



Science & Technology  
Facilities Council

Technical Report  
RAL-TR-2015-002

# Lectures on Neutron Science - Tor Vergata 2015

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**March 2015**

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**ISSN 1358-6254**

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## Lectures on Neutron Science – Tor Vergata 2015

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This lecture series was given in February 2015 as part of the *International Joint Chairs Programme* at the *Università degli Studi di Roma – Tor Vergata* (Italy). They provide an introduction to contemporary neutron science, including the foundations of neutron-scattering techniques, a survey of applications in condensed-matter research, neutron production and utilisation, and the use of computational materials modelling to add value to increasingly complex experimental studies. The first lecture gives an overview of neutron scattering with an emphasis on the merits and strengths of the technique in comparison with other probes, followed by a presentation of the general formalism to calculate and understand neutron-scattering observables. The second lecture applies the concepts introduced above to specific situations, including the mathematical formalism needed to describe the time-averaged and dynamical response of ordered and disordered matter. The third lecture provides an up-to-date account of neutron production and instrumentation, with an emphasis on the increasing use of accelerator technology to produce pulsed neutron beams. A number of recent and ongoing projects around the globe to build both small- and large-scale facilities are described, alongside emerging concepts aimed at maximising neutron production in the foreseeable future. The fourth and last lecture introduces the use of first-principles materials modelling to interpret neutron-scattering data and design new experiments, a growing area of synergy across experiment and theory. In this respect, this last lecture constitutes the *in silico* counterpart of the preceding three, and explores in some depth the rationale underpinning the need for computational experiments in the context of neutron science and the benefits derived from this increasingly important synergy. All throughout this lecture series, key concepts are illustrated by reference to recent work on phenomena of technological relevance including gas storage and sequestration in nanoporous materials, nanostructured matter, ionic conduction and charge storage, chemical catalysis, and quantum phenomena.

The primary objective of this lecture series is to provide a self-contained introduction to contemporary neutron science. They were first presented in February 2015 as part of *International Joint Chairs Programme* supported by the *Università degli Studi di Roma – Tor Vergata* (Italy). Course materials have been primarily drawn from: the recent thematic volume *Neutron Scattering – Fundamentals*;<sup>1</sup> a number of lectures and courses given at *University College London*,<sup>2</sup> *Oxford University*,<sup>3</sup> *Università degli Studi di Milano – Bicocca*,<sup>4</sup> and the *Cockcroft Institute*;<sup>5</sup> and recent research carried out primarily at the *ISIS Facility*<sup>6</sup> and, in particular, by the *ISIS Molecular Spectroscopy Group*.<sup>7,8</sup> The primary audience are graduate or advanced undergraduate students in physics, chemistry, materials science, and engineering seeking to explore the use of neutron-scattering techniques in their specific areas of research. Each lecture has been designed to last for two hours, and the entire series could be delivered quite comfortably over a two-week period. Participants are expected to have a working knowledge of quantum mechanics, crystallography, and spectroscopy at a level typically covered during a first degree in the physical sciences.

*Lecture I (Fundamentals)* is primarily concerned with the *why*, that is, why neutron scattering is the technique

*par excellence* to explore *where atoms are* (structure) and *what atoms do* (dynamics). To provide a relevant starting point, a number of recent and ongoing projects involving the Italian community<sup>9–13</sup> are first presented, followed by a qualitative account of neutron-matter interactions and the definition of fundamental observables such as total and differential scattering cross sections for elastic and inelastic processes. The latter task includes explicit calculations of count rates in neutron-scattering experiments, to illustrate the quantitative character of the technique. Recent examples to illustrate basic concepts and terminology are given in topical research areas such as materials for energy applications<sup>14</sup> or quantum matter,<sup>15</sup> with an emphasis on nuclear scattering and spectroscopic studies. This discussion is complemented by a comparison between neutron scattering and other techniques such as photon-based spectroscopies (both X-ray and optical), nuclear magnetic resonance, and dielectric spectroscopy. A discussion of the main *pro et contra* of neutron scattering wraps up this discussion, with a view to exploring these in more depth in subsequent lectures. This semi-quantitative account is then extended by introducing the basic formalism of neutron scattering during the second part of this lecture. Although we necessarily need to make recourse to a fair amount of mathematics, emphasis

is placed on gaining an intuitive understanding of the underlying formalism, as opposed to attaining the requisite level of mathematical dexterity to derive specific results from first principles. In this spirit, we adopt a rigorous definition of the (single) Differential Cross Section (DCS) in terms of a total transition rate between initial and final states of the neutron-target system. This quantity is evaluated using Fermi's Golden Rule and generalized to include the exchange of energy between neutron and target. Using the *Master Formula*, we link the Double Differential Cross Section (DDCS) to a sum of transition probabilities. The *Master Formula* is then evaluated for the case of nuclear scattering by an extended ensemble of atoms representing a generic material. This exercise is a useful one so as to illustrate the importance of a time-dependent picture to express the DDCS in terms of a thermal average of spatio-temporal correlation functions weighted by products of scattering lengths, naturally leading to the decoupling between nuclear parameters (scattering lengths, the realm of nuclear physics) and the intrinsic spatial and temporal correlations of the system (quantities of interest to the condensed-matter scientist). The concepts of coherent and incoherent scattering can be derived from these considerations in terms of an average scattering length (coherent scattering) and its associated variance owing to intrinsic spin or isotope disorder (incoherent scattering). This first lecture concludes with a formal definition of scattering laws (or dynamic structure factors) and associated intermediate scattering functions. In preparation for the next session, students are asked to think of a definition of a solid. For a more detailed presentation of the concepts presented in this lecture, including the interaction of neutrons with electron and nuclear spins, the reader is referred to *Chapter 1* and the *Appendix* in Ref. 1.

Building upon the conceptual framework presented above, *Lecture II (Applications)* addresses the *what, i.e.,* what is neutron scattering useful for? It kicks off with a group discussion of what a solid is and offers an operational definition of a so-called *canonical solid* as a *physical system in which each atom has a well-defined (and fixed) equilibrium position over the duration of the measurement*. We stress that this definition includes disordered materials such as metastable states of matter (*i.e.*, glasses), of certain relevance to contemporary materials research. It excludes quantum systems like helium where intrinsic quantum-mechanical delocalization of individual atomic species requires a many-body treatment from the outset. It also excludes an increasingly relevant class of systems (typically regarded as solids) where atoms can undergo translational diffusion (*i.e.*, the anode and cathode materials in the battery of your mobile phone). From a conceptual viewpoint, our definition of a *canonical solid* brings to the fore the importance of time-dependent properties (dynamics) in establishing the nature of scattering observables. With this definition in mind, scattering functions for the canonical solid are derived and then specialized to the cases of

harmonic displacements and ordered systems. Explicit expressions are given and illustrated with recent examples for the case of coherent<sup>16</sup> and incoherent<sup>17</sup> inelastic scattering. The former case illustrates the measurement of phonon-dispersion relations in crystalline materials, a well-known and celebrated case with many examples to be found in conventional texts. The latter case and, in particular, its use in the study of hydrogenous materials is perhaps less known to the audience, yet these data are also relatively straightforward to interpret for those already familiar with Raman scattering or infrared spectroscopy. To fill this gap, reference is given to an extensive compilation of inelastic neutron-scattering data.<sup>18</sup> We also take the opportunity to introduce the direct link between inelastic neutron-scattering data and state-of-the-art computational modelling techniques,<sup>19,20</sup> as well as recent applications in chemical catalysis<sup>21-24</sup> and molecular<sup>25-30</sup> and macromolecular<sup>31-37</sup> intercalation in nanoporous and layered materials. As complement to the above, we extend the above presentation to illustrate the use of low-energy neutron spectroscopy in the study of Terahertz vibrations in supramolecular frameworks,<sup>38</sup> quantum-mechanical tunnelling of molecular adsorbates,<sup>39</sup> and quantum rotations.<sup>27,28,30,40</sup> The examples provided in this discussion also bring to the fore the need for the development of increasingly complex sample-environment equipment to emulate realistic conditions,<sup>41</sup> the use of complementary techniques alongside neutron measurements,<sup>42</sup> and industrial applications.<sup>43</sup>

Moving beyond the concept of a *canonical solid* requires revisiting the definition of the scattering functions introduced earlier and, in particular, taking a closer look at their counterparts in both real time and space (Van Hove correlation functions). To this end, structure factors are re-cast in terms of particle-density operators and these quantities are then related to (experimentally accessible) DCSs and DDCSs. This approach constitutes the essence of so-called *total scattering techniques*, as illustrated by the classic case of liquid argon<sup>44</sup> or metal-ion solvation in aqueous media.<sup>45</sup> For an up-to-date compilation of neutron data for disordered materials, the reader is also referred to Ref. 46. A closer look at the properties of the DDCS and associated dynamic structure factor starts with a qualitative analysis of the incoherent and coherent scattering functions for liquid argon and it is put on firmer mathematical grounds in terms of its moments and conditions of reality and detailed balance. These fundamental properties of the dynamic structure factor are further analysed within the context of the static and impulse approximations. The static approximation constitutes the starting point for total-scattering measurements, best performed via the use of epithermal neutrons from spallation neutron sources. Likewise, the impulse approximation constitutes the starting point for a discussion of neutron-Compton-scattering techniques, a unique area of research for electron-volt neutrons, including fundamental studies of water,<sup>47-50</sup> hydrogen-storage materials<sup>51-53</sup> or ferroelectrics,<sup>54,55</sup> not to forget requisite and

parallel developments and advances in instrumentation (see Refs. 56–61 and references therein). To close this discussion on non-canonical solids, the case of stochastic diffusion and relaxation in liquids is considered by explicit reference to quasielastic neutron-scattering experiments on liquid hydrogen fluoride.<sup>62,63</sup> The most salient features of the dynamic structure factor of simple liquids are illustrated via recourse to an explicit model for a diatomic fluid, including the limiting case of a plastic-crystalline phase where translational motions of the molecular centre of mass are arrested. The application of quasielastic neutron scattering techniques to the study of technological materials is finally introduced in the context of protonics<sup>64–66</sup> and liquid diffusion in confined media.<sup>67</sup>

*Lecture III (Neutron Sources – State-of-the-Art and Perspectives)* provides a self-contained account on neutron production and utilisation, the *how* underpinning neutron science. To set the scene, we begin by summarising the most salient features of neutron scattering techniques in the study of condensed matter. Neutron production is then covered in a chronological fashion, from the pioneering experiments of Chadwick and Fermi, to the advent of intense neutron sources over the past seventy years. We discuss the primary differences between fission-based research reactors and accelerator-driven facilities, and explain how the past two decades have witnessed a golden age of the latter technology leading to an unprecedented increase in capacity. Taking the *ISIS Facility*<sup>6</sup> as an example of a world-leading spallation neutron source, we describe its operation, from ion production and acceleration all the way to neutron moderation, transport to the point of use in an instrument, and data collection and subsequent analysis. As interlude, we also provide a brief explanation of muon production, along with selected examples of muon science. Pulsed neutron instrumentation is covered in some depth, including how it differs from the use of continuous sources, the primary components of a neutron instrument, and ways to boost the useful neutron flux by either the use of neutron-guide technology or multiplexing techniques.<sup>68–73</sup> This discussion is followed by the description of other major sources around the world such as *SINQ* in Switzerland,<sup>74</sup> *SNS* in the USA,<sup>75</sup> *MLF* in Japan,<sup>76</sup> *CSNS* in China,<sup>77</sup> and *ESS* in Sweden.<sup>78</sup> We also cover parallel efforts worldwide to develop medium-size<sup>79,80</sup> and compact<sup>81,82</sup> neutron sources for specific applications, examples of which include the *RIKEN Accelerator Neutron Source*<sup>83</sup> or (closer to home), the *Frascati Neutron Generator*<sup>84</sup> and the *Neutron Beam Test Facility*,<sup>85</sup> not to forget heroic and seminal attempts to develop compact neutron sources in Italy at the end of the last century.<sup>86</sup> In the last section of this lecture, we present a number of challenges and opportunities. These include the optimisation of cold-neutron production at spallation sources, and materials and engineering challenges associated with the use of high-power proton accelerators. Further into the future, we explore the enticing possibility of combining accelerator and reactor technologies into a single neutron facility, an option

which still needs to be explored in greater detail, as explained recently in Ref. 87. We close by considering the use of inertial fusion for neutron production, a possibility that remains well beyond current technologies yet it most definitely sets a horizon for future developments.<sup>88</sup> The last few minutes of this lecture serve as a timely reminder of 27 February 1932, the beginning of neutron science,<sup>89</sup> and a milestone soon to be followed by seminal advances by Fermi and collaborators not far away from where these lectures were first given.<sup>90</sup> The (brave) student is referred to *Chapters 2* and *3* in Ref. 1 for further reading.

*Lecture IV (First-principles Materials Modelling – A Primer)* may be regarded as the *in silico* counterpart of the preceding three lectures, and seeks to explore the *why*, *what*, and *how* associated with the use of state-of-the-art electronic-structure methods to calculate and predict the properties and neutron-scattering response of materials. The past two decades have witnessed a revolutionary step change in the use of these tools to describe the materials world around us from first principles, either as a predictive tool in and of itself or as a means of performing ‘computational experiments’ to interpret neutron data or design new experimental campaigns. A link to contemporary neutron science is made by reference to recent research,<sup>9,91–94</sup> and ongoing efforts to provide a unified data-analysis framework in the context of neutron-scattering experiments.<sup>95–99</sup> Beyond these general considerations, we explain in some depth the inner machinery generic to these methods, and provide a conceptual distinction between so-called *wave-function* vs. *density-functional-theory* (DFT) approaches. As on earlier lectures, we place emphasis on gaining an intuitive understanding for the differences between these two methodologies, as well as the pre-eminence of DFT in recent years in spite of its well-known limitations to describe weak interactions.<sup>100</sup> Armed with these insights, we proceed to describe the main ingredients of first-principles calculations to obtain static and dynamical properties of relevance to neutron-scattering experiments, including the incoherent<sup>38</sup> and coherent<sup>102</sup> dynamical response of technological materials. To this end, we revisit in more depth a number of the examples covered in previous lectures, and extend some of these by considering quantitative comparisons between classical<sup>101</sup> and path-integral<sup>49</sup> molecular dynamics simulations and neutron data.

In closing this introduction, I wish to thank Prof R Senesi, my *Tor Vergata* counterpart in the *International Joint Chairs Programme*, as well as Prof C Andreani for their hospitality, encouragement, and undeterred enthusiasm over the course of my stay in Rome in February 2015. I am also indebted to Profs S Licocchia and G Paradossi for enjoyable and insightful discussions on the application of neutron scattering in physical and materials chemistry.

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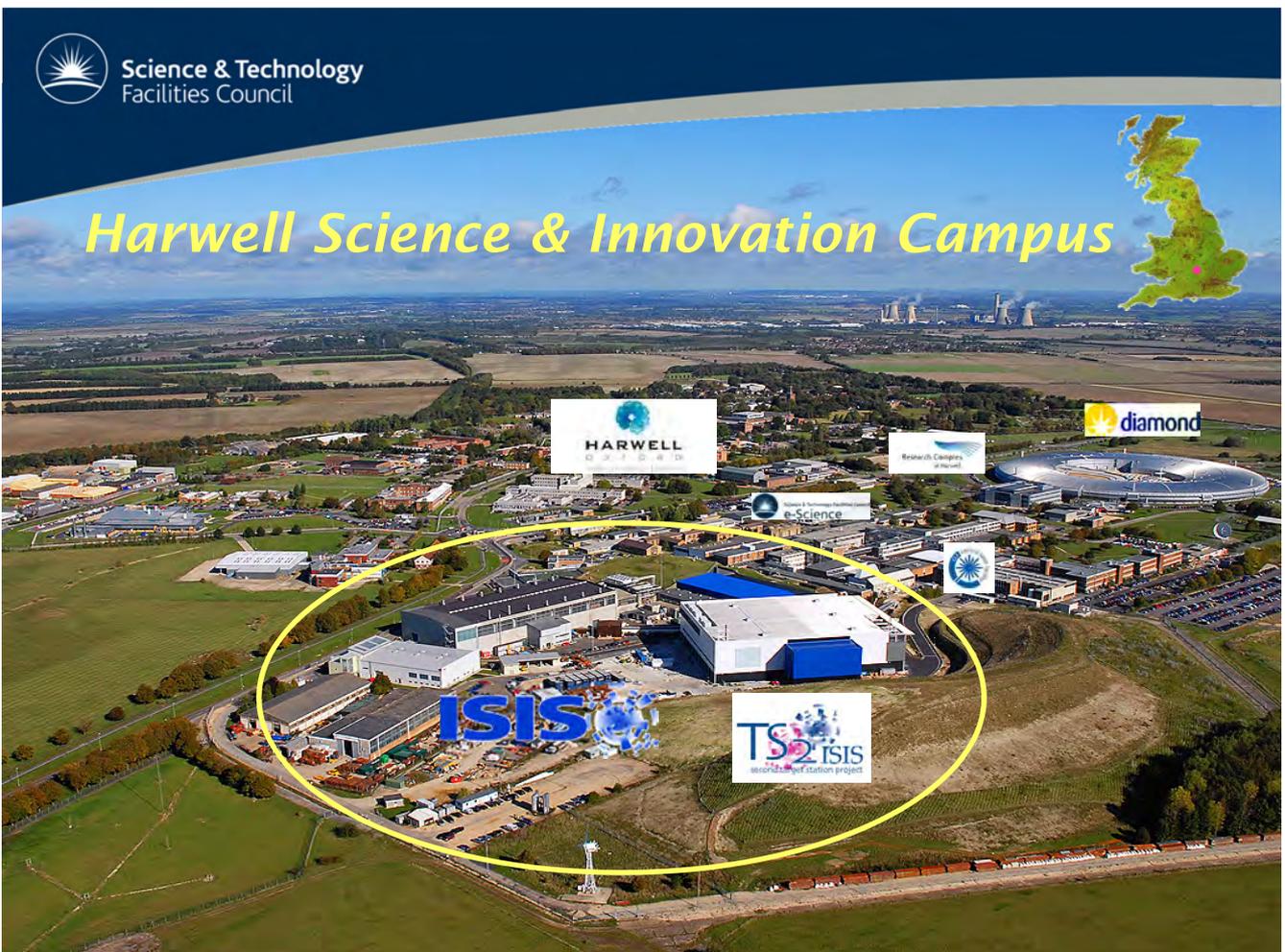
# Lecture I: Neutron Scattering

## *Fundamentals*

Roma, February 2015



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# ISIS Pulsed Neutron and Muon Source

## Structure (& morphology):

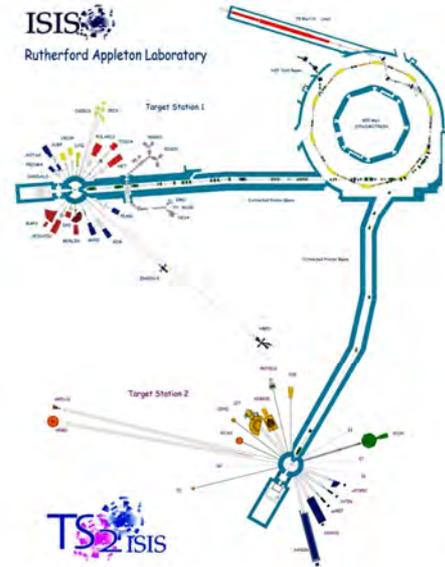
- Powder diffractometers
- Liquid diffractometers
- Small angle scattering
- Reflectometers
- Imaging/tomography

## Dynamics:

- Neutron spectrometers (inelastic & quasielastic)
- Muon spectrometers

## Other:

- Support laboratories
- Irradiation facility
- Test facilities



## Some Metrics for ISIS



~1200 users/yr

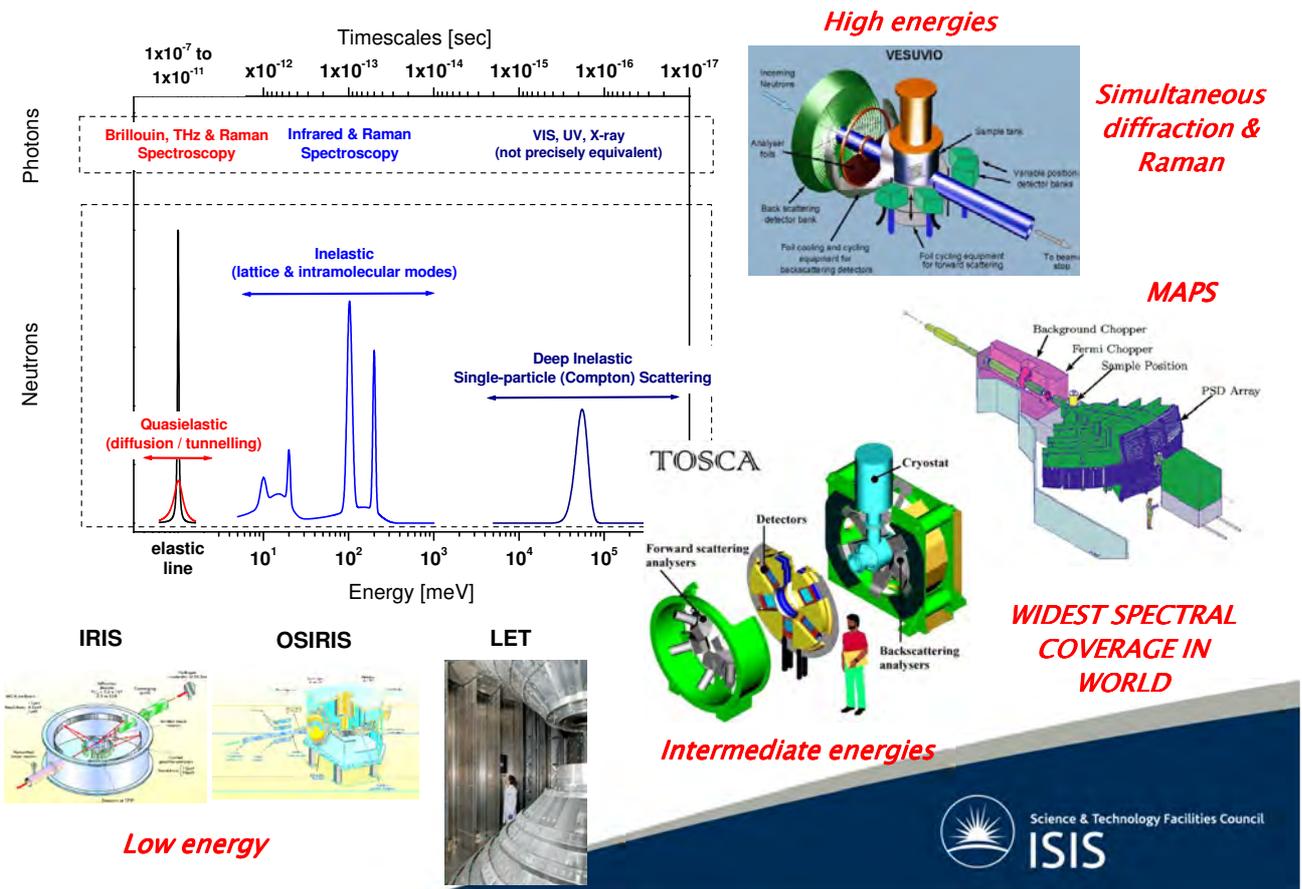
~700 experiments/yr

150 days running (50 industry)

~450 publications/yr (1/3 high impact)

12,000+ publications to date

# Molecular Dynamics & Spectroscopy at ISIS

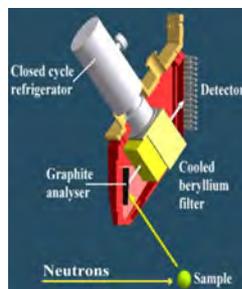


## The CNR-ISIS TOSCA Project



*TOSCA remains to this day the highest-resolution INS spectrometer in the world for the energy transfer range 25-4000  $\text{cm}^{-1}$ .*

*TOSCA was  $\frac{2}{3}$  funded by CNR to replace TFXA at ISIS. The instrument was installed in two stages: TOSCA I at 12 m (1998) had improved sensitivity and better resolution. TOSCA II was installed in 2000 at 17 m.*



*Above: cross section through a TOSCA analyser module*

*Below: assembly of an analyser module*



**Both TOSCA I and II were largely designed and built in Italy.**

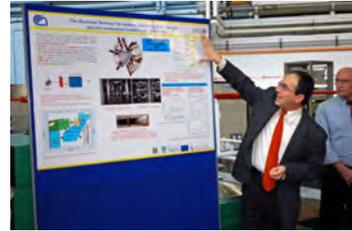


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# Fast Neutrons and Italy



*VESUVIO is a unique neutron spectrometer, with incident energies orders of magnitude higher than any other neutron instrument. Deep inelastic neutron scattering measurements on VESUVIO yield fundamental insights into the quantum nature of condensed matter via access to atomic momentum distributions, with an increasing emphasis in chemical applications..*



*The pioneering eVS instrument at ISIS was substantially upgraded to VESUVIO in 1998, with further developments under the e-VERDI project in 2002. Novel detector designs, backscattering detection, and unrivalled spectral resolution continue to provide a strong scientific output over an energy range unique to spallation neutron sources.*



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## Outline [today]

- *Fundamentals*
- Applications.
- Neutron production.
- First-principles materials modelling.



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# “Neutral Protons” as Condensed Matter Probes

## Neutron



- Mass 1 amu
- Spin  $\frac{1}{2}$
- Charge 0
- Interaction Nuclear

## Photon

- Rest mass 0 amu
- Spin 1
- Charge 0
- Interaction E/B dipole ...

### Thermal Neutrons (T = 300 K)

- |                       |   |
|-----------------------|---|
| - Energies (meV)      | motions in condensed matter (e.g., vibrations). |
| - Wavelengths (Å)     | interatomic distances.                          |
| - Neutral particles   | high penetration power.                         |
| - Nuclear interaction | $\delta$ -like (s-wave scattering).             |
| - Spin                | magnetic dipole moment $\sim 1.9\mu_N$          |
| - Stable              | lifetime $\sim 15$ min                          |

**Observables easy to calculate & link to theoretical predictions**



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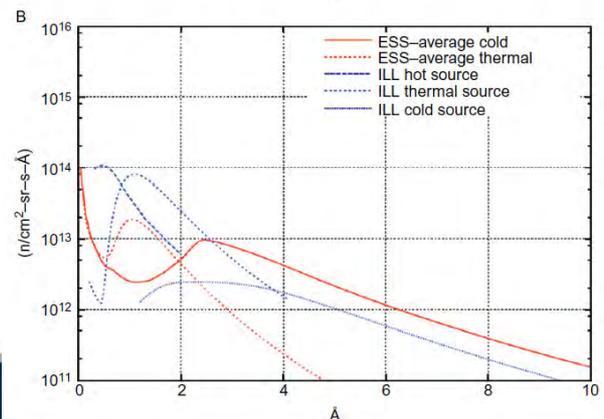
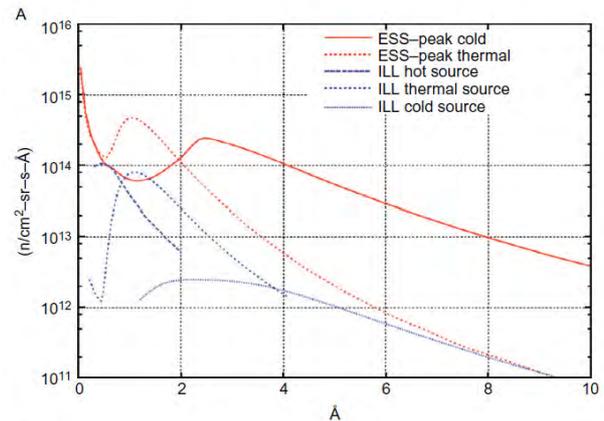
# “Neutral Protons” as Condensed Matter Probes

$$E_n = \frac{h^2}{2m_n \lambda_n^2} = \frac{\hbar^2 k_n^2}{2m_n} = k_B T$$

**TABLE 1.1** Properties of the Neutron at Selected Kinetic Energies

Quantity	Unit	Definition	Ultracold	Cold	Thermal	Epithermal
Energy $E_n$	meV <sup>a</sup>		$2.5 \times 10^{-4}$	1	25	1000
Temperature $T$	K	$E_n/k_B$	$2.9 \times 10^{-3}$	12	290	12,000
Wavelength $\lambda_n$ <sup>b</sup>	Å	$h/(2m_n E_n)^{1/2}$	570	9.0	1.8	0.29
Wave vector $k_n$ <sup>c</sup>	Å <sup>-1</sup>	$(2m_n E_n)^{1/2}/\hbar$	0.011	0.7	3.5	22
Velocity $v_n$ <sup>d</sup>	m s <sup>-1</sup>	$(2E_n/m_n)^{1/2}$	6.9	440	2,200	14,000

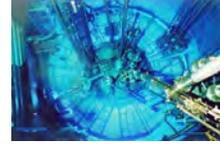
For definitions of the various symbols and associated numerical values, see the *List of Commonly Used Symbols* and references therein.  
<sup>a</sup>1 meV =  $1.6022 \times 10^{-22}$  J, the amount of energy necessary to move an electron against a potential difference of one millivolt (1 mV).  
<sup>b</sup> $\lambda_n$  (Å) =  $9.0446 [E_n (\text{meV})]^{-1/2}$ .  
<sup>c</sup> $k_n$  (Å<sup>-1</sup>) =  $0.69469 [E_n (\text{meV})]^{1/2}$ .  
<sup>d</sup> $v_n$  (m s<sup>-1</sup>) =  $437.39 [E_n (\text{meV})]^{1/2}$ .



# Reactor and Accelerator-based Neutron Sources

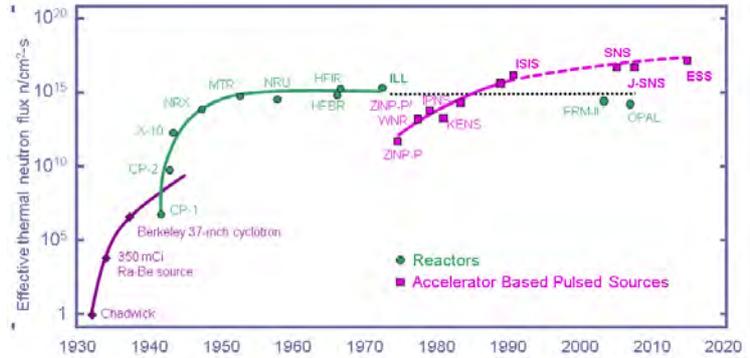
## Reactor-based source:

- Neutrons produced by fission reactions
- Continuous neutron beam
- 1 neutron/fission .



## Accelerator-based source:

- Neutrons produced by spallation reaction
- 10s of neutrons/proton
- Neutrons are pulsed, follow proton beam time structure.
- A pulsed beam with precise  $t_0$  allows neutron energy measurement via TOF ( $v=d/t$ )



Updated from *Neutron Scattering*, K. Skold and D. L. Price, eds., Academic Press, 1986.

**Accelerator based-sources have not yet reached their limit and hold out the promise of higher intensities.**



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# The Golden Age of Spallation Neutron Sources

*Operational*

**More in Lecture III**

*Under Construction or Planned*



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# Units, units, units

$$E_n = \frac{h^2}{2m_n \lambda_n^2} = \frac{\hbar^2 k_n^2}{2m_n} = k_B T$$

**TABLE 1.2** Common Quantities Used to Denote Energy or Energy Transfer

Quantity	Definition	Value at $E = 1$ meV
Radian frequency $\omega$	$E/\hbar$	$1.5193 \times 10^{12}$ rad s <sup>-1</sup>
Frequency $\nu$	$E/h$	$0.24180 \times 10^{12}$ Hz = 0.24180 THz
Spectroscopic wave number (or kayser) $\tilde{\nu}$	$E/hc$	$8.0655$ cm <sup>-1</sup>
Temperature $T$	$E/k_B$	11.605 K

For definitions of the various symbols and associated numerical values, see the *List of Commonly Used Symbols* and references therein.

*Of particular relevance to these lectures*

**Good to memorize them!**



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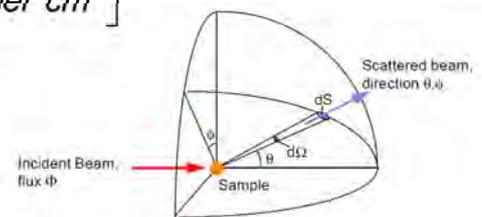
## Basic Observables: Scattering Cross Sections

Given an incident beam:  $\Phi = [\text{incident neutrons per cm}^2]$

This is what we can measure:

(1) Transmission experiment:

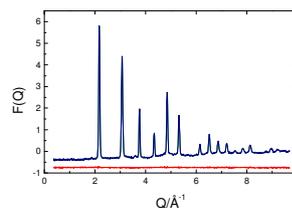
$$\sigma = \frac{[\text{scattered neutrons}]}{\Phi}$$



Cross sections also depend on polarisation of incident & scattered neutron.

