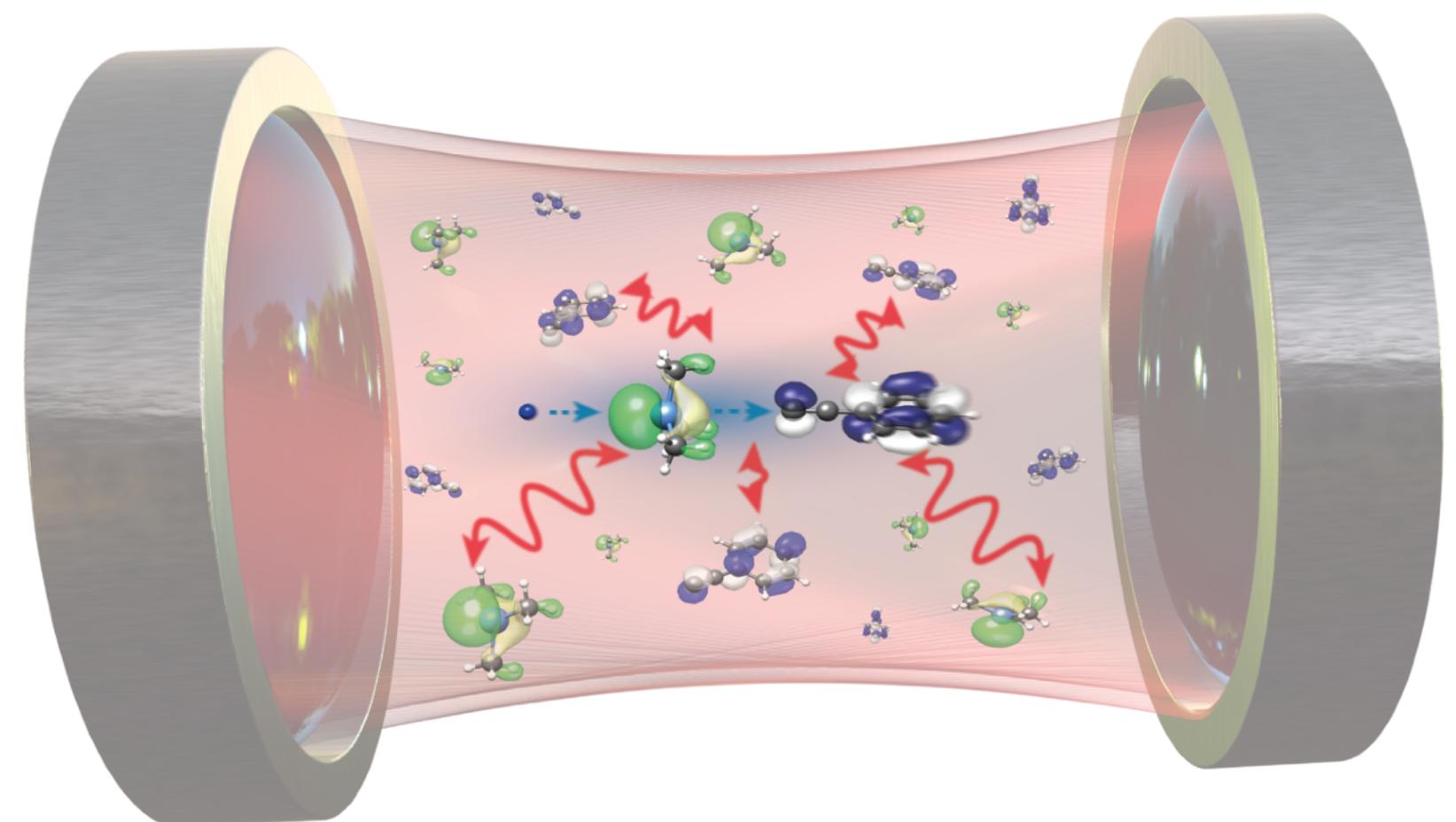
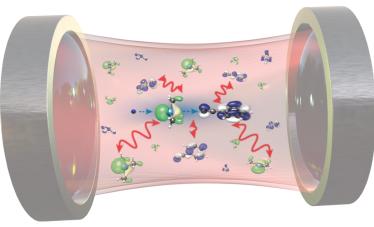


Dominik Sidler, 2025

Polaritonic / QED Chemistry

Lecture 1: Introduction

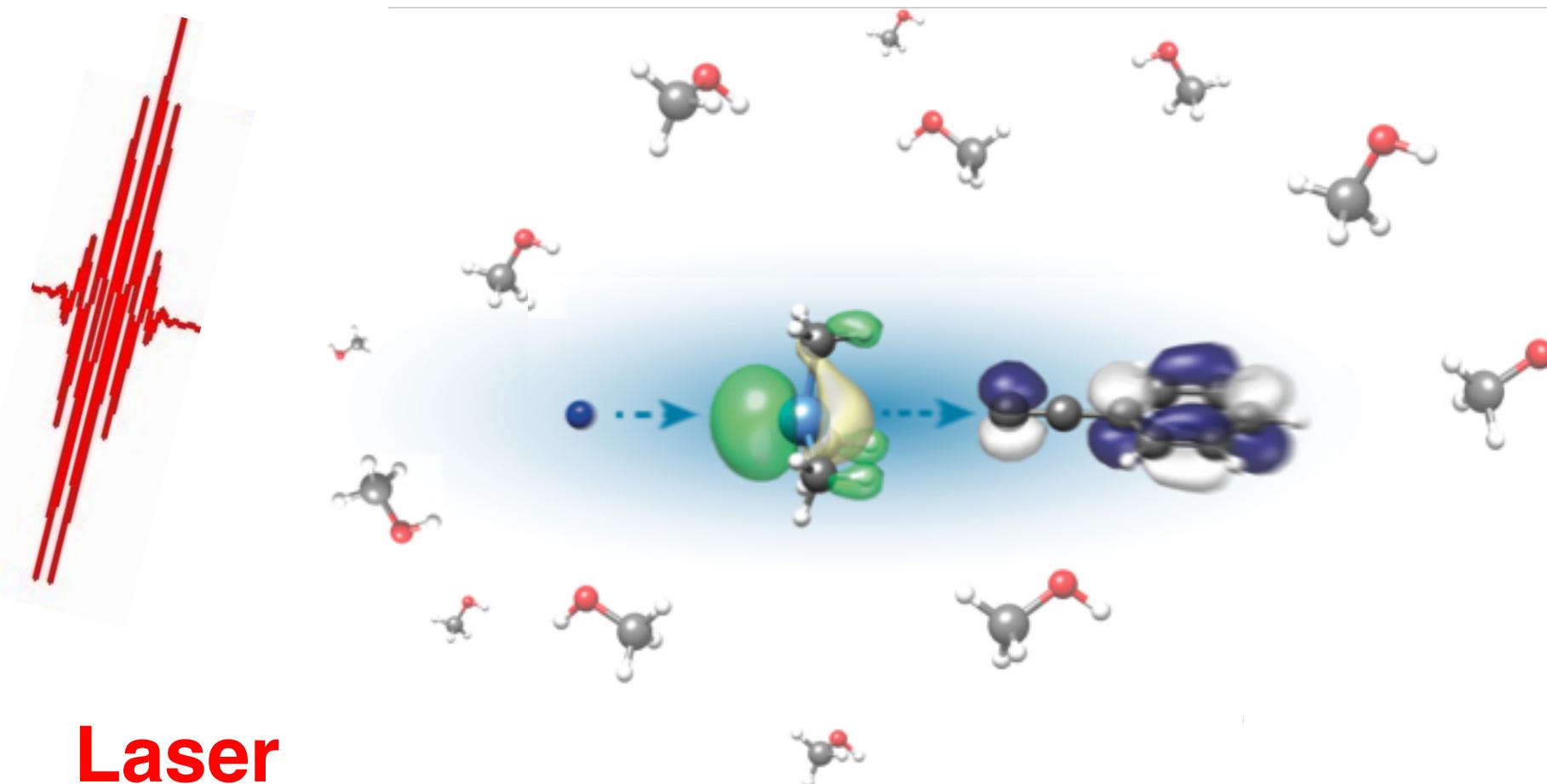




Polaritonic Chemistry

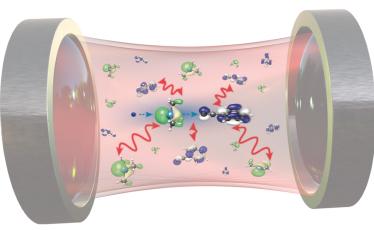
Coupling Light and Matter

Frequency (bond / site) selective control of chemistry?



