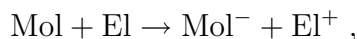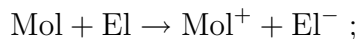## 2.4 Heterogeneous Electron Transfer

we will consider two types of transfer reactions: charge transfer from the metal surface into the molecule (formation of a molecular anion)

$$\mathrm{Mol} + \mathrm{El} \rightarrow \mathrm{Mol}^- + \mathrm{El}^+ \ ,$$

and charge transfer from the molecule into the metal electrode (formation of a molecular cation)

$$\mathrm{Mol} + \mathrm{El} \rightarrow \mathrm{Mol}^+ + \mathrm{El}^- \ ;$$

the latter process includes as a special case the electron transfer from a molecule into a semiconductor;
we considered single–electron transfer leading in the first case to the anionic state of the molecule and in the second case to a molecular cationic state;
since the metal electrons form a Fermi–sea with Fermi energy E_F the second reaction is possible if the extra electron is put above the Fermi energy E_F; ET from the metal into the molecule requires the jump of an electron out of the Fermi–sea;

the metal will be described by quasi–particle states with energy:

$$E_\mathbf{k} = \hbar \varepsilon_\mathbf{k} \ ;$$

these energies should be spin–degenerated; at $T = 0$ the quasi–particles form a Fermi–sea of completely occupied states

$$|\phi_\mathrm{F}\rangle = \prod_{|\mathbf{k}| \leq k_\mathrm{F}, s} a^+_{\mathbf{k},s} |0\rangle \ ;$$

in the bulk case electrons form Bloch–states which are occupied up to the Fermi–vector k_F defined by

$$E_\mathrm{F} = E_{|\mathbf{k}| = k_\mathrm{F}} \ ;$$

considering a metal surface, $\mathbf{k}$ covers bulk and surface states;
since the metal surface – the *electrode* – represents a macroscopic system a grand–canonical statistical description becomes necessary; at finite temperatures the electron distribution is given by the Fermi–distribution

$$f_\mathrm{F}(E_\mathbf{k} - \mu) = \frac{1}{e^{(E_\mathbf{k} - \mu)/k_\mathrm{B}T} + 1} \ ;$$

μ is the chemical potential of the metal;
it is useful to introduce a notation which directly accounts for the continuous electronic energy levels of the electrode; therefore the electrode density of states (DOS)

$$\mathcal{N}(\Omega) = \sum_\mathbf{k} \delta(\Omega - \varepsilon_\mathbf{k})$$

is introduced; the DOS gives the number of energy levels per frequency interval and we get

$$\int d\Omega \, \mathcal{N}(\Omega) = \sum_\mathbf{k} 1 = N_\mathrm{states} \ ;$$

we note for an arbitrary function $F_{\mathbf{k}} \equiv F(\varepsilon_{\mathbf{k}})$

$$\sum_{\mathbf{k}} F_{\mathbf{k}} = \int d\Omega\, \mathcal{N}(\Omega) F(\Omega) \ ;$$

when discussing the electronic states of the molecule we have to consider the neutral molecule as well as different charged states (presence of *excess* electrons) with

$$N = \pm 1, \pm 2, ...$$

excess electrons (holes); if $N = 0$ we consider the neutral molecule; the related total electronic energy is written as E_N; it refers to the electronic ground–state at the presence of N excess electrons;

let us consider the transfer of a single electron from the electrode into the molecule being so far in a neutral state; such an ET becomes possible if the following energy balance relation is fulfilled:

$$\sum_{|\mathbf{k}| \leq k_{\mathrm{F}}, s} E_{\mathbf{k}} + E_0 = \sum_{|\mathbf{k}| \leq k_{\mathrm{F}}, s} E_{\mathbf{k}} - E_{\mathbf{q}} + E_1 \ ;$$

here the quasi–wavevector has to fulfill $\mathbf{q} < k_{\mathrm{F}}$ since only occupied states contribute; if N_{el} is the number of electrons in the electrode and if $E_{\mathrm{el}}(N_{\mathrm{el}})$ is the respective energy we may write:

$$E_{\mathrm{el}}(N_{\mathrm{el}}) - E_{\mathrm{el}}(N_{\mathrm{el}} - 1) \geq E_1 - E_0 \ ;$$

in a grand–canonical description it reads

$$\frac{E_{\mathrm{el}}(N_{\mathrm{el}}) - E_{\mathrm{el}}(N_{\mathrm{el}} - 1)}{N_{\mathrm{el}} - (N_{\mathrm{el}} - 1)} \equiv \frac{\partial E_{\mathrm{el}}}{\partial N_{\mathrm{el}}} = \mu \geq E_1 - E_0 \ ;$$

the chemical potential μ of the electrode should be equal or larger than the change of the molecular energy upon charging with a single electron, i.e. if $\mu \geq E_1 - E_0$, there are electrons in the electrode which have energy identical to $E_1 - E_0$ and the molecule becomes singly charged; sometimes $E_1 - E_0$ is named *charging energy*;
if the molecule is in a $N - 1$–fold charged state N–fold charging is possible:

$$\mu \geq E_N - E_{N-1} \ ;$$

ET out of the neutral molecule becomes possible if

$$\mu \leq E_0 - E_{-1} \ ;$$

so far we assumed that E_N gives the total electronic energy of the molecule in the N–fold charged state but for the case that it is completely isolated from the metal surface; however, it is necessary to account for polarization effects of the Fermi–sea if the molecule is charged and for the back–reaction; hence for a realistic evaluation if ET is possible the E_N have to be re–interpreted as energies formed if the molecule is at the metal surface;

2.4.1   Electron Transfer from the Electrode into the Molecule

in the following we concentrate on the ET:

$$\mathrm{Mol} + \mathrm{El} \rightarrow \mathrm{Mol}^- + \mathrm{El}^+ \ ,$$
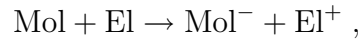
it becomes possible if

$$\mu \geq E_1 - E_0 \ ;$$

the description of ET will be done in an effective single electron picture (the charging energy is taken as a single electron energy);
in the initial state the electron to be transferred is in the electrode with energy $\hbar\varepsilon_{\mathbf{k}}$; in the final state it occupies the molecular level with energy $\hbar\varepsilon_1$ corresponding to the anionic (singly charged) state; the initial and final state have to be extended by the vibrational Hamiltonian H_0 and H_1, respectively; the neutral ground–state before charge transfer is φ_0 and that afterwards is φ_1;
accordingly the related Hamiltonian is separated into a molecular part, the electrode contribution, and a respective coupling

$$H = H_{\mathrm{mol}} + H_{\mathrm{el}} + H_{\mathrm{el-mol}} \ ;$$

for the Hamiltonian H_{mol} we get

$$H_{\mathrm{mol}} = (\hbar\varepsilon_1 + H_1)|\varphi_1\rangle\langle\varphi_1| \ ;$$

here,

$$H_1 = T_{\mathrm{vib}} + U_1$$

denotes the vibrational Hamiltonian which belongs to the state φ_1; for notational convenience we separate the energy

$$\hbar\varepsilon_1 \equiv U_1^{(0)} + \Delta E_1^{(\mathrm{zp})} \ ,$$

i.e. we split off the minimum of the complete potential energy surface $U_1^{(0)}$ together with the zero–point energy of the vibrations; therefore, the vibrational spectrum $\hbar\omega_{1M}$ starts at zero energy; the related vibrational wave functions read χ_{1M}; consequently we have

$$H_1|\chi_{1M}\rangle = \hbar\omega_{1M}|\chi_{1M}\rangle \ ;$$

the Hamiltonian which describes the vibrational dynamics of the neutral molecule (if the excess electron is absent) is written as H_0 and defines

$$H_0|\chi_{0M}\rangle = \hbar\omega_{0M}|\chi_{0M}\rangle \ ;$$

it will be combined with the band energies

$$E_{\mathbf{k}} \equiv \hbar\varepsilon_{\mathbf{k}} \ ;$$

consequently, the electrode Hamiltonian reads

$$H_{\mathrm{el}} = \sum_{\mathbf{k}} (\hbar\varepsilon_{\mathbf{k}} + H_0)|\varphi_{\mathbf{k}}\rangle\langle\varphi_{\mathbf{k}}| \ ;$$

