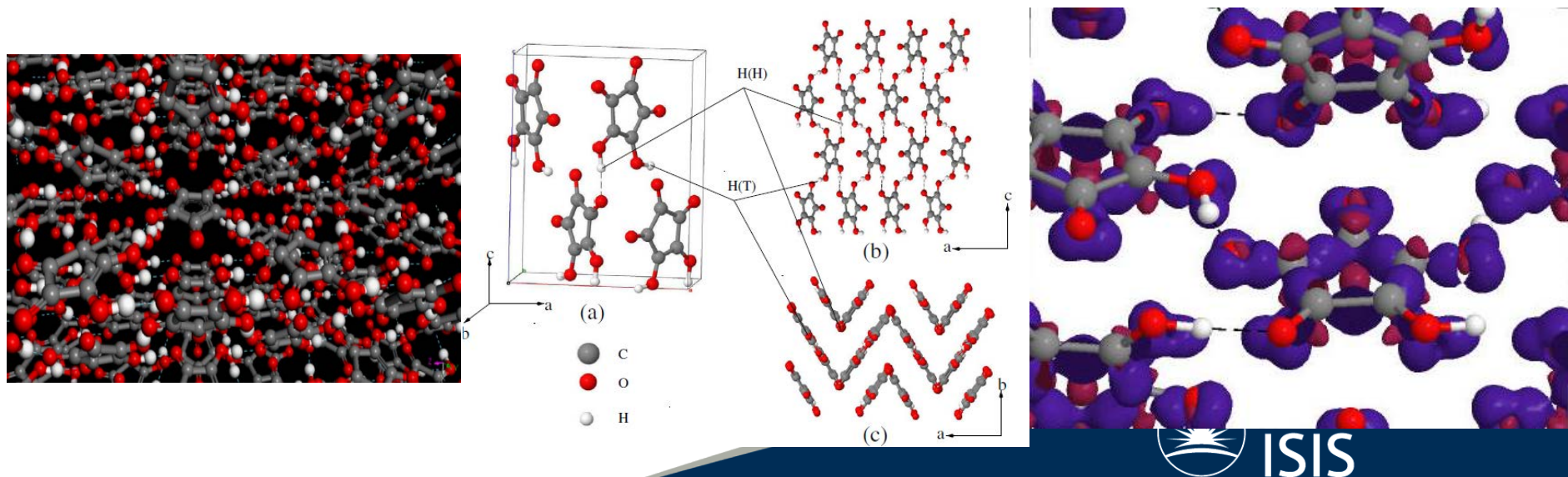# Introduction to Electronic Structures and Lattice Dynamics
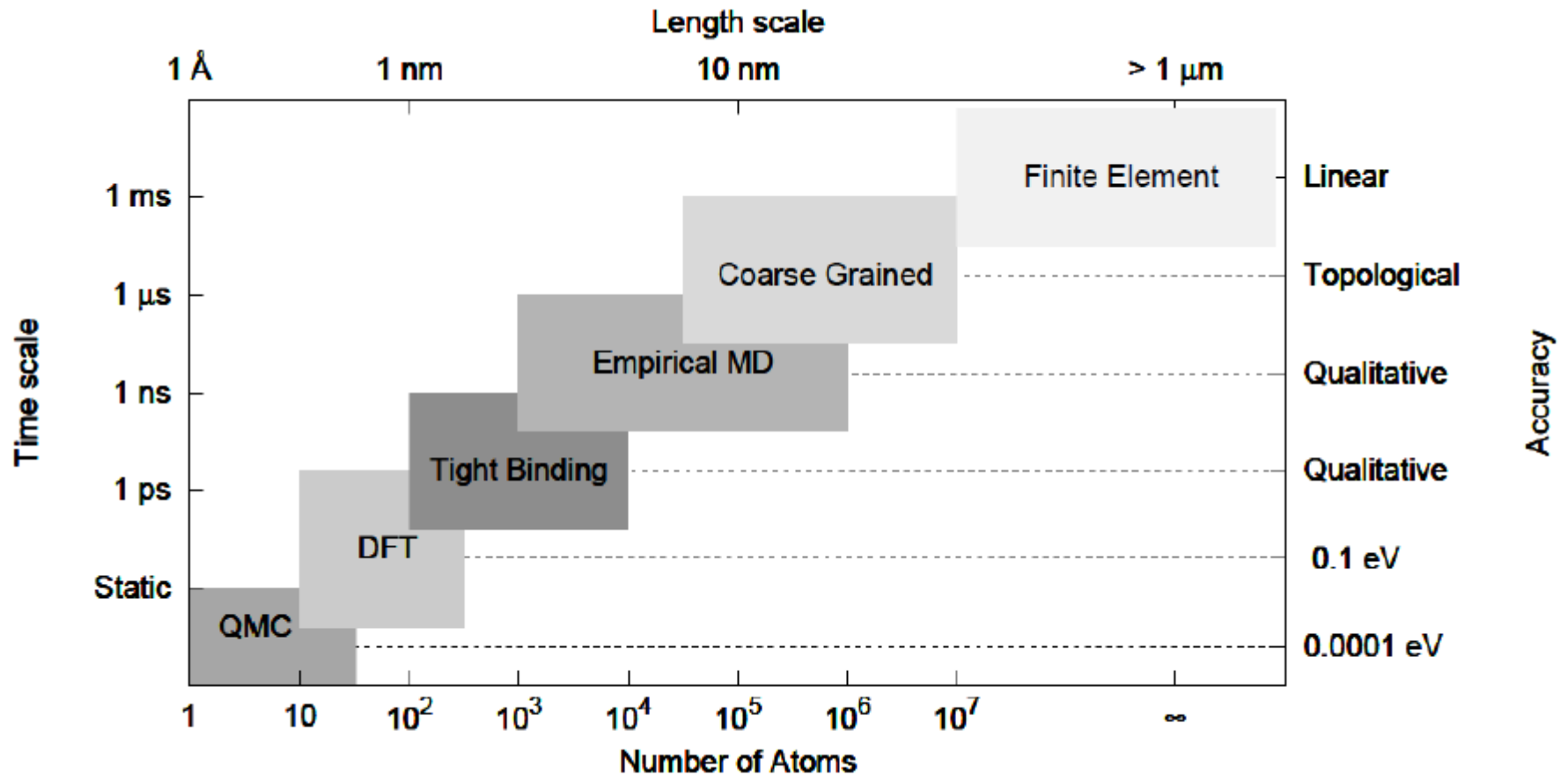
Sanghamitra Mukhopadhyay

