Problem definition

We are looking for solution of this Schrodinger equation:

$$\left[-\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} + V_0(\phi)\right]\psi_m(\phi) = E_m\psi_m(\phi), where$$

$$V_0(\phi) = \frac{1}{2}[V_2(1-\cos 2\phi) + V_4(1-\cos 4\phi) + V_6(1-\cos 6\phi)] + C$$

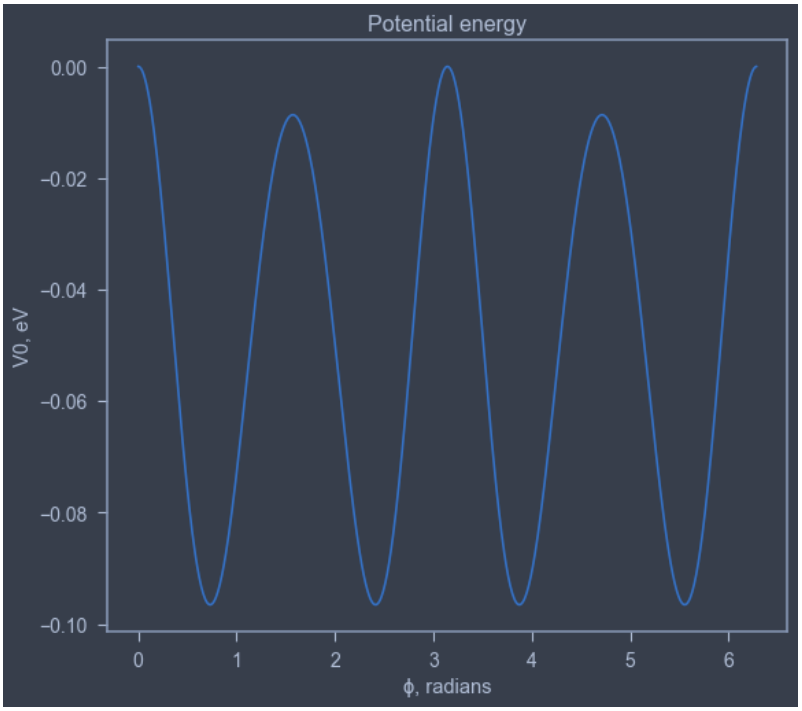
ref: Torsional potential of biphenyl: Ab initio calculations with the Dunning correlation consisted basis sets.

The boundary conditions are:

$$\psi(0) = \psi(2\pi),$$

$$\psi'(0) = \psi'(2\pi).$$

The plot of the potential:



3 methods were used to solve this equation: Finite Difference Method, Exponential Fourier Basis and Sines and Cosines Fourier Basis.

0. Finite Difference Method

Solution 0. Finite Difference Method

Using the fact that

$$\frac{d^2\psi}{dx^2}(x_i) \approx \frac{-2\psi_i + \psi_{i-1} + \psi_{i+1}}{\Delta x^2}$$

we can rewrite the Schrodinger equation as

$$\frac{2\psi_i - \psi_{i-1} - \psi_{i+1}}{\Delta x^2} + V_i\psi_i = E\psi_i$$

Since this holds for all ψ_i, it can be expressed as a matrix eigenvalue equation (note, the top left and bottom right corners are okay since $\psi_0 = 0$ and $\psi_{N-1} = 0$). Our Schrodinger equation $H\psi = E\psi$ then becomes the equation below. Note that the Hamiltonian is now a matrix

$$\begin{bmatrix} \frac{2}{\Delta x^2} + V_1 & -\frac{1}{\Delta x^2} & 0 & 0... \\ -\frac{1}{\Delta x^2} & \frac{2}{\Delta x^2} + V_2 & -\frac{1}{\Delta x^2} & 0... \\ ... & ... & ... & -\frac{1}{\Delta x^2} \\ ...0 & 0 & -\frac{1}{\Delta x^2} & \frac{2}{\Delta x^2} + V_{N-1} \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ ... \\ \psi_{N-1} \end{bmatrix} = E \begin{bmatrix} \psi_1 \\ \psi_2 \\ ... \\ \psi_{N-1} \end{bmatrix}$$

This works only when $\psi_0 = \psi_N = 0$ is the boundary condtion.

Source:
https://github.com/lukepolson/youtube_channel/blob/main/Python%20Metaphysics%20Series/vid33.ipynb?short_path=4cccb3e
and
https://medium.com/modern-physics/finite-difference-solution-of-the-schrodinger-equation-c49039d161a8

