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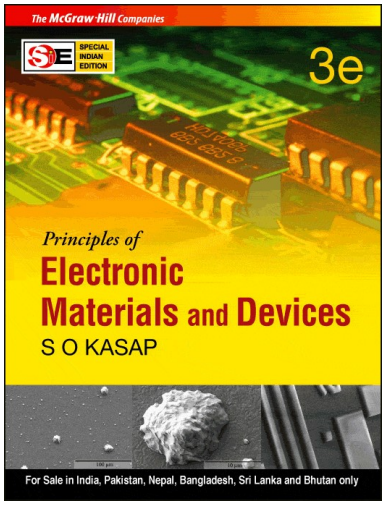

Chapter 4

Modern Theory of Solids

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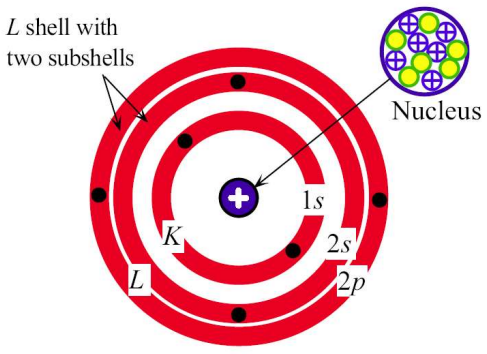
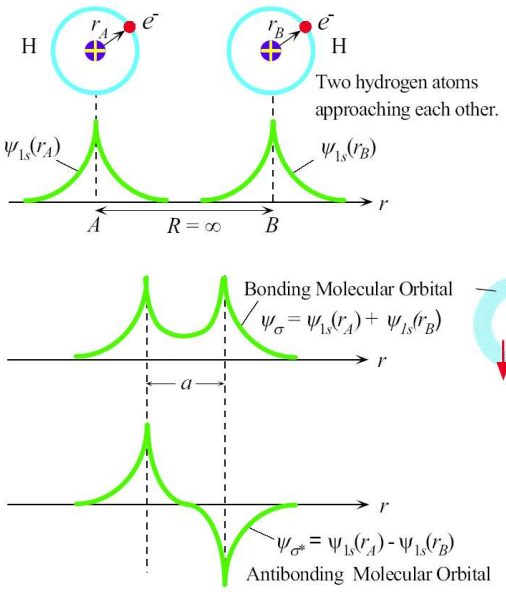
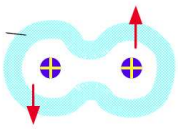


$1s^2 2s^2 2p^2$ or $[He]2s^2 2p^2$

The shell model of the atom in which electrons are confined to live within certain shells and in subshells within shells

3





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.

4

Linear Combination of Atomic Orbitals

Two identical atomic orbitals ψ_{1s} on atoms A and B can be combined linearly in two different ways to generate two separate molecular orbitals ψ_σ and ψ_{σ^*}

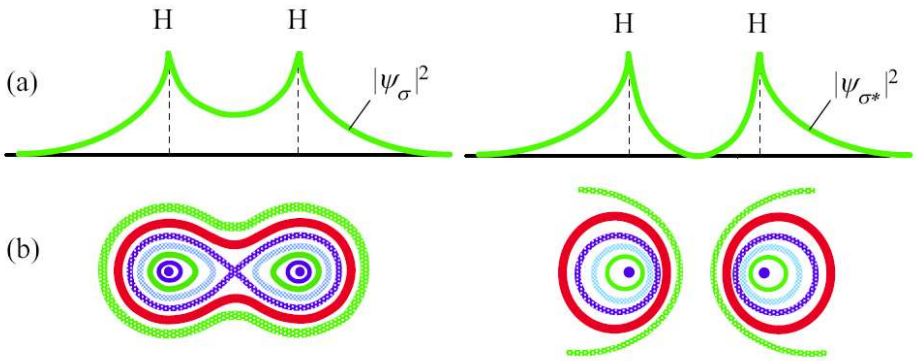
ψ_σ and ψ_{σ^*} generated from a
linear combination of atomic orbitals (LCAO)

Wavefunction around A

Wavefunction around B

$$\psi_\sigma = \psi_{1s}(r_A) + \psi_{1s}(r_B)$$

$$\psi_{\sigma^*} = \psi_{1s}(r_A) - \psi_{1s}(r_B)$$



(a) Electron probability distributions for bonding and antibonding orbitals, ψ_σ and ψ_{σ^*}.
(b) Lines representing contours of constant probability (darker lines represent greater relative probability).

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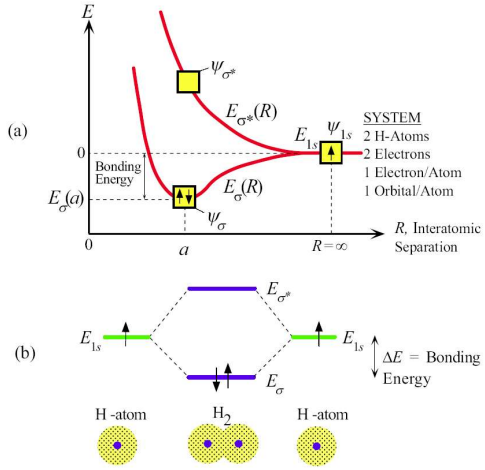

(a) Energy of ψ_σ and ψ_{σ^*} vs. the interatomic separation R.
(b) Schematic diagram showing the changes in the electron energy as two isolated H atoms, far left and far right, come together to form a hydrogen molecule.

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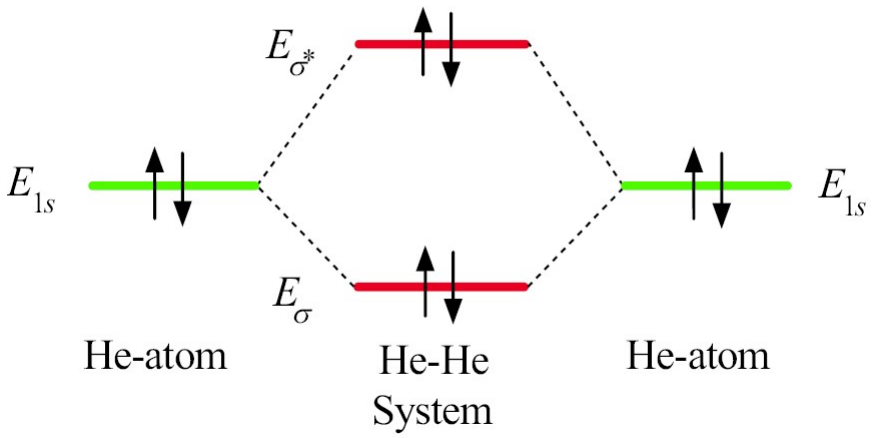
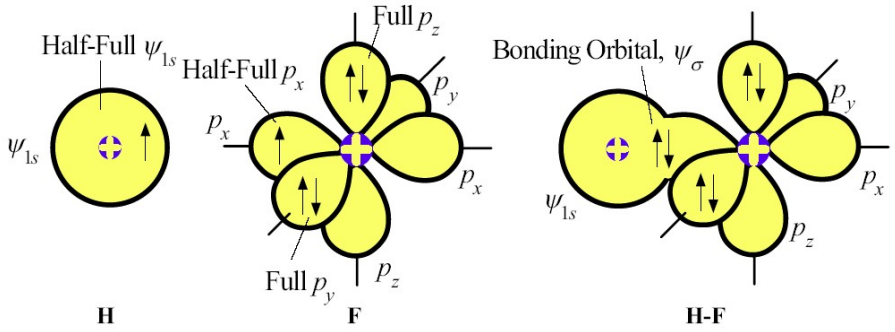
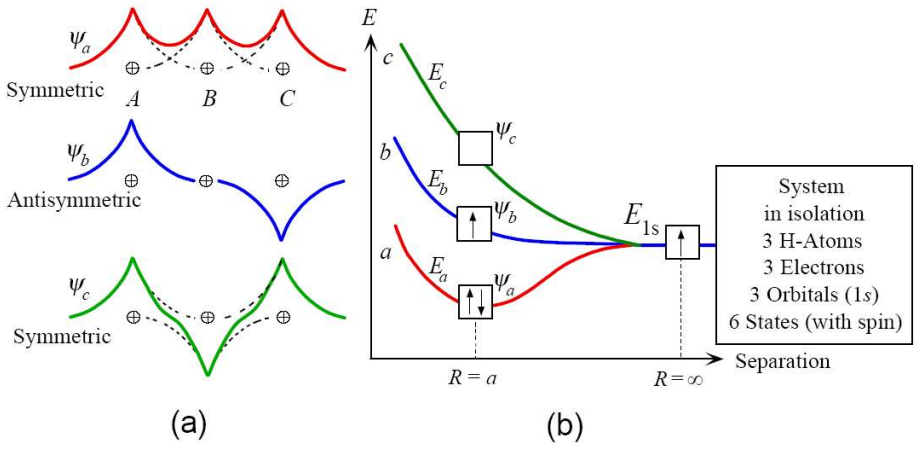


Two He atoms have four electrons. When He atoms come together, two of the electrons enter the E_{σ} level and two the E_{σ^*} level, so the overall energy is greater than two isolated He atoms.

