

### 2.3. Molecules

From atoms to molecular self-assembly, we are witnessing the continual emergence of new properties.

The most complex edifices, ie molecules, are organized by the grouping together of atoms. It is the properties of these molecules that give us the world in which we evolve.

In fact, the grouping of atoms reveals the notion of functionality; from acid carrying hydrogen with one atom, up to large molecules in living organisms, genes and long chains of molecules assembled in a helix. The latter carries the building blocks of living organisms<sup>2</sup> which are not only present in the nanoworld but also in our world.

#### ***2.3.1. From the smallest molecule to the largest and their spectacular properties***

*The water molecule: H<sub>2</sub>O*

The extraordinary subtlety of the hydrogen bond means that humanity is unable to work out the different characteristics of its phases; for example, a liquid which solidifies itself into an ice crystal is less dense than water. Water is necessary for life on earth. Another example is a solid snow structure whose infinite complexity allows researchers to carry out up-to-date research in order to optimize the friction coefficient. We are witnessing the emergence of new properties which are replacing those of their

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<sup>2</sup> In a time when we can save hours of music onto an MP3 player, would it not be easier to imagine our life coded on one giant molecule? We could then believe we come from spontaneous creation or from homonculus, ie miniature versions of man that alchemists once pretended they were able to create.

atomic components. This will be the same for structures with an increasing complexity.

### *Proteins*

These molecules, which have enormous edifices with multiple configurations and functions, have developed a soft chemical catalyst by using the lock and key effect to interact. Here, an atom has its own unique place: carbon, which has four electrons in its outer shell (a half-full shell), is at the heart of the chemistry of living things along with hydrogen, oxygen, nitrogen, and some other elements. The atom is at the origin of the extraordinary variety of proteins which replicate themselves, join together, construct and deconstruct.

### *Carbon nanotubes*

These new objects, which are between the size of a molecule and an aggregate, will perhaps replace silicon which is the current leader in the world of electronics.

### **2.3.2. *Functionality***

The notion of functionality is fundamental. With bricks we can build a house; however, we can no longer see the individual components that make up the house once it is complete. In general, we are unable to predict the functionalities of a new molecule. When possible, a step-by-step construction of the molecule lets chemists work out its properties, at least in theory. If this is not possible, then the properties are discovered by trial and error, as is the case most of the time.

However, simulation, which is an extremely powerful approach based on the use of computers with advanced calculating capabilities and on the possibilities of unlimited information storage, has come to our rescue. This will be discussed later in this chapter.

## **2.4. Solid matter**

After molecules, another important construction is that of solid bodies, some of which have a particular status in the nanoworld. How can we consider an atomic aggregate of several nanometers in diameter to be an insulator or conductor with the magnetic and electrical properties according to size? First of all, we need to understand the behavior of the electron in solids when affected by external factors which is the case for crystalline bodies. After this, we will be able to analyze the effect of the size of the aggregates.

Whether the solid is an insulator, conductor or semi-conductor, everything depends on the circulation of electrons within it.

### **2.4.1. *Insulators or conductors***

The fact that a body is an insulator or a conductor is only the consequence of the electron's ability to move.

Let us take the example of an insulating material. It has no free electrons because they are all taking part in interatomic bonds. One particular class of insulator corresponds to transparent bodies. All the electrons are so tightly packed together that the luminous photons do not have enough energy to unlock them and the light travels through the solid body without being absorbed, as in the

case of glass (silicon oxide) or diamonds (covalent crystal of carbon).

On the other hand, metal is a conducting material. Its properties can be described in a relatively simple way by considering it as a “box” with free electrons. This “box” is made up of atoms of ionized metal that are positively charged. The resistance characterizes the shocks of the electrons with the ions, which increases with thermal agitation and therefore the temperature. Knowing that there is one electron for one ion, the density of electrons is very large and therefore the current is important. In the case of aggregates, where the number of atoms and therefore electrons is reduced, we start to notice the individual behavior of the electrons, for example in surface interactions which give particular optic properties. Without being fully aware of its properties, ancient glassmakers used gold dust to color glass.

