An Introduction to Nanoscience and Nanotechnology

Alain Nouailhat

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The Physicists

"Leaning over the screens of powerful machines
They watch the rise of a world previously unknown
From within their instruments new phenomena appear."

(José Maria de Heredia, *Les Conquérants*, adapted by the author)

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Foreword

Alain Nouailhat's book takes us on a journey to a newly discovered magical realm. This is the world of the small and the smallest parts, of micro and nanotechnologies. The discovery of this world is, of course, not a recent one, but one which began a long time ago. The ancient Greeks imagined the atom as the smallest unit which could not be split. There then followed a long evolution comprising several different stages before the eventual development of the quantum mechanics model. Recently, a very important step was taken to improve the technology of microscopes. At last we are able to see atoms (in some ways this was already possible with the invention of transmission electron microscopy). However, now we can also manipulate them individually, change their position one by one and use them to create a new code; this is a difficult task but nevertheless it is possible. In fact, we can only create something we can actually see.

In the beginning, there were only two dimensions in nanotechnologies. Specialists in optics then created almost perfect surfaces. The difficulty lay, and still lies, in how to deal with the third dimension. Specialists in electronics working with integrated circuits took part in the miniaturization race going from micro to submicrodimensions, all the while getting closer and closer to the nanometer. Once they reach the stage where they will finally be using a single electron as the basis of electronics (and this day is still far in the future) the whole idea of electronics will need to be rethought.

This evolution does not only concern electronics, since other fields of study such as mechanics, optics, chemistry and biology have also started creating their own nanoworld; today we refer to these as microsystems. The first example of mass production of microsystems which was not purely electronic was the silicon accelerometer of airbags which can be found in the majority of cars. On the contrary, nanosystems do not yet exist. It will still take some time before they make it out of the laboratories.

As expected, these technological evolutions, not to speak of revolutions, bring with them some concerns since change does not come naturally to humanity and societies. We must therefore be aware of the ongoing challenges and of what is at stake.

I would like to invite the reader to follow Alain Nouailhat on his journey. Let us discover this new world in all its varieties. Alain Nouailhat describes it with the realism of an engineer as well as with the imagination of a researcher; in doing so he shows us a part of his dream.

Jean-Jacques GAGNEPAIN
Research Director at the CNRS,
former Director at the Department of Technology
in the Ministry for Research (France)

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To all those who have participated in the illustration of this book.

To the OMNT (Observatory for Micro and Nanotechnology) and ADIT (French agency for the diffusion of technological information) which have been my main sources of information due to their scientific and technological knowledge in an area of perpetual evolution.

To Isabelle Denizet, for carefully proofreading the original manuscript.

Preface

The term "nanoworld" is understood differently by many experts. Do we have to restrict ourselves to the field of nanomaterials, which consists of building nanometric structures made up of a limited number of atoms? Should we include the miniaturized world which is largely dominated by microelectronics and in which the dimensions of its devices are smaller than a hundredth of a nanometer?

How do we approach concepts which at first glance seem to be very different, ie the link between volume and surface of the different aggregates, the functionality of macromolecules and the complexity brought about by our electronic systems?

In fact, all different scientific disciplines, including every single sector (such as nanomaterials, micro and nanomachines, micro and nanoelectronics), have their own paradigm[1]. This is why innovations and industrial developments are profoundly different. However, these fields are strongly interlinked. It is therefore necessary to make our studies more interdisciplinary in order to enable us to understand the nanoworld.

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1 "A paradigm is an image of the world; it describes a way of seeing things, a coherent model which lies on a previously defined basis (a matrix according to the scientific discipline). It refers to a theoretic model in a specific field of science" (Wikipedia).

Taking this idea as a basis for our work, we would like to introduce nanosciences and nanotechnologies in the broadest scale possible by showing their common scientific basis as well as their multiple interconnections.

We will cover different fields in the chapters to come. This is not a straight textbook; those are easily accessible in libraries or on the Internet. The following chapters will both provoke reflection and provide the reader with a better understanding of the subject. This is a guided tour of the discovery of the nanoworld which we hope will arouse the reader's curiosity so that they will engage more profoundly with the subject.

In many different fields we can observe a tidal wave of new products which are directly linked to nanosciences. Therefore, the basic ideas will be introduced and a brief outline will be given in Chapter 1.

Yet, it remains difficult to understand how so many complex domains work together. An understanding of the basic concepts of quantum physics is of great importance as these laws rule the nanoworld. A basic introduction to these ideas will be given in Chapter 2.

In Chapter 3 the functioning of the tools needed to explore the nanoworld will be explained.

We have entered the nano era: progress in the domains of electronics, information technology and telecommunications allows us to bring together fields which were once separate. Microelectronics, which is covered in Chapter 4, has merged with molecular and cellular biology.

Chapter 5 will introduce this convergence and the impressive new perspectives that it opens up. Silicon-based circuits are constantly improving and we can observe the functioning of our neuronal circuits via MRI[2]. The transistors connect to the biological neurons and enable us to create prostheses which were unheard of before.

The latest innovations, examples of which will be given in Chapter 6, show the applications of nanotechnologies in the domains of materials, motors, energy and also micro and nanosystems. The convergence of these technologies allows for the creation of complex systems.

In Chapter 7 we will deal with the impact on society that these new technologies will have. The chapter focuses on computer simulations which were greatly improved due to better databases and an increased performance in the processing capabilities of computers. These computer simulations have become an essential tool in predicting future developments and in supporting industrial innovations. A large part of our work takes place in a virtual world, which in turn enables us to understand the nanoworld. The object becomes the actor.

Nanosciences and nanotechnologies are leading to a major turning point in our understanding of nature. Such a force has its consequences or in the words of a famous fictional character: every force has its dark side. Our future depends on how we use new discoveries and what risks they bring upon humanity and our natural environment. The ethical implications of this must therefore be discussed.

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2 Magnetic resonance imaging.

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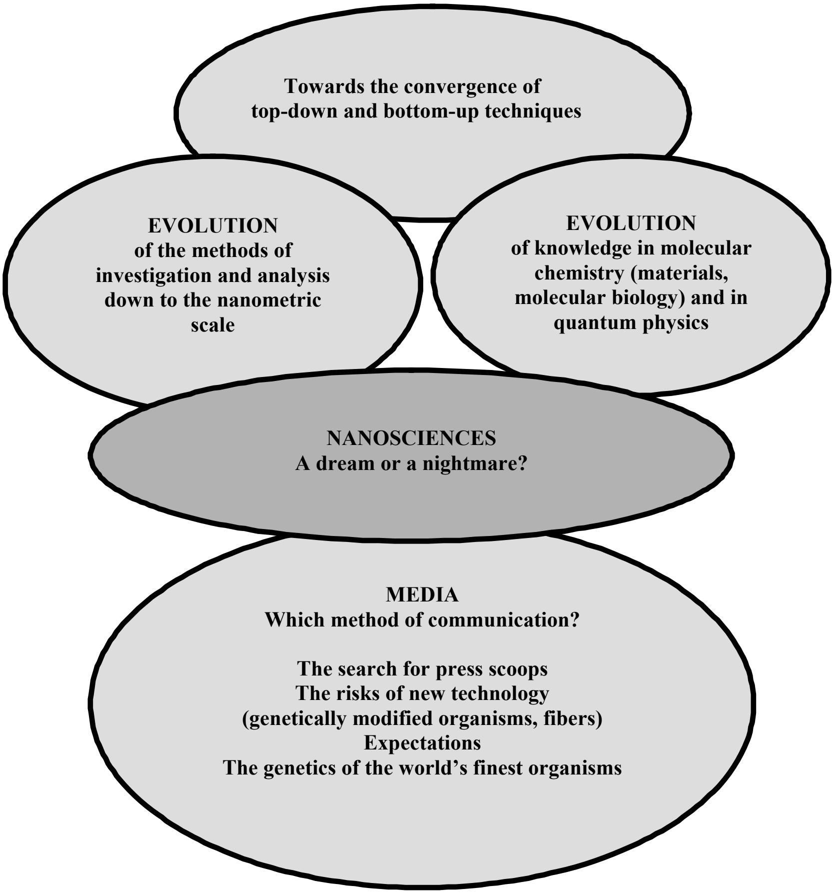
Chapter 1

What are Nanos?
Putting Things into Perspective


Towards the convergence of
top-down and bottom-up techniques
EVOLUTION
of the methods of
investigation and analysis
down to the nanometric
scale
EVOLUTION
of knowledge in molecular
chemistry (materials,
molecular biology) and in
quantum physics
NANOSCIENCES
A dream or a nightmare?
MEDIA
Which method of communication?
The search for press scoops
The risks of new technology
(genetically modified organisms, fibers)
Expectations
The genetics of the world's finest organisms

A nanometer = 10^{-9} meter

1.1. What are we talking about?

We are talking about the “nano tidal wave”. Not a single day passes without the press reporting on major innovations in this area. Large industrialized countries spend considerable amounts of money, around US$10 billion per year, on this field of study. This should have a positive effect on the economy and on employment[1].

Microelectronics and the steady miniaturization of components has become commonplace. Moore’s Law (a doubling of the number of transistors for the same surface every 18 months) illustrates this idea. This also makes us think of the production of chips in laboratories. With their engineers and technicians in uniform, these laboratories can be considered as the technological cathedrals of our times. Microcomputers, microprocessors, mobile phones and MP3 players with a USB connection are available to the general public. For several decades now, this technology has been largely submicronic, and the idea of nanoelectronics was created in the laboratories. The current technological limits will soon be reached, even if ongoing innovations will push them beyond these limits. Emerging technologies such as carbon nanotubes will take over.

1 In Grenoble, France, the first European center for micro and nanotechnologies, Minatec, has been created. It was inaugurated in June 2006, and with an area of 45,000 m^2 it is home to 4,000 engineers and researchers who work in the fields of microelectronics, biotechnologies and information technology.

The nanoworld is the intermediary between the atom and the solid, from the large molecule or the small solid object to the strong relationship between surface and volume. Strictly speaking, the nanoworld has existed for a long time and it is up to chemists to study the structures and properties of molecules. They have learnt (with the help of physicists) to manipulate them and build more and more complex structures. Progress in observation tools (electron microscopes, scanning-tunneling microscopes and atomic force microscopes) as well as in analysis tools (particularly X-ray, neutron and mass spectometry) has been a decisive factor. The production of nanoscopic material is constantly improving, as is the case for the process of catalysis and surfaces used in the nanoworld. A substantial number of new materials with nano elements such as ceramics, glass, polymers and fibers are making their way onto the market and are present in all shapes and forms in everyday life, from washing machines to architecture.

In 1959, the physicist Richard Feynman, Nobel Prize winner for Physics in 1965, came up with the brilliant concept of the nano when he said "there is plenty of room at the bottom" during a conference of the American Physical Society.

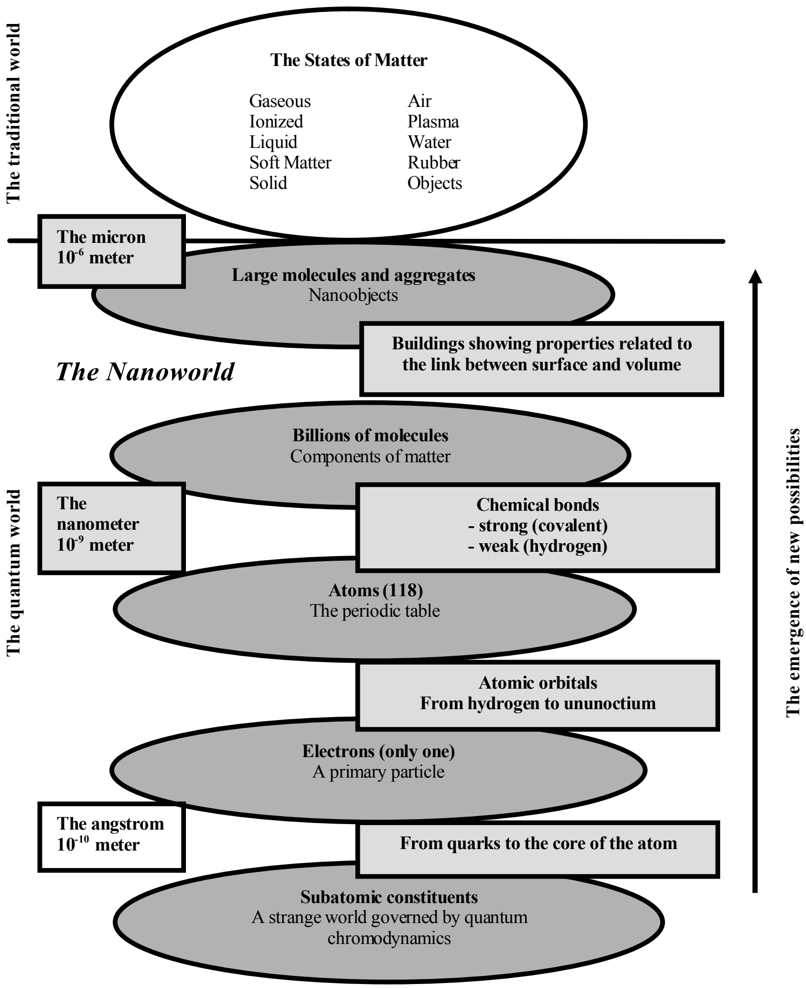


Figure 1.1. *Where can we find the nanoworld?*

Biology has been molecular for a long time. The areas of DNA, proteins, and cellular machinery are all subjects of multidisciplinary research. Investigations into these fields have been carried out by biologists, chemists, and physicists. Furthermore, the tools that have been developed have created new areas of specialization, such as bioinformatics. Observation, image-processing and simulation all benefit from the advances in information technology and, once more, conceptual progress goes hand in hand with technical expertise.

