11 Time evolution

11.1 The Schrödinger equation

The time evolution of quantum states is often described by way of time-dependent wave functions, column vectors or ket vectors satisfying the Schrödinger equation. E.g.,

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi(x,y,z,t) \tag{11.1}$$

if we describe the quantum states of the system by time-dependent wave functions $\Psi(x,y,z,t)$, or

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle \tag{11.2}$$

if we describe them by time-dependent state vectors $|\Psi(t)\rangle$.

You probably remember to have seen most of the following results and definitions, if not all of them:

1. The operator $\hat{H}$ appearing in Eq. (11.2) is a Hermitian operator called the Hamiltonian of the system.
2. The inner product $\langle\Phi(t)|\Psi(t)\rangle$ is constant if $|\Phi(t)\rangle$ and $|\Psi(t)\rangle$ evolve in time according to the Schödinger equation: $\langle\Phi(t)|\Psi(t)\rangle = \langle\Phi(t')|\Psi(t')\rangle$ for any t, t'. In particular, the norm of a state vector does not change under time evolution.

> ☞ Proof: We see from Eq. (11.2) that to first order in δt,
>
> $$|\Psi(t+\delta t)\rangle = |\Psi(t)\rangle + \frac{1}{i\hbar}\hat{H}|\Psi(t)\rangle\delta t. \tag{11.3}$$
>
> Similarly,
>
> $$\langle\Phi(t+\delta t)| = \langle\Phi(t)| - \frac{1}{i\hbar}\langle\Phi(t)|\hat{H}^\dagger\delta t. \tag{11.4}$$
>
> Therefore, to first order in δt,
>
> $$\langle\Phi(t+\delta t)|\Psi(t+\delta t)\rangle = \langle\Phi(t)|\Psi(t)\rangle + \frac{1}{i\hbar}\langle\Phi(t)|\hat{H}|\Psi(t)\rangle\delta t - \frac{1}{i\hbar}\langle\Phi(t)|\hat{H}^\dagger|\Psi(t)\rangle\delta t. \tag{11.5}$$
>
> The second and third terms in the right-hand side cancel since $\hat{H}$ is Hermitian. Hence, to first order in δt,
>
> $$\langle\Phi(t+\delta t)|\Psi(t+\delta t)\rangle = \langle\Phi(t)|\Psi(t)\rangle. \tag{11.6}$$
>
> Therefore
>
> $$\lim_{\delta t\to 0}\frac{\langle\Phi(t+\delta t)|\Psi(t+\delta t)\rangle - \langle\Phi(t)|\Psi(t)\rangle}{\delta t} = 0, \tag{11.7}$$
>
> which means that $\mathrm{d}\langle\Phi(t)|\Psi(t)\rangle/\mathrm{d}t = 0$. □

3. As the Schrödinger equation is linear and of first order in time, giving $\hat{H}$ and specifying $|\Psi(t)\rangle$ at a time t_0 determines $|\Psi(t)\rangle$ at all times (at least in principle, in practice the Schrödinger equation may be impossible to solve to sufficient accuracy).

4. The eigenvalues and eigenvectors of $\hat{H}$ are defined by the equation

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle, \tag{11.8}$$

and similarly for the continuum eigenstates of $\hat{H}$ if there are any (but then in terms of generalized eigenvalues and generalized eigenvectors, see Section 6.9). The eigenvalues E_n are called the eigenenergies of the system. Since $\hat{H}$ is Hermitian, the eigenergies are real (not complex).

5. $\hat{H}$ may or may not depend on time. For example, the Hamiltonian used in the Term 1 course to describe an unperturbed hydrogen atom,

$$-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r},$$

does not depend on time. By contrast, the Hamiltonian

$$-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + e\,\mathbf{F}(t)\cdot\mathbf{r},$$

which describes an atom of hydrogen perturbed by a time-dependent electric field $\mathbf{F}(t)$, does depend on time. The Hamiltonian is normally time-independent, unless the system it represents is subject to a time-dependent interaction with the rest of the world.

