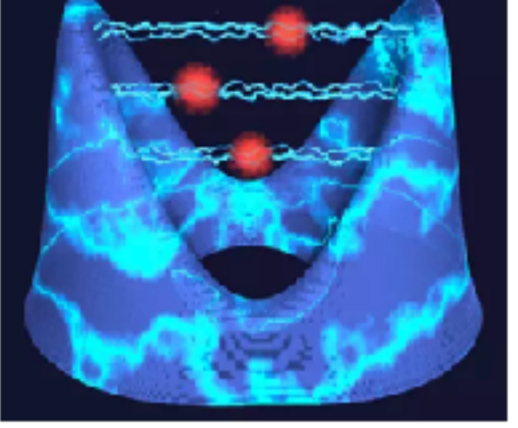
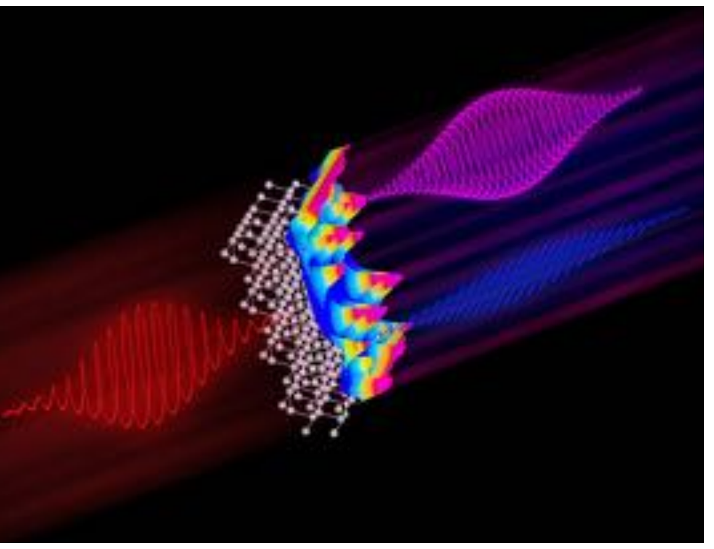


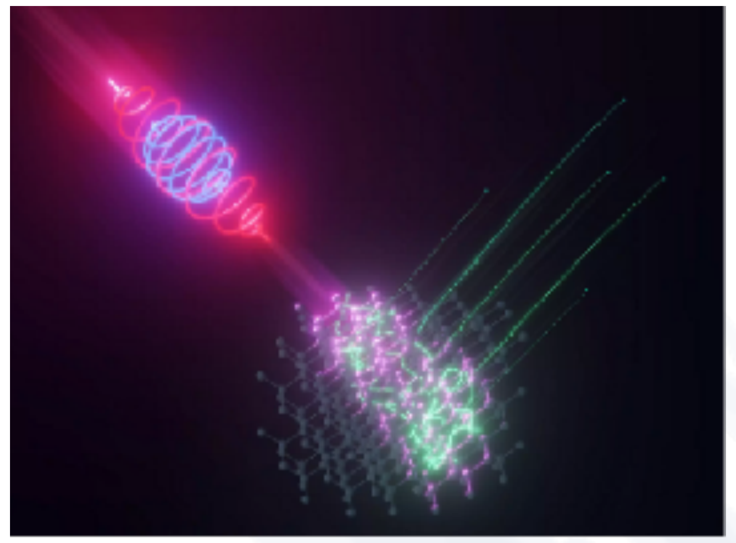
Engineering Quantum Materials via Cavity Vacuum Fluctuations: an ab initio QEDFT framework

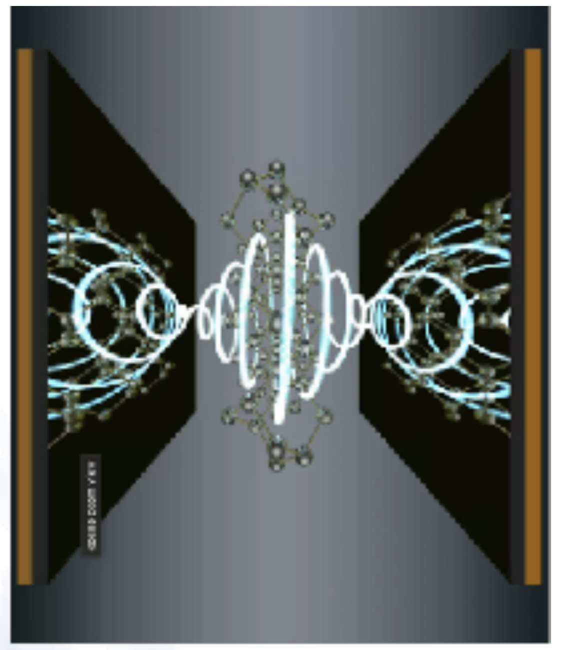
Angel Rubio

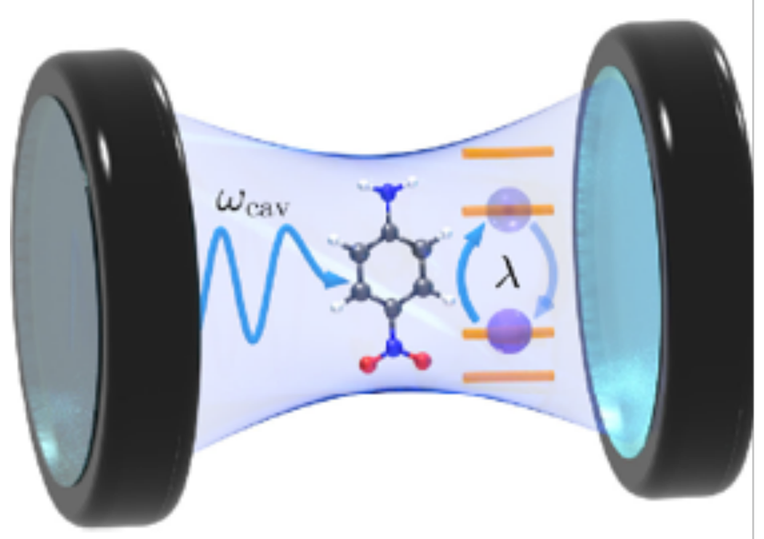
Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany

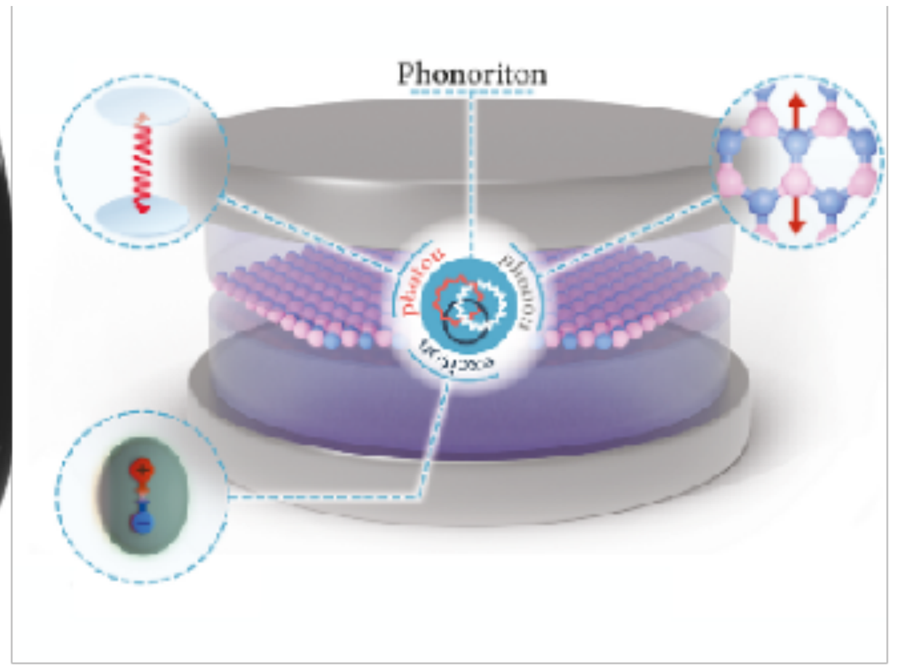
Initiative for Computational Catalysis (ICC) and
Center for Computational Quantum Physics (CCQ), Flatiron Institute-Simons Foundation NY, USA

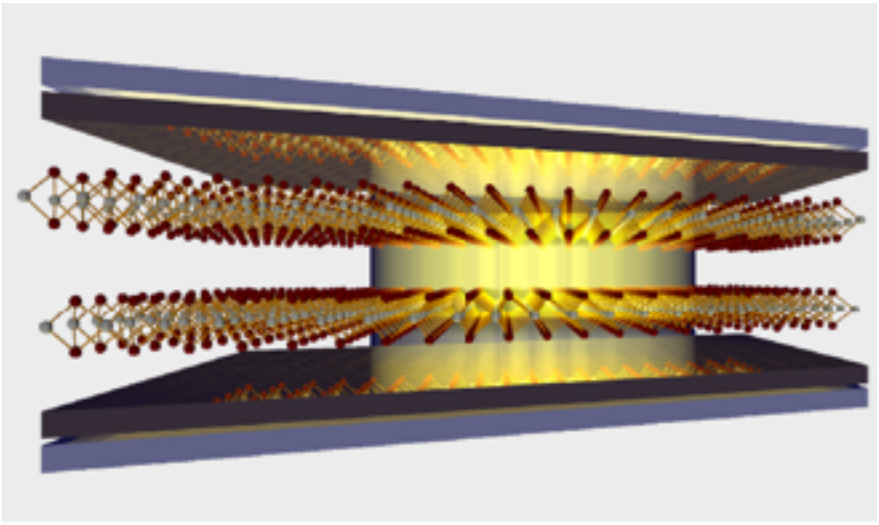


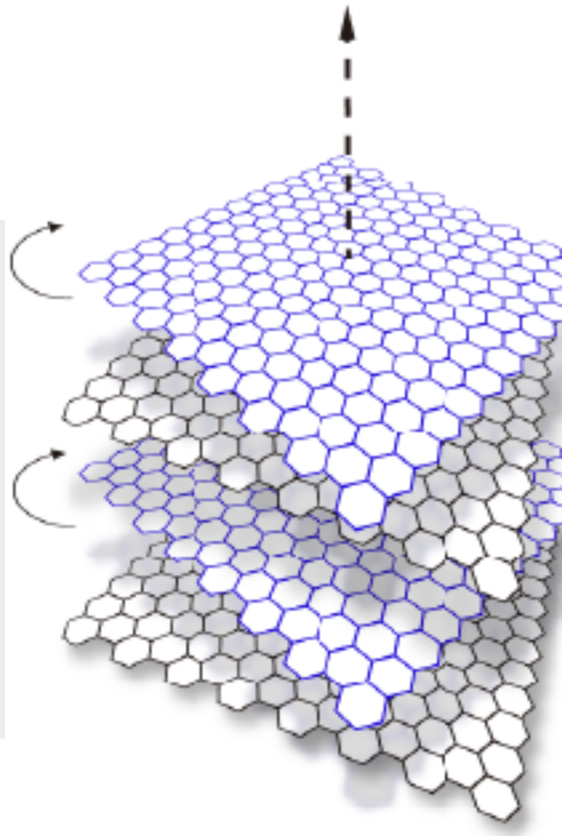












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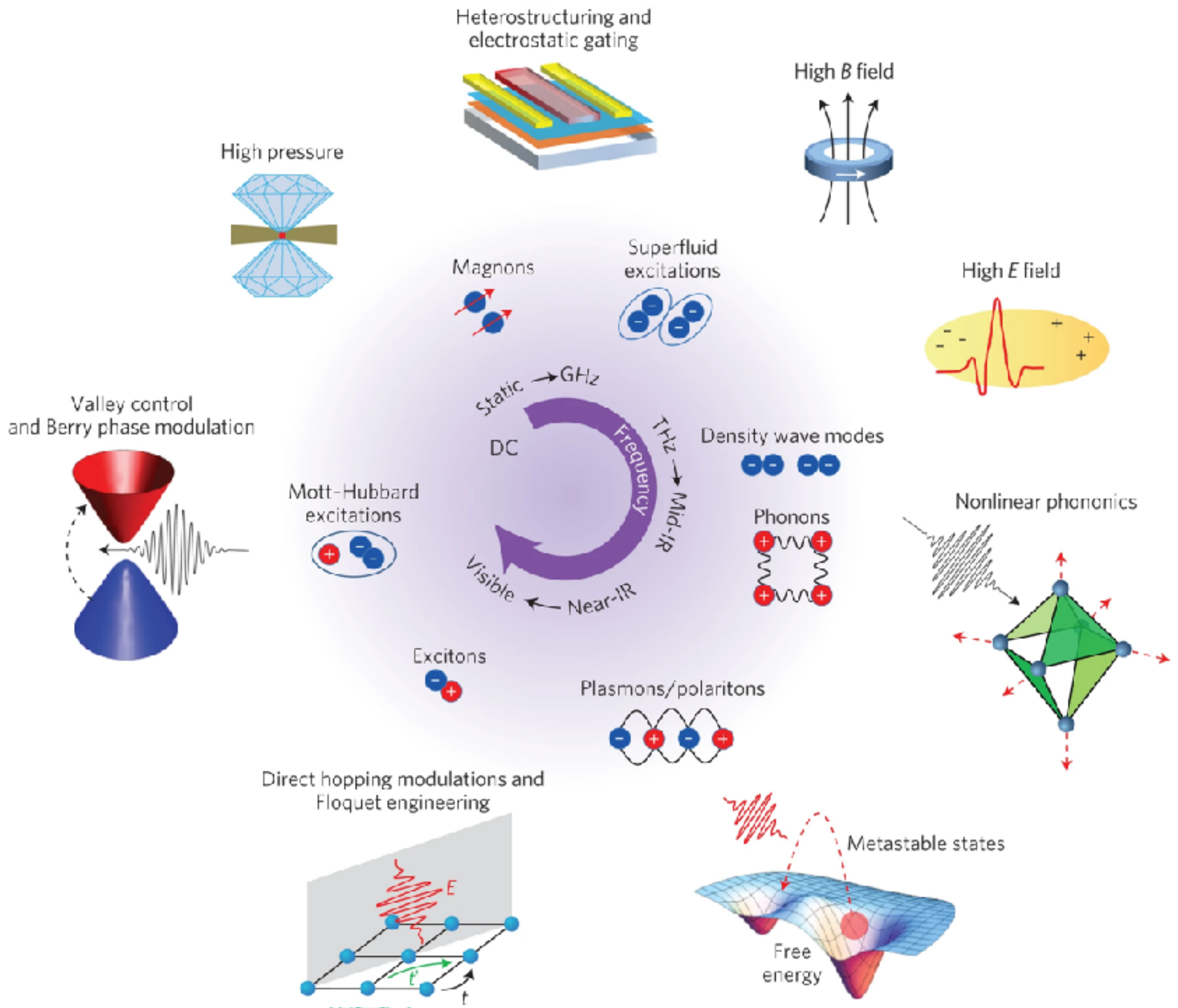
SIMONS FOUNDATION

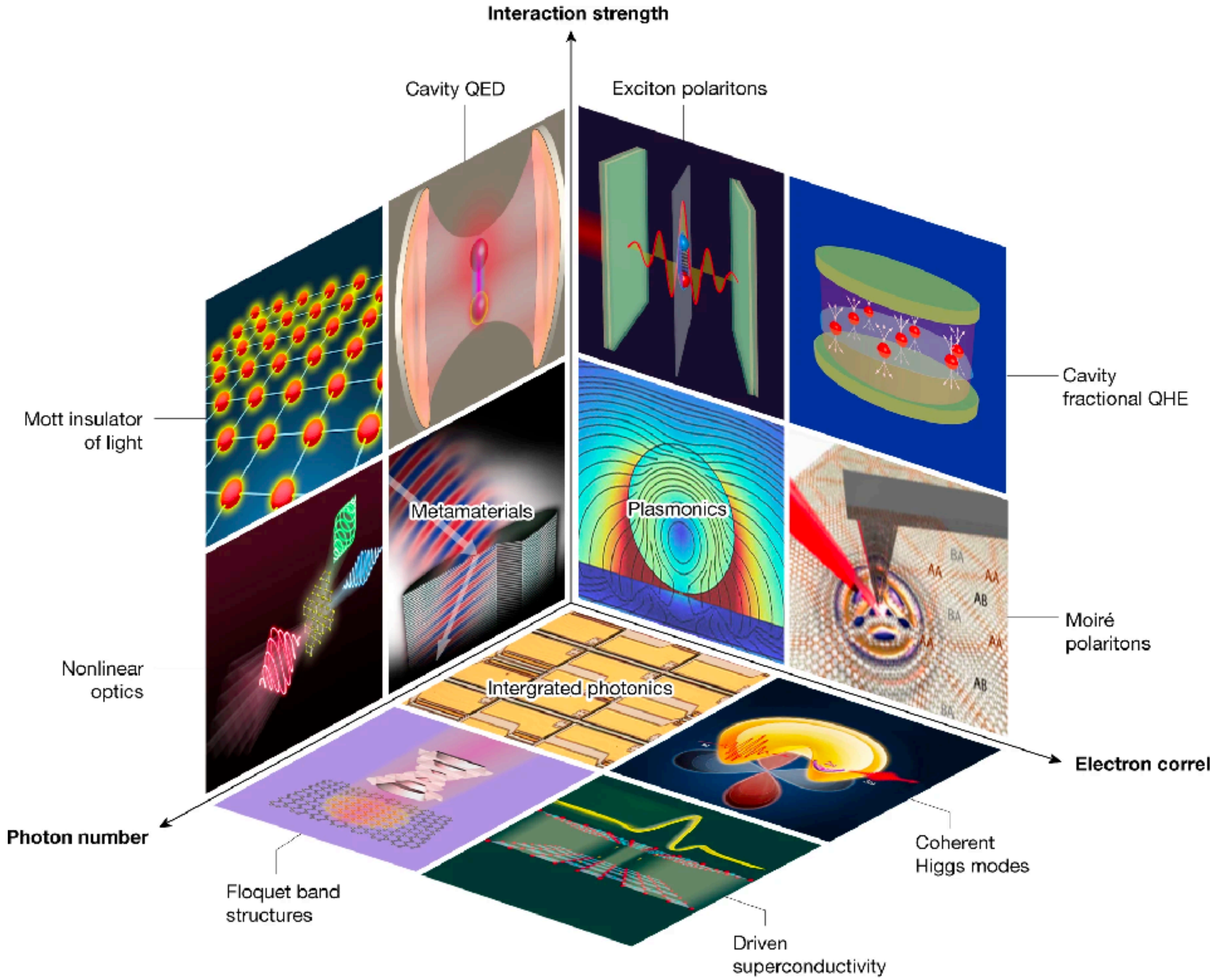
How to manipulate the properties of quantum materials?

Methods for controlling quantum materials and quantum phases.
Elementary excitations in quantum materials and select control techniques arranged (clockwise) in order of ascending frequency.
Basov, Averitt and Hsieh, Nature Materials 16, 1077 (2017).



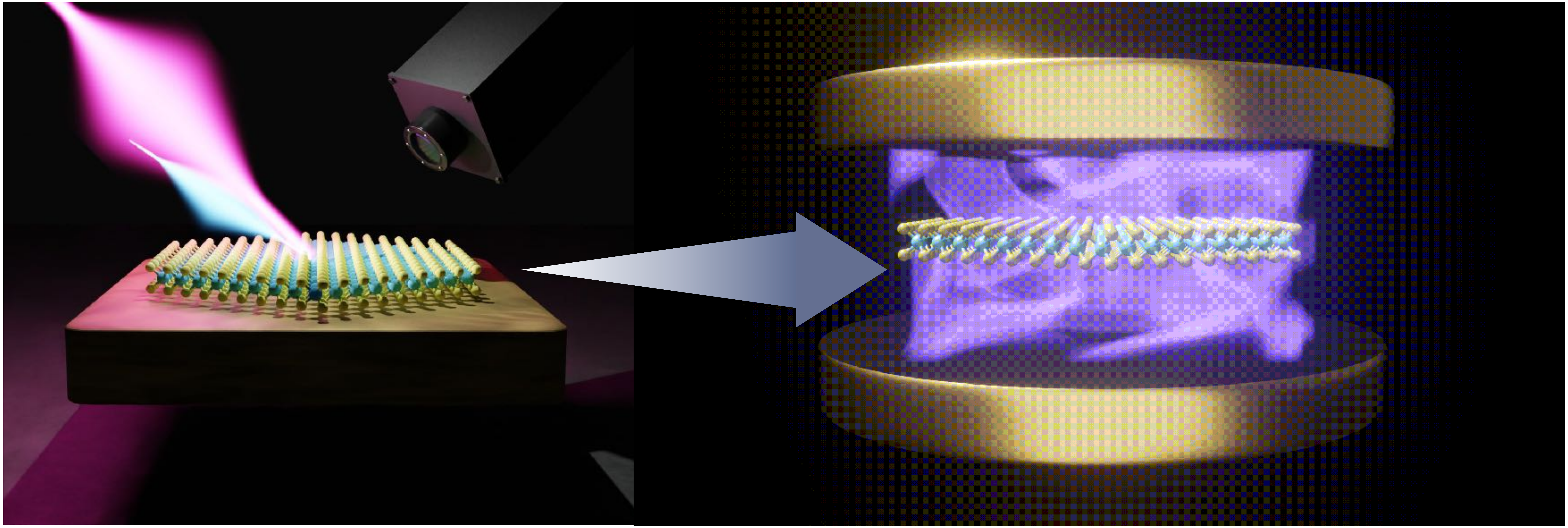
J. Bloch, A. Cavalleri, V. Galitski, M. Hafezi, AR,, Nature 606 41-48 (2022)

Map of strongly correlated electron–photon systems



Strong Light-Matter Coupling without Lasers: Cavity Material Engineering

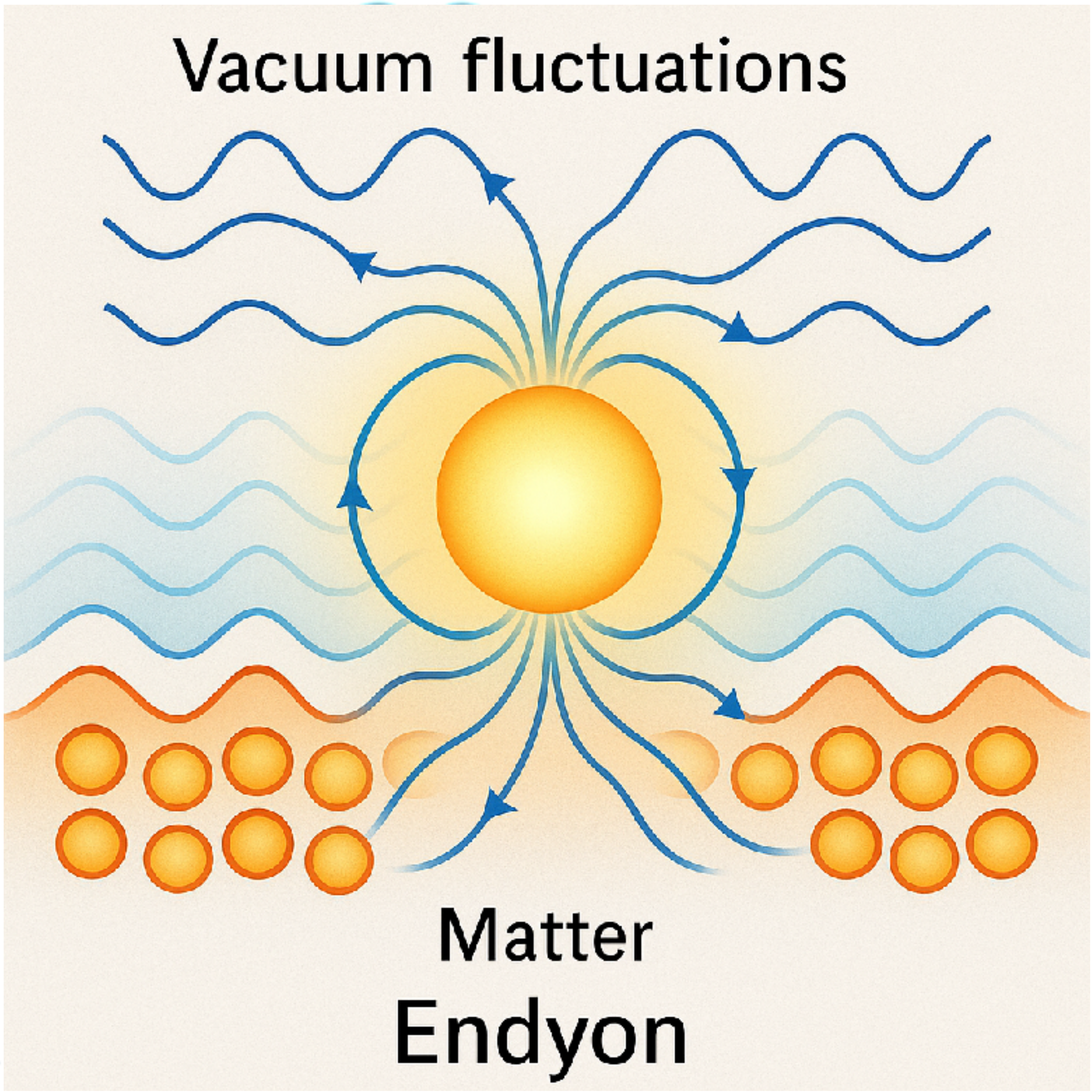
Laser-Induced **Cavity-Induced**



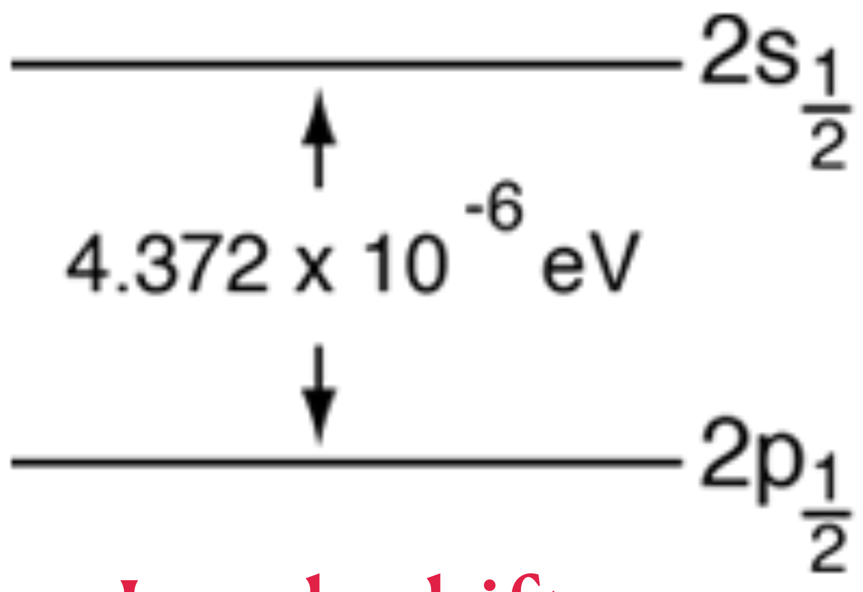
H. Hubener, U. De Giovannini, C,. Schafer, M. Ruggenthaler, J. Faist, AR Nature Materials (2021)

Light-Matter Coupling in a Cavity :

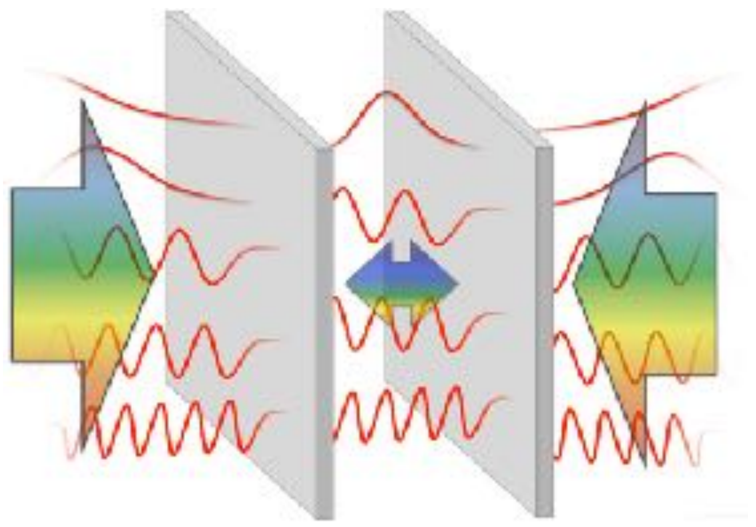
$$E = \frac{1}{2}\hbar\omega \qquad \rho_{\rm vac}(\omega) = \frac{\hbar\omega^3}{2\pi^2 c^3}$$



Zero-point field effects are usually miniscule



Lamb shift



$$F = -\frac{\pi^2\hbar c}{240 d^4}$$

Casimir effect

Van der Waals forces

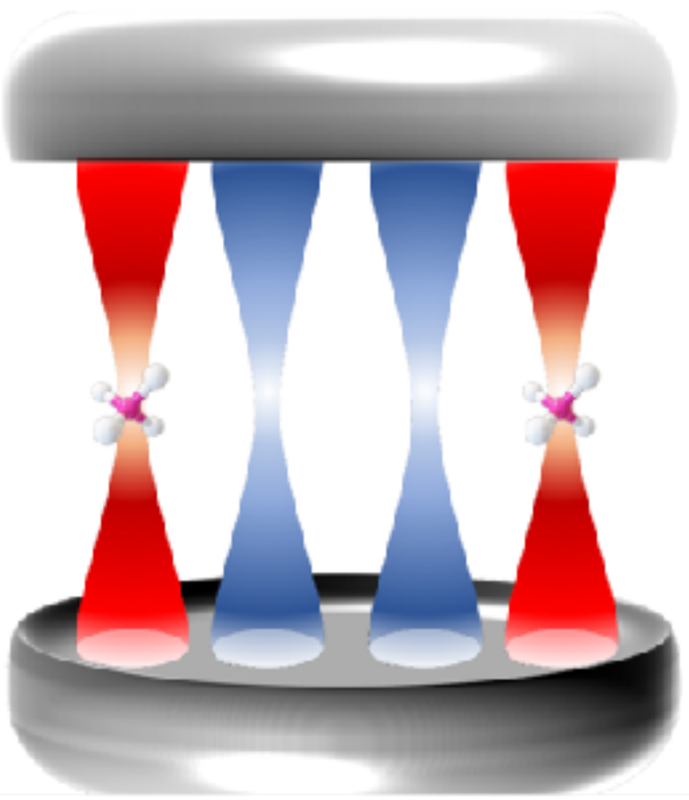
=> No chemical impact expected

- Coupling Scales as $\propto \frac{1}{\sqrt{V_{\rm eff}}}$
- Coupling is Collective $\propto \sqrt{N_{\rm dipoles}}$
- Vacuum Fluctuations play a role as $\langle \hat{\mathbf{E}} \rangle_{\rm eq} = 0$

