1-28-2009

The Driven Harmonic Oscillator in Chemistry

Carl W. David
University of Connecticut, Carl.David@uconn.edu

The Driven Harmonic Oscillator in Chemistry

Carl W. David
Department of Chemistry
University of Connecticut
Storrs, Connecticut 06269-3060

Abstract

The molecular dynamical simulation of the normal vibrational mode of water which involves H-O-H angle deformation, when driven by an external force, can be used to see how a driven harmonic oscillator, classically, is associated with the infra-red spectrum of water (and the absorption for this particular normal mode). *The incredible delay in refereeing this paper prompts me to place it here in case I die before its published.*

Introduction

In earlier work(1,2), the molecular mechanics (using Maple) of vibration of simple molecules has been presented, with the idea that the interpretations obtainable from classical mechanics are appropriate for appreciating the non-classical interpretations of the same system's functioning when appropriate quantum mechanics is employed.

Specifically, it was shown that the three normal modes of vibration were obtainable from a molecular dynamics simulation where the frequencies of vibration were associated with the IR absorption frequencies as studied in elementary physical chemistry. The “hapinstance” that the classical frequency coincided with the absorption frequency allows one to adjust the potential energy parameters to give vibrational frequencies which agree with the obeserved infra-red spectrum of water.

But the classical picture even includes an inkling of what happens when a photon approaches a molecule. One can approximate what happens by assuming an electric field of known frequency (color) which interacts with the molecule (technically, through its dipole moment), leading classically to a driven harmonic oscillator, and quantum mechanically, to an absorption of the incident photon with its resultant demise.

In this piece, the classical driven oscillator is simulated for the water case, in the normal mode which treats the H-O-H angle as the primary variable.

Geometry of the Water Molecule

We place the water molecule with its oxygen at the origin, and its protons in the x-y plane $z_{H_1} = z_{H_2} = z_O$ such that $x_{H_1} = x_{H_2}$ and $y_{H_1} = -y_{H_2}$. The H-O-H angle is nominally set at 104.5^o but will be varying in the normal mode under discussion here, while $r_{OH} = 0.9584$ Angstrom .

Perturbation Force

In order to drive the oscillator, we perturb the molecule using a force on the protons of the form $F_{y_{H_1}} = A\cos\left(\frac{f\left(\frac{2\pi}{180}\right)i}{n_{points}}\right) = -F_{y_{H_2}}$ where *f* is a variable we choose trying to tune to the "resonant" frequency corresponding to the infra-red transition and the classical frequency of vibration. The "strength" of the perturbation (*A*) is arbitrary, chosen to make things work. "*i*" is the index which increments by one for each time step from 1 to n_{points}. *A*, in our example, was 1×10^4.

Maple Integration of Newton's Equations of Motion

Earlier work was employed for this extension. All that was required was to add the lines of code which perturbed the motion (as noted above) and find a suitable strength of perturbation.

Resultant Motion

One sees from the figures that the motion when *f* is too small or too large leads to beating, while when *f* is close to "right", the resonance pheonomenon takes hold in an intuitively appealing manner.

