PHYS 3803: Quantum Mechanics I, Spring 2021

Lecture 14, March 18, 2021 (Thursday)

- Reading: Harmonic Oscillator [Griffiths 2.3]
- Assignment: Problem Set 7 due March 24 (Wednesday).
  Submit your homework assignments to Canvas.

Topics for Today:
Schrödinger Equation [Chapter 2 in Griffiths]

3.6 Schrödinger Equation

(d) Finite Square Well [Griffiths 2.6]

3.7 Stationary State Solutions

Topics for Next Lecture:
Harmonic Oscillator [Griffiths 2.3]

3.8 Equation of continuity

4.1 Introduction

4.2 Energy Eigenstates of the Harmonic Oscillator

3.6 The Schrödinger Equation

In the x basis, the state vector is represented by a wave function

$$\Psi(x,t) = \langle x|\Psi(t)\rangle$$

and an operator is represented by matrix elements

$$\Omega_{xy} = \langle x|\Omega|y\rangle\,.$$

For example, the matrix elements of X, D, K, and P in the x basis are

$$\begin{aligned}
X_{xy} &= \langle x|X|y\rangle = \langle x|y|y\rangle = y\langle x|y\rangle = y\delta(x-y) \quad \text{and} \\
D_{xy} &= \langle x|D|y\rangle = \frac{d}{dx}\delta(x-y) \\
K_{xy} &= \langle x|K|y\rangle = \langle x|-iD|y\rangle = -i\frac{d}{dx}\delta(x-y) \quad \text{and} \\
P_{xy} &= \langle x|\hbar K|y\rangle = -i\hbar\langle x|D|y\rangle = -i\hbar\frac{d}{dx}\delta(x-y)\,.
\end{aligned}$$

In the Hilbert space, the Schrödinger equation is

$$i\hbar \frac{d|\Psi(t)\rangle}{dt} = H|\Psi(t)\rangle \,.$$

In the x basis, the matrix element of the Hamiltonian is

$$H_{xy} \equiv \langle x|H|y\rangle = \langle x|\frac{P^2}{2m} + V(X)|y\rangle = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(y)\right]\delta(x-y)$$

and the Schrödinger equation becomes

$$i\hbar \frac{d}{dt}\langle x|\Psi(t)\rangle = \langle x|H|\Psi(t)\rangle = \int \langle x|H|y\rangle\langle y|\Psi(t)\rangle dy = \int \langle x|H|y\rangle\, \Psi(y,t)\, dy$$

or

$$i\hbar \frac{\partial}{\partial t}\Psi(x,t) = \int \langle x|H|y\rangle \Psi(y,t)\, dy = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x,t) \,.$$

Introducing separation of variables $\Psi(x,t) = f(t)u(x)$, we obtain

$$\begin{aligned} i\hbar\left(\frac{df}{dt}\right)u(x) &= f(t)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]u(x) \\ i\hbar\frac{df/dt}{f} &= \frac{1}{u}\left[-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} + V(x)u(x)\right] = E\,. \end{aligned}$$

Since the left-hand side depends only on time and the right-hand side depends only on spatial coordinates, both sides must be equal to a constant which we call E. Thus

$$\begin{aligned} i\hbar\frac{df}{dt} = Ef\,, \quad \text{or} \quad \frac{df}{dt} + \frac{i}{\hbar}Ef &= 0\,, \quad \text{with} \quad f(t) = A_t e^{-(\frac{i}{\hbar})Et} \\ \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]u(x) &= Eu(x)\,. \end{aligned}$$

In the energy basis

$$\Psi(x,t) = u(x)f(t) = u(x)e^{-(\frac{i}{\hbar})Et} = \psi(x)e^{-(\frac{i}{\hbar})Et}$$

where we have absorbed the normalization constant A_t into $u(x)$.

If the Hamiltonian does not depend on time explicitly, the Schrödinger equation becomes an eigenvalue equation

$$H\psi_n(x) = E_n\psi_n(x)$$

where E_n are eigenvalues of the Hamiltonian operator H.

The general solution to the equation of motion becomes

$$\Psi(x,t) = \sum_{n=0}^{\infty} c_n\psi_n(x)e^{-(\frac{i}{\hbar})E_n t} = \sum_{n=0}^{\infty} c_n\Psi_n(x,t)\,.$$

The separable solutions

$$\Psi_n(x,t) = \psi_n(x)e^{-(\frac{i}{\hbar})E_n t}$$

are stationary states, such that probabilities and expectation values are independent of time.

