

# Computer Modelling Project Report

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## 1 Aim

The aim of this project was to accurately measure the vibrational frequencies of the diatomic molecules  $N_2$  &  $O_2$  using computer simulations implementing different time integrators, and determine the ‘best’<sup>1</sup> method in which we can determine an accurate model for the particles.

## 2 Background & Method

To simulate the vibrational frequency of these molecules, we used two separate time integration methods;

Symplectic Euler

$$\vec{v}(t) = \vec{v}(t + dt) - \dot{\vec{v}}(t + dt)dt + \frac{1}{2}\ddot{\vec{v}}(t + dt)dt^2 \mp \dots$$

$$\vec{x}(t + dt) = \vec{x}(t) + \vec{v}(t)dt$$

$$\vec{v}(t + dt) = \vec{v}(t) + \frac{1}{m}\vec{F}(t)dt$$

Velocity Verlet

$$\vec{v}(t) = \vec{v}(t) + \frac{1}{2m}(\vec{F}(t) + \vec{F}(t + dt))dt$$

$$\vec{x}(t + dt) = \vec{x}(t) + \vec{v}(t)dt + \frac{1}{2m}\vec{F}(t)dt^2$$

Using these methods, we are able to predict and simulate the velocity and position of the two particles, but to do this we need to know the forces acting upon said particles.

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<sup>1</sup>best here meaning we not only consider the accuracy, but whether or not adding 30 seconds of processing time adds any valuable accuracy

As we are trying to simulate diatomic molecules, we will be looking at the pairwise forces that occur when two atoms are bonded. These forces form the Morse potential which we will be using to determine the potential energy of the atoms.

$$U_m(\mathbf{r}_1, \mathbf{r}_2) = D_e((1 - \exp[-\alpha(r_{12} - r_e)])^2 - 1)$$

$$F_1(\mathbf{r}_1, \mathbf{r}_2) = 2\alpha D_e((1 - \exp[-\alpha(r_{12} - r_e)])\exp[-\alpha(r_{12} - r_e)])\hat{\mathbf{r}}_{12}$$

$\mathbf{r}_{1,2}$  - position vectors of each particle w.r.t. centre point  
 $D_e, \alpha, r_e$ , - Constants  
 $r_{12}$  - separation between particles  
 $\hat{\mathbf{r}}_{12}$  - unit vector of the two separation vector  
 $\mathbf{r}_2 - \mathbf{r}_1$  - separation vector

Using these equations, and applying our time integration methods we can determine the separations of the atoms and the total energy of the system with relative ease.

Due to the shape of the Morse potential well, the particles will oscillate in a predictable fashion. If we plot the time and separation, and take two peaks, we can determine the period of the oscillations and hence the vibrational frequency of the particles.

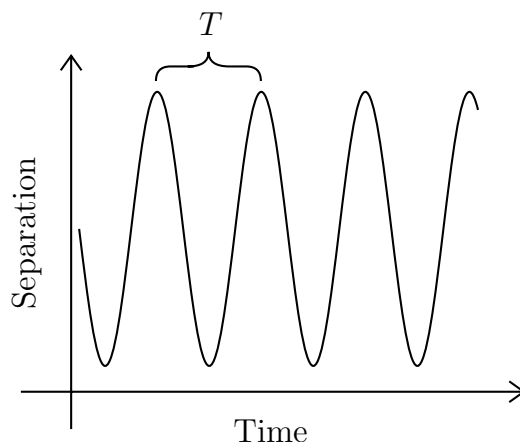


Figure 1: Theoretical Results demonstrating how to determine the period.

The code was written with each time integrator such that particles would be created from a source file, and constants would be given to the program via another file. The particle data would then be used to determine its movement within the system considering the pairwise forces over a space of time, with the time being

updated by a user deterined time interval,  $dt^2$ . The total energy of the system was then determined, this was done to look at the uncertainty in the method, as the energy *should* be constant. The positions & total energies were then output to separate files and plotted with respect to time using *matplotlib*. The code was run for both  $N_2$  &  $O_2$  for the determined timesteps.

## 3 Analysis

### 3.1 Symplectic Euler vs Velocity Verlet

Using the results from our simulations, the most suitable method for determining the particles frequency can be determined.

It is clear from the data that Symplectic Euler is unfit for the task, as its change in total energy decreased rather slowly with the increase in steps, compared to the Velocity Verlet method, which decreases rapidly but becomes more ineffective at higher time steps.

Time step	$\Delta E$
0.5	N/A
0.1	0.055657...
0.01	0.005456...
0.001	0.000545...
0.0001	0.000054...

Table 1: Change in energy of  $O_2$  for Symplectic Euler.

Time step	$\Delta E$
0.5	N/A
0.1	0.00421
0.01	$813 \times 10^{-9}$
0.001	$425 \times 10^{-9}$
0.0001	$4 \times 10^{-9}$

Table 2: Change in energy of  $O_2$  for Velocity Verlet

This shows that the Symplectic is too inaccurate (and therefore inefficent) to use for determining accurate data without using too much processing power compared to its rival. The energy shouldn't change, but due to the use of time integration methods<sup>3</sup> this isn't feasible, so the smaller the change in energy the better.

