



Project Report # 1

CHEM 548-Molecular Electronic Structure: Advanced Quantum
Chemistry & Numerical Methods Spring 2017

Course Instructor

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1 Computational Project- 1 Programming Homework 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.

2 Numerical Solutions of the Schrödinger Equation

The basic problem in quantum mechanics is to solve the stationary Schrödinger equation

$$-\frac{\hbar^2}{2m}\Delta^2\Psi_n(\vec{x}) + V(\vec{x})\Psi_n(\vec{x}) = E_n\Psi_n(\vec{x}) \quad (1)$$

for the energy eigenvalues and the associated energy eigenfunctions (stationary states) Ψ_n . There are a number of cases in which we can solve the Schrödinger equation analytically, but in most of the practical cases of interest obtaining an exact solution is not possible so approximate numerical methods are used. In this project we use the Finite difference method – an approximate second order scheme to solve for the eigenvalues and eigenfunctions for various potentials, namely particle in a box, finite well, harmonic oscillator etc.

3 Finite-Difference Method

In elementary calculus we define a derivative as :

$$u'(x) = \lim_{\Delta x \rightarrow 0} \frac{u(x + \Delta x) - u(x)}{\Delta x} \quad (2)$$

However, on a computer memory we cannot deal with $\Delta x \rightarrow 0$ so we need to define a discrete analogue of the continuous case. In this process of discretization, the set of points in which this function is defined is finite and the value of the function is available on these set of points. The approximations to the derivatives are derived from these discrete values of the functions at the points that are considered.

The figure below [1] shows the discrete set of points x_i where the function is known. We can use the notation $u_i = u(x_i)$ to denote the value of the function at the i -th node of the grid on computer. The nodes divide the axis into a set of intervals of width $\Delta x = x_{i+1} - x_i$. All the intervals are made to be of equal size in our case.

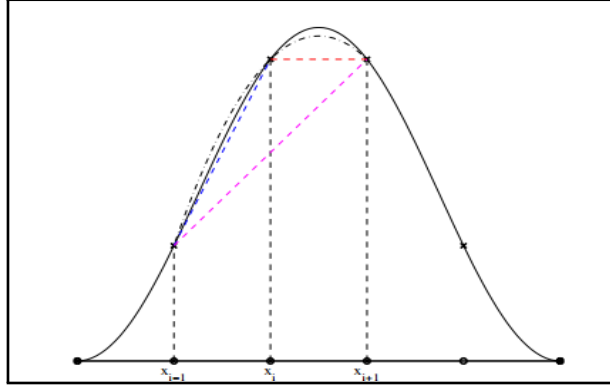


Figure 1: The grids used in computation and examples of forward, backward and central approximation to the derivative at point x_i

We can extend the definition of derivative in the continuous case to the discrete case as :

$$u'(x) \approx \frac{u(x_i + \Delta x) - u(x_i)}{\Delta x} = \frac{u_{i+1} - u_i}{\Delta x} \quad (3)$$

where now Δx is finite and assumed to be very small, although not zero. This is something known as the Forward Euler approximation since it uses forward differencing. We can see that as $\Delta x \rightarrow 0$ the approximation improves. In addition to the above forward differencing we also have:

Backward Difference:

$$u'(x) \approx \frac{u(x_i) - u(x_i - \Delta x)}{\Delta x} = \frac{u_i - u_{i+1}}{\Delta x} \quad (4)$$

Central Difference:

$$u'(x) \approx \frac{u(x_i + \Delta x) - u(x_i - \Delta x)}{2\Delta x} = \frac{u_{i+1} - u_{i-1}}{2\Delta x} \quad (5)$$

Although all these definitions are equivalent in the continuous case but these are but lead to different approximations in the discrete case. We now use the Taylor series expansion to study the truncation error associated with each of these difference methods. We look at the Forward difference first. We expand the function at x_{i+1} about the point x_i as

$$u(x_i + \Delta x_i) = u(x_i) + \Delta x_i \frac{\partial u}{\partial x} \Big|_{x_i} + \frac{\Delta x_i^2}{2!} \frac{\partial^2 u}{\partial x^2} \Big|_{x_i} + \frac{\Delta x_i^3}{3!} \frac{\partial^3 u}{\partial^3 x^3} \Big|_{x_i} + \dots \quad (6)$$

The above expression can be rearranged as :

$$\frac{u(x_i + \Delta x_i) - u(x_i)}{\Delta x_i} - \frac{\partial u}{\partial x} \Big|_{x_i} = \underbrace{\frac{\Delta x_i^2}{2!} \frac{\partial^2 u}{\partial x^2} \Big|_{x_i} + \frac{\Delta x_i^3}{3!} \frac{\partial^3 u}{\partial^3 x^3} \Big|_{x_i} + \dots}_{\text{Truncation Errors}} \quad (7)$$

The above expression shows that the forward difference formula correspond to the truncating the Taylor series after the first term. This is called the truncating error which is defined as the difference between the partial derivative and its finite difference approximation. The general exact behavior of the error is not know but we can characterize it as $\Delta x \rightarrow 0$ and write the above expression as :

$$\frac{\partial u}{\partial x} \Big|_{x_i} = \frac{u(x_i + \Delta x_i) - u(x_i)}{\Delta x_i} + O(\Delta x) \quad (8)$$

