Chapter 2

Electron Transfer

2.1   Introduction

electron transfer (ET) – one of the basic types of chemical processes (initial step of a number of reactions like the making and breaking of chemical bonds or the change of molecular conformations)
corrosion is caused by the ET between some metal surface and oxygen
in biological systems ET reactions are a basic step of enzymatic activity in the living cells of bacteria, plants and animals
ET in proteins or protein complexes plays an important role in the cell metabolism and energy balance
photosynthesis - a transmembrane potential is created which acts as a proton pump to produce ATP

ET – a *spontaneous* charge redistribution between an initially prepared reactant state and a well defined product state
transferred electron remains in a bound state with respect to the particular molecule or molecular system – ET reactions occur as *tunneling processes*
in many reactions the change of the electronic charge density corresponds to the change induced by a single electron; sufficient to discuss ET as the result of the transition of a *single* electron;

change of the electronic charge distribution during an ET reaction → internal electrostatic field of the molecular complex is modified → new equilibrium positions of the nuclei;
in the case of ET there exists a coupling V between the reactant and the product state;
if V is small, one is in the limit of *nonadiabatic* ET; in the reactant state the transferred electron is localized at the electron donor part; then, it moves to the acceptor region;
if V is large, one is in the limit of *adiabatic* transfer; it is *not* connected with a characteristic spatial redistribution of charge; the internal energy of the reaction (or if entropic effects are important, the free energy) is considered in dependence on a reaction coordinate; the metastable initial (reactant) state and the stable final (product) state are separated by a potential barrier along this reaction coordinate; to overcome this barrier the reaction requires thermal activation, or a tunneling transition through the barrier is possible;

we introduce the donor (D) and acceptor (A) states of a molecular system; common structure formed by the D and A is called donor–acceptor (DA) *complex*;
the ET reaction is most simply characterized by the following scheme (ET of an *excess* electron)

$$D^-A \rightarrow DA^- ;$$
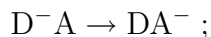
donor and acceptor belong to the same molecule → *intramolecular* ET or alternatively *unimolecular* ET
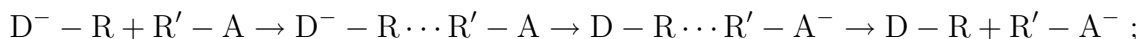donor and acceptor belong to different molecules →*intermolecular* ET or *bimolecular* ET

photoinduced ET

$$D^*A \rightarrow D^+A^- ;$$
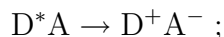
an unexcited electron may move in the opposite direction from the acceptor HOMO to the donor HOMO, this so–called *hole transfer*:

$$D^*A \rightarrow D^-A^+ .$$
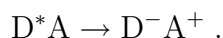
bimolecular ET in solution → *formation* of the DA complex, the so–called *encounter complex*

$$D^- - R + R' - A \rightarrow D^- - R \cdots R' - A \rightarrow D - R \cdots R' - A^- \rightarrow D - R + R' - A^- ;$$

if the ET is influenced mainly by solvent molecules it is of *outer–sphere* type;
if intramolecular nuclear motions it is of *inner–sphere* type;

ET reactions which proceed directly from the donor to the acceptor, although some bridging units are separating them, are called *through–space* transfer (DA distances less than 20 Å);
if some LUMOs of the bridge participate in the ET, the reaction is called *through–bond* transfer = *bridge–assisted* ET → *long–range* ET

$$D^-BA \rightarrow DB^-A \rightarrow DBA^- .$$

electron moves from the donor to the acceptor via different bridge molecules (B) = *spacers* (fix the donor and the acceptor at a particular distance one from another);
two distinct mechanisms for bridge–mediated ET:
superexchange ET (bridge units provide a means for delocalization of the donor state wave function across the whole bridge);
sequential or *hopping* transfer (charge jumps stepwise from one part to the other of the whole DBA chain);

