From Quantum Motion of Electrons to Multi-scale Behavior of Solids

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QM100 Conference, ICTS
January 14, 2024

Funded by the Dept of Science and Technology, GoI

Part I: Introduction (general audience)
Part II: Power and Success of Quantum Methods: Materials
Part III: New Experimental Spectroscopy from Quantum Geometry

UNESCO International Year of Quantum Science & Technology (IYQ)

Mission: "… help raise public awareness of the importance and impact of quantum science and applications on all aspects of life."

Health & Wellbeing

Quantum photonics is advancing medical imaging and diagnosis.

Quantum chemistry is supporting the development of new vaccines and drugs.

Reduced Inequalities

Open science and gender equity in education and research will ensure that **quantum solutions** are accessible to all.

Industry & Infrastructure

Quantum science is essential for developing new materials that drive technological innovation.

Economic Growth

Quantum science and technologies are integral to many industries; future economic and financial infrastructures will be secured by **quantum information**.

Climate Action

Quantum physics will inform next-generation sensors for environmental monitoring; quantum computers will improve the accuracy of long-term climate models.

Clean Energy

Quantum engineering is leading to more energy efficient and affordable solar cells and low emission LED light sources.

Materials

https://quantum2025.org/about/

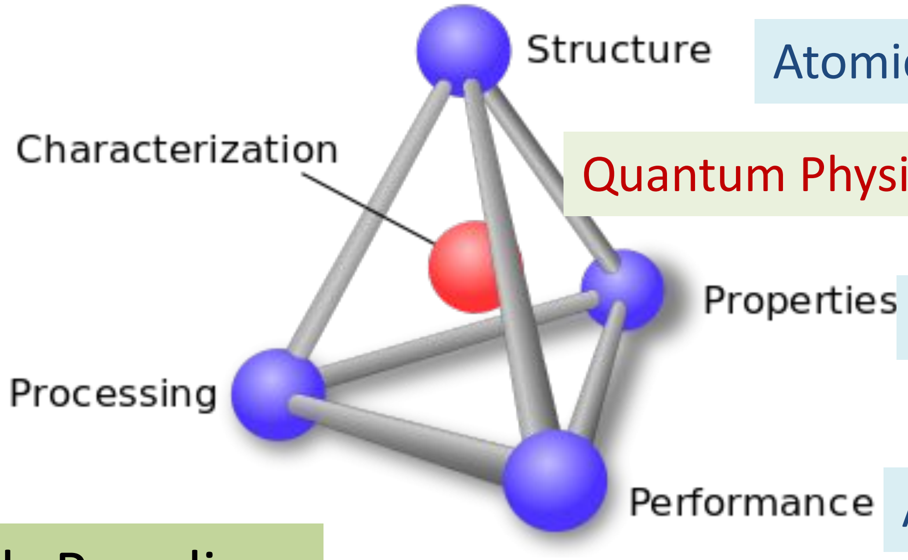
Materials Science

How the history of a material (its *processing*) influences its structure, and thus the material's properties and performance.

Experiment +Theory

Atomic-nano-micro-macro

Quantum Physics



Interaction with fields

Kinetics

Applications

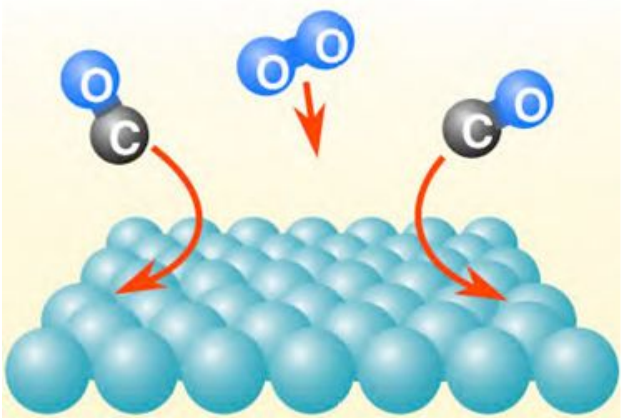
Materials Paradigm

https://en.wikipedia.org/wiki/Materials_science

Truly exciting, interdisciplinary science that affects society

First-principles Theory

How atoms interact with each other via electrons?



First-principles Theoretical Approach:

Total Energy Function

Chemistry: Z_I: *Atomic numbers* of atoms in a given material

Structure: R_I: *Atomic positions* of atoms in a given material

Quantum Mechanics   Electrostatic Energy

$$E_{tot}(Z_I, R_I) = E_G^{el}(Z_I, R_I) + E_{Coulomb}^{ion}(Z_I, R_I)$$

Minimum energy quantum state of electrons: *Density Functional Theory [**DFT**], W Kohn et al* (1964)

$E[n(\vec{r})]$

Kohn: Nobel (Chem) 1998

- Inter-atomic interaction *T=0K*
- Hamiltonian of a collection of atoms

Stat Mech →

Free Energy
$T > 0\,K$

First-principles Quantum Simulations

Marvin Cohen: "*Standard Model*" of materials

Total energy: Interatomic Interactions

What do we obtain?

Minimization of E_{tot}

3 levels of structure

Geometric, Dynamical and Electronic

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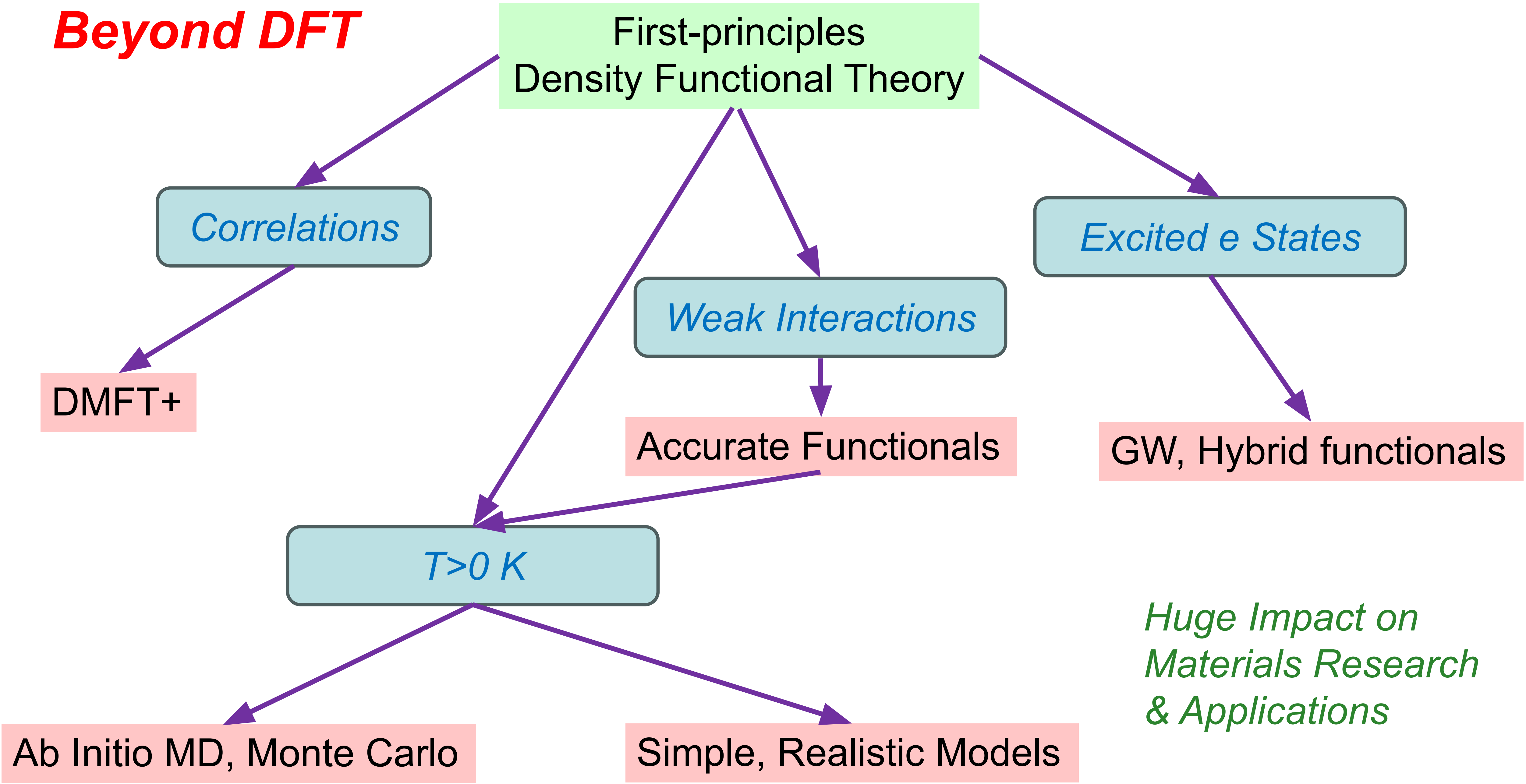
Properties of a material:

Derivatives of total energy!

Beyond DFT



Huge Impact on Materials Research & Applications

Current Societal Challenges:
Energy and Environment

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"… help raise public awareness of the importance and impact of quantum science and applications on all aspects of life."

https://quantum2025.org/about/

Clean Energy

- Diminishing fossil fuels and global warming have prompted the need and use of
- **Renewable energy**: solar, wind, tidal, and geothermal en

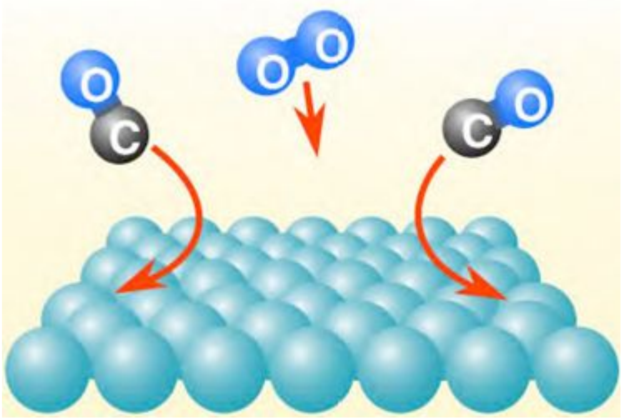
ue b

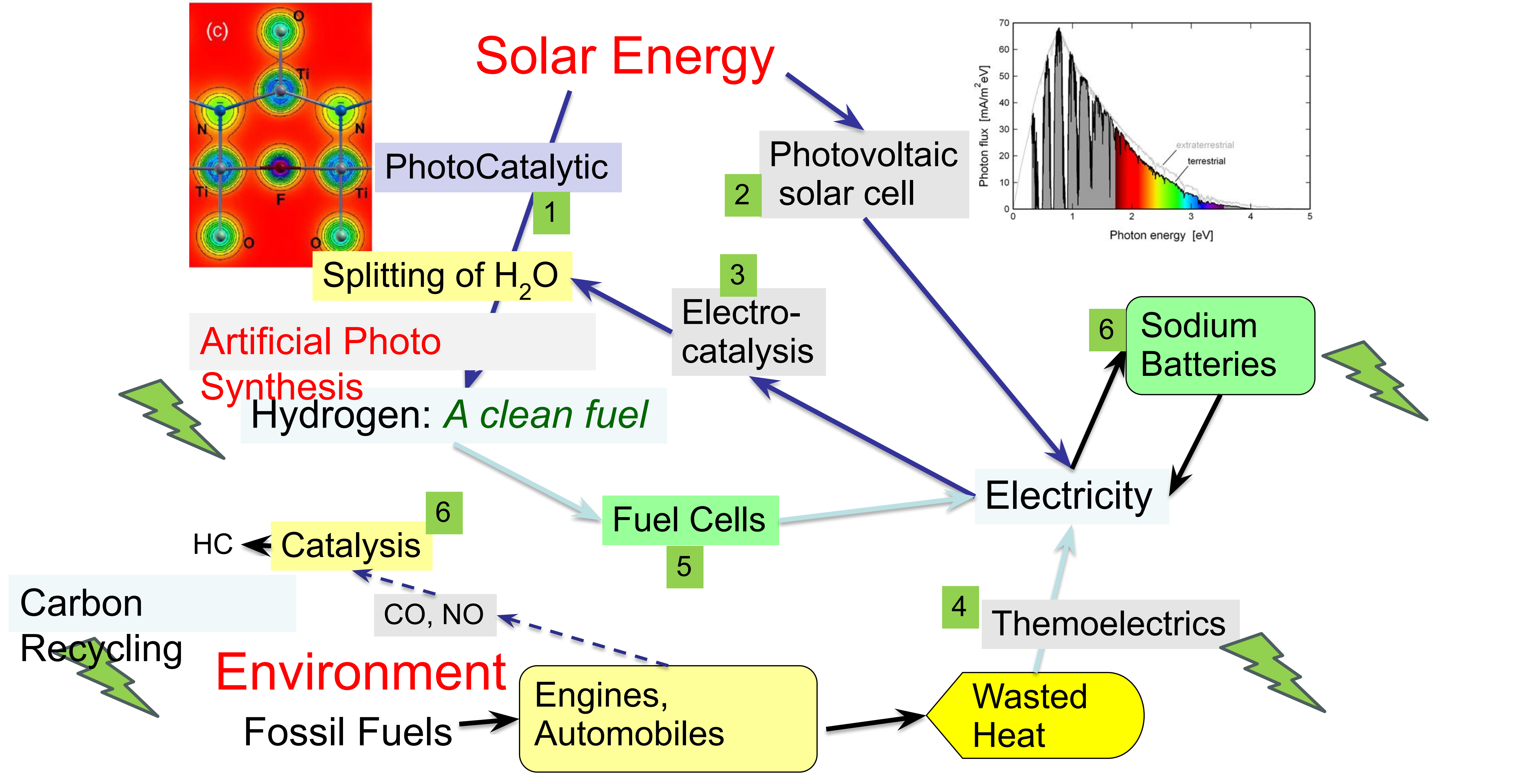
mgsenergy.com

www.hydrogencarsnow.com

First-principles DFT based Simulations

How atoms interact with each other via electrons?





Materials are key to the technologies to address the current challenges of E & E: ***DFT***

First-principles Simulations

Phase Transitions, why?

Ferroelectric Functional Properties: *Structural Instability*

$BaTiO_3$, $PbTiO_3$

Ferroelectric Structural Transition

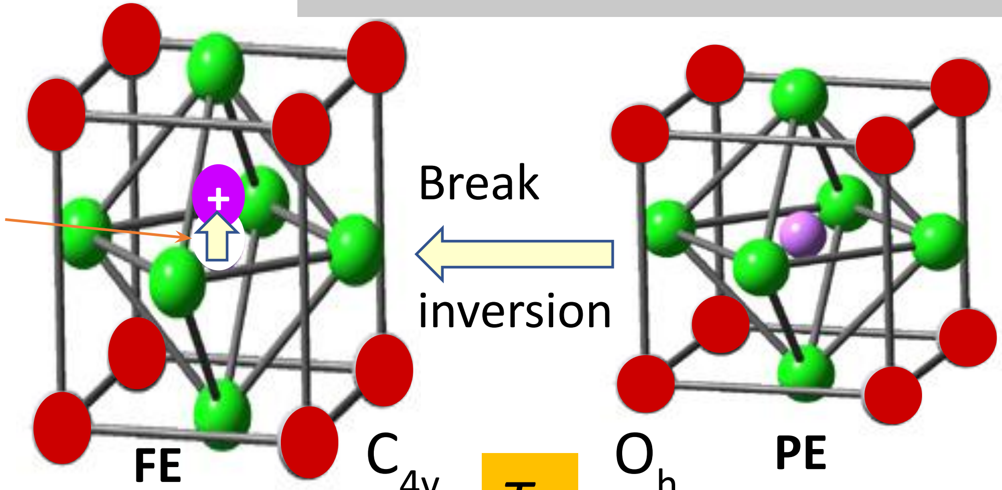
Ba, Pb

Ti^{4+}

O^{2-}

Electric Dipole *p*

Strain *c/a*



Break inversion

Centrosymmetric

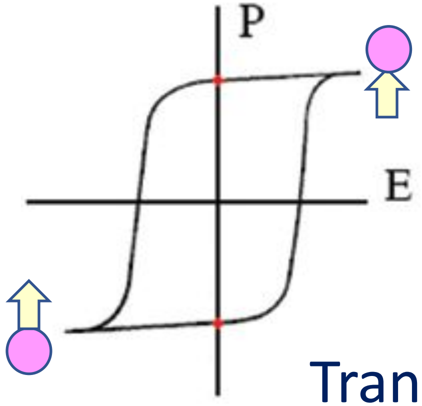
C_{4v} T_o O_h *T*

New Functional Properties ($T<T_o$):

Applications

Linear Piezoelectric → Sensors, Actuators, MEMS, Speakers, Heart-beat monitors,...

Nonlinear Hysteresis → Memory



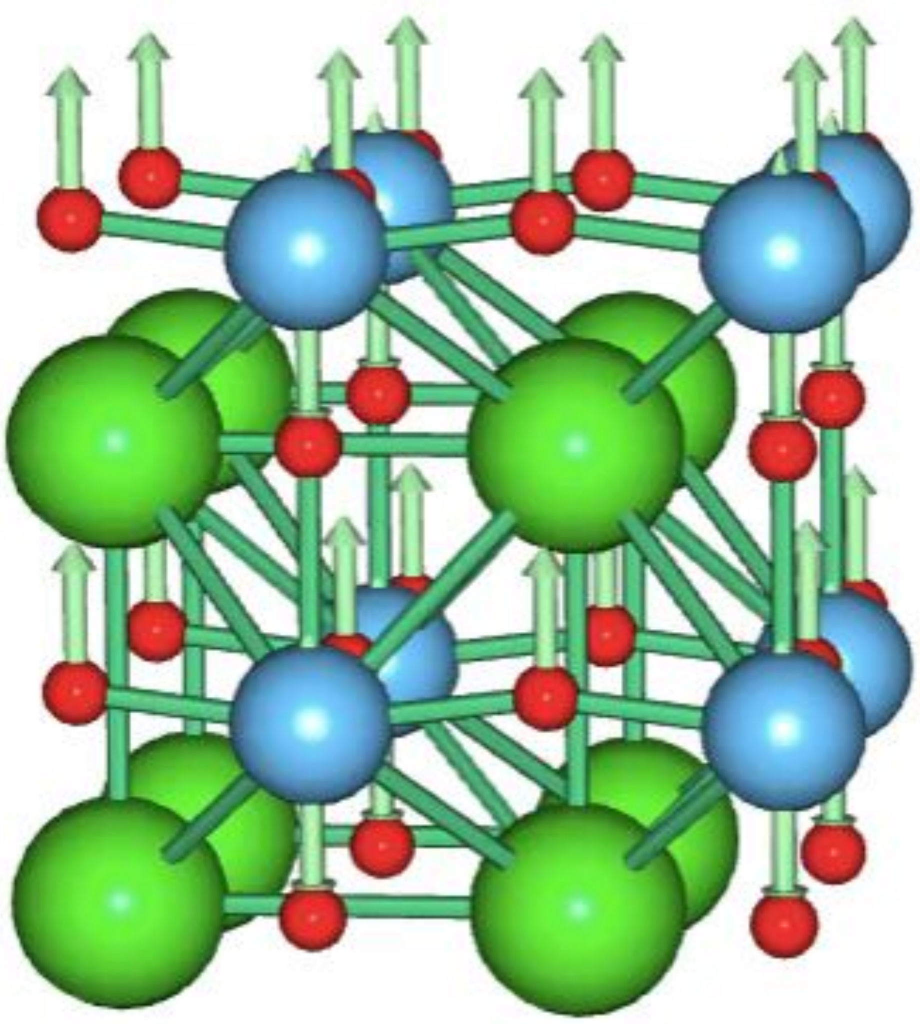
Near the Transition:

- Colossal piezo, dielectric properties
- Instability of Ti off-centering important!

Physics of Ferroelectrics, Rabe, Ahn and Triscone, Springer Nature (2007)

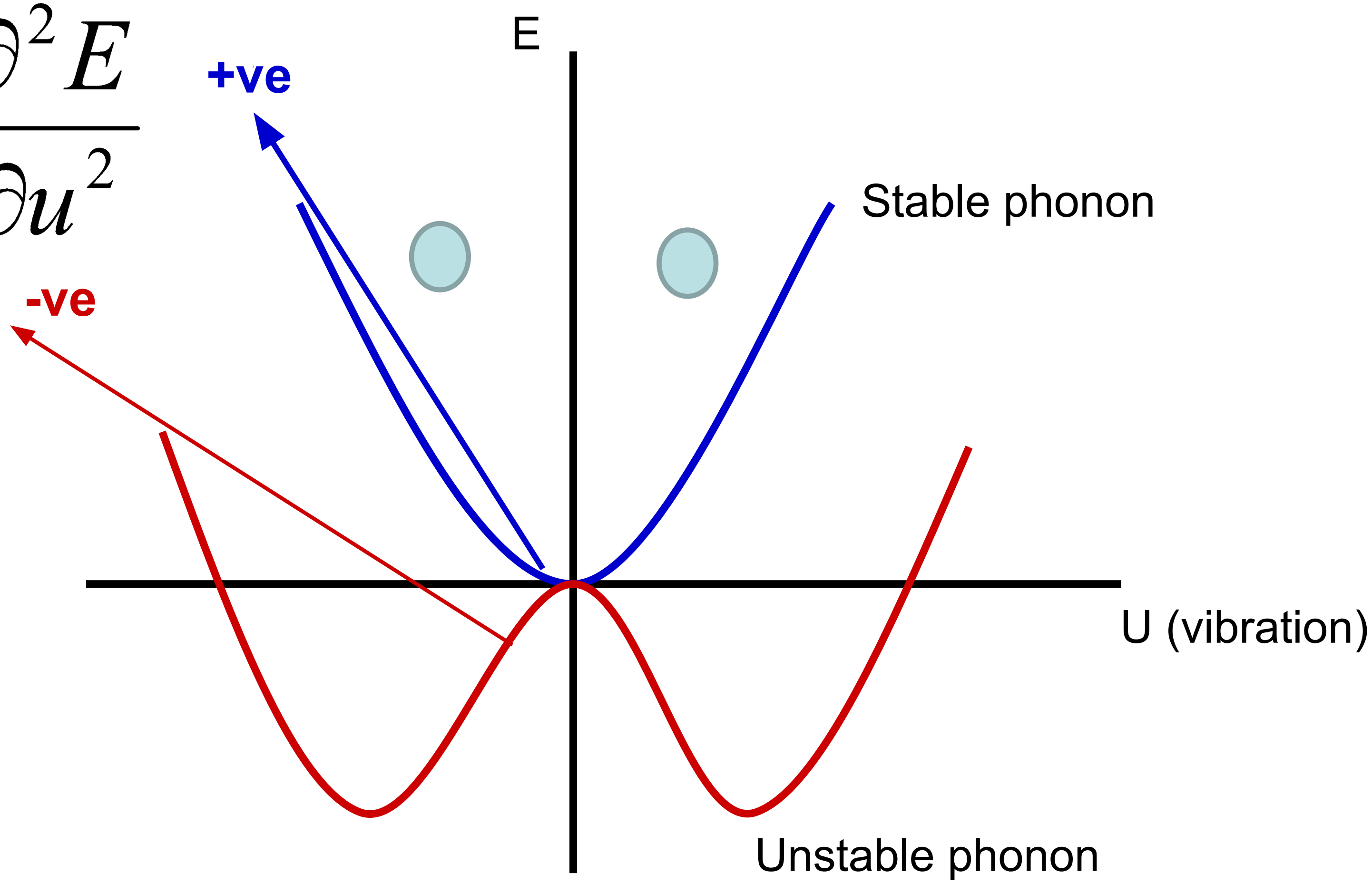
Transitions govern the properties relevant to applications

Vibration (Phonon)
Associated with
Ferroelectric Instability:
$BaTiO_3$



Crystal Structure Instability: *Link with vibrations or phonon*!

$$\omega^2 \propto \frac{\partial^2 E}{\partial u^2}$$



E.g. **Instability** → T-dependent structural transition

First-principles quantum theory

Scientific Challenges in Theory of Structural Transitions

Need *first-principles* density functional theory:
Mixed bonding, materials-specific properties

1. *Small* differences in *large* energies of high & low *T* structures:
   e.g. 0.01 eV in *O*(1000) eV

2. Temperature dependent phase transition:
   Simple quasi-harmonic approximation invalid

   Strong anharmonicity (nonlinear phonon-phonon or phonon spin interactions)
   Needs *Molecular Dynamics (MD) or Monte Carlo (MC)*

3. Phase Transition (occurs strictly in $L \to \infty$ limit):
   MD & MC with *large* system sizes (N_a > 10,000) !

Ab Initio MD or MC are computationally too expensive!