Also, we rearrange the Schrodinger equation for FDM, so it's easier to solve:

$$\left[-\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} + V_0(\phi)\right]\psi_m(\phi) = E_m\psi_m(\phi)$$

$$-C\frac{d^2}{d\phi^2}\psi_m(\phi) + V_0(\phi)\psi_m(\phi) = E_m\psi_m(\phi)$$

$$-\frac{d^2}{d\phi^2}\psi_m(\phi) + \frac{1}{C}V_0(\phi)\psi_m(\phi) = \frac{1}{C}E_m\psi_m(\phi)$$

where

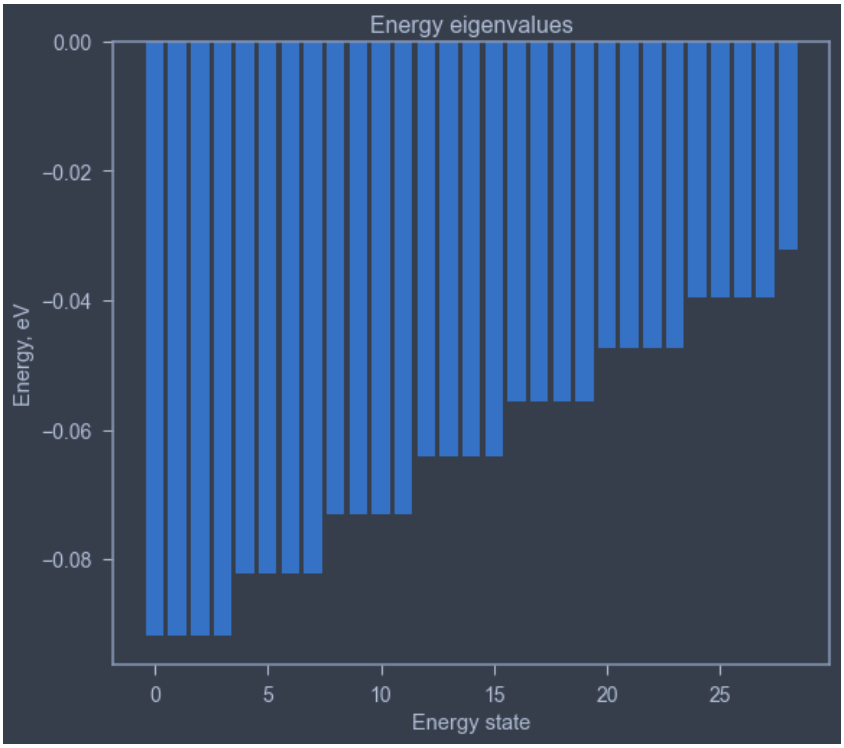
$$C = \frac{\hbar^2}{2I}.$$

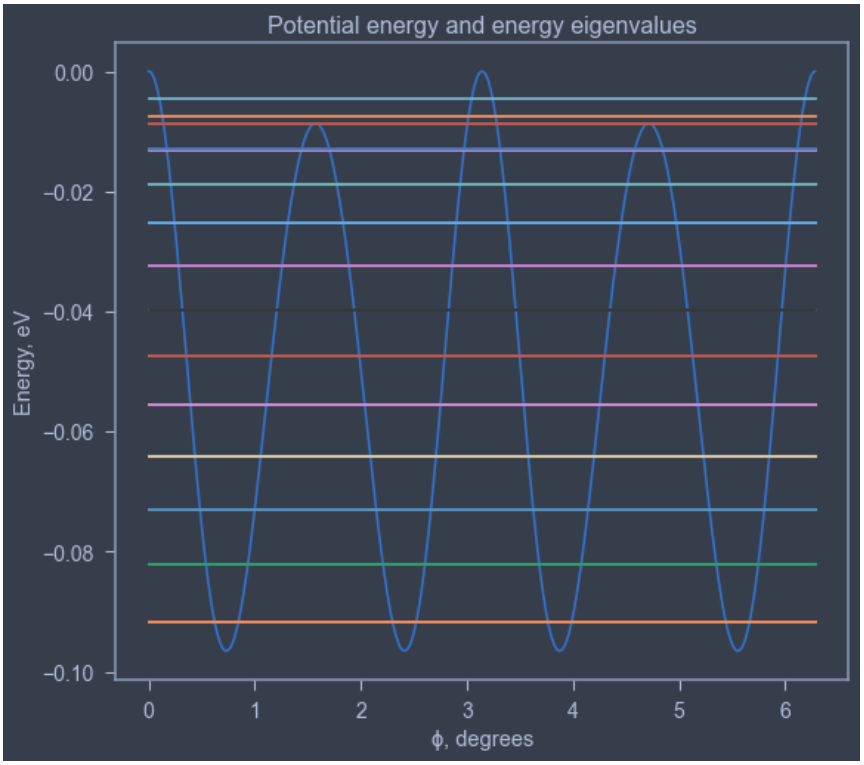
So, when we multiply the potential by constant C, and when we get the eigenvalues, their value in eV should be E=E*C.

