V) Iff a system is in a pure state $\mathrm{Tr}\,\hat{\rho}^2 = (\mathrm{Tr}\,\hat{\rho})^2$ (1.11)

proof: $\hat{\rho} = |\psi\rangle\langle\psi| \Rightarrow \hat{\rho}^2 = |\psi\rangle\underbrace{\langle\psi|\psi\rangle}_{=1}\langle\psi| = |\psi\rangle\langle\psi| = \hat{\rho}$

$\Rightarrow \mathrm{Tr}\,\hat{\rho}^2 = \mathrm{Tr}\,\hat{\rho}$. But $\mathrm{Tr}\,\hat{\rho} = (\mathrm{Tr}\,\hat{\rho})^2 = 1$

The opposite direction is slightly more difficult.

- in general $\mathrm{Tr}\,\hat{\rho}^2 \leq (\mathrm{Tr}\,\hat{\rho})^2$

proof: $\hat{\rho} = \sum_n W_n |\psi_n\rangle\langle\psi_n|$. Let us first assume a simpler form $\hat{\rho} = \sum_n W_n |\phi_n\rangle\langle\phi_n|$ (Diagonal in an orthonormal basis)

$$\Rightarrow \hat{\rho}^2 = \sum_{n_1 n_2} W_{n_1} W_{n_2} |\phi_{n_1}\rangle\underbrace{\langle\phi_{n_1}|\phi_{n_2}\rangle}_{\delta_{n_1 n_2}}\langle\phi_{n_2}| = \sum_n W_n^2 |\phi_n\rangle\langle\phi_n|$$

$$\sum_n (W_n^2) \leq \underbrace{\left(\sum_n W_n\right)^2}_{= \sum_n W_n^2 + A(\{W_n\})} \quad \text{simply because } W_n \geq 0 \ \forall n.$$

$A \geq 0$

- $\mathrm{Tr}\,\hat{\rho}^2 = \mathrm{Tr}\,\hat{\rho}$?

$A(\{W_n\}) = \sum_n \sum_{m \neq n} W_n W_m$. $A = 0$ only if each term of the sum vanishes. Since $W_n = 0 \ \forall n$ is not allowed ($\mathrm{Tr}\,\hat{\rho} = 1$!), the only possibility is that $\exists \bar{n} : W_{\bar{n}} = 1$ and $W_n = 0$ if $n \neq \bar{n}$.

$$\sum_n (W_n^2) = \left(\sum_n W_n\right)^2 \Rightarrow \hat{\rho} = |\phi_{\bar{n}}\rangle\langle\phi_{\bar{n}}| \Rightarrow \hat{\rho} \text{ represents a pure state.}$$

1.3. Coherence vs. Incoherence

One of the basic concepts in quantum mechanics is the superposition principle. If a system has at disposal state $|\psi_1\rangle$ and $|\psi_2\rangle$ => its most general state is

$$|\psi\rangle = a|\psi_1\rangle + b|\psi_2\rangle$$

This is a third quantum state. This superposition principle is the mathematical background of the interference phenomena.

▲ How does the density matrix theory express the quantum interference and the superposition principle?

Def. The system is a <u>coherent superposition</u> of basis states $|\phi_n\rangle$ if its density matrix is <u>not diagonal</u> in the $|\phi_n\rangle$ representation.
If in addition the system is in a pure state it is said to be <u>completely coherent</u>.

Def. If ρ_{ij} ($\hat{\rho}$, loosely speaking) is <u>diagonal</u> the system is said to be in an <u>incoherent superposition</u> of the basis states. (providing more than 1 diagonal element $\neq 0$)
Cohen-Tannoudji (1962)

<u>Note</u>: The concept of coherent superposition depends on the choice of the representation basis for the density matrix.
For example, let $\{|\psi_n\rangle\}$ be ON then $\hat{\rho} = \sum_n W_n |\psi_n\rangle\langle\psi_n|$ is an incoherent superposition of states $|\psi_n\rangle$, but in general due to (1.6) a coherent superposition of basis states.

<u>Note</u>: The diagonal element ρ_{ii} (<u>population</u>) expresses the probability of finding the system in the basis state $|\phi_i\rangle$. The off-diagonal elements, (<u>coherences</u>) are associated with interference effects.

▲ Why shall we call a pure state completely coherent?

$$\hat{\rho}_{pure} = |\psi\rangle\langle\psi| \quad \longleftrightarrow \quad \rho_{pure} = \left(\begin{array}{c|c} 1 & 0 \\ \hline 0 & 0 \end{array}\right)$$

- ρ_{pure} has off-diagonal elements in any representation not containing $|\psi\rangle$ in the basis.