Literature Cited

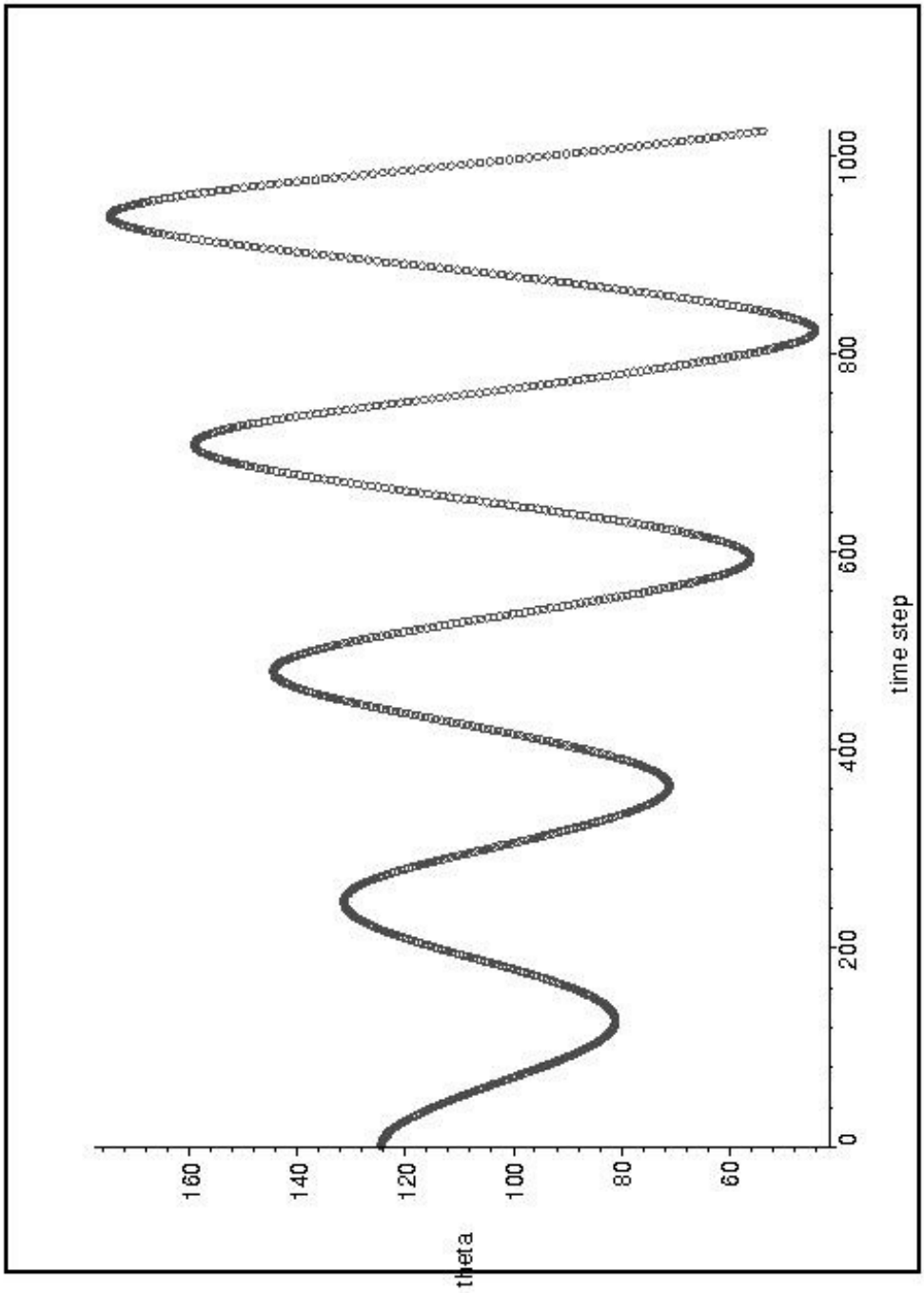
(1) David, C. W.; http://digitalcommons.uconn.edu/chem_educ/11/

