Projects - CH-452

AY 2025-2026

Project 1: Non-adiabatic dynamics using trajectories: Tully Surface Hopping and the Multiple Spawning approach

Introduction

The exact solution of the coupled channel equation for highly dimensional systems is currently out of reach due to the exponential scaling of available algorithms with the number of degrees of freedom. In contrast, algorithms for classical dynamics scale essentially linearly with the number of degrees of freedom. This motivates several attempts to derive, or intuit, approximate schemes for non-adiabatic dynamics based on the propagation of ensembles of classical (or classical-like) trajectories.

Tasks

This project entails studying the most popular non-adiabatic scheme, Tully surface hopping, and a more recent idea called multiple spawning. In particular:

1. Frame the discussion by deriving the coupled-channel equation in the so-called Born-Huang expansion.
2. Consider the Born-Oppenheimer limit of this equation.
3. Describe the Tully surface hopping scheme, and identify the key assumptions in it.
4. Describe the multiple spawning scheme, and identify the key assumptions in it.
5. Compare the properties of the two schemes: What can spawning do that surface hopping can't? What are the computational bottlenecks of the two methods?
6. Write a code implementing Tully surface hopping and use it to compute the populations on the two-level system included in the M-SOFT code provided in class.

References

1. Non-adiabatic dynamics based on trajectories. F. de Carvhalo, M. Bouduban, B. Courchod, and I. Tavernelli, *Entropy*, sections 1 to 2.1.3.
2. Molecular dynamics with electronic transitions. Tully, J.C., *Journal of Chemical Physics*, 93, 1061-1071 (1990).
3. Multi-electronic-state molecular dynamics: A wave function approach with applications. Martinez, T.J.; Ben-Nun, M.; Levine, R.D. *J. Phys. Chem.*, 100, 7884-7895 (1996).

Project 2: Non-adiabatic dynamics using trajectories: Ehrenfest dynamics and the Exact Factorization method

Introduction

The exact solution of the coupled channel equation for highly dimensional systems is currently out of reach due to the exponential scaling of available algorithms with the number of degrees of freedom. In contrast, algorithms for classical dynamics scale essentially linearly with the number of degrees of freedom. This motivates several attempts to derive, or intuit, approximate schemes for non-adiabatic dynamics based on the propagation of ensembles of classical (or classical-like) trajectories.

Tasks

This project entails studying a common mean-field method to do so, Ehrenfest, and a recent promising development based on a similar starting idea, the exact factorization scheme. In particular:

1. Frame the discussion by deriving the coupled-channel equation in the so-called Born-Huang expansion.
2. Consider the Born-Oppenheimer limit of this equation.
3. Describe Ehrenfest dynamics, and identify the key assumptions in it.
4. Describe the exact factorization method, and identify the key assumptions in it.
5. Compare the properties of the two schemes.
6. Write a code implementing Ehrenfest dynamics and use it to compute the populations on the two-level system included in the M-SOFT code provided in class.

References

1. Non-adiabatic dynamics based on trajectories. F. de Carvhalo, M. Bouduban, B. Courchod, and I. Tavernelli, *Entropy*, sections 1, 2, 2.1, 2.2, 2.2.1, 2.2.2.
2. Exact Factorization of the Time-Dependent Electron-Nuclear Wave Function. Abedi, A.; Maitra, N.; Gross, E. *Phys. Rev. Lett.*, 2010, 105, 123002.

Project 3: Quantum dynamics using Wigner's formulation

0.1 Introduction

In 1932, E. Wigner introduced a formulation of quantum mechanics that highlighted interesting formal analogies with classical mechanics, both in the expression of expectation values of operators on quantum states and in the form of the time evolution equation for the state. This formalism is today at the root of many approximate methods to solve quantum dynamics.

