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APPLICATION OF A DIATOMIC MOLECULE MODEL POTENTIAL TO A SERIES OF HOMO- AND HETERODIATOMIC MOLECULES


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APPLICATION OF A DIATOMIC MOLECULE MODEL POTENTIAL TO A SERIES OF HOMO- AND HETERODIATOMIC MOLECULES

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We apply a one-dimensional classical model of a diatomic molecule model potential with modifications to H₂, HF, LiF, N₂, and CO. We obtain the unknown parameters of this model by digitizing plots of the potential curves for the molecules from a published, Hartree-Fock based theoretical electron correlation calculation (Piris 2017). We then apply the method of successive approximations to the model in order to calculate the wavenumber for each molecule in the series. The wavenumber depends on a parameter which in turn depends on the initial conditions. The value of this parameter for each individual molecule gives zero percent error for the corresponding molecule's wavenumber, but an average is used in the final calculation of all molecules' wavenumbers. The resulting wavenumbers are all within seven percent of the experimental values.

Keywords: mechanics, model potential, wavenumber, successive approximations, diatomic molecule

INTRODUCTION

The Lennard-Jones potential (Lennard-Jones 1931; Kittel 1986; Hasbun and Datta 2019) is an equation that models the potential between two atoms or molecules within a solid. The equation is composed of a term representing the short-range repulsive force caused by the Pauli Exclusion Principle and a second term representing the long-range attractive force due to the Van der Waals interaction. The derivation of the Van der Waals term relies on the assumption that the charge separation on each particle is significantly less than the distance between the particles (Kittel 1986). An example of such a system is shown in Figure 1.

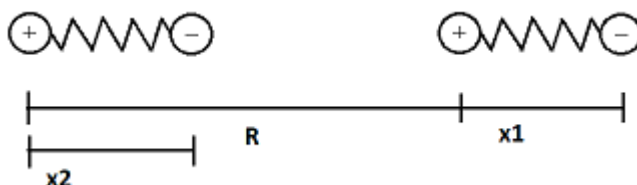


Figure 1. Diagram of two neutral particles with charge separations $x1$ and $x2$, separated by a distance R . This system follows the Lennard-Jones potential model.

The Lennard-Jones potential for a system such as that in Figure 1 can be written as

$$V(R) = \frac{B}{R^{12}} - \frac{A}{R^6}, \quad (1)$$

where A and B are positive constants (Kittel 1986; Hasbun and Datta 2019). The graph of potential versus the distance between the particles generated by Equation (1) will have the general characteristics of the plot shown in Figure 2.

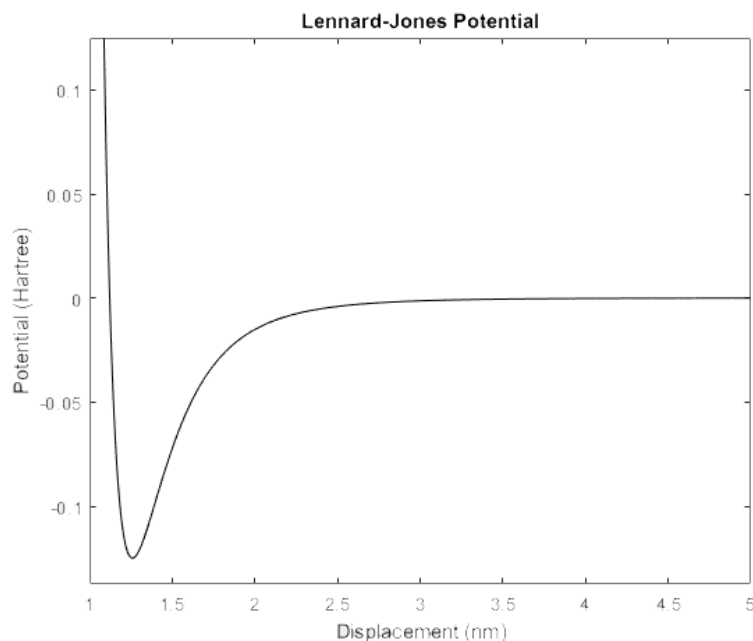


Figure 2. Example plot of the Lennard-Jones potential (Equation (1))

In the case of a diatomic molecule, the internuclear distance of the atoms is approximately equal to the sum of the charge separation on each atom. This makes the approximation used in the derivation of the Lennard-Jones potential invalid and so the Lennard-Jones potential model is not a good representation of this system. However, the plot of potential versus internuclear distance for two atoms forming a diatomic molecule has a distinct shape which is similar to that produced by the Lennard-Jones potential (Piris 2017). It is this similarity that inspired the diatomic molecule model potential. Based on the Lennard-Jones potential, this model has a short-range repulsive term and a long-range attractive term.

$$V(x) = \frac{A}{x^3} - \frac{B}{x^2}, \quad (2)$$

where A and B are positive constants and x is the internuclear distance of the atoms (Timberlake and Hasbun 2008; Hasbun 2009).

To test the accuracy of the model potential, we compare the wavenumbers calculated using the model to those obtained experimentally (Piris 2017). We also compare the plots of potential versus internuclear distance to those generated by a Hartree-Fock (Hartree 1935) based theoretical electron correlation calculation (Piris 2017).

