Numerical solution to the time-independent Schrödinger equation for HCl in a Morse potential using finite difference

Jackson Sheppard

Chemistry Department, University of California, Santa Barbara, CA 93106-9530

(Dated: February 8, 2022)

Abstract

Here we present a numerical solution to the time-independent Schrödinger equation for the diatomic molecule HCl in a Morse potential well using the method of finite difference to calculate the energy eigenvalues and corresponding eigenstates in r-coordinate space, where r is the interatomic separation between the hydrogen and chlorine atoms. This method considers the continuous radial coordinate r as an evenly spaced grid of n points and approximates the derivative of the function $f(r)$ as $\Delta f/\Delta r$. In doing so, one can solve the eigenvalue equation $HU(r) = EU(r)$ as a discrete problem yielding n energy eigenvalues $\{E_n\}$ and n eigenvectors $\{U_n(r)\}$, each evaluated at the n radial coordinates. Implementing these methods for HCl using Python yields a ground state energy $E_0 = -4.434$ eV, in excellent agreement with that found from the analytical solution to this differential equation.

INTRODUCTION

The Morse potential $V(r)$, first introduced by Philip M. Morse, describes the interaction between atoms in a diatomic molecule and can be thought of as the energy stored in the bond as function of atomic separation r. This potential energy takes the form of an anharmonic oscillator with respect to r and thus has energy eigenvalues perturbed from that of the standard quantum harmonic oscillator. The Morse potential takes the form:

$$V(r) = D_e(1 - e^{-a(r-r_e)})^2 - D_e \tag{1}$$

Here D_e is the well-depth (the diatomic molecule dissociation energy), r_e is the equilibrium separation between the two atoms, and the parameter a is defined as $a = \sqrt{k_e/2D_e}$, where k_e is the spring force constant calculated at the minimum of the well $r = r_e$. We note that the offset of D_e is arbitrary and applied for mathematical convenience. One can then rewrite Eq. 1 as follows:

$$V(r) = D_e(e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}) \tag{2}$$

giving the functional form employed in this analysis.

The time-independent Schrödinger equation for the wave function $U(r)$ is then:

$$-\frac{\hbar^2}{2m}\frac{d^2U(r)}{dr^2} + V(r)U(r) = EU(r) \tag{3}$$

$$HU(r) = EU(r) \tag{4}$$

where $m = m_H m_{Cl}/(m_H + m_C l)$ is the reduced mass of HCl and $H = K + V$ is the Hamiltonian operator expressed as a sum of the kinetic energy $K = (-\hbar^2/2m)d^2/dr^2$ and Morse potential energy $V = V(r)$ terms.

Next we employ the method of finite difference by approximating the derivative of the wave function $U(r)$ evaluated at a discrete radial position r_i as follows:

$$\left.\frac{dU}{dr}\right|_{r=r_i} \approx \left.\frac{\Delta U}{\Delta r}\right|_{r=r_i} = \frac{U(r_{i+1}) - U(r_{i-1})}{r_{i+1} - r_{i-1}} = \frac{U_{i+1} - U_{i-1}}{2d} \tag{5}$$

where d is the incremental step size in r. To evaluate the second derivative, we consider the Taylor expansion of the continuous function $f(x)$ shifted by small amounts $+\Delta x$ and $-\Delta x$, giving:

$$f(x + \Delta x) \approx f(x) + \frac{df}{dx}\Delta x + \frac{1}{2}\frac{d^2f}{dx^2}\Delta x^2 \tag{6}$$

$$f(x - \Delta x) \approx f(x) - \frac{df}{dx}\Delta x + \frac{1}{2}\frac{d^2f}{dx^2}\Delta x^2 \tag{7}$$

Adding the two expressions above yields:

$$f(x + \Delta x) + f(x - \Delta x) \approx 2f(x) + \frac{d^2 f}{dx^2}\Delta x^2 \tag{8}$$

$$\frac{d^2 f}{dx^2} \approx \frac{f(x + \Delta x) - 2f(x) + f(x - \Delta x)}{\Delta x^2} \tag{9}$$

We can then translate the expression above to our discrete system allowing us to numerically calculate the value of $d^2 U/dr^2$ in the time-independent Schrödinger equation at each radial point in our grid. We thus have:

$$\left. \frac{d^2 U}{dr^2} \right|_{r=r_i} \approx \frac{U_{i+1} - 2U_i + U_{i-1}}{d^2} \tag{10}$$

