A.5 Stationary and non-stationary states

a. Stationary states (Hemmer p 34, Griffiths p 21)

In Hemmer p 34 or Griffiths p 21, you can see how the concept of a **stationary state** arises naturally if one tries to separate the space and time dependence of the Schrödinger equation, by writing

$$\Psi(x,t) = \psi(x)f(t).$$

It then turns out that the separation of the partial differential Schrödinger equation is possible only if

- (i) $\hat{H}$ is time independent,

- (ii) $\psi(x)$ is an eigenfunction of $\hat{H}$,

that is, ψ must be a solution of the time-independent Schrödinger equation, $\hat{H}\psi_E(x) = E\psi_E(x)$.

It is then very easy to find $f(t)$. The time-dependent Schrödinger equation gives

$$i\hbar \frac{\partial f}{\partial t} \cdot \psi_E(x) = f(t)\,\hat{H}\psi_E(x) = f(t)\,E\,\psi_E(x).$$

Here, the partial derivative $\partial/\partial t$ means d/dt with x kept fixed. And keeping x fixed, it is very easy to integrate the equation above over time, from 0 to t:

$$\frac{df}{f} = -\frac{iE}{\hbar}\,dt \qquad \Longrightarrow \qquad \ln f(t) = \ln f(0) - \frac{iEt}{\hbar}, \qquad \Longrightarrow$$

$$f(t) = f(0)\,e^{-iEt/\hbar}.$$

Absorbing the constant $f(0)$ into $\psi(x)$, we then have

$$\boxed{\Psi_E(x,t) = \psi_E(x)\,e^{-iEt/\hbar}.}$$

This is called a **stationary solution** of the Schrödinger equation, because

- the probability density $|\Psi_E(x,t)|^2 = |\psi_E(x)|^2$ is time independent (doesn't "move")

- all observables which do not depend explicitly on time, like x, p_x, E etc, have time-independent expectation values in the stationary state $\Psi_E(x,t)$. Thus, if $F = F(x, p_x)$, then

$$\begin{aligned}
\langle F \rangle_{\Psi_E} &= \int \Psi_E^*(x,t)\,\hat{F}(x,\hat{p}_x)\,\Psi_E(x,t)dx \\
&= \int \psi_E^*(x)\,\hat{F}(x,\hat{p}_x)\,\psi_E(x)dx = \text{constant},
\end{aligned}$$

(since the time-dependent exponentials in the integrand cancel). This means that the exponential $\exp(-iEt/\hbar)$ really doesn't matter for a stationary state, it can not be measured, and it has no measurable consequences. Thus, there is no measurable development in time in a stationary state; *nothing happens*. So the state really deserves its name. Why, then, are we so interested in these states? There are (at least) four reasons:

Reason 1: When the system has the lowest possible energy (in the ground state), all the properties of the system are determined by the energy eigenfunction of this state. So, even if nothing happens in this stationary state, the wave function is what determines the **form** and the **size** of the system. This goes for a single atom, but also for aggregate states like more or less complex molecules, crystals, etc. The same applies for excited states, for which the size and the form will in principle be different.

Reason 2: Since $\psi_E(x)$ [and also $\Psi_E(x,t) = \psi_E(x)\exp(-iEt/\hbar)$] are eigenfunctions of $\hat{H}$ (and $\hat{H}^2$) with eigenvalues E (and E^2), *the energy is sharply defined* in a stationary state, with $\Delta E = 0$. [Remember that $(\Delta E)^2 = \langle\,(E - \langle\,E\,\rangle)^2\,\rangle = \langle\,E^2\,\rangle - \langle\,E\,\rangle^2$.] These energies are important when the system is excited or de-excited. (Cf **spectral lines**, and see for example the discussion pp 165 – 175 in Brehm & Mullin.)

b. Non-stationary states

Reason 3: According to the superposition principle (section A.1), any linear combination of the stationary states $\Psi_n(x,t) = \psi_n(x)\exp(-iE_nt/\hbar)$ is a solution of the Schrödinger equation, and thus represents a possible physical state for the system:

$$\boxed{\Psi(x,t) = \sum_n c_n\,\Psi_n(x,t) = \sum_n c_n\,\psi_x(x)\,e^{-iE_nt/\hbar}.}$$

Here, the coefficients c_n are arbitrary complex constants, and $\Psi(x,t)$ is normalized if $\sum_n |c_n|^2 = 1$ (provided that the set $\psi_n(x)$ is orthonormal). In fact, this expansion is the most general solution of the Schrödinger equation, that is, *all* solutions can be expanded in stationary states.

