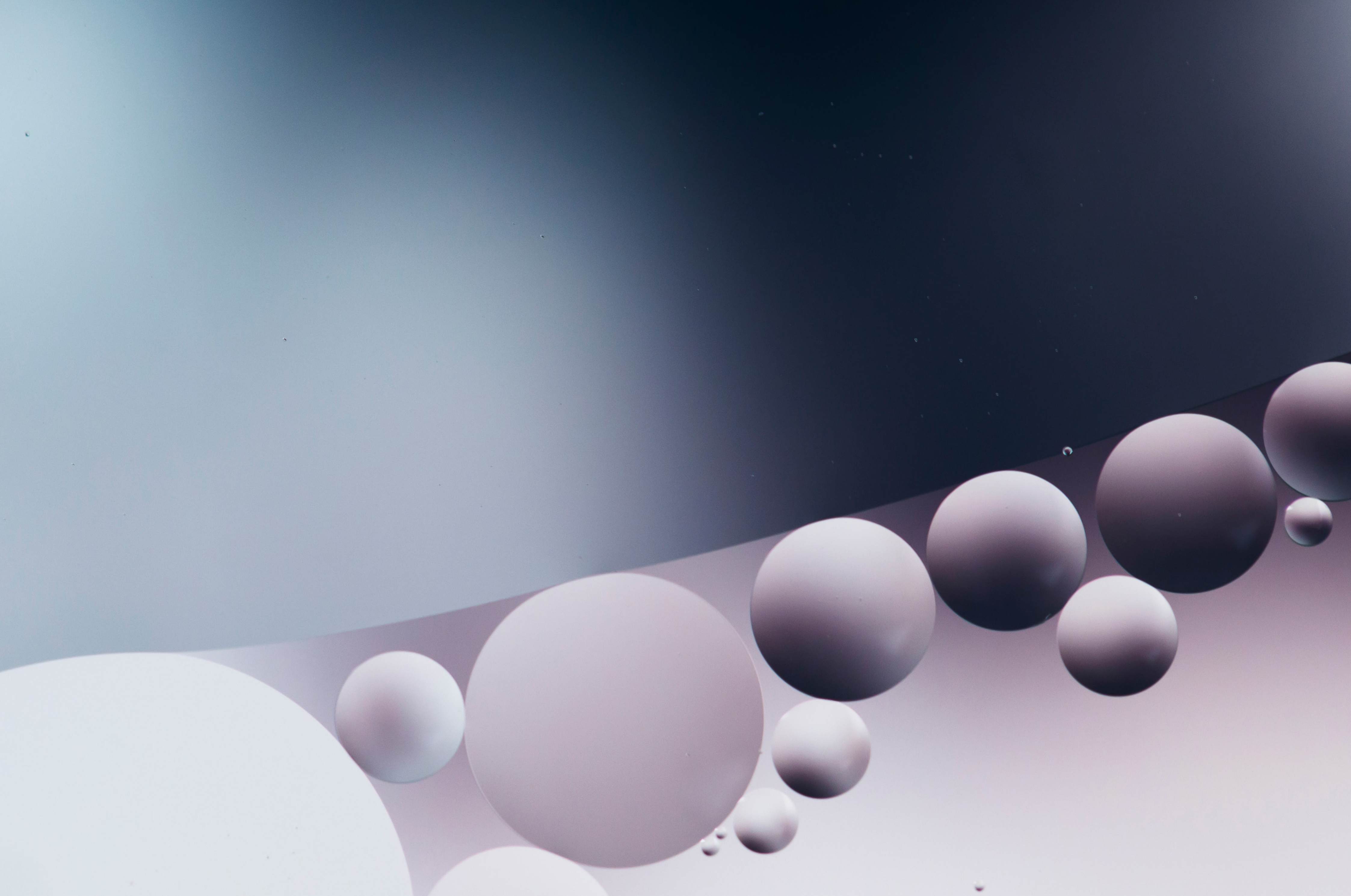

Università
Ca'Foscari
Venezia

**Dipartimento di
Scienze Molecolari
e Nanosistemi**

Orbital-optimized density functional calculations of challenging electronic excitations in molecules, molecules in solution, and solids

9 settembre 2024, ore 10.00
Aula Delta 2A, Scientific Campus, Mestre (Venice)
link zoom: **https://zoom.us/j/86879148120** passcode: seminar1

Gianluca Levi

Calculating electronic excitations in molecules and condensed-phase systems involved in energy-conversion processes poses significant challenges. The systems are often too big for accurate but computationally costly wave function methods, and the excitations typically involve significant rearrangements of the electron density, which is problematic for affordable time dependent density functional theory (TDDFT) calculations. Time-independent orbital-optimized density functional calculations, where excited states are obtained as saddle points on the electronic energy surface, offer a computationally efficient and accurate alternative. I will present new strategies for excited state orbital optimized calculations. In a first constrained optimization step, where the orbitals involved in the excitation are fixed, the saddle point order of the target excited state is estimated. Thereby, approximate second-order direct optimization algorithms, such as a generalized mode following approach, are used to converge on target saddle points. This novel method shows significant improvements in density functional calculations of charge transfer and Rydberg excited states of molecules, outperforming TDDFT. The method has also been applied in multiscale molecular dynamics simulations of photoexcited metal complexes in solution. Calculations of the long-debate excitations of the charged nitrogen-vacancy center in diamond yield results in close agreement with high-level many-body calculations.