Charge transport in molecular devices.

Nanoscience and nanotechologies: new science?

Nanoscience and nanotechnologies are fields of research that have attracted a lot of interest and large financing in the last few years both in USA, with a large program started by the Clinton administration, and in Europe. China and other developing countries are also joining in this scientific effort.

What does nanoscience and nanotechnology mean exactly? Literally these words indicate science and technology that deal with objects that are confined to the scale of "nanometers", that is one billionth of a meter, in practice everything from the single atom scale (the typical dimension of which is one Angstrom i.e. one tenth of a nanometer) to 100 nanometers. Consider that the typical dimensions of cells are in the micron range even if they can vary dramatically.



But a question arises: is there something new in this science and technology or is it just a fancy way of calling old-fashioned science in order to obtain more easily research grants from government

agencies? Indeed it could be argued that for example chemistry, when dealing with the synthesis of new molecules, is really acting at the nanometer scale since the chemist is putting together atoms or molecules to form new objects which all have nano- or sub-nanometric dimensions. Nanoparticles of various materials have had technological uses for hundreds of years, a typical example are gold particles that at nanometers dimension change their color as a function of the precise dimension, they don't appear yellowish anymore but they could be more reddish or greenish according to their exact size and for these properties were used since early medieval time for coloring glass. Molecular biology is also another example of an intrinsic nanoscale science that existed before "nanoscience". So we can now reformulate our question: what is new in science and technology that really deserves a new discipline name, new research centers, new university departments? Is there something like a scientific "revolution" how it is often claimed by "nanoscientists" (I'm not referring with the prefix to their dimensions or scientific abilities)?

I think is difficult to judge a scientific revolution when you are in the middle of it since this is usually mostly made by many small advancements that only retrospectively appear as a revolution. Anyway if there is a revolution, at least two main breakthroughs and exciting novelties have helped this "revolution" to start. These are two new tools, one on the experimental side and one on the theoretical side, that have appeared in the last twenty years or so.

On the experimental side we have had the development of a new class of microscopic tools, called microscopic scanning probes, starting with the Scanning Tunnelling Microscope (STM)whose invention earned Binnig and Rohrer the physics Nobel Prize in year 1986 and that really changed our approach to microscopy. We make a short detour to describe this wonderful instrument since most of the research in nanoscience-technology involves the use of it at least as a complementary tool. The concept underlying the functioning of the (STM) experimental apparatus is very simple, we have a very thin tip, which ideally should be terminated by a single atom, that can be moved around with a precision better than an angstrom (Å, one tenth of a nanometer). We apply a voltage between the tip and the sample that we want to image and we measure the current that is flowing.

This apparently very simple method allows us to "see" single atoms or if you prefer "sense" them by measuring a current map.





Nickel surface image with atomic resolution.

While the first pictures with atomic resolution were obtained by moving the STM tip around the surface of a solid kept in so-called Ultra High Vacuum (UHV) (10⁻¹⁰ mbar not a very simple condition to obtain or very natural except in interstellar space) by the inventors of the technique, single atoms can nowadays be routinely seen in different environments, even in liquids.



Moreover by applying particular voltages it is possible to capture single atoms from a surface atomic site, move them around and place them in a well-defined position. In this way researchers have been able to write words with single atoms on a surface. Even electrochemical reactions can be localized with atomic precision by using STM-like instruments in electrochemical cells. There are some difficulties on the other hand to make these procedures more than a test or a game for skilled researchers and transform them into useful tools for technological applications, in fact the atomic writing, for example, has been obtained by keeping the system at temperatures very near 0 Kelvin, otherwise the temperature related casual movements of the atoms would both blur the atomic resolution of the microscope and make the atom diffuse much faster than the time required to position them with the tip. I discuss this point because the Holy Grail of nanoscience would be to form molecules and in general atomic structures artificially by positioning atoms in the desired location with an appropriate tool, this being a forecast of a famous physicist called Feynman at the beginning of the sixties. Of course these structure should be stable but these types of technological applications are still far away from our present capabilities.

