Equations and Derivations for Episode 1

Let's Talk QM Podcast

by

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Time independent Schrödinger equation

The time independent Schrödinger equation

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{1}$$

In 1-d this reduces to

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

The solution in the case of the infinite potential well,

$$V(x) = \begin{cases} 0, & -L/2 < x < L/2 \\ \infty, & L/2 < |x| \end{cases} \tag{3}$$

leads to discrete energy eigenvalues,

$$E = n^2\frac{\pi^2\hbar^2}{8mL^2} \tag{4}$$

where $n = 1, 2, 3, \ldots$

The operator on the left in (1) is the usual Hamiltonian

$$H \equiv \frac{-\hbar^2}{2m}\nabla^2 + V \tag{5}$$

so we have

$$H\psi = E\psi, \tag{6}$$

an eigenvalue equation, with ψ as the eigenstates.

Time dependent equation and probability density

The time dependent Schrödinger equation is

$$i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t} = H\psi(\boldsymbol{r},t) \tag{7}$$

where the $V(\boldsymbol{r},t)$ in H can be time dependent (and hence, H is time dependent). The notation of the bold symbol $\boldsymbol{r}$ is to denote the vector nature of the position $\boldsymbol{r}$. In general, the wave function

$$\psi \in \mathbb{Z}, \tag{8}$$

i.e., the set of complex numbers.

How is ψ interpreted?

$$\rho(\boldsymbol{r},t) = |\psi|^2 = \psi^*\psi \tag{9}$$

is the probability density function (pdf) provided

$$\int \mathrm{d}^3r\, \rho(\boldsymbol{r},t) = 1 \tag{10}$$

Here ψ^* is the complex conjugate (c.c.) of ψ. If ψ is not normalizable this way, we have relative probabilities.

The continuity equation is

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\boldsymbol{j} = 0 \tag{11}$$

where $\boldsymbol{j}$ is defined as the probability current density. To derive this, we use (7) and multiply it with the c.c., ψ^*,

$$\begin{aligned} i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t}\times\psi^*(\boldsymbol{r},t) &= (H\psi)\times\psi^* \\ &= \frac{-\hbar^2}{2m}(\nabla^2\psi)\psi^* + V(\boldsymbol{r},t)|\psi|^2 \end{aligned} \tag{12}$$

Next, assume V to be real, and take the c.c. of the above equation, obtaining,

$$-i\hbar\frac{\partial\psi^*(\boldsymbol{r},t)}{\partial t}\times\psi(\boldsymbol{r},t) = \frac{-\hbar^2}{2m}(\nabla^2\psi^*)\psi + V(\boldsymbol{r},t)|\psi|^2 \tag{13}$$

Subtracting the above two equations we obtain,

$$i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t}\psi^*(\boldsymbol{r},t)+i\hbar\frac{\partial\psi^*(\boldsymbol{r},t)}{\partial t}\psi(\boldsymbol{r},t)=\frac{\hbar^2}{2m}\left(\psi\nabla^2\psi^*-\psi^*\nabla^2\psi\right) \tag{14}$$

This leads to,

$$i\hbar\frac{\partial(\psi\psi^*)}{\partial t}=i\hbar\frac{\partial\rho}{\partial t}=\frac{\hbar^2}{2m}\nabla\cdot\left(\psi\nabla\psi^*-\psi^*\nabla\psi\right) \tag{15}$$

With

$$\boldsymbol{j}\equiv\frac{\hbar}{2mi}\left(\psi^*\nabla\psi-\psi\nabla\psi^*\right) \tag{16}$$

as the current density, we have the continuity equation (11).

If the normalization integral (10) holds, then it should hold for all time t, i.e.,

$$\frac{\partial}{\partial t}\int \mathrm{d}^3r\,\rho(\boldsymbol{r},t)=0 \tag{17}$$

Using the continuity equation we have,

$$\int \mathrm{d}^3r\,\frac{\partial\rho(\boldsymbol{r},t)}{\partial t}=-\int \mathrm{d}^3r\,\nabla\cdot\boldsymbol{j}=0, \tag{18}$$

using the divergence theorem.

Expectation values and Fourier transforms

The expectation value of position is

$$\langle\boldsymbol{r}\rangle=\int \mathrm{d}^3r\,\boldsymbol{r}\,|\psi|^2 \tag{19}$$

and also for any function of position, i.e.,

$$\langle f(\boldsymbol{r})\rangle=\int \mathrm{d}^3r\,f(\boldsymbol{r})\,|\psi|^2 \tag{20}$$

But how are operator expectation values calculated in quantum mechanics—for example, $\langle\boldsymbol{p}\rangle$ and $\langle H\rangle$?