#### **2.4.2. *Semi-conductors***

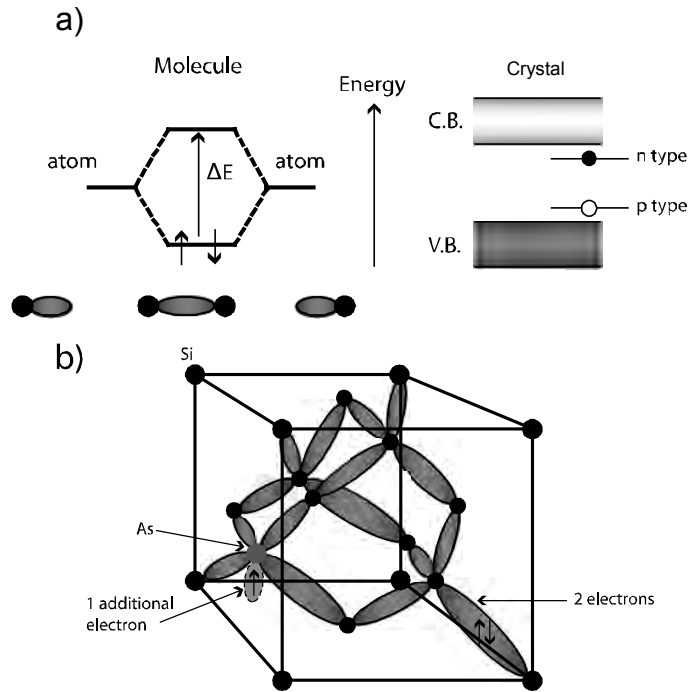
One particular item is essential for solid-state electronics and that is semi-conductors. They conduct electricity, but in a weaker way than a metal does. They allow for the manufacturing of components, such as the famous chip.

##### *2.4.2.1. Silicon crystal*

If we look at what happens in a crystal such as silicon, we notice that the silicon atom has, like germanium, four electrons on its outer shell; therefore it has four possible bonds. In silicon crystal, each atom is surrounded by four others and all the available electrons are used in the bonding process; no electrons can be free to participate in conduction. The crystal is therefore an insulator.

Let us then introduce some phosphorus into the silicon crystal in a weak concentration (doping is the term used when referring to semi-conductors). One phosphorus atom per million is a weak doping and one phosphorus atom per thousand is a strong doping. The phosphorus atoms randomly take the place of the silicon atoms without disrupting the crystalline lattice. The silicon crystal now becomes a conductor. Why? The phosphorus atom has five electrons on its outer shell, of which four are used to bond with their four neighboring atoms. The fifth electron is free and is only slightly held back by its original atom whose outer layer has eight electrons and is therefore saturated. It can consequently move within the crystal. We talk about n-type conduction (n for negative) and n-type silicon where the current is electronic.

Now let us see what happens when we introduce a weak concentration of indium atoms into the silicon crystal. They will also randomly take the place of the silicon atoms. In this case, the crystal also becomes a conductor. Yet the indium atom only has three outer electrons which are all used in the bonding process. However, one bond is not paired and an electron from a neighboring atom is able to come and make a pair with the remaining indium atom (there is no need for energy) to leave a partially unoccupied bond. The electron that moves leaves an equal and opposing charge and we can consider this conduction as the movement of a positive hole. We talk about p-type conduction and p-type silicon.



**Figure 2.6.** Molecular orbitals and the band structure of crystalline silicon

a) The chemical bond between two atoms is due to the joining of two electrons on a molecular orbital created by the interaction. The orbital possesses two energy levels, bonding and anti-bonding, separated by an energy  $\Delta E$ . In a solid, these levels widen to become bands, the valence band (VB) and the conduction band (CB) respectively.

b) For silicon (Si) which has four electrons on its outer shell, each electron bonds with one of the four neighboring atoms in the crystal. All the electrons take part in the bonding process. Thus, the valence band is full and there is no possible displacement of charge.

If a silicon atom is replaced by an atom from column 5 of the periodic table, such as arsenic (As), the fifth electron is weakly bonded and passes to the conduction band. The silicon crystal becomes a n-type conductor. If a silicon atom is replaced by an atom from column 3, there is an electron missing. This creates a hole which lets an electron move into the valence band. The silicon crystal becomes a p-type conductor.

