Calculation of the Quantum Mechanical Effusion Rate out of a 2D Box

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CALCULATION OF THE QUANTUM MECHANICAL EFFUSION RATE OUT OF A 2D BOX

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15 ECTS thesis submitted in partial fulfillment of a
Baccalaureus Scientiarum degree in Chemistry

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Abstract

In recent years there has been much interest in expansions of transition state theory to include quantum mechanical effects such as tunnelling and zero-point energy. Many attempts have been put forward to formulate a quantum transition state theory. To determine the quality of those expansions they must be compared to known results.

Effusion can be taken as an example, as the classical rate of effusion can be calculated using both classical transition state theory and the kinetic theory of gasses. The purpose of this study was to calculate the quantum mechanical rate of effusion for a system which displayed strong quantum mechanical characteristics.

Útdráttur

Mikill áhugi hefur verið undanfarin ár á útvíkkunum á virkjunarástandskenningunni til þess að taka tillit til skammtafræðilegra áhrifa eins og smug og núllpunktsorku. Margar tilraunir hafa verið gerðar til þess að setja fram skammtafræðilega virkjunarástandskenningu. Til þess að geta metið gæði/réttmæti útvíkkanna þurfa þau að vera borin saman við þekktar niðurstöður.

Útsveim getur verið gott dæmi, þar sem klassíski hraðafastinn fyrir útsveim má reikna bæði með virkjunarástandskenningunni og kvikfræði gasa. Tilgangur þessarar rannsóknar vað að reikna út skammtafræðilega hraðafasta fyrir útsveim á kerfi sem sýndi sterklega skammtafræðilega eiginleika.

Preface

When I was first introduced to this problem of expanding transition state theory into quantum mechanics, it intrigued me that nobody had yet calculated this simple system of effusion according to quantum mechanics before and I wanted to learn more. I started out by reading and researching more on the subject and on methods to calculate quantum mechanical rate constants. Then I received code from Gregory K. Schenter where he had started to dabble a bit with this problem. My first task was to understand it better and relate it to methods used to calculate the rate constants.

When I subsequently started to work more with the code, what had at first seemed to be a simple problem to solve turned out to be much more complicated than I first had thought. Small changes to how the calculation proceeded were necessary to get results. Then, once I again could start to calculate somethings, it became apparent that it was necessary to check for convergence with regards to a variety of factors. Among these were the space of the area outside of the box that was calculated (representing infinite space), the thickness of the walls, the convergence of the correlation functions used to calculate the rates, and various other things.

Despite all these challenges I decided to continue with the project until I could get some usable results. Through some ups and downs I managed with the support of various people around me to push through the challenges and get some results.

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Abbreviations

C_f: Flux-Flux Correlation Function
$C_{f,s}$: Side-Flux Correlation Function
C_s: Side-Side Correlation Function
TST: Transition State Theory
QTST: Quantum Transition State Theory

Acknowledgements

I would like to thank all of my friends and family that supported me through the process of doing this project and writing this.

Special thanks go to my advisor, Hannes Jónson, for his guidance and support with this project, Gregory K. Schenter for providing a rough draft of the code which I developed further, Elvar Örn Jónsson for technical assistance, and my brother James Elías Sigurðarson for always helping me when I had the stupidest questions.

1. Introduction

The purpose of this study is to calculate rate constants for effusion of a particle described by quantum mechanics. The results from this study will hopefully be able to be used to compare different formulations of quantum transition state theories.

1.1. TST and QTST

Transition State Theory (TST) is a useful tool to calculate reaction rates for chemical reactions at different temperatures. The theory is in the realm of classical mechanics. A dividing surface is determined between the two states that are considered. The rate is subsequently approximated as the product of the probability of the system reaching the dividing surface if it is in thermal equilibrium and the flux passing through the dividing surface in the direction to the product region.

A key part in the theory are four assumptions:

- the Born-Oppenheimer approximation (adiabatic),

- classical behaviour,

- Boltzmann distribution in the initial state (thermal equilibrium),

- there is no recrossing of the dividing surface.

This last assumption is weak and depends on a good choice of the transition state.

Various attempts have been made to expand TST to include quantum mechanics. Especially significant are the effects of zero-point energy and tunnelling. For systems at low temperature these effects become significant. Therefore, various

attempts have been made to expand TST into Quantum Transition State Theory (QTST). Among these are for example reversible action-space work QTST (RAW-QTST, see [1]) and harmonic QTST (HQTST, see [2]).

1.2. Effusion

To determine if a form of QTST is correct it is necessary to compare results using the theory with a known result. For this it is possible to look at the problem of effusion and compare it to the classical case. Effusion is the phenomenon when a gas particle passes through a gap which is smaller than the mean free path.

In the realm of classical mechanics both TST and the Kinetic Theory of gasses give the same result:

$$k = \sqrt{\frac{k_B T}{2\pi m}} \frac{A}{V} \tag{1.1}$$

Where k_B is the Boltzmann constant, T is the temperature, m the mass of the particle, A the area of the gap (length in two dimensions), and V the Volume of the box (area in two dimensions).

This fact is often used as an example to show that TST gives reliable results. In this case all the assumptions that TST requires are true; this is an adiabatic system, can be reliably described in thermal equilibrium and thus with Boltzmann distribution, and there is zero possibility of recrossing the transition state (the gap).

Our objective is to calculate this same system through quantum mechanics. This will give results that can be used to determine the reliability of different forms of QTST.

1.3. Correlation functions

Quantum mechanical reaction rates can be calculated using correlation functions. The rate can be expressed as the limit of correlation functions as time goes to

infinity:

$$kQ = \int_0^\infty C_f(t), \tag{1.2}$$

$$kQ = \lim_{x \to \infty} C_{f,s}(t), \tag{1.3}$$

$$kQ = \lim_{x \to \infty} \frac{d}{dt} C_s(t) \tag{1.4}$$

Where,

$$C_f(t) = tr\left[\hat{F} \exp\left(\frac{i\hat{H}t}{\hbar}\right) \exp\left(-\frac{\beta\hat{H}}{2}\right) \hat{F} \exp\left(-\frac{\beta\hat{H}}{2}\right) \exp\left(-\frac{i\hat{H}t}{\hbar}\right)\right], \tag{1.5}$$

$$C_{f,s}(t) = tr\left[\hat{F} \exp\left(\frac{i\hat{H}t}{\hbar}\right) \exp\left(-\frac{\beta\hat{H}}{2}\right) \hat{h} \exp\left(-\frac{\beta\hat{H}}{2}\right) \exp\left(-\frac{i\hat{H}t}{\hbar}\right)\right], \tag{1.6}$$

$$C_s(t) = tr\left[\hat{h} \exp\left(\frac{i\hat{H}t}{\hbar}\right) \exp\left(-\frac{\beta\hat{H}}{2}\right) \hat{h} \exp\left(-\frac{\beta\hat{H}}{2}\right) \exp\left(-\frac{i\hat{H}t}{\hbar}\right)\right], \tag{1.7}$$

$$C_f(t) = \dot{C}_{f,s}(t) = \ddot{C}_s(t) \tag{1.8}$$

Where $\hat{F}$ is the flux operator:

$$\langle\phi|\hat{F}|\psi\rangle = \frac{1}{2m}[\phi^*\hat{p}\psi - \psi^*\hat{p}\phi] \tag{1.9}$$

Where $\hat{p}$ is the quantum mechanical momentum operator.
$\hat{h}$ is a projection (step) operator which gives:

$$\hat{h} = \begin{cases} 1, & \text{if particle is on the product side of the dividing surface} \\ 0, & \text{if particle is NOT on the product side of the dividing surface} \end{cases} \tag{1.10}$$

$\hat{H}$ is the quantum mechanical Hamiltonian and $\beta = \frac{1}{k_B T}$. k is the rate constant and Q is the partition function for the reactant area.[3][4]

Using a finite basis set of bound eigenstates of the Hamiltonian C_f can be expressed as:

$$C_f = \sum_{i,j} \exp\left[-\frac{\beta(E_i + E_j)}{2}\right] \cos\left[\frac{(E_i - E_j)t}{\hbar}\right] |\langle i|\hat{F}|j\rangle|^2 \tag{1.11}$$

Where i, j are eigenstates of the Hamiltonian and E_i and Ej are their respective

1. Introduction

eigenvalues. The Flux squared factors are calculated with:

$$|\langle i|\hat{F}|j\rangle|^2 = |\langle i|s\rangle\langle s|\hat{F}|s'\rangle\langle s'|j\rangle|^2 = \left|\int ds \int ds' \psi_i^*(s)\langle s|\hat{F}|s'\rangle\psi_j(s')\right|^2$$
$$= \int_{\partial R} ds \left(\frac{\hbar}{2m}\right)^2 \left|\frac{\partial\psi_i(s)}{\partial n}\psi_j(s) - \psi_j'(s)\psi_i(s)\right|^2 \tag{1.12}$$

Where ∂R is a path along the dividing surface and $\frac{\partial}{\partial n}$ is the derivative across the surface towards the product region.

Integrating 1.11 gives:

$$C_{f,s} = \sum_{i,j} \exp\left[-\frac{\beta(E_i + E_j)}{2}\right] \frac{\hbar \sin\left[\frac{(E_i - E_j)t}{\hbar}\right]}{(E_i - E_j)} |\langle i|\hat{F}|j\rangle|^2 \tag{1.13}$$

However, this function does not formally have a limit at infinite time as the sine functions continue to fluctuate. If the system is "well behaved" enough, it can reach the "limit" at an intermediate time before the instability caused by the discretisation of the energy spectrum makes the expression inaccurate.

Therefore, to evaluate the value of kQ, the function in 1.13 has to be examined to see if it converges to a value before it becomes unstable. [3] Examples of these functions can be seen on figures 1.1 and 1.2.

