Computational Physics and Chemistry of Phonons

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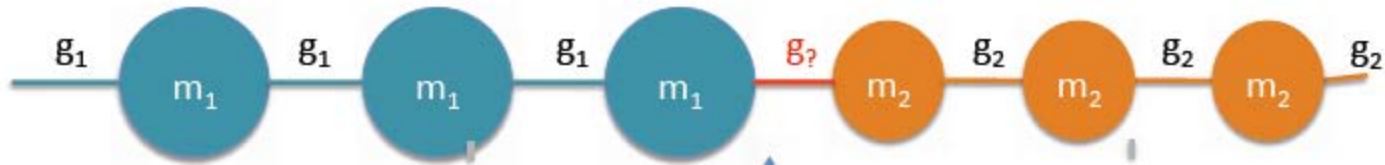**Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560 064**

http://www.jncasr.ac.in/waghmare

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Applications of
Density Functional Theory:
Computational Materials Science

Goal *[Tutorials + Lab Exercise]:*

To understand theoretical background and
practical aspects of first-principles calculations of
structure and **phonons** in bulk and nano-scale
materials: provide non-empirical inputs to
nano-electronics and nano-phononics,
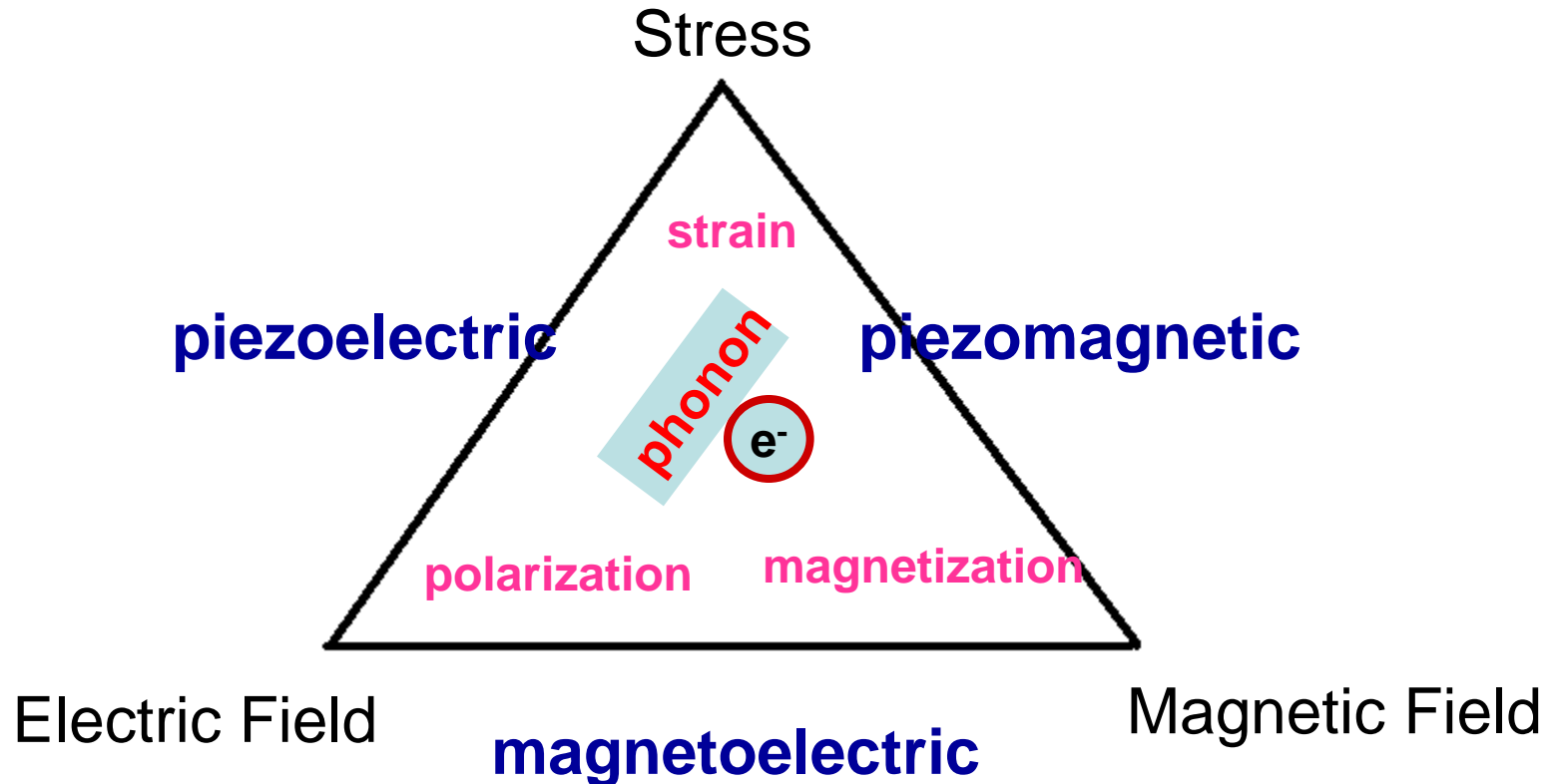use through *nanohub*.

