II.3 Probabilistic description of quantum mechanical systems

In this section, we first recall in § II.3.1 the basics of the density-operator formalism for the description of quantum systems with a large number of degrees of freedom—which for brevity will often be referred to as "macroscopic systems". We then discuss the time evolution of the density operator (§ II.3.2) as well as that of the expectation values of observables of the system (§ II.3.3). Eventually, we consider the case in which the Hamilton operator governing the evolution of the system can be split into two terms, namely a time-independent one and a time-dependent "perturbation" that is switched on at some initial instant (§ II.3.4).

II.3.1 Randomness in quantum mechanical systems

Unlike classical physics, whose predictions for the outcome of measurements are deterministic when the (micro)state of a system is known, quantum mechanics already involves probabilities for predictions on "exactly" prepared systems, described as pure states. Accordingly, there are two

---

[30] The case $N = 0$ has to be considered as well, corresponding here to a 0-dimensional phase space reduced to a single point.

levels of randomness when describing a quantum-mechanical system with many degrees of freedom: that arising at the pure-state level, and that due to the incomplete knowledge of the microstate.

II.3.1 a Randomness in pure states

In the "classical" formalism of quantum mechanics, the state of a system—if it is exactly known, in which case it is referred to as a *pure state*—is described by a normalized vector $|\Psi\rangle$ of a Hilbert[(aa)] space $\mathscr{H}$. In turn, observables are modeled by Hermitian operators $\hat{O}(t)$ on $\mathscr{H}$.

Conceptually, a pure state of a quantum-mechanical system is entirely determined by the results of measurements of quantities associated with the operators of a complete set of commuting observables, where the latter are Hermitian linear operators on the system Hilbert space $\mathscr{H}$.

As is well known, the result of a measurement performed on a pure state $|\Psi\rangle$ might already be a random variable, in case $|\Psi\rangle$ is not an eigenstate of the observable $\hat{O}$ associated to the measured quantity. In that case, repeated measurements will give the expectation value of the observable according to

$$\langle\hat{O}\rangle_\Psi \equiv \frac{\langle\Psi|\,\hat{O}\,|\Psi\rangle}{\langle\Psi\,|\,\Psi\rangle}. \tag{II.21}$$

One can similarly express the variance σ_O^2 of the outcome of the measurements, which is given by $\langle(\hat{O}-\langle\hat{O}\rangle)^2\rangle_\Psi$.

II.3.1 b Randomness in mixed states

In realistic cases, the microstate $|\Psi\rangle$ of a macroscopic system is not exactly determined. Instead, one only knows that the system can be with probability p_1 in microstate $|\Psi_1\rangle$, with probability p_2 in another microstate $|\Psi_2\rangle$, and so on, where the states $|\Psi_1\rangle,\ldots,|\Psi_m\rangle,\ldots$ are not necessarily orthogonal, while the probabilities $p_1,\ldots,p_m,\ldots$ satisfy

$$p_m \geq 0 \quad \forall m \quad \text{and} \quad \sum_m p_m = 1.$$

One then speaks of a *statistical ensemble* or *statistical mixture* of states, or in short—and somewhat misleadingly—of a *mixed state*. To simplify notations,[(31)] we assume that the states $\{|\Psi_m\rangle\}$ are normalized to unity, i.e. $\langle\Psi_m\,|\,\Psi_m\rangle = 1$ for all m.

Remark: A mixed state should not be confused with a linear combination of states. In the latter case, the system is still in a pure state, corresponding to a single vector of the Hilbert space.

The expectation value of an observable for a system in a mixed state is the weighted sum of the expectation values in the pure states:

$$\langle\hat{O}\rangle = \sum_m p_m\langle\Psi_m|\,\hat{O}\,|\Psi_m\rangle. \tag{II.22a}$$

To express such expectation values in a convenient way, one introduces the *density operator* (also called *statistical operator* or *density matrix*)[(32)]

$$\hat{\rho} = \sum_m p_m\,|\Psi_m\rangle\langle\Psi_m|. \tag{II.22b}$$

One then has the identity

$$\langle\hat{O}\rangle = \text{Tr}\big(\hat{\rho}\,\hat{O}\big), \tag{II.22c}$$

where Tr denotes the trace of an operator.

