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The Power of Density Functional Theory for Materials Physics and Chemistry

Date 12.09.19

Keith Refson

ROYAL
HOLLOWAY
UNIVERSITY
OF LONDON

Third mode of science

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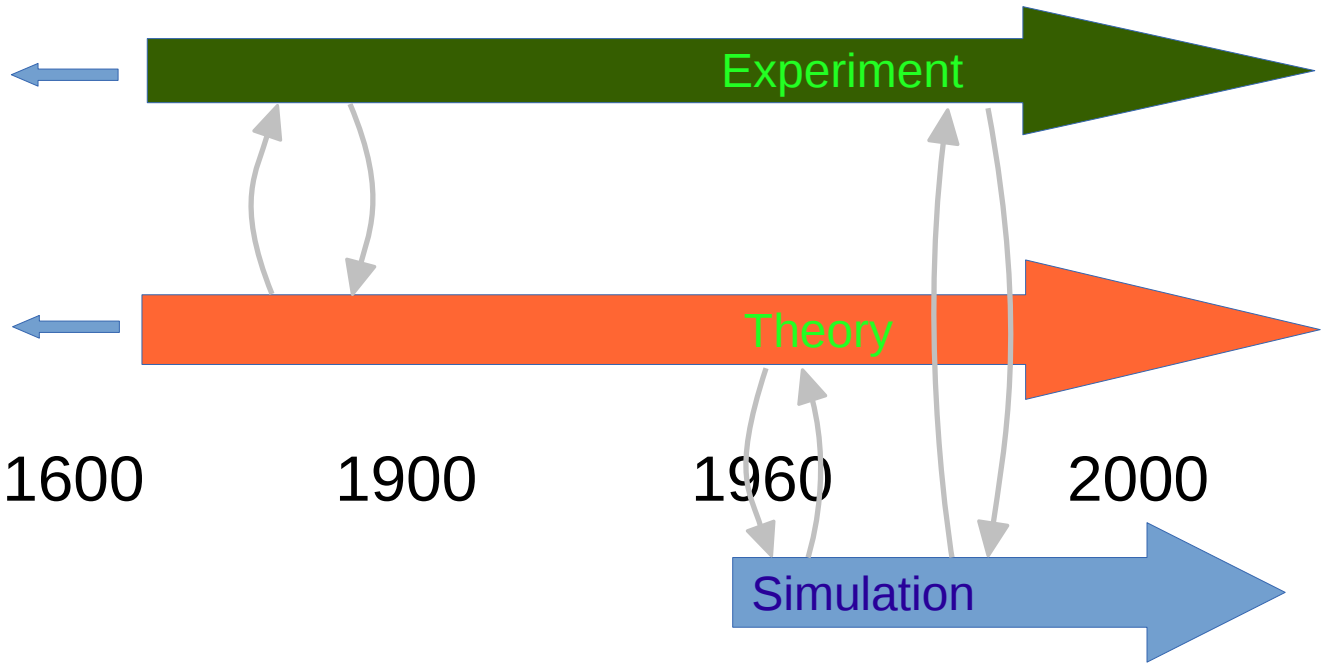

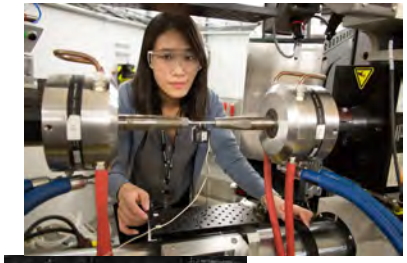

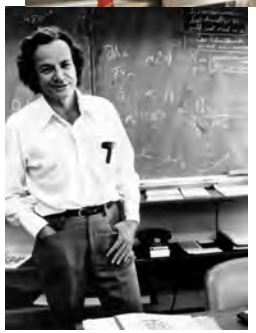

"During its spectacular rise, the computational has joined the theoretical and experimental branches of science, and is rapidly approaching its two older sisters in importance and intellectual respectability."

Peter D Lax, J. Stat. Phys. **43**, 749 (1986)

Quantum Mechanics and Density Functional Theory

The quantum Toolbox

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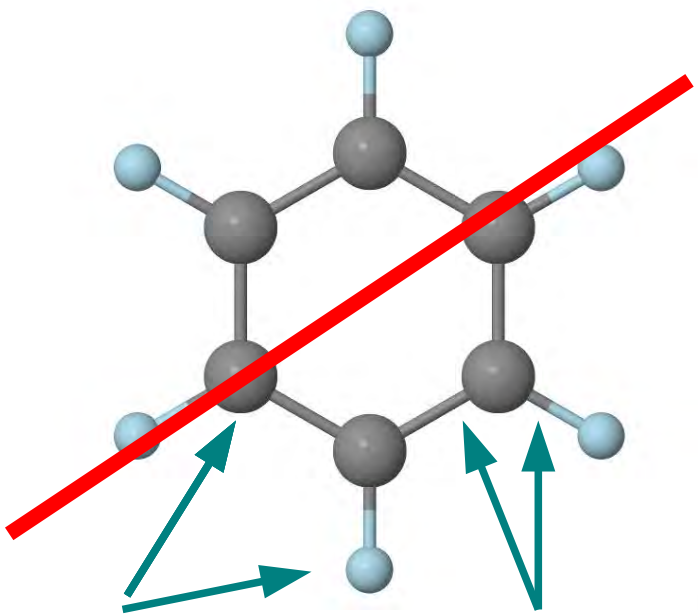
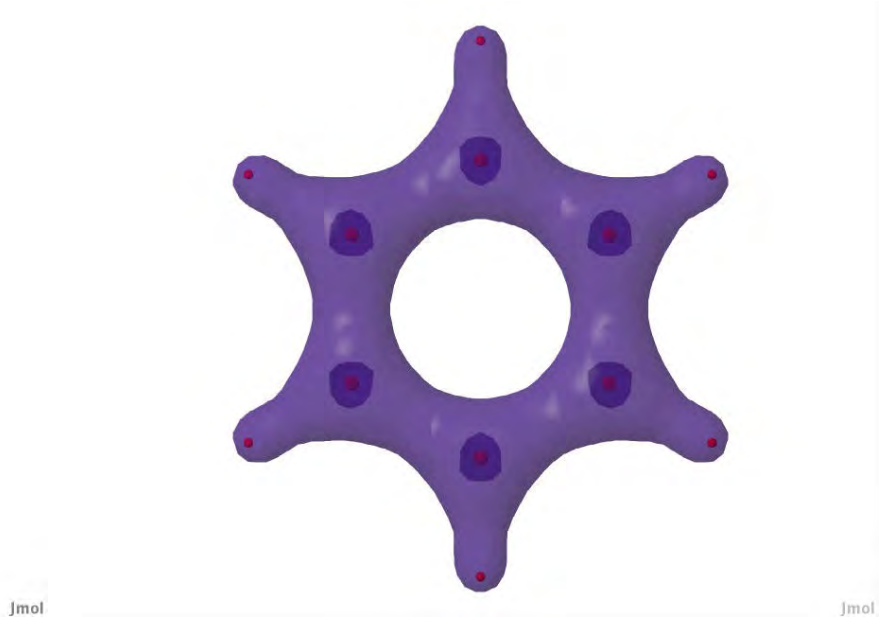


Atoms Bonds



Nuclei Electrons

F = m a

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

The Theory of Everything

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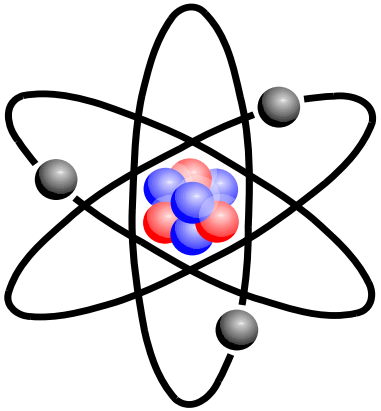
"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the application of these laws leads to equations much too complicated to be soluble."

P.A.M. Dirac, Proceedings of the Royal Society **A123**, 714 (1929)

Why?

Each electron interacts with the nucleus
Every electron also interacts with every other electron.



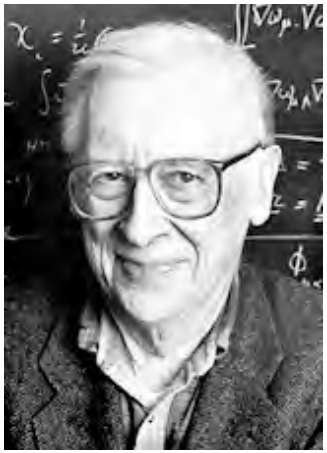
In Lithium (Z=3) there are 3 e-e interactions to consider.
In Boron (Z=5) there are 10 e-e interactions to consider.
In Iron (Z=26) there are 325 e-e interactions to consider.
In Uranium (Z=92) there are 4186 e-e interactions to consider.

.. and that's just isolated atoms. We need to model crystals and molecules containing hundreds of atoms.

QM of multi-electron atoms still too complex to solve on Powerful supercomputers in 2019 (and forseeable future)..

Approximate quantum mechanics

Walter Kohn 1923-2016



John Pople 1925-2004

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)

Density Functional Theory

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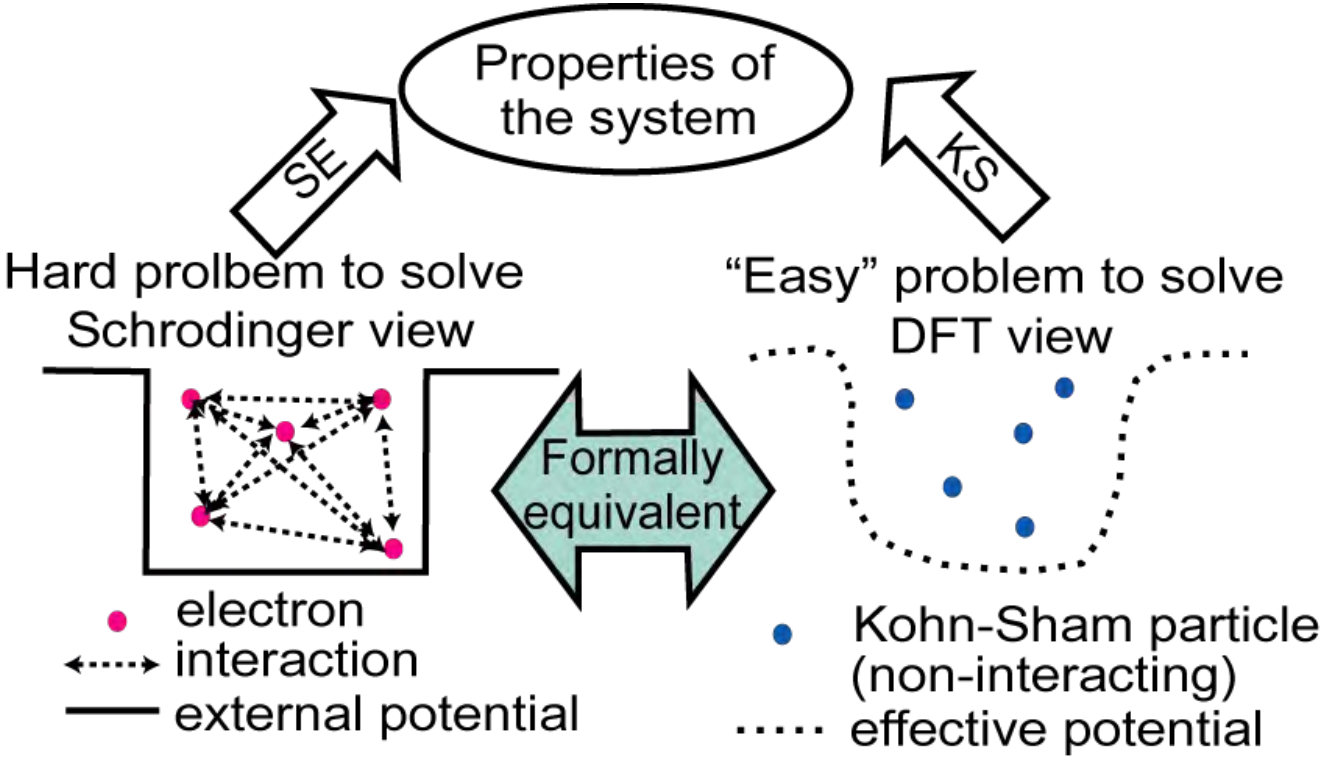

Approximate e-e interaction with
- local density approximation (LDA)
- generalized gradient approximation (GGA)
- Hybrids, DMFT, GW, …

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

Kohn-Sham equations

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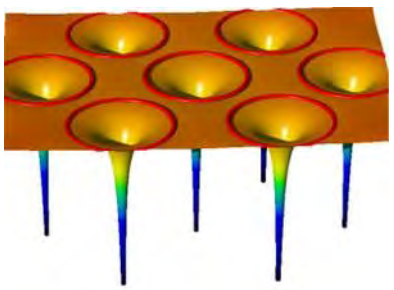
$$\left\{\frac{1}{2}\nabla^2 + V_{\text{ext}}(\vec{r}) + V_H(\vec{r}) + V_{\text{xc}}([n(\vec{r})])\right\}\phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r})$$



$$n(\vec{r}) = \sum_i^{occ} |\phi_i^2(\vec{r})|$$

$$V_H(\vec{r}) = \int d\vec{r}\,' \frac{n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$$

Self-consistent solution required.

LDA and GGAs

LDA

$$V_{xc}[n] \approx V_{xc}(n(\vec{r}))$$

$$V_{xc} \equiv \frac{\delta E_{xc}[n]}{\delta n(\vec{r})}$$

Parameterized from uniform electron gas

- *Cohesive energies ~ 1eV too large*
- *lattice parameters and bond lengths -1-2%*
- *Band gaps too small*
- *Hund's rule for open shells not always obeyed*
- *Van der Waals forces not included*

GGAs

$$V_{xc}[n] \approx V_{xc}(n(\vec{r}), \nabla n(\vec{r}))$$

e.g. PBE, PW91, BLYP, ...

Parameterized from non-uniform electron gas and atoms

- *Cohesive energies error of ~ 100 meV*
- *lattice parameters and bond lengths -1-2%*
- *Band gaps too small*
- *Hund's rule for open shells not always obeyed*
- *Van der Waals forces not included*

Meta GGAs and Hybrids

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Meta-GGA $V_{xc}[n] \approx V_{xc}(n(\vec{r}), \nabla n(\vec{r}), \tau_s(\vec{r}))$ $\tau_s(\vec{r}) = \frac{1}{2} \sum_{mk} |\nabla \phi_{mk}(\vec{r})|^2$

Added dependency on kinetic-energy density

- *Early forms (TPSS) not fully self-consistent.*
- *SCAN & rSCAN fitted to exact results and QMC.*
- *lattice parameter error ~ 0.007A*
- *Self-interaction error still present (Hund's rule not always obeyed)*
  Cohesive energies accurate to ~ 30 meV
- *Van der Waals forces still not included*

Hybrids

$$E_{xc}^{PBE0} \equiv \frac{3}{4} E_x^{PBE} + \frac{1}{4} E_x^{HF} + E_c^{PBE}$$

e.g. PBE0, B3LYP, HSE06...

Linear admixture of DFT and Hartree-Fock exchange

- *Cohesive energies and lattice parameters slightly better than GGAs*
- *Partially self-inteaction corrected – band gaps improved*
- *Hund's rule for open shells obeyed*
- *Van der Waals forces not included*

Plane-waves and pseudopotentials

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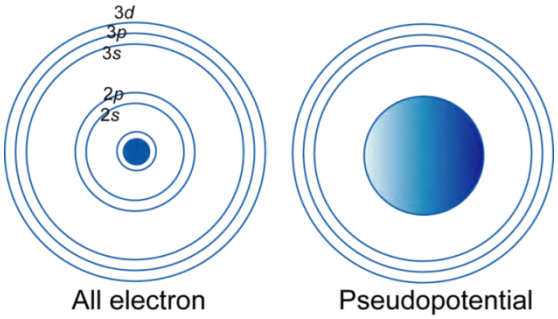
Plane-wave basis set

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}},$$

$$u_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}}\sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}}e^{i\mathbf{G}\mathbf{r}}$$

- Well-adapted for crystalline and solid/liquid modelling
- Systematic control of basis set convergence

Pseudopotential for ionic interactions



- “All electron” method but frozen core.
- Retain chemically relevant valence electrons
- Good scaling/large systems

Pseudopotentials

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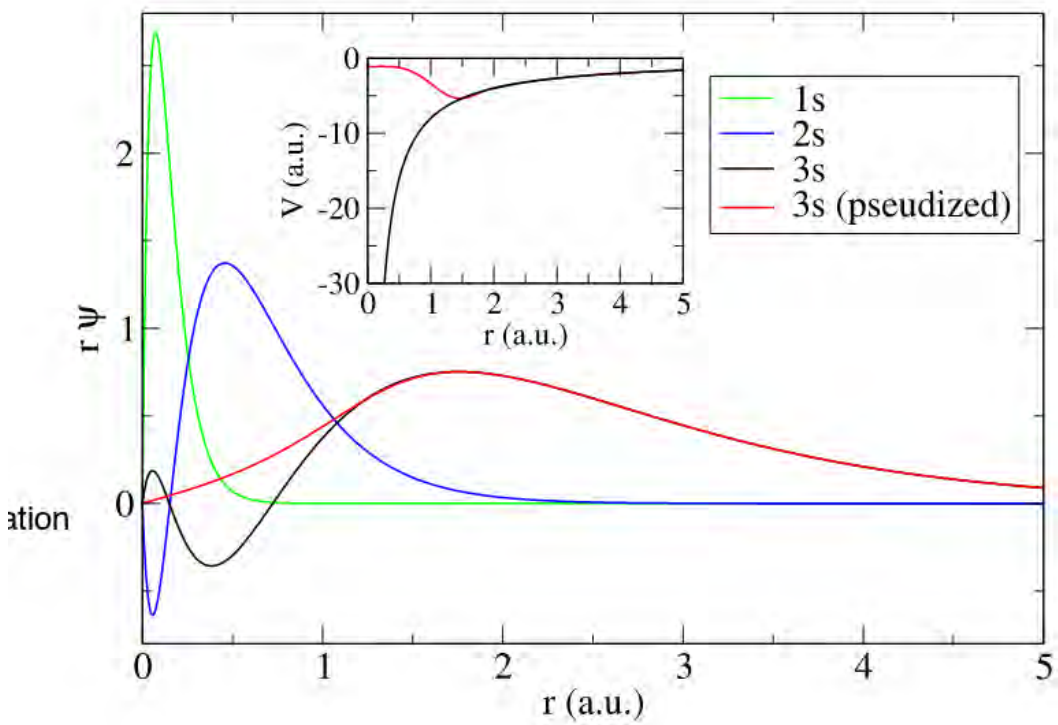

Valence orbitals determined by DFT calculation on isolated atom
Pseudization finds potential which retains large-r form
N.B. use relativistic atom solver to include relativity in plane-wave calc.
- correct treatment of heavy atoms.

and

PAW

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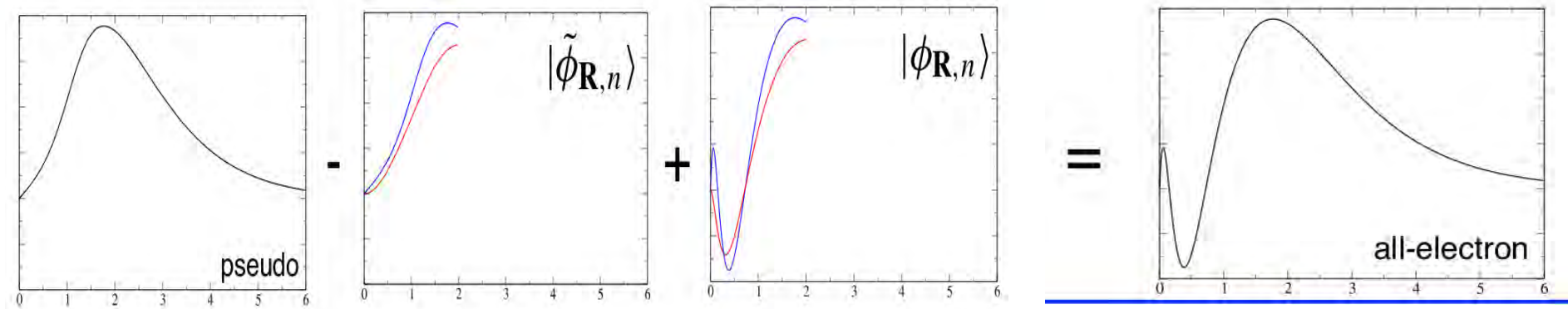
$$|\Psi\rangle = \mathcal{T}|\tilde{\Psi}\rangle$$

$$\mathcal{T} = \mathbf{1} + \sum_{\mathbf{R},n} [|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle]\langle\tilde{p}_{\mathbf{R},n}|$$

all-electron pseudo



PAW is extension of pseudopotential method.
Restores atomic nodal form of plane-wave orbitals near nucleus
Sometimes called “all-electron”, but core electrons not included!