Our next step in the method of finite difference is to insert the approximation of the second derivative in Eq. 10 into Eq. 3. In doing so, we consider the continuous functions $U(r)$ and $V(r)$ as discrete functions evaluated at each grid point i, where i ranges from 1 to n. This gives:

$$-\frac{\hbar^2}{2md^2}(U_{i+1} - 2U_i + U_{i-1}) + V_i U_i = EU_i \tag{11}$$

We can then rewrite Eq. 11 by noting the first and second terms include an n by n kinetic energy matrix K with 2 along the diagonal and -1 above and below the diagonal and an n by n diagonal potential energy matrix V with elements equal to the Morse potential $V(r)$ evaluated at each radial coordinate, respectively. Each multiplies an n-element column vector U whose entries are the wave function evaluated at each radial coordinate. This gives:

$$-\frac{\hbar^2}{2md^2} \begin{bmatrix} -2 & 1 & 0 & \dots & 0 \\ 1 & -2 & 1 & \dots & 0 \\ 0 & 1 & -2 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & 1 \\ 0 & 0 & 0 & \dots & -2 \end{bmatrix} \begin{bmatrix} U_1 \\ U_2 \\ U_3 \\ \vdots \\ U_n \end{bmatrix} + \begin{bmatrix} V_1 & 0 & 0 & 0 & \dots \\ 0 & V_2 & 0 & 0 & \dots \\ 0 & 0 & V_3 & 0 & \dots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & V_n \end{bmatrix} \begin{bmatrix} U_1 \\ U_2 \\ U_3 \\ \vdots \\ U_n \end{bmatrix} = E \begin{bmatrix} U_1 \\ U_2 \\ U_3 \\ \vdots \\ U_n \end{bmatrix} \tag{12}$$

Eq. 12 can then be written compactly as:

$$KU + VU = EU \tag{13}$$

$$(K + V)U = EU \tag{14}$$

$$HU = EU \tag{15}$$

The method of finite difference in the context of the time-independent Schrödinger equation therefore leads to the diagonalization of the Hamiltonian H in Eq. 15, where K and V

are defined in Eq. 12, to numerically determine the energy eigenvalues and corresponding eigenstates for HCl in a Morse potential.

METHODS

We complete the diagonalization of Eq. 15 and visualization of the corresponding energy states using Python. After initializing physical constants for HCl in a Morse potential $V(r)$, we use NumPy to define the discrete radial coordinate r in Å as a vector of 4000 evenly spaced steps from 10 nm to 10 Å. The potential energy is then calculated at each radial coordinate according to Eq. 2 and added to a matrix V following Eq. 12. We then build the kinetic energy matrix K with the grid spacing d defined as the difference between adjacent radial coordinates. Adding the matrices K and V yields the Hamiltonian H whose eigenvalues and eigenvectors are found using the SciPy function `eigh`. This yields the first 4000 energy levels and corresponding eigenstates (since H is an n by n matrix, where $n = 4000$) which we then visualize using Matplotlib.

Calculation Details

Physical constants for HCl in the Morse potential were taken from Elok Fidiani's "Modeling of diatomic molecule using the Morse potential and the Verlet algorithm". The remaining physical constants in Eq. 12 were taken from NIST by rewriting the constant $\hbar^2/2md^2$ as follows:

$$\frac{\hbar^2}{2md^2} = \frac{(\hbar c)^2}{2mc^2 d^2} \tag{16}$$

Where m is the reduced mass of the HCl diatomic system whose atomic masses are given in amu. These parameters are summarized in Table I and produce the plot of the corresponding Morse potential shown in Fig. 1. The full source code for replication of the following results is then accessible through GitHub at https://github.com/jsheppard95/Morse_Potential.

RESULTS

Applying the previously described method of finite difference to the diatomic molecule HCl with parameters shown in Table I yields a calculated ground state energy $E_0 = -4.434$

eV. This and the next six excited state energy levels are shown in Table II and displayed alongside the Morse potential in Fig. 2 and Fig. 3, the latter of which includes higher energy levels closer to the dissociation energy. We then compare the energy levels calculated using finite difference to those found using the following analytical result:

$$E_n = h\nu_0(n + 1/2) - \frac{[h\nu_0(n + 1/2)]^2}{4D_e} \tag{17}$$

$$\nu_0 = \frac{a}{2\pi}\sqrt{\frac{2D_e}{m}} \tag{18}$$

$$\implies h\nu_0 = a\hbar c\sqrt{\frac{2D_e}{mc^2}} \tag{19}$$

Note that we must subtract the constant energy offset D_e from each analytically calculated energy level since $E = 0$ is defined as the minimum of the Morse well for the analytical solution as opposed to the dissociation energy D_e as was defined in this numerical calculation. Here we see that low energy levels have roughly even spacing, agreeing with that of the traditional quantum harmonic oscillator. It is only at higher energy level that anharmonic effects have a noticeable perturbation on the energy level spacing.

