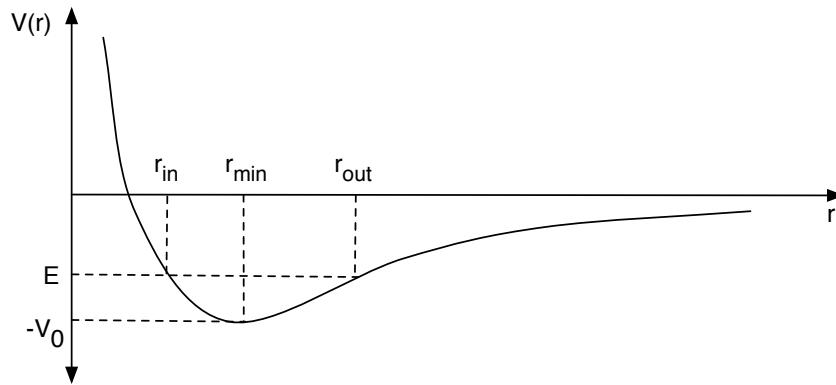


Project 1
Due on November 18th, 2011

Semiclassical Quantization of Molecular Vibration

Definition of problem: Consider the bond of a diatomic molecule, such as H_2 . Two nuclei are bound together by the e^- “cloud.” It is possible to model a potential describing this binding, and such a potential is seen in the following sketch:



This indicates a repulsive force when the two nuclei are close to each other, and attractive force if they are away from each other. Thus, if the total energy of the system is E , then the nuclei vibrates between r_{in} and r_{out} .

Quantum mechanics dictates that there are discrete levels of allowed energies for this system. The goal of the project is finding those levels numerically using an empirical model of $V(r)$, and comparing the results with the observed values.

One dimensional Schrödinger equation yields a solution for such a system with total energy E :

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V(r) \right] \psi = E\psi$$

where m is the reduced mass of the system ($1/m = 1/m_1 + 1/m_2$).

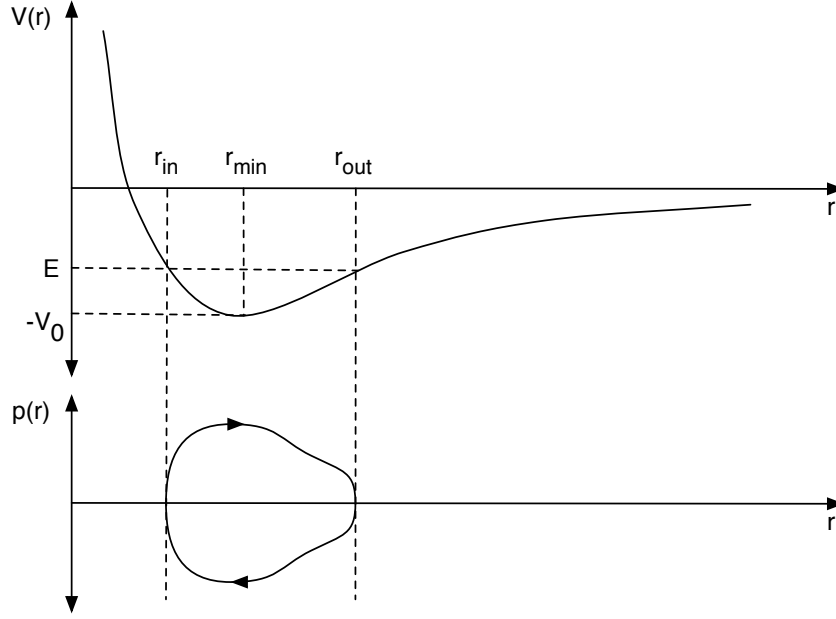
Classically, this system oscillates between r_{in} and r_{out} at any $-V_0 < E < 0$, provided that the total energy is conserved:

$$\text{Kinetic Energy} \iff \text{Potential energy}$$

where, the total energy, $E = \frac{p^2}{2m} + V(r)$ is constant. Then, the momentum $p(r)$ is simply:

$$p(r) = [2m(E - V(r))]^{1/2}$$

Then, the trajectory defined by $p(r)$ is shown as in the following sketch:



To quantize this, we write the dimensionless action at a given energy E :

$$S(E) = \oint k(r) dr$$

where $k(r) = \hbar^{-1}p(r)$ is *de Broglie* wave number. Note that, the path integral is written for full cycle. Since, the momentum, $p(r)$ above the r -axis and below the r -axis shown in the above sketch are symmetrical, we can write the same integral for one of these pieces, and multiply it by two:

$$S(E) = \oint k(r) dr = 2 \int_{r_{\text{in}}}^{r_{\text{out}}} k(r) dr$$

Thus, we get

$$S(E) = 2 \left(\frac{2m}{\hbar^2} \right)^{1/2} \int_{r_{\text{in}}}^{r_{\text{out}}} [E - V(r)]^{1/2} dr \quad (1)$$

Then, the quantization of the problem is done by stating that the *de Broglie* wave number should be $(n + \frac{1}{2})2\pi$, where n are nonnegative integers. Thus, we get:

$$S(E_n) = \left(n + \frac{1}{2} \right) 2\pi \quad (2)$$

For a given state, n , we can solve this numerically for E_n once we know the potential function $V(r)$. We know the energy levels of these states experimentally, and it is listed in the following table:

n	E_n (eV)	n	E_n (eV)
0	-4.477	8	-1.151
1	-3.962	9	-0.867
2	-3.475	10	-0.615
3	-3.017	11	-0.400
4	-2.587	12	-0.225
5	-2.185	13	-0.094
6	-1.811	14	-0.017
7	-1.466		

An early attempt to model $V(r)$ was done by Lennard-Jones as:

$$V(r) = 4V_0 \left[\left(\frac{a}{r} \right)^{12} - \left(\frac{a}{r} \right)^6 \right]$$

For simplicity, let's define the following unitless quantities:

$$\epsilon \equiv \frac{E}{V_0} \quad x \equiv \frac{r}{a} \quad \gamma \equiv \left(\frac{2ma^2V_0}{\hbar^2} \right)^{1/2}$$

Then, we define the scaled potential as:

$$v(x) = 4 \left(\frac{1}{x^{12}} - \frac{1}{x^6} \right)$$

Note that, γ defines the quantum nature of the system.

$$\begin{aligned} \gamma &= \text{large} & \rightarrow & \text{classical system} \\ \gamma &= \text{small} & \rightarrow & \text{quantum system} \end{aligned}$$

Then, we can write the Equation 2 using the above definition as:

$$\begin{aligned} s(\epsilon_n) &= \frac{1}{2} S(E_n) \\ s(\epsilon_n) &= \gamma \int_{x_{in}}^{x_{out}} [\epsilon_n - v(x)]^{1/2} dx = (n + 1/2)\pi \end{aligned} \quad (3)$$

Part 1

Consider the H_2 molecule:

$$\begin{aligned} \gamma &= 21.7 \\ V_0 &= 4.747 \text{ eV} \end{aligned}$$

Question 1: Find x_{min} analytically for which $\frac{dv(x)}{dx} = 0$.

Question 2: Analytically, find the solutions for $\epsilon - v(x) = 0$. These are your x_{in} and x_{out} .

Question 3: Write a function that calculates $s(\epsilon)$ numerically. Use extended formula for the integration, and take $N = 1000$. Note that, the only input to that function is going to be ϵ , the rest of the variables in this function are constants. You determine the integral limits analytically using the information in Question 2 for the given ϵ . The function will look like:

`double action(double e)` C language¹

Question 4: Draw² $s(\epsilon)$ as a function of ϵ for the range of $\epsilon = (-1, 0)$. Observe the behavior of the *action*.

¹Note that you can use any programming language. Here, the C prototype is given.

²You can use Matlab or your favorite utility for graphing.

Question 5: Now, define another function that uses `action` as:

$$f(\epsilon, n) = s(\epsilon) - (n + 1/2)\pi$$

Note that this function vanishes for ϵ_n and n according to Equation 3:

$$f(\epsilon_n, n) = 0$$

Call this function “`funct(e,n)`”.

