Quantum change for nanotubes

Jing Kong, Leo Kouwenhoven, Cees Dekker

From
Physics World
July 2004

ISSN: 0953-8585

Institute of Physics Publishing
Bristol and Philadelphia

Quantum change for nanotubes

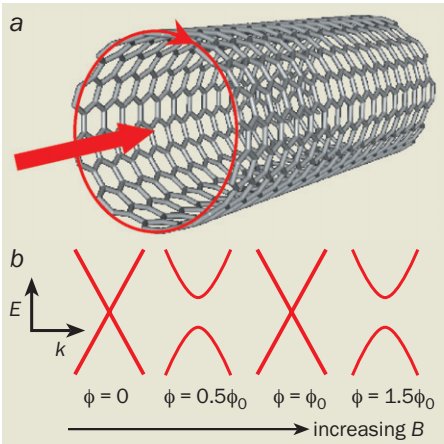
A metallic carbon nanotube can be made into a semiconductor and vice versa when a magnetic field is combined with a little quantum mechanics

From **Jing Kong**, **Leo Kouwenhoven** and **Cees Dekker** at the Kavli Institute of Nanoscience, Delft University of Technology, the Netherlands

We all remember the infamous experiments carried out by Jan Hendrik Schön in 1999. In his hands, materials that were notorious insulators became conductors when a voltage was changed. Those claims, alas, turned out to be false, and Schön's publications were later retracted. Indeed, in reality it is very difficult to change an insulator into a metal, and vice versa, without, say, applying extreme pressures.

For nano-scale materials, however, things may be different. The electronic properties of a carbon nanotube, for example, depend on its chirality, which, in turn, depends on the direction in which the graphene sheet has been rolled up to form the nanotube. About two-thirds of nanotubes are semiconductors, and the remaining third are metals. Semiconducting nanotubes have a band gap in their energy spectrum where electrons cannot exist, whereas such a gap is absent in metallic nanotubes.

The electronic fate of a nanotube is therefore determined once it has been grown. However, this is not quite the end of the story. For instance, researchers have tried (with some limited success) to alter the band gaps of nanotubes by applying strain or by filling them with molecules. Now three independent teams – led by Paul McEuen at Cornell University, Junichiro Kono at Rice University and Alexey Bezryadin at the University of Illinois at Urbana-Champaign – have demonstrated that this feat can be achieved with a magnetic field. Indeed, the three experiments show that one can convert a semiconducting nanotube into a metallic one, and vice versa, at least in principle.



Magnetic magic – carbon nanotubes are rolled-up cylinders of graphite with diameters of about 1–10 nm, and they have been the focus of intense research since they were discovered in 1991. (*a*) A magnetic field (red arrow) introduces a phase factor to the electron wavefunction in the circumferential direction (red circle) via the Aharonov–Bohm effect. As a result, the electronic properties of a nanotube can be modulated by a magnetic field. (*b*) The energy spectrum (red lines) is a plot of energy (E) versus wavevector (k). As the magnetic flux, ϕ, increases, the energy-band structure of the nanotube oscillates from that of a metal to that of a semiconductor. The transformation of a semiconducting nanotube into a metallic one is a little more complicated because the band gap first decreases to zero and then widens again.

Quantum phase

The magnetic field comes into play via the Aharonov–Bohm effect. This is a quantum phenomenon in which the wavefunction of an electron acquires a phase shift as it follows a trajectory that encloses a magnetic flux (such as the path round the surface of a cylinder in a magnetic field). This phase shift alters the way the electron trajectories interfere, and therefore affects the electronic properties of the material.

The Aharonov–Bohm effect has become famous in mesoscopic physics, where it causes the resistance of micron-sized metallic and semiconducting cylinders and rings to oscillate as a function of the strength of an applied magnetic field. One period of oscillation, which is the result of a phase shift of 2π in the electron wavefunction, corresponds to adding a quantum of magnetic flux, ϕ_0, through the cylinder: $\phi_0 = h/e$, where h is Planck's constant and e is the charge of the electron. Plugging in the numbers, one finds that the resistance of a ring with a diameter of 1 μm oscillates with a period of 5 mT.

In 1999 Adrian Bachtold and co-workers in Christian Schönenberger's group at the University of Basel, Switzerland, explored the Aharonov–Bohm effect in a multiwalled carbon nanotube that had a diameter of just 16 nm (see *Physics World* June 2000 pp37–41). Here the Aharonov–Bohm period corresponds to a magnetic field of 18 T, which is about the maximum field that is commercially available.