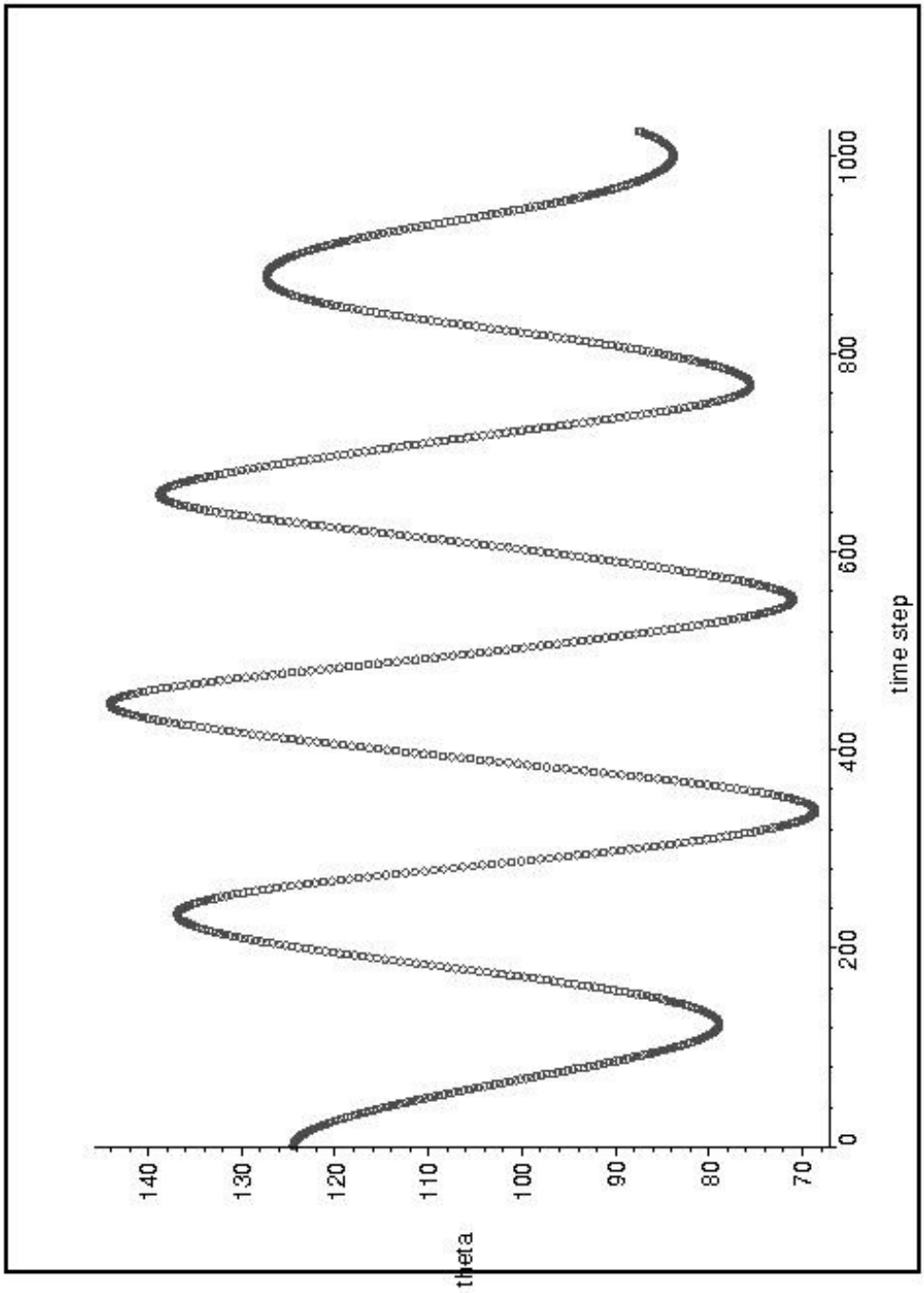
(2) David, C. W.; Chem. Educator, *11*, 1-4 , **2006**