ISIS Facility, STFC Rutherford Appleton Laboratory Oxfordshire
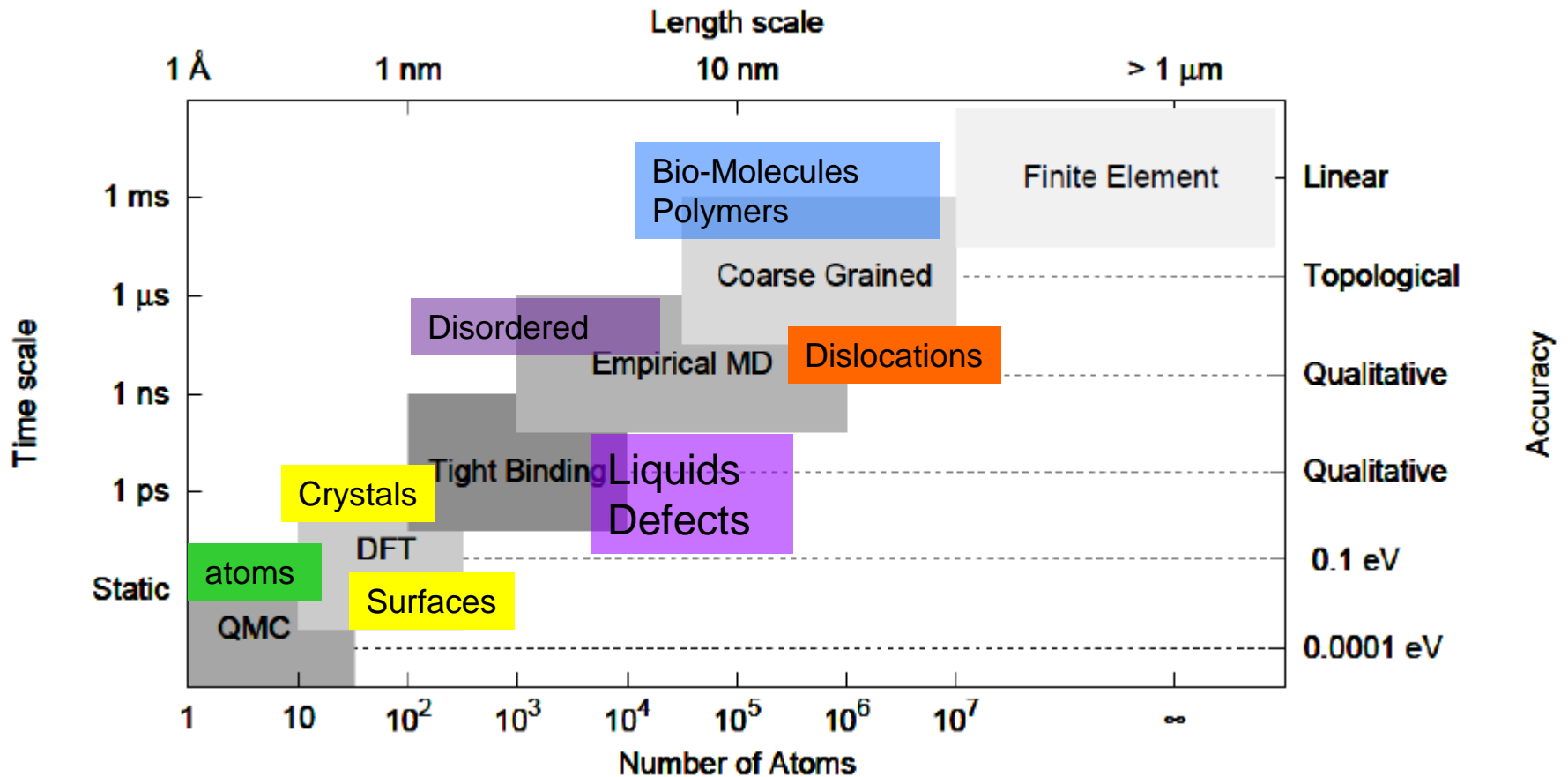

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Level of Approximations

Comparison between computational costs, accuracy and generality

Multiscale simulations in Mat. Sc., J. Grotendorst et al., NIC Series, Vol 12 (2009).

Level of Approximations

Comparison between computational costs, accuracy and generality

Alphabets of the Materials World
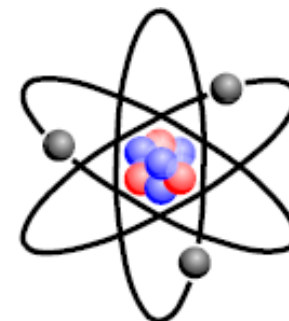
Properties depend on electronic structures

Essential Ingredients of Electronic Structures

- Consider nucleus as point mass with positive charge
- Consider each electron as point mass with negative charge
- Apply Coulomb's interactions between nucleus-electron, electron-electron
- Apply force law, laws of motion, conservation of energy, momentum

$$
\hat{H} = \overbrace{\hat{T}_n}^{\text{Nucl. kin. energy}} + \overbrace{\hat{T}_e}^{\text{Elec. kin. energy}}
$$
$$
+ \underbrace{\hat{v}_{ne}}_{\text{Elec.-nucl. attraction}} + \underbrace{\hat{v}_{ee}}_{\text{Elec.-elec repulsion}} + \underbrace{\hat{v}_{nn}}_{\text{Nucl.-nucl repulsion}}
$$
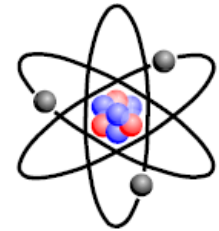
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Essential Ingredients of Electronic Structures

- Consider nucleus as point mass with positive charge
- Consider each electron as point mass with negative charge
- Apply Coulomb's interactions between nucleus-electron, electron-electron
- Apply force law, laws of motion, conservation of energy, momentum

$$\hat{H} = -\sum_{a=1}^{No} \frac{\hbar^2}{2\,\mathbf{M_a}} \vec{\nabla}^2_{\vec{R}_a} - \sum_{i=1}^{N} \frac{\hbar^2}{2\,\mathbf{m_e}} \vec{\nabla}^2_{\vec{r}_i}$$

$$-\frac{e^2}{4\pi\epsilon_0} \sum_{a=1}^{No} \sum_{i=1}^{N} \frac{Z_a}{|\vec{R}_a - \vec{r}_i|} + \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{j=1}^{i-1} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{e^2}{4\pi\epsilon_0} \sum_{a=1}^{No} \sum_{b=1}^{a-1} \frac{Z_a Z_b}{|\vec{R}_a - \vec{R}_b|}$$

