



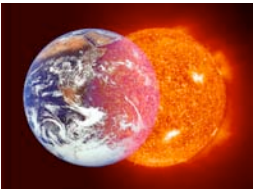
# Essentials of Quantum Physics

## References

Direct energy conversion by S.W. Angrist, Ch 3. (out of print text book)

Essential Quantum Physics by Peter Landshoff, Allen Metherell and Gareth Rees, 1997, Cambridge University Press.

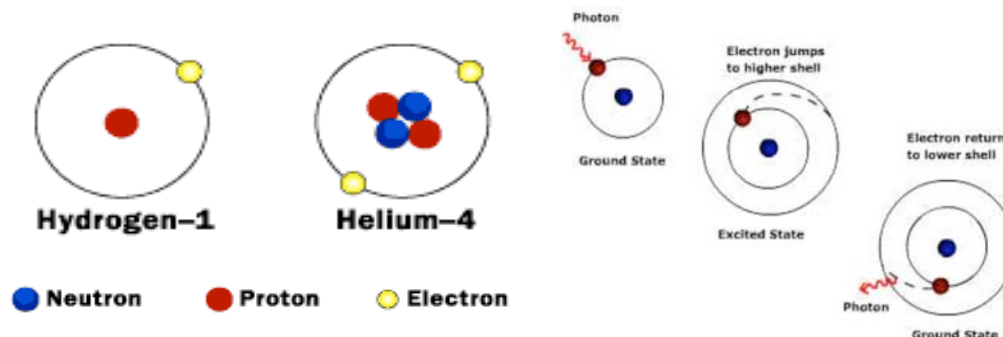


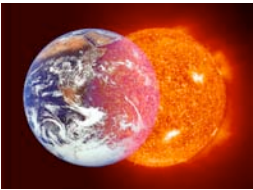


# Atoms

Atoms are believed to be the basic building blocks of matter. An atom consists of a positively charged **nucleus** together with a number of negatively charged **electrons**. Inside the nucleus there are **protons** and **neutrons** that carry positive charge and no charge respectively. The diameter of the whole atom is about  $10^{-10}$  m. Since the diameter of the nucleus is of the order of  $10^{-15}$  m, it may be considered as a point charge. The mass of the proton or neutron is some 2000 times that of the electron (mass =  $9.1 \times 10^{-31}$  kg; charge =  $-1.6 \times 10^{-19}$  Coulombs), hence nearly all the mass of the atom is in the nucleus.

Electrons carry a negative charge and circle the nucleus, in special orbits, because of the attractive electrostatic force according to Coulomb's law. When they jump between these special orbits, they would cause radiation with a little bursts of light (electromagnetic energy) generally referred to as **photons**. This energy is known to change only in little jumps, called **quanta**. Atoms do not obey classical mechanics and one resorts to **Quantum mechanics** for their behavior.





# Photons

**Photon:** a quantum of electromagnetic energy having both particle and wave properties.

A photon has no electric charge or mass but possesses momentum, energy and spin. In the present context, the focus is on the interaction of electromagnetic waves (*photons*) with *electrons* to understand the creation and absorption of light.

Electromagnetic waves have wavelengths ranging from 1 nm ( $10^{-9}$  m) for x-rays to 1 km for radio waves. All electromagnetic radiation, in vacuum, moves at the speed of light ( $c = 3 \times 10^8$  m/s). The speed of the photons changes when they pass through different media, such as water, glass and air.

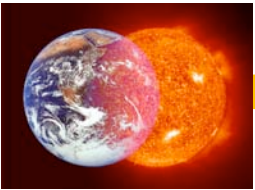
In a metal, the atoms are anchored to fixed sites by the electrostatic forces due to all the other atoms. The outermost orbital electrons of the atoms are almost free, and move through the metal when an electric field is applied.

It is known that if one shines a beam of light on a clean surface of a metal, electrons can escape from the metal surface and can be detected as electric current - *photoelectric effect*. The light has to exceed a certain energy to remove electrons from the metal surface. The number of electrons that escape in a given time rises with the light beam intensity. However, the energy with which they escape does not depend on the beam intensity, rather it depends on the *frequency* of light,  $\nu$  (in Hz). The energy  $E$  of each photon is proportional to frequency.

$$E = h\nu$$

Where  $h$  is Planck's constant that is equal to  $6.626 \times 10^{-34}$  J s.