To calculate the wavenumber, we first calculate the angular frequency of the system. For this, we use the method of successive approximations (Hasbun 2009; Chow 1995; Hill and Hasbun 2018) to account for the anharmonicity of the system described by the model potential. This results in a more accurate calculation of the wavenumber than is obtained using a harmonic approximation. Following the method of successive approximations, for a system acted on by a force $f(x)$, such that

$$m \frac{d^2 x}{dt^2} = f(x), \quad (3)$$

we calculate the frequency by making a third order Taylor expansion (Boas 2006) of the force about the equilibrium position, x_0 ,

$$f(x) \cong f_0(x_0) + \frac{1}{1!} f'(x_0)(x - x_0) + \frac{1}{2!} f''(x_0)(x - x_0)^2 + \frac{1}{3!} f'''(x_0)(x - x_0)^3. \quad (4)$$

The force at $x = x_0$ is zero, so the first term vanishes. We then define the new parameters $k_{\text{eff}} = -f'(x_0)$, $a_2 = \frac{1}{2!m} f''(x_0)$, and $a_3 = \frac{1}{3!m} f'''(x_0)$ and combine and rewrite equations (3) and (4) as

$$\frac{d^2 x}{dt^2} + \omega_0^2 (x - x_0) = a_2 (x - x_0)^2 + a_3 (x - x_0)^3, \quad (5)$$

where $\omega_0^2 = \frac{k_{\text{eff}}}{m}$, with $k_{\text{eff}} = -f'(x_0)$. We make a guess solution of the form

$$x = A_0 + A_1 \cos(\omega t) + A_2 \cos(2\omega t) + A_3 \cos(3\omega t), \quad (6)$$

which we substitute into equation (5) to find the corrected angular frequency,

$$\omega = \omega_0 \sqrt{1 - 3a_3 \left(\frac{A_1}{2}\right)^2}, \quad (7)$$

where A_1 is determined by the initial conditions (Hasbun 2009).

Once we have calculated the angular frequency, we calculate the wavenumber starting with the oscillation frequency,

$$f = \frac{\omega}{2\pi}. \quad (8)$$

We then calculate the wavelength using the formula

$$\lambda = \frac{c}{f}, \quad (9)$$

where c is the wave speed. Finally, the wavenumber (Hecht 1998) is given by

$$N = \frac{1}{\lambda}. \quad (10)$$

Combining equations (8) through (10), we obtain a formula for the wavenumber from the angular frequency as

$$N = \frac{\omega}{2\pi c}. \quad (11)$$

THEORY

The equation for the potential between two atoms forming a diatomic molecule given by equation (2) assumes the potential approaches zero for an infinite internuclear distance. To make the model more generic, we add a constant parameter, V_{inf} . We then further modify equation (2) to better fit the data obtained by digitizing plots of potential generated using a Hartree-Fock (Hartree 1934) based theoretical electron correlation calculation (Piris 2017). This is done by replacing the variable x with $x - x_s$. Therefore, equation (2) becomes

$$V(x) = \frac{A}{(x-x_s)^3} - \frac{B}{(x-x_s)^2} + V_{\text{inf}}. \quad (12)$$

The addition of the new parameter x_s serves to stretch the model potential to better conform to the digitized data (Piris 2017).

To find the values of the parameters in equation (12), we extract several values from the digitized data (Piris 2017). First, the bond length, x_b , which is the internuclear distance where the potential is minimized. Next, the potential at the bond length, V_{min} , and the potential as the internuclear distance becomes large, V_{inf} . Last, we obtain the internuclear distance less than x_b where the potential equals V_{inf} , x_0 . These values are illustrated in Figure 3.

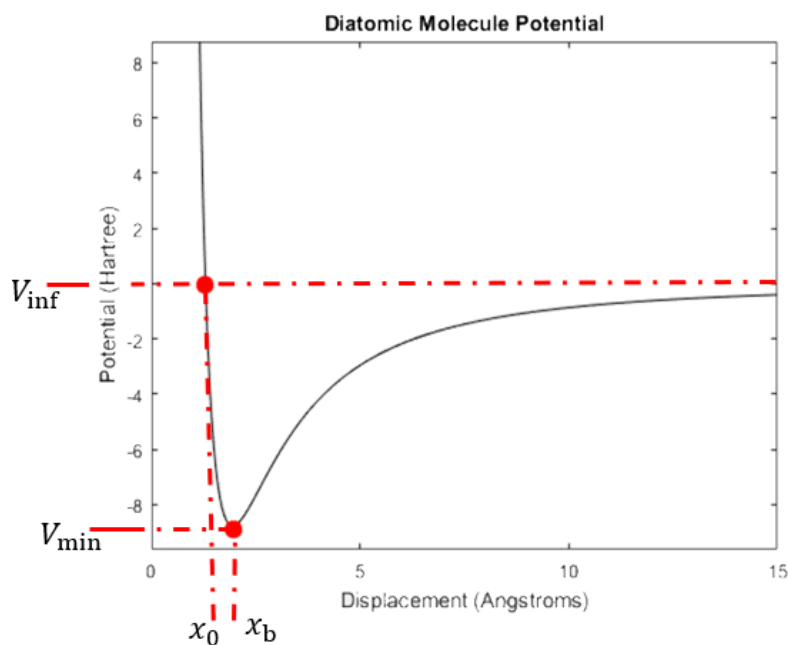


Figure 3. Plot of the potential for a diatomic molecule illustrating the known parameters of the molecule.

