5.2 The thermodynamic equilibrium

is defined by an effective zero-flux for all states, i.e. per time period the same number of electrons will flow into each state as are leaving the state. It is impossible to calculate this "steady state" just from the matrix elements (5.1) taking into account all possible perturbations of the system. The number of particles and parameters is much too high. But especially this high number of particles serves the perfect solution for the problem**, the statistical Thermodynamics**:
For the system only macro states exist, which have the most probable microstates. This leads to the fundamental equation that the probability W_k for a microstate k is proportional to the Boltzmann factor

$$W_k \propto \exp\left(-\frac{E_k}{kT}\right) \tag{5.2}$$

If the energy E_k described as a sum of independent states, it is quite easy to use Eq. (5.2) for the mathematical analysis of the system. In the one electron approximation all electrons are independent. But there exists a coupling of all particles due to the constant number of electrons. To overcome this limitation we define the chemical potential μ. Eq. (5.2) changes to

$$W_k \propto \exp\left(-\frac{\sum_i (E_i - \mu)}{kT}\right) = \prod_i \exp\left(-\frac{(E_i - \mu)}{kT}\right) = \prod_i W_{k,i} \tag{5.3}$$

where i sums up all one electron states of the macrostate. E_i is the energy of the microstate i.

HINT: If a state is not occupied with an electron it will not add to the complete energy.

- In quantum mechanics as well as in classical physics only the energy values of a state define the fraction of this state to the complete ensemble in thermodynamic equilibrium.
- The type and the character of the thermally induced excitation do not matter at all.
- **No** transfer matrix elements have to be calculated in order to describe the thermodynamic equilibrium.
- Diagonalization of the Hamiltonian gives the Eigenvalues and the Eigenvectors; but only the Eigenvalues are necessary for the description of the thermodynamic equilibrium.
- For any additional perturbation (excitation) which is not induced thermally we have to calculate again the transfer matrix elements.
- The thermodynamics is a very powerful instrument and supplies a number of concepts to decide (depending on the strength of the perturbation), if
  - a perturbation has to be considered at all,
  - a semi classical approach is enough to calculate the changes of the system
  - or if we need a complete new quantum mechanical analysis of the problem, i.e. if we have to diagonalize the new Hamiltonian exactly.