

2 Examples of a System Reservoir Separation

we present different examples of a system (the primary, active quantum system) coupled to a reservoir (environment, thermal bath);

the overall Hamiltonian is written as

$$H = H_S + H_{S-R} + H_R$$

the system part is denoted by H_S and the reservoir part by H_R ;

the system-reservoir coupling will be written as

$$H_{S-R} = \sum_u K_u \Phi_u$$

the K_u are operators acting in the state space of the active system;

the Φ_u are operators acting in the state space of the reservoir;

2.1 Harmonic Oscillator Reservoir

we assume that the reservoir can be represented by normal mode oscillators;
respective coordinates are $Z = \{Z_\xi\}$;
the reservoir Hamiltonian can be written as

$$H_R = \sum_{\xi} \hbar\omega_{\xi}(C_{\xi}^+ C_{\xi} + 1/2)$$

the ω_{ξ} are the normal mode frequencies;
 C_{ξ}^+ and C_{ξ} denote normal mode oscillator creation and annihilation operators, respectively;
harmonic oscillator eigenstates are

$$|N_{\xi}\rangle = \frac{(C_{\xi}^+)^{N_{\xi}}}{\sqrt{N_{\xi}!}}|0_{\xi}\rangle$$

they are labeled by the oscillator quantum numbers N_{ξ} ;

we perform a Taylor expansion of H_{S-R} with respect to the reservoir coordinates;
in the lowest-order H_{S-R} becomes linear with respect to $Z = \{Z_{\xi}\}$;
dropping the index u we can write

$$H_{S-R} = K(s) \sum_{\xi} \hbar\gamma_{\xi} Z_{\xi}$$

γ_{ξ} is the system-reservoir coupling constant;

in terms of the creation and annihilation operators the reservoir coordinates are written as

$$Z_\xi = \sqrt{\hbar/2\omega_\xi}(C_\xi + C_\xi^+)$$

it is more suitable to define Φ in terms of

$$Q_\xi = C_\xi + C_\xi^+$$

just writing

$$\Phi = \hbar \sum_{\xi} \omega_{\xi} g_{\xi} Q_{\xi}$$

with the dimensionless coupling constant

$$g_{\xi} = \gamma_{\xi} \sqrt{\hbar/2\omega_{\xi}^3}$$

the obtained system-reservoir coupling reads

$$H_{S-R} = K\Phi$$

2.2 Electron-Phonon Interaction in Solid-State Systems

electrons in a solid state system form the active system and the lattice vibrations the reservoir

we start with the Hamiltonian of the valence electrons moving across the background of ions forming a regular lattice

$$H = H_{\text{el}} + H_{\text{el-ion}} + H_{\text{ion}}$$

electron Hamiltonian

$$H_{\text{el}} = \sum_j \frac{\mathbf{p}_j^2}{2m_{\text{el}}} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

electron-ion interaction

$$H_{\text{el-ion}} = \sum_{j,n} V_{\text{el-ion}}(\mathbf{r}_j - \mathbf{R}_n)$$

Hamiltonian of the ions

$$H_{\text{ion}} = \sum_n \frac{\mathbf{P}_n^2}{2M_n} + \frac{1}{2} \sum_{m,n} V_{\text{ion}}(\mathbf{R}_m - \mathbf{R}_n)$$

the regular lattice is characterized by the equilibrium configuration of the ions $\mathbf{R}_n^{(0)}$; small deviations are denoted by $\Delta\mathbf{R}_n$;

it results the Bloch-electron Hamiltonian (single band picture of a metal) including electron-electron interaction

$$\mathcal{H}_{\text{el}} = \sum_j \left(\frac{\mathbf{p}_j^2}{2m_{\text{el}}} + \sum_n V_{\text{el-ion}}(\mathbf{r}_j - \mathbf{R}_n^{(0)}) \right) + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \rightarrow \sum_{\mathbf{k},s} \varepsilon(\mathbf{k}) a_{\mathbf{k}s}^+ a_{\mathbf{k}s} + V_{\text{el-el}}$$

the Hamiltonian of harmonic lattice vibrations defines the phonon Hamiltonian (the acoustic branch)

$$H_{\text{ion}} \approx \frac{1}{2} \sum_{m,n} V_{\text{ion}}(\mathbf{R}_m^{(0)} - \mathbf{R}_n^{(0)}) + \sum_n \frac{\mathbf{P}_n^2}{2M_n} + \frac{1}{2} \sum_{m,n} \kappa_{mn} \Delta \mathbf{R}_m \Delta \mathbf{R}_n \rightarrow \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} (b_{\mathbf{q}}^+ b_{\mathbf{q}} + 1/2)$$