As the particle is originally in a box; the partition function can be calculated from the eigenvalues for a particle in a box. The eigenvalues for a 1D box are shown in equation 1.14

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \tag{1.14}$$

Where $\hbar$ is the reduced Planck constant, L is the length of the box, and n is a natural number.

This can be expanded into two dimensions as is done in

$$E_{n_x,n_y} = \frac{n_x^2\pi^2\hbar^2}{2mL_x^2} + \frac{n_y^2\pi^2\hbar^2}{2mL_y^2} \tag{1.15}$$

Where the system has been expanded into to dimensions with an x-axis and a y-axis.
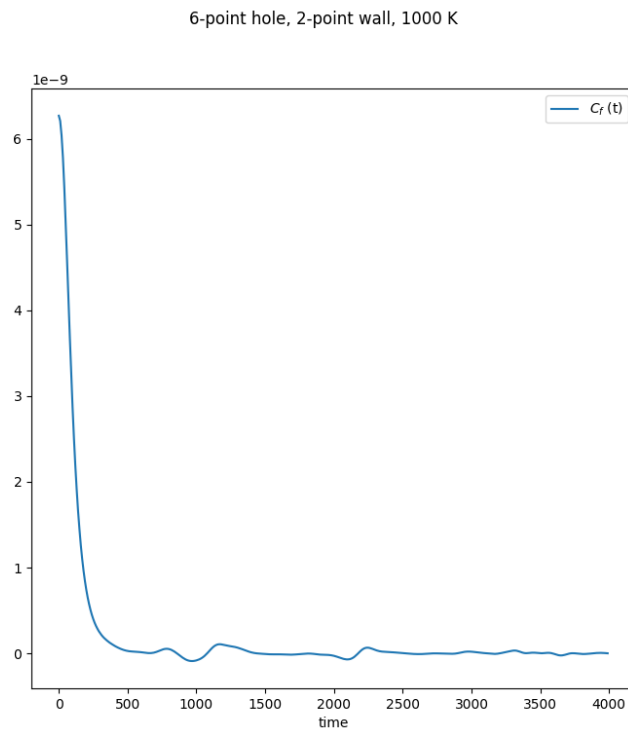
Figure 1.1: Example of a well behaved C_f, or flux-flux correlation function. Note how the function quickly approaches its limit at 0.
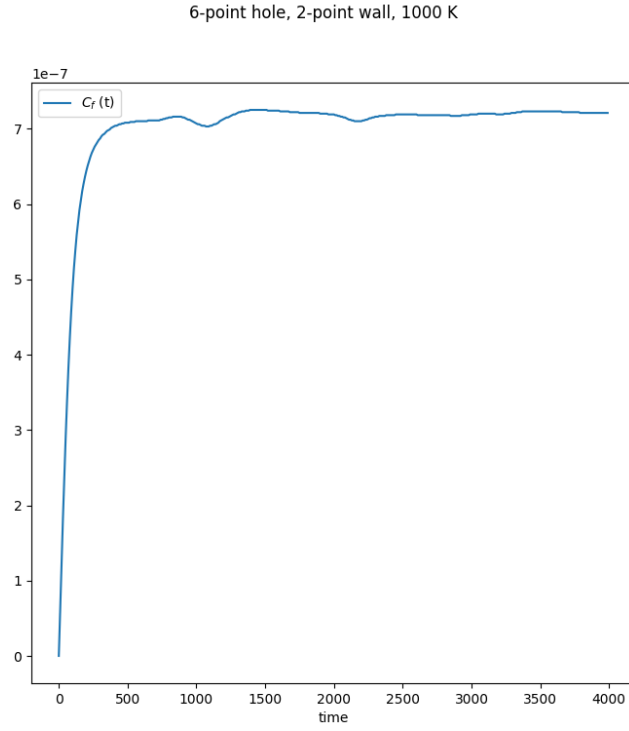
*Figure 1.2: Example of a well behaved $C_{f,s}$, or flux-side correlation function cor-
responding to the C_f, or flux-flux correlation function shown in figure 1.1. The
function reaches its limit, shown as a plateau on the graph, which gives the value
of kQ. Note, this is the same system as shown on figure 2.5, but plotted for a
shorter timescale.*

The partition function can then be calculated:

$$Q(T) = \sum_{n_x, n_y} \exp\left[\frac{n_x^2 \pi^2 \hbar^2}{2mL_x^2} + \frac{n_y^2 \pi^2 \hbar^2}{2mL_y^2}\right] = \sum_{n_x} \exp\left[\frac{n_x^2 \pi^2 \hbar^2}{2mL_x^2}\right] \cdot \sum_{n_y} \exp\left[\frac{n_y^2 \pi^2 \hbar^2}{2mL_y^2}\right]$$

$$(1.16)$$

2. Methods

The system that was calculated was that of two boxes. One was smaller $(1\text{Å} \times 1\text{Å})$ and was defined as the "reactant region" or original position of the particle, and the other much larger represented the "outside" of the box, where the particle had escaped. The outside needed to be large enough to accurately represent the infinite space outside of the box. This is shown in figure 2.1.

The thickness of the wall and size of the hole were varied in the calculations. The value eventually used were the limit as the thickness of the wall went to zero. The mass of the particle was defined as 1 a.m.u. $(1.660539066 \times 10^{-27}$ kg).
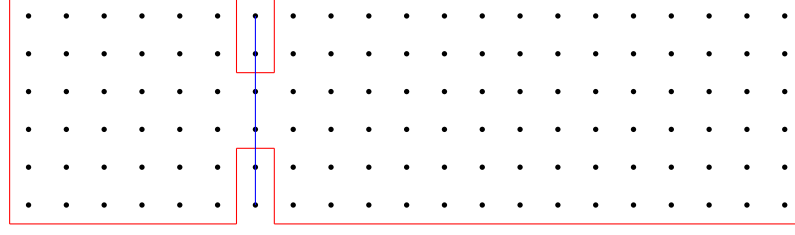
Figure 2.1: Diagram showing what the system looks like (Not to scale). The black points represent points in the grid used for calculation. The red lines represent walls; everything outside of them is set to zero. The left side of the diagram represents the box where the particle is originally placed. The right side represents the area where the particle has escaped out of the box. The blue line represents the dividing surface separating the two boxes, and the points it goes through were later used to calculate the flux.

2.1. The Code

The code was structured in the following way:

- Creation of the Hamiltonian matrix

- Solving the eigenstates and eigenvalues of the Hamiltonian

- Normalisation of the eigenstates.

- Calculation of the derivative of each state along the dividing surface

- Calculation of values in the flux matrix (squared)

- Calculation of the C_f and $C_{f,s}$ functions

Everything was calculated in Hartree atomic units for simplification. The Code was programmed in Python, using the numpy and scipy packages.

Hamiltonian Matrix

The Hamiltonian matrix was constructed in the following way:

The area was divided into $N \times M$ points, having N points on the x-axis and M points on the y-axis. The space between each point was $dx = \frac{x_{length}}{N}$ and $dy = \frac{y_{length}}{M}$. Each point (x_i, y_j) was renumbered as $n = j + N \times i$. The second derivative in each direction was described with a centred finite difference approximation, with the weights taken as the limit as the number of points extends to infinity.[5] This was deemed possible as all points outside of the area considered were set to zero.

For points inside the "wall" the value of the wavefunction was also predefined as zero. This was done by replacing all points c_{wk} or c_{kw} relating to that point w inside the wall with 0, setting $c_{ww} = -1$ and subsequently throwing out all eigenstates with a eigenvalue of -1. This is all shown in Algorithm 1

Solving for eigenstates and values

The routine numpy.linalg.eigh was used to find the eigenstates and eigenvalues of the Hamiltonian matrix. All the eigenstates with negative eigenvalues were subsequently removed.

Normalisation

The eigenstates were normalised by summing the values squared, multiplied by the spacing between points, and then dividing the values of the eigenstate by one over the square root of that value.

$$\psi = \frac{1}{\sqrt{\left(\sum (p_k \cdot dx \cdot dy)\right)}} \tag{2.1}$$

Derivative

The derivative over the dividing surface which is placed through the wall and the hole, is calculated using centred finite difference approximations of the fourth order.

2. Methods

for $i, j \leq N$ **do**
  for $h, k \leq M$ **do**
    if $i = h$ **then**
      if $j = k$ **then**
        | $H_{(i,j),(h,k)} = H_{(i,j),(h,k)} + \frac{\pi^2}{3} \cdot \frac{\hbar^2}{2mdy^2}$
      else
        | $H_{(i,j),(h,k)} = H_{(i,j),(h,k)} + (-1)^{j-k} \cdot \frac{2}{(j-k)^2} \cdot \frac{\hbar^2}{2mdy^2}$
      end
    if $j = k$ **then**
      if $i = h$ **then**
        | $H_{(i,j),(h,k)} = H_{(i,j),(h,k)} + \frac{\pi^2}{3} \cdot \frac{\hbar^2}{2mdx^2}$
      else
        | $H_{(i,j),(h,k)} = H_{(i,j),(h,k)} + (-1)^{j-k} \cdot \frac{2}{(i-h)^2} \cdot \frac{\hbar^2}{2mdx^2}$
      end
    else
      | $H_{(i,j),(h,k)} = 0$
    end
    if (i, j) *is a point inside the wall* **then**
      if $i = h$ *&* $j = k$ **then**
        | $H_{(i,j),(h,k)} = -1$
      else
        | $H_{(i,j),(h,k)} = 0$;
        | $H_{(h,k),(i,j)} = 0$
      end
    end
  end
end

Algorithm 1: Construction of the Hamiltonian matrix.

forall i **do**
  | $\vec{z} = |\vec{\psi_i}|^2$;
  | $s = \sqrt{sum(\vec{z})}$;
  | $\vec{\psi_i} = \frac{\vec{\psi_i}}{s}$
end

Algorithm 2: Normalisation of the eigenstates.

forall i **do**
  for *points on the dividing surface* **do**
    $\left|\quad \frac{\partial \psi_i}{\partial y}(x) = \frac{\psi_{i,(x,y-2)} - 8\psi_{i,(x,y-1)} + 8\psi_{i,(x,y+1)} - \psi_{i,(x,y+2)}}{12 dy}\right.$
  end
end

        Algorithm 3: First derivative over the dividing surface.