Outline

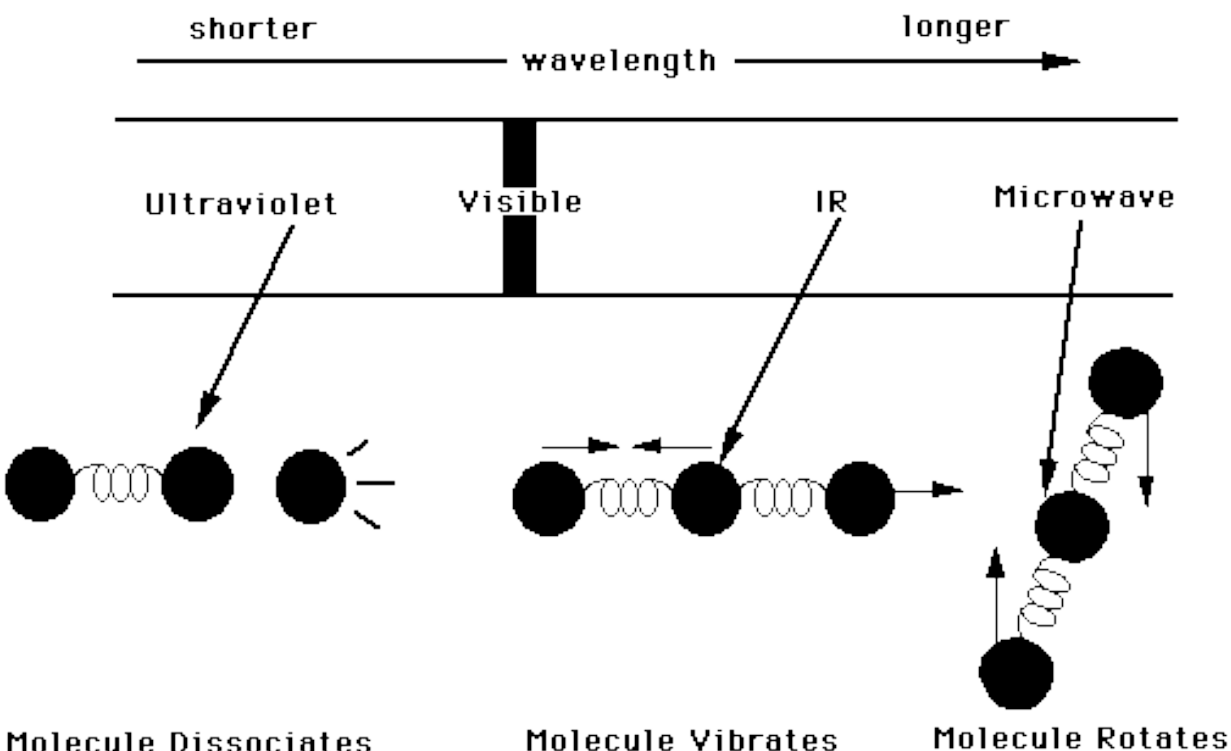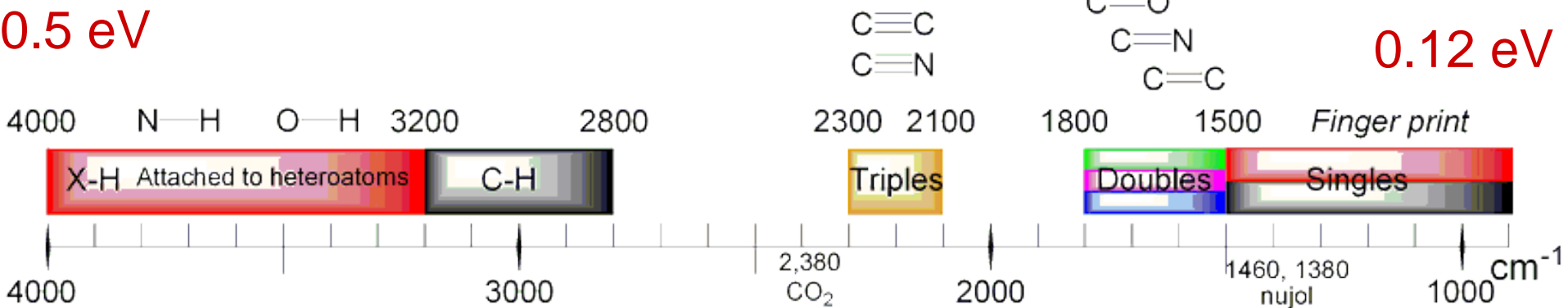Introduction: Phonons, soft modes
Introduction: Computational Materials Science
First-principles Density Functional Theory

Important Fields and Couplings in *smart functional materials*

Introduction: *Vibrations*

0.5 eV

C≡C
C≡N

C=O
C=N
C=C

0.12 eV

4000	N—H	O—H	3200	2800		2300	2100	1800	1500	*Finger print*

X-H Attached to heteroatoms   C-H   Triples   Doubles   Singles

4000   3000   2,380   2000   1460, 1380   1000 cm⁻¹
                            CO₂   nujol

shorter → wavelength → longer

Ultraviolet   Visible   IR   Microwave

Vibrational frequency:
ω ~ measure of
   stiffness of a
   bond

Molecule Dissociates   Molecule Vibrates   Molecule Rotates
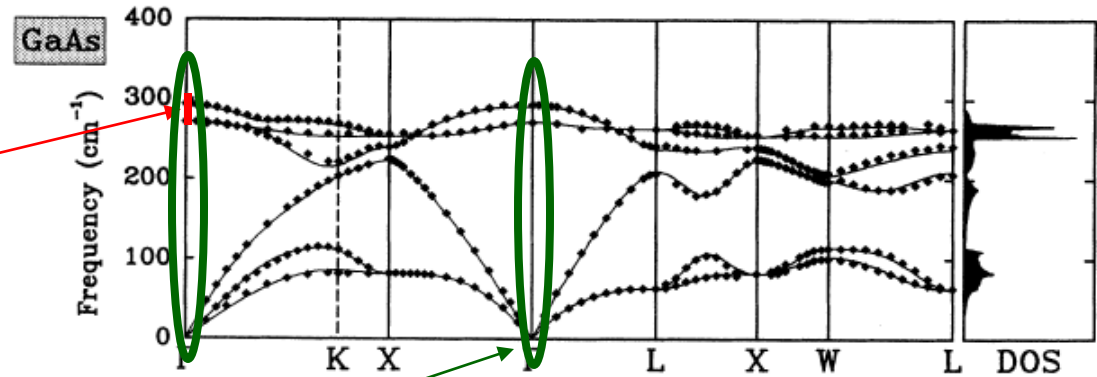
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Vibrations of a Crystal