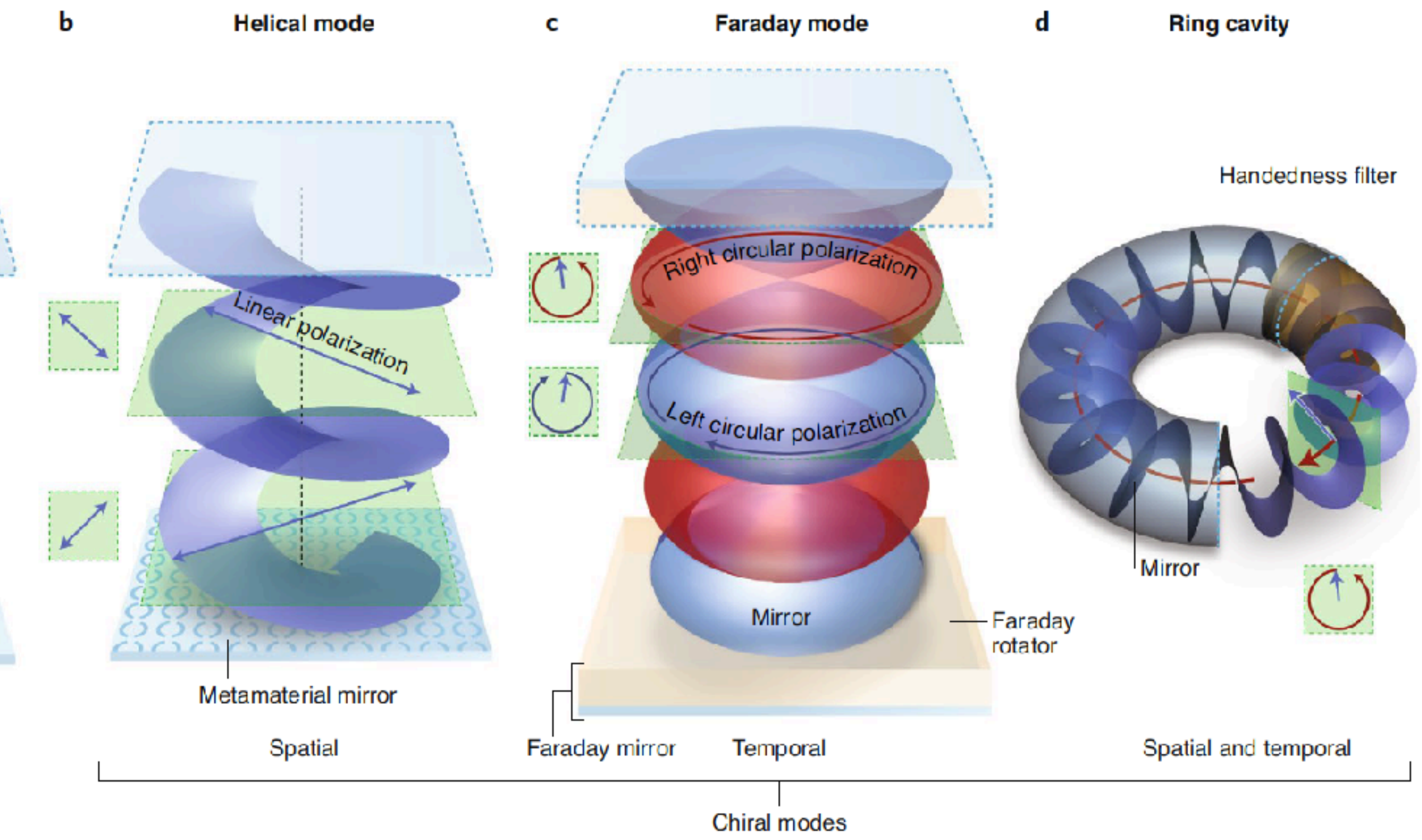
order - disorder transition from vacuum

Focus on the matter modified due to photon quantum fluctuations

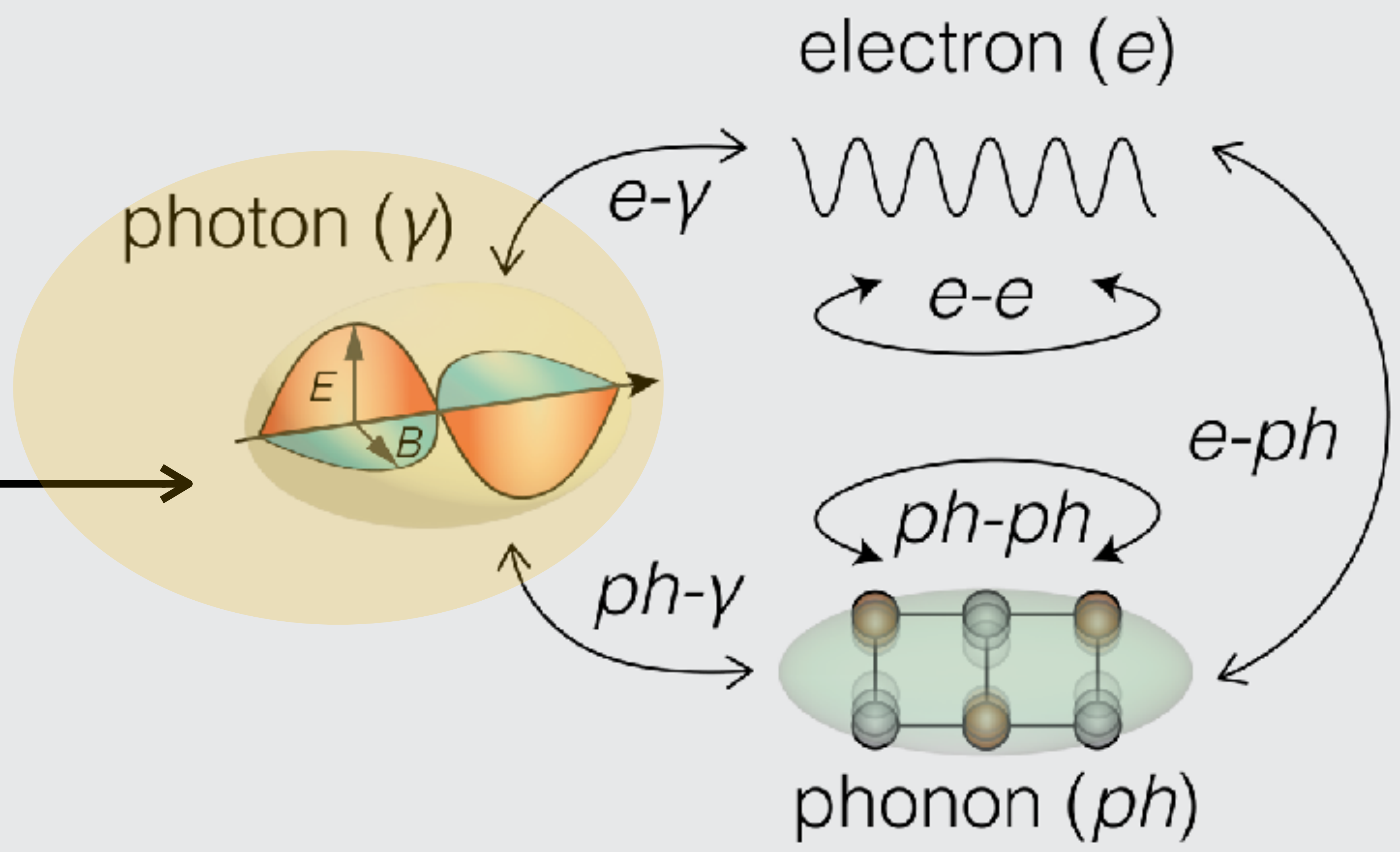
- Mode structure is d ptical cavity configuration



Cavity design

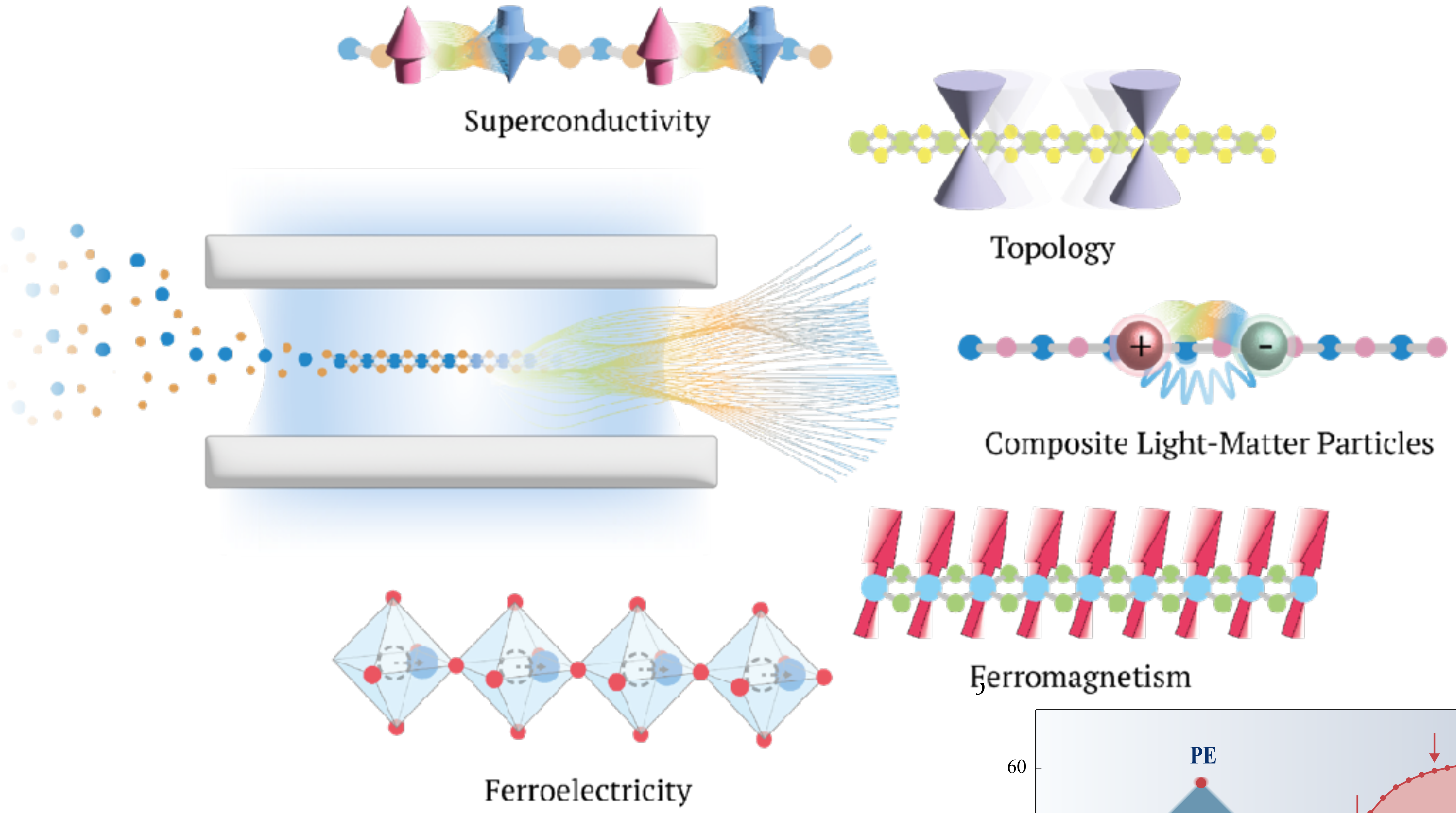


- Study how electrons and phonons are modified inside the effective modes

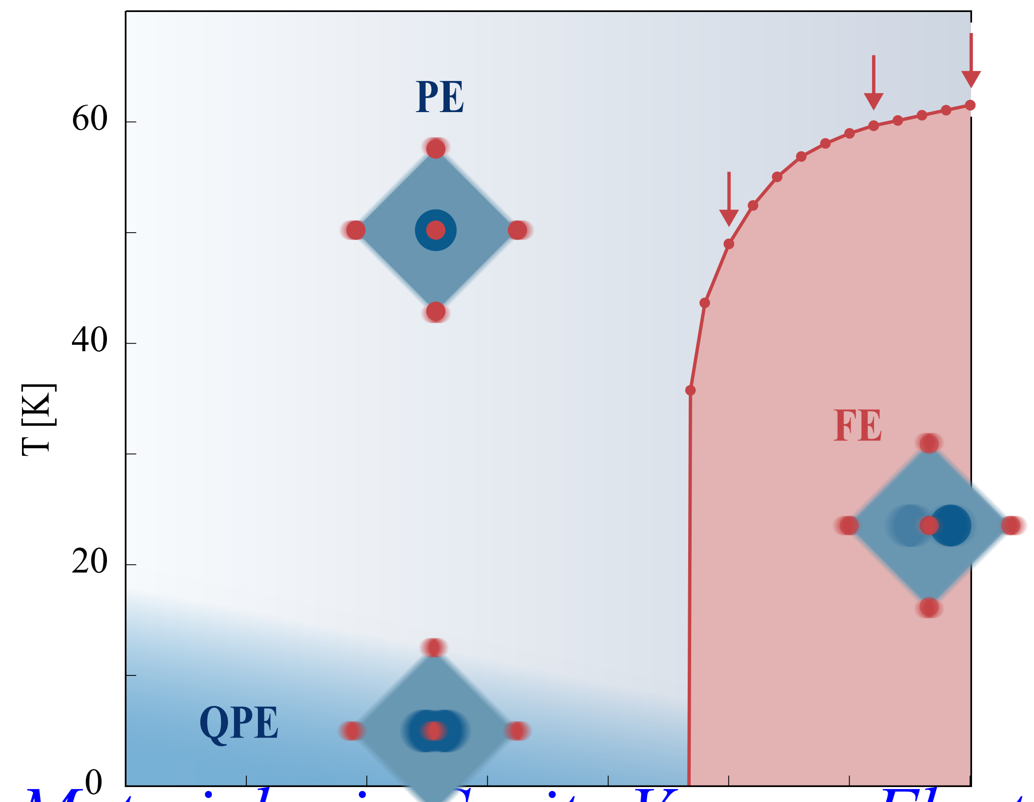


Focus on the matter modified due to photon quantum fluctuations

control the ground state of a quantum material with vacuum fluctuations?



A new Photo-Phase Diagram for STO



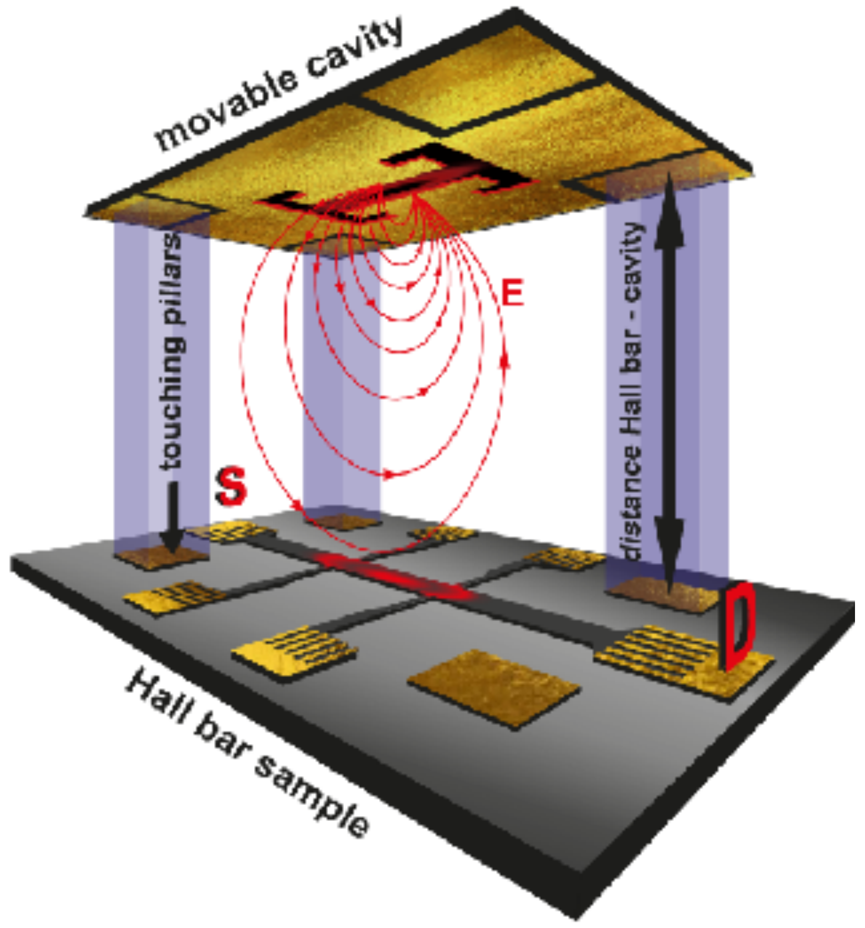
The Ferroelectric Photo-Groundstate of SrTiO3,: Cavity Materials Engineering, S. Latini, D. Shin, S.A. Sato, C. Schäfer, U. De Giovannini, H. Hübener, AR PNAS (2021)

1. Can we modify electrical conductivity with vacuum photons?
2. Can we increase the transition temperature of a superconductor?
3. Can we modify the topology of an electronic band using circularly polarized cavity vacuum fields?
4. Can we create or destroy phases of matter using engineered vacuum fields?

Can we modify chemical reaction rates, energy transfer, enantiomeric selectivity … chemistry? **"Polaritonic chemistry"**

Quantum vacuum fluctuations can be used to modify a wide range of solid-state materials ground state properties

- **Quantum Hall effect**

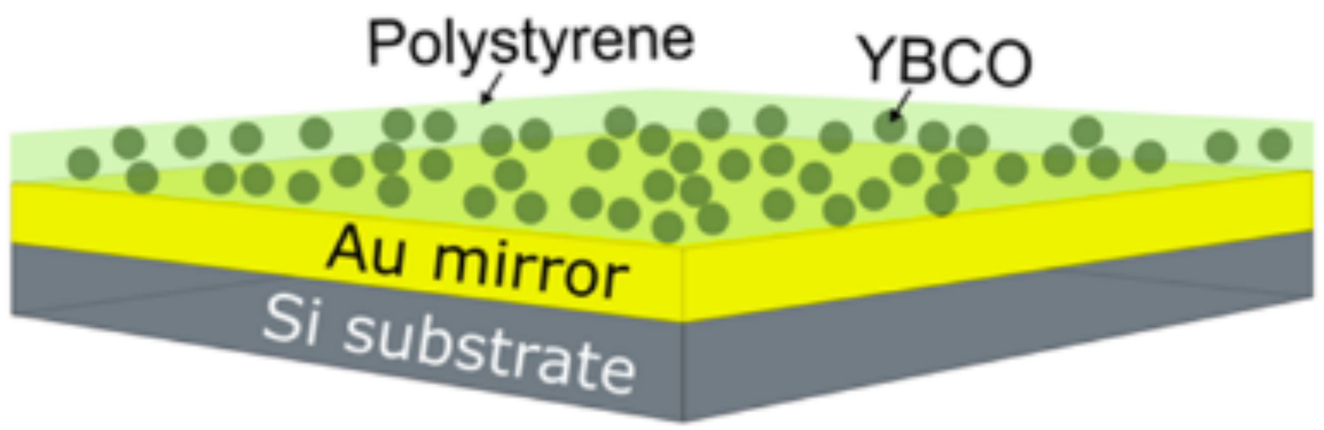


F. Appugliese et al., Science 375, 1030-1034 (2022)

J. Enkner et al., Nature 641, 884-889 (2025)

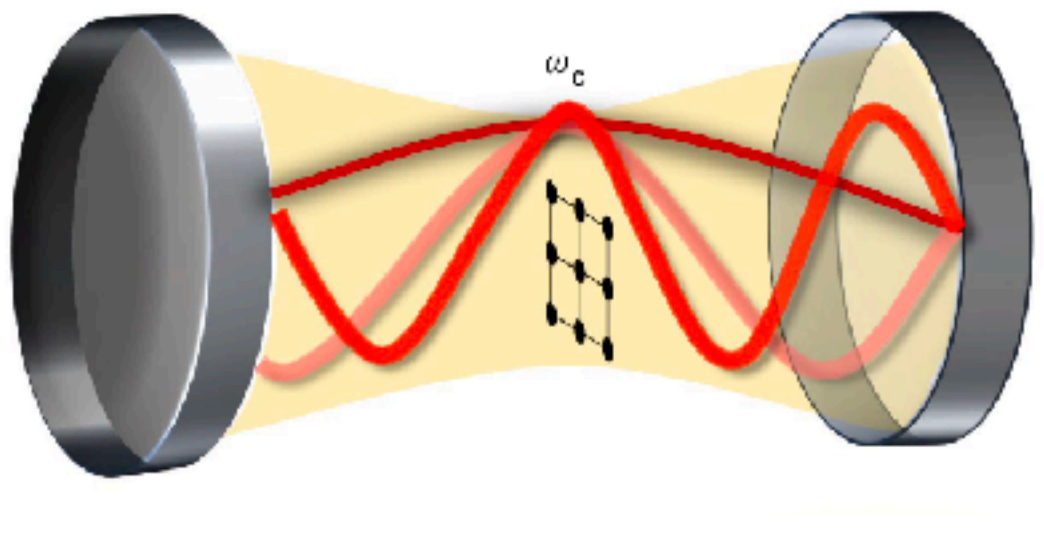
L. Graziotto et al., arXiv:2502.15490 (2025)

- **Ferromagnetism**



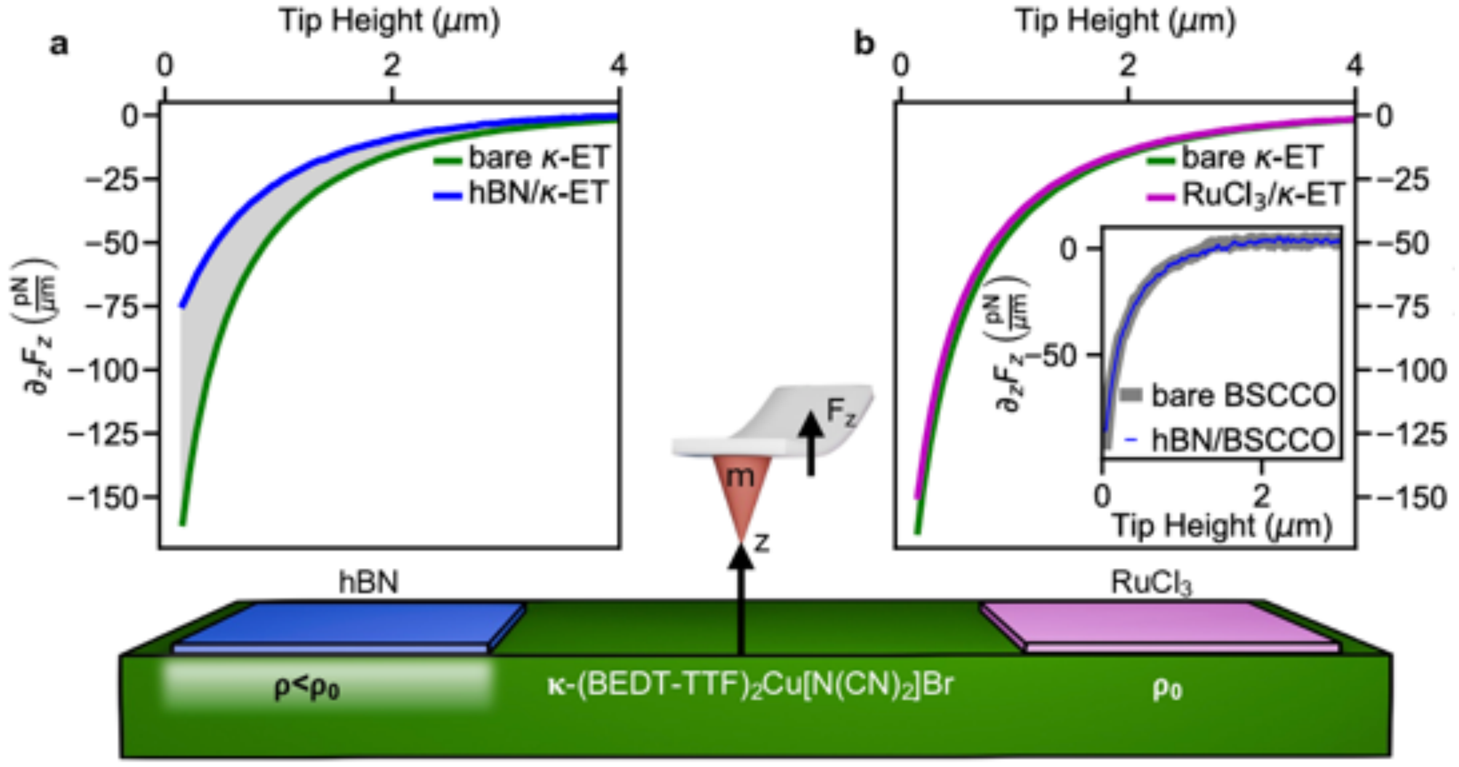
A. Thomas *et al.*, Nano Letters 21, 4365 (2021)

- **Metal-to-insulator transition**



G. Jarc et al., *Nature* 622, 487 (2023)

- **Superconductivity**



I. Keren et al., arXiv:2505.17378 (2025)

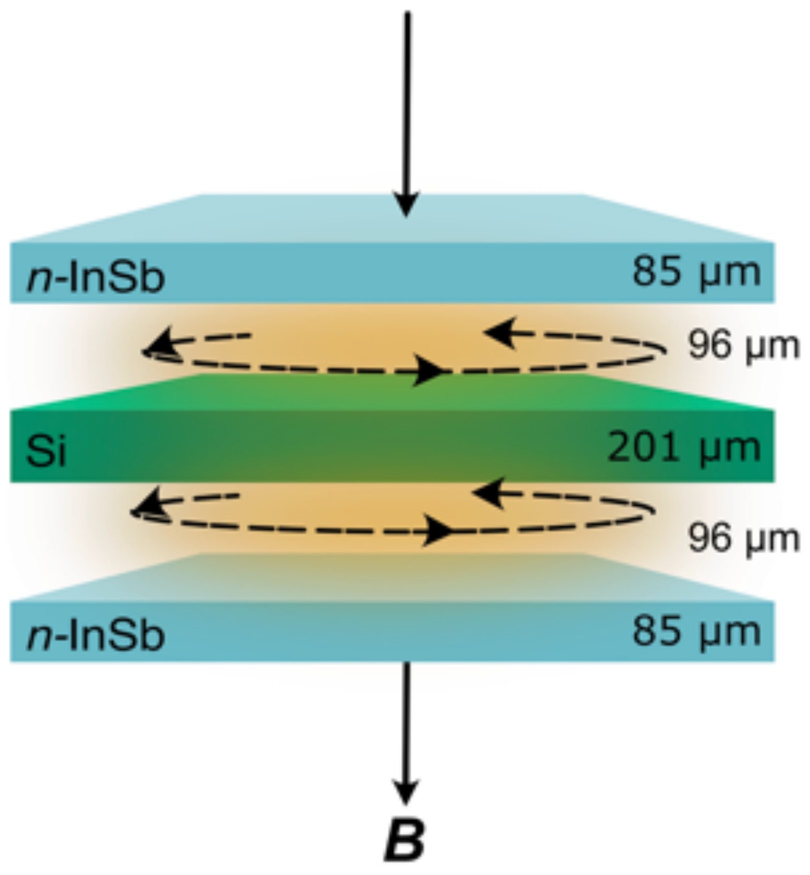
A. Thomas et al., *J. Chem. Phys.* 162, 134701 (2025)

- **Other cavity platforms**

P. Forn-Díaz et al., Rev. Mod. Phys. 91, 025005 (2019)

A. F. Kockum et al., Nat. Phys. 1, 19 (2019)

THz chiral cavity to break time-reversal symmetry



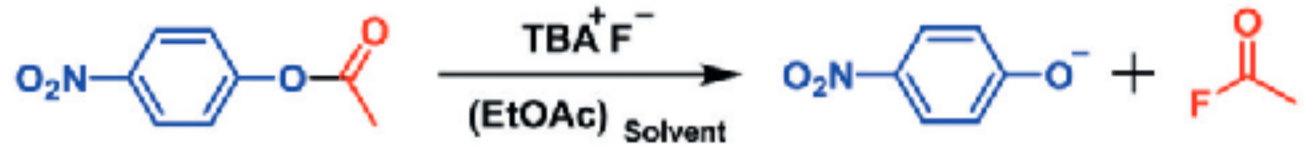
K. M. Kulkarni et al., arXiv:2509.14366 (2025)

F. Tay et al., Nat. Commun. 16, 5270 (2025)

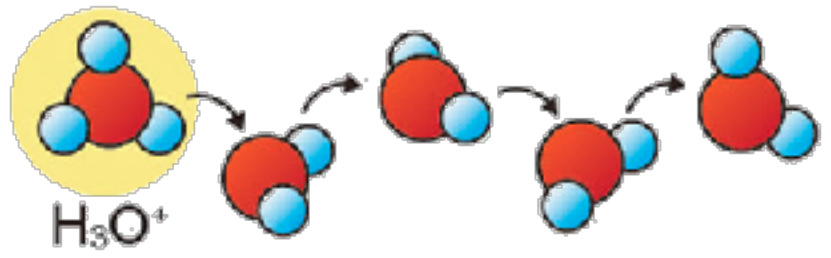
Seminal Experiments

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

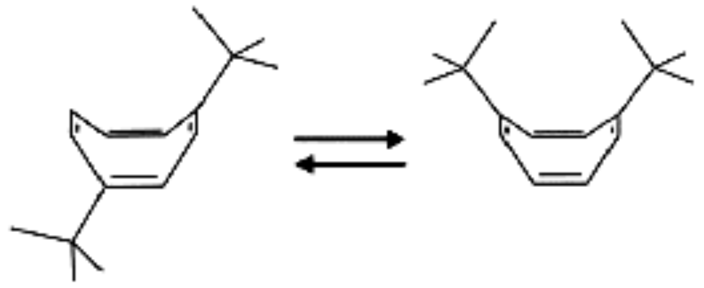
Hydrolysis reaction
Lather et al., *Angew. Chem.* 2019



Ionic conductivity of water
Fukushima et al., *JACS* 2022

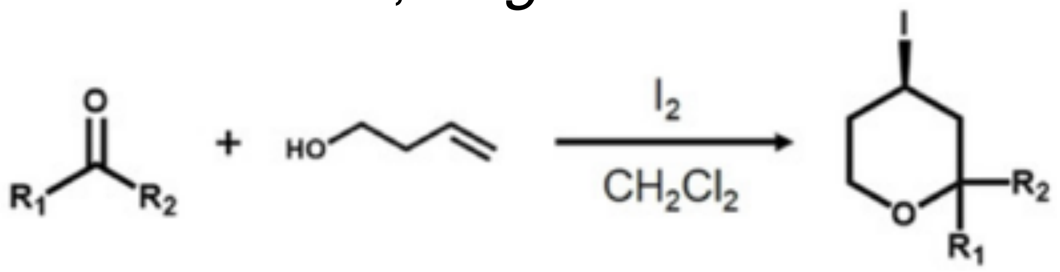


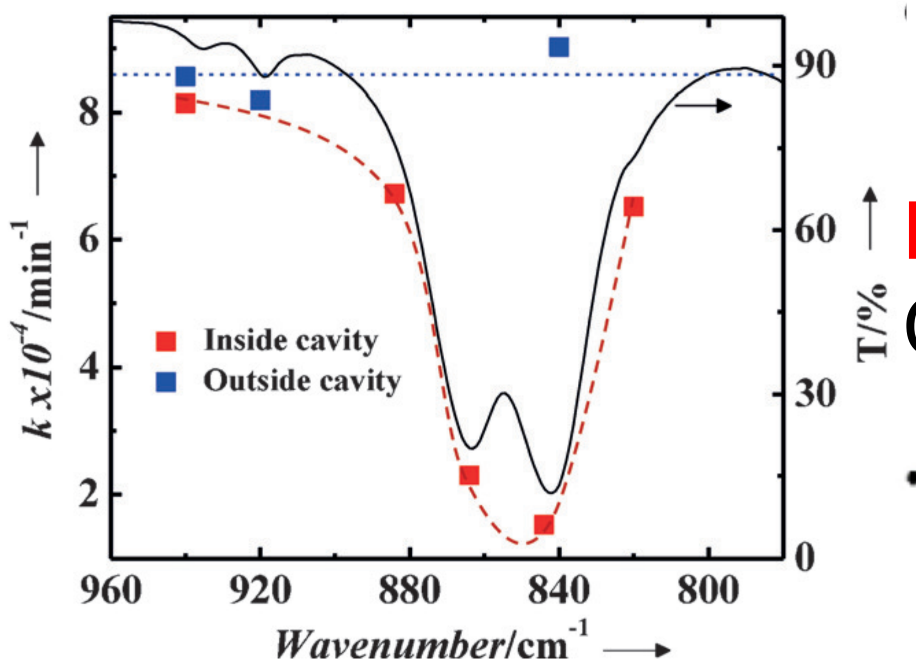
Isomerization reaction
Patrahau et al.,
Angew. Chem. 2024



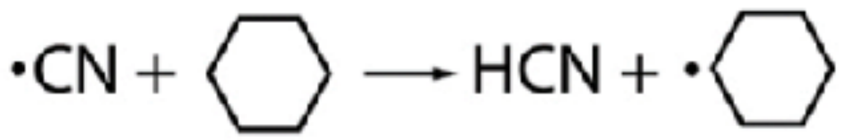
Deprotection reaction
Thomas et al.,
Angew. Chem. 2016