**Laser
driving
with
undesired
heating**

**Control chemistry by
temperature,
pressure, solvent,
catalyst,...**

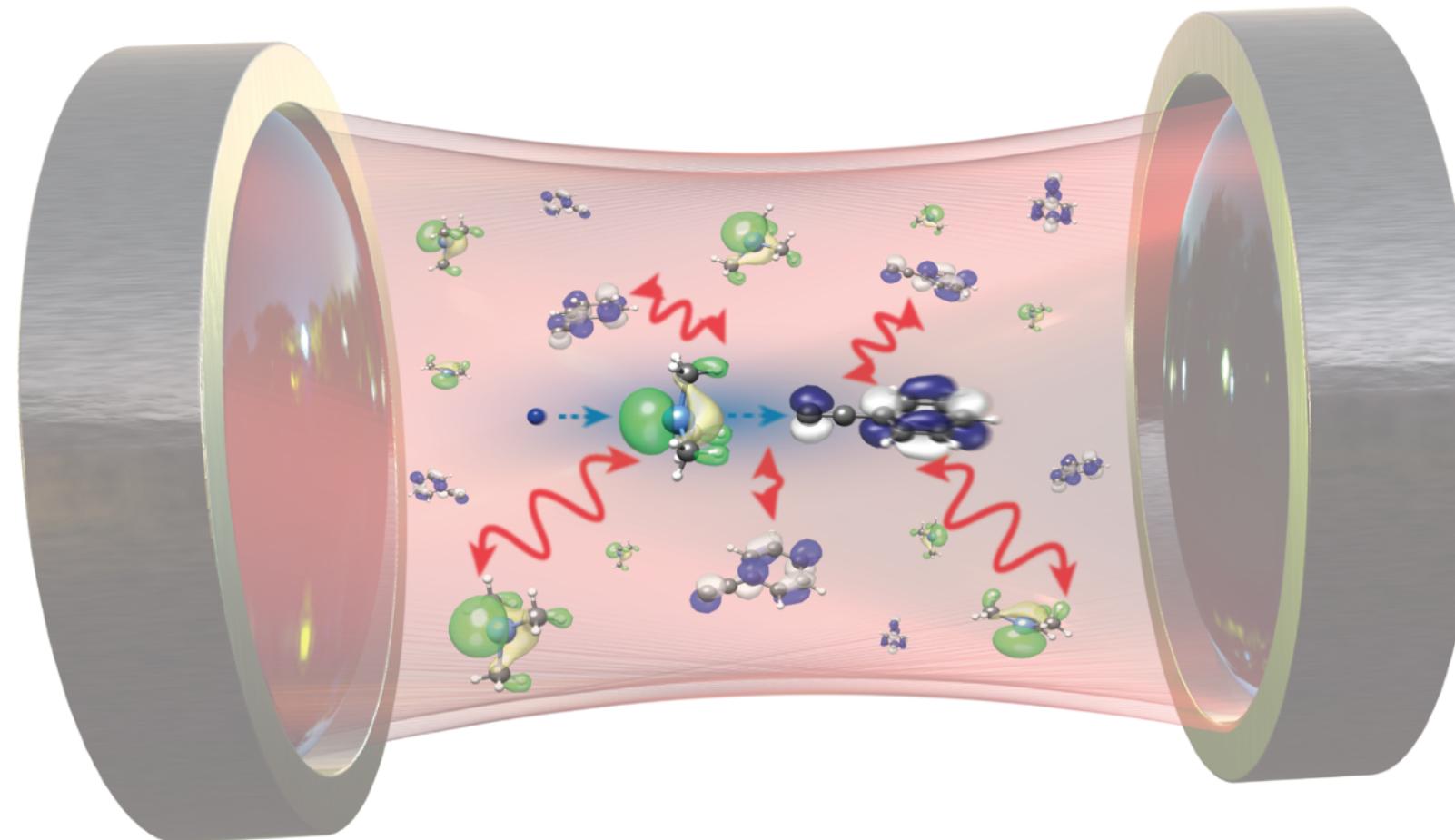


Polaritonic Chemistry

Coupling Light and Matter Strongly

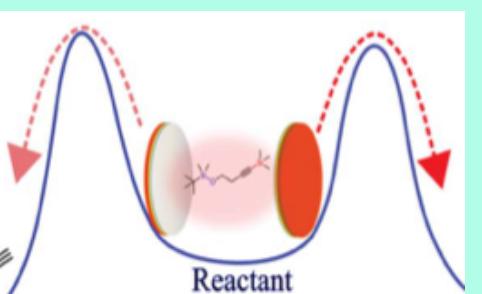
Frequency (bond / site) selective control of chemistry?

Optical cavity



Restructuring vacuum modes
Hybridisation of quantum light and matter

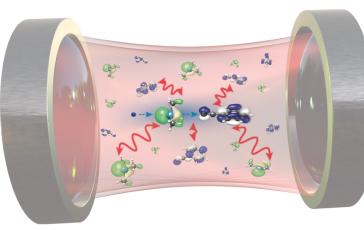
Experimental success



Engineer equilibrium properties

Novel chemical effects

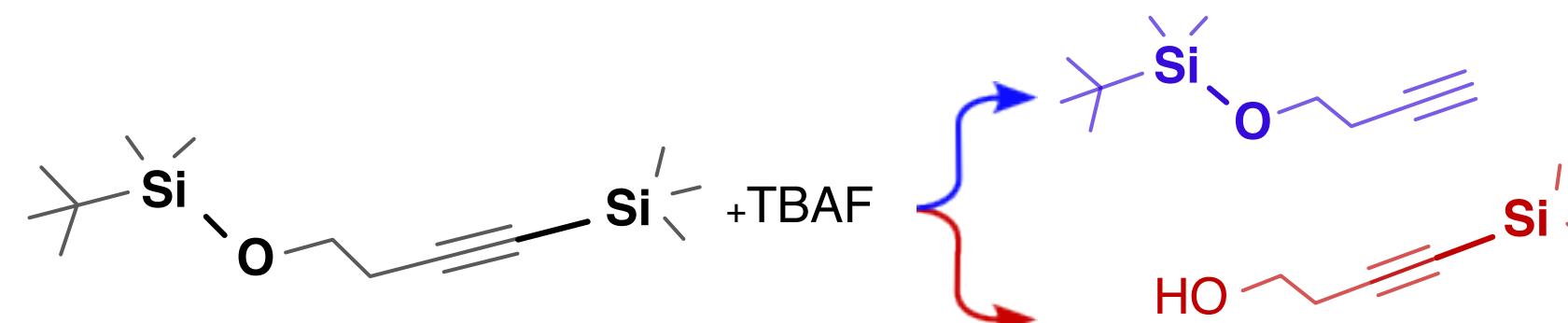
Industrial relevance



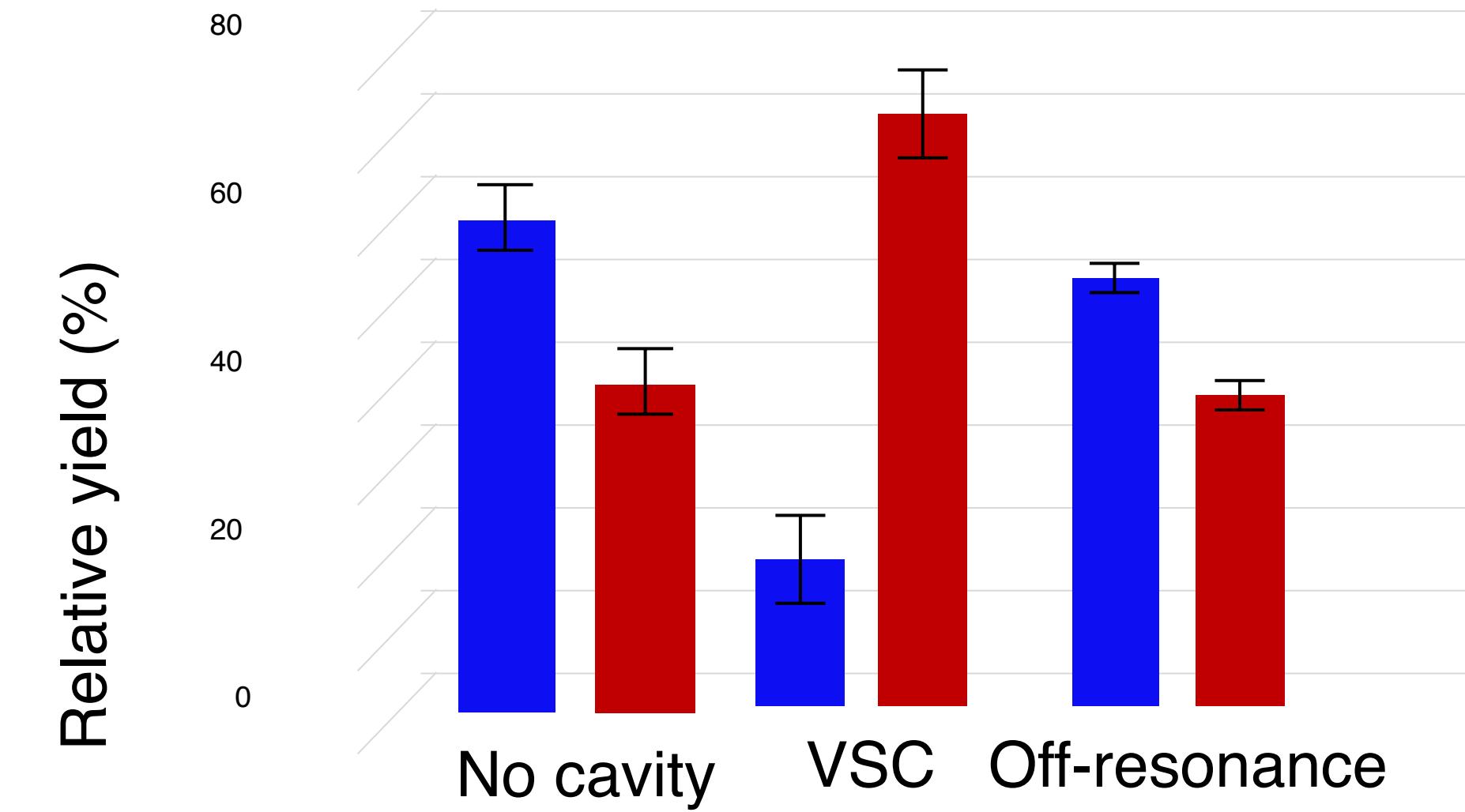
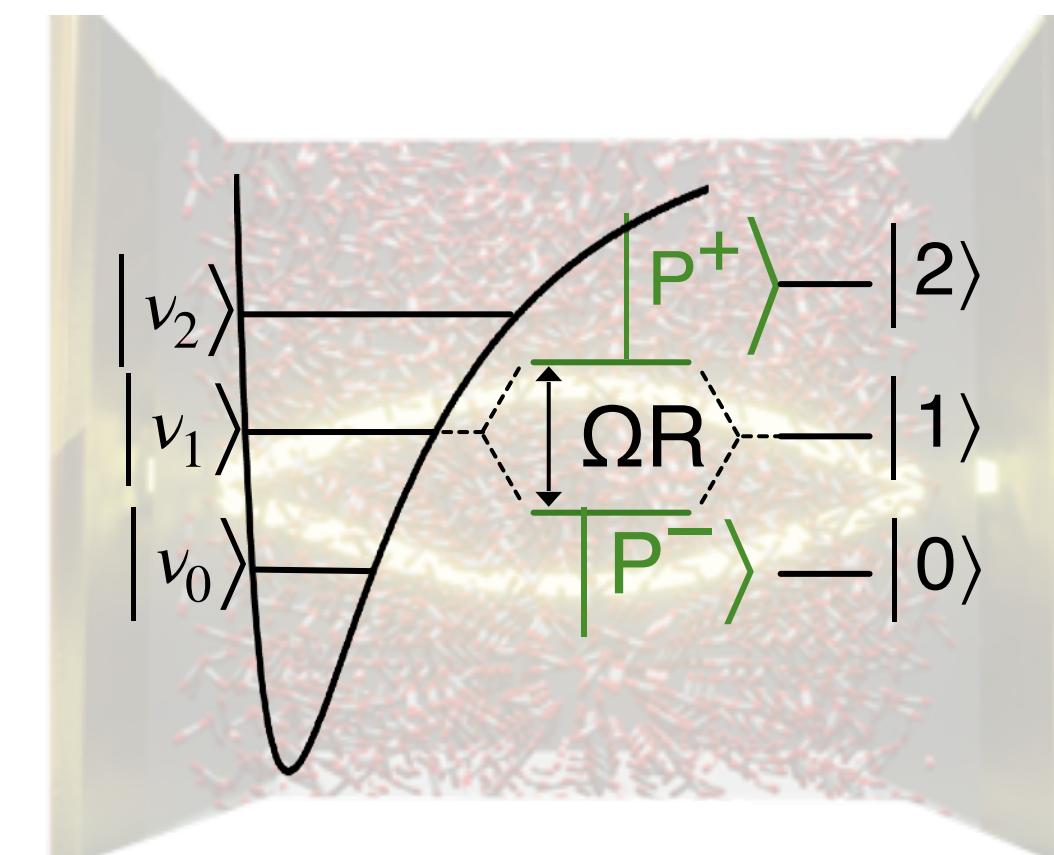
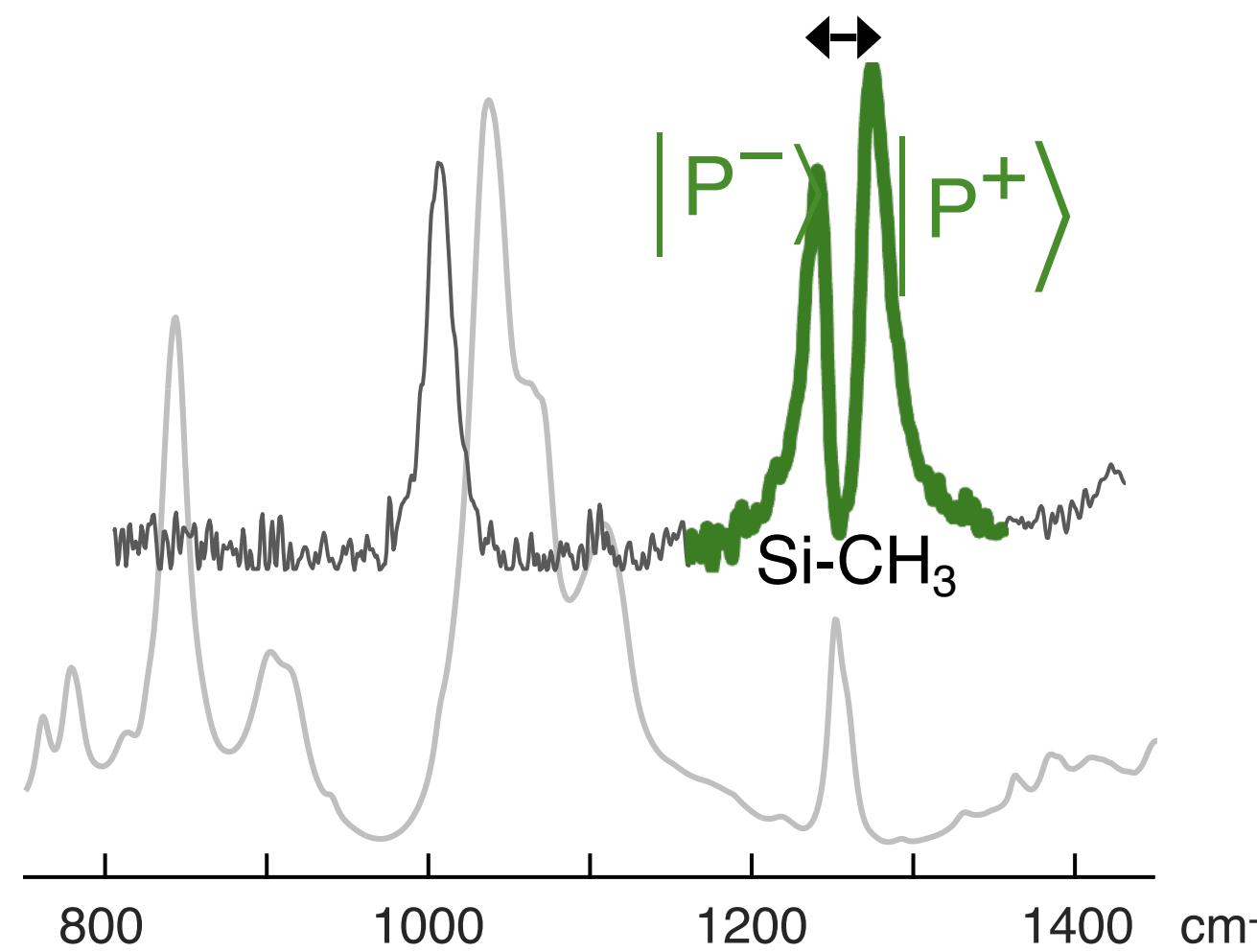
Seminal Experiments