The Delta Project

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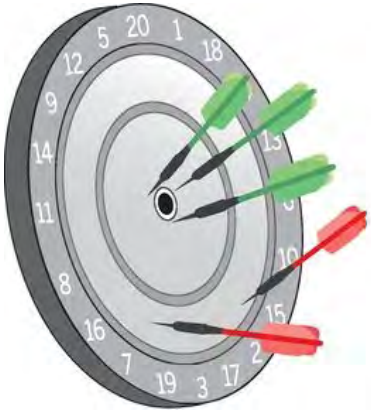
RESEARCH ARTICLE

DFT METHODS

Reproducibility in density functional theory calculations of solids

Kurt Lejaeghere,[1*] Gustav Bihlmayer,[2] Torbjörn Björkman,[3,4] Peter Blaha,[5] Stefan Blügel,[2] Volker Blum,[6] Damien Caliste,[7,8] Ivano E. Castelli,[9] Stewart J. Clark,[10] Andrea Dal Corso,[11] Stefano de Gironcoli,[11] Thierry Deutsch,[7,8] John Kay Dewhurst,[12] Igor Di Marco,[13] Claudia Draxl,[14,15] Marcin Dułak,[16] Olle Eriksson,[13] José A. Flores-Livas,[12] Kevin F. Garrity,[17] Luigi Genovese,[7,8] Paolo Giannozzi,[18] Matteo Giantomassi,[19] Stefan Goedecker,[20] Xavier Gonze,[19] Oscar Grånäs,[13,21] E. K. U. Gross,[12] Andris Gulans,[14,15] François Gygi,[22] D. R. Hamann,[23,24] Phil J. Hasnip,[25] N. A. W. Holzwarth,[26] Diana Iuşan,[13] Dominik B. Jochym,[27] François Jollet,[28] Daniel Jones,[29] Georg Kresse,[30] Klaus Koepernik,[31,32] Emine Küçükbenli,[9,11] Yaroslav O. Kvashnin,[13] Inka L. M. Locht,[13,33] Sven Lubeck,[14] Martijn Marsman,[30] Nicola Marzari,[9] Ulrike Nitzsche,[31] Lars Nordström,[13] Taisuke Ozaki,[34] Lorenzo Paulatto,[35] Chris J. Pickard,[36] Ward Poelmans,[1,37] Matt I. J. Probert,[25] Keith Refson,[38,39] Manuel Richter,[31,32] Gian-Marco Rignanese,[19] Santanu Saha,[20] Matthias Scheffler,[15,40] Martin Schlipf,[22] Karlheinz Schwarz,[5] Sangeeta Sharma,[12] Francesca Tavazza,[17] Patrik Thunström,[41] Alexandre Tkatchenko,[15,42] Marc Torrent,[28] David Vanderbilt,[23] Michiel J. van Setten,[19] Veronique Van Speybroeck,[1] John M. Wills,[43] Jonathan R. Yates,[29] Guo-Xu Zhang,[44] Stefaan Cottenier[1,45*]



New methods
Mutual agreement

Old methods
Different values

Scorecard

	0.3	0.3	0.6	1.0	0.9	0.3	1.5	0.6	0.9	0.4	1.0	0.4	0.4	6.3	13.5	1.1	2.1	0.7	1.4
0.3		0.1	0.5	0.9	0.8	0.2	1.5	0.6	0.8	0.4	1.0	0.5	0.3	6.3	13.4	1.1	2.1	0.7	1.4
0.3	0.1		0.5	0.9	0.8	0.2	1.5	0.6	0.8	0.4	0.9	0.5	0.3	6.3	13.4	1.1	2.1	0.7	1.4
0.6	0.5	0.5		0.8	0.6	0.4	1.5	0.6	0.8	0.6	1.0	0.7	0.5	6.3	13.2	1.0	1.9	0.6	1.3
1.0	0.9	0.9	0.8		0.9	0.9	1.8	0.9	1.3	1.0	1.4	1.0	0.9	6.4	13.0	1.2	1.8	1.0	1.6
0.9	0.8	0.8	0.6	0.9		0.8	1.7	0.7	1.1	0.8	1.3	1.0	0.8	6.5	13.2	1.1	1.8	0.8	1.5
0.3	0.2	0.2	0.4	0.9	0.8		1.5	0.5	0.8	0.3	1.0	0.5	0.3	6.2	13.4	1.0	2.0	0.6	1.4

PAW vs USP accuracy

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		AE							
		Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc	**average < Δ >**
PAW	GBRV12/ABINIT	0.9	0.8	0.8	0.9	1.3	1.1	0.8	0.9
	GPAW09/ABINIT	1.3	1.3	1.3	1.3	1.7	1.5	1.3	1.4
	GPAW09/GPAW	1.5	1.5	1.5	1.5	1.8	1.7	1.5	1.6
	JTH02/ABINIT	0.6	0.6	0.6	0.6	0.9	0.7	0.5	0.6
	PSlib100/QE	0.9	0.8	0.8	0.8	1.3	1.1	0.8	0.9
	VASPGW2015/VASP	0.5	0.4	0.4	0.6	1.0	0.9	0.4	0.6
USPP	GBRV14/CASTEP	1.1	1.1	1.0	1.0	1.4	1.3	1.0	1.1
	GBRV14/QE	1.0	1.0	0.9	1.0	1.4	1.3	1.0	1.1
	OTFG9/CASTEP	0.4	0.5	0.5	0.7	1.0	1.0	0.5	0.7
	SSSP/QE	0.4	0.3	0.3	0.5	0.9	0.8	0.3	0.5
	Vdb2/DACAPO	6.3	6.3	6.3	6.3	6.4	6.5	6.2	6.3

Ionic bonding in NaCl

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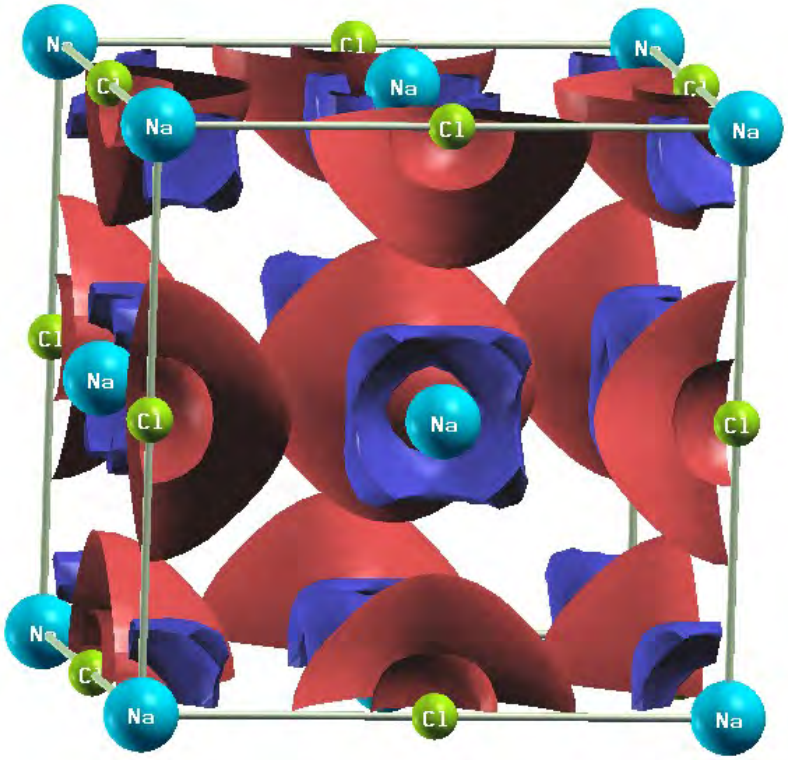
Charge transfer from Na to Cl

Unlike Si, no build up of charge between atoms



Covalent bonding in silicon

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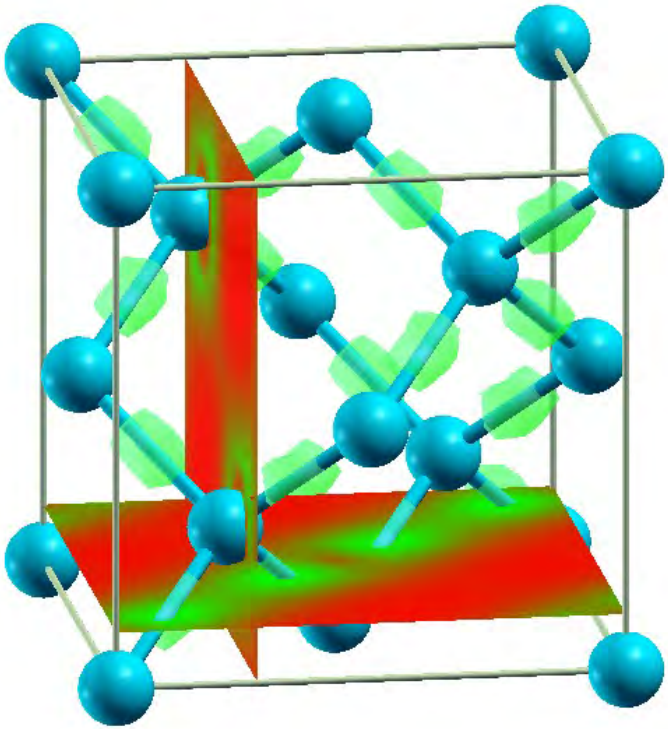
Covalent bonding arises from build up of -ve charge between +ve nuclei.

Chemical bond is emergent property of electron-ion system

Not merely qualitative description – can compute bond and cohesive energy.
(E_{coh}=5.45 eV; expt 4.62 eV)
Lattice Parameter a_0=0.549nm (0.5431nm)



Metallic bonding in aluminium

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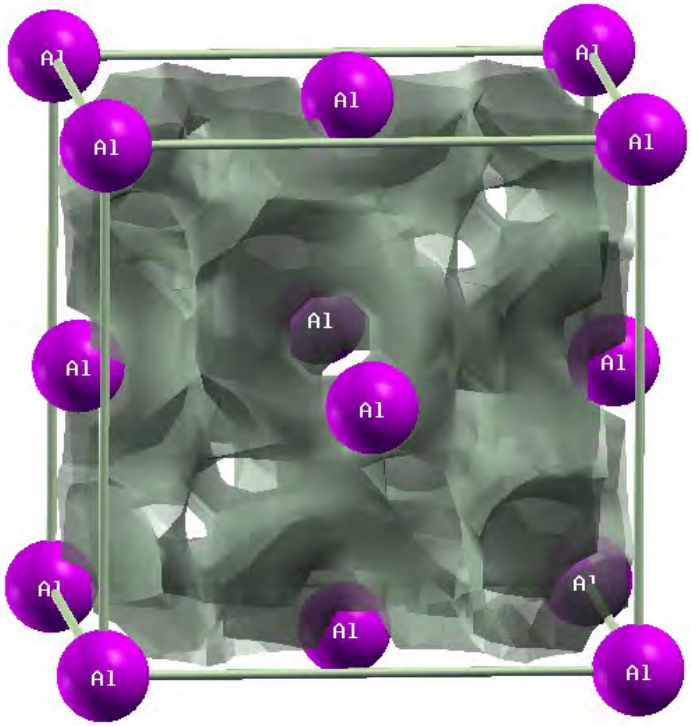
Valence electrons are spread out – metallic state.

Calculation shows no band gap; correctly predicts Al is metallic.



No van Der Waals Bonding

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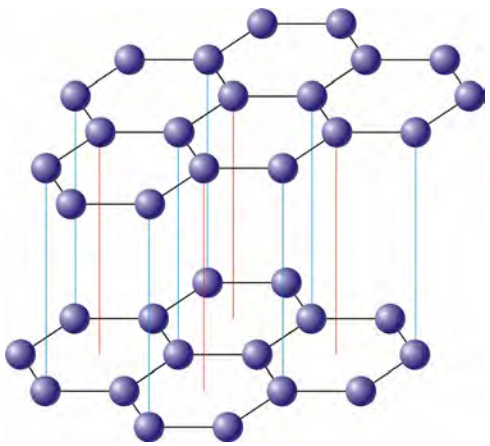
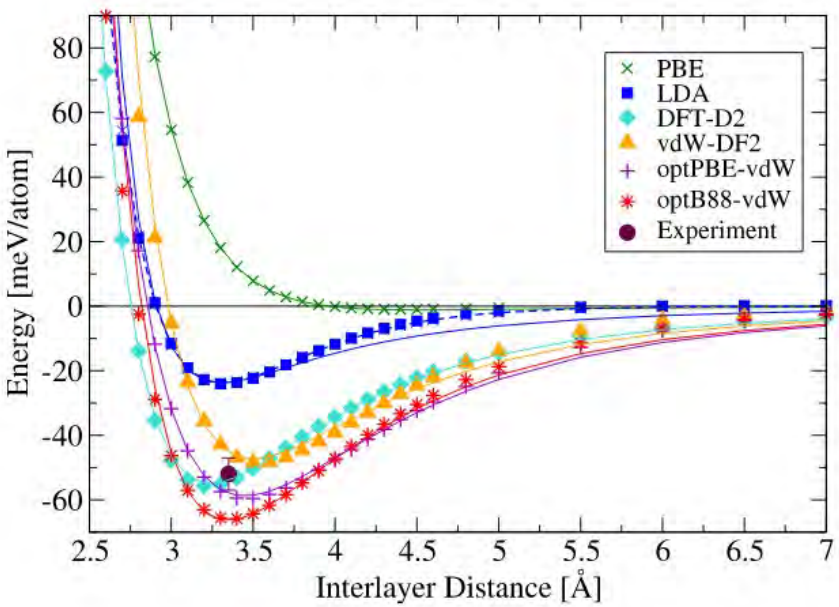
LDA, GGA, m-GGA and hybrids do not include non-bonded van-der Waals interactions.
3
Example: Graphite

Non-polar molecular crystals can be completely unbound!

A variety of semi-empirical correction schemes exist to add missing interaction.





Electronic Spectra

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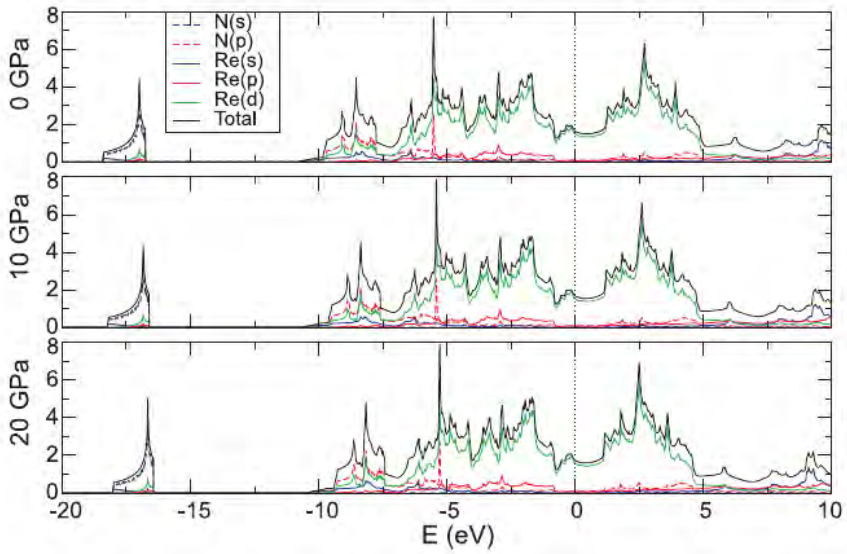
Strictly, DFT has no basis to describe excited states. However unoccupied K-S states do resemble single-electron excitations. It is predictive for some spectroscopies, ignoring band-gap error:

- UV-Vis (but not excitons)
- EELS and Xanes

But some excitations have no K-S counterpart.

- Magnons
- Excitons

and a higher level of theory treatment is required. (eg Bethe-Salpeter)



From bands to properties

Band-theory perspective

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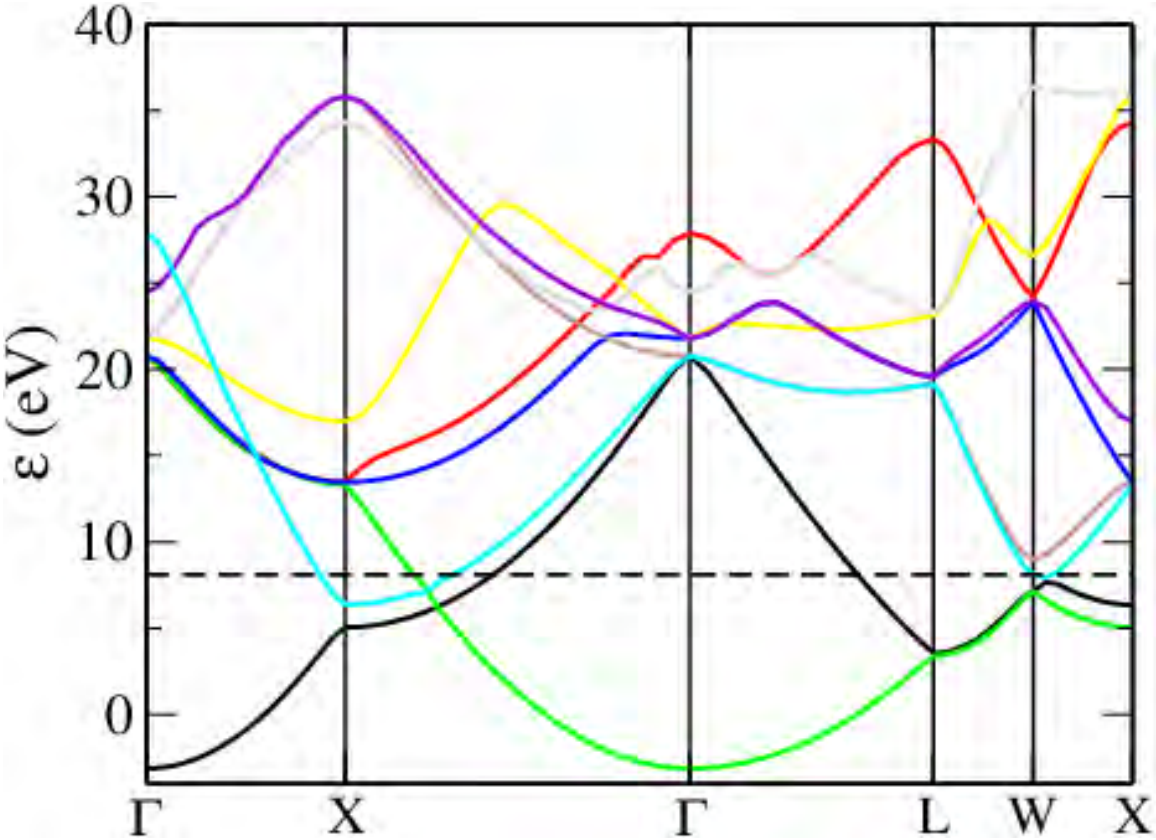
$$\hat{H}\Psi_i = \epsilon_i \Psi_i$$



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?

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

Totally Useless?

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

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

$$F_j = -\frac{dE_{tot}}{dR_j}$$

$$\Phi_{i,j} = \frac{d^2 E_{tot}}{dR_i dR_j}$$

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

Totally Useless?

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

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

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

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

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

$$I_{m,i,j}^{raman} \propto \frac{d^3 E_{tot}}{d E_i d E_j d Q_m}$$

$$\chi_{i,j,k}^{(2)} \propto \frac{d^3 E_{tot}}{d E_i d E_j d E_j}$$

$$\frac{\delta \omega}{\omega} \sim \frac{d^3 E_{tot}}{d R_i d R_j d R_k}$$

The Optimization Problem

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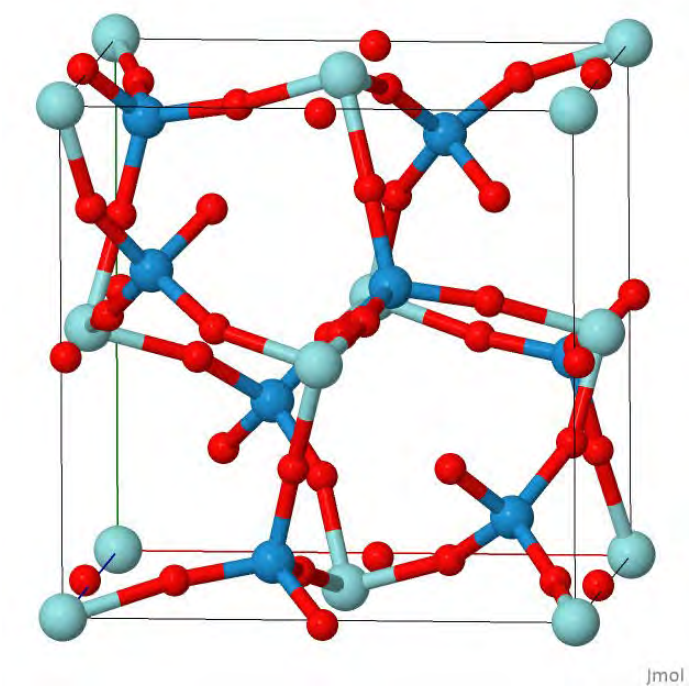

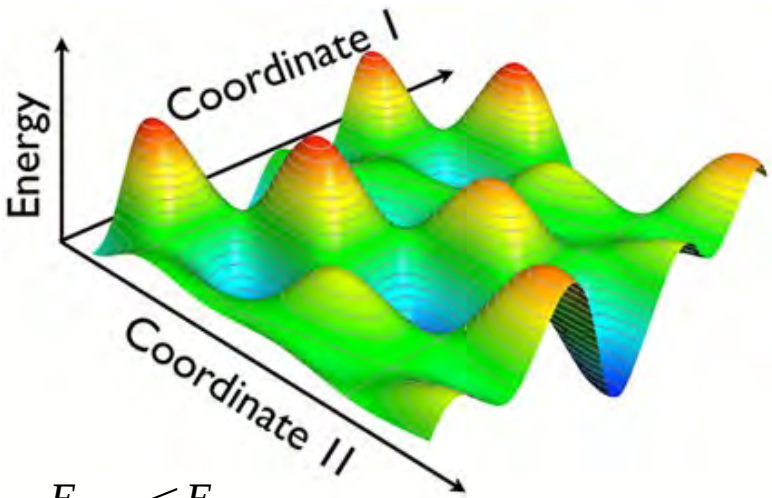

$E_{global} \leq E_{local}$

$E(x1, y1, z1, \ldots) \leq E_0$

iterative downhill optimization methods can find local mini

Forces and Geometry

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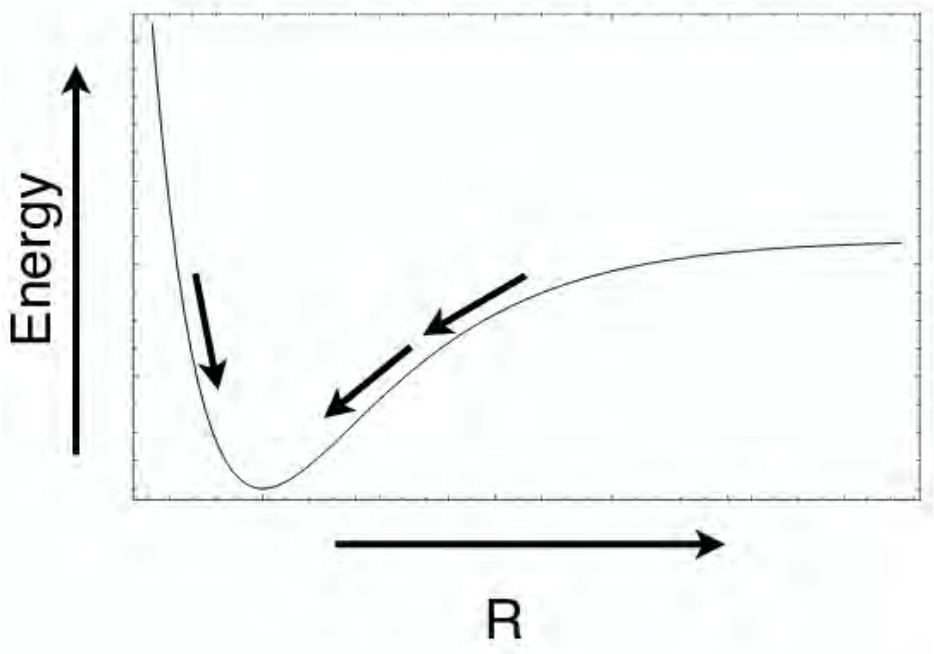
The Hellman-Feynman Theorem gives forces if ground state known

$$F_i = -\langle \Psi_0 | \frac{dE}{dx_i} | \Psi_0 \rangle$$

Can move atoms in response to computed forces.

