Quantum Mechanics I (141) Problem Set 2

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I. Solutions overview

Given an initial wavefunction $\Psi(x,0)$, we are tasked to find possible values for energy, the probability of measuring the energy at each state, and deriving a general expression for the wavefunction $\Psi(x,t)$.

II. Time Independent Schrodinger Equation - Infinite Square Well Potential

Recall that the 1D time-dependent Schrodinger equation (TDSE) is

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)+V(x)\Psi(x,t)=i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{1}$$

Finding the stationary state solutions via a separable ansatz $\Psi(x,t) = \phi(t)\psi(x)$, one can directly find the temporal solution

$$\phi(t)=e^{-\frac{iEt}{\hbar}} \tag{2}$$

where we have absorbed the integration constant (to be used as the normalization constant) into the solution of the time-independent Schrodinger equation (TISE) expressed as

$$\frac{-\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+V(x)\psi(x)=E\psi(x) \tag{3}$$

The solution to TISE depends on the potential of the quantum system. In this case, we are dealing with an infinite square well with potential

$$V=\begin{cases}0, & 0\le x\le a\\ \infty, & \text{otherwise}\end{cases} \tag{4}$$

This translates to the following boundary condition

$$\psi(0)=\psi(a)=0 \tag{5}$$

To find the general expression of the wavefunction $\Psi(x,t)$ as a linear combination of the stationary states, we will use the initial wavefunction $\Psi(x,0)$ to find the series coefficients. In this case, it is expressed as

$$\Psi(x,0)=\begin{cases}\sqrt{\frac{2}{a/2}}\sin(\frac{2\pi x}{a}), & 0\le x\le a/2\\ 0, & a/2\le x\le a\end{cases} \tag{6}$$

Inside the well using Eq. (3) and Eq. (4), TISE reduces to

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}=-\frac{2mE}{\hbar^2}\psi(x) \tag{7}$$

Observe that $\frac{2mE}{\hbar^2}\ge 0$. To see this more clearly, we can introduce a constant k such that

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}=-k^2\psi(x) \tag{8}$$

This is an equation of a simple harmonic motion with a general solution

$$\psi(x)=A\sin(kx)+B\cos(kx) \tag{9}$$

Boundary conditions from Eq. (5) gives us $B=0$ and $k=n\pi/a$, $n\in Z_+$ ($A=0$ will be a non-normalizeable solution). With these, the spatial solution is

$$\psi(x)=A\sin(kx) \tag{10}$$

Since k is discrete, E must be discrete. From the definition of k, possible values of E takes the following form with each state n

$$E_n=\frac{n^2\pi^2\hbar^2}{2ma^2},\qquad n\in Z_+ \tag{11}$$

Then,

$$k_n^2=\frac{2mE_n}{\hbar^2}=\frac{n^2\pi^2}{a^2} \tag{12}$$

Normalizing this yields using $\sin^2(x)=1/2(1-\cos(2x))$ to convert into elementary integrals,

$$A=\frac{1}{\sqrt{\int_0^a\sin^2(kx)}}=\sqrt{\frac{2}{a}} \tag{13}$$

Hence, we obtain the energy eigenstates (in position basis)

$$\psi_n(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \tag{14}$$

We proceed to find a general solution. Now that we have already found the energy eigenstates ψ_n, we can find propagator operator to generalize with any arbitrary initial wavefunction which might come in handy later. This might also be a good point to start switching to Dirac notation. We start by expressing the state vector $|\Psi(t)\rangle$ in the energy eigenbasis $|\psi_n\rangle$

$$|\Psi(t)\rangle=\sum_n|\psi_n\rangle\langle\psi_n|\Psi(t)\rangle \tag{15}$$

$$\equiv\sum_n a_n(t)|\psi_n\rangle \tag{16}$$

To find $a_n(t)$, we act $i\hbar\,\partial/\partial t-\hat{H}$ on both sides and noting that $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ and that the state vector satisfies TDSE.