We next extract the eigenstates of this spectral analysis and normalize those of the first three energy levels for visualization of the corresponding probability distributions, the results of which are shown in Fig. 4. Here we see similar results to that of the traditional quantum harmonic oscillator, in which the ground state has interatomic separation close to the equilibrium value with highest probability. Multiple separations of high probability then develop and shift from the equilibrium separation as n increases.

Finally, we find the interatomic separation probability distribution for the first eigenstate with calculated energy greater than the dissociation energy D_e. We find this to be the $n = 142$ state with energy $E_{142} = 4.65$ eV (slightly greater than $D_e = 4.618$ eV) and show the corresponding probability distribution in Fig. 5. Here we see unstable oscillations with high probability of zero-potential energy separations, indicating that dissociation of the diatomic molecule can occur.

CONCLUSION AND FURTHER ANALYSIS

We have thus presented a spectral decomposition of the diatomic molecule HCl in a Morse potential $V(r)$ shown in Eq. 2. We determine the ground state energy of this system to be

5

$E_0 = -4.434$ eV and display the next six excited state energy levels in Table II. Here we see excellent agreement between the energy levels determined by finite difference and analytical methods. Fig. 2 shows that low energy levels are roughly equally spaced, agreeing with the result of the traditional quantum harmonic oscillator, while Fig. 3 shows higher energy states are more closely separated due to anharmonic effects. This is also shown in Fig. 5 by unstable oscillations in this high-energy wave function leading to dissociation.

Considering future work, one could first optimize the calculation by considering only $r \leq 5$ Å, beyond which $V(r) \to 0$. In addition, one could develop a more quantitative comparison between the energy levels of the Morse potential to those of the traditional quantum harmonic oscillator by numerically calculating successive energy level differences and comparing to those determined by anharmonicity constants of the HCl system. Further, one could consider the time evolution of this system using the time evolution operator $U = \exp\left(-iHt/\hbar\right)$, where H is the discrete Hamiltonian calculated using finite difference. Finally, it would be interesting to perform a molecular dynamics simulation by considering the system classically and applying the Verlet algorithm in which the force acting on each atom is calculated as $F = -dV/dr$ and the atomic positions are computed by solving Newton's equation. This would allow for the use molecular dynamics software to visualize molecular motion at low energy states and those near the dissociation energy where bonds can break from unstable oscillations.

REFERENCES

[1] Srnec MN, Upadhyay S, Madura JD. 2017. A Python Program for Solving Schrodinger's Equation in Undergraduate Physical Chemistry. J Chem Educ. 94:813-814

[2] Pulliam T.H. Matrix Form of Finite Difference Schemes. NASA Ames. 2018; [accessed 2022 Feb 6].

https://www.nas.nasa.gov/assets/pdf/ams/2018/introtocfd/Intro2CFD_Lecture2_Pulliam_Matrix_ODE.pdf.

[3] Fidiani E. Modeling of diatomic molecule using the Morse potential and the Verlet algorithm. AIP Conference Proceedings 1719, 030001 (2016); https://doi.org/10.1063/1.4943696. Published Online: 11 March 2016.

[4] reduced Planck constant times c in MeV fm. The NIST Reference on Constants, Units, and Uncertainty; [accessed 2022 Feb 6]. https://physics.nist.gov/cgi-bin/cuu/Value?hbcmevf.