Vibrational Strong Coupling (VSC): A Novel Tool for Tailoring Reactivity

Example: Site-selective silyl bond cleavage



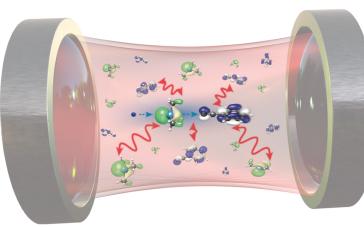
Rabi splitting Ω_R



A “different” molecule with modified properties

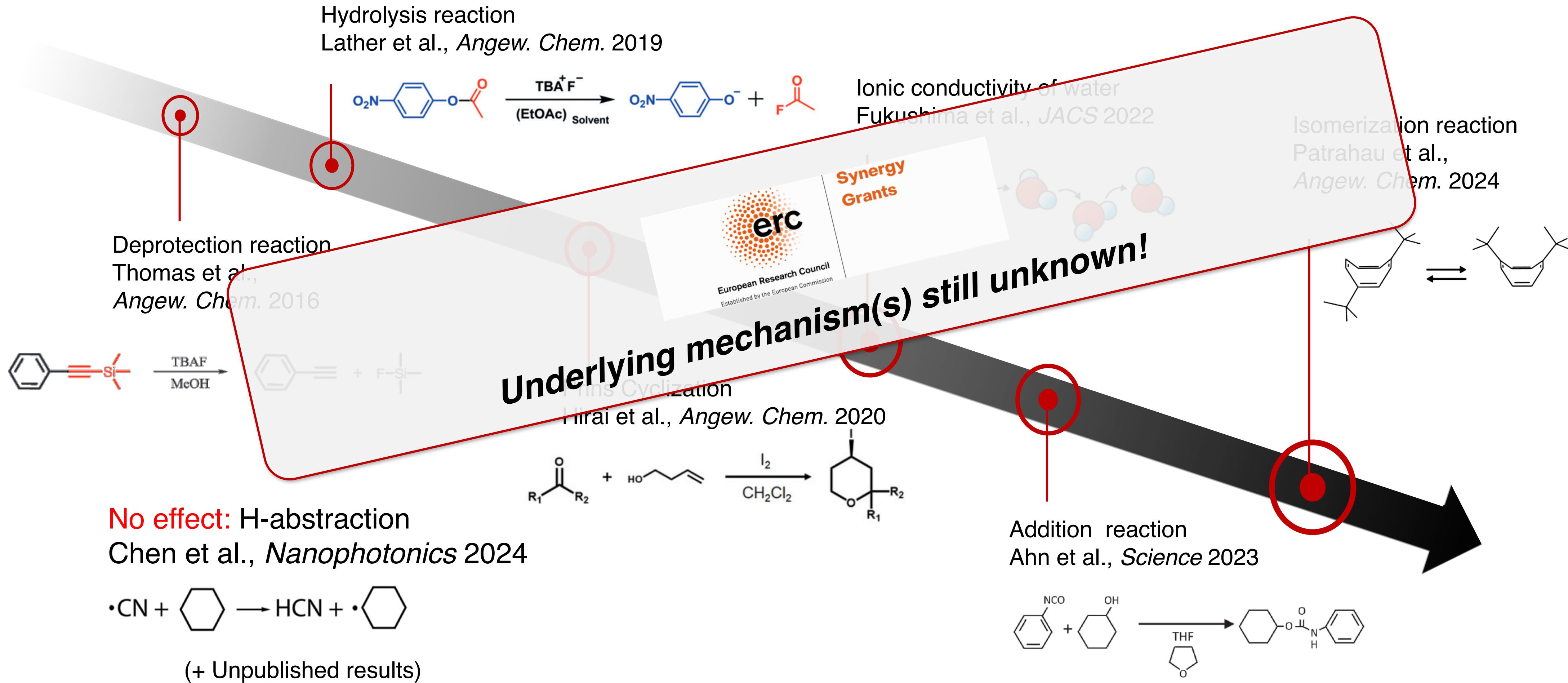
*** In the “dark”

