The Power of First-Principles Simulation

From electronic structure to real materials

Keith Refson
Scientific Computing Department
STFC Rutherford Appleton Laboratory

Science & Technology Facilities Council

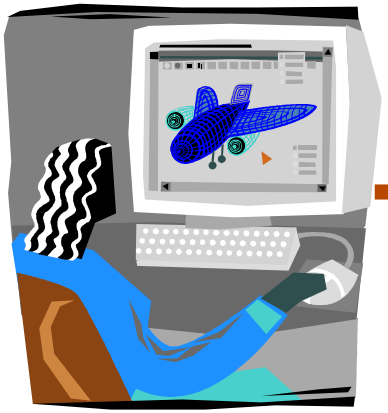
Computer Simulation

Supercomputer

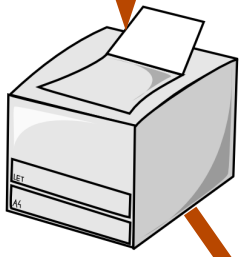
Laws of Physics

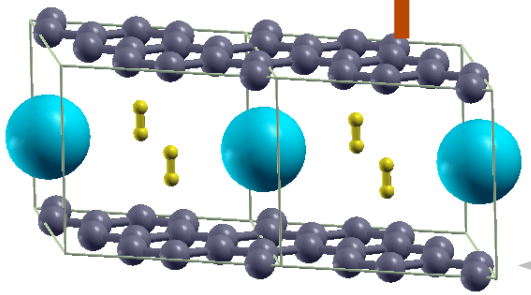
$$H\Psi = -i\hbar\, d\Psi / dt$$

$$F = m\,a$$



Computer Program





Initial input data

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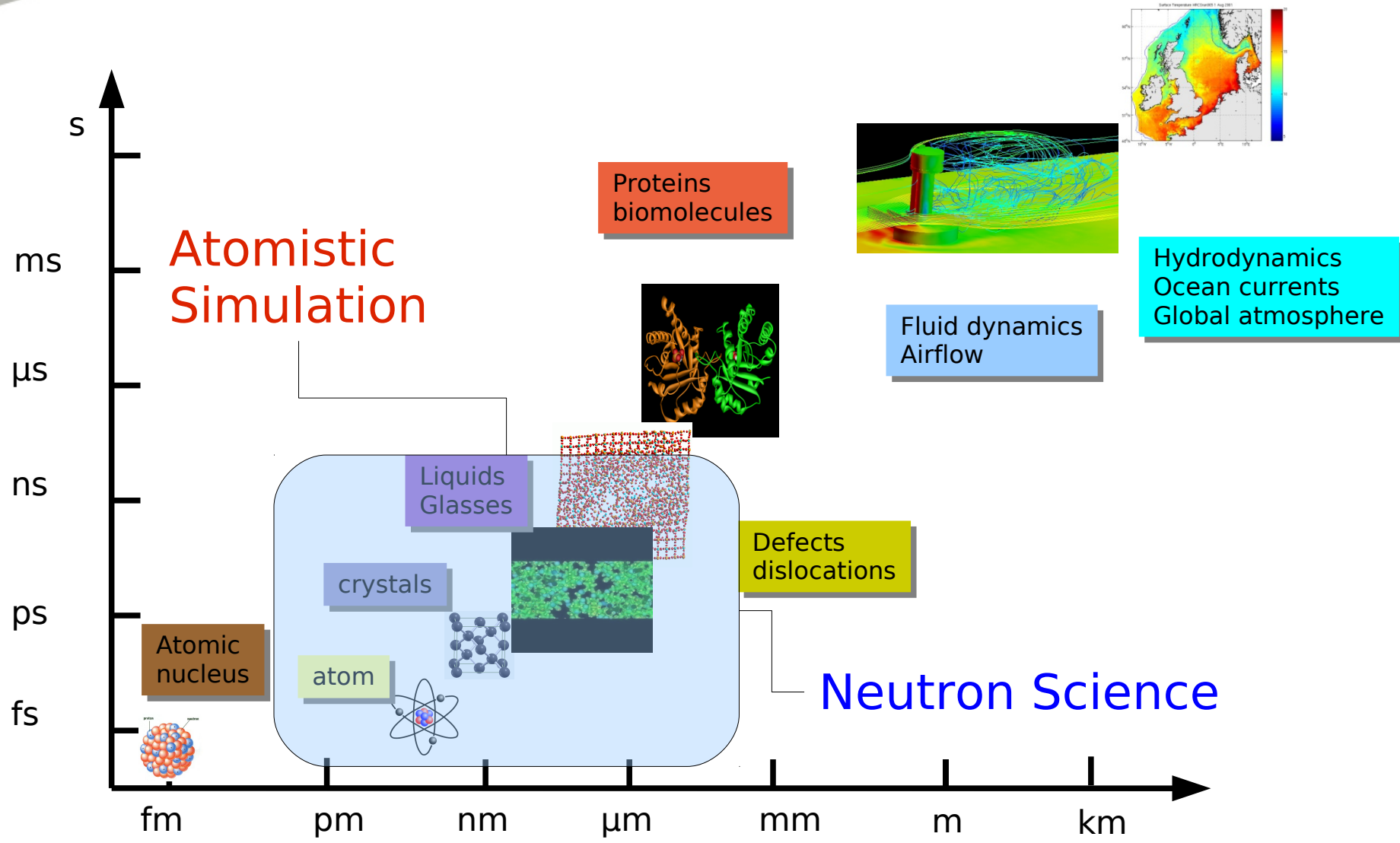
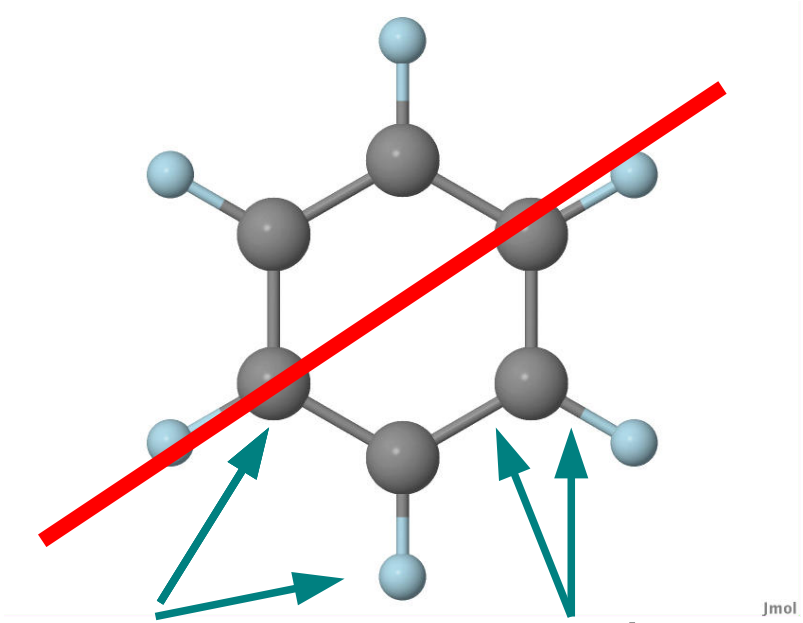
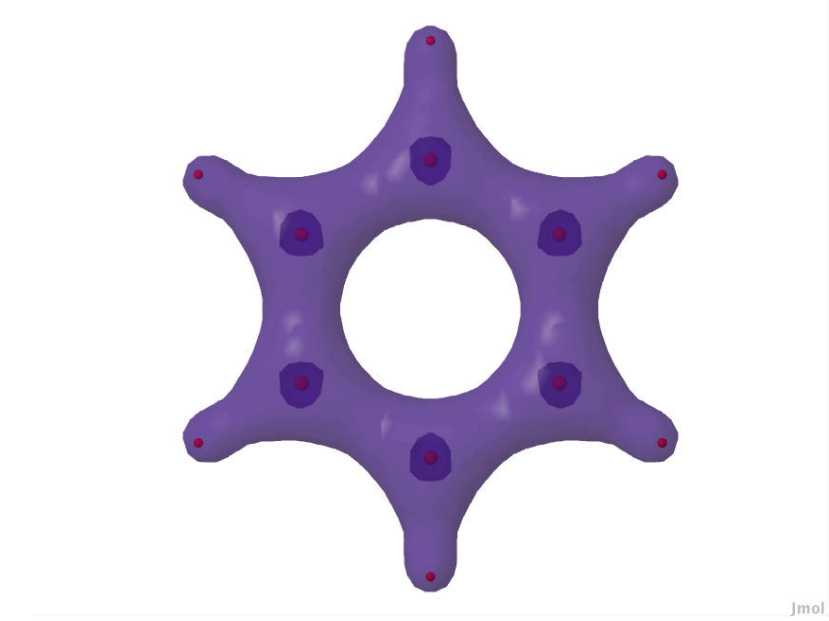
Simulation scales



A Chemistry Toolbox



Atoms Bonds



Nuclei Electrons

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

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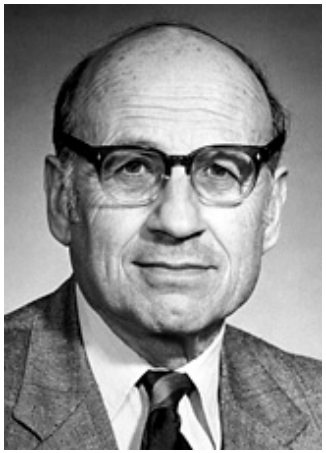
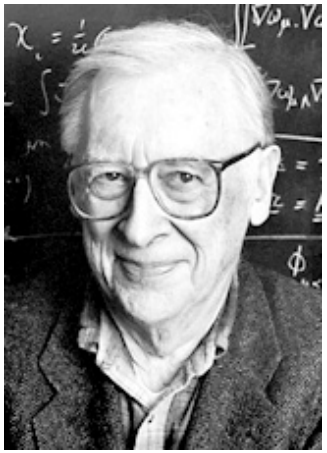
Approximate quantum mechanics





The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry".

Key developments dating back to 1960s and 70s were approximate quantum theories which were nevertheless “good enough”.

Density Functional Theory- Local Density Approximation

Hartree-Fock approximation, MP2, CI, CCSD(S,T)

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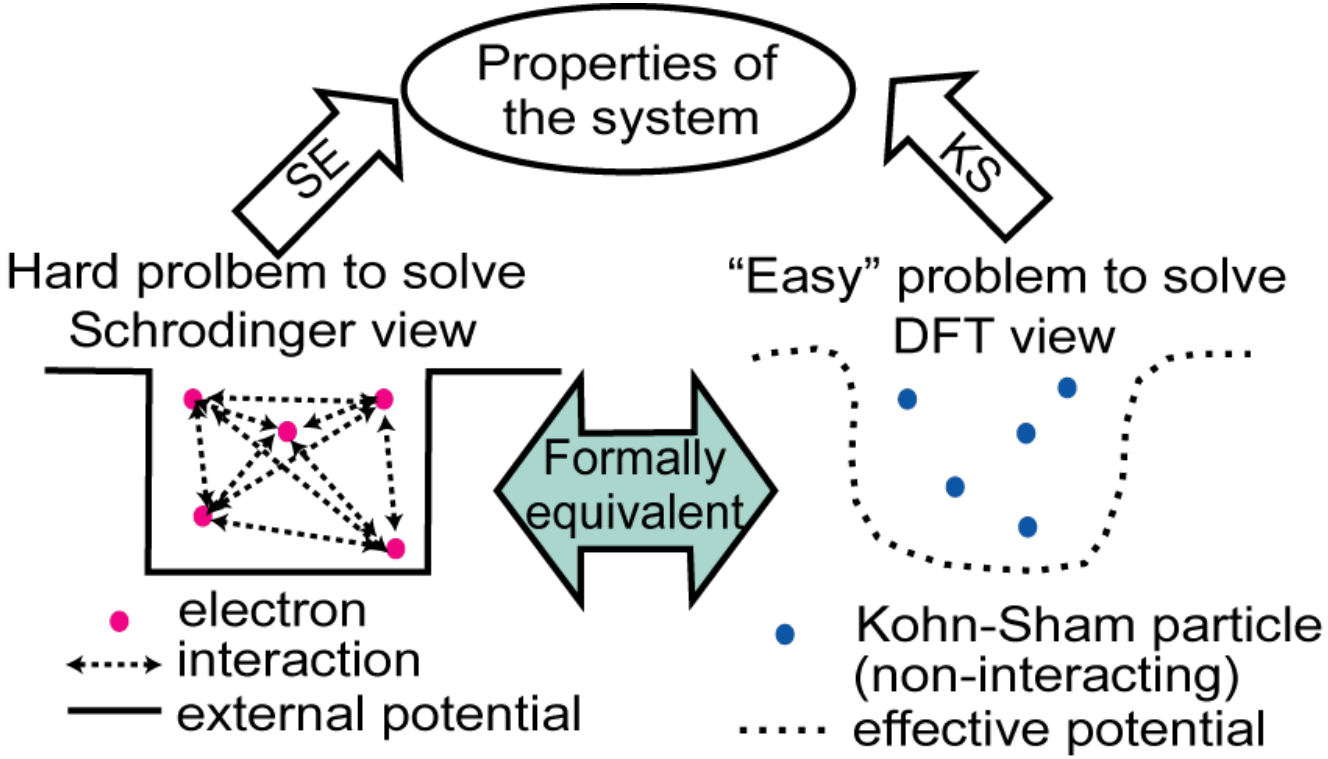
Density Functional Theory

