Chapter 2
Basics of Quantum Mechanics

*Those who are not shocked when they first come across
quantum theory cannot possibly have understood it.*

— N. Bohr [1]

Abstract Before we can start with the quantum mechanical approach to thermodynamics we have to introduce some fundamental terms and definitions of standard quantum mechanics for later reference. This chapter should introduce the reader only to some indispensable concepts of quantum mechanics necessary for the text at hand, but is far from being a complete overview of this subject. For a complete introduction we refer to standard textbooks [2–7].

2.1 Introductory Remarks

The shortcomings of classical theories had become apparent by the end of the 19th century. Interestingly enough, one of the first applications of quantum ideas has been within thermodynamics: Planck's famous formula for black body radiation was based on the hypothesis that the exchange of energy between the container walls and the radiation field should occur in terms of fixed energy quanta only. Later on, this idea has been put on firmer ground by Einstein postulating his now well-known rate equations [8].

Meanwhile quantum mechanics has become a theory of unprecedented success. So far, its predictions have always been confirmed by experiment.

Quantum mechanics is usually defined in terms of some loosely connected axioms and rules. Such a foundation is far from the beauty of, e.g., the "principles" underlying classical mechanics. Motivated, in addition, by notorious interpretation problems, there have been numerous attempts to modify or "complete" quantum mechanics.

A first attempt was based on so-called "hidden variables" [9]. Its proponents essentially tried to expel the non-classical nature of quantum mechanics. More recent proposals intend to "complete" quantum mechanics not within mechanics, but on a higher level: by means of a combination with gravitation theory [10], with psychology [11], or with (quantum-) information theory [12, 13].

While the emergence of classicality from an underlying quantum substrate has enjoyed much attention recently, it has so far not been appreciated that the under-

standing of quantum mechanics may benefit also from subjects like quantum thermodynamics.

2.2 Operator Representations

In quantum mechanics we deal with systems (Hamilton models), observables, and states. They all are represented by Hermitian operators. Their respective specification requires data (parameters), which have to be defined with respect to an appropriate reference frame. These frames are operator representations. Let us in the following consider some aspects of these operator representations in detail. First we will concentrate on simple systems and their representation.

2.2.1 Transition Operators

If we restrict ourselves to systems living in a finite and discrete Hilbert space $\mathscr{H}$ (a complex vector space of dimension n_{tot}), we may introduce a set of orthonormal state vectors $|i\rangle \in \mathscr{H}$. From this orthonormal and complete set of state vectors with

$$\langle i|j\rangle = \delta_{ij} , \quad i, j = 1, 2, \ldots, n_{\text{tot}} , \tag{2.1}$$

we can define n_{tot}^2 transition operators (in general non-Hermitian)

$$\hat{P}_{ij} = |i\rangle\langle j| , \quad \hat{P}_{ij}^{\dagger} = \hat{P}_{ji} . \tag{2.2}$$

These operators are, again, orthonormal in the sense that

$$\text{Tr}\left\{\hat{P}_{ij}\,\hat{P}_{i'j'}^{\dagger}\right\} = \delta_{ii'}\delta_{jj'} , \tag{2.3}$$

where $\text{Tr}\{\ldots\}$ denotes the trace operation. Furthermore, they form a complete set in so-called Liouville space, into which any other operator $\hat{A}$ can be expanded,

$$\hat{A} = \sum_{i,j} A_{ij}\,\hat{P}_{ij} , \tag{2.4}$$

$$A_{ij} = \text{Tr}\left\{\hat{A}\,\hat{P}_{ij}^{\dagger}\right\} = \langle i|\hat{A}|j\rangle . \tag{2.5}$$

The n_{tot}^2 parameters are, in general, complex ($2n_{\text{tot}}^2$ real numbers). For Hermitian operators we have, with

$$\hat{A}^{\dagger} = \sum_{i,j} A_{ij}^{*} \hat{P}_{ij}^{\dagger} = \sum_{i,j} A_{ji} \hat{P}_{ji} = \hat{A} \ , \qquad (2.6)$$

$$A_{ij}^{*} = A_{ji} \ , \qquad (2.7)$$

i.e., we are left with n_{tot}^{2}-independent real numbers. All these numbers must be given to uniquely specify any Hermitian operator $\hat{A}$.

