Introduction and Theory

A python program "simulate_particle" was used to conduct a computational experiment with the aim being to simulate the vibrational motion of O2 and N2, with and without spin, using the morse potential for covalent bonds. Two-time integrators, Sympletic Euler and Velocity Verlet, are implemented and compared for the spin and no spin situations. The aim is obtaining the wavenumber (also referred to as vibrational frequency) of molecules interacting via the Morse potential and compare to experimental data to evaluate our code and time integrators.

The Morse potential, as used in the simulation, describes the interaction between molecules and clusters through covalent bonds. The constants De, α and re are specific to each molecule. The distance between two particle positions, represented by vectors $\boldsymbol{r1}$ and $\boldsymbol{r2}$ is needed to compute it. Potential energy reaches its minimum value when the distance is re.

The Morse potential energy is given by equation 1, The force derived from the Morse potential, used to update the velocities in both Euler and Verlet integration methods (as per Newton's 2nd and 3rd laws), is given by equation 2:

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

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Adapted units are used, since we are in the world of atomic physics, to minimise precision loss due to rounding errors. These include eV, electronvolts, for the energy. Å, angstorm, for length. u, atomic mass unit for mass. This sets the units and amount for time so one time unit will be T, where T = 1.0180e−14s. The wavenumber we are looking for is expressed in 1/cm since that is the convention.

Method

Particle3D class is used , assigning the features of label, mass, position, and velocity. Energy and wavenumber inaccuracies according to reading material are computed and used to compare the quality of different timesteps. If timestep parameter is too high, the simulation will be inaccurate. The smaller it is, the longer the simulation takes so for efficiency we identify a timestep with wavenumber inaccuracy less than 0.05% and use that for the rest of the simulation, this initial search is done using the oxygen data with no spin. Then the experiment is repeated for O2 and N2 using the ideal timestep that was found.

Results

dt	0.5	0.1	0.01	0.001	0.0001	0.00001
Energy mean [eV]	201.19	-4.863	-4.861	-4.861	-4.861	-4.861
Energy inaccuracy	-42.12	-2.12e-2	-2.09e-5	-2.09e-7	-2.09e-9	-2.101e-11
Wavenumber [cm^{-1}]	1310.61	1489.33	1523.97	1526.09	1525.60	1525.59
Wavenumber inaccuracy	0.14	0.024	0.0011	0.00033	4.7e-06	N/A ~ 0

Table 1 Energy mean, energy inaccuracy, wavenumber and wavenumber inaccuracy for different values of dt when simulation is ran on O2 molecule with no spin
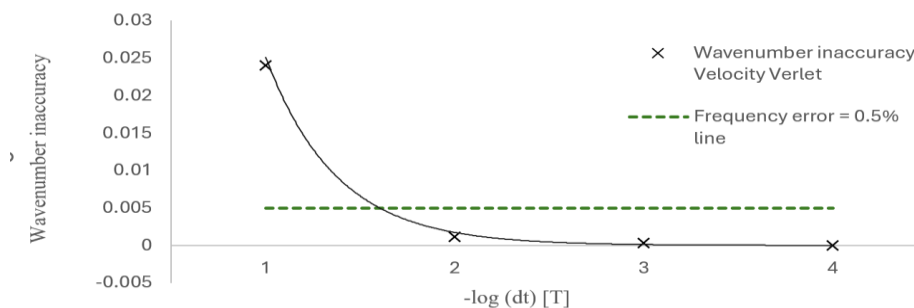

Figure 1 Wavenumber inaccuracy for different values of dt (in negative log$_{10}$ scale). The line for which error is 0.5% visualised as to show which dt values lay below. Best Fit line drawn through points exponential.

