Universität Rostock Traditio et Innovatio

INSTITUT FÜR PHYSIK

Dynamics and Spectroscopy of Molecular Systems: From the Infrared to the X-ray Regime

Prof. Oliver Kühn

Institute of Physics, University of Rostock,
Albert-Einstein-Str. 23-24, 18059 Rostock
Email: oliver.kuehn@uni-rostock.de
http://web.physik.uni-rostock.de/quantendynamik

Table of Contents

- Concepts of Molecular Physics
- Concepts of (Non-)linear Spectroscopy
- Dynamics and Spectroscopy of Hydrogen Bonds
- Frenkel Excitons in Natural and Artifical Light-Harvesting
- X-Ray Spectroscopy of Core Levels

Literature (general)

V. May, O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems*, Wiley-VCH, Weinheim, 2011.

S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*, Oxford University Press, New York, 1995.

P. Hamm, M. Zanni, *Concepts and Methods of 2D Infrared Spectroscopy*, Cambridge University Press, Cambridge, 2011.

F. de Groot, A. Kotani, *Core Level Spectroscopy of Solids*, CRC, Boca Raton, 2008

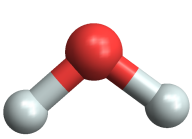
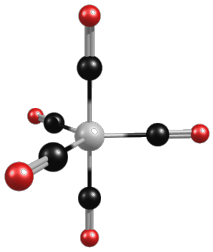
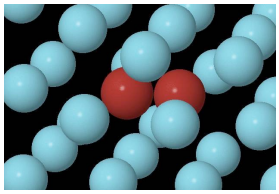
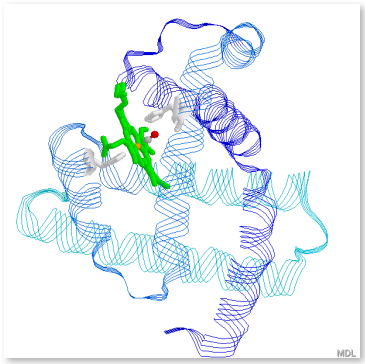
Universität Rostock Traditio et Innovatio

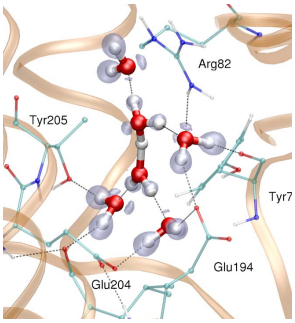
INSTITUT FÜR PHYSIK

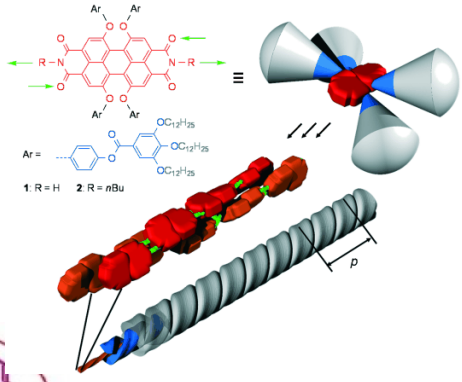
Lecture One:
Concepts of Molecular Physics

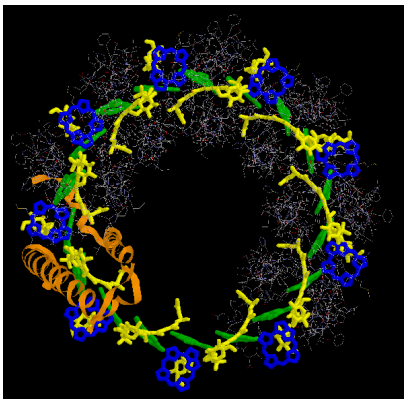
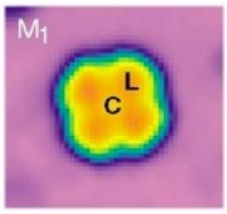
Oliver Kühn

The Molecular World

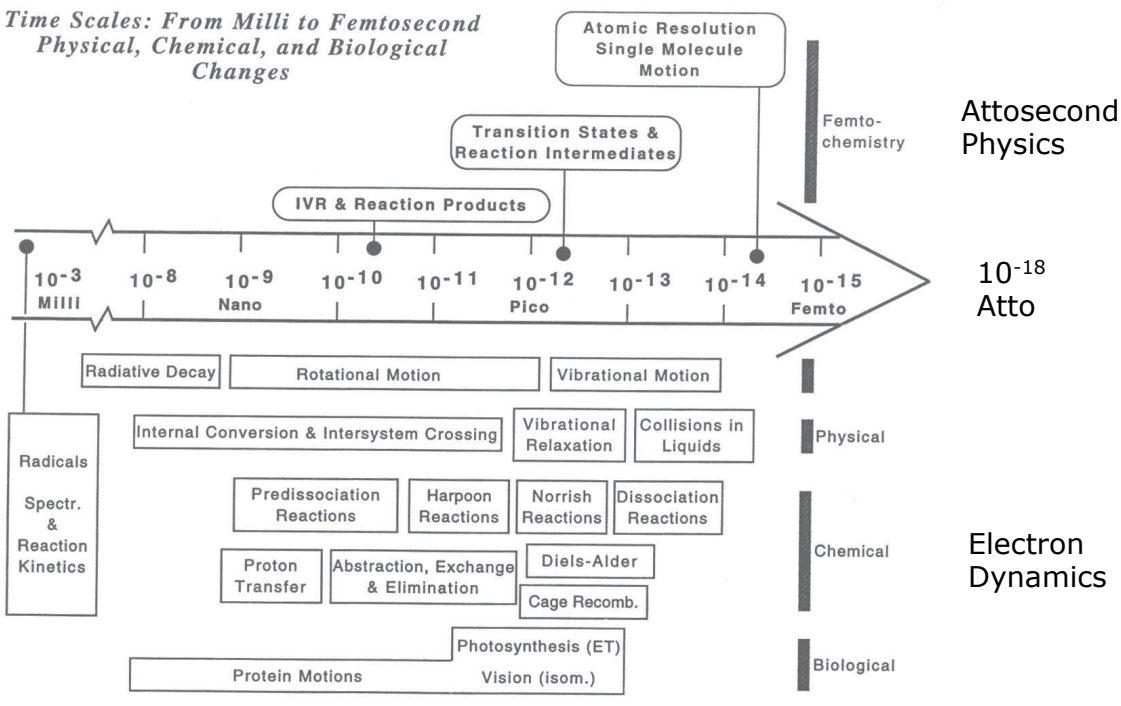




5

Time Scales



Attosecond Physics

10^{-18} Atto

Electron Dynamics

A.H. Zewail
Femtochemistry—Ultrafast Dynamics of the Chemical Bond, Vols. I and II, World Scientific, New Jersey, Singapore (1994)

6

Overview

- Born-Oppenheimer ansatz and potential energy surfaces
- electronic structure in a nutshell
- harmonic oscillators everywhere
- condensed phase models
- quantum dynamics, from coherent to incoherent

Born-Oppenheimer Ansatz

- molecular Hamiltonian

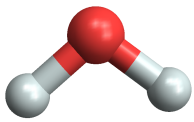
$$H_{\mathrm{mol}} = T_{\mathrm{el}} + V_{\mathrm{el-nuc}} + V_{\mathrm{el-el}} + T_{\mathrm{nuc}} + V_{\mathrm{nuc-nuc}}$$

kinetic energy

$$T_{\mathrm{el}} = \sum_{j=1}^{N_{\mathrm{el}}} \frac{\mathbf{p}_j^2}{2m_{\mathrm{el}}}$$

Coulomb interaction

$$V_{\mathrm{el-el}} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$



$(N_{\mathrm{el}}, \mathbf{r}_j, \mathbf{p}_j, m_{\mathrm{el}})$

$(N_{\mathrm{nuc}}, Z_A, \mathbf{R}_A, \mathbf{P}_A, M_A)$

- molecular Schrödinger equation

$$H_{\mathrm{mol}} \Psi_\lambda(r, R) = E_\lambda \Psi_\lambda(r, R) \quad \longrightarrow \quad m_{\mathrm{el}}/M_{\mathrm{A}} < 10^{-3}$$

- electronic Hamilton operator for fixed nuclei

$$H_{\mathrm{el}}(R) = T_{\mathrm{el}} + V_{\mathrm{el-nuc}}(R) + V_{\mathrm{el-el}}$$

- electronic Schrödinger equation: adiabatic electronic states

$$H_{\mathrm{el}}(R)\, \psi_a(r; R) = E_a(R)\, \psi_a(r; R)$$

- assuming a complete adiabatic basis
- ansatz for molecular wave function

$$\Psi(r;R) = \sum_a \chi_a(R)\,\psi_a(r;R)$$

- expansion coefficients are nuclear wavefunctions and obey

$$\left(T_{\rm nuc} + E_a(R) + V_{\rm nuc-nuc} + \Theta_{aa} - E\right)\,\chi_a(R) = -\sum_{b\neq a}\Theta_{ab}\chi_b(R)$$

- nonadiabaticity operator

$$\Theta_{ab} = \int dr\;\psi_a(r;R)\,T_{\rm nuc}\,\psi_b(r;R) + \sum_n \frac{1}{M_n}\left[\int dr\;\psi_a(r;R)\mathbf{P}_n\psi_b(r;R)\right]\mathbf{P}_n$$

- potential energy surfaces (PES)