In the early metal-ring experiments the electrical conductance was only slightly modified by the Aharonov–Bohm effect. Now, however, the experiments of McEuen, Kono, Bezryadin and their co-workers demonstrate that it is possible to use the effect to alter the energy spectrum of the nanotubes.

In order to see how this happens, consider the electron wavefunction along the circumferential direction of a nanotube. The Bloch theorem – which tells us what an electron wavefunction looks like in a solid with a periodic lattice structure – states that the wavefunction has a phase factor that depends on the electron's wavevector, which is the reciprocal of its wavelength. Because the electron is confined to move along the circumference of the nanotube, standing waves arise that have discrete wavelengths. This means that the wavevector, k, is also quantized: $k = (n - \nu/3)/R$, where R is the radius of the nanotube, n is an integer and ν is a parameter that equals 0 or ± 1 depending on the chirality of the nanotube.

For the lowest lying mode, $n = 0$, the energy band gap is proportional to k. As a result, we have a metallic nanotube with a zero band gap if $\nu = 0$, or a semiconducting nanotube if $\nu = \pm 1$. When a magnetic field is applied along the axis of the nanotube, however, the electron wavefunction acquires an additional phase shift due to the Aharonov–Bohm effect. As a result, the wavevector is modified: $k = (n - \nu/3 + \phi/\phi_0)/R$, where ϕ is the magnetic flux through the tube.

This allows one to tune the wavevector, and therefore change the band-gap structure of the nanotube, by varying the magnetic field. Note that every time that the ratio ϕ/ϕ_0 becomes an integer, the Aharonov–Bohm effect is cancelled by n, which means that the band-gap modulation is periodic as a function of the magnetic field.

Experimental confirmation

This simple and elegant way to change the electronic properties of a carbon nanotube was predicted by Hiroshi Ajiki and Tsuneya Ando of University of Tokyo 10 years ago, just after nanotubes were discovered. However, efforts to test their ideas have been hampered by the fact that magnetic fields of up to 5266 T are required to observe one Aharonov–Bohm period in a nanotube with a diameter of 1 nm. This is far beyond the reach of even specialized magnet labs, where the maximum continuous field that is available is about 45 T. The Cornell, Rice and Illinois teams have now managed to get round this, and have provided a complete confirmation of Ajiki and Ando's predictions.

The Cornell researchers found that even a tiny fraction of a full Aharonov–Bohm

period can still lead to observable electronic effects. Indeed, the 8 T field in their 2.6 nm and 5 nm diameter nanotube devices allowed them to investigate just 0.1% of one period. By making sensitive measurements of the electron transport at low temperatures, the team observed a significant shift in the energy states near the band edge, which showed that the semiconducting gap was getting smaller as the field increased (E D Minot *et al.* 2004 *Nature* **428** 536).

The Rice team worked on nanotubes with a diameter of about 1 nm, and used special facilities at the high-field magnet lab in Florida State University to apply a magnetic field as high as 45 T. This is almost 1% of a full Aharonov–Bohm period (S Zaric *et al.* 2004 *Science* **304** 1129). The spectra of optical absorption and photoluminescence in the nanotubes showed a clear redshift, which also revealed that the band gap of semiconducting nanotubes shrinks in the presence of a magnetic field. The Cornell and Rice groups have therefore observed the first steps of a process in which a semiconducting nanotube becomes a metal at very high field, and their results are in excellent agreement with the predictions of Ajiki and Ando.

The only way to obtain a larger fraction of the Aharonov–Bohm period, and therefore to truly turn a semiconducting nanotube into a metal, and vice versa, is to increase the diameter of the nanotube. This was the approach chosen by Bezryadin and co-workers, who used a multiwalled nanotube with a diameter of 30 nm (U C Coskun *et al.* 2004 *Science* **304** 1132).

Compared with the Cornell and Rice experiments, this method reduces the magnetic field required for one Aharonov–Bohm period to about 6 T, which is readily available in the lab. In their low-temperature electron-transport measurements, the Illinois researchers observed the predicted modulation of electrical conductance with a period equal to h/e.

Fields of dreams

These experiments provide a consistent confirmation of the combined effect of the Bloch theorem and the Aharonov–Bohm effect, although some of the details still need to be resolved. The fact that a magnetic field can be used to tune the energy spectrum of carbon nanotubes also provides a powerful extra "knob" for nanotube researchers. Indeed, our group at Delft has recently taken advantage of this to obtain a tunable multilevel Kondo effect.