[(31)]Otherwise, one needs to divide by $\langle\Psi_m\,|\,\Psi_m\rangle$ in Eqs. (II.22a) and (II.22b).
[(32)]See e.g. Refs. [27] chapter E$_{\text{III}}$ or [3] § 5.

[(aa)]D. HILBERT, 1862–1943

Using the matrix elements ρ_{ij} and O_{ij} of $\hat\rho$ and $\hat O$ in an arbitrary basis $\{|\phi_j\rangle\}$ of $\mathscr{H}$, as well as two decompositions of the identity, one finds at once

$$\langle \hat O \rangle = \sum_{i,j} \sum_m p_m \langle \Psi_m \,|\, \phi_i \rangle \langle \phi_i |\, \hat O \,| \phi_j \rangle \langle \phi_j \,|\, \Psi_m \rangle = \sum_{i,j} \rho_{ij} O_{ji} = \mathrm{Tr}\big(\hat\rho\,\hat O\big). \qquad \Box$$

Remarks:

$*$ The probabilities $p_1, \ldots, p_m, \ldots$ are clearly the eigenvalues of the density operator $\hat\rho$.

$*$ The density-operator formalism easily accommodates the description of both mixed states and pure states. Thus, a normalized microstate $|\Psi\rangle \in \mathscr{H}$ can be equivalently represented by the density operator $\hat\rho = |\Psi\rangle\langle\Psi|$ acting on the Hilbert space $\mathscr{H}$.

Properties of the density operator

1. $\hat\rho$ is Hermitian: $\hat\rho^\dagger = \hat\rho$.
   As a consequence, the expectation value of every observable is real.

   > The proof follows from the hermiticity of $\hat O$ and the invariance of the trace under cyclic permutations: $\langle \hat O \rangle^* = \big[\mathrm{Tr}\big(\hat\rho\,\hat O\big)\big]^* = \mathrm{Tr}\big(\hat O^\dagger \hat\rho^\dagger\big) = \mathrm{Tr}\big(\hat O\,\hat\rho\big) = \mathrm{Tr}\big(\hat\rho\,\hat O\big) = \langle \hat O \rangle.$ $\qquad \Box$

2. $\hat\rho$ is positive: $\forall \,|\phi\rangle \in \mathscr{H}, \ \langle\phi|\,\hat\rho\,|\phi\rangle \geq 0$.
   Thus, the expectation value of every positive operator is a positive number.

3. $\hat\rho$ is normalized to unity: $\mathrm{Tr}\,\hat\rho = 1$.
   This means that the expectation value of the identity operator on $\mathscr{H}$ equals 1.

The whole information on the system is encoded in its density operator $\hat\rho$. If one considers its matrix elements ρ_{ij} in an arbitrary basis $\{|\phi_j\rangle\}$, then each diagonal element, called *population*, ρ_{ii} is the probability to find the system in state $|\phi_i\rangle$.

The off-diagonal elements ρ_{ij} with $i \neq j$ are called *coherences*, and represent an information on the quantum-mechanical correlations between the possible states $|\phi_i\rangle$ and $|\phi_j\rangle$ of the system, which is absent in a classical description.

Remark: From the positivity of the density operator follows that of each of its minors in a given basis, in particular the inequality $\rho_{ii}\rho_{jj} - \rho_{ij}\rho_{ji} \geq 0$. Since $\rho_{ji} = \rho_{ij}^*$, one sees that the coherence between two states can only be non-zero when the populations of these states do not vanish.

II.3.1 c Fluctuating number of particles

To account for possible fluctuations in the number of particles in a quantum-mechanical system, one introduces the *Fock*[(ab)] *space*, that is the Hilbert space $\mathscr{H}$ defined as direct sum of the Hilbert spaces $\mathscr{H}_N$ corresponding to the N-particle problems, including the one-dimensional space $\mathscr{H}_0$ spanned by the *vacuum state* $|0\rangle$ describing the absence of particles.

The density operator $\hat\rho$ then simply acts on this Fock space and allows one to compute the expectation value of an observable—represented as an Hermitian operator on $\mathscr{H}$—through the usual formula (II.22c).

