

The EPFL logo is rendered in a bold, red, sans-serif font. The letters 'E', 'P', and 'F' are connected at the top, while the 'L' is separate. The logo is positioned to the right of a vertical red bar that runs down the left side of the slide.

Génie Electrique et Electronique
Master program
Prof. Elison Matioli

EE-557 Semiconductor devices I

Energy bang gap and band diagrams

Outline of the lecture

1. Introduction
2. Energy gap and energy bands
3. Important bits of knowledge

References:

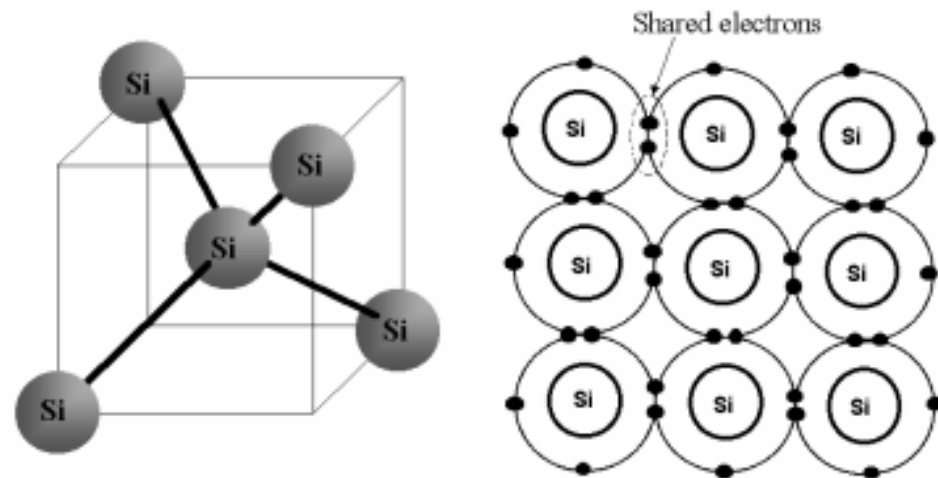
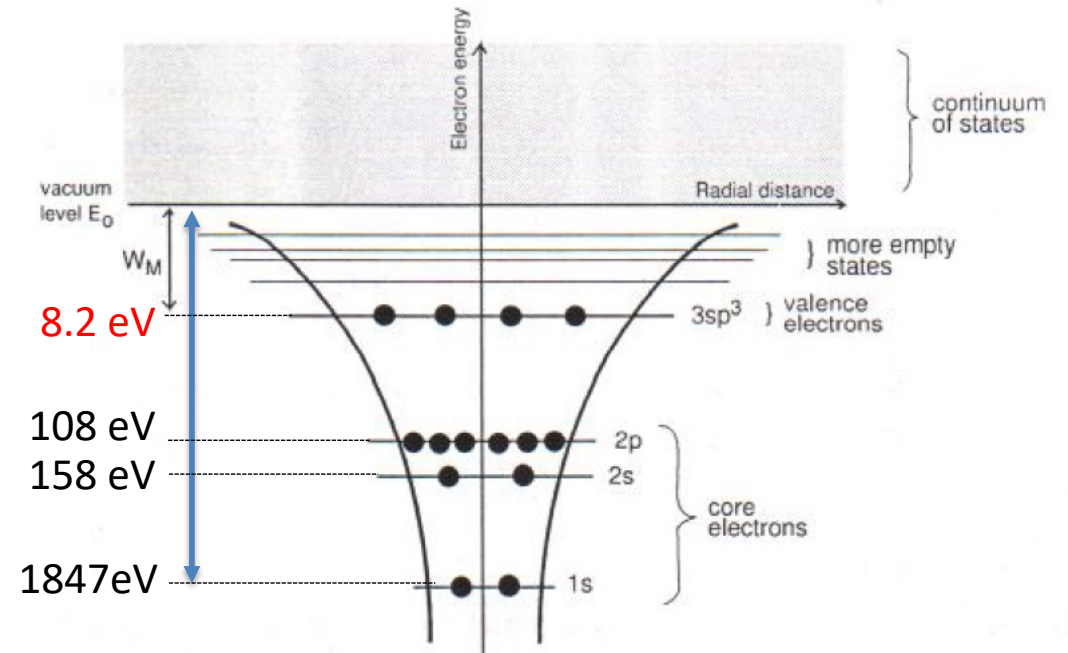
- J. A. del Alamo, course materials for 6.720J Integrated Microelectronic Devices, Spring 2007. MIT OpenCourseWare (<http://ocw.mit.edu/>)
- C. Kittel, Introduction to Solid State Physics, John Wiley & Sons, 2005

- What is a semiconductor?
- What is an energy band gap?
- How do we treat electrons in a solid?
- How do atoms arrange themselves? And the consequences...
- How do electrons arrange themselves (in energy) in an electronic system?

Energy band-gap

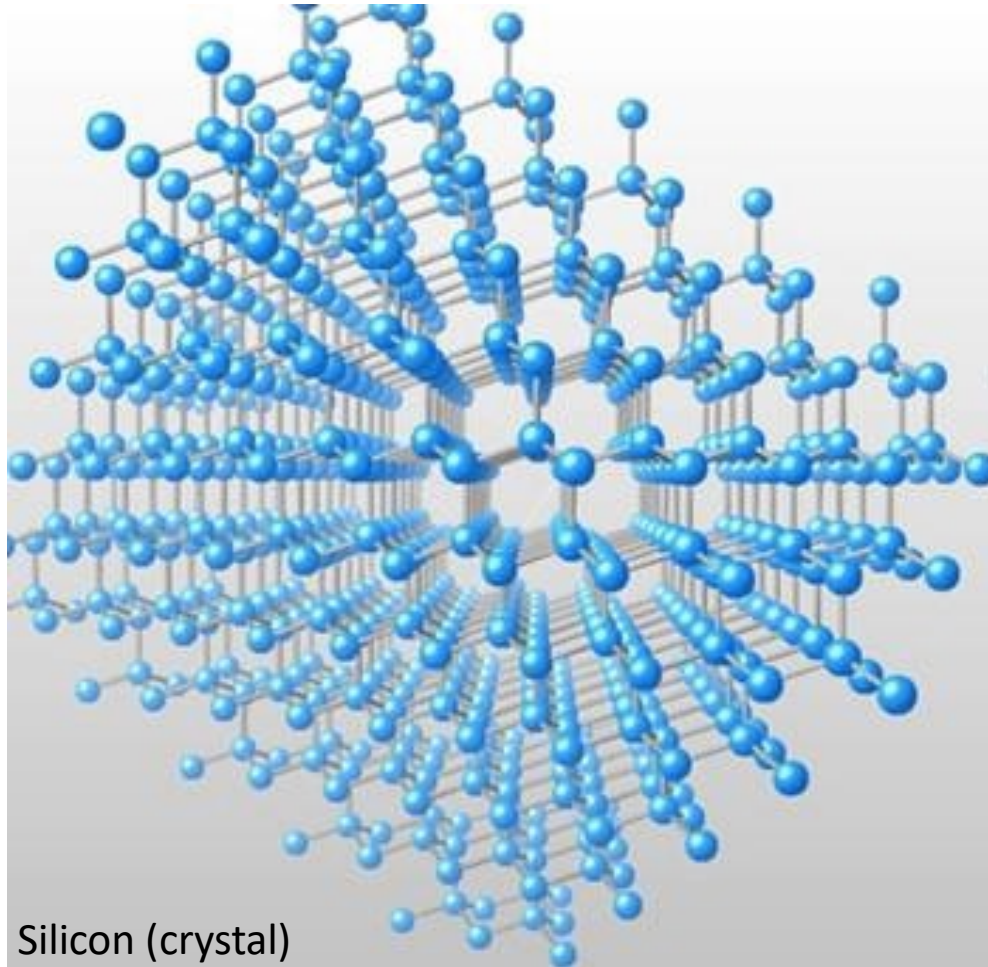
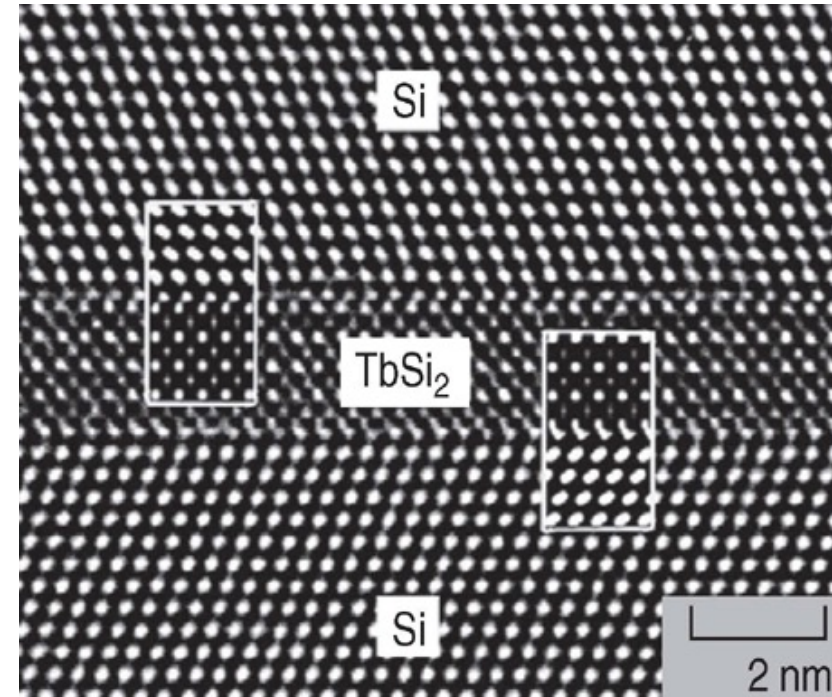
Single silicon atom

