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# Dipole–Environment Interaction

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July 30, 2014

## Harmonic Oscillators

- ❖ The Harmonic Oscillator
- ❖ Solution Methods
- ❖ Damping
- ❖ Forces
- ❖ Langevin
- ❖ Fluctuations
- ❖ Coupling
- ❖ Langevin
- ❖ Other uses
- ❖ TST
- ❖ Kramers
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- ❖ Solvent Effects
- ❖ Common Features
- ❖ Effective
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- ❖ Classical
- Conclusions

## Two-Level Systems

## Exercises and Problems

# *Harmonic Oscillators*

# The Harmonic Oscillator

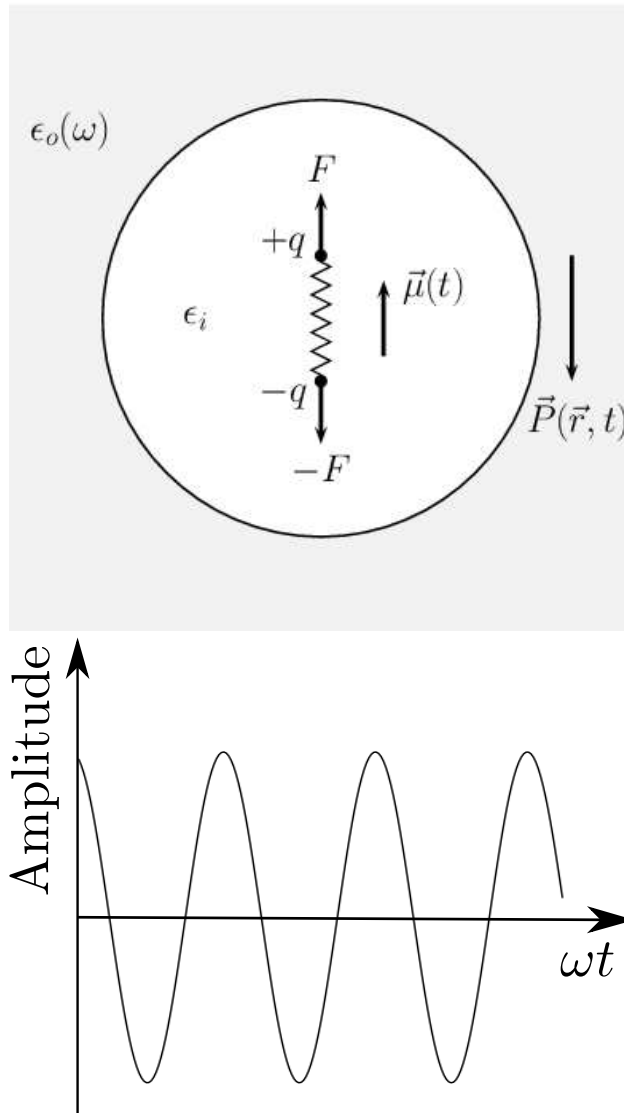
## Harmonic Oscillators

### ❖ The Harmonic Oscillator

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## Two-Level Systems

## Exercises and Problems



- Hamiltonian of the unperturbed oscillator:

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \quad (1)$$

- Equation of Motion:

$$m \frac{d^2 x}{dt^2} = -m\omega_0^2 x \quad (2)$$

- Solution:

$$x(t) = A \cos(\omega_0 t + \phi) \quad (3)$$

# Solution Methods

## Harmonic Oscillators

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## Two-Level Systems

- Exercises and Problems

- Trial and error (mostly taught in elementary courses): try an exponential  $e^{\alpha t}$ . This gives  $\alpha^2 = -\omega_0^2$ , or  $\alpha = \pm i\omega_0$ . General solution is then

$$A_1 e^{i\omega_0 t} + A_2 e^{-i\omega_0 t} \quad (4)$$

$A_1$  and  $A_2$  follow from initial conditions.

- For linear initial value problems: use Laplace Transform.

$$\hat{f}(s) = \int_0^\infty dt e^{-st} f(t) \quad (5)$$

with inverse:

$$f(t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} ds e^{st} \hat{f}(s) \quad (6)$$

# The Damped Oscillator

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## Two-Level Systems

- Exercises and Problems

### ● Equation of Motion:

$$m \frac{d^2 x}{dt^2} = -m\omega_0^2 x - \zeta \frac{dx}{dt} \quad (7)$$

### ● Laplace Transform:

$$\left( s^2 + s \frac{\zeta}{m} + \omega_0^2 \right) = \dot{x}_0 + s x_0 + \frac{\zeta}{m} x_0 \quad (8)$$

### ● Solution:

$$x(t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} ds \frac{\dot{x}_0 + (s + \zeta/m)x_0}{s^2 + s\zeta/m + \omega_0^2} e^{st} \quad (9)$$

# The Damped Oscillator 2

## Harmonic Oscillators

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## Two-Level Systems

## Exercises and Problems

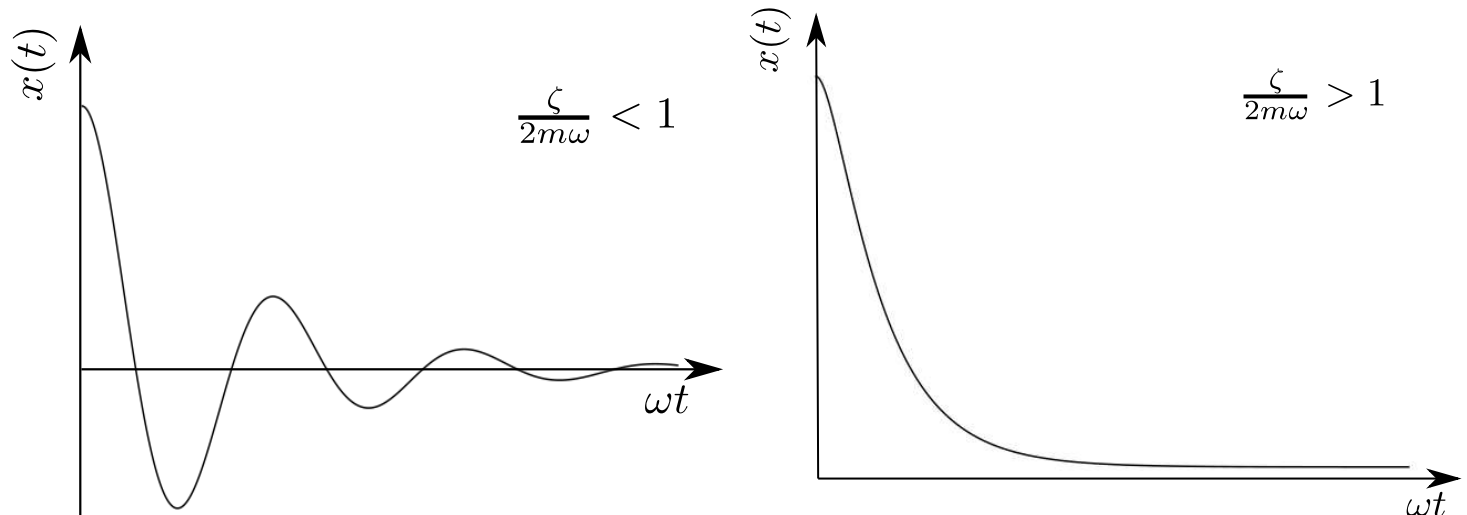
- Solution for  $t \geq 0$ :

$$x(t) = \frac{(\dot{x}_0 + (s_1 + \zeta/m)x_0) e^{s_1 t} - (\dot{x}_0 + (s_2 + \zeta/m)x_0) e^{s_2 t}}{s_1 - s_2} \quad (10)$$

with

$$s_{1,2} = \omega_0 \left[ -\frac{\zeta}{2m\omega_0} \pm \sqrt{\left(\frac{\zeta}{2m\omega_0}\right)^2 - 1} \right] \quad (11)$$

- Graphs for underdamped and overdamped motion; cf Eq. (10).