electron-phonon coupling is defined in the lowest order with respect to $\Delta \mathbf{R}_n$

$$H_{\text{el-ion}} \approx \sum_{j,n} \nabla_{\mathbf{R}_n} V_{\text{el-ion}}(\mathbf{r}_j - \mathbf{R}_n^{(0)}) \Delta \mathbf{R}_n \rightarrow \sum_{\mathbf{k},\mathbf{q},s} T_{\mathbf{k}+\mathbf{q},\mathbf{k}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^+) a_{\mathbf{k}+\mathbf{q}s}^+ a_{\mathbf{k}s}$$

we compare the obtained expressions with the general form of the system-reservoir coupling written as

$$H_{\text{S-R}} = \sum_u K_u \Phi_u$$

the following identifications become possible

$$K_u = K_{\mathbf{q}} = \sum_{\mathbf{k},s} T_{\mathbf{k}+\mathbf{q},\mathbf{k}} a_{\mathbf{k}+\mathbf{q}s}^+ a_{\mathbf{k}s}$$

and

$$\Phi_u = \Phi_{\mathbf{q}} = b_{\mathbf{q}} + b_{-\mathbf{q}}^+$$

2.3 An Atom Interacting with the Quantized Radiation Field

electrons in an atom form the active system and the photons of the radiation field the reservoir

in order to introduce photons and to derive atom-photon interaction we take the Coulomb gauge which let become the vector potential transversal, i.e. $\nabla \mathbf{A} = 0$;

the longitudinal part of the radiation field is accounted for by the instantaneous Coulomb interaction among charge distributions;

the atom radiation field Hamiltonian reads

$$H = \sum_u \frac{1}{2m_u} \left[\mathbf{p}_u - \frac{q_u}{c} \mathbf{A}(\mathbf{x}_u, t) \right]^2 + \frac{1}{2} \sum_{u \neq v} \frac{q_u q_v}{|\mathbf{x}_u - \mathbf{x}_v|} + H_{\text{field}}$$

field quantization can be achieved by expanding the vector potential $\mathbf{A}(\mathbf{r})$ in terms of plane waves with wave vectors \mathbf{k} pointing in propagation direction;

usually this is done assuming that the radiation field is contained in a volume L^3 (box with lengths L , quantization volume)

$$\mathbf{A}(\mathbf{r}) = \sum_{\lambda, \mathbf{k}} N_{\mathbf{k}} \mathbf{n}_{\lambda \mathbf{k}} \left[\hat{a}_{\lambda \mathbf{k}} e^{i\mathbf{k}\mathbf{r}} + \text{H.c.} \right].$$

the vector potential is a transverse field and every partial wave can be characterized by two (linear independent) transverse ($\mathbf{k} \mathbf{n}_{\lambda \mathbf{k}} = 0$) polarization directions with unity vectors $\mathbf{n}_{\lambda \mathbf{k}}$ ($\lambda = 1, 2$);

we introduced the normalization constant $N_{\mathbf{k}} = (2\pi \hbar c^2 / L^3 \omega_{\mathbf{k}})^{1/2}$

as well as the photon dispersion relation $\omega_{\mathbf{k}} = c|\mathbf{k}|$;

we have the photon creation and annihilation operators, $\hat{a}_{\lambda\mathbf{k}}^+$ and $\hat{a}_{\lambda\mathbf{k}}$, respectively, which fulfill the commutation relations of harmonic oscillator operators;

with the help of these operators the energy of the photon field can be written as

$$H_{\text{phot}} = \sum_{\lambda,\mathbf{k}} \hbar\omega_{\mathbf{k}}(a_{\lambda\mathbf{k}}^+ a_{\lambda\mathbf{k}} + 1/2) .$$

to describe atom photon interaction we assume that the radiation field is of low intensity such that the term $\propto \mathbf{A}^2$ can be neglected as compared with the one $\propto \mathbf{p}_j \mathbf{A}$;

specifying our consideration to electronic transitions only, the interaction Hamiltonian follows as (note $\mathbf{p}_j \mathbf{A} \sim \nabla_j \mathbf{A} = 0$)