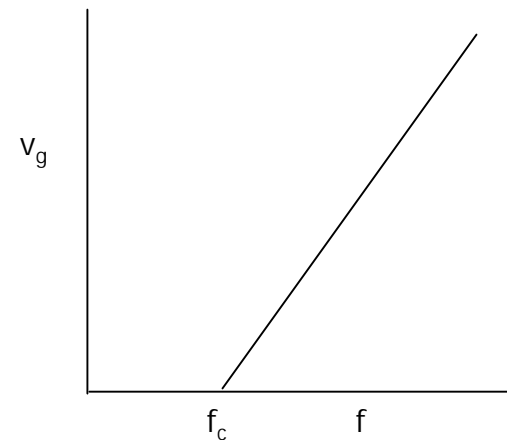
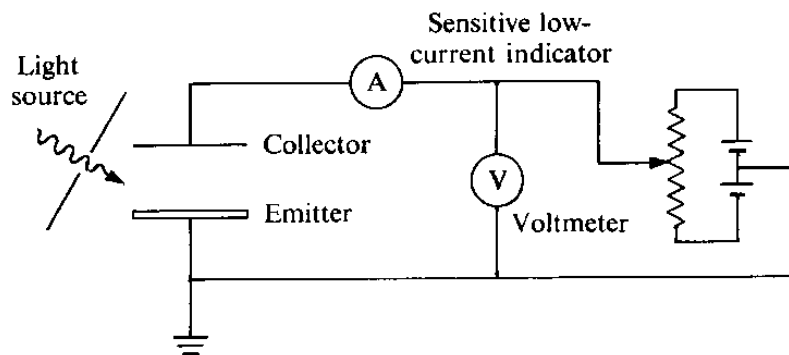




# Photoelectric Emission

The understanding of the physics of semiconductors requires some knowledge of pertinent parts of quantum mechanics.

**The photoelectric emission of electrons:** If a light of certain frequency is allowed to fall on a metal (emitter) plate, some electrons will receive enough energy to be released from the plate. The positive bias supplied by the battery in the circuit causes these free electrons to be attracted to the collector and a current is caused to flow. By making the voltage of the collector plate negative, the current can be made to go to zero. The voltage that reduced the current to zero is called  $V_g$ , the *stopping potential*. Using a monochromatic light it can be shown that the photocurrent increases with the intensity of light. The minimum frequency of light that will cause electrons to be released is called *threshold frequency* ( $f_c$ ) of the material. When light of a frequency less than the threshold frequency is applied to the material, regardless of its intensity, no electrons are released.





# Photons

The kinetic energy  $T$ , with which the electrons escape is given by:  $h\nu = T + W$

Here  $h$  is Planck's constant, and  $W$  is the energy that must be given to the electron to enable it to overcome the electrostatic attraction of the metal. For a given metal, there is a minimum value  $W_0$ , that is referred to as *work function* of the metal. The electron is ejected from the metal when one of the photons collides with it and is absorbed by it, so giving up all its energy to the electron.

The energy of the particle is given by the laws of special relativity as

$$E = \frac{mc^2}{\sqrt{1 - \left(\frac{u^2}{c^2}\right)}}$$

where the particle speed is  $u$  and whose rest mass is  $m$ . When  $u = c$  the energy can be finite only if  $m = 0$ ; i.e. photons have zero mass. In terms of the momentum  $p$  of the particle, the above equation can be written as

$$E = c\sqrt{m^2c^2 + p^2}$$

So that for a photon

$$E = cp$$





# Compton Effect

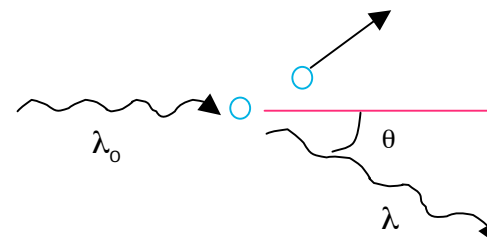
Classical electromagnetic theory indicates that when radiation passes through matter, the resulting scattered radiation should have the same frequency as the incident radiation. Using monochromatic X rays, Compton found that the scattered radiation from a surface gives rise to a higher wavelength in addition to the incident light wavelength. The conservation of momentum and energy requires that the photon must have a lower energy, and hence lower frequency, than the incident photon. The energy of photon is reduced by just that amount of energy that the electron gains. The associated wavelength is given by

$$\lambda = \frac{h}{p} = \frac{h}{mu}$$

Where  $p$  is the momentum of a "particle" with mass  $m$  and velocity  $u$ .

$$\lambda = \lambda_o + \frac{h}{mc}(1 - \cos\theta) \approx \lambda_o + 0.0024(1 - \cos\theta)$$

$$m_e = 9.11 \times 10^{-31} \text{ kg}$$





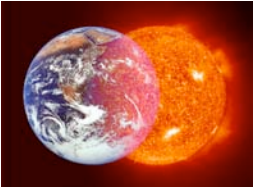
# Atomic Spectra

According to the results of quantum mechanics, the allowed energy levels of the electrons in atoms are discrete. If a beam of light is shone on a collection of atoms, the photons can be absorbed by the atoms if, and only if, their energy is equal to the difference between the energies of two electron levels. The absorption of the photon then excites the atom sending the electron from the lower to higher level. Thus only **photons with certain discrete frequencies are absorbed**. Conversely, an atom in an excited state can decay by emitting a photon; the frequency of the photon depends on the difference between the initial and final energies:

$$h\nu = E_2 - E_1$$

The energy levels of an atom depends on properties of the element. The spectrum of frequencies absorbed and emitted provides a way of identifying substances.