Question 6: Now, write a root finding function that finds the root of $f(\epsilon, n)$ for the given n . Call this function “`normalized_energy`”, such as:

```
double normalized_energy(int n)           C language
```

Explain why using Newton-Raphson method may not be desirable (Hint: Use $s(\epsilon)$ plot you made for explaining this.). Use binary-search method for root finding. Now, you can solve the Equation 3 for ϵ_n for a given n . Then, $E_n = V_0 \epsilon_n$ which is the n^{th} energy level for this system.

Question 7: Call your `normalized_energy` function for $n = [0, \dots, 5]$, and make a table showing E_n for these 6 energy levels. Compare your results with the experimental values shown in the above table.

Question 8: Try calling `normalized_energy` function for $n = 6$. Does it fail? Explain why?

Part 2

In the previous part, we have seen that Lennard-Jones potential yields *marginally* reasonable solutions for the bound state energies only when n is small, and fails to give any result for $n > 5$. So, do not be surprised if you could not get numbers that are close to the experimental values in Part 1.

It is clear that a better analytic form of the potential with more parameters is required to produce both low energy (vibrations) solutions and high energy solutions simultaneously.

One such potential is known as the Morse potential:

$$V(r) = V_0 \left[\left[1 - e^{-(r-r_{min})/\beta} \right]^2 - 1 \right]$$

which has two parameters besides V_0 : r_{min} is used to define the lowest point of the potential, and β is used to adjust the width of the potential. r_{min} is experimentally known to be 0.74166 \AA . β is unknown and can be adjusted as a fit parameter. The goal of this part is finding the value of β for which the solution for E_0 (ground state) is exactly equal to the experimental value, and finding the rest of the energy levels using this β value.

Use the following units for the constants we need:

$$\begin{aligned} \hbar &= 6.5821 \times 10^{-16} \text{ eV sec} \\ V_0 &= 4.747 \text{ eV} \\ r_{min} &= 0.74166 \text{ \AA} \\ m &= 1.04222 \times 10^{-28} \text{ eV}/(\text{\AA} / \text{sec})^2 \end{aligned}$$

Question 9: Show that:

$$\left. \frac{dV(r)}{dr} \right|_{r=r_{min}} = 0$$

Question 10: Analytically, find the solutions for $E - V(r) = 0$. These are your r_{in} and r_{out} .

Question 11: Write a function that calculates action, S , numerically for a given E and β ; $S(E, \beta)$. Use extended formula for the integration, and take $N = 1000$. Note that, the inputs to that function are going to be E and β .

You can analytically determine the integral limits using the the expression found in Question 10 for a given E and β . The function will look like:

```
double action(double E, double beta)      C language
```

Question 12: Now, define another function that uses `action` as:

$$f(E, n, \beta) = S(E, \beta) - (n + 1/2)2\pi$$

Note that this function vanishes for E_n and n for *correct* β according to Equation 2:

$$f(E_n, \beta, n) = 0$$

Call this function “`funct(E,beta,n)`”.

Question 13: Now, write a root finding function that finds the root of $f(E, \beta, n)$ for the given n and β . Call this function “`energy`”, such as:

`double energy(double beta, int n)` C language

Use binary-search method for root finding. Now, you can solve the Equation 2 for E_n for a given n and β . E_n is the n^{th} energy level for this system.

Question 14: We need to determine β for which the “energy(beta,0)” gives correct E_0 . Write a function that finds the root of “E-energy(beta, n)” function for the given E and n . The prototypes will look like:

`double find_beta(double E, int n)` C language

Call this function with $E = -4.477$ eV and $n = 0$ according to the experimental data provided in above table. Print out the value of β found by this function which will be in angstrom. Hint: beta is at the order of unity; start your search at $\beta = 1 \text{ \AA}$.

Note that your latest root-finding function uses another root-finding function that uses a numerical integration! The optimization of such a problem is important as it may require too much CPU time when not optimized properly. You can also eliminate one of the root-finding stage with a little effort.

Question 15: Call your `energy` function for $n = [0, \dots, 14]$ with the above β , and make a table showing E_n for these 15 energy levels. Compare your results with the experimental values shown in the above table. Does this potential gives reasonable results?