Scanning probe microscopies have been further developed with many new tools that make us able to measure forces, magnetic properties, etc at the nanometer scale. The results of these developments are instruments like the Atomic Force Microscope (AFM) and the Magnetic Force Microscope. The latter, as its name says, allows us to measure magnetic properties with almost atomic resolution. Instead by AFM it has been recently demonstrated that is even possible to press a single molecule and study its reaction to this external mechanical stimulus. Moreover the introduction of the AFM has made it possible to determine the structure and morphology of non-conducting samples (being a conductor was a real limitation of STM samples) and to open also a wider range of applications of scanning probes to biomaterials.

The second great tool is a set of ever more powerful computing codes for the calculation of the relevant properties of nanoscale objects. Up to now powerful theoretical methods (the so-called Car-Parinello method invented in Trieste) and computers have reached an impressive capability of simulating and predicting the properties of molecules and molecules interacting with other objects like surfaces of metals and semiconductors.

A not so rapid but a more continuous transformation (maybe induced by the competition with the incredible resolution of the Scanning Probe microscopies) has brought various other more classical experimental techniques to a level of spatial resolution that makes it possible to study single objects of nanometer size. Examples are the very precise Transmission Electron Microscopes (TEM) of the last generation that make use of beams of electrons with transverse dimensions of the order of the Å. Nowadays also these instruments are routinely able to visualize single atoms, even if with some drastic limitations on the type of sample to be imagined. Chemically sensitive microscopy has been obtained by developing X-ray microscopes. These very recent instruments require the use of synchrotron radiation sources which are usually very large machines (storage rings where particles travel at speeds very near the speed of light the speed difference being typical one part over 10^{-9}) with diameters of hundreds of meters, so we have the paradox that to see the extremely small we need very big machines. Thank to the same machine we can also study with unprecedented resolution the electronic energy level of atoms and molecules and also determine the structure i.e. the relative positions of atomic nuclei in molecules and solids and even at the devilish (see below) surfaces of solids. This information allow us to reach an understanding of how, where and why certain atom and molecules bind to other atoms or molecules or surfaces.



Aerial view of Elettra synchrotron light source in Trieste.



Typical scheme of a synchrotron light source

Besides these practical tools or maybe as a consequence of their exploitation a very important change has occurred in the science related to this type of research and a new scientific approach has become an obliged choice when studying nanosize objects. Scientists are forced not to think anymore in terms of old style disciplines (even if this is a very difficult jump to make for old-fashioned scientists) like physics, chemistry, biology since, when you are dealing with nanoscale object properties it is very difficult to say if you are doing physics, chemistry or in certain cases biology. Moreover the only way to obtain substantial advances in this field is to put together research groups with a range of competences as wide as possible: a chemist with the sensibility to choose the right molecules to reach a certain aim (build an electronic device based on organic molecules), the understanding of a physicist for the basic processes to calculate, predict, measure the system properties of interest (charge transport, mechanical properties...).

So in the end I believe that there is something really new and worthy of a new name and is related to our much improved capability of measuring, predicting the behaviour and making nano-objects. Still I think we are just at the beginning of this "revolution".

Nanoscience in my research group in Trieste.

For at least 30 years systems of nanometer dimensions have been within the reach of current science and technology, this is the science and technology of thin and ultrathin films. It has been possible to control the deposition of various materials with a precision better than a single atomic layer and in the last 20 years the properties of these films have been studied with experimental and theoretical techniques that have been developed or arranged for this use. The technology of thin films is nowadays widely used in particular in the electronic industry. This science has been my research subject in the last few years in Trieste.

Two main effects produce a change of objects properties when they reach nanometric dimensions: one appears to be more a quantitative difference but it can have dramatic consequences and is that the surface to volume ratio increases when an object becomes smaller. A famous physicist

(Wolfgang Pauli) stated that the bulk of the material was created by God and the surface invented by the devil to signify that surfaces are quite a more difficult system to study than bulk periodic materials (remember that most of the solid materials are in crystalline form, it means periodic in space and therefore easier to study experimentally and to calculate theoretically by physicists who very much like symmetries and order), on the other hand many of the most important physical and chemical processes occur at the surface of materials, the most classical example being catalysis. We can appreciate the missing symmetry at the surface when we move from well inside a crystalline material where the inner landscape is boring and perfectly periodic up to the surface where suddenly we see no more material around us. This change of landscape strongly affects the chemical properties of the first few atomic layers. Materials made by nanoparticles which are mostly surface can therefore have completely different chemical properties with respect to their bulk counterpart but also mechanical properties are affected and so called nanocomposites i.e. materials made of nanoparticles pressed together can be very different with respect to a uniform material: for example nickel composite made by binding together nickel nanoparticles can have mechanical properties comparable with the hardest stainless steel while normal nickel is much softer.