$$\begin{aligned} H_{\text{int}} &= -\frac{e}{m_{\text{el}}c} \sum_j \mathbf{p}_j \mathbf{A}(\mathbf{r}_j) = -\frac{e}{m_{\text{el}}c} \sum_j \sum_{\lambda,\mathbf{k}} N_{\mathbf{k}}[\mathbf{p}_j \mathbf{n}_{\lambda\mathbf{k}}] \left[\hat{a}_{\lambda\mathbf{k}} e^{i\mathbf{k}\mathbf{r}_j} + \text{H.c.} \right] \\ &= -\frac{e}{m_{\text{el}}c} \sum_{\lambda,\mathbf{k}} N_{\mathbf{k}} \hat{a}_{\lambda\mathbf{k}} \sum_{a,b} \langle \psi_a | \sum_j [\mathbf{n}_{\lambda\mathbf{k}} \mathbf{p}_j] e^{i\mathbf{k}\mathbf{r}_j} | \psi_b \rangle | \psi_a \rangle \langle \psi_b | + \text{H.c.} \end{aligned}$$

next we focus on transitions between the electronic ground state ψ_g of the atom and a particular excited state ψ_e ;

if only photons are of interest which wavelength is large compared to the spatial extension of the atom $\mathbf{k}\mathbf{r}_j$ becomes a small quantity; a replacement of the exponential function in the matrix element by 1 can be carried out; this corresponds to the dipole approximation, since one can replace the electronic matrix element of the momentum operator by the transition dipole moment;

to show this we start with the equation of motion for the electronic coordinate operator \mathbf{r}_j given by

$$i\hbar \frac{\partial}{\partial t} \mathbf{r}_j = [\mathbf{r}_j, H_{\text{el}}]_- = i\hbar \frac{\mathbf{p}_j}{m_{\text{el}}}$$

the matrix elements of the momentum operator can be written as

$$\begin{aligned} \langle \psi_e | \sum_j \mathbf{n}_{\lambda \mathbf{k}} \mathbf{p}_j | \psi_g \rangle &= -i \frac{m_{\text{el}}}{\hbar} \mathbf{n}_{\lambda \mathbf{k}} \sum_j \langle \psi_e | (\mathbf{r}_j H_{\text{el}} - H_{\text{el}} \mathbf{r}_j) | \psi_g \rangle \\ &= \frac{m_{\text{el}}}{i\hbar} \mathbf{n}_{\lambda \mathbf{k}} (E_g - E_e) \sum_j \langle \psi_e | \mathbf{r}_j | \psi_g \rangle = i \frac{m_{\text{el}}}{\hbar e} (E_e - E_g) \mathbf{n}_{\lambda \mathbf{k}} \mathbf{d}_{eg} \end{aligned}$$

\mathbf{d}_{eg} is the transition dipole matrix element (which should be independent on the nuclear coordinates) and E_e and E_g are electronic energy levels;

we only combine photon absorption with electronic excitation and vice versa and get ($\hbar\omega_{eg} = E_e - E_g$)

$$\begin{aligned} H_{\text{int}} &= -\frac{e}{m_{\text{el}} c} \sum_{\lambda, \mathbf{k}} \sqrt{\frac{2\pi \hbar c^2}{L^3 \omega_{\mathbf{k}}}} \hat{a}_{\lambda \mathbf{k}} i \frac{m_{\text{el}} \omega_{eg}}{e} [\mathbf{n}_{\lambda \mathbf{k}} \mathbf{d}_{eg}] |\psi_e\rangle \langle \psi_g| + \text{H.c.} \\ &= -i \sum_{\lambda, \mathbf{k}} \sqrt{\frac{2\pi \hbar \omega_{eg}^2}{L^3 \omega_{\mathbf{k}}}} [\mathbf{n}_{\lambda \mathbf{k}} \mathbf{d}_{eg}] \hat{a}_{\lambda \mathbf{k}} |\psi_e\rangle \langle \psi_g| + \text{H.c.} \end{aligned}$$

we compare the obtained expressions with the general form of the system-reservoir coupling written as

$$H_{S-R} = \sum_u K_u \Phi_u$$

the following identifications become possible

$$K_1 = |\psi_e\rangle\langle\psi_g| = K_2^+$$

and

$$\Phi_1 = -i \sum_{\lambda, \mathbf{k}} \sqrt{\frac{2\pi\hbar\omega_{eg}^2}{L^3\omega_{\mathbf{k}}}} [\mathbf{n}_{\lambda\mathbf{k}} \mathbf{d}_{eg}] \hat{a}_{\lambda\mathbf{k}} = \Phi_2^+$$

2.4 An Electron in a Supramolecular Systems Interacting with the Environmental Vibrations

the electron represents the active system and the molecular vibrations the reservoir