With Velocity Verlet, the relative frequency error was determined to be under 1% when using the Time step 0.1. For Symplectic Euler, the time step required to be below 1% was between 0.1 and 0.01. This once again shows that Velocity Verlet is the better method of the two for creating accurate simulations.

<sup>2</sup>The timesteps used were 0.5, 0.1,  $10^{-2}$ ,  $10^{-3}$  &  $10^{-4}$

<sup>3</sup>This code can only handle discrete time intervals, the only way to completely remove uncertainty would be to have a continuous time system, which would take a **LOT** of power.

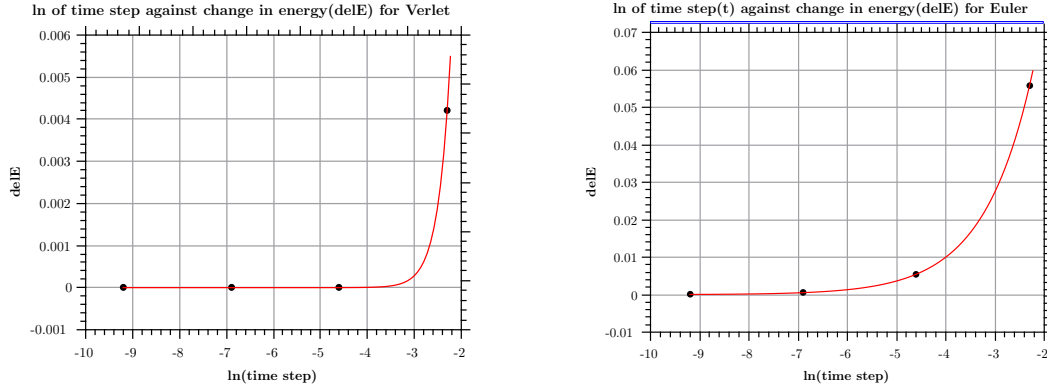


Figure 2: Natural log of the time step against the change in energy shows that for small time steps (large -ve values) the inaccuracy in the Verlet method drops off significantly quicker than the inaccuracy in the Euler method.

The previous figures and discussion in this section have clearly shown that the Velocity Verlet method is superior for decreasing inaccuracy while keeping the processing time reasonable when compared to the Symplectic Euler method.

### 3.2 Comparing with Experimental

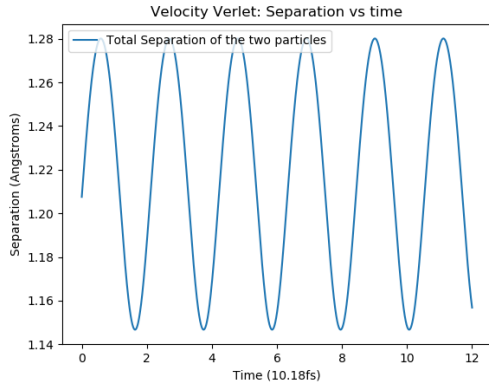
Using the results from our Velocity Verlet method, the vibrational frequencies of  $N_2$  &  $O_2$  were found to be  $2338cm^{-1}$  &  $1556cm^{-1}$ . Comparing these to their experimental values ( $2359cm^{-1}$  &  $1580cm^{-1}$ ) shows that there is still some inaccuracies that have not been accounted for in the system that would need to be further taken into account.

### 3.3 Particles with spin

The oxygen and nitrogen particles were simulated with velocity in the y axis with a suitable timestep, and their vibrational frequencies were determined to be  $2236cm^{-1}$  for  $N_2$  &  $1402cm^{-1}$  for  $O_2$ . As we can tell the frequencies are smaller than our previous values by a significant amount. This system introduces the mechanics of ‘Rotational-Vibrational coupling’, which means that the particles have to consider the conservation of angular momentum when vibrating & rotating, this new degree of freedom means that the vibrational energy that creates the oscillation forces will make up less of the total energy of the system, and such vibrate at a slower rate overall.

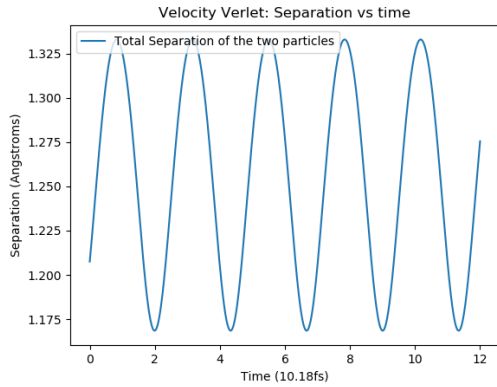
## 4 Particle Separation Graphs

### 4.1 $O_2$ for vibrational oscillations



Initial conditions;  
Particle 1:  $x = 0.60376, y = 0, z = 0,$   
 $v_x = 0.1, v_y = 0, v_z = 0, m = 16$   
Particle 2:  $x = -0.60376, y = 0, z = 0,$   
 $v_x = -0.1, v_y = 0, v_z = 0, m = 16$

### 4.2 $O_2$ for vibrational & rotational oscillations



Initial conditions;  
Particle 1:  $x = 0.60376, y = 0, z = 0,$   
 $v_x = 0.1, v_y = 0.3, v_z = 0, m = 16$   
Particle 2:  $x = -0.60376, y = 0, z = 0,$   
 $v_x = -0.1, v_y = -0.3, v_z = 0, m = 16$