Since $-i\hbar\nabla$ (equivalently the x-component is, $-i\hbar\partial_x$) is associated with momentum $\boldsymbol{p}$; and $i\hbar\partial_t$ is associated with H, we have

$$\langle \boldsymbol{p} \rangle = \int \mathrm{d}^3 r\, \psi^* (-i\hbar\nabla\psi) \tag{21a}$$

$$\langle H \rangle = \int \mathrm{d}^3 r\, \psi^* (i\hbar\frac{\partial}{\partial t}\psi) \tag{21b}$$

So the operators are inserted in between ψ^* and ψ.
Consistency of (21b) with the time dependent Schrödinger equation (7) can be seen by multiplying ψ^* on the left, i.e.,

$$\psi^*(\boldsymbol{r},t) \times i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t} = \psi^*(\boldsymbol{r},t) H \psi(\boldsymbol{r},t) \tag{22}$$

and integrating over all space. A formal derivation of (21a) this is obtained using the Fourier transform (FT) pair

$$\psi(\boldsymbol{r},t) = \frac{1}{(2\pi\hbar)^{3/2}} \int \mathrm{d}^3 p\, \phi(\boldsymbol{p},t) \exp\left(\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right) \tag{23a}$$

$$\phi(\boldsymbol{p},t) = \frac{1}{(2\pi\hbar)^{3/2}} \int \mathrm{d}^3 r\, \psi(\boldsymbol{r},t) \exp\left(-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right) \tag{23b}$$

If $|\psi|^2$ is the pdf in position coordinates, $|\phi|^2$ has the analogous interpretation in momentum coordinates. Therefore, the momentum expectation value is

$$\begin{aligned} \langle \boldsymbol{p} \rangle &= \int \mathrm{d}^3 p\, \boldsymbol{p}\, |\phi|^2 = \int \mathrm{d}^3 p\, \boldsymbol{p}\, \phi^* \phi \\ &= \int \mathrm{d}^3 p\, \boldsymbol{p} \frac{1}{(2\pi\hbar)^{3/2}} \int \mathrm{d}^3 r\, \psi^*(\boldsymbol{r},t) \exp\left(+\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right) \phi(\boldsymbol{p},t) \end{aligned} \tag{24}$$

where ϕ^* has been replaced using c.c. of (23b). Using the trick,

$$\boldsymbol{p} \exp\left(\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right) = \frac{\hbar}{i}\nabla \exp\left(\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right), \tag{25}$$

we write the above as

$$\begin{aligned} &\frac{1}{(2\pi\hbar)^{3/2}} \int \mathrm{d}^3 p \int \mathrm{d}^3 r\, \psi^*(\boldsymbol{r},t) \frac{\hbar}{i} \nabla \exp\left(\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right) \phi(\boldsymbol{p},t) \\ &= \int \mathrm{d}^3 r\, \psi^*(\boldsymbol{r},t) \frac{\hbar}{i} \nabla \frac{1}{(2\pi\hbar)^{3/2}} \int \mathrm{d}^3 p\, \phi \exp\left(\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right) \\ &= \int \mathrm{d}^3 r\, \psi^*(\boldsymbol{r},t) \frac{\hbar}{i} \nabla \psi(\boldsymbol{r},t) = \langle \boldsymbol{p} \rangle, \end{aligned} \tag{26}$$

where the momentum integration is FT (23a). More generally,

$$\langle f(\boldsymbol{p})\rangle = \int \mathrm{d}^3 r\, \psi^*(\boldsymbol{r},t)\, f\left(\frac{\hbar}{i}\nabla\right)\psi(\boldsymbol{r},t) \tag{27}$$

Similarly the position expectation (20) can be calculated in momentum space as,

$$\langle f(\boldsymbol{r})\rangle = \int \mathrm{d}^3 p\, \phi^*(\boldsymbol{p},t) f(i\hbar\nabla_{\boldsymbol{p}})\phi(\boldsymbol{p},t) \tag{28}$$

emphasizing the dual relationship shared between the operators $\boldsymbol{r}$ and $\boldsymbol{p}$ in quantum mechanics, summarized as,

$$\begin{aligned}
&\text{(position space)}\quad \boldsymbol{r} \leftrightarrow i\hbar\nabla_{\boldsymbol{p}} \quad \text{(momentum space)}\\
&\text{(position space)}\quad \frac{\hbar}{i}\nabla \leftrightarrow \boldsymbol{p} \quad \text{(momentum space)}
\end{aligned} \tag{29}$$