					18 VIII A	
					2 He Helium 4.003 2	
	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	
	5 B Boron 10.81 2-3	6 C Carbon 12.01 2-4	7 N Nitrogen 14.007 2-5	8 O Oxygen 15.999 2-6	9 F Fluorine 18.998 2-7	10 Ne Neon 20.180 2-8
	13 Al Aluminium 26.982 2-3	14 Si Silicon 28.085 2-4	15 P Phosphorus 30.974 2-5	16 S Sulfur 32.06 2-6	17 Cl Chlorine 35.45 2-7	18 Ar Argon 39.948 2-8
12 IB	31 Ga Gallium 69.723 2-3	32 Ge Germanium 72.630 2-4	33 As Arsenic 74.922 2-3	34 Se Selenium 78.971 2-4	35 Br Bromine 79.904 2-7	36 Kr Krypton 83.798 2-8
10 n	49 In Indium 114.82 2-3	50 Sn Tin 118.71 2-4	51 Sb Antimony 121.76 2-3	52 Te Tellurium 127.60 2-6	53 I Iodine 126.90 2-7	54 Xe Xenon 131.29 2-8
8 d	81 Tl Thallium 204.38 2-3	82 Pb Lead 207.2 2-4	83 Bi Bismuth 208.98 2-3	84 Po Polonium 209 2-6	85 At Astatine [210] 2-7	86 Rn Radon [222] 2-8
10 g	81 Tl Thallium 204.38 2-3	82 Pb Lead 207.2 2-4	83 Bi Bismuth 208.98 2-3	84 Po Polonium 209 2-6	85 At Astatine [210] 2-7	86 Rn Radon [222] 2-8



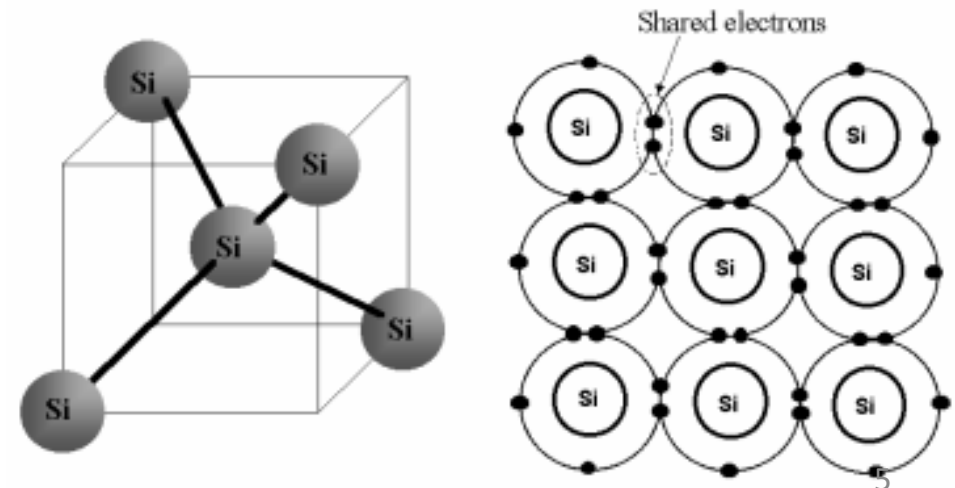
Covalent bonds

Transmission electron microscope (TEM)



Silicon (crystal)

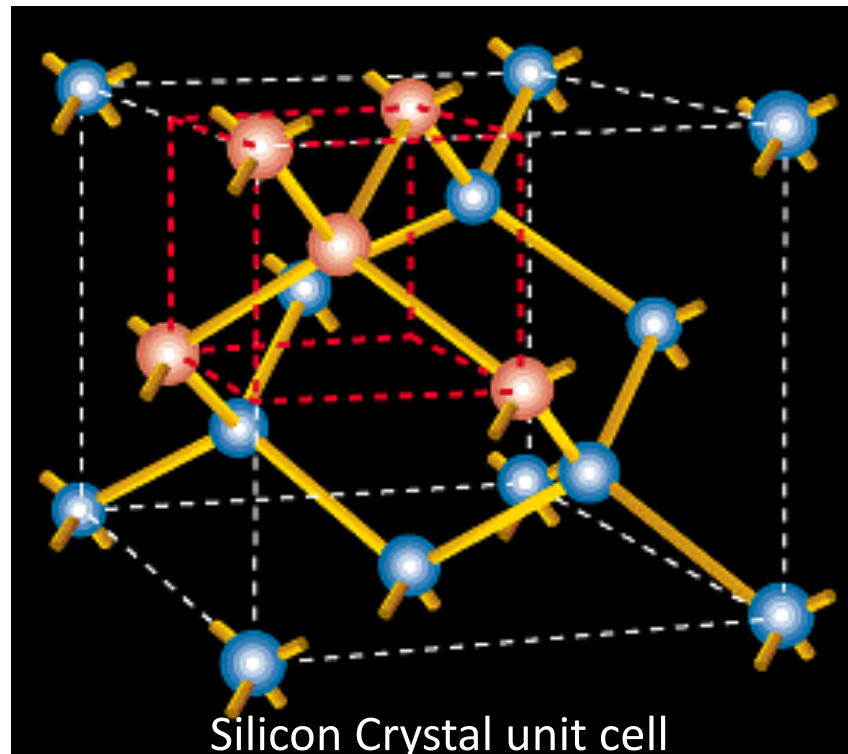
Take a look at this link to "play" its crystal structure:
<https://sketchfab.com/3d-models/silicon-crystal-lattice-73e292f32ffe4ca490e166faeba317e7>



