CH-453

# Molecular quantum dynamics

Vanicek Jiri

| Cursus | Sem. | Type |
|---|---|---|
| Chemistry and Chemical Engineering | | Opt. |
| Chimiste | MA2, MA4 | Opt. |
| Computational science and Engineering | MA2, MA4 | Opt. |
| Computational science and engineering minor | E | Opt. |
| Minor in Quantum Science and Engineering | E | Opt. |
| Quantum Science and Engineering | MA2, MA4 | Opt. |

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| Language of teaching | English |
| Credits | 3 |
| Session | Summer |
| Semester | Spring |
| Exam | Oral |
| Workload | 90h |
| Weeks | 14 |
| **Hours** | **3 weekly** |
| Courses | 2 weekly |
| Exercises | 1 weekly |
| **Number of positions** | |

## Summary

The course covers several exact, approximate, and numerical methods to solve the time-dependent molecular Schrödinger equation, and applications including calculations of molecular electronic spectra. More advanced topics include introduction to the semiclassical methods and Feynman path integral.

## Content

1. Review of classical molecular dynamics.
Langrangian and Hamiltonian formalisms, phase space.
Classical molecular dynamics and thermodynamics in phase space.
2. Exact real-time quantum dynamics.
Time-dependent Schrödinger's equation. Born-Oppenheimer approximation and potential energy surfaces.
Time-correlation functions.
Methods of quantum propagation of wave functions.
Split operator method and the fast Fourier transform.
3. Approximate methods for quantum dynamics.
Sudden approximation.
Adiabatic approximation.
Time-dependant perturbation theory.
Fermi's Golden Rule.
Time-dependent Hartree method.
4. Semiclassical dynamics.
Old quantum theory and the WKB approximation.
Wigner function.
Van Vleck propagator.
Semiclassical initial value representation.
5. Quantum thermodynamics.
Feyman path integral approach
- interpreted as imaginary-time dynamics
- interpreted as classical thermodynamics of a polymer chain.
Path integral Monte Carlo method.
Path integral molecular dynamics.

## Learning Outcomes

By the end of the course, the student must be able to:

- Solve the time-dependent Schrödinger equation with a basis method.
- Derive and apply the sudden and adiabatic approximations.
- Derive the time-dependent perturbation theory and Fermi's Golden Rule.
- Apply the time-dependent perturbation theory and Fermi's Golden Rule to molecular transitions induced by

electromagnetic field.

• Expound the connections between the Newtonian, Lagrangian, and Hamiltonian approaches to classical mechanics.

• Expound how electronic spectra can be computed via the autocorrelation functions.

• Apply the Fourier and split-operator methods to solve the time-dependent Schrödinger equation numerically.

• Expound the connection between quantum dynamics and quantum thermodynamics and how it can be used to compute molecular quantum thermodynamic properties with the Feynman path integral.

## Assessment methods

Grade: 25% exercises during the semester; 75% oral exam

## Supervision

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| Office hours | Yes |
| Assistants | Yes |

## Resources

### Bibliography

• Quantum mechanics in chemistry / Schatz

• Introduction to quantum mechanics / Tannor

### Ressources en bibliothèque

• Quantum mechanics in chemistry / Schatz

• Introduction to quantum mechanics / Tannor

### Websites

• http://scgc.epfl.ch/telechargement_cours_chimie

### Moodle Link

• https://go.epfl.ch/CH-453