Lecture 8

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1 Wave mechanics

Although the more abstract approach we used for the harmonic oscillator has many advantages, it is not generalizable for more general potentials where there is not simple algebraic structure that allows us to solve the problem without specifying a basis. In particular, for the problem of a particle subject to a general potential $\hat{V}$ which is diagonal in position space and depends only on position $\langle x'|\hat{V}|x\rangle = \delta(x - x')V(x)$, it is convenient to work explicitly in the position basis. Starting from the general Schrödinger equation for state kets, we can write

$$i\hbar\langle x|\frac{d}{dt}|\psi, t\rangle = \langle x|\frac{\hat{p}^2}{2m} + \hat{V}|\psi, t\rangle \quad (1)$$

Recall that the position basis $|x\rangle$ is defined via $\hat{x}|x\rangle = x|x\rangle$. Since operators are time-independent in the Schrödinger picture, the basis kets $|x\rangle$ are also time-independent. Thus, $\langle x|\frac{d}{dt}|\psi, t\rangle = \frac{d}{dt}\langle x|\psi, t\rangle = \frac{d}{dt}\psi(x, t)$. We can also simplify the action of $\hat{p}$ and $\hat{V}$ using $\langle x|\hat{p} = i\hbar\frac{d}{dx}\langle x|$ and $\langle x|\hat{V} = V(x)\langle x|$ leading to the celebrated time-dependent Schrödinger wave equation

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

We note that in many approaches introducing quantum mechanics, the Schrödinger wave equation is introduced as the fundamental object. However, in our approach it appears as a special case for the more general basis-independent Schrödinger equation for the time evolution operator.

For a stationary state with $\psi(x, t) = \psi(x)e^{-\frac{i}{\hbar}Et}$, we get the time-independent Schrödinger wave equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x) \quad (3)$$

In most cases, the potential $V(x)$ is taken to grow at infinity, e.g. for the harmonic oscillator $V(x) \sim x^2$. This serves to confine the particle in a finite region. For $E < \lim_{x\to\pm\infty} V(x)$, we have the condition $\lim_{x\to\infty}\psi(x) = 0$. This boundary condition leads to the quantization of energy eigenvalues E similar to the case of a vibrating string. In the following, we will discuss cases where this assumption does not hold leading to a continuous rather than discrete spectrum.

2 Solutions to the Schrödinger wave equtions

2.1 Free particle in 3D

Consider the case of a free particle in 3D where $V(\boldsymbol{x}) = 0$. We can solve the time-independent Schrödinger equation in two ways. First, we can use the separation of variables ansatz $\psi(x, y, z) = \psi_x(x)\psi_y(y)\psi_z(z)$ and introduce the variables $k_{x,y,z}$ such that $E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$ (notice that at this point, we do not assume

$k_{x,y,z}$ are real). Then, we find that we can solve the Schrödinger equation using separation of variables by dividing both sides by $\psi(x, y, z)$

$$\left[\frac{1}{\psi_x(x)}\frac{d^2\psi_x(x)}{dx^2} + k_x^2\right] + \left[\frac{1}{\psi_y(y)}\frac{d^2\psi_y(y)}{dy^2} + k_y^2\right] + \left[\frac{1}{\psi_z(z)}\frac{d^2\psi_z(z)}{dz^2} + k_z^2\right] = 0 \tag{4}$$

