Equations and Derivations for Episode 2

Let's Talk QM Podcast

by

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Equations from the previous episode

$$i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t} = H\psi(\boldsymbol{r},t) \tag{1}$$

with

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

The continuity equation is

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\boldsymbol{j} = 0 \tag{3}$$

where $\rho = |\psi|^2$, with

$$\boldsymbol{j}(\boldsymbol{r},t) = \frac{\hbar}{2mi}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) \tag{4}$$

We, therefore, have,

$$\begin{aligned} j_x &= \frac{\hbar}{2mi}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right) \\ j_y &= \frac{\hbar}{2mi}\left(\psi^*\frac{\partial\psi}{\partial y} - \psi\frac{\partial\psi^*}{\partial y}\right), \text{etc.} \end{aligned} \tag{5}$$

Ehrenfest's theorem

$$\langle \boldsymbol{r} \rangle = \int \mathrm{d}^3 r\, \psi^* \boldsymbol{r}\, \psi \tag{6}$$

$$\frac{\mathrm{d}\langle \boldsymbol{r} \rangle}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t} \int \mathrm{d}^3 r\, \psi^* \boldsymbol{r} \psi \tag{7}$$

Recall that $\boldsymbol{r} = x\hat{x} + y\hat{y} + z\hat{z}$, so we can look at,

$$\begin{aligned}
\frac{\mathrm{d}\langle x \rangle}{\mathrm{d}t} &= \int \mathrm{d}^3 r\, \frac{\partial \psi^*}{\partial t} x\psi + \int \mathrm{d}^3 r\, \psi^* x \frac{\partial \psi}{\partial t} \\
&= -\frac{1}{i\hbar} \int \mathrm{d}^3 r\, (H\psi^*) x\psi + \frac{1}{i\hbar} \int \mathrm{d}^3 r\, \psi^* x H\psi \\
&= \frac{\hbar}{2mi} \int \mathrm{d}^3 r\, \left[(\nabla^2 \psi^*) x\psi - \psi^* x \nabla^2 \psi \right]
\end{aligned} \tag{8}$$

Using integration by parts,

$$\nabla \cdot ((\nabla \psi^*) x\psi) = \left(\nabla^2 \psi^* \right) x\psi + (\nabla \psi^*) \cdot \nabla(x\psi), \tag{9}$$

the term $\int (\nabla^2 \psi^*) x\psi$ in (8) above is,

$$\begin{aligned}
\int \mathrm{d}^3 r\, (\nabla^2 \psi^*) x\psi &= \int \mathrm{d}^3 r\, \nabla \cdot ((\nabla \psi^*) x\psi) - \int \mathrm{d}^3 r\, \nabla \psi^* \cdot \nabla(x\psi) \\
&= -\int \mathrm{d}^3 r\, \nabla \psi^* \cdot \nabla(x\psi)
\end{aligned} \tag{10}$$

Using integration by parts again,

$$\nabla \cdot (\psi^* \nabla(x\psi)) = \nabla \psi^* \cdot \nabla(x\psi) + \psi^* \nabla^2(x\psi) \tag{11}$$

we have,

$$-\int \mathrm{d}^3 r\, \nabla \psi^* \cdot \nabla(x\psi) = -\int \mathrm{d}^3 r\, \nabla \cdot (\psi^* \nabla(x\psi)) + \int \mathrm{d}^3 r\, \psi^* \nabla^2(x\psi) \tag{12}$$

So we rewrite (8)

$$\frac{\mathrm{d}\langle x \rangle}{\mathrm{d}t} = \frac{\hbar}{2mi} \int \mathrm{d}^3 r\, \left[\psi^* \nabla^2(x\psi) - \psi^* x \nabla^2 \psi \right] \tag{13}$$