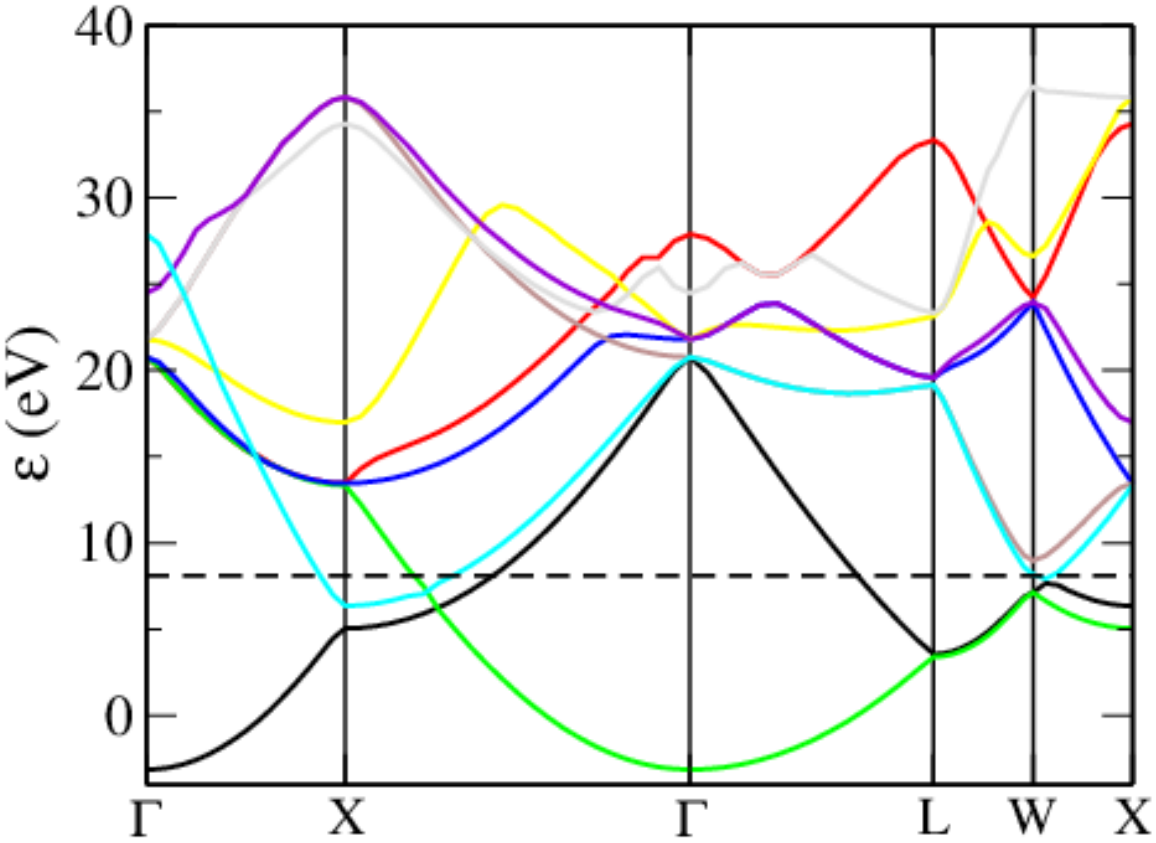


Approximate e-e interaction with
- local density approximation (LDA)
- generalized gradient approximation (GGA)
- Hybrids, DMFT, GW, ...

Modified from Mattsson et al., (2005) Modeling. Simul. Mater. Sci. Eng. 13, R1.

1970s: Bandstructure Calculations

$$\hat{H}\Psi_i = \epsilon_i \Psi_i$$



1980s: Total Energy Calculations

$$E_{tot} = \langle \Psi | \hat{H} | \Psi \rangle = E_{BS} + E_{I-I} - E_{e-e}$$

Total energy calculations in solid state physics

J Ihm†

Bell Communications Research, Murray Hill, New Jersey 07974, USA

Abstract

Total energy calculations for the study of atomic and electronic structures of solids are reviewed. A history of total energy calculations in solid state physics from the emergence of quantum physics to the mid 1970s is briefly summarised. Important developments in the last decade, the period during which computing capability has grown explosively all over the world, are then described. Modern computational method are discussed in detail, with emphasis on the tight-binding, quantum-chemical

Totally Useless?

$$E_{tot} = E_{BS} + E_{I-I} - E_{e-e}$$

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Totally Useless?

$$E_{tot} = E_{BS} + E_{I-I} - E_{e-e}$$

$$P = -\frac{dE_{tot}}{dV}$$

$$F_j = -\frac{dE_{tot}}{d} R_j$$

$$\Phi_{i,j} = \frac{d^2 E_{tot}}{d R_i d R_j}$$

$$\alpha_{ij} = \frac{d^2 E_{tot}}{d E_i d E_j}$$

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Totally Useless?

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$$\alpha_{ij} = \frac{d^2 E_{tot}}{dE_i dE_j}$$

$$I^{raman}_{m,i,j} \propto \frac{d^3 E_{tot}}{dE_i dE_j dQ_m}$$

$$\chi^{(2)}_{i,j,k} \propto \frac{d^3 E_{tot}}{dE_i dE_j dE_j}$$

$$\frac{\delta\omega}{\omega} \sim \frac{d^3 E_{tot}}{dR_i dR_j dR_k}$$

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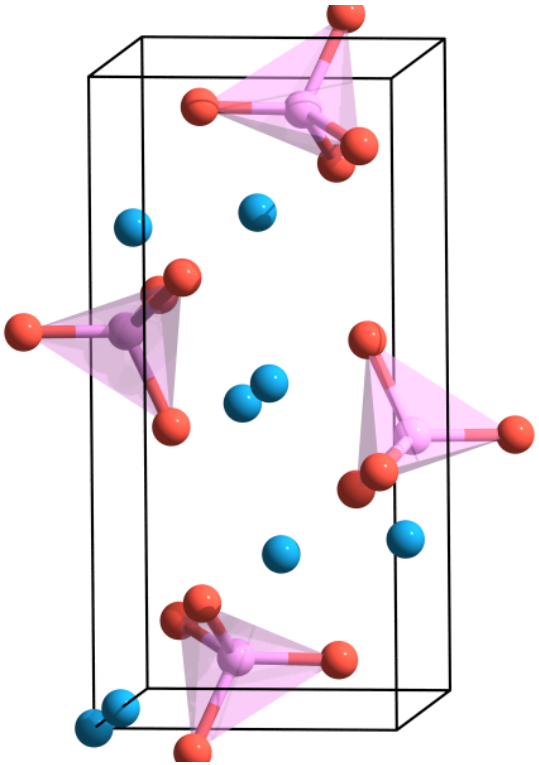
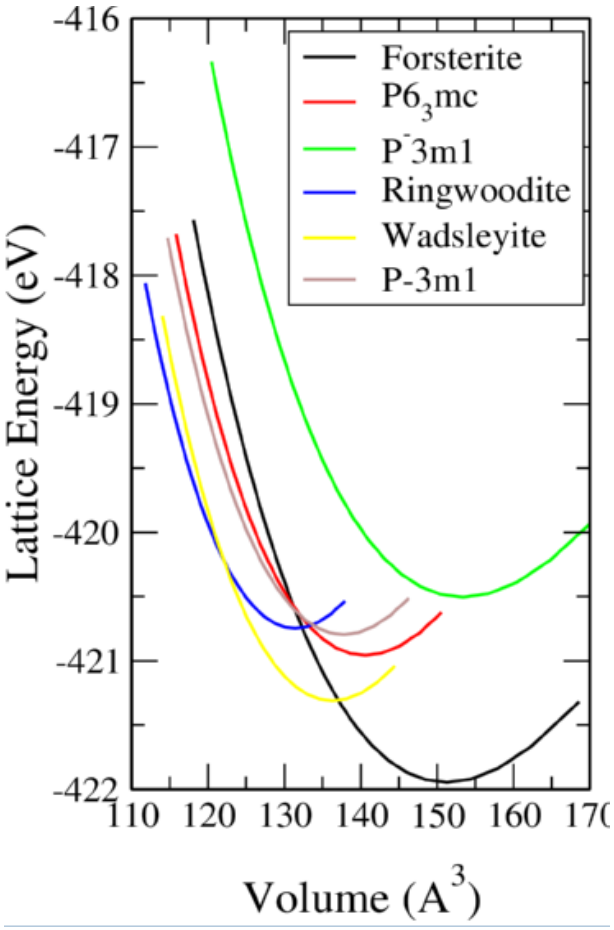
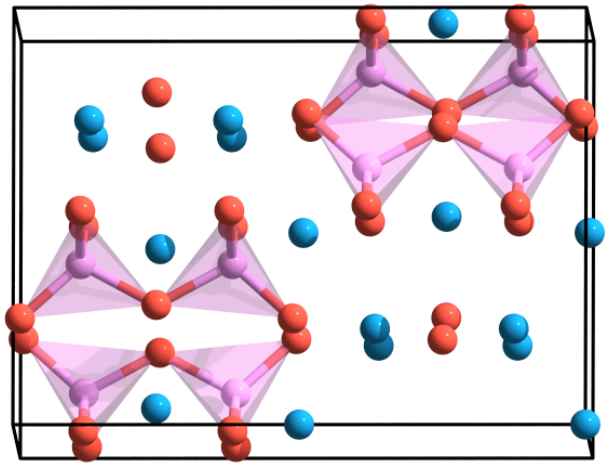
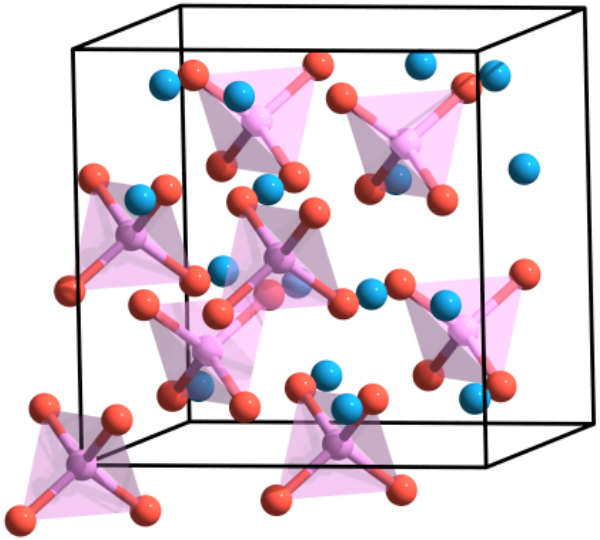
From electronic to crystal structure

Polymorphs of Mg_2SiO_4







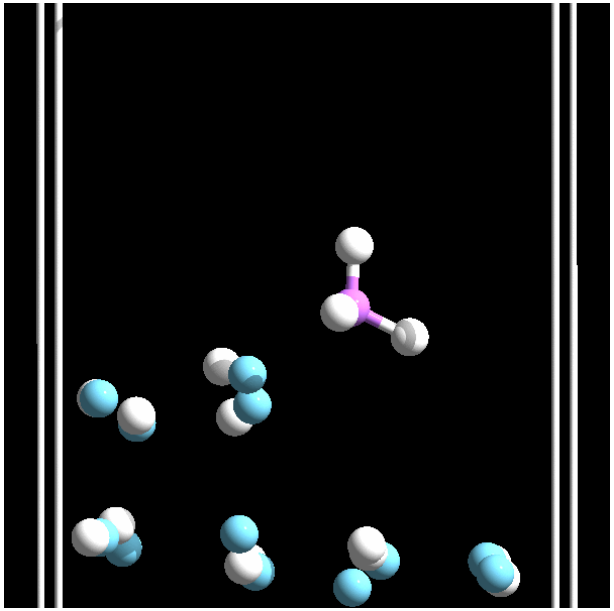


Ab-initio modelling of condensed matter

- Modelling of solids, liquids, surfaces, nanostructures
- Ingredients: atomic nuclei and electrons
- Quantum-mechanical description of interactions.
- Mostly Density Functional Theory (DFT)
- Contains good description of metallic, covalent, ionic bonding.
- Post – DFT approximations (SX, hybrid) more expensive.
- Quantum-mechanical forces allow geometry optimisation and molecular dynamics simulation.
- Electronic effects, polarisation, spectra also available.
- Many other properties can be calculated from first principles.

