First-Principles Vibrational spectroscopy and lattice dynamics of materials in the solid state

Keith Refson
Computational Science and Engineering Department
STFC Rutherford Appleton Laboratory
First principles modelling

\[ -\frac{\hbar^2}{2m_e} \Psi + \hat{V} \Psi = E \Psi \]
Density Functional Theory

Approximations to exchange and correlation
• Local Density Approximation (LDA)
• Generalised Gradient Approximation (GGA)

Modified from Mattsson et al., (2005)
DFT with a Plane-wave basis

➢ Periodic boundary conditions applied to ions orbitals, electron densities.
➢ Electron density represented on grid.
➢ Basis coefficients of orbitals also stored on grid in \( G \)-space.
➢ Use FFTs to evaluate terms in Hamiltonian.
➢ Never construct Hamiltonian, only compute effect of operator.
➢ Kohn–Sham equations solved using SCF
➢ PW basis is efficient, accurate, robust.
➢ PW basis requires pseudopotentials.
➢ Mature technology – good algorithms.
➢ Robust in use, even by non experts.
The CASTEP project

- Original 1990s CASTEP code by Mike Payne/Accelrys reached end of life.

- Complete re-engineering of a new plane-wave code from scratch beginning 1999.

- Core “Developer Group” of P. Hasnip, S. Clark, M. Probert, C. Pickard, M. Segall, P. Lindan, (Payne) and in 2002, K. Refson.

- Commercialised by Accelrys and integrated into Materials Studio

- Aim: build a flexible, well-engineered development platform for new physics using modular software practices and documented API specification.


- Now at release 6.0.

- Excellent “Core” functionality with many additional capabilities; Structure, dynamics and many properties.
CASTEP Capabilities

CASTEP Capabilities

CASTEP has a variety of Hamiltonians and XC functionals

- Pure local DFT (LDA, LSDA, PBE, RPBE, WC,...)
- Hybrid HF exchange methods (HF, Screened HF, PBE0, B3LYP)
- Model methods (LDA+U)
- More under development (TDDFT, GW,..).

CASTEP can perform many spectroscopic calculations

- IR and raman spectroscopy (vibrational/phonon)
- INS and IXS spectroscopy (vibrational phonon)
- Conduction-band optical dielectric spectra (EELS etc)
- Core level spectroscopy (ELNES, XANES)
- NMR chemical shifts
Vibrational Spectroscopy in CASTEP

- Full *ab-initio* lattice dynamics code
- Plane-wave basis with 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)
Parallel supercomputing enables large calculations and high throughput.

http://hpcsg.esc.rl.ac.uk/scarf/

http://www.hector.ac.uk
Approaches to first principles
Lattice Dynamics

**Density–Functional Perturbation Theory**
- Works with LDA/GGA Hamiltonians
- Only primitive cell calculations required
- Fourier interpolation of dynamical matrices to entire BZ from grid of q-points.
- Can compute dielectric permittivity and Born effective charges
- LO/TO splitting included.
- IR absorptivity or Raman activity included.
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

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

\[
A_{\alpha, \beta}^m = \sum_{\kappa, \gamma} \frac{\partial^3 E}{\partial \mathcal{E}_\alpha \partial \mathcal{E}_\beta \partial u_{m, \kappa, \gamma}} u_{m, \kappa, \gamma} = \sum_{\kappa, \gamma} \frac{\partial e_{\alpha \beta}}{\partial u_{m, \kappa, \gamma}} u_{m, \kappa, \gamma}
\]

Inelastic neutron cross section

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

Spectral response to light depends on response of electrons; for neutrons only nuclei.
NH4F studied in the ISIS TOSCA spectrometer.
Collaborator: Mark Adams (ISIS)
Structurally isomorphic with ice Ih
INS spectrum modelled using ACLIMAX software (A. J. Ramirez Cuesta)
Predicted INS spectrum agrees with experiment
NH4 libration modes in error by ? 5%.
Complete mode assignment achieved.