Infinitely many bonds and
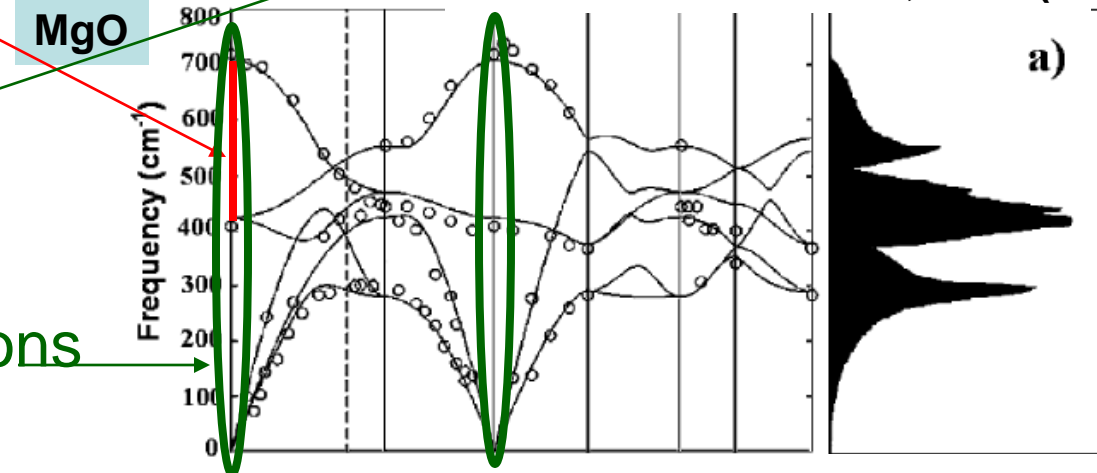 vibrational modes:
Bloch vector k = $\frac{2\pi}{\lambda}$
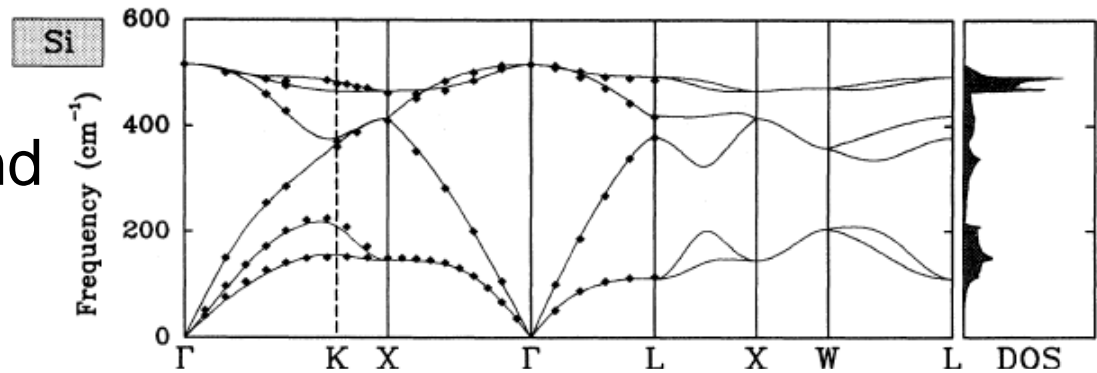
LO-TO splitting:
 measure of coupling
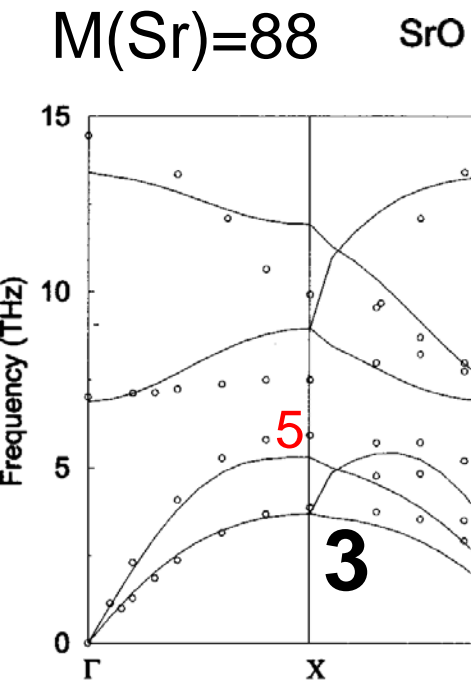 with electric field
 screened by electrons

IR and Raman
Spectra:
long wave-length phonons

Giannozzi et al PRB 43, 7236 (1991).

Ghose et al, Phys Rev Lett 96, 035507 (2006).