II.3.2 Time evolution of the density operator

Consider a macroscopic system with Hamilton operator $\hat H(t)$. Starting from the Schrödinger[(ac)] equation

$$\mathrm{i}\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = \hat H(t)|\Psi(t)\rangle, \tag{II.23}$$

[(ab)]V. A. Fock (or Fok), 1898–1974 [(ac)]E. Schrödinger, 1887–1961

which holds for every pure state $|\Psi_m\rangle$ in which a statistical mixture can be, one finds that the time evolution of the density operator $\hat{\rho}(t)$ is governed by the *Liouville–von Neumann*[(ad)] *equation*

$$\frac{\partial\hat{\rho}(t)}{\partial t} = \frac{1}{\mathrm{i}\hbar}\big[\hat{H}(t),\hat{\rho}(t)\big], \tag{II.24}$$

where the square brackets denote the commutator of two operators.

Considering the Hermitian conjugate equation to the Schrödinger equation, one finds

$$\frac{\partial\hat{\rho}(t)}{\partial t} = \sum_m p_m\bigg(\frac{\partial|\Psi_m\rangle}{\partial t}\langle\Psi_m| + |\Psi_m\rangle\frac{\partial\langle\Psi_m|}{\partial t}\bigg) = \sum_m p_m\bigg(\frac{1}{\mathrm{i}\hbar}\,\hat{H}|\Psi_m\rangle\langle\Psi_m| + \frac{1}{-\mathrm{i}\hbar}\,|\Psi_m\rangle\langle\Psi_m|\,\hat{H}\bigg),$$

which is readily recast as Eq. (II.24). $\square$

The solution of this differential equation for a given initial condition $\hat{\rho}(t_0)$ at some time $t = t_0$ can be expressed in terms of the *time-evolution operator* $\hat{\mathcal{U}}(t,t_0)$.[(33)] Recall that the latter evolves pure states of the system—described as vectors of $\mathscr{H}(t)$—between the initial time t_0 and time t

$$|\Psi(t)\rangle = \hat{\mathcal{U}}(t,t_0)|\Psi(t_0)\rangle. \tag{II.25a}$$

As such, the time-evolution operator is solution to the first-order differential equation

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\hat{\mathcal{U}}(t,t_0) = \hat{H}(t)\hat{\mathcal{U}}(t,t_0), \tag{II.25b}$$

with the initial condition

$$\hat{\mathcal{U}}(t{=}t_0,t_0) = \hat{\mathbb{1}}, \tag{II.25c}$$

with $\hat{\mathbb{1}}$ the identity operator on $\mathscr{H}$. One easily checks[(34)] that the solution to Eq. (II.24) is

$$\hat{\rho}(t) = \hat{\mathcal{U}}(t,t_0)\,\hat{\rho}(t_0)\,\hat{\mathcal{U}}(t_0,t), \tag{II.26}$$

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

This follows from differentiating the proposed solution and using the Hermitian conjugate equation to Eq. (II.25b). $\square$

Introducing the *Liouville operator* $\hat{\tilde{\mathcal{L}}}(t)$ (or at times *superoperator*, since the objects it acts upon are the operators on the Hilbert space $\mathscr{H}$) defined by

$$\mathrm{i}\hat{\tilde{\mathcal{L}}}(t) \equiv \frac{1}{\mathrm{i}\hbar}\big[\,\cdot\,,\hat{H}(t)\big], \tag{II.27}$$

the Liouville–von Neumann equation takes the form

$$\frac{\partial\hat{\rho}(t)}{\partial t} = -\mathrm{i}\hat{\tilde{\mathcal{L}}}(t)\hat{\rho}(t), \tag{II.28}$$

formally analogous to the classical Liouville equation (II.12).

II.3.2 a Isolated systems

If the system under consideration is isolated, its Hamilton operator $\hat{H}$ is actually time independent, so that the equation (II.25b) governing the time-evolution operator is readily integrated, yielding

$$\hat{\mathcal{U}}(t,t_0) = \mathrm{e}^{-\mathrm{i}(t-t_0)\hat{H}/\hbar}. \tag{II.29}$$

[(33)] See e.g. Ref. [27] chapter F_{III}.