The concept of the nanoworld is based on the convergence of a real mix of scientific and technological domains which once were separate.

Even though the laws of quantum mechanics based on wave corpuscle duality are not directly visible in our everyday world, except for lasers and semi-conductor components, they do govern the nanoworld. In the future, the quantum effects will be used in a large number of applications, and in objects with new properties, such as quantum cryptography, quantum computers, teletransportation, etc.

The evolution of our know-how, and of technological innovations, is already having significant consequences. The Internet is the fruit of the union between information technology and telecommunications, just as biochips are for electronics and biology. Imaging on a molecular level revolutionized the techniques of medical examinations. The borders between chemistry, physics, mechanics and biology are disappearing with the emergence of new materials, such as intelligent systems, nanomachines, etc.

This is where the nano tidal wave, which will have considerable impact on society, can be found. A comprehensive public debate is required on real or possible risks and their consequences. Will humanity be able to master these new applications or are we taking on an unfamiliar role?

1.2. References

1.2.1. *Two basic facts*

The evolution of knowledge

This is a fabulous adventure where the frontier between fundamental science and applied science becomes an area of exchange and innovation. If the laws of electricity make the electric motor possible, then we can make the same comparison for the electron and television. We are going from the macroscopic to the microscopic.

Technological expertise

Progress in metallurgy and in chemistry has allowed scientists to process silicon. Physicists, in particular, have highlighted its semi-conductor properties. The understanding of these allowed the invention and the production of the transistor. A long succession of successful discoveries and innovations has meant that integrated circuits are now present in everyday objects. If an object can be understood in detail at the microscopic level, we can use our knowledge to apply it to the macroscopic level.

Furthermore, the concept of nano is becoming fashionable as it combines what we already know with new concepts and it conveys the idea of modern technology (eg carbon nanotubes used in top of the range tennis rackets, bicycle frames, or golf clubs).

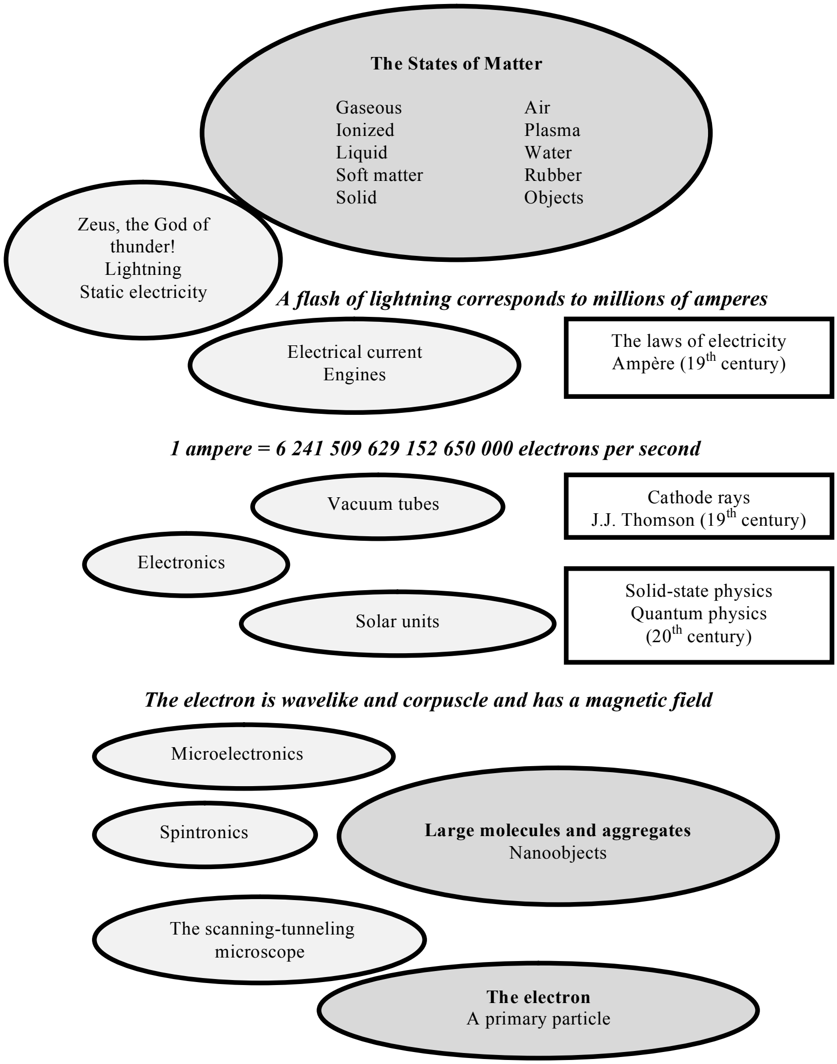


Figure 1.2. *The scientific approach is advancing on all fronts: from lightning to the electron, from the thunder of Zeus to the scanning-tunneling microscope*

1.2.2. *Two approaches*

It seems that the level of knowledge and technical know-how has never been as advanced. This in turn allows for the manufacture of intelligent objects which result from the merging of two approaches:

– top-down, which enables us to control the manufacture of smaller, more complex objects, as illustrated by micro and nanoelectronics;

– bottom-up, which enables us to control the manufacture of atoms and molecules, as illustrated by supramolecular chemistry.

The traditional world has come together with the quantum world. Sectors that were once separate are now coming together. The natural world is of interest to physicists as well as to computer scientists and mathematicians. The divisions between the different disciplines are disappearing and paving the way for new paradigms.

These approaches come together in the nanometric domain.

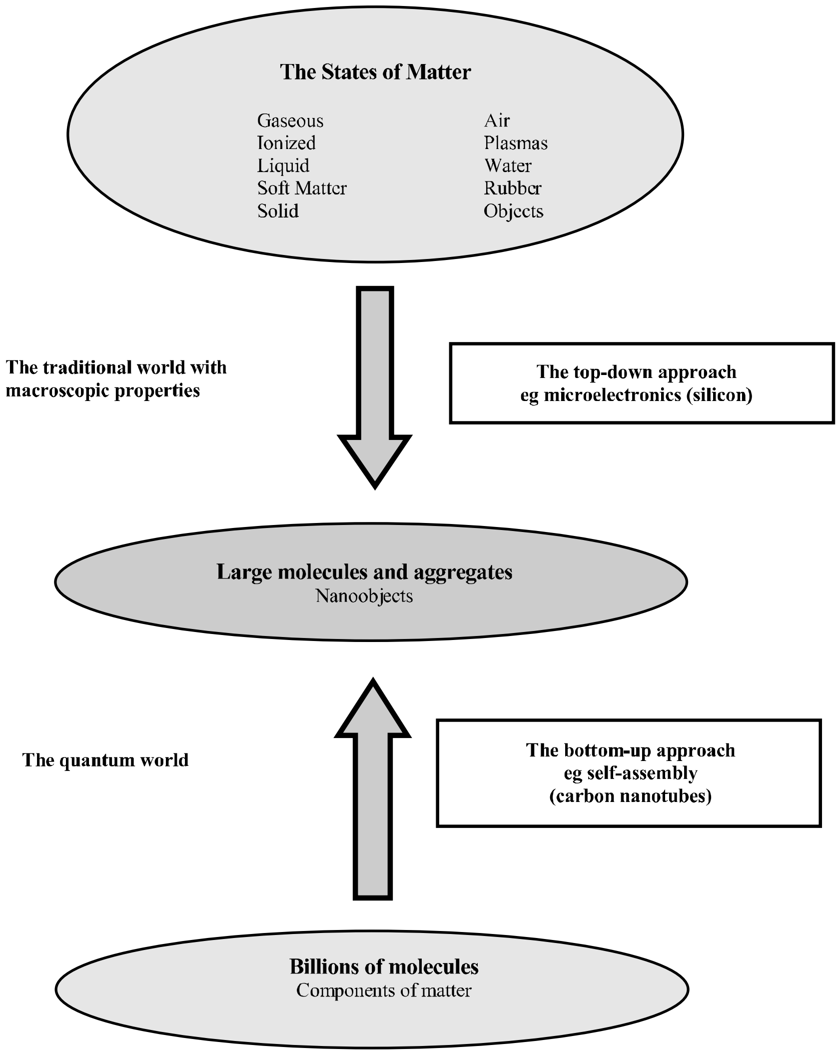


Figure 1.3. *Two technological approaches to the nanoworld: top-down and bottom-up*

1.2.3. *Two key points*

Miniaturization

This process makes it possible to see, work on and manufacture ever smaller objects. In order to do so, increasingly sophisticated technology is required.

Complexity

The integration of ever smaller objects, coupled with a rise in their number, leads to the emergence of new implementations. The appearance of algorithms, with sometimes unpredictable results, brings objects that have been inspired by human genius closer together with objects found in the biological world. The complexity of objects in the biological world is strictly organized and at the same time they are self-organizing. The processes of supramolecular chemistry and of the chemistry of self-assembling materials function in the same fashion.

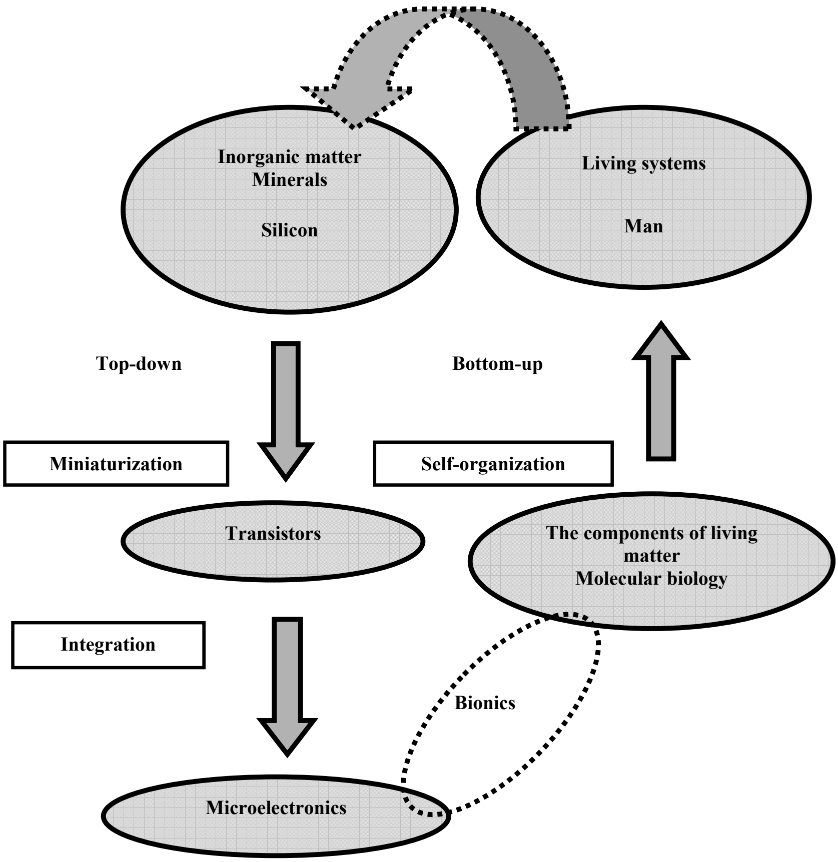


Figure 1.4. *Two key points: miniaturization and complexity. Self-organization in the bottom-up approach (eg living systems), and miniaturization integration in the top-down approach (eg micro and nanoelectronics)*

1.3. Some bonus material for economists

Recent government measures aim to discover what impacts these new technologies will have on the economy. These measures bring considerable investment in developed countries: the global effort was US$10 billion in 2004 and this was double the figure from 2003. Large American companies, such as IBM, HP and 3M, invest about one-third of their research and development budget in nanotechnologies. There are more than 1,000 start-ups that have declared that they are carrying out research in the area of nanos.

However, these figures should not to be taken as definitive since they depend on the generally restrictive definition that is given to the area of nanotechnology. Nanotechnologies often share some common ground with microtechnologies from which they are partly derived. Strictly speaking, nanotechnologies do not include technologies measuring up to several tens microns in size, at least not at present. This is frequently the case for MEMS (Micro Electro Mechanical Systems). Furthermore, an ambiguous common ground, if one exists, divides traditional chemistry from modern chemistry in the area of molecular auto-binding, the aim of which is to lead to self-organized materials and systems.

