QUANTUM MECHANICS
Lecture 5
Stationary states

Enrico Iacopini

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D. J. Griffiths: paragraph 2.1

Stationary states

1. It is time, now, to see how to **solve the Schrődinger equation**

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

2. We will proceed under the hypothesis that the potential energy $V=V(x)$ is **time independent.**

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Stationary states

1. The Schrödinger equation is a linear differential equation, which means that if $\mathbf{\Psi}_a$ and $\mathbf{\Psi}_b$ are solutions, then also
$\mathbf{\Psi} = \alpha\,\mathbf{\Psi}_a + \beta\,\mathbf{\Psi}_b$
is a solution, for any value of the complex numbers α and β.

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Stationary states

1. However, which are the "**simple**" solutions that we have in mind ?
2. Let us look for solutions in which the spatial and time dependence are factorized

$$\mathbf{\Psi}(x,t) = \psi(x)\cdot\phi(t)$$

3. From the Schrödinger equation, we obtain

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

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1. Now, if we divide both sides of the equation by $\mathbf{\Psi}(x,t) = \psi(x)\cdot\phi(t)$, we get

$$\frac{1}{\phi(t)}\left[i\hbar\frac{d\phi(t)}{dt}\right] = \frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right]$$

2. But the left hand side of the equation depends only on the time t, whereas the right hand side depends only on the position x.
3. The only possibility to satisfy the equation is that **both sides are in fact constant.** Let us call E this constant.
4. We will see in a moment that E must also to be a **real quantity**.

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Stationary states

1. The original Schrödinger linear partial differential equation then factorizes in two ordinary linear differential equations

$$i\hbar\frac{d\phi(t)}{\partial t} = \mathbf{E}\ \phi(t) \qquad (1)$$

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

2. The solution of equation (1) is quite straightforward:

$$\phi(t) = A\, e^{-iEt/\hbar} \quad \rightarrow \quad \phi(t) = e^{-iEt/\hbar}$$

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Equation (2)

$$\widehat{H}\,\psi(x) \equiv -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\;\psi(x)$$

is called the **time-independent Schrödinger equation** and, to solve it, we need to know the esplicit form of the potential energy $V(x)$.

Stationary states

In conclusion, the "*simple*" solutions of the Schrödinger equation that we were looking for, have the following general structure

$$\mathbf{\Psi}(x,t) = e^{-iEt/\hbar}\ \psi(x)$$

where ψ is a solution of the time-independent Schrödinger equation for the energy value E and, for these "*simple*" solutions, both the following equations are satisfied

$$\begin{aligned} i\hbar\frac{\partial\mathbf{\Psi}(x,t)}{\partial t} &= E\,\mathbf{\Psi}(x,t) \\ \widehat{H}\,\mathbf{\Psi}(x,t) &\equiv \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\mathbf{\Psi}(x,t) = \\ &= E\,\mathbf{\Psi}(x,t)\end{aligned}$$

Why E must be real

Before considering in more detail the properties of these solutions, let us convince ourselves that **the constant E, that couples the two equations, must be real.**

Why E must be real

We have already anticipated in the previous lecture that the hamiltonian operator $\mathbf{\widehat{H} \equiv -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)}$ is such that

$$\int dx\,\Psi_2^*(x,t)\cdot\left[\widehat{H}\Psi_1(x,t)\right] =$$
$$= \int dx\left[\widehat{H}\Psi_2(x,t)\right]^*\cdot\Psi_1(x,t)$$

for any wave functions Ψ_1 and Ψ_2 which are square-integrable (in the x variable).

Why E must be real

1. Assume now $\Psi_1 = \Psi_2 \equiv \Psi$: we have

$$\int dx \left(\widehat{H}\Psi\right)^* \psi = \int \Psi^* \left(\widehat{H}\Psi\right)$$

2. but, in our case, $\widehat{H}\Psi = E\,\Psi$, therefore

$$E^* \int dx\,|\Psi|^2 = E \int dx\,|\Psi|^2$$

Since the integral is certainly different from zero (it is equal to 1 if Ψ is normalized ...), **this requires that $\mathbf{E} = \mathbf{E}^*$.**

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Stationary states

1. Let us come, now, to consider in more detail the properties of the "*simple*" solutions

$$\Psi(x,t) = e^{-iEt/\hbar}\,\psi(x)$$

of the Schrödinger equation.