Hamiltonian describing the motion of a single excess electron across different molecules labeled by m

$$H = \sum_{m,n} (\delta_{m,n} H_m + (1 - \delta_{m,n}) V_{mn}) |\varphi_m\rangle \langle \varphi_n|$$

expansion with respect to states ϕ_m localized at the various molecules results in transfer matrix elements V_{mn} ;

the electron shall couple to intramolecular vibrations;

the vibrational Hamiltonian $H_m = T_{\text{vib}} + U_m$ corresponds to the state where the excess electron is localized at molecule m ;

the potential energy surface (PES) U_m is the one of molecule m in its charged state and all other molecules in their neutral state

$$U_m(Q) = u_m^{(-)}(Q_m) + \sum_{n \neq m} u_n^{(0)}(Q_n)$$

we introduced the set of vibrational coordinates $Q_m = \{Q_{mj}\}$ which belong to molecule m ;

if those are dimensionless and all PES of harmonic type we get

$$u_m^{(-)}(Q_m) = u_m^{(-)} + \sum_j \frac{\hbar\omega_{mj}}{4} (Q_{mj} - Q_{mj}^{(-)})^2$$

and

$$u_m^{(0)}(Q_m) = u_m^{(0)} + \sum_j \frac{\hbar\omega_{mj}}{4} Q_{mj}^2$$

the shift of the vibrational configuration of molecule m upon its charging can be translated into a linear electron-vibrational coupling

$$U_m(Q) = \sum_n u_n^{(0)}(Q_n) + u_m^{(-)}(Q_m) - u_m^{(0)}(Q_m) = U_0(Q) + u_m^{(-)} - u_m^{(0)} + \sum_j \frac{\hbar\omega_{mj}}{4} Q_{mj}^{(-)2} - \sum_j \frac{\hbar\omega_{mj}}{2} Q_{mj}^{(-)} Q_{mj}$$

the diagonal part of the original Hamiltonian can be rewritten

$$H_0 = \sum_m H_m |\varphi_m\rangle \langle \varphi_m| = \sum_m \left(T_{\text{vib}} + u_0(Q) \right) |\varphi_m\rangle \langle \varphi_m| + \sum_m \left(u_m^{(-)} - u_m^{(0)} + \sum_j \frac{\hbar\omega_{mj}}{4} Q_{mj}^{(-)2} \right) |\varphi_m\rangle \langle \varphi_m| - \sum_m \sum_j \frac{\hbar\omega_{mj}}{2} Q_{mj}^{(-)} Q_{mj} |\varphi_m\rangle \langle \varphi_m|$$

we assume the introduction of harmonic oscillator operators for all vibrations

$$Q_{mj} = a_{mj} + a_{mj}^+$$

we abbreviate (note the inclusion of the vibrational zero-point energy)

$$E_m = u_m^{(-)} - u_m^{(0)} + \sum_j \frac{\hbar\omega_{mj}}{4} (Q_{mj}^{(-)2} + 2)$$

and

$$K_{mj} = -\frac{\hbar\omega_{mj}}{2} Q_{mj}^{(-)}$$

it follows

$$H_0 = H_{\text{vib}} + \sum_m E_m |\varphi_m\rangle\langle\varphi_m| + H_{\text{el-vib}}$$

the vibrational Hamiltonian is (reference energy has been set equal to zero)

$$H_{\text{vib}} = \sum_{m,j} \hbar\omega_{mj} a_{mj}^+ a_{mj}$$

and the electron-vibrational coupling reads

$$H_{\text{el-vib}} = \sum_{m,j} K_{mj} (a_{mj} + a_{mj}^+) |\varphi_m\rangle\langle\varphi_m|$$

accordingly the total Hamiltonian is written as

$$H = H_{\text{el}} + H_{\text{el-vib}} + H_{\text{vib}}$$

with

$$H_{\text{el}} = \sum_{m,n} h_{mn} |\varphi_m\rangle \langle \varphi_n|$$

and

$$h_{mn} = \delta_{m,n} E_m + (1 - \delta_{m,n}) V_{mn}$$

we compare the obtained expressions with the general form of a system-reservoir coupling; the following identifications become possible

$$H_{\text{S-R}} = H_{\text{el-vib}} = \sum_m K_m \Phi_m$$

with

$$K_m = |\varphi_m\rangle \langle \varphi_m|$$

and

$$\Phi_m = \sum_j K_{mj} (a_{mj} + a_{mj}^+)$$