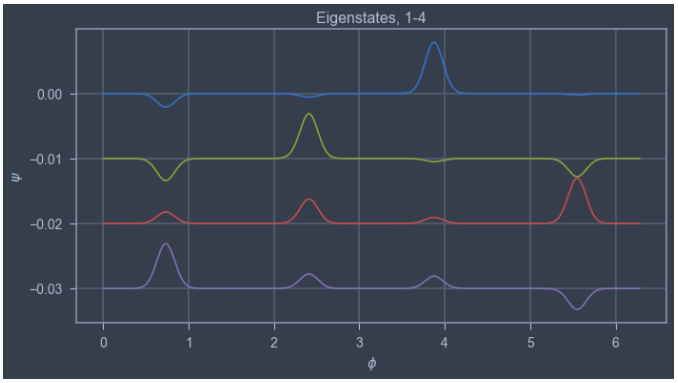
I used this set of constants for solving Schrodinger equation:

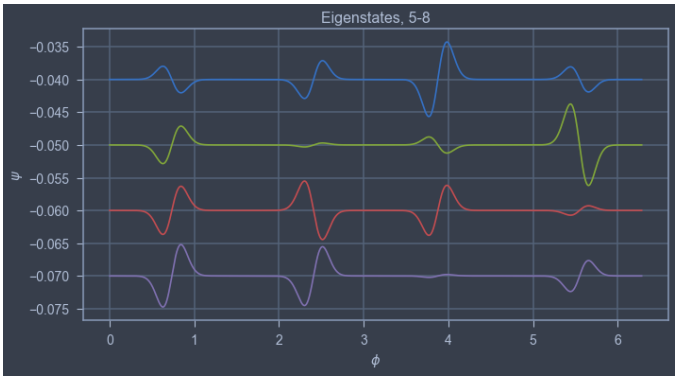
```
# Potential energy constants
V_2 = 0.09 * 0.043361254529175 # Convert from kcal/mol to eV/particle
V_4 = -2.10 * 0.043361254529175 # Convert from kcal/mol to eV/particle
V_6 = -0.29 * 0.043361254529175 # Convert from kcal/mol to eV/particle
# SE constants
h_bar = 6.626070150 * 10**-34 # Plancks constant, kg*m^2/s
M = 1.9944733 * 10**-26 # Mass of carbon, kg
# d = 0.417 * 10**-9 # Diameter of benzene ring, m
d = 1.7  * 10**-9 # Diameter of benzene ring (not sure about this one), m
I = 1/2 * M * d ** 2 # Moment of inertia
KE_C = h_bar**2 / (2 * I) # Kinetic energy operator's constant, J
KE_C = KE_C * 6.241509 * 10**18 # Convert from J to eV
```

Results:

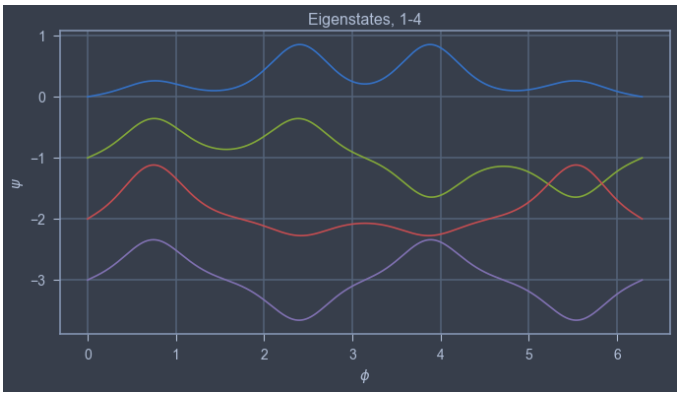

Energy eigenvalues
0.00
−0.02
−0.04
−0.06
−0.08
Energy, eV
0
5
10
15
20
25
Energy state

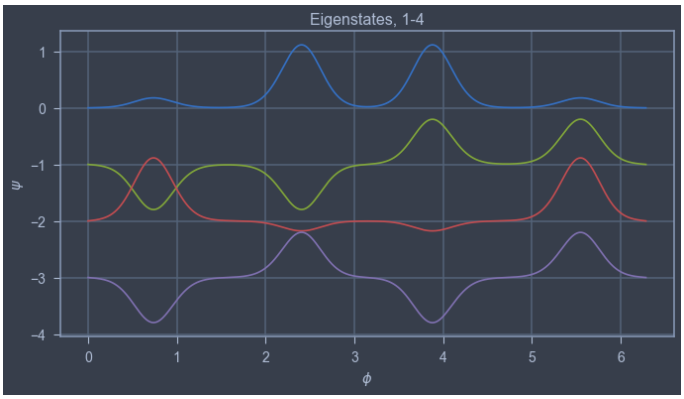

Potential energy and energy eigenvalues
0.00
−0.02
−0.04
−0.06
−0.08
−0.10
Energy, eV
0
1
2
3
4
5
6
ϕ, degrees

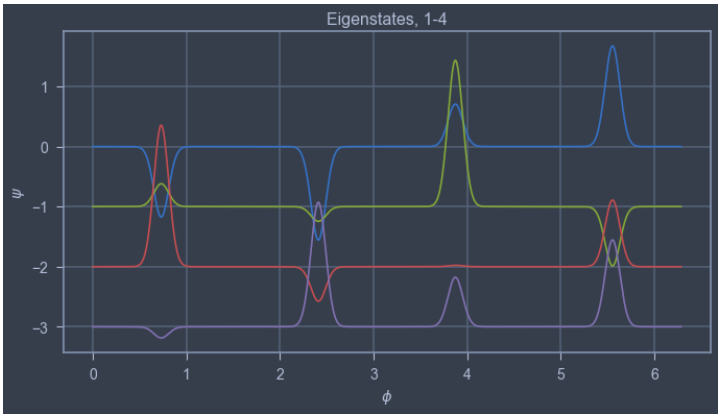




Also, depending on the value of the radius of benzene ring (I wasn't sure, what it was exactly) we get different results:







In some cases, finite difference method becomes very inaccurate because we take our boundary conditions as $\psi(0) = \psi(2\pi)\ and\ \psi'(0) = \psi'(2\pi)$, which sometimes isn't right. This isn't a problem in the next solving methods.