▲ Can you think about a state which is „completely" incoherent?

$$\hat{\rho} = \sum_{n=1}^{N} \frac{1}{N} |\phi_n\rangle\langle\phi_n| \quad \longleftrightarrow \quad \rho = \frac{1}{N} \mathbb{1}$$

this state is a statistical mixture in whatever representation.

1.4 Time evolution of statistical mixtures

▲ How is time entering in the density matrix theory?

In steps:

• 1.4.1 Time-evolution operator

The time evolution of quantum mechanical states is described by the Schrödinger eq. (SE)

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle \qquad (1.12)$$

Rather than solving directly the SE, we move the problem to the identification of a time-evolution operator $\hat{U}(t)$ defined by

$$|\psi(t)\rangle := \hat{U}(t,t_0) |\psi(t_0)\rangle \qquad (1.13)$$

with the convention $\hat{U}(t) := \hat{U}(t,0)$.

From (1.12) it follows $i\hbar \frac{\partial \hat{U}}{\partial t} |\psi(0)\rangle = \hat{H}(t) \hat{U}(t) |\psi(0)\rangle$ and, due to the arbitrary choice of $|\psi(0)\rangle$

$$i\hbar \frac{\partial}{\partial t} \hat{U}(t) = \hat{H}(t) \hat{U}(t) \quad (1.14)$$

$$-i\hbar \frac{\partial}{\partial t} \hat{U}^{+}(t) = \hat{U}^{+}(t) \hat{H}^{+}(t) \quad (1.14b)$$

Properties of $\hat{U}(t)$

i) (1.13) $\Rightarrow$ $\hat{U}(0) = \mathbb{1}$

ii) (1.14 + 1.14b) $i\hbar \frac{\partial}{\partial t}(U^{+}U) = 0 \Rightarrow U^{+}(t)U(t)$ is constant

but $U^{+}(0)U(0) = \mathbb{1} \Rightarrow U$ is unitary.

proof

$$i\hbar \frac{\partial}{\partial t}(U^{+}U) = i\hbar\left(\frac{\partial}{\partial t}U^{+}\right)U + U^{+} i\hbar\left(\frac{\partial}{\partial t}U\right) = -U^{+}HU + U^{+}HU = 0$$

$i\hbar \frac{\partial}{\partial t}(UU^{+}) = 0$ along the same lines.

1.4.2 Time evolution of $\hat{\rho}(t)$

Suppose that at time $t=0$ a certain mixture is represented by the density operator

$$\hat{\rho}(0) = \sum_n W_n |\psi_n(0)\rangle\langle\psi_n(0)| \quad (1.15)$$

The states vary in time according to (1.13). It follows

$$\hat{\rho}(t) = \sum_n W_n |\psi_n(t)\rangle\langle\psi_n(t)| =$$

$$\sum_n W_n \hat{U}(t) |\psi_n(0)\rangle\langle\psi_n(0)| U^{+}(t)$$

$$\Rightarrow \boxed{\hat{\rho}(t) = \hat{U}(t)\hat{\rho}(0)\hat{U}^{+}(t)} \quad 1.16$$

Moreover, differentiating (1.16) with respect to time it follows

$$\boxed{i\hbar \frac{\partial}{\partial t} \hat{\rho}(t) = \left[\hat{H}(t), \hat{\rho}(t)\right]} \qquad (1.17)$$

known as Liouville-von Neumann eq. because it assumes the same form as the equation of motion for the phase space probability distribution in classical mechanics.

$$\rho\,(q,p) = \rho\,(q(t), p(t))$$

$$\frac{d}{dt}\rho = \frac{\partial \rho}{\partial q}\dot{q} + \frac{\partial \rho}{\partial p}\dot{p}\ .$$

If the system has an hamiltonian dynamics described by the Hamilton function $H(q,p)$

$$\begin{cases} \dot{q} = \dfrac{\partial H}{\partial p} \\ \dot{p} = -\dfrac{\partial H}{\partial q} \end{cases}$$

$$\frac{d}{dt}\rho = \frac{\partial \rho}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial \rho}{\partial p}\frac{\partial H}{\partial q} = \{\rho, H\}_{\text{Poisson}} \longleftarrow \boxed{\text{Liouville equation}}$$

where we have introduced the Poisson brackets:

$$\{f,g\}_{\text{Poisson}} = \frac{\partial f}{\partial q}\frac{\partial g}{\partial p} - \frac{\partial f}{\partial p}\frac{\partial g}{\partial q}$$

the following correspondence can be derived:

$$\frac{i}{\hbar}[\ ,\ ] \longleftrightarrow \{\ ,\ \}_{\text{Poisson}}$$

Note: Eq. (1.10) and (1.17) are the basic equations of the theory out of which one gets the dynamics of the observables.