Prins Cyclization
Hirai et al., *Angew. Chem.* 2020



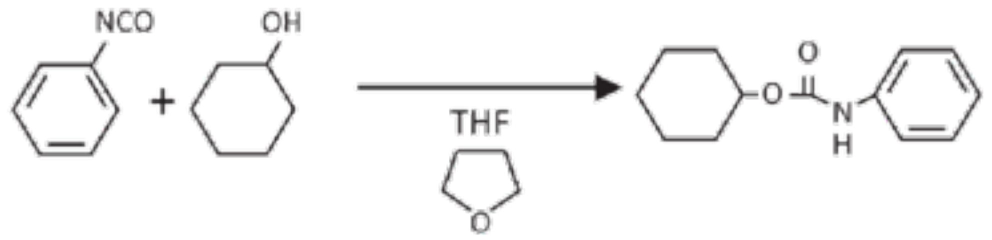


No effect: H-abstraction
Chen et al., *Nanophotonics* 2024



(+ Unpublished results)

Addition reaction
Ahn et al., *Science* 2023



Theoretical Developments: QEDFT

QEDFT: Quantum electrodynamical density functional theory

fermions+bosons: electron photons phonons…

"New States of Matter"

QED-materials

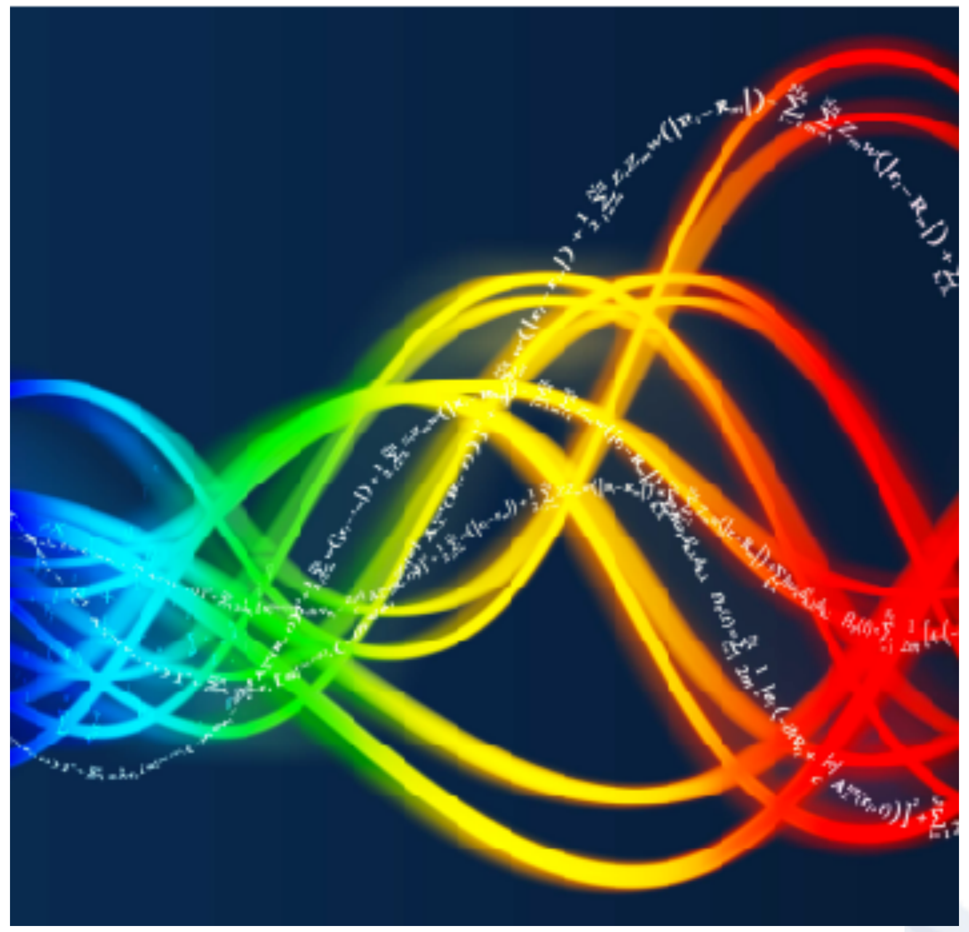
Octopus project

nature REVIEWS

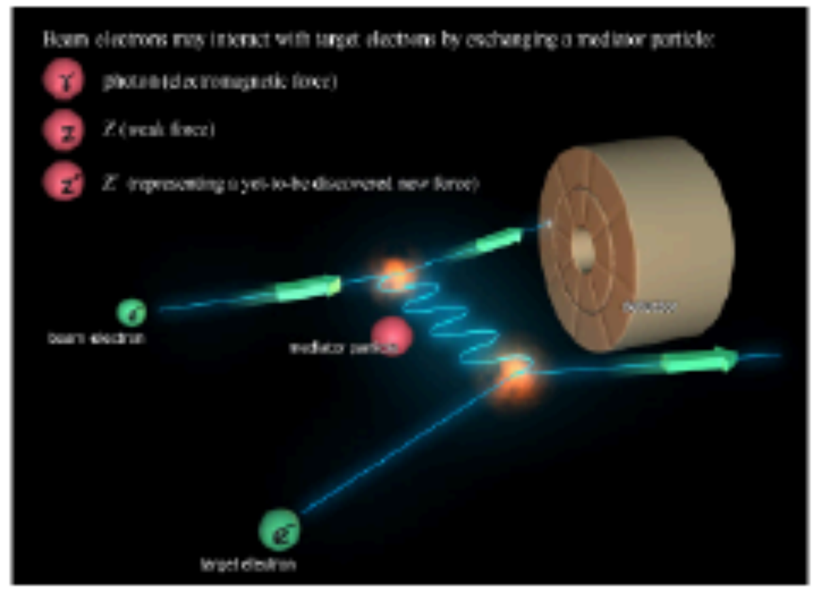
March 2018 volume 2 no. 3

www.nature.com/reviews

CHEMISTRY



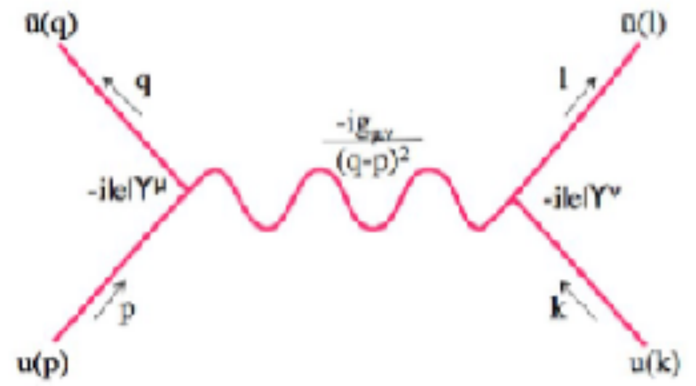
Matter and light (quantum electrodynamics)



project.slac.stanford.edu/e158/experiment.html

- $\hat{H}_{\text{int}} = \int d^3r \hat{J}_\mu(\mathbf{r})\hat{A}^\mu(\mathbf{r})$
- $\hat{J}_\mu(\mathbf{r})$ charge current
- $\hat{A}^\mu(\mathbf{r}) =$ $\sum\!\!\!\!\!\!\int \frac{d^3k}{\sqrt{2|k|}}\lambda^\mu\left[\hat{a}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \hat{a}^\dagger_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}}\right]$

Matter (e.g. chemistry



askamathematician.com/2010/10/

- $\hat{H}_{\text{int}} \rightarrow \sum_{i>j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$
- Particles only

M. Ruggenthaler, et al, PRA (2014), Nature Reviews Chemistry (2018)

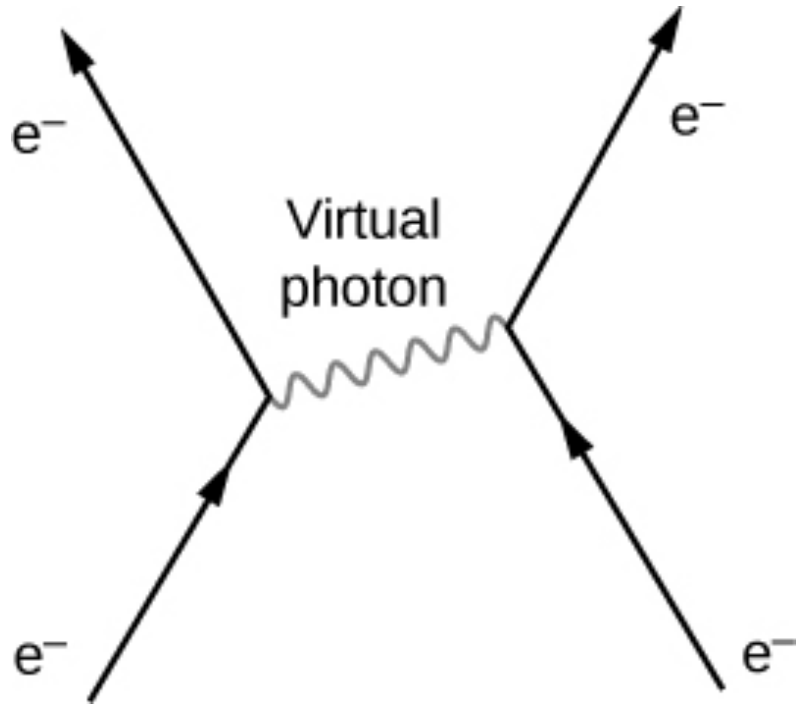
J. Flick, et al, PNAS (2015), PNAS (2017), JCTC (2017); ACS Photonics (2018)

The Pauli-Fierz (PF) Hamiltonian serves as the foundation for (quantum) light-matter coupled systems

Transverse — Longitudinal

$$\hat{H}_{\mathrm{PF}} = \sum_{i=1}^{N_e}\left[\frac{\left(\hat{\mathbf{p}}_i + |e|\hat{\mathbf{A}}_\perp(\mathbf{r}_i)\right)^2}{2m_{e,b}} + \frac{|e|\hbar}{2m_{e,b}}\sigma_i\cdot\hat{\mathbf{B}}(\mathbf{r}_i)\right] + \frac{1}{2}\sum_{i\neq j}^{N_e}\frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i-\mathbf{r}_j|} - \sum_{i=1}^{N_e}\sum_{I=1}^{N_n}\frac{Z_I e^2}{4\pi\epsilon_0|\mathbf{r}_i-\mathbf{R}_I|}$$

$$+\sum_{I=1}^{N_n}\left[\frac{\left(\hat{\mathbf{P}}_I - Z_I|e|\hat{\mathbf{A}}_\perp(\mathbf{R}_I)\right)^2}{2M_{I,b}} - \frac{Z_I|e|\hbar}{2M_{I,b}}\mathbf{S}_I\cdot\hat{\mathbf{B}}(\mathbf{R}_I)\right] + \frac{1}{2}\sum_{I\neq J}^{N_n}\frac{Z_I Z_J e^2}{4\pi\epsilon_0|\mathbf{R}_I-\mathbf{R}_J|} + \sum_{\mathbf{n},\lambda}\hbar\omega_{\mathbf{n}}\hat{a}^\dagger_{\mathbf{n},\lambda}\hat{a}_{\mathbf{n},\lambda}$$

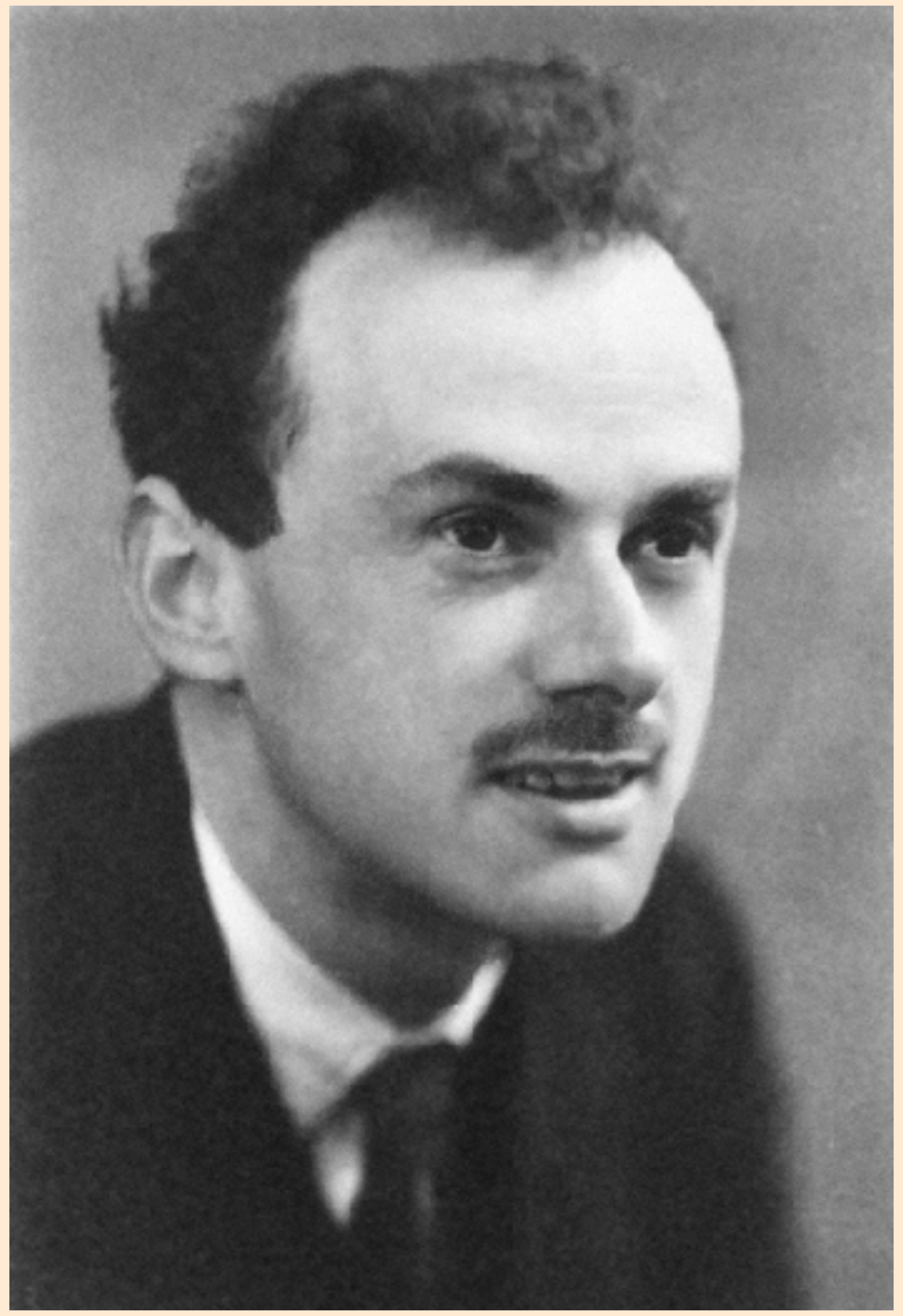


$$\hat{\mathbf{A}}(\mathbf{r}) = \sqrt{\frac{\hbar c^2}{\epsilon_0 L^3}}\sum_{\mathbf{n},\lambda}\frac{\boldsymbol{\epsilon}_{\mathbf{n},\lambda}}{\sqrt{2\omega_{\mathbf{n}}}}\left(a_{\mathbf{n},\lambda}e^{i\mathbf{k}_{\mathbf{n}}\cdot\mathbf{r}} + a^\dagger_{\mathbf{n},\lambda}e^{-i\mathbf{k}_{\mathbf{n}}\cdot\mathbf{r}}\right)$$

M. Ruggenthaler, D. Sidler, & A. Rubio, *Chem. Rev.* **123**, 11191–11229 (2023)

M. Ruggenthaler, N. Tancogne-Dejean, J. Flick, H. Appel, & A. Rubio, *Nat. Rev. Chem.* **2**, 1–16 (2018)

Why don't we just solve the many-body SE?



The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

P.A.M. Dirac, Proceedings of the Royal Society of London. Series A **123**, 792 (1929)

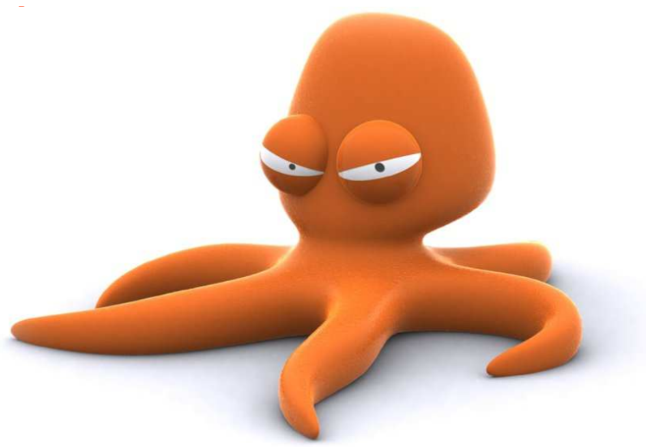
Complexity — Disorder / order (symmetries) — Open quantum systems

Theoretical Developments: QEDFT

QEDFT: Quantum electrodynamical density functional theory
fermions+bosons: electron photons phonons…

"New States of Matter"

QED-materials



Octopus project

QEDFT Theorem

Electronic system $\mapsto \{\mathbf{r}_i\}_{i=1}^{N}$, photons $\mapsto \{q_\alpha, p_\alpha, \omega_\alpha\}_{\alpha=1}^{M}$

$$\mathrm{i}\hbar\frac{d}{dt}\Psi(t) = \hat{H}_{\mathrm{PF}}(t)\Psi(t) \Rightarrow \Psi(t) \overset{1:1}{\leftrightarrow} \{\boldsymbol{J}(\boldsymbol{r},t), \boldsymbol{A}_{\perp}(\boldsymbol{r},t)\}$$

Self-consistent coupled Maxwell– Kohn–Sham–Pauli equations

Riemann-Silberstein

M. Ruggenthaler, et al, PRA (2014), Nature Reviews Chemistry (2018), Chemical Reviews (2023)
J. Flick, et al, PNAS (2015), PNAS (2017), JCTC (2017); ACS Photonics (2018)
D. Sidler, et al JCP (2022), JPCL (2020), C. Schaefer PRA (2018), PNAS(2019), Nat. Comm (2023)

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Quantum electrodynamical density functional theory (QEDFT) in nutshell

$$\hat{H}_{\rm PF} = \frac{1}{2}\sum_{l=1}^{N_e}\left(-i\nabla_l + \frac{1}{c}\hat{\mathbf{A}}(\mathbf{r}_l)\right)^2 + \frac{1}{2}\sum_{l\neq k}^{N_e} w(\mathbf{r}_l, \mathbf{r}_k) + \sum_{l=1}^{N_e} v_{\rm ext}(\mathbf{r}_l) + \sum_{\alpha=1}^{M_p}\omega_\alpha\left(\hat{a}_\alpha^\dagger\hat{a}_\alpha + \frac{1}{2}\right) - \frac{1}{c}\int d^3r\, \mathbf{j}_{\rm ext}(\mathbf{r})\cdot\hat{\mathbf{A}}(\mathbf{r})$$

$$(V_{\rm ext}, \mathbf{j}_{\rm ext}) \leftrightarrows |\Psi\rangle \leftrightarrows (\rho(\mathbf{r}), \mathbf{A}(\mathbf{r})) \leftrightarrows |\Phi\rangle \leftrightarrows (V_{\rm KS}, \mathbf{j}_{\rm KS})$$

Non-interacting system

M. Ruggenthaler, arXiv:1509.01417 (2017) (Ground-state QEDFT)

M. Ruggenthaler et al., *PRA* **90**, 012508 (2014) (Relativistic and non-relativistic QEDFT)

Maxwell-KS system

$$\hat{h} = \frac{1}{2}\left(-i\nabla + \frac{1}{c}\mathbf{A}_{\rm KS}(\mathbf{r})\right)^2 + v_{\rm KS}(\mathbf{r})$$

$\mathbf{A}_{\rm KS}$ long-wavelength approximation

$$v_{\rm KS}(\mathbf{r}) = v_{\rm ext}(\mathbf{r}) + v_{\rm H}(\mathbf{r}) + v_{\rm xc}(\mathbf{r}) + v_{\rm pxc}(\mathbf{r})$$

e-e interaction ($v_{\rm xc}$)

e-photon interaction ($v_{\rm pxc}$)

I-T. Lu et al, AR., PRA 109, 052823 (2024)

L. Weber et al, AR PRL 135, 126901 (2025)

Effective photon-free KS Hamiltonian for light-matter interaction

Kohn-Sham (KS) Hamiltonian in the presence of photons

$$H_{\mathrm{PKS}} = -\frac{1}{2}\nabla^2 + v_{\mathrm{ex}}(\mathbf{r}) + v_{\mathrm{Hxc}}(\mathbf{r}) + v_{\mathrm{px}}(\mathbf{r}) + v_{\mathrm{pc}}(\mathbf{r})$$

External potential

Hatree potential + xc potential

photon-exchange potential

photon-correlation potential

C. Schäfer et al, PNAS **118**, (2021)

I-T. Lu et al, AR., *PRA* 109, 052823 (2024)

Options for the px potential (wave function or LDA)

$$\nabla^2 v_{\mathrm{px}}(\mathbf{r}) = -\eta\nabla\cdot\left[\sum_{\alpha=1}^{M_p}\frac{\tilde{\lambda}_\alpha^2}{2\tilde{\omega}_\alpha^2}\frac{(\tilde{\boldsymbol{\varepsilon}}_\alpha\cdot\nabla)\langle\left\{\tilde{\boldsymbol{\varepsilon}}_\alpha\cdot\hat{\mathbf{J}}_p,\hat{\mathbf{j}}_p(\mathbf{r})\right\}\rangle_\Phi}{\rho(\mathbf{r})}\right]$$

$$\nabla^2 v_{\mathrm{pxLDA}}(\mathbf{r}) = -\eta\sum_{\alpha=1}^{M_p}\kappa\frac{2\pi^2\tilde{\lambda}_\alpha^2}{\tilde{\omega}_\alpha^2}\left(\tilde{\boldsymbol{\varepsilon}}_\alpha\cdot\nabla\right)^2\left(\frac{\rho(\mathbf{r})}{2V_d}\right)^{2/d}$$

pc potential $v_{\mathrm{pc}}(\mathbf{r}) = \eta v_{\mathrm{pm}}(\mathbf{r})$

where $v_{\mathrm{pm}}(\mathbf{r}) = \sum_{\alpha=1}^{M_p} e^{-\frac{\tilde{\lambda}_\alpha^2}{\tilde{\omega}_\alpha^2 - N_e\tilde{\lambda}_\alpha^2}}\frac{\tilde{\lambda}_\alpha^2}{4\tilde{\omega}_\alpha^3}(\tilde{\boldsymbol{\varepsilon}}_\alpha\cdot\nabla)^2 v_{\mathrm{ex}}(\mathbf{r})$

scaling factor

$$\eta = \eta_0 + (1-\eta_0)(1 - e^{-\beta_s\frac{\lambda^2}{\omega^2}})$$

η_0 is obtained using a small coupling to get the correct energy correction in perturbation regime

Our QEDFT toolbox for QED solid-state materials

Electron-photon systems

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$$v_{\mathrm{KS}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{xc}}(\mathbf{r}) + v_{\mathrm{pxc}}(\mathbf{r})$$

e-e interaction   e-γ interaction

I-T. Lu et al, AR., *PRA* 109, 052823 (2024)

Nuclear motion (classical ions)

$$M_I\frac{d^2\mathbf{R}_I}{dt^2} = \mathbf{F}_I + Z_I\mathbf{E}$$

Hellmann-Feynman forces $\mathbf{F}_I$

Dark cavity, i.e., $\mathbf{E} = 0$

Phonon properties (harmonic approximation)

Density functional perturbation theory (DFPT)

$$\partial_{\nu\mathbf{q}}v_{\mathrm{KS}}(\mathbf{r}) \leftrightarrow \partial_{\nu\mathbf{q}}\rho(\mathbf{r})$$

including $\partial_{\nu\mathbf{q}}v_{\mathrm{pxc}}(\mathbf{r})$

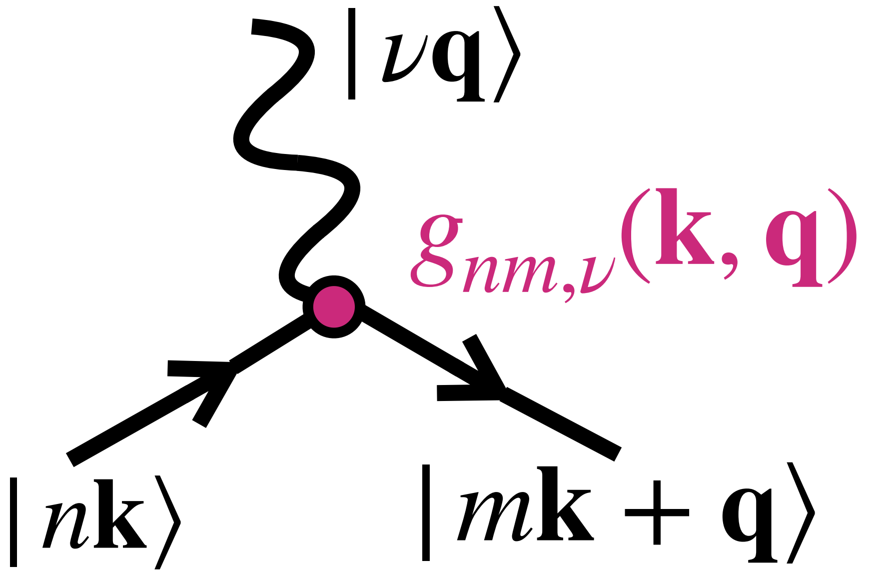
I-T. Lu et al. AR, PNAS 121, e2415061121 (2024)

Phonon dispersion

$\omega_{\nu\mathbf{q}}$ and $|\nu\mathbf{q}\rangle$

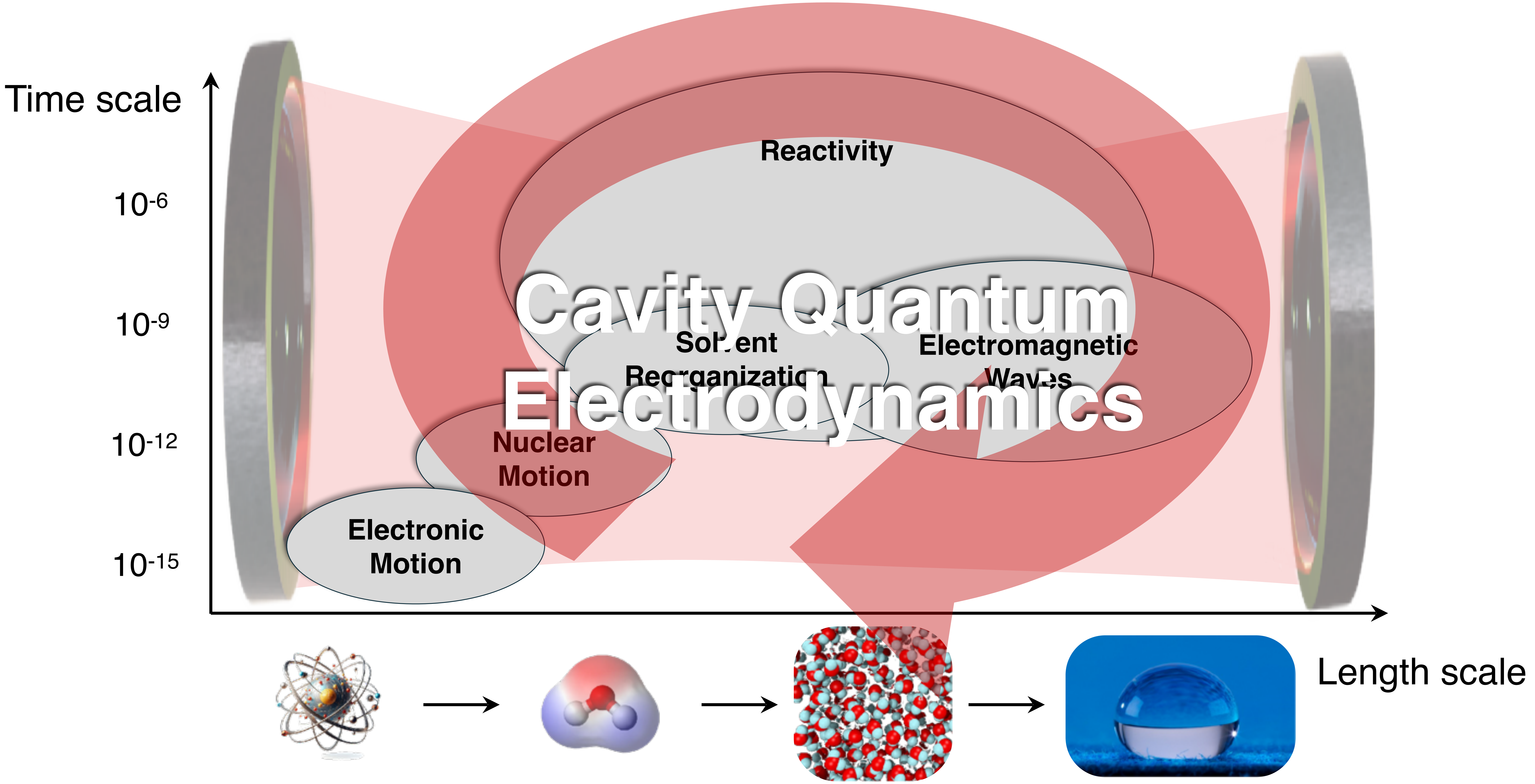
Electron-**phonon** coupling

$$g_{mn,\nu}(\mathbf{k},\mathbf{q}) = \langle m\mathbf{k}+\mathbf{q}|\partial_{\nu\mathbf{q}}v_{\mathrm{KS}}|n\mathbf{k}\rangle$$