Silicon intrinsic: $\rho = 3.2 \times 10^5 \Omega\text{cm} = 3.2 \times 10^3 \Omega\text{m}$

Semiconductors are solids

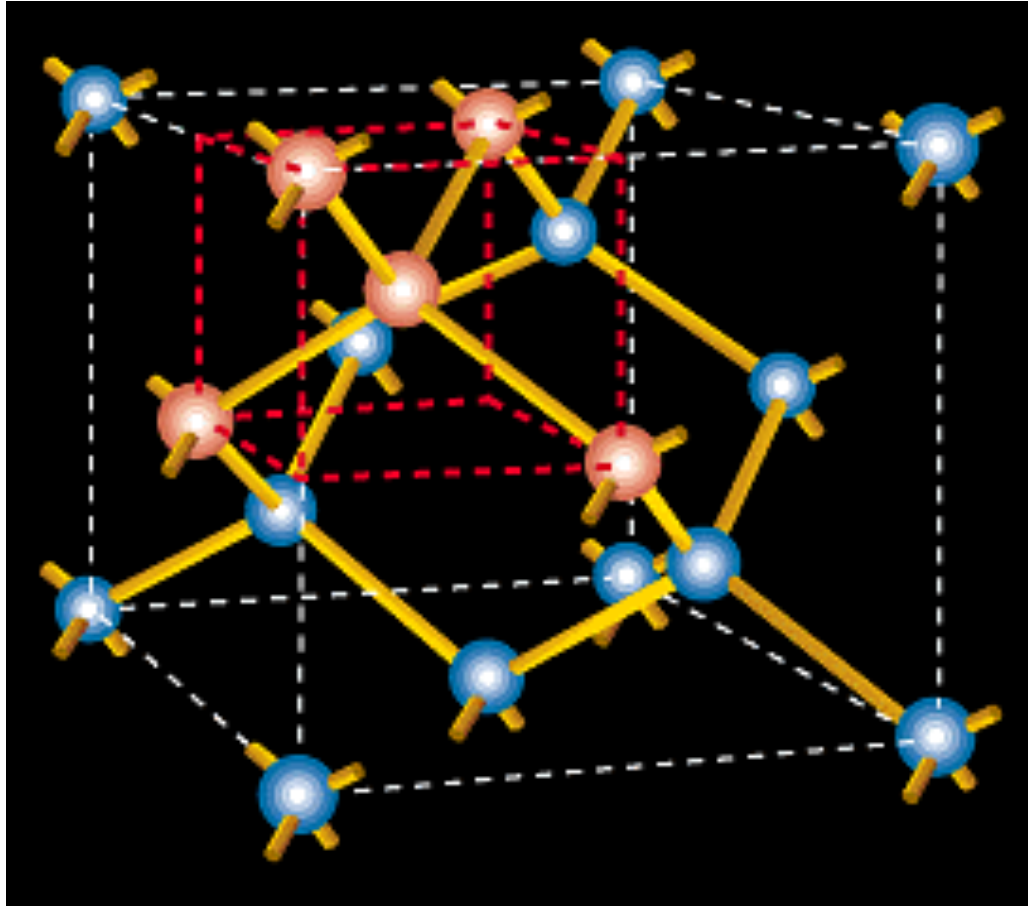
- Semiconductors are **crystalline solids**
- Crystalline solid = elemental atomic arrangement, or unit cell, repeated “ad infinitum” in space in three dimensions.
 - Si lattice constant: 0.54 nm
 - Si atomic spacing: 0.24 nm
- Solid is an electronic system with **periodic potential**



Structure is held together by covalent bonding 4 valence electrons shared with 4 neighbors:
lowest energy situation (stable configuration)

See: <http://www.science.oregonstate.edu/~gablek/CH231H/Silicon.htm>
<https://sketchfab.com/3d-models/silicon-crystal-lattice-73e292f32ffe4ca490e166faeba317e7>

