LF61: Low-dimensional strongly correlated electron systems, spin-Hall effect and nanoscale science and technology

S. Bellucci (Resp. Naz.), M. Benfatto, M. Cini (Ass.), L. Coderoni (Bors.), K. Hatada (Borsista PD), K. Hayakawa (Borsista PD), F. Micciulla (Ass. Ric.), C. Natoli (Ass.), F. Palumbo (Ass.), N. Pugno (Ass.), I. Sacco (Bors.), G. Stefanucci (Ass.)

 External collaborating Institutions:

IHEP-Protvino, Russia
Univ. Pavia, Italy
Belorus State Univ. Minsk,
Department of Physics, Yerevan State University, Armenia
Department of Physics, Univ. Roma Tor Vergata, Italy
Institute of Solid State Physics, University of Latvia, Kengaraga Str. 8, 1063 Riga, Latvia
Instituto de Ciencia de Materiales de Aragon, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain.
ICB, UMR 5209 Universite' de Bourgogne - CNRS, BP 47870, F-21078 Dijon, France
Institut de Physique de Rennes, UMR UR1-CNRS 6251, Campus de Beaulieu, Universite' de Rennes1, 35042 Rennes-cedex, France

Research Activity

Our theoretical study in collaboration with Riga, Latvia focused on the fundamental properties of various CNT-metal (Me), GNR-Me, and CNT-graphene interconnects. The cluster approach based on the multiple scattering theory as well as effective medium approximation were used to model the dispersion law, electronic density of states (DOS), and conductivity, etc. Multiple scattering problems were solved for nanostructures with radial (quantum dots) and axial (nanowires, nanotubes) symmetry. Interconnect capacitances and impedances have been evaluated in the GHz and THz regimes. Parametrical numerical simulations of conductivity were carried out for zig-zag (m,0), armchair (m,m), and chiral (m,n) CNTs, and the sensitivity of conductivity to the local electronic DOS in CNTs with local impurities (N and B atoms) was demonstrated. CNTs, CNT-Me, and GNR-Me based nanostructures are prospective nanosensor structures [1].

Cluster approach based on the multiple scattering theory formalism, realistic analytical and coherent potentials, as well as the effective medium approximation (EMA-CPA), can be effectively used for modeling of nano-sized systems. This allows us to calculate the dispersion law $E(k)$, the electronic density of states, the conductivity, etc. The multiple scattering problems are stated for radial (e.g., quantum dots) and axial (e.g., nanowires, nanotubes) symmetry approaches. Basic attention is paid now for applications on carbon nanotubes (CNTs) of various morphology which possess the unique physical properties in nanoelectronics, e.g., contacts of CNTs with other conducting elements of a nanocircuit which can be promising candidates for interconnects in a high-speed electronics. The main problems solving for resistance in nanotube junctions with metal particles appear due to the influence of chirality effects in the interconnects of single-wall (SW) and multi-wall (MW) CNTs with the fitting metals (Me = Ni, Cu, Ag, Pd, Pt, Au) for predefined CNT geometry. Using the model of 'effective bonds' developed in the framework of presented approach and Landauer theory, we can predict the resistivity

properties for both SW and MW CNT-Me interconnects. We have also developed the model of the inter-wall interaction inside the MW CNTs, which demonstrates the possible 'radial current' losses [2].

To predict a growth mechanism for carbon nanotubes (CNTs) upon a metal particle as synthesized in the porous membrane block then incorporated in the nanoelectronic device, we have performed a series of large-scale DFT-LCAO calculations using the CRYSTAL-06 code. Carbon adatoms can appear upon the densely-packed Ni(111) catalyst surface due to dissociation of hydrocarbon molecules (e.g., CH4) when applying the CVD method for the nanotube growth. We have started with adsorption properties of carbon atoms. Then, we have simulated the regular C/Ni(111) interface, where adatoms initially form a monolayer which can be disintegrated to nanoflakes gradually transforming into CNT embryos (in the form of semi-fullerenes) and, finally, into the capped CNTs (d C–C $\approx$ 1.42 Å) with either armchair or zigzag chirality. Periodicity of this system results in models of infinite arrays (bundles) of single-walled (SW) CNTs with a diameter 8.0–8.2 Å and the inter-tube distance 4.2–4.6 Å (depending on chirality). Analyzing the results of calculations on the CNT/Ni interconnect, we have observed a considerable transfer of the electronic charge from the metallic catalyst towards the nanotube (up to ~1.4 e per contacting C atom) accompanying by substantial redistribution of the electronic density, especially in the case of nanostructured Ni(111) containing nickel nanoclusters. The nanostructured morphology of metal substrate has been found to be the most effective for the growth of CNT bundles [3].