MgO — M(Mg)=24

CaO — M(Ca)=40

SrO — M(Sr)=88
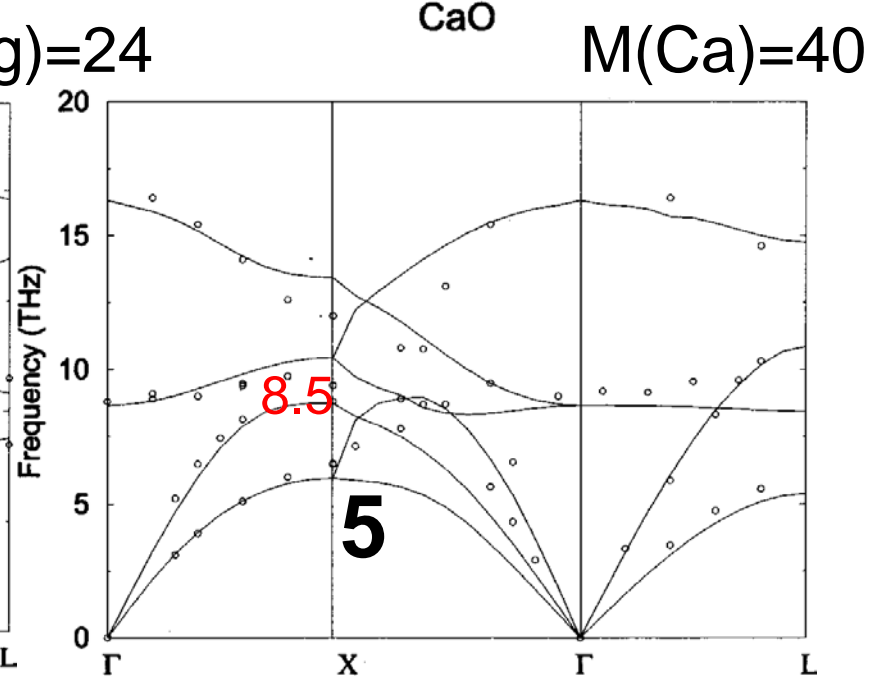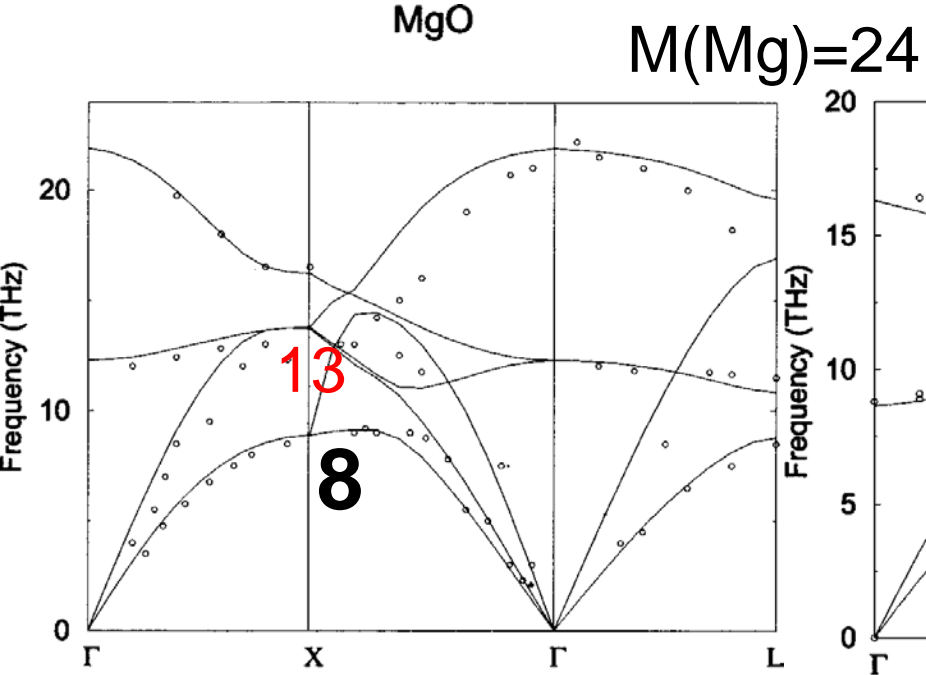
Wu and Ceder, JAP 89, 5630 (01)

Gupta et al, SRX Mat Sc (2010)

	C_{11}(GPa)	C_{12}(GPa)	C_{44}(GPa)
MgO	299	96	157
CaO	221	58	80
SrO	172	45	56
BaO	121	50	38

Vibrational spectra:
Finger-print of a material

Eg. Graphene: use of Raman to characteize
no of layers, disorder, level of doping

Can you hear the shape of a drum? - Feynman

The α-β; Transformation of Quartz
C. V. RAMAN & T. M. K. NEDUNGADI

Abstract
In the hope of obtaining an insight into these remarkable phenomena, a careful study has been made of the spectrum of monochromatic light scattered in a quartz crystal at a series of temperatures ranging from that of liquid air to nearly the transition point. Significant changes are observed which are illustrated in the accompanying illustration, reproducing part of the spectrum excited by the 4358 A. radiation of the mercury arc.

W

Tc

T

Soft mode
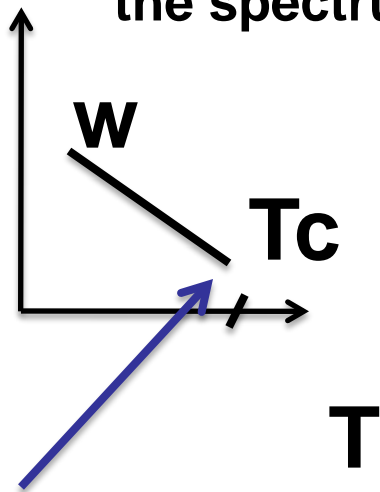
The behaviour of the 220 cm^{-1} line clearly indicates that the binding forces which determine the frequency of the corresponding mode of vibration of the crystal lattices diminish rapidly with rising temperature. It appears therefore reasonable to infer that the increasing excitation of this particular mode of vibration with rising temperature and the deformations of the atomic arrangement resulting therefrom are in a special measure responsible for the remarkable changes in the properties of the crystal already mentioned, as well as for inducing the transformation from the α to the β form.