(2) Diffraction experiment:

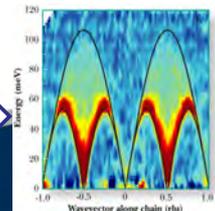
$$\frac{\partial \sigma}{\partial \Omega} = \frac{[\text{scattered neutrons into } \partial \Omega]}{\Phi \partial \Omega}$$



Diffraction pattern (crystallography)

(3) Spectroscopy experiment:

$$\frac{\partial \sigma}{\partial \Omega \partial E} = \frac{[\text{scattered neutrons into } \partial \Omega \text{ \& } \partial E]}{\Phi \partial \Omega \partial E}$$



"Dynamic" Diffraction pattern

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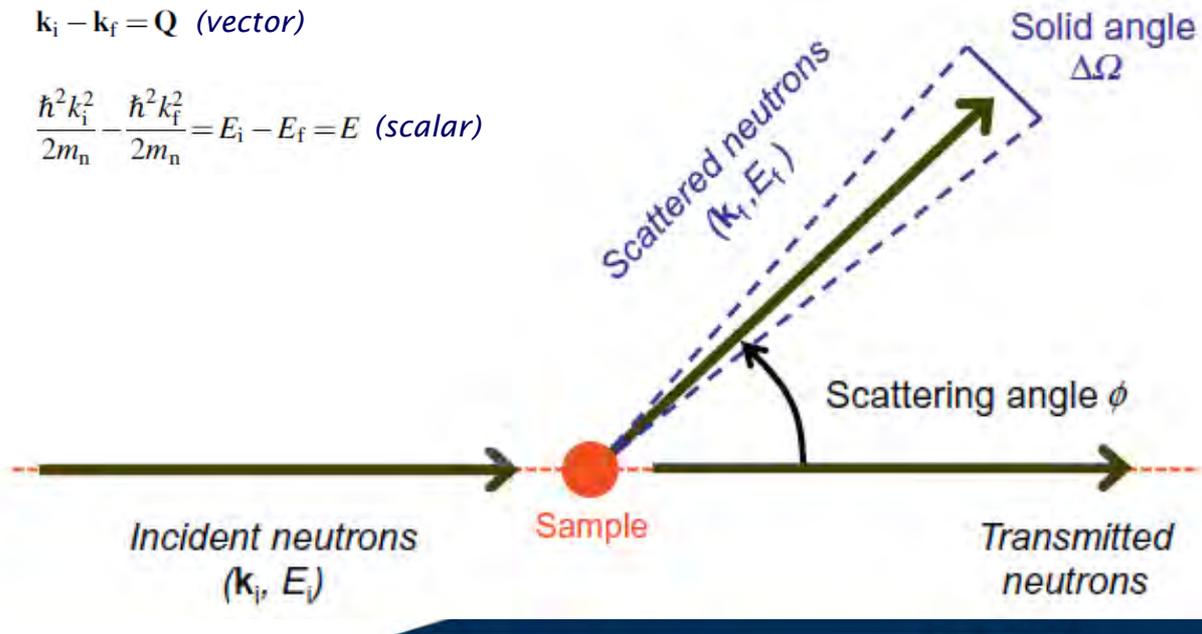
# A Neutron-scattering Experiment

Count rate:  $C = \eta \Phi N \left( \frac{d\sigma}{d\Omega} \right) \Delta\Omega.$

Conservation laws:

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

$\frac{\hbar^2 k_i^2}{2m_n} - \frac{\hbar^2 k_f^2}{2m_n} = E_i - E_f = E$  (scalar)



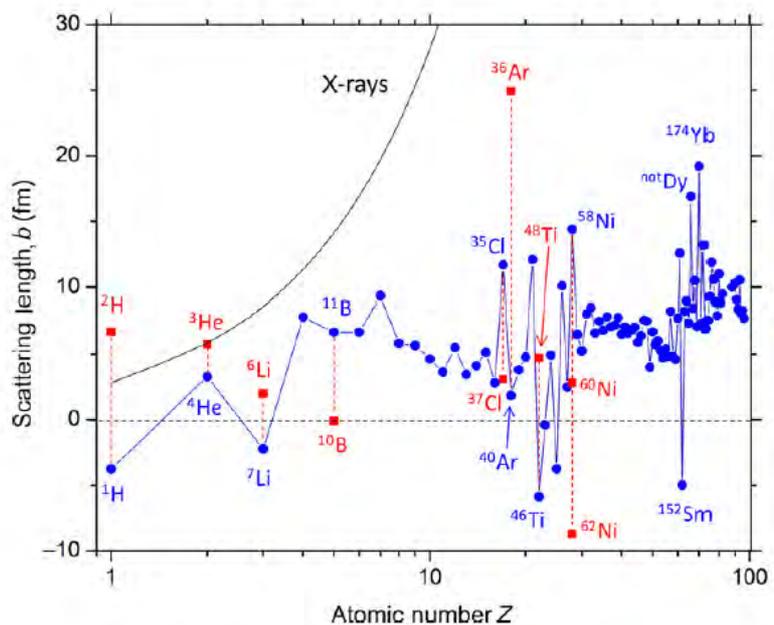
Q

## Nuclear Scattering

Identical & noninteracting nuclei

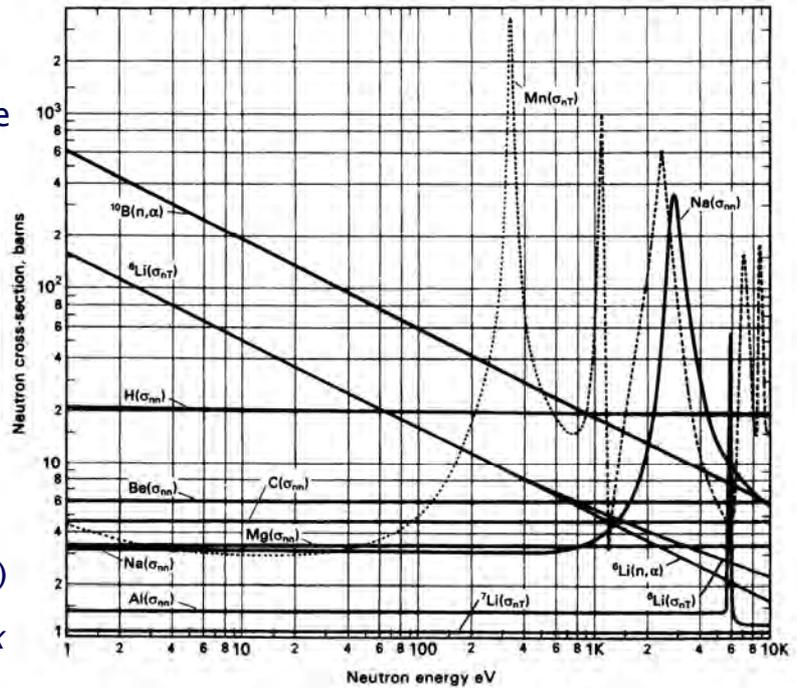
$\frac{d\sigma}{d\Omega} = b^2$

- Scattering length  $b$  dependent on isotope and spin state.
- $b$ 's in range of fm, and can be negative (not for X-rays).
- X-rays quite insensitive to light nuclides.
- Cross sections: barn =  $100 \text{ fm}^2 = 10^{-28} \text{ m}^2$ .
- These are tabulated extensively - more later.



# Beyond Thermal Neutron Scattering: Nuclear Absorption and Resonances

- Thermal neutron scattering assumes scattering lengths are energy independent.
- Nuclear absorption and resonant capture complicate the above.
- Absorption (from direct nuclear reaction): follows  $1/v$  law, can be corrected form in terms of an attenuation term.
- Resonant capture (compound-nucleus formation) leads anomalous scattering (rapidly changing and *complex* scattering length) and it is typically avoided altogether.

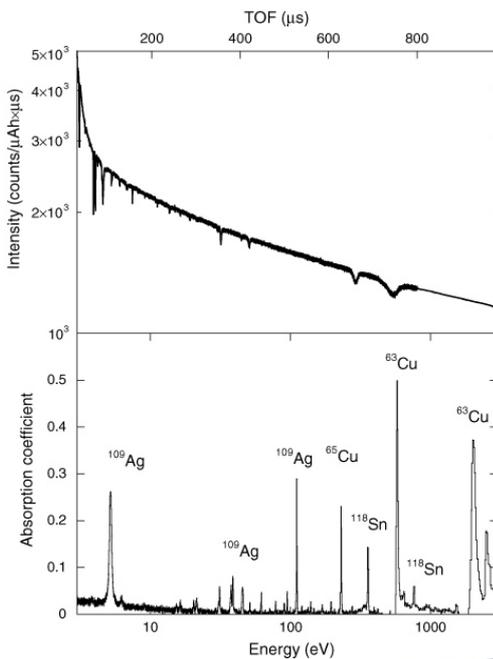


## Resonant Neutron Scattering

In the presence of resonances, scattering length must be modified to include Breit-Wigner terms

$$b = R + \frac{\Gamma_{n,r}/2k}{E - E_r + i\Gamma_r/2} = R + b_r(E)$$

*R* represents scattering length due to potential (direct) scattering



In thermal/epithermal region, resonances can be used to identify specific elements.



## Absorption: Elements to Watch Out for ...

**TABLE A.5** Absorption Cross Sections for Nuclides That Have Significant Charged-Particle Reactions with Thermal Neutrons (Cross Sections in Barns)

Nuclide	$\sigma_a$	$\sigma_\gamma$	$\sigma_p$	$\sigma_\alpha$	$\sigma_f$
$^3\text{He}$	5333	0.000031	5333	0	0
$^6\text{Li}$	940	0.0385	0	940	0
$^{10}\text{B}$	3835	0.5	0	3834	0
$^{14}\text{N}$	1.91	0.075	1.83	0	0
$^{17}\text{O}$	0.236	0.00054	0	0.235	0
$^{33}\text{S}$	0.54	0.35	0.002	0.19	0
$^{35}\text{Cl}$	44.1	43.6	0.489	0	0
$^{40}\text{K}$	35	30	4.4	0.39	0
$^{233}\text{U}$	575	46	0	0	529
$^{235}\text{U}$	681	98	0	0	583
$^{238}\text{Pu}$	558	540	0	0	17.9
$^{239}\text{Pu}$	1017	269	0	0	748

Quite useful for  
neutronics.

Can you think why?

## Resonance Scattering: Elements to Watch For ...

**TABLE A.4** Radiative-Capture Cross Sections and Resonance Energies of Naturally Occurring Nuclides Having ( $n,\gamma$ ) Resonances at Thermal Neutron Energies

Nuclide	$\sigma_\gamma$ (b)	$E_0$ (meV)
$^{113}\text{Cd}$	20,600	178
$^{149}\text{Sm}$	42,080	97.3
$^{151}\text{Eu}$	9100	321
$^{155}\text{Gd}$	61,100	26.8
$^{157}\text{Gd}$	259000	31.4
$^{176}\text{Lu}$	2065	141.3
$^{180}\text{Tm}$	563	200

In most cases, well-defined low-energy resonances only occur for heavy nuclei ( $n > p$ ).



# Structure

Two-body collision:  $E = \frac{2E_i m_n}{M} (1 - \cos \phi) + O\left(\frac{m_n}{M}\right)^2$  Recoil:  $E = \frac{\hbar^2 Q^2}{2M}$

Note: energy transfer  $E$  goes to zero as  $M$  increases, (and  $M$  is referenced to neutron mass)

For purely elastic scattering  $|\mathbf{k}_i| = |\mathbf{k}_f|$

And vector relation  $\mathbf{k}_i - \mathbf{k}_f = \mathbf{Q}$  implies  $2k_i \sin(\phi/2) = Q$

For a crystalline material,  $Q$  must match a reciprocal lattice vector of crystal:

$$\mathbf{Q} = 2\pi \left( \frac{h}{a}, \frac{k}{b}, \frac{l}{c} \right) \text{ or } Q = \frac{2\pi}{d}$$

In terms of neutron wavelength  $k_i = 2\pi/\lambda_i$

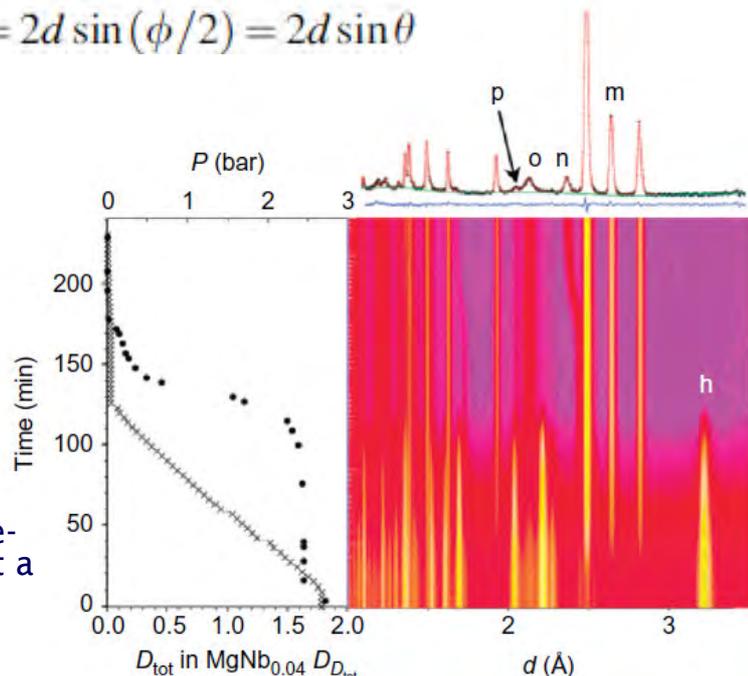
Bragg condition for diffraction:  $\lambda_i = \lambda_f = 2d \sin(\phi/2) = 2d \sin \theta$

Note distinction between Bragg vs scattering angle

## Structure: Example

$$\lambda_i = \lambda_f = 2d \sin(\phi/2) = 2d \sin \theta$$

- Two types of measurement.
- Elastic scattering is typically *assumed*.
- Important to distinguish between *elastic* and *total* (more on this later).
- Data corresponds to variable-lambda/fixed-theta method at a pulsed spallation source.



# Electron and Nuclear Spins

Ensemble of randomly oriented spins (paramagnet):

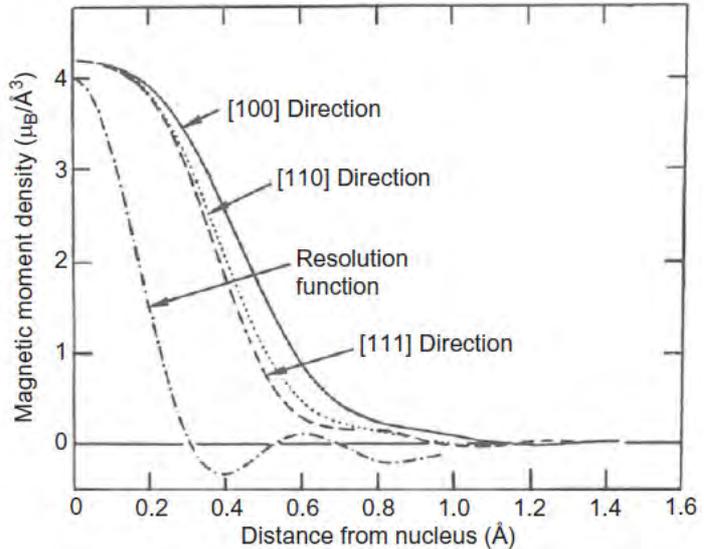
$$\frac{d\sigma}{d\Omega} = (\gamma r_0)^2 [f(\mathbf{k}_i - \mathbf{k}_f)]^2 S(S+1)$$

- Scattering length  $\gamma r_0 = 5.4$  fm (commensurate with nuclear processes).

- Second term is the magnetic form factor: Fourier transform of the spatial distribution of unpaired electron density.

- Also note decoupling between scattering & spatial properties.

- Note absolute units in figure (bulk iron).



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For more ...

**NEUTRON SCATTERING - FUNDAMENTALS**

Edited by  
**FELIX FERNANDEZ-ALONSO**  
**DAVID L. PRICE**

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EXPERIMENTAL METHODS IN THE PHYSICAL SCIENCES

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## Structure: Practical Considerations

$$C = \eta \Phi N \left( \frac{d\sigma}{d\Omega} \right) \Delta\Omega$$

$$\frac{d\sigma}{d\Omega} = b^2$$

$$C = \eta \Phi N \left( \frac{d\sigma}{d\Omega} \right) \Delta\Omega \approx \eta \Phi(\lambda_i) \Delta\lambda_i N b^2 \Delta\Omega$$

$$\Phi(\lambda_i) \Delta\lambda_i \approx 10^9 \text{ n/cm}^2 \text{ s}$$

$$b^2 \approx 2 \times 10^{-25} \text{ cm}^2$$

$$\Delta\Omega \approx 10^{-4}$$

*Typical values, 1% bandwidth*

$$C \approx 10^{-22} N$$

For a count rate of 1 Hz on a single detector, require  $10^{+22}$  atoms (ca. 1 g).



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## Structure: Neutrons & Photons

- X-rays: surface vs bulk response can be tricky to separate.
- Access to high-Q information is harder with X-rays – important for the study of disordered matter using total-scattering techniques.
- X-rays not sensitive to isotope, thus scattering is coherent (interparticle correlations). Neutron scattering can also tell you about single-particle correlations (incoherent scattering).
- X-ray cross sections can be energy dependent (anomalous scattering), and therefore can be element specific, i.e., EXAFS, XANES (much harder with neutrons – isotopic substitution, nuclear-spin alignment, or recoil scattering of epithermal neutrons).
- X-rays interact very weakly with magnetic materials, yet these studies are still possible (circular dichroism).



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# Adding Motion: Dynamics & Spectroscopy

## Conservation laws:

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

$$\frac{\hbar^2 k_i^2}{2m_n} - \frac{\hbar^2 k_f^2}{2m_n} = E_i - E_f = E \quad (\text{scalar})$$

$$k_i^2 - 2k_i k_f \cos \phi + k_f^2 = Q^2$$

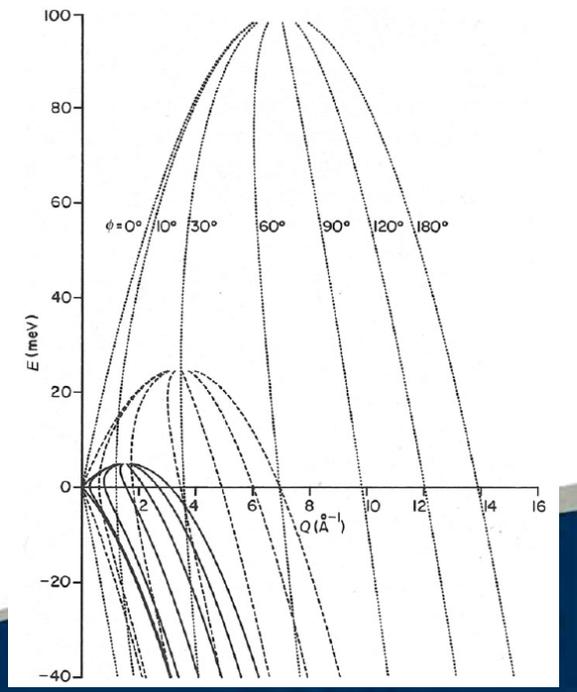
$$2 \left[ 1 - (1 - E/E_i)^{1/2} \cos \phi \right] - E/E_i = Q^2/k_i^2$$

## Observables:

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{C}{\Phi N(\Delta\Omega)\eta\Delta E}$$

$$\frac{d\sigma}{d\Omega} = \int_{-\infty}^{E_0} \frac{d^2\sigma}{d\Omega dE_f} dE \quad \text{Total scattering}$$

$$\sigma_t = \int_{4\pi} \frac{d\sigma}{d\Omega} d\Omega \quad \text{Cross section (transmission)}$$



## A Health Warning on Jargon

### What We Mean by “Elastic” and “Inelastic” Scattering

- Thermal neutrons (meV energies) can only exchange kinetic energy with target (unless they undergo nuclear absorption).
- Strictly speaking, thermal neutrons can only undergo elastic (s-wave) scattering in the scattering (centre-of-mass) frame.
- The condensed-matter scientist always refers to scattering in the laboratory frame (typically with target at rest).
- In lab frame, two types of thermal neutron scattering:
  - “Elastic”: velocity of neutron does not change.
  - “Inelastic”: velocity of neutron changes due to atomic motions (a Doppler shift).

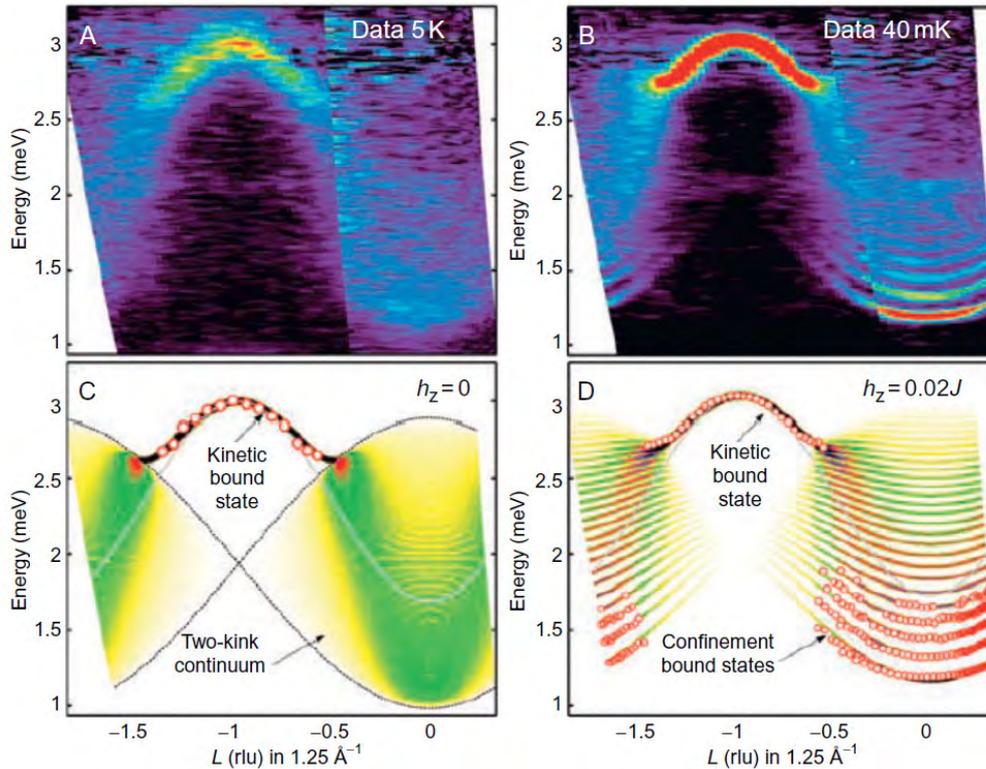
Keep this in mind, to avoid confusion



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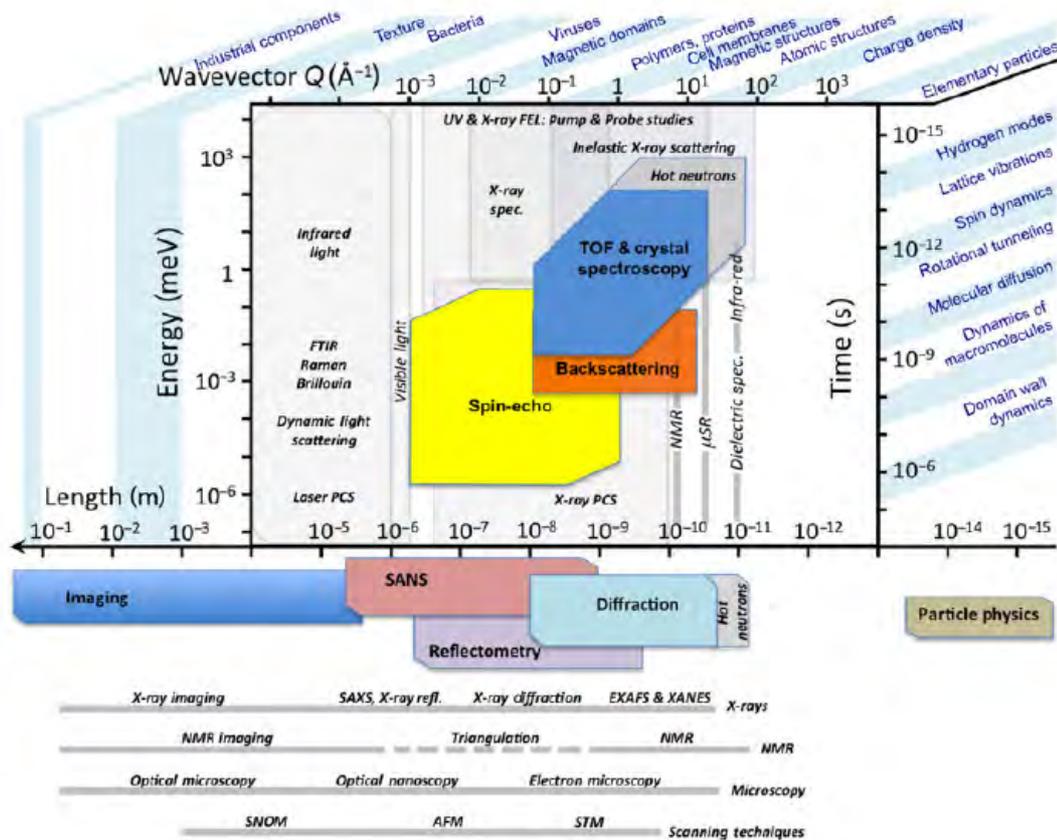
# Example



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# The Power of Inelastic Neutron Scattering



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# Dynamics: Neutrons and Other Probes

- IXS: very similar, no kinematic restrictions (e.g., low  $Q$  and high  $E$ ), requires high photon energies to access relevant  $Q$ , energy resolution limited to meV (neV possible with neutrons, also possible with XPCS in real space).
- Brillouin, THz, IR, Raman: highly complementary to INS, much more restricted  $Q$  range, optical selection rules ... link to theory with INS is far more direct.
- NMR (and Muon): to probe stochastic/relaxation phenomena, typically no information on  $Q$  (exception PFG-NMR).
- Dielectric spectroscopy: very wide time range, no information on spatial scales, hard to interpret.
- Computer simulation: highly complementary to neutron scattering, a real synergy.



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## Pro et Contra

### Pro

1. Neutrons carry no charge and therefore have high penetrating power into bulk samples
2. Thermal neutron wavelengths and energies match interatomic distances and excitation energies in condensed matter
3. Neutron-scattering lengths vary irregularly with  $Z$ —generally good for light atoms (especially hydrogen) and for discriminating between nearby elements in the periodic table
4. Scattering lengths vary irregularly with  $A$ —isotopic substitution can be used to provide information about a particular element, most notably hydrogen. Resonant and recoil scattering have also been used to achieve element specificity. See [Section 1.4.3.2](#) and [Chapters 4–6](#)
5. Scattering intensities can be *quantitatively* related to the structural and dynamical properties of the sample—the main subject of later sections in this chapter
6. Scattering from nuclei can be both incoherent and coherent, thus sensitive to single- and two-particle spatiotemporal correlations in condensed matter. See [Section 1.2.5](#)
7. Scattering from unpaired electrons constitutes a unique probe of magnetism. See [Sections 1.5 and 1.6](#)
8. Scattering from nuclei with nonzero spin can be used to probe nuclear magnetism. See [Section 1.7](#)
9. Neutron-scattering experiments offer a direct link to the predictions of computational experiments—a recurring theme throughout the present and future volumes in this series

### Contra

1. High-intensity neutron beams can only be produced at central facilities, i.e., you cannot (yet!) perform neutron-scattering experiments on your lab bench. See [Chapter 2](#) for the most recent developments
2. Beam intensities may be too low to measure very small specimens, although current neutron instrumentation has improved significantly over the past two decades. See [Chapter 3](#)
3. Being neutral, neutrons are difficult to manipulate, e.g., focus into small spot sizes. See [Chapter 3](#)

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# Formalism



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## DCS and Fermi's Golden Rule

$$\left(\frac{d\sigma}{d\Omega}\right)_{\mathbf{k}_i\sigma_i\tau_i \rightarrow \mathbf{k}_f\sigma_f\tau_f} = \frac{1}{N\Phi\Delta\Omega} W_{\mathbf{k}_i\sigma_i\tau_i \rightarrow \mathbf{k}_f\sigma_f\tau_f} \quad \text{Recall} \quad C = \eta\Phi N \left(\frac{d\sigma}{d\Omega}\right) \Delta\Omega$$

*Transition rate  $W$ : number of transitions per second from initial to final states*

*$W$  evaluated using Fermi's Golden Rule:*

$$W_{\mathbf{k}_i\sigma_i\tau_i \rightarrow \mathbf{k}_f\sigma_f\tau_f} = \frac{2\pi}{\hbar} |\langle \mathbf{k}_f\sigma_f\tau_f | V | \mathbf{k}_i\sigma_i\tau_i \rangle|^2 \rho_{\mathbf{k}_f\sigma_f}(E_f) = C/\eta$$

*Rate = Transition Probability  $\times$  Final states per unit energy*

*Approach works because neutron-matter interactions are weak (first-order perturbation theory applies).*



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# Fermi's Golden Rule, DCS, and DDCS

$$W_{\mathbf{k}_i \sigma_i \tau_i \rightarrow \mathbf{k}_f \sigma_f \tau_f} = \frac{2\pi}{\hbar} |\langle \mathbf{k}_f \sigma_f \tau_f | V | \mathbf{k}_i \sigma_i \tau_i \rangle|^2 \rho_{\mathbf{k}_f \sigma_f}(E_f)$$

Incident and scattered neutrons are spin-half plane waves:  $V_0^{-1/2} e^{i\mathbf{k}_i \cdot \mathbf{r}} |\sigma_i\rangle$   
 $V_0^{-1/2} e^{i\mathbf{k}_f \cdot \mathbf{r}} |\sigma_f\rangle$

Number of states over energy interval:  $\rho_{\mathbf{k}_f \sigma_f}(E_f) dE_f = \frac{V_0}{8\pi^3} d\mathbf{k}_f = \frac{V_0}{8\pi^3} k_f^2 dk_f \Delta\Omega$   
 $\rho_{\mathbf{k}_f \sigma_f}(E_f) = \frac{V_0}{8\pi^3} \frac{m_n k_f}{\hbar^2} \Delta\Omega$

Incident flux:  $\Phi = \frac{1}{V_0} v_i = \frac{\hbar k_i}{V_0 m_n}$

Such that DCS:  $\left(\frac{d\sigma}{d\Omega}\right)_{\mathbf{k}_i \sigma_i \tau_i \rightarrow \mathbf{k}_f \sigma_f \tau_f} = \left(\frac{1}{N}\right) \frac{k_f}{k_i} \left(\frac{m_n V_0}{2\pi \hbar^2}\right)^2 |\langle \mathbf{k}_f \sigma_f \tau_f | V | \mathbf{k}_i \sigma_i \tau_i \rangle|^2$

And DDCS requires implicit energy conservation:  $E = E_i - E_f = E_{\tau_f} - E_{\tau_i}$

$$\left(\frac{d^2\sigma}{d\Omega dE_f}\right)_{\mathbf{k}_i \sigma_i \tau_i \rightarrow \mathbf{k}_f \sigma_f \tau_f} = \left(\frac{1}{N}\right) \frac{k_f}{k_i} \left(\frac{m_n V_0}{2\pi \hbar^2}\right)^2 |\langle \mathbf{k}_f \sigma_f \tau_f | V | \mathbf{k}_i \sigma_i \tau_i \rangle|^2 \delta(E + E_{\tau_i} - E_{\tau_f})$$

## Master Formula for the DDCS

DDCS from previous slide:

$$\left(\frac{d^2\sigma}{d\Omega dE_f}\right)_{\mathbf{k}_i \sigma_i \tau_i \rightarrow \mathbf{k}_f \sigma_f \tau_f} = \left(\frac{1}{N}\right) \frac{k_f}{k_i} \left(\frac{m_n V_0}{2\pi \hbar^2}\right)^2 |\langle \mathbf{k}_f \sigma_f \tau_f | V | \mathbf{k}_i \sigma_i \tau_i \rangle|^2 \delta(E + E_{\tau_i} - E_{\tau_f})$$

Need to sum over ALL initial and final states of both neutron and target

For a system in thermal equilibrium (no off-diagonal density-matrix elements), the DDCS reads:

$$\left(\frac{d^2\sigma}{d\Omega dE_f}\right)_{\mathbf{k}_i \rightarrow \mathbf{k}_f} = \left(\frac{1}{N}\right) \frac{k_f}{k_i} \left(\frac{m_n V_0}{2\pi \hbar^2}\right)^2 \sum_{\tau_i \sigma_i} p_{\tau_i} p_{\sigma_i} \sum_{\tau_f \sigma_f} |\langle \mathbf{k}_f \sigma_f \tau_f | V | \mathbf{k}_i \sigma_i \tau_i \rangle|^2 \delta(E + E_{\tau_i} - E_{\tau_f})$$

Formally speaking, all neutron scattering is reduced to the solution of this MASTER FORMULA

# Application to Nuclear Scattering

Interaction with single nucleus described by a Fermi pseudopotential

$$\frac{2\pi\hbar^2}{m_n} b_{\sigma\tau} \delta(\mathbf{r} - \mathbf{R})$$

Note: Fermi pseudopotential depends on identity of nucleus as well as relative orientation of neutron and nuclear spins (more on this later)

Total (neutron-target) interaction potential:

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} \sum_j b_j \delta(\mathbf{r} - \mathbf{R}_j)$$

And bra-ket in Master Formula:

$$\langle k_f | V | k_i \rangle = \frac{2\pi\hbar^2}{m_n V_0} \sum_j b_j \int e^{-ik_f \cdot \mathbf{r}} \delta(\mathbf{r} - \mathbf{R}_j) e^{ik_i \cdot \mathbf{r}} d\mathbf{r} = \frac{2\pi\hbar^2}{m_n} \sum_j b_j e^{i\mathbf{Q} \cdot \mathbf{R}_j} \quad \text{with} \quad \mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$$

And a Master Formula of the form:  $\frac{d^2\sigma}{d\Omega dE_f} = \left(\frac{1}{N}\right) \frac{k_f}{k_i} \sum_{\tau_i} p_{\tau_i} p_{\sigma_i} \left| \sum_{\tau_f} \sum_j b_j \langle \sigma_f \tau_f | e^{i\mathbf{Q} \cdot \mathbf{R}_j} | \langle \sigma_i \tau_i \rangle \right|^2 \delta(E + E_{\tau_i} - E_{\tau_f})$

For unpolarized neutron beams:

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N} \frac{k_f}{k_i} \sum_{\tau_i} p_{\tau_i} \left| \sum_{\tau_f} \sum_j b_j \langle \tau_f | e^{i\mathbf{Q} \cdot \mathbf{R}_j} | \tau_i \rangle \right|^2 \delta(E + E_{\tau_i} - E_{\tau_f})$$

## The DDCS and Dynamics

Need to evaluate square mtx element in Master Formula:

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N} \frac{k_f}{k_i} \sum_{\tau_i} p_{\tau_i} \left| \sum_{\tau_f} \sum_j b_j \langle \tau_f | e^{i\mathbf{Q} \cdot \mathbf{R}_j} | \tau_i \rangle \right|^2 \delta(E + E_{\tau_i} - E_{\tau_f})$$

Most convenient in time domain using

$$\delta(E + E_{\tau_i} - E_{\tau_f}) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \exp\left[-i\frac{t}{\hbar}(E + E_{\tau_i} - E_{\tau_f})\right] dt$$

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N} \left(\frac{k_f}{k_i}\right) \frac{1}{2\pi\hbar} \sum_{\tau_i} p_{\tau_i} \sum_{\tau_f} \sum_{j,j'} b_j^* b_{j'} \int_{-\infty}^{\infty} \langle \tau_i | e^{i\mathbf{Q} \cdot \mathbf{R}_j} | \tau_f \rangle$$

$$\langle \tau_f | e^{iHt/\hbar} e^{i\mathbf{Q} \cdot \mathbf{R}_j} e^{-iHt/\hbar} | \tau_i \rangle e^{-iEt/\hbar} dt,$$

$$\text{with} \quad e^{iHt/\hbar} | \tau_i \rangle = e^{iE_i t/\hbar} | \tau_i \rangle$$

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N} \left(\frac{k_f}{k_i}\right) \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \sum_{j,j'} e^{-iEt/\hbar} \langle b_j^* b_{j'} e^{-i\mathbf{Q} \cdot \mathbf{R}_j} e^{iHt/\hbar} e^{i\mathbf{Q} \cdot \mathbf{R}_{j'}} e^{-iHt/\hbar} \rangle_{\tau_i} dt$$

with

$$e^{i\mathbf{Q} \cdot \mathbf{R}_j(t)} \equiv e^{iHt/\hbar} e^{i\mathbf{Q} \cdot \mathbf{R}_j} e^{-iHt/\hbar}$$

Real-time representation of the DDCS (a key result):

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N} \left(\frac{k_f}{k_i}\right) \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \sum_{j,j'} \langle b_j^* b_{j'} e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_{j'}(t)} \rangle e^{-iEt/\hbar} dt$$

# Good-bye to Nuclear Physics

For randomly distributed isotopes and nuclear-spin orientations in target, scattering lengths  $b$  and positions  $R$  can be treated independently

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N} \left( \frac{k_f}{k_i} \right) \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \sum_{dd'} \sum_{j \in d, j' \in d'} \overline{b_j^* b_{j'}} \left\langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_{j'}(t)} \right\rangle e^{-iEt/\hbar} dt$$

Nuclear Physics  
Physics, Chemistry, Biology ...

where  $(d, d')$  refer to different elements and the bar represents an average over the spin and isotope distributions for the corresponding element pairs

Let's look at this expression in more detail in some specific situations ...