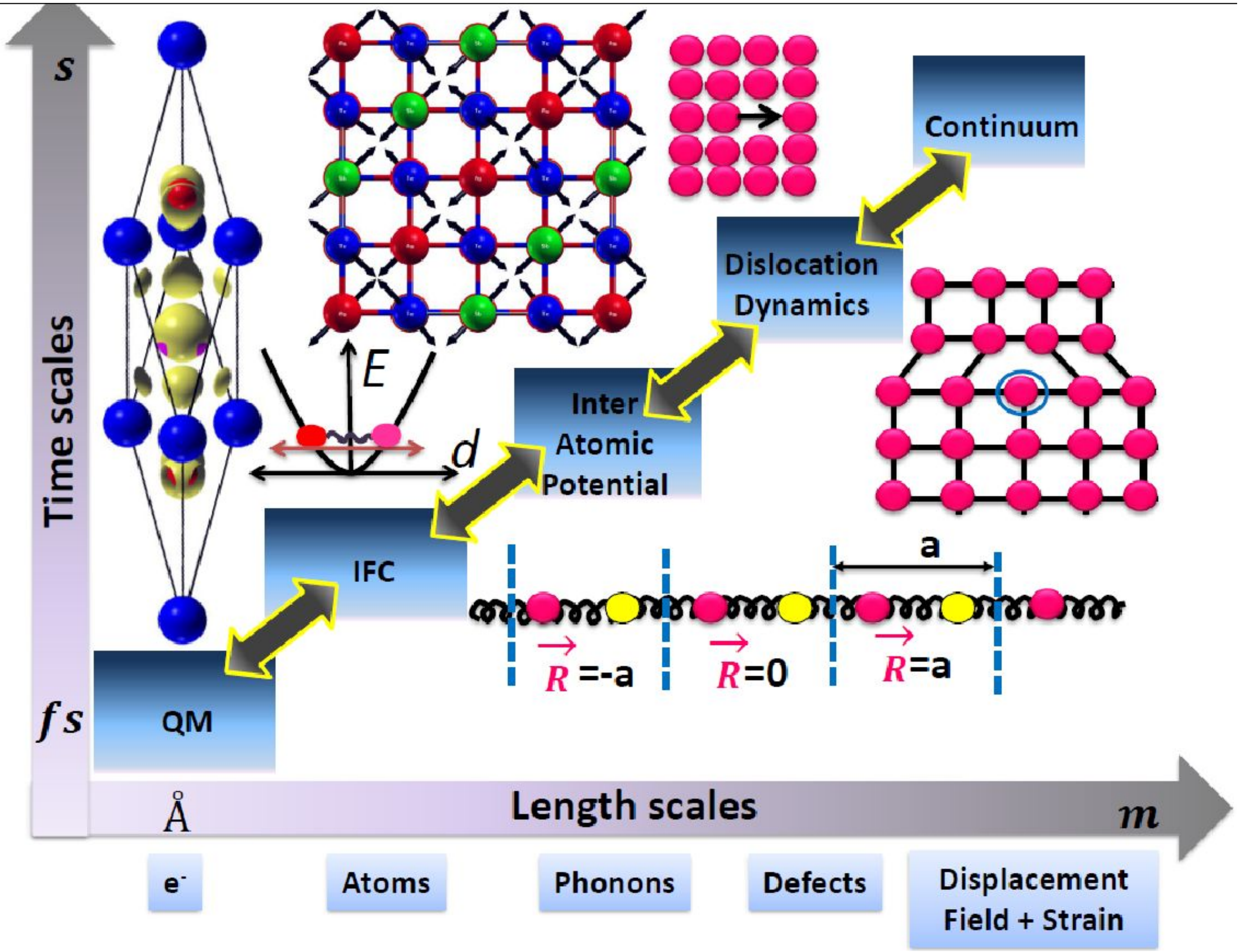
Challenges of First-principles Quantum Simulations

Computationally Expensive

CPU time: $O(N^3)$

Memory: $O(N^2)$

Material behavior: a *multi-scale* problem



→ Need multi-scale *modeling* strategy to bridge scales!

Multi-scale Modeling

First-principles DFT: Energy, Complete space of phonons — 1-2 nm

↓ *Coarse-graining in t domain*

Integrate out high energy phonons
$\omega > \omega_c \sim 40$ meV, $\tau < 0.1$ ps

A subset of phonons: *Model Hamiltonian*

↓ 10-20 nm

MD → Phase Transitions, Phase Diagrams

↓ *Coarse-graining in r domain*

1. Constrained P: *Polostat*
2. Thermodynamic Integration

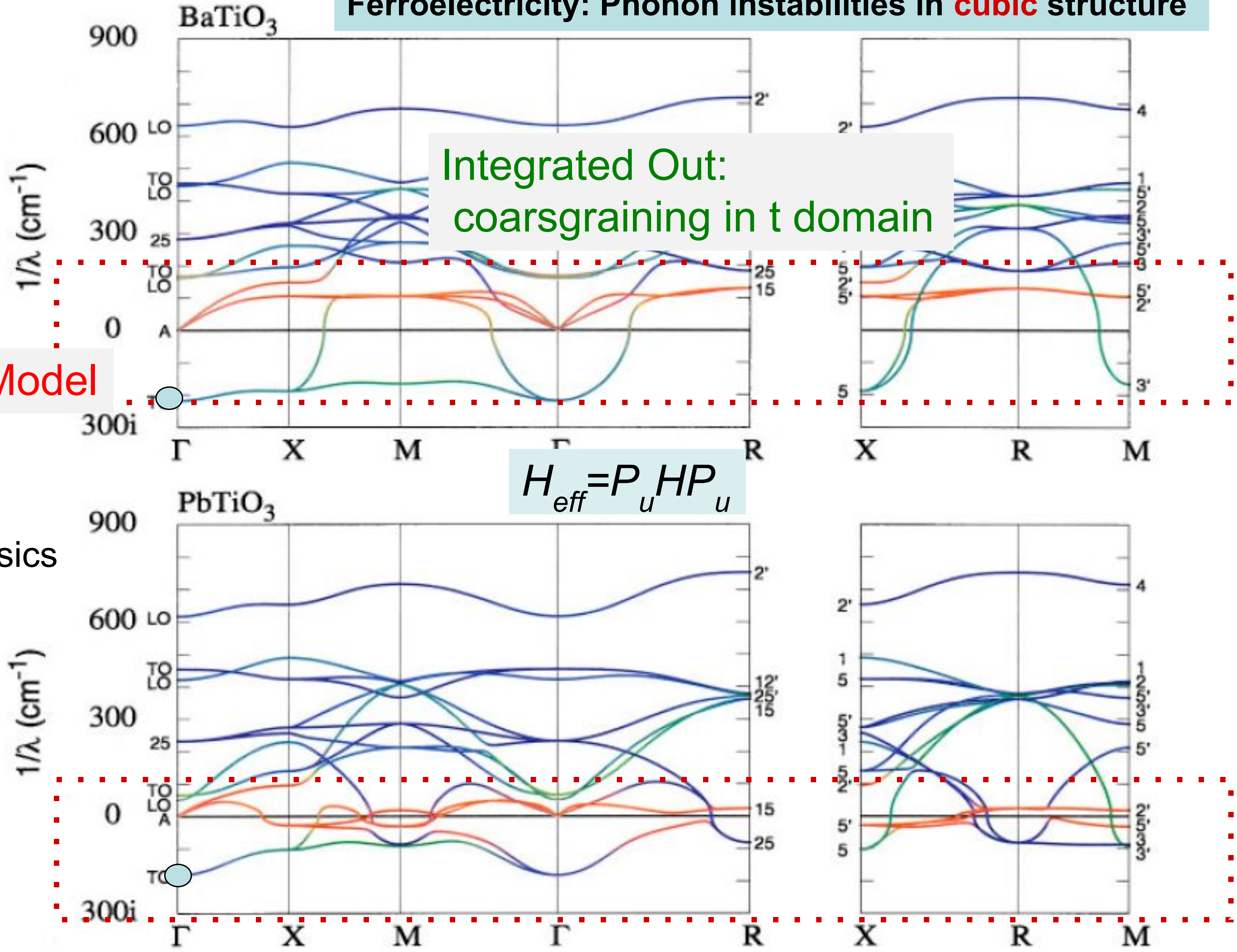
Landau-Ginzburg Free Energy Functional

↓ >100 nm

Fundamental Understanding of Phase Transitions, Simulations of Devices

U V Waghmare, Acc. Chem. Res. 47, 322 (2014)

Ferroelectricity: Phonon instabilities in cubic structure



Integrated Out:
coarsgraining in t domain

Model

$H_{eff}=P_u H P_u$

Ferroelectricity

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Low Energy Physics

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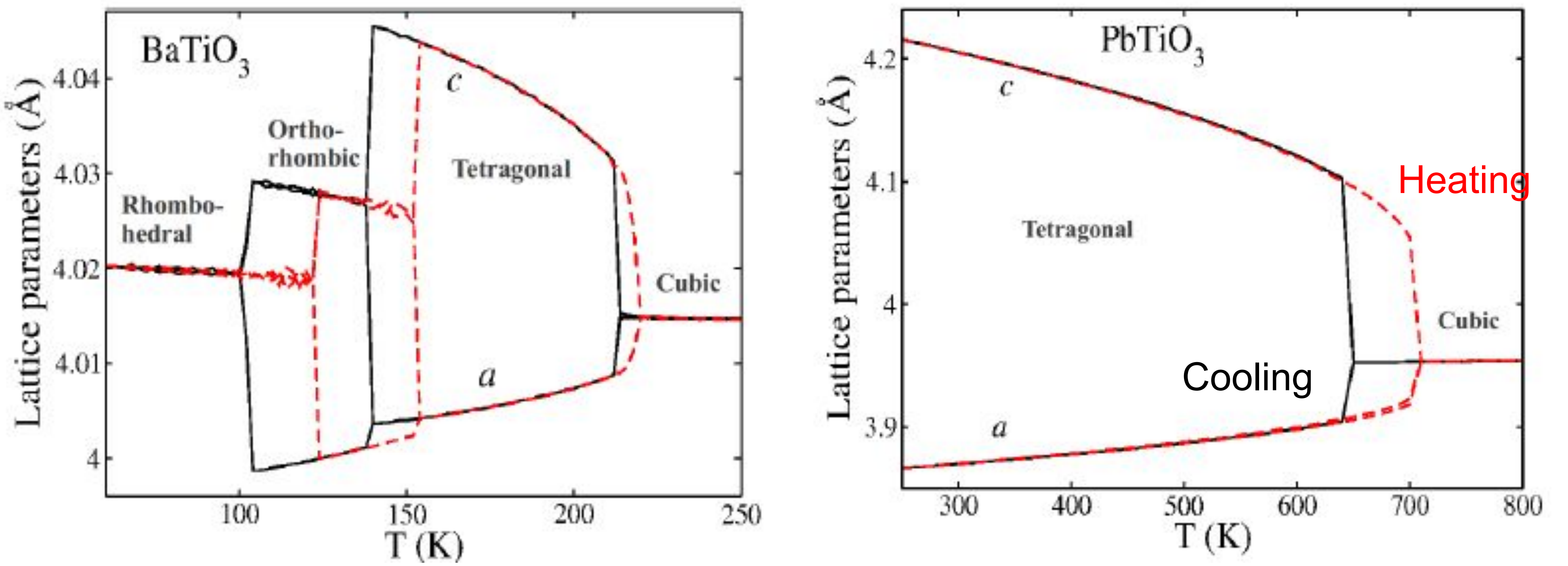
Lattice Instabilities

Structural Phase Transitions from SCAN meta-GGA

Earlier flavors of DFT (e.g. LDA): notable underestimates of T_c's



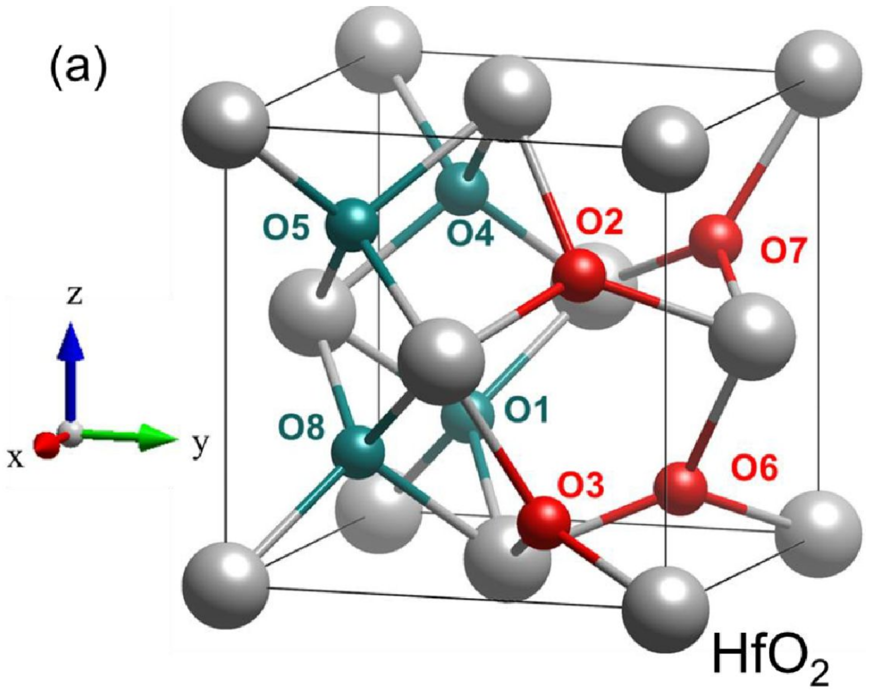
Material-specific Phase Transitions
Reasonably accurate T_c's

The errors in models obtained with coarse-graining →10 % errors in T_c

A. Paul. J Sun, J P Perdew and U V Waghmare, Phys Rev B 95, 054111 (2017).

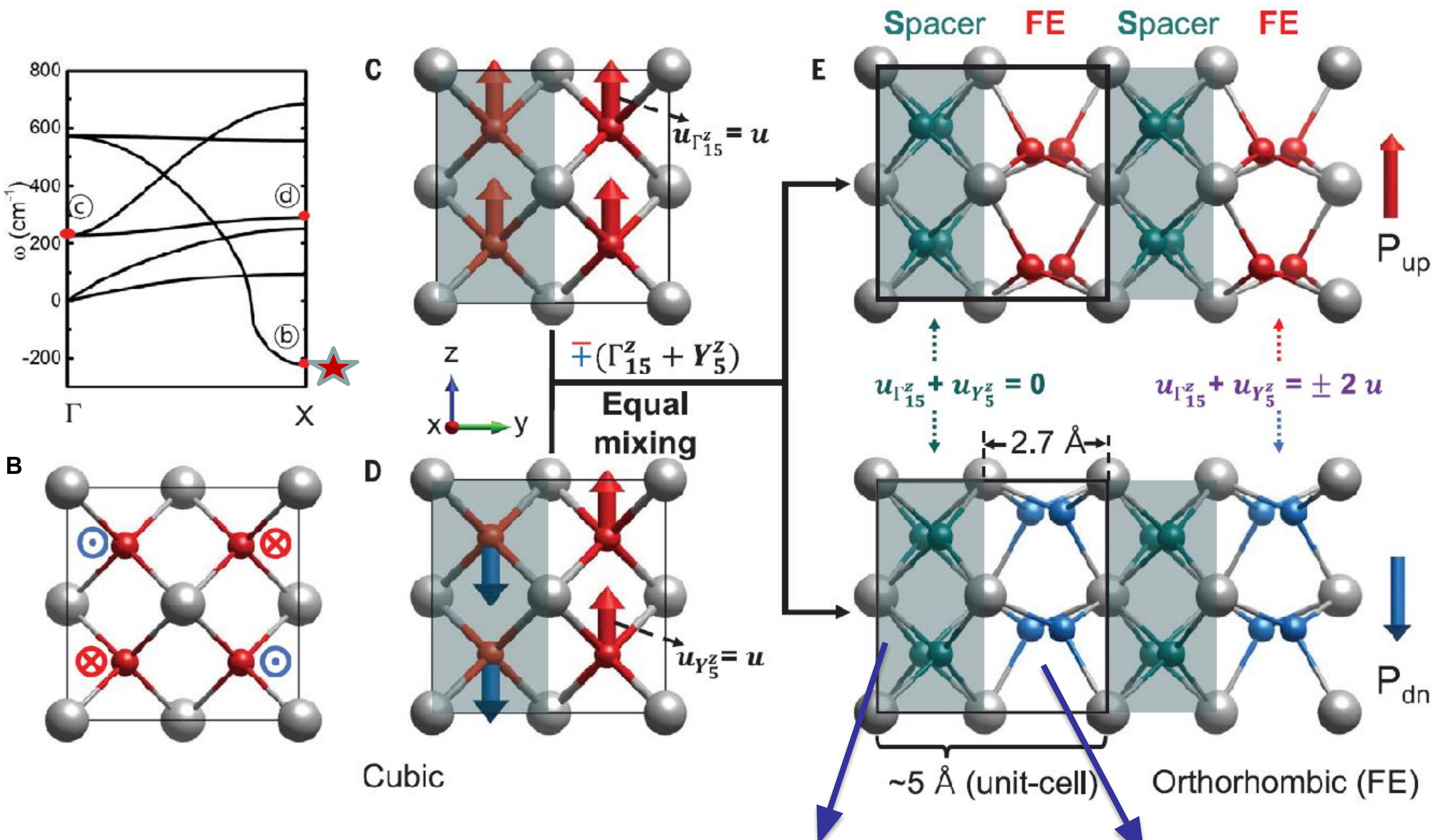
Instabilities of Phonon Pairs:
A Scale-free Ferroelectric

o-HfO_2



- HfO_2: readily integrable into Si technology!