2.2 Theoretical Model for Donor–Acceptor Electron Transfer

2.2.1 The Single–Electron Hamiltonian of a Donor–Acceptor Complex

ET comes along with the modification of many molecular orbitals;
we will proceed with a simple and intuitive picture of the motion of a single *excess*

electron injected from the outside into the DA complex;
an effective potential experienced by the excess electron after entering the DA complex is introduced

$$V(\mathbf{r}) = \sum_m V_m(\mathbf{r}) \; ;$$

$V_m(\mathbf{r})$ belongs to the donor, the acceptor, or to some bridging molecules; it can be understood as a so–called *pseudo–potential*; the electronic part of the DA–Hamiltonian takes the form

$$H_{\mathrm{el}}^{(\mathrm{DBA})} = T_{\mathrm{el}} + V(\mathbf{r}) \; ;$$

the single–electron Schrödinger equation which determines the single–particle energies E_m and wave functions $\varphi_m(\mathbf{r})$ reads as:

$$(T_{\mathrm{el}} + V_m(\mathbf{r})) \, \varphi_m(\mathbf{r}) = E_m \varphi_m(\mathbf{r}) \; ;$$

only the lowest eigenvalue E_m is of interest;
since the E_m correspond to different sites in the complex they are usually called *site energies*;
in general, the set of states φ_m does not form a normalized and orthogonal basis; however, we will assume that this is valid in an approximate form: $\langle \varphi_n | \varphi_m \rangle \approx \delta_{nm}$;

an expansion of the electronic part of the DA–Hamiltonian gives

$$H_{\mathrm{el}}^{(\mathrm{DBA})} = \sum_{m,n} \langle \varphi_m | H_{\mathrm{el}}^{(\mathrm{DBA})} | \varphi_n \rangle | \varphi_m \rangle \langle \varphi_n | \; ,$$

with the matrix elements

$$\langle \varphi_m | H_{\mathrm{el}}^{(\mathrm{DBA})} | \varphi_n \rangle = \delta_{m,n} \Big(E_m + \sum_{k \neq m} \langle \varphi_m | V_k | \varphi_m \rangle \Big) + (1 - \delta_{m,n}) \langle \varphi_m | T_{\mathrm{el}} + \sum_k V_k | \varphi_n \rangle \; ;$$

we will introduce the approximations that all three–center integrals are neglected;
the two–center integrals of the type $\langle \varphi_m | V_k | \varphi_m \rangle$, introduce a shift of the site energies E_m;
two–center integrals $\langle \varphi_n | V_n | \varphi_m \rangle$ couple the state $|\varphi_m\rangle$ to the state $|\varphi_n\rangle$ via the tail of the potential V_n at site m;
the matrix elements of $H_{\mathrm{el}}^{(\mathrm{DBA})}$ reduce to:

$$\langle \varphi_m | H_{\mathrm{el}}^{(\mathrm{DBA})} | \varphi_n \rangle = \delta_{m,n} \Big(E_m + \sum_{k \neq m} \langle \varphi_m | V_k | \varphi_m \rangle \Big) + (1 - \delta_{m,n}) \langle \varphi_m | T_{\mathrm{el}} + V_m + V_n | \varphi_n \rangle \; ;$$

the off–diagonal part can be rewritten as

$$\langle \varphi_m | T_{\mathrm{el}} + V_m + V_n | \varphi_n \rangle = \frac{1}{2} \langle \varphi_m | (T_{\mathrm{el}} + V_m) + (T_{\mathrm{el}} + V_n) + (V_m + V_n) | \varphi_n \rangle$$

$$= \frac{1}{2} \langle \varphi_m | E_m + E_n + (V_m + V_n) | \varphi_n \rangle = \frac{1}{2} \langle \varphi_m | V_m + V_n | \varphi_n \rangle = V_{mn} \; ;$$

V_{mn} is called *transfer integral* or alternatively *inter–state coupling*; the term *tunneling* matrix element is also common;
one can also write V_{mn} $(m \neq n)$ in terms of the matrix element of the kinetic energy operator:

$$V_{mn} = \langle \varphi_m | T_{\mathrm{el}} + V_m + T_{\mathrm{el}} + V_n - T_{\mathrm{el}} | \varphi_n \rangle$$

$$= \langle \varphi_m | E_m + E_n - T_{\text{el}} | \varphi_n \rangle = -\langle \varphi_m | T_{\text{el}} | \varphi_n \rangle \; ;$$

the complete electronic Hamiltonian for the DA complex reads (we included the diagonal matrix elements of the pseudo–potentials into the definition of the site energies E_m)

$$H_{\text{el}}^{(\text{DBA})} = \sum_m E_m |\varphi_m\rangle\langle\varphi_m| + \sum_{m,n} V_{mn} |\varphi_m\rangle\langle\varphi_n| \; ;$$