C V RAMAN
T M K NEDUNGADI

Department of Physics
Indian Institute of Science, Bangalore
11 December

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Soft **Modes**

Vibrational modes of frequencies < 100 cm^{-1} (hv < 12.5 meV)

Analogy with electrons at or near the Fermi energy

Relevance to low-energy / temperature phenomena

Smaller the frequency, greater is the response:

k_{hard}

q

$k_{soft} < k_{hard}$

k_{soft}

Soft m

E

d

Electric Field
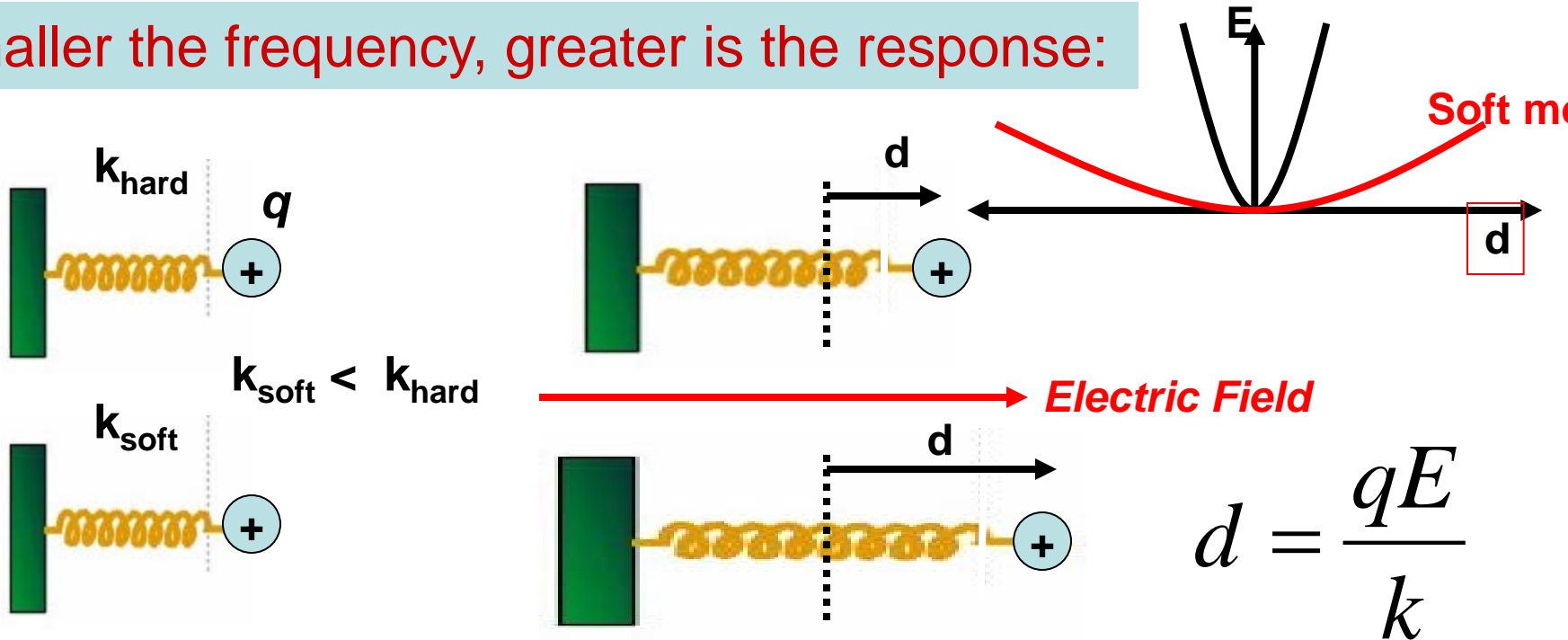
$$d = \frac{qE}{k}$$

$$k \sim w^2$$

HARD Materials: B > 0.10 B$_{Diamond}$

Soft **Modes (contd)**

Vibrational modes of frequencies < 100 cm⁻¹ (hv < 12.5 meV)
Relevance to Temperature Dependent STABILITY