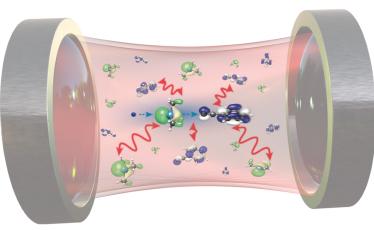
*** At room temperature



Seminal Experiments

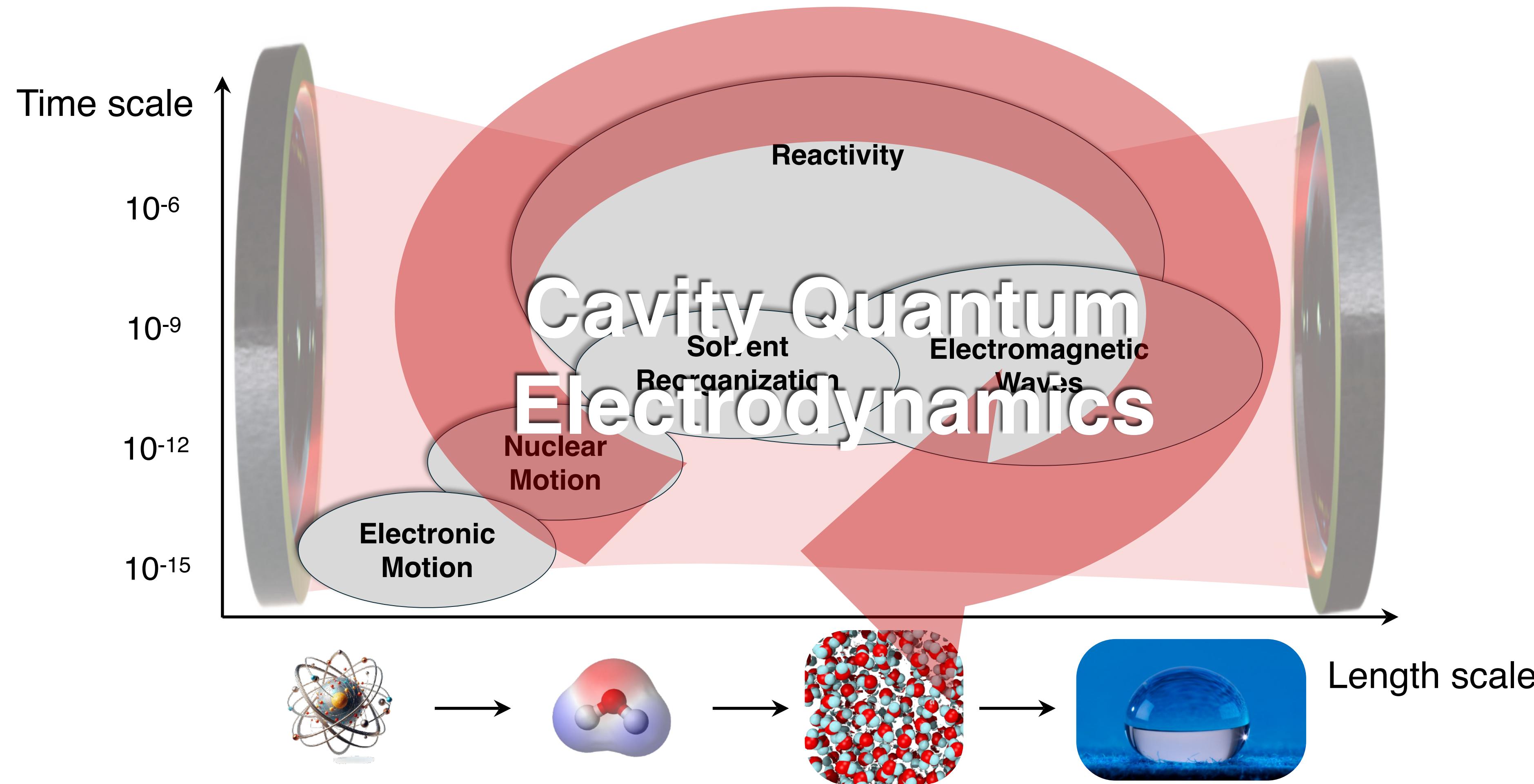
VSC: A Novel Tool for Tailoring Reactivity

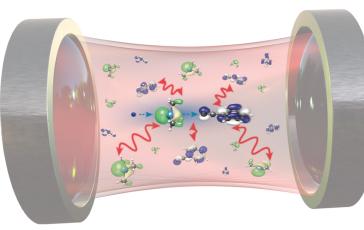




Polaritonic Chemistry

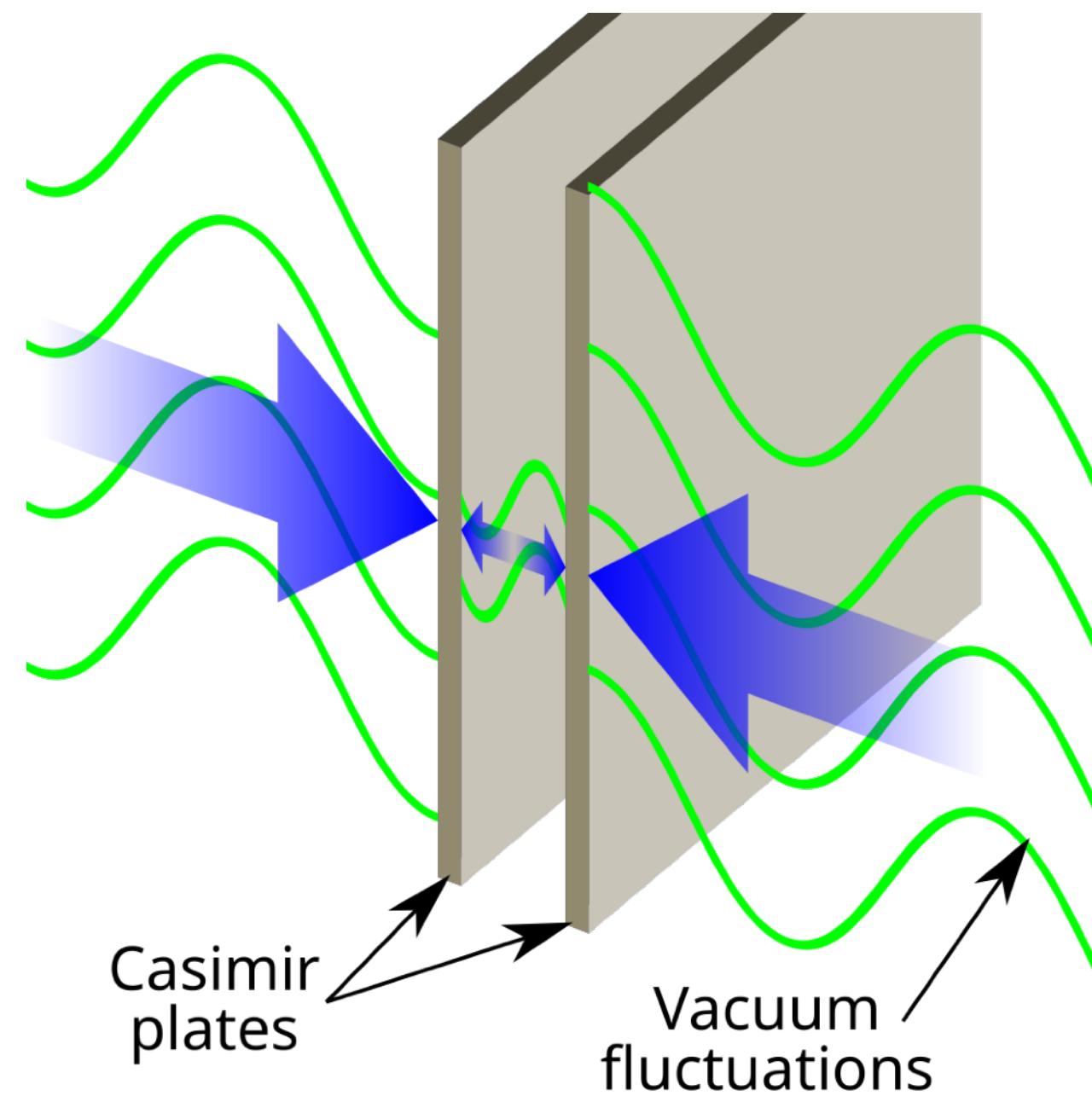
A Multiscale Challenge



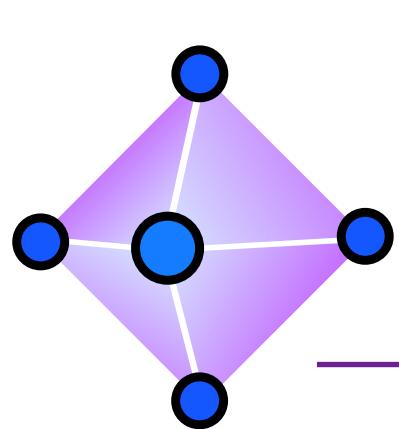


Why Quantum Light?

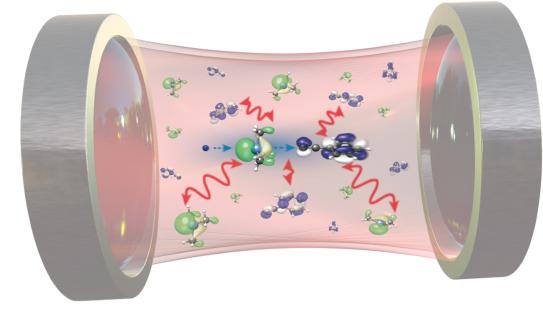
Famous Example: Casimir Forces



- Metal plates (cavity) **impose boundary conditions (BC)** on electromagnetic field.
- Only **discrete number of field modes** are allowed in cavity.
- **Breaks isotropy of space** / vacuum field is restructured that introduces **attractive force on metal plates**.



Lecture: Aims and Concept



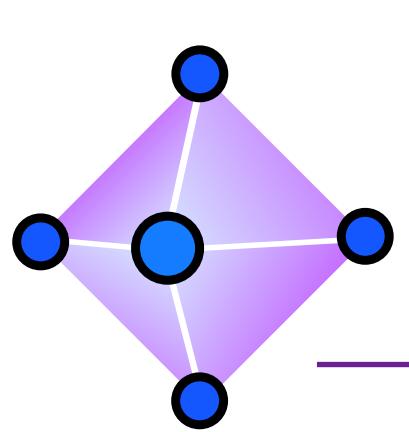
Polaritonic chemistry is a young and active research discipline and no general consensus about the relevant theoretical mechanism has been achieved!

1. Introduce fundamental theoretical concepts.
2. Focus on ab-initio methods, complementary with standard quantum / computational chemistry approaches.
3. Standard numerical solution strategies adjusted for optical cavities.
4. Illustrate several open theoretical questions.
5. Equip students to contribute their expertise to the highly interdisciplinary theoretical developments in the field.
6. Practical python exercises to familiarize with some key features.
7. Short presentations

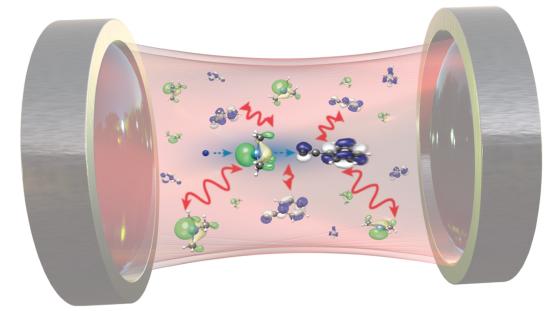
Be critical! Polaritonic chemistry is not established knowledge!
There are a lot of research opportunities awaiting for you!

Open PhD and postdoc positions at MPSD!
Synergy Grants
erc
European Research Council
Established by the European Commission

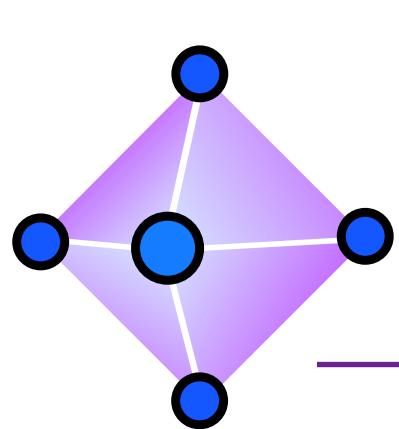




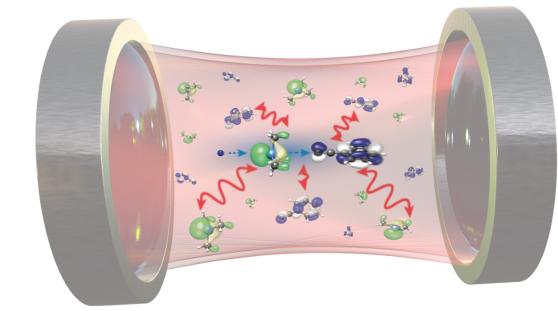
Who are you?



