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Compound semiconductors and molecular complexes

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Introduction

Most properties of matter can be evaluated from its electronic structure, the quantum state and dynamics of the electrons involved. Therefore, finding reliable solutions to this many-body problem is of extreme importance. The density-functional theory (DFT) is the practical approach for large and complex systems like nanostructures or solids [1]. Furthermore, the challenging task of describing the excited states needs to be solved for the optical properties and effects of finite temperature. In this field, success in research intimately depends on sound theoretical modeling, and finally, available computational resources. Here is a brief presentation of our studies at the Institute of Physics at Tampere University of Technology concerning compound semiconductors and molecular complexes. The contributing researchers are acknowledged, below, and also found as authors of the original publications listed in the bibliography.

Compound semiconductor structures

Compound semiconductors offer a multitude of possibilities for designing new materials. The number of possible binary compounds is very large, already, let alone the combinations of more than two components. Furthermore, doping and use of layered and quantum confined structures allows one to tune the electrical and optical properties of semiconductor materials. We have studied GaInNAs-family compounds starting from GaAs, first doping with N [2]. Finding the basic material properties is always a good starting point for more sophisticated investigations. In Figure 17.1, the electronic band structure and density-of-states (DOS) of dilute nitride GaAsN is shown, emphasizing the impurity contribution.

Further studies relate to various roles and forms of N impurities in GaAs,

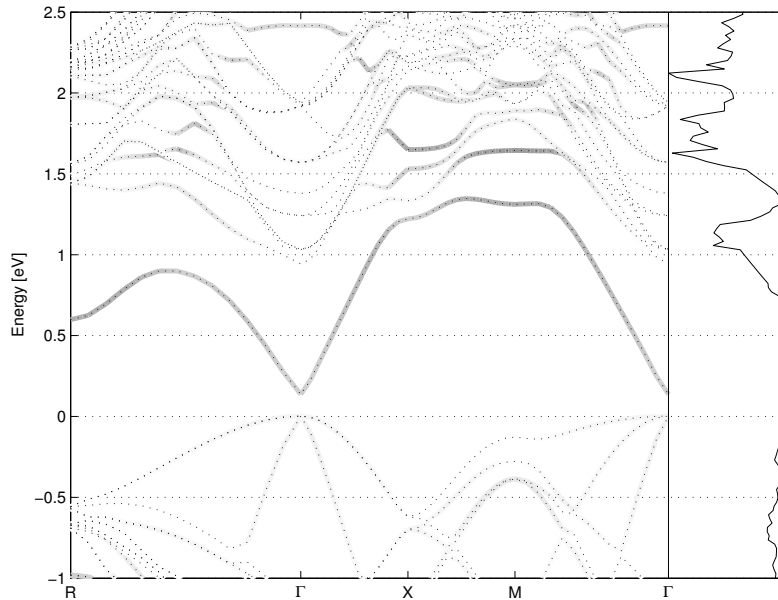


Figure 17.1: Calculated electronic band structure of N-doped GaAs in some high-symmetry directions. The impurity contribution is pointed out with line thickness. The semiconductor band gap problem appearing with conventional approximations to DFT is clearly demonstrated. On the right hand, the corresponding DOS is shown. (Courtesy of Hannu-Pekka Komsa)

impurity dynamics and GaAs/GaAsN interfaces. Surfaces, adsorbates, surface defects and other surface structures can be experimentally investigated by STM methods. Depth profiles can be obtained by perpendicularly cleaving the surface for STM imaging. This is called cross-sectional STM (X-STM). Because STM probes the contours of a constant local DOS (LDOS), heterointerfaces made of different types of atoms on the opposite sides are revealed by image contrast. Interpretation of such subtle effects calls for high-level electronic structure modeling. We have modeled surface electronic structures with so-called slab model, which is illustrated in Figure 17.2, where also two different type of electronic states are shown: surface resonance and bulk state [3].

The optical properties like refraction index, absorption coefficient, *etc.* can be evaluated from the complex dielectric function. This is the technique we have used in our studies of a wide-band-gap semiconductor SnO_2 , and the surface contribution to the optical parameters, in particular [4].