This leads to the solution $\psi(x, y, z) = Ce^{i(k_x x + k_y y + k_z z)}$ where $k_{x,y,z}$ has to be real otherwise, ψ will blow up in some direction at ∞. We notice that there are at least six degenerate solutions corresponding to $\pm k_x$, $\pm k_y$ and $\pm k_z$. This can be incorporated by assuming $k_{x,y,z}$ can take positive or negative real values. Note that, we could have found the eigenstates by just noting that the Hamiltonian only depends on $\hat{\boldsymbol{p}} = \hbar\hat{\boldsymbol{k}}$, thus its eigenstates are the momentum or wavevector eigenstates $|\boldsymbol{k}\rangle$ introduced in Lecture 4. We have seen that $|\boldsymbol{k}\rangle$ are related to the $|\boldsymbol{x}\rangle$ by Fourier transform

$$|\boldsymbol{k}\rangle = C\int \frac{d^2\boldsymbol{x}}{(2\pi)^2} e^{i\boldsymbol{k}\cdot\boldsymbol{x}}|\boldsymbol{x}\rangle \tag{5}$$

which implies

$$\psi_{\boldsymbol{k}}(\boldsymbol{x}) = C\langle\boldsymbol{x}|\boldsymbol{k}\rangle = Ce^{i\boldsymbol{k}\cdot\boldsymbol{x}} \tag{6}$$

To normalize the wavefunctions, we need to put the system in a box of dimensions $L_x \times L_y \times L_z$ and impose periodic boundary conditions $\psi(x_i + L) = \psi(x_i)$. This leads to the quantization of $k_{x,y,z}$ via

$$k_i = \frac{2\pi n_i}{L_i}, \tag{7}$$

The normalization can then be computed as $C = \frac{1}{\sqrt{L_x L_y L_z}}$. The energy eigenvalues are

$$E = \frac{2\pi^2\hbar^2}{m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right] \tag{8}$$

Notice that unlike the case of the Harmonic oscillator, the eigenfunctions $\psi_{\boldsymbol{k}}(\boldsymbol{x})$ do not decay at infinity in the limit $L_i \to \infty$. In addition, the spectrum becomes contineous in this limit such that any energy window ΔE around a positive energy E contains infinitely many states. It is useful to define a continuous function that characterizing how dense energy levels are at different energies. We consider an energy E and ask how many energy eigenvalues exists in an energy window $(E - \Delta E/2, E + \Delta E/2)$, which we denote by $N_{\Delta E}(E)$. Visually, the constant energy surface describes a sphere in 3D and $N_{\Delta E}(E)$ counts the number of energy eigenvalues on a shell of thickness ΔE and radius E. Clearly, this number is proportional to ΔE in the limit $\Delta E \to 0$. It is also proportional to the total volume (since larger $L_{x,y,z}$ yields smaller grid size). Thus, we can define a function that is generally continuous and finite through the limit

$$D(E) = \lim_{\Delta E\to 0}\lim_{L_x, L_y, L_z\to\infty} \frac{N_{\Delta E}(E)}{L_x L_y L_z \Delta E} \tag{9}$$

The function $D(E)$ is called the density of states. It plays an important role in the theory of solids since it determines how many states are available to scatter to or tunnel into at a given energy.

2.2 Harmonic Oscillator

Let us now revisit the harmonic oscillator from the point of view of wave mechanics. In the context of a particle in a potential $V(x)$, the harmonic oscillator plays a fundamental role since the expansion of the potential around any local minimum has the form $V(x) = V_0 + \frac{1}{2}V''(x_0)(x - x_0)^2$. Thus, the harmonic oscillator forms the basis of approximating the solution to any potential close to its minima. The time-independent Schrödinger equation for the harmonic oscillator has the form

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2x^2\right]\psi(x)=E\psi(x) \tag{10}$$

First, we notice that for every solution of this equation $\psi(x)$, $\psi(-x)$ is also a solution. This arises from the inversion or parity symmetry of the potential $V(x)=V(-x)$. Note that this does **not** imply the spectrum is doubly degenerate since $\psi(-x)$ may be proportional to $\psi(x)$. If that is the case, then we have $\psi(-x)=\lambda\psi(x)$ which implies $\psi(x)=\lambda\psi(-x)=\lambda^2\psi(x)$ yielding $\lambda=\pm1$. In fact, from the algebraic treatment, we saw that the eigenstates of the harmonic oscillator were labelled by an integer $|n\rangle$ with eigenvalues $\hbar\omega(n+1/2)$ which means that the spectrum is non-degenerate. We will later see that this is a general property of the discrete spectrum of the Schrödinger equation in one dimension.

