



CHEM 548: Advanced Electronic Structure

Project #1 Report

Course Instructor

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by

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1 Abstract

This report presents a discussion on using the finite difference method for solving bound systems with arbitrary potentials. It also provides a demonstration of a simulated vibrational progression for 2 displaced potential surfaces.

2 Questions

1. Write a program that solves the one-dimensional Schrödinger equation for an arbitrary bound potential using a finite-difference method.
2. Solve the particle in a box problem numerically with this program and compare the results with the analytical solutions. Plot the wave functions if possible.
3. Solve the particle in a finite depth well problem. Examine the degree of permeation of wave functions into the wall.
4. Solve the particle in a box problem with a rectangular barrier in the middle. Observe the tunneling splitting of energies.
5. Solve the harmonic and Morse oscillator problems. Compute Franck–Condon factors across two (displaced) potentials and simulate a vibrational progression in an electronic absorption spectrum.

3 1D Schrodinger Equation

The basic crux of quantum mechanics involves solving the schrodinger equation. The 1 Dimensional Schrodinger equation is given as follows:

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \quad (1)$$

However, we can write the time independent schrodinger equation for stationery states:

$$\hat{H} |\Psi(x)\rangle = E |\Psi(x)\rangle \quad (2)$$

Where \hat{H} is the hamiltonian, which is expressed as the sum of the kinetic energy and potential energy operators. Solving this equation gives us the stationery eigenstates of the system, along with their energies.

4 Finite-Difference Method

The schrodinger equation can be solved analytically for only a few small systems, and numerical solutions are often required to solve the equation.

The finite-difference method is a numerical method used to discretise the position into a grid made of discrete grid-points, converting the differential equation into a set of linear equations. This system of equations can be readily solved by computers to provide approximate solutions.

A function $f(x)$ can be represented by it's taylor series:

$$f(x + h) = f(x) + hf'(x) + O(h^2), \quad (3)$$

where we truncate after the first derivative.

The derivative of a function $f(x)$ at a point x is defined by rearranging the above equation

$$\lim_{h \rightarrow 0} \frac{f(x + h) - f(x)}{h} - f'(x) = O(h) \quad (4)$$

This gives us a "first order" approximation to the first derivative of a funtion.

WE can find the exact derivative by taking an infintely small h , but in practice, our computers cannot have infinite precision, so we must resort to using numerical approximations.

We can convert our domain into a grid, and we can convert our continuous wavefunction into a discrete wavefunction. Therefore, our h gets converted to Δx where, Δx is the unit length, or the distance between point x_i and point x_{i+1} on the grid. The function has values $f(x_i)$ and $f(x_{i+1})$ at those points respectively.

If $h > 0$, $h = \Delta x$, we get the *forward difference approximation*:

$$f'(x) = \frac{f(x + \Delta x) - f(x)}{\Delta x} + O(\Delta x) \quad (5)$$

Similary, for $h < 0$, $h = -\Delta x$, we get the *backward difference approximation*:

$$f'(x) = \frac{f(x) - f(x - \Delta x)}{\Delta x} + O(\Delta x) \quad (6)$$

We can get an even better approximation by combining both forward and backward difference terms.

Expaning the taylor series around $x + \Delta x$ and $x - \Delta x$ and combining them gives us the *centered difference* approximation.

$$f(x + \Delta x) = f(x) + \Delta x f'(x) + \frac{\Delta x^2}{2!} f''(x) + O(\Delta x^3) \quad (7)$$

$$f(x - \Delta x) = f(x) - \Delta x f'(x) + \frac{\Delta x^2}{2!} f''(x) - O(\Delta x^3) \quad (8)$$

Subtracting the 2 equations and rearranging, we get

$$\frac{f(x + \Delta x) - f(x - \Delta x)}{2\Delta x} - f'(x) = O(\Delta x^2) \quad (9)$$

The error here is now proportional to Δx^2 , and is thus reduced.

The hamiltonian contains a double derivative:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (10)$$

Using the same Taylor expansions, and adding the 2 equations instead, we can get the second-order centered difference approximation of the second derivative:

$$\frac{f(x + \Delta x) - 2f(x) + f(x - \Delta x)}{\Delta x^2} - f''(x) = O(\Delta x^2) \quad (11)$$

Using the grid we defined previously, the i^{th} point on the grid is x_i , therefore $x - \Delta x$ becomes x_{i-1} , and $x + \Delta x$ becomes x_{i+1} . The wavefunction $\Psi(x)$ can be represented by $\Psi(x_i)$ and x_i .

Rewriting the kinetic energy operator by its approximation, we can write it as:

$$\nabla^2\Psi(x) = \frac{\Psi(x + \Delta x) - 2\Psi(x) + \Psi(x - \Delta x)}{2\Delta x^2} = \frac{\Psi(x_{i+1}) - \Psi(x) + \Psi(x_{i-1}))}{2\Delta x^2} \quad (12)$$

The Schrodinger equation thus becomes:

$$\left(\frac{-\hbar^2}{2m}\right)\frac{\Psi(x_{i+1}) - \Psi(x) + \Psi(x_{i-1}))}{2\Delta x^2} + V(x_i)\Psi(x_i) = E\Psi(x_i) \quad (13)$$

This can be converted into system of equations, which can be represented by a matrix equation:

$$-\frac{\hbar^2}{2m\Delta x^2} \begin{bmatrix} -2 & 1 & 0 & \cdots & 0 \\ 1 & -2 & 1 & \cdots & 0 \\ 0 & 1 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & -2 & 1 \\ 0 & \cdots & 0 & 1 & -2 \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_{n-1} \\ \Psi_n \end{bmatrix} + \begin{bmatrix} V_1 & 0 & \cdots & 0 \\ 0 & V_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & V_n \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_{n-1} \\ \Psi_n \end{bmatrix} = E \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_{n-1} \\ \Psi_n \end{bmatrix}$$

This is the same as a the eigenvalue equation:

$$A\Psi = E\Psi \quad (14)$$

Where A is our hamiltonian operator.