The unknown parameters A , B , and x_s can then be calculated as follows:

We take the derivative of equation (12) with respect to x .

$$V'(x) = -\frac{3A}{(x-x_s)^4} + \frac{2B}{(x-x_s)^3}. \quad (13)$$

Equation (13), being the derivative of equation (12) is zero at the minimum of equation (12), which occurs at $x = x_b$. Therefore,

$$-\frac{3A}{(x_b-x_s)^4} + \frac{2B}{(x_b-x_s)^3} = 0, \quad (14)$$

which we rearrange to find

$$\frac{3A}{2B} = x_b - x_s. \quad (15)$$

We then evaluate equation (12) at $x = x_0$, substitute $V(x_0) = V_{inf}$, and rearrange to obtain

$$\frac{A}{B} = x_0 - x_s. \quad (16)$$

Combining equations (15) and (16) provides us with a formula for x_s in terms of the known parameters x_0 and x_b ,

$$x_s = 3x_0 - 2x_b. \quad (17)$$

To find A and B , we evaluate equation (12) at $x = x_b$, substitute $V(x_b) = V_{min}$ to obtain

$$V_{min} = \frac{A}{(x_b-x_s)^3} - \frac{B}{(x_b-x_s)^2} + V_{inf}. \quad (18)$$

Substituting equation (15) into equation (18) and simplifying, we find

$$-\frac{4B^3}{27A^2} = V_{min} - V_{inf}, \quad (19)$$

which, by factoring out $-\frac{B}{3}$, substituting equation (15), and rearranging, gives us

$$B = -3(x_b - x_s)^2 \cdot (V_{min} - V_{inf}). \quad (20)$$

Combining equations (20) and (15), we then find

$$A = -2(x_b - x_s)^3 \cdot (V_{min} - V_{inf}). \quad (21)$$

Once we have obtained the parameters for the model (Tables I and II), we calculate the wavenumber. We begin by making a second order Taylor expansion (Boas 2006) of the potential, equation (2), about $x = x_b$.

$$V(x) \cong V_0(x_b) + \frac{1}{1!}V'(x_b)(x - x_b) + \frac{1}{2!}V''(x_b)(x - x_b)^2. \quad (22)$$

The second term on the right-hand side of equation (22) is proportional to the derivative of the potential at a local minimum, and so becomes zero. The first term is the minimum of the potential, V_{\min} , but, because potential is relative, this term can be ignored without affecting the calculation of the wavenumber. Therefore, upon evaluating the second derivative of potential at $x = x_b$, equation (22) becomes

$$V(x) \cong \frac{1}{2} \frac{32B^5}{81A^4} (x - x_b)^2, \quad (23)$$

which is the equation of potential for a simple harmonic oscillator with an effective spring constant given by

$$k_{\text{eff}} = \frac{32B^5}{81A^4}. \quad (24)$$

The angular frequency for such a system is

$$\omega_0 = \sqrt{\frac{k_{\text{eff}}}{M}}, \quad (25)$$

where M is the reduced mass of the system, given by

$$M = \frac{m_1 \cdot m_2}{m_1 + m_2}, \quad (26)$$

with m_1 and m_2 being the masses of the two atoms. From the angular frequency, we can calculate the wavenumber (Table III) for this harmonic approximation using equation (11) with the wave speed being the speed of light, $3 \cdot 10^{10}$ centimeters per second (Hasbun 2009).

To account for the anharmonicity of the system, we apply the method of successive approximations. Because this requires a third order Taylor expansion of the force, and since force, in one dimension, is related to potential by

$$f(x) = -\frac{dV(x)}{dx}, \quad (27)$$

we make a fourth order Taylor expansion of the potential about $x = x_b$,

$$V(x) \cong V_0(x_b) + \frac{1}{1!} V'(x_b)(x - x_b) + \frac{1}{2!} V''(x_b)(x - x_b)^2 + \frac{1}{3!} V'''(x_b)(x - x_b)^3 + \frac{1}{4!} V^{(IV)}(x_b)(x - x_b)^4 \quad (28)$$

To calculate force, we take the derivative of equation (28) with respect to x . The zeroth order term becomes zero, and the first order term, being proportional to the derivative at a minimum, becomes zero. Therefore, we obtain

$$f(x) \cong V''(x_b)(x - x_b) + \frac{1}{2} V'''(x_b)(x - x_b)^2 + \frac{1}{3!} V^{(IV)}(x_b)(x - x_b)^3, \quad (29)$$

where $V''(x_b) = \frac{32B^5}{81A^4}$, $V'''(x_b) = \frac{-512B^6}{243A^5}$, and $V^{(IV)}(x_b) = \frac{2560B^7}{243A^6}$.

Comparing equation (29) with equation (4), we see that the coefficients from equation (5) for the model potential are

$$\omega_0^2 = \frac{1}{M} V''(x_b), \quad (30)$$

$$a_2 = \frac{1}{2M} V'''(x_b), \quad (31)$$

$$a_3 = \frac{1}{3M} V^{(IV)}(x_b). \quad (32)$$

Equation (30) is the angular frequency calculated using the simple harmonic oscillator approach and is therefore equivalent to equation (25).

