

# Numerical Simulation Methods applied to Diatomic O<sub>2</sub> and N<sub>2</sub> molecules

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## Abstract

We have determined diatomic Oxygen and Nitrogen to have near-equilibrium spinless oscillation frequencies of 1556,2261 cm<sup>-1</sup> respectively. Introducing molecular spin we have observed anharmonicity of an effective potential, with frequencies of 1401,2164 cm<sup>-1</sup>. Euler, symplectic Euler and Velocity Verlet time integration techniques have been examined with optimal timesteps determined for spinless O<sub>2</sub> and N<sub>2</sub>, with the unique result of this quantity being larger for the symplectic Euler than the Velocity Verlet in the case of N<sub>2</sub>.

## 1 Introduction

Diatomic Oxygen and Nitrogen O<sub>2</sub> and N<sub>2</sub> have total potential energy readily described by the Morse potential<sup>[1]</sup>  $U_M(\mathbf{r}_1, \mathbf{r}_2)$ , given by

$$D_e((1 - \exp[-\alpha(r_{21} - r_e)])^2 - 1)$$

where  $D_e, \alpha$  are the depth and “width” of the well, and  $r_e$  is the equilibrium bond distance.  $\mathbf{r}_{1,2}$  denote the vector positions of the two particles relative to some origin.  $r_{21}$  denotes the separation of the two atoms, given by the magnitude of the vector  $\mathbf{r}_{21} = \mathbf{r}_1 - \mathbf{r}_2$ .

Taking  $-\nabla U_M$  the force can be determined for either particle, i.e. for the particle at  $\mathbf{r}_1$  the force  $\mathbf{F}_1(\mathbf{r}_1, \mathbf{r}_2)$  is given by

$$-2\alpha D_e(1 - \exp[-\alpha(r_{21} - r_e)]) \exp[-\alpha(r_{21} - r_e)] \hat{\mathbf{r}}_{21}$$

where the force  $\mathbf{F}_2$  is given by  $-\mathbf{F}_1$  via consideration of Newton’s Third Law.

In this experiment we aim to obtain the oscillation frequencies for atomic separation in O<sub>2</sub> and N<sub>2</sub> in the case of molecules both with and without spin, based on the Morse potential. This will be done using numerical time integration techniques<sup>[2]</sup>. We aim to minimise the processing required for this, thus attempting to discern a maximum timestep  $\Delta t_{max}$  that can be used before the simulation results are unsatisfactory, using a relative frequency error maximum of 0.01 as our gauge.

## 2 Methods

Three integration techniques will be utilised. Euler (EU), symplectic Euler (SEU), and Velocity Verlet (VV). A detailed treatise on these techniques can be had<sup>[2]</sup>, where symplecticity can also be examined<sup>[3]</sup>.

Python is used for simulation using these techniques. A particle class is created, which contains

the requisite methods for integration. These include  $\mathbf{r}$  and  $\mathbf{v}$  steps for both the SE and VV integration methods. The simulation program is then run based on the particle objects created with the system parameters defined in a file, which is read into the program.

The complete set of Morse parameters and atomic masses to be used are shown in 1. From this, it can be seen that the units of time are given by  $T = \text{\AA}(\frac{amu}{eV})^{0.5}$ ,  $\approx 10.18$  fs if the data is not converted by the program, which it isn’t. As mentioned, both a spinless molecule and a molecule with spin will be simulated. When spinless,  $\mathbf{r}_1, \mathbf{v}_1 = (\frac{r_e}{2}, 0, 0), (0.1, 0, 0)$  and with a spin,  $\mathbf{v}_1 = (0.1, 0.3, 0)$ .  $\mathbf{r}_2, \mathbf{v}_2 = -\mathbf{r}_1, -\mathbf{v}_1$ .

**Table 1:** Table showing Morse parameters for O<sub>2</sub> and N<sub>2</sub>, alongside atomic mass.

Quantity	O <sub>2</sub>	N <sub>2</sub>
$D_e/\text{V}$	5.213 22	9.905 23
$r_e/\text{\AA}$	1.207 52	1.097 68
$\alpha/\text{\AA}^{-1}$	2.653 74	2.688 67
$m/\text{amu}$	16.000 00	14.010 00

The general process used by the simulation program is as follows. The file containing start parameters is read in. Following this, a array is created which contains the diatomic atom as a pair of particle objects. Iterators are ran for the array, each one returning an array of five lists: separation, potential energy, kinetic energy, total system energy, and the time elapsed, the first four lists a time series of the fifth.

