Quantum Mechanics I - PSet 6

Telmo Cunha

November 2025

Exercise 1

Consider the following wavefunction for a particle of mass m in an infinite square well of width a

$$\Psi(x,0) = \frac{1}{\sqrt{3}}\sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right) + \frac{2}{\sqrt{3}}\sqrt{\frac{2}{a}}\sin\left(\frac{3\pi x}{a}\right). \tag{1.1}$$

- (a) For $\Psi(x,0)$ to be an energy eigenstate it needs to satisfy the eigenvalue equation for the Hamiltonian operator, i.e.

$$\hat{H}\Psi(x,0) = E\Psi(x,0), \tag{1.2}$$

or equivalently

$$\hat{H}\Psi(x,0) - E\Psi(x,0) = 0. \tag{1.3}$$

Instead of verifying this let us compute directly the eigenstates for the infinite square-well of width a. Let $\psi(x) := \Psi(x,0)$, the TISE is given by

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x), \tag{1.4}$$

with solutions

$$\psi(x) = A\sin(kx) + B\cos(kx), \tag{1.5}$$

where $k = \sqrt{2mE}/\hbar$. From the boundary data $\psi(0) = \psi(a) = 0$, we have $B = 0$ and

$$ka = n\pi, \tag{1.6}$$

where we consider $n \in \mathbb{N}$ since $\sin(-\alpha) = -\sin(\alpha)$, giving the same state. This leads to

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}, \;\; n \in \mathbb{N}. \tag{1.7}$$

We find A by enforcing normalization, i.e.

$$1 = |A|^2\int_0^a \sin^2(kx)dx = |A|^2\frac{a}{2}, \tag{1.8}$$

which, considering $A \in \mathbb{R}$, leads to $A = \sqrt{2/a}$. To conclude, the energy eigenstates are given by

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right), \;\; n \in \mathbb{N}. \tag{1.9}$$

Clearly, $\Psi(x,0)$ is a linear combination of the eigenstates $\psi_2(x)$ and $\psi_3(x)$ and therefore it is not an energy eigenstate. To find $\Psi(x,t)$ we just need to add the time dependence corresponding to each eigenstate, since each one separately is a solution and Schrödinger's equation is linear, i.e. linear combinations are also solutions. We have then

$$\Psi(x,t) = \frac{1}{\sqrt{3}}\sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right)e^{-\frac{iE_2 t}{\hbar}} + \frac{2}{\sqrt{3}}\sqrt{\frac{2}{a}}\sin\left(\frac{3\pi x}{a}\right)e^{-\frac{iE_3 t}{\hbar}}. \tag{1.10}$$

Briefly, recall that we consider solutions of the form $\Psi(x,t) = f(x)g(t)$ leading to two equations, one for t and one for x, each equal to the same constant E.

- (b) By the measurement postulate the probability of measuring the energy corresponding to state n is $|c_i|^2$, where c_i is the coefficient of eigenstate i. For $n = 1$ since it's coefficient in $\Psi(x,0)$ is zero, the probability is zero. For $n = 2$ this corresponds to $1/3$ and for $n = 3$ it is $2/3$, summing to 1 as it should.

- (c) We have

$$\Psi(x,t) = c_2\psi_2(x)e^{-\frac{iE_2 t}{\hbar}} + c_3\psi_3(x)e^{-\frac{iE_3 t}{\hbar}}, \tag{1.11}$$

$c_2, c_3 \in \mathbb{R}$. Thus

$$\begin{aligned}
\langle\hat{x}\rangle(t) &= \langle\Psi(x,t)|x|\Psi(x,t)\rangle \\
&= \int_0^a \Big[c_2^2 x\psi_2^2 + c_3^2 x\psi_3^2 + c_2c_3\psi_2\psi_3 x e^{-i(E_3-E_2)\frac{t}{\hbar}} \\
&\qquad + c_2c_3\psi_2\psi_3 x e^{-i(E_2-E_3)\frac{t}{\hbar}}\Big]dx \\
&= \int_0^a c_2^2 x\psi_2^2 + c_3^2 x\psi_3^2 + 2\Re\left(c_2c_3e^{-i(E_3-E_2)t/\hbar}\langle\psi_2|x|\psi_3\rangle\right)dx.
\end{aligned} \tag{1.12}$$

