"The Effective Potentials of Density Functional Theory: from Exact Properties to Accurate Approximations"

Special Theoretical and Computational Seminar

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Abstract:
Density functional theory (DFT) is the leading theoretical framework used to describe electronic structure of materials. The most common approach in DFT is that of Kohn and Sham: it describes a material, namely, a system of N interacting electrons, via a fictitious system of N non-inteacting electrons subject to an effective potential termed the Kohn-Sham (KS) potential. The KS potential – a central quantity DFT – is almost never known exactly. But we do know some of its properties: for example, it exhibits sharp, non-analytic steps, in various scenarios, such as dissociation, ionization, excitation and charge transfer. These sharp features are rarely modelled in common approximations.
In this talk I discuss the step structure of the KS potential, highlight the common origin of steps that appear in different situations and underscore the significance of steps, serving the bridge between the real, many-electron energy differences and the fictitious Kohn-Sham energies. I further show that the Pauli potential – a central quantity in orbital-free DFT (OF-DFT) and in the emerging exact electron factorization (EEF) method – exhibits steps, as well. Surprisingly, detailed analytic characterization of the Pauli steps opens the door to accurately approximate also the KS potential. I suggest ways to incorporate potential steps in new approximations to exchange and correlation in DFT.

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