Linear augmented-cylindrical-wave method in the band theory of nanotubes

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The linear augmented-cylindrical-wave (LACW) method was suggested, elaborated, and implemented as software for calculation of the electronic structure of polymers with an approximate cylindrical symmetry, such as pristine and metal-doped nanotubes. This method is the extension of the linear augmented-plane-wave method to cylindrical systems.

Consideration was carried out in the muffin-tin (MT) and local density functional approximations for the electron potential. We consider that the electron potential is spherically symmetric in the vicinity of atoms and constant in the interatomic space up to two cylindrical potential barriers: the exterior cylinder of radius *a* and the interior cylinder of radius *b*. These radii are chosen so that the region confined by these barriers accommodates a significant portion of the electron density of the system under consideration. To construct basis wave functions, the solutions of the wave equation for the interspherical (cylindrical waves) and MT regions are sewn together so that the resulting LACWs and their derivatives are continuous at the boundaries of the MT spheres. Inside the MT spheres, the LACW is expanded in spherical harmonics. The addition theorem for cylindrical functions is used to equate these functions and their derivatives at the boundaries of the MT spheres. In this basis, we obtained the analytical expressions for the overlap integrals Hamiltonian matrix elements of the secular equation, the roots of which determine the electron spectrum of nanotube.

We discuss the results of application of the LACW method, beginning with monatomic chains, namely, a carbyne (linear chain of carbon atoms) and 3*d* metallic chains both with and without alternation of bonds. Particularly, this calculation shows that carbyne with alternating the bond lengths is a narrow-gap semiconductor with an indirect transition from the σ_s^* to π_p^* band. The chemical bond strength and band stuctures in 3*d*-metal chains is determined by the bonding and antibonding character of the bands and by their filling with electrons. The calculations predict an increase in the stability of the chains to metal–metal bond dissociation in the series Sc–Cr. Beginning with the chain of manganese atoms there must be a weakening of chemical bonding. The chains of Ni, Cu, and Zn atoms should be unstable since they are stabilized only by weak δ interactions. Therefore, upon the increase in the atomic number of a transition metal, the stability of the $[M]_\infty$ chains should first increase to the middle of the period and then decrease.

The band structures of single-wall carbon nanotubes are calculated. As is known, all armchair carbon nanotubes have a metal-type electronic structure. The Fermi level for them is located at the intersection of two π-bands at point $k = (2/3)(\pi/c)$. Carbon (*n*, 0) nanotubes, depending on parameter *n*, can be both semiconductors with a direct gap in the center of the Brillouin zone and semimetals when the top of the valence band and the bottom of the conduction band touch each other at $k = 0$. This is clearly reproduced by the LACW method. The results of calculations of the armchair tubes are used to correlate the minimum direct energy gaps E_{11} between the conduction and valence band singularities with the nanotube diameter and optical absorption spectra. Significant deviations from the equation $E_{11} \sim d^{-1}$ are observed. The ππ* gap energy increases monotonically with 1/*d*, whereas the σπ* gap width shows a minimum at $n = 10$. In the (3, 3) tube, the conduction band singularity coincides with the Fermi level resulting in a drastic increase of the density of states on this level.

We have calculated the electronic structure of $[M@C_{20}]_\infty$ nanotubes representing a (5, 5)-type carbon shell doped with 3*d* transition metal atoms M. These band structures are compared with the data for the pristine (5, 5) carbon tube and metallic chains. In the doped tubes, the Fermi level is intersected not only by the carbon π bands, but also by the partially filled metallic bonding bands. Dependences of the electronic structure of $[M@C_{20}]_\infty$ nanowires on composition are demonstrated by the curves of total and partial densities of states too. These curves indicate that the electronic states located at a distance up to 10 eV from the bottom of the valence band do not depend on the metal nature: they correspond to the roughly undisturbed carbon 2*s*-states. The metal exerts a relatively weak effect on the deep-seated carbon p_σ-states. The most sensitive to the metal nature is the region adjacent to the Fermi level where the C p_π-states mix with the metal 4*s*- and 3*d*-states. For the pristine carbon (5, 5) tube, the Fermi level is located in the vicinity of the depression in the curve of the p_π density of states. As a result, the density of state at the Fermi level for the carbon tube appears to be rather low. Intercalating the metal fills the corresponding depression by the valence states of the intercalant. In some systems ($[Ti@C_{20}]_\infty$, $[V@C_{20}]_\infty$, $[Cr@C_{20}]_\infty$, $[Mn@C_{20}]_\infty$), the Fermi level correspond to the peak of the density of states.

We calculated the pure and intercalated boron nitride nanotubes. A hollow armchair and zigzag BN nanotubes are dielectrics. The band structures and total densities of states of intercalated boron nitride nanotubes show that these systems are the conductors.

1. P. N. D'yachkov, O. M. Kepp, and A. V. Nikolaev, *Dokl. Chem. (Engl. Trans.)* **365**, 67-72, (1999); in *Science and Application of Nanotubes*, editors D. Tomanek and R. J. Enbody (Kluwer Academic / Plenum Publishers, NY, 2000), 77-82.
2. P. N. D'yachkov and D. V. Kirin, *Dokl. Chem. (Engl. Trans.)* **369**, 326, (1999); *Ital. Phys. Soc., Conf. Proc.*, **74**, 203–211 (2001).
3. Kirin, D.V., D'yachkov, P.N. (2001), *Dokl. Phys. Chem. (Engl. Trans.)* **380**, 217–223.
4. P. N. D'yachkov, H. Hermann, D.V. Kirin, *Appl. Phys. Lett.*, **81** (2002).