Since the Schrödinger equation is second order partial differential equation we now derive the finite difference approximations for the second order, again from the definition of the derivative.

$$\frac{\partial^2 u}{\partial x^2} = \lim_{\Delta x \rightarrow 0} \frac{\frac{\partial u}{\partial x}(x + \frac{\Delta x}{2}) - \frac{\partial u}{\partial x}(x - \frac{\Delta x}{2})}{\Delta x} \quad (9)$$

$$= \lim_{\Delta x \rightarrow 0} \frac{1}{\Delta x} \left[\frac{u(x + \Delta x) - u(x)}{\Delta x} - \frac{u(x) - u(x - \Delta x)}{\Delta x} \right] \quad (10)$$

$$= \lim_{\Delta x \rightarrow 0} \frac{1}{\Delta^2 x} [u(x + \Delta x) - 2u(x) + u(x - \Delta x)] \quad (11)$$

Now we can use this discretized form of the differential operator in our wave function equation

$$\frac{\partial^2}{\partial x^2} \Psi \approx \frac{\Psi(x + d) - 2\Psi(x) + \Psi(x - d))}{d^2} \approx \frac{\Psi_{n-1} - 2\Psi_n + \Psi_{n+1}}{d^2} \quad (12)$$

Where we have replaced the interval between the grid points Δx by d . The Schrödinger equation now reads:

$$-\frac{\hbar}{2m} \frac{\Psi_{n-1} - 2\Psi_n + \Psi_{n+1}}{d^2} + V_n \Psi_n = E \Psi_n \quad (13)$$

We immediately realize that this is a matrix equation of the form:

$$-\frac{\hbar}{2md^2} \begin{bmatrix} -2 & 1 & & & \\ 1 & -2 & 1 & & \\ & \ddots & \ddots & \ddots & \\ & & 1 & -2 & 1 \\ & & & 1 & -2 \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_{n-1} \\ \Psi_n \end{bmatrix} + \begin{bmatrix} V_1 & & & & \\ & V_2 & & & \\ & & \ddots & & \\ & & & V_{n-1} & \\ & & & & V_n \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_{n-1} \\ \Psi_n \end{bmatrix} = E \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_{n-1} \\ \Psi_n \end{bmatrix}$$

where n is the number of mesh/grid points. So, its now clear that we have an eigenvalue equation of the form:

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

4 Particle in a Box Problem using the Finite-Difference Method

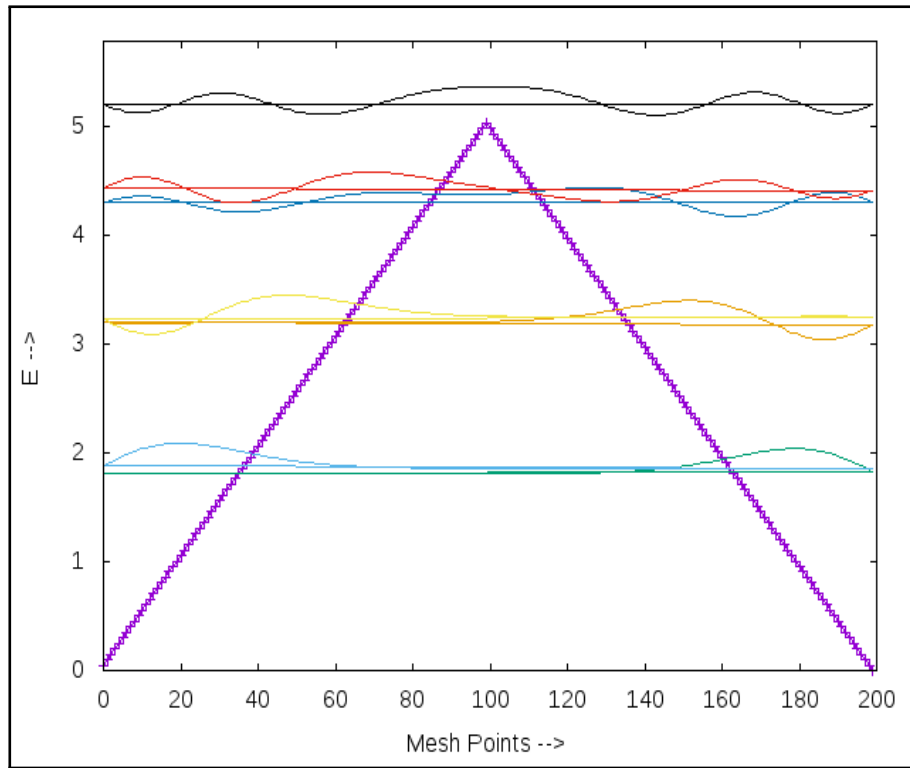


Figure 2: The form of the wave functions for an particle in arbitrary potential

The codes for Finite difference method for an arbitrary potential were written. The plot of the wave functions is shown above. We then solved for the particle in a box. The potential was included in the codes as shown below. The portion of the code used to define Finite Depth Well potential:

```
write(*, '("particle_in_a_box")')  
do i=1,points  
  potent(i)=0d0  
enddo
```

