Numerical Approaches for Quantum Mechanics

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The presentation and the codes are available for download at https://github.com/raghurama123/NumQM

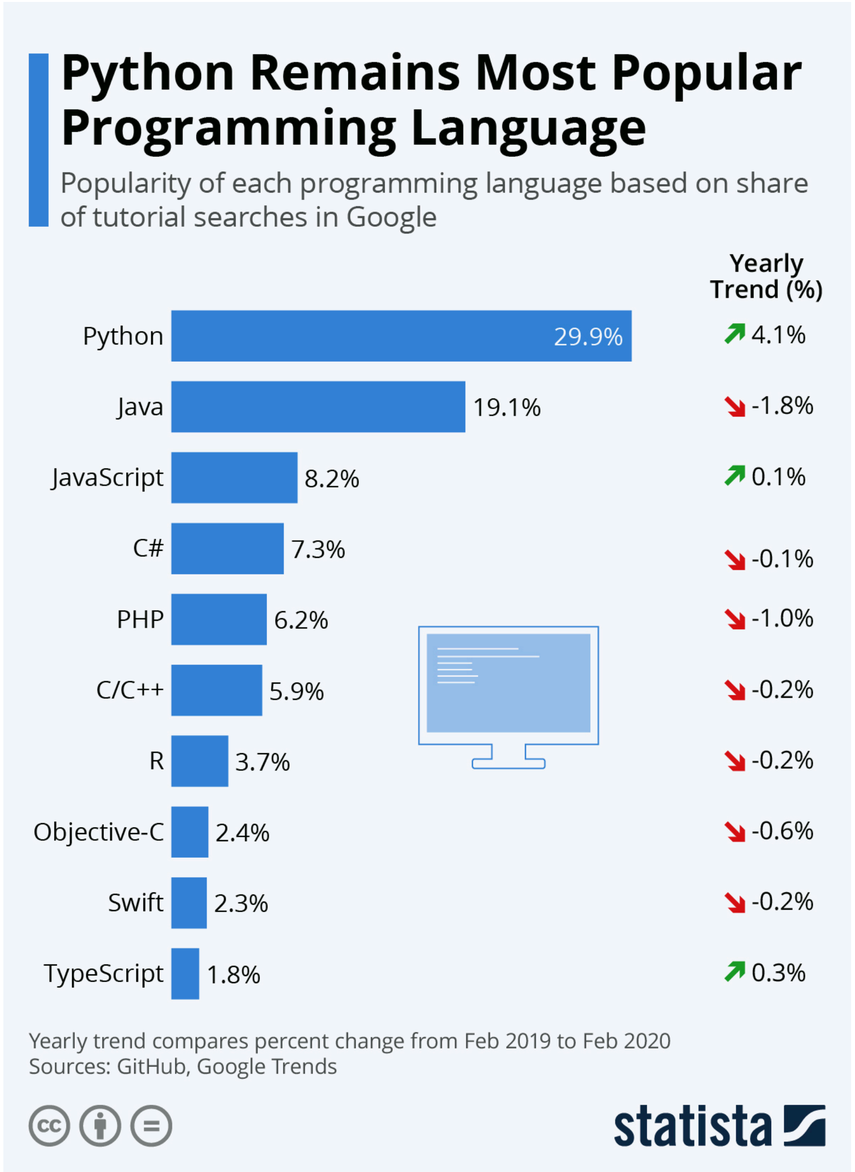
Purpose of this presentation

- To give a flavour for numerical modelling of quantum mechanical problems.
- To demonstrate how a bit of programming can clarify important concepts.
- To highlight the connections between concepts learned in quantum mechanics and the mathematics encountered in numerical computation.
- To provide sample programs that you can download, modify and enhance your understanding.

Why Numerical Approaches?

- Except for simple cases, quantum mechanical problems are mathematically intensive.
- Numerical modelling provides quick solutions to analytically complicated problems.
- When combined with visualisation of results, computer modelling provides deep insights.
- One can perform virtual experiments that may not even be feasible to perform in a laboratory.
- Free software can help fast-track coding efforts.
- Possible to combine to symbolic computation with numerical computation.

Choosing a programming language



Q: What's the best programming language to learn for science student with no previous programming experience

A: Python

Python is

- free
- easy to reference in the internet
- has a lot of libraries for visualisation, numerical methods, and data-analysis
- more libraries means less coding effort *so that one can focus on the research problem at hand*

I want to have Python in my computer but I don’t know how to install it. What to do?

Don’t be shy to ask around.

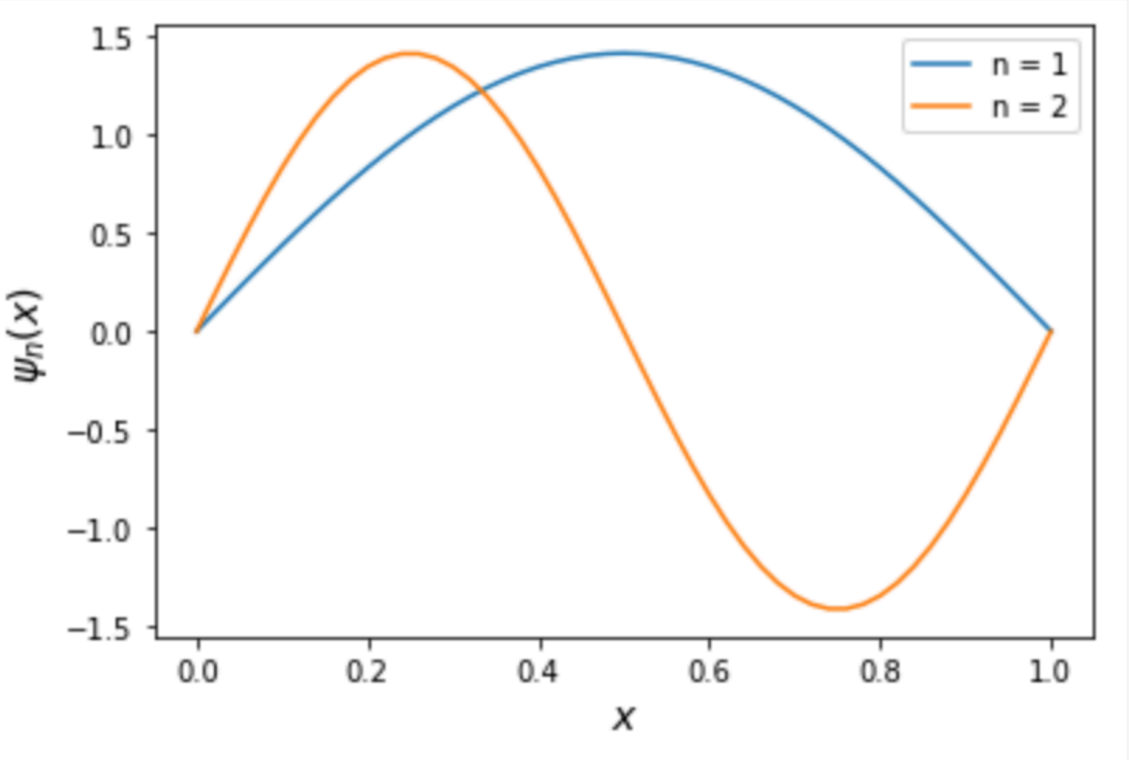
Take help from friends, teachers, or research scholars in your institute.

Mathematics and Numerical Methods

Equations	Root-finding (Newton-Raphson, simplex, etc.)
Functions	Optimization: minimization (Newton-Raphson, simplex, etc.)
Function approximation	Least-squares regression (Gaussian elimination, LU decomposition, etc.), interpolation
Eigenvalue problems	Similarity transformation (Jacobi method), Iterative method (power method, Lanczos, etc.)
Differentiation/Integration	Finite-derivatives, trapezoidal method, quadratures, etc.
Differential equations	Euler method, Runge-Kutta, etc.

