Electronic Bandstructures

Topics in Kittel's Ch. 7

Bandstructure ≡ E(k)

- We are interested in understanding the ***PHYSICS*** of the behavior of electronic energy levels in crystalline solids as a function of wave vector **k** or "momentum" **p = ħk.**
  - Much of our discussion will be valid ***in general***, for metals, insulators, & semiconductors.
- **Group Theory:** The math of ***symmetry*** that can be useful to simplify calculations of **E(k).** We won't be doing this in detail. But we will introduce some of it's results & notation.

Bandstructure Theory: ***A Very Mathematical Subject!***

- Detailed math coverage will be kept to a minimum. Results and the ***PHYSICS*** will be emphasized over math!

Many Methods to *Numerically* Calculate E(k):

- They are highly sophisticated & computational!
- We'll only have an overview of the most important methods.

Basic knowledge that I ***must assume*** that you know:

1. Electron **energies** are **quantized** (***discrete***).
2. You have at least seen the **Schrödinger Equation**
   - It is the **fundamental equation** that ***governs*** (non-relativistic) **quantum mechanics**
   - If you are weak on this or need a review, please ***get & read*** an undergraduate quantum mechanics book!
3. You understand the basic **Crystal Structures** of some common crystals (as in **Kittel's Ch. 1**).
4. In a crystal, **electronic energy levels** form into **regions of allowed energy (*bands*)** & **forbidden energy (*gaps*).**

Overview

- A qualitative & semi-quantitative treatment now. Later, a more detailed & quantitative treatment.

Electronic Energy Bands ≡
Bandstructure ≡ E(k)

- The bandstructure gives the dependence of the electronic energy levels in crystalline materials as a function of **wave vector k** or "momentum" **$p = \hbar k$**.
- **For *FREE* electrons, $E(k) = (p)^2/2m_o = (\hbar k)^2/2m_o$**

  (m_o= free electron mass)
- **In Crystalline Solids, E(k)** forms into regions of allowed energies (***bands***) & regions of forbidden energies (***gaps***).

As we'll see,

- **Often** in solids, for **k** in some high symmetry regions of the **1st Brillouin Zone**, a ***Good Approximation*** is:

$$E(k) = (\hbar k)^2/2m^*$$

m^* is *not* m_o!

In general, m^* is a tensor, not a scalar & it is k dependent!

$m^* = m^*(k)$ = "effective mass"

The E(k) can be complicated!

- Calculation of **E(k)** requires sophisticated quantum mechanics ***AND*** computational methods to obtain them numerically!

Bands in "r-space" (functions of position in the solid)

- One way to distinguish between solid types is by ***how the electrons fill the bands & by the band gaps!***

