Theoretical Spectroscopy (iMOS)

Module	Credits	Workload	Term	Frequency	Duration
9 RC	5 CP	150 h	2. Sem.	Each SuS	1 Semester
Courses			**Contact hours**	**Self-Study**	**Group size**
a) Lectures b) Exercises			a) 2 SWS b) 1 SWS	105 h	10 – 20 Students

Prerequisites

Undergraduate level knowledge in classical mechanics, statistical mechanics and time-independent non-relativistic quantum mechanics and advanced knowledge at the level of the Dynamics and Simulation M.Sc. course

Learning outcomes

Students understand and are able to explain theoretical approaches relying on time-dependent methods to compute observables which are obtained experimentally using spectroscopic, scattering, and diffraction techniques. They are able to assess the scope and limitations of such methods in the context of Solvation Science with a focus on (bio)molecular condensed phase systems, in particular aqueous solutions and soft matter.

Content

Review of standard molecular spectroscopy: Approximate decoupling of time-independent Schrödinger equation in terms of translational, rotational, vibrational and electronic contributions, ro-vibrational spectroscopy of diatomics based on rigid rotor/harmonic oscillator approximation, selection rules, vibronic effects in the Frank-Condon approximation, Frank-Condon principle applied to the solvation of chromophores, normal mode analysis of vibrations of polyatomic molecules

Time-dependence in quantum mechanics: Time-dependent Schrödinger equation and its wavepacket solutions, properties of free particle and Gaussian wavepackets, quantum/classical correspondence and Ehrenfest theorem, time-evolution operator formalism and Dyson equation, Schrödinger versus Heisenberg versus Dirac pictures of quantum dynamics, time-dependent variational principle (Dirac-Frenkel TDVP), linear TDVP, essentials of the time-dependent Hartree (TDH) method and its multiconfiguration (MCTDH) extension, Gaussian wavepacket propagation methods (Heller, Singer)

Time-dependent perturbation theory for spectroscopy: Formalism and applications to important schematic models, linear TDVP in Dirac picture, first- and second-order diagrams, virtual states and transitions, Fermi's Golden Rule

Molecular systems in the radiation field for spectroscopy: Transition probability, absorption cross section, dipole approximation, transition dipole, semiclassical approach to molecule-radiation field coupling, basics of the quantization of the radiation/electromagnetic field for spontaneous emission, multi-photon processes and non-linear spectroscopy, Raman scattering process, transformation of spectroscopy formulated in the static Schrödinger picture to the dynamic Heisenberg picture (Kubo-Gordon formalism to compute spectra), time-autocorrelation functions and spectral line shape function, time-domain versus frequency-domain spectroscopy

Neutron scattering and x-ray diffraction: van Hove formalism, first Born approximation, dynamic and static structure factor, scattering length and form factors, coherent and incoherent scattering, van Hove correlation function and the structural dynamics of liquids, pair correlation functions, radial distribution functions

Teaching methods

Lectures and exercises with problems for self-studying, Q&A and discussion sessions with presentations given by the participants, digital material provided via TheoChem Cloud.

Mode of assessment Written or oral end-of-semester exam and homework
Requirement for the award of credit points Passing the end-of-semester exam
Module applicability M.Sc. iMOS; M.Sc. Chemistry; M.Sc. Biochemistry (Focal Point Program "Biomolecular Chemistry")
Weight of the mark for the final score According to CP
Module coordinator and lecturer(s) D. Marx
Further information Module can be integrated CP-relevant in M.Sc. Biochemistry within the Focal Point Program "Biomolecular Chemistry"