2.2.2 Pauli Operators

There are many other possibilities to define basis operators, besides the transition operators. For $n_{\mathrm{tot}} = 2$ a convenient set is given by the so-called Pauli operators $\hat{\sigma}_{i}$ ($i = 0, \ldots, 3$). The new basis operators can be expressed in terms of transition operators

$$\hat{\sigma}_{1} = \hat{P}_{12} + \hat{P}_{21} \ , \qquad (2.8)$$

$$\hat{\sigma}_{2} = i(\hat{P}_{12} - \hat{P}_{21}) \ , \qquad (2.9)$$

$$\hat{\sigma}_{3} = -\hat{P}_{11} + \hat{P}_{22} \ , \qquad (2.10)$$

$$\hat{\sigma}_{0} = \hat{1} \ . \qquad (2.11)$$

These operators are Hermitian and – except for $\hat{\sigma}_{0}$ – traceless. The Pauli operators satisfy several important relations: $(\hat{\sigma}_{i})^{2} = \hat{1}$ and $[\hat{\sigma}_{1}, \hat{\sigma}_{2}] = 2i\hat{\sigma}_{3}$ and their cyclic extensions. Since the Pauli operators form a complete orthonormal operator basis, it is possible to expand any operator in terms of these basis operators. Furthermore we introduce raising and lowering operators, in accordance with

$$\hat{\sigma}_{+} = 1/2(\hat{\sigma}_{1} + i\hat{\sigma}_{2}) \ , \quad \hat{\sigma}_{-} = 1/2(\hat{\sigma}_{1} - i\hat{\sigma}_{2}) \ . \qquad (2.12)$$

Also for higher dimensional cases, $n_{\mathrm{tot}} \geq 2$, one could use as a basis the Hermitian generators of the SU(n_{tot}) group.

2.2.3 State Representation

The most general way to define the state of a quantum mechanical system is by its density matrix, ρ_{ij}, which specifies the representation of the density operator,

$$\hat{\rho} = \sum_{i,j} \rho_{ij} \hat{P}_{ij} \qquad (2.13)$$

subject to the condition

$$\mathrm{Tr}\,\{\hat{\rho}\} = \sum_i \rho_{ii} = 1 \ . \tag{2.14}$$

The expectation value for some observable $\hat{A}$ in state $\hat{\rho}$ is now given by

$$\langle A \rangle = \mathrm{Tr}\,\{\hat{A}\hat{\rho}\} = \sum_{i,j} A_{ij}\rho_{ij} \ . \tag{2.15}$$

The density matrix $\rho_{ij} = \langle i|\hat{\rho}|j\rangle$ is a positive definite and Hermitian matrix. The number of independent real numbers needed to specify $\hat{\rho}$ is thus $d = n_{\mathrm{tot}}^2 - 1$. For the density operator of an arbitrary pure state $|\psi\rangle$ we have $\hat{\rho} = |\psi\rangle\langle\psi|$. In the eigenrepresentation one finds, with $W_i = \rho_{ii}$,

$$\hat{\rho} = \sum_i W_i \hat{P}_{ii} \ , \tag{2.16}$$

which may be interpreted as a "mixture" of pure states $\hat{P}_{ii} = |i\rangle\langle i|$ with the statistical weight W_i. From this object the probability $W(|\psi\rangle)$ to find the system in an arbitrary pure state, expanded in the basis $|i\rangle$

$$|\psi\rangle = \sum_i \psi_i |i\rangle \ , \tag{2.17}$$

can be calculated as

$$W(|\psi\rangle) = \langle\psi|\hat{\rho}|\psi\rangle = \sum_i |\psi_i|^2 W_i \ . \tag{2.18}$$

To measure the distance of two arbitrary, not necessarily, pure states given by $\hat{\rho}$ and $\hat{\rho}'$ we define a "distance measure"

$$D_{\hat{\rho}\hat{\rho}'}^2 = \mathrm{Tr}\,\{(\hat{\rho} - \hat{\rho}')^2\} \ . \tag{2.19}$$

This commutative measure (sometimes called Bures metric) has a number of convenient properties: $D_{\hat{\rho}\hat{\rho}'}^2 \geq 0$ with the equal sign holding if and only if $\hat{\rho} = \hat{\rho}'$; the triangle inequality holds as expected for a conventional distance measure; for pure states

$$D_{|\psi\rangle|\psi'\rangle}^2 = 2\left(1 - |\langle\psi|\psi'\rangle|^2\right) \leq 2 \tag{2.20}$$

and D^2 is invariant under unitary transformations. A second measure of distance is the fidelity defined by [14]

$$F_{\hat{\rho}\hat{\rho}'} = \mathrm{Tr}\,\left\{\left(\sqrt{\hat{\rho}}\,\hat{\rho}'\sqrt{\hat{\rho}}\right)^{1/2}\right\} \ . \tag{2.21}$$

For pure states F is just the modulus of the overlap: $F_{|\psi\rangle|\psi'\rangle} = |\langle\psi|\psi'\rangle|$.

