

## **Electronic and optical properties in density functional theory and beyond**

Density functional theory (DFT) is a formally exact theory, in which the total energy is a functional of the electronic density  $n(\mathbf{r})$ . In the Kohn-Sham theory, which is the most common realization of DFT, the electronic density is described in terms of mean-field “independent particle” Kohn-Sham orbitals residing in an effective one-particle potential determined by  $n(\mathbf{r})$ . Many-particle effects are accounted for in an effective manner through an exchange-correlation (xc) functional. Striking a good balance between accuracy and speed, successive developments of DFT has made the method the by far most widely used theoretical method to obtain atom-level insight and “hard numbers” on electronic, structural, and energetic properties of materials and chemical processes. DFT finds usage in condensed matter physics, chemistry, and increasingly in adjacent fields such as geology and biology.

DFT lends itself to studies of van der Waals bonded material at the microscopic level by using van-der Waals inclusive xc-functionals. For macroscopic systems beyond reach of standard DFT implementation (which is typically limited to around 1000 atoms) or in conceptual studies, an alternative is to generate dielectric functionals or polarizabilities of materials and molecules without relying on empirical experimental data and use these as input to Casimir-Lifschitz theory

In the final Friday lecture, I will introduce basic concepts of DFT with emphasis on electronic and dielectric properties in the Kohn-Sham formalism. Calculation of the dielectric functional in the independent particle approximation will be discussed in detail, followed by an overview of how effects such as local-field effects and two-particle ‘excitonic’ effects can be accounted for by going beyond DFT using many-particle perturbation theory.

*Active student participation in discussions is expected and highly encouraged in all my lectures.*

### **van der Waals density functional theory: Dispersion forces in density functional theory**

For a long time, lack of dispersion forces was a hallmark shortcoming of DFT, but this has been resolved during the last 15 years. In this early Saturday lecture, I will discuss the exchange-correlation functional of DFT in more detail and explain what physical effects can be described at different level of theory. I will next outline various approaches to include dispersion forces in DFT calculations. One of the most successful and robust methods for describing these forces in DFT is the Chalmers-Rutgers van der Waals density functional (vdW-DF). I will outline a derivation of the van der Waals density functional (vdW-DF) and connect it earlier developments such as the Anderson-Langreht-Lundqvist (ALL) functional. For the latest theoretical developments within vdW-DF, I refer to topics covered in my workshop talk.

### **van der Waals density functional theory: Applications**

In this lecture, I will provide several examples of how DFT using vdW-DF and related methods has provided insight into van der Waals binding at the nanoscale. In particular, many important systems are characterized by a competition between chemical bonding and non-covalent interactions, challenging the textbook notion that van der Waals forces are ‘weak’ and can be disregarded for covalently-bonded systems. I will also exemplify cases where different vdW-DF variants and related methods give qualitative contradicting predictions, highlighting why care much be taken when selecting the most appropriate vdW inclusive DFT method. Shortcomings of vdW-DF beyond typical binding separations will also be discussed, such as incorrect power asymptotic laws for certain systems and geometries.