Let's begin with a plot

In [1]:
```
import numpy as np
import matplotlib.pyplot as plt

def psi(n,L,x):
    psi=np.sqrt(2.0/L)*np.sin(n*np.pi*x/L)
    return psi

L=1.0

x=np.linspace(0.0, L, 51)

f1=np.zeros(51)
f2=np.zeros(51)

for i in range(51):
    f1[i]=psi(1,L,x[i])
    f2[i]=psi(2,L,x[i])

plt.plot(x,f1)
plt.plot(x,f2)
plt.legend(['n = 1','n = 2'])

plt.xlabel("$x$", fontsize=14)
plt.ylabel("$\psi_n(x)$", fontsize=14)
plt.savefig('PIB.png')
plt.show()
```



see: NumQM_Basic01.ipynb

Non-stationary states and their time-evolution

Recall:

- Eigenstates of a system are stationary. When a system is in one of the eigenstates, all quantum mechanical observables (expectation values, $\langle n | \hat{O} | n \rangle$) are conserved in time.

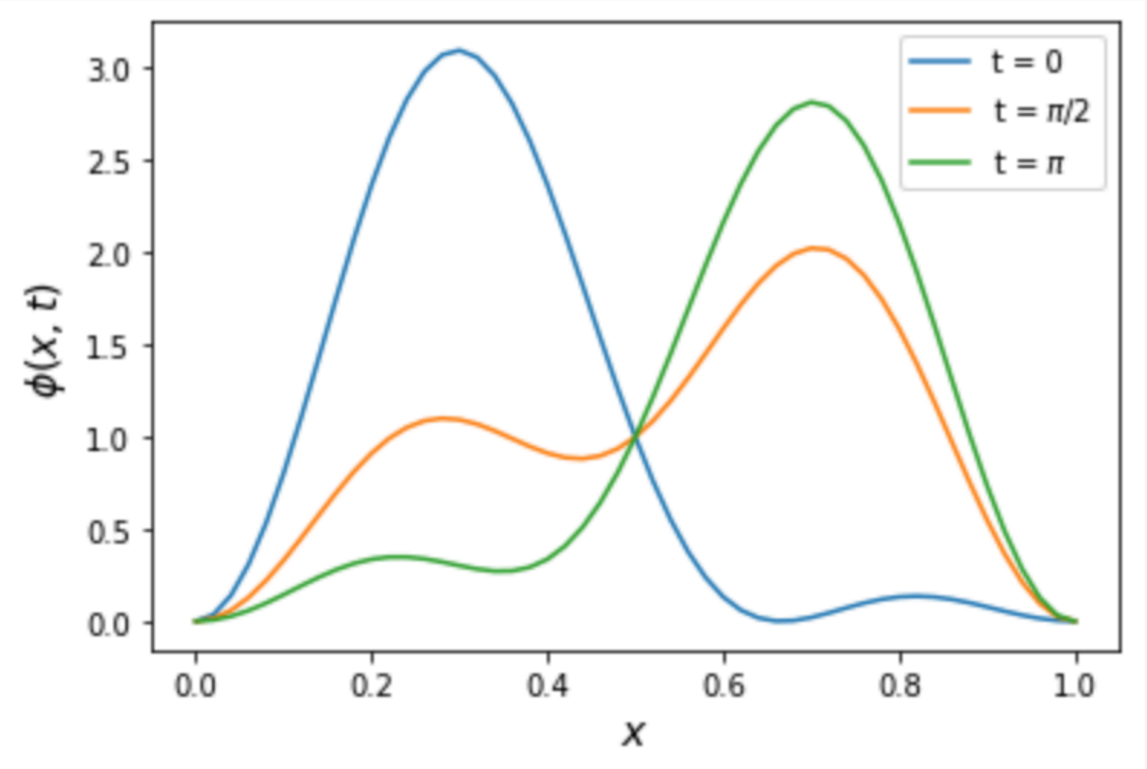
- Linear combinations of eigenfunctions are not stationary. Consider $\phi(x) = \left[\psi_m(x) + \psi_n(x)\right]/\sqrt{2}$

$$\phi(x,t) = \exp\left(-it\hat{H}/\hbar\right)\left[\psi_m(x) + \psi_n(x)\right]/\sqrt{2} = \left[\exp\left(-itE_m/\hbar\right)\psi_m(x) + \exp\left(-itE_n/\hbar\right)\psi_n(x)\right]/\sqrt{2}$$

$$|\phi(x,t)|^2 = \phi^*(x,t)\phi(x,t)$$
$$= \left(|\psi_m(x)|^2 + |\psi_n(x)|^2\right)/2 + \text{Real}\left[\exp(-it\omega_{mn})\psi_n^*(x)\psi_m(x)\right]; \qquad \omega_{mn} = (E_m - E_n)/\hbar$$
$$= \left(|\psi_m(x)|^2 + |\psi_n(x)|^2\right)/2 + \cos(\omega_{mn}t)\psi_n^*(x)\psi_m(x)$$

Let's watch the wave function evolve in time

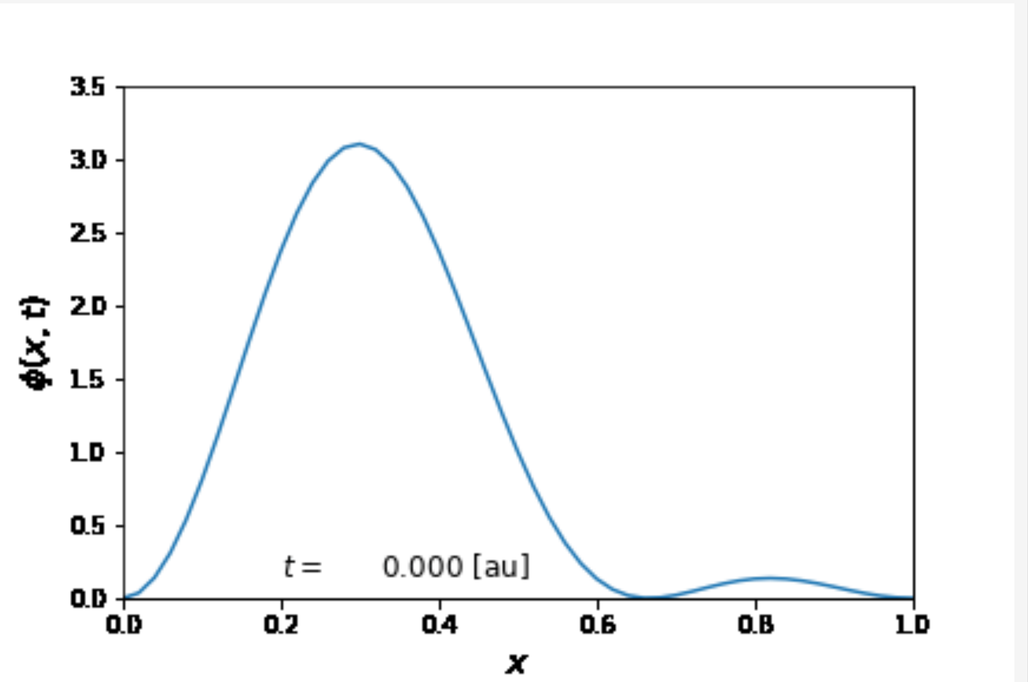
In [2]:
```
t=np.linspace(0.0, 1.0, 51)

hbar=1                  # in atomic units
mass_e=1                # in atomic units

h=2*np.pi * hbar

E1=1**2 * h**2/(8*mass_e*L**2)
E2=2**2 * h**2/(8*mass_e*L**2)
w21 = (E2-E1)/hbar

def phi(t):
    phi=np.zeros(51)
    phi=(f1**2 + f2**2)/2+np.cos(w21*t)*f1*f2
    return phi

plt.plot(x,phi(0))
plt.plot(x,phi(np.pi/2))
plt.plot(x,phi(np.pi))
plt.legend(['t = 0','t = $\pi$/2','t = $\pi$'])

plt.xlabel("$x$", fontsize=14)
plt.ylabel("$\phi(x,t)$", fontsize=14)
plt.savefig('PIB_2.png')
plt.show()
```



see: NumQM_Basic01.ipynb

Movie time!