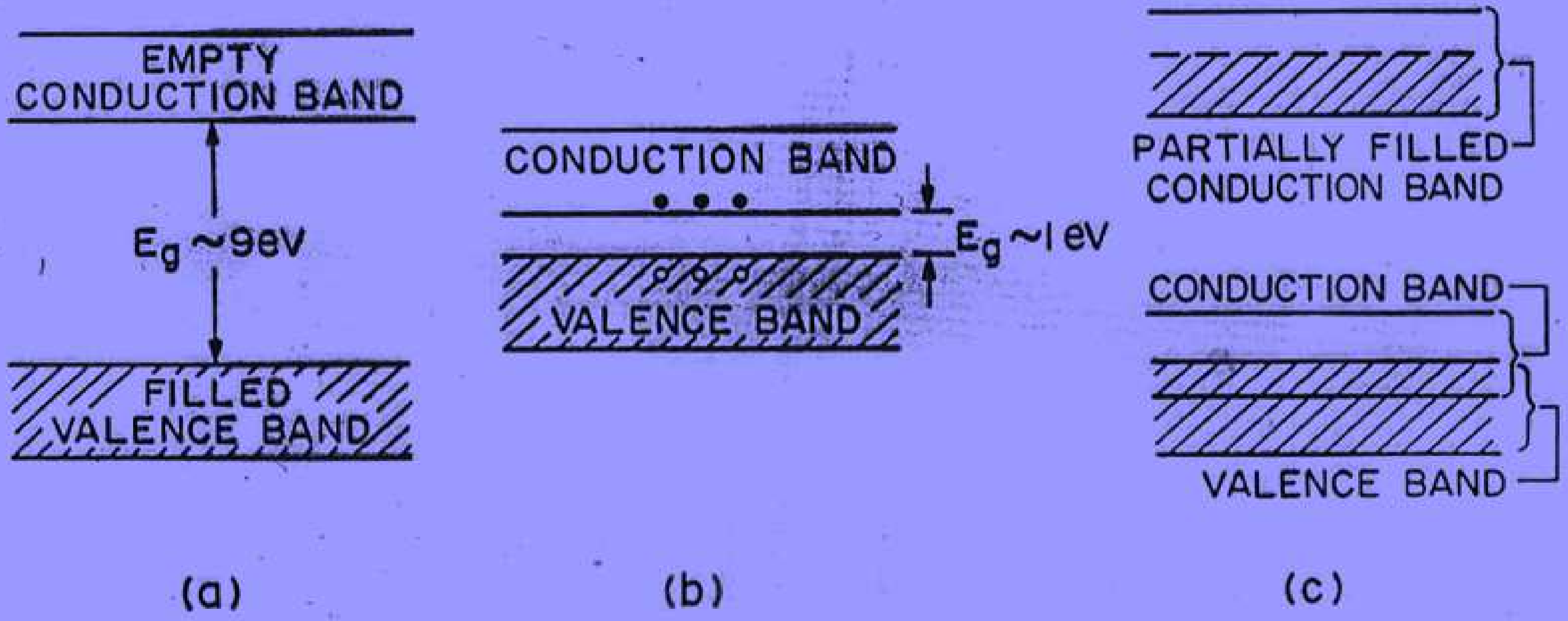
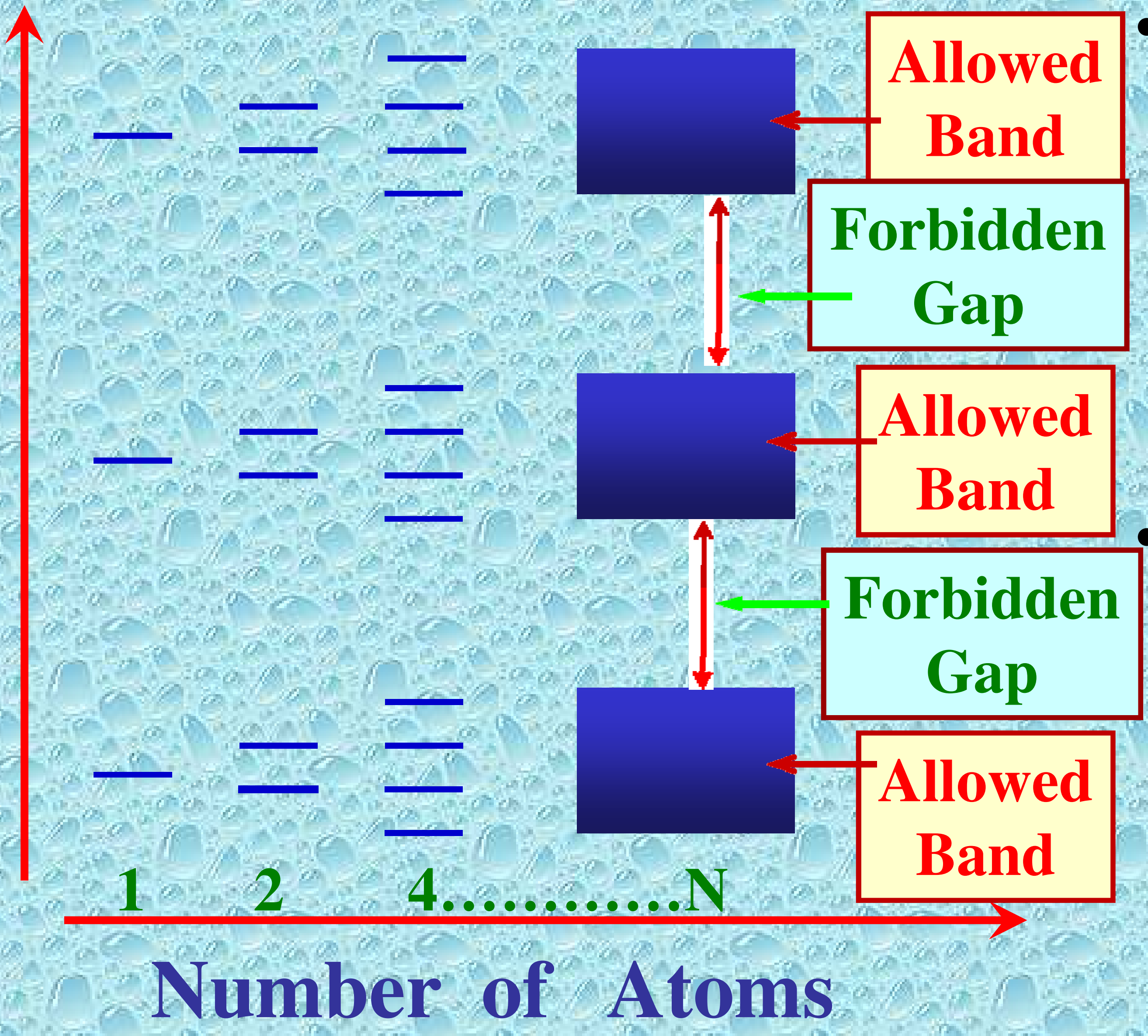