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finally we give the coupling Hamiltonian between the molecule and the electrode

$$H_{\mathrm{el-mol}} = \sum_{\mathbf{k}} V_{\mathbf{k}} |\varphi_{\mathbf{k}}\rangle\langle\varphi_1| + \mathrm{H.c.} \; ;$$

when introducing the DOS $\mathcal{N}(\Omega)$ of the metal electrode it becomes possible to replace the electrode–molecule coupling matrix element by $V(\Omega)$;
the whole Hamiltonian represents a special realization of our general Hamiltonian for a DBA system;
note that the model introduced so far has neglected any Coulomb interaction between the anionic state of the molecule and the Fermi–sea of metal electrons; the correct description represents a complicated many–particle problem;
a simple approximate attempt is given by the mirror charge approach of macroscopic electrostatics; let us assume that the electrode fills the half space for $x < 0$; moreover the excess electron should be completely localized within the molecule and positioned at $x = d, y = 0, z = 0$; than the respective electrostatic potential formed by the excess electron and the polarized metal electrons reads

$$\phi_{\mathrm{pol}}(\mathbf{r}) = \frac{e}{|\mathbf{r} - d\mathbf{e}_x|} - \frac{e}{|\mathbf{r} + d\mathbf{e}_x|} \; ;$$

the interaction energy follows as $-e^2/4d$; below, however, we will neglect this effect;

ET into the Molecule: Second–Order Rate Expression

to characterize the transfer of an electron from the metal electrode into the molecule we have to calculate the basic transition–rate $k_{\mathbf{k}\to 1}$; it includes the transition of an electron of the metal Fermi–sea with energy $\hbar\varepsilon_{\mathbf{k}}$ at the presence of various possible molecular vibrational energies $\hbar\omega_{0M}$ into an anionic level $\hbar\varepsilon_1$ of the molecule at the vibrational energies $\hbar\omega_{1N}$;
we will assume that the transfer is *irreversible*; this would be the case if the coupling $V_{\mathbf{k}}$ is weak and if the transfer is accompanied by fast relaxation of the transfered electron; than $k_{\mathbf{k}\to 1}$ can be determined in the second–order with respect to $V_{\mathbf{k}}$;
once $k_{\mathbf{k}\to 1}$ has been computed the overall rate follows as

$$k_{\mathrm{ET}} = \sum_{\mathbf{k}} f_{\mathrm{F}}(E_{\mathbf{k}} - \mu) k_{\mathbf{k}\to 1}$$

since a single–electron theory is used the appearance of the Fermi–distribution cannot be deduced from a more general formula;
let us calculate the second–order rate

$$k_{\mathbf{k}\to 1} = \frac{|V_{\mathbf{k}}|^2}{\hbar^2} \int dt \; e^{i(\varepsilon_{\mathbf{k}} - \varepsilon_1)t} \mathrm{tr}_{\mathrm{vib}}\{\hat{R}_0 e^{iH_0 t/\hbar} e^{-iH_1 t/\hbar}\}$$

$$\equiv \frac{|V_{\mathbf{k}}|^2}{\hbar^2} \mathcal{D}_{0\,1}(\varepsilon_{\mathbf{k}} - \varepsilon_1) \; ;$$

note the introduction of the combined DOS for the molecular transition

$$\mathcal{D}_{0\,1}(\omega) = \int dt \; e^{i\omega t} \mathrm{tr}_{\mathrm{vib}}\{\hat{R}_0 e^{iH_0 t/\hbar} e^{-iH_1 t/\hbar}\} \; ;$$

before further considering this expression we denote the overall rate by introducing the DOS:

$$k_{\mathrm{ET}} = \int d\Omega \, \mathcal{N}(\Omega) f_{\mathrm{F}}(\hbar\Omega - \mu) k_1(\Omega)$$

$$\equiv \int d\Omega \, \mathcal{N}(\Omega) f_{\mathrm{F}}(\hbar\Omega - \mu) \frac{|V(\Omega)|^2}{\hbar^2} \mathcal{D}_{0\,1}(\Omega - \varepsilon_1) \; ;$$

we introduce the electrode–molecule coupling function (spectral density)

$$\Gamma(\Omega) = \mathcal{N}(\Omega) \frac{|V(\Omega)|^2}{\hbar^2} \equiv \frac{1}{\hbar^2} \sum_{\mathbf{k}} |V_{\mathbf{k}}|^2 \delta(\Omega - \varepsilon_{\mathbf{k}}) \; ;$$

the so–called *broad–band* approximation is obtained if one neglects any frequency dependency of $\mathcal{N}(\Omega)$ and of $V(\Omega)$ and replaces both quantities by averaged (frequency–independent) expressions $\bar{\mathcal{N}}$ and of $\bar{V}$, respectively; it follows

$$\Gamma(\Omega) \approx \bar{\mathcal{N}} \frac{|\bar{V}|^2}{\hbar^2} \; ;$$

this approximation is valid if the frequency range contributing to $\Gamma(\Omega)$ is far away from the metal conduction–band edges;
with the definition of $\Gamma(\Omega)$ we arrive at

$$k_{\mathrm{ET}} = \int d\Omega \, f_{\mathrm{F}}(\hbar\Omega - \mu) \Gamma(\Omega) \mathcal{D}_{0\,1}(\Omega - \varepsilon_1) \; ;$$

we first give an estimate by considering the high temperature case with respect to the combined molecular DOS

$$\mathcal{D}_{0\,1}(\Omega - \varepsilon_1) = \frac{1}{\sqrt{4\pi k_{\mathrm{B}} T E_\lambda}} \exp\left\{ -\frac{(\hbar\Omega - \hbar\varepsilon_1 - E_\lambda)^2}{4 E_\lambda k_{\mathrm{B}} T} \right\} \; ;$$

next we consider the case valid for all temperatures; the trace can be calculated by introducing the vibrational states χ_{0M} and χ_{1N} of the neutral molecule and of the state with a single excess electron, respectively:

$$\mathcal{D}_{0\,a}(t) \equiv \mathrm{tr}_{\mathrm{vib}}\{\hat{R}_0 e^{iH_0 t/\hbar} e^{-iH_a t/\hbar}\}$$

$$= \sum_M f_{0M} \langle \chi_{0M}| e^{i\omega_{0M} t} \sum_N |\chi_{1N}\rangle \langle \chi_{1N}| e^{-i\omega_{1N} t} |\chi_{0M}\rangle$$

$$= \sum_{M,N} f_{0M} |\langle \chi_{0M}|\chi_{1N}\rangle|^2 e^{i(\omega_{0M} - \omega_{1N}) t} \; ;$$

here,

$$f_{0M} = \langle \chi_{0M}|\hat{R}_0|\chi_{0M}\rangle$$

is the thermal distribution with respect to the vibrational states (of the neutral molecule); if inserted into the overall rate we get

$$k_{\mathrm{ET}} = 2\pi \sum_{M,N} f_{0M} |\langle \chi_{0M}|\chi_{1N}\rangle|^2$$

$$\times \int d\Omega \, f_{\mathrm{F}}(\hbar\Omega - \mu) \Gamma_a(\Omega) \delta(\Omega + \omega_{0M} - \varepsilon_a - \omega_{1N})$$

after taking the Ω–integral it follows

$$k_{\mathrm{ET}} = 2\pi \sum_{M,N} f_{0M} |\langle \chi_{0M} | \chi_{1N} \rangle|^2 f_{\mathrm{F}}(\hbar[\varepsilon_1 + \omega_{1N} - \omega_{0M}] - \mu)\Gamma(\varepsilon_1 + \omega_{1N} - \omega_{0M})$$