We calculate the corrected angular frequency using equations (7), (25), and (32). However, equation (7) depends on the parameter A_1 , which depends on the initial conditions. To obtain the value of A_1 , we rearrange equation (7) to find

$$A_1 = 2 \sqrt{\frac{1 - (\omega/\omega_0)^2}{3 \cdot a_3}}. \quad (33)$$

We then calculate the experimental angular frequencies for the molecules H_2 , HF , LiF , N_2 , and CO from the experimental wavenumbers (Piris 2017) using equation (11). These values are substituted along with ω_0 and a_3 for each molecule, respectively. This provides five values of A_1 (Table IV), the average of which is computed and used in the final calculation for all the molecules. The average we obtain is

$$\overline{A_1} = 2.309 \cdot 10^{-11} \text{ m} \cdot \text{s}. \quad (34)$$

Once we calculate the corrected angular frequency; that is,

$$\omega = \omega_0 \sqrt{1 - 3a_3 \left(\frac{A_1}{2}\right)^2}, \quad (35)$$

we calculate the corrected wavenumber using equation (11).

We compare the calculated wavenumbers, corrected and uncorrected, to the experimental values using the percent error, which is given by

$$Error = 100 \cdot \left| \frac{N_{exp} - N}{N_{exp}} \right|, \quad (36)$$

where N_{exp} is the experimental wavenumber.

RESULTS

All calculations are done using MATLAB (MathWorks). The MATLAB script in Appendix A calculates all resultant values for dihydrogen and produces a graph comparing the potential curves for dihydrogen from the model potentials and the Lennard-Jones potential to the experimental data (Piris 2017). The known parameters for the molecules are listed in Table I. These values were extracted by using MATLAB (MathWorks) to digitize the potential curves generated by a Hartree-Fock based theoretical electron correlation calculation (Piris 2017).

Table I. Known parameters of the model potential obtained by using the MATLAB (MathWorks) to digitize plots of potential generated by a Hartree-Fock based theoretical electron correlation calculation (Piris 2017).

Molecule	V_{\min} (Hartree)	V_{\inf} (Hartree)	x_b (Angstrom)	x_0 (Angstrom)
H ₂	-1.17	-1.00	0.743	0.378
HF	-100.15	-100.02	0.917	0.654
LiF	-107.07	-106.91	1.564	1.110
N ₂	-109.11	-108.82	1.098	0.849
CO	-112.90	-112.62	1.128	0.866

The known parameters in Table I were used to calculate the unknown parameters for the model potential given by equation (2). These parameters are listed in Table II.

Table II. Unknown parameters for the model potential calculated from equations (17), (20), and (21) using MATLAB and the known parameters in Table I.

Molecule	A (Hartree Angstroms cubed)	B (Hartree Angstroms squared)	x_s (Angstrom)
H ₂	0.4536	0.6210	-0.353
HF	0.1329	0.2522	0.127
LiF	0.7870	0.8676	0.203
N ₂	0.2408	0.4837	0.351
CO	0.2762	0.5278	0.343

The wavenumbers calculated using the harmonic oscillator approach of equation (25) are only reasonably accurate for H₂, HF, N₂, and CO, with the average percent error for these molecules being 21.52 percent. However, for LiF, the harmonic oscillator approach is moderately accurate, having a percent error of only 5.76 percent. Using the method of successive approximations with the average value of A_1 from equation (7) for all the molecules significantly improves the calculated wavenumber. The corrected wavenumbers for all the molecules differ by less than seven percent from their respective experimental values (Piris 2017). Table III presents the experimental

wavenumbers, calculated harmonic angular frequencies, and wavenumbers, and the percent error for each calculated wavenumber. Table IV displays the experimental wavenumbers, the values of A_1 and a_3 calculated for the method of successive approximations, the corrected angular frequencies, the corrected wavenumbers, and the percent error for each improved wavenumber.

Table III. Experimental wavenumbers, angular frequencies and wavenumbers calculated from the harmonic oscillator approximation (Equation (25)) and the percent error for the molecules in the series.

Molecule	N_{exp} (cm ⁻¹)	ω_0 (rad/s)	N_0 (cm ⁻¹)	Percent Error
H ₂	4401	$6.701 \cdot 10^{14}$	3557.6	19.16
HF	4138	$5.953 \cdot 10^{14}$	3160.6	23.62
LiF	911	$1.617 \cdot 10^{14}$	858.5	5.76
N ₂	2359	$3.417 \cdot 10^{14}$	1813.9	23.11
CO	2170	$3.263 \cdot 10^{14}$	1732.2	20.18

Table IV. Experimental wavenumbers, values of parameters A_1 , a_2 , and a_3 , angular frequencies and wavenumbers calculated using the method of successive approximations (Equations (32) and (35) which replaces Equation (7)), and the percent error for the molecules in the series.