Here, n is the number of points in the grid we choose, the higher the n, the closer the approximation is to the analytical value.

We can solve this equation by diagonalising the hamiltonian and getting our eigenvectors and eigenvalues.

5 Calculation Parameters and System Details

The assignment was done in python, with the numpy library being used for matrix calculations, and matplotlib library being used for plotting results.

A box of length **20** Angstrom was used, with a potential barrier of 8 eV being used in the finite well and rectangular barrier.

The arbitrary potential well was a right angle triangle well, starting from **-L** at **0eV** to **+L** at **8eV**, it is similar to a particle being in a constant electric field.

The value of omega used for the harmonic well was **2.5e15**.

The values for morse potential well were as follows:

dissociation energy = **8 eV**

morse width = **0.2**

displacement = **5 Angstrom**

6 Code and Implementation

The code is available on [Github](#)

7 Arbitrary bound potential using a finite-difference method

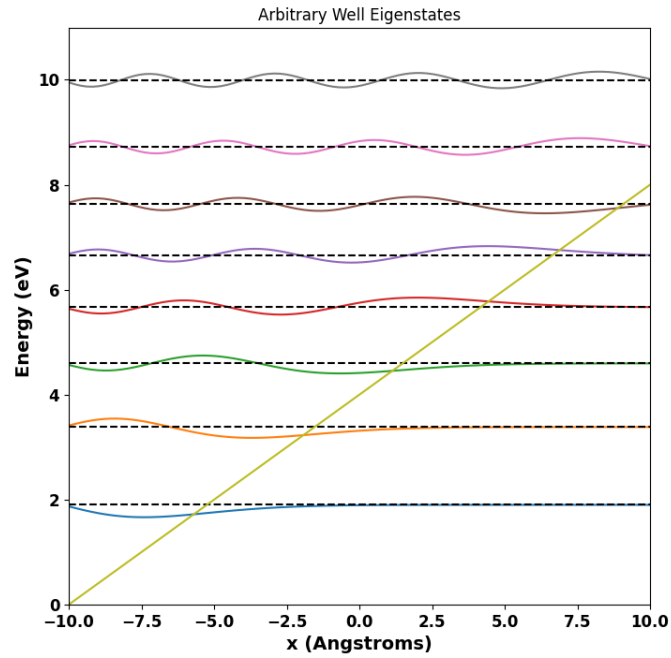


Figure 1: Arbitrary triangle potential and Eigenstates

	Energy(eV)
1	1.90098507
2	3.38324031
3	4.59618985
4	5.66801282
5	6.65429413
6	7.62986534
7	8.71664917
8	9.98880987

Table 1: Energy levels and their corresponding energy values in eV.

8 Free Particle in a box Solutions

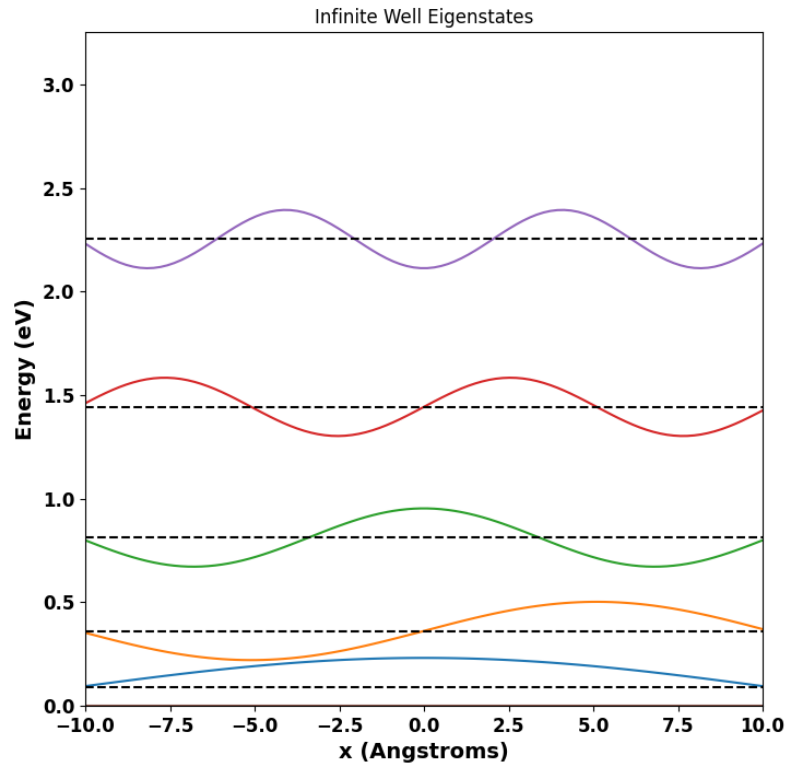


Figure 2: Eigenstates of a particle in an infinite well

The analytical solution to the particle in an infinite well is given by:

$$E_n = \frac{n^2 h^2}{8ml^2} \quad (15)$$

Comparing energy values obtained by finite difference method with analytical solution:

As we can see in Figure 3, the finite-difference method does approximate lower energy levels to an acceptable degree, but the error drastically increases with increasing energy levels.