In the few-electron quantum-confined structures the many-body phenomena or correlations become pronounced. For studies of quantum dots we employ computationally demanding quantum Monte Carlo (QMC) technique. With the path-integral QMC we are able to examine the electronic structures even at a finite temperature [5].

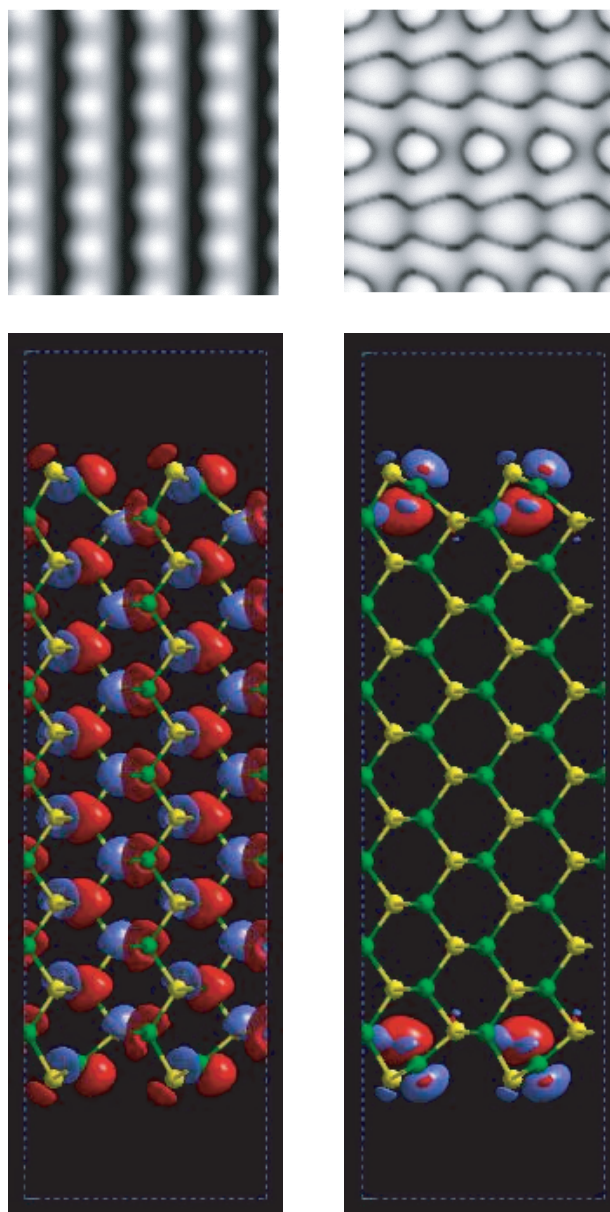


Figure 17.2: Supercell of the slab model for GaAs(110) surface. One of the bulk state and surface resonance wave functions are demonstrated on the left and right, respectively. The upper panels show their contributions to the STM images. (Courtesy of Ville Arpiainen, 2004)

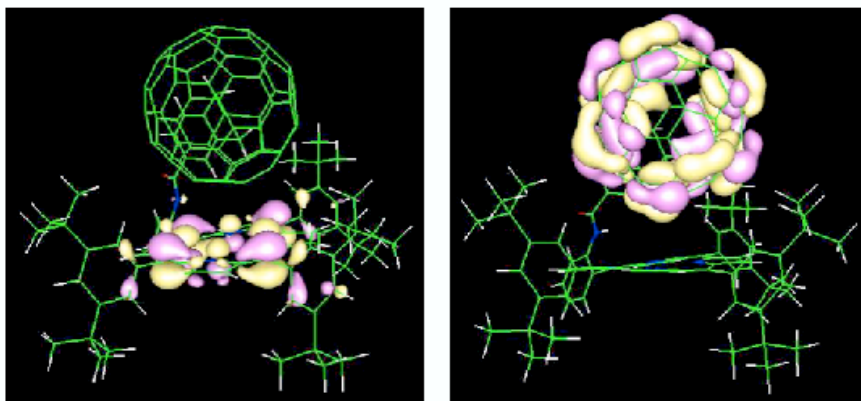


Figure 17.3: Porphyrin-fullerene dyad with the *HOMO* and *LUMO* orbital wave functions illustrated on the left and right, respectively. (Courtesy of Oana Cramariuc)