$$\left(i\hbar\frac{\partial}{\partial t} - \hat{H}\right)|\Psi(t)\rangle = \left(i\hbar\frac{\partial}{\partial t} - \hat{H}\right)\sum_n a_n(t)\,|\psi_n\rangle \tag{17}$$

$$= \sum_n (i\hbar\dot{a_n}(t) - E_n a_n(t))\,|\psi_n\rangle \quad = 0 \tag{18}$$

which means

$$i\hbar\dot{a_n}(t) = E_n a_n(t) \tag{19}$$

Solving this ODE gives us

$$a_n(t) = a_n(0)e^{-iEt/\hbar} \tag{20}$$

We employ Fourier's trick in abstract form by taking the inner product of the expansion in Eq. (15) at $t = 0$

$$\langle\psi_m|\Psi(0)\rangle = \sum_n a_n(0)\,\langle\psi_m|\psi_n\rangle = a_m(0) \tag{21}$$

Hence,

$$a_n(t) = \langle\psi_m|\Psi(0)\rangle\, e^{-iEt/\hbar} \tag{22}$$

and the general expansion is

$$|\Psi(t)\rangle = \sum_n \langle\psi_n|\Psi(0)\rangle\, e^{-iEt/\hbar}\,|\psi_n\rangle \tag{23}$$

$$|\Psi(t)\rangle = \hat{U}(t)\,|\Psi(0)\rangle \tag{24}$$

where the propagator operator is

$$\hat{U}(t) = \sum_n |\psi_n\rangle\,\langle\psi_n|\, e^{-iEt/\hbar} \tag{25}$$

The probability of getting the energy eigenvalue E_n associated with the eigenbasis $|\psi_n\rangle$ is

$$(|c_n(t)|)^2 = (\langle\psi_n|\Psi(t)\rangle)^2 = (\langle\psi_n|\Psi(0)\rangle)^2 \tag{26}$$

where the exponential vanishes due to squaring. Now that we have built stuff up, it is time to go into the appropriate basis to solve the inner products. We aim to expand the general solution in terms of energy eigenbasis. In the process, we shall first evaluate the probability amplitude at Eq. (26) and plug it into the general expansion at Eq. (23). To do so, we go into the position basis where the inner product is

$$\int_{-\infty}^{\infty} \psi_n(x)^*\Psi(x,0)\mathrm{d}x \tag{27}$$

Using the given initial wavefunction at Eq. (6),

$$c_n = \int_0^{a/2} \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)\sqrt{\frac{2}{a/2}}\sin\left(\frac{2\pi x}{a}\right)\mathrm{d}x \tag{28}$$

$$= \frac{\sqrt{8}}{a}\int_0^{a/2} \sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)\mathrm{d}x \tag{29}$$

Observe that the integrand is only nonzero for odd values of n and for $n = 2$. Consider the following integral where n is odd

$$c_n = \frac{\sqrt{8}}{a}\int_0^{a/2} \sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)\mathrm{d}x \tag{30}$$

Using trigonometric relation $\sin(\alpha)\sin(\beta) = \cos(\alpha-\beta) - \cos(\alpha+\beta)$, the integral becomes

$$c_n = \frac{\sqrt{8}}{2a}\int_0^{a/2} \cos(\epsilon_-) - \cos(\epsilon_+)\mathrm{d}x \tag{31}$$

where $\epsilon_\pm(x) := (\pi x/a)(n \pm m)$ is defined for convenience. Evaluating the integral and setting m=2,

$$c_n = \frac{\sqrt{8}}{2\pi}\left(\left(\frac{\sin\left(\frac{\pi(2-n)}{2}\right)}{(2-n)}\right) - \left(\frac{\sin\left(\frac{\pi(2+n)}{2}\right)}{(2+n)}\right)\right) \tag{32}$$

which simplifies to

$$c_n = \frac{4\sqrt{2}\,\sin(n\pi/2)}{\pi(4-n^2)}; \qquad n = 1,3,5,... \tag{33}$$