Molecule	N_{exp} (cm ⁻¹)	A_1 (m·s)	a_2 (m ⁻¹ ·s ⁻²)	a_3 (m ⁻² ·s ⁻²)	ω (rad/s)	N (cm ⁻¹)	Percent Error
H ₂	4401	$2.91 \cdot 10^{-11}$	$-1.64 \cdot 10^{40}$	$-3.74 \cdot 10^{50}$	$7.74 \cdot 10^{14}$	4107.8	6.66
HF	4138	$2.44 \cdot 10^{-11}$	$-1.79 \cdot 10^{40}$	$-5.67 \cdot 10^{50}$	$7.62 \cdot 10^{14}$	4047.6	2.19
LiF	911	$1.76 \cdot 10^{-11}$	$-7.69 \cdot 10^{38}$	$-1.41 \cdot 10^{49}$	$1.78 \cdot 10^{14}$	946.7	3.92
N ₂	2359	$2.27 \cdot 10^{-11}$	$-6.25 \cdot 10^{40}$	$-2.09 \cdot 10^{50}$	$4.48 \cdot 10^{14}$	2377.1	0.77
CO	2170	$2.16 \cdot 10^{-11}$	$-5.42 \cdot 10^{39}$	$-1.73 \cdot 10^{50}$	$4.19 \cdot 10^{14}$	2224.5	2.51

The plots of potential versus internuclear distance for the molecules are compared to the data obtained by digitizing the potential curves generated by a Hartree-Fock based theoretical electron correlation calculation (Piris 2017). The plots for each molecule match the data well near the bond length as well as for distances less than the bond length. However, the model potential (Equation (12)) approaches V_{inf} much more slowly than the data. The plots of potential versus internuclear distance for dihydrogen, as an example, are shown in Figure 4. This plot shows the model potential modified only by adding V_{inf} , the model potential with V_{inf} and x_s , and the quartic approximation of the model used to calculate the corrected wavenumber superimposed on the data. This plot also shows the Lennard-Jones potential applied to the dihydrogen molecule to show that it is a poor representation of the potential between the atoms within a diatomic molecule.

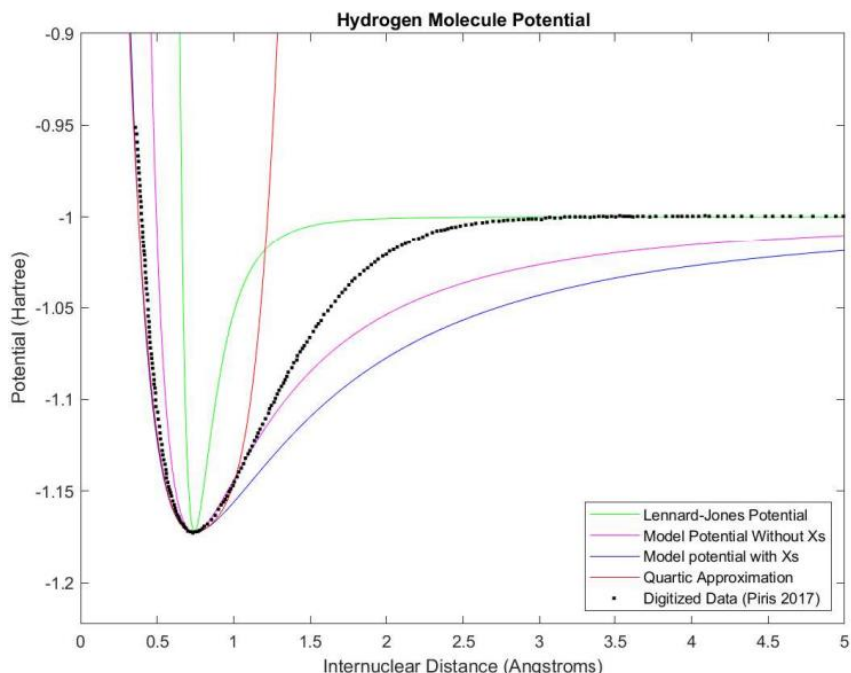


Figure 4. Plots of potential for dihydrogen generated by the model potential (Equation (2)) with the V_{inf} correction, the model with x_s (Equation (3)), the quartic approximation used to calculate the wavenumber (Equation (28)), and the Lennard-Jones potential (Equation (1)) with the V_{inf} correction superimposed on the digitized data (Piris 2017).

DISCUSSION

The purpose of this project is to test the accuracy of the diatomic molecule model potential (Timberlake and Hasbun 2008; Hasbun 2009). With the modifications of adding the potential for a large internuclear distance (V_{inf}) and the parameter x_s improved the model potential so that it better fits the data. This data is obtained by digitizing the potential curves generated using a Hartree-Fock based theoretical electron correlation calculation (Piris 2017). Applying the method of successive approximations to the modified model potential, we calculated the wavenumbers of the molecules H_2 , HF, LiF, N_2 , and CO to within seven percent of the experimental values (Piris 2017). To use the method of successive approximations, we calculated the values of the parameter A_1 for each molecule based on the experimental wavenumbers, then used the average to calculate the theoretical wavenumber. The calculated wavenumbers can possibly be improved by using the method of successive approximations for a higher order Taylor expansion of the model potential as well as by performing further iterations of the method. Furthermore, by deriving the formula for A_1 in terms of the initial conditions, one could use the values for A_1 to calculate the amplitude of the molecules' oscillations. Finally, for the purpose of the interested reader, we have included the MATLAB script that reproduces the above potential curves and prints the parameters and calculated values.

