I. 1D HARMONIC OSCILLATOR

Let us consider a mono-dimensional system composed by a single particle with mass m. The particle position is described by the cartesian coordinate x and its momentum by p. Assuming that the particle experiences an harmonic potential with equilibrium position at $x = 0$, the system's Hamiltonian can be written as

$$H_{1D} = \frac{p^2}{2m} + \frac{1}{2}m\omega x^2 \,, \tag{1}$$

where ω is the typical harmonic vibrational frequency.
This Hamiltonian is often transformed in an equivalent form by mean of a coordinates transformation that renders x and p unit-less. The new position and momentum $\bar{x}$ and $\bar{p}$ are defined as

$$\bar{p} = \sqrt{\frac{1}{m\hbar\omega}}p \,, \quad \bar{x} = \sqrt{\frac{m\omega}{\hbar}}x \,. \tag{2}$$

The Hamiltonian 1 in this new basis becomes

$$H_{1D} = \frac{\hbar\omega}{2}(\bar{p}^2 + \bar{x}^2) \,, \tag{3}$$

It is also convenint to introduce creation and annihilation operators

$$a^\dagger = \frac{1}{\sqrt{2}}(\bar{x} - i\bar{p}) \quad \text{and} \quad a = \frac{1}{\sqrt{2}}(\bar{x} + i\bar{p}) \,, \tag{4}$$

with commuting rule $[a, a^\dagger] = 1$ and by means of which we finally obtain a third, equivalent, form of the system Hamiltonian

$$H_{1D} = \hbar\omega(\hat{n} + \frac{1}{2}) \,, \tag{5}$$

where $\hat{n} = a^\dagger a$ is the particle number operator.

II. DFT - N-1D HARMONIC OSCILLATORS MAPPING

A molecular system made by N interacting particles can be described in the harmonic approximation assuming the potential energy surface U to be well described by its Taylor expansion around the $T = 0K$ equilibrium position. In this case

$$U(\vec{\mathbf{x}}) = \frac{1}{2}\sum_{ij}^{3N}\frac{\partial E_{el}}{\partial x_i \partial x_j}x_i x_j \,, \tag{6}$$

where E_{el} is the adiabatic electronic energy and $\vec{\mathbf{x}}$ is a $3N$ dimensional vector describing the system configuration. This system can still be mapped on a set of 3N decoupled 1D harmonic oscillators by introducing the normal mode of vibration. We first start defining mass-weighted cartesian coordinates $u_i = \sqrt{m_i}x_i$ and by diagonalizing the force-constant matrix of the energy second-order derivatives $\mathbf{H}$

$$\frac{1}{2}\sum_{ij}^{3N}\frac{\partial E_{el}}{\partial x_i \partial x_j}x_i x_j = \frac{1}{2}\sum_{ij}^{3N}\frac{\partial E_{el}}{\partial u_i \partial u_j}u_i u_j = \frac{1}{2}\sum_{ij}^{3N}H_{ij}u_i u_j \rightarrow \frac{1}{2}\sum_{i}^{3N}diag(\mathbf{H})_{ii}q_i^2 \tag{7}$$

The system Hamiltonian can now be written as is eq. 1 by mapping the q_i coordinates, expressed by the $\mathbf{H}$ eigenvectors L_{ij}, on the 1D mass-weighted cartesian coordinates $\sqrt{m}x$ of last section. Doing so, the frequencies of normal vibrations are defined as $\omega_i = \sqrt{diag(\mathbf{H})_{ii}}$ while q_i coordinates are defined as function of cartesian coordinates x_j through $\mathbf{H}$ eigenvectors L_{ij}

$$q_j = \sum_{i}^{3N}L_{ij}\sqrt{m_i}x_i \tag{8}$$

As done in the previous section we here define a set of unit-less normal modes $\bar{q}_i$

$$\bar{q}_j = \sqrt{\frac{\omega_j}{\hbar}} \sum_i^{3N} L_{ij} \sqrt{m_i} x_i \tag{9}$$

and the inverse transformation that defines the cartesian displacement associated to a unit-less normal mode $\bar{q}_j$ amount of displacement

$$\bar{x}_i = \sqrt{\frac{\hbar}{m_i \omega_j}} L_{ij} \bar{q}_j \, . \tag{10}$$

Finally, we can also write the i- unit-less normal mode as function of creation and annihilation operators as

$$\bar{q}_i = \frac{1}{\sqrt{2}} (a_i^\dagger + a_i). \tag{11}$$

with the usual commutation rule $[a_i, a_j^\dagger] = \delta_{ij}$ and total Hamiltonian

$$H_N = \sum_i \hbar\omega (\hat{n}_i + \frac{1}{2}) \, , \tag{12}$$

where $\hat{n}_i = a_i^\dagger a_i$ is the number operator for the i-normal mode.

III. REDFIELD EQUATIONS

First order in coupling strength and first order in time-dependent perturbation theory

Second order in coupling strength and first order in time-dependent perturbation theory

First order in coupling strength and second order in time-dependent perturbation theory