Week ②

PHY 303 Quantum Mechanics
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1.6 The basic structure of quantum mechanics

Armed with the mathematical framework that we developed in section 1.5, we shall now revisit the essential structure of quantum mechanics that you already learnt in PHY106, also deepening the math level. Later we will do a second step of deepening the math content in section 3. There will not be many examples in this section, since the following weeks provide many.

1.6.1 Normalisation and phase of wavefunctions

We already reviewed in section 1.4 that the quantum state of a particle is given by a <u>complex</u> wave function $\Psi(x,t)$ that is a solution of the TDSE (1.2). Importantly, (1.2) is <u>linear</u>, which means that (i) if we have one solution $\Psi(x,t)$ then $\Psi_c(x,t) = c\Psi(x,t)$ is also a solution, for an arbitrary <u>complex</u> number c, and (ii) If we found two solutions $\Psi_1(x,t)$ and $\Psi_2(x,t)$, then also $\Psi_3(x,t) = \overline{\Psi_1(x,t)} + \Psi_2(x,t)$ is a solution. The latter is called the <u>superposition principle</u>, and holds for any linear wave equation (see also PHY106).

We can use property (i), to always make sure of

Wavefunction normalisation Since we know that $|\Psi(x,t)|^2 dx$ ought to be the probability at time t to find the particle between x and $x + dx$ (for infinitesimal dx), and the total probability has to be unity (see section 1.5.2), we require:

$$\int_{-\infty}^{\infty} dx \, |\Psi(x,t)|^2 = 1. \tag{1.27}$$

- Due to property (i) above, if we have any wavefunction $\tilde{\Psi}$ in $\mathbb{L}_2$ solving the TDSE that is <u>not</u> normalised to one, say instead $\int_{-\infty}^{\infty} dx |\tilde{\Psi}(x,t)|^2 = A$, then we know also $\Psi(x,t) = \tilde{\Psi}(x,t)/\sqrt{A}$ is a solution, and this one IS normalized to one (mini exercise).

- For physical quantum states, we should only ever consider states in $\mathbb{L}_2$ for which this procedure is possible.

- However we will later see (and have already seen in PHY106), that it is sometimes useful for math, and instructive for physics to also consider states that are non-normalizable for

$-\infty < x < \infty$ (these are thus not part of $\mathbb{L}_2$). The most important example is the infinite plane wave $\exp[ikx]$, for which $A \to \infty$. We will see some tricks on how to handle those functions anyway in section 2.1.

- You can show as a relative simply but instructive exercise, or read up in Griffith, that if at any given time t the wavefunction is normalized, the TDSE (1.2) ensures that it also remains normalized for all later times $t' > t$. This is also called conservation of probability.

Let us write the complex factor c form above in polar notation as $c = re^{i\varphi}$, with amplitude $r \in \mathbb{R}$ and phase φ. We see that the normalisation condition (1.27) fixes r but not φ. For a quantum state, its so-called global phase is thus undefined. Later we see that φ is not physically relevant (cannot be measured).

1.6.2 Momentum and other operators

While the state of a particle becomes a wavefunction in quantum mechanics, observables dependent on this state are represented by operators, introduced in section 1.5.4. The reason is ultimately that we need a mathematical formalism that gives rise to Heisenberg's uncertainty principle (see PHY106, week6), which is observed in nature. We shall see in section 3 why observables thus have to be operators, and what precisely is meant by "represented by...".

The simplest operator is the position operator, which is just the multiplication by x, i.e. $\hat{x}\Psi(x,t) = x\Psi(x,t)$. Since we already know that $|\Psi(x,t)|^2$ it the position space probability density of the particle, we can use the basic definition Eq. (1.6) and write the

> **Expectation value of position**
>
> $$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} dx\, x|\Psi(x,t)|^2 = \int_{-\infty}^{\infty} dx\, \Psi^*(x,t)\hat{x}\Psi(x,t) \qquad (1.28)$$

- We shall see shortly that for expectation values of an operator, the operator has to be sandwiched between the wave functions. Of course once we realize that in the case of the position operator, the operation is merely a multiplication, this no longer matters. For other operators it DOES matter.