Recall that,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{14}$$

and w.r.t. the y, z terms, $\nabla^2_{y,z}(x\psi) = x\nabla^2_{y,z}\psi$, so we need to only keep track of

$$\psi^* \frac{\partial^2(x\psi)}{\partial x^2} - \psi^* x \frac{\partial^2 \psi}{\partial x^2} \tag{15}$$

We have,

$$\frac{\partial^2(x\psi)}{\partial x^2} = \frac{\partial}{\partial x}\left(\psi + x\frac{\partial\psi}{\partial x}\right) = 2\frac{\partial\psi}{\partial x} + x\frac{\partial^2\psi}{\partial x^2} \tag{16}$$

Therefore equation (13) becomes,

$$\begin{aligned}
\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} &= \frac{\hbar}{2mi}\int \mathrm{d}^3r\, \psi^* \left[2\frac{\partial\psi}{\partial x} + x\frac{\partial^2\psi}{\partial x^2} - x\frac{\partial^2\psi}{\partial x^2}\right] \\
&= \frac{\hbar}{mi}\int \mathrm{d}^3r\, \psi^* \frac{\partial\psi}{\partial x} \\
&= \frac{\langle p_x\rangle}{m},
\end{aligned} \tag{17}$$

as

$$\langle p_x\rangle = \frac{\hbar}{i}\int \mathrm{d}^3r\, \psi^* \frac{\partial\psi}{\partial x} \tag{18}$$

With

$$\langle \boldsymbol{p}\rangle = \frac{\hbar}{i}\int \mathrm{d}^3r\, \psi^* \nabla\psi \tag{19}$$

we generalize this to,

$$\frac{\mathrm{d}\langle \boldsymbol{r}\rangle}{\mathrm{d}t} = \frac{\langle \boldsymbol{p}\rangle}{m} \tag{20}$$

The equation (8)

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{\hbar}{2mi}\int \mathrm{d}^3r\, \left[(\nabla^2\psi^*)x\psi - \psi^* x\nabla^2\psi\right] \tag{21}$$

can be manipulated using integration by parts on both terms,

$$\begin{aligned}
\nabla\cdot((\nabla\psi^*)x\psi) &= \left(\nabla^2\psi^*\right)x\psi + (\nabla\psi^*)\cdot\nabla(x\psi) \\
\nabla\cdot(\psi^* x\nabla\psi) &= \psi^* x\nabla^2\psi + \nabla(\psi^* x)\cdot\nabla\psi
\end{aligned} \tag{22}$$

So the integral becomes,

$$\begin{aligned}
\int \mathrm{d}^3r\, \left[(\nabla^2\psi^*)x\psi - \psi^* x\nabla^2\psi\right] &= \int \mathrm{d}^3r\, \nabla\cdot((\nabla\psi^*)x\psi - \psi^* x\nabla\psi) \\
&\quad - \int \mathrm{d}^3r\, ((\nabla\psi^*)\cdot\nabla(x\psi) - \nabla(\psi^* x)\cdot\nabla\psi)
\end{aligned} \tag{23}$$

Using the product rule, one term in the expression $(\nabla\psi^*)\cdot\nabla(x\psi) - \nabla(\psi^* x)\cdot\nabla\psi$ is

$$x\nabla\psi^*\cdot\nabla\psi - \nabla\psi^*\cdot(\nabla\psi)x \equiv 0 \tag{24}$$

the other term being,

$$\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi \tag{25}$$

Referring to equation (5) we recognize that with $\frac{\hbar}{2mi}$ this is j_x and therefore equation (21) becomes

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \int \mathrm{d}^3r\, j_x \tag{26}$$

Generalising,

$$\frac{\mathrm{d}\langle \boldsymbol{r}\rangle}{\mathrm{d}t} = \int \mathrm{d}^3r\, \boldsymbol{j} \tag{27}$$

