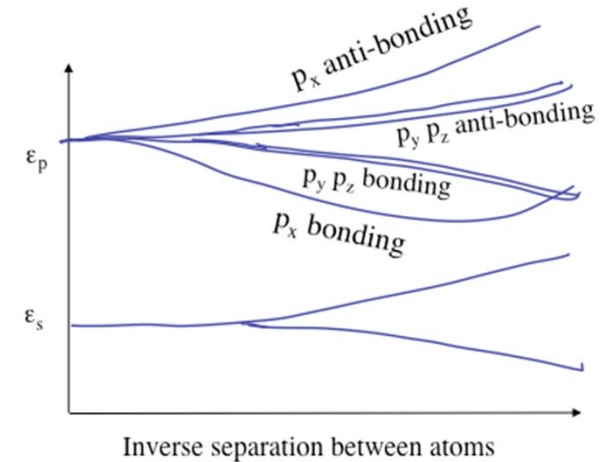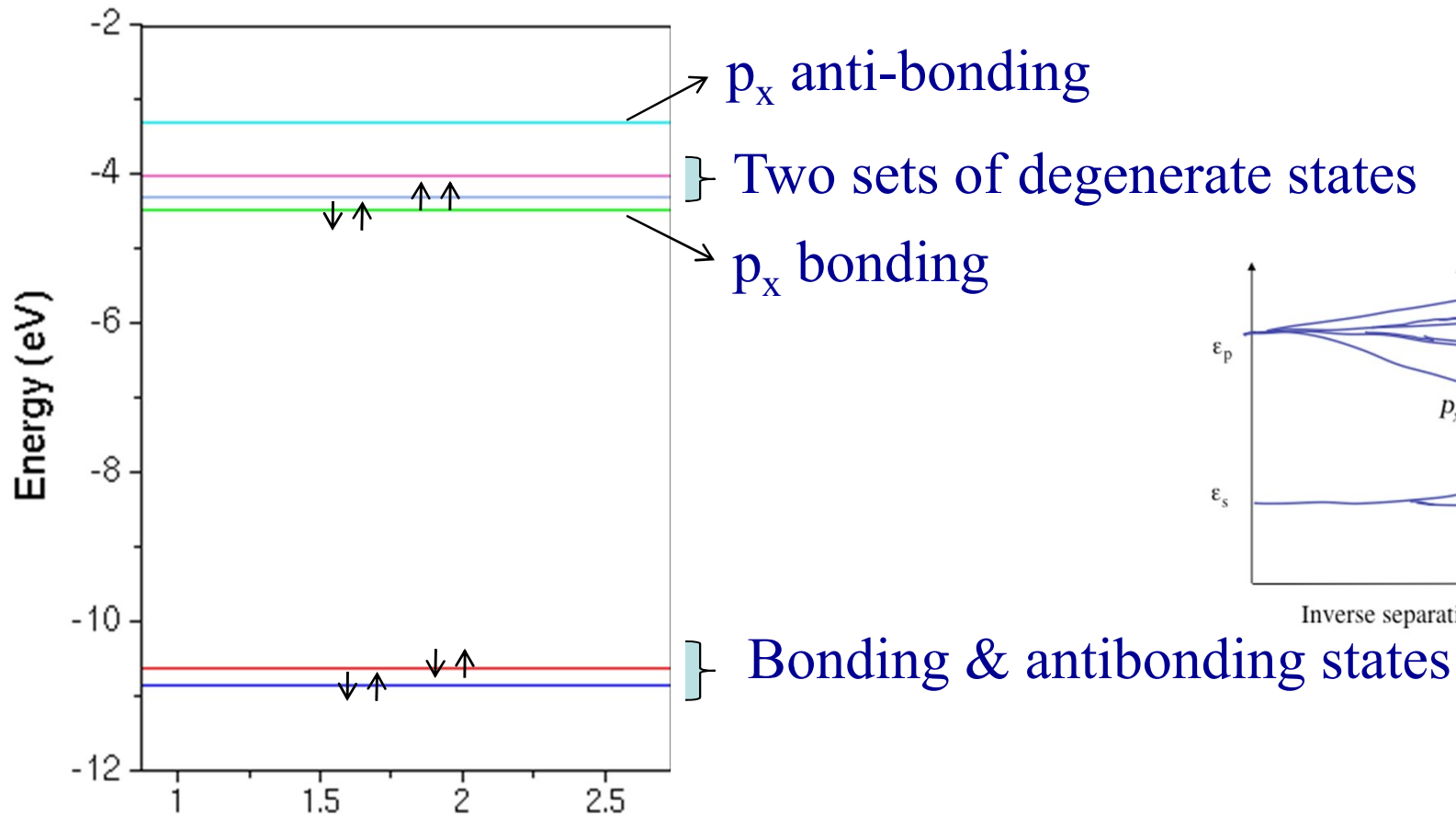3s state