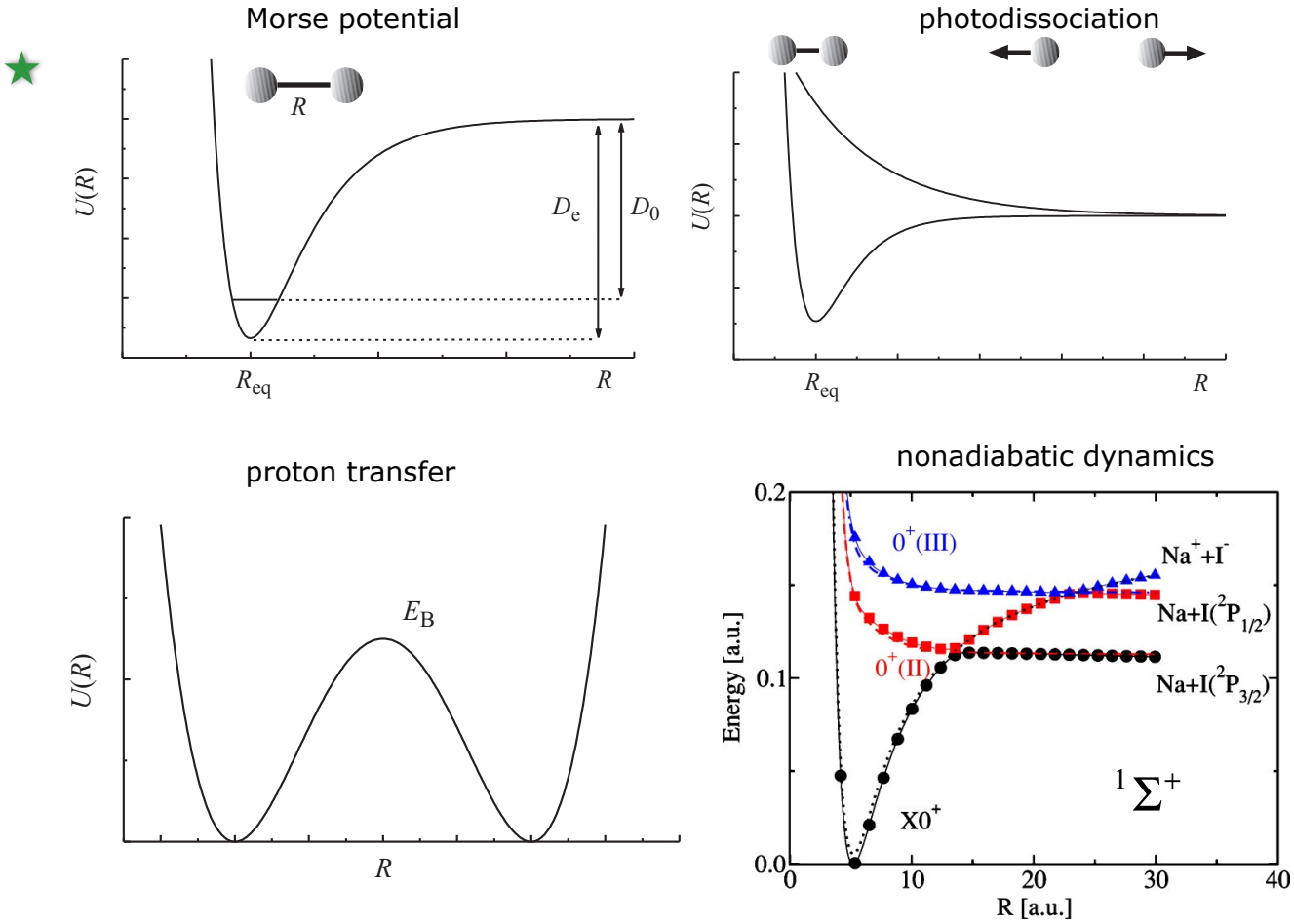
$$U_a(R) = E_a(R) + V_{\rm nuc-nuc}(R) + \Theta_{aa}$$

- PES: $3N_{\rm nuc}$-dimensional hypersurfaces
  - $3N_{\rm nuc}$-6 internal degrees of freedom (DOF) + 3 rotations + 3 translations
  - stationary points $\quad \nabla U_a(R)|_{R=R^{(a)}} = 0$

$$\nabla U_a(R) = \{\partial U_a(R)/\partial R_1, \ldots, \partial U_a(R)/\partial R_{3N_{\rm nuc}}\}$$

  - Hessian matrix $\quad \kappa^{(a)}_{mn} = \dfrac{\partial^2 U_a(R)}{\partial R_m \partial R_n} \quad (m,n = 1,\ldots,3N_{\rm nuc})$

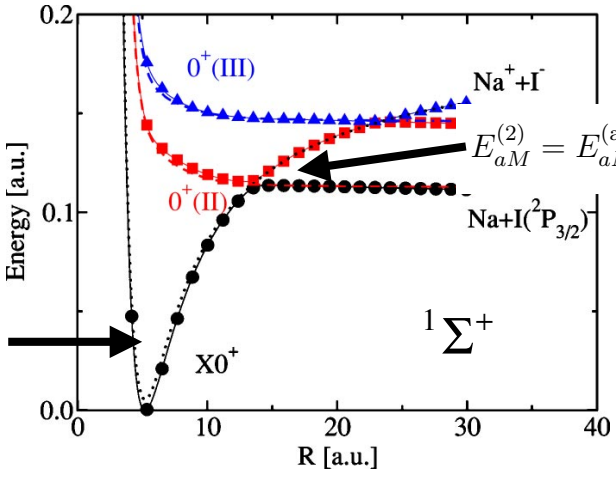
  - degeneracies of electronic states $\quad U_a(R) \approx U_b(R)$



- nonadiabatic effects & Born-Oppenheimer approximation

$$(T_{\rm nuc} + E_a(R) + V_{\rm nuc-nuc} + \Theta_{aa} - E)\ \chi_a(R) = -\sum_{b\neq a} \Theta_{ab}\chi_b(R)$$

$$\Theta_{ab} = \int dr\ \psi_a(r;R)\, T_{\rm nuc}\, \psi_b(r;R) + \sum_n \frac{1}{M_n}\left[\int dr\ \psi_a(r;R)\mathbf{P}_n\psi_b(r;R)\right]\mathbf{P}_n$$



$$E^{(2)}_{aM} = E^{(\rm adia)}_{aM} + \sum_{bN} \frac{|\langle\chi_{aM}|\Theta_{ab}|\chi_{bN}\rangle|^2}{E^{(\rm adia)}_{aM} - E^{(\rm adia)}_{bN}}$$

BO approximation

$\Theta_{ab} = 0$

adiabatic molecular wavefunction: $\Psi^{(\rm adia)}_{aM}(r;R) = \chi_{aM}(R)\psi_a(r;R)$

Electronic Structure in a Nutshell

- electronic Schrödinger equation for fixed nuclei

$$H_{\mathrm{el}}(R)\,\psi_a(r;R) = E_a(R)\,\psi_a(r;R)$$

  - wavefunction (Hartree-Fock, MPn, CI, MCSCF, CC etc.) and density (DFT) based methods

many particle state	single particle molecular orbital (MO)	linear combination of atomic orbitals (LCAO MO)

$$\psi_a(r;R) \quad \rightarrow \quad \varphi_i(r;R) = \psi_i(r;R)g(m_s) \quad \rightarrow \quad \sum_\mu C_{\mu i}\phi_\mu(\mathbf{r};\mathbf{R})$$

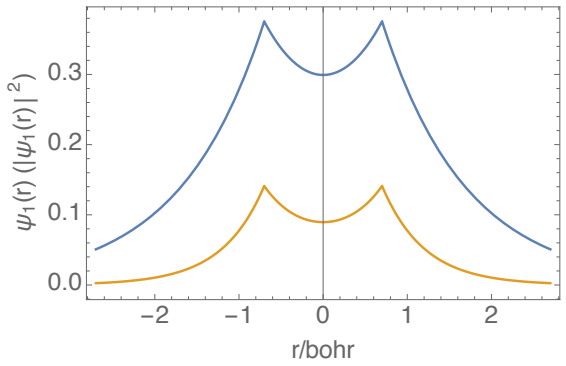
- illustration for H_2

- LCAO-MO approach (H_2)
  - minimal basis of one atomic 1s function per nucleus

$$\psi_i(r;R) = \sum_{\mu=1}^{2} C_{\mu i}\phi_\mu(\mathbf{r};\mathbf{R}) \qquad \longrightarrow \qquad \phi_\mu(\mathbf{r}-\mathbf{R}_\mu) = \frac{1}{\sqrt{\pi}}\,e^{-|\mathbf{r}-\mathbf{R}_\mu|}$$

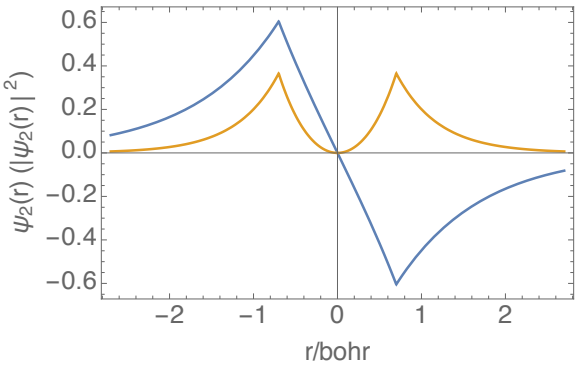
  - coefficients follow from linear variation principle

$\psi_1 = \sigma_g = [2(1+S_{12})]^{-1/2}\,(\phi_1+\phi_2)$



bonding MO

$\psi_2 = \sigma_u = [2(1-S_{12})]^{-1/2}\,(\phi_1-\phi_2)$

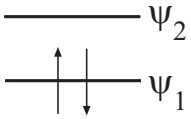


antibonding MO

- many-electron states
  - four possible spin-orbitals

$$\varphi_1(\mathbf{x}) = \psi_1(\mathbf{r})\alpha(m_s) \qquad \varphi_2(\mathbf{x}) = \psi_1(\mathbf{r})\beta(m_s) \qquad \varphi_3(\mathbf{x}) = \psi_2(\mathbf{r})\alpha(m_s) \qquad \varphi_4(\mathbf{x}) = \psi_2(\mathbf{r})\beta(m_s)$$

  - Pauli principle requires antisymmetric wavefunction
  - fulfilled if many-electron wavefunction is chosen as in Slater determinant form