- Be careful about the name "expectation value". It does not mean the expected outcome of a measurement of position. Neither does it even have to be one of the possible outcomes of a measurement of position. It instead means the expected (and then indeed certain) average of a very large number of measurements of positions of particles that are identically prepared, such that they are described by the wavefunction Ψ. Again, not repeated measurements of the position of the same particle.

- Importantly, the expectation value thus makes reference to the wavefunction $\Psi(x,t)$. It of course be different for different wavefunctions.

We had already seen arguments in PHY106, how one is lead to the

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Momentum operator in one dimension

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}.\tag{1.29}$$

- In PHY106 week8, we saw how this can extract information about the momentum since the latter is encoded in the wavelength or wavenumber of $\Psi(x,t)$, and the wavenumber k in a plane-wave e^{ikx} is appearing as multiplication after applying the momentum operator.

- We will still use the 1D version (1.30) for a while, but for completeness already mention the 3D momentum operator

$$\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}.\tag{1.30}$$

Note, that this is now a <u>vector of operators</u> or <u>vectoroperator</u>, $\hat{\mathbf{p}} = -i\hbar[\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial x}]^T$. Its application onto a <u>wavefunction</u> will again be a <u>vector</u>.

To see another line of thought that motivates the choice (1.30) for the momentum operator, consider the rate of change of a position expectation value:

$$\frac{\partial}{\partial t}\langle x\rangle = \frac{\partial}{\partial t}\int_{-\infty}^{\infty}dx\ \Psi^*(x,t)x\Psi(x,t) = \cdots.\tag{1.31}$$

A common trick in derivations like this, is to exchange the order of differentiation and integration for two different variables[6]. We can then use the product rule inside the integrand

$$\cdots = \int_{-\infty}^{\infty}dx\left[\left(\frac{\partial}{\partial t}\Psi^*(x,t)\right)x\Psi(x,t) + \Psi^*(x,t)x\left(\frac{\partial}{\partial t}\Psi(x,t)\right)\right]\tag{1.32}$$

$$\overset{Eq.\ (1.2)}{=}\int_{-\infty}^{\infty}dx\left[\left(\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)\frac{\Psi^*(x,t)}{-i\hbar}\right)x\Psi(x,t) + \Psi^*(x,t)x\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)\frac{\Psi(x,t)}{i\hbar}\right].$$

For the left part of the last line, we had to first take the complex conjugate of Eq. (1.2), in order to get an equation involving $\Psi^*(x,t)$. We see that the terms involving the potential $V(x)$ cancel and the rest becomes

$$\cdots = -\frac{i\hbar^2}{2m}\int_{-\infty}^{\infty}dx\ x\underbrace{\left[\left(\frac{\partial^2}{\partial x^2}\Psi^*(x,t)\right)\Psi(x,t) - \Psi^*(x,t)\left(\frac{\partial^2}{\partial x^2}\Psi(x,t)\right)\right]}_{=\frac{\partial}{\partial x}\left(\frac{\partial\Psi^*(x,t)}{\partial x}\Psi(x,t)-\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}\right)}.\tag{1.33}$$

We can now do integration by parts to "shift the $\partial/\partial x$ onto the x". We should get an additional boundary term $x\left(\frac{\partial\Psi^*(x,t)}{\partial x}\Psi(x,t) - \Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}\right)\Big|_{-\infty}^{\infty}$, but this has to vanish since $\lim_{x\to 0}\Psi(x,t) =$

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[6]Mathematicians allow you this only for integrands that are "sufficiently nice", but this will usually be the case in physics.

0, if $\Psi(x,t)$ is supposed to be normalized as in (1.27). After than and one more integration by parts, we finally reach

$$\frac{\partial}{\partial t}\langle x \rangle = -\frac{i\hbar}{m}\int_{-\infty}^{\infty}dx\,\Psi^*(x,t)\frac{\partial}{\partial x}\Psi(x,t) = \langle \hat{p}/m \rangle. \tag{1.34}$$

For our earlier definition of $\hat{p}$, the rate of change of the position expectation value is thus the velocity expectation value, which seems to make sense.