Background, expectations, interests, ...?

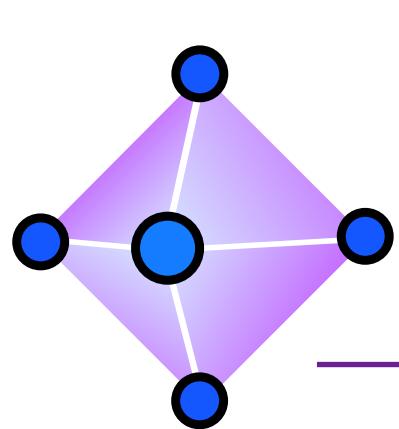


Outline

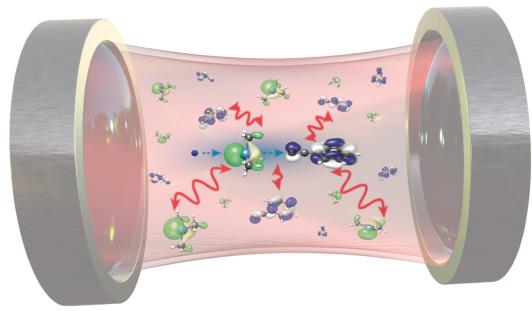


Course overview

Dates	Topic
24.02.2025	1) Introduction
03.03.2025	2) Macroscopic cavities / Maxwell's equations
10.03.2025	3) Quantum optics
24.03.2025	4) Pauli-Fierz theory
31.03.2025	5) Electronic strong coupling: Hartree Fock
07.04.2025	6) Vibration strong coupling: Cavity Born-Oppenheimer molecular dynamics
14.04.2025	No lecture (programming task)
21.04.2025	No lecture (Easter Monday)
28.04.2025	No lecture (Sechseläuten)
05.05.2025	7) Fundamental open questions: Local vs. collective and thermodynamics
12.05.2025	8) Advanced topic: Electron correlation and connection to a spin glass
19.05.2025	9) Advanced topic: TBD (e.g. polaritonic reaction rates, or advanced electronic structure methods)
26.05.2025	Presentations / literature seminar / ongoing research



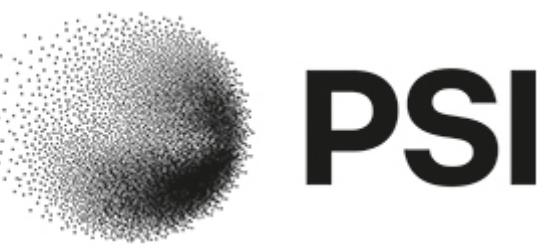
Course Informations



This course is based on the 2024 CECAM school: „Ab initio quantum electrodynamics for quantum materials engineering“. (<https://memento.epfl.ch/event/cecam-school-ab-initio-quantum-electrodynamics-for/>)



Lecturer: Dr. Dominik Sidler (dominik.sidler@psi.ch)
Scientist at PSI and Groupleader at MPSD (Prof. A. Rubio)



Python exercises and lecture notes:

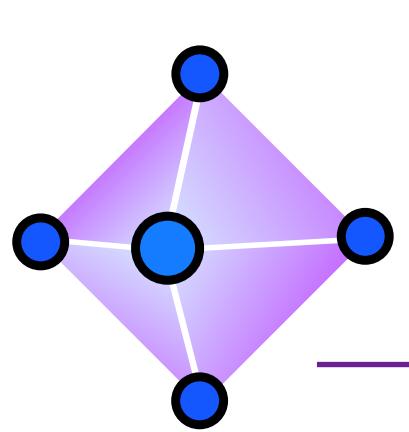
Git access: git clone https://github.com/sidu85/polaritonic_chemistry_lecture_public.git

Run exercises with *jupyter notebook* on your personal notebook.

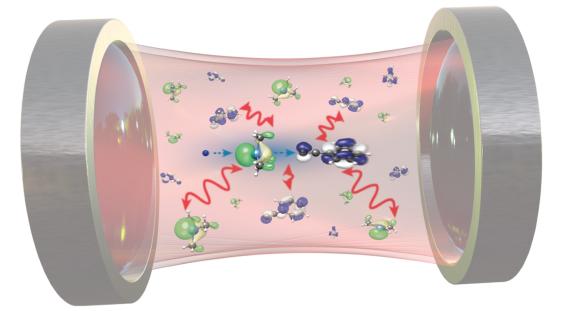
Recommended to install python with anaconda: <https://docs.anaconda.com/anaconda/install/>

Programming exercises start during lecture 2. Be prepared!

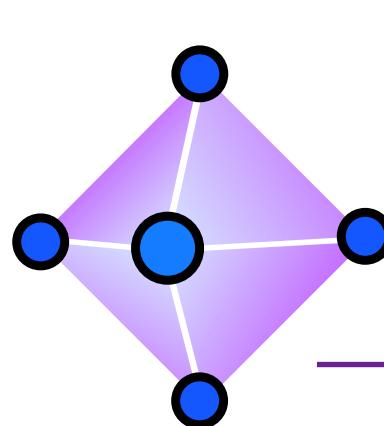




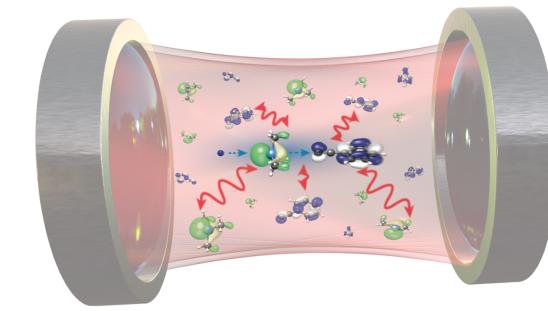
Notebook 1



Test jupyter, git access etc. Please run at home...



Theoretical Complexity



The beauty and the beast

correlations
stochastic resonances

real space vs.
k-space
gauge choice

matter vs. light
degeneracy

**solid, liquid,
gaseous phase**

**resonance
effects**

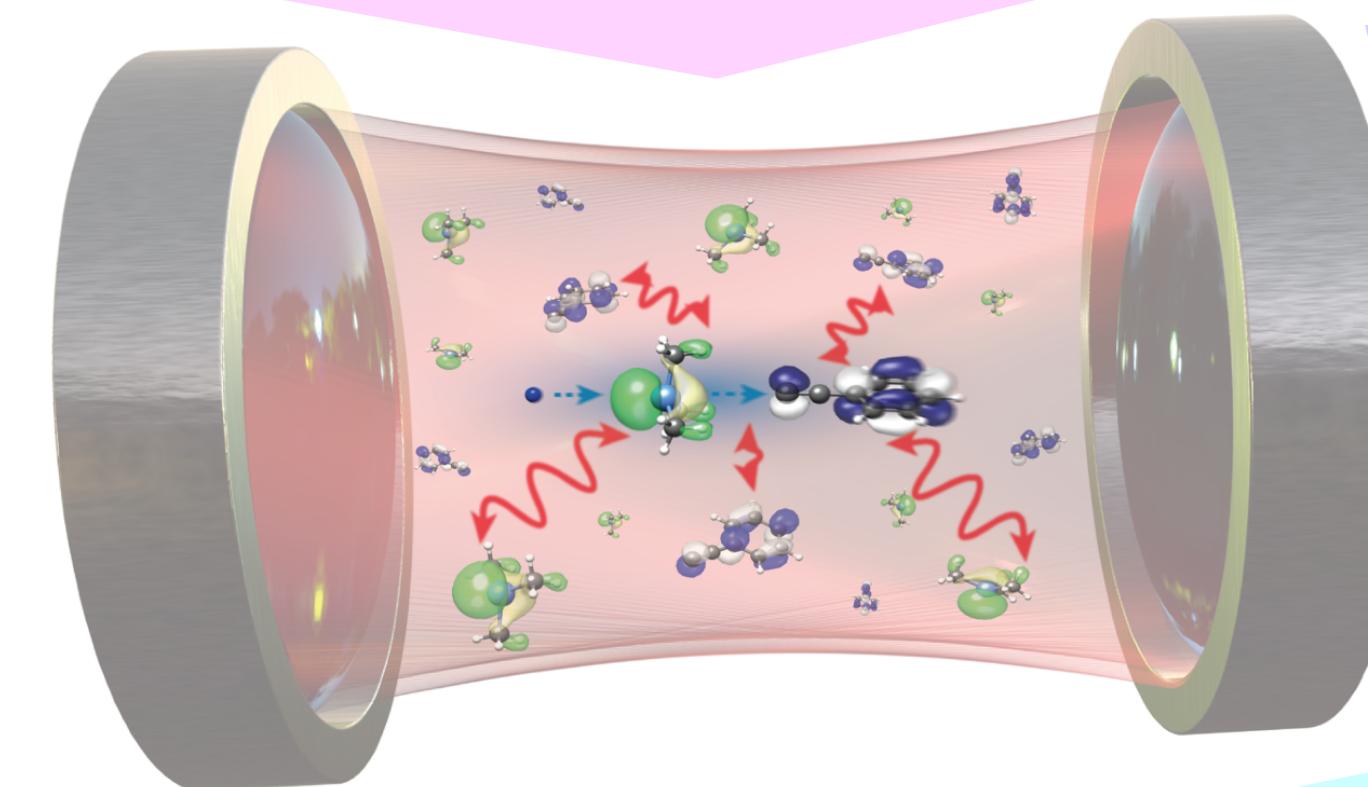
symmetry breaking

IR
NMR
Raman
Optical Activity

**experimental
observables**

collective vs. local

spin glass thermodynamic limit
Tavis-Cummings model



modified response
mirror material losses
engineer cavity / mode structure

partitioning of wave-function
photochemical processes
nucelar dynamics

**electronic vs.
vibrational coupling**

thermodynamics

minimal statistical entity
Boson vs. Fermion
free energy and entropy
frustration

external driving

electric / magnetic
pumping
time-resolved
static

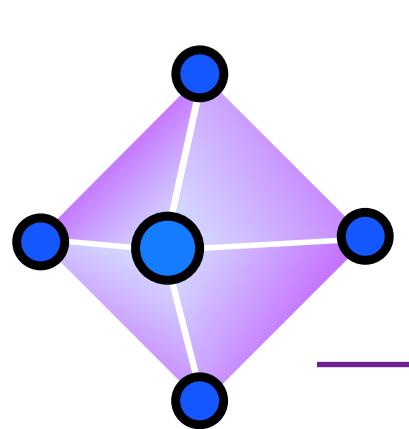
numerics

QEDFT
cavity CC
MD

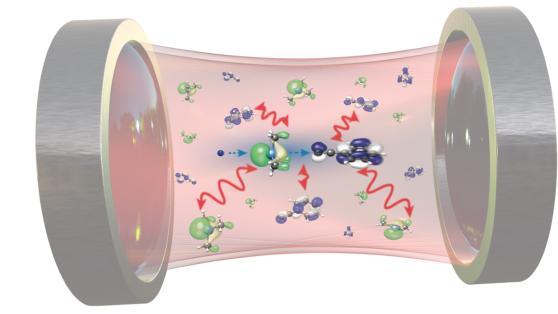
reactions

cavity HF
multi reference
kinetics vs. PES

No-one possess expertise in all relevant fields, but cavity connects them!