concentrating on a simple model with a single vibrational coordinate (the set of vibrational quantum numbers M and N reduces to single numbers) and on $k_{\mathrm{B}}T \ll \hbar\omega_{\mathrm{vib}}$ ($f_{0M} = \delta_{M,0}$) we get

$$k_{\mathrm{ET}} = 2\pi \sum_{N} |\langle \chi_{00} | \chi_{1N} \rangle|^2 f_{\mathrm{F}}(\hbar[\varepsilon_1 + \omega_{1N}] - \mu)\Gamma(\varepsilon_1 + \omega_{1N})$$

Some Estimations
lets undertake an estimate for k_{ET}; we will concentrate on a situation where $f_{\mathrm{F}} = 1$ and where the frequency dependency of Γ is weak; it results

$$k_{\mathrm{ET}} \approx 2\pi\Gamma = 2\pi\frac{\bar{\mathcal{N}}}{\hbar}\frac{|\bar{V}|^2}{\hbar} \approx 2\pi\frac{10^3}{\mathrm{eV}}\frac{(10^{-3}\mathrm{eV})^2}{6.5\ 10^{-16}\mathrm{eVs}} \approx \frac{10^{13}}{\mathrm{s}} = \frac{10}{\mathrm{ps}} \equiv \frac{1}{100\mathrm{fs}}$$

accordingly the ET time is about 100 fs;

2.5 Sequential Charge Transmission through Single Molecules

formula for the current:
electric current = amount of charge which moves per time through a given conductor cross section

$$I = \frac{\Delta Q}{\Delta t} = GV = \frac{V}{R} \; ;$$

current through the left contact (terminal) of the molecule

$$I = -|e|\frac{\partial}{\partial t}N_{\mathrm{L}} \; ;$$

the number of electrons in the left electrode are denoted by N_{L};
if $\partial N_{\mathrm{L}}/\partial t < 0$: charge flow from L to R
$\Longrightarrow I > 0$;

an estimation:
typical value of I if a current flows through a single molecule: 1 nA
residence time:

$$\Delta t = \frac{|e|}{I} = \frac{1.6\,10^{-19}\,\mathrm{As}}{10^{-9}\mathrm{A}} \approx 10^{-10}\,\mathrm{s} = 100\,\mathrm{ps} \; ;$$

to compute IV–characteristics for charge transmission we will consider sequential ET through a molecule using the rate equation approach;
ET starts at the left electrode states $\varphi_{L\mathbf{k}}$, goes through the molecular level φ_1 and ends up in the right electrode states $\varphi_{R\mathbf{q}}$; of course, the reverse process takes also place; the respective Hamiltonian reads:

$$H = H_{\mathrm{mol}} + H_{\mathrm{el}} + H_{\mathrm{el-mol}} \; ;$$

the molecular part is given by that one introduced in the foregoing section

$$H_{\mathrm{mol}} = (\hbar\varepsilon_1 + H_1)|\varphi_1\rangle\langle\varphi_1| \; ,$$

with

$$H_1|\chi_{1M}\rangle = \hbar\omega_{1M}|\chi_{1M}\rangle \; ;$$

note $\omega_{1M=0} = 0$; the part of the electrodes covers two contributions with $X = L, R$

$$H_{\mathrm{el}} = \sum_{X,\mathbf{k}}(\hbar\varepsilon_{X\mathbf{k}} + H_0)|\varphi_{X\mathbf{k}}\rangle\langle\varphi_{X\mathbf{k}}| \; ;$$

the vibrational Hamiltonian H_0 of the neutral molecule obeys

$$H_0|\chi_{0M}\rangle = \hbar\omega_{0M}|\chi_{0M}\rangle \; ;$$

note again $\omega_{0M=0} = 0$; the electrode–molecule coupling takes the following form

