

Computation of vibrational frequencies for N2 and O2 molecules

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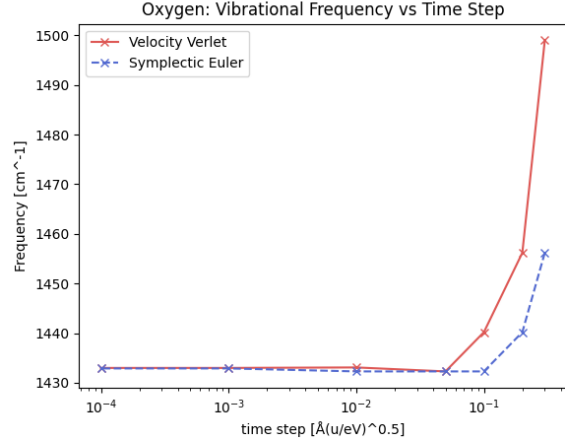
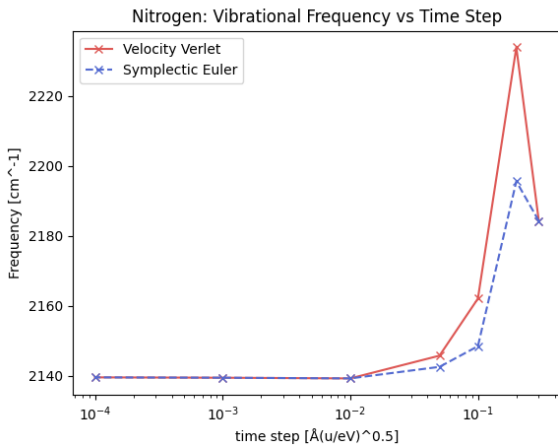
Computational Experiment

This computational experiment aims to calculate the vibrational frequencies of nitrogen and oxygen molecules. This is done by simulating their atoms interacting via a Morse potential for ~ 200 fs with the use of a time integrator (either Symplectic Euler or Velocity Verlet). Due to the parameters used for the Morse potential, the units of time for the computation are $\text{\AA}\sqrt{\frac{u}{\text{eV}}} \sim 10.18$ fs. Unless otherwise stated, all times will be given in these units. Hence, the calculated vibrational frequency is then converted to the more traditional units for spectroscopy of cm^{-1} . Due to conservation of energy, the fluctuations of total energy throughout the simulation can then be used as a measure of the accuracy of the simulation where the less deviation from the starting energy the better. Both this measure and a comparison to the most accurate frequency calculated (using the smallest time step) can then be used to quantify the accuracy of the simulation with a given time step.

Results

The total simulation time for all data was fixed at 20 ($20\text{\AA}\sqrt{\frac{u}{\text{eV}}} \sim 204$ fs). The simulations logged the separation-time data as well as (total energy)-time data. The separation-time data is then fed into a program that calculates its vibrational period using `scipy.signal.find_peaks`, which takes the times of the first and last peaks and divides their difference by the number of periods in between. The units are then converted to cm^{-1} .

Pure Vibration



Where the used time steps were¹:

0.5*, 0.4*, 0.3, 0.2, 0.1, 0.05, 0.01, 0.001, 0.0001

A caveat in the used method of finding frequencies is that the algorithm might still find a vibrational period even if there is no vibrational motion. While the frequency finder program always threw an error when this was the case in the simulations (namely for 0.4 and 0.5, in the case of both integrators) it is theoretically possible that the separation has one small peak before increasing forever, resulting in a calculated frequency based on the simulation time. This occurrence can be avoided by paying attention to the energy deviation as later explained.

Both time integrators quickly converge for time steps smaller than 0.1. The most accurate results give: 2140cm^{-1} for Nitrogen and 1433 cm^{-1} for Oxygen.

The largest time steps (to 3dp) that produce a relative frequency error (with respect to the most accurate simulation) under 0.5% are:

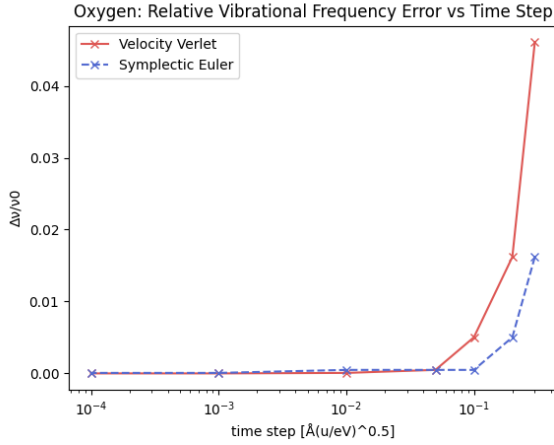
	Nitrogen	Oxygen
Symplectic Euler	0.100	0.117
Velocity Verlet	0.065	0.099

These results were given by simulating the particles with an initial time step of 0.05 and increasing by 0.001 until a simulation gave an out-of-bounds relative error.