What is the time dependent Schrödinger equation (7)

$$i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t} = H\psi(\boldsymbol{r},t) = \frac{-\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r},t) + V(\boldsymbol{r},t)\psi(\boldsymbol{r},t)$$

in momentum space? Using the FT (23b) and the above, we have,

$$\begin{aligned}
i\hbar\frac{\partial\phi(\boldsymbol{p},t)}{\partial t} &= \frac{i\hbar}{(2\pi\hbar)^{3/2}}\int \mathrm{d}^3 r\, \frac{\partial\psi(\boldsymbol{r},t)}{\partial t}\exp\left(-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right)\\
&= \frac{1}{(2\pi\hbar)^{3/2}}\int \mathrm{d}^3 r\, H\psi(\boldsymbol{r},t)\exp\left(-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right)\\
&= \frac{1}{(2\pi\hbar)^{3/2}}\int \mathrm{d}^3 r\, \left(\frac{-\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r},t) + V(\boldsymbol{r},t)\psi(\boldsymbol{r},t)\right)\exp\left(-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right)
\end{aligned} \tag{30}$$

To evaluate the RHS, we use back and forth FT's and integration by parts. So here goes—first, the $\int V\psi\exp\left(-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right)$ piece:

$$\frac{1}{(2\pi\hbar)^3}\int \mathrm{d}^3 r\, \mathrm{d}^3 q\, V(\boldsymbol{r},t)\phi(\boldsymbol{q},t)\exp\left(-\frac{i}{\hbar}(\boldsymbol{p}-\boldsymbol{q})\cdot\boldsymbol{r}\right) \tag{31}$$

where ψ has been replaced by its FT ϕ (23a). Next using (23b), the $\int \mathrm{d}^3 r$ is evaluated to yield,

$$\frac{1}{(2\pi\hbar)^{3/2}}\int \mathrm{d}^3 q\, V(\boldsymbol{p}-\boldsymbol{q},t)\phi(\boldsymbol{q},t) \tag{32}$$

This is known as a convolution integral.

The other piece, $\int \nabla^2\psi \exp\left(-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right)$, on the RHS is evaluated using repeated integration by parts,

$$\begin{aligned}
&\frac{1}{(2\pi\hbar)^{3/2}}\int \mathrm{d}^3r\, \frac{-\hbar^2}{2m}\left(\nabla^2\psi(\boldsymbol{r},t)\right)\exp\left(-\tfrac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right)\\
&=\frac{1}{(2\pi\hbar)^{3/2}}\left[\int \mathrm{d}^3r\,\frac{-\hbar^2}{2m}\nabla\cdot\left((\nabla\psi)\exp(-\tfrac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r})\right)-\frac{i\hbar}{2m}\int \mathrm{d}^3r\,(\boldsymbol{p}\cdot\nabla\psi)\exp(-\tfrac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r})\right]\\
&=\frac{1}{(2\pi\hbar)^{3/2}}\left[\int \mathrm{d}^3r\,\frac{-\hbar^2}{2m}\nabla\cdot\left(\nabla\psi\exp(-\tfrac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r})\right)-\frac{i\hbar}{2m}\int \mathrm{d}^3r\,\boldsymbol{p}\cdot\nabla(\psi\exp(-\tfrac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}))\right.\\
&\qquad\left.+\frac{i\hbar}{2m}\int \mathrm{d}^3r\,\psi\boldsymbol{p}\cdot\nabla\exp(-\tfrac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r})\right]
\end{aligned}\tag{33}$$

In the last line above, the first two terms are a result of integration by parts and the use of (25) to evaluate $\nabla\exp\left(-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right)$. These two terms vanish; and the remaining third term in the last line above becomes,

$$\frac{1}{(2\pi\hbar)^{3/2}}\times\frac{1}{2m}\int \mathrm{d}^3r\,\psi\,\boldsymbol{p}\cdot\boldsymbol{p}\exp(-\tfrac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r})=\frac{p^2}{2m}\phi(\boldsymbol{p},t)\tag{34}$$

where once again FT (23b) is used.

Putting the convolution term (32) and the above together, (30) becomes

$$i\hbar\frac{\partial\phi(\boldsymbol{p},t)}{\partial t}=\frac{p^2}{2m}\phi(\boldsymbol{p},t)+\frac{1}{(2\pi\hbar)^{3/2}}\int \mathrm{d}^3q\,V(\boldsymbol{p}-\boldsymbol{q},t)\phi(\boldsymbol{q},t)\tag{35}$$

So the time dependent Schrödinger differential equation in position space, is an integro-differential equation in momentum space.

End of Podcast Episode 1.