Solving the Schrödinger equation for Many-body Electron System

Schrödinger equation:

$$\hat{H}\Psi = E\Psi$$

$$\frac{-\hbar^2}{2m_e}\Psi + \hat{V}\Psi = E\Psi$$

$$\hat{H}_e = \hat{T}_e + \hat{v}_{ne} + \hat{v}_{ee} + v_{nn}$$

$$= \sum_{i=1}^{N}\left[-\frac{\hbar^2}{2\,m_e}\vec{\nabla}_{\vec{r}_i}^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{a=1}^{N_0}\frac{Z_a}{|\vec{R}_a - \vec{r}_i|}\right] + \sum_{i=1}^{N}\sum_{j=1}^{i-1}\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r}_i - \vec{r}_j|} + v_{nn}$$

$$= \underbrace{\sum_{i=1}^{N}\hat{h}_1(\vec{r}_i)}_{\text{simple}} + \underbrace{\sum_{i=1}^{N}\sum_{j=1}^{i-1}\hat{h}_2(\vec{r}_i, \vec{r}_j)}_{\text{difficult}} + v_{nn}$$

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Approximate Solution: DFT

Interacting electrons in an external potential

Non-interacting electrons in an effective potential

These non-interacting electrons are called as Kohn-Sham particles

Approximate e-e interactions with
- Local density approximation
- Generalized gradient approximation
- Hybrid …

Problem is that the exact form of this functionals are unknown.

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Kohn-Sham Equation

$$\left\{\frac{1}{2}\nabla^2 + V_{\text{ext}}(\vec{r}) + V_H(\vec{r}) + V_{\text{xc}}([n(\vec{r})])\right\}\varphi_i(\vec{r}) = \epsilon_i \varphi_i(\vec{r})$$

Electron density $\qquad n(\vec{r}) = \sum_i^{occ} |\varphi_i^2(\vec{r})|$

Hartree energy is the self interaction energy of the density n(r) treated as a classical charge density

Hartree exchange can be calculated exactly, but e-e correlation is unknown

Local Density Approximation

The $\hat{v}_{\text{xc}}[n]$ functionals

- **LDA/LSDA** Local Density Approximation
  $\hat{v}_{\text{xc}}[n] =$ homogeneous $\bar{e}$ gas
  Perdew et Zunger (PZ), Vosko Wilkes and Nusiar (VWN)

  - Easy, fast
  - OK for Fermi $\bar{e}$ of metals

  - Bad for core $\bar{e}$
  - Only local $f(n(\vec{r}))$
    exch.-corr. : non local $f(\vec{r}, \vec{r}')$
  - Self-inter. pb
  - Overdelocalize
  - Underestimates gaps
  - No dispersion forces

Generalised Gradient Approximation

The $\hat{v}_{\text{xc}}[n]$ functionals

- **GGA** Generalized Gradient Approximation
  Add semi-local terms : $f(n(\vec{r}), \vec{\nabla}_{\vec{r}}(n(\vec{r})))$
  Perdew-Burke-Ernzerhof (PBE, PBESOL), Perdew-Wang 91
  (PW91), BLYP, second order (SOGGA), Perdew-Wang (PW),
  Wu-Cohen (WC)

  - A little better than LDA

Hybrid Functionals

The $\hat{v}_{xc}[n]$ functionals

- **Hybrids functionals**
  Mix of LDA - GGA - HF exact exchange
  B3LYP, B3PW, PBE0 and PBESOL0, B1PW, B1WC

  - Good structures
  - Part self-inter. pb
  - Gaps

  - No dispersion forces
  - More costly
  - Cooking recipe

Solving Electronic Structures: Recipe

1ē Hamiltonian $\hat{F}$ depends on its solution $\Rightarrow$ SCF
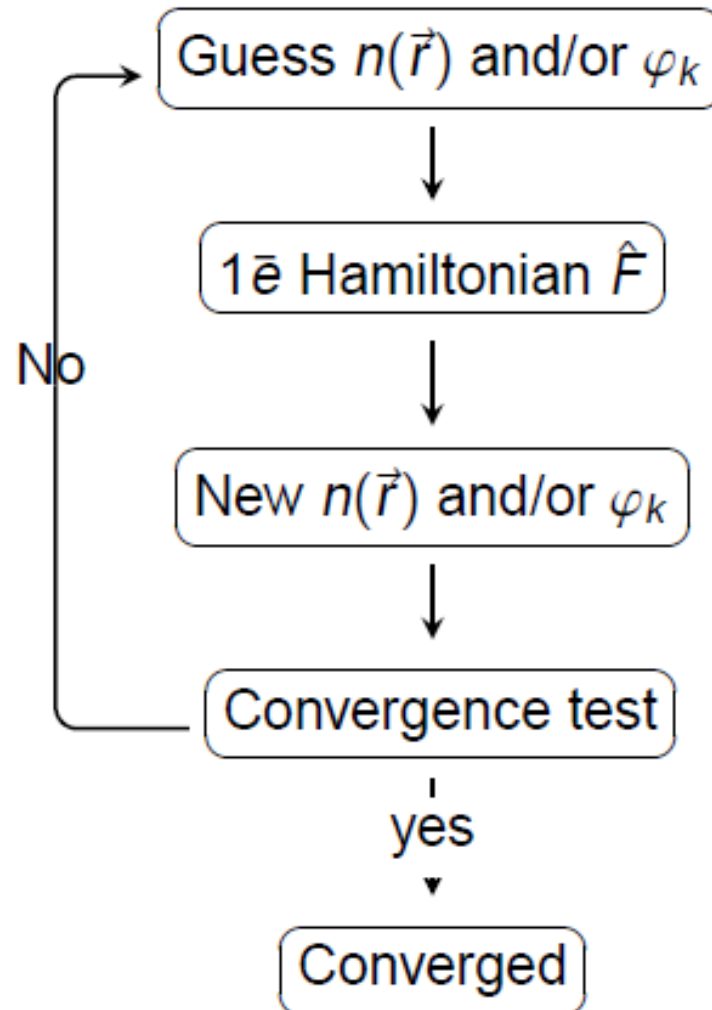
Periodic Solid
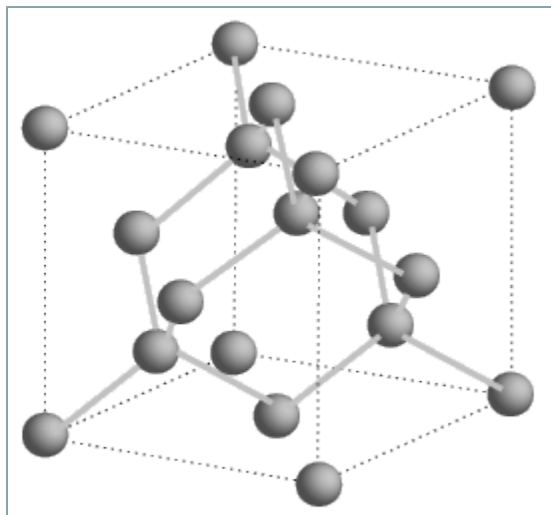
Crystal structure = lattice +basis