Q

## Coherent and Incoherent Scattering

Define  $S_{jj'}(\mathbf{Q}, E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \left\langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_{j'}(t)} \right\rangle e^{-iEt/\hbar} dt$  i.e., all except kinematics and nuclear physics

And the DDCS then reads  $\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N} \left( \frac{k_f}{k_i} \right) \sum_{dd'} \sum_{j \in d, j' \in d'} \overline{b_j^* b_{j'}} S_{jj'}(\mathbf{Q}, E)$

Uncorrelated nuclear spins and isotopes imply  $\overline{b_j^* b_{j'}} = \begin{cases} \overline{b_d^* b_{d'}}, & j \neq j', \\ |\overline{b_d^*}|^2, & j = j', \end{cases}$   
 $\overline{b_j^* b_{j'}} = \overline{b_d^* b_{d'}} + \left( |\overline{b_d^*}|^2 - |\overline{b_d}|^2 \right) \delta_{jj'} \delta_{dd'}$

DDCS is then the sum of TWO distinct terms

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE_f} &= \frac{1}{N} \left( \frac{k_f}{k_i} \right) \sum_{dd'} \sum_{j \in d, j' \in d'} \left[ \overline{b_d^* b_{d'}} + \left( |\overline{b_d^*}|^2 - |\overline{b_d}|^2 \right) \delta_{jj'} \delta_{dd'} \right] S_{jj'}(\mathbf{Q}, E) \\ &= \frac{1}{N} \left( \frac{k_f}{k_i} \right) \sum_{dd'} \overline{b_d^* b_{d'}} \sum_{j \in d, j' \in d'} S_{jj'}(\mathbf{Q}, E) + \frac{1}{N} \left( \frac{k_f}{k_i} \right) \sum_d \left( |\overline{b_d^*}|^2 - |\overline{b_d}|^2 \right) \sum_{j \in d} S_{jj}(\mathbf{Q}, E) \end{aligned}$$

Atom pairs (coherent) Individual atoms (incoherent)



# Coherent and Incoherent Cross Sections

$$\sigma_c^d = 4\pi |\bar{b}_d|^2 \text{ (coherent cross section),}$$

$$\sigma_i^d = 4\pi \left[ |\bar{b}_d|^2 - |\bar{b}_d|^2 \right] \text{ (incoherent cross section)}$$

Can be regarded as properties of a given element

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N} \left( \frac{k_f}{k_i} \right) \sum_{dd'} \bar{b}_d^* \bar{b}_{d'} \sum_{j \in d, j' \in d'} S_{jj'}(\mathbf{Q}, E) + \frac{1}{N} \left( \frac{k_f}{k_i} \right) \sum_d \frac{\sigma_i^d}{4\pi} \sum_{j \in d} S_{jj}(\mathbf{Q}, E)$$

$$\sigma_c^d / 4\pi$$

For same atom type



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TABLE A.2 Bound Scattering Lengths and Cross Sections of the Elements and Their Isotopes

Element	Z	A	$I(\pi)$	$c_s$	$\bar{b}$	$b^+$	$b^-$	$b_l$	$\sigma_c$	$\sigma_i$	$\sigma_s$	$\sigma_a$
n	0	1	1/2(+)		-37.8(8)	0	-37.8 (8)	0	44.89 (4)	0	44.89 (4)	0
H	1				-3.7390 (11)				1.7568 (10)	80.26(6)	82.02 (6)	0.3326 (7)
<sup>1</sup> H	1	1	1/2(+)	99.9885	-3.7423 (12)	10.817 (5)	-47.420 (14)	25.217(6)	1.7589 (11)	79.91(4)	81.67 (4)	0.3326 (7)
<sup>2</sup> H	1	2	1(+)	0.0115	6.674(6)	9.53 (3)	0.975 (60)	4.03(3)	5.597 (10)	2.04(3)	7.64(3)	0.000519 (7)
<sup>3</sup> H	1	3	1/2(+)	12.32 y	4.792(27)	4.18 (15)	6.56(37)	-1.04(17)	2.89(3)	0.14(4)	3.03(5)	<6E-06
He	2				3.26(3)				1.34(2)	0	1.34(2)	0.00747 (1)
<sup>3</sup> He	2	3	1/2(+)	0.000134	5.74(7) - 1.483(2)i	4.5(3)	9.3(5)	-2.1(3) + 2.568(3)i	4.42 (10)	1.38(16)	5.8(2)	5333.0 (7.0)
<sup>4</sup> He	2	4	0(+)	99.999866	3.26(3)			0	1.34(2)	0	1.34(2)	0
Li	3				-1.90(3)				0.454 (10)	0.92(3)	1.37(3)	70.5(3)
<sup>6</sup> Li	3	6	1(+)	7.59	2.00(11) - 0.261(1)i	0.67 (14)	4.67(17)	-1.89 (10) + 0.26 (1)i	0.51(5)	0.46(5)	0.97(7)	940.0 (4.0)

**Note:**

- Bound cross sections (stationary target).
- Assumes 300K neutrons (2200 m/s) - important for absorption xsections.



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# Bound vs Free Cross Sections

All scattering lengths discussed so far are BOUND (assume stationary nucleus, of infinite mass).

Free nuclei (e.g., gas), require solving two-body problem in CENTER-OF-MASS FRAME where we can define a free-atom scattering length  $a$  and a reduced mass of the neutron-nucleus system.

Resulting cross section is reduced by a factor

$$a = \left( \frac{A}{A+1} \right) b$$

Scattering cross section

$$\sigma_{s, \text{free}} = \left( \frac{A}{A+1} \right)^2 \sigma_s$$

Absorption cross section

$$\sigma_{a, \text{free}} = \sigma_a$$



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<sup>149</sup> Sm	*	149	7/2(-)	13.82	18.7(28)– 11.7(1)i	±31.4 (6)–10.3i	63.5(6)	137.0 (5.0)	200.0 (5.0)	42080.0 (400.0)
<sup>150</sup> Sm		150	0(+)	7.38	14.0(3.0)	0	25.0 (11.0)	0	25.0 (11.0)	104.0 (4.0)
<sup>152</sup> Sm		152	0(+)	26.75	–5.0(6)	0	3.1(8)	0	3.1(8)	206.0 (6.0)
<sup>154</sup> Sm		154	0(+)	22.75	8.0(1.0)	0	11.0 (2.0)	0	11.0 (2.0)	8.4(5)
Eu		63			5.3(3)– 1.26(1)i		6.57(4)	2.5(4)	9.2(4)	4530.0 (40.0)
<sup>151</sup> Eu	*	151	5/2(+)	47.81	6.92(15)– 2.53(3)i	±4.5(4)– 2.14(2)i	5.5(2)	3.1(4)	8.6(4)	9100.0 (100.0)
<sup>153</sup> Eu		153	5/2(+)	52.19	8.22(12)	±3.2(9)	8.5(2)	1.3(7)	9.8(7)	312.0 (7.0)
Gd		64			9.5(2)– 13.82(3)i		29.3(8)	151.0 (2.0)	180.0 (2.0)	49700.0 (125.0)
<sup>152</sup> Gd		152	0(+)	0.2	10.0(3.0)E	0	13.0 (8.0)	0	13.0 (8.0)	735.0 (20.0)
<sup>154</sup> Gd		154	0(+)	2.18	10.0(3.0)E	0	13.0 (8.0)	0	13.0 (8.0)	85.0 (12.0)
<sup>155</sup> Gd	*	155	3/2(-)	14.8	13.8(3)– 17.0(1)i	±5.5(5)– 13.16(9)i	40.8(4)	25.0(6.0)	66.0 (6.0)	61100.0 (400.0)
<sup>156</sup> Gd		156	0(+)	20.47	6.3(4)	0	5.0(6)	0	5.0(6)	1.5(1.2)

**Careful, you are hitting a resonance.**

**Careful, most neutrons will be absorbed**



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# Spin vs Isotope Contributions to Incoherent Scattering

**TABLE A.3** Contributions to Spin and Isotope Incoherence to the Total Bound Incoherent Scattering Cross Sections of Selected Elements, Listed in Order of Increasing Ratio of Isotope Incoherence to Total Incoherence (Cross Sections in Barns)

Element	Z	$\sigma_j$	$\sigma_j$ (spin)	$\sigma_j$ (isotope)	$\sigma_j$ (isotope)/ $\sigma_j$
H	1	80.26	80.26	0.006	<0.0001
V	23	5.08	5.06	0.02	0.00
Li	3	0.92	0.76	0.16	0.18
Cl	17	5.3	3.56	1.74	0.33
Gd	64	151	65.36	85.64	0.57
Cr	24	1.83	0.56	1.27	0.69
Ti	22	2.87	0.29	2.58	0.90
W	74	1.63	0.23	1.40	0.86
Ni	28	5.2	0.02	5.18	1.00
Ar	18	0.23	0.00	0.23	1.00

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## Scattering Functions

Q

Coherent dynamic structure factor (or 'scattering function')

$$S_c^{dd'}(\mathbf{Q}, E) = \frac{1}{(N_d N_{d'})^{1/2}} \sum_{j \in d, j' \in d'} S_{jj'}(\mathbf{Q}, E) = \frac{1}{(N_d N_{d'})^{1/2}} \left( \frac{1}{2\pi\hbar} \right) \sum_{j \in d, j' \in d'} \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_{j'}(t)} \rangle e^{-iEt/\hbar} dt$$

Incoherent counterpart

$$S_i^d(\mathbf{Q}, E) = \frac{1}{N_d} \sum_{i \in d} S_{ii}(\mathbf{Q}, E) = \frac{1}{N_d} \left( \frac{1}{2\pi\hbar} \right) \sum_{j \in d} \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_j(t)} \rangle e^{-iEt/\hbar} dt$$

DDCS in its most general form

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} \left( \sum_{dd'} \left[ c_d^{1/2} c_{d'}^{1/2} \bar{b}_d^* \bar{b}_{d'} \right] S_c^{dd'}(\mathbf{Q}, E) + \sum_d \left[ c_d \frac{\sigma_i^d}{4\pi} \right] S_{dd}(\mathbf{Q}, E) \right)$$



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# Intermediate Scattering Functions

Intermediate scattering function

$$I^{dd'}(\mathbf{Q}, t) = \frac{1}{(N_d N_{d'})^{1/2}} \sum_{j \in d, j' \in d'} \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_{j'}(t)} \rangle$$

*DDCS probes  $S(\mathbf{Q}, E)$*

Self-intermediate scattering function

$$I_s^d(\mathbf{Q}, t) = \frac{1}{N_d} \sum_{j \in d} \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_j(t)} \rangle$$

*ISFs can be probed directly via spin-echo methods.*

Defined in a way such that they represent the time-energy Fourier transform of the corresponding dynamic structure factors.

$$\begin{aligned} S_c^{dd'}(\mathbf{Q}, E) &= \frac{1}{(N_d N_{d'})^{1/2}} \sum_{j \in d, j' \in d'} S_{jj'}(\mathbf{Q}, E) \\ &= \frac{1}{(N_d N_{d'})^{1/2}} \left( \frac{1}{2\pi\hbar} \right) \sum_{j \in d, j' \in d'} \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_{j'}(t)} \rangle e^{-iEt/\hbar} dt \end{aligned}$$

$$S_i^d(\mathbf{Q}, E) = \frac{1}{N_d} \sum_{i \in d} S_{ii}(\mathbf{Q}, E) = \frac{1}{N_d} \left( \frac{1}{2\pi\hbar} \right) \sum_{j \in d} \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_j(t)} \rangle e^{-iEt/\hbar} dt$$



Q

## Next Lecture

**Applications, with an emphasis on neutron spectroscopy applied to chemical & molecular systems.**

**To think about: what is a solid for you?**



# Lecture II: Neutron Scattering

## *Applications*

*Roma, February 2015*



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## Outline [today]

- Fundamentals.
- *Applications.*
- Neutron production.
- First-principles materials modelling.



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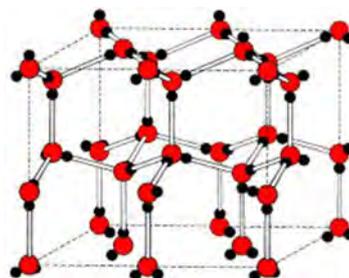
# What is a solid? (discussion)



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## Solids, An Operational Definition

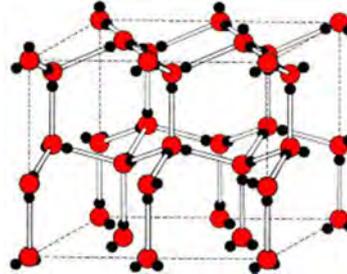
***A solid is a physical system in which each atom has a well-defined (and fixed) equilibrium position over the duration of the measurement.***



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# Solids, An Operational Definition

*A solid is a physical system in which each atom has a well-defined (and fixed) equilibrium position over the duration of the measurement.*



Note: order is not a prerequisite to define a solid (includes glasses, amorphous matter).

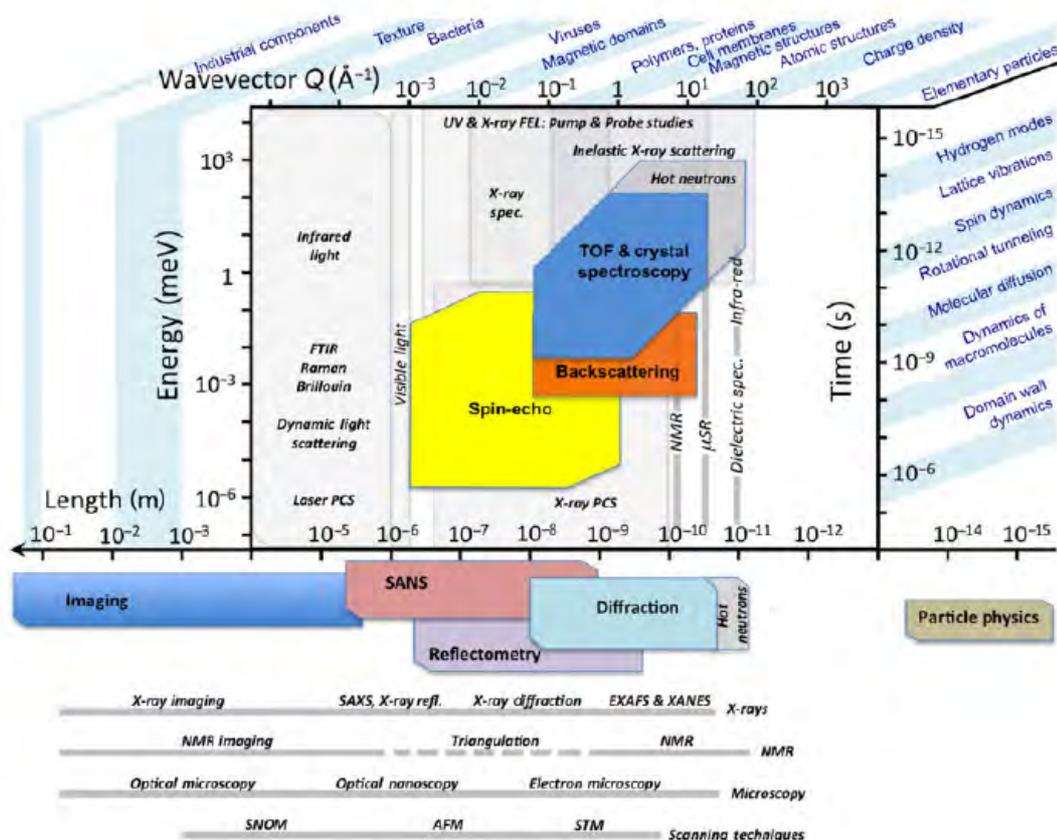
This definition excludes:

- Quantum solids (Helium).
- The battery on your mobile phone: materials where atoms or ions undergo translational diffusion.



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# The Power of Inelastic Neutron Scattering



# Scattering Functions For a Solid

Each atom occupies a well-defined site, with an instantaneous displacement given by:

$$\mathbf{R}_j(t) = \mathbf{j} + \mathbf{u}_j(t), j = 1, \dots, n.$$

Recall definition of scattering function from previous lecture:

$$S_{jj'}(\mathbf{Q}, E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q}\cdot\mathbf{R}_j(0)} e^{i\mathbf{Q}\cdot\mathbf{R}_{j'}(t)} \rangle e^{-iEt/\hbar} dt$$

Coherent and incoherent (self) are then given by

$$S_c(\mathbf{Q}, E) = \frac{1}{N} \left( \frac{1}{2\pi\hbar} \right) \sum_{jj'} \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q}\cdot\mathbf{u}_j(0)} e^{i\mathbf{Q}\cdot\mathbf{u}_j(t)} \rangle e^{i\mathbf{Q}\cdot(\mathbf{j}'-\mathbf{j})} e^{-iEt/\hbar} dt$$

$$S_i(\mathbf{Q}, E) = \frac{1}{N} \left( \frac{1}{2\pi\hbar} \right) \sum_j \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q}\cdot\mathbf{u}_j(0)} e^{i\mathbf{Q}\cdot\mathbf{u}_j(t)} \rangle e^{-iEt/\hbar} dt.$$

Note that time-dependent part is all related to instantaneous displacements from equilibrium.

Will assume these motions are *harmonic*.



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## Normal Modes of Vibration

Q

Harmonic displacement vectors (second quantization picture):

$$\mathbf{u}_j(t) = \sum_k \left( \frac{\hbar}{2M_k\omega_k} \right)^{1/2} \left[ \mathbf{e}_j^k e^{-\omega_k t} a_k + \mathbf{e}_j^{k*} e^{\omega_k t} a_k^+ \right]$$

Mode polarization vectors for *j*th atom

Eigenvalues of dynamical mtx:

$$\mathbf{D}_{jj'} = \frac{1}{(M_j M_{j'})^{1/2}} f_{jj'}$$

With force constants:

$$U - U_0 = \frac{1}{2} \mathbf{u}_j f_{jj'} \mathbf{u}_{j'}$$

Quantum harmonic oscillator implies:

$$\langle e^{-i\mathbf{Q}\cdot\mathbf{u}_j(0)} e^{i\mathbf{Q}\cdot\mathbf{u}_{j'}(t)} \rangle = e^{-[W_j(\mathbf{Q}) + W_{j'}(\mathbf{Q})]} e^{\langle \mathbf{Q}\cdot\mathbf{u}_j(0) \mathbf{Q}\cdot\mathbf{u}_{j'}(t) \rangle}$$

$$e^{-W_j(\mathbf{Q})} = e^{-1/2 \langle [\mathbf{Q}\cdot\mathbf{u}_j(0)]^2 \rangle} \quad \text{Debye-Waller factor}$$

$$e^{\langle \mathbf{Q}\cdot\mathbf{u}_j(0) \mathbf{Q}\cdot\mathbf{u}_{j'}(t) \rangle} = 1 + \langle \mathbf{Q}\cdot\mathbf{u}_j(0) \mathbf{Q}\cdot\mathbf{u}_{j'}(t) \rangle + \frac{1}{2!} \langle \mathbf{Q}\cdot\mathbf{u}_j(0) \mathbf{Q}\cdot\mathbf{u}_{j'}(t) \rangle^2 + \dots$$



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# Debye-Waller Factor for Harmonic Vibrations

For a given atom, sum over all polarization vectors:

$$W_j(\mathbf{Q}) = \frac{\hbar}{3M_j} \sum_k \frac{|\mathbf{Q} \cdot \mathbf{e}_j^k|^2}{\omega_k} \langle 2n_k + 1 \rangle$$

With a Bose population factor:

$$\langle n_k \rangle = \frac{1}{e^{\hbar\omega_k/k_B T} - 1}$$

Simplest (and most commonly used) case: angular average

$$2W(Q) = \frac{1}{3} Q^2 \langle u^2 \rangle$$

defined in terms of a mean-square displacement.

(used for example in the study of proteins)



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## Purely Elastic Scattering (Coherent)

$$S_c(\mathbf{Q}, E) = \frac{1}{N} \left( \frac{1}{2\pi\hbar} \right) \sum_{jj'} \int_{-\infty}^{+\infty} \langle e^{-i\mathbf{Q} \cdot \mathbf{u}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{u}_j(t)} \rangle e^{i\mathbf{Q} \cdot (\mathbf{j}' - \mathbf{j})} e^{-iEt/\hbar} dt$$

$$\langle e^{-i\mathbf{Q} \cdot \mathbf{u}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{u}_{j'}(t)} \rangle = e^{-[W_j(\mathbf{Q}) + W_{j'}(\mathbf{Q})]} e^{i\mathbf{Q} \cdot \mathbf{u}_j(0) \cdot \mathbf{Q} \cdot \mathbf{u}_{j'}(t)}$$

$$e^{i\mathbf{Q} \cdot \mathbf{u}_j(0) \cdot \mathbf{Q} \cdot \mathbf{u}_{j'}(t)} = 1 + \langle \mathbf{Q} \cdot \mathbf{u}_j(0) \cdot \mathbf{Q} \cdot \mathbf{u}_{j'}(t) \rangle + \frac{1}{2!} \langle \mathbf{Q} \cdot \mathbf{u}_j(0) \cdot \mathbf{Q} \cdot \mathbf{u}_{j'}(t) \rangle^2 + \dots$$

Gives (note Dirac-delta in time):

$$S_{c,el}(\mathbf{Q}, E) = \frac{1}{N} \left( \frac{1}{2\pi\hbar} \right) \sum_{jj'} \int_{-\infty}^{+\infty} e^{-[W_j(\mathbf{Q}) + W_{j'}(\mathbf{Q})]} e^{i\mathbf{Q} \cdot (\mathbf{j}' - \mathbf{j})} e^{-iEt/\hbar} dt$$

$$= \left[ \frac{1}{N} \sum_{jj'} e^{-[W_j(\mathbf{Q}) + W_{j'}(\mathbf{Q})]} e^{i\mathbf{Q} \cdot (\mathbf{j}' - \mathbf{j})} \right] \delta(E),$$

And energy integration gives the *Elastic Structure Factor*

$$S_{el}(\mathbf{Q}) = \frac{1}{N} \sum_{jj'} e^{-[W_j(\mathbf{Q}) + W_{j'}(\mathbf{Q})]} e^{i\mathbf{Q} \cdot (\mathbf{j}' - \mathbf{j})}$$



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# Purely Elastic Scattering (Incoherent)

$$S_i(\mathbf{Q}, E) = \frac{1}{N} \left( \frac{1}{2\pi\hbar} \right) \sum_j \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q}\cdot\mathbf{u}_j(0)} e^{i\mathbf{Q}\cdot\mathbf{u}_j(t)} \rangle e^{-iEt/\hbar} dt.$$

$$\langle e^{-i\mathbf{Q}\cdot\mathbf{u}_j(0)} e^{i\mathbf{Q}\cdot\mathbf{u}_j(t)} \rangle = e^{-[W_j(\mathbf{Q}) + W_j'(\mathbf{Q})]} e^{i\mathbf{Q}\cdot\mathbf{u}_j(0)\mathbf{Q}\cdot\mathbf{u}_j(t)}$$

$$e^{i\mathbf{Q}\cdot\mathbf{u}_j(0)\mathbf{Q}\cdot\mathbf{u}_j(t)} = 1 + \langle \mathbf{Q}\cdot\mathbf{u}_j(0)\mathbf{Q}\cdot\mathbf{u}_j(t) \rangle + \frac{1}{2!} \langle \mathbf{Q}\cdot\mathbf{u}_j(0)\mathbf{Q}\cdot\mathbf{u}_j(t) \rangle^2 + \dots$$

Gives (note Dirac-delta in time):  $S_{i,\text{el}}(\mathbf{Q}, E) = \left[ \frac{1}{N} \sum_j e^{-2W_j(\mathbf{Q})} \right] \delta(E)$

And energy integration gives *average Debye-Waller Factor*

$$S_{i,\text{el}}(\mathbf{Q}) = \int S_{i,\text{el}}(\mathbf{Q}, E) dE = \frac{1}{N} \sum_j e^{-2W_j(\mathbf{Q})}$$



# Purely Elastic Scattering in Ordered Solids

Q

Crystalline solid with lattice sites at  $\mathbf{j} = \mathbf{l} + \mathbf{d}$ .

Elastic structure factor involves a sum over reciprocal lattice vectors  $\boldsymbol{\tau}$

$$S(\mathbf{Q})_{\text{el}}^{\text{dd}'} = \frac{(2\pi)^3}{v_0} e^{-[W_d(\mathbf{Q}) + W_{d'}(\mathbf{Q})]} e^{i\mathbf{Q}\cdot(\mathbf{d}' - \mathbf{d})} \sum_{\boldsymbol{\tau}} \delta(\mathbf{Q} - \boldsymbol{\tau})$$

*Bragg peaks*

The *elastic coherent differential scattering cross section*

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{c,el}} = \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}} |F(\boldsymbol{\tau})|^2 \delta(\mathbf{Q} - \boldsymbol{\tau}) \quad \text{with} \quad F(\boldsymbol{\tau}) = \sum_{\mathbf{d}} \bar{b}_{\mathbf{d}} e^{-W_{\mathbf{d}}(\boldsymbol{\tau})} e^{i\boldsymbol{\tau}\cdot\mathbf{d}}$$

*unit-cell structure factor*

The *incoherent scattering cross section*

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{i,el}} = \sum_{\mathbf{d}} c_{\mathbf{d}} \sigma_{\mathbf{d}}^{\text{i}} e^{-2W_{\mathbf{d}}(\mathbf{Q})}$$



# Inelastic (One-Phonon) Scattering

$$S_c(\mathbf{Q}, E) = \frac{1}{N} \left( \frac{1}{2\pi\hbar} \right) \sum_{jj'} \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q}\cdot\mathbf{u}_j(0)} e^{i\mathbf{Q}\cdot\mathbf{u}_j(t)} \rangle e^{i\mathbf{Q}\cdot(\mathbf{j}'-\mathbf{j})} e^{-iEt/\hbar} dt$$

$$\langle e^{-i\mathbf{Q}\cdot\mathbf{u}_j(0)} e^{i\mathbf{Q}\cdot\mathbf{u}_j(t)} \rangle = e^{-[W_j(\mathbf{Q})+W_{j'}(\mathbf{Q})]} e^{\langle \mathbf{Q}\cdot\mathbf{u}_j(0)\mathbf{Q}\cdot\mathbf{u}_j(t) \rangle}$$

$$e^{\langle \mathbf{Q}\cdot\mathbf{u}_j(0)\mathbf{Q}\cdot\mathbf{u}_j(t) \rangle} = 1 + \langle \mathbf{Q}\cdot\mathbf{u}_j(0)\mathbf{Q}\cdot\mathbf{u}_j(t) \rangle + \frac{1}{2!} \langle \mathbf{Q}\cdot\mathbf{u}_j(0)\mathbf{Q}\cdot\mathbf{u}_j(t) \rangle^2 + \dots$$

Scattering function now depends implicitly on time via displacement terms

$$S_{c,1}(Q, E) = \frac{1}{N} \left( \frac{1}{2\pi\hbar} \right) \sum_{jj'} \int_{-\infty}^{+\infty} e^{-[W_j(\mathbf{Q})+W_{j'}(\mathbf{Q})]} \langle \mathbf{Q}\cdot\mathbf{u}_j(0)\mathbf{Q}\cdot\mathbf{u}_j(t) \rangle e^{i\mathbf{Q}\cdot(\mathbf{j}'-\mathbf{j})} e^{-iEt/\hbar} dt$$

Also note quadratic  $Q$  dependence within brackets.



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# Harmonic (Coherent) Case

$Q$

$$S_{c,1}(\mathbf{Q}, E) = \frac{1}{N} \left( \frac{1}{4\pi} \right) \sum_{jj'} \int_{-\infty}^{+\infty} e^{-[W_j(\mathbf{Q})+W_{j'}(\mathbf{Q})]} \sum_k \frac{(\mathbf{Q}\cdot\mathbf{e}_j^k)^* (\mathbf{Q}\cdot\mathbf{e}_{j'}^k)}{(M_j M_{j'})^{1/2} \omega_k} \times \\ \times [e^{-i\omega_k t} \langle n_k + 1 \rangle + e^{i\omega_k t} \langle n_k \rangle] e^{i\mathbf{Q}\cdot(\mathbf{j}'-\mathbf{j})} e^{-iEt/\hbar} dt.$$

And time integral now carries additional terms satisfying the creation or annihilation of normal modes of vibration (phonons)

$$S_{c,+1}(\mathbf{Q}, E) = \frac{1}{2N} \sum_{jj'} e^{-[W_j(\mathbf{Q})+W_{j'}(\mathbf{Q})]} e^{i\mathbf{Q}\cdot(\mathbf{j}'-\mathbf{j})} \times \quad \text{with} \quad E_k = \hbar\omega_k \\ \times \sum_k \frac{\hbar^2 (\mathbf{Q}\cdot\mathbf{e}_j^k)^* (\mathbf{Q}\cdot\mathbf{e}_{j'}^k)}{(M_j M_{j'})^{1/2} E_k} \langle n_k + 1 \rangle \delta(E - E_k)$$

$$S_{c,-1}(\mathbf{Q}, E) = \frac{1}{2N} \sum_{jj'} e^{-[W_j(\mathbf{Q})+W_{j'}(\mathbf{Q})]} e^{i\mathbf{Q}\cdot(\mathbf{j}'-\mathbf{j})} \times \\ \times \sum_k \frac{\hbar^2 (\mathbf{Q}\cdot\mathbf{e}_j^k)^* (\mathbf{Q}\cdot\mathbf{e}_{j'}^k)}{(M_j M_{j'})^{1/2} E_k} \langle n_k \rangle \delta(E + E_k)$$



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# Harmonic (Incoherent) Case

$$S_{i,+1}(\mathbf{Q}, E) = \frac{1}{2N} \sum_j e^{-w_j(\mathbf{Q})} \sum_k \frac{\hbar^2 |\mathbf{Q} \cdot \mathbf{e}_j^k|^2}{M_j E_k} \langle n_k + 1 \rangle \delta(E - E_k)$$

$$S_{i,-1}(\mathbf{Q}, E) = \frac{1}{2N} \sum_j e^{-w_j(\mathbf{Q})} \sum_k \frac{\hbar^2 |\mathbf{Q} \cdot \mathbf{e}_j^k|^2}{M_j E_k} \langle n_k \rangle \delta(E + E_k)$$

*Appealingly simple!*



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# Case of an Ordered Solid

Long-range order defined as  $\mathbf{j} = \mathbf{l} + \mathbf{d}$

Polarization vectors exploit translational invariance:

$$\mathbf{e}_d^k = \frac{1}{N_c^{1/2}} \sum_{\mathbf{q}} \mathbf{e}_d^k(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{l}}$$

Leading to an additional momentum-transfer condition

$$S_{c,+1}^{dd'}(\mathbf{Q}, E) = \frac{1}{2N_c} (2\pi)^3 e^{-[w_d(\mathbf{Q}) + w_{d'}(\mathbf{Q})]} \sum_{\mathbf{q}k} \frac{\hbar^2 (\mathbf{Q} \cdot \mathbf{e}_d^k(\mathbf{q}))^* (\mathbf{Q} \cdot \mathbf{e}_{d'}^k(\mathbf{q}))}{(M_d M_{d'})^{1/2} E_k(\mathbf{q})} \times e^{i\mathbf{Q} \cdot (\mathbf{d}' - \mathbf{d})} \langle n_{\mathbf{q}k} + 1 \rangle \sum_{\boldsymbol{\tau}} \delta(\mathbf{Q} - \mathbf{q} - \boldsymbol{\tau}) \delta(E - E_k(\mathbf{q}))$$

And DDCS

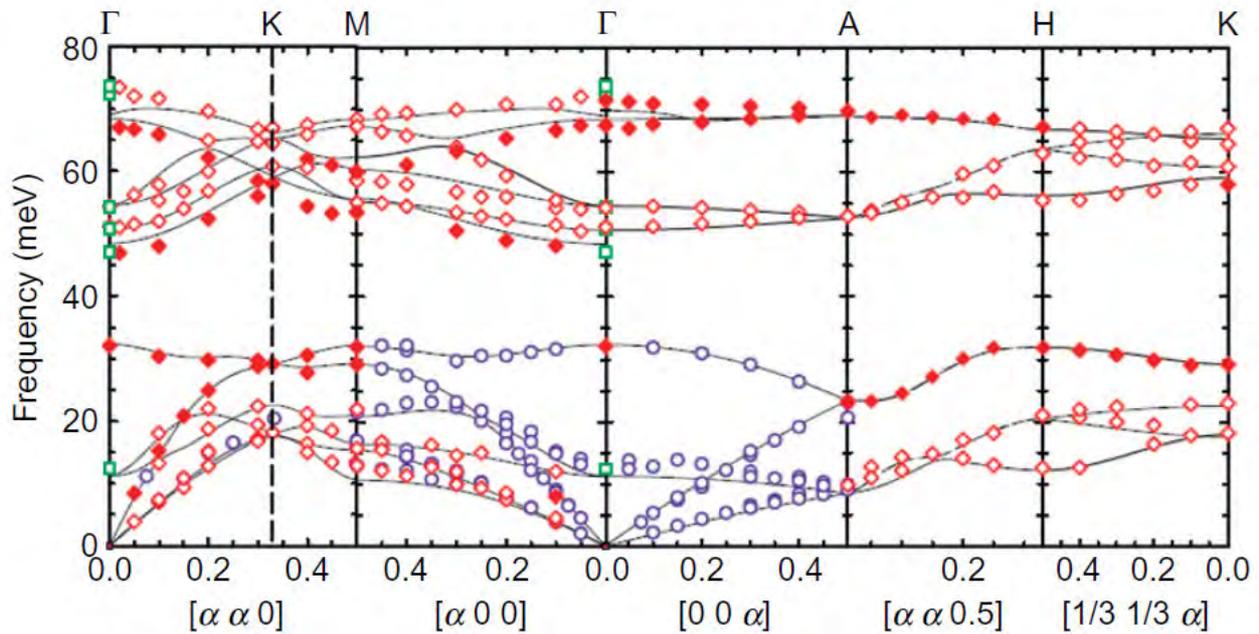
$$\left( \frac{d^2 \sigma}{d\Omega dE_f} \right)_{c,+1} = \frac{k_f}{k_i} \left[ \frac{(2\pi)^3}{2N_c v_0} \right] \sum_{\boldsymbol{\tau}} \sum_{\mathbf{q}k} |F_1(\mathbf{Q}, \mathbf{q}k)|^2 \frac{\hbar^2 \langle n_{\mathbf{q}k} + 1 \rangle}{E_k(\mathbf{q})}$$

$$\delta(\mathbf{Q} - \mathbf{q} - \boldsymbol{\tau}) \delta(E - E_k(\mathbf{q})),$$

One-phonon structure factor  $F_1(\mathbf{Q}, \mathbf{q}k) = \sum_d \frac{\bar{b}_d}{M_d^{1/2}} e^{-w_d(\mathbf{Q})} e^{i\mathbf{Q} \cdot \mathbf{d}} [\mathbf{Q} \cdot \mathbf{e}_d^k(\mathbf{q})]$

# Phonon Dispersion Relations

$$\mathbf{Q} = \boldsymbol{\tau} \pm \mathbf{q}, \quad E = E_k(\mathbf{q})$$



Zinc oxide



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## Incoherent Case

$$\left( \frac{d^2 \sigma}{d\Omega dE_f} \right)_{i,+1} = \frac{k_f}{k_i} \left( \frac{1}{2N} \right) \sum_{\mathbf{d}} \frac{1}{M_{\mathbf{d}}} \frac{\sigma_{\mathbf{d}}^{\mathbf{d}}}{4\pi} e^{-2W_{\mathbf{d}}(\mathbf{Q})} \sum_{\mathbf{qk}} \frac{\hbar^2 |\mathbf{Q} \cdot \mathbf{e}_{\mathbf{d}}^k(\mathbf{q})|^2}{E_k(\mathbf{q})} \langle n_{\mathbf{qk}} + 1 \rangle \delta(E - E_k(\mathbf{q}))$$

with only one selection rule, associated with energy:  $E = \pm E_k(\mathbf{q})$

Or in terms of the *one-phonon vibrational density of states*  $Z(E)$ :

$$\left( \frac{d^2 \sigma}{d\Omega dE_f} \right)_{i,+1} = \frac{k_f}{k_i} \sum_{\mathbf{d}} \frac{3 \sigma_{\mathbf{d}}^{\mathbf{d}}}{24\pi} e^{-2W_{\mathbf{d}}(\mathbf{Q})} \frac{\overline{\hbar^2 |\mathbf{Q} \cdot \mathbf{e}_{\mathbf{d}}^k(\mathbf{q})|^2}}{M_{\mathbf{d}} E} \langle n + 1 \rangle Z(E)$$

$$\text{with } \langle n + 1 \rangle = \frac{1}{2} \left[ 1 + \coth \left( \frac{E}{2k_B T} \right) \right]$$



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# Incoherent Case for a Single Mass

$$\left(\frac{d^2\sigma}{d\Omega dE_f}\right)_{i,+1} = \frac{k_f}{k_i} \left(\frac{\hbar^2 Q^2}{2M}\right) e^{-2W(Q)} \frac{\langle n+1 \rangle}{E} Z(E)$$

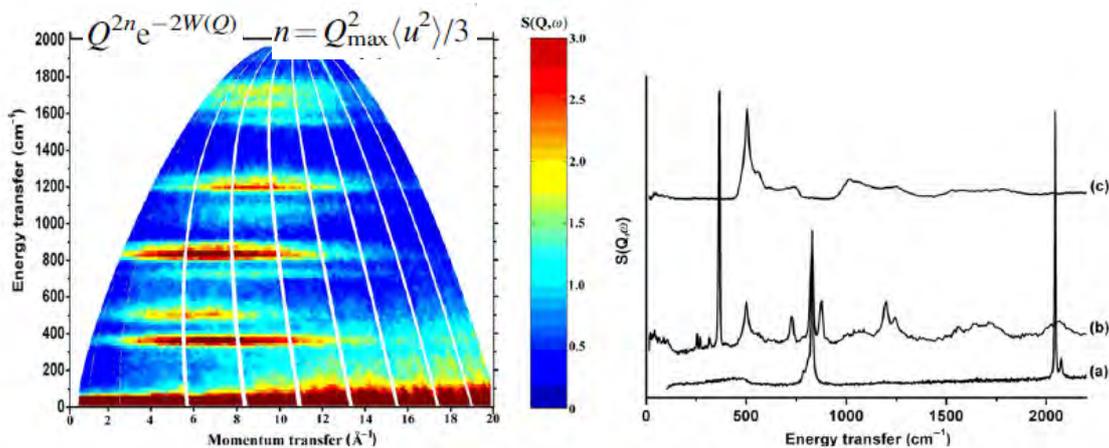
Extensively used for hydrogen-containing systems.