# Quantum Numbers

The Bohr model of the atom involves a single quantum number, the integer  $n$  that appears in the expression for the energy of an electron in an orbit. ( $n$ : any integer from 1 to  $\infty$ )

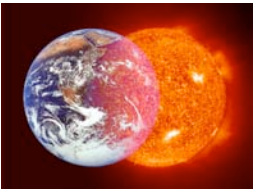
But a full quantum mechanical treatment requires four quantum numbers to characterize the electron orbitals. These are known as the **principal quantum number,  $n$** , the **orbital quantum number,  $L$**  the **magnetic quantum number,  $m_L$** , and the **spin quantum number,  $m_s$** . These are all associated with particular physical properties.  $n$ , the principal quantum number.

The **orbital quantum number  $L$** , is connected to the total angular momentum of the electron. (integer from 0 to  $n-1$ )

The energy of any orbital depends on the **magnetic quantum number,  $m_L$**  only when the atom is in an external magnetic field. (integer from  $-L$  to  $+L$ )

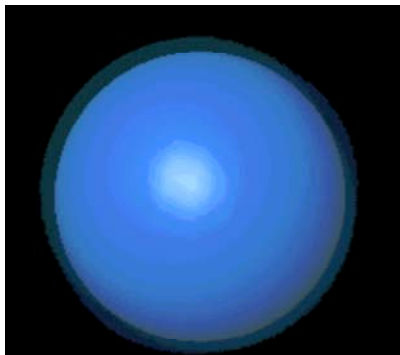
The **spin quantum number,  $m_s$**  is related to the spin angular momentum of the electron. There are only two possible states for this quantum number, often referred to as spin up and spin down. ( $\pm 1/2$ )



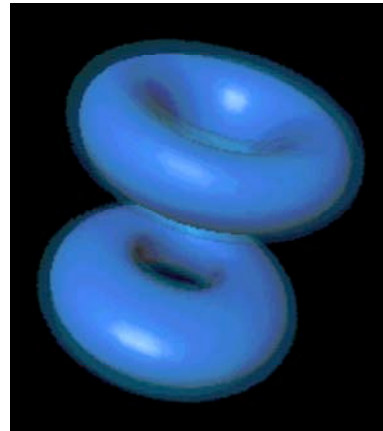


# Quantum Numbers

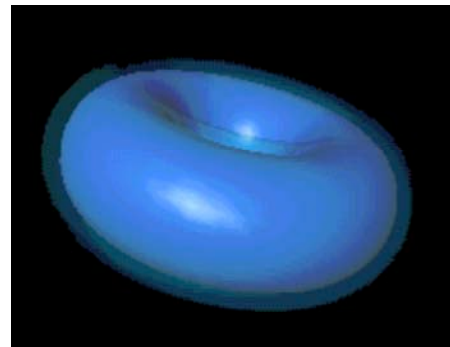
We need all four to completely describe the state an electron occupies in the atom.



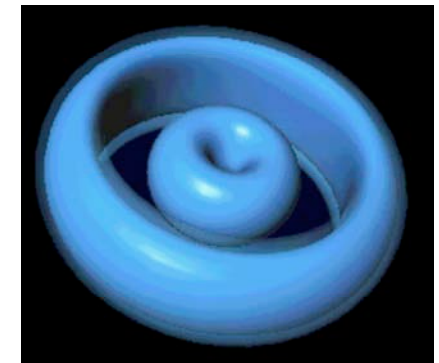
$n=1, L=0, m_L=0$



$n=1, L=2, m_L=1$



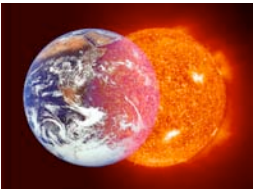
$n=3, L=2, m_L=2$



$n=4, L=2, m_L=2$

Electron probability clouds: An electron in an atom is no longer considered to be moving in a simple orbit. Rather, its exact location and velocity at any time is unknown, but its probability of being found at any point is known. Thus the electron is spread out in a probability cloud which has a wave-like character around the nucleus. These electron probability clouds have interesting shapes which are described precisely by the mathematics of quantum mechanics





# Schrodinger Equation

It is a wave equation that encompasses all the quantum mechanics principles and it replaces the familiar  $F=ma$  of classical mechanics. The variable used in this equation is the *wave function*, denoted by  $\psi$ . This variable although does not corresponds no physical occurrence, it represents the probability of finding an electron in a certain region of space. For example, concentrations of electrons will occur in those regions where  $|\psi|^2$  is high.

The Schrodinger equation describes non-relativistic particles, whose energy  $E$  and momentum  $p$  are related by

$$E = \frac{p^2}{2m}$$

This equation is valid so long as the energy  $E$  is not comparable or larger than  $mc^2$ . We recall that:

$$\nu = \frac{E}{h} \quad \text{and} \quad \lambda = \frac{h}{p}$$





# Schrodinger Equation

It is convenient to introduce the angular frequency  $\omega = 2\pi\nu$  and the wave vector  $\mathbf{k}$ , whose direction is in the direction of wave propagation and whose magnitude is  $k = 2\pi/\lambda$ . We define (pronounced as "h-cross")

$$\hbar = \frac{h}{2\pi}$$

to have

$$\vec{p} = \hbar\vec{k}$$

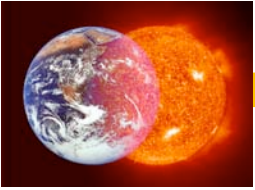
$$E = \hbar\omega$$

For a free particle which is not interacting with any other particle, we note that  $p$  and  $E$  are constants. Hence we expect such a particle to be described by a wave for which  $\mathbf{k}$  and  $\omega$  are constant.

$$\Psi(\vec{r}, t) = Ne^{-i(\vec{k}\cdot\vec{r} - \omega t)}$$

Here  $\mathbf{r}$  denotes the position vector and  $N$  is a constant. The function  $\Psi$  represents a plane wave and is a simplest example of a wave function for a free particle.





