L6

Transition probabilities and couplings

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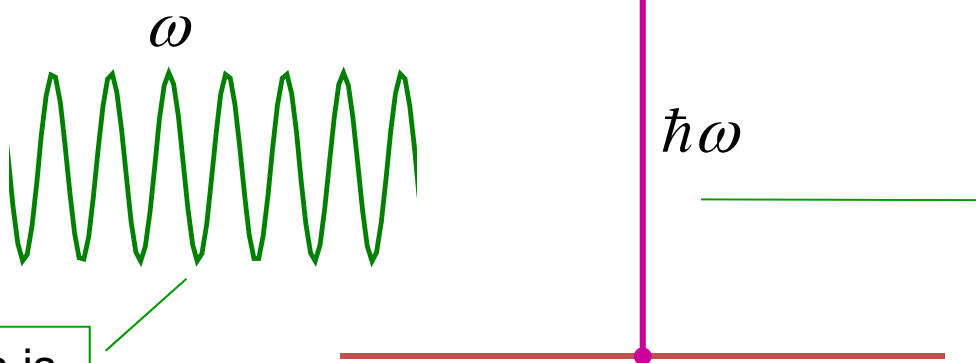
Fermi's golden rule

Fermi's Golden Rule

Transition rate: $$W_k = \frac{2\pi}{\hbar}\left|\langle i|H_p|k\rangle\right|^2 \rho_k$$



Quantum levels of the non-perturbed system

Perturbation is applied

Transition is induced

Derivation of Fermi's Golden Rule

Time-dependent formulation

$$\left(i\hbar \frac{\partial}{\partial t} - H \right) \Phi = 0$$

$$H = H_0 + H_p \quad \begin{cases} H_0 - \text{Non-perturbated Hamiltonian} \\ H_p - \text{Perturbation Hamiltonian} \end{cases}$$

$\{|n\rangle\}$ which solves: $(H_0 - E_n)|n\rangle = 0$

$\langle i | j \rangle = \delta_{ij}$ and $|E_i - E_j| \equiv \hbar\omega_{ij}$

$$\Phi = \sum_n a_n(t) e^{-iE_n t} |n\rangle$$

$$H = H_0 + H_p$$

$$\left(i\hbar \frac{\partial}{\partial t} - H \right) \Phi = 0$$

Multiply by $\langle k |$ at left and integrate

Prove it!

$$i\hbar \frac{da_k(t)}{dt} = \sum_n \langle k | H_p | n \rangle a_n(t) e^{i\omega_{kn} t}$$

An approximate way to solve the differential equation

$$i\hbar \frac{da_k(t)}{dt} = \sum_n \langle k | H_p | n \rangle a_n(t) e^{i\omega_{kn}t}$$

Guess the "0-order" solution: $a_n^{(0)}(t)$

Use this guess to solve the equation and to get the 1st-order approximation: $a_k^{(1)}(t)$

$$i\hbar \frac{da_k^{(1)}(t)}{dt} \approx \sum_n \langle k | H_p | n \rangle a_n^{(0)}(t) e^{i\omega_{kn}t}$$

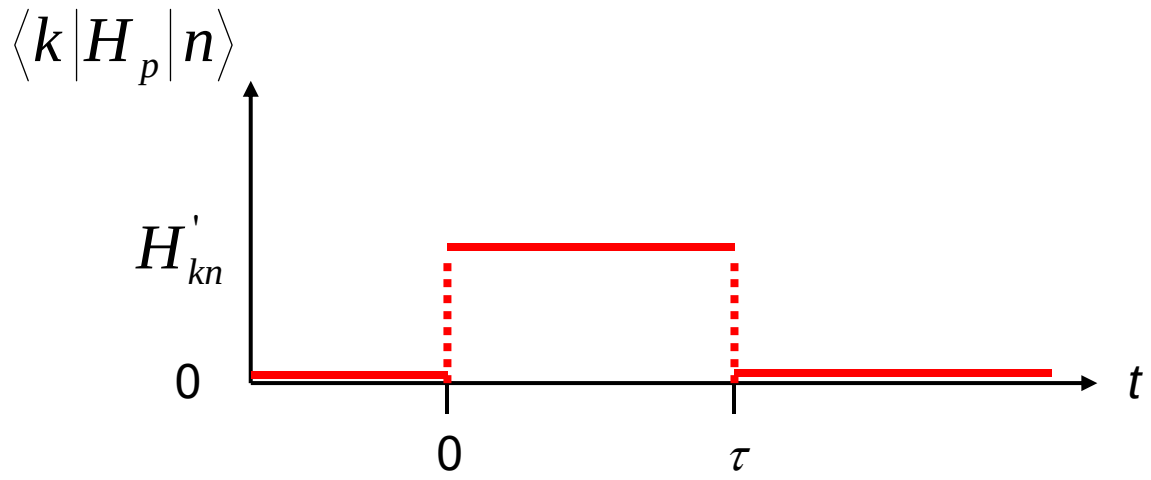
Use the 1st-order to get the 2nd-order approximation and so on.

$$i\hbar \frac{da_k^{(p)}(t)}{dt} \approx \sum_n \langle k | H_p | n \rangle a_n^{(p-1)}(t) e^{i\omega_{kn}t}$$

First case: constant perturbation

Suppose the simplified perturbation:

$$\langle k|H_p|n\rangle = \begin{cases} H'_{kn} & \text{Constant between } 0 \text{ and } \tau \\ 0 & \text{Otherwise} \end{cases}$$



First order approximation

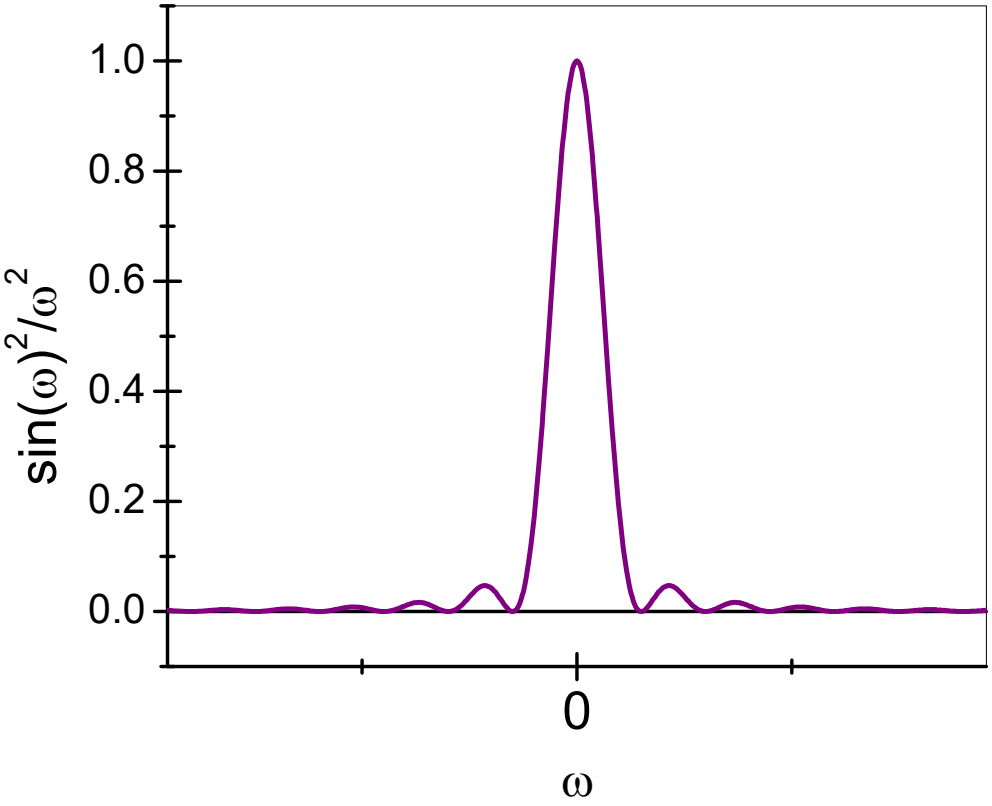
$$i\hbar \frac{da_k^{(1)}(t)}{dt} \approx \begin{cases} \sum_n H'_{nm}\delta_{ni} e^{i\omega_{kn}t} & \text{Between } 0 \text{ and } \tau \\ 0 & \text{Otherwise} \end{cases}$$

$$i\hbar a_k^{(1)}(\tau) \approx H'_{ik}\int_0^\tau e^{i\omega_{ki}t}dt = 2H'_{ik}e^{i\omega_{kn}\tau/2}\frac{\sin(\omega_{ki}\tau/2)}{\omega_{ki}}$$

It was used: $$\int_0^a e^{ikx}dx = 2e^{ika/2}\frac{\sin(ka/2)}{k}$$

Transition probability

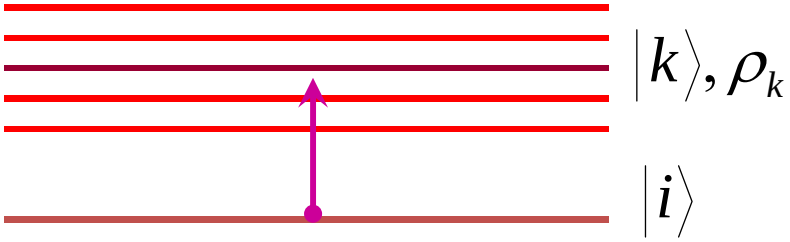
$$P_{ik} = \left|a_k(\tau)\right|^2 \approx 4\left|H'_{ik}\right|^2 \frac{\sin^2(\omega_{ki}\tau/2)}{\hbar^2\omega_{ki}^2}$$



Only transitions with $\omega \sim 0$ take place.