If the sum contains terms with *different* energies E_n, this sum is *not* an eigenfunction of the Hamiltonian $\hat{H}$, and $\Psi(x,t)$ is a non-stationary state. For such a state, the probability density $|\Psi(x,t)|^2$ and (some of) the expectation values $\langle\,F\,\rangle_\Psi$ will depend on the time. The reason of course is that the phase factors $\exp(-iE_nt/\hbar)$ "run around the unit circle with different speeds", or different periods $T_n = 2\pi\hbar/E_n$. So here these phase factors (or rather the ratios between them) become important.

Reason 4: In the generic quantum problem, we are given an initial wave function $\Psi(x,0)$ at time $t=0$, and are asked to find $\Psi(x,t)$. Since $\Psi(x,t)$ can always be expanded in stationary states,

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

the problem is essentially solved if we can find the expansion coefficients c_n. These are determined by the initial state, for which the expansion becomes

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

This should tell us at once that c_n is the projection of $\Psi(x,0)$ on the eigenfunction $\psi_n(x)$, but it is also very easy to do the calculation:

$$\langle\,\psi_n,\Psi(0)\,\rangle = \left\langle\,\psi_n,\sum_k c_k\psi_k\,\right\rangle = \sum_k c_k\langle\,\psi_n,\psi_k\,\rangle = \sum_k c_k\delta_{nk} = c_n, \quad \text{q.e.d.}$$

Thus, the time-dependent wave function is

$$\Psi(x,t) = \sum_n \langle \psi_n, \Psi(0) \rangle \, \psi_n(x) \, e^{-iE_n t/\hbar},$$

where the projection of the initial state on ψ_n is

$$\langle \psi_n, \Psi(0) \rangle \equiv \int_{-\infty}^{\infty} \psi_n^*(x) \Psi(x,0) dx.$$

The *trivial* example is if we choose one of the energy eigenfunctions as the initial state, $\Psi(x,0) = \psi_i(x)$. Then,

$$c_n = \langle \psi_n, \Psi(0) \rangle = \langle \psi_n, \psi_i \rangle = \delta_{ni},$$

and the system *stays* in the corresponding stationary state:

$$\Psi(x,t) = \sum_n \delta_{ni} \psi_n(x) \, e^{-iE_n t/\hbar} = \psi_i(x) \, e^{-iE_i t/\hbar} \equiv \Psi_i(x,t).$$

Conclusion: The first line of attack for any quantum-mechanical problem with a time-independent Hamiltonian is to find the set of energy eigenfunctions $\psi_n(x)$ and the corresponding stationary states $\Psi_n(x,t) = \psi_n(x) \exp(-iE_n t/\hbar)$.

c. When $\hat{H}$ is time dependent, $\hat{H} = \hat{H}(t)$,

it follows from the argument in Hemmer that stationary solutions do not exist. As an example, consider a hydrogen atom influenced by an electromagnetic wave, $\mathcal{E} = \mathcal{E}_0 \cos(\mathbf{k}\cdot\mathbf{r} - \omega t)$.

If one neglects the interaction with this electromagnetic field, the system is described by the time-independent Hamiltonian $\hat{H}_0 = -(\hbar^2/2m)\nabla^2 - e^2/(4\pi\epsilon_0 r)$, with the well-known bound-state eigenfunctions $\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta,\phi)$.