Meanwhile, in the case of n=2,

$$c_n = \frac{\sqrt{8}}{a}\int_0^{a/2} \sin^2\left(\frac{2\pi x}{a}\right)\mathrm{d}x \tag{34}$$

which, again, can be evaluated using $\sin^2(x) = 1/2(1 - \cos(2x))$ giving us

$$c_n = \frac{1}{\sqrt{2}} \tag{35}$$

Collecting the coefficients, we have

$$c_n = \begin{cases} \frac{4\sqrt{2}\,\sin(n\pi/2)}{\pi(4-n^2)}, & n = 1,3,5,.. \\ \frac{1}{\sqrt{2}}, & n = 2 \end{cases} \tag{36}$$

and

$$|c_n|^2 = \begin{cases} \frac{32\sqrt{2}\,\sin(n\pi/2)}{\pi^2(4-n^2)^2}, & n = 1,3,5,.. \\ \frac{1}{2}, & n = 2 \end{cases} \tag{37}$$

Numerically evaluating the first three $|c_n|^2$ for odd n, 0.360253, 0.129691, 0.0073521, which rapidly converges to 1/2. Putting this together with n=2 case, we prove that $\sum_n |c_n|^2 = 1$ and the coefficients are valid. With these, the probability of energies are as follows. If the ground state n=1 corresponds to E_0 [1] with probability $|c_1|^2$ and so on,

$$P(E_1) = |c_2|^2 = 0.500000 \tag{38}$$

$$P(E_2) = |c_3|^2 = 0.129691 \tag{39}$$

Using Eqs. (36) and (23), the general solution is

[1] I am confused by this convention since ground states are usually denoted by n=1(?).

$$|\Psi(t)\rangle = \sum_{n=1,3,5...} \frac{4\sqrt{2}\,\sin(n\pi/2)}{\pi(4-n^2)} e^{-iE_nt/\hbar} |\psi_n\rangle + \frac{1}{\sqrt{2}} e^{-iE_2t/\hbar} |\psi_2\rangle \tag{40}$$

Expressing in position basis and simplifying a bit,

$$\Psi(x,t) = \sum_{n=1,3,5...} \frac{8\,\sin(n\pi/2)}{\pi\sqrt{a}(4-n^2)} \sin\left(\frac{n\pi x}{a}\right) e^{-iE_nt/\hbar} + \frac{1}{\sqrt{a}} \sin\left(\frac{2\pi x}{a}\right) e^{-iE_2t/\hbar} \tag{41}$$

III. Shifting an Infinite Well

We solve TISE again with form

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{42}$$

but now with boundary conditions

$$V = \begin{cases} 0, & -a/2 \le x \le a/2 \\ \infty, & \text{otherwise} \end{cases} \tag{43}$$

Mathematically, what changed here are the boundary conditions. Hence, we still have the same general solution

$$\psi(x) = A\text{sin}(kx) + B\text{cos}(kx) \tag{44}$$

Invoking the conditions that the wavefunctions must be zero at both $x = -a/2$ and $x = a/2$, this gives us two equations to solve

$$A\text{sin}\left(k\frac{a}{2}\right) + B\text{cos}\left(k\frac{a}{2}\right) = 0 \tag{45}$$

$$-A\text{sin}\left(k\frac{a}{2}\right) + B\text{cos}\left(k\frac{a}{2}\right) = 0 \tag{46}$$

where we have exploited symmetries of sines and cosines. Adding the second equation into the first equation, we get

$$2B\text{cos}\left(k\frac{a}{2}\right) = 0 \iff k = \frac{n\pi}{a} \tag{47}$$

where n must be odd. Subtracting the second equation from the first equation, we get

$$2A\text{sin}\left(k\frac{a}{2}\right) = 0 \iff k = \frac{n\pi}{a} \tag{48}$$

where n must be even. Hence, the general solution as a linear combination of sines and cosines is

$$\psi(x) = A\text{sin}\left(\frac{n_{even}\pi x}{a}\right) + B\text{sin}\left(\frac{n_{odd}\pi x}{a}\right) \tag{49}$$