Major attention is paid now to applications of carbon nanotubes (CNTs) and graphene nanoribbons (GNRs) with various morphology which possess unique physical properties in nanoelectronics, e.g., contacts of CNTs or (GNRs) with other conducting elements of a nanocircuit, which can be promising candidates for interconnects in high-speed electronics. The main problems solving for resistance C-Me junctions with metal particles appear due to the influence of chirality effects in the interconnects of single-wall (SW) and multi-wall (MW) CNTs, single-layer (SL) and multi-layer (ML) GNRs with the fitting metals (Me = Ni, Cu, Ag, Pd, Pt, Au) for the predefined carbon system geometry. Using the models of 'liquid metal' and 'effective bonds' developed in the framework of the presented approach and Landauer theory, we can predict resistivity properties for the considered interconnects. We have also developed the model of the inter-wall interaction inside MW CNTs, which demonstrates possible 'radial current' losses. CNT- and GNR- Metal interconnects in FET-type nanodevices provide nanosensing possibilities for local physical (mechanical), chemical and biochemical influences of external medium. At the same time, due to high concentrations of dangling bonds CNT- and GNR-Metal interconnects as interfaces are also considered as electrically, magnetically and chemically sensitive elements for novel nanosensor devices [4].

Also, double-wall (DW) CNTs consisting of two coaxial single-wall (SW) constituents, possess mechanical, structural and electronic properties which are superior to SW CNTs. DW CNT is also the simplest model of multi-wall (MW) carbon nanotube. In our study, we have simulated DW NTs with not only commensurate (6, 6)@(11, 11) and (10, 0)@(19, 0) morphologies (analogously to those doublewall carbon nanotubes studied so far), but also incommensurate (6, 6)@(19, 0) and (10, 0)@(11, 11) ones, all described by asymmetric P1 rod group. Inter-shell distances in aforementioned nanotubes are changed from 3.37 to 3.54 Å, within the interval of DW CNT stability. Due to essential difference between the translation periods of SW CNTs with (n1, n1) and (n2, 0) chirality indices (their ratio is 1/√3), we have been able to use the first-principles DFT-LCAO method only for detailed calculations on the first two nanotube configurations mentioned above (using unit cell model), while the semi-empirical self-consistent-charge density-functional tight-binding (SCC-DFTB) method has been applied for calculations of all four DW NT configurations (in the framework of super-cell model

characterized by large translation length unit of incommensurate double-wall nanotube achieving 4.24 nm). Combining both methods for calculations on SW and DW CNTs, we have analyzed their electronic properties (e.g., band structure, density of states as well as electronic charge redistribution) [5].

The process of photon emission by a high-energy electron or positron moving in a bent single crystal with a constant curvature is considered. The relations for differential energy losses of particles and polarization of emitted photons are obtained. Corrections due to multiphoton production are found. The comparison of calculations with existing experimental data is carried out. The process of photoproduction of electron-positron pairs in a bent single crystal is also studied. The differential probabilities of the process taking into account the photon polarization are presented. Equations are obtained which determine the variation of the Stokes parameters of γ quanta, and their solutions are given [6].

The effects of long-range interactions in quantum transport are still largely unexplored, mainly due to the difficulty of devising efficient embedding schemes. In this work we present a substantial progress in the interacting resonant level model by reducing the problem to the solution of Kadanoff-Baym-like equations with a correlated embedding self-energy. The method allows us to deal with short- and long-range interactions and is applicable from the transient to the steady-state regime. Furthermore, memory effects are consistently incorporated and the results are not plagued by negative densities or nonconservation of the electric charge. We employ the method to calculate densities and currents with long-range interactions appropriate to low-dimensional leads, and show the occurrence of a jamming effect, which drastically reduces the screening time and suppresses the zero-bias conductance. None of these effects are captured by short-range model interactions [7].