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APPENDIX A

```

% Potential_Calculator.m (11/2022) By Dorien Carpenter and J. Hasbun
% This uses the known parameters of a diatomic molecule to calculate the
% potential curve of the two atoms using the 3-2 potential (Hasbun 2009).
% The wavenumber of the molecule is calculated using a quadratic
% approximation of the potential and using the method of successive
% approximations to obtain a more accurate wavenumber from the quartic
% approximation of the potential. A plot of potential vs. internuclear
% distance is created comparing the model potential, the model potential
% with xs and its quartic approximation, and the Lennard-Jones potential to
% the digitized experimental data (Piris 2017).
% References
% Piris, M. 2017. Global Method for Electron Correlation. Physical Review
% Letters.119(6),063002
% Hasbun, J.E. 2009. Classical Mechanics with MATLAB Applications, 1st
% Ed.(Jones and Bartlet Publishers,LLC, Sadbury, Massachusetts)
clear;

% Parameters obtained from Piris for hydrogen
Vmin=-1.172455;    % minimum of potential (hartree) (Piris 2017)
Vinf=-1;          % potential at infinite distance (hartree) (Piris 2017)
Xb=0.743;         % Bond Length, distance at Vmin(angstroms) (Piris 2017)
X0=0.3778;       % internuclear distance less than Xb at which the
                 % potential equals Vinf (angstroms) (Piris 2017)
Nexp=4401;       % experimental wavenumber (1/cm) (Piris 2017)

% Data from potential plot of Hydrogen molecule (Piris 2017)
X_angstrom = [0.357853,0.366799,0.369781,0.372763,0.375746,0.378728,...
              0.378728,0.38171,0.384692,0.387674,0.387674,0.390656,0.393638,...
              0.39662,0.39662,0.399602,0.402584,0.405567,0.405567,0.408549,...
              0.411531,0.414513,0.417495,0.420477,0.420477,0.423459,0.426441,...
              0.429423,0.429423,0.435388,0.43837,0.441352,0.441352,0.447316,...
              0.447316,0.450298,0.450298,0.45328,0.456262,0.462227,0.465209,...
              0.468191,0.471173,0.477137,0.480119,0.480119,0.486083,0.489066,...
              0.489066,0.492048,0.503976,0.506958,0.515905,0.518887,0.521869,...
              0.530815,0.533797,0.536779,0.542744,0.55169,0.557654,0.560636,...
              0.560636,0.569583,0.575547,0.581511,0.587475,0.593439,0.602386,...
              0.611332,0.617296,0.62326,0.632207,0.641153,0.647117,0.656064,...
              0.670974,0.676938,0.688867,0.700795,0.718688,0.733598,0.742545,...
              0.757455,0.769384,0.781312,0.796223,0.808151,0.829026,0.855865,...
              0.879722,0.900596,0.918489,0.9334,0.945328,0.957256,0.969185,...
              0.981113,0.996024,1.00497,1.022863,1.034791,1.049702,1.064612,...
              1.076541,1.094433,1.106362,1.121272,1.136183,1.151093,1.16004,...
              1.171968,1.189861,1.207753,1.228628,1.234592,1.246521,1.264414,...
              1.27336,1.285288,1.297217,1.312127,1.327038,1.335984,1.347913,...
              1.356859,1.380716,1.392644,1.413519,1.416501,1.434394,1.449304,...
              1.461233,1.479125,1.497018,1.520875,1.538767,1.553678,1.571571,...
              1.589463,1.616302,1.637177,1.664016,1.687873,1.708748,1.729622,...
              1.753479,1.774354,1.792247,1.82505,1.851889,1.875746,1.899602,...
              1.923459,1.944334,1.974155,1.998012,2.018887,2.045726,2.069583,...
              2.099404,2.12326,2.147117,2.176938,2.209742,2.236581,2.263419,...
              2.299205,2.329026,2.355865,2.379722,2.400596,2.424453,2.451292,...

```

```

2.481113,2.516899,2.555666,2.582505,2.627237,2.657058,2.695825,...
2.734592,2.764414,2.791252,2.827038,2.862823,2.895626,2.925447,...
2.949304,2.976143,3.011928,3.038767,3.065606,3.09841,3.137177,...
3.164016,3.196819,3.232604,3.265408,3.295229,3.331014,3.363817,...
3.393638,3.423459,3.447316,3.477137,3.503976,3.530815,3.554672,...
3.575547,3.596421,3.617296,3.647117,3.682903,3.727634,3.766402,...
3.832008,3.87674,3.909543,3.936382,3.972167,4.007952,4.04672,...
4.088469,4.115308,4.171968,4.2167,4.270378,4.327038,4.392644,...
4.482107,4.529821,4.595427,4.643141,4.714712,4.792247,4.878728,...
4.941352,4.992048];