# Schrodinger Equation

To determine wave functions that describe particles that are not free, we perform simple manipulations on the expression  $\Psi(\vec{r}, t) = Ne^{-i(\vec{k}\cdot\vec{r}-\omega t)}$  to yield the following equation.

$$\left(-i\hbar\frac{\partial}{\partial x_j}\right)\Psi = p_j\Psi; (j = 1, 2, 3)$$

or

$$(-i\hbar\nabla)\Psi = \vec{p}\Psi$$

Here  $\Psi$  is an eigenfunction of the operator  $\left(-i\hbar\frac{\partial}{\partial x_j}\right)$  with eigenvalue  $p_j$ .

The energy of a free particle is given by  $\mathbf{p}^2/2m$ . The corresponding differential operator is simply given by

$$\frac{(-i\hbar\nabla)^2}{2m} \text{ or } \frac{-\hbar^2\nabla^2}{2m}$$

If the particle has a potential energy  $P(r)$ , this operator becomes

$$H = \left(\frac{-\hbar^2}{2m}\right)\nabla^2 + P(\vec{r})$$

Where H is called the Hamiltonian operator.





# Schrodinger Equation

To find the possible energy levels  $E$  of the particle, we must find the eigen values  $E$  of  $H$  by solving the following equation with appropriate boundary conditions.

$$H\Psi = E\Psi$$
$$\left[ \left( \frac{-\hbar^2}{2m} \right) \nabla^2 + P(\vec{r}) \right] \Psi(\vec{r}, t) = E\Psi(\vec{r}, t)$$

This equation is the *time-independent Schrodinger equation*.

In general  $P$  depends explicitly on the time  $t$  as well as the position  $r$  of the particle. Using the plane-wave solution appropriate to a free particle, we now write the *time-dependent Schrodinger equation* as

$$\left[ \left( \frac{-\hbar^2}{2m} \right) \nabla^2 + P(\vec{r}, t) \right] \Psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t)$$

Where  $h$  is Planck's constant,  $P$  is the particle potential energy and  $i$  is the imaginary number. In general, solutions to the above equation are tedious and can be only obtained for some special cases.





# One-dimensional Potential Well

Example: For an electron bound in an atom, the values of  $E$  that are allowed by the time-independent Schrodinger equation are discrete. That is, the energy levels of a bound state are quantized. The simplest mathematical model of a bound state situation is as follows.

Suppose that the wave function  $\psi$  depends on only one coordinate  $x$ . Let the potential be the infinite square well

$$\begin{aligned} p &= 0 & 0 < x < a \\ p &= \infty & \text{otherwise} \end{aligned}$$

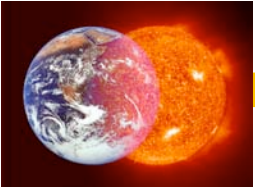
To find the states of definite energy  $E$  we solve the following equation.

$$\left[ \left( \frac{-\hbar^2}{2m} \right) \frac{d^2}{dx^2} + P \right] \Psi(x) = E \Psi(x)$$

In the region  $0 < x < a$  the above equation reduces to

$$\left( \frac{-\hbar^2}{2m} \right) \psi''(x) = E \psi(x)$$





# One-dimensional Potential Well

Using the conditions at  $x = 0$  and  $x = a$ , the allowed wave functions are given by

$$\psi_n(x) = C_n \sin\left(\frac{n\pi x}{a}\right) \quad 0 < x < a$$
$$\psi_n(x) = 0 \quad \textit{otherwise}$$

The corresponding allowed energy values are

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2ma^2} \quad n = 1, 2, \dots$$

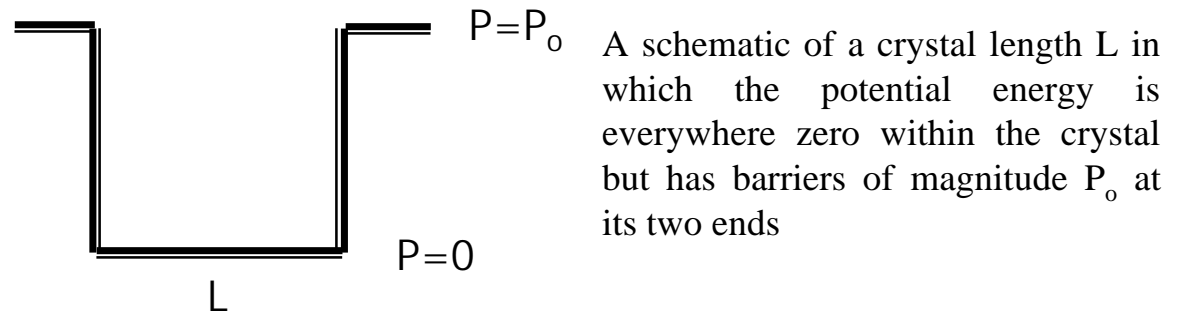
That is the allowed energy values for the bound system are discrete.