#### 2.4.2.2. *Electrons and holes*

A simple representation of the concept of hole conduction can be created with the following analogy. We are driving on a road and if there are not many of people on the road then it is not difficult to get from one place to another; there is enough space for everyone. If there is a lot of traffic, our movement is then dependent on the number of available spaces. This image lets us understand the idea of hole conduction.

If we observe a large crowd of people, where one free place in the crowd allows gradual movement, movement appears to occur as if the “holes” travel in the opposite direction of the people who use them in order to move forward, as is the case for bubbles that rise in a liquid and represent the displacement towards the bottom of the corresponding liquid.

#### 2.4.2.3. *Junctions*

When a n-type silicon comes into contact with a p-type silicon, they form what is known as a junction. The current can only pass in one direction. In fact, if we look at it in terms of energy, the electrons from the “n” side do not have the same energy as those from the “p” side; these latter electrons take part in the bonding process and are strongly bonded in the crystalline lattice. The “n” electrons, which are free, are now more energetic. What happened to their contact? What happens when we try to join two liquid bodies of two different levels? What happens is that there is a flow of one into the other. But here, the liquid is electrically charged, and the passage of the electrons from the “n” crystal to the “p” crystal leads to the appearance of a difference in potential which balances the system. This is equal to the energy difference in volts of the banded-electron linked to the free electron states as is the case for silicon. If we directly polarize the atom, where the negative pole is on the “n”, then the current will flow. As a consequence, the “n” and “p” parts of a crystal automatically

isolate themselves, which is a property used in semi-conductor components.

On the basis of these components, technology lets us engrave billions of microscopic transistors together on the same plate, which when appropriately organized helps us create microprocessors.

### **2.4.3. *Nanomaterials***

As is the case with metals, we can produce structures with one, two or three nanometric dimensions. The most common structures are thin layers whose different production techniques enable us to precisely control the depth of the layer, measured in nanometers. Two examples include the self-cleaning surfaces of spectacles (the lotus effect) and silver bactericidal nanocatalysts in certain washing machines.

On this level, purely quantum effects will arise. We are talking about metamaterials, quantum wells, and other remarkable objects which are fascinating scientists, and becoming more and more a part of our daily life.

## **2.5. Quantum boxes: between the atom and the crystal**

The spherical, semi-conductor nanocrystal atoms, ranging in size from 2 to 50 nm (nanometers), also called quantum boxes or quantum dots, have intermediary properties between those of a molecule and a solid. The electron's energy is no longer spread out in bands of energy as in an ordinary semi-conductor, but in discrete, quantified levels as in an atom or in a molecule. The distribution of energy on these levels is relative to the size of the crystal. It results in the fact that the wavelength from the light source, which corresponds to the relative recombination of these



pseudo atoms under excitation, can be adjusted in the visible domain. This technique is largely used in the medical world where nanocrystals are used as fluorescent markers. We find a similar explanation for quantum well lasers.

## 2.6. Some bonus material for physicists

Let us now address the laser effect. What does laser mean? Laser stands for Light Amplification by Stimulated Emission of Radiation.

A laser is a common, visible object: from blackboard pointers to disco lights, we recognize lasers because they have a perfectly defined color – they are monochrome – and because the beams are straight. Their rays diverge much less than a normal projector.

The qualities mentioned above are linked because we use the properties of a cavity<sup>3</sup> in order to amplify and monochromatize the light. This light is normally emitted spontaneously from certain materials by the fundamental process of luminescence.

### 2.6.1. Luminescence

We have seen that electrons in an atom occupy a clearly defined state of energy. In their basic state, they occupy the electronic state with the lowest energy. If we put an electron into a superior electronic state, it becomes excited. Very quickly it will become de-excited by emitting energy.

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<sup>3</sup> This cavity in the optical world of electromagnetic waves is analog in the field of acoustics: a resonance cavity amplifies sound waves corresponding to stationary waves. This resonance cavity is fixed by the dimensions and shapes of the musical instruments.