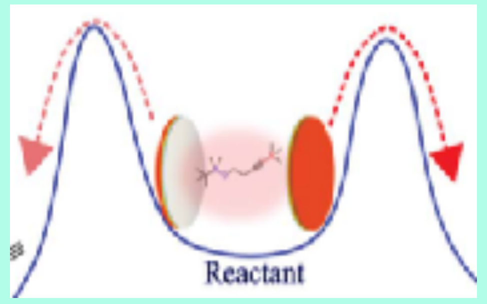


Polaritonic chemistry

A Multiscale Challenge



Experimental success

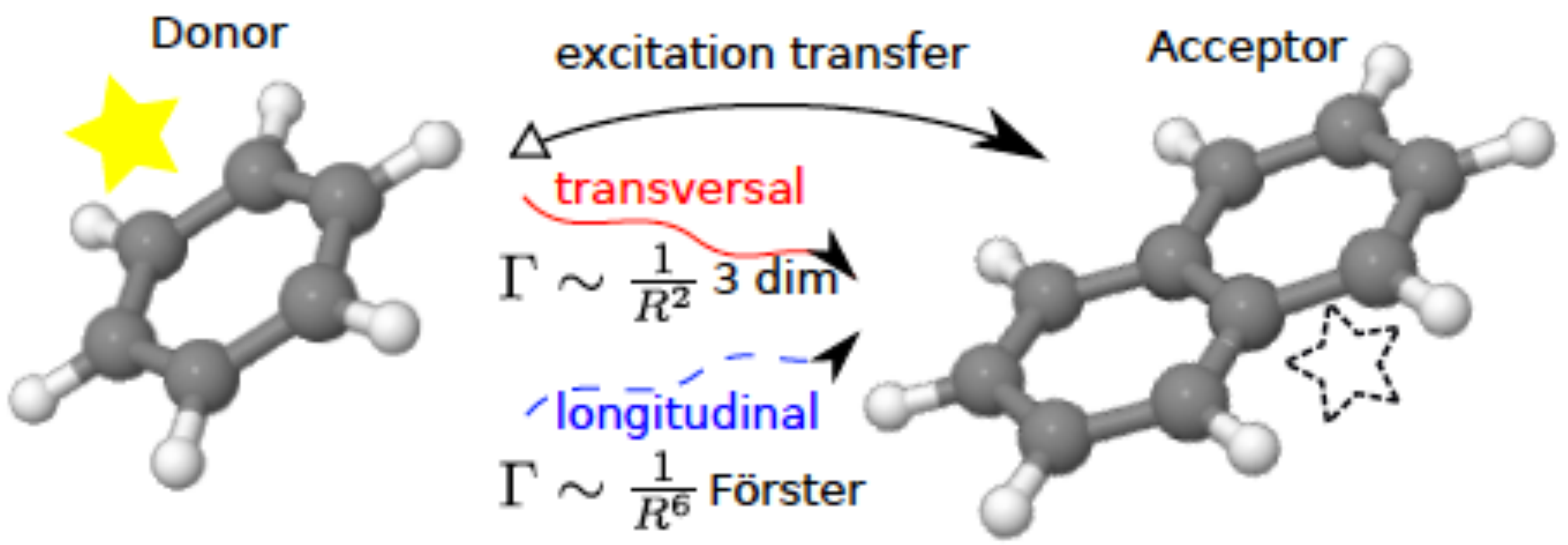


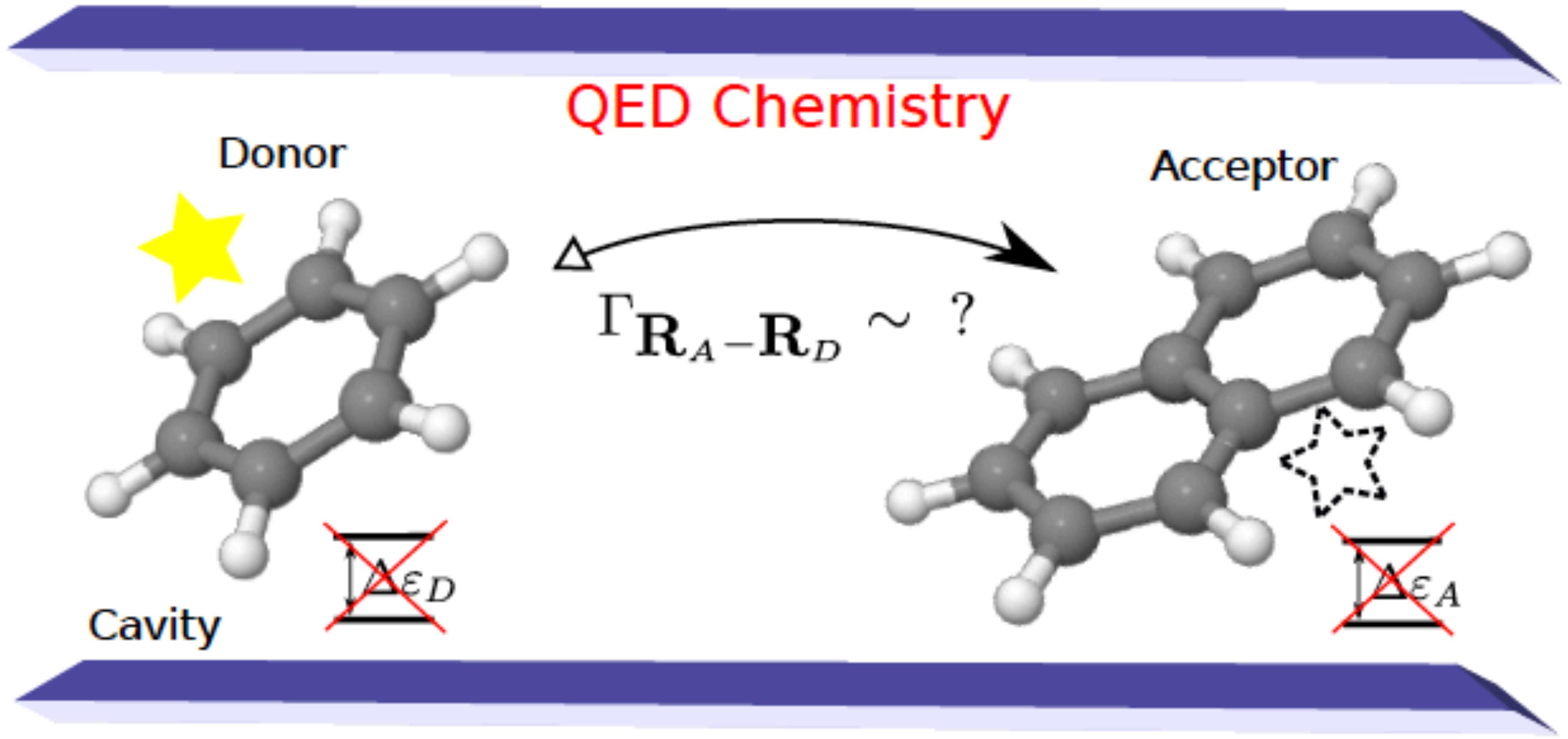
D. Sidler, et al JCP (2022), JPCL (2020), Chem.Rev (2025)
M. Ruggenthaler et al, Chem.Rev (2023))

Cavity QED-Chemistry "polaritonic chemistry"

Modifying Chemical Landscapes by Coupling to Vacuum Fields

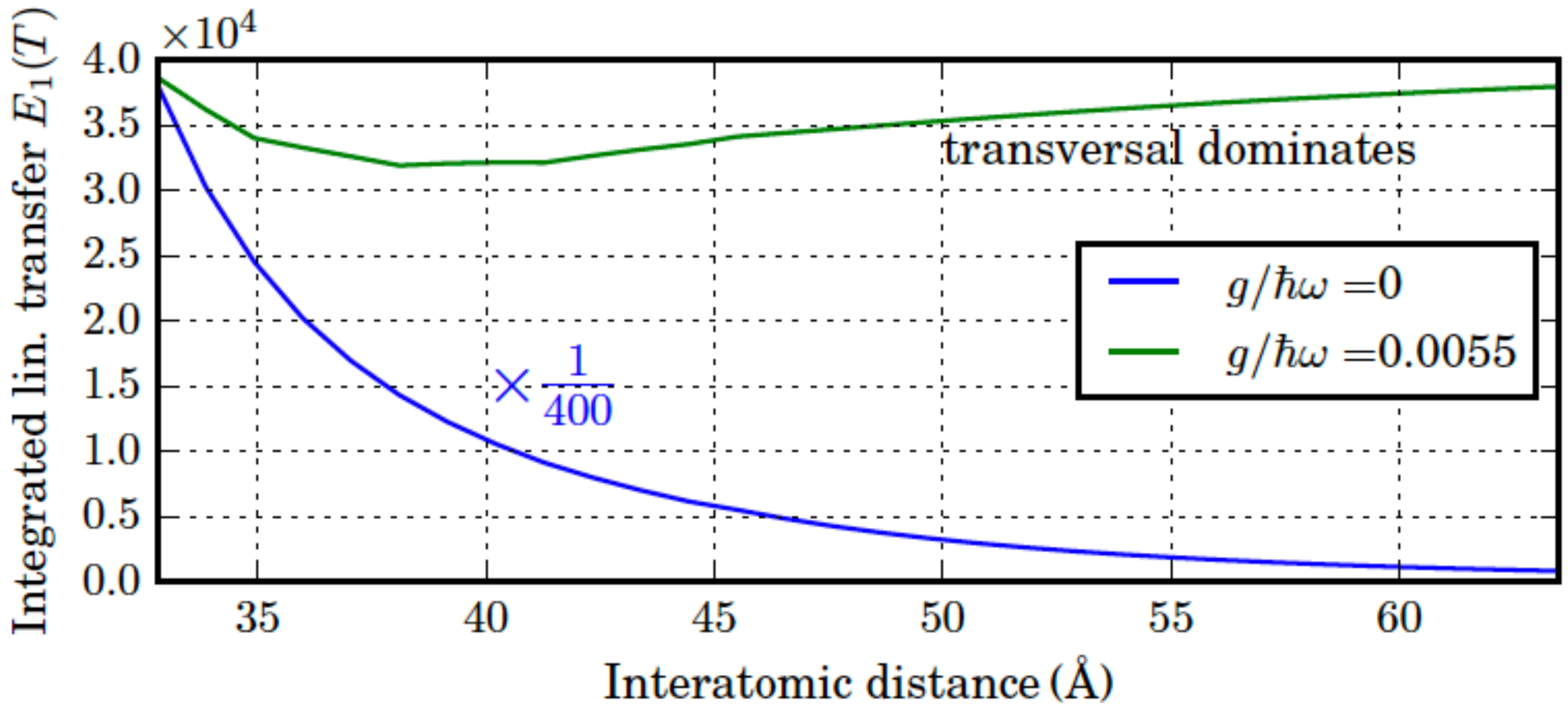
Molecular Energy Transfer





Avoid few-level approximation to properly capture electronic behavior

C. Schäfer, M. Ruggethaler, A. Rubio, PNAS (2018)

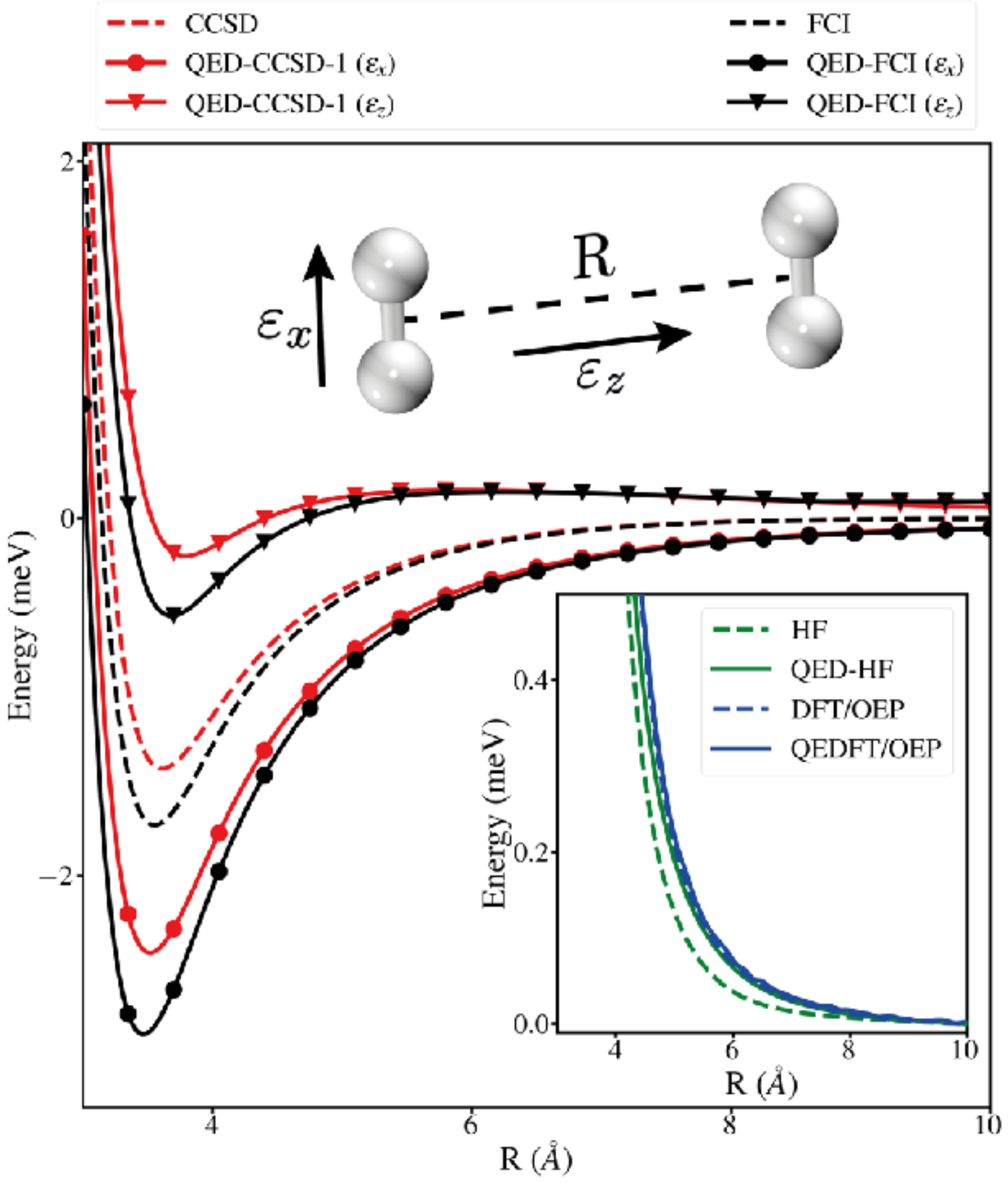


Experimental evidence:
Thomas Ebbesen's group
Angewandte Chemie International Edition (2017)

Few (!) molecular electronic strong coupling

Different computational methods inside/outside a cavity

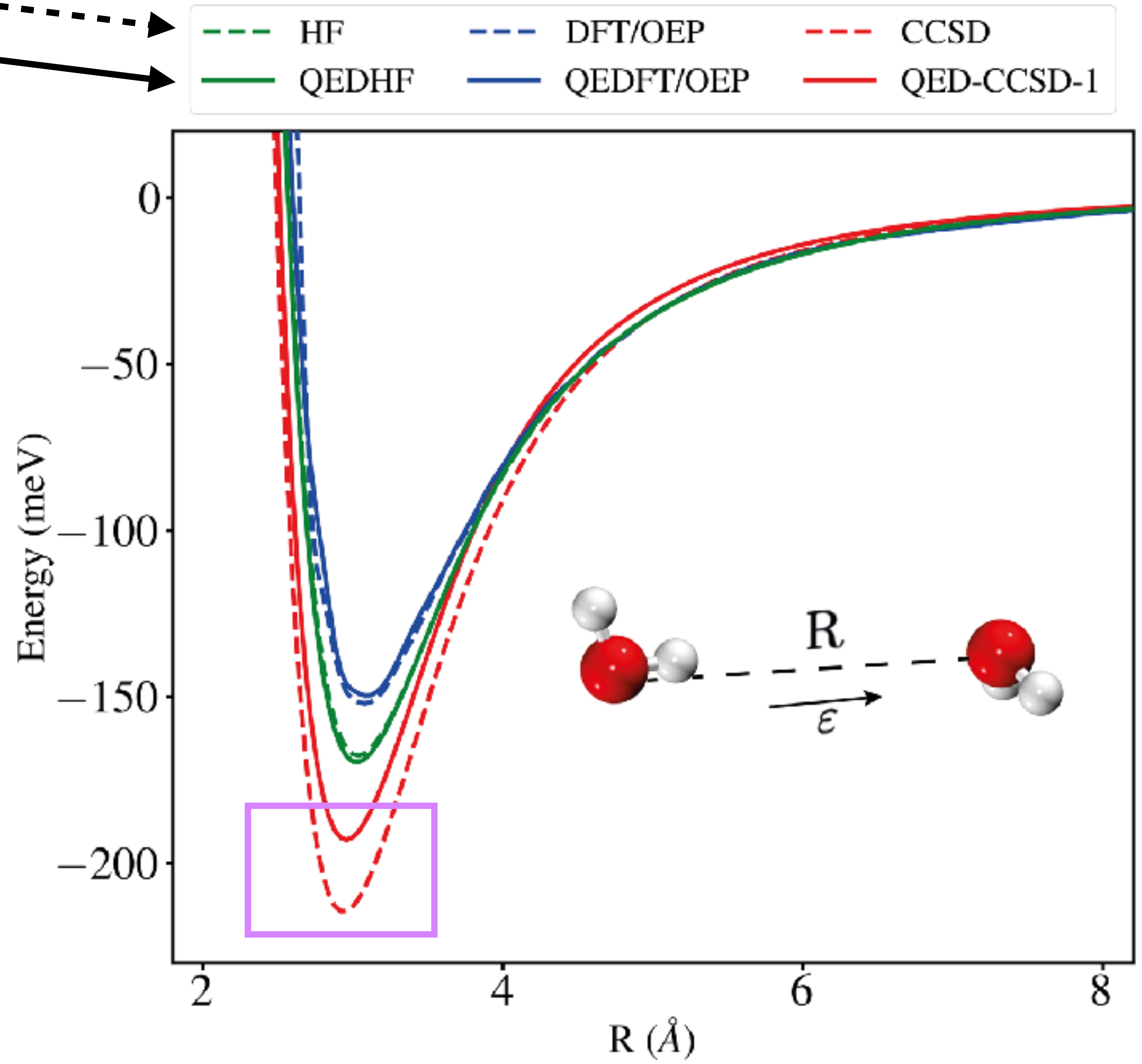
van der Waals



no Cavity

Cavity

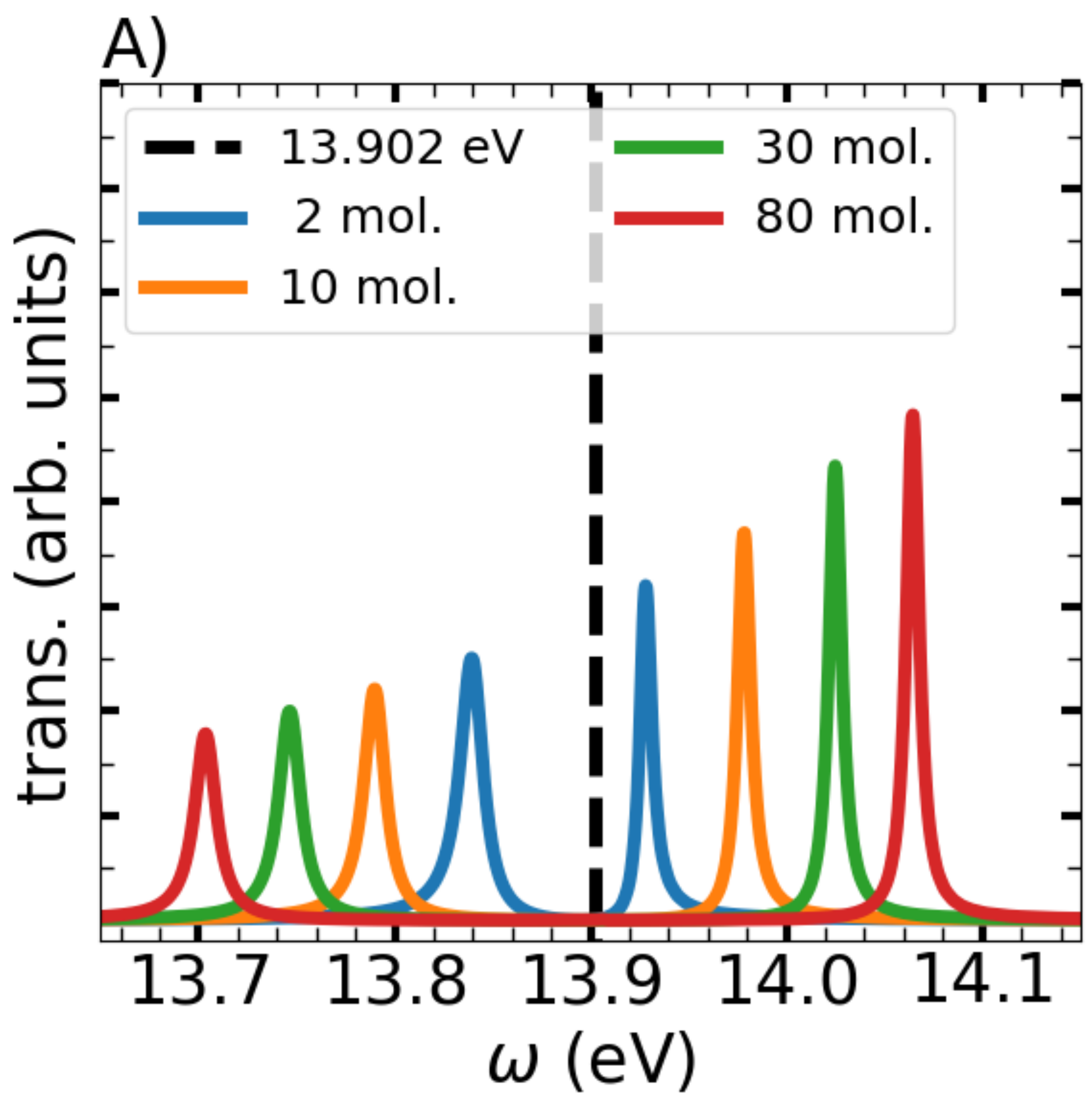
Hydrogen Bonds

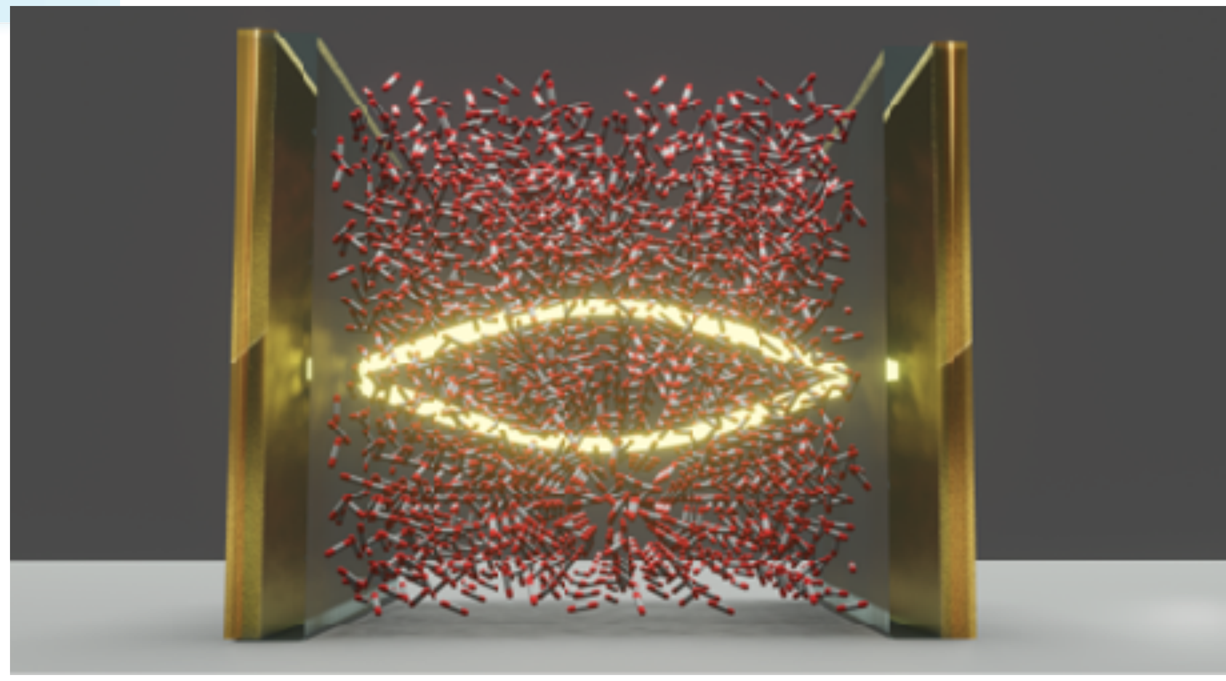


T. Haugland et al., J. Chem. Phys., 154, 094113, 2021

Collective Strong Coupling

Rabi-Splitting Scaling Mystery





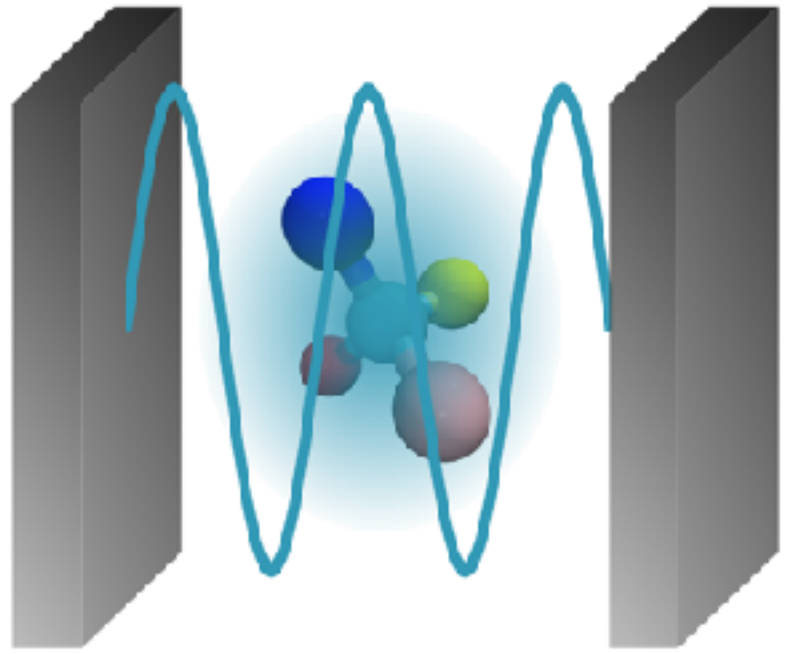
$N \approx 10^4 - 10^{12}$

=> Light-matter coupling λ_α of single molecule extremely small!

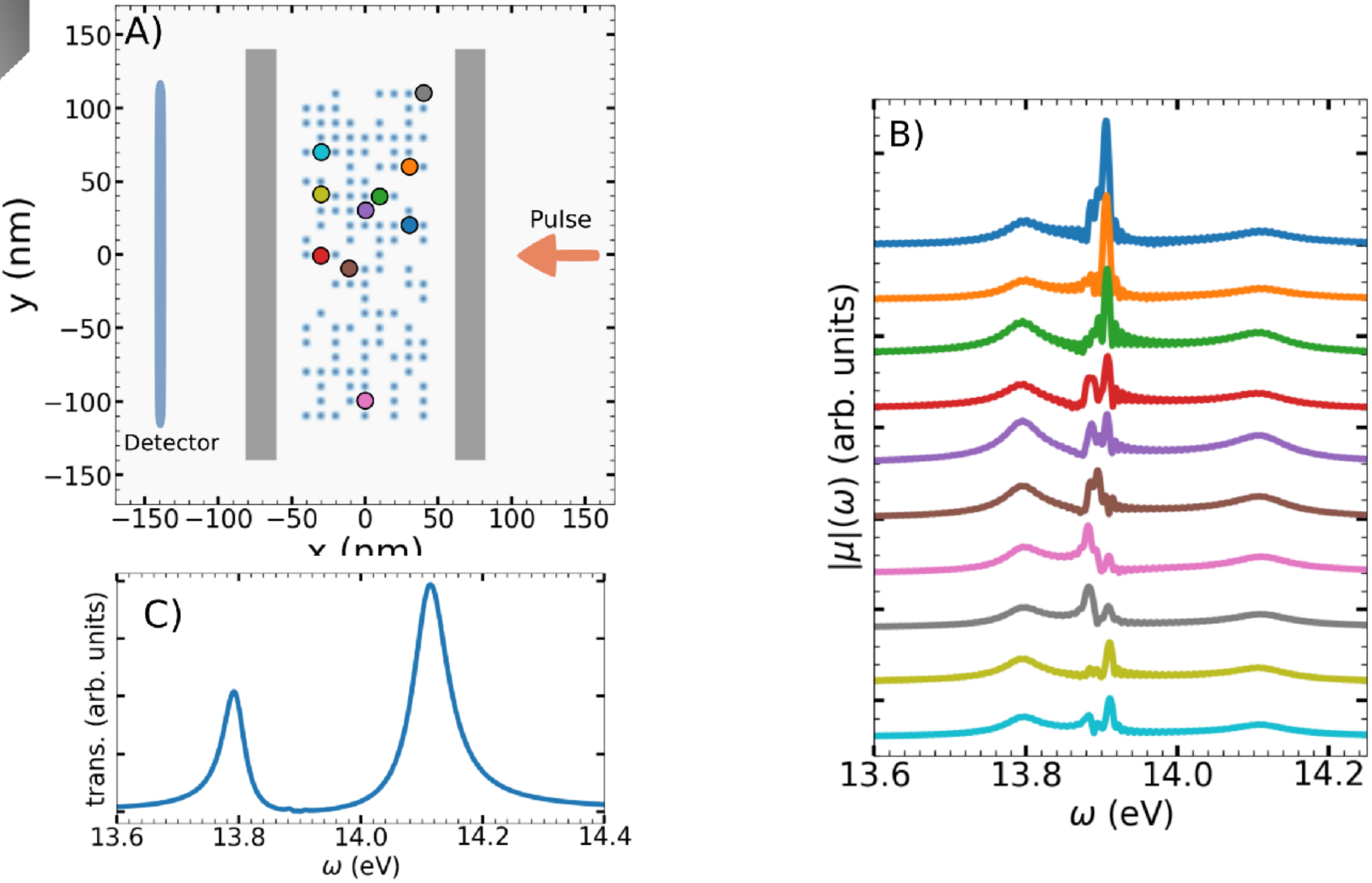
=> No chemical impact expected

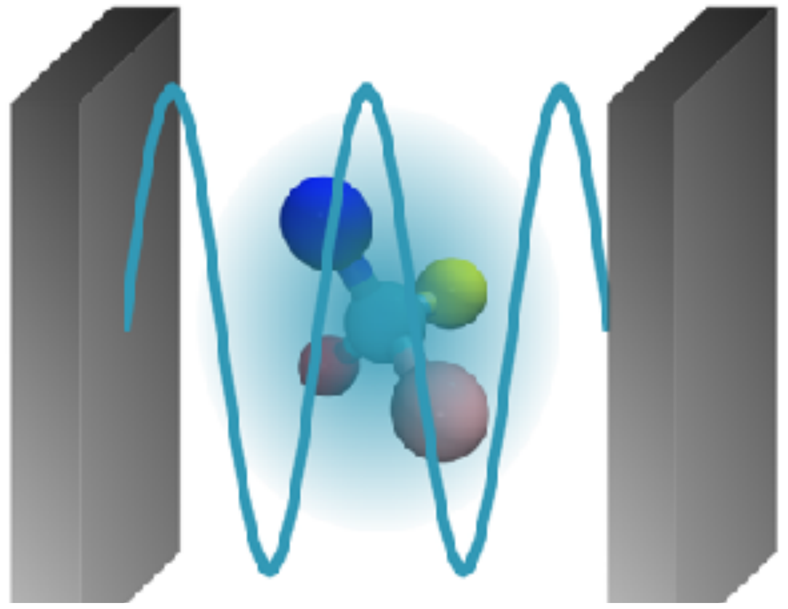
Collective (!) scaling of light-matter interaction

$\Omega \propto \sqrt{N}$



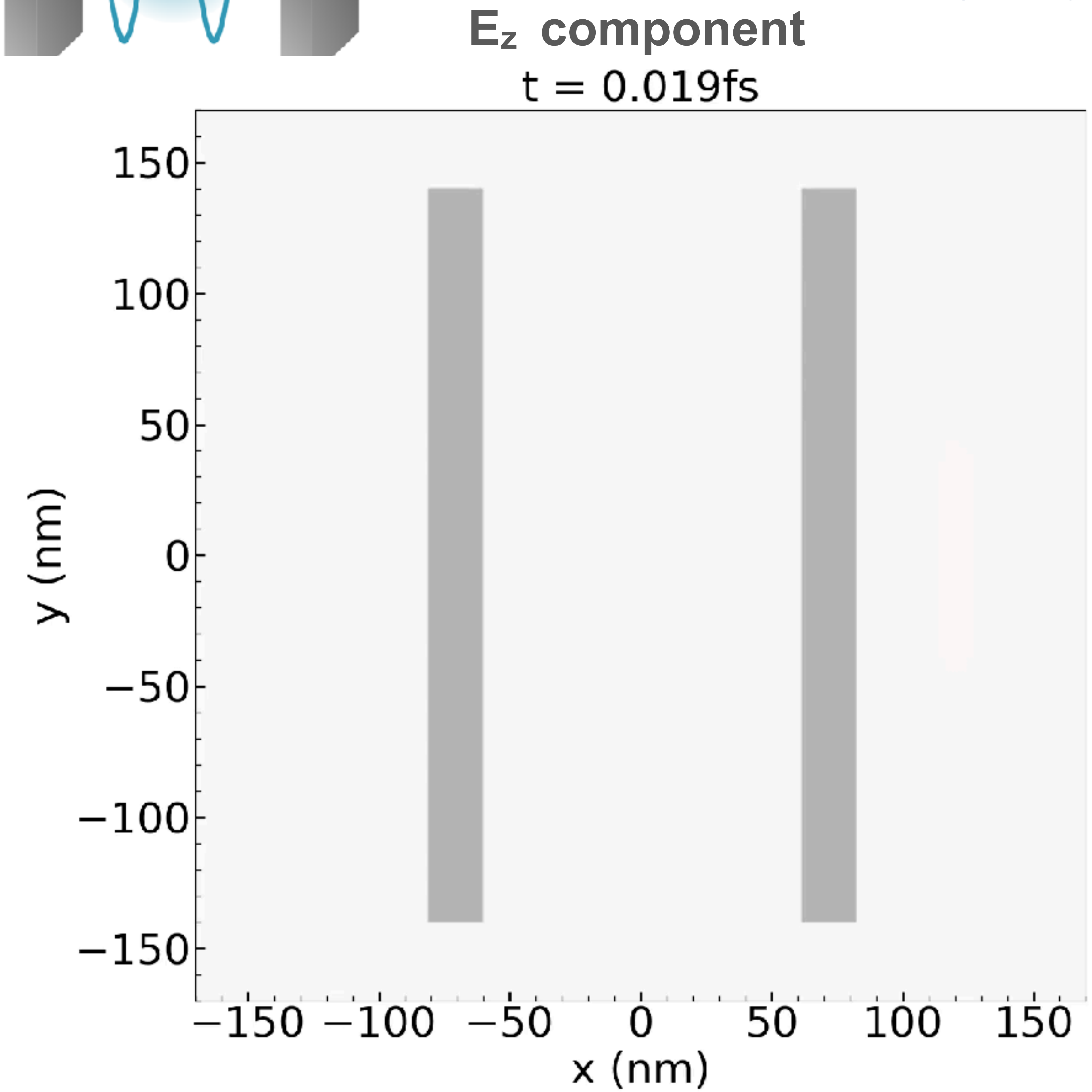
N_2 under electronic strong coupling (ESC)