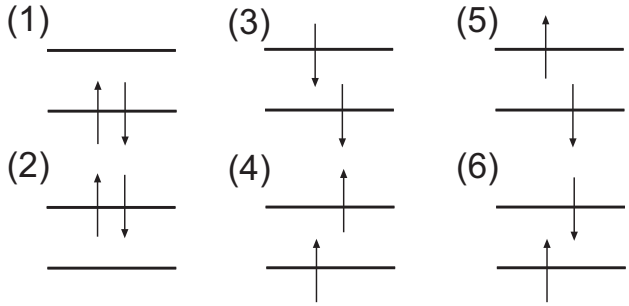
electronic ground state

$$\Psi_0(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}(\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) - \varphi_1(\mathbf{x}_2)\varphi_2(\mathbf{x}_1))$$

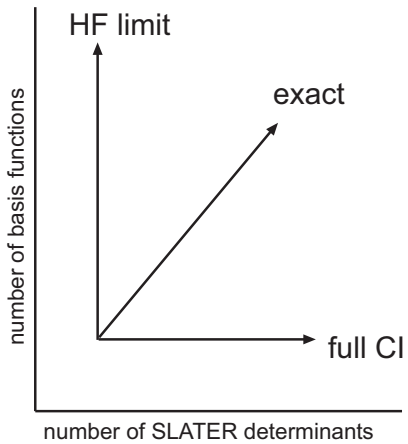
$$= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_2(\mathbf{x}_1) \\ \varphi_1(\mathbf{x}_2) & \varphi_2(\mathbf{x}_2) \end{vmatrix}$$

  - restriction to a single determinant description: Hartree-Fock theory

- excited determinants



- configuration interaction
  - correlation effects
  - electronically excited states



but…
number of configurations for *N* electrons and 2K spin orbitals

$$(2K)!/(N!(2K-N)!)$$

- ab initio wavefunction-based methods (selection)

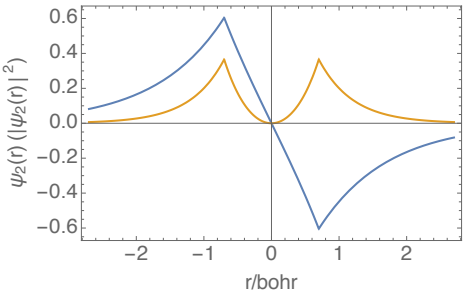
HF	CI	MCSCF
$\|\boldsymbol{\kappa}\rangle = \hat{U}(\boldsymbol{\kappa})\|0\rangle$	$\|\mathbf{C}\rangle = \sum_i C_i \|i\rangle$	$\|\boldsymbol{\kappa}, \mathbf{C}\rangle = \hat{U}(\boldsymbol{\kappa}) \sum_i C_i \|i\rangle$

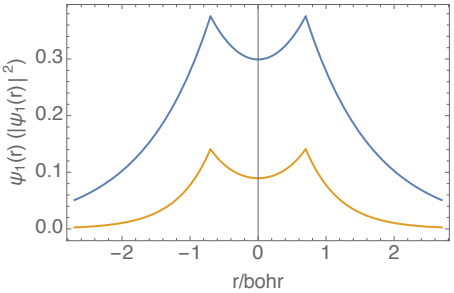
- density functional theory
  - energy functional of electron density (Hohenberg-Kohn)

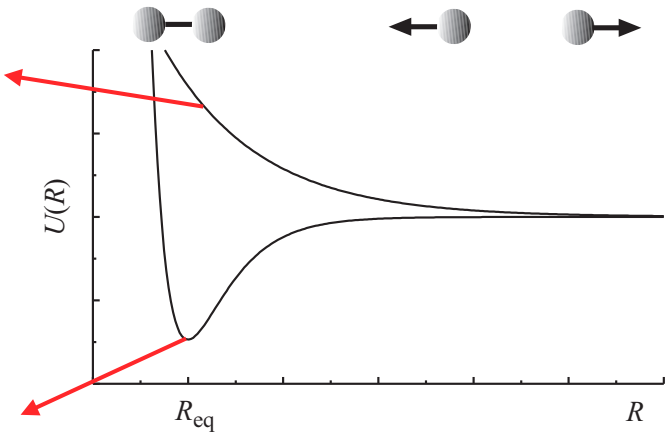
$$E[\rho] = e \int d^3\mathbf{x}\, V_{\mathrm{el-nuc}}(\mathbf{x})\, \rho(\mathbf{x}) + T_{\mathrm{el}}[\rho] + \frac{e^2}{2} \int d^3\mathbf{x}\, d^3\mathbf{x}'\, \frac{\rho(\mathbf{x})\rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} + E_{\mathrm{XC}}[\rho]$$

  - holy grail: exchange correlation functional
  - electronically excited states: linear response theory

- electronic states vs. potential energy curves







Harmonic Oscillators

- assumption: Born-Oppenheimer approximation is valid
- PES

$$U_a(R) = E_a(R) + V_{\mathrm{nuc-nuc}}(R) + \Theta_{aa}$$

- choice of internal coordinates depends on problem
  - reactive dynamics & floppy molecules: bond distances, angles, dihedrals - complicated kinetic energy
- close to equilibrium: harmonic approximation
  - small deviations w.r.t. geometry of stationary point

$$\Delta R_n^{(a)} = R_n^{(a)} - R_n \; (n = 1, \ldots, 3N_{\mathrm{nuc}})$$

  - Taylor expansion of PES

$$H_a = U_a(R^{(a)}) + \sum_{n=1}^{3N_{\mathrm{nuc}}} \frac{P_n^2}{2M_n} + \sum_{m,n=1}^{3N_{\mathrm{nuc}}} \frac{1}{2} \kappa_{mn}^{(a)} \Delta R_m^{(a)} \Delta R_n^{(a)}$$

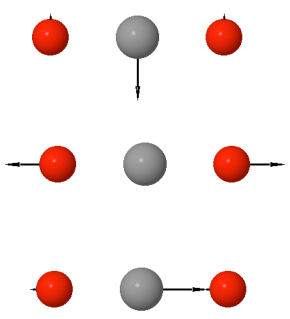
- diagonalization of Hessian by linear trafo to mass-weighted normal mode coordinates

$$\Delta R_n^{(a)} = \sum_{\xi} M_n^{-1/2} A_{n\xi}^{(a)} q_{a,\xi}$$

- normal mode Hamiltonian

$$H_a = U_a(q_{a,\xi} = 0) + H_a^{(\mathrm{nm})} \qquad H_a^{(\mathrm{nm})} = \frac{1}{2} \sum_{\xi} \left(p_\xi^2 + \omega_{a,\xi}^2 q_{a,\xi}^2 \right)$$

Normal Mode Vibrations of CO_2

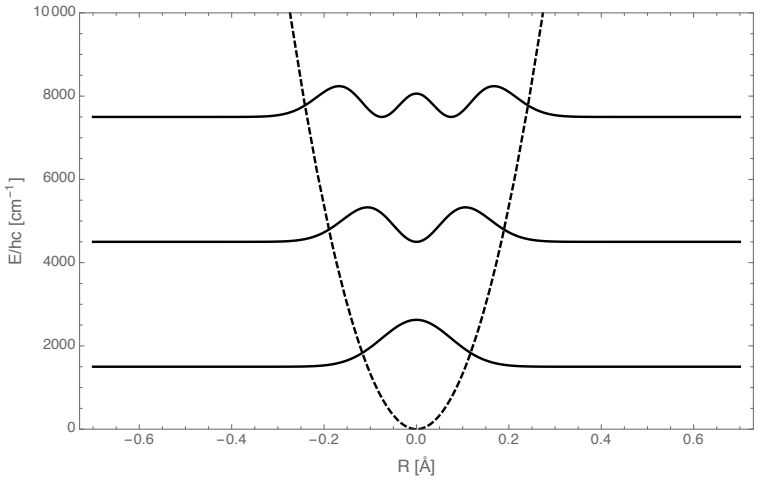


- eigenvalue problem for harmonic oscillators

$$H_a^{(\mathrm{nm})}\chi_{aN}(q) = E_{aN}\chi_{aN}(q) \qquad N = \{N_1, N_2, \ldots\}$$

$$E_{aN} = \sum_\xi \hbar\omega_{a,\xi}(N_\xi + \frac{1}{2}) \qquad N_\xi = 0, 1, 2, \ldots$$

$$\chi_{aN_\xi}(q_{a,\xi}) = \frac{\sqrt{\lambda_{a,\xi}}}{\sqrt{\sqrt{\pi}\, 2^{N_\xi}\, N_\xi!}} \exp\Big(-\frac{1}{2}\lambda_{a,\xi}^2 q_{a,\xi}^2 \Big)\; H_{N_\xi}(\lambda_{a,\xi}\, q_{a,\xi})$$



$$\lambda_{a,\xi}^2 = \omega_{a,\xi}/\hbar$$

- two electronic states:shifted oscillator model
  - different equilibrium positions

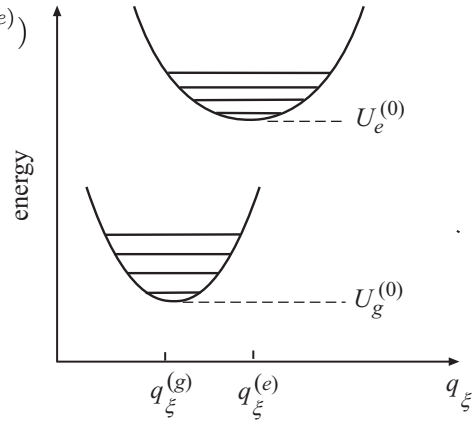
$$U_{a=g/e}(R) \to R^{(g/e)} \qquad U_e(R) = U_e(R^{(e)}) + \sum_{m,n=1}^{3N_{\mathrm{nuc}}} \frac{1}{2}\, \kappa_{mn}^{(e)}\, \Delta R_m^{(e)}\, \Delta R_n^{(e)}$$

  - assume same normal modes

$$\Delta R_n^{(e)} = R_n - R_n^{(g)} - (R_n^{(e)} - R_n^{(g)}) = \sum_\xi M_n^{-1/2} A_{n\xi}^{(g)} (q_\xi - q_\xi^{(e)})$$