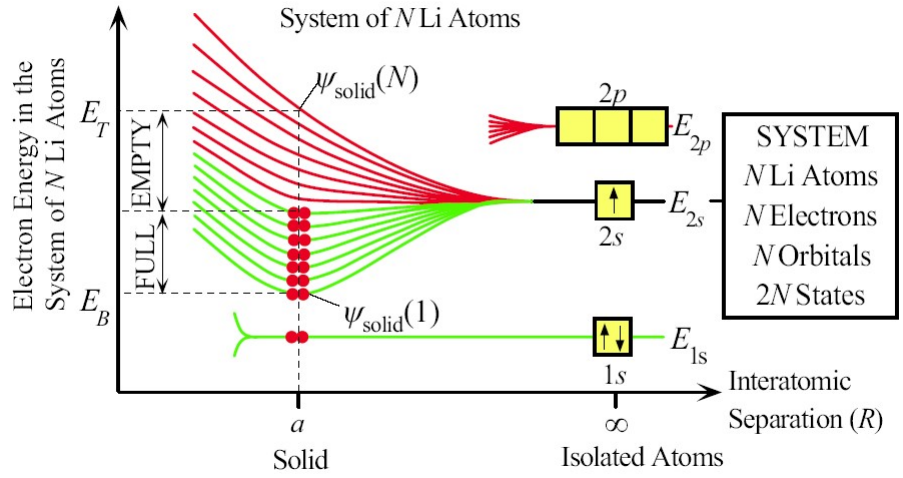


H has one half-empty ψ_{1s} orbital.

F has one half-empty p_x orbital but full p_y and p_z orbitals. The overlap between ψ_{1s} and p_x produces a bonding orbital and an antibonding orbital. The two electrons fill the bonding orbital and thereby form a covalent bond between H and F.



(a) Three molecular orbitals from three ψ_{1s} atomic orbitals overlapping in three different ways. (b) The energies of the three molecular orbitals, labeled a, b, and c, in a system with three H atoms.



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

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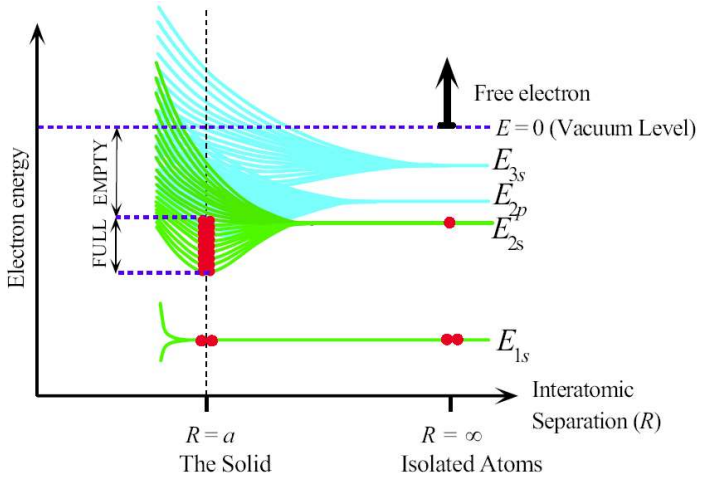

As Li atoms are brought together from infinity, the atomic orbitals overlap and give rise to bands. Outer orbitals overlap first. The 3*s* orbitals give rise to the 3*s* band, 2*p* orbitals to the 2*p* band, and so on. The various bands overlap to produce a single band in which the energy is nearly continuous.

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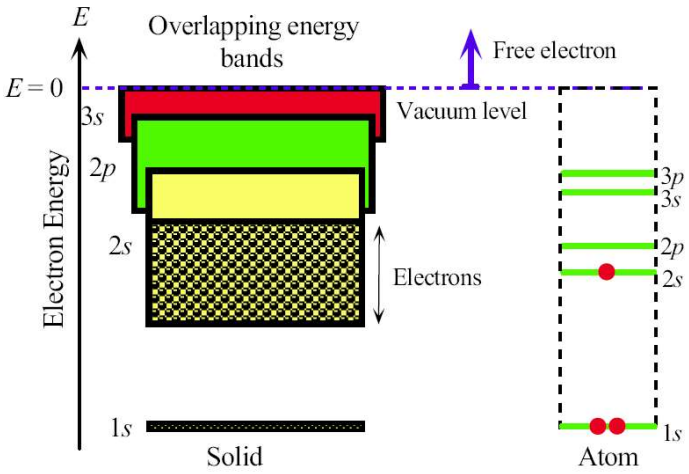

In a metal, the various energy bands overlap to give a single energy band that is only partially full of electrons. There are states with energies up to the vacuum level, where the electron is free.

Electron Energy Band Structures

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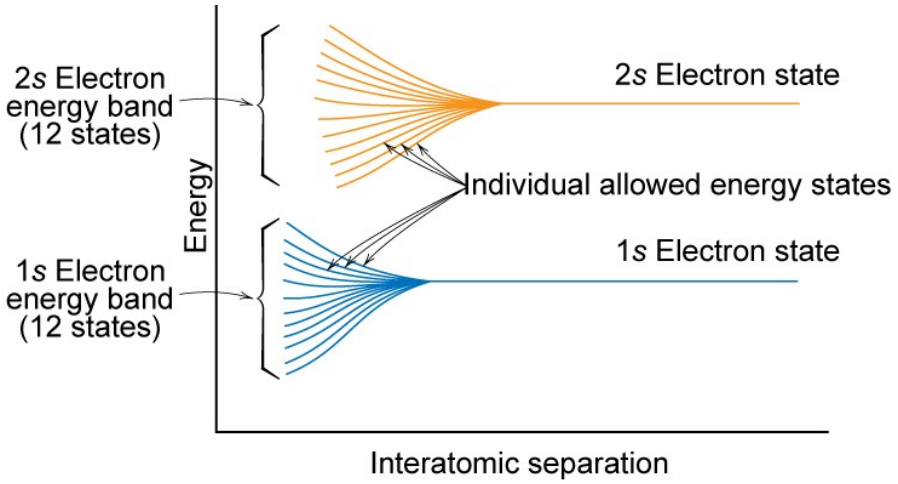

Adapted from Fig. 18.2, *Callister & Rethwisch 8e.*

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Band Structure Representation

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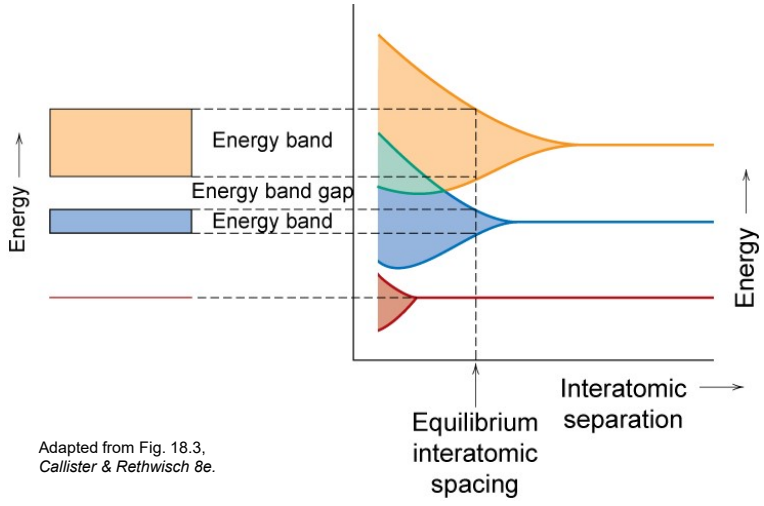