Apply machinery of optimization theory:
E.g. quasi-Newton methods (BFGS) to find equilibrium crystal structure.



DFT Simulation Codes

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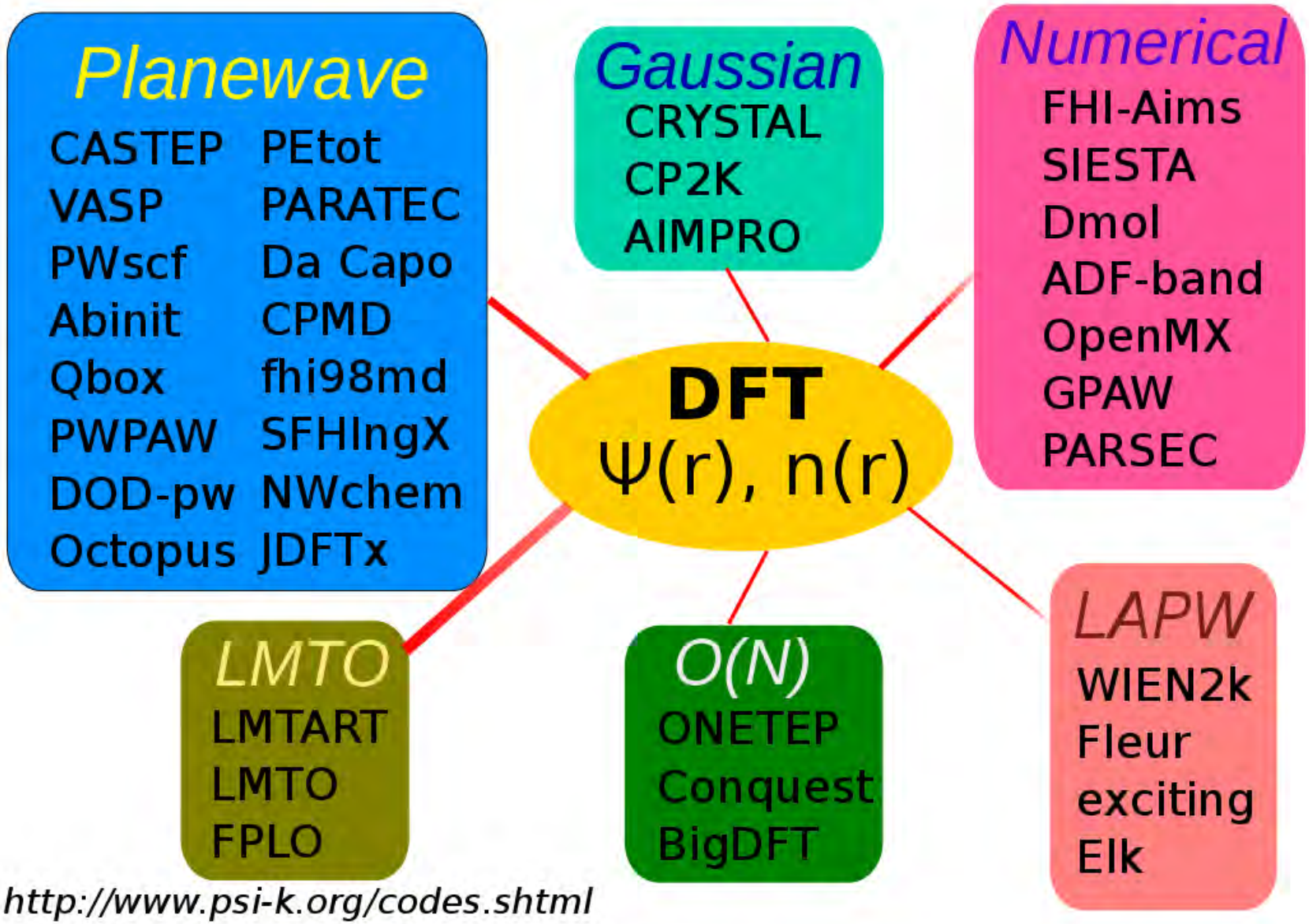

http://www.psi-k.org/codes.shtml

Popularity of DFT

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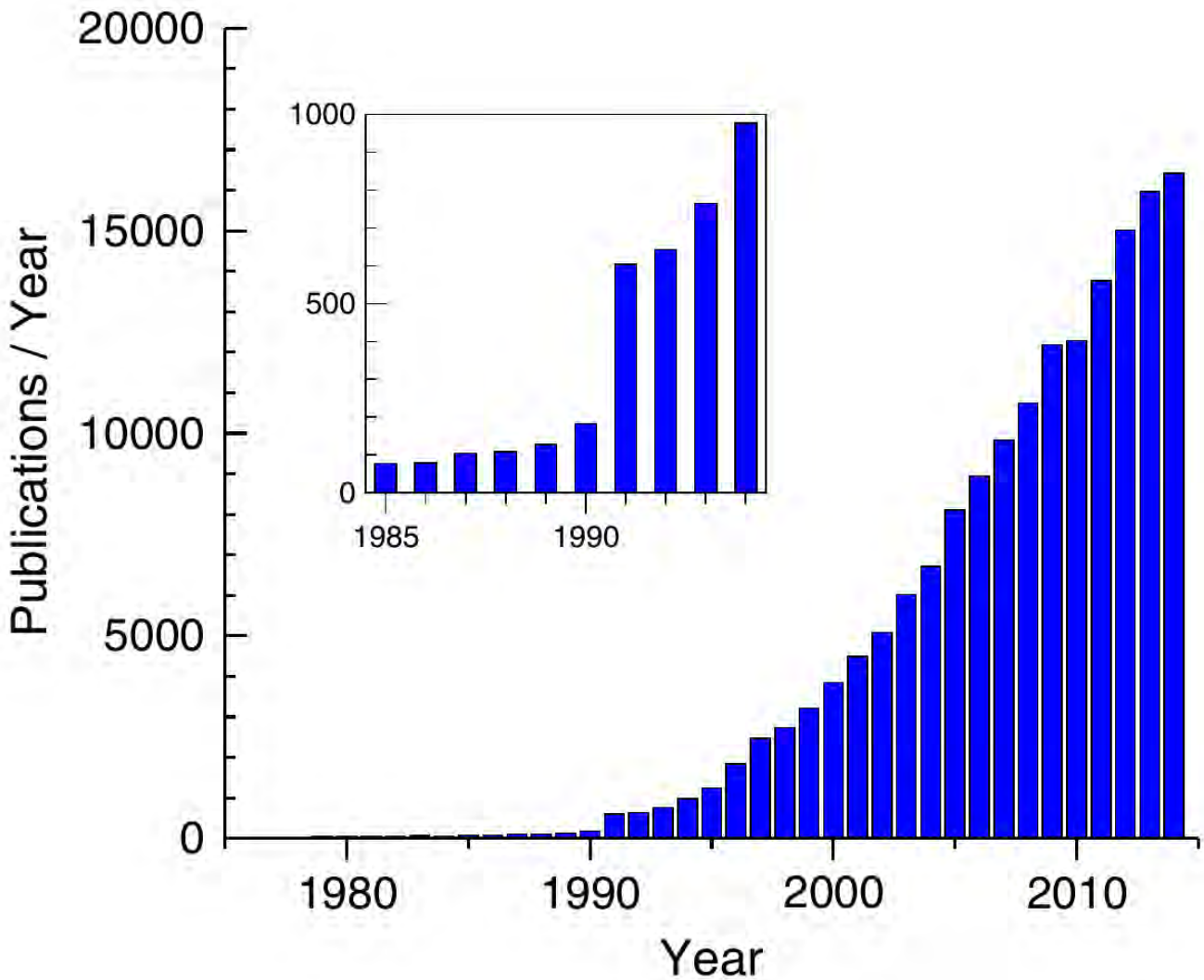

Electronic Structure

Charged Defects in ZnO

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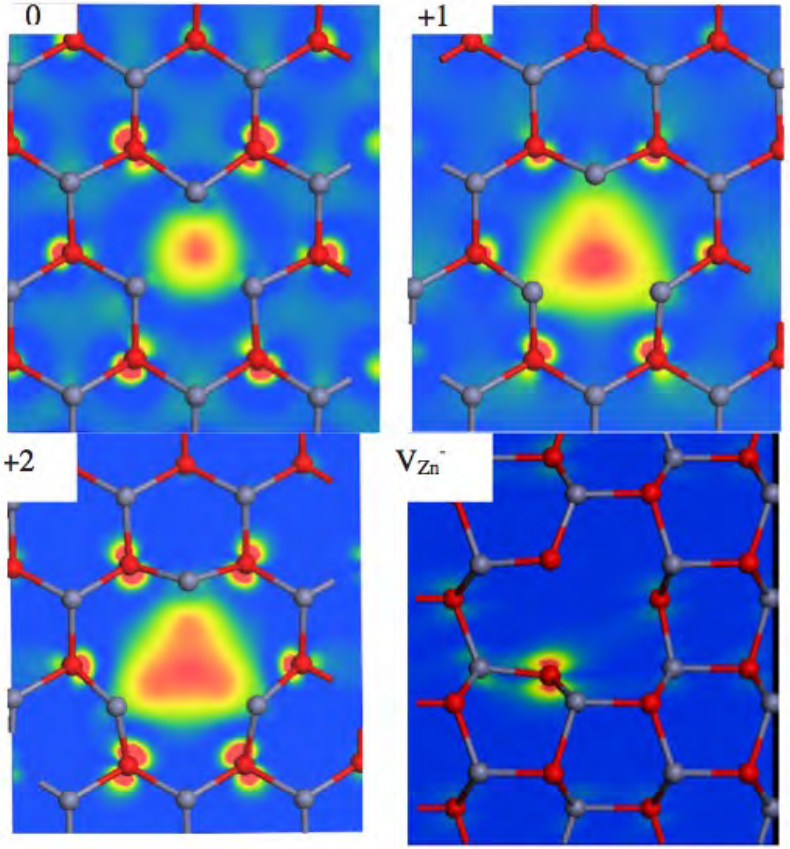

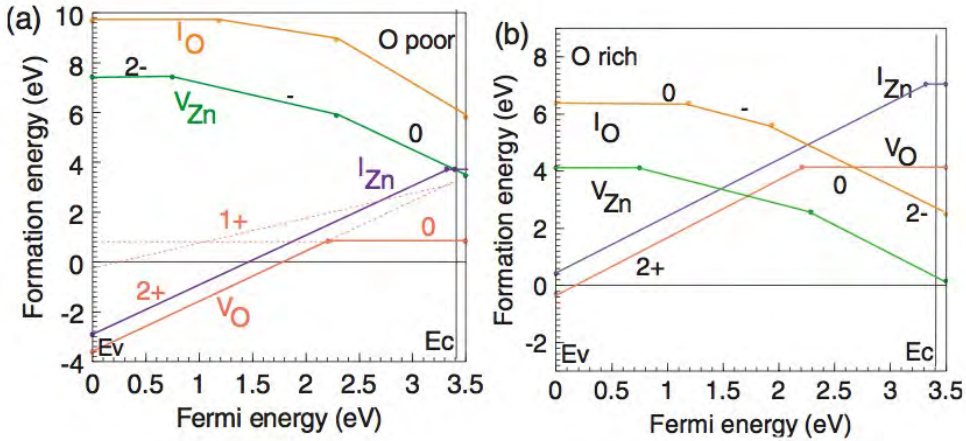

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Clark, Zunger, et al., PRB 81, 115311 (2010)

Charge ordering (with DFT+U)

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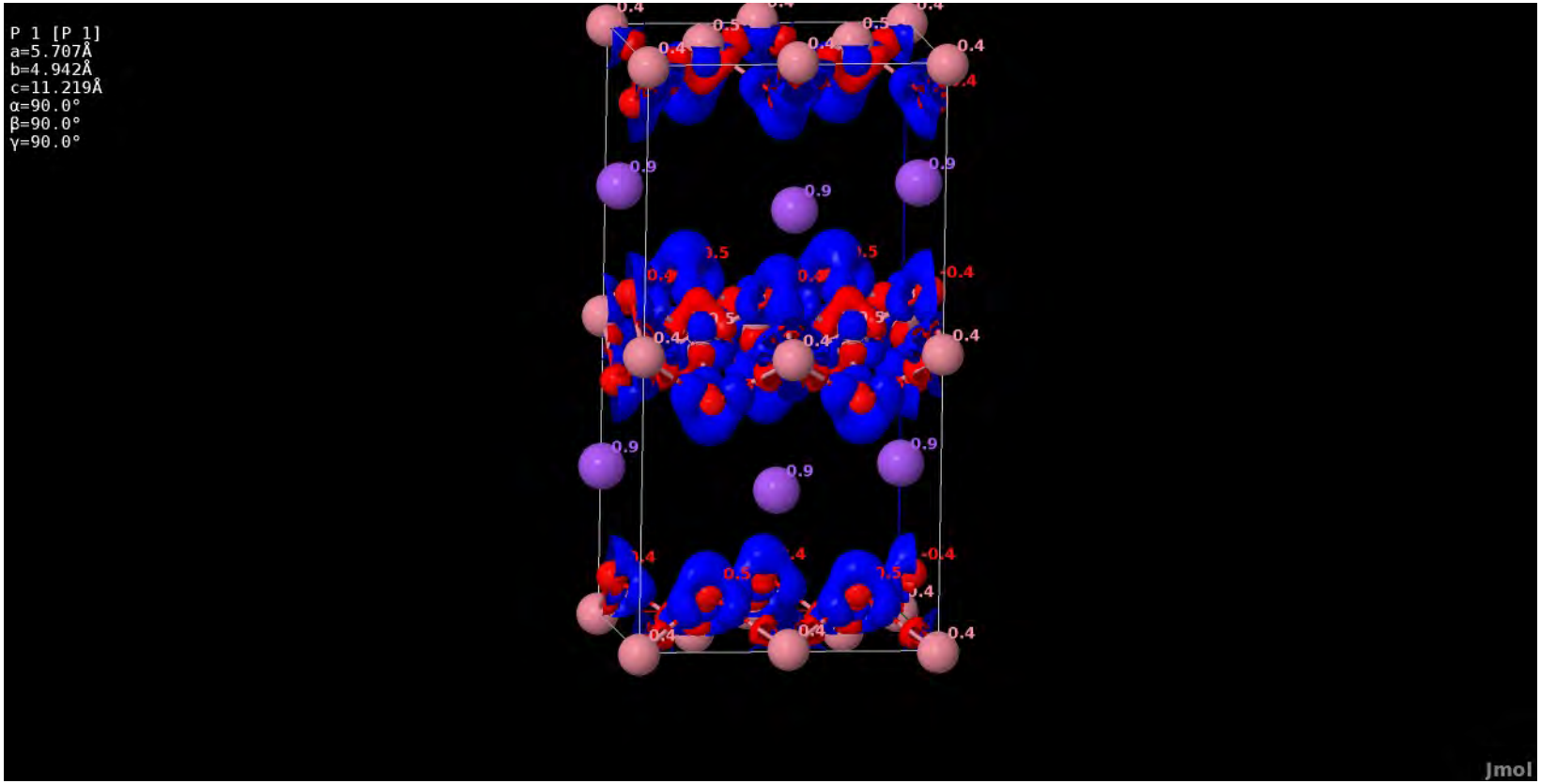

Crystal Structure

AIRSS: Prediction of Crystal Structures

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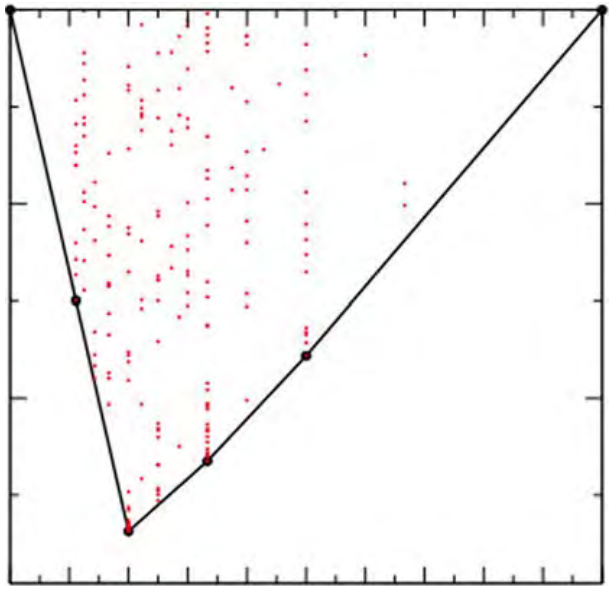
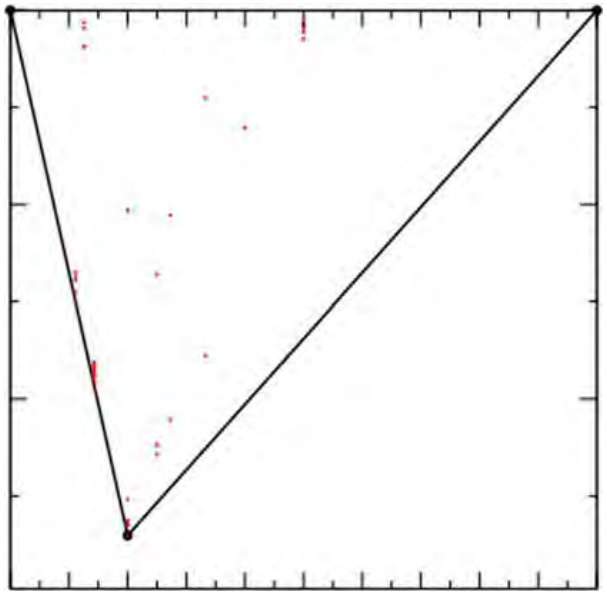
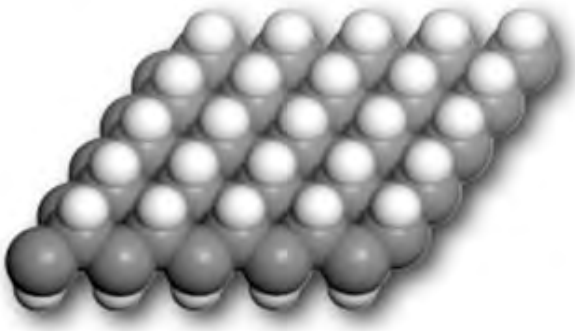




methane

polyethane



graphane

Predicting Structure

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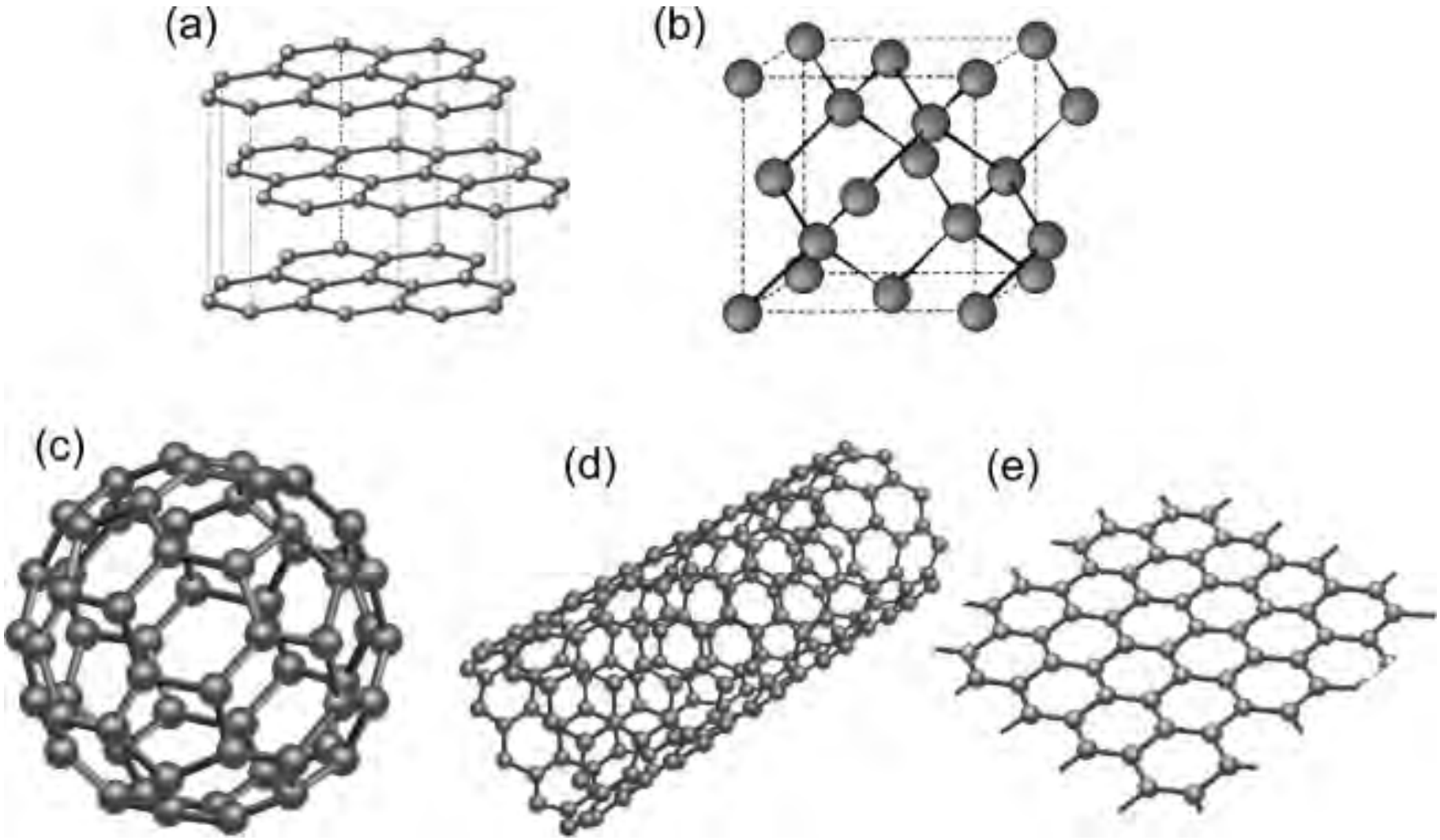
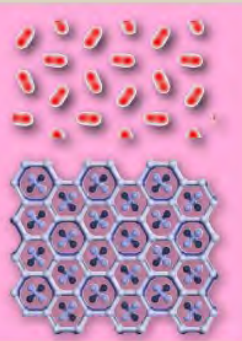