# One-dimensional Square Well

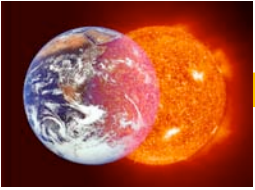
Consider a problem of a potential energy well as shown below. Idealized crystal (a collection of atoms arranged in a regular way) constitutes many such wells.



At the two ends of the well the electron is forbidden from leaving the crystal by high potential barrier  $P_0$ . If we further assume that the potential barrier to be infinite, the following relationship must hold:

$$\frac{2\pi}{h} \sqrt{2m\varepsilon} L = n\pi$$
$$n = 1, 2, 3, \dots$$





## One-dimensional Square Well

From the previous relationship, we observe that the energy can only assume discrete values, referred to as *eigenvalues*

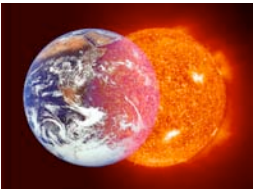
$$\epsilon_n = \frac{h^2 n^2}{8mL^2}$$

The quantity  $n$  in this equation is called the *quantum number*. In real crystal the height of the potential barrier is determined in a complex way by the crystal's surface energies.

When examining the solutions of Schrodinger equation in complex situations, we find that the dependence of the energy upon four different quantum numbers including the principle quantum number  $n$ . The electron's orbital angular momentum and the orientation of the angular momentum vector gives raise to two other quantum numbers that specify a possible state of the electron. The fourth quantum number represents the electron spin.

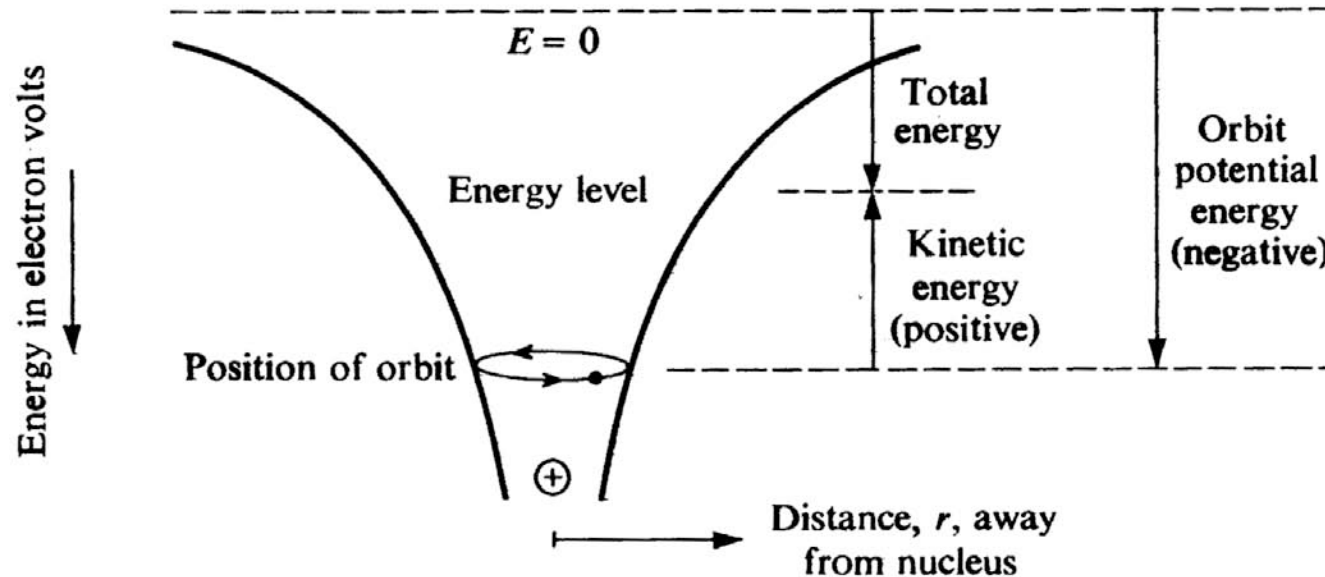
Pauli's principle states that no two electrons in an atom can have exactly the same set of four quantum numbers - *Pauli exclusion principle*.

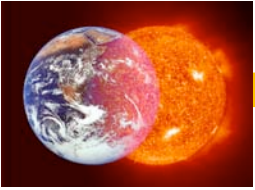




# Electron Energy

Crystals consists of a large number of atoms brought together in a orderly fashion. The energy of an electron (negative energy) placed at an infinite distance from nucleus (positive energy) is taken to be zero. As the electrons move toward the nucleus, their energy level goes down as depicted below. The total electron energy is the sum of its potential and kinetic energies.