6. If the Hamiltonian is time-independent, then

   (a) The eigenenergies E_n and the energy eigenstates $|\psi_n\rangle$ are also time-independent, and so is Eq. (11.8). This equation is often referred to as the time-independent Schrödinger equation. Eq. (11.2) is the time-dependent Schrödinger equation.

   (b) Given an energy eigenstate $|\psi_n\rangle$ and the corresponding eigenenergy E_n, the ket $|\psi_n\rangle\exp(-iE_nt/\hbar)$ is a solution of Eq. (11.2):

$$\begin{aligned} i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi_n\rangle\exp(-iE_nt/\hbar) &= i\hbar|\psi_n\rangle\frac{\mathrm{d}}{\mathrm{d}t}\exp(-iE_nt/\hbar) \\ &= i\hbar|\psi_n\rangle(-iE_n/\hbar)\exp(-iE_nt/\hbar) \\ &= E_n|\psi_n\rangle\exp(-iE_nt/\hbar) \\ &= \hat{H}|\psi_n\rangle\exp(-iE_nt/\hbar). \end{aligned} \tag{11.9}$$

(c) Imagine an experiment in which the system of interest is prepared in the state $|\psi_n\rangle \exp(-iE_n t/\hbar)$ and a certain observable A is measured on that system at a time t. We assume, for simplicity, that $|\psi_n\rangle$ is an eigenvector of $\hat{H}$ in the usual meaning of the term, not a generalized eigenvector describing a continuum state. Therefore $|\psi_n\rangle$ can be normalized in the usual way ($\langle\psi_n|\psi_n\rangle = 1$), and so does $|\psi_n\rangle \exp(-iE_n t/\hbar)$. As seen in Section 4.2, the probability of each possible outcome of this measurement is given by the square of the modulus of the inner product of $|\psi_n\rangle \exp(-iE_n t/\hbar)$ with a normalized eigenvector $|phi\rangle$ of the Hermitian operator representing A,

$$|\langle\phi|\psi_n\rangle \exp(-iE_n t/\hbar)|^2,$$

or by a sum of such square moduli in case of degenerate eigenvalues. (Again, for simplicity we assume that the eigenvalues of interest are discrete, so that the corresponding eigenvectors are normalizable in the usual way.) Since E_n is real, $|\exp(-iE_n t/\hbar)| = 1$ and therefore

$$\begin{aligned} |\langle\phi|\psi_n\rangle \exp(-iE_n t/\hbar)|^2 &= |\langle\phi|\psi_n\rangle|^2 \, |\exp(-iE_n t/\hbar)|^2 \\ &= |\langle\phi|\psi_n\rangle|^2. \end{aligned} \tag{11.10}$$

This result shows that the probability of each possible outcome of a measurement does not depend on the instant at which the measurement is made. It is easy to see that we would arrive to the same conclusion for the probability densities we would need to consider if the eigenvalues of interest belonged to a continuum. As we have not assumed anything specific about the measured observable, the conclusion is that the probability distribution of the results of any measurement which can be made on the system is constant in time. In other words, the eigenvectors of the Hamiltonian describe stationary states, i.e., states whose physical properties are the same at all times.

Stationary states are also states of well defined energy: Since the vector $|\psi_n\rangle \exp(-iE_n t/\hbar)$ is an eigenvector of $\hat{H}$ and eigenvectors corresponding to different eigenenergies are orthogonal, a measurement of the energy in the state $|\psi_n\rangle \exp(-iE_n t/\hbar)$ would give E_n with probability 1. Correspondingly, the uncertainty ΔE in the value of the energy is zero in that state.