(d) Finite square well potential

The time-independent Schrödinger equation in the x basis is

$$H\psi(x) = E\psi(x) \quad \text{i.e.} \quad \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x)\,.$$

Let us consider the potential for the bound state with $V_0 > E > 0$:

$$V(x) = \begin{cases} 0 & \text{for } x^2 < a^2, \text{ and} \\ V_0, & \text{for } x^2 \geq a^2. \end{cases}$$

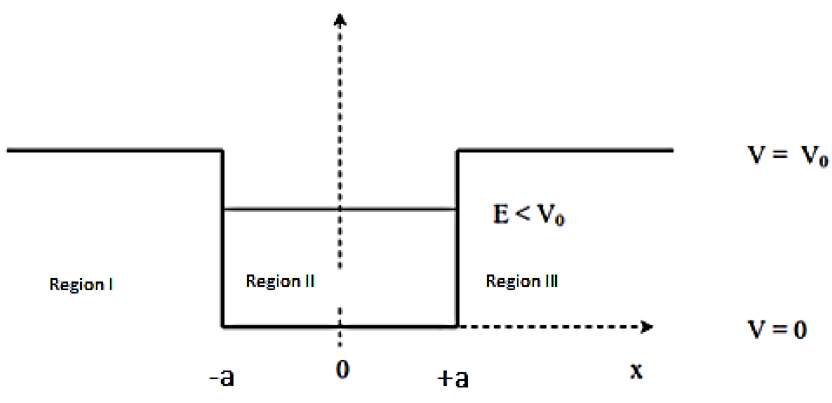

Figure 1: The finite square well potential.

Region (I): $x \leq -a$, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V_0\psi(x) = E\psi(x)$$

or in the standard form

$$\frac{d^2\psi}{dx^2} - \frac{2m}{\hbar^2}(V_0 - E)\psi(x) = 0\,, \quad \text{with} \quad V_0 > E > 0\,.$$

The characteristic equation is

$$\lambda^2 - \frac{2m}{\hbar^2}(V_0 - E) = 0 \quad \text{with roots} \quad \lambda_{1,2} = \mp\sqrt{\frac{2m}{\hbar^2}(V_0 - E)}\,.$$

Hence

$$\psi_1(x) = A_1 e^{-\lambda x} + B_1 e^{\lambda x} \quad \text{with} \quad \lambda = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$$

where A_1 and B_1 are constants. The physical solution requires $A_1 = 0$. Thus for $x \leq -a$,

$$\psi_1(x) = B_1 e^{\lambda x}\,.$$

Region (III): $x \geq a$, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V_0\psi(x) = E\psi(x)$$

or

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}(V_0 - E)\psi(x) = \lambda^2\psi\,, \quad V_0 > E > 0\,.$$

Hence

$$\begin{aligned}\psi_3(x) &= A_3 e^{-\lambda x} + B_3 e^{\lambda x} \\ \lambda &= \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}\end{aligned}$$

where A_3 and B_3 are constants. The physical solution requires $B_3 = 0$. Thus for $x \geq a$,

$$\psi_3(x) = A_3 e^{-\lambda x}\,.$$

Region (II): $-a < x < a$, the Schrödinger equation is

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

or

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \text{with} \quad k^2 = \frac{2mE}{\hbar^2}\,.$$

Hence

$$\psi_2(x) = Ae^{-ikx} + Be^{ikx} = C\sin(kx) + D\cos(kx)$$

where A, B, C and D are constants.

In this system there is no divergence in the potential energy, solutions and their derivatives must be continuous at the boundaries.

We have found the wave functions

$$\begin{aligned}
\psi_1(x) &= B_1 e^{\lambda x}\,, \quad x \leq -a \\
\psi_2(x) &= C\sin(kx) + D\cos(kx)\,, \quad -a < x < a \\
\psi_3(x) &= A_3 e^{-\lambda x}\,, \quad x \geq a\,.
\end{aligned}$$

Let us apply boundary conditions: (a) Dirichlet condition (the values of the solution), and (b) Neumann condition (the values of the derivative).

(i) The matching solutions at $x = -a$ leads to

$$\begin{aligned}
\psi_1(-a) &= \psi_2(-a) \\
B_1 e^{-\lambda a} &= -C\sin(ka) + D\cos(ka) \qquad \text{(I)}\,.
\end{aligned}$$

(ii) The matching solutions at $x = +a$ leads to

$$\begin{aligned}
\psi_3(a) &= \psi_2(a) \\
A_3 e^{-\lambda a} &= C\sin(ka) + D\cos(ka) \qquad \text{(II)}\,.
\end{aligned}$$