2.2.4 Purity and von Neumann Entropy

For a pure state in eigenrepresentation all matrix elements in (2.13) of the density matrix are zero except $\rho_{ii} = 1$, say, i.e., the density operator $\hat{\rho} = \hat{P}_{ii}$ is a projection operator. Obviously in this case $\hat{\rho}^2 = \hat{\rho}$, due to the properties of the projection operator, so that the so-called purity becomes

$$P = \text{Tr}\left\{\hat{\rho}^2\right\} = 1 . \tag{2.22}$$

In general, we have

$$P(\hat{\rho}) = \sum_{i,j}\sum_{i',j'} \rho_{ij}\,\rho_{i'j'}\,\text{Tr}\left\{\hat{P}_{ij}\,\hat{P}_{i'j'}^{\dagger}\right\} = \sum_{i,j}|\rho_{ij}|^2 > \frac{1}{n_{\text{tot}}} . \tag{2.23}$$

Because of the Cauchy–Schwarz relation

$$|\rho_{ij}|^2 \leq \rho_{ii}\,\rho_{jj} , \tag{2.24}$$

we conclude that $P \leq 1$. The equality sign holds for pure states only. P can be calculated for any density matrix without prior diagonalization. In the diagonal representation (cf. (2.16)) the purity is simply the sum of the squares of the probabilities W_i to find the system in a respective eigenstate,

$$P(\{W_i\}) = \text{Tr}\left\{\hat{\rho}^2\right\} = \sum_i W_i^2 . \tag{2.25}$$

Note that the purity itself is invariant with respect to unitary transformations. Its value does not depend on the representation chosen.

Furthermore, a very important quantity is another measure called the von Neumann entropy [14]. Also this measure is defined for any state $\hat{\rho}$ as

$$S(\hat{\rho}) = -k_{\text{B}}\text{Tr}\left\{\hat{\rho}\,\ln\hat{\rho}\right\} \geq 0 , \tag{2.26}$$

where k_{B} denotes a proportional constant, the Boltzmann constant. (At this point the inclusion of k_{B} is arbitrary and not yet meant to anticipate any connection to thermodynamics.) For a pure state the minimum entropy $S = 0$ is reached. The maximum entropy obtains for

$$\rho_{ij} = \frac{1}{n_{\text{tot}}}\,\delta_{ij} , \quad i, j = 1, 2, \ldots, n_{\text{tot}} , \tag{2.27}$$

i.e., for a density matrix proportional to the normalized unit matrix, with the entropy

$$S_{\text{max}} = k_{\text{B}} \ln n_{\text{tot}} \ . \tag{2.28}$$

In the same limit the purity P is minimal,

$$P_{\text{min}} = \frac{1}{n_{\text{tot}}} \ . \tag{2.29}$$

The maximum entropy (or minimum purity) is thus found for the broadest possible probability distribution, the equipartition over all pure states (remember (2.27)). Therefore S and P are both measures for the "broadness" of the distribution.

The purity can be expressed as a rather simple function of the full state, the evaluation of which does not require the diagonalization of a matrix, as opposed to the calculation of the von Neumann entropy. We will thus mainly consider P rather than S.

In general, though, these two measures do not uniquely map onto each other. Nevertheless in the limits of maximum S (minimum P) and maximum P (minimum S) they do. The formal approximation $\ln \hat{\rho} \approx \hat{\rho} - \hat{1}$ leads to the "linearized" entropy

$$S_{\text{lin}} = k_{\text{B}}(1 - P) \geq 0 \ . \tag{2.30}$$

Since, as will be shown in Sect. 2.4, S is a constant of motion, the question for the possible origin of $S > 0$ arises. One interpretation is essentially classical and traces a finite S back to subjective ignorance. In the eigenrepresentation of the density operator (see (2.16)) the density operator can be seen as a "mixture" of pure states $\hat{P}_{ii} = |i\rangle\langle i|$ and the entropy then reads

$$S = -k_{\text{B}} \sum_i W_i \ln W_i \ . \tag{2.31}$$

Alternatively, a nonpure state may result from the system under consideration being entangled with another system, while the total state is pure. In this case S indicates a principal uncertainty. It is always possible to find such an embedding, as will be discussed in the next section.