Dynamics of nuclei

With forces calculated from DFT
Can also calculate dynamics:
- Molecular dynamics – time evolution
- Lattice dynamics - spectroscopy



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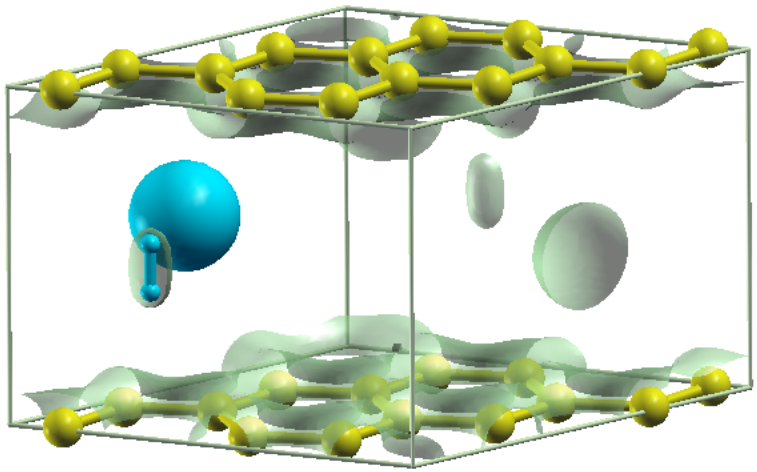
CASTEP

UK plane-wave materials simulation code

Emphasis on properties calculation

- Electronic properties: band structure, DOS, PDOS,
  Mulliken and Hirshfeld population analysis
  ELF, Wannier Functions.
  Core hole spectroscopy – EELS, XANES
  EFG
- Response properties
  NMR chemical shifts, J-coupling
- Vibrational spectroscopy
  Density Functional perturbation for phonons
  Quasi-harmonic thermodynamics.
  Dielectric response and polarizability
  Born effective charges
  ir and Raman intensities.



Roadmap

- Time-dependent DFT
- More efficient hybrid exchange functional approximations
- Spin-Orbit coupling
- Non-collinear magnetism
- GW

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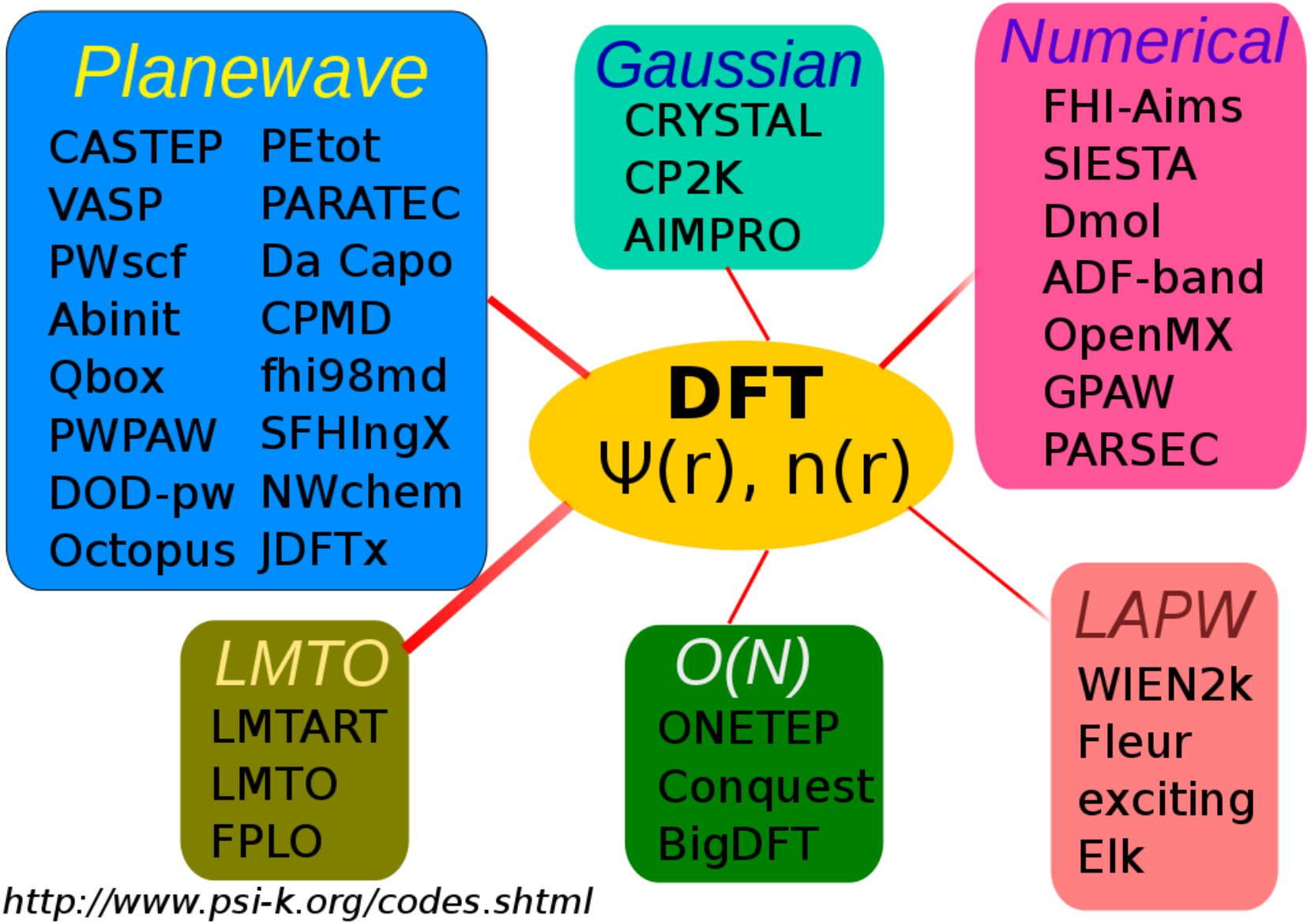
DFT Codes



http://www.psi-k.org/codes.shtml

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Parallel Supercomputing

Parallel supercomputing enables large calculations and high

http://www.hector.ac.uk

http://www.stfc.ac.uk/hartree

http://www.top500.org

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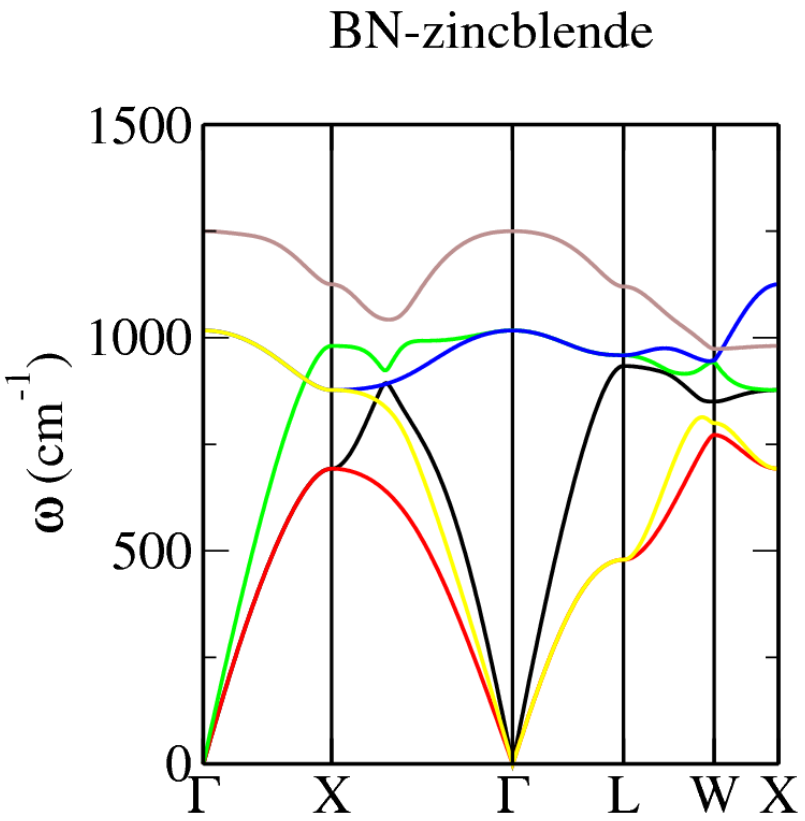
Vibrational Spectroscopy in CASTEP

- Full *ab-initio* lattice dynamics code
- Plane-wave basis w pseudopotentials
- DFPT and supercell methods
- Phonons across full BZ by interpolation
- Symmetry analysis of eigenvectors
- Highly parallel for HPC use (can use 1000's of cores)



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Modelling the spectrum

Orientationally averaged infrared absorptivity

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

Raman cross section

$$I^m_{\text{raman}} \propto \left| \boldsymbol{e_i} \cdot \boldsymbol{A^m} \cdot \boldsymbol{e_s} \right|^2 \frac{1}{\omega_m} \left(\frac{1}{\exp(\hbar \omega_m / k_B T) - 1} + 1 \right)$$

$$A^m_{\alpha,\beta} = \sum_{\kappa,\gamma} \frac{\partial^3 E}{\partial \boldsymbol{\mathcal{E}}_\alpha \partial \boldsymbol{\mathcal{E}}_\beta \partial u_{\kappa,\gamma}} u_{m,\kappa,\gamma} = \sum_{\kappa,\gamma} \frac{\partial \epsilon_{\alpha\beta}}{\partial u_{\kappa,\gamma}} u_{m,\kappa,\gamma}$$

Inelastic neutron cross section

$$S^n(\omega_m) = \int d\boldsymbol{Q} \sum_\kappa \sigma_\kappa \left\langle \frac{(Q \cdot u_{m,\kappa})^{2n}}{n!} \exp(-(Q \cdot u_{m,\kappa})^2) \right\rangle$$

Spectral response to light depends on response of electrons; for neutrons only nuclei.

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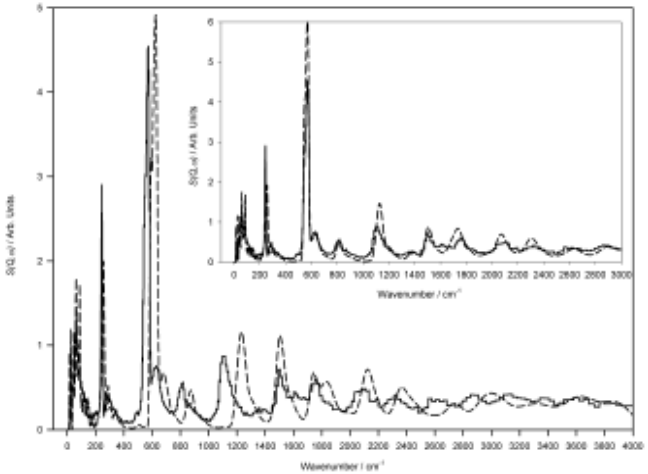
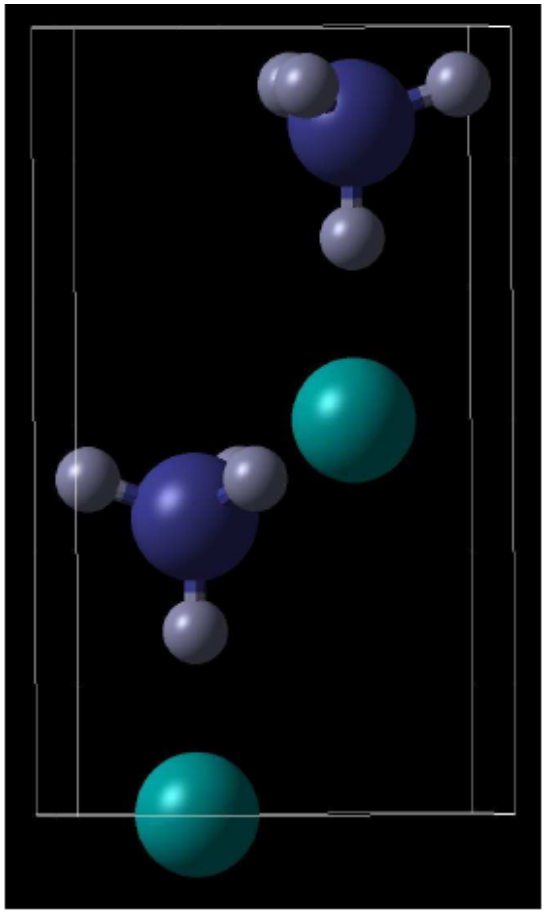
INS Spectrum of Ammonium Fluoride

- **NH_4F** is one of a series of ammonium halides studied in the ISIS TOSCA spectrometer.
- Collab. Mark Adams (ISIS)
- Structurally isomorphic with ice ih
- INS spectrum modelled using ACLIMAX software (A. J. Ramirez Cuesta, ISIS)
- Predicted INS spectrum agrees with experiment
- NH4 libration modes in error by ≈ 5%.
- Complete mode assignment achieved.





