Computational Report: Diatomic Molecules

Introduction

To model the oscillations of atoms in diatomic molecules, a Python model utilising the symplectic Euler and the velocity Verlet integration algorithms was developed, in accordance with specifications from the instruction sheet for the third exercise of the University of Edinburgh School of Physics and Astronomy's Computer Modelling module. This report outlines the nature of the oscillations being modelled, how a time interval parameter for the algorithms was found and assesses the accuracy of each algorithm in modelling rotating and non-rotating Nitrogen and Oxygen molecules.

Background: Algorithms

The positions and velocities of a particle after a small time interval can be found using Taylor expansions. However, only the second derivative of position can be easily found using physical laws.

The Euler integration algorithm therefore uses a first order truncation of the position and velocity Taylor expansions. It first calculates the particle's position after a short interval using its current velocity. Then, for the case of a diatomic molecule, it calculates the Morse force, and thus the acceleration using Newton's second law at the new positions. It then calculates the new velocity and repeats these steps.

There is a source of inaccuracy in the Euler algorithm due to higher order terms in the Taylor expansion being neglected, and the fact that the acceleration is taken as constant during the interval. Consequently, the Verlet algorithm attempts to improve accuracy by computing the position expansion to the second order and by computing the velocity after the time interval using the time-averaged acceleration.

Background: Physics

When the separation of atoms in a diatomic molecule is near the equilibrium separation, a second order Taylor expansion may be applied to the Morse force equation from the exercise instructions. Then, by applying Newton's second law, the differential equation $\frac{d^2r}{dt^2} = -\frac{4D}{m}\alpha^2(r - r_e)$ is obtained, where m is the mass of the particles, r is their separation, D and α describe the shape and depth of the potential minimum and r_e is the equilibrium separation. This is the result for a simple harmonic oscillator. The separation of the particles with respect to time can thus be expressed as $r(t) = r_0 \sin\left(2\alpha\sqrt{\frac{D}{m}}t + \phi\right) + r_e$, where r_0 is the maximum separation, set by boundary conditions and ϕ is a phase shift set by boundary conditions. The computational model presented in this report replicates behaviour near the equilibrium separation, so this result implies that the Python simulation should output a sinusoidal variation of separation with time.

For such a system, total energy should remain constant. Therefore, the accuracy of the simulation was assessed by determining the fractional error in the total energy, defined as the difference between the maximum and minimum calculated energies divided by the initial calculated total energy.

The frequency of oscillation of the atoms determines the wavenumber of the photons emitted and absorbed by the molecule. The wavenumber is given by $\bar{v} = \frac{v}{c}$, where v is the combined vibrational and rotational frequency of the atoms. The model calculates the vibrational frequency by finding the inverse of the average period between subsequent peaks in particle separation modelled by each algorithm. The model does not calculate rotational frequency, which is the frequency of rotation about the particles' centre of mass. The accuracy of the simulation can be assessed by calculating the fractional error in the calculated wavenumber compared to the experimentally verified values of 1580cm^{-1} for oxygen and 2359cm^{-1} for nitrogen.

Implementation

To find suitable time interval for the algorithms described previous section, another python algorithm was developed, which repeated the simulation for various values of the time interval and calculated the fractional error in total energy each time. The maximum allowable error was chosen to be 5%. An interval of $0.13 \text{ Å}\sqrt{\text{amu/eV}}$ was chosen, as it achieved approximately this error across all molecular systems tested for both algorithms. A lower interval was not chosen to avoid unnecessary computational cost.

Results and Discussion

Graphs showing the time variation of particle separation for the rotating (spun) and non-rotating (unspun) oxygen molecules using the Euler and the Verlet algorithms are shown in figure 1.
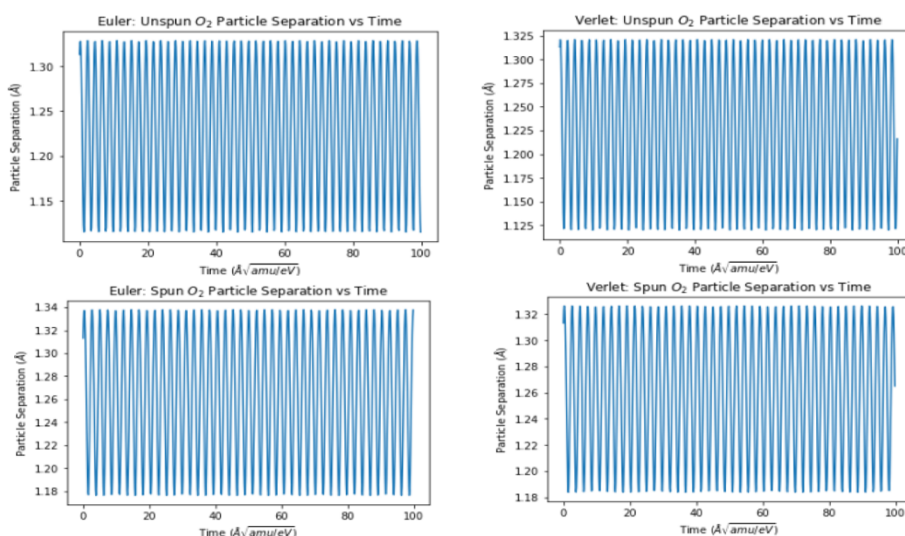

Figure 1: Particle separations over time as simulated by Euler and Verlet algorithms for spun and unspun oxygen atoms.

The shape of the oscillations is sinusoidal, as expected, and was similar for the Nitrogen molecules. This implies that the simulation correctly models the shape of the vibrational oscillations of the atoms near their equilibrium separation.

The table below displays the wavenumber (rounded to the nearest integer), wavenumber error and energy error outcomes of both algorithms for the spun and unspun oxygen and nitrogen molecules.

System Modelled	Euler $\bar{v}$ (cm⁻¹)	Error	Verlet $\bar{v}$ (cm⁻¹)	Error	Euler Energy Error	Verlet Energy Error
Rotating O_2	1383	12.4%	1389	12.1%	3.1%	0.1%
Non-rotating O_2	1530	0.3%	1536	0.3%	3.9%	0.4%
Rotating N_2	2203	6.6%	2216	6.1%	3.7%	0.4%
Non-rotating N_2	2309	2.1%	2324	1.4%	5.2%	0.7%

Both algorithms gave wavenumbers near the experimental values, but were less accurate for the rotating molecules. This was expected since the model only calculates vibrational frequency, and therefore does not account for the impact of rotational oscillations on photon absorption and emission. The Verlet algorithm was only slightly more accurate in calculating the wavenumber. Both algorithms returned wavenumbers below the experimental values, which may be due to a source of systematic error in the model, or because the oscillations weren't perfectly harmonic. The Verlet algorithm was far more effective than the Euler in conserving energy. This was expected given the advantages of the Verlet algorithm over the Euler discussed above.

Conclusion

Both algorithms were effective in modelling the general behaviour of the vibrational oscillations in each molecular system, however both lacked in accuracy in determining the wavenumber of rotating molecules. The Euler algorithm was far less effective in maintaining conservation of energy. The Verlet algorithm is therefore a superior choice for modelling such system and is useful in modelling the general behaviour of diatomic molecules.

Algorithm Specification

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