	Finite Difference (eV)	Analytical (eV)
1	0.09031405	0.09400754
2	0.36116882	0.37603015
3	0.81230227	0.84606784
4	1.44327797	1.50412061
5	2.25348549	2.35018845
6	3.24214099	3.38427136
7	4.40828803	4.60636936
8	5.75079843	6.01648242
9	7.26837340	7.61461057
10	8.95954478	9.40075379

Table 2: Comparison of finite difference and analytical energy values (eV).

Grid Points	Deviation
100	0.0036934907429467256356759
500	0.0007493666459807701851759
1000	0.0003753560709318232158083
2000	0.0001878464633337240119459
5000	0.0000751791736073176286581

Table 3: Deviation from the analytical solution for different grid sizes.

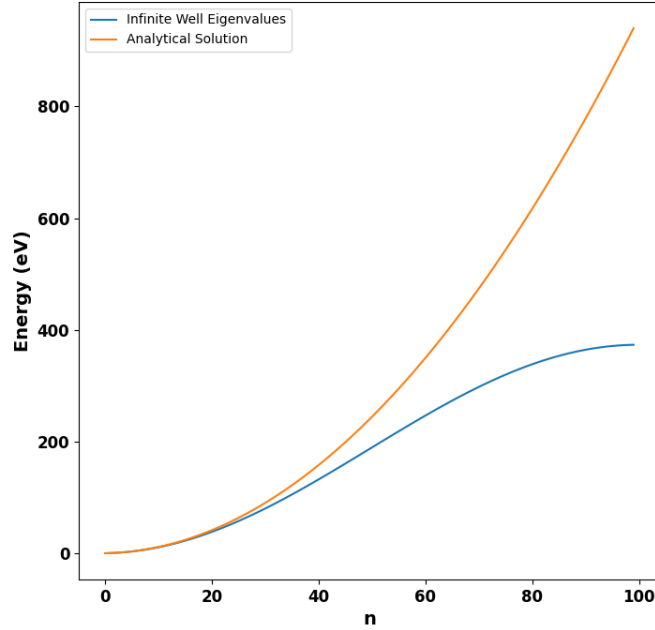


Figure 3: Comparing approximate solutions with analytical results

9 Finite Well Solutions

A finite potential well depth was added from $-L$ to $-L/2$ and $L/2$ to L with a height of 8 eV. The eigenstates were observed as follows:

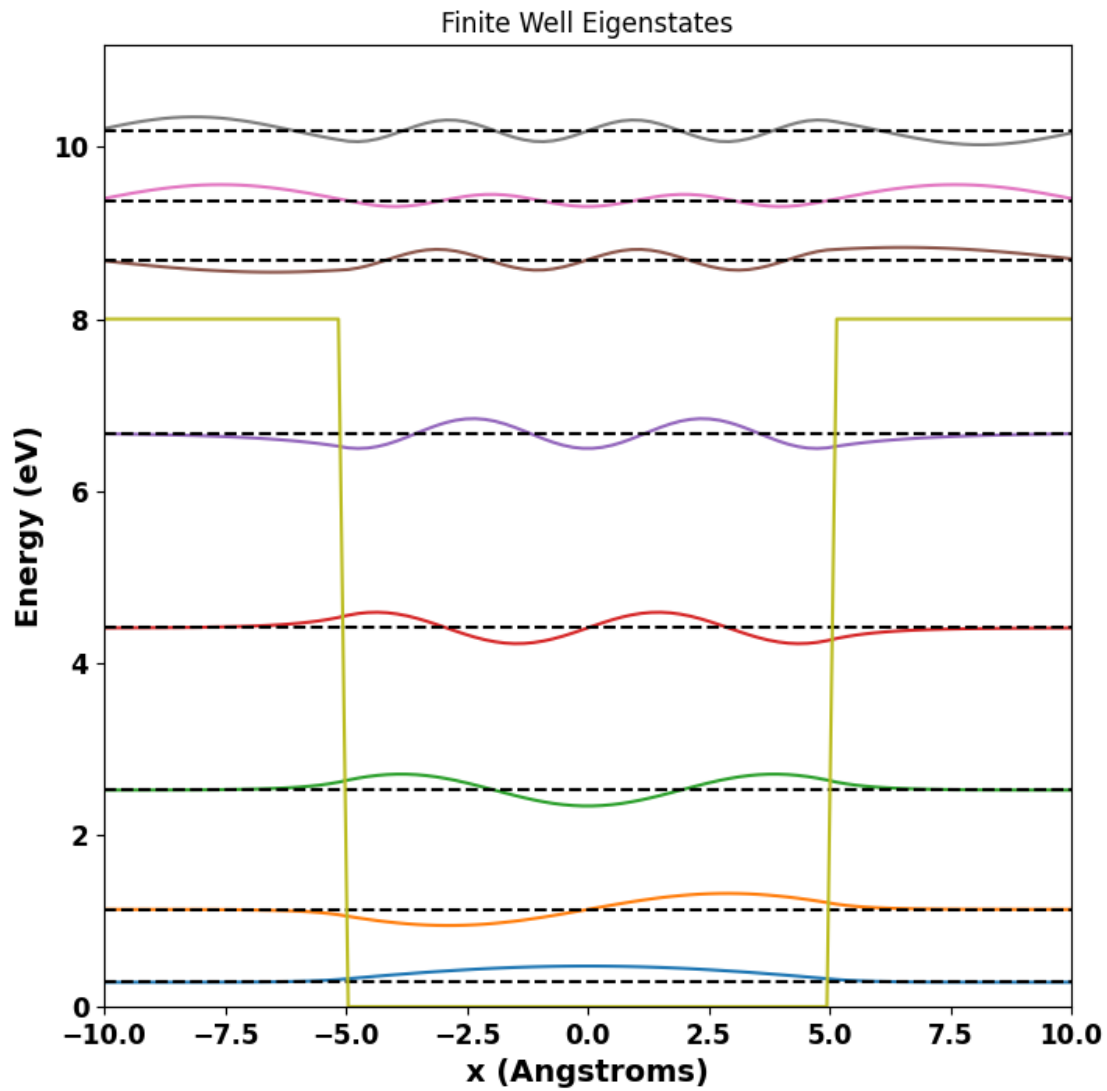


Figure 4: Finite Potential Well Eigenstates

The eigenvalues were observed as follows:

	Energy(eV)
1	0.28407318
2	1.13049088
3	2.51940894
4	4.40563601
5	6.66750561
6	8.68938817
7	9.37975585
8	10.1896967

Table 4: Energy levels for the finite potential well (eV).

In classical mechanics, if a particle has an energy lower than an energy barrier, it cannot pass through. In quantum mechanics, a phenomenon known as tunneling becomes prevalent, where the particle has a small probability to tunnel through.

For the finite well, there were observed to be 5 bound states, and the degree of permeation is shown below:

The permeation increases as the energy of the particle increases. The wavefunction exponentially decays inside the barrier, and has the form:

$$\Psi = Ae^{-\alpha x}, \alpha = \sqrt{\frac{2m(V_o - E)}{\hbar^2}} \quad (16)$$

It is evident that as the potential barrier reaches infinity, the probability of the particle tunneling decreases. Similarly, for a finite potential barrier, the probability of the particle tunneling, and therefore the tunneling depth increases with particle energy.

	Permeation Percentage
1	0.4284649629940675
2	1.7925581851450247
3	4.399208536214323
4	9.174395689592718
5	20.169492733411373

