CYLINDRICAL-WAVE METHOD IN THEORY OF PRISTINE AND METAL-DOPED NANOTUBES AND NANOWIRES

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Abstract

The linear augmented-cylindrical-wave (LACW) method was suggested, elaborated, and implemented as software for calculation of the electronic structure of inorganic polymers with approximate cylindrical symmetry, such as pristine and metal-doped nanotubes. Consideration was carried out in the muffin-tin (MT) and local density functional approximations for the electron potential. The analytical expressions for the Hamiltonian matrix elements and overlap integrals were found. The LACW method was applied to calculation of the band structure of carbyne, linear chains formed by 3d metals, pristine and metal-intercalated carbon and boron–nitrogen nanotubes. Introducing transition-metal atoms into the interior of nanotubes was found to change the character of the conductivity of nanowires, which can be used for creating nanosized heterojunctions.

1. Introduction

Nanotubes, a novel class of surface carbon forms, were discovered in the early 1990s [1–7]. Nanotubes are hollow extended cylinders whose surface, like a graphite layer, is formed by fused benzene rings. Actual structures are 3 to 200 Å in diameter and can be up to several micrometers long. Nanotubes can exhibit either a high metallic conductivity or semiconducting properties depending on their thickness and the orientation of the surface benzene rings about the tube axis. Nanotubes exhibit superconductivity [8–10] and a high current density associated with the ballistic mechanism of electron transfer without scattering by defects and phonons [11–13]. Nanotubes have a highly ordered structure, which is responsible
for their high mechanical strength. This property, in combination with the high conductivity, renders them suitable for fabricating the probe of a scanning electron microscope and allows one to increase its resolution by several orders of magnitude [14, 15]. Nanotubes have excellent emission characteristics, which permit their use for designing LEDs and displays [16, 17]. Their high specific surface area and chemical inertness make them attractive for chemical engineering, in particular, for catalysis. The most intriguing field of possible application of carbon nanotubes is nanoelectronics [1–7]. This is a new field of electronics in which separate atoms and molecules should act as electronic components [18]. Based on nanotubes, diodes [19], field and one-electron transistors [20, 21], voltage inverters [22], and nanosized sensors [23] have been already created. Carbon nanotubes can function as nanowires interconnecting separate components of nanosized electronic devices.

From the chemical standpoint, the most extraordinary properties of nanotubes are associated with the existence of a hollow channel running the entire length of the tube along its axis. This channel can accommodate hydrogen and alkali, transition, noble, and rare-earth metals; in addition, nanotubes can be intercalated with compounds, for example, binary compounds, such as transition-metal carbides and oxides [24]. Introducing different atoms and molecules into nanotubes results in materials with new properties. Carbon nanotubes filled with metals are fabricated by the electric arc method in the presence of a catalyst. Some metals encapsulated in a nanotube form nanowires of constant diameter running the entire length of the tube along its axis [25].

The electronic structure of all-carbon nanotubes was first studied by the MO LCAO method in \( \pi \)-electron and local density functional approximations and, later, by other quantum-chemical methods [26–31]. However, the LCAO methods are inapplicable to calculations of the electronic structure of nanotubes intercalated with heavy atoms, e.g., transition metals. In a series of our recent works, we suggested and implemented a new quantum-chemical method referred to as the linear augmented-cylindrical-wave (LACW) method. This method is the extension of the linear augmented-plane-wave (LAPW) method to cylindrical systems. The LAPW method is one of the most exact approaches in the band theory of bulk solids and is applicable, in particular, to transition-metal compounds [32–37]. In this paper, the LACW method is expounded and its application to calculation of the band structure of carbyne; all-carbon and boron–nitrogen nanotubes, both pristine and intercalated with \( 3d \) metals; metallic nanowires; and some other systems is described.