Whether the eigenfunctions are degenerate or not, the fact that $\psi(x)$ and $\psi(-x)$ are eigenfunctions of the same energy, means we can form the linear combinations

$$\psi_\pm(x)=\frac{1}{2}(\psi(x)\pm\psi(-x)) \tag{11}$$

which satisfy $\psi_\pm(-x)=\pm\psi(x)$. This means we can solve the Schrödinger equation once for even parity states $\psi_+(-x)=\psi_+(x)$ and once for odd parity states $\psi_-(-x)=-\psi_-(x)$. This usually simplifies the solution.

Second, we can again define $l=\sqrt{\frac{\hbar}{m\omega}}$ and introduce the dimensionless quantities

$$r=\frac{x}{l},\qquad \epsilon=\frac{2E}{\hbar\omega} \tag{12}$$

Eq. 10 then simplifies to

$$\psi''(r)+[\epsilon-r^2]\psi(r)=0 \tag{13}$$

In the limit $r\to\pm\infty$ for fixed ϵ, we can ignore the term $\epsilon\psi(r)$ and find $\psi(r)\sim r^ne^{-\frac{1}{2}r^2}$, where the $\sim$ sign here indicates that we are keeping only the leading power of r in the pre-exponent. This motivates the ansatz

$$\psi(r)=f(r)e^{-\frac{1}{2}r^2} \tag{14}$$

Substituting in (13), we get

$$f''(r)-2rf'+\lambda f=0,\qquad \lambda=\epsilon-1 \tag{15}$$

To solve this equation, we write a power series in r. We can separately consider solutions of even or odd parity. For even parity, we have

$$f_+(r)=\sum_n f_nr^{2n} \tag{16}$$

Substituting in (15) and matching the coefficients for each power of r, we get

$$f_{n+1}=\frac{4n-\lambda}{(2n+1)(2n+2)}f_n \tag{17}$$

If the series does not terminate, we see that $f_+(r)$ behaves as e^{r^2} for large r since $\frac{f_{n+1}}{f_n}=\frac{1}{n}$. This would lead to a non-normalizable state. Thus, we conclude that the series has to terminate which is only possible if $\lambda=4n$ for some n. This leads to the energy

$$\epsilon=4n+1=2(2n)+1,\quad\Longrightarrow\quad E=\hbar\omega(2n+1/2) \tag{18}$$

A similar analysis for the odd parity gives $\lambda=4n+2$ leading to the energies

$$\epsilon=4n+3,\quad\Longrightarrow\quad E=\hbar\omega(2n+1+1/2) \tag{19}$$

These are the same eigenvalues we obtained from the algebraic solution with even n corresponding to even parity states and odd n corresponding to odd parity states. This is something we could have guessed from the form $|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle$ by noticing that $|0\rangle$ was a simple Gaussian and thus have even parity. $\langle x|0\rangle = \langle -x|0\rangle$ and also noting that the action of the creation operator $a^\dagger$ flips parity since it is odd in both $\hat{x}$ and $\hat{p}$. We can combine both results by writing $\lambda = 2n$ for some integer n.