2.2.2 The Electron–Vibrational Hamiltonian of a Donor–Acceptor Complex

one can distinguish between *accepting modes* which change their equilibrium configuration if the electronic charge density changes, and *promoting modes*, which enter the transfer integral and thus may accelerate the ET;
including the vibrational degrees of freedom, $\{R_u\} \equiv R$ (note that we use the index u instead of n), the complete Hamiltonian of the DA complex becomes

$$H_{\text{DBA}} = H_{\text{el}}^{(\text{DBA})}(R) + T_{\text{nuc}} + V_{\text{nuc−nuc}}(R)$$

$$= \sum_m \Big[\big(T_{\text{nuc}} + E_m(R) + V_{\text{nuc−nuc}}(R) \big) + \Theta_{mm} \Big] |\varphi_m\rangle\langle\varphi_m| + \sum_{m \neq n} (V_{mn}(R) + \Theta_{mn}) |\varphi_m\rangle\langle\varphi_n| \; ;$$

we can introduce PES which relate to those state with the excess electron localized at site m:

$$U_m(R) = E_m(R) + V_{\text{nuc−nuc}}(R) + \Theta_{mm} \; ;$$

we neglect the nonadiabatic coupling and the total electron–vibrational Hamiltonian is obtained as

$$H_{\text{DBA}} = \sum_m \big(T_{\text{nuc}} + U_m(R) \big) |\varphi_m\rangle\langle\varphi_m| + \sum_{m \neq n} V_{mn}(R) |\varphi_m\rangle\langle\varphi_n| \; ;$$

we introduce normal mode coordinates $\{q_\xi\} \equiv q$ with a reference configuration for the neutral DA complex; it is supposed to be characterized by the PES $U_g(R)$ having the equilibrium configuration at $\{R_u^{(g)}\} \equiv R^{(g)}$;
we carry out an expansion of $U_g(R)$ around $R^{(g)}$ up to the second order with respect to the deviations $\Delta R_u^{(g)} = R_u - R_u^{(g)}$ and obtain

$$U_g(R) = U_g^{(0)} + \frac{1}{2} \sum_{u,u'} \kappa_{uu'}^{(g)} \Delta R_u^{(g)} \Delta R_{u'}^{(g)} \; ;$$

we used $U_g(R^{(g)}) = U_g^{(0)}$, and the $\kappa_{uu'}^{(g)}$ denote the second derivatives of the PES;
mass-weighted normal mode coordinates are introduced according to the linear transformation

$$\Delta R_u^{(g)} = \sum_\xi M_u^{-1/2} A_{u\xi}^{(g)} q_\xi \; ;$$

it leads to a diagonalization of the vibrational Hamiltonian with the potential energy given by

$$U_g(R) \equiv U_g(q) = U_g^{(0)} + \frac{1}{2} \sum_\xi \omega_{g,\xi}^2 q_\xi^2 \; ;$$

we consider the PES $U_m(R)$ relevant if the excess electron is localized at site m; let us suppose that this electronic state can be described by the same normal mode coordinates; the expansion of the PES $U_m(R)$ reads

$$U_m(R) = U_m^{(0)} + \frac{1}{2} \sum_{u,u'} \kappa_{uu'}^{(m)} \Delta R_u^{(m)} \Delta R_{u'}^{(m)} \; ;$$

with $U_m(R^{(m)}) = U_m^{(0)}$ and $\Delta R_u^{(m)} = R_u - R_u^{(m)}$;
we note

$$\Delta R_u^{(m)} = (R_u - R_u^{(g)}) - (R_u^{(m)} - R_u^{(g)}) = \sum_\xi M_u^{-1/2} (A_{u\xi}^{(g)} q_\xi - A_{u\xi}^{(g)} q_\xi^{(m)}) \; ,$$

