Chapter 2

Outline of density matrix theory

2.1 The concept of a density matrix

A physical experiment on a molecule usually consists in observing in a macroscopic ensemble[1] a quantity that depends on the particle's degrees of freedom (like the measure of a spectrum, that derives for example from the absorption of photons due to vibrational transitions). When the interactions of each molecule with any other physical system are comparatively small[2], it can be described by a state vector $|\psi_i(t)\rangle$ whose time evolution follows the time–dependent Schrödinger equation

$$|\dot{\psi}_i(t)\rangle = -i\hat{H}|\psi_i(t)\rangle, \tag{2.1}$$

where $\hat{H}$ is the system Hamiltonian, depending only on the degrees of freedom of the molecule itself.

Even if negligible in first approximation, the interactions with the environment usually bring the particles to a distribution of states where many of them behave in a similar way because of the periodic or uniform properties of the reservoir (that can just consist of the other molecules of the gas). For numerical purposes, this can

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[1] There are interesting exceptions to this, the "single molecule spectroscopies" [44, 45].

[2] Of course with the exception of the electromagnetic or any other field probing the system!

be described as a discrete distribution. The interaction being small compared to the internal dynamics of the system, the macroscopic effect will just be the incoherent sum of the observables computed for every single group of similar particles times its weight[3]:

$$< \hat{A} > (t) = \sum_{i=0}^{\infty} \rho_i \langle \psi_i(t) | \hat{A} | \psi_i(t) \rangle \tag{2.2}$$

If we skip the time dependence, we can think of (2.2) as a thermal distribution, in this case the ρ_i would be the Boltzmann factors:

$$\rho_i := \frac{e^{-\frac{E_i}{k_b T}}}{Q} \tag{2.3}$$

where E_i is the energy of state i, and k_b and T are the Boltzmann constant and the temperature of the reservoir, respectively . Q is the partition function defined as

$$Q := \sum_{i=0}^{\infty} e^{-\frac{E_i}{k_b T}}.$$

With this formalism, the weights ρ_i must be left time independent because we do not have an equation for the distribution but only a formula to derive the expectation values (2.2).

What we need is a quantum mechanical equivalent of the phase space distribution or micro-canonical ensemble of classical statistical mechanics. Because of the superposition principle of quantum mechanics, a simple sum generates interferences, that should not exist between the elements of a statistical ensemble (using again the time independent formalism for states in equilibrium):

$$|\psi_{stat}\rangle \;=\; \sum_{i=0}^{\infty} a_i |\psi_i\rangle \quad \Rightarrow \quad < \hat{A} > = \langle \psi_{stat} | \hat{A} | \psi_{stat} \rangle \;=\; \sum_{i,j=0}^{\infty} a_j^* a_i \langle \psi_j | \hat{A} | \psi_i \rangle.$$

To derive the quantum mechanical equivalent of a Liouville distribution, we may introduce an identity operator $\hat{I}$ on the left of $\hat{A}$ in (2.2)

$$< \hat{A} > = \sum_{i=0}^{\infty} \rho_i \langle \psi_i | \sum_{j=0}^{\infty} |\phi_j\rangle \langle \phi_j | \hat{A} | \; \psi_i \rangle \;=\; \sum_{i,j=0}^{\infty} \rho_i \langle \psi_i | \phi_j \rangle \langle \phi_j | \hat{A} | \psi_i \rangle$$

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[3] The number of states is set to infinity, for a finite number of states N, it is enough to set the coefficients with index larger than N to zero.

and rearrange the order of the terms

$$< \hat{A} >= \sum_{j=0}^{\infty} \langle \phi_j | \hat{A} \ \big(\sum_{i=0}^{\infty} \rho_i |\psi_i\rangle\langle\psi_i| \big) \ |\phi_j\rangle \quad .$$

Accordingly, expectation values of quantum mechanical operators $\hat{A}$ for ensembles can be derived from the trace operation

$$\langle \hat{A} \rangle = \mathrm{tr}\left(\hat{A}\hat{\rho}\right) , \tag{2.4}$$

where the equilibrium statistical operator $\hat{\rho}$ is defined as

$$\hat{\rho} = \sum_{i=0}^{\infty} \rho_i |\psi_i\rangle\langle\psi_i| \quad . \tag{2.5}$$

It is possible to generalize the definition (2.5) by introducing a basis and time dependent coefficients[4]:

$$\hat{\rho}(t) := \sum_{i,j=0}^{\infty} \rho_{ij}(t) |\phi_i\rangle\langle\phi_j| \quad . \tag{2.6}$$

To have the properties equivalent to a microcanonical ensemble, the density operator must be Hermitean and positive semidefinite[5] because when brought back to diagonal form the coefficients $\rho_{ij}(t) = \delta_{ij}\rho_i(t)$ have the meaning of probabilities, so they must be real and positive. Once the density operator is generalized, the problem arises whether (2.6) can always be rewritten as (2.5); being Hermitean, it can always be diagonalized; but if there are states with the same population, the transformation is not unique anymore. Any orthogonal set of state vectors spanning the subspace of the degenerate eigenvectors can be used in (2.5); but all of them will give rise to the same expectation values as can be verified by rewriting the equations for $\hat{\rho}$ and using different sets for the functions belonging to the degenerate eigenvalues. So the orthogonalization procedure may be problematic, but the resulting density operator will have anyway the correct physical properties.

