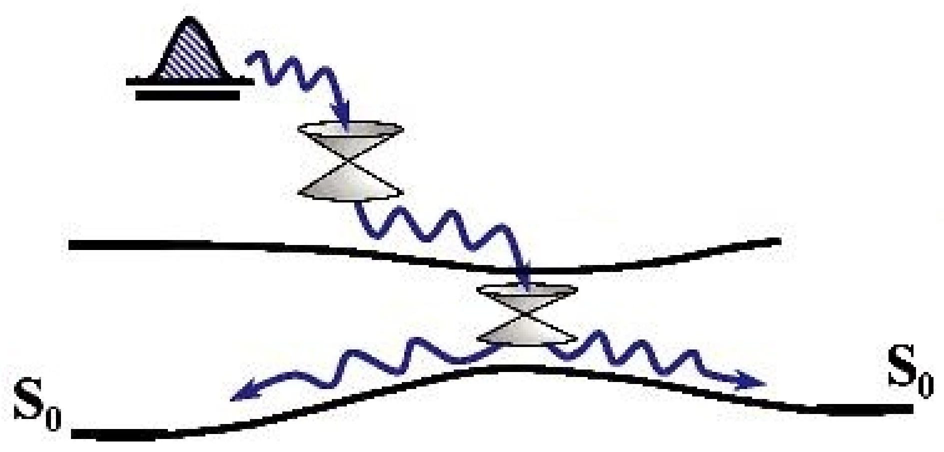
Theoretical Photochemistry WiSe 2016/17

Lecture 11



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http://www.theochem.uni-frankfurt.de/teaching/ ⟶ Theoretical Photochemistry

Topics

1. Photophysical Processes
2. The Born-Oppenheimer approximation
3. Wavepackets
4. Beyond Born-Oppenheimer – non-adiabatic transitions
5. The Franck-Condon picture of electronic transitions
6. Interaction with light: allowed and forbidden transitions; symmetry considerations
7. Conical intersections
8. Examples: Ethene, Protonated Schiff Bases (Retinal), Azobenzene
9. Some electronic structure aspects
10. Dynamics: trajectories or wavefunctions?

11. **Wavefunction propagation techniques**
12. **Trajectory surface hopping techniques**
13. **Transition rates: Fermi's Golden Rule**
14. **Non-linear optical spectroscopy: calculation of spectroscopic signals**
15. **Extended systems: Excitons, light-harvesting, etc.**
16. **Solvent/environmental effects**

Fermi's Golden Rule

Transition probability between quantum states that are subject to a perturbation

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

e.g., $\hat{V}(t) = -\hat{\mu}\, E_0\, (e^{i\omega t} + e^{-i\omega t})$ **"perturbation"**

Transition rate between two states $a \rightarrow b$
(in 2nd order perturbation theory):

$$\Gamma_{a\rightarrow b} = \frac{2\pi}{\hbar} |\langle \psi_b^{(0)} | \hat{\mu} | \psi_a^{(0)} \rangle|^2 \; \delta(E_b^0 - E_a^0 \pm \hbar\omega)$$

where $E_b^0 - E_a^0 = \hbar\omega_{ba}$ **- resonance condition!**

Derivation

We refer to the following reference by A. Wacker:

www.matfys.lth.se/staff/andreas.wacker/Scripts/fermiGR.pdf

The Hamiltonian is given as above:

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

and we assume that $\hat{H}_0|\varphi_n\rangle = E_n^0|\varphi_n\rangle$.

The wavefunction can be written as follows, using the eigenfunctions of the *unperturbed* Hamiltonian ($\hat{H}_0$) as a basis:

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-iE_n^0 t/\hbar}|\varphi_n\rangle$$

The time-dependent phase factor is arbitrary (but convenient, as this factor represents the time evolution under $\hat{H}_0$).

Inserting the above wavefunction into the TDSE:

$$i\hbar\frac{\partial}{\partial t}\sum_n c_n(t)e^{-iE_n^0 t/\hbar}|\varphi_n\rangle = (\hat{H}_0 + \hat{V}(t))\sum_n c_n(t)e^{-iE_n^0 t/\hbar}|\varphi_n\rangle$$

i.e.:

$$i\hbar\sum_n\Big(\dot{c}_n(t) + c_n(t)(-\frac{iE_n^0}{\hbar}\Big)e^{-iE_n^0 t/\hbar}|\varphi_n\rangle = (\hat{H}_0 + \hat{V}(t))\sum_n c_n(t)e^{-iE_n^0 t/\hbar}|\varphi_n\rangle$$

i.e.:

$$\begin{aligned} i\hbar\sum_n\Big(\dot{c}_n(t) + c_n(t)(-\frac{iE_n^0}{\hbar}\Big)e^{-iE_n^0 t/\hbar}|\varphi_n\rangle \quad &= \quad \sum_n c_n(t)E_n^0 e^{-iE_n^0 t/\hbar}|\varphi_n\rangle \\ &\quad + \hat{V}(t)\sum_n c_n(t)e^{-iE_n^0 t/\hbar}|\varphi_n\rangle \end{aligned}$$

