

SEMICONDUCTOR PHYSICS REVIEW – BONDS, BANDS, EFFECTIVE MASS

February 21, 2012

The University of Toledo, Department of Physics and Astronomy
SSARE, PVIC

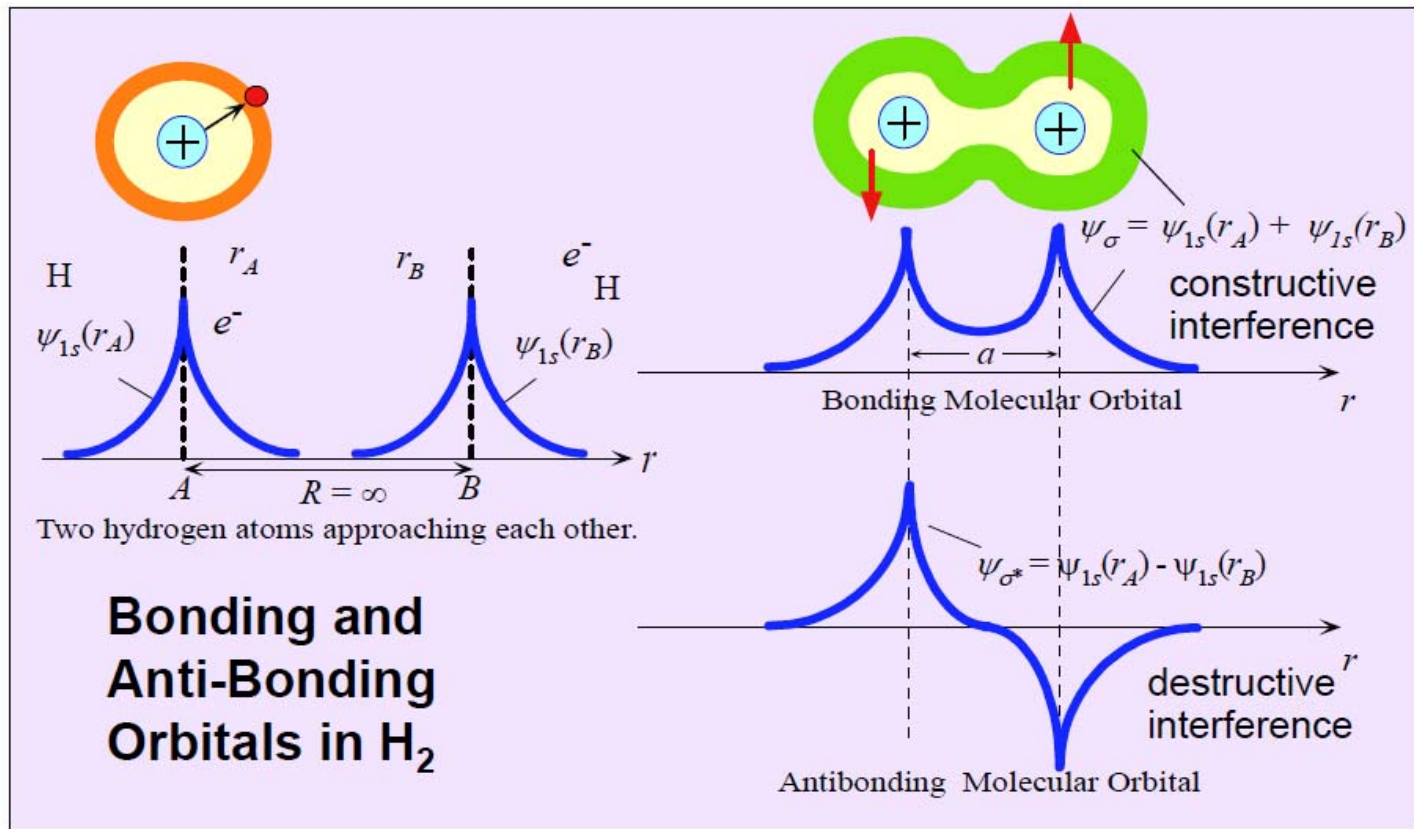
Principles and Varieties of Solar Energy (PHYS 4400)
and
Fundamentals of Solar Cells (PHYS 6980)



On today's menu

- Review of semiconductor physics
 - bonds and bands in crystals
 - electrons and holes
 - valence/conduction bands,
 - HOMO-LUMO concepts
- drift and diffusion
- photogenerated carriers
 - Absorption coefficient, depth dependence
 - direct vs. indirect gap
- recombination mechanisms





Formation of molecular orbitals, bonding and antibonding (ψ_{σ} and ψ_{σ^*}) when two H atoms approach each other. The two electrons pair their spins and occupy the bonding orbital ψ_{σ} .

5Fig 4.1

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Molecular Orbitals of H₂

In bringing the two atoms together, the two identical 1s atomic orbitals indicated by the wavefunctions $\psi_{1s}(\mathbf{r})$, that can accommodate two electrons each in the two isolated atoms, evolve into two molecular orbitals that can do the same in the molecule, but without violation of the Pauli Exclusion Principle.

Thus, as the two atomic orbitals interact, they lead to two new one electron wavefunctions with different energy levels and accommodating two electrons each, with four different sets of quantum numbers, i.e., four states in all.

The interaction can lead to constructive or destructive interference of the one electron wavefunctions:

$$\psi_{\sigma}^{(g)} = \frac{\psi_{1s}(\mathbf{r}_A) + \psi_{1s}(\mathbf{r}_B)}{[2(I + 1)]} \quad \psi_{\sigma^*}^{(u)} = \frac{\psi_{1s}(\mathbf{r}_A) - \psi_{1s}(\mathbf{r}_B)}{[2(I + 1)]}$$

I is an "overlap integral" used for normalization. This approach to generating molecular orbitals is the LCAO method described on the previous slide.

The + sign corresponds to a molecular orbital that is spatially symmetric with respect to the midpoint between the atoms (labeled "g" for *gerade* or *even*) and

the – sign corresponds to a spatially antisymmetric orbital ("u" for *ungerade* or *odd*).

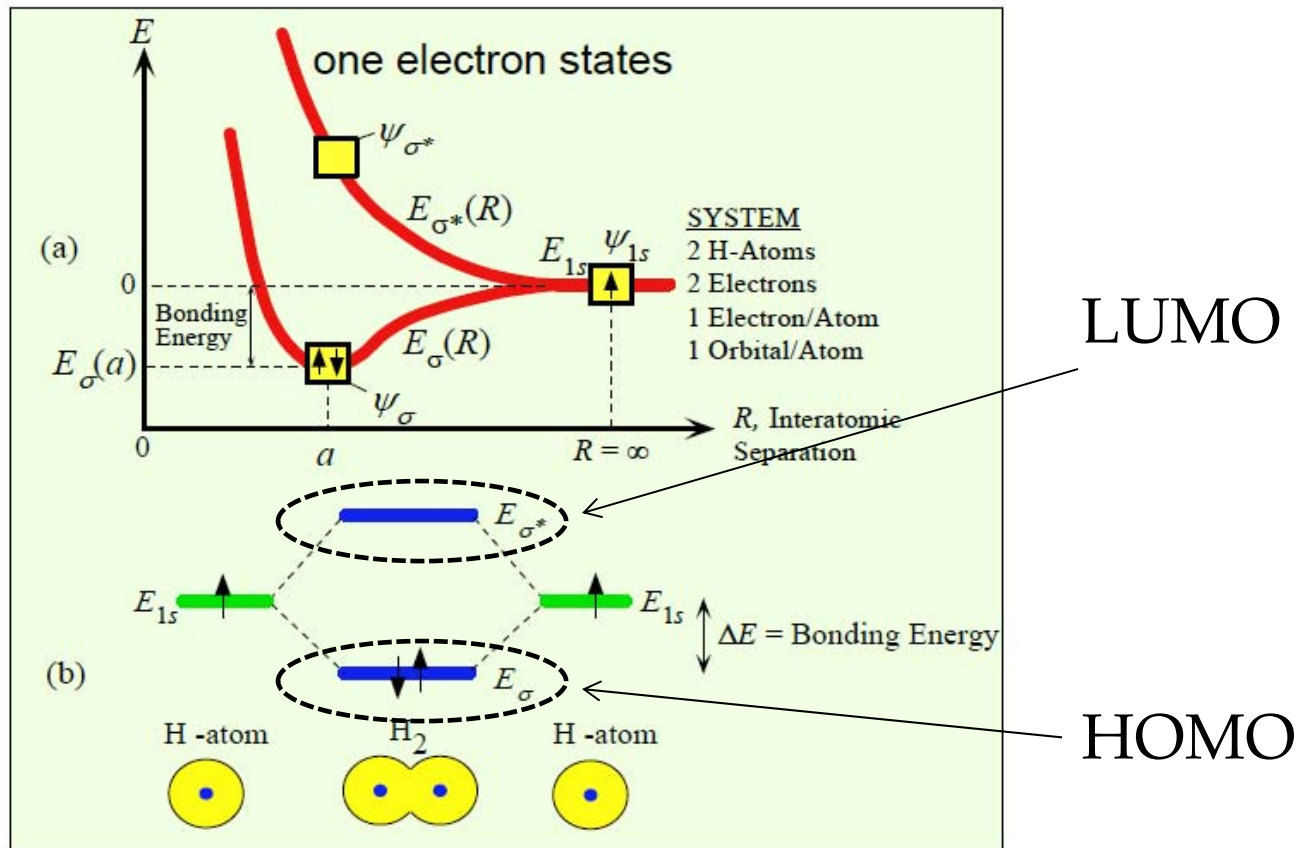
For the + sign, the electron density between the two protons is higher;

this effect leads to a lower potential energy by enabling the electron density to be close to two protons simultaneously, a characteristic of a *bonding orbital*.

For the – sign, a node in the electron density exists between the atoms; this configuration leads to a higher energy level, a characteristic of an *antibonding orbital*.



Electronic Energy Levels of the H₂ Molecule



Electron energy in the system comprising two hydrogen atoms. (a) Energy of ψ_σ and ψ_{σ^*} vs. the interatomic separation, R . (b) Schematic diagram showing the changes in the electron energy as two isolated H atoms, far left and far right, come together to form a hydrogen molecule.