Using the data obtained from the iterator, the *SciPy*<sup>[4]</sup> package is used. Setting a timestep of  $\Delta t = 0.00001$  for roughly  $\approx 1.5$  oscillations it is possible to attain a reasonable sinusoidal curve fit of the data, of the form  $r_{21}(t) = a \sin(bt + c) + d$  for the separation as a function of time. This is done using the *scipy.optimize.curve\_fit* task.

An example fit is shown in fig 1. The angular frequency  $b$  is converted into spectroscopic frequency for comparative purposes.

We then determine the error on frequency  $\nu$  as a function of  $\Delta t$  for all three integration techniques. The true frequency  $\nu_0$  of the oscillator is judged to be that of the VV simulation for  $\Delta t_{base} = 0.00001$ . Oscillation frequency is calculated for  $\Delta t$ , initially  $\Delta t_{base}$ . It is then subtracted from and subsequently normalised by the true frequency, giving relative frequency error. This is then repeated for a new timestep,  $\Delta t = \Delta t + \Delta t_{base}$ . Simultaneously this is done for energy fluctuation, following the exact same technique. The result is a time-step series for  $\frac{\delta \nu}{\nu_0}$  and  $\frac{\delta E}{E_0}$ . Example graphs are shown in fig 1.<sup>1</sup>

### 3 Results and Discussion

The determined values for  $\nu, \Delta t_{max}$  are shown in table 2. Representative plots for the N<sub>2</sub> run with and without spin are shown in fig 1.

**Table 2:** Table showing calculated spectroscopic frequencies  $\nu$ , and estimates for  $\Delta t_{max}$  for EU, SEU & VV time integration methods. S and NS represent a spin and a lack thereof. Error only shown for NS for brevity.

Quantity	O <sub>2</sub>	N <sub>2</sub>
$\nu/\text{cm}^{-1}$ NS	1556	2261
$\nu/\text{cm}^{-1}$ S	1401	2164
$\Delta t_{max}/\text{T}$ NS EU	0.010	0.003
$\Delta t_{max}/\text{T}$ NS SEU	0.180	0.154
$\Delta t_{max}/\text{T}$ NS VV	0.180	0.106

The determined values of  $\nu$  for O<sub>2</sub> without spin agree with the accepted values<sup>[1]</sup> of  $1580 \text{ cm}^{-1}$  to within 1.5% percentage error. For N<sub>2</sub> this drops to 4.2%, which is less satisfactory.

When spin is introduced,  $\nu$  increases for the oscillators. For small oscillations, the Morse potential behaves quadratically, i.e. the oscillations are harmonic. Considering the addition of angular momentum to the system, the oscillations are now described by an effective potential. This concept is described well by Taylor<sup>[5]</sup> in his treatise on the motions of bound kepler orbits. For small angular momentum of the system, oscillations are limited near the equilibrium of the effective potential, which yields harmonic oscillations. As angular momentum of the system increases, an anharmonic component is introduced,

which increases the period of oscillation. It's interesting to note that the Morse potential itself admits anharmonicity<sup>[6]</sup> though that will not be discussed.

It's interesting to note that  $\Delta t_{max}$  for the SEU simulation mirrors that of the VV simulation for O<sub>2</sub> exactly, while being even lower than it for the VV simulation. In both cases the expectation of  $\Delta t_{max}$  for the EU simulation being the lowest is satisfied. The method used to obtain  $\Delta t_{max}$  seems inherently flawed, as indicated by the rather colourful display shown by the plots in fig 1. The error plots for the runs for O<sub>2</sub> had some interesting oscillatory phenomena for the EU simulations, further indicating a possible error in the methods utilised. The key reason behind this flaw almost certainly lies with the single-oscillation *scipy.optimize.curve\_fit* methodology we hastily adopted. In the future, fitting for a significant number of oscillations would be pertinent to examine this.

Also of interest is total energy of the system. For VV and SEU simulations it oscillates but remains roughly constant. For EU simulations however, it perpetually increases, indicating poor conservation, even for a subjectively low timestep. For larger timesteps, the total energy rapidly diverges, which can be seen in the energy fluctuation curves in fig 1.