Flux matrix

The Flux matrix is calculated as described in 1.12.

forall i,j **do**
  $\hat{F}_{i,j} = \sum_{x \in dividingsurface} \frac{\hbar}{2m}\left(\frac{\partial \psi_i}{\partial y}(x) \cdot \psi_j(x) - \frac{\partial \psi_j}{\partial y}(x) \cdot \psi_i(x)\right) \cdot dy;$
  $\hat{F}_{i,j}^2 = \hat{F}_{i,j}^2$
end

        Algorithm 4: Calculation of the Flux squared.

Correlation functions

The correlation functions were calculated as described in 1.11 and 1.13 on page 3.

forall *t that are considered* **do**

$C_f(t) = 0$;

$C_{f,s}(t) = 0$;

forall *i, j* **do**

$s_f = \exp\left[-\frac{\beta(E_i+E_j)}{2}\right] \cos\left[\frac{(E_i-E_j)t}{\hbar}\right] |\langle i|\hat{F}|j\rangle|^2$;

if $i = j$ **then**

$s_{s,f} = \exp\left[-\frac{\beta(E_i+E_j)}{2}\right] t |\langle i|\hat{F}|j\rangle|^2$

else

$s_{s,f} = \exp\left[-\frac{\beta(E_i+E_j)}{2}\right] \frac{\hbar \sin\left[\frac{(E_i-E_j)t}{\hbar}\right]}{(E_i-E_j)} |\langle i|\hat{F}|j\rangle|^2$

end

$C_f = C_f + s_f$;

$C_{f,s} = C_{f,s} + s_{f,s}$

end

end

Algorithm 5: Calculation of the Correlation functions.

2.2. Evaluations & Convergence

Various things had to be evaluated to check if they converged properly. Among these were various constraints of the system such as the size of the space on the outside, the number of points in the grid, the correlation functions and the thickness of the wall.

2.2.1. Constraints

It was important for the space outside the box representing the particle going out to infinity was large enough to accurately represent that space. Various different proportions were considered. This is shown in figure 2.2; where the "inside" box was 30×30 points and the ratio inside:outside was 1:3, 1:7, 1:11,... etc. Absolute convergence was reached at 1:15 proportions, but the difference was so small that 1:7 was deemed sufficiently converged for this study, in order to save on computational load.

It was also necessary to evaluate the convergence with respect to the number of points used in the grid/spacing between the points. This can be seen in figure 2.3.

Figure 2.2: Value of kQ with differing sizes of the area outside of the box with insert of values close to convergence.

Here the ratio was fixed at 1:7 as noted before, and the number of total points in the grid was varied. Both the results from using a full routine that calculated all the eigenvalues using the whole matrix, and from a sparse routine that calculated a limited number of eigenvalues can be seen.

It was determined that using $N = 28800$ points with the full routine was sufficiently converged for the purposes of this study, although it gives slightly too high values. This corresponded to having 60×60 points inside the box.

2.2.2. Correlation functions

It was also very important to evaluate the value of kQ accurately. The problems related to this are described in section 1.3. A couple of examples of different correlation functions are shown in figures 2.4 to 2.8.

The value of the rate constant k was then determined by dividing by the partition function given in equation 1.16, and changing from the Hartree atomic units to SI units (s^{-1}).
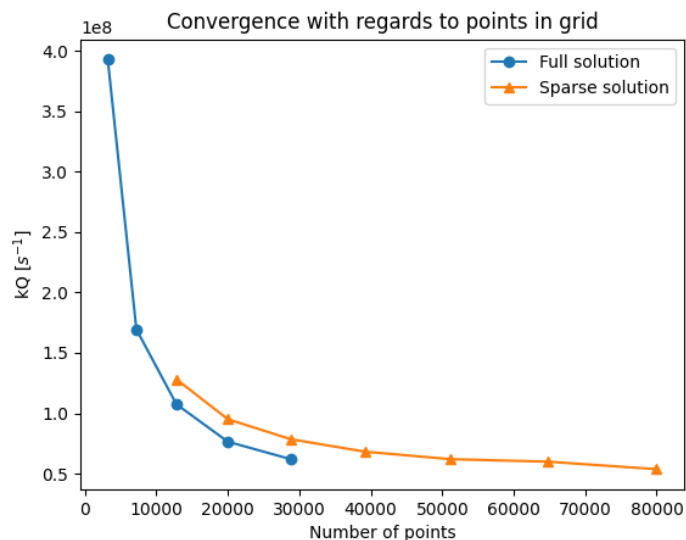
Figure 2.3: Convergence of the value kQ with differing number of points.

2.2.3. Thickness of the wall

It was also necessary to evaluate the limit as the thickness of the wall went to zero. In order to do that a couple of points were calculated for each gap and for each temperature, with varying thicknesses of the wall. An example of this can be seen in figure 2.9, using data found in table 3.7.

Plotting the logarithm of these values gave a straight line which could be fitted and the value at zero thickness of the wall could be extrapolated. This is shown in figure 2.10.

The natural logarithm of the rate constant as the thickness of the wall tended to zero could then be determined, and therefore the rate constant as well. Subsequently the unit of the rate constant could be changed from the inverse of the Hartree time unit to inverse seconds.
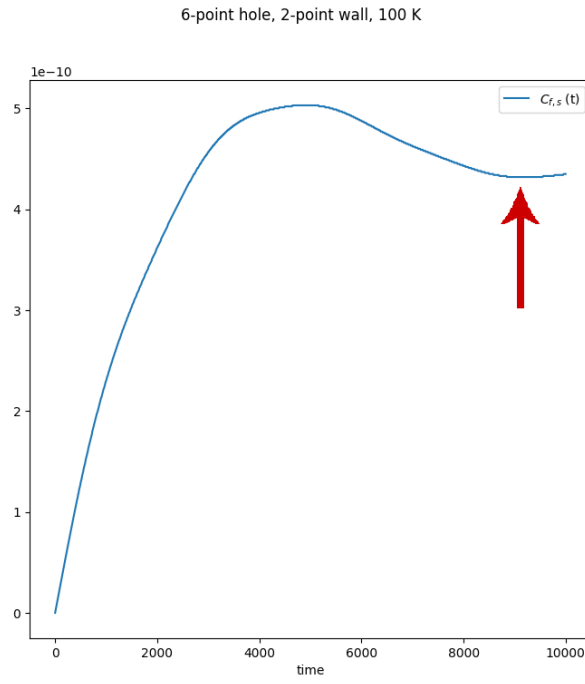
Figure 2.4: $C_{f,s}$ function for system with a 6-point hole and 2-point wall at 100 K. Here the Correlation function takes a long time to reach a plateau which gives the value of kQ. The red arrow roughly marks the area where the value for kQ was taken.

6-point hole, 2-point wall, 1000 K
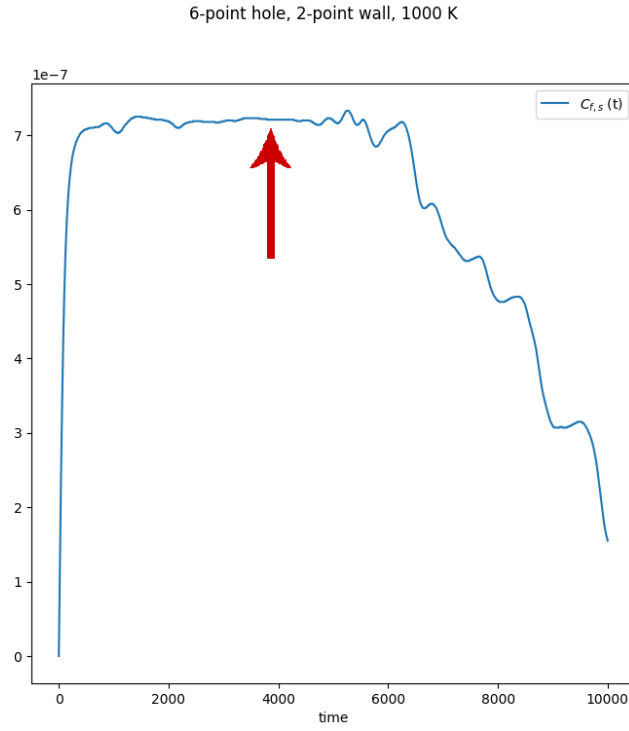
Figure 2.5: $C_{f,s}$ function for system with a 6-point hole and 2-point wall at 1000 K. Here the Correlation function reaches a plateau which gives the value of kQ relatively early and stays around the same value for a significant amount of time. The red arrow roughly marks the area where the value for kQ was taken. Note, this is the same system as is plotted on figure 1.2, but here plotted for a slightly longer timescale to show where the instability comes in.

