Molecular quantum dynamics: Solutions 8

a)

The coefficients of the exact solution for the TDSE are

$$\dot{c}_k(t) = -\frac{i}{\hbar}\sum_m e^{-i\omega_{km}t}V_{km}(t)c_m(t), \tag{1}$$

where $\omega_{km} = (E_m - E_k)/\hbar$. Therefore, we get

$$\dot{c}_a(t) = -\frac{i}{2\hbar}Ue^{i(\omega-\omega_{ab})t}c_b(t) \tag{2}$$
$$\dot{c}_b(t) = -\frac{i}{2\hbar}Ue^{-i(\omega-\omega_{ab})t}c_a(t). \tag{3}$$

Differentiating $\dot{c}_a(t)$ and substituting $\dot{c}_b(t)$ and $c_b(t)$, we obtain

$$\ddot{c}_a(t) = -\frac{i}{2\hbar}Ue^{i(\omega-\omega_{ab})t}\dot{c}_b(t) + \frac{\omega-\omega_{ab}}{2\hbar}Ue^{i(\omega-\omega_{ab})t}c_b(t) \tag{4}$$
$$= -\frac{U^2}{4\hbar^2}c_a(t) + i(\omega-\omega_{ab})\dot{c}_a(t) \tag{5}$$

This is a second order differential equation of the following type:

$$\ddot{x} + b\dot{x} + kx = 0 \tag{6}$$

and if $b^2 < 4k$, the solution is

$$x(t) = e^{\alpha t}[C_1\cos(\beta t) + C_2\sin(\beta t)], \tag{7}$$

where $\alpha = -b/2$ and $\beta = (1/2)\sqrt{4k-b^2}$. In our case, $b = -i(\omega-\omega_{ab})$ and $k = U^2/(4\hbar^2)$ so $b^2 < 4k$. The solution for $c_a(t)$ is given as

$$c_a(t) = e^{i(\omega-\omega_{ab})t/2}[C_1\cos(\omega_r t) + C_2\sin(\omega_r t)] \tag{8}$$

Similarly for $c_b(t)$,

$$\ddot{c}_b(t) + i(\omega-\omega_{ab})\dot{c}_b(t) + \frac{U^2}{4\hbar^2}c_b(t) = 0 \tag{9}$$

with the solution

$$c_b(t) = e^{-i(\omega-\omega_{ab})t/2}[D_1\cos(\omega_r t) + D_2\sin(\omega_r t)]. \tag{10}$$

From $c_a(t=0) = 1$ we obtain $C_1 = 1$ and from $c_b(t=0) = 0$, $D_1 = 0$.
We need to know $\dot{c}_a(t=0)$ and $\dot{c}_b(t=0)$ to figure out C_2 and D_2.

$$\dot{c}_a(0) = -\frac{iU}{2\hbar}c_b(0) = 0 \tag{11}$$
$$\dot{c}_b(0) = -\frac{iU}{2\hbar}c_a(0) = -\frac{iU}{2\hbar}. \tag{12}$$

On the other hand, differentiating the solutions of ODEs give

$$\dot{c}_a(t) = \frac{i(\omega - \omega_{ab})}{2} c_a(t) + e^{i(\omega-\omega_{ab})t/2}[\omega_r C_2 \cos(\omega_r t) - \omega_r \sin(\omega_r t)] \tag{13}$$

$$\dot{c}_b(t) = -\frac{i(\omega - \omega_{ab})}{2} c_b(t) + e^{-i(\omega-\omega_{ab})t/2} \omega_r D_2 \cos(\omega_r t) \tag{14}$$

Substituting $t = 0$ to Eq. (13) and Eq. (14) gives

$$\dot{c}_a(0) = \frac{i(\omega - \omega_{ab})}{2} + \omega_r C_2 \tag{15}$$

$$\dot{c}_b(0) = \omega_r D_2 \tag{16}$$

Finally, we obtain $C_2 = -i(\omega - \omega_{ab})/(2\omega_r)$ and $D_2 = (-iU)/(2\hbar\omega_r)$ to get the final solution as

$$c_a(t) = e^{i(\omega-\omega_{ab})t/2}[\cos(\omega_r t) - \frac{i(\omega - \omega_{ab})}{2\omega_r} \sin(\omega_r t)] \tag{17}$$

$$c_b(t) = e^{-i(\omega-\omega_{ab})t/2}[\frac{-iU}{2\hbar\omega_r} \sin(\omega_r t)] \tag{18}$$

b)

The transition probability $P_{a\to b}(t)$ is given by

$$P_{a\to b}(t) = |c_b(t)|^2 = \frac{U^2}{4\hbar^2} \frac{\sin^2(\omega_r t)}{\omega_r^2} = \frac{(U/\hbar)^2}{(\omega - \omega_{ab})^2 + (U/\hbar)^2} \sin^2(\omega_r t). \tag{19}$$

Both the fraction and $\sin^2(\omega_r t)$ do not exceed 1 so the transition probability also doesn't.

$$|c_a(t)|^2 = \cos^2(\omega_r t) + \frac{(\omega - \omega_{ab})^2}{4\omega_r^2} \sin^2(\omega_r t) \tag{20}$$

$$= \cos^2(\omega_r t) + \left(1 - \frac{U^2/\hbar^2}{4\omega_r^2}\right) \sin^2(\omega_r t) \tag{21}$$

Finally,

$$|c_a(t)|^2 + |c_b(t)|^2 = \cos^2(\omega_r t) + \sin^2(\omega_r t) = 1 \tag{22}$$

c)

When

$$\left(\frac{U}{\hbar}\right)^2 << (\omega - \omega_{ab})^2, \tag{23}$$

i.e, if $U << \hbar(\omega - \omega_{ab})$ then $\omega_r \approx (\omega - \omega_{ab})/2$. This gives

$$P_{a\to b}(t) = \frac{U^2}{4\hbar^2} \frac{\sin^2[(\omega - \omega_{ab})t/2]}{[(\omega - \omega_{ab})/2]^2} \tag{24}$$

$$= \left(\frac{U}{2}\right)^2 \frac{\sin^2[(E_a - E_b + E)t/2\hbar]}{[(E_a - E_b + E)/2]^2}, \tag{25}$$

which agrees with the TDPT result we derived in the lecture.

d)

For a normalized quantum state ψ, both ψ and $\lambda\psi$ represent the same physical state, where λ is a non-zero complex number satisfying $|\lambda| = 1$. [Such a λ can be written as $\lambda = \exp(i\phi)$.] Therefore, as long as $|c_b|^2 = 0$, the system returns to the original state. The systesm first returns to its original state at

$$t^* = \frac{\pi}{\omega_r} \tag{26}$$