This result can also be obtained by noting that

$$\begin{aligned}\langle\boldsymbol{r}\rangle &= \int \mathrm{d}^3r\,\psi^*\boldsymbol{r}\psi = \int \mathrm{d}^3r\,\boldsymbol{r}\psi^*\psi = \int \mathrm{d}^3r\,\boldsymbol{r}\rho \\ \Rightarrow \frac{\mathrm{d}\langle\boldsymbol{r}\rangle}{\mathrm{d}t} &= \int \mathrm{d}^3r\,\boldsymbol{r}\frac{\partial\rho}{\partial t} = -\int \mathrm{d}^3r\,\boldsymbol{r}\nabla\cdot\boldsymbol{j}\end{aligned} \tag{28}$$

where (3) has been used.

Next we have

$$\frac{\mathrm{d}\langle \boldsymbol{p}\rangle}{\mathrm{d}t} = -i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\int \mathrm{d}^3r\,\psi^*\nabla\psi \tag{29}$$

Once again, with a particular coordinate direction,

$$\begin{aligned}\frac{\mathrm{d}\langle p_x\rangle}{\mathrm{d}t} &= -i\hbar\int \mathrm{d}^3r\,\left[\frac{\partial\psi^*}{\partial t}\frac{\partial\psi}{\partial x} + \psi^*\frac{\partial}{\partial x}\frac{\partial\psi}{\partial t}\right] \\ &= \int \mathrm{d}^3r\,\left[(H\psi^*)\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial}{\partial x}H\psi\right] \\ &= \frac{\hbar^2}{2m}\int \mathrm{d}^3r\,\left[\psi^*\frac{\partial}{\partial x}\nabla^2\psi - (\nabla^2\psi^*)\frac{\partial\psi}{\partial x}\right] + \int \mathrm{d}^3r\,\psi^*\left(V\frac{\partial\psi}{\partial x} - \frac{\partial}{\partial x}(V\psi)\right)\end{aligned} \tag{30}$$

The first term can be manipulated using Green's theorem,

$$\int \mathrm{d}^3r\,(T\nabla^2U - U\nabla^2T) = \int (T\nabla U - U\nabla T)\cdot\mathrm{d}\boldsymbol{S} \tag{31}$$

Note that,

$$\frac{\partial}{\partial x}\nabla^2\psi = \nabla^2\frac{\partial\psi}{\partial x} \tag{32}$$

and so we identify

$$T = \psi^*; U = \frac{\partial\psi}{\partial x} \tag{33}$$

So we have,

$$\begin{aligned}\frac{\mathrm{d}\langle p_x\rangle}{\mathrm{d}t} &= \int \mathrm{d}^3r\,\psi^*\left(V\frac{\partial\psi}{\partial x} - \frac{\partial}{\partial x}(V\psi)\right) = -\int \mathrm{d}^3r\,\psi^*\frac{\partial V}{\partial x}\psi \\ &= \left\langle -\frac{\partial V}{\partial x}\right\rangle\end{aligned} \tag{34}$$

Once again, generalizing,

$$\frac{\mathrm{d}\langle \boldsymbol{p}\rangle}{\mathrm{d}t} = \langle -\nabla V\rangle \tag{35}$$

Combining with equation (20) above,

$$\frac{\mathrm{d}^2\langle \boldsymbol{r}\rangle}{\mathrm{d}t^2} = \frac{1}{m}\frac{\mathrm{d}\langle \boldsymbol{p}\rangle}{\mathrm{d}t} = \frac{1}{m}\langle -\nabla V\rangle \tag{36}$$

When we have

$$\boldsymbol{F}(\boldsymbol{r},t) = -\nabla V(\boldsymbol{r},t) \tag{37}$$

then,

$$\frac{\mathrm{d}^2\langle \boldsymbol{r}\rangle}{\mathrm{d}t^2} = \frac{1}{m}\frac{\mathrm{d}\langle \boldsymbol{p}\rangle}{\mathrm{d}t} = \frac{\langle \boldsymbol{F}\rangle}{m} \tag{38}$$

In particular, if $\langle \boldsymbol{F}(\boldsymbol{r},t)\rangle = \boldsymbol{F}(\langle \boldsymbol{r}\rangle,t)$, then $\langle \boldsymbol{r}\rangle$ behaves like a classical particle.