# Adding an External Force

## Harmonic Oscillators

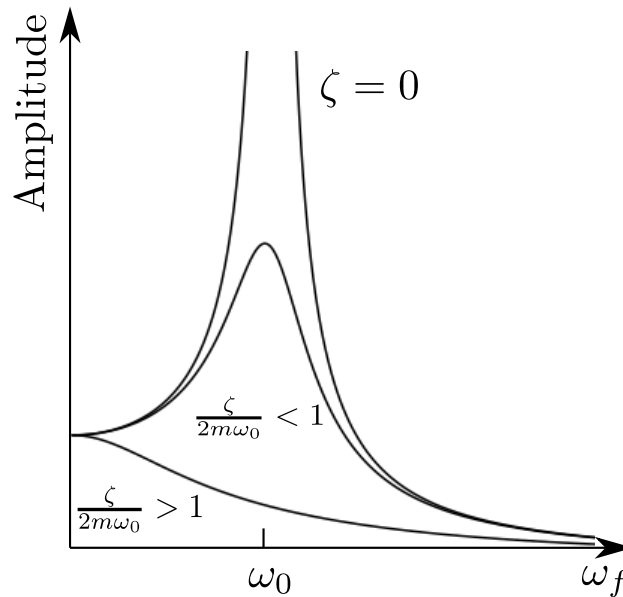
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## Two-Level Systems

## Exercises and Problems



### ● Equation of Motion:

$$m \frac{d^2 x}{dt^2} = -m\omega_0^2 x - \zeta \frac{dx}{dt} + F_0 \cos \omega_f t \quad (12)$$

- On the left: amplitude for the undamped, underdamped, and overdamped oscillator for an oscillating force.

### ● Solution (for times $t \gg (\zeta/2m)^{-1}$ ):

$$x(t) = \frac{F_0/m}{(\omega_0^2 - \omega_f^2)^2 + 4\omega_0^2\omega_f^2(\zeta/2m\omega_0)^2} \cos(\omega_f t + \phi) \quad (13)$$

with

$$\tan \phi = \frac{\zeta/2m\omega_0}{\omega_0^2 - \omega_f^2} \quad (14)$$

# Role in Planck's Thinking

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## Two-Level Systems

## Exercises and Problems

### ● Equation of Motion (Planck):

$$m \frac{d^2 x}{dt^2} + \frac{2e^2 \omega_0^2}{3mc^3} \frac{dx}{dt} + m\omega_0^2 x = \frac{e}{m} E(t) \quad (15)$$

- Friction term is due to 'radiation damping' and the external force is the electric field in the cavity.

The study of conservative damping appears to me to be of fundamental importance due to the fact that through it one's view is opened towards the possibility of a general explanation of irreversible processes with the help of conservative forces.

M. Planck, 1896.

Boltzmann disagreed and pointed out that Planck's system was also microscopically reversible. Eventually Planck abandoned this idea.

# The Langevin Equation

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## Two-Level Systems

## Exercises and Problems

The oscillator is constantly buffeted by molecules in the environment. This leads to friction *and* random forces. External Force is a random force due to fluctuations in the medium (Brownian Motion).

- Equation of motion:

$$m \frac{d^2 x}{dt^2} + \zeta \frac{dx}{dt} + m\omega_0^2 x = F_R(t) \quad (16)$$

- Random Force:

$$\langle F_R(t) \rangle = 0 \quad \text{and} \quad \langle F_R(t) F_R(t') \rangle = C \delta(t - t') \quad (17)$$

The average of the force is zero and is uncorrelated for different times.

# Fluctuation–Dissipation Theorem

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## Two–Level Systems

## Exercises and Problems

For long times the system should go to equilibrium:

$$\langle x^2 \rangle = \frac{k_B T}{m \omega_0^2} \quad \text{and} \quad \langle v^2 \rangle = \frac{k_B T}{m} \quad (18)$$

- Formal Solution (ignore initial conditions which decay rapidly anyway):

$$x(t) = \frac{1}{2\pi i} \int_{-i\infty}^{\infty} ds \frac{\hat{F}_R(s)/m}{(s - s_1)(s - s_2)} \quad (19)$$

- Consequence: strength of the random force is correlated with the friction

$$\lim_{t \rightarrow \infty} \langle x(t)^2 \rangle = \frac{k_B T}{m \omega_0^2} \implies C = 2k_B T \zeta \quad (20)$$

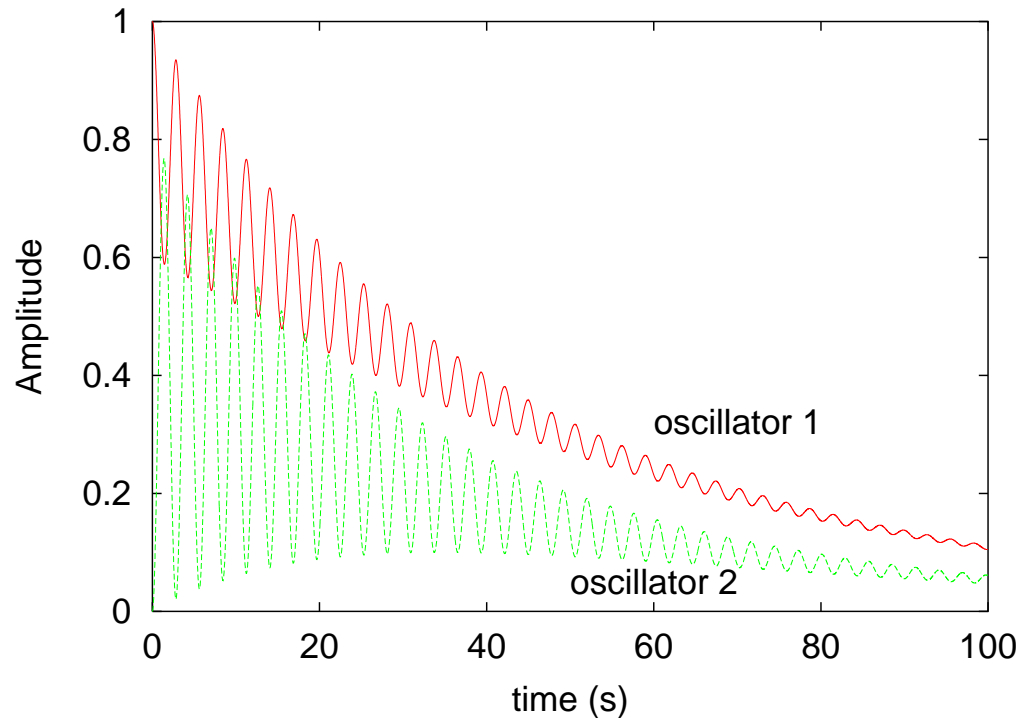
# Coupled Oscillators

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## Two-Level Systems

Exercises and Problems



$m_1$	1
$m_2$	1
$\omega_1$	1
$\omega_2$	2
$\gamma$	0.2
$\zeta$	0.1

## Equations of motion:

$$m_1 \frac{d^2 x_1}{dt^2} = -\omega_1^2 x_1 + \gamma x_2$$

$$m_2 \frac{d^2 x_2}{dt^2} = -\omega_2^2 x_2 - \zeta \frac{dx_2}{dt} + \gamma x_1$$

# Langevin Equations, Non-Markovian Behavior

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## Two-Level Systems

## Exercises and Problems

### ● Coupled equations

$$\begin{aligned} m_1 \frac{d^2 x_1}{dt^2} &= -m_1 \omega_1^2 x_1 + \gamma x_2 \\ m_2 \frac{d^2 x_2}{dt^2} &= -m_2 \omega_2^2 x_2 - \zeta \frac{dx_2}{dt} + \gamma x_1 + F_R(t) \end{aligned} \quad (21)$$

lead to non-Markovian behavior of oscillator 1.