In [3]:
```
import os
import imageio
filenames = []
for it in range (100):
    t=it*0.01

    plt.plot(x,phi(t))

    plt.xlim(0, L)
    plt.ylim(0, 3.5)
    plt.xlabel("$x$", fontsize=14)
    plt.ylabel("$\phi(x,t)$", fontsize=14)

    filename='_tmp_'+str(it).zfill(5)+'.png'
    filenames.append(filename)
    plt.savefig(filename)

    plt.close()

# build animated gif
with imageio.get_writer('PIB_t.gif', mode='I') as writer:
    for filename in filenames:
        image = imageio.imread(filename)
        writer.append_data(image)

# remove temporary files
for filename in set(filenames):
    os.remove(filename)
```



see: NumQM_Basic01.ipynb

Homework

Exercise 1: It appears from the animation shown in the previous slide that the initial wave function seems to get back its shape after evolving for some time. This time period is called as the wave packet revival time. Can you derive an analytic expression for the revival time and compare it with the simulation?

Hint: You can generate the animation yourself using the interactive notebooks at https://mybinder.org/v2/gh/raghurama123/NumQM_Basic/HEAD

Does wave packet revival remind you of any classical phenomenon, where the system comes back to its initial configuration after a bit of time-evolution?

Wavefunctions in x and p representations

Suppose a system is in a state denoted by the ket $|n\rangle$, then the corresponding wave function of the system is obtained by representing the ket in the position or momentum eigen kets.

$$\psi_n(x) = \langle x|n\rangle; \qquad \phi_n(p) = \langle p|n\rangle$$

The definition of the basis kets $|x\rangle$ and $|p\rangle$ has to be taken as one of the postulates of quantum mechanics. They are related to one another by Fourier transformation.

	x-representation	p-representation
$\|x_0\rangle$	$\langle x\|x_0\rangle = \delta(x - x_0)$	$\langle p\|x_0\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp(-ipx_0/\hbar)$
$\|p_0\rangle$	$\langle x\|p_0\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp(ip_0x/\hbar)$	$\langle p\|p_0\rangle = \delta(p - p_0)$

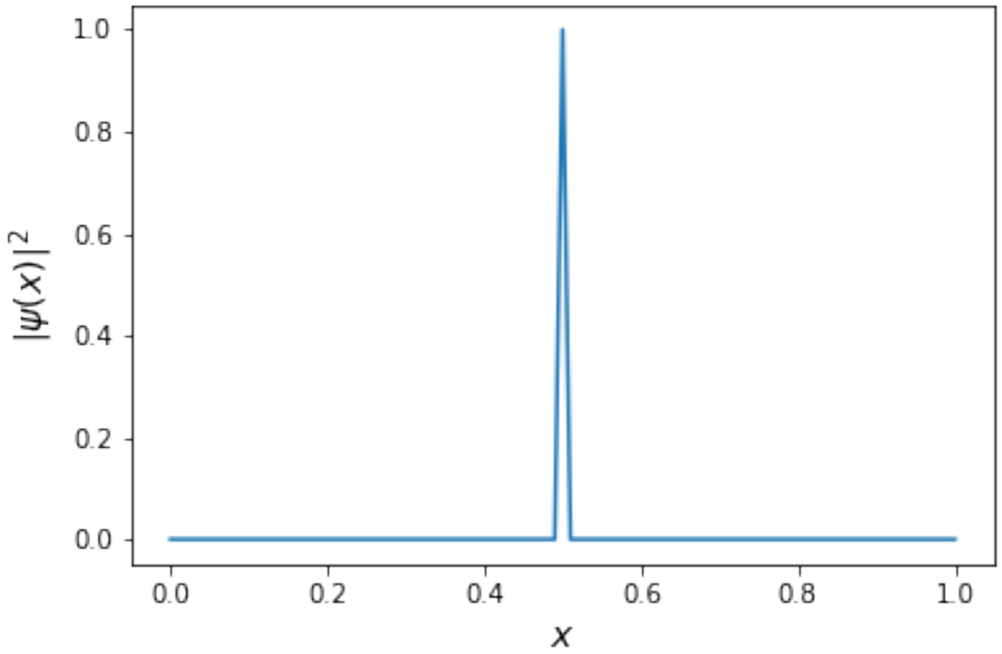
Changing representations

$$\begin{aligned}\phi_n(p) &= \langle p \,|\, n \rangle \\ &= \langle p \,|\, \hat{I} \,|\, n \rangle \\ &= \langle p \,|\, \int dx \,|\, x \rangle\langle x \,|\, n \rangle \\ &= \int dx \langle p \,|\, x \rangle\langle x \,|\, n \rangle \\ &= \int dx \langle p \,|\, x \rangle \psi_n(x) \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int dx \exp(-ipx/\hbar)\psi_n(x)\end{aligned}$$

$$\begin{aligned}\psi_n(x) &= \langle x \,|\, n \rangle \\ &= \langle x \,|\, \hat{I} \,|\, n \rangle \\ &= \langle x \,|\, \int dp \,|\, p \rangle\langle p \,|\, n \rangle \\ &= \int dp \langle x \,|\, p \rangle\langle p \,|\, n \rangle \\ &= \int dp \langle x \,|\, p \rangle \phi_n(p) \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int dp \exp(ipx/\hbar)\phi_n(p)\end{aligned}$$

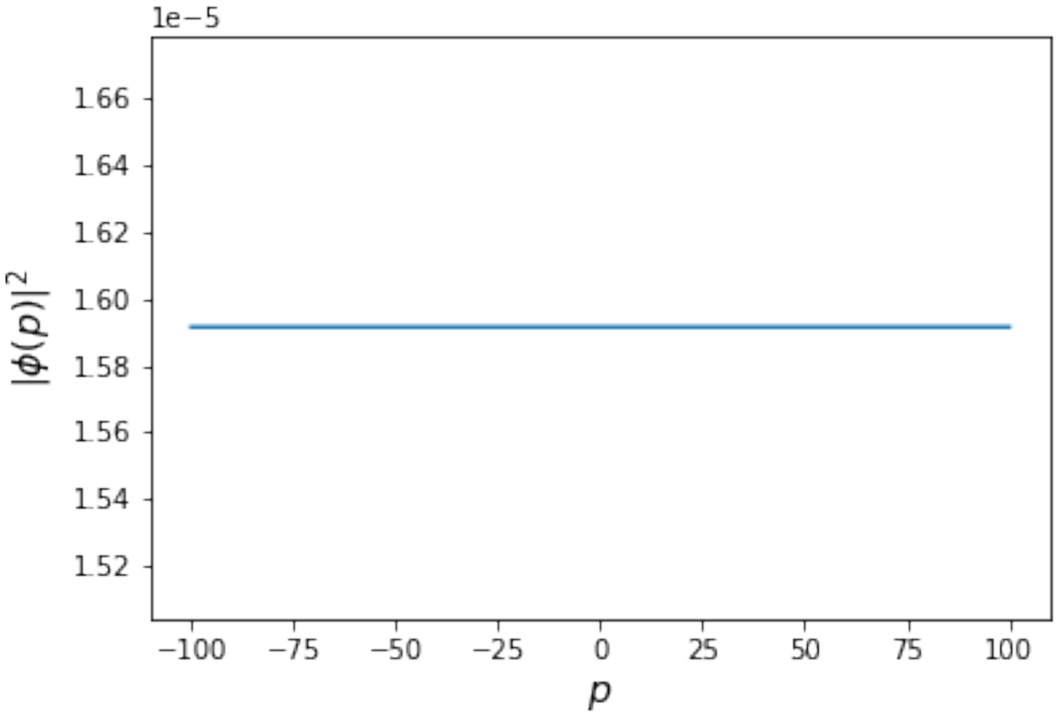
$\hat{I} = \int dx \,|\, x \rangle\langle x \,| = \int dp \,|\, p \rangle\langle p \,|$ is called as the completeness relation