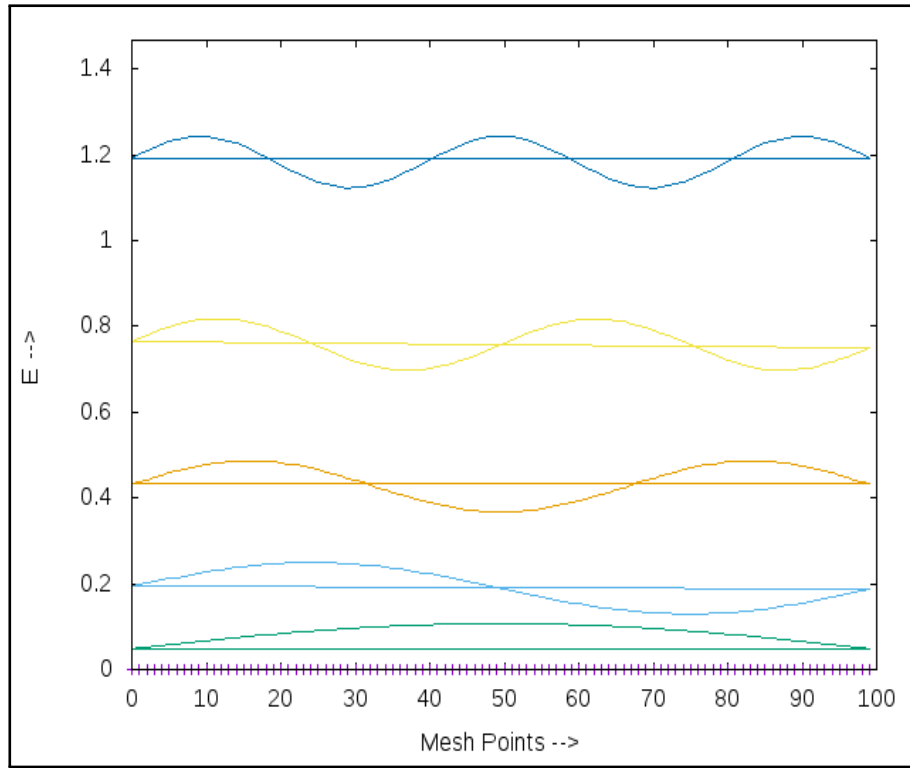


Figure 3: The particle in a box wave functions.

Table 1: Particle in a box enegies :

| | |
|---|------------------------|
| 1 | 0.04932828634628094733 |
| 2 | 0.19731314046657644212 |
| 3 | 0.44395454783807514199 |
| 4 | 0.78925248407176684662 |
| 5 | 1.23320691505796276033 |

5 Particle in a Finite Depth Well Problem

The portion of the code used to define Finite Depth Well potential:

```

write(*, '(" particle_finite_well_potential" ) ')
do i=1,points
  if ((i.le.50).or.(i.ge.(points-50))) then
    potent(i)=7
  else
    potent(i)=0
  end if
enddo

```

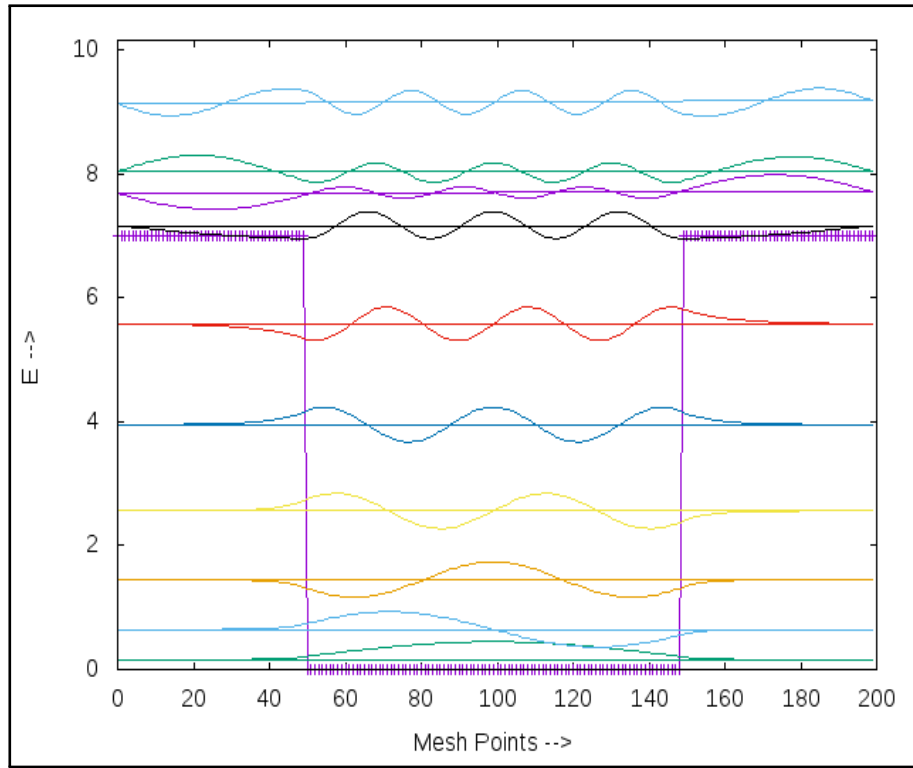


Figure 4: Particle in a finite well wave functions

Table 2: Particle in a finite dimensional box energies in a.u:

| | |
|----|------------------------|
| 1 | 0.16230756297106554986 |
| 2 | 0.64759851279880809027 |
| 3 | 1.45051041084737164510 |
| 4 | 2.56012065295287571942 |
| 5 | 3.95454137203869082740 |
| 6 | 5.58009527020730988767 |
| 7 | 7.17211857692431919986 |
| 8 | 7.69915763596709723515 |
| 9 | 8.02114919354751343405 |
| 10 | 9.15804009973776267373 |

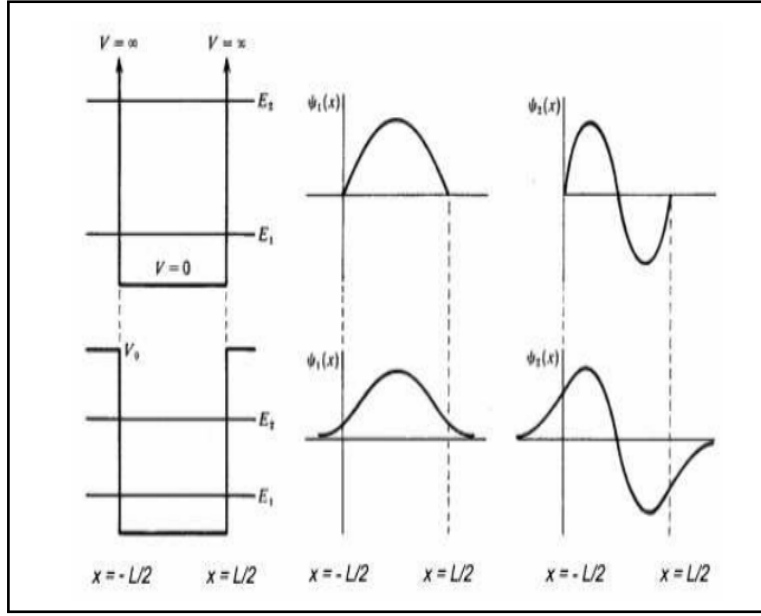


Figure 5: Comparison between the finite and infinite well wavefunctions[4].

Table 3: Comparison between the finite and infinite well wavefunctions

| Infinite well | Finite well |
|-----------------------------------|---------------------------------------|
| $\Psi(x)$ is confined to the well | $\Psi(x)$ is not confined to the well |
| infinite tower of states | finite tower of states |
| there are no unbound states | unbound states for $E > V_0$ |

We observe a quantum tunnelling effect in case of the finite wall potential well.

For $x > L/2$ the wavefunction is $\Psi(x) \propto \exp^{-\alpha x}$

For $x < -L/2$ the wavefunction is $\Psi(x) \propto \exp^{\alpha x}$

where penetration depth α is defined as :

$$\alpha = \frac{2m(V_0 - E)}{\hbar^2} > 0 \quad (15)$$

So we have as $V \rightarrow \infty \Rightarrow \alpha \rightarrow \infty \Rightarrow \frac{1}{\alpha} \rightarrow 0$ and

$V \rightarrow 0 \Rightarrow \alpha \rightarrow 0 \Rightarrow \frac{1}{\alpha} \rightarrow \infty$

Non-zero wavefunction in classically forbidden regions ($KE < 0$) is a purely quantum mechanical effect. It allows tunnelling between classically allowed regions and it follows from the fact that we require that both $\Psi(x)$ and its first derivative $\Psi'(x)$ to be continuous.

6 Particle in a Box Problem with a Rectangular Barrier in the Middle

The portion of the code used to define the rectangular barrier:

```
write(*, '("particle_in_a_box_with_rectangular_potential_in_the_middle")')
do i=1,points
  if((i.ge.90).and.(i.le.110)) then
    potent(i)=60d0*xxx
  else
    potent(i)=0d0
  end if
enddo
```