The first two terms are of the form

$$\begin{aligned}
c_n^2\int_0^a x\psi_n^2 dx =& c_n^2\int_0^a x\frac{2}{a}\sin^2\left(\frac{n\pi x}{a}\right) = \frac{2c_n^2}{a}\int_0^a x\left(\frac{1-\cos(2n\pi x/a)}{2}\right)dx \\
&= \frac{2c_n^2}{a}\left[\frac{a^2}{4} - \int_0^a x\left(\frac{\cos(2n\pi x/a)}{2}\right)dx\right] \\
&= \frac{2c_n^2}{a}\left[\frac{a^2}{4} - \frac{1}{2}\int_0^a x\cos(2n\pi x/a)dx\right] \\
&= \frac{2c_n^2}{a}\left[\frac{a^2}{4} - \frac{1}{2}\left(\frac{a}{2n\pi}x\sin(2n\pi x/a)\Big|_0^a\right) - \frac{a}{2n\pi}\int_0^a \sin(2n\pi x/a)dx\right] \\
&= \frac{2c_n^2}{a}\left[\frac{a^2}{4} - \frac{1}{2}\left(\frac{a}{2n\pi}x\sin(2n\pi x/a)\Big|_0^a\right) + \frac{a^2}{4n^2\pi^2}\cos(2n\pi x/a)\Big|_0^a\right] \\
&= c_n^2\frac{a}{2},
\end{aligned} \tag{1.13}$$

while

$$\begin{aligned}
\langle\psi_n|x|\psi_m\rangle &= \frac{2}{a}\int_0^a x\sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)dx \\
&= \frac{1}{a}\int_0^a x\cos\left(\frac{n\pi x}{a} - \frac{m\pi x}{a}\right) - x\cos\left(\frac{n\pi x}{a} + \frac{m\pi x}{a}\right)dx \\
&= \frac{1}{a}\int_0^a x\cos\left(\frac{(n-m)\pi x}{a}\right) - x\cos\left(\frac{(n+m)\pi x}{a}\right)dx,
\end{aligned} \tag{1.14}$$

which leads to

$$\begin{aligned}\int_0^a x\cos(k\pi x/a)dx &= \frac{a}{k\pi}x\sin(k\pi x/a)\Big|_0^a - \frac{a}{k\pi}\int_0^a \sin(k\pi x/a)dx \\ &= \frac{a^2}{k^2\pi^2}\cos(k\pi x/a)\Big|_0^a dx \\ &= \begin{cases} -\frac{2a^2}{k^2\pi^2}, & \text{if } k \text{ is odd,} \\ 0, & \text{if } k \text{ is even.}\end{cases}\end{aligned} \tag{1.15}$$

So, the integral above becomes

$$\langle\psi_n|x|\psi_m\rangle = \begin{cases} \frac{2a}{\pi^2}\left(\frac{1}{(n+m)^2} - \frac{1}{(n-m)^2}\right), & \text{if } n-m \text{ (and thus } n+m) \text{ is odd,} \\ 0, & \text{if if } n-m \text{ (and thus } n+m) \text{ is even,}\end{cases} \tag{1.16}$$

In particular

$$\langle\psi_2|x|\psi_3\rangle = -\frac{48a}{25\pi^2}. \tag{1.17}$$

Finally, we have

$$\langle\hat{x}\rangle(t) = \frac{a}{2} - \frac{32\sqrt{2}a}{25\pi^2}\cos\left(\frac{5\pi^2\hbar}{2ma^2}t\right). \tag{1.18}$$