1. Rewriting wave function in exponential Fourier basis

$$\Psi(\phi) = \sum_{m=-\infty}^{\infty} c_m \Phi_m(\phi)\,, where$$

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}.$$

$$H_{mm'} = \int_0^{2\pi} \Phi_m^{\star}(\phi)\hat{\mathcal{H}}\,\Phi_{m'}(\phi)\,d\phi$$

$$\begin{aligned}
H_{mm'} &= \frac{1}{2\pi}\int_0^{2\pi} e^{-im\phi}\left[-\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} + V_0(\phi)\right] e^{im'\phi}\,d\phi \\
&= \frac{1}{2\pi}\int_0^{2\pi} e^{-im\phi}\left[-\frac{\hbar^2(im')^2}{2I} + V_0(\phi)\right] e^{im'\phi}\,d\phi \\
&= \frac{1}{2\pi}\int_0^{2\pi} e^{i\phi(m'-m)}\left[\frac{\hbar^2 m'^2}{2I} + V_0(\phi)\right] d\phi \\
&= \frac{1}{2\pi}\int_0^{2\pi} \big(cos\big(\phi(m'-m)\big) + i\,sin\big(\phi(m'-m)\big)\big)\left[\frac{\hbar^2 m'^2}{2I} + V_0(\phi)\right] d\phi \\
&= \frac{1}{2\pi}\int_0^{2\pi} \big(cos\big(\phi(m'-m)\big) + i\,sin\big(\phi(m'-m)\big)\big)\left[\frac{\hbar^2 m'^2}{2I} + V_0(\phi)\right] d\phi \\
&= \frac{1}{2\pi}\int_0^{2\pi} cos\big(\phi(m'-m)\big)\left[\frac{\hbar^2 m'^2}{2I} + V_0(\phi)\right] d\phi \\
&+ i\frac{1}{2\pi}\int_0^{2\pi} sin\big(\phi(m'-m)\big)\left[\frac{\hbar^2 m'^2}{2I} + V_0(\phi)\right] d\phi.
\end{aligned}$$

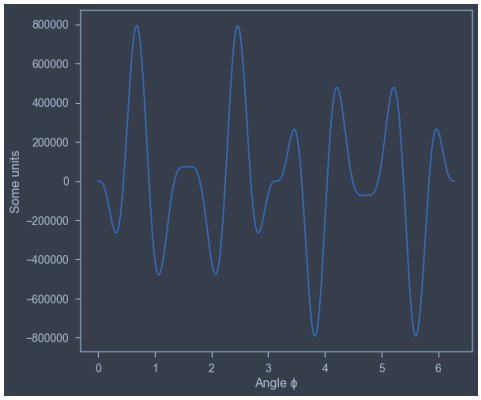
We have two parts, *cos* and *sin*. The sin part is 0, as the graph is antisymmetric around the point $\phi = \pi$. The part $sin\big(\phi(m' - m)\big)$ is antisymmetric and the $V_0(\phi) = \frac{1}{2}[V_2(1 - \cos 2\phi) + V_4(1 - \cos 4\phi) + V_6(1 - \cos 6\phi)] + C$ is symmetric. For example, for $m = 2, m' = 5, \hbar = 1, I = 1$:

```
In [47]: def integrand_test(phi, m, m_s):
             return np.sin(phi * (m + m_s)) * (
                     h_bar ** 2 * m_s ** 2 / 2 / I + potential(phi) * potential_factor)

In [48]: print(quad(integrand_test, 0, 2 * np.pi, args=(2, 5))[0])

         1.3955842759675618e-09
```

The result is not 0 because of floating numbers, but it is very small.

