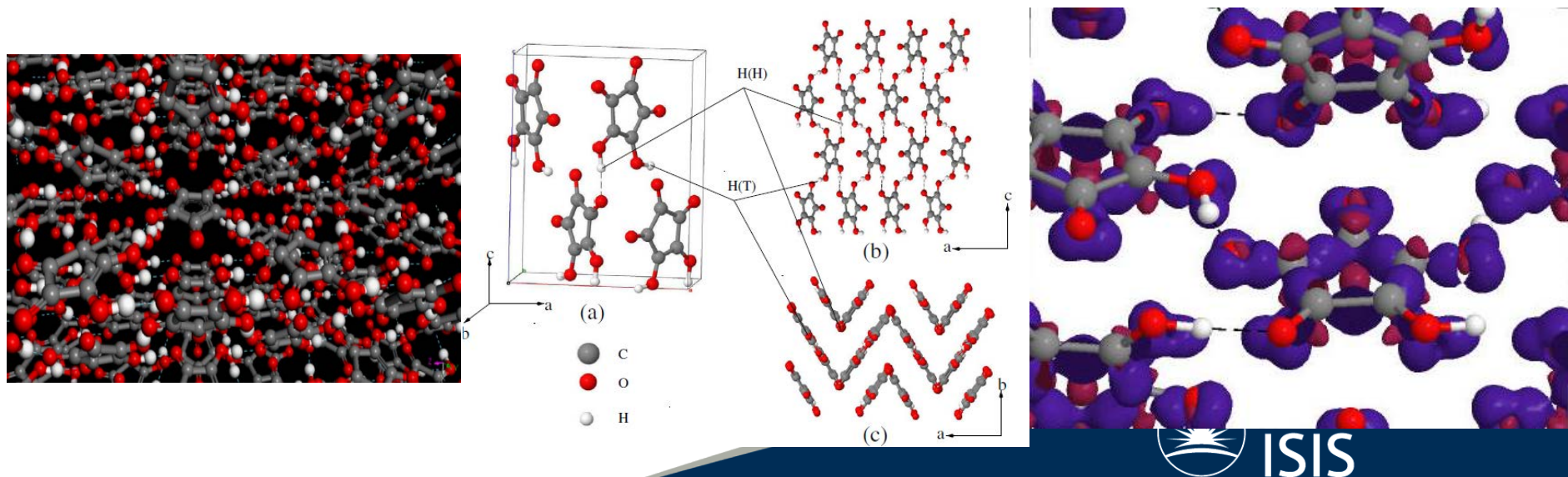


Introduction to Electronic Structures and Lattice Dynamics

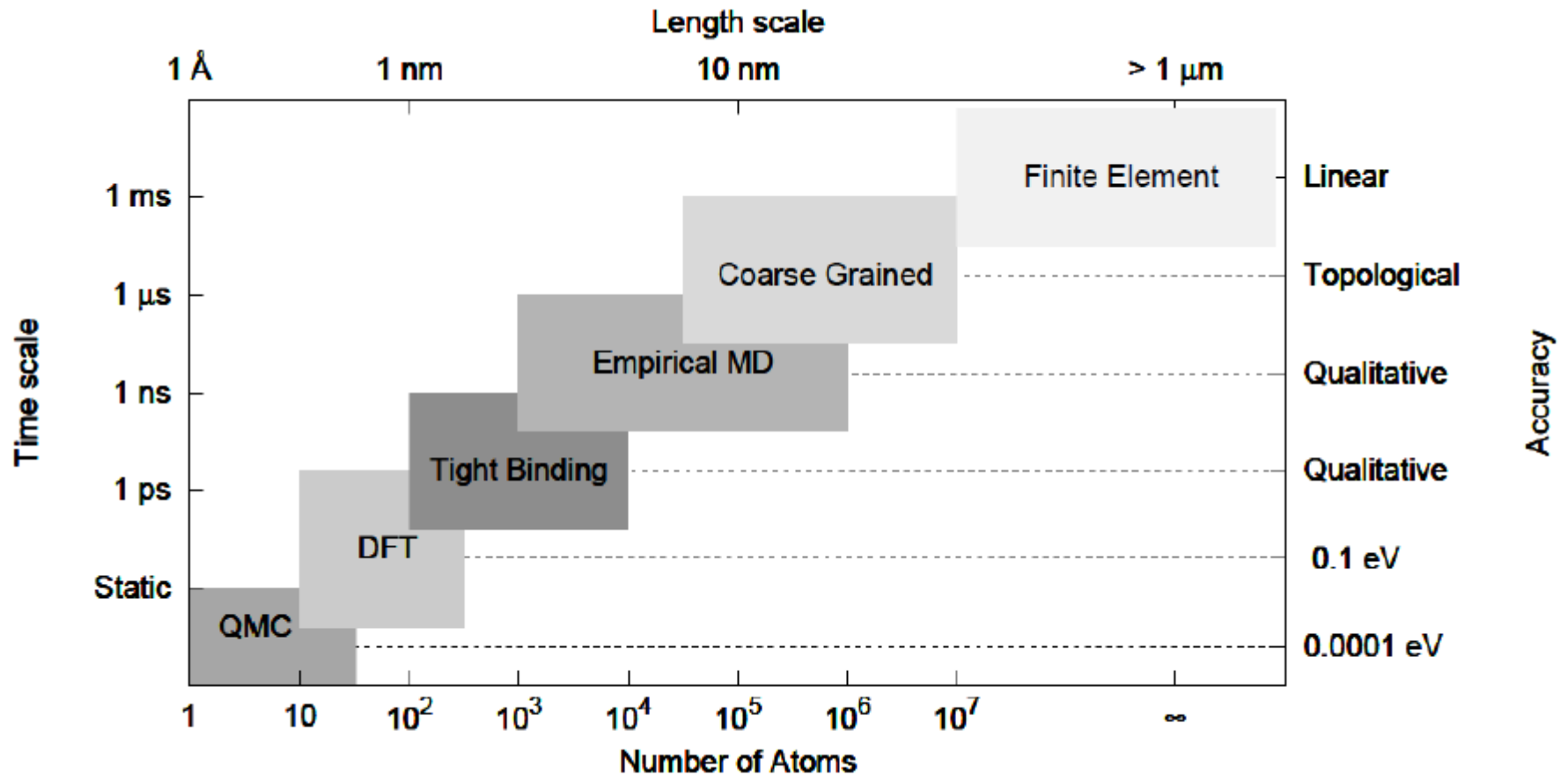
Sanghamitra Mukhopadhyay

*ISIS Facility, STFC Rutherford Appleton Laboratory
Oxfordshire*



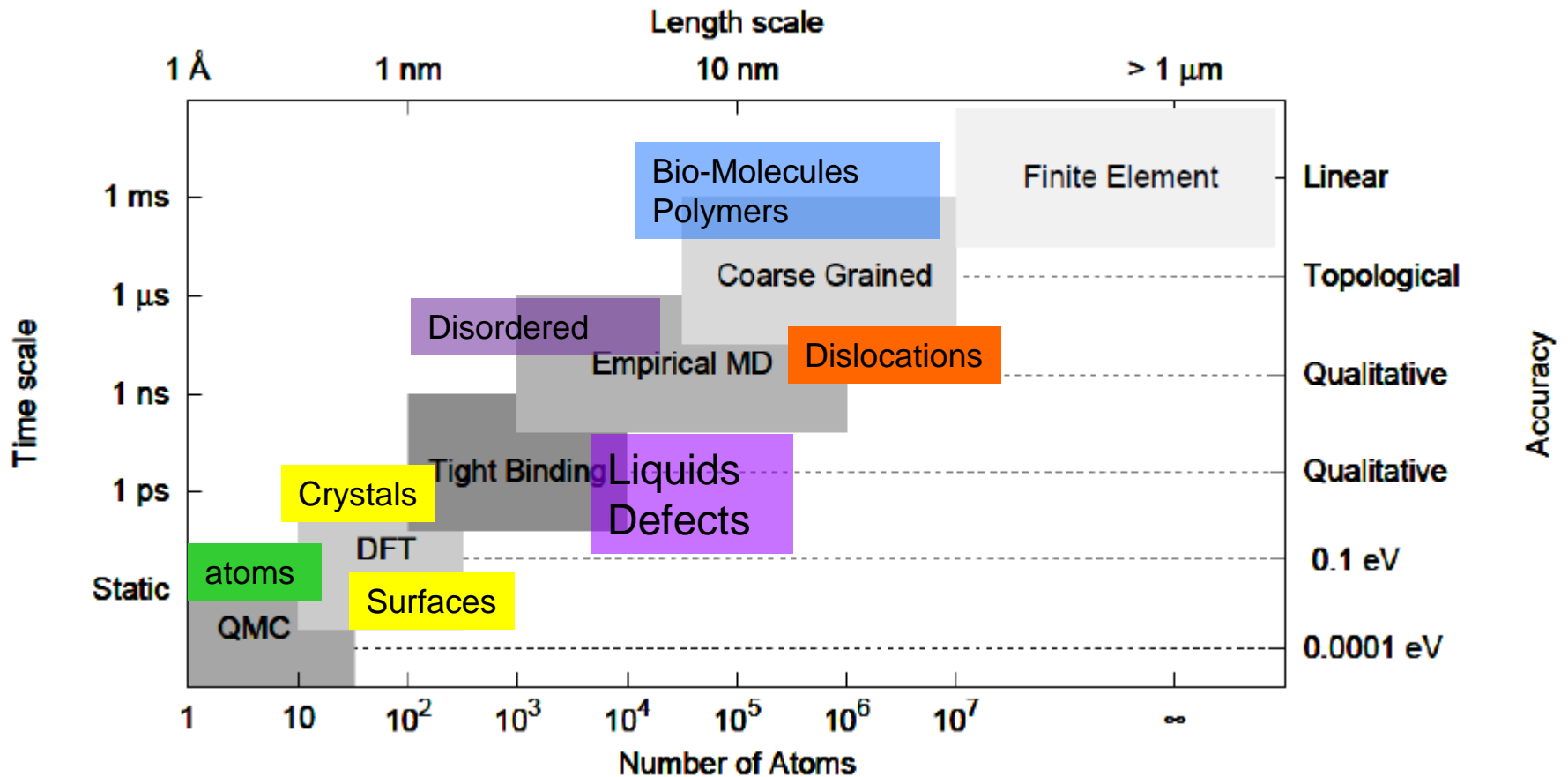
Level of Approximations

Comparison between computational costs, accuracy and generality



Level of Approximations

Comparison between computational costs, accuracy and generality

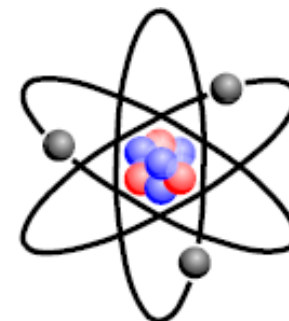


Alphabets of the Materials World



WebElements: the periodic table on the world-wide web

www.webelements.com



Properties depend
on electronic
structures

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
hydrogen 1 H 1.0079																	helium 2 He 4.0026		
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180		
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948		
<div>Key:</div> <div>element name atomic number symbol atomic weight (mean relative mass)</div>																			
potassium 19 K 39.098	calcium 20 Ca 40.078											gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80		
rubidium 37 Rb 85.468	strontium 38 Sr 87.62											indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29		
cesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *											lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]		
francium 87 Fr [223]	radium 88 Ra [226]	89-102 **											ununbium 112 Uub [286]	ununtrium 113 Uut [288]	ununquadium 114 Uuq [289]	ununpentium 115 Uup [291]	ununhexium 116 Uuh [293]	ununseptium 117 Uus [294]	ununoctium 118 Uuo [296]

