Part VI

Elementary photoinduced processes

18 Molecular states

In the following we consider a molecule without translational or rotational motion

18.1 Born-Oppenheimer separation

In molecular physics usually the Born-Oppenheimer separation of electronic (r) and nuclear motion (Q) is used. The molecular Hamiltonian (without considering spin or relativistic effects) can be written as

$$H = T_N(Q) + T_{el}(r) + V_N(Q) + V_{eN}(Q,r) + V_{ee}(r)$$

with kinetic energy

$$T_N = \sum_j -\frac{\hbar^2}{2m_j}\frac{\partial^2}{\partial Q_j^2} \qquad T_{el} = \sum -\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial r_k^2}$$

and the Coulombic interaction

$$V = V_N(Q)+V_{eN}(Q,r)+V_{ee}(r) = \sum_{j,j'}\frac{Z_j Z_{j'} e^2}{4\pi\epsilon|R_j - R_{j'}|} - \sum_{j,k}\frac{Z_j e^2}{4\pi\epsilon|R_j - r_k|} + \sum_{k,k'}\frac{e^2}{4\pi\epsilon|r_k - r_{k'}|}$$

The BO wavefunction is a product

$$\psi(r,Q)\chi(Q)$$

where the electronic part depends parametrically on the nuclear coordinates.

The nuclear masses are much larger than the electronic mass. Therefore the kinetic energy of the nuclei is neglected for the electronic motion. The electronic wavefunction is approximately obtained from the Eigenvalue problem

$$(T_{el} + V)\psi_s(r,Q) = E_s(Q)\psi_s(r,Q)$$

which has to be solved for each set of nuclear coordinates separately. Using now the BO product ansatz we have

$$H\psi_s(r,Q)\chi_s(Q) = T_N\psi_s(r,Q)\chi_s(Q) + E_s(Q)\psi_s(r,Q)\chi_s(Q)$$

$$= \psi_s(r,Q)(T_N + E_s(Q))\chi_s(Q) - \sum_j \frac{\hbar^2}{2m_j}\left(\chi_s(Q)\frac{\partial^2\psi_s(r,Q)}{\partial Q_j^2} + \frac{\partial\chi_s(Q)}{\partial Q_j}\frac{\partial\psi_s}{\partial Q_j}\right)$$

The sum constitutes the so called nonadiabatic interaction V_{nad} . If it is neglected in lowest order the nuclear wavefunction is a solution of the Eigenvalue problem

$$(T_N + E_s(Q))\chi_s(Q) = E\chi_s(Q)$$

often the potential energy $E_s(Q)$ can be expanded around the equilibrium configuration Q_{0s} [42]

$$E_s(Q) = E_s(Q_{0s}) + \frac{1}{2}\sum_{j,j'} \frac{\partial^2}{\partial Q_j \partial Q_{j'}} E_s + \cdots$$

Within the harmonic approximation the matrix of second derivatives is diagonalized and the nuclear motion becomes a superposition of independent normal modes Q_r with reduced masses M_r and frequencies ω_r [43]

$$E_s(Q) = E_s^{(0)} + \sum_r \frac{M_r^{(s)} \omega_r^{(r)2}}{2} Q_r^2$$

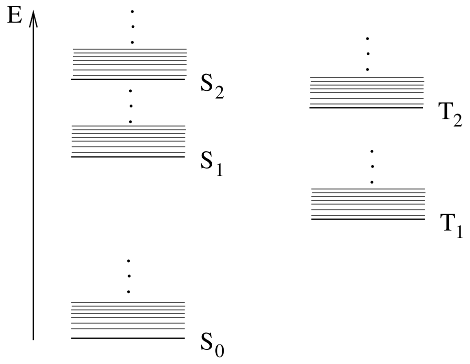
$$\chi_s(Q) = \prod_r \chi_{s,r,n(r)}(Q_r)$$

and the total energy of a molecular state is

$$E_s^0 + \sum_r \hbar\omega_r^{(s)}(n(r) + \frac{1}{2})$$

For biological molecules the vibrations form a very dense manifold of states.This is often schematically represented in a Jablonsky-diagram [44]

Figure 90: Jablonsky diagram



18.2 Nonadiabatic interaction

The nonadiabtic interaction couples the adiabatic electronic states.[45] If we expand the wavefunction as a linear combination of the adiabatic wavefunctions which form a complete basis at each configuration Q

$$\Psi = \sum_s C_s \psi_s(r, Q)\chi_s(Q)$$

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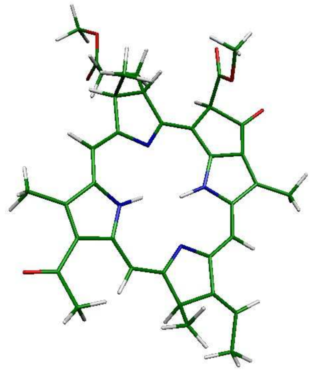
[42] which will be different for different electronic states s in general

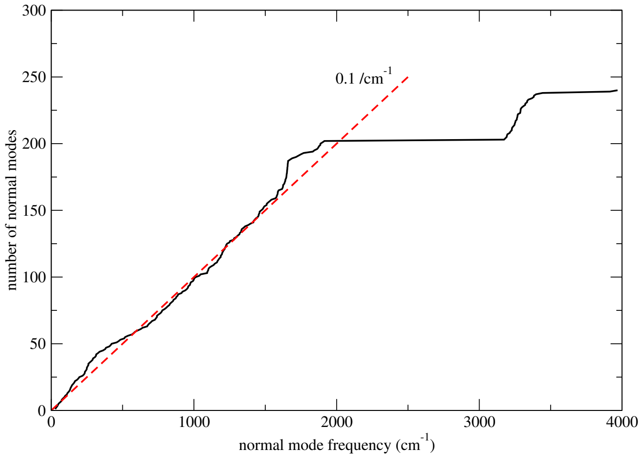
[43] all these quantities will be different for different electronic states s of course

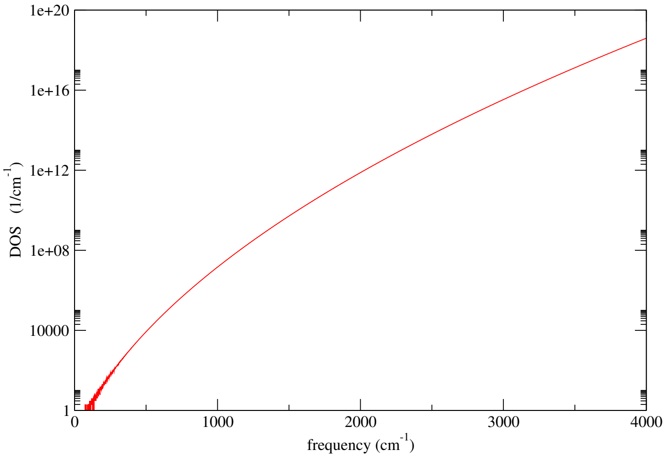
[44] which usually also shows electronic states of higher multiplicity

[45] sometimes called channels

Figure 91: Bacteriopheophytine model
The normal modes are calculated quantum chemically. The densitiy of vibrational states is evaluated with a simple counting method







we have to consider the nonadiabatic matrix elements[46]

$$V_{s,s'}^{nad} = \int dr\, dQ\, \chi_{s'}(Q)\psi_{s'}(r,Q)\, V_{nad}\, \psi_s(r,Q)\chi_s(Q)$$

$$= -\sum_j \frac{\hbar^2}{2m_j} \int dQ\, \chi_{s'}(Q)\, \chi_s(Q) \int dr\, \psi_{s'}(r,Q) \left(\frac{\partial^2}{\partial Q_j^2} \psi_s(r,Q) \right)$$

$$- \sum \frac{\hbar^2}{2m_j} \int dQ\, \chi_{s'}(Q) \left(\frac{\partial}{\partial Q_j} \chi_s(Q) \right) \int dr\, \psi_{s'}(r,Q)\, \left(\frac{\partial}{\partial Q_j} \psi_s(r,Q) \right)$$

The first term is generally small. If we evaluate the second at an equilibrium configuration $Q^{(0)}$ of the state s and neglect the dependence on Q [47]we have

$$V_{s,s'}^{nad} \approx -V_{s,s'}^{nad,el} \sum \frac{\hbar^2}{2m_j} \int dQ\, \chi_{s'}(Q) \left(\frac{\partial}{\partial Q_j} \chi_s(Q) \right)$$

$$V_{s,s'}^{nad,el} = \int dr\, \psi_{s'}(r, Q^{(0)})\, \left(\frac{\partial}{\partial Q_j} \psi_s(r, Q^{(0)}) \right)$$

Within the harmonic approximation the gradient operator can be expressed as

$$\frac{\partial}{\partial Q_r} = \sqrt{\frac{M_r \omega_r}{2\hbar}} (b_r^+ - b_r)$$

and the nonadiabatic matrix element becomes

$$V_{s',n(r'),s,n(r)}^{nad} = -V_{s,s'}^{nad,el} \sum \frac{\hbar^2}{2M_r} \sqrt{\frac{M_r \omega_r}{2\hbar}} \int dQ \left(\prod_{r'} \chi_{s'r'n(r')} \right) \times$$

$$\times \left(\prod_{r'' \neq r} \chi_{s,r'',n(r'')} \right) \left(\sqrt{n(r)+1}\chi_{s,r,n(r)+1} + \sqrt{n(r)}\chi_{s,r,n(r)-1} \right)$$

This expression simplifies considerably if the mixing of normal modes in the state s' can be neglected (the socalled parallel mode approximation). Then the overlap integral factorizes into a product of Franck-Condon factors

$$V_{s',n(r'),s,n'(r)}^{nad} = -V_{s,s'}^{nad,el} \sum \frac{\hbar^2}{2M_r} \sqrt{\frac{M_r \omega_r}{2\hbar}} \times$$

$$\times \left(\prod_{r' \neq r} FC_{r'}^{s's}(n', n) \right) \left(\sqrt{n_r+1} FC_r^{s's}(n'_r, n_r+1) + \sqrt{n_r} FC_r^{s's}(n'_r n_r - 1) \right)$$

with

$$FC_r^{s's}(n'_r n_r) = \int dQ\, \chi_{s'r,n'(r)}(Q)\, \chi_{s,r,n(r)}(Q)$$

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[46] Without a magnetic field the molecular wavefunctions can be chosen real valued.