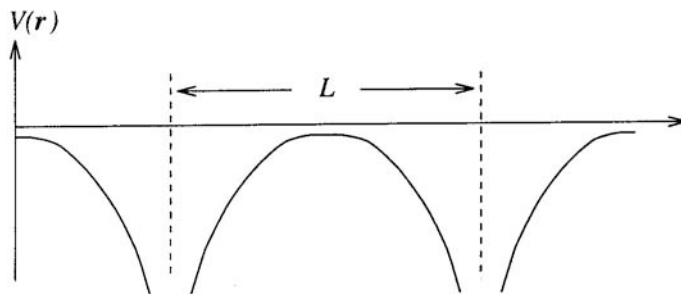




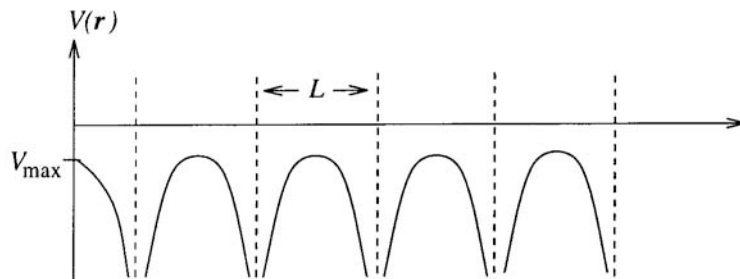
# Band Structure of Crystals

The energy of an electron bound to an atom is restricted to certain values.

We can assemble a crystal of identical atoms whose spacing  $L$  can be altered at will. If  $L$  is large enough, the electron motion in one atom will minimally be affected by the electrons and nuclei of other atoms. Then each atom behaves as if it were isolated, with its electrons in discrete bound states.

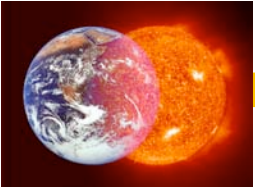


Atoms are widely separated



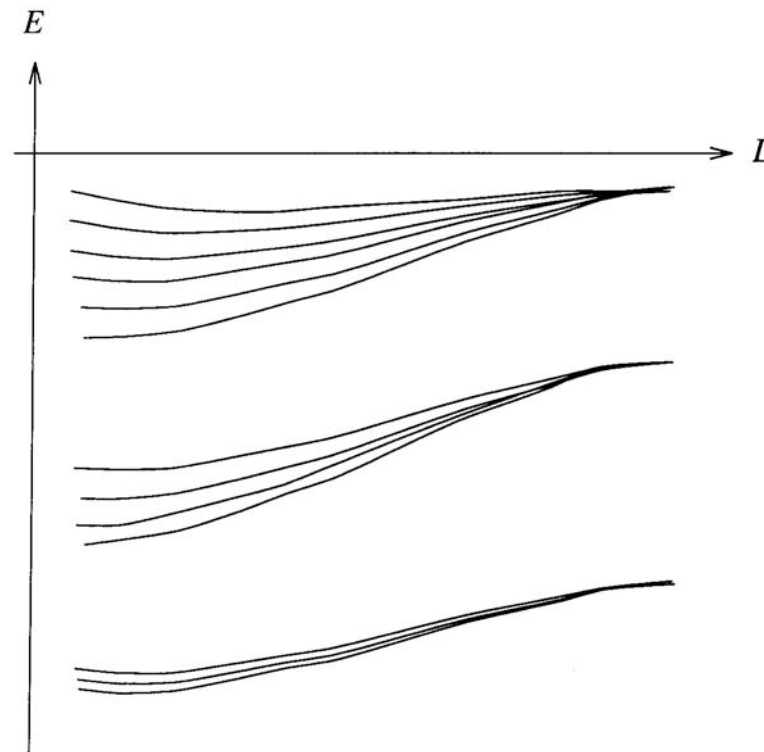
Atoms are close together

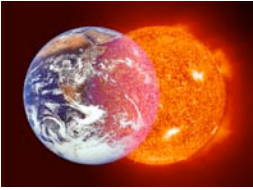




# Band Structure of Crystals

When  $L$  is reduced each original discrete atomic energy level spreads out into *bands* of closely spaced levels. These bands are separated by *energy gaps* that are forbidden to the electrons. This band structure is important in determining the properties of electrons in crystals. The band structure of a material has profound effect on its physical properties such as electrical conductivity and its optical properties. A solid is classified as an insulator or a semiconductor based on largely according to how good conductor it is.