To take into account the **perturbative force** from the electromagnetic field, we would have to add a time-dependent term $\hat{H}'(t)$ to $\hat{H}_0$, corresponding to the oscillatory force. With the resulting time-dependent Hamiltonian, $\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$, the Schrödinger equation $i\hbar\partial\Psi/\partial t = \hat{H}\Psi$ has *no* stationary solutions. And, of course, the stationary solutions for the unperturbed system, which include the bound states

$$\Psi_{nlm}(\mathbf{r},t) = R_{nl}(r)Y_{lm}(\theta,\phi) \, e^{-iE_n t/\hbar},$$

are *not* solutions of $i\hbar\partial\Psi/\partial t = \hat{H}\Psi$. However, these unperturbed solutions, denoted for simplicity by $\Psi_k^{(0)}(\mathbf{r},t)$ (where k is shorthand for the necessary indices) still turn out to be very useful:

Firstly, we are still allowed to choose one of them, $\psi_i^{(0)}(\mathbf{r})$, as the *initial state* of the system at $t = 0$. (We are allowed to choose *any* initial state.) For example, we can prepare the hydrogen atom in the unperturbed ground state at $t = 0$, even in the presence of an electromagnetic wave.

Secondly, it turns out to be useful to expand the unknown wave function $\Psi(\mathbf{r},t)$ for the perturbed system in the **un**perturbed solutions:

$$\Psi(\mathbf{r},t) = \sum_k c_k(t)\Psi_k^{(0)}(\mathbf{r},t).$$

This is allowed because the unperturbed set $\Psi_k^{(0)}(\mathbf{r}, t) = \psi_k^{(0)}(\mathbf{r}) \exp(-iE_k t/\hbar)$ is complete. But note that in this case the expansion coefficients c_k are not time independent:

   With the initial state $\Psi(\mathbf{r}, 0) = \psi_i^{(0)}(\mathbf{r})$, we thus start out with the coefficient $c_0 = 1$,   while all the others are equal to zero. But, since the unperturbed state $\Psi_i^{(0)}(\mathbf{r}, t)$ is not a solution of $i\hbar \partial \Psi/\partial t = \hat{H}\Psi$, the system will not stay in this state. This means that the coefficient $c_i(t)$ (which is the probability amplitude to find the system in the initial state) will be reduced from 1, while some of the other coefficients start to increase from zero. We remember that $|c_k(t)|^2$ is the probability to measure the energy E_k and leave the system in the corresponding eigenstate, or as we frequently put it: to "find" the system in the eigenstate $\psi_k^{(0)}$ of $\hat{H}_0$. Thus, for $k \neq i$, $|c_k(t)|^2$ are **transition probabilities**; the atom which was prepared for example in the ground state at $t = 0$,   can after time t be "found" in excited states.

   In the next course on quantum mechanics, you will learn to calculate such transition probabilities with the help of **time-dependent perturbation theory**, which is an approximate method. (In most cases, this is the *only* method to treat such problems; see Hemmer p 221 and Griffiths p 298.)

A.6 The free particle. Wave packets

a. Stationary states for the free particle

Consider a free particle in one dimension, $V(x) = 0$. In this case, it is very easy to solve the time-independent Schrödinger equation,

$$\hat{H}\,\psi(x) = E\,\psi(x),$$

which takes the form

$$\frac{d^2\psi}{dx^2} = -k^2\,\psi, \qquad \text{with} \quad k \equiv \frac{1}{\hbar}\sqrt{2mE}.$$

As solutions we could use $\sin kx$ and $\cos kx$ (which we recognize from the discussion of the one-dimensional box), but here we shall use instead $\exp(\pm ikx)$.