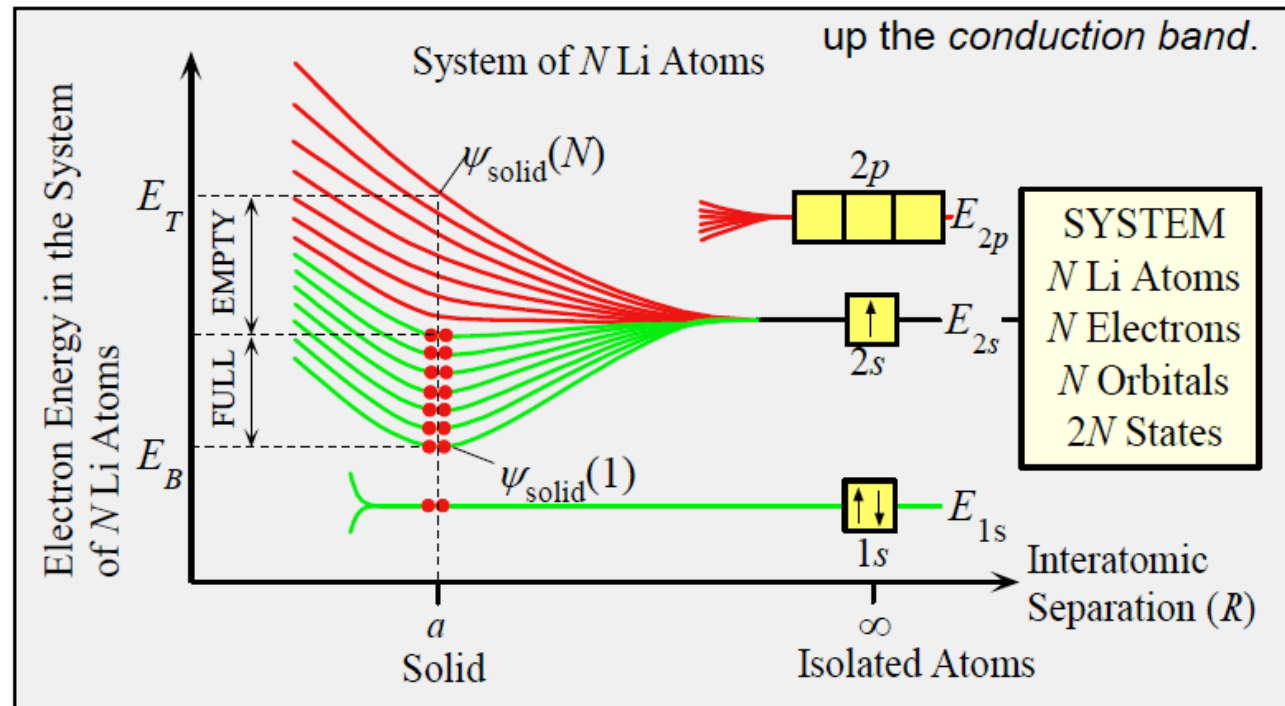
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Band Theory of Solids

The full 1s atomic states form full 1s core states in the solid.

The half-filled 2s atom states form half-filled 2s valence states in the solid that make

N "levels"
 $2N$ "states"

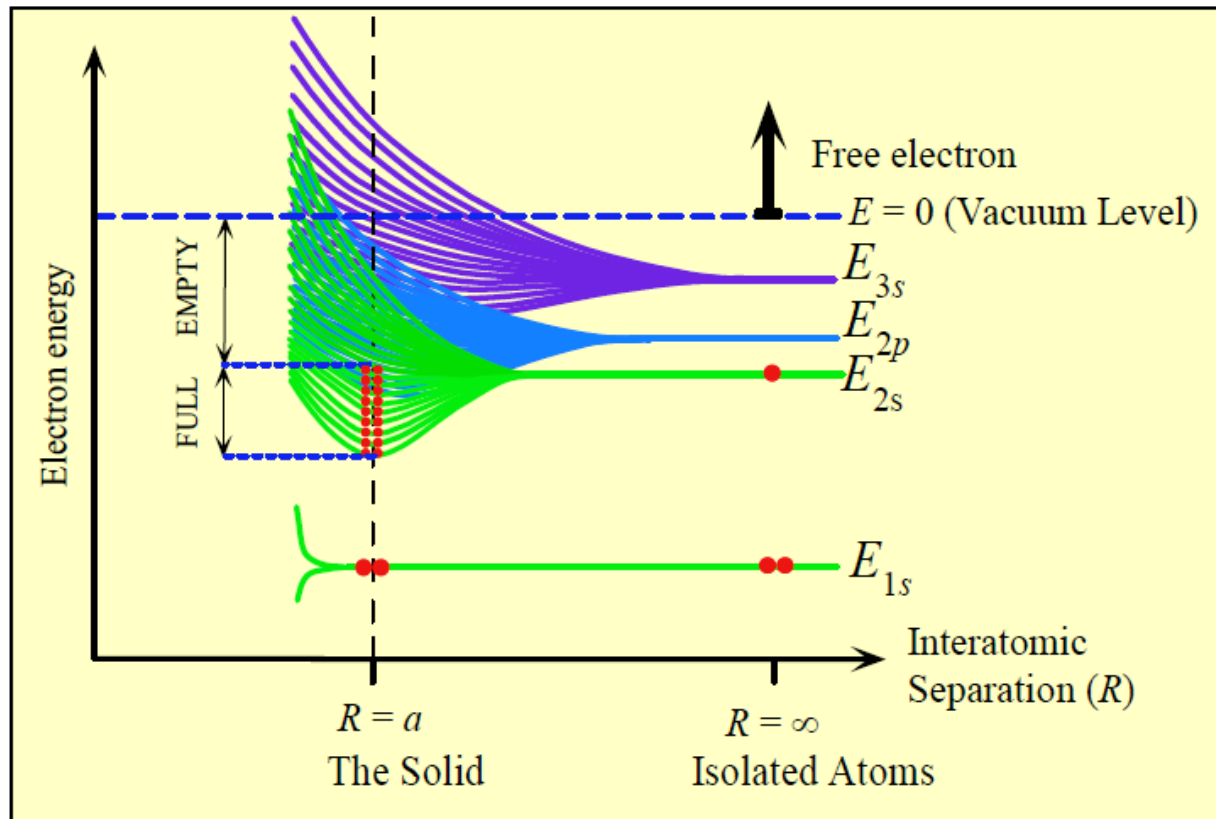


The formation of a 2s-energy band from the 2s-orbitals when N Li atoms come together to form the Li solid. There are N 2s-electrons but $2N$ states in the band. The 2s-band therefore is only half full. The atomic 1s orbital is close to the Li nucleus and remains undisturbed in the solid. Thus each Li atom has a closed K-shell (full 1s orbital).

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Band Theory of Solids



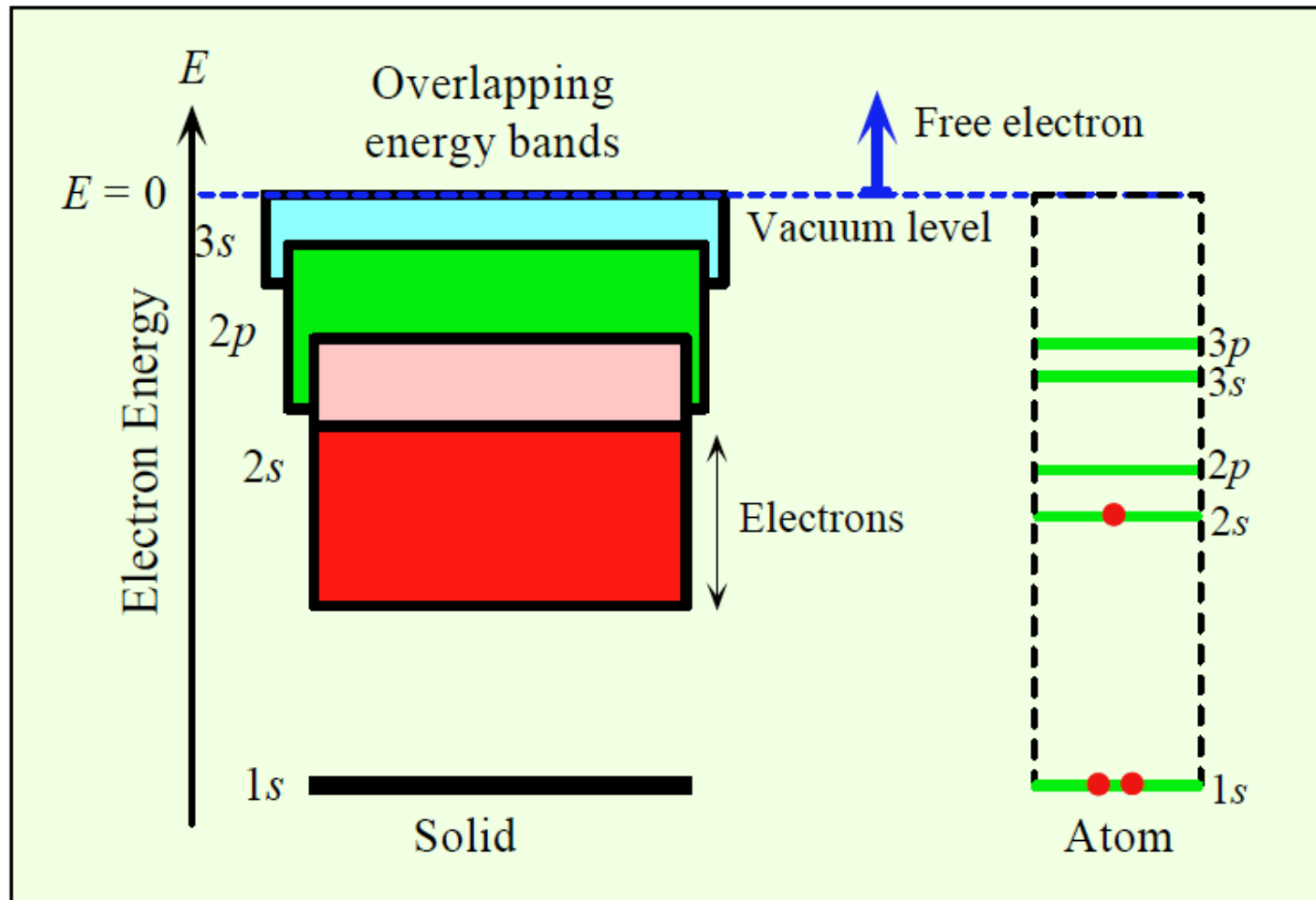
As solid atoms are brought together from infinity, the atomic orbitals overlap and give rise to bands. Outer orbitals overlap first. The 3s orbitals give rise to the 3s band, 2p orbitals to the 2p band and so on. The various bands overlap to produce a single band in which the energy is nearly continuous.