Furthermore, matching the derivatives at the boundaries, we have

(iii) $x = -a$,

$$
\begin{aligned}
\frac{d\psi_1(x)}{dx}\Big|_{x=-a} &= \frac{d\psi_2}{dx}\Big|_{x=-a} \\
\lambda B_1 e^{-\lambda a} &= k\left[C\cos(ka) + D\sin(ka)\right] \qquad \text{(III)}
\end{aligned}
$$

(iv) $x = +a$,

$$
\begin{aligned}
\frac{d\psi_3(x)}{dx}\Big|_{x=a} &= \frac{d\psi_2}{dx}\Big|_{x=a} \\
-\lambda A_3 e^{-\lambda a} &= k\left[C\cos(ka) - D\sin(ka)\right] \qquad \text{(IV)}
\end{aligned}
$$

Adding Eqs. (I) and (II), we have

$$2D\cos(ka) = (B_1 + A_3)e^{-\lambda a} = (A_3 + B_1)e^{-\lambda a}\,.$$

Also subtracting them, we obtain

$$2C\sin(ka) = (A_3 - B_1)e^{-\lambda a}\,.$$

Similarly, adding and subtracting Eqs. (III) and (IV), we have

$$\begin{aligned} 2kC\cos(ka) &= -\lambda(A_3 - B_1)e^{-\lambda a} \\ 2kD\sin(ka) &= \lambda(B_1 + A_3)e^{-\lambda a} = \lambda(A_3 + B_1)e^{-\lambda a}\,. \end{aligned}$$

Let $A_3 - B_1 = F$ and $A_3 + B_1 = G$, then we have two sets of equations

$$\begin{aligned} 2C\sin(ka) - Fe^{-\lambda a} &= 0 \\ 2kC\cos(ka) + \lambda Fe^{-\lambda a} &= 0 \end{aligned}$$

and

$$\begin{aligned} 2D\cos(ka) - Ge^{-\lambda a} &= 0 \\ 2kD\sin(ka) - \lambda Ge^{-\lambda a} &= 0\,. \end{aligned}$$

The first set has a nontrivial solution if

$$\det\begin{pmatrix} 2\sin(ka) & -e^{-\lambda a} \\ 2k\cos(ka) & \lambda e^{-\lambda a} \end{pmatrix} = 0\,.$$

That leads to

$$2\lambda \sin(ka)e^{-\lambda a} + 2k\cos(ka)e^{-\lambda a} = 0$$

or

$$k\cot(ka) = -\lambda \qquad (a)$$

The second set has a nontrivial solution if

$$\det\begin{pmatrix} 2\cos(ka) & -e^{-\lambda a} \\ 2k\sin(ka) & -\lambda e^{-\lambda a} \end{pmatrix} = 0$$

or

$$-2\lambda\cos(ka)e^{-\lambda a} + 2k\sin(ka)e^{-\lambda a} = 0$$

or

$$k\tan(ka) = \lambda \qquad (b)$$

However, it is impossible to satisfy both (a) and (b) simultaneously. Therefore, we have two classes of solutions:

(a) Odd solution with $D = 0 = G$ and $k \cot(ka) = -\lambda$.

(b) Even solution with $C = 0 = F$ and $k \tan(ka) = \lambda$.

N.B. $F = A_3 - B_1$ and $G = A_3 + B_1$.

In either of the relations (a) and (b), energy is the only unknown quantity. Thus we see that motion is allowed only if the energy satisfies certain conditions. Let us analyze the two cases in detail.

Case (I) Let $\xi = ka$ and $\eta = \lambda a$, then

$$\begin{aligned} \eta^2 + \xi^2 &= a^2(\lambda^2 + k^2) \\ &= a^2\left(\frac{2m}{\hbar^2}(V_0 - E) + \frac{2m}{\hbar^2}E\right) = \frac{2m}{\hbar^2}a^2 V_0 \end{aligned}$$

This is the equation of a circle. Furthermore, relation (a) can be written as

$$\begin{aligned} ka\cot(ka) &= -\lambda a \\ \xi\cot\xi &= -\eta \end{aligned}$$

Plotting the two functions on the 1st quadrant only, we have

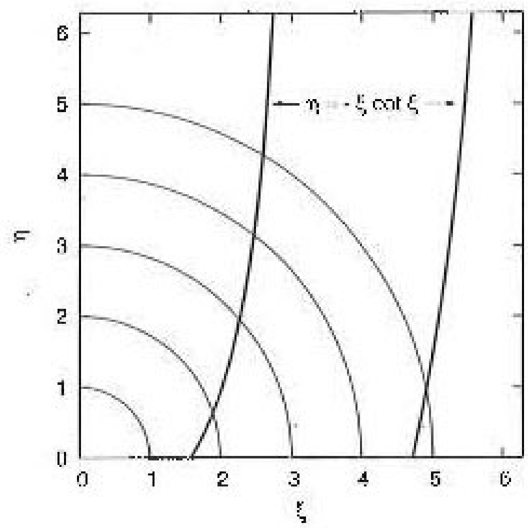

Figure 2: Odd function solutions $\xi \to \eta$.