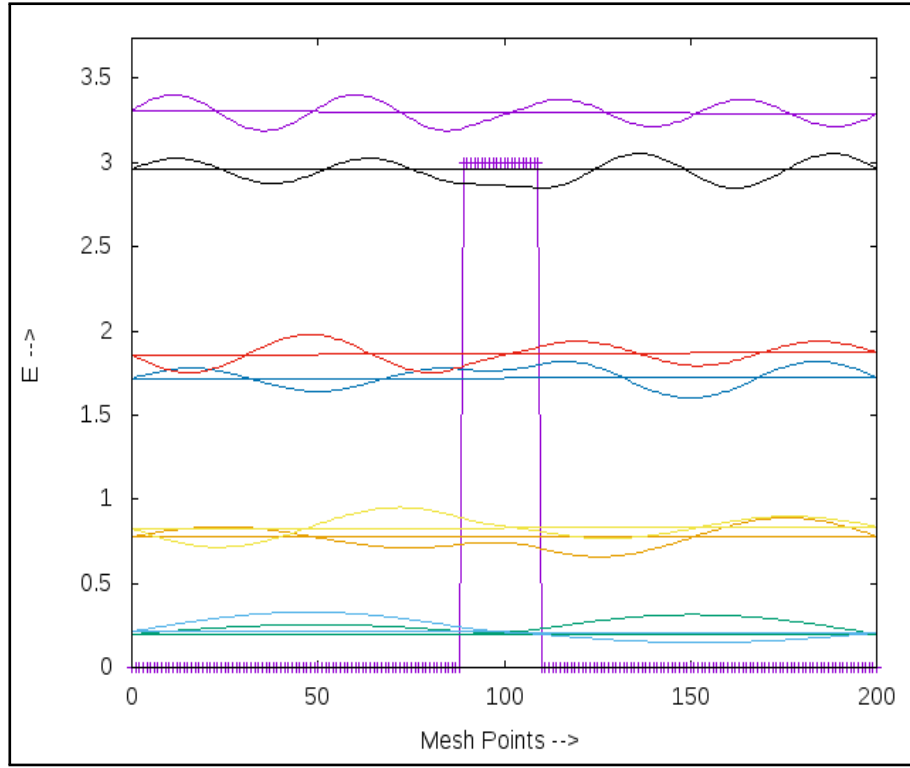


Figure 6: The particle in a box wavefunctions with a rectangular barrier in the box

Table 4: Particle in a box with rectangular box potential energies in a.u :

| | |
|---|------------------------|
| 1 | 0.19532170202806756198 |
| 2 | 0.20886224845015990970 |
| 3 | 0.77396029177840808266 |
| 4 | 0.83304656364252582801 |
| 5 | 1.70963511132301015927 |
| 6 | 1.86545404978419049336 |
| 7 | 2.95000952906981650514 |
| 8 | 3.29493788964326528301 |

7 Harmonic and Morse oscillator problems

The portion of the code used to define the Harmoic Oscillator-Potential

```
write(*, '("harmonic_oscillator_potential")')
do i=1,points
  potent(i)=0.5d0*(exp((dble(i-1)-dble((points-1)/2))*xxx))**2
enddo
```

Table 5: Harmonic Potential energies in a.u using 3000 mesh points:

| | |
|---|------------------------|
| 0 | 0.49999965262031764723 |
| 1 | 1.49999826628845767118 |
| 2 | 2.49999556465263639282 |
| 3 | 3.49999250121254679158 |
| 4 | 4.49999806088089915335 |

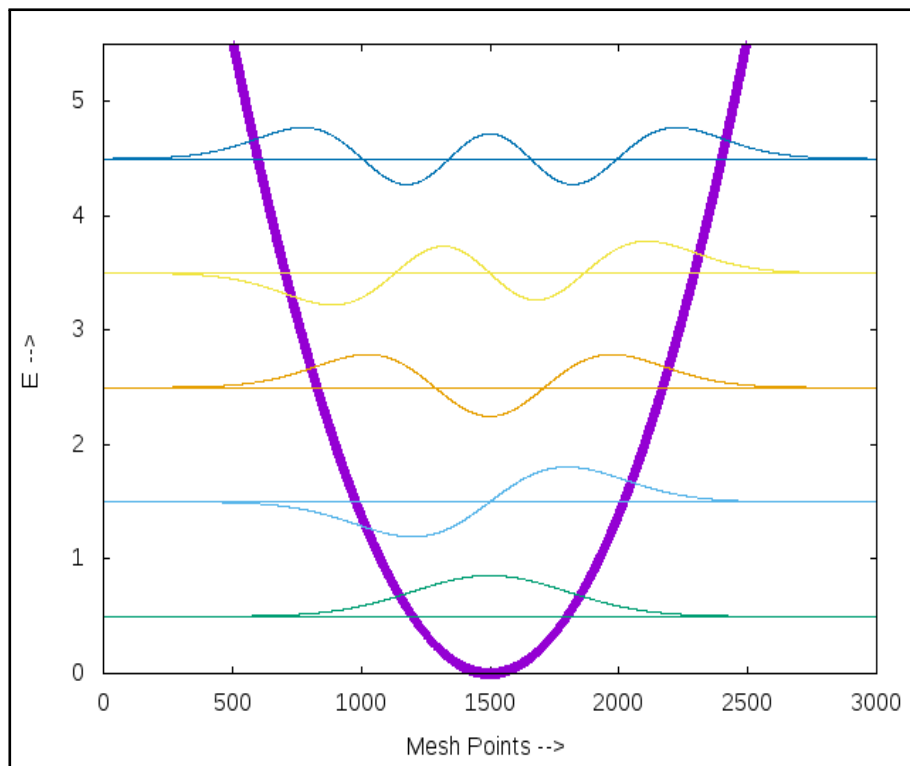


Figure 7: The harmonic oscillator wave functions.