Physically meaningful quantity

$$W_k = \frac{1}{\tau} \sum_{k' \, near \, k} P_{ik'}$$



Near *k*: *density of states* $\rho_k = \frac{dn}{dE}$

$$W_k = \frac{1}{\tau} \sum_{k' \, near \, k} P_{ik'} = \frac{1}{\tau} \int P_{ik} \rho_k dE_k = \frac{\hbar}{\tau} \int P_{ik} \rho_k d\omega_{ki}$$

$$W_k = \frac{1}{\tau}\sum_{k' \, near \, k} P_{ik'} = \frac{1}{\tau}\int P_{ik}\rho_k dE_k = \frac{\hbar}{\tau}\int P_{ik}\rho_k d\omega_{ki}$$

Using $$P_{ik} = 4\left|H'_{ik}\right|^2 \frac{\sin^2(\omega_{ki}\tau/2)}{\hbar^2\omega_{ki}^2}$$

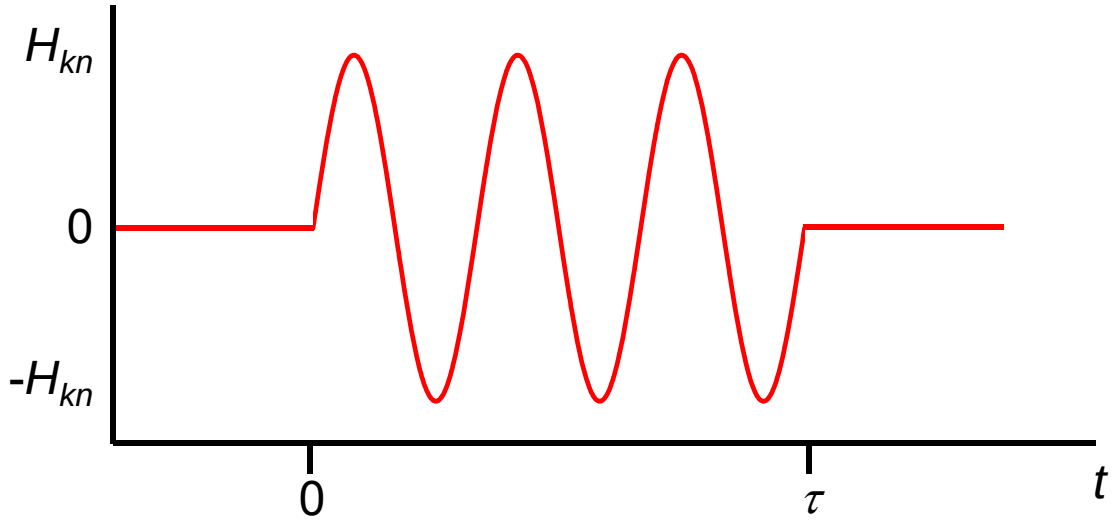
$$W_k = \frac{1}{\hbar}4\left|H'_{ik}\right|^2\rho_k \underbrace{\int_{-\infty}^{\infty}\frac{1}{\tau}\frac{\sin^2(\omega_{ki}\tau/2)}{\omega_{ki}^2}d\omega_{ki}}_{\pi/2}$$

$$\boxed{W_k = \frac{2\pi}{\hbar}\left|H'_{ik}\right|^2\rho_k}$$

Second case: harmonic perturbation

Suppose the harmonic perturbation:

$$\langle k | H_p | i \rangle = H_{kn} e^{i\omega t} + H_{kn}^{\dagger} e^{-i\omega t}$$



First order approximation

$$i\hbar a_k^{(1)}(\tau) \approx \int_0^{\tau} \left(H_{ki} e^{i\omega t} + H_{ki}^{\dagger} e^{-i\omega t} \right) e^{i\omega_{ki} t} dt$$

$$= \left[\frac{1 - e^{i(\omega_{ki} + \omega)t}}{\omega_{ki} + \omega} H_{ki} + \frac{1 - e^{i(\omega_{ki} - \omega)t}}{\omega_{ki} - \omega} H_{ki}^{\dagger} \right]$$

.
.
. Repeat same steps as before

$$W_{i \to k} = \frac{2\pi}{\hbar} \left| H_{ki} \right|^2 \delta\left(E_k - E_i \pm \hbar\omega \right)$$

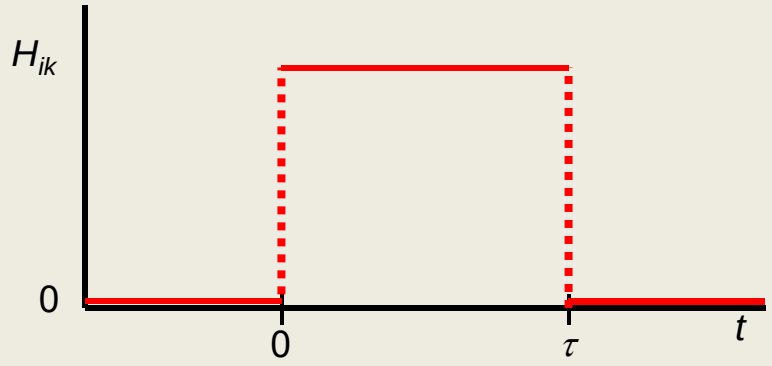
Fermi's Golden Rule in a nutshell

Transition rate between states *i* and *k*:

$$W_k = \frac{2\pi}{\hbar}\left|\langle i|H_p|k\rangle\right|^2 \rho_k$$

(First order time-dependent perturbation theory)

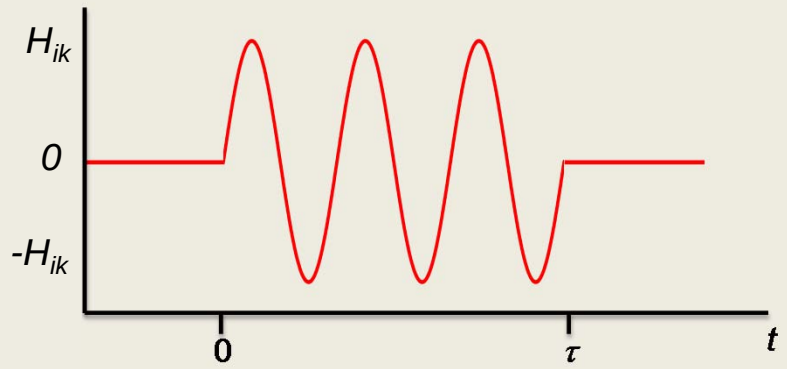
$\langle i|H_p|k\rangle$ constant



$P_{i\to k}$ is max for $\Delta E_{i\to k} = 0$

(Internal conversion, collision)

$\langle i|H_p|k\rangle$ Oscillating (ω)



$P_{i\to k}$ is max for $\Delta E_{i\to k} = \hbar\omega$

(Photoinduced)


Transition dipoles
Einstein coefficients
Oscillator strengths

Fermi's Golden Rule: photons and molecules

Light-matter perturbation Hamiltonian in **dipole approximation**:

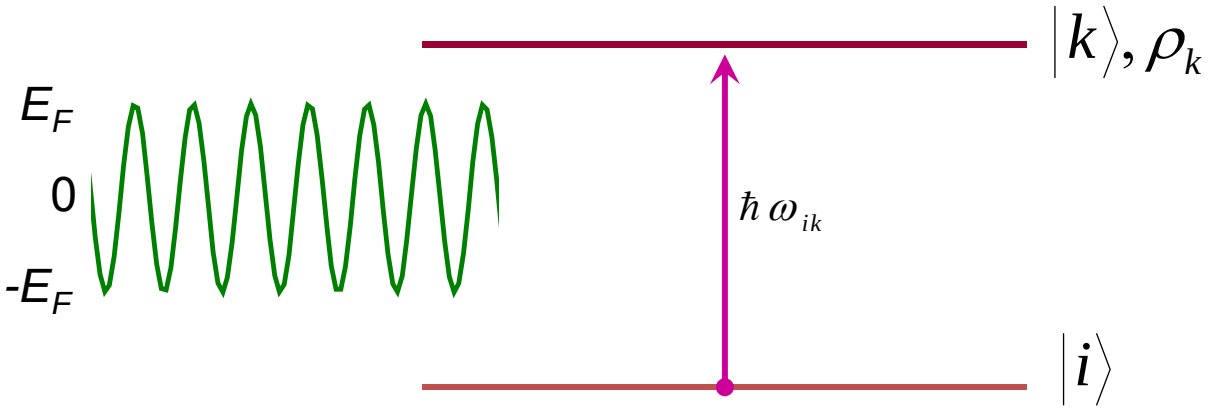
$$\langle k|H_p|i\rangle = \boldsymbol{\mu}\cdot\mathbf{E}_F\cos(\omega t) = \frac{1}{2}\boldsymbol{\mu}\cdot\mathbf{E}_F\left(e^{i\omega t}+e^{-i\omega t}\right)$$

$$H_{ki} = \frac{1}{2}\left(\boldsymbol{\mu}\cdot\mathbf{E}_F\right)$$

Molecular dipole

Electric field amplitude

Transition rate: $W_{i\to k} = \frac{\pi}{2\hbar^2}\left|\langle i|\boldsymbol{\mu}|k\rangle\cdot\mathbf{E}_F\right|^2\delta\left(\omega_{ik}\pm\omega\right)$



Transition dipole moment

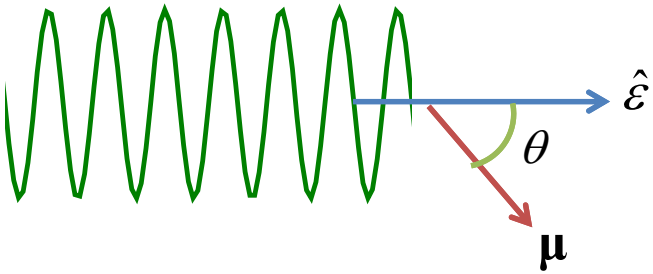
$$W_{i\to k} = \frac{\pi}{2\hbar^2}\left|\langle i|\boldsymbol{\mu}|k\rangle \cdot \mathbf{E}_F\right|^2 \delta\left(\nu_{ik} \pm \nu\right)$$

$$\langle i|\boldsymbol{\mu}|k\rangle = \langle i|e\left[\sum_{n=1}^{N_{at}} Z_n \mathbf{R}_n + \sum_{m=1}^{N_{el}} \mathbf{r}_m\right]|k\rangle = \boldsymbol{\mu}_N \delta_{ik} + \langle i|\boldsymbol{\mu}_e|k\rangle$$

