8 From quantum dynamics to macroscopic kinetics

8.1 Quantum states, level densities and level numbers of composite quantum systems

8.1.1 Harmonic oscillator

\[ E_v = h\nu(v + \frac{1}{2}), \quad v = 0, 1, 2, 3, \ldots \infty \]  

(8.1)

Number of states with energy \( E_v < E \) given by

\[ W(E) = \sum_{v=0}^{\infty} h(E - E_v), \]  

(8.2)

Figure 8.1: Potential energy \( V(q) \) and energy eigenvalues \( E_v \) of the harmonic oscillator.

where \( h(x) \) is the Heaviside step function defined as
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\[ h(x) = 0 \quad \text{for} \quad x < 0 \]
\[ h(x) = 1 \quad \text{for} \quad x > 0 \]  

\textbf{Density of states} is defined as

\[ \rho(E) = \frac{dW(E)}{dE} = \sum_{v=0}^{\infty} \delta(E - E_v) \]  

Instead of \( W(E) \), one often works with the smoothed version \( \langle W(E) \rangle \) which describes the averaged behaviour

\[ \langle W(E) \rangle = v + 1 = \frac{E}{\hbar \nu} + \frac{1}{2} = \frac{E + E_z}{\hbar \nu} \]  

The deviation of \( \langle W(E) \rangle \) with respect to energy provides the averaged level density:

\[ \langle \rho(E) \rangle = \frac{d \langle W(E) \rangle}{dE} = \frac{1}{\hbar \nu} \simeq \frac{\Delta W(E)}{\Delta E} \]

Both averaged quantities are only meaningful in the limit of many quantum states per energy interval.

\textbf{8.1.2 Many harmonic oscillators}

The levels of a quantum system composed of 2 subsystems are given by

\[ E_m = E_{n_1,n_2} = E_{n_1} + E_{n_2} \]  

For example, we consider 2 harmonic oscillators

\[ E_k = E_{v_1,v_2} = (v_1 + \frac{1}{2})\hbar \nu_1 + (v_2 + \frac{1}{2})\hbar \nu_2 \]

Expressed in the level densities, we have

\[ N_1(E_1) = \rho_1(E_1)|dx| \equiv \rho_1(E')|dE'| \]
\[ N_2(E_2) = \rho_2(E_2)|dx| \equiv \rho_2(E'')|dE''| \]

The total number of levels that fulfill \( E_1 + E_2 = E \) (\( |dx| << E \)) is given by

\[ N_{1,2} = N_1 N_2 = \rho_1(E_1)\rho_2(E_2)(dx)^2 \]

The corresponding level density for \( E_1 = x \) and \( E_2 = E - x \) is

\[ \rho_{1,2}(E_1 = x, E_2 = E - x, E) = \frac{dN_{1,2}}{dx} = \rho_1(x)\rho_2(E - x)dx \]
Figure 8.2: Number of states $W(E)$ and the density of states $\rho(E)$ for a harmonic oscillator.

The total level density at energy $E$ is then obtained by integrating over the variable $x$. 

\[ W'(E) = E/hv + 1/2 \]
\[ W''(E) = E/hv \]
\[ \rho_{1,2}(E_2) = \int_{x=0}^{x=E} \rho_1(x)\rho_2(E - x)dx 
= \int_{E' = E}^{E'' = 0} \rho_1(E')\rho_2(E'')dE'' , \]

which corresponds to the convolution of the functions \( \rho_1 \) and \( \rho_2 \), which is also written

\[ \rho_{1,2} = \rho_1 \otimes \rho_2 = \rho_2 \otimes \rho_1 \]

Figure 8.3: Convolution of the densities of states of two spectra \( E_1 + E_2 = E \), see text).