Adams, Refson & Gabrys, Phys. Chem. Chem. Phys 7, 3685 (2005)

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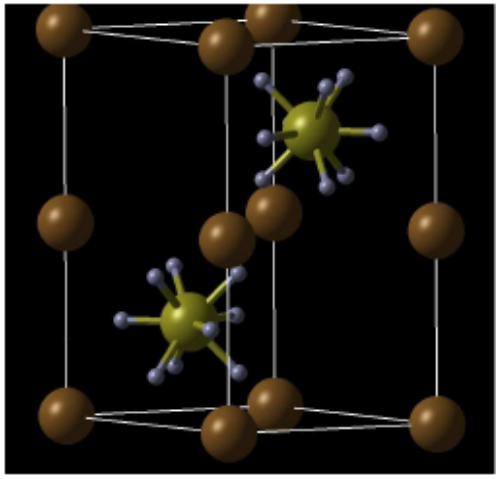
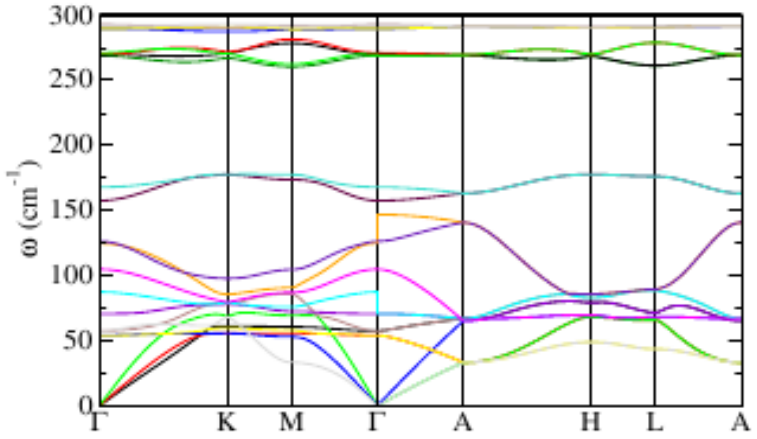
INS Spectrum of Ba ReH_9

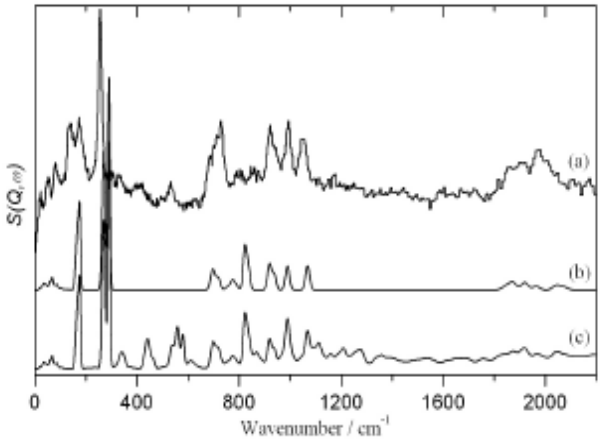


- Collab with S. F. Parker, ISIS facility, RAL.
- BaReH9 with unusual $ReH_9$2+ ion has very high molar hydrogen content.
- INS spectrum modelled using A-CLIMAX software (A. J. Ramirez Cuesta, ISIS)

Predicted INS spectrum in mostly excellent agreement with experiment

- LO/TO splitting essential to model INS.
- Librational modes in error (c.f NH4 F)
- Complete mode assignment achieved.





Parker et. al. Inorg. Chem 45, 10951 (2006)

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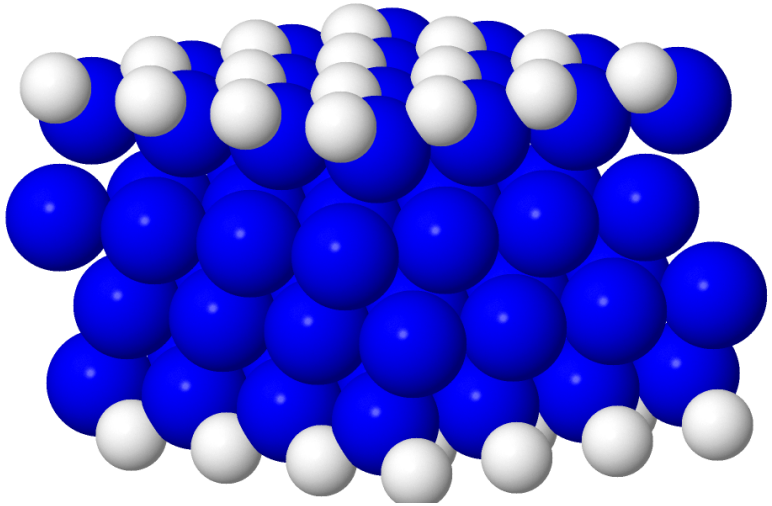
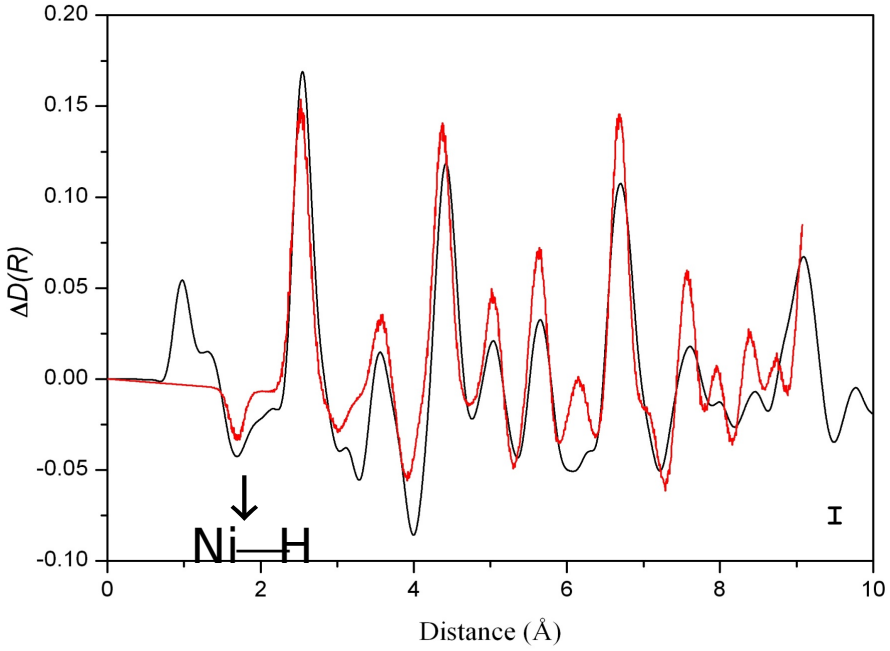
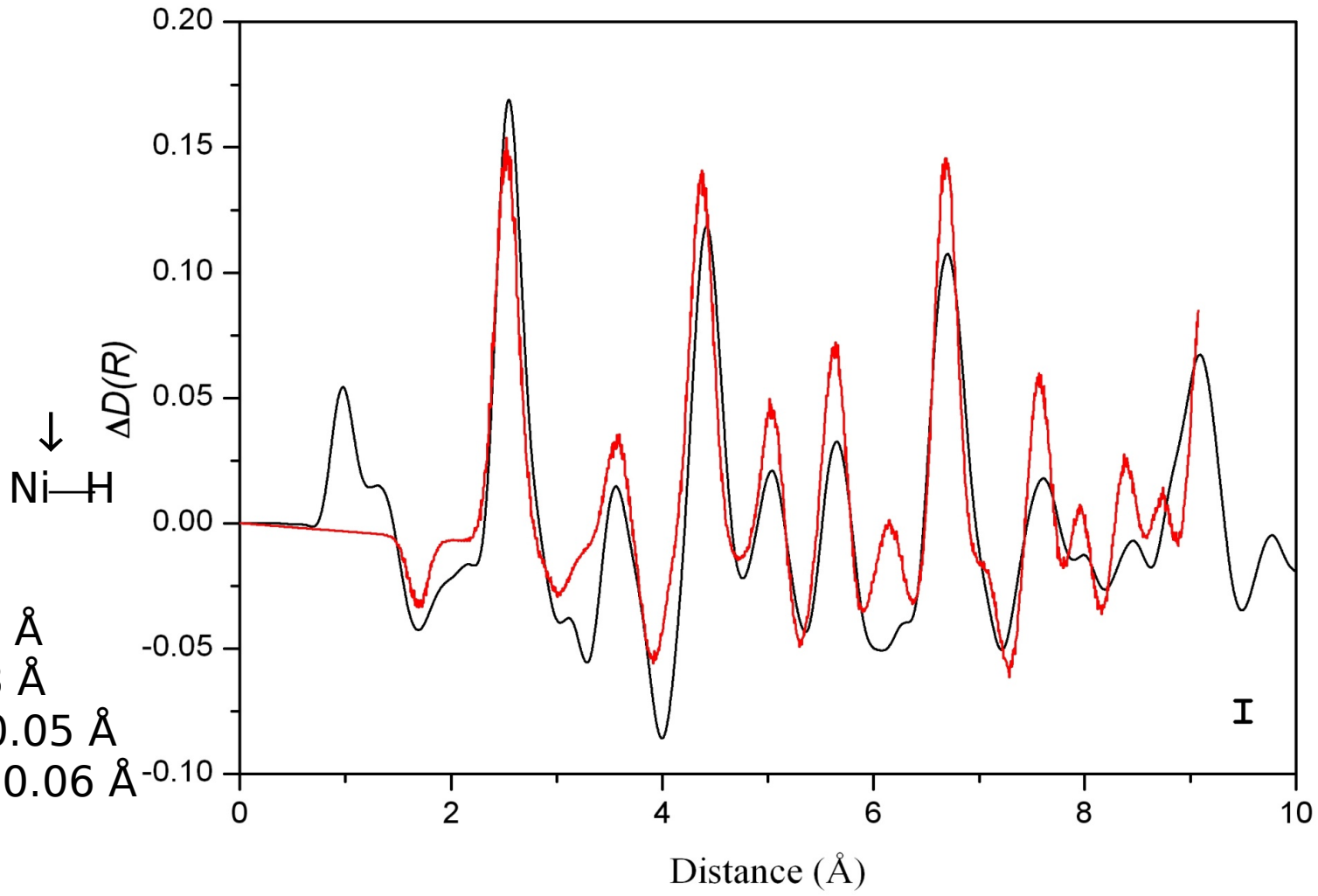
Raney(TM) Ni Catalyst



Difference pair distribution ΔD(r) with and without H (SANDALS measurement)
Calculated ΔD(r) from simulation



Ni-H distance
Neutron: 1.68 Å
Ab initio: 1.68 Å
LEIS: 1.65 ± 0.05 Å
LEED: 1.84 ± 0.06 Å



Ni—H

Neutron: 1.68 Å

Ab initio: 1.68 Å

LEIS: 1.65 ± 0.05 Å

LEED: 1.84 ± 0.06 Å

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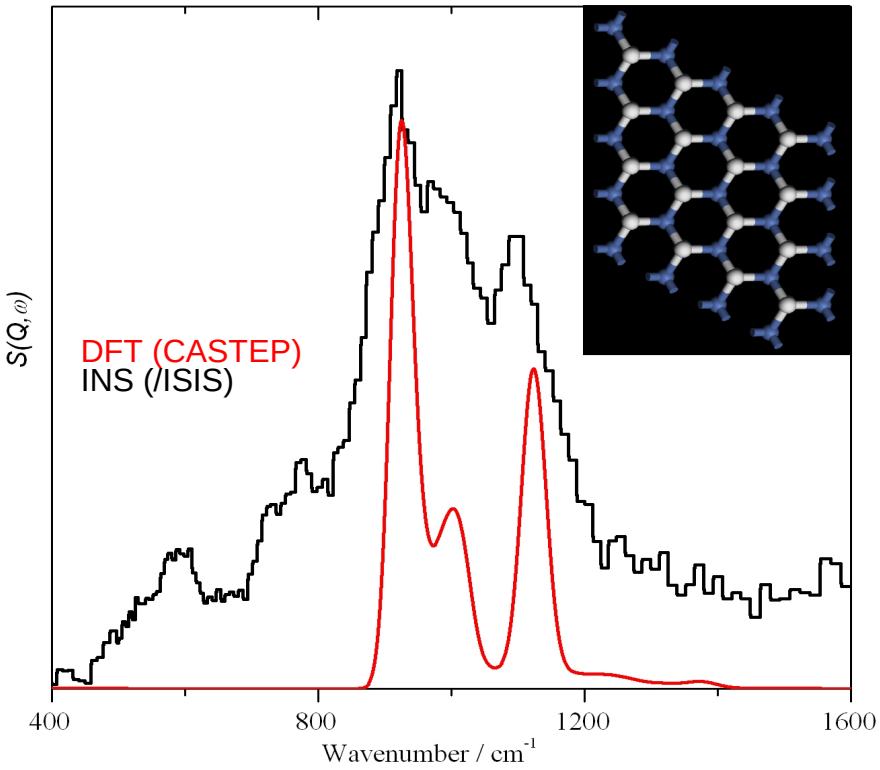
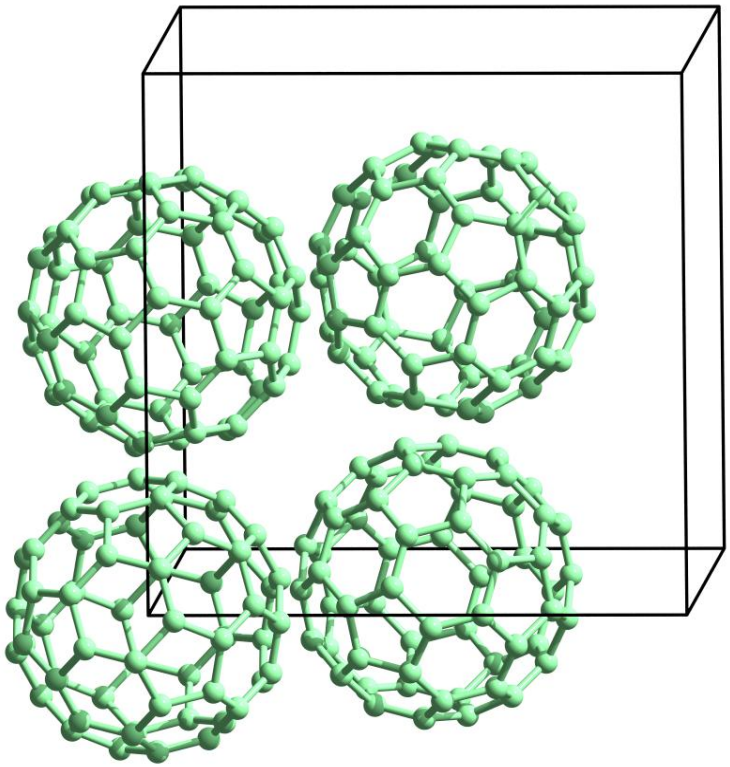
Structure determination of adsorbed hydrogen on a real catalyst.