$q_\xi^{(m)}$ corresponds to the linear transformation of the difference $R_u^{(m)} - R_u^{(0)}$; we get

$$U_m(q) = U_m^{(0)} + \frac{1}{2} \sum_\xi \omega_{m,\xi}^2 (q_\xi - q_\xi^{(m)})^2 \; ;$$

this result reflects the assumption that the linear transformation used for the electronic ground–state of the DBA–complex is also valid for those states where an excess electron is located at a particular site;
the related vibrational Hamiltonian reads

$$H_m(q) = T_{\text{vib}} + U_m(q) = U_m^{(0)} + \frac{1}{2} \sum_\xi \left\{ p_\xi^2 + \omega_{m,\xi}^2 \left(q_\xi - q_\xi^{(m)} \right)^2 \right\} \; ;$$

in the general case the inter–site couplings V_{mn} also depend on the nuclear coordinates; since the magnitude of V_{mn} is mainly determined by the overlap of the exponential tail of the wave functions localized at sites m and n, we expect an exponential dependence on the distance x_{mn} between the two sites:

$$V_{mn}(R) = V_{mn}^{(0)} \exp \left\{ -\beta_{mn}(x_{mn} - x_{mn}^{(0)}) \right\} \; ;$$

for further use we remove $U_m^{(0)}$ from H_m and get the total Hamiltonian as

$$H_{\text{DBA}} = \sum_{m,n} \{ \delta_{mn}(U_m^{(0)} + H_m(q)) + (1 - \delta_{mn})V_{mn} \} |\varphi_m\rangle\langle\varphi_n| \; ;$$

since the vibrational dynamics are described via normal–mode harmonic oscillators we introduce respective oscillator operators

$$c_\xi^+ = \sqrt{\frac{\omega_\xi}{2\,\hbar}} \, q_\xi \; - \; i \, \frac{1}{\sqrt{2\,\hbar\,\omega_\xi}} \, p_\xi \; ,$$

$$c_\xi = \sqrt{\frac{\omega_\xi}{2\,\hbar}} \, q_\xi \; + \; i \, \frac{1}{\sqrt{2\,\hbar\,\omega_\xi}} \, p_\xi \; ;$$

here we assumed that the normal–mode frequencies do not depend on the diabatic state, i.e. $\omega_{m\xi} = \omega_\xi$;
the reverse relation reads

$$q_\xi = \sqrt{\frac{\hbar}{2\,\omega_\xi}} \, (c_\xi \; + \; c_\xi^+) \; ,$$

$$p_\xi = -i \sqrt{\frac{\hbar \omega_\xi}{2}} \left(c_\xi \ - \ c_\xi^+ \right) ;$$

introducing the dimensionless electron–vibrational coupling constant

$$g_m(\xi) \ \equiv \ -\sqrt{\frac{\omega_\xi}{2\hbar}} \, q_\xi^{(m)}$$

the vibrational Hamiltonians may be written as

$$H_m = \sum_\xi \hbar\omega_\xi \left((c_\xi^+ \ + \ g_m(\xi))(c_\xi \ + \ g_m(\xi)) \ + \ \frac{1}{2} \right) ;$$

it is useful to give a representation of the DA Hamiltonian using the complete diabatic electron–vibrational basis defined by the states

$$|\Psi\mu\rangle \equiv |\Psi_{mM}\rangle \equiv |\varphi_m\rangle |\chi_{mM}\rangle ;$$

the vibrational states $|\chi_{mM}\rangle$ which belong to the electronic states $|\varphi_m\rangle$ are the eigenstates of the vibrational Hamiltonian:

$$H_m |\chi_{mM}\rangle = E_{mM} |\chi_{mM}\rangle ;$$

the respective eigenvalues

$$E_{mM} = U_m^{(0)} + \sum_\xi \hbar\omega_{m\xi}(M_\xi + 1/2)$$

give the energy spectrum of the normal mode oscillators;
the Hamiltonian can be expanded in the diabatic electron–vibrational basis as follows

$$H_{\mathrm{DBA}} = \sum_{\mu\nu} \left(\delta_{\mu\nu} E_\mu + V_{\mu\nu} \right) |\Psi_\mu\rangle \langle\Psi_\nu| .$$

if the transfer integral V_{mn} is coordinate independent the coupling matrix element follows as $V_{\mu\nu} = V_{mn}\langle\chi_{mM}|\chi_{nN}\rangle$, where $\langle\chi_{mM}|\chi_{nN}\rangle$ is the overlap integral of the vibrational wave functions belonging to different sites (Franck–Condon factor)