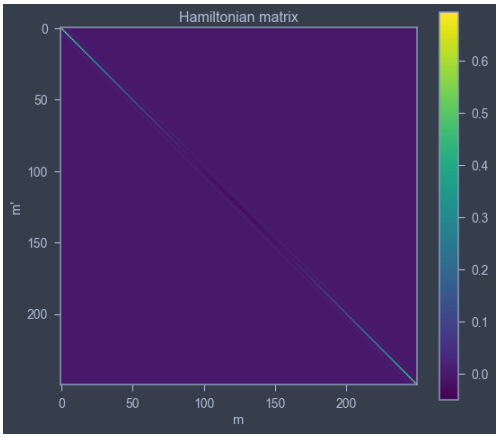


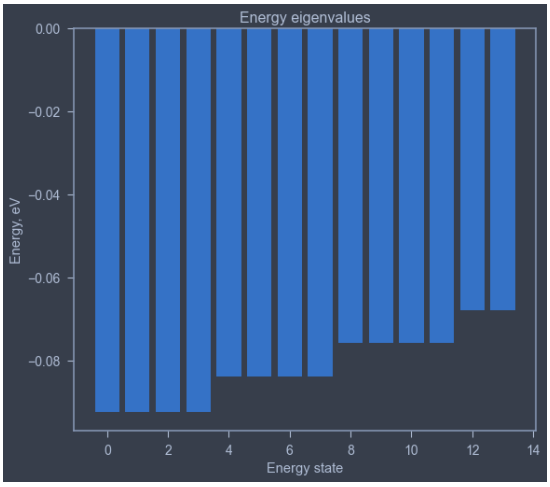
Graph is antisymmetric.

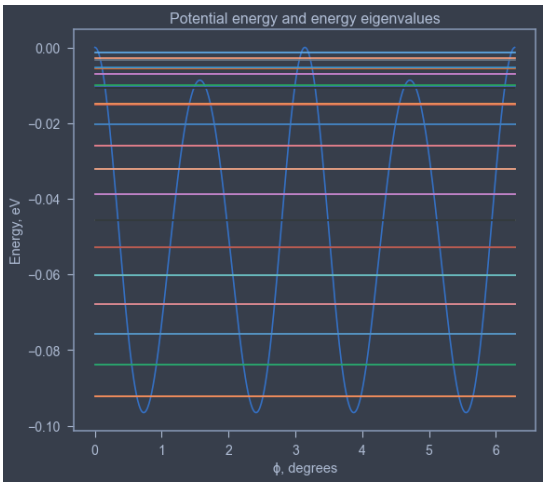
So, we have:

$$H_{mm'} = \frac{1}{2\pi}\int_0^{2\pi} cos\big(\phi(m' - m)\big)\left[\frac{\hbar^2 m'^2}{2I} + V_0(\phi)\right] d\phi.$$

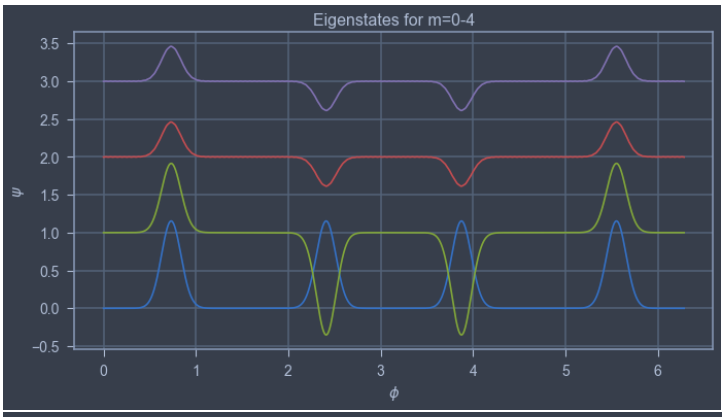
Results:

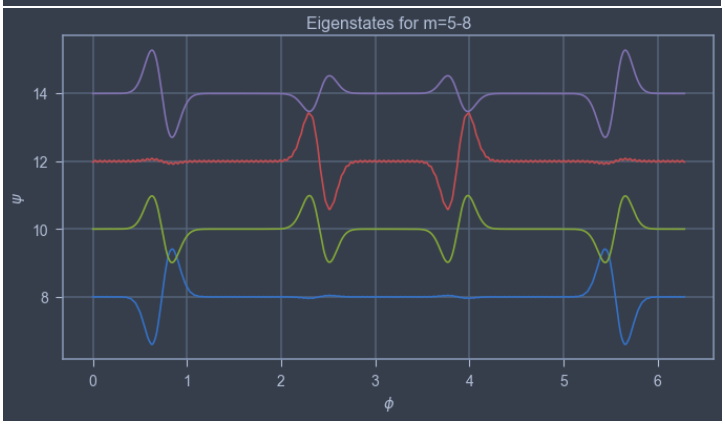






If M (number of exponents in the Fourier basis) is not big enough, or accuracy of calculating integrals is low, some oscillations can be seen:





2. Rewriting wave function in sines and cosines Fourier basis

$$\Psi(\phi) = \sum_{m=-\infty}^{\infty} \left(a_m \Phi_{mc}(\phi) + b_m \Phi_{ms}(\phi)\right), where$$

$$\Phi_{mc}(\phi) = \frac{1}{\sqrt{\pi}} \cos m\phi \, , \Phi_{ms}(\phi) = \frac{1}{\sqrt{\pi}} \sin m\phi .$$

$$H_{mm'} = \int_0^{2\pi} \Phi_m^{\star}(\phi) \hat{\mathcal{H}} \, \Phi_{m'}(\phi) \, d\phi$$