*lanthanoids

Lanthanum 57 La 138.91	Cerium 58 Ce 140.12	Praseodymium 59 Pr 140.91	Neodymium 60 Nd 144.24	Promethium 61 Pm [145]	Samarium 62 Sm 150.36	Europium 63 Eu 151.96	Gadolinium 64 Gd 157.25	Terbium 65 Tb 158.93	Dysprosium 66 Dy 162.50	Holmium 67 Ho 164.93	Erbium 68 Er 167.26	Thulium 69 Tm 168.93	Ytterbium 70 Yb 173.06
Actinium 89 Ac [227]	Thorium 90 Th 232.04	Protactinium 91 Pa 231.04	Uranium 92 U 238.03	Np 93 Np [237]	Pu 94 Pu [244]	Am 95 Am [243]	Cm 96 Cm [247]	Bk 97 Bk [247]	Cf 98 Cf [251]	Es 99 Es [252]	Fm 100 Fm [257]	Md 101 Md [258]	No 102 No [259]

**actinoids

Symbols and names: the symbols and names of the elements, and their spellings are those recommended by the International Union of Pure and Applied Chemistry (IUPAC - <http://www.iupac.org>). Names have yet to be proposed for the most recently discovered elements beyond 112 and so those used here are IUPAC's temporary systematic names. In the USA and some other countries, the spellings californium and cesium are correct while in the UK and elsewhere the common spelling is californ and caesium.

Group labels: the numeric system (1-10) used here is the current IUPAC convention.

Atomic weights (mean relative masses): Apart from the heaviest elements, these are the IUPAC 2007 values and given to 5 significant figures. Elements for which the atomic weight is given within square brackets have no stable isotopes and are represented by the element's longest lived isotope reported at the time of writing.

©2007 Dr Mark J Winter (WebElements Ltd) and University of Sheffield. webelements@sheffield.ac.uk All rights reserved. For updates to this table see http://www.webelements.com/news/Printable_Periodic_Table_Version.doc. 21 September 2007.



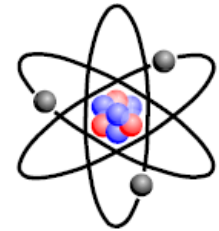
Science & Technology Facilities Council

ISIS

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

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



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

$$\hat{H} = -\sum_{a=1}^{N_b} \frac{\hbar^2}{2M_a} \nabla_{\vec{R}_a}^2 - \sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_{\vec{r}_i}^2 - \frac{e^2}{4\pi\epsilon_0} \sum_{a=1}^{N_b} \sum_{i=1}^N \frac{Z_a}{|\vec{R}_a - \vec{r}_i|} + \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{j=1}^{i-1} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{e^2}{4\pi\epsilon_0} \sum_{a=1}^{N_b} \sum_{b=1}^{a-1} \frac{Z_a Z_b}{|\vec{R}_a - \vec{R}_b|}$$



Solving the Schrödinger equation for Many-body Electron System

Schrödinger equation:

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

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

$$\begin{aligned}\hat{H}_e &= \hat{T}_e + \hat{v}_{ne} + \hat{v}_{ee} + v_{nn} \\&= \sum_{i=1}^N \left[-\frac{\hbar^2}{2m_e} \nabla_{\vec{r}_i}^2 - \frac{e^2}{4\pi\epsilon_0} \sum_{a=1}^{N_b} \frac{Z_a}{|\vec{R}_a - \vec{r}_i|} \right] + \sum_{i=1}^N \sum_{j=1}^{i-1} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_i - \vec{r}_j|} + v_{nn} \\&= \underbrace{\sum_{i=1}^N \hat{h}_1(\vec{r}_i)}_{\text{simple}} + \underbrace{\sum_{i=1}^N \sum_{j=1}^{i-1} \hat{h}_2(\vec{r}_i, \vec{r}_j)}_{\text{difficult}} + v_{nn}\end{aligned}$$

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.



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 $\bar{n}(\vec{r}) = \sum_i^{\text{occ}} |\varphi_i(\vec{r})|^2$

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

- **LDA/LSDA** Local Density Approximation

$\hat{v}_{xc}[n]$ = 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 $\hat{v}_{xc}[n]$ 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

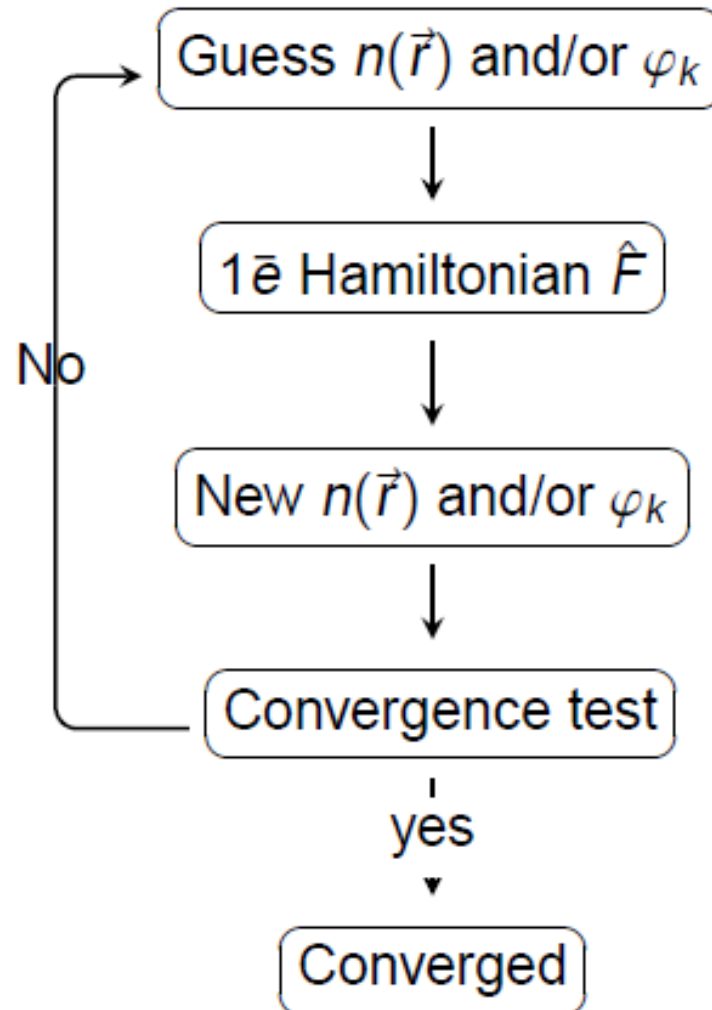
B3LYP, B3PW, PBE0 and PBESOL0, B1PW, B1WC