- (d) Similarly, we have

$$\begin{aligned}\langle\hat{p}\rangle(t) &= -i\hbar\int_0^a \left[c_2^2\psi_2\psi_2' + c_3^2\psi_3\psi_3' + c_2c_3\psi_2\psi_3'e^{-i(E_2-E_3)\frac{t}{\hbar}} + c_2c_3\psi_2'\psi_3e^{-i(E_3-E_2)\frac{t}{\hbar}}\right]dx \\ &= -i\hbar c_2c_3e^{-i(E_2-E_3)\frac{t}{\hbar}}\int_0^a(\psi_2\psi_3')\,dx - i\hbar c_2c_3e^{-i(E_3-E_2)\frac{t}{\hbar}}\int_0^a(\psi_2'\psi_3)\,dx \\ &= i\hbar Ac_2c_3\left(e^{i\omega t} - e^{-i\omega t}\right) \\ &= 2\hbar c_2c_3A\sin(\omega t) \\ &= \frac{16\sqrt{2}\hbar}{5a}\sin\left(\frac{E_3-E_2}{\hbar}t\right) \\ &= \frac{16\sqrt{2}\hbar}{5a}\sin\left(\frac{5\pi^2\hbar}{2ma^2}t\right),\end{aligned} \tag{1.19}$$

where we use $\sin(a)\cos(b) = 1/2(\sin(a+b) + \sin(a-b)$ and define A as

$$\begin{aligned}A := \int_0^a \psi_2\psi_3'dx &= \frac{6\pi}{a^2}\int_0^a \sin\left(\frac{2\pi x}{a}\right)\cos\left(\frac{3\pi x}{a}\right)dx \\ &= \frac{3\pi}{a^2}\int_0^a \sin\left(\frac{5\pi x}{a}\right) - \sin\left(\frac{\pi x}{a}\right)dx \\ &= \frac{3\pi}{a^2}\left(\frac{2a}{5\pi} - \frac{2a}{\pi}\right) \\ &= -\frac{24}{5a},\end{aligned} \tag{1.20}$$

using the fact that

$$\int_0^a \psi_n\psi_n'dx = \sqrt{\frac{a}{2}}\psi_n^2(x)\Big|_0^a = 0, \tag{1.21}$$

and also that

$$\int_0^a \psi_n \psi_m' dx = -\int_0^a \psi_n' \psi_m dx, \tag{1.22}$$

using integration by parts and the fact that the wavefunctions vanish at the boundary. Thus, we conclude that

$$\langle \hat{p} \rangle (t) = \frac{16\sqrt{2}\hbar}{5a} \sin\left(\frac{5\pi^2\hbar}{2ma^2}t\right). \tag{1.23}$$

Exercise 2

This corresponds to exercise 2.44, page 78, of [GS18]. Prove the following: In one dimension ($-\infty < x < \infty$) there are no degenerate bound states (where scalar multiples of a solution is considered to be the same solution).

Suppose we have bound states ψ_1 and ψ_2 with the same energy E and such that $\psi_1 \neq \psi_2$. Then

$$\begin{cases} \hat{H}\psi_1 = E\psi_1, \\ \hat{H}\psi_2 = E\psi_2, \end{cases} \tag{1.24}$$

equivalently

$$\begin{cases} \frac{d^2\psi_1}{dx^2} = -\frac{2mE}{\hbar^2}\psi_1 + \frac{2m}{\hbar^2}V(x)\psi_1, \\ \frac{d^2\psi_2}{dx^2} = -\frac{2mE}{\hbar^2}\psi_2 + \frac{2m}{\hbar^2}V(x)\psi_2. \end{cases} \tag{1.25}$$

Multiply the first equation by ψ_2, the second by ψ_1 and subtract to obtain

$$\psi_1''\psi_2 - \psi_2''\psi_1 = \frac{d}{dx}\left(\psi_1'\psi_2 - \psi_2'\psi_1\right) = 0. \tag{1.26}$$