Table 5: Permeation percentages for the first 5 energy levels in the finite well

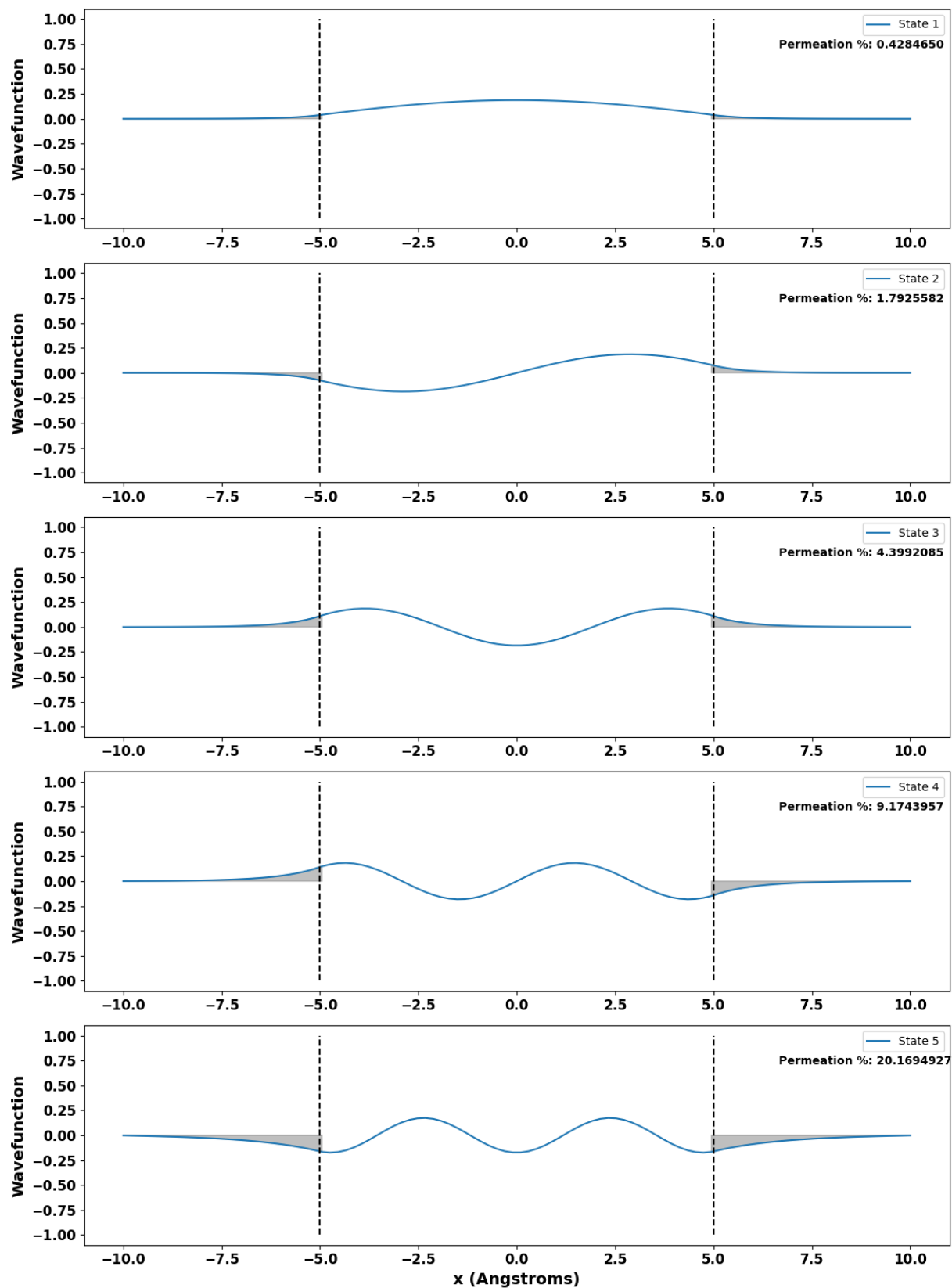


Figure 5: Permeation for Finite Well

10 Rectangular Barrier Potential Solutions

A rectangular potential barrier with a height of 8 eV was placed between $-L/4$ to $L/4$.

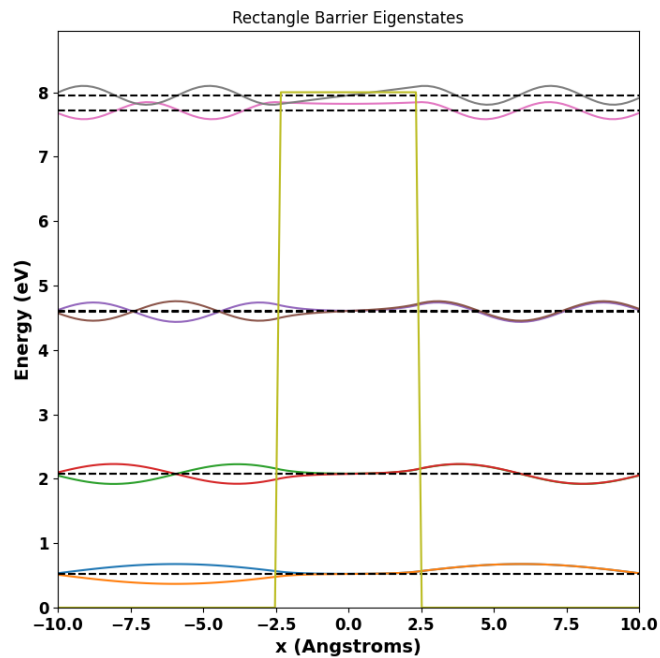


Figure 6: Rectangular barrier eigenstates

	Energy (eV)
1	0.52216376
2	0.52254355
3	2.07291789
4	2.07568489
5	4.58574844
6	4.60489438
7	7.71423157
8	7.95254957

Table 6: Energy levels for the rectangular barrier (eV).

By plotting the wave functions separately, we can observe the splitting of the energies due to the barrier.