After we applied the definitions of expectation values from section 1.5.2 to quantum mechanical operators, we can do the same for the standard deviations, to define:

Position and momentum uncertainties in the state $\Psi(x,t)$:

$$\text{Position uncertainty: } \sigma_x = \sqrt{\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2}, \tag{1.35}$$

$$\text{Momentum uncertainty: } \sigma_p = \sqrt{\langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2}. \tag{1.36}$$

This is defined in analogy to (1.8).

Luckily all other physical observables in mechanics can be expressed in terms of position and momentum. Hence also the corresponding operators can be written accordingly in terms of the position and momentum operator. For example

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Mechanical observables

$$\text{Kinetic energy: } \qquad \hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, \tag{1.37}$$

$$\text{Potential energy: } \qquad \hat{V} = V(\hat{x}), \tag{1.38}$$

$$\text{Total energy: } \qquad \hat{H} = \hat{T} + \hat{V}, \tag{1.39}$$

$$\text{Angular momentum: } \qquad \hat{L} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}. \tag{1.40}$$

- The total energy operator get special name, the Hamiltonian, in association with the "Hamiltonian function $H = \frac{p^2}{2m} + V(x)$ in classical mechanics (PHY305). We also recognize this as the operator on the RHS of Schrödinger's equation (1.2), which we could thus write as $i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t)$.

- We can see that all operators in the list above are Hermitian per (1.24) (exercise, use integration by parts).

- For any of the above operators $\hat{O}(\hat{x},\hat{p})$ the expectation value is then found as

$$\langle \hat{O} \rangle = \int_{-\infty}^{\infty}dx\,\Psi^*(x,t)O(x,-i\hbar\frac{\partial}{\partial x})\Psi(x,t),. \tag{1.41}$$

and its uncertainty via

$$\sigma_O = \sqrt{\langle \hat{O}^2 \rangle - \langle \hat{O} \rangle^2}.. \tag{1.42}$$

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While particularly the appearance of the momentum operator as a derivative wrt. x makes all the above look very different from classical mechanics, it still contains much of the same gist, as we had shown you from a simulation in example 1. We can also analytically see this in

> **Example 11, Ehrenfest's theorem:** The expectation values of position and momentum are linked as in classical physics[a], i.e. Eq. (1.34) and
>
> $$\frac{\partial}{\partial t}\langle \hat{p}\rangle = -\langle \frac{\partial}{\partial x}V(x)\rangle. \tag{1.43}$$
>
> *Proof: Exercise, follow similar steps as for Eq. (1.34).* Note, that Ehrenfest's theorem does not tell us how uncertainties evolve, only averages. Since in the initial times of example 1 uncertainties are small, the mean and center position remain almost at the same place, hence the theorem explains why the support region of the probability density just follows Newton's equations.
>
> ───────────
> [a]Via Hamilton's equations, see PHY305.

1.6.3 Heisenberg's uncertainty principle

We know from PHY106, that the momentum is encoded in a wavefunction $\Psi(x,t)$ through its wavelength. The specific link is given by the

> **De-Broglie wavelength**
>
> $$\lambda_{\mathrm{dB}} = \frac{h}{p}, \tag{1.44}$$
>
> where h is Planck's constant (1.3) and $p = |\mathbf{p}|$ the momentum (modulus).

- In one dimension an example of a wavefunction with a well defined momentum p is $\Psi(x) = e^{i\frac{p}{\hbar}x}/\sqrt{(V)}$ (but see section 1.6.1 regarding normalisation issues).

- With the usual conversion from wavelength to wavenumber $\mathbf{k}$, we can also write

$$\mathbf{p} = \hbar\mathbf{k}. \tag{1.45}$$

Note these are now 3D vectors. The 3D wavevector $\mathbf{k} = [k_x, k_y, k_z]^T$ defines a planewave $\Psi(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{x}}/\sqrt{V}$.