Raman and ir spectroscopy of $C_{60}$

- Above 260K takes Fm3m structure with dynamic rotational 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.
- Full CASTEP DFPT lattice dynamics calculation on Fm–3 and Pa3 phases
GGA Raman spectrum of C_{60}
Fig. 6  INS spectra of the internal modes of $C_{60}$ in the $P\bar{a}3$ phase: recorded on TOSCA at 20 K (blue), recorded on MARI at 5 K with 1815 cm$^{-1}$ (olive green) and 1452 cm$^{-1}$ (black) incident energy compared with that generated from the CASTEP calculation (red).
GGA infrared spectrum of C$_{60}$
Approaches to first principles
Lattice Dynamics

Finite displacement and supercells
• Works with most general Hamiltonians (PBE0/B3LYP, LDA+U, DFT+D, USPs)
• Accurate, but computationally expensive
• Can not compute dielectric permittivity or Born effective charges
• Can not include LO/TO splitting.
• Can not compute IR or Raman absorptivity/activity
Re3N at high pressure

High Pressure – Re$_3$N

Phys Rev B 82, 244106 (2010)
INS spectrum of hydrogen on Raney Ni.

expt (TOSCA)

Full dispersion calc. for Ni(111)/H (scaled by 0.93).

Pair distribution function, $D(R)$, for hydrogen on Raney nickel. Fourier transform of the normalised difference between the two $S(Q)$. 

![Graph showing the pair distribution function $D(R)$ for hydrogen on Raney nickel. The x-axis represents distance in Å, and the y-axis represents the value of $D(R)$ ranging from -0.10 to 0.20. Peaks are observed at regular intervals, indicating the distribution of hydrogen atoms around the nickel sites.](image)
Ni—H
Neutron: 1.68 Å
Ab initio: 1.68 Å
LEIS: 1.65 ± 0.05 Å
LEED: 1.84 ± 0.06 Å
H–storage materials

H transport in LiBH4
Raman studies of H transport

Expts: A. Borgschulte, EMPA
With A.J. Ramirez Cuesta, ISIS

@ low temperature
transport of intact BH₄ units

@ >225°C
all isotopomers are present
CASTEP Raman calculation

Measurement  Calculation

$\text{LiBD}_4$

$x = 1$

$v_1$, $2v_4$, $v_3^*$, $v_{3'}$

$x = 0.87$

$v_1$, $v_3^*$

$x = 0.72$

$v_1$, $v_3^*$

$x = 0.45$

$v_1(D)$, $v_2(D)$, $v_3(D)$

$x = 0.14$

$v_1(D)$, $v_2(D)$, $v_3(D)$

$\text{LiB(H}_3\text{D}_x)_4$

$\text{Raman shift [cm}^{-1}\text{]}$

$1500$ to $1800$

R. Gremaud et al, PRB 80 100301(R) (2009)
Diaspore (AlOOH)

Canonical example of hydrous mineral
Inelastic X-Ray scattering of diaspore

Conventional wisdom: OH groups interact weakly and modes show little dispersion.

Ab-initio calculations frequently show significantly dispersive OH stretch modes.

INS is not feasible in OH stretch range of 3000–4000 cm\(^{-1}\).

First IXS measurement of OH stretch dispersion ever performed at ID28 at ESRF

B. Winkler, *et. al.*
OH dispersion in diaspore
Developments in CASTEP

HPC performance and scaling
• Band parallelism
• Shared-memory node optimizations of FFT
• Wavefunction read/write optimizations
• Memory optimization
• Distributed $\langle \beta | \phi \rangle$

Recently added properties and capabilities
• DFT+D
• Hirshfeld atomic Charges
• NMR Hyperfine Coupling
• New GGAs (PBEsol, WC)
• Hybrid functionals (PBEh, B3LYP), SX
• LDA+U
• EELS and XANES with d core–hole final states
• Raman and infrared intensity/spectroscopy
• Electron localization functions (ELF)
• DFPT phonons for metallic systems
DFPT Phonons for Metals

- Metallic phonon DFPT
- Fourier interpolation for full DOS and dispersion calculations.

MgB2
LDA q=5x5x5 k=15x15x12
Under Development

Much faster Raman activities using DFPT

DFPT for magnetic systems

Non-collinear magnetism

GW for many-body perturbation theory
Treatment of excitations
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