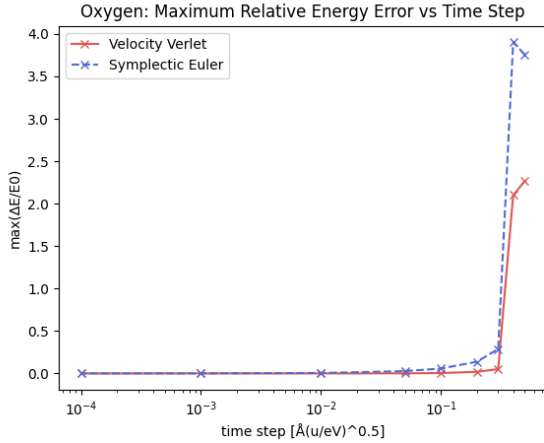
¹The starred values did not result in vibrational motion for either integrator and hence were excluded from diagrams

In-Depth Results: Oxygen

Accuracy of time integrators



The results show that the Symplectic Euler converges significantly faster than Velocity Verlet. Further supported by the time step values in the table above.



The only measure in which Velocity Verlet is superior is maintaining a lower maximum relative energy error in its simulations. This diagram, along with its counterpart for Nitrogen is a clear measure that for time steps 0.4 and 0.5, where the energy error spikes, that the motion is not vibrational and hence any respective calculated frequencies should be excluded.

Given these results, we conclude that the most accurate time integrator is Symplectic Euler by all important measures. Not only giving more accurate data per time step also on average being $\sim 25\%$ faster simulating the particles than Velocity Verlet.

Comparison

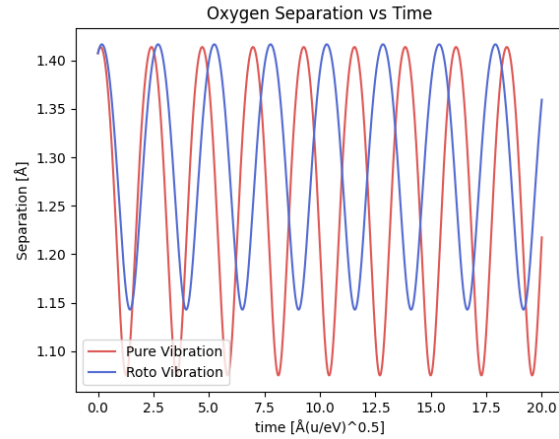
Experimental data shows: $\nu(N_2) = 2359 \text{ cm}^{-1}$ and $\nu(O_2) = 1580 \text{ cm}^{-1}$.² The relative errors in the results are then 9.3% for both Nitrogen and Oxygen.

²Computer Modelling notes, University of Edinburgh, 2020.

By Taylor expanding the Morse potential we can estimate the vibrational frequencies for small amplitudes. This gives a comparison for our model that doesn't include simulations. Doing so gives: $T = 2\pi\sqrt{\frac{\mu}{2D_e a^2}}$. Plugging in the respective values for each particle and changing units gives: $\nu_M(N_2) = 2358 \text{ cm}^{-1}$ and $\nu_M(O_2) = 1580 \text{ cm}^{-1}$. Hence the theoretical values in the model agree with the experimental data. The large discrepancy between the small amplitude/experimental frequency and the simulated frequencies can be attributed to the initial conditions for which the pure vibration was calculated. An initial separation closer to r_e , such as $r_e + 0.02$ results in: $\nu(O_2) = 1566 \text{ cm}^{-1}$ and $\nu(N_2) = 2350 \text{ cm}^{-1}$. This is to no surprise, as the closer we get to the stable separation in the potential the closer it resembles its quadratic, small-amplitude form for which the vibrational frequencies match the experimental ones.

Pure Vibration and Rotational Vibration

Results shown for Symplectic Euler integration and a time step of 0.001:



Utilising rotational initial conditions result in lower rovibrational frequencies of 1294 cm^{-1} for Oxygen and 2043 cm^{-1} for Nitrogen. We expect this decrease in frequency as in the non-inertial reference frame of the system, the fictitious centrifugal force implies a larger stable separation value (r_e). This results in a lower force than for the pure vibration system, which produces larger periods of oscillations, and hence lower frequencies.

Conclusions

Simulations showed lower frequencies than experimental data, which could be attributed to the initial conditions straying too far away from the small-amplitude case which is known to give the matching results. Within the simulations, the Symplectic Euler algorithm outperformed Velocity Verlet both in accuracy and computation time.