However, since n can't be both odd and even at the same time, the solution must either be A or B. With this, we see that $A = B$ and we have already normalized this previously from Eq. (14). That is,

$$A = B = \sqrt{\frac{2}{a}} \tag{50}$$

Hence,

$$\boxed{\psi(x) = \sqrt{\frac{2}{a}}\left(\text{sin}\frac{n\pi x}{a} + B\text{sin}\frac{n\pi x}{a}\right)} \tag{51}$$

Where n can take any integer noting that sine factor cancels out when n is odd while cosine factor cancels out when n is even. Observe that we are still using the same frequency and wave number k. That is,

$$k = \frac{n\pi x}{a} \tag{52}$$

And since (12) still holds, the expression is similar to the original unshifted infinite well expressed as

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}, \qquad n \in Z_+ \tag{53}$$

Hence, the shifted infinite well would still have the same energies from before . Observe that making substitution of form $x \to x - a/2$ to Eq. (14) gives us

$$\psi_n(x-a/2) = \sqrt{\frac{2}{a}}\text{sin}\left(\frac{n\pi x}{a}(x-a/2)\right) = \sqrt{\frac{a}{2}}\text{sin}\left(\frac{n\pi x}{a} - \frac{n\pi}{2}\right) \tag{54}$$

Using the sine difference identity, we get

$$\sqrt{\frac{a}{2}}\left(\text{sin}\left(\frac{n\pi x}{a}\right)\text{cos}\left(\frac{n\pi}{2}\right) + \text{cos}\left(\frac{n\pi x}{a}\right)\text{sin}\left(\frac{n\pi}{2}\right)\right) \tag{55}$$

where we have absorbed the negative sign into the cosine function. Since the factors with parameter $n\pi/2$ will either be cancelled or simply be unity, we can simply express them as

$$\psi(x) = \sqrt{\frac{2}{a}}\left(\text{sin}\frac{n\pi x}{a} + B\text{sin}\frac{n\pi x}{a}\right) \tag{56}$$

where the sine factor cancels at odd n while cosine factor cancels at even n. This is precisely our result from Eq. fin thus proving that the shift of the potential well towards the left by $a/2$ is expressed by the substitution $x \to x - a/2$

IV. Expectation values as function of time

Consider the initial state vector $|\Psi(0)\rangle$ as linear superposition of the first two stationary states $|\psi_1(t)\rangle := |\psi_1\rangle\, e^{-iE_1t/\hbar}$ and $|\psi_2(t)\rangle := |\psi_2\rangle\, e^{-iE_2t/\hbar}$

$$|\Psi(0)\rangle = A(|\psi_1(t)\rangle + |\psi_2(t)\rangle) \tag{57}$$

First task is to normalize $\Psi(0)$,

$$\langle\Psi(0)|\Psi(0)\rangle = A^*A(\langle\psi_1| + \langle\psi_2|)(|\psi_1\rangle + |\psi_2\rangle) \tag{58}$$

$$= A^2(\langle\psi_1|\psi_1\rangle + \langle\psi_1|\psi_1\rangle + 2\,\langle\psi_1|\psi_2\rangle) \tag{59}$$

Since stationary states are pairwise orthonormal, we have $\langle\psi_m|\psi_n\rangle = \delta_{mn}$, which is a convenient property.

$$|\Psi(0)|^2 = A^2(\langle\psi_1|\psi_1\rangle + \langle\psi_2|\psi_2\rangle) = 2A^2 = 1 \tag{60}$$

Giving us the normalization constant

$$A = \frac{1}{\sqrt{2}} \tag{61}$$

We proceed to use the propagator operator at Eq. (25) of infinite well potential to immediately derive the general solution.

$$\begin{aligned} |\Psi(t)\rangle &= \hat{U}(t)\,|\Psi(0)\rangle &(62)\\ &= \frac{1}{\sqrt{2}}(\sum_n |\psi_n\rangle\,\langle\psi_n|\,e^{-iEt/\hbar})(|\psi_1\rangle + |\psi_2\rangle) &(63)\end{aligned}$$