A second qualitative change in the material properties at nanometric scale is due to the fact that quantum effects come into play when the pieces of materials approach the atomic dimensions. What does this mean? The main effect is the so called quantum size effect (QSE) mainly due to the electrons contained in the very small piece of material which we consider. From the quantum mechanical point of view particles, in particular with small mass like electrons (that is why we don't need to care too much about protons and neutrons that are the other constituents of everyday matter for what concerns quantum mechanic effects), have also a wave nature and the wavelength of the electron is related to its energy (wavelength= distance between two crests or two valleys of a wave). The problems i.e. the quantum size effects come into play when the dimension of the piece

of material in which the electrons are confined become comparable with wavelength of the electrons. You can think of the piece of material as a box where the electron wave is contained. To have a wave in a stationary state you must have that an integer number of wave lengths can be contained in the box, if this is not the case you either have to change the dimension of the box to accommodate the wave or change the energy of the electron to adjust the wavelength to the dimension of the object. Now the capability of atoms or atomic aggregates to bond with other atoms or molecules i.e. their chemical reactivity, is strictly related to the energy levels of their electrons. This is one of the scientific subjects that I have been studying in Trieste for the last few years in particular for metallic thin films. What we have discovered is that really both things happen at the same time, the adjustment of the box dimensions and of the electron energy and there is an interplay between these two effects. The interesting point, apart from the scientific satisfaction of understanding a new piece of the laws of nature, is that these changes of electron energies and box dimensions can drastically change the chemical and electronic properties of materials and therefore it is conceivable, at least in principle, that the reactivity of materials covered by very thin layers of material can be modulated by changing the number of atomic layers of the film i.e. the dimension of the box.

It has been discovered that, due to the same QSE, small particles of gold, the by "antonomasia" noble (i.e. completely non-reactive, not even when attacked by extremely reactive acids) metal can be turned into a very effective catalysts, i.e. a piece of material that, thanks of its high reactivity, helps chemical reactions that are in its absence very slow, to occur at a much faster rate. In recent years there has been a constantly growing interest in studying and if possible controlling the formation of thin films or in the general nanostructure of organic materials with the aim of substituting the expensive silicon electronics with the much cheaper organic based electronics. Organic material based devices can be economically cheap but more importantly also less energetically consuming to realize and could for example render photovoltaic cells a more energy efficient system able to satisfy our growing energy demand by exploiting the renewable solar

energy. The most efficient photovoltaic cell presently available, based on high purity, highly ordered (mono crystalline) silicon wafers, need to operate many years before they repay the energy cost of production.

One of the applications of organic electronics that has already reached the stage of industrial production is the so called Organic LED (OLED) which can be build at very low costs and is a much more efficient and therefore environmental friendly light source than the filament bulb lights. Consider that almost one quarter of the electricity power in US is used for lighting and that it is mostly obtained by incandescent bulbs that have an efficiency in light production of only 10%. But the most sought after application is the building of much cheaper and smaller chips for computers. To reach this goal various steps have to be considered: these new chips can't be made exclusively of organic materials, metals are also needed for stable contacts, therefore the interaction of organic molecules with metals have to be studied; moreover complex structures shaped according to the requests of electronic engineers have to be designed. Presently there are two different approaches to form complex and extended nanostructures, one indicated by the expression "top-down" where circuits or more in general nanostructures are designed on the material by using techniques like lithography (now nanolithography), where the "writing on the stone" is obtained by directing beams of electrons, photons or ions with nanometer resolution on the material to machine. This is a very time-consuming method. The alternative is the so called "bottom up" approach where the hope is to let nature do the slave work. Since organic molecules present high capability to auto aggregate in complex fashions (life could be seen as the most complex auto-aggregation process of organic molecules) the idea is to opportunely guide this desire of the molecules in order to obtain the required nanostructures in a process that is called self-assembly. There are many examples of these type of processes, we have recently studied the formation of very long molecular wires of aminoacids on metal surfaces. Our aim is not only to look at the nice (from the nanoscientist's viewpoint...) structures that are formed on the metallic surface (this can be done with the STM technique) but also to understand at the atomic level why these structures form, how the molecules

bind to the metals and to each other, to be able to predict the formation of such structures in other cases. This information and knowledge can be obtained by measuring properties like energy and wavefunction spatial distribution of the electrons of the molecules by using for example synchrotron radiation techniques.