[5] Conversion from u to eV. The NIST Reference on Constants, Units, and Uncertainty; [accessed 2022 Feb 6]. https://physics.nist.gov/cgi-bin/cuu/Convert?exp=0num=1From=uTo=evAction=Convert+value+and+show+factor.
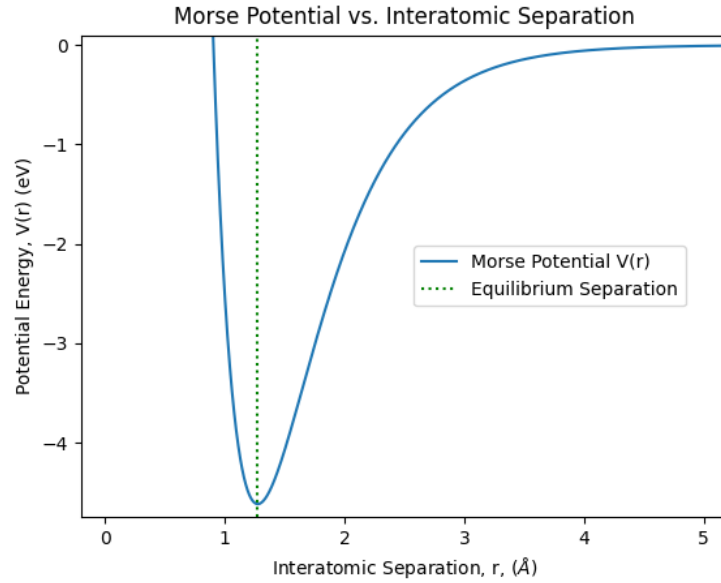
FIGURES

FIG. 1.   Plot of the Morse potential $V(r)$ in eV for the diatomic molecule HCl versus the interatomic separation r in Å, centered on the region surrounding the equilibrium separation r_e.
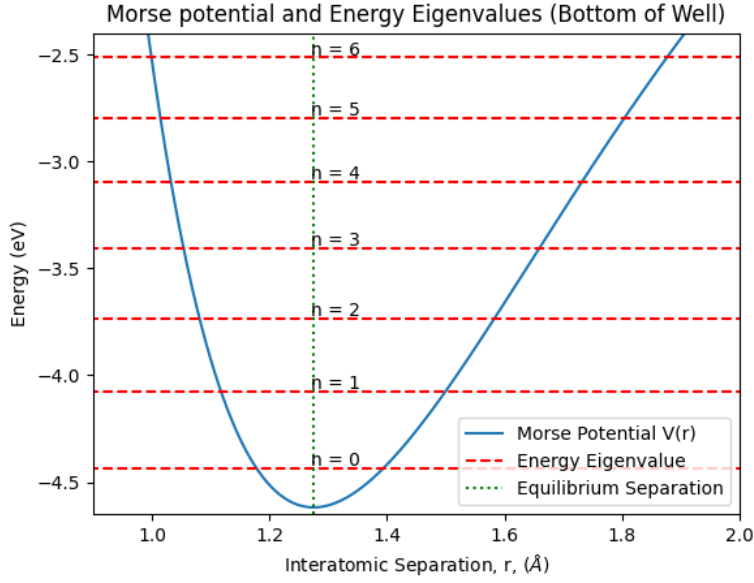
FIG. 2.   Plot of the first seven energy levels alongside the Morse potential $V(r)$ in eV for the diatomic molecule HCl versus the interatomic separation r in Å calculated using finite difference.
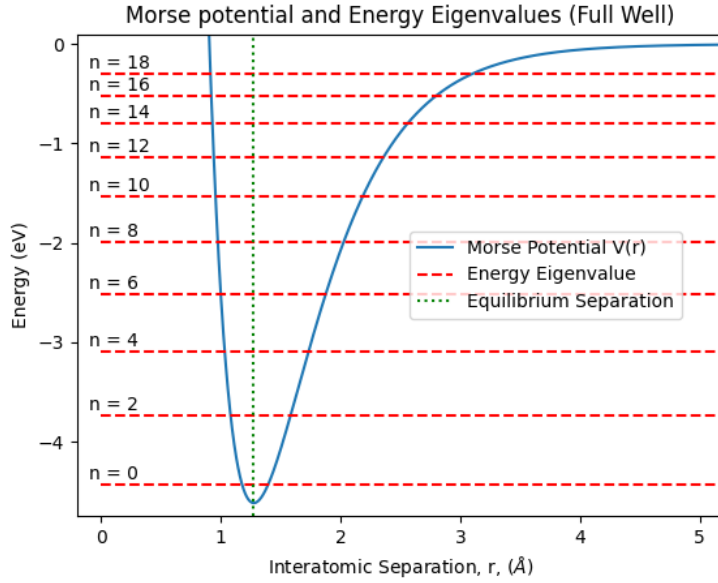