2.2.5 Bipartite Systems

Systems typically consist of subsystems. In the case of a bipartite system, the total Hilbert space can be decomposed into a product space

$$\mathcal{H} = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)} \ , \tag{2.32}$$

with dimension $n_{\text{tot}} = n^{(1)} \cdot n^{(2)}$. A complete set of orthonormal vectors is then given by the product states ($\otimes$ means tensor product of the vectors involved)

$$|ij\rangle = |i\rangle \otimes |j\rangle \,, \tag{2.33}$$

with $i = 1, 2, \ldots, n^{(1)}$ numbering the states in $\mathscr{H}^{(1)}$ and $j = 1, 2, \ldots, n^{(2)}$ in $\mathscr{H}^{(2)}$. The states fulfill the orthonormality relation

$$\langle ij|i'j'\rangle = \delta_{ii'}\,\delta_{jj'} \,. \tag{2.34}$$

Based on this we can define the transition operators

$$\hat{P}_{ij|i'j'} = |ij\rangle\langle i'j'| = \hat{P}^{(1)}_{ii'} \otimes \hat{P}^{(2)}_{jj'} \,, \tag{2.35}$$

where $\hat{P}^{(\mu)}_{ii'}$ is a transition operator in the subspace of the subsystem $\mu = 1, 2$. These, again, form a complete orthogonal set such that any operator $\hat{A}$ can be expanded in the form

$$\hat{A} = \sum_{i,j} \sum_{i',j'} A_{ij|i'j'}\, \hat{P}_{ij|i'j'} \,. \tag{2.36}$$

For a pure state

$$|\psi\rangle = \sum_{i,j} \psi_{ij}\, |i\rangle \otimes |j\rangle \tag{2.37}$$

the density operator $\hat{\rho} = |\psi\rangle\langle\psi|$ has the matrix representation

$$\rho_{ij|i'j'} = \psi_{ij}\, \psi^{*}_{i'j'} \,. \tag{2.38}$$

If we are interested in the state of one of the subsystems alone we have to trace over the other subsystem. The reduced density operator of the system of interest is now given by

$$\hat{\rho}^{(1)} = \text{Tr}_2\{\hat{\rho}\} = \sum_{i,i'}\sum_{j}\langle ij|\hat{\rho}|i'j\rangle\, |i\rangle\langle i'|$$
$$= \sum_{i,i'} \rho_{ii'}\, \hat{P}^{(1)}_{ii'} \,, \tag{2.39}$$

with $\rho_{ii'} = \sum_{j} \rho_{ij|i'j}$. Here $\text{Tr}_2\{\ldots\}$ means trace operation within Hilbert space $\mathscr{H}^{(2)}$. The result for subsystem 2 is obtained by exchanging the indices of the two subsystems.

The expectation value for any local operator $\hat{A}^{(1)} \otimes \hat{1}^{(2)}$ can be calculated from

$$\langle \hat{A}^{(1)}\rangle = \text{Tr}_1\left\{\hat{A}^{(1)}\hat{\rho}^{(1)}\right\} \,. \tag{2.40}$$

The corresponding purity, say, for the reduced state of the first subsystem, is

$$P\big(\hat{\rho}^{(1)}\big) = \sum_{i,i'} |\rho_{ii'}|^2 = \sum_{i,i'} \sum_{j,j'} \rho_{ij|i'j} \; \rho_{i'j'|ij'} \; . \tag{2.41}$$

Furthermore, the reduced von Neumann entropies are given by

$$S\big(\hat{\rho}^{(\mu)}\big) = -k_{\mathrm{B}} \mathrm{Tr}_{\mu} \left\{ \hat{\rho}^{(\mu)} \ln \hat{\rho}^{(\mu)} \right\} \;, \quad \mu = 1, 2 \; . \tag{2.42}$$

One easily convinces oneself that for

$$\hat{\rho} = \hat{\rho}^{(1)} \otimes \hat{\rho}^{(2)} \tag{2.43}$$

the total entropy is additive,

$$S = S\big(\hat{\rho}^{(1)}\big) + S\big(\hat{\rho}^{(2)}\big) \; . \tag{2.44}$$

In general, the theorem by Araki and Lieb [15] tells us that

$$\big|S\big(\hat{\rho}^{(1)}\big) - S\big(\hat{\rho}^{(2)}\big)\big| \le S \le S\big(\hat{\rho}^{(1)}\big) + S\big(\hat{\rho}^{(2)}\big) \; . \tag{2.45}$$

This theorem implies that if the total system is in a pure state ($S = 0$) then $S(\hat{\rho}^{(1)}) = S(\hat{\rho}^{(2)})$, no matter how the system is partitioned. Under the same condition $P(\hat{\rho}^{(1)}) = P(\hat{\rho}^{(2)})$. Then if $S(\hat{\rho}^{(1)}) = S(\hat{\rho}^{(2)}) > 0$, it follows that (2.44) does not apply and the total (pure) state cannot be written in a product form. This is interpreted to result from "entanglement," for which the local entropies $S(\hat{\rho}^{(1)}) = S(\hat{\rho}^{(2)})$ thus constitute an appropriate measure.