Fourier transform of one position eigenstate



full-localisation at one point in the x-representation

$$\psi(x) = \langle x \,|\, x = 0.5 \rangle = \delta(x - 0.5)$$

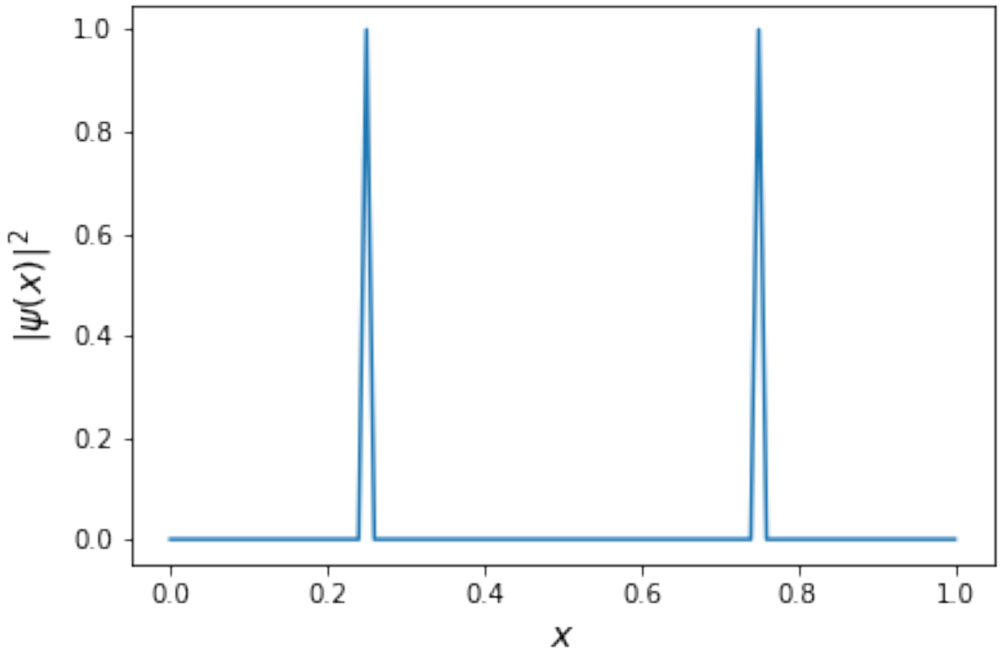


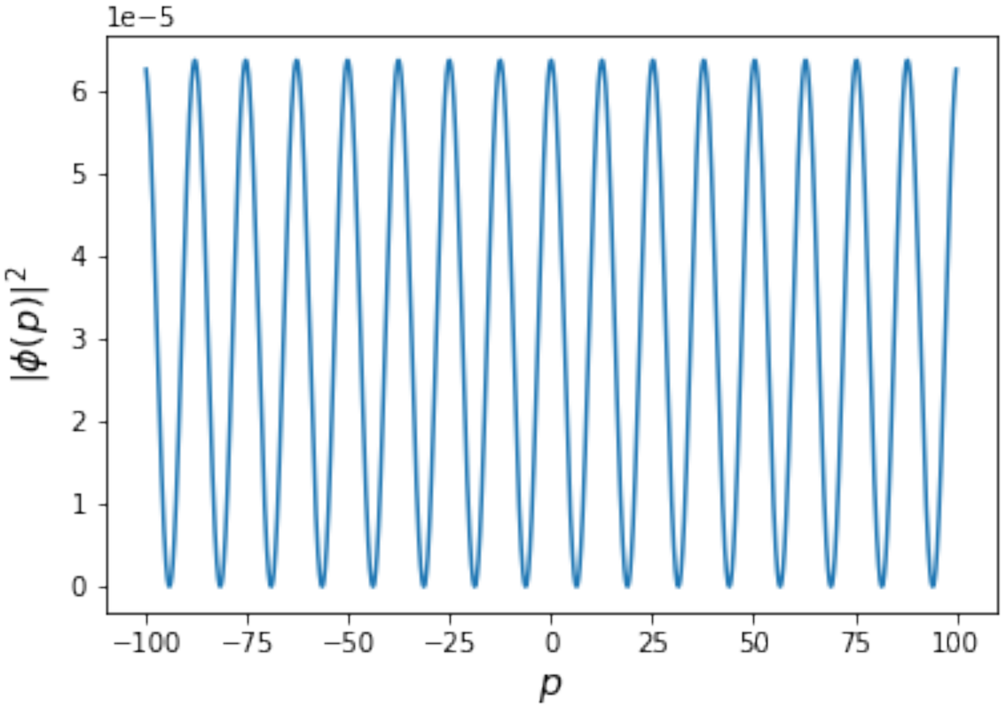
completely delocalised in the p-representation

$$\phi(p) = \langle p \,|\, x = 0.5 \rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp(-ipx/\hbar)$$

