HW2 – Semiclassical quantization of molecular vibrations

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According to quantum mechanics, in a diatomic molecule such as H_2, there are just an integer number of allowed energies. In this project, a search of the quantized energy levels are going to be searched numerically using two different models of the potential that describes the binding of the nucleus.

We consider the dimensionless action at a given energy

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

where $k(r) = p(r)/\hbar$ is the local de Broglie wave number and

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

is the momentum that, classically, describes the oscillation of the system between r_{in} and r_{out}.

The quantization of the system is achieved by stating that the de Broglie wave number, $k(r)$, should be $(n + 1/2)2\pi$, with $n \in \mathbb{N}$. This gives us

$$S(E_n) = 2 \int_{r_{in}}^{r_{out}} \left(\frac{2m}{\hbar^2}\right)^{1/2} [E_n - V(r)]^{1/2} \, dr = \left(n + \frac{1}{2}\right) 2\pi \tag{1}$$

For the diatomic molecule, H_2, $\gamma = 21.7$ and $V_0 = 4.747\,\mathrm{V}$. Also, experimentally, the quantized energies are

Table 1: Quantized energies for the diatomic molecule H_2

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		

0.1 Modelling with the Lennard-Jones potential

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

Given the Lennard-Jones potential we can define

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

and the scaled potential as

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

to get

$$s(\epsilon_n) = \gamma \int_{x_{in}}^{x_{out}} \left[\epsilon_n - v(x)\right]^{1/2} dx = \left(n + \frac{1}{2}\right)\pi \tag{2}$$

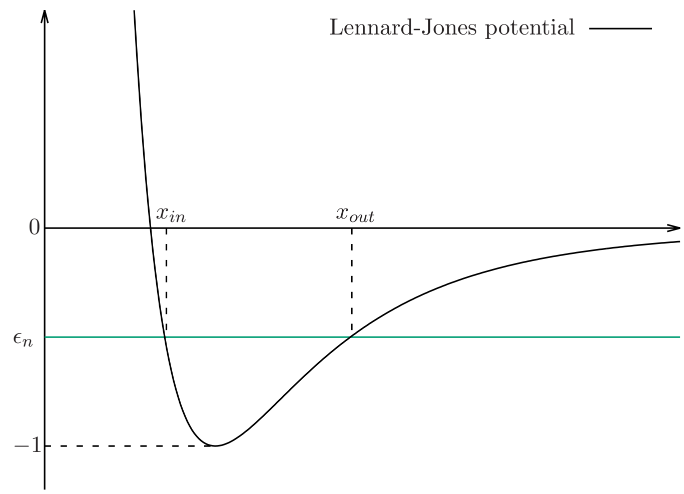

Figure 1: Scaled Lennard-Jones potential

Analytically, x_{in} and x_{out} can be obtained by finding the roots of the equation $\epsilon - v(x) = 0$. This roots are

$$x_{in} = \sqrt[6]{\frac{2}{\epsilon}\left(-1+\sqrt{1+\epsilon}\right)}$$
$$x_{out} = \sqrt[6]{\frac{2}{\epsilon}\left(-1-\sqrt{1+\epsilon}\right)}$$

Knowing x_{in} and x_{out}, the integral in equation 1 can be calculated. Bode's rule was used to calculate the action, s, for each energy $\epsilon \in (-1, 0)$.

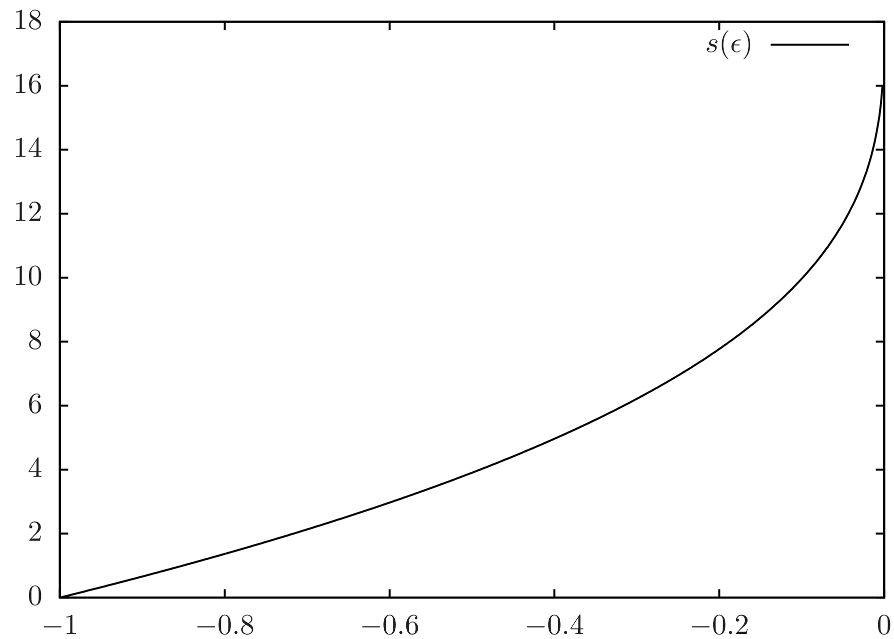

Figure 2: Action for each dimensionless energy ϵ.