We can, again, take advantage of the orthonormality of the eigenstates to find that

$$\begin{aligned} &\frac{1}{\sqrt{2}}\sum_n |\psi_n\rangle\,\langle\psi_n|\psi_1\rangle\,e^{-iE_nt/\hbar} + &(64)\\ &\frac{1}{\sqrt{2}}\sum_n |\psi_n\rangle\,\langle\psi_n|\psi_2\rangle\,e^{-iE_nt/\hbar} \\ &|\Psi(t)\rangle = \frac{1}{\sqrt{2}}(|\psi_1\rangle\,e^{-iE_1t/\hbar} + |\psi_2\rangle\,e^{-iE_2t/\hbar}) &(65)\end{aligned}$$

Using the allowable energies of the infinite well at Eq. (53) and the expressions of the energy eigenstate in position basis at Eq. (14), we express the general solution in position basis as

$$\Psi(x,t) = \tfrac{1}{\sqrt{a}}\left(\sin\left(\tfrac{\pi x}{a}\right)e^{-iE_1t/\hbar} + \sin\left(\tfrac{2\pi x}{a}\right)e^{-iE_2t/\hbar}\right) \tag{66}$$

where $E_1 = \pi^2\hbar^2/2ma^2$ and $E_2 = 4\pi^2\hbar^2/2ma^2$. We can get rid of the exponentials by defining $\omega := E_n/n\hbar = \pi^2\hbar/2ma^2$. Using Euler's formula, $e^{-i\omega t} = \cos(\omega t) + i\,\sin(\omega t)$,

$$\begin{aligned} \Psi(x,t) = &\tfrac{1}{\sqrt{a}}\left(\sin\left(\tfrac{\pi x}{a}\right)\cos(\omega t) + \sin\left(\tfrac{2\pi x}{a}\right)\cos(4\omega t)\right) &(67)\\ &+\tfrac{i}{\sqrt{a}}\left(\sin\left(\tfrac{\pi x}{a}\right)\sin(\omega t) + \sin\left(\tfrac{2\pi x}{a}\right)\sin(4\omega t)\right)\end{aligned}$$

Since $(a+ib)(a-ib) = a^2+b^2$, and the trigonometric identities $\sin^2(a)+\cos^2(a) = 1$, and $\cos(a)\cos(b)+\sin(a)\sin(b) = \cos(a-b)$ squaring Eq. (67) gives

$$\begin{aligned} |\Psi(x,t)|^2 = &\frac{1}{a}\left(\sin^2\left(\frac{\pi x}{a}\right) + \sin^2\left(\frac{2\pi x}{a}\right)\right) &(68)\\ &+\frac{2}{a}\left(\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)\cos(3\omega t)\right) &(69)\end{aligned}$$

Solving for $\langle x\rangle$,

$$\begin{aligned} \langle x\rangle &= \int_0^a x|\Psi(x,t)|^2\mathrm{d}x &(70)\\ &= \int_0^a \frac{x}{a}\left(\sin^2\left(\frac{\pi x}{a}\right) + \sin^2\left(\frac{2\pi x}{a}\right)\right)\mathrm{d}x \\ &+ \int_0^a \frac{2x}{a}\left(\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)\cos(3\omega t)\right)\mathrm{d}x \\ & &(71)\end{aligned}$$

Observe how in the identity expansion of $\sin^2(\epsilon x) = 1/2 - \cos(2\epsilon x)/2$, integration by parts will give us $1/4x^2 - 1/4\epsilon\,\sin(2\epsilon a) - 1/8\epsilon^2\cos(2\epsilon a)$. The trigonometric terms go to zero giving us an integral of $x^2/4$ for all ϵ. Hence,

$$\int_0^a \frac{x}{a}\left(\sin^2\left(\frac{\pi x}{a}\right) + \sin^2\left(\frac{2\pi x}{a}\right)\right)\mathrm{d}x = 2\frac{a^2}{4a} = \frac{a}{2} \tag{72}$$