- 1.4.3 <u>The interaction picture</u>

In general either $\hat{U}(t)$ is not known or an exact solution of (1.17) is not possible. We shall see later different methods to determine $\hat{\rho}$ either exactly or approximately. Here we start to address the case in which we can write:

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \qquad (1.18)$$

whereby $\hat{V}$ is a possibly time-dependent perturbation. Then, it is convenient to reformulate the Liouville eq. in the <u>interaction picture</u>

The interaction picture is defined by the relation:

$$|\psi(t)\rangle_s = \hat{U}_0(t)\,|\psi(t)\rangle_I \quad (1.19) \quad \Leftrightarrow \quad |\psi(t)\rangle_I = \hat{U}_0^{+}(t)\,|\psi(t)\rangle_s \quad (1.19b)$$

where the subscript s denotes the Schrödinger name of the time evolution picture considered so far. $\hat{U}_0(t)$ is the ev. operator associated with $\hat{H}_0$. Since, the expectation value of an observable is independent of the time evolution picture:

$$\langle \hat{O} \rangle_s = \langle \hat{O} \rangle_I$$

${}_I\langle \psi(t)|\,\hat{O}\,|\psi(t)\rangle_s = {}_I\langle \psi(t)|\, U_0^{+}(t)\,\hat{O}\,U_0(t)\,|\psi(t)\rangle_I$ naturally defines the time evolution of operators in the interaction picture:

$$\hat{O}_I(t) = U_0^{+}(t)\,\hat{O}_s\,U_0(t) \qquad (1.20)$$

Note: $|\psi(0)\rangle_s = |\psi(0)\rangle_I$ at time $t=0$ the two representation coincide.

$\hat{O}_I(0) = \hat{O}_s(0)$

▲ The question is now: which is the time evolution operator in interaction picture?

$$|\psi(t)\rangle_I := \hat{U}_I(t)\,|\psi(0)\rangle_I$$

but from 1.19b $\quad |\psi(t)\rangle_I = U_0^+(t)\,U(t)\,|\psi(0)\rangle_s = U_0^+(t)\,U(t)\,|\psi(0)\rangle_I$

thus

$$\boxed{U_I(t) := U_0^+(t)\,U(t)} \qquad (1.21)$$

The importance of the interaction picture is first achieved by differentiating (1.21) with respect of time:

$$i\hbar\frac{\partial}{\partial t}U_I(t) = i\hbar\left(\frac{\partial}{\partial t}U_0^+(t)\right)U(t) + U_0^+(t)\,i\hbar\frac{\partial}{\partial t}U(t) \overset{1.14-1.14b}{=}$$

$$= U_0^+(t)\left(-H_0\right)U(t) + U_0^+(t)\,H\,U(t) = U_0^+(t)\,V(t)\,U(t)$$

$$= U_0^+(t)\,V(t)\,U_0(t)\,U_0^+(t)\,U(t) = V_I(t)\,U_I(t)$$

Summarizing

$$\boxed{i\hbar\frac{\partial}{\partial t}U_I(t) = V_I(t)\,U_I(t)} \qquad (1.22)$$

The equation of motion of the time evolution operator in interaction picture is only determined by the interaction component of the Hamiltonian.

▲ Which are the consequences for the density operator $\hat{\rho}$ of this time evolution picture?

We start from the definition

$$\hat{\rho}_I(t) = \sum_n W_n \, |\psi(t)\rangle_I \langle \psi(t)| \qquad (1.23)$$

From (1.19b) it follows

$$\hat{\rho}_I(t) = \hat{U}_0^+(t)\, \hat{\rho}_s(t)\, \hat{U}_0(t) \qquad (1.24)$$

← Note: the time evolution of $\hat{\rho}$ follows the rules defined for a generic operator $\hat{O}$.

Finally, we can derive the Liouville equation in interaction picture

$$\frac{d}{dt}\rho_I(t) = \left(\frac{d}{dt}U_0^+(t)\right)\rho_s(t)\,U_0(t) + U_0^+(t)\left(\frac{d}{dt}\rho_s(t)\right)U_0(t) + U_0^+(t)\rho_s(t)\frac{d}{dt}U_0(t)$$

$$= \underbrace{U_0^+ \frac{i}{\hbar}H_0\rho_s U_0 + U_0^+\left(-\frac{i}{\hbar}\right)H\rho_s U_0}_{} + U_0^+\rho_s\left(\frac{i}{\hbar}\right)HU_0 + U_0^+\rho_s\left(-\frac{i}{\hbar}\right)H_0 U_0(t)$$

$$= -\frac{i}{\hbar}U_0^+ V\rho_s U_0 \qquad + \frac{i}{\hbar}U_0^+\rho_s V U_0$$

$$= -\frac{i}{\hbar}U_0^+VU_0\,U_0^+\rho_s U_0 + \frac{i}{\hbar}U_0^+\rho_s U_0\,U_0^+VU_0$$