*Direct measure of Z(E), quite unique to neutrons*



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# Incoherent Inelastic Neutron Scattering



***Conceptually analogous to IR, Raman***

For many more examples, see INS database

<http://www.wisis2.isis.rl.ac.uk/INSdatabase/>

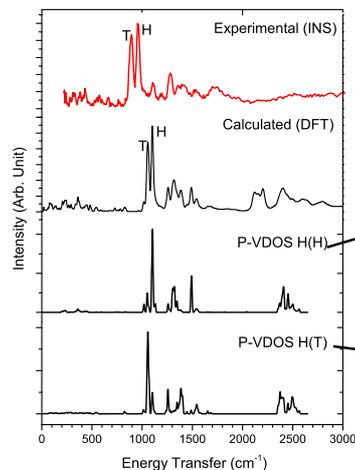
*Data collected on TOSCA at ISIS.*

ilities Council

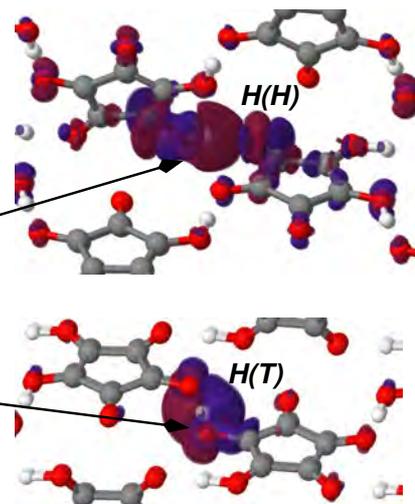
# In-silico Neutron Spectroscopy

**Croconic acid**  
(organic ferroelectric)

**TOSCA, SXD**  
+  
**Lagrange (ILL)**



Experimental INS compared with Calculations



Response charge densities of hydrogen ions

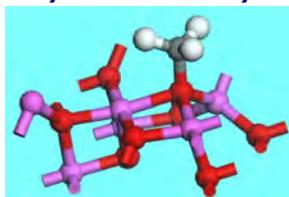
**vdw-DFT key to explain structure, hydrogen-bond dynamics, and ferroelectric response.**



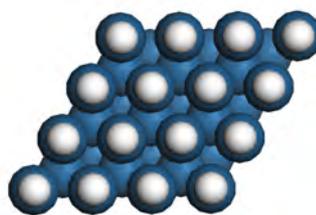
## Chemical Catalysis



### Methyl Chloride Synthesis

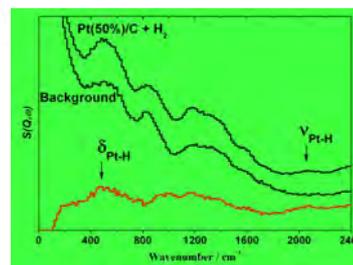


Neutron results: £4M cost saving to industrial partner.

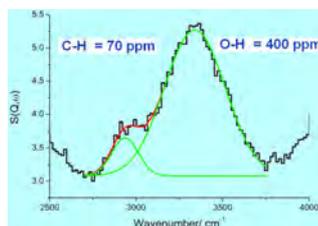
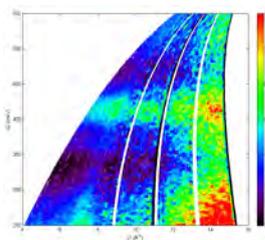


First observation of on-top hydrogen on an industrial Pt fuel-cell catalyst. *Catalysis Today*, 114 (2006) 418.

### Fuel Cells

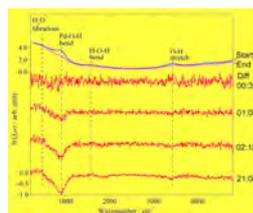


### Dry Reforming of Methane

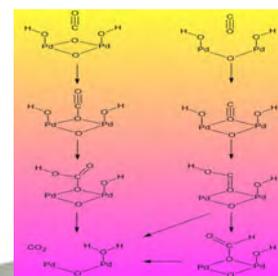


Quantitation of hydroxyl and adsorbed hydrocarbon *Phys Chem Chem Phys* 12 (2010) 3102.

### Operando Neutron Studies



Two hydroxyls are required for CO oxidation. *Chem Comm* 47 (2011) 1998.



# In Situ, Operando & Simultaneous Techniques



## Back to Spectroscopy: Polymer Intercalation in Graphene-related Materials

www.rsc.org/softmatter Soft Matter, 2011, 7, 7173 COMMUNICATION

**Polymers under extreme two-dimensional confinement: Poly(ethylene oxide) in graphite oxide†**

Fabienne Barroso-Bujans,<sup>a,c</sup> Felix Fernandez-Alonso,<sup>b</sup> Silvina Cerveny,<sup>a</sup> Stewart F. Parker,<sup>b</sup> Angel Alegria<sup>a,c</sup> and Juan Colmenero<sup>a,d</sup>

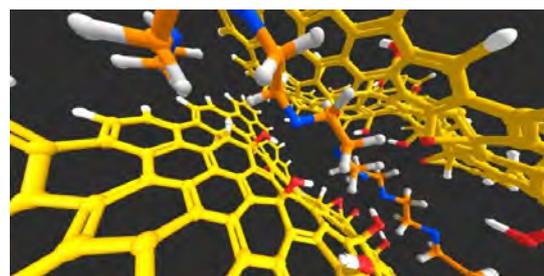
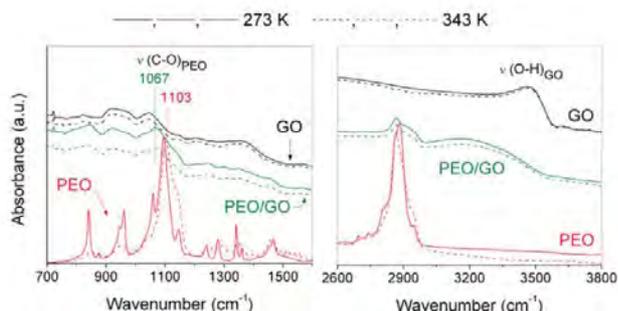
Received 13th April 2011, Accepted 31st May 2011  
DOI: 10.1039/c1sm05661a

CARBON 50 (2012) 5232-5241

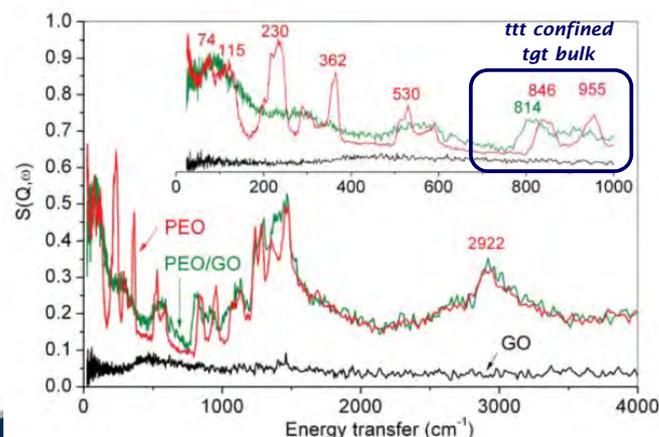
**Tunable uptake of poly(ethylene oxide) by graphite-oxide-based materials**

Fabienne Barroso-Bujans<sup>a,c</sup>, Felix Fernandez-Alonso<sup>b,c</sup>, Jose A. Pomposo<sup>a,d,e</sup>, Eduardo Enciso<sup>f</sup>, Jose Luis G. Fierro<sup>g</sup>, Juan Colmenero<sup>a,e,h</sup>

Optical (FTIR+Raman)



**Intercalate conformation:  
only with neutrons**



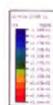
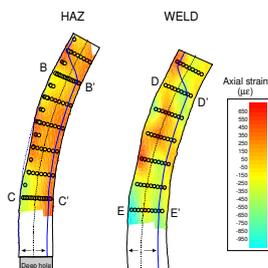
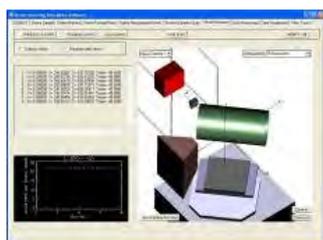
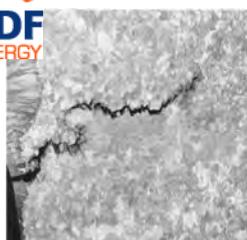
*TOSCA Xpress: Soft Matter Comm 7 7173 (2011).  
ACS Macro Lett 1 550 (2012).  
Macromolecules 45 3137 (2012).  
Carbon 50 5232 (2012).  
Soft Matter 9 10960 (2013).*



# Engineering & Industry: Stress, Strain, and Materials Performance



Diagnosing cracks in advanced gas-cooled reactors



Courtesy of SY Zhang (ISIS)



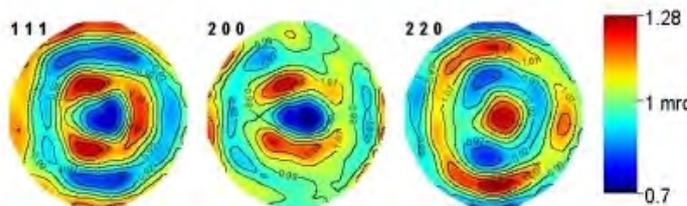
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## Neutrons and Archaeology

### Analysis of Ancient Greek Helmets



National Museum of Wales, Cardiff



Texture of Archaic Greek helmet

Questions :

- Origin: Archaic or Classical period?
- Technology: single piece of bronze?
- Preservation state: harmful corrosion products?
- Authenticity: are these the original?



Manchester Museum

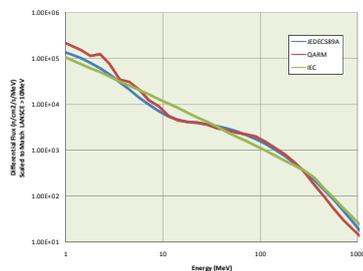
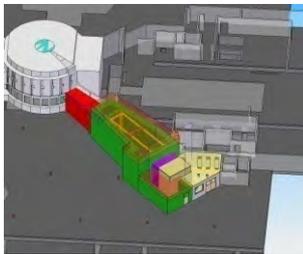


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# Neutrons Helping the Semiconductor Industry



- Atmospheric neutrons collide with microchips and upset microelectronic devices every few seconds.
- 300x at high altitudes.
- Spallation sources provide same fast neutron spectrum at much higher intensities (1 ISIS-hr ~ 100 years.)
- Manufacturers can mitigate against the problem of cosmic radiation.



## Below & Above Molecular Vibrations: An Operational Definition

*Use the H<sub>2</sub> molecule as 'yardstick'*

- H-H stretch is highest-known vibrational frequency for a molecule:
  - $\omega_{vib} = 4400 \text{ cm}^{-1} = 550 \text{ meV} = 133 \text{ THz}$
  - **High energies**  $> \omega_{vib}$

*Spallation sources (ISIS) can access up to 100-200 eV.*

- H<sub>2</sub> rotational constant (free molecule) also highest known.
  - $B_{rot} = 58.8 \text{ cm}^{-1} = 7.35 \text{ meV} = 1.8 \text{ THz}$
  - **Low energies**  $< 2B_{rot} = 15 \text{ meV} = 3.6 \text{ THz}$  (rotational band head)

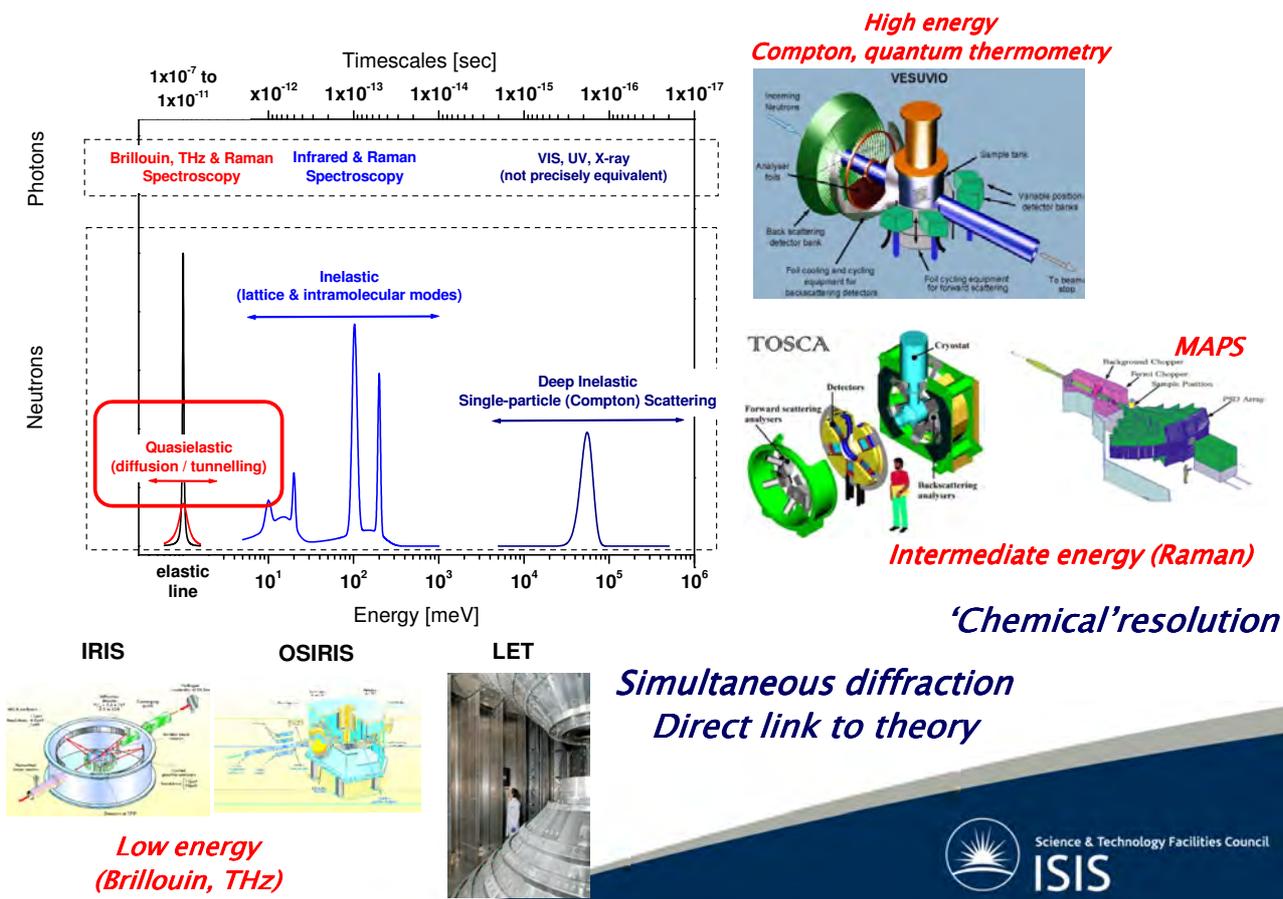
*With neutrons, access to sub-THz frequencies is routine. Reactor sources (ILL) best for cold neutrons.*



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# Below Molecular Vibrations



# Below Molecular Vibrations

*Lower energies: larger (supramolecular) objects.*

Recall : 
$$\omega_{vib} = \sqrt{\frac{k}{\mu}}$$

# Neutron Spectroscopy of Framework Materials

PHYSICAL REVIEW LETTERS

## Identifying the Role of Terahertz Vibrations in Metal-Organic Frameworks: From Gate-Opening Phenomenon to Shear-Driven Structural Destabilization

Matthew R. Ryder,<sup>1,2,3</sup> Bartolomeo Civalleri,<sup>4</sup> Thomas D. Bennett,<sup>5</sup> Sebastian Henke,<sup>5</sup> Svemir Rudic,<sup>2</sup>  
Gianfelice Cinque,<sup>2</sup> Felix Fernandez-Alonso,<sup>2,6</sup> and Jin-Chong Tan<sup>1,2</sup>

<sup>1</sup>Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, United Kingdom  
<sup>2</sup>ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, United Kingdom

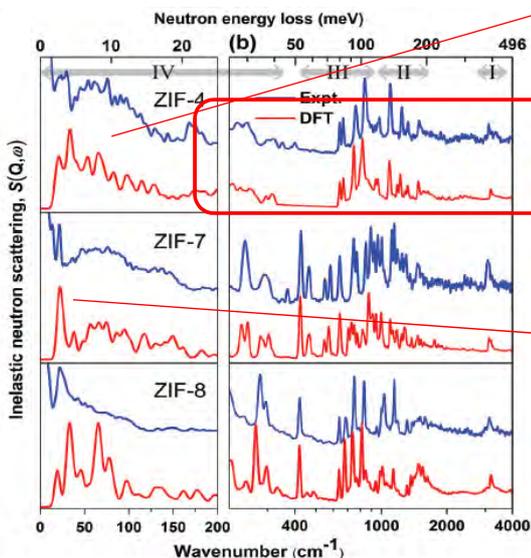
<sup>3</sup>Diamond Light Source, Harwell Campus, Didcot, Oxford OX11 0DE, United Kingdom

<sup>4</sup>Department of Chemistry, NIS and INSTM Reference Centre, University of Turin, via P. Giuria 7, 10125 Torino, Italy

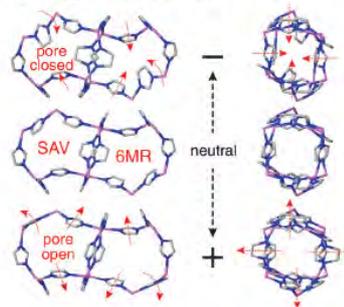
<sup>5</sup>Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB3 0ES, United Kingdom

<sup>6</sup>Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

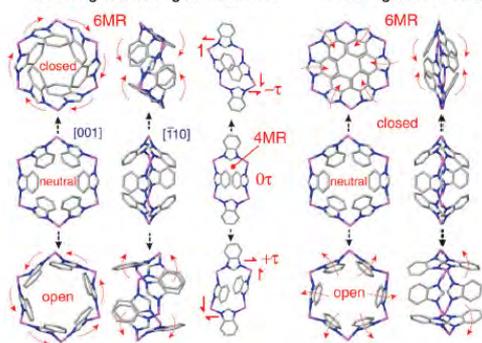
(Received 1 August 2014)



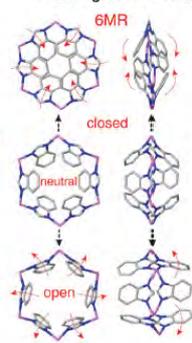
### Gate-opening mechanism at ~1 THz



### Breathing & shearing at 0.654 THz



### Breathing at 1.47 THz



## Below Molecular Vibrations

*Low energies also give access to:*

*Quantum tunnelling in H<sub>2</sub>, CH<sub>4</sub>, hydrocarbons, methyl groups in many materials like polymers, ...*

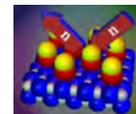
*No classical counterpart (not vibrations per se)*



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# Molecular Tunnelling on Surfaces



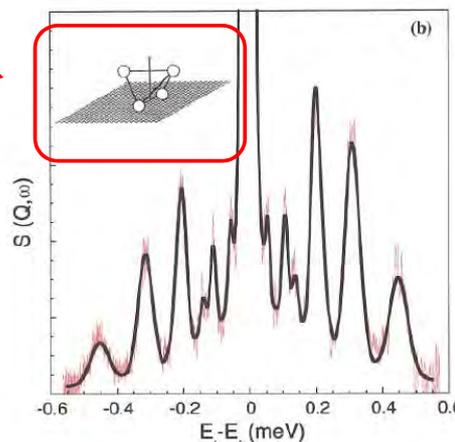
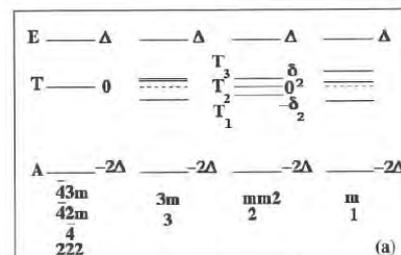
## Tracking the Evolution of Interatomic Potentials with High Resolution Inelastic Neutron Spectroscopy

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 (Received 27 October 2000; published 26 October 2001)

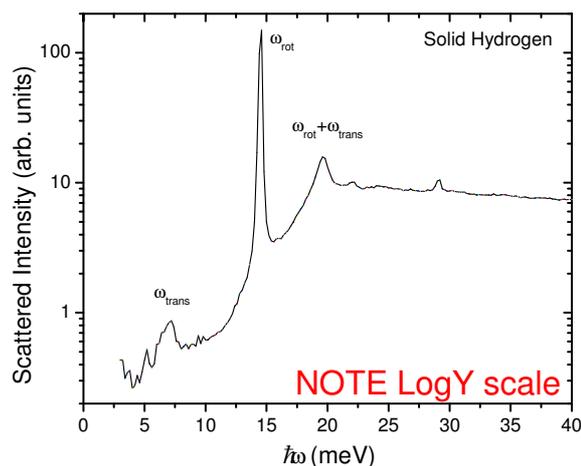
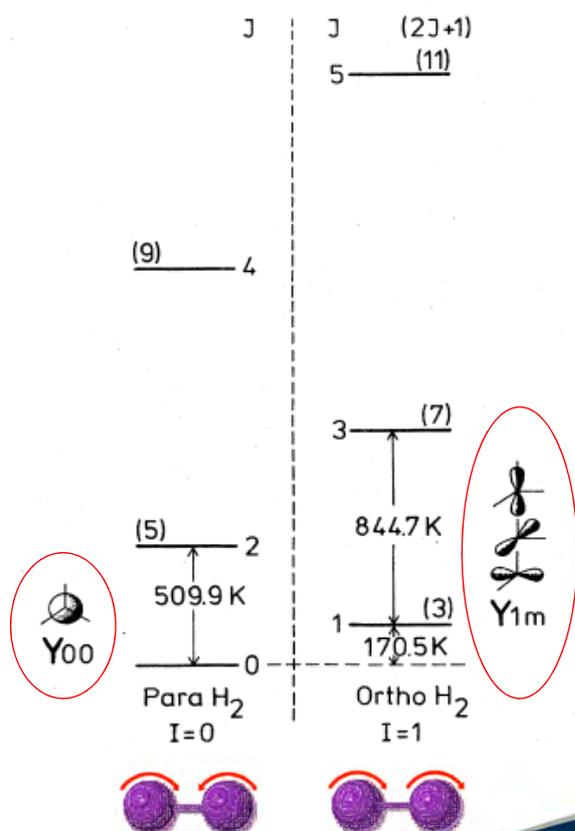
### Structure of CH<sub>4</sub> films on MgO(100) surfaces

TABLE I. Comparison of model calculations (Ref. [10]) with fits to data in Fig. 1(b) using Bayesian analysis. Model calculations use molecule-to-surface distance of 3.30 Å and molecular field of 21.8 cm<sup>-1</sup> and level diagram (mm2, 2).

Transition	Model (μeV)	Experiment (μeV)
E → T3	59	56.6 ± 0.5
T2 → T1	110	108.2 ± 0.4
T3 → T2	134	139.7 ± 0.7
E → T2	193	200.0 ± 2.1
T1 → A	212	218.0 ± 3.7
T3 → T1	Not Allowed	Not Observed
E → T1	300	306.2 ± 0.4
T2 → A	322	324.0 ± 2.5
T3 → A	456	450.4 ± 0.7



## Beyond Vibrations: Molecular Hydrogen



- (0→1) rotational transition is purely incoherent & strong (strong for neutrons but optically forbidden)
- M-level splitting of J=1 state is a sensitive probe of local environment.

# Rotational Levels in Presence of Angular Potential

## Free diatomic rotor

$$Y_{JM}(\Theta, \phi) = |JM\rangle \quad \text{with} \quad \langle J'M' | H_{rot} | JM \rangle = B_{rot} J(J+1) \delta_{J'J} \delta_{M'M}$$

## Additional hindering potential

$$H_{total} = H_{rot} + V(\Theta, \phi) \quad \text{with} \quad V(\Theta, \phi) = \sum_{J_v M_v} V_{J_v M_v} Y_{J_v M_v}(\Theta, \phi)$$

$$\langle J'M' | H_{tot} | JM \rangle = B_{rot} J(J+1) \delta_{J'J} \delta_{M'M} + \sum_{J_v M_v} V_{J_v M_v} \langle J'M' | Y_{J_v M_v}(\Theta, \phi) | JM \rangle$$

$$\langle J'M' | Y_{J_v M_v}(\Theta, \phi) | JM \rangle = (-1)^{M'} \sqrt{\frac{(2J'+1)(2J_v+1)(2J+1)}{4\pi}} \begin{pmatrix} J' & J_v & J \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J' & J_v & J \\ -M' & M_v & M \end{pmatrix}$$

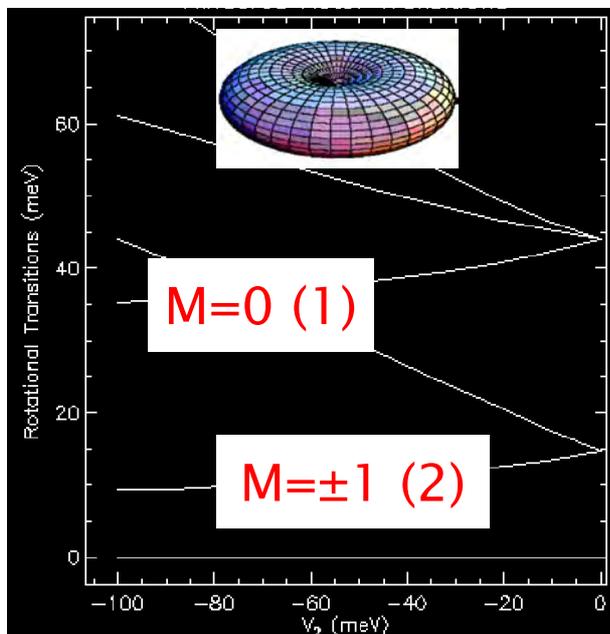


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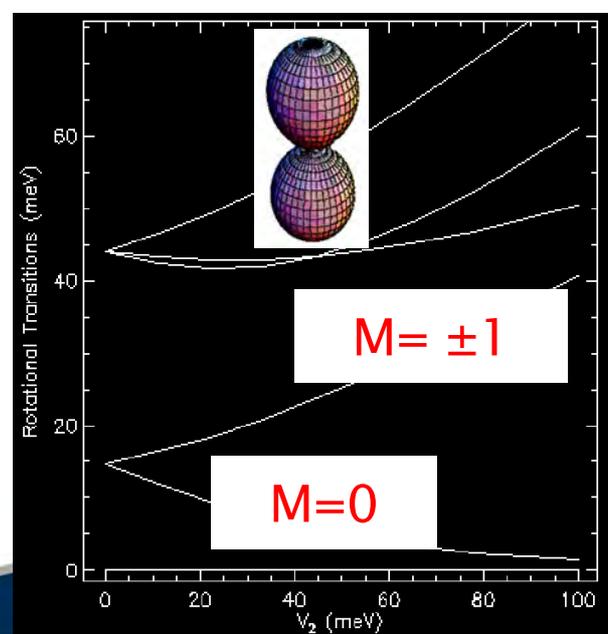
## Pinning H<sub>2</sub> along an Axis or a Plane

Lowest-order term for a homonuclear diatomic:  $V(\Theta, \phi) = V_{\Theta} \sin^2 \Theta$

### Free Rotation on Plane



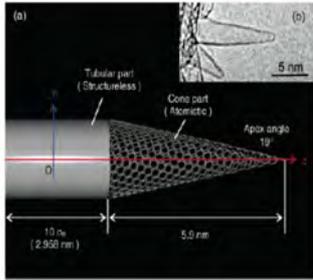
### Libration along axis



# H<sub>2</sub> Rotations in Carbon Nanostructures

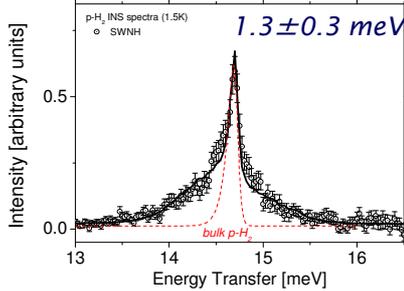
PRL 98, 215501 (2007) PHYSICAL REVIEW LETTERS week ending 25 MAY 2007

**Nature of the Bound States of Molecular Hydrogen in Carbon Nanoforms**  
 F. Fernandez-Alonso,<sup>1,4</sup> F. J. Bernice,<sup>2,1</sup> C. Cabelli,<sup>2</sup> R. O. Loth,<sup>3</sup> V. Lesn,<sup>4</sup> and M. L. Saboung<sup>4</sup>  
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 (Received 5 January 2007; published 25 May 2007)

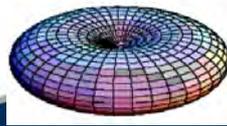
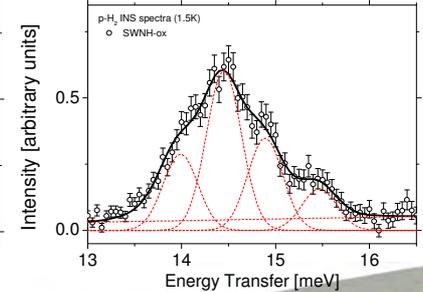
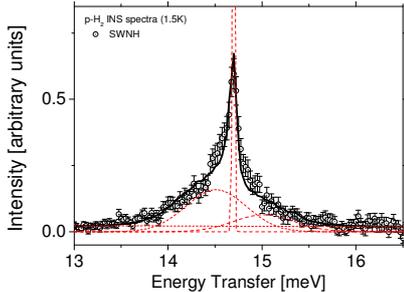
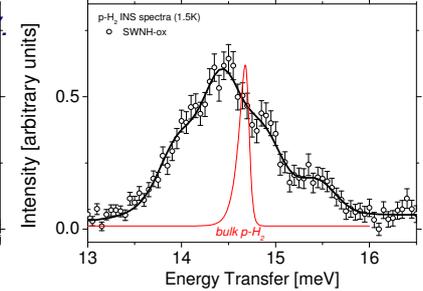


- Case of extreme confinement (surface areas > 1000 m<sup>2</sup>/g).
- Cylindrically symmetric environment: molecular alignment parallel to surface.
- Orientational barriers are a few meV (4x than nanotubes).

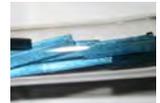
**Closed Tips (exohedral adsorption)**



**Open Tips (tube filling)**

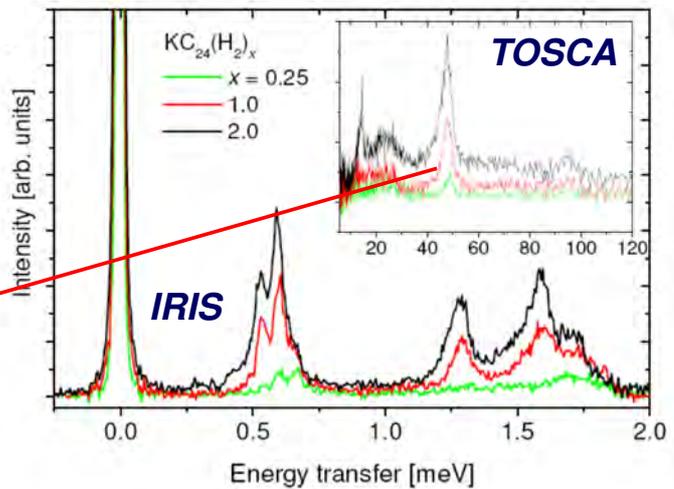
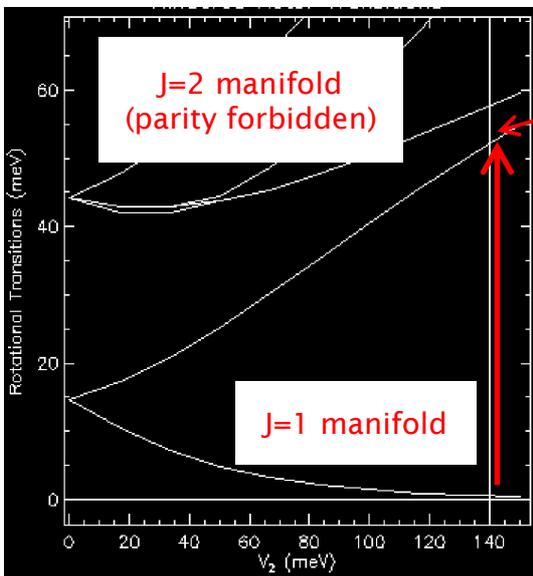


# H<sub>2</sub> in Metal-doped Carbon Nanostructures



PRL 101, 126101 (2008) PHYSICAL REVIEW LETTERS week ending 19 SEPTEMBER 2008

**Quantum Delocalization of Molecular Hydrogen in Alkali-Graphite Intercalates**  
 Arthur Lovell,<sup>1,\*</sup> Felix Fernandez-Alonso,<sup>1,\*</sup> Neal T. Skipper,<sup>2</sup> Keith Refson,<sup>3</sup>  
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 (Received 7 March 2008; published 18 September 2008)



**Orientational barriers ~30x than carbon-only materials**

**Structure & energetics**



**H<sub>2</sub> pinned along quantization axis.**

# Beyond Canonical Solids

Materials exhibiting particle diffusion within time of measurement are not 'canonical solids' per se.

Need to revisit the definition of intermediate scattering functions introduced earlier:

$$I^{dd'}(\mathbf{Q}, t) = \frac{1}{(N_d N_{d'})^{1/2}} \sum_{j \in d, j' \in d'} \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_{j'}(t)} \rangle$$

$$I_s^d(\mathbf{Q}, t) = \frac{1}{N_d} \sum_{j \in d} \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_j(t)} \rangle$$

And look at their space Fourier transforms (Van Hove correlation functions):

$$G^{dd'}(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int I^{dd'}(\mathbf{Q}, t) e^{-i\mathbf{Q} \cdot \mathbf{r}} d\mathbf{Q}$$

'self'  $G_s^d(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int I_s^d(\mathbf{Q}, t) e^{-i\mathbf{Q} \cdot \mathbf{r}} d\mathbf{Q}$



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## Van Hove Correlation Functions

Recalling the time-dependent representation of the Dirac delta-function, we can write

$$G^{dd'}(\mathbf{r}, t) = \frac{1}{(N_d N_{d'})^{1/2}} \sum_{\substack{j \in d \\ j' \in d'}} \int \langle \delta[\mathbf{r}' - \mathbf{R}_j(0)] \delta[\mathbf{r}' + \mathbf{r} - \mathbf{R}_{j'}(t)] \rangle d\mathbf{r}'$$

$$G_s^d(\mathbf{r}, t) = \frac{1}{N_d} \sum_{j \in d} \int \langle \delta[\mathbf{r}' - \mathbf{R}_j(0)] \delta[\mathbf{r}' + \mathbf{r} - \mathbf{R}_j(t)] \rangle d\mathbf{r}'$$

Physical meaning more transparent if we define particle-density operators:

$$\rho_d(\mathbf{r}, t) = \sum_{j \in d} \delta[\mathbf{r} - \mathbf{R}_j(t)] \quad \text{and in momentum space} \quad \rho_d(\mathbf{Q}, t) = \int \rho_d(\mathbf{r}, t) e^{i\mathbf{Q} \cdot \mathbf{r}} d\mathbf{r} = \sum_{j \in d} e^{i\mathbf{Q} \cdot \mathbf{R}_j(t)}$$

So that  $G^{dd'}(\mathbf{r}, t) = \frac{1}{(N_d N_{d'})^{1/2}} \int \langle \rho_d(\mathbf{r}', t) \rho_{d'}(\mathbf{r}' + \mathbf{r}, t) \rangle d\mathbf{r}'$

$$I^{dd'}(\mathbf{Q}, t) = \frac{1}{(N_d N_{d'})^{1/2}} \langle \rho_d(-\mathbf{Q}, 0) \rho_{d'}(\mathbf{Q}, t) \rangle$$



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# Pair Distribution Functions

Define a pair-density function  $\rho^{dd'}(\mathbf{r}) = \left(\frac{N_d}{N_{d'}}\right) \sum_{\substack{j \in d' \\ (0 \in d)}} \langle \delta[\mathbf{r}' - \mathbf{R}_0(0) + \mathbf{R}_j(0)] \rangle$

That is, the average instantaneous density of particles of type  $d'$  with respect to one atom of type  $d$  sitting at an (arbitrary) origin.