[(34)] Note that this form can also be deduced from definition (II.22b) and equation (II.25a).

[(ad)] J. VON NEUMANN, 1903–1957

Accordingly, relation (II.26) becomes

$$\hat{\rho}(t) = \mathrm{e}^{-\mathrm{i}(t-t_0)\hat{H}/\hbar}\,\hat{\rho}(t_0)\,\mathrm{e}^{\mathrm{i}(t-t_0)\hat{H}/\hbar}, \tag{II.30}$$

with $\hat{\rho}(t_0)$ the initial density operator at $t = t_0$.

Denoting by $\{|\phi_j\rangle\}$ the orthonormal basis formed by the eigenstates of the Hamilton operator, with respective eigenvalues ϵ_j, and by ρ_{ij} the matrix elements of the density operator in this basis, Eq. (II.30) reads

$$\rho_{ii}(t) = \rho_{ii}(t_0), \qquad \rho_{ij}(t) = \rho_{ij}(t_0)\,\mathrm{e}^{-\mathrm{i}(\epsilon_i - \epsilon_j)(t-t_0)/\hbar} \quad \text{for } i \neq j. \tag{II.31}$$

That is, the populations in the energy eigenbasis do not evolve with time, while the corresponding coherences oscillate with the respective Bohr frequencies.

In turn, the Liouville superoperator is also time-independent, and the Liouville–von Neumann equation (II.28) can formally be integrated as

$$\hat{\rho}(t) = \mathrm{e}^{-\mathrm{i}(t-t_0)\hat{\hat{\mathcal{L}}}}\,\hat{\rho}(t_0), \tag{II.32}$$

which parallels Eq. (II.13) for classical systems, and is totally equivalent to Eq. (II.30).

II.3.2 b Time-dependent Hamiltonian

When the Hamilton operator $\hat{H}$ depends on time, the corresponding time-evolution operator $\hat{\mathcal{U}}(t, t')$ is given by the *Dyson*[(ae)] *series*

$$\hat{\mathcal{U}}(t, t') = \hat{\mathbb{1}} - \frac{\mathrm{i}}{\hbar}\int_{t'}^{t}\hat{H}(t_1)\,\mathrm{d}t_1 + \left(\frac{-\mathrm{i}}{\hbar}\right)^2\int_{t'}^{t}\left[\int_{t'}^{t_1}\hat{H}(t_1)\hat{H}(t_2)\,\mathrm{d}t_2\right]\mathrm{d}t_1 + \cdots. \tag{II.33a}$$

If t is a later time than t', then the time arguments on the right hand side obey $t' \leq \cdots \leq t_2 \leq t_1 \leq t$, i.e. the latest time argument is that of the leftmost integral, the second latest time is that of the second integral from the left, and so on. Accordingly, one may write

$$\hat{\mathcal{U}}(t, t') = \mathcal{T}\exp\left[-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}\hat{H}(u)\,\mathrm{d}u\right] \quad \text{for } t \geq t', \tag{II.33b}$$

with $\mathcal{T}$ the Dyson time-ordering operator, which orders each product of (Hamilton) operators in the expansion of the exponential with growing time arguments from the right to the left.

On the other hand, if $t < t'$ in the Dyson series (II.33a), then the time arguments are actually ordered the other way round: $t \leq t_1 \leq t_2 \leq \cdots \leq t'$, i.e. the latest one is rightmost. Thus, one now writes

$$\hat{\mathcal{U}}(t, t') = \mathcal{T}^{\mathrm{a}}\exp\left[\frac{\mathrm{i}}{\hbar}\int_{t}^{t'}\hat{H}(u)\,\mathrm{d}u\right] \quad \text{for } t \leq t', \tag{II.33c}$$

with $\mathcal{T}^{\mathrm{a}}$ the anti-chronological time-ordering operator, which orders each product of operators in the expansion of the exponential with growing time arguments from the left to the right.

