1.2   The Time–Dependent Schrödinger Equation

using the state vector notation we get

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = H|\Psi(t)\rangle$$

the initial value of the state vector is $|\Psi_0\rangle \equiv |\Psi(t_0)\rangle$;
if the Hamiltonian is time–independent a formal solution is given by

$$|\Psi(t)\rangle = e^{-iH(t-t_0)/\hbar}|\Psi_0\rangle$$

introduction of the time–evolution operator

$$U(t,t_0) \equiv U(t-t_0) = e^{-iH(t-t_0)/\hbar}$$

$U(t,t_0)$ is unitary and obeys the following equation of motion

$$i\hbar\frac{\partial}{\partial t}U(t,t_0) = HU(t,t_0)$$

with the initial condition $U(t_0,t_0) = 1$;
the time–evolution operator has the important property that it can be decomposed as

$$U(t,t_0) = U(t,t_{N-1})U(t_{N-1},t_{N-2})\ldots U(t_2,t_1)U(t_1,t_0)$$

where $t_1 \leq t_2 \ldots \leq t_{N-1}$ are arbitrary times in the interval $[t_0,t]$;
if the solution of the stationary Schrödinger equation

$$H|\lambda\rangle = E_\lambda|\lambda\rangle$$

with eigenstates $|\lambda\rangle$ and eigenvalues E_λ is known, on can solve the time–dependent Schrödinger equation via an expansion with respect to the states $|\lambda\rangle$

$$|\Psi(t)\rangle = \sum_\lambda c_\lambda(t)|\lambda\rangle \ .$$

$$c_\lambda(t) = \langle\lambda|e^{-iE_\lambda(t-t_0)/\hbar}|\Psi_0\rangle = e^{-iE_\lambda(t-t_0)/\hbar}c_\lambda(t_0) \ ,$$

$$|\Psi(t)\rangle = \sum_\lambda c_\lambda(t_0)e^{-iE_\lambda(t-t_0)/\hbar}|\lambda\rangle$$

the superposition state is known as a *wave packet*;
since the state vector $|\Psi(t)\rangle$ is given here as a superposition of (time–dependent) states $c_\lambda(t)|\lambda\rangle$, it is alternatively called *coherent* superposition state;
let us calculate the time–dependent expectation value of the operator $\hat{O}$:

$$O(t) = \langle\Psi(t)|\hat{O}|\Psi(t)\rangle = \sum_{\lambda,\kappa} c_\lambda^*(t_0)c_\kappa(t_0)\langle\lambda|\hat{O}|\kappa\rangle e^{i(E_\lambda - E_\kappa)(t-t_0)/\hbar}$$

the different time–dependent contributions are determined by *transition frequencies* $\omega_{\lambda\kappa} = (E_\lambda - E_\kappa)/\hbar$;

1.2.1 The Interaction Representation

we assume

$$H = H_0 + V$$

where V represents a small perturbation of the dynamics given by H_0;
a perturbation expansion with respect to V can be performed; the solution of the time–dependent Schrödinger equation reads

$$|\Psi(t)\rangle = U(t, t_0)|\Psi(t_0)\rangle$$

is conveniently written as

$$|\Psi(t)\rangle = U_0(t, t_0)|\Psi^{(\mathrm{I})}(t)\rangle$$

this representation makes use of the formal solution which is available for the unperturbed time–dependent Schrödinger equation for H_0, i.e.

$$U_0(t, t_0) = e^{-iH_0(t-t_0)/\hbar}$$

the new state vector $|\Psi^{(\mathrm{I})}(t)\rangle$ is called the state vector in the *interaction representation*; since $U(t_0, t_0) = 1$ we have

$$|\Psi^{(\mathrm{I})}(t_0)\rangle = |\Psi(t_0)\rangle$$

the equation of motion for the state vector in the interaction representation follows directly from the original time–dependent Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = U_0(t, t_0)\left(H_0|\Psi^{(\mathrm{I})}(t)\rangle + i\hbar\frac{\partial}{\partial t}|\Psi^{(\mathrm{I})}(t)\rangle\right) = H|\Psi(t)\rangle$$

after some rearrangement we get (note that $U^{-1} = U^+$)