- Raney® Ni is large-scale industrial catalyst (e.g. hydrogenation of fats)
- Combined neutron diffraction, inelastic neutron scattering (ISIS) and *ab initio* DFT (CASTEP/CSED) studies reveal structure and dynamics of monolayer H on Ni (111).
- Ni-H distance is 1.68Å (expt), 1.68Å(DFT)
- DFT vibrational spectrum shows 3 peaks in agreement with inelastic neutron scattering (TOSCA instrument, ISIS).
- Structure-property relationship confirms geometry of Ni(111)/H monolayer.



S. F. Parker, D. T. Bowron, S. Imberti, A. K. Soper, K. Refson, E. S. Lox, M. Lopez, and P. Albers, *Chem. Comm.* **46**, 2959-61 (2010).

Raman and ir spectroscopy of C



- Above 260K takes Fm3m structure with dynamical orientational disorder
- m3m point group lower than I_h molecular symmetry
- Selection rules very different from gas-phase.
- Intramolecular modes and factor group splitting seen.
- Try ordered Fm3 model for crystal spectral calculation.

Parker et al, PCCP **13**, 7780 (2011)

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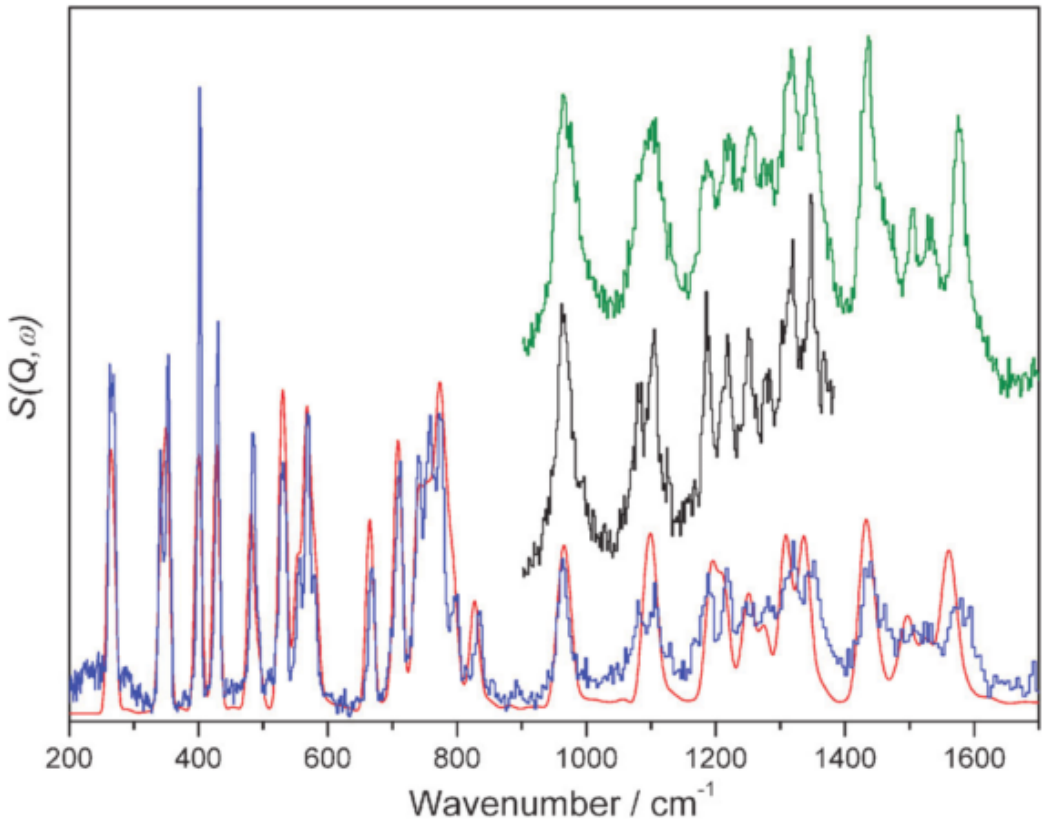
INS -Tosca



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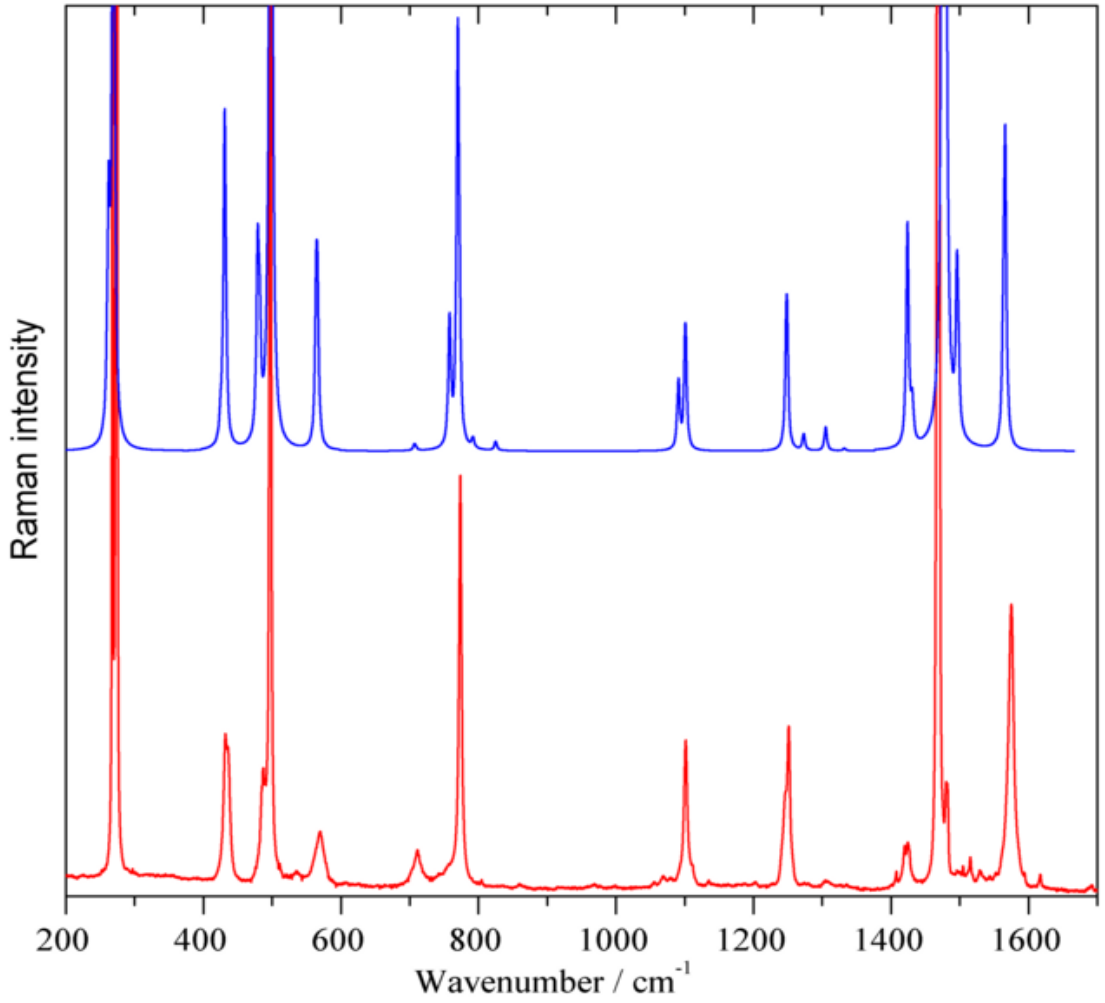
GGA Raman spectrum of C_{60}



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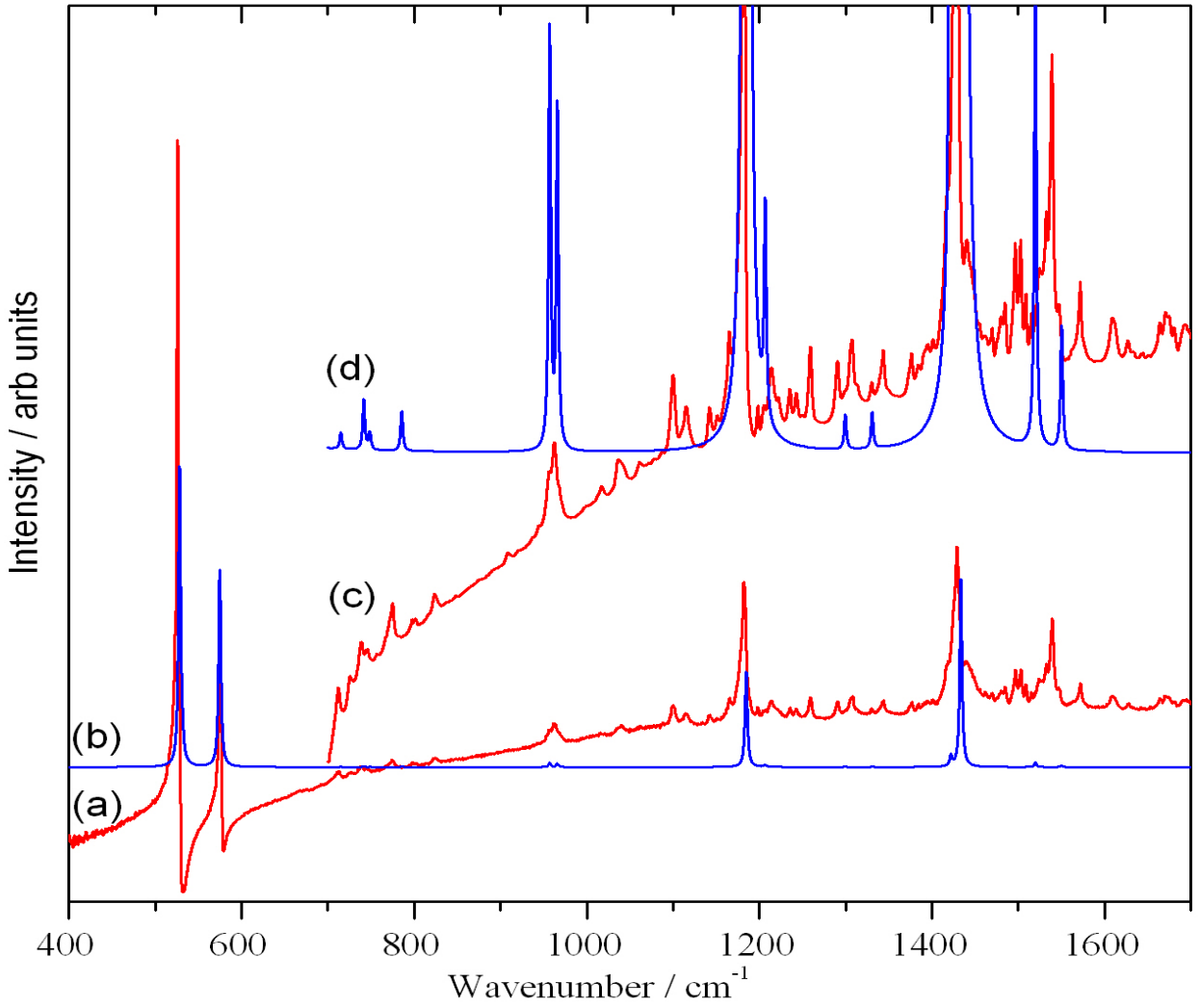
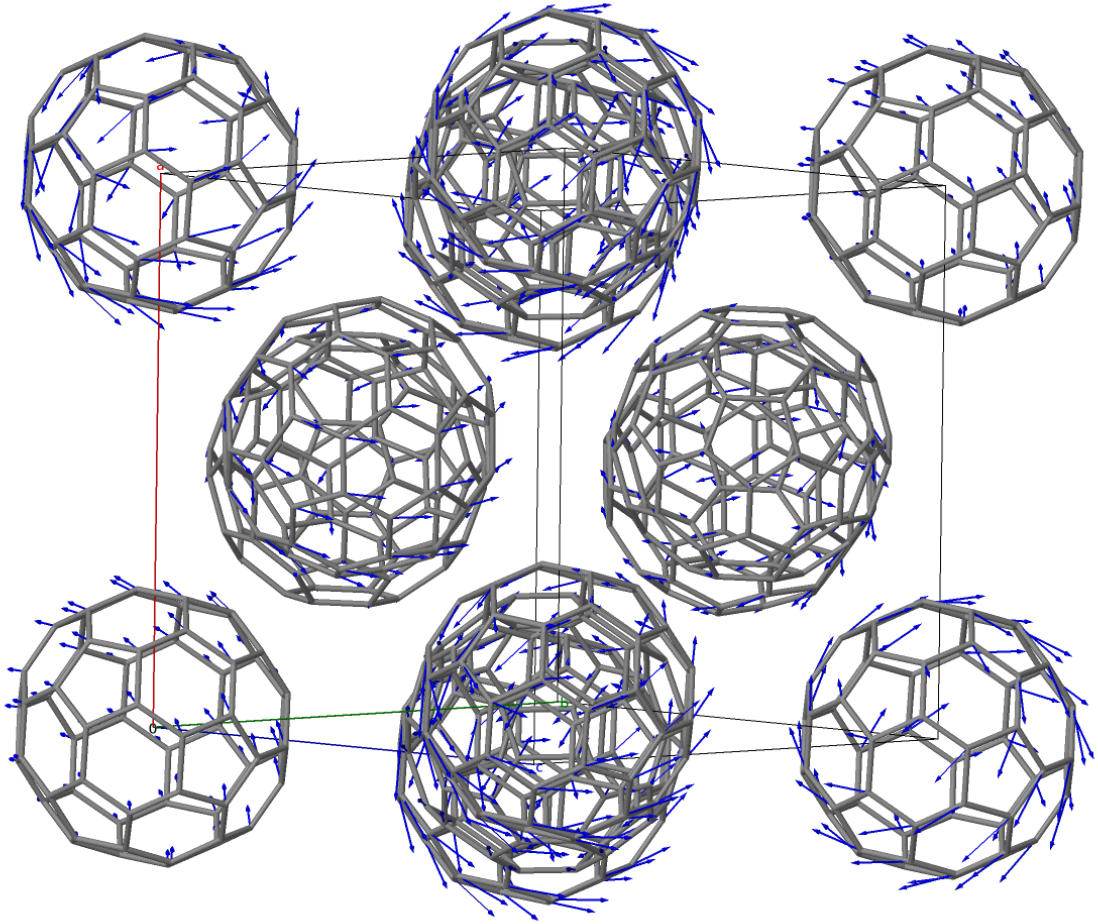
GGA infrared spectrum of C_{60}