Armed with these results, we may now express the density operator (II.26). Assuming—since this is the case we shall in practice consider—that the instant t_0 at which the boundary condition is fixed is really the initial time, one has

$$\hat{\rho}(t) = \mathcal{T}\exp\left[-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t}\hat{H}(u)\,\mathrm{d}u\right]\hat{\rho}(t_0)\,\mathcal{T}^{\mathrm{a}}\exp\left[\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t}\hat{H}(u)\,\mathrm{d}u\right] \quad \text{for } t \geq t_0. \tag{II.34}$$

Remark: If the values of the Hamilton operator at two arbitrary different times t', t'' always commute, $\big[\hat{H}(t'), \hat{H}(t'')\big] = 0$, then the time-ordering operators (chronological or anti-chronological) are not necessary.

[(ae)]F. Dyson, 1923–2020

II.3.3 Time evolution of observables and of their expectation values

Consider now an observable $\hat{O}$ for a time-dependent quantum-mechanical system with Hilbert space $\mathscr{H}$. As is well known, there are two approaches to compute its expectation value (II.21) in a pure state, namely either considering that the latter is described by a time-evolving vector $|\Psi(t)\rangle$ of $\mathscr{H}$ obeying the Schrödinger equation, or by letting the state-vector remain constant, while the time evolution is entirely attached to the observable.[35] Here we extend this dual point of view to the computation of expectations values of observables in statistical mixtures of states, described by a density operator $\hat{\rho}$.

II.3.3 a Schrödinger picture

Let $\hat{O}(t)$ denote an observable of the system, where for the sake of generality we allowed for an explicit time dependence of the operator. In the Schrödinger picture, the density operator $\hat{\rho}(t)$ evolves with time according to the Liouville–von Neumann equation, while $\hat{O}(t)$ is what it is—in particular, $\hat{O}$ remains constant in time if it has no explicit dependence on t.

Using the general formula (II.22c) under consideration of Eq. (II.26), the expectation value of the observable at time t then reads

$$\langle\hat{O}(t)\rangle = \mathrm{Tr}\big[\hat{\rho}(t)\,\hat{O}(t)\big] = \mathrm{Tr}\Big[\hat{\mathcal{U}}(t,t_0)\,\hat{\rho}(t_0)\,\hat{\mathcal{U}}(t_0,t)\,\hat{O}(t)\Big]. \tag{II.35}$$

In the following, (pure) states or operators without subscript will automatically refer to their representation in the Schrödinger picture.

II.3.3 b Heisenberg picture

In the Heisenberg[af] picture, the state of the system is kept fixed at its value at a given reference time t_0: for a pure state, $|\Psi\rangle_\mathrm{H} \equiv |\Psi(t_0)\rangle$; for a statistical mixture of states, $\hat{\rho}_\mathrm{H} \equiv \hat{\rho}(t_0)$.

In turn, observables are represented by operators $\hat{O}_\mathrm{H}(t)$ related to those in the Schrödinger representation by

$$\hat{O}_\mathrm{H}(t) \equiv \hat{\mathcal{U}}(t_0,t)\,\hat{O}(t)\,\hat{\mathcal{U}}(t,t_0), \tag{II.36}$$

which ensures the identity $_\mathrm{H}\langle\Psi|\,\hat{O}_\mathrm{H}(t)\,|\Psi\rangle_\mathrm{H} = \langle\Psi(t)|\,\hat{O}(t)\,|\Psi(t)\rangle$ for the expectation value of the observable in a pure state in either picture. The operator $\hat{O}_\mathrm{H}(t)$ obeys the *Heisenberg equation*

$$\frac{\mathrm{d}\hat{O}_\mathrm{H}(t)}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar}\big[\hat{O}_\mathrm{H}(t),\hat{H}_\mathrm{H}(t)\big] + \left(\frac{\partial\hat{O}(t)}{\partial t}\right)_\mathrm{H}, \tag{II.37}$$

where the second term on the right-hand side vanishes when $\hat{O}$ has no explicit time dependence. Under this assumption and using the Liouville operator (II.27) computed with $\hat{H}_\mathrm{H}$, this equation becomes

$$\boxed{\frac{\mathrm{d}\hat{O}_\mathrm{H}(t)}{\mathrm{d}t} = \mathrm{i}\hat{\tilde{\mathcal{L}}}_\mathrm{H}(t)\hat{O}_\mathrm{H}(t),} \tag{II.38}$$

to be compared with Eq. (II.16) for a classical system.

