# Molecular quantum dynamics: Solutions 7

## Problem 1: Nonadiabatic transitions

(a) The Hamiltonian for the whole system is

$$\hat{H} = \hat{H}_0(t) + \hat{V}, \tag{1}$$

where

$$\hat{H}_0(t) = \begin{pmatrix} \alpha_1 t & 0 \\ 0 & \alpha_2 t \end{pmatrix} \text{ and } \hat{V} = \begin{pmatrix} 0 & V_{12} \\ V_{12} & 0 \end{pmatrix}. \tag{2}$$

We first solve the problem in the absence of perturbation, i.e., for $\hat{H}_0(t)$. The states 1 and 2 form a slowly changing adiabatic basis $|n(t)\rangle$ that satisfies at all times the relation

$$\hat{H}_0(t)|n(t)\rangle = E_n(t)|n(t)\rangle \tag{3}$$

for $n = 1, 2$. We may expand the solution to the TDSE in the form of

$$|\psi(t)\rangle = \sum_{n=1,2} f_n(t)|n(t)\rangle. \tag{4}$$

From the lecture notes, with the adiabatic approximation, if the non-adibatic couplings $D_{kn} = \langle k|\dot{n}\rangle$ can be neglected, we have for each $n$

$$i\hbar \dot{f}_n(t) = E_n(t) f_n(t) \tag{5}$$

with the solution

$$\begin{aligned} f_n(t) =& f_n(0) e^{-i\int_0^t E_n(\tau)d\tau/\hbar} & (6)\\ =& f_n(0) e^{-i\int_0^t \alpha_n \tau d\tau/\hbar} & (7)\\ =& f_n(0) e^{-\frac{i}{2\hbar}\alpha_n t^2}. & (8) \end{aligned}$$

We set $f_n(0) = 1$ for each $n$, and obtain the time-dependence of the probability amplitude $f_n(t)$ for the system to be in state $|n(t)\rangle$ as $f_n(t) = e^{-\frac{i}{2\hbar}\alpha_n t^2}$.
The states $|n(t)\rangle$ evolve slowly and we may neglect their time-dependence and take $|n\rangle = |n(t)\rangle$ for simplification. Now we use the following ansatz to solve the wavefunction for the perturbed system:

$$|\psi(t)\rangle = \sum_{n=1,2} c_n(t) f_n(t) |n\rangle , \tag{9}$$

and the full Hamiltonian from Eq. (1).

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle \tag{10}$$

$$\begin{aligned} & i\hbar \dot{c}_1(t) f_1(t) |1\rangle + \alpha_1 t c_1(t) f_1(t) |1\rangle + i\hbar \dot{c}_2(t) f_2(t) |2\rangle + \alpha_2 t c_2(t) f_2(t) |2\rangle \\ = \; & \alpha_1 t c_1(t) f_1(t) |1\rangle + c_2(t) f_2(t) V_{12} |1\rangle + \alpha_2 t c_2(t) f_2(t) |2\rangle + c_1(t) f_1(t) V_{12} |2\rangle \end{aligned} \tag{11}$$

We see that two terms on the left-hand side cancel out with two terms on the right-hand side and we obtain

$$i\hbar\dot{c}_1(t)f_1(t)\,|1\rangle + i\hbar\dot{c}_2(t)f_2(t)\,|2\rangle = c_2(t)f_2(t)V_{12}\,|1\rangle + c_1(t)f_1(t)V_{12}\,|2\rangle \tag{12}$$

Multiplying from the left by $\langle 1|$ gives

$$i\hbar\dot{c}_1(t)f_1(t) = c_2(t)f_2(t)V_{12}\,, \tag{13}$$

whereas multiplying from the left by $\langle 2|$ gives

$$i\hbar\dot{c}_2(t)f_2(t) = c_1(t)f_1(t)V_{12}\,. \tag{14}$$

Finally, we apply perturbation theory to the results in Eqs. (13–14). We assume that all the population was originally on state 1. The zero-order (unperturbed) coefficients are then $c_1^{(0)} = 1$ and $c_2^{(0)} = 0$; they correspond to the coefficients at time $t \to -\infty$. First-order perturbation theory expression is obtained by replacing $c_1(t)$ in Eq (14) with its time-independent zero-order approximation $c_1^{(0)}$:

$$\begin{aligned}
i\hbar\dot{c}_2(t)f_2(t) &= c_1^{(0)}V_{12}f_1(t) && (15)\\
\dot{c}_2(t) &= -\frac{i}{\hbar}\frac{f_1(t)}{f_2(t)}V_{12} && (16)\\
\dot{c}_2(t) &= -\frac{i}{\hbar}e^{i(\alpha_2-\alpha_1)t^2/2\hbar}V_{12} && (17)
\end{aligned}$$