Operators and commutators

Operators act on functions. In coordinate representation

$$\phi(x) = O\psi(x) \tag{39}$$

Already seen two examples x and p_x; or more generally $\boldsymbol{r}$ and $\boldsymbol{p}$, which lead to

$$\begin{aligned}\phi(\boldsymbol{r}) &= \boldsymbol{r}\psi(\boldsymbol{r}) \\ \phi(\boldsymbol{r}) &= \boldsymbol{p}\psi(\boldsymbol{r}) = -i\hbar\nabla\psi(\boldsymbol{r})\end{aligned} \tag{40}$$

The order in which operators act on a function is important:

$$O_1 O_2 \psi(\boldsymbol{r}) \neq O_2 O_1 \psi(\boldsymbol{r}) \tag{41}$$

For example,

$$\frac{\partial}{\partial x} x\psi \neq x \frac{\partial}{\partial x}\psi \tag{42}$$

The commutator of two operators is an operator,

$$[O1, O2] \equiv O_1 O_2 - O_2 O_1 \tag{43}$$

In general for any operator O,

$$\begin{aligned} i\hbar \frac{\mathrm{d}\langle O\rangle}{\mathrm{d}t} &= i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \int \mathrm{d}^3 r\, \psi^* O \psi \\ &= \int \mathrm{d}^3 r\, \left(\psi^* O H \psi - (H\psi^*)(O\psi)\right) + i\hbar \int \mathrm{d}^3 r\, \psi^* \frac{\partial O}{\partial t} \psi \end{aligned} \tag{44}$$

We want to move ψ^* to the left of H, in the term,

$$-(H\psi^*)(O\psi) \to -\psi^* H O \psi \tag{45}$$

Then we have,

$$i\hbar \frac{\mathrm{d}\langle O\rangle}{\mathrm{d}t} = \int \mathrm{d}^3 r\, \psi^* (OH - HO)\psi + i\hbar \left\langle \frac{\partial O}{\partial t} \right\rangle \tag{46}$$

This becomes,

$$i\hbar \frac{\mathrm{d}\langle O\rangle}{\mathrm{d}t} = \langle [O, H] \rangle + i\hbar \left\langle \frac{\partial O}{\partial t} \right\rangle \tag{47}$$

If $[O, H] = 0$ and O does not have any explicit time dependence,

$$\frac{\mathrm{d}\langle O\rangle}{\mathrm{d}t} = 0, \tag{48}$$

i.e., O is a conserved quantity or constant of motion.

So how do we move ψ^* to the left of H?

$$-\int \mathrm{d}^3 r\, (H\psi^*)(O\psi) = \int \mathrm{d}^3 r\, \left(\frac{\hbar^2}{2m}\nabla^2 \psi^* - V\psi^*\right)(O\psi) \tag{49}$$

Focusing on the $(\nabla^2\psi^*)(O\psi)$ term, note that we can write this as

$$\int \mathrm{d}^3r\,(O\psi)\frac{\hbar^2}{2m}\nabla^2\psi^* \tag{50}$$

Identifying

$$T = O\psi; U = \psi^* \tag{51}$$

in Green's theorem,

$$\int \mathrm{d}^3r\,(T\nabla^2 U - U\nabla^2 T) = \int (T\nabla U - U\nabla T)\cdot \mathrm{d}\boldsymbol{S} \tag{52}$$

we have

$$\begin{aligned} \frac{\hbar^2}{2m}\int \mathrm{d}^3r\,\big((O\psi)\nabla^2\psi^* - \psi^*\nabla^2(O\psi)\big) = 0 \\ \Rightarrow \frac{\hbar^2}{2m}\int \mathrm{d}^3r\,(O\psi)\nabla^2\psi^* = \frac{\hbar^2}{2m}\int \mathrm{d}^3r\,\psi^*\nabla^2(O\psi) \end{aligned} \tag{53}$$