Rotational eigenvectors



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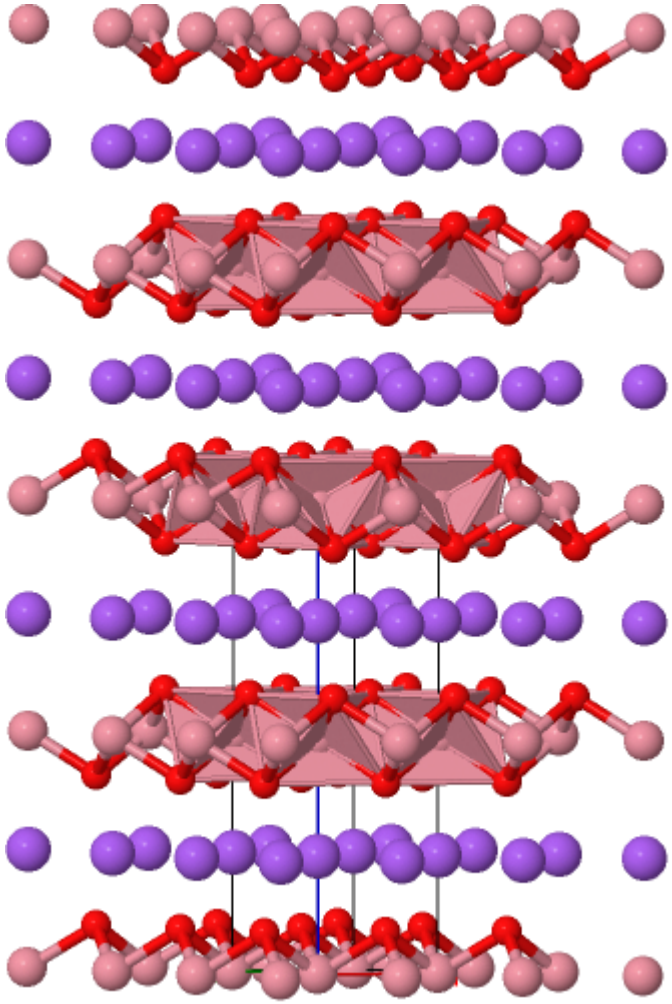
Na_xCoO_2

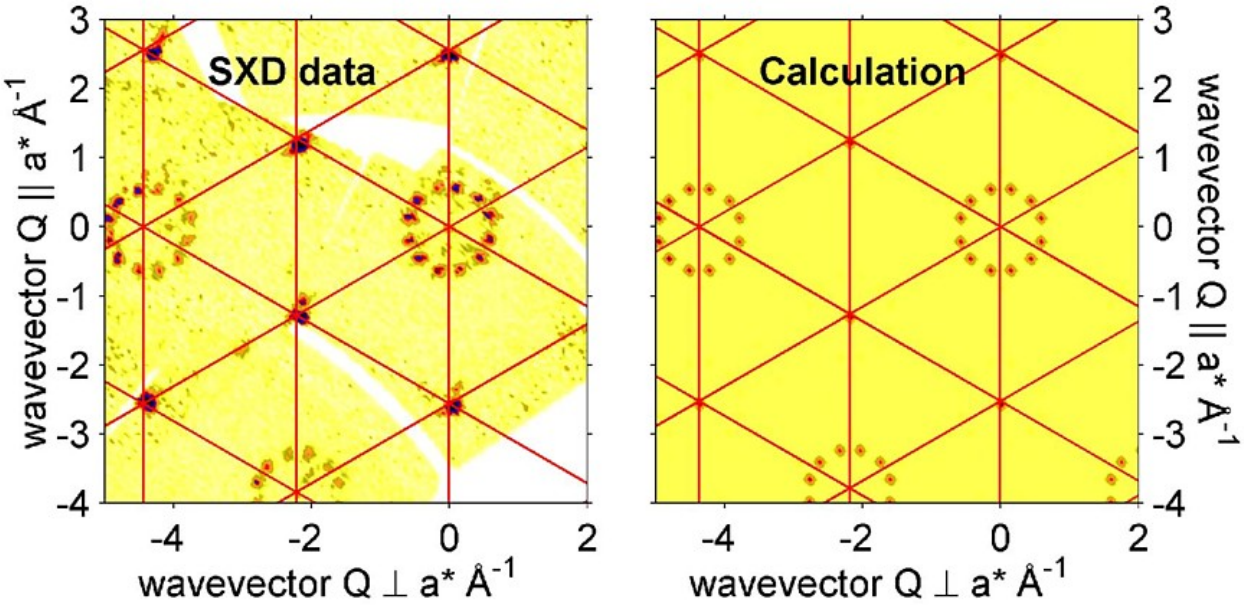


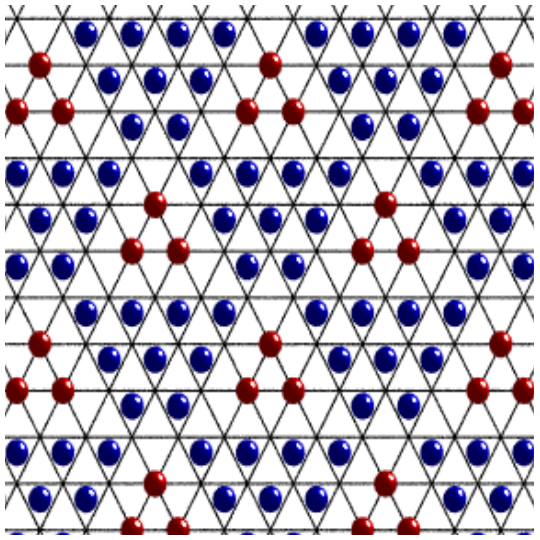
D. J. Voneshen, , K. Refson, et al.
Nature Materials (2013): 2. doi:10.1038/nmat3739.

Thermoelectric $Na_{0.8}CoO2$

12-fold rings, $L = 11$, $T = 150$ K

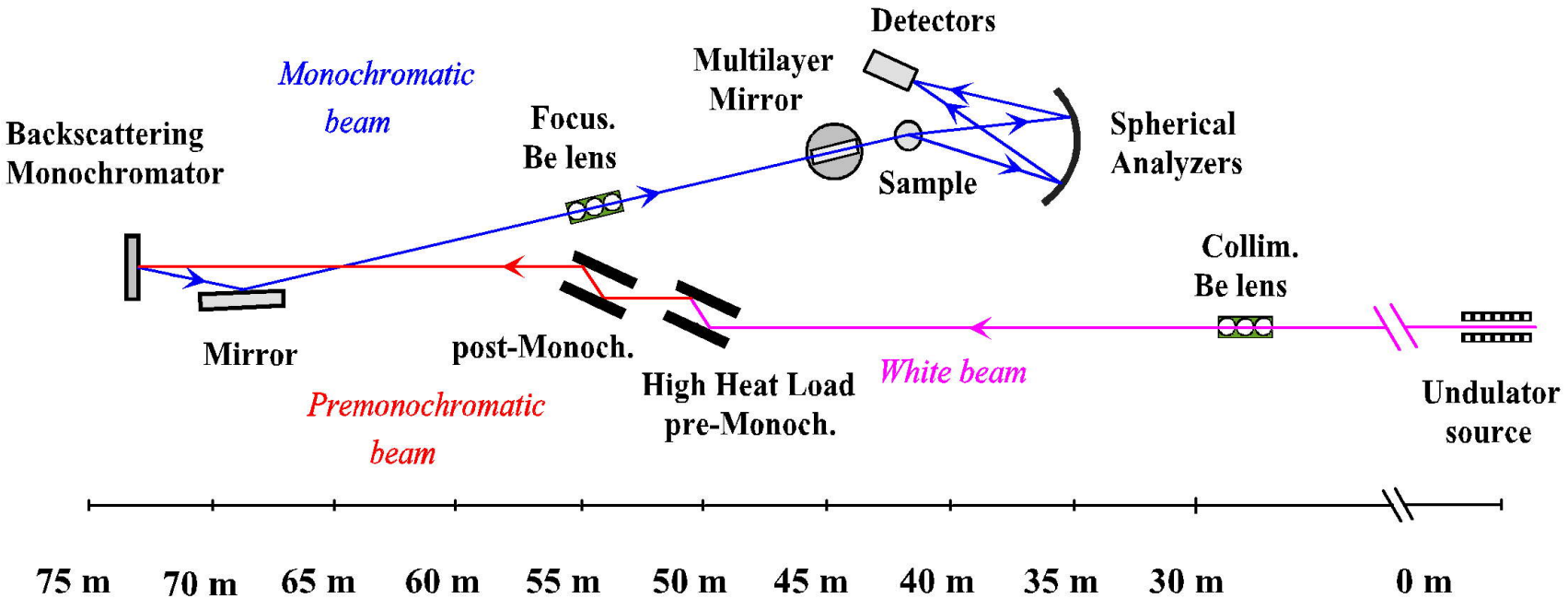
Square phase





Roger, M., *et al*., Patterning of sodium ions and control of electrons in sodium cobaltate. *Nature* **445**, 631 (2007)

Inelastic X-ray Scattering (IXS)