Therefore

$$\psi_1'\psi_2 - \psi_2'\psi_1 = C, \tag{1.27}$$

for some $C \in \mathbb{R}$. Since we are considering bound states, which are normalizable, they decay to zero at infinity, therefore we must in fact have $C = 0$. In a neighborhood of x_0 such that $\psi_1(x) \neq 0$, by continuity and because otherwise $\psi_1(x) \equiv 0$, we have

$$\left(\frac{\psi_2}{\psi_1}\right)' = \frac{\psi_2\psi_1'}{\psi_1^2} - \frac{\psi_2'\psi_1}{\psi_1^2} = \frac{C}{\psi_1^2} = 0. \tag{1.28}$$

Integrating from x_0 to x we obtain

$$\psi_2(x) = \frac{\psi_2(x_0)}{\psi_1(x_0)}\psi_1(x) =: c\psi_1(x), \tag{1.29}$$

around a neighborhood of x_0. Consider now

$$f(x) := \psi_2(x) - c\psi_1(x), \tag{1.30}$$

where $f(x_0) = 0$ by definition, and

$$f'(x_0) = \frac{\psi_1(x_0)}{\psi_1(x_0)}\psi_2'(x_0) - \frac{\psi_2(x_0)}{\psi_1(x_0)}\psi_1'(x_0) = 0. \tag{1.31}$$

Because ψ_1 and ψ_2 solve the same linear second order ODE so does f, since it is a linear combination. Therefore, the IVP with initial data $f(x_0) = 0$ and $f'(x_0) = 0$ implies $f(x) \equiv 0$ is the unique solution for all x and thus

$$\psi_2(x) = c\psi_1(x), \ \ \forall x \in \mathbb{R}, \tag{1.32}$$

concluding the proof.

Exercise 3

- (a) The 2D TISE within the well is given by

$$-\frac{\hbar^2}{2m}\Delta\psi(x,y) = E\psi(x,y), \tag{1.33}$$

which we solve using the usual separation of variables trick. Suppose

$$\psi(x,y) = f(x)g(y), \tag{1.34}$$

then

$$\frac{f''(x)}{f(x)} + \frac{g''(y)}{g(y)} = -\frac{2mE}{\hbar^2}. \tag{1.35}$$

This implies that

$$\begin{cases} f''(x) = Af(x), \\ g''(y) = Bg(y), \end{cases} \tag{1.36}$$

for some constants $A, B \in \mathbb{R}$ and such that

$$A + B = -\frac{2mE}{\hbar^2}. \tag{1.37}$$

Depending on the sign of A and B one can have several different solutions. However, for the solution to represent a bound state, we can not have exponential terms since those do not satisfy the boundary condition. From the boundary conditions we have that

$$f(0) = f(L_x) = 0. \tag{1.38}$$

Suppose $A > 0$, then

$$f(x) = e^{Ax} + e^{-Ax}. \tag{1.39}$$

However, in this case, $f(0) \neq 0$. Similarly, if $A = 0$, we have

$$f(x) = Cx + D, \tag{1.40}$$

and from $f(0) = 0$ we have $D = 0$ and from $f(L_x) = 0$ we have $C = 0$, which gives the trivial solution. Thus, we must have $A < 0$ and we define $A = -k_x^2$ leading to

$$f(x) = A_x \sin(k_x x) + B_x \cos(k_x x). \tag{1.41}$$

From $f(0) = 0$ we have $B_x = 0$ and from $f(L_x) = 0$ we have

$$k_x = \frac{n_x\pi}{L_x}, \tag{1.42}$$

$n_x \in \mathbb{N}$. Similarly, defining $B = -k_y^2$, for $g(y)$ we have

$$g(y) = A_y \sin(k_y y), \tag{1.43}$$

and from $g(L_y) = 0$ we have

$$k_y = \frac{n_y \pi}{L_y}, \tag{1.44}$$

$n_y \in \mathbb{N}$. Then, we have

$$\frac{2mE}{\hbar^2} = \frac{n_x^2 \pi^2}{L_x^2} + \frac{n_y^2 \pi^2}{L_y^2}, \tag{1.45}$$

for $n_x, n_y \in \mathbb{N}$ leading to

$$E = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right), \quad n_x = 1, 2, 3, ..., \quad n_y = 1, 2, 3, ... \tag{1.46}$$