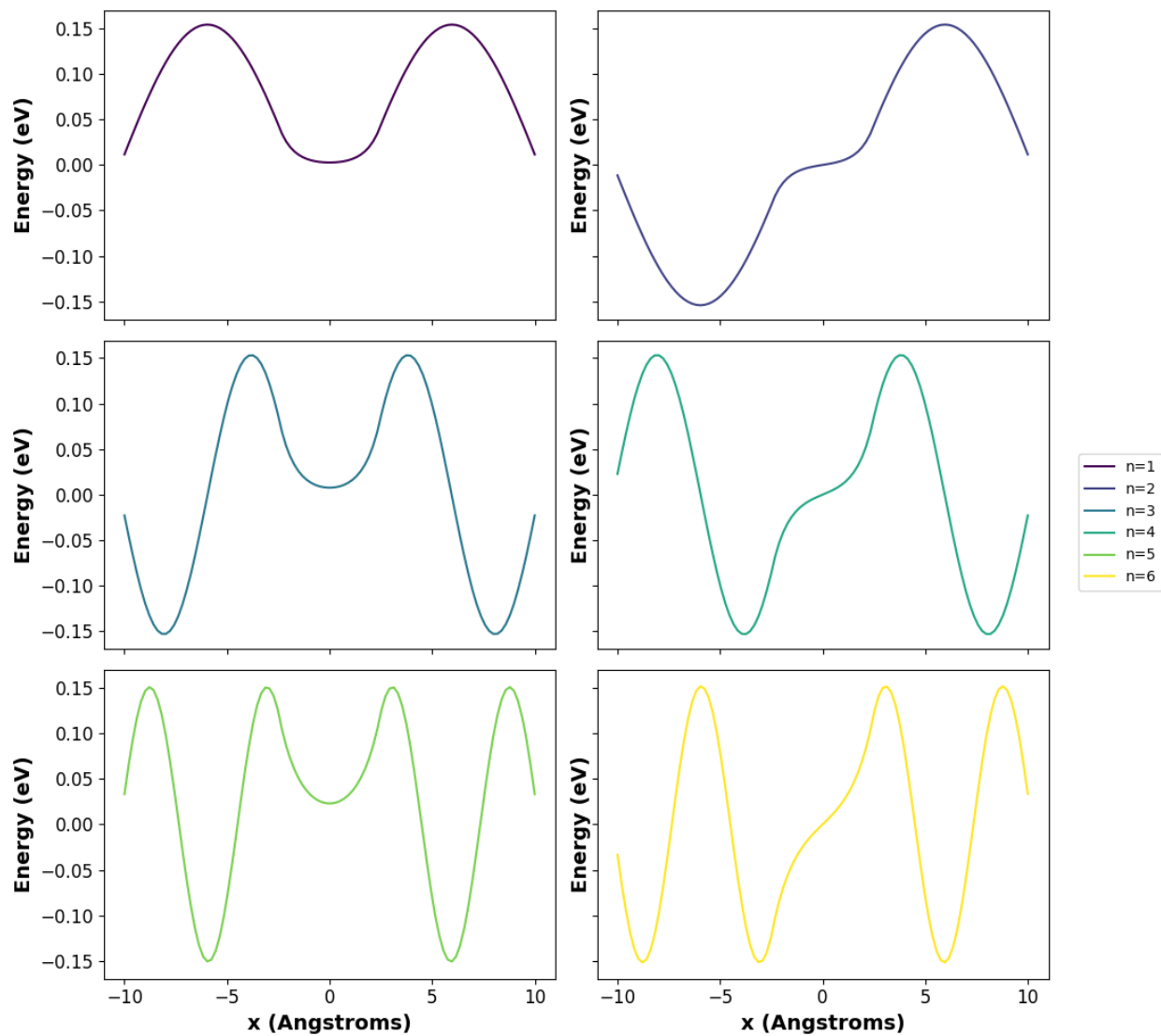


Figure 7: Rectangular barrier eigenstates

11 Harmonic and Morse Potential Solutions

Solutions were computed for a Harmonic potential and a Morse Potential.

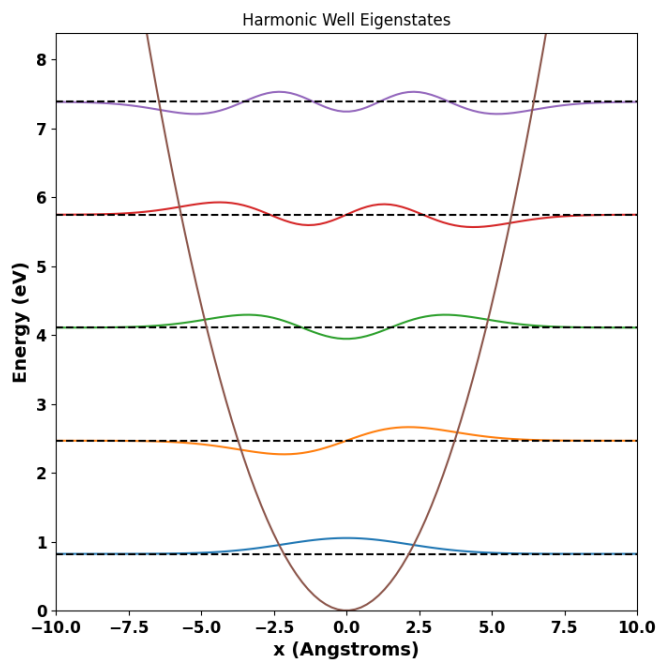


Figure 8: Harmonic Potential Eigenstates

	Finite Difference (eV)	Analytical (eV)
1	0.82231147	0.82276492
2	2.46602654	2.46829477
3	4.10792547	4.11382461
4	5.74801826	5.75935446
5	7.38640512	7.40488430

Table 7: Comparison of finite difference and analytical energy values for the harmonic oscillator (eV).

A similar trend to that of the infinite well solution comparison was observed when comparing the numerical solutions to the analytical solutions of the harmonic oscillator. The analytical solutions are given by the formula:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \quad (17)$$