It is clear that for

$$0 \leq \frac{2m}{\hbar^2}(a^2 V_0) < (\frac{\pi}{2})^2$$

there is no solution. For

$$(\frac{\pi}{2})^2 \leq \frac{2m}{\hbar^2}(a^2 V_0) \leq (\frac{3\pi}{2})^2$$

there is one solution and so on.

Case (II) Let $\xi = ka$ and $\eta = \lambda a$, then

$$\eta^2 + \xi^2 = \frac{2m}{\hbar^2}(a^2 V_0) \quad ka \tan(ka) = \lambda a\,, \quad \xi \tan \xi = \eta\,.$$

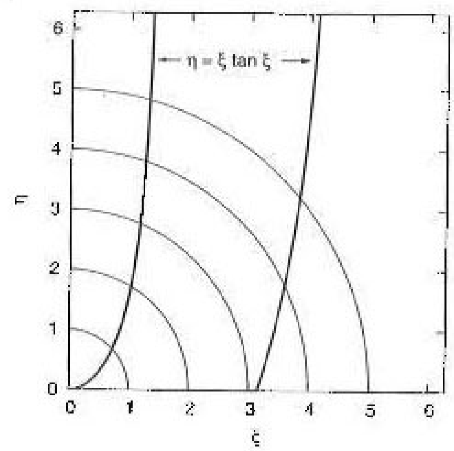

Figure 3: Even function solutions $\xi \to \eta$.

Plotting these functions on the 1st quadrant only, we see that they intersect once if

$$0 \leq \frac{2m}{\hbar^2}(a^2 V_0) < \pi^2\,.$$

Parity

In the cases of the infinite well and the finite square well, we have classified solutions as even and odd. The Schrödinger equation is

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

Let us assume that the potential is symmetric about $x = 0$, i.e., $V(x) = V(-x)$. Then changing $x \to -x$, the Schrödinger equation becomes

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(-x) = E\psi(-x)\,.$$

- This shows that if $\psi(x)$ is an eigenstate, so is $\psi(-x)$.
- Therefore, they must be related by a multiplicative constant, i.e.,

$$\psi(-x) = \epsilon\psi(x)\,.$$

Normalization would give

$$\epsilon^2 = 1$$
$$\epsilon = \pm 1\,.$$

- The constant ϵ can be chosen to be real by adjusting the phase of $\psi(x)$.
- This shows that all eigenfunctions of a symmetric potential are either even or odd under change of sign of x and are said to have even or odd parity.

3.7 Stationary State Solutions

Let us consider the case where the Hamiltonian is independent of time. The Schrödinger equation is

$$i\hbar \frac{d|\Psi(t)\rangle}{dt} = H|\Psi(t)\rangle \,.$$

This is a first order differential equation in time.

We can think of

$$|\Psi(t)\rangle = U(t,t_0)|\Psi(t_0)\rangle \quad \text{or} \quad |\Psi(t)\rangle = U(t)|\Psi(0)\rangle \,.$$

To find $U(t)$, let us consider the eigenbasis of the Hamiltonian H:

$$H|E_n\rangle = E_n|E_n\rangle \quad \text{or} \quad H|E\rangle = E|E\rangle$$

where $|E_n\rangle$ form a complete set of orthonormal basis

$$\langle E_m|E_n\rangle = \delta_{mn} \quad \text{and} \quad \sum_n |E_n\rangle\langle E_n| = \mathrm{I} \,.$$

In terms of this basis we can write

$$\begin{aligned}|\Psi(t)\rangle &= \sum_n |E_n\rangle\langle E_n|\Psi(t)\rangle \quad \text{completeness relation} \\ &= \sum a_E(t)|E_n\rangle \\ a_E(t) &= \langle E|\Psi(t)\rangle = \langle E_n|\Psi(t)\rangle\,.\end{aligned}$$

- If the eigenvalues of H are discrete, then we use a summation.
- However, if the eigenvalues E take continuous values then we must replace the sum by an integral.

Thus

$$\begin{aligned} i\hbar\frac{d}{dt}|\Psi(t)\rangle &= H|\Psi(t)\rangle \quad \text{leads to} \\ i\hbar\sum \dot{a}_E|E\rangle &= \sum E\, a_E(t)|E\rangle \quad \text{or} \quad \sum_n \left[i\hbar\dot{a}_E - E\, a_E(t)\right]|E_n\rangle = 0\,.\end{aligned}$$

What is the standard form of the differential equation for $a_E(t)$?