And finally, with the quantization rule in the right hand side of equation 1 we can obtain the permitted energy levels by getting the roots of the function

$$f(\epsilon, n) = s(\epsilon) - \left(n + \frac{1}{2}\right)\pi$$

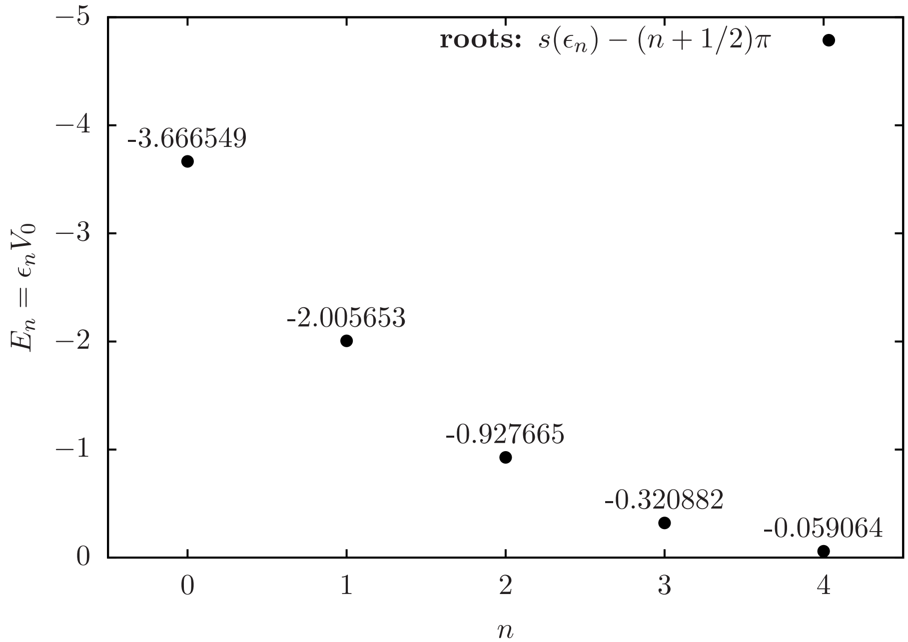

Figure 3: Quantized energy levels E_n.

It can be seen, by comparing figure 3 with table 1, that we don't get exactly the energies that the experiment shows. The Lennard-Jones model only predicts energies for $n < 5$, with $n \geq 5$ the energy diverges for this model.

0.2 Modelling with the Morse potential

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

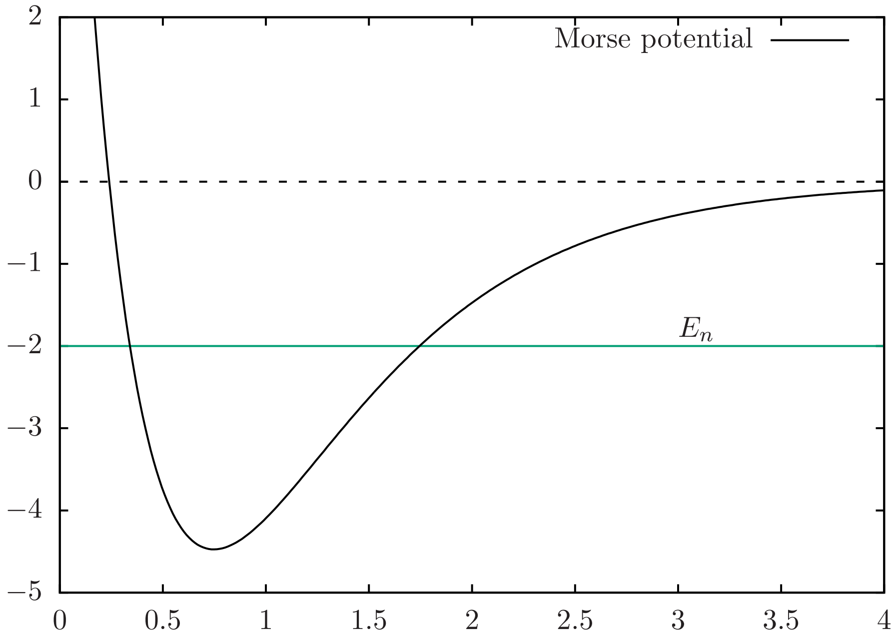

Figure 4: Morse potential.