From this data we can calculate the highest dt for which the error is below 0.5% is 0.0256. Therefore, a dt of 0.02 was used for the main values of experiment. With numstep 1000 for nice graphs:
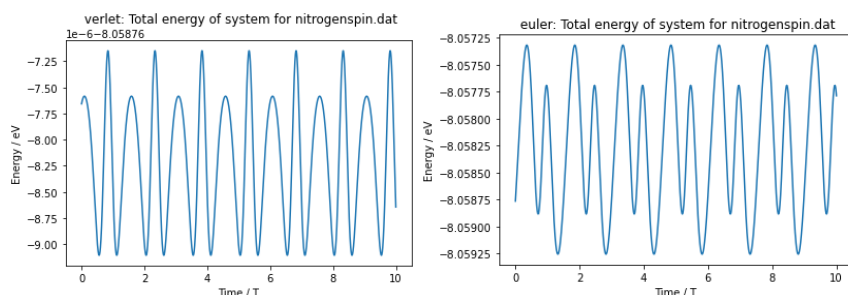

Figure 2 Energy variation with time for same particle and initial conditions, difference being integration method
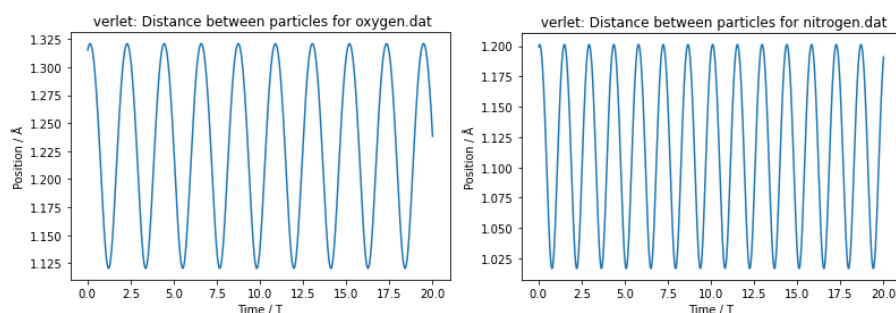

Figure 3 Vibration ossiclation for O2 and N2 with no spin side by side for comparision

Time integration method used:	Wavenumber [cm⁻¹]:			
	Oxygen	Oxygen with spin	Nitrogen	Nitrogen with spin
Sympletic Euler	1531.09	1388.36	2275.36	2184.35
Velocity Verlet	1516.91	1376.69	2307.41	2184.35
Error of closest method [%]	3.1	12.1	2.2	7.4

Table 2 Summary of results of wavenumbers found for O2 and N2 with and without spin for the two integration methods Sympletic Euler and Velocity Verlet running particle_simulation with dt 0.02 and numstep 1000.

Discussion

The wavenumbers for both O2 and N2 provided in the Exercise 3 manual for non-rotating wavenumbers are 1580 cm-1 for O2 and 2359 cm-1 respectively. Our closest result for oxygen both oxygen and nitrogen is the non-spinning data however euler integration gave a closer result for oxygen whereas verlet gave a closer result for nitrogen. The values obtained were 1531.09 cm-1 and 2307.41 cm-1, this gives the error of 3.1% and 2.2% respectively.

In the context of simulating the vibrational motion of molecules we expect velocity Verlet integrator to be more accurate than the symplectic Euler method, as it is a second-order integrator, meaning it provides higher precision in calculating both positions and velocities by accounting for the forces at both the current and predicted positions however in our simulation the euler method seems to work better for oxygen in both the spin and non-spin case. Oxygen has a smaller frequency and maybe this makes the difference, or this could indicate a problem with the code, however since both values from the verlet and euler for non- spinning oxygen are very close to the real value it might be euler works better with these initial conditions. All in all the investigation of the modes showed that the Verlet mode is more accurate, providing the lowest energy inaccuracy. This was proven during the analysis of the ideal time-step δt and can be seen in figure2.

Both integrators give lower wavenumbers than expected when the particles spin, the errors here are significantly higher at 7% and 12%, this may be an indication that these methods become less precise when used on particles with spin and should be avoided. The simulation with the chosen time step is good as it does not require a long time to run (seconds) and many initial conditions could be tested very quickly. However, it needs the further improvement, maybe a different time integrator, to be used rotating particles.

As expected a smaller dt does not seem to help as a dt of 10^{-6} was tried and seems to reach the limits of the simulation, providing an identical wavenumber. The pattern in the fluctuation of is broken. This could be that the computer error is bigger than the error is simulation or that the floating point error is smaller than precision.

verlet Total Energy of system over time