Theoretical investigation of small diameter carbon nanotubes

Thesis points of the PhD Thesis

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2005

1 Introduction

Single walled carbon nanotubes are long cage-like molecules with a structure very similar to that of fullerenes, except that they are extremely elongated in one direction. While their diameter (d) is in the range of nanometers, their typical length falls in the region of micrometers – and can extend up to millimeters – which makes them quasi one-dimensional solids. They are often described as a rolled up sheet of graphene (single sheet of graphite) and many of their most characteristic physical properties are indeed possible to trace back to graphite.

The physical properties of a nanotube greatly depend on how the hexagons are aligned with respect to the tube axis; this can be given by two integer numbers, the (n, m) chiral indices. The electronic band structure of a nanotube can be easily calculated from that of graphene by zone folding. Carbon nanotubes can be either metallic or semiconducting. Being quasi one-dimensional systems, nanotubes exhibit Van Hove singularities in their density of states, which leaves a mark on many of their physical properties, e.g. their optical and resonant Raman spectra. The majority of the Raman spectrum of carbon nanotubes shows a large resemblance to that of graphene, e.g. the two most characteristic Raman bands of graphene – the D and the G bands – can be found in the Raman spectrum of carbon nanotubes as well. Yet all carbon nanotubes have one Raman active mode which cannot be traced back to graphite, the so-called radial breathing mode (RBM), which is the most characteristic vibrational mode of carbon nanotubes. This is a totally symmetric mode, where all nuclei are vibrating almost completely radially in the same phase. Simple continuum elastic theory predicts that the RBM frequency is inversely proportional to the diameter of the tube; first principles calculations and measurements have both shown that for large diameters this is indeed the case.

Carbon nanotubes have many potential application possibilities, especially in the field of nanoelectronics, but also as nanomechanical parts and biological nanotools. They can be used e.g. as field emitters in scanning tunneling electron microscopes or flat displays, as tips for STM or AFM to allow for increased resolution, as field effect transistors, as high quality fibers with high tensile strengths which do not break at knots, as efficient biological tools for targeted delivery of molecules within an organism, or even to improve neural signal transfer by growing neuronal circuits on a carbon nanotube grid.

For the nanotubes with a diameter of about 1-2 nm the simple graphene folding description works fairly well. But at lower diameters, deviations can be expected from this ideal behavior, and a higher level of theory is necessary to treat small diameter tubes. The

accurate theoretical investigation of single walled carbon nanotubes with small diameters has become important recently, because such tubes can now be produced by several methods. Nanotubes with diameters down to about 0.7 nm can be produced by the HiPCO method, annealing of fullerene-nanotube peapods at high temperatures results in double-walled carbon nanotubes where the diameter of the inner tube can be as low as 0.5 nm, and nanotubes with an extremely small diameter of about 0.4 nm can be produced inside AFI-zeolite channels. These kinds of small diameter nanotubes have a highly curved surface, and this can have a strong effect on the physical properties of the nanotubes, thus methods which include curvature effects are required to describe them, preferably on the first principles level.

2 The aim of our research

Our aim was to perform the first systematic analysis of the physical properties of a large number of different single walled carbon nanotubes in the diameter region of 0.3 to 1.6 nm focusing on the small diameter tubes and including chiral tubes, using first principles methods. Below we summarize the particular physical properties that we sought to examine in our investigations.

2.1 Geometry

While the simplest theoretical methods based on the zone folding approximation can describe the large diameter tubes well, deviations from this approximation can be expected at small diameters where the curvature of the tubes is very high and the discreteness of the atoms cannot be neglected. The most important geometrical parameters, the diameter, lattice constant, bond lengths and bond angles can all be influenced by the high curvature. Beyond studying these parameters, we also meant to examine some less trivial geometrical parameters, the so-called misalignment angles and the pyramidalization angle.