Fig. 9 Schematic energy band representations of (*a*) an insulator, (*b*) a semiconductor and (c) conductors.

- **Note:** Bandstructures **E(k)** are bands in **"k-space"** (functions of **k** or momentum in solids), which is *a completely different picture* than is shown here.

Electronic Energy Bands

Qualitative Picture



- Electrons occupying the quantized energy states around a nucleus must obey the ***Pauli Exclusion Principle.***
- This prevents more than 2 electrons (of opposite spin) from occupying the same level.

- In a solid, the energy differences between each of the discrete levels is so tiny that it is reasonable to consider each of these sets of energy-levels as being continuous ***BANDS*** of energy, rather than considering an enormous number of discrete levels. On solving the **Schrödinger Equation**, it is found that

  1. There are regions of energy **E** for which a solution exists (that is, where **E** is real). These regions are called the

Allowed Bands

(or just the Bands!).

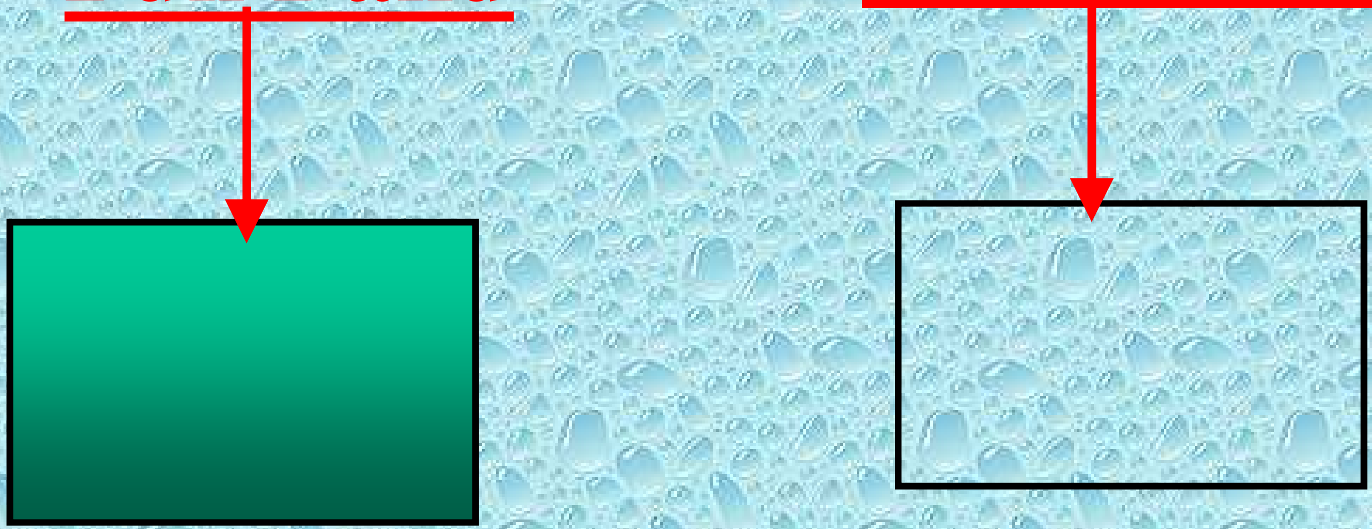
- On solving the **Schrödinger Equation**, it is also found that

