

1. Molecular Dynamics

In this problem you will develop an approach for evaluating the vibrational dynamics of molecules that treats nuclei as classical particles which move according to the Newtonian equations of motion (EOM), $F = ma$. In this expression, m is the particle mass, $a = \frac{d^2R}{dt^2}$ (the acceleration) the second derivative of the particle positions R with respect to time t , and $F = -\nabla_R V(R)$ is the conservative force exerted on the particle, given by the negative gradient of the potential, $V(R)$. The EOM is a second order ordinary differential equation in time and can be integrated to solve for the time evolution of the classical particle's position (and velocity).

In this assignment (**Part I**) you will derive and implement the working equations for one of the most commonly used methods for numerically integrating the classical EOM (the “velocity Verlet” algorithm) and analyze the error associated with the method. In **Part II** of this exercise you will be using the method you derive here along with an *ab initio* potential energy surface (PES) from Gaussian to perform molecular dynamics for the HCl molecule.

(a) Derive the working equations for the velocity Verlet algorithm (**Must show all work for the credit**)

- i. Express the classical EOM, a second-order differential equation, as a system of two-coupled first-order differential equations. This can be done by identifying the first time derivative of the position, $\dot{R}(t)$ (where differentiation with respect to time is indicated with over-dots in the following convention: $\dot{x} = \frac{dx}{dt}$, $\ddot{x} = \frac{d^2x}{dt^2} \dots$) with the velocity $v(t)$, i.e. $v(t) = \dot{R}(t)$
- ii. Write out the Taylor series for the position, $R(t + \Delta t)$, and the velocity, $v(t + \Delta t)$, expanded about $R(t)$ and $v(t)$. Truncate both at the third term in the series and account for the leading error term using the “Big O” notation, i.e. $\mathcal{O}(\Delta t^x)$, where x would be the exponent for the Δt in the next term in the Taylor series after truncation.
- iii. Here is the trick to completing the derivation: Taylor expand the time derivative of the velocity, $\dot{v}(t + \Delta t)$, about $\dot{v}(t)$ to first order in Δt . Solve for $\ddot{v}(t)$ and substitute this expression in for the corresponding term in your Taylor series expansion of $v(t + \Delta t)$. Finally, use the equation of motion to get the resulting expressions for $R(t + \Delta t)$ and $v(t + \Delta t)$ into the following form (but including the Big O terms showing the estimated error):

$$R(t + \Delta t) = R(t) + \Delta t v(t) + \frac{\Delta t^2}{2m} F(R(t)) \quad (1)$$

$$v(t + \Delta t) = v(t) + \frac{\Delta t}{2m} (F(R(t + \Delta t)) + F(R(t))) \quad (2)$$

- iv. To what power of the “time-step”, Δt , is the leading error term for this algorithm proportional to?

- v. Run the python molecular dynamics script for the harmonic oscillator. Print the total, kinetic and potential energies for each point of the simulation. If the integration is performed exactly the total energy should be conserved during the simulation, with oscillating kinetic and potential energies. Demonstrate the change in energy conservation with changing Δt .
 - vi. Implement the velocity Verlet algorithm in place of the “euler” function in the python molecular dynamics script. Demonstrate the change in energy conservation between the two integration schemes.
- (b) calculate the electronic energy as a function of bond length for HCl, and fit a Morse potential to the resulting *ab initio* surface.
- i. Perform a “Rigid Scan” of the H-Cl distance using **spin unrestricted** DFT with **B3LYP** functional and a **6-311g** basis set. Start from a H-Cl distance of 0.8Å and do 36 steps of 0.1Å each. At the bottom of the .log file for this Gaussian job you will find a section headed with the string “Summary of the potential surface scan”. This section collects the PES information in units of Hartree for the energies and Å for the scan coordinates. **The MD code requires consistent use of atomic units, so convert the bond-lengths to Bohr.**
 - ii. In your favourite numerical analysis software package (i.e. Python, Mathematica, Gnuplot, etc), determine the best (least-squares) fit of a Morse potential ($V(R) = D_e(1 - e^{-a(R-R_e)})^2 + c$) to the PES from your scan. Here, R is the bond distance, R_e is the equilibrium bond distance, D_e is the dissociation energy, c accounts for the arbitrary zero of potential energy, and a is a curvature parameter that will be determined from your least squares fit. Plot your PES scan data points and the resulting fitted function on the same axis. Report the functional form of your fitted Morse potential (including the parameters determined from your fitting procedure). You will use this potential energy surface in **Part II** of the assignment.
- (c) Unit Analysis: The potential that drives the nuclear dynamics in our python program is supplied in the atomic unit of energy (i.e. Hartree, E_H). This directly determines the units for our time step through the reciprocal relationship between energy and time. use the facts that energies carry the dimension of $\text{mass} \times \text{length}^2 \times \text{time}^{-2}$, and that the atomic unit of length and mass are the Bohr radius and the electron rest mass respectively, to derive the conversion factor from atomic units of time to seconds. What is the period of a typical C-H stretch (assume a frequency of 3000 cm^{-1}) expressed in atomic units of time?

2. Molecular Dynamics, Part II

Run the molecular dynamics program that you’ve modified to perform the velocity Verlet integration with your fitted HCl Morse potential from **Part I** in place of the default harmonic potential (and the corresponding acceleration). This will require you to differentiate (by hand) the fitted Morse potential, and to modify some portions of the python program (the potential, acceleration, and a reduced mass). Generate an MD trajectory started with zero initial velocity and an initial bond length stretched

- by 5% relative to the equilibrium geometry. This initial condition corresponds to a ‘classical turning point’ for the diatomic’s sole vibrational mode. Perform 100,000 velocity Verlet steps with 10.0 a.u. time step (**be sure to change the reduced mass to that of HCl**). Include a plot of the energy as a function of time, and the vibrational spectrum generated at the end of this simulation.
3. Perform a standard frequency calculation for the HCl molecule (starting from the optimized geometry) using the same level of theory that you used for the PES scan in **Part I**. Compare the H-Cl stretching frequency from the frequency calculation to the frequency peak in your vibrational power spectrum.
 - (a) Does the vibrational frequency exactly match that from the MD? To what do you attribute any differences you may see between the two spectra?