Adapted from Fig. 18.3, *Callister & Rethwisch 8e.*

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Conduction & Electron Transport

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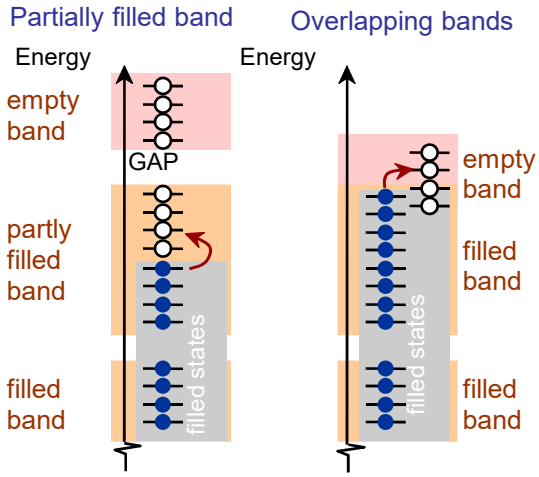
- Metals (Conductors):

-- for metals empty energy states are adjacent to filled states.

-- thermal energy excites electrons into empty higher energy states.

-- two types of band structures for metals
- partially filled band
- empty band that overlaps filled band



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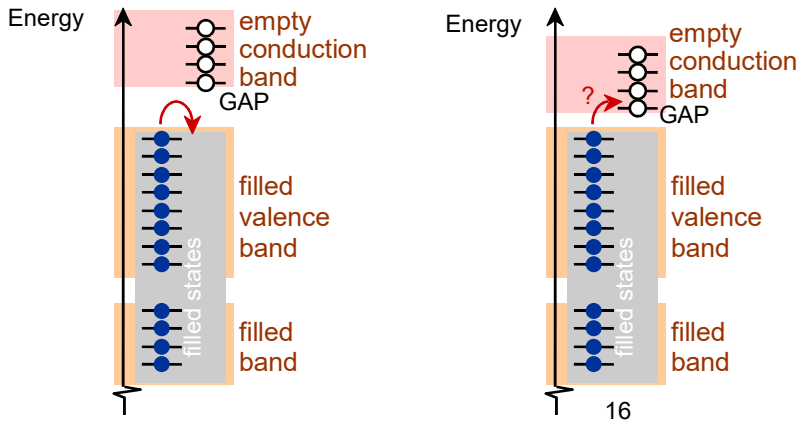
Energy Band Structures: Insulators & Semiconductors

- Insulators:
  -- wide band gap (> 2 eV)
  -- few electrons excited across band gap

- Semiconductors:
  -- narrow band gap (< 2 eV)
  -- more electrons excited across band gap



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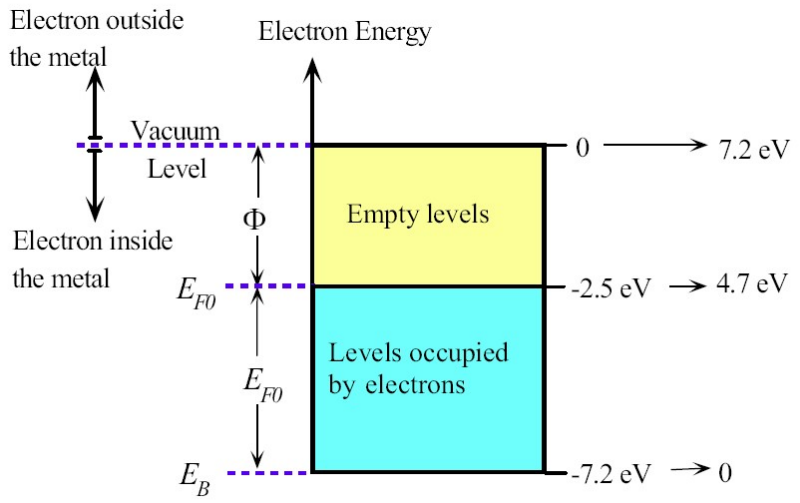

Typical electron energy band diagram for a metal.
All the valence electrons are in an energy band, which they only partially fill. The top of the band is the vacuum level, where the electron is free from the solid ($PE = 0$).

18

Work function Φ

The energy required to excite an electron from the Fermi level to the vacuum level, that is, to liberate the electron from the metal, is called the **work function** Φ of the metal.

Electron gas in a metal

The electrons in the energy band of a metal are loosely bound valence electrons, which become free in the crystal and thereby form a kind of **electron gas** within the crystal. It is this electron gas that holds the metal ions together in the crystal structure and constitutes the metallic bond.

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Table 4.1 Fermi energy and work function of selected metals

	Metal							
	Ag	**Al**	**Au**	**Cs**	**Cu**	**Li**	**Mg**	**Na**
Φ (eV)	4.5	4.28	5.0	2.14	4.65	2.3	3.7	2.75
E_{FO} (eV)	5.5	11.7	5.5	1.58	7.0	4.7	7.1	3.2

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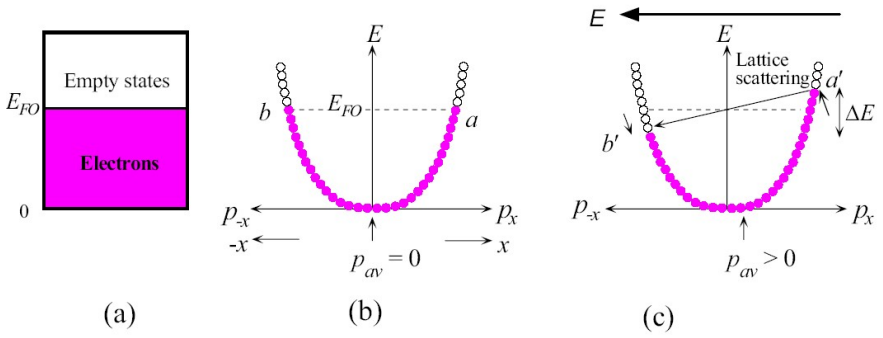

(a) Energy band diagram of a metal. (b) In the absence of a field, there are as many electrons moving right as there are moving left. The motions of two electrons at each energy cancel each other as for a and b. (c) In the presence of a field in the *x* direction, the electron a accelerates and gains energy to a' where it is scattered to an empty state near E_{FO} but moving in the -x direction. The average of all momenta values is along the +*x* direction and results in a net electrical current.

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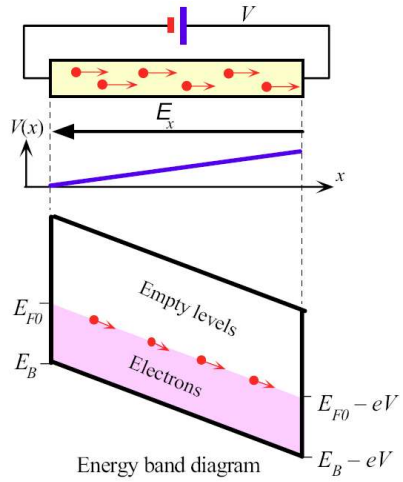

Conduction in a metal is due to the drift of electrons around the Fermi level. When a voltage is applied, the energy band is bent to be lower at the positive terminal so that the electron's potential energy decreases as it moves toward the positive terminal.