10-point hole, 6-point wall, 4500 K
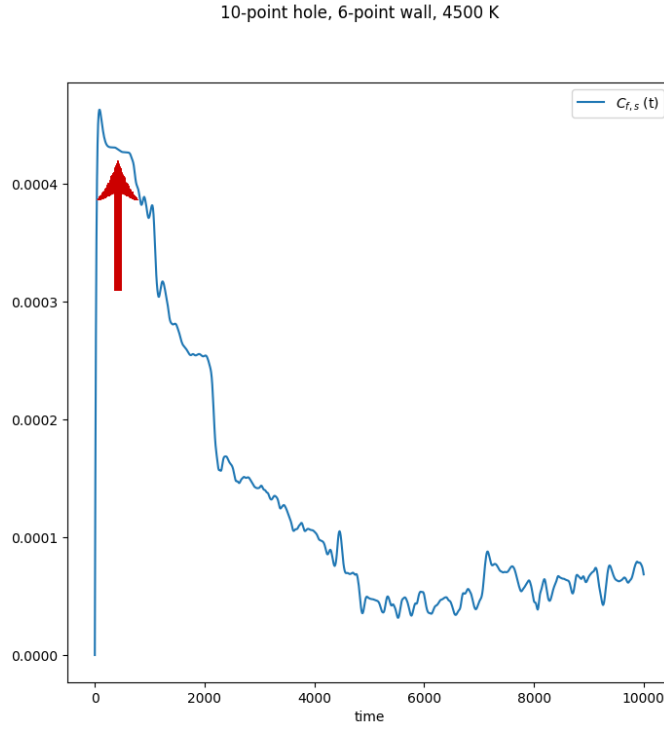
Figure 2.6: $C_{f,s}$ function for system with a 10-point hole and 6-point wall at 4500 K. Here the Correlation function reaches the plateau which gives the value of kQ on a comparatively short timescale. The red arrow roughly marks the area where the value for kQ was taken.
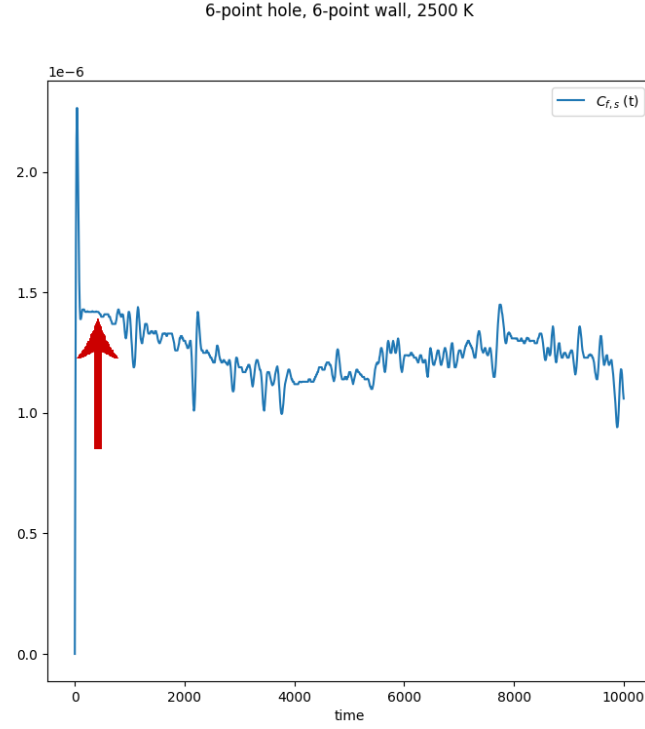
Figure 2.7: $C_{f,s}$ function for system with a 6-point hole and 6-point wall at 2500 K. Here the Correlation function reaches a plateau which gives the value of kQ after a sharp peak at a small timescale. The plateau only lasts for a relatively short time period, before the function shows instability. The red arrow roughly marks the area where the value for kQ was taken.

6-point hole, 2-point wall, 5000 K
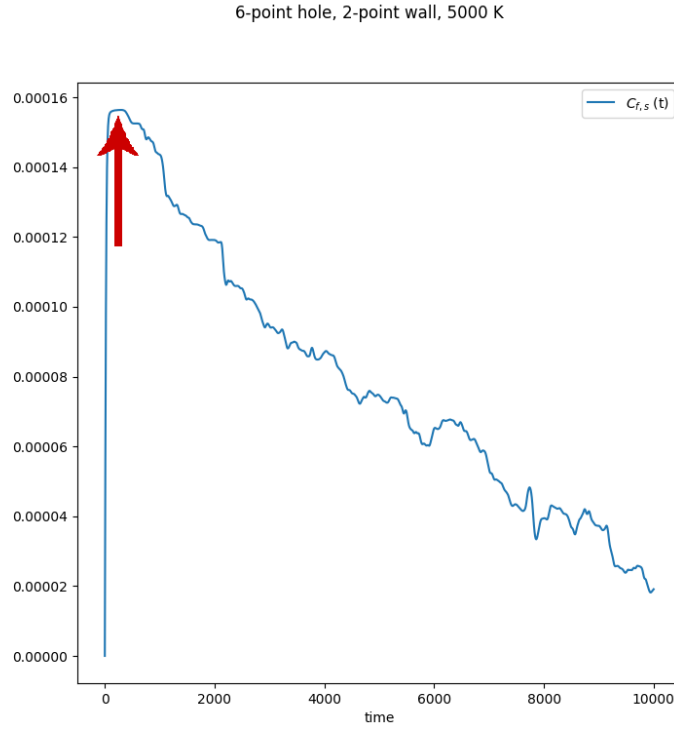
Figure 2.8: $C_{f,s}$ *function for system with a 6-point hole and 2-point wall at 5000 K. Here the Correlation function reaches the plateau which gives the value of kQ very quickly and it only stays there for a short time period before becoming unstable. The red arrow roughly marks the area where the value for kQ was taken.*
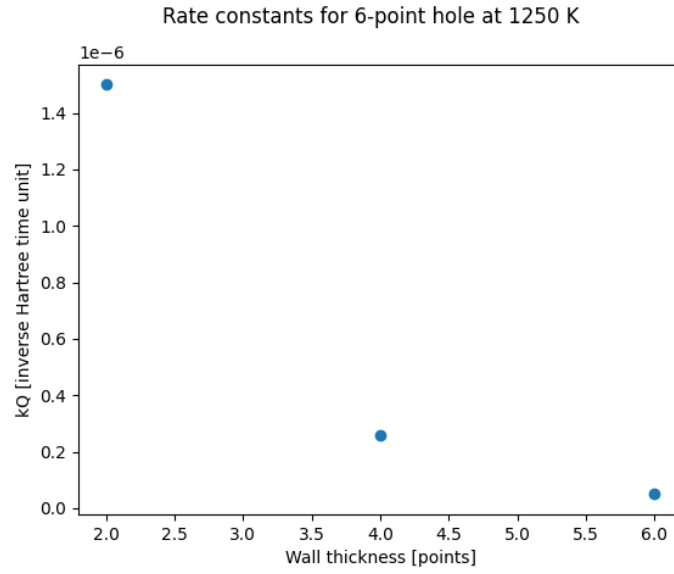
Figure 2.9: Rate constants for 6-point hole at 1250 K.
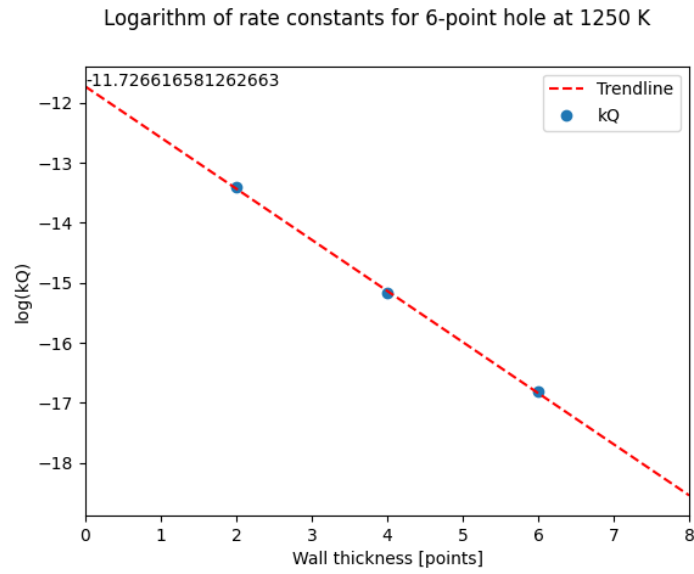
Figure 2.10: Logarithm of rate constants for 6-point hole at 1250 K, with fitted trendline and extrapolated value.

3. Results

The system described was calculated, with the box being 1Å × 1Å, the weight of the particle being 1 a.m.u. ($1.660539066 \times 10^{-27}$ kg), and the size of the gap varying between 6-, 8-, 10-, and 12-points (0.100 Å, 0.133 Å, 0.167 Å, and 0.200 Å respectively), and the thickness of the wall varying between 2-, 4-, and 6-points (0.033 Å, 0.067 Å, and 0.100 Å respectively). The results of the calculation for kQ are shown in tables 3.1 to 3.16.

The values for all gaps as the wall tended towards zero were extrapolated as described in subsection 2.2.3. The value was then divided by the partition function at the temperature calculated according to equation 1.16. This was done for a range of temperatures up to 5000 K. The results of this are shown in table 3.17 and figures 3.2 and 3.1. Table 3.17 shows the values in Hartree atomic units; while the graphs on the figures have been converted into SI-units (s^{-1}).

More useful is to plot this over the square root of the temperature, as there, the classical rate constants form a straight line. This is done in figures 3.4 and 3.3.

The ratios between the quantum mechanical rate over the classical rate is displayed in figures 3.6 and 3.5.

Table 3.1: kQ in Hartree atomic units at 100 K.

Wall thickness\Gap size	6	8	10	12
2	4.32E-10	1.74E-09	5.19E-09	1.27E-08
4	5.58E-11	3.72E-10	1.51E-09	4.56E-09
6	8.40E-12	8.81E-11	4.75E-10	1.74E-09

3. Results

Table 3.2: kQ in Hartree atomic units at 200 K.

Wall thickness\Gap size	6	8	10	12
2	5.53E-09	2.24E-08	6.67E-08	1.61E-07
4	7.18E-10	4.84E-09	1.98E-08	5.98E-08
6	1.09E-10	1.16E-09	6.32E-09	2.34E-08

Table 3.3: kQ in Hartree atomic units at 400 K.