[47] this is known as the Condon approximation

19 crossing of two electronic states

19.1 adiabatic and diabatic states

We consider the avoided crossing of two electronic states along a nuclear coordinate Q . The two states are described by adiabatic wavefunctions

$$\psi_{1,2}^{ad}(r,Q)$$

and the wavefunction

$$\psi_1^{ad}(r,Q)\chi_1(Q)+\psi_2^{ad}(r,Q)\chi_2(Q)$$

will be also written in matrix notation as

$$\left(\begin{array}{cc} \psi_1^{ad}(r,Q) & \psi_2^{ad}(r,Q) \end{array}\right)\left(\begin{array}{c} \chi_1(Q) \\ \chi_2(Q) \end{array}\right)$$

From the adiabatic energies

$$\int dr\, \psi_s^{ad}(T_{el}+V)\psi_{s'}^{ad}=\delta_{s,s'}E_s^{ad}(Q)$$

and the nonadibatic interaction matrix elements

$$-\frac{\hbar^2}{2m}\int dr\, \psi_s^{ad}(r,Q)\left(\frac{\partial}{\partial Q}\right)\psi_{s'}^{ad}(r,Q)\frac{\partial}{\partial Q}$$

$$=-\frac{\hbar^2}{2m}V_{s,s'}^{nad}(Q)\frac{\partial}{\partial Q}$$

we construct the Hamiltonian for the nuclear wavefunction

$$H(Q)=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial Q^2}+E^{ad}(Q)-\frac{\hbar^2}{2m}V^{nad}(Q)\frac{\partial}{\partial Q}$$

with the matrices

$$E^{ad}(Q)=\left[\begin{array}{cc} E_1^{ad}(Q) & \\ & E_2^{ad}(Q) \end{array}\right] \qquad V^{nad}(Q)=\left[\begin{array}{cc} V_{11}^{nad}(Q) & V_{12}^{nad}(Q) \\ V_{21}^{nad}(Q) & V_{22}^{nad}(Q) \end{array}\right]$$

and the nuclear part of the wavefunction is determined by the Eigenvalue equation

$$H(Q)\left(\begin{array}{c} \chi_1(Q) \\ \chi_2(Q) \end{array}\right)=E\left(\begin{array}{c} \chi_1(Q) \\ \chi_2(Q) \end{array}\right)$$

We want to define a new basis of so called diabatic electronic states for which the nonadiabatic interaction vanishes. Therefore we introduce a transformation with a unitary matrix

$$C=\left(\begin{array}{cc} c_{11} & c_{12} \\ c_{21} & c_{22} \end{array}\right)$$

and form the linear combinations

$$\psi^{dia}=\left(\begin{array}{cc} \psi_1^{dia}(r,Q) & \psi_2^{dia}(r,Q) \end{array}\right)=\left(\begin{array}{cc} \psi_1^{ad}(r,Q) & \psi_2^{ad}(r,Q) \end{array}\right)C=\psi^{ad}C$$

The nonadibatic interaction in the new basis is

$$\int dr\, \psi^{dia\,\dagger}(r,Q)\frac{\partial}{\partial Q}\psi^{dia}(Q) =$$

$$= \int dr\, C^\dagger \psi^{ad\,\dagger}\left(\frac{\partial \psi^{ad}}{\partial Q}C + \psi^{ad}\frac{\partial C}{\partial Q}\right)$$

$$C^\dagger V^{nad}(Q)C + C^\dagger \frac{\partial C}{\partial Q}$$

which vanishes if we chose C to be a solution of

$$\frac{\partial C}{\partial Q} = -V^{nad}(Q)C$$

which can be formally solved by

$$C = \exp\left\{\int_Q^\infty V^{nad}(Q)dQ\right\}$$

Now generally we have

$$V^{nad}_{ss'}(Q) = \int dr\, \psi^{ad}_s(r,Q)\frac{\partial}{\partial Q}\psi^{ad}_{s'}$$

$$= \frac{\partial}{\partial Q}\int dr\, \psi^{ad}_s(r,Q)\psi^{ad}_{s'}(r,Q) - \int dr\, \left(\frac{\partial}{\partial Q}\psi^{ad}_s\right)\psi^{ad}_{s'}$$

$$= 0 \quad - V^{nad}_{s's}(Q)$$

and therefore the matrix V^{nad} is antisymmetric

$$V^{nad} = \begin{pmatrix} 0 & V^{nad}_{12} \\ -V^{nad}_{12} & 0 \end{pmatrix}$$

end the exponential function can be easily evaluated to give

$$C = \begin{pmatrix} \cos\zeta(Q) & \sin\zeta(Q) \\ -\sin\zeta(Q) & \cos\zeta(Q) \end{pmatrix} \qquad \zeta(Q) = \int_Q^\infty V^{nad}_{12}(Q)dQ$$

The matrix elements of the electronic hamiltonian are

$$\int dr\, \psi^{dia\,\dagger}(T_{el}+V)\psi^{dia} = \int dr\, C^\dagger \psi^{ad\,\dagger}(T_{el}+V)\psi^{ad}C$$

$$\widetilde{H} = C^\dagger E^{ad}(Q)C$$

$$= \begin{pmatrix} \cos^2\zeta E^{ad}_1 + \sin^2\zeta E^{ad}_2 & \sin\zeta\cos\zeta(E^{ad}_1 - E^{ad}_2) \\ \sin\zeta\cos\zeta(E^{ad}_1 - E^{ad}_2) & \cos^2\zeta E^{ad}_2 + \sin^2\zeta E^{ad}_1 \end{pmatrix}$$

At the crossing point

$$(\cos^2\zeta_0 - \sin^2\zeta_0)(E^{ad}_1 - E^{ad}_2) = 0$$

which implies

$$\cos^2\zeta_0 = \sin^2\zeta_0 = \frac{1}{2}$$

Expanding the sine and cosine functions around the crossing point we have

$$\widetilde{H} \approx \begin{pmatrix} \frac{E_1+E_2}{2} + (E_2-E_1)(\zeta-\zeta_0)+\cdots & (E_1-E_2)(\frac{1}{2}+(\zeta-\zeta_0)^2+\cdots) \\ (E_1-E_2)(\frac{1}{2}+(\zeta-\zeta_0)^2+\cdots) & \frac{E_1+E_2}{2} - (E_2-E_1)(\zeta-\zeta_0)+\cdots \end{pmatrix}$$

and expanding also the matrix elements

$$E_1^{ad}(Q) = \bar{E} + \frac{\Delta}{2} + v_1(Q-Q_0)+\cdots$$

$$E_2^{ad} = \overline{E} - \frac{\Delta}{2} + v_2(Q-Q_0)+\cdots$$

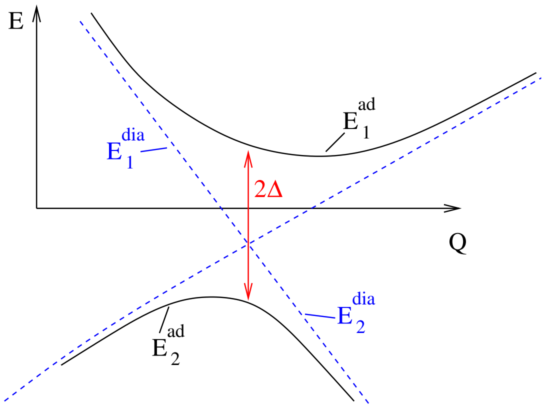
$$\zeta-\zeta_0 = -V_{12}^{nad}(Q-Q_0)$$

where $\Delta$is the splitting of the adiabatic energies at the crossing point, the interaction matrix then becomes

$$H = \overline{E} + \frac{v_1+v_2}{2}Q + \begin{pmatrix} -V_{12}^{nad}(Q_0)\Delta(Q-Q_0) & \frac{\Delta}{2} \\ \frac{\Delta}{2} & V_{12}^{nad}(Q_0)\Delta(Q-Q_0) \end{pmatrix} + \cdots$$

We see that in the diabatic basis the interaction is given by half the splitting of the adiabatic energies at the crossing.