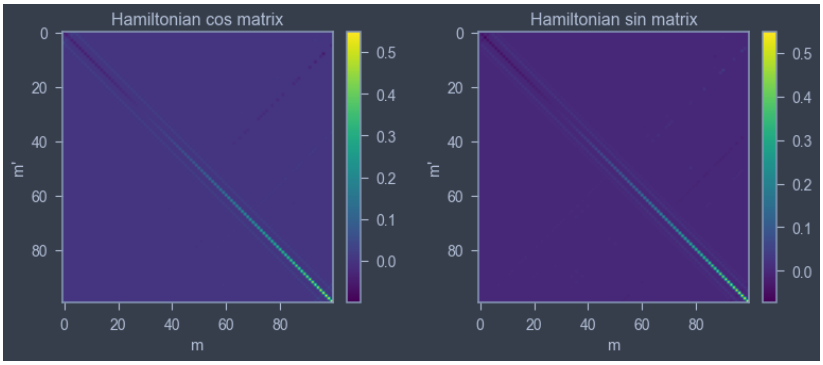
Cosine part:

$$\begin{aligned} H_{cmm'} &= \int_0^{2\pi} \frac{1}{\sqrt{\pi}} \cos m\phi \left[-\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2} + V_0(\phi) \right] \frac{1}{\sqrt{\pi}} \cos m'\phi \, d\phi \\ &= \frac{1}{\pi} \int_0^{2\pi} \cos m\phi \left[-\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2} + V_0(\phi) \right] \cos m'\phi \, d\phi \\ &= \frac{1}{\pi} \int_0^{2\pi} \cos m\phi \left[\frac{\hbar^2 m'^2}{2I} + V_0(\phi) \right] \cos m'\phi \, d\phi . \end{aligned}$$

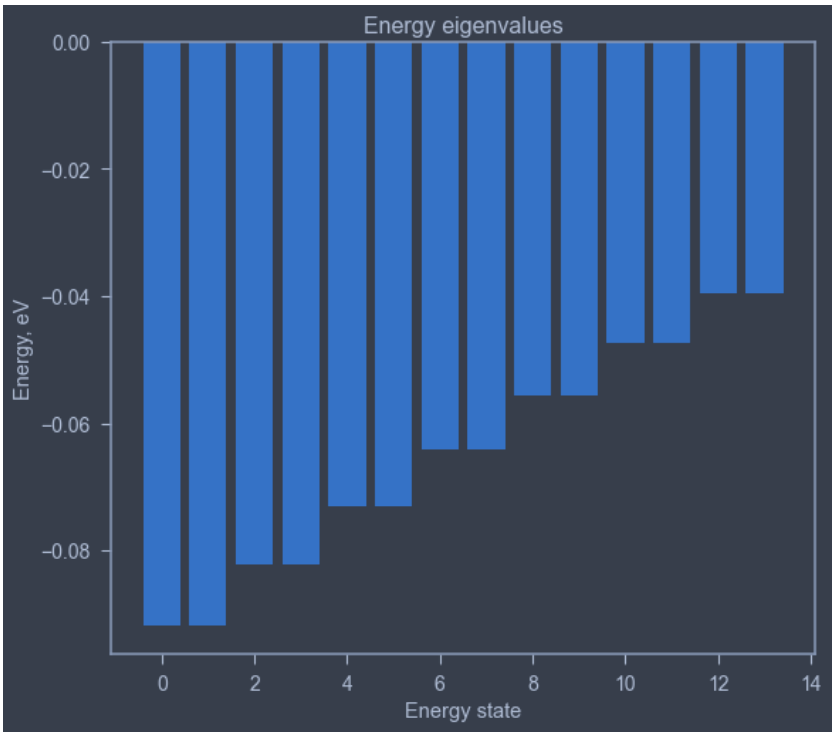
Sine part:

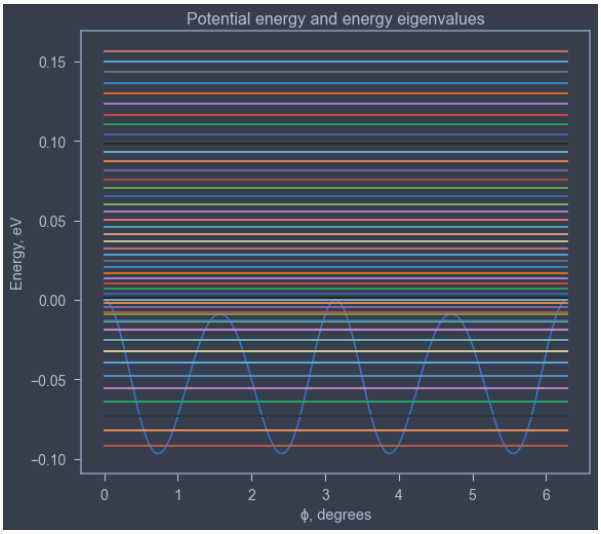
$$H_{smm'} = \frac{1}{\pi}\int_0^{2\pi} \sin m\phi \left[\frac{\hbar^2 m'^2}{2I} + V_0(\phi)\right] \sin m'\phi \, d\phi.$$

Hamiltonians:

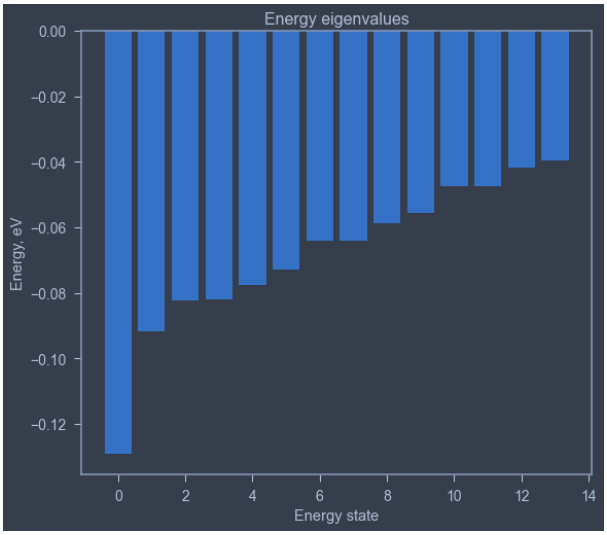


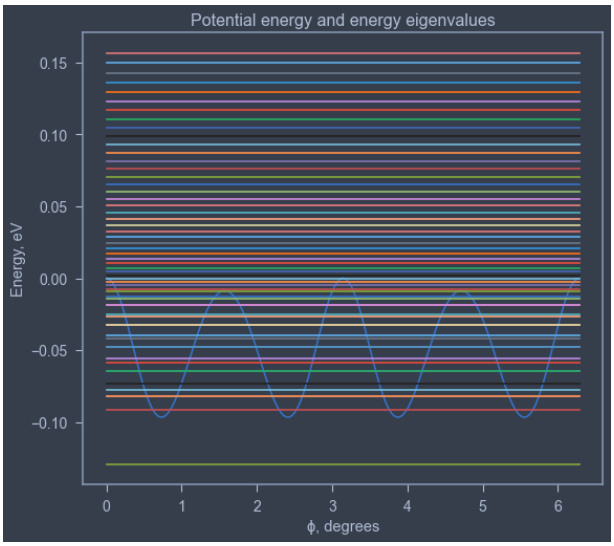
This is how eigenvalue problem solutions for sine Hamiltonian look like:





And cosine Hamiltonian:





Some questions

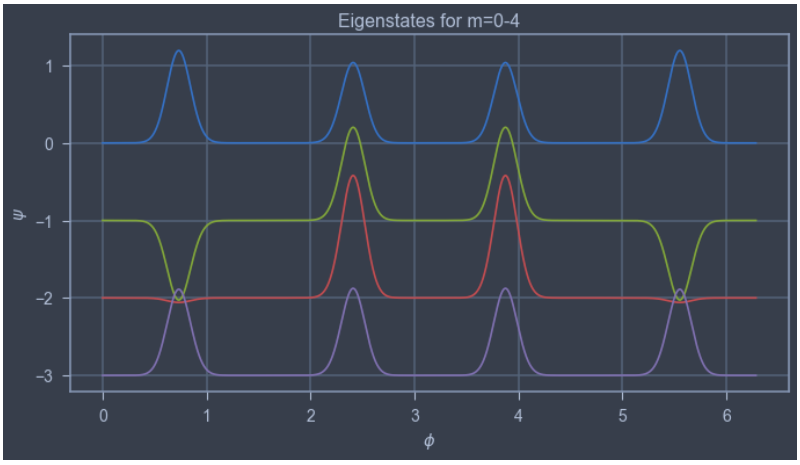
1. Did I get it right, that we can rewrite these formulas like this:

$$\int_0^{2\pi} \Phi_m^\star(\phi)\, \Phi_{m'}(\phi)\, d\varphi = \langle \Phi_m | \Phi_{m'} \rangle = \delta_{mm'},$$

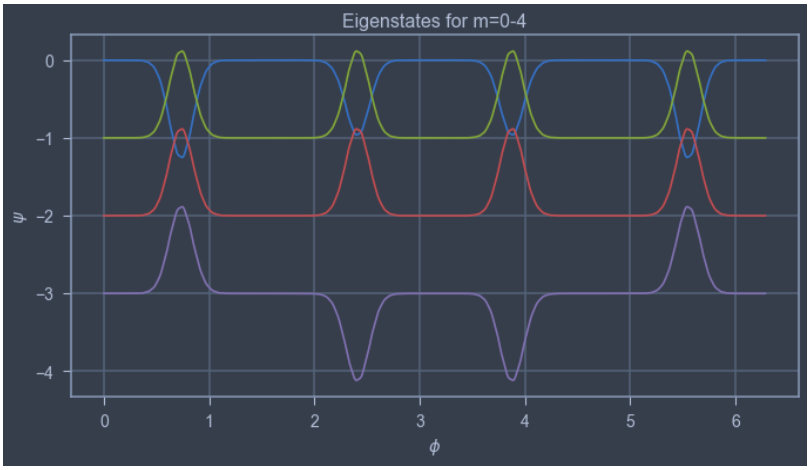
$$\int_0^{2\pi} \Phi_m^\star(\phi) \widehat{\mathcal{H}}\, \Phi_{m'}(\phi)\, d\varphi = \langle \Phi_m \left| \widehat{\mathcal{H}} \right| \Phi_{m'} \rangle = \mathcal{H}_{mm'}?$$

2. After increasing accuracy for exponentials Fourier basis, the pattern of wave function eigenstates changed (when “hills” are facing up or down), and there never were --++ and +-+- patterns (which are the only antisymmetric patterns).