- Good structures
- Part self-inter. pb
- Gaps
- No dispersion forces
- More costly
- Cooking recipe

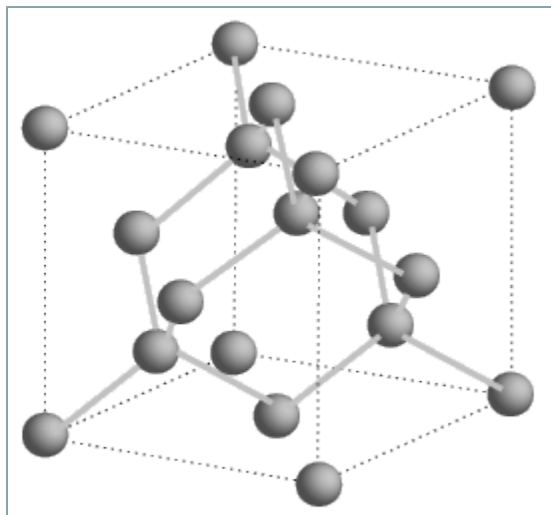


Solving Electronic Structures: Recipe

1 \bar{e} 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>



Science & Technology Facilities Council

ISIS

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 \Rightarrow 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



Introduction to Lattice Dynamics

Motivations for *ab initio* lattice dynamics II

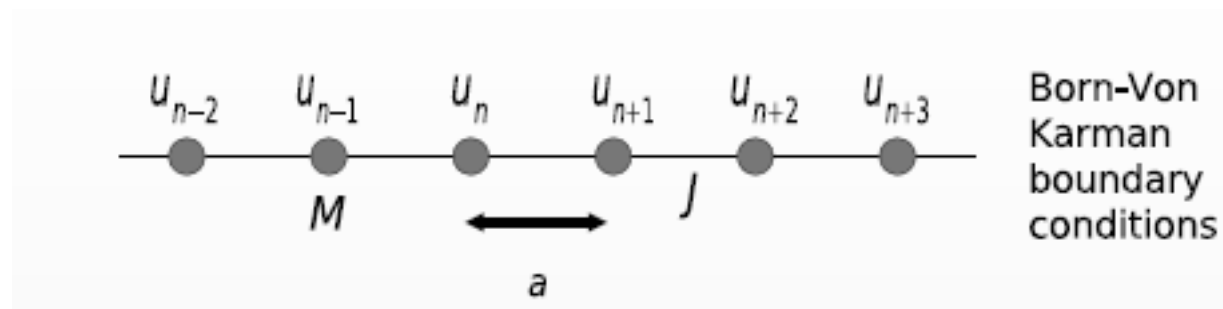
Motivations from predictive modelling

- 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)



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

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

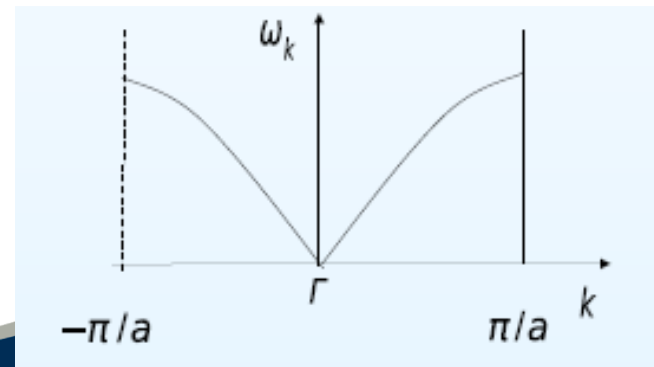
When this expression is inserted in the equation of motion one obtains:

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

Which leads to the following dispersion curve

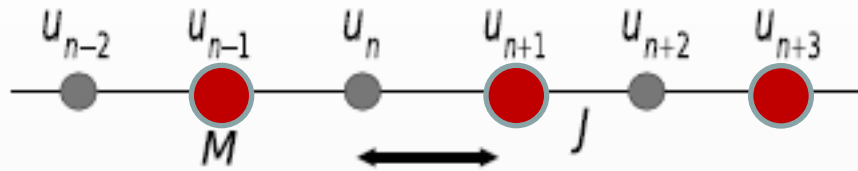
$$\omega_k = \sqrt{\frac{4J}{M}} |\sin(ka/2)|$$