If the coupling with the bath is negligible or its coordinates are included in (2.6), the Schrödinger dynamics can be mapped directly onto the density matrix space to

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[4] The basis set being complete a time dependence on the functions is not necessary.

[5] Positive semidefinite operators have eigenvalues real positive or null.

get the nondissipative Liouville–von Neumann equation [37, 46]

$$\dot{\hat{\rho}}(t) = \mathcal{L}\hat{\rho}(t) \equiv \mathcal{L}_H\hat{\rho}(t) \equiv -i\left[\hat{H},\ \hat{\rho}(t)\right], \tag{2.7}$$

where $\mathcal{L}_H$ is the Hamiltonian Liouvillian superoperator. The dynamics are unitary and the eigenvalues consequently do not change in time, keeping the distribution constant. The equations for isolated systems follow always the Hamiltonian dynamics, being by definition independent of external forces. Eqn.(2.7) is completely equivalent to a set of time dependent Schrödinger equations plus the averaging (2.2). The practical solution of (2.7), however, requires the propagation of matrices rather than state vectors. This disadvantage of density matrices is outweighed only in rare cases by the advantage that both the propagation of mixed and pure initial states can be done with the same effort.

When the strength of the interactions with the external modes cannot be neglected (like in condensed phases) each molecule will behave according to the slightly different environment it is in, thus modifying the distribution (2.6). The dynamics is even more perturbed when we look at the properties of small parts of molecules like the chromophores of a macromolecule or the absorption properties of the active groups of chlorophyll or rhodopsin,[6] both embedded in large biological systems. Here with the time evolution appears the phenomenon of IVR (Intramolecular Vibrational Redistribution). This could be modeled using a distribution of molecular Hamiltonians (source of the inhomogeneous broadening in spectroscopy) and/or fluctuating forces (homogeneous broadening). All these phenomena can again be more elegantly, and often more efficiently, be handled in the framework of density matrix theory. Here, the bath can be left out of the dynamics, but its effects on the system can be reproduced directly in the equations of motion of the system via the (non-Markovian) dissipative Liouville-von Neumann equation [37]

$$\dot{\hat{\rho}}(t) = \mathcal{L}\hat{\rho}(t) = -i\left[\hat{H}_s,\ \hat{\rho}(t)\right] + \int_0^t d\tau \mathcal{L}_D(t,\tau)\{\hat{\rho}(\tau)\}. \tag{2.8}$$

The relevant observables are then directly computed with $\hat{\rho}(t)$ and relation (2.4). In (2.8), the Hamiltonian is indicated with $\hat{H}_s$ to stress that it refers only to the coordinates of the smaller system. One usually talks about the “reduced dynamics”

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[6] Molecules involved in the photosynthesis and in the visual process respectively.

of the “reduced density operator”. $\hat{H}_s$ is an effective Hamiltonian because even if it depends only on the system modes, it includes the static (averaged) distortion of the system dynamics that is due to the environmental degrees of freedom, like the additional electrostatic field of a crystal cavity.

The term

$$\int_0^t d\tau \mathcal{L}_D(t,\tau)\{\hat{\rho}(\tau)\}$$

enters in (2.8) as a dissipative corrective to the Hamiltonian evolution to describe the dynamical coupling of the system to an unobserved environment and depends on the fluctuations of the bath variables. It accounts for energy and phase relaxation,*i.e.*, the modification of distribution (2.5), or equivalently, of the eigenvalues of (2.6). The derivation of the dissipative term may lead to a non-Markovian evolution (as in Eqn.(2.8)), then the time evolution of the density operator depends upon its past, the system develops a “memory”.

Under the Markov approximation (*i.e.*, when memory effects are neglected), the equations of motion turn into [37, 46, 4]:

$$\dot{\hat{\rho}}(t) = \mathcal{L}\hat{\rho}(t) = -i\left[\hat{H}_s,\ \hat{\rho}(t)\right] + \mathcal{L}_D\left(\hat{\rho}(t)\right). \tag{2.9}$$

Here, $\mathcal{L}_D\left(\hat{\rho}(t)\right)$ is a function of $\hat{\rho}$ at time t only and is usually linear. The expression “dissipative Liouville-von Neumann equation” normally refers to this equation and not to (2.8).