In an atom, the energy exchanges are carried out by photons. Excitation and de-excitation correspond to the absorption and emission of a photon respectively during energy exchanges between two different energy states. The emission is completed either spontaneously or by stimulation by the photons themselves following an entrainment process. There cannot be any amplification in this case since the more the atom becomes excited, the more it will become de-excited. At most, we have a balance between the atoms in their basic state and in their excited state.

Let us now consider a system with three states of energy: the basic electronic state  $F$  and two excited electronic states with superior energy,  $E1$  and  $E2$ , with  $E2$  having more energy than  $E1$ . We excite an electron so that it can pass into the  $E2$  state. It comes back to its basic state by either directly emitting a photon of the same energy as what it has absorbed, or “in cascade”, by passing through the intermediary level  $E1$ . In the second case, it emits two photons whose additional energy corresponds to the unique energy of the direct transition. The excited electron has the choice between these two mechanisms. If the transit via the intermediary level  $E1$  is the quickest path, then it is clear that this is the path that will be taken by the electron.

This is what happens to certain atoms when they are introduced into solid bodies. The first, most commonly known example is chromium when it is introduced into an alumina lattice, which gives us rubies. It absorbs green light (transition  $A$ : from the basic state  $F$  to the superior excited state  $E2$ ) and emits red light (transition  $E$ : from the intermediary state  $E1$  to the basic state  $F$ ).

This emission technique can be explained in the following way: the chromium atom is not isolated and the transition from the superior excited state  $E2$  towards the intermediary is influenced by the presence of the lattice. In effect, the  $E2$  level corresponds to a state far from the nucleus of the chromium atom and it mixes with the states of neighboring atoms. It results in the fact that this level is no longer a purely atomic level; it acquires a wider energy band.

Furthermore, the transition towards the E1 level is a lot faster than the direct transition to the basic state, and is carried out by a non-radiation process producing heat.

This technique is essential because we have the possibility, by using green light, of having more atoms in the excited state than in the basic state during the lifetime of the E1 state, which is not subject to the absorbed photons by the E2 state. This phenomenon is known as population inversion. An amplification of light in this case is possible: for red light, the absorption is weaker than the stimulated emission that it will lead to, thus the laser effect is attained.

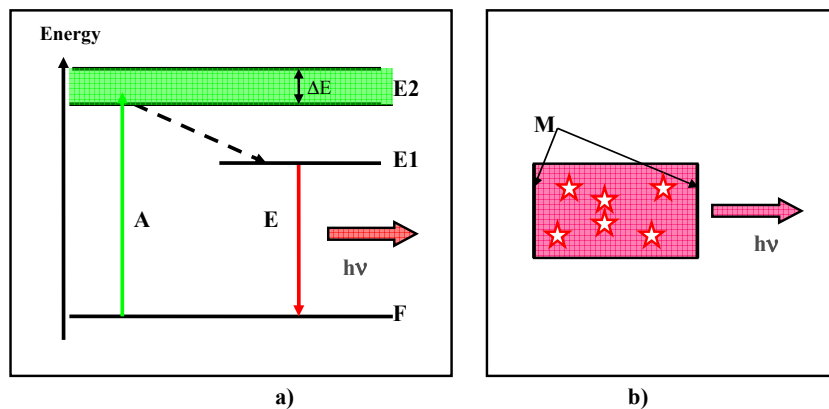
### **2.6.2. *The laser device***

If the amplifying medium is placed between two parallel mirrors forming a resonant cavity, then the red light will spontaneously release itself by auto-stimulation. The coherent stimulated amplification is then made by following a type of resonance which creates a very monochrome and guided beam of light following the axis of the cavity; the cavity being the mirror which is slightly transparent. We now have the laser effect.

Many other materials that possess light-emitting centers are used to create lasers of different wavelengths. If we continue the permanent excitation of atoms, or optical pumping, we have continuous wave lasers. If the excitation comes from a flash source, then we have a pulse laser.