  - general shifted oscillator Hamiltonian

$$H_a = U_a(q_\xi = q_\xi^{(a)}) + \frac{1}{2}\sum_\xi \Big(p_\xi^2 + \omega_{a,\xi}^2 (q_\xi - q_\xi^{(a)})^2 \Big)$$



$$\chi_{aN_\xi}(q_\xi) = \frac{\sqrt{\lambda_{a,\xi}}}{\sqrt{\sqrt{\pi}\, 2^{N_\xi}\, N_\xi!}} \exp\Big(-\frac{1}{2}\lambda_{a,\xi}^2 (q_\xi - q_\xi^{(a)})^2 \Big)\; H_{N_\xi}(\lambda_{a,\xi}(q_\xi - q_\xi^{(a)}))$$

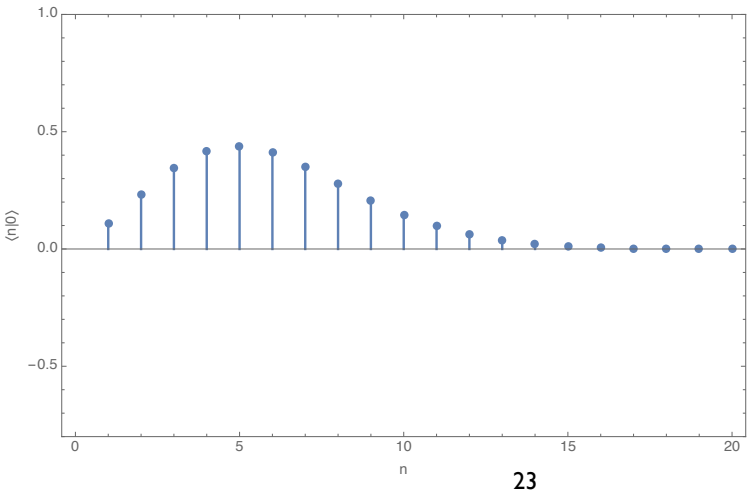
- Franck-Condon factor

$$\langle \chi_{aM} | \chi_{bN} \rangle = e^{-(\Delta g_{ab})^2/2} \sum_{m=0}^{M} \sum_{n=0}^{N} \frac{(-1)^n (\Delta g_{ab})^{m+n}}{m!n!} \times \sqrt{\frac{M!N!}{(M-m)!(N-n)!}} \delta_{M-m,N-n}$$

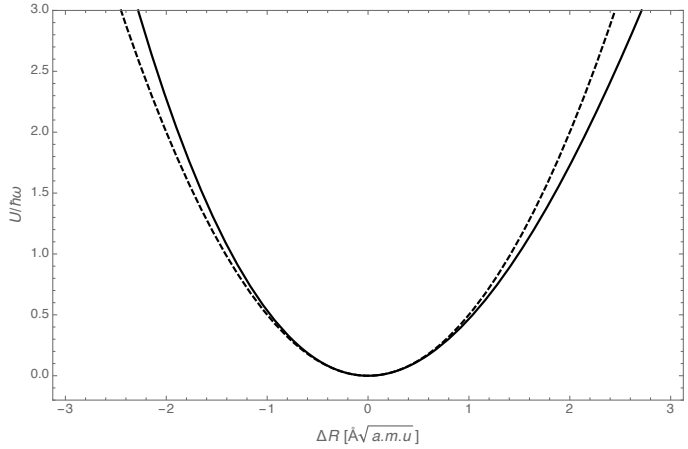
PES shift

$$\Delta g_{ab} = \sqrt{\frac{\omega_\xi}{2\hbar}} (q_\xi^{(b)} - q_\xi^{(b)})$$

  - special case: Poisson distribution $|\langle \chi_{aM} | \chi_{b0} \rangle|^2 = e^{-(\Delta g_{ab})^2} \frac{(\Delta g_{ab})^{2M}}{M!}$



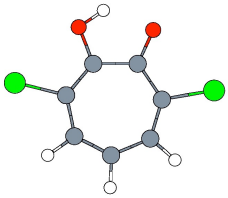
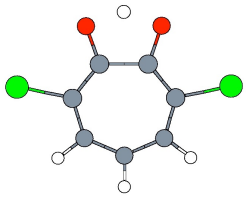
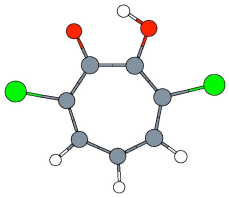
- anharmonic corrections
  - use normal mode coordinates to express higher order terms in the Taylor expansion



$$V^{(\mathrm{anh})} = \frac{1}{3!} \sum_{klm} K_{klm} q_k q_l q_m + \frac{1}{4!} \sum_{klmn} K_{klmn} q_k q_l q_m q_n + \dots$$

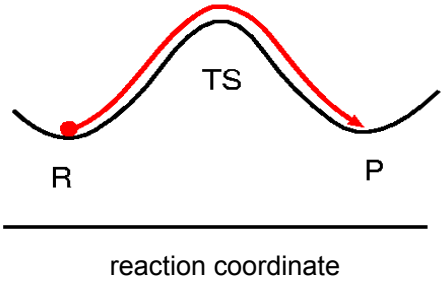
Reaction Surfaces

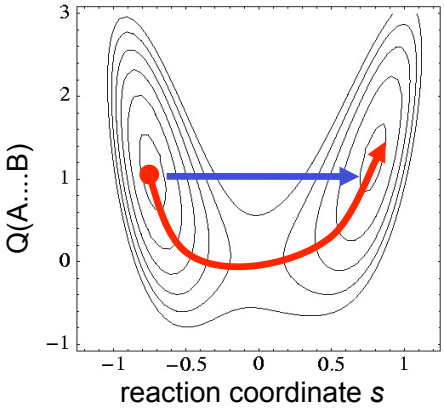
- combination of large amplitude and harmonic motion
- example: proton transfer

3,7-dichlorotropolone

A-H ...B ↦ A..H..B ↦ A...H-B





- divide nuclear DOF into active, ***s***, and spectator, ***Z***, coordinates
- expand w.r.t. a meaningful reference configuration

$$U(R) \approx U(\mathbf{s}, \mathbf{Z}^{(0)}) + \underbrace{\left(\frac{\partial U(\mathbf{s},\mathbf{Z})}{\partial \mathbf{Z}}\right)_{\mathbf{Z}=\mathbf{Z}^{(0)}}}_{-\mathbf{f}(\mathbf{s})} \Delta\mathbf{Z} + \frac{1}{2}\Delta\mathbf{Z}\underbrace{\left(\frac{\partial^2 U(\mathbf{s},\mathbf{Z})}{\partial \mathbf{Z}\partial \mathbf{Z}}\right)_{\mathbf{Z}=\mathbf{Z}^{(0)}}}_{\kappa(\mathbf{s})}\Delta\mathbf{Z}$$

- normal mode trafo

$$\Delta\mathbf{Z}(\mathbf{s}) = \mathbf{M}^{-1/2}\mathbf{A}\mathbf{q}$$

- reaction surface Hamiltonian

$$H = \mathbf{T_s} + U(\mathbf{s}, \mathbf{Z}^{(0)}) + \mathbf{T_q} + \frac{1}{2}\mathbf{q}\mathbf{K}(\mathbf{s})\mathbf{q} - \mathbf{F}(\mathbf{s})\mathbf{q}$$

mode mixing

forces on modes

$$\mathbf{K}(\mathbf{s}) = \mathbf{A}^{+}\mathbf{M}^{-1/2}\kappa(\mathbf{s})\mathbf{M}^{-1/2}\mathbf{A} \qquad \mathbf{F}(\mathbf{s}) = \mathbf{f}(\mathbf{s})\mathbf{M}^{-1/2}\mathbf{A}$$

(re)active system — spectator modes

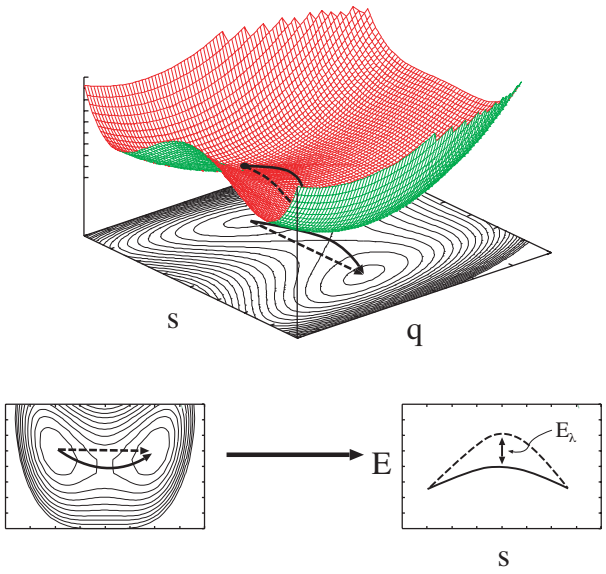
$$H = \mathbf{T_s} + U(\mathbf{s}, \mathbf{Z}^{(0)}) - E_{\mathrm{reorg}}(\mathbf{s}) + \mathbf{T_q} + \frac{1}{2}(\mathbf{q} - \mathbf{q}^{(0)}(\mathbf{s}))\mathbf{K}(\mathbf{s})(\mathbf{q} - \mathbf{q}^{(0)}(\mathbf{s}))$$

reorganization energy

$$E_{\mathrm{reorg}}(\mathbf{s}) = \frac{1}{2}\mathbf{q}^{(0)}(\mathbf{s})\mathbf{K}(\mathbf{s})\mathbf{q}^{(0)}(\mathbf{s})$$

displacements

$$\mathbf{q}^{(0)}(\mathbf{s}) = -[\mathbf{K}(\mathbf{s})]^{-1}\,\mathbf{F}(\mathbf{s})$$



Coupled Electronic States

- consider two-state one coordinate (curve-crossing) system
  - adiabatic representation (dynamic coupling)

$$\mathbf{H}^{\mathrm{ad}} = \begin{pmatrix} T_{\mathrm{nuc}} & \Theta_{+-} \\ \Theta_{+-} & T_{\mathrm{nuc}} \end{pmatrix} + \begin{pmatrix} U_+(R) & 0 \\ 0 & U_-(R) \end{pmatrix} \qquad \mathbf{H}^{\mathrm{ad}} \begin{pmatrix} \chi_+ \\ \chi_- \end{pmatrix} = E \begin{pmatrix} \chi_+ \\ \chi_- \end{pmatrix}$$