0

Electronic transition dipole moment

$$W_{i\to k} = \frac{\pi E_F^2}{2\hbar^2}\left|\langle i|\boldsymbol{\mu}_e \cdot \hat{\varepsilon}|k\rangle\right|^2 \delta\left(\omega_{ik} \pm \omega\right)$$



Anisotropic case:

$$W_{i\to k} = \frac{1}{3}\frac{\pi E_F^2}{\left(2\hbar^2\right)}\left|\langle i|\mu_e|k\rangle\right|^2 \delta\left(\omega_{ik} \pm \omega\right)$$

Transition dipole moment

$$W_{i\to k} = \frac{\pi E_F^2}{6\hbar^2}\left|\langle i|\mu_e|k\rangle\right|^2 \delta(\omega_{ik} \pm \omega)$$

$$= \frac{\pi\left|\langle i|\mu_e|k\rangle\right|^2}{3\varepsilon_0\hbar^2} \mathrm{P}(\omega)\delta(\omega_{ik} \pm \omega)$$

Where the density of radiant energy is:

$$\mathrm{P}(\omega) = \frac{1}{2}\varepsilon_0 E_F^2$$

$$W'_{i\to k} = \int W_{i\to k}\, d\omega = \underbrace{\frac{\pi\left|\langle i|\mu_e|k\rangle\right|^2}{3\varepsilon_0\hbar^2}} \mathrm{P}(\omega_{ik})$$

Einstein coefficient *B* for absorption

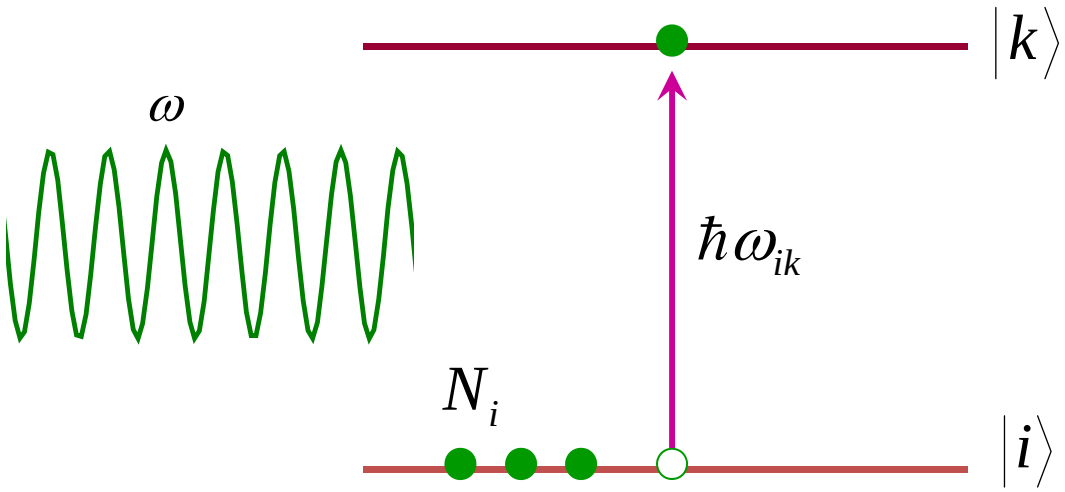
Einstein coefficients

Rate of absorption $i \rightarrow k$ $\quad W_{ik}^{a} = B_{ik} N_i$

Einstein coefficient B for absorption

$$B_{ik} = \frac{g_k}{g_i} \frac{\pi \left| \langle i | \mu_e | k \rangle \right|^2}{3\varepsilon_0 \hbar^2}$$

g_n - degeneracy of state n

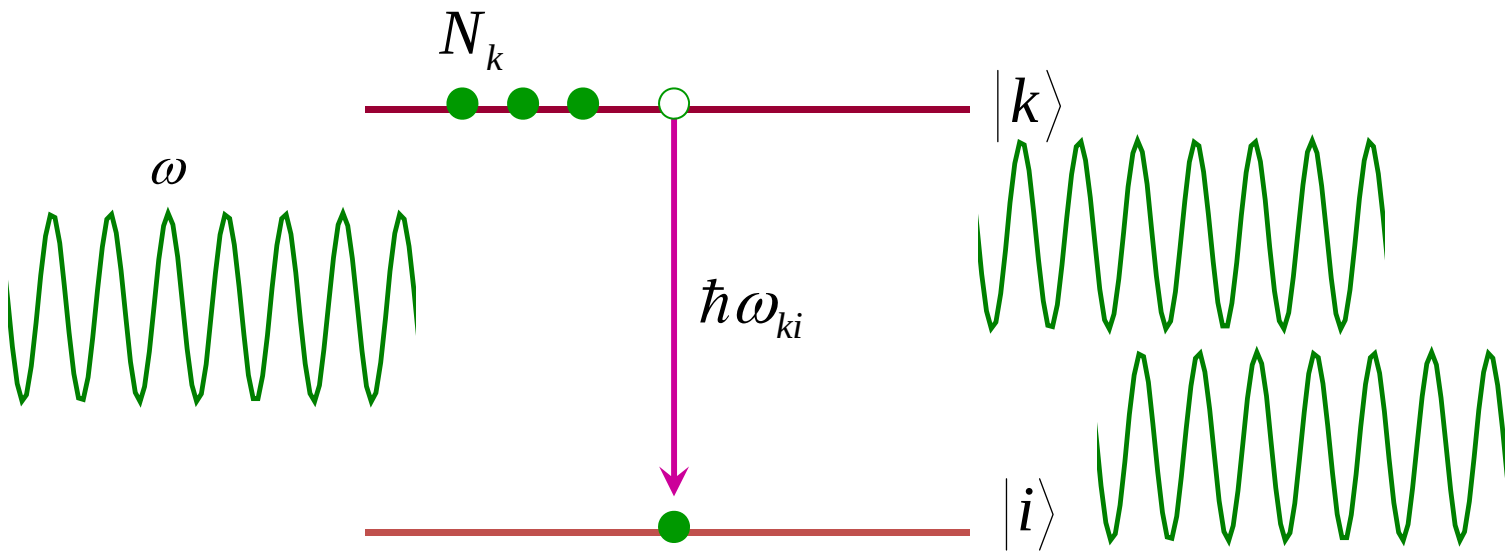


Einstein coefficients

Rate of stimulated emission $k \rightarrow i$ $\quad W_{ki}^{st} = B_{ki} N_k$

Einstein coefficient B for stimulated emission

$$B_{ik} = \frac{g_i}{g_k} B_{ki}$$

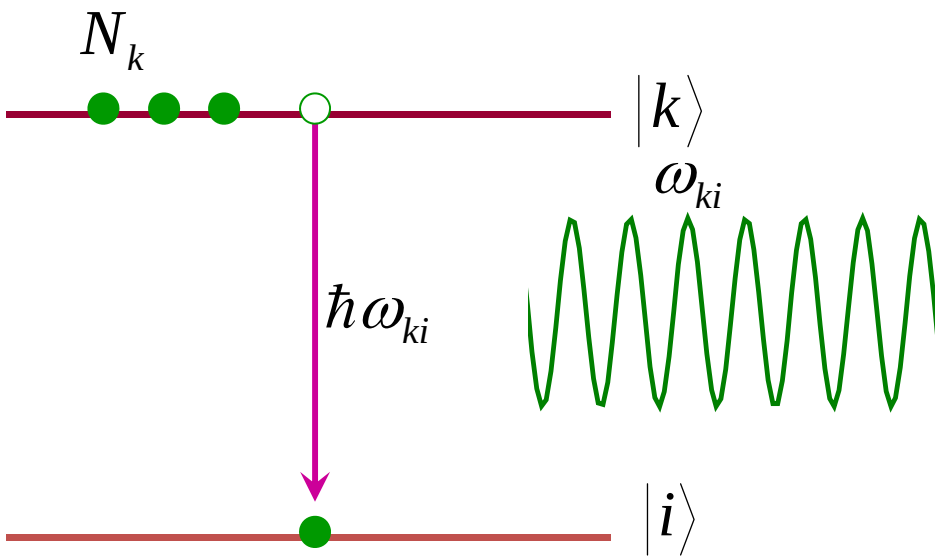


Einstein coefficients

Rate spontaneous decay $k \rightarrow i$ $\quad W_{ki}^{sp} = A_{ki} N_2$

Einstein coefficient *A* for spontaneous emission

$$A_{ki} = \frac{\hbar \omega_{ki}^3}{\pi^2 c^3} B_{ki}$$



Einstein coefficient and oscillator strength

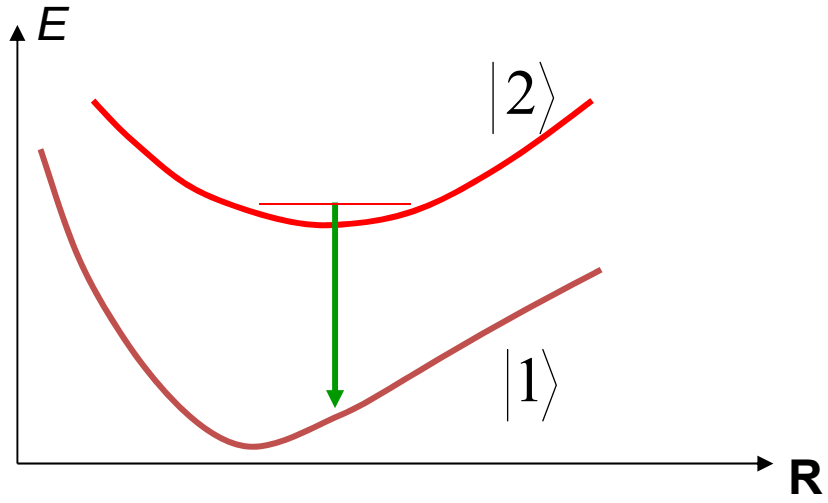
$$f_{ki} = -\frac{2\pi\varepsilon_0 mc^3}{\omega_{ki}^2 e^2} A_{ki}$$

In atomic units:

$$f_{ki} = -\frac{c^3}{2\Delta E_{ki}^2} A_{ki}$$

Einstein coefficient and lifetime

$$\tau_{ki} = \frac{1}{A_{ki}} = -\frac{c^3}{2\Delta E^2 f_{ki}}$$



If ΔE_{21} = 4.65 eV and f_{21} = -0.015, what is the lifetime of the excited state?