Semi-conductor lasers function in a different way: luminescence occurs when the recombination of electrons and holes on the “pn” junction level is radiative, which is the case for certain materials such as gallium arsenide. Strictly speaking, this junction has to be directly polarized when we want to emit light. We produce electroluminescent diodes and semi-conductor lasers using the

same techniques that are used in microelectronics. Thus, at present we are able to develop hybrid circuits integrating lasers on silicon circuits, mainly for use in the world of telecommunications.



**Figure 2.7.** Light-emitting diodes and lasers: general principles

a) The electron of a light-emitting source, for example the ion  $\text{Cr}^{+3}$ , in the aluminum matrix for a ruby laser is excited from its basic structure F up to a state of energy E2 width  $\Delta E$  (absorption band). It quickly passes to the discrete state E1 by losing its energy in a non-radiative way.

b) The lifetime in the E1 state lets us keep a majority of electrons in this excited state during a strong illumination in the absorption band (optical pumping A). We also say that there is a population inversion. This system collectively de-excites itself by stimulation (the emission of energy  $E = h\nu$ ). If the material is placed in a resonant cavity with parallel mirrors (M), known as a Perrot-Fabry cavity, then the emission takes place in the form of a very thin ray (cavity resonance mode), and leaves through the semi-transparent mirror following a beam of light parallel to the axis of the cavity. There are three characteristics for laser lighting: monochromaticity, phase coherence, and directivity.

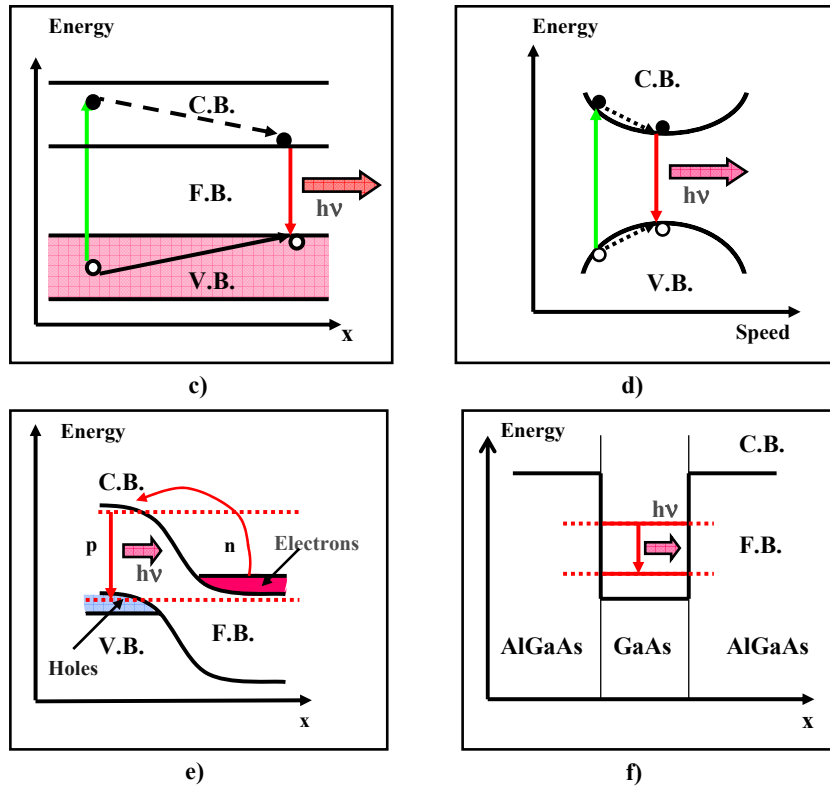


Figure 2.8. Semi-conductor lasers

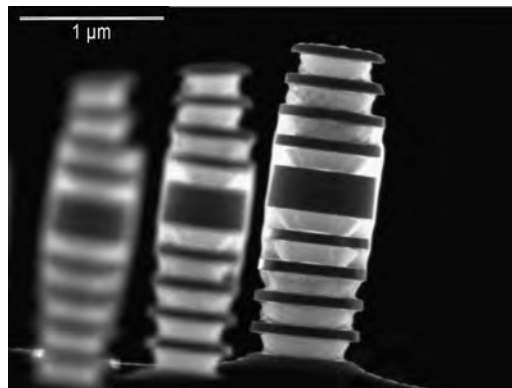
c) Diagram of a band. The valence band (VB), the forbidden band (FB) and the conduction band (CB). An electron is excited and passes into the conduction band. It immediately relaxes with the minimum energy of the conduction band. Furthermore, the hole that it leaves relaxes at the top of the valence band, otherwise known as the minimum energy principle, which is always used by electrons. The electron comes back to its basic state by emitting a photon of energy  $h\nu$ .