Tasks

This project entails:

1. Understanding the definition of the Wigner transform of a state and of simple operators (position, momentum, Hamiltonian).
2. Exploring the properties of the Wigner formalism, in particular with respect to quantum expectation values.
3. Using the formalism to study the quantum harmonic oscillator.
4. Deriving the time-evolution for the Wigner transform of the state (this is the counterpart of the time-dependent Schrödinger equation in this formulation of quantum mechanics).
5. Analyzing the classical limit of the evolution.
6. Outlining an algorithm to solve the evolution and obtain the propagated state in the classical limit. How can we go beyond this approximation?
7. (Optional) Writing a code to compute the Wigner representation of a pure and a mixed state for a harmonic oscillator.

References

1. Wigner functions and Weyl transforms for pedestrians. W. B. Case, *American Journal of Physics*, vol. 76, 937-946 (2008).

Project 4: Semi-classical Born-Oppenheimer dynamics

0.2 Introduction

The exact solution of the time-dependent Schrödinger equation for highly dimensional systems is currently out of reach due to the exponential scaling of available algorithms with the number of degrees of freedom. In contrast, algorithms for classical dynamics scale essentially linearly with the number of degrees of freedom. This motivates several attempts to derive approximate dynamics schemes based on the propagation of ensembles of classical (or classical-like) trajectories.

Tasks

This project entails studying one of the most popular approaches, semi-classical dynamics, which is based on the path integral representation of the quantum propagator. In particular:

1. Frame the discussion by writing the path integral expression for the quantum propagator and the time-evolved wave-function.
2. Consider a stationary phase approximation of the time-evolved wave-function. Show that the stationary paths are classical trajectories specified in terms of boundary conditions. Show that the integral involving the second order variations of the phase can be done analytically.
3. Clarify the relation between the stationary phase interpretation and the classical limit, and interpret the result of the integral on the second order variations.
4. Determine the evolution equation of the function resulting from the integral on the second order variations.
5. Define an algorithm, based on the propagation of classical (or classical-like) trajectories, to propagate the wave-function.
6. What are the main limitations of this algorithm?
7. Show that, when computing averages over the state (consider for simplicity the average of the position operator), it is possible to change variables and identify the stationary paths as classical trajectories identified by initial (not boundary) conditions, and discuss the corresponding algorithm.

References

1. Introduction to quantum mechanics: A time-dependent perspective. D. J. Tannor, University Science Books , Chap. 10.

Project 5: Methods for adiabatic dynamics

Introduction

The fundamental assumption underlying most first-principle (ab initio) calculations performed today is the Born-Oppenheimer approximation. Within this approximation, the difference in mass between nuclei and electrons is such that complete time-scale separation of the motions occurs. The energy of the interacting system depends on both sets of degrees of freedom but, due to their much faster motion, for every nuclear configuration, the electrons "have time" to relax to an energy minimum. The Born-Oppenheimer evolution then couples a nuclear time-step, typically performed via classical mechanics, with the minimization of the energy for the electronic degrees of freedom.

Methods for first-principle dynamics then differ in two main ingredients: the electronic structure method employed to compute the electronic energy functional and the minimization method to enforce the Born-Oppenheimer minimum condition.

Tasks

In this project, we assume that the electronic structure method (e.g., density functional theory) is given and focus on understanding and comparing different methods for the energy minimization with respect to the electronic degrees of freedom. In particular:

1. Identify the approximations to move from the general coupled-channel dynamics to first-principle molecular dynamics with classical evolution of the nuclear degrees of freedom.
2. Describe the algorithm for a single time-step in the MD, detailing the conceptual steps for the calculation of the force acting on the nuclear degrees of freedom.
3. Understand and describe the conjugate gradient method for minimization of the energy with respect to the electronic degrees of freedom.
4. Understand and describe the Car-Parrinello approach for the dynamics.
5. Compare conjugate gradient and Car-Parrinello dynamics.
6. Recently, a new approach – called Mass-Zero constraint dynamics (MaZe) – has been proposed to propagate adiabatically separated systems. Derive the evolution equations in MaZe.
7. Compare the properties of MaZe with Car-Parrinello and conjugate gradient dynamics.
8. Would it be possible to go beyond classical evolution for the nuclear degrees of freedom? Consider a one-dimensional nuclear system and describe how to adapt the SOFT algorithm to first-principle molecular dynamics.