We investigated the effects of the electron-electron interaction between a molecular junction and the metallic leads in time-dependent quantum transport. We showed that the molecule-lead interaction changes substantially the transient and steady-state transport properties. We first show that the mean-field Hartree-Fock (HF) approximation does not capture the polarization effects responsible for the renormalization of the molecular levels neither in nor out of equilibrium. Furthermore, due to the time-local nature of the HF self-energy, there exists a region in parameter space for which the system does not relax after the switch-on of a bias voltage. These and other artifacts of the HF approximation disappear when including correlations at the second-Born or GW levels. Both these approximations contain polarization diagrams, which correctly account for the screening of the charged molecule. We find that by changing the molecule-lead interaction, the ratio between the screening and relaxation time changes, an effect which must be properly taken into account in any realistic time-dependent simulation. Another important finding is that while in equilibrium the molecule-lead interaction is responsible for a reduction of the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap and for a substantial redistribution of the spectral weight between the main spectral peaks and the induced satellite spectrum, in the biased system it can have the opposite effect, i.e., it sharpens the spectral peaks and opens the HOMO-LUMO gap [8]

We presented a compact and simplified proof of a generalized Wick theorem to calculate the Green's function of bosonic and fermionic systems in an arbitrary initial state. It was shown that the decomposition of the noninteracting n-particle Green's function is equivalent to solving a boundary problem for the Martin-Schwinger hierarchy; for noncorrelated initial states, a one-line proof of the standard Wick theorem is given. Our result leads to new self-energy diagrams, and an elegant relation with those of the imaginary-time formalism is derived. The theorem is easy to use and can be combined

with any ground-state numerical technique to calculate time-dependent properties [9].

The possibility of finding multistability in the density and current of an interacting nanoscale junction coupled to semi-infinite leads was studied at various levels of approximation. The system is driven out of equilibrium by an external bias and the nonequilibrium properties are determined by real-time propagation using both time-dependent density functional theory (TDDFT) and many-body perturbation theory (MBPT). In TDDFT the exchange-correlation effects are described within a recently proposed adiabatic local density approximation (ALDA). In MBPT the electron-electron interaction is incorporated in a many-body self-energy which is then approximated at the Hartree-Fock (HF), second-Born, and GW level. Assuming the existence of a steady state and solving directly the steady-state equations we find multiple solutions in the HF approximation and within the ALDA. In these cases we investigate whether and how these solutions can be reached through time evolution and how to reversibly switch between them. We further show that for the same cases the inclusion of dynamical correlation effects suppresses bistability [10].

We showed that the energy functional of ensemble density functional theory (DFT) in systems with attractive interactions is a convex function of the fractional particle number N and is given by a series of straight lines joining a subset of ground-state energies. As a consequence the exchange-correlation (XC) potential is not discontinuous for all N. We highlight the importance of this exact result in the ensemble-DFT description of the negative-U Anderson model. In the atomic limit the discontinuity of the XC potential is missing for odd N while for finite hybridizations the discontinuity at even N is broadened. We demonstrate that the inclusion of these properties in any approximate XC potential is crucial to reproduce the characteristic signatures of the charge-Kondo effect in the conductance and charge susceptibility [11].

We proposed a new type of experiment to observe scissors modes in crystals. These experiments are based on the assumption that in systems in which the spin-orbit coupling is much larger than the crystal field, an applied magnetic field should rotate both spin and charge density profile (spin-orbit locking). Rare earth compounds should provide examples of spin-orbit locking, since their 4f electrons have standard values of the crystal field energies one order of magnitude smaller than the spin-orbit coupling. Such standard values, however, have been questioned by a recent experiment suggesting that crystal field and spin-orbit coupling should be comparable in rare earths. Our experiments should also help to settle this issue. [12]

We proposed a comparative and critical assessment of multiple scattering expansions. The so-called multiple scattering series expansion is much used in the description of spectroscopies at higher energies. However, it is plagued with convergence problems when operated at lower energies. We compare this method to related methods that can be found in the literature, relying both on finite and infinite expansions. After discussing the pros and cons of these methods, we establish a simple alternative to multiple scattering series expansion which has a wider and faster range of convergence [13].