Fabry-Pérot Cavity



Prototypical Cavity Setup

Assume normal incident light

speed of light $c = c_0/n$

refractive index n

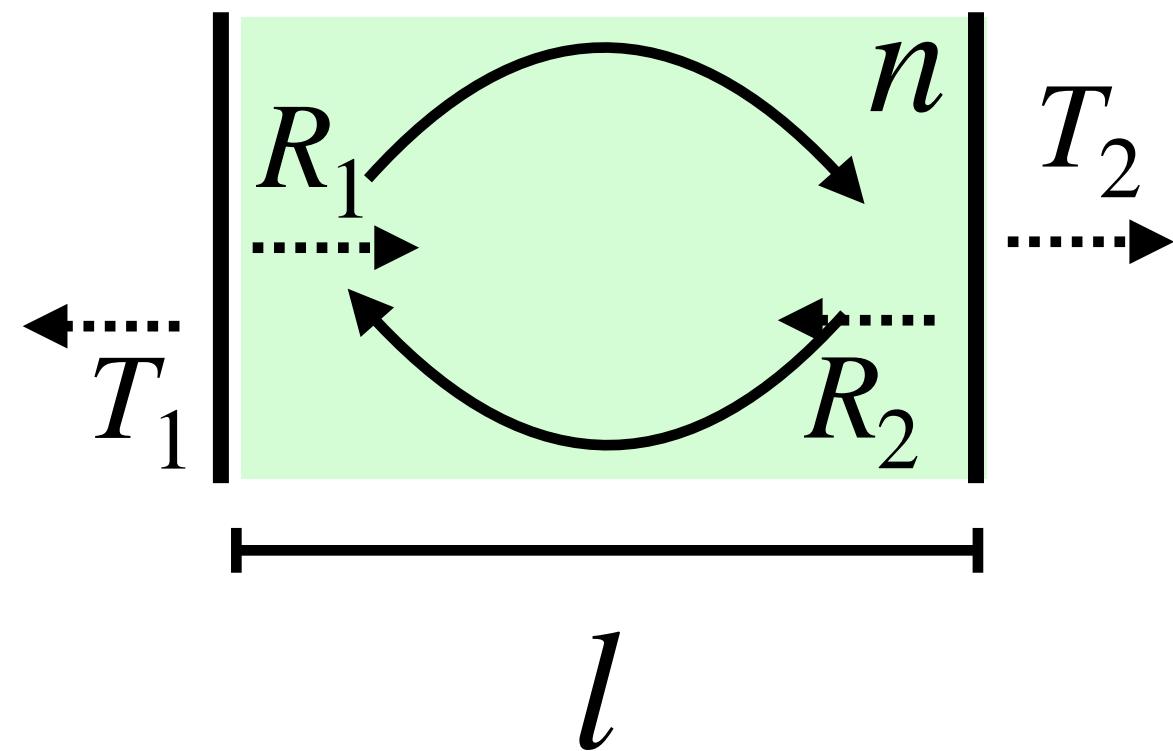
round-trip time $t_{RT} = \frac{2l}{c}$

electric-field r_i^2 or intensity reflectivity R_i

transmitted intensity T_i

losses at mirror τ_i

$$R_i = 1 - T_i = e^{-\frac{t_{RT}}{\tau_i}}$$



photon decay time of resonator $\frac{1}{\tau_c} = \sum_i \frac{1}{\tau_i}$

number of photons decay as $\varphi(t) = \varphi(0)e^{-t/\tau_c}$

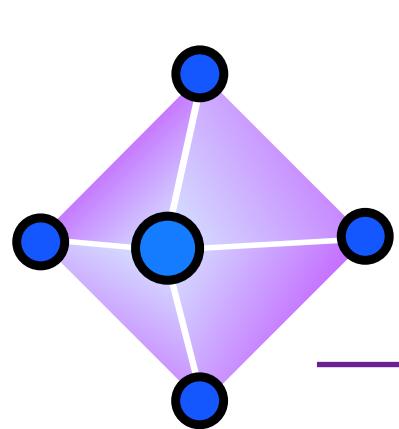
single-pass phase shift $\phi(\nu)$ at frequency ν

resonance condition for constructive interference

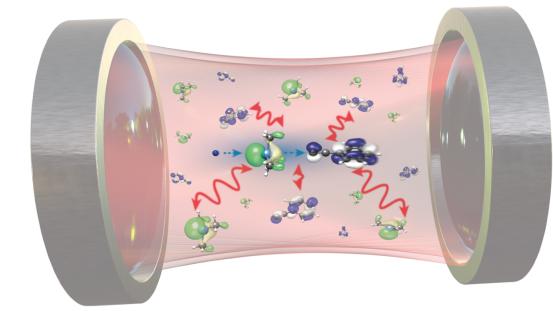
$$2\phi = 2\pi\Delta\nu_{FSR}t_{RT} \stackrel{!}{=} 2\pi$$

free spectra range $\Delta\nu_{FSR} = 1/t_{RT}$

resonance frequency $\nu_q = q\Delta\nu_{FSR}$, $q \in \mathbb{Z}$, of mode q



Fabry-Pérot Cavity



Lorentzian Finesse

Can we resolve different resonator modes?

Use Taylor criterion: Two spectral lines resolved if the individual lines cross at half intensity.

Assume electric field at frequency ν_q represented by damped harmonic oscillator of the following form: $E_q(t) = E e^{i2\pi\nu_q t} e^{-t/(2\tau_c)}$

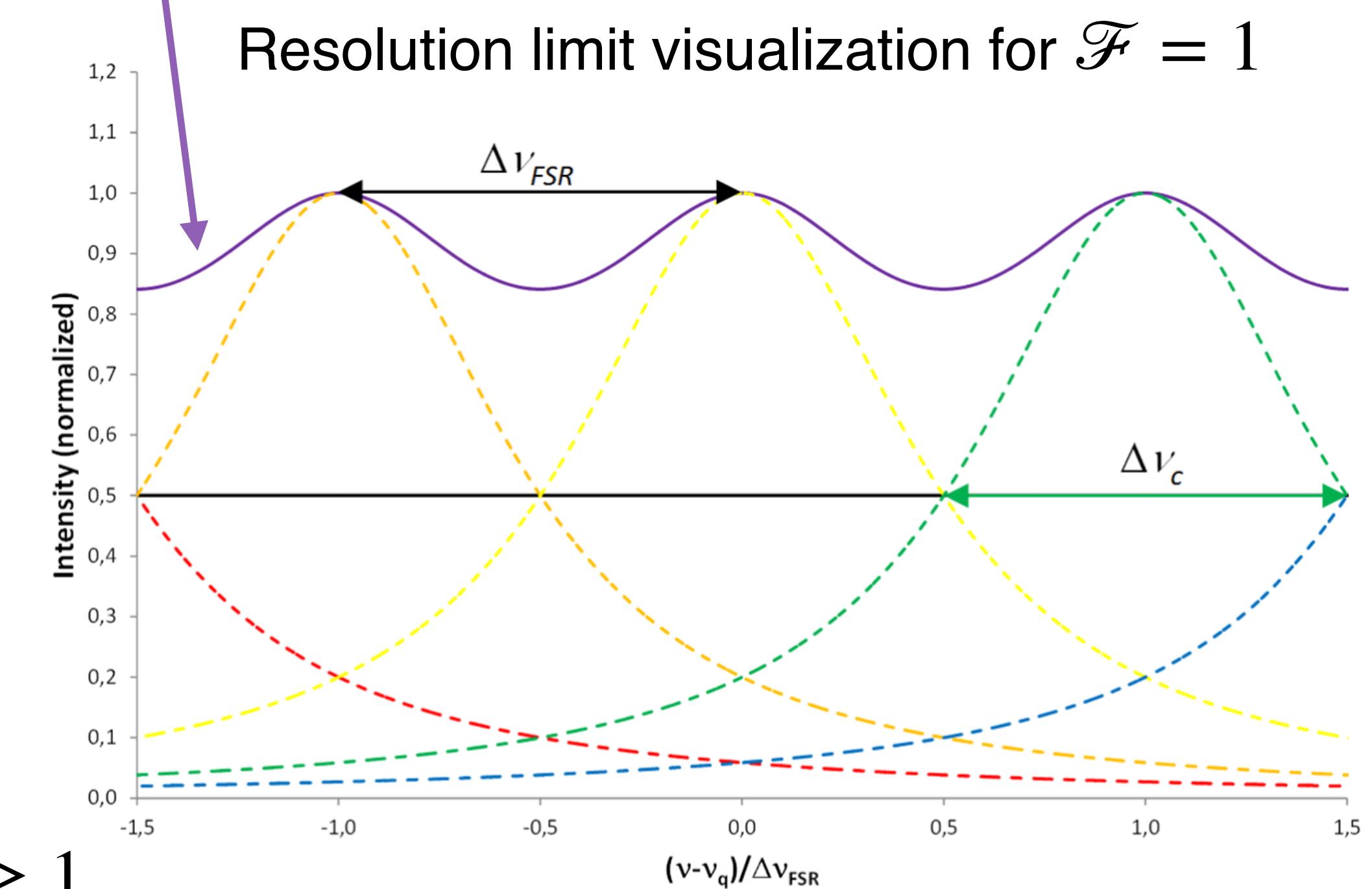
Normalized spectral line shape per mode (Lorentzian):