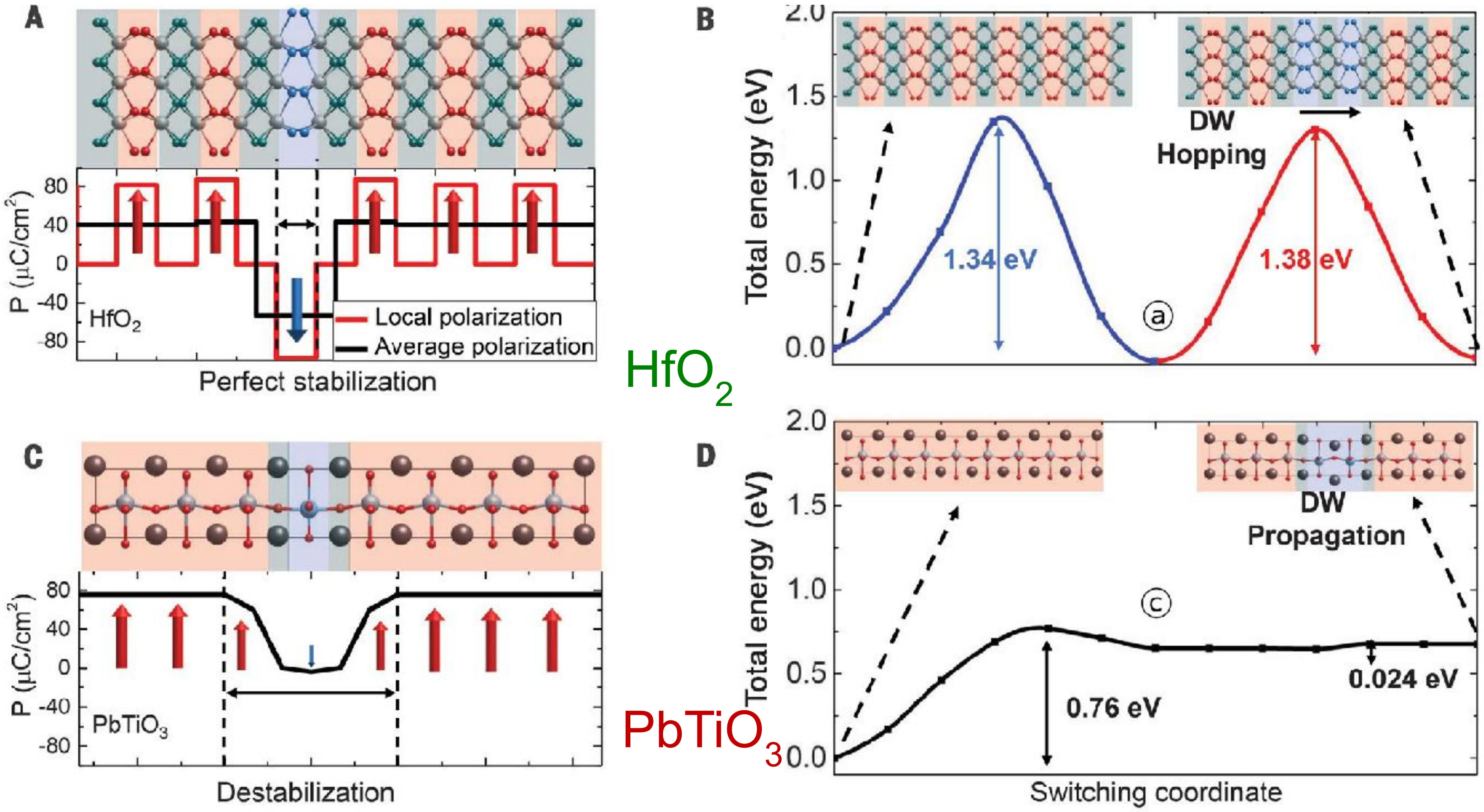
Multiple Phonon Instabilities: *Ferroelectricity in o-HfO_2*



Alternating 2D sheets of spacer (P=0) and ferroelectric (P≠0)

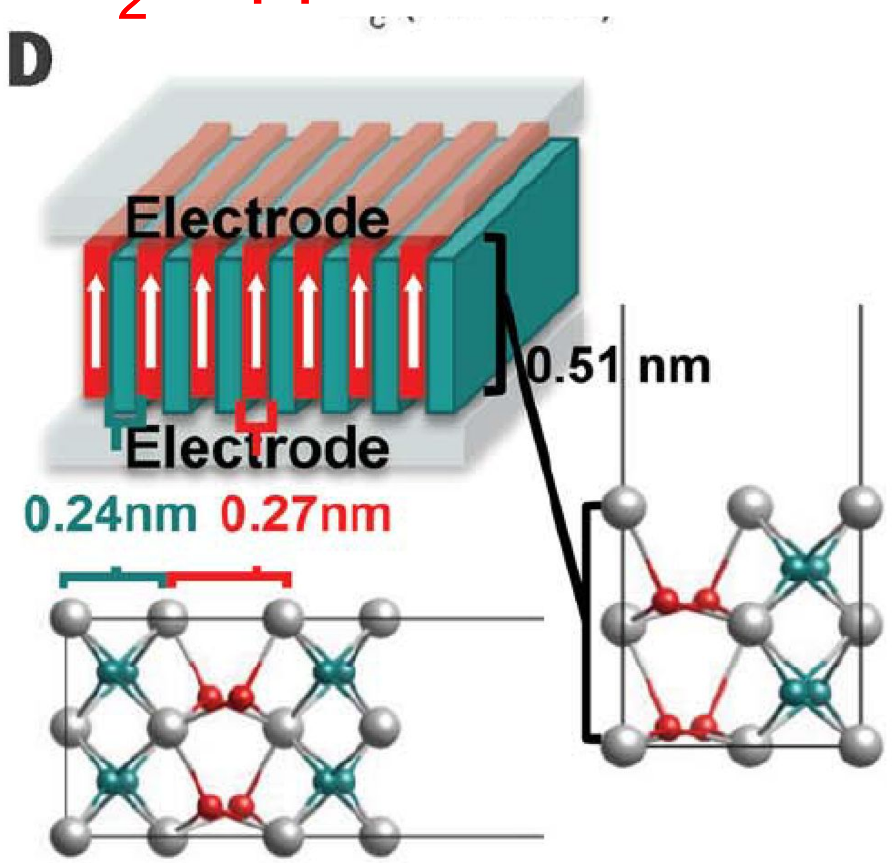
Anionic Ferroelectricity!

Robust Stability of Ferroelectric Domains in HfO_2



Nonvolatile Memory Unit → each dipolar sheet of HfO_2:
2 bits per nm!

Ferroelectric HfO_2: Applications



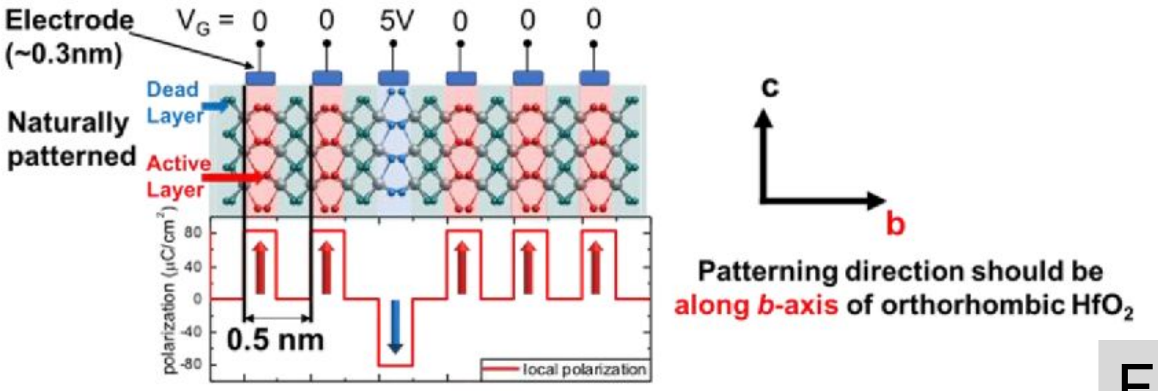
High coercive fields:
scale-free (local and collective) dipole switching at the same E field

No size limit:
Ultimately high density storage devices

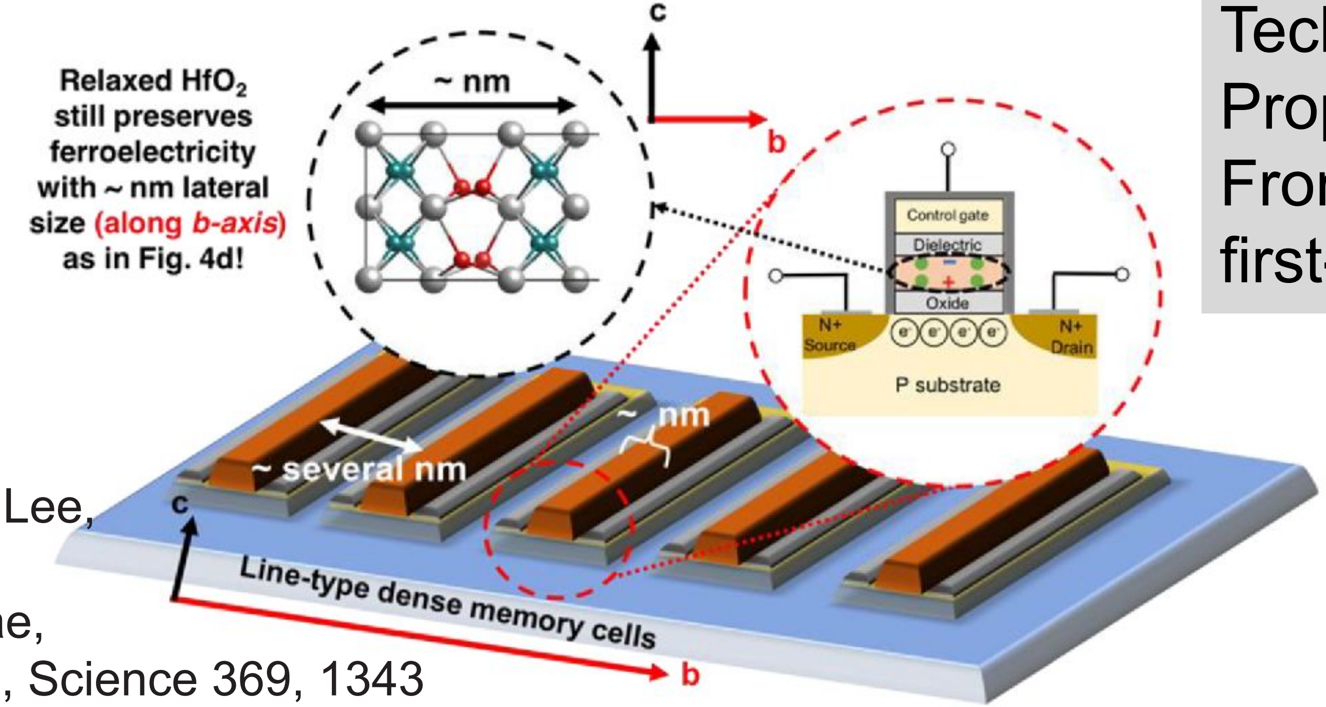
Antipolar Phonon Drives the Polar Phonon Instability: Robust Functional Behavior

Hyun-Jae Lee, Minseong Lee, Kyoungjun Lee, Jinhyeong Jo, Hyemi Yang, Yungyeom Kim,

Applications of Ferroelectric HfO_2



A. Ideal case (sub-nm) with ultra-fine electrode pattering for the future

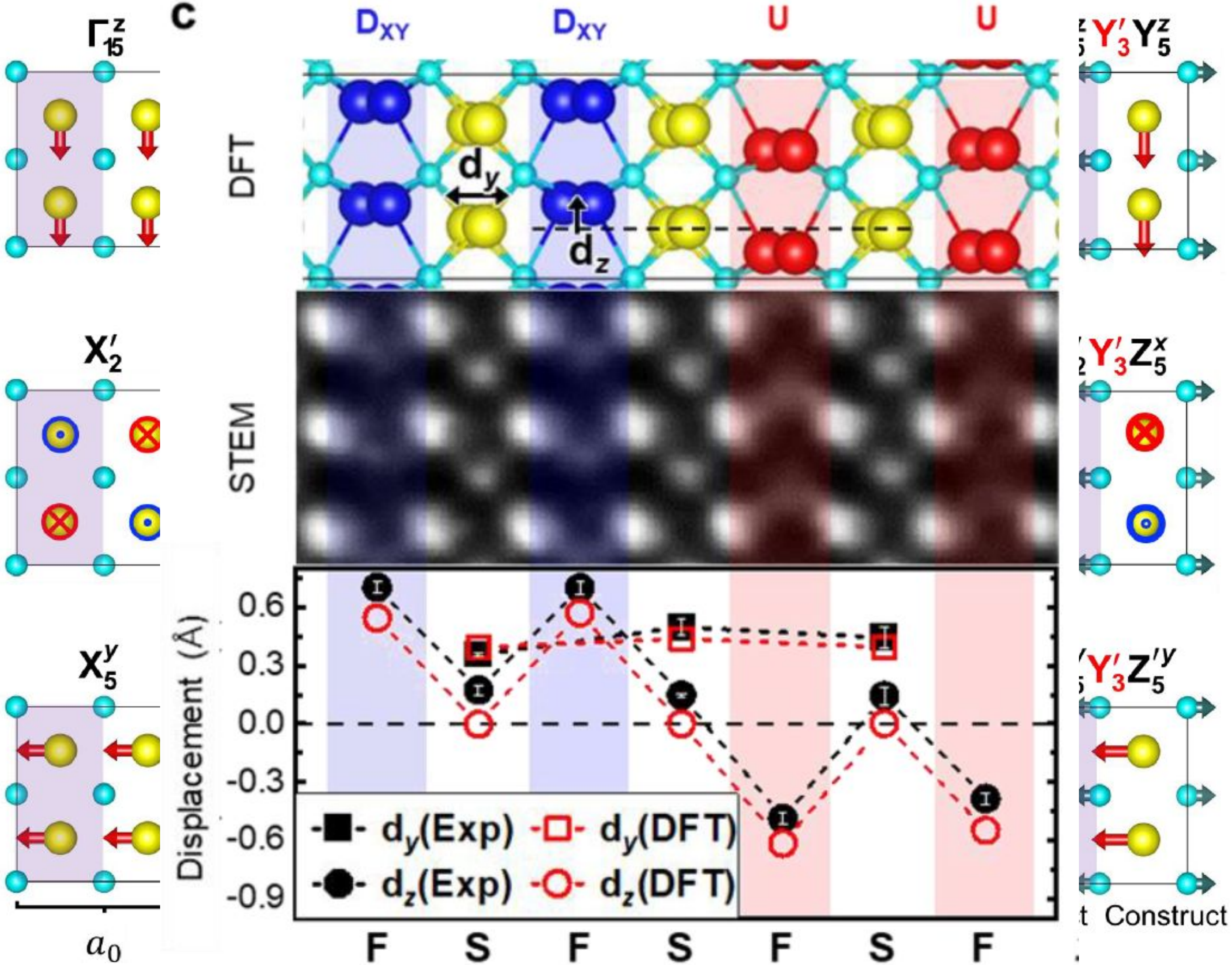


B. More practical case : Since ferroelectricity is preserved in ~ nm lateral size by flat bands, ~nm pattering (along b direction) can be used for dense memories of line-type.

Futuristic Memory Technology Proposed From first-principles

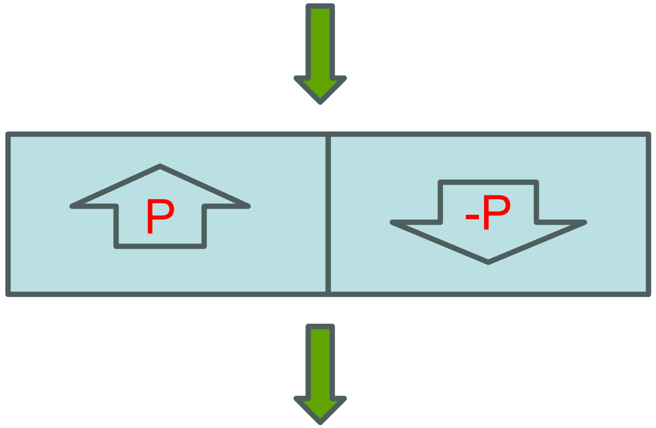
Hyun-Jae Lee, Minseong Lee, K Lee, Jinhyeong Jo, Hyemi Yang, Yungyeom Kim, Seung Chul Chae, Umesh Waghmare, Jun Hee Lee, Science 369, 1343 (2020)

Phonon Pairing in HfO_2 : *Unusual Domain Walls*



Y_3' mode binds two phonons through 3rd order coupling to form pairs:

$$Q_{\Gamma_{15}^{z}} \, Q_{Y_3'} \, Q_{Y_5^z}$$



Domain Wall with ***Bulk-like structure***!
~0 energy

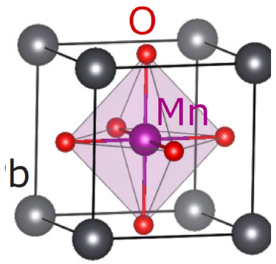
Lee et al, arXiv:2403.01415

Designing
Crystals with
Broken Symmetries

Transition Metal Oxides

A*TM*O_3 perovskites

Symmetry Lowering Ordering: Emergence of Properties



Ferroelectrics
$d^{n=0} \longrightarrow P$

BiFerroics

Ferromagnets
$d^{n\neq 0} \longrightarrow S$

Insulators

Metals

Half-metals

Polarity

Inversion symmetry

Polar Half-metallic Ferromagnet?

Puggioni et al, Phys Rev Mat 2, 114403 (2018)

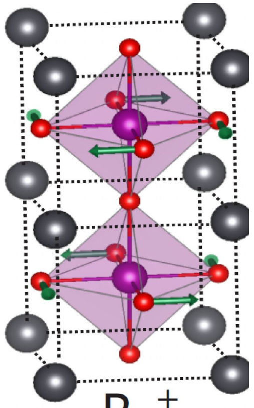
- Metallic in one spin channel: Ferromagnet
- Gapped in the states of other spin channel: Polarization

Engineering polar phases in $PbMnO_3$

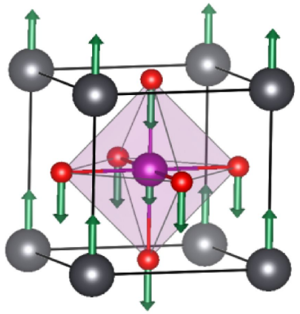
Mn^{4+}: d^3 (Half-filled)

Cubic $PbMnO_3$

Ferromagnetic
Half-metal



R_4^+



Γ_4^-

Unstable modes: R_4^+ and M_3^+
Rotation of MnO_6 octahedra

Unstable polar phonon mode: Γ_4^-

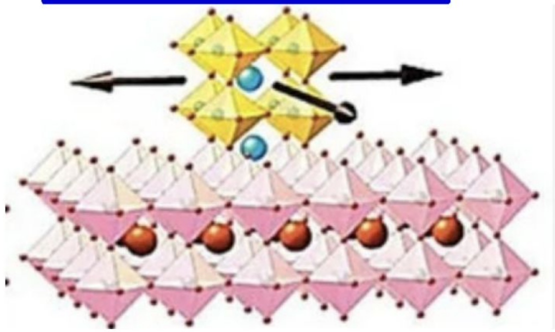
Nonpolar orthorhombic phase

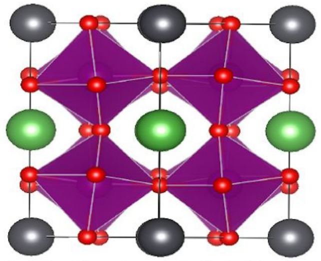
Ferromagnetic
Half-metal

Competition

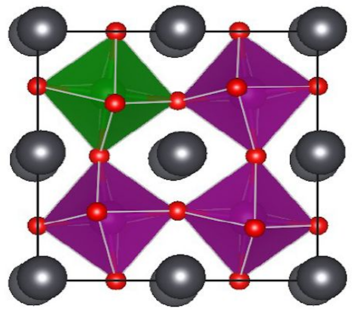
Stabilizing polar phases

- X Epitaxial strain
- √ Hetero-structuring
- X Cation substitution



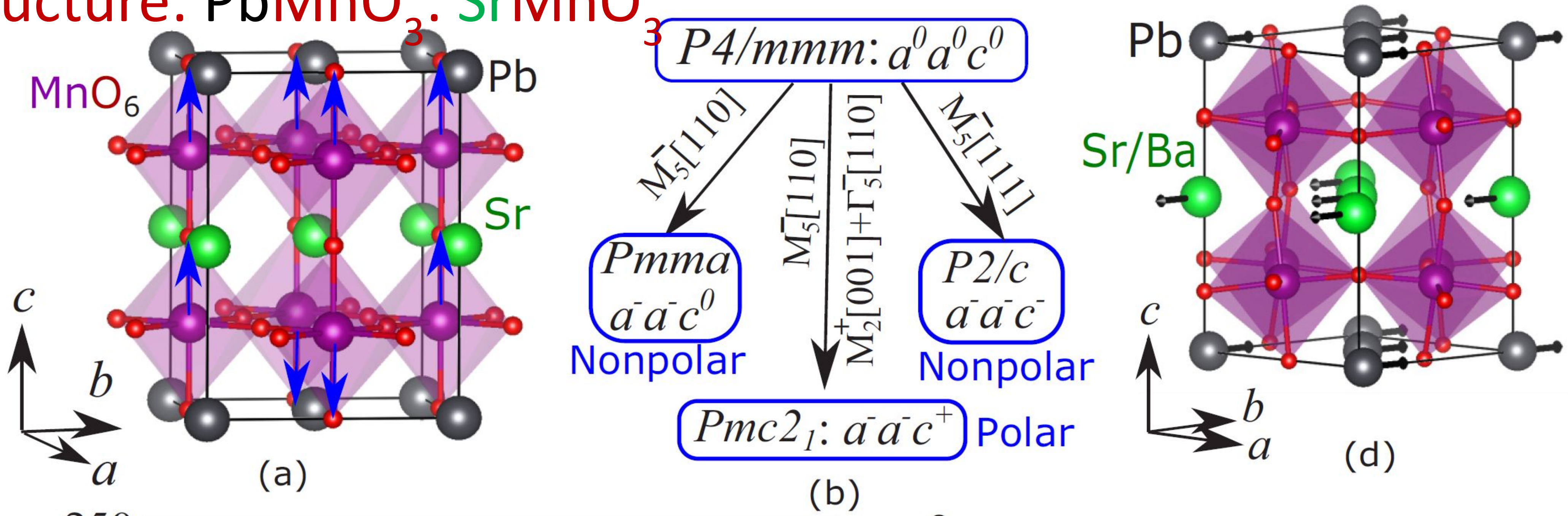


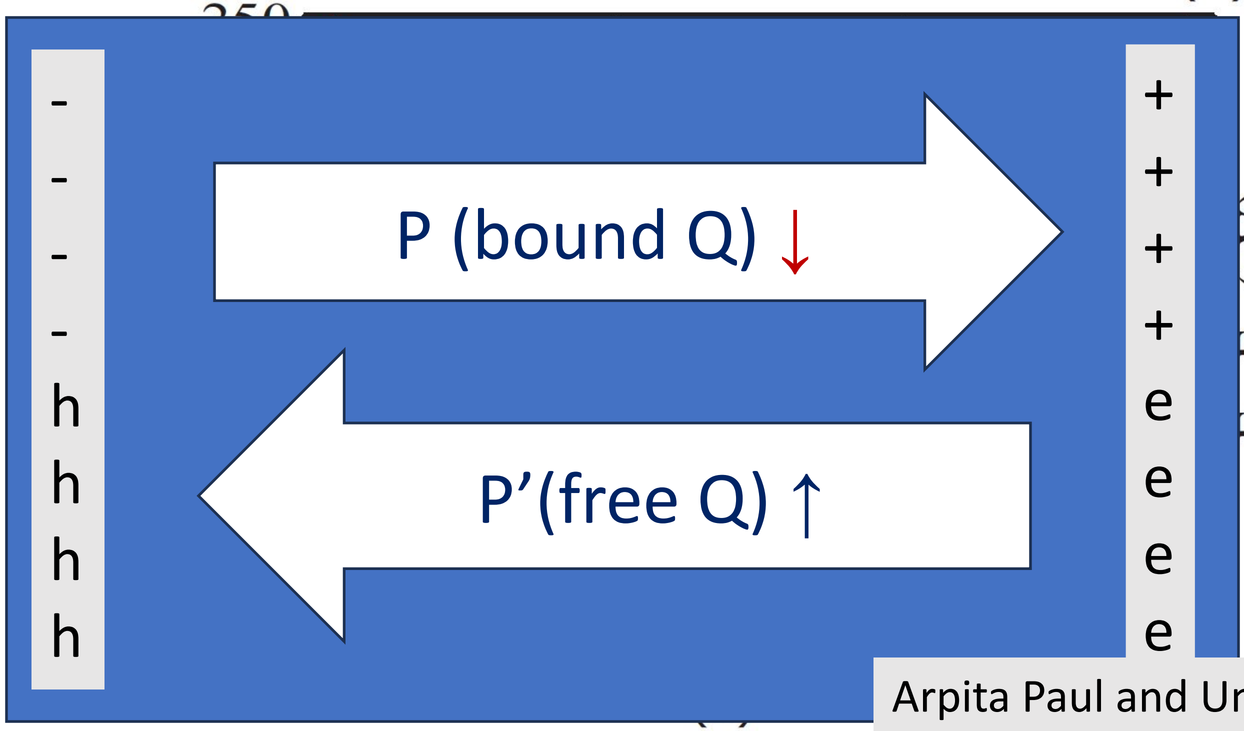
$(ABO_3)_1/(A'BO_3)_1$

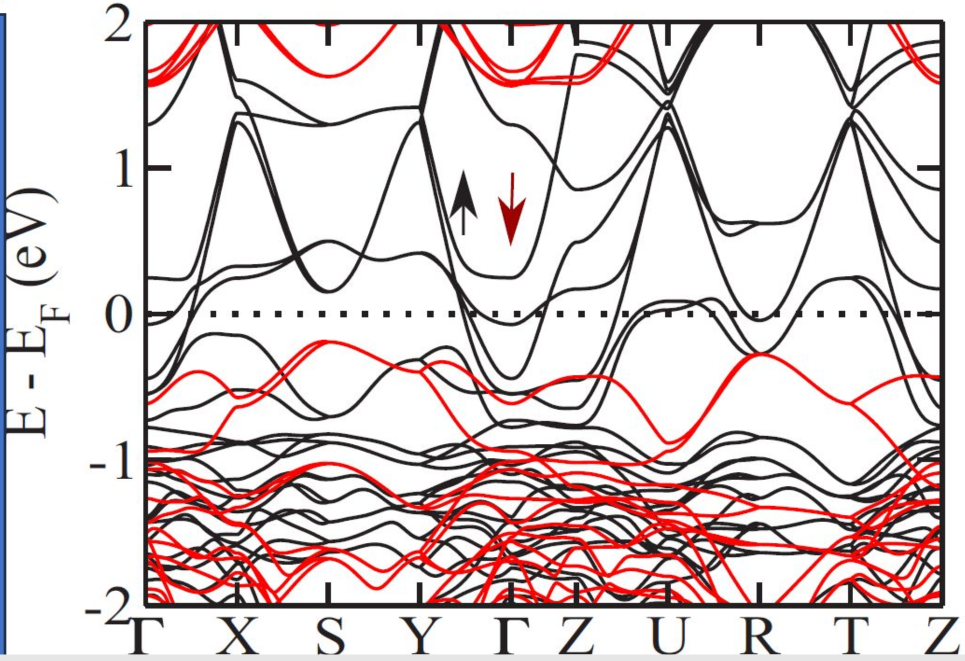


Mn site

Heterostructure: $PbMnO_3$: $SrMnO_3$







Arpita Paul and Umesh V Waghmare, Phys Rev B 110, 184110 (2024)