Similarly, the number of levels can also be obtained by convolution
\[ W_{1,2}(E) = \int_0^E W_1(E')\rho_2(E - E')dE' \]
\[ = W_1 \otimes \rho_2 = \rho_1 \otimes W_2 \quad (8.14) \]
\[ = \int_0^E \rho_{1,2}(x)dx \]

The level density of a system composed of \( n \) subsystems can be obtained by a sequence of convolutions

\[ \rho_{1,2,3}(E) = \int_0^E \rho_{1,2}(x)\rho_3(E - x)dx \]
\[ = \int_0^E \rho_{1,2}(E - E'')\rho_3(E'')dE'' \quad (8.15) \]

The application of these formula to the smoothed level density of harmonic oscillators is particularly simple because the level densities are not energy dependent:

\[ \rho_{1,2,3} = (h\nu_1)^{-1}(h\nu_2)^{-1}(h\nu_3)^{-1} \int_0^E E''dE''' \]
\[ = (h\nu_1 h\nu_2 h\nu_3)^{-1} \frac{1}{2} E^2 \quad (8.16) \]

For \( s \) harmonic oscillators we therefore find

\[ \rho_{1,2,3,...,s}(E) = \frac{E^{s-1}}{(s - 1)! \prod_{i=1}^{s} h\nu_i} \quad (8.17) \]

The number of levels is obtained by integration

\[ W_{1,2,3,...,s} = \frac{E^s}{s! \prod_{i=1}^{s} h\nu_i} \]
\[ = \int_0^E \rho_{1,2,3,...,s}(E'''...)dE'''... \quad (8.18) \]

These simple formulae represent an approximate result following from the use of the smoothed density function \( \langle \rho(E) \rangle \approx (h\nu_i)^{-1} \). A more accurate calculation provides the following better approximation

\[ \rho_{1,2,3,...,s} = \frac{(E + aE_z)^{s-1}}{(s - 1)! \prod_{i=1}^{s} (h\nu_i)} \]
\[ W_{1,2,3,...,s} = \frac{(E + aE_z)^s}{s! \prod_{i=1}^{s} (h\nu_i)} \quad (8.19) \]
where $E_z$ is the total zero-point energy of the $s$ harmonic oscillators

$$E_z = \sum_{i=1}^{s} \frac{1}{2}(h\nu_i)$$  \hspace{1cm} (8.20)

Figure 8.4: Logarithm (base 10) of the density of states for 30 vibrational degrees of freedom in C$_6$H$_5$F. Symbol x="semiclassical approximation" with $a = 1$ in Equation.(8.19); Symbol o="classical approximation". The solid line results from a step function in quantum mechanics "exact" step function $W(E)$, (from Chem.Phys. 51,353 (1980)). Wave number units have been used, which are related to energy by $E = h\nu$ for the density of states $\rho(E) = \frac{\rho}{hc}$.

and $a$ is an energy-dependent parameter which can be chosen as $a = 1$ for the purpose of a simple approximation. This yields a upper boundary for $\rho(E)$ whereas $a = 0$ represents a lower boundary. $a = 1$ is often called the "semi-classical approximation", whereas $a = 0$ is the "classical-approximation".
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8.1.3 Many particles in a box (model for ideal gas)

Energy levels of a particle of mass \( m \) in one-dimensional box of length \( a \) are given by

\[
E_n = \frac{n^2 \hbar^2}{8ma^2}, \quad n = 1, 2, 3, \ldots \tag{8.21}
\]

The quantum number \( n \) counts the number of levels, hence

\[
W(E) = n = \frac{2a}{\hbar} \sqrt{2mE} \tag{8.22}
\]

The level density is obtained through derivation

\[
\rho(E) = \frac{dW(E)}{dE} = \frac{2a}{\hbar} \sqrt{2m \frac{1}{2} E^{-\frac{1}{2}}} = \frac{a}{\hbar} \sqrt{2mE^{-\frac{1}{2}}} \tag{8.23}
\]

The level density for a particle in a three-dimensional box is obtained by convolution

\[
\rho_d = \rho_{x,y,z} = \rho_x \otimes \rho_y \otimes \rho_z = m^{\frac{3}{2}} \frac{a^3}{\pi} \hbar^{-\frac{3}{2}} E^{\frac{3}{2}} \tag{8.24}
\]

In contrast to the spectrum of the harmonic oscillator, the level densities for a particle in a box (1D or 3D) depend on the energy. Explicit integration yields,

\[
W_d(E) = \int \rho_d(E) dE = \pi V \hbar^{-3} m^{\frac{3}{2}} \frac{5}{3} E^{\frac{3}{2}} \tag{8.25}
\]

One can again show that a slightly better approximation of the step-like level-number function is possible:

\[
\ln[W_d(x)] = \frac{3}{2} x - ce^{-bx} + h\left(\frac{\pi}{6}\right)
\]

\[
x = \ln(8ma^2 \frac{E}{\hbar^2}) \tag{8.26}
\]