Wall thickness\Gap size	6	8	10	12
2	4.33E-08	1.82E-07	5.55E-07	1.35E-06
4	5.86E-09	4.17E-08	1.79E-07	5.53E-07
6	9.17E-10	1.04E-08	6.11E-08	2.39E-07

Table 3.4: kQ in Hartree atomic units at 600 K.

Wall thickness\Gap size	6	8	10	12
2	1.45E-07	6.32E-07	1.98E-06	4.99E-06
4	2.09E-08	1.57E-07	6.89E-07	2.03E-06
6	3.40E-09	4.20E-08	2.59E-07	1.09E-06

Table 3.5: kQ in Hartree atomic units at 750 K.

Wall thickness\Gap size	6	8	10	12
2	2.90E-07	1.28E-06	3.71E-06	7.83E-06
4	4.34E-08	3.38E-07	1.48E-06	4.05E-06
6	7.33E-09	9.60E-08	6.30E-07	2.17E-06

Table 3.6: kQ in Hartree atomic units at 1000 K.

Wall thickness\Gap size	6	8	10	12
2	7.21E-07	3.38E-06	1.07E-05	2.50E-05
4	1.16E-07	9.63E-07	4.54E-06	1.38E-05
6	2.11E-08	3.03E-07	2.11E-06	8.26E-06

Table 3.7: kQ in Hartree atomic units at 1250 K.

Wall thickness\Gap size	6	8	10	12
2	1.50E-06	7.17E-06	2.19E-05	4.79E-05
4	2.57E-07	2.27E-06	1.03E-05	2.89E-05
6	4.97E-08	8.10E-07	5.44E-06	1.91E-05

Table 3.8: kQ in Hartree atomic units at 1500 K.

Wall thickness\Gap size	6	8	10	12
2	2.78E-06	1.32E-05	3.84E-05	7.93E-05
4	5.15E-07	4.64E-06	1.98E-05	5.12E-05
6	1.10E-07	1.87E-06	1.16E-05	3.62E-05

Table 3.9: kQ in Hartree atomic units at 1750 K.

Wall thickness\Gap size	6	8	10	12
2	4.70E-06	2.19E-05	6.06E-05	1.19E-04
4	9.49E-07	8.48E-06	3.37E-05	8.09E-05
6	2.22E-07	3.84E-06	2.13E-05	6.03E-05

Table 3.10: kQ in Hartree atomic units at 2000 K.

Wall thickness\Gap size	6	8	10	12
2	7.45E-06	3.38E-05	8.85E-05	1.65E-04
4	1.64E-06	1.42E-05	5.25E-05	1.18E-04
6	4.35E-07	7.11E-06	3.53E-05	9.14E-05

Table 3.11: kQ in Hartree atomic units at 2500 K.

Wall thickness\Gap size	6	8	10	12
2	1.61E-05	6.76E-05	1.61E-04	2.79E-04
4	4.22E-06	3.28E-05	1.05E-04	2.11E-04
6	1.42E-06	1.92E-05	7.73E-05	1.74E-04

Table 3.12: kQ in Hartree atomic units at 3000 K.

Wall thickness\Gap size	6	8	10	12
2	3.00E-05	1.16E-04	2.55E-04	4.17E-04
4	9.25E-06	6.27E-05	1.78E-04	3.29E-04
6	3.85E-06	4.10E-05	1.39E-04	2.80E-04

Table 3.13: kQ in Hartree atomic units at 3500 K.

Wall thickness\Gap size	6	8	10	12
2	5.03E-05	1.79E-04	3.67E-04	5.75E-04
4	1.78E-05	1.05E-04	2.69E-04	4.69E-04
6	8.75E-06	7.44E-05	2.19E-04	4.08E-04

3. Results

Table 3.14: kQ in Hartree atomic units at 4000 K.

Wall thickness\Gap size	6	8	10	12
2	7.78E-05	2.56E-04	4.97E-04	7.51E-04
4	3.11E-05	1.61E-04	3.78E-04	6.26E-04
6	1.73E-05	1.20E-04	3.17E-04	5.74E-04

Table 3.15: kQ in Hartree atomic units at 4500 K.

Wall thickness\Gap size	6	8	10	12
2	1.13E-04	3.46E-04	6.41E-04	9.45E-04
4	5.00E-05	2.29E-04	5.02E-04	8.00E-04
6	3.06E-05	1.79E-04	4.31E-04	7.21E-04

Table 3.16: kQ in Hartree atomic units at 5000 K.

Wall thickness\Gap size	6	8	10	12
2	1.56E-04	4.49E-04	8.00E-04	1.15E-03
4	7.52E-05	3.10E-04	6.40E-04	9.90E-04
6	4.96E-05	2.50E-04	5.60E-04	9.02E-04

Table 3.17: Extrapolated rate constants in Hartree atomic units.

| Temperature [K]\Gap size	12	10	8	6
100	3.24E-08	1.6E-08	7.07E-09	2.67E-09
200	3.97E-07	1.99E-07	8.69E-08	3.02E-08
400	2.97E-06	1.56E-06	6.85E-07	2.44E-07
600	8.71E-06	4.85E-06	2.21E-06	7.98E-07
750	1.17E-05	8.1E-06	4.45E-06	1.43E-06
1000	3.37E-05	1.79E-05	8.71E-06	3.52E-06
1250	7.49E-05	4.31E-05	2.09E-05	8.04E-06
1500	0.000116	6.86E-05	3.43E-05	1.36E-05
1750	0.000164	0.0001	5.11E-05	2.11E-05
2000	0.00022	0.000137	7.14E-05	2.99E-05
2500	0.00035	0.000228	0.000123	5.19E-05
3000	0.000502	0.000339	0.000189	7.97E-05
3500	0.000674	0.000467	0.000269	0.000114
4000	0.000845	0.000611	0.000362	0.000156
4500	0.001071	0.00077	0.000468	0.000206
5000	0.001292	0.000941	0.000585	0.000263
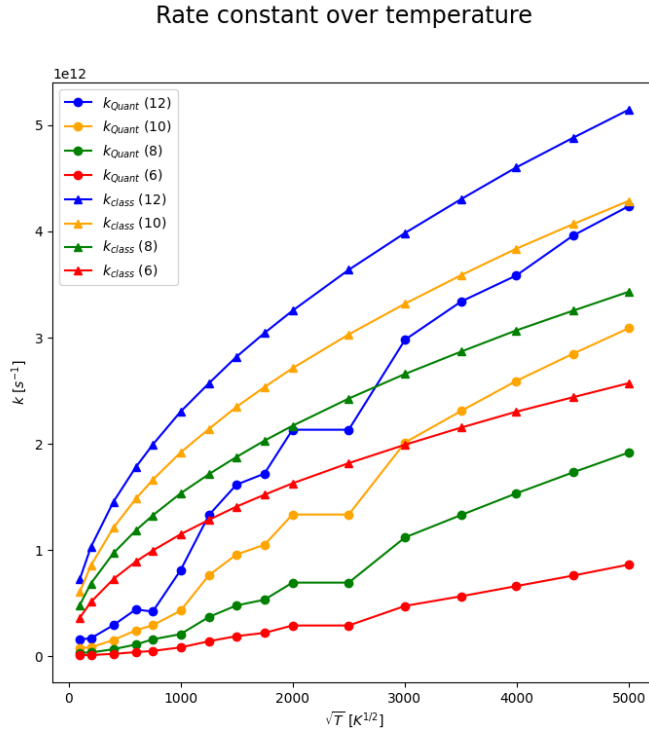
Figure 3.1: Rate constant of different sized holes over temperature. The holes are referred to by their size in points on the grid. 'k_{Quant} (12)' for example shows the quantum mechanical rate constants for the hole that was 12 points in size (0.200 Å).
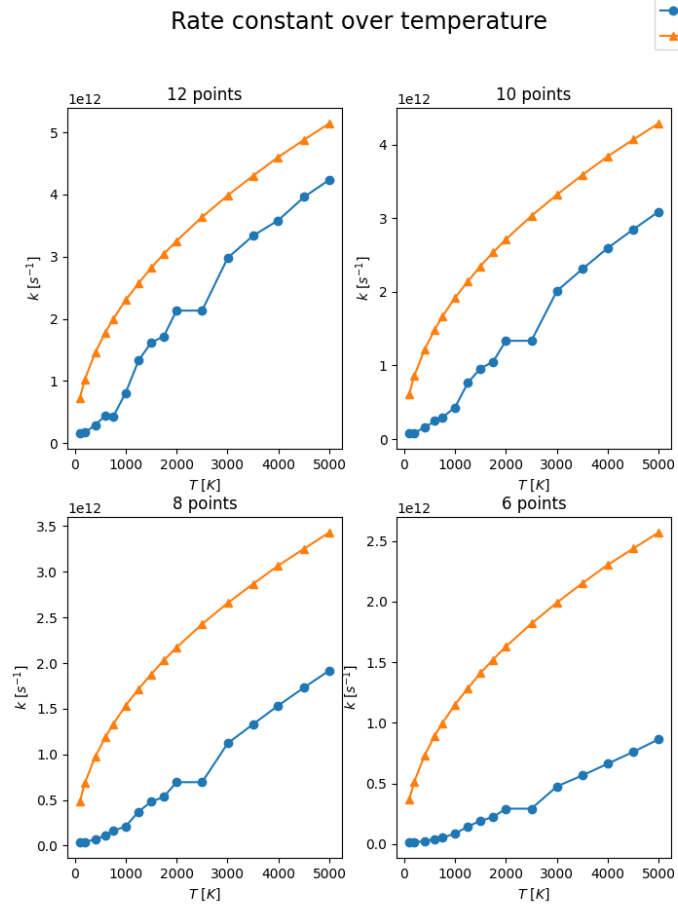
Figure 3.2: Rate constant of different sized holes over temperature, split view. The holes are referred to by their size in points on the grid. The graph '12 points' for example shows the classical and quantum mechanical rate constants for the hole that was 12 points in size (0.200 Å).