The eigenfunctions are given by

$$\psi(x, y) = A_x A_y \sin\left(\frac{n_x \pi}{L_x} x \right) \sin\left(\frac{n_y \pi}{L_y} y \right). \tag{1.47}$$

The normalization conditions gives

$$\begin{aligned} 1 &= A_x^2 A_y^2 \int_0^{L_x} \sin^2\left(\frac{n_x \pi}{L_x} x \right) dx \int_0^{L_y} \sin^2\left(\frac{n_y \pi}{L_y} y \right) dy \\ &= A_x^2 A_y^2 \frac{L_x}{2} \frac{L_y}{2}, \end{aligned} \tag{1.48}$$

Thus

$$A_x A_y = \frac{2}{\sqrt{L_x L_y}}, \tag{1.49}$$

and the normalized eigenstates are

$$\psi_{n_x, n_y}(x, y) = \frac{2}{\sqrt{L_x L_y}} \sin\left(\frac{n_x \pi}{L_x} x \right) \sin\left(\frac{n_y \pi}{L_y} y \right), \quad n_x, n_y \in \mathbb{N}, \tag{1.50}$$

with energies

$$E(n_x, n_y) = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right), \quad n_x, n_y \in \mathbb{N}. \tag{1.51}$$

- (b) Suppose that $L_x = L_y = L$, then the eigenfunctions are given by

$$\psi_{n_x, n_y}(x, y) = \frac{2}{L} \sin\left(\frac{n_x \pi}{L} x \right) \sin\left(\frac{n_y \pi}{L} y \right), \quad n_x, n_y \in \mathbb{N}, \tag{1.52}$$

with energies

$$E(n_x, n_y) = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2 + n_y^2}{L^2} \right), \quad n_x, n_y \in \mathbb{N}. \tag{1.53}$$

The simple symmetry consideration comes from switching n_x with n_y, i.e. $E(n_x, n_y) = E(n_y, n_n)$. However, there are other "accidental" symmetries, the given example is $n_x = 7, n_y = 1$ and $n_x = 5, n_y = 5$, leading to the same energy. Another such example is $n_x = 10, n_y = 5$ and $n_x = 2, n_y = 11$ since $10^2 + 5^2 = 11^2 + 2^2 = 125$.

- (c) We have

$$E(n_x, n_y) = \frac{\pi^2 \hbar^2}{2m} \left(\frac{L_y^2 n_x^2 + L_x^2 n_y^2}{L_y^2 L_x^2} \right), \quad n_x, n_y \in \mathbb{N}. \tag{1.54}$$

To have a degeneracy we must have

$$L_y^2 n_x^2 + L_x^2 n_y^2 = L_y^2 a + L_x^2 b = L_y^2 c + L_x^2 d, \tag{1.55}$$

for some $a, b, c, d \in \mathbb{N}$ with $(a, b) \neq (c, d)$. However, this leads to

$$\frac{L_x^2}{L_y^2} = \frac{c-a}{b-d}, \tag{1.56}$$

which is impossible since the LHS is an irrational number and the RHS is a rational number. When $b = d$ we have immediately $a = c$ so there is never degeneracy in this case.