We had discussed at some length in PHY106 week6, that there is a tradeoff between how well we know the wavelength of some wavefunction versus how well we know its "position":

Example 12, Wave localisation versus wavelength:
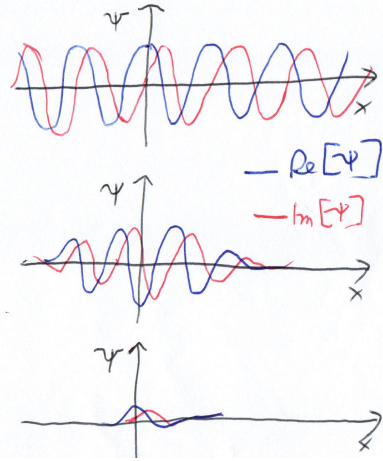
left: Three examples of complex wavefunctions with differently strong spatial localisation, and differently well defined wavelength. (top) Plane wave $\sim e^{ikx}$ has a perfectly well defined wavelength, but no localisation. (middle) A wavepacket is somewhat localized, but we saw in PHY106 and will see more formally later, how this comes at a tradeoff of some spread in wavelengths. (bottom) Sub-cycle wave: Here it becomes very difficult to even read of any wavelength.

This tradeoff gives rise to

Heisenberg's uncertainty principle (HUP)

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}, \tag{1.46}$$

for the position uncertainty σ_x and momentum uncertainty σ_p defined in Eq. (1.35)-(1.36).

- For now we just remind you that you have seen this in PHY106. This time we shall formally prove it in week 6, based on operator algebra (see section 1.5.4). We will then also generalize the HUP to other operators than position and momentum.

- Let us repeat that the HUP has nothing to do with imperfections in the position and momentum measurement apparatuses. It represents a fundamental limitation in simultaneously knowing position and momentum of a particle, which arises immediately once we realize that the particle must be described by a wavefunction.

1.6.4 Probability currents

The complex wave function $\Psi(x,t)$ can always be expressed through to real functions using the polar representation

$$\Psi(x,t) = \sqrt{\rho(x,t)}e^{i\varphi(x,t)}. \tag{1.47}$$

We already know to interpret $\rho(x,t) = |\Psi(x,t)|^2$ as local probability density. Let us clarify a bit further the meaning of the complex phase $\varphi(x,t)$. Inserting (1.47) into the TDSE (1.2) we can

write:

$$i\hbar\left[\dot{\rho}(x,t)\frac{1}{2\sqrt{\rho(x,t)}}e^{i\varphi(x,t)} + i\dot{\varphi}(x,t)\sqrt{\rho(x,t)}e^{i\varphi(x,t)}\right]$$

$$= -\frac{\hbar^2}{2m}\left(\frac{\rho''(x,t)}{2\sqrt{\rho(x,t)}} + i\sqrt{\rho(x,t)}\varphi''(x,t) - \sqrt{\rho(x,t)}\varphi'(x,t)^2 + i\frac{\rho(x,t)'\varphi'(x,t)}{\sqrt{\rho(x,t)}}\right.$$

$$\left. - \frac{\rho(x,t)'^2}{4\rho(x,t)^{3/2}}\right)e^{i\varphi(x,t)} + V(x)\sqrt{\rho(x,t)}e^{i\varphi(x,t)}. \tag{1.48}$$

We have used the notation $\frac{\partial^2}{\partial x^2}f(x) = f''$ and otherwise just used the chain and product rules for differentiation. At this point we can divide both sides by $e^{i\varphi(x,t)}$ and then separately equate the real and imaginary parts of the left and right hand sides, since all variables are now real. This yields:

$$-\hbar\dot{\varphi}(x,t)\sqrt{\rho(x,t)} = -\frac{\hbar^2}{2m}\left(\frac{\rho''(x,t)}{2\sqrt{\rho(x,t)}} - \sqrt{\rho(x,t)}\varphi'(x,t)^2 - \frac{\rho'(x,t)^2}{4\rho(x,t)^{3/2}}\right) + V(x)\sqrt{\rho(x,t)}, \tag{1.49}$$

$$\hbar\dot{\rho}(x,t)\frac{1}{2\sqrt{\rho(x,t)}} = -\frac{\hbar^2}{2m}\left(\sqrt{\rho(x,t)}\varphi''(x,t) + \frac{\rho'(x,t)\varphi'(x,t)}{\sqrt{\rho(x,t)}}\right). \tag{1.50}$$