For \( N \) particles of the same mass \( m \) in a box we find

\[
\rho_n^{(E)} = \rho_{d_1} \otimes \rho_{d_2} \otimes \rho_{d_3} \otimes \ldots \otimes \rho_{d_N} \tag{8.27}
\]

The corresponding number of states is

\[
W_N(E) = \int_0^{(E)} \rho_N(x) dx = \alpha E^{\frac{3N}{2}} \tag{8.28}
\]

where

\[
\alpha = [2\pi V \frac{(2m)^{\frac{3}{2}}}{\hbar^3}]^N \frac{[\Gamma(\frac{3}{2})]^N}{\Gamma[\frac{3}{2}N + 1]}
\]

where \( a^3 \) is the volume \( V \) of the box and we call the properties of the gamma function
\[
\Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2}
\]
\[
\Gamma(n) = (n - 1)! \quad \text{for} \quad n = 1, 2, 3... \quad (8.29)
\]

In the case of \(N\) identical, non-distinguishable particle, such as gas atoms of the same isotope, we need to take into account the Pauli principle, i.e. the fact that only a function \((N!)^{-1}\) of these states is allowed. Therefore

\[
W_{N,\text{Pauli}}(E) = \alpha (N!)^{-1} E^{\frac{3N}{2}} \quad (8.30)
\]

Figure 8.5: Partition function \(W(E)\) for the three-dimensional translational motion of a particle in the box, exact step function and continuous approximations (appr. 1, appr.2 (logarithmic scale)). The approximation 2 (appr.2) has the particular advantage that \(W(E) = 1\) for \(E = E_z(3\epsilon, \text{Zero-point energy})\) and is of the form in Eq. (8.26) with \(c = [1.5\ln 3 + \ln\left(\frac{7}{12}\right)]e^{b\ln 3}\), where \(b = 0.413\) is a good approximation (variable). The approximation 1 corresponds to Eq. (8.26) with \(c = 2.35, b = 0.48, \epsilon = \frac{\hbar^2}{8ma^2}\).
This simple correction by division through \( N! \) is only valid for high energies \( E \) and very large values of \( W(E) \).

These results obtained so far allowed us to draw the following conclusions about quantum levels and properties of macroscopic systems:

1. The average energy-level separation of neighbouring quantum states is given by the inverse average level density and becomes unmeasurably small for all known forms of spectroscopy.

2. As a consequence of 1, it is experimentally impossible to prepare single quantum levels as stationary energy eigenstates. The concept of stationary states therefore looses its usefulness when mesoscopic or macroscopic systems are considered.

3. Since the experimentally observable quantum states of macroscopic systems are therefore always superposition of many energy levels, they have to always be considered as time-dependent states.

4. The very large numbers involved suggest or require the application of statistical methods.

### 8.2 Laplace transformation for derivation of level densities and level numbers via partition function

The derivation of the level densities from convolutions can be more accurately obtained via the Laplace transformation. In general, the Laplace transform \( g(y) \) of a function \( f(x) \) is defined as

\[
g(y) = \int_0^\infty f(x)e^{-xy}dx
\]

In operator notation:

\[
g(y) = \hat{L}[f(x)],
\]

The Laplace transformation operator \( \hat{L} \) is an integral operator. The inverse transformation with the operator \( \hat{L}^{-1} \) corresponds to integration in the complex plane

\[
f(x) = \hat{L}^{-1}[g(y)]
\]

\[
f(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} g(y)e^{xy}dy
\]

The following properties are important for our purpose: Convolution theorem: With \( F=f_1 \otimes f_2 \) the convolution of functions \( f_1(x) \) and \( f_2(x) \), and \( g_1(y) = \hat{L}f_1(x), g_2(y) = \hat{L}f_2(x) \), the function \( G = g_1 \cdot g_2 = \hat{L}F \). This means that convolution in the function space becomes a simple product in the space of the Laplace transforms. This theorem can now be exploited to obtain a basic access to level densities, provided that the Laplace
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The transform of the level density of the sub-systems is known. We define the partition function (German: Zustandssumme) $q$ as the Laplace transform of the level density

$$q(\beta) = \int_0^\infty \rho(E)e^{-\beta E}dE = \hat{L}[\rho(E)]$$

$$= \sum_{j=0}^\infty e^{-\beta E_j}$$

$$= \sum_{j=0}^\infty g_j e^{-\beta E_j}$$

where we have used a property of the Dirac $\delta$-function

$$\int_{-\infty}^\infty \delta(x-x_0)f(x)dx = f(x_0)$$

$$\int_{-\infty}^\infty \delta(E-E_j)e^{-\beta E} = e^{-\beta E_j}$$

and $\beta = (kT)^{-1}$ with the Boltzmann constant $k$ and the temperature $T$.