Figure 92: curve crossing



19.2 Semiclassical treatment

Landau and Zener investigated the curve crossing process treating the nuclear motion classically by introducing a trajectory

$$Q(t) = Q_0 + vt$$

where they assumed a constant velocity in the vicinity of the crossing point. They investigated the time dependent model Hamiltonian

$$H(t) = \begin{pmatrix} E_1(Q(t)) & W \\ W & E_2(Q(t)) \end{pmatrix} = \begin{pmatrix} -\frac{1}{2}\frac{\partial \Delta E}{\partial t}t & W \\ W & \frac{1}{2}\frac{\partial \Delta E}{\partial t}t \end{pmatrix}$$

and solved the time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = H(t) \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

which reads explicitely

$$i\hbar \frac{\partial c_1}{\partial t} = E_1(t)c_1 + Wc_2$$

$$i\hbar \frac{\partial c_2}{\partial t} = E_2(t) + Wc_1$$

Substituting

$$c_1 = a_1 e^{\frac{1}{i\hbar}\int E_1(t)dt}$$

$$c_2 = a_2 e^{\frac{1}{i\hbar}\int E_2(t)dt}$$

the equations simplify

$$i\hbar \frac{\partial a_1}{\partial t} = We^{\frac{1}{i\hbar}\int (E_2(t)-E_1(t)dt} a_2$$

$$i\hbar \frac{\partial a_2}{\partial t} = We^{-\frac{1}{i\hbar}\int (E_2(t)-E_1(t)dt} a_1$$

Let us consider the limit of small W and calculate the transition probability in lowest order. From the initial condition $a_1(-\infty) = 1$, $a_2(-\infty) = 0$ we get

$$\int_0^t (E_2(t') - E_1(t'))dt' = \frac{\partial \Delta E}{\partial t}\frac{t^2}{2}$$

$$a_2(\infty) \approx \frac{1}{i\hbar} W \int_{-\infty}^{\infty} e^{-\frac{1}{i\hbar}\frac{\partial \Delta E}{\partial t}\frac{t^2}{2}} dt = \frac{W}{i\hbar}\sqrt{\frac{2\pi\hbar}{-i\frac{\partial \Delta E}{\partial t}}}$$

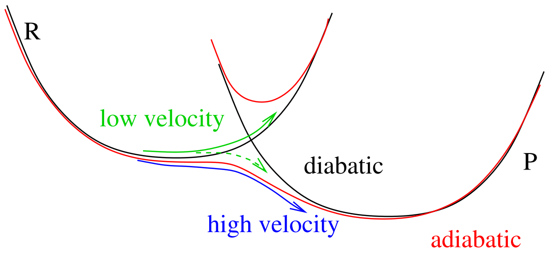
and the transition probability is

$$P_{12} = |a_2(\infty)|^2 = \frac{2\pi W^2}{\hbar |\frac{\partial \Delta E}{\partial t}|}$$

Landau and Zener calculated the transition probability for arbitrary coupling strength

$$P_{12}^{LZ} = 1 - \exp\left(-\frac{2\pi W^2}{\hbar |\frac{\partial \Delta E}{\partial t}|} \right)$$

Figure 93: velocity dependence of the transition rate



19.3 application to diabatic ET

If we describe the diabatic potentials as displaced harmonic oscillators

$$E_1(Q) = \frac{m\omega^2}{2}Q^2 \qquad E_2(Q) = \Delta G + \frac{m\omega^2}{2}(Q-Q_1)^2$$

the energy gap is with

$$Q_1 = \sqrt{\frac{2\lambda}{m\omega^2}}$$

$$E_2 - E_1 = \Delta G + \frac{m\omega^2}{2}(Q_1^2 - 2Q_1Q) = \Delta G + \lambda - \omega\sqrt{2m\lambda}Q$$

the time derivative of the energy gap is

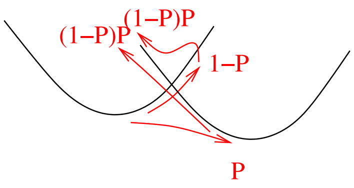
$$\frac{\partial(E_2(Q) - E_1(Q))}{\partial t} = -\omega\sqrt{2m\lambda}\frac{\partial Q}{\partial t}$$

and the average velocity is

$$< \frac{\partial Q}{\partial t} >= \frac{\int_{-\infty}^{\infty}|v|e^{-mv^2/2kT}}{\int_{-\infty}^{\infty}e^{-mv^2/2kT}} = \sqrt{\frac{2kT}{m\pi}}$$

The probability of curve crossing during one period of the oscillation is given by $2P_{12}$ (see figure).

Figure 94: multiple crossing



Together this gives a transmission coefficient

$$\kappa_{el} = 2\frac{2\pi W^2}{\hbar|\omega\sqrt{2\lambda}\sqrt{\frac{2kT}{\pi}}|} = \frac{2\pi W^2}{\hbar}\frac{2\pi}{\omega}\frac{1}{\sqrt{4\pi\lambda kT}}$$

and a rate of

$$k = \frac{2\pi W^2}{\hbar} \frac{1}{\sqrt{4\pi\lambda kT}} e^{-\Delta G_a/kT}$$

19.4 crossing in more dimensions

The definition of a diabatic basis is not so straightforward in more dimensions. The reason is essentially that the gradient $\frac{\partial}{\partial Q_i}C$ has a longitudinal as well as a transversal component (in three dimensions these are the components with $div = 0$ and $rot = 0$. Therefore only part of the nonadiabatic coupling can be eliminated. Often a crude diabatic is used which refers to a fixed configuration near the crossing point and does not depend on the nuclear coordinates at all. In a diabatic representation the Hamiltonian of a two-state system has the general form

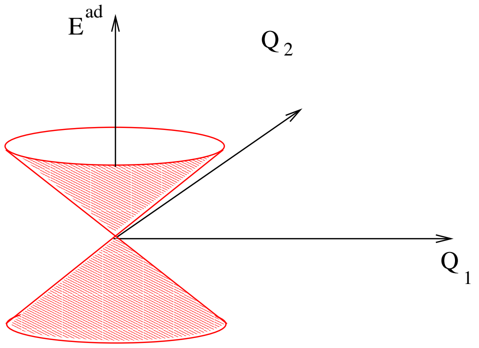
$$H = \begin{pmatrix} H_{11}(Q_i) & H_{12}(Q_i) \\ H_{12}(Q_i)^\dagger & H_{22}(Q_i) \end{pmatrix}$$

A crossing of the corresponding adiabatic curves (the Eigenvalues of H) is very unlikely in one dimension since it occurrs only if simultaneously the two conditions

$$H_{11}(Q) - H_{22}(Q) = H_{12}(Q) = 0$$

are fullfilled.[48] In two dimensions this is generally the case in a single point which leads to a so called conical intersection. This type of curve crossing is very important for ultrafast transitions. In more than two dimensions crossings appear at higher dimensional surfaces. The terminology of conical intersections is also used here.

Figure 95: conical intersection



20 Dynamics of an excited state

We want to describe the dynamics of an excited state $|s>$ which is prepared e.g. by electronic excitation due to absorption of radiation. This state is an Eigenstate of the diabatic Hamiltonian with energy E_s^0. Close in energy to $|s>$ there

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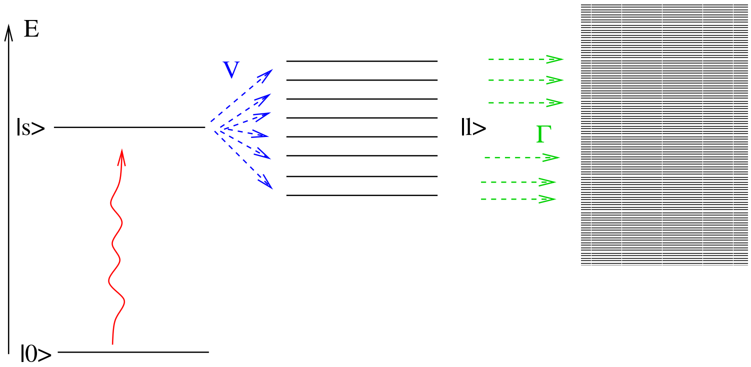
[48] if the two states are of different symmetry then $H_{12} = 0$ and a crossing is possible in one dimension.

is a manifold of other states $\{|l>\}$ which are not populated during the short time excitation since from the ground state only the transition $|0> \rightarrow |s>$ is optically allowed. The states l are weakly coupled to a continuum of bath states[49] and therefore have a finite lifetime. The bath states will not be considered explicitly. Instead we use a non hermitian Hamiltonian for the subspace spanned by $|s>$ and $\{|l>\}$. We assume that the Hamiltonian is already diagonal[50] with respect to the manifold $\{|l>\}$ which has complex energies [51]

$$E_l^0 = \epsilon_l - i\frac{\Gamma_l}{2}$$

This describes the exponential decay $\sim e^{-\Gamma_l t}$ of the l-states into the continuum states.