$$\forall k \in \text{BZ}$$

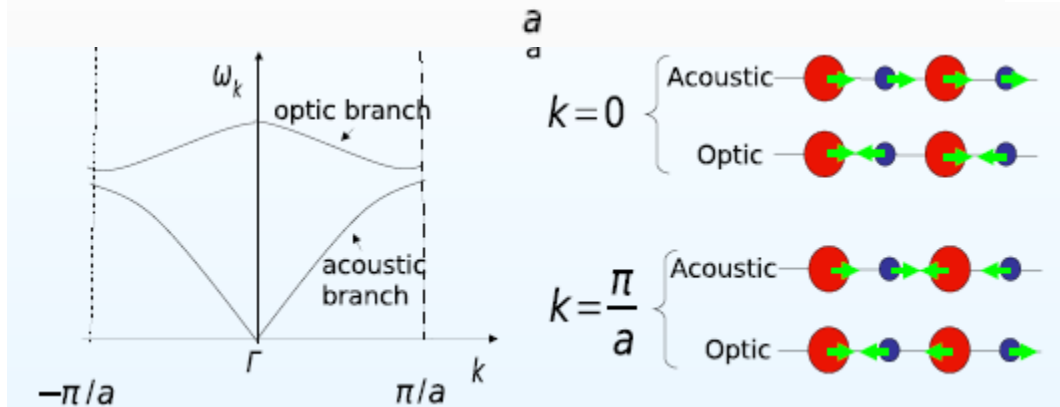


Lattice Dynamics in Crystals (Cont.)

Diatomic Crystal in 1d (II)



More than one atom in unit cell gives rise to optic modes



$\omega(q)$ relation is called vibrational dispersion relation

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



Science & Technology Facilities Council

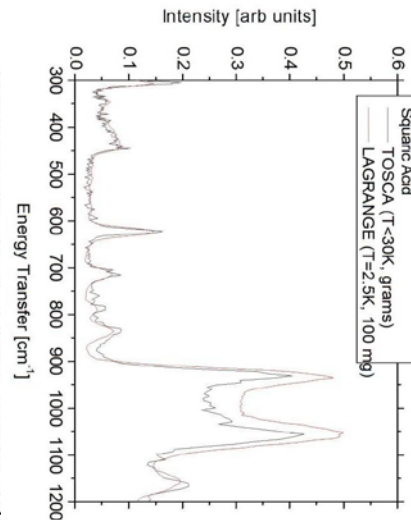
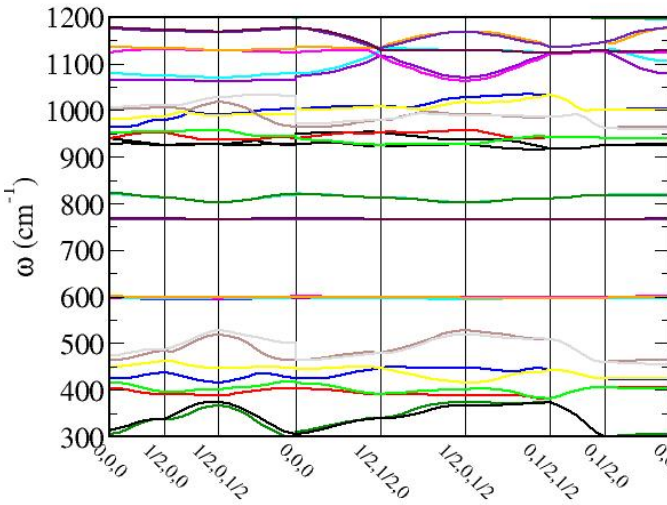
ISIS

Lattice Dynamics to Vibrational Spectroscopy

Phonons represent across Brillouin zone by

- phonon dispersion and
- vibrational densities of states (VDOS)

squaric acid



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:

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

At equilibrium \parallel
0

$$\frac{\partial^2 E}{\partial \mathbf{u}_{\kappa, \alpha} \partial \mathbf{u}_{\kappa', \alpha'}}$$

\leq $\begin{vmatrix} & & & \\ & & & \\ & & & \\ & & & \end{vmatrix}$
Force constant
matrix

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

$$\mathbf{u}_{\kappa,\alpha} = \boldsymbol{\epsilon}_{m\kappa,\alpha\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{R}_{\kappa,\alpha} - \omega t)$$

We get the eigenvalue equation,

$$D_{\alpha,\alpha'}^{\kappa,\kappa'}(\mathbf{q}) \boldsymbol{\epsilon}_{m\kappa,\alpha\mathbf{q}} = \omega_{m,\mathbf{q}}^2 \boldsymbol{\epsilon}_{m\kappa,\alpha\mathbf{q}}$$

Solutions of this eigenvalue equation correspond to normal modes

where,

$$D_{\alpha,\alpha'}^{\kappa,\kappa'}(\mathbf{q}) = \frac{1}{\sqrt{M_{\kappa}M_{\kappa'}}} C_{\alpha,\alpha'}^{\kappa,\kappa'}(\mathbf{q}) = \frac{1}{\sqrt{M_{\kappa}M_{\kappa'}}} \sum_a \Phi_{\alpha,\alpha'}^{\kappa,\kappa'}(a) e^{-i\mathbf{q} \cdot \mathbf{R}_a}$$

|-----|
Force constant matrix

ω = vibrational frequency

Solution can be obtained by:

- Finite Displacement + supercell method
- Density Functional perturbation + linear response method

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 :

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

Polarisability :

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

Dielectric permittivity :

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

Born Effective charge tensor :

$$Z_{\alpha,\beta}^* = \Omega \frac{\partial P_{\beta}}{\partial u_{\kappa,\alpha}} = \frac{\partial F_{\kappa,\alpha}}{\partial \epsilon_{\beta}} = \frac{\partial^2 E}{\partial u_{\kappa,\alpha} \partial \epsilon_{\beta}}$$

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 $I_m = \left| \sum_{\kappa,b} \frac{1}{\sqrt{M_\kappa}} \underset{\text{Born effective charge}}{\underset{\parallel}{Z_{\kappa,a,b}^*}} u_{m,\kappa,b} \right|^2$

Raman Spectroscopy

Intensity of Raman active peaks depend on the Raman activity tensor

$$I_{\alpha\beta}^{\text{Raman}} = \frac{d^3 E}{d\varepsilon_\alpha d\varepsilon_\beta dQ_m} = \frac{d\varepsilon_{\alpha\beta}}{dQ_m}$$