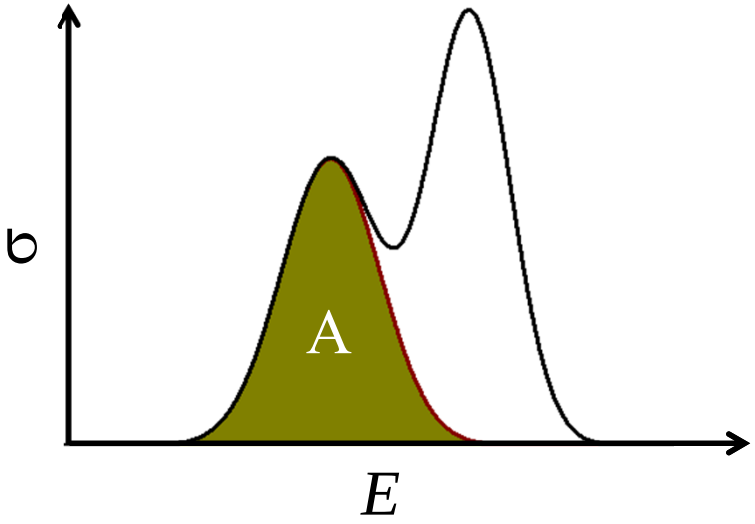
$$\Delta E_{21} = 4.65\ eV$$
$$= 4.65 / 27.211396$$
$$= 0.170884\ au$$

$$\tau_{21} = -\frac{(137)^3}{2(0.170884)^2(-0.015)}$$
$$= 0.29 \times 10^{10}\ au$$

Converting to nanoseconds:

$$\tau_{21} = 0.29 \times 10^{10} \left(2.4189 \times 10^{-17}\ s\right)$$
$$= 70\ ns$$

Oscillator strength and experiments



$$f = \frac{4mc\varepsilon_0}{he^2n^2}\underbrace{\int \sigma(E)\,dE}_{A}$$

For a Gaussian peak:

$$\sigma(E) = \sigma_{\max}\, e^{-\frac{(E-E_{\max})^2}{\Delta E^2}}$$

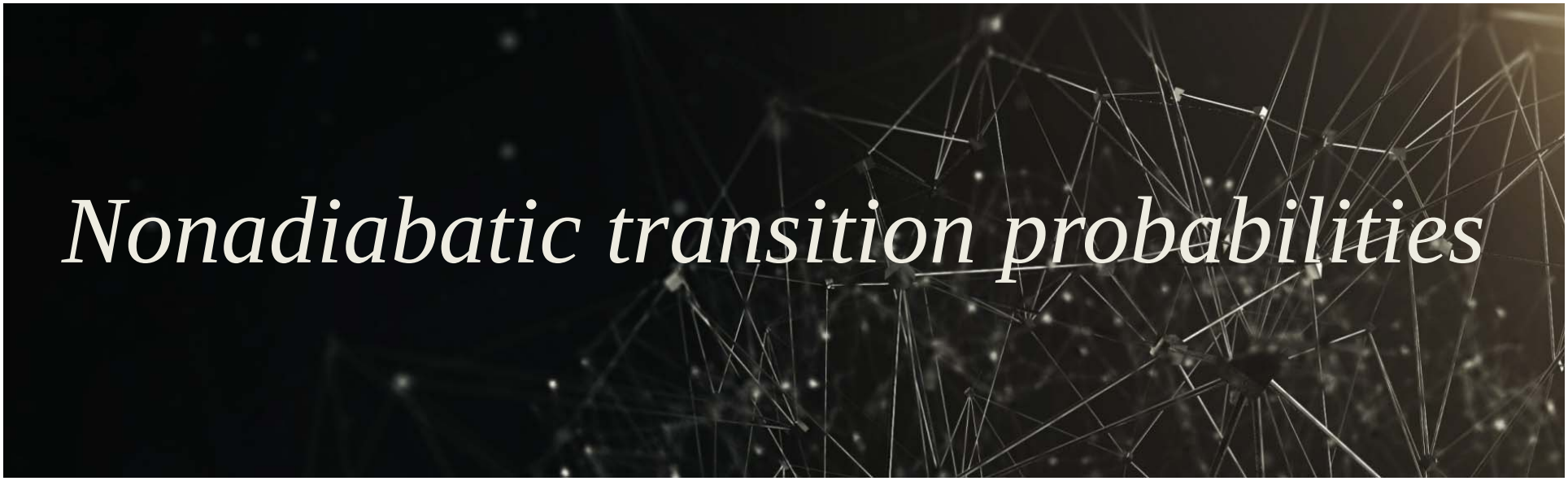
$$f = 1.6\Delta E\sigma_{\max} \quad \begin{cases} \Delta E \text{ in eV} \\ \sigma_{\max} \text{ in Å}^2/\text{molecule} \end{cases}$$

Example:

$$B_{12}^{\omega} = \frac{g_2}{g_1}\frac{\pi^2 c^3}{\hbar\omega_{21}^3}A_{21}$$

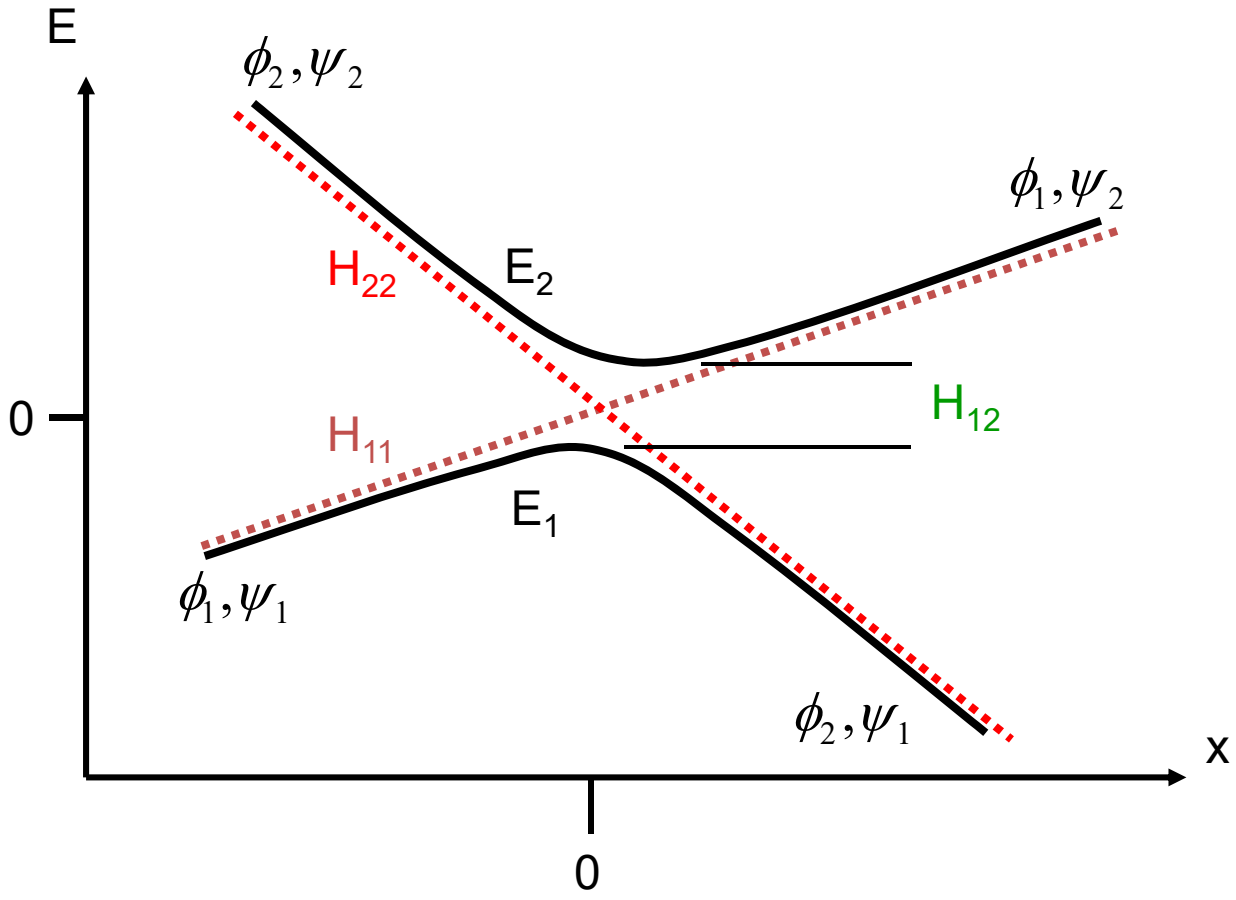
- Hilborn, Am J Phys **50**, 982 (1982)

	A_{21}						
A_{21}	1	B_{12}^{ω}					
B_{12}^{ω}	$\frac{g_2}{g_1}\frac{\pi^2 c^3}{\hbar\omega_{21}^3}$	1	B_{12}^{f}				
B_{12}^{f}	$\frac{g_2}{g_1}\frac{c^3}{8\pi h f^3}$	$\frac{1}{2\pi}$	1	σ_0			
σ_0	$\frac{g_2}{4g_1}\lambda_{21}^2$	$\frac{\hbar\omega_{21}}{c}$	$\frac{h\omega_{21}}{c}$	1	f_{12}		
f_{12}	$\frac{g_2}{g_1}\frac{2\pi\varepsilon_o mc^3}{\omega_{21}^2 e^2}$	$\frac{2\varepsilon_o m\hbar\omega_{21}}{\pi e^2}$	$\frac{4\varepsilon_o m\hbar\omega_{21}}{e^2}$	$\frac{2\varepsilon_o mc}{\pi e^2}$	1	μ_{21}^2	
μ_{21}^2	$\frac{3\varepsilon_o hc^3}{2\omega_{21}^3}$	$3\frac{g_1}{g_2}\frac{\varepsilon_o\hbar^2}{\pi}$	$6\frac{g_1}{g_2}\varepsilon_o\hbar^2$	$3\frac{g_1}{g_2}\frac{\varepsilon_o\hbar c}{\pi\omega_{21}}$	$\frac{3g_1}{2g_2}\frac{\hbar e^2}{m\omega_{21}}$	1	S_{21}
S_{21}	$g_2\frac{3\varepsilon_o hc^3}{2\omega_{21}^3}$	$3\frac{g_1\varepsilon_o\hbar^2}{\pi}$	$6g_1\varepsilon_o\hbar^2$	$3\frac{g_1\varepsilon_o\hbar c}{\pi\omega_{21}}$	$\frac{3g_1\hbar e^2}{2\omega_{21}m}$	g_2	1



Nonadiabatic transition probabilities

Problem: if the molecule prepared in state 2 at x = $-\infty$ moves through a region of crossing, what is the probability of ending in state 1 at x = $+\infty$?