### 4 Conclusion

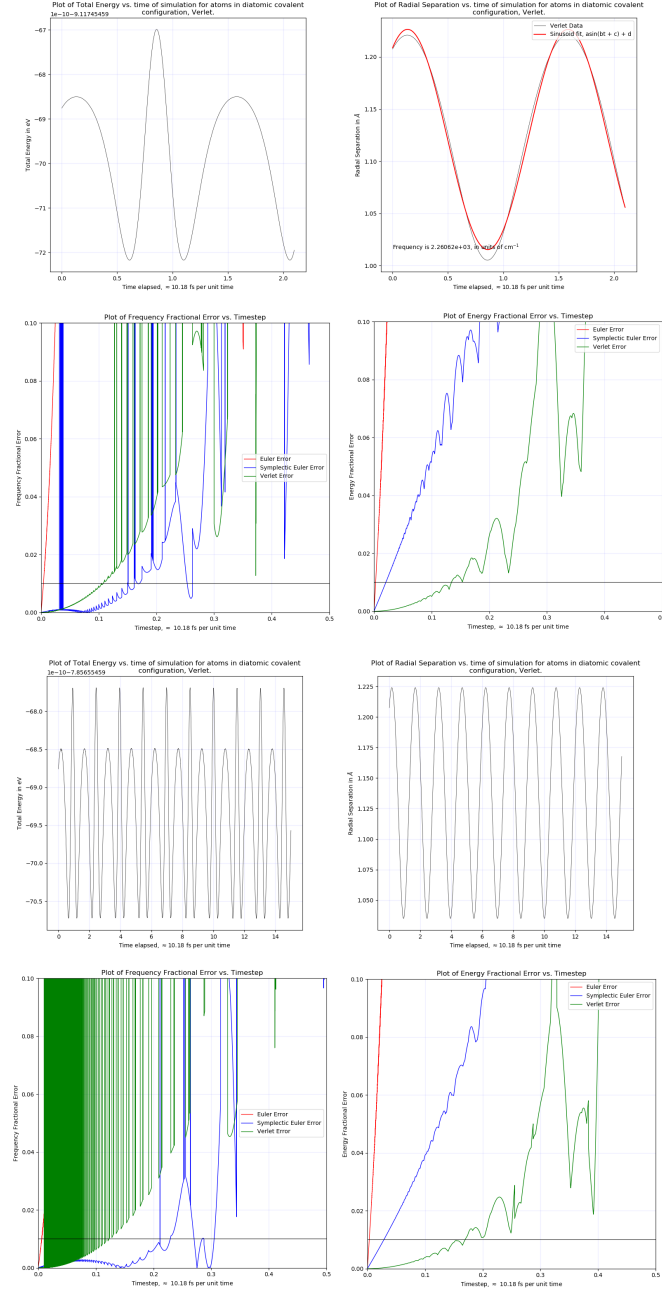
Simulating the oscillation of oxygen and nitrogen within spinless O<sub>2</sub> and N<sub>2</sub> under the Morse potential near equilibrium we have determined the oscillatory frequencies to be  $1556, 2261 \text{ cm}^{-1}$  respectively, agreeing to accepted values within 1.5, 4.2 %. Introducing a significant spin, we observed the expected result that the oscillation frequencies would decrease, returning frequencies of  $1401, 2164 \text{ cm}^{-1}$  respectively.

We have examined three different time integration methods for particle simulation: Euler, symplectic Euler, and Velocity Verlet. Considering relative error in the obtained frequency vs. the best possible frequency we could obtain, with a maximum error of 1%, we have determined maximum integration timestep for the three methods on both spinless O<sub>2</sub> and N<sub>2</sub>. Surprisingly, we discovered that the maximum timestep was larger

<sup>1</sup>I've only shown one oscillation, purely to show the curve fit. By setting the max time far higher you can get a longer oscillation if you so wish, in the program that is.

for the symplectic euler method in comparison to the velocity verlet method for nitrogen, defying expectations.

We have determined that the program developed requires improvement and an alternate curve fitting method to estimate frequency could be better utilised in the future.



**Figure 1:** Selection of graphs for  $N_2$  run with and without spin, lower four graphs with, upper four without. The Velocity Verlet total energy and separation graphs without spin are pictured for roughly one oscillation, while shown for roughly 9 with spin:  $\nu$  error/energy fluctuation are both for  $\approx$  one oscillation.

## Acknowledgements

I went over the page limit. I know I did. The graphs are also tiny. To be fair, you guys wanted representative plots for a run with and without spin, that's already a load of graphs. Then tables, too. The references, too. That's easily 3/8 of the entire paper (if it were 2 pages)! The introduction needs the physics, with quantities marked, also quite verbose. No marks are given out for the actual introduction or methods (according to the mark scheme) even though they take up an equal volume to the results/conclusions, too ;-;

## References

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