We can construct the wavefunctions explicitly from the series solution, but there is a more clever way. Let us denote the unnormalized eigenfunction corresponding to the eigenvalue $\lambda = 2n$ by $H_n(r)$ and consider the series

$$g(r,t) = \sum_{n=0}^{\infty} \frac{t^n}{n!} H_n(r) \tag{20}$$

Such function is called the generating function for the series $H_n(r)$. First, we can choose the normalization of H_n such that $H_{2n}(0) = (-1)^n \frac{(2n)!}{n!}$ which gives $g(0,t) = e^{-t^2}$. We now notice that

$$\left[\frac{d^2}{dr^2} - 2r\frac{d}{dr}\right] g(r,t) = -2\sum_{n=0}^{\infty} n\frac{t^n}{n!} H_n(r) = -2t\frac{d}{dt} g(r,t) \tag{21}$$

It is easy to see that this equation with the boundary condition $g(0,t) = e^{-t^2}$ is solved by choosing $g(r,t) = e^{-t^2+2rt}$. The functions $H_n(r)$ which are called the Hermite polynomials can be extracted from $g(r,t)$ via

$$H_n(r) = \frac{d^n}{dt^n} g(r,t)|_{t=0} = \frac{d^n}{dt^n} e^{r^2-(t-r)^2}|_{t=0} = (-1)^n e^{r^2} \frac{d^n}{dr^n} e^{-r^2} \tag{22}$$

2.3 Properties of bound states in one dimension

The bound states we found for the harmonic oscillator seemed to have several interesting features that we can summarize as follows:

(1) Eigenstates has either even or odd parity. We have seen that this follows from the parity symmetry of the potential $V(-x) = V(x)$.

(2) Eigenstates are all non-degenerate.

(3) Eigenfunctions are real.

(4) Ground state has no zeros and the n-th excited state is proportional to an n-th order polynomial and thus have n zeros.

Properties (2)-(4) turn out to be general features of bound states in one dimension as we will show now.

For (2), we will show that bound states are non-degenerate in one dimension i.e. if two eigenfunctions ϕ and ψ correspond to the same eigenvalue E, then they are proportional $\phi = \lambda\psi$ which means that they describe the same state. To see this, let us consider the following quantity

$$W(x) = \phi(x)\psi'(x) - \phi'(x)\psi(x) \tag{23}$$

This quantity is called the Wronskian and it plays an important role in the theory of second order differential equations. Assuming ϕ and ψ are eigenfunctions with the same eigenvalue, we find

$$W'(x) = \phi(x)\psi''(x) - \phi''(x)\psi(x) = -\frac{2m}{\hbar^2}[(E-V)\phi(x)\psi(x) - (E-V)\psi(x)\phi(x)] = 0 \tag{24}$$

This means that the Wronksian is a constant. Since ϕ and ψ describe bound states, they vanish at infinity, which implies W also vanishes at infinity, but since it is a constant, it has to be zero everywhere. Thus,

$$\frac{\phi'(x)}{\phi(x)} = \frac{\psi'(x)}{\psi(x)}, \implies \frac{d}{dx}\ln\phi(x) = \frac{d}{dx}\ln\psi(x) \implies \ln\phi(x) = \ln\psi(x) + C \implies \phi(x) = \lambda\psi(x) \tag{25}$$

which means that ϕ and ψ describe the same state. Notice that our proof relies crucially on the vanishing of the states at infinity. For extended plane wave states, this does not hold as we have seen for the free particle which has two degenerate eigenstates $e^{\pm ikx}$.

(3) follows by combining (2) with the observation that whenever $\psi(x)$ is an energy eigenstate $\psi^*(x)$ is also an eigenstate. The above argument then implies that $\psi^*(x) = e^{i\chi}\psi(x)$ for some real phase χ. However, since the phase of ψ is arbitrary, we can define $\tilde{\psi} = e^{i\chi/2}\psi$ such that $\tilde{\psi}^* = \tilde{\psi}$.

Proving (4) is beyond the scope of this course. We note one simple statement though. All zeros of the eigenstates of the Schrödinger equation has to be single zeros. To see this, note that a wavefunction with a double zero at point x_0 will have $\psi(x_0) = \psi'(x_0) = 0$, but since the Schrödinger equation is a second order differential equation, this immediatly implies $\psi''(x_0) = \psi'''(x_0) = \cdots = 0$ which means that $\psi(x) = 0$ for all x.