  - diabatic representation (static coupling)

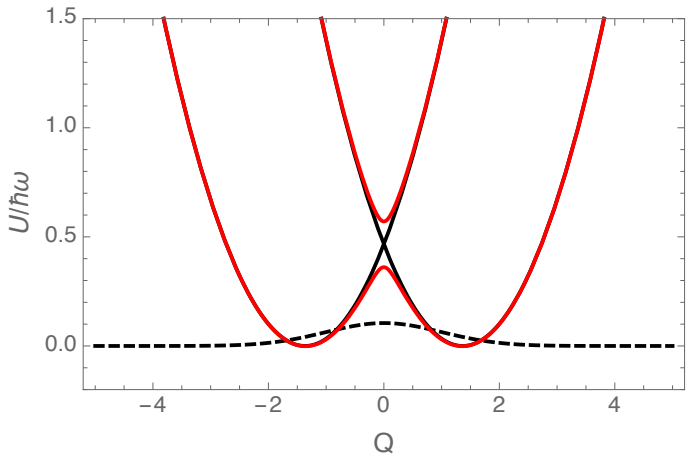
$$\mathbf{H}^{\mathrm{d}} = \begin{pmatrix} T_{\mathrm{nuc}} & 0 \\ 0 & T_{\mathrm{nuc}} \end{pmatrix} + \begin{pmatrix} U_1^{\mathrm{d}}(R) & V_{12}(R) \\ V_{12}(R) & U_2^{\mathrm{d}}(R) \end{pmatrix} \qquad \mathbf{H}^{\mathrm{d}} \begin{pmatrix} \chi_1^{\mathrm{d}} \\ \chi_2^{\mathrm{d}} \end{pmatrix} = E \begin{pmatrix} \chi_1^{\mathrm{d}} \\ \chi_2^{\mathrm{d}} \end{pmatrix}$$

  - related via an orthogonal transformation

$$\begin{pmatrix} \chi_+ \\ \chi_- \end{pmatrix} = \mathbf{C} \begin{pmatrix} \chi_1^{\mathrm{d}} \\ \chi_2^{\mathrm{d}} \end{pmatrix} \qquad \mathbf{C} = \begin{pmatrix} \cos\gamma(R) & \sin\gamma(R) \\ -\sin\gamma(R) & \cos\gamma(R) \end{pmatrix}$$

$$\text{mixing angle} \quad \gamma(R) = \frac{1}{2}\arctan\left(\frac{2|V_{12}(R)|}{|U_1^{\mathrm{d}}(R) - U_2^{\mathrm{d}}(R)|}\right)$$

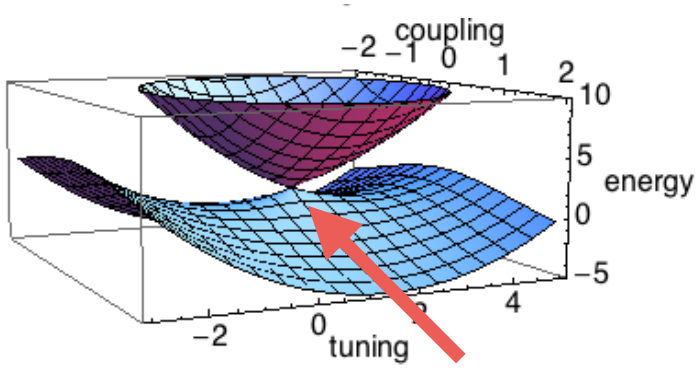
- diabatic vs. adiabatic representation



$$U_{\pm}(R) = \frac{1}{2}\left(U_1^{\mathrm{d}}(R) + U_2^{\mathrm{d}}(R) \pm \sqrt{[U_1^{\mathrm{d}}(R) - U_2^{\mathrm{d}}(R)]^2 + 4|V_{12}(R)|^2} \right)$$

- diabatic states can cross
- adiabatic crossing requires diabatic crossing and vanishing coupling
- non-crossing rule: adiabatic states of the same symmetry do not cross

- vibronic coupling model



conical intersection

$$H_{\mathrm{mol}} = \sum_{ab} \left(\delta_{ab} H_a(R) + (1 - \delta_{ab}) V_{ab}(R)\right) |\psi_a\rangle\langle\psi_b|$$

$$H_0 = \frac{1}{2} \sum_{\xi} \left(p_\xi^2 + \omega_\xi^2 q_\xi^2 \right)$$

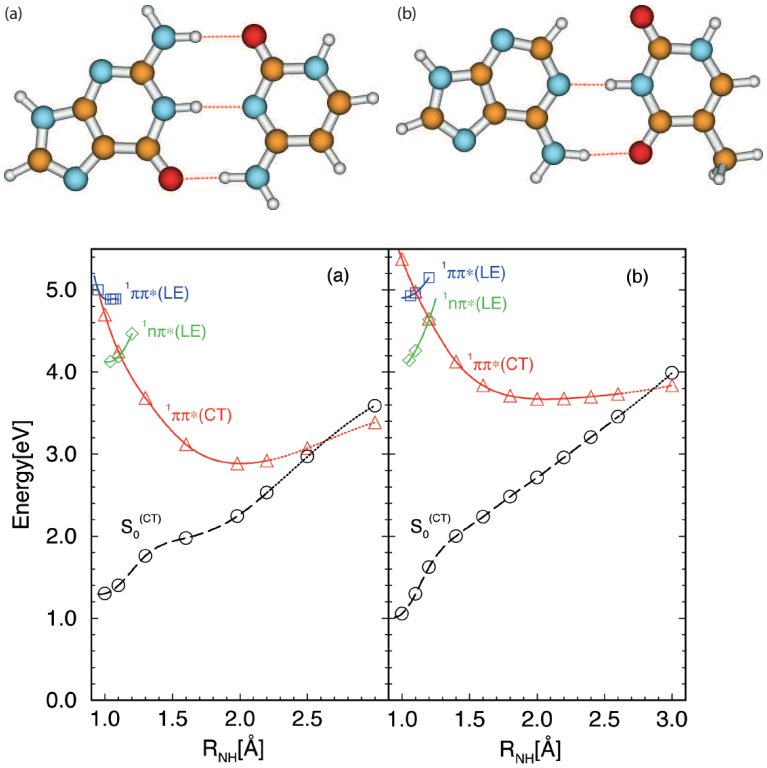
$$H_{a>0}(q_\xi) = H_0 + E_a + \sum_{\xi} \kappa_\xi^{(a)} q_\xi + \ldots$$

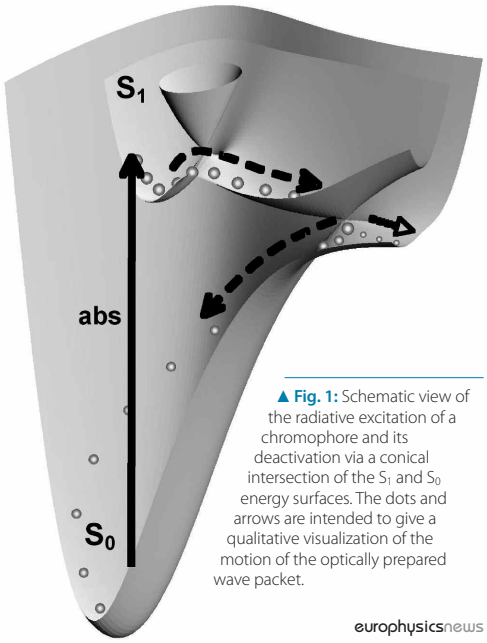
- tuning modes

$$V_{ab}(q_\xi) = V_{ab}(q_\xi = 0) + \sum_{\xi} \lambda_\xi^{(ab)} q_\xi + \ldots$$

- coupling modes

- example: photostability of life





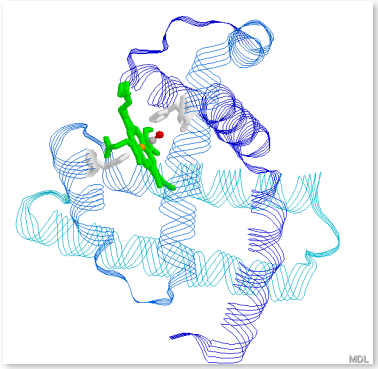
▲ **Fig. 1:** Schematic view of the radiative excitation of a chromophore and its deactivation via a conical intersection of the S_1 and S_0 energy surfaces. The dots and arrows are intended to give a qualitative visualization of the motion of the optically prepared wave packet.

europhysicsnews

Sobolewski, Domcke, Europhys. News 37, 20 (2006)

Molecules in the Condensed Phase

- examples:
  - solute-solvent system
  - host-guest solid state
  - chromophores in biomolecules



potentials

QM, MM, QM/MM

on-the-fly

a priori PES, models

trajectories

classical, quasi-classical, semiclassical

quantum propagation

wavefunction, reduced density

- from PES to classical force fields
  - Newton's equation for classical nuclei

$$M_A \frac{d^2\mathbf{R}}{dt^2} = -\nabla_A U(\{\mathbf{R}(t)\})$$

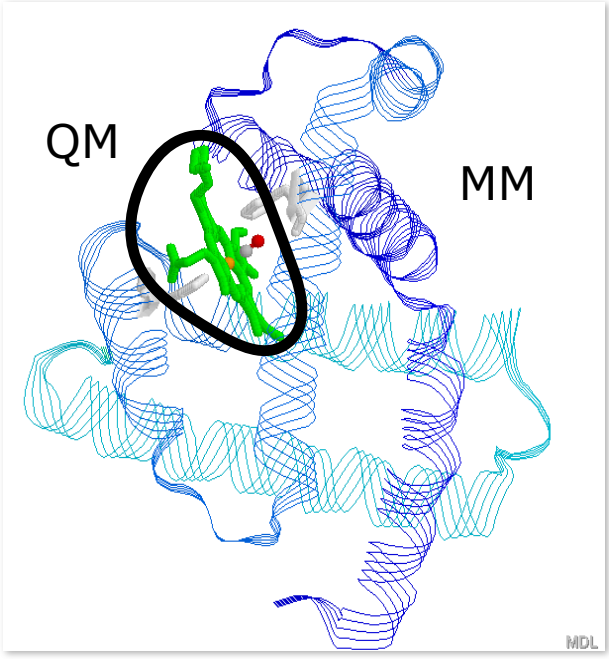
  - ab initio Born-Oppenheimer Molecular Dynamics (AIMD)
  - Molecular Mechanics (MM) force fields

$$U(\{\mathbf{R}\}) \approx \sum_A v_1(\mathbf{R}_A) + \sum_{A<B} v_2(\mathbf{R}_A, \mathbf{R}_B) + \ldots$$