Such pure entangled states have been of central interest now for almost 70 years. They can have properties that seem to contradict intuition. If a local measurement on one subsystem is made, i.e., a projection of only one subsystem state is performed, the local state of the other subsystem can be severely affected, which has raised the question of whether quantum mechanics could be valid at all [16]. Nevertheless, these states can theoretically be shown to result from product states, if the subsystems are allowed to interact for a while. On a small scale such a buildup has been demonstrated experimentally; it is a widespread belief that entanglement as a fundamental quantum mechanical property should show up mainly between very small objects.

2.2.6 Multipartite Systems

Alternatively, one may consider a network of N subsystems of dimension n each. Then $n_{\mathrm{tot}} = n^N$. As a consequence of the direct product structure, the number of parameters required to specify a density operator then grows exponentially with N

$$d = n^{2N} - 1 \; . \tag{2.46}$$

For the classical system of N point particles we would need $6N$ real parameters, i.e., we would just have to specify position and momentum of each individual particle. This so-called phase space is the direct sum of the individual particle spaces. The analog in the quantum case would be to specify the local states of the N subsystems, for which we would need $(n^2 - 1)N$ parameters. (This was the dimension of the direct sum of subsystem Liouville spaces.) Defining

$$\gamma = \frac{d}{(n^2 - 1)N} \, , \tag{2.47}$$

we see that for $n = 2$, $N = 3$, $\gamma = 7$, but for $N = 10$, $\gamma \approx 30\,000$. The tremendous information needed over the local parameters is due to the fact that correlations (entanglement) dominate, in general. For product states $\gamma = 1$.

The blowup of γ is a typical quantum property, closer to the heart of quantum mechanics than the famous Heisenberg uncertainty relation. Both are due to the non-commutativity of the underlying operators, though.

The number of parameters needed to specify a Hamilton model typically grows only polynomially with N. This is because direct interactions are usually restricted to finite clusters, e.g., up to pairs.

2.3 Dynamics

So far, we have considered some properties of Hilbert spaces, the basis operators and appropriate states. We turn now to some dynamical aspects of quantum systems.

The unitary dynamics of a closed system generated by a Hamilton operator $\hat{H}$ is given by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle \tag{2.48}$$

for the time-dependent pure state $|\psi(t)\rangle$. This is the fundamental equation specifying the so-called Schrödinger picture: here the state vectors $|\psi(t)\rangle$ carry all dynamics, while the basic operators are time independent. But note that the Hamiltonian could include explicitly time-dependent potentials. These would render the system non-autonomous, though.

From the Schrödinger equation one can easily derive the evolution equation directly for the density operator. This is the Liouville–von Neumann equation

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}] \, , \tag{2.49}$$

with $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ defining the commutator. This equation can be written in the form

$$\frac{\partial \hat{\rho}}{\partial t} = \hat{\mathcal{L}} \hat{\rho} \,, \tag{2.50}$$

where $\hat{\mathcal{L}}$ is a so-called superoperator acting (here) on the operator $\hat{\rho}$ to produce the new operator

$$\hat{\mathcal{L}} \hat{\rho} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] \,. \tag{2.51}$$

Modified superoperators control the dynamics of open quantum systems, which we will consider in detail in Sect. 4.8.

The Liouville–von Neumann equation can formally be solved by

$$\hat{\rho}(t) = \hat{U}(t) \, \hat{\rho}(0) \, \hat{U}^{\dagger}(t) \,, \tag{2.52}$$

where the unitary time evolution operator, $\hat{U}^{\dagger}\hat{U} = \hat{U}\hat{U}^{\dagger} = \hat{1}$, also obeys the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \hat{U}(t) = \hat{H}(t) \, \hat{U}(t) \,. \tag{2.53}$$

For $\partial \hat{H}/\partial t = 0$, i.e., no explicit time-dependent Hamiltonian, it has the formal solution

$$\hat{U}(t) = e^{-i\hat{H}t/\hbar} \,. \tag{2.54}$$

When represented with respect to a specific set of basis operators, the Liouville–von Neumann equation is equivalent to

$$i\hbar \frac{\partial}{\partial t} \rho_{ij}(t) = \text{Tr} \left\{ [\hat{H}, \hat{\rho}(t)] \, \hat{P}_{ij}^{\dagger} \right\} \,. \tag{2.55}$$

This equation determines the evolution of the matrix elements of the density operator. The solution $\rho_{ij}(t)$, subject to the condition $\sum_i \rho_{ii} = 1$, can thus be visualized as a deterministic quantum trajectory in Liouville space, controlled by the Hamiltonian and by the initial state $\hat{\rho}(0)$.

