Solids

This course is targeted to students who are interested or are starting to learn about the application of theoretical methods and techniques to the study of the physics and chemistry of the solid state. After two initial days where the fundamentals of theory of the treatment of the electronic structure of solids will be presented to the students, the remaining of the course will be devoted to the examination of specific and hot areas like characterization of chemical bonding in solids and relationship to macroscopic properties, calculation of thermoelectric parameters, structure and reactivity at solid surfaces, including layered systems and highly correlated oxides, and magnetic properties. The afternoons will be dedicated to practical hand-on tutorials using programs like (but not limited to) Quantum Espresso, Vasp, Vesta, jmol, Critic2g or SCALE-UP. Getting familiar with the different codes and their possibilities requires an adequate training that merges theory and practice in substantial amounts.

Standard methods in solid-state simulations allow for relatively large supercells containing up to 1000 atoms at zero temperature. However, predicting or interpreting many experimental results is still a great challenge due to finite temperature effects and defects like impurities, surfaces, grain boundaries, etc. For that reason, there is an on-going effort in the solid-state community to develop methods that can be applied to larger and larger systems. We will devote a theoretical session to discuss the factors that limit the application of first-principles simulations to these larger supercells and the kind of techniques that can be applied to overcome these problems. We will discuss the construction of Hamiltonians in localized basis sets and linear scaling techniques with a very brief incursion on the idea of model-Hamiltonians and QM/MM techniques. One practical session will be devoted to discussing these methods with applications on the calculation of optical properties in solids and the simulation of polarons in crystals so that the students get a more detailed look at how some of these complex topics are realized in specific applications.

Scientific content

From the theoretical side, the course briefly covers the basics of electronic structure methods in solids, with a focus on DFT, and provides some insight on perturbation theory to quickly move to applications. This includes an overview of bulk thermodynamical properties, the relationship between bonding and electronic structure in solids, phase transitions, temperature and pressure effects, magnetic and spectroscopic properties. Solid surfaces' structures (relaxation, rumpling and reconstruction), electronic properties, influence of structural vacancies and their relationships to chemical reactivity will be examined in two of the morning sessions. The course will cover the fundamentals and the practical use of a state-of-the-art codes for the calculation of the electronic structure of bulk solids, surfaces, and defects and impurities in solids. At the end of the course, the students will have acquired the basic knowledge on which Solid State Chemistry is founded. They will be able to apply this knowledge to understand and analyze more complex concepts and phenomena in the field. Finally, they will be able to perform computational simulations on periodic and semi-periodic systems choosing with critical thinking the one that best suits the nature of the system or phenomenon to be studied.

List of topics to the covered

- Summary of basic concepts. Space groups. Tensor quantities. Crystal strain. Bloch theorem. The symmetry of the wavefunction under periodic boundary conditions. Reciprocal space. Mean field solution of the electronic problem in solids and electron-correlation methods.

- Cluster and periodic models. Atomistic models. Kohn-Sham equations and DFT methodologies. Electronic structure calculations. Phonons and crystal searching.
- Thermodynamic properties: Static models. Equation of state of solids. Phase transitions.Mechanisms and kinetics of phase transitions. Thermal effects.
- Optical properties of Solids. Macroscopic Maxwell equations: conductivity and dielectric tensors, polarization, and currents. Microscopic interpretation. Simple models: metals and insulators. Multiband transitions. Examples. Hamiltonians for light-matter interaction. Time-dependent evolution of a periodic system under electric fields. Absorption and reflectivity.
- Multiscale methods. Current difficulties in solid-state calculations. Scaling in the construction of the Hamiltonian of different methods. Scaling in diagonalization.
- Construction of sparse Hamiltonian matrix. Linear scaling techniques. Metals, insulators, and the Fermi energy. Force fields in solid state. QM/MM and combination of force-fields and electronic structure codes. Applications: Excitons and polarons.
- Computational models in Surface Science. Structure of surfaces: Tasker's classification of ionic surfaces. Relaxation, rumpling, and reconstruction of surfaces. Surface energies. Surface defects: O vacancies in metal oxides. Adsorption at surfaces. Case studies: organic molecules and transition metal atoms at oxide surfaces. Reactivity at surfaces: organic molecules at simple surfaces. Role of point defects.
- Topologies of scalar fields in crystals. Electron density, electron localization function and reduced density gradient chemical functions. Chemical origin of compressibility. Chemical bonding reconstruction along a phase transition.
- Phonons and dispersion curves. Free energy. Quasi-harmonic approximation. Thermal properties: Heat capacity, Debye temperature, Gruneisen parameters and thermal expansion coefficient. Temperature-dependent mechanical and elastic properties. Anharmonicity and thermal transport.
- Spin Hamiltonians. Effective Hamiltonian theory. Magnetism in condensed matter. Spin waves for ferromagnets. Antiferromagnetic lattices. Electron transport. Quantum Chemical approach to solid state magnetism. Four center interactions in cuprates. Magnetic anisotropy, Double exchange and spin wave theory.

Practical work

Four practical sessions lasting for a total of 16 hours will be offered during the afternoons. The topics to be covered and the corresponding lecturers include: Electronic structure calculations (Cristina Díaz). Methods for the calculations of magnetic and optical properties and polarons. (Pablo García Fernández). Structure and reactivity at ionic surfaces. (Antonio M. Márquez). Topology of chemical functions. (Julia Contreras). The proposed problems can be solved on commodity PC-type computers in a reasonable amount of time within the scheduled time.

Teachers

Contreras García, Julia. Université Pierre et Marie Curie, Paris (Francia).

Díaz Blanco, Cristina. Universidad Complutense de Madrid (Spain).

García Fernández, Pablo. Universidad de Cantabria, Santander (Spain).

Márquez Cruz, Antonio M. Universidad de Sevilla (Spain).

Plata Ramos, José Javier. Universidad de Sevilla (Spain).

Ribas Ariño, Jordi. Universidad de Barcelona (Spain).