see: NumQM_Basic02.ipynb

Adding one more position eigenstate



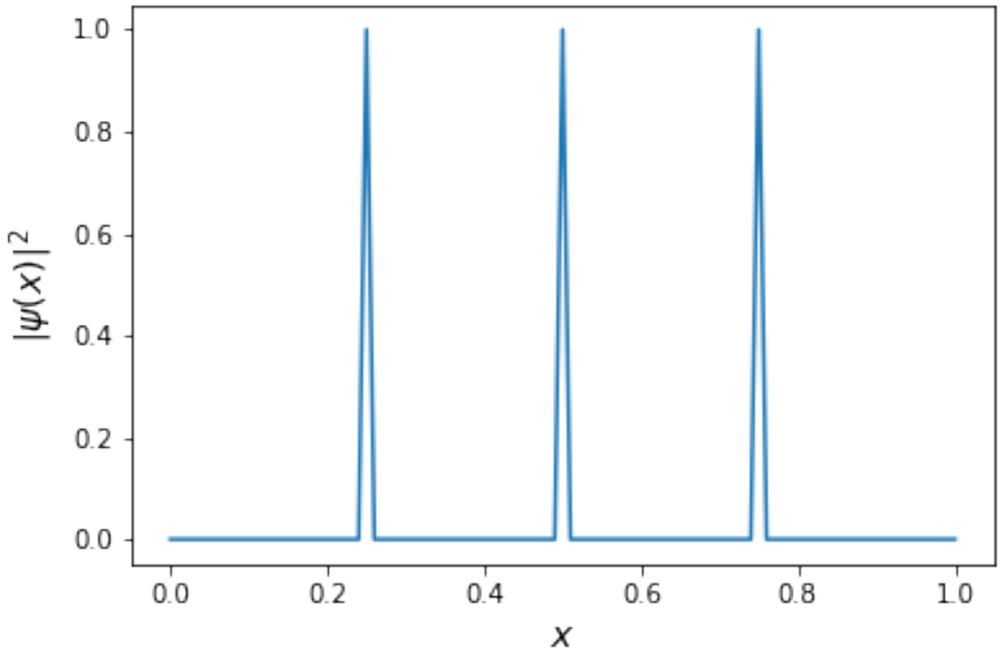


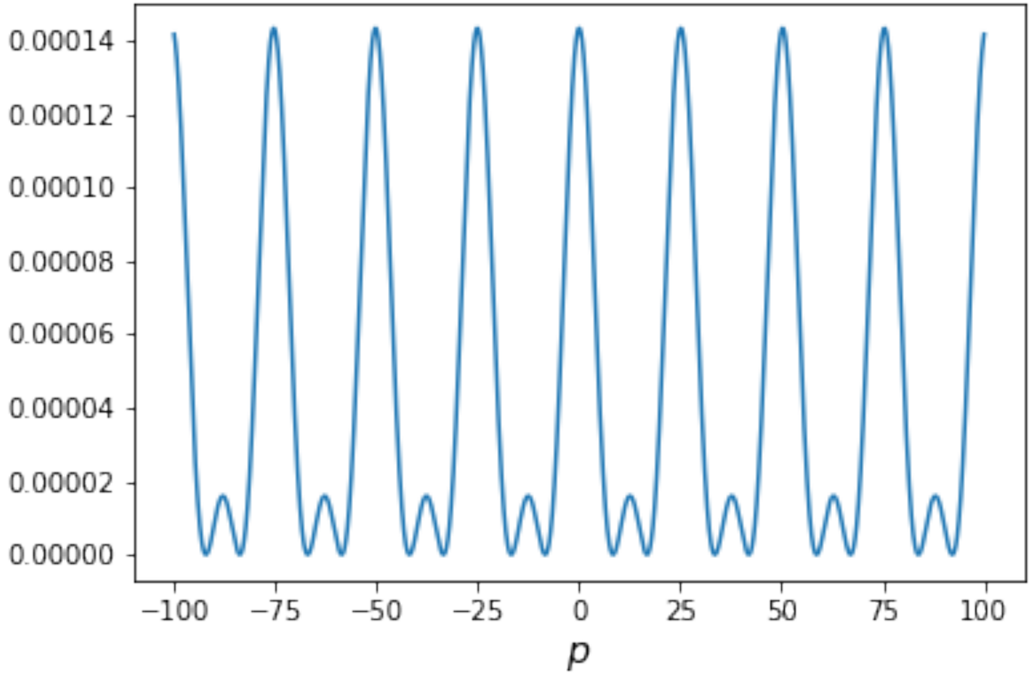
$$\psi(x) = \langle x|0.25\rangle + \langle x|0.75\rangle$$

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int dx \exp(-ipx/\hbar)\psi_n(x)$$