For every $|E\rangle = |E_n\rangle$, we have

$$i\hbar \dot{a}_E(t) = E a_E(t)$$

The standard form of this first order linear differential equation is

$$\frac{da_E}{dt} + \frac{i}{\hbar} E a_E = 0$$

with the characteristic equation

$$\lambda + \frac{i}{\hbar} E = 0 \quad \text{or} \quad \lambda = -\frac{i}{\hbar} E\,.$$

The general solution becomes

$$a_E(t) = A e^{\lambda t} = a_E(0) e^{-(\frac{i}{\hbar})Et}\,.$$

And the state vector can be expanded as

$$|\Psi(t)\rangle \;\; = \;\; \sum a_E(t)|E\rangle = \sum a_E(0) e^{-(\frac{i}{\hbar})Et}|E\rangle.$$

On the other hand,

$$\begin{aligned}
|\Psi(t)\rangle &= \sum a_E(0) e^{-(\frac{i}{\hbar})Et}|E\rangle \\
&= \sum e^{-(\frac{i}{\hbar})Et}\langle E|\Psi(0)\rangle|E\rangle \\
&= \sum e^{-(\frac{i}{\hbar})Et}|E\rangle\langle E|\Psi(0)\rangle \\
&= (\sum e^{-(\frac{i}{\hbar})Et}|E\rangle\langle E|)|\Psi(0)\rangle \\
&= U(t)|\Psi(0)\rangle
\end{aligned}$$

where $U(t) = \sum e^{-(\frac{i}{\hbar})Et}|E\rangle\langle E|$.

This determines the operator $U(t)$ which leads to time evolution of physical states. If the eigenvalues of H are degenerate, then we must introduce a label α for the degeneracy and then

$$U(t) = \sum_{\alpha}\sum_{E} e^{-(\frac{i}{\hbar})Et}|E,\alpha\rangle\langle E,\alpha|$$

and $U(t, t_0)$ is the time evolution operator for the state vector.

Clearly the solutions

$$|E(t)\rangle = e^{-(\frac{i}{\hbar})Et}|E\rangle$$

satisfy Schrödinger equation.

- Such states are called stationary states.
- Because in such states the probability for measurement of any operator Ω is time independent.

Thus

$$\begin{aligned} P(\omega, t) &= |\langle\omega|E(t)\rangle|^2 \\ &= |\langle\omega|E\rangle e^{-(\frac{i}{\hbar})Et}|^2 \\ &= |\langle\omega|E\rangle|^2 \\ &= P(\omega, 0)\,. \end{aligned}$$

Now clearly the time evolution operator can also be written as

$$
\begin{aligned}
U(t) &= \sum |E\rangle\langle E| e^{-(\frac{i}{\hbar})Et} = \sum_n |E_n\rangle\langle E_n| e^{-(\frac{i}{\hbar})E_n t} \\
&= \sum |E_n\rangle\langle E_n| e^{-(\frac{i}{\hbar})Ht} \quad \text{(eigenvalue equation)} \\
&= \left(\sum_n |E_n\rangle\langle E_n|\right) e^{-(\frac{i}{\hbar})Ht} \quad \text{(completeness relation)} \\
&= e^{-(\frac{i}{\hbar})Ht}.
\end{aligned}
$$

Although the convergence of this series is hard to prove, it is clear that this expression is formally true even if the eigenvalues of H are degenerate. Since H is Hermitian, it is clear that $U(t)$ is unitary. Thus

$$U^\dagger(t)U(t) = I \quad \text{and} \quad \langle\Psi(t)|\Psi(t)\rangle = \langle\Psi(0)|U^\dagger U|\Psi(0)\rangle = \langle\Psi(0)|\Psi(0)\rangle .$$

If the Hamiltonian depends on time, i.e.,

$$H = H(t)$$

then the evolution operator takes the following form

$$U(t) = e^{-\left(\frac{i}{\hbar}\right)\int_0^t H(\tau)d\tau}.$$

In this case, the operator U depends on the initial and the final time. Thus

$$U = U(t_2, t_1)$$

so that

$$U(t_2, t_1)|\Psi(t_1)\rangle = |\Psi(t_2)\rangle$$

Furthermore, they satisfy the following relations

$$\begin{aligned} U(t_3, t_2)U(t_2, t_1) &= U(t_3, t_1) \\ U^\dagger(t_2, t_1) &= U^{-1}(t_2, t_1) = U(t_1, t_2). \end{aligned}$$