Note that the terms marked in red cancel out, such that only two terms are left.

$$i\hbar \sum_n \dot{c}_n(t) e^{-iE_n^0 t/\hbar} |\varphi_n\rangle \quad = \quad \hat{V}(t) \sum_n c_n(t) e^{-iE_n^0 t/\hbar} |\varphi_n\rangle$$

Now we multiply from the left by $\langle\varphi_k| e^{iE_k^0 t/\hbar}$ such as to single out the time evolution of a particular coefficient c_k:

$$i\hbar \dot{c}_k(t) \quad = \quad \sum_n c_n(t) e^{-i(E_n^0 - E_k^0)t/\hbar} \langle\varphi_k|\hat{V}(t)|\varphi_n\rangle$$

Integration yields:

$$i\hbar(c_k(t) - c_k(0)) \quad = \quad \int_0^t dt' \sum_n c_n(t') e^{-i(E_n^0 - E_k^0)t'/\hbar} \langle\varphi_k|\hat{V}(t')|\varphi_n\rangle$$

Now we assume that only one coefficient $n = j$ is initially non-zero: $c_j(t = 0) = 1$, such that only $n = j$ contributes on the r.h.s. (to linear order) and we approximate as follows:

$$i\hbar(c_k(t) - c_k(0)) \quad \simeq \quad \int_0^t dt'\, e^{-i(E_j^0 - E_k^0)t'/\hbar} \langle \varphi_k | \hat{V}(t') | \varphi_j \rangle$$

We continue to solve the integral for the specific form of the interaction: $\hat{V}(t) = \hat{F} e^{i\omega t}$ which includes constant interactions and oscillatory interactions (e.g., external fields). In detail:

$$\begin{aligned} i\hbar(c_k(t) - c_k(0)) \quad &\simeq \quad \Big(\int_0^t dt'\, e^{-i(E_j^0 - E_k^0)t'/\hbar} e^{i\omega t}\Big) \langle \varphi_k | \hat{F} | \varphi_j \rangle \\ &\simeq \quad \Big(\int_0^t dt'\, e^{-i(E_j^0 - E_k^0 - \hbar\omega)t'/\hbar}\Big) \langle \varphi_k | \hat{F} | \varphi_j \rangle \\ &\equiv \quad \Big(\int_0^t dt'\, e^{-i\Delta E t'/\hbar}\Big) \langle \varphi_k | \hat{F} | \varphi_j \rangle \end{aligned}$$

where

$$\int_0^t dt'\, e^{-i\Delta E t'/\hbar} = \frac{\hbar}{-i\Delta E}\Big(e^{-i\Delta E t} - e^0\Big) = \frac{i\hbar}{\Delta E}\Big(e^{-i\Delta E t} - 1\Big)$$

Using $c_k(0) = 0$, we have

$$c_k(t) = \frac{e^{-i\Delta E t} - 1}{\Delta E} \langle \varphi_k | \hat{F} | \varphi_j \rangle$$

and for the *transition probability*:

$$\begin{aligned} P_k(t) = |c_k(t)|^2 &= \left| \frac{e^{-i\Delta E t} - 1}{\Delta E} \right|^2 |\langle \varphi_k | \hat{F} | \varphi_j \rangle|^2 \\ &= \left| e^{-i\frac{\Delta E}{2}t} \frac{e^{-i\frac{\Delta E}{2}t} - e^{i\frac{\Delta E}{2}t}}{\Delta E} \right|^2 |\langle \varphi_k | \hat{F} | \varphi_j \rangle|^2 \\ &= \frac{4\ \sin^2(\frac{\Delta E}{2} t/\hbar)}{\Delta E^2} |\langle \varphi_k | \hat{F} | \varphi_j \rangle|^2 \end{aligned}$$

The time-dependent function (i.e., square of a “sinc” function) turns out to be an approximation of the Dirac δ function:

$$\frac{4\ \sin^2(\frac{\Delta E}{2} t/\hbar)}{\Delta E^2} \sim \frac{2\pi t}{\hbar} \delta(\Delta E)$$

such that we finally get the transition rate:

$$\Gamma_{j\rightarrow k} = \frac{P_k(t)}{t} = \frac{2\pi}{\hbar}\delta(E_j^0 - E_k^0 - \hbar\omega)|\langle\varphi_k|\hat{F}|\varphi_j\rangle|^2$$

If we go to quasi-continuum of states, with a *density of states* ρ:

$$\Gamma_E = \frac{2\pi}{\hbar}\rho(E - \hbar\omega)|\langle\varphi_k|\hat{F}|\varphi_j\rangle|^2$$

Note that the derivation relies on various approximations (weak perturbation, short-time limit, etc.) and the validity needs to be checked in particular cases. In practice, Fermi's Golden Rule works fine for describing:

- interactions with the electromagnetic field (absorption, emission)
- transfer processes to a continuum of states (e.g., Förster theory, in case of a quasi-continuum of vibronic states)