In the Heisenberg picture, the dynamics is carried by time-dependent observables

$$\hat{A}_{\text{H}}(t) = \hat{U}^{\dagger}(t) \, \hat{A} \, \hat{U}(t) \,, \tag{2.56}$$

while the states are constant, $\hat{\rho}_{\text{H}}(t) = \hat{\rho}(0)$. If $\partial \hat{A}/\partial t = 0$ in the Schrödinger picture, the corresponding evolution equation for the now time-dependent operators reads

$$i\hbar \frac{d}{dt} \hat{A}_{\text{H}} = -[\hat{H}, \hat{A}_{\text{H}}] \,. \tag{2.57}$$

In either picture the time dependence of the expectation value of an operator $\langle \hat{A} \rangle = \mathrm{Tr}\left\{ \hat{A}\,\hat{\rho} \right\} = \mathrm{Tr}\left\{ \hat{A}_{\mathrm{H}}\,\hat{\rho}(0) \right\}$ is given by

$$i\hbar\, \frac{\partial}{\partial t}\, \langle \hat{A} \rangle = \mathrm{Tr}\left\{ [\hat{H}, \hat{\rho}]\, \hat{A} \right\} = -\mathrm{Tr}\left\{ [\hat{H}, \hat{A}_{\mathrm{H}}]\, \hat{\rho}(0) \right\}$$
$$= -\langle [\hat{H}, \hat{A}_{\mathrm{H}}] \rangle\,, \tag{2.58}$$

which is known as the "Ehrenfest theorem." Since this evolution equation is similar to the classical equation of motion based on the Poisson bracket, this theorem can be interpreted to state that "the classical equations of motion are valid for expectation values in quantum mechanics."

2.4 Invariants

According to the Heisenberg equation of motion (2.57), conserved quantities are those which commute with the system Hamiltonian $\hat{H}$. In eigenrepresentation $\hat{H}$ can be written as

$$\hat{H} = \sum_{i=1}^{n_{\mathrm{tot}}} E_i\, \hat{P}_{ii}\,. \tag{2.59}$$

As a consequence, the projectors commute with the Hamiltonian itself,

$$[\hat{P}_{jj}, \hat{H}] = 0\,, \quad j = 1, \ldots, n_{\mathrm{tot}}\,. \tag{2.60}$$

Since commutators are invariant under unitary transformations, the above relation thus holds in the Schrödinger as well as in the Heisenberg pictures. For the change of the energy distribution we find

$$i\hbar\, \frac{\partial}{\partial t}\, W_j = i\, \frac{\partial}{\partial t}\, \mathrm{Tr}\left\{ \hat{P}_{jj}\, \hat{\rho} \right\} = -\mathrm{Tr}\left\{ [\hat{H}, \hat{P}_{jj}^{(\mathrm{H})}]\, \hat{\rho}(0) \right\} = 0\,, \tag{2.61}$$

i.e., the energy distribution, the probability of finding the system in state j, is a constant of motion.

Furthermore, defining the expectation value of an arbitrary function of the density operator $\hat{\rho}$

$$\langle f(\hat{\rho}) \rangle = \mathrm{Tr}\left\{ \hat{\rho}\, f(\hat{\rho}) \right\}\,, \tag{2.62}$$

one infers that

$$i\hbar \frac{\partial}{\partial t} \langle f(\hat{\rho}) \rangle = i\hbar \operatorname{Tr} \left\{ \frac{\partial}{\partial t} \hat{\rho} f(\hat{\rho}) \right\} + i\hbar \operatorname{Tr} \left\{ \hat{\rho} \frac{\partial}{\partial t} f(\hat{\rho}) \right\}$$
$$= \operatorname{Tr} \left\{ [\hat{H}, \hat{\rho}] f(\hat{\rho}) \right\} + \operatorname{Tr} \left\{ \hat{\rho} [\hat{H}, f(\hat{\rho})] \right\} . \tag{2.63}$$

Here we have made use of the Liouville equation (2.49) and its variant

$$i\hbar \frac{\partial}{\partial t} f(\hat{\rho}) = [\hat{H}, f(\hat{\rho})] . \tag{2.64}$$

Observing the invariance of the first trace term in (2.63) under cyclic permutations, we see that the right-hand side cancels,

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle f(\hat{\rho}) \rangle = 0 . \tag{2.65}$$

Taking now $f(\hat{\rho}) = \hat{\rho}$, the term $\langle f(\hat{\rho}) \rangle = \operatorname{Tr} \left\{ \hat{\rho}^2 \right\}$ is just the purity, so that

$$\frac{\mathrm{d}}{\mathrm{d}t} P = 0 . \tag{2.66}$$

For $f(\hat{\rho}) = \ln \hat{\rho}$ one concludes that the von Neumann entropy is invariant, too. In fact, any moment $\operatorname{Tr} \left\{ (\hat{\rho})^k \right\}$ is a constant of motion in closed quantum systems. But note that the local reduced von Neumann entropy of a part of the system defined in (2.42) is not necessarily conserved under a unitary time evolution of the full system (see Sect. 6.1).