The proper choice of this dissipative part is still a matter of dispute, so we dedicate to this issue a separate section.

2.2 Equations of motion

The Liouville–von Neumann equation with dissipative terms does not have a unique form[7], and even its general properties are not yet clearly understood. Already in

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[7] At least there are the non–Markovian (2.8) and the Markovian (2.9) alternatives.

the derivation of the equations of motion, two main approaches are possible: One is to start from the complete system and to eliminate through projection operator techniques [47] the environmental degrees of freedom, leaving them only as operators of the Hilbert space describing the "essential" modes. The other one consists in taking a phenomenological viewpoint, that is devising proper dissipation operators for the Liouville–von Neumann equation, mainly using empirical knowledge on the system. The two techniques should be equivalent in principle, given that the underlying physics is the same, but the effects of the environment are often not only theoretically complex to disentangle[8], but also poorly known[9]. Moreover, coarse approximations have to be made on the system and bath models just to be able to derive the equations of motion, thus making the two approaches very different. Both solutions have their advantages and shortcomings, and both rely on the separability of the system from the bath. Unfortunately, this assumption contradicts the quantum mechanical character of the dynamics because, when systems get in contact with one another, they are entangled and "cannot be divided" (as tell the famous Einstein–Podolski–Rosen correlations). Indeed, it was recently shown by Lindblad [48] that a reduced dynamics cannot have all the mathematical properties we would expect for its physical interpretability[10].

Nevertheless, the complexity of many reactions makes the use of a reduced dynamics interesting, if not unavoidable, because the approximations that have to be introduced to describe the complete dynamics of the system plus reservoir would be too poor. So, we follow the idea of eliminating the bath degrees of freedom from the dynamics, while keeping only the coordinates necessary to compute the physical observables relevant to the phenomenon of interest. First, the environmental degrees of freedom are projected out of the dynamics, then an inverse mapping is constructed to the complete space in order to determine the equations of motion (in simple words: "What would do the bath if it would have been propagated together

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[8] For instance, where the asymptotic evolution should lead, and which are the mathematical restrictions that the dynamics should satisfy.

[9] The evaluation of potential energy surfaces for the strongly coupled coordinates is already a very complicated numerical task.

[10] This depends on the basic algebraic structure of quantum mechanics, the so called von Neumann (noncommutative with involution) algebras, see in [48] and references for a more detailed discussion of this issue.

with the system"). This is the source of the non-Markovian terms because the present "answer of the environment" depends on how the smaller system behaved in the past. Therefore, the elimination of the bath from the dynamics creates a link to the past, a memory, that otherwise wouldn't be there, because quantum mechanics is Markovian[11]. This is why in order to have a reduced dynamics local in time, an additional approximation has to be made, namely the already mentioned Markov approximation. It is valid when the correlation time of the reservoir is much smaller than the characteristic time scale of the system (that is the bath needs much less time to go back to equilibrium than the system to change significantly); in other cases, *e.g.*, when the bath correlation times are long (slowly moving solvent molecules, low frequency phonons), it breaks down. This assumption depends also on the weakness of the coupling, being exact in the zero coupling limit. An example of the failure of the Markov approximation is when the system dynamics is very fast because ultrashort lasers are used in the system Hamiltonian [49].

Many of the models based on projection operators have to make the assumption that the bath and the system are initially uncorrelated; this may turn out to be a major source of errors in addition to the neglected non-Markovian character of the reduced dynamics. The so called build up of memory effects or "system slips" [50, 51], are thus generated. In this case the reduced dynamics resembles the true dynamics (for the solvable cases) only after an initial stage, and if the reduced operator phases are changed (slipped) in the derivation of the equations. Physically this corresponds to set a correction for the initial correlations in the global system. An extensive study aimed at finding a consistent solution for these problems is being done in the group of Tannor [52].

The size and complexity of many condensed phase problems makes probably the use of a Markovian dynamics the minor of the passable approximations, especially in the case of the gas surface problems we are interested in. The Redfield theory [53, 54] and the mathematical, phenomenological approach of Lindblad and Gorini–

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[11] This happens also in the case of Time Dependent Self Consistent Field equations [20], for cases where some of the coupled equations are analytically solvable (like harmonic oscillators subject to a time dependent force) and can be included in the other equations as non-Markovian nonlinear terms. In [20], a nice example is reported.

Kossakowski–Sudarshan [55, 56, 46] are the most prominent Markovian approaches to open quantum systems [57].