We again consider two subsystems with energy levels $E_{n_1}, E_{n_2}$. The partition functions are

$$q_1(\beta) = \sum_{n_1=0}^\infty e^{-\beta E_{n_1}}$$

$$q_2(\beta) = \sum_{n_2=0}^\infty e^{-\beta E_{n_2}}$$

The partition function of the total system is

$$q_{1,2} = q_1 \cdot q_2 = (\sum_{n_1=0}^\infty e^{-\beta E_{n_1}})(\sum_{n_2=0}^\infty e^{-\beta E_{n_2}})$$

$$= \sum_{n_1=0}^\infty \sum_{n_2=0}^\infty e^{-\beta(E_{n_1}+E_{n_2})}$$

$$= \sum_{m=0}^\infty e^{-\beta E_m}$$

Without the need of approximations, the properties of the Laplace transformation thus lead to the result

$$\rho_{1,2} = \hat{L}^{-1}(q_1 \cdot q_2)$$

$$= \hat{L}^{-1}(\hat{L}(\rho_1 \otimes \rho_2))$$

$$= \rho_1 \otimes \rho_2 \quad q.e.d$$

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We now show that the results of section 8.1.3 can be obtained in a more straightforward way by using the Laplace transform. We start from the translational partition function $q_x$ using a smoothed level density $\rho_x$:

\[
q_x = \int_0^\infty \rho_x e^{-\beta E} dE = \frac{a}{h} (2m)^{\frac{1}{2}} \int_0^\infty E^{-\frac{1}{2}} e^{-\beta E} dE \tag{8.38}
\]

Using

\[
\int_0^\infty x^n e^{-bx} dx = \frac{\Gamma(n+1)}{b^{n+1}} \tag{8.39}
\]

for all real $n > -1$ and all $b > 0$. We further recall that $\Gamma(n+1) = n!$ for all integer $n$.

Here we need $n = -\frac{1}{2}$ and $\Gamma(\frac{1}{2}) = \sqrt{\pi}$, therefore

\[
q_x = \frac{a}{h} (2m)^{\frac{1}{2}} \frac{\sqrt{\pi}}{\beta^{\frac{1}{2}}} = \left(\frac{2\pi m a^2}{\beta h^2}\right)^{\frac{1}{2}} \tag{8.40}
\]

The product is therefore given by

\[
q_d = q_x q_y q_z = \left(\frac{2\pi m a^2}{\beta h^2}\right)^{\frac{3}{2}} = V \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}} \tag{8.41}
\]

Using the following properties of the Laplace transform:

\[
\hat{L}^{-1}\left(\frac{1}{\beta^n}\right) = \left(\frac{E^{n-1}}{\Gamma(n)}\right) \quad \text{and} \quad \hat{L}\left(\frac{E^{n-1}}{\Gamma(n)}\right) = \frac{1}{\beta^n} \tag{8.42}
\]

We obtain

\[
\hat{L}^{-1}(q_d) = \rho_d = V \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}} \frac{2E^{\frac{1}{2}}}{\sqrt{\pi}}, \tag{8.43}
\]

which is identical with Equation (8.24) The partition function for $N$ particles is then a product

\[
Q = q_d^N = V^N \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}} \tag{8.44}
\]

The inverse of the Laplace transform with $n = \frac{3N}{2}$ provides

\[
\hat{L}^{-1}(Q) = \rho_N = V^N \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}} E^{(3N/2-1)}/\Gamma(3N/2) \tag{8.45}
\]

\[
W_N(E) = \int_0^E \rho_N(x) dx = V^N \left(\frac{2\pi m}{h^2}\right)^{\frac{3N}{2}} \frac{E^{\left(\frac{3N}{2}\right)}}{\Gamma\left(\frac{3N}{2}\right)} \tag{8.45}
\]

Using the properties $\Gamma(x+1) = x\Gamma(x)$ and $\Gamma(\frac{3}{2}) = \frac{\sqrt{\pi}}{2}$ leads back to equation (8.28).
8.3 Recurrence times in dense spectra

The high level densities of "dense" spectra typical of large molecules excited to high energies or mesoscopic/macroscopic systems lead to very long recurrence times

$$\tau(E) \geq \hbar \langle \rho(E) \rangle,$$

where $$\langle \rho(E) \rangle$$ is the average level density. The equality holds for an equidistant spectrum ($$\langle \rho(E) \rangle = \frac{1}{\delta} = \text{constant}$$).