Geometry of lattice can be obtained from X-ray or neutron diffraction experiments

Database of CIF files:

National Chemical Database Service

http://cds.rsc.org/

Inorganic Crystal Structure Database

https://www.fiz-karlsruhe.de/de/leistungen/kristallographie/icsd.html

Basis sets

One electron projected on finite basis set

- Plane wave (CASTEP, VASP)

- Linear Combination of Atomic Orbitals (LCAO) (CRYSTAL, GAUSSIAN)

- Atom centered numerical basis set (SIESTA)

Treatment of inner electrons

- Pseudopotentials
- All electrons
- Atomic functions with muffin-tin spheres

Things to Remember

Test numerical parameters

- Type of pseudopotential

- Heavy elements : relativistic corrections

- Plane waves : energy cutoff

- Atomic basis sets : basis set quality

- $\vec{k}$ points convergence

- Metals : smearing temperature

- Phonons : geom. opt. convergence (negative phonons)

Introduction to Lattice Dynamics

Motivations for *ab initio* lattice dynamics I

Motivations from experimental spectroscopy:

· Vibrational spectroscopy is sensitive probe of structure and dynamics of materials.

· IR and Raman have inactive modes

· Hard to distinguish fundamental and overtone (multi-phonon) processes in spectra

· No experimental technique provides complete

Lattice dynamics provides:

· eigenvector information ⇒ mode assignment

· based on similar materials, chemical intuition, guesswork.

· Hard to find accurate model potentials to describe many systems

· Fitted force-constant models only feasible for small, high symmetry systems

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Introduction to Lattice Dynamics

Motivations for *ab initio* lattice dynamics II

Motivations from predictive modelling

- Lattice dynamics (LD) calculation is direct test of stability or otherwise of putative structure

- Thermodynamics: LD can compute zero-point energy (ZPE) and phonon entropy contributions to Free energy

- LD gives direct information on interatomic forces.

- Some phase transitions are direct result of "soft" phonon mode instability.

- Electron - phonon coupling is origin of (BCS) superconductivity.

Lattice Dynamics in Crystals

Monatomic Crystal in 1d (I)

Born-Von Karman boundary conditions
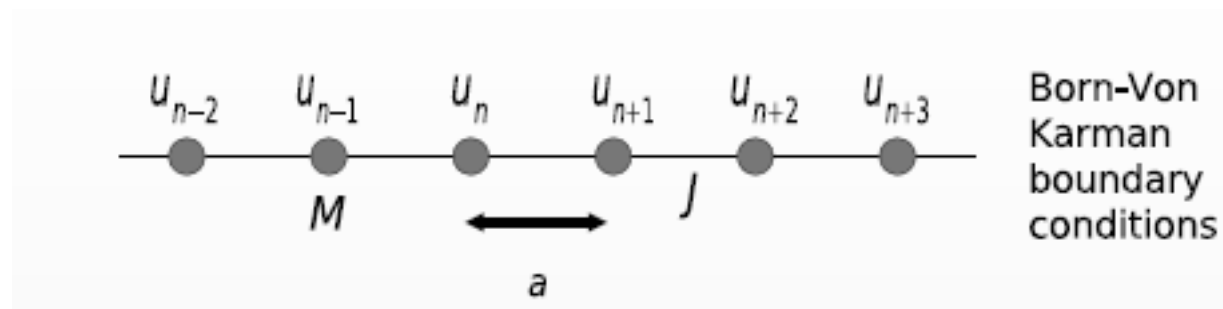
If only nearest neighbours interact:

$$E^{harm} = \frac{1}{2} J \sum_n (u_n - u_{n+1})^2$$

where $J = \Phi_{nn'}$ force constant

Equation of motion of n-th atom:

$$M \frac{\partial^2 u_n}{\partial t^2} = -\frac{\partial E^{harm}}{\partial u_n} = -J(2u_n - u_{n+1} - u_{n-1})$$

Lattice Dynamics in Crystals (Cont.)

Monatomic Crystal in 1d (II)

Solution is known to be the equation of a travelling wave

$$u_n(t) = \sum_k \tilde{u}_k \exp[i(kx - \omega_k t)]$$

When this expression is inserted in the equation of motion one obtains:

$$M\omega_k^2 = 2J[1 - \cos(ka)]$$

Which leads to the following dispersion curve

$$\omega_k = \sqrt{\frac{4J}{M}} |\sin(ka/2)|$$

$$\forall k \in BZ$$
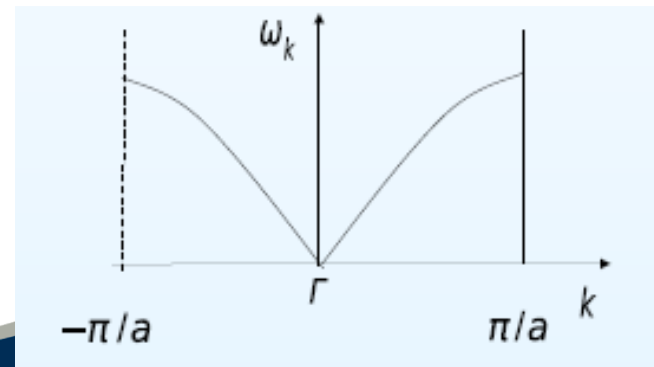
Lattice Dynamics in Crystals (Cont.)

Diatomic Crystal in 1d (II)
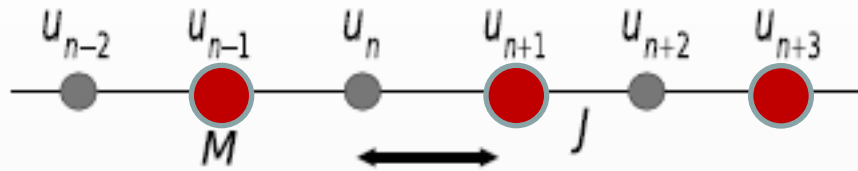
More than one atom in unit cell gives rise optic modes
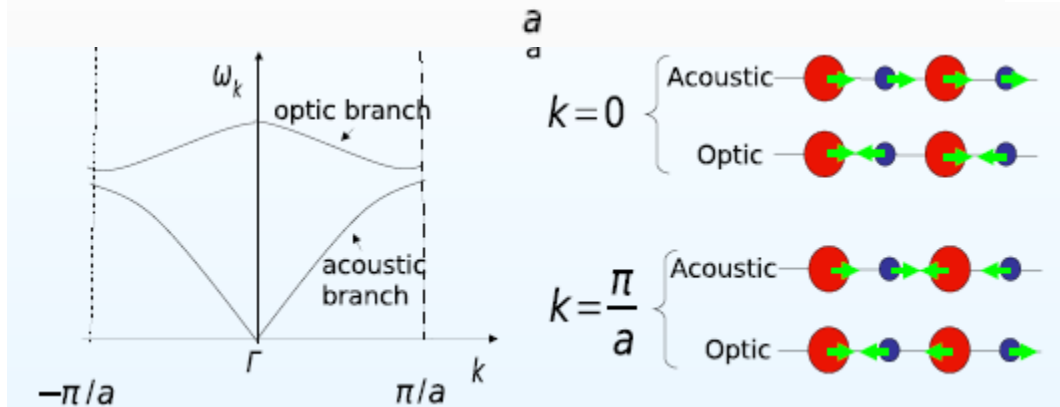
ω(q) relation is called vibrational dispersion relation