$$i\hbar\frac{\partial}{\partial t}|\Psi^{(\mathrm{I})}(t)\rangle = U_0^+(t, t_0)VU_0(t, t_0)|\Psi^{(\mathrm{I})}(t)\rangle \equiv V^{(\mathrm{I})}(t)|\Psi^{(\mathrm{I})}(t)\rangle$$

the quantity $V^{(\mathrm{I})}(t)$ is the interaction representation of the perturbational part of the Hamiltonian;
the formal solution is obtained by introducing the so–called S–operator (the scattering matrix)

$$|\Psi^{(\mathrm{I})}(t)\rangle = S(t, t_0)|\Psi^{(\mathrm{I})}(t_0)\rangle \equiv S(t, t_0)|\Psi(t_0)\rangle$$

it follows

$$U(t, t_0) = U_0(t, t_0)S(t, t_0)$$

the S–operator can be determined by the iterative solution of the equation of motion; formal time–integration gives

$$|\Psi^{(\mathrm{I})}(t)\rangle = |\Psi^{(\mathrm{I})}(t_0)\rangle - \frac{i}{\hbar}\int_{t_0}^{t} d\tau\, V^{(\mathrm{I})}(\tau)|\Psi^{(\mathrm{I})}(\tau)\rangle$$

this equation is suited to develop a perturbation expansion with respect to $V^{(\mathrm{I})}$. If there is no interaction one gets

$$|\Psi^{(\mathrm{I},0)}(t)\rangle = |\Psi^{(\mathrm{I})}(t_0)\rangle$$

next we get the state vector in the interaction representation, which is the first–order correction to $|\Psi^{(\text{I},0)}(t)\rangle$ in the presence of a perturbation,

$$|\Psi^{(\text{I},1)}(t)\rangle = -\frac{i}{\hbar} \int_{t_0}^{t} d\tau_1 V^{(\text{I})}(\tau_1) |\Psi^{(\text{I},0)}(\tau_1)\rangle$$

upon further iteration of this procedure one obtains the nth–order correction as

$$|\Psi^{(\text{I},n)}(t)\rangle = -\frac{i}{\hbar} \int_{t_0}^{t} d\tau_n V^{(\text{I})}(\tau_n) |\Psi^{(\text{I},n-1)}(\tau_n)\rangle$$

the total formally exact state vector in the interaction representation is

$$|\Psi^{(\text{I})}(t)\rangle = \sum_{n=0}^{\infty} |\Psi^{(\text{I},n)}(t)\rangle$$

let us consider the total wave function containing the effect of the interaction up to the order n

$$|\Psi^{(\text{I},n)}(t)\rangle = \left(-\frac{i}{\hbar}\right)^{n} \int_{t_0}^{t} d\tau_n V^{(\text{I})}(\tau_n) \int_{t_0}^{\tau_n} d\tau_{n-1} V^{(\text{I})}(\tau_{n-1}) \times \ldots$$

$$\ldots \times \int_{t_0}^{\tau_2} d\tau_1 V^{(\text{I})}(\tau_1) |\Psi^{(\text{I})}(t_0)\rangle$$

$$= \left(-\frac{i}{\hbar}\right)^{n} \frac{1}{n!} \hat{T} \int_{t_0}^{t} d\tau_n \ldots d\tau_1 V^{(\text{I})}(\tau_n) \ldots V^{(\text{I})}(\tau_1) |\Psi^{(\text{I})}(t_0)\rangle$$

in the last part of this expression all integrals are carried out to the upper limit t; double counting is compensated for by the factor $1/n!$; in order to account for the fact that the time–dependent operators $V^{(\text{I})}$ do not commute for different time arguments the *time ordering operator* $\hat{T}$ has been introduced; it orders time–dependent operators from the right to the left with increasing time arguments, i.e., if $t_1 > t_2$, $\hat{T}[V^{(\text{I})}(t_2)V^{(\text{I})}(t_1)] = V^{(\text{I})}(t_1)V^{(\text{I})}(t_2)$;
this formal rearrangement enables us to write for the exact state vector in the interaction representation

$$|\Psi^{(\text{I})}(t)\rangle = \hat{T} \sum_{n=0}^{\infty} \frac{1}{n!} \prod_{k=1}^{n} \left(-\frac{i}{\hbar} \int_{t_0}^{t} d\tau_k V^{(\text{I})}(\tau_k)\right) |\Psi^{(\text{I})}(t_0)\rangle \,.$$

the summation on the right–hand side is formally identical to the expansion of the exponential function

$$S(t,t_0) = \hat{T} \, \exp\left\{-\frac{i}{\hbar} \int_{t_0}^{t} d\tau V^{(\text{I})}(\tau)\right\} \,.$$