• Desouter-Lecomte and Lorquet, J Chem Phys 71, 4391 (1979)

Models for non-adiabatic transitions

1. Landau-Zener

$$H_{11} - H_{22} = \Delta F_{12}\, x$$
$$H_{12}, \Delta F_{12} = \text{constant}$$

$$P = \exp\left\{ -\frac{2\pi}{\hbar v} \frac{|H_{12}|^2}{|\Delta F_{12}|} \right\}$$

2. Demkov / Rosen-Zener

$$E_1 - E_2 = \text{constant}$$
$$h_{12} = h_{12}^x \,\text{sech}[x/\beta]$$

$$P = \text{sech}^2\left[\frac{\pi(E_1 - E_2)}{4\hbar v h_{12}^x} \right]$$

3. Nikitin

$$H_{11} - H_{22} = \Delta\varepsilon - A\cos\omega_0 \exp(-\alpha x)$$
$$H_{12} = -\frac{A}{2}\sin\omega_0 \exp(-\alpha x)$$

$$P = \frac{\exp\left(\lambda \cos^2(\omega_0/2)\right) - 1}{\exp\lambda - 1}$$
$$\lambda = \frac{2\pi}{\hbar v \alpha} \Delta\varepsilon \tan^2\omega_0 \cot^2\omega_0$$

4. Bradauk; 5. Delos-Thorson; 6. …

Derivation of Landau-Zener formula

$$|\Phi\rangle = \sum_n a_n(t)\exp\left[-\frac{i}{\hbar}\int^t H_{nn}(t)dt\right]|\phi_n\rangle$$

$$\left(i\hbar\frac{\partial}{\partial t} - H\right)|\Phi\rangle = 0$$

Multiply by $\langle\phi_k|$ at left and integrate

$$i\hbar\frac{da_k(t)}{dt} = \sum_{n\neq k} H_{kn}a_n(t)e^{\gamma_n}$$

$$H_{kn} \equiv \langle\phi_k|H|\phi_n\rangle$$

$$\gamma_n \equiv -\frac{i}{\hbar}\int^t H_{nn}dt$$

In the deduction it was used:

$$\frac{d}{dt}\int^t H_{nn}dt = H_{nn}$$

- Wittig, J Phys Chem B **109**, 8428 (2005)

Since there are only two states:

$$i\hbar\frac{da_k(t)}{dt}=\sum_{n\neq k}H_{kn}a_n(t)e^{\gamma_n}$$

$$\begin{cases}\dfrac{da_1(t)}{dt}=-\dfrac{i}{\hbar}H_{12}a_2(t)e^{\gamma_{21}} & \text{(i)}\\[2ex] \dfrac{da_2(t)}{dt}=-\dfrac{i}{\hbar}H_{21}a_1(t)e^{\gamma_{12}} & \text{(ii)}\end{cases}$$

$$\gamma_{ij}\equiv\gamma_i-\gamma_j$$

Solving (i) for a_2 and taking the derivative:

$$\frac{(H_{11}-H_{22})e^{\gamma_{12}}}{H_{12}}\frac{da_1}{dt}+\frac{i\hbar e^{\gamma_{12}}}{H_{12}}\frac{d^2a_1(t)}{dt^2}=\frac{da_2(t)}{dt}\quad\text{(iii)}$$

Substituting (iii) in (ii):

$$\frac{d^2a_1}{dt^2}-\frac{i}{\hbar}(H_{11}-H_{22})\frac{da_1}{dt}+\frac{1}{\hbar^2}|H_{12}|^2a_1=0$$

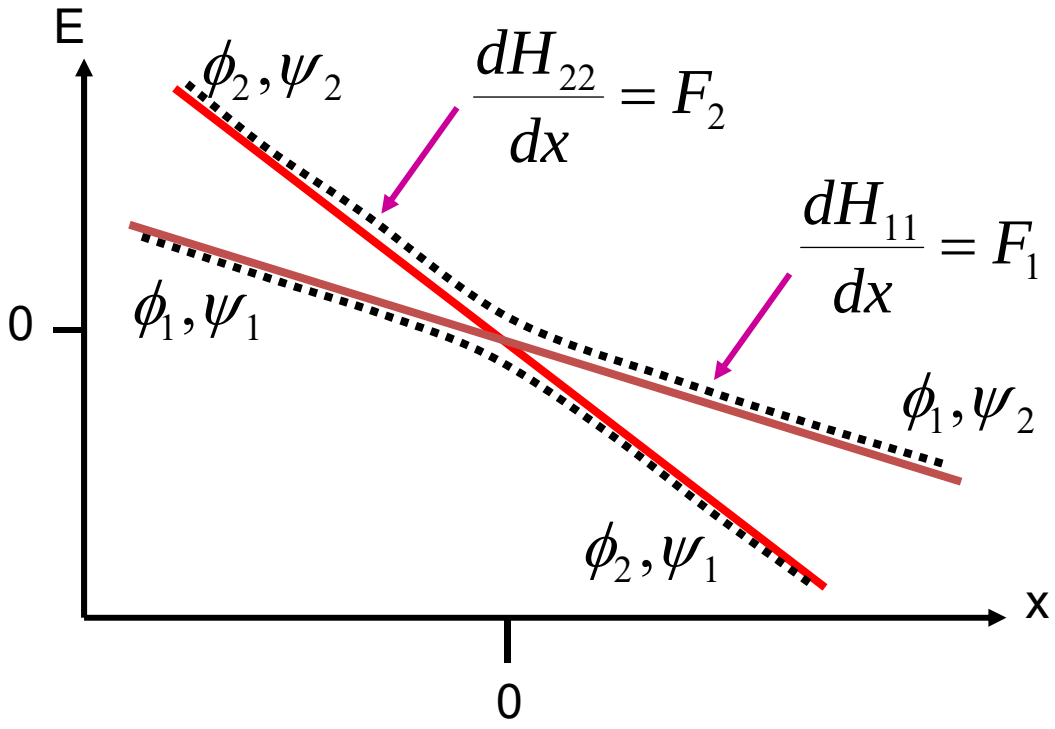
$$\frac{d^2a_1}{dt^2} - \frac{i}{\hbar}(H_{11} - H_{22})\frac{da_1}{dt} + \frac{1}{\hbar^2}|H_{12}|^2 a_1 = 0$$

Zener approximation: $H_{11} - H_{22} = \alpha t$

$$\begin{cases} H_{11} = F_1 x = F_1 v t \\ H_{22} = F_2 x = F_2 v t \end{cases}$$

$$H_{11} - H_{22} = -|F_1 - F_2| v t$$

$$\alpha = -|\Delta F_{12}| v$$



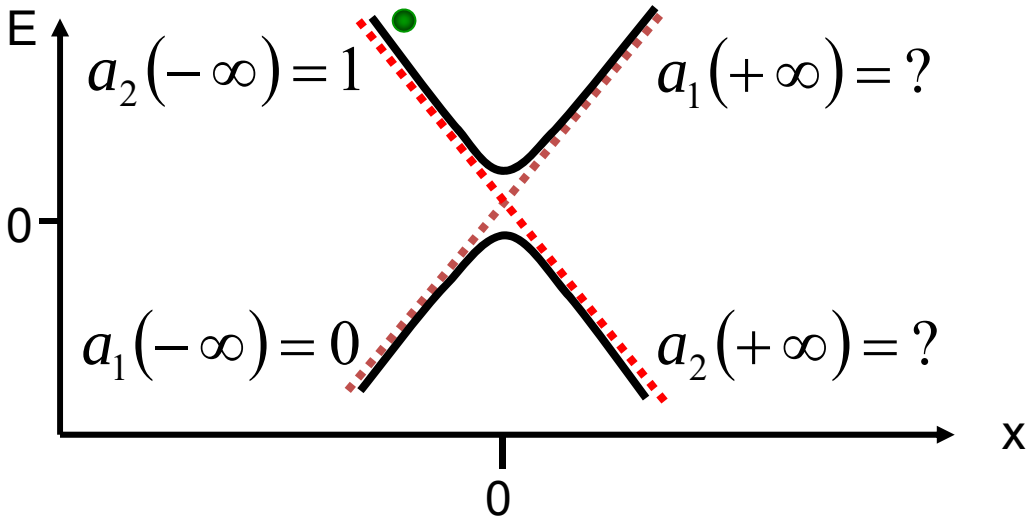
$$\frac{d^2a_1}{dt^2} + \frac{i}{\hbar}|\Delta F_{12}|vt\frac{da_1}{dt} + \frac{1}{\hbar^2}|H_{12}|^2 a_1 = 0$$

$$\frac{d^2a_2}{dt^2} - \frac{i}{\hbar}|\Delta F_{12}|vt\frac{da_2}{dt} + \frac{1}{\hbar^2}|H_{12}|^2 a_2 = 0$$

Problem: Find $a_2(+\infty)$ subject to the initial condition $a_2(-\infty) = 1$.