d) The coordinate representation of the speeds of electrons. A radiative transition can only take place if the minimum conduction band corresponds to the maximum valence band, which is the case for the majority of III-V composites (elements from groups 3 and 5 of the periodic table) such as

*GaAs (Gallium Arsenide). We say that the semi-conductor is a direct gap semi-conductor<sup>4</sup>.*

*e) Representation of the emission technique in a “pn” junction. Strictly speaking, electrical excitation takes place in a direct polarized junction by the introduction of carriers: electrons from the conduction band “n” recombine at the junction with the holes from the valence band “p”. By altering the make up of composite compounds, we can adjust the emitting wavelength by changing the width of the forbidden band. A multitude of different types of more or less sophisticated light emitting diodes (LEDs) are produced using this technology. When the structure of the diode is a Perrot-Fabry cavity we have a laser diode.*

*f) Quantum wells. These are created with compatible materials from different forbidden bands. When the thickness of the shell is nanometers deep and the shell is sandwiched between the shells of more important forbidden bands (example: AlGaAs/GaAs/AlGaAs) then we see atomic pseudo-states starting to appear just as in quantum boxes, giving rise to a new type of quantum optoelectronics.*



**Figure 2.9.** *Quantum dot for single photon experiments: 400-nm-diam micropillar, produced by e-beam lithography and reactive ion etching from a GaAs/AlAs-layered planar structure grown by molecular-beam epitaxy*

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4 The emission of a photon that has zero mass occurs without any variation in the momentum of the electron. Momentum is the product of the mass and the velocity ( $v$ ). The minimum value of CB and the maximum value of VB must correspond to the same value of  $v$ , which is the vertical transition on diagram d.

### **The theory of symmetry groups**

From the atom, and indeed from the subatomic to the solid, the theory of symmetry groups gives a powerful definition of the above listed areas of science and can be easily adapted to the quantum world.

It is based on operator algebra. For example, the “rotation” operator (R) enables us to rotate a body. If the body is of spherical symmetry any type of rotation transforms the body in itself. The particular states of this operator<sup>5</sup> are well known mathematically; they are known as spherical harmonics.

As far as the atom is concerned, its electrons occupy defined states of symmetry using the coulomb potential. The operator that lets us calculate the energy of the states is known as the Hamiltonian (H). It is clear that the energy from the atom is independent of any geometric rotation that we can subject it to, which translates mathematically by the fact that the operators R and H can switch places with one another. This means that we can apply the two operators in one state in any order so that  $RH = HR$  for the same result.

In operator algebra, an important theory states that when two operators commute they have the same basic functions. The particular states of the rotation operator therefore create a basis for the quantum states of the atom, which in turn explain the distribution into successive layers and all the quantum numbers of the electronic states. This is truly amazing.

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<sup>5</sup> In algebra, an operator is an application that transforms one function into another function. It is represented by a matrix in a space called a vectorial. The particular states correspond to base vectors in which the shape of the matrix is diagonal. For atoms, the particular states represent independent states that the electrons will occupy.

In a periodic solid, the application of the “conservation law of momentum” from the electron to the operator of translation gives the functional shape of the quantum state waves, the famous Bloch functions and band theories. We cannot really say anything more; all we can do is admire a theory based on a fundamental concept, that of symmetry. When theory becomes a work of art it almost resembles poetry: “There’ll be nothing but beauty, wealth, pleasure, with all things in order and measure”<sup>6</sup>.

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6 “L’invitation au voyage” in *Les Fleurs du mal*, Charles Baudelaire (English translation by Roy Campbell, *Poems of Baudelaire*, 1952, New York: Pantheon Books).