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1.3 Golden Rule Rate Formula

the Golden Rule rate formula offers a simple way to determine the transition rate between different quantum states of some zeroth–order Hamiltonians in the presence of a small coupling;

basic assumption is that the transitions are irreversible (transition into a macroscopic number of final states);

mutual interferences among the final states and with the initial state preclude any recurrence of probability back into the initial state;

recurrences are additionally suppressed when the coupling between the initial and final states is sufficiently weak;

irreversible transition can also be found if a fast relaxation from the final state to further additional states is possible; the final state itself may be discrete, but there is a coupling to another continuum of states;

the rate of *internal conversion (IC)* between an excited electronic state ϕ_e and the electronic ground–state ϕ_g will be considered as an example;

electronic excitation energy is distributed among the different vibrational degrees of freedom; since the radiation field does not take part in this type transition, it is also called *radiationless transition*; often the internal conversion is slow compared to the time scale of vibrational relaxation within an electronic state and therefore it can be characterized by a transition rate; (for stronger nonadiabatic coupling one cannot assume complete vibrational equilibrium for every step of the transition; if vibrational relaxation can be completely neglected a description in terms of wave functions becomes possible)

the respective Hamiltonian in the electron vibrational state representation reads

$$H_{\mathrm{IC}} = \sum_{a=e,g} \sum_{\mu} E_{a\mu} |\Psi_{a\mu}\rangle\langle\Psi_{a\mu}| + \sum_{\mu,\nu} \Big(\Theta_{e\mu,g\nu} |\Psi_{e\mu}\rangle\langle\Psi_{g\nu}| + \mathrm{H.c.} \Big)$$

1.3.1 Transition from a Single State into a Continuum

we consider quantum transitions between the single state $|\Psi_{e\mu}\rangle$ into the continuum of states $|\Psi_{g\nu}\rangle$;

the related transfer of occupation probability can be characterized by looking at the population of state $|\Psi_{e\mu}\rangle$ (survival probability) which reads

$$P_{e\mu}(t) = |\langle\Psi_{e\mu}|U(t)|\Psi_{e\mu}\rangle|^2$$

to get this quantity let us derive equations of motion for general matrix elements of the time–evolution operator (*transition amplitude*)

$$A_{\alpha\beta}(t) = \theta(t)\langle\Psi_\alpha|U(t)|\Psi_\beta\rangle$$

the unit–step function $\theta(t)$ has been introduced to restrict non–zero values of $A_{\alpha\beta}(t)$ to times larger than zero;

the equations of motion for the transition amplitudes read

$$i\hbar\frac{\partial}{\partial t}A_{\alpha\beta} = i\hbar\delta(t)\delta_{\alpha,\beta} + \sum_{\gamma} \langle\Psi_\alpha|H_{\mathrm{IC}}|\Psi_\gamma\rangle A_{\gamma\beta}$$

in order to solve this equation we introduce the Fourier transform of the transition amplitudes

$$A_{\alpha\beta}(\omega) = \int dt \; e^{i\omega t} A_{\alpha\beta}(t)$$

we obtain for the transition amplitudes the following equations

$$\hbar\omega A_{\alpha\beta}(\omega) = i\hbar\delta_{\alpha,\beta} + \sum_{\gamma} \langle\Psi_\alpha|H_{\mathrm{IC}}|\Psi_\gamma\rangle A_{\gamma\beta}(\omega)$$

in particular for $\alpha = \beta = e\mu$ this gives

$$\hbar\omega A_{e\mu,e\mu}(\omega) = i\hbar + E_{e\mu} A_{e\mu,e\mu}(\omega) + \sum_\nu \Theta_{e\mu,g\nu} A_{g\nu,e\mu}(\omega)$$