   We arrive at the same solutions if we start with the plane-wave eigenfunctions

$$\psi_p(x) = (2\pi\hbar)^{-1/2}\, e^{ipx/\hbar}$$

of the momentum operator $\hat{p}_x$: Since

$$\hat{p}_x\psi_p(x) = p\,\psi_p(x),$$

we have

$$\hat{H}\,\psi_p(x) = \frac{\hat{p}_x^2}{2m}\,\psi_p(x) = \frac{p^2}{2m}\,\psi_p(x).$$

Thus, $\psi_p(x)$ is an energy eigenfunction (for the free particle) with energy E if we choose either of the two p-values

$$p = \pm\sqrt{2mE} = \pm\hbar k.$$

In any case, we find *two* unbound energy eigenfunctions for each energy $E > 0$ (degeneracy 2). For $E = 0$, there is only one solution, $\psi = (2\pi\hbar)^{-1/2} = $ constant. Thus the spectrum is $E \in [0, \infty)$. This means that the complete set of momentum eigenfunctions $\psi_p(x)$ is also a complete set of eigenfunctions of the free-particle Hamiltonian $\hat{H} = \hat{p}_x^2/2m$. And the corresponding set of stationary solutions,

$$\boxed{\Psi_p(x,t) = \psi_p(x)\, e^{-i(p^2/2m)t/\hbar}, \qquad\qquad (E = p^2/2m),}$$

is also complete.

b. Non-stationary states for the free particle

Since the plane waves require delta-function normalization (see section A.3.g), none of the stationary states represents a physically realizable state, strictly speaking. A localized (square integrable) state therefore has to be non-stationary. Inspired by the discussion above (cf "Reason 4"), we understand that the wave function $\Psi(x,t)$ for such a state can be determined once the initial state $\Psi(x,0)$ is specified, in the following way:

(i) $\Psi(x,t)$ can always be written as a superposition of the stationary plane waves $\Psi_p(x,t)$:

$$\Psi(x,t) = \int_{-\infty}^{\infty} \phi(p)\, \Psi_p(x,t)dp.$$

[Here, the coefficient function $\phi(p)$ plays the role of the expansion coefficient.]

(ii) Setting $t = 0$, we have

$$\Psi(x,0) = \int_{-\infty}^{\infty} \phi(p)\, \psi_p(x)dp.$$

This means that $\phi(p)$ is the projection of the initial state $\Psi(x,0)$ on $\psi_p(x)$,

$$\phi(p) = \langle\, \psi_p, \Psi(0)\, \rangle \equiv \int_{-\infty}^{\infty} \psi_p^*(x)\Psi(x,0)dx,$$

and this can be calculated once $\Psi(x,0)$ is specified.

(iii) Putting $\phi(p)$ back into the integral for $\Psi(x,t)$, we can find out how $\Psi(x,t)$ develops with time. We shall use this method in an exercise to study the behaviour of a free-particle wave packet.

c. Phase velocity. Dispersion

Without specifying $\Psi(x,0)$, it is still possible to investigate some of the general properties of free-particle wave functions. We start by noting that the plane wave entering the integral for $\Psi(x,t)$ is of the form

$$e^{i(kx-\omega t)},$$

with

$$k = \frac{p}{\hbar} \qquad \text{and} \qquad \omega = \frac{E}{\hbar} = \frac{\hbar k^2}{2m}.$$

Let us make a digression, and consider for a moment electromagnetic waves in *vacuum*, for which $\omega = c|\mathbf{k}|$. This means that a harmonic electromagnetic wave travelling in the x-direction is described essentially by a wave function of the form

$$e^{i(kx-\omega t)} = e^{ik(x-ct)}$$

(or rather the real part of this). The crests of this wave travel with the velocity

$$v_{ph} = \frac{\omega}{k} = c.$$

Thus, the so-called **phase velocity** is independent of the wave number k; waves with different wave lengths all travel with the same velocity:
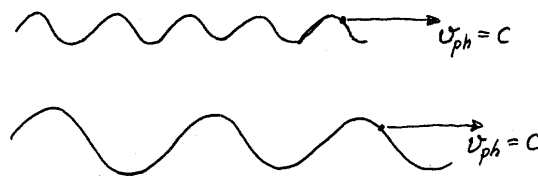
By superposing plane harmonic waves like these, we can make a wave packet,

