Let's use the time-propagator in a model calculation that we will refer to often. It is common to reduce or map quantum problems onto a two level system (2LS). We will pick the most important states for our problem and find strategies for discarding or simplifying the influence of the remaining degrees of freedom. Consider a 2LS with two unperturbed or “zeroth order” states $|\varphi_a\rangle$ and $|\varphi_b\rangle$ with energies $\epsilon_a$ and $\epsilon_b$, which are described by a zero-order Hamiltonian $H_0$:

$$H_0 = |\varphi_a\rangle \epsilon_a \langle \varphi_a| + |\varphi_b\rangle \epsilon_b \langle \varphi_b|$$

These states interact through a coupling $V$ of the form

$$V = |\varphi_a\rangle V_{ab} \langle \varphi_b| + |\varphi_b\rangle V_{ba} \langle \varphi_a|$$

The full Hamiltonian for the two coupled states is $\hat{H}$:

$$\hat{H} = H_0 + V$$

The zero-order states are $|\varphi_a\rangle$ and $|\varphi_b\rangle$. The coupling mixes these states, leading to two eigenstates of $\hat{H}$, $|\varphi_+\rangle$ and $|\varphi_-\rangle$, with corresponding energy eigenvalues $\epsilon_+$ and $\epsilon_-$, respectively.

We will ask: If we prepare the system in state $|\varphi_a\rangle$, what is the time-dependent probability of observing it in $|\varphi_b\rangle$? Since $|\varphi_a\rangle$ and $|\varphi_b\rangle$ are not eigenstates of $\hat{H}$, and since our time-propagation will be performed in the eigenbasis using Equation \ref{1.29}, we will need to find the transformation between these bases.

We start by searching for the eigenvalues of the Hamiltonian (Equation \ref{1.35}). Since the Hamiltonian is Hermitian, \(\langle\psi|H\psi\rangle = \langle H\psi|\psi\rangle\), we write
\[ V_{ab} = V_{ba}^* = V e^{-i\varphi} \label{1.36} \]

\[ \hat{H} = \begin{pmatrix} \varepsilon_a & V e^{-i\varphi} \\ V e^{+i\varphi} & \varepsilon_b \end{pmatrix} \label{1.37} \]

Often the couplings we describe are real, and we can neglect the phase factor \(\varphi\). Now we define variables for the mean energy and energy splitting between the uncoupled states

\[ E = \frac{\varepsilon_a + \varepsilon_b}{2} \]

\[ \Delta = \frac{\varepsilon_a - \varepsilon_b}{2} \label{1.39} \]

We can then obtain the eigenvalues of the coupled system by solving the secular equation

\[ \text{det} (H - \lambda I) = 0 \]

giving

\[ \varepsilon_{\pm} = E \pm \Omega \label{1.41} \]

Here I defined another variable

\[ \Omega = \sqrt{\Delta^2 + V^2} \label{1.42} \]

To determine the eigenvectors of the coupled system \(\{\varphi_{\pm}\}\), it proves to be a great simplification to define a mixing angle \(\theta\) that describes the relative magnitude of the coupling relative to the zero-order energy splitting through

\[ \tan 2\theta = \frac{V}{\Delta} \label{1.43} \]

\[ \sin 2\theta = \frac{V}{\Omega} \]
\[ \cos 2\theta = \frac{\Delta}{\Omega} \label{1.45} \]

In this representation the Hamiltonian (Equation \ref{1.37}) becomes

\[ \hat{H} = E \overline{I} + \Delta \begin{pmatrix} 1 & \tan 2\theta e^{-i\varphi} \\ \tan 2\theta e^{+i\varphi} & 1 \end{pmatrix} \]

We see that the mixing angle adopts values such that \(0 \leq \theta \leq \pi / 4\). Also, we note that

\[ \sin 2\theta = \frac{V}{\Omega} \]

\[ \cos 2\theta = \frac{\Delta}{\Omega} \]

In this representation the Hamiltonian (Equation \ref{1.37}) becomes
and we can express the eigenvalues as

\[\varepsilon_{\pm} = E \pm \Delta \sec 2 \theta\]  \hspace{1cm} \text{(1.47)}

Next we want to find \(S\), the transformation that diagonalizes the Hamiltonian and which transforms the coefficients of the wavefunction from the zero-order basis to the eigenbasis. The eigenstates can be expanded in the zero-order basis in the form

\[|\varphi_{\pm}\rangle = c_{a} |\varphi_{a}\rangle + c_{b} |\varphi_{b}\rangle\]  \hspace{1cm} \text{(1.48)}

So that the transformation can be expressed in matrix form as

\[
\left(\begin{array}{l}
\varphi_{+} \\
\varphi_{-}
\end{array}\right) = S \left(\begin{array}{l}
\varphi_{a} \\
\varphi_{b}
\end{array}\right)
\]  \hspace{1cm} \text{(1.49)}

To find \(S\), we use the Schrödinger equation \(\hat{H} |\varphi_{\pm}\rangle = \varepsilon_{\pm} |\varphi_{\pm}\rangle\) substituting Equation (1.48). This gives

\[S = \left(\begin{array}{ll}
\cos \theta & e^{-i \varphi / 2} \\
-sin \theta & e^{i \varphi / 2}
\end{array}\right)\]  \hspace{1cm} \text{(1.50)}