Figure 3.3: *Rate constant of different sized holes over the square root of the temperature. The holes are referred to by their size in points on the grid. 'k$_{Quant}$ (12)' for example shows the quantum mechanical rate constants for the hole that was 12 points in size (0.200 Å).*

Figure 3.4: Rate constant of different sized holes over the square root of the temperature, split view. The holes are referred to by their size in points on the grid. The graph '12 points' for example shows the classical and quantum mechanical rate constants for the hole that was 12 points in size (0.200 Å).
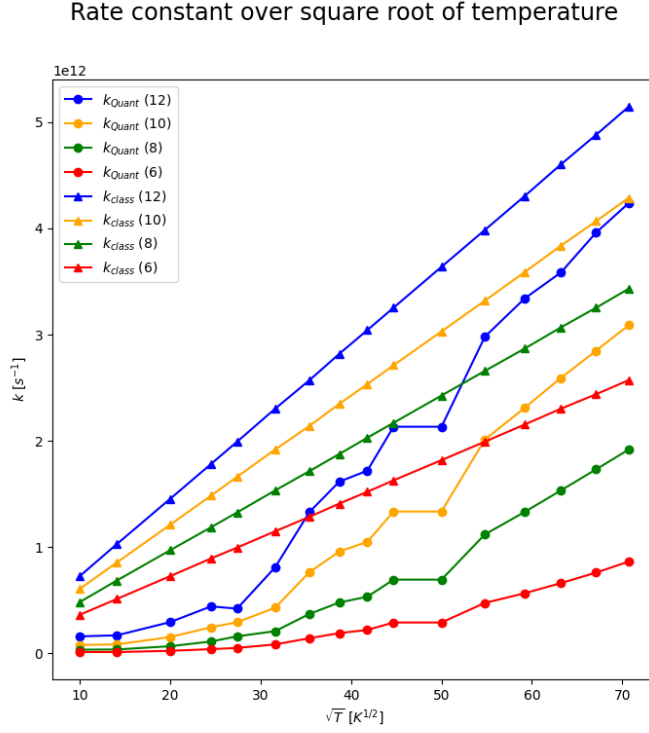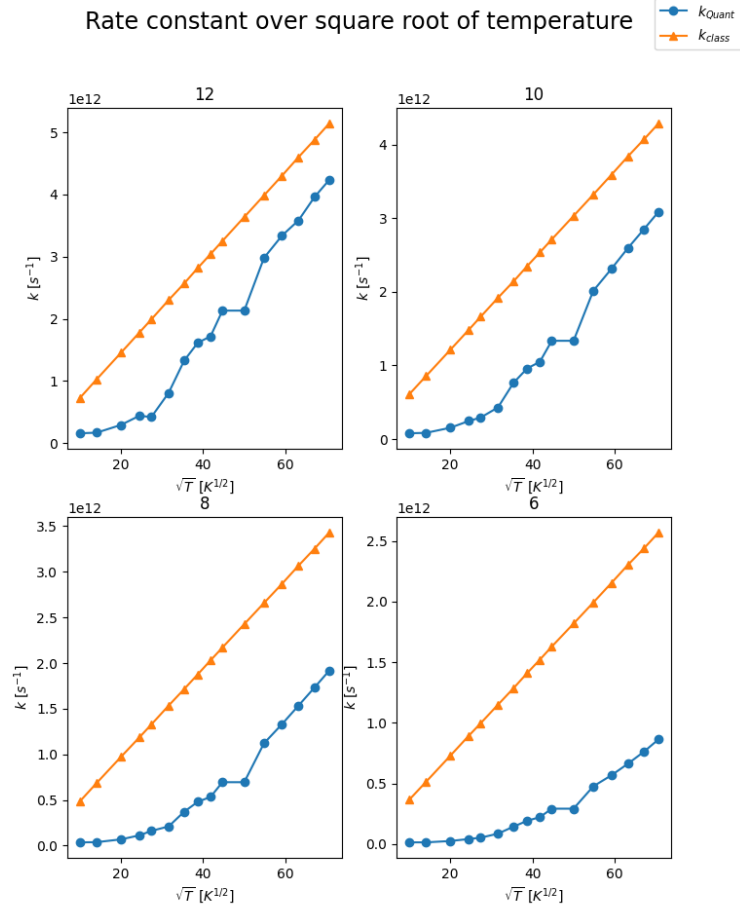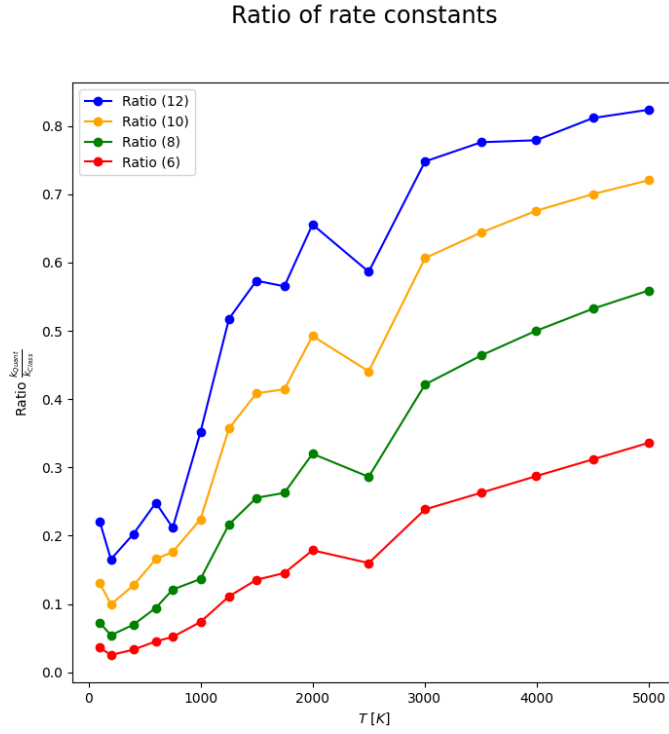
Figure 3.5: Ratio of the quantum mechanical rate constant to the classical rate over temperature. The holes are referred to by their size in points on the grid. 'Ratio (12)' for example shows the ratio between the quantum mechanical rate over the classical rate for the hole that was 12 points in size (0.200 Å).
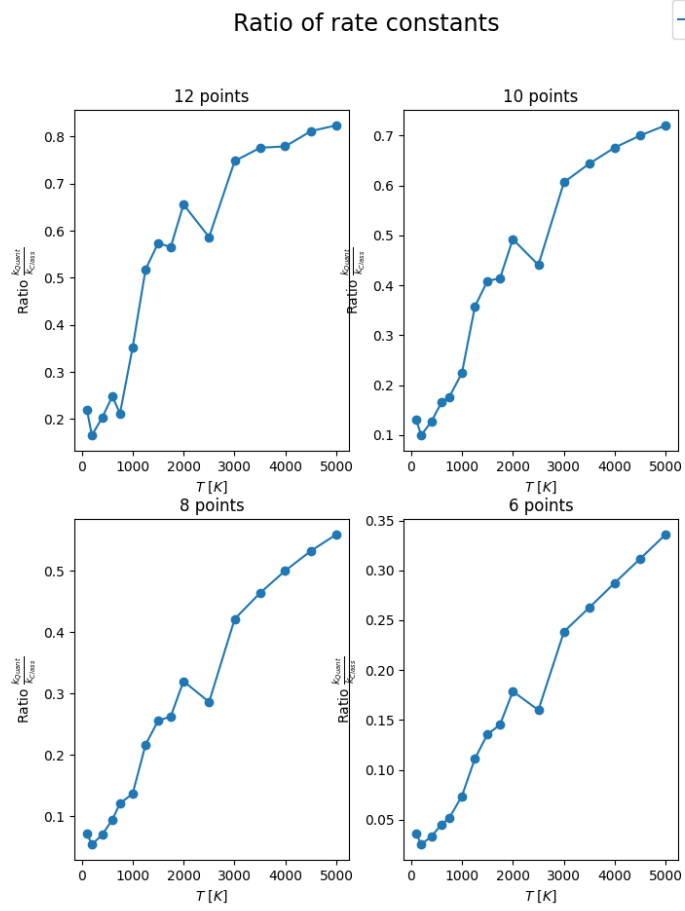
Figure 3.6: Ratio of the quantum mechanical rate constant to the classical rate over temperature, split view. The holes are referred to by their size in points on the grid. The graph '12 points' for example shows the ratio between the quantum mechanical and classical rate constants for the hole that was 12 points in size (0.200 Å).

4. Discussion

The rates calculated in this experiment deviate significantly from the classical rates. This was to be expected as the size of the box was very small and the particle was very light, meaning that there would be significant quantum mechanical effects. Under these circumstances the system behaves closer to a wave passing through a gap rather than a particle passing through a gap. The rate does not go linearly towards the classical rate, but rather fluctuates towards it. The way that the rate approaches the classical rate is also dependent on the size of the gap.

Continuing study of this system should consider both a larger box, and a heavier particle. Presumably a similar pattern would occur on a shorter temperature scale. This has though yet to be researched and confirmed.

Another interesting field for further study would be to consider placing the gap at different places in the wall (other than the centre as in this study). Possibly this will affect the rates at temperatures and circumstances where quantum effects are significant, as for a particle in a box the lower eigenstates are more centred in the middle and have a lower value close to the edges.

Error factors in this study are both a possible need for greater convergence with regards to the space outside the box, number of points in the grid and estimation of the value kQ from the correlation function (This is limited by the computational power however). Another error factor present is the inherent error with the method of evaluating the correlation functions using bound states with a discreet energy spectrum. For more information on this see [3].