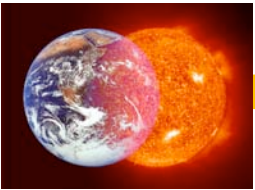
## Energy Bands

Electron energy levels are grouped into bands according to the solutions to Schrodinger equation. The properties of semiconductors are discussed in terms of *state* and *level*. The state of an electron is fixed by four quantum numbers and they specify both the wave function and the energy. For example consider two sets of quantum numbers: (3, 1, 1, 1/2) and (3, 1, -1, 1/2). These numbers will determine two different wave functions. The electron energy is simply the sum of the squares of the first three quantum numbers

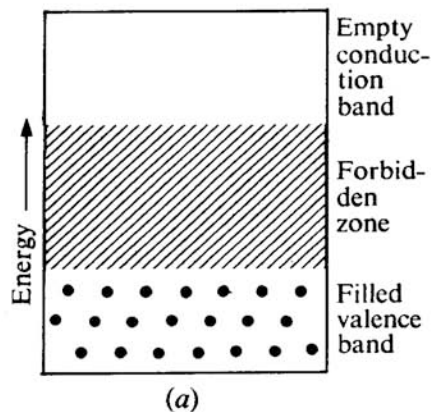
$$\varepsilon = (3^2 + 1^2 + 1^2) = (3^2 + 1^2 + (-1)^2)$$

Thus we observe that in this situation the energy levels are the same but the states are different. A situation in which energy levels are made up of more than one quantum state is called *degenerate*.

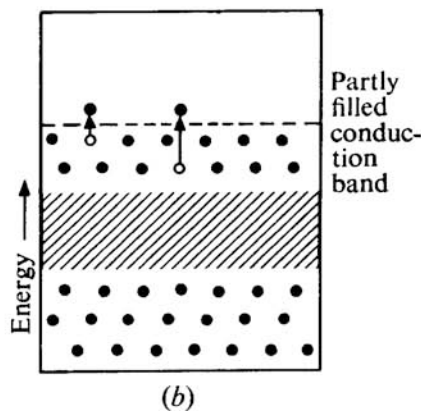




# Energy Bands

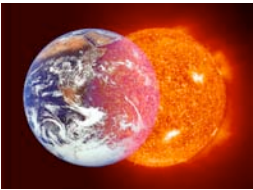


The energies of the electrons are restricted to energetically separated ‘energy bands’: the lower lying so-called valance band and energetically higher lying conduction band. The two bands are energetically separated by a band gap. Under the condition of thermal equilibrium the valance band of a pure semiconductor is practically fully occupied by immobile electrons sitting between neighboring semiconductor atoms and the conduction band is empty. Under these conditions no electrons can move about freely in the solid and the semiconductor behaves like an insulator

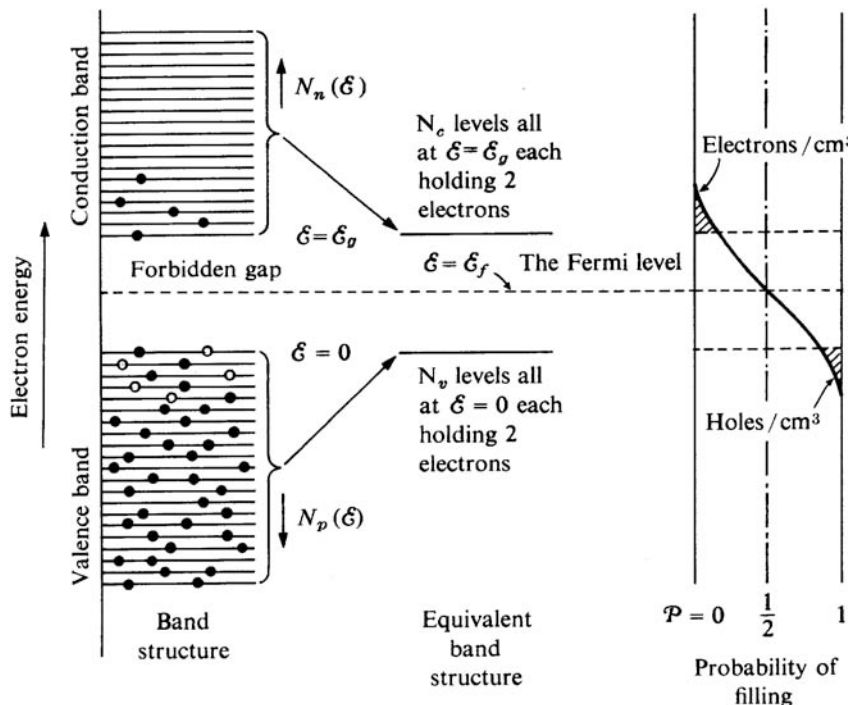


When a photon is absorbed in the semiconductor, thereby transferring energy to a bound immobile electron in the valance band which is then excited across the band gap into the conduction band, where it is free to move about the solid. The photon must carry more energy than required to transfer the electron across the gap. The electron that has been excited to the conduction band leaves a place in the valance band that is now not occupied by an electron. Such an empty energy state of a negatively charged electron behaves like a positively charged particle- a so-called [hole](#). These charge carrying holes are also comparatively free to move about the semiconductor solid.





# Electron-Hole pair



There is an attractive force between the negatively charged electron in the conduction band and the positively charged hole in the valence band resulting in a locally confined electron-hole pair. The attractive force creating this pair has to be overcome and the electron-hole pair split spatially in order to produce a useful electric current. If left alone, the excited electron will eventually recombine either with the original hole of the electron-hole pair or any other hole within reach to produce a photon or waste heat. It is therefore essential (in a solar cell application) to separate the charges in the photogenerated electron hole-pairs as soon as possible and to collect the charge at the external electrodes before they combine.