We integrate the last expression over the whole time that the perturbation is "on", meaning from $-\infty$ to some time $t$:

$$c_2(t) = -\frac{i}{\hbar}V_{12}\int_{-\infty}^{t} e^{i(\alpha_2-\alpha_1)\tau^2/2\hbar}d\tau \tag{18}$$

Now we look for the transition probability at time $t \to \infty$ (long time after the crossing):

$$\begin{aligned}
P &= \lim_{t\to\infty}\left|c_2^{(1)}(t)\right|^2 && (19)\\
&= \frac{V_{12}^2}{\hbar^2}\left|\int_{-\infty}^{\infty} e^{i(\alpha_2-\alpha_1)\tau^2/2\hbar}d\tau\right|^2 && (20)\\
&= \frac{2\pi V_{12}^2}{\hbar\,|\alpha_2-\alpha_1|} && (21)
\end{aligned}$$

The integral is solved in the following way:

$$\begin{aligned}
\int_{-\infty}^{\infty} e^{i(\alpha_2-\alpha_1)\tau^2/2\hbar}d\tau &= 2\int_{0}^{\infty} e^{i(\alpha_2-\alpha_1)\tau^2/2\hbar}d\tau && (22)\\
&= 2\left(\int_0^\infty \cos\frac{(\alpha_2-\alpha_1)\tau^2}{2\hbar}d\tau + i\int_0^\infty \sin\frac{(\alpha_2-\alpha_1)\tau^2}{2\hbar}d\tau\right) && (23)
\end{aligned}$$

Introduce a change of variables: $x = \sqrt{(\alpha_2-\alpha_1)/2\hbar}\tau$, $dx = \sqrt{(\alpha_2-\alpha_1)/2\hbar}d\tau$.

$$\begin{aligned}
&\int_{-\infty}^{\infty} e^{i(\alpha_2-\alpha_1)\tau^2/2\hbar}d\tau && (24)\\
&\qquad = 2\sqrt{\frac{2\hbar}{\alpha_2-\alpha_1}}\left(\sqrt{\frac{\pi}{8}} + i\sqrt{\frac{\pi}{8}}\right) && (25)
\end{aligned}$$

Then the transition probability expression reads:

$$P_{12} = \frac{4V_{12}^2}{\hbar^2}\frac{2\hbar}{|\alpha_2-\alpha_1|}\left|\sqrt{\frac{\pi}{8}}+i\sqrt{\frac{\pi}{8}}\right|^2 \tag{26}$$

$$= \frac{2\pi V_{12}^2}{\hbar\,|\alpha_2-\alpha_1|} \tag{27}$$

(b) The Landau-Zener expression for the transition probability is $P_{12} = 1 - e^{-2\pi\gamma}$. Taylor expansion of the second term around $\gamma = 0$ leads to

$$P_{12} = 1 - (1 - 2\pi\gamma) + \ldots \tag{28}$$

$$= 2\pi\gamma + \ldots . \tag{29}$$

Therefore,

$$P_{12} \underset{V_{12}\to 0}{\longrightarrow} 2\pi\gamma = \frac{2\pi V_{12}^2}{\hbar v|s_1 - s_2|}. \tag{30}$$

Since

$$\alpha_n = \frac{dE_n}{dt} = \frac{dE_n}{dr}\frac{dr}{dt} = s_n v, \quad \text{for} \quad n = 1, 2, \tag{31}$$

we get $v|s_1 - s_2| = |\alpha_1 - \alpha_2|$, and

$$P_{12} \underset{V_{12}\to 0}{\longrightarrow} \frac{2\pi V_{12}^2}{\hbar|\alpha_1 - \alpha_2|}. \tag{32}$$