If the Hamiltonian $\hat{H}$ is time independent, then $\hat{H}_\mathrm{H} = \hat{H}$ and the Liouville operator $\mathrm{i}\hat{\tilde{\mathcal{L}}}_\mathrm{H}$ is time-independent. Equation (II.38) is straightforwardly integrated as

$$\hat{O}_\mathrm{H}(t) = \mathrm{e}^{\mathrm{i}(t-t_0)\hat{\tilde{\mathcal{L}}}_\mathrm{H}}\,\hat{O}_\mathrm{H}(t_0) = \mathrm{e}^{\mathrm{i}(t-t_0)\hat{H}/\hbar}\,\hat{O}_\mathrm{H}(t_0)\,\mathrm{e}^{-\mathrm{i}(t-t_0)\hat{H}/\hbar}, \tag{II.39}$$

which under consideration of Eq. (II.29) is exactly equivalent to relation (II.36) since $\hat{O}_\mathrm{H}(t_0) = \hat{O}(t_0)$.

---

[35] See e.g. Refs. [27] chapter G$_\mathrm{III}$ or [28] § 13.

[af] W. HEISENBERG, 1901–1976

Remarks:

∗ The evolution equations for the density operator (in Schrödinger representation) and for observables (in Heisenberg representation), Eqs. (II.28) and (II.38), differ by a minus sign, which shows that the former, despite its possessing some of the "good" properties (hermiticity), is not an observable.[36]

∗ The Liouville operator is sometimes defined with a different convention from Eq. (II.27), namely as

$$\hat{\hat{\mathcal{L}}}' \equiv -\big[\,\cdot\,,\hat{H}\big], \tag{II.40}$$

without the factor $1/\hbar$. The advantage of this alternative definition is that the evolution equation of observables then becomes

$$i\hbar\frac{\mathrm{d}\hat{O}(t)}{\mathrm{d}t} = -\hat{\hat{\mathcal{L}}}'\hat{O}(t), \tag{II.41}$$

instead of Eq. (II.37). It is thus now quite similar—up to the minus sign—to the Schrödinger equation (II.23): the Liouville superoperator plays the role of the (negative of the) Hamilton operator, while the role of the kets of the Hilbert space $\mathscr{H}$ is taken by the operators on $\mathscr{H}$.
The drawback of this definition is that one loses the usual recipe for going from the quantum-mechanical to the classical case by replacing Poisson brackets $\{\,\cdot\,,\,\cdot\,\}$ with $\big[\,\cdot\,,\,\cdot\,\big]/i\hbar$.

II.3.3 c Time evolution of expectation values in statistical ensembles

Multiplying both sides of Eq. (II.36) with the density operator $\hat{\rho}_{\mathrm{H}} = \hat{\rho}(t_0)$ and taking the trace yields the expectation value

$$\big\langle\hat{O}_{\mathrm{H}}(t)\big\rangle = \mathrm{Tr}\big[\hat{\rho}_{\mathrm{H}}\,\hat{O}_{\mathrm{H}}(t)\big] = \mathrm{Tr}\Big[\hat{\rho}(t_0)\hat{\mathcal{U}}(t_0,t)\,\hat{O}(t)\hat{\mathcal{U}}(t,t_0)\Big]. \tag{II.42}$$

Using the invariance of the trace under cyclic permutations, this is clearly the same as Eq. (II.35) in the Schrödinger picture, i.e. $\big\langle\hat{O}_{\mathrm{H}}(t)\big\rangle = \big\langle\hat{O}(t)\big\rangle$.