Europe has adopted an active policy so that its member states can remain frontrunners in this competition. Europe is supporting nanoelectronics via the 7th Framework Programme for Research and Technological Development by increasing infrastructure, initiatives relating to health, security and the environment, and introducing a new system of European patent control (see Appendix A).

Miniaturization and complexity

What do the development of cells and organisms have in common with the day-to-day running of a town or society? The answer is complexity. Complexity, under different variants, is present everywhere in the nanoworld.

With regard to products originating from the top-down approach, except when used industrially (when referring to complex industrial systems), it seems that true complexity lies in software or, in other words, in the intelligent objects themselves. The duplication of millions of identical elements, as well as the links between them, admittedly leads to complications. However, complexity can be found in both self-repair and self-learning programs. Thus, hierarchical organization defined in terms of components, machines and systems is moving ever closer to the organization we see in biological systems. In the technology of the future, the recognition of error management and of corrections will reinforce this analogy.

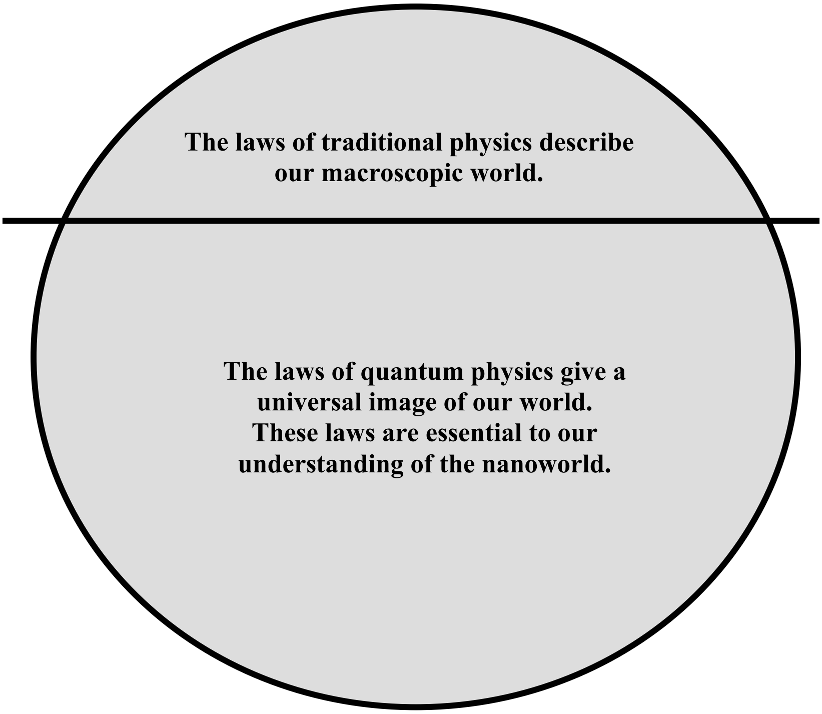
Complexity is a notion that brings unpredictability into play. If biosystems are strongly hierarchical in terms of their level, ie molecules, cells, organisms, and populations, then these four systems are, unlike computers, interdependent. Complexity comes from unpredictable emerging functions in the bottom-up approach. These functions not only provide organisms with the sturdiness they need in order to live, but also create opportunities for evolutionary adaptation depending on the external conditions. It is this concept that is being discovered in new emerging phenomena, which is, of course, understandable, but at the same time is occasionally unpredictable. For example, the multiplicity of interaction loops makes their analysis with genes extremely difficult. Remember that each protein has its own gene code, meaning that each gene determines the chain of a certain number of amino acids. This is only the beginning of understanding how molecular machinery works.

The idea of complexity is, in essence, multidisciplinary. Not only does it introduce us to the graph theory, supramolecular synthesis, modelization and simulation, and thermodynamics of systems that are not in equilibrium, it also introduces us to the information theory, meaning mathematical, chemical, IT, and physical approaches. Observation and calculation techniques, as well as general expertise, are needed in order to advance our understanding of complex systems.

Chapter 2

Some Science to Get You Started

The Necessary Toolkit


The laws of traditional physics describe our macroscopic world.
The laws of quantum physics give a universal image of our world. These laws are essential to our understanding of the nanoworld.

2.1. Quantum physics

2.1.1. *From the traditional world to the quantum world*

The nanoworld is part of our world, but in order to understand this, concepts other than the normal ones, such as force, speed, weight, etc., must be taken into consideration.

The nanoworld is subject to the laws of quantum physics, yet evolution has conditioned us to adapt to this ever changing world. This observation has led us to further investigate theories based on the laws of physics that deal with macroscopic phenomena.

Therefore, the law linking the pressure of a gas "P", its volume "V" and its temperature "T", following the equation $P \times V/T$ = a constant, is one of astounding simplicity. It describes how engines work. Each liter of gas, at atmospheric pressure, contains approximately 10,000 billion billion atoms, and because of this immense size we are unable to predict the individual movement of the atoms. This movement can only be observed in exceptional vacuum conditions and in exceptionally low temperatures, but the laws of physics that are applied will no longer be the same.

Let us take Ohm's Law, $V = R \times I$, which in the field of electricity deals with the relationship between the potential difference from one terminal point on a conductor to the other "V", its resistance "R" and the flow of electric current "I". The simplicity and elegance of this equation come from the statistical translation of the number of different behaviors that electrons have; electrons being the fundamental particles for the flow of electricity in the conductor. An ampere, which is a unit of electric current, is the equivalent of approximately 10 billion billion of these small particles moving around per second. Resistance represents a statistical value resulting from the interactions of electrons with atoms. In a gas, the number of electrons is much higher. We can observe the behavior of a single electron, but there again the laws of physics will no longer be the same. If the notion of electric current is intuitive and does not create any problems of representation, such as fluid analogies, then the electrons in the final component state will not be the same.

Furthermore, in the macroworld, sizes are continuous; however this is not the case in the nanoworld. When we investigate and try to understand what is happening on this scale, we have to, strictly speaking, change the way we look at things. New concepts of quantum physics can only come directly from our surroundings. However, our world is fundamentally quantum. Our common sense in this world has no value in the nanoworld; we have to invent new concepts. This does not happen overnight: little by little, scientists have been able to interpret all known phenomena and give them a joint, common theory which has never been called into question.

This is recent history. In fact, we had to wait for the 20th century and the observation of the atomic world to reach the real limits of traditional physics and create a new branch of physics, quantum physics.

Also known as quantum or wave mechanics, this branch of physics was created by Max Planck (Nobel Prize winner for Physics in 1918) who showed that the exchange of energy between matter and radiation occurred in discontinuous quantities (quanta). The physicist Louis de Broglie (Nobel Prize winner for Physics in 1929) founded wave mechanics. Erwin Schrödinger and Paul Dirac (who shared the Nobel Prize for Physics in 1933) developed the general formulae of quantum mechanics. Finally, Wolfgang Pauli (Nobel Prize winner for Physics in 1945), who is well known for his exclusion principle which governs the states of particles, and other physicists took this theory to the highest degree of accurate prediction in the atomic world.

Until now, no observation has proved the theories of quantum physics wrong and it remains an area that is still under investigation.

Quantum physics also describes an extraordinary world with entirely new properties that are difficult to imagine, but which give us a better understanding of chemistry, transistors and lasers.

2.1.2. *Two fundamental concepts*

2.1.2.1. *Wave-corpuscle duality*

Particles can behave like waves. This property, particularly for electrons, is used in different investigative instruments in the atomic scale:

– The scanning-tunneling microscope, which lets us look at atoms on the surface of a lattice, uses an effect of quantum physics, the tunneling effect, which allows particles to pass through a barrier.

– The electronic microscope whose function is based on the wave properties of electrons, and whose wavelength and speed both correspond to light with a very short wavelength.

Waves can also act like particles: the photoelectric effect shows the corpuscular properties of light.

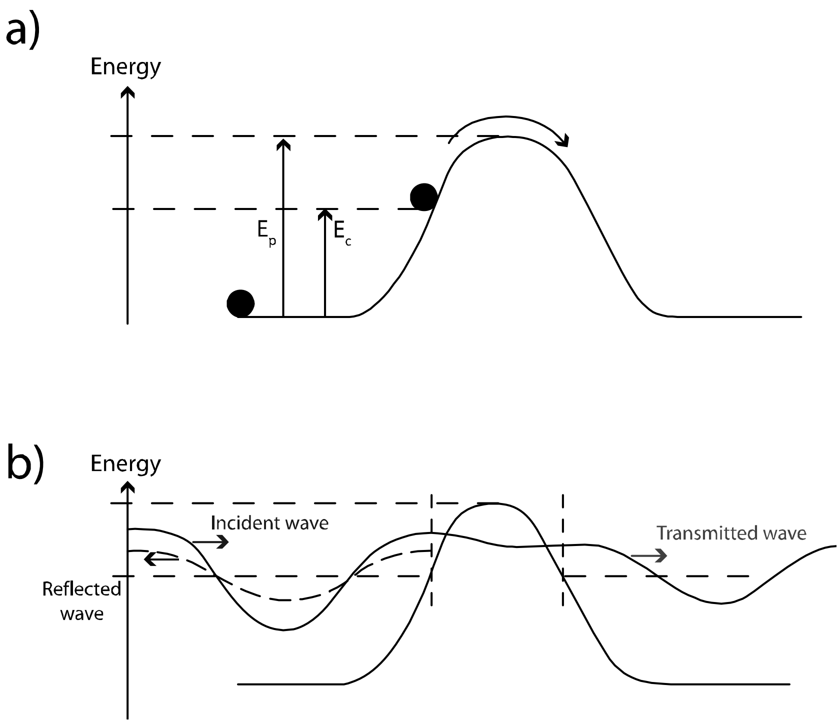


Figure 2.1. *An effect of quantum physics: the tunneling effect*

a) The passage of a particle through a barrier in the traditional world: the particle does not pass if $E_c < E_p$ and the particle passes if $E_c > E_p$.

b) The passage of a particle through a barrier in the quantum world: the probability of passage is not zero when $E_c < E_p$ and the probability increases with E_c to reach 1 when $E_c = E_p$.

2.1.2.2. *Probability in the quantum world*

Quantum physics gives a completely different version of the world on the nanometric scale than that given by traditional physics. A molecule is described by a cloud of probability with the presence of electrons at discrete energy levels; this can only be represented as a simulation.

All measurable sizes are subject to the laws of quantum physics which condition every organism in our world, from the atom to the different states of matter.

The nanoworld must therefore be addressed with quantum concepts.
Chemistry is quantum.
The chemistry of living organisms is quantum.

Is the functioning of our brain closer to the concept of a quantum computer or to the most sophisticated microprocessors?

All properties of matter are explicable only by quantum physics. Traditional physics, which is certainly efficient and sufficient in the macroscopic domain, only deals with large objects (remember that there are nearly 10^{23} atoms per cm^3 in a solid), while quantum physics only deals with small discrete objects. However, the evolution of techniques and the use of larger and larger objects stemming from scientific discoveries make us aware of the quantum nature of our world in all its domains. Our vision of this has been completely transformed, and our lives have been changed as a result.

Just as Alice did in *Alice in Wonderland*, we are going to have a look at things from the reverse side. Before leaping into the submicronic world we need to understand some of the key ideas that await us there.

Fasten your seatbelts!

2.2. The key players

2.2.1. *The electron*

2.2.1.1. *The cornerstone of matter*

Everything starts with the atom, the building block of the nanoworld, and also of our world. Mass is predominantly concentrated in the nucleus of the atom, which is made up of particles called protons which have a positive electric charge, and of neutrons which are neutral, but which have the same mass as protons. The neutrons stabilize the confinement of the protons which are subject to their mutual electrostatic repulsion. This nucleus is packed with negatively charged particles called electrons which are equal in number to the number of protons. The atomic unit is therefore neutral. It is the distribution of electrons that is the origin of the atom's chemical properties.

The electron is a particle. It has a weak mass, almost 1/2,000 of that of a proton, and it carries the basic electric charge that creates electricity. Like the proton, it has a magnetic field called spin that leads to magnetism which has multiple uses; we will see more of this later. But this is not all; the electron is also a wave, the frequency of which depends on its energy. Without it, the world would not exist. It is not enough to compare the image of small electrons orbiting around the nucleus to the planets orbiting around the sun, or to compare the electrostatic force of attraction in atoms to the force of gravitational attraction for the planets. It neither explains the stability of the system, for example any perturbation ends with the electron falling on the nucleus, nor does it explain the organization of the electrons around the nucleus. It is their undulatory structure that explains the atomic structure: electrons group themselves into zones according to the stationary modes of their corresponding waves. Everyone can see how stationary modes work by observing resonance phenomena in the field of acoustics, for example in the vibration of guitar strings.

2.2.1.2. *Electronic states*

It is clear that for the atom, things start to become more complicated.

Electrons occupy discrete states, in other words quantum states. In the quantum world, the continuous does not exist and places are numbered. The various different states are predefined and are identified by a number.