$$H_{\mathrm{el-mol}} = \sum_{X,\mathbf{k}}V_{X\mathbf{k}}|\varphi_{X\mathbf{k}}\rangle\langle\varphi_1| + \mathrm{h.c.} \; ;$$

the standard rate equation to be used in the following reads

$$\frac{\partial}{\partial t}P_m = -\sum_n(k_{m\to n}P_m - k_{n\to m}P_n) \; .$$

we specify it for the considered ET and get

$$\frac{\partial}{\partial t}P_{L\mathbf{k}}(t) = -k_{L\mathbf{k}\to 1}P_{L\mathbf{k}}(t) + k_{1\to L\mathbf{k}}P_1(t) \; ,$$

$$\frac{\partial}{\partial t}P_1(t) = -\left(\sum_{\mathbf{k}}k_{1\to L\mathbf{k}} + \sum_{\mathbf{q}}k_{1\to R\mathbf{q}}\right)P_1(t)$$

$$+ \sum_{\mathbf{k}}k_{L\mathbf{k}\to 1}P_{L\mathbf{k}}(t) + \sum_{\mathbf{q}}k_{R\mathbf{q}\to 1}P_{R\mathbf{q}}(t) \; ,$$

and

$$\frac{\partial}{\partial t}P_{R\mathbf{q}}(t) = -k_{R\mathbf{q}\to 1}P_{R\mathbf{q}}(t) + k_{1\to R\mathbf{q}}P_1(t) \; ;$$

the rates appearing in these rate–equations will be specified later;
the current from electrode $X = L, R$ into the molecule follows as

$$I_X = -|e|\frac{\partial}{\partial t}\sum_{\mathbf{k}}P_{X\mathbf{k}}(t)$$

stationary conditions $I = I_L = -I_R$;
assumptions necessary to get the current are:
electrodes are macroscopic systems, staying in equilibrium; therefore the electrode populations on the right–hand side of the rate equations can be replaced by Fermi–distributions abbreviated here as

$$f_{X\mathbf{k}} = f_{\mathrm{F}}(\hbar\varepsilon_{X\mathbf{k}} - \mu_X)$$

since stationary conditions are chosen P_1 is time–independent;
the formation of a vibrational equilibrium in the molecule is fast compared to the time of charge transmission;
therefore it is possible to introduce the rates

$$k_{X\to 1} = \sum_{\mathbf{k}}f_{X\mathbf{k}}k_{X\mathbf{k}\to 1} \; ;$$

to get the correct reverse rates which account for the filled and empty states in the electrodes we have to include the Fermi–blocking

$$k_{1\to X} = \sum_{\mathbf{k}}\left(1 - f_{X\mathbf{k}}\right)k_{1\to X\mathbf{k}} \; ,$$

this is a particular consequence of the used single–electron theory;
from the rate equations we may deduce (for example at the left electrode)

$$I/|e| = k_{L\to 1} - k_{1\to L}P_1 \; ;$$

P_1 follows from the balance equation

$$0 = -(k_{1\to L} + k_{1\to R})P_1 + k_{L\to 1} + k_{R\to 1} \; ;$$

this results in

$$I/|e| = \frac{k_{L\to 1}k_{1\to R} - k_{R\to 1}k_{1\to L}}{k_{1\to L} + k_{1\to R}} \; ;$$

the expression contains contributions to the forward current (from left to right) proportional to $k_{L\to 1}k_{1\to R}/(k_{1\to L} + k_{1\to R})$ and respective contributions to the backward current; in the given expression $k_{1\to L} + k_{1\to R}$ represents the overall rate of a charge to leave the molecule (into the left or right electrode); the rate of forward charge motion through the molecule follows by the combined rate $k_{L\to 1}k_{1\to R}$ for the left–electrode molecule and molecule right–electrode transition divided by the rate of overall charge outflow from the molecule;

the respective rates have been already calculated; since fast vibrational relaxation has been assumed electron transfer into as well as out of the molecule starts from an vibrational equilibrium distribution;
as a consequence we use the following rate expression for electron transfer into the molecule