  2. There are regions of energy **E** for which no solution exists (for real **E**). These regions are called the

  Forbidden Gaps.

- Obviously, electrons can only be found in the ***Allowed Bands*** & they can’t be found in the ***Forbidden Gaps.***

Semiconductors, Insulators, Conductors



Full Band

All energy levels are occupied (contain electrons)

Empty Band

All energy levels are empty

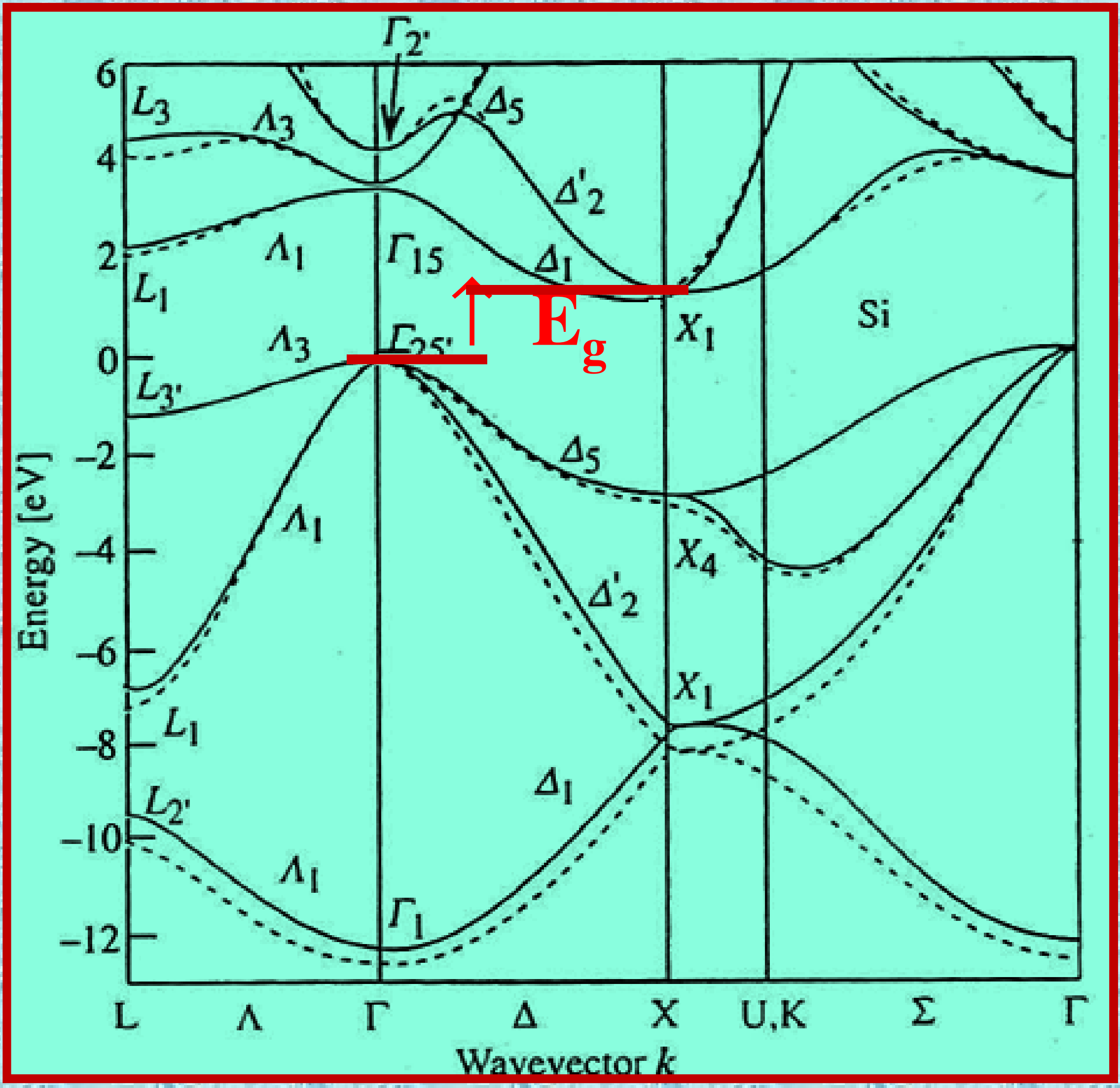
It can be shown that

Neither full nor empty bands participate in electrical conduction.

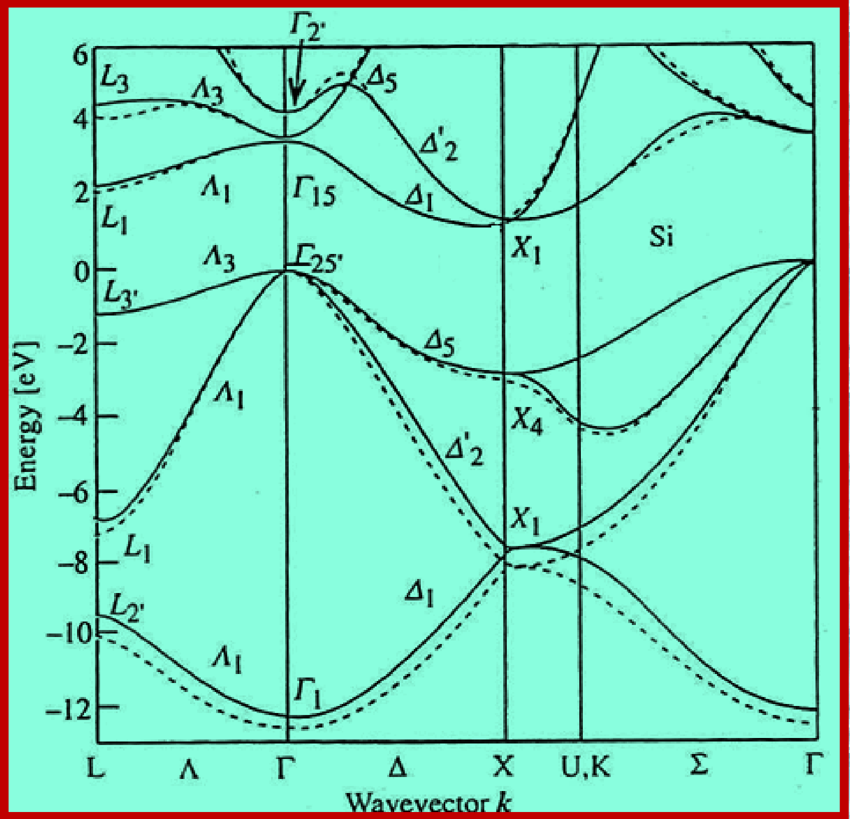
FYI: Calculated Si Bandstructure

Fig. 2.10. Electronic band structure of Si calculated by the pseudopotential technique. The *solid* and the *doted lines* represent calculations with a **nonlocal** and a **local pseudopotential**, respectively. [Ref. 2.6, p. 81]

Note: Si has
an indirect
Fundamental
Band Gap E_g



Calculated Si Bandstructure



GOALS

After this chapter, you should:

1. Understand the underlying physics behind the existence of bands & gaps.

2. Understand how to interpret this figure.

3. Have a rough, general idea about how realistic bands are calculated.

4. Be able to calculate energy bands for some simple models of a solid.

Brief Review of Quantum Mechanics

- **QM results** :
  Utilization of

  The Schrödinger Equation

  describes electrons i.e.
- Solutions to the **Schrödinger Equation** result in ***quantized*** (discrete) **energy levels** for electrons.