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Band Theory of Solids

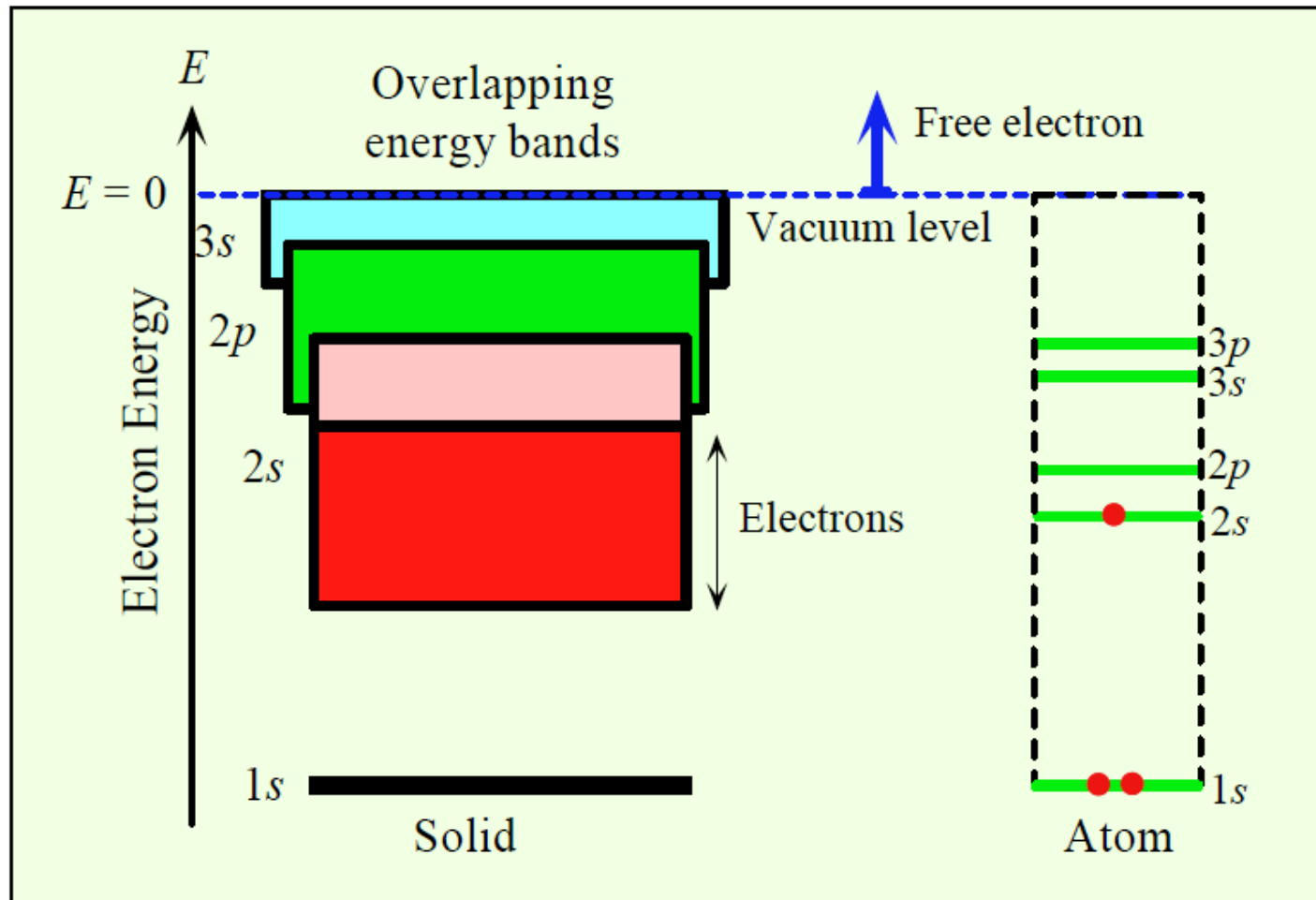


In a metal the various energy bands overlap to give a single band of energies that is only partially full of electrons. There are levels with energies up to the vacuum level where the electron is free.

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Band Theory of Solids



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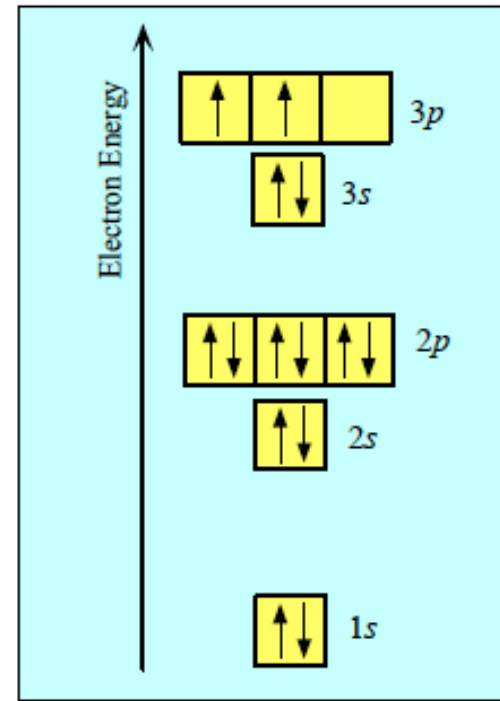
Semiconductors

As a prototypical semiconductor, consider Si which has 14 electrons.

When atoms are brought together to form a solid, the filled $n = 1$ and $n = 2$ shells act as core electrons and do not participate in the bonding. Thus, they show little energy spread in the solid.

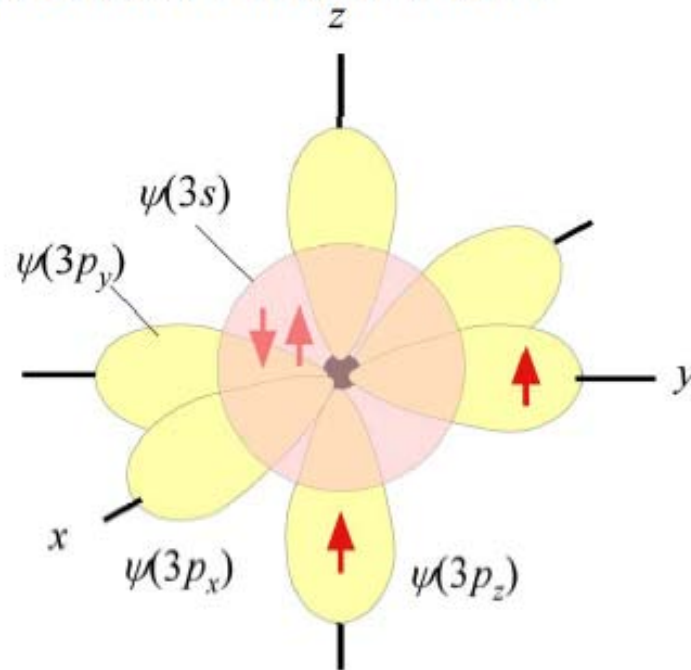
The 4 valence electrons with $n = 3$ have energies that are relatively close. So when five Si atoms are brought together, the orbitals that interact are the $3p$ and $3s$. What is found is that the orbitals reorganize to maximize the overlap in three dimensions in a process called *hybridization*.

The valence electrons of atoms considered so far have been in partially filled s states ($l = 0$) which are non-directional and so do not show such an effect. As a result, an atom such as Li forms a BCC crystal and one electron per Li atom is free to move throughout the crystal.



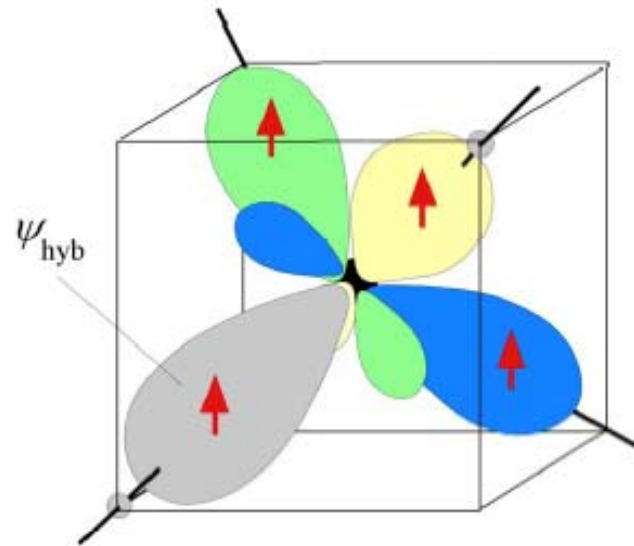
The four atomic orbitals $\psi(3s)$, $\psi(3p_x)$, $\psi(3p_y)$, $\psi(3p_z)$ with a capacity of 8 electrons hybridize into four sp^3 molecular orbitals oriented in a tetrahedron also with a capacity of 8 electrons (see next slide).