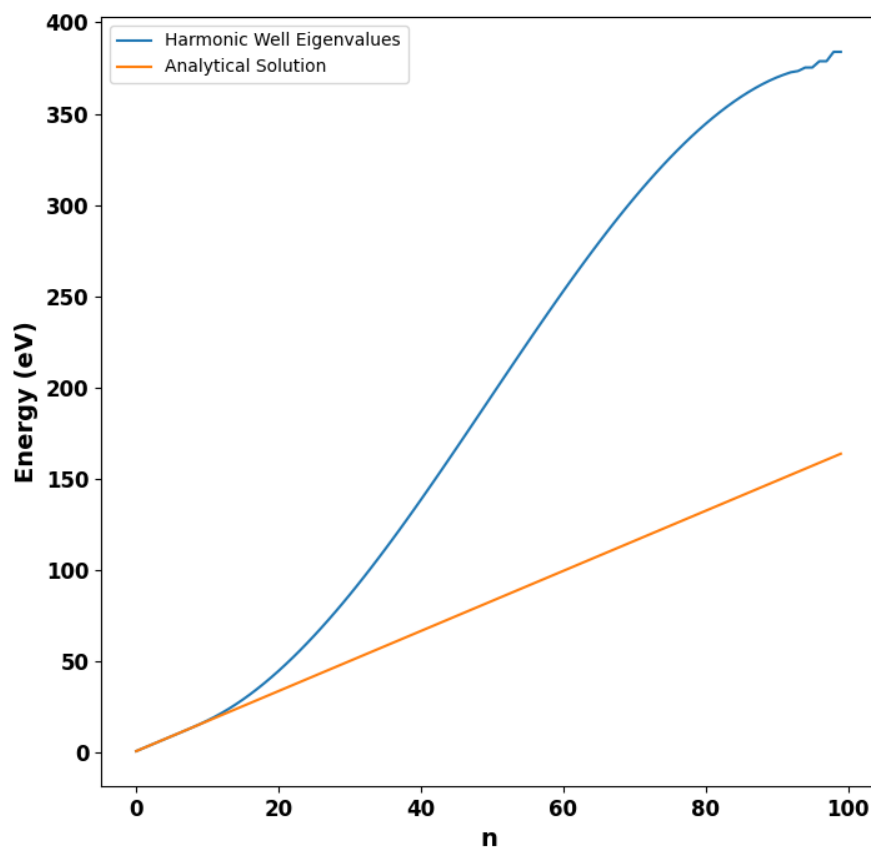


Figure 9: Comparison of Energies of Harmonic Oscillator

Through plotting the morse wavefunctions, they are not symmetrical around the equilibrium distance, or the displacement, unlike the harmonic oscillator.

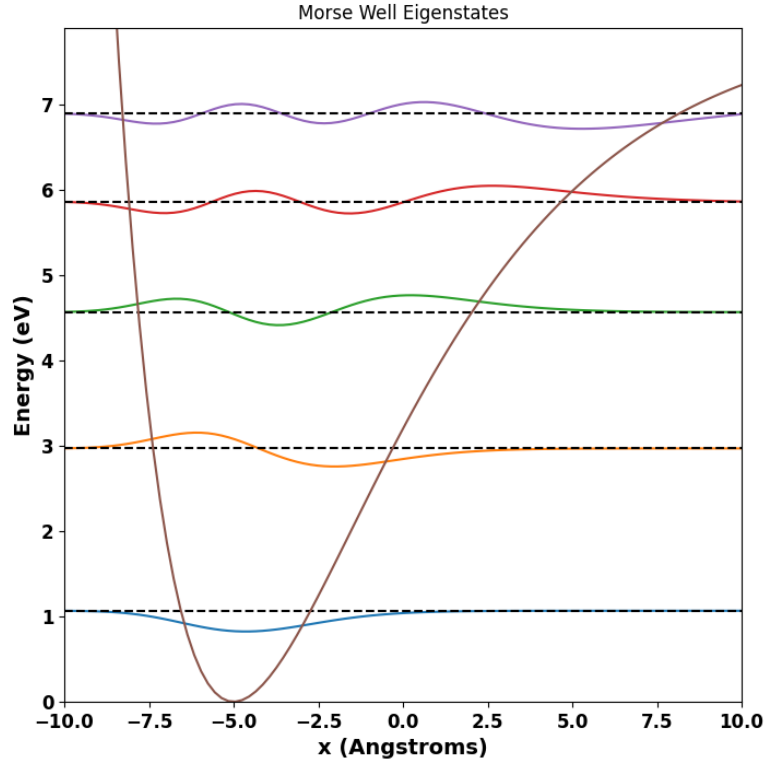


Figure 10: Morse Potential Eigenstates

	Energy (eV)
1	1.06535049
2	2.96689294
3	4.56325117
4	5.85690833
5	6.89089171

Table 8: Energy levels for the Morse potential (eV).

12 Frank Condon Factors - Vibrational Progression

A vibrational progression was simulated by calculating the frank condon factors of wave-functions for excitation for vibrational energy levels of a ground state morse potential, to the vibrational levels of an excited state morse potential.

The excited morse potential well was shifted up by 10 eV, and right by 3 Angstrom.

The energies and eigenstates were found to be as follows:

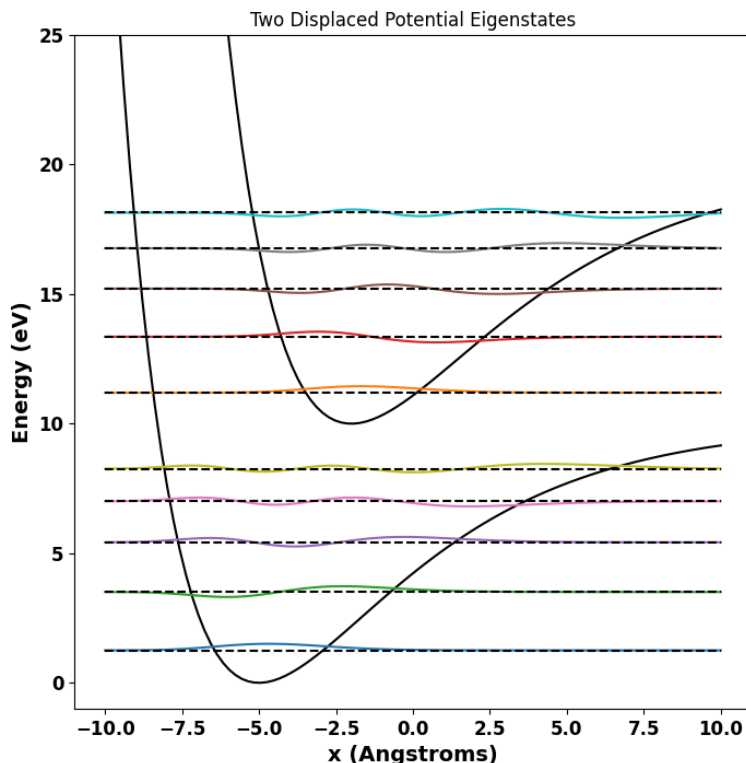


Figure 11: Eigenstates of 2 displaced morse potentials

The energies of the ground state and excited state were as follows:

ν	Ground State Energy (eV)
1	1.25319380
2	3.50664092
3	5.42320255
4	7.00471466
5	8.26237933

Table 9: Ground state energies for different values of ν (eV).

