The vibrational frequencies of Nitrogen and Oxygen molecules

Computer Modelling Exercise 3

E Forster

Introduction and Theory:

The aim of this exercise was to simulate Oxygen and Nitrogen molecules under various initial conditions to find their wavenumber and compare them to experimental values.

The particles were to interact with each other via the Morse Potential:

$$U_M(\mathbf{r}_1, \mathbf{r}_2) = D_e \{ \left[1 - e^{-\alpha (r_{12} - r_e)} \right]^2 - 1 \}$$

Where: $\mathbf{r}_{12} = \mathbf{r}_2 - \boldsymbol{r_1}$ and $r_{12} = |\mathbf{r}_{12}|$

The force on the particle at $\mathbf{r}_1$ is then:

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

Where: $\boldsymbol{F}_2 = -\boldsymbol{F}_1$ and $\hat{\boldsymbol{r}}_{12} = \frac{\mathbf{r}_{12}}{|\mathbf{r}_{12}|}$

The unit for time is $\dot{A} \sqrt{\frac{amu}{eV}}$ in simulation so must be multiplied by 1.018050571 x 10^{-14} to convert into seconds [1.].

Computational Method:

Experiments were done computationally using Python language, with methods describing the Morse Potential and making a particle class that could hold and use information of a three-dimensional particle.

The symplectic Euler method and the velocity Verlet time integrators were implemented to model the evolution of two interacting particles. The Euler scheme updates the particle positions based on their velocities, then uses the updated positions to obtain updated forces and velocities at each time-step. The Verlet method expands positions to second order derivatives and updates the velocity by averaging the current and new forces. The Verlet scheme updates the particle position, then the force and then updates the velocity at each time-step.

Convergence was analysed in repeating the simulation for Oxygen molecules at different time-steps to find the ideal time-step parameter that was the maximum time-step that had a relative frequency error under 0.5%. This gave an idea of which method was more accurate.

Finally, Nitrogen was analysed to investigate the difference between no-spin Nitrogen and rotating molecule of Nitrogen. The values of wavenumber for the molecules were compared to experimental values given in Reference 1 and their differences were considered.

Results and Analysis:

First, v-nought was obtained by running the simulation at a dt = 10e-5 which gave a wavenumber of 1525.6 cm^-1. Then a graph with logarithmic scaling of energy inaccuracy vs. dt and wavenumber inaccuracy vs. dt were plotted for both methods, as seen in Figures 1 and 2.

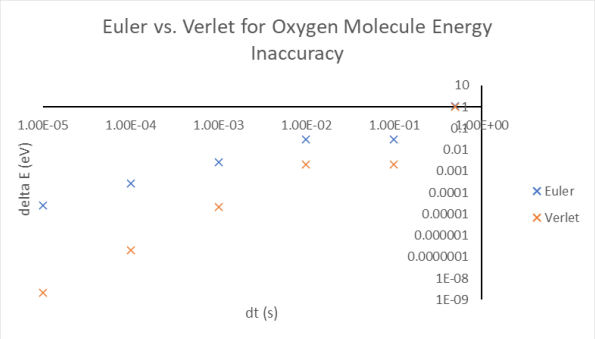

Figure 1: Method Comparison of Energy Inaccuracy vs. dt

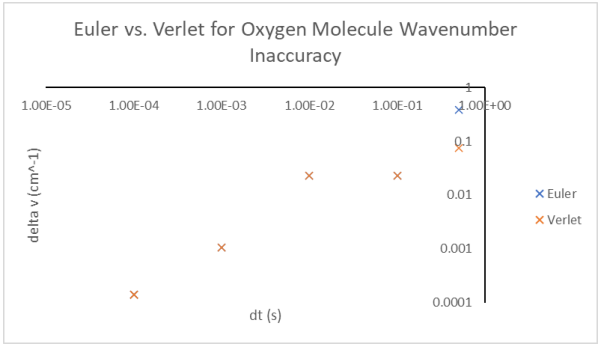

Figure 2: Method Comparison of Wavenumber Inaccuracy vs. dt

The figures demonstrate that a smaller dt means a more accurate simulation. From this, the Verlet method is shown to be more accurate than the Euler method.

The position vs. time in Verlet method for a Nitrogen molecule and a rotating Nitrogen molecule were obtained and compared as seen in Figures 3 and 4.

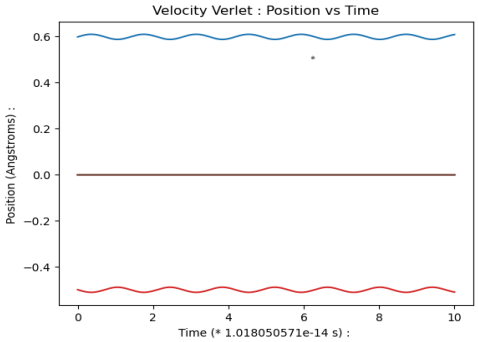

Figure 1: Verlet method for Nitrogen Molecule

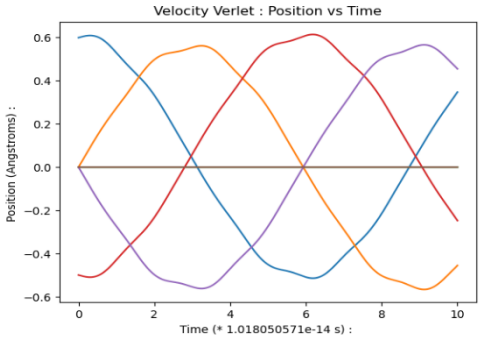

Figure 4: Verlet method for rotating Nitrogen molecule

The rotating Nitrogen molecule has a much more interesting plot with a longer period than the non-rotating Nitrogen.

Table 1 gives the Euler and Verlet simulations for the various molecules being analysed.

Result:	Euler			Verlet		
	O2	N2	N2 spin	O2	N2	N2 Spin
Wavenumber :	1525.585	2353.637	2249.57	1525.585	2353.637	2249.57
delta Wavenumber	0	0.542777	0.474562	0	0.542777	0.474562

Table 1: Wavenumber and inaccuracies for Euler and Verlet simulations for molecules

The experimental wavenumbers for Nitrogen and Oxygen are 2359 cm^-1 and 1580 cm^-1 respectively.

Conclusions:

The Verlet method is more accurate compared to the Euler method. Compared to experimental wavenumbers, the Nitrogen molecule was closest. For some reason, the table shows the wavenumbers being the same and due to time constraints this could not be further investigated.

References:

1.) Exercise 3: Time Integration, Computer Modelling Assignment, accessed via The University of Edinburgh's LEARN page. Date accessed: 4th December 2021.