The portion of the code used to define the Morse-Potential

```
do i=1,points
  potent2(i)=4d0*(1-exp(-0.4*(dble(i-dble(1.5*points/3))*xxx))**2
enddo
```

Table 6: Morse Potential energies in a.u using 1000 mesh points:

| | |
|---|------------------------|
| 0 | 0.61244520368495614093 |
| 1 | 1.71732614791903848150 |
| 2 | 2.66219779753077956386 |
| 3 | 3.44707717940468727491 |
| 4 | 4.07200762638626745371 |
| 5 | 4.54096380891701389970 |

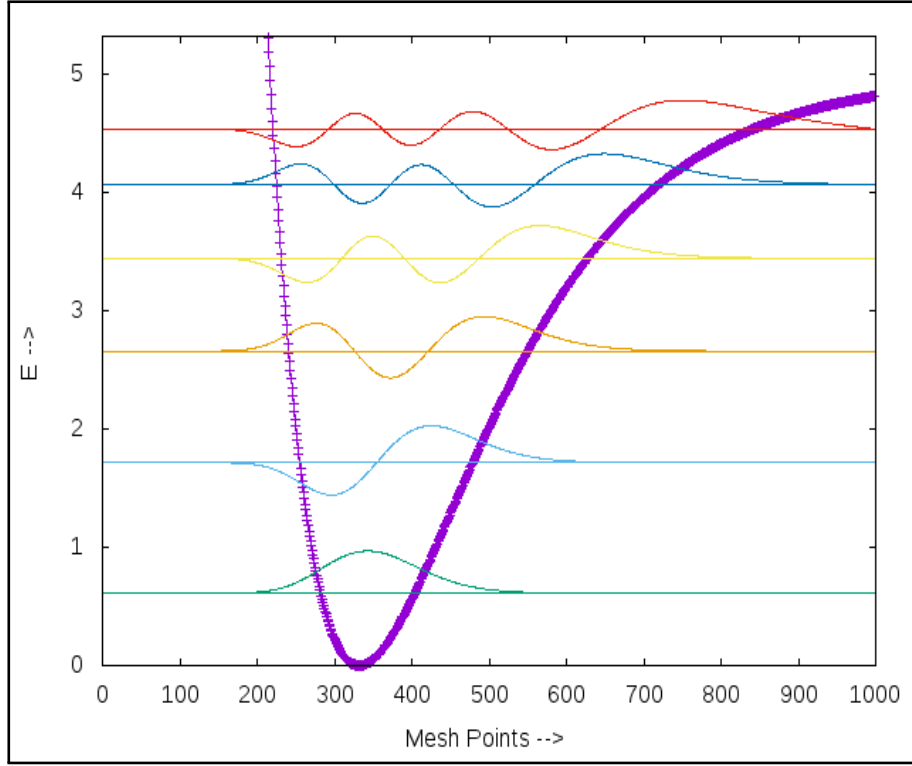


Figure 8: The Morse potential wavefunctions

7.1 Franck-Condon Principle

Visualizing the vertical transition from ground to excited electronic state as taking place from a vibrational wave function – that gives a probability distribution of finding the nuclei in a give region of space – the probability of transition to a given vibrational level can be determined by the $S_{v',v}$ this gives the overlap of the vibrational wave function in the ground and excited state.

The v'' quantum numbers refer to the ground state and the v' quantum numbers refer to the excited state. The total transition probability is the square of the transition moment which in turn can be separated into electronic and nuclear parts using the Condon approximation.

Condon approximation: the electronic transition occurs on a time scale short compared to nuclear motion so that the transition probability can be calculated at a fixed nuclear position.

The Franck-Condon principle is based on the Born-Oppenheimer approximation, which allows separation of the electronic q and nuclear Q wave functions given the total wavefunction.[5]

$$|\Psi_{total}(Q, q)\rangle = |\Psi_{nuclear}(Q)\rangle |\Psi_{electronic}(Q; q)\rangle \quad (16)$$

Since the transition operator, $\hat{\mu}(q)$, is dependent only on the electronic component, the nuclear components can be separated from the transition moment integral that dictates the probability of the transition occurring:

$$\langle \Psi_{total}^*(Q, q) | \hat{\mu}(q) | \Psi_{total}(Q, q) \rangle = \langle \Psi_{nuclear}(Q) | \Psi_{electronic}(Q; q) | \hat{\mu} | \Psi_{nuclear}(Q) \Psi_{electronic}(Q; q) \rangle \quad (17)$$

$$= \underbrace{\langle \Psi_{nuclear}(Q) | \Psi_{nuclear}(Q) \rangle}_{\text{nuclear overlap}} \langle \Psi_{electronic}(Q; q) | \hat{\mu} | \Psi_{electronic}(Q; q) \rangle \quad (18)$$

The Frank-Condon factor/coefficient is the square of this overlap integral between the two vibrational states(excited and ground states).