- $PbMnO_3$: HM FM in ***Pnma*** structure (nonpolar)
- Nonpolar structure robust against epitaxial strain or substitution
- $PbMnO_3$:$SrMnO_3$: An excellent Polar Ferromagnetic Half-Metal

Ongoing Work:

Domains in polar FM HM

Quantum Geometric Features into Multi-Ferroics

Arpita Paul and Umesh V Waghmare, Phys Rev B 110, 184110 (2024)

Sensing Vibrations Using Quantum Geometry of Electrons

Proposal using *First-principles Theory*

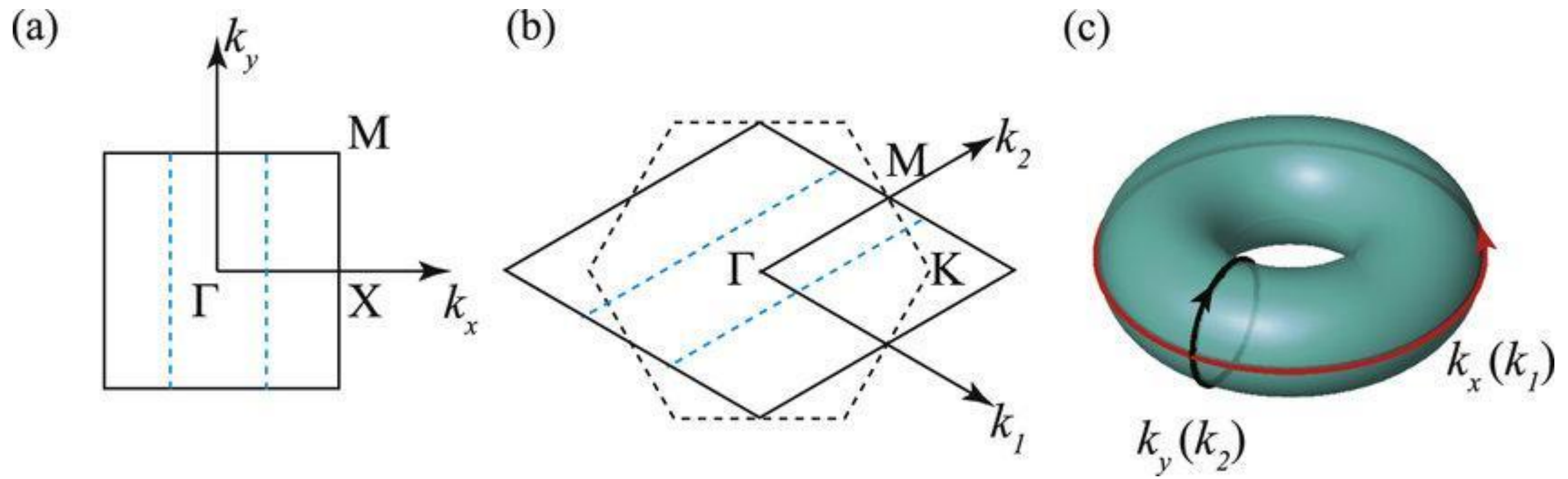
New Class of Spectroscopies based on Quantum Geometry

Demonstration of a Vibrational Spectroscopy In 2D Materials

R Bhuvaneswari, M M Deshmukh and U V Waghmare, Physical Review B 110, 014305 (2024)

100 (+1) years of Raman Effect

Periodicity of a Crystal: in real & reciprocal spaces



Wang et al, New J of Phys (2019)

$$Force = -eE = \hbar\dot{k} = ma$$

Trajectory of an electron $k \Rightarrow k + \Delta k$

Electron going across the Brillouin Zone: ***A closed path!***

Geometric or Pancharatnam or Zak or Berry phase

Bloch Electron

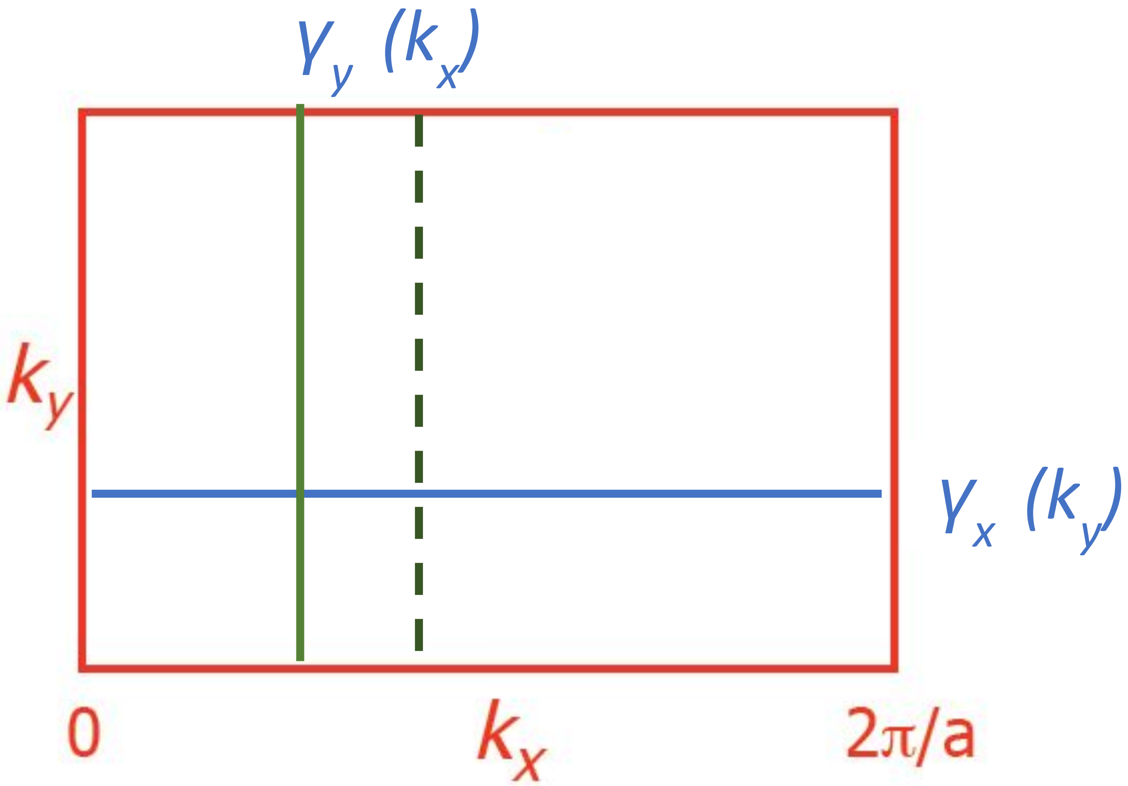
Geometric Phase

Average Position

$$\gamma_\alpha = i \int_{-\pi/a}^{\pi/a} d\boldsymbol{k} \left\langle u_{\boldsymbol{k}} \left| \frac{\partial}{\partial k_\alpha} \right| u_{\boldsymbol{k}} \right\rangle \sim \frac{\langle r_\alpha \rangle}{a}(2\ \pi)$$

Ref. 1. R. D. King-Smith and D. Vanderbilt, Theory of polarization of crystalline solids, *Phys. Rev. B.* **47**, 3 (1993).
Ref. 2. S. Pancharatnam, Generalized theory of interference and its applications. Part I. Coherent pencils, *Proc. Ind. Acad. Science* **A44**, 247 (1956).
Ref. 3. M. V. Berry, Quantal Phase factors accompanying adiabatic changes, *Proc. Roy. Soc. (London)* **392**, 45 (1984).

Geometric Phases in 2D



Berry potential:

$$\mathbf{A}(\mathbf{k}) = -\mathrm{Im}\,\langle u_{\mathbf{k}}|\nabla_{\mathbf{k}}|u_{\mathbf{k}}\rangle$$

Berry phase:

$$\phi = \oint \mathbf{A}(\mathbf{k}) \cdot d\mathbf{k}$$

Berry curvature:

$$\Omega(\mathbf{k}) = \nabla \times \mathbf{A}$$

γ_α : <x> and <y>

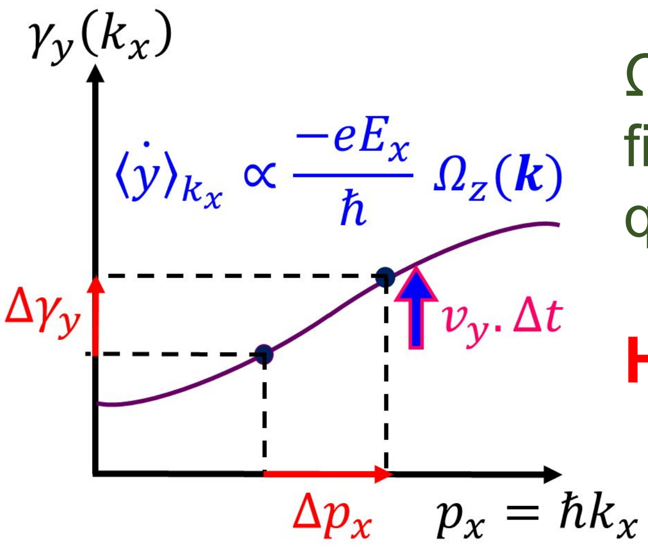
If $\Omega \neq 0$

Applied Electric Field, E_x,

► causes change in momentum $\hbar\Delta k_x$

► in shift in <y>, change in phase $\gamma_y(k_x)$

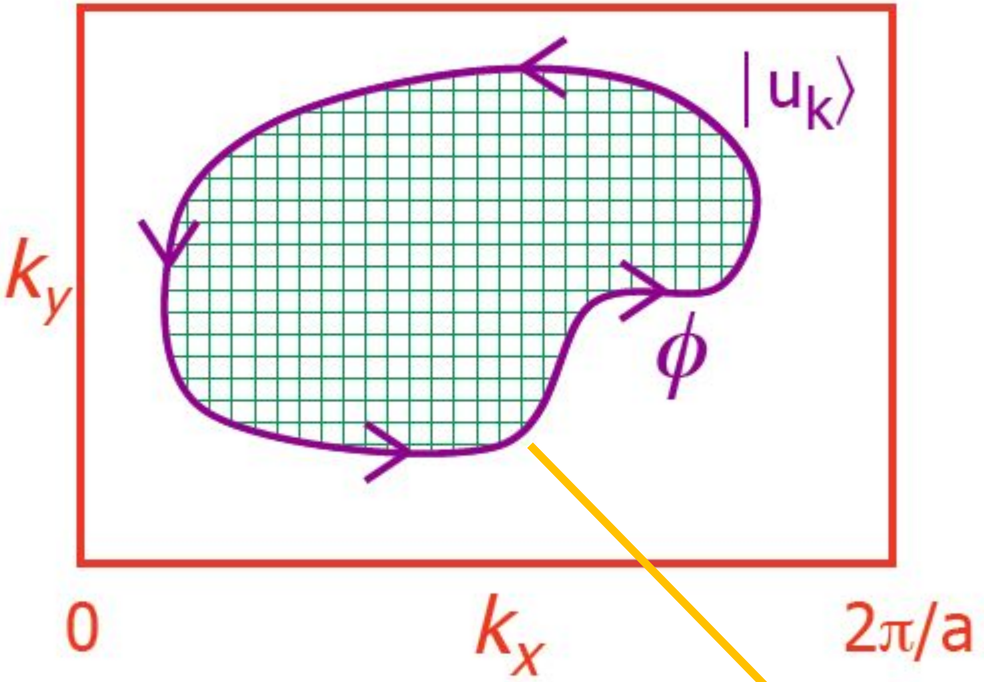
anomalous velocity v_y



$\Omega \neq 0$ acts like a magnetic field emerging from quantum geometry

Hall Effect with $B_{ext}=0$

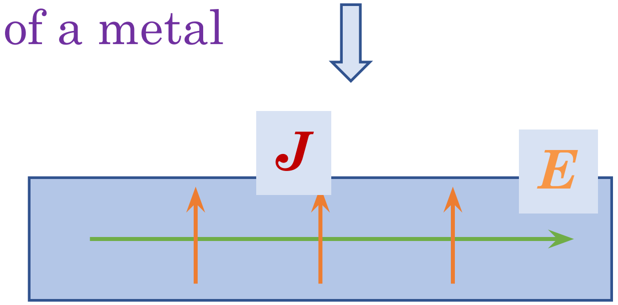
Geometric Phases and Anomalous Hall Conductivity:
Hall effect with out magnetic field!



$$\vec{v} = -\frac{e}{c}\vec{E} \times \vec{\Omega}(\vec{k})$$

E_x causes j_y

Fermi Surface of a metal



Stokes Theorem: $\phi = \int d^2k\, \Omega_z(k)$

Anomalous Hall Conductivity $\sigma_{xy} = \frac{-e^2}{2\pi h}\phi$

Karplus & Luttinger; Sundaram & Niu

Quantum Geometry & Topology of Electrons: *Emerging Fields*

Geometric band theory

Electromagnetism (gauge fields)

Consequences of Symmetry

Time Reversal Symmetry
$t \longrightarrow -t$

$$\Omega(-k) = -\Omega(k)$$

Inversion Symmetry
$(xyz) \longrightarrow -(xyz)$

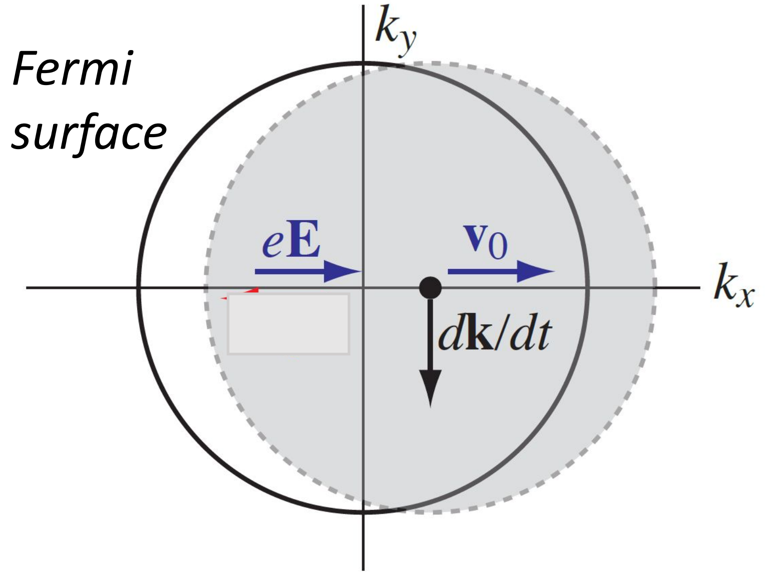
$$\Omega(-k) = \Omega(k)$$

In centrosymmetric, non-magnetic crystals $\Omega(k) = 0!$
Most metals, Si, …

Nonlinear Hall effect

Anomalous <*linear*> Hall Effect σ_{xy}: **Broken time-reversal symmetry**

$$\boldsymbol{\Omega}(-\boldsymbol{k}) = -\boldsymbol{\Omega}(\boldsymbol{k})$$



Applied E-field lowers the inversion symmetry

Shift in the Fermi surface: asymmetry in occupied states

First moment of $\boldsymbol{\Omega}(\boldsymbol{k})$ can be nonzero.

Theoretical Prediction

Second order non-linear Hall current: $j_y \propto E_x^2 . D$

Generates w=0 rectification or 2w (SHG) Hall signal for E_x(w)

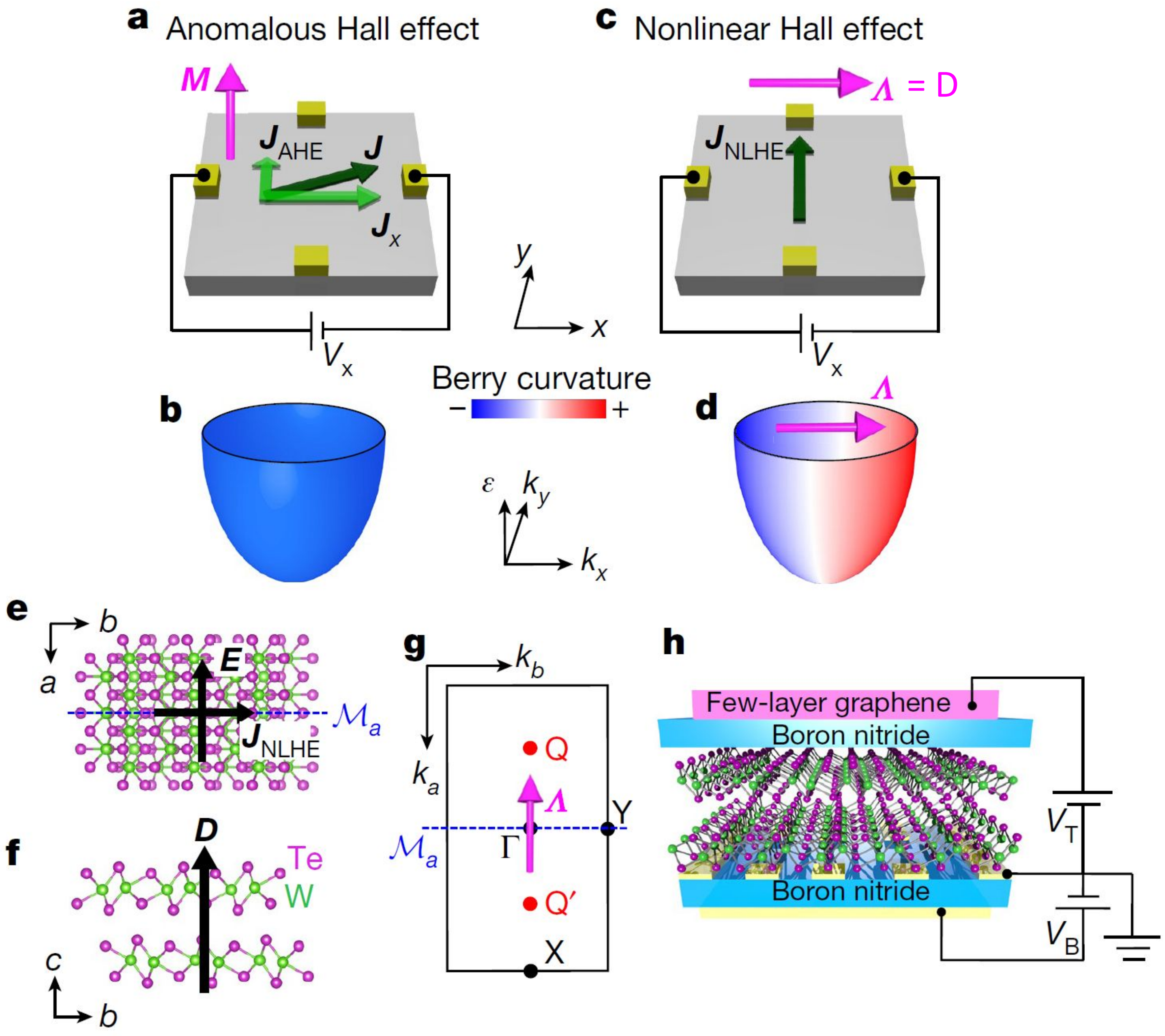
where D is the first moment of Berry curvature (Berry curvature dipole)

$$D = \iint f(\varepsilon_{\boldsymbol{k}}) \left[\frac{\partial}{\partial k_x} \Omega_z(\boldsymbol{k}) \right] = -\frac{1}{\hbar} \iint v_x(\boldsymbol{k}) \left[\frac{\partial}{\partial \varepsilon_k} f(\varepsilon_{\boldsymbol{k}}) \right] \Omega_z(\boldsymbol{k})$$

Ref. I. Sodemann and L. Fu, Quantum Nonlinear Hall Effect induced by Berry Curvature Dipole in Time-Reversal Invariant Materials, *Phys. Rev. Lett.* **115**, 216806 (2015).