Isolated Silicon Atom



(a) Isolated Si

Silicon Atom in a Solid



(b) Si before it bonds

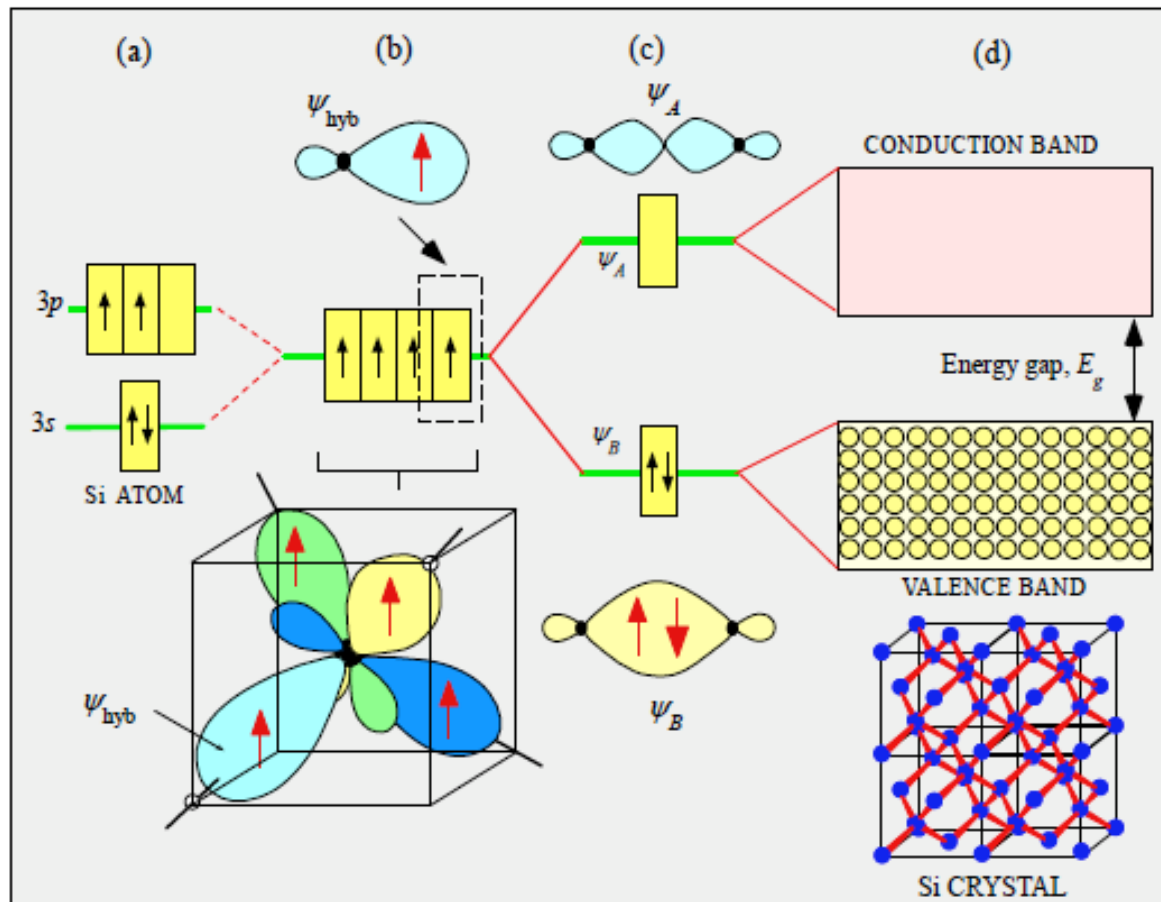
Molecular Orbitals from Hybridization of Atomic Orbitals

(a). Si is in Group IV in the Periodic Table. An isolated Si atom has 2 electrons in the 3s and 2 electrons in the 3p orbitals. (b) When Si is about to bond, the *one* 3s-orbital and the *three* 3p-orbitals become perturbed and mixed to form four hybridized orbitals, ψ_{hyb} , called sp^3 orbitals which are directed towards the corners of a tetrahedron. The ψ_{hyb} orbital has a large major lobe and a small back lobe. Each ψ_{hyb} orbital takes one of the four valence electrons.

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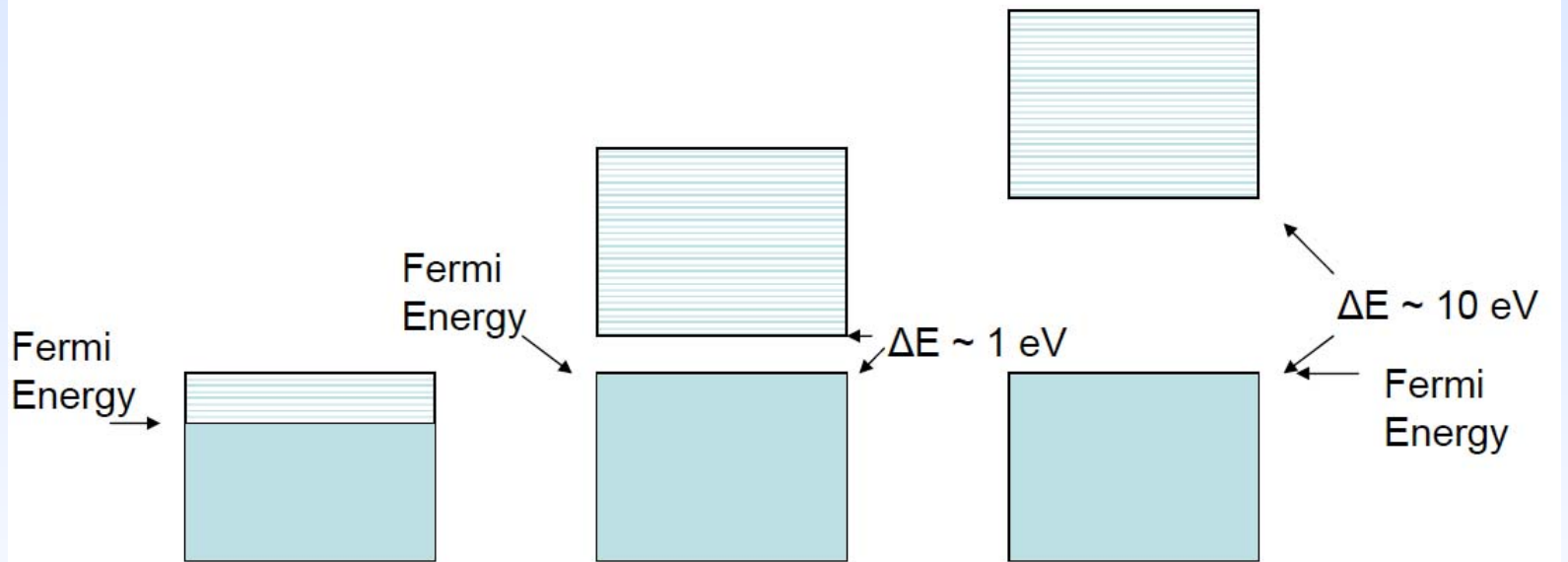
Formation of Energy Bands in Si by Splitting of Hybridized Molecular Orbitals



(a) Formation of energy bands in the Si crystal first involves hybridization of 3s and 3p orbitals to four identical ψ_{hyb} orbitals which make 109.5° with each other as shown in (b). (c) ψ_{hyb} orbitals on two neighboring Si atoms can overlap to form ψ_B or ψ_A . The first is a bonding orbital (full) and the second is an antibonding orbital (empty). In the crystal ψ_B overlap to give the valence band (full) and ψ_A overlap to give the conduction band (empty).

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Conductors, Insulators, Semiconductors



Conductor:
Fermi energy lies within a band of accessible states

Semiconductor:
Fermi energy lies in the gap, gap is relatively small in size ($\sim 1 \text{ eV}$) so that some e^- 's can be excited

Insulator: Fermi energy lies in the gap, gap is relatively large in size ($\sim 10 \text{ eV}$ – electrons cannot be excited to higher states)

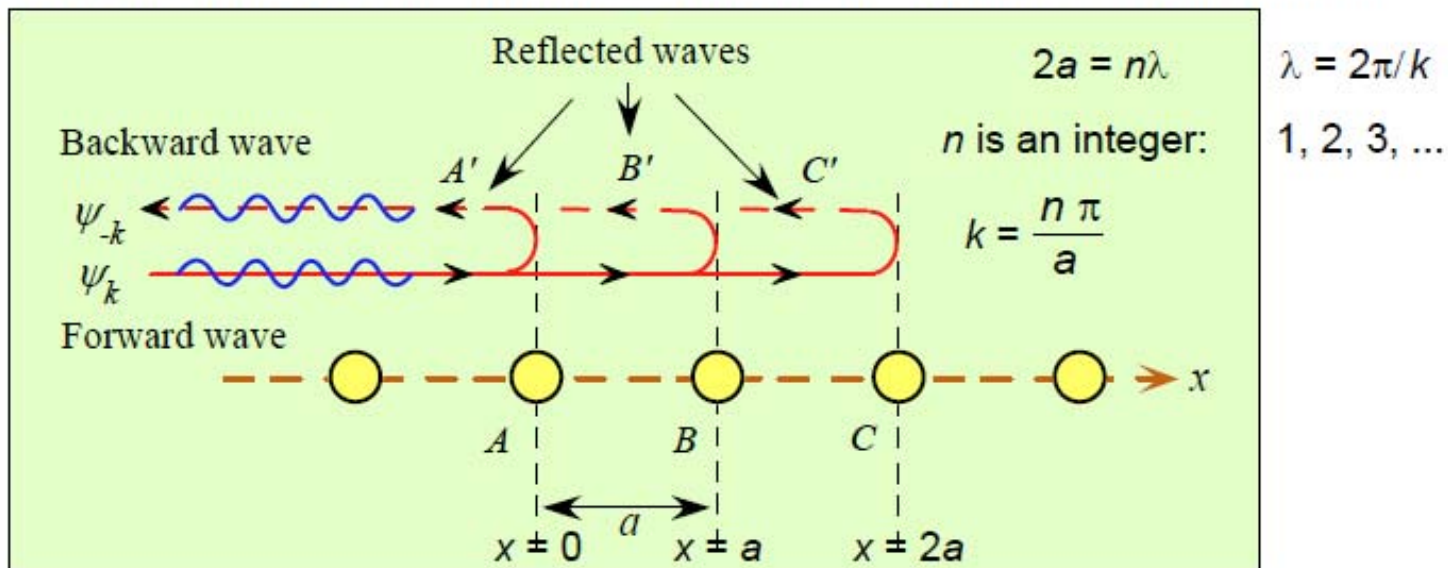
Charge carriers increasingly “feel” the crystal potential



Transport and Nearly-Free-Electron Model

Although we approximate $V(x) = 0$ within the crystal, the lattice sites generate periodic perturbations that lead to electron *diffraction* inside the crystal. This can happen in covalently bonded crystals also... the concept is not confined to metals.

Diffraction occurs with a reinforcing backward wave when the EPD or electron path difference, $2a$, is matched by an integral number of wavelengths $n\lambda$.