Lower the frequency, greater is the entropy and lower free energy:
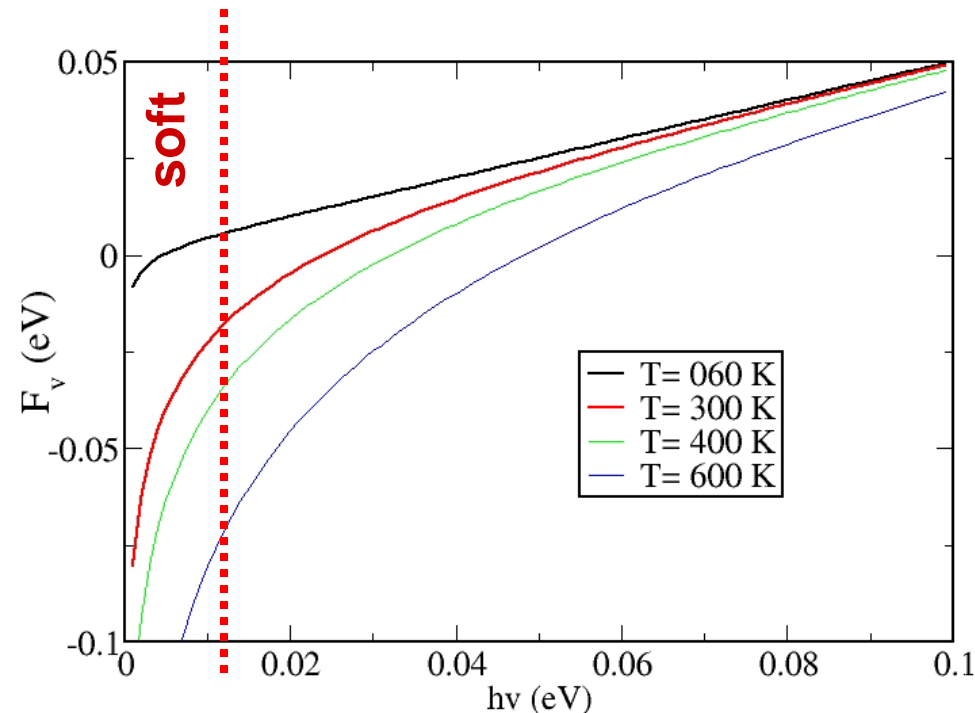
$$F_{vib} = + k_B T \sum_{iq} \log \left[2 \sinh \left(\frac{\hbar \omega_{iq}}{2 k_b T} \right) \right]$$

Soft modes give lower free
 energy particularly as T increases

Effects of anharmonicity are large:
T-dependent structural transitions.

soft

	T= 060 K
	T= 300 K
	T= 400 K
	T= 600 K

Determination of phonon dispersion

First-principles Simulations [T=0 K]

1. Obtain K-matrices at various wave-vectors (q) in the Brillouin zone using DFT-linear response
2. Use iFourier series to transform K(q) to K(R) = real-space force constant matrices
3. Use Fourier series to obtain K(q) at arbitrary wave vector q
4. Eigen-spectrum of $D(q)=K/\sqrt{(M_i M_j)}$ gives *all* phonons!

Experiment

1. **First-order Raman: some optic phonons at $q \rightarrow 0$**
2. **Second-order Raman: in-principle all phonons, not dispersion**
3. **Brillouin spectroscopy: Acoustic phonons at $q \rightarrow 0$**
4. **Neutron scattering: phonon dipsersion w(q), eigenvectors may not be accessible.**

Introduction to First-principles Density Functional Theory
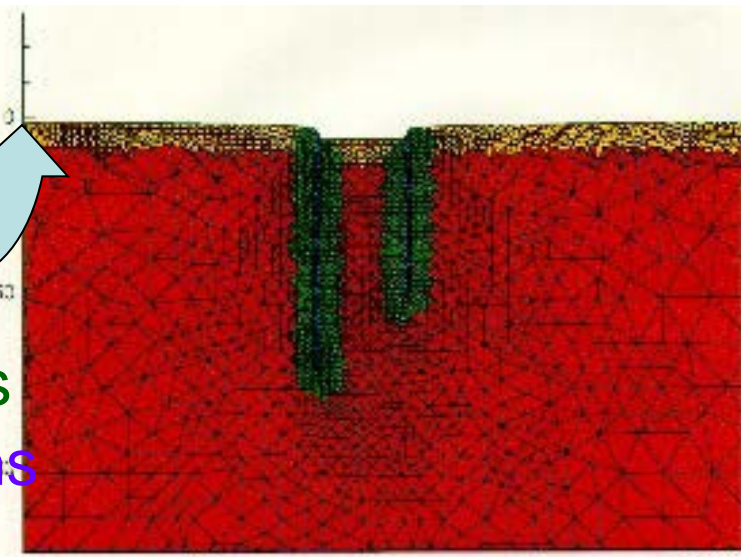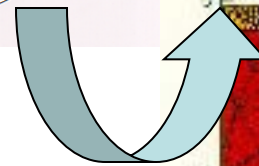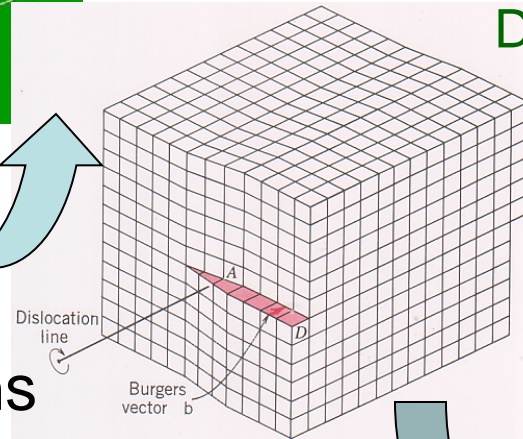
Theoretical and Computational Materials Science

"First-principles" or "*Ab Initio*"

Electronic orbitals,
Nuclei, vibrations Material-specific microscopic info
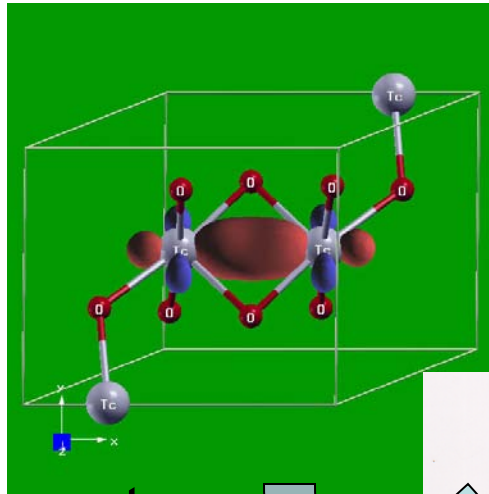
Defects, eg. grains, dislocations

Sub-angstrom

Intermediate-scale
structure: properties

Nano-m, microns

Dislocation line

Burgers vector b

μ, mm

Continuum analysis

Landau-theory Devices, applications

INTRODUCTION: Computational Materials Science

- Diversity in the Solid State
  * Chemical constitutents: example, Si and C
           Combination of elements: *complex* materials
  * Structure:example, graphite, Fullerene and diamond
           Size, scale

- *Change (transition) from one state to another*
  Change in Symmetry
   --- Signatures in material properties
  Advanced Materials: are on the edge of many such transitions !