see: NumQM_Basic02.ipynb

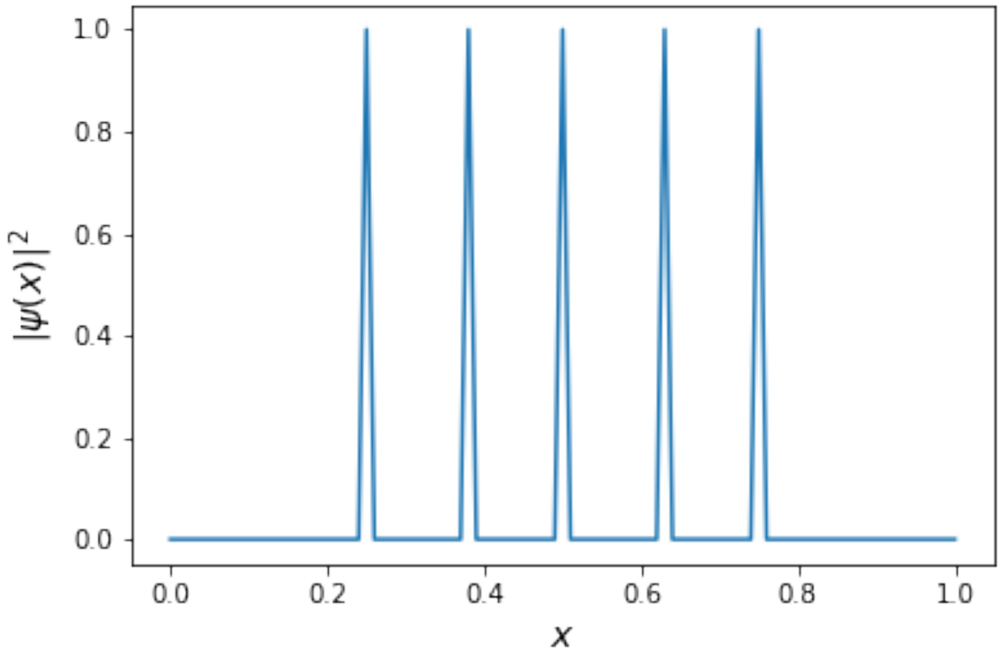
Sum of three position eigenstates



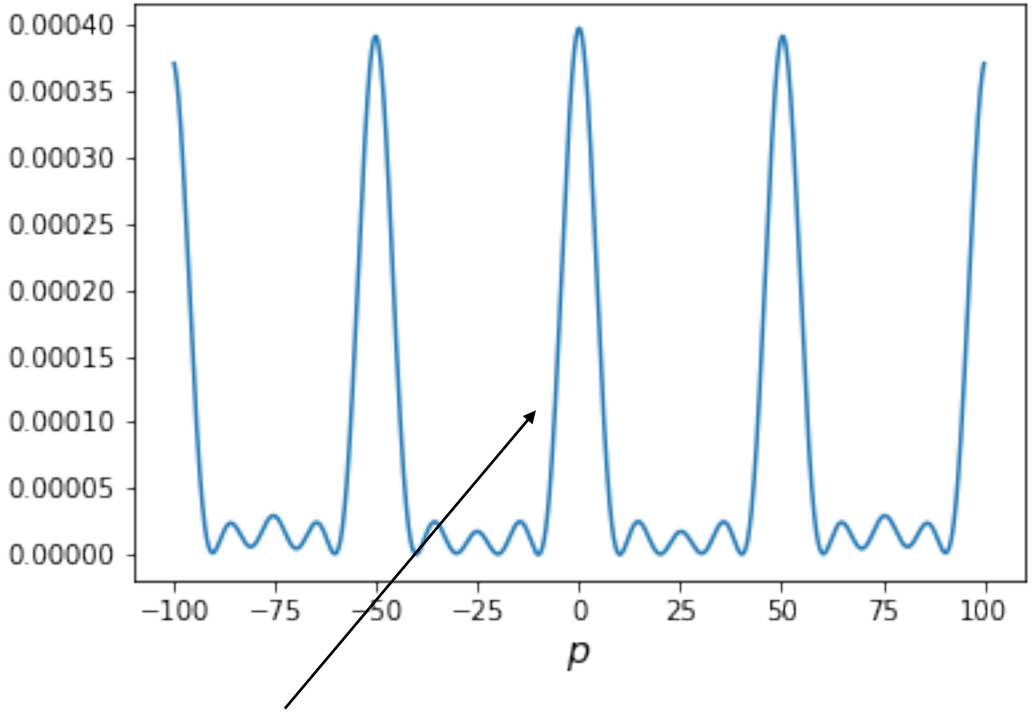


see: NumQM_Basic02.ipynb

Sum of five position eigenstates



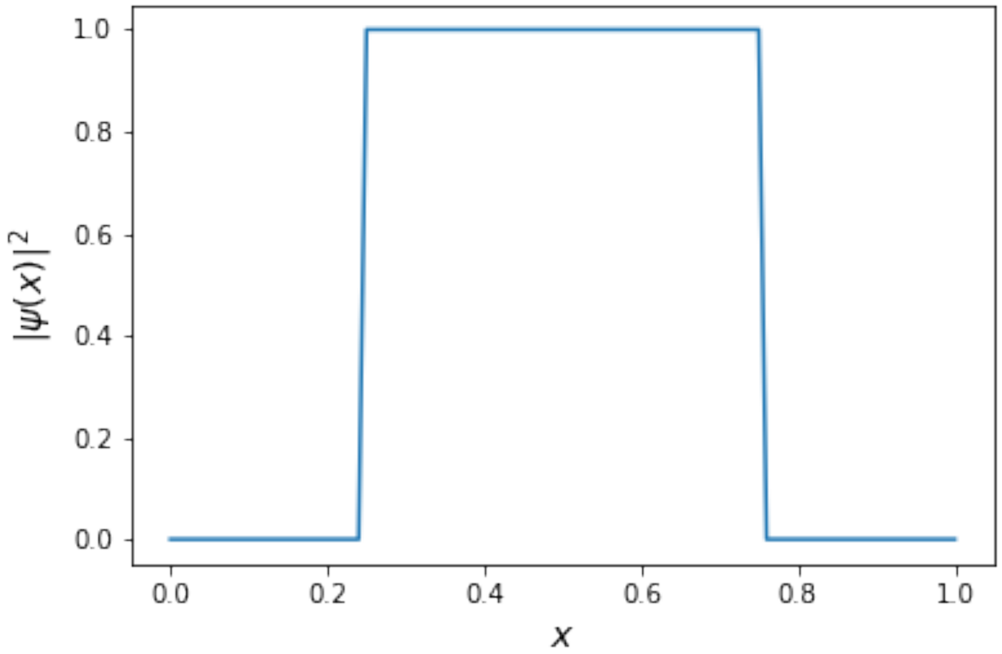
beginning to spread in the x-representation