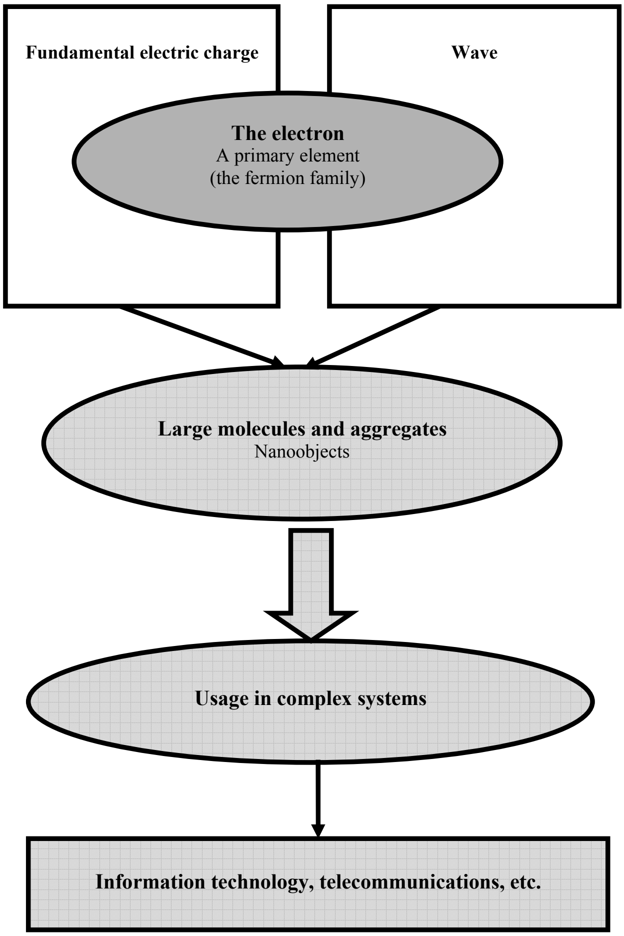


Figure 2.2. *The electron, a universal actor*

Two electrons can occupy, at most, one state, which is due to the existence of two spin values[1]. As we look closer, the atom becomes heavier and the number of electrons increases. They are divided in an orderly fashion around the nucleus, forming concentric shells starting with the one closest to the nucleus, just as you would fill up a theater from the front row to the back. Each shell has a limited number of states. The most important shell for interactions between atoms is the outer shell which has four states, meaning that there is enough space for eight electrons, except for hydrogen and helium. This has fundamental consequences.

The ranking of atoms by their mass in relation to their chemical properties highlights this periodicity; in other words Mendeleev's periodic table of elements. Thus, when there is only one electron on the external shell we are dealing with alkali metals, such as lithium, sodium, potassium, and rubidium, all of which come from the first column of the periodic table. When the outer shell is full, meaning that when there are eight electrons on the shell, we are then dealing with the noble gases, such as helium, neon, and argon, which make up the eighth column of the periodic table. Hydrogen, which has one proton and one electron, plays a key role in molecular construction and in our world in general. Its external configuration determines other chemical properties.

2.2.1.3. *The quantification of energy*

A key idea in the atomic world is that of quantification. As no two states are the same, every exchange that occurs between them must be carried out through "packets" of energy, each with a

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1 Particles with half-integer spin, which are called fermions (the electron), and particles with integer spin, which are called bosons (the photon), have different quantum statistics. In particular, several bosons can simultaneously occupy the same state. Pauli's Exclusion Principle does not apply to bosons, but is applicable to fermions.

defined value which corresponds to the energy difference between them. In the atomic world, every process must be carried out step by step; there are no short cuts. It is still possible for an electron to be excited if it receives enough energy to progress to a superior level, if one is available and not already occupied. This energy can be supplied by a shock, in particular by light stimulation. It is the process of atomic absorption which lets us probe the atoms in order to find out more about their different states. The reverse occurs if we remove an electron from one of the outer shells. In this case, there will be a knock-on effect leading to the source of the light. The balance that is reached always corresponds to a minimum level of energy.

All of these properties are used in nanometric objects.

2.2.1.4. *Bonds*

Thanks to their surface electrons, atoms form more complex edifices: molecules or solids which create new properties. The fixing between atoms is known as chemical bonding.

The concept of bonding is as old as that of the atom. Its most famous interpretation comes from the Greek philosopher Democritus who saw that the bonding between atoms was a property linked to their shape, smoothness, and ability to lock onto other atoms. Chemical bonding can only really be explained with the knowledge of the quantum nature of the electron.

We have seen that the outer shell has between one and eight electrons. Chemical bonding between atoms is due to the pooling of one or several electrons from their outer shells in order to make sure that each shell is surrounded by eight electrons. This is known as covalent bonding. This allows atoms to join with one another and allows for the creation of complex atomic edifices known as molecules. A good example is given by stacking pieces of Lego together in order to create larger complete structures. The bonding force for atoms is based on the fact that the energy from the state created by the two shared electrons is weaker than the two independent states. More precisely, while the atoms approach one another, the atomic states taking part in the covalent bond will form two molecular states, one of which is bonding and the other, with a superior energy level, is anti-bonding. Each state accepts two electrons of opposing spin; the bonding molecule is full and the other anti-bonding one is empty.

Physicists talk about molecular orbitals, often represented in chemical formulae by a line, for example the C-C bond between two carbon atoms. This idea of a molecular orbital is very useful for visualizing the bonds between atoms. This is the most solid bond in chemistry, the universal adhesive which forms the basis of semi-conductor materials such as molecules of living organisms.

Other types of bonds exist based on electrostatic interactions; in particular the bond that is associated with the presence of hydrogen. These are very useful for carrying out reversible fixing like the adhesive on Post-its. In large organic molecular edifices we find these structures mixing with strongly bonded parts (covalent bonds), joined together by easy to remove fasteners (hydrogen bonds), ensuring the robustness and suppleness of the dynamic world of living organisms. These strong and weak bonds are found in nature.

2.2.2. *The photon*

2.2.2.1. *The wave*

We live in a world of photons made up of the electromagnetic spectrum which goes from radio waves to X-rays and then gamma rays. We have a very limited perception of the electromagnetic spectrum; visible light is the only part of the spectrum that is directly captured by the eye. Our body perceives infrared rays in the form of heat through sensors in our skin and reacts to ultraviolet rays by tanning and sunburning as well as, unfortunately, developing skin cancers.

We have only been aware of the existence of radio waves due to developments in electricity, and of X-rays thanks to research on atomic structure at the end of the 19th century. Light travels at a speed of 300,000 km per second in a vacuum, which definitely comes from Maxwell's electromagnetic theory in the 19th century which in turn explains all the phenomena linked to electricity and magnetism through the use of four mathematical equations.

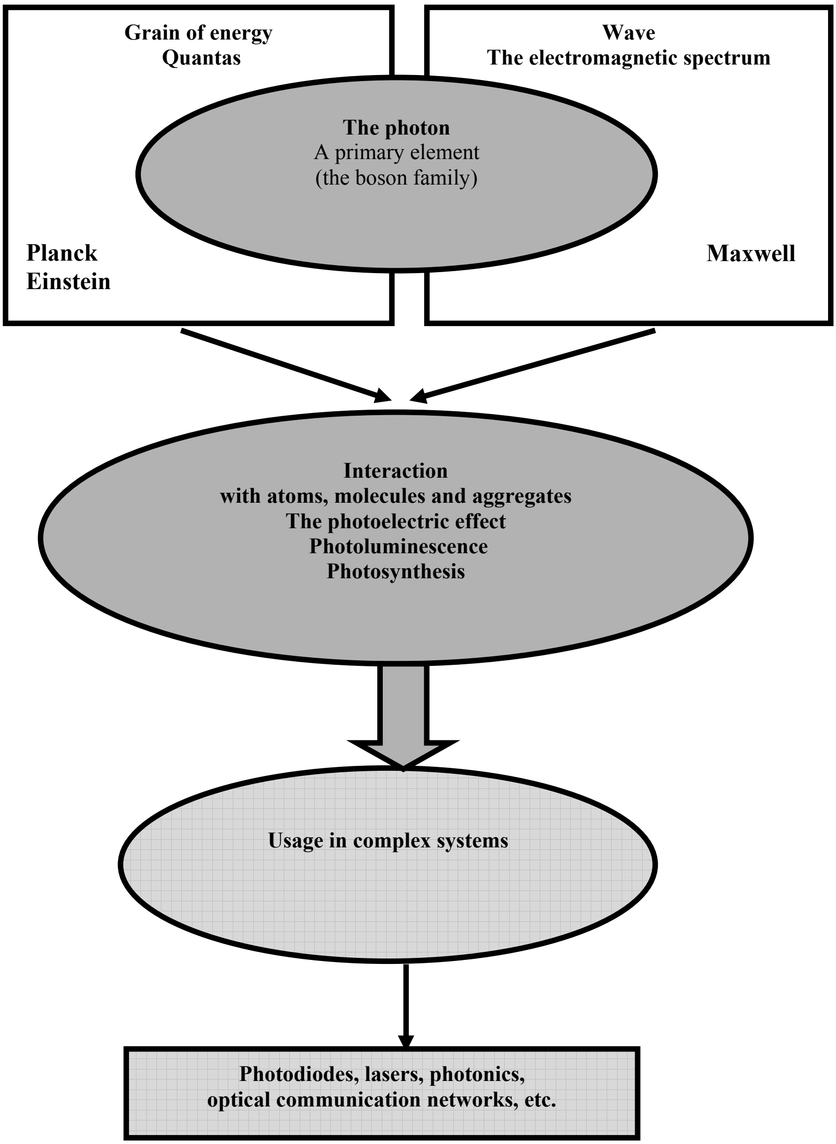


Figure 2.3. *The photon, a super fast messenger*

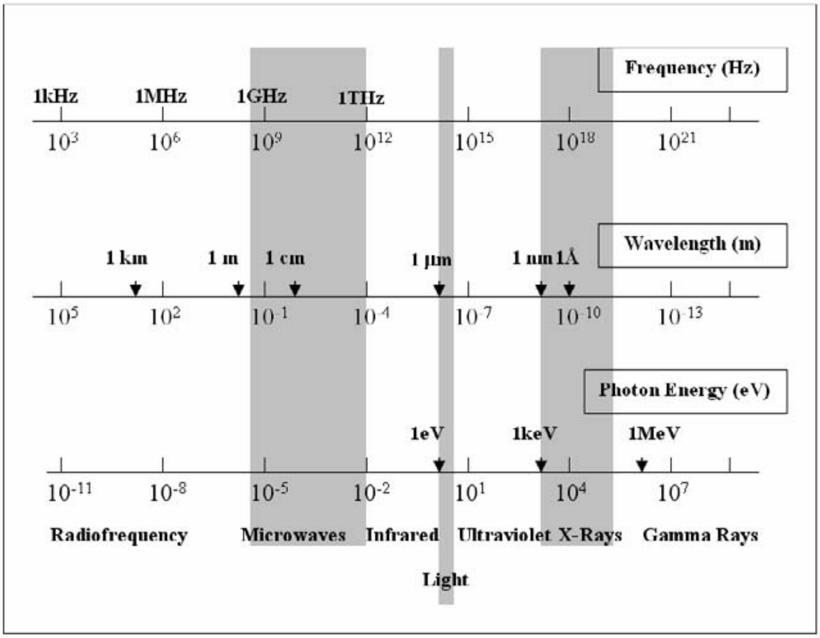


Figure 2.4. *The electromagnetic spectrum*

Units of abbreviations:

Hz	***hertz***	***m***	***meter***	***eV***	***electronvolt***
THz	*terahertz*	*Å*	*angstrom*	*MeV*	*mega-electronvolt*
GHz	*gigahertz*	*nm*	*nanometer*	*keV*	*kilo-electronvolt*
MHz	*megahertz*	*µm*	*micron*		
kHz	*kilohertz*	*cm*	*centimeter*		
		km	*kilometer*		

2.2.2.2. *The energy grain*

However, a small phenomenon has appeared and raised doubt in peoples' minds and revolutionized our conception of light: the phenomenon is that of the photoelectric effect.

Some time will be spent on this development because it signifies the division between traditional and quantum physics. When a beam of monochrome light is sent onto a solid object, the solid object will only emit electrons from a certain frequency of this light. The interpretation, which was given by the famous physicist Albert Einstein, is that light carries its energy "E" by discrete packets which are proportional to its frequency "ν": $E=h\nu$! These discrete packets are known as quanta, which give their name to the new area of physics known as quantum physics.

Just like the waves in optic microscopes with their properties of propagator interference and diffraction, light is also corpuscular. When we look at our world on a smaller scale, the idea of the continuous disappears and everything stops with ultimate countable quantities. An example of this would be if you look at an image in a newspaper. If the photo is enlarged, dots, which are the final component of the printing process, will be visible. These dots are obviously still part of the traditional world and correspond to the resolution of the image. If the image is enlarged again there is no doubt that ink molecules will be found and in this instance we are dealing with the nanoworld.

