ETH Zürich: Departement Informationstechnologie und Elektrotechnik

COMPENDIUM EXERCITATIONUM

Molecular and Materials Modelling: FS 2023

Wednesday 30 May 2023

Raymond Amador, Daniele Passerone, Carlo Pignedoli
ramador@ethz.ch

0 Preface

This document represents my response to the behest of a few students, that a summarising document be drawn up in preparation for the upcoming oral exams for the course *Molecular and Materials Modelling* offered at the ETH Zürich during the FS 2023. Before we begin, a few words of caution:

- the current document is not — and can not — be a substitute for the body of literature, Powerpoint slides, and Jupyter notebooks, which have been accrued over the course of the semester;
- rather, the current document should merely be used as a sort of *Sammelstelle*, which could be useful to pull together overarching ideas and themes from the lectures and exercises.
- this document is **not** comprehensive — and in particular, while covering topics from both the lectures and the exercises, should not be used as the sole learning material.

All this being said, if you know, and can do, most/all of the things in this outline, you are also probably quite well prepared for the lectures portion of the oral exam :D.

0.1 Interaction with the terminal

The following commands (as well as any respective flags and options) should be quite familiar to you by now:

- standard navigation: `pwd`, `mv`, `cd`, `cp`, `ls`, `rm`
- text manipulation and extraction: `grep`, `awk`. See for example the application in Exercise 8, Assignment 3:

```
$ grep <string expression for total energy> |
tail <flags to extract only the last line> | awk '{print $3}'
```

1 Exercise 1: determination of lattice constants via equations of state and a general second-degree polynomial fit

- the Atomistic Simulation Environment (ASE)
- equations of state: ideal gas, van der Waals gas, virial expansion, Burch-Murnaghan

2 Exercise 2: simulation of the 2D Ising Model

- description and implementation of Ising model
- basics of Monte-Carlo simulations
- phenomenology near/at critical temperature
- see self-check questions at end of scripts

3 Exercise 3: Optimization of Lennard-Jones clusters

- form and appearance of the Lennard-Jones potential: be able to identify the short- vs. long-range interaction terms in the potential and explain their physical meaning thereto
- general meaning of an energy landscape
- geometry optimizations: why are they necessary?
- (Steinhardt) order parameters: what are they and what are they used for; what functions are they defined in terms of (answer: the spherical harmonics). **Please don't memorize any formulae here...**

4 Exercises 4 and 5: Band Theory of Crystals I and II

- recognise and identify bandstructure plots: k-points, direct vs. indirect bandgap, energy scale, etc.
- lattices and bases: direct (real) space and reciprocal space
- lattice vectors: direct (real) space and reciprocal space; Brillouin zone
- importance of symmetry operations
- Bohr model vs. Sommerfeld model of the electron
- planewave diffraction, Bragg's law
- Bloch's theorem
- Born von Karman boundary conditions
- see self-check questions at end of scripts

5 Exercise 6: the formation of molecular oxygen using molecular orbital theory

- from Schrödinger to Hartree-Fock: variational principle; Born-Oppenheimer approximation; secular equation
- Hartree-Fock approximation: formulation in terms of Slater determinants; direct and exchange integrals; problems and limitations
- molecular orbital theory: bonding vs. antibonding orbitals; Aufbau principle; Hund's rules; Pauli exclusion
- triplet vs. singlet oxygen: which is the ground state of molecular oxygen and why?
- Hückel theory
- explain the paramagnetism of molecular oxygen
- fermionic character of electrons
- (basics of) basis sets: what are they, what are they used for, and why?
- summary of exercise: show the paramagnetism of molecular oxygen

6 Exercise 7: the dehydration of ethanol

- Hartree-Fock vs. density-functional theory
- Hohenberg-Kohn theorems
- practical solution and implementation: Kohn-Sham equations; single particle formulation, etc.
- exchange-correlation energy: differences between LDA, GGA, meta-GGA, hybrids
- basis sets; construction and solution of Kohn-Sham matrix
- self consistency
- summary of exercise: examine reaction energetics using different classes — GGA vs. hybrid — of xc-functionals and reproduce published results

7 Exercise 8: hydrocarbons on platinum: functional-sensitive adsorption energies

- Basis set superposition error; counterpoise correction
- modifying and solving the secular equation: exact diagonalization with Cholesky decomposition vs. pseudo-diagonalization; orbital transofrmation; purification methods; formulation and advantages and disadvantages of each
- procedure for calculation of an adsorption energy
- influence and implementation of van der Waals interactions

- summary of exercise: investigate influence of adsorption energy of three diffferent hydrocarbons on the Pt(111) surface using different xc-functionals with van der Waals corrections; reproduced published results

8 Exercise 9: molecular dynamics of Lennard-Jones clusters

- statistical mechanical ensembles: microcanonical, canonical, grand canonical, isothermal-isobaric; thermodynamic variables of each
- obtaining expectation values from trajectories
- Hamilton's principle; Hamilton's equations
- time integration algorithms, *especially* Verlet algorithm; problems and limitations, especially regarding stability; energy drift
- predictor-corrector algorithms
- periodic boundary conditions in simulation
- radial distribution function: its features and derived quantities thereof (as implemented in the exercise)
- summary of exercise: use classical molecular dynamics to obtain the $g(r)$, from which we calculate thermodynamic quantities

9 Exercises 10 and 11: Data and dimensionality reduction

- creation of trajectories; representations of data
- selection of landmarks
- dimensionality reduction: PCA, MDS
- SOAP: basic concepts
- differences between "random sampling", "farthest point sampling", "well tempered FPS"
- explain "dimensionality reduction", "data reduction"; give an example
- see self-check questions at end of script

10 Exercise 12: Replica exchange for Lennard-Jones clusters

- thermostats: what are they and why are they used (within the scope of MD of course...)
- temperature rescaling and different types of thermostats; pros and cons of each
- dispersion interactions: properties

- summary: using parallel tempering (ie replica exchange) to obtain statistical averages, we reproduce thermodynamic quantities of interest — namely the heat capacity, its derivative, and the Q_4 order parameter — of the 38atom Lennard Jones cluster; reproduced published results

11 Exercise 13: Nudged elastic band and free energy calculations

- potential energy surface:locating transition states, locating extrema
- the nudged elastic band: different flavours (original, climbing image, tangent); idea, setup, and problems
- free energy vs. total energy; differences in free energy, physical meaning thereof
- sampling the free energy surface: umbrella sampling; constrained molecular dynamics; collective variables; choosing collective variables
- metadynamics: basic principles
- machine learning potentials: basic concepts, structure, philosophy