The Two-Level System

There are many situations where the relevant molecular system can be modeled as an effective two–level system. In the following we will study the eigenstates as well as the population dynamics of a generic two–level system. This exactly solvable model will provide a reference case for the subsequent discussions.

The Hamiltonian for a two–level system can be written in two alternative ways. First, we can assume that we know the eigenstates $|\pm\rangle$ and eigenenergies $\mathcal{E}_\pm$. Then we can write

$$H = \sum_{\kappa=\pm} \mathcal{E}_\kappa |\kappa\rangle\langle\kappa| \; . \tag{1}$$

If we do not know the eigenstates but some zeroth–order states $|1\rangle$ and $|2\rangle$ which correspond to a situation where, for instance, the coupling between the left and the right well in Fig. **??** is switched off, the Hamiltonian reads

$$\bar{H} = \varepsilon_1 |1\rangle\langle 1| + \varepsilon_2 |2\rangle\langle 2| + V|1\rangle\langle 2| + V^*|2\rangle\langle 1| \tag{2}$$

Here, the level energies of the zeroth–order states are denoted $\varepsilon_{a=1,2}$ and the coupling between these states is given by V. Independent of the specific situation the Hamiltonian (2) can be transformed to take the form (1). In the following we will outline how this diagonalization of (2) is achieved.

In a first step we determine the eigenvalues and eigenstates which follow from the stationary Schrödinger equation

$$H|\Psi\rangle = \mathcal{E}|\Psi\rangle \; . \tag{3}$$

We expand the state vector with respect to the states $|a = 1, 2\rangle$

$$|\Psi\rangle = C(1)|1\rangle + C(2)|2\rangle \; , \tag{4}$$

which leads to a matrix equation for the expansion coefficients $C(a = 1, 2)$,

$$\begin{pmatrix} \varepsilon_1 & V \\ V^* & \varepsilon_2 \end{pmatrix} \begin{pmatrix} C(1) \\ C(2) \end{pmatrix} = \mathcal{E} \begin{pmatrix} C(1) \\ C(2) \end{pmatrix} \; . \tag{5}$$

The eigenvalues are obtained from the secular equation

$$(\mathcal{E} - \varepsilon_1)(\mathcal{E} - \varepsilon_2) - |V|^2 = 0 \; . \tag{6}$$

Solving this quadratic equation gives

$$\mathcal{E}_{\kappa=\pm} = \frac{1}{2}\left\{\varepsilon_1 + \varepsilon_2 \pm \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4|V|^2}\right\} . \tag{7}$$

To determine the expansion coefficients and thus the eigenstates the $\mathcal{E}_{\kappa=\pm}$ are inserted into the eigenvalue equation (5),

$$\begin{pmatrix} \mathcal{E}_\kappa - \varepsilon_1 & -V \\ -V^* & \mathcal{E}_\kappa - \varepsilon_2 \end{pmatrix} \begin{pmatrix} C_\kappa(1) \\ C_\kappa(2) \end{pmatrix} = 0 . \tag{8}$$

Note, that the expansion coefficients $C(m)$ have been labeled by the quantum numbers $\kappa = \pm$. If we make use of the normalization condition

$$\sum_m |C_\kappa(m)|^2 = 1 \tag{9}$$

we obtain

$$|C_\kappa(1)|^2 = \frac{(\mathcal{E}_\kappa - \varepsilon_2)^2}{(\mathcal{E}_\kappa - \varepsilon_2)^2 + |V|^2} . \tag{10}$$

From Eq. (7) we get the relations

$$(\mathcal{E}_\kappa - \varepsilon_1)(\mathcal{E}_\kappa - \varepsilon_2) = |V|^2 \tag{11}$$

and

$$\mathcal{E}_+ + \mathcal{E}_- = \varepsilon_1 + \varepsilon_2 , \tag{12}$$

which, if inserted into (10), gives

$$\begin{aligned} |C_\kappa(1)|^2 &= \frac{(\mathcal{E}_\kappa - \varepsilon_2)^2}{(\mathcal{E}_\kappa - \varepsilon_2)^2 + (\mathcal{E}_\kappa - \varepsilon_1)(\mathcal{E}_\kappa - \varepsilon_2)} = \frac{\mathcal{E}_\kappa - \varepsilon_2}{\mathcal{E}_\kappa - \varepsilon_2 + \mathcal{E}_\kappa - \varepsilon_1} \\ &= \frac{\mathcal{E}_\kappa - \varepsilon_2}{\mathcal{E}_\kappa - \mathcal{E}_{\bar\kappa}} . \end{aligned} \tag{13}$$

To have compact notation we introduced $\bar\kappa = \pm$, if $\kappa = \mp$. The complex expansion coefficient itself reads

$$C_\kappa(1) = \sqrt{\frac{\mathcal{E}_\kappa - \varepsilon_2}{\mathcal{E}_\kappa - \mathcal{E}_{\bar\kappa}}}\, e^{i\chi_1(\kappa)} , \tag{14}$$

where the phase $\chi_1(\kappa)$ remains open at this point. In a similar manner we can derive

$$|C_\kappa(2)| = \sqrt{\frac{\mathcal{E}_\kappa - \varepsilon_1}{\mathcal{E}_\kappa - \mathcal{E}_{\bar\kappa}}} . \tag{15}$$