$$f(x,t) = \int_{-\infty}^{\infty} \phi(k)\, e^{i(kx-\omega t)} dk = \int_{-\infty}^{\infty} \phi(k)\, e^{ik(x-ct)} dk.$$
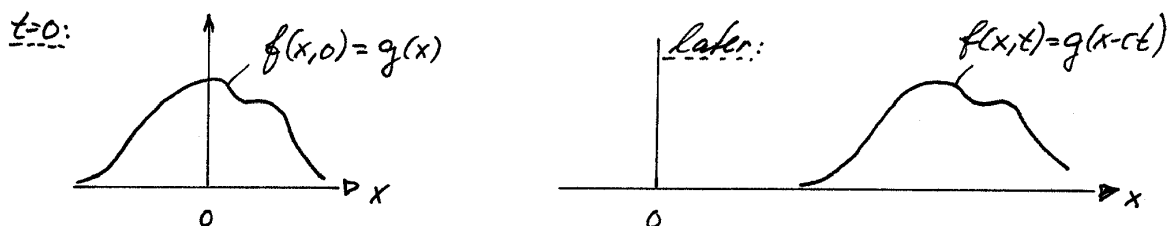
Each component wave $\exp[ik(x-ct)]$ in this superposition moves with the same speed c. Then we understand that also the resulting *sum* (the integral) of these waves will travel with speed c and *unchanged form.*

This also follows from the formula above. If we denote

$$f(x,0) = \int_{-\infty}^{\infty} \phi(k)\, e^{ikx} dk$$

by $g(x)$, we see from the right-hand side further up on the page that

$$f(x,t) = g(x - ct) :$$

Thus a plane electromagnetic pulse travels with unchanged form in vacuum.

In an optical fiber, on the other hand, the phase velocity depends slightly on the wavelength, and the component waves of a pulse will travel with slightly different velocities. The pulse will then be distorted during propagation. This means that if we start out with a sharp pulse corresponding to a broad band of wavelengths, it will after some time tend to spread. This is known as **dispersion**, and is the reason for calling the relation

$$\omega = \omega(k)$$

the **dispersion relation**.

d. Group velocity

After this digression, let us see what we can learn from the dispersion relation

$$\omega = \frac{\hbar}{2m} k^2$$

for the free-particle plane wave

$$\Psi_p(x,t) = \psi_p(x)e^{-i(p^2/2m)t/\hbar} \ \propto \ e^{i(kx-\omega t)}.$$

Firstly, we note that the phase velocity of this harmonic wave,

$$v_{ph} = \frac{\omega}{k} = \frac{\hbar k}{2m} = \frac{p}{2m},$$

is half the classical velocity of the particle. This desn't bother us at all. The phase velocity, like the phase itself, of the de Broglie wave is not observable, and neither is the phase of any other quantum-mechanical wave function. This is contrary to the case for classical waves, like for example surface waves in water.

Secondly, we note that the phase depends strongly on the wavelength, being proportional to k. To see what this means, let us make a wave packet,

$$\Psi(x,t) = \int_{-\infty}^{\infty} \phi(k)\, e^{i(kx-\omega t)} dk, \qquad \omega = \omega(k),$$

using a wave-number distribution $\phi(k)$ reasonably narrowly peaked about a central value k_0, corresponding to a momentum distribution around $p_0 = \hbar k_0$:
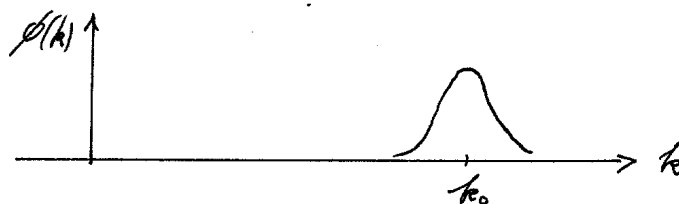
We suppose that the width (Δk) of the distribution is not very large. It is then natural to consider the Taylor expansion of $\omega(k)$ about the central value k_0,

$$\omega(k) = \omega(k_0) + (k - k_0) \left.\frac{d\omega}{dk}\right|_{k_0} + \frac{1}{2!}(k - k_0)^2 \left.\frac{d^2\omega}{dk^2}\right|_{k_0}.$$