Let's start with the electronic
structure of the atom

Electronic configuration of Si :
[Ne] $3s^2 3p^2$
Si has 4 valence states and
4 valence electrons

• Isolated atoms in a system simply have discrete energy eigenvalues
• No dependence of energy on k
• Note the energy level splitting in Si (3s and 3p are different energies) as compared to hydrogen arises from electron-electron interactions.

Let's explore bonding and band structure in Si

What happens when we bring two Si atoms together?

p_x anti-bonding

Two sets of degenerate states

p_x bonding

p_x anti-bonding

p_y p_z anti-bonding

p_y p_z bonding

p_x bonding

ε_p

ε_s

Inverse separation between atoms

Bonding & antibonding states

nanoHUB.org calculation

This is an isolated molecule, no k dependence
Remember k tells you how the WF in one unit cells differs from that in the next one
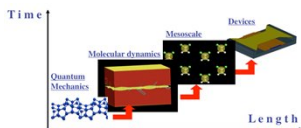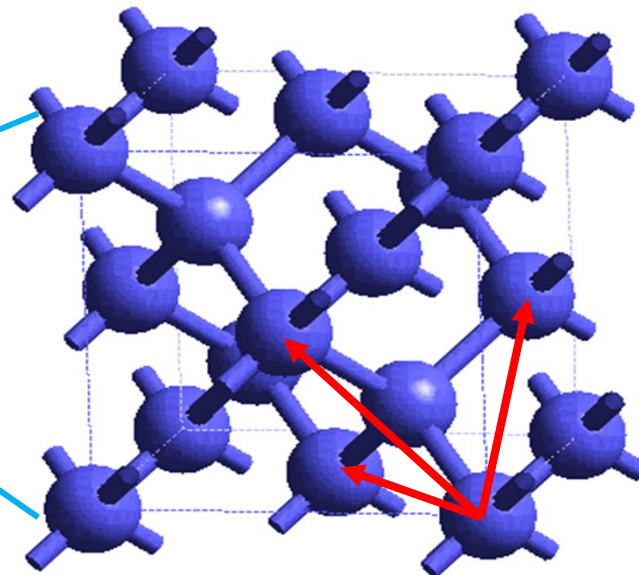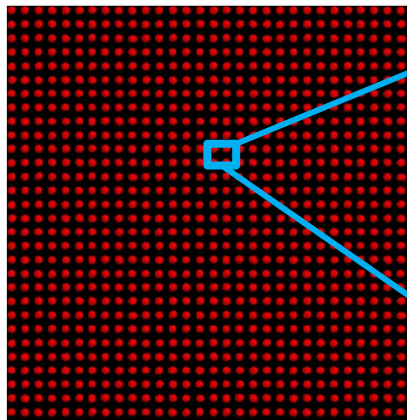
Now we will simulate a crystal

Solids contain atoms of order 10^{23} atoms/cm$^{3.}$

Description of this order is overwhelming to do all the individual atoms. How do we describe them?