Using either picture—which we do by not specifying whether the time dependence is attached to $\hat{\rho}$ or $\hat{O}$ and by dropping the subscript H—one finds that the time derivative of the expectation value of an observable with no explicit time dependence obeys the equation

$$\frac{\mathrm{d}\langle\hat{O}\rangle}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\big[\mathrm{Tr}\big(\hat{\rho}\,\hat{O}\big)\big] = \frac{1}{i\hbar}\,\mathrm{Tr}\big(\big[\hat{H},\hat{\rho}\big]\hat{O}\big) = \frac{1}{i\hbar}\,\mathrm{Tr}\big(\hat{\rho}\big[\hat{O},\hat{H}\big]\big). \tag{II.43}$$

The third term is proven by attaching the time dependence to $\hat{\rho}$ (Schrödinger picture) and using the Liouville–von Neumann equation (II.24); The fourth term follows from differentiating $\hat{O}_{\mathrm{H}}(t)$ and inserting the Heisenberg equation (II.37) without the partial-derivative term. The equivalence between the third and fourth terms is easily checked and follows from the invariance of the trace under cyclic permutations.

II.3.3 d Time contour

Invoking the invariance of the trace under cyclic permutations, Eqs. (II.35) or (II.42) can be rewritten as

$$\big\langle\hat{O}(t)\big\rangle = \big\langle\hat{O}_{\mathrm{H}}(t)\big\rangle = \mathrm{Tr}\Big[\hat{\mathcal{U}}(t_0,t)\,\hat{O}(t)\hat{\mathcal{U}}(t,t_0)\,\hat{\rho}(t_0)\Big]. \tag{II.44}$$

Reading the operator product in the argument of the trace from right to left, one begins with the system at an "initial" time t_0, evolves until time t—which might actually be prior to t_0, yet in practice we shall always take $t \geq t_0$—; then the operator $\hat{O}$ acts on the system at time t. Eventually, the system evolves "back" from t to t_0.

---

[36] A further hint to this difference is given by the fact that, in the interaction picture, observables evolve with the "unperturbed" Hamiltonian $\hat{H}_0$ while the density operator evolves with the perturbation $\hat{W}(t)$, see § II.3.4.
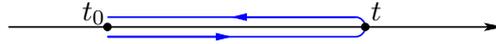
<div align="center">**Figure II.3.1**</div>

The corresponding path "in time" is pictured in Fig. II.3.1 as a *time contour* or *Keldysh*[ag] *contour* (in the complex plane of the variable t) along the real axis, starting at t_0, going forward until t, then back to t_0. Note that for the readability of the figure both forward and backward parts of the contour have been slightly displaced away from the real axis, although in fact they lie on it.

II.3.4 Time evolution of perturbed systems

An often encountered scenario consists in the following setup:

- Until some "initial" time t_0, the quantum-mechanical system under consideration is governed by a time-independent Hamilton operator $\hat{H}_0$—whose eigenvalues and eigenstates are often assumed to be known—and the (macro)state of the system at t_0 is known: $\hat{\rho}(t_0)$.

- At t_0 a time-dependent "perturbation" is turned on, corresponding to an extra term $\hat{W}(t)$ in the Hamiltonian, resulting in the total Hamilton operator

$$\hat{H}(t) = \hat{H}_0 + \hat{W}(t) \quad \text{for } t \geq t_0. \tag{II.45}$$

The goal is then to compute the evolution of the system—in particular of $\hat{\rho}(t)$—or the expectation value of some observable(s) at $t > t_0$.

In that case, it is fruitful to work in the *interaction* or *Dirac picture*, introducing on one hand vectors of the Hilbert space $\mathscr{H}$

$$|\Psi(t)\rangle_{\mathrm{I}} \equiv \mathrm{e}^{\mathrm{i}(t-t_0)\hat{H}_0/\hbar} |\Psi(t)\rangle = \hat{\mathcal{U}}_0(t,t_0)^\dagger |\Psi(t)\rangle \tag{II.46a}$$

and on the other hand operators on $\mathscr{H}$

$$\hat{O}_{\mathrm{I}}(t) \equiv \mathrm{e}^{\mathrm{i}(t-t_0)\hat{H}_0/\hbar} \hat{O}(t) \, \mathrm{e}^{-\mathrm{i}(t-t_0)\hat{H}_0/\hbar} = \hat{\mathcal{U}}_0(t,t_0)^\dagger \hat{O}(t) \hat{\mathcal{U}}_0(t,t_0). \tag{II.46b}$$

In these definitions, $\hat{\mathcal{U}}_0(t,t_0)$ denotes the time-evolution operator associated with $\hat{H}_0$ alone, here given by Eq. (II.29).