### ● Formally solve the second equation (use Fourier transforms):

$$x_2(\omega) = \frac{\gamma x_1(\omega) + F_R(\omega)}{m_2(\omega_2^2 - \omega^2) - i\omega\zeta} \quad (22)$$

### ● And substitute in the first:

$$m_1(\omega_1^2 - \omega^2)x_1(\omega) - \frac{\gamma^2 x_1(\omega)}{m_2(\omega_2^2 - \omega^2) - i\omega\zeta} = \frac{\gamma F_R(\omega)}{m_2(\omega_2^2 - \omega^2) - i\omega\zeta} \quad (23)$$

# Langevin Equations, Non-Markovian Behavior

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## Two-Level Systems

## Exercises and Problems

- Some minor rearrangement:

$$m_1(\omega_{\text{pmf}}^2 - \omega^2)x_1(\omega) - i\omega\zeta_1(\omega)x_1(\omega) = \overline{F}_R(\omega) \quad (24)$$

- Potential of Mean Force (“Equilibrium Solvation”):

$$\omega_{\text{pmf}}^2 = \omega_1^2 \left( 1 - \frac{\gamma^2}{\omega_1^2 \omega_2^2} \right) \quad (25)$$

- Frequency dependent friction:

$$\zeta_1(\omega) = \frac{\gamma^2}{\omega_2^2} \frac{-i\omega + \zeta/m_2}{m_2(\omega_2^2 - \omega^2) - i\omega\zeta} \quad (26)$$

- Fluctuation–Dissipation Theorem:

$$\langle \overline{F}_R(\omega) \overline{F}_R(\omega') \rangle = 2k_B T \zeta_1(\omega) 2\pi \delta(\omega - \omega') \quad (27)$$

# Other uses for Oscillators

## Harmonic Oscillators

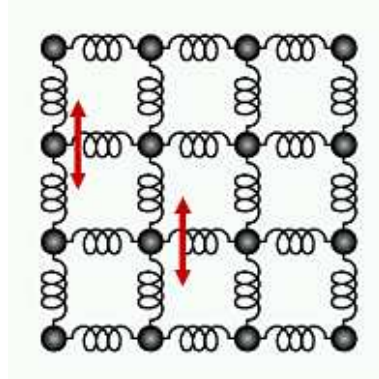
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## Two-Level Systems

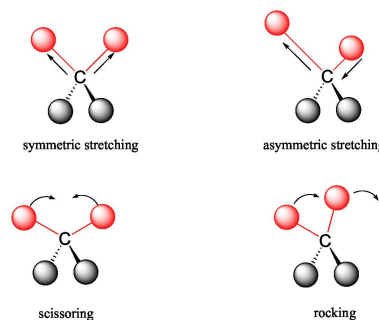
## Exercises and Problems

In almost any field of physics the harmonic oscillator plays a crucial role as one of the few systems that can be solved analytically.

Two notable fields are:



- Vibrations of crystals. Low temperature thermodynamics.



- Molecular vibrations. Raman and Infrared spectroscopy.

# Crystal Vibrations

## Harmonic Oscillators

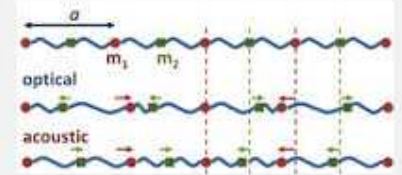
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## Two-Level Systems

## Exercises and Problems



# Beyond Transition State Theory

## Harmonic Oscillators

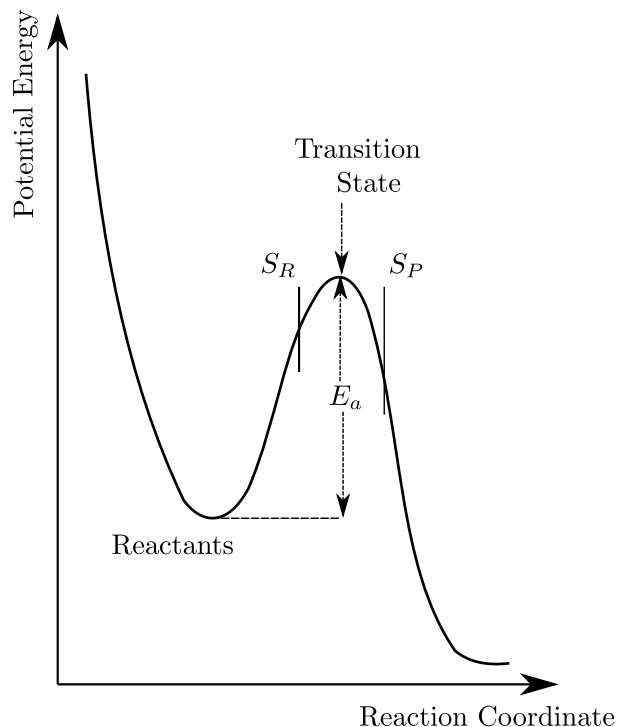
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## Two-Level Systems

## Exercises and Problems



- The reactant well is harmonic.
- One of the normal modes of the reactive complex is a harmonic barrier.
- The rate is the (average) current over the barrier:

$$k = \int_0^\infty dt \langle j_i(S_R) j_o^*(S_P, t) \rangle_R \quad (28)$$

The rate is determined by the dynamics in the barrier region: how many particles enter it through the reactant surface  $S_R$ , and how many of those leave through the product surface  $S_P$  some time later.

Trivial TST Dynamics: Every particle that reaches the top is reactive.

$$k^{\text{TST}} = \frac{k_B T}{h} e^{-\Delta G^\ddagger / k_B T} \quad (29)$$

# Kramers Rate Equation

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## Two-Level Systems

## Exercises and Problems

- The barrier is an inverted parabola:

$$V(x) = \frac{1}{2}m\omega_b^2 x^2 \quad (30)$$

- ❖ Reaction coordinate:  $x$ , position near the barrier top.
- ❖ Barrier frequency:  $\omega_b$ , curvature of the barrier top.
- ❖ Reduced mass:  $m$ , mass of the normal, reactive, mode.

- Reactive motion is Brownian motion over the barrier.

$$m \frac{d^2 x}{dt^2} = -m\omega_b^2 x - \zeta \frac{dx}{dt} + F_R(t) \quad (31)$$

Note: Kramers used the Fokker–Planck equation, but for this problem (and for most others) the Langevin approach is completely equivalent.

# Kramers' Result

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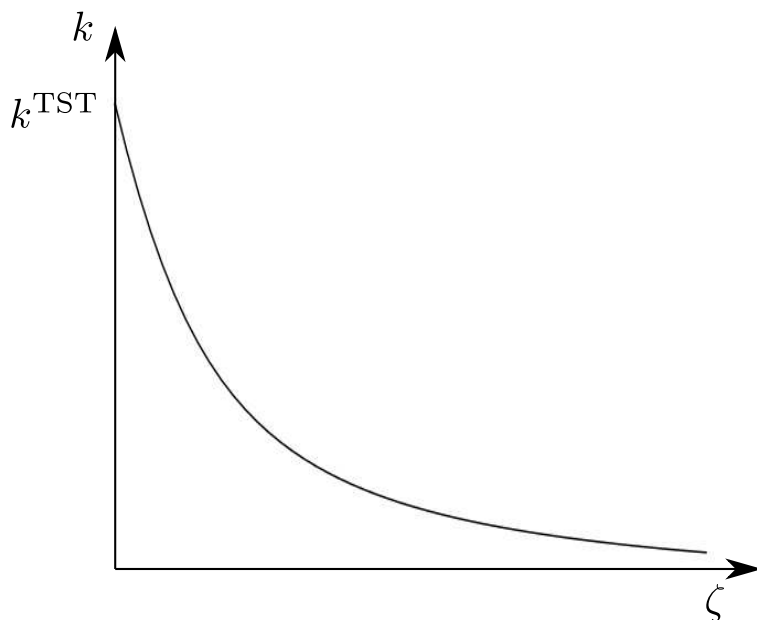
## Two-Level Systems

## Exercises and Problems

### Eigenvalues: (note the change of sign!)

$$s_{1,2} = -\omega_b \left[ \frac{\zeta}{2m\omega_b} \pm \sqrt{\left( \frac{\zeta}{2m\omega_b} \right)^2 + 1} \right] \quad (32)$$

The positive eigenvalue (pole), the reactive frequency  $\omega_r$ , indicates exponential motion away from the barrier top: a *reaction*.



- Reaction rate

$$k = k^{\text{TST}} \frac{\omega_r}{\omega_b} \quad (33)$$

- The rate goes to zero for high friction.

# Kramers' Problem

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## Two-Level Systems

## Exercises and Problems

- Solvents need time to adjust. Typical (polarization) relaxation times  $\tau_r$  are of the order of a picosecond (in water).
- Barrier passage times are related to the barrier frequency  $\omega_b$ : high frequencies mean rapid motion.
- Kramers result is based on the solvent being adjusted to the motion over the barrier, the friction is a steady state friction.
- Expectation: for high barrier frequency ( $\omega_b \tau_r \gg 1$ ) the solvent is static, for low barrier frequency ( $\omega_b \tau_r \ll 1$ ) Kramers should apply.