Then  $G^{dd'}(\mathbf{r}, 0) = \delta_{dd'}\delta(\mathbf{r}) + \left(\frac{N_d}{N_{d'}}\right)\rho^{dd'}(\mathbf{r})$  and  $G_s^d(\mathbf{r}, 0) = \delta(\mathbf{r})$

From which we define structure factors as energy integrals of  $S(\mathbf{Q}, E)$

$$S^{dd'}(\mathbf{Q}) = \int_{-\infty}^{\infty} S_c^{dd'}(\mathbf{Q}, E) dE = I^{dd'}(\mathbf{Q}, 0)$$

$$\int S^{dd'}(\mathbf{Q}) e^{-i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{Q} = \int I^{dd'}(\mathbf{Q}, 0) e^{-i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{Q} = (2\pi)^3 \left[ \delta_{dd'}\delta(\mathbf{r}) + \left(\frac{N_d}{N_{d'}}\right)^{1/2} \rho^{dd'}(\mathbf{r}) \right] \xrightarrow{\text{coherent}} \frac{1}{(2\pi)^3} \int [S^{dd'}(\mathbf{Q}) - \delta_{dd'}] e^{-i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{Q} = \left(\frac{N_d}{N_{d'}}\right)^{1/2} \rho^{dd'}(\mathbf{r})$$

$$\int_{-\infty}^{\infty} S_i^d(\mathbf{Q}, E) dE = I_s^d(\mathbf{Q}, 0) = 1 \quad \text{incoherent}$$

## Total Scattering

$$S^{dd'}(\mathbf{Q}) = \int_{-\infty}^{\infty} S_c^{dd'}(\mathbf{Q}, E) dE = I^{dd'}(\mathbf{Q}, 0) \quad \text{Structure factors sought after in a so-called 'total-scattering experiment'}$$

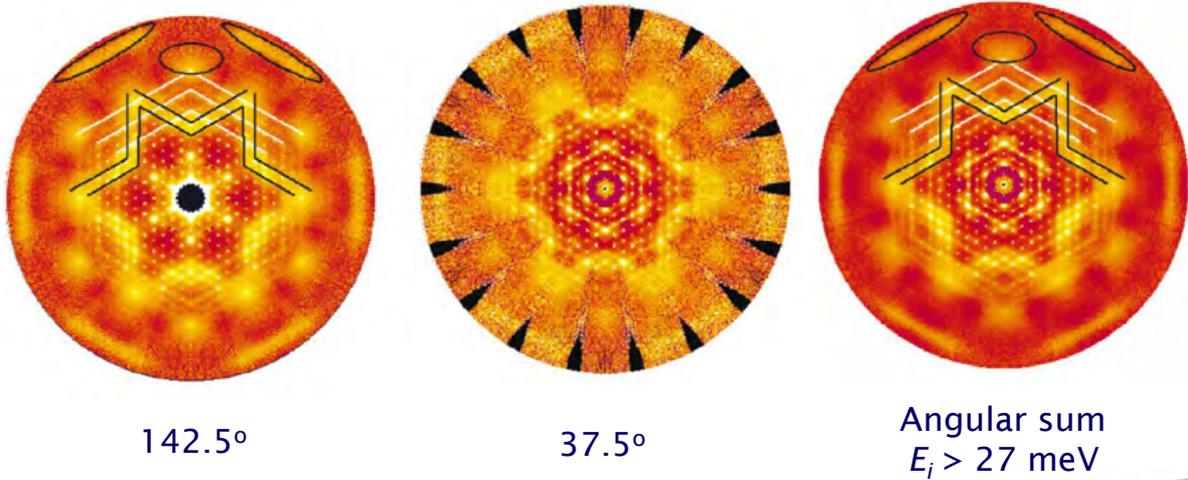
Relationship between differential cross section (measured) and structure factors

$$\left. \frac{d\sigma}{d\Omega} \right|_{\mathbf{Q}} = \int_{-\infty}^{E_i} \frac{d^2\sigma}{d\Omega dE_f} dE_f \approx \sum_{dd'} c_d^{1/2} c_{d'}^{1/2} \overline{b_d^* b_{d'}} S^{dd'}(\mathbf{Q}) + \sum_d c_d \frac{\sigma_i^d}{4\pi}$$

$$= \sum_{dd'} c_d^{1/2} c_{d'}^{1/2} \overline{b_d^* b_{d'}} [S^{dd'}(\mathbf{Q}) - \delta_{dd'}] + \sum_d c_d \frac{\sigma_i^d}{4\pi}$$

# From Order to Disorder: Diffuse Scattering

Reciprocal-space sections  $hk0$  of single-crystal D-benzyl



Intensity under and between Bragg peaks: static & dynamical disorder.

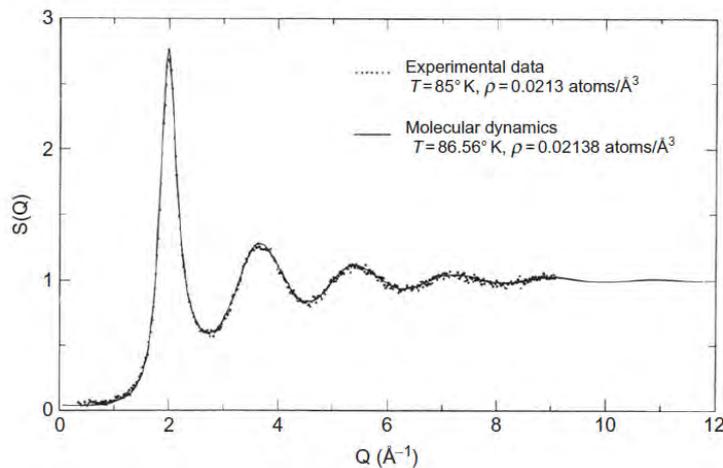


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## The Structure of Liquids & Glasses

$$S^{dd}(\mathbf{Q}) = \int_{-\infty}^{\infty} S_c^{dd'}(\mathbf{Q}, E) dE = I^{dd}(\mathbf{Q}, 0)$$

Information on instantaneous (ensemble-averaged) positions



For many more examples, see disordered materials database

<http://www.isis.stfc.ac.uk/groups/disordered-materials/database/database-of-neutron-diffraction-data6204.html>

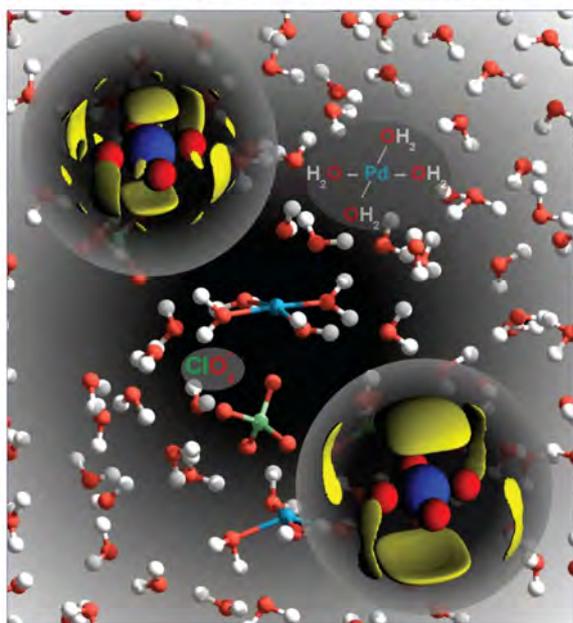


# Heavy Metals in Solution: From Catalysis to Pharmacy

January 18, 2012  
Volume 134  
Number 2  
pubs.acs.org/JACS

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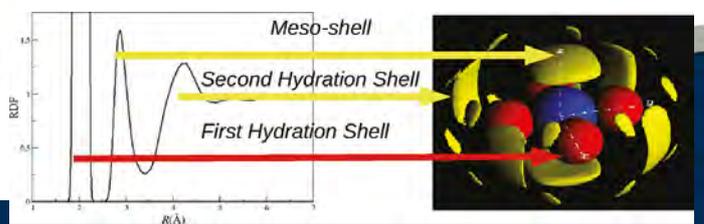
## Axial Structure of the Pd(II) Aqua Ion in Solution

Daniel T. Bowron,<sup>†</sup> Elizabeth C. Beret,<sup>†||</sup> Eloisa Martin-Zamora,<sup>§</sup> Alan K. Soper,<sup>†</sup> and Enrique Sánchez Marcos<sup>\*,†</sup>

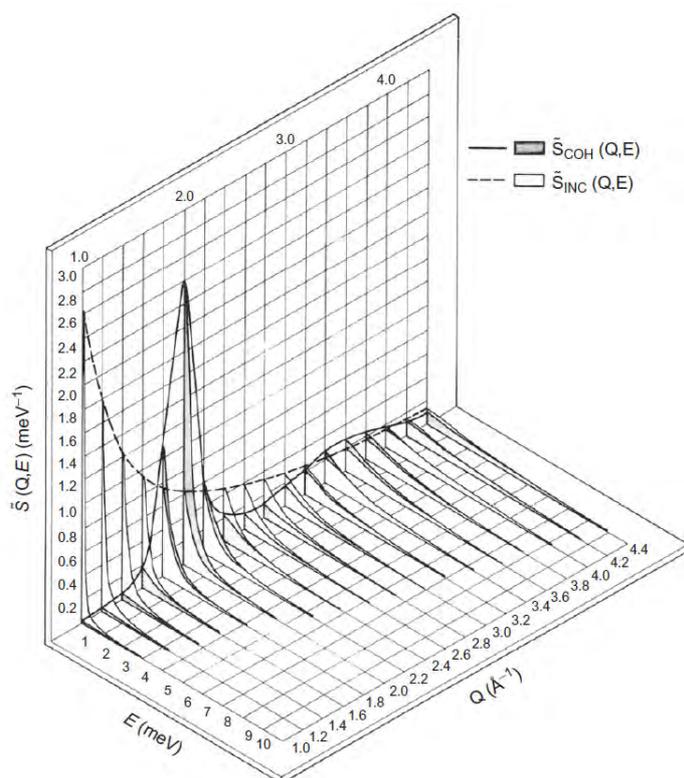
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- *Solution structure of Pt(II) and Pd(II) ions of relevance to homogeneous catalysis and pharmacological activity of drugs.*
- *Pd-O axial coordination related to reactivity.*
- *What neutrons (with X-rays) tell us:*
  - *It is located between 1<sup>st</sup> and 2<sup>nd</sup> hydration shells*
  - *Strong competition between solvent and counterion to occupy this region.*



## Associated Dynamic Structure Factor



No 'elastic' scattering

Incoherent:  $S(Q, E=0)$  decreases due to increase in energy widths (direct measure of diffusion)

$$\int_{-\infty}^{\infty} S_i^d(Q, E) dE = I_s^d(Q, 0) = 1$$

Coherent: oscillatory (density correlations), de Gennes narrowing.

$$\frac{1}{(2\pi)^3} \int [S^{dd}(\mathbf{Q}) - \delta_{dd}] e^{-i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{Q} = \left(\frac{N_d}{N_{d'}}\right)^{1/2} \rho^{dd'}(\mathbf{r})$$



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# Properties of the Dynamic Structure Factor

It is real (as any observable):  $S_c^{dd'}(\mathbf{Q}, E) = S_c^{dd'*}(\mathbf{Q}, E),$

$$S_i^d(\mathbf{Q}, E) = S_i^{d*}(\mathbf{Q}, E).$$

Must satisfy detailed balance:  $S_c^{dd'}(\mathbf{Q}, E) = e^{E/k_B T} S_c^{dd'}(-\mathbf{Q}, -E),$  *Transition probabilities are same in either direction*

$$S_i^d(\mathbf{Q}, E) = e^{E/k_B T} S_i^d(-\mathbf{Q}, -E).$$

Zeroeth moment:  $\int_{-\infty}^{\infty} S_c^{dd'}(\mathbf{Q}, E) dE = S^{dd'}(\mathbf{Q})$  and  $\int_{-\infty}^{\infty} S_i^d(\mathbf{Q}, E) dE = 1$

First moment:  $\int_{-\infty}^{\infty} S_c^{dd'}(\mathbf{Q}, E) E dE = \frac{\hbar^2 Q^2}{2M_d} \delta_{dd'}$  and  $\int_{-\infty}^{\infty} S_i^d(\mathbf{Q}, E) E dE = \frac{\hbar^2 Q^2}{2M_d}$

Second moment:  $\int_{-\infty}^{\infty} S_i^d(\mathbf{Q}, E) E^2 dE = \left(\frac{\hbar^2 Q^2}{2M_d}\right)^2 + \hbar^2 Q^2 \langle (\mathbf{v} \cdot \hat{\mathbf{Q}})^2 \rangle$



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## Total Scattering and Static Approximation

For energy changes in target much smaller than the incident energy:

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N} \frac{k_f}{k_i} \sum_{\tau_i} p_{\tau_i} \left| \sum_{\tau_f} \sum_j b_j \langle \tau_f | e^{i\mathbf{Q} \cdot \mathbf{R}_j} | \tau_i \rangle \right|^2 \delta(E + E_{\tau_i} - E_{\tau_f}) \delta(E)$$

And the differential cross section:

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \int_{-\infty}^{E_i} \frac{d^2\sigma}{d\Omega dE_f} dE_f = \frac{1}{N} \sum_{\tau_i} p_{\tau_i} \sum_{j \in d, j' \in d'} \overline{b_j^* b_{j'}} \langle e^{-i\mathbf{Q}_0 \cdot (\mathbf{R}_j - \mathbf{R}_{j'})} \rangle \\ &= \sum_{dd'} c_d^{1/2} c_{d'}^{1/2} \overline{b_d^* b_{d'}} S^{dd'}(\mathbf{Q}_0) + \sum_d c_d \frac{\sigma_i^d}{4\pi}. \end{aligned}$$

Common expression to analyse data (wrong first moment though!).

Good approximation for  $E_i \gg \hbar^2 Q^2 / 2M$  and  $k_i \gg Q/A^{1/2}$

Best done with eV (not thermal) neutrons.



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# Free Particles and Impulse Approximation

For N independent (and structureless) particles in a volume V, translational wavefunction:

$$|\tau\rangle = \frac{1}{V^{1/2}} e^{i\mathbf{p}\cdot\mathbf{R}/\hbar}$$

Dynamic structure factor:

$$\langle \tau_f | e^{i\mathbf{Q}\cdot\mathbf{R}} | \tau_i \rangle = \delta_{\mathbf{Q}, (\mathbf{p}_f - \mathbf{p}_i)/\hbar}$$

$$E_{\tau_f} - E_{\tau_i} = \frac{\hbar^2}{2M} (p_f^2 - p_i^2) = \frac{\hbar^2}{2M} \left( Q^2 + \frac{2\mathbf{Q}\cdot\mathbf{p}_i}{\hbar} \right)$$



$$S(\mathbf{Q}, E) = \frac{1}{N} \sum_{\tau_i} p_{\tau_i} \sum_{\tau_f} \langle \tau_f | e^{i\mathbf{Q}\cdot\mathbf{R}} | \tau_i \rangle^2 \delta(E + E_{\tau_i} - E_{\tau_f})$$

$$= \sum_{\mathbf{p}_i} n(\mathbf{p}_i) \delta\left(E - \frac{\hbar^2 Q^2}{2M} - \frac{\hbar \mathbf{Q}\cdot\mathbf{p}_i}{M}\right)$$

Properties:

Zeroth moment  $\sum_{\mathbf{p}_i} n(\mathbf{p}_i) = 1$

First moment (recoil energy)

$$E_R = \frac{\hbar^2 Q^2}{2M}$$

Second moment

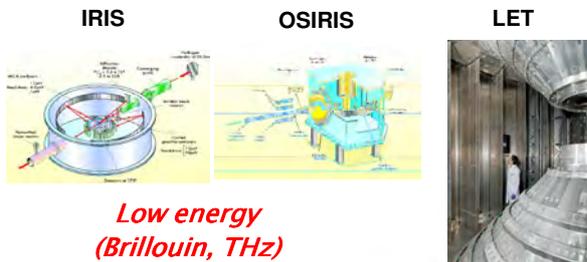
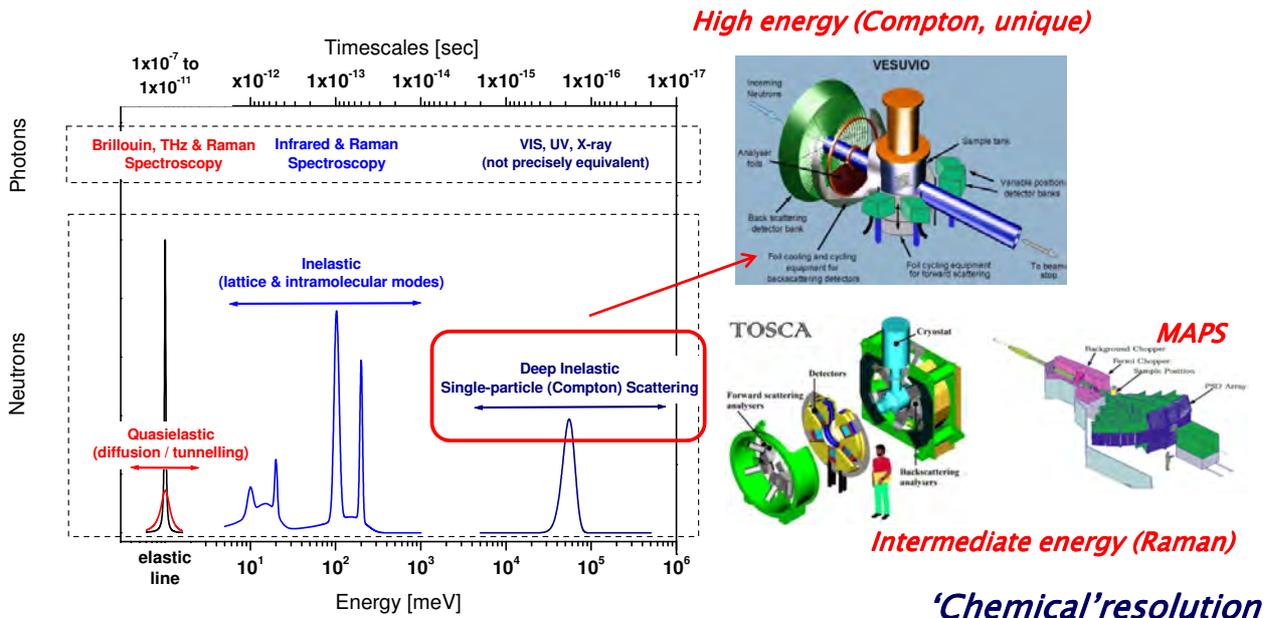
$$E_R^2 + 2E_R \sum_{\mathbf{p}_i} n(\mathbf{p}_i) \frac{(\mathbf{p}_i \cdot \mathbf{Q})^2}{M} = E_R^2 + \frac{2E_R \langle p_i^2 \rangle}{3M}$$

All three satisfied

Impulse approximation  
(measures momentum distribution)



## Above Molecular Vibrations: Atoms



Simultaneous diffraction  
Direct link to theory



# Neutron Compton Scattering

Measured Compton profile:

$$J(\hat{Q}, y) = \hbar \int n(\mathbf{p}) \delta(\hbar y - \mathbf{p} \cdot \hat{Q}) d\mathbf{p}$$

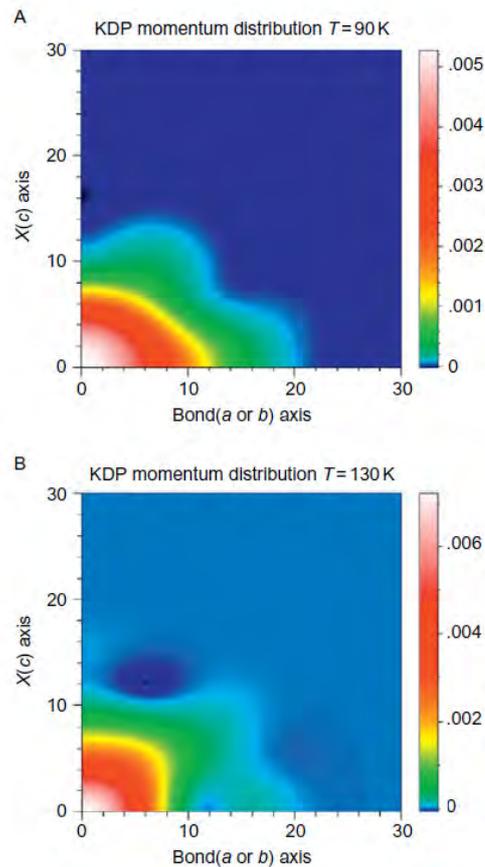
Three-dimensional momentum distribution:

$$n(\mathbf{p}) = \frac{1}{2\pi\hbar^3} \int d\mathbf{r} d\mathbf{r}' e^{i/\hbar(\mathbf{p} \cdot (\mathbf{r} - \mathbf{r}'))} \frac{\rho(\mathbf{r}, \mathbf{r}')}{Z}$$

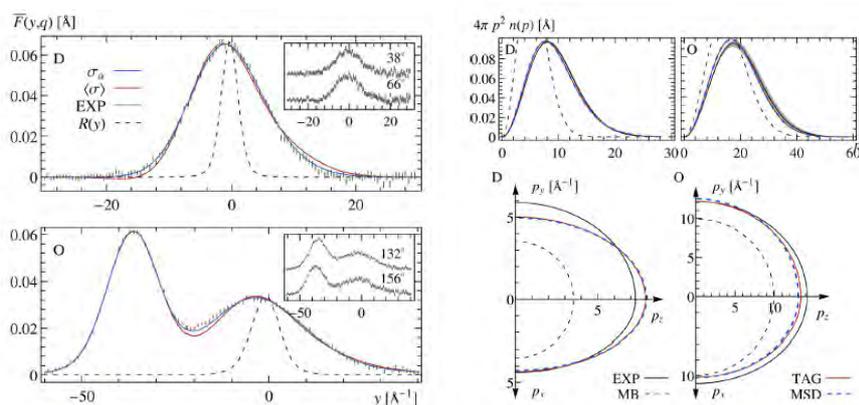
High-Qs required, atomic recoil.

*In principle, can measure the single-particle wavefunction.*

VESUVIO at ISIS



## Nuclear Quantum Effects and the Melting of Heavy Water



Physical Chemistry Letters

**Direct Measurement of Competing Quantum Effects on the Kinetic Energy of Heavy Water upon Melting**

Corrado Rovelli,<sup>1</sup> Michele Ceriotti,<sup>2\*</sup> David R. Manolopoulos,<sup>3</sup> Claudia Pasquini,<sup>1,4</sup> Roberto Serra,<sup>5\*</sup> and Carlo Andreani<sup>6</sup>

<sup>1</sup>Department of Chemistry, University of Cambridge, 120Z, Lensfield Road, Cambridge CB2 3RQ, United Kingdom; <sup>2</sup>Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3PS, United Kingdom; <sup>3</sup>Department of Chemistry, University of Cambridge, 120Z, Lensfield Road, Cambridge CB2 3RQ, United Kingdom; <sup>4</sup>Department of Chemistry, University of Cambridge, 120Z, Lensfield Road, Cambridge CB2 3RQ, United Kingdom; <sup>5</sup>Department of Chemistry, University of Cambridge, 120Z, Lensfield Road, Cambridge CB2 3RQ, United Kingdom; <sup>6</sup>Department of Chemistry, University of Cambridge, 120Z, Lensfield Road, Cambridge CB2 3RQ, United Kingdom

**ABSTRACT:** Even at room temperature, quantum mechanics plays a major role in determining the quantum behavior of light nuclei, changing significantly the value of physical quantities such as the heat capacity. However, their detailed description is still strongly hindered by the computational cost of the many-body Schrödinger equation. We report here a direct measurement of the kinetic energy of heavy water upon melting, which is compared to the results of the many-body Schrödinger equation. The present study is the first experimental determination of the kinetic energy of heavy water upon melting, which is compared to the results of the many-body Schrödinger equation. The present study is the first experimental determination of the kinetic energy of heavy water upon melting, which is compared to the results of the many-body Schrödinger equation. The present study is the first experimental determination of the kinetic energy of heavy water upon melting, which is compared to the results of the many-body Schrödinger equation.

**KEYWORDS:** Liquid, Chemical and Physical Processes in Liquids

**INTRODUCTION:** The structure and dynamics of liquid water are directly influenced by quantum mechanics, not only at the level of the hydrogen and oxygen nuclei, but also at the level of the electron system. Indeed, nuclear quantum effects (NQEs) include zero-point energy, tunneling, and the formation of a protonic network, which are not captured by the classical description of water. The present study is the first experimental determination of the kinetic energy of heavy water upon melting, which is compared to the results of the many-body Schrödinger equation. The present study is the first experimental determination of the kinetic energy of heavy water upon melting, which is compared to the results of the many-body Schrödinger equation.

- Intra and intramolecular nuclear quantum dynamics of D and O: detailed line shape analysis gives nuclear momentum distribution (not just width).
- Use of state-of-art first-principles methods (PIMD) to be quantitative.
- Direct benchmark of theoretical methods.

# Beyond Structure: Nuclear Quantum Dynamics on VESUVIO

PHYSICAL REVIEW B RE. 174306 (2010)

Nuclear quantum effects in *ab initio* dynamics: Theory and experiments for lithium imide

Michela Cerretti,<sup>1a</sup> Giacomo Miceli,<sup>2a</sup> Antonio Pietropaolo,<sup>3</sup> Daniela Cristofolini,<sup>4</sup> Angeloskaido Nale,<sup>2</sup> Michele Catti,<sup>2</sup> Marco Bernasconi,<sup>2</sup> and Michele Parrinello<sup>1a</sup>

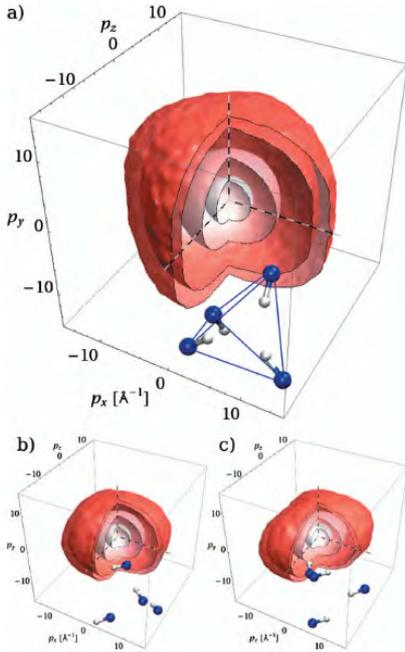
<sup>1</sup>Computational Science, D-CHAB, ETH Zurich, USI Campus, via G. Baffi 13, CH-6900 Lugano, Switzerland

<sup>2</sup>Department of Materials Science, Università di Milano-Bicocca, via R. Cozzi 53, I-20125 Milano, Italy

<sup>3</sup>INFM UdR Roma Tor Vergata and Centro NAST, Università degli Studi di Roma Tor Vergata, via della Ricerca Scientifica 1, I-00133 Roma, Italy

<sup>4</sup>Istituto dei Sistemi Complessi, CNR, via Madonna del Piano 10, 50019 Firenze, Italy

(Received 15 September 2010; revised manuscript received 28 October 2010; published 23 November 2010)



- Direct access to proton momentum distributions with neutrons.
- Quantum effects essential to explain material properties.
- Extension to other masses of technological interest (e.g., Li, O).

Chemical Physics Letters 518 (2011) 1–6



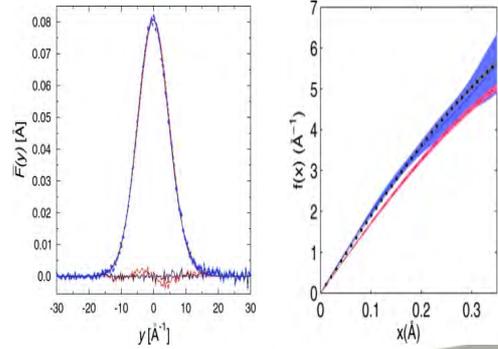
FRONTIERS ARTICLE

Ground state proton dynamics in stable phases of water

C. Andreani<sup>a,\*</sup>, D. Colognesi<sup>b</sup>, A. Pietropaolo<sup>a</sup>, R. Senesi<sup>a</sup>

<sup>a</sup>Università degli Studi di Roma Tor Vergata, Dipartimento di Fisica and Centro NAST, Via della Ricerca Scientifica 1, 00133 Roma, Italy

<sup>b</sup>Consiglio Nazionale delle Ricerche, Istituto dei Sistemi Complessi, Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy



ETH

Eidgenössische Technische Hochschule Zürich  
Swiss Federal Institute of Technology Zürich



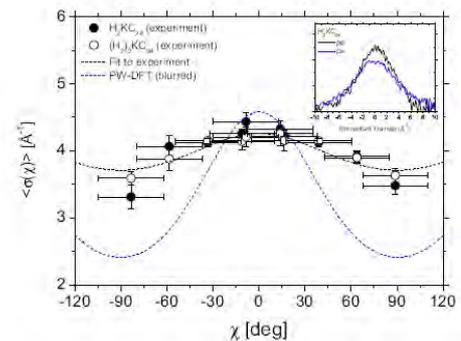
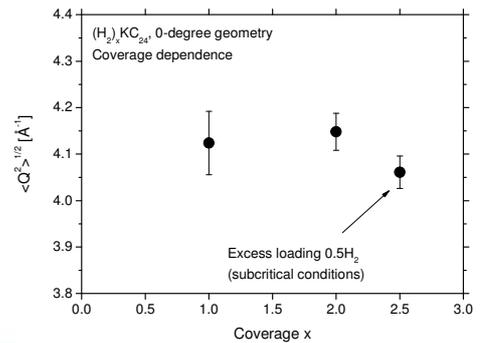
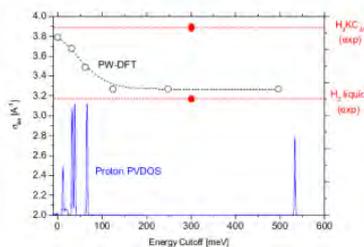
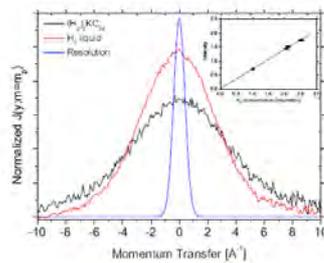
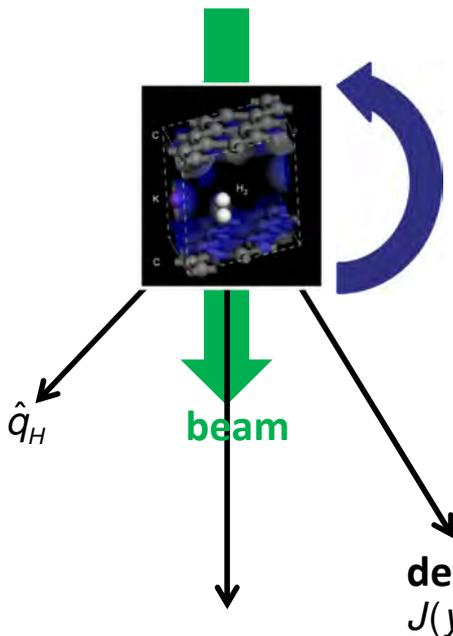
Science & Technology Facilities Council  
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This journal is © The Royal Society of Chemistry 2011

Faraday Discuss., 2011, 151, 171–197

## Probing the binding and spatial arrangement of molecular hydrogen in porous hosts *via* neutron Compton scattering

Maciej Krzystyniak,<sup>ab</sup> Mark A. Adams,<sup>a</sup> Arthur Lovell,<sup>ac</sup> Neal T. Skipper,<sup>c</sup> Stephen M. Bennington,<sup>ac</sup> Jerry Mayers<sup>a</sup> and Felix Fernandez-Alonso<sup>abc</sup>

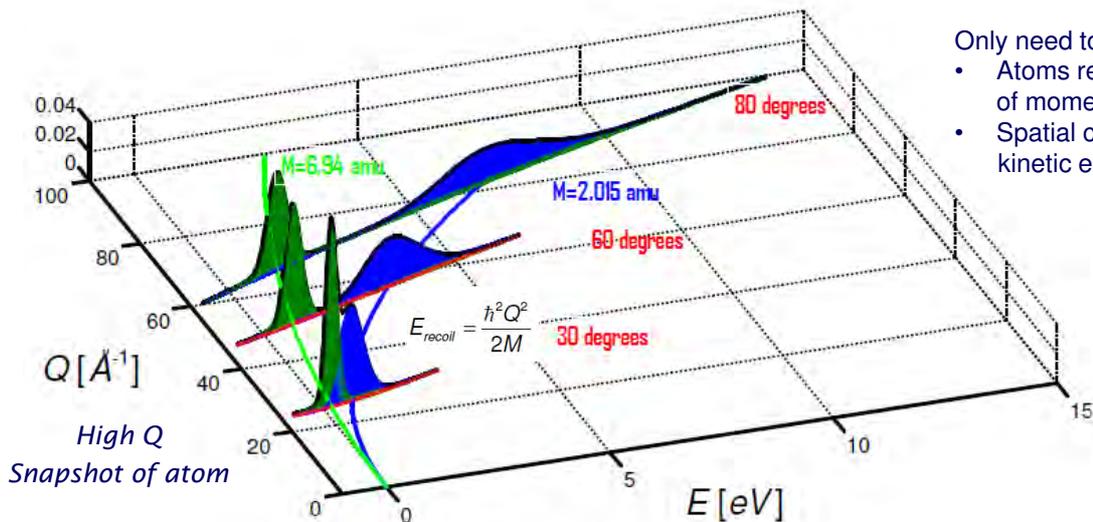


- Calculations to dissect recoil profiles.
- Access to adsorbate-adsorbate interactions.
- Direct probe of molecular alignment.



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# MASS-selective Neutron SpEctroscopy - MANSE



Only need to know that:

- Atoms recoil (conservation of momentum).
- Spatial confinement raises kinetic energy (ZPE).

## Atomic Quantum Thermometry:

- Mass selectivity from atomic recoil (kinematics).
- Width of recoil peaks: kinetic energy or 'chemical temperature' of an atom (binding).
- Already demonstrated up to 20 amu.

PHYSICAL REVIEW B 88, 184304 (2013)

Mass-selective neutron spectroscopy of lithium hydride and deuteride: Experimental assessment of the harmonic and impulse approximations

Maciej Krzys̄ymiak<sup>1</sup> and Selena E. Richards

<sup>1</sup>School of Science and Technology, Nottingham Trent University, Clifton campus, Nottingham NG11 8NS, United Kingdom and ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom

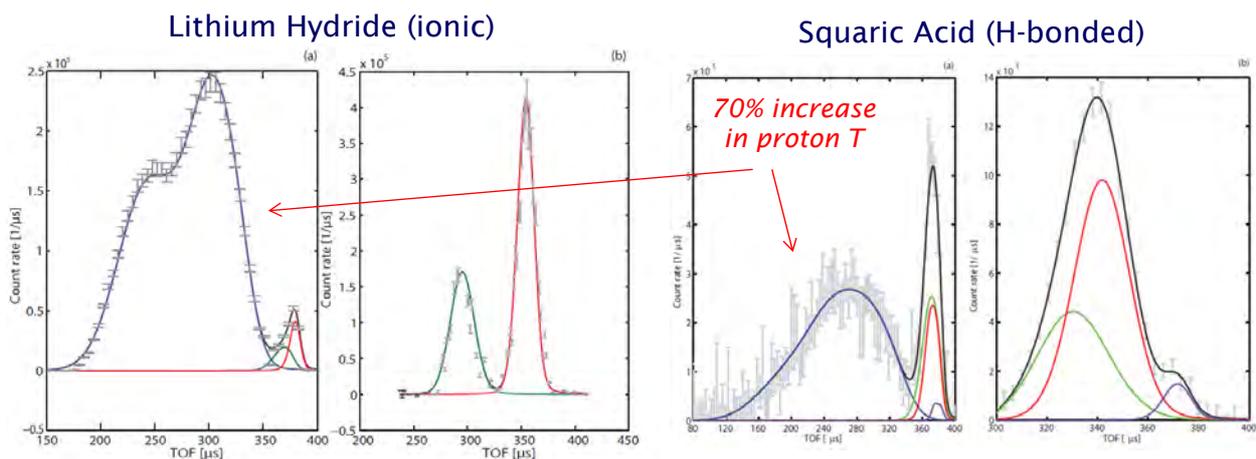
Andrew G. Seal and Felix Fernandez-Alonso<sup>1</sup>

<sup>1</sup>ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom (Received 26 July 2013; revised manuscript received 22 October 2013; published 19 November 2013)



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## MANSE: Unique Chemical Information from Recoil Data



Journal of Physics: Conference Series 571 (2014) 012002

## Mass-selective Neutron Spectroscopy Beyond the Proton

M. Krzys̄ymiak<sup>1,2</sup>, A.G. Seal<sup>1</sup>, S.E. Richards<sup>1,2</sup>, M.J. Gutmann<sup>1</sup>, and F. Fernandez-Alonso<sup>1,3</sup>

<sup>1</sup> ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom

<sup>2</sup> School of Science and Technology, Nottingham Trent University, Clifton Campus, Nottingham NG11 8NS, United Kingdom

<sup>3</sup> Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

- Two modes of operation (similar to xtallography):
  - Coarse resolution (forward scattering, H)
  - High resolution (backscattering)
- Peak integration: head count with sub-ppm sensitivity for H.
- Sensitive to chemical environment (temperature) around an atom, a consequence of binding forces and dimensionality of bonding network
- Mass resolution could be improved further.