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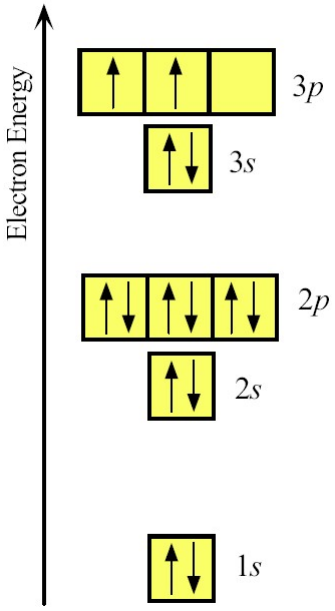

The electronic structure of Si

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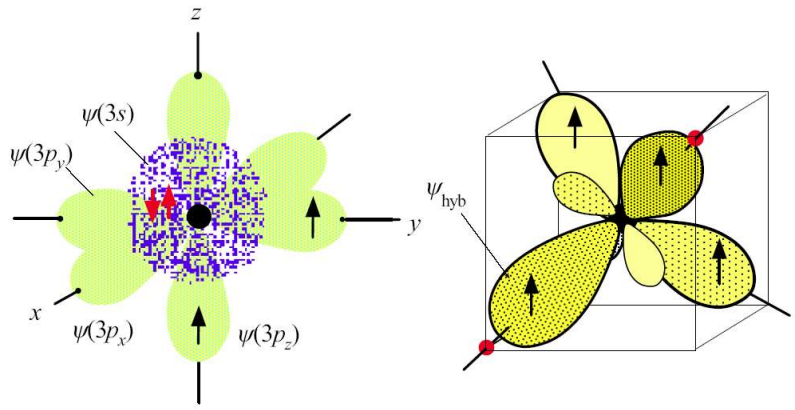

(a) Isolated Si (b) Si preparing to bond

(a) Si is in Group IV in the Periodic Table. An isolated Si atom has two electrons in the 3*s* and two electrons in the 3*p* orbitals.
(b) When Si is about to bond, the one 3*s* orbital and the three 3*p* orbitals become perturbed and mixed to form four hybridized orbitals, ψ_{hyb}, called sp^3 orbitals, which are directed toward 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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Hybridization

sp^3 hybridization

The 3*s* and 3*p* energy levels are quite close, and when five Si atoms approach each other, the interaction results in the four orbitals $\psi(3s)$, $\psi(3p_x)$, $\psi(3p_y)$ and $\psi(3p_z)$ mixing together to form four new hybrid orbitals, which are directed in tetrahedral directions; that is, each one is aimed as far away from the others as possible.

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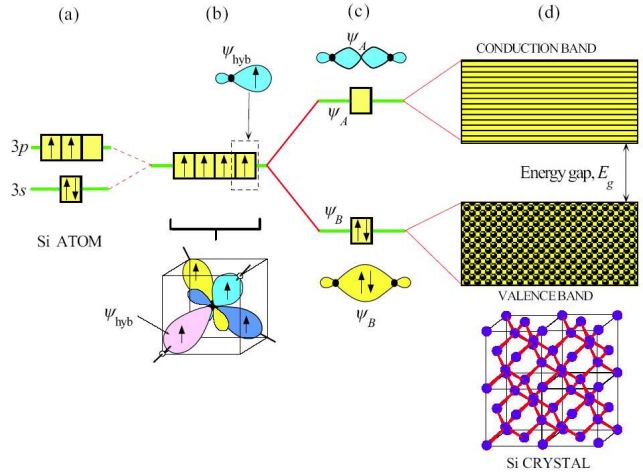

(a) Formation of energy bands in the Si crystal first involves hybridization of 3*s* and 3*p* orbitals to four identical ψ_{hyb} orbitals which make 109.5° with each other as shown in (b). (c) ψ_{hyb} orbitals on two neighboring Si atoms can overlap to form ψ_B or ψ_A. The first is a bonding orbital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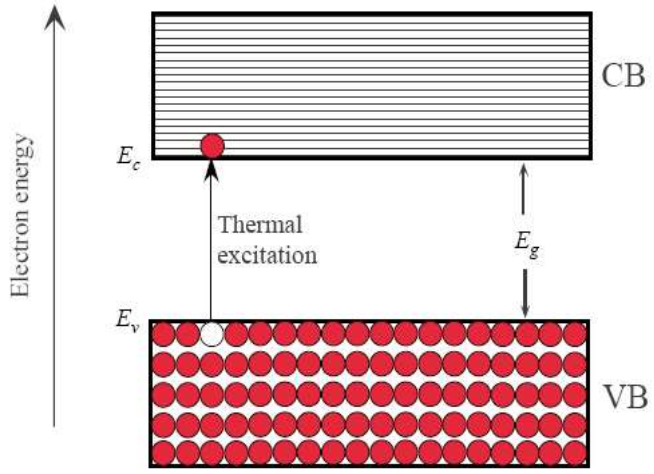

Energy band diagram of a semiconductor. CB is the conduction band and VB is the valence band. AT 0 K, the VB is full with all the valence electrons.

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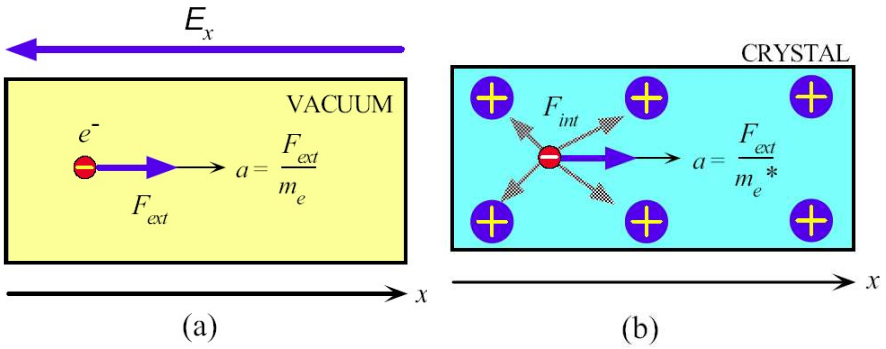

(a) An external force F_{ext} applied to an Electron in a vacuum results in an acceleration $a_{vac} = F_{ext} / m_e$.

(b) An external force F_{ext} applied to an electron in a crystal results in an acceleration $a_{cryst} = F_{cryst} / m_{e*}$

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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

Density of States

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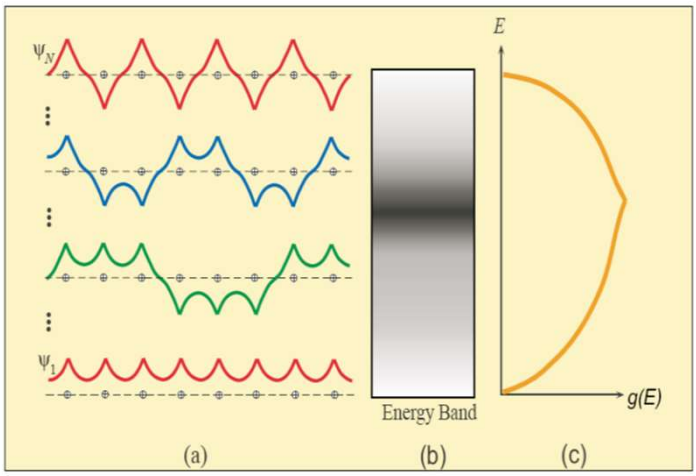

(a) In the solid there are N atoms and N extended electron wavefunctions from ψ_1 all the way to ψ_N. There are many wavefunctions, states, that have energies that fall in the central regions of the energy band.
(b) The distribution of states in the energy band; darker regions have a higher number of states.
(c) Schematic representation of the density of states $g(E)$ versus energy E.

Density of States

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$g(E)$ = Density of states

$g(E)\,dE$ is the number of states (*i.e.,* wavefunctions) in the energy interval E to $(E + dE)$ per unit volume of the sample.

$$g(E) = \left(8\pi 2^{1/2}\right)\left(\frac{m_e}{h^2}\right)^{3/2} E^{1/2}$$

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Number of Electrons/ Volume

$f(E)$ = Probability that a state with energy E is occupied

$g(E)$ = Density of states

$$n = \int_{Band} f(E)g(E)dE$$

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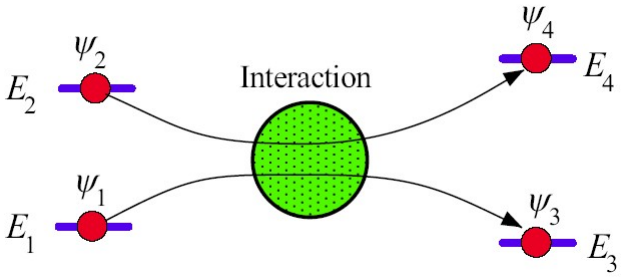
Boltzmann Classical Statistics



Two electrons with initial wavefunctions ψ_1 and ψ_2 at E_1 and E_2 interact and end up different energies E_3 and E_4. Their corresponding wavefunctions are ψ_3 and ψ_4.