References

1. Ab initio molecular dynamics: Basic theory and advanced methods. D. Marx, J. Hutter, Cambridge University Press, Chap. 2.3, 2.4, 2.5, 2.6.

2. Adiabatic motion and statistical mechanics via mass-zero constrained dynamics. S. Bonella, A. Coretti, R. Vuilleumier, G. Ciccotti, *Physical Chemistry Chemical Physics*, 2020, 22, 10775.

Project 6. Path integral simulation of H_2O-H_2O interaction

Programs used: CP2K 3.0
VMD Theoretical topic: Path-Integral

Introduction

In molecular dynamic, the forces of the system are computed by using quantum calculations (Born-Oppenheimer or generally Ab Initio MD) or a parametrized force field (classical MD). In both cases however the hydrogen's nucleus is treated as a classical particle and this is a question- able assumption. Path integral theory allows to model the quantum behaviour of the nucleus as multiple replicas of the same atom connected by an harmonic potential ("Ring Polymer") with a value quantified by the theory. This model applied to water molecules is able to improve the simulation and the understanding of experimental observations.

Tasks

The scope of the project is to model two interacting molecules of water using the standard method and the path integral method and compare the different statistical characteristics of the H bond formed. CP2K is a versatile program able to perform both AIMD and MD: a reactive force field (no harmonic bonds between atoms) is suggested to start the study (because of the speed of analytically computed forces), then a DFT method can be chose to compute the forces Ab Initio. Average properties can be computed using VMD or writing simple programs.

References

1. CP2K tutorial on AIMD
2. CP2K manual on Path Integral
3. Reactive force field: Pinilla et al., Ab initio parameterization of an all-atom polarizable and dissociable force field for water, J. Ch. Ph., 2012
4. Tuckerman Statistical Mechanics: Theory and Molecular Simulations, Chapter 12

Project 7. Hartree-Fock Implementation

Programming Language: Preferred Programming Language (e.g. Python, Mathematica, etc.).
Theoretical Topics: Hartree-Fock, SCF, variational principle

Introduction

Hartree–Fock (HF) theory provides the starting point for many ab initio quantum chemistry methods. It approximates the many-electron wavefunction as a single Slater determinant, leading to a set of self-consistent equations for the molecular orbitals.

In *Modern Quantum Chemistry* by Szabo and Ostlund, a 12-step algorithm for restricted HF is outlined and illustrated with a two-electron example (HeH^+ in a minimal basis). This example forms the basis for a compact implementation which is the goal of this project.

Tasks

1. Understand the theory: This includes understanding the limitations of HF theory and the concept of minimal basis set.
2. Understand the algorithm: By writing a pseudocode, mapping each step to objects in code, and producing a flowchart.
3. Reproduce the HF cycle for the HeH^+ molecule in your preferred programming language and compare your results with the values found in the literature.
4. Explore extensions of the program: Basis sets size and type, additional molecules, etc.
5. Extend to (at least one) different system(s): Use this program as a base to perform an HF calculation on a different simple system. You should be able to explain how this is done in a theoretical, algorithmic, and computational way.
6. (Optional) The Configuration Interaction (CI) method can be seen as an extension of HF. Can you extend your HF program to perform a simple CI computation? You can start by understanding the main differences from a theoretical perspective, then in the algorithm and if you feel confident, in the code!

References

- Szabo, A., & Ostlund, N. S. Modern *Quantum Chemistry: Introduction to Advanced Electronic Structure Theory.* Dover, 1996.
- Piela, Lucjan. *Ideas of Quantum Chemistry.* Elsevier, 2007.