In the present case, there are no higher-order terms in this expansion, because ω goes as k^2. We find

$$\begin{aligned}
\omega(k_0) &= \frac{\hbar}{2m} k_0^2 \equiv \omega_0, \\
\left.\frac{d\omega}{dk}\right|_{k_0} &= \frac{\hbar}{m} k_0 \equiv v_g, \\
\left.\frac{d^2\omega}{dk^2}\right|_{k_0} &= \frac{\hbar}{m}.
\end{aligned}$$

With this notation, the (exact) expansion of $\omega(k)$ around k_0 is

$$\omega(k) = \omega_0 + v_g(k - k_0) + \frac{\hbar}{2m}(k - k_0)^2.$$

Since we are assuming a narrow distribution $\phi(k)$, the last term must be small. So, let us try to drop this term, using the approximation

$$\omega(k) \approx \omega_0 + v_g(k - k_0).$$

Inserting this into the integral for $\Psi(x,t)$, and moving the factors which do not depend on the integration variable k outside the integral, we get

$$\begin{aligned}
\Psi(x,t) &\approx \int_{-\infty}^{\infty} \phi(k) \, e^{i(kx - [\omega_0 + v_g(k-k_0)]t)} dk \\
&= e^{-i\omega_0 t} e^{ik_0 v_g t} \int_{-\infty}^{\infty} \phi(k) \, e^{ik(x - v_g t)} dk.
\end{aligned}$$

For $\quad t = 0, \quad$ this simplifies to

$$\Psi(x,0) = \int_{-\infty}^{\infty} \phi(k) \, e^{ikx} dk \equiv g(x).$$

Inspired by the digression above, we here denote the latter integral by $g(x)$. Then the integral in the expression for $\Psi(x,t)$ obviously is $\quad g(x - v_g t) = \Psi(x - v_g t, 0)$. Thus, without actually doing any calculations, we find that the approximation $\quad \omega \approx \omega_0 + v_g(k - k_0)$ leads to the result

$$\Psi(x,t) \approx e^{-it(\omega_0 - k_0 v_g)} \, \Psi(x - v_g t, 0).$$

Apart from the unimportant phase factor, we see that the wave packet has the same form as for $\quad t = 0; \quad$ it has only moved a distance $v_g t$ during time t. Thus, the quantity v_g, which was defined as $\quad v_g \equiv d\omega/dk|_{k_0}, \quad$ is the velocity of the wave packet, or wave "group", as we sometimes prefer to call it. From this we may conclude with the following rule:

> A wave packet containing a narrow distribution $\phi(k)$ of wave numbers centered around the value k_0 will move with the **group velocity**
> $$v_g = \left. \frac{d\omega}{dk} \right|_{k_0}.$$

In the present case, with the dispersion relation $\quad \omega = \hbar k^2/2m, \quad$ we found a group velocity

$$v_g = \frac{\hbar k_0}{m}.$$

We note that this is the classical velocity for a particle with momentum $\quad p_0 = \hbar k_0$, corresponding to the central Fourier component of the wave packet.

We also see that neglecting the quadratic term in the expansion

$$\omega(k) = \omega(k_0) + (k - k_0) \left. \frac{d\omega}{dk} \right|_{k_0} + \frac{1}{2!}(k - k_0^2) \left. \frac{d^2\omega}{dk^2} \right|_{k_0}$$

is the same as neglecting the dispersion of the wave packet. If the quadratic term is included (which in the present case corresponds to using the exact dispersion relation $\omega(k) = \hbar k^2/2m$), one finds that the the wave packet changes form as it propagates.

If one chooses a narrow distribution $\phi(k)$ (small $\Delta p_x = \hbar \Delta k$), corresponding to a large width of the wave packet (large Δx), it takes a long time before the dispersion (spreading) of the wave packet shows up.

If one insists on a narrow packet in x-space (small Δx), this requires a broad distribution of wave numbers (large $\Delta p_x = \hbar \Delta k$), and the dispersion will be much stronger and show up in a short time. (Cf exercises.)