Boltzmann Classical Statistics

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Boltzmann probability function

$$P(E) = A \exp\left(-\frac{E}{kT}\right)$$

Boltzmann Statistics for two energy levels

$$\frac{N_2}{N_1} = \exp\left(-\frac{E_2 - E_1}{kT}\right)$$

Boltzmann Classical Statistics

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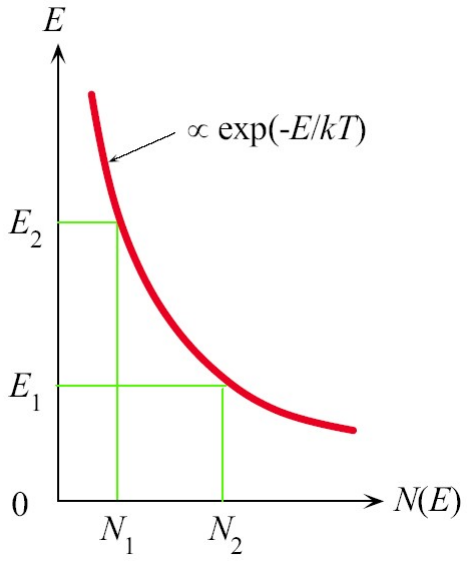

The Boltzmann energy distribution describes the statistics of particles, such as electrons, when there are many more available states than the number of particles.

Fermi-Dirac Statistics

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The Fermi-Dirac function

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

where E_F is a constant called the **Fermi energy**.

$f(E)$ = the probability of finding an electron in a state with energy E is given

Fermi-Dirac Statistics

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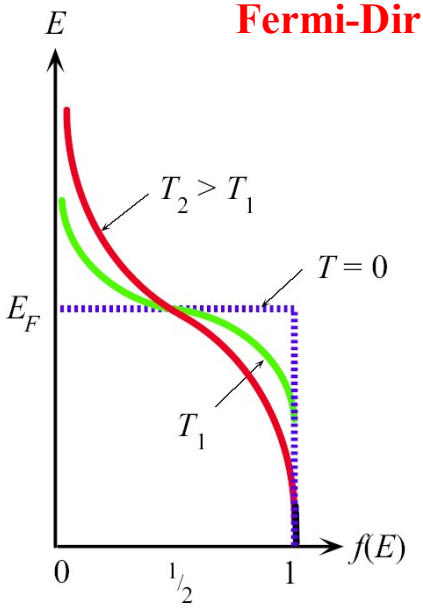
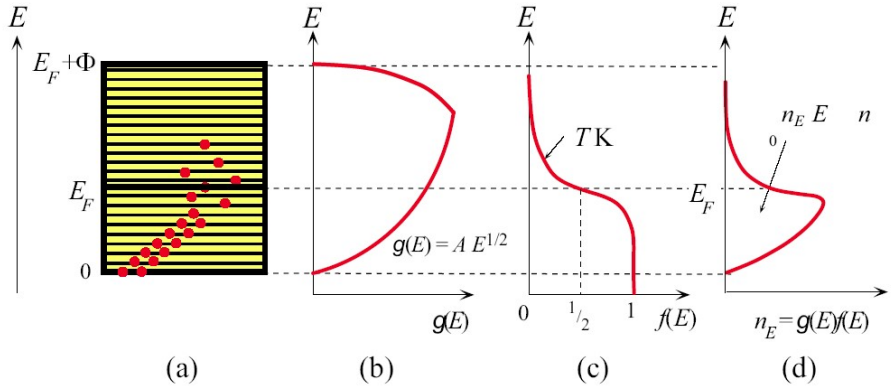


The fermi-Dirac $f(E)$ describes the statistics of electrons in a solid. The electrons interact with each other and the environment, obeying the Pauli exclusion principle.

Electrical Conduction

37



(a) Above 0K, due to thermal excitation, some of the electrons are at energies above E_F.
(b) The density of states, $g(E)$ versus E in the band.
(c) The probability of occupancy of a state at an energy E is $f(E)$.
(d) The product of $g(E)\,f(E)$ is the number of electrons per unit energy per unit volume, or the electron concentration per unit energy. The area under the curve on the energy axis is the concentration of electrons in the band.

Fermi Energy

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Fermi energy at $T = 0$ K

$$E_{FO} = \left(\frac{h^2}{8m_e}\right)\left(\frac{3n}{\pi}\right)^{2/3}$$

n is the concentration of conduction electrons (free carrier concentration)

Fermi energy at T (K)

$$E_F(T) = E_{FO}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{FO}}\right)^2\right]$$

Average energy per electron

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Average energy per electron at 0 K

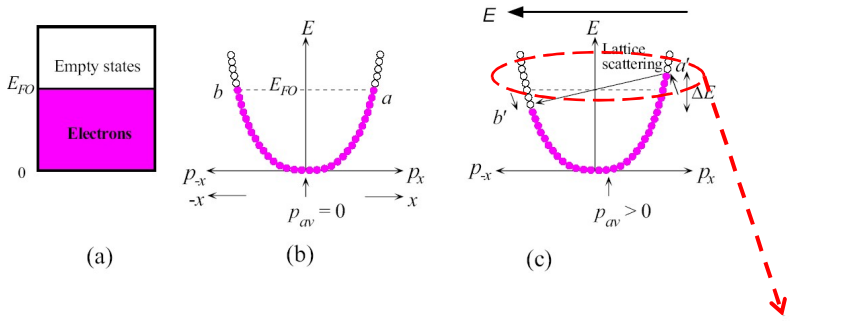
$$E_{\text{av}}(0) = \frac{3}{5} E_{FO}$$

Average energy per electron at *T* (K)

$$E_{\text{av}}(T) = \frac{3}{5} E_{FO}\left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{E_{FO}}\right)^2\right]$$

Conduction in Metals

40



$$\sigma = \frac{1}{3} e^2 v_F^2 \tau g(E_F)$$

Effect of $g(E_F)$: Cu and Mg

Effect of τ: Ni – 3d and 4s bands

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Fermi Energy Significance

For a given metal the Fermi energy represents the free energy per electron called the **electrochemical potential**. The Fermi energy is a measure of the potential of an electron to do electrical work ($e \times V$) or nonmechanical work, through chemical or physical processes.

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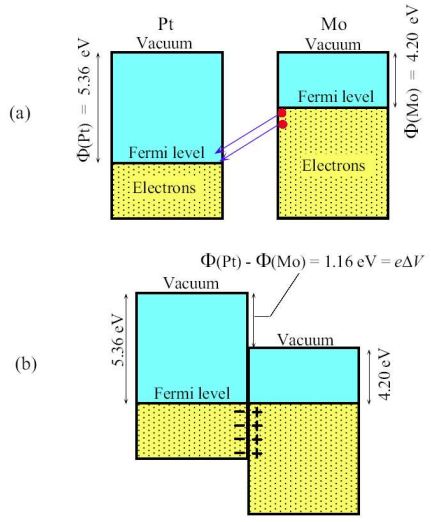
Metal-Metal Contact: Contact potential



(a) Electrons are more energetic in Mo, so they tunnel to the surface of Pt.
(b) Equilibrium is reached when the Fermi levels are lined up.
When two metals are brought together, there is a contact potential ΔV.

Metal-Metal Contact: Contact potential

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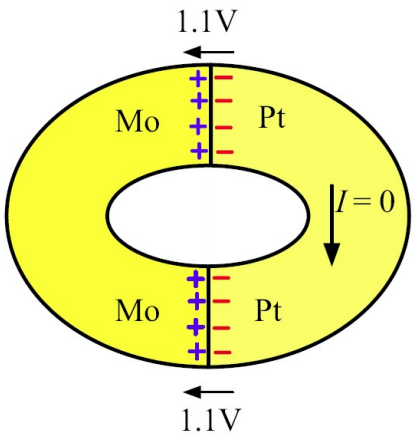

There is no current when a closed circuit is formed by two different metals, even though there is a contact potential at each contact.
The contact potentials oppose each other.