Shift current: S M Young and A M Rappe, Phys Rev Lett 109, 116601 (2012).

Nonlinear Hall effect



Demonstrated experimentally
in noncentrosymmetric
T_d-WTe_2 type-II Weyl semimetal
$\Lambda = D \neq 0$

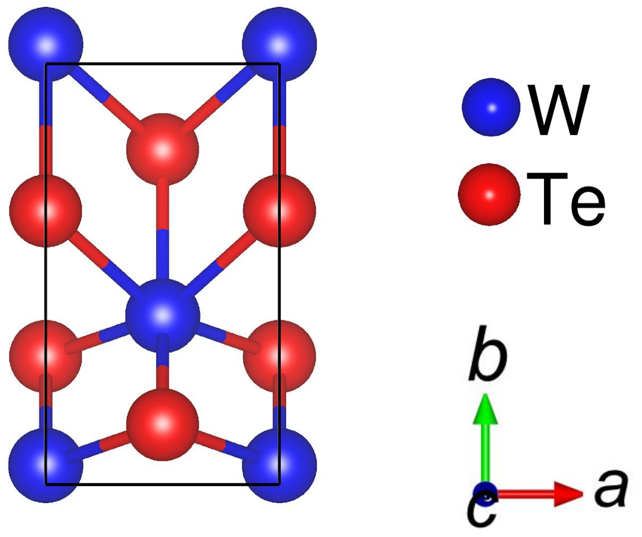
Q Ma et al, Nature 565, 337 (2019)

Nonlinear Hall effect: *Berry Curvature Dipole*

Time reversal symmetry

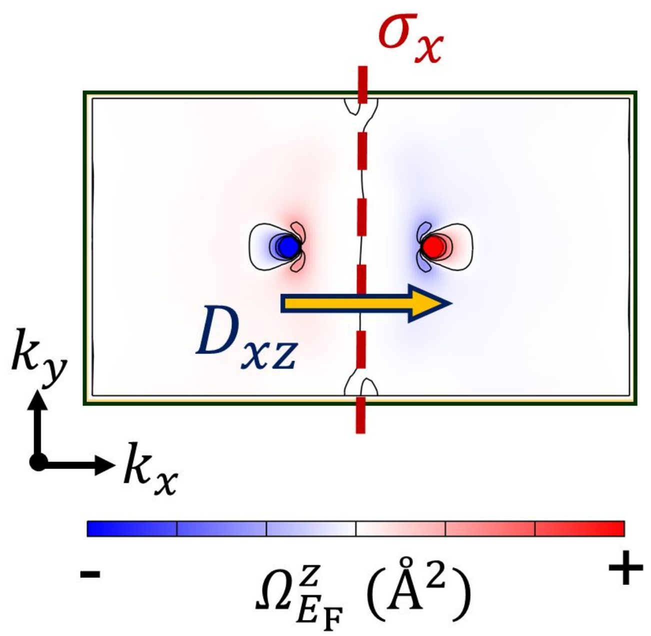
Band-gap should be *small*: Ω≠0

Crystal structural symmetry: **Low**



WTe$_2$ Monolayer:

low-symmetry structure (only σ_x),



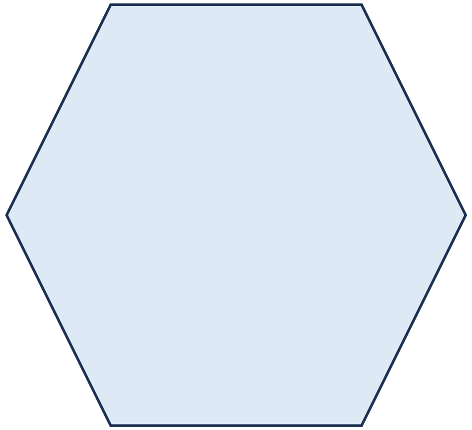
Bhuvaneswari, Deshmukh, Waghmare (2024)

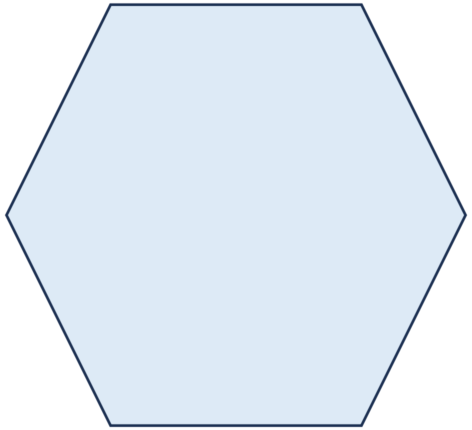
Our work: Crystal Structural Symmetry can be *dynamically* lowered!

The Basic Idea

Vibration

A Dynamical State with Lower Symmetry





Berry Curvature Dipole

= 0

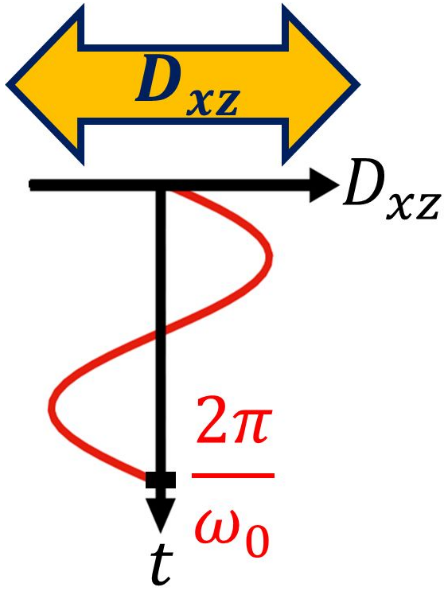
≠ 0

Vibration causes oscillations in Berry Curvature Dipole

Oscillations in Nonlinear Hall Current

Spectroscopy based on Geometry of Quantum Electronic Structure (GQuES)

Dynamical Lowering of Crystal Symmetry



Dynamical Excitations:

Vibration of a lattice lowers its symmetry (function of t): induce oscillations in the quantum geometry of electrons

If $\partial D/\partial u \neq 0$

where u is the amplitude of vibrational mode at w=w_0

Frequency-dependent non-linear Hall current proposed in the work:

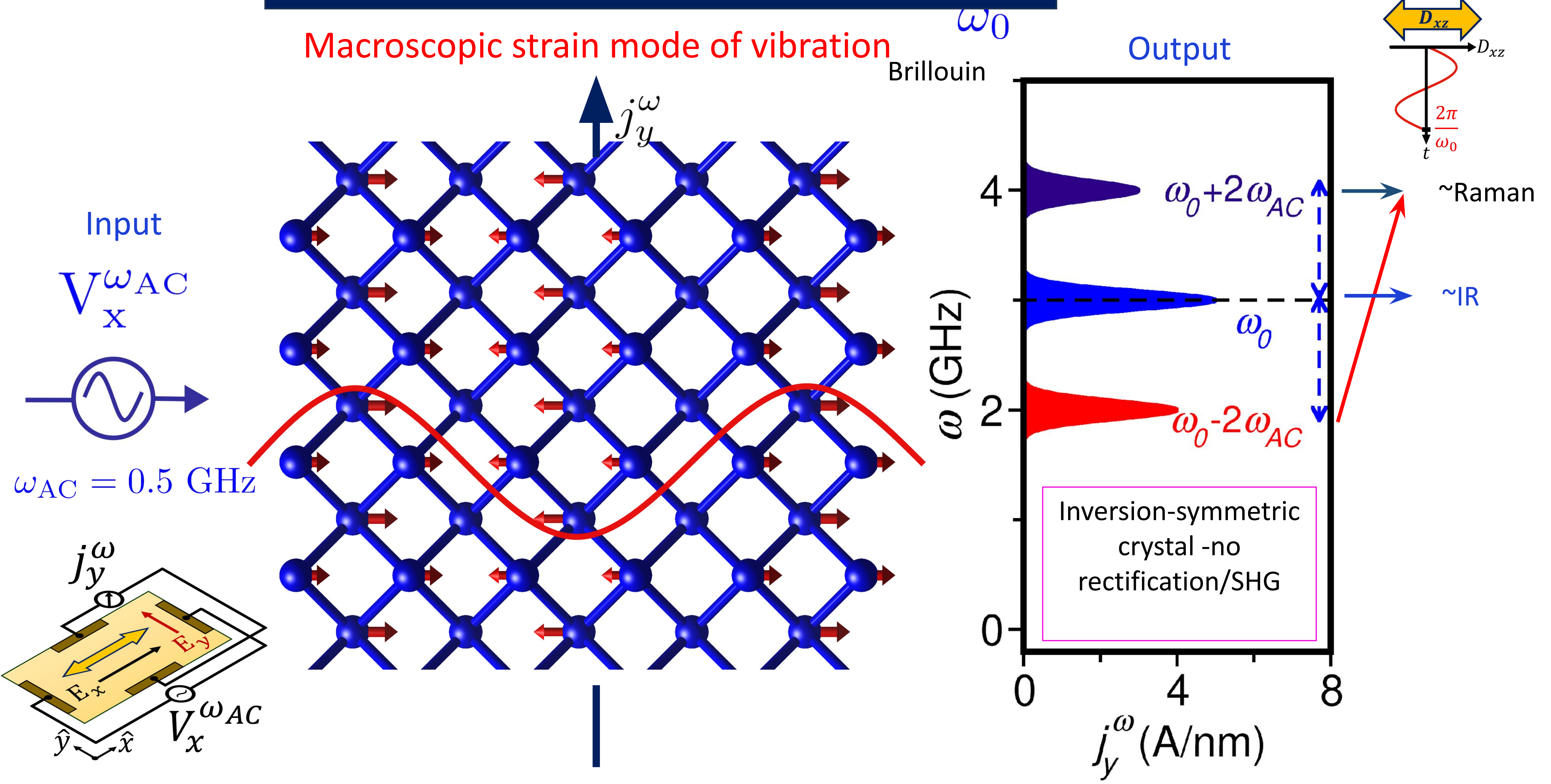
$$j_y(\omega) \propto E_x^2 \left\{ 2\boldsymbol{D}[\delta(\omega - 2\omega_{AC}) + \delta(\omega)] + u_0 \frac{\partial \boldsymbol{D}}{\partial \boldsymbol{u}}\Big|_{u=0} \begin{bmatrix} \delta(\omega - (\omega_0 + 2\omega_{AC})) + \\ \delta(\omega - |\omega_0 - 2\omega_{AC}|) + \\ 2\delta(\omega - \omega_0) \end{bmatrix} \right\}$$

SHG Rectification

Even a centrosymmetric, non-magnetic material that leads to vanishing *Ω:*

has nontrivial $j_y(\omega)$ through $\frac{\partial D}{\partial u}$

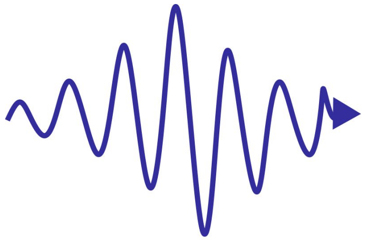
GQuES Transport Spectroscopy



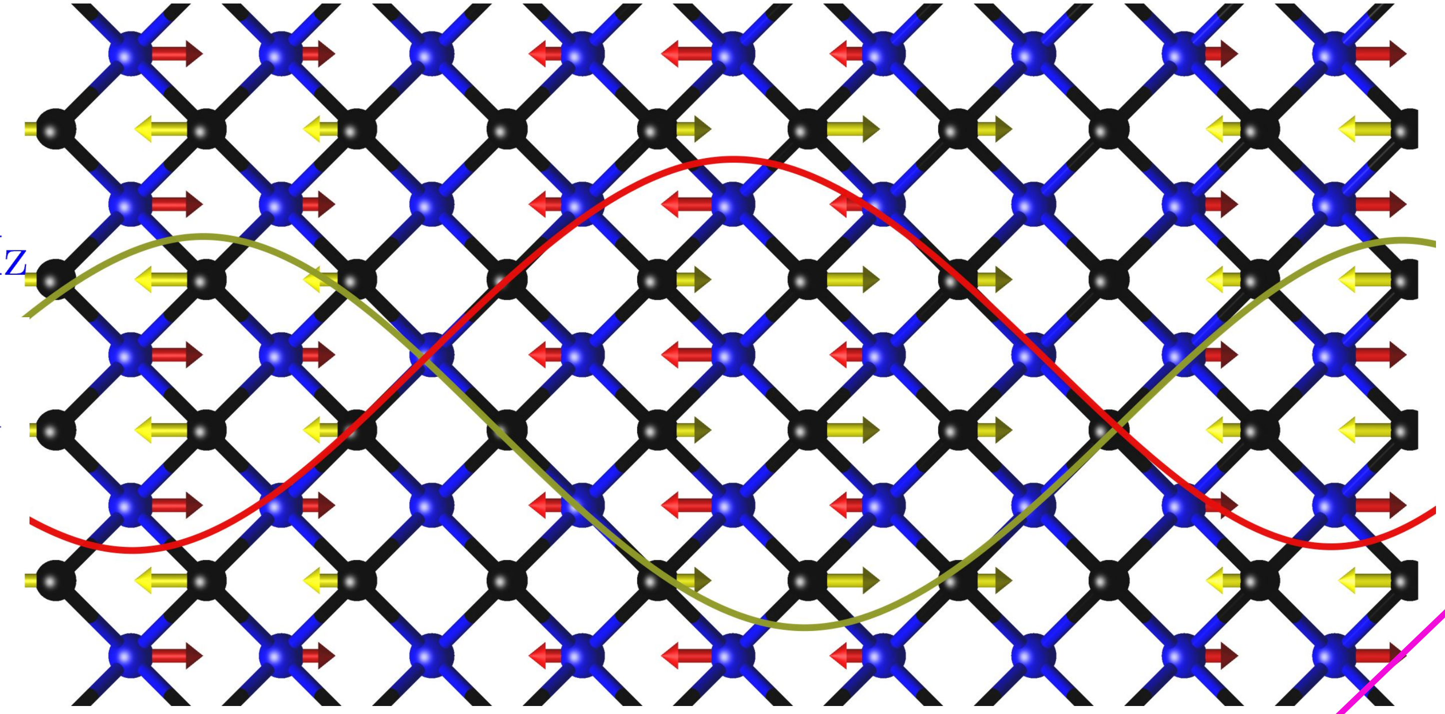
GQuES-Emission Spectroscopy

Laser

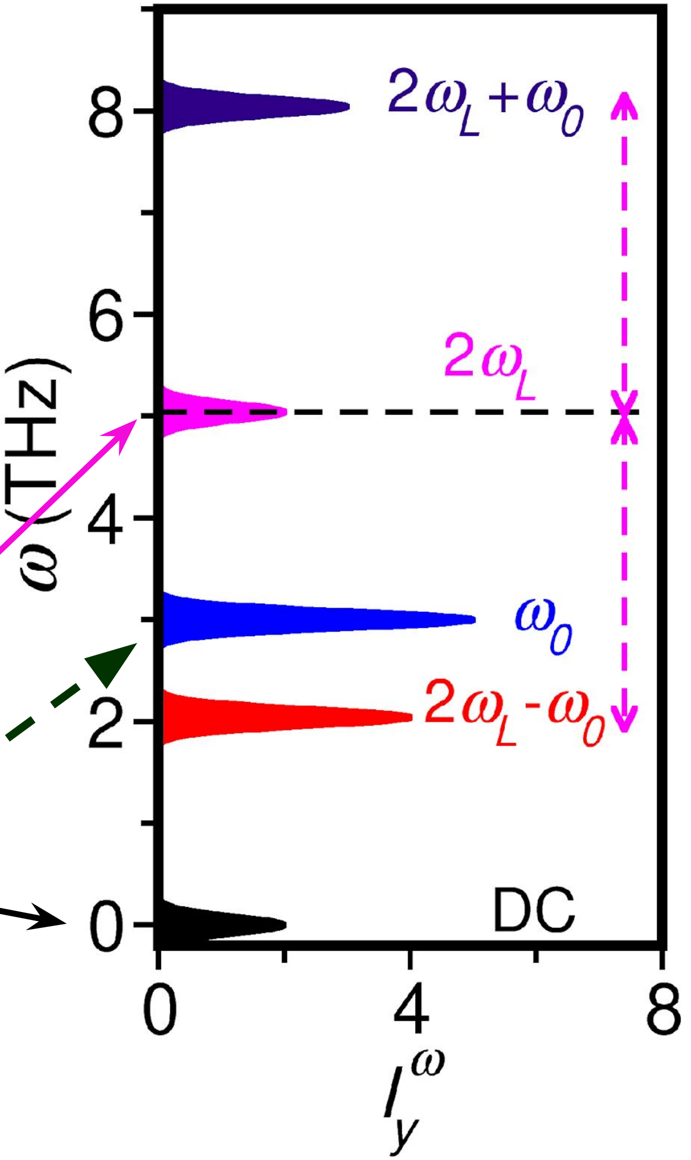
$\omega_{\mathrm{L}} = 2.52\ \mathrm{THz}$



Commercially available



$2\omega_L > \omega_0$



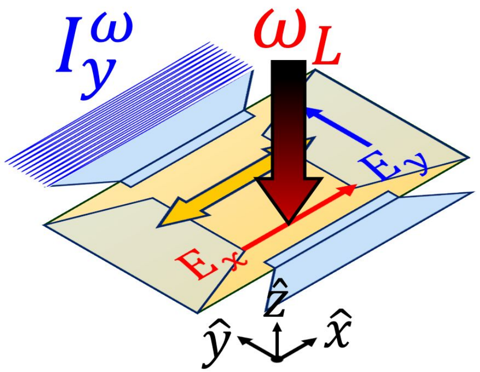
Inversion-asymmetric crystal - DC and SHG

Stokes and Anti-stokes like Raman peaks

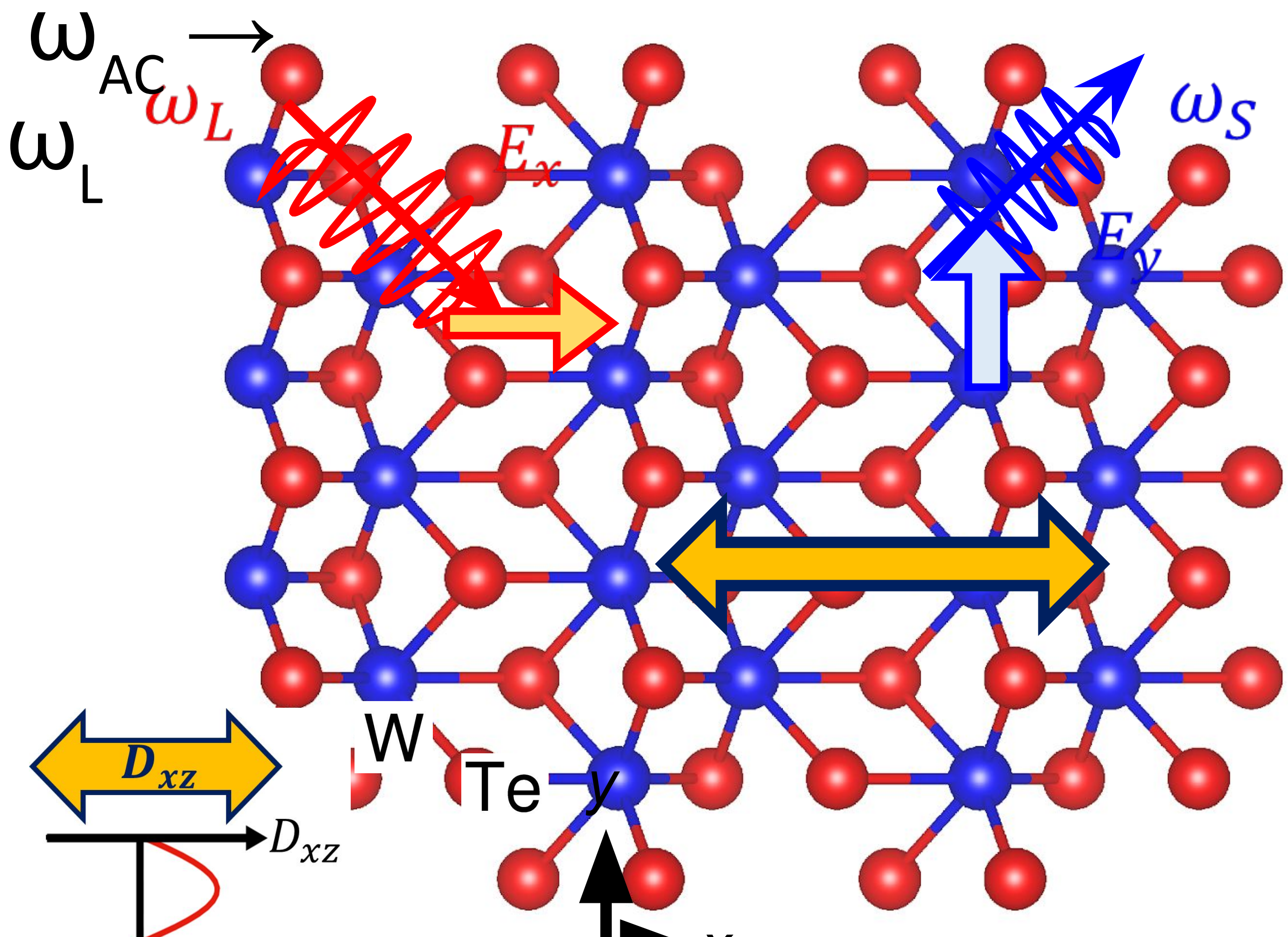
$2\omega_L - \omega_0$ $2\omega_L + \omega_0$