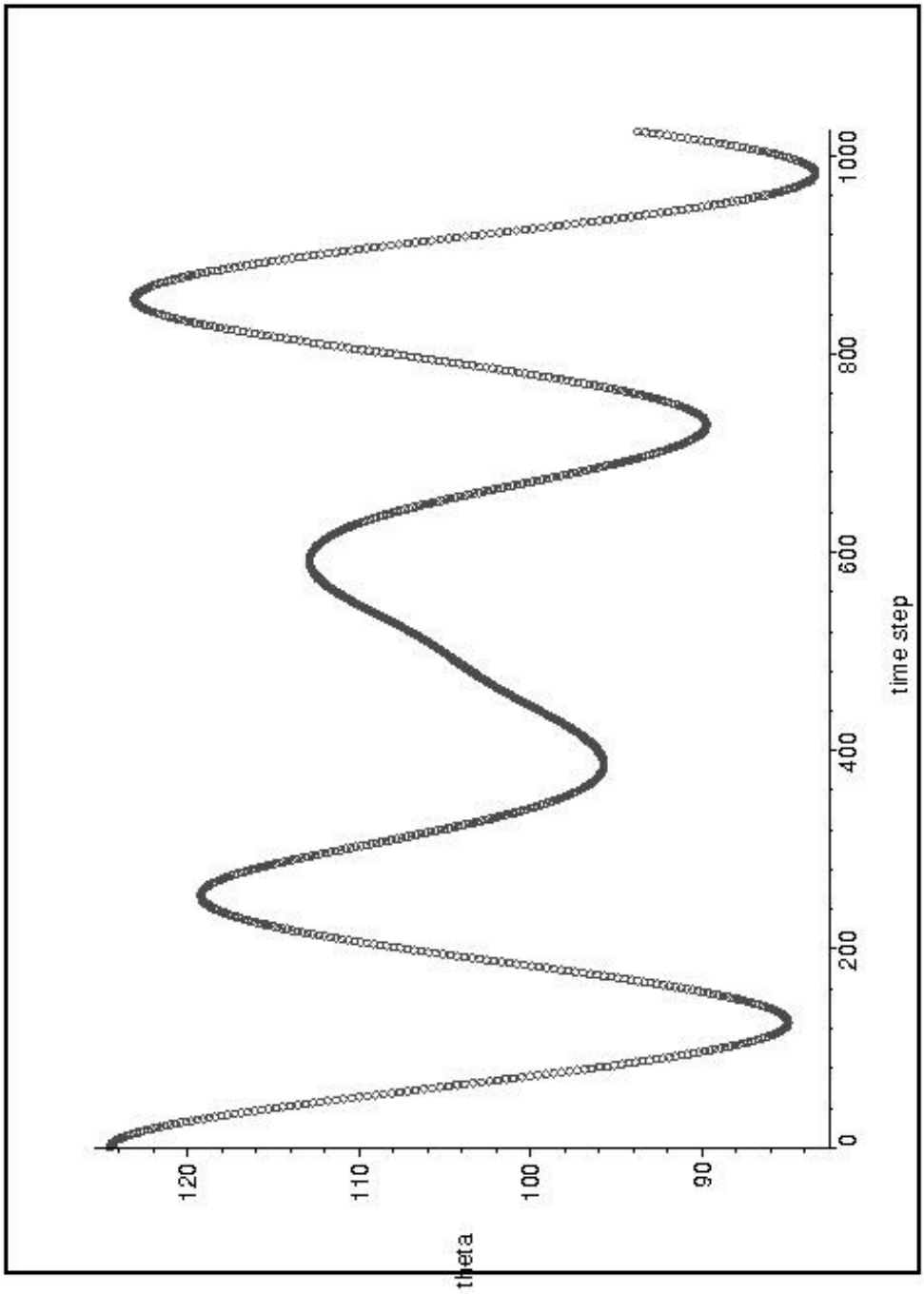
FIGURES

Figure 1; f = 4.65, time step = 0.965×10^{-16} seconds, H-O-H angle versus time step (i). This choice corresponds to near resonance, resulting in energy being inserted into the molecule from an outside driver. This is the classical analog of absorption of a photon of the proper frequency resulting in transiting to a higher vibration level.

Figure 2 & 3; f = 5.65 and 3.65, time step = 0.965×10^{-16} seconds, H-O-H angle versus time step (i). Beating can be seen in both these plots.


160
140
120
100
80
60
theta
0
200
400
600
800
1000
time step


140
130
120
110
100
90
80
70
theta
0
200
400
600
800
1000
time step


theta
120
110
100
90
0
200
400
600
800
1000
time step