Seebeck Effect

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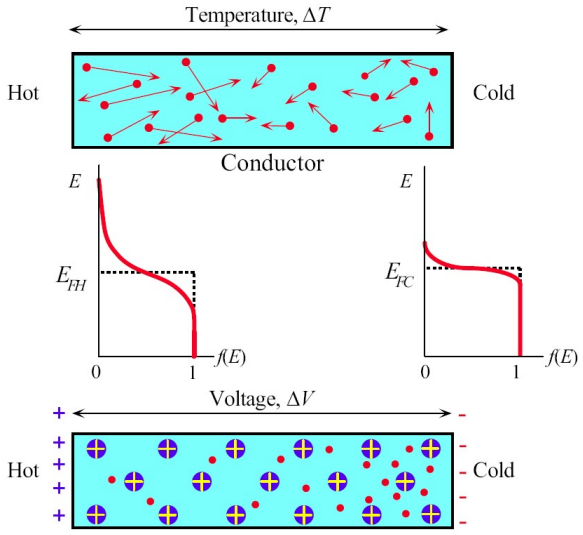


The Seebeck effect. A temperature gradient along a conductor gives rise to a potential difference.

Seebeck Effect

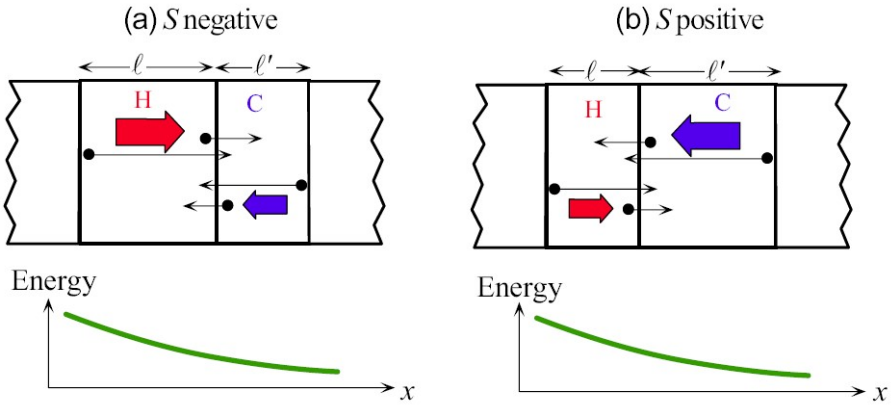
Seebeck effect (thermoelectric power)

is the built-in potential difference ΔV across a material due to a temperature difference ΔT across it.

$$S = \frac{\Delta V}{\Delta T}$$

Sign of *S*

is the potential of the cold side with respect to the hot side; negative if electrons have accumulated in the cold side.



Consider two neighboring regions H (hot) and C (cold) with widths corresponding to the mean Free paths l and l' in H and C.
Half the electrons in H would be moving in the +*x* direction and the other half in the –*x* direction.
Half of the electrons in H therefore cross into C, and half in C cross into H.

Seebeck coefficient for metals

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$$S \approx -\frac{\pi^2 k^2 T}{3eE_{FO}} x$$

Mott and Jones thermoelectric power equation

x = a numerical constant that takes into account how various charge transport parameters, such as the mean free path ℓ, depend on the electron energy.

x values are tabulated in Table 4.3

DOES NOT APPLY TO MATERIALS HAVING OVERLAPPING BANDS – e.g. Ni

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Table 4.3 Seebeck coefficients of selected metals (from various sources)

Metal	S at 0 °C ($\mu V\ K^{-1}$)	S at 27 °C ($\mu V\ K^{-1}$)	E_F (eV)	x
Al	−1.6	−1.8	11.6	2.78
Au	+1.79	+1.94	5.5	−1.48
Cu	+1.70	+1.84	7.0	−1.79
K		−12.5	2.0	3.8
Li	+14		4.7	−9.7
Mg	−1.3		7.1	1.38
Na		−5	3.1	2.2
Pd	−9.00	−9.99		
Pt	−4.45	−5.28		

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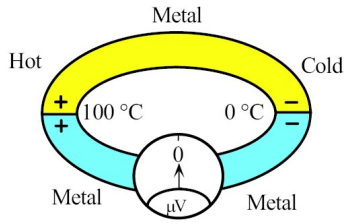
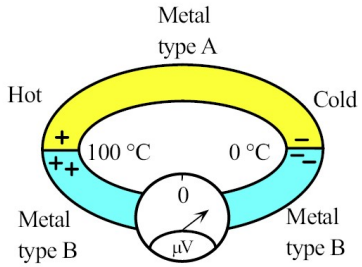
(a)



(b)



(a) If Al wires are used to measure the Seebeck voltage across the Al rod, then the net emf is zero. (b) The Al and Ni have different Seebeck coefficients. There is therefore a net emf in the Al-Ni Circuit between the hot and cold ends that can be measured.

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Thermocouple

We can only measure differences between thermoelectric powers of materials.

When two different metals *A* and *B* are connected to make a **thermocouple**, then the net EMF is the voltage difference between the two elements.

$$V_{AB} = \int_{T_o}^{T} (S_A - S_B) dT = \int_{T_o}^{T} S_{AB} dT$$

Thermocouple Equation

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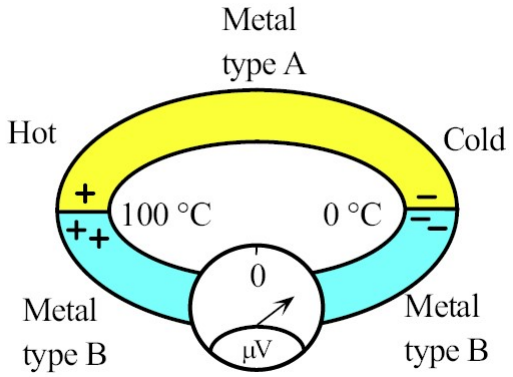

$$V_{AB} = a\Delta T + b(\Delta T)^2$$

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Table 4.4 Thermoelectric emf for metals at 100 and 200 °C with respect to Pt and the reference junction at 0 °C

Material	emf (mV)	
	At 100 °C	At 200 °C
Copper, Cu	0.76	1.83
Aluminum, Al	0.42	1.06
Nickel, Ni	−1.48	−3.10
Palladium, Pd	−0.57	−1.23
Platinum, Pt	0	0
Silver, Ag	0.74	1.77
Alumel	−1.29	−2.17
Chromel	2.81	5.96
Constantan	−3.51	−7.45
Iron, Fe	1.89	3.54
90% Pt–10% Rh (platinum-rhodium)	0.643	1.44

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Thermocouples are widely used to measure the temperature.

LEFT: A thermocouple pair embedded in a stainless steel sheath-probe. The thermocouple junction inside the probe is in thermal contact with the probe tip, and, electrically insulated from the probe metal.