# The Polarization Field

## Harmonic Oscillators

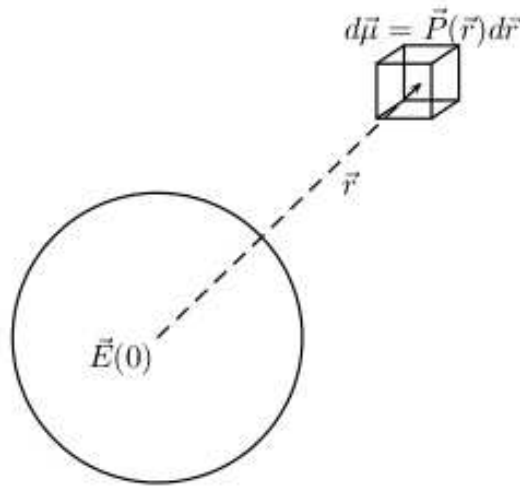
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## Two-Level Systems

## Exercises and Problems



- Polarization is a fluctuating quantity.
- Free energy functional

$$G[\vec{P}] = \frac{1}{2\chi} \int d\vec{r} \vec{P}(\vec{r}) \cdot \vec{P}(\vec{r}) + \frac{1}{2} \int d\vec{r} \int d\vec{r}' \frac{\vec{\nabla} \cdot \vec{P}(\vec{r}) \vec{\nabla}' \cdot \vec{P}(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (34)$$

- Electric field at the origin:

$$d\vec{E} = \frac{3\epsilon_r}{2\epsilon_r + 1} \frac{1}{4\pi\epsilon_0\epsilon_r r^3} [1 - 3\hat{r}\hat{r}] \cdot \vec{P}(\vec{r}) d\vec{r} \quad (35)$$

- Fields:

$$\langle \vec{E} \rangle = 0 \quad \text{and} \quad \langle \vec{E} \cdot \vec{E} \rangle = \frac{k_B T}{4\pi\epsilon_0\epsilon_r a^3} \frac{2(\epsilon_r - 1)}{2\epsilon_r + 1} \quad (36)$$

# Polarization Dynamics

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## Two-Level Systems

## Exercises and Problems

- Debye polarization dynamics:

$$\frac{d\vec{P}(\vec{r}, t)}{dt} = \frac{\chi \vec{E}(\vec{r}, t) - \vec{P}(\vec{r}, t)}{\tau_D} \quad (37)$$

$\tau_D$ : Debye relaxation time, related to solvent molecule reorientation time.

$\chi$ : Dielectric susceptibility.

- Frequency dependent dielectric constant

$$\epsilon_r(\omega) = \frac{\epsilon_r - i\omega\tau_D}{1 - i\omega\tau_D} \quad (38)$$

- In all calculations electronic polarization is neglected, only orientational polarization is taken into account.

# *How does the solvent couple to the reaction?*

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## Two-Level Systems

## Exercises and Problems

- Solvent molecules have dipole moments (and higher moments) that cause electric fields in the solvent.
- The solvent responds by becoming polarized.
- The polarization creates an electric field at the position of the molecule.
- The electronic distribution of the molecule changes.
- This leads to both static and dynamic effects.
- Which need to be solved self-consistently.
- See QM/MM and implementations of polarization in quantum chemistry programs.

# Solvent Effects on Reaction Rates

## Harmonic Oscillators

- ❖ The Harmonic Oscillator
- ❖ Solution Methods
- ❖ Damping
- ❖ Forces
- ❖ Langevin
- ❖ Fluctuations
- ❖ Coupling
- ❖ Langevin
- ❖ Other uses
- ❖ TST
- ❖ Kramers
- ❖ Polarization
- ❖ **Solvent Effects**
- ❖ Common Features
- ❖ Effective
- ❖ Reactive
- ❖ Dynamics
- ❖ Classical
- ❖ Conclusions

## Two-Level Systems

- Exercises and Problems

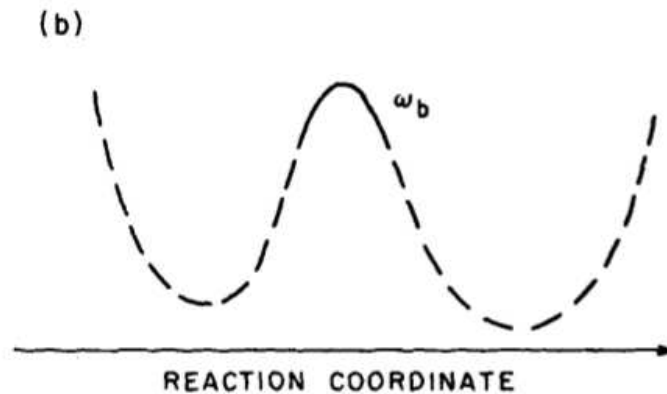
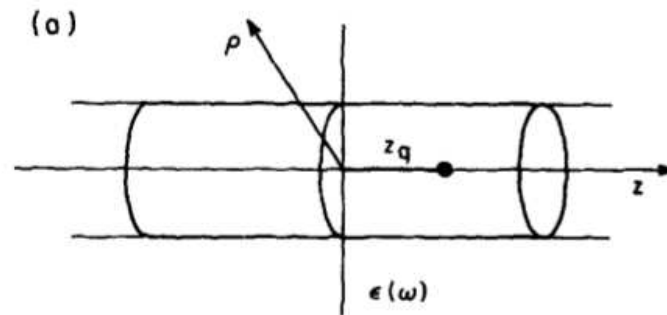


FIG. 1. Model for charge transfer reaction. (a) Infinite cylindrical cavity of radius  $\rho_0$  and dielectric constant  $\epsilon_\infty$  containing the charge  $q$  at position  $z_q$ . The cavity is surrounded by a dielectric continuum with frequency dependent dielectric constant  $\epsilon(\omega)$ . The high frequency limit of  $\epsilon(\omega)$  is  $\epsilon_\infty$ . (b) Schematic free energy diagram for the charge transfer.

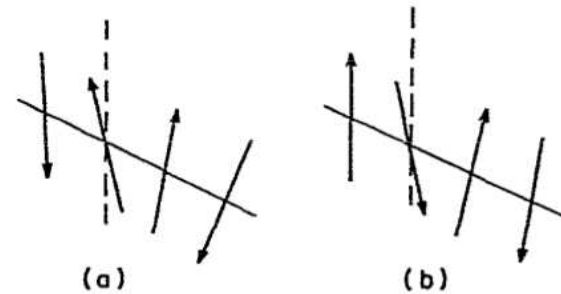
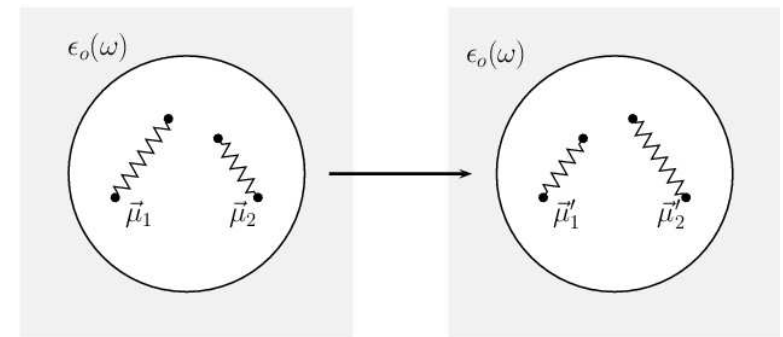


Fig 1 Reaction and solvent model in the (a) transition state and (b) reactant neighborhoods

## Isomerization Reactions.



## Tautomerization reactions.

# Common Features

## Harmonic Oscillators

- ❖ The Harmonic Oscillator
- ❖ Solution Methods
- ❖ Damping
- ❖ Forces
- ❖ Langevin
- ❖ Fluctuations
- ❖ Coupling
- ❖ Langevin
- ❖ Other uses
- ❖ TST
- ❖ Kramers
- ❖ Polarization
- ❖ Solvent Effects