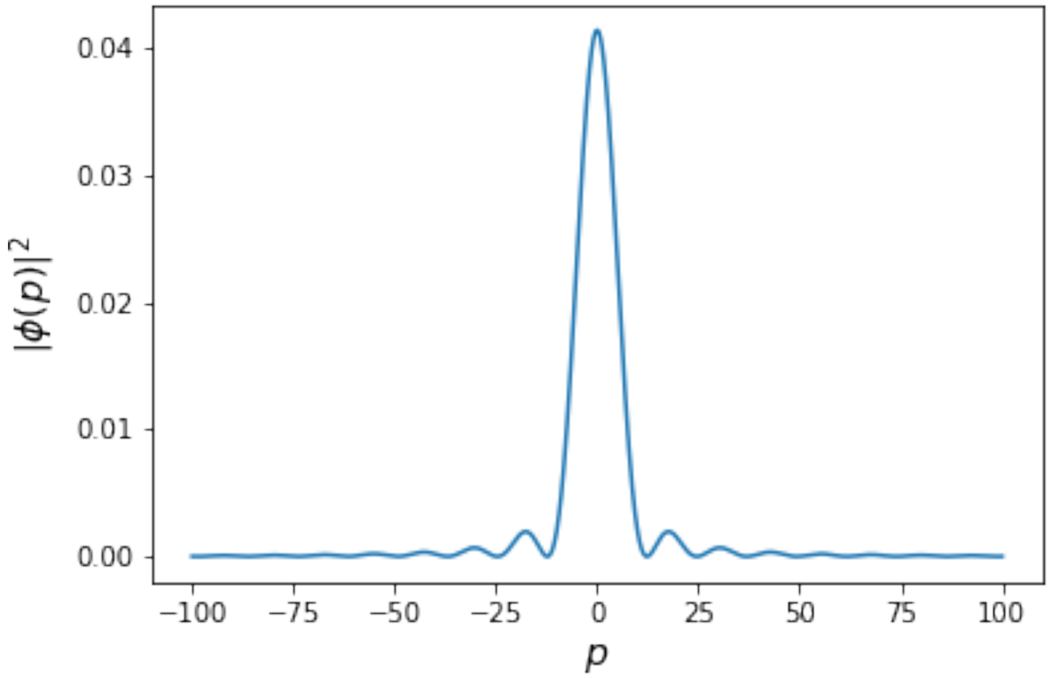


quasi-localisation in the p-representation emerges

see: NumQM_Basic02.ipynb

Integration over position eigenstates

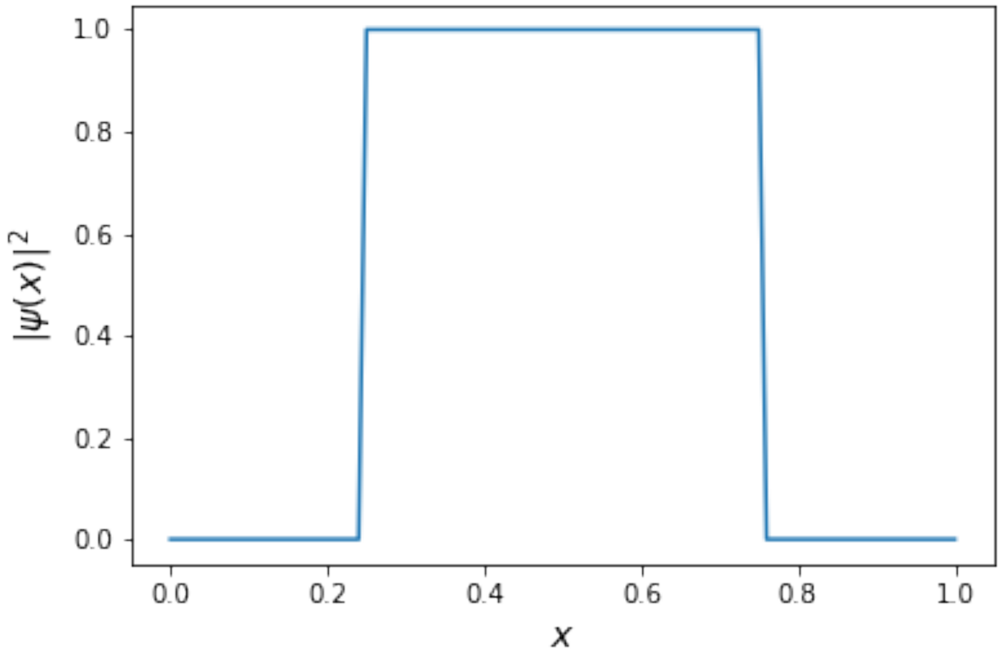


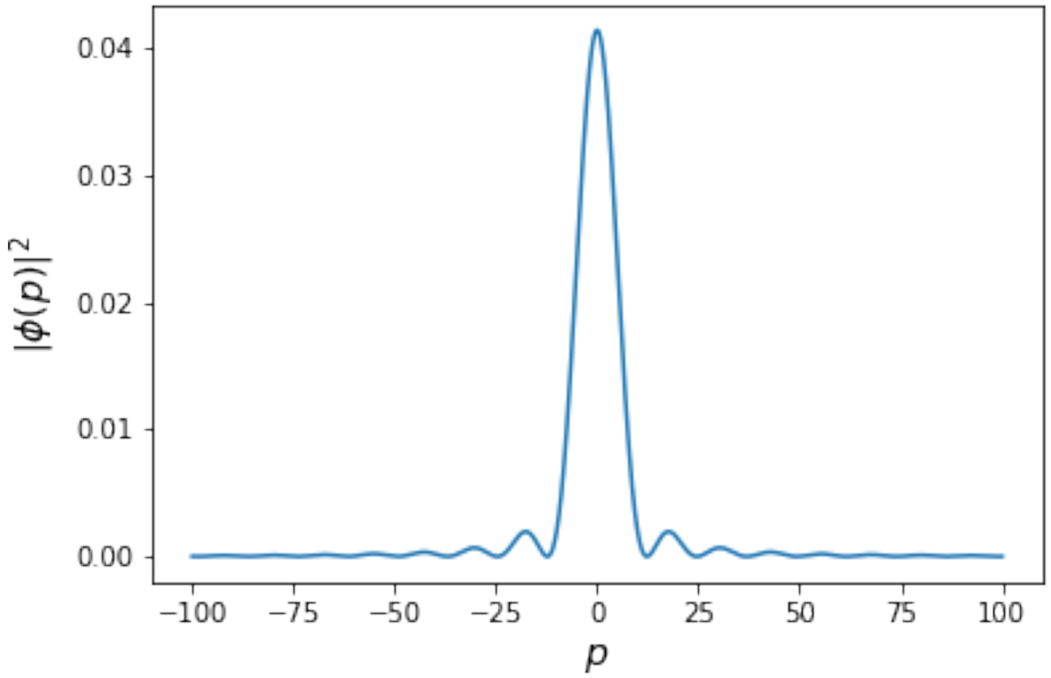


full-localisation in the p-representation

see: NumQM_Basic02.ipynb

Integration over position eigenstates

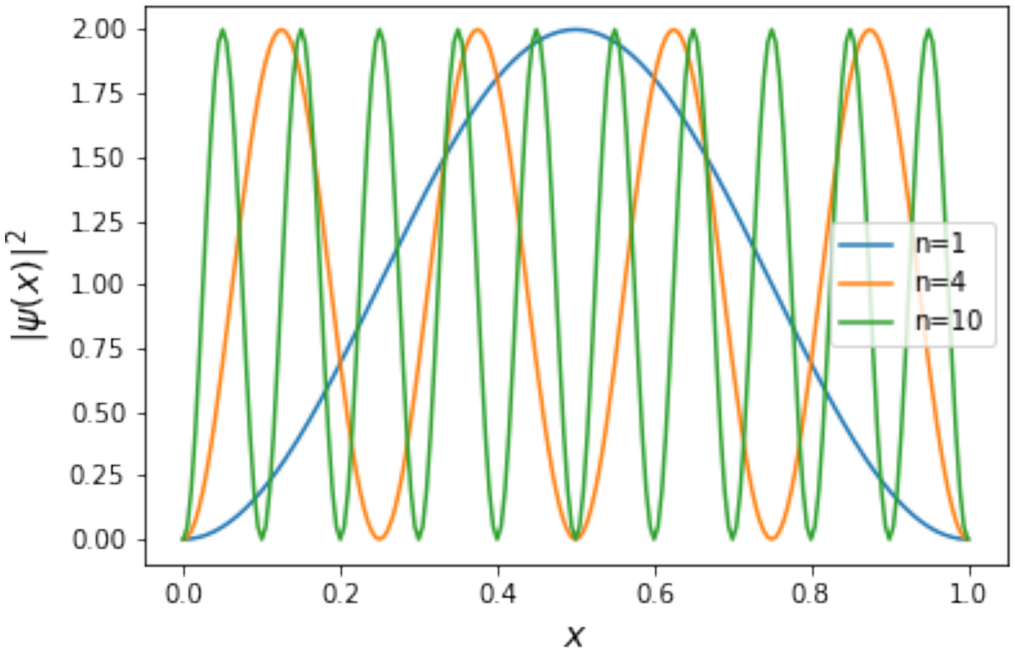


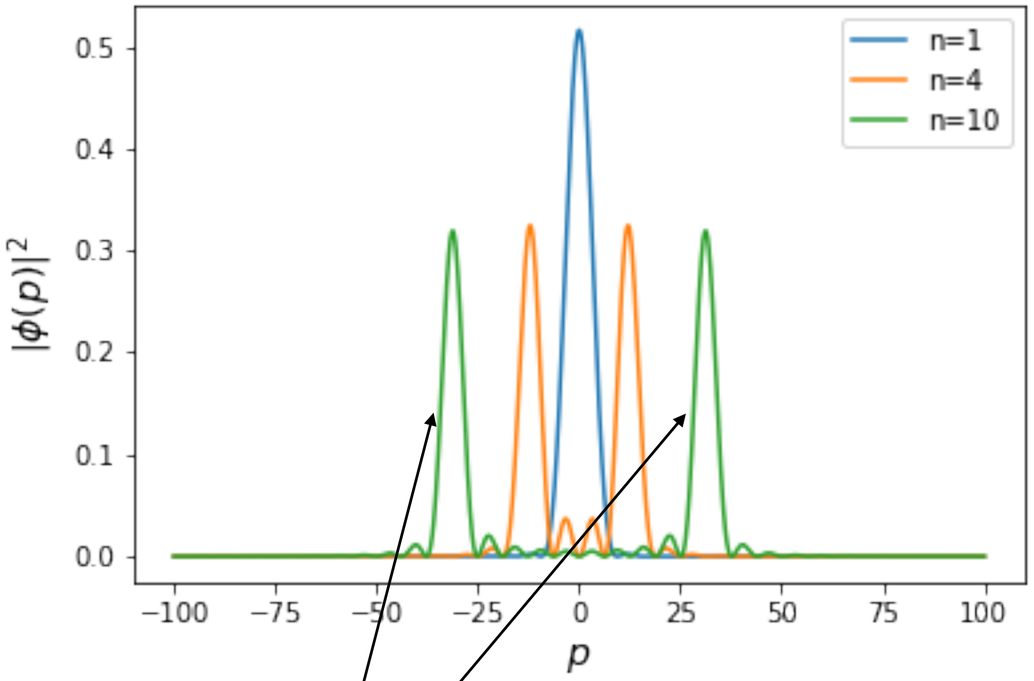


Have you seen this function before? Can you guess the mathematical expression for this function?

see: NumQM_Basic02.ipynb

Particle-in-a-box in the p-representation





high-energy states correspond to particles
traveling towards left and right with definite momentum

see: NumQM_Basic03.ipynb

Homework

Exercise 2: Plot the probability distributions for a classical particle-in-a-box in position and momentum representations. Can you interpret these plots using the ideas discussed in the previous slides?

A linear variational problem

An approximation technique in QM is to expand the eigenfunctions of a new problem as linear combinations of basis functions that are eigenfunctions of a known problem.

$$\psi_n^{\text{new}}(x) = \sum_k c_{k,n}\psi_k^{\text{known}}(x) \text{ or simply } \psi_n(x) = \sum_k c_{k,n}\chi_k(x)$$

The best wavefunctions for the new problem are obtained by varying the coefficients $\{c_{k,n}\}$ that minimise the energy eigenvalues of the new problem.

The procedure for finding these coefficients is by representing the Hamiltonian operator of the new problem using the eigenfunctions of the known problem. The eigenvectors of the Hamiltonian matrix provide $\{c_{k,n}\}$.

Let's apply this method to find the eigenvalues and eigenfunctions of the quantum harmonic oscillator (new problem) in terms of particle-in-a-box (known problem) eigenfunctions.

Numerical solution to the harmonic oscillator

In [4]:
```
def fn_V(x):
    psi_i=np.sqrt(1/L)*np.sin((i+1)*(x-L)*np.pi/(2*L))
    psi_j=np.sqrt(1/L)*np.sin((j+1)*(x-L)*np.pi/(2*L))
    fn_V=psi_i * k * x**2/2 * psi_j
    return fn_V

for iN in range(0,6):

    N=2**iN    # No. of basis functions

    V=np.zeros([N,N])
    T=np.zeros([N,N])
    H=np.zeros([N,N])

    for i in range(N):
        for j in range(N):
            Int_V=integrate.quadrature(fn_V, -L, L,maxiter=1000)
            V[i][j]=Int_V[0]
        #kinetic energy part is same as in the particle-in-a-box
        T[i][i]=(i+1)**2 * hbar**2 * np.pi**2 / (8 * m * L**2)

    H=T+V

    E,V=eigen(H)

    print("Number of basis: ", N, ", ground state energy is:", E[0])
```

```
Number of basis:  1 , ground state energy is: 6.546885307943112
Number of basis:  2 , ground state energy is: 6.546885307943112
Number of basis:  4 , ground state energy is: 2.2409822186260655
Number of basis:  8 , ground state energy is: 0.7712925817042399
Number of basis:  16 , ground state energy is: 0.5026588346751345
Number of basis:  32 , ground state energy is: 0.49999999991960487
```