```

```

Y_hartree=[-0.951196,-0.954785,-0.95927,-0.963158,-0.966746,-0.969737,...
-0.973325,-0.976017,-0.979605,-0.982895,-0.985885,-0.988876,...
-0.991567,-0.994557,-0.998146,-1.001734,-1.005024,-1.008313,...
-1.011005,-1.013995,-1.016388,-1.019079,-1.021172,-1.024163,...
-1.027153,-1.030742,-1.034031,-1.036423,-1.039713,-1.042703,...
-1.045993,-1.051077,-1.054665,-1.057656,-1.060646,-1.063337,...
-1.066029,-1.069019,-1.07201,-1.075299,-1.077691,-1.080383,...
-1.083074,-1.086364,-1.089354,-1.091746,-1.09384,-1.096531,...
-1.100419,-1.104007,-1.106998,-1.110885,-1.114773,-1.118361,...
-1.121651,-1.124641,-1.127931,-1.130323,-1.133014,-1.135407,...
-1.138397,-1.14049,-1.142883,-1.145275,-1.147667,-1.149462,...
-1.150957,-1.152751,-1.155443,-1.157536,-1.15933,-1.161124,...
-1.162919,-1.164115,-1.16561,-1.167105,-1.168002,-1.169498,...
-1.170395,-1.17189,-1.172189,-1.172787,-1.172189,-1.172189,...
-1.17189,-1.171292,-1.170395,-1.169199,-1.168002,-1.16561,...
-1.163218,-1.159928,-1.157536,-1.156041,-1.154545,-1.152751,...
-1.150359,-1.148864,-1.147069,-1.144976,-1.142285,-1.139593,...
-1.1375,-1.135108,-1.132117,-1.129725,-1.127931,-1.125538,...
-1.122548,-1.120455,-1.118361,-1.116268,-1.113577,-1.110586,...
-1.107596,-1.105203,-1.103409,-1.101615,-1.099522,-1.097129,...
-1.095036,-1.092943,-1.091148,-1.089354,-1.08756,-1.085167,...
-1.082775,-1.080084,-1.078589,-1.076196,-1.074103,-1.072309,...
-1.070813,-1.06872,-1.066328,-1.063038,-1.060347,-1.058852,...
-1.057057,-1.053768,-1.051675,-1.049282,-1.046591,-1.0439,...
-1.041806,-1.040012,-1.03762,-1.035526,-1.034031,-1.031938,...
-1.029844,-1.028349,-1.026555,-1.02506,-1.023565,-1.02177,...
-1.020873,-1.019079,-1.018182,-1.016986,-1.015789,-1.014892,...
-1.013995,-1.0125,-1.011902,-1.011005,-1.009809,-1.008612,...
-1.007715,-1.007416,-1.007117,-1.006519,-1.005921,-1.005622,...
-1.005024,-1.004426,-1.004127,-1.003529,-1.00323,-1.002931,...
-1.002333,-1.002333,-1.002033,-1.001734,-1.001734,-1.001435,...
-1.001435,-1.001136,-1.001136,-1.001136,-1.001435,-1.000538,...
-1.000239,-1.000538,-1.000538,-0.99994,-0.99994,-0.99994,...
-0.99994,-0.99994,-1.000239,-0.99994,-0.999641,-0.999641,...
-0.99994,-0.999641,-0.99994,-0.999342,-0.999641,-0.999641,...
-0.999641,-0.99994,-0.999641,-0.999641,-0.99994,-0.999641,...
-0.999641,-0.999641,-0.999641,-0.999641,-0.999641,-0.999641,...
-0.999641,-0.999342,-0.999641,-0.999641,-0.999641,-0.999641,...
-0.999641,-0.999641,-0.999641,-0.999641,-0.999641,-0.999641,...
-0.999641,-0.999641,-0.999641,-0.999641,-0.999641];

```

```
% Known Parameters
```

```

C=3*10^(8);           % speed of light (m/s) (Hasbun 2009)
m1=1.007947;         % mass of atom 1 (amu)