The nature of the photon is, however, very different to that of the electron. First of all, it has zero mass, it travels at a speed that particles with mass cannot even dream of reaching, and it can travel in a group in the same energy state. Therefore, photons can be stacked together in any number in the same space. This last property is the basis of the laser effect: a laser beam is in fact made up of photons of the same type, meaning the same energy.

Physicists talk about different families; remember that the electron belongs to the fermion family and the photon belongs to the boson family. We, as humans, are closer to the fermion family!

Let us come back to the photoelectric effect. We know that the energy of electrons varies under a discontinuous form, or to be precise, it occupies specific predefined states of energy.

In order to change state, in this case moving from one energy level in a specific material to an energy level in a vacuum, a single grain of energy is required. This corresponds to the difference in level from where the threshold (the minimum level of energy required in order to pass to the next level) appears. Generally, all interactions between electrons and photons are quantified, thus giving rise to the phenomenon of luminescence that can be seen in the nanoworld, particularly in the area of imagery.

The corpuscular concept enables us to have a better understanding of why ultraviolet rays and X-rays are dangerous. The photons which make up these rays are projectiles whose energy destroys our cells.

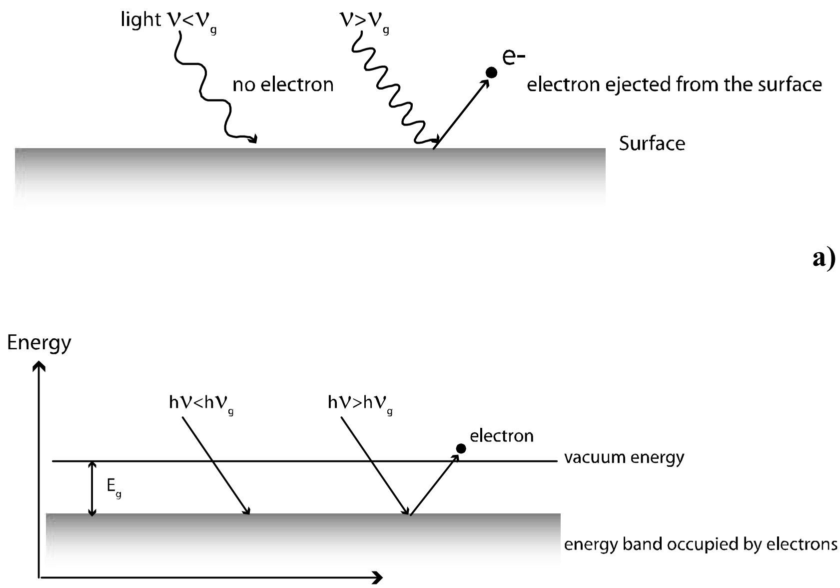
The quantum nature of the photon is used in a spectacular way in protecting confidential information.

In order to ensure communication security, man has always invented very elaborate coding systems; this is known as cryptography. Unfortunately, because of the power of calculation in modern computers, the codes always end up being cracked due to the fact that they are primarily based on arithmetic. This is especially evident in the world of banking where there is always a need for more sophisticated coding.

With photons, a new type of cryptography is starting to appear, especially in state-of-the-art laboratories which have very sophisticated instruments; this is known as quantum cryptography. This is based on the absolute ban on reproduction, which means that it is impossible to copy information. In the quantum world, measuring devices change the quantity of the measured object, so, if we measure a given state of a photon, we then transform it. It is like a locksmith who sees the lock change every time he tries to put the key in it.

This new method is imperative as it is the definitive weapon against theft.

Other uses of photons, which would be worthy of science fiction, are already up most scientists' sleeves.



a)

b)

Figure 2.5. *The photoelectric effect*

a) Experience. While the surface of a metal vacuum is illuminated with monochrome light, the surface will emit electrons if its frequency ν *is more than a certain value* ν_g.

b) Physics. Light is made up of energy photons $E = h\nu$. *While* $E < E_g$ *(*E_g *being the electron bond in the metal), the electrons will not reach the necessary energy level to break the vacuum in order to be able to escape. While* $E > E_g$*, the electrons are emitted by the surface.*

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[2] 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_2O

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

2 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.

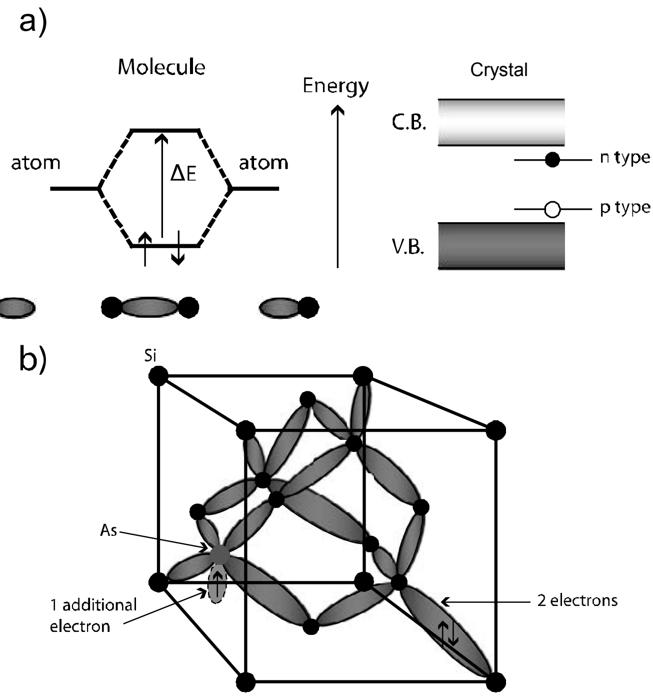


Figure 2.6. *Molecular orbitals and the band structure of crystalline silicon*

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 ΔE. 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[3] 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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3 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 protons 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.

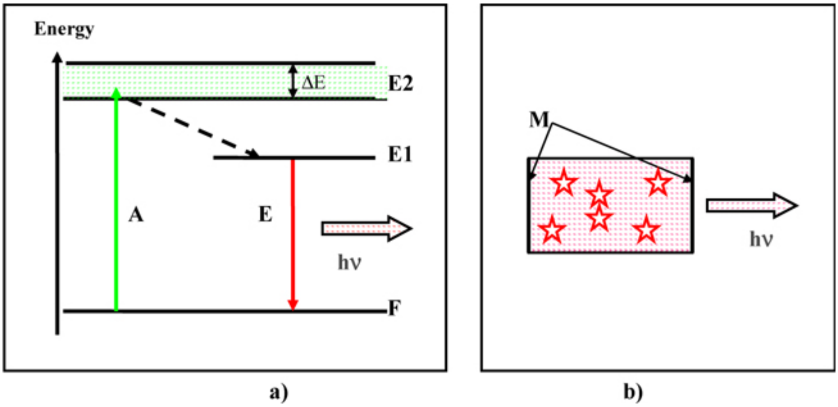

Figure 2.7. *Light-emitting diodes and lasers: general principles*

a) The electron of a light-emitting source, for example the ion 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 ΔE (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: monochromicity, phase coherence, and directivity.*

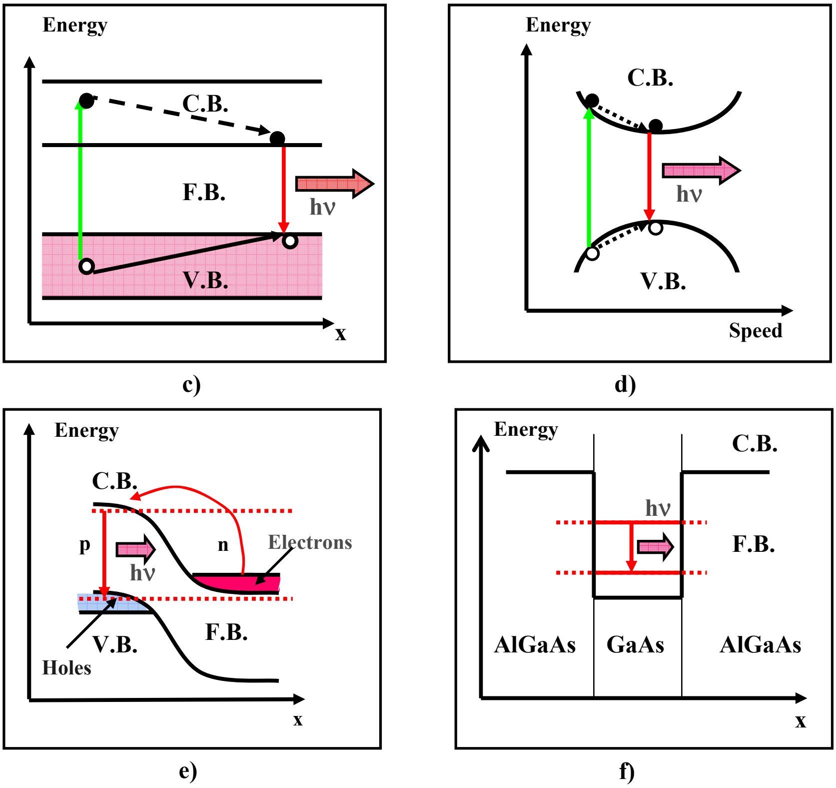

Figure 2.8. *Semi-conductor lasers*

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 hv.

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[4].

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.

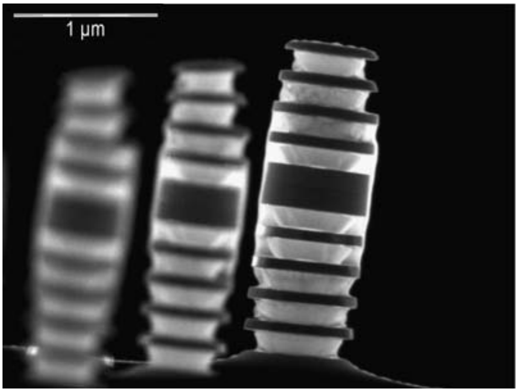

Figure 2.9. *Quantum dot for single photon experiments: 400-nm-diam micropillar, produced by e-beam lithography and reactive ion etching from a GaAs/AlAs-layered planar structure grown by molecular-beam epitaxy*

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[5] 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.

5 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"[6].

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).

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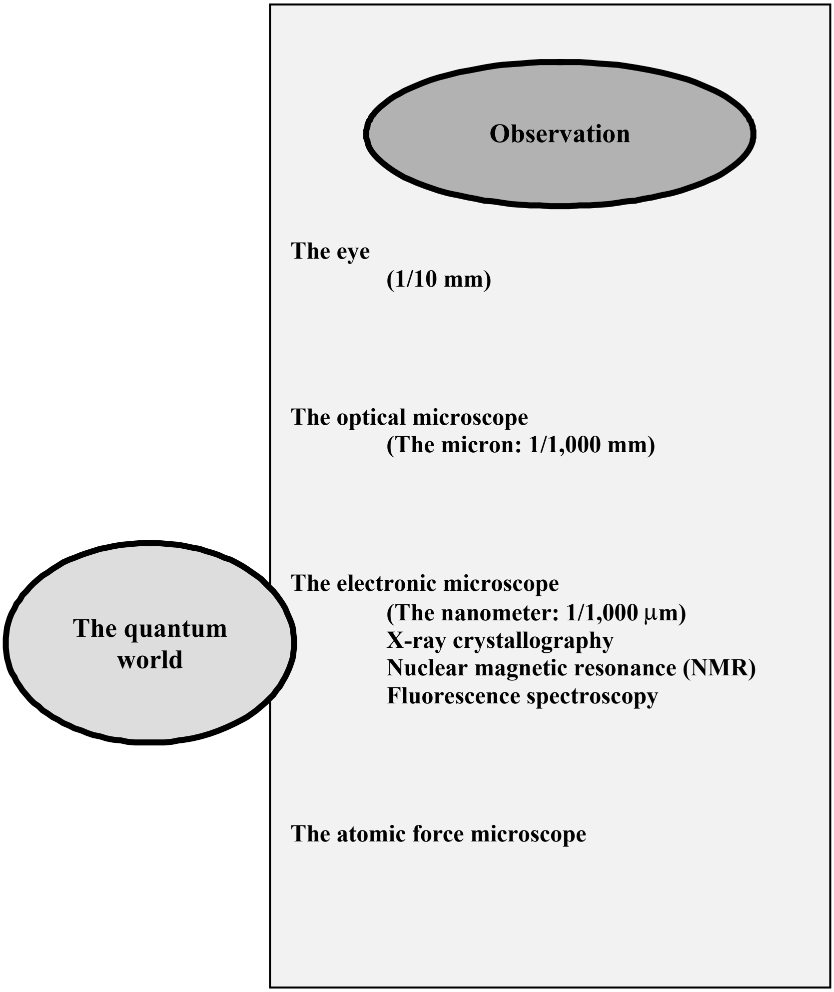
Chapter 3

The Revolution in Techniques Used in Observation and Imagery


Observation
The eye
(1/10 mm)
The optical microscope
(The micron: 1/1,000 mm)
The electronic microscope
(The nanometer: 1/1,000 μm)
X-ray crystallography
Nuclear magnetic resonance (NMR)
Fluorescence spectroscopy
The atomic force microscope
The quantum world

Observation is at the origin of all scientific discoveries.