the off–diagonal elements, $A_{g\nu,e\mu}(\omega)$, can be obtained from

$$\hbar\omega A_{g\nu,e\mu}(\omega) = E_{g\nu} A_{g\nu,e\mu}(\omega) + \Theta_{g\nu,e\mu} A_{e\mu,e\mu}(\omega)$$

note the restriction to the single vibrational state in the excited electronic state, i.e. we set

$$\sum_\kappa \Theta_{g\nu,e\kappa} A_{e\kappa,e\mu}(\omega) \approx \Theta_{g\nu,e\mu} A_{e\mu,e\mu}(\omega)$$

in a more general frame this approximation corresponds to the case of a weak non–adiabatic coupling (higher order contributions are neglected);
inserting the solution of this equation into the equation for $A_{e\mu,e\mu}$ yields a closed equation for this quantity which can be solved to give

$$A_{e\mu,e\mu}(\omega) = i\hbar \left(\hbar\omega - E_{e\mu} - \sum_\nu \frac{|\Theta_{e\mu,g\nu}|^2}{\hbar\omega - E_{g\nu} + i\varepsilon} + i\varepsilon \right)^{-1}$$

here, ε has to be understood as a small and positive number which we will let go to zero at the end of the calculation;
the contributions in the denominator of $A_{e\mu,e\mu}(\omega)$, which are proportional to the square of the coupling matrix, result in a complicated frequency dependence of $A_{e\mu,e\mu}(\omega)$; one effect is apparent: the coupling to the continuum shifts the energy $E_{e\mu}$ of the initial state to a new value; this shift, which is in general a complex quantity, is commonly called *self–energy*

$$\Sigma_{e\mu}(\omega) = \sum_\nu \frac{|\Theta_{e\mu,g\nu}|^2}{\hbar\omega - E_{g\nu} + i\varepsilon}$$

the separation into a real and imaginary part gives

$$\Sigma_{e\mu}(\omega) \equiv \hbar\Delta\Omega_{e\mu}(\omega) - i\hbar\Gamma_{e\mu}(\omega) = \sum_\nu \mathcal{P}\frac{|\Theta_{e\mu,g\nu}|^2}{\hbar\omega - E_{g\nu}} - i\pi \sum_\nu |\Theta_{e\mu,g\nu}|^2\delta(\hbar\omega - E_{g\nu})$$

if the coupling matrix does not strongly depend on the vibrational quantum number ν, the variation of the self–energy in the region where $\hbar\omega \approx E_{g\nu}$ can be expected to be rather weak; this means that the frequency dependence of $A_{e\mu,e\mu}(\omega)$ is dominated by the resonance at $\hbar\omega = E_{e\mu}$; since this will give the major contribution to the inverse Fourier transform we can approximately replace $\hbar\omega$ in $\Sigma_{e\mu}(\omega)$ by $E_{e\mu}$;
to carry out the inverse Fourier transformation we replace the quantity $\Sigma_{e\mu}(\omega)$ by the

frequency–independent value $\Sigma(E_{e\mu}/\hbar)$ and obtain the desired state population $P_{e\mu}(t)$ as

$$P_{e\mu}(t) = \left| \int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{i\hbar}{\hbar\omega - (E_{e\mu} + \hbar\Delta\Omega(E_{e\mu}/\hbar)) + i\hbar\Gamma(E_{e\mu}/\hbar)} \right|^2 = \theta(t)\, e^{-2\Gamma(E_{e\mu}/\hbar)t}$$

the integral has been calculated using the residue theorem of the theory of complex functions; we may close the ω–integral in the complex plane; to guarantee convergence via $\exp -i\omega t$ and at positive time–arguments this has to be done in the lower half–plane

$$\frac{1}{2\pi} \oint d\omega\, e^{-i\omega t} \frac{i\hbar}{\hbar\omega - (E_{e\mu} + \hbar\Delta\Omega(E_{e\mu}/\hbar)) + i\hbar\Gamma(E_{e\mu}/\hbar)}$$