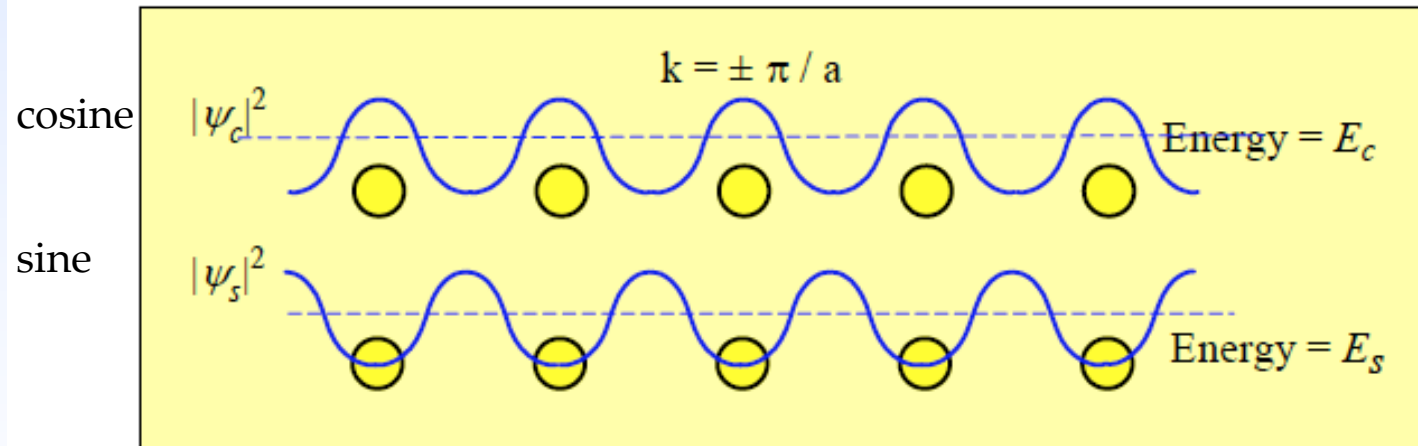
An electron wave propagation through a linear lattice. For certain k values the reflected waves at successive atomic planes reinforce each other to give rise to a reflected wave travelling in the backward direction. The electron then cannot propagate through the crystal.

At the Brillouin boundary



Nearly-Free-Electron Model

Given a single electron placed in a fixed periodic potential of positively charged atomic cores, the electron will achieve a lower energy configuration when it overlaps the cores most strongly. The potential energy will be negative in this case... call it $-V_n$. Now, $V_c + V_s$ is proportional to the average potential in the crystal, which for a weak potential vanishes. In addition, even if one adds the lowest order Fourier component to make the small potential periodic, then $V = V_0 \cos(2\pi x/a)$ and this also vanishes in the average.



Forward and backward waves in the crystal with $k = \pm \pi/a$ give rise to two possible standing waves, ψ_c and ψ_s . Their probability density distributions, $|\psi_c|^2$ and $|\psi_s|^2$, have maxima either at the ions or between the ions.



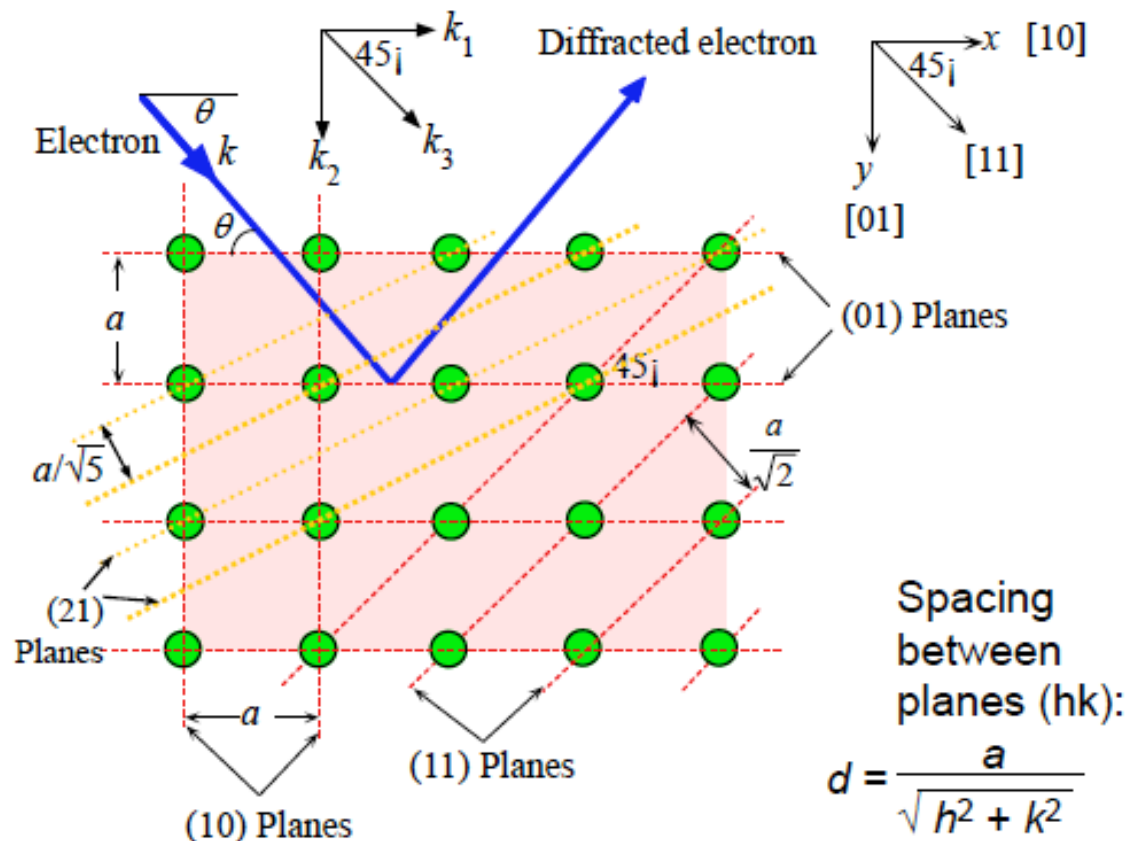
Nearly-Free-Electron Model

Consider the lowest band gap due to diffraction of electrons traveling in different directions:

For k along $[10]$, the first band gap occurs at $k = \pm \pi/a$ due to the (10) diffracting planes. For k along $[01]$ the behavior is the same.

For k along $[11]$, the first band gap occurs at $k = \pm \sqrt{2} (\pi/a)$ due to the $\{10\}$ diffracting planes with spacing a and $\theta=45^\circ$.

Diffraction also occurs for this same k due to the (11) planes with $\theta=0^\circ$ and spacing $a/\sqrt{2}$.



Diffraction of the electron in a two dimensional cubic crystal. Diffraction occurs whenever k has a component satisfying $k_1 = \pm n\pi/a$, $k_2 = \pm n\pi/a$ or $k_3 = \pm n\pi/a$. In general terms, when $k \sin \theta = n\pi/a$.



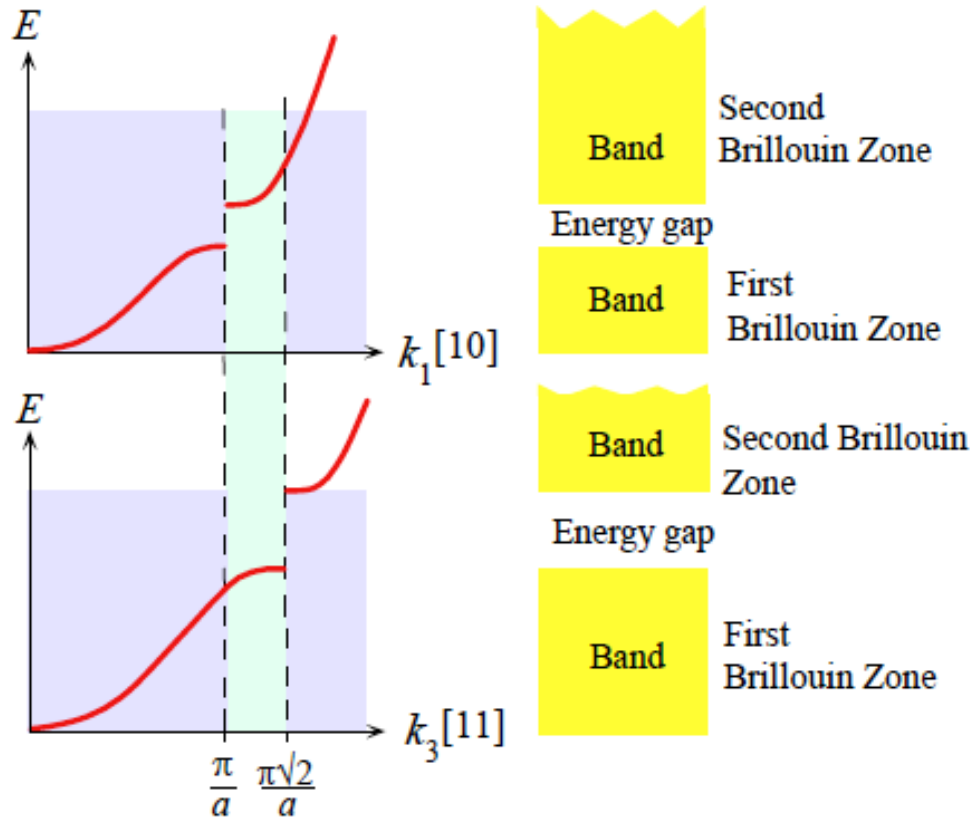
Nearly-Free-Electron Model

This figure shows that the position of the energy gap along a particular direction in k space and its magnitude depends on the direction.

The same general concept can be applied in three dimensions, as well.

Spacing between planes (hkl) in 3d in a cubic crystal:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$



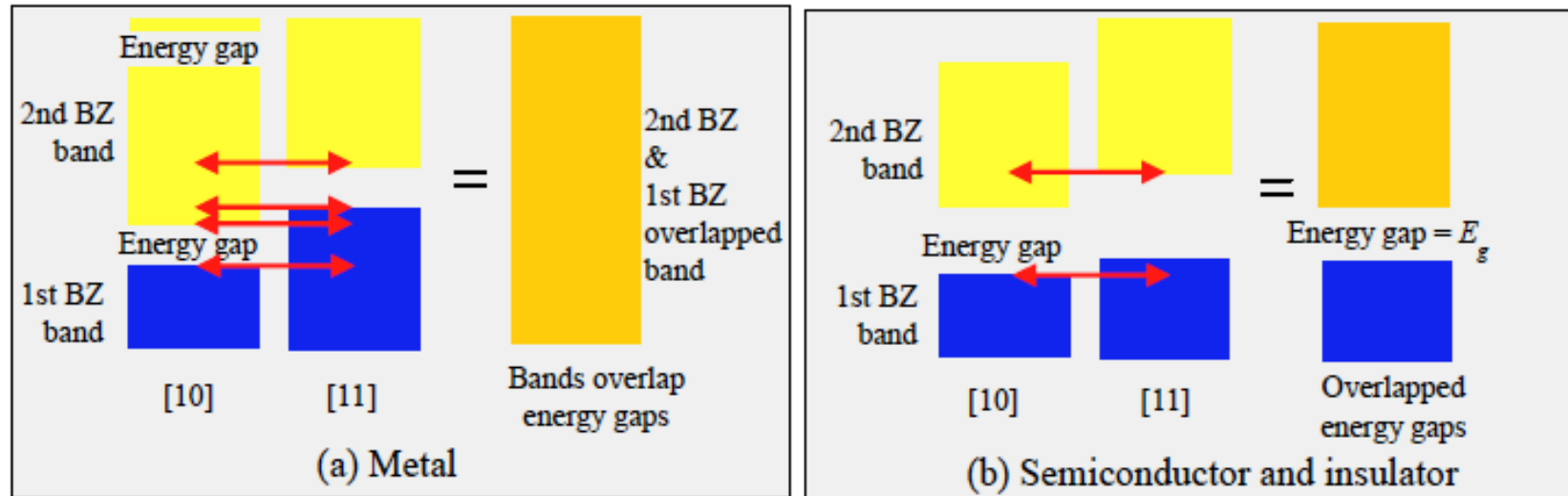
The E - k behavior for the electron along different directions in the two dimensional crystal. The energy gap along $[10]$ is at π/a whereas it is at $\pi\sqrt{2}/a$ along $[11]$.