Summarizing

$$\boxed{i\hbar\frac{d}{dt}\hat{\rho}_I(t) = \left[\hat{V}_I(t), \hat{\rho}_I(t)\right]} \qquad (1.25)$$

Note: Eq. (1.25) can be formally integrated

$$\hat{\rho}_I(t) = \hat{\rho}_I(0) - \frac{i}{\hbar}\int_0^t d\tau \left[\hat{V}_I(\tau), \rho_I(\tau)\right] \qquad (1.26)$$

Replacing (1.26) in (1.25

$$i\hbar\frac{d}{dt}\hat{\rho}_I(t) = \left[V_I(t), \rho_I(0)\right] - \frac{i}{\hbar}\int_0^t d\tau \left[\hat{V}_I(t), \left[\hat{V}_I(\tau), \hat{\rho}_I(\tau)\right]\right] \qquad (1.27)$$

Eq.(1.27) represents the starting point for a perturbative solution of (1.25).

1.5 systems in thermal equilibrium

A peculiar density matrix particularly usefull in the study of system bath models is the one describing a system in thermal equilibrium with the surrounding medium. For such systems, as shown by statistical mechanics

$$\hat{\rho}_{eq} := \frac{e^{-\beta\hat{H}}}{Z} \quad (1.28) \qquad Z = \mathrm{Tr}\, e^{-\beta\hat{H}} \quad (1.28b)$$

if the system can exchange energy but NOT particles with the surrounding. (CANONICAL ENSEMBLE)

$$\hat{\rho}_{eq} := \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{Z} \quad (1.28c) \qquad Z = \mathrm{Tr}\, e^{-\beta(\hat{H}-\mu\hat{N})} \quad (1.28d)$$

if the system can exchange energy and particles with the surrounding (GRANDCANONICAL ENSEMBLE)

Note: in the energy representation, given $\hat{H}|m\rangle = E_m|m\rangle$

$$\rho_{nm} = \langle n|\hat{\rho}_{eq}|m\rangle = \delta_{nm}\frac{e^{-\beta E_n}}{Z}$$

$$\Rightarrow \boxed{\hat{\rho}_{eq} = \frac{1}{Z}\sum_n e^{-\beta E_n}|n\rangle\langle n|} \quad (1.29)$$

Hence, a system in thermal equilibrium is an incoherent statistical mixture of energy eigenstates with weights $W_n = e^{-\beta E_n}/Z$.

Analogously, in the grand canonical ensemble

$$\hat{H}|N,m\rangle = E_{N,m}|N,m\rangle \qquad \rho_{Nn,Mm} = \langle N,n|\hat{\rho}_{eq}|M,m\rangle =$$

$$\Rightarrow \boxed{\hat{\rho}_{eq} = \frac{1}{Z}\sum_{N,n} e^{-\beta(E_{N,n}-\mu N)}|N,n\rangle\langle N,n|} = \delta_{NM}\delta_{nm}\frac{e^{-\beta(E_{N,m}-\mu N)}}{Z} \quad (1.29b)$$

Chapter 2: COUPLED SYSTEMS

2.1 The non-separability of QM systems after an interaction

Let us consider two QM systems Φ_1 and Φ_2 described by the complete set of ON state vectors $\{|\phi_i^{(1)}\rangle\}$ and $\{|\phi_j^{(2)}\rangle\}$, respectively. The two systems, initially separated, are brought together a time $t=0$ and allowed to interact.

If before the interaction the two systems are in the pure states $|\phi_\alpha^{(1)}\rangle$ and $|\phi_\beta^{(2)}\rangle$ then prior the interaction the combined system is represented by the state vector

$$|\psi_{in}\rangle := |\phi_\alpha^{(1)}\rangle|\phi_\beta^{(2)}\rangle \qquad (2.1)$$

in the composite Hilbert space. During the interaction time, the time evolution is determined by the time evolution operator in the composite space

$$|\psi_{in}\rangle \longrightarrow |\psi_{out}(\alpha,\beta)\rangle \qquad (2.2)$$

In general

$$|\psi_{out}(\alpha,\beta)\rangle = \sum_{ij} a(ij,\alpha\beta)\,|\phi_i^{(1)}\rangle|\phi_j^{(2)}\rangle \qquad (2.3)$$

with the coefficients a yielding the probability amplitude of finding a particle of Φ_1 in $|\phi_i^{(1)}\rangle$ and <u>simultaneously</u> one particle of Φ_2 in $|\phi_j^{(2)}\rangle$.