(d) Linear combinations of eigenvectors belonging to *different* eigenenergies do *not* describe stationary states. In fact, any solution of Eq. (11.2) can be written as an expansion on the eigenvectors and generalized eigenvectors of $\hat{H}$. Namely, if $|\Psi(t)\rangle$ is a time-dependent

state vector and the Hamiltonian is time-independent, there exists a set of constant coefficients c_n and c_k such that

$$|\Psi(t)\rangle = \sum_n c_n \exp(-iE_n t/\hbar)|\psi_n\rangle + \int c_k \exp(-iE_k t/\hbar)|\psi_k\rangle \, \mathrm{d}k, \tag{11.11}$$

where the $|\psi_n\rangle$'s and $|\psi_k\rangle$'s are, respectively, eigenvectors and generalized eigenvectors of $\hat{H}$ corresponding to the energies E_n and E_k. (As usual, n and k represent the sets of quantum numbers which must be specified to identify each of these eigenstates unambiguously.)

11.2 The evolution operator

Under time evolution, the state of a quantum system changes from one represented at time t_0 by a vector $|\Psi(t_0)\rangle$ to one represented at time t by a vector $|\Psi(t)\rangle$. This time evolution can be described as a transformation of $|\Psi(t_0)\rangle$ into $|\Psi(t)\rangle$, this transformation being effected by an operator $\hat{U}(t, t_0)$ depending on t_0 and t:

$$|\Psi(t)\rangle = \hat{U}(t, t_0)|\Psi(t_0)\rangle. \tag{11.12}$$

More precisely, we define $\hat{U}(t, t_0)$ as being the operator which maps any vector $|\Psi(t_0)\rangle$ to the vector $|\Psi(t)\rangle$ that $|\Psi(t_0)\rangle$ changes into under the time evolution governed by the Schrödinger equation, for any t_0 and any t. This operator is called the evolution operator (or time evolution operator).

The requirement that $|\Psi(t)\rangle$ obeys the Schrödinger equation implies that

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \hat{U}(t, t_0) = \hat{H}\hat{U}(t, t_0). \tag{11.13}$$

Together with the initial condition that $\hat{U}(t = t_0, t_0) = \hat{I}$ (the identity operator), Eq. (11.13) determines the evolution operator at all times once $\hat{H}$ is given.

☞ Proof: Differentiating Eq. (11.12) with respect to time and multiplying each side by $i\hbar$ yields

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t}|\Psi(t)\rangle = i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \hat{U}(t, t_0)|\Psi(t_0)\rangle. \tag{11.14}$$

We also have, from Eq. (11.2),

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle = \hat{H}\,\hat{U}(t, t_0)|\Psi(t_0)\rangle. \tag{11.15}$$

Hence, for any $|\Psi(t_0)\rangle$,

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \hat{U}(t, t_0)|\Psi(t_0)\rangle = \hat{H}\,\hat{U}(t, t_0)|\Psi(t_0)\rangle. \tag{11.16}$$

Eq. (11.13) follows. □

Note that solving Eq. (11.13) is, in general, as difficult as solving Eq. (11.2). The usefulness of introducing the time evolution operator lies primarily in the interesting theoretical developments possible in this approach. However, in the frequent case where the Hamiltonian $\hat{H}$ is time-independent, a formal solution of Eq. (11.13) can be written as

$$\hat{U}(t, t_0) = \exp[-i\hat{H}(t - t_0)/\hbar]. \tag{11.17}$$

(See Section 3.3 for the definition of the exponential of an operator.) We stress that Eq. (11.17) only applies to the case where $\hat{H}$ is time-independent. This equation is generally not correct for time-dependent Hamiltonians.

Whether Eq. (11.17) applies or not, the evolution operator has the following properties:

1. $\hat{U}(t_0, t_0) = \hat{I}$ since we must have that $|\Psi(t_0)\rangle = \hat{U}(t_0, t_0)|\Psi(t_0)\rangle$ for any $|\Psi(t_0)\rangle$.

2. For any t_0, t_1 and t,

$$\hat{U}(t, t_0) = \hat{U}(t, t_1)\hat{U}(t_1, t_0), \tag{11.18}$$

   since going from time t_0 to time t_1 and then from t_1 to t is equivalent to going from t_0 to t.