The nanoworld is becoming more important and is even becoming an area of scientific discovery thanks to the progress that has been made in the techniques of observation.

3.1. Observing with photons

3.1.1. *The optical microscope in visible light*

The optical microscope was the first instrument that enabled man to observe objects normally invisible to the naked eye. As the microscope is subject to the laws of optics, its resolution is limited to several tenths of a micron. In order to study samples from living organisms, the samples must be prepared with coloration techniques.

A new generation of microscope which uses laser light appeared in the 1980s. It has enabled scientists to create three-dimensional images at different levels of depth of the matter being studied by using focalization and laser beam scanning. This type of microscope is known as a confocal microscope[1] and is particularly adapted for use in the natural world.

One very interesting use of these microscopes corresponds to their ability to work with fluorescent markers. The laser beam excites a fluorescent substance which has been added to the sample, for which we know the affinity for certain molecular sites. Thanks to these markers we can, for example, selectively view certain reactions. The fluorescent signals are detected by electronic

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1 A diaphragm situated in the focal plane image of the microscope only detects the photons coming from the convergence point of excitation, in other words the focal plane object.

sensors and these signals are then amplified. The image is then processed by computer.

3.1.2. *X-ray machines*

X-rays are photons with a wavelength that is much shorter than the wavelength of ultraviolet light. X-rays are produced from an accelerated shock of electrons against a metallic target.

One of the first applications of machines using X-rays was in the macroscopic domain. The X-rays benefit from the fact that this radiation has a strong penetrating power in materials with the rate of absorption depending on the density of the material. Radiation transmitted through a body coated with a phosphorescent or photosensitive substance is commonly known as radio waves. A sophisticated version of this type of machine is the X-ray scanner. The transmitter turns around the object at the same time as the receptor does, measuring the intensity of the X-rays transmitted. The data is processed by a computer which reconstructs cross-sections of the object, in other words 3-D imagery. The resolution is determined by the quality of the X-ray beam used. This type of machine is used in many applications, especially in medical imagery.

Another type of machine, which uses the interactive properties of X-rays with crystalline structures, is used in X-ray spectroscopy. These machines enable scientists to investigate objects in the nanoworld. Their operation rests on the following principle: a crystal is made up of identical patterns of atoms following a particular lattice whose chain is the same size as the wavelength of the X-ray. The X-rays are realigned by selective reflection in predetermined directions and then form diffraction figures. The information contained in the diffraction figures clearly deals with the structure of the lattice and, more specifically, the rather complex three-dimensional structures of atomic patterns. This analysis is possible, firstly, due to the quality of today's machines and, secondly, because of the sophisticated calculation techniques used. This type of machine is an essential tool for chemists who want to assemble molecules in crystalline form in order to study their atomic pattern. This method enabled the discovery of the double helix by Francis Crick and James Watson in 1953[2].

3.2. Observing with electrons

Electron microscopy uses the wave properties of electrons. However, as particles they need a vacuum in order to travel. Microscopes are in the form of a metal vacuum enclosure in which the following can be found:

– The electron gun, such as in cathode ray tubes used in television sets.

– The different elements of electronic optics, such as electromagnetic lenses (equivalent to traditional optic lenses) which control the trajectories of the electrons as well as the support of the object to be studied.

There are two types of electron microscope.

3.2.1. *The transmission electron microscope (TEM)*

In this type of microscope, as with X-rays, the beam interacts with the crystalline sample and creates a diffraction figure, or hologram. The analysis of the diffraction figure enables us to study the atomic structure of the sample being analyzed. The final resolution is related to the associated wavelength of the electrons

2 This discovery won them the Nobel Prize for Medicine in 1962.

and therefore to their energy. The most powerful machines work with voltages in the region of hundreds of thousands of volts.

3.2.2. *The scanning electron microscope (SEM)*

The surface of the sample under study is scanned with an electron beam. The size of the scanned surface depends on the level of enlargement desired. The interaction between the electrons and the sample gives rise to different signals (the emission of electrons and photons) which when gathered and analyzed bring together the image of the surface of the observed sample without using any mathematical process, contrary to the process of the TEM.

The resolution of this type of instrument, limited by the machine's technology, enables scientists to view objects at an atomic scale (1/10 of a nanometer).

A significant restriction of this microscope, as is the case for the TEM, is that it needs a vacuum. The samples need to be prepared in a specific manner, in other words they need to be plated, cooled, and cut into thin sections, all of which are clearly impossible when observing living organisms.

A new generation of SEM has overcome this restriction; they are known as environmental scanning electron microscopes. These SEMs enable scientists to observe objects in their natural state. The difference between the environmental scanning electron microscope and the conventional ones, which need a high vacuum on all levels of the columns that make up the microscope, is that the sample remains at a determined pressure thanks to a differential diaphragm pump system used in the observation room.

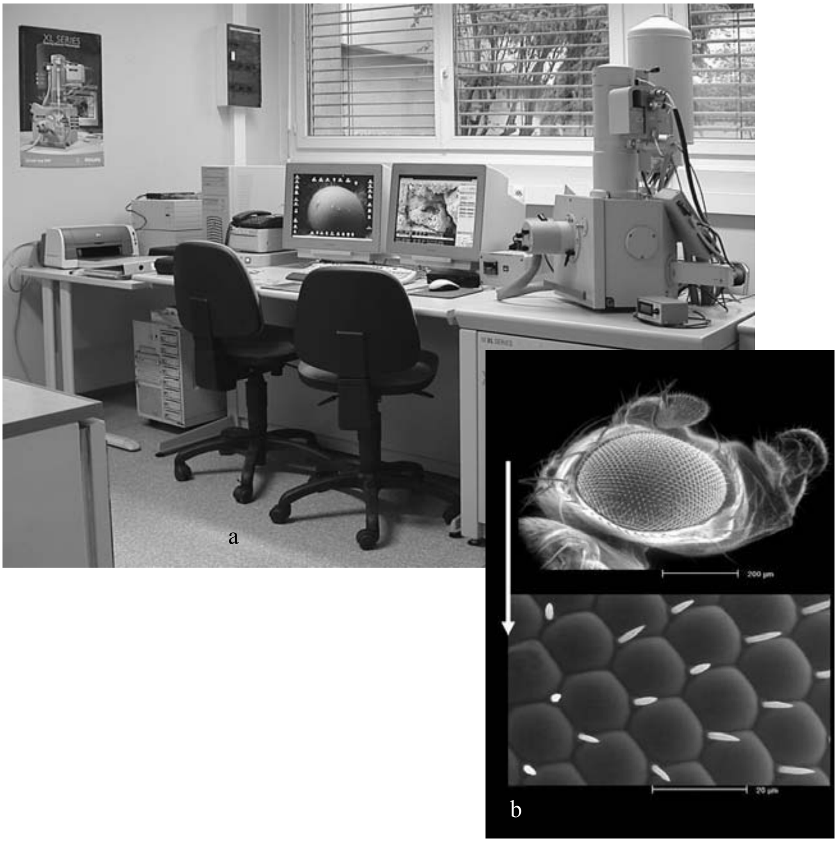

Figure 3.1. *The environmental scanning electron microscope: a) a general view of the environmental scanning electron microscope, b) example: detailed makeup of the eye of a drosophila*

3.3. Touching the atoms

The atomic microscope is mainly used in research laboratories. It works on a simple principle, but with very sophisticated technology.

Scientists create an image of vertical displacement from a point on the surface of a sample. This point is made up of some atoms (eg thinned down tungsten microcrystal atoms) and the precision of displacement is to the nearest 1/10 of a nanometer.

In the first version invented by IBM researchers[3] in 1981, the control signal is the current, albeit extremely weak, existing between the point of the microscope and the surface of the sample without any contact between the microscope and the sample. However, they are at a distance where the electrons can pass through by using the tunnel effect. In this case, we are referring to the scanning-tunneling microscope.

When there is contact between the point of the microscope and the surface of the sample, the microscope is called an atomic force microscope. This is the nano equivalent of our old gramophones. This type of microscope enables scientists to analyze surfaces with insulating properties, which is impossible with the scanning-tunneling microscope.

An optical version has existed for a short time now, and it is based on the presence of an optical wave that does not move. This evanescent wave is present on the illuminated surface of a sample which can only be detected on a nanoscopic level.

With these instruments, scientists can see the atoms of a surface, but they can also use these instruments to move the atoms, form

3 Gerd Binning and Heinrich Rohrer, Nobel Prize winners for Physics in 1986.

aggregates and construct atomic objects in order to study the properties of the atoms.

New generations of microscopes are being created which enable scientists to work on both the atomic and molecular scale.

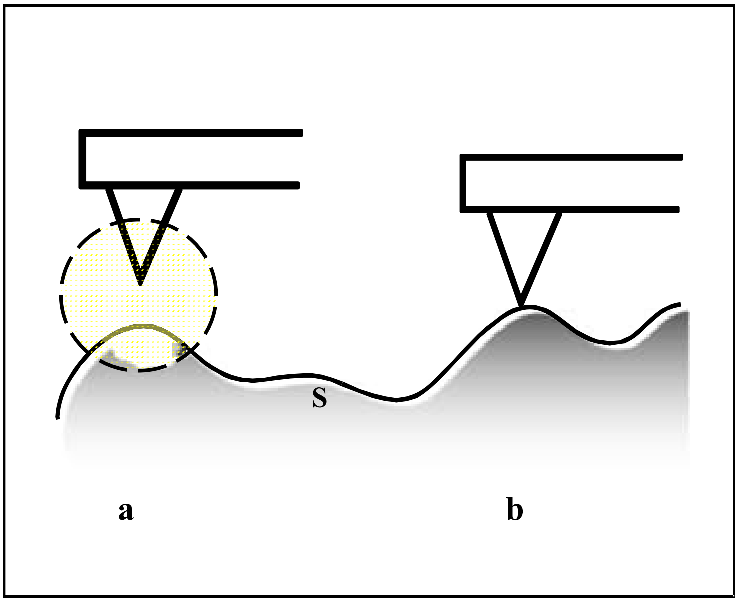

Figure 3.2. *The principle of atomic microscopes*

a) The scanning-tunneling microscope. Electrical charges pass from the surface of an object to the point of the microscope without there being any contact. The current varies strongly with distance. The movement of the point of the microscope is controlled with a specific current value in order to follow exactly the surface of the sample.

b) The atomic force microscope. A derivative of the scanning-tunneling microscope, it enables scientists to study the insulating surfaces. There is contact between the point of the microscope and the surface. The control is regulated by the force of pressure.

3.4. Observing how our brain functions

3.4.1. *Nuclear magnetic resonance*

A new generation of machine, primarily used by chemists, is becoming increasingly important in the field of medicine because it allows for 3-D imagery inside the organism. It uses nuclear magnetic resonance.

Remember that the proton, which has a nucleus, can be considered as a small magnet with two states called spin-up and spin-down, just like the electron. Certain nuclei, according to the number of protons they have, possess a magnetic moment. The nucleus of the hydrogen atom, in other words its proton, is the probe that is the most used. In a magnetic field, the two spin states have different levels of energy. If the proton is subject to a radio-frequency electromagnetic field whose energy is equal to the difference of these two states, there will be a resonance mechanism producing a signal which may be detected. This signal depends on the proton's environment. This is in fact a preferred method used by scientists for organic chemistry analysis.

Nuclear magnetic resonance is used in medical imagery due to the fact that it is non-destructive and enables scientists to carry out 3-D investigations with a resolution that is actually comparable[4] to X-ray scanners. The 3-D investigation is obtained by creating a magnetic field gradient in the body. The zone corresponding to the resonance of the protons of water molecules produces a signal at a determined frequency which is fixed by the nuclear magnetic resonance machine. The zone of resonance can be moved by varying the magnetic field.

4 The information obtained from these two methods is different.

The three-dimensional resolution is related to the frequency of resonance, and therefore to the intensity of the magnetic field which leads to the use of supra-conductor coils[5] which are only capable of generating sufficient magnetic fields for large objects.

3.4.2. *Functional magnetic resonance imaging*

One extremely promising technique associated with nuclear magnetic resonance is functional magnetic resonance imaging (fMRI). This enables scientists to study how the brain works. The excitation of groups of neurons can be observed by the amplification of the resonance signal and the rise in blood flow which is caused by the increase in the metabolism of the neurons. Scientists are therefore able to see how the brain functions. This type of imagery is currently under development.

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5 Supra-conductor coils are created with alloys which have a zero electric resistance at low temperature, allowing for considerable electric currents without any loss.