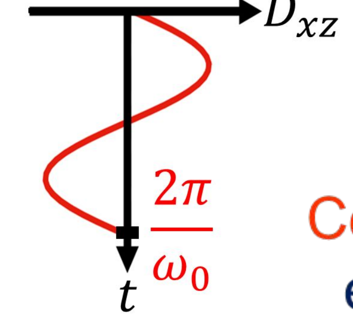
Peak at vibrational frequency ~ IR

ω_0

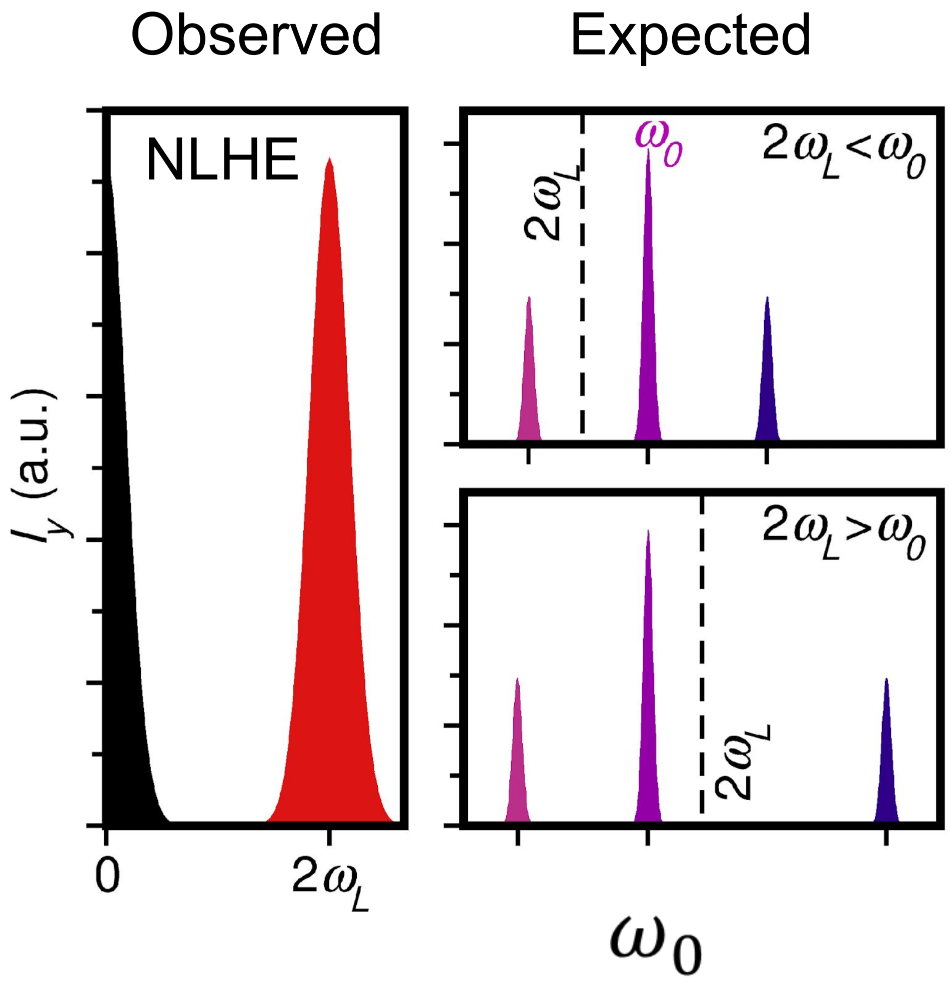


GQuES Optical Spectroscopy





Coupling between *quantum* geometry of electronic structure & excitations (ω_0)

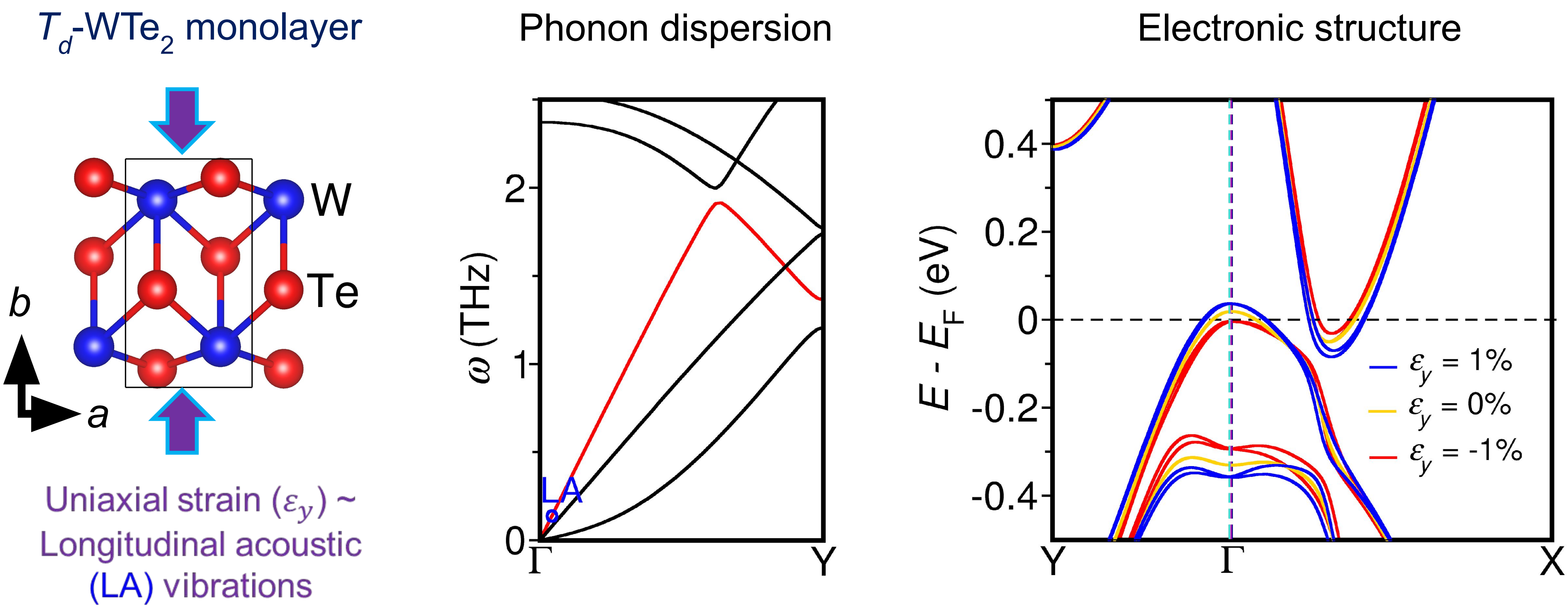


Similarity with IR and Raman spectroscopies

GQuES spectroscopy:
Specific predictions from first-principles

Electron-Phonon Coupling

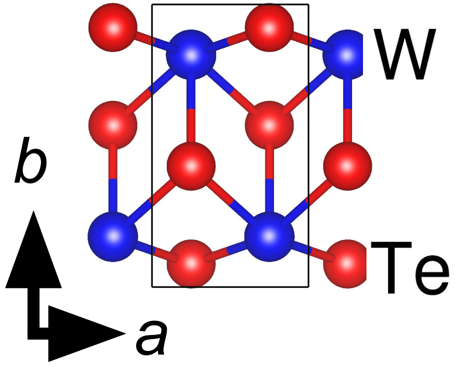
Coupling of electrons with excitations: Vibrations-induced electronic structure modulation

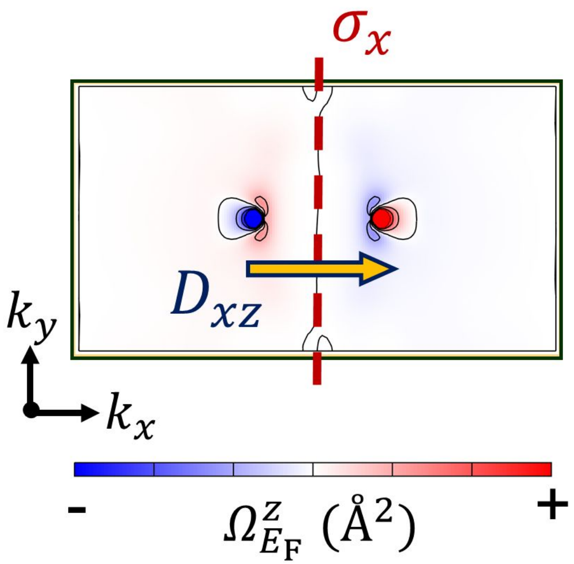


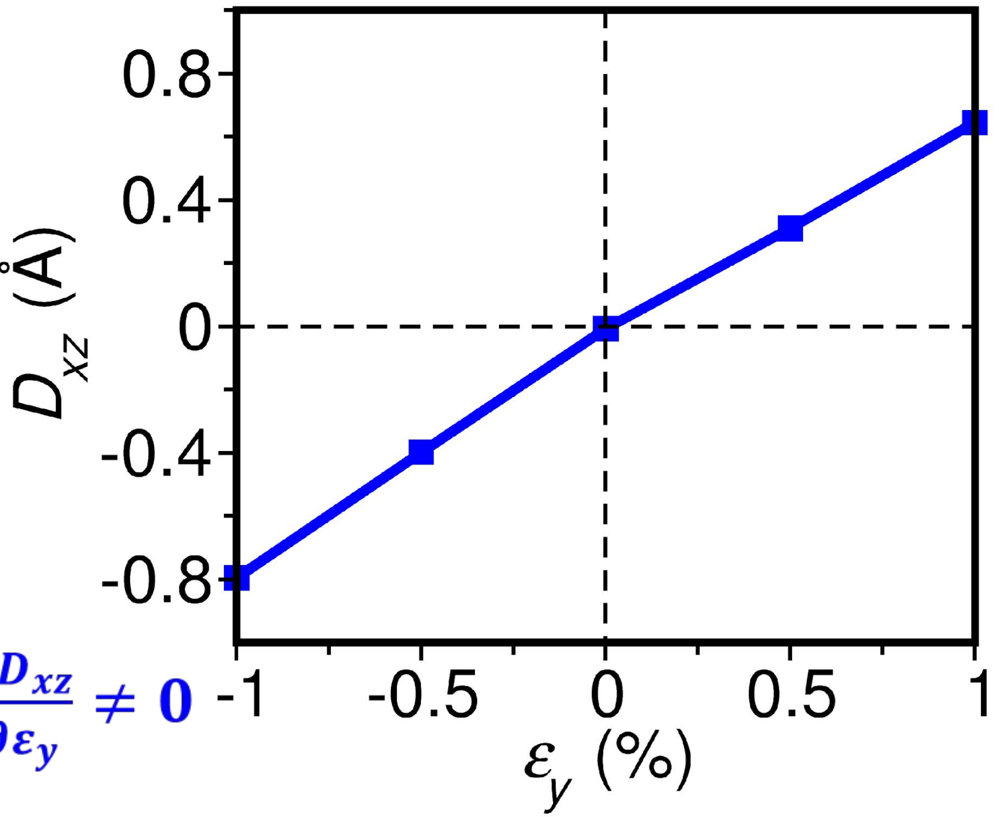
Changes in the geometry of quantum electronic structure (GQuES): *sense* vibrations?

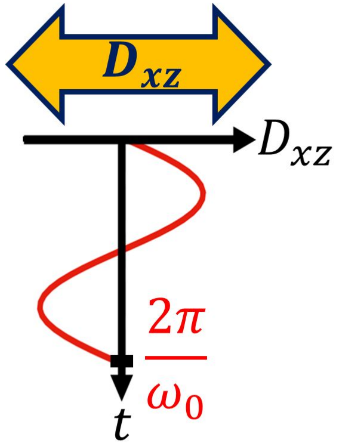
Selection Rule for GQuES Spectroscopy

Non-centrosymmetric T_d-WTe_2 monolayer









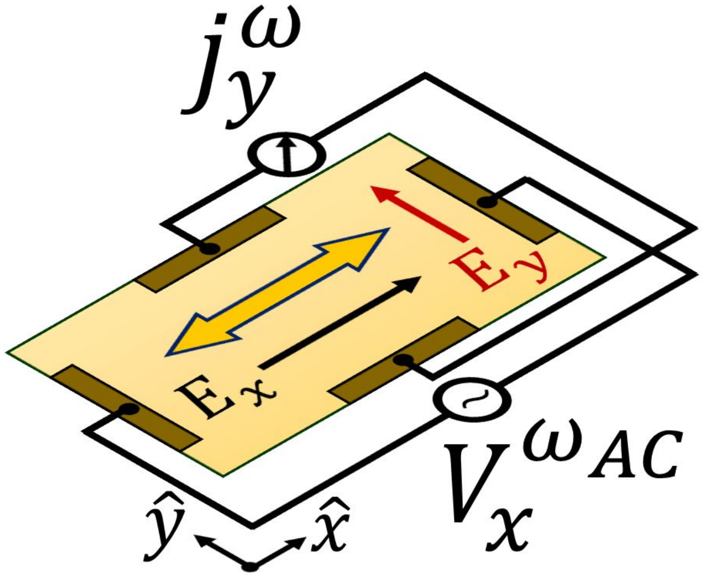
Selection rule for spectroscopy: $\frac{\partial D_{xz}}{\partial \varepsilon_y} \neq 0$

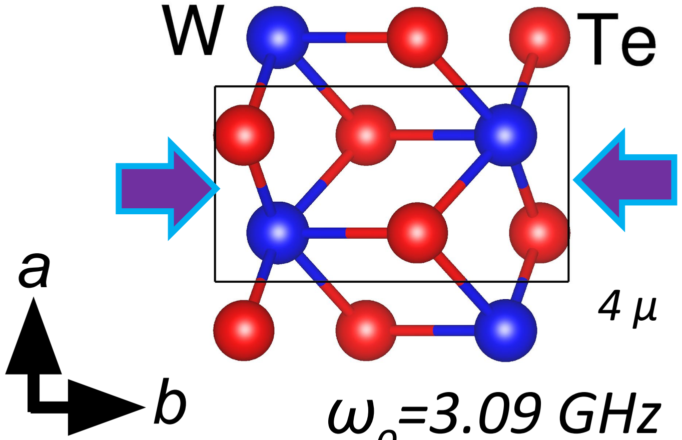
Spectroscopic signatures

Expected at $\omega = \omega_0, |\omega_0 \pm 2\omega_{AC}|$ due to $\frac{\partial D}{\partial u} \neq 0$

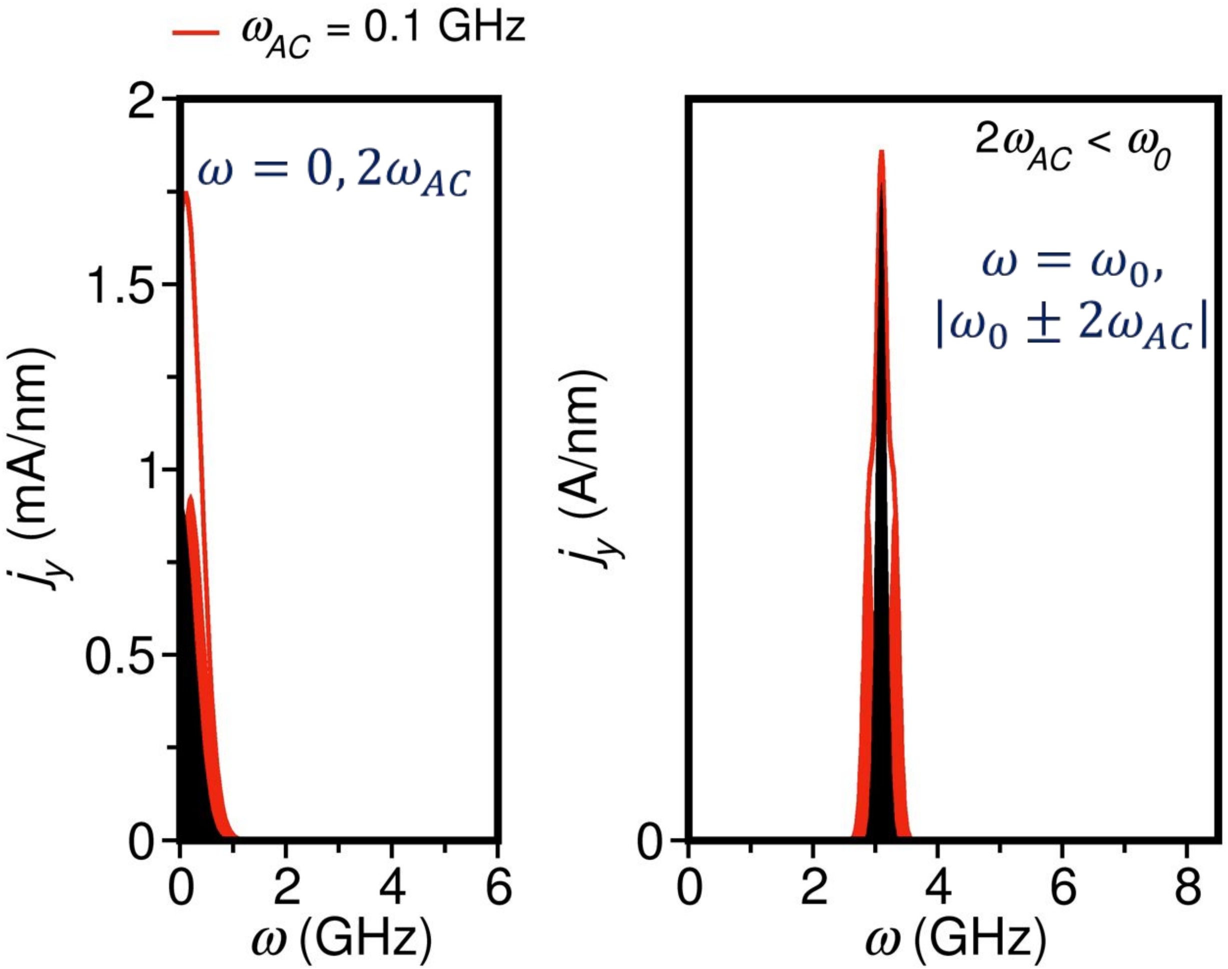
GQuES Transport Spectroscopy (GHz)

Uniaxial strain ε_y ~(longitudinal acoustic phonon) vibration of T_d-WTe_2 monolayer



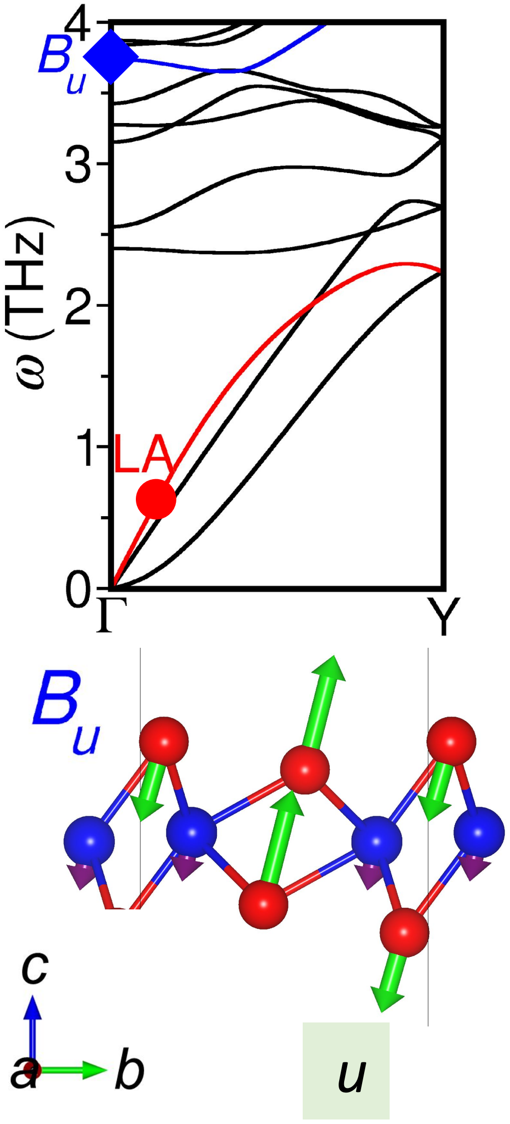


ω_0=3.09 GHz

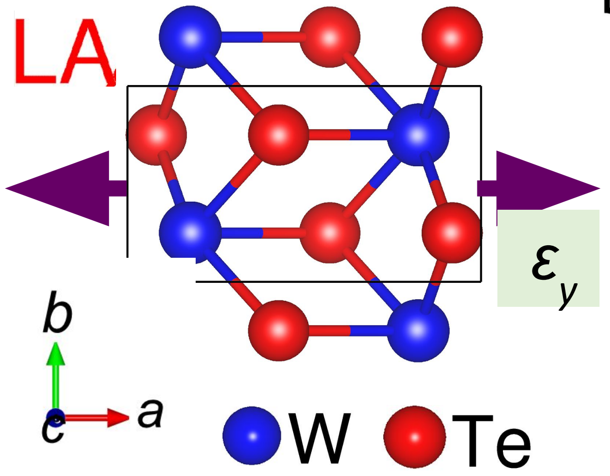


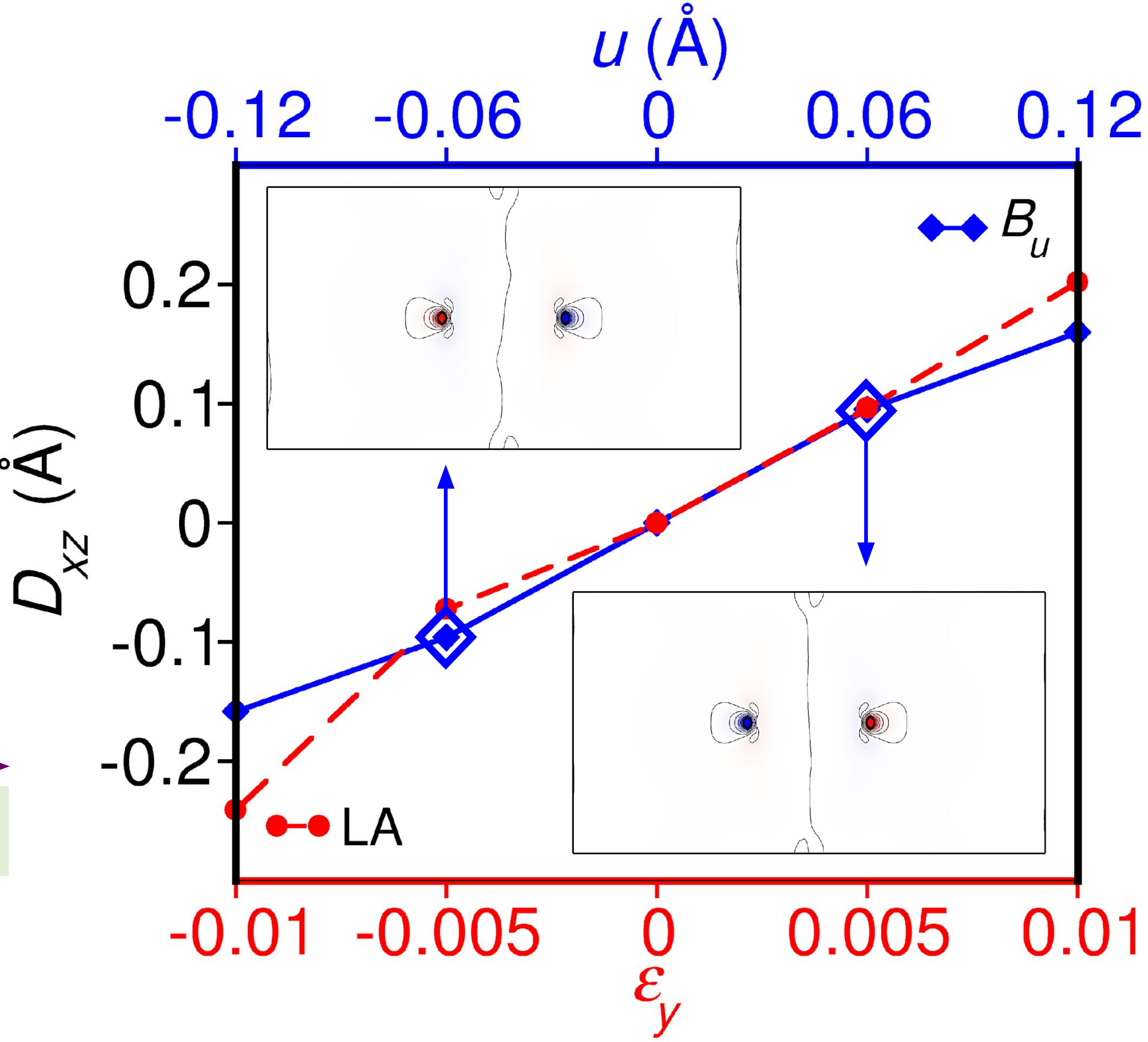
ω_{AC} helps track down the phonon peak!