For later reference we finally investigate a bipartite system with the total Hamiltonian $\hat{H}$. Here we may encounter a situation for which

$$[\hat{A}^{(1)}, \hat{H}] = 0 , \quad [\hat{B}^{(2)}, \hat{H}] = 0 , \tag{2.67}$$

where the operator

$$\hat{A}^{(1)} = \sum_i A_i \, \hat{P}_{ii}^{(1)} \tag{2.68}$$

acts only on subsystem 1, and

$$\hat{B}^{(2)} = \sum_j B_j \, \hat{P}_{jj}^{(2)} \tag{2.69}$$

acts only on subsystem 2. As a consequence,

$$[(\hat{A}^{(1)})^k, \hat{H}] = \sum_i A_i^k [\hat{P}_{ii}^{(1)}, \hat{H}] = 0 . \tag{2.70}$$

As this has to hold for any k, we conclude that

$$[\hat{P}_{ii}^{(1)}, \hat{H}] = 0 \;, \tag{2.71}$$

and correspondingly,

$$[\hat{P}_{jj}^{(2)}, \hat{H}] = 0 \;. \tag{2.72}$$

According to these considerations the expectation value

$$W_{ij}^{(12)} = \text{Tr}\left\{ \hat{P}_{ii}(1)\, \hat{P}_{jj}(2)\, \hat{\rho} \right\} \tag{2.73}$$

is thus a conserved quantity, too. This expectation value is the joint probability for finding subsystem 1 in state i and subsystem 2 in state j.

2.5 Time-Dependent Perturbation Theory

Just as in classical mechanics or any other theoretical framework, there are very few examples that allow us to achieve an exact analytical solution. In quantum mechanics even numerical solutions are seriously constrained by exponential explosion of state parameters (cf. Sect. 2.2.6). Many, quite powerful, approximation schemes have been developed. For later reference we summarize here the basics of standard perturbation theory.

To consider time-dependent phenomena it is often very helpful – if not unavoidable – to use a perturbation theory instead of a full solution of the time-dependent problem. To outline such a theory, we use in addition to the Schrödinger and the Heisenberg pictures the interaction or Dirac picture.

2.5.1 Interaction Picture

In the interaction picture, both observables and states are time dependent. We consider the Hamilton operator

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \;, \tag{2.74}$$

where $\hat{H}_0$ represents the unperturbed Hamiltonian and $\hat{V}(t)$ the time-dependent perturbation. According to the unitary transformation

$$\hat{U}_0(t, t_0) = \exp\left(-\frac{i}{\hbar} \hat{H}_0 (t - t_0) \right) \;, \tag{2.75}$$

where t_0 is the time at which the perturbation is switched on, one can transform the states as well as the operators of the Schrödinger picture into the interaction picture (index I)

$$|\psi(t)\rangle = \hat{U}_0(t, t_0) |\psi_{\mathrm{I}}(t)\rangle \;, \tag{2.76}$$

$$\hat{A}_{\mathrm{I}} = \hat{U}_0^\dagger(t, t_0) \,\hat{A}\, \hat{U}_0(t, t_0) \;. \tag{2.77}$$

Based on these transformations, the Schrödinger equation reads

$$i\hbar \Big(\frac{\partial}{\partial t} \hat{U}_0 \Big)|\psi_{\mathrm{I}}(t)\rangle + i\hbar \hat{U}_0 \frac{\partial}{\partial t}|\psi_{\mathrm{I}}(t)\rangle = (\hat{H}_0 + \hat{V})\hat{U}_0|\psi_{\mathrm{I}}(t)\rangle \;. \tag{2.78}$$