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 interact with any Q of phonons
- There is no selection rule, so all modes can be visible

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

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

$$\mathbf{Q} = (\mathbf{k}_i - \mathbf{k}_f)$$

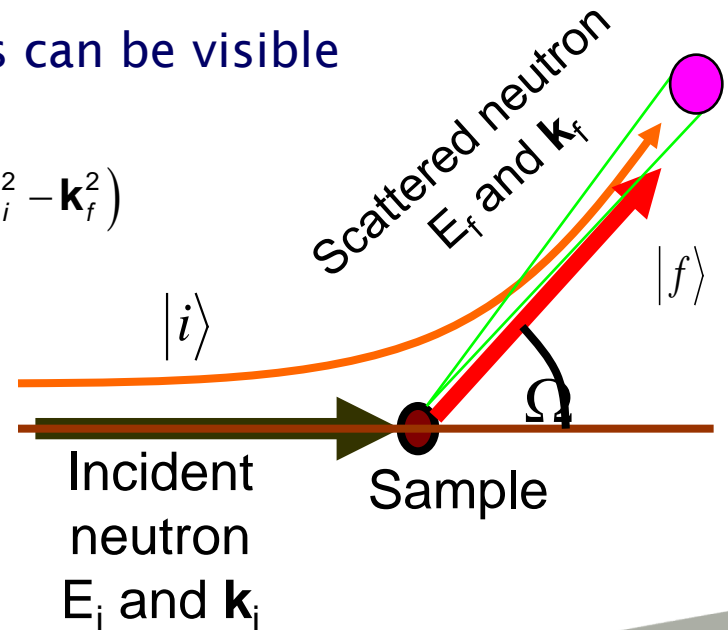
INS spectrum

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

σ = scattering cross section

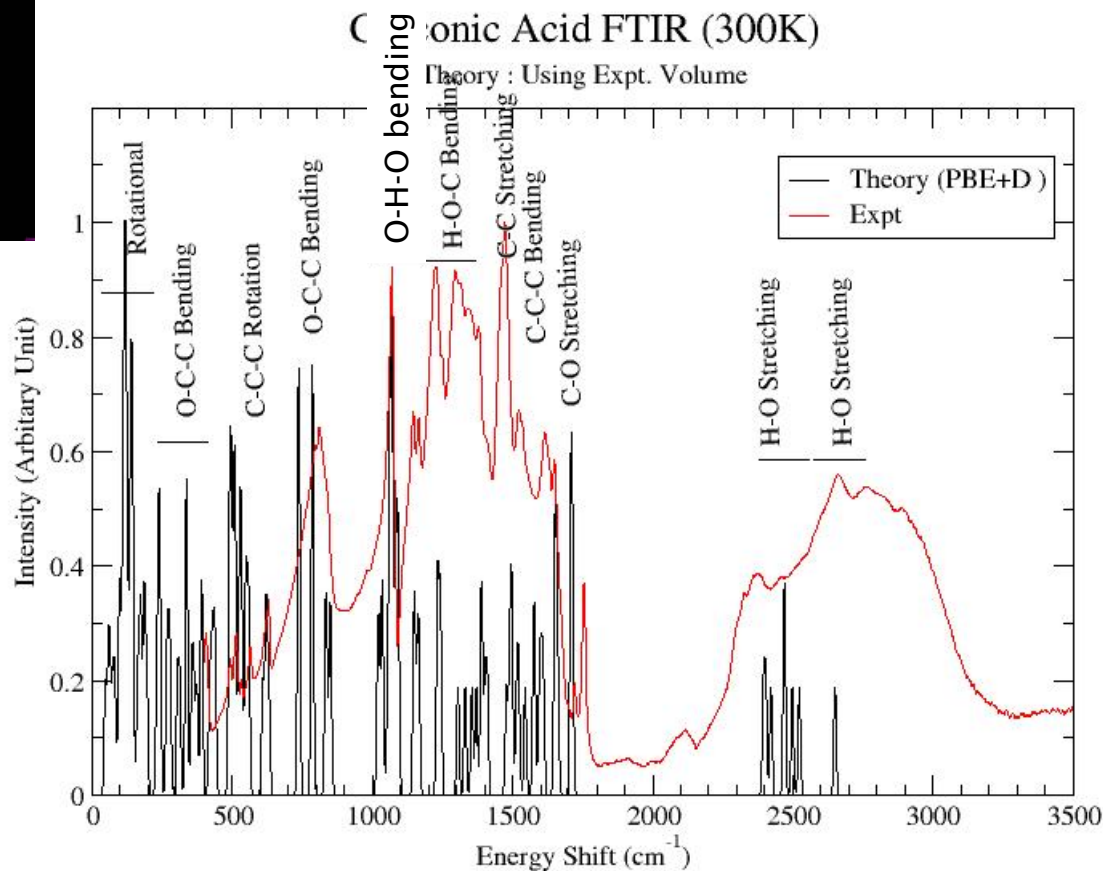
u = atomic displacement

n = transition number



abINS algorithm in Mantid can calculate INS from DFT phonon information

Example : IR Spectrum (Croconic Acid)