The solution is:

$$a_2(+\infty) = \exp\left\{-\frac{\pi}{\hbar v}\frac{|H_{12}|^2}{|\Delta F_{12}|}\right\}$$

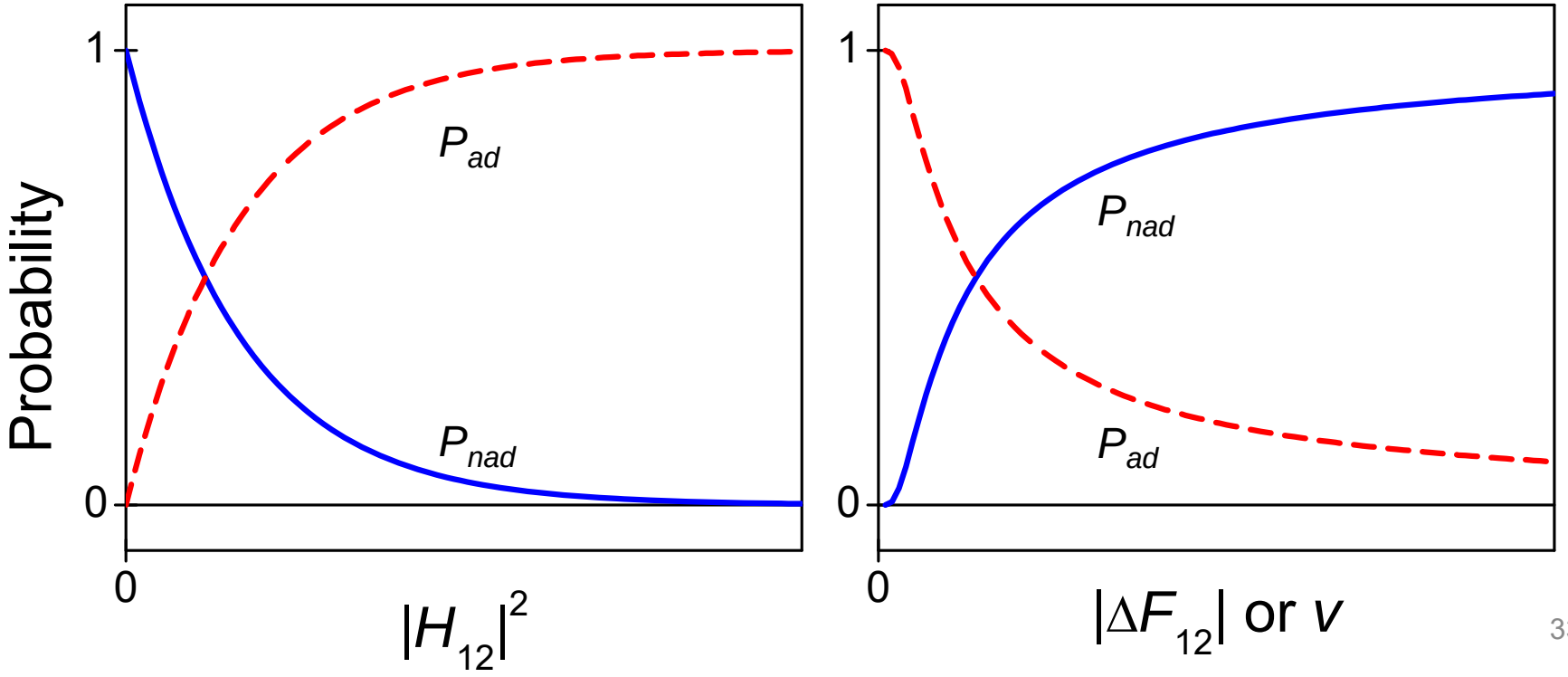


The probability of finding the system in state 2 is:

$$P_{nad} = |a_2(\infty)|^2 = \exp\left\{-\frac{2\pi}{\hbar v}\frac{|H_{12}|^2}{|\Delta F_{12}|}\right\}$$

The probability of finding the system in state 1 is:

$$P_{ad} = 1 - P_{nad} = 1 - \exp\left\{-\frac{2\pi}{\hbar v}\frac{|H_{12}|^2}{|\Delta F_{12}|}\right\}$$



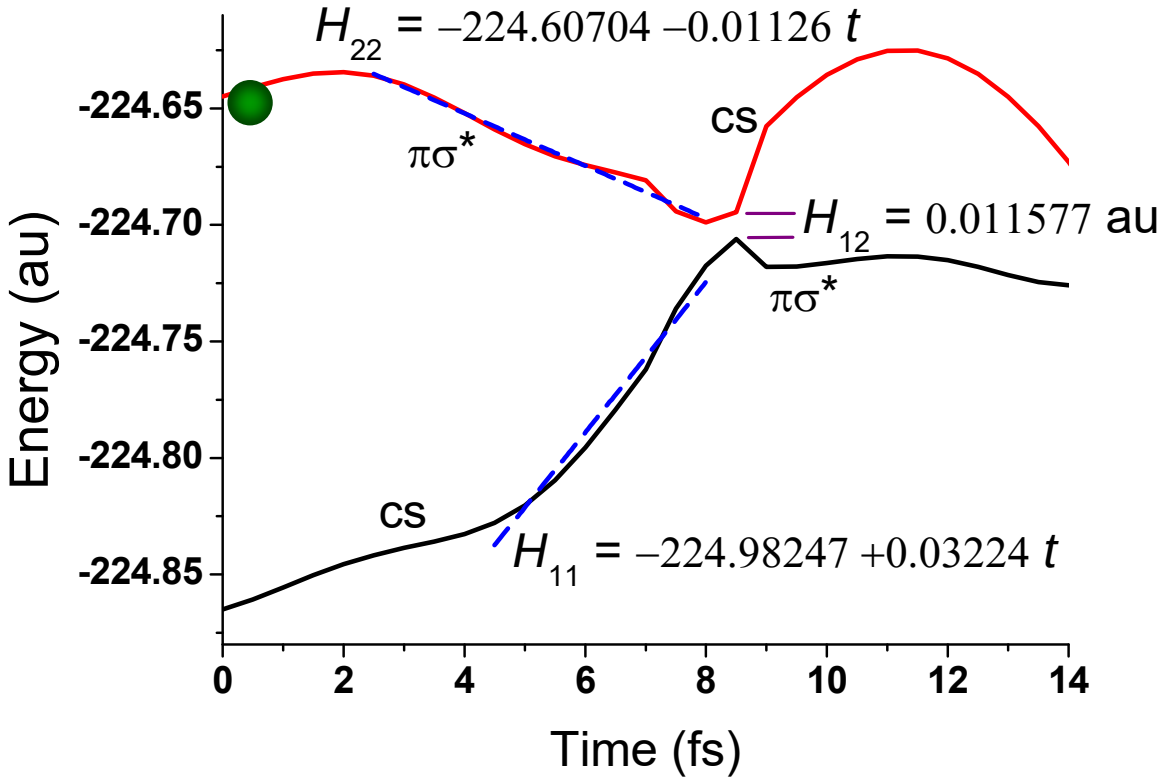
Example: In trajectory in the graph, what are the probability of the molecule to remain in the $\pi\sigma^*$ state or to change to the closed shell state?

$$P_{\pi\sigma^*\to\pi\sigma^*} = \exp\left\{-2\pi\frac{|H_{12}|^2}{|\alpha|}\right\} \qquad \alpha = -|\Delta F_{12}|v \qquad \hbar = 1$$

$$H_{11} - H_{22} = \alpha t$$

$$\alpha = 0.03224 - (-0.01126)$$

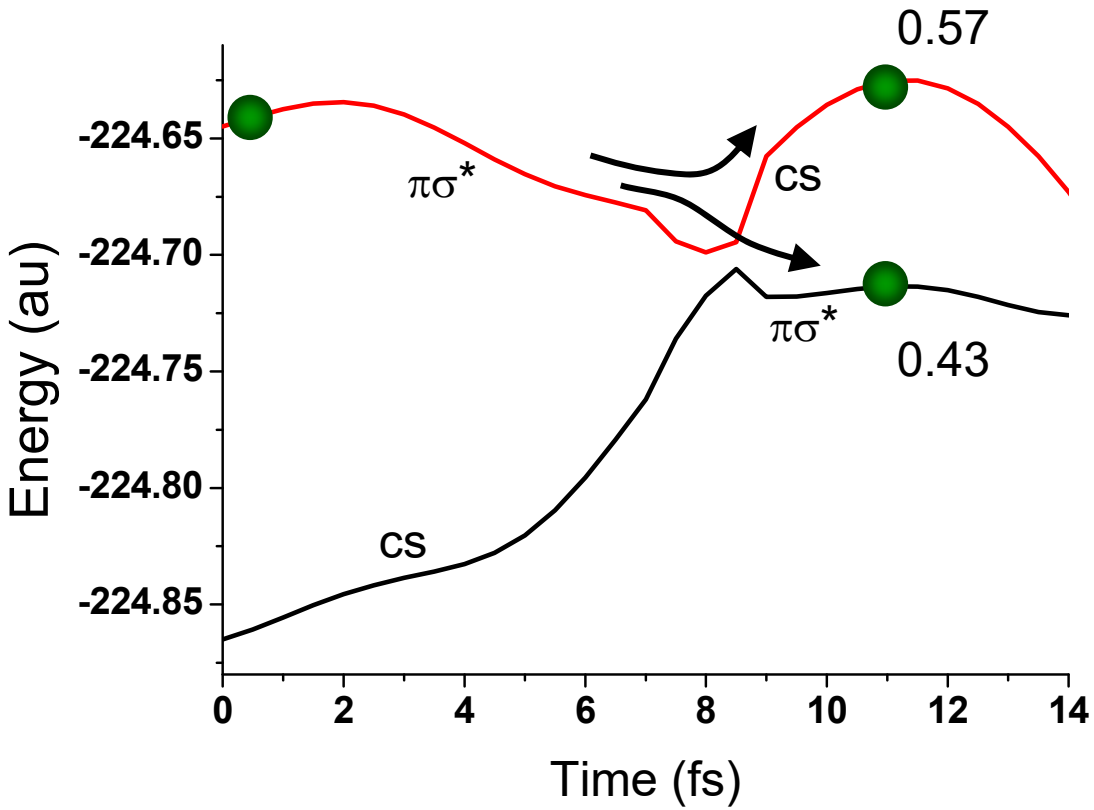
$$= 0.0435 \text{ au/fs} = 0.001 \text{ au} \qquad \left(1 \text{ au}_{\text{time}} = 2.4\times10^{-2} \text{ fs}\right)$$



Example: In trajectory in the graph, what are the probability of the molecule to remain in the $\pi\sigma^*$ state or to change to the closed shell state?