3. In particular, $\hat{U}(t_0, t_0) = \hat{U}(t_0, t_1)\hat{U}(t_1, t_0)$. Hence

$$\hat{U}(t_0, t)\hat{U}(t, t_0) = \hat{I} = \hat{U}(t, t_0)\hat{U}(t_0, t) \tag{11.19}$$

   for any t_0 and t. Therefore the evolution operator is invertible and

$$\hat{U}(t_0, t) = \hat{U}^{-1}(t, t_0). \tag{11.20}$$

4. $\hat{U}(t, t_0)$ is a unitary operator. Hence

$$\hat{U}^{\dagger}(t, t_0) = \hat{U}^{-1}(t, t_0). \tag{11.21}$$

> ☞ Proof: Let us assume, to start, that the domain of $\hat{H}$ is the whole of the relevant Hilbert space (we'll revisit this assumption at the end of this proof). Consider the inner product of two ket vectors taken at a time t_0, $\langle\Phi(t_0)|\Psi(t_0)\rangle$. We saw, in Section 11.1, that this quantity remains invariant when these two ket vectors evolve according to the Schrödinger equation: $\langle\Phi(t)|\Psi(t)\rangle = \langle\Phi(t_0)|\Psi(t_0)\rangle$ if $|\Psi(t)\rangle = \hat{U}(t, t_0)|\Psi(t_0)\rangle$ and $|\Phi(t)\rangle = \hat{U}(t, t_0)|\Phi(t_0)\rangle$. In terms

of the bra vectors conjugate to the ket vectors $|\Phi(t)\rangle$ and $|\Phi(t_0)\rangle$, $\langle\Phi(t)| = \langle\Phi(t_0)|\hat{U}^\dagger(t,t_0)$. Hence

$$\langle\Phi(t_0)|\hat{U}^\dagger(t,t_0)\hat{U}(t,t_0)|\Psi(t_0)\rangle = \langle\Phi(t_0)|\Psi(t_0)\rangle. \tag{11.22}$$

This equation can also be written as

$$\langle\Phi(t_0)|\hat{U}^\dagger(t,t_0)\hat{U}(t,t_0) - \hat{I}|\Psi(t_0)\rangle = 0 \tag{11.23}$$

and must be true for any $|\Phi(t_0)\rangle$ and any $|\Psi(t_0)\rangle$. In particular, it must be true for any $|\Psi(t_0)\rangle$ and for

$$|\Phi(t_0)\rangle = [\hat{U}^\dagger(t,t_0)\hat{U}(t,t_0) - \hat{I}]|\Psi(t_0)\rangle. \tag{11.24}$$

However, with this choice of ket $|\Phi_0\rangle$, Eq. (11.23) reduces to the equation $\langle\Phi(t_0)|\Phi(t_0)\rangle = 0$, which implies that $|\Phi(t_0)\rangle$ is the zero vector. The operator $\hat{U}^\dagger(t,t_0)\hat{U}(t,t_0) - \hat{I}$ thus maps every vector to the zero vector, which is possible only if $\hat{U}^\dagger(t,t_0)\hat{U}(t,t_0) = \hat{I}$. Multiplying this equation on the right by the inverse of $\hat{U}(t,t_0)$ gives $\hat{U}^\dagger(t,t_0) = \hat{U}^{-1}(t,t_0)$. Therefore $\hat{U}^\dagger(t,t_0)$ is a unitary operator. □