ID28 at the ESRF

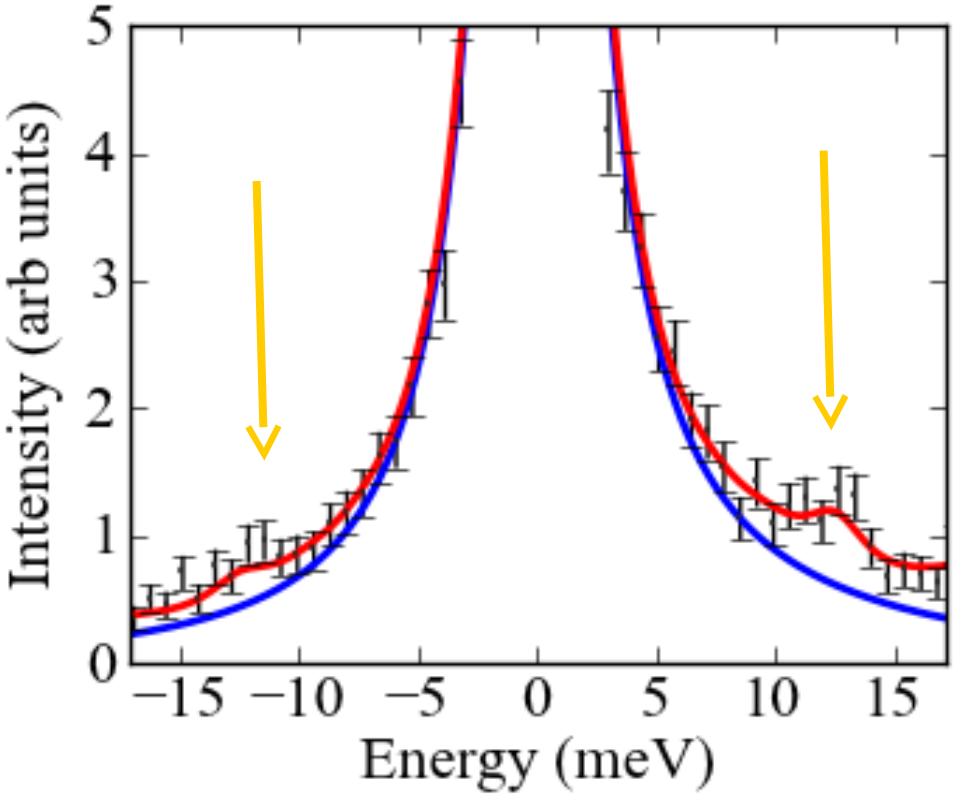
- Study sub-millimetre single crystals throughout Brillouin zone
- Energy resolution ~ 1meV

Inelastic X-ray Scattering (IXS)

Low energy transfer

Q = (1.25,1.25,1)

Arrows indicate position of **rattling mode**



- Typical IXS data in the square phase at $T \sim 200$ K
- Sharp energy line shapes show that it is **not a phonon glass**

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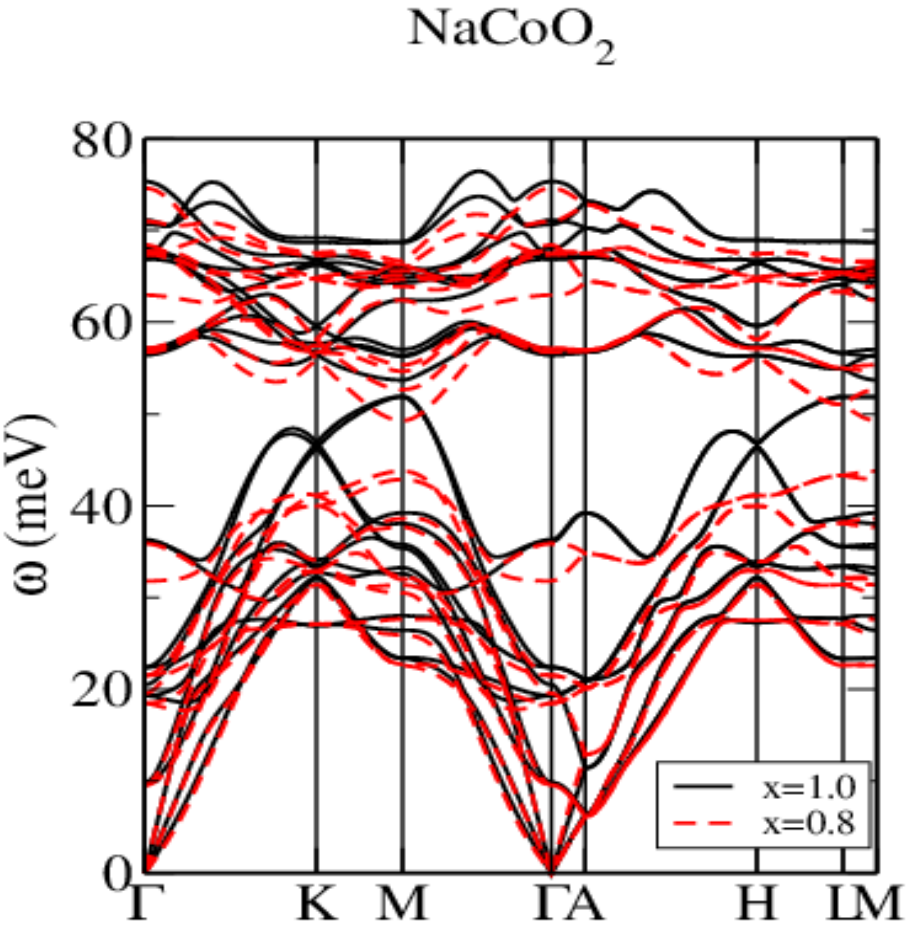
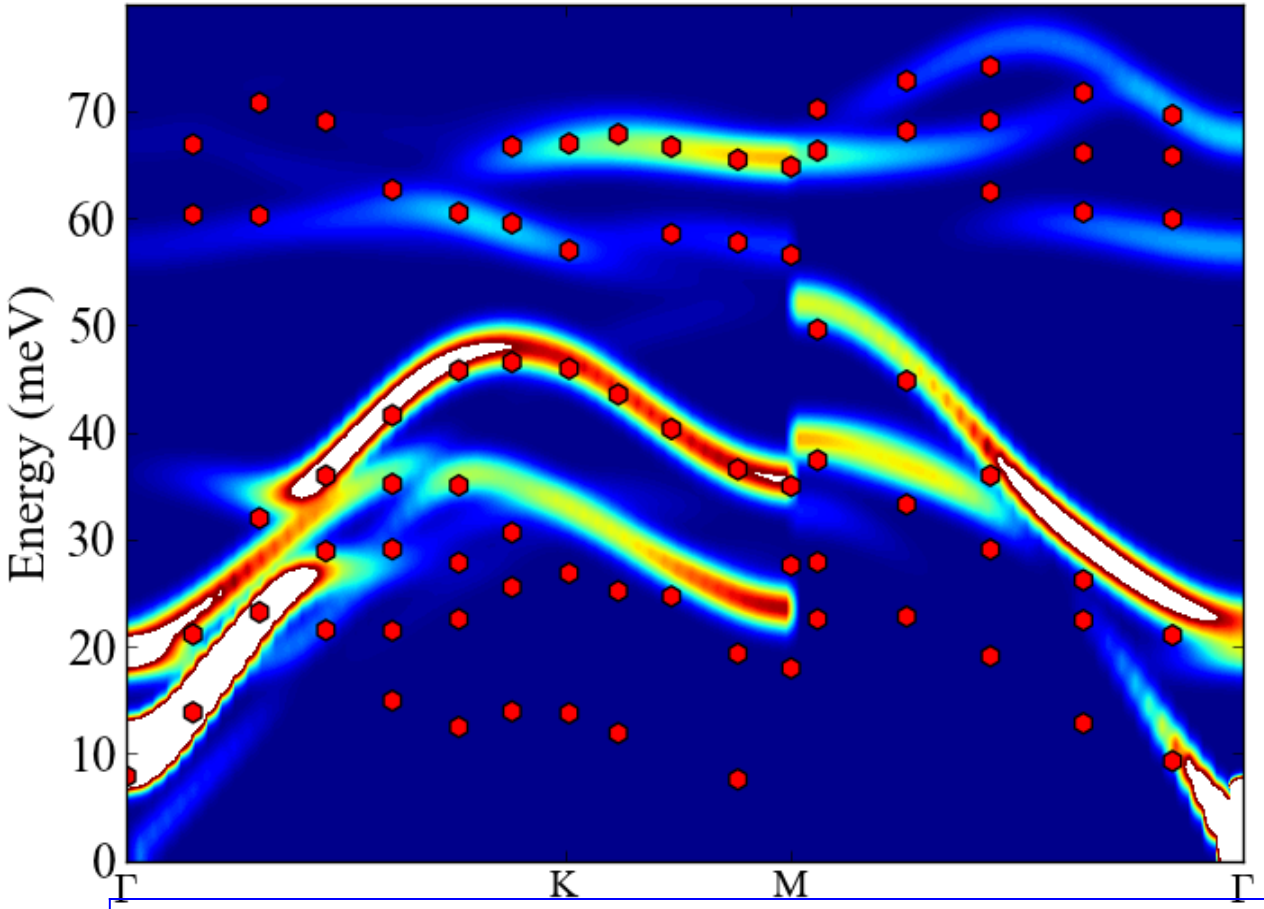
Vibrational Spectroscopy in CASTEP

- Full *ab-initio* DFT lattice dynamics code
- Plane-wave basis + pseudopotentials
- DFPT and supercell methods
- Phonons across full BZ by interpolation
- Symmetry analysis of eigenvectors
- Highly parallel for HPC use (can use 1000's of cores)

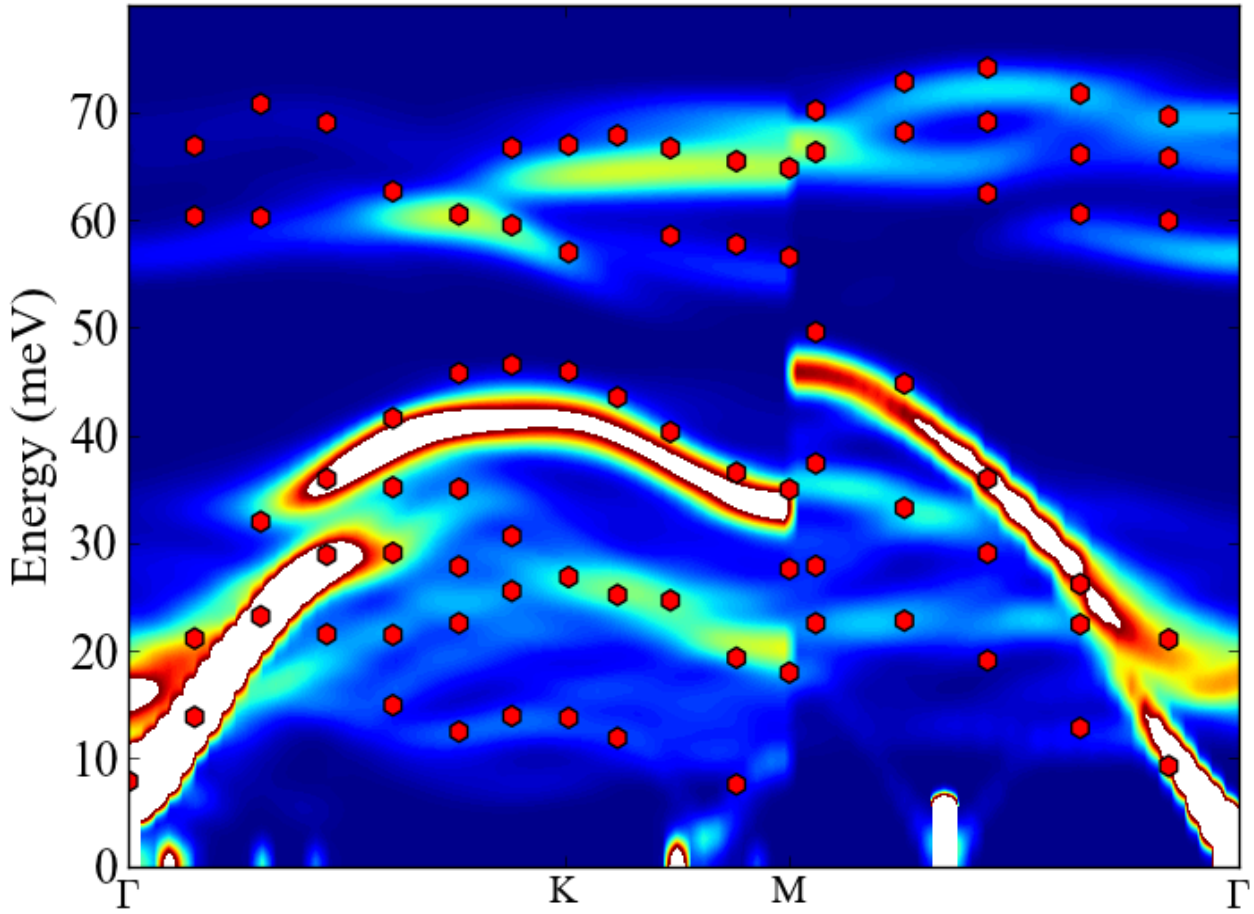


Inelastic X-ray Scattering (IXS)



- Phonon dispersion determined by IXS
- CASTEP calculation for **$NaCoO_2$**

Inelastic X-ray Scattering (IXS)



- Phonon dispersion determined by IXS
- CASTEP calculation for **$Na_{0.8}CoO_2$**