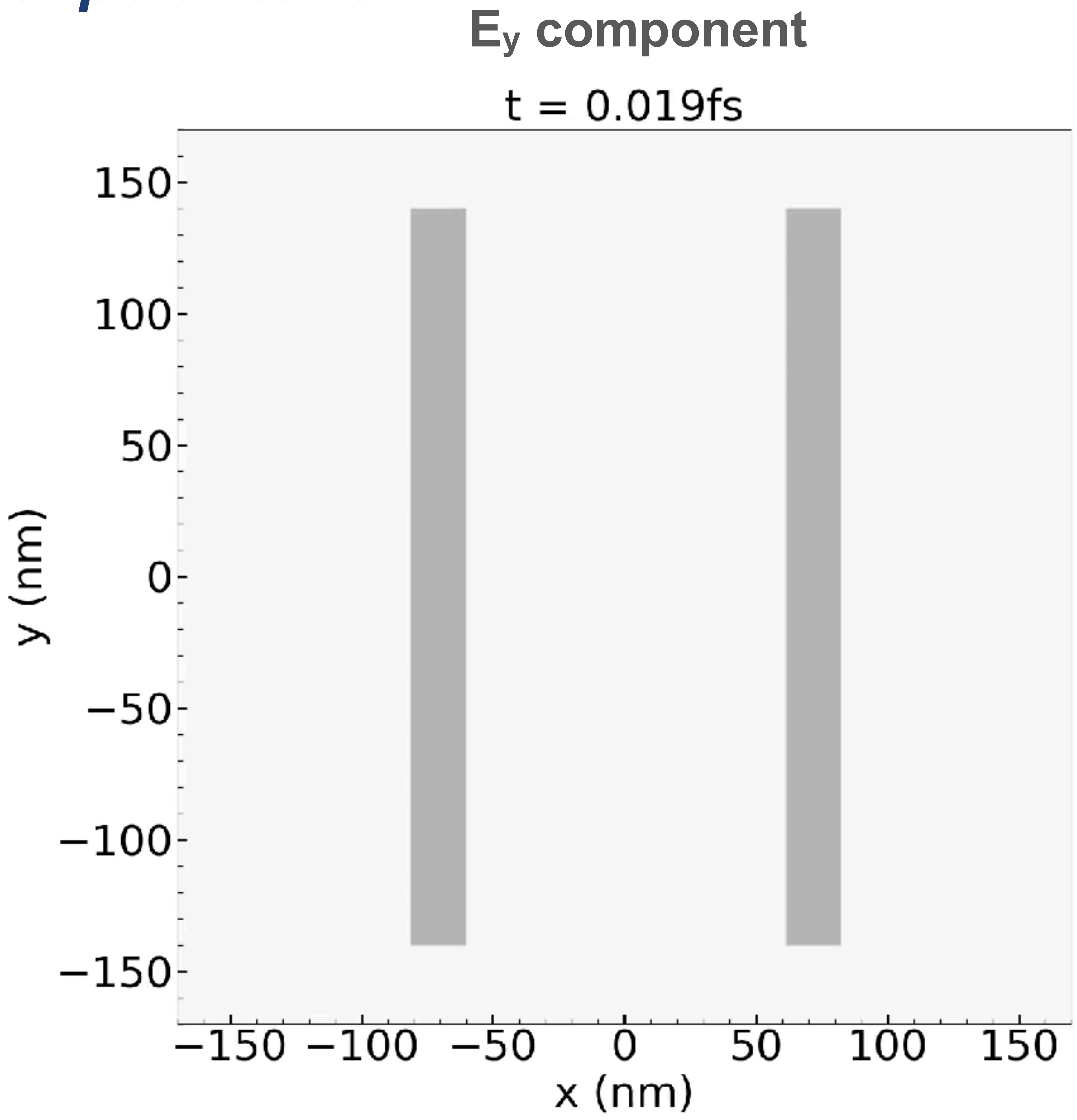




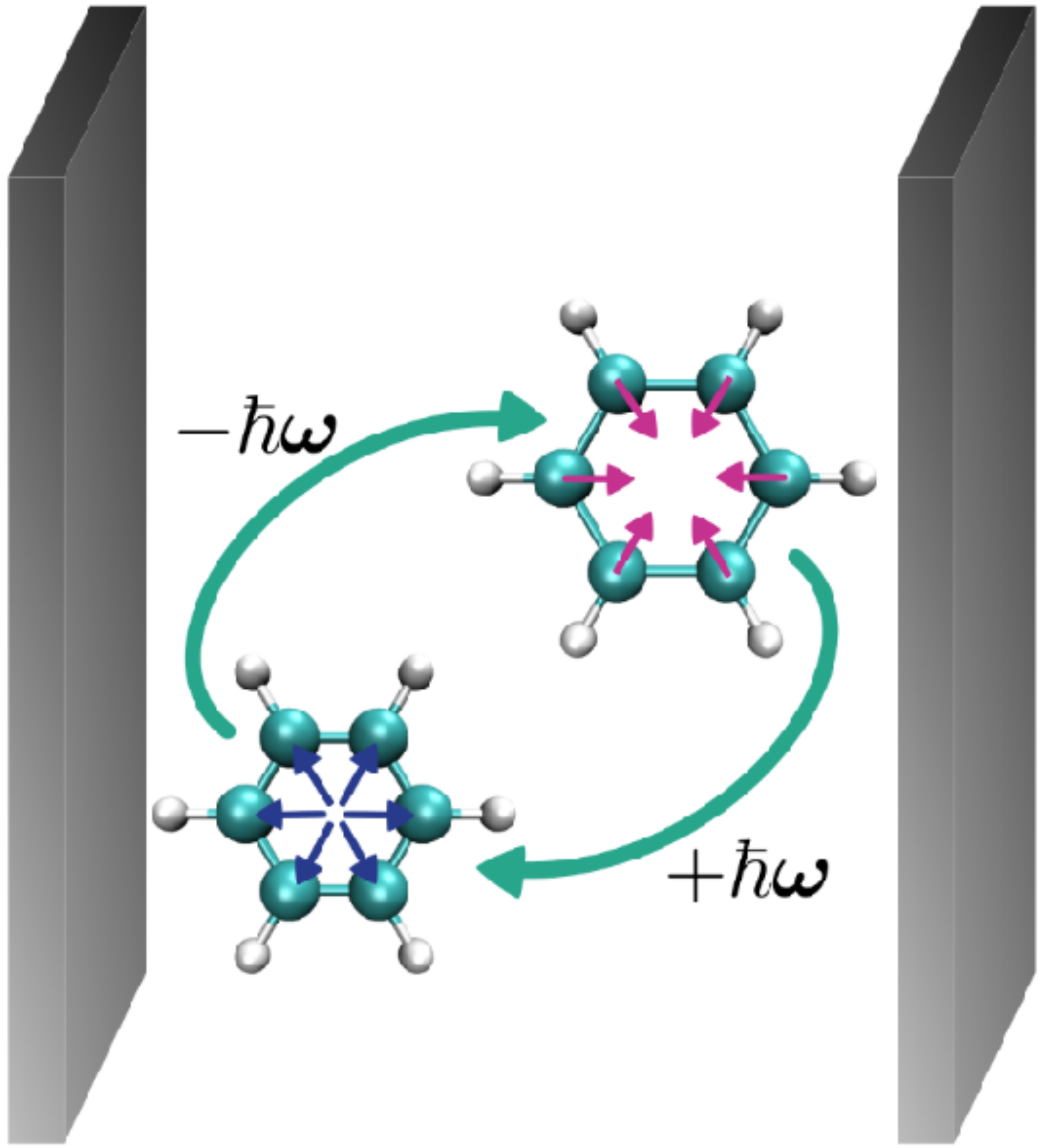
N_2 under electronic strong coupling (ESC)

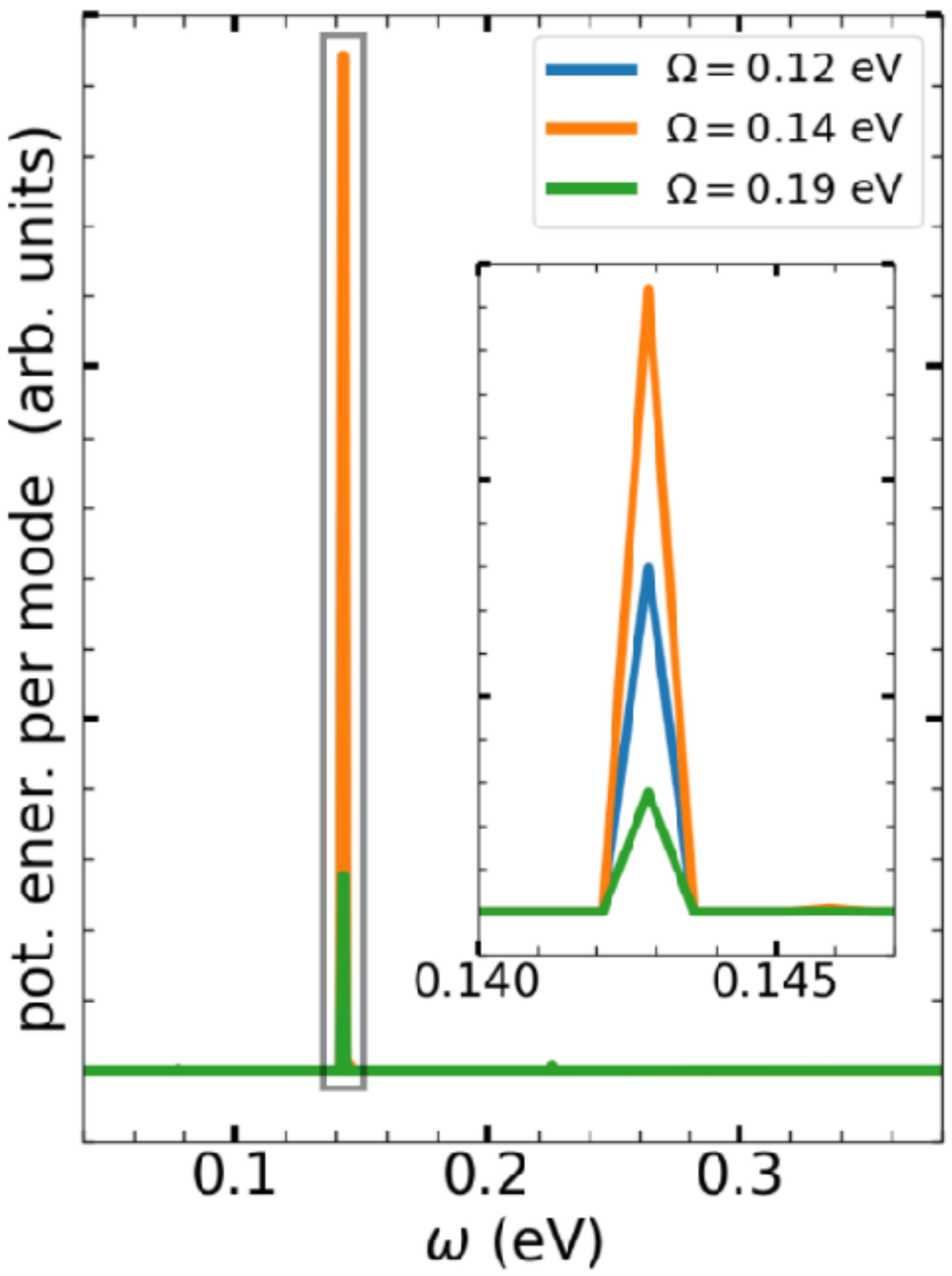
formation of polaritons

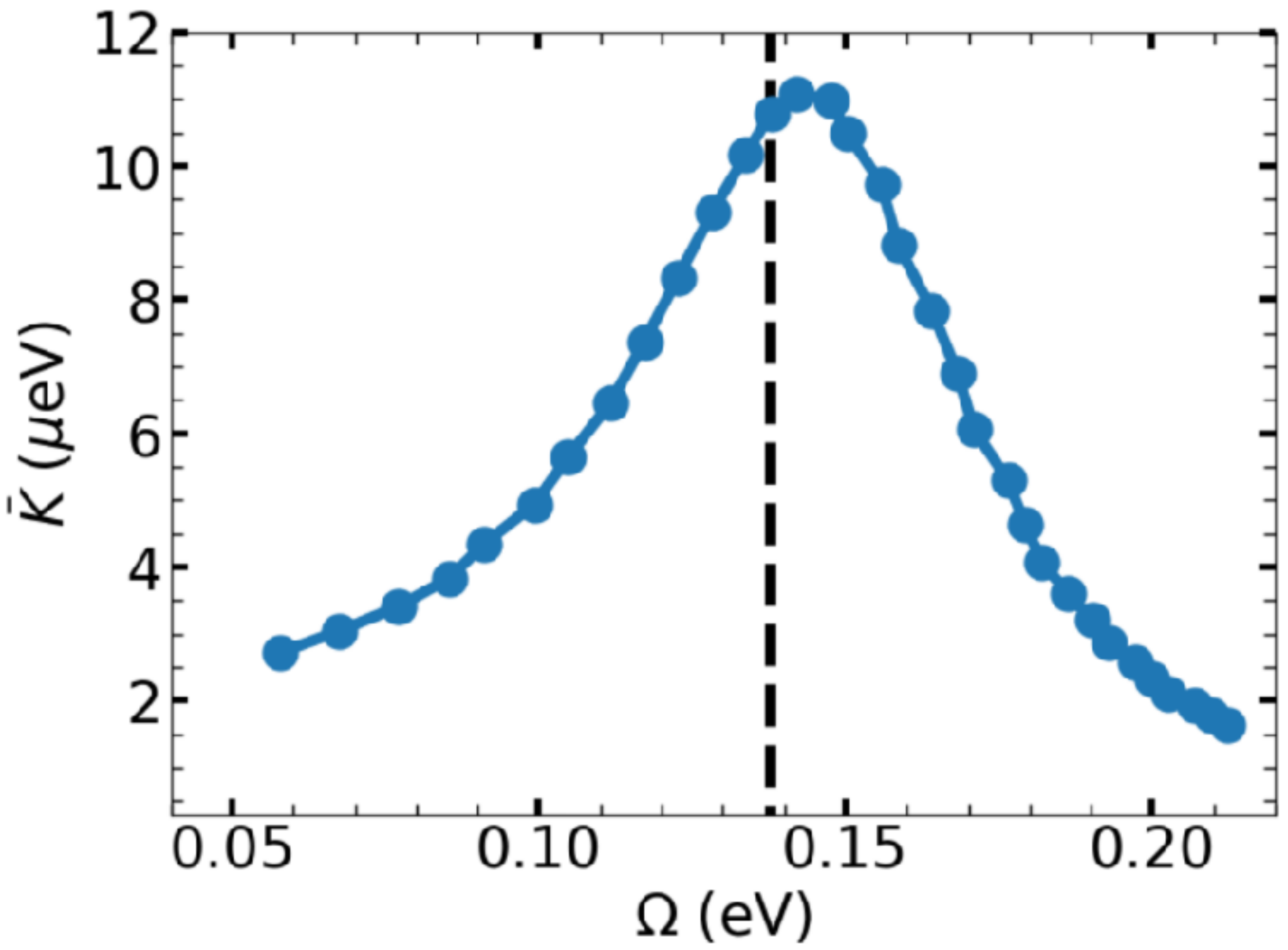




Benzene under ESC with Ehrenfest dynamics







general effect : As long as the excited state forces activate one particular vibrational mode

Collective Electron Correlation Challenge

Electron-Electron Interaction

Bare Matter

Coulomb (longitudinal): $\hat{V}^{(2)}_{\text{long,ij}} = \frac{e^2}{|\hat{\boldsymbol{r}}_i - \hat{\boldsymbol{r}}_j|}$

Relatively **localized** intra- and inter-molecular **correlations**.

Established, but computationally demanding:

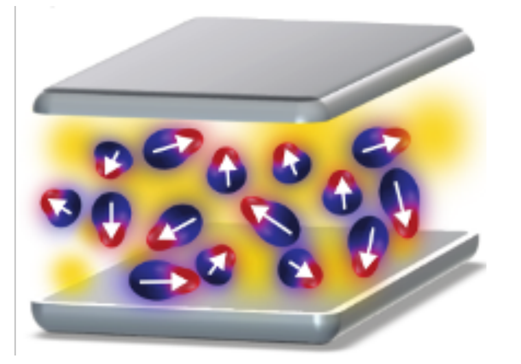
- Configuration Interaction
- Coupled Cluster
- Multi-configuration SCF methods
- Sophisticated exchange-correlation functionals in DFT
- …

$$E^e_{\text{tot}} = E^e_{\text{cH}} + \underbrace{E^e_{\text{xc,Coul}}}_{\frac{e^2}{|\hat{\boldsymbol{r}}_i - \hat{\boldsymbol{r}}_j|}} + \underbrace{E^e_{\text{xc,trans}}}_{\lambda_\alpha^2 e^2 \hat{x}_i \hat{x}_j}$$

Cavity

Dipole Self-energy $\hat{V}^{(2)}_{\text{trans,ij}} = \lambda_\alpha^2 e^2 \hat{x}_i \hat{x}_j$

Long-range inter-molecular **correlations**.



$E_{\text{corr}} \mapsto \sum_{i<j}^{N} J_{ij} s_i s_j$

Collective correlations

require new

computational methods!

Spin Glass mapping — Spherical Sherrington-Kirkpatrick (SSK) Model

$$E_{\text{xc,trans}} \mapsto -\sum_{i<j}^{N} J_{ij} s_i s_j, \quad \sum_{i}^{N} s_i^2 = 1, \; J_{ij} \sim \mathcal{N}(0, \sigma_\lambda^2)$$

Random — Normalization

J. M. Kosterlitz et al., Phys. Rev. Lett. 36, 20 (1976),
D. Sidler, M. Ruggenthaler and A. Rubio, arXiv:2409.08986, (2024)

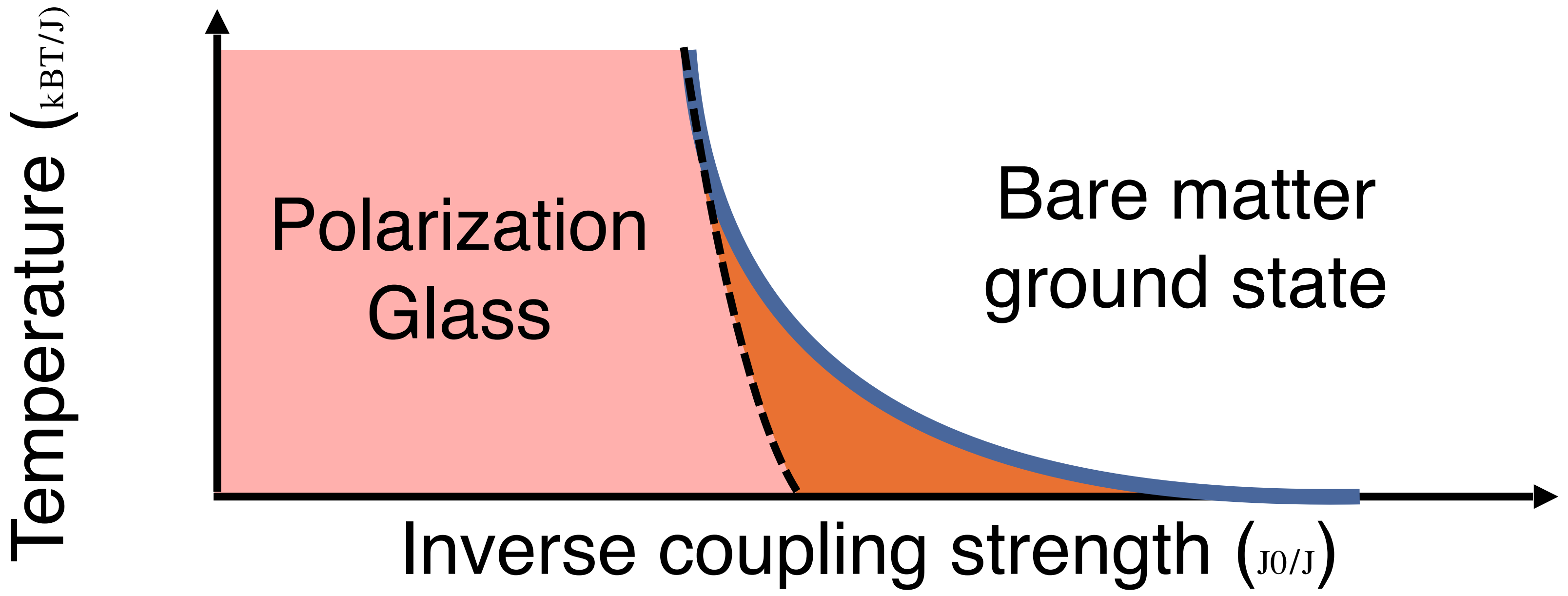
The Spin Glass Hypothesis

European Research Council
Established by the European Commission
Synergy Grants

Spin glass-like electron correlations

Electronic structure (ab initio):

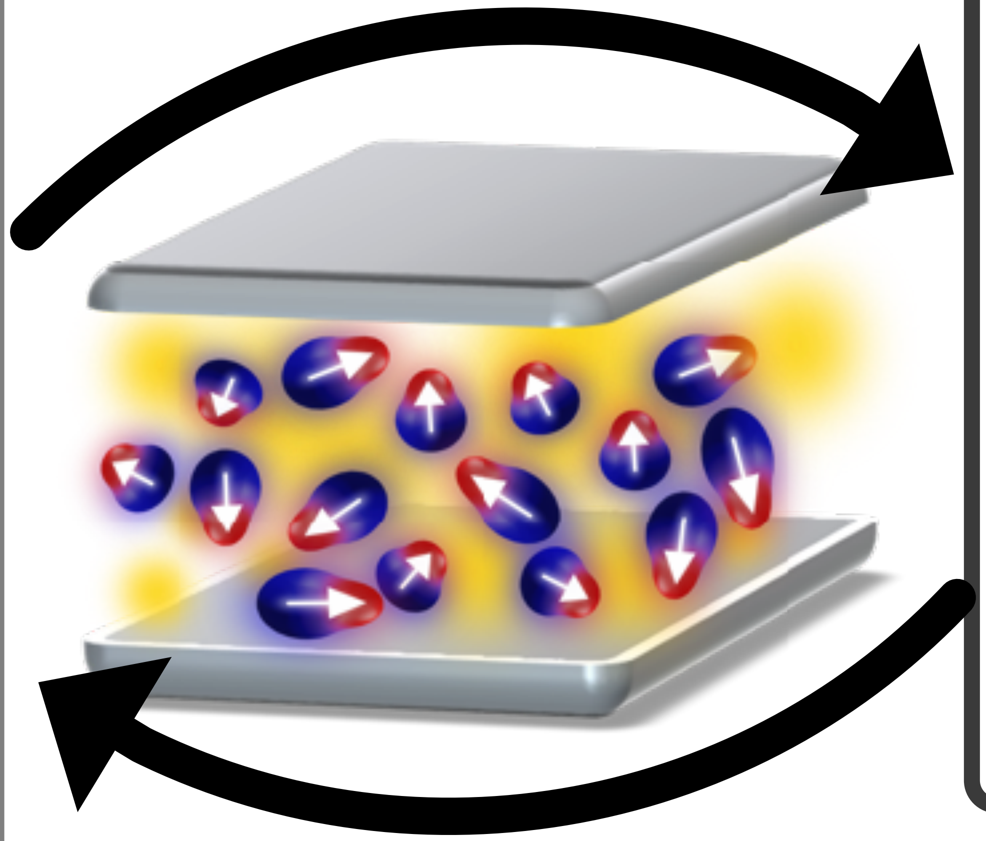
$$\left\langle \hat{H}^e\left(\mathbf{R}, q_\beta\right)\right\rangle = \sum_i^N \left[\left\langle \hat{H}_i^{m,e}\right\rangle_i - q_\beta\omega_\beta\left\langle \hat{x}_i\right\rangle_i + \left\langle \hat{x}_i^2\right\rangle_i/2 + 2\sum_{j<i}\left\langle \hat{x}_j\right\rangle_j\left\langle \hat{x}_i\right\rangle_i\right]$$



Seed of VSC (mapping to a spin glass model)

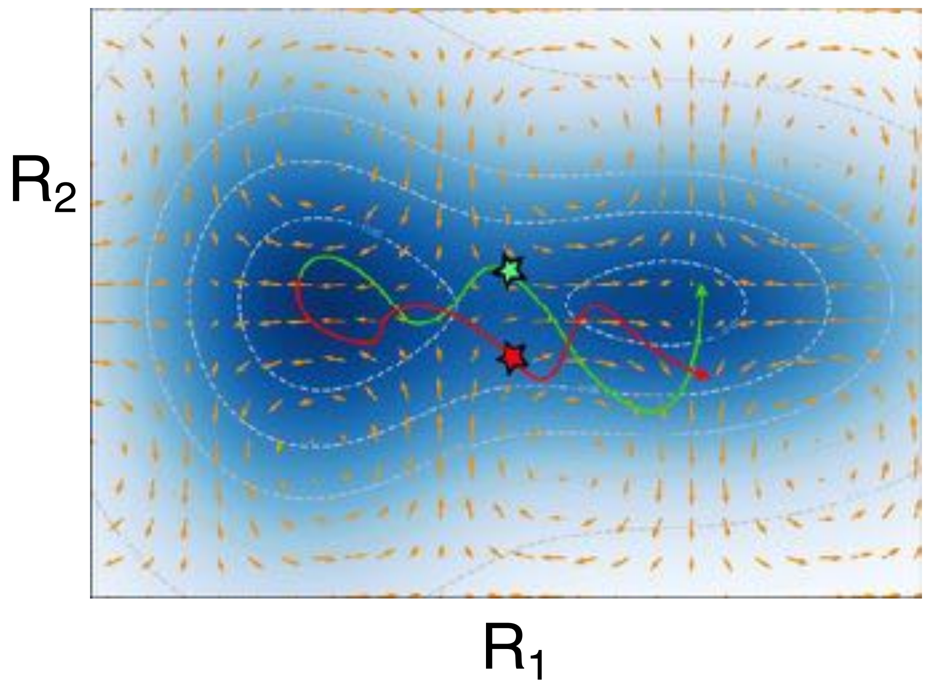
Collectively induced polarization instability

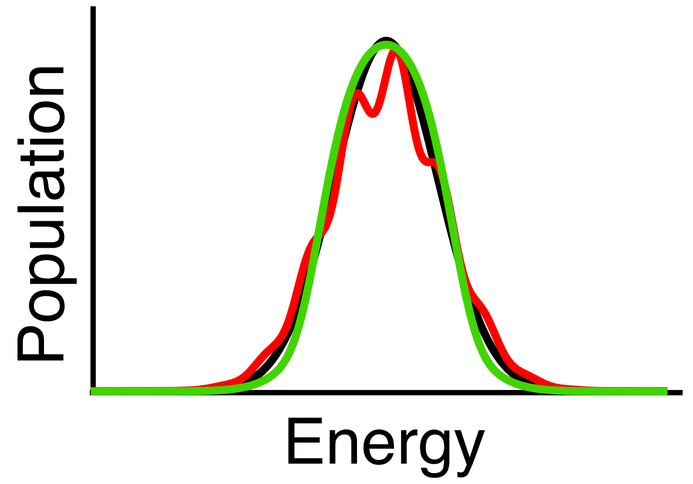
Replica **symmetry breaking** & dynamic frustration



Nuclei–photon interactions (MD)

$$H^{\mathrm{m}}\left(\mathbf{R}(t), q_\beta(t)\right) + \frac{p_\beta^2}{2} + \frac{\omega_\beta^2}{2}\left(q_\beta - \frac{X_\beta}{\omega_\beta}\right) + \mathscr{E}\left(\mathbf{R}(t), q_\beta(t), t\right)$$





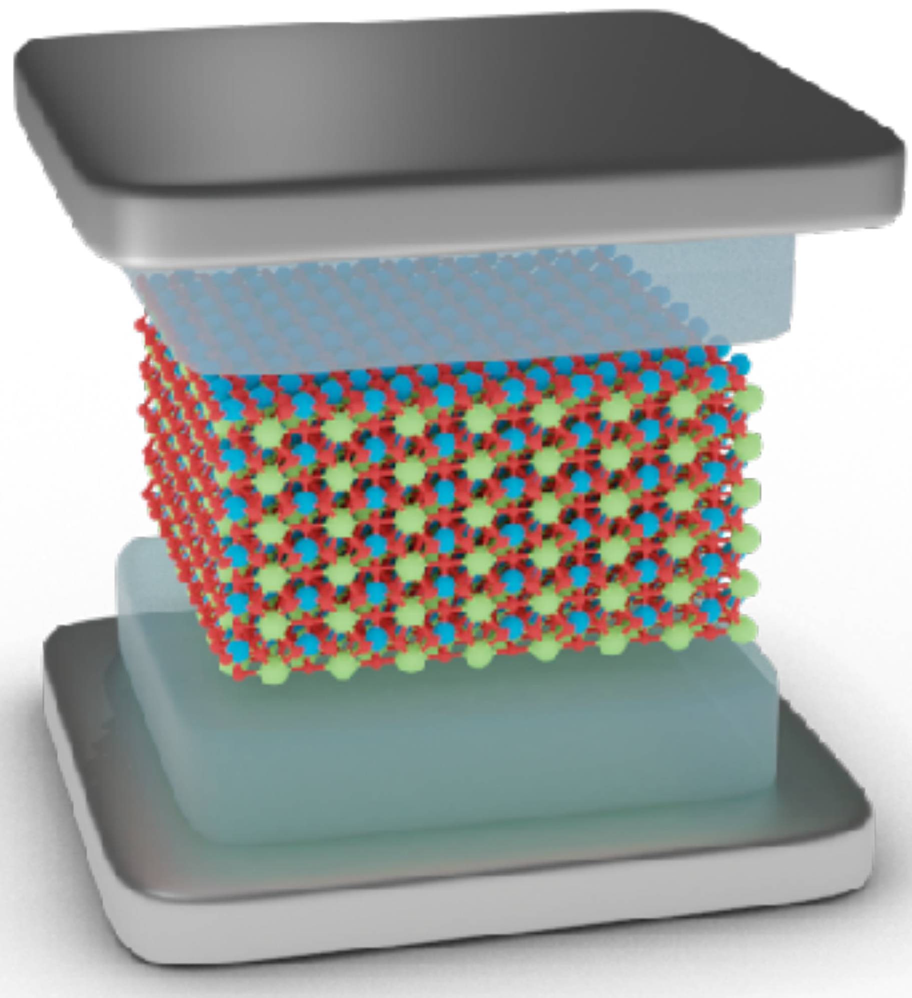
Stochastic Resonances:

Non-equilibrium thermodynamics

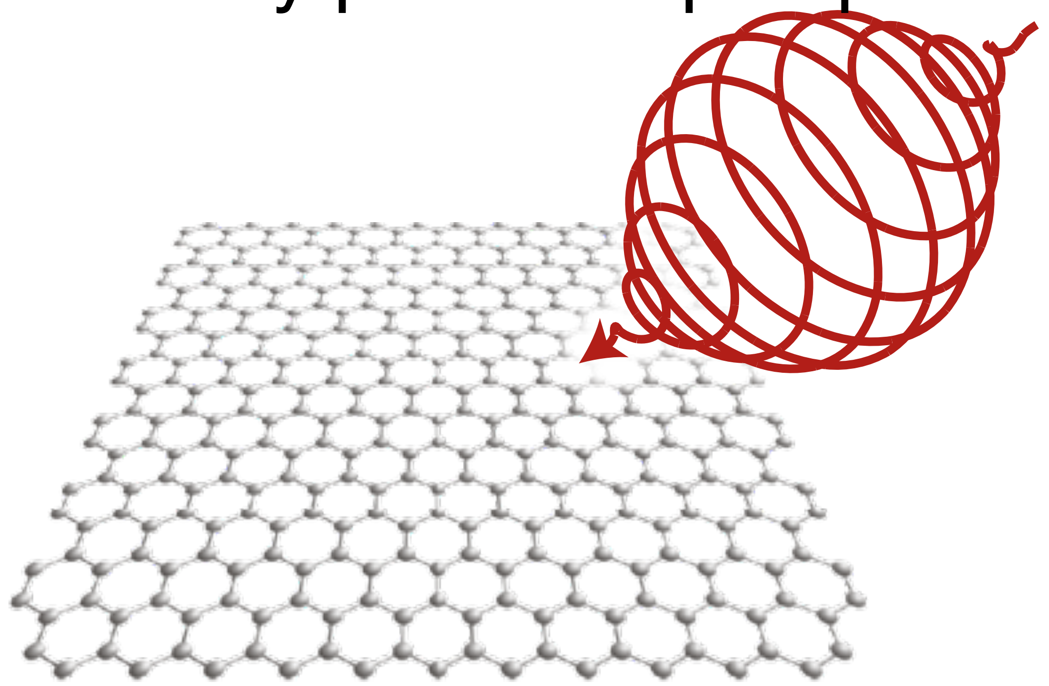
The connection of polaritonic chemistry with the physics of a spin glass
D. Sidler, M. Ruggenthaler, AR arXiv:5853629

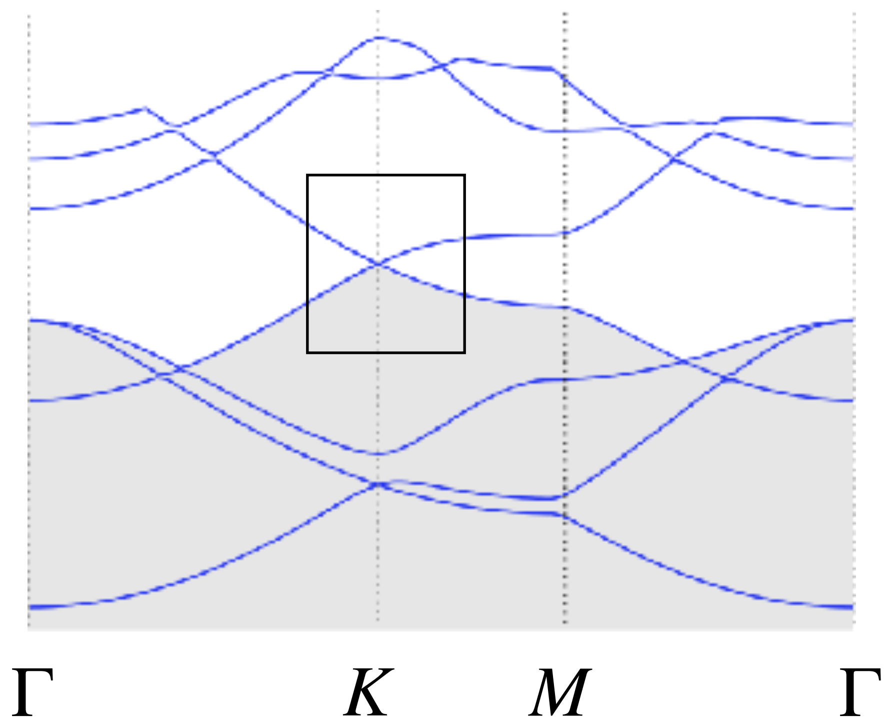
what about the main question

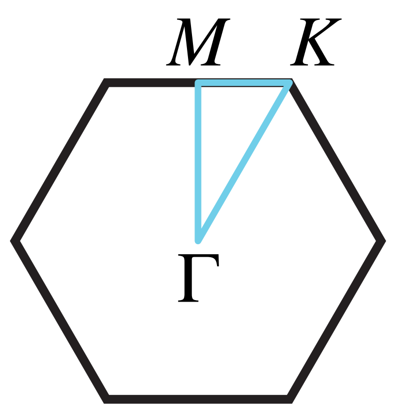
modifying the ground state of a quantum material with with vacuum fluctuations?