N atoms in unit cell produces 3N branches
3 acoustic branches and 3N-3 optic branches

Lattice Dynamics to Vibrational Spectroscopy

Phonons represents across Brillouin zone by
- phonon dispersion and
- vibrational densities of states (VDOS)
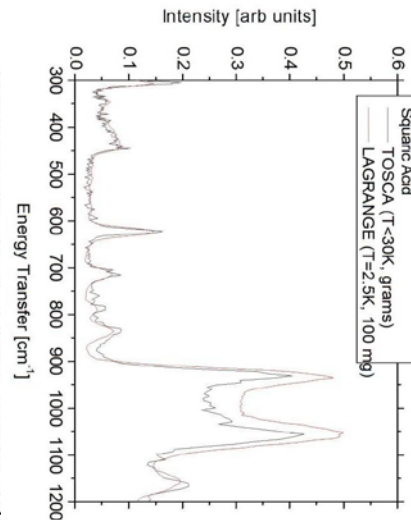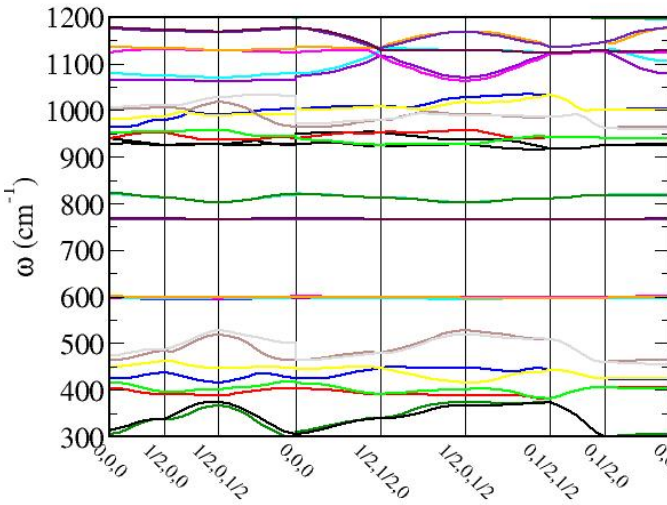
Both of them can be measured experimentally through neutron spectroscopy

- Experimental vibrational spectroscopy is a sensitive probe of structure and dynamics of materials
- No direct experimental methods can provide accurate eigenvectors
- Fitted force field models cannot describe interatomic forces accurately

Vibrational Spectroscopy using DFT

Ab-initio lattice dynamics can give accurate information on interatomic forces

Expanding total energy about structural equilibrium coordinates:

$$E = E_0 + \sum_{\kappa,\alpha} \frac{\partial E}{\partial \boldsymbol{u}_{\kappa,\alpha}} . \boldsymbol{u}_{\kappa,\alpha} + \frac{1}{2} \sum_{\kappa,\alpha,\kappa',\alpha'} \boldsymbol{u}_{\kappa,\alpha} . \Phi_{\alpha,\alpha'}^{\kappa,\kappa'} . \boldsymbol{u}_{\kappa',\alpha'} + ...$$

At equilibrium $\|$
0

$|\_\_\_\_\_|$
Force constant matrix

$$\frac{\partial^2 E}{\partial \boldsymbol{u}_{\kappa,\alpha} \partial \boldsymbol{u}_{\kappa',\alpha'}} \quad <=$$

In harmonic approximations all terms beyond the second term are considered as zero

Vibrational Spectroscopy using DFT

Assuming Born-von-Karman periodic boundary conditions, and substituting plane wave

$$u_{\kappa,\alpha} = \varepsilon_{m\kappa,\alpha q} \, exp(i\mathbf{q}.\mathbf{R}_{\kappa,\alpha} - \omega t)$$

We get the eigenvalue equation,

$$D^{\kappa,\kappa'}_{\alpha,\alpha'}(\mathbf{q}) \varepsilon_{m\kappa,\alpha q} = \omega^2_{m,q} \varepsilon_{m\kappa,\alpha q}$$

Solutions of this eigenvalue equation correspond to normal modes

where,

$$D^{\kappa,\kappa'}_{\alpha,\alpha'}(\mathbf{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} C^{\kappa,\kappa'}_{\alpha,\alpha'}(\mathbf{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_a \Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a) e^{-i\mathbf{q}.\mathbf{R}_a}$$

|_____|
Force constant matrix

ω = vibrational frequency

Solution can be obtained by:
- Finite Displacement + supercell method
- Density Functional perturbation + linear response method

K. Refson, P. R. Tulip and S. J Clark
Phys. Rev. B **73**, 155114 (2006)

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Experimental Observables using DFT

IR Spectroscopy :

$$\frac{\partial \mu_i}{\partial R_k} = -\frac{\partial^2 E}{\partial G_i \partial R_k}$$

μ = dipole moment

G = Electric field perturbation

Raman Spectroscopy :

$$\frac{\partial \widetilde{\alpha}_{ij}}{\partial R_k} = -\frac{\partial^3 E}{\partial G_i \partial G_j \partial R_k}$$

Polarisability :

$$\alpha^{\infty}_{\alpha,\beta} = -\frac{1}{\Omega}\frac{\partial^2 E}{\partial \varepsilon_\alpha \partial \varepsilon_\beta}$$

Dielectric permittivity :

$$\epsilon^{\infty}_{\alpha,\beta} = \delta_{\alpha,\beta} - \frac{4\pi}{\Omega}\frac{\partial^2 E}{\partial \varepsilon_\alpha \partial \varepsilon_\beta}$$

Born Effective charge tensor :

$$Z^{*}_{\alpha,\beta} = \Omega\frac{\partial P_\beta}{\partial u_{\kappa,\alpha}} = \frac{\partial F_{\kappa,\alpha}}{\partial \varepsilon_\beta} = \frac{\partial^2 E}{\partial u_{\kappa,\alpha} \partial \varepsilon_\beta}$$

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Vibrational Spectroscopy : Experiments