- *Design of New (better) Materials and*
           Structures of reducing size need:
  * Microscopic understanding
  * Atomistic Modeling   } **Reduce the phase space of exploration/design**

Theoretical Model of Materials

Capture both *material-specific* and *universal* properties

Goals:

1. Identify microscopic mechanisms
2. Complement experimental probes
3. Predict new materials or structures

Ingredients:

Electrons: Need Quantum Mechanics

   Interacting many-body problem

   Approximate ground state: Density Functional Theory

   * *Not-so-good* for strongly correlated systems

Nuclei: Often classical mechanics suffices

   * Needs the inter-atomic potential

Electrons and nuclei interacting via Electromagnetic fields

P. A. M. Dirac (1929)

"The underlying physical laws necessary for 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".

Proc. Roy. Soc. (London) A123, 714 (1929).

Born-Oppenheimer Approximation

If I had access to an *infinite* computer, I would solve *H* quantum mechanically:

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i \neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I \neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

$H_e(Z_I, R_I)$

Very small, because $M_I \gg m_e$.

Classical term: $E_c(R_I)$

e: Ground state   **$H_e(Z_I, R_I)\ \Psi_G(Z_I, R_I) = E_G(Z_i, R_i)\ \Psi_G(Z_I, R_I)$**

$E_{total}(Z_I, R_I) = E_G(Z_i, R_i) + E_c(Z_I, R_I)$

E_{total} **has all the material-specific information** *except for electronic excitations.*
E_G is the part that is hard to determine!

Energy Function: $E(d_i, Z_i)$

T=0 properties:

Structure: Min $E_{total}(d_i, Z_i)$
$\{d_i\}$

E

d
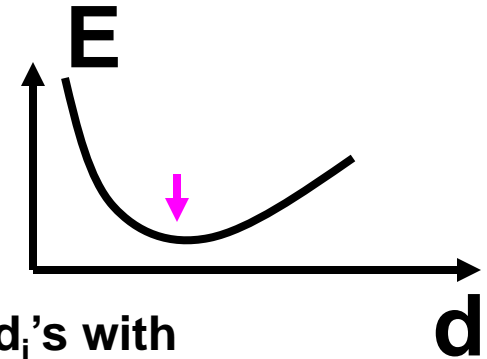
Energy can be written as a Taylor expansion in d_i's with
the minimum energy structure as a reference: $E_0 + \sum K_{ij} d_i d_j$
+ …

Symmetry principles: E has to have the symmetry of the minimum energy
structure
Restrictions (symm. properties) on K follow naturally.

$E_{total}(d_i, Z_i)$: *Hamiltonian* governing the motion of nuclei
: Inter-atomic potential
: Force – field $F_i = - \partial E_{tot} / \partial d_i$

Various external fields coupling with a material:
Electric field (E), Magnetic Field (H) and Stress (σ)
conjugate material properties:
Electric Polarization (P), Magnetization (M) and strain (ε)
are all related to first derivatives of E_{total} with respect to fields.

Example: O₂ molecule

E

Bond length

Cohesive energy

$$K = \frac{\partial^2 E}{\partial d^2} \bigg|_{d=d_0}$$

E=E$_c$+(1/2) K (d-d$_0$)²

$$E = E_c + (1/2)\, K\, (d-d_0)^2$$

vibrational frequency
w = √(K/M)