In other words, a particular state $|\phi_i^{(1)}\rangle$ is correlated to one or several states $|\phi_j^{(2)}\rangle$. It follows the principle of non-separability:

In general it is not possible to write $|\psi_{out}\rangle = |\phi^{(1)}\rangle|\phi^{(2)}\rangle$, i.e. to assign a single state vector to either of the two subsystems.

If $\hat{Q}_1$ is an observable of system Φ_1 and $\hat{Q}_2$ an observable of Φ_2

$$\langle \hat{Q}_1\hat{Q}_2\rangle (t=0) = \langle \psi_{in}|\hat{Q}_1\hat{Q}_2|\psi_{in}\rangle = \langle \phi_\alpha^{(1)}|\hat{Q}_1|\phi_\alpha^{(1)}\rangle\langle \phi_\beta^{(2)}|\hat{Q}_2|\phi_\beta^{(2)}\rangle$$

and this is valid for the entire probability distribution of $\hat{Q}_1$ and $\hat{Q}_2$ with respect of the one of $\hat{Q}_1\hat{Q}_2$ $P_{Q_1Q_2} = P_{Q_1}P_{Q_2}$.

$$\langle \hat{Q}_1\hat{Q}_2\rangle (t>0) = \sum_{ij i'j'} a^*(i'j',\alpha\beta)\, a(ij\,\alpha\beta)\, \langle \phi_{i'}^{(1)}|\hat{Q}_1|\phi_i^{(1)}\rangle\langle \phi_{j'}^{(2)}|\hat{Q}_2|\phi_j^{(2)}\rangle.$$

It follows an important consequence for the case in which only one system, say Φ_1, is observed after interaction:
Although both systems were in pure states, at a later time Φ_1 will be found in a mixed state due to its correlations with Φ_2.

$\Rightarrow$ $\boxed{\text{The non observation of the } \Phi_2 \text{ system results in a loss of coherence in the } \Phi_1 \text{ system}}$

2.2. The reduced density matrix

Consider two (or more) interacting QM systems. In meny cases only one of the component systems, say Φ_1, is of interest, while the other, say Φ_2, is left undetected.

As a consequence the Φ_1 system is in a mixed state (cf sec 2.1)
We wish to construct the relevant density operator $\hat{\rho}(\Phi_1, t)$ (so called <u>reduced</u> density operator) characterizing the system Φ_1 alone.

Let us consider an operator $\hat{Q}_1$ acting on the Φ_1 system only.
Then, with $\hat{\rho}_{tot}(t)$ the density operator of the composite system,

$$\langle \hat{Q}_1 \rangle = \mathrm{Tr}\{\hat{\rho}_{tot}\, \hat{Q}_1\} = \sum_{i'j'} \langle \phi_{i'}^{(1)} \phi_{j'}^{(2)} | \hat{\rho}_{tot} \hat{Q}_1 | \phi_{i'}^{(1)} \phi_{j'}^{(2)} \rangle =$$

$$= \sum_{iji'j'} \langle \phi_{i'}^{(1)} \phi_{j'}^{(2)} | \hat{\rho}_{tot} | \phi_i^{(1)} \phi_j^{(2)} \rangle \underbrace{\langle \phi_i^{(1)} \phi_j^{(2)} | \hat{Q}_1 | \phi_{i'}^{(1)} \phi_{j'}^{(2)} \rangle}_{\delta_{jj'} \langle \phi_i^{(1)} | \hat{Q}_1 | \phi_{i'}^{(1)} \rangle}$$

$$= \sum_{i'i} \langle \phi_{i'}^{(1)} | \underbrace{\sum_j \langle \phi_j^{(2)} | \hat{\rho}_{tot} | \phi_j^{(2)} \rangle}_{\hat{\rho}_{red}} | \phi_i^{(1)} \rangle \langle \phi_i^{(1)} | \hat{Q}_1 | \phi_{i'}^{(1)} \rangle$$

$$= \mathrm{Tr}_{\Phi_1}\{\hat{\rho}_{red}\, \hat{Q}_1\}$$

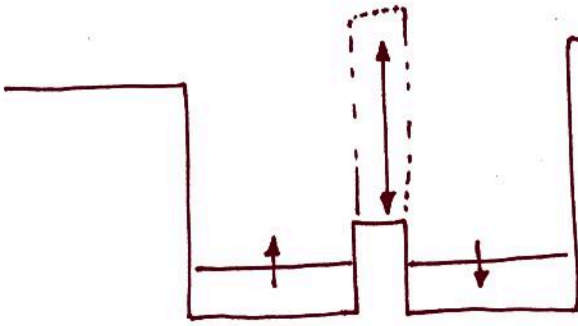
Defining thus the reduced density matrix

$$\hat{\rho}_{red} := \sum_i \langle \phi_i^{(2)} | \hat{\rho}_{tot} | \phi_i^{(2)} \rangle := \mathrm{Tr}_{\Phi_2}\{\hat{\rho}_{tot}\} \qquad (2.4)$$