AIRSS - A tool for discovery

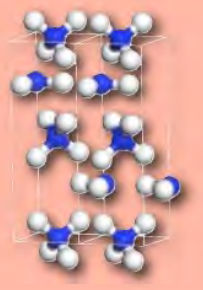
Hydrogen is polar and "graphene"

Nature Physics, 2007
Physical Review B, 2012



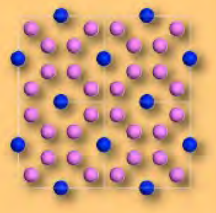
Ammonia is ionic

Nature Materials, 2008



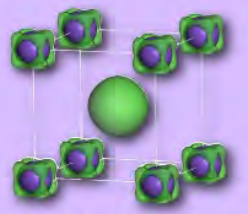
Aluminium is complicated

Nature Materials, 2010



Magnetic potassium

Physical Review Letters, 2011



Molecular Dynamics

Dynamics of nuclei

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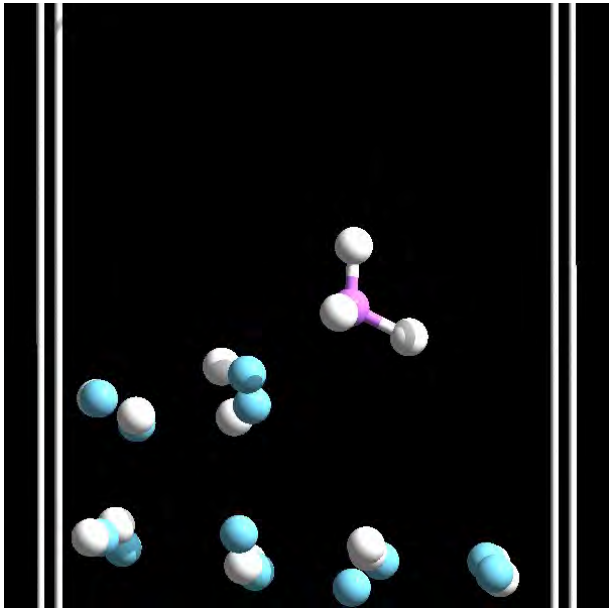
With forces calculated from DFT
Can also calculate dynamics:

- Molecular dynamics – time evolution
- Lattice dynamics - spectroscopy

$$r(t+\delta t)=r(t)+v(t)\delta t+\frac{1}{2}a(t)\delta t^2$$

$$v(t+\delta t)=v(t)+\frac{1}{2}[a(t)+a(t+\delta t)]\delta t$$

$$a(t+\delta t)=\frac{1}{m}F(t+\delta t)$$



Water on metal Surfaces

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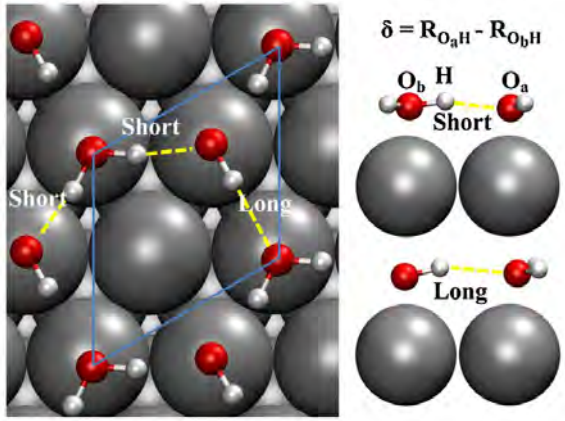

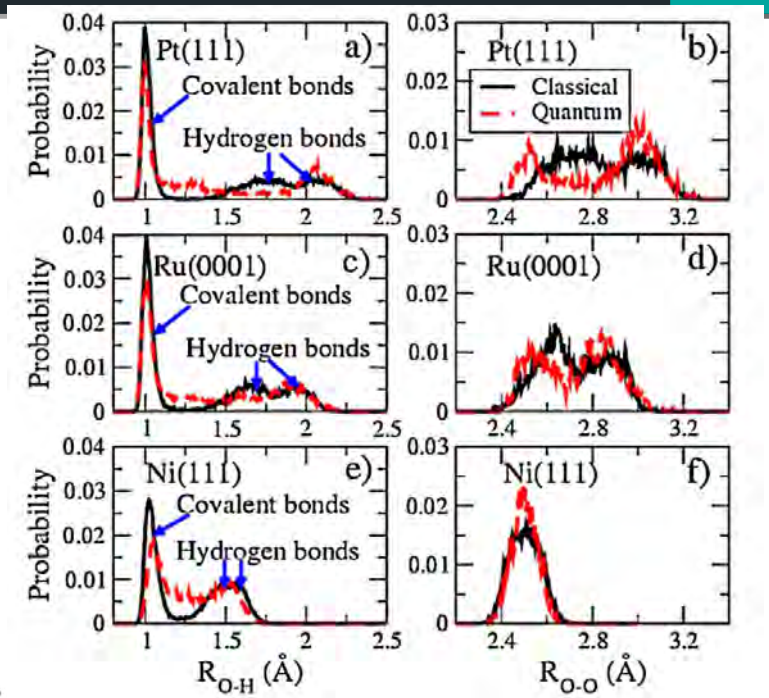

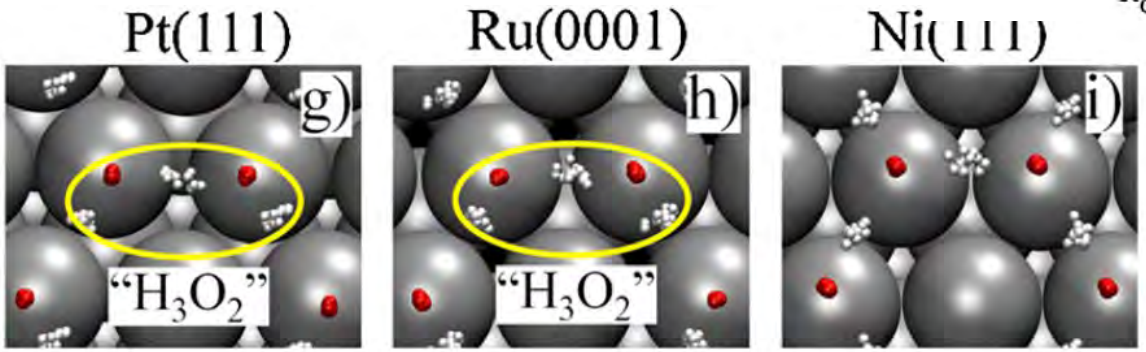

Li, Probert, Alavi, Michaelides, PRL **104**, 066102 (2010)

Fast-ion conduction in $LiBH_4$

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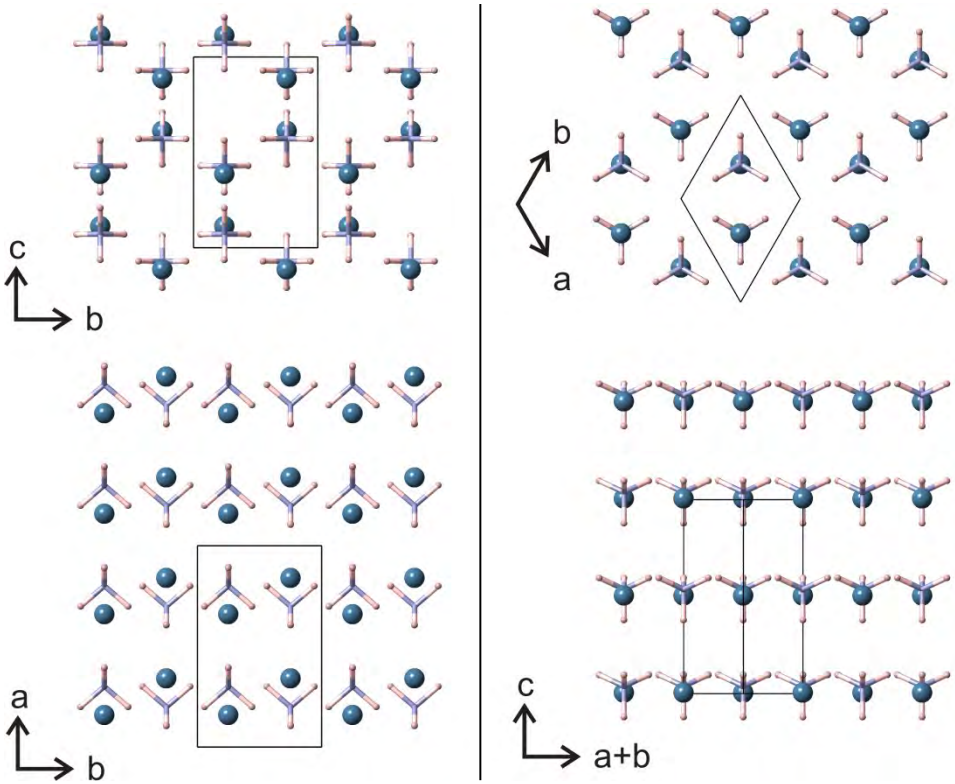

< 390 K
Orthorhombic (Pnma)

> 390 K
Hexagonal (P63/mmc)
Disordered
Superionic conductivity

> 560 K: liquid
> 650 K: decomposition

A little knowledge?

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unsuccessful attempts to model high-temperature phase by optimisation and lattice dynamics:

- Miwa, K. et al., 2004. First-principles study on lithium borohydride LiBH4. Physical Review B, 69(24), 245120.

  "The finite temperature effects are probably crucial to study the structural properties in this phase."

- Tekin, A. et al., 2010. First-Principles Determination of the Ground-State Structure of $LiBH_4$. PRL, 104(21), p.215501.

- Łodziana, Z. & Vegge, T., 2004. Structural Stability of Complex Hydrides: $LiBH_4$ Revisited. PRL, 93(14), p.145501.

  "At finite temperatures a stable crystalline structure requires all phonon frequencies to be positive definite: $\omega^2 > 0$. ... a significant part of the phonon spectrum for the P63mc phase is imaginary—which means that this structure is unstable at T>0K. This surprising result, considering the experimental predictions ... "

- Łodziana, Z. & Vegge, T., 2006. Łodziana and Vegge Reply: Physical Review Letters, 97(11), p.119602.

  "A system which is unstable within the harmonic approach can be stabilized by entropy, in which case it must posses more than dynamical disorder."

AIMD – computational details

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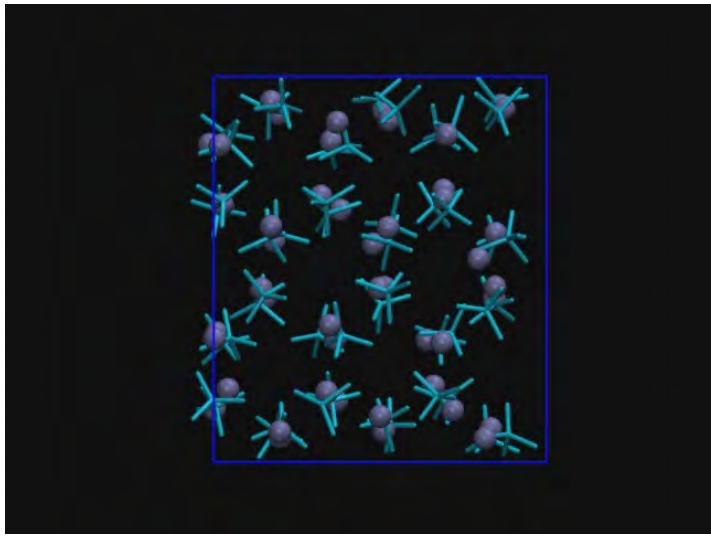
- Code: CP2K (out-of-the-box)
- Born-Oppenheimer molecular dynamics in isokinetic ensemble (Gaussian thermostat)
- Forces evaluated by DFT using the QUICKSTEP method
- Supercell: 288 atoms (48 formula units)
- Time step: 0.5 fs
- Run lengths 20-30 ps after equilibration
- PBE exchange-correlation functional
- Dual basis set (Gaussian DZ orbitals & plane waves up to 280 Ry) and Goedecker pseudopotentials are used



Equilibrium MD picture

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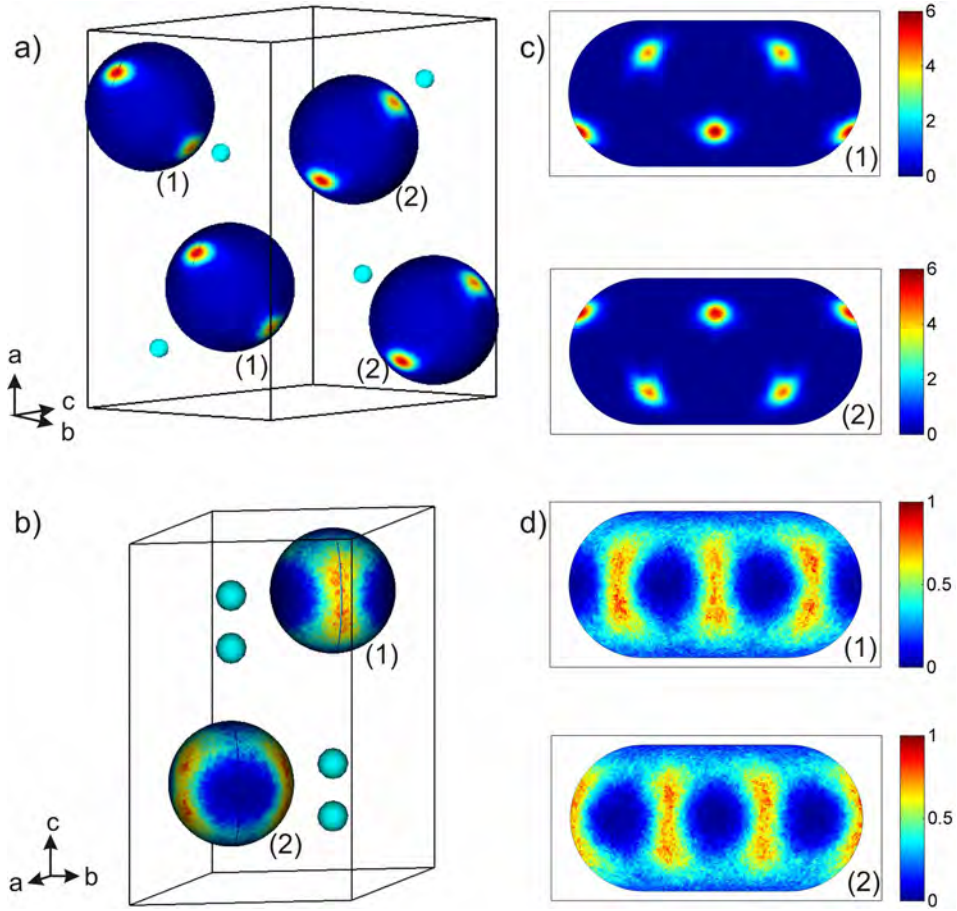
BH4 rotational disorder:



298K

473K

Equilibrium MD picture

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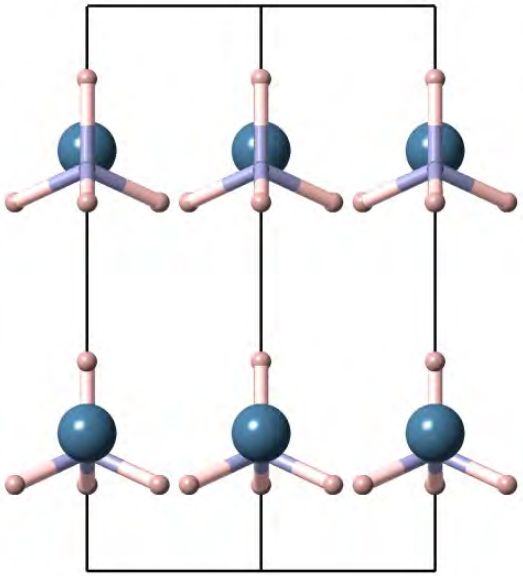
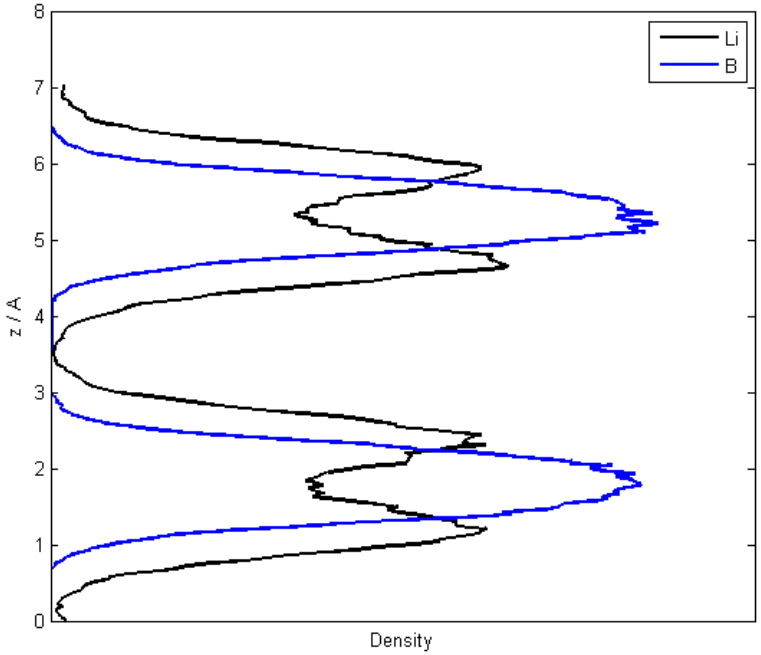
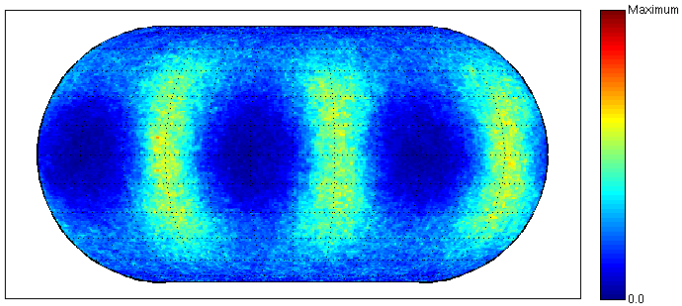
Li dynamical disorder:





BH4 rotational disorder:



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ARTICLE

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The Nature of BH_4^- Reorientations in Hexagonal $LiBH_4$

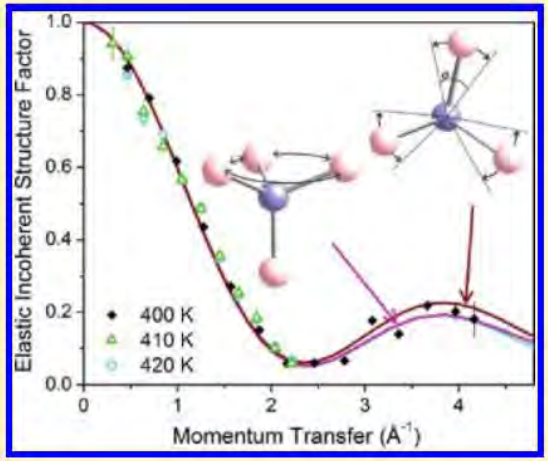
Nina Verdal,*[,†] Terrence J. Udovic,[†] and John J. Rush[†,‡]

[†]NIST Center for Neutron Research, National Institute of Standards and Technology, 100 Bureau Dr., MS 6102, Gaithersburg, Maryland 20899-6102, United States

[‡]Department of Materials Science and Engineering, University of Maryland, 2135 Chemical & Nuclear Engineering Bldg., College Park, Maryland 20742-2115, United States

S *Supporting Information*

ABSTRACT: Lithium borohydride ($LiBH_4$) has lately been the subject of intense inquiry within the hydrogen storage community. Quasi-elastic neutron scattering spectra were measured for $LiBH_4$ in the high-temperature hexagonal crystal phase. The elastic incoherent structure factor associated with the rapid BH_4^- anion reorientations was determined at 400, 410, and 420 K for momentum transfers as high as 4.2 $Å^{-1}$. The results strongly suggest a BH_4^- reorientational mechanism approaching quasi-free, trigonal-axis rotation of three borohydride H atoms, combined with reorientational jump exchanges between these delocalized "orbiting" H atoms and the remaining axial borohydride H atom. This mechanism is consistent with previously reported diffraction and spectroscopy studies.