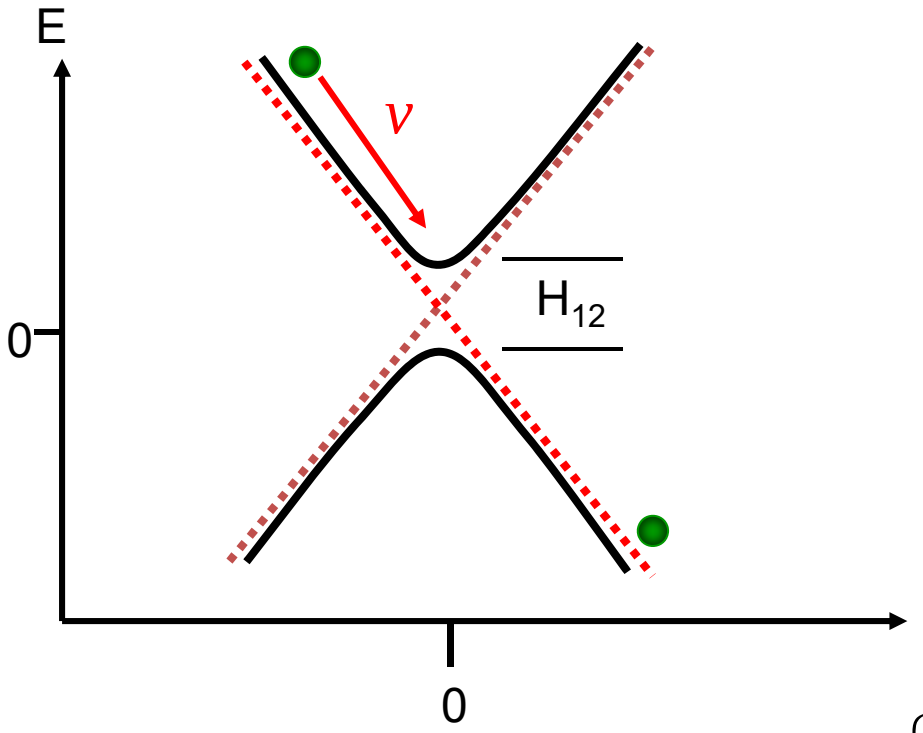
$$P_{\pi\sigma^*\rightarrow\pi\sigma^*} = \exp\left\{-2\pi\frac{0.011577^2}{0.001}\right\} = 0.43$$

$$P_{\pi\sigma^*\rightarrow cs} = 1 - P_{\pi\sigma^*\rightarrow\pi\sigma^*} = 0.57$$

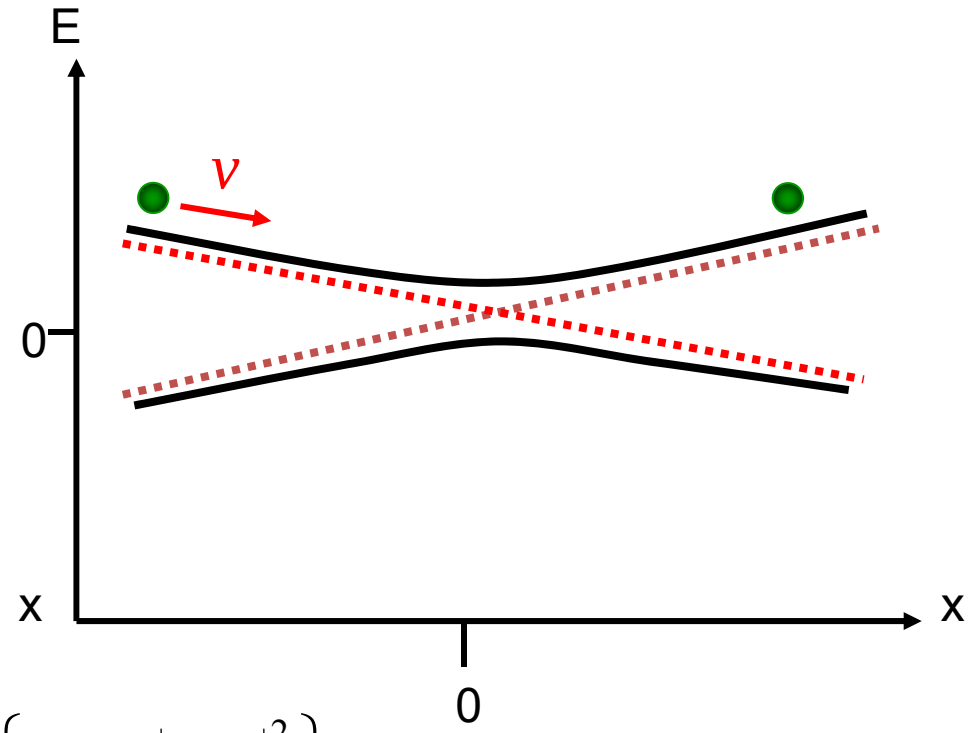


For the same H_{12}, Landau-Zener predicts:

Non-adiabatic (diabatic)



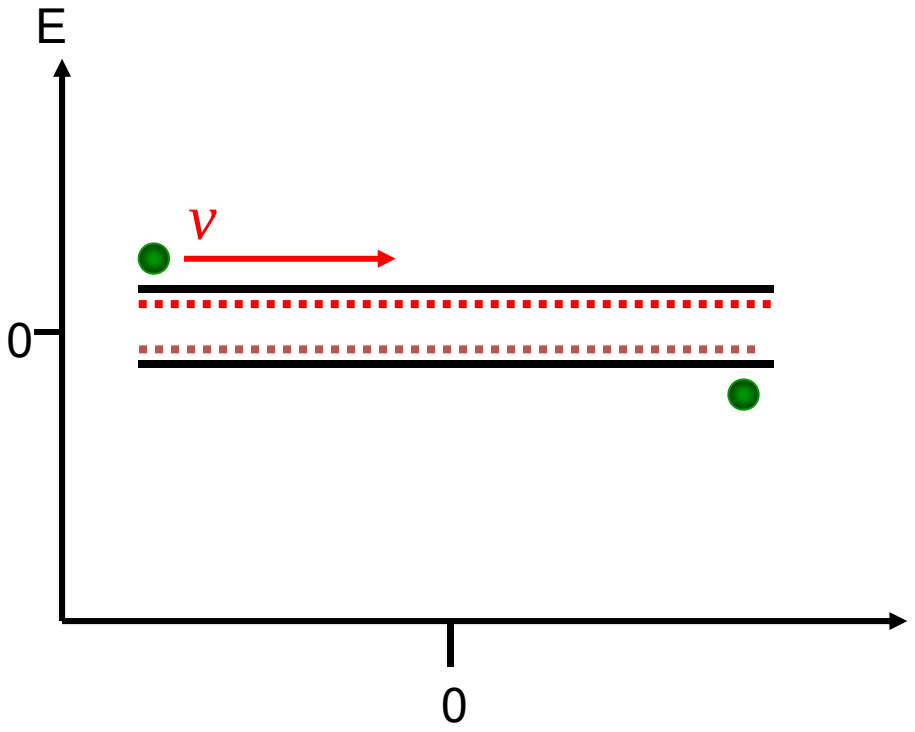
Adiabatic



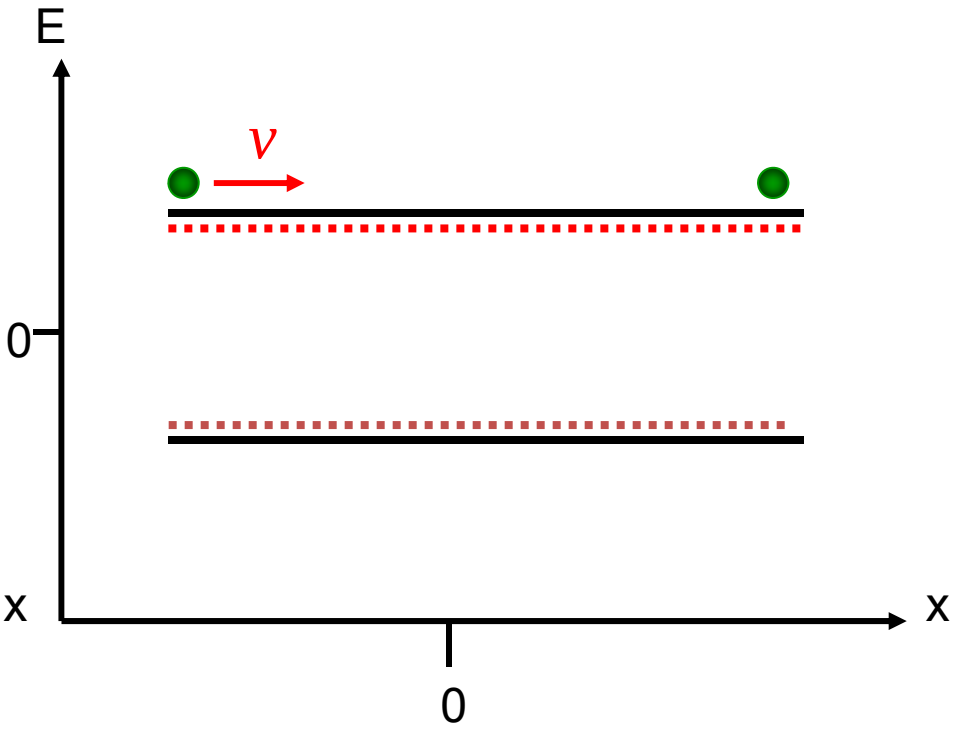
$$P_{nad} = \exp\left\{-\frac{2\pi}{\hbar v}\frac{|H_{12}|^2}{|\Delta F_{12}|}\right\}$$

For the same h_{12}^{x} , Rosen-Zener predicts:

Non-adiabatic (but not diabatic!)