Silicon Crystal unit cell



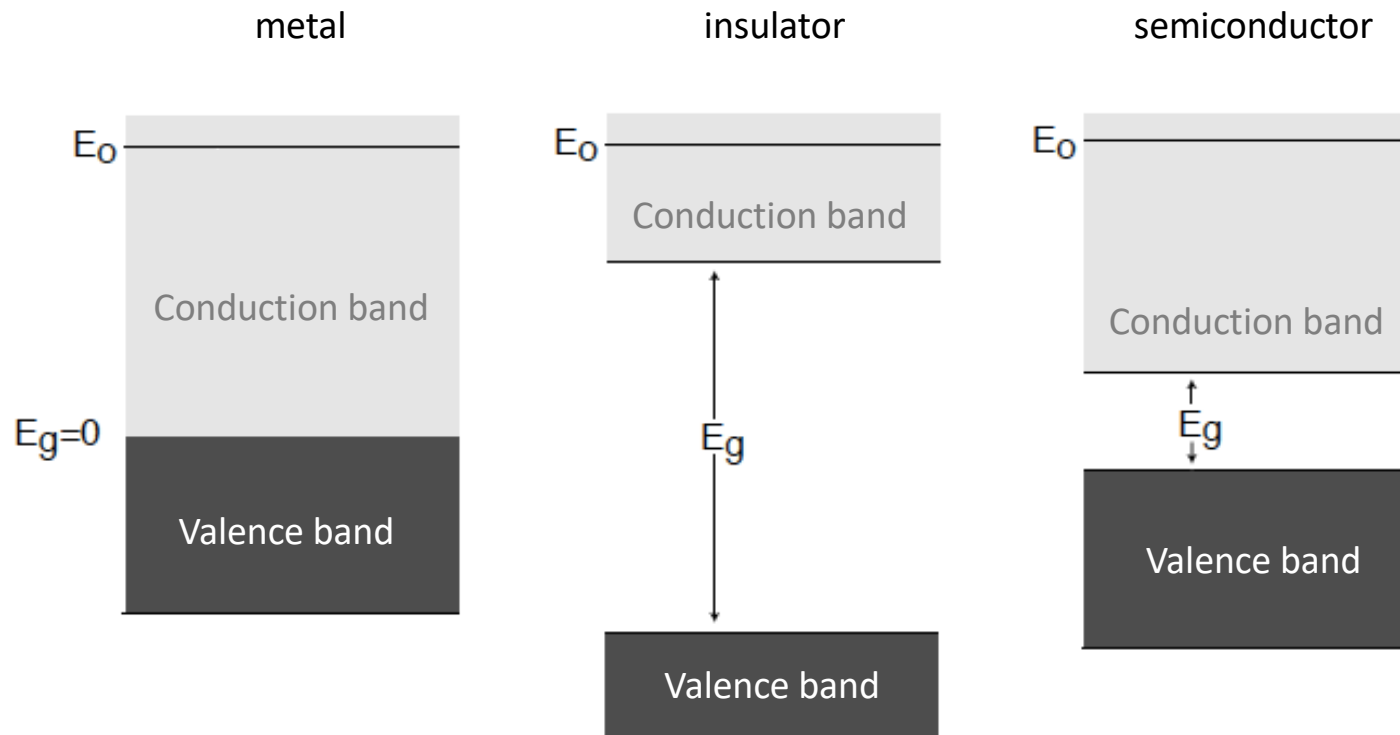
“diamond cubic” lattice

- Each Si atom has 4 nearest neighbors
- lattice constant = 5.431 Å

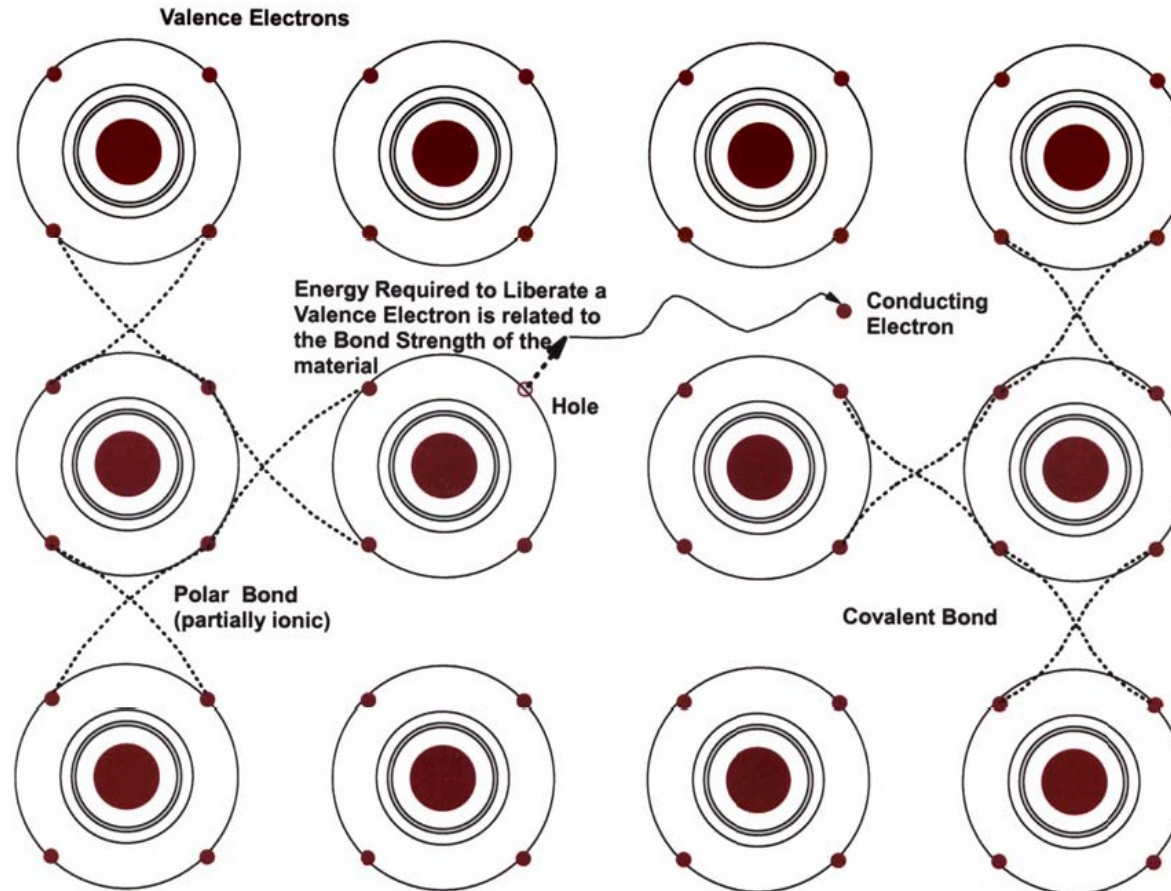
How Many Silicon Atoms per cm^3 ?



What is an energy band gap E_g ?

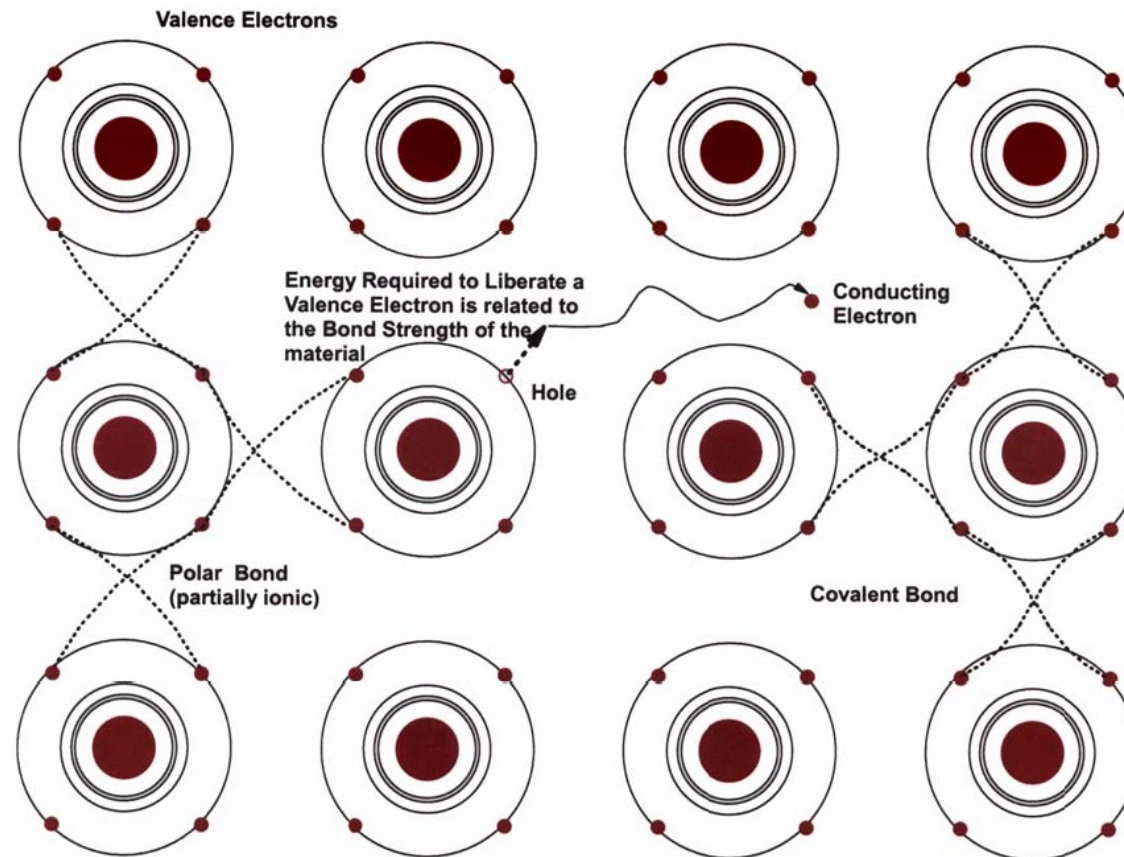


What is a Semiconductor Energy Bandgap?



- For metals, the electrons can jump from the valence orbits (outermost core energy levels of the atom) to any position within the crystal (free to move throughout the crystal) with no “extra energy needed to be supplied”
- For insulators, it is VERY DIFFICULT for the electrons to jump from the valence orbits and requires a huge amount of energy to “free the electron” from the atomic core.
- For semiconductors, the electrons can jump from the valence orbits but does require a small amount of energy to “free the electron” from the atomic core.

What is a Semiconductor Energy Bandgap?