We multiply Eq. (1.49) by $-(\hbar\sqrt{\rho(x,t)})^{-1}$ and Eq. (1.50) by $2\sqrt{\rho(x,t)}/\hbar$ to reach

$$\dot{\varphi}(x,t) = -\frac{\hbar}{2m}\left(\frac{\rho''(x,t)}{2\rho(x,t)} + \varphi'(x,t)^2 + \frac{\rho'(x,t)^2}{4\rho(x,t)^2}\right) - V(x)/\hbar, \tag{1.51}$$

$$\dot{\rho}(x,t) = -\frac{\hbar}{m}\left(\rho(x,t)\varphi''(x,t) + \rho'(x,t)\varphi'(x,t)\right) = -J'(x,t), \tag{1.52}$$

where we have used the

Probability current for a wavefunction $\Psi(x,t)$ is

$$J(x,t) = \frac{i\hbar}{2m}\left[\Psi\frac{\partial\Psi^*}{\partial x} - \Psi^*\frac{\partial\Psi}{\partial x}\right] = \frac{\hbar}{m}\mathfrak{Im}\left[\Psi^*\frac{\partial\Psi}{\partial x}\right] = \frac{\hbar}{m}\rho(x,t)\frac{\partial\varphi(x,t)}{\partial x} \tag{1.53}$$

The second equation, (1.52), takes the form of a continuity equation involving the probability density and probability current, just like we would have e.g. in hydrodynamics for the particle density and particle current.[7]

Integrating the LHS of (1.52) over $\int_a^b dx\cdots$, we can write for the total probability in the interval $[ab]$ that

$$\dot{P}_{ab} = J(a) - J(b), \tag{1.54}$$

see section 1.5.2, i.e. the total probability in that interval changes according to the difference of the ingoing and outgoing probability current.

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[7]We can even write Eq. (1.51) in a form similar to Bernoulli's equation in hydrodynamics, but now involving a so-called quantum pressure

1.6.5 Stationary states

So far, we have spent most of this section with a general discussion of quantum mechanical principles. In the next section we want to finally start solving stuff and seeing real examples. Solving the TDSE (1.2) analytically is not possibly in all cases. Particularly note that this is a partial differential equation (PDE), containing partial derivatives with respect to at least two variables, x and t.

A huge simplification is possible, whenever the Hamiltonian $\hat{H}$ in (1.39) does not explicitly depend on time. This would for example be true for a plain harmonic oscillator potential $V(x) = \frac{1}{2}m\omega^2 x^2$, but not the driven oscillator potential $V(x,t) = \frac{1}{2}m\omega^2(x - x_0\cos[\omega t])^2$. Note that we are talking about the potential energy function $V(x)$ in the Hamiltonian, not the actual potential energy of the particle, which is $\langle V(x) \rangle = \int dx \Psi^*(x,t)V(x)\Psi(x,t)$. The latter may be time dependent even if $V(x)$ is not.

For a time-independent Hamiltonian, we can tackle the TDSE with

> **Separation of variables:** This is a trick to reduce the complexity of PDEs. Consider a generic PDE for a function $f(a,b)$ of two variables a, b
>
> $$P\left[a, \frac{\partial}{\partial a}, b, \frac{\partial}{\partial b}, f(a,b)\right] = 0. \tag{1.55}$$
>
> We make the attempt to write the solution as a product $f(a,b) = g(a)h(b)$ of two functions that depend only on one variable, and insert this into (1.55).
> We then attempt to segregate everything that depends on a on the LHS and everything that depends on b on the RHS to write
>
> $$P_1\left[a, \frac{\partial}{\partial a}, g(a)\right] = P_2\left[b, \frac{\partial}{\partial b}, g(b)\right], \tag{1.56}$$
>
> we conclude that *both sides have to be equal to the same constant*:
>
> $$P_1\left[a, \frac{\partial}{\partial a}, g(a)\right] = const = P_2\left[b, \frac{\partial}{\partial b}, g(b)\right]. \tag{1.57}$$
>
> We can now solve the two equations obtained separately, which is much easier since they each involve *only one variable*.