Figure 96: Dynamics of an excited state



The model Hamiltonian thus has the form

$$H = H^0 + V = \begin{pmatrix} E_s^0 & V_{s1} & \cdots & V_{sL} \\ V_{1s} & E_1^0 & & \\ \vdots & & \ddots & \\ V_{Ls} & & & E_L \end{pmatrix}$$

20.1 Green's formalism

The corresponding Greens operator or resolvent [52] is defined as

$$G(E) = (E - H)^{-1} = \sum_n |n> \frac{1}{E - E_n} < n|$$

For a hermitian Hamiltonian the poles of the Greens operator are on the real axis and the time evolution operator (the so called propagator) is defined by

$$\widetilde{G}(t) = G_+(t) - G_-(t)$$

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[49] for instance the field of electromagnetic radiation

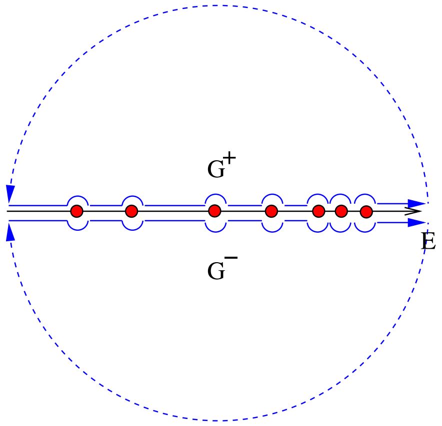
[50] for non Hermitian oerators we have to distinguish left- and right Eigenvectors

[51] This is also known as the damping approximation

[52] see for instance E.N.Economou , Green's functions in quantum physics, Springer

$$G_\pm(t) = \frac{1}{2\pi i}\int_{-\infty\pm i\epsilon}^{\infty\pm i\epsilon} e^{-\frac{iE}{\hbar}t}G(E)$$

Figure 97: integration contour



For times $t<0$ $(t>0)$the integration path can be closed in the upper (lower) half of the complex plane and therefore

$$G_+(t) = 0 \quad \text{for} \quad \text{t<0}$$

$$G_-(t) = 0 \quad \text{for} \quad \text{t>0}$$

and we can express

$$G_+(t) = \theta(t)\widetilde{G}(t)$$

We use the relation

$$\lim_{\epsilon\to 0}\frac{1}{E+i\epsilon-E_n} = P\frac{1}{E-E_n} + i\pi\delta(E-E_n)$$

to find

$$\widetilde{G}(t) = \frac{1}{2\pi i}\sum|n> P\int_{-\infty}^{\infty} dE\frac{e^{-\frac{iE}{\hbar}t}}{E-E_n} < n| + \sum|n>\int_{-\infty}^{\infty}\delta(E-E_n)e^{-\frac{iE}{\hbar}t}dE < n|$$

$$= \sum|n> e^{-\frac{iE}{\hbar}t} < n| = \exp\left(\frac{t}{i\hbar}H\right)$$

Hence G_+ is the time evolution operator for $t>0$. For times $t<0$ there are additional interactions which prepare the initial state

$$\psi(t=0) = |s>$$

For a non hermitian Hamiltonian the integration contour can be chosen as the real axis for $G_+(t)$ which now becomes the Fourier transform of the resolvent.

Dividing the Hamiltonian in the diagonal part H^0 and the interaction V we have

$$(G^0)^{-1} = E - H^0$$
$$G^{-1} = E - H = (G^0)^{-1} - V$$

Multiplication from left with G^0 and from right with G gives the socalled Dyson equation

$$G = G^0 + G^0 V G$$

We iterate that once more

$$G = G^0 + G^0 V(G^0 + G^0 V G) = G^0 + G^0 V G^0 + G^0 V G^0 V G$$

and project on the state $|s>$

$$< s|G|s >=< s|G^0|s > + < s|G^0 V G^0|s > + < s|G^0 V G^0 V G|s >$$

Now G^0 is diagonal and V is non diagonal. Therefore

$$< s|G^0 V G^0|s >=< s|G^0|s >< s|V|s >< s|G^0|s >= 0$$

and

$$< s|G^0 V G^0 V G|s >=< s|G^0|s >< s|V|l >< l|G^0|l >< l|V|s >< s|G|s >$$

$$G_{ss} = G^0_{ss} + \sum_l G^0_{ss} V_{sl} G^0_{ll} V_{ls} G_{ss}$$

$$G_{ss} = \frac{G^0_{ss}}{1 - G^0_{ss} \sum_l V_{sl} G^0_{ll} V_{ls}} = \frac{1}{E - E^0_s - R_s}$$

with the level shift operator

$$R_s = \sum_l \frac{|V_{sl}|^2}{E - \epsilon_l + i\frac{\Gamma_l}{2}}$$

The poles of the Green's function G_{ss} are given by the implicit equation

$$E_p = E^0_s + \sum_l \frac{|V_{sl}|^2}{E_p - E^0_l}$$

Generally the Green's function is meromorphic and can be represented as

$$G_{ss}(E) = \sum_p \frac{A_p}{E - E_p}$$

where the residuals are defined by

$$A_p = \lim_{E \to E_p} G_{ss}(E)(E - E_p)$$

The probability to find the system still in the state $|s>$ at time $t > 0$ is

$$P_s(t) = | < s|\widetilde{G}(t)|s > |^2 = |\widetilde{G}_{ss}(t)|^2$$

where the propagator is the Fourier transform of the Green's function

$$\widetilde{G}_{+ss}(t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} e^{\frac{E}{i\hbar}t} G_{ss}(E) dE = \theta(t) \sum_p A_p e^{\frac{E_p}{i\hbar}t}$$

20.2 Bixon Jorner model

We want now to study a simplified model which can be solved analytically. The energy of $|s>$ is set to zero. The manifold $\{|l>\}$ consists of infinitely equally spaced states with equal width

$$E_l^0 = \alpha + l\Delta\epsilon - i\frac{\Gamma}{2}$$

and the interaction $V_{sl} = V$ is taken independent on l. With this simplifications the poles are solutions of

$$E_p = \sum_{l=-\infty}^{l=\infty} \frac{V^2}{E_p - \alpha - l\Delta\epsilon + i\frac{\Gamma}{2}}$$

which can be written using the identity [53]

$$\cot(z) = \sum_{l=-\infty}^{\infty} \frac{1}{z - l\pi}$$

as

$$E_p = \frac{V^2\pi}{\Delta\epsilon} \cot\left(\frac{\pi}{\Delta\epsilon}\left(E_p - \alpha + i\frac{\Gamma}{2}\right)\right)$$

For the following discussion it is convenient to measure all energy quantities in units of $\pi/\Delta\epsilon$ and define

$$\widetilde{\alpha} = \alpha\pi/\Delta\epsilon \quad \widetilde{\Gamma} = \Gamma\alpha\pi/\Delta\epsilon$$

$$\widetilde{E}_p = E_p\alpha\pi/\Delta\epsilon \quad \widetilde{V} = V\alpha\pi/\Delta\epsilon$$

to have

$$\widetilde{E}_p = \widetilde{E}_p^r - \frac{i\widetilde{\Gamma}_p}{2} = \widetilde{V}^2 \cot\left\{\widetilde{E}_p - \widetilde{\alpha} + i\frac{\widetilde{\Gamma}}{2}\right\}$$

which can be split into real and imaginary part

$$\frac{\widetilde{E}_p^r}{\widetilde{V}^2} = \frac{\sin(2(\widetilde{E}_p^r - \widetilde{\alpha}))}{\cosh(\widetilde{\Gamma_p} - \widetilde{\Gamma}) - \cos(2(\widetilde{E}_p^r - \widetilde{\alpha}))}$$

$$-\frac{\widetilde{\Gamma}_p}{2\widetilde{V}^2} = \frac{\sinh(\widetilde{\Gamma}_p - \widetilde{\Gamma})}{\cosh(\widetilde{\Gamma_p} - \widetilde{\Gamma}) - \cos(2(\widetilde{E}_p^r - \widetilde{\alpha}))}$$

We have to distinguish now two limiting cases.

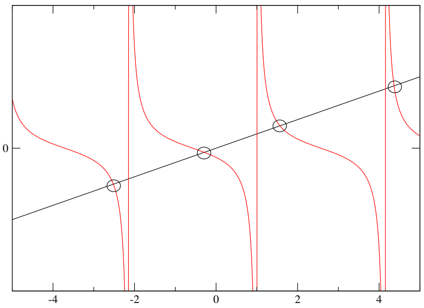
---

[53] The cotangens has single poles at $z = l\pi$ with residues $\lim_{z\to l\pi}\cot(z)(z - l\pi) = 1$

The small molecule limit

For small molecules the density of state $1/\Delta\epsilon$ is small. If we keep the lifetime of the l-states fixed then $\widetilde{\Gamma}$ is small in this limit. The poles are close to the real axis. [54]