$$= -\frac{1}{2\pi i}\theta(t)(-2\pi i)\exp\left(-i[E_{e\mu} + \hbar\Delta\Omega(E_{e\mu}/\hbar)) - i\hbar\Gamma(E_{e\mu}/\hbar)]t/\hbar\right)$$

the absolute square of the expression gives the result already quoted above;
as expected the occupation probability of the initially occupied state $|e\mu\rangle$ decreases in time due to transitions into the manifold of states $|g\nu\rangle$;
the rate of change of the survival probability is defined as

$$k_{e\mu} = 2\Gamma_{e\mu} = \frac{2\pi}{\hbar} \sum_\nu |\Theta_{e\mu,g\nu}|^2 \delta(E_{e\mu} - E_{g\nu})$$

this type of expression is known as the *Golden Rule* of quantum mechanics;
the delta function appearing in the rate expression can be interpreted as the energy conservation law for the transition; only those transitions from $|\Psi_{e\mu}\rangle$ to $|\Psi_{g\nu}\rangle$ are possible for which the energy of the initial state $E_{e\mu}$ matches some energy $E_{g\nu}$ of the final states;

1.3.2   Transition Rate for a Thermal Ensemble

we consider an *ensemble* of N_{mol} independent but identical molecules (with a weak intramolecular nonadiabatic coupling); in this case the initially prepared state $|\Psi_{e\mu}\rangle$ may be different for each member of the ensemble;
all molecules are counted by the additional index m; the population $P_{me\mu}(t)$ gives the probability the molecule m is in the particular electron–vibrational state; its time–dependence follows as

$$P_{me\mu}(t) = \theta(t)e^{-k_{e\mu}t}P_{me\mu}(0)$$

where $P_{me\mu}(0)$ defines the probability to have molecule m initially in the particular electron–vibrational state;
since different molecules are in different vibrational states it makes sense to introduce the quantity

$$P_{me}(t) = \sum_\mu P_{me\mu}(t)$$

it gives the probability to have molecule m in the electronic state independent on the actual vibrational state; it represents a *reduced probability*; often observables measured in the experiment are only determined by this quantity; in the following we will focus on its computation;

we assume that initially all molecules have been in the excited electronic state, then, we get

$$\sum_m P_{me}(0) = N_{\mathrm{mol}}$$

it is suitable, to introduce the probability $P_{e\mu}(t)$ to have the state $|\Psi_{e\mu}\rangle$ realized in the ensemble

$$P_{e\mu}(t) = \frac{1}{N_{\mathrm{mol}}} \sum_m P_{me\mu}(t)$$

if we assume that the ensemble stays initially in thermal equilibrium with some environment at temperature T we can write

$$P_{e\mu}(0) = f_{e\mu}$$

where we introduced the quantum statistical equilibrium distribution

$$f_{e\mu} = \frac{\exp(-E_{e\mu}/k_{\mathrm{B}}T)}{\sum_\nu \exp(-E_{e\nu}/k_{\mathrm{B}}T)}$$

to discuss this case where a finite coupling to the environment is present, two characteristic times will be introduced; first, we have the time scale $\tau_{\mathrm{S-R}}$ which characterizes the coupling of the different members of the ensemble to the thermal reservoir; second, the nonadiabatic coupling introduces a time scale given by $1/k_{e\mu}$;
now we can distinguish the cases $\tau_{\mathrm{S-R}} \gg 1/k_{e\mu}$ (slow thermalization compared to the transition), $\tau_{\mathrm{S-R}} \ll 1/k_{e\mu}$ (fast thermalization), and $\tau_{\mathrm{S-R}} \approx 1/k_{e\mu}$ (intermediate case);
Case $\tau_{\mathrm{S-R}} \gg 1/k_{e\mu}$:
we suppose that the interaction with an external field promotes the ensemble into the state manifold $\{|\Psi_{e\mu}\rangle\}$, where each state occurs $N_{e\mu}$ times in the ensemble; since the interaction with the environment is weak compared to the state coupling the population will evolve according to