Bonded: $\sum K_b(b-b_0)^2$; $\sum K_\theta(\theta-\theta_0)^2$; $\sum V_n\left[1-\cos(n\phi-\phi_n^0)\right]$; $\sum K_\chi \chi^2$; $\sum K_{b\theta}(b-b_0)^2(\theta-\theta_0)^2$

Nonbonded: Electrostatic $\sum \frac{q_i q_j}{\varepsilon r_{ij}}$; Repulsion-dispersion $\sum \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^{6}}$

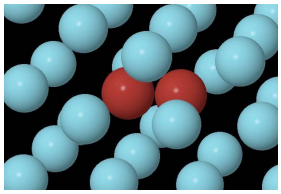
- Quantum Mechanics/Molecular Mechanics (QM/MM) method



- Quantum Mechanics: System-Bath models
  - recall reaction surface Hamiltonian

$$H = \underbrace{\mathbf{T_s} + U(\mathbf{s}, \mathbf{Z}^{(0)})}_{\text{relevant system}} + \underbrace{\mathbf{T_q} + \frac{1}{2}\mathbf{q}\mathbf{K}(\mathbf{s})\mathbf{q}}_{\text{bath}} - \underbrace{\mathbf{F}(\mathbf{s})\mathbf{q}}_{\text{system-bath coupling}}$$

  - spectrum of bath modes arbitrary



  - Caldeira-Leggett model

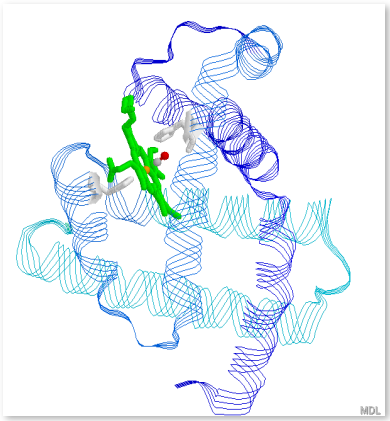
$$H = H_{\mathrm{S}} + \frac{1}{2}\sum_{\xi}[p_\xi^2 + \omega_\xi^2 q_\xi^2] + s\sum_{\xi} c_\xi q_\xi$$

  - fluctuating force picture

$$H = H_{\mathrm{S}} + \delta H_{\mathrm{S}}(t)$$

  - stochastic models (Kubo, Haken-Strobl-Reineker)

$$\langle \delta H_{\mathrm{S}}(t)\delta H_{\mathrm{S}}(0)\rangle_{\mathrm{bath}} = f(t)$$



Quantum Dynamics: Schrödinger Equation

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

- standard approach
  - formal solution via time evolution operator

$$|\Psi(t)\rangle = U(t)|\Psi(0)\rangle \qquad U(t) = e^{-iHt/\hbar}$$

  - if eigenstates are known

$$H|a\rangle = E_a|a\rangle \qquad |\Psi(t)\rangle = \sum_a c_a(t)|a\rangle \quad \rightarrow c_a(t) = c_a(0)e^{-iE_at/\hbar}$$

  - if eigenstates are unknown, but some meaningful basis exists

$$|\Psi(t)\rangle = \sum_n c_n(t)|n\rangle \qquad i\hbar\frac{dc_n(t)}{dt} = \sum_m H_{nm}c_m(t)$$

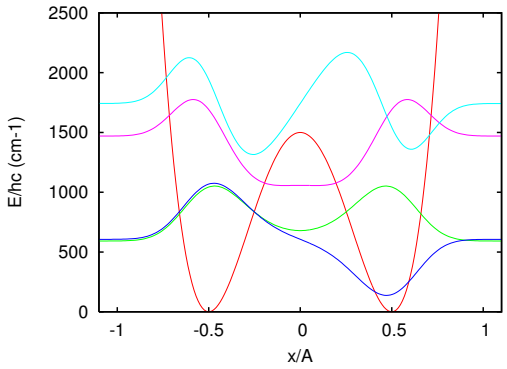
  - follows from Dirac-Frenkel variational principle

$$\langle\delta\Psi|H - i\hbar\frac{\partial}{\partial t}|\Psi\rangle = 0$$

- Simple example: Dynamics in a double well

$$V(x) = \frac{E_{barrier}}{x_0^4}(x - x_0)^2(x + x_0)^2$$

$$\Psi_{L/R}(x;0) = \frac{1}{\sqrt{2}}\left(\phi_0(x) \pm \phi_1(x)\right)$$

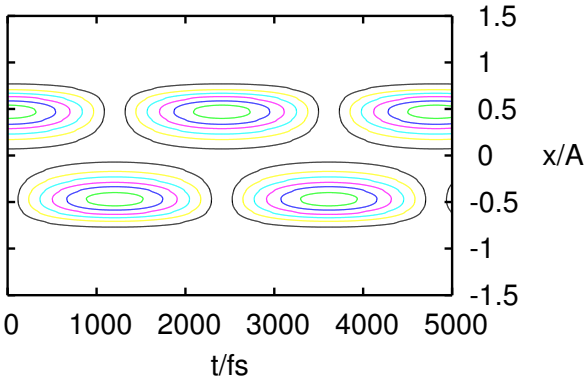


$$|\Psi_{L/R}(x;t)|^2 = \frac{1}{2}\left(e^{-iE_0t/\hbar}\phi_0(x) \pm e^{-iE_1t/\hbar}\phi_1(x)\right)\left(e^{iE_0t/\hbar}\phi_0^*(x) \pm e^{iE_1t/\hbar}\phi_1^*(x)\right)$$

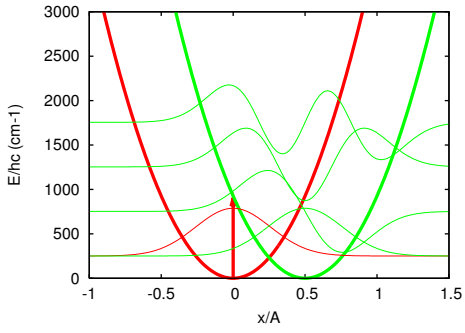
$$= \frac{1}{2}\left(|\phi_0(x)|^2 + |\phi_1(x)|^2\right) \pm \phi_0(x)\phi_1(x)\cos((E_1 - E_0)t/\hbar)$$

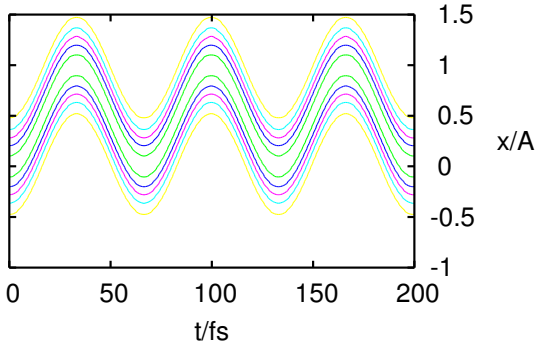
- tunneling frequency

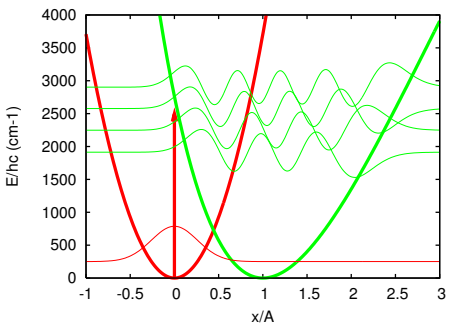
$$\omega_{10} = 2\pi\nu_{10} = 2\pi/\tau_{10} = (E_1 - E_0)/\hbar$$

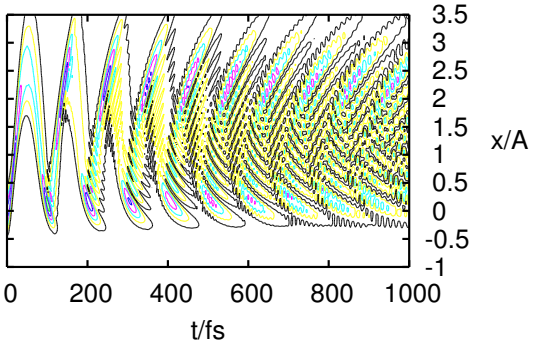


- harmonic vs. Morse oscillator









- wave packet dephasing

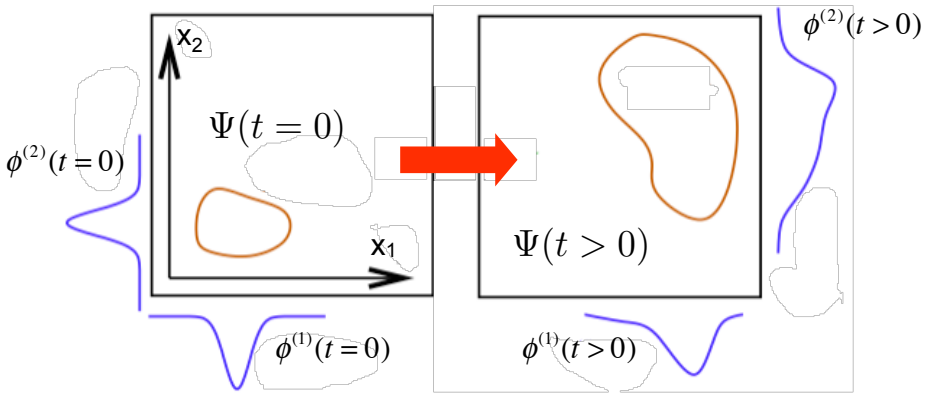
- multi-dimensional extension (*f* DOF)

$$\Psi(x_1,\dots x_f,t)=\sum_{j_1=1}^{N_1}\cdots\sum_{j_f=1}^{N_f}C_{j_1\dots j_f}(t)\,\phi_{j_1}^{(1)}(x_1)\cdots\phi_{j_f}^{(f)}(x_f)$$

$$i\hbar\dot{C}_{j_1,\dots,j_f}=\sum_{k_1,\dots,k_f}\langle\phi_{j_1}^{(1)}\dots\phi_{j_f}^{(f)}|H|\phi_{k_1}^{(1)}\dots\phi_{k_f}^{(f)}\rangle C_{k_1,\dots,k_f}$$