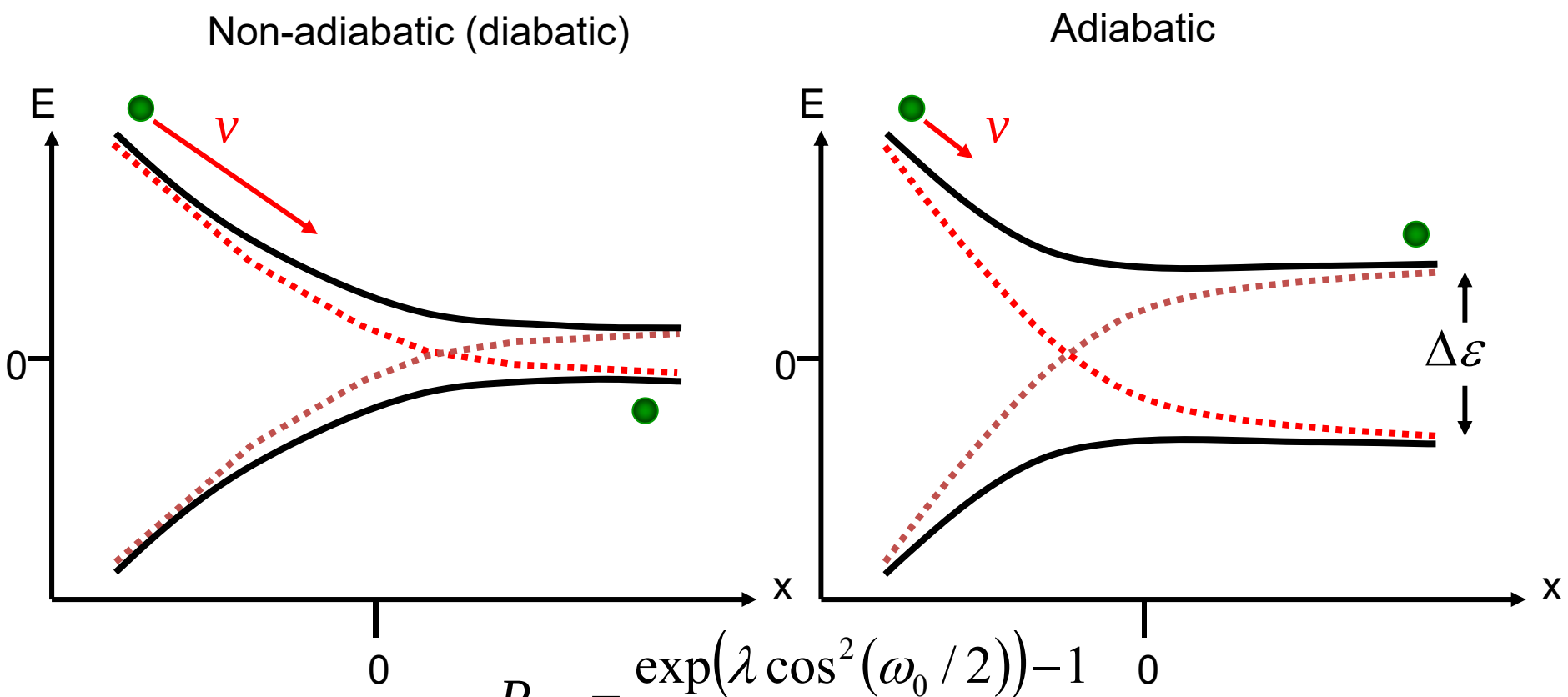


Adiabatic



$$P_{nad} = \operatorname{sech}^2\left[\frac{\pi\left(E_1 - E_2\right)}{4\hbar v h_{12}^{x}}\right]$$

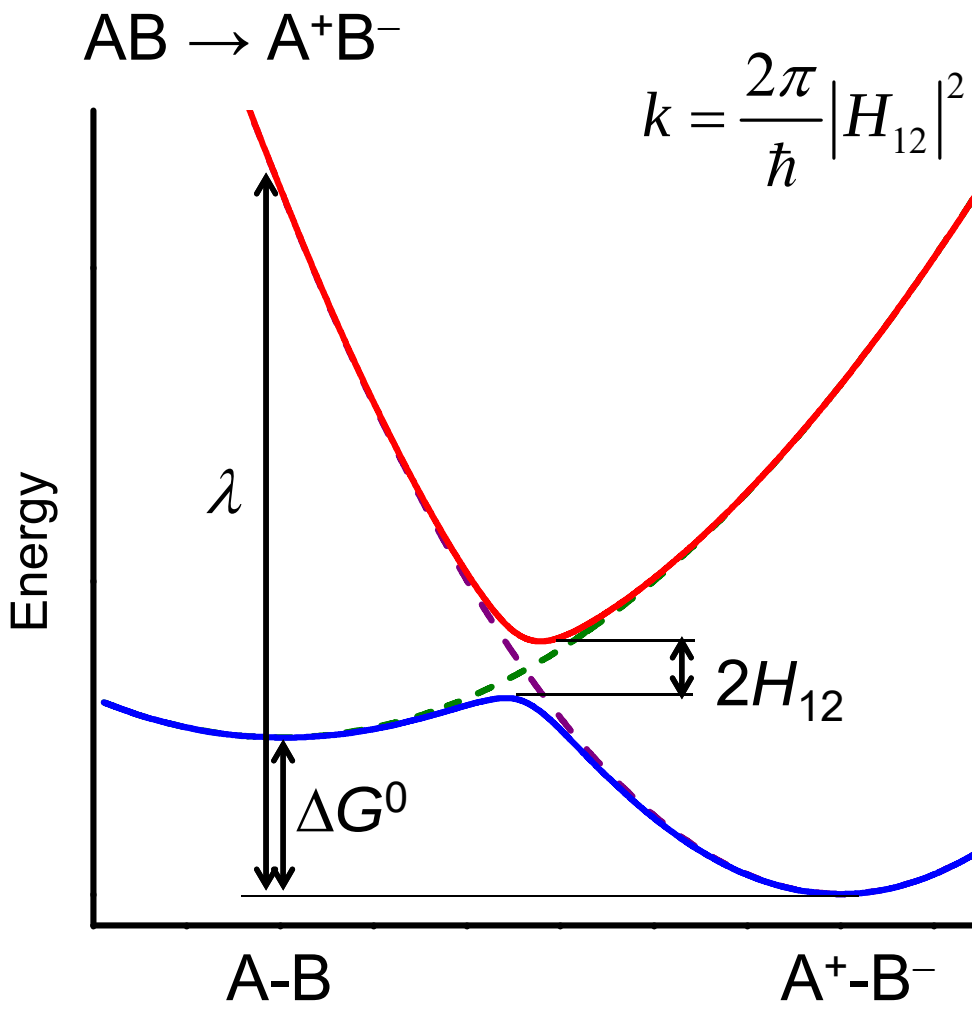
For the same ω_0 (H_{12}), Nikitin predicts:



$$P_{nad} = \frac{\exp\left(\lambda \cos^2(\omega_0/2)\right) - 1}{\exp\lambda - 1}$$

$$\lambda = \frac{2\pi}{\hbar v \alpha} \Delta\varepsilon \tan^2 \omega_0 \cot^2 \omega_0$$

Marcus Model ($\lambda \neq 0$)

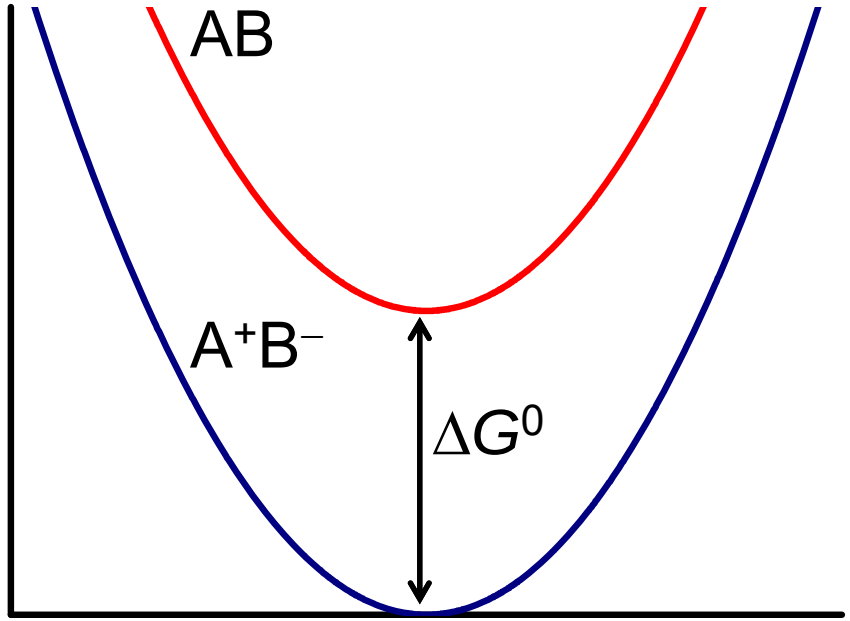


$$k = \frac{2\pi}{\hbar}\left|H_{12}\right|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{\left(\lambda + \Delta G^0\right)^2}{4\lambda k_B T}\right)$$

Gap Law ($\lambda = 0$)

$AB \rightarrow A^+B^-$

$$k \propto \left|H_{12}\right|^2 \exp\left(-\alpha \Delta G^0\right)$$



- Jortner and Bixon, Adv Chem Phys **106**, 35 (1999)

The problem with the previous formulations is that they only predict the total probability at the end of the process.

If we want to perform dynamics, it is necessary to have the instantaneous probability.

Fewest-switches surface hopping is a good option.

Key points

- Femi's Golden Rule is the key to describe transfer between states.
- There are many different ways of computing nonadiabatic transition probabilities.
- It is important to have an intuition about when transition is more probable.