2. They describe **stationary states.**

No matter the value of E is, the pdf $|\Psi(x,t)|^2$ is **time-independent.** In fact

$$|\Psi(x,t)|^2 = e^{iEt/\hbar}\,\psi^*(x)\;\; e^{-iEt/\hbar}\,\psi(x) = |\psi(x)|^2$$

3. This means that the probability density $|\Psi(x,t)|^2\,dx$ to find the particle between x and $x + dx$ **does not change with time.**

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Stationary states

On a stationary state, **any dynamical variable** Q, represented by the operator $\mathcal{Q}(x, -i\hbar\frac{\partial}{\partial x})$, **will have its expectation value time-independent**: in fact

$$< Q > \; = \; \int dx\, \Psi^*(x,t) \Big[\mathcal{Q}\left(x, -i\hbar\frac{\partial}{\partial x}\right) \Psi(x,t) \Big] =$$

$$= \int dx\, e^{iEt/\hbar} \psi^*(x) \Big[\mathcal{Q}\left(x, -i\hbar\frac{\partial}{\partial x}\right) e^{-iEt/\hbar} \psi(x) \Big] =$$

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1. In particular, the expectation value of the position x will be time-independent

$$\begin{aligned} < x(t) > \; &= \int dx\, e^{iEt/\hbar}\psi^*(x)\, x\, e^{-iEt/\hbar}\psi(x) = \\ &= \int dx\, |\psi(x)|^2 \cdot x \end{aligned}$$

   and, therefore (Ehrenfest theorem) $< p > \equiv m\frac{d}{dt} < x(t) > = 0$ at any time.

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1. Let us show, now, that the **stationary states have a definite total energy.**
2. We have already remarked that the operator

$$\hat{H} \equiv -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

represents the dynamical variable $H(p,x) = \frac{p^2}{2m} + V(x)$, which is the *hamiltonian* of the system.

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Stationary states

1. We have also seen that, on a stationary state, the $time-independent$ Schrödinger equation simply reads

$$\widehat{H}\,\Psi(x) = E\,\Psi(x)$$

2. Therefore, the hamiltonian expectation value on a stationary state is

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Stationary states

1. More important, **on a stationary state there is no energy uncertainty.** In fact

$$< H^2 > = \int dx\,\psi^*(x)\left(\hat{H}^2\psi(x)\right) = E^2 \int dx\,|\psi|^2 = E^2$$

which implies a null standard deviation

$$\sigma_H^2 = < H^2 > - < H >^2 = 0$$

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Orthogonality of the ψ_n

1. Let us show, now, that **time-independent solutions of the Schrödinger equation corresponding to different energies, are mutually orthogonal:**

$$\int dx \; \psi_1^*(x)\, \psi_2(x) = 0$$

   where, by hypothesis, $\hat{H}\psi_1 = E_1\psi_1$, $\hat{H}\psi_2 = E_2\psi_2$ and $E_1 \neq E_2$.

2. We already know that $\hat{H}$ is such that, for any ψ_1 and ψ_2 square-integrable, we have

$$\int dx\, \psi_1^* \left(\hat{H}\psi_2\right) = \int dx \, \left(\hat{H}\psi_1\right)^* \psi_2$$

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therefore we obtain that

$$E_1\int dx\,\psi_1^*\psi_2 = E_2\int dx\,\psi_1^*\psi_2$$

2. Since $E_1 \neq E_2$ by hypothesis, the integral

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General solution of the Schrödinger equation

1. Up to now, we have seen some interesting properties of the solutions ψ of the *time-independent* Schrödinger equation.

2. But how these functions can help, in order to find the most **general solution** of the **time-dependent** Schrödinger equation ?

3. In other words, if we know that a given physical state is represented, at $t = 0$, by the wave function $\Psi(x, 0)$ (initial condition), **what should we do in order to determine the wave function at any other time t ?**

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1. The procedure to find the **general solution** of **the time dependent** Schrödinger equation is as follows.
2. We start by solving the time-independent Schrödinger equation, which, in general, has infinite solutions $\psi_1(x), \ldots, \psi_n(x), \ldots$ corresponding to the energies $E_1, \ldots, E_n, \ldots$
3. It turns out that $\Psi(x,0)$ **can always** be written as a linear combination of the stationary solutions, i.e.

$$\Psi(x,0) = \sum_n c_n \, \psi_n(x)$$

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1. Let us define,now, the function

$$\Psi(x,t) = \sum_n c_n \, e^{-iE_n t/\hbar} \, \psi_n(x)$$

2. Since it is a linear combination of solutions of the $time - dependent$ Schrödinger equation, it is certainly one of its possible solutions.
3. At $t = 0$, $\Psi(x,t)$ satisfies the initial condition that we have assumed, therefore **it is the solution that we were looking for**, ***because the solution with a given initial condition is unique.***

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