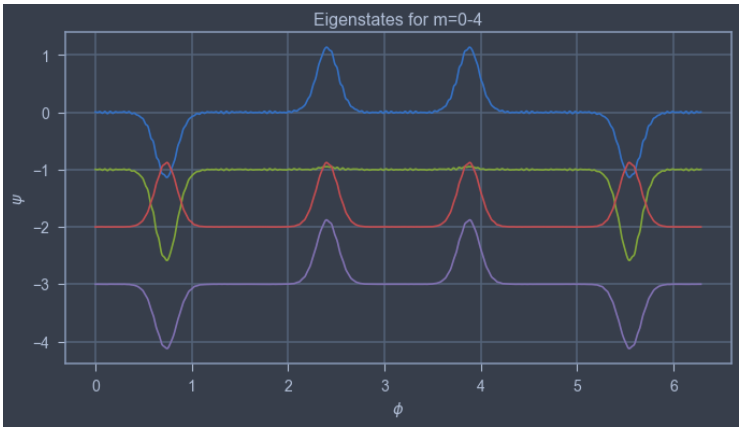
   M=100:



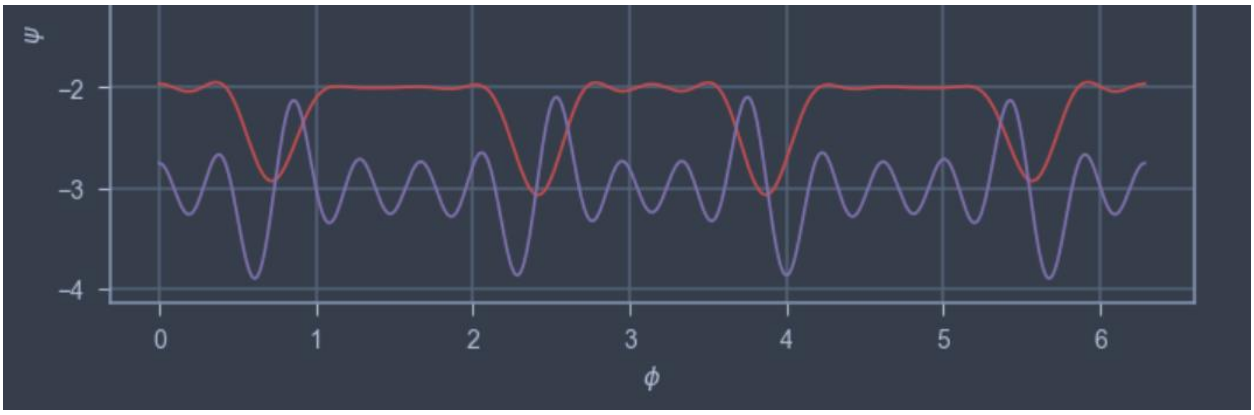
   M=220:



   M=250:



And also if M is small, some eigenstates oscillate badly, while other look more or less ok. M=30:

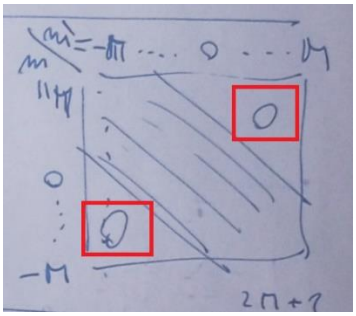


Is this supposed to look like that for small M, or I did a mistake somewhere?

3. Is it okay that probability distribution is bigger in some regions than in others?

4. How should I find wave function coefficients and energy eigenvalues in case of rewriting wave function in sines and cosines Fourier basis? I noticed that energy eigenvalues of sine Hamiltonian matrix looks like every second energy eigenvalue of exponential Hamiltonian matrix, but I'm not sure how to find all eigenvalues and wave function coefficients.

5. I'm also not sure about Hamiltonian matrix values in corners:



$$H_{-M,-M} = \frac{1}{2\pi}\int_0^{2\pi} e^{iM\phi}\left[-\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} + V_0(\phi)\right]e^{-iM\phi}\,d\phi$$
$$= \frac{1}{2\pi}\int_0^{2\pi} e^{iM\phi}\,e^{-iM\phi}\left[\frac{\hbar^2 M^2}{2I} + V_0(\phi)\right]d\phi$$
$$= \frac{1}{2\pi}\int_0^{2\pi}\left[\frac{\hbar^2 M^2}{2I} + V_0(\phi)\right]d\phi\,.$$

This value doesn't seem to converge to 0. Did I make a mistake somewhere, or I misunderstood something?