  - example: *f*=6, *N*=20 there are 20^6=64x10^6 basis functions
  - requires 3GB of memory for propagation
  - dimensionality bottleneck

- (partial) solution: time-dependent basis functions



$$\Psi(x_1,\dots,x_f;t)=\underbrace{\phi^{(1)}(x_1;t)\times\dots\times\phi^{(f)}(x_f;t)}_{\text{Hartree product}}$$

- application to reaction surface Hamiltonian

$$H=H_S+\frac{1}{2}\sum_\xi[p_\xi^2+\omega_\xi^2q_\xi^2]+\sum_\xi F_\xi(s)q_\xi$$

- coupled equations of motion (via Frenkel-Dirac principle)
  - active coordinate

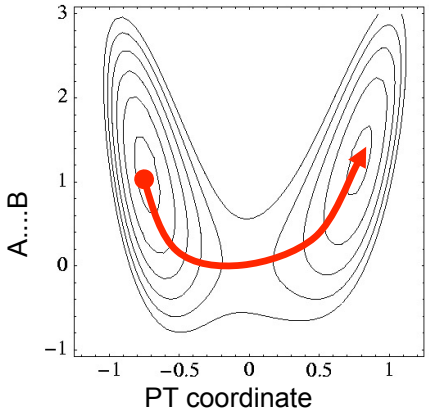
$$i\hbar\frac{\partial}{\partial t}\phi(s,t) = [T_s + V_{\rm SCF}(s,t)]\phi(s,t)$$

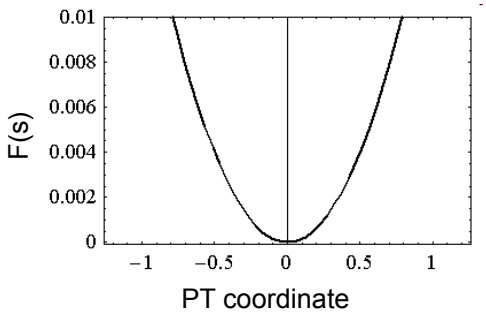
  - spectator modes = driven oscillators

$$i\hbar\frac{\partial}{\partial t}\phi(q_\xi,t) = \big[\frac{p_\xi^2}{2} + \frac{1}{2}\omega_\xi^2 q_\xi^2 - \bar{F}_\xi(t)q_\xi\big]\phi(q_\xi,t)$$

  - mean fields

$$\bar{F}_\xi(t) = \int ds\, \phi^*(s;t)F_\xi(s)\phi(s;t)$$





41

- multi-configuration time-dependent Hartree (MCTDH) approach (**Heidelberg group**, H.D. Meyer, L. Cederbaum and coworkers)

$$\Psi(\mathbf{x};t) = \sum_{j_1\ldots j_f} A_{j_1,\ldots,j_f}(t)\,\phi_{j_1}^{(1)}(x_1;t)\times\ldots\times\phi_{j_f}^{(f)}(x_f;t) = \sum_J A_J(t)\Phi_J(\mathbf{x};t)$$

  - time-dependent compact basis
  - optimal representation of moving with wave packet
  - correlations included via superposition of Hartree products
  - high-dimensional dynamics via multi-layer extension (ML-MCTDH)
  - coupled equations of motion from Dirac-Frenkel principle

coefficient vector: $i\hbar\dot{A}_J = \sum_K H_{JK}A_K$

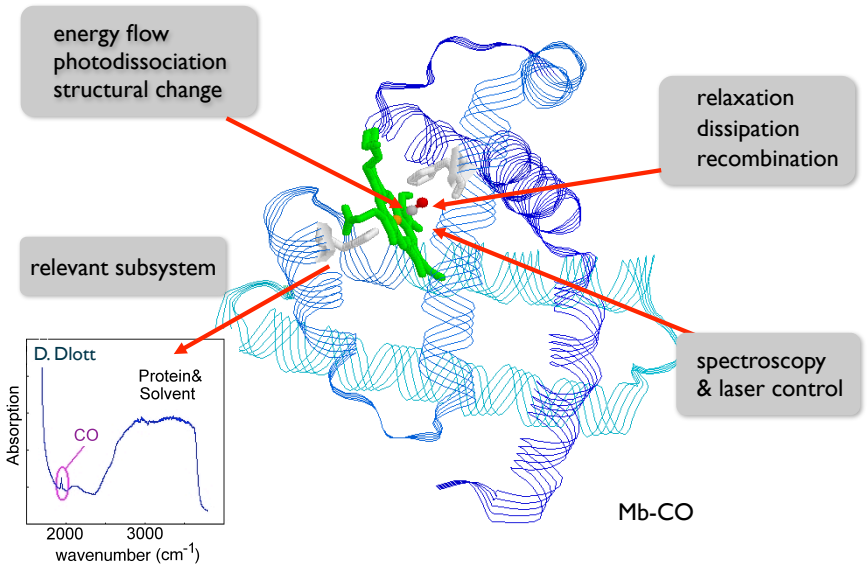
vector of single particle functions: $\bar{\phi}^{(\kappa)} = (\phi_1^{(\kappa)},\ldots,\phi_{n_\kappa}^{(\kappa)})^T$

$$i\hbar\dot{\bar{\phi}}^{(\kappa)} = (1-P^{(\kappa)})(\rho^{(\kappa)})^{-1}\mathcal{H}^{(\kappa)}\bar{\phi}^{(\kappa)}$$

42

Dissipative Quantum Dynamics

elementary processes in complex systems



- system-bath (reservoir) situation

- system-bath Hamiltonian

$$H = H_{\mathrm{S}} + H_{\mathrm{S-R}} + H_{\mathrm{R}}$$

- system defined by observable

$$\langle O \rangle(t) = \int ds\, dZ\, \Psi^*(s, Z, t) O(s) \Psi(s, Z, t) \equiv \mathrm{tr}_{\mathrm{S+R}}\{W(t) O\}$$

- introduction of reduced density operator

$$\rho(s, \bar{s}, t) = \int dZ\, \Psi^*(s, Z, t) \Psi(\bar{s}, Z, t) \quad \rightarrow \quad \rho(t) = \mathrm{tr}_{\mathrm{R}}\{W(t)\}$$

$$\langle O \rangle(t) = \int ds\, [O(\bar{s}) \rho(s, \bar{s}, t)]_{s=\bar{s}} = \mathrm{tr}_{\mathrm{S}}\{\rho(t) O\}$$

- Liouville-von Neumann equation for total statistical operator

$$\frac{\partial}{\partial t} W(t) = -\frac{i}{\hbar} [H, W(t)]$$

- derivation of the Quantum Master Equation (QME)
  - interaction representation

$$U_0(t-t_0) = \exp\Big(-\frac{i}{\hbar}H_{\rm S}(t-t_0)\Big)\ \exp\Big(-\frac{i}{\hbar}H_{\rm R}(t-t_0)\Big)$$

$$W^{(\rm I)}(t) = U_0^{+}(t-t_0)W(t)U_0(t-t_0)$$

$$\frac{\partial}{\partial t}W^{(\rm I)}(t) = -\frac{i}{\hbar}[H^{(\rm I)}_{\rm S-R}(t), W^{(\rm I)}(t)]$$

  - equation of motion for reduced density density operator

$$\frac{\partial}{\partial t}\rho^{(\rm I)}(t) = -\frac{i}{\hbar}{\rm tr}_{\rm R}\Big\{[H^{(\rm I)}_{\rm S-R}(t), W^{(\rm I)}(t)]\Big\}$$

  - equation not closed, use perturbation theory based on formal solution

$$W^{(\rm I)}(t) = W^{(\rm I)}(t_0) - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ \Big[H^{(\rm I)}_{\rm S-R}(t'), W^{(\rm I)}(t')\Big]$$

  - assumptions: factorized S-R coupling & bath stays in equilibrium

$$W^{(\rm I)}(t) = \rho^{(\rm I)}(t)\otimes R_{\rm eq} \qquad R_{\rm eq} = e^{-H_{\rm R}/k_{\rm B}T}/{\rm tr}_{\rm R}\{e^{-H_{\rm R}/k_{\rm B}T}\}$$

$$H_{\rm S-R} = \sum_u K_u\Phi_u \qquad \langle\Phi_u\rangle_{\rm R} = 0$$

  - second-order EOM for reduced density operator

$$\frac{\partial}{\partial t}\rho^{(\rm I)}(t) = -\frac{1}{\hbar^2}\int_{t_0}^{t} dt'\ {\rm tr}_{\rm R}\Big\{[H^{(\rm I)}_{\rm S-R}(t), [H^{(\rm I)}_{\rm S-R}(t'), R_{\rm eq}\rho^{(\rm I)}(t')]]\Big\}$$

  - four terms due to commutators

$$\begin{aligned}\frac{\partial}{\partial t}\rho^{(\rm I)}(t) \;=\; -\sum_{uv}\int_{t_0}^{t} dt'\ \Big(&C_{uv}(t-t')[K^{(\rm I)}_u(t), K^{(\rm I)}_v(t')\rho^{(\rm I)}(t')]\\ &-C_{vu}(-t+t')[K^{(\rm I)}_u(t), \rho^{(\rm I)}(t')K^{(\rm I)}_v(t')]\Big)\end{aligned}$$