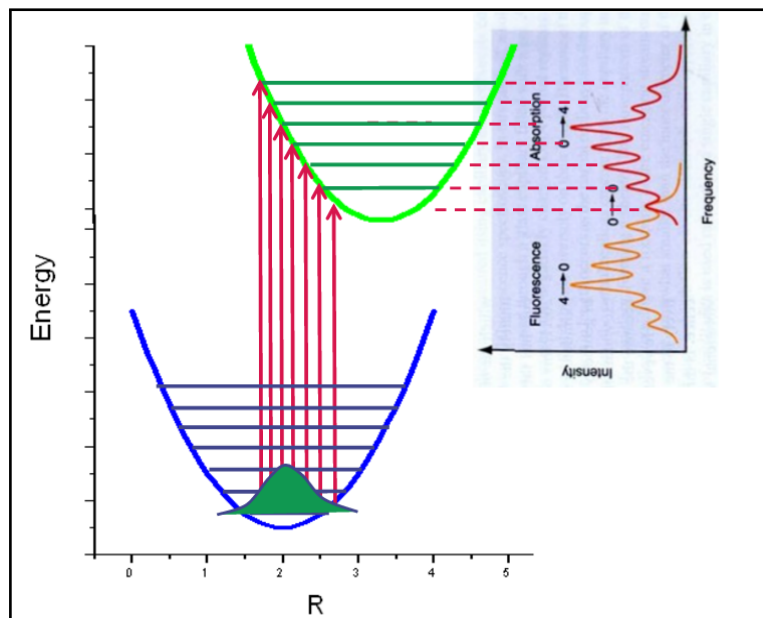


Figure 9: Franck-Condon principle energy diagrams are shown here. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $v = 0$ and $v = 2$. [2]

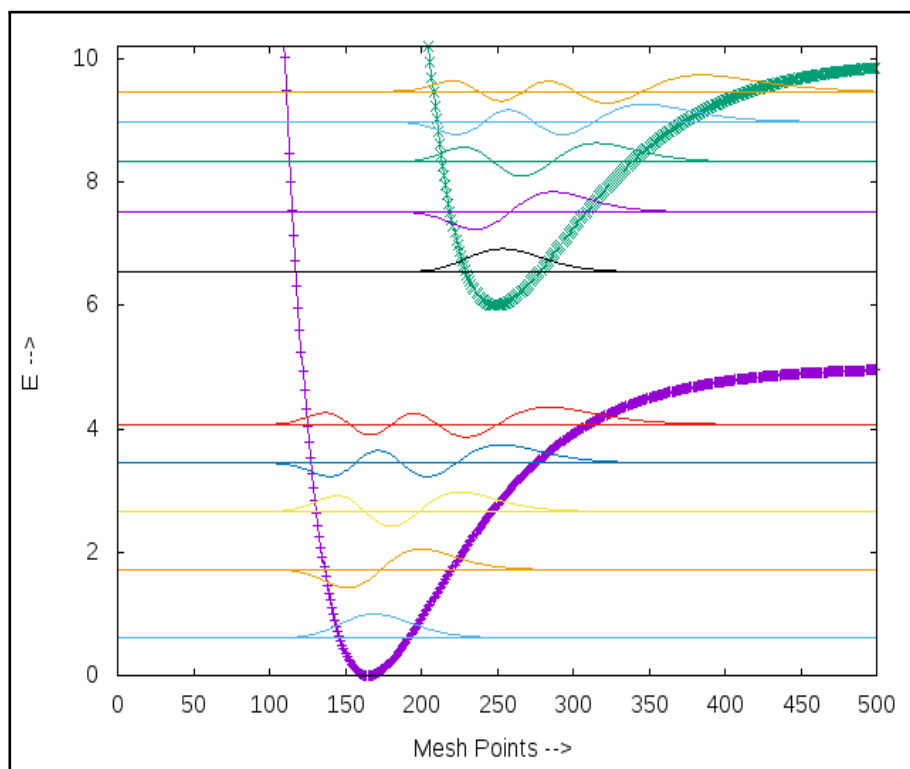


Figure 10: The ground electronic state and the excited electronic state potential energy surfaces obtained by setting the energy of the excited state higher by 6 a.u.

The ground and excited state energies for the Morse potential (used in determination of the Franck-Condon Coefficients) are shown in the tables below.

Table 7: The energies of the ground state in a.u:

| | |
|------------|------------------------|
| $v'' = 1$ | 0.61238187609305338999 |
| $v'' = 2$ | 1.71707818247003318746 |
| $v'' = 3$ | 2.66170820024868248765 |
| $v'' = 4$ | 3.44639288484202710450 |
| $v'' = 5$ | 4.07121213206735799162 |
| $v'' = 6$ | 4.53621740416869467794 |
| $v'' = 7$ | 4.84517085141899794820 |
| $v'' = 8$ | 5.06873827998376302872 |
| $v'' = 9$ | 5.33831377811080276530 |
| $v'' = 10$ | 5.67148648260862842108 |

Table 8: The energies of the excited state in a.u:

| | |
|-----------|-------------------------|
| $v' = 1$ | 6.54562711999247426320 |
| $v' = 2$ | 7.51683533087035193887 |
| $v' = 3$ | 8.32800937025043985784 |
| $v' = 4$ | 8.97925120024521561390 |
| $v' = 5$ | 9.47135663446098696738 |
| $v' = 6$ | 9.83285981783623519448 |
| $v' = 7$ | 10.19488055525867764572 |
| $v' = 8$ | 10.64155574230201928287 |
| $v' = 9$ | 11.16716110119765126285 |
| $v' = 10$ | 11.76214199279432470746 |

