Molecular quantum dynamics: Exercise series 8

Reading list: Schatz and Ratner: 4.1, 4.2 (basis set solution of TDSE = one of the first lectures), 4.3.1-4.3.4 (general TDPT = previous lecture), 4.5.1, 4.5.2, 4.5.4 (specific cases of TDPT = today's lecture).

Problem 1: Exact solution for a two level system interacting with electromagnetic field

As it turns out, a two-level system with a periodic interaction of the type $V(t) = \frac{1}{2}Ue^{i\omega t}$ discussed in the lecture today can be solved *exactly*, without invoking the time-dependent perturbation theory. An example is an atom or a molecule with only two most important electronic states, interacting with a laser field. [More generally, for interaction of the type $V(t) = U\cos\omega t = \frac{1}{2}U\left(e^{i\omega t} + e^{-i\omega t}\right)$, for a given transition $a \to b$, only one term ($e^{i\omega t}$ or $e^{-i\omega t}$) is important and the other can be neglected. This is called *rotating wave approximation* and is valid much more generally than the TDPT.]

(a) Solve exactly the time-dependent Schrödinger equation with a Hamiltonian, including the periodic interaction $V(t)$,

$$H = H_0 + V(t) = \begin{pmatrix} E_a & 0 \\ 0 & E_b \end{pmatrix} + \begin{pmatrix} 0 & \frac{1}{2}Ue^{i\omega t} \\ \frac{1}{2}Ue^{-i\omega t} & 0 \end{pmatrix}.$$

Use the initial conditions $c_a(t=0) = 1$ and $c_b(t=0) = 0$. Express your results [$c_a(t)$ and $c_b(t)$] in terms of the *Rabi flopping frequency*,

$$\omega_r := \frac{1}{2}\sqrt{(\omega - \omega_{ab})^2 + |U|^2/\hbar^2},$$

where $\omega_{ab} := (E_b - E_a)/\hbar$.

Hint: Use the basis set method for exact solution of TDSE from one of the first lectures and also discussed in Schatz and Ratner Chapter 4.2.

(b) Determine the transition probability, $P_{a\to b}(t)$, and show that it never exceeds 1. Confirm that $|c_a(t)|^2 + |c_b(t)|^2 = 1$ for all times.

(c) Check that $P_{a\to b}(t)$ reduces to the perturbation theory result form today's lecture when the perturbation is "small," and state precisely what small *means* in this context, as a constraint on U.

(d) At what time does the system first return to its original state?