Observing that

$$i\hbar \, \frac{\partial}{\partial t} \hat{U}_0 = \hat{H}_0 \, \hat{U}_0 \tag{2.79}$$

and

$$\hat{U}_0 \hat{U}_0^\dagger = \hat{1} \;, \tag{2.80}$$

the above equation reduces to an effective Schrödinger equation for $|\psi_{\mathrm{I}}(t)\rangle$

$$i\hbar \, \frac{\partial}{\partial t}|\psi_{\mathrm{I}}(t)\rangle = \hat{V}_{\mathrm{I}}(t) \, |\psi_{\mathrm{I}}(t)\rangle \;, \tag{2.81}$$

identifying $\hat{V}_{\mathrm{I}}(t) = \hat{U}_0^\dagger \hat{V}(t)\hat{U}_0$. This equation has the formal solution

$$|\psi_{\mathrm{I}}(t)\rangle = \hat{U}_{\mathrm{I}}(t, t_0) \, |\psi_{\mathrm{I}}(t_0)\rangle, \tag{2.82}$$

with the evolution equation

$$i\hbar \, \frac{\partial}{\partial t} \hat{U}_{\mathrm{I}}(t, t_0) = \hat{V}_{\mathrm{I}}(t) \, \hat{U}_{\mathrm{I}}(t, t_0) \;. \tag{2.83}$$

The corresponding dynamics for observables in the interaction picture (remember (2.77)) is then controlled by

$$\frac{\mathrm{d}\hat{A}_{\mathrm{I}}}{\mathrm{d}t} = \frac{1}{i\hbar}[\hat{A}_{\mathrm{I}}(t), \hat{H}_0] + \hat{U}_0^\dagger \frac{\partial \hat{A}}{\partial t} \, \hat{U}_0 \;. \tag{2.84}$$

2.5.2 Series Expansion

The formal solution (2.82) of the effective Schrödinger equation (2.81) may be written as

$$\hat{U}_I(t, t_0) = \hat{1} - \frac{i}{\hbar} \int_{t_0}^t \mathrm{d}t_1 \, \hat{V}_{\mathrm{I}}(t_1) \, \hat{U}_{\mathrm{I}}(t_1, t_0) \;. \tag{2.85}$$

This integral equation can be solved for $\hat{U}_\mathrm{I}(t, t_0)$ by iteration,

$$\hat{U}_\mathrm{I}(t, t_0) = \hat{1} + \frac{\mathrm{i}}{\hbar} \int_{t_0}^{t} \mathrm{d}t_1 \, \hat{V}_\mathrm{I}(t_1) + \left(\frac{\mathrm{i}}{\hbar}\right)^2 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_2 \, \hat{V}_\mathrm{I}(t_1) \, \hat{V}_\mathrm{I}(t_2) + \cdots$$

$$= \sum_{n=0}^{\infty} \left(\frac{\mathrm{i}}{\hbar}\right)^n \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_2 \cdots \int_{t_0}^{t_{n-1}} \mathrm{d}t_n \, \hat{V}_\mathrm{I}(t_1) \cdots \hat{V}_\mathrm{I}(t_n) , \qquad (2.86)$$

which is called the Dyson series expansion. In first order the transition probability due to $\hat{V}_\mathrm{I}(t)$ is given by

$$W_{ij}(t) = \left| \delta_{ij} + \frac{1}{\mathrm{i}\hbar} \int_{t_0}^{t} \mathrm{d}t_1 \, \langle j| \hat{V}_\mathrm{I}(t_1) |i \rangle \right|^2 . \qquad (2.87)$$

For $i \neq j$ and going back to the Schrödinger picture, we find

$$W_{ij}(t) = \frac{1}{\hbar^2} \left| \int_{t_0}^{t} \mathrm{d}t_1 \, \exp\left(\frac{\mathrm{i}(E_j - E_i)t_1}{\hbar}\right) \langle j| \hat{V}(t_1) |i \rangle \right|^2 . \qquad (2.88)$$

Let the time-dependent perturbation be

$$\hat{V}(t) = \begin{cases} 0 \\ \hat{V} \end{cases} \quad \text{for} \quad \begin{matrix} t \leq 0 \\ t > 0 \end{matrix} \qquad (2.89)$$

and

$$\frac{E_j - E_i}{\hbar} = \omega_{ji} . \qquad (2.90)$$

Then we find for the transition probability

$$W_{ij}(t) = \frac{1}{\hbar^2} \left| \frac{\mathrm{e}^{\mathrm{i}\omega_{ji}t} - 1}{\omega_{ji}} \langle j| \hat{V} |i \rangle \right|^2 \qquad (2.91)$$

$$= \frac{1}{\hbar^2} \left| \frac{\sin(\omega_{ji} t/2)}{\omega_{ji}/2} \right|^2 |\langle j| \hat{V} |i \rangle|^2 , \qquad (2.92)$$

which gives Fermi's golden rule for large times

$$W_{ij}(t) = t \, \frac{2\pi}{\hbar} \, \delta(E_j - E_i) |\langle j| \hat{V} |i \rangle|^2 , \qquad (2.93)$$

i.e., a constant transition rate.

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