14Fig 4.15

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Nearly-Free-Electron Model



(a) Metal: For the electron in a metal there is no apparent energy gap because the 2nd BZ (Brillouin Zone) along [10] overlaps the 1st BZ along [11]. Bands overlap the energy gaps. Thus the electron can always find an energy by changing its direction.

(b) Semiconductor or insulator: For the electron in a semiconductor there is an energy gap arising from the overlap of the energy gaps along [10] and [11] directions. The electron can never have an energy within this energy gap, E_g .

The red arrows show possible phonon scattering events which carry significant momentum and very little energy. Phonon scattering allows electrons in metals to increase and decrease continuously in energy without gaps simply by changing direction.

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Nearly-Free-Electron Model

The total energy of the electrons having wavefunctions ψ_c and ψ_s are:

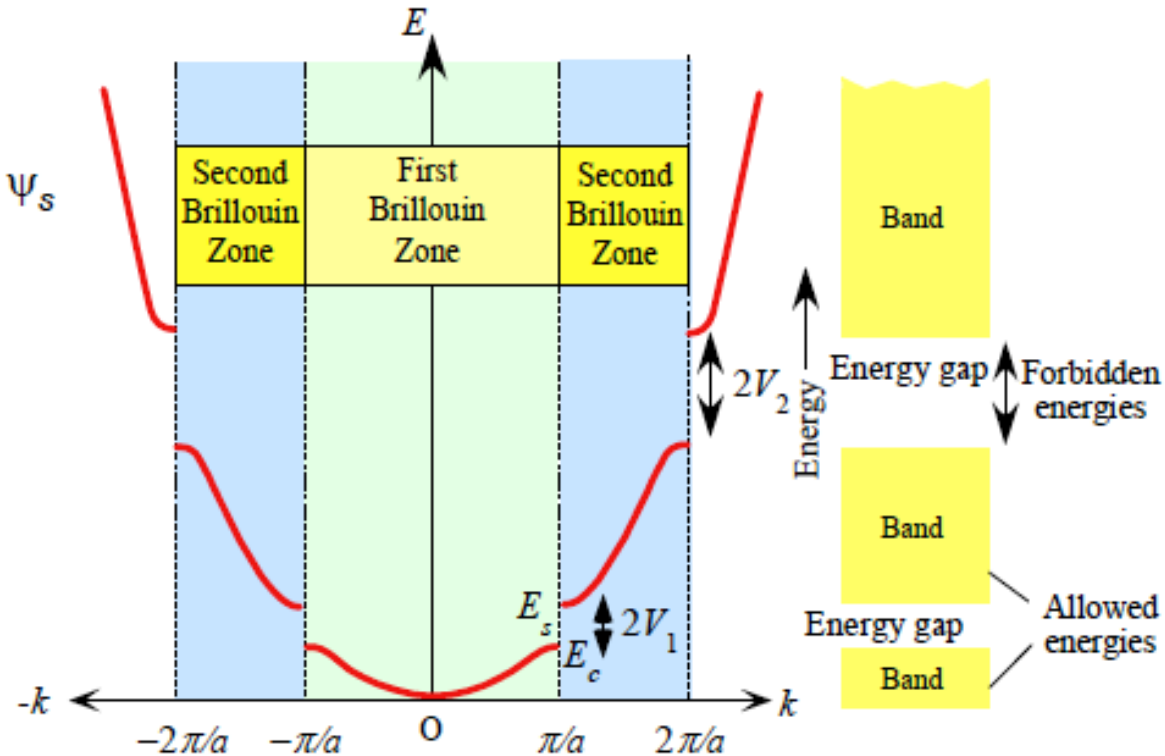
$$E_c \approx \frac{\hbar^2 k^2}{2m_e} - V_n$$

$$E_s \approx \frac{\hbar^2 k^2}{2m_e} + V_n$$

These wavefunctions have the same wave vector quantum number k but different energies by virtue of the different PE's.

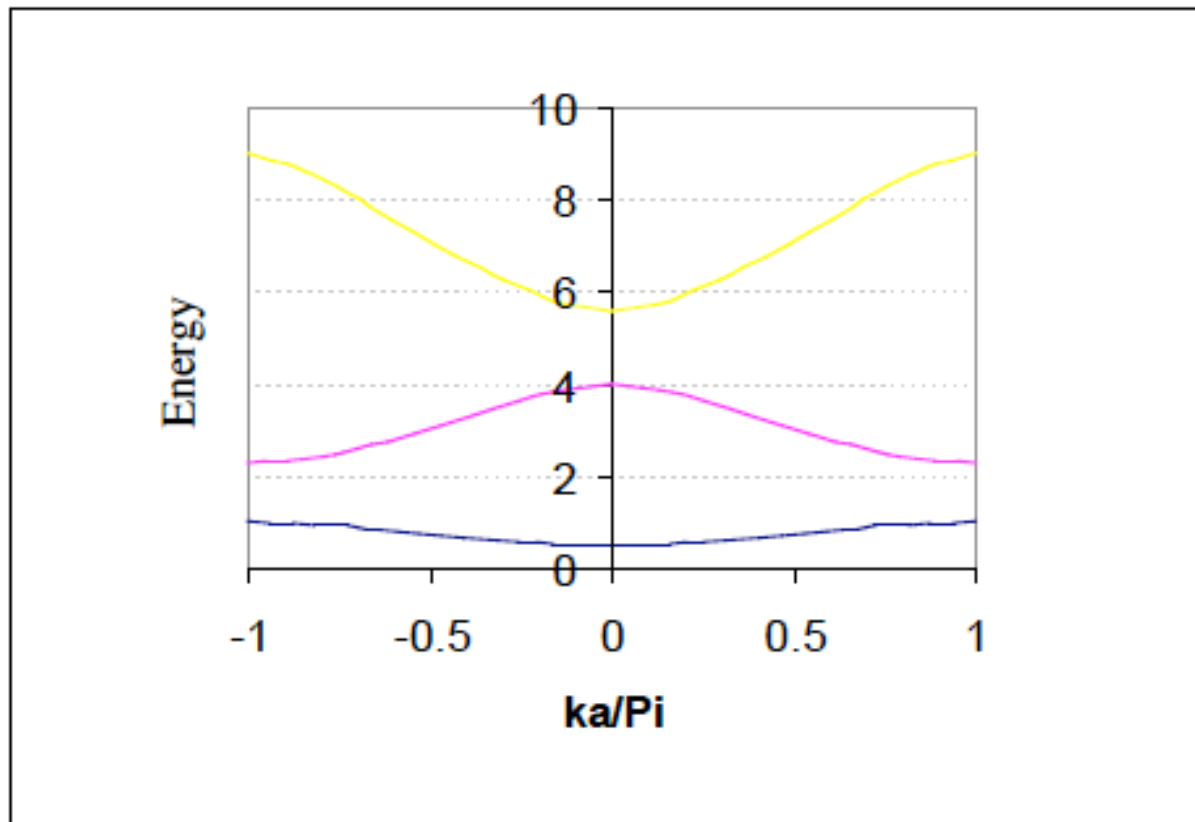
For k values away from the

Bragg reflection condition of $k=n\pi/a$, the waves continue to act as traveling waves.



The energy of the electron as a function of its wavevector k inside a one-dimensional crystal. There are discontinuities in the energy at $k = \pm n\pi/a$ values where the waves suffer Bragg reflections in the crystal. There are energy gaps at these k values. For example, there can be no energy value for the electron between E_c and E_s . $E_s - E_c$ is therefore an energy gap at $k = \pm\pi/a$. Away from the critical k values, the E - k behavior is like that of a "free" electron, E increasing with k as $E = (\hbar k)^2/2m_e$. These energies fall within an energy band inside a solid.