Figure 98: small molecule limit



graphical solution of $x = cot(x-1)$

We approximate the real part by solving the real equation

$$\widetilde{E}_P^{(0)} = \widetilde{V}^2 \cot\left(\widetilde{E}_P^{(0)} - \widetilde{\alpha}\right)$$

and consider first the solution which is closest to zero. Expanding around $\widetilde{E}_P^{(0)}$ we find

$$\widetilde{E}_P^{(0)} + \xi = \widetilde{V}^2 \cot\left(\widetilde{E}_P^{(0)} + \xi - \widetilde{\alpha} + \frac{i\widetilde{\Gamma}}{2}\right)$$

$$= \widetilde{V}^2 \cot\left(\widetilde{E}_P^{(0)} - \widetilde{\alpha}\right) - \widetilde{V}^2(1 + \cot\left(\widetilde{E}_P^{(0)} - \widetilde{\alpha}\right)^2)(\xi + \frac{i\Gamma}{2})$$

which simplifies to

$$\xi = -\widetilde{V}^2(1 + \cot\left(\widetilde{E}_P^{(0)} - \widetilde{\alpha}\right)^2)(\xi + \frac{i\Gamma}{2})$$

and has the solution

$$\xi = -\frac{i}{2}\widetilde{\Gamma}_p = -\frac{i}{2}\widetilde{\Gamma}\frac{\widetilde{V}^2(1 + \frac{\widetilde{E}_P^{(0)2}}{\widetilde{V}^4})}{1 + \widetilde{V}^2(1 + \frac{\widetilde{E}_P^{(0)2}}{\widetilde{V}^4})}$$

which in the case $\widetilde{V}$ small but $\widetilde{V} > \widetilde{E}_P^{(0)}$ gives

$$\widetilde{\Gamma}_p \approx \widetilde{V}^2\widetilde{\Gamma}$$

$$\Gamma_p \approx \pi^2 \frac{\widetilde{V}^2}{\Delta\epsilon^2}\Gamma$$

---

[54] we assume that $\alpha \neq 0$

The other poles are approximately undisturbed

$$\widetilde{E}_p^r = \widetilde{\alpha} + l\pi$$

$$\widetilde{\Gamma_p} = \widetilde{\Gamma}\frac{\widetilde{V}^2 + \frac{\widetilde{E}_p^{r2}}{\widetilde{V}^2}}{1 + \widetilde{V}^2 + \frac{\widetilde{E}_p^{r2}}{\widetilde{V}^2}} \to \widetilde{\Gamma}$$

and the residuum of the Green's function follows from

$$\frac{1}{(\widetilde{E}_p + dE) - \widetilde{V}^2 \cot(\widetilde{E}_p + dE - \widetilde{\alpha} + \frac{i\widetilde{\Gamma}}{2})}$$

$$= \frac{1}{(\widetilde{E}_p + dE) - \widetilde{V}^2 \cot(\widetilde{E}_p - \widetilde{\alpha} + \frac{i\widetilde{\Gamma}}{2}) + \widetilde{V}^2 dE(1 + \cot(\widetilde{E}_p - \widetilde{\alpha} + \frac{i\widetilde{\Gamma}}{2})^2) + \cdots}$$

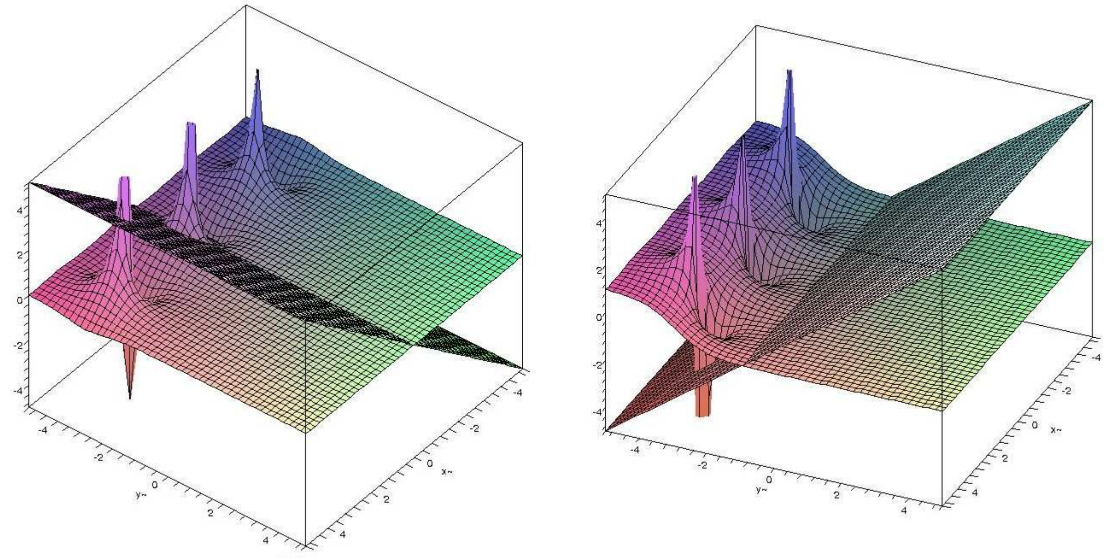
$$\frac{1}{dE(1 + \widetilde{V}^2(1 + \cot(\widetilde{E}_p - \widetilde{\alpha} + \frac{i\widetilde{\Gamma}}{2})^2)} = \frac{1}{dE}\frac{1}{\widetilde{V}^2 + \widetilde{E}_p}$$

which shows that only the contributions from poles close to zero are important.

The statistical limit

Consider now the limit $\widetilde{\Gamma}_p > 1$ and $\widetilde{V} > 1$. This condition is usually fullfilled in biomolecules.

Figure 99: complex cotangens



Real and imaginary part of $\cot(z + 3i)$ are shown

If the poles are far away enough from the real axis, then on the real axis the cotangens is very close to -1 and

$$R_s = \frac{V^2\pi}{\Delta\epsilon}\cot\left(\frac{\pi}{\Delta\epsilon}\left(E_p - \alpha + i\frac{\Gamma}{2}\right)\right) \approx -i\frac{V^2\pi}{\Delta\epsilon}$$

and thus

$$G_{ss}(E) = \frac{1}{E + i\frac{V^2\pi}{\Delta\epsilon}}$$

and the initail state decays as

$$P(t) = |e^{\frac{-iV^2\pi}{i\hbar\Delta\epsilon}t}|^2 = e^{-kt}$$

with the rate

$$k = \frac{2\pi V^2}{\hbar\Delta\epsilon} = \frac{2\pi V^2}{\hbar}\rho$$

20.3 A more general ladder model

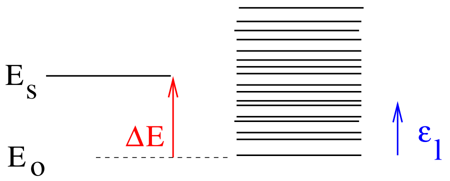
We consider now a more general model where the spacing of the states is not constant and the matrix elements are different. The Hamiltonian now has the form

$$H = \begin{pmatrix} E_s & V_{s1} & \cdots & V_{sL} \\ V_{1s} & E_1 & & \\ \vdots & & \ddots & \\ V_{Ls} & & & E_L \end{pmatrix}$$

We take the energies relative to the lowest l-state

$$E_s = E_0 + \Delta E \quad E_l = E_0 + \epsilon_l$$

Figure 100: more general ladder model



We start from the Golden rule expression

$$k = \sum_l \frac{2\pi V_{sl}^2}{\hbar}\delta(E_s - E_l) = \sum_l \frac{2\pi V_{sl}^2}{\hbar}\delta(\Delta E - \epsilon_l)$$

where the density of final states is given by

$$\rho(E_s) = \sum_l \delta(E_s - E_l) = \sum_l \delta(\Delta E - \epsilon_l)$$

We represent the delta function by a Fourier integral

we should check the sign in the exponent

$$\delta(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t} dt$$

$$\omega = \frac{E}{\hbar} \rightarrow \delta(E) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{\frac{E}{i\hbar}t} dt$$

$$k = \sum_l \frac{V_{sl}^2}{\hbar^2}\int_{-\infty}^{\infty} e^{\frac{\Delta E - \epsilon_l}{i\hbar}t} dt$$

Interchanging integration and summation we find

$$k = \int_{-\infty}^{\infty} dt \sum_l \frac{V_{sl}^2}{\hbar^2} e^{\frac{\Delta E - \epsilon_l}{i\hbar}t}$$

We introduce

$$z = \sum_l \frac{V_{sl}^2}{\hbar^2} e^{\frac{i\epsilon_l}{\hbar}t}$$

and write the rate as

$$k = \int_{\infty}^{\infty} dt\, e^{-\frac{i}{\hbar}\Delta E\, t + \ln(z)}$$

This integral will now be evaluated approximately with the saddle point method[55].