GQuES-active Modes of *Centrosymmetric* T'-WTe_2 Monolayer



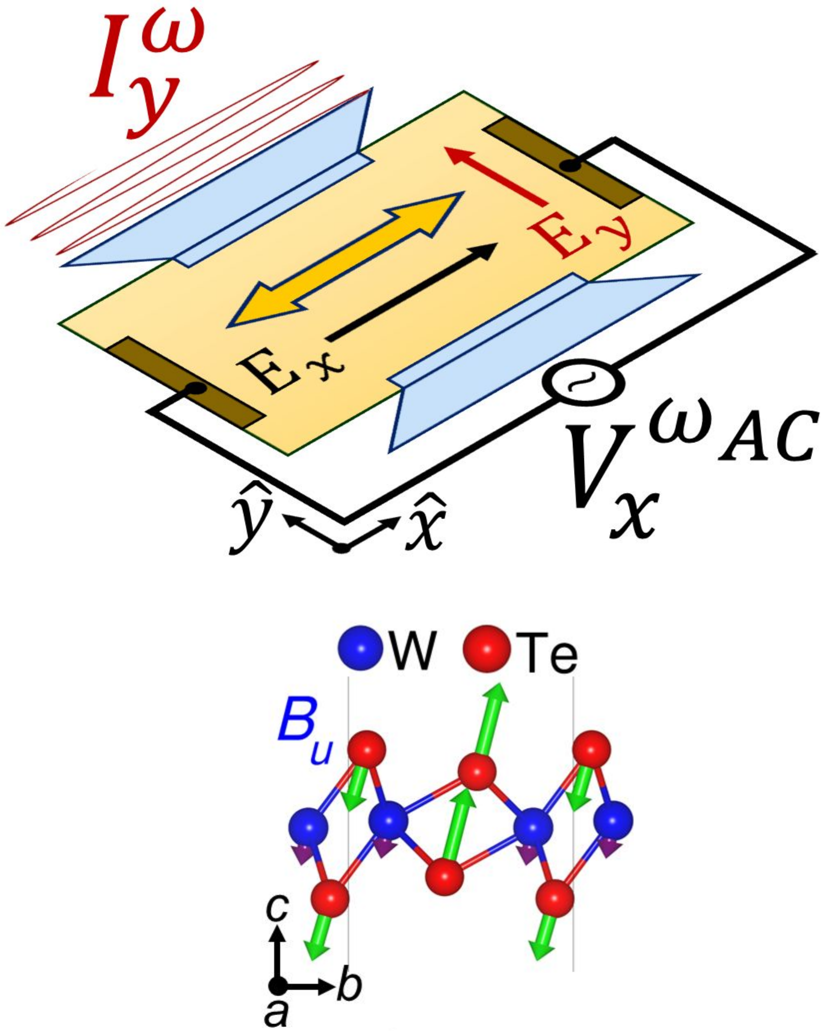
GQuES-active B_u and LA mode *dynamically* lower the inversion symmetry of T'-WTe_2 → $D \neq 0$ with distortions

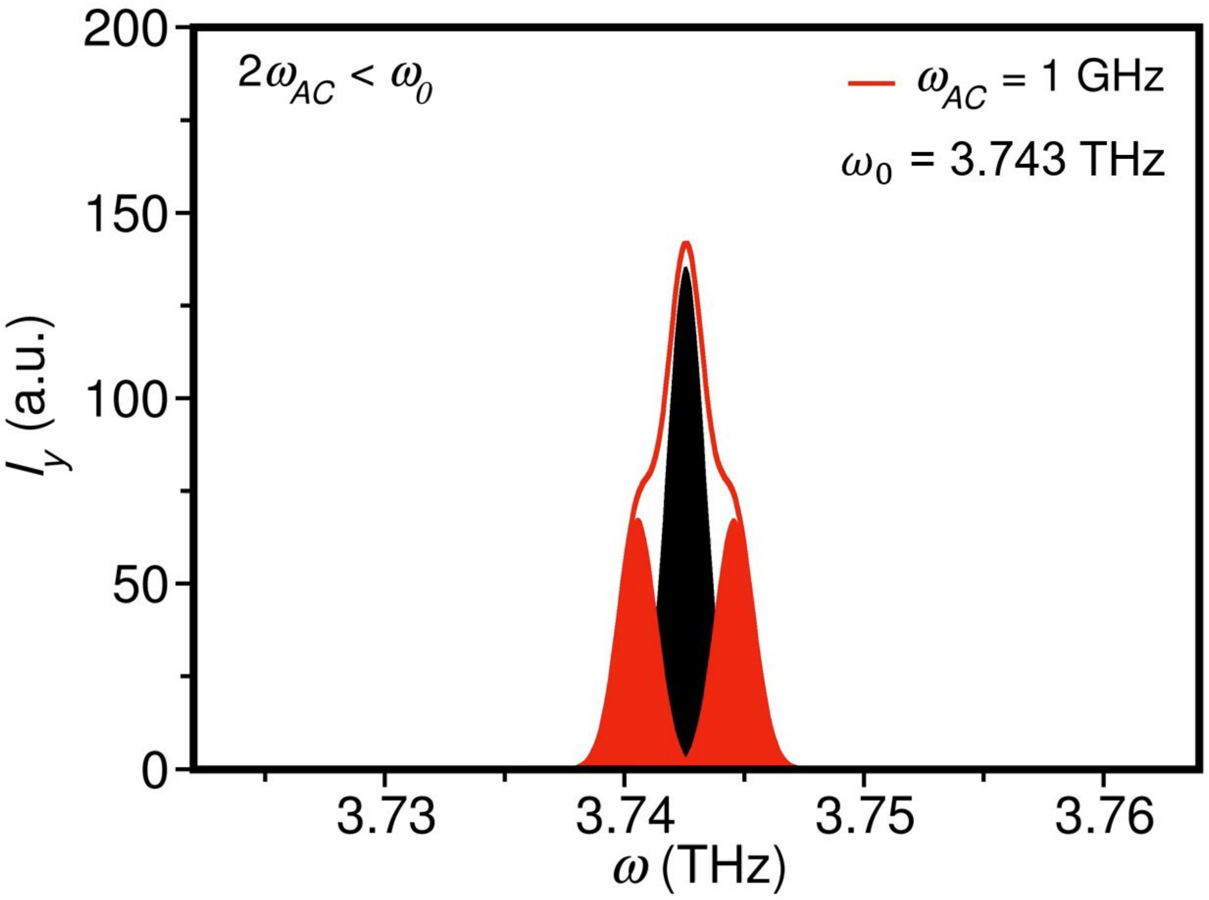




GQuES Transport Spectroscopy (GHz THz)

B_u mode of centrosymmetric T'-WTe_2 monolayer





Possibility of conversion of FM signals from GHz to THz

Our idea of dynamical lowering of symmetry works:
Introduces a new type of spectroscopy

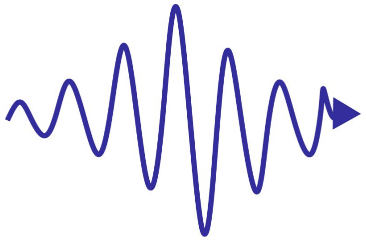
However, the ideas appear still ***restrictive*** to narrow band gap crystals… and those which have the potential of nontrivial quantum geometry!

We overcome this by interfacing an ***inert*** material
(e.g. large band-gap h-BN)
with one with a narrow gap or nontrivial quantum geometry!
(e.g. graphene)

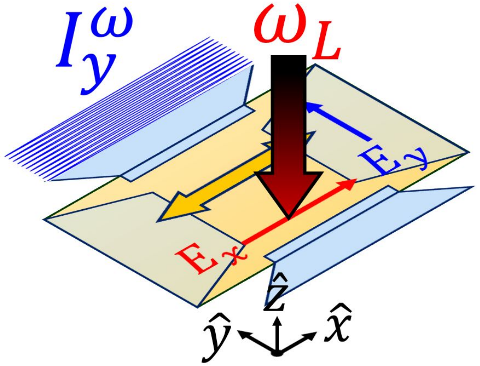
Substrate-induced GQuES (THz)

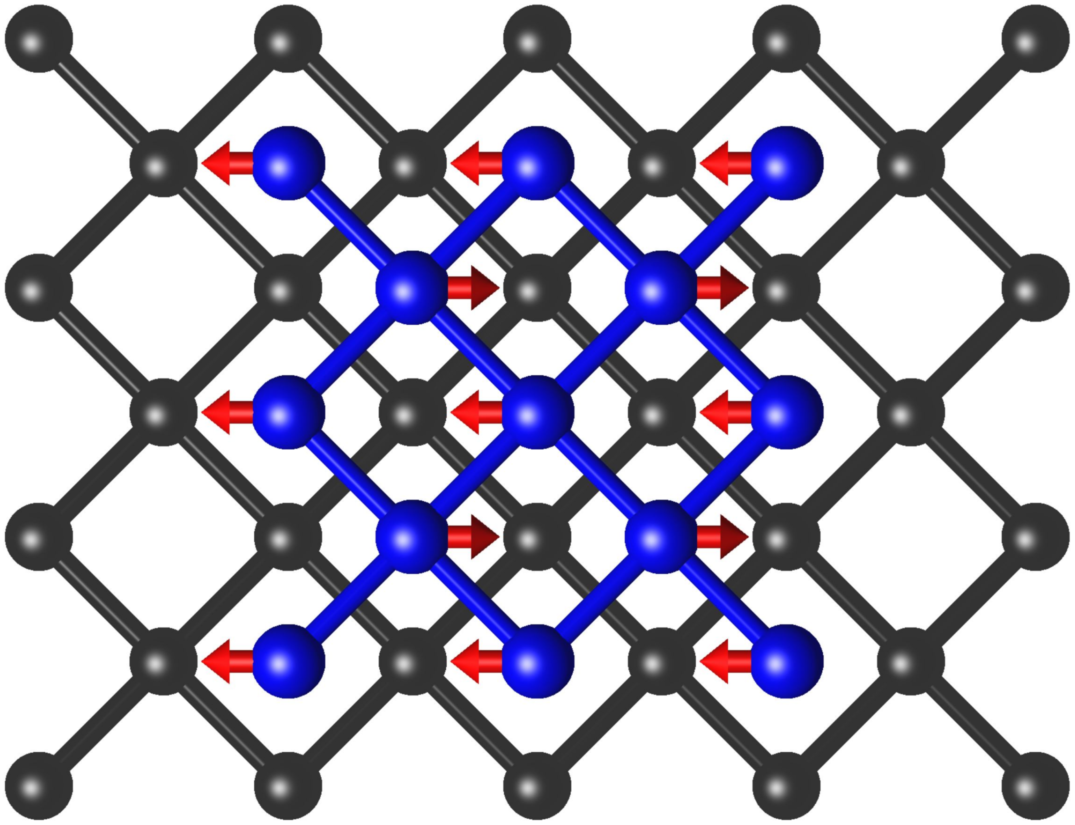
Laser

$\omega_L = 2.52$ THz

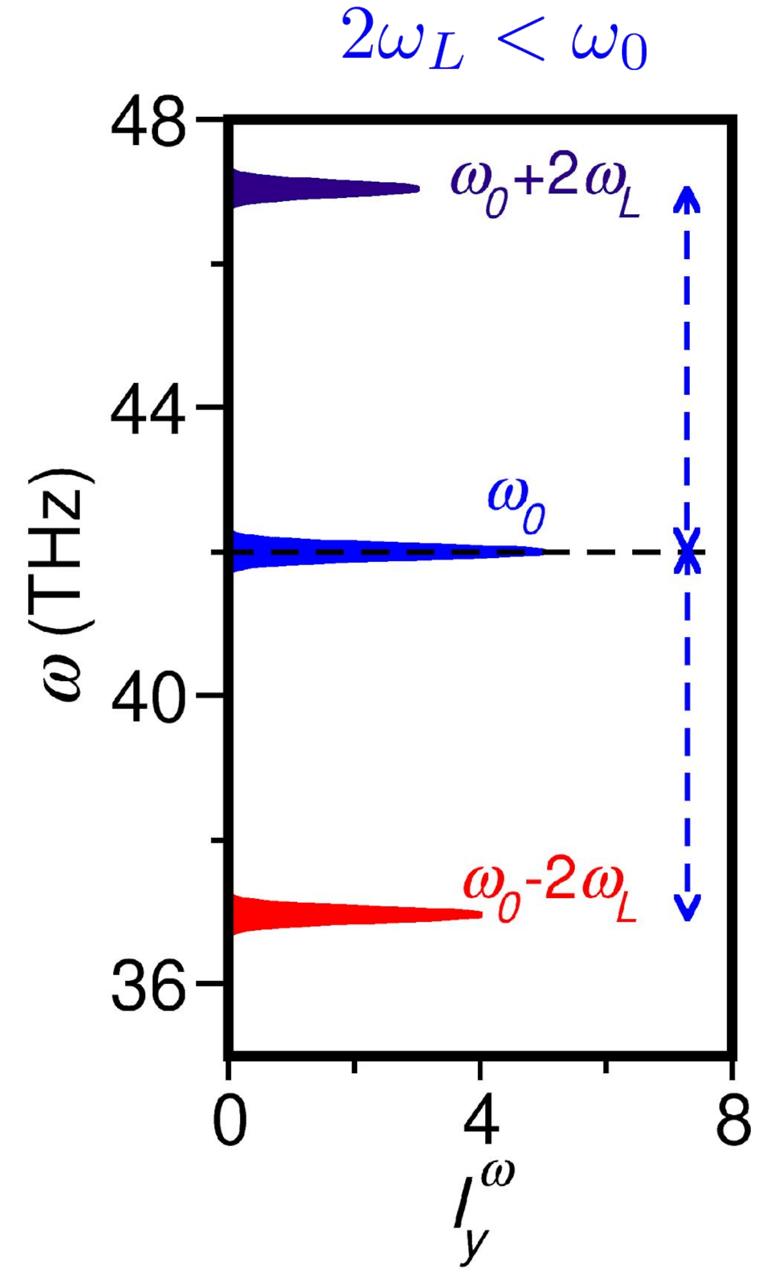


*Commercially available

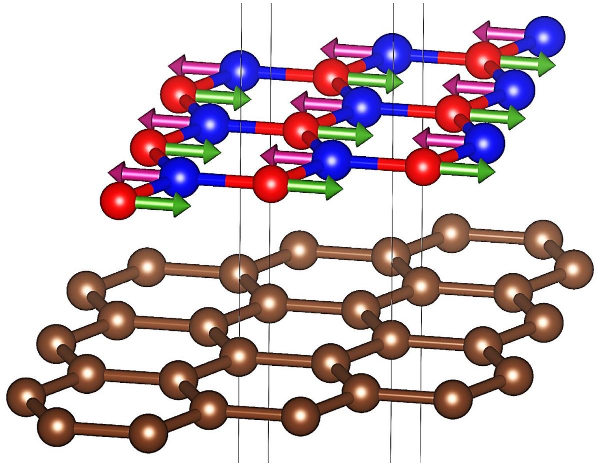




Vibrations of layer 1 couples to the non-trivial quantum electronic geometry of layer 2 through proximal interaction

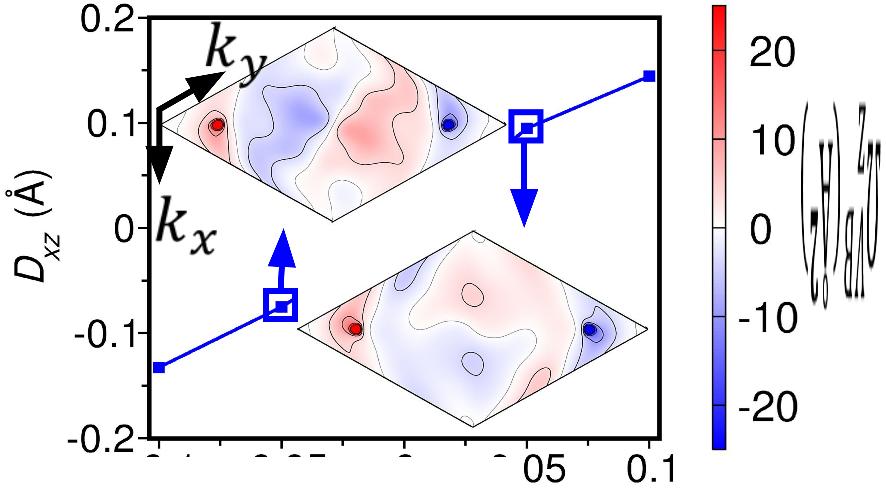


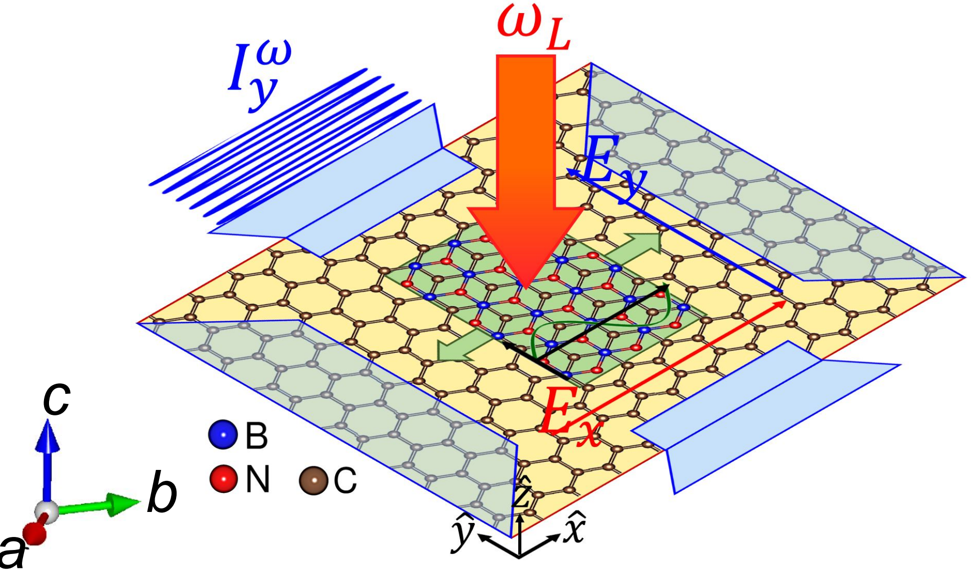
Substrate-induced GQuES activity in aligned gr-hBN



41.9 THz

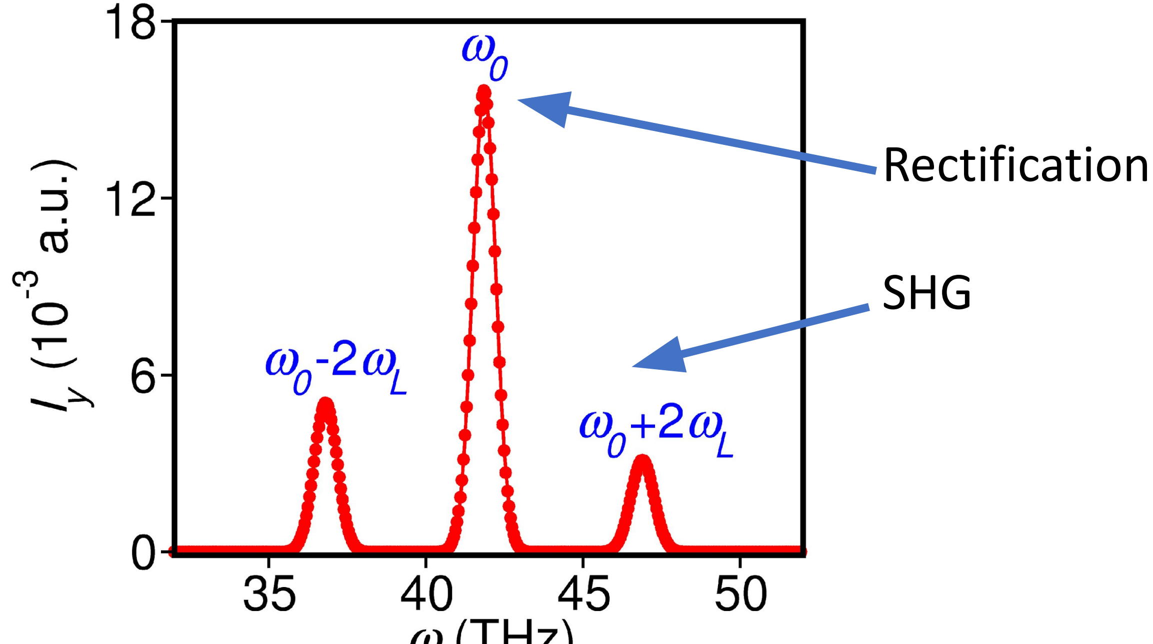
E mode of aligned hBN dynamically lowers the C_{3z} symmetry and induces $D \neq 0$