$$P_e(t) = \sum_\mu \frac{N_{e\mu}}{N_{\mathrm{mol}}} \exp(-k_{e\mu}t)$$

as stated above (absence of thermalization on the time–scale of the transfer).
Case $\tau_{\mathrm{S-R}} \ll 1/k_{e\mu}$:
thermalization proceeds at every time–step of the transfer; to derive the appropriate equations typical for thermalization let us introduce the time–step $\Delta t \approx \tau_{\mathrm{S-R}}$; usually we will be interested in the time evolution of the system on time scales much longer than Δt such that we can consider Δt to be a continuous quantity on the time scale of observation (*coarse graining* of the time axis);
at the initial time the population of the manifold $\{|\Psi_{e\mu}\rangle\}$ is thermalized; starting at $t = 0$ we get for $t = \Delta t$

$$P_{e\mu}(\Delta t) \simeq (1 - k_{e\mu}\Delta t)P_{e\mu}(0) = (1 - k_{e\mu}\Delta t)f_{e\mu}$$

we note

$$1 = P_e(0) = \sum_\mu f_{e\mu}$$

and obtain for the total electronic state population

$$P_e(\Delta t) \approx 1 - \sum_\mu k_{e\mu}f_{e\mu}\Delta t = P_e(0) - \sum_\mu k_{e\mu}f_{e\mu}P_e(0)\Delta t$$

because we are using a course–grained time axis where the state population $P_{e\mu}(t)$ is thermalized within the time step Δt we can generalize this expression and obtain for each t

$$P_e(t + \Delta t) \approx P_e(t) - \sum_\mu k_{e\mu} f_{e\mu} P_e(t) \Delta t$$

since Δt has been assumed to be very small we can rewrite the expression for the total population as

$$\frac{P_e(t + \Delta t) - P_e(t)}{\Delta t} \approx \frac{\partial}{\partial t} P_e(t) = -k_{e\to g} P_e(t) \;,$$

where we introduced the rate for transitions from a thermalized state manifold

$$k_{e\to g} = \sum_\mu f_{e\mu} k_{e\mu} = \frac{2\pi}{\hbar} \sum_{\mu,\nu} f_{e\mu} |\Theta_{e\mu,g\nu}|^2 \, \delta(E_{e\mu} - E_{g\nu})$$

the strong coupling of the system of interest to a thermal reservoir leads to a thermalization which is fast compared to the transfer, i.e., every step of probability transfer from the manifold of initial states to the manifold of final states starts from a thermalized initial state population;

Case $\tau_{\mathrm{S-R}} \approx 1/k_a$:

in this case one can no longer make a separation of time scales and the reasoning used in the previous two cases breaks down; a more general description of the simultaneous influence of the interstate coupling and the coupling to the reservoir is necessary; this more general approach is offered by the *density matrix theory*;

1.3.3   Consideration of the Transition Rate

Principle of Detailed Balance

up to now our discussion has been concentrated on the transitions from the states $|\Psi_{e\mu}\rangle$ (the initial states) to the states $|\Psi_{g\nu}\rangle$ (the final states); of course, one can consider also the reverse process along the same line of arguments; we expect that the reverse rate $k_{g\to e}$ follows by interchanging $E_{e\mu}$ with $E_{g\nu}$ in the thermal distribution (transfer starts from the thermalized distribution at the state manifold $|\Psi_{g\nu}\rangle$)

$$k_{g\to e} = \frac{2\pi}{\hbar} \sum_{\nu,\mu} f_{g\nu} |\Theta_{g\nu,e\mu}|^2 \, \delta(E_{g\nu} - E_{e\mu})$$

we relate both rates to each other; noting the presence of the δ–function we may replace in $k_{g\to e}$ the distribution $f_{g\nu}$ by the new distribution

$$\tilde{f}_{e\mu} = \frac{\exp(-E_{e\mu}/k_\mathrm{B}T)}{\sum_\kappa \exp(-E_{g\kappa}/k_\mathrm{B}T)} = \frac{\sum_\lambda \exp(-E_{e\lambda}/k_\mathrm{B}T)}{\sum_\kappa \exp(-E_{g\kappa}/k_\mathrm{B}T)} \times f_{e\mu}$$

this already gives

$$k_{g\to e} = \frac{\sum_\lambda \exp(-E_{e\lambda}/k_\mathrm{B}T)}{\sum_\kappa \exp(-E_{g\kappa}/k_\mathrm{B}T)} k_{e\to g} = k_{e\to g} \exp\left(-[E_e - E_g]/k_\mathrm{B}T\right) \frac{\sum_\lambda \exp(-\Delta E_{e\lambda}/k_\mathrm{B}T)}{\sum_\kappa \exp(-\Delta E_{g\kappa}/k_\mathrm{B}T)}$$