- Semiconductor materials are a sub-class of materials distinguished by the existence of a range of disallowed energies between the energies of the valence electrons (outermost core electrons) and the energies of electrons free to move throughout the material.
- The energy difference (**energy gap or bandgap**) between the states in which the electron is bound to the atom and when it is free to conduct throughout the crystal is related to the bonding strength of the material, its density, the degree of ionicity of the bond, and the chemistry related to the valence of bonding.
- High bond strength materials (diamond, SiC, AlN, GaN etc...) tend to have large energy bandgaps.
- Lower bond strength materials (Si, Ge, etc...) tend to have smaller energy bandgaps.

How do energy bands and band gaps form?

Energy band-gap

Simple case: Hydrogen atom

Electron experiences an electrostatic Coulomb attraction to the nucleus

$$V = -\frac{e^2}{4\pi\epsilon_0 r}$$

Hamiltonian for this problem (time-independent Schroedinger's equation):

$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi}_{\text{Kinetic energy}} + \underbrace{V\psi}_{\text{Potential energy}} = \underbrace{E\psi}_{\text{total energy}}$$

Energies electrons are allowed to have

Wavefunction of an electron

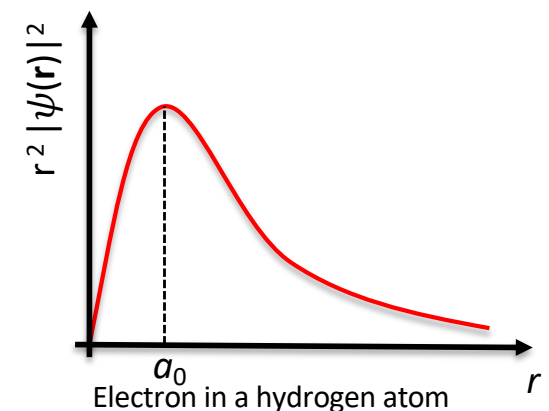
After writing the Laplacian ∇^2 in spherical coordinates:

$$H = -\frac{\hbar^2}{2m_e r^2} \left\{ \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right\} - \frac{e^2}{4\pi\epsilon_0 r}$$

$$E_n = -\frac{\hbar^2}{2m_e a_0^2} \frac{1}{n^2} \quad n = 1, 2, 3, \dots \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \approx 0.5291772107 \cdot 10^{-10} \text{ m}$$

The wave nature of electrons results in only a few allowed energies (like a guitar string)

$|\psi(\mathbf{r})|^2$ gives the probability of finding an electron in a given position \mathbf{r}



Energy band-gap

Simple case: Hydrogen atom

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Energies electrons are allowed to have

Wavefunction of an electron

After writing the Laplacian ∇^2 in spherical coordinates:

$$H = -\frac{\hbar^2}{2m_e r^2} \left\{ \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} - \frac{e^2}{4\pi\epsilon_0 r}$$

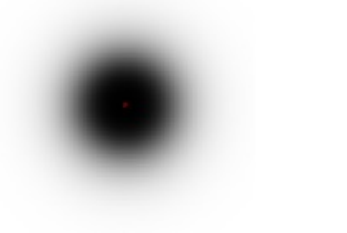
$$E_n = -\frac{\hbar^2}{2m_e a_0^2} \frac{1}{n^2} \quad n = 1, 2, 3, \dots$$

Ground state:

$$E_1 = -13.6 \text{ eV}$$

$$\psi_{100}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

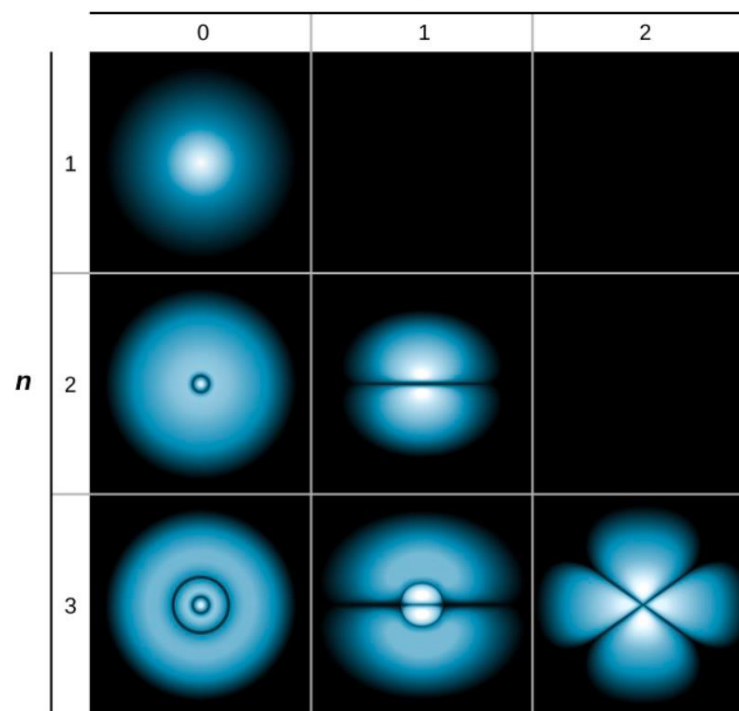
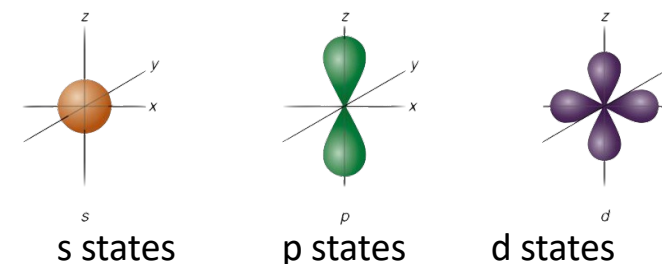
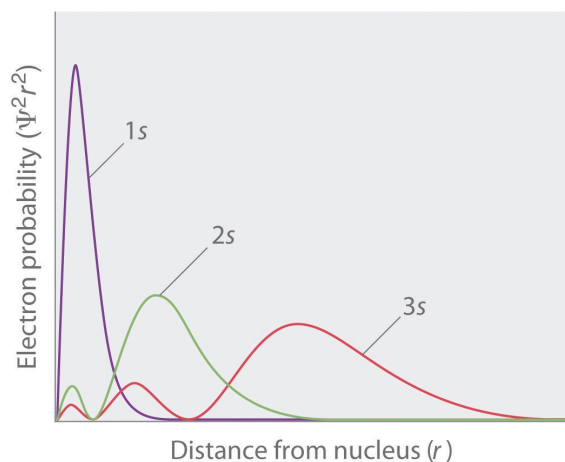
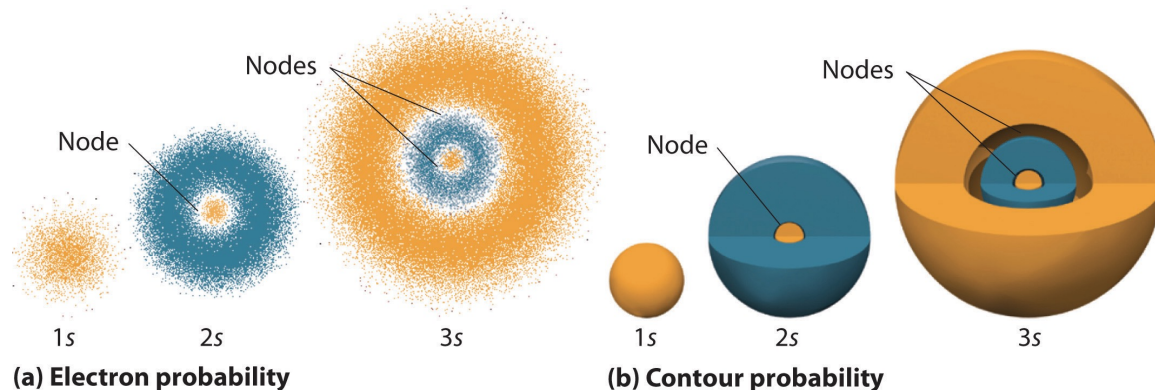
1s orbital