5. Conclusion

This study shows that at low temperatures, for very light particles or for very small systems where quantum mechanical effects are significant the effusion rate is considerable smaller than the classical rate. The rate is presumably closer to some type of diffraction of a wave through a gap (Fresnel diffraction) than the classical model of a particle passing through a gap. This needs to be studied further.

Bibliography

[1] G. Mills, G. Schenter, D. Makarov, and H. Jónsson, "Generalized path integral based quantum transition state theory", *Chemical Physics Letters*, vol. 278, no. 1-3, pp. 91–96, 1997. DOI: `10.1016/s0009-2614(97)00886-5`.

[2] V. Ásgeirsson, A. Arnaldsson, and H. Jónsson, "Efficient evaluation of atom tunneling combined with electronic structure calculations", *The Journal of Chemical Physics*, vol. 148, no. 10, p. 102 334, 2018. DOI: `10.1063/1.5007180`.

[3] W. H. Miller, S. D. Schwartz, and J. W. Tromp, "Quantum mechanical rate constants for bimolecular reactions", *The Journal of Chemical Physics*, vol. 79, no. 10, pp. 4889–4898, 1983. DOI: `10.1063/1.445581`.

[4] D. E. Manolopoulos, "Chemical reaction dynamics lecture notes", 2008, [Online]. Available: `http://manolopoulos.chem.ox.ac.uk/`.

[5] B. Fornberg and N. Flyer, "Brief summary of finite difference methods", in *A primer on radial basis functions with applications to the geosciences*. Society for Industrial and Applied Mathematics, 2015, pp. 1–17.

Appendices

A. Code

A.1. Flux.py

An example of the program used to calculate the eigenvalues and the flux matrix (here for a 6-point gap with the wall thickness set at 2 points) is shown below:

```python
import numpy as np
import scipy.linalg as la
from matplotlib import pyplot as plt

# Boltzmann consta in Hartree
kb = 3.166830e-6

# In Ångstöm
a0 = 0.529177258
# In amu
me = 5.485799e-4
# In cm-1
har = 2.194746e5

# fjÃ¶ldi falla notaÃ°
nn = 10000
# lengd stensils fyrir fyrstu afleiÃ°u
nd = 2

# Skalinn er Ã°t frÃ¡ Bohr lengd, massa rafeindar og Hartree orku
xmin = 0.0 / a0
xmax = 1.0 / a0
nx = 60
ymin = 0.0 / a0
ymax = 8.0 / a0
```

A. Code

```python
ny = 480

m = 1.0 / me

hbar = 1.0
pi = np.pi

cd = np.zeros(nd)

for k in range(nd):
    zz = 1.0
    for j in range(nd):
        if j != k:
            zz *= (((j + 1) ** 2) / ((j + 1) ** 2 - (k + 1) ** 2))
        else:
            continue
    cd[k] = zz / (2 * (k + 1))

dx = (xmax - xmin) / (nx - 1)
dy = (ymax - ymin) / (ny - 1)

H = np.zeros((nx * ny, nx * ny))

i = -1
for i1 in range(nx):
    for i2 in range(ny):
        i = i + 1

        j = -1
        for j1 in range(nx):
            for j2 in range(ny):
                j = j + 1

                if i2 == j2:
                    if i1 == j1:
                        zz = pi ** 2 / 3.0
                    else:
                        zz = 2.0 / (i1 - j1) ** 2
                    zz = zz * (-1) ** (i1 - j1)
                    zz = zz * hbar ** 2 / (2.0 * m * dx ** 2)
```

```python
            H[i][j] = H[i][j] + zz

        if i1 == j1:
            if i2 == j2:
                zz = pi ** 2 / 3.0
            else:
                zz = 2.0 / (i2 - j2) ** 2
            zz = zz * (-1) ** (i2 - j2)
            zz = zz * hbar ** 2 / (2.0 * m * dy ** 2)
            H[i][j] = H[i][j] + zz

    x = dx * i1 + xmin
    y = dy * i2 + ymin
    if (1.0 / a0) < y < (1.0 / a0 + 2.0 * dy):
        if x < (0.5 * xmax - 3.0 * dx) or x > (0.5 * xmax + 3.0 * dx):
            H[i] = np.zeros(nx * ny)
            H[:, i] = np.zeros(nx * ny)
            H[i, i] = -1

eigvals, eigvecs = np.linalg.eigh(H)

psi = eigvecs.transpose()
psi = psi[np.argsort(eigvals)]
E = eigvals[np.argsort(eigvals)].real

cut = np.where(E > 0)
E = E[cut]
psi = psi[cut]

for i in range(nn):
    zz = psi[i]
    zz = zz * zz
    zz *= dy * dx
    s = np.sum(zz)
    s = np.sqrt(s)
    psi[i] = psi[i] / s


y = 1.0 / a0 + 1.0 * dy
i0 = int((y - ymin) / dy)
```

```python
for j in range(nn):
    for i2 in range(nx):
        ix = ny * i2 + i0
        zz = 0.0
        for k in range(nd):
            kk = k + 1
            zz += cd[k] * (psi[j][ix + kk] - psi[j][ix - kk])
        zz = zz / dy
        dpsi[j, i2] = zz

for j1 in range(nn):
    for j2 in range(nn):
        zz = 0.0
        for i2 in range(nx):
            ix = ny * i2 + i0
            zz0 = dpsi[j1, i2] * psi[j2, ix] - psi[j1, ix] * dpsi[j2, i2]
            zz0 = zz0 * dy / (2.0 * m)
            zz += zz0
        zz = zz ** 2
        fx2[j1, j2] = zz

with open("Energy.npz", "wb") as f:
    np.savez(f, E=E, fx2=fx2)
```

A.2. Correlation.py

The program used to calculate the correlation functions is shown below:

```python
import numpy as np
from matplotlib import pyplot as plt

# Boltzmann in Hartree
kb = 3.166830e-6

# In cm-1
har = 2.194746e5
```

```python
Trange = np.array([100, 200, 400, 600, 750, 1000, 1250, 1500, 1750, 2000, 2500, 3000,

tmin = 0
tmax = 10000
nt = 1000
dt = (tmax - tmin) / nt


hbar = 1.0


with np.load('Energy.npz') as data:
    E = np.array([data['E']])
    fx2 = data['fx2']

nn = np.shape(fx2)[0]
epsilon = np.log(1e-16)
Zero = E[0]


dE = E - E.transpose()
sE = E + E.transpose()


dEm = dE.copy()
np.fill_diagonal(dEm, 1)


ttot = np.arange(tmin, tmax+1, dt)
CF = np.zeros((2, nt + 1))
CS = np.zeros((2, nt + 1))
CF[0] = ttot
CS[0] = ttot


for T in Trange:
    beta = 1 / (kb * T)
    cut = 2 * epsilon / beta
    over = np.where(E > Zero - cut)
    if np.shape(over) == 0:
        print(f'not converged at {T}')
        Q = nn
    else:
        print(f'At {T}K, {over[0]} functions are significant')
        if over[0] <= nn:
            Q = over[0]
```

A. Code

```python
        else:
            Q = nn

    for it in range(nt + 1):
        t = tmin + it * dt
        zz = np.exp(-beta * 0.5 * sE[0:Q,0:Q]) * fx2[0:Q,0:Q]
        CF1 = zz * np.cos(dE[0:Q,0:Q] * t)
        zzd = np.diagonal(zz)
        CS1 = zz * np.sin(dE[0:Q,0:Q] * t) / dEm[0:Q,0:Q]
        CSd = zzd * t
        np.fill_diagonal(CS1, CSd)

        CF[1, it] = np.sum(CF1)
        CS[1, it] = np.sum(CS1)

    with open(f'Side-Flux{T}.txt', 'w') as f:
        np.savetxt(f, CS, fmt='%1.4e')

    with open(f'Flux-Flux{T}.txt', 'w') as f:
        np.savetxt(f, CF, fmt='%1.4e')
```

B. Eigenstate examples

Examples of the eigenstates of the system are shown in the figures below:

B. Eigenstate examples
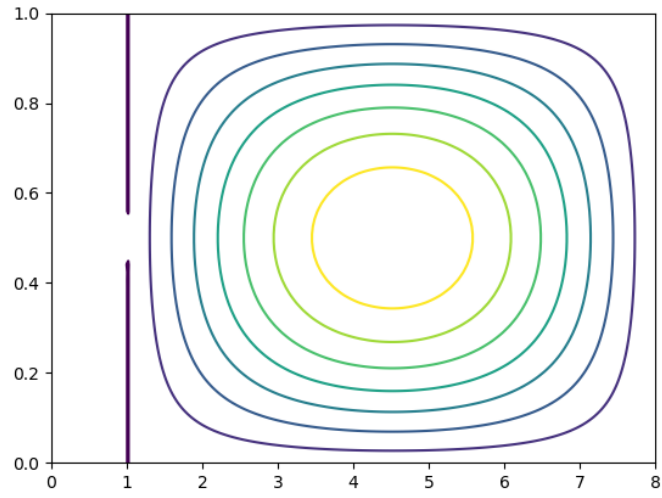
Figure B.1: Wavefunction for the ground state of a system with a 6-point gap and a 2-point wall.
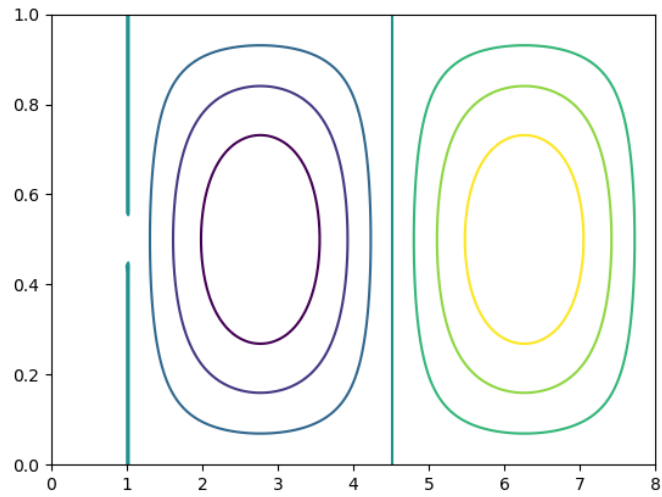
Figure B.2: Wavefunction for the first excited state of a system with a 6-point gap and a 2-point wall.
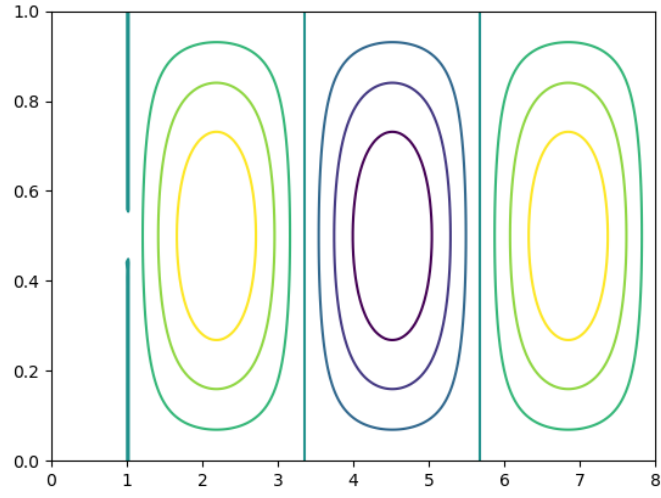
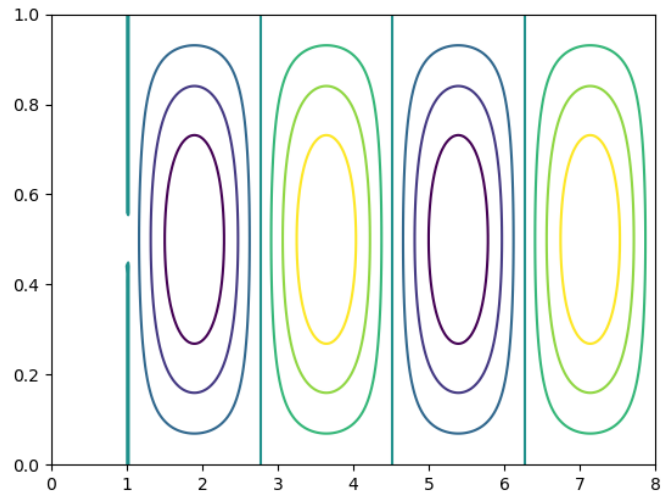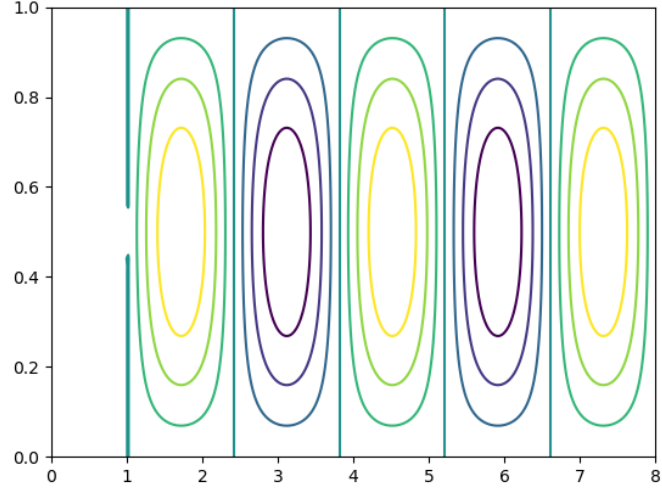Figure B.3: Wavefunction for the second excited state of a system with a 6-point gap and a 2-point wall.

Figure B.4: Wavefunction for the third excited state of a system with a 6-point gap and a 2-point wall.

B. Eigenstate examples

Figure B.5: *Wavefunction for the fourth excited state of a system with a 6-point gap and a 2-point wall.*
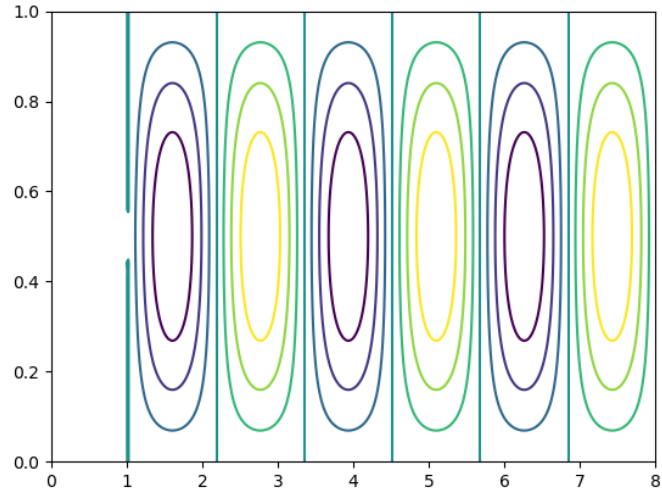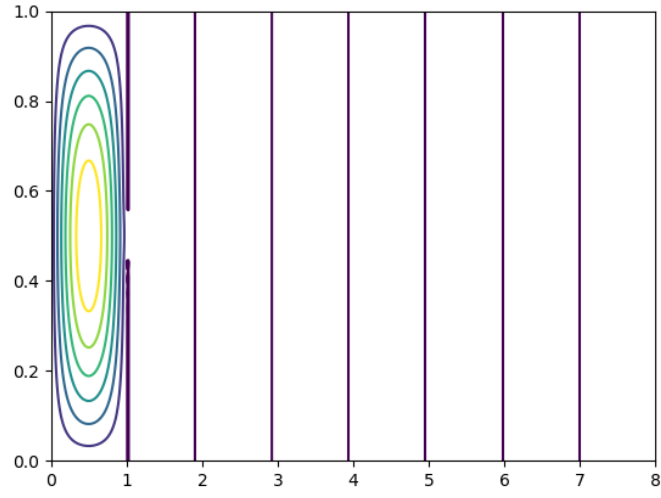

Figure B.6: *Wavefunction for the fifth excited state of a system with a 6-point gap and a 2-point wall.*

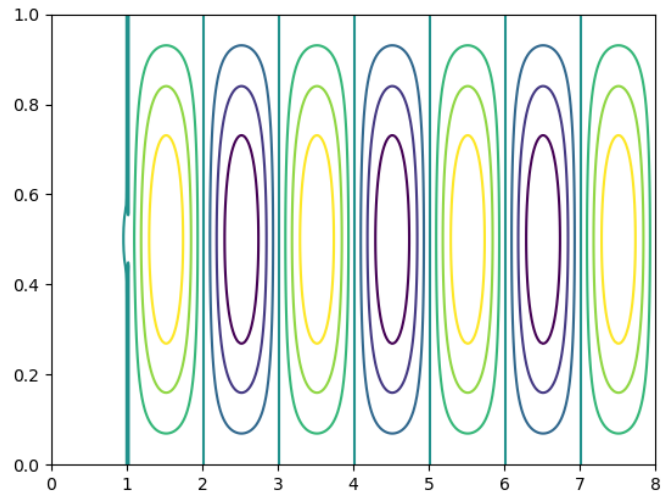*Figure B.7: Wavefunction for the sixth excited state of a system with a 6-point gap and a 2-point wall.*

Figure B.8: Wavefunction for the seventh excited state of a system with a 6-point gap and a 2-point wall.
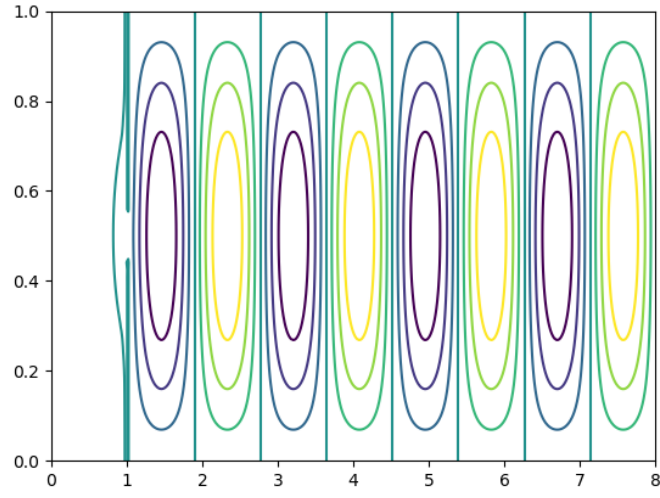
Figure B.9: Wavefunction for the eighth excited state of a system with a 6-point gap and a 2-point wall.
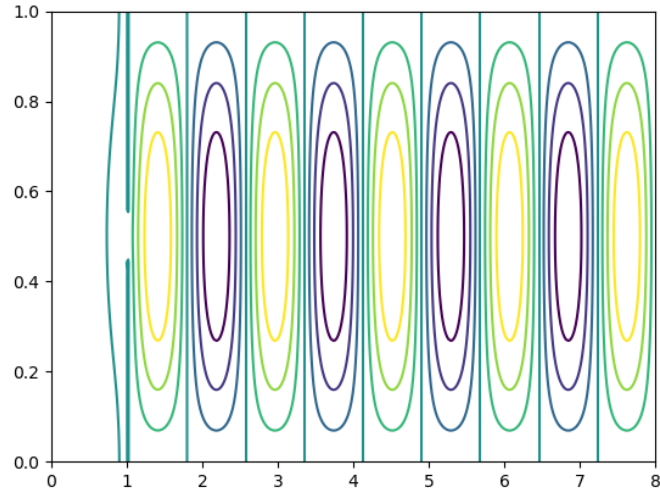

Figure B.10: Wavefunction for the ninth excited state of a system with a 6-point gap and a 2-point wall.