In this model, 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 0.741 66 Å. β was adjusted by trial and error to give correctly the known energies for H_2

To integrate equation 1 we obtain analytically r_{in} and r_{out}.

$$r_{in} = r_{min} - \beta \log\left(1 + \sqrt{\frac{E}{V_0} + 1}\right)$$
$$r_{out} = r_{min} - \beta \log\left(1 - \sqrt{\frac{E}{V_0} + 1}\right)$$

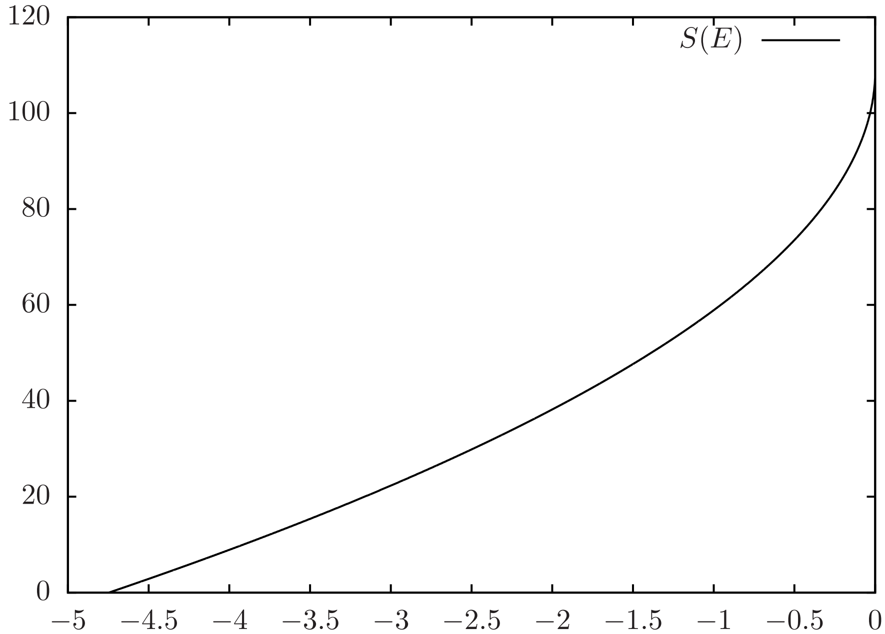

Figure 5: Action for each classical energy E.

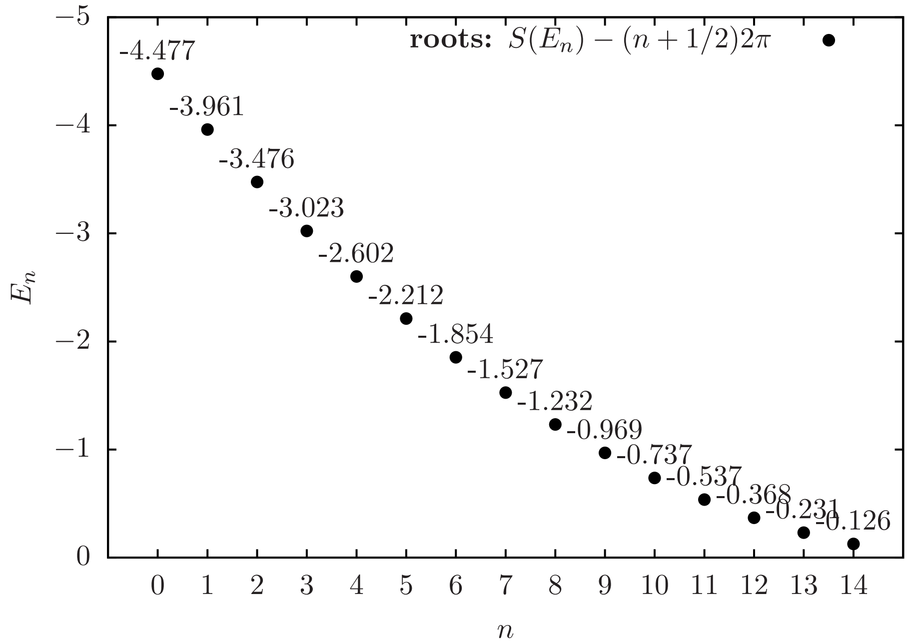

Figure 6: Quantized energy levels E_n.