One then quickly finds that pure states $|\Psi(t)\rangle_{\mathrm{I}}$ evolve according to

$$\mathrm{i}\hbar \frac{\partial |\Psi(t)\rangle_{\mathrm{I}}}{\partial t} = \hat{W}_{\mathrm{I}}(t)|\Psi(t)\rangle_{\mathrm{I}}, \tag{II.47a}$$

i.e. under the influence of the "perturbation" $\hat{W}(t)$ alone, while accordingly the density operator in interaction representation $\hat{\rho}_{\mathrm{I}}(t)$ is governed by

$$\frac{\partial \hat{\rho}_{\mathrm{I}}(t)}{\partial t} = \frac{1}{\mathrm{i}\hbar} \big[\hat{W}_{\mathrm{I}}(t), \hat{\rho}_{\mathrm{I}}(t) \big]. \tag{II.47b}$$

Eventually, definition (II.46b) leads to

$$\frac{\mathrm{d}\hat{O}_{\mathrm{I}}(t)}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar} \big[\hat{O}_{\mathrm{I}}(t), \hat{H}_0 \big] + \left(\frac{\partial \hat{O}(t)}{\partial t} \right)_{\mathrm{I}}. \tag{II.47c}$$

Remarks:

∗ The "initial time" t_0 is also often taken to lie in the infinitely remote past, $t_0 \to -\infty$. This in particular allows one to consider if need be that the perturbation $\hat{W}(t)$ is turned on "adiabatically", i.e. slowly enough.[37]

---

[37]The corresponding *adiabaticity*, which takes here a different meaning from that of thermodynamics (absence of heat exchange), is discussed for instance in Refs. [29] chapter XVII § 7–14 or [30] chapter 10.

[ag]L. V. KELDYSH, born 1931

∗ Irrespective of whether t_0 is finite or not, it is often assumed that the system is at time t_0 in a state of thermodynamic equilibrium with respect to the Hamiltonian $\hat{H}_0$. For instance, the system is in equilibrium with a thermostat at temperature T, leading to the canonical equilibrium distribution

$$\hat{\rho}(t_0) = \frac{1}{Z(\beta)} e^{-\beta \hat{H}_0} \quad \text{with} \ \ Z(\beta) \equiv \text{Tr } e^{-\beta \hat{H}_0}$$

and $\beta \equiv 1/k_B T$. The exponential term entering this density operator can be written in term of the time-evolution operator associated with $\hat{H}_0$

$$e^{-\beta \hat{H}_0} = \hat{\mathcal{U}}_0(t_0, t_0 - i\hbar\beta),$$

corresponding formally to an evolution in imaginary time, from $t_0 - i\hbar\beta$ to t_0. Accordingly, the expectation value (II.44) becomes

$$\langle \hat{O}(t) \rangle = \langle \hat{O}_{\text{H}}(t) \rangle = \frac{1}{Z(\beta)} \text{Tr} \left[\hat{\mathcal{U}}(t_0, t) \, \hat{O}(t) \, \hat{\mathcal{U}}(t, t_0) \, \hat{\mathcal{U}}_0(t_0, t_0 - i\hbar\beta) \right], \quad (\text{II}.48)$$

where one has to pay attention that the system does not evolve with the same Hamiltonian "before" t_0 and afterwards, resulting in different time-evolution operators $\hat{\mathcal{U}}_0$, $\hat{\mathcal{U}}$. Corresponding to the time sequence, read from right to left, one can associate the Keldysh contour pictured in Fig. II.3.2, with a first part parallel to the imaginary axis.
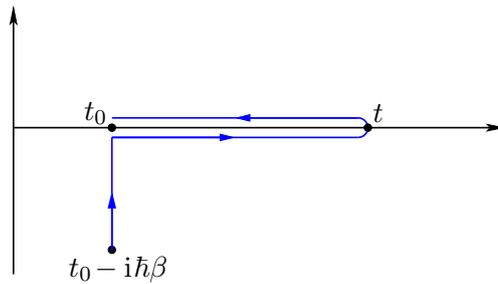

Figure II.3.2