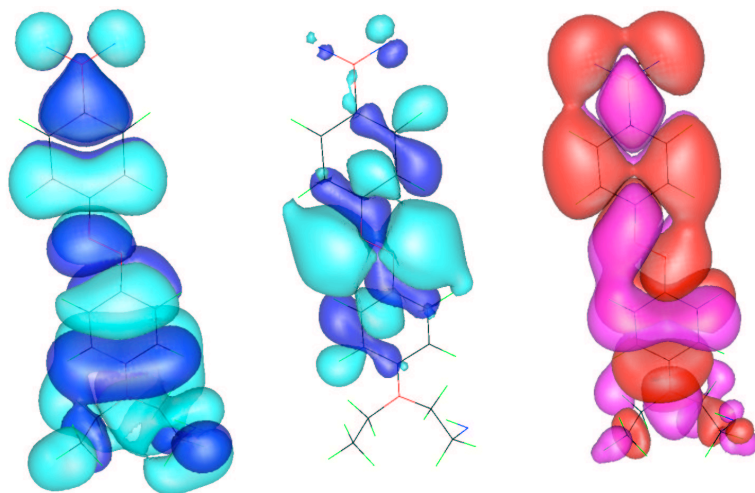


Figure 17.4: The *HOMO-1*, *HOMO*, and *LUMO* orbital wave functions of the *DR1* molecule. The occupied and unoccupied states are depicted by blue and red colors, respectively. (Courtesy of Jussi Ojanen, 2005)

Molecular complexes

Molecular nanoelectronics searches for a way to use molecules or molecular complexes as functional electronic devices. Individual molecules are orders of magnitude smaller than the smallest features conceivably attainable by conventional technologies. Thus, electronic devices constructed from molecules will be orders of magnitude smaller than their semiconductor-based counterparts, and furthermore, individual molecules are easily made identical. Heading for molecular optoelectronics, we have studied the near UV-vis region photo-absorption-induced electron transfer in porphyrin-fullerene dyads, Figure 17.3, in which porphyrins act as donors and fullerenes as acceptors [6]. The charge transfer results from the electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) located in porphyrin and fullerene, respectively. The long-living charge-separated excited states are applicable as light-emitting material, and the opposite mechanism, photon energy conversion to voltage, as a solar cell.

Delocalized electronic states of molecules typically result in nonlinear optical properties. In Figure 17.4 we show a series of orbital wave functions including the HOMO and LUMO of the disperse-red-1 (DR1) molecule. A closer inspection shows the different symmetry of HOMO and LUMO resulting in a negligible overlap and intensity of the corresponding lowest energy transition.

Computational tools and facilities

All the electronic and atomic structure calculations have been carried out by using state-of-the-art first-principles plane-wave pseudopotential (PWPP) or projected augmented wave (PAW) DFT or TDDFT methods. These include both academic and commercial software. Our own software development relates to QMC approach but advanced DFT software development has also been initiated recently¹.

Beyond our own desktop computers, we use the computing facilities at CSC. CSC provides computational facilities of all scales up to supercomputers, and furthermore, a large palette of commercial software that has proven to be indispensable for our research. In addition, starting from the beginning of 2005 we have a new national computer Grid (M-grid²) devoted to materials physics research. This enterprise, funded by the Academy of Finland, consists of ten sites of Linux clusters in Finland coupled to form a delocalized supercomputing facility.

Acknowledgements

The author acknowledges Jouko Nieminen, Eero Arola, Matti Mäki-Jaskari, Oana Cramariuc, Markku Leino, Hannu-Pekka Komsa, Ville Arpiainen, Jussi

¹<http://www.csc.fi/physics/mika/>

²<http://www.csc.fi/proj/mgrid/>

Ojanen and others, who have contributed to the research work at the Theoretical and Computational Materials Physics reviewed here.

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