2.2 Totally symmetric vibrational modes

The diameter dependence of the RBM frequency allows for an assignment of the chiral indices of a tube simply by measuring the RBM frequency in Raman measurements, combined with other experimental methods. In order to make the assignment however, one needs accurate knowledge of the diameter dependence of the RBM frequency. The

continuum model prediction only works for large diameter tubes, and even for large diameter tubes there is a slight difference between the case of zigzag $(n, 0)$ and armchair (n, n) tubes, suggesting that there is no simple one-to-one correspondence between diameter and frequency, and in fact chirality plays an important role. By calculating the RBM frequency of a large number of tubes in a wide diameter range on the first principles level, we intended to study the chirality-dependence of the RBM frequency in detail.

There is another effect which has been largely neglected in the literature before. The radial breathing mode is a totally symmetric mode, and in principle, it can mix with any of the other totally symmetric modes of the nanotube. Depending on the chiral indices, nanotubes have one or two totally symmetric modes beside the RBM, which correspond to a tangential movement of the nuclei along the nanotube cylinder. We meant to increase the accuracy of the RBM frequency calculations by including the coupling of the RBM with these modes.

2.3 Electronic band structures

The electronic properties of carbon nanotubes are important to know accurately to efficiently realize any of the possible nanoelectronic applications. The simplest way to determine the electronic band structure of a single walled carbon nanotube, is to use the zone folding approximation, which however neglects many physical effects that are very important to be taken into account for small diameter tubes. First principles calculations on the actual, curved surfaced nanotubes are necessary to include these effects. First principles level calculations have been sparse in the literature so far, there are especially very few previous calculations for chiral tubes in the low diameter region ($\lesssim 0.8$ nm). Our main goal was to perform a systematic study of the electronic properties of a large number of different carbon nanotubes on the first principles level, including as many chiral tubes as possible.

3 Method

We performed all calculations with the density functional theory (DFT) based Vienna *ab initio* simulation package (VASP). The code uses a plane-wave basis set and periodic boundary conditions. It was primarily designed to examine three-dimensional solids, but lower dimensional solids and molecules can also be examined with VASP as long as a large enough separation is applied between the periodically repeated instances of the system.

The interaction between ions and electrons can be described by either ultrasoft Vanderbilt pseudopotentials or by the projector-augmented wave (PAW) method. The exchange-correlation energy is described within the framework of the local density approximation (LDA), based on the Ceperley-Alder parameterization scheme. Optionally, generalized gradient (GGA) corrections can be included. For the PAW method, two kinds of GGA functionals can be used, the PW91 or the PBE functional. For the ultrasoft pseudopotentials, only the PW91 GGA functional is available. We used the PAW method and the LDA functional in all of our calculations.

4 Thesis points

My PhD thesis sums up the results of our calculations on the physical properties of various single walled carbon nanotubes in a wide diameter range, focusing on small diameter tubes. Our investigations were the first systematic analysis of 40 different nanotubes, including 14 chiral tubes, on the first principles level of theory. The most important results of my PhD thesis can be summarized in the following thesis points.

1. Single walled carbon nanotubes show strong individuality and chirality-dependence in all of their physical properties, especially below a diameter of 1 nm.

2. The folding energy, the diameter, the lattice constant, the bond lengths, and the bond angles show significant, chirality-dependent deviation from the prediction of the simple graphene folding model. The misalignment angles are small, but not neglectible at small diameters. The magnitude of the pyramidalization angle exceeds that of C_{60} for the smallest diameter tubes. The zigzag tubes show a "triad structure" in almost every geometrical parameter due to the "trigonal warping effect".

3. The RBM frequency does not follow the simple $1/d$ diameter dependence of the continuum model below a diameter of 1 nm, but shows a significant, strongly chirality-dependent softening, and furthermore, the coupling of the radial breathing mode with the totally symmetric tangential mode(s) is small, but not neglectible.

4. The frequencies of the totally symmetric tangential modes form two well-defined branches when plotted as a function of tube diameter. Some exceptions occur, which again are an indication of the strong individuality of small diameter carbon nanotubes.

5. The Fermi wave vector of armchair tubes shifts to lower values from the zone folding prediction as the diameter decreases, as a consequence of increasing curvature. The downshift is proportional to the inverse diameter square.

6. Similar to the triad structure in the geometrical parameters, the band gap of the zigzag tubes as a function of the diameter shows a "buckling". This buckling is enhanced in the DFT calculation as compared to what is expected from tight binding approximation, showing that the anisotropy, that is, the trigonal warping effect is actually larger than what is predicted by simple tight binding.