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# Fast-neutron Detector Development



## Below Molecular Vibrations: Atomic & Molecular Transport



# Stochastic Diffusion & Relaxation

No well-defined equilibrium sites – use Van Hove formalism

Translational diffusion:

$$G_s(\mathbf{r}, t) = [4\pi\gamma(t)]^{-3/2} \exp[-r^2/4\gamma(t)]$$

*Gaussian Approximation*

Mean-square displacement:

$$\gamma(t) = \frac{1}{6} \langle r^2(t) \rangle = \frac{1}{6} \int r^2 G_s(\mathbf{r}, t) d\mathbf{r}$$

Intermediate scattering function:

$$G_s^d(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int I_s^d(\mathbf{Q}, t) e^{-i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{Q}$$

$$I_s(\mathbf{Q}, t) = \exp[-Q^2\gamma(t)]$$

MSD defines problem

Gas  $\gamma(t) = \frac{1}{6} \langle v^2 \rangle t^2 = \frac{k_B T}{2M} t^2$



$$S_i(\mathbf{Q}, E) = \left[ \frac{M}{4\pi k_B T \hbar^2 Q^2} \right]^{1/2} \exp\left[ -\frac{ME^2}{2k_B T \hbar^2 Q^2} \right]$$

Liquid  $\gamma(t) = Dt$



$$S_i(\mathbf{Q}, E) = \frac{1}{\pi E^2 + (\hbar D Q^2)^2}$$



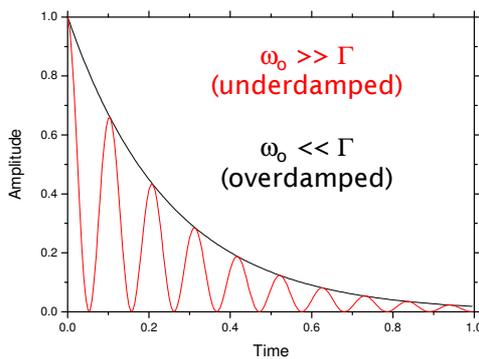
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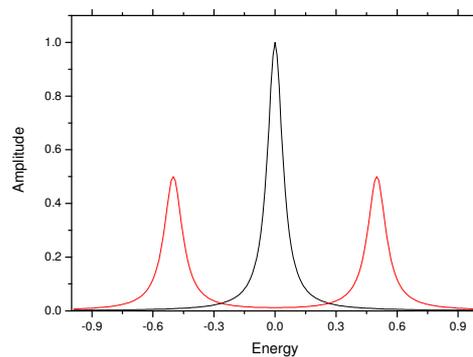
## “Inelastic” vs “Quasielastic”

Spectral peaks characterized by a frequency  $\omega_0$  and damping  $\Gamma$  (decay)

Time Domain



Energy (frequency) Domain



- Underdamped motions: ‘proper’ spectroscopic peaks, e.g.,  $H_2$  molecule rotations & vibrations.
- Overdamped motions: not enough time to define period of oscillation
  - Centered at zero frequencies (elastic scattering of probe – e.g., neutrons).
  - Broadening proportional to damping.
  - Example: diffusion in a crowded environment.

**Note: transition from ‘INS’ to ‘QENS’ is continuous (e.g., with temperature)**



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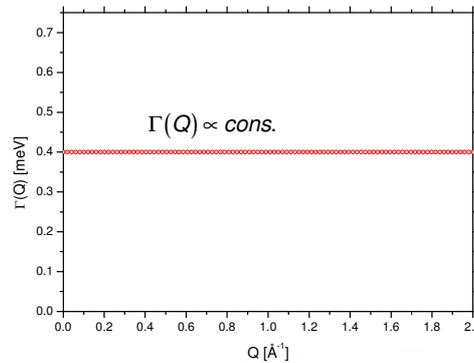
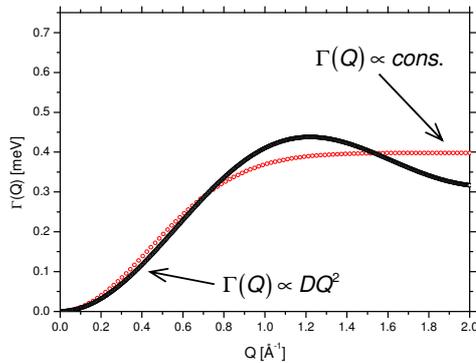
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# The Added Dimension (Neutrons Only)

If neutron  $Q$  range matches characteristic length scales of motion  $R$  ( $Q \sim 1/R$ ), then QENS broadening  $\Gamma$  will be sensitive to it.

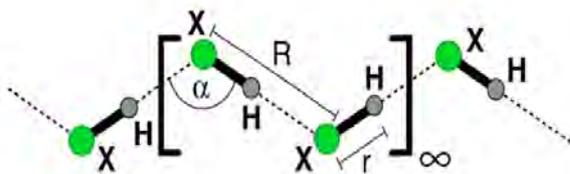
Two limits of interest:

- Translational diffusion: motion of molecular center of mass.
- Localized diffusion: motion about the molecular CM



Lorentzian line shape: 
$$\frac{\Gamma(Q)}{E^2 + \Gamma^2(Q)}$$

## Stochastic Motions in the Simplest Hydrogen-bonded Liquid

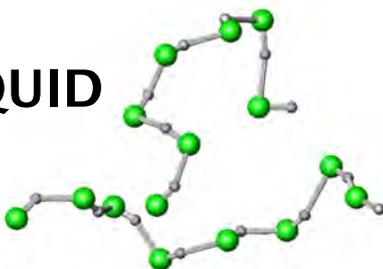


**SOLID**

- Quintessential H-bonded liquid.
  - Linear geometry ( $R_{HF} = 0.94 \text{ \AA}$ ).
  - Strongest hydrogen bond ( $\sim 250 \text{ meV}$ ).

• Abundant theoretical and simulation studies.

**LIQUID**



• Very few experiments (very aggressive material)

Snapshot of liquid HF from computer simulation. The length of the  $(HF)_n$  chains displays a strong temperature dependence

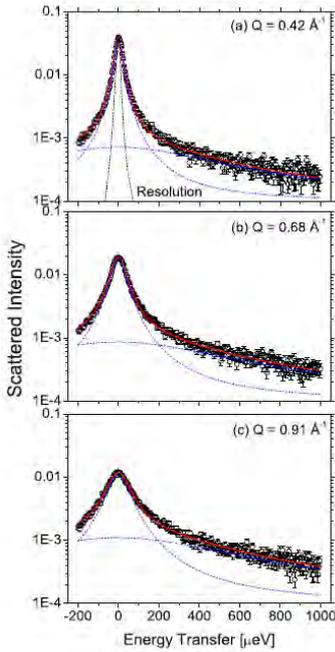
# Dynamics of Liquids: Hydrogen Fluoride

PRL 98, 077801 (2007) PHYSICAL REVIEW LETTERS week ending 16 FEBRUARY 2007

## Observation of Fractional Stokes-Einstein Behavior in the Simplest Hydrogen-Bonded Liquid

F. Fernandez-Alonso,<sup>1,\*</sup> F. J. Bermejo,<sup>2,1</sup> S. E. McLean,<sup>1</sup> J. F. C. Turner,<sup>2</sup> J. J. Molaison,<sup>2</sup> and K. W. Herwig<sup>2</sup>  
<sup>1</sup>ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom  
<sup>2</sup>CSIC-Instituto Estructural de la Materia & Department of Electricity and Electronics, University Basque Country, P.O. Box 644, Bilbao 48960, Spain  
<sup>3</sup>Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996-1500, USA  
<sup>4</sup>Spallation Neutron Source, Oak Ridge National Laboratory, Scarborough Road, Oak Ridge, Tennessee 37830, USA  
 (Received 24 October 2006; published 14 February 2007)

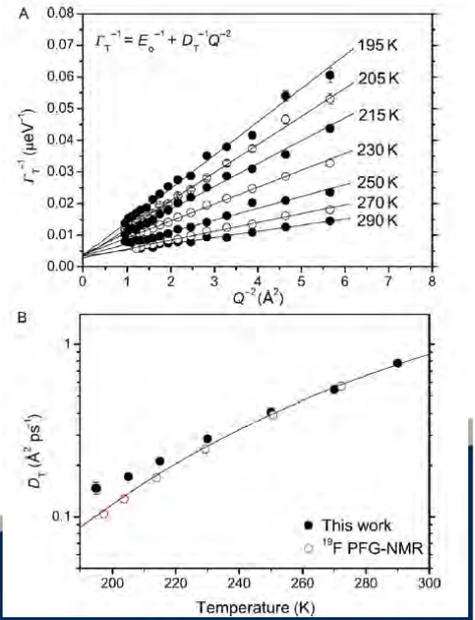
### 'Quasielastic' data



$$\left[ \frac{1}{\pi E^2 + \Gamma_T(Q)} \right]$$

$$\Gamma_T(Q) = \hbar \left[ \frac{D_T Q^2}{1 + D_T Q^2 \tau_0} \right]$$

### Spectral Analysis



## Constructing the Dynamic Structure Factor

Decoupled CM trans and internal rotations:

$$I_S(Q, t) = I_T(Q, t) I_R(Q, t)$$

Associated dynamic structure factors:

$$S_i(Q, E) = S_T(Q, E) \otimes S_R(Q, E)$$

CM translations and cage vibrations:

$$S_T(Q, E) = e^{-Q^2 \langle u^2 \rangle / 3} \left[ \frac{1}{\pi E^2 + \Gamma_T(Q)^2} \right]$$

Internal rotations:

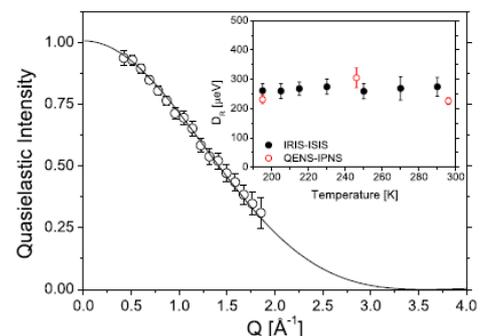
$$S_R(Q, E) = j_0^2(QR) \delta(E) + \sum_{l>0} (2l+1) j_l^2(QR) \left[ \frac{1}{\pi E^2 + (l(l+1)\Gamma_R)^2} \right]$$

Total (incoherent) dynamic structure factor:

$$S_i(Q, E) = e^{-Q^2 \langle u^2 \rangle / 3} \left\{ j_0^2(QR) \left[ \frac{1}{\pi E^2 + \Gamma_T(Q)^2} \right] + \sum_{l>0} (2l+1) j_l^2(QR) \left[ \frac{1}{\pi E^2 + \Gamma_{RT}(l; Q)^2} \right] \right\}$$

$$\Gamma_{RT}(l; Q) = \Gamma_T(Q) + l(l+1)\Gamma_R$$

Simultaneous information on molecular shape and motions



$$S_i(Q, E) = e^{-Q^2 \langle u^2 \rangle / 3} \left\{ j_0^2(QR) \left[ \frac{1 - \Gamma_T(Q)}{\pi E^2 + \Gamma_T(Q)^2} \right] + \sum_{l>0} (2l+1) j_l^2(QR) \left[ \frac{1 - \Gamma_{RT}(l; Q)}{\pi E^2 + \Gamma_{RT}^2(l; Q)} \right] \right\}$$



## Frozen Translations

$$S_T(Q, E) \rightarrow e^{-Q^2 \langle u^2 \rangle / 3} \delta(E)$$

$$S_i(Q, E) = e^{-Q^2 \langle u^2 \rangle / 3} \left\{ j_0^2(QR) \delta(E) + \sum_{l>0} (2l+1) j_l^2(QR) \left[ \frac{1 - l(l+1)\Gamma_R}{\pi E^2 + (l(l+1)\Gamma_R)^2} \right] \right\}$$

*Elastic term*

*Elastic scattering always originates if there is a finite probability to return to same place (fixed CM or spatial confinement)*

*Is this a canonical solid?*



# Disordered Solids

(important applications to proton, ionic conductors)

Basic picture: discontinuous jumps across sites.

Basic rate equation: 
$$\frac{\partial}{\partial t} P(\mathbf{r}, t) = \frac{1}{n\tau} \sum_{k=1}^n [P(\mathbf{r} + \mathbf{d}_k, t) - P(\mathbf{r}, t)]$$

with jump-distance  $d$  and residence time  $\tau$

With boundary condition  $P(\mathbf{r}, 0) = \delta(\mathbf{r})$  we have  $G_s^D(\mathbf{r}, t) = P(\mathbf{r}, t)$

Leading to 
$$I_s^D(\mathbf{Q}, t) = \exp\left[-\frac{\Gamma(\mathbf{Q})}{\hbar} t\right] \quad S_i^D(\mathbf{Q}, E) = \frac{1}{\pi E^2 + \Gamma^2(\mathbf{Q})}$$

$$\Gamma(\mathbf{Q}) = \frac{\hbar}{\tau n} \sum_{k=1}^n [1 - e^{-i\mathbf{Q} \cdot \mathbf{d}_k}]$$

For a cubic lattice with lattice parameter  $a$

$$\Gamma(\mathbf{Q}) = \frac{\hbar}{3\tau} (3 - \cos Q_x a - \cos Q_y a - \cos Q_z a)$$

And at low  $Q$

$$\Gamma(Q) = \hbar \frac{Q^2 a^2}{6\tau} \equiv \hbar D Q^2$$



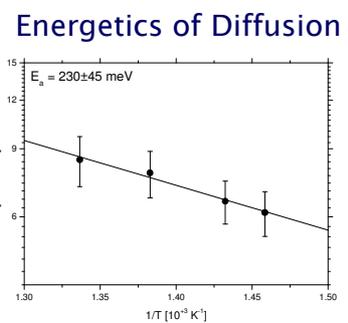
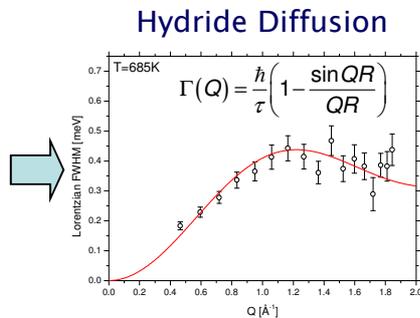
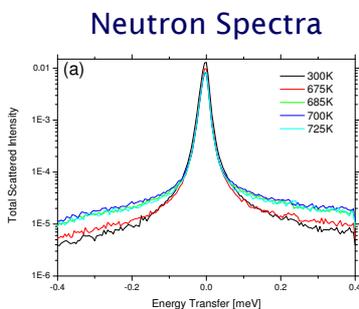
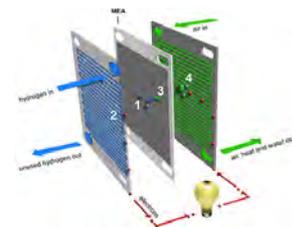
## Mass & Charge Transport: Fuel-cell & Battery Materials

COMMUNICATION

Adv. Mater. 2006, 18, 3304–3308

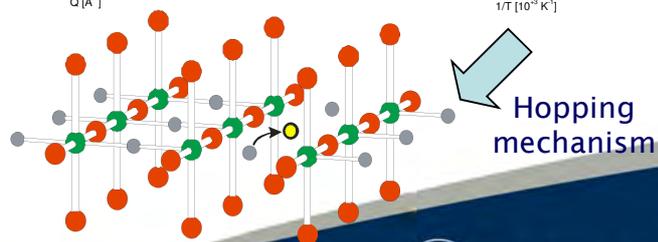
### Observation of Hydride Mobility in the Transition-Metal Oxide Hydride $\text{LaSrCoO}_{3-x}\text{H}_x$

By Craig A. Bridges, Felix Fernandez-Alonso, Jon P. Goff, and Matthew J. Rosseinsky



**Order-of-magnitude increase in conductivity compared to other proton conductors.**

**Only way to obtain microscopic diffusion directly**



# Vibrations and Elastic Scattering

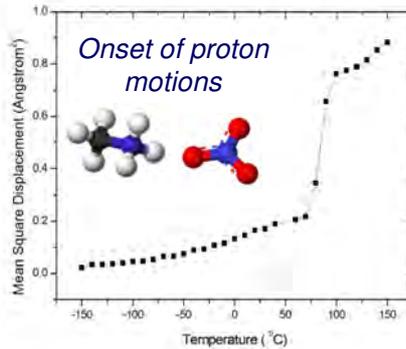
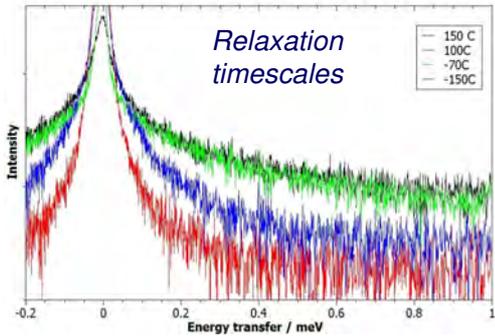
- Well-defined vibrations lead to modulation of elastic-line intensities

- Debye-Waller factor (as in diffraction): 
$$I(Q) = e^{-\frac{r^2 Q^2}{3}}$$

- “Elastic-window” scans: T-dependence of mean-square displacement.

**Atom-specific (H) ‘neutron calorimetry’ with spatial and temporal resolution – quick measurements, backbone of Xpress programme**

Methylammonium nitrate (ionic liquid)



KR Seddon et al

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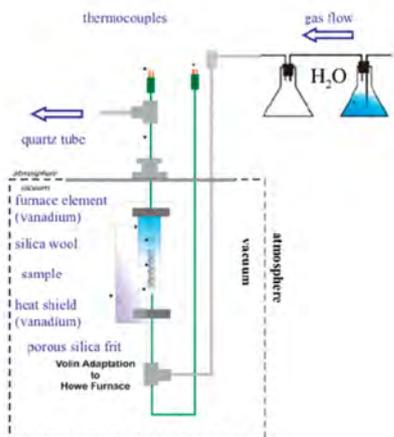
# Solid Electrolytes under Operating Conditions

*J. Phys. Chem. C* 2007, *111*, 6574–6580

Proton-Containing Lanthanum-Doped Barium Cerate: A Simultaneous Structural and Dynamic Study by Neutron Scattering

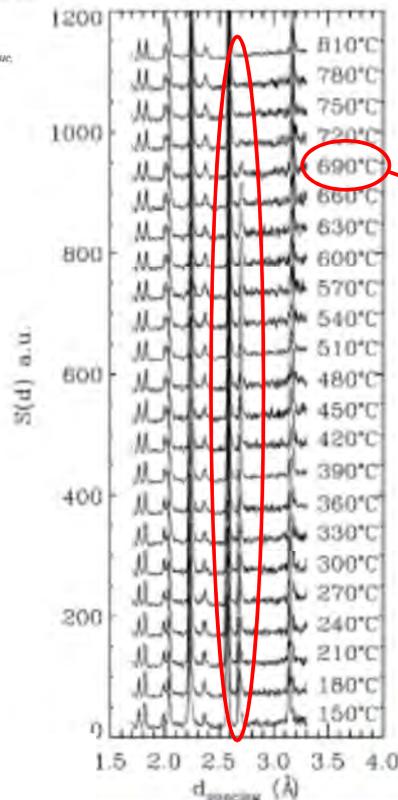
N. Malikova,<sup>1,2,4</sup> C.-K. Loong,<sup>3</sup> J.-M. Zanotti,<sup>1</sup> and F. Fernandez-Alonso<sup>5,1</sup>  
Intense Pulsed Neutron Source Division, Argonne National Laboratory, 9700 S Cass Avenue, Argonne, Illinois 60439, Laboratoire Léon Brillouin (CEA-CNRS), CEA Saclay, 91191 Gif-sur-Yvette cedex, France, and ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom

Yttrium-doped Barium Cerate (perovskite-type)

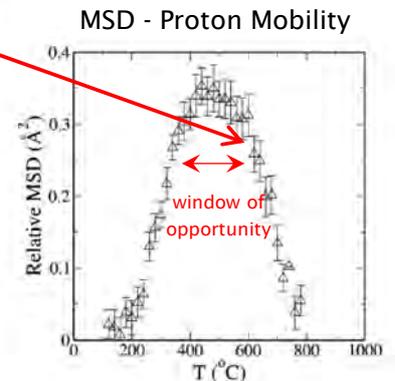


Experimental conditions to emulate operating fuel cell

Simultaneous Diffraction



Rhombohedral → cubic phase transition



Dehydration & proton mobility occur before phase transition at 700°C

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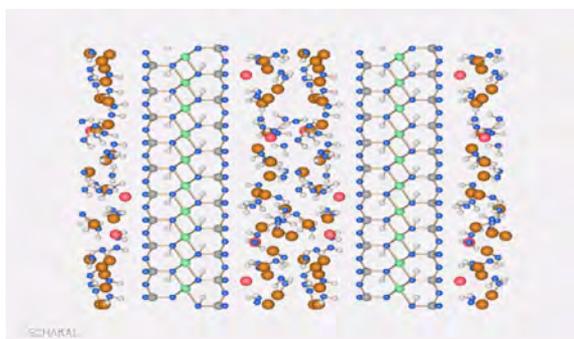
# Diffusion of Organic Contaminants in Hydrated Clays

Chemical Geology 230 (2006) 182–196

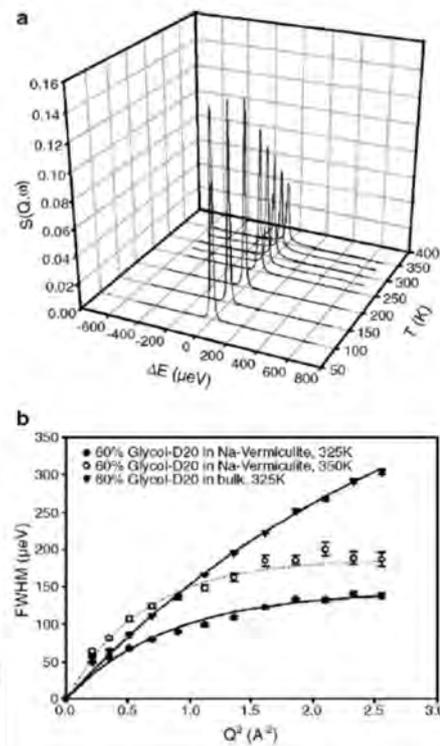
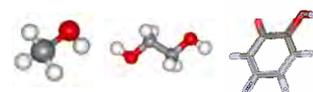
The structure and dynamics of 2-dimensional fluids in swelling clays

Neal T. Skipper<sup>a,\*</sup>, Peter A. Lock<sup>a</sup>, James O. Titiloye<sup>b</sup>, Jan Swenson<sup>c</sup>,  
Zakaria A. Mirza<sup>a</sup>, W. Spencer Howells<sup>d</sup>, Felix Fernandez-Alonso<sup>d</sup>

<sup>a</sup> Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK  
<sup>b</sup> Department of Chemical Engineering and Applied Chemistry, Asian University, Birmingham, B4 7ET, UK  
<sup>c</sup> Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden  
<sup>d</sup> ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK

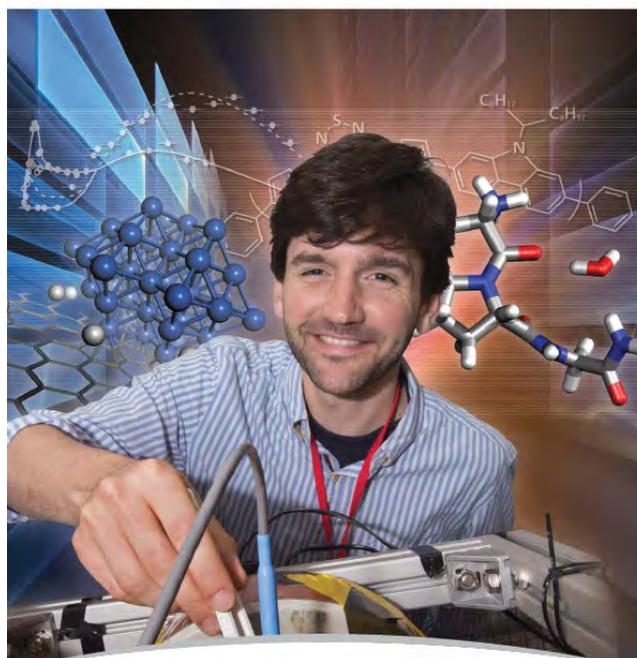


- Diffusion of organic molecules close to bulk solutions: unexpected high mobility inside clay.
- Pressures and temperatures in order to emulate geophysical environments a few Km in depth.



For Much More ...

**ISIS** 2014  
neutron and muon source annual review



[www.isis.stfc.ac.uk](http://www.isis.stfc.ac.uk)



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# What to Remember a Year from Now

- **Neutron scattering for condensed matter research:** plenty of opportunities across  $(Q,E)$  space!
- **In-silico neutron scattering:** can't do without it – computational modelling and neutron scattering experiments go hand-in-hand.
- **Increasing complexity:** sample environment for in-situ and operando studies (of direct industrial relevance), other techniques (simultaneous diffraction or Raman).



# Lecture III: Neutron Sources

## State-of-the-art and Perspectives

*Roma, February 2015*



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## Outline [today]

- Fundamentals.
- Applications.
- *Neutron production.*
- First-principles materials modelling.



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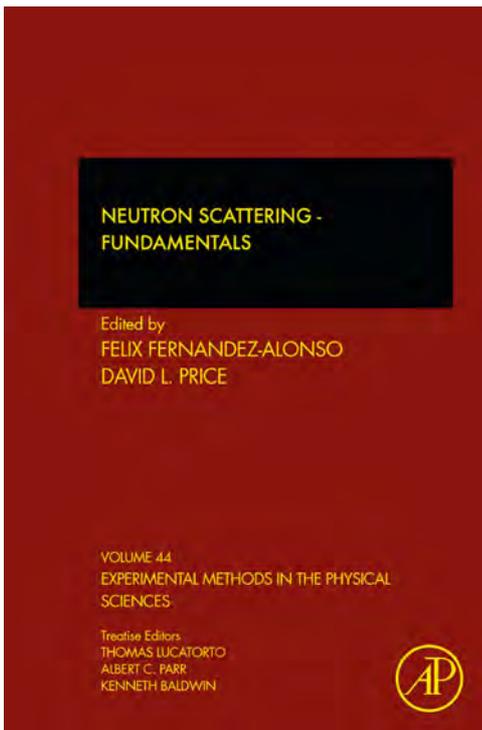
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# Outline

- Why neutrons are so special – quick recap.
- Neutron production: why we need accelerators.
- How accelerator-based neutron (and muon) sources work.
- Challenges & perspectives.



# For Much More



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# “Neutral Protons” as Condensed Matter Probes

## Neutron



- Mass 1 amu
- Spin  $\frac{1}{2}$
- Charge 0
- Interaction Nuclear

## Photon

- Rest mass 0 amu
- Spin 1
- Charge 0
- Interaction E/B dipole ...

## Thermal Neutrons (T = 300 K)

- |                       |   |
|-----------------------|---|
| - Energies (meV)      | motions in condensed matter (e.g., vibrations). |
| - Wavelengths (Å)     | interatomic distances.                          |
| - Neutral particles   | high penetration power.                         |
| - Nuclear interaction | $\delta$ -like (s-wave scattering).             |
| - Spin                | magnetic dipole moment $\sim 1.9\mu_N$          |
| - Stable              | lifetime $\sim 15$ min                          |

**Hard to produce , no lab equivalent.  
Direct link to theoretical predictions.**



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## Basic Observables: Scattering Cross Sections

Given an incident beam:  $\Phi = [\text{incident neutrons per cm}^2]$

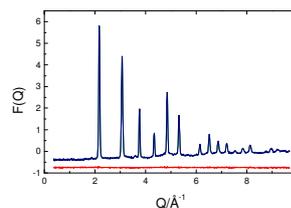
This is what we can measure:

(1) Transmission experiment:

$$\sigma = \frac{[\text{scattered neutrons}]}{\Phi}$$

(2) Diffraction experiment:

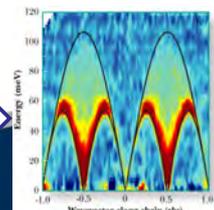
$$\frac{\partial \sigma}{\partial \Omega} = \frac{[\text{scattered neutrons into } \partial \Omega]}{\Phi \partial \Omega}$$



Diffraction pattern (crystallography)

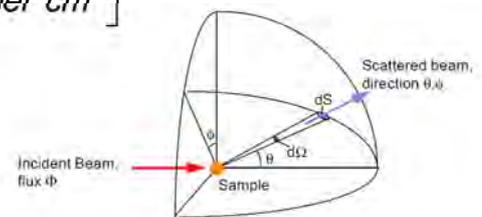
(3) Spectroscopy experiment:

$$\frac{\partial \sigma}{\partial \Omega \partial E} = \frac{[\text{scattered neutrons into } \partial \Omega \text{ \& } \partial E]}{\Phi \partial \Omega \partial E}$$



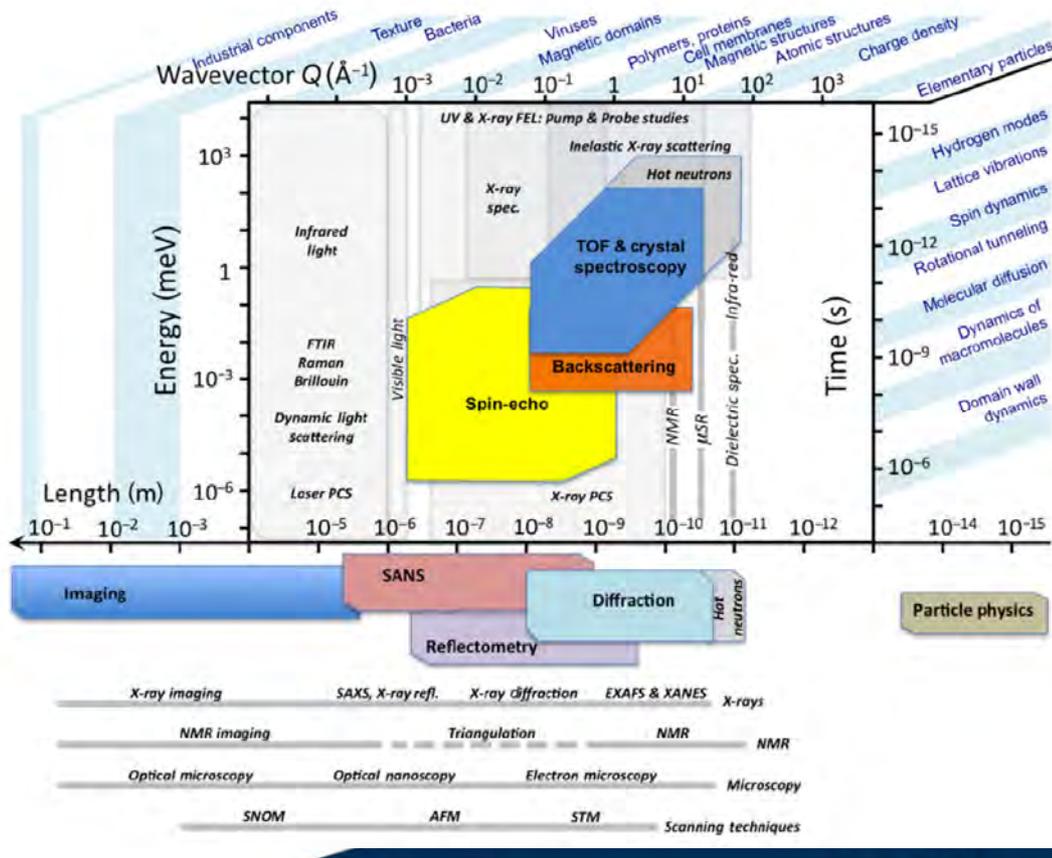
“Dynamic” Diffraction pattern

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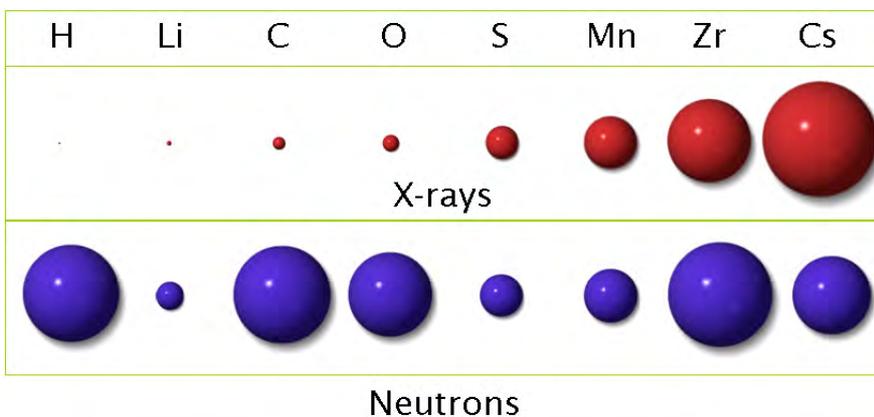
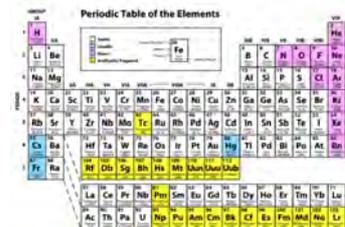
Cross sections also depend on polarisation of incident & scattered neutron.

# Where Atoms Are and Do: Neutrons

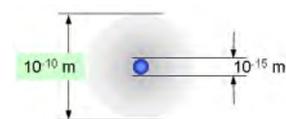


## The Periodic Table: X-rays vs. Neutrons

- X-rays: see electron clouds.
- Neutrons: see the atomic nucleus.



Nuclear scattering



- Hydrogen: large cross section, largely invisible to X-rays.
- Different nuclear isotopes can have very different neutron cross sections.

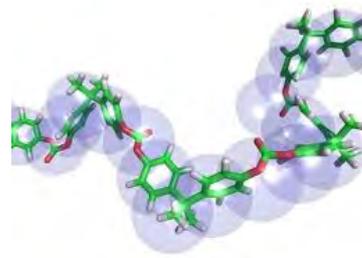
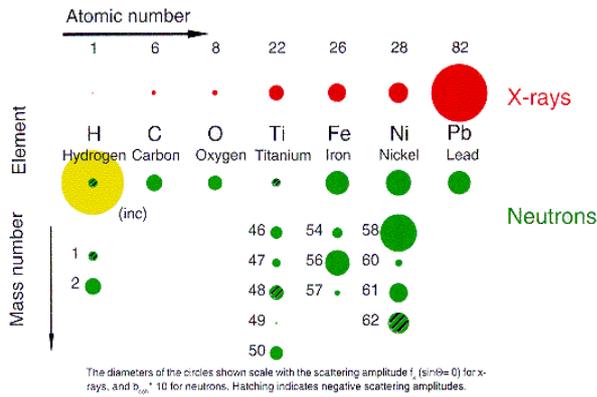
*Isotopes: what do we gain?*



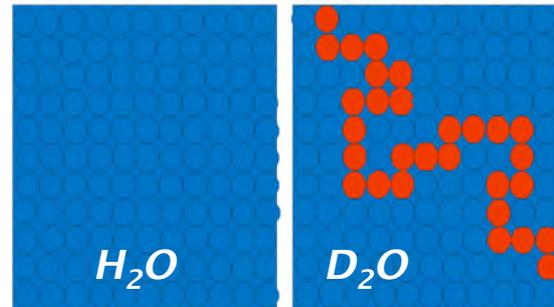
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# Contrast Variation: The Added Dimension



A polymer (mostly H) in water ...