- Proof: The LHS will overall be a function of a, and the RHS of b. The equation (1.56) implies that LHS=RHS for all possible combinations of values for a and b. Suppose the equation is correct for some values a_0, b_0 hence $LHS(a_0) = RHS(b_0)$, if either of them was not constant (say RHS), we can find another value $b \neq b_0$ such that $RHS(b_0) \neq RHS(b)$, hence also $LHS(a_0) \neq RHS(b)$, which proves the assertion by contradiction.

- We only discussed the case of two variables above, but it may work also for many. In that case we first "separate off" one of them as above (bring it to LHS and all others to the RHS). We then repeat the process with the equation we reached for the RHS. We shall see an example in chapter (4), dealing with the Hydrogen atom.

- In the box above we mentioned "attempt to" many times: The procedure of course *does not work* for most PDEs. If it does, we are lucky.

- IF it does work however, we typically know that we have found ALL solutions, despite the apparent restrictiveness of our "guess" $f(a,b) = g(a)h(b)$. This is due to some theorem the mathematicians can provide that tells us how many different solutions a certain PDE can have. In our cases, it will mean IF the guess works, it is ALL the solutions.

Let us now apply "Separation of variables" to the TDSE for the case of a time-independent Hamiltonian, which will also serve as a practical example. We make the Ansatz $\Psi(x,t) = \phi(x)c(t)$ as in the box above ($a \to x$, $b \to t$), insert this into (1.2) and apply derivatives, to find:

$$i\hbar\phi(x)\frac{\partial}{\partial t}c(t) = -\frac{\hbar^2}{2m}c(t)\frac{\partial^2}{\partial x^2}\phi(x) + V(x)\phi(x)c(t). \tag{1.58}$$

We now divide both sides by $\phi(x)c(t)$:

$$i\hbar\frac{\frac{\partial}{\partial t}c(t)}{c(t)} = -\frac{\hbar^2}{2m}\frac{\frac{\partial^2}{\partial x^2}\phi(x)}{\phi(x)} + V(x). \tag{1.59}$$

At this point we have reached the form (1.56) where all time dependence is on the left and all space dependence on the right. LHS and RHS thus have to be equal to the same constant. We call that constant E, and re-write the two resultant equations as:

$$i\hbar\frac{\partial}{\partial t}c(t) = Ec(t), \tag{1.60}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi(x) + V(x)\phi(x) = E\phi(x). \tag{1.61}$$

We have now turned the PDE (1.2) into two *ordinary differential equations* (ODEs). The first one (1.60) is easy to solve as $c(t) = c(0)e^{-iEt/\hbar}$. Since we care only about the product $\phi(x)c(t)$ later, we can absorb $c(0)$ into $\phi(x)$ and write $c(t) = e^{-iEt/\hbar}$ for now. The second equation is called

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Time-independent Schrödinger equation (TISE) for the <u>Hamiltonian</u> $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\phi_n(x) = \hat{H}\phi_n(x) = E_n\phi_n(x). \tag{1.62}$$

- Note that we have added the subscript n to $\phi(x)$ in Eq. (1.62), to indicate that an equation of type (1.62) typically has many solutions, as you have already seen in PHY106 (weeks 8 and 9). Often we can take these as countably infinite, then we use an integer $n \in \mathbb{Z}$. They can also be uncountably infinite, so we should better use a real label k to distinguish different solutions $\phi(k,x)$.