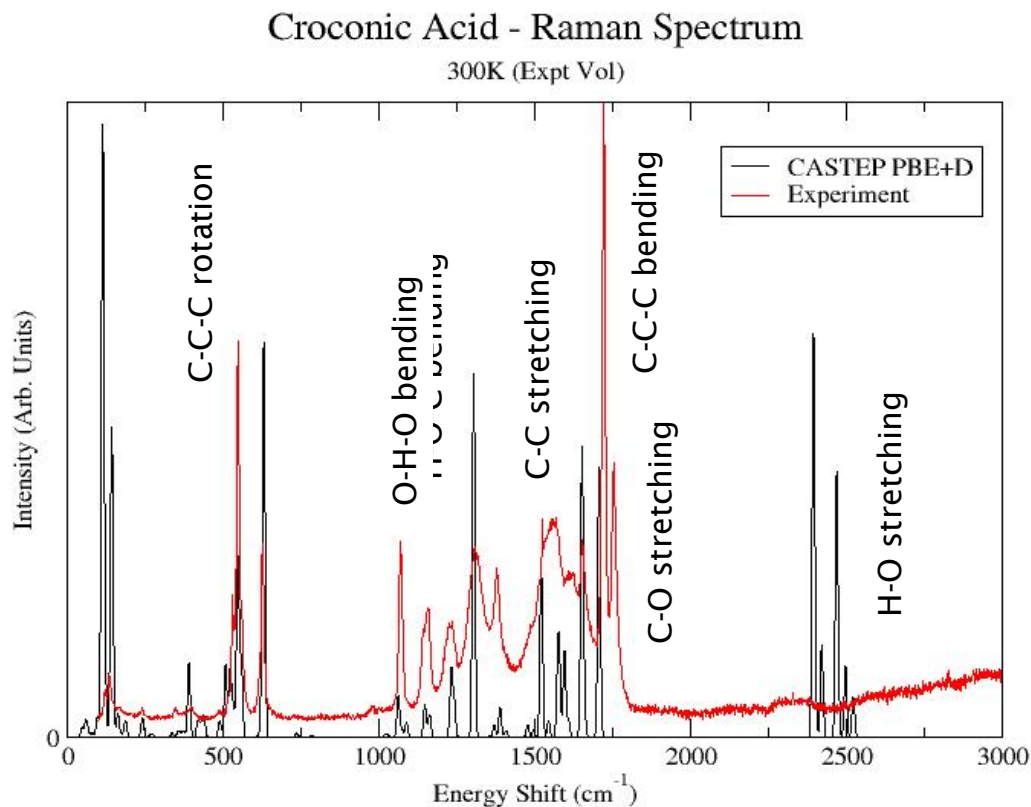
Total modes 144
IR active modes 106



Science & Technology Facilities Council

ISIS

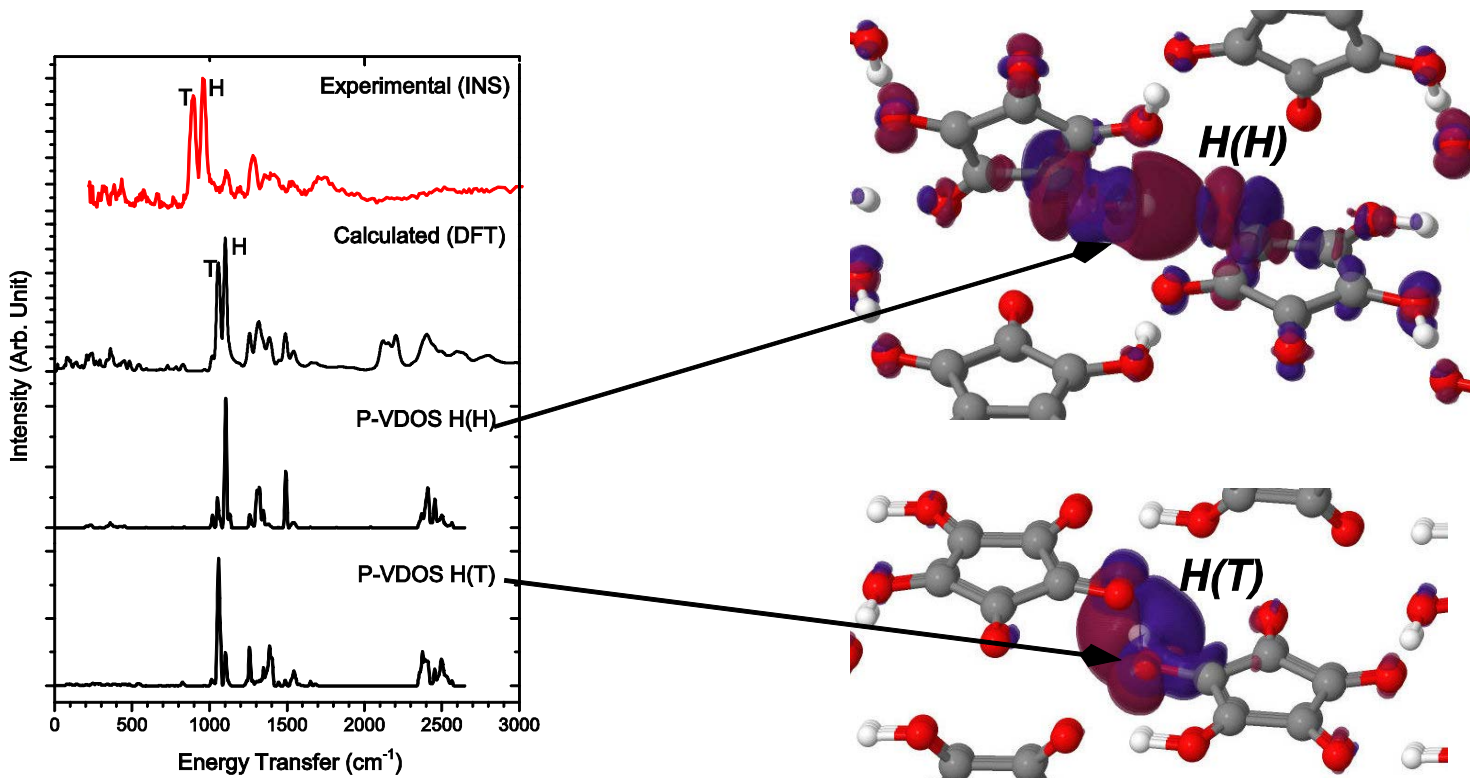
Example : Raman Spectrum (Croconic Acid)



All 144 modes are Raman active



Example : INS Spectrum (Croconic Acid)