Energy band-gap

The dual nature of the electron

This results in different levels with principal quantum number n , and with sub-levels s, p, d, \dots defined by the angular momentum number l, \dots



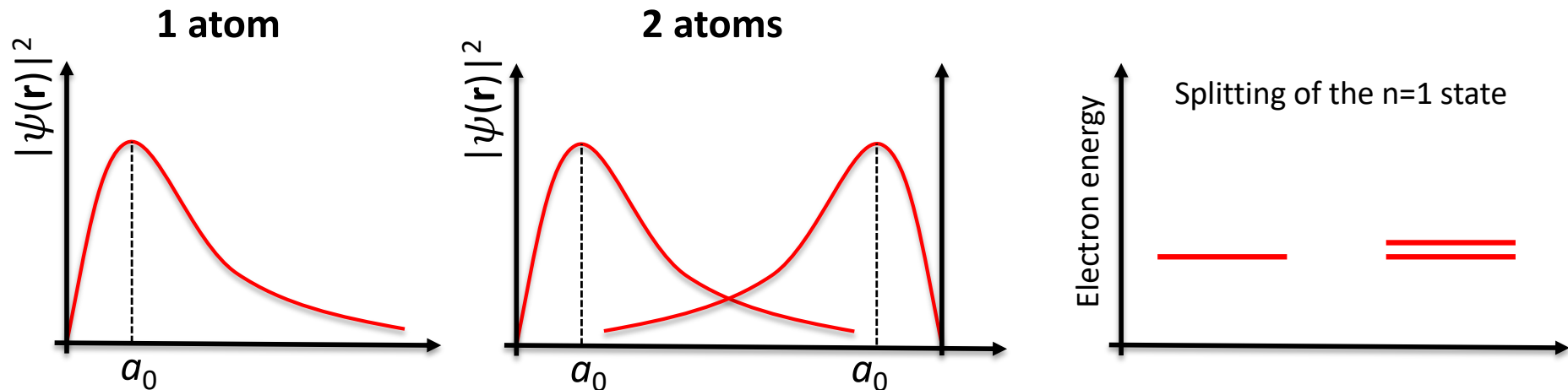
What happens when atoms come together?

Pauli exclusion principle: no two electrons occupying the same space, can have the same energy.

Thus, as **atoms are brought closer** towards one another and begin to bond together, their **energy levels must split** into bands of discrete levels so closely spaced in energy that they can be considered a continuum of allowed energy.

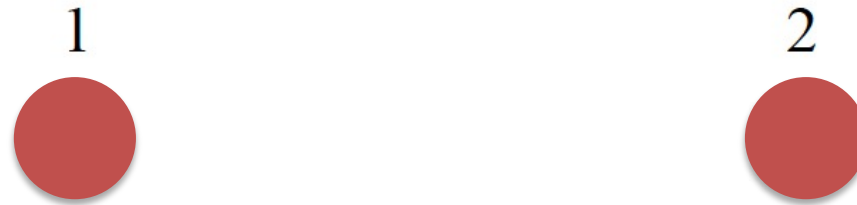
The wavefunction of the electrons overlap: two electrons will interact

This perturbation results in discrete quantized energy levels **splitting into two discrete energy levels**



Strongly bonded materials tend to have small interatomic distances between atoms. Thus, the strongly bonded materials can have larger energy bandgaps than weakly bonded materials.

What happens when atoms come together?



$$H_1\varphi_1 = E_{01}\varphi_1$$

$$H_2\varphi_2 = E_{02}\varphi_2$$

When atoms come close to each other, the electron wavefunction is delocalized on atoms 1 and 2 :

$$\psi = (c_1\varphi_1 + c_2\varphi_2) \quad \text{Linear combination of atomic orbitals}$$

$$\frac{p^2}{2m}\psi + (V_1 + V_2)\psi = E\psi$$

What happens when atoms come together?

Develop and project on φ_1 and φ_2

$$c_1 E_{01} + c_2 E_{02} \langle \varphi_1 | \varphi_2 \rangle + c_2 \langle \varphi_1 | V_1 | \varphi_2 \rangle + c_1 \langle \varphi_1 | V_2 | \varphi_1 \rangle = E c_1 + c_2 E \langle \varphi_1 | \varphi_2 \rangle$$

$$c_1 E_{01} \langle \varphi_2 | \varphi_1 \rangle + c_2 E_{02} + c_2 \langle \varphi_2 | V_1 | \varphi_2 \rangle + c_1 \langle \varphi_2 | V_2 | \varphi_1 \rangle = E c_2 + c_1 E \langle \varphi_2 | \varphi_1 \rangle$$

$$\begin{vmatrix} (E_{01} - E) + \langle \varphi_1 | V_2 | \varphi_1 \rangle & (E_{02} - E) \langle \varphi_1 | \varphi_2 \rangle + \langle \varphi_1 | V_1 | \varphi_2 \rangle \\ (E_{01} - E) \langle \varphi_2 | \varphi_1 \rangle + \langle \varphi_2 | V_2 | \varphi_1 \rangle & (E_{02} - E) + \langle \varphi_2 | V_1 | \varphi_2 \rangle \end{vmatrix} = 0$$

- Can be solved as it is 😊
- But it can be simplified by introducing assumptions which are done in the real semiconductor band structure calculations based on this approach (Tight Binding) 😊 😊

What happens when atoms come together?

$$\begin{vmatrix} (E_{01} - E) + \langle \varphi_1 | V_2 | \varphi_1 \rangle & (E_{02} - E) \langle \varphi_1 | \varphi_2 \rangle + \langle \varphi_1 | V_1 | \varphi_2 \rangle \\ (E_{01} - E) \langle \varphi_2 | \varphi_1 \rangle + \langle \varphi_2 | V_2 | \varphi_1 \rangle & (E_{02} - E) + \langle \varphi_2 | V_1 | \varphi_2 \rangle \end{vmatrix} = 0$$

$\langle \varphi_1 | \varphi_2 \rangle = 0$ Not strictly true. In addition $E_{02} - E$ is expected to be small

$\langle \varphi_1 | V_2 | \varphi_1 \rangle = \langle \varphi_2 | V_1 | \varphi_2 \rangle$ by symmetry

Describes the effect of the potential of atom 2 on the energy in atom 1, and vice versa. It is a shift of the energy, with no important effect.

(when atoms are different or with less trivial symmetries, it has an effect).