Measurements of Li mobility

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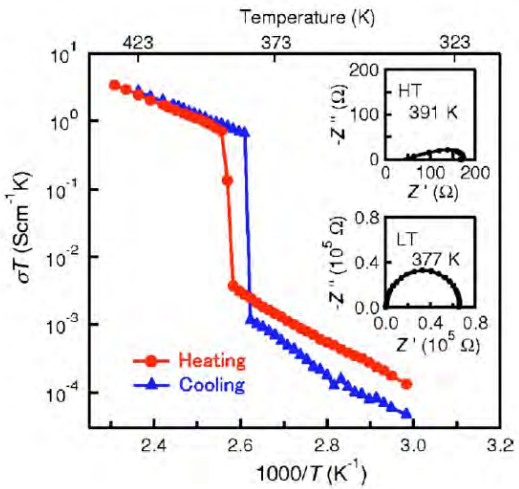
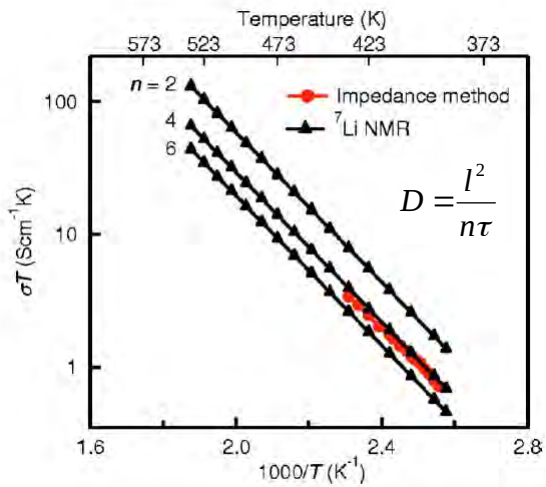
Motoaki Matsuo et al., Applied Physics Letters **91**, 224103 (2007).



A/C impedance measurements



Li-7 NMR measurements

At 535K: $\sigma = 0.139$ S/cm ⟷ $D_{Li} = 2.28 \cdot 10^{-6}$ cm^2/s

Calculating diffusion by AIMD

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Diffusion coefficient calculated by…

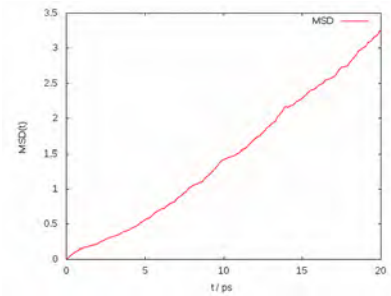
Einstein-Sutherland equation

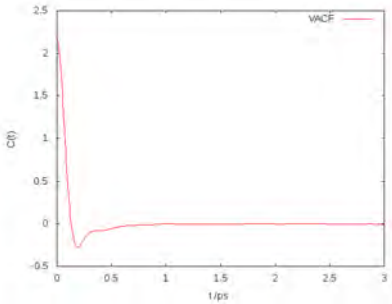
$$D = \frac{1}{n}\frac{d\langle r^2(t)\rangle}{dt}$$

Green-Kubo formula

$$D = \frac{2}{n}\int_0^\infty dt\langle v(0)\cdot v(t)\rangle$$

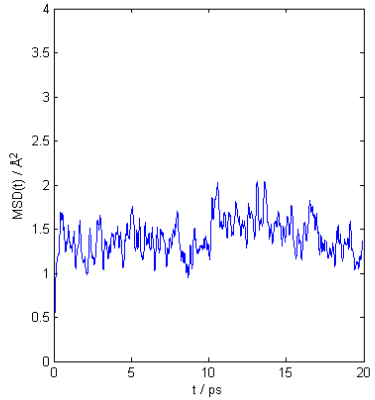
Lennard-Jonesium
(mimicking liquid Argon)

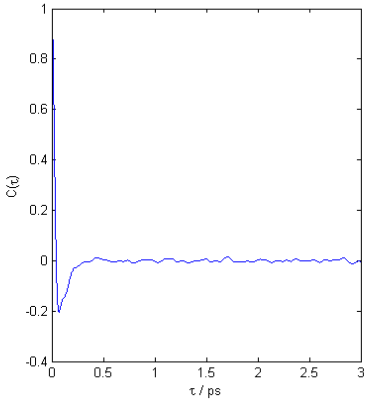




Fast diffusion

LiBH4 at 535 K





Diffusion by ion jumps
(rare events)
which are often
followed by a jump back
to the original position

Limits of AIMD: diffusion in fluids with $D > 10^{-5}$ cm^2/s

Nonequilibrium Molecular Dynamics

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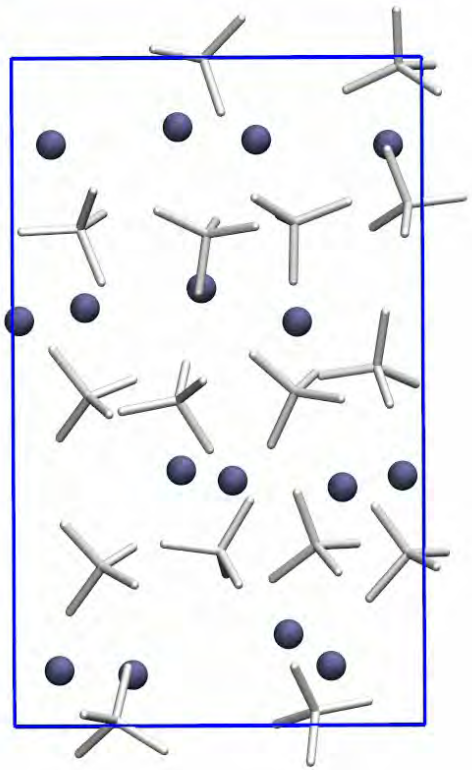

- An external field ***Fe*** is applied that couples to a fictitious atomic property ("colour", *ci*):

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + c_i \mathbf{F}_e$$

- The (fictitious) field and its induced response are related by (real) transport coefficients:

$$D = \frac{k_B T}{\rho_c} \lim_{t \to \infty} \lim_{F_e \to 0} \frac{\langle J_c(t) \rangle}{F_e}$$

- NEMD functionality implemented in CASTEP and CP2K
- *ab initio* nature of the method allows mechanism discovery

Results – F_e = 0.05 eV/Å

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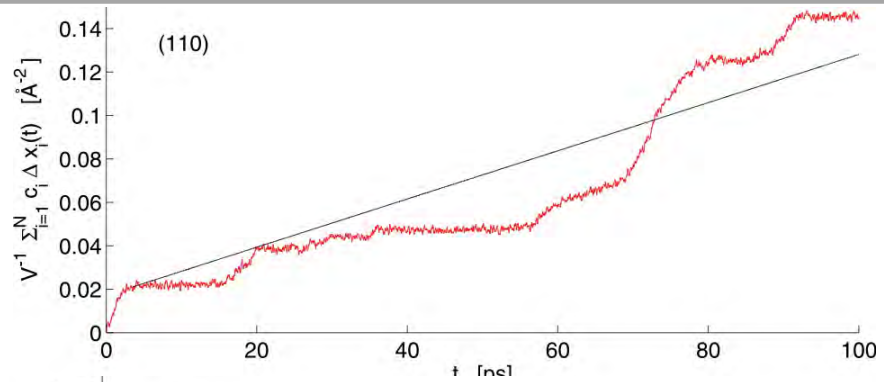
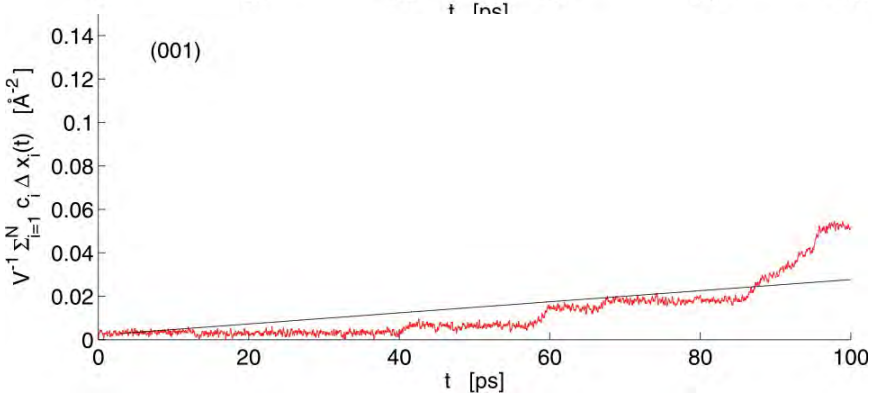
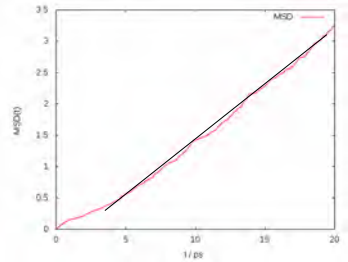


$D_{Li} = 5.82 \cdot 10^{-6}$ cm²/s



$D_{Li} = 1.34 \cdot 10^{-6}$ cm²/s

(Measured: $D_{Li} = 2.28 \cdot 10^{-6}$ cm²/s)



Compare: $D = \frac{1}{n} \frac{d\langle r^2(t) \rangle}{dt}$ vs $D = \frac{k_B T}{\rho_c} \lim_{t \to \infty} \lim_{F_e \to 0} \frac{\langle J_c(t) \rangle}{F_e}$

linear response domain

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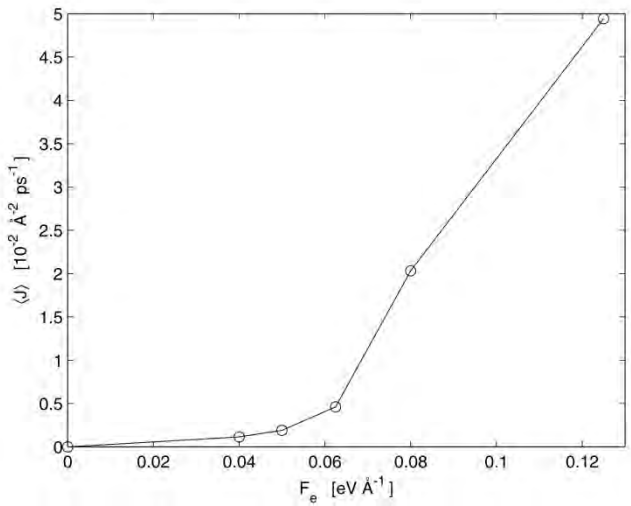

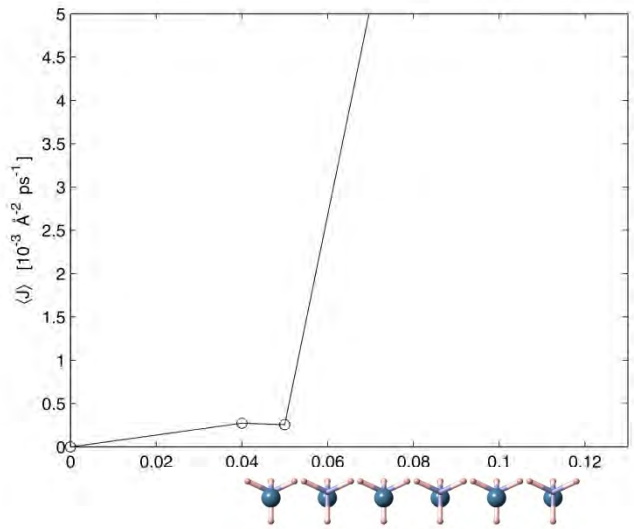

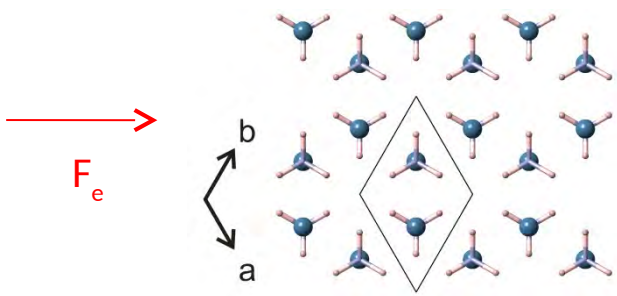

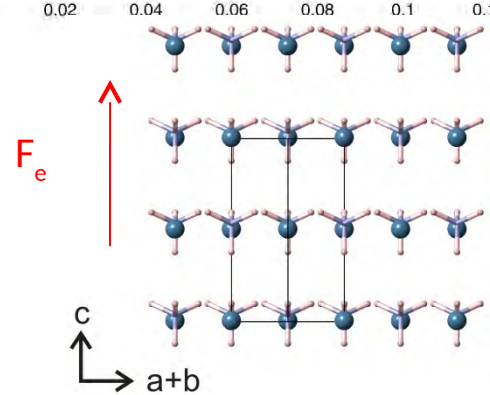

Maximum field strength in linear regime: 0.05 eV/Å

$D(110)/(001) = 5.8\times10^{-6}/1.3\times10^{-6}\ cm^2s^{-1}$

$D(expt, avg.) = 2.3\times10^{-6}\ cm^2s^{-1}$

Diffusion Pathway

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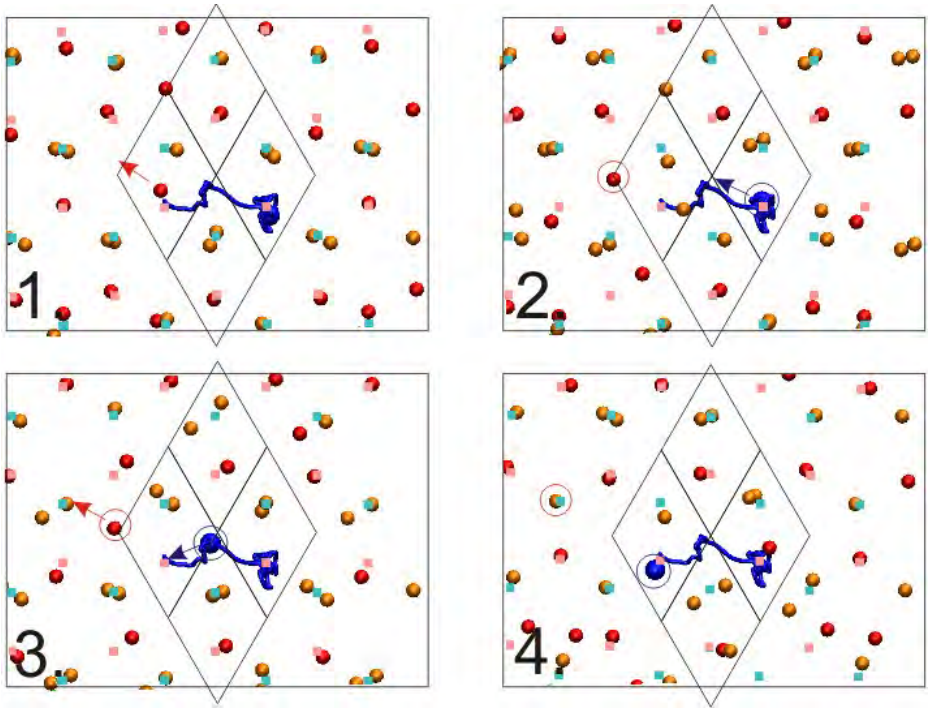
Inspection of the NEMD trajectory:



hopping is via jumps from a lattice site into an empty interstitial site (2 & 3), and from there on to another lattice site (4).

P.C. Aeberhard, S. Williams, D. Evans, K. Refson, and W.I.F. David, Physical Review Letters 108, 095901 (2012).

Vibrations, Phonons and Spectroscopy

Vibrational Spectroscopy

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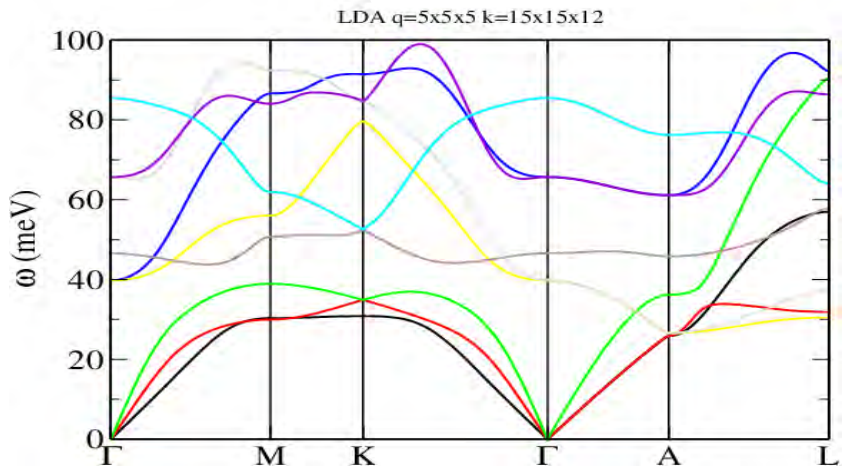
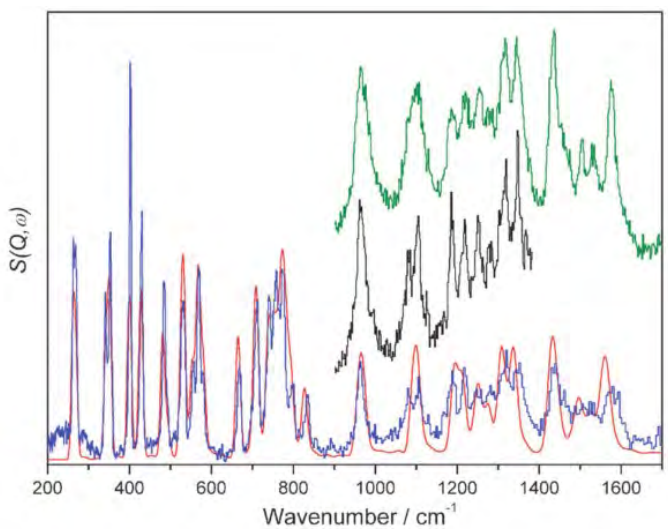
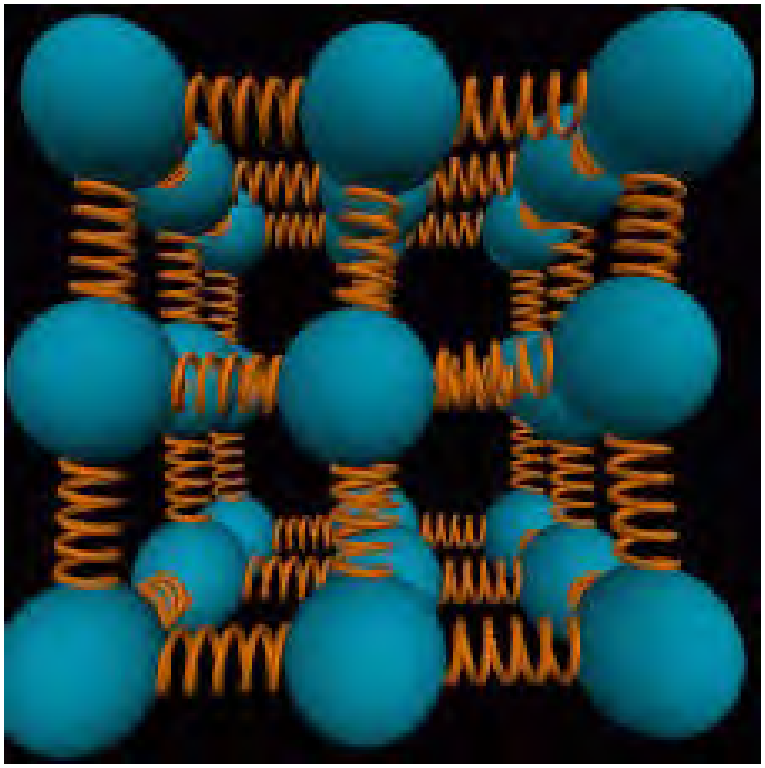


$$\Phi^{\kappa\alpha}_{\kappa'\alpha'}(\mathbf{0},\boldsymbol{R}) = \frac{\partial^2 E}{\partial r_{\kappa\alpha}\,\partial r_{\kappa'\alpha'}}$$