Concerning applications, the future is not as bright. Magneto-optical and magneto-electronic nanotube devices based on the Aharonov–Bohm effect will probably always be out of reach because they require a magnet that can produce a field of 1000 T. Such a device is a dream that not even Hendrik Schön would be able to publish. But the fact that we now know that it is possible, in principle, to turn a semiconducting nanotube into a metallic one is an important step forward for the nanotube community.

Magical helium clusters

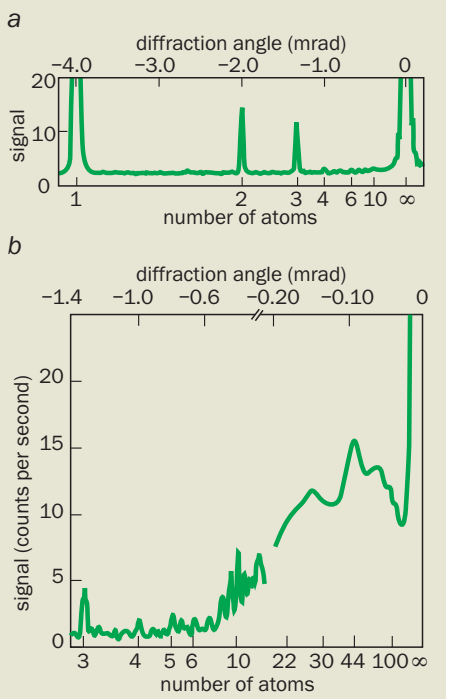
Helium-4 atoms prefer to form clusters of a certain size

From **Peter V E McClintock** in the Physics Department at Lancaster University, UK

Physicists are well acquainted with the concept of magic numbers. In nuclear physics, for example, a nucleus is more stable if it contains a magic number (e.g. 2, 8, 20, 28,…) of protons or neutrons. As a result, there is an abundance of nuclides in nature of a certain size. Similar patterns are seen in small atomic systems, such as the closed shells of valence electrons in metal clusters.

There are explicit theoretical predictions, however, that magic numbers of this kind – which are related to an enhanced stability of the ground state – should not occur for clusters of helium-4 atoms. Rather, the ground-state properties of the cluster should change smoothly as the number of atoms it contains increases. At first sight it therefore seems astonishing that Peter Toennies of the Max Planck Institute for Flow Research in Göttingen, Germany, and co-workers have recently observed magic numbers in helium-4 clusters (R Brühl *et al.* 2004 *Phys. Rev. Lett.* **92** 185301).

To create the helium clusters, Toennies and colleagues in Spain and the US allowed fluid helium to expand at cryogenic temperatures and form a collimated beam. The researchers then directed this beam through a transmission grating that had a period of 100 nm, which diffracted the clusters into a mass spectrometer. Since the de Broglie wavelength of a cluster is inversely proportional to its mass, clusters of different sizes were diffracted at different angles. By plotting the signal from the mass spectrometer as a function of the diffraction angle, the team was therefore able to plot the size distributions of the clusters with excellent resolution (see figure).



Preferential peaks – when clusters of helium atoms are transmitted through a periodic grating, the angle of diffraction depends on the momentum and therefore the mass of the clusters. Plotting the current detected by a mass spectrometer as a function of this diffraction angle (top axis) therefore yields the distribution of cluster sizes (bottom axis). Instead of a smooth dependence, Peter Toennies and co-workers found a series of peaks that shows helium-4 prefers to form clusters of 10/11, 14, 22, 26/27 and 44 atoms.

Contrary to what is expected, certain cluster sizes appear to be favoured more than others. Toennies and co-workers carried out several tests to check that the peaks in the size distribution were independent of conditions in the source region and in the detector. They also varied the angle of the diffraction grating relative to the incident beam of clusters, and concluded that the peaks definitely indicated magic numbers corresponding to cluster sizes of 10/11, 14, 22, 26/27 and 44 atoms.

Magic clusters

Why does this pattern arise? A preference for particular cluster sizes presumably reflects events that take place when the clusters are created. For example, one would assume that these preferred sizes were more stable and therefore energetically favoured during the creation processes. But this seems to be ruled out by calculations that estimate the binding energy of the ground state of helium-4 clusters. However, there is no reason why stability considerations should be applied only to the ground state. Given the relatively high temperature of the source region (6.7 K), and the turmoil that leads to cluster production, it is highly plausible that the helium-4 clusters will often be created in excited states.

Toennies and co-workers therefore calculate the energies of excited states of the cluster taking into account its angular momentum radial vibration modes, and their calculations produced some very interesting results. By comparing the excitation energies of clusters with their chemical potential