SOURCE: Courtesy of Omega

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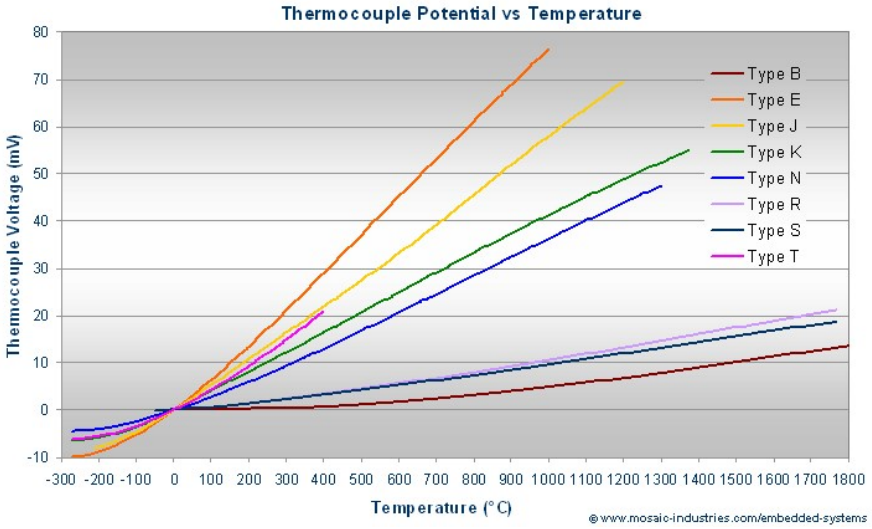

Examples of vacuum tubes using thermionic emission

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TOP: UHF Tetrode vacuum tubes that can handle up to 30 kW, and provide gains up to 17 dB

|SOURCE: Courtesy of Thales

LEFT: Klystrons are used as the final amplifier stage in many UHF television transmitters.

|SOURCE: Courtesy of Thales

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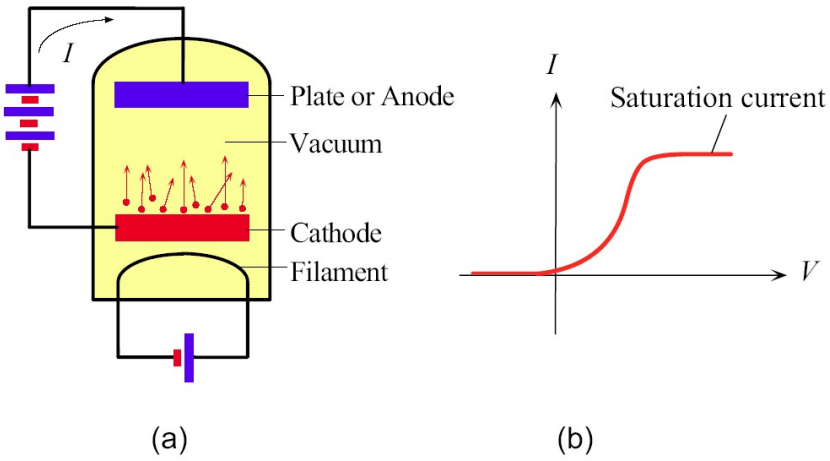

(a) Thermionic electron emission in a vacuum tube.
(b) Current-voltage characteristics of a vacuum diode.

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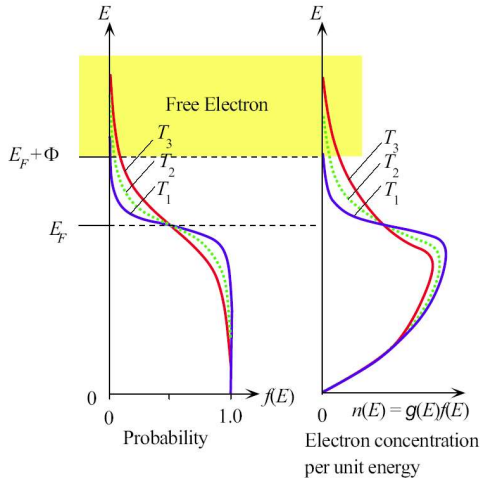

Fermi-Dirac function $f(E)$ and the energy density of electrons $n(E)$ (electrons per unit energy and per unit volume) at three different temperatures. The electron concentration extends more and more to higher energies as the temperature increases. Electrons with energies in excess of $E_F+\Phi$ can leave the metal (thermionic emission)

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Thermionic Emission

Richardson-Dushman thermionic emission equation

$$J = B_o T^2 \exp\left(-\frac{\Phi}{kT}\right)$$

$B_o = 4\pi e m_e k^2/h^3 = 120\times10^6$ A m^{-2} K^{-2}

Richardson-Dushman constant

$$J = B_e T^2 \exp\left(-\frac{\Phi}{kT}\right)$$

where B_e = effective emission constant = (1-R) B_0

R = Reflection coefficient

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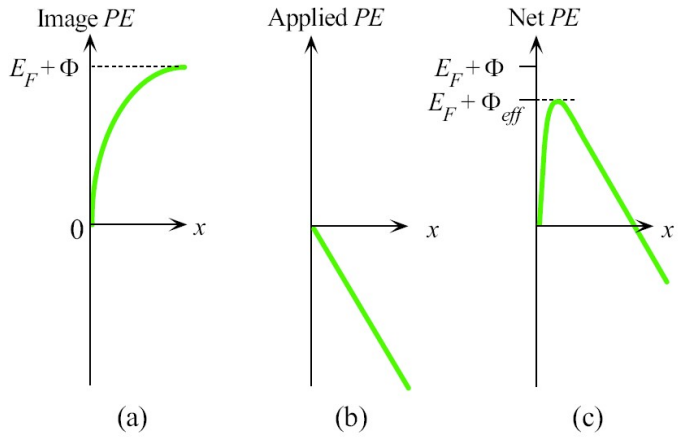

(a) PE of the electron near the surface of a conductor.
(b) Electron PE due to an applied field, that is, between cathode and anode.
(c) The overall PE is the sum.

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Schottky effect

When a positive voltage is applied to the anode with respect to the cathode, the electric field at the cathode helps the thermionic emission process by lowering the *PE* barrier Φ by an amount $\beta_S \mathcal{E}^{1/2}$. The current density in field assisted thermionic emission is

Metal's work function — Schottky coefficient

$$J = B_e T^2 \exp\left(-\frac{\Phi - \beta_S \mathcal{E}^{1/2}}{kT}\right)$$

Field assisted emission is field assisted tunneling from the cathode

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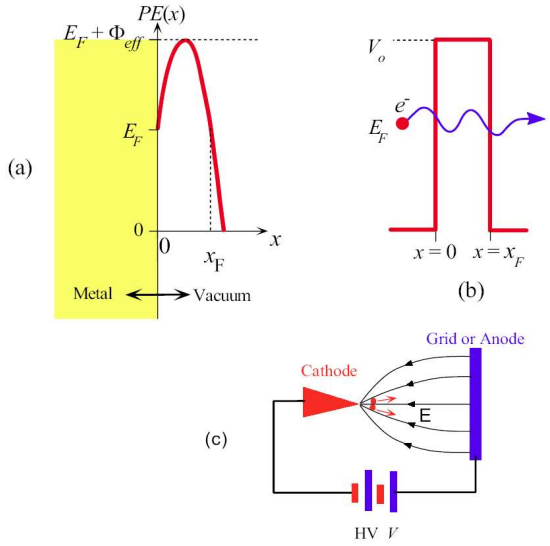

(a) Field emission is the tunneling of an electron at an energy E_F through narrow *PE* barrier induced by a large applied field.
(b) For simplicity, we take the barrier to be rectangular.
(c) A sharp point cathode has the maximum field at the tip where the field emission of electrons occurs.

Field-assisted Tunneling

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Field-assisted tunneling probability

Effective work function due to the Schottky effect

$$p \approx \exp\left[-\frac{2\left(2m_e\Phi_{\text{eff}}\right)^{1/2}\Phi}{e\hbar\mathcal{E}}\right]$$

Field-assisted tunneling: the Fowler-Nordheim equation

Constants

$$J_{\text{field-emission}} \approx C\mathcal{E}^2 \exp\left(-\frac{\mathcal{E}_c}{\mathcal{E}}\right)$$

Applied field at the cathode

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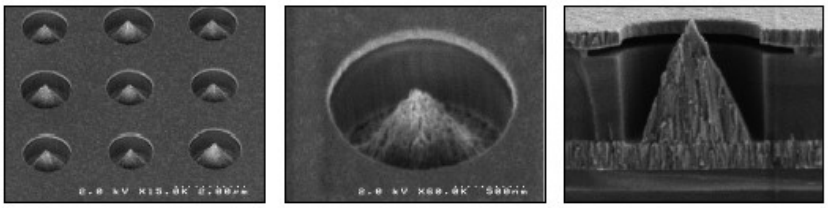

Left: A scanning electron microscope image of an array of electron field emitters (icebergs). Center: One iceberg. Right: A cross section of a field emitter. Each iceberg is a source of electron emission arising from Fowler–Nordheim field emission; for further information see B. Chalamala, et al., *IEEE Spectrum,* April 1998, pp. 42–51.