Molecular rows of Lmethione formed on the Ag surface. The length of the rows can reach microns. In the right panel the fine structure of the rows can be observed, the single molecule are distinguishable and it can be appreciated that the rows are formed by couples of molecules.

Nanoscience and charge transfer in single molecules at Columbia.

At the Nanoscale Science and Engineering Center of Columbia University the main aim is to reach the ultimate miniaturization of electronic devices and be able to have a transistor made mainly by a single molecule. The idea is to use an organic molecule that is complex enough to have the characteristic required by an active electronic component. To achieve this goal it is necessary to gain many skills in producing atomically defined contacts, to master the electrode-molecule contact formation etc. At a more deeply physical level there is the need to understand how the electrons travel across the single molecule from one contact to the other. A better understanding of these processes would be of interest also for biologists since the charge transport is relevant also in various biological processes, for example electronic excitations and the motion of electric charges are known to play a significant role in a wide range of bio-macromolecules and the electron transfer in DNA plays an important role in radiation damage and repair and in biosynthesis. A recent achievement of the NanoCenter has been the first incorporation of a single molecule in an actual electronic circuit. A complex path has been followed. Two pieces of a wonderful nanomaterial called carbon nanotube have been used as electrodes. Carbon nanotubes ar objects formed by one or a few sheets of a graphitic-like material which is rolled in the shape of a tube with a diameter of the order of the nanometer. This is one of the many incredible forms that carbon can assume and has been recently discovered, not long after the discovery of another form of carbon which is also intrinsically "nano": the soccer ball-like fullerene or C60, where the C atoms sit on the corner of geometrical structure composed by hexagons and pentagons very much like a soccer ball. Fullerenes and C-nanotubes belong to the same family of C compounds.



C60 molecule formed by hexagons and pentagons



Single walled Carbon nanotube. You can imagine obtaining it by wrapping a single layer of graphite (graphene) onto a cylinder.

With a typical top-down approach NSEC scientists have managed to cut a nanotube with high precision nanolitographic methods and to bind an organic molecule between the cut obtaining a real single molecule device.



A combined work of physicists and chemists to produce a real single molecule electronic device.

More very interesting research work that has recently been pursued at the Columbia Nanocenter concerned the measurement of the electrical "resistance" of a single molecule. This type of measurements really makes it possible to investigate the basis of the charge transfer process. Very important results have been obtained showing that molecules formed mainly by C rings (like the molecule of benzene) have different resistance according to the relative orientation of the rings. This resistance has been measured between gold electrodes with a very simple but clever method. Of course to understand the meaning of these measurements it is necessary the help of a chemist with the chemical intuition and the capability to create the proper compounds, of a theoretical physicist able to calculate the energy levels and spatial distributions of our old friends the electrons of the molecule. Moreover we are going to try to understand in greater detail the formation of the bonding of the molecule is important first of all to create the contact but then is also To obtain this information we go back to our large machine the synchrotron source.



Conclusions?

To end this rather boring discussion, I think nonetheless there is still an interesting aspect to consider when studying these systems. When considering the conduction through a single molecule we have the molecule, an intrinsically quantum object, that means that it has to be treated using QM laws, but to measure its conductance we have to bring it into contact with some macroscopic objects which will follow classical mechanical laws. Quantum objects have some funny properties, for example they can travel through a wall (in QM language they **tunnel**), it means they can cross regions where their velocity becomes imaginary (if you remember the effect on the mind of the young Toerless of his first encounter with imaginary numbers you can guess which problems an imaginary velocity could cause to an unsettled mind!), their position cannot be precisely determined

if not at the expense of making their velocity completely undetermined, their evolution in time is defined only by their probability to be in a certain point of space (related to the square of their wave function); but if you put enough quantum objects together at a certain point they start to follow the classical mechanic laws, it means their behaviour becomes completely deterministic. Now you could ask yourself at which point objects stop tunnelling and why you need to open the door to move to an other room. Maybe the study of the interaction of macroscopic classical objects with single molecules could shed light on this, I think, still unresolved problem of the foundations of quantum mechanics.