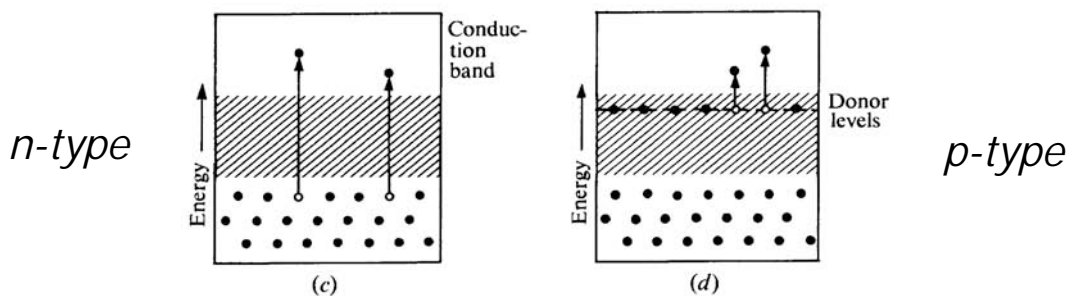


# Semiconductors

Recombination process between electrons and holes occur with high probability at distributed crystal sites. Surfaces represent areas of crystal imperfections and they can be avoided by depositing suitable coatings on the surface.

To manipulate electrical conductivity of a semiconductor is done by introducing well-controlled small amounts of dopant atoms. For example, the electrical conductivity in silicon can be significantly increased by replacing every one-millionth silicon atom by a phosphorus or a boron atom. The phosphorus atom has one electron more than the silicon atom. This leads to the fact that we have more freely mobile electrons than holes in the semiconductor, which is then said to be *n-doped*.

In contrast, the boron atom has one less electron than the silicon atom. The boron atom easily binds an electron from the valance band and produces a hole there, leading to *p-type* conduction. This p- and n-type conduction forms the basis of all semiconductors.





# Semiconductors

1. Materials, both compounds and elements, can be classified according to how well they conduct electricity. There are materials such as metals which conduct electricity well and those which conduct electricity poorly, called insulators. There are a few materials which fall in between. They conduct electricity a little bit. These materials are called semiconductors.
2. With the development of quantum theory and the band theory description of the (electrical) properties of elements, it became possible to understand what differentiated conductors, insulators and semiconductors in a comprehensive and testable theory.
3. The Pauli Exclusion Principle applied to electrons bound to an atom defines a series of distinct energy shells which electrons can fill. These shells are filled from the lowest energy level upwards. The Periodic Table arises with each element adding a proton and the filling of each shell taking one 'period' of the table.
4. The semiconducting elements form a loose band on the table; not quite metals and not quite insulators. Compounds formed from various crystalline and amorphous mixtures are also semiconducting.
5. On top of which, the electrical characteristics of semiconductors can be changed by introducing traces of other elements in minute proportions. This is called doping and is how n-type and p-type semiconductors are constructed.
6. By applying voltages and bias currents, semiconductors can function as switches forming the basis of transistors and by applying light radiation, semiconductors can function as photovoltaic devices.





# Semiconductors

Silicon is the most commonly used semiconductor, but there are many others. Examples are:

- \* gallium arsenide
- \* germanium
- \* selenium
- \* cuprous oxide
- \* lead telluride
- \* lead sulfide
- \* silicon carbide
- \* cadmium telluride
- \* indium gallium arsenide nitride
- \* copper indium gallium selenium





# Band Gaps

The band gap of a semiconductor, measured in electron volts [eV], is the difference between the valence band and the conduction band potentials. Each type of semiconductor has a unique band gap, most of which fall in the range 1.0 to 2.6 eV.

Semiconductor	Band Gap [eV]
Silicon	1.1
Gallium Arsenide	1.34
Copper Indium Delenide	1.0
Germanium	0.72
Indium antimonide	0.18
Cadium Sulfide	2.45
Zinc Oxide	3.3

The point to note here is that a photovoltaic material can only capture those photons which have an energy greater than or equal to the band gap of that material. Silicon, for example, will be transparent to photons with an energy of less than 1.1 eV. It might seem therefore, that the thing to do is use a very low band gap material, but the strength of the electric field created by the conjunction of n-type and p-type material is also dependent upon the band gap. One has to make a tradeoff between photon energy and field strength.





## Summary

With the development of quantum theory and the band theory description of the (electrical) properties of elements, it became possible to understand what differentiated conductors, insulators and semiconductors in a comprehensive and testable theory. The Pauli Exclusion Principle applied to electrons bound to an atom defined a series of distinct energy shells which the electrons could fill, from the lowest energy levels upward in distinct steps or quanta.

When many atoms are aggregated in a crystal structure, the distinct energy shells become bands. The lowest level shells, which may be partially filled, are called the valence band; while the higher unfilled levels are called the conduction band. The highest filled level of the atom at absolute zero is called the Fermi level. This marks a dividing line between the valence and conduction bands, in the centre of a forbidden energy gap, also known as the band gap.

In conductors, i.e. metals, the band gap is near zero, while insulators have a relatively high band gap and semiconductors are in the middle.