Ans: periodic boundary conditions

Bravais Lattice and Periodicity:

Basis: 2 Si atoms
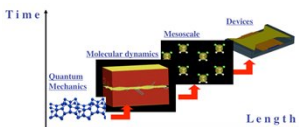
$$a_0(0,0,0)$$
$$a_0(0.25,0.25,0.25)$$

Bravias lattice:

$$\vec{a} = a_0(0.5,0.5,0)$$
$$\vec{b} = a_0(0.5,0,0.5)$$
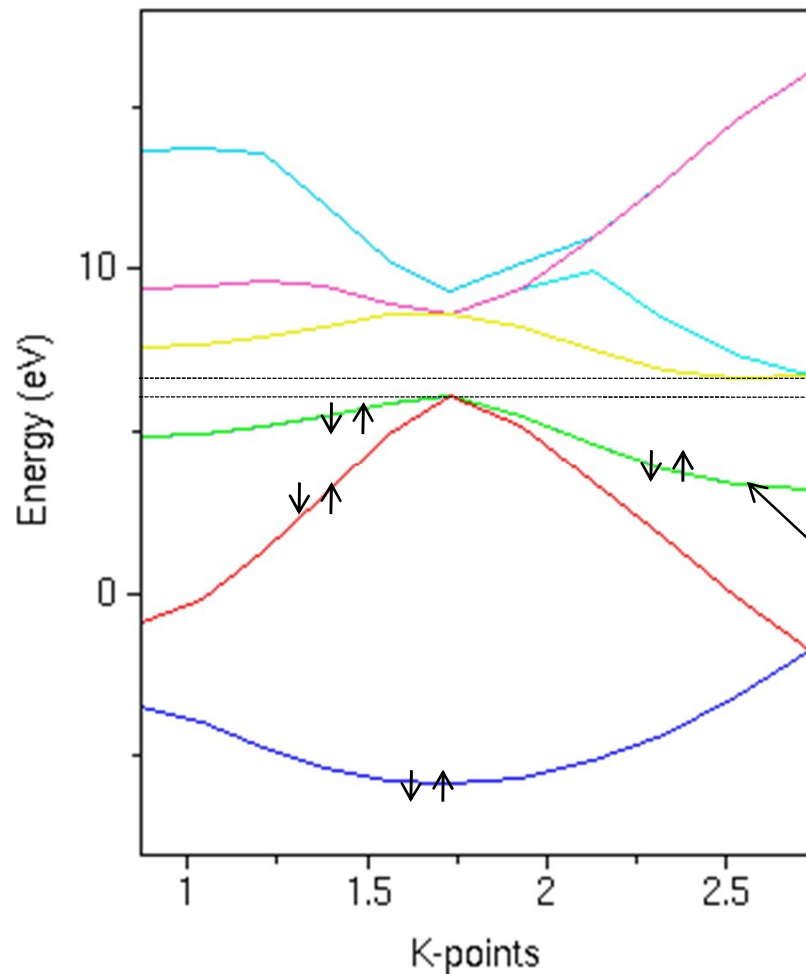$$\vec{c} = a_0(0,0.5,0.5)$$

Translation vector:

$$R = l\bar{a} + m\bar{b} + n\bar{c}$$
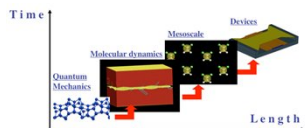
Si diamond structure

Band structure of the crystal

We have to assign 4 valence electrons per atom: total 8
The 4 bands with lower energy will be occupied

Band gap

Degenerate band (two electrons per atom)

nanoHUB.org calculation

What you will learn

- Use online electronic structure calculations to explore:
    - Bonding in Si
    - How the band structure of the solid forms as atoms are brought together

- Explore band structures and bonding in other semiconductors

- Explore band structures and bonding in metals

  Now: go over the tutorial and run your own electronic structure calculations to explore bonding and bandstructures