20
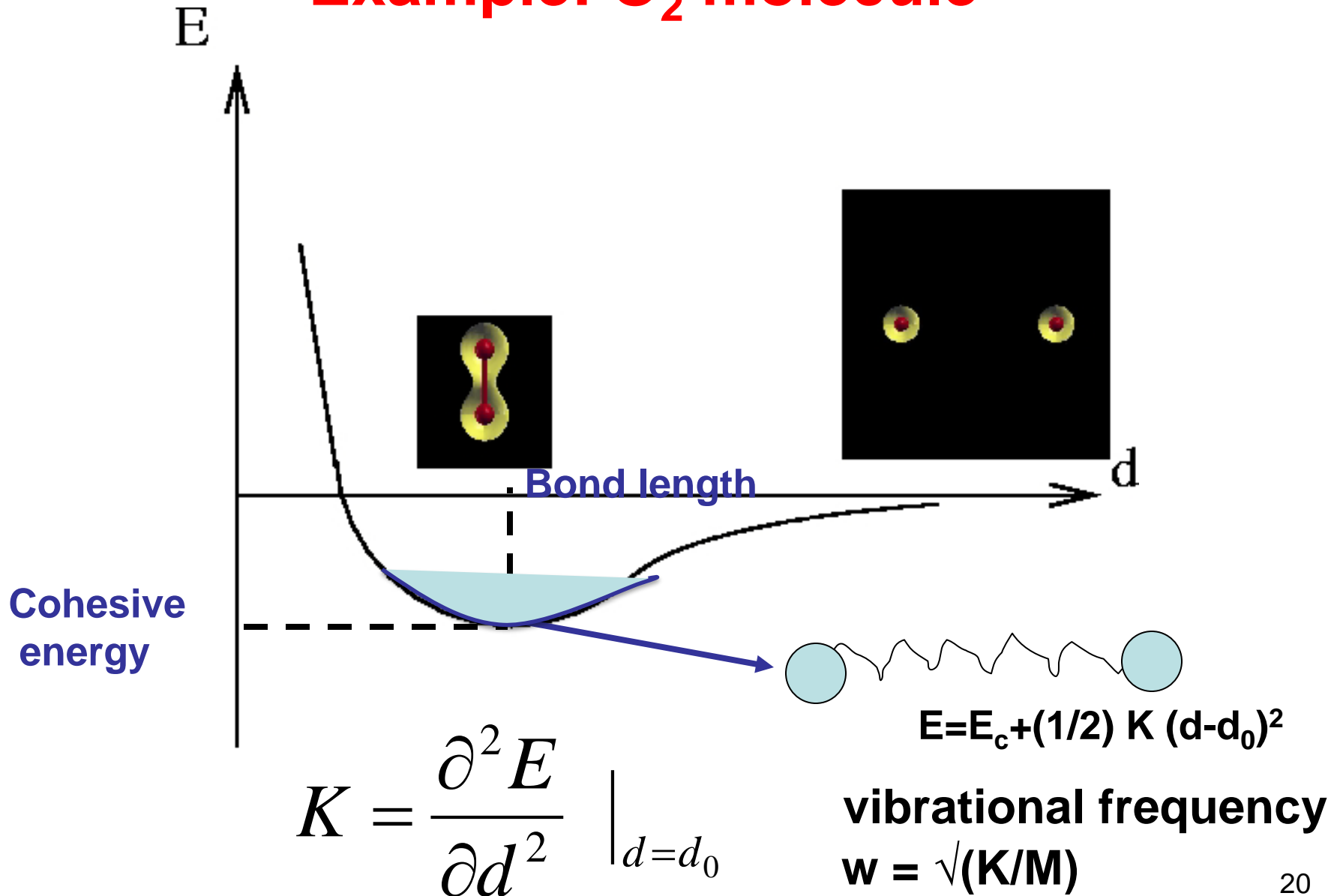
Energy Function: $E_{total}(d_i, Z_i) = E_G + E_c$

T≠ 0 : $E_{total} \rightarrow$ tools of statistical mechanics $\rightarrow$ free energy F

| Second derivative of E_{tot} or F wrt	Physical property
d_i, d_i (atomic displacement)	Force spring const: phonons
E, E (E-field)	Dielectric constant
ε, ε (strain)	Elastic constant
E, ε	Piezo-electric constant
E, d_i	Born Dynamical charge
ε, d_i	Strain-phonon coupling
H, H (magnetic field)	Magnetic susceptibility
E, H	Magneto-electric constant
H, ε	Piezo-magnetic constant

Energy: Symmetry Principles

Energy of a system can not change when it is transformed with its symmetry. Eg. H_2O molecule

Reflection plane σ

$$E([H_2O]) = E(\sigma \cdot [H_2O])$$
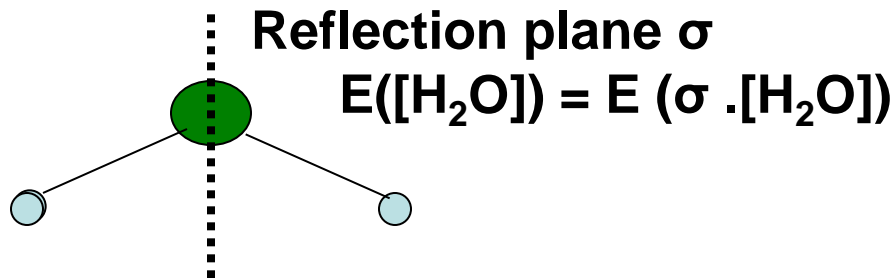
Energy of a system ↔ Hamiltonian of the system: statics and dynamics

Derivatives of energy: properties of the system
 symmetry restriction on energy   symmetry restriction on properties!
 eg. Dielectric constant of a cubic crystal: $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz}$

of a tetragonal crystal: $\varepsilon_{xx} = \varepsilon_{yy} \neq \varepsilon_{zz}$

Energy Function: $E(d_i, Z_i)$ (contd)

T ≠ 0 properties: statistical mechanics

Free energy

$$F(T, V) = - k_B T \, \text{Log} \int dR_I \, \text{Exp}(-E_{total}(Z_I, R_I)/k_B T)$$

Derivatives of Free energy ↔ Physical properties at finite T

It seems that E_{total} should be adequate to determine all the macroscopic properties of a material!

Except those which involve excitation of electrons (eg. Optical spectra)

Born-Oppenheimer approximation does break down (rarely):

Eg. explosion of RDX under pressure

How to access $E_{total}(Z_I, R_I)$?

1. Empirical approach: Have Nature solve all the equations!

2. First-principles approach: Have a computer solve all the equations!

Energy Function:

Empirical	First-principles
eg interatomic potential, MM	eg. density functional theory based methods
Cost: LOW	Much higher
Accuracy: Good in properties used in fit	Uniformly good
Applicability: Simple cases-elements	General
Many parameters eg. Si: 13 parameters	Parameter-free
	Unbiased, Reliable, great predictability!

Atomic Number of Elements in the solid, Structure	▷	Quantitative Information on Material-specific Properties

Microscopics, Chemical Trends   Macroscopic Bahavior