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we introduced electronic reference energies E_a including the zero point energy of the molecular vibrations according to

$$E_{a\mu} = E_a + \Delta E_{a\mu}$$

we further assume

$$\sum_\lambda \exp(-\Delta E_{e\lambda}/k_\mathrm{B}T) = \sum_\kappa \exp(-\Delta E_{g\kappa}/k_\mathrm{B}T)$$

and arrive at the *detailed balance principle* ($\Delta E = E_e - E_g$)

$$k_{g\to e} = e^{-\Delta E/k_\mathrm{B}T} k_{e\to g}$$

in the case of IC, ΔE amounts values of 1 ... 3 eV; it is much larger than thermal energy (at room temperature) and thus $k_{g\to e} \approx 0$

Representation of the Rate by a Correlation Function

next we present an alternative notation which takes into account the structure of the molecular states; to stay simple we neglect the operator character of Θ_{ab} and consider it as a simple complex valued matrix element

$$\Theta_{e\mu,g\nu} = \langle \chi_{e\mu} | \hat\Theta_{eg} | \chi_{g\nu} \rangle = \langle \chi_{e\mu} | \left(\langle \phi_e | [T_\mathrm{nuc} | \phi_g \rangle] + \sum_n \frac{1}{M_n} \langle \phi_e | [\mathbf{P}_n | \phi_g \rangle] \mathbf{P}_n \right) | \chi_{g\nu} \rangle$$

$$\approx \Theta_{eg} \langle \chi_{e\mu} | \chi_{g\nu} \rangle$$

moreover, the δ–function is replaced by a time integral; altogether results in

$$k_{e\to g} = \frac{2\pi |\Theta_{eg}|^2}{\hbar} \sum_{\mu,\nu} f_{e\mu} |\langle \chi_{e\mu} | \chi_{g\nu} \rangle|^2 \int \frac{dt}{2\pi\hbar} e^{i(E_{e\mu} - E_{g\nu})t/\hbar}$$

$$= \frac{|\Theta_{eg}|^2}{\hbar^2} \int dt \sum_{\mu,\nu} f_{e\mu} \langle \chi_{e\mu} | e^{iE_{e\mu}t/\hbar} e^{-iE_{g\nu}t/\hbar} | \chi_{g\nu} \rangle \langle \chi_{g\nu} | \chi_{e\mu} \rangle$$

$$= \frac{|\Theta_{eg}|^2}{\hbar^2} \int dt \; \mathrm{tr}_\mathrm{vib} \{ \hat R_e e^{iH_e t/\hbar} e^{-iH_g t/\hbar} \}$$

we used the definition of the trace with respect to the vibrational states

$$\mathrm{tr}_\mathrm{vib}\{...\} = \sum_\mu \langle \chi_{e\mu} | ... | \chi_{e\mu} \rangle$$

and introduced the equilibrium statistical operator according to

$$\langle \chi_{e\mu} | f_{e\mu} = \langle \chi_{e\mu} | \hat R_e$$

consequently it has the structure

$$\hat R_e = \frac{\exp(-H_e/k_\mathrm{B}T)}{\mathrm{tr}_\mathrm{vib}\{\exp(-H_e/k_\mathrm{B}T)\}}$$