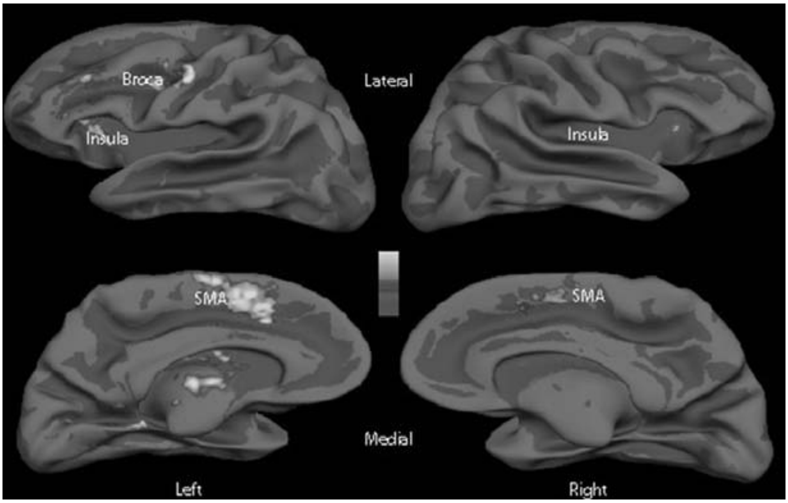

Figure 3.3. *Functional magnetic resonance imaging (fMRI)*

Application to functional imagery:

Activations obtained during the cognitive task. The anatomic image of the brain is represented here after cortical inflation allowing us to have a more detailed image of fissions or sulci (dark grey) and convolutions or gyri (light grey). The obtained activations, encoded according to a red-yellow color scale, highlight the neuronal fields involved in this task, primarily in the left hemisphere.

We have seen the main methods and observation tools that scientists use in order to study the nanoworld. Others exist which generally correspond to more sophisticated versions of the machines already described in this chapter. The use of nuclear technology in the field of medicine, such as the use of radio-isotopes, will not be discussed here.

3.5. Some bonus material for researchers

Synchrotron radiation involves the emission of light from electrons spinning in rotation.

In order to probe the nucleus of the atoms, physicists use electrons as projectiles in order to split them. To do this, the electrons are accelerated in order to supply them with energy. The first machines of this type were linear electrostatic accelerators which were replaced by more powerful ring-shaped instruments known as synchrotrons. The synchrotrons propel the electrons at speeds close to the speed of light[6]. A packet of electrons is introduced and each solo circuit receives supplementary energy. Unfortunately, at each turn the electrons lose energy by emitting electromagnetic radiation. This phenomenon limits the ultimate performance of the machine and, as a result, large machines have been created in order to minimize the loss of the electron's energy. An example is the large hadron collider which belongs to the European Organization for Nuclear Research whose 27 km circumference is larger than that of Geneva.

However, this light, which is undesirable for high energy physicists, has many exceptional properties.

Light is emitted during each rotation of the packets of electrons. Each beam of light possesses a continuous spectrum from infrared rays to X-rays.

Physicists, followed by chemists and then biologists, have been quick to use this source of light by "parasiting" certain accelerators. In France this is what is happening at the Laboratory for the Use of Electromagnetic Radiation (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE)) in Orsay[7]. Some light lines have been altered which did not please

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6 Speed limit impassable. The energy of a particle with a non-zero mass becomes infinite at this speed.

7 "LURE has completely fulfilled its mission as a national center of synchrotron radiation. Much has been achieved between its creation in October 1971 and the decision to create SOLEIL in September 2000. Its history is made up of many scientific and technological firsts, such as ground breaking experiments and the development of instruments and machines. […] LURE contributed strongly to the

nuclear physicists who saw this as a type of parasiting of the light lines in order to please other scientists[8].

Very quickly this source of intense light was put to use in multiple scientific fields. Here are two particular examples:

– The first is in the area of microelectronics, such as UV and X-ray sources, in order to push back the ultimate limits of lithography.

– The second is in the area of biology. Biochemists use an intense radiation of X-rays to enable them to carry out experiments that were previously impossible.

This new source of light was optimized and large machines dedicated to synchrotron radiation were created throughout the world. This is the case for SOLEIL in France.

Thus, a parasite light stemming from the theory of relativity and the physics of particles has become one of the most powerful instruments used to study matter on a nanometric scale.

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creation, definition and defense of the more recent project known as SOLEIL." Adieu LURE, Welcome to SOLEIL and CLIO-ELYSE. A message from A. Tadjeddine, Directing Manager of LURE, September 26, 2005.

8 The electrons spin millions of times on a stable trajectory to the nearest 1/10 of a millimeter in tubes which have an extremely tight vacuum. The use of the light emitted by the synchrotron needs vacuum drains linked to the ring in which the electrons spin.

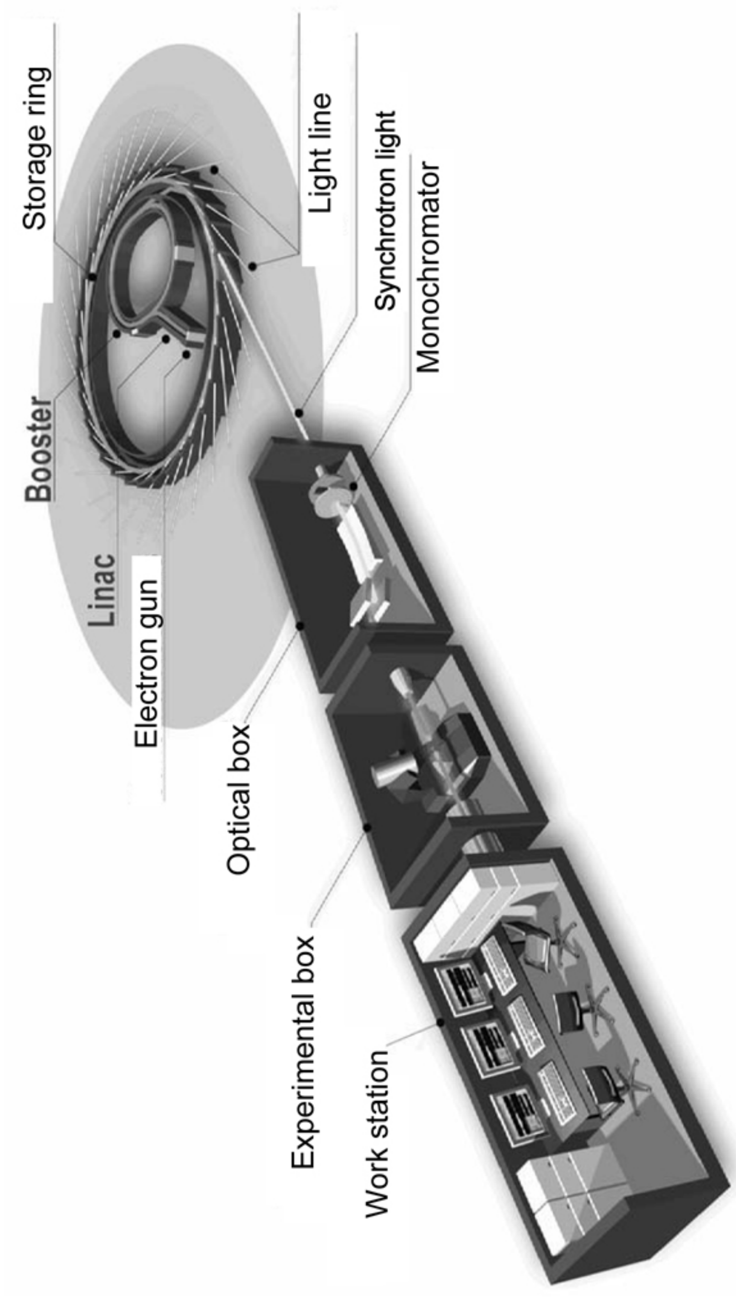


Figure 3.4. *SOLEIL: a synchrotron in France. Diagram of a light line*

Observation helps us see more clearly

Observation has always been the starting point in the progress made towards greater knowledge and mankind has invented instruments to study the infinitesimal, as well as the infinitely large.

Optic microscopy has made remarkable progress, in particular in the latest generation of confocal microscopes. 3-D images of the subject matter to be studied are obtained by the scanning of a laser beam whose absorption only occurs in sites where the frequency of excitation corresponds to twice the frequency of the light used. This property, called two-photon absorption, has two interesting points: first, the matter is transparent for one-photon absorption and, secondly, it only occurs at the focal point of a beam which provides excellent photographic detail. Two-photon laser scanning fluorescence microscopy, which is based on the same principle, is the most sophisticated method of microscopy that uses fluorescent markers.

A new generation of scanning electron microscopes, known as environmental scanning electron microscopes, makes it possible to study specimens without the preparations that are required for traditional electronic microscopy. These microscopes enable scientists to observe in vitro with a resolution of less than a nanometer.

The atomic microscope, which is only used in laboratories, is the best microscope used for the analysis of surfaces on a subnanometric scale.

Scanners using nuclear magnetic resonance have made extraordinary advances in medical imagery. MRIs continue to improve their resolution by using more intense magnetic fields.

To facilitate the observation process or to make it possible, coloration techniques are used. Biochemists have been using coloring or fluorescent substances for a long time in order to identify molecules, enabling their identification by absorption or fluorescence[9]. Molecular biology has also brought with it some innovations in this field, for example green fluorescent protein[10]. This molecular marker enables scientists to see the dynamics of proteins in the natural world. The techniques used to manipulate the molecules of living organisms can bind the molecules with fluorescent markers which act as real markers for the observation process. It is possible to selectively study how our molecular structures, proteins, repairing enzymes, and hormone signal transfers function.

Furthermore, nanoscience has made immense progress in imagery by controlling the fabrication of nanostructures, nanoparticles, and nanocrystals with a specific molecular fixation. Scientists can therefore appreciate the biological molecules of nanocrystals or quantum dots which have optic properties superior to those of fluorphores[11].

The cell lights up under our microscopes in the same way as a town does at night-time.

9 The emission of light under optic or electronic excitation.

10 This protein, which is extracted from the jellyfish, *Aequorea victoria*, is coded with a gene that can be introduced into the genome of a cell by genetic manipulation. We can genetically produce rabbits which glow fluorescent green under ultraviolet radiation.

11 The spherical nanocrystal is made up of atoms taken from groups 2–6 and groups 3–5 of the periodic table. This crystal is also made up of a packet of organic liquids.

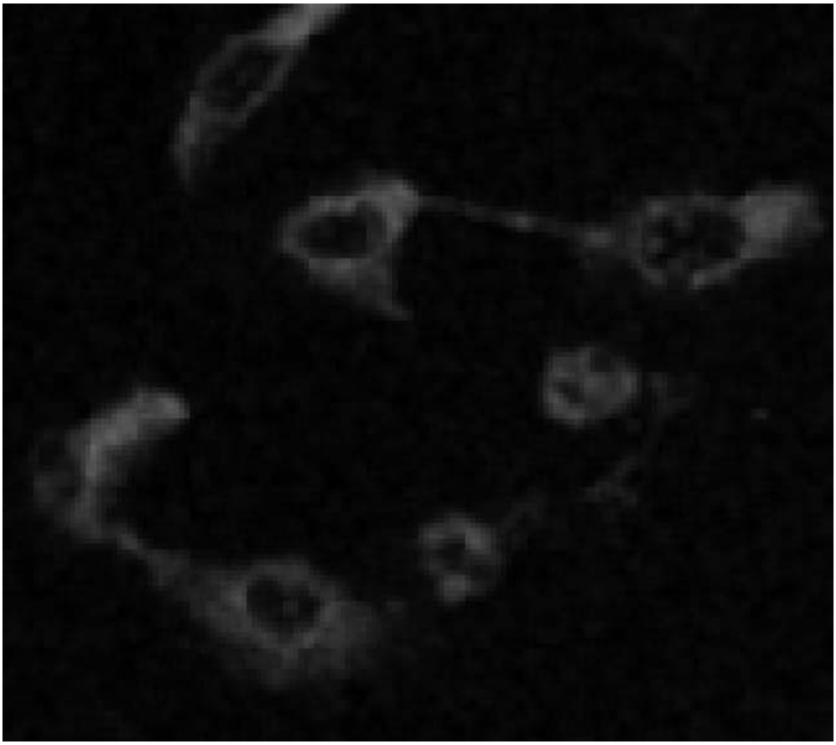
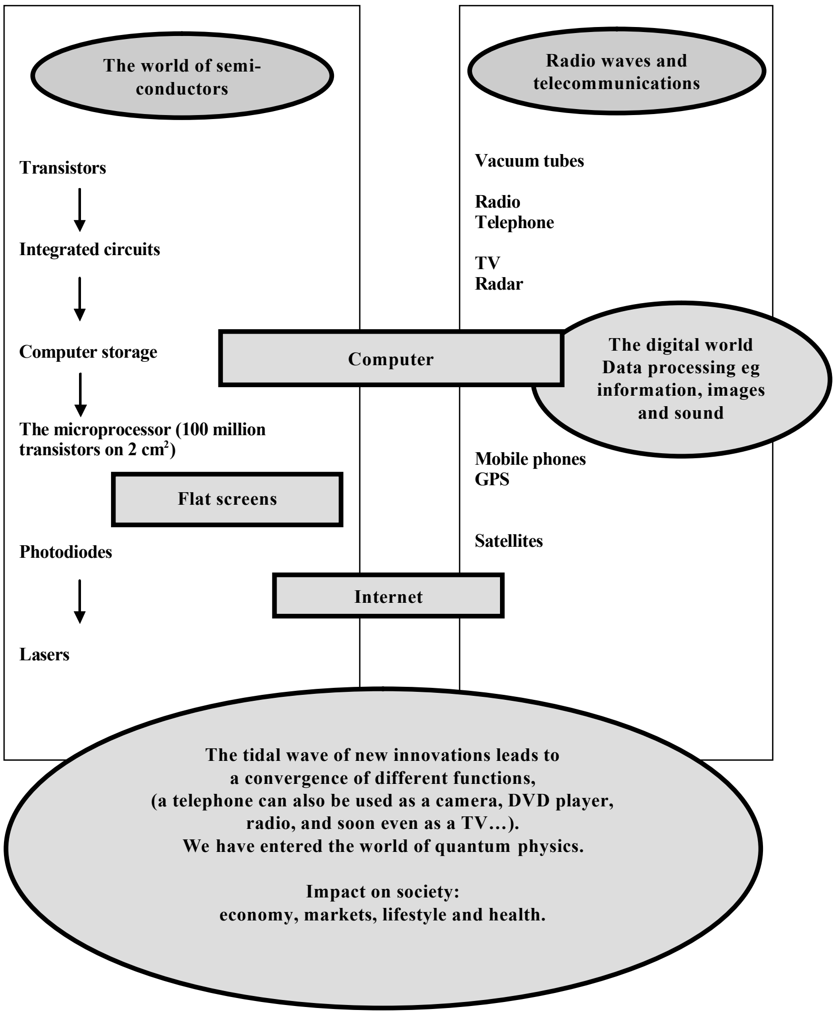