IR Spectroscopy

- IR photons interacts with phonons very close to Γ point

- There are selection rules for IR active modes

IR Intensity $\quad I_m = \left| \sum_{\kappa,b} \frac{1}{\sqrt{M_\kappa}} Z^*_{\kappa,a,b} u_{m,\kappa,b} \right|^2$

$\|$

Born effective charge

Raman Spectroscopy

Intensity of Raman active peaks depend on the Raman activity tensor

$$I^{Raman}_{\alpha\beta} = \frac{d^3 E}{d\varepsilon_\alpha d\varepsilon_\beta dQ_m} = \frac{d\epsilon_{\alpha\beta}}{dQ_m}$$

It is the derivative of the dielectric permittivity with respect to the displacement along mode eigenvectors

Vibrational Spectroscopy : Experiments

Inelastic neutron scattering (INS) Spectroscopy

- Thermal neutron has same magnitude of energy and momenta as of phonon, so can interacts with any Q of phonons

- There is no selection rule, so all modes can be visible

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\sigma_{TOT}}{4\pi}\left(\frac{k_f}{k_i}\right)S(\mathbf{Q},\omega)$$

$$\hbar\omega = (E_i - E_f) = \frac{\hbar}{2m}(\mathbf{k}_i^2 - \mathbf{k}_f^2)$$
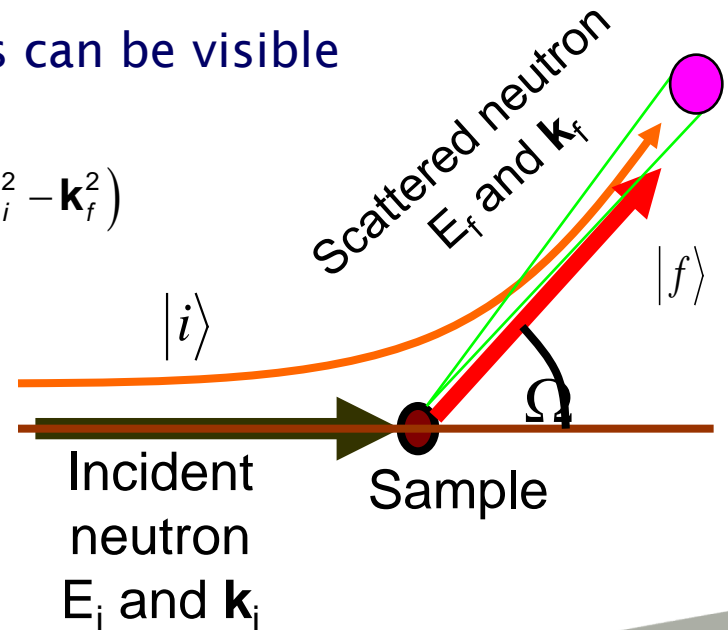
$$\mathbf{Q} = (\mathbf{k}_i - \mathbf{k}_f)$$

INS spectrum

$$S(\mathbf{Q}, \omega)^v = \frac{\sigma l}{4\pi}\frac{[Q.u]^{2n}}{n!}\exp(-(Q.\textstyle\sum_{k=0}^{n} ul) ** 2)$$
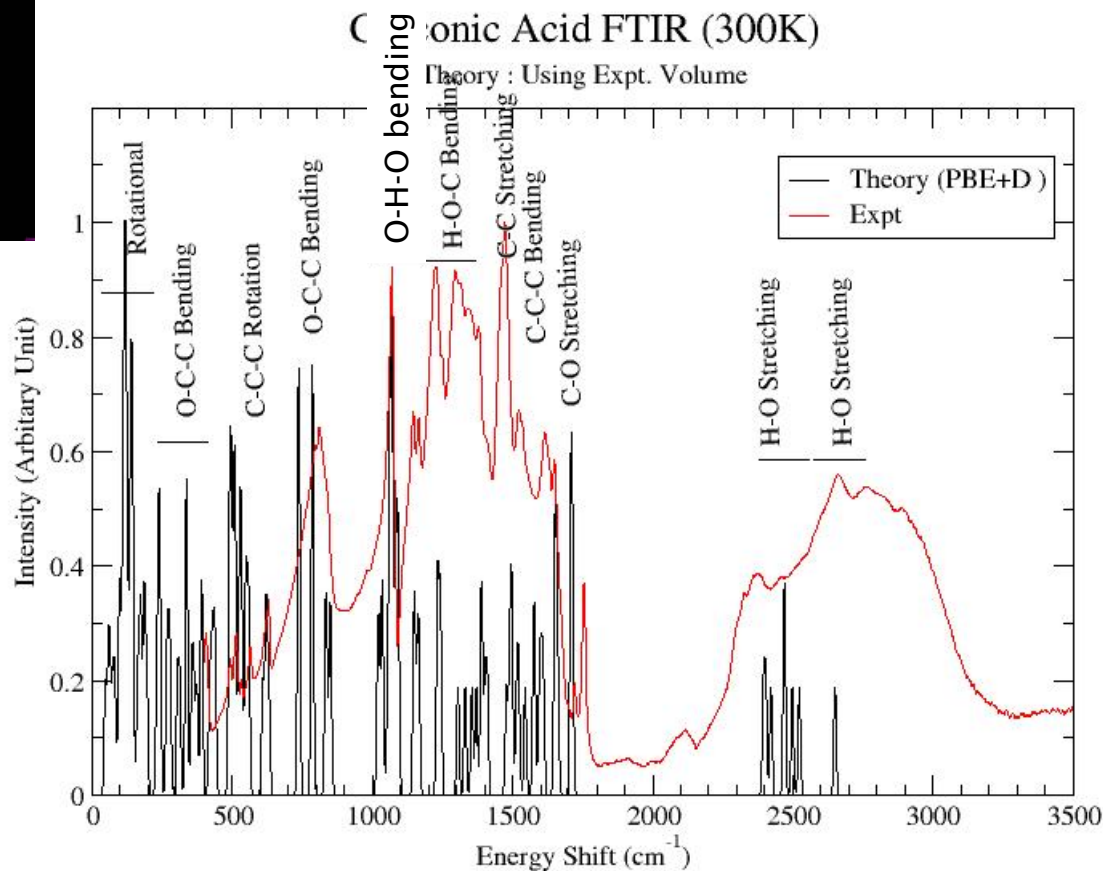
σ = scattering cross section