see: NumQM_Basic04.ipynb

Higher states converge slowly

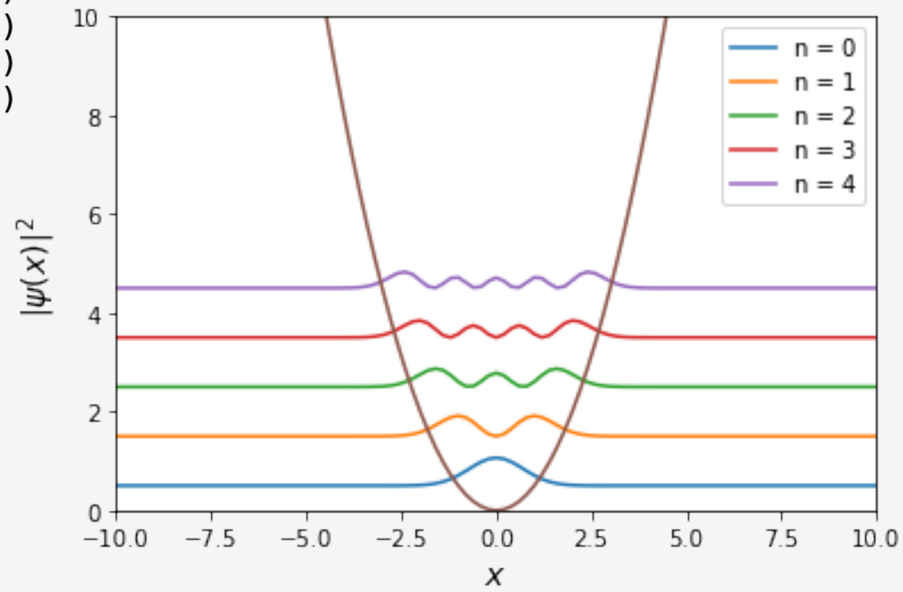
In [5]:
```
for i in range(N):
    print(i,E[i])
```

```
0 0.49999999991960487
1 1.500000003533623
2 2.5000000246525915
3 3.5000000749476574
4 4.500003826380895
5 5.500009108730652
6 6.500213561983046
7 7.500380483848162
8 8.50489994173305
9 9.507109605274334
10 10.550503775703861
11 11.563037889597
12 12.757188589561512
13 13.790161054294524
14 15.274948394336956
15 16.323820558552228
16 18.175821285164076
17 19.22309685760712
18 21.47078218078809
19 22.495304266567338
20 25.155539320689343
21 26.135710969665308
22 29.225350687266882
23 30.13958386030048
24 33.67696348822975
25 34.50365514827044
26 38.50946635546445
27 39.22763463005119
28 43.745025808894155
29 44.34804530869218
30 50.588924425384036
31 51.22056108474399
```

see: NumQM_Basic04.ipynb

Eigenfunctions as linear combination of basis

In [6]:
```
x=np.linspace(-L, L, 101)
Vharm=k*x**2/2

psi0=np.zeros(101)
psi1=np.zeros(101)
psi2=np.zeros(101)
psi3=np.zeros(101)
psi4=np.zeros(101)
for i in range(N):
    psi0=psi0+V[i][0]*np.sqrt(1/L)*np.sin((i+1)*(x-L)*np.pi/(2*L))
    psi1=psi1+V[i][1]*np.sqrt(1/L)*np.sin((i+1)*(x-L)*np.pi/(2*L))
    psi2=psi2+V[i][2]*np.sqrt(1/L)*np.sin((i+1)*(x-L)*np.pi/(2*L))
    psi3=psi3+V[i][3]*np.sqrt(1/L)*np.sin((i+1)*(x-L)*np.pi/(2*L))
    psi4=psi4+V[i][4]*np.sqrt(1/L)*np.sin((i+1)*(x-L)*np.pi/(2*L))

plt.plot(x,np.abs(psi0)**2+E[0])
plt.plot(x,np.abs(psi1)**2+E[1])
plt.plot(x,np.abs(psi2)**2+E[2])
plt.plot(x,np.abs(psi3)**2+E[3])
plt.plot(x,np.abs(psi4)**2+E[4])
plt.plot(x,Vharm)
plt.xlabel("$x$", fontsize=14)
plt.ylabel("$|\psi(x)|^2$", fontsize=14)
plt.savefig('psi_harm.png')
plt.legend(['n = 0','n = 1','n = 2','n = 3','n = 4'])
plt.ylim(0,10)
plt.show()
```



see: NumQM_Basic04.ipynb

One-dimensional molecule

The method can be extended easily to any arbitrary 1D problem. Let's apply to 1D diatomic molecule

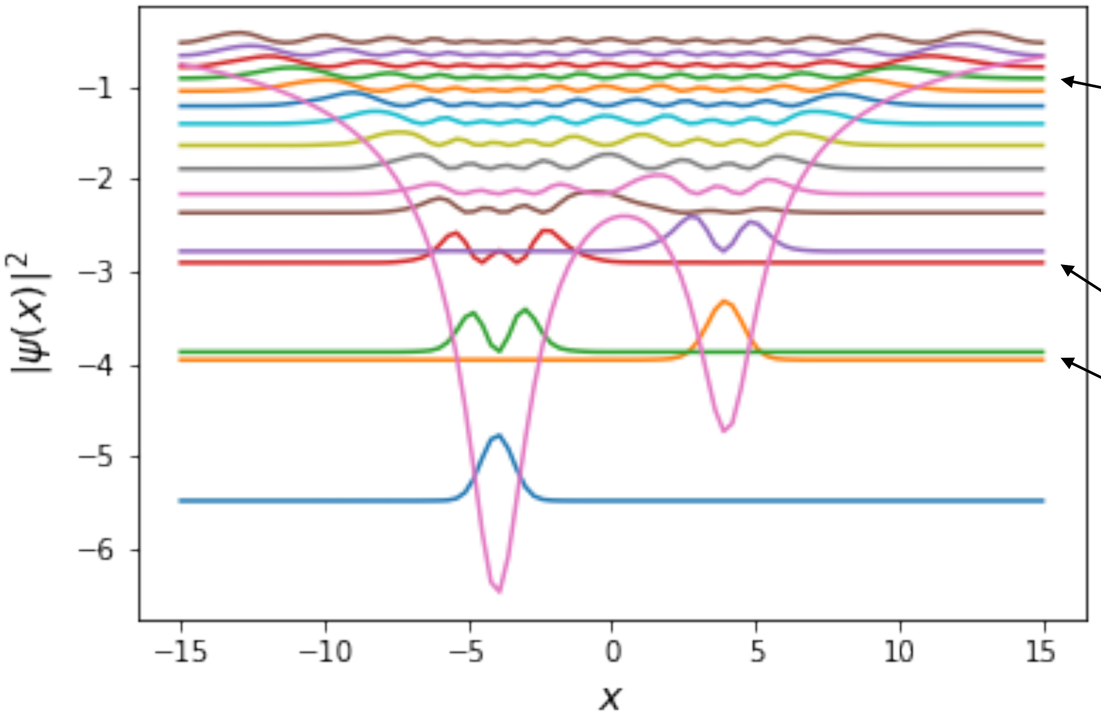
$$V(x) = -\left[\frac{Z_A}{\sqrt{|x - x_A|^2 + \alpha}} + \frac{Z_B}{\sqrt{|x - x_B|^2 + \alpha}}\right]$$

The constant $\alpha \geq 0$ 'softens' the Coulomb potential (let's set it to 1.0). Can you think of some reasons for why should we soften the potential?

see: NumQM_Basic05.ipynb

$$V(x) = -\left[\frac{6}{\sqrt{|x+4|^2+1}} + \frac{4}{\sqrt{|x-4|^2+1}}\right]$$

A heteronuclear diatomic molecule



Approaching continuum

Tunneling splitting of energy levels

see: NumQM_Basic05.ipynb

Thank you for your attention!

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