Figure 3.5. *Fluorescence imaging.*
This image represents fibroblasts which are found inside carbon nanotubes

Chapter 4

The Marriage of Software and Hardware *or Intelligence Engraved in Silicon*


The world of semi-conductors
Transistors
Integrated circuits
Computer storage
The microprocessor (100 million transistors on 2 cm^2)
Flat screens
Photodiodes
Lasers
Radio waves and telecommunications
Vacuum tubes
Radio
Telephone
TV
Radar
Computer
The digital world
Data processing eg information, images and sound
Mobile phones
GPS
Satellites
Internet
The tidal wave of new innovations leads to a convergence of different functions,
(a telephone can also be used as a camera, DVD player, radio, and soon even as a TV…).
We have entered the world of quantum physics.
Impact on society:
economy, markets, lifestyle and health.

> In terms of size [of transistor] you can see that we're approaching the size of atoms which is a fundamental barrier, but it'll be two or three generations before we get that far but that's as far out as we've ever been able to see. We have another 10 to 20 years before we reach a fundamental limit. By then they'll be able to make bigger chips and have transistor budgets in the billions.
>
> (Gordon Moore, Co-founder of Intel, 2005)

4.1. Small is beautiful

One way of reaching the nanoworld is by miniaturizing the objects of our world. This process is called top-down. The forerunner in this field is evidently microelectronics, now referred to as nanoelectronics. As the primary component in this field, the transistor becomes ever smaller. The consequences for the domain of information technology and telecommunications are tremendous. Furthermore, this scientific progress will enable the fabrication of billions of copies of this component. Being highly complex, reliable, energy-saving and in possession of gigantic memories, they could even be classed as the beginning of a form of intelligence. In order to produce these copies we need a very advanced scientific level and high-tech equipment. Obviously we cannot create a new neighborhood just by building houses next to one another. We need a structure, all sorts of networks and circuits that allow us to control the entire system. A microprocessor is really just a city in this sense, but reduced to the size of a pinhead.

4.2. Miniaturization

It took John Bardeen, William B. Shockley and Walter H. Brattain's (winners of the Nobel Prize for Physics in 1956) discovery of the transistor to begin the adventure. The electronic amplification device had previously been created with the help of the triode[1] which could not be miniaturized and consumed high amounts of energy. Several thousands of these tubes were used to create the first electronic calculators, which needed a good 10 kWh to work.

This changed with the appearance of solid semi-conductors. Their size became ever smaller and has reached a tenth of a micron in today's production, and in the area of research these semi-conductors are even smaller. At the same time, the appearance of the binary numeral system for calculators and the development of computers enabled the rapid development of a new technology with an exceptionally high performance. This technology is based on Metal Oxide Semi-conductor Field Effect Transistor (MOSFET) and it made silicon the most important material in electronics. As all possible information is coded using the binary numeral system of 0 and 1, which could also be described as an on/off system, the MOS transistor is perfectly adapted to it. This transistor relies on an electric field which is applied to an electrode to control the shape and hence the conductivity of a channel. The same principle applies to water pipes in which the pressure controls the water flow. This kind of device is not the only one which exists, but due to its simplicity, its geometry, and its relatively easy production, it is the best suited to large scale integration.

4.3. Integration

4.3.1. *The silicon planet*

With relation to the fabrication of integrated circuits, we moved from LSI (Large Scale Integration, at the level of thousands of

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1 In this vacuum tube the heated filament (cathode) causes a flow of electrons that hits the plate, a positively charged electrode (anode). The anode will receive the electrons. A third electrode (wire grid), which is polarized more or less negatively, is placed between both of them and controls the flow of electrons.

transistors) on to ULSI (Ultra Large Scale Integration, at the level of millions of transistors). Producing a primary device is one thing, but integrating millions of transistors per square centimeter without any errors is something else. The smaller the devices, the bigger the factory producing these circuits. This is a consequence of scientific, technical and economic needs:

– Scientific needs: the smaller a device becomes, the less energy it consumes. This is essential if we want millions of these devices to work on a small surface and increase the frequency of operations carried out. Currently, integration still continues to follow Moore's Law.

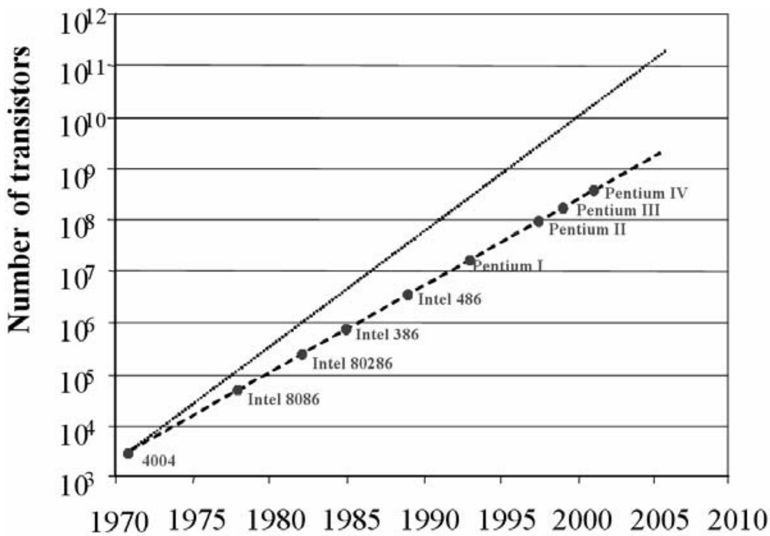

Figure 4.1. *Moore's Law*

– Technical needs: the smaller a device becomes, the more difficult its fabrication. In fact, it is essential that no problems occur that could interfere with the functioning of the device. A high level of integration forces all operations required in the creation of the final product to be exactly the same. The working environment needs to be entirely dust-free; these are the so-called clean rooms where employees wear specialized clothing and all products used in the process need to be at a high level of purity.

– Economic needs: the smaller a device becomes, the higher the cost of production. A maximum amount of circuits therefore needs to be engraved on each circuit board so that the diameter increases. Currently the limit of the diameter lies at 30 centimeters. An economic balance can only be reached if the price of the machines is not too high. The photorepeater[2] exposes the synthetic resin in preparation for the process of engraving. To reduce the dimensions of the devices in accordance with the law of optics (which states that the resolution of an image is subject to the light wave used), researchers are currently trying to produce powerful sources of light in the spectrum of ultraviolet waves. The research in the field of optics is restricted by the extremely expensive material.

Extraordinarily high integration demands an extremely high investment. In France, one example of this is the technological complex in Crolles near Grenoble. This research center is an international collaboration between Philips, Motorola, and STMicroelectronics.

2 The photorepeater exposes a surface on each circuit board and repeats this action for the entire time it is working on it. All other operations of storage or engraving are carried out in exactly the same way across the entire circuit board.

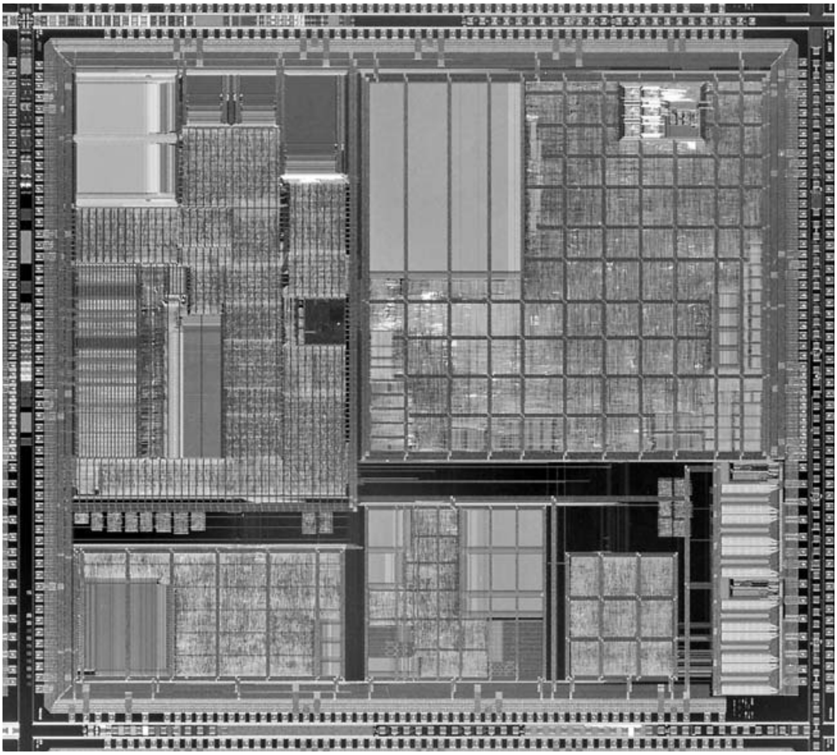

Figure 4.2. *An example of a device for integrated circuits on silicon*

Figure 4.3. *View of a 300 mm clean room (STMicroelectronics, Crolles2)*

The emblematic circuit in microelectronics, the microprocessor, is made up of one unit that deals with mathematical and logistical tasks needed to process and store given data (computer memories), as well as a control unit that runs the microprocessor as a whole. The control unit transmits commands given by the relevant software.

The production of a microprocessor, or computer-assisted devices, goes through the following steps:

– The new device which is defined in the feature specification is drawn in functional blocks.

– It is then subdivided into smaller components with specified characteristics which are applied according to the information in the relevant database.

– The layout is then documented in an optimized technological plan.

– Using the database, the technological plan is subdivided into different levels corresponding to the operation of photolithography. It is used to produce the “mask”[3].

– The production takes place in the laboratory and is controlled at each stage.

– The circuit boards are cut down to the required size and the circuits are tested.

– This process is followed by surface passivation and packaging.

3 Every phase in photolithography corresponds to a mask that defines which parts of the circuit board will be exposed.

4.3.2. *An expanding universe*

Thousands of technological innovations have been applied to the chips that are used today. They are now made up of several million transistors per square millimeter. This is possible thanks to a miracle of nature: silicon and its oxide form a perfect couple[4] and have enabled the development of the MOSFET transistor. We are part of this triumphant technological era. Intelligence is engraved in silicon.

Reducing the dimensions of transistors, as stated in Moore's Law, leads to a decrease in their energy consumption and the time needed to operate. Therefore, it is possible to increase their data storage as well as the speed at which they process it. This leads to the emergence of ever more complex systems which become smaller and smaller, as well as higher performance communication tools with a greater degree of flexibility. The latest mobile phones combine different functions, such as dictaphone, MP3 player, digital camera, PC games, and payment facilities as well as, of course, the telephone itself.

The last boundary in the realm of physics will be reached only when information can be stored on one single electron. This is unattainable with today's technology, even if in the laboratory objects can be manipulated at the level of a single electron. Other obstacles make the possibility of a computer made up of one single electron a dream rather than a reality. New technology which supports molecular electronics to enable such integration would be required. Nature deals with this in a very efficient, but certainly different, way: our brain!

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4 Silicon and its oxide are crystallographically compatible without any weaknesses in the interface which is unique in the domain of semi-conductors.