## ❖ Common Features

- ❖ Effective
- ❖ Reactive
- ❖ Dynamics
- ❖ Classical
- Conclusions

## Two-Level Systems

## Exercises and Problems

## Polarization dynamics (“Solvent coordinate”):

$$\frac{d\vec{P}(\vec{r}, t)}{dt} = \frac{\chi \vec{E}(\vec{r}, t) - \vec{P}(\vec{r}, t)}{\tau_D}$$

(or more complicated dynamics: Polarization diffusion, presence of ions, short time inertial behavior)

coupled to Barrier Motion:

$$m \frac{d^2 x(t)}{dt^2} = m \omega_b^2 x(t) + F[\vec{P}(\vec{r}, t)]$$

*a/ways* leads to a Generalized Langevin Equation

$$m \frac{d^2 x(t)}{dt^2} = m \omega_{\text{eff}}^2 x(t) - \int_0^t d\tau \zeta_D(t - \tau) \frac{dx(\tau)}{d\tau}$$

# Effective frequency and Polarization Caging.

## Harmonic Oscillators

- ❖ The Harmonic Oscillator
- ❖ Solution Methods
- ❖ Damping
- ❖ Forces
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- ❖ Fluctuations
- ❖ Coupling
- ❖ Langevin
- ❖ Other uses
- ❖ TST
- ❖ Kramers
- ❖ Polarization
- ❖ Solvent Effects
- ❖ Common Features

## ❖ Effective

- ❖ Reactive
- ❖ Dynamics
- ❖ Classical
- Conclusions

## Two-Level Systems

- Exercises and Problems

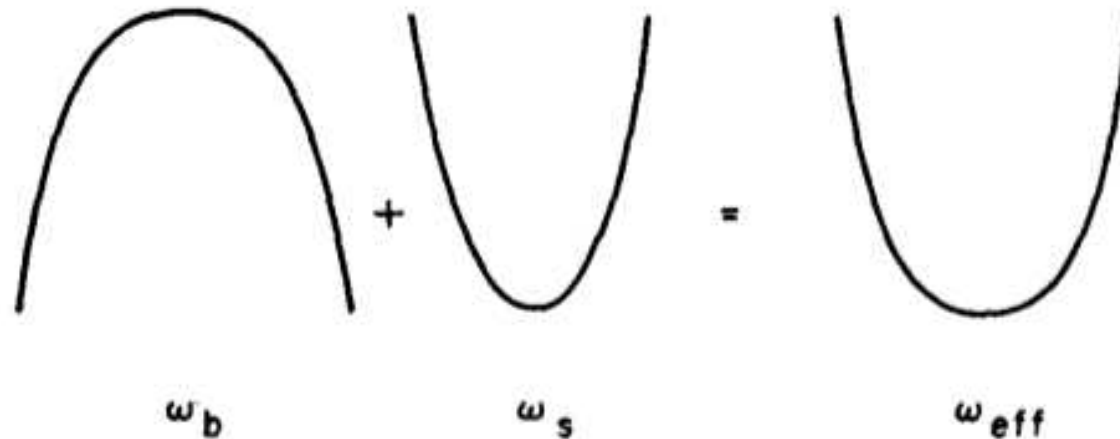


FIG. 4. Schematic illustration of the effective solvent well in the strong solvent force regime.

The solvent frequency  $\omega_s$  is the frequency at the bottom of the (non-equilibrium free energy) well the charge distribution dug for itself in the dielectric (see also Marcus' theory).

$$\omega_s = \zeta_D(t = 0)$$

# Reactive Trajectories

## Harmonic Oscillators

- ❖ The Harmonic Oscillator
- ❖ Solution Methods
- ❖ Damping
- ❖ Forces
- ❖ Langevin
- ❖ Fluctuations
- ❖ Coupling
- ❖ Langevin
- ❖ Other uses
- ❖ TST
- ❖ Kramers
- ❖ Polarization
- ❖ Solvent Effects
- ❖ Common Features
- ❖ Effective
- ❖ **Reactive**
- ❖ Dynamics
- ❖ Classical Conclusions

## Two-Level Systems

## Exercises and Problems

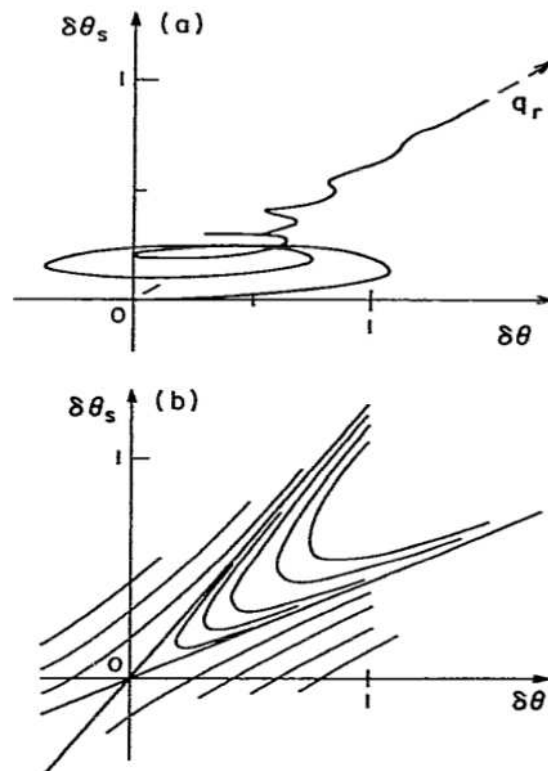


Fig 8 (a) An average trajectory in the polarization caging regime, illustrating the trapping and ultimate approach to the reaction coordinate  $q_r$ .

- Initially motion is trapped in the solvent well, but after relaxation the reaction can proceed.
- The reaction involves both nuclear motion (in the reacting system) as well as solvent motion.
- Repeated crossings do not contribute to the rate.
- Kramers (sometimes dramatically) overestimates the effect of the friction.

# TST, Kramers, Dynamical Solvent

## Harmonic Oscillators

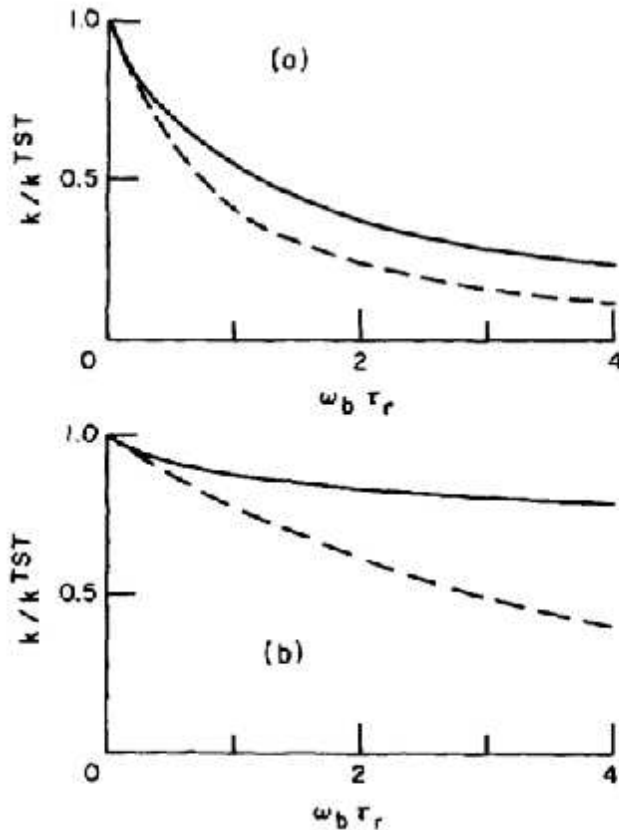
- ❖ The Harmonic Oscillator
- ❖ Solution Methods
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- ❖ Forces
- ❖ Langevin
- ❖ Fluctuations
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- ❖ Kramers
- ❖ Polarization
- ❖ Solvent Effects
- ❖ Common Features
- ❖ Effective
- ❖ Reactive

## ❖ Dynamics

- ❖ Classical
- Conclusions

## Two-Level Systems

- Exercises and Problems



- Dashed lines are Kramers result.
- Top: Strong solvent force regime. For strong solvent forces and high friction the rate goes to zero.
- Bottom: weak solvent force regime. In this case the rate remains finite, even if the friction goes to infinity.