(i) **Solutions $\phi(x)$ of the TISE are stationary states:** The complete wave function $\phi(x)e^{-iEt/\hbar}$ does depend on time, however in such a way that the probability density $\rho(x)$ does not:

$$\rho(x,t) = |\Psi(x,t)|^2 = \Psi^*(x,t)\Psi(x,t) = \phi^*(x)e^{iEt/\hbar}\phi(x)e^{-iEt/\hbar} = |\phi(x)|^2 \equiv \rho(x). \tag{1.63}$$

The same will be true for the expectation value (see Eq. (1.41)) of any operator (exercise).

(ii) **Solutions $\phi_n(x)$ of the TISE have a definite energy:** We had seen in section 1.6.2 that the total energy is represented by the Hamiltonian $\hat{H}$. For its expectation value in the state $\phi_n(x)$ we can thus write

$$\langle \hat{H} \rangle = \int dx\, \phi_n^*(x) \hat{H} \phi_n(x) \overset{Eq.\ (1.62)}{=} \int dx\, \phi_n^*(x) E_n \phi_n(x) = E_n \int dx\, |\phi_n(x)|^2 \overset{Eq.\ (1.27)}{=} E_n. \tag{1.64}$$

Similarly we can calculate the uncertainty using Eq. (1.42) and find $\sigma_H^2 = 0$ (exercise/Griffith). The state thus has energy E_n (which is why we used that letter to denote the constant arising in separation of variables) and that energy has no fluctuations (it is definite).

(iii) **The set of all solutions $\phi_n(x)$ of the TISE also provides us with all solutions of the TDSE:** For this, we compare Eq. (1.62) with Eq. (1.23), to see that the TISE is the eigenvalue equation of the Hamiltonian, thus E_n are its eigenenergies and $\phi_n(x)$ the corresponding eigenfunctions. Since $\hat{H}$ is a Hermitian operator (see Eq. (1.24)), we know that all energies E_n have to be real and that the eigenfunctions $\phi_n(x)$ always form a complete orthonormal basis of the Hilbertspace, see Eq. (1.25). This is an extremely powerful statement, as we shall see now. Recall from the comment after Eq. (1.2), that the TDSE predicts the future wavefunction $\Psi(x, t > 0)$ from some initial state $\Psi(x, t = 0) \equiv \Psi_0(x)$. Since the $\phi_n(x)$ form a basis, we can expand the initial state as

$$\Psi_0(x) = \sum_n c_n(0) \phi_n(x), \tag{1.65}$$

for some *complex or real* coefficients $c_n(0)$. Due to the orthogonality Eq. (1.26) of the eigenfunctions $\phi_n(x)$, we can find these coefficients using:

$$c_k(0) = \int dx\, \phi_k^*(x) \Psi_0(x), \tag{1.66}$$

as you can show as an exercise. The same expansion must be possible at any later time, so we write

$$\Psi(x, t) = \sum_n c_n(t) \phi_n(x), \tag{1.67}$$

and insert this into the TDSE (1.2). We obtain

$$i\hbar \sum_n \dot{c}_n(t) \phi_n(x) = \sum_n c_n(t) \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \phi_n(x),$$

$$\overset{Eq.\ (1.62)}{=} \sum_n c_n(t) E_n \phi_n(x). \tag{1.68}$$

We now integrate both sides over $\int dx \phi_k^*(x) \cdots$. This is called "projecting the equation onto $\phi_k(x)$ and completely analogous to taking the scalar product $\mathbf{v} \cdot \ldots$ on both sides of a vector equation (this would be called "projecting onto $\mathbf{v}$"). Using again (1.26), this gives us (after dividing by $\phi_k(x)$):

$$i\hbar \dot{c}_k(t) = c_k(t) E_k, \tag{1.69}$$

which is solved by $c_k(t) = c_k(0)e^{-iE_k t/\hbar}$. We already know that $c_k(0)$ is given by Eq. (1.66), with $\Psi_0(x)$ assumed known. We thus reached the

General solution of the TDSE for a time-independent Hamiltonian:

$$\Psi(x,t) = \sum_n c_n(0)e^{-iE_n t/\hbar}\phi_n(x). \qquad (1.70)$$

We will come back to all statements in this week in the next few weeks, which serve as extensive example collection.