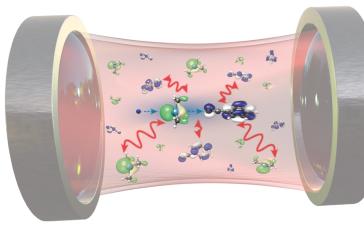
$$\gamma_q(\nu) = \frac{1}{\tau_c} \left| \frac{FT\{E_q(t)\}}{E} \right|^2 = \frac{1}{\pi} \frac{\Delta\nu_c/2}{(\Delta\nu_c/2)^2 + (\nu - \nu_q)^2}, \quad \Delta\nu_c = \frac{1}{2\pi\tau_c}$$

$$\text{Lorentzian finesse } \mathcal{F} = \frac{\Delta\nu_{\text{FSR}}}{\Delta\nu_c}$$

Single modes resolved if $\mathcal{F} \geq 1$

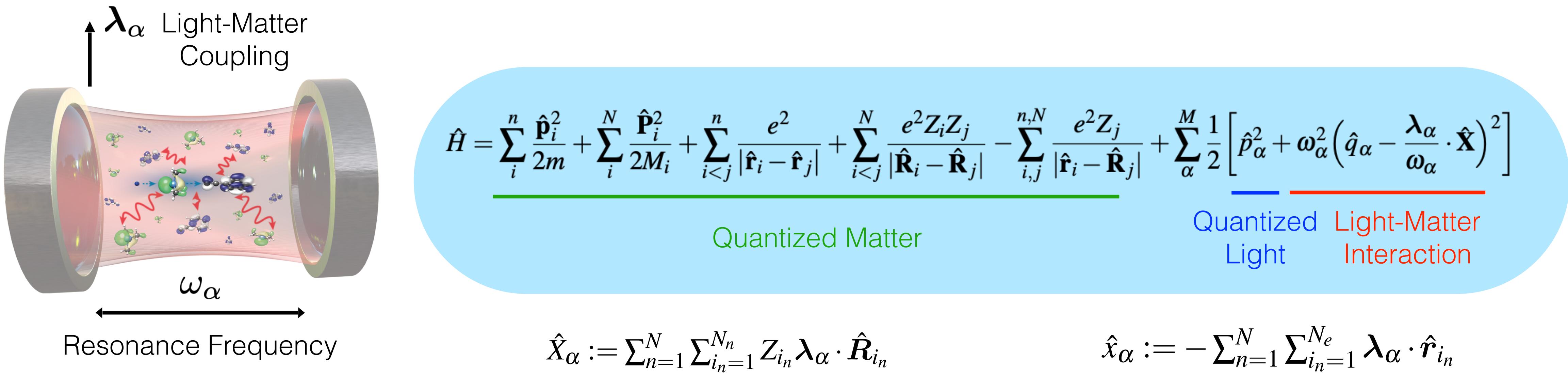
Airy distribution (from superposition of modes)



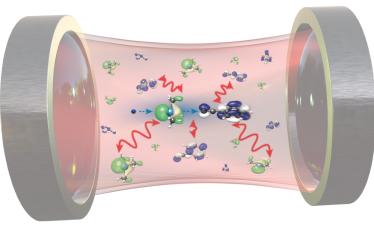


Ab-initio Quantum Theory

Pauli-Fierz Hamiltonian (in Dipole Approximation)



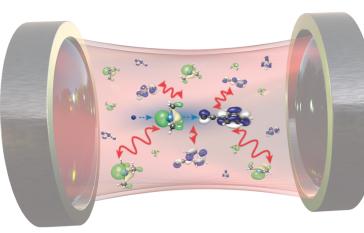
- Non-relativistic limit of quantum electrodynamics
 - Schrödinger-type equation
 - Possesses ground-state (variational principle applicable)



Repetition of Quantum Mechanics

Quantum Harmonic Oscillator, Perturbation Theory, Polarizability

Blackboard



Summary Quantum Harmonic Osc.

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{k}{2}\hat{x}^2 = \hbar\omega\left(\hat{N} + \frac{1}{2}\right) = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right)$$

$$\omega = \sqrt{k/m}$$

Ladder operator method

$$\hat{p} = i\sqrt{\frac{\hbar m\omega}{2}}(a^\dagger - a) \quad \hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a)$$

Creation Op.

$$a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle \quad \langle n | m \rangle = \delta_{nm}$$

Annihilation Op.

$$a |n\rangle = \sqrt{n} |n-1\rangle \quad a |0\rangle = 0 \quad [a^\dagger, a] = 1$$

Energy eigenvalues

$$E_n = \langle n | \hat{H} | n \rangle = \hbar\omega(n + \frac{1}{2})$$

Apply static external electric field ϵ

$$\hat{H}(\epsilon) = \frac{\hat{p}^2}{2m} + \frac{k}{2}\hat{x}^2 + \epsilon e \hat{x}$$

Polarizability

$$\alpha = \frac{d}{d\epsilon} \langle 0 | e \hat{x} | 0 \rangle$$

Assume $\epsilon \approx 0$, use 2nd order perturbation theory

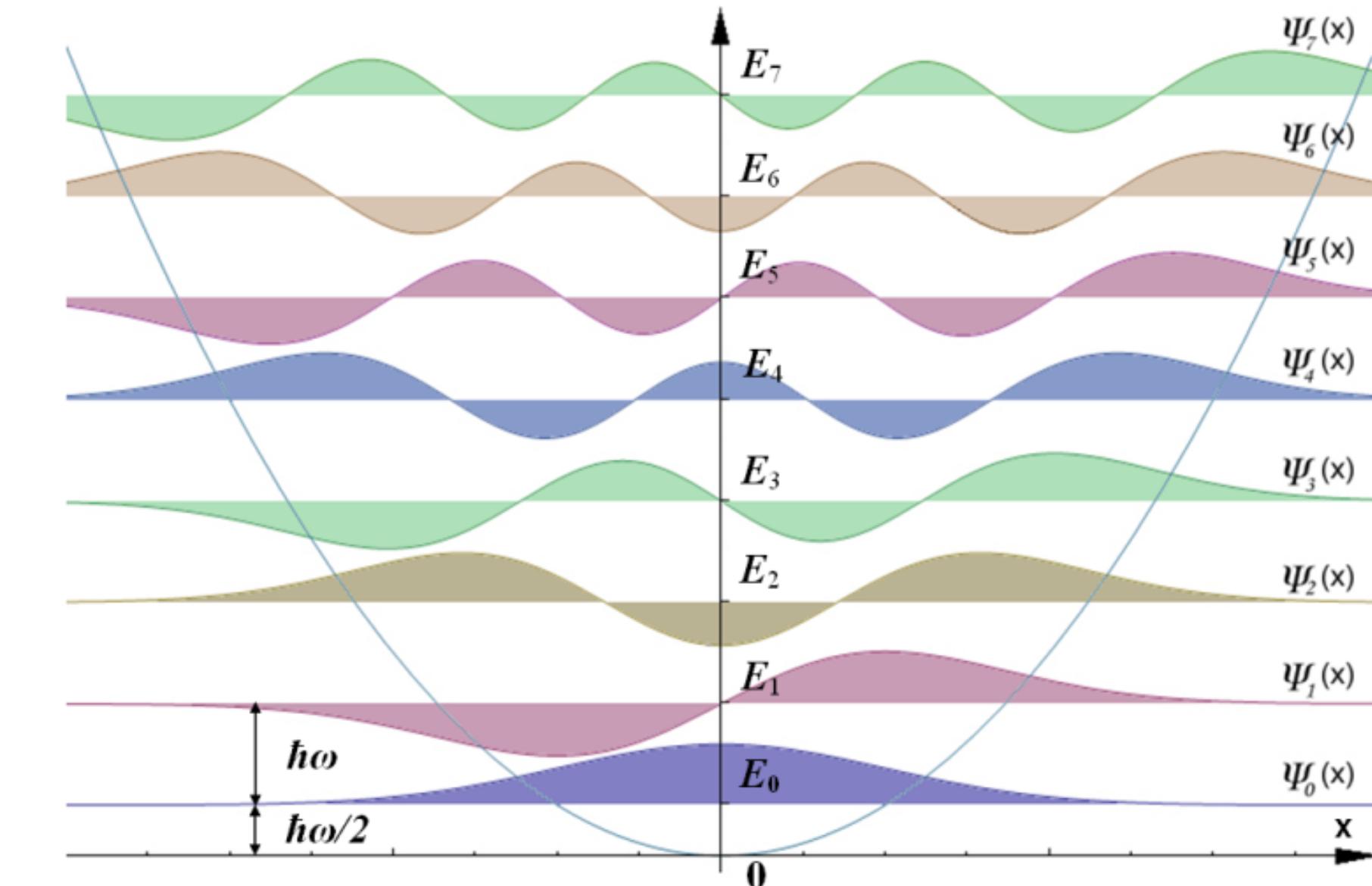
$$\Rightarrow \alpha = \frac{e^2}{k}$$

Using Hellmann-Feynman theorem

$$\langle 0 | e \hat{x} | 0 \rangle = \frac{d}{d\epsilon} \langle 0 | \hat{H}(\epsilon) | 0 \rangle$$

$$E_n(\epsilon) = E_n + \epsilon \langle n | e \hat{x} | n \rangle + \epsilon^2 \sum_{k \neq n} \frac{|\langle k | e \hat{x} | n \rangle|^2}{E_n - E_k} + O(\epsilon^3)$$

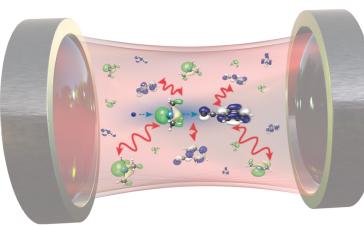
Outlook: Perturbation theory can break down for electronic structure under strong light-matter coupling in optical cavities even for $\epsilon \approx 0$.