Estimate of the Rate

finally we present an estimate of the rate for the case that only a single vibrational coordinate defines the vibrational states (diatomic molecule, or only a single normal mode vibration of a polyatomic molecules changes strongly upon electronic transitions); according to the derivation of the rate formula this case of discrete final state energies requires the introduction of additional decay processes of the electronic ground–state vibrational states; it might be possible be introducing a finite life time τ of these states; the vibrational energies are written as

$$E_{a\mu} = E_a + \hbar\omega_{\mathrm{vib}}\mu$$

the energy E_a defines the electronic energy plus zero–point energy of the harmonic vibrations; the respective vibrational energy quantum $\hbar\omega_{\mathrm{vib}}$ is considered to be identical for both electronic states; moreover we take the approximation

$$\Theta_{e\mu,g\nu} \approx \Theta_{eg}\langle\chi_{e\mu}|\chi_{g\nu}\rangle$$

and consider the zero–temperature case; then, the rate takes the form

$$k_{e\to g} = \frac{2\pi|\Theta_{eg}|^2}{\hbar} \sum_{\nu=0}^{\infty} |\langle\chi_{e\mu}|\chi_{g\nu}\rangle|^2 \, \delta(E_e - E_g - \hbar\omega_{\mathrm{vib}}\nu)$$

the formula indicates that strict coincidence of initial and final state energy of the transition is necessary; the divergent behavior indicates that for the present case no meaningful rate can be defined;
we change to a δ–function which has been broadened by the inverse life time of vibrational states

$$\delta(E_e - E_g - \hbar\omega_{\mathrm{vib}}\nu) \to \frac{1/\pi\tau}{(E_e - E_g - \hbar\omega_{\mathrm{vib}}\nu)^2 + (1/\tau)^2} \tag{1.1}$$

if $E_e = E_g + \hbar\omega_{\mathrm{vib}}\nu$ this gives the rate as

$$k_{e\to g} \approx \frac{2\tau|\Theta_{eg}|^2}{\hbar}|\langle\chi_{e\mu}|\chi_{g\nu}\rangle|^2$$

it is mainly determined by the vibrational overlap expressions $\langle\chi_{e\mu}|\chi_{g\nu}\rangle$

1.3.4   Rate Equations for Internal Conversion

if we account for the back transfer we have to set

$$\frac{\partial}{\partial t}P_e(t) = -k_{e\to g}P_e(t) + k_{g\to e}P_g(t)$$

however, the single rate equation for $P_e(t)$ has to be completed by that for $P_g(t)$

$$\frac{\partial}{\partial t}P_g(t) = -k_{g\to e}P_g(t) + k_{e\to g}P_e(t)$$

we obtained the *Pauli Master Equations*;
it is easy to find the solution of the above given coupled rate equations; because conservation of probability $P_e(t) + P_g(t) = 1$ holds, the two equations can be transformed

to a single one for $P_e(t) - P_g(t)$; taking as the initial condition $P_e(0) = 1$ the solutions read (note $K = k_{e \to g} + k_{g \to e}$)

$$P_e(t) = \frac{1}{K}\left(k_{e \to g}e^{-Kt} + k_{g \to e}\right)$$

$$P_g(t) = \frac{k_{e \to g}}{K}\left(1 - e^{-Kt}\right) \ .$$

It is instructive to put both solutions ($a = g, e$) into the form

$$P_a(t) = P_a(\infty) + \left(P_a(0) - P_a(\infty)\right)e^{-Kt} \ .$$

with $P_e(\infty) = k_{g \to e}/K$ and $P_g(\infty) = k_{e \to g}/K$;
as it has to be expected the result indicates a complete depletion of the initial state if there is no back–transfer ($k_{g \to e} = 0$); otherwise both manifolds remain populated;

a generalization of the Pauli Master Equation to a larger set of different states is straightforward; to obtain a general solution of the related rate equations we denote the right–hand side as $-\sum_b K_{ab}P_b$ with the general rate–matrix $K_{ab} = \delta_{ab}\sum_{c \neq a} k_{a \to c}$ $-(1 - \delta_{ab})k_{b \to a}$; given the eigenvalues $\kappa(\eta)$ and (normalized) eigenvectors $e_a(\eta)$ of K_{ab}, the general solution for the population of state $|a\rangle$ reads as (η counts the rate–matrix eigenvalues)

$$P_a(t) = \sum_\eta c(\eta)e_a(\eta)\exp(-\kappa(\eta)t)$$

the additional factors $c(\eta)$ are determined from the initial conditions; the decay of the various populations is multi–exponential; since the smallest $\kappa(\eta)$ equals zero the respective term in $P_a(t)$ fixes $P_a(\infty)$; it is obvious that the given solution (except some special examples) can be only achieved by numerical computations;