Quantum Mechanics (QM)

The Schrödinger Equation:

(**time independent**)

$$H\psi = E\psi$$

- This is a differential (or matrix) eigenvalue equation.

H ≡ Hamiltonian operator for the system

(energy operator)

E ≡ Energy eigenvalue, ψ ≡ wavefunction

Particles are QM waves!

$|\psi|^2$ ≡ probability density

ψ is a function of ***ALL*** coordinates

of ***ALL*** particles in the problem!

The Physics **Behind E(k)**

E(k) ≡ Solutions to the **Schrödinger Equation** for an electron in a solid.

QUESTIONS

Why (***qualitatively***) are there bands?

Why (***qualitatively***) are there gaps?

Bands & Gaps

- These can be understood from

  2 very different

  qualitative pictures!!
- The 2 pictures are models & are the

  Opposite Limiting Cases

  of the true situation!
- Consider an electron in a perfectly periodic crystalline solid: The potential seen by this electron is perfectly periodic

The existence of the periodic potential the cause of the bands & the gaps!

Qualitative Picture #1

" Physicist's viewpoint"- Looked at the solid **"collectively"**

The *Almost* Free Electron Picture

(done in detail in Kittel's Ch. 7!)

- **For *free electrons*,**

$$E(k) = (p)^2/2m_o = (\hbar k)^2/2m_o$$

The Almost Free Electron Picture

- Start with the free electron **E(k)**, add a small (weakly perturbing) ***periodic* potential V**. This breaks up **E(k)** into bands (allowed energies) & gaps (forbidden energy regions).
- **Gaps** occur at the **k** where the electron waves (incident on atoms & scattered from atoms) undergo **constructive interference** (Bragg reflections!)

Qualitative Picture #1

Forms the starting point for **REALISTIC** bandstructure computational methods!

- Starting from the ***almost free electron*** viewpoint & adding a high degree of sophistication & theoretical + computational rigor:
- Results in a method that works ***VERY WELL*** for calculating **E(k)** for ***metals & semiconductors!***

An "alphabet soup" of computational techniques:

- **OPW**: **O**rthogonalized **P**lane **W**ave method
- **APW**: **A**ugmented **P**lane **W**ave method
- **ASW**: **A**ntisymmetric **S**pherical **W**ave method
- Many, many others

The Pseudopotential Method

(the modern method of choice!)

Qualitative Picture #2

“Chemist’s Viewpoint”:

The solid is looked at as a collection of atoms & molecules.

Atomic / Molecular **Electrons**

- Atoms (with discrete energy levels) come together to form the solid
- Interactions between electrons on neighboring atoms cause the atomic energy levels to split, hybridize, & broaden.

(*Quantum Chemistry!*)

Qualitative Picture #2

"Chemist's Viewpoint":

The solid is looked at as a collection of atoms & molecules.

(***Quantum Chemistry!***)

- ***First Approximation*: Small Interaction V!**
  - The interaction **V** is periodic.
  - Groups of levels come together to form bands (also gaps).
  - The bands **E(k)** retain much of the character of their "parent" atomic levels (**s**-like and **p**-like bands, etc.)
  - **Gaps:** Also occur at the **k** where the electron waves (incident on atoms & scattered from atoms) undergo ***constructive interference*** (Bragg reflections!)

Qualitative Picture #2

Forms the starting point for ***REALISTIC*** bandstructure computational methods!