Where ???

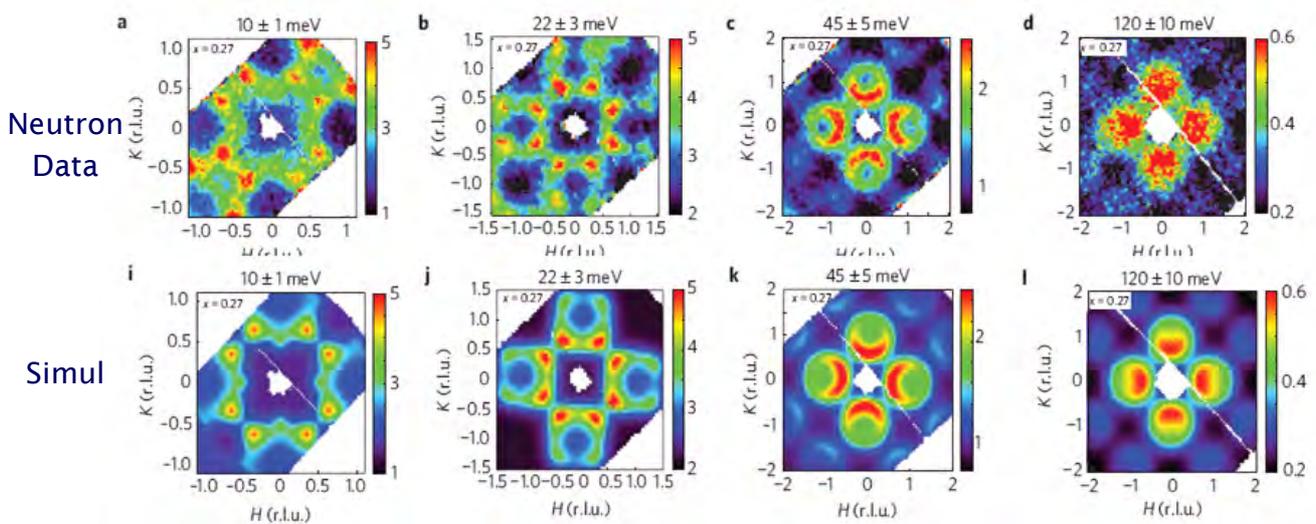
There !!!

- H/D substitution is at the heart of many neutron experiments.
- Hydrogen: central to biology, organic chemistry, soft matter, aqueous chemistry, energy, catalysis ...
- Same principle applies to all elements (if you can get the isotope!)



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# Magnetic Scattering: No Neutrons, No Insight

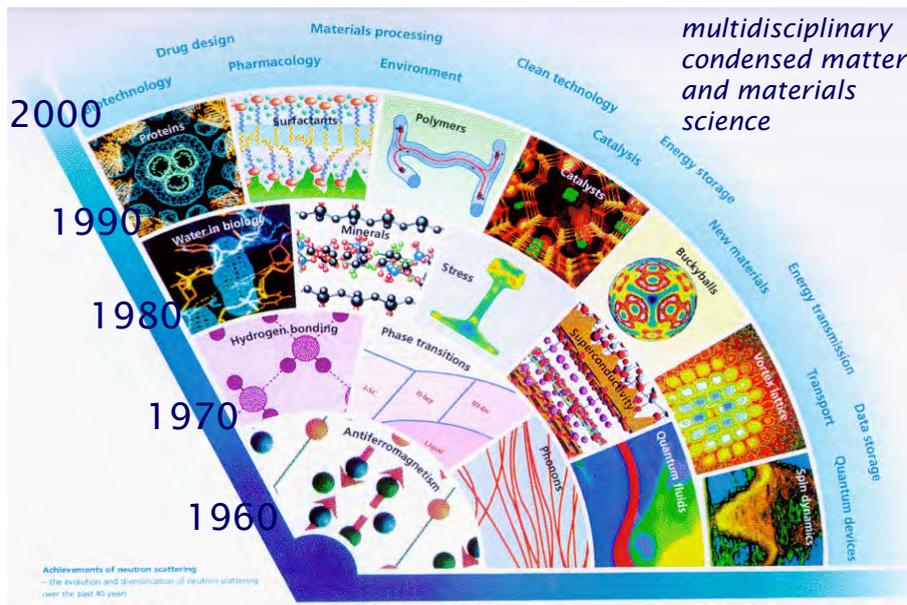


Iron-based superconductor  $\text{Fe}_{1.04}\text{Te}_{0.73}\text{Se}_{0.27}$

*Nature Physics* 5 555 (2009)



# One Probe, Many Questions



*Particularly  
to study  
hydrogen-  
containing  
materials and  
magnetism.*



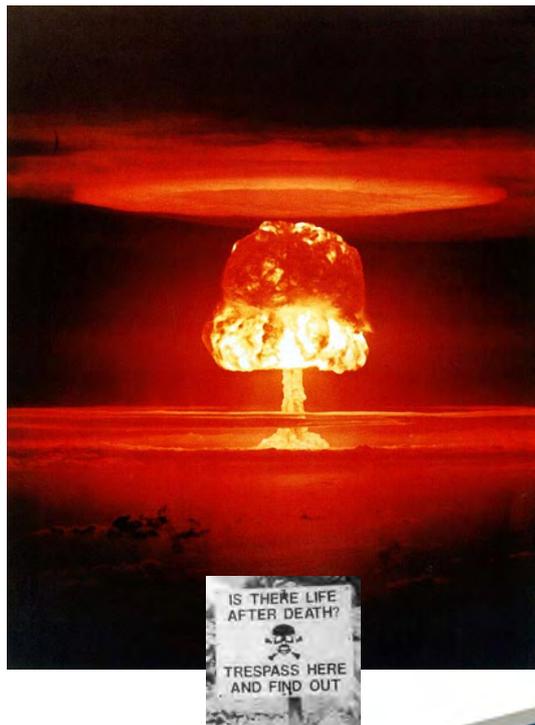
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## Neutron Production



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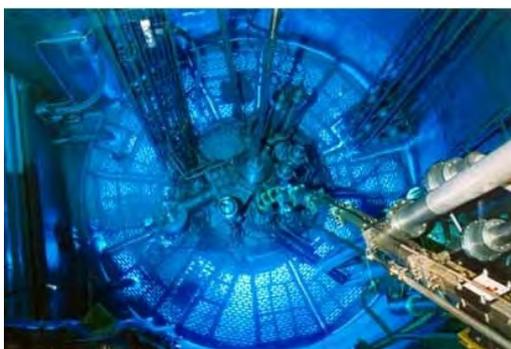
# The Quick-and-dirty Way to Produce Neutrons



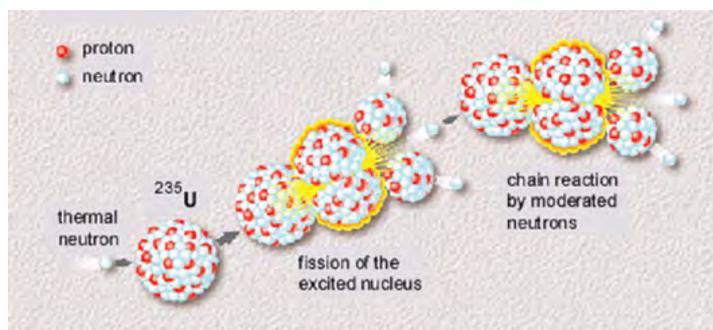
Not a wise option

## A Safer Option: The Nuclear Reactor

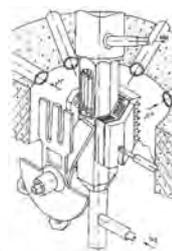
ILL Reactor, France  
(58 MW)



(Controlled!) Nuclear Fission

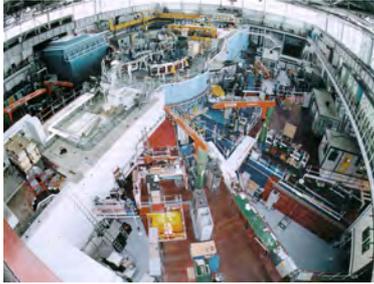


- Requires fissile material (e.g., Uranium).
- Chain reaction.
- Continuous operation – exception: IFR pulsed (!) reactor in Dubna, Russia (2MW/1.5GW average/peak power).

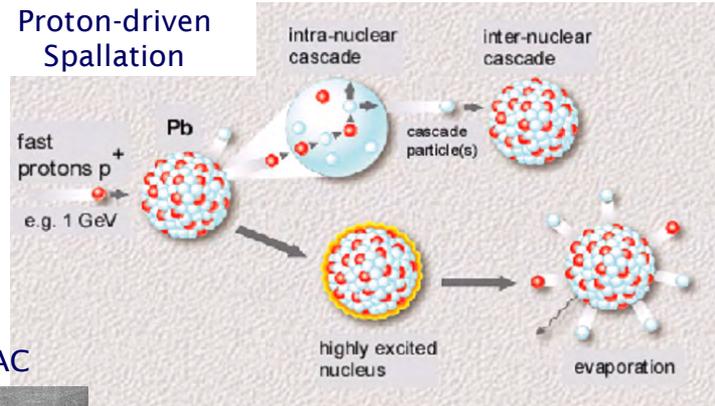


# An Even Safer (and cleaner) Option: A Particle Accelerator

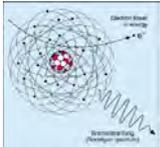
ISIS Facility, United Kingdom  
(operational since 1984)



## Proton-driven Spallation



Its predecessor: the Harwell e-LINAC

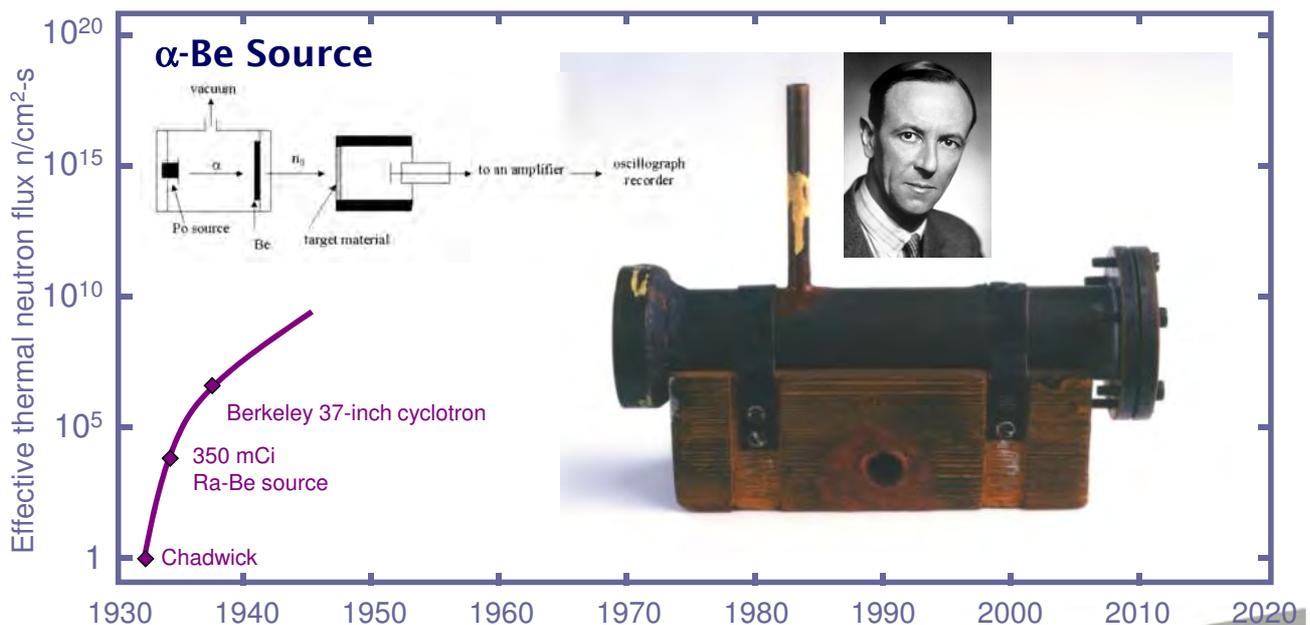


- A fast particle, normally a proton, chips or 'spalls' nucleons from a nucleus.
- There is no chain reaction.
- Neutrons are produced with MeV energies.



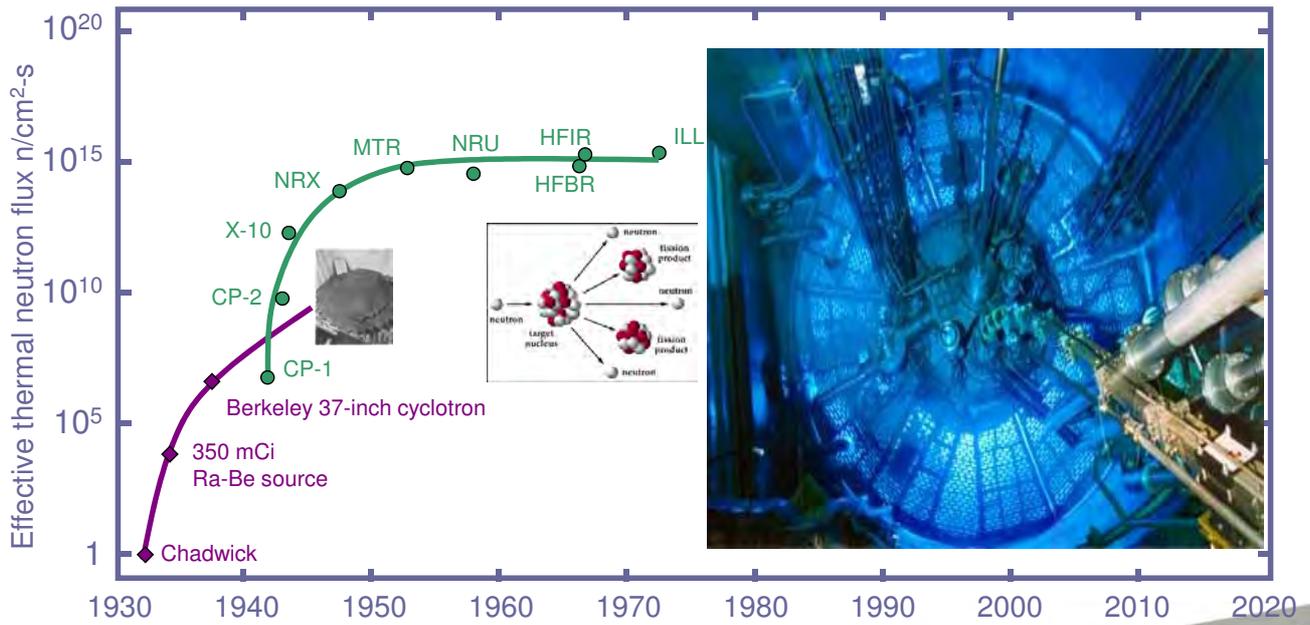
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## Historical Evolution of Neutron Sources

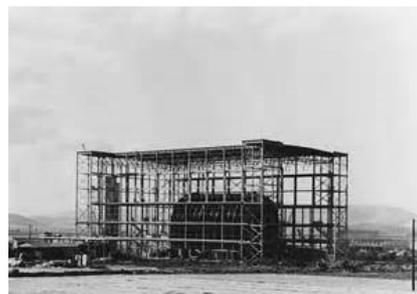


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# Historical Evolution of Neutron Sources



## Materials Testing Accelerator (Lawrence, 1950s)

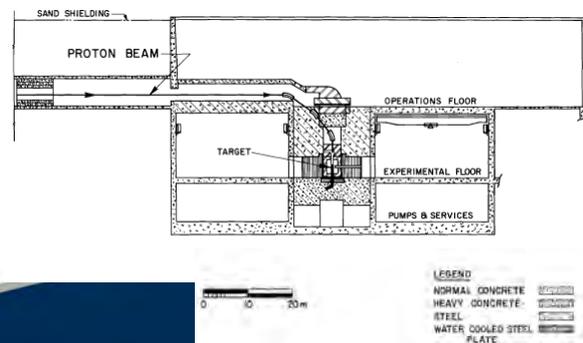
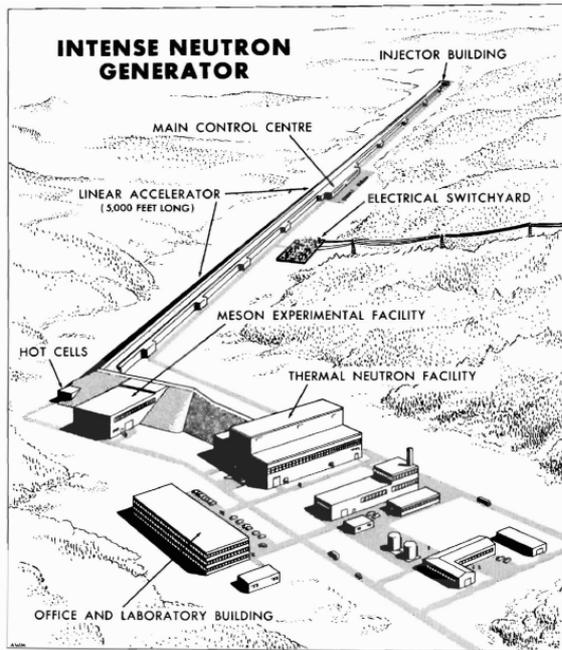


A gram of neutrons a day.

Ahead of its time.

Precursor to Lawrence Livermore Lab.

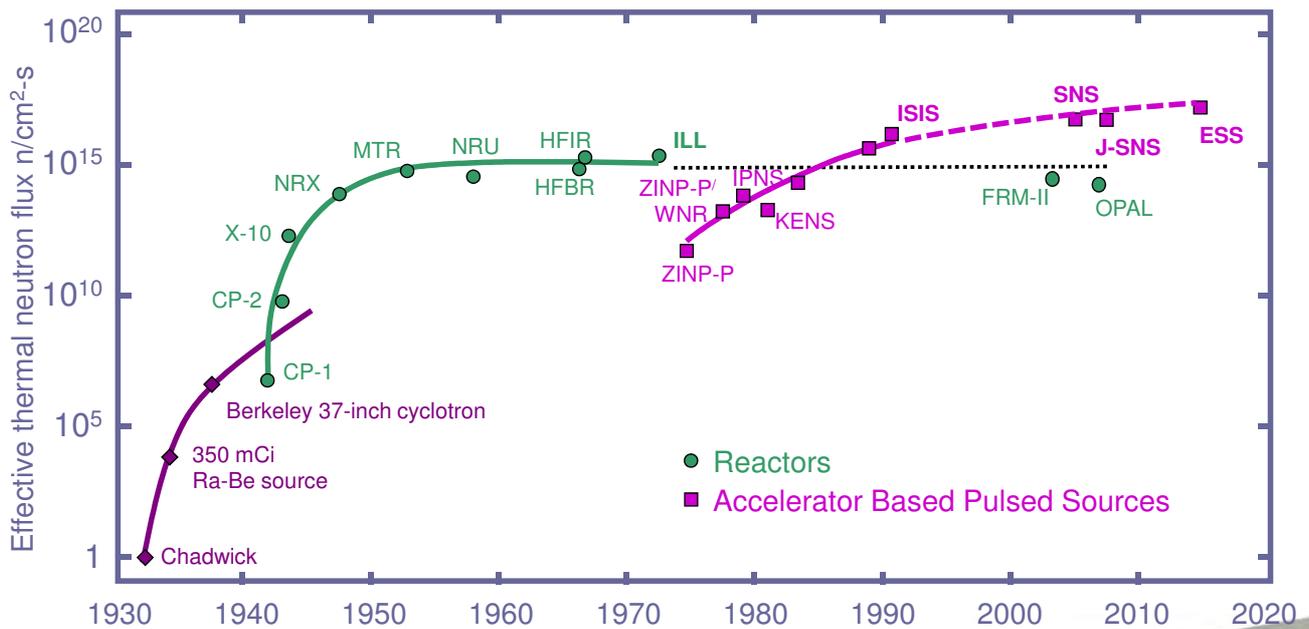
# Intense Neutron Generator (Canada, 1960s)



Cancelled in 1968 due to perceived high cost and insufficient political support.

Precursor to present-day spallation sources.

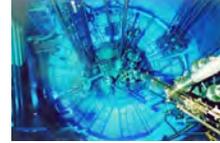
## Historical Evolution of Neutron Sources



# Reactor vs Accelerator-based Neutron Sources

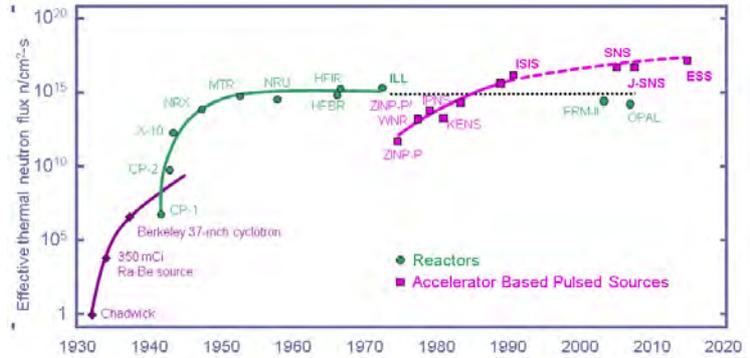
## Reactor-based source:

- Neutrons produced by fission reactions
- Continuous neutron beam
- 1 neutron/fission .



## Accelerator-based source:

- Neutrons produced by spallation reaction
- 10s of neutrons/proton
- Neutrons are pulsed, follow proton beam time structure.
- A pulsed beam with precise  $t_0$  allows neutron energy measurement via TOF ( $v=d/t$ )



Updated from *Neutron Scattering*, K. Skold and D. L. Price, eds., Academic Press, 1986.

**Accelerator based-sources have not yet reached their limit and hold out the promise of higher intensities.**



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# The Golden Age of Spallation Neutron Sources

## Operational



## Under Construction or Planned



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# How Spallation Neutron (and Muon) Sources Work

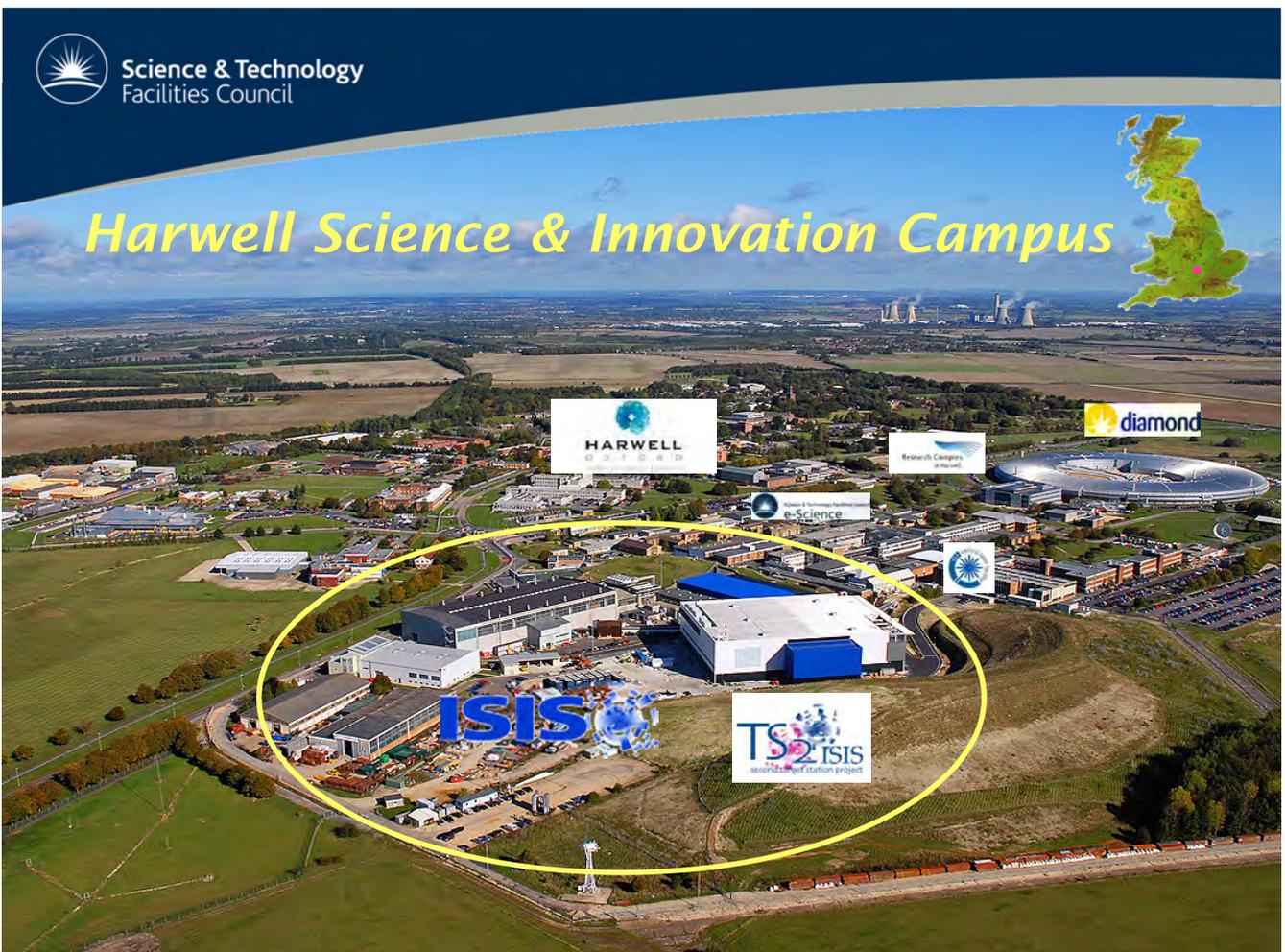


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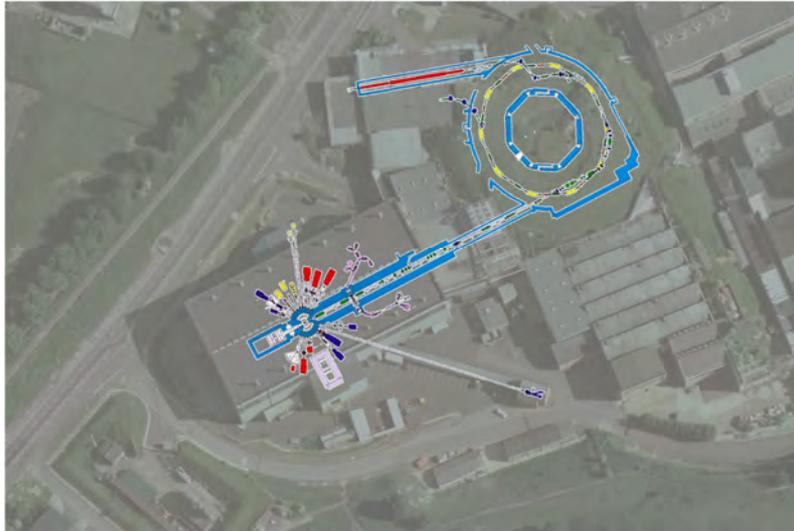


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## Harwell Science & Innovation Campus



# ISIS Target Station I



Formerly NIMROD  
(particle physics)

200  $\mu$ amp proton beam  
at 800 MeV hitting heavy-  
metal target (50 Hz rep  
rate, 200 kW).

1984  
(30 years Dec 2014)



Protons are used to produce  $>10^{16}$  n/s.

Neutron pulses are short ( $\mu$ sec).

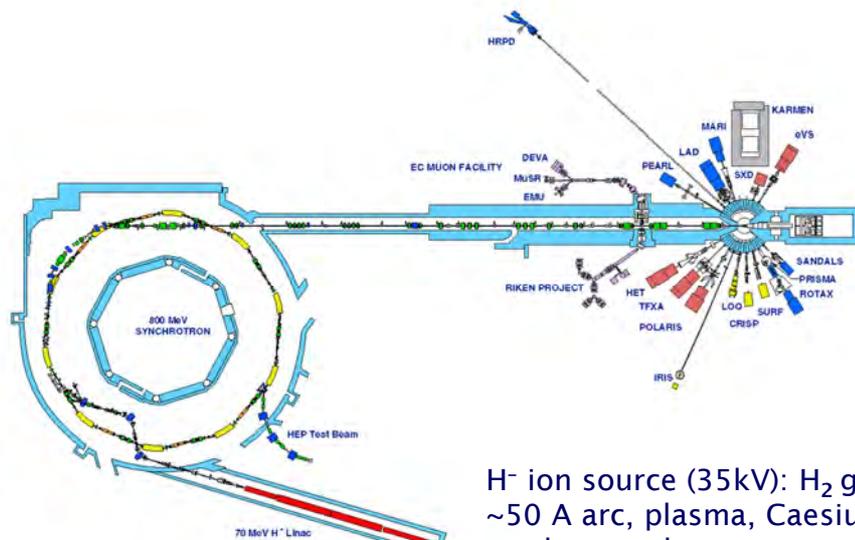
How many neutrons produced since 1984?



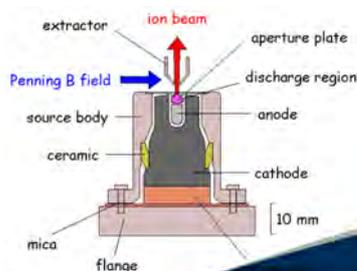
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## Neutrons from Spallation: The Ion Source



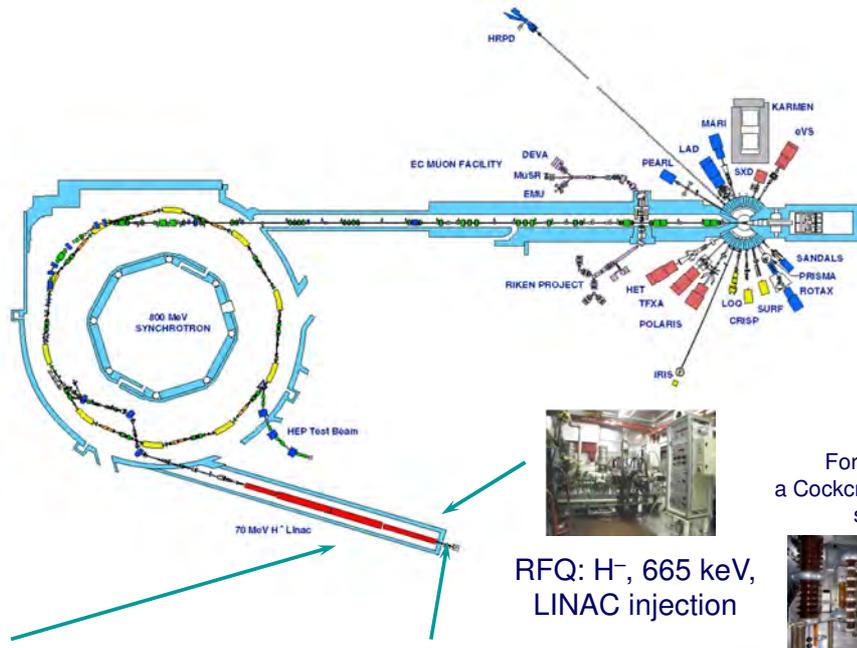
H<sup>-</sup> ion source (35kV): H<sub>2</sub> gas,  
~50 A arc, plasma, Caesium  
as electron donor.