20.3.1 The saddle point method

The saddle point method is an asymptotic method to calculate integrals of the type

$$\int_{-\infty}^{\infty} e^{n\phi(x)} dx$$

for large n. If the function $\phi(x)$ has a maximum at x_0 then the integrand also has a maximum there which becomes very sharp for large n. Then the integral can be approximated by expanding the exponent around x_0

$$n\phi(x) = n\phi(x_0) + \frac{1}{2}\frac{d^2(n\phi(x))}{dx^2}_{|x_0}(x - x_0)^2 + \cdots$$

as a Gaussian integral

$$\int_{-\infty}^{\infty} e^{n\phi(x)} dx \approx n\phi(x_0)\sqrt{\frac{2\pi}{n|\phi''(x_0)|}}$$

The method can be extended to integrals in the complex plane

$$\int_C e^{n\phi(z)} dz = \int_C e^{n\Re(\phi(z))} e^{in\Im(\phi(z))} dz$$

If the integration contour is deformed such that the imaginary part is constant, then the Laplace method is applicable and gives

$$\int_C e^{n\phi(z)} dz = e^{in\Im(\phi(z_0))}\int_{C'} e^{n\Re(\phi(z))} dz$$

---

[55] also known as method of steepest descent or Laplace method

The contour C' and the expansion point are determined from

$$\phi'(z_0) = 0$$

$$\phi(z) = u(z) + iv(z) = u(z) + iv(z_0)$$

Now consider the imaginary part as a function in $\mathbb{R}^2$. The gradient is

$$\bigtriangledown v(x,y) = (\frac{\partial v}{\partial x}, \frac{\partial v}{\partial y})$$

now for an analytic function $\phi(x+iy)$ we have

$$u(x+dx+iy+idy)+iv(x+dx+iy+idy)-(u(x+iy)+iv(x+iy)) = \frac{\partial(u+iv)}{\partial x}dx+\frac{\partial(u+iv)}{\partial y}dy$$

which can be written as

$$\frac{d\phi}{dz}dz = \frac{d\phi}{dz}(dx+idy)$$

only if

$$i\frac{\partial(u+iv)}{\partial x} = \frac{\partial(u+iv)}{\partial y}$$

or

$$\frac{\partial u}{\partial x} = \frac{\partial v}{\partial y} \quad \frac{\partial v}{\partial x} = -\frac{\partial u}{\partial y}$$

Hence the gradient of the imaginary part

$$\bigtriangledown v(x,y) = (-\frac{\partial u}{\partial y}, \frac{\partial u}{\partial x})$$

which is perpendicular on the gradient of the real part

$$\bigtriangledown u(x,y) = (\frac{\partial u}{\partial x}, \frac{\partial u}{\partial y})$$

which gives the direction of steepest descent.

The method is known as saddle point method since a maximum of the real part always is a saddle point which can be seen from the expansion

$$\phi(z) = \phi(z_0) + \frac{1}{2}\phi''(z_0)(z-z_0)^2 + \cdots$$

now

$$dz^2 = dx^2 - dy^2 + 2idx\,dy$$

and for the real part we find

$$\Re(\phi(z)) = \Re(\phi(z_0)) - \frac{1}{2}\left(\Re(\phi''(z_0))(dx^2-dy^2) - 2\Im(\phi''(z_0))dx\,dy\right)$$

$$= \Re(\phi(z_0)) - \frac{1}{2}(dx,dy)\begin{pmatrix} \Re(\phi'') & -\Im(\phi'') \\ -\Im(\phi'') & -\Re(\phi'') \end{pmatrix}\begin{pmatrix} dx \\ dy \end{pmatrix}$$

The Eigenvalues of the matrix are

$$\pm\sqrt{\Re(\phi'')^2 + \Im(\phi'')^2} = \pm|\phi''|$$

20.3.2 Application to the ladder model

The saddle point equation for the ladder model becomes

$$-\frac{i}{\hbar}\Delta E + \frac{d\ln z}{dt} = 0$$

and calculating the derivative

$$\frac{d\ln z}{dt} = \frac{1}{z}\sum_l \frac{V_{sl}^2}{\hbar^2}\frac{i\epsilon_l}{\hbar}e^{\frac{i\epsilon_l}{\hbar}t}$$

we find

$$\Delta E = \frac{1}{z}\sum_l \frac{V_{sl}^2}{\hbar^2}\epsilon_l e^{\frac{i\epsilon_l}{\hbar}t}$$

Since ΔE is real, we look for a saddle point on the imaginary axis and write

$$\frac{it_s}{\hbar} = -\beta$$

where the new variable β is real. The saddle point equation now has a quasi-thermodynamic meaning

$$\Delta E = \frac{1}{z}\sum_l \frac{V_{sl}^2}{\hbar^2}\epsilon_l e^{-\beta\epsilon_l} =< \epsilon_l >$$

where β plays the role of $1/kT$ and $g_l = V_{sl}^2/\hbar^2$ that of a degeneracy factor. The second derivative relates to the width of the energy distribution

$$\frac{d^2\ln z}{dt^2} = \frac{d}{dt}\left(\frac{\frac{d\ln z}{dt}}{z}\right) = \frac{\frac{d^2\ln z}{dt^2}}{z} - \left(\frac{d\ln z}{dt}\right)^2 = \frac{1}{z}\sum_l g_l\frac{-\epsilon_l^2}{\hbar^2}e^{-\beta\epsilon_l} - \frac{1}{z^2}\left(\sum_l g_l\frac{i\epsilon_l}{\hbar}e^{-\beta\epsilon}\right)^2$$

$$= -<\frac{\epsilon^2}{\hbar^2}> + <\frac{\epsilon}{\hbar}>^2$$

We approximate now the integral by the contribution around the saddle point.

$$k = \int_{\infty}^{\infty} dt\, e^{-\frac{i}{\hbar}\Delta E\, t+\ln(z)} = z(t_s)e^{\beta\Delta E}\sqrt{\frac{2\pi\hbar^2}{<\epsilon^2> - <\epsilon>^2}}$$

$$= \sum_l \frac{V_{sl}^2}{\hbar}e^{-\beta(\epsilon_l-\Delta E)}\sqrt{\frac{2\pi}{<\epsilon^2> - <\epsilon>^2}}$$

For comparison let us consider the simplified model with $V_{sl} = V$,$\epsilon_l = l\Delta\epsilon$. Then

$$z = \frac{V^2}{\hbar^2}\sum_{l=0}^{\infty} e^{-\beta l\Delta\epsilon} = \frac{V^2}{\hbar^2}\frac{1}{1-e^{-\beta\Delta\epsilon}}$$

The saddle point equation is

$$\Delta E = -\frac{\partial}{\partial\beta}\ln z = \frac{\Delta\epsilon}{e^{\beta\Delta\epsilon}-1}$$

which determines the 'temperature'

$$\beta = \frac{1}{\Delta\epsilon}\ln(1+\frac{\Delta\epsilon}{\Delta E}) \approx \frac{1}{\Delta E}$$

if $\Delta\epsilon \ll \Delta E$. Then

$$< \epsilon_l > = \frac{\Delta\epsilon}{e^{\Delta\epsilon/\Delta E}-1} \approx \Delta E$$

$$< \epsilon_l^2 > - < \epsilon >^2 = \frac{\partial^2}{\partial\beta^2}\ln z = \frac{\Delta\epsilon^2 e^{\Delta\epsilon/\Delta E}}{\left(e^{\Delta\epsilon/\Delta E}-1\right)^2} \approx \Delta E^2$$

$$z(t_s) = \frac{V^2}{\hbar^2}\frac{1}{1-e^{-\Delta\epsilon/\Delta E}} \approx \frac{V^2}{\hbar^2}\frac{\Delta E}{\Delta\epsilon}$$

and the rate becomes

$$k = \frac{V^2}{\hbar^2}\frac{\Delta E}{\Delta\epsilon}e^1\sqrt{\frac{2\pi\hbar^2}{\Delta E^2}} = \frac{2\pi V^2}{\hbar\Delta\epsilon}e^1\sqrt{\frac{1}{2\pi}}$$

where the numerical value of $e/\sqrt{2\pi} = 1.08$

20.4 The displaced oscillator model

We want now to discuss a more specific model for the transition between the vibrational manifolds of two electronic states. We assume that the Born Oppenheimer separation of nuclear and electronic motion is applicable. Furthermore we use the Condon and the parallel mode approximations to write the rate expression as a product of an electronic matrix element and Franck-Condon factors of the independent normal modes[56]

$$V_{if}^2 = V^2\prod_r FC_r(n_r^i, n_r^f)$$

$$\epsilon_i = \sum_r n_r^i\hbar\omega_r \quad \epsilon_l = \sum_r n_r^f\hbar\omega_r$$

Figure 101: displaced oscillator model

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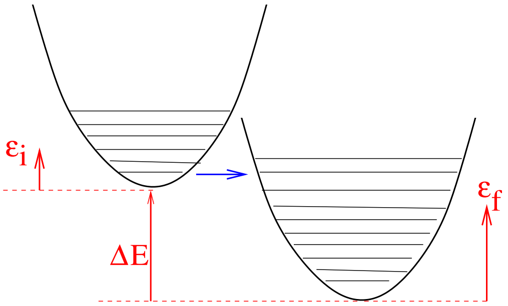

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[56] The zero point energies are included in ΔE

The rate expression follows from averaging over the possible initial states and summing over the possible final states

$$k = \frac{2\pi V^2}{\hbar} \sum_{n_r^i, n_r^f} P(\{n_r^i\} \prod_r FC_r(n_r^i, n_r^f) \delta(\Delta E + (n_r^i - n_r^f)\hbar\omega_r)$$

In the following we assume a canonical distribution of initial states

$$P(\{n_r^i\}) = \prod_r \frac{e^{-n_r^i \hbar\omega_r/kT}}{Z_r}$$

The Franck Condon factors are the overlaps of oscillator functions

$$FC_r(n_r^i, n_r^f) = | < n_r^i | n_r^f > |^2 =< n_r^i | n_r^f >< n_r^f | n_r^i >$$

Let us first consider the zero temperature limit.
Replacing again the delta function by a Fourier integral we have

$$k = \frac{V^2}{\hbar^2} \int_{-\infty}^{\infty} dt\, e^{\frac{-it}{\hbar}\Delta E} \sum_{n_r^f} < 0_r^i | n_r^f > e^{itn_r^f\omega_r} < n_r^f | 0_r^i >$$

$$= \frac{V^2}{\hbar^2} \int_{-\infty}^{\infty} dt\, e^{\frac{-it}{\hbar}\Delta E} < 0_r^i | e^{\frac{it}{\hbar}H_f} | 0_r^i >= \frac{V^2}{\hbar^2} \int_{-\infty}^{\infty} dt\, e^{\frac{-it}{\hbar}\Delta E} F(t)$$

where H_f is the Hamiltonian of the nuclear vibrations in the final state.