For the next integral, a substitution $\sin(a)\sin(a) = 1/2(\cos(a-b) - \cos(a+b))$ will reduce it into an IBP'able integral

$$\frac{2\,\cos(3\omega t)}{a}\int_0^a x\cos(\frac{\pi x}{a}) - \cos(\frac{3\pi x}{a})\mathrm{d}x \tag{73}$$

Integrating $x\cos(\epsilon x)$ gives us $(x/\epsilon)\sin(\epsilon x)+(1/\epsilon^2)\cos(\epsilon x)$. For the first integral where $\epsilon = \pi/a$, the sine term vanishes leaving us with $(-2/\epsilon^2) = -2a^2/\pi^2$. For the second integral where $\epsilon = 3\pi/a$, the sine term also vanishes leaving us with $(-2/\epsilon^2) = -2a^2/9\pi^2$. Subtracting the latter from the former,

$$\begin{aligned} &\int_0^a \frac{2x}{a}\left(\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)\cos(3\omega t)\right)\mathrm{d}x &(74)\\ &= \frac{a}{2}\frac{32}{9\pi^2}\cos(3\omega t) &(75)\end{aligned}$$

and hence,

$$\langle x(t)\rangle = \frac{a}{2} - \frac{a}{2}\frac{32}{9\pi^2}\cos(3\omega t) \tag{76}$$

The second term serves as the oscillation term. Observe that it has an amplitude of

$$\text{amplitude} = \frac{a}{2}\frac{32}{9\pi^2} \tag{77}$$

while its angular frequency is

$$\text{angular frequency} = 3\omega = \frac{3\pi^2\hbar}{2ma^2} \tag{78}$$

To "kveekly" find the momentum expectation value, we can use Ehrenfest's theorem

$$\begin{aligned} \langle p\rangle &= m\frac{\mathrm{d}\,\langle x\rangle}{\mathrm{d}t} &(79)\\ &= m\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{a}{2} - \frac{a}{2}\frac{32}{9\pi^2}\cos(3\omega t)\right) \\ &= \frac{32ma}{6}\omega\,\sin(3\omega t) \\ &= \frac{8\hbar}{3a}\sin(3\omega t) &(80)\end{aligned}$$

where we have used the definition $\omega := \pi^2\hbar/2ma^2$. To find the energy expectation value, observe that the general solution at Eq. (66) has contributions from two eigenstates with energies E_1 and E_2. It might be unnecessary hassle to find $\langle H\rangle$ directly. Hence, it is important to observe that in Eq. (65), both eigenstates have equal contribution to the general solution. $|c_n|^2 = 1/2$ for both eigenstates. Hence,

$$\langle H \rangle = \frac{1}{2}(E_1 + E_2) = \frac{1}{2}\left(\frac{\pi^2\hbar^2}{2ma^2} + \frac{2\pi^2\hbar^2}{ma^2}\right) \tag{81}$$

$$= \frac{5\pi^2\hbar^2}{4ma^2} \tag{82}$$

Of course, it is the average of the two possible energies. If a classical particle has this energy inside the $V = 0$ infinite well,

$$\frac{5\pi^2\hbar^2}{4ma^2} = \frac{1}{2}mv^2 \tag{83}$$

It's velocity is then,

$$v = \frac{5\pi\hbar}{2ma} \tag{84}$$

Since $T = 2a/v$ by imagining the particle starting at $x = 0$ bouncing at $x = a$ then returning again at $x = 0$, $f = 1/T = v/2a$, and $\omega = 2\pi f$, we have $\omega = \pi v/a$. The classical angular frequency ω_c is then,

$$\omega_c = \frac{5\pi^2\hbar}{ma} \tag{85}$$

Which is higher than the quantum counterpart, ω_q, by $5/(3/2)$ or

$$\frac{\omega_c}{\omega_q} = \frac{10}{3} \tag{86}$$