Position representation: $\Psi_\nu(x) \propto H_\nu(\beta x)e^{-\beta x^2/2}$

Examples of Hermite Polynomials

0	1
1	$2z$
2	$4z^2 - 2$
3	$8z^3 - 12z$
4	$16z^4 - 48z^2 + 12$

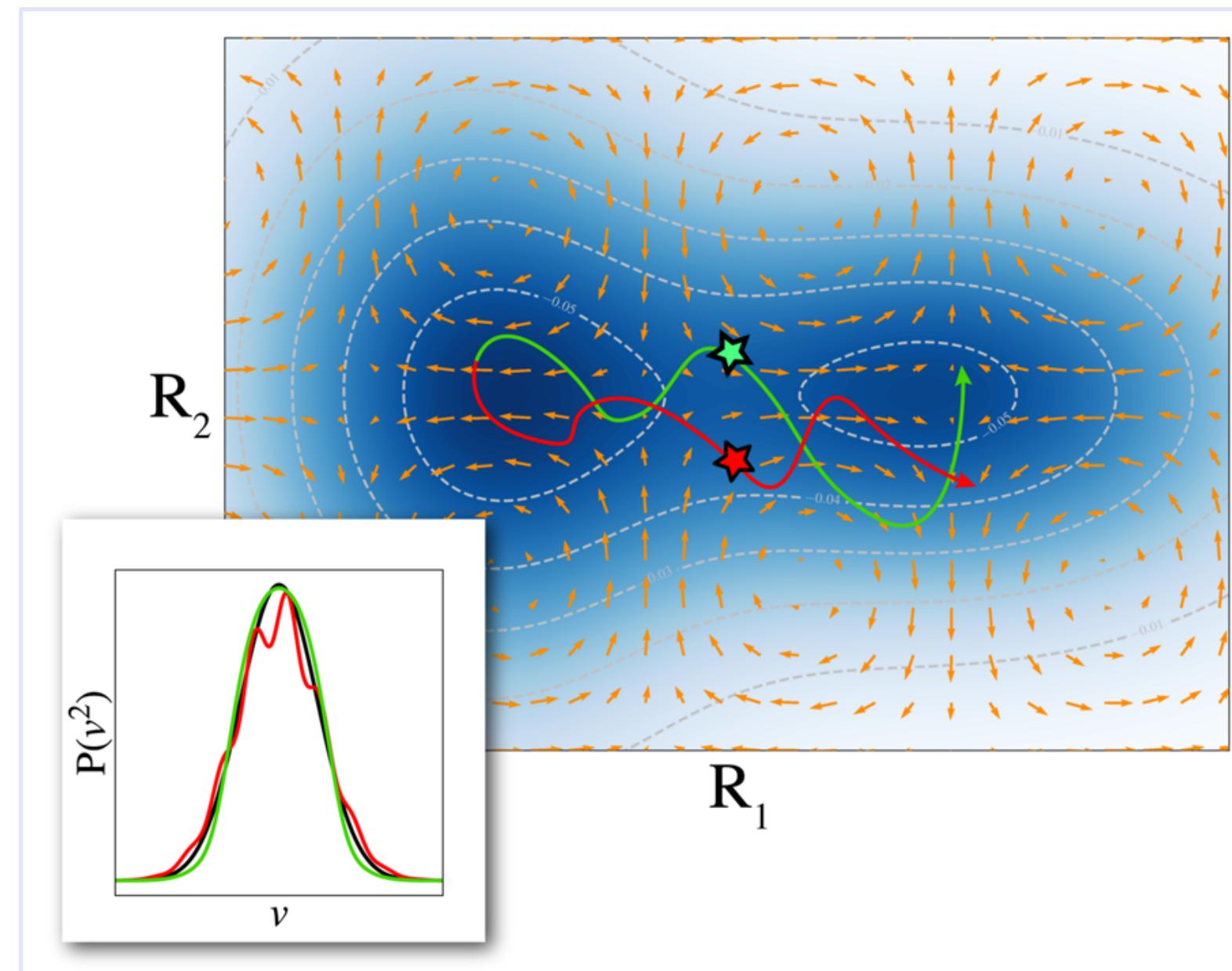


Outlook: What About the Nuclei?

Electronic structure problem will be complex

Classical Cavity Born-Oppenheimer Molecular Dynamics

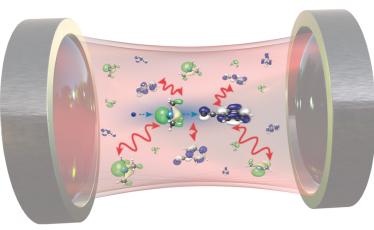
$$H^{\text{hyp}} := H_m^n + \sum_{\alpha=1}^M \left(\frac{p_\alpha^2}{2} + \frac{\omega_\alpha^2}{2} \left(q_\alpha - \frac{X_\alpha}{\omega_\alpha} \right)^2 + \langle \psi_0 | \hat{H}_e(\underline{\mathbf{R}}, \underline{q}) | \psi_0 \rangle \right)$$



Electronic problem:
Cavity correlations (aging effects) may introduce
explicit **time-dependent electronic forces**

Add (nuclear) temperature:
Classical Langevin equations of motion.

**Non-conservative forces imply non-canonical (!)
dynamics and possibly stochastic resonances.**

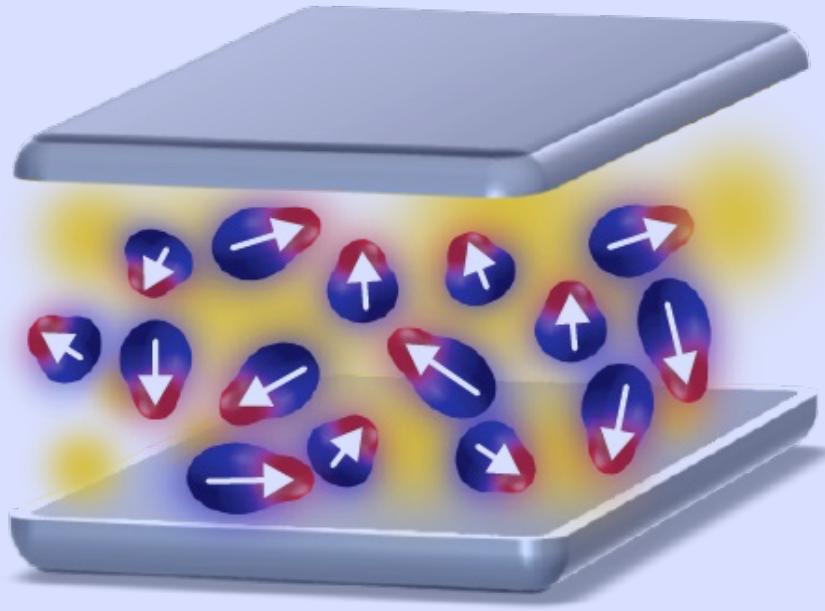


Outlook

Non-trivial Feedback in VSC

Electronic Structure

$$\langle \Psi | \sum_i^{N_e} \left\{ \frac{\hat{\mathbf{p}}_i^2}{2} - \frac{1}{2} \sum_l^{N_N} \frac{Z_n}{|\hat{\mathbf{r}}_i - \mathbf{R}_l|} + \frac{1}{2} \sum_j^{N_e} \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} \right\} + \left(\frac{1}{2} \hat{x}^2 + \hat{x}X - \omega_\beta \hat{x}q_\beta \right) |\Psi\rangle$$



Seed of VSC:

*Collectively induced polarization instability.
Replica symmetry breaking & (dynamic)
frustration.*

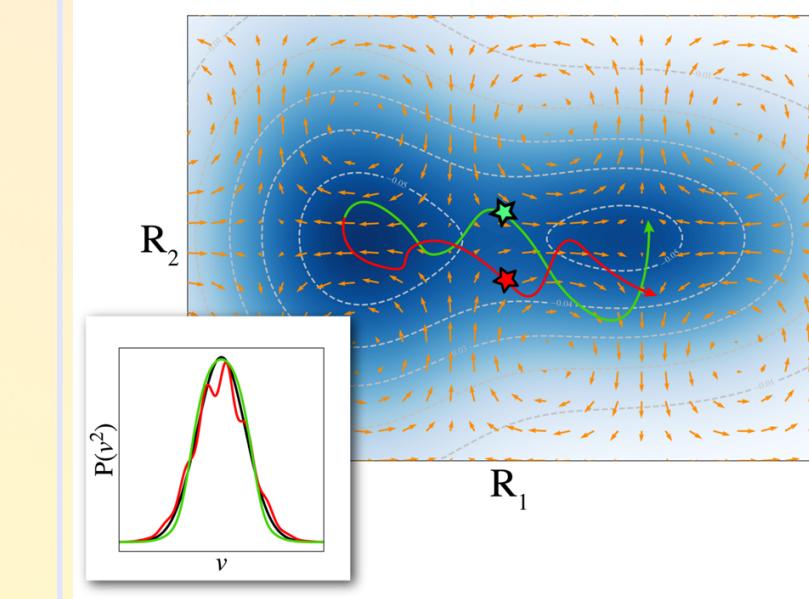
?



European Research Council
Established by the European Commission

Synergy Grants

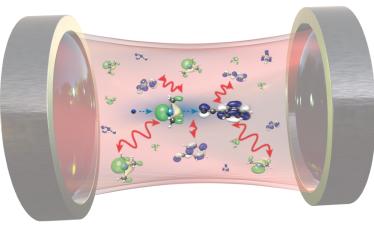
$$H^{\text{npt}} := H_m^n + \sum_{\alpha=1}^M \left(\frac{p_\alpha^2}{2} + \frac{\omega_\alpha^2}{2} \left(q_\alpha - \frac{X_\alpha}{\omega_\alpha} \right)^2 + \langle \psi_0 | \hat{H}_e(\underline{\mathbf{R}}, \underline{q}) | \psi_0 \rangle \right)$$



Nuclei

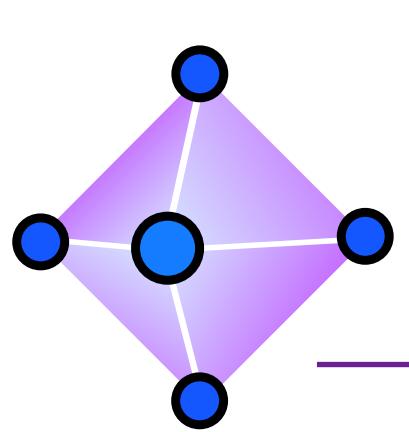
Stochastic Resonances:
non-equilibrium thermodynamics

Displacement Field

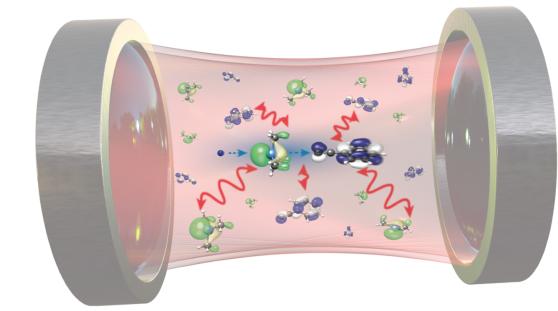


Summary and Conclusion

1. Feedback between spatiotemporal scales makes polaritonic chemistry theoretically hard.
2. Quantized light-matter interaction a priori required (Casimir).
3. Brief repetition of quantum mechanics and perturbation theory.
4. Quantum harmonic oscillator will play a crucial role to describe photons.
5. Many fundamentally open questions make polaritonic chemistry a highly active field of research.



Feedback?



**Should I provide more basic introductions to QM,
electrodynamics, programming etc. or stay more advanced?**

Did you like the blackboard calculations?