H<sup>-</sup> ion source



# Neutrons from Spallation: RFQ & LINAC



Formerly a Cockcroft-Walton set

RFQ: H<sup>-</sup>, 665 keV, LINAC injection

H<sup>-</sup> ions accelerated to 70MeV in LINAC

H<sup>-</sup> ion source



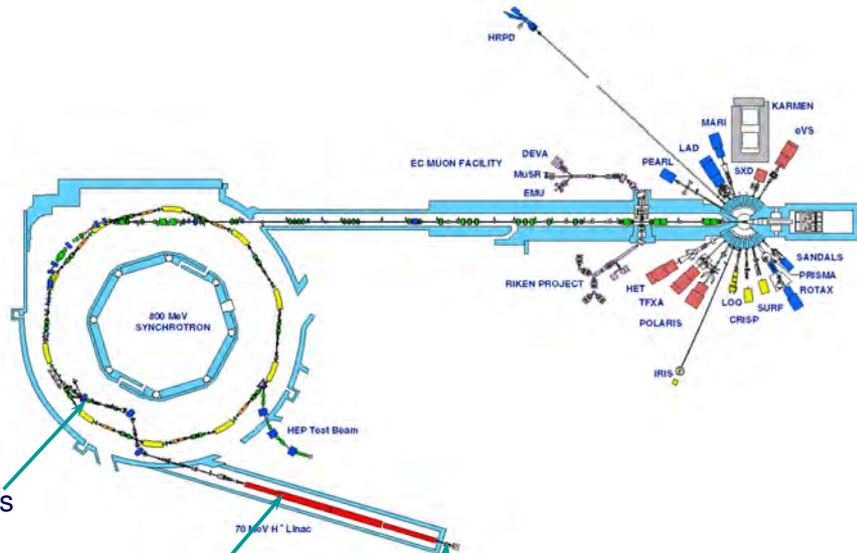
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# Neutrons from Spallation: Charge Stripping

Al<sub>2</sub>O<sub>3</sub>, 0.25 μm  
Creation of p<sup>+</sup> and injection into synchrotron



Stripped of electrons  
H<sup>-</sup> ⇨ p<sup>+</sup>



H<sup>-</sup> ion source



H<sup>-</sup> ions accelerated to 70MeV in LINAC



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# Neutrons from Spallation: Synchrotron



$p^+$  accelerated to 800MeV and bunched into two 0.3 $\mu$ s pulses

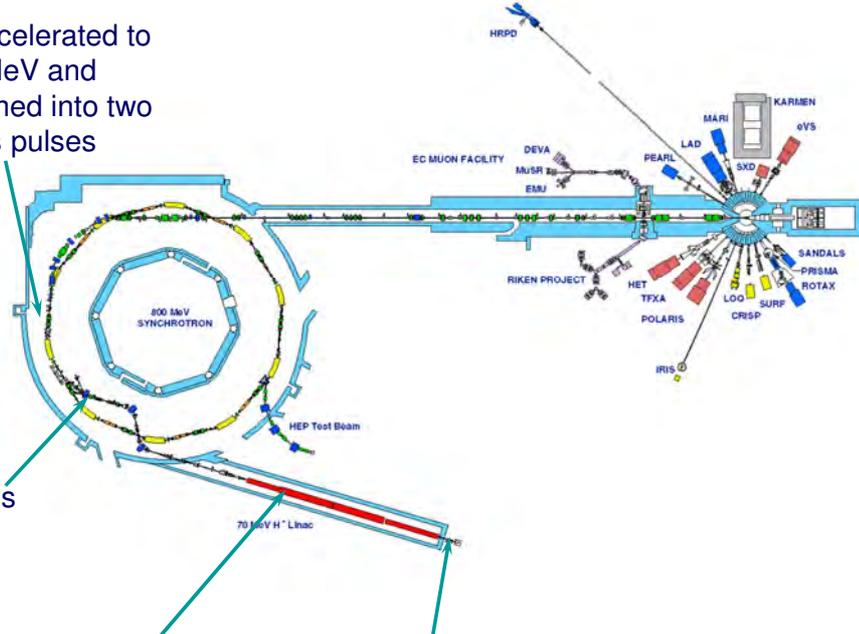


Stripped of electrons  
 $H^- \Rightarrow p^+$



$H^-$  ions accelerated to 70MeV in LINAC

$H^-$  ion source



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# Neutrons from Spallation: Beam Extraction



$p^+$  accelerated to 800MeV and bunched into two 0.3 $\mu$ s pulses



Stripped of electrons  
 $H^- \Rightarrow p^+$

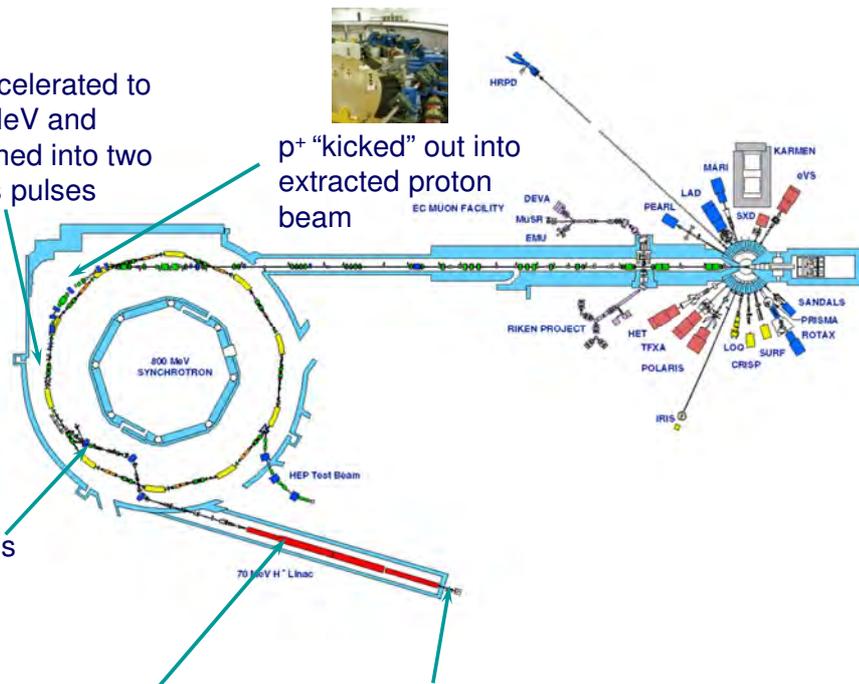


$H^-$  ions accelerated to 70MeV in LINAC

$H^-$  ion source

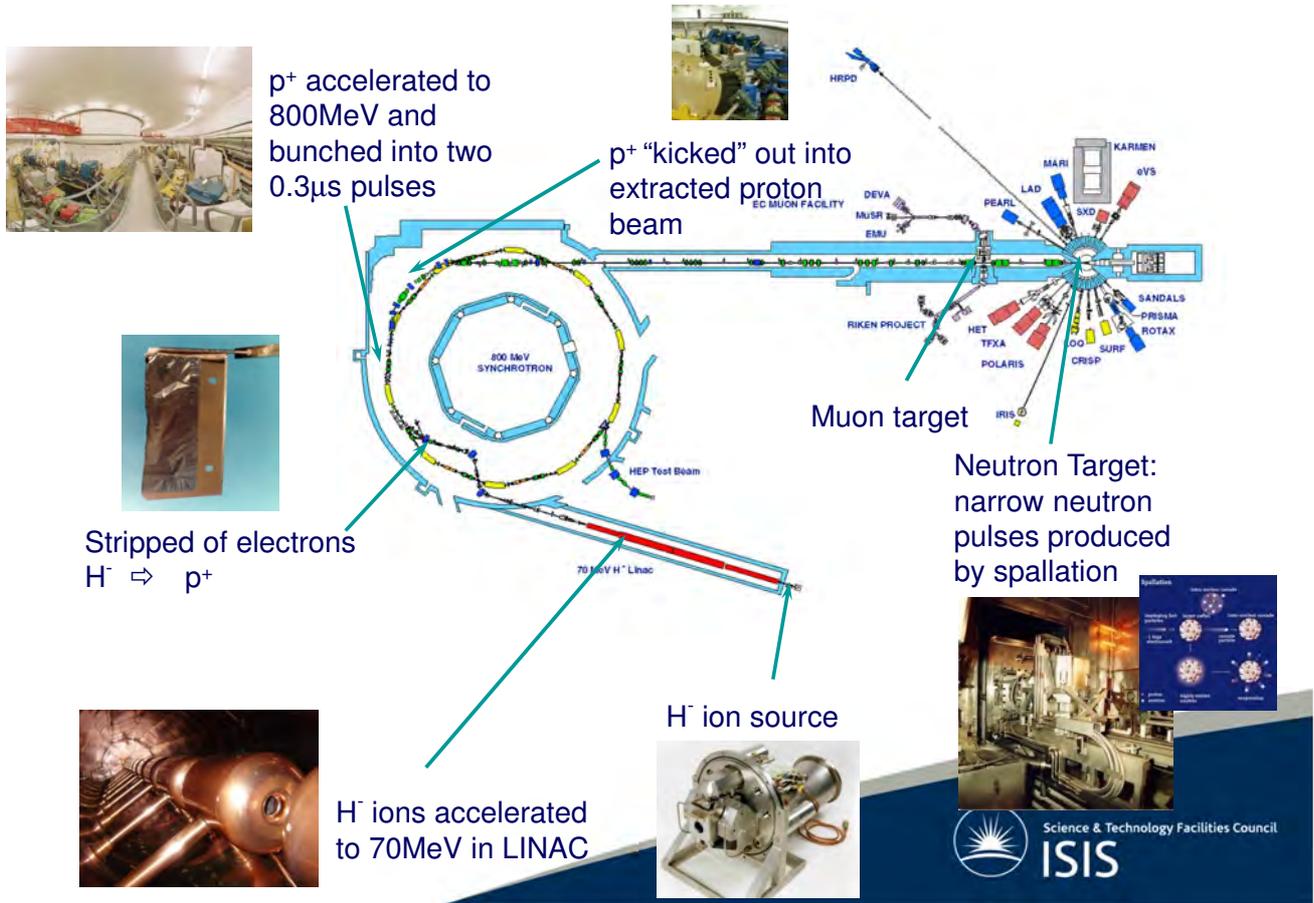


$p^+$  "kicked" out into extracted proton beam



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# Neutrons from Spallation: Muon and Neutron Production

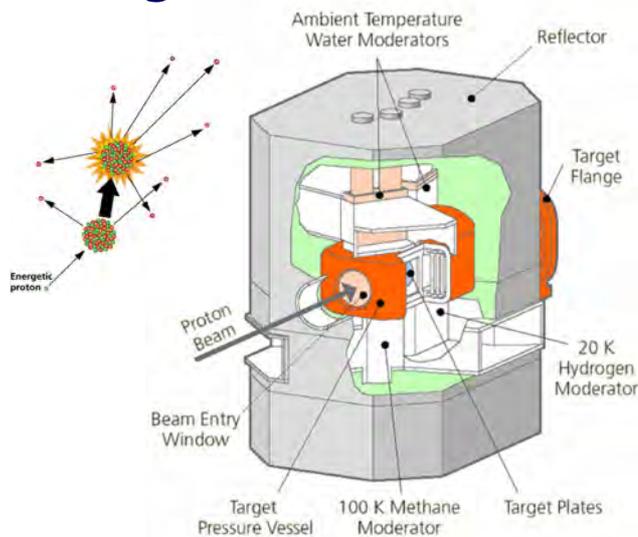


## Extracted Proton Beam



Frequency of extraction determines source repetition frequency (50Hz)  
4/5 into TS1, 1/5 into TS2

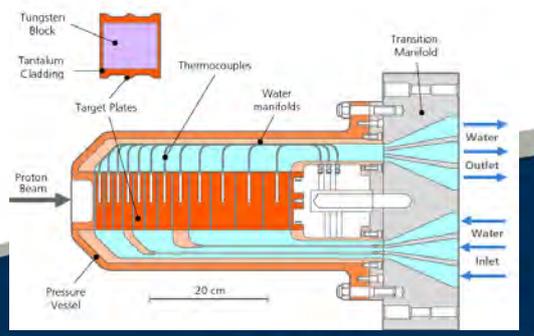
# Spallation Target



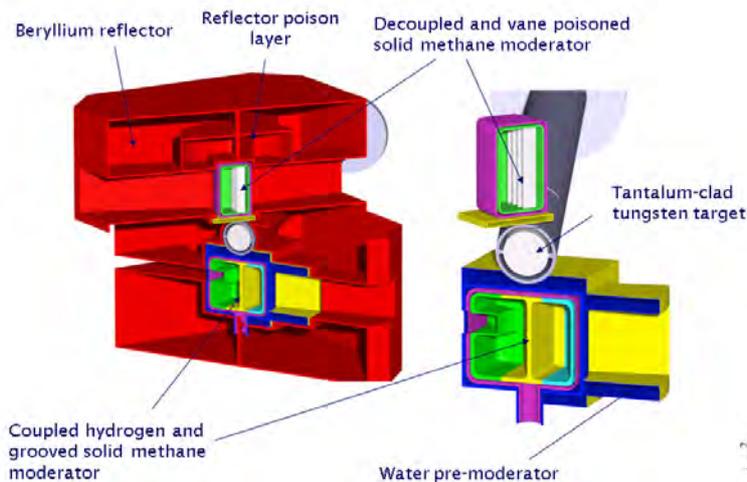
$\sim 2.5 \times 10^{13}$  protons per pulse onto tungsten target (50 pps)

$\sim 15\text{--}20$  neutrons / proton,  $\sim 4 \times 10^{14}$  neutrons / pulse

Primary neutrons from spallation: evaporation spectrum ( $E \sim 1$  MeV, still not useful).

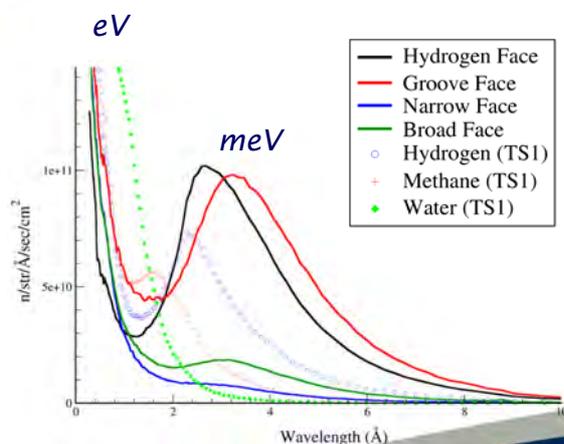


## Neutron Moderation: From “M” to “m” eV



- Elastic nuclear scattering in a hydrogenous material.
- Temperature determines position of moderated “hump.”

- Three moderators: liquid hydrogen (20 K), methane (100 K), water (315 K).
- Moderation is incomplete, to preserve time structure of pulse ( $\mu\text{sec}$ ).
- Number of collisions needed about 10-20.
- Quite inefficient (1/10000 are useful)



# Condensed Matter Science at a Spallation Neutron Source

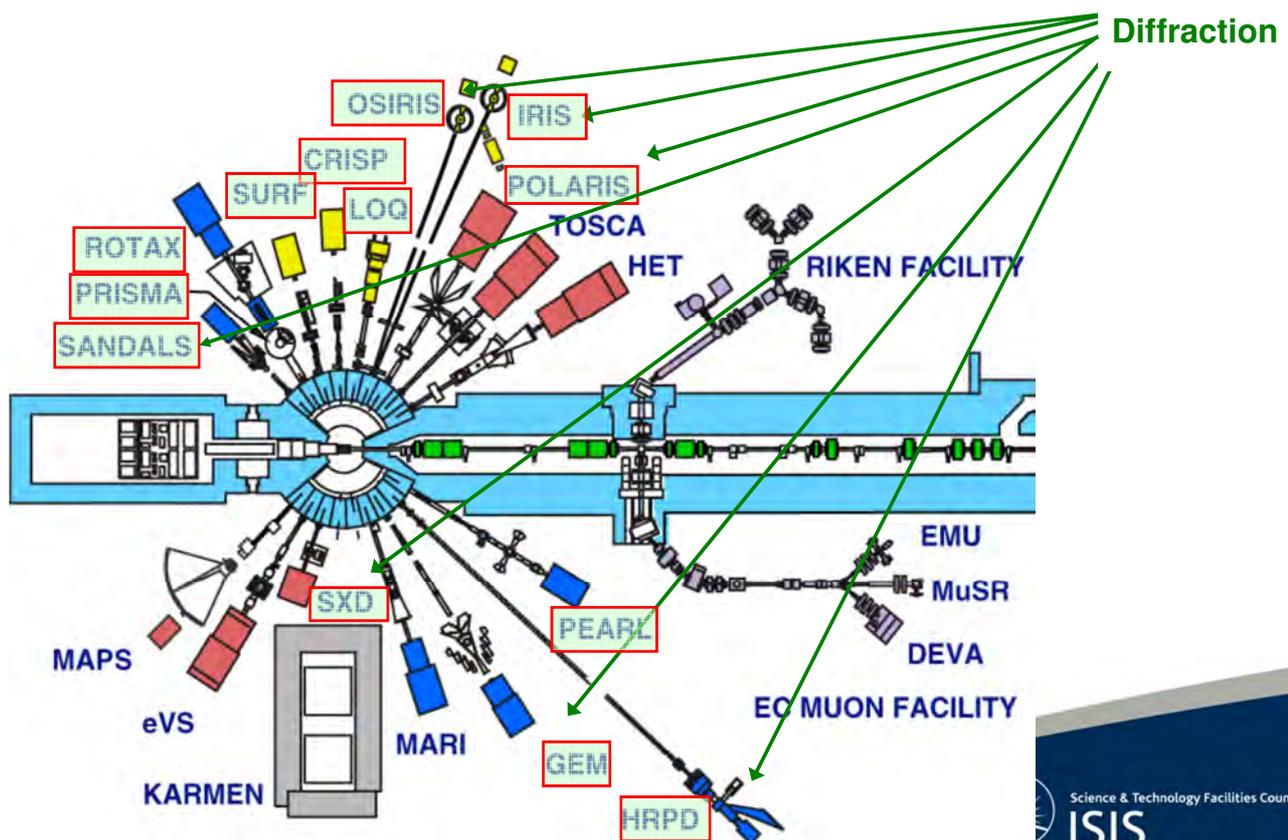


ISIS Experimental Halls



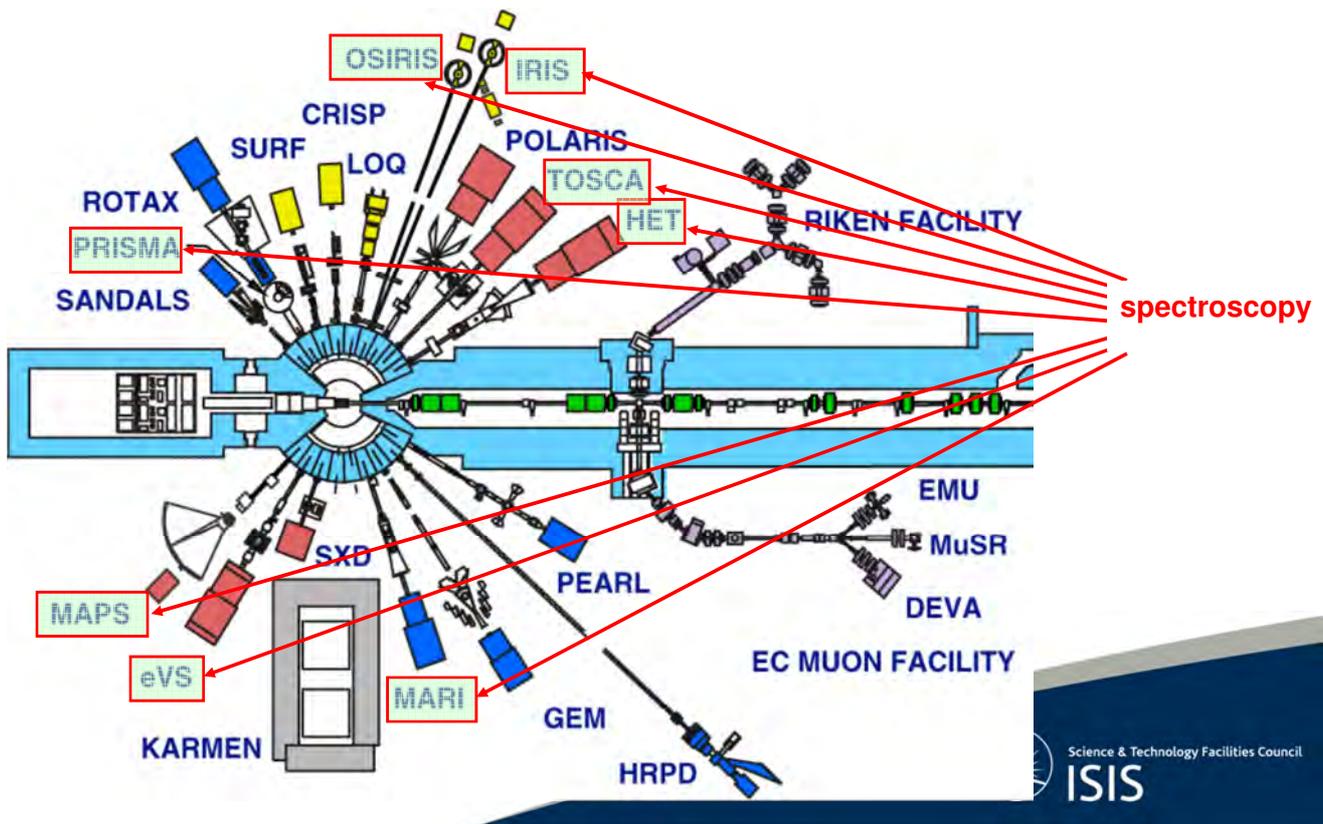
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## ISIS Neutron Instruments: Where Atoms Are (Structure)



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# ISIS Neutron Instruments: What Atoms Do (Dynamics)



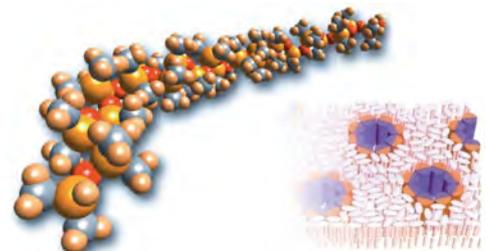
## ISIS Target Station II

*Takes one proton pulse out of five (10 Hz, 40 kW)*

Aimed to meet scientific needs in key areas:

- Soft Matter
- Advanced Materials
- Bio-molecular Science
- Nanoscience

*Optimised for cold neutrons.*



2008

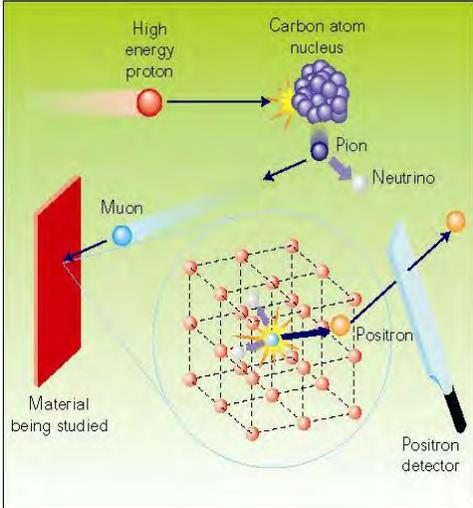
*Neutronic performance higher than TS1 with 1/5 power.*

TS<sub>2</sub> ISIS

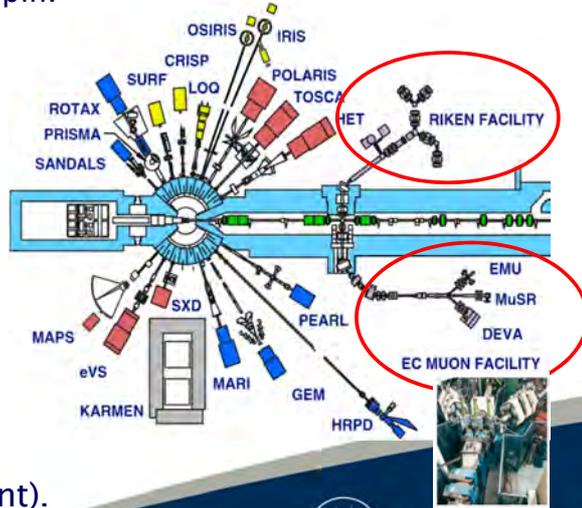


# Brief Detour: ISIS Muons

Courtesy of AD Hillier (ISIS)



- High-energy protons collide with carbon nuclei producing pions.
- Pions decay into spin-polarised muons:  $\pi^+ \rightarrow \mu^+ + \nu_\mu$
- Muons decay in  $2.2\mu\text{s}$ :  $\mu^+ \rightarrow e^+ + \nu_e + \nu_\mu$
- Positrons are emitted preferentially along direction of muon spin.

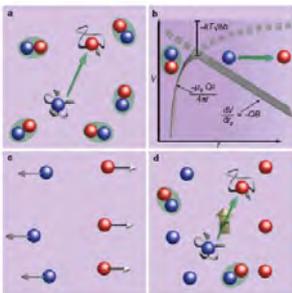


Muons are used as:

- Local magnetic probes (physics).
- Ultralight protons (chemistry).
- A source of neutrinos (MICE experiment).

# Brief Detour: Whetting Your Appetite for Muons

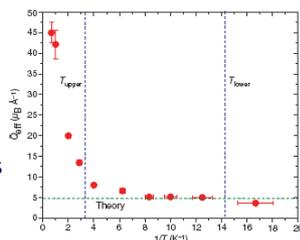
## “Magneticity”



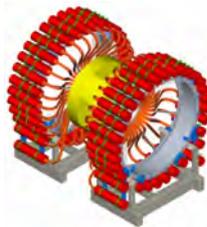
Emergent magnetic monopoles in “spin ices”

*Nature* 461 956 (2009)

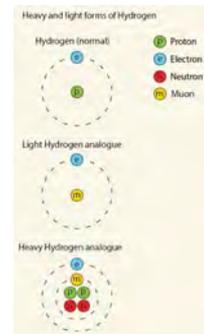
Muons give the effective charge of these quasiparticles



**This is the subject of an entirely separate talk!**

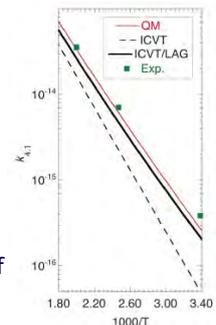


## Muonium Chemistry



The  $\text{H}+\text{H}_2$  reaction: the “quark” of chemistry.

Use of muons as an ultralight hydrogen atom to benchmark our understanding of chemical reactivity.



*Science* 331 448 (2011)

# Some Metrics for ISIS



~1200 users/yr

~700 experiments/yr

150 days running (50 industry)

~450 publications/yr (1/3 high impact)

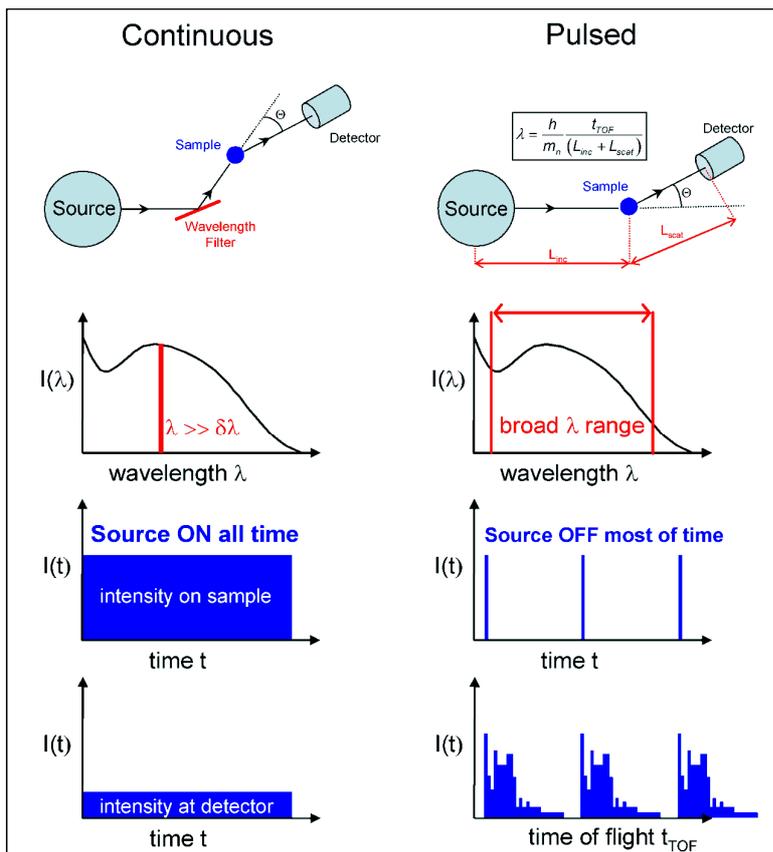
12,000+ publications to date



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## The Merits of Pulsed Neutrons



### Pulsed Sources:

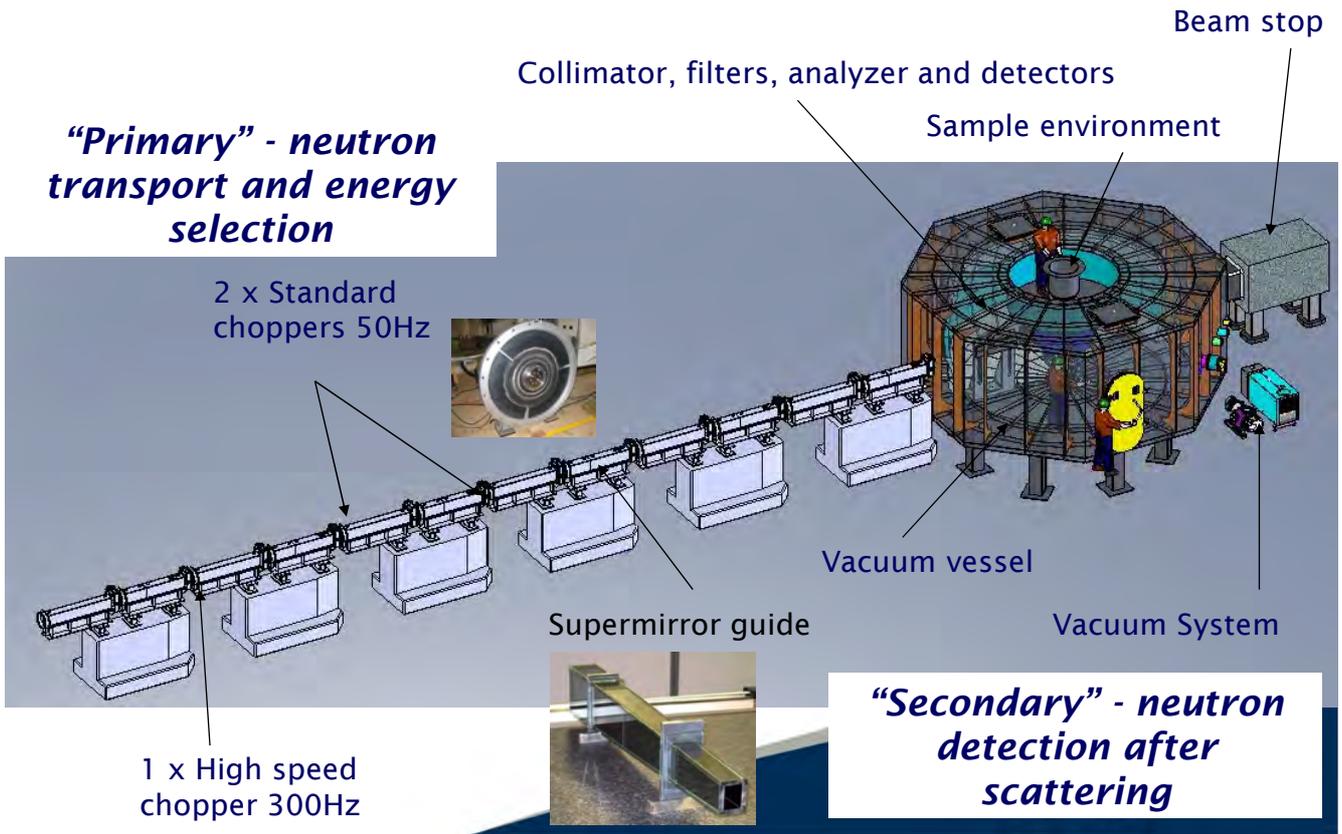
- Time-of-flight spectrum is trivially related to neutron wavelength spectrum.
- Broad range of neutron energies (from meV to eV).
- Tight pulses: good resolution.
- Multiplexing advantage: broad range of wavelengths can be used simultaneously (more efficient experiments)
- Source is OFF most of the time (backgrounds are low).
- Source repetition frequency determines dynamic range.



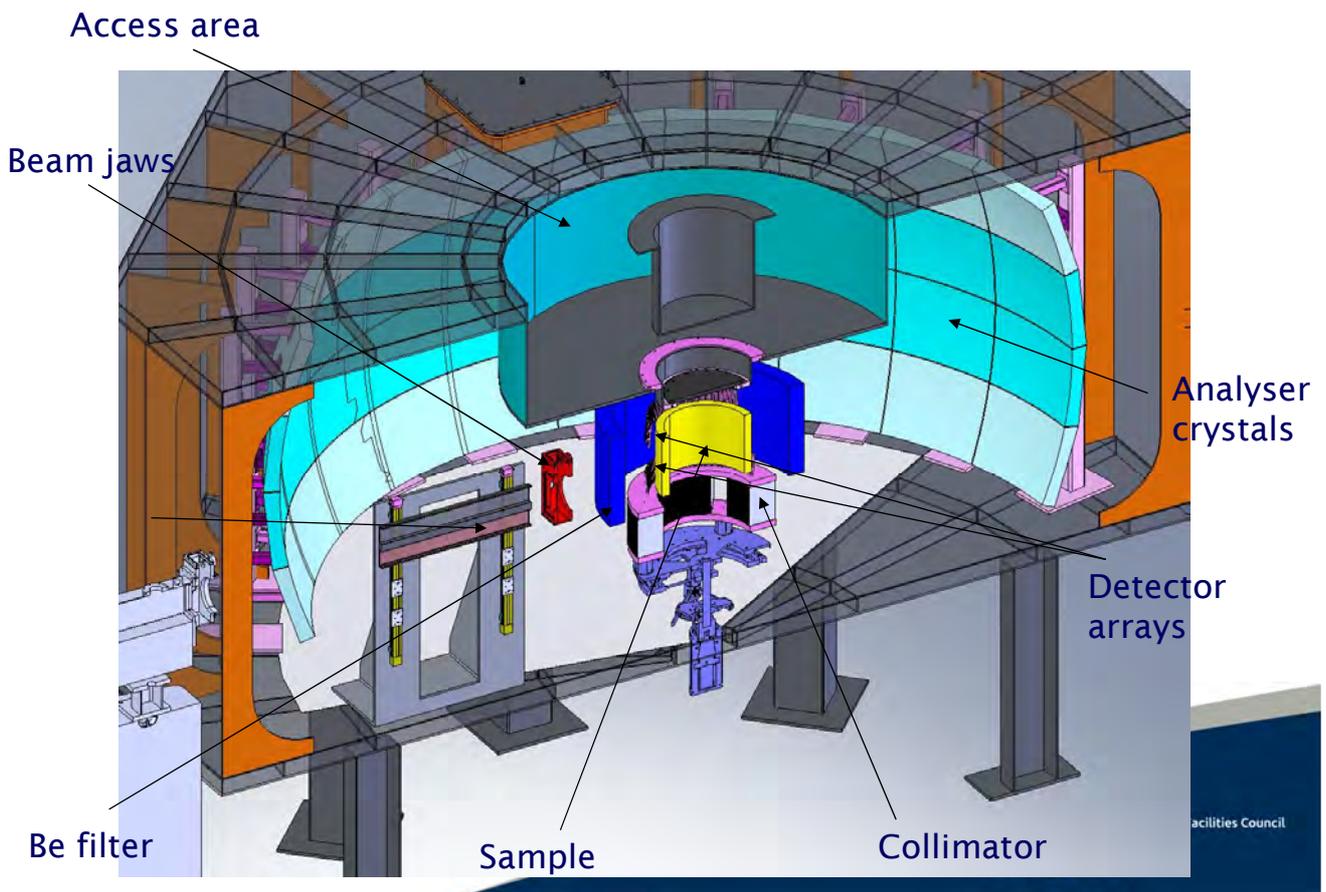
Science & Technology Facilities Council

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# The Anatomy of an Instrument



## The Anatomy of a Neutron Instrument: The “Secondary”



# Neutronics – Where Science Meets Engineering

JPCS 554 012003 (2014)

Recent and future developments on TOSCA at ISIS

Stewart F. Parker,<sup>1</sup> Felix Fernandez-Alonso,<sup>1,2</sup> Anibal J. Ramirez-Cuesta,<sup>1,3</sup> John Tomkinson,<sup>4</sup> Sverrir Rudi,<sup>5</sup> Roberto S. Pina,<sup>6</sup> Giuseppe Gorini<sup>7</sup> and Javier Fernandez Castanon.<sup>8,9</sup>

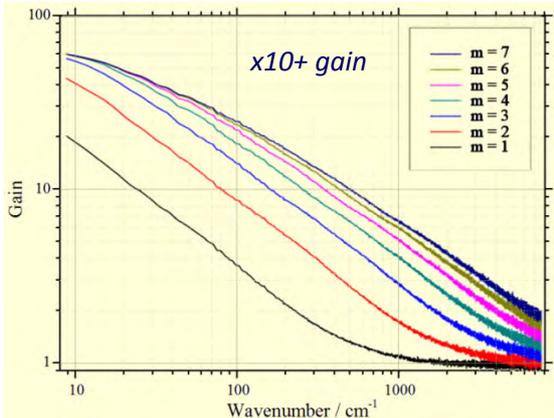
<sup>1</sup> ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK  
<sup>2</sup> Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK  
<sup>3</sup> Present address: CEMOS, Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge TN 37831, USA  
<sup>4</sup> CNISM, Università degli Studi di Milano-Bicocca, Piazza della Scienza 3, 20126 Milano, Italy  
<sup>5</sup> Facultad de Ciencias, Universidad de Oviedo, Calvo Sotelo, 33007 Oviedo, Spain  
<sup>6</sup> Present address: ILL, 6 rue Jules Horowitz, BP 156, F-38042 Grenoble Cedex 9, France

EPJ 83 03013 (2015)

Monte carlo simulations of the TOSCA spectrometer: Assessment of current performance and future upgrades

Roberto S. Pina<sup>1,2</sup>, Sverrir Rudi<sup>5</sup>, Stewart F. Parker<sup>1</sup>, Giuseppe Gorini<sup>7</sup> and Felix Fernandez-Alonso<sup>1,3</sup>

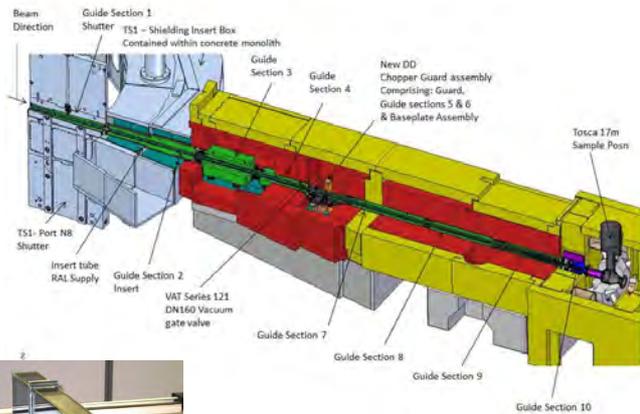
<sup>1</sup> ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK  
<sup>2</sup> CNISM, Università degli Studi di Milano-Bicocca, Piazza della Scienza 3, 20126 Milano, Italy  
<sup>3</sup> Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK



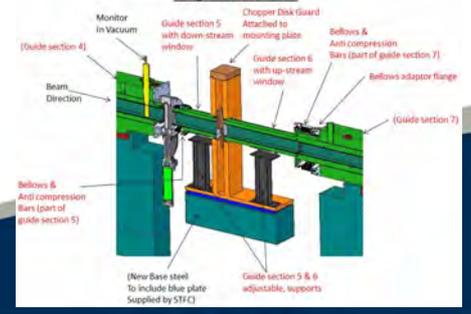
Engineering design & tendering on track.

Aiming for completion in 2016

Sectional view showing Tosca Guide & Chopper Project.



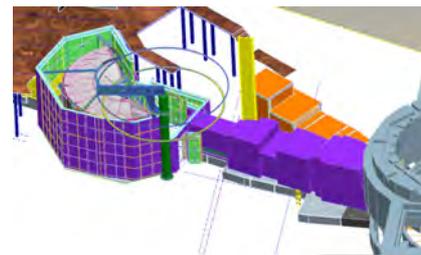