Let us renormalize the energies :

$$E_1 = E_{01} + \langle \varphi_1 | V_2 | \varphi_1 \rangle$$

$$E_2 = E_{02} + \langle \varphi_2 | V_1 | \varphi_2 \rangle$$

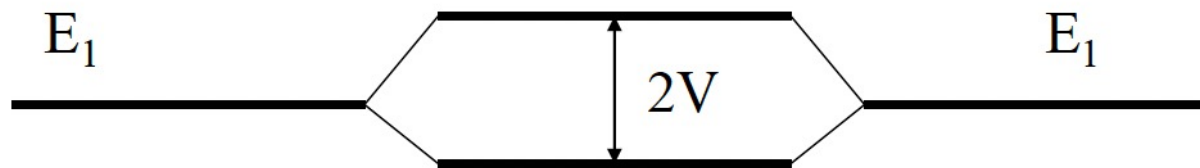
What happens when atoms come together?

$$\begin{vmatrix} (E_1 - E) & \langle \varphi_1 | V_1 | \varphi_2 \rangle \\ \langle \varphi_2 | V_2 | \varphi_1 \rangle & (E_2 - E) \end{vmatrix} = 0$$

We introduce : $\langle \varphi_1 | V_1 | \varphi_2 \rangle \times \langle \varphi_2 | V_2 | \varphi_1 \rangle = V^2$

$$E = \frac{(E_1 + E_2)}{2} \pm \sqrt{\left(\frac{E_1 - E_2}{2}\right)^2 + V^2}$$

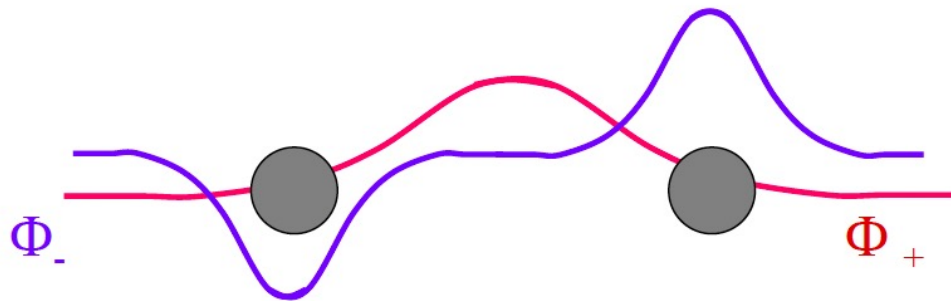
If atoms are identical: $E_1 = E_2$ $E = E_1 \pm |V|$



2 new energy eigenvalues

What happens when atoms come together?

2 new eigen states



$$\Phi_+ = \frac{1}{\sqrt{2}} (\varphi_1 + \varphi_2)$$

Lowest energy: bonding state

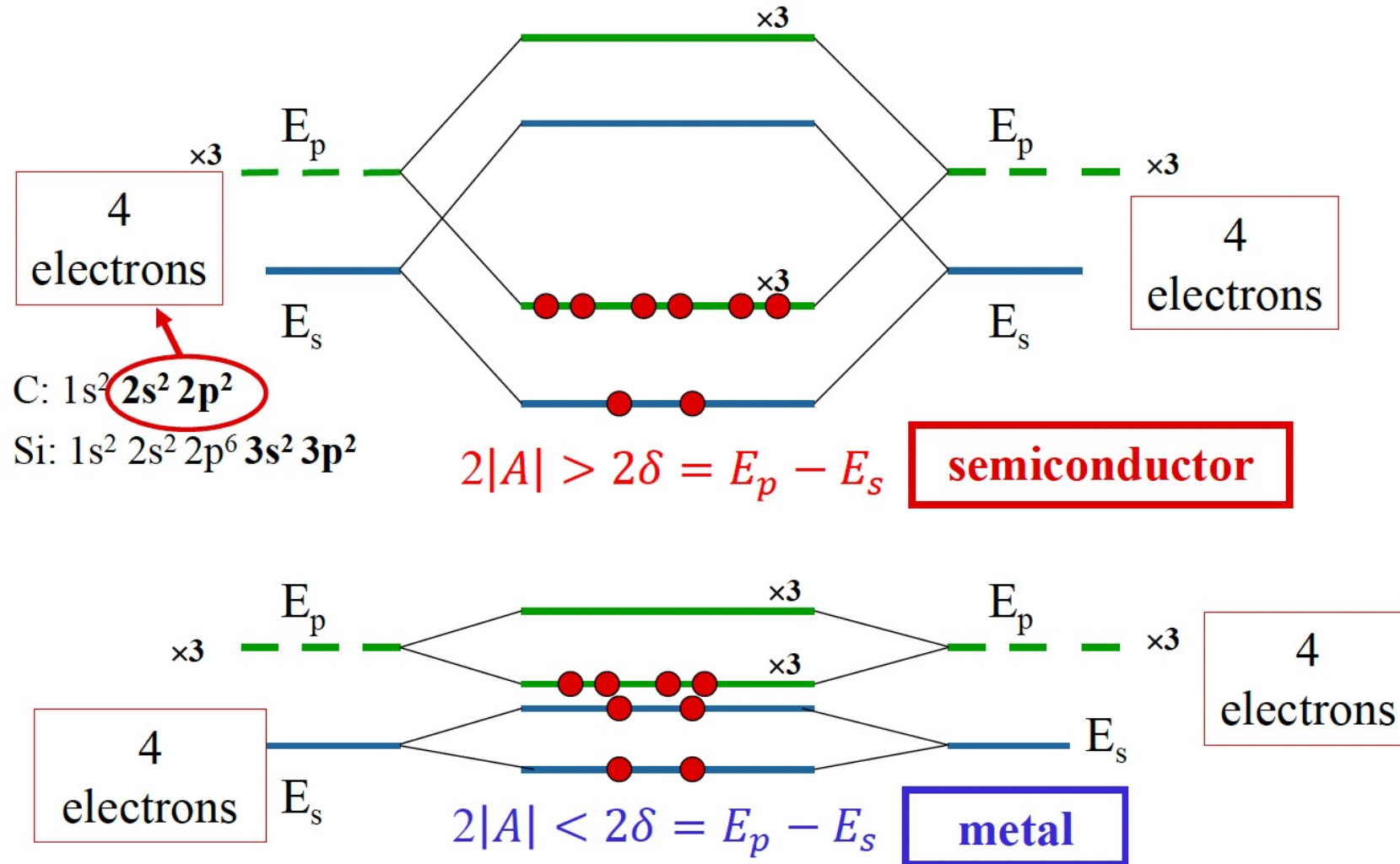
$$\Phi_- = \frac{1}{\sqrt{2}} (\varphi_1 - \varphi_2)$$