```



```

m2=1.007947;           % mass of atom 2 (amu)
M=m1*m2/(m1+m2);     % reduced mass of the molecule (amu)
A1=2.9133*10^(-11);  % A1 parameter for the molecule

% Conversion factors
m_to_cm=100;          % conversion from meters to centimeters
h_to_J=4.35975.*10.^(-18); % conversion from hartree to Joule
A_to_m=10.^(-10);    % conversion from angstrom to meter
U_to_Kg=1.6605402*10.^(-27); % conversion from atomic mass unit to kg

% Conversion of units
c=C*m_to_cm;         % Speed of light in cm/s

VminJ=Vmin*h_to_J;   % Convert potentials to Joules
VinfJ=Vinf*h_to_J;

Xbm=Xb*A_to_m;       % Convert distances to meters
X0m=X0*A_to_m;

MKg=M*U_to_Kg;       % Convert mass to Kg

% Quadratic Approximation
Xs = 3*X0-2*Xb;       % calculate Xs in angstroms
Xsm = Xs*A_to_m;     % calculate Xs in meters
A = -2*((Xbm-Xsm)^3)*(VminJ-VinfJ); % calculate parameters A and B
B = -3*((Xbm-Xsm)^2)*(VminJ-VinfJ);

k=(32*B^5)/(81*A^4); % Effective spring constant
w_quad=sqrt(k/MKg);  % Frequency of oscillation (rad/s)
f=w_quad/(2*pi);     % Frequency converted to Hz
n_quad=f/c;          % Wavenumber (1/lamda; 1/cm)
err_quad=100*abs(n_quad-Nexp)/Nexp; % Percent error for quad approx

% Method of Successive Approximation
a3=(120*B/((Xbm-Xsm)^6)-360*A/((Xbm-Xsm)^7))/(6*MKg); % a3 for correction
w_correction=w_quad*sqrt(1-((A1.^2)*(3*a3)/(4*w_quad^2))); % corr ang freq
n_correction=w_correction/(2*pi*c); % corrected wavenumber
err_correction=100*abs(n_correction-Nexp)/Nexp; % percent error

% Lennard-Jones Potential Model
Alj=2.*(Xbm.^6).*(VinfJ-VminJ); % a and b for Lennard-Jones model
Blj=(Xbm.^12).*(VinfJ-VminJ);
klj=156.*Blj.*(Xbm.^(-14))-42.*Alj.*(Xbm.^(-8)); % eff spring cnst
wlj=sqrt(klj./M); % angular frequency
nlj=wlj./(2*pi*c); % wavenumber
errlj=100.*abs(nlj-Nexp)./Nexp; % percent error
Aplotlj=2.*(Xb.^6).*(Vinf-Vmin); % a and b for Lennard-Jones plot
Bplotlj=(Xb.^12).*(Vinf-Vmin);
vlj=Bplotlj./(X_angstrom.^12)-Aplotlj./(X_angstrom.^6)+Vinf; % Potential
figure
plot(X_angstrom,vlj,'g')
hold on

% Model potential without Xs for plotting
A_noXs=2.*(Xb.^3).*(Vinf-Vmin); % A & B for model without Xs

```



```

B_noXs=3.*(Xb.^2).*(Vinf-Vmin);
V_3_2 = A_noXs./(X_angstrom.^3)-B_noXs./(X_angstrom.^2)+Vinf; % Potential
plot(X_angstrom,V_3_2,'m') % plot calculated potential

% Model potential with Xs for plotting
x_plot=[0:0.01:5]; % generate x values for plot
a_hA3 = -2*((Xb-Xs)^3)*(Vmin-Vinf); % a and b in units for plotting
b_hA2 = -3*((Xb-Xs)^2)*(Vmin-Vinf);
v_plot = a_hA3./((x_plot-Xs).^3)-b_hA2./((x_plot-Xs).^2)+Vinf; % Potential
plot(x_plot,v_plot,'b') % plot calculated potential curve
ylim([Vmin-0.05 Vinf+0.1]); % set y limits for best view of plot
xlabel('Internuclear Distance (Angstroms)');
ylabel('Potential (Hartree)');

% Quartic approximation of potential
X_m = x_plot.*A_to_m; % convert x values to meters
a1V = (32*B.^5)./(81*A.^4); % coefficients of pot. taylor series
a2V = (-512*B.^6)./(243*A.^5);
a3V = (2560*B.^7)./(243*A.^6);
V_Approx = VminJ + (1/2)*a1V*(X_m-Xbm).^2 + (1/6)*a2V*(X_m-Xbm).^3 + ...
(1/12)*a3V*(X_m-Xbm).^4; % calculate potential at each x value
V_Approx_hartree = V_Approx./h_to_J; % convert from Joule to hartree
plot(x_plot,V_Approx_hartree,'r') % plot quartic potential

% calculate coefficients of taylor series of force
w0_squared = a1V/MKg;
a2 = a2V/(2*MKg);
a3 = a3V/(6*MKg);

% plot data from (Piris 2017)
plot(X_angstrom,Y_hartree,'k.')
title('Hydrogen Molecule Potential');
legend('Lennard-Jones Potential','Model Potential Without Xs',...
'Model potential with Xs','Quartic Approximation',...
'Digitized Data (Piris 2017)',Location='southeast')

% Print results of calculations
format_1a = 'Parameters:\n Xb = %5.4E angstroms\n X0 = %5.4E angstroms\n';
format_1b = ' Vmin = %5.4E hartree\n Vinf = %5.4E hartree\n';
format_1c = ' Xs = %5.4E angstroms\n A = %5.4E hartree*angstrom^3\n';
format_1d = ' B = %5.4E hartree*angstrom^2\n w0^2 = %5.4E (rad/s)^2\n';
format_1e = ' a2 = %5.4E (m^-1)(s^-2)\n a3 = %5.4E (m*s)^-2\n\n';
format1=strcat(format_1a,format_1b,format_1c,format_1d,format_1e);
fprintf(format1,Xb,X0,Vmin,Vinf,Xs,a_hA3,b_hA2,w0_squared,a2,a3);
format_2a = 'Results:\n Calculated Frequency: %5.4E rad/s \n';
format_2b = 'Calculated Wavenumber: %5.4E cm-1 \n\t\t';
format_2c = 'Percent Error: %2.4f \n\n Corrected Frequency: %5.4E rad/s';
format_2d = ' \n Corrected Wavenumber: %5.4E cm-1 \n\t\t';
format_2e = 'Percent Error: %2.4f\n';
format2=strcat(format_2a,format_2b,format_2c,format_2d,format_2e);
fprintf(format2,w_quad,n_quad,err_quad,w_correction,n_correction,...
err_correction);

```