Let us come back to the assumption made at the start that the domain of $\hat{H}$ is the whole Hilbert space (this assumption was made necessary by our use of the Schrödinger equation, which makes sense only for vectors in the domain of the Hamiltonian). This assumption is not inocuous in infinite dimensional Hilbert spaces, but removing it would require to add to the proof a detailed discussion of what the domains of $\hat{H}$, of $\hat{H}^\dagger$, of $\hat{U}(t,t_0)$ and of $\hat{U}^\dagger(t,t_0)$ actually are. However, this complication is unnecessary: time evolution can be defined from the onset as being a unitary transformation effected by a unitary operator $\hat{U}(t,t_0)$ obeying Eq. (11.18), and the Hamiltonian can then be introduced as the self-adjoint operator $\hat{H}$ such that $\hat{U}(t,t_0)$ satisfies Eq. (11.13). (The Hamiltonian is indeed a self-adjoint operator, i.e., $\hat{H}^\dagger = \hat{H}$, not merely a Hermitian operator.) The mathematical basis of this latter approach is an important theorem of functional analysis called the Stone's theorem.

11.3 The Schrödinger picture and the Heisenberg picture

Recall that the expectation value $\langle A\rangle(t)$ of a dynamical variable A represented by an operator $\hat{A}$ is $\langle\Psi(t)|\hat{A}|\Psi(t)\rangle$ if the state of the system is described by the normalized time-dependent vector $|\Psi(t)\rangle$. It is often the case that operators describing dynamical variables do not depend on time (think, e.g., to the position operator, the momentum operator, the orbital angular momentum operator, the spin operator — none of them dependss on t). Hence, to keep the discussion as

simple as possible, we will assume that $\hat{A}$ does not vary in time. Now, since

$$\langle\Psi(t)|\hat{A}|\Psi(t)\rangle = \langle\Psi(t_0)|\hat{U}^\dagger(t,t_0)\hat{A}\hat{U}(t,t_0)|\Psi(t_0)\rangle, \tag{11.25}$$

$\langle A\rangle(t)$ can also be seen as the expectation value of the time-dependent operator

$$\hat{A}_{\rm H}(t) = \hat{U}^\dagger(t,t_0)\hat{A}\hat{U}(t,t_0) \tag{11.26}$$

in the state represented by the time-independent vector $|\Psi(t_0)\rangle$:

$$\langle A\rangle(t) = \langle\Psi(t_0)|\hat{A}_{\rm H}(t)|\Psi(t_0)\rangle. \tag{11.27}$$

Note that Eq. (11.26) can also be written as

$$\hat{A}_{\rm H}(t) = \hat{U}(t_0,t)\hat{A}\hat{U}^\dagger(t_0,t), \tag{11.28}$$

since $\hat{U}^\dagger(t_0,t) = \hat{U}^{-1}(t_0,t) = \hat{U}(t,t_0)$. This alternative form is completely consistent with what we have seen in Section 3.13 about how operators transform under a unitary transformation. Here the transformation is taken to be a time evolution from t to t_0; under this transformation, the vector $|\Psi(t)\rangle$ transforms to $\hat{U}(t_0,t)|\Psi(t)\rangle$ and the operator $\hat{A}$ to $\hat{U}(t_0,t)\hat{A}\hat{U}^\dagger(t_0,t)$. (The operator $\hat{A}_{\rm H}(t)$ is usually time-dependent even when $\hat{A}$ isn't, but we will see in Section 11.4 that there is an important exception to this general rule.)

Remember what we have seen about calculating the probability of finding a particular value of a dynamical variable in a measurement — e.g, that the probability of finding the eigenvalue λ_n of $\hat{A}$ is $|\langle\psi_n|\Psi(t)\rangle|^2$ if λ_n is non-degenerate, if $\hat{A}|\psi_n\rangle = \lambda_n|\psi_n\rangle$ and if the ket vectors $|\psi_n\rangle$ and $|\Psi(t)\rangle$ are normalized. Since $\hat{A}_{\rm H}(t) = \hat{U}(t_0,t)\hat{A}\hat{U}^\dagger(t_0,t)$ and $\hat{U}(t_0,t)$ is a unitary operator, the operator $\hat{A}_{\rm H}(t)$ has the same eigenvalues as the operator $\hat{A}$ (see page 135 in Part 10 of these notes). Moreover, if $\hat{A}|\psi_n\rangle = \lambda_n|\psi_n\rangle$, then (1) $\hat{A}_{\rm H}(t)|\psi_n^{\rm H}(t)\rangle = \lambda_n|\psi_n^{\rm H}(t)\rangle$, where $|\psi_n^{\rm H}(t)\rangle = \hat{U}^\dagger(t,t_0)|\psi_n\rangle$ (i.e., $|\psi_n^{\rm H}(t)\rangle$ is an eigenvector of $\hat{A}_{\rm H}(t)$ corresponding to the eigenvalue λ_n), and also (2) $|\langle\psi_n|\Psi(t)\rangle|^2 = |\langle\psi_n^{\rm H}(t)|\Psi(t_0)\rangle|^2$. (The proof of these two assertions is left as an exercise for the reader.) Thus