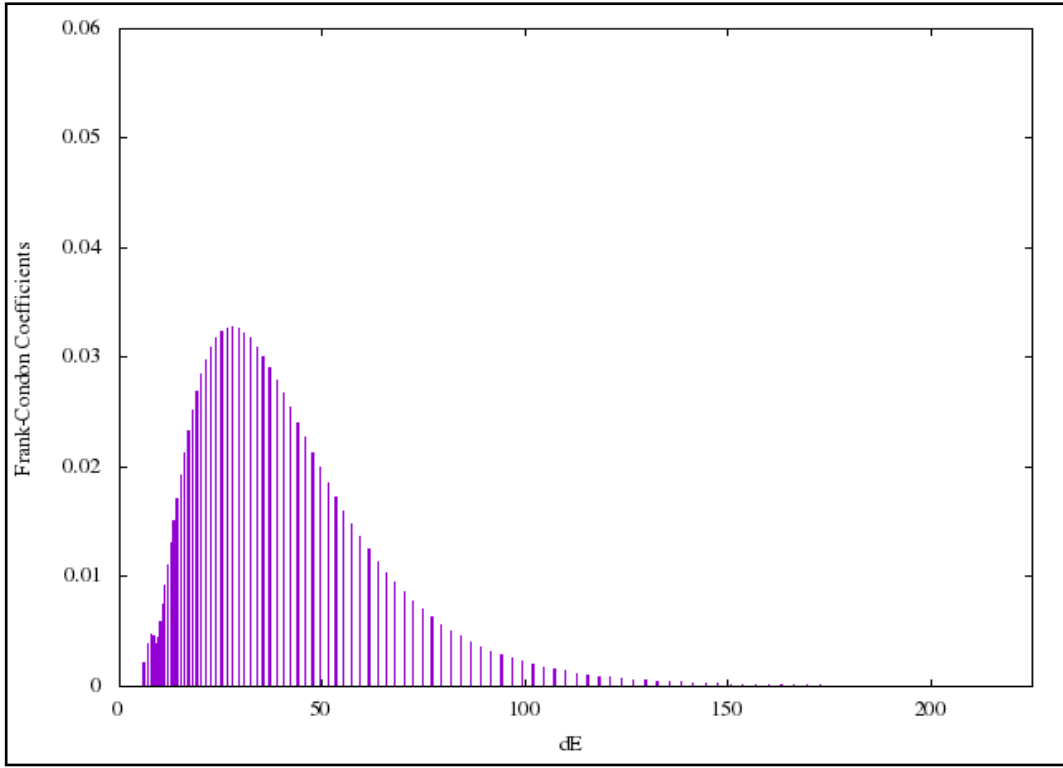


Figure 11: Vibrational progression in an electronic absorption spectrum. This plots shows the Frank-Condon coefficients for transition from the ground vibrational state of the ground electronic state to 100 other states of the electronically excited state.

Table 9: Franck-Condon Coefficients

| Ground state | Excited state | Franck-Condon Coefficients : |
|--------------|---------------|------------------------------|
| $v''=0$ | $v'=0$ | 0.0022299737679933135867105 |
| $v''=0$ | $v'=1$ | 0.0038975937083522461945595 |
| $v''=0$ | $v'=2$ | 0.0046835738264243307812928 |
| $v''=0$ | $v'=3$ | 0.0046077313831085096526574 |
| $v''=0$ | $v'=4$ | 0.0038642654274414537339533 |
| $v''=0$ | $v'=5$ | 0.0034177806512801925734046 |
| $v''=0$ | $v'=6$ | 0.0044724716445935707928583 |
| $v''=0$ | $v'=7$ | 0.0059432112217992051975135 |
| $v''=0$ | $v'=8$ | 0.0075187236209745614279321 |
| $v''=0$ | $v'=9$ | 0.0092263503685435857559760 |

8 Conclusions

The finite difference method was implemented using the FORTRAN programming language. The plots for the questions were included. It was observed that the energy levels in the finite well potential are lower than of the infinite wall potential well because the wavefunction spreads out (by penetrating the classically forbidden region) and therefore reduces its kinetic energy. We also note that as we increased the number of mesh points the numerical results moved closer to the exact analytical results.

The ground state energy value for the Harmonic oscillator potential was to be 0.49999965262031764723 using 3000 mesh points which is quite close to the exact analytical results of 0.5. We also plotted as vibronic transition spectra by calculating the Franck-Condon coefficients for various transitions.

9 References

- [1] MSC321 Lecture notes by M. Iskandarani, ROsentile School of Marine and Atmospheric Sciences.
- [2] Chemistry-2 Lecture 11 Electronic spectroscopy of polyatomic molecules on slideplayer.com
- [3] [https : //en.wikipedia.org/wiki/FranckCondon_principle](https://en.wikipedia.org/wiki/FranckCondon_principle) accessed on 8th February
- [4] Physics 202 Lecture notes by Prof. Gennady Gusev.
- [5] Chemistry LibreText – [https : //chem.libretexts.org](https://chem.libretexts.org)