

Time Integration

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1 Aim

In this experiment, time integration algorithms of Euler and Verlet are used to determine the algorithms are used to simulate the O_2 and N_2 molecules under different set initial parameters.

2 Theory

The particles in this simulation interact with each other using the Morse potential stated in equation 1. Covalent bonds in molecules or clusters are described by this pair-potential. This is defined as:

$$U_M(r_1, r_2) = D_e \left\{ \left[1 - e^{-\alpha(r_{12}-r_e)} \right]^2 - 1 \right\} \quad (1)$$

for two particles at \mathbf{r}_1 and \mathbf{r}_2 where $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ and $r_{12} = |\mathbf{r}_{12}|$. The force on the particle at \mathbf{r}_1 is given as

$$\mathbf{F}_1(r_1, r_2) = 2\alpha D_e \left[1 - e^{-\alpha(r_{12}-r_e)} \right] e^{-\alpha(r_{12}-r_e)} \hat{\mathbf{r}}_{12} \quad (2)$$

and $\mathbf{F}_1 = -\mathbf{F}_2$ also, $\hat{\mathbf{r}}_{12} = \mathbf{r}_{12}/r_{12}$. The parameters r_e , D_e , and α control the position, depth and curvature, respectively, of the potential minimum. These are dependent on the system.[1] These simulation were conducted on Spyder.

3 Method

The time integrator methods Symplectic Euler and velocity Verlet in updating the positions of the particles using the changes in velocity and by using 2nd order Taylor expansions combined with their 1st order expansions of their corresponding velocities, respectively.[2]

Output files are generated through the command line and this data was then used to analyse the data for the Energy inaccuracy, the frequency and the frequency inaccuracy.

4 Results and Analysis

The algorithms mentioned in the method were used and the following graphs in figure 1 were produced:

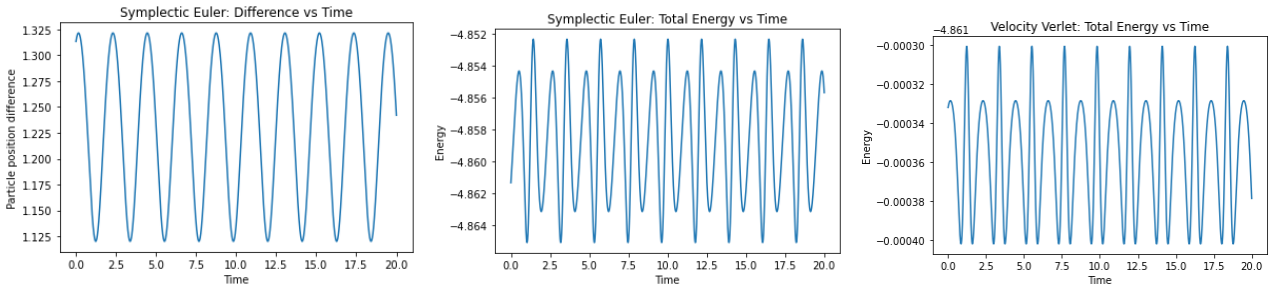


Figure 1: Graphs produced from the 2 simulation on the Oxygen particles that have no spin. The first graph shows the particle difference over time and the last 2 graphs produced using the Euler and Verlet algorithms. These are taken with "numstep" as 2000 to make the graph easier to read.

The maximum time step δt_{max} was estimated for both time integrators, that could simulate the system with a relative frequency inaccuracy under 0.5%. This time step was then used as a constant in the simulations that followed.

The simulations also showed that the data was achieved using the Verlet algorithm had a more less energy inaccuracy. Figure 2, below, shows how this decision was made. This algorithm was then used to make calculations.

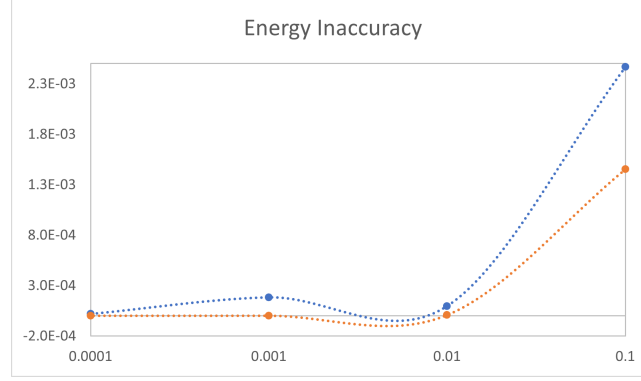


Figure 2: The blue line is data from produced using the Euler algorithm. The orange line is by using Verlet.

$\delta t(s^{-1})$	$E_{inaccuracy}$	Wave Number (cm^{-1})	$f (cm s^{-1})$	$f_{inaccuracy}$
10^{-1}	-1.454×10^{-3}	1560.24	4.677×10^{-13}	0.023
10^{-2}	-7.180×10^{-6}	1523.95	4.569×10^{-13}	-0.0011
10^{-3}	-5.060×10^{-8}	1525.37	4.573×10^{-13}	-0.00014
10^{-4}	-5.052×10^{-10}	1525.58	4.574×10^{-13}	0

Table 1: Data found using the chosen Verlet for the simulation for Oxygen particles.

It is seen that as the timestep increases, the frequency increases as well. However, the energy decreases. Using the data in table 1, the optimal that was selected for simulations is 10^{-3} . This value is less than 0.5% and has the least frequency inaccuracy. The following results made using this value is shown in the table below. These are done for Nitrogen with and without spin, and Oxygen with spin.

Element	$E_{inaccuracy}$	Wave Number (cm^{-1})	$f (cm s^{-1})$
Nitrogen	-1.14×10^{-9}	2291.26	6.87×10^{-13}
Nitrogen (with spin)	-1.22×10^{-7}	2188.71	6.56×10^{-13}
Oxygen (with spin)	-2.98×10^{-9}	1384.24	4.15×10^{-13}

Table 2: Data found from the simulations with the chosen $\delta t (10^{-3})$.

In the above table 2, the data produced with the spin on the particles has a lower wave number, Energy inaccuracy and frequency. This is because the energy distributed into the spin of the particle as rotational energy. However, this simulation does not account for the rotational energy.

Using the harmonic approximation,

$$\bar{\nu} = \frac{\alpha}{2\pi} \sqrt{\frac{2D_e}{m}}$$

The harmonic frequencies calculated using the above equation for Nitrogen (N_2) and Oxygen (O_2) are $1665 cm^{-1}$ and $1364 cm^{-1}$, respectively. This is less than the $\bar{\nu}(N_2) = 2359 cm^{-1}$ and $\bar{\nu}(O_2) = 1580 cm^{-1}$ which are the recorded known values.

References

- [1] M. Martinez-Canales, J. Zuntz (2021) Exercise 3: Time Integration [Coding Instructions]
- [2] M. Martinez-Canales, J. Zuntz (2021) Computer Modelling Course Notes [Course Notes]