And the expectation value es

$$\langle \hat{Q}_1 \rangle = \sum_i \langle \phi_i^{(1)} | \hat{\rho}_{red}\, \hat{Q}_1 | \phi_i^{(1)} \rangle := \mathrm{Tr}_{\Phi_1}\{\hat{\rho}_{red}\, \hat{Q}_1\}. \qquad (2.5)$$

A (hopefully clarifying) example



The initial state is $|\uparrow\rangle_L |\downarrow\rangle_R := |\uparrow\downarrow\rangle$. The Hamiltonian

$$H = \sum_{i\sigma} \varepsilon\, c^\dagger_{i\sigma} c_{i\sigma} + \sum_{\sigma} t\left(c^\dagger_{1\sigma} c_{2\sigma} + c^\dagger_{2\sigma} c_{1\sigma} \right)$$

No more particles can enter the system. The Hilbert space has dimension 6

(*) $|\uparrow\uparrow\rangle$ $|\uparrow\downarrow\rangle$ $|\downarrow\uparrow\rangle$ $|\downarrow\downarrow\rangle$ $|2\,0\rangle$ $|0\,2\rangle$

Short notation for the occupation number representation

(**) $|1100\rangle$ $|1001\rangle$ $|0110\rangle$ $|0011\rangle$ $|1010\rangle$ $|0101\rangle$

with the single particle states ordering $1\uparrow, 2\uparrow, 1\downarrow, 2\downarrow$. It is not difficult to prove that H in the ordered basis (*) or (**) reads

$$H = \left(\begin{array}{cccc|cc} 2\varepsilon & & & & 0 & 0 \\ & 2\varepsilon & & & t & t \\ & & 2\varepsilon & & t & t \\ & & & 2\varepsilon & 0 & 0 \\ \hline 0 & t & t & 0 & 2\varepsilon & 0 \\ 0 & t & t & 0 & 0 & 2\varepsilon \end{array}\right)$$

This matrix we want to diagonalize to obtain the eigenvalues E_i and eigenvectors $|\varphi_i\rangle$ such that.

$$|\uparrow\downarrow\rangle(t) = \sum_i \langle \varphi_i | \uparrow\downarrow\rangle\, |\varphi_i\rangle\, e^{i E_i t/\hbar}$$

And, consequently:

$$\rho_{tot}(t) = \sum_{ij} \langle \varphi_i | \uparrow\downarrow \rangle \langle \uparrow\downarrow | \varphi_j \rangle \; |\varphi_i \rangle\langle \varphi_j | \, e^{i(E_i - E_j)t/\hbar}$$

Finally

$$\rho_{red,1} = {}_R\langle 0 | \rho_{tot} | 0 \rangle_R + {}_R\langle \uparrow | \rho_{tot} | \uparrow \rangle_R +$$

$$ {}_R\langle \downarrow | \rho_{tot} | \downarrow \rangle_R + {}_R\langle 2 | \rho_{tot} | 2 \rangle_R \, .$$

Now that we defined the program, let us realize it: for the diagonalization one notices that the Hamiltonian is invariant under:

S_F * spin flip $\quad \uparrow \to \downarrow$ and $\downarrow \to \uparrow$

W_F * well flip $\quad 1 \to 2$ and $2 \to 1$

Moreover $[S_F, W_F] = 0$. Thus we can organize the basis in terms of eigenstates for S_F and W_F. Namely:

		S_F W_F
NO	$\frac{1}{\sqrt{2}}\left(\overset{c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}}{|\uparrow\uparrow\rangle} + \overset{c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}}{|\downarrow\downarrow\rangle}\right)$	$|1, -1\rangle$
NO	$\frac{1}{\sqrt{2}}\left(\overset{c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}}{|\uparrow\uparrow\rangle} - \overset{c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}}{|\downarrow\downarrow\rangle}\right)$	$|-1, -1\rangle$
	$\frac{1}{\sqrt{2}}\left(\overset{c^\dagger_{1\uparrow}c^\dagger_{2\downarrow}}{|\uparrow\downarrow\rangle} + \overset{c^\dagger_{2\uparrow}c^\dagger_{1\downarrow}}{|\downarrow\uparrow\rangle}\right)$	$|-1, +1\rangle$
✓	$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$	$|1, -1\rangle$
	$\frac{1}{\sqrt{2}}\left(\overset{c^\dagger_{1\uparrow}c^\dagger_{1\downarrow}}{|2,0\rangle} + \overset{c^\dagger_{2\uparrow}c^\dagger_{2\downarrow}}{|0,2\rangle}\right)$	$|-1, +1\rangle$
✓	$\frac{1}{\sqrt{2}}\left(|2,0\rangle - |0,2\rangle\right)$	$|-1, -1\rangle$

Note: $c^\dagger_{1\uparrow} c^\dagger_{2\uparrow} = - c^\dagger_{2\uparrow} c^\dagger_{1\uparrow}$.

$|\varphi_i\rangle \quad i = 1 \ldots 6$

eigenstate

eigenstate

Considering that $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ are already eigenstates of H.

the procedure allows to identify already also

$$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \quad \text{and} \quad \frac{1}{\sqrt{2}}\left(|2,0\rangle - |0,2\rangle\right)$$

as eigenstates of the system. By symmetry they can only couple to $|1,-1\rangle$ and $|-1,-1\rangle$ states, but the latter are decoupled due to system specific properties.

$$|\varphi_1\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle\right) \qquad E_1 = 2\varepsilon$$

$$|\varphi_2\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\uparrow\rangle - |\downarrow\downarrow\rangle\right) \qquad E_2 = 2\varepsilon$$

$$|\varphi_3\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \qquad E_3 = 2\varepsilon$$

$$|\varphi_4\rangle = \frac{1}{\sqrt{2}}\left(|2,0\rangle - |0,2\rangle\right) \qquad E_4 = 2\varepsilon$$

In the basis $\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)$, $\frac{1}{\sqrt{2}}\left(|2,0\rangle + |0,2\rangle\right)$ H reads

$$H_{red} = \begin{pmatrix} 2\varepsilon & 2b \\ 2b & 2\varepsilon \end{pmatrix}$$

$$|\varphi_5\rangle = \frac{1}{2}\left(|2,0\rangle + |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle + |0,2\rangle\right) \qquad E_5 = 2\varepsilon + 2b$$

$$|\varphi_6\rangle = \frac{1}{2}\left(|2,0\rangle - |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle + |0,2\rangle\right) \qquad E_6 = 2\varepsilon - 2b$$

$$|\uparrow\downarrow\rangle = e^{i\frac{2\varepsilon}{\hbar}t}\left[\frac{1}{\sqrt{2}}|\varphi_3\rangle + \frac{1}{2}e^{i\frac{2b}{\hbar}t}|\varphi_5\rangle - \frac{1}{2}e^{-i\frac{2b}{\hbar}t}|\varphi_6\rangle\right]$$

$$|\uparrow\downarrow\rangle\langle\uparrow\downarrow| = \frac{1}{2}|\varphi_3\rangle\langle\varphi_3| + \frac{1}{4}|\varphi_4\rangle\langle\varphi_4| + \frac{1}{4}|\varphi_5\rangle\langle\varphi_5| +$$
$$\frac{1}{\sqrt{8}}|\varphi_3\rangle\langle\varphi_4|e^{-i2bt/\hbar} - \frac{1}{\sqrt{8}}|\varphi_3\rangle\langle\varphi_5|e^{i2bt/\hbar} + \frac{1}{\sqrt{8}}|\varphi_4\rangle\langle\varphi_3|e^{i2bt/\hbar}$$
$$-\frac{1}{4}|\varphi_4\rangle\langle\varphi_5|e^{i2bt/\hbar} - \frac{1}{\sqrt{8}}|\varphi_5\rangle\langle\varphi_3|e^{-i2bt/\hbar} - \frac{1}{4}|\varphi_5\rangle\langle\varphi_4|e^{-i2bt/\hbar}$$

For the projection into the factorized basis, it is convenient to calculate.

$$|\uparrow\downarrow(t)\rangle = e^{i\,2\varepsilon/\hbar\, t}\Big[\frac{1}{2}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) + \frac{1}{4}\left(|2,0\rangle + |\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle + |0,2\rangle\right) e^{i\,2b/\hbar\, t} + $$
$$ - \frac{1}{4}\left(|2,0\rangle - |\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle + |0,2\rangle\right) e^{-i\,2b/\hbar\, t}\Big]$$

$$= e^{i\,2\varepsilon/\hbar\, t}\Big[\left(\frac{1}{2} + \frac{1}{2}\cos\left(\frac{2b}{\hbar}t\right)\right)|\uparrow\downarrow\rangle + \left(-\frac{1}{2} + \frac{1}{2}\cos\left(\frac{2b}{\hbar}t\right)\right)|\downarrow\uparrow\rangle + \frac{i}{2}\sin\left(\frac{2b}{\hbar}t\right)\left(|2,0\rangle + |0,2\rangle\right)\Big]$$