However, the phase of $C_\kappa(2)$ is not free but has to be determined from

$$C_\kappa(2) = |C_\kappa(2)|e^{i\chi_2(\kappa)} = \frac{|V|e^{-i\arg(V)}}{\mathcal{E}_\kappa - \varepsilon_2}\sqrt{\frac{\mathcal{E}_\kappa - \varepsilon_2}{\mathcal{E}_\kappa - \mathcal{E}_{\bar{\kappa}}}}\, e^{i\chi_1(\kappa)} \; . \tag{16}$$

We note that for $\kappa = +$, it is $\mathcal{E}_\kappa > \varepsilon_2$ and for $\kappa = -$, one has $\mathcal{E}_\kappa < \varepsilon_2$. Consequently, the phase $\chi_2(\kappa)$ is given by $\chi_2(+) = \chi_1(+) - \arg(V)$ and $\chi_2(-) = \chi_1(-) - \arg(V) + \pi$.

Coherent Dynamics

The time–evolution operator for the isolated two–level system $U(t) = e^{-iHt/\hbar}$ is conveniently expressed in terms of the eigenstates $|\kappa = \pm\rangle$. One obtains

$$U(t) = \sum_{\kappa,\lambda=\pm} \langle\kappa|U(t)|\lambda\rangle\, |\kappa\rangle\langle\lambda| = \sum_{\kappa=\pm} e^{-i\mathcal{E}_\kappa t/\hbar}|\kappa\rangle\langle\kappa| \; . \tag{17}$$

This expression can be used to determine, for instance, how the initially prepared zeroth–order state $|1\rangle$ evolves in time. To this end we calculate the probability for transitions between $|1\rangle$ and $|2\rangle$ which is defined as

$$P_{1\to 2}(t) = |\langle 2|U(t)|1\rangle|^2 \; . \tag{18}$$

Once this quantity is known the survival probability is obtained as $P_{1\to 1}(t) = 1 - P_{1\to 2}(t)$. Using Eqs. (14) and (16) we get ($\hat{\kappa} = \mp$, if $\kappa = \pm$)

$$\begin{aligned}
\langle 2|U(t)|1\rangle &= \sum_{\kappa=\pm} e^{-i\mathcal{E}_\kappa t/\hbar}\langle 2|\kappa\rangle\langle\kappa|1\rangle = \sum_{\kappa=\pm} e^{-i\mathcal{E}_\kappa t/\hbar}\, C_\kappa(2)\, C^*_\kappa(1) \\
&= \sum_{\kappa=\pm} e^{-i\mathcal{E}_\kappa t/\hbar}\left(\frac{\mathcal{E}_\kappa - \varepsilon_2}{\mathcal{E}_\kappa - \mathcal{E}_{\hat{\kappa}}}\quad\frac{\mathcal{E}_\kappa - \varepsilon_1}{\mathcal{E}_\kappa - \mathcal{E}_{\hat{\kappa}}}\right)^{\frac{1}{2}} e^{i(\chi_2(\kappa) - \chi_1(\kappa))} \\
&= e^{-i\arg(V)}\frac{|V|}{\mathcal{E}_+ - \mathcal{E}_-}\left(e^{-i\mathcal{E}_+ t/\hbar} - e^{-i\mathcal{E}_- t/\hbar}\right) \; .
\end{aligned} \tag{19}$$

This gives for the transition probability

$$\begin{aligned}
P_{1\to 2}(t) &= \frac{|V|^2}{(\hbar\Omega)^2}\left|e^{-i\mathcal{E}_- t/\hbar}\{e^{-i\Omega t} - 1\}\right|^2 \\
&= \frac{|V|^2}{(\hbar\Omega)^2}\left([\cos(\Omega t) - 1]^2 + \sin^2(\Omega t)\right) \; ,
\end{aligned} \tag{20}$$

where we introduced

$$\hbar\Omega = \mathcal{E}_+ - \mathcal{E}_- \equiv \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4|V|^2} \; . \tag{21}$$

Using

$$[\cos(\Omega t) - 1]^2 + \sin^2(\Omega t) = 2\,(1 - \cos(\Omega t)) = 4\sin^2\frac{\Omega t}{2} \tag{22}$$

we finally get

$$P_{1\to 2}(t) = \frac{4|V|^2}{(\hbar\Omega)^2}\sin^2(\Omega t/2)\ . \tag{23}$$

For the case that the zeroth–order states have the same energy this expression simplifies to

$$P_{1\to 2}(t) = \sin^2\left(|V|t/\hbar\right)\ . \tag{24}$$

From (23) we realize that $P_{1\to 2}(t)$ will oscillate with frequency $\Omega/2$ which depends on the detuning. Given a constant coupling V the oscillation frequency will increase with increasing detuning. At the same time, due to the prefactor in Eq. (23), the transfer will be less complete. A complete population switching occurs only if the two zeroth–order states are degenerate.d The oscillation frequency is then $V/\hbar$ and according to Eq. (24) a complete transfer is realized for the condition $t = (2N+1)\pi\hbar/2|V|$ where N is an integer.

We would like to point out that this simple result reflects the general statement made earlier namely that time–dependent phenomena in a closed quantum system appear whenever a non–eigenstate, that is, a superposition of eigenstates has been prepared initially. In the present case the initial preparation of state $|1\rangle$ corresponds to a particular superposition of the two eigenstates $|+\rangle$ and $|-\rangle$.