- General expression for the rate for a generalized Langevin equation:

$$k = k^{\text{TST}} \frac{\omega_r}{\omega_b} \quad \text{with} \quad \omega_r = \frac{\omega_b^2}{\omega_r + \zeta_D(\omega_r)} \quad (39)$$

# Classical Conclusions

## Harmonic Oscillators

- ❖ The Harmonic Oscillator
- ❖ Solution Methods
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- ❖ Fluctuations
- ❖ Coupling
- ❖ Langevin
- ❖ Other uses
- ❖ TST
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- ❖ Polarization
- ❖ Solvent Effects
- ❖ Common Features
- ❖ Effective
- ❖ Reactive
- ❖ Dynamics

## ❖ Classical Conclusions

## Two-Level Systems

## Exercises and Problems

- Even though ultimately we may not understand irreversibility, we do have a set of equations giving a satisfactory description of many if not all of its features.
- Coupling of a mechanical to a dissipative system can be done self-consistently.
- Rates can be measured, dielectric friction can be measured, experimental evidence (also from Molecular Dynamics) confirms the model.
- Basically all aspects displayed in the figure on slide 3 can be accounted for, both statically and dynamically.
- How About Quantum Mechanics?

Harmonic Oscillators

**Two–Level Systems**

- ❖ Two–level systems
- ❖ QC
- ❖ Onsager
- ❖ QC
- ❖ Final Remarks

Exercises and  
Problems

# *Two–Level Systems*

# Two-level systems

Harmonic Oscillators

Two-Level Systems

❖ Two-level systems

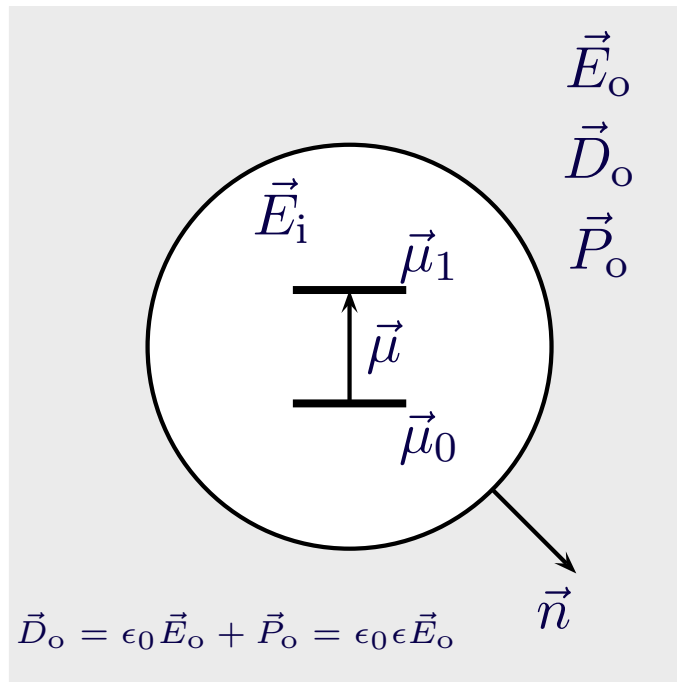
❖ QC

❖ Onsager

❖ QC

❖ Final Remarks

Exercises and Problems



- Basis States:  $|0\rangle$  and  $|1\rangle$ .
- Hamiltonian:  $\mathcal{H}_0 = \epsilon |1\rangle \langle 1|$
- Dipole Operator:  

$$\hat{\vec{\mu}} = \vec{\mu}_0 |0\rangle \langle 0| + \vec{\mu}_1 |1\rangle \langle 1| + \vec{\mu} [|0\rangle \langle 1| + |1\rangle \langle 0|]$$
- Dynamics: Schrödinger Equation.

Two-Level System in a static external electric field:

$$\mathcal{H} = \mathcal{H}_0 - \hat{\vec{\mu}} \cdot \vec{E} \quad \mathcal{H} |\psi\rangle = \lambda |\psi\rangle \quad (40)$$

with

$$|\psi\rangle = c |0\rangle + s e^{i\phi} |1\rangle \quad c^2 + s^2 = 1 \quad (41)$$

# Quantum Chemistry in polarizable media.

Harmonic Oscillators

Two-Level Systems

❖ Two-level systems

❖ QC

❖ Onsager

❖ QC

❖ Final Remarks

Exercises and  
Problems

## Basic Assumptions:

- Quantum system ‘feels’ classical (reaction) field:

$$\mathcal{H} = \mathcal{H}_0 - \hat{\vec{\mu}} \cdot \vec{E}_R \quad (42)$$

- Classical system ‘feels’ the expectation value of the dipole operator:

$$\vec{E}_R = A \langle \hat{\vec{\mu}} \rangle \quad (43)$$

- $A$  is a proportionality factor depending on the shape and size of the cavity: for instance Onsager:

$$A = \frac{1}{4\pi\epsilon_0 a^3} \frac{2(\epsilon - 1)}{2\epsilon + 1} \quad (44)$$

# Sidebar: Onsager Reaction Field

Harmonic Oscillators

Two-Level Systems

❖ Two-level systems

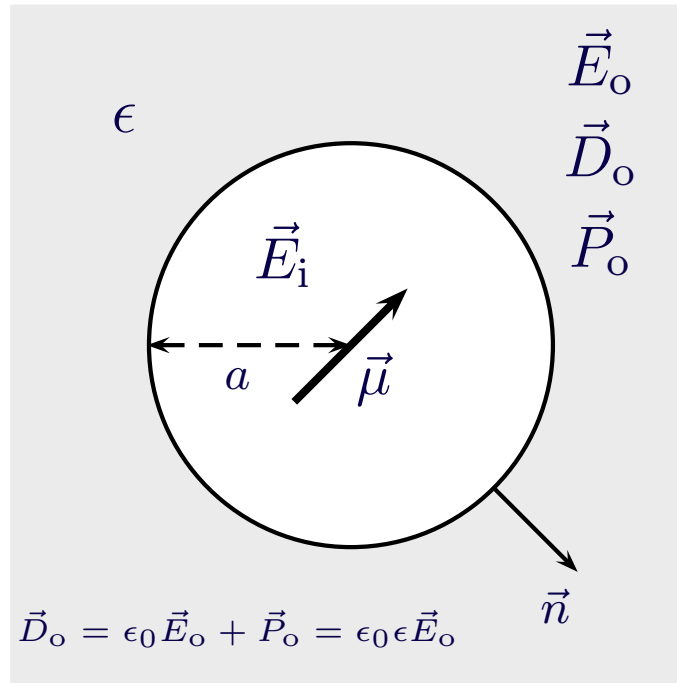
❖ QC

❖ **Onsager**

❖ QC

❖ Final Remarks

Exercises and Problems



Maxwell equations:

$$\vec{\nabla} \cdot \vec{E}_i = \frac{\rho}{\epsilon_0} = -\frac{\vec{\mu} \cdot \vec{\nabla} \delta(\vec{r})}{\epsilon_0}$$

$$\vec{\nabla} \cdot \vec{D}_o = 0$$

Boundary conditions

$$\vec{n} \cdot \vec{D}_o = \vec{n} \cdot \vec{E}_i$$

$$\vec{n} \times \vec{E}_o = \vec{n} \times \vec{E}_i$$

Solution:  $\vec{E}_i = E_{\text{vac}} + \vec{E}_R = \vec{E}_{\text{vac}} + \frac{1}{4\pi\epsilon_0 a^3} \frac{2(\epsilon-1)}{2\epsilon+1} \vec{\mu} \equiv \vec{E}_{\text{vac}} + A\vec{\mu}$

Energy:  $U = -\vec{\mu} \cdot \vec{E}_R = -A\mu^2$  Free energy:  $F = -\frac{1}{2} A\mu^2$

2 D dipole, cavity radius 0.5 nm:  $U \approx 200 \text{ cm}^{-1}$ .

NB:  $k_B T \approx 200 \text{ cm}^{-1}$  at room temperature.

# Quantum Chemistry in polarizable media. 2

Harmonic Oscillators

Two-Level Systems

❖ Two-level systems

❖ QC

❖ Onsager

❖ QC

❖ Final Remarks

Exercises and  
Problems

- Solve for the ground state of the molecule. This gives a charge density.
- Construct a surface around the molecule, and calculate, using the charge density, the polarization in the medium.
- Calculate the reaction field inside the cavity, and solve for the ground state in equilibrium with that reaction field.
- Iterate until a stable solution is found.