VibrationalSpectroscopy

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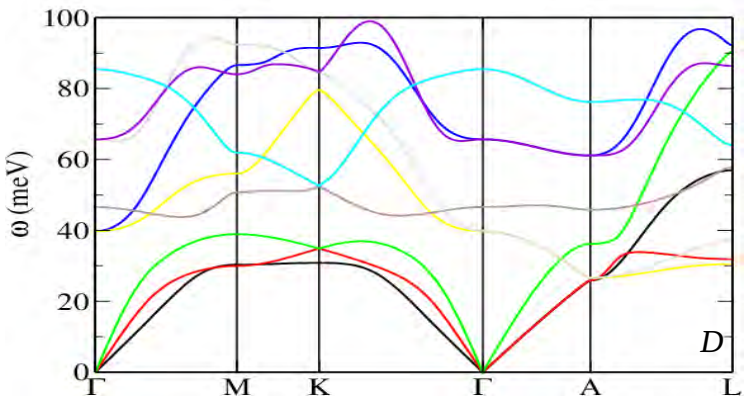
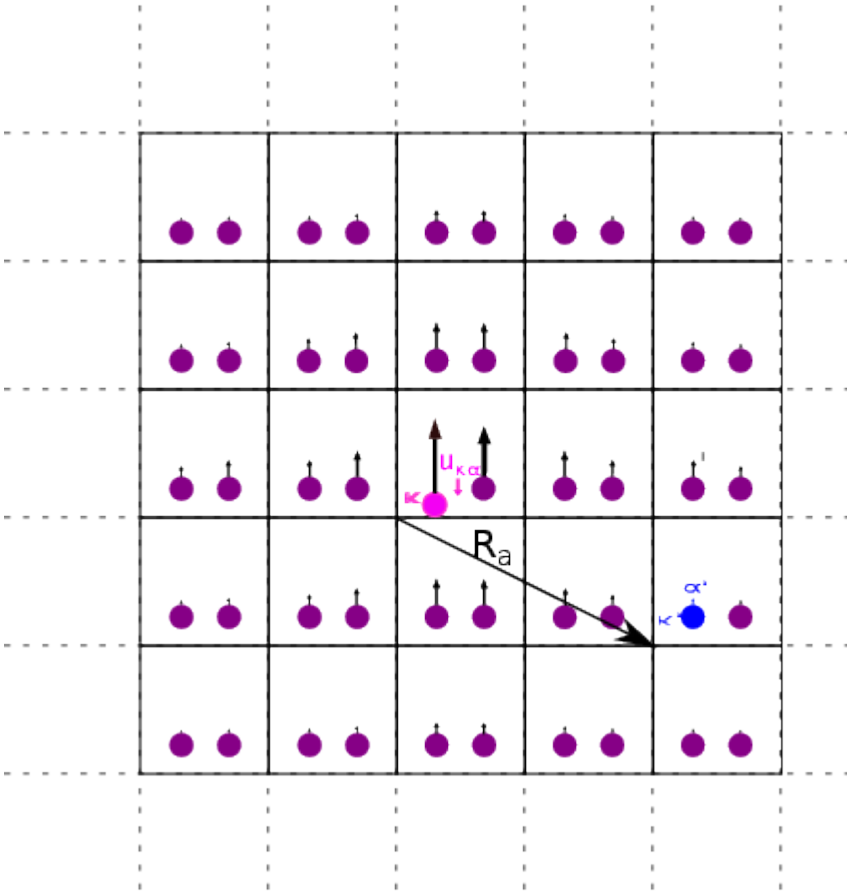


$$\Phi^{\kappa\alpha}_{\kappa'\alpha'}(\mathbf{0},\boldsymbol{R}) = \frac{\partial^2 E}{\partial r_{\kappa\alpha}\,\partial r_{\kappa'\alpha'}}$$



Lattice dynamics from first principles

$$D^{\kappa\alpha}_{\kappa'\alpha'}(\boldsymbol{q}) = \int \Phi^{\kappa\alpha}_{\kappa'\alpha'}(\mathbf{0},\boldsymbol{R})\, e^{i\boldsymbol{q}\cdot\boldsymbol{R}}\, d\boldsymbol{R}$$

$$D^{\kappa\alpha}_{\kappa'\alpha'}(\boldsymbol{q})\,\epsilon_{m\kappa\alpha} = \omega_m^2\,\epsilon_{m\kappa\alpha}$$

The Supercell Method

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Build large supercell model

Optimize Geometry: $F_{\kappa\alpha}=0$

Displace atom I by $\delta x_{\kappa\alpha}$

Compute *all* Forces $\delta F_{\lambda\beta}$

$$\Phi_{\kappa\alpha\lambda\beta}=-\frac{\delta F_{\lambda\beta}}{\delta x_{\kappa\alpha}}$$

Repeat for all i

$$D^{\kappa\alpha}_{\lambda\beta}(\boldsymbol{q})=\int \Phi^{\kappa\alpha}_{\lambda\beta}(\boldsymbol{0},\boldsymbol{R})e^{i\boldsymbol{q}.\boldsymbol{R}}d\boldsymbol{R}$$

$$D^{\kappa\alpha}_{\lambda\beta}(\boldsymbol{q})\epsilon_{m\kappa\alpha}=\omega_m^2\epsilon_{m\lambda\beta}$$

Repeat for any q

End

Expensive DFT calculation

The Nondiagonal Supercell Method

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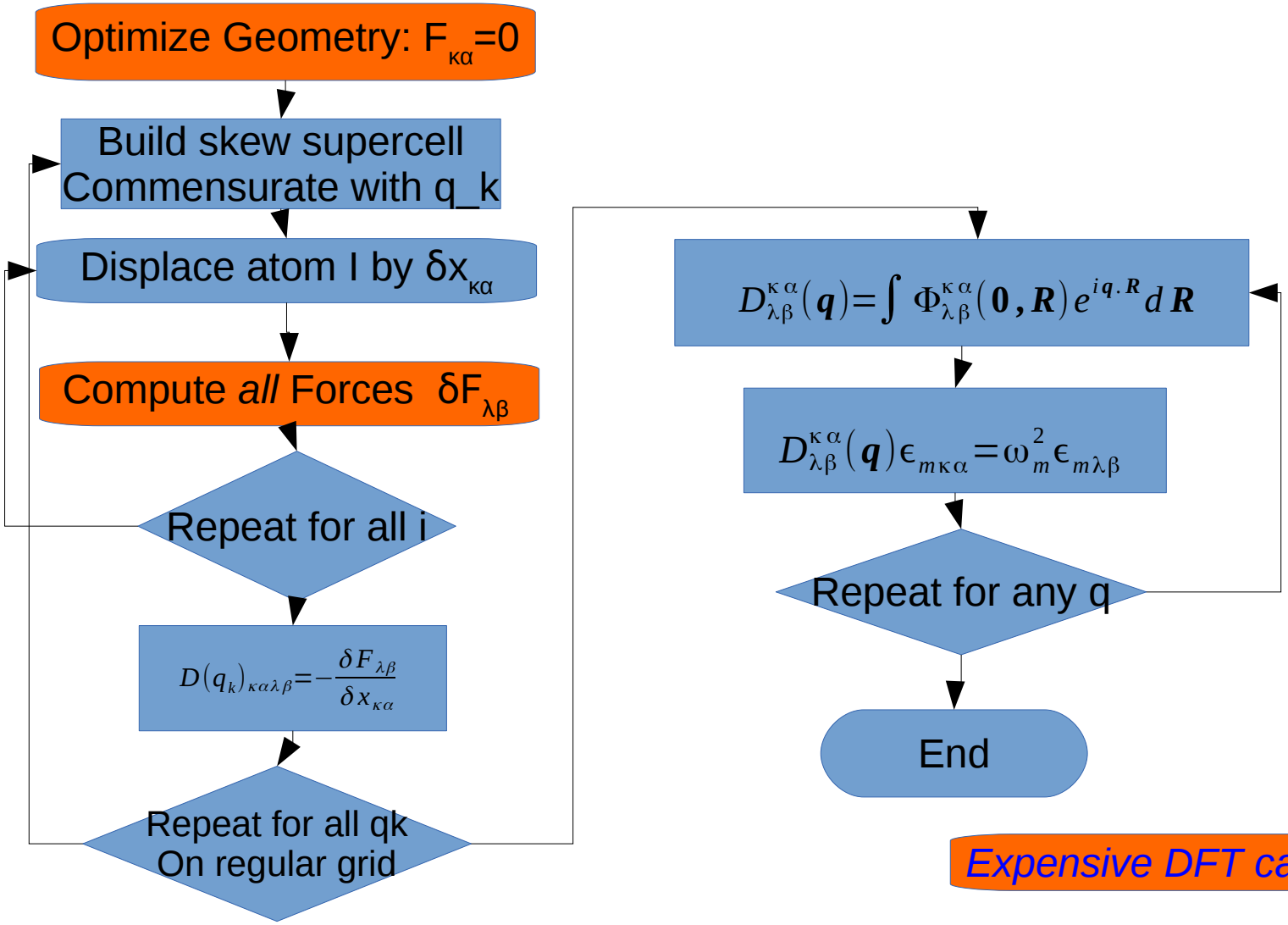

Expensive DFT calculation

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

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

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

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.

Vibrational spectroscopy of C_{60}

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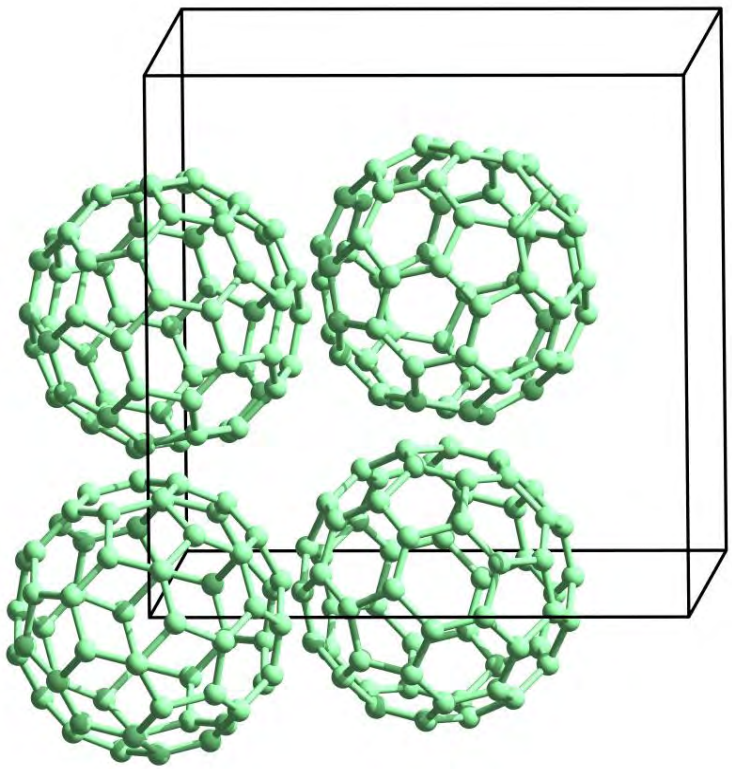

- Above 260K takes Fm3m structure with dynamical orientational disorder
- m3m point group lower than I_h molecular symmetry
- Selection rules very different from gas-phase.
- Intramolecular modes and factor group splitting seen.
- Try ordered Fm3 model for crystal spectral calculation.

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

GGA Raman spectrum of C_{60}

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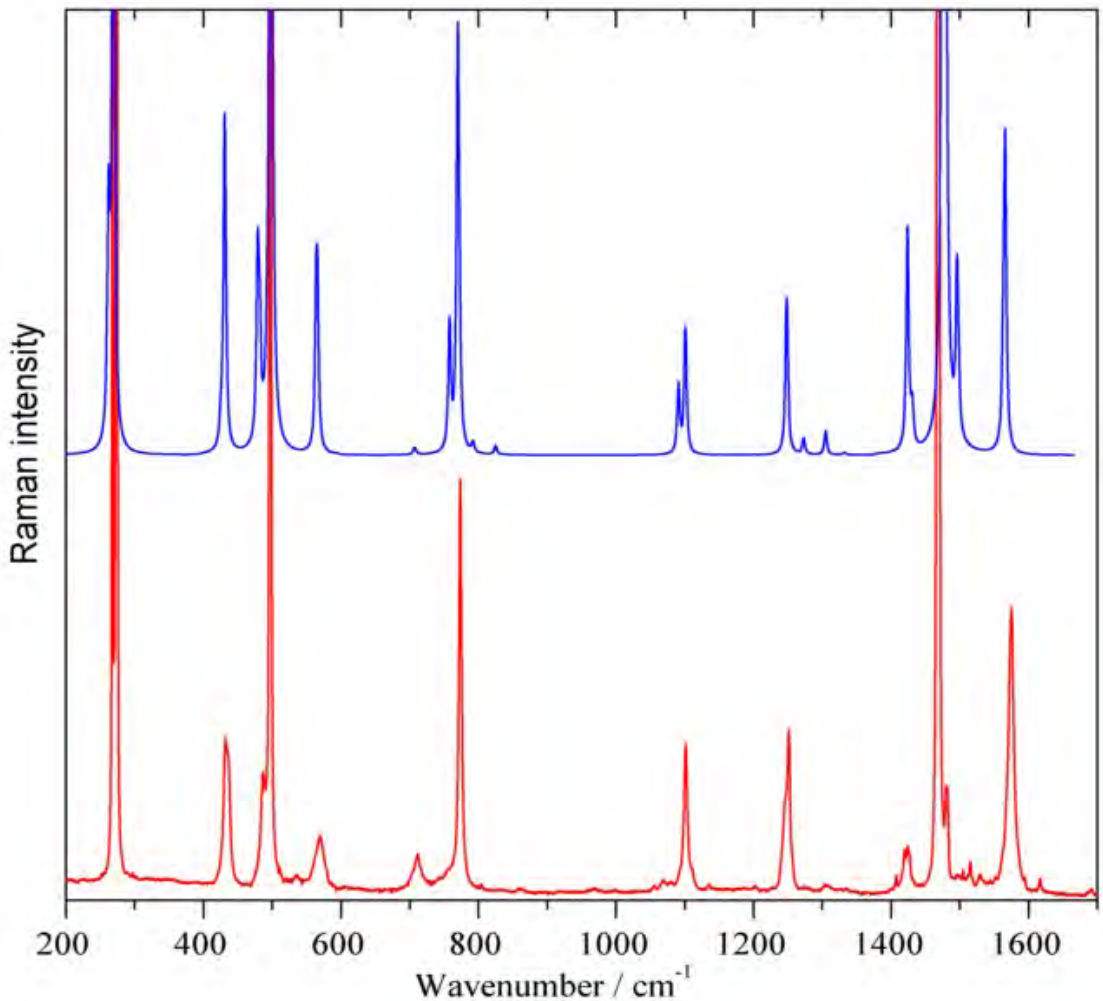

C_{60} INS -Tosca

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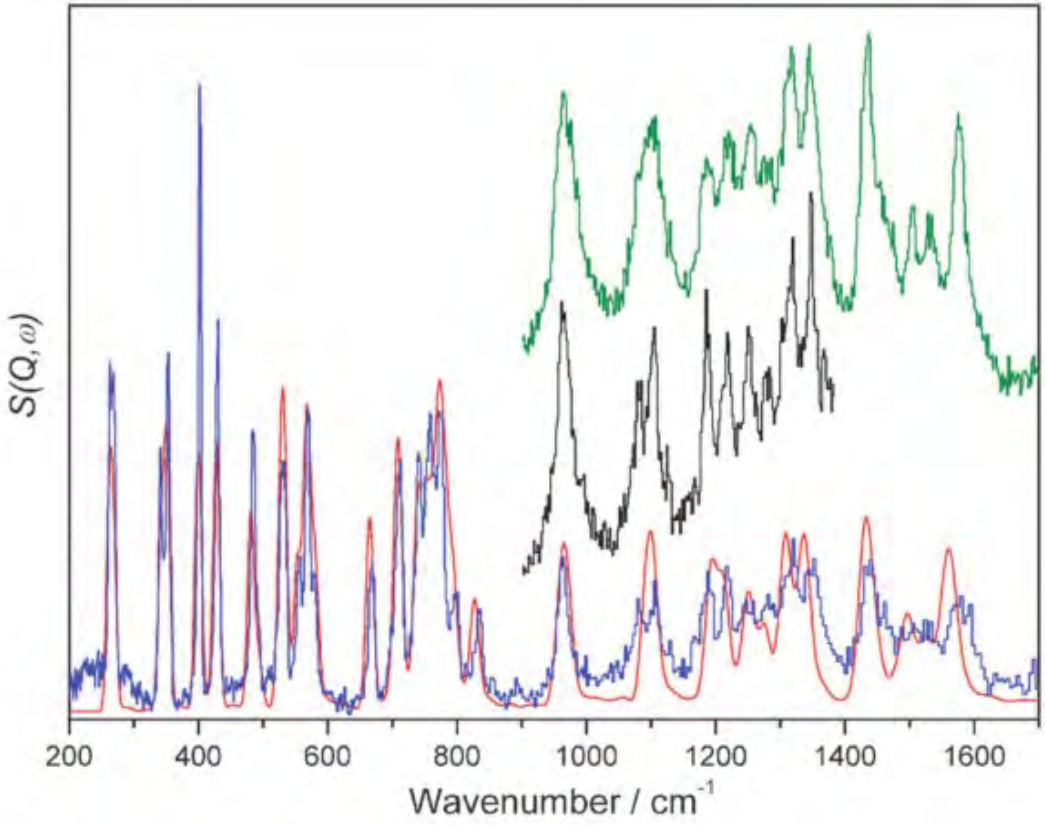

GGA infrared spectrum of C_{60}

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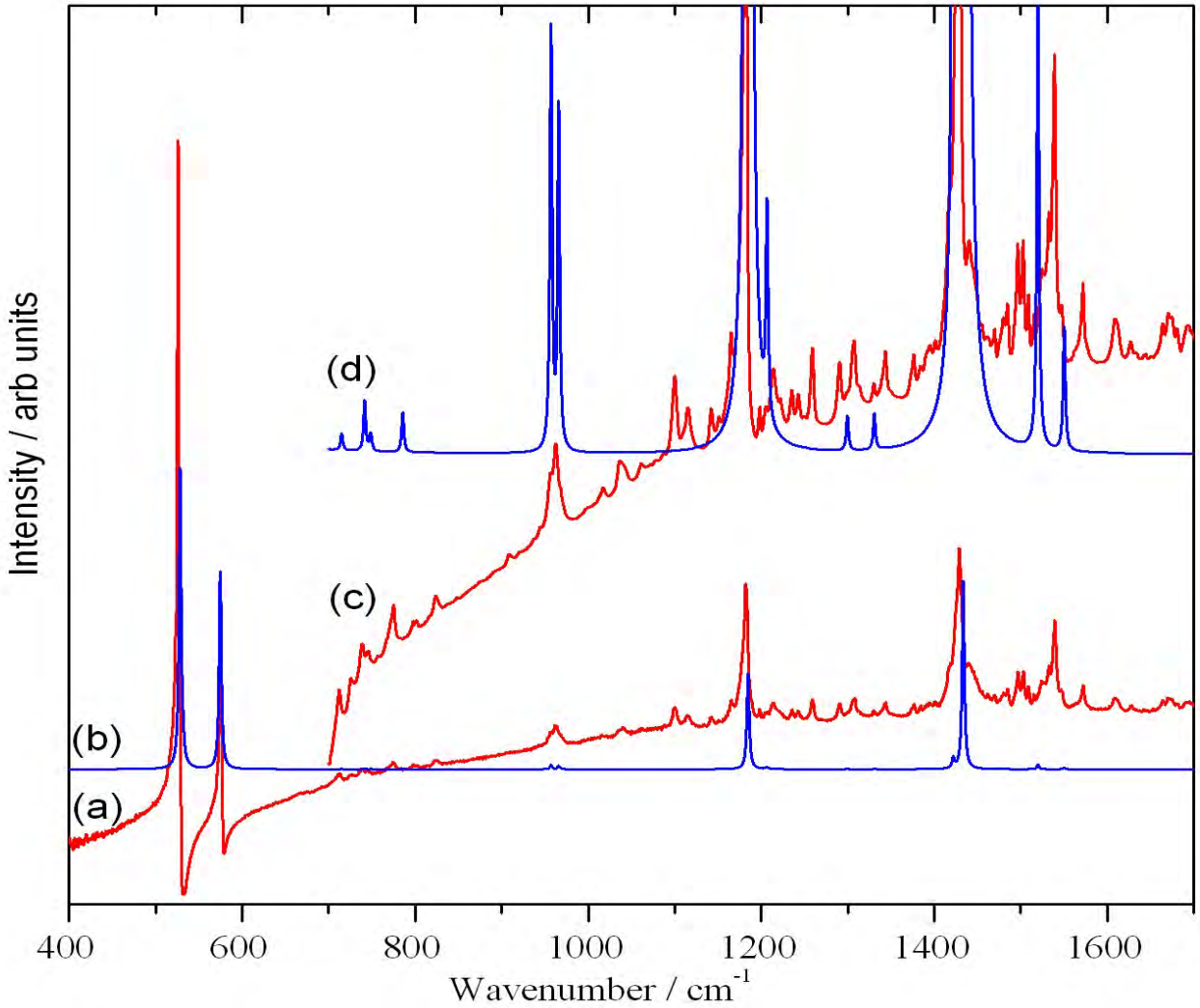