Example:

1. C₆H₅F excited to 18000 cm⁻¹: $$\tau_R' \geq 0.3 \text{ s},$$
2. (CF₃)₃CH excited to 15000 cm⁻¹: $$\tau_R'' \geq 0.3 \times 10^5 \text{ s} \approx 4 \text{ days}$$
3. 1 mole of Hg(s) with internal energy of 4 kJ: $$\tau_R \geq 10^{10^{24}} \text{ s}.$$

Compare to the age of universe: $$\tau \approx 1.5 \times 10^9 \text{ a} \ll 10^{18} \text{ s} \ll \tau_R''.$$

These results show that the periodicity of quantum dynamics is irrelevant for macroscopic systems. This however does not exclude the existence of (seemingly) periodic motion on much shorter time scales (e.g. motion of a pendulum, motion of planets). However, these motions are never really periodic but always damped on longer time scales.

8.4 Pauli equations and micro-canonical equilibrium

This section brings us back to the question as to how the oscillatory character of the solutions of the TDSE $$c_k e^{-iE_k t/\hbar}$$ can lead to the irreversible relaxation behaviour that is commonly observed in chemical kinetics. We only provide here a simple discussion of this complex problem. We start from an idealized quantum system that is assumed to be exactly isolated and therefore possesses a constant energy following the probability distribution $$p_k(E_k) = |c_k|^2$$. In statistical mechanics, such a system is called "microcanonical ensemble". We first consider a quantum system consisting of two levels coupled by a matrix element $$V$$. The inversion motion of the ammonia molecule may serve as an example. The time-dependent wavefunction

$$\psi(t) = c_0 e^{-iE_{0} t/\hbar} \phi_0 + c_1 e^{-iE_{1} t/\hbar} \phi_1$$

is assumed to be such that $$|c_0|^2 = |c_1|^2 = \frac{1}{2}$$. $$\psi(t)$$ is periodically varying with time without relaxation. The spectrum of macroscopic systems is, however, very different from this example. We should consider many quantum levels of very similar energies that we can group to "states" with a level number $$N_k$$. These states can then be considered to be coupled by matrix elements $$V$$. These states are not eigenstates of the Hamiltonian and hence lack a well-defined energy. The eigenstates however can again be obtained by solving the Schrödinger equation. Choosing the initial conditions such that $$N_1$$ levels of the state 1 are statistically occupied (irregular phase factors $$e^{i\alpha_k}$$ of the basis vectors $$\phi_k$$)
and calculating the occupations of single quantum levels that belong to the same state (upper-case indices are used for distinction):

\[
p_L = \sum_{k=1}^{N_L} p_k(L)
\]  

leads in the case of a typical model calculation to the result shown in Fig. (8.8).
Figure 8.7: Energy-level scheme with closely spaced quantum states in "states" with the occupations $p_L$.

Such "numerical experiments" using the TDSE systematically lead to a relaxation behaviour that can be well approximated by generalized first-order kinetics

$$\frac{dp}{dt} = Kp \quad (8.49)$$

The vector of level populations is $p = (p_1, p_2, ..., p_L)^T$ and the matrix $K$ contains the rate coefficients $K_{IJ}$ for the transition of state $J$ to state $I$ according to generalized first-order kinetics. We do not give here the detailed derivation of equation (8.49) from the Schrödinger equation, which was first given by Wolfgang Pauli in 1927.