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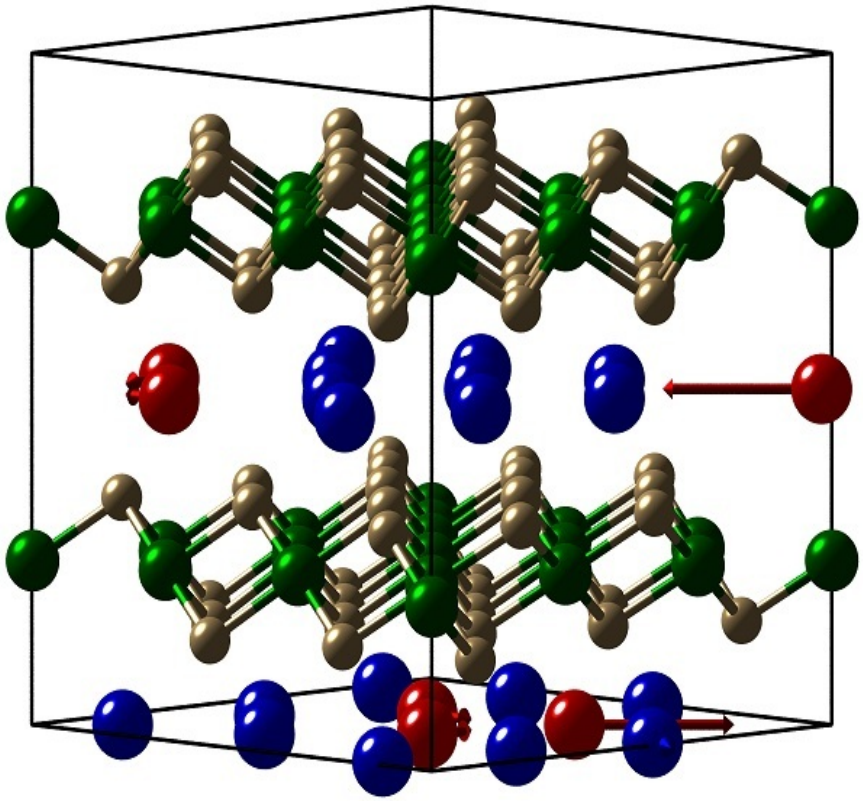
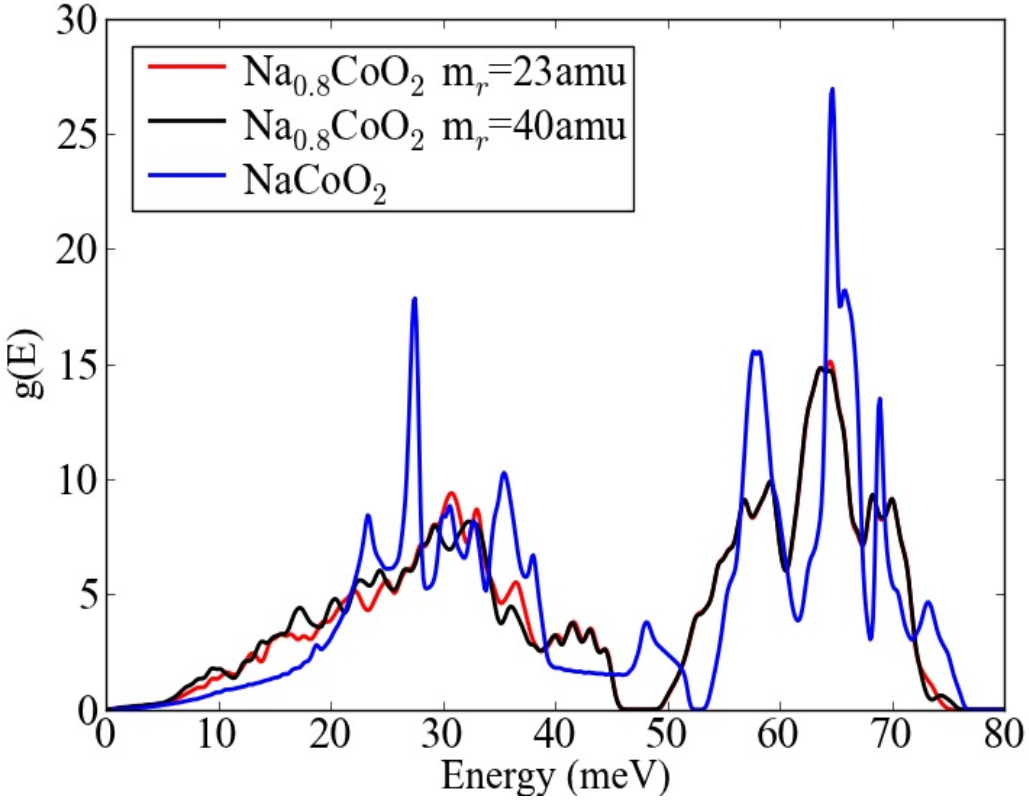
Phonon modes



- **Rattling mode** observed using IXS
- Na 2*b* ions have large-amplitude vibrations

Phonon density of states

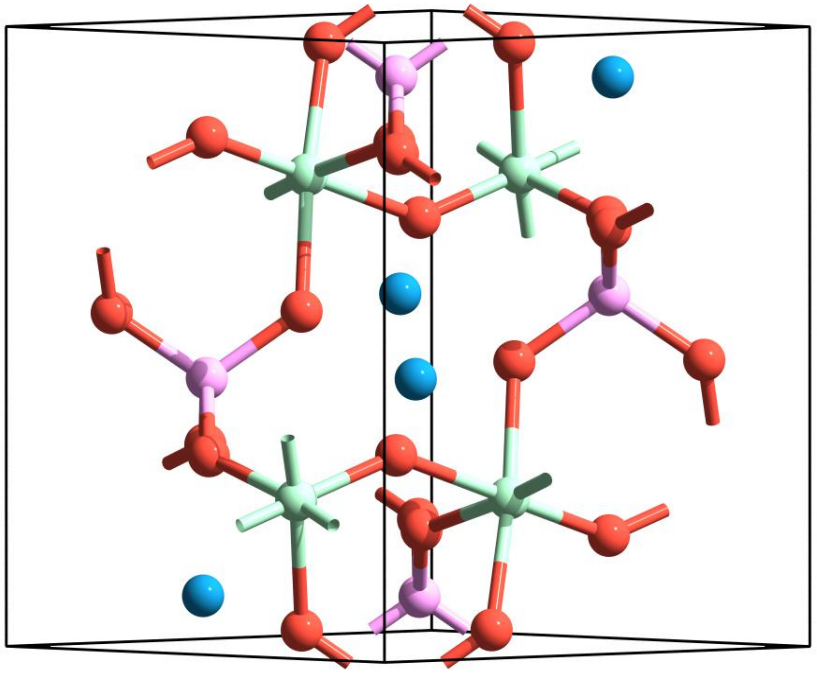


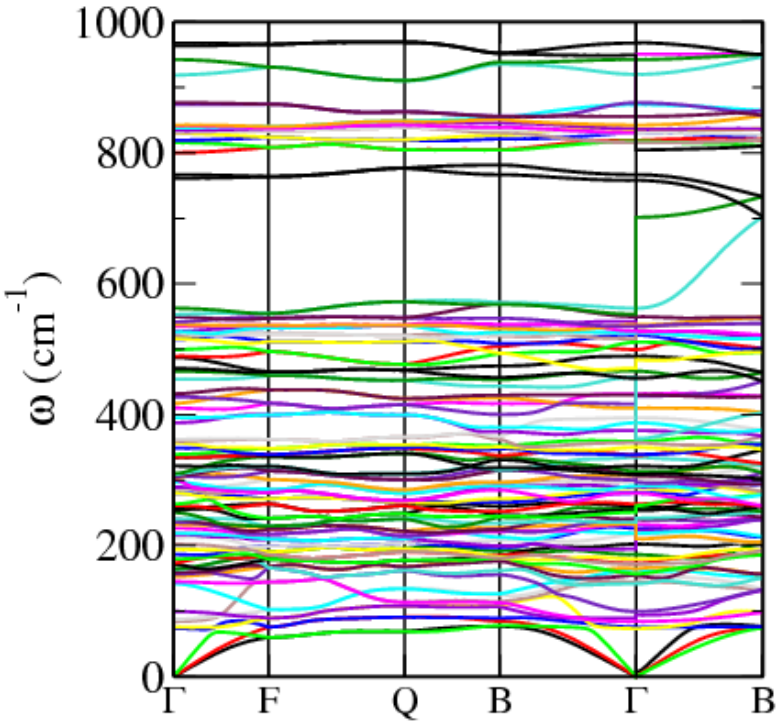
- Rattler only affects modes below $E \sim 40$ meV
- Transfer from sharp peaks to low energy

Conclusions

- Approximate quantum mechanical calculations of thousands of electrons and ions can are practical today.
- Chemical bonds, crystal structure, atomic dynamics arise as emergent properties.
- Density Functional-based approximations good enough for vast range of (but not all) materials and properties.
- Combination with neutron is a productive match.

The Phonons of Sphene

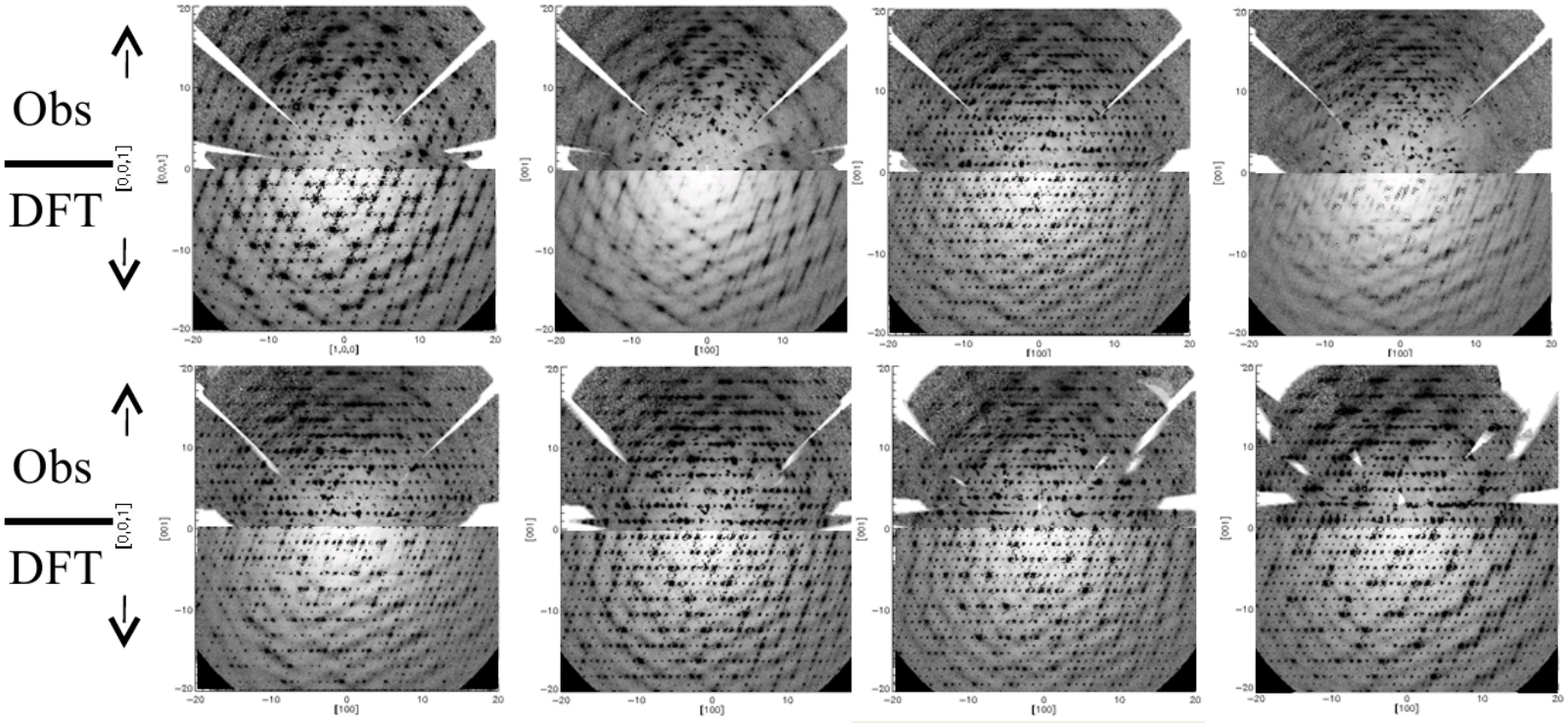




$CaTiSiO_5$ “sphene” or “titanite" is Calcium titanate mineral

Antiferroelectric distortion at R.T. Phase transition at 500K

Anomalous phonon dispersion and LO/TO splitting along Γ-B

Thermal diffuse scattering

- Thermal diffuse scattering measured on SXD (ISIS) 300K
- TDS calculated from *ab -initio* eigenvectors and frequencies
- Sharp features sensitive to acoustic phonons
- Broad features are sensitive to optic modes