ν'	Excited State Energy (eV)
1	11.19546276
2	13.35690399
3	15.21276428
4	16.77241935
5	18.14219855

Table 10: Excited state energies for different values of ν' (eV).

The frank condon coefficients are defined as the square of the overlap between the wavefunctions of 2 energy levels involved in a transition under the Born Oppenheimer Approximation.

The vibrational progression was plotted with energy difference on the x axis:

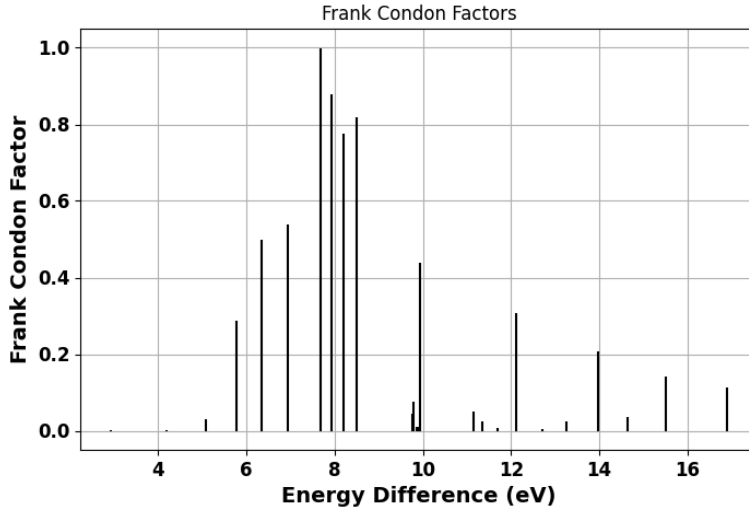


Figure 12: Eigenstates of 2 displaced morse potentials

Since there is uncertainty when making measurements during experiments, errors are introduced, due to human error or the limitation of the instrument. The sharp peaks also broaden due to the doppler effect, which is caused by thermal motion of the molecule relative to the observer. [1]

So instead of plotting sharp peaks at the energy differences, a plot was made by superimposing gaussian peaks centered around their respective origins. A dummy value of 0.05 was used as a width of the peak.

The vibrational progression thus observed was the following:

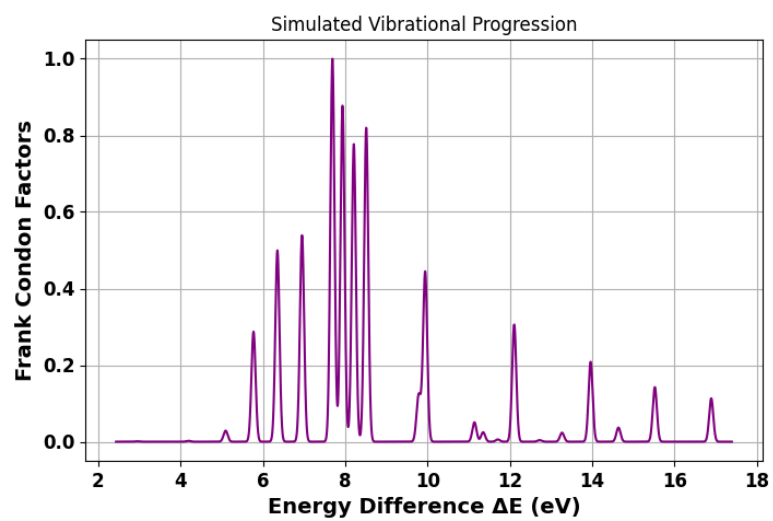


Figure 13: Eigenstates of 2 displaced morse potentials with Spectral Line Broadening

The frank condon coefficients were found to be the following:

ν	ν'	Franck-Condon Coefficient
1	1	0.25280006
1	2	0.17685404
1	3	0.12057201
1	4	0.08237028
1	5	0.06545649
2	1	0.57809218
2	2	0.00639364
2	3	0.00341116
2	4	0.01353616
2	5	0.02131853
3	1	0.16612436
3	2	0.50729859
3	3	0.04302380
3	4	0.01425726
3	5	0.00236011
4	1	0.00139117
4	2	0.28878232
4	3	0.44920858
4	4	0.02591095
4	5	0.02928720
5	1	0.00064882
5	2	0.01666241
5	3	0.31157149
5	4	0.47391371
5	5	0.00587487

Table 11: Franck-Condon factors for different vibrational transitions ($\nu \rightarrow \nu'$).

References

- [1] Spectral Lines Broadening - PhysicsOpenLab — physicsopenlab.org, <https://physicsopenlab.org/2017/09/07/spectral-lines-broadening/>, [Accessed 25-02-2025].