  - correlation function of bath fluctuations

$$C_{uv}(t) = \frac{1}{\hbar^2}\langle\Delta\Phi_u(t)\Delta\Phi_v(0)\rangle_{\rm R} = \frac{1}{\hbar^2}\langle\Phi^{(\rm I)}_u(t)\Phi^{(\rm I)}_v(0)\rangle_{\rm R} - \frac{1}{\hbar^2}\langle\Phi_u\rangle_{\rm R}\langle\Phi_v\rangle_{\rm R}$$

- EOM in Schrödinger representation

$$\frac{\partial}{\partial t}\rho = -\frac{i}{\hbar}[H_{\rm S},\rho] + \left(\frac{\partial\rho}{\partial t}\right)_{\rm diss}$$

$$\left(\frac{\partial\rho}{\partial t}\right)_{\rm diss} = -\sum_{u,v}\int_0^{t-t_0} d\tau\Big(C_{uv}(\tau)\Big[K_u, U_{\rm S}(\tau)K_v\rho(t-\tau)U_{\rm S}^{+}(\tau)\Big] - C_{vu}(-\tau)\Big[K_u, U_{\rm S}(\tau)\rho(t-\tau)K_vU_{\rm S}^{+}(\tau)\Big]\Big)$$

- r.h.s. contains free and dissipative evolution
- retarded time argument leads to memory effects: non-Markovian dynamics
- memory time determined by bath correlation function, usually

$$C_{uv}(\tau) \propto \exp(-\tau/\tau_{\rm mem})$$

- Markov approximation ($C_{uv}(\tau) \propto \delta(\tau)$)

$$\begin{aligned}\rho(t-\tau) &= U_{\rm S}(t-\tau-t_0)\rho^{(\rm I)}(t-\tau)U_{\rm S}^{+}(t-\tau-t_0)\\ &\approx U_{\rm S}(-\tau)U_{\rm S}(t-t_0)\rho^{(\rm I)}(t)U_{\rm S}^{+}(t-t_0)U_{\rm S}^{+}(-\tau) = U_{\rm S}^{+}(\tau)\rho(t)U_{\rm S}(\tau)\end{aligned}$$

- Quantum Master Equation (QME)

$$\left(\frac{\partial\rho}{\partial t}\right)_{\rm diss} = -\sum_{u,v}\int_0^{\infty} d\tau\,\Big\{C_{uv}(\tau)\,\big[K_u, K_v^{(\rm I)}(-\tau)\rho(t)\big]_- - C_{vu}(-\tau)\,\big[K_u,\rho(t)K_v^{(\rm I)}(-\tau)\big]_-\Big\}$$

$$C_{uv}(t) = \frac{1}{\hbar^2}\langle\Delta\Phi_u(t)\Delta\Phi_v(0)\rangle_{\rm R} \qquad K_v^{(\rm I)}(-\tau) = U_{\rm S}(\tau)K_vU_{\rm S}^{+}(\tau)$$

- beyond the Markovian and perturbative QME
  - path integral method
  - hierarchy equations of motion

- multi-level Redfield equations
  - eigenstates of the relevant system $H_{\rm S}|a\rangle = E_a|a\rangle$

$$\left(\frac{\partial\rho}{\partial t}\right)_{\rm diss} = -\sum_{u,v}\int_0^\infty d\tau\,\left\{C_{uv}(\tau)\left[K_u, K_v^{(\rm I)}(-\tau)\rho(t)\right]_- - C_{vu}(-\tau)\left[K_u, \rho(t)K_v^{(\rm I)}(-\tau)\right]_-\right\}$$

$$\left(\frac{\partial\rho_{ab}}{\partial t}\right)_{\rm diss.} = -\sum_{cd} R_{ab,cd}\rho_{cd}(t)$$

  - Redfield relaxation tensor

$$R_{ab,cd} = \delta_{ac}\sum_e \Gamma_{be,ed}(\omega_{de}) + \delta_{bd}\sum_e \Gamma_{ae,ec}(\omega_{ce}) - \Gamma_{ca,bd}(\omega_{db}) - \Gamma_{db,ac}(\omega_{ca})$$

  - damping matrix

$$\Gamma_{ab,cd}(\omega) = {\rm Re}\sum_{u,v} K_{ab}^{(u)} K_{cd}^{(v)} \int_0^\infty d\tau\; e^{i\omega\tau} C_{uv}(\tau)$$

- harmonic oscillator bath (Caldeira-Leggett model)

$$H_{\rm R} = \sum_\xi \frac{\hbar\omega_\xi}{2}\Big(-\frac{\partial^2}{\partial Q_\xi^2} + Q_\xi^2\Big) \qquad (Q_\xi = x_\xi/\sqrt{\hbar/m_\xi\omega_\xi})$$

$$H_{\rm S-R} = K(s)\sum_\xi \hbar\omega_\xi g_\xi Q_\xi$$

  - correlation function

$$C(t) = \sum_\xi \omega_\xi^2 S_\xi([(1+n(\omega_\xi)]e^{-i\omega_\xi t} + n(\omega_\xi)e^{i\omega_\xi t}) \qquad S_\xi = g_\xi^2/2$$

$$C(\omega) = 2\pi\omega^2[1+n(\omega_\xi)][J(\omega) - J(-\omega)]$$

  - spectral density

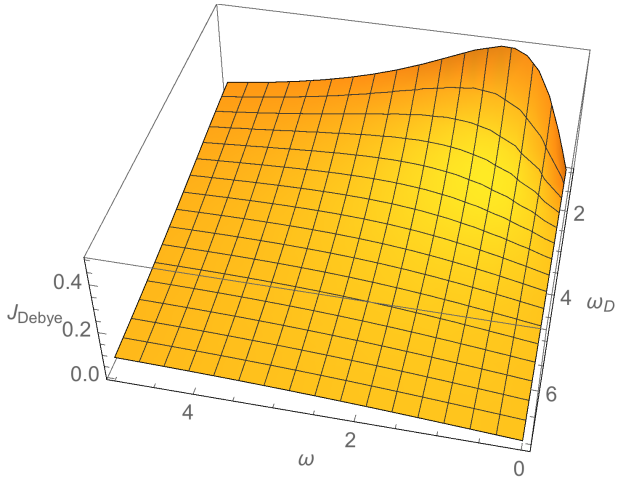
$$J(\omega) = \sum_\xi S_\xi\delta(\omega-\omega_\xi)$$

$$C(t) = \int_0^\infty d\omega\left(\cos(\omega t)\coth\left(\frac{\hbar\omega}{2k_{\rm B}T}\right) - i\sin(\omega t)\right)\omega^2 J(\omega)$$

- model spectral densities
  - Ohmic spectral density with cut-off: $\omega^2 J(\omega) = \Theta(\omega)\, j_0\, \omega\, e^{-\omega/\omega_c}$
  - Debye spectral density (solutes in polar solvents)

$$\omega^2 J(\omega) = \Theta(\omega)\, \frac{j_0 \omega}{\omega^2 + \omega_D^2}$$

in high temperature limit $C(t) = \dfrac{\pi j_0}{2\hbar\omega_D}\, (2k_B T - i\,\mathrm{sgn}(t)\hbar\omega_D)\, e^{-\omega_D |t|}$



correlation time: ω_D^{-1}

Ohmic limit $\omega_D^{-1} \to 0$

$C(\omega) \propto \omega$

Markov dynamics: $C(t) \approx \delta(t)$

- Redfield tensor: $R_{ab,cd}$
  - population transfer (a=b, c=d)

$$R_{aa,cc} = 2\delta_{ac} \sum_e \Gamma_{ae,ea}(\omega_{ae}) - 2\Gamma_{ca,ac}(\omega_{ca}) = \delta_{ac} \sum_e k_{ae} - k_{ca}$$

energy relaxation rate $k_{ab} = 2\Gamma_{ab,ba}(\omega_{ab}) = \sum_{u,v} K_{ab}^{(u)} K_{ba}^{(v)} C_{uv}(\omega_{ab})$

  - coherence dephasing (a≠b,a=c,b=d)

$$R_{ab,ab} \equiv \gamma_{ab} = \sum_e \left(\Gamma_{ae,ea}(\omega_{ae}) + \Gamma_{be,eb}(\omega_{be})\right) - \Gamma_{aa,bb}(0) - \Gamma_{bb,aa}(0)$$

dephasing rate due to energy relaxation $\gamma_{ab} = \frac{1}{2}\sum_e k_{ae} + \frac{1}{2}\sum_e k_{be} + \gamma_{ab}^{(\mathrm{pd})}$

pure dephasing rate $\gamma_{ab}^{(\mathrm{pd})} = -\sum_{u,v} K_{aa}^{(u)} K_{bb}^{(v)} C_{uv}(\omega = 0)$

- a simple example: the damped harmonic oscillator

$$\frac{\partial}{\partial t}\rho_{MN} = -\delta_{MN}\sum_K \left(k_{MK}\rho_{MM} - k_{KM}\rho_{KK}\right) - (1-\delta_{MN})\,(i\Omega_{\rm s}(M-N) + \gamma_M + \gamma_N)\rho_{MN}$$

$$k_{MN} = |\langle M|K(s)|N\rangle|^2\, C(\omega_{MN}) \qquad \gamma_M = \textstyle\sum_N k_{MN}/2$$

$$\langle M|K(s)|N\rangle = \left(\sqrt{N}\,\delta_{M,N-1} + \sqrt{N+1}\,\delta_{M,N+1}\right)$$

  - relaxation rates

$$k_{MN} = \left(\delta_{M,N-1}(M+1)C(-\Omega_{\rm s}) + \delta_{M,N+1}MC(\Omega_{\rm s})\right)$$

  - life times

$$\tau_M^{-1} = \sum_N k_{MN} = \left((M+1)C(-\Omega_{\rm s}) + MC(\Omega_{\rm s})\right)$$