$$\Pr(\lambda_n;|\Psi(t)\rangle) = |\langle\psi_n|\Psi(t)\rangle|^2 = |\langle\psi_n^{\rm H}(t)|\Psi(t_0)\rangle|^2. \tag{11.29}$$

We see that the probability of finding λ_n can be calculated either in terms of the ket vector $|\Psi(t)\rangle$ and an eigenvector of $\hat{A}$ or in terms of the ket vector $|\Psi(t_0\rangle$ and an eigenvector of $\hat{A}_{\rm H}(t)$, and these two approaches are completely equivalent. They correspond to two alternative descriptions of quantum systems. The first one is probably the most familiar of the two: quantum states are described

by time-dependent vectors and observables by (usually) time-independent operators. This description is referred to as the Schrödinger picture of Quantum Mechanics (or the Schrödinger representation). The alternative description, in which the states are represented by time-independent vectors and the observables by (usually) time-dependent operators, is referred to as the Heisenberg picture of Quantum Mechanics (or Heisenberg representation).

In the Schrödinger picture, time evolution is governed by the time-dependent Schrödinger equation, Eq. (11.2). Its counterpart in the Heisenberg picture is the Heisenberg equation of motion. If $\hat{A}$ does not depend on time, this equation reads

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \hat{A}_{\mathrm{H}}(t) = [\hat{A}_{\mathrm{H}}(t), \hat{H}_{\mathrm{H}}(t)], \tag{11.30}$$

where

$$\hat{H}_{\mathrm{H}}(t) = \hat{U}(t_0, t) \hat{H} \hat{U}^\dagger(t_0, t). \tag{11.31}$$

☞ These considerations generalize to the case of observables represented by a time-dependent operator even in the Schrödinger picture. E.g., for a time-dependent $\hat{A}(t)$, Eq. (11.28) simply reads $\hat{A}_{\mathrm{H}}(t) = \hat{U}(t_0, t) \hat{A}(t) \hat{U}^\dagger(t_0, t)$. However, Eq. (11.30) only applies to the case where $\hat{A}(t)$ is constant in t. Instead, the Heisenberg equation of motion for the "Heisenberg operator" $\hat{A}_{\mathrm{H}}(t)$ corresponding to a time-dependent "Schrödinger operator" $\hat{A}(t)$ reads

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \hat{A}_{\mathrm{H}}(t) = [\hat{A}_{\mathrm{H}}(t), \hat{H}_{\mathrm{H}}(t)] + i\hbar \hat{U}(t_0, t) \frac{\mathrm{d}\hat{A}}{\mathrm{d}t} \hat{U}^\dagger(t_0, t). \tag{11.32}$$

Proof: Let $\hat{A}_{\mathrm{H}}(t) = \hat{U}^\dagger(t, t_0) \hat{A}(t) \hat{U}(t, t_0)$. Differentiating this product of operators is done by differentiating one operator at a time, as for ordinary functions:

$$\begin{aligned} i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \hat{A}_{\mathrm{H}}(t) = &\left[i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \hat{U}^\dagger(t, t_0) \right] \hat{A}(t) \hat{U}(t, t_0) + \hat{U}^\dagger(t, t_0) \left[i\hbar \frac{\mathrm{d}\hat{A}}{\mathrm{d}t} \right] \hat{U}(t, t_0) \\ &+ \hat{U}^\dagger(t, t_0) \hat{A}(t) \left[i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \hat{U}(t, t_0) \right]. \end{aligned} \tag{11.33}$$

