Notations and conventions

Notations

Operators and operations

Here we explain the most important notations used in this dissertation. We add information about the operations that are typical of density matrix theory, which is extensively used in this work, but not generally in quantum dynamics, an excellent account of which can be found in Ref. [1].

- $\hat{A}$ is used to indicate an operator. Operators will sometimes be called matrices (especially the density operator), because they are often handled within the matrix formalism [1].

- $\hat{I} := \sum_{i=0}^{\infty} |\psi_i\rangle\langle\psi_i|$ is the identity operator expressed in an orthonormal basis $\{|\psi_i\rangle\}$. An integral should appear instead of the sum if continuous indices are involved [1]. However, in the numerical calculations the Hilbert space will always be finite or at least separable, so it will be discretized [2]. Continuous indices are consequently not necessary in the following and the basis will always be taken as discrete.

- $\hat{A} = \mathcal{O}\,\hat{B}$ indicates an operator $\mathcal{O}$ that acts on an operator $\hat{B}$ connecting each element of it with every element of $\hat{A}$[1]. In particular $\mathcal{L}$, indicates the generator of the dynamics of the density operator and is often called Liouvillian super-operator or simply Liouvillian.

- $\mathrm{tr}\left(\hat{A}\right)$ indicates the trace of an operator $\hat{A}$, provided it exists, $\mathrm{tr}\left(\hat{A}\right) := \sum_{i=0}^{\infty}\langle\psi_i|\hat{A}|\psi_i\rangle$, where $\{|\psi_i\rangle\}$ is any orthonormal basis.

- $\left[\hat{A},\ \hat{B}\right]$ is the commutator $\hat{A}\,\hat{B} - \hat{B}\,\hat{A}$.

- $\left[\hat{A},\ \hat{B}\right]_+$ is the anticommutator $\hat{A}\,\hat{B} + \hat{B}\,\hat{A}$.

- “System” will often refer to the few degrees of freedom over which the observables of interest are defined, plus possibly the modes strongly coupled to them. For the other modes of the global physical system the expression “bath”, “environment” or “reservoir” are used following the nomenclature of macroscopic thermodynamics.

- The expressions “open” system dynamics is used to indicate that the system can exchange energy and phase with the environment. The corresponding expression in thermodynamics would be “closed”, because there, “open” is used for systems that exchange matter [3]. In density matrix theory the systems are always considered as trace preserving, *i.e.*, they are “closed” in thermodynamical sense, so “open” and “closed” refer here to energetics.

Density matrix norm and scalar product

Sometimes

$$(\hat{A}, \hat{B}) := \mathrm{tr}\left(\hat{A}^{\dagger}\,\hat{B}\right), \tag{0.1}$$

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[1] Usually $\mathcal{O}$ is called a super-operator or a tensor, because in matrix form it has a rank that is the square of the one of the operators on which it acts. It actually represents a mapping $\mathcal{O} : \mathcal{B}(\mathcal{H}) \to \mathcal{B}(\mathcal{H})$ where $\mathcal{B}(\mathcal{H})$ is the algebra of linear bounded operators defined on $\mathcal{H}$, the Hilbert space of the system.

is used as a scalar product between operators (matrices). This implies a norm of the form

$$||\hat{A}|| := \sqrt{\mathrm{tr}\left(\hat{A}^{\dagger}\,\hat{A}\right)}, \tag{0.2}$$

which is called a Frobenius norm. The use (0.2) is incompatible with the postulates of quantum mechanics, because if applied to a matrix representing a statistical mixture, like Eqn.(2.5) below when more than one $|\psi_i\rangle$ has weight different from zero, one would compute expectation values different from the incoherent sum over the ensemble (see chapter 2). Accordingly for density matrices, one defines the norm as[2]

$$\mathrm{tr}\left(\hat{A}\right), \tag{0.3}$$

that will be shown in chapter 2 to have the correct properties[3]. This implies the absence of a scalar product in the density matrix space (so it is not a Hilbert space, but a Banach space [4]). The use of the scalar product (0.1) and relative norm (0.2) is consequently restricted to numerical or analytical purposes, and has no strict physical meaning.

Conventions and units

In the following chapters, unless otherwise specified, atomic units will be used, consequently $\hbar$ is set to one [1]. Exceptions are: temperature, measured in Kelvin, time often indicated in fs (10^{-15} s) and energy expressed in eV, because these are the most used units in quantum molecular dynamics, as can be seen in Ref.[5], that is an extremely detailed review of time dependent quantum dynamics. The conversion of units and the numerical values of the constants relevant for this work are presented in table 0.1. The atomic unit of mass corresponds to the mass of one electron, and the atomic unit of charge to the charge of one proton.

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[2] This definition is not a norm for general operators, because it can be negative; but density operators are positive semidefinite

[3] For general trace class operators the norm should be $tr|\hat{A}|$.

Table 0.1: Conversion of atomic units into S.I. units, plus values of some important constants.

Unit	atomic	S.I.	other common units
distance	1 a_0	$5.29177 \cdot 10^{-11}$ m	.529177 Å
energy	1 E_h	$4.3597455 \cdot 10^{-18}$ J[a]	27.211379 eV
			$2.194746 \cdot 10^{5}$ cm^{-1}
time	1 $\hbar/E_h$	$2.41888 \cdot 10^{-17}$ s	$2.41888 \cdot 10^{-2}$ fs
mass	1 m$_e$	$9.1093897 \cdot 10^{-31}$ kg	
charge	1 e	$1.602177 \cdot 10^{-19}$ A·s	
Constant			
Planck / 2π, $\hbar$	= 1 $\hbar$	1.05457 ·10^{-34} J·s	
Boltzmann, k_b	= 3.166829·10^{-6} E_h·K^{-1}	1.38066 ·10^{-23} J·K^{-1}	

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[a] 1 J = 1 $m^2kg \cdot s^{-2}$