FIG. 3.   Plot of higher energy levels alongside the Morse potential $V(r)$ in eV for the diatomic molecule HCl versus the interatomic separation r. Here we see anharmonic effects developing at higher energy levels with the separation between adjacent levels decreasing as n increases.
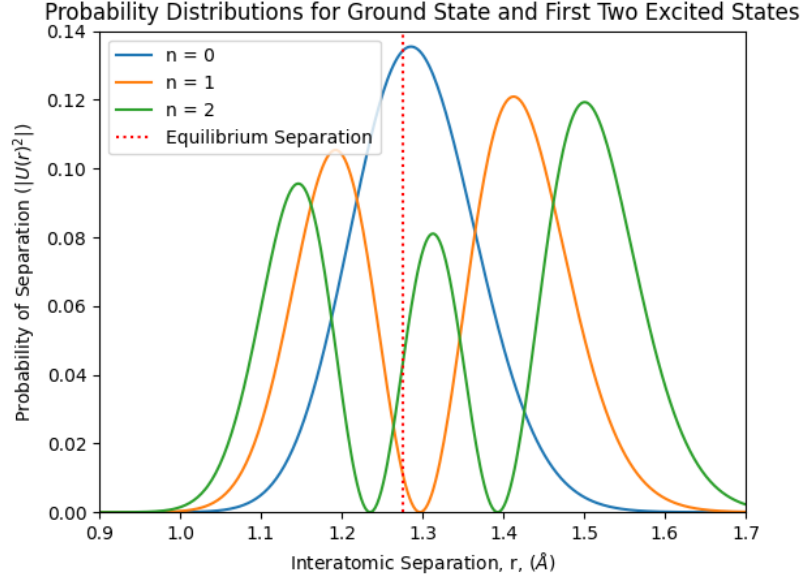
FIG. 4.   Plot of probability distributions for the lowest three energy eigenstates $U_0(r)$, $U_1(r)$, and $U_2(r)$ of HCl in the Morse potential. Here we see modest deviations from the result of the traditional quantum harmonic oscillator.
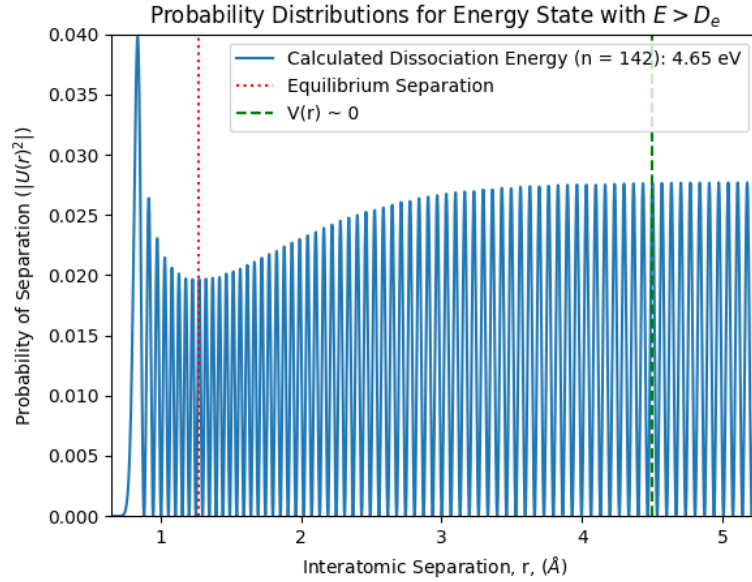

FIG. 5.   Plot of the probability distribution for the $n = 142$ eigenstate $U_{142}(r)$ of HCl in the Morse potential with energy $E_{142} = 4.65$ eV, just over the dissociation energy $D_e = 4.618$ eV. The equilibrium separation along with the separation beyond which the potential energy approaches zero are shown by the dotted red and dashed green lines, respectively.

9

TABLES

TABLE I. Morse potential physical constants for the diatomic molecule HCl.

Parameter	Value	Unit
Dissociation Energy, D_e	4.618	eV
a	1.869	Å
Equilibrium Separation, r_e	1.275	Å
$\hbar c$	1973	eVÅ
Mass of Hydrogen, m_H	1	amu
Mass of Chlorine, m_{Cl}	35	amu
Conversion Factor amu/(eV/c^2)	931.49432×10^6	1

TABLE II. First seven energy levels for the diatomic molecule HCl calculated using finite difference and analytical methods.

Energy Level, n	Numerical Value (eV)	Analytical Value (eV)
0	-4.43368	-4.43367
1	-4.07632	-4.07629
2	-3.73399	-3.73393
3	-3.40670	-3.40657
4	-3.09442	-3.09424
5	-2.79717	-2.79692
6	-2.51494	-2.51461