- Starting from the ***atomic / molecular electron*** viewpoint & adding a high degree of sophistication & theoretical & computational rigor.
- Results in a method that works ***VERY WELL*** for calculating **E(k)** (mainly the valence bands) for ***insulators & semiconductors!*** (Materials with covalent bonding!)
- **An "*alphabet soup*" of computational techniques:**

LCAO: Linear Combination of Atomic Orbitals method

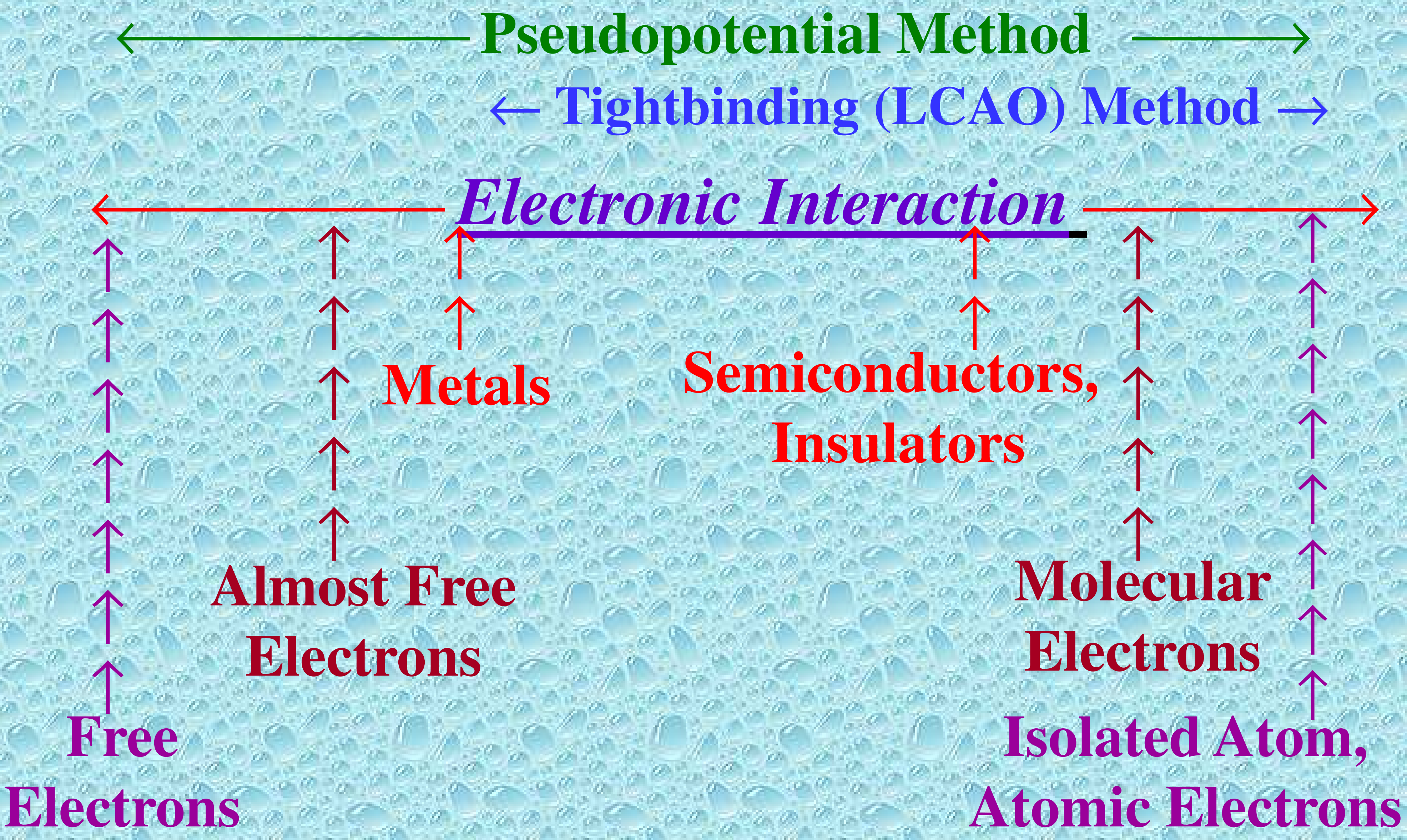
LCMO: Linear Combination of Molecular Orbitals method

- The "***Tightbinding***" method & many others.

The Pseudopotential Method

(the modern method of choice!)

Theories of Bandstructures in Crystalline Solids



← Pseudopotential Method →

← Tightbinding (LCAO) Method →

← *Electronic Interaction* →

Metals

Semiconductors, Insulators

Almost Free Electrons

Molecular Electrons

Free Electrons

Isolated Atom, Atomic Electrons