LASER frequency ω_L=2.52 THz

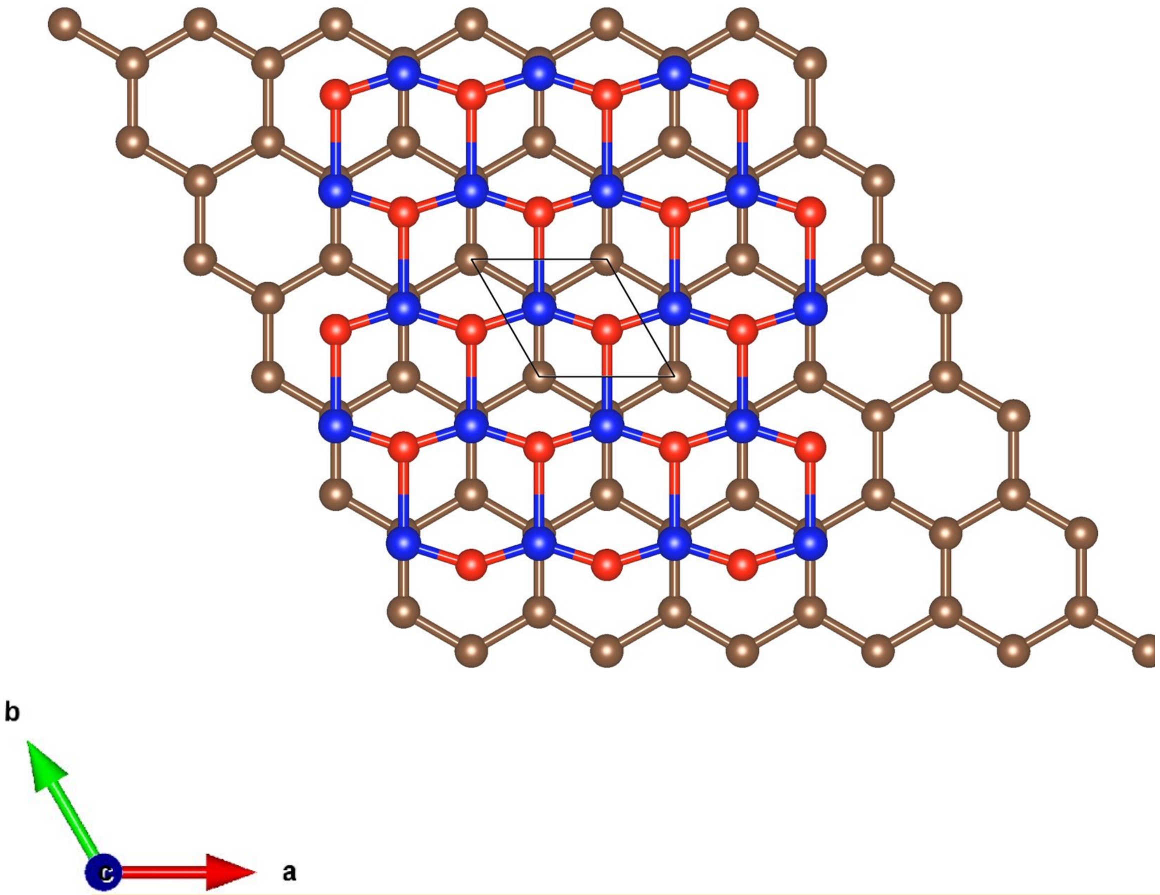
(λ_L=118.9 μm)

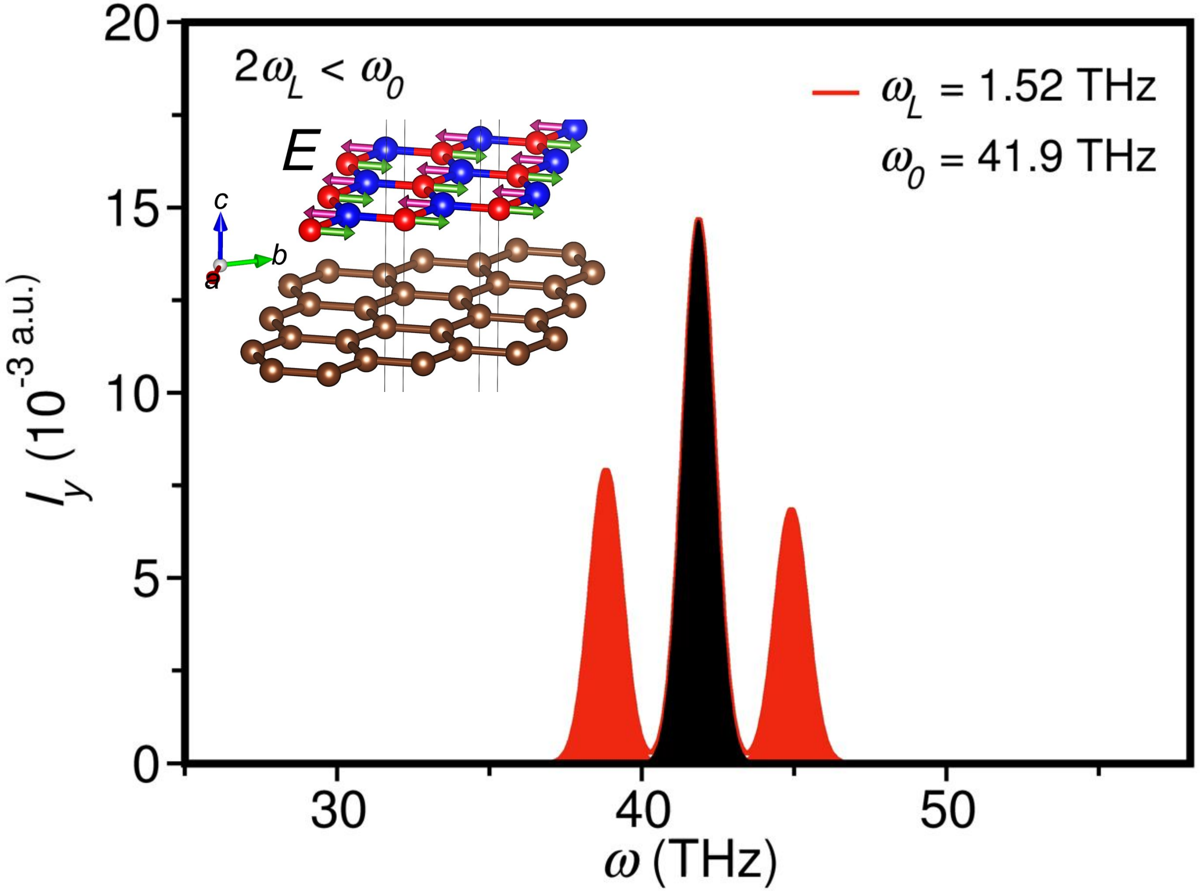


Substrate-based Optical GQuES (THz)

GQuES-active mode in hexagonal-Boron Nitride + GQuES-inert Graphene (non-trivial geometry)

E mode of hexagonal-Boron nitride

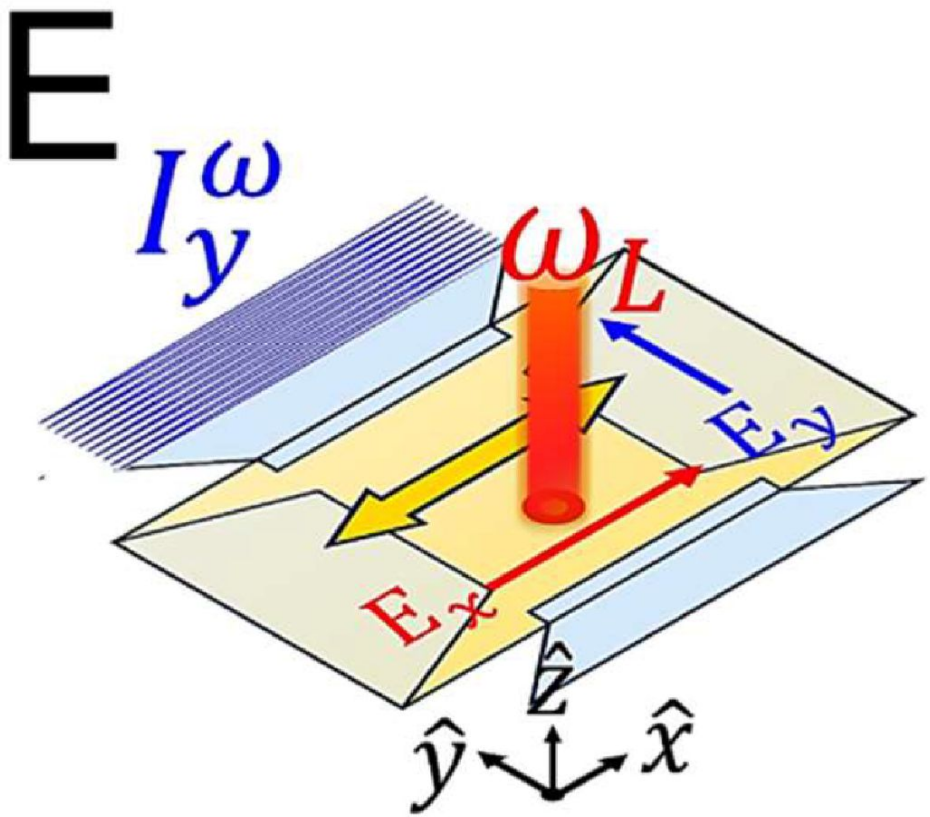




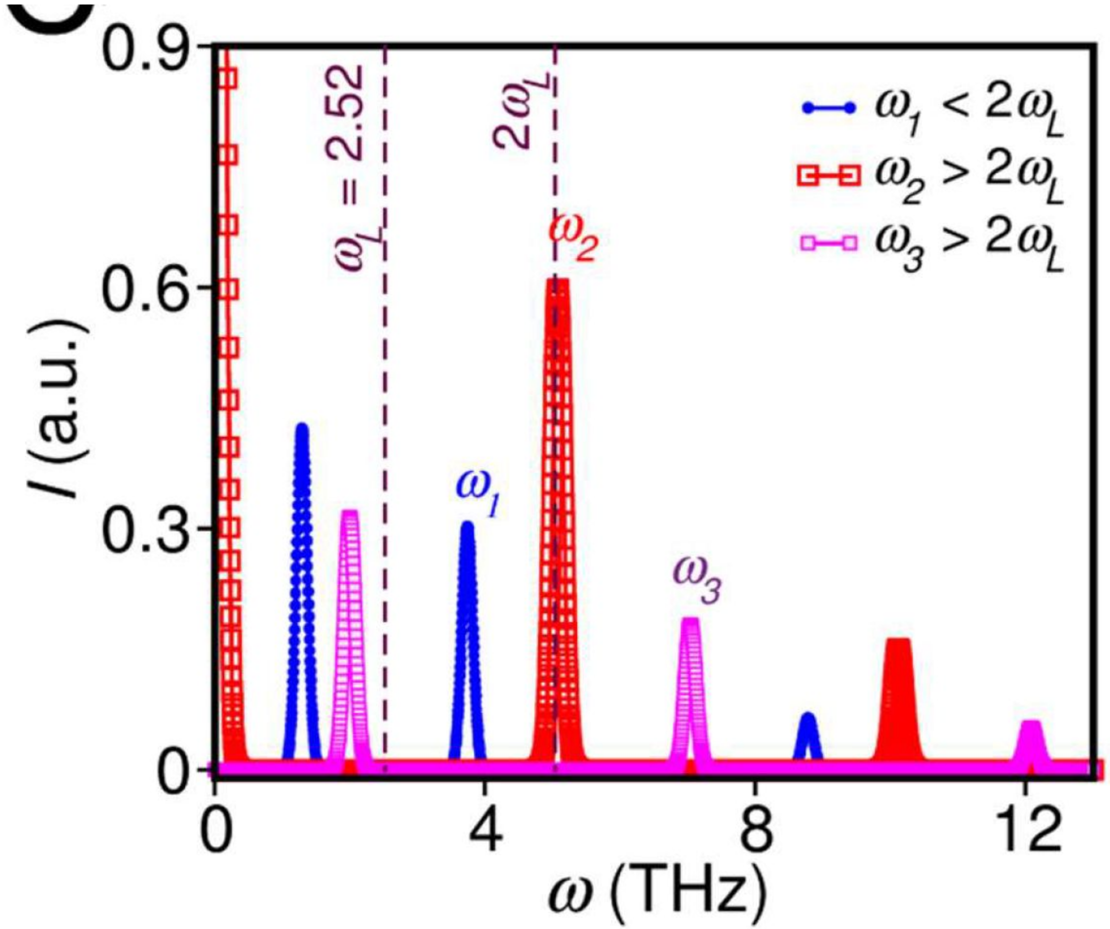
Application of quantum materials, like Graphene, as substrate in GQuES

GQuES spectrum of T'-WTe_2

Rich Spectrum



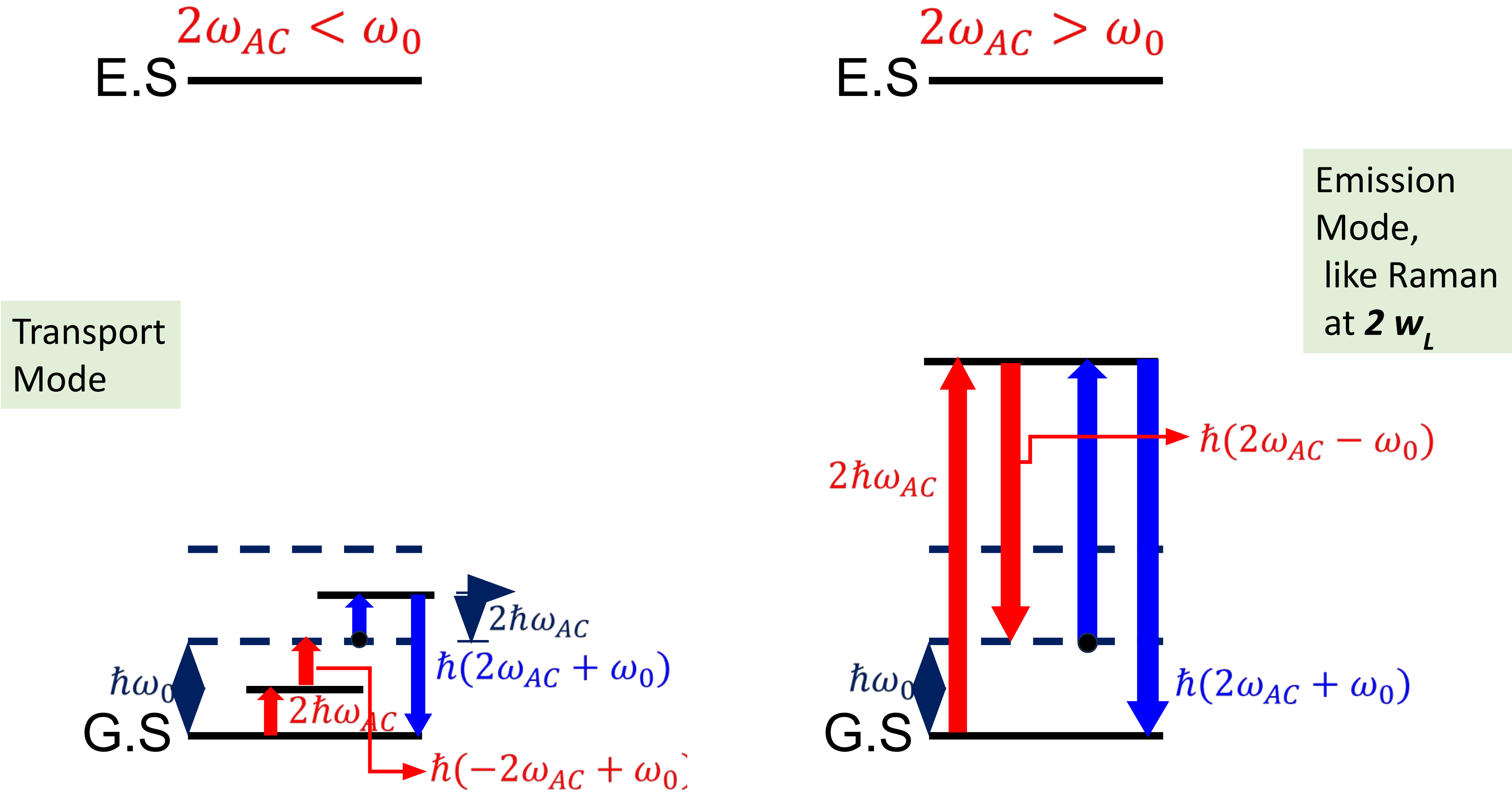
LASER frequency ω_L=2.52 THz
(λ_L=118.9 μm)



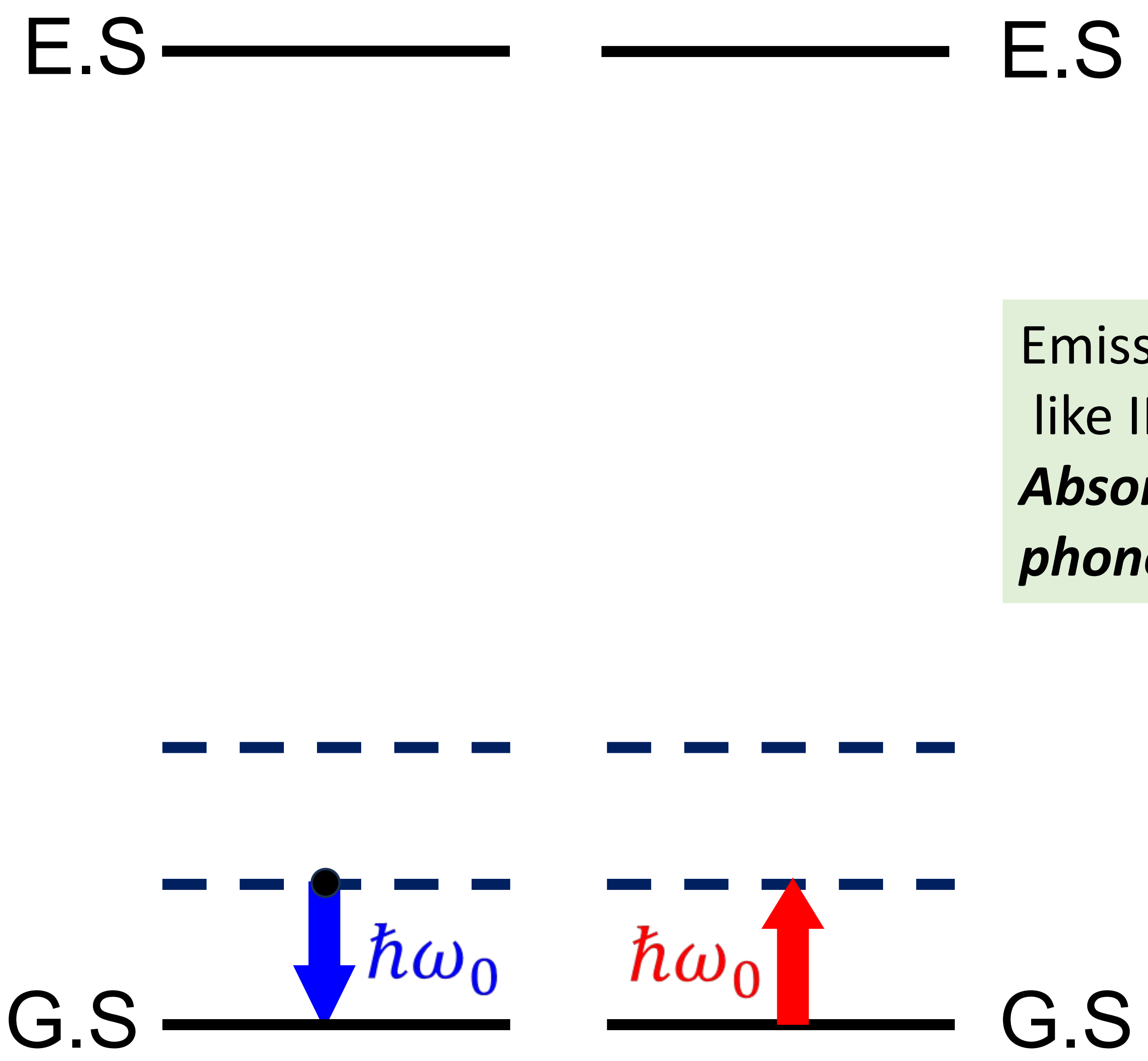
3.74
5.08
7.04
THz

Similarity to IR and
Raman (w_1 Stokes and Antistokes centered at 2 w_L)

Quantum Picture of GQuES



Quantum Picture of GQuES (Rectification)



Emission Mode,
like IR:
Absorption and emission of phonon at w_0

$$\epsilon + \frac{4\pi}{\omega} i\sigma(\omega)$$

$Re[\epsilon]$

Raman

${\sigma^{(2)}}_{xy}$

BCD

GQuES

Sensing Vibrations Using Quantum Geometry of Electrons

R Bhuvaneswari, M M Deshmukh and U V Waghmare, Physical Review B 110, 014305 (2024)

Raman
100 years!

GQuES spectra
Light
Circuit $w_L = w_{AC}$

Summary

- Introduced **GQuES vibrational spectroscopy**: transport and emission modes
  Combines capabilities of IR, Raman and Brillouin

- May be generalized to *other dynamical excitations* (eg magnon, plasmon)

- Quantum Geometry ideas applicable to wider set of systems, including 3D crystals

R Bhuvaneswari, M M Deshmukh and U V Waghmare arXiv: 2403.05872 (2024)

Physical Review B 110, 014305 (2024)

Acknowledgements

R Bhuvaneswari (JNCASR)
Pawan Kumar (JNCASR → UNIST)

Arpita Paul (IIT Jammu)

Mandar Deshmukh (TIFR)

J Sun, John Perdew and Group (Temple)

Hyun Jae Lee, Jun Hee Lee and Group (UNIST)

THANK YOU!