Note that \(S\) is unitary since \(S^{\dagger} = S^{-1}\) and \((S^{T})^{*} = S^{-1}\). Also, the eigenbasis is orthonormal:

\[
\langle \varphi_{\pm} | \varphi_{\pm} \rangle + \langle \varphi_{\pm} | \varphi_{\pm} \rangle = 1.
\]

Now, let’s examine the eigenstates in two limits:

1. **Weak coupling** (\(|V| / \Delta \ll 1\)). Here \(\hat{\theta} \approx 0\), and \(|\varphi_{+}\rangle\) corresponds to \(|\varphi_{a}\rangle\) weakly perturbed by the \(V_{ab}\) interaction. \(|\varphi_{-}\rangle\) corresponds to \(|\varphi_{b}\rangle\). In another way, as \(\theta \rightarrow 0\), we find \(\varphi_{+} \rightarrow \varphi_{a}\) and \(\varphi_{-} \rightarrow \varphi_{b}\).

2. **Strong coupling** (\(|V| / \Delta \gg 1\)). In this limit \(\hat{\theta} = \pi / 4\), and the \(|a/b\rangle\) basis states are indistinguishable. The eigenstates are symmetric and antisymmetric combinations: \(|\varphi_{+}\rangle \rangle = \frac{1}{\sqrt{2}} (|\varphi_{a}\rangle + |\varphi_{b}\rangle)\). Note from Equation (1.50) that the sign of \(V\) dictates whether \(|\varphi_{+}\rangle \rangle\) or \(|\varphi_{-}\rangle \rangle\) corresponds to the symmetric or antisymmetric eigenstate. For negative \(V\), \(\theta = -\pi / 4\), and the correspondence in Equation (1.51) changes to \(\mp\).

We can schematically represent the energies of these states with the following diagram. Here we explore the range of \(|E_{\pm}\rangle\rangle\) available given a fixed coupling \(|V\rangle\rangle\) and varying the splitting \(|\Delta\rangle\rangle\).
This diagram illustrates an avoided crossing effect. The strong coupling limit is equivalent to a degeneracy point ($\Delta = 0$) between the states $|\varphi_a\rangle$ and $|\varphi_b\rangle$. The eigenstates completely mix the unperturbed states, yet remain split by the strength of interaction $2V$. We will return to the discussion of avoided crossings when we describe potential energy surfaces and the adiabatic approximation, where the dependence of $V$ and $\Delta$ on position $R$ must be considered.

Now we can turn to describing dynamics. The time evolution of this system is given by the time-propagator

$$U(t) = |\varphi_+\rangle e^{-i\omega_+ t} \langle\varphi_+| + |\varphi_-\rangle e^{-i\omega_- t} \langle\varphi_-| \quad \label{1.52}$$

where $\omega_\pm = \varepsilon_\pm / \hbar$. Since $\varphi_a$ and $\varphi_b$ are not the eigenstates, preparing the system in state $|\varphi_a\rangle$ will lead to time evolution! Let’s prepare the system so that it is initially in $|\varphi_a\rangle$.

$$|\psi(0)\rangle = |\varphi_a\rangle \quad \label{1.53}$$

Evaluating the time-dependent amplitudes of initial and final states with the help of $\langle \rangle$, we find

$$c_a(t) = \langle \varphi_a | U(t) | \varphi_a \rangle = e^{-iE t} \left[ \cos^2 \theta e^{i\Omega_R t} + \sin^2 \theta e^{-i\Omega_R t} \right] \quad \label{1.54}$$
$$c_b(t) = \langle \varphi_b | U(t) | \varphi_a \rangle = 2 \sin \theta \cos \theta e^{-iE t} \sin \Omega_R t \quad \label{1.55}$$

So, what is the probability that it is found in state $|\varphi_b\rangle$ at time $t$?

$$P_{ba}(t) = |c_b(t)|^2 = \frac{V^2}{V^2 + \Delta^2} \sin^2 \Omega_R t \quad \label{1.56}$$
where

\[
\Omega_R = \frac{1}{\hbar} \sqrt{\Delta^2 + V^2} \label{1.57}
\]

\(\Omega_R\), the Rabi Frequency, represents the frequency at which probability amplitude oscillates between \(\varphi_a\) and \(\varphi_b\) states.

Notice for the weak coupling limit (\(V \rightarrow 0\)), \(\varphi_{\pm} \rightarrow \varphi_{a,b}\) (the eigenstates resemble the stationary states), and the time-dependence disappears. In the strong coupling limit (\(V \gg \Delta\)), amplitude is exchanged completely between the zero-order states at a rate given by the coupling: \(\Omega_R \rightarrow V/\hbar\). Even in this limit it takes a finite amount of time for amplitude to move between states. To get \(P=1\) requires a time \(\tau\):

\[
\tau = \frac{\pi}{2\Omega_R} = \frac{\hbar\pi}{2V}. \nonumber
\]

**Readings**