Using this in (49), we have

$$-\int \mathrm{d}^3r\,(H\psi^*)(O\psi) = \int \mathrm{d}^3r\,\psi^*(\frac{\hbar^2}{2m}\nabla^2(O\psi) - VO\psi) = -\int \mathrm{d}^3r\,\psi^* HO\psi \tag{54}$$

giving equation (46), with the term in brackets, the commutator (47)

Coming back to commutators,

$$\begin{aligned} &[x, p_x] = [y, p_y] = [z, p_z] = i\hbar \\ &[x, p_y] = 0 \end{aligned} \tag{55}$$

If A, B, C are operators, we have

$$[A, B] = -[B, A] \tag{56a}$$

$$[AB, C] = A[B, C] + [A, C]B \tag{56b}$$

Another identity (cyclic) is

$$[A, [B, C]] + [C, [A, B]] + [B, [C, A]] = 0 \tag{57}$$

To show this, expand the above,

$$A[B, C] - [B, C]A + C[A, B] - [A, B]C + B[C, A] - [C, A]B \tag{58}$$

Combining terms, one can obtain terms like LHS of equation (56b).

$$\begin{aligned} A[B, C] - [C, A]B &= A[B, C] + [A, C]B = [AB, C] \\ -[B, C]A + C[A, B] &= [C, B]A + C[A, B] = [CA, B] \end{aligned} \tag{59}$$

We have,

$$[A, [B, C]] + [C, [A, B]] + [B, [C, A]] = [AB, C] + [CA, B] + [BC, A] = 0 \tag{60}$$

Another useful identity set

$$\begin{aligned} [A, B^n] &= nB^{n-1}[A, B] \\ [A^n, B] &= nA^{n-1}[A, B] \end{aligned} \tag{61}$$

provided that $[A, [A, B]] = [B, [A, B]] = 0$.

For $n = 2$, we have $[A, B^2] = B[A, B] + [A, B]B = 2B[A, B]$. So for the induction step, we have to show that

$$[A, B^{n+1}] = (n + 1)B^n[A, B] \tag{62}$$

assuming $[A, B^n] = nB^{n-1}[A, B]$ holds. The above follows because,

$$\begin{aligned} [A, B^{n+1}] &= [A, B \cdot B^n] = B[A, B^n] + [A, B]B^n \\ &= B(nB^{n-1}[A, B]) + B^n[A, B] \end{aligned} \tag{63}$$

Here is an example that applies the above result: Let

$$f(x) = \sum_{n=0}^{\infty} a_n x^n \tag{64}$$

be an operator that has a power series expansion in the coordinate operator x. What is the commutator, $[p_x, f(x)]$? Note that we already know the result for $[p_x, x] = -[x, p_x] = -i\hbar$ (equation (55)). We have,

$$[p_x, f(x)] = \left[p_x, \sum a_n x^n\right] = \sum a_n[p_x, x^n] \tag{65}$$

With the above identity (61), we obtain

$$[p_x, f(x)] = \sum a_n n x^{n-1}[p_x, x] = -i\hbar \sum a_n n x^{n-1} = -i\hbar \frac{\mathrm{d}f}{\mathrm{d}x} \tag{66}$$

Note that

$$[x, [p_x, x]] = 0 \tag{67}$$

as required.
Therefore the action of the operator $[p_x, f(x)]$ on a function $\psi(x)$ is,

$$[p_x, f(x)]\psi(x) = -i\hbar \frac{\mathrm{d}f}{\mathrm{d}x}\psi(x) \tag{68}$$

and this is a multiplicative operator in coordinate space.

End of Podcast Episode 2.