Molecular quantum dynamics: Exercise series 7

Read Tannor 9.4.1., Schatz & Ratner 4.3.1, 4.3.2.

Problem 1: Nonadiabatic transitions

Consider a collision between two atoms in which two electronic potential curves cross to cause a change of state (as in $\mathrm{Na} + \mathrm{I} \rightarrow \mathrm{Na}^{+} + \mathrm{I}^{-}$). To a first approximation, the transition probability can be calculated by first-order perturbation theory, with the motions of the nuclei treated classically.

(a) Suppose that the interaction matrix element V_{12} between the two states 1 and 2 is a constant independent of time, while the energies E_1 and E_2 of each state are linear functions of time (i.e., $E_1 = \alpha_1 t$ and $E_2 = \alpha_2 t$ where α_1 and α_2 are constants). Here $t = 0$ is taken to be the moment when the two curves intersect. What is the time dependence of each state in the absence of V_{12}? What is the perturbation theory expression for the transition probability P_{12} between states 1 and 2?

Hints:

1) The perturbation theory equation

$$P_k(t) = |c_k^{(1)}(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t d\tau \, V_{km}(\tau) \, e^{i\omega_{km}\tau} \right|^2$$

from the lecture will have to be slightly modified (i.e., rederived) for the case where the zero-order energies are time-dependent. (You should look back at one of the older lectures where we derived the exact differential equations for c_k's for the case of a time-dependent Hamiltonian and start from there.)

2) The following integral will be useful:

$$\int_0^\infty \sin x^2 \, dx = \int_0^\infty \cos x^2 \, dx = \left(\frac{\pi}{8}\right)^{1/2}.$$

(b) One way to rationalize the linear dependence of $E_1 - E_2$ on time is to assume that the nuclei move with a constant velocity v in the vicinity of the crossing point. Show that under these circumstances P_{12} is identical to the limit for small V_{12} of the Landau-Zener expression for the transition probability,

$$P_{12} = 1 - e^{-2\pi\gamma}$$

where $\gamma = V_{12}^2/\hbar v|s_1 - s_2|$ and $s_1 - s_2$ is the difference between the slopes of the potential curves at their point of intersection.