The rate coefficients in the matrix $K$ can be determined using perturbation theory

$$K_{IJ} = \frac{4\pi^2}{\hbar} \langle |V_{IJ}|^2 \rangle \rho_L \quad (8.50)$$

with the average of the coupling matrix elements

$$\langle |V_{IJ}|^2 \rangle = \frac{1}{N_L N_M} \sum_{i=1}^{N_i} \sum_{j=1}^{N_j} |V_{i(I),j(J)}|^2 \quad (8.51)$$

The solutions of these equations are already known from PC II- chemical kinetics:

$$p(t) = e^{Kt}p(0) \quad (8.52)$$

where $e^{Kt}$ can be obtained from

$$e^{Kt} = \sum_{n=0}^{\infty} \frac{(Kt)^n}{n!} \quad (8.53)$$
Figure 8.8: Time-dependent state occupations for model systems with many ($\simeq 50$) levels per state (see text and M. Quack, Nuovo Cim. B 69,359 (1981)). There is a reduced time axis in the form of the product $Vt$, where $V$ is a typical coupling matrix element.

It can be shown that under certain circumstances all eigenvalues $\lambda_k$ of $K$ are negative with the exception of one value $\lambda_1 = 0$.

This directly leads to the relaxation into a well-defined equilibrium state in which all $e^{\lambda_k t}$ with $k > 1$ have decayed to zero for $t \rightarrow \infty$. The corresponding vector of equilibrium populations for $t \rightarrow \infty$ is

$$ p_{eq}^J = \frac{N_J}{Z} = \frac{\rho_J}{Z} $$

with "microcanonical partition function"
\[ Z = \sum J N_J \]
\[ Z' = \sum J \rho_J \]  

(8.56)

where \( N_J \) is the number of levels in the state, \( \rho_J \) is the level density. The rate coefficients fulfill the principle of detailed balance

\[ \frac{K_{IJ}}{K_{JI}} = \frac{N_I}{N_J} \frac{\rho_I}{\rho_J} = \frac{p_{eq}^I}{\rho_I} \]

(8.57)

The ratios of rate coefficients can be obtained from the result of perturbation theory Eq. (8.50), stating that the rate coefficient is proportional to the density of levels in the final state (remember \( K_{LM} = K_{L-M} \)).

The equilibrium distribution for the microcanonical system takes on an even simpler form when working with the average occupation number \( \langle p_j \rangle \) of individual non-degenerate quantum levels

\[ \langle p_j \rangle = \frac{p_J}{N_J} \]

and \[ \langle p_{eq}^j \rangle = \frac{p_{eq}^J}{N_J} = \frac{1}{Z} \]  

(8.58)

The average occupation of each level at equilibrium is thus simply equal to the inverse of the total number \( Z \) of levels occupied at this energy. One can therefore speak of a "democracy of quantum levels". However, one should remember that the true level occupations \( p_J(t) \) are not equal but different even at equilibrium and are time dependent. The differences in occupation and their time dependence within one state however cancels, such that \( p_{eq}^J \) is time independent, except for small fluctuations.

The main results of the section are the following:

1. Neglecting small fluctuations, the time-dependent state populations \( p_L \) are described by generalized first-order kinetics according to the Pauli equations.

2. After sufficiently long times \( t \to \infty \), the system reaches an equilibrium with occupation numbers \( p_{eq}^J = \frac{N_J}{Z} \). These equilibrium populations are time independent.

3. This leads to equal level populations on average

\[ \langle p_{eq}^J \rangle = \frac{p_{eq}^J}{N_J} = \frac{1}{Z} \]  

(8.59)

for all single, non-degenerate quantum states. At equilibrium all quantum levels have the "same probability" ("democracy of quantum levels").

4. This equilibrium is kinetic in nature, because the effective time independence follows from the property that processes \( I \to J \) with rate coefficient \( K_{IJ} \) are compensated by processes \( J \to I \) (with \( K_{JI} \)), i.e. \( K_{IJ} p_{eq}^J = K_{JI} p_{eq}^I \).
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8.5 Microcanonical entropy and 2\textsuperscript{nd} law of thermodynamics:

The relaxation into equilibrium leads to the 2\textsuperscript{nd} law of thermodynamics. It is therefore intuitive to define a function that possesses the properties of the entropy

\[ S = -k \sum_{J=1}^{X} p_{J} \ln \left( \frac{p_{J}}{N_{J}} \right) \] (8.60)

where we use the summation convention for X states with \(N_{J}\) levels of state \(J\). The introduction of average occupation numbers for single, non-degenerate quantum states leads to

\[ S = -k \sum_{J=1}^{X} N_{J} \langle p_{J(J)} \rangle \ln \langle p_{J(J)} \rangle \]
\[ = -k \sum_{j=1}^{Z} \langle p_{j} \rangle \ln \langle p_{j} \rangle \] (8.61)