# Final Remarks

Harmonic Oscillators

Two-Level Systems

❖ Two-level systems

❖ QC

❖ Onsager

❖ QC

❖ Final Remarks

Exercises and  
Problems

- The quantum–classical equilibrium methods appear to be well developed, and lead to few immediate questions.
- For the dynamics it is a different matter. The non–linear Schrödinger approach does not seem to be helpful:
  - ❖ You cannot put friction in it.
  - ❖ There is no thermodynamic equilibrium state to go to.
- A new formalism is needed: the density operator. This will be developed in the next set of notes.
- We'll get to coupled 2LS systems (and entanglement) after that.

Harmonic Oscillators

Two-Level Systems

**Exercises and  
Problems**

- ❖ Exercises
- ❖ R Program for the Damped Oscillator
- ❖ Problems
- ❖ Problems 2
- ❖ Problems 3
- ❖ Literature
- ❖ List of papers on coupled oscillators.
- ❖ 2LS Onsager

# *Exercises and Problems*

# Exercises

Harmonic Oscillators

Two-Level Systems

Exercises and Problems

❖ Exercises

❖ R Program for the Damped Oscillator

❖ Problems

❖ Problems 2

❖ Problems 3

❖ Literature

❖ List of papers on coupled oscillators.

❖ 2LS Onsager

1. Use Laplace transform to derive Eq. (8).
2. Derive Eq. (10) from Eq. (9). You need complex integration for this, and use Cauchy's theorem. Prove first that the poles  $s_{1,2}$  are in the negative half of the complex plane.
3. Install R on your computer if you haven't already done so, and run the program on the next slide. Vary the parameters and rationalize what you see. Also check that the imaginary part of the solution is zero for all times. Investigate also the behavior of the poles as a function of the friction.
4. Use the Laplace transform to derive the solution of the forced oscillator Eq. (13). Ignore all terms related to the initial conditions or turning on the force.
5. Prove the fluctuation dissipation theorem, Eq. (20). Actually this involves quite a bit of work, and you may want to consult literature. Also about the relevance of this type of theorems.
6. Prove Eq. (39). This is easier than you might think.
7. What does the other, negative, root of Eq. (32) signify?

# Exercises 2

Harmonic Oscillators

Two-Level Systems

Exercises and Problems

❖ Exercises

❖ R Program for the Damped Oscillator

❖ Problems

❖ Problems 2

❖ Problems 3

❖ Literature

❖ List of papers on coupled oscillators.

❖ 2LS Onsager

8. Find the eigenvalues and eigenvectors of the Hamiltonian in Eq. (40) for the case the state dipole moments are zero. Sketch the energy difference as a function of  $E$ . Calculate the state dipole moments, the transition moment and the polarizability for finite electric field strength. The (static) polarizability  $\vec{\alpha}$  of a system is defined as:

$$\vec{\mu}_g = \vec{\alpha} \cdot \vec{E} \quad (45)$$

where  $\vec{\mu}_g$  is the expectation value of the dipole operator in the ground state.

9. Solution of Eqs. (9) and (10) is much harder. Sometimes this is referred to as a non-linear Schrödinger equation since the equation depends on the expectation value of the eigenfunction it is supposed to give. Nevertheless I leave it as an exercise. Again ignore state dipole moments:  $\vec{\mu}_0 = \vec{\mu}_1 = 0$ .
10. Show that for strong enough interaction ( $2A\mu^2 > \epsilon$ ) the quantum system can spontaneously develop a ground state dipole moment. For some help on the last two problems, see the four blue sheets at the end of this lecture.

# *R Program for the Damped Oscillator*

Harmonic Oscillators

Two-Level Systems

Exercises and  
Problems

❖ Exercises

❖ R Program for the  
Damped Oscillator

❖ Problems

❖ Problems 2

❖ Problems 3

❖ Literature

❖ List of papers on  
coupled oscillators.

❖ 2LS Onsager

```
// the poles
```

```
s1 <- function(alpha){-alpha+sqrt(as.complex(alpha^2-1))}
```

```
s2 <- function(alpha){-alpha-sqrt(as.complex(alpha^2-1))}
```

```
//parameters and initial conditions
```

```
alpha = 1.2
```

```
dotx0 = 0
```

```
x0 = 1
```

```
HO <- function(t){
```

```
  Re(( (dotx0+(s1(alpha)+2*alpha)*x0)*exp(s1(alpha)*t)-  
        (dotx0+(s2(alpha)+2*alpha)*x0)*exp(s2(alpha)*t))/  
        (s1(alpha)-s2(alpha)))
```

```
}
```

```
t <- seq(0,20, by = 0.01)
```

```
plot(t, HO(t), type = "l", lwd = 2)
```

# Problems

Harmonic Oscillators

Two-Level Systems

Exercises and Problems

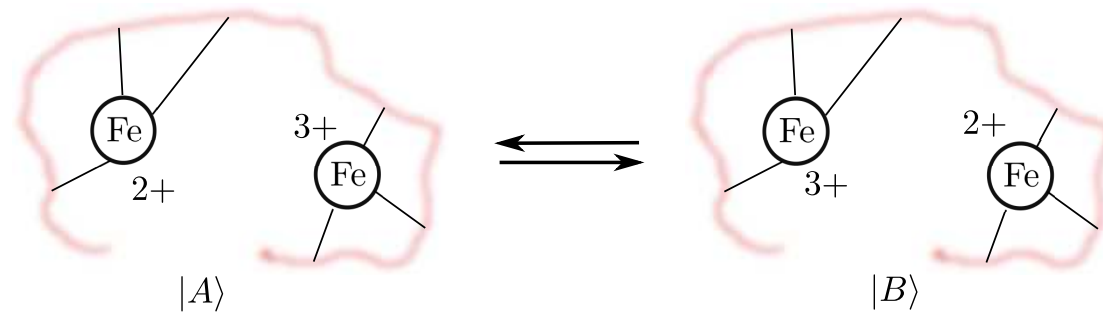
- ❖ Exercises
- ❖ R Program for the Damped Oscillator

❖ Problems

- ❖ Problems 2
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Here is a problem from Chandler's *Introduction to Modern Physics* which deals some of the issues in this lecture.

In this problem you consider the behavior of solvated mixed valence compounds, a depiction of which is given in the figure:



The compound, consisting of two Fe atoms in a given oxidized state can exist in two states  $|A\rangle$  and  $|B\rangle$  which differ in the position of the electron. In the absence of the environment the Hamiltonian of the compound is given by  $\mathcal{H}_0$  with matrix elements

$$\langle A | \mathcal{H}_0 | A \rangle = \langle B | \mathcal{H}_0 | B \rangle = 0 \quad \text{and} \quad \langle A | \mathcal{H}_0 | B \rangle = -\Delta \quad (46)$$

# Problems 2

Harmonic Oscillators

Two-Level Systems

Exercises and Problems

- ❖ Exercises
- ❖ R Program for the Damped Oscillator
- ❖ Problems
- ❖ **Problems 2**
- ❖ Problems 3
- ❖ Literature
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- ❖ 2LS Onsager

The dipole moment for each of the states is given by

$$\mu = \langle A | \hat{\mu} | A \rangle = - \langle B | \hat{\mu} | B \rangle \quad (47)$$

The overlap  $\langle A | B \rangle$  and the transition dipole moment  $\langle A | \hat{\mu} | B \rangle$  are both zero.

The surrounding medium (crystal, protein, the reddish stuff), has a crystal field  $E$  which couples to the dipole moment. The Hamiltonian of the complete system is  $\mathcal{H} = \mathcal{H}_0 - \hat{\mu}E$ .

1. Show that when  $E = 0$  the eigenstates of the Hamiltonian are

$$|\pm\rangle = \frac{1}{\sqrt{2}} [|A\rangle \pm |B\rangle] \quad (48)$$

and the energy levels are  $\pm\Delta$ .