Reduced Zone Scheme

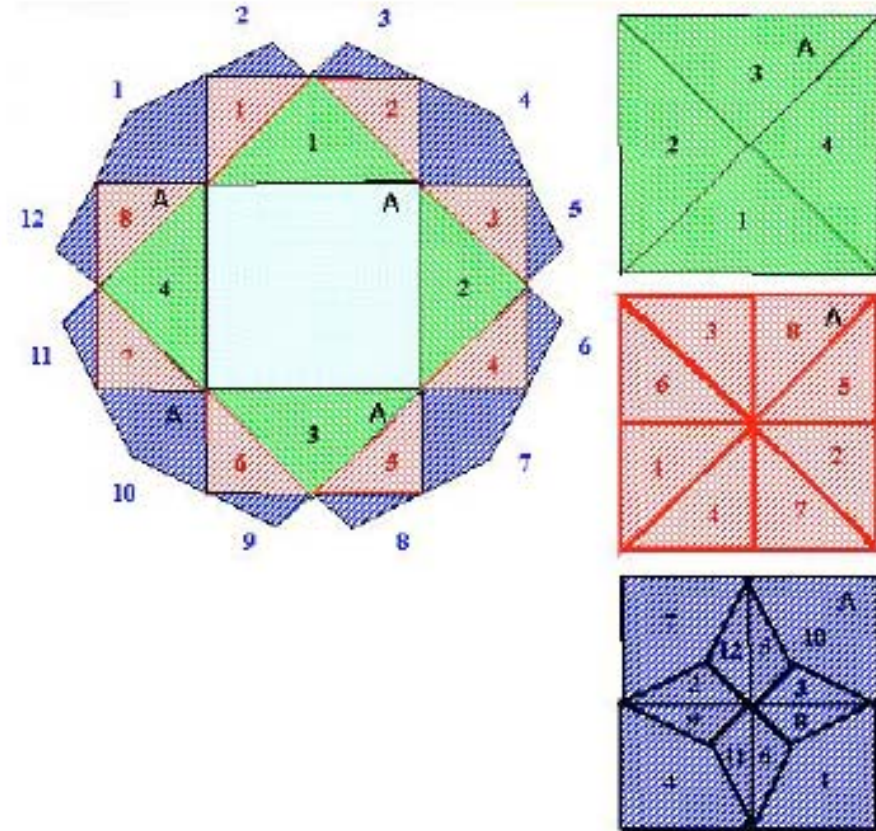


- Bands folded into First Brillouin Zone

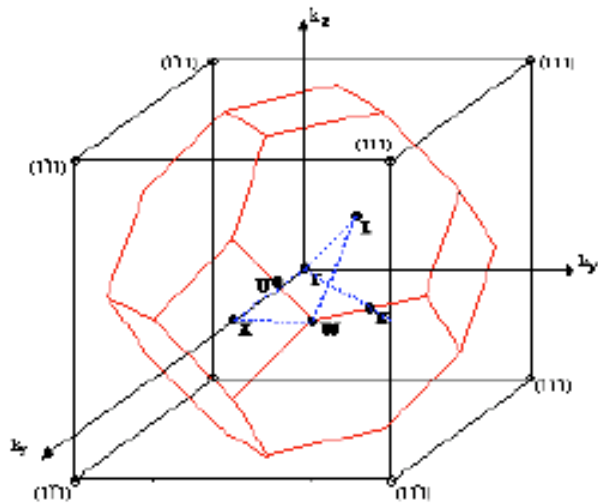


Brillouin zones -2D

- higher order zones can be mapped directly onto the 1st BZ by simple translation
- all BZs have exactly the same area/volume
- 1BZ corresponds to the primitive lattice cell in reciprocal space



Free electron bands for fcc structure



Γ – center of the BZ

X – [100] intercept;

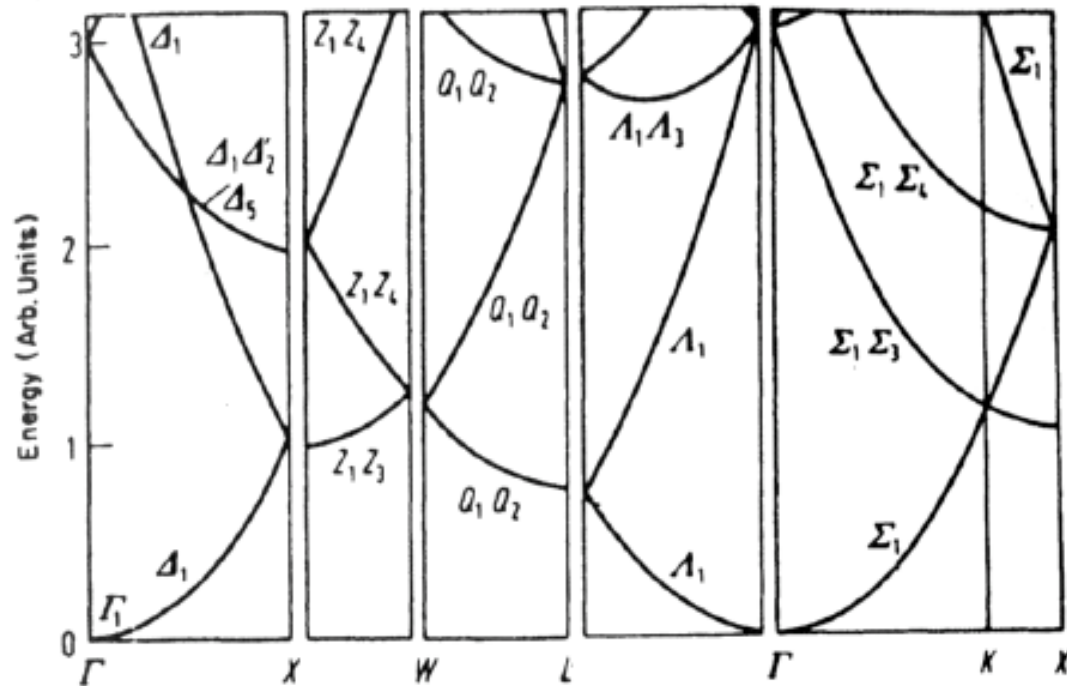
K – [110] intercept;

L – [111] intercept;

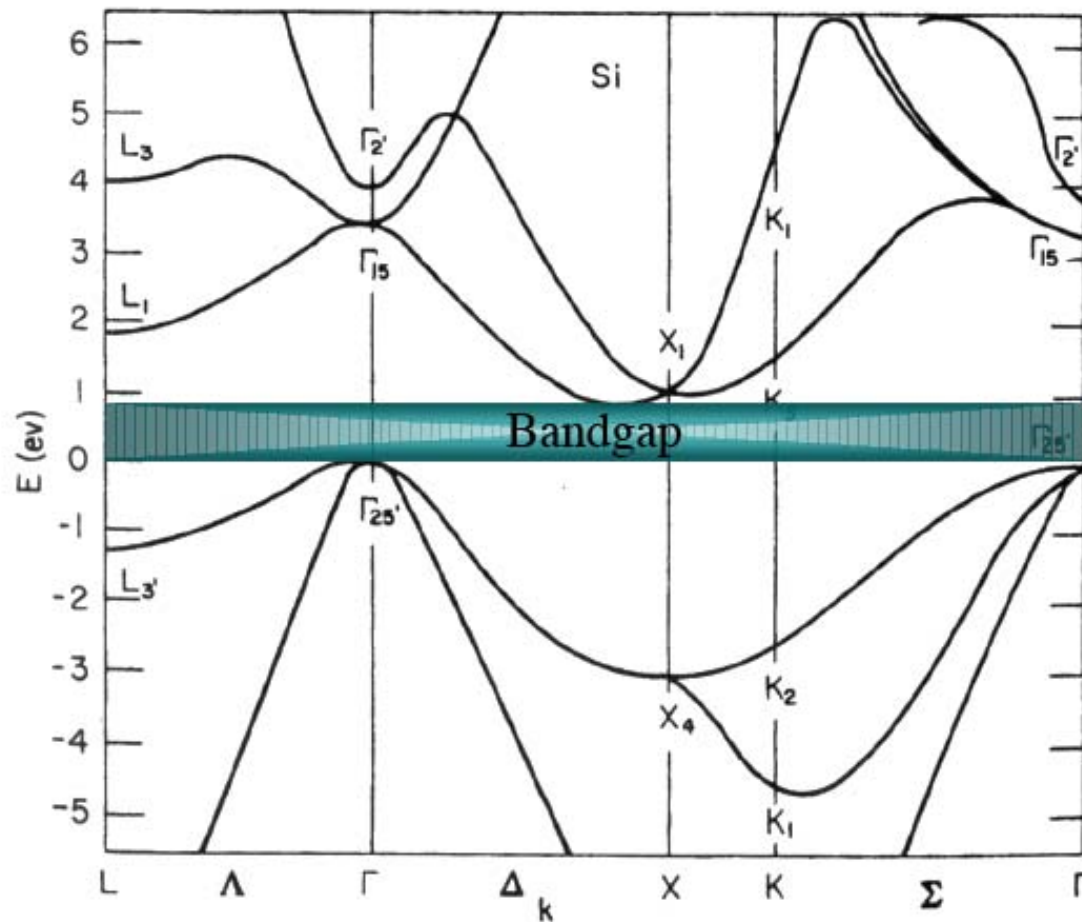
Γ – X path Δ

Γ – K path Σ

Γ – L path Λ



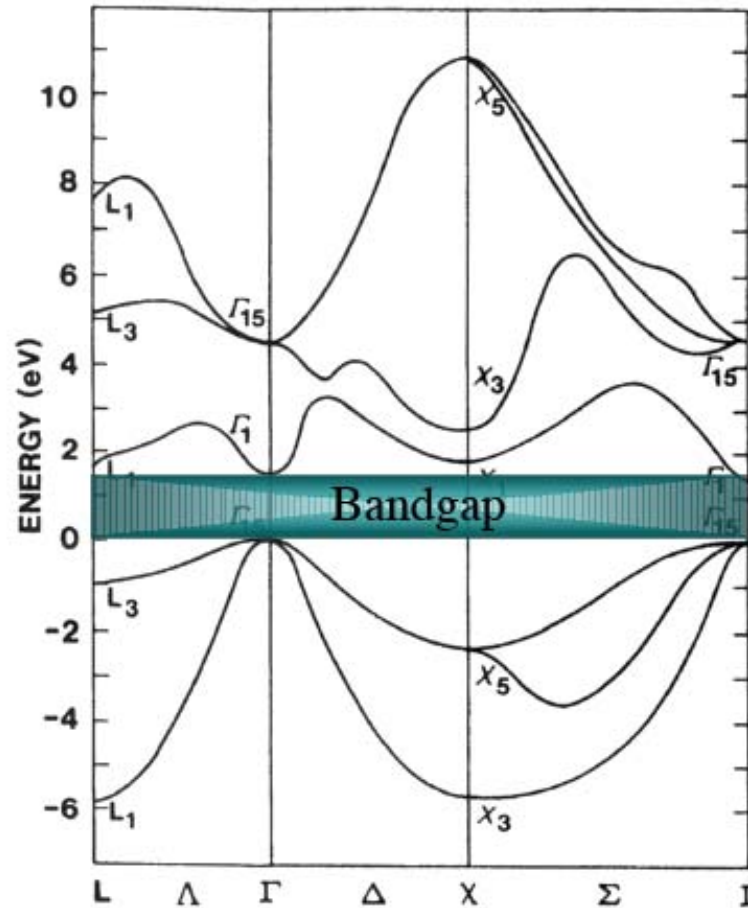
Band structure of Si (diamond)



Indirect Gap



Band structure of GaAs (zb)