We have accomplished Methodological advances in multiple scattering theory (MST) in both wave and Green's function version for the calculation of electronic ground and excited state properties of condensed matter systems with emphasis on core-level photoemission and absorption spectra. We have reviewd Full-Potential MST and have extended it to non-local potentials. Likewise we have reformulated Multichannel MST in terms of the multichannel density matrix whereby strong electron

correlation of atomic multiplet type can be accounted for in both ground and excited states [14].

Cu K-edge extended X-ray absorption fine structure (EXAFS) and Minuit X-ray absorption near-edge structure (MXAN) analyses were combined to evaluate the structure of the copper(II) imidazole complex ion in liquid aqueous solution. Both methods converged to the same square-pyramidal inner coordination sphere [Cu(Im)4Lax]2+ (Lax indeterminate) with four equatorial nitrogen atoms at EXAFS, 2.02 ± 0.01 Å, and MXAN, 1.99 ± 0.03 Å. A short-axial N/O scatterer (Lax) was found at 2.12 ± 0.02 Å (EXAFS) or 2.14 ± 0.06 Å (MXAN). A second but very weak axial Cu–N/O interaction was found at 2.9 ± 0.1 Å (EXAFS) or 3.0 ± 0.1 Å (MXAN). In the MXAN fits, only a square-pyramidal structural model successfully reproduced the doubled maximum of the rising K-edge X-ray absorption spectrum, specifically excluding an octahedral model. Both EXAFS and MXAN also found eight outlying oxygen scatterers at 4.2 ± 0.3 Å that contributed significant intensity over the entire spectral energy range. Two prominent rising K-edge shoulders at 8987.1 and 8990.5 eV were found to reflect multiple scattering from the 3.0 Å axial scatterer and the imidazole rings, respectively. In the MXAN fits, the imidazole rings took in-plane rotationally staggered positions about copper. The combined (EXAFS and MXAN) model for the unconstrained cupric imidazole complex ion in liquid aqueous solution is an axially elongated square-pyramidal core, with a weak nonbonded interaction at the second axial coordination position and a solvation shell of eight nearest-neighbor water molecules [15].

The environment of sulfur in dissolved aqueous L-cysteine has been examined using K-edge x-ray absorption spectroscopy (XAS), extended continuum multiple scattering (ECMS) theory, and density functional theory (DFT). For the first time, bound-state and continuum transitions representing the entire XAS spectrum of L-cysteine sulfur are accurately reproduced by theory. Sulfur K-edge absorption features at 2473.3 eV and 2474.2 eV represent transitions to LUMOs that are mixtures of S–C and S–H σ* orbitals significantly delocalized over the entire L-cysteine molecule. Continuum features at 2479, 2489, and 2530 eV were successfully reproduced using extended continuum theory. The full L-cysteine sulfur K-edge XAS spectrum could not be reproduced without addition of a water-sulfur hydrogen bond. Density functional theory analysis shows that although the Cys(H)S···H–OH hydrogen bond is weak (~2 kcal) the atomic charge on sulfur is significantly affected by this water. MXAN analysis of hydrogen-bonding structures for L-cysteine and water yielded a best fit model featuring a tandem of two water molecules, 2.9 Å and 5.8 Å from sulfur. The model included a Scys···H–Ow1H hydrogen-bond of 2.19 Å and of 2.16 Å for H2Ow1···H–Ow2H. One hydrogen-bonding water-sulfur interaction alone was insufficient to fully describe the continuum XAS spectrum. However, density functional theoretical results are convincing that the water-sulfur interaction is weak and should be only transient in water solution. The durable water-sulfur hydrogen bond in aqueous L-cysteine reported here therefore represents a break with theoretical studies indicating its absence. Reconciling the apparent disparity between theory and result remains the continuing challenge [16].

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