$t = 0$ one obtains back $|\uparrow\downarrow\rangle$ ✓

$\frac{2b}{\hbar}t = \pi \Leftrightarrow t = \frac{\hbar\pi}{2b}$ $\quad -|\downarrow\uparrow\rangle e^{i\frac{2\varepsilon}{\hbar}\cdot\frac{\hbar\pi}{2b}} = -|\downarrow\uparrow\rangle e^{i\pi\varepsilon/b}$ separable

$\frac{2b}{\hbar}t = \pi/2$ $\quad |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle + i\left(|2,0\rangle + |0,2\rangle\right)$ for example, non separable.

$$\hat{\rho}_{tot}(t) = \frac{\left[1+\cos\left(\frac{2b}{\hbar}t\right)\right]^2}{4}|\uparrow\downarrow\rangle\langle\uparrow\downarrow| + \frac{\left[1-\cos\left(\frac{2b}{\hbar}t\right)\right]^2}{4}|\downarrow\uparrow\rangle\langle\downarrow\uparrow|$$
$$+ \frac{\sin^2\left(\frac{2b}{\hbar}t\right)}{4}\left(|2,0\rangle\langle 2,0| + |2,0\rangle\langle 0,2| + |0,2\rangle\langle 2,0| + |0,2\rangle\langle 0,2|\right)$$
$$+ \frac{-1+\cos^2\left(\frac{2b}{\hbar}t\right)}{4}\left(|\uparrow\downarrow\rangle\langle\downarrow\uparrow| + |\downarrow\uparrow\rangle\langle\uparrow\downarrow|\right) - \frac{i\sin\left(\frac{2b}{\hbar}t\right)\left(1+\cos\left(\frac{2b}{\hbar}t\right)\right)}{4}$$
$$\left(|\uparrow\downarrow\rangle\langle 2,0| + |\uparrow,\downarrow\rangle\langle 0,2|\right) + \frac{i\sin\left(\frac{2b}{\hbar}t\right)\left(1+\cos\left(\frac{2b}{\hbar}t\right)\right)}{4}\left(|2,0\rangle\langle\uparrow\downarrow| + |0,2\rangle\langle\uparrow\downarrow|\right)$$
$$+ \frac{i\sin\left(\frac{2b}{\hbar}t\right)\left(1-\cos\left(\frac{2b}{\hbar}t\right)\right)}{4}\left(|\downarrow\uparrow\rangle\langle 2 0| + |\downarrow\uparrow\rangle\langle 0 2|\right) - \frac{i\sin\left(\frac{2b}{\hbar}t\right)\left(1-\cos\left(\frac{2b}{\hbar}t\right)\right)}{4}$$
$$\left(|0,2\rangle\langle\downarrow\uparrow| + |2,0\rangle\langle\downarrow\uparrow|\right)$$

$$\hat{\rho}_{red}(t) = \frac{[1+\cos(\omega t)]^2}{4}\,|\uparrow\rangle\langle\uparrow| + \frac{[1-\cos(\omega t)]^2}{4}\,|\downarrow\rangle\langle\downarrow|$$

$$+ \frac{\sin^2(\omega t)}{4}\left(|2\rangle\langle 2| + |0\rangle\langle 0|\right) \qquad , \omega = \frac{2b}{\hbar}$$

which is a statistical mixture except for $t = \frac{n\pi}{\omega} = \frac{n\pi\hbar}{2b} = \frac{nh}{4b}$. when the system 1 is either in the pure state $|\uparrow\rangle\langle\uparrow|$ (n even) or in the pure state $|\downarrow\rangle\langle\downarrow|$ (n odd). Notice that

$$\mathrm{Tr}_{\Phi_1}\,\hat{\rho}_{red} = \frac{2 + 2\cos^2(\omega t) + 2\sin^2(\omega t)}{4} = 1 .$$

$$\hat{\rho}_{red,1} = P_\uparrow(t)\,|\uparrow\rangle\langle\uparrow| + P_\downarrow(t)\,|\downarrow\rangle\langle\downarrow| + P_0(t)\,|0\rangle\langle 0| + P_2(t)\,|2\rangle\langle 2|$$

Note $P_0 = P_2 \quad \forall t$