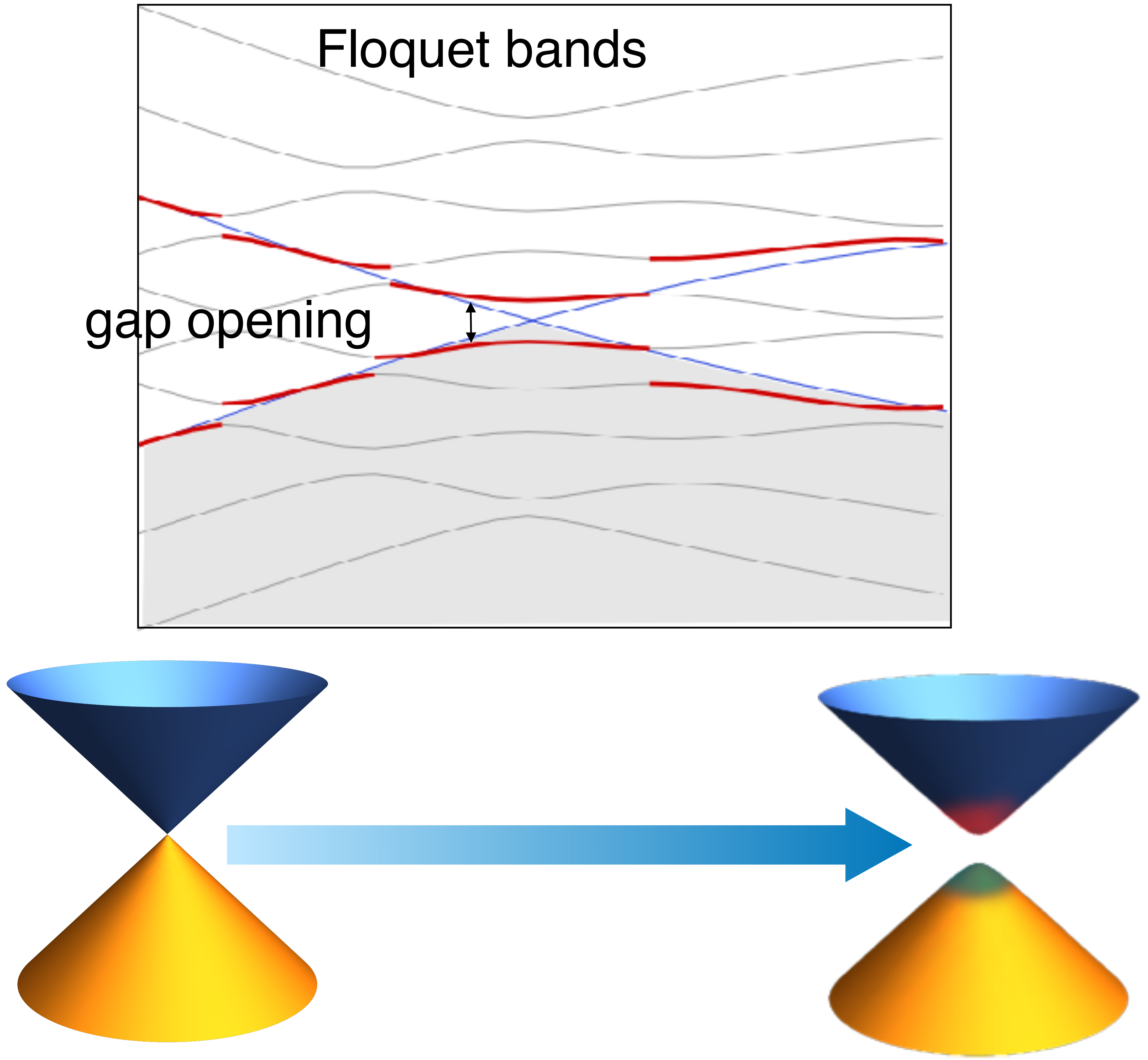
A famous proposal:
Floquet topology in driven graphene





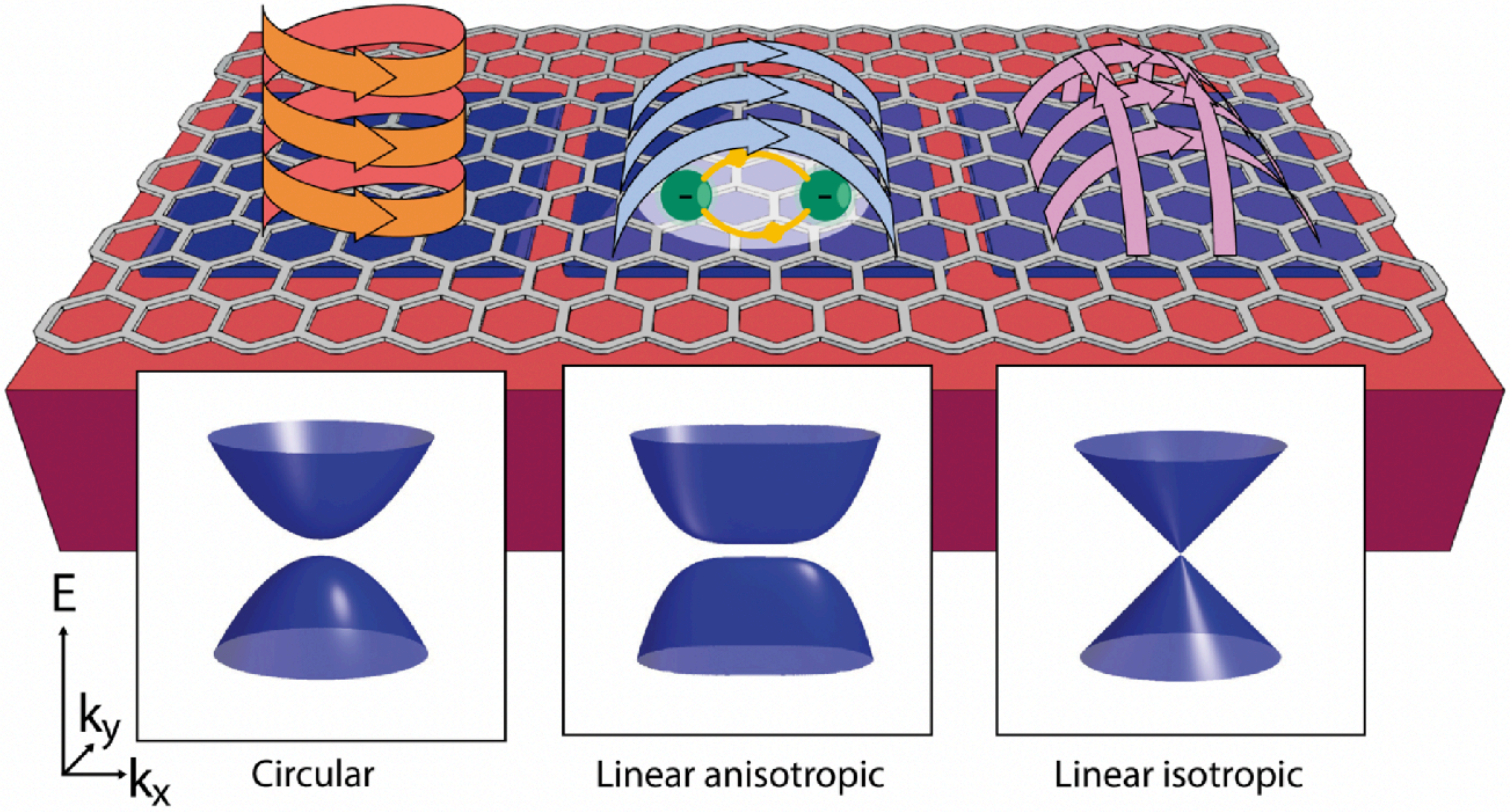


topological Chern insulator -> anomalous Hall current



T. Oka and H. Aoki, Phys. Rev. B 79, 081406(R) (2009)

Engineering graphene with optical cavities



Cavity-Mediated Electron-Electron Interactions: Renormalizing Dirac States in Graphene,
Hang Liu, Francesco Troisi, Hannes Hubener, Simone Latini, AR, Science Advances 11, eadz1855 (2025)

Electron-photon interacting Hamiltonian

Pauli-Fierz Hamiltonian

N_e electrons

$$\hat{H}_e = \sum_i^{N_e} \left[\frac{\hat{\mathbf{p}}_i^2}{2m} + \hat{V}(\mathbf{r}_i) \right]$$

A single photon

$$\hat{\mathbf{A}} = A_0 \left(\hat{a}^\dagger \mathbf{e}^* + \hat{a}\mathbf{e} \right)$$

e.g., $\mathbf{e} = \mathbf{e}_x, \mathbf{e} = (\mathbf{e}_x + i\mathbf{e}_y)/\sqrt{2}$

Pauli-Fierz Hamiltonian (long wave)

$$\hat{H} = \sum_i^{N_e} \left[\frac{(\hat{\mathbf{p}}_i - q\hat{\mathbf{A}})^2}{2m} + \hat{V}(\mathbf{r}_i) \right] + \hbar\omega \left(\frac{1}{2} + \hat{a}^\dagger \hat{a} \right)$$

Dressed photon: Diamagnetism removed

$$\hat{H} = \hat{H}_e + \hbar\tilde{\omega} \left(\frac{1}{2} + \hat{\tilde{a}}^\dagger \hat{\tilde{a}} \right) - \frac{q}{m} \sum_i^{N_e} \hat{\mathbf{p}}_i \cdot \hat{\tilde{\mathbf{A}}}$$

$$\hat{\tilde{\mathbf{A}}} = \tilde{A}_0 \left(\hat{\tilde{a}}^\dagger \mathbf{e}^* + \hat{\tilde{a}}\mathbf{e} \right)$$

Circular: $\tilde{\omega} = \omega \left(1 + \zeta \frac{N_e A_0^2}{\omega} \right)$ $\quad \tilde{A}_0 = A_0$ $\quad \zeta = \frac{q^2}{m\hbar}$

Linear: $\tilde{\omega} = \omega \sqrt{1 + \zeta \frac{2N_e A_0^2}{\omega}}$ $\quad \tilde{A}_0 = A_0 \frac{\sqrt{u+1} - \sqrt{u-1}}{\sqrt{2}}$ $\quad u = \frac{\zeta N_e A_0^2 + \omega}{\sqrt{(2\zeta N_e A_0^2 + \omega)\omega}}$

Matrix in the dressed photon space

$\langle\tilde{0}\|\hat{H}\|\tilde{0}\rangle$	$\langle\tilde{0}\|\hat{H}\|\tilde{1}\rangle$	0	0
$\langle\tilde{1}\|\hat{H}\|\tilde{0}\rangle$	$\langle\tilde{1}\|\hat{H}\|\tilde{1}\rangle$	$\langle\tilde{1}\|\hat{H}\|\tilde{2}\rangle$	0
0	$\langle\tilde{2}\|\hat{H}\|\tilde{1}\rangle$	$\langle\tilde{2}\|\hat{H}\|\tilde{2}\rangle$	$\langle\tilde{2}\|\hat{H}\|\tilde{3}\rangle$
0	0	$\langle\tilde{3}\|\hat{H}\|\tilde{2}\rangle$	$\langle\tilde{3}\|\hat{H}\|\tilde{3}\rangle$

$\ddots$

$$\langle\tilde{n}|\hat{H}|\tilde{n}\rangle = \langle\tilde{0}|\hat{H}|\tilde{0}\rangle + \tilde{n}\hbar\tilde{\omega}$$
$$\langle\tilde{n}|\hat{H}|\tilde{n}+1\rangle = \sqrt{\tilde{n}+1}\langle\tilde{0}|\hat{H}|\tilde{1}\rangle$$

Downfolding at high frequency (off resonant)!

Electron-photon interacting Hamiltonian

Photon-free effective Hamiltonian

$$\hat{H}_{\mathrm{eff}} = \hat{H}_{\mathrm{e}} + \sum_{\alpha}^{N_{\mathrm{p}}} \left(\frac{\hbar\tilde{\omega}_\alpha}{2} + \hat{H}_{\mathrm{l},\alpha} + \hat{H}_{\mathrm{nl},\alpha} \right)$$

$$\hat{H}_{\mathrm{l},\alpha} = -\zeta \frac{\tilde{A}_{0\alpha}^2}{\tilde{\omega}_\alpha} \sum_i^{N_{\mathrm{e}}} (\hat{\mathbf{p}}_i \cdot \tilde{\mathbf{e}}_\alpha)(\hat{\mathbf{p}}_i \cdot \tilde{\mathbf{e}}_\alpha^*)$$

local interaction (one body) - Floquet

$$\hat{H}_{\mathrm{nl},\alpha} = -\zeta \frac{\tilde{A}_{0\alpha}^2}{\tilde{\omega}_\alpha} \sum_i^{N_{\mathrm{e}}} \sum_{j\neq i}^{N_{\mathrm{e}}} (\hat{\mathbf{p}}_i \cdot \tilde{\mathbf{e}}_\alpha)(\hat{\mathbf{p}}_j \cdot \tilde{\mathbf{e}}_\alpha^*)$$

nonlocal interaction (two body)

$$\text{Coulomb:} \sum_i^{N_{\mathrm{e}}} \sum_{j\neq i}^{N_{\mathrm{e}}} \frac{1}{\mathbf{r}_i - \mathbf{r}_j} \quad \text{vs.} \quad \text{QED:} \sum_i^{N_{\mathrm{e}}} \sum_{j\neq i}^{N_{\mathrm{e}}} (\nabla_i \cdot \mathbf{e})(\nabla_j \cdot \mathbf{e}^*)$$

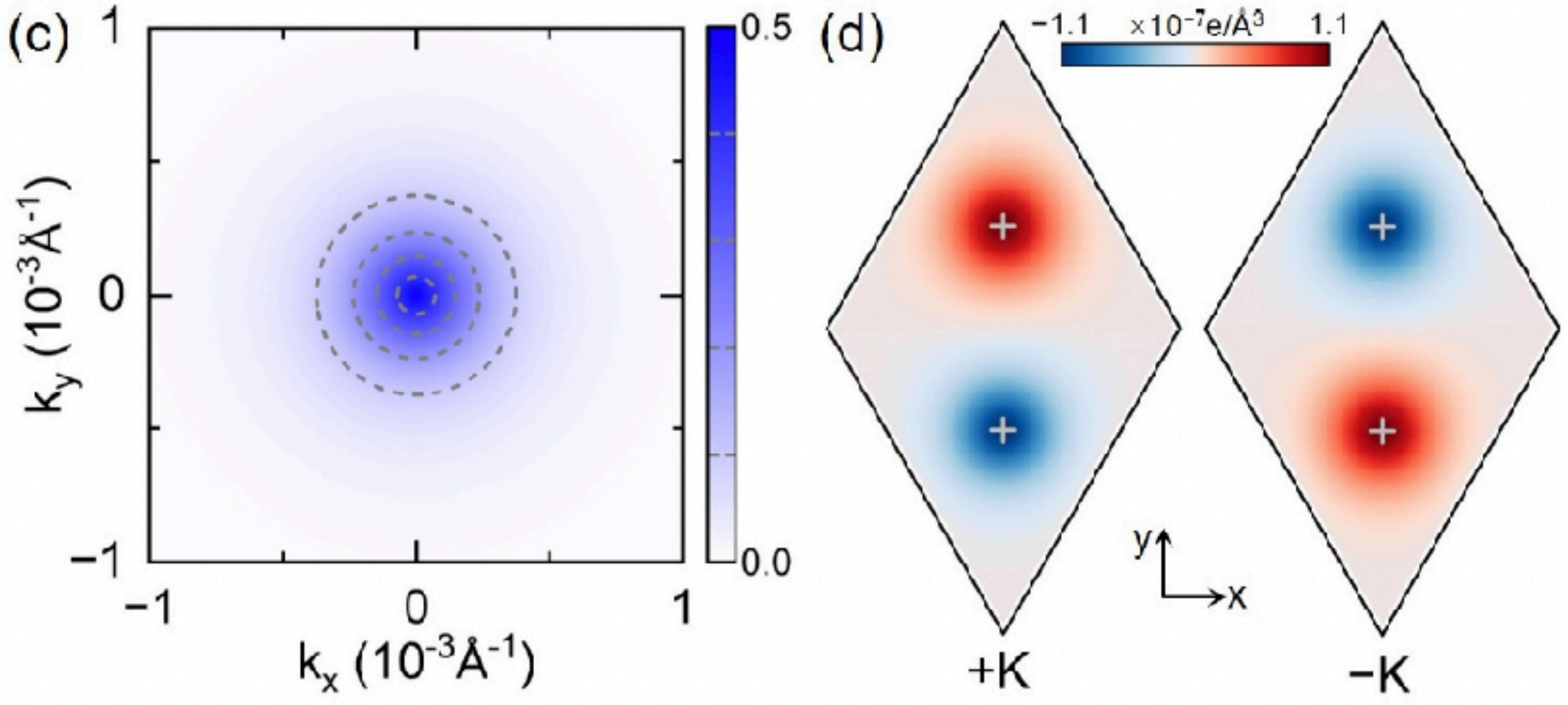
Solution at the Hartree-Fock (HF) approximation, QED-HF.

Hang Liu, Francesco Troisi, Hannes Hubener, Simone Latini, AR, Science Advances 11, eadz1855 (2025)

Engineering graphene with CHIRAL optical cavities

$$\Delta = \kappa \frac{A_0^2}{\omega}$$

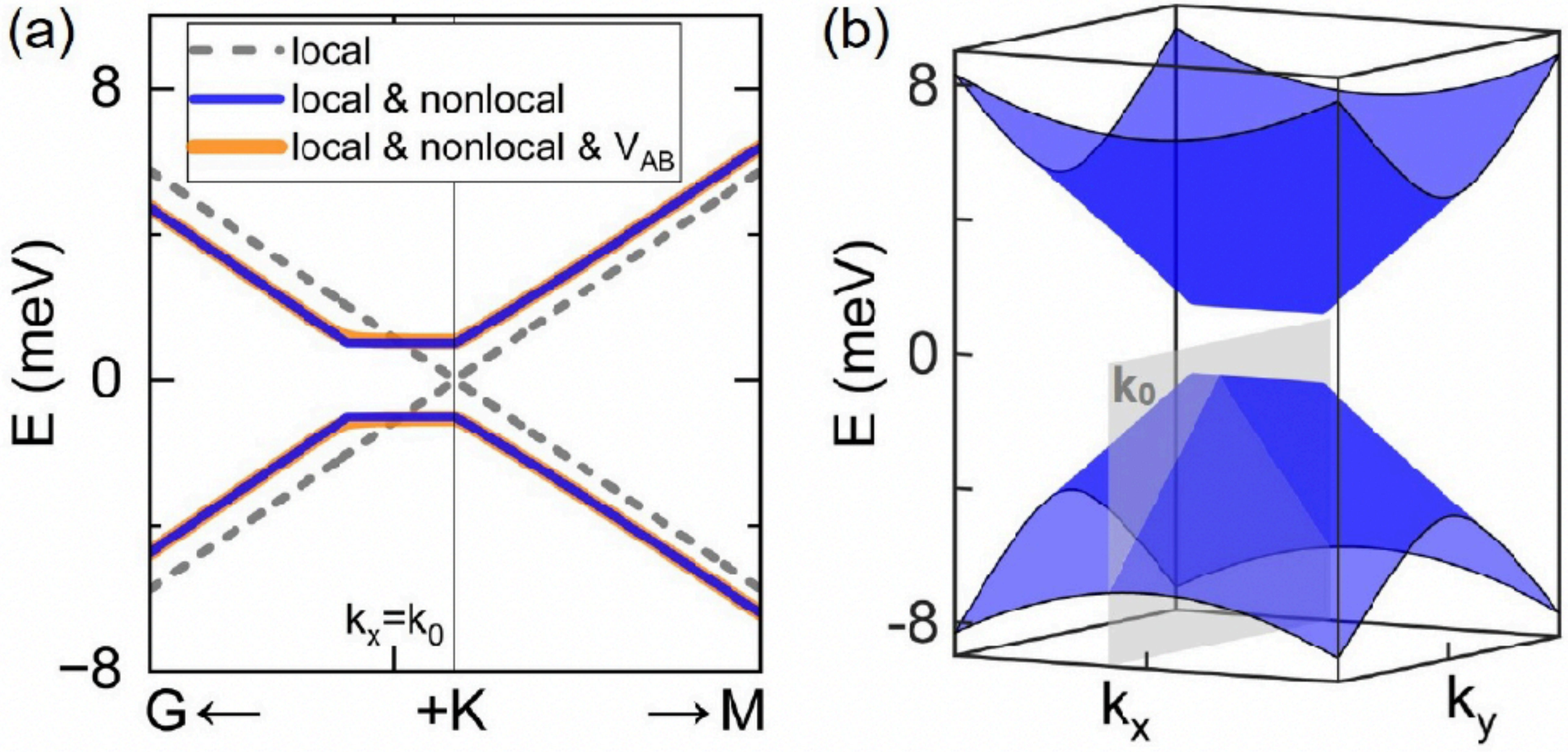
Isotropic Dirac gap ~ 4 meV (same at –K valley)



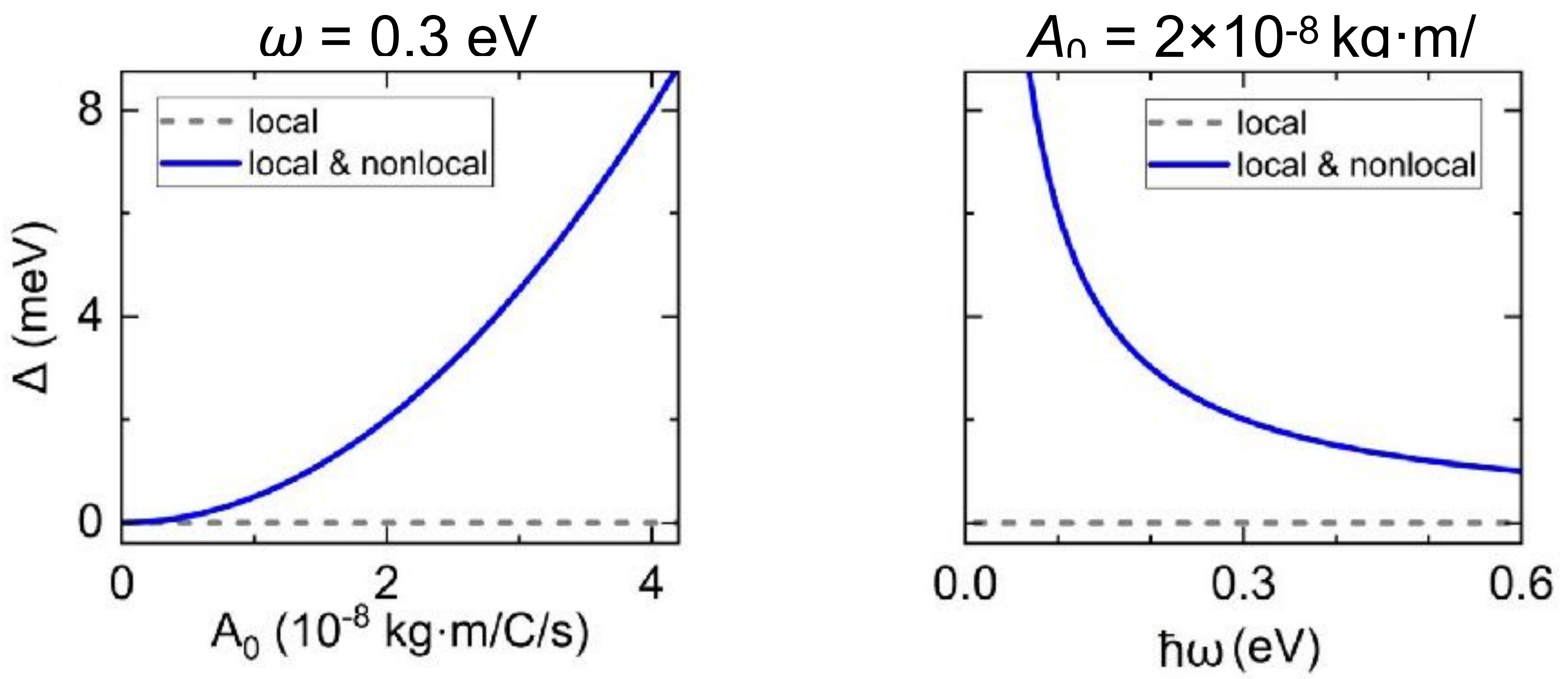
$$|\varphi_{v,+K}(\mathbf{r})|^2 \neq |\varphi_{v,-K}(\mathbf{r})|^2$$

Time-reversal symmetry breaking

Engineering graphene with LINEAR optical cavities



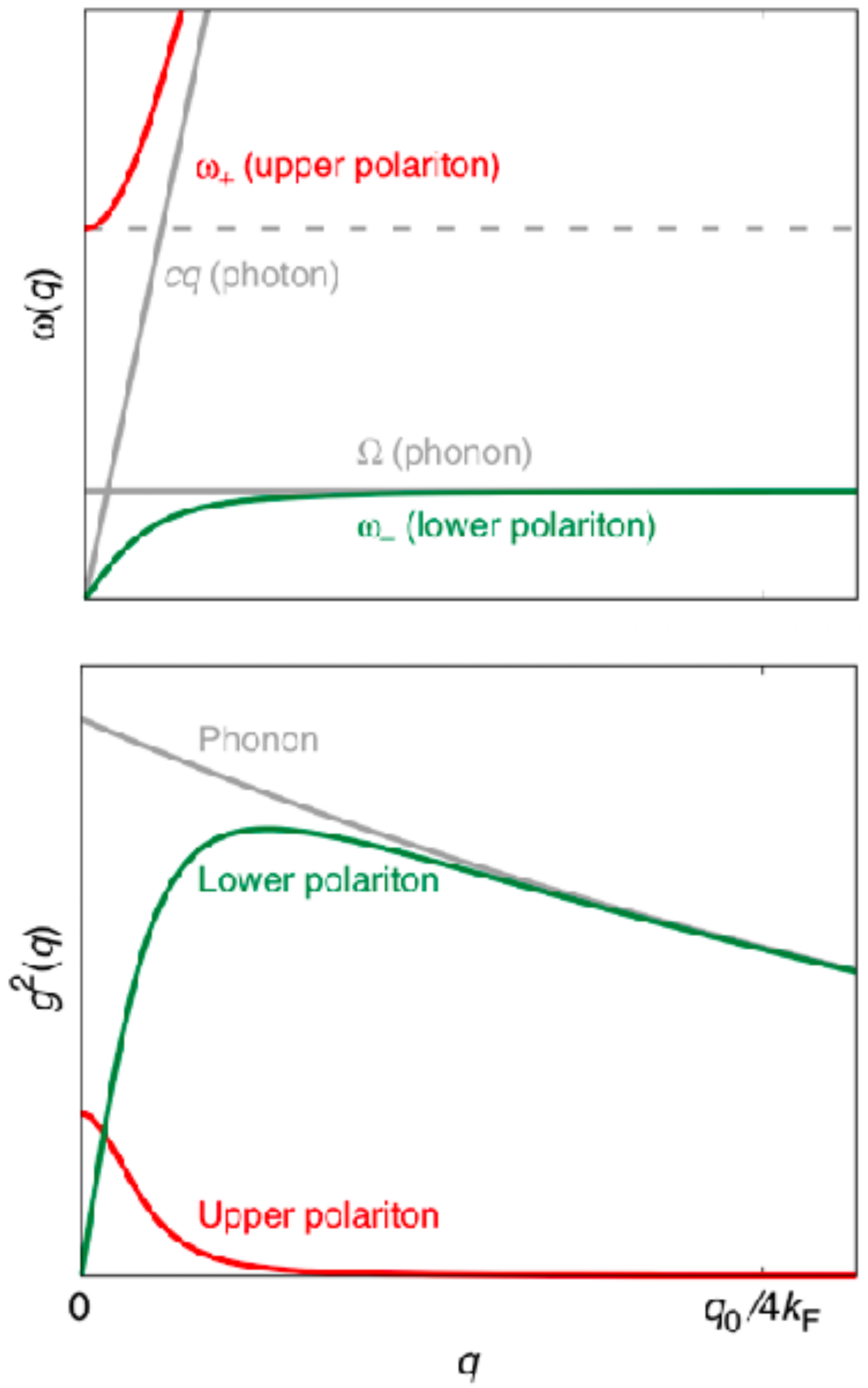
$$\Delta = \xi \frac{A_0^2}{\omega}$$



Gap opening from nonlocal interaction!