$$k_{X\to 1} = 2\pi \sum_{M,N} f_{0M} |\langle \chi_{0M}|\chi_{1N}\rangle|^2 f_{\mathrm{Fermi}}(\hbar[\varepsilon_1 + \omega_{1N} - \omega_{0M}] - \mu_X)$$

$$\times \Gamma_X(\varepsilon_1 + \omega_{1N} - \omega_{0M}) \; ;$$

note the introduction of the electrode–molecule coupling function

$$\Gamma_X(\Omega) = \mathcal{N}_X(\Omega)\frac{|V_X(\Omega)|^2}{\hbar^2} \; ;$$

the rate for electron transfer out of the molecule takes the following form:

$$k_{1\to X} = 2\pi \sum_{M,N} f_{1M} |\langle \chi_{1M}|\chi_{0N}\rangle|^2 \Big(1 - f_{\mathrm{Fermi}}(\hbar[\varepsilon_1 + \omega_{1M} - \omega_{0N}] - \mu_X)\Big)$$

$$\times \Gamma_X(\varepsilon_1 + \omega_{1M} - \omega_{0N})$$

note the inclusion of the chemical potentials μ_X; if we provide a symmetrically applied voltage they read
$$\mu_L = E_{\mathrm{F}} + |e|V/2 \; ,$$
and
$$\mu_R = E_{\mathrm{F}} - |e|V/2 \; ;$$

Example

we consider a molecule with a single vibrational mode with $\hbar\omega_{\mathrm{vib}} > k_{\mathrm{B}}T$; moreover, the energy dependence of the single coupling function Γ should be weak; then, the transition rates read

$$k_{X\to 1} = 2\pi\Gamma \sum_{N} |\langle \chi_{00}|\chi_{1N}\rangle|^2 f_{\mathrm{Fermi}}(\hbar[\varepsilon_1 + \omega_{1N}] - \mu_X) \; ,$$

and
$$k_{1\to X} = 2\pi\Gamma \sum_{N} |\langle \chi_{10}|\chi_{0N}\rangle|^2 \Big(1 - f_{\mathrm{Fermi}}(\hbar[\varepsilon_1 - \omega_{0N}] - \mu_X)\Big) \; ;$$

to calculate the vibrational overlap expression we assume a simple parabolic PES for the neutral molecular level
$$U_0 = \frac{\omega_{\mathrm{vib}}^2}{2}q^2 \equiv \frac{\hbar\omega_{\mathrm{vib}}}{4}Q^2 \; ,$$

and for the presence of a single excess electron

$$U_1 = \frac{\omega_{\text{vib}}^2}{2}(q - \Delta q)^2 \equiv \frac{\hbar\omega_{\text{vib}}}{4}(Q + 2\Delta g)^2 \; ;$$

note that the vibrational frequency is the same for both states; accordingly the overlap reads

$$\langle \chi_{00} | \chi_{1N} \rangle = \langle 0 | D^+(\Delta g) | N \rangle$$

where we introduced the N'th excited state of a harmonic oscillator

$$|N\rangle = \frac{C^{+N}}{\sqrt{N!}} |0\rangle \; ,$$

and the shift operator

$$D^+(\Delta g) = \exp\left(\Delta g C - \text{h.c.}\right) \; ;$$

we further note

$$\langle 0 | \exp\left(\Delta g C - \Delta g C^+\right) | N \rangle = e^{-\Delta g^2/2} \langle 0 | \exp\left(-\Delta g C^+\right) \exp\left(\Delta g C\right) | N \rangle$$

$$= e^{-\Delta g^2/2} \langle 0 | \frac{(\Delta g C)^N}{N!} | N \rangle = e^{-\Delta g^2/2} \Delta g^N \frac{\sqrt{N!}}{N!} \; ;$$

so we arrive at

$$|\langle \chi_{00} | \chi_{1N} \rangle|^2 = \frac{\Delta g^{2N}}{N!} e^{-\Delta g^2} \; ;$$