Direct Gap

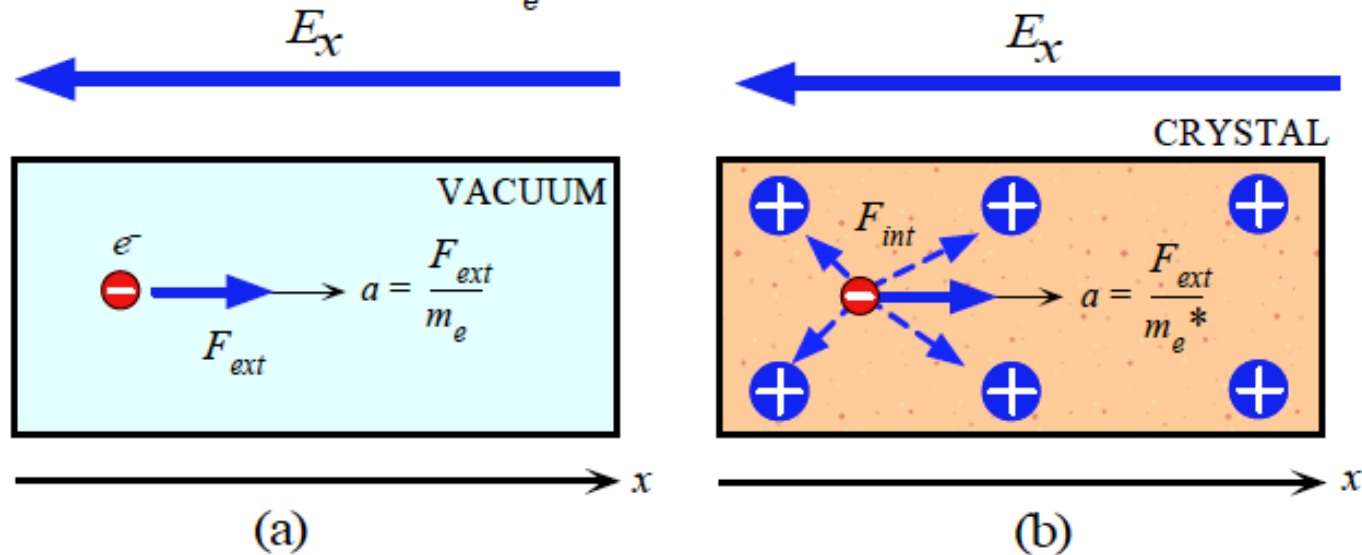


Electron Effective Mass

The acceleration of an electron in a crystal a_c is influenced by both external and internal forces:

$$\mathbf{a}_c = (\mathbf{F}_{ext} + \mathbf{F}_{int})/m_e = (\mathbf{F}_{ext} - \vec{\nabla}V)/m_e \equiv \mathbf{F}_{ext}/m_e^*$$

When the band is not full, all the effects of both internal and external forces are incorporated into an effective mass m_e^* .



(a) An external force F_{ext} applied to an electron in vacuum results in an acceleration $a_{vac} = F_{ext} / m_e$. (b) An external force F_{ext} applied to an electron in a crystal results in an acceleration $a_{cryst} = F_{ext} / m_e^*$. (E_x is the electric field.)

Electron Effective Mass

One can apply the concept of the group velocity to a wavefunction defined as a traveling wave $\Psi(x, t) = A \exp\{i(k_x x - \omega t)\}$; $\omega = E_k/\hbar$ with wave vector k_x .

The group velocity is $v_{gx} = \frac{d\omega}{dk_x}$

$$\frac{dv_{gx}}{dt} = \frac{1}{\hbar} \frac{d^2 E_k}{dk_x^2} \frac{dk_x}{dt} \quad \text{Note that:} \quad \hbar \frac{dk_x}{dt} = F_x$$

$$\frac{dv_{gx}}{dt} = \frac{1}{\hbar^2} \frac{d^2 E_k}{dk_x^2} F_x \quad \text{Note that:} \quad m_{xx}^* \frac{dv_{gx}}{dt} = F_x$$

$$\frac{1}{m_{xx}^*} = \frac{1}{\hbar^2} \frac{d^2 E_k}{dk_x^2} \quad \text{In general:} \quad \frac{1}{m_{\mu\nu}^*} = \frac{1}{\hbar^2} \frac{d^2 E_k}{dk_\mu dk_\nu}$$

In three-dimensional k -space, the effective mass is in general a tensor which must be diagonalized to find the principal axis coordinate system and the principal components.

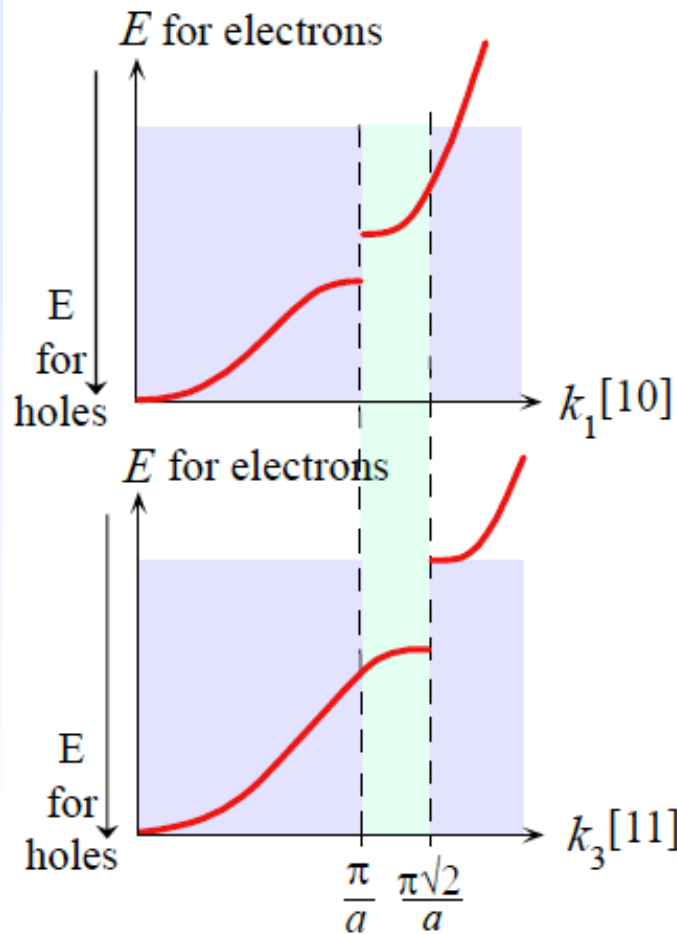
Table 4.2 Effective mass m_e^* of electrons in some metals

Metal	Ag	Au	Bi	Cu	K	Li	Na	Ni	Pt	Zn
$\frac{m_e^*}{m_e}$	0.99	1.10	0.047	1.01	1.12	1.28	1.2	28	13	0.85

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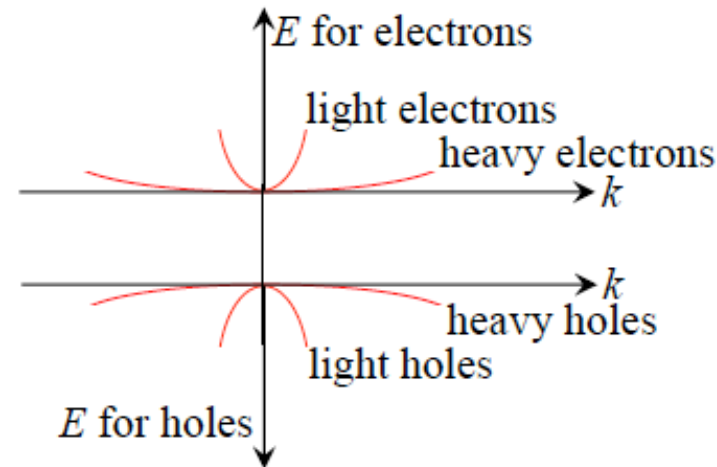
Electron Effective Mass



The effective mass is inversely proportional to the curvature of the E_k function.

At the lowest energies of each band, the effective mass is positive (upward curvature) and assigned to electrons of positive mass and negative charge whose energy increases upward.

At the highest energies of each band, the effective mass is negative (downward curvature) and assigned to holes of positive mass and positive charge whose energy increases downward.



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Comparison of Li ($1s^2 2s^1$) and Si ($1s^2 2s^2 2p^4 3s^2 3p^2$)

Model for Li (BCC):

- *Molecular Orbital Picture*

One-electron wavefunctions are considered as delocalized within the solid. For a given wavefunction, there can be either constructive or destructive interference of neighboring atomic orbitals. The electronic level is determined by the number of occurrences of destructive interference, i.e., by the number of nodes of the wavefunction between the atoms. The collection of N atoms lead to N levels that are continuously distributed in energy. Because there are two spin states per level, $N/2$ levels are filled with N electrons. In addition, the empty $2p$ and $3s$ band states overlap the $2s$ states, leading to a continuous distribution of states from the Fermi level to the vacuum level.

- *Band Picture*

The N electrons fill up one-half the states in the first Brillouin zone in k -space. Electrons can move from the Fermi level to the vacuum level with a large number of infinitesimal energy jumps. When the boundary of the first Brillouin zone is reached, there is a band gap for the given direction of k ; however, by changing its direction in a scattering event, the electron can avoid this gap and cross into the second Brillouin zone with no energy gain.



Comparison of Li ($1s^2 2s^1$) and Si ($1s^2 2s^2 2p^4 3s^2 3p^2$)

Model for Si (diamond cubic):

- *Molecular Orbital Picture*

The four 3s and 3p atomic orbitals hybridize to form four sp^3 molecular orbitals with the ability to accommodate 8 electrons. Because of the localized nature of the electron wavefunctions in the solid, the four molecular orbitals split into bonding and antibonding levels with 4 electrons per atom accommodated in each. In forming the solid from N atoms, the bonding states split into a *valence band* that accommodates $4N$ electrons total and the antibonding states split into the conduction band that also accommodate $4N$ electrons. So the valence band is fully occupied in the solid and the conduction band is empty.

- *Band Picture*

Valence and conduction band states -- $4N$ of each -- can be formed through a linear combination of the localized bonding and antibonding molecular orbitals respectively. The $4N$ electrons fill up the first Brillouin zone in k -space. (There are $2N$ levels in the first Brillouin zone since the Bravais lattice has a 2 atom basis.) At the Brillouin zone boundary there is a band gap, and the lowest energy state in the second zone lies at a higher energy than the highest energy state in the first zone. Thus, the only way to move the electron to the second Brillouin zone is to provide an energy equal to this lowest gap which is simply the *band gap* of Si.

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