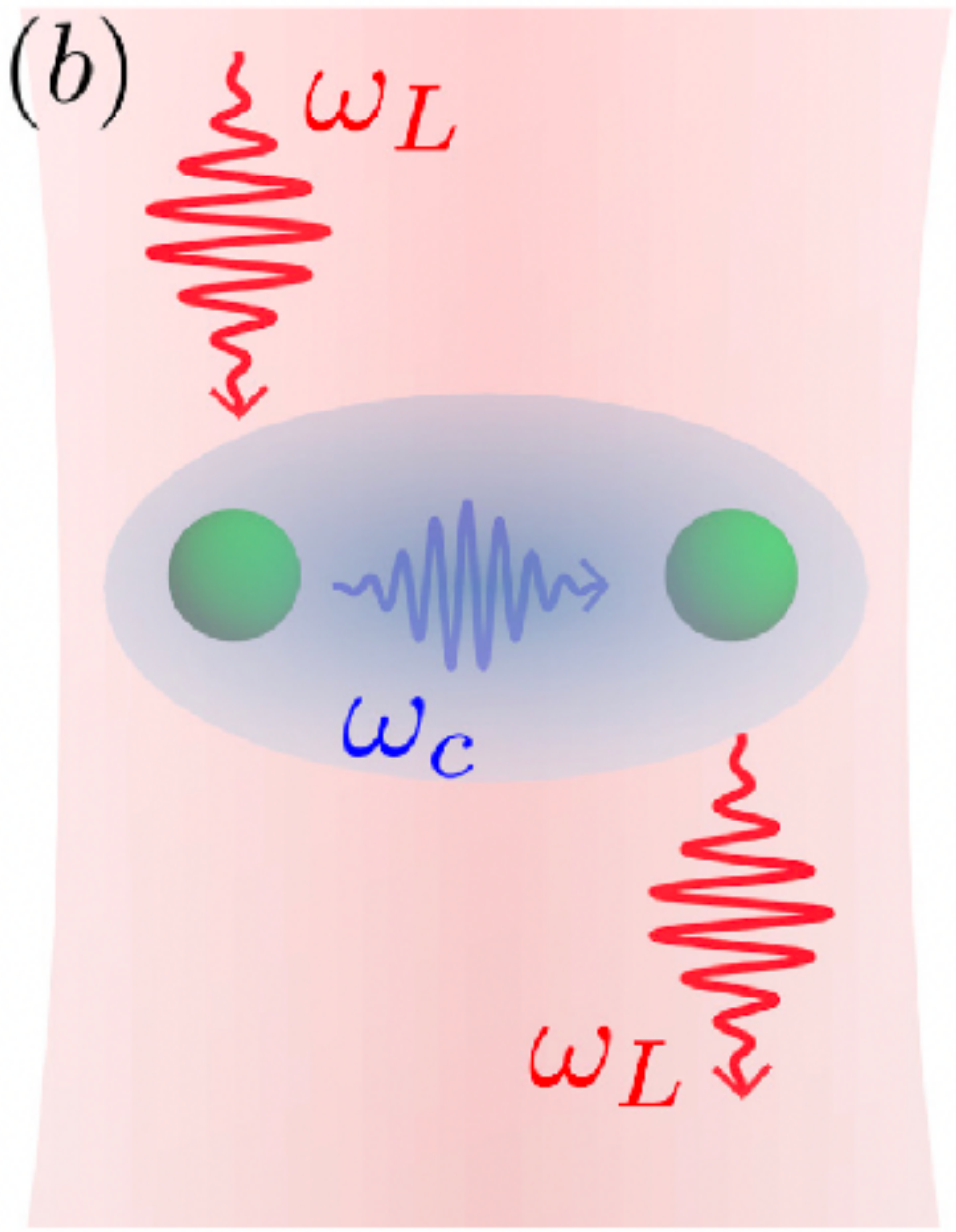
Tuning superconductivity inside a cavity

Use hybrid states
(phonon-polariton)

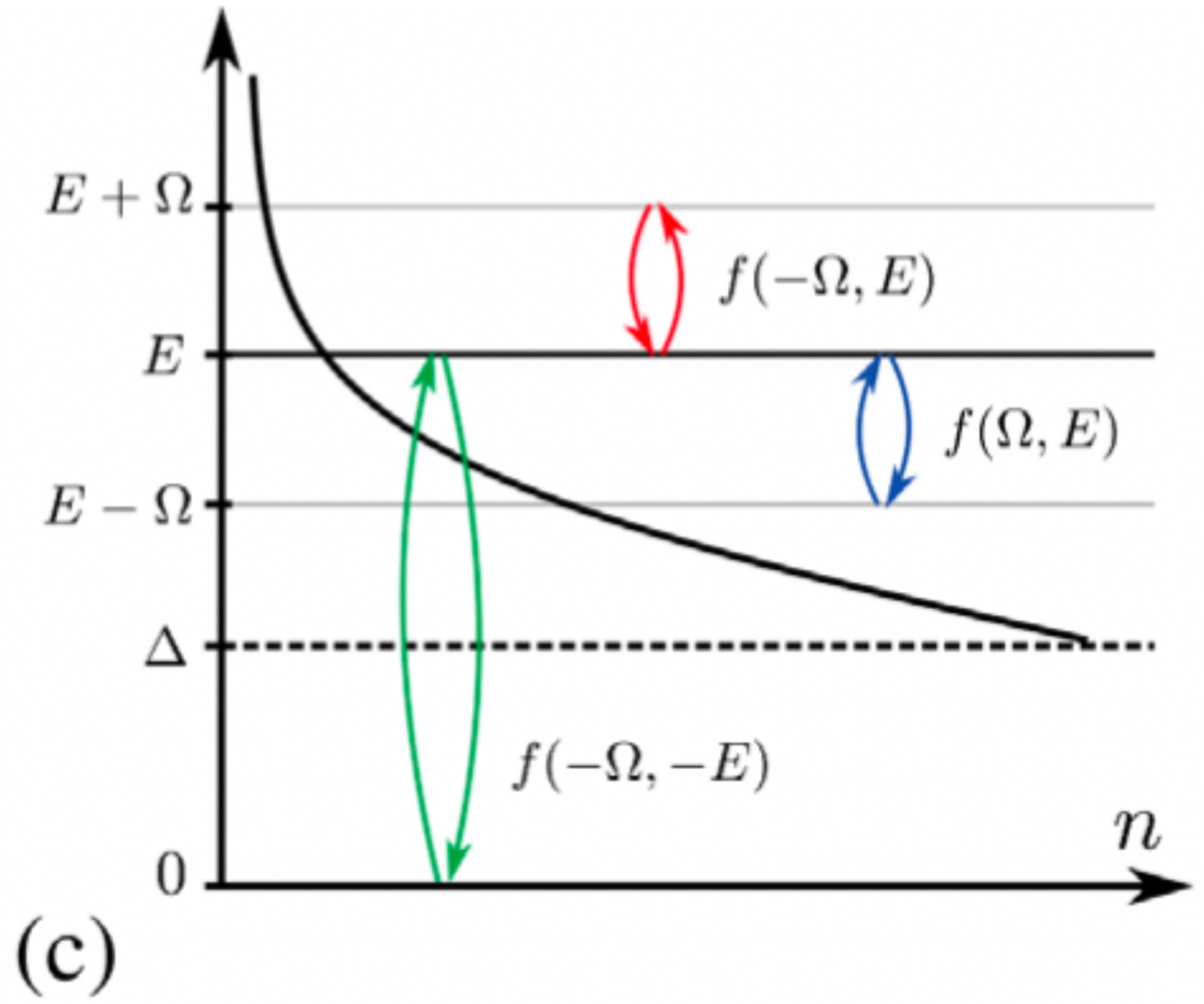


Cavity-photon
mediated interaction

"Amperean" pairing instability



Non equilibrium state
(quantum Eliashberg effect)



Sentef, M. A., Ruggenthaler, M. & Rubio, A., *Science Advances* **4**, eaau6969 (2018)

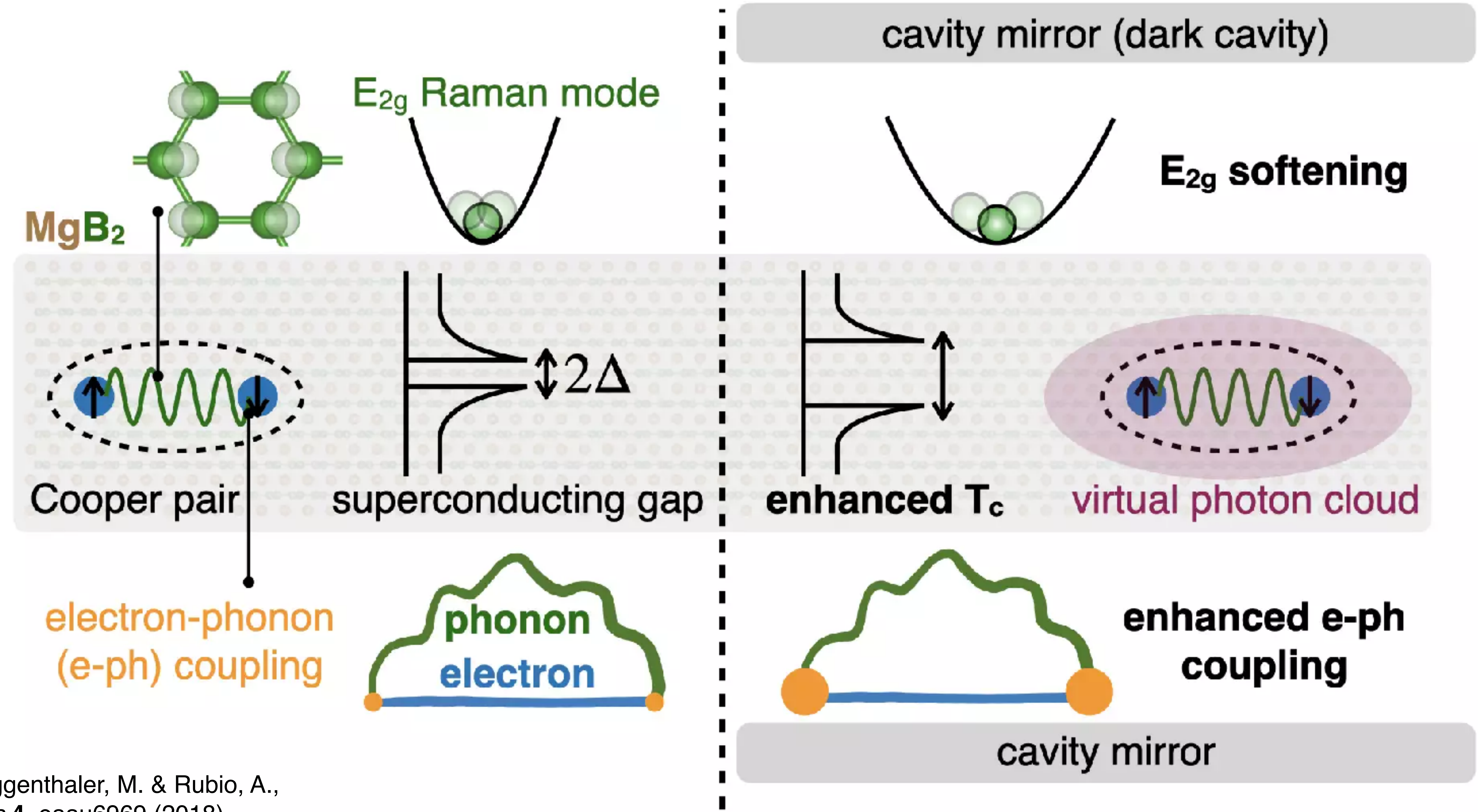
Schlawin, F., Cavalleri, A. & Jaksch, D. *Phys. Rev. Lett.* **122**, 133602 (2019)

Curtis, J. B., Raines, Z. M., Allocca, A. A., Hafezi, M. & Galitski, V. M. *Phys. Rev. Lett.* **122**, 167002 (2019)

How **cavity-modified ground states** change the superconductivity

Tuning superconductivity inside a cavity

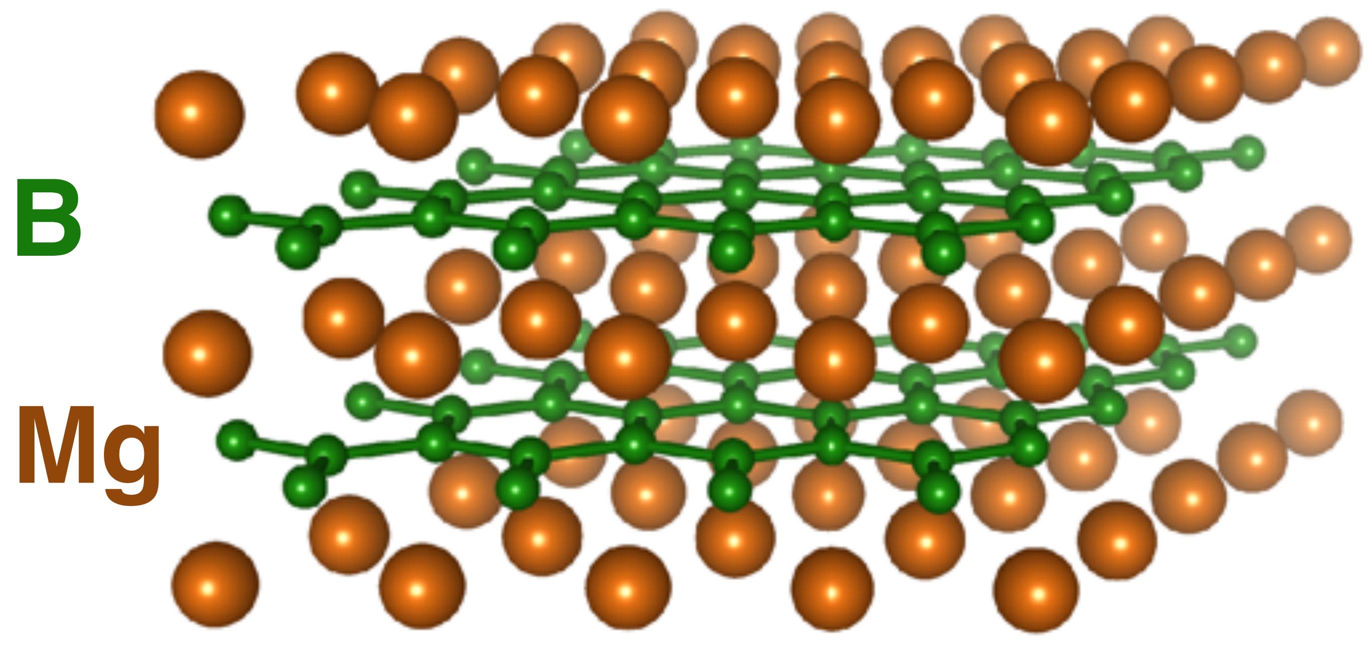
I-T. Lu, …, A. Rubio PNAS (2024)



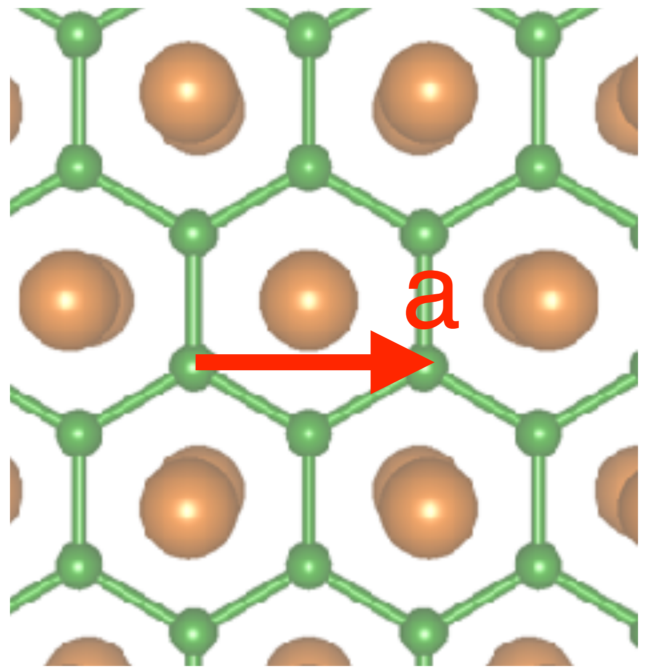
Sentef, M. A., Ruggenthaler, M. & Rubio, A., *Science Advances* **4**, eaau6969 (2018)

MgB_2 : Phonon-mediated superconductivity

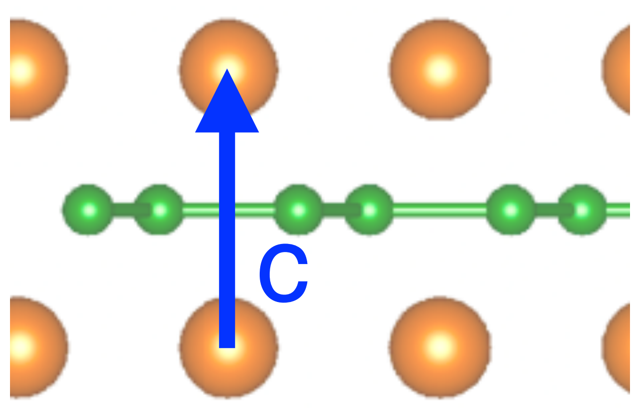
MgB_2 Hexagonal structure



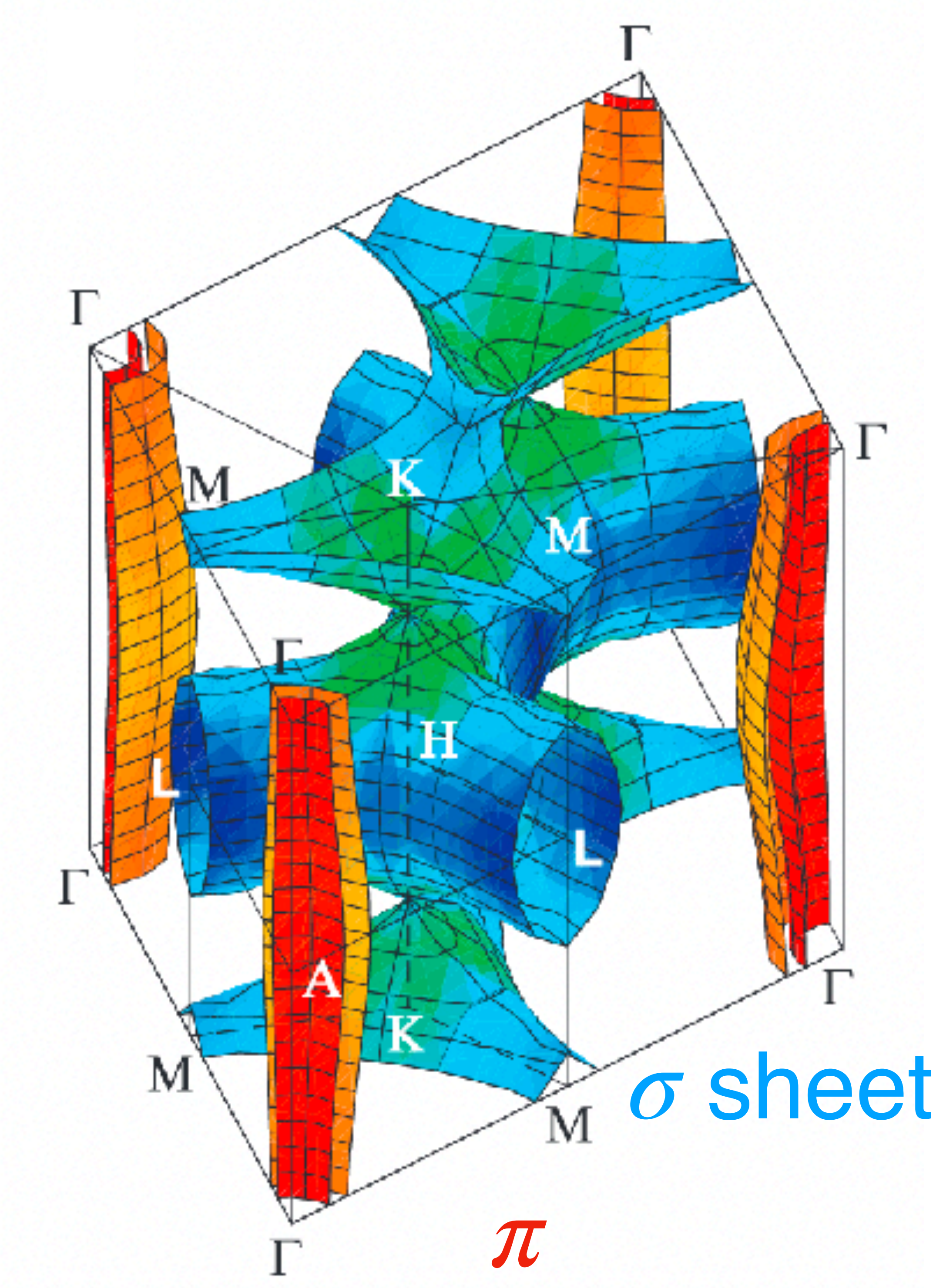
top view

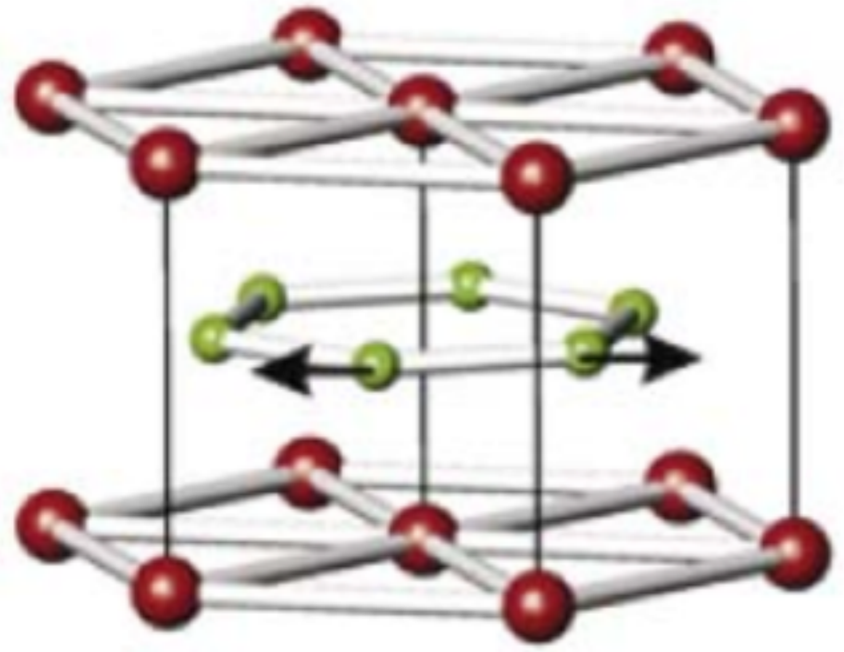


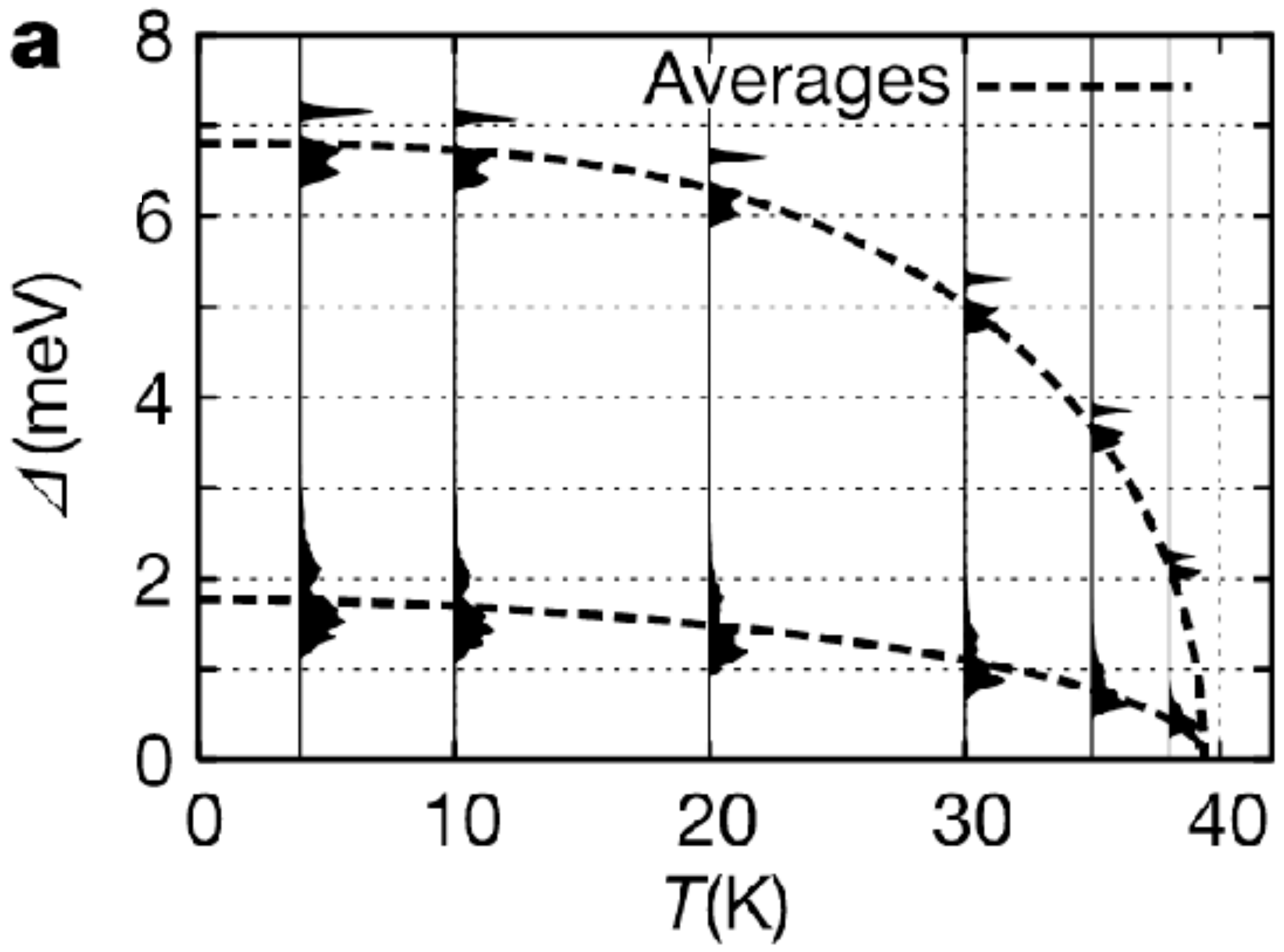
side view



$a = 3.084$ Å
$c = 3.523$ Å

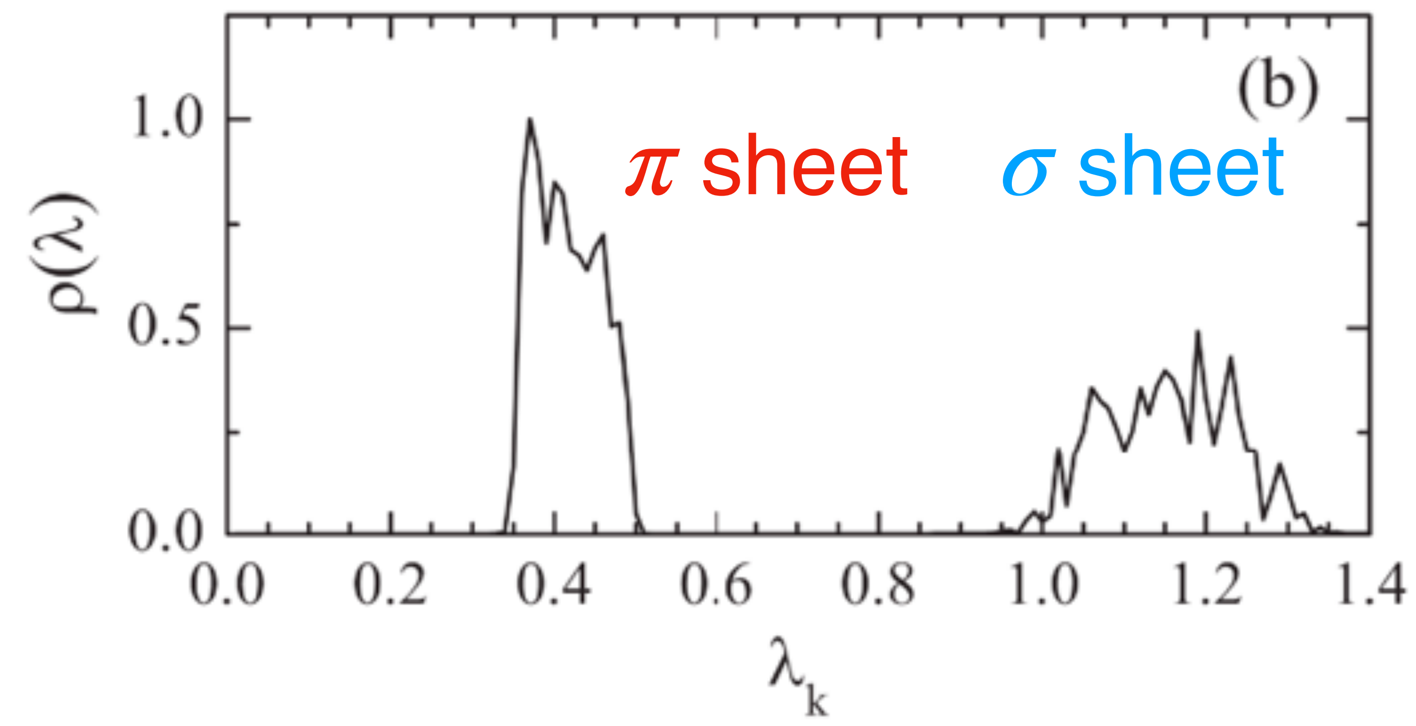






Choi, H. J., Roundy, D., Sun, H., Cohen, M. L. & Louie, S. G. *Nature* 418, 758–760 (2002)

Margine, E. R. & Giustino, F. *Phys. Rev. B* **87**, 024505 (2013)



Solve anisotropic Eliashberg equations to get superconducting gaps

QEDFT + DFPT provides all the ingredients to solve the anisotropic Eliashberg equations

Eliashberg Eqs. requires **e-ph coupling**, **electronic band structure**, and **phonon frequency** as inputs

$$Z(\mathbf{k}s, i\omega_n) = 1 + \frac{\pi k_B T}{\omega_n N(0)} \sum_{\mathbf{k}'s',n'} \frac{\omega_{n'}\delta(\epsilon_{\mathbf{k}'s'} - \epsilon_F)}{\sqrt{\omega_{n'}^2 + \Delta^2(\mathbf{k}'s', i\omega_{n'})}} \lambda(\mathbf{k}s, \mathbf{k}'s', n - n')$$

Mass renormalization function

e-ph matrix element

$$Z(\mathbf{k}s, i\omega_n)\, \Delta(\mathbf{k}s, i\omega_n) = \frac{\pi k_B T}{N(0)} \sum_{\mathbf{k}'s',n'} \frac{\Delta(\mathbf{k}'s', i\omega_{n'})\delta(\epsilon_{\mathbf{k}'s'} - \epsilon_F)}{\sqrt{\omega_{n'}^2 + \Delta^2(\mathbf{k}'s', i\omega_{n'})}} [\lambda(\mathbf{k}s, \mathbf{k}'s', n - n') - \mu^*]$$

Superconducting gaps

Coulomb screened parameter

T_c can be found when the **superconducting gaps vanish**, i.e., $\Delta(\mathbf{k}s, 0) = 0$

e-ph matrix element $$\lambda(n\mathbf{k}, m\mathbf{k}', l - l') = \int_0^\infty d\omega \frac{2\omega}{(\omega_l - \omega_{l'})^2 + \omega^2} \alpha^2 F(n\mathbf{k}, m\mathbf{k}', \omega)$$

Use isotropic Eliashberg function to peek into it superconductivity

Anisotropic Eliashberg function

$$F(n\mathbf{k}, m\mathbf{k}', \omega) = N_F \sum_{\nu} |g^{SE}_{mn,\nu}(\mathbf{k},\mathbf{q})|^2 \delta(\omega - \omega_{\nu,\mathbf{q}=\mathbf{k}-\mathbf{k}'})$$

