1 The Pauli master equation

In this exercise, we study the derivation of the Pauli master equation. A master equation is an effective probabilistic equation of motion. There are a wide variety of master equations for different purposes, and the Pauli master equation is used for example to study the dynamics of large molecules or electron transport in nano-structures.

We are concerned with a dynamic process, e.g. a chemical reaction, and we want to investigate if and how its microscopic description can be simplified if the number of available states of the system is large enough that statistical methods may be used. It is also assumed that there is a large number of similar processes which differ only in the initial conditions and which are ultimately averaged.

Given is a time-independent Hamiltonian of a molecular system,
\[ \hat{H} = \hat{H}_0 + V \]
with some small perturbation \( V \), as well as the spectrum of \( \hat{H}_0 \),
\[ \hat{H}_0 |\psi_n\rangle = E_n |\psi_n\rangle. \]
Those are normalized as \( \langle \psi_m | \psi_n \rangle = \delta_{mn} \). The system is initially in a state \( |\Psi(0)\rangle \). The state at time \( t \) is given by the time-dependent Schrödinger equation
\[ i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \]
which can be expanded in terms of the eigenstates of \( \hat{H}_0 \) as
\[ |\Psi(t)\rangle = \sum_{n=0}^{\infty} c_n(t) |\psi_n\rangle. \]

The formal solution of (3) is
\[ |\Psi(t)\rangle = \hat{U}(t) |\Psi(0)\rangle := e^{-i\hat{H}_0 t/\hbar} |\Psi(0)\rangle \]
where the exponential is defined in terms of its power series.

1.1 Show that the coefficients \( c_n(t) \) at time \( t \) are related to the initial coefficients as
\[ c_m(t) = \sum_n c_n(0) \langle \psi_m | \hat{U}(t) | \psi_n \rangle =: \sum_n c_n(0) U_{mn}(t). \]

Here, \( U_{mn}(t) \) are defined as the matrix elements of the operator \( \hat{U} \) in the basis of the states \( |\psi_n\rangle \).

1.2 What would happen to \( U_{mn} \) and hence to the time-evolution of the coefficients \( c_m(t) \) if there was no perturbation \( V \) in (1)?
We assume that there is a large number of rather dense energy levels $E_n$ and that the dynamics of the system can be described by grouping energy levels together. This coarse-graining is achieved by partitioning the set of all energy levels and by summing the population of these sets. The effective population $p_I$ of a set of energy levels with quantum numbers from $n_I + 1$ to $n_{I+1}$ is

$$p_I(t) := \sum_{i=n_I+1}^{n_{I+1}} |c_i(t)|^2. \tag{7}$$

In the following, we use upper-case indices $I, J$ to denote the sets, while the corresponding lower-case indices $i, j$ run over all elements of the set, e.g. the index $i$ always runs from $n_I + 1$ to $n_{I+1}$. This convention is very important to understand the following derivation.

Next, we approximate the time-development of those populations as

$$p_I(t) \approx \sum_J \sum_j \sum_i |U_{ij}(t)|^2 |c_j(0)|^2 \tag{8}$$

1.3 What is the exact expression for $p_I(t)$ in terms of $c_j(0)$? What approximation was made in (8) and how can it be justified? Would there be differences in the quality of this approximation if the dynamical molecular process is thermally induced (incoherent) or if it is induced by laser light (coherent)?

*Hint:* The sums over $J$ and $j$ in (8) taken together are equivalent to a sum over all states.

In the coarse-grained picture, we assume that we can only measure $p_J$ but do not know (or care about) the true populations $|c_j|^2$ of the individual levels combined in $p_J$. From this ignorance follows that our best guess for the individual initial populations in the set of levels from $n_J + 1$ to $n_{J+1}$ is the average

$$|c_j(0)|^2 \approx \frac{p_J(0)}{n_{J+1} - n_J} \tag{9}$$

and the coarse-grained populations from (8) are approximated as

$$p_I(t) \approx \sum_J \frac{p_J(0)}{n_{J+1} - n_J} \sum_j \sum_i |U_{ij}(t)|^2 =: \sum_J p_J(0)Y_{IJ}(t). \tag{10}$$

If we define $\vec{p}$ as the vector of all $p_I$ and $Y$ as the matrix with entries $Y_{IJ}$, we can write this equation as

$$\vec{p}(t) = Y(t)\vec{p}(0). \tag{11}$$

1.4 Show that

$$Y(t_1 + t_2) = Y(t_1)Y(t_2) = Y(t_2)Y(t_1). \tag{12}$$

To satisfy the requirements (12), we make the ansatz

$$Y(t) = e^{Kt} \tag{13}$$
for the function \( Y(t) \) with a matrix \( K \). From (11) follows that

\[
\frac{\partial}{\partial t} \vec{p} = K \vec{p}.
\]  

(14)

This is the Pauli master equation. It is a first-order rate equation for the populations with rate coefficients \( K_{IJ} \). Those coefficients may be estimated with the help of perturbation theory for \( V \).

1.5 The Pauli master equation describes irreversible dynamics, although we started from the time-dependent Schrödinger equation, which is time-reversible. Where and how did we change from a time-reversible to a time-irreversible description of the process?

The Pauli master equation is rarely stated in the form of (14), but typically as

\[
\frac{\partial}{\partial t} p_n(t) = \sum_{m \neq n} (K_{nm} p_m(t) - K_{mn} p_n(t)).
\]

(15)

1.6 Derive (15) from (14).

\textit{Hint: } After writing (14) explicitly for the components \( p_n \) of \( \vec{p} \), you need to replace the diagonal element \( K_{nn} \) by a suitable relation. To obtain this relation, you may use the requirement of conservation of the total population, i.e. the sum of populations \( \sum_n p_n(t) \) is constant for all times \( t \). This relationship needs to be fulfilled for any population vector \( \vec{p} \), in particular also for an initial \( \vec{p} \) where only one level is populated.

Finally, to “apply” (14), we set up a simple model for a population inversion, the process underlying laser technology. Let us assume that we have three levels as depicted in the figure, and we allow only transitions from level 1 to level 2 with rate \( k_1 \), from level 2 to level 3 with rate \( k_2 \), and from level 3 to level 1 with rate \( k_3 \).

\[ \begin{array}{c}
\text{level} \ 1 \\
\downarrow \\
\text{level} \ 2 \\
\downarrow \\
\text{level} \ 3
\end{array} \]

\[ \begin{array}{c}
k_1 \\
\downarrow \\
k_2 \\
\downarrow \\
k_3
\end{array} \]

Figure 1: Left: 3-state model for transitions between states 1, 2, and 3 as given by the arrows. Right: Change of populations of the levels with time for an initial population vector \( \vec{p} = (1, 0, 0) \) with rate constants as given above the figure.
1.7 Set up the matrix $K$ of the Pauli master equation (14) for this model.

1.8 Determine the population vector $\vec{p}$ corresponding to equilibrium for the case $k_1 = 1.0, k_2 = 1.0, k_3 = 0.1$ shown in the figure.

For questions regarding the tasks, please contact Daniel Hammerland (daniel.hammerland@phys.chem.ethz.ch).