Highest energy: anti-bonding state

Energy band-gap

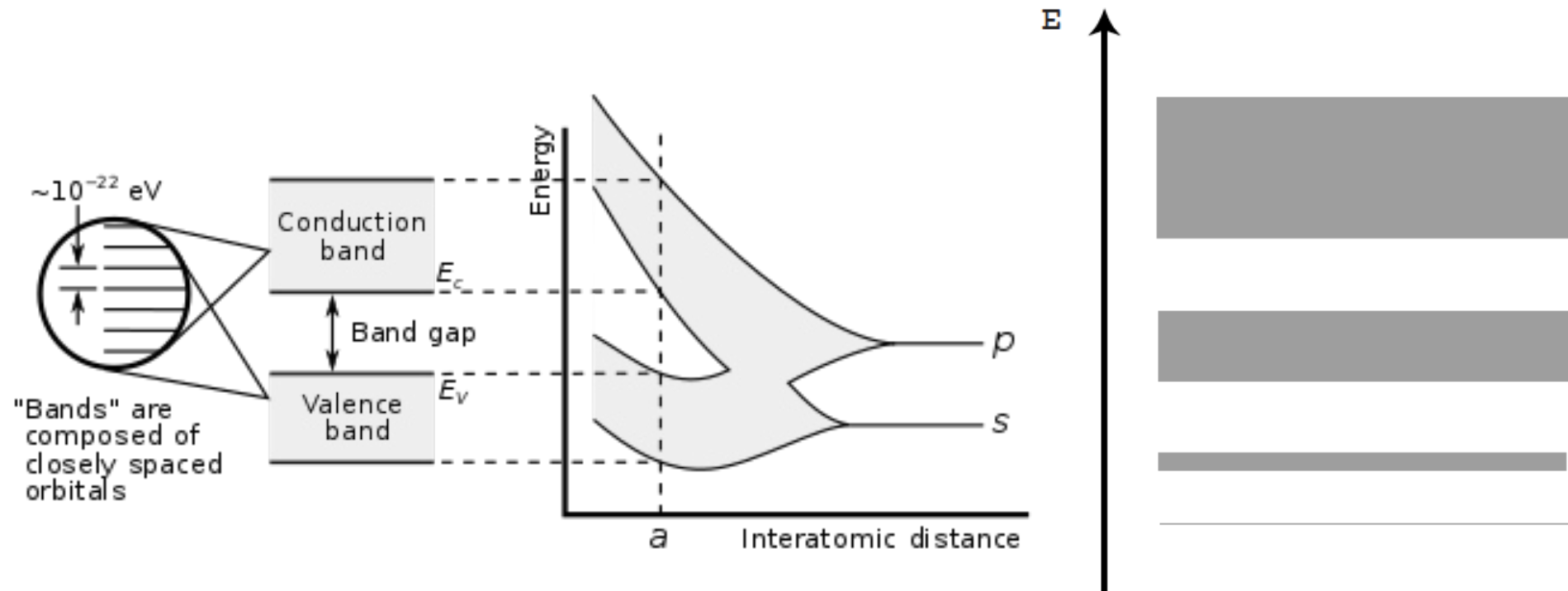
What happens when atoms come together?

Metals versus semiconductors



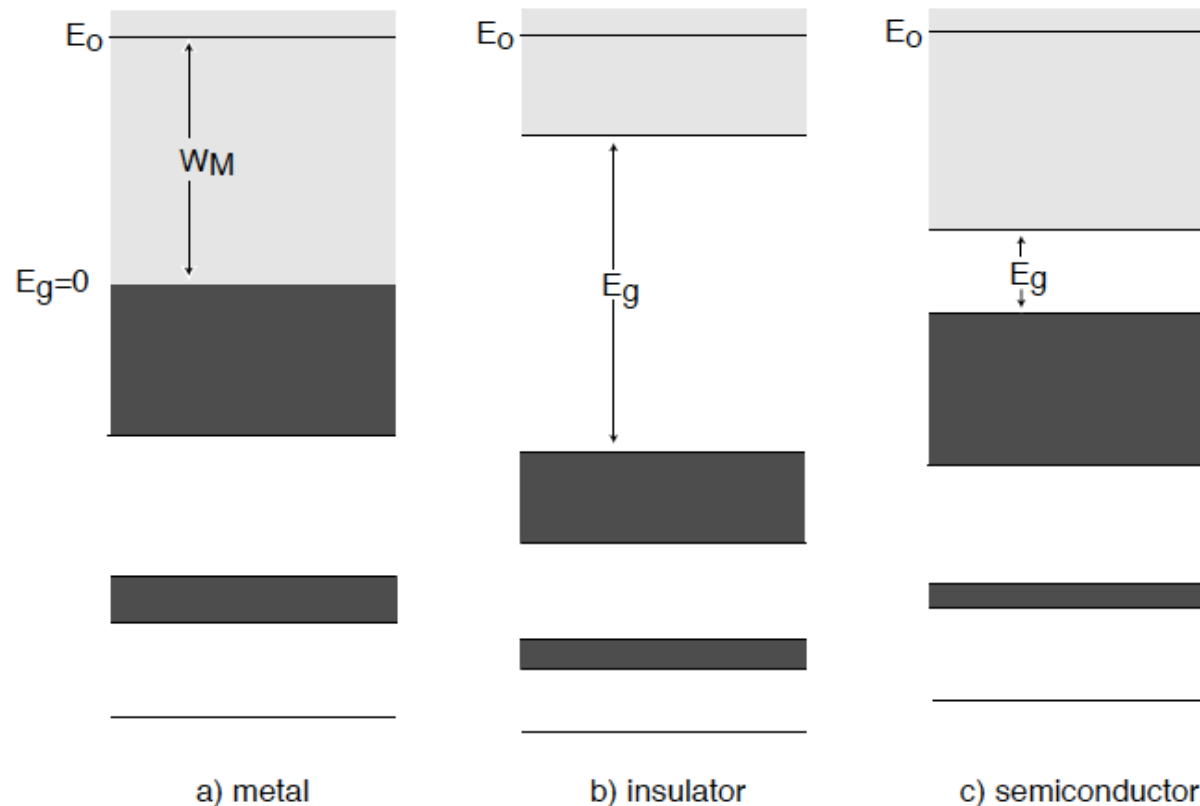
Energy band-gap

Quantum states cluster in bands leaving bandgaps (regions without allowed states) in between.



Electronic structure of semiconductors

Quantum states filled with one electron per state starting from lowest energy state (Pauli exclusion principle)



At 0 K: the energy of the top-most energy state filled is called the **Fermi level**

No conduction is possible in a full band insulators: semiconductors do not conduct at 0 K.

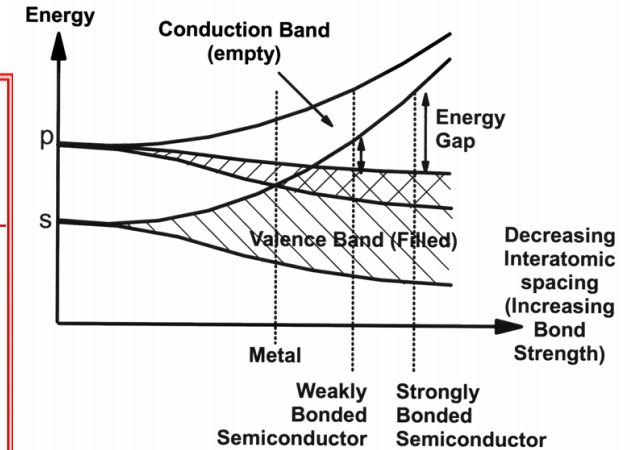
Conduction requires a partially filled band: metals conduct at 0 K.

But in semiconductors at finite temperatures, some electrons populate next band above bandgap conduction becomes possible.

Energy band-gap

Consider the case of the group 4 elements, all covalently bonded

Element	Atomic Radius/Lattice Constant (How closely spaced are the atoms?)	Bandgap
C	0.91/3.56 Angstroms	5.47 eV
Si	1.46/5.43 Angstroms	1.12 eV
Ge	1.52/5.65 Angstroms	0.66 eV
α -Sn	1.72/6.49 Angstroms	~ 0.08 eV*
Pb	1.81/** Angstroms	Metal



*Only has a measurable bandgap near 0K

**Different bonding/Crystal Structure due to unfilled higher orbital states

How Energy Bands and Energy Gap are calculated?

The dual nature of the electron

If it is a wave, we can define a wavevector: $\psi(x, t) = A \cos(kx - \omega t + \varphi)$

where:

$$\omega = \frac{2\pi}{T} \text{ and } k = \frac{2\pi}{\lambda}$$