Thermoelectric Heat Recovery

TiNiSn-based Half-Heusler Alloys

The Half-Heusler Crystal Structure

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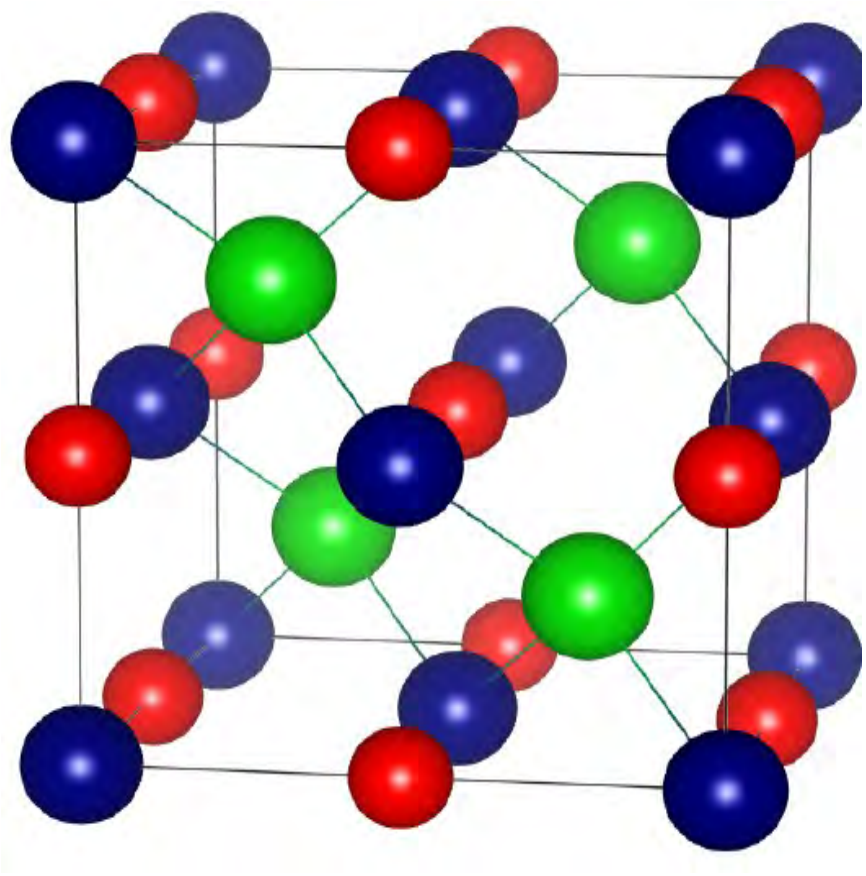
- Chemical Formula ABC
- A, B, C are elemental metallic elements
- Closed-shell “18-electron” results in insulating band-gap.
- TiNiSn with excess Ni or Cu show high themoelectic ZT.
- Investigate phonon origin of low thermal conductivity.
- MARI experiments performed on on Ti/Zr/Hf NiSn
- MARI experiments on excess Ni and Cu in TiNiSn



Ti/Zr/Hf series

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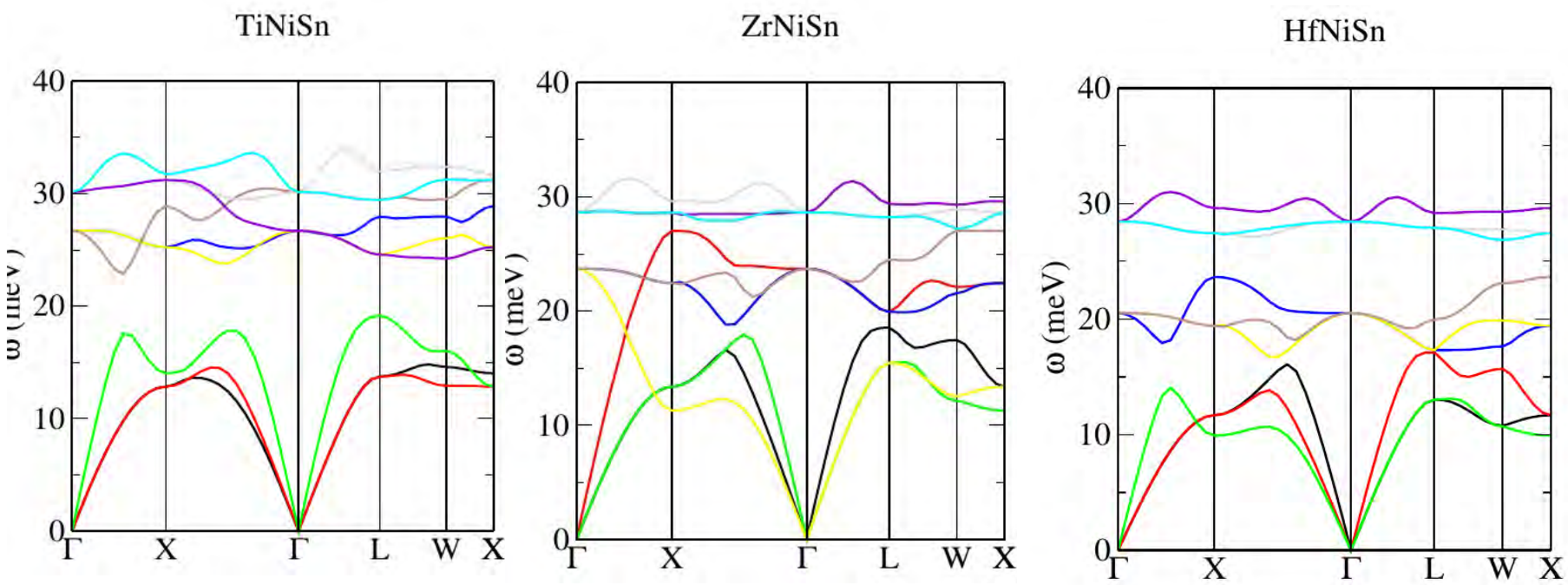
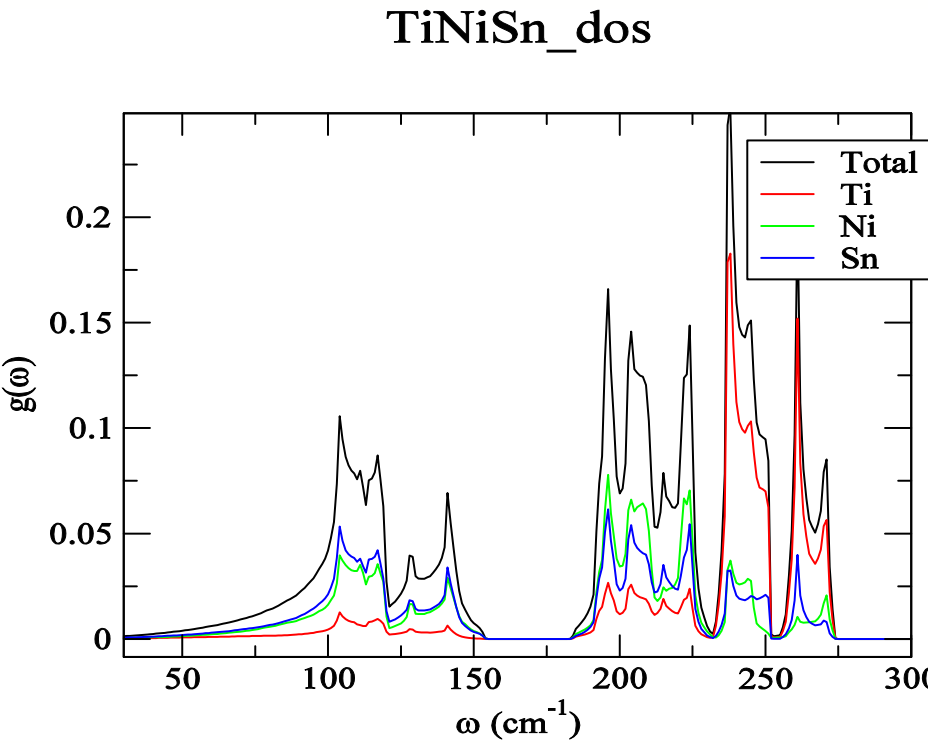
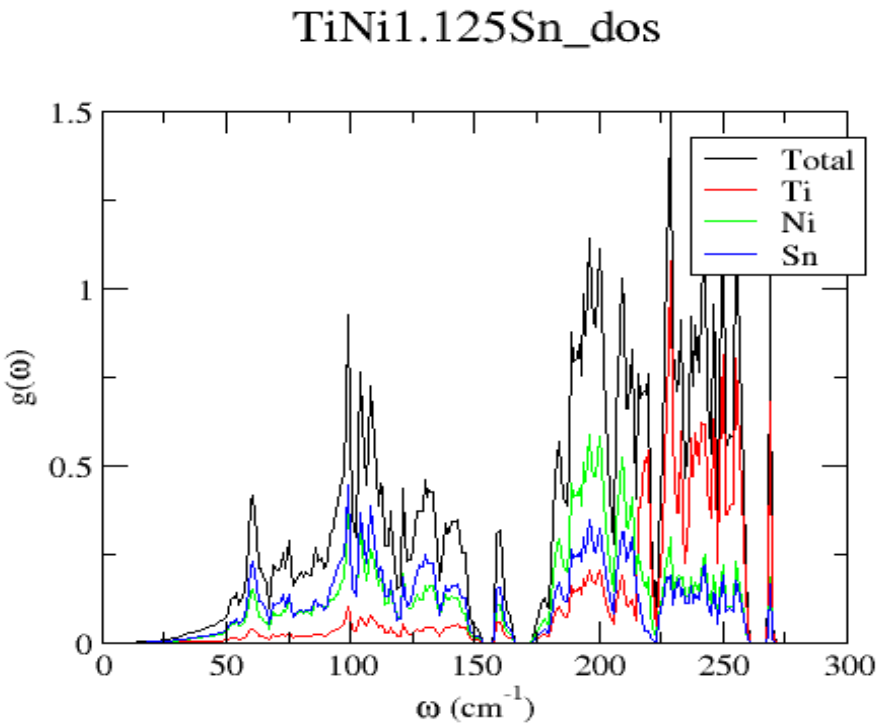
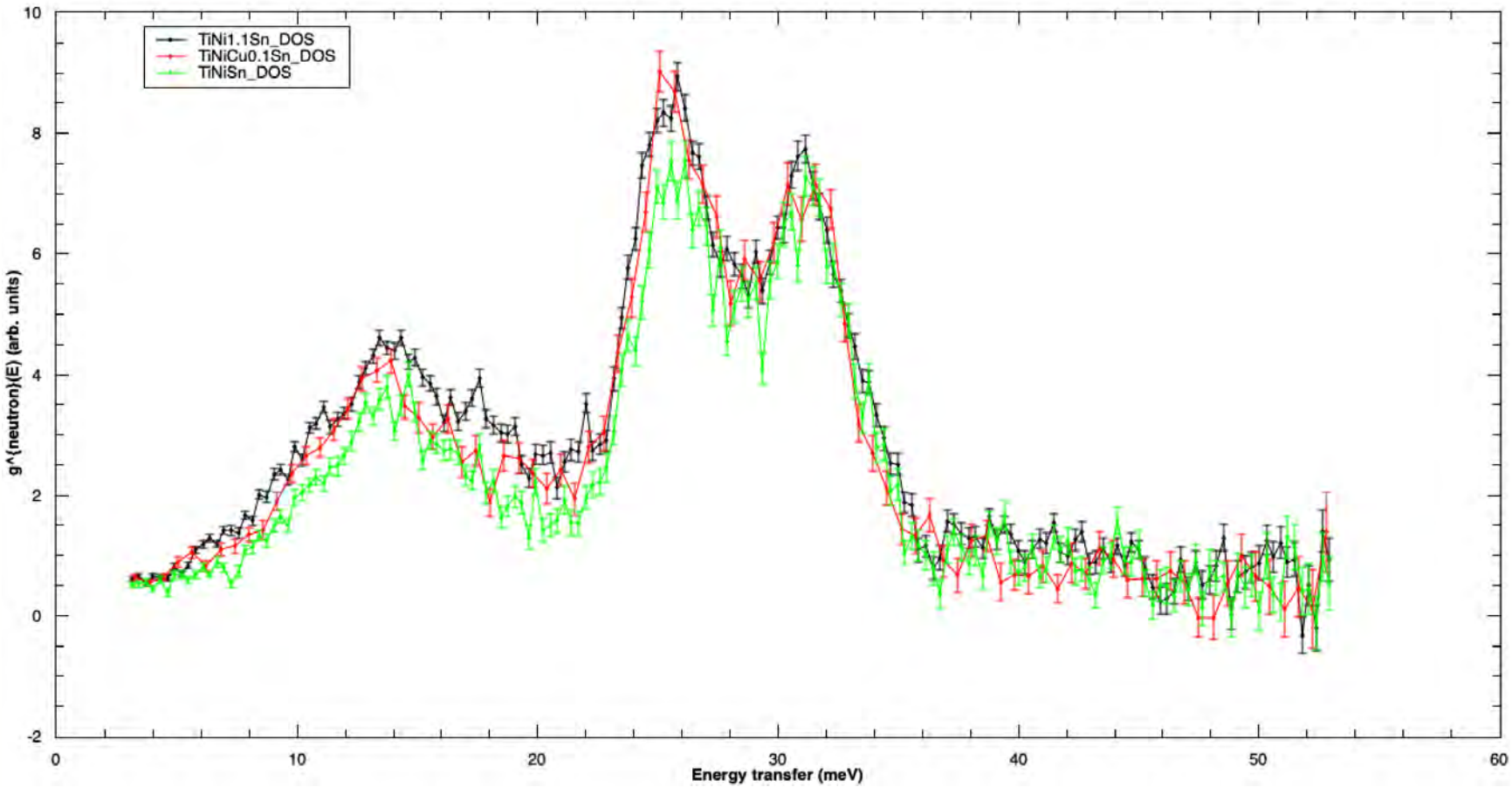


Effect of Excess Ni in TiNiSn

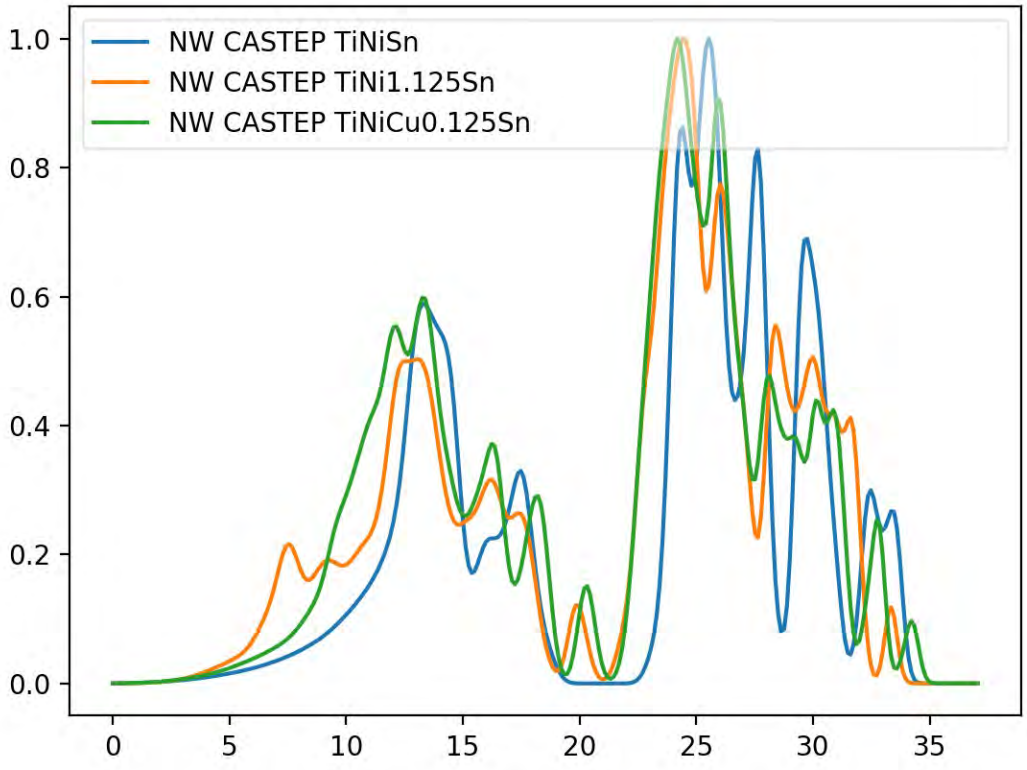




MARI TiNiSn, TiNi1.1Sn, TiNiCu0.125Sn



Neutron Weighted Phonon DOS



Rattler mode in thermoelectric $Na_{0.8}CoO_2$

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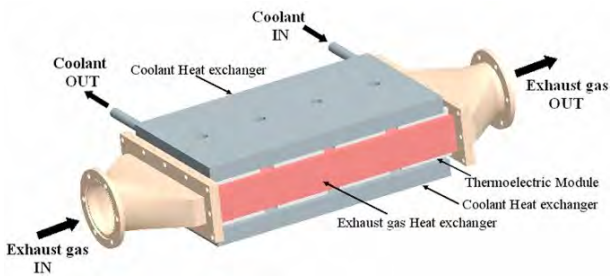
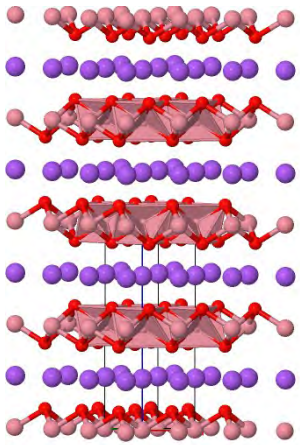
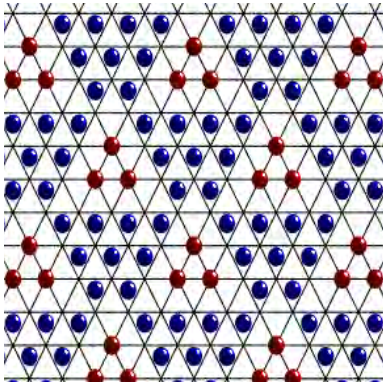


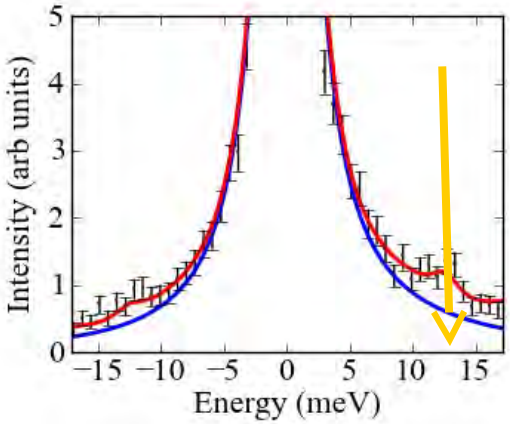


Thermoelectric
"figure of merit"

$$zT = \frac{S^2 T \sigma}{\kappa}$$



"Square Phase" Na ordering at 150K



Inelastic X-Ray spectrum measured at ESRF

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

Ab initio Lattice Dynamics

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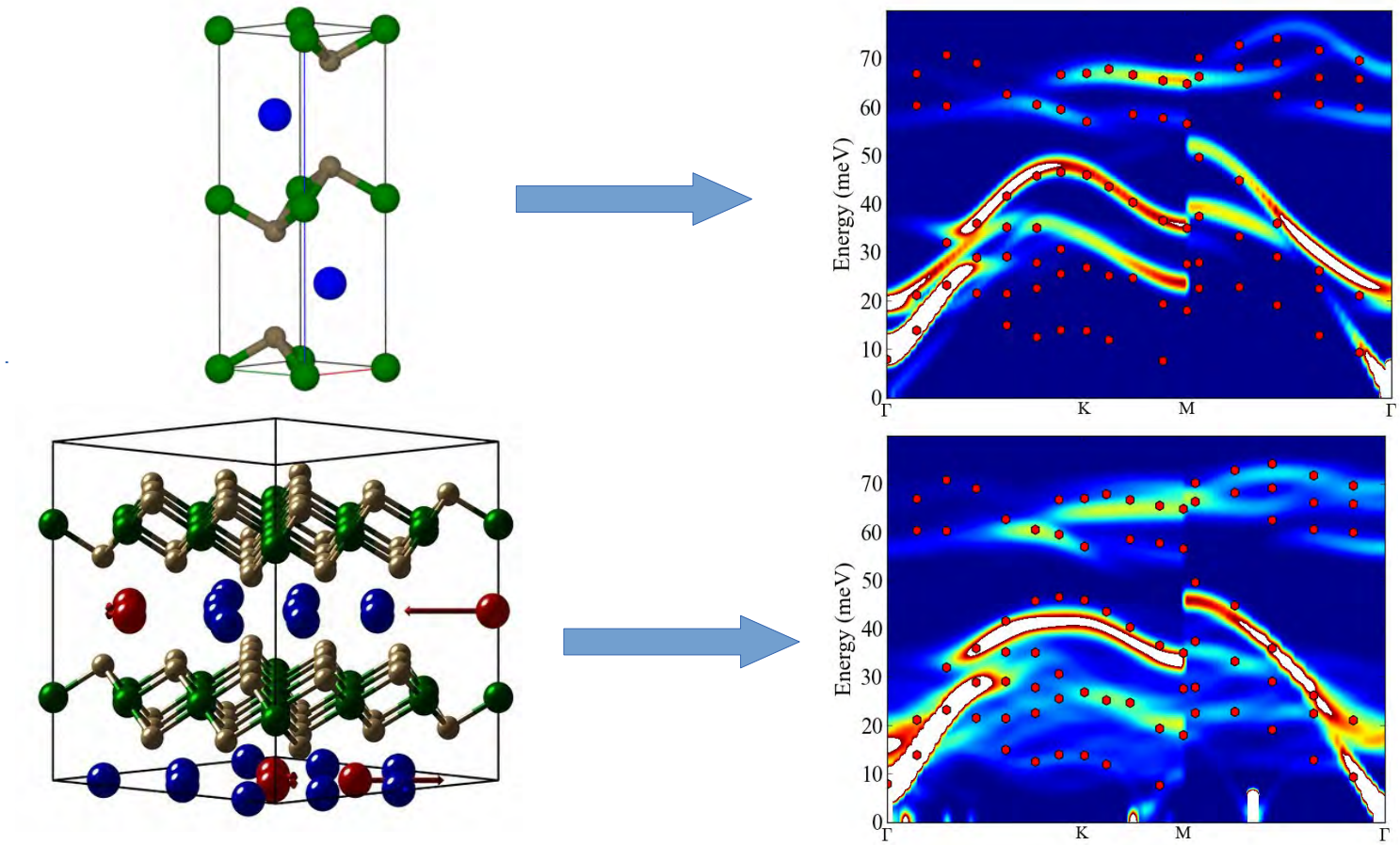

D. Voneshen et al.,*Suppression of thermal conductivity by rattling modes in thermoelectric sodium cobaltate*. Nature Materials **12**, 1028 (2013)