u = atomic displacement

n = transition number

Scattered neutron E_f and $\mathbf{k}_f$

$|i\rangle$ $|f\rangle$

Ω

Incident neutron E_i and $\mathbf{k}_i$

Sample

abINS algorithm in Mantid can calculate INS from DFT phonon information
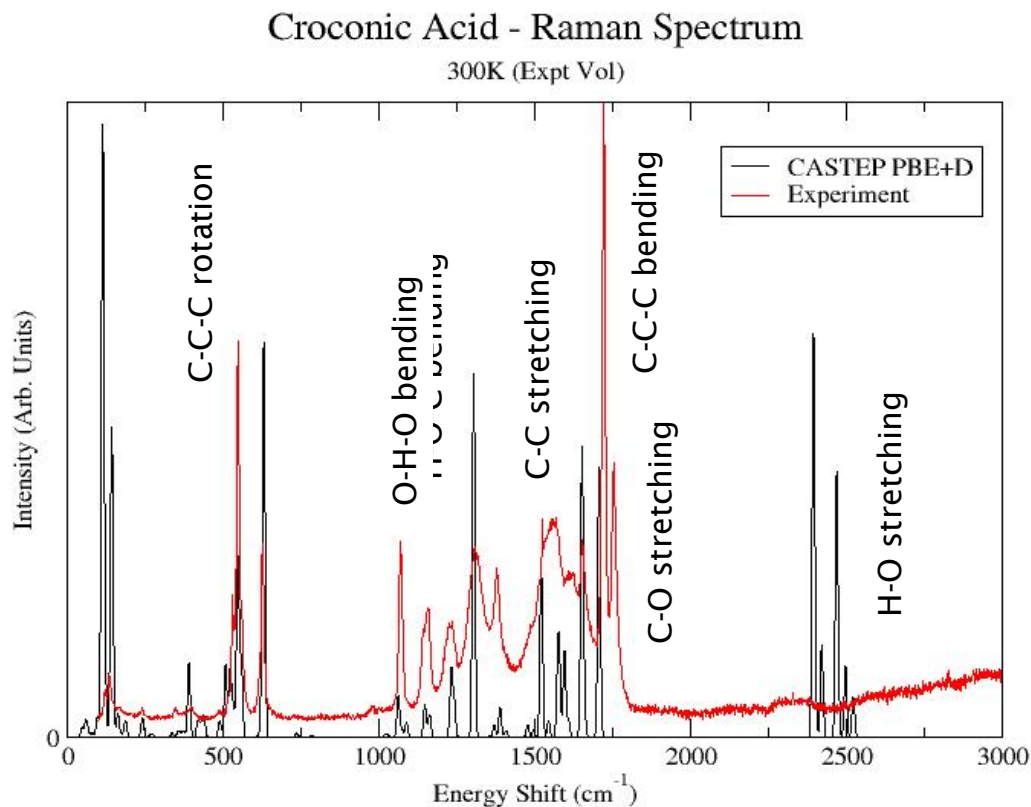
Example : IR Spectrum (Croconic Acid)

Total modes 144
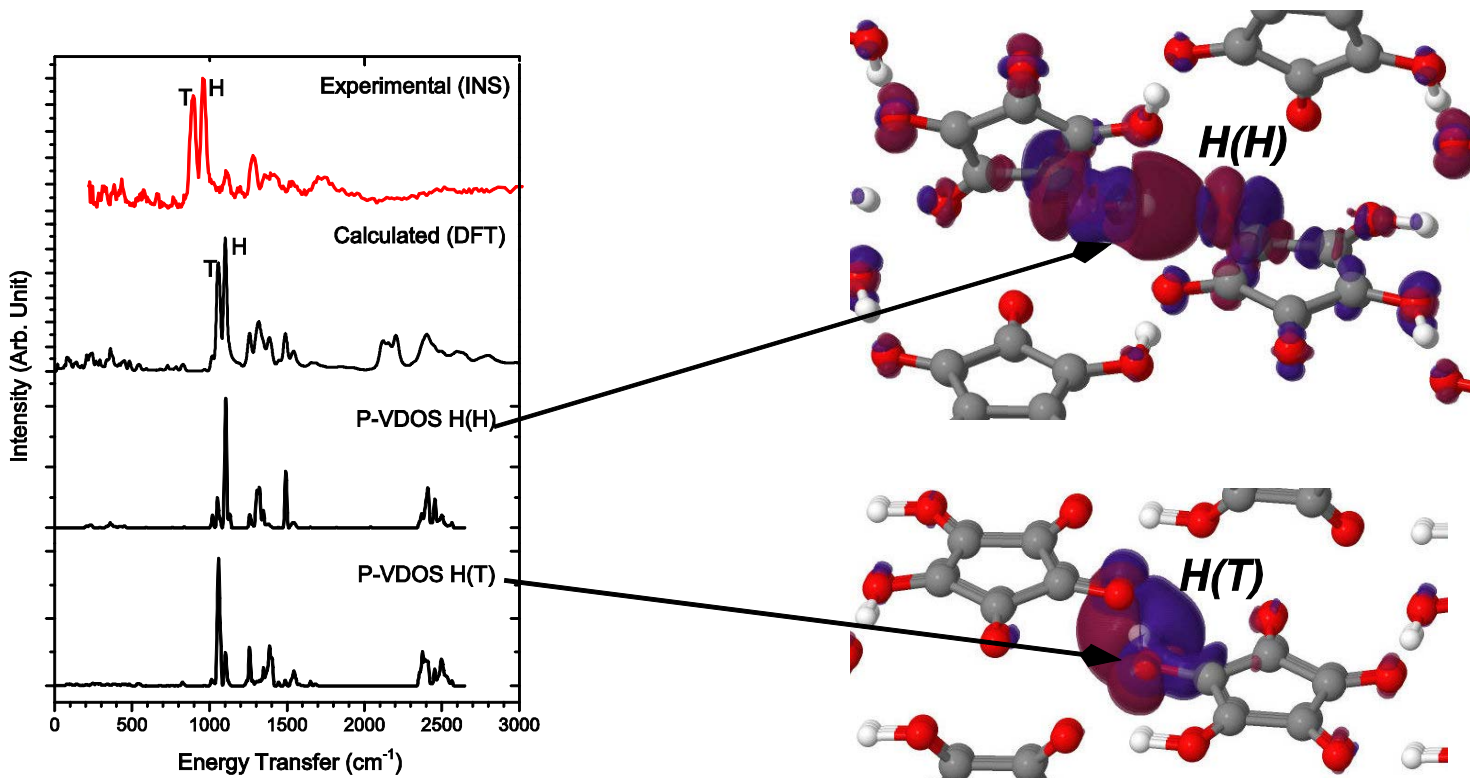IR active modes 106

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Example : Raman Spectrum (Croconic Acid)

Croconic Acid - Raman Spectrum
300K (Expt Vol)

All 144 modes are Raman active

Example : INS Spectrum (Croconic Acid)