Experimental INS compared with Calculations

Response charge densities of hydrogen ions

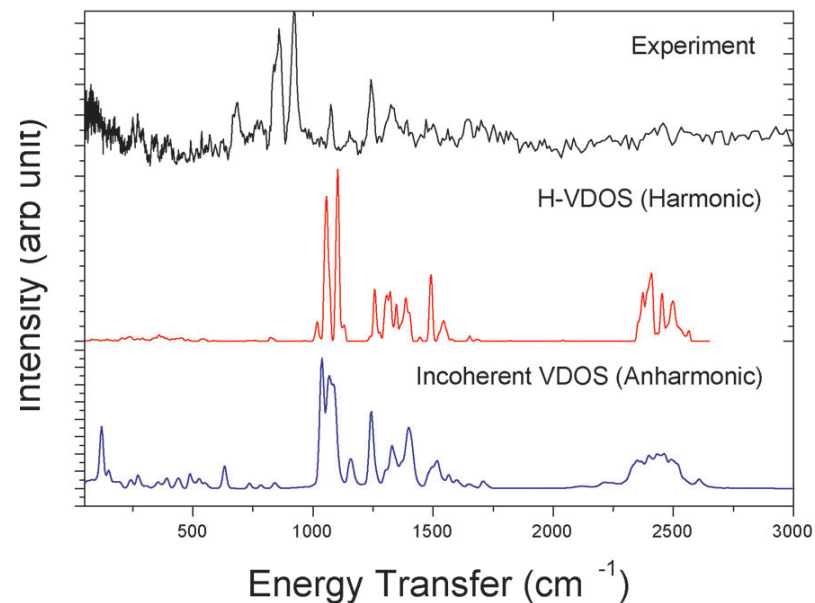
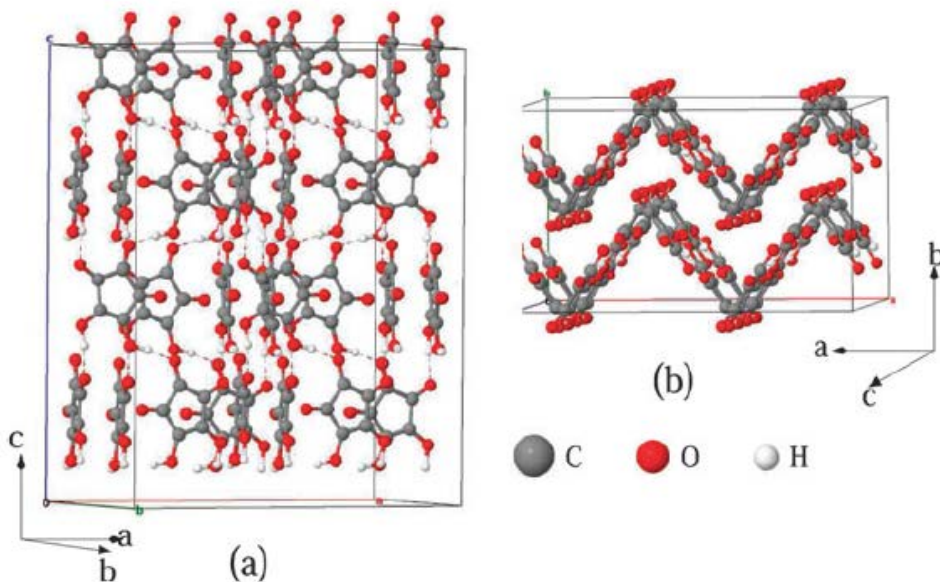
S, Mukhopadhyay et. al, J. Chem Phys, 427, 95 (2013)

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

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

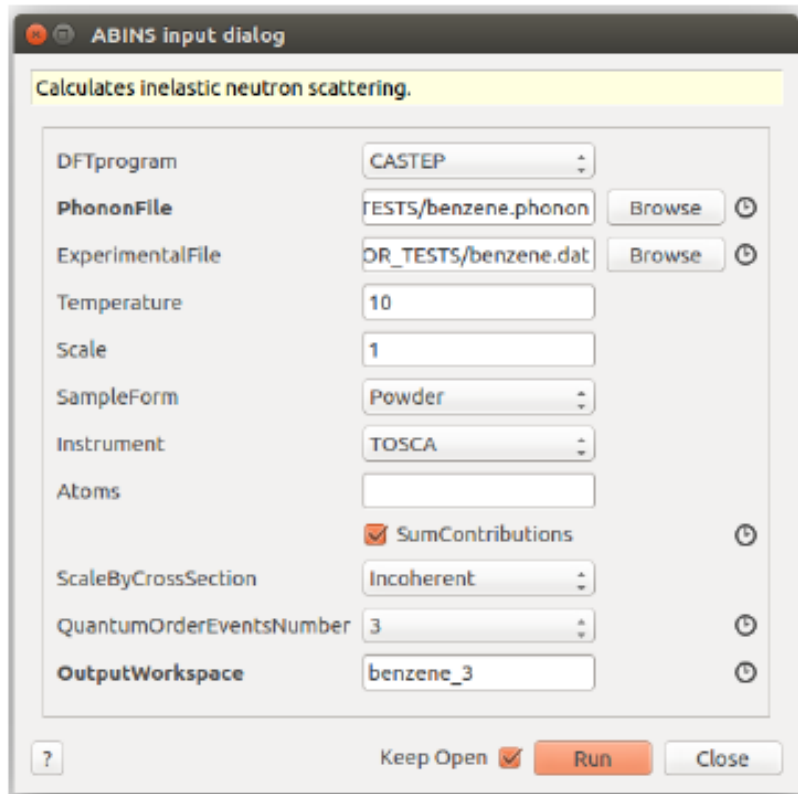
Example : INS Spectrum (Croconic Acid)

Anharmonic DOS is compared with
INS experiments



MD simulations on supercells are required for simulating anharmonicity

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



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



Science & Technology Facilities Council
ISIS