20.4.1 The time correlation function F(t)

In the approximation of independent displaced oscillators we have

maybe we replace λ_r by g_r ?

$$H_i = \sum_r \hbar\omega_r b_r^\dagger b_r \quad H_f = \sum_r \hbar\omega_r (b_r^\dagger - \lambda_r)(b_r - \lambda_r)$$

Consider the following unitary transformation

$$A = e^{\lambda(b^\dagger - b)} b^\dagger b e^{-\lambda(b^\dagger - b)}$$

and make a series expansion

$$A = A(0) + \lambda \frac{dA}{d\lambda} + \cdots$$

where the derivatives are

$$\frac{dA}{d\lambda}|_{\lambda=0} = [b^\dagger - b, b^\dagger b] = b^\dagger [b^\dagger, b] + [-b, b^\dagger] b$$

$$= -(b + b^+)$$

$$\frac{d^2 A}{d\lambda^2}|_{\lambda=0} = [b^\dagger - b, [b^\dagger - b, b^\dagger b]]$$

$$= -[b^\dagger - b, b^\dagger + b] = 2$$

$$\frac{d^n A}{d\lambda^n}|_{\lambda=0} = 0 \quad \text{for } n \geq 3$$

and finally

$$A = b^\dagger b - \lambda(b^\dagger + b) + \lambda^2 = (b^\dagger - \lambda)(b - \lambda)$$

Hence

$$H_f = e^{\sum \lambda_r (b_r^\dagger - b_r)} H_i e^{-\sum \lambda_r (b_r^\dagger - b_r)} = \sum e^{\lambda_r (b_r^\dagger - b_r)} \hbar\omega_r b_r^\dagger b_r e^{-\lambda_r (b_r^\dagger - b_r)}$$

and

$$F(t) = \prod_r F_r(t)$$

with

$$F_r(t) =< 0|e^{\lambda_r (b_r^\dagger - b_r)} \exp\left\{ \frac{it}{\hbar} \hbar\omega_r b_r^\dagger b_r \right\} e^{-\lambda_r (b_r^\dagger - b_r)}|0 >$$

Now consider

$$A = e^{\beta b^\dagger b} b e^{-\beta b^\dagger b} \quad \beta = -i\omega t$$

Making again a series expansion

$$\frac{dA}{d\beta} = [b^+ b, b] = -b$$

$$\frac{d^2 A}{d\beta^2} = [b^+ b, -b] = b \quad \text{etc.}$$

$$A = b(1 - \beta + \frac{\beta^2}{2} - \cdots) = b(1 + it\omega + \frac{(it\omega)^2}{2} + \cdots) = b\, e^{i\omega t}$$

and taking the hermitian conjugate we have also

$$e^{-i\omega t b^\dagger b} b^+ e^{i\omega t b^\dagger b} = b^\dagger e^{-i\omega t}$$

and therefore

$$F_r(t) =< 0| \exp\left\{ \frac{it}{\hbar} \hbar\omega_r b_r^\dagger b_r \right\} \exp\left\{ \lambda_r (b_r^+ e^{-i\omega t} - b_r e^{i\omega t}) \right\} e^{-\lambda_r (b_r^\dagger - b_r)}|0 >$$

$$=< 0| \exp\left\{ \lambda_r (b_r^+ e^{-i\omega t} - b_r e^{i\omega t}) \right\} e^{-\lambda_r (b_r^\dagger - b_r)}|0 >$$

since the first exponential gives one.

As the commutator $|b, b^+] = 1$ is a constant we can write the exponentials as products according to the rule

$$e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]}$$

$$\exp\left\{ \lambda_r (b_r^+ e^{-i\omega t} - b_r e^{i\omega t}) \right\} = \exp\left\{ \lambda_r b_r^+ e^{-i\omega t} \right\} \exp\left\{ -\lambda_r b_r e^{i\omega t} \right\} e^{-\lambda^2/2}$$

$$e^{-\lambda_r (b_r^\dagger - b_r)} = e^{-\lambda_r b_r^\dagger} e^{\lambda_r b_r} e^{-\lambda^2/2}$$

and we find

$$F_r(t) = e^{-\lambda^2} < 0|e^{-\lambda_r b_r e^{i\omega t}} e^{-\lambda_r b_r^+}|0 >$$

and from

$$e^A e^B = e^B e^A e^{-[B,A]}$$

$$F_r(t) = e^{-\lambda^2} < 0|e^{-\lambda_r b_r^+} e^{-\lambda_r b_r e^{i\omega t}} e^{\lambda^2 e^{i\omega t}}|0 >$$

$$F_r(t) = e^{-\lambda^2} e^{\lambda^2 e^{i\omega t}} = e^{g_r(t)}$$

with

$$g_r(t) = \lambda^2(e^{i\omega t} - 1)$$

Expansion of $F_r(t)$ gives

$$e^{\lambda^2(e^{i\omega t}-1)} = \sum_j \frac{\lambda^{2j}}{j!} e^{-\lambda^2} e^{ji\omega t}$$

which corresponds to a progression of overtones $ni\omega$ with Franck-Condon factors

$$FC(0, j) = \frac{\lambda^{2j}}{j!} e^{-\lambda^2}$$

At finite temperatures the correlation function generalizes to

$$F_r(t) = \sum P(n^i) < n^i|e^{\frac{t}{i\hbar}\hbar\omega(n^i - n^f)}|n^f >< n^f|n^i >$$

which can be written as

$$F_r(t) = \frac{1}{Z_r} Tr(e^{-\beta H_i} e^{\frac{-it}{\hbar} H_i} e^{\frac{it}{\hbar} H_f})$$

which after some more operator algebra can be evaluated as[57]

$$F_r(t) = \exp\left\{\lambda^2 \left[(\overline{n} + 1)(e^{i\omega t} - 1) + \overline{n}(e^{-i\omega t} - 1)\right]\right\}$$

with the average phonon number

$$\overline{n} = \frac{1}{e^{\beta\hbar\omega} - 1}$$

Finally considering a large number of displaced oscillators the rate expression becomes

$$k = \frac{V^2}{\hbar^2} \int_{-\infty}^{\infty} dt\, e^{\frac{-it}{\hbar}\Delta E} \exp\left\{\sum_r \lambda_r^2 \left[(\overline{n}_r + 1)(e^{i\omega_r t} - 1) + \overline{n}_r(e^{-i\omega_r t} - 1)\right]\right\}$$

For discussion let us first apply

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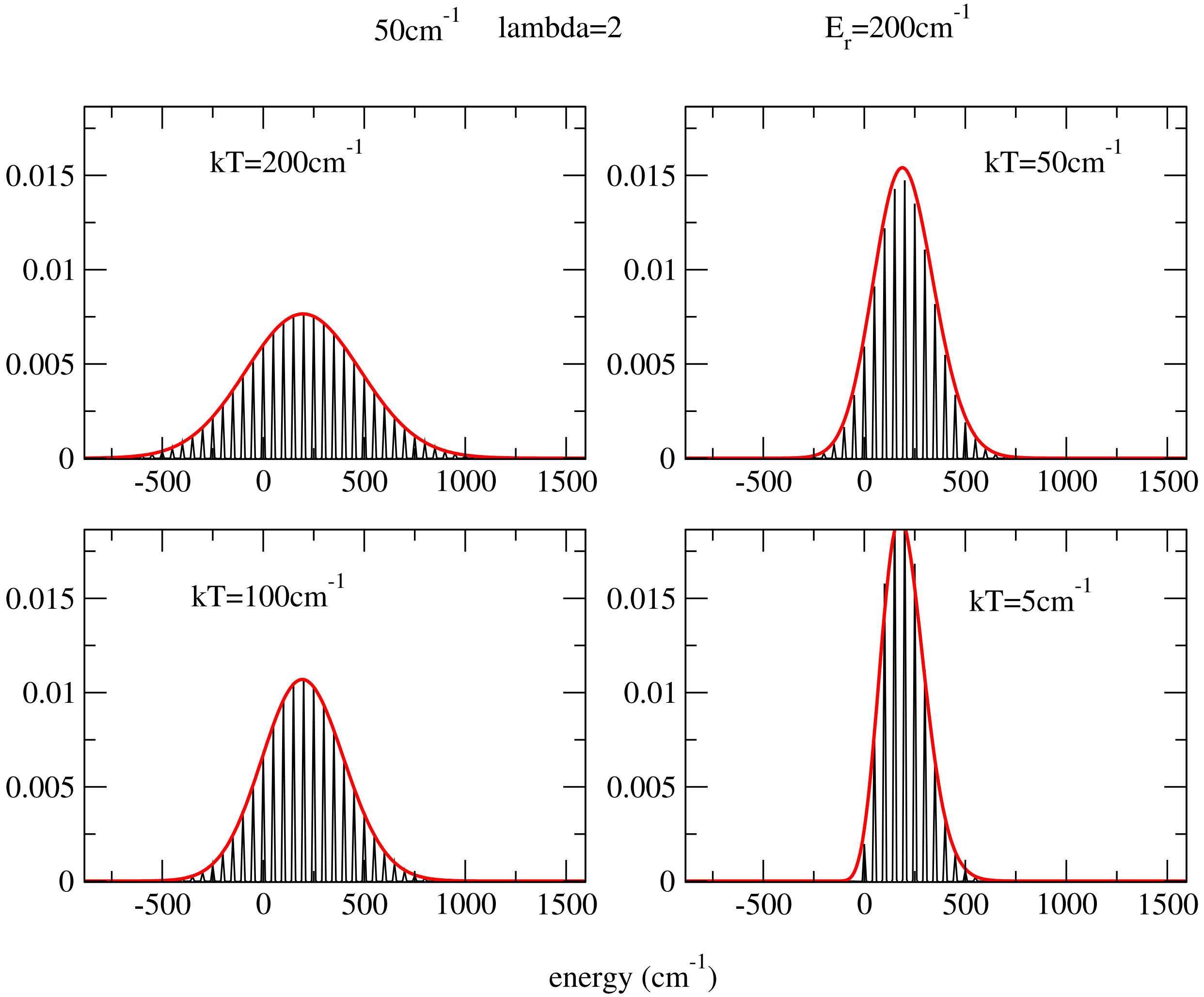
[57] In the literature sometimes a different sign convention for the Fourier transform of the delta function is used which leads to a sign change of the frequency here.