The derivative of $\hat{U}(t, t_0)$ is given by Eq. (11.13). Transforming that equation into an equation for the adjoint operators gives

$$-i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \hat{U}^\dagger(t, t_0) = \hat{U}^\dagger(t, t_0) \hat{H}^\dagger, = \hat{U}^\dagger(t, t_0) \hat{H}, \tag{11.34}$$

where in the last step we have used the fact, mentioned in the note at the end of Section 11.2, that $\hat{H}$ is self-adjoint. Making use of these two relations in Eq. (11.33) yields Eq. (11.32). □

☞ It follows from Eqs. (11.27) and (11.32) and from Eq. (11.36) of Section 11.4 that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle(t) = \frac{1}{i\hbar}\,\langle\Psi(t)|[\hat{A},\hat{H}]|\Psi(t)\rangle + \langle\Psi(t)|\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}|\Psi(t)\rangle, \tag{11.35}$$

which is a general form of the Ehrenfest theorem (you have encountered this theorem in the Term 1 QM course).

11.4 Constants of motion

We now focus on the important case of an observable A represented by an operator $\hat{A}$ which, in the Schrödinger picture, (1) does not depend on time, and (2) commutes with the Hamiltonian.

We have seen, in Section 10.2, how commutators transform under a unitary transformation. Here, Eq. (10.14) says that

$$[\hat{A}_{\mathrm{H}}(t), \hat{H}_{\mathrm{H}}(t)] = \hat{U}(t_0,t)[\hat{A},\hat{H}]\hat{U}^{\dagger}(t_0,t). \tag{11.36}$$

Thus $[\hat{A}_{\mathrm{H}}(t), \hat{H}_{\mathrm{H}}(t)] \equiv 0$ if $[\hat{A},\hat{H}] \equiv 0$. In that case, Eq. (11.30) says that

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\,\hat{A}_{\mathrm{H}}(t) \equiv 0. \tag{11.37}$$

Therefore $\hat{A}_{\mathrm{H}}(t)$ is constant in time and $\hat{A}_{\mathrm{H}}(t) \equiv \hat{A}$ if $\hat{A}$ commutes with $\hat{H}$. In turns, this implies that the probability of finding any given value of the observable A remains the same as t varies. On account of these facts, and by analogy with Classical Mechanics, a dynamical variable represented by an operator $\hat{A}$ commuting with the Hamiltonian is said to be a constant of motion.

☞ For example, take the case of an atom of hydrogen exposed to an external electric field $F_{\mathrm{ext}}(t)\,\hat{\mathbf{z}}$, which varies in time but is spatially uniform ($F_{\mathrm{ext}}(t)$ depends on t but not the position variables x, y and z). The potential energy of the electron changes by $eF_{\mathrm{ext}}(t)z$ due to this electric field, and the Hamiltonian takes on the following form:

$$H = -\frac{\hbar^2}{2\mu}\,\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\,\frac{1}{r} + eF_{\mathrm{ext}}(t)z. \tag{11.38}$$

Because of the interaction term $eF_{\mathrm{ext}}(t)z$, the solutions of the time-dependent Schrödinger equation may be extremely complicated. However, this Hamiltonian commutes with L_z, the z-component of the orbital angular momentum operator. Hence, the z-component of the orbital angular momentum of the electron is a constant of motion. For instance, if at some time the atom is in in a eigenstate of L_z with eigenvalue $m\hbar$, so

that the z-component of the electron's orbital angular momentum is well defined and equal to $m\hbar$, then the atom will remain in an eigenstate of L_z corresponding to that eigenvalue at all times, however complicated the wave function might become as time increases.