Exercise 4

We are given the potential

$$V(x) = \begin{cases} \infty, & \text{for } x < 0 \\ 0, & \text{for } 0 < x < a \\ V_0, & \text{for } a < x < 2a \\ \infty, & \text{for } x > 2a \end{cases} \tag{1.57}$$

- (a) The TISE for $0 < x < a$ is given by

$$\psi_1''(x) = -\frac{2mE}{\hbar^2}\psi_1(x), \tag{1.58}$$

with solutions

$$\psi_1(x) = A\sin(kx) + B\cos(kx). \tag{1.59}$$

The boundary data $\psi_1(0) = 0$ forces $B = 0$ and thus

$$\psi_1(x) = A\sin(kx), \quad 0 \leq x < a. \tag{1.60}$$

The TISE for $a < x < 2a$ is given by

$$\psi_2''(x) = \frac{2m(V_0 - E)}{\hbar^2}\psi_2(x), \tag{1.61}$$

where $0 < E < V_0$. Thus, the solutions are of the form

$$\psi_2(x) = Ce^{\kappa x} + De^{-\kappa x}. \tag{1.62}$$

The boundary data $\psi_2(2a) = 0$ gives

$$Ce^{2\kappa a} + De^{-2\kappa a} = 0, \tag{1.63}$$

leading to

$$-\frac{D}{C} = e^{4\kappa a}, \tag{1.64}$$

or

$$D = -Ce^{4\kappa a}, \tag{1.65}$$

and thus

$$\psi_2(x) = C\left(e^{\kappa x} - e^{\kappa(4a-x)}\right). \tag{1.66}$$

We further have

$$\psi_1(a) = \psi_2(a) \tag{1.67}$$

leading to

$$A\sin(ka) = C\left(e^{\kappa a} - e^{3\kappa a}\right). \tag{1.68}$$

and

$$\psi_1'(a) = \psi_2'(a) \tag{1.69}$$

leading to

$$kA\cos(ka) = \kappa C\left(e^{\kappa a} + e^{3\kappa a}\right). \tag{1.70}$$

Dividing (1.68) by (1.70) we obtain

$$\tan(ka) = \frac{k}{\kappa}\frac{e^{\kappa a} - e^{3\kappa a}}{e^{\kappa a} + e^{3\kappa a}}. \tag{1.71}$$

From

$$\begin{cases} \eta = ka, \\ \xi = \kappa a, \end{cases} \tag{1.72}$$

and

$$\xi^2 + \eta^2 = z_0^2, \tag{1.73}$$

we have

$$\frac{\tan(\eta)}{\eta} = \frac{1}{\xi}\frac{e^{\xi} - e^{3\xi}}{e^{\xi} + e^{3\xi}} = \left(\frac{1}{\xi}\right)\frac{1 - e^{2\xi}}{1 + e^{2\xi}} = -\frac{\tanh(\xi)}{\xi}. \tag{1.74}$$

So, we have the two equations

$$\begin{cases} \frac{\tan(\eta)}{\eta} = -\frac{\tanh(\xi)}{\xi}, \\ \xi^2 + \eta^2 = z_0^2 = \frac{2ma^2V_0}{\hbar^2}. \end{cases} \tag{1.75}$$

- (b) We have

$$\xi = \sqrt{z_0^2 - \eta^2}, \tag{1.76}$$

since $\xi > 0$. Solving these equations for $z_0 = 2\pi$ leads to a unique solution

$$\eta \approx 5.28. \tag{1.77}$$

Thus, we have a single state. Since we do not know a we can only specify E in terms of V_0 where

$$\frac{E}{V_0} = \frac{\hbar^2\eta^2/(2ma^2)}{\hbar^2 z_0^2/(2ma^2)} = \frac{\eta^2}{z_0^2} \approx 0.7075. \tag{1.78}$$

Exercise 5

Computational (to solve later).

Exercise 6

Computational (to solve later).

References

[GS18] David J. Griffiths and Darrell F. Schroeter. *Introduction to quantum mechanics*. Third edition. Cambridge ; New York, NY: Cambridge University Press, 2018. ISBN: 978-1-107-18963-8.