50cm-1 lambda=2
Er=200cm-1
kT=200cm-1
kT=50cm-1
kT=100cm-1
kT=5cm-1
0.015
0.01
0.005
0
-500
0
500
1000
1500
energy (cm-1)

20.4.2 the short time approximation

expanding the oscillating functions

$$e^{i\omega_r t} = 1 + i\omega_r t - \frac{\omega_r^2 t^2}{2}$$

we have the approximation

$$k = \frac{V^2}{\hbar^2}\int_{-\infty}^{\infty} dt\, e^{\frac{-it}{\hbar}\Delta E} \exp\left\{\sum_r \lambda_r^2 i\omega_r t - \sum_r \lambda_r^2(2\bar{n}_r+1)\frac{\omega_r^2 t^2}{2}\right\}$$

$$= \frac{V^2}{\hbar^2}\sqrt{\frac{2\pi}{\sum_r \lambda_r^2\omega_r^2(2\bar{n}_r+1)}} \exp\left\{-\frac{(\frac{\Delta E}{\hbar} - \sum_r \lambda_r^2\omega_r)^2}{2\left(\sum_r \lambda_r^2\omega_r^2(2\bar{n}_r+1)\right)}\right\}$$

and with the definition of reorganization energy

$$E_r = \sum_r \lambda_r^2 \hbar\omega_r =< \hbar\omega_r >$$

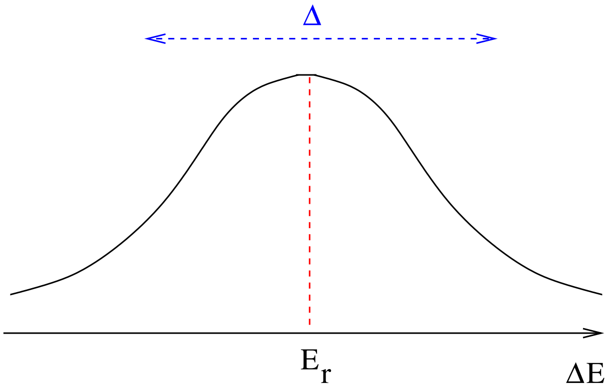
and width

$$\Delta^2 = \sum_r \lambda_r^2(\hbar\omega_r)^2(2\bar{n}_r+1) =< (\hbar\omega)^2 >$$

this takes the form

$$k = \frac{V^2}{\hbar^2}\sqrt{\frac{2\pi\hbar^2}{\Delta^2}} \exp\left\{-\frac{(\Delta E - E_r)^2}{2\Delta^2}\right\}$$

Figure 103: Gaussian envelope



If all modes can be treated clasically $\hbar\omega_r \ll kT$ the phonon number is $\bar{n}_r = kT/\hbar\omega_r$ and

$$\Delta^2 \approx 2kT\sum_r \lambda_r^2\hbar\omega_r = 2kTE_r$$

which gives the rate in the classical limit the Marcus expression

$$k = \frac{2\pi V^2}{\hbar}\sqrt{\frac{1}{4\pi kTE_r}} \exp\left\{-\frac{(\Delta E - E_r)^2}{4E_r kT}\right\}$$

20.4.3 Application of the saddle point method

We want now to apply the saddle point. The saddle point equation is

$$-\frac{i}{\hbar}\Delta E = \sum_r \lambda_r^2 \left[i\omega_r(\overline{n}_r+1)e^{i\omega_r t} - i\omega_r\overline{n}_r e^{-i\omega_r t}\right]$$

$$= i\sum_r \lambda_r^2\omega_r \left[(\overline{n}_r+1)e^{-i\omega_r t} - \overline{n}_r e^{i\omega_r t}\right]$$

which we solve approximately by linearization

$$-i\Delta E = i\hbar\sum_r \lambda_r^2\omega_r \left[1-(2\overline{n}_r+1)i\omega_r t+\cdots\right] =$$

$$= iE_r - \Delta^2\,\frac{t}{\hbar}+\cdots$$

$$t_s = -i\hbar\frac{\Delta E - E_r}{\Delta^2}$$

At the saddle point we have

$$-\frac{it_s}{\hbar}\Delta E + g(t_s) = -\frac{it_s}{\hbar}\Delta E + \sum_r \lambda_r^2\left[(\overline{n}_r+1)(i\omega_r t_s) - \overline{n}_r i\omega_r t_s+\cdots\right]$$

$$= -\frac{it_s}{\hbar}\Delta E + i\sum_r \lambda_r^2\omega_r t_s - \frac{\Delta^2}{\hbar^2}\frac{t_s^2}{2} = -\frac{it_s}{\hbar}(\Delta E - E_r) - \Delta^2\frac{-(E_r-\Delta E)^2}{2\Delta^4}$$

$$= -\frac{(\Delta E - E_r)^2}{2\Delta^2}$$

the second derivative is

$$-\sum_r \lambda_r^2\omega_r^2\left[(\overline{n}_r+1)e^{-i\omega_r t} + \overline{n}_r e^{i\omega_r t}\right] = -\frac{\Delta^2}{\hbar^2}+\cdots$$

and finally the rate is again

$$k = \frac{V^2}{\hbar^2}\sqrt{\frac{2\pi\hbar^2}{\Delta^2}}\exp\left\{-\frac{(\Delta E - E_r)^2}{2\Delta^2}\right\}$$

At low temperatures $kT \ll \hbar\omega$ the saddlepoint equation simplifies to

$$\Delta E = \sum_r \lambda_r^2\hbar\omega_r e^{i\omega_r t}$$

To solve this equation we introduce an average frequency (major accepting modes) $\widetilde{\omega}$ with

$$\sum_r \lambda_r^2\hbar\omega_r = \sum_r \lambda_r^2\hbar\widetilde{\omega} = S\hbar\widetilde{\omega}$$

$$\widetilde{\omega} = \frac{\sum_r \lambda_r^2\omega_r}{S} \qquad S = \sum_r \lambda_r^2$$

which after insertion into the saddle point equation gives the approximation

$$\Delta E = S\hbar\widetilde{\omega}e^{it_s\widetilde{\omega}}$$

with the solution

$$it_s = \frac{1}{\widetilde{\omega}} \ln \frac{\Delta E}{S\hbar\widetilde{\omega}}$$

The second erivative is

$$-\sum_r \lambda_r^2 \omega_r^2 e^{i\omega_r t_s} \approx -S\widetilde{\omega}^2 e^{\ln(\Delta E/S\hbar\widetilde{\omega})} = -\frac{1}{\hbar}\Delta E\widetilde{\omega}$$

and the rate is

$$k = \frac{V^2}{\hbar^2}\sqrt{\frac{2\pi\hbar}{\Delta E\widetilde{\omega}}} \exp\left\{-\frac{\Delta E}{\hbar}\frac{1}{\widetilde{\omega}} \ln \frac{\Delta E}{S\hbar\widetilde{\omega}} + S\frac{\Delta E}{S\hbar\widetilde{\omega}} - S\right\}$$

$$k = \frac{V^2}{\hbar}\sqrt{\frac{2\pi}{\Delta E\hbar\widetilde{\omega}}} \exp\left\{-S - \frac{\Delta E}{\hbar\widetilde{\omega}}\left[\ln \frac{\Delta E}{S\hbar\widetilde{\omega}} - 1\right]\right\}$$

which is known as the energy gap law