The former belongs to the class of methods that combine projection operator techniques [47] with perturbation theory to treat the system bath coupling microscopically. Redfield theory can be shown to converge to the exact dynamics in the weak coupling limit[12] [58]. It is also known to generate negative eigenvalues (probabilities) in case of violation of the perturbative hypothesis or for a time scale shorter than the bath correlation time [59]. This is the "coarse graining" assumption,*i.e.*, the dynamics is meaningful only if averaged over timesteps larger than the bath correlation time.

The Redfield equations of motion, derived for the matrix elements of $\hat{\rho}(t)$ in the basis of the eigenfunctions of the effective Hamiltonian, are

$$\dot{\rho}_{ij}(t) = -i\omega_{ij}\rho_{ij}(t) + \sum_{kl} \mathcal{R}_{ij,kl}\rho_{kl}(t) \tag{2.10}$$

where $\omega_{ij} = E_i - E_j$ is the transition frequency between states i and j, and $\mathcal{R}_{ij,kl}$ is the Redfield tensor, a matrix with the square of the rank of the density matrix.

The Lindblad approach belongs to the branch of the completely positive dynamical semigroups[13]. Here, the so called Lindblad operators are used in the equations of motion to treat the relaxation in the framework of the system only. One asks which are the possible forms for $\mathcal{L}_D$ in (2.9) that give to the dynamics of the physical system the correct mathematical and physical properties; it is, consequently, a semiphenomenological mathematical approach. Information from microscopic knowledge on the system bath coupling can be included also in this model [43, 60]. This second approach allows for the probabilistic interpretation of the diagonal elements of the density matrix at any instant of time, while the Redfield theory does not.

One of the requirements made in the Lindblad approach is the restrictive complete positivity [46, 55]; this can intensify the coarse character of the dynamics as

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[12] Through the use of numerical simulations and for an harmonic oscillator coupled with a bath of harmonic oscillators, that is the only system for which a direct solution is possible.

[13] "Semigroups", because the inverse of the dynamical map does not exist [46], reflecting an irreversible evolution.

illustrated in numerous works [61, 62, 63, 64], because of the weakness of the reduced dynamics approach in quantum systems [48]. Nevertheless, this approach is general and allows to introduce the known properties of the system under study phenomenologically, even when a proper microscopical model approach is impractical. The mathematical form of the Lindblad generator was derived by Gorini, Kossakowski, and Sudarshan [56] for finite dimensional Hilbert spaces and by Lindblad [55] for infinite Hilbert spaces:

$$\mathcal{L}_D\hat{\rho} = \sum_{i=0}\left\{\hat{C}_i\hat{\rho}\hat{C}_i^\dagger - \frac{1}{2}\left[\hat{C}_i^\dagger\hat{C}_i,\ \hat{\rho}\right]_+\right\} \quad . \tag{2.11}$$

The $\hat{C}_i$ are the Lindblad operators. They belong to the algebra of the bounded linear operators acting on Hilbert space of the system with the condition that $\sum_i \hat{C}_i^\dagger\hat{C}_i$ must be bounded [55].

There are other approaches derived from the projection operator technique, the Caldeira–Leggett model [65, 66] being one example of these. As far as shortcomings are concerned it shares the nonpositive character with the Redfield theory. As a matter of fact, the original derivation of the Caldeira–Leggett model is made in the Feynmann-Vernon formalism from which one gets a path integral formulation for the system density matrix dynamics with so called influence functionals that represent the effect of the environment [67]. This last formalism is often used to model small systems in condensed phases, but because of its complexity it cannot be directly applied to large systems.

An interesting discussion on Markovian dynamics is given in the series of papers of Tannor and coworkers [63, 64].

To deal with stronger couplings between system and bath, time dependent operator techniques can be used. Here the perturbation approach is not needed; they generate a Markovian, but nonlinear dynamics. These methods are more accurate, but computationally intense and were therefore used only for small and simple systems [68]. Another way to deal with strongly interacting baths is to use higher order perturbation theory (the Redfield theory being only second order in the bath coupling); master equations of this kind are derived and discussed in [69].

We have used Lindblad forms for almost all our dissipation models, because of the complexity of the system studied (with electron hole pairs, phonons and multiple electronic surfaces) that renders almost impossible to derive sensible dissipation operators microscopically. Moreover, we often need a strict positive density matrix, because we are interested in small probabilities, and the only alternative to a Lindblad form would be to abandon the Markovian or the linear approaches in the hope that the less approximate dynamics would correct the arising of negative probabilities [52]. This approach is presently technically impossible for our large systems. Moreover our dissipation is often connected with the motion of electrons, whose speed compared to the nuclei renders the Markov approach very reasonable.