Universität Regensburg Wintersemester 13-14

Density Matrix Theory

Prof. Andrea Donarini 5.0.21, Tuesdays, 10:15

Sheet 1

1. Time evolution for a closed three level system (analytics)

Consider a three level system described by the Hamiltonian in the "position basis":

$$H = \begin{pmatrix} \varepsilon_1 & b & b \\ b & \varepsilon_2 & b \\ b & b & \varepsilon_3 \end{pmatrix},$$

which you can take as the Hueckel Hamiltonian of a three-atomic molecule, where ε_i with $i = 1, 2, 3$ are the on-site energies of the three atoms and b describes the hopping between the atoms. Study the quantum dynamics of the system by means of the Liouville equation:

$$\dot{\rho} = -\frac{i}{\hbar}[H, \rho]$$

where ρ is the (single particle) density matrix for the molecule. In particular:

1. Write the Liouville equation explicitly in components ($\dot{\rho}_{ij} = \ldots$) in the position basis. Is the dynamics of the populations decoupled from the one of the coherences?

2. Repeat the operation done at the first point but this time in the energy basis instead of the position basis. Is the dynamics of the populations decoupled from the one of the coherences?

   (Hint: Do not try to find explicitly the transformation that diagonalizes the Hamiltonian. Just concentrate on the fact that H is diagonal in its eigen-basis)

3. Consider the homoatomic case ($\varepsilon_1 = \varepsilon_2 = \varepsilon_3$) and calculate explicitly the time evolution of the density matrix both in energy and position representation in terms of a generic initial condition:

$$\rho(t=0) = \begin{pmatrix} \rho^0_{11} & \rho^0_{12} & \rho^0_{13} \\ \rho^0_{21} & \rho^0_{22} & \rho^0_{23} \\ \rho^0_{31} & \rho^0_{32} & \rho^0_{33} \end{pmatrix}$$

   (Hint: Every operator $\hat{\mathcal{O}}$ (including the density operator $\hat{\rho}$) has different matrix representations depending on the choice of the basis in the Hilbert space of the system. Nevertheless all representation are equivalent and connected by unitary transformation.

$$\tilde{\mathcal{O}} = U\mathcal{O}U^\dagger$$

   Find the transformation that diagonalizes the Hamiltonian and solve the problem first in the representation in which H is diagonal.)

2. Time evolution for a closed three level system (numerics)

Consider the same problem of the first exercise. But this time look for a numerical solution to the problem. The basic idea is to discretize the time and to calculate the density matrix at time $t + \Delta t$ according to the formula:

$$\rho(t + \Delta t) = \rho(t) - \frac{i}{\hbar}[H, \rho(t)]\Delta t$$

1. Plot the populations as a function of time for different initial conditions. What happens if for example you prepare the electron on the first atom of the molecule at time $t = 0$?
2. Can you plot the results also in the energy basis?
3. What happens to the dynamics if you prepare the system in a statistical mixture in the energy basis?
4. Compare the results with the analytical ones: is the numerics acceptable?
5. What happens if you make the Δt smaller?

An example for the two-level system is on-line at:

`http://homepages-nw.uni-regensburg.de/~doa17296/fisica/Teaching/WT1314_DMT/WT1314_DMT.html`

Frohes Schaffen!