We will show later that this definition of the entropy, introduced by W. Pauli, displays the known, thermodynamic properties of entropy. It is known as ”microcanonical entropy”. The goal of this section is to show that the function \(S\) reaches a maximal value at equilibrium (for \(t \to \infty\)), just like the thermodynamic entropy. At equilibrium we find using \(p_{J}^{eq}\)

\[ S_{eq} = -k \sum_{j=1}^{Z} \left( \frac{1}{Z} \right) \ln \left( \frac{1}{Z} \right) = k \ln Z \] (8.62)

This is identical with the known Boltzmann formula if we replace \(W\) by \(Z\). We now show that \(S_{eq} = S_{\text{max}}\) by ”adding zero”

\[ \frac{S}{k} = - \sum_{J=1}^{X} p_{J} \ln \frac{p_{J}}{N_{J}} + \ln Z - \ln Z \] (8.63)

and substitute

\[ - \ln Z = \sum_{J=1}^{X} N_{J} \frac{1}{Z} \ln \left( \frac{1}{Z} \right) = - \sum_{J=1}^{X} p_{J}^{eq} \ln Z \] (8.64)

to obtain

\[ \left( \frac{S}{k} \right) = \ln Z - \sum_{J=1}^{X} (p_{J} \ln p_{J} - p_{J} \ln N_{J}) - \sum_{J=1}^{X} p_{J}^{eq} \ln Z \] (8.65)

We now add \(0 = p_{J} \ln Z - p_{J} \ln Z\) to each term of the first sum and simplify all terms into a single sum

\[ \left( \frac{S}{k} \right) = \ln Z - \sum_{J=1}^{X} (p_{J} \ln p_{J} - p_{J} \ln \left( \frac{N_{J}}{Z} \right) - p_{J} \ln Z + p_{J}^{eq} \ln Z) \] (8.66)
The summation over the last 2 terms yields
\[
\sum_{J=1}^{X} p_J \ln Z = \sum_{J=1}^{X} p_{eq}^J \ln Z
\]  
(8.67)

since
\[
\sum_{J=1}^{X} p_J = \sum_{J=1}^{X} p_{eq}^J = 1
\]  
(8.68)

Therefore
\[
\left( \frac{S}{k} \right) = \ln Z - \sum_{J=1}^{X} (p_J \ln p_J - p_J \ln p_{eq}^J - p_J + p_{eq}^J)
\]  
(8.69)

The general form of this sum is
\[
F(x, y) = x \ln x - x \ln y - x + y
\]  
(8.70)

for which we can use the property (Klein lemma for \(x, y\) real positive, \(x\) may be zero):
\[
F(x, y) > 0 \quad \text{for} \quad x \neq y
\]
\[
F(x, y) = 0 \quad \text{for} \quad x = y
\]  
(8.71)

Therefore \(\frac{S}{k} \leq \ln Z\) with the maximal value for \(p_J = p_{eq}^J\)
\[
S_{eq} = S_{max} = k \ln Z
\]  
(8.72)

The function \(S\) thus reaches a maximum at equilibrium under constant energy, just like the thermodynamic entropy in the equilibrium formulation of the 2nd law of thermodynamics. Similar considerations based on the Pauli equations allow to show that the "non-equilibrium" entropy fulfills
\[
\frac{dS}{dt} \geq 0
\]  
(8.73)

according to the non-equilibrium formulation of the 2nd law for irreversible processes in closed systems. The Pauli equations thus describe the average behaviour without taking the small fluctuations into account. These small fluctuation can, however, be calculated from the TDSE, which is illustrated here using the dynamics of intramolecular vibrational relaxation of CF\(_2\)HCl (see Fig. 8.9).
Figure 8.9: a) Schematic illustration of the time-dependent entropy following Boltzmann (with fluctuations exaggerated). b) Microscopic example of the quantum entropy of the dynamics of three strongly-coupled oscillators in the molecule CF$_3$HCl, with large "fluctuations" calculated exactly quantum mechanically (J. Mol. Struct. 292 (1993) 171). The right-hand panel of the figure shows the process after "time-reversal" (pulse inversion) at 2 ps.