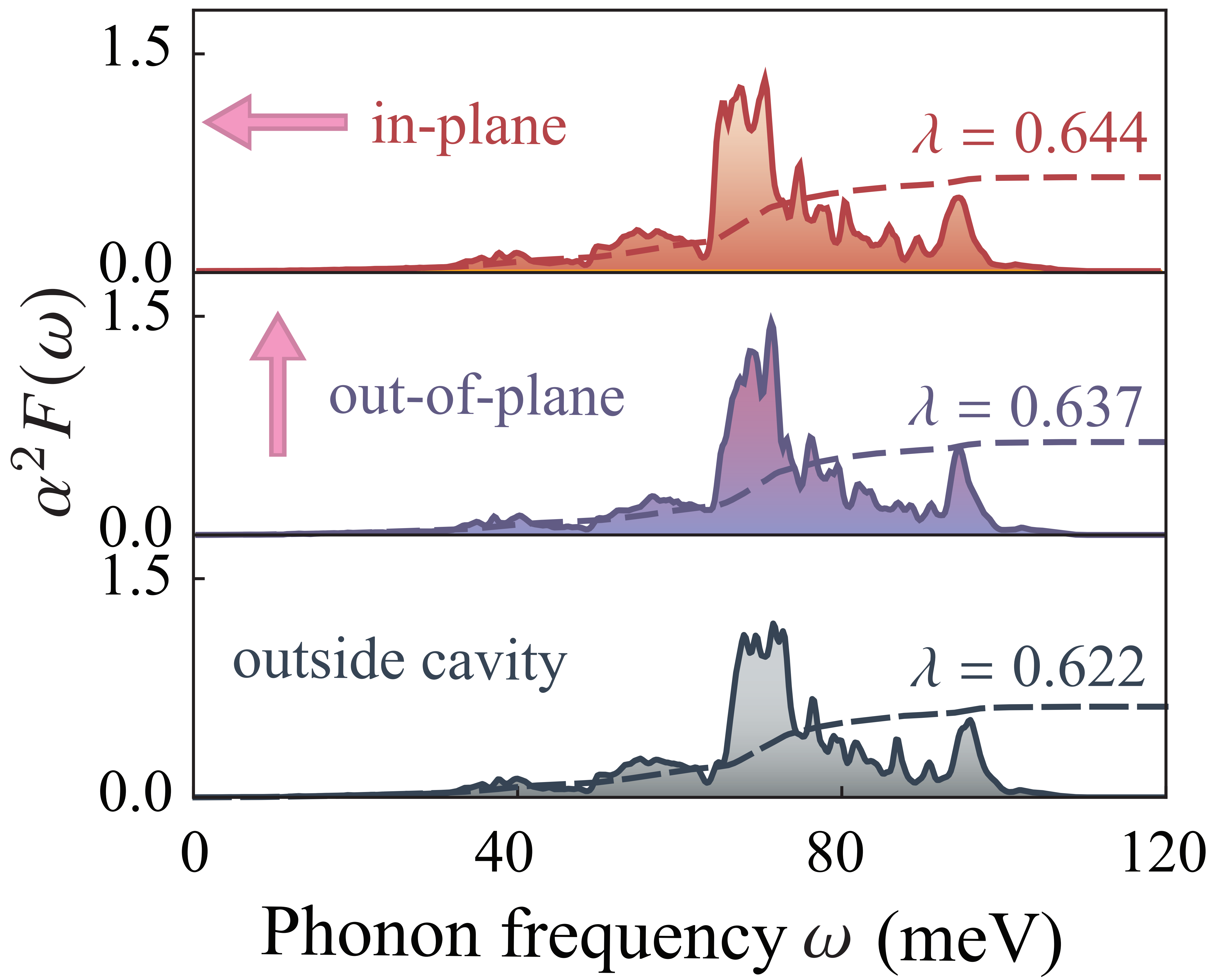
where $g^{SE}_{mn,\nu}(\mathbf{k},\mathbf{q}) = \left(2\omega_{\nu\mathbf{q}}\right)^{-1/2} g_{mn,\nu}(\mathbf{k},\mathbf{q})$

Isotropic Eliashberg function

$$\alpha^2 F(\omega) = \sum_{n\mathbf{k}, m\mathbf{k}'} W_{n\mathbf{k}} W_{m\mathbf{k}'} \alpha^2 F(n\mathbf{k}, m\mathbf{k}', \omega)$$

where $W_{n\mathbf{k}} = \delta(\epsilon_{n\mathbf{k}})/N_F$ $\quad N_F$: density of states at Fermi energy

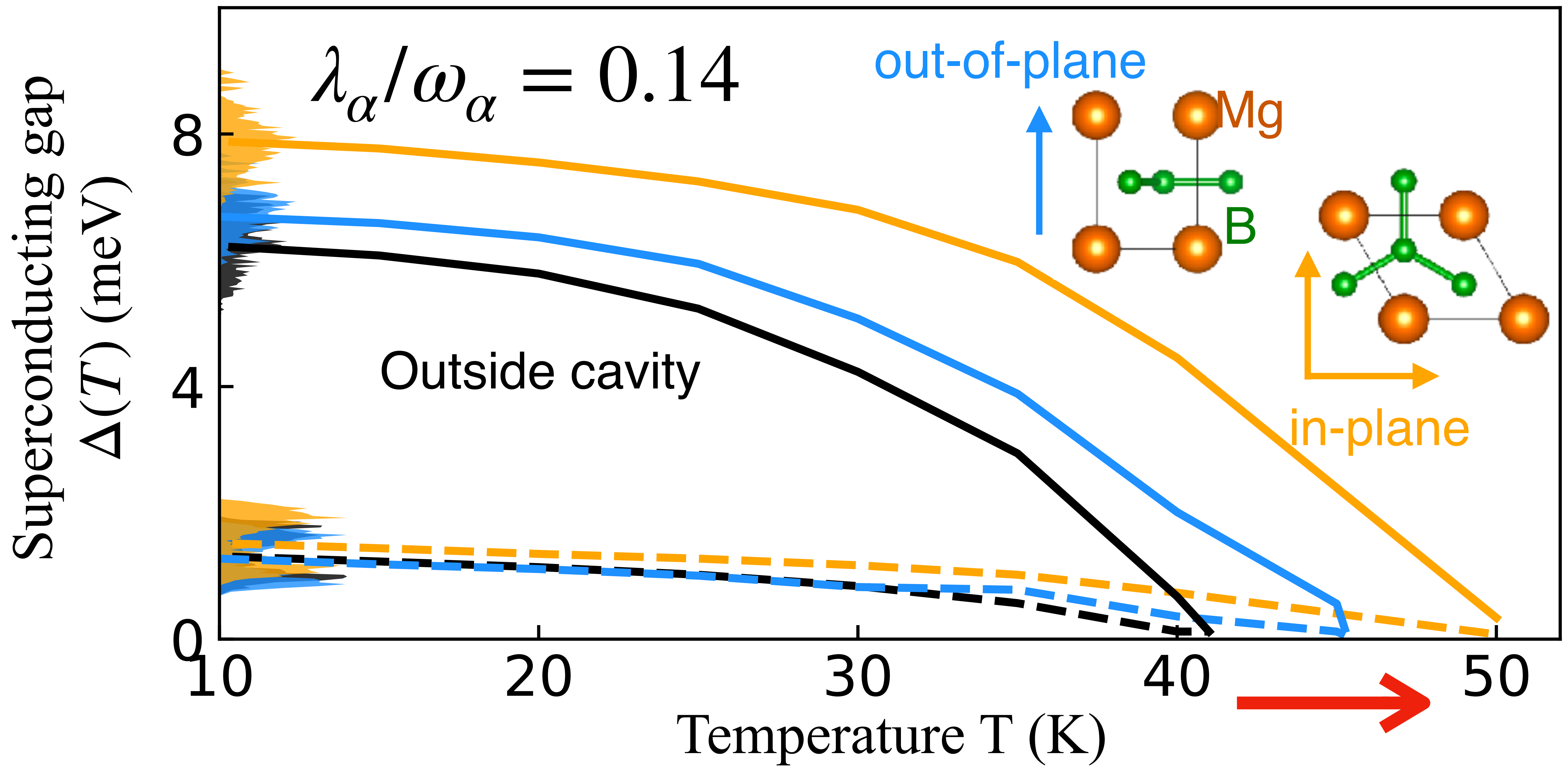
Total electron-phonon coupling strength $\quad \lambda(\omega) = 2\int_0^{\omega} d\omega' \frac{\alpha^2 F(\omega')}{\omega'}$



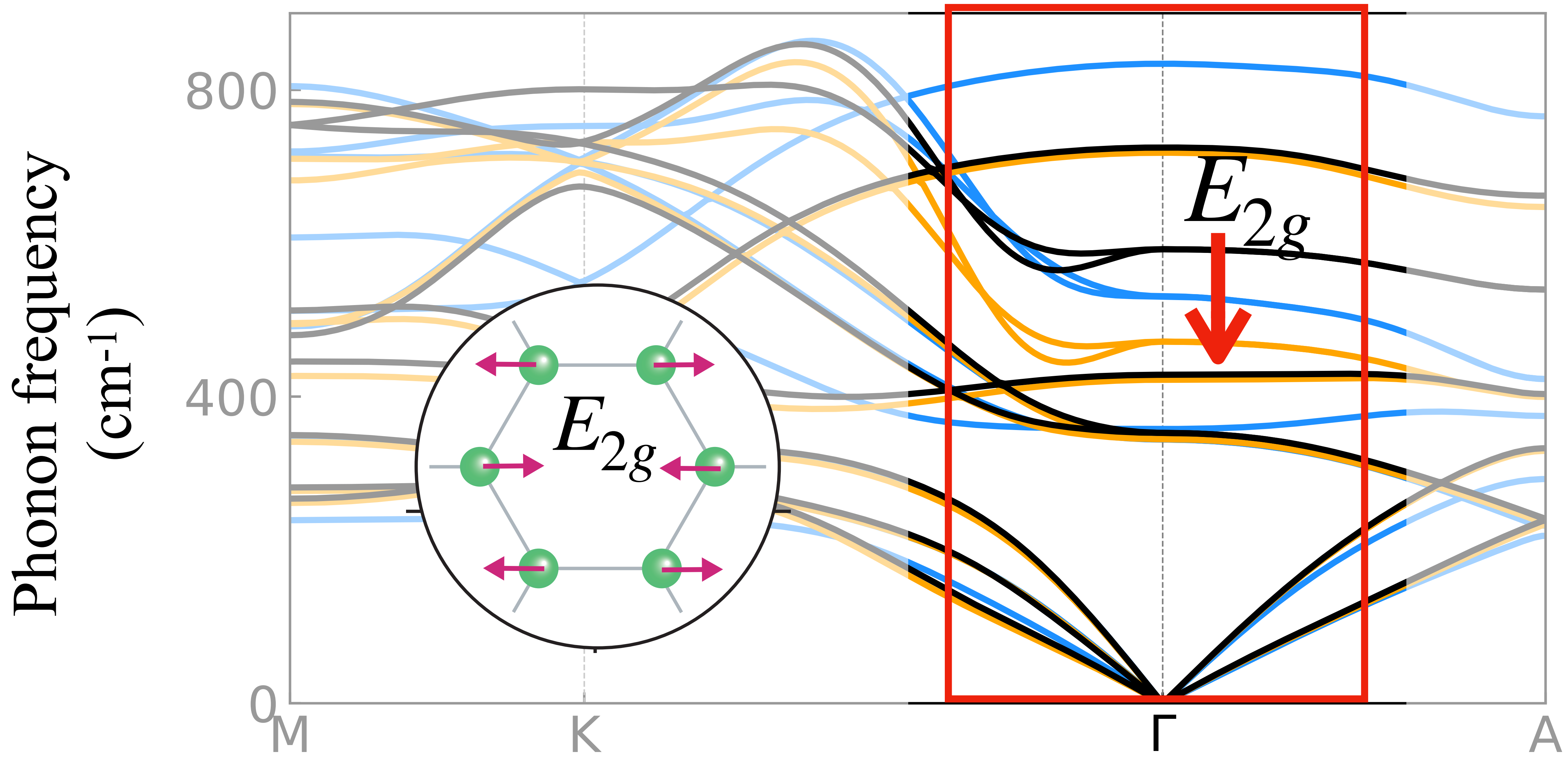
Cavity engineered phonon-mediated superconductors

Bulk MgB_2

$\Delta(T)$ from **anisotropic Eliashberg** eq.



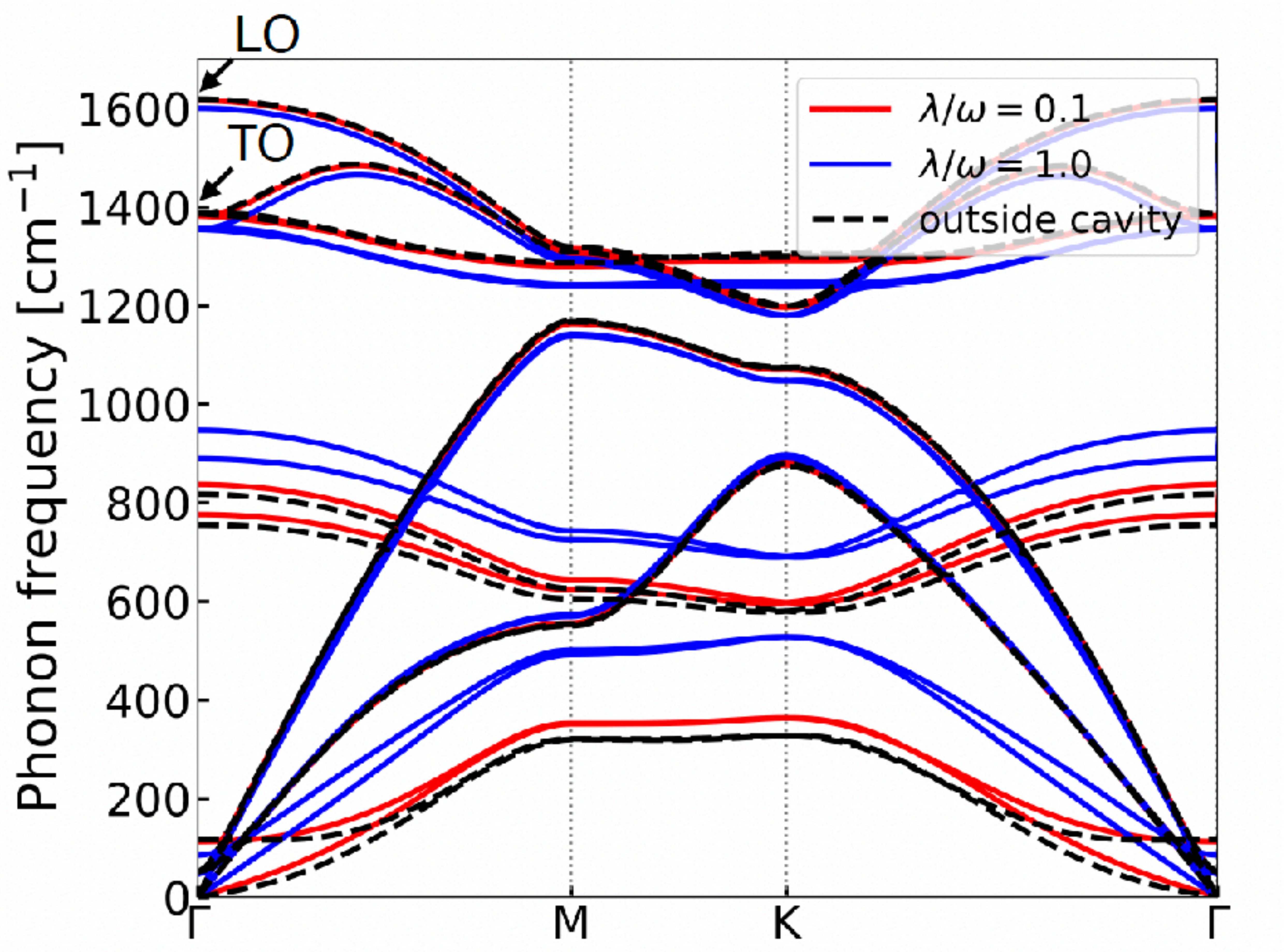
Due to the **softened** E_{2g} mode

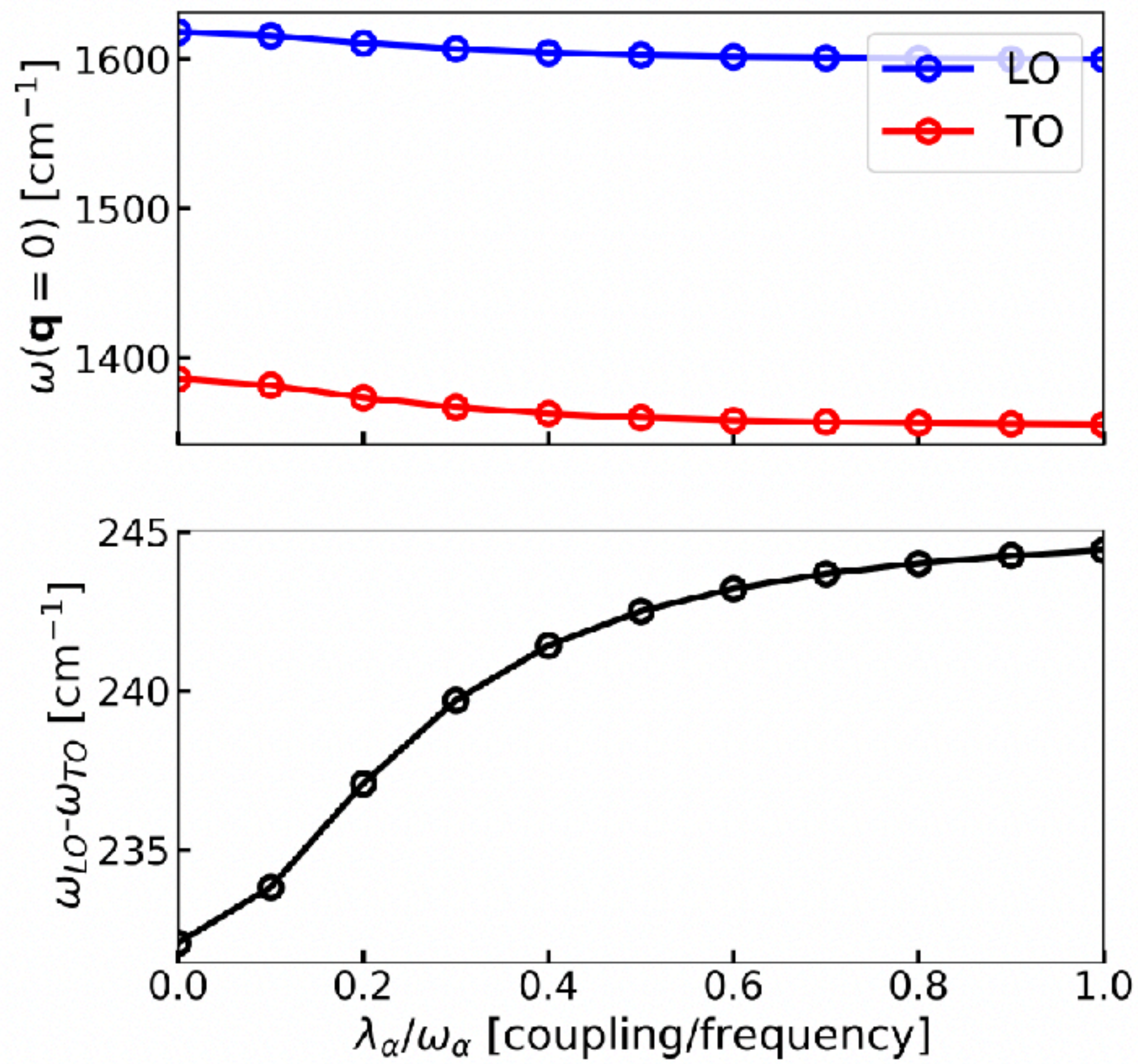


I-T. Lu, …, A. Rubio, arXiv:2404.08122 (2024), PNAS (2024)

Cavity engineered phonon-band structure: Born effective Charges

LO-TO splitting of bulk hBN is enhanced inside a cavity

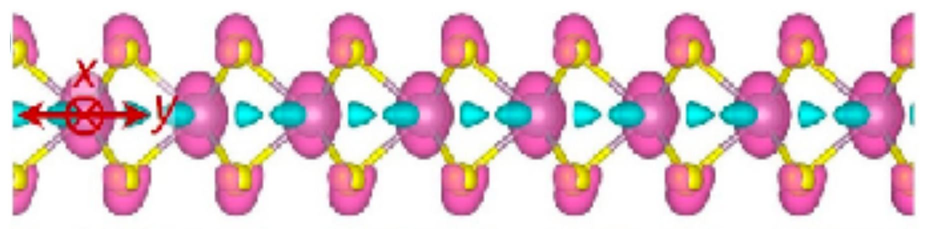




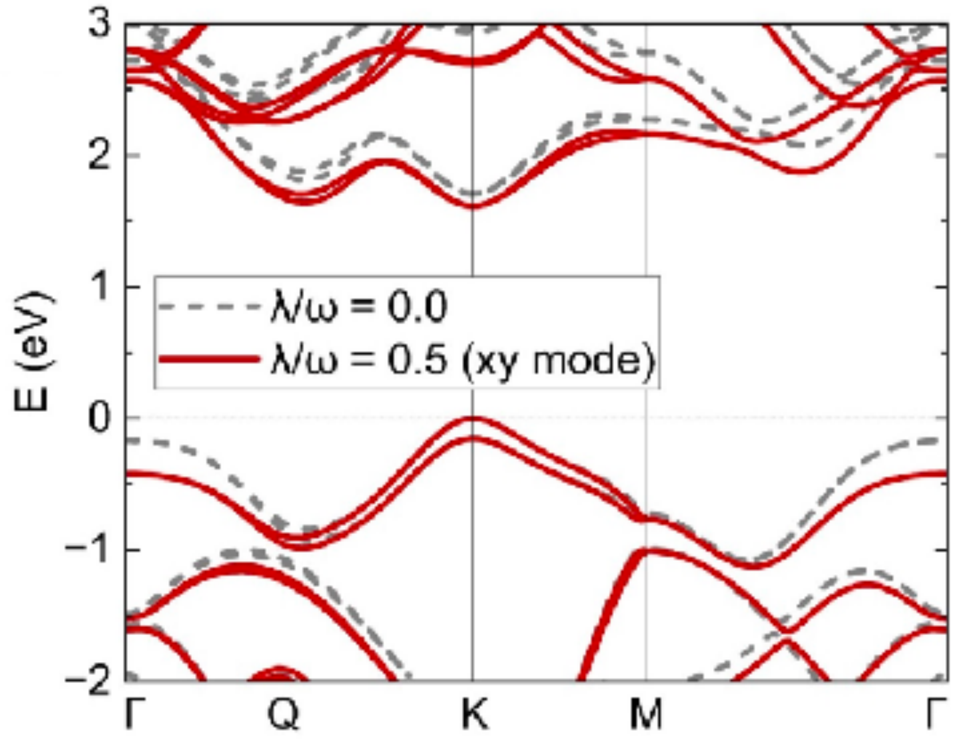
Using cavity to engineer other materials properties

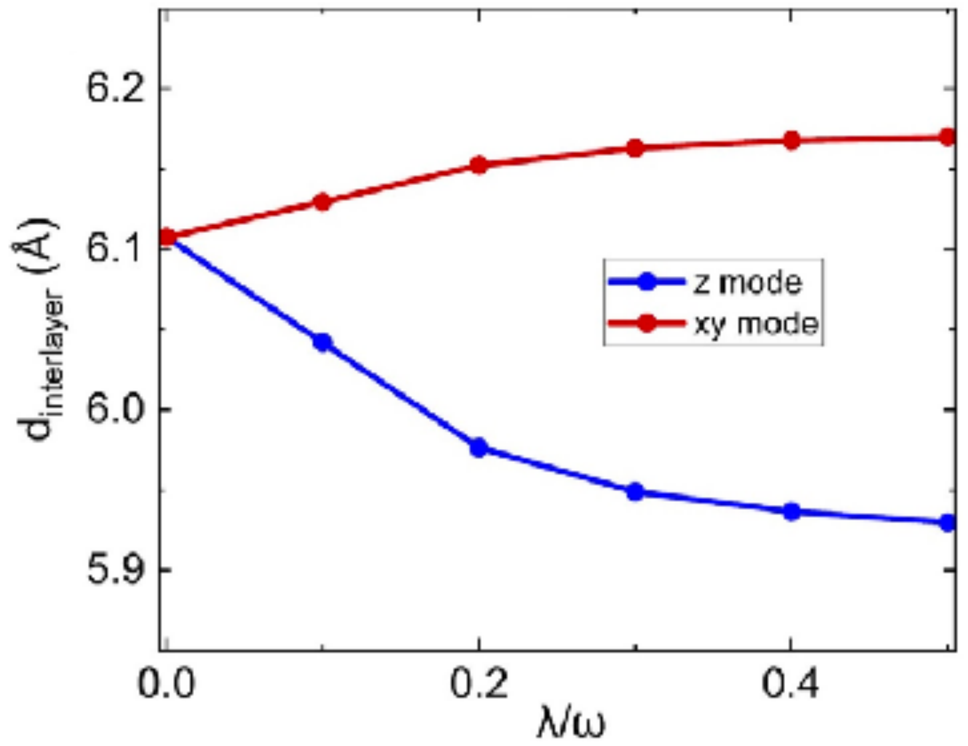
- Cavity-modified 2D van der Waals

Monolayer 2H-MoS_2

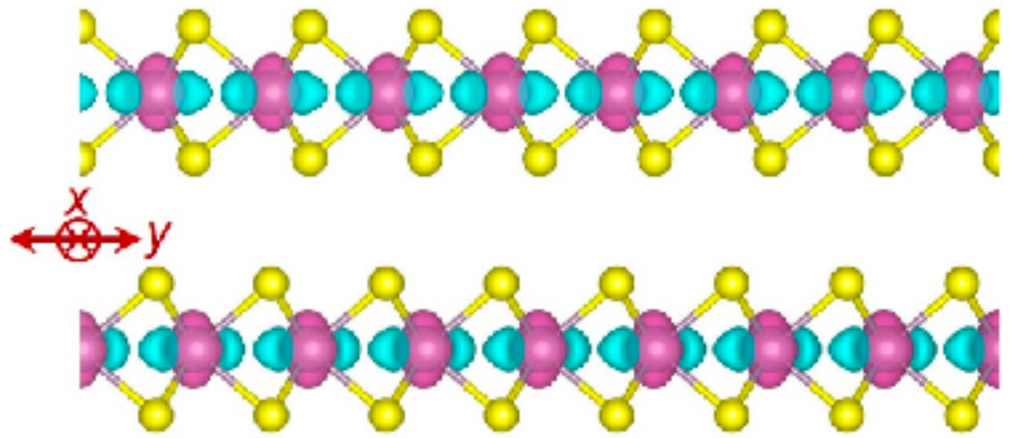


direct to indirect E_g





Bilayer 2H-MoS_2

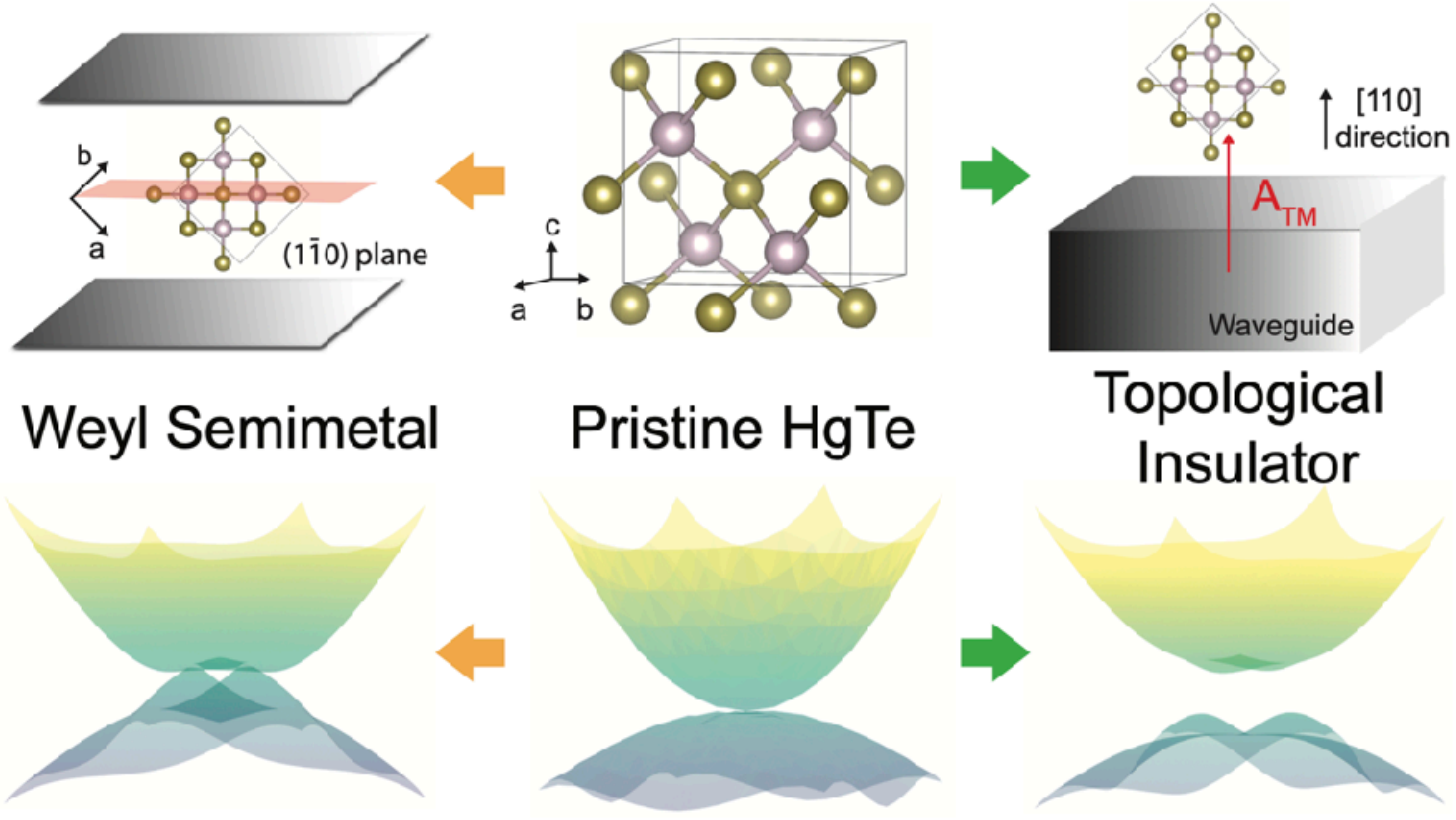


Tune interlayer distance

H. Liu et al., Opt. Mater. Express 15(9), 2105 (2025)

- Cavity-modified topological properties

Break symmetry using photon modes



D. Shin et al., arXiv:2506.23494 (2025)

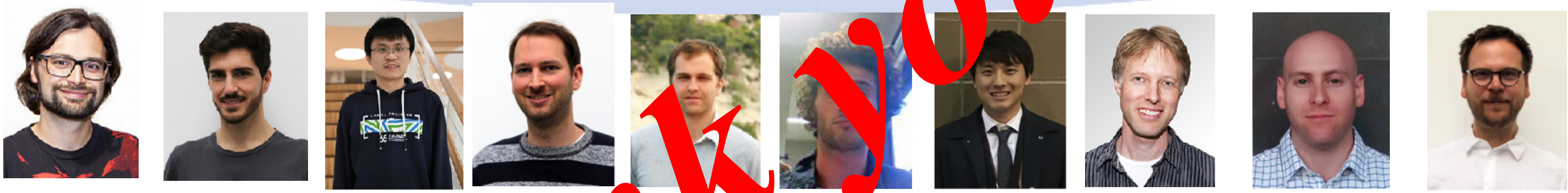
Short summary

New field of Cavity and Floquet materials engineering:
Interdisciplinary field connecting materials science, chemistry and quantum optics
grounded on tailoring
quantum fluctuations, light matter coupling and electron/ phonon correlations

QEDFT: Rigorous first principles: Pauli-Fierz Hamiltonian

New phases of matter: **quantum polaritonic matter**

Thank you!



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