SOURCE: Courtesy of Dr. Babu Chalamala, Flat Panel Display Division, Motorola.

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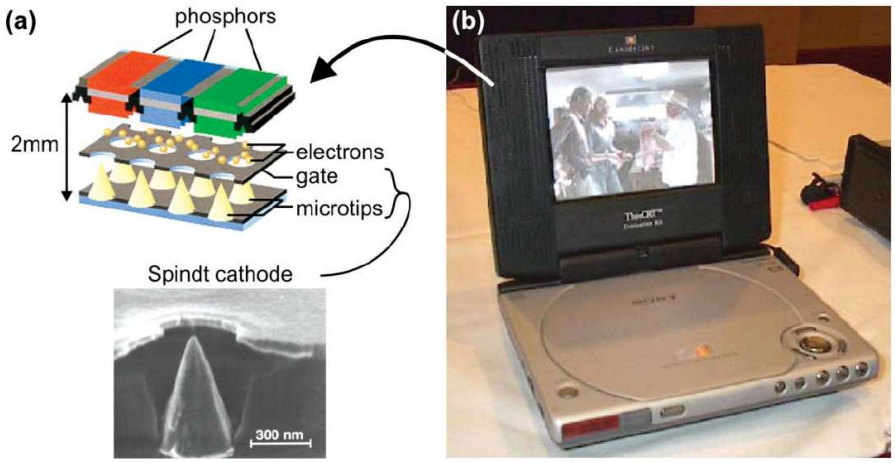
Motorola's prototype flat panel display based on the Fowler-Nordheim field emission principle. The display is 14 cm in diagonal and 3.5 mm thick with a viewing angle 160°. Each pixel (325 μm thick) uses field emission of electrons from microscopic sharp point sources (icebergs). Emitted electrons impinge on colored phosphors on a screen and cause light emission by cathodoluminescence. There are millions of these microscopic field emitters to constitute the image.

SOURCE: Courtesy of Dr. Babu Chalamala, Flat Panel Display Division, Motorola.



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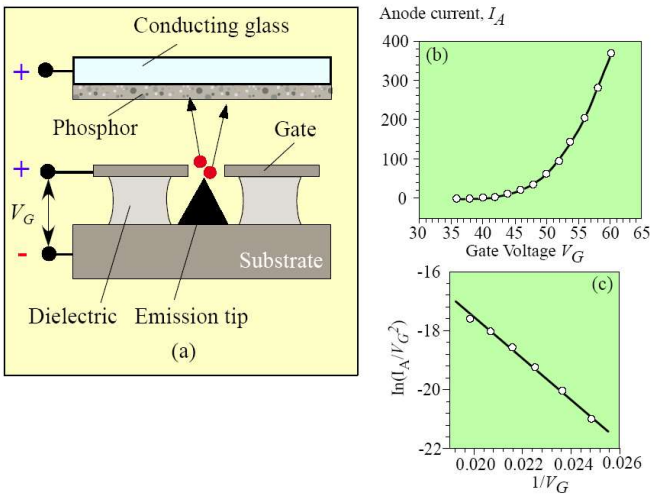
Cross-section of a field emission display showing a Spindt tip cathode, (b) Sony portable DVD player using a field emission display.

SOURCE: Courtesy of Professor W.I. Milne, University of Cambridge, England. *Carbon nanotubes as field emission sources,* W. I. Milne, K. B. K. Teo, G. A. J. Amaratunga, P. Legagneux, L. Gangloff, J.-P. Schnell, V. Semet, V. Thien Binh and O. Groening, *Journal of Materials Chemistry,* **14**, 933, 2004



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(a) Spindt-type cathode and the basic structure of one of the pixels in the FED.
(b) Emission (anode) current versus gate voltage.
(c) Fowler-Nordheim plot that confirms field emission.

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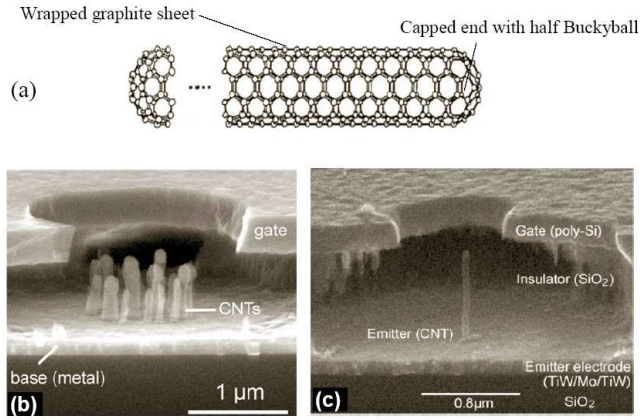

(a) A carbon nanotube (CNT) is a whisker-like very thin and long carbon molecule with rounded ends; almost a perfect shape as an electron field-emitter. **(b)** Multiple CNTs as electron emitters. **(c)** A single CNT as an emitter.
|SOURCE: Courtesy of Professor W.I. Milne, University of Cambridge; G. Pirio *et al*, *Nanotechnology*, **13**, 1, 2002.

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CNT (Carbon NanoTube)

A carbon nanotube (CNT) is a very thin filament-like carbon molecule whose diameter is in the nanometer range but whose length can be quite long, e.g., 10-100 microns, depending on how it is grown or prepared.

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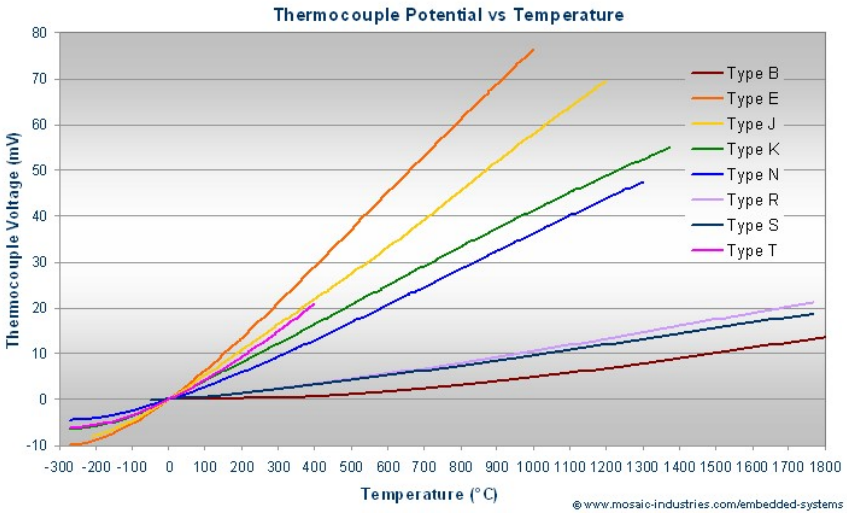

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Thermocouple Types			
Type	**Composition**	**Sensitivity**	**Temperature range**
Type B	(+) Platinum - 30% Rhodium (−) Platinum - 6% Rhodium	5 to 10 µV/°C	+250 to +1820 °C
Type E	(+) Chromel (Ni-Cr) (−) Constantan (Cu-Ni)	40 to 80 µV/°C	−270 to +1000 °C
Type J	(+) Iron (−) Constantan (Cu-Ni)	50 to 60 µV/°C	−210 to +1200 °C
Type K	(+) Chromel (Ni-Cr) (−) Alumel (Ni-Al)	28 to 42 µV/°C	−250 to +1250 °C
Type N	(+) Nicrosil (Ni-Cr-Si) (−) Nisil (Ni-Si-Mg)	24 to 38 µV/°C	−250 to +1300 °C
Type R	(+) Platinum (−) Platinum - 13% Rhodium	8 to 14 µV/°C	−50 to +1768 °C
Type S	(+) Platinum (−) Platinum - 10% Rhodium	8 to 12 µV/°C	−50 to +1768 °C
Type T	(+) Copper (−) Constantan (Cu-Ni)	17 to 58 µV/°C	−250 to +400 °C

Table 1 Table of thermocouple wire alloy composition and useful temperature ranges for different thermocouple types.

http://www.mosaic-industries.com/embedded-systems/microcontroller-projects/temperature-measurement/thermocouple/types-wire-element

For more information, check with: https://en.wikipedia.org/wiki/Thermocouple