2. Compute the canonical partition function for the system of mixed valence compounds when  $E = 0$  by (i) performing the Boltzmann weighted sum with energy eigenvalues, and (ii) performing the matrix trace of  $e^{-\beta\mathcal{H}_0}$ , using the configurational states  $|A\rangle$  and  $|B\rangle$ . The latter states diagonalize  $\hat{\mu}$  but not  $\mathcal{H}_0$ . Nevertheless the two calculations yield the same result. Why?

# Problems 3

Harmonic Oscillators

Two-Level Systems

Exercises and Problems

- ❖ Exercises
- ❖ R Program for the Damped Oscillator
- ❖ Problems
- ❖ Problems 2
- ❖ **Problems 3**
- ❖ Literature
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- ❖ 2LS Onsager

3. When  $E = 0$  determine the average dipole moment, the average of the absolute value of the dipole moment, and the deviation from the average dipole moment.
4. When  $E \neq 0$  the surroundings couple to the compound and there is a free energy of solvation  $A(E) - A(0)$ . Compute this free energy by (i) determining the energy as a function of  $E$  and then performing the Boltzmann weighted sum; or (ii) performing the trace with  $e^{-\beta\mathcal{H}}$ . These two calculations should again give the same answer.
5. Calculate  $\langle \hat{\mu} \rangle$  for  $E \neq 0$ . Why does this quantity increase with increasing  $E$ ?

# Literature

Harmonic Oscillators

Two-Level Systems

Exercises and Problems

- ❖ Exercises
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- ❖ Literature
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- ❖ 2LS Onsager

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2. J. Mehra and H. Reichenberg, *The Historical Development of Quantum Theory*, Springer, (2001).

# List of papers on coupled oscillators.

## Harmonic Oscillators

## Two-Level Systems

## Exercises and Problems

- ❖ Exercises
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- ❖ Literature
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Harmonic Oscillators

Two-Level Systems

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## Self-consistency: Onsager revisited (1)

2LS in a spherical cavity in polarizable medium.

- Expectation value of the dipole operator in the ground state causes polarization in the medium, and a reaction field.
- Reaction field changes the state of the system

Hamiltonian:

$$\mathcal{H} = \epsilon |0\rangle \langle 0| - \vec{\mu} \cdot \vec{E}_R$$

Reaction field:

$$\vec{E}_R = \frac{1}{4\pi\epsilon_0 a^3} \frac{2(\epsilon_r - 1)}{2\epsilon_r + 1} \langle \vec{\mu} \rangle_g \equiv A \vec{\mu}_g$$

Remember: a rotation over  $\theta$  with:

$$t = \tan \theta = \frac{\epsilon - \Delta \vec{\mu} \cdot \vec{E}_R - \sqrt{(\epsilon - \Delta \vec{\mu} \cdot \vec{E}_R)^2 + 4(\vec{\mu} \cdot \vec{E}_R)^2}}{2\vec{\mu} \cdot \vec{E}_R}$$

diagonalizes the Hamiltonian, and

$$\vec{\mu}_g = \frac{1}{1+t^2} (\vec{\mu}_0 + 2t\vec{\mu} + t^2\vec{\mu}_1)$$

## Harmonic Oscillators

## Two-Level Systems

## Exercises and Problems

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## Onsager revisited (2). Symmetry breaking.

This leads to a fourth order equation in  $t$ :

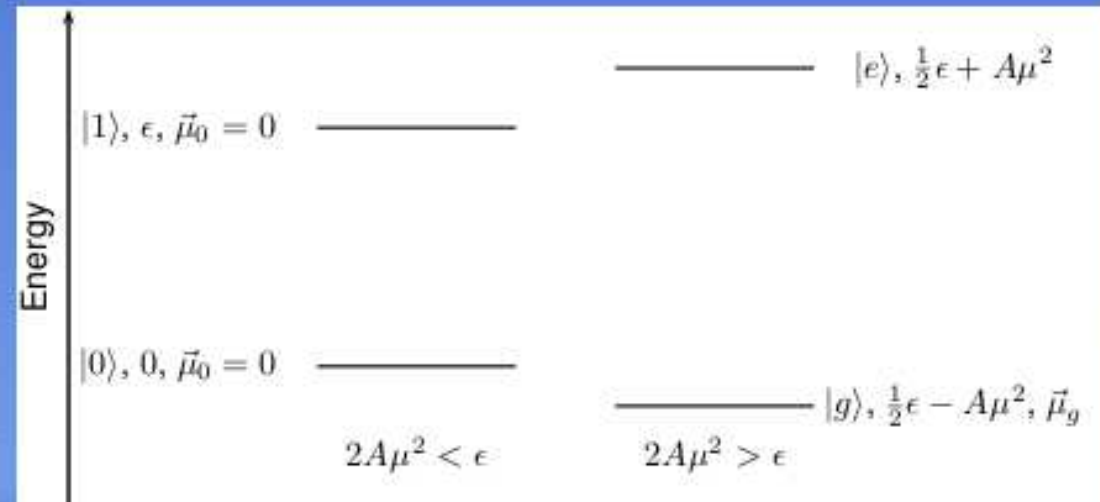
$$A\vec{\mu} \cdot \vec{\mu}_1 t^4 + t^3 [2A\mu^2 + A\mu_1^2 - \epsilon] + A\vec{\mu} \cdot \Delta\vec{\mu} t^2 + t [A\vec{\mu}_0 \cdot \Delta\vec{\mu} - 2A\mu^2 - \epsilon] - A\vec{\mu}_0 \cdot \vec{\mu} = 0$$

Simple case:  $\vec{\mu}_0 = \vec{\mu}_1 = 0$

$$t^3 [2A\mu^2 - \epsilon] - t [2A\mu^2 + \epsilon] = 0$$

Solution:

$$t = 0 \quad \text{and} \quad t^2 = \frac{2A\mu^2 + \epsilon}{2A\mu^2 - \epsilon} \quad \text{if} \quad 2A\mu^2 \geq \epsilon$$



## Harmonic Oscillators

## Two-Level Systems

## Exercises and Problems

- ❖ Exercises
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- ❖ 2LS Onsager

## Onsager revisited (3). Free energy and polarization fluctuations.

Free energy related to electric field fluctuations at the origin of the cavity (see also sheet 27):

$$G[\vec{E}] = \frac{E^2}{2A} \quad \text{with} \quad A = \frac{1}{4\pi\epsilon_0 a^3} \frac{2(\epsilon_r - 1)}{2\epsilon_r + 1}$$

Free energy of quantum system in fluctuating field:

$$G[\Psi, \vec{E}] = \langle \Psi | \mathcal{H}_0 | \Psi \rangle - \langle \Psi | \hat{\vec{\mu}} | \Psi \rangle \cdot \vec{E} + \frac{E^2}{2A}$$

Minimize  $G$  with respect to the state, and to the fields:

$$\frac{\delta G}{\delta \Psi} = 0 \quad \text{gives} \quad \left[ \mathcal{H}_0 - \hat{\vec{\mu}} \cdot \vec{E} \right] |\Psi\rangle = \epsilon |\Psi\rangle$$

( $\epsilon$  is an undetermined Lagrange multiplier put in to keep  $|\Psi\rangle$  normalized), and

$$\frac{\delta G}{\delta \vec{E}} = 0 \quad \text{gives} \quad \vec{E} = A \langle \Psi | \hat{\vec{\mu}} | \Psi \rangle$$

## Harmonic Oscillators

## Two-Level Systems

## Exercises and Problems

- ❖ Exercises
- ❖ R Program for the Damped Oscillator
- ❖ Problems
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## Classical-Quantum coupling in equilibrium

Equilibrium density operator:

$$\rho_{eq} = \frac{1}{Q} e^{-\beta[\mathcal{H}_0 - \vec{\mu} \cdot \vec{E} + E^2/2A]} = \frac{1}{Q} \left[ e^{-\beta(\epsilon_g + E^2/2A)} |g\rangle \langle g| + e^{-\beta(\epsilon_e + E^2/2A)} |e\rangle \langle e| \right]$$

with

$$Q = \int d\vec{E} \operatorname{Tr} e^{-\beta[\mathcal{H}_0 - \vec{\mu} \cdot \vec{E} + E^2/2A]}$$

Quantum equivalent of potential of mean force ("average Hamiltonian"):

$$\vec{\rho}_{eq} \equiv \sigma_{eq} = \int d\vec{E} \rho_{eq}$$

also called: reduced density matrix