Thermal Diffuse Scattering in Titanite

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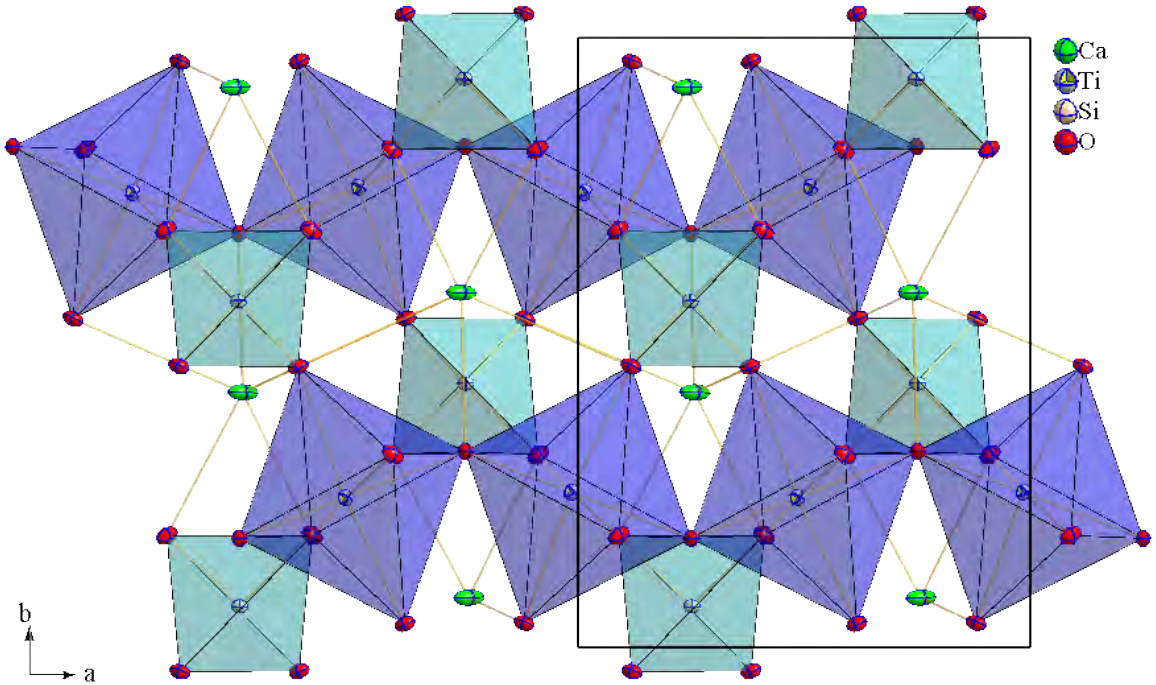

Motivation

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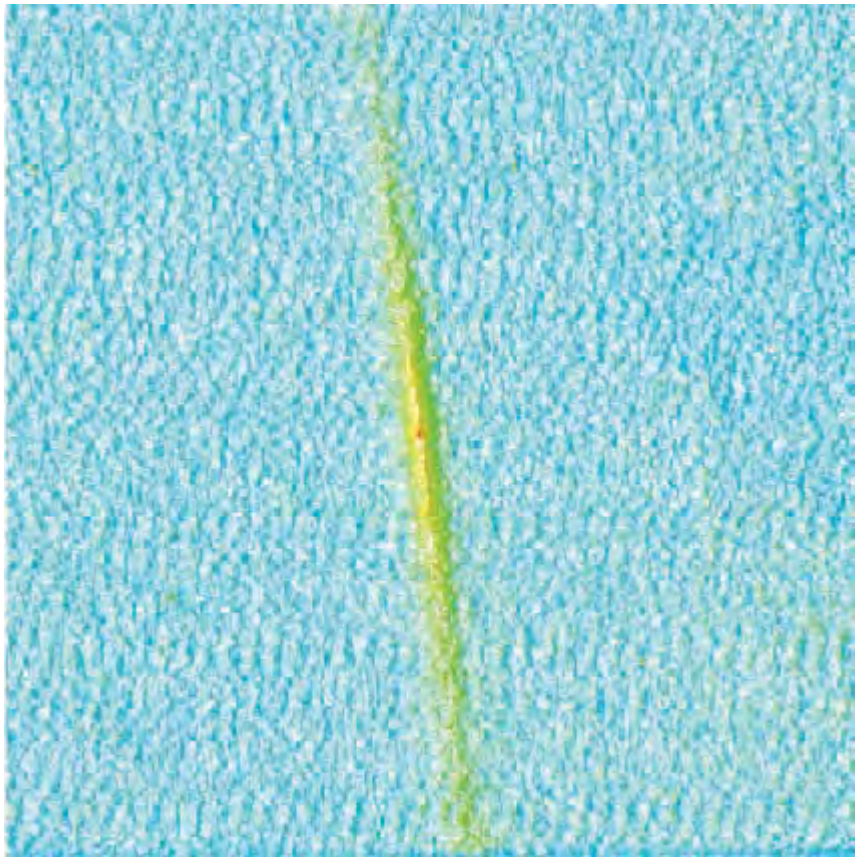

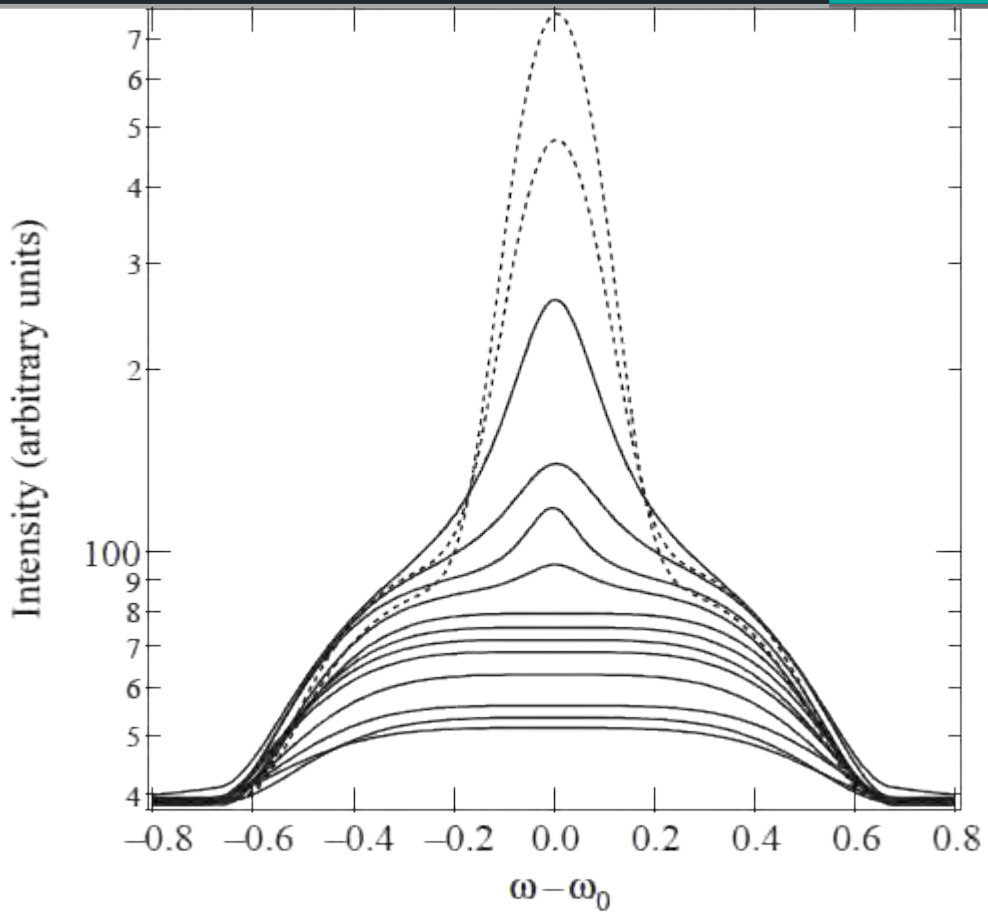

T. Malcherek *et al.*, J. Appl. Cryst. **34** (2001), 108.

Experiment

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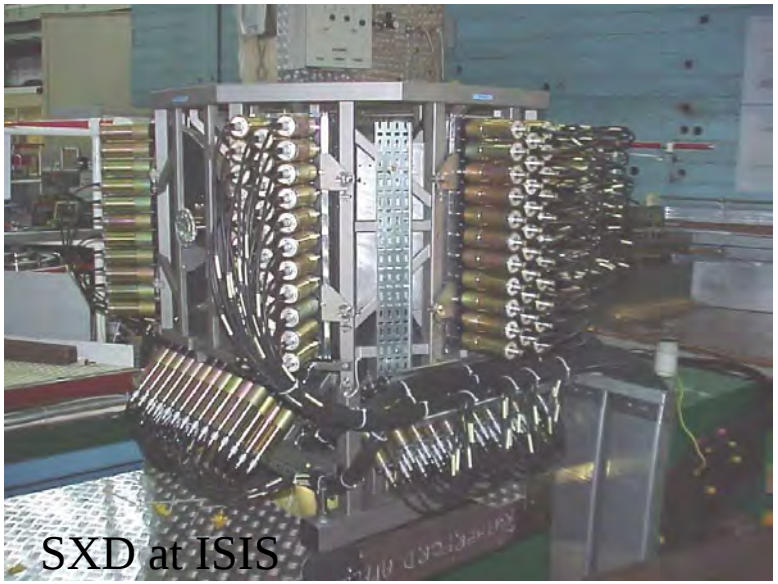

SXD at ISIS

BW5 at DESY

Diffuse scattering

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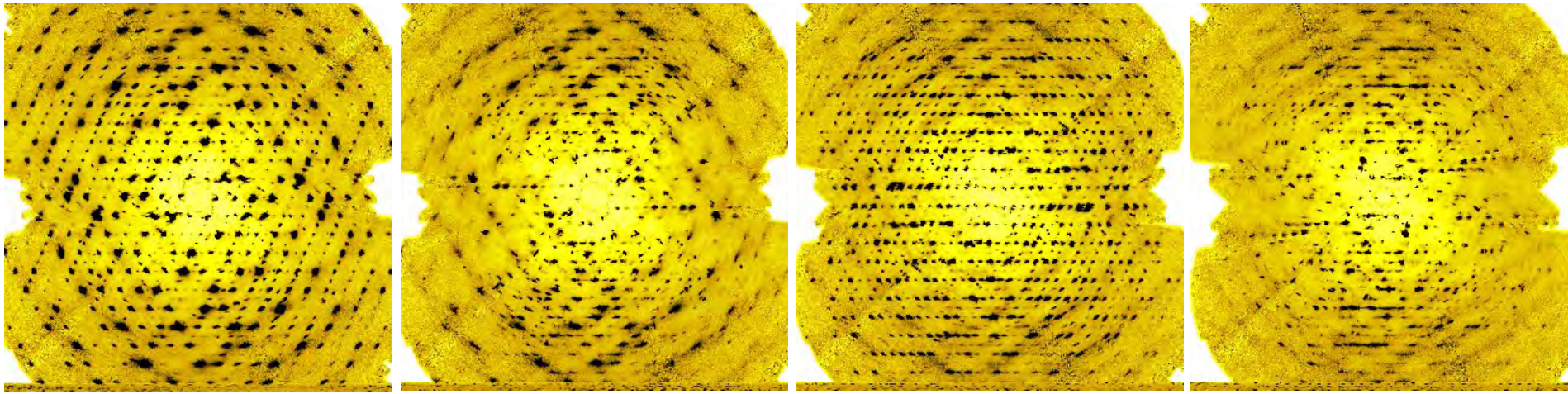
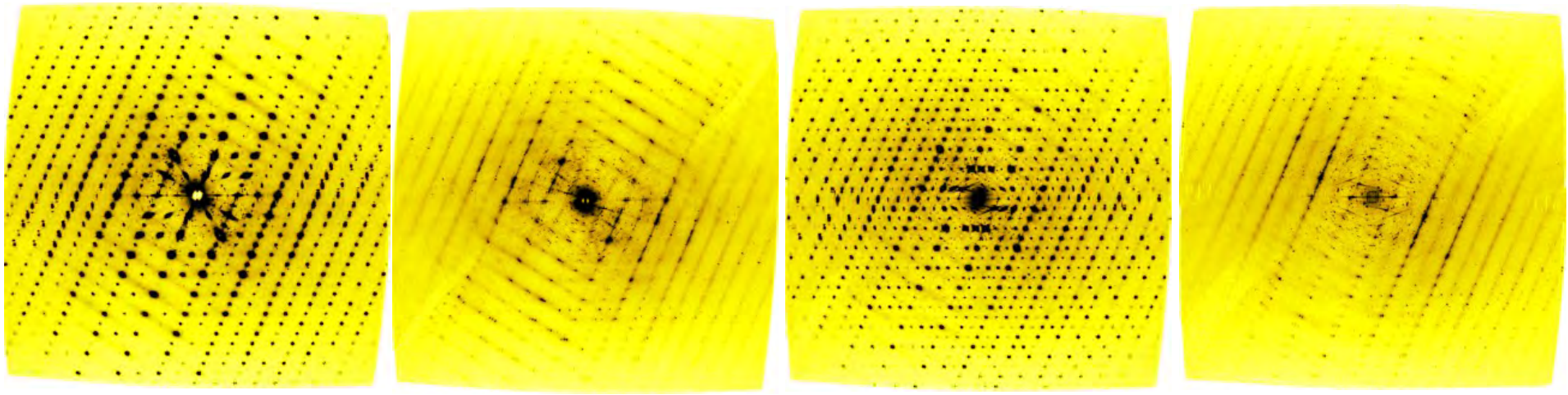


Neutron



X-Ray

Phonons and diffraction

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$$F_j(\vec{q}) = \sum_s \frac{f_s}{\sqrt{\mu_s}} \cdot e^{-M_s} \cdot (\vec{q} \cdot \vec{e}_{\vec{q},j,s}) \cdot e^{-i\vec{q}\cdot\vec{r}_s}$$

$$I_{TDS} = \frac{\hbar N I_e}{2} \sum_j \frac{1}{\omega_{\vec{q},j}} \coth\left(\frac{\hbar \omega_{\vec{q},j}}{k_B T}\right) |F_j(\vec{q})|^2$$

R. Xu and T. C. Chiang, Z. Kristallogr. **220** (2005), 1009.

Dispersion curves from DFPT

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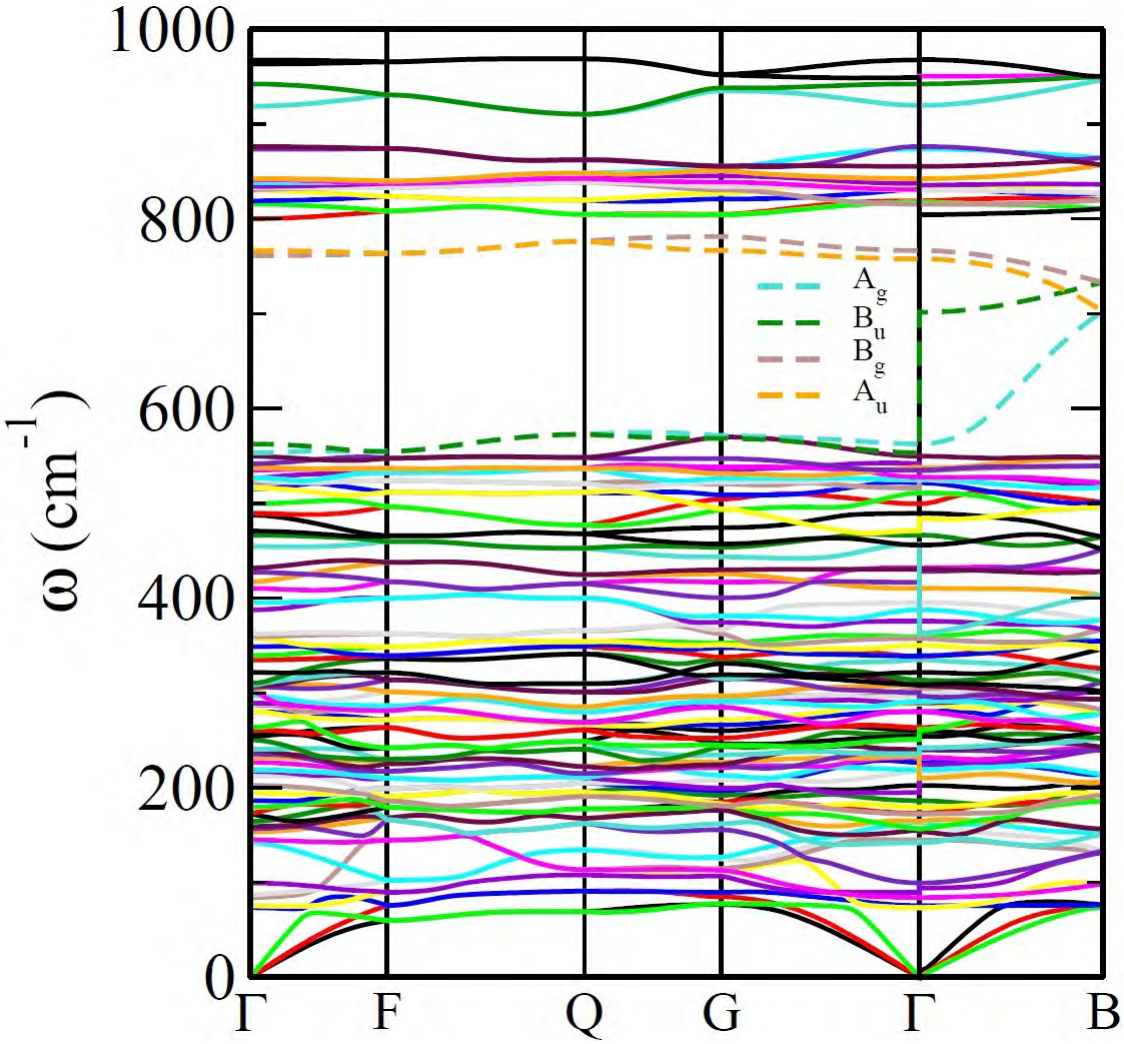

Comparison with data

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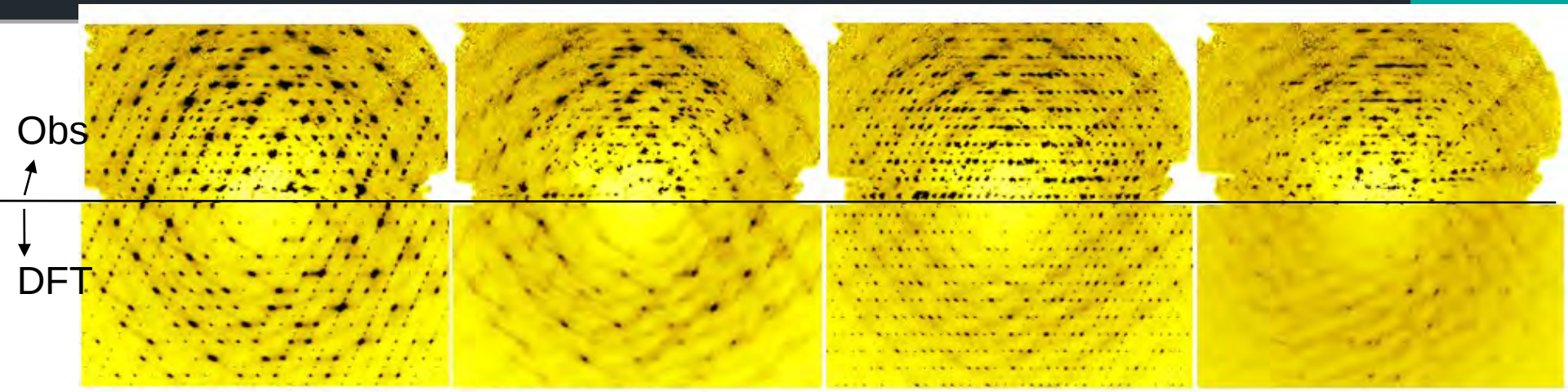
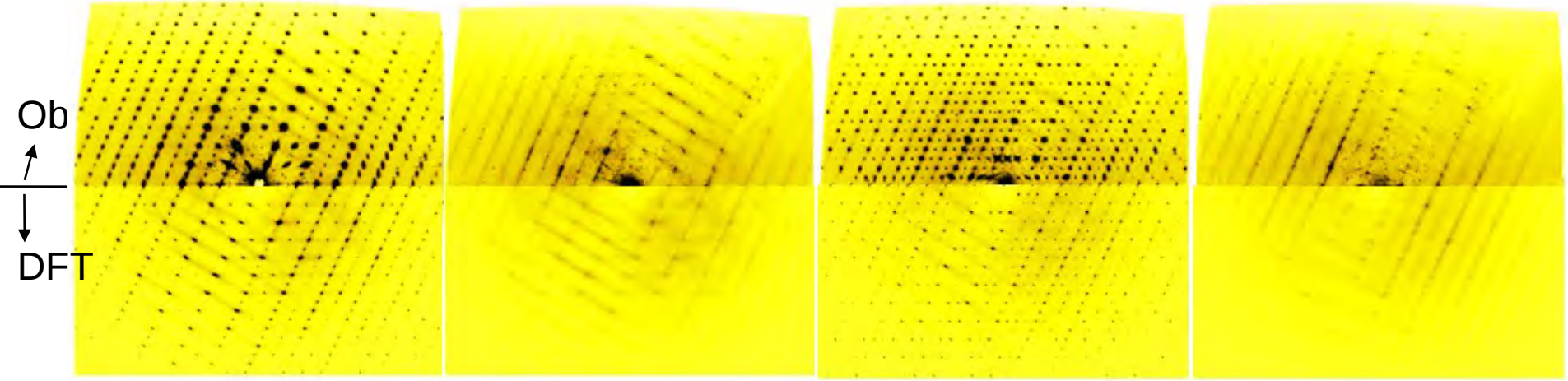


Neutron



X-Ray