Experimental INS compared with Calculations
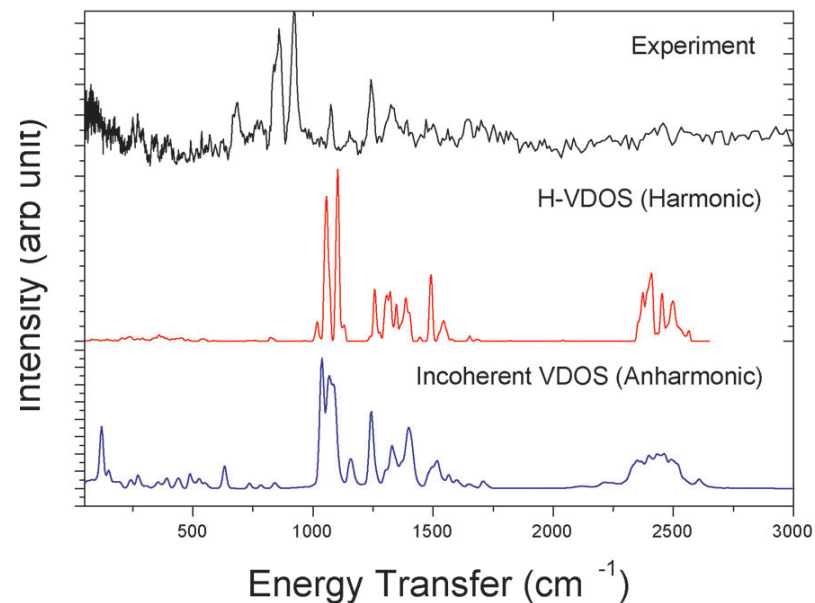
Response charge densities of hydrogen ions
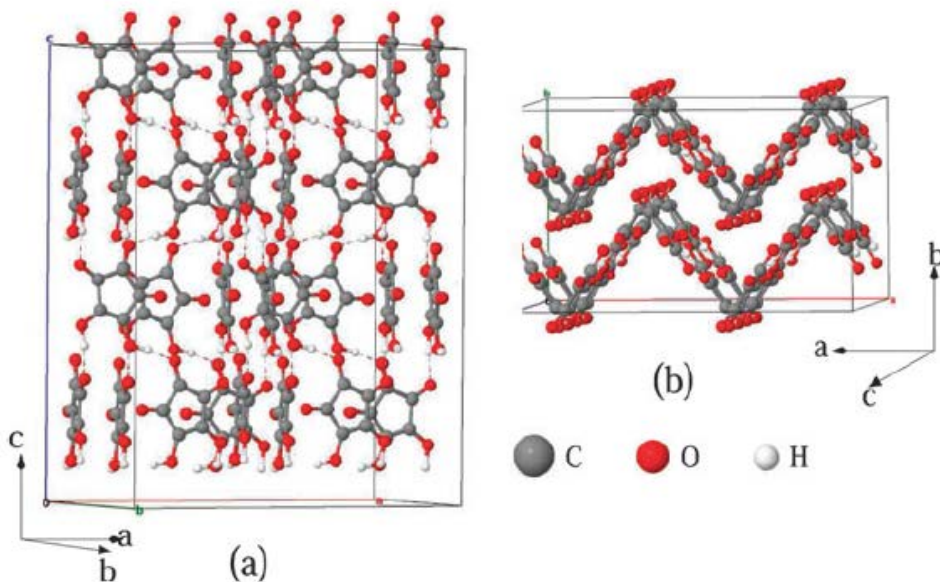
S, Mukhopadhyay et. al, J. Chem Phys, **427**, 95 (2013)

F. Fernandez-Alonso et al, J. Phys. Soc. Jap **82**, SA001 (2013)

S, Mukhopadhyay et. al, Phys. Chem. Chem. Phys. , **19**, 32216 (2017)

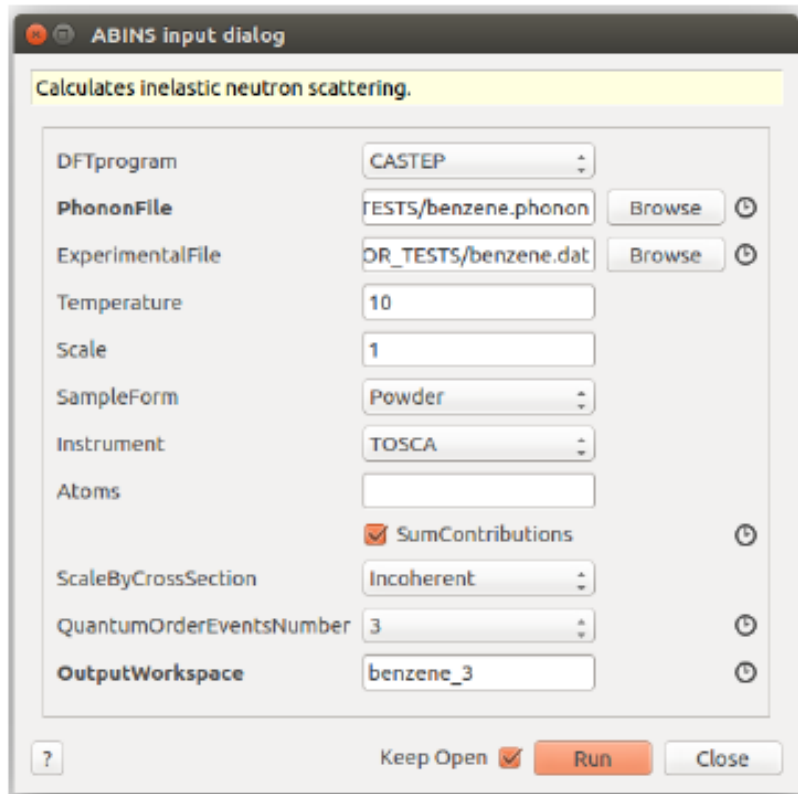nce & Technology Facilities Council

Example : INS Spectrum (Croconic Acid)

Anharmonic DOS is compared with INS experiments

MD simulations on supercells are required for simulating anharmonicity

S. Mukhopadhyay et al, Phys. Chem. Chem. Phys, (2014).

AbINS : Inelastic neutron scattering simulations from ab-initio lattice dynamics

- Allows direct comparison of simulated and measured inelastic neutron scattering spectra

- Implemented as a plugin to Mantid data reduction and visualisation tool

- User friendly GUI based on Mantid

- User can plot data by means of Mantid plotting functions

- All data is saved to ASCII file so that user can later visualise it in the software of choice

K Dymkowski SF Parker F Fernandez-Alonso S Mukhopadhyay, Phys. B (published on-line) (2018).

Summary

- Electronic structures of materials help to correlate structure-property relationship from first principles.

- Lattice dynamics simulations are used to compare experimental IR, Raman and INS of materials

- AbINS is available in Mantid for calculations of INS spectra

Thank you

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