7. A curvature induced secondary gap appears in zone folding metallic non-armchair tubes as a consequence of curvature, while all armchair tubes remain metallic. Anomalous diameter dependence is found for the secondary gap of zigzag tubes, this is possibly due to the lack of considering many-electron effects in our calculations.

8. At very small diameters, $\sigma - \pi$ rehybridization makes almost every nanotube metallic. In the case of zone folding semiconducting tubes, this effect appears only at diameters below about 0.4 nm, whereas in the case of zone folding metallic tubes, it already appears at diameters as large as about 0.5 nm. Some of the zone folding semiconducting tubes remain semiconducting; this slight chirality-dependence is another indication of the strong individuality of small diameter carbon nanotubes.

5 Conclusions

The most important conclusions of my PhD thesis can be summed up as follows.

Small diameter single walled carbon nanotubes show strong individuality and chirality-dependence in their geometrical, vibrational, and electronic properties. The geometrical parameters significantly deviate from the prediction of the simple graphene wrapping model. The RBM frequency shows a chirality-dependent softening from the continuum approximation. Coupling between the RBM and the totally symmetric tangential modes is small, but not neglectible. The trigonal warping effect is found to be larger than predicted by simple tight binding. Curvature induces a small secondary gap in the band structure of zone folding metallic non-armchair tubes and a downshift of the Fermi wave vector of armchair tubes. Anomalous diameter scaling is found for the secondary gap, possibly due to neglecting many-electron effects. The band gap of the smallest diameter tubes disappears in almost every case due to $\sigma - \pi$ rehybridization.

6 List of publications

6.1 Publications closely related to the thesis

1. Publications in refereed international scientific journals:

   (a) R. Pfeiffer, H. Kuzmany, Ch. Kramberger, Ch. Schaman, T. Pichler, H. Kataura, Y. Achiba, J. Kürti, and V. Zólyomi: "Unusual high degree of unperturbed environment in the interior of single-wall carbon nanotubes", *Phys. Rev. Lett.* **90**, 225501 (2003); impact factor: 7.035; independent citations: 12.

   (b) J. Kürti, V. Zólyomi, M. Kertesz and G.Sun: "The geometry and the radial breathing mode of carbon nanotubes: beyond the ideal behaviour", *New J. Phys.* **5**, 125 (2003), Focus issue on Carbon Nanotubes; impact factor: 2.480; independent citations: 14.

   (c) C. Kramberger, R. Pfeiffer, H. Kuzmany, V. Zólyomi and J. Kürti: "Assignment of chiral vectors in carbon nanotubes", *Phys. Rev. B* **68**, 235404 (2003); impact factor: 2.962; independent citations: 6.

   (d) J. Kürti, V. Zólyomi, M. Kertesz, G.Sun, R. H. Baughman and H. Kuzmany: "Individualities and average behavior in the physical properties of small diameter single-walled carbon nanotubes", *Carbon* **42**, 971 (2004); impact factor: 3.120; independent citations: 3.

   (e) V. Zólyomi and J. Kürti: "First-principles calculations for the electronic band structures of small diameter single-wall carbon nanotubes", *Phys. Rev. B* **70**, 085403 (2004); impact factor: 2.962; independent citations: 1.

2. Publications in conference proceedings:

   (a) J. Kürti and V. Zólyomi: "Theoretical Investigation of Small Diameter Single-Wall Carbon Nanotubes" in *Molecular Nanostructures, AIP Conference Proceedings* **685** edited by H. Kuzmany, J. Fink, M. Mehring and S. Roth (Melville, New York, 2003), p. 456; independent citations: 2.

   (b) V. Zólyomi and J. Kürti: "First principles calculations for the electronic band structures of small diameter zone folding metallic single wall carbon nanotubes"

in *Electronic Properties of Synthetic Nanostructures, AIP Conference Proceedings* **723** edited by H. Kuzmany, J. Fink, M. Mehring and S. Roth (Melville, New York, 2004), p. 343; independent citations: 0.

(c) J. Kürti and V. Zólyomi: "First principles calculations for the electronic band structures of small diameter zone folding non-metallic single wall carbon nanotubes" in *Electronic Properties of Synthetic Nanostructures, AIP Conference Proceedings* **723** edited by H. Kuzmany, J. Fink, M. Mehring and S. Roth (Melville, New York, 2004), p. 377; independent citations: 0.

3. Scientific lectures:

(a) V. Zólyomi: "The effects of curvature on the electronic band structure of single wall carbon nanotubes", 2nd Szeged International Workshop on Advances in Nanoscience (SIWAN04) September 30th - October 2nd, 2004, Szeged, Hungary

Sum of impact factors: ≈**18.6**. Sum of independent citations: **38**.

6.2 Further publications

1. Publications in refereed international scientific journals:

(a) J. Kürti, V. Zólyomi, A. Grüneis, and H. Kuzmany: "Double resonant Raman phenomena enhanced by van Hove singularities in single wall carbon nanotubes", *Phys. Rev. B* **65**, 165433 (2002); impact factor: 2.962; independent citations: 19.

(b) V. Zólyomi and J. Kürti: "Calculating the discrepancy between the Stokes and anti-Stokes Raman D band of carbon nanotubes using the double resonance theory", *Phys. Rev. B* **66**, 073418 (2002); impact factor: 2.962; independent citations: 5.

(c) V. Zólyomi, J. Kürti, A. Grüneis, and H. Kuzmany: "Origin of the fine structure of the Raman D band in single-wall carbon nanotubes", *Phys. Rev. Lett.* **90**, 157401 (2003); impact factor: 7.035; independent citations: 9.

(d) F. Simon, Ch. Kramberger, R. Pfeiffer, H. Kuzmany, V. Zólyomi, J. Kürti, P. M. Singer, and H. Alloul: "Isotope engineering of carbon nanotube systems", *Phys. Rev. Lett.* **95**, 017401 (2005); impact factor: 7.035; independent citations: 0.

2. Publications in conference proceedings:

   (a) J. Kürti, V. Zólyomi, A. Grüneis, and H. Kuzmany: "Disorder Induced Triple Resonant Raman Phenomena in Single-Wall Carbon Nanotubes" in *Structural and Electronic Properties of Molecular Nanostructures, AIP Conference Proceedings* **633** edited by H. Kuzmany, J. Fink, M. Mehring and S. Roth (Melville, New York, 2002), p. 347; independent citations: 0.

   (b) V. Zólyomi, J. Kürti, and H. Kuzmany: "Calculating the Structure of the Raman D Band of Bundles of Single-Wall Carbon Nanotubes" in *Molecular Nanostructures, AIP Conference Proceedings* **685** edited by H. Kuzmany, J. Fink, M. Mehring and S. Roth (Melville, New York, 2003), p. 443; independent citations: 0.

3. Scientific lectures:

   (a) V. Zólyomi: "Double resonance enhanced by Van Hove singularities in the Raman spectrum of single wall carbon nanotubes", Invited seminar lecture, December 18th, 2001, Institut für Materialphysik, Universität Wien, Strudlhofgasse 4, A–1090 Wien, Austria

   (b) V. Zólyomi: "A D-sáv eredete szén nanocsövek Raman spektrumában", ELTE TTK Biológiai Fizika Tanszék, Tanszéki szeminárium, 2002. február 21.

   (c) V. Zólyomi: "Isotope Engineering in Carbon Nanotube Systems", ELTE TTK Biológiai Fizika Tanszék, Tanszéki szeminárium, 2004. november 11.

   (d) V. Zólyomi: "Single linear chain of carbon atoms in the interior of a single walled carbon nanotube", HUNS 2005 meeting March 21st-22nd, 2005, Budapest, Hungary

   (e) V. Zólyomi: "Charge transfer and band structure calculations in nanotube systems", Invited seminar lecture, June 20th, 2005, Institut für Materialphysik, Universität Wien, Strudlhofgasse 4, A–1090 Wien, Austria

Sum of impact factors: $\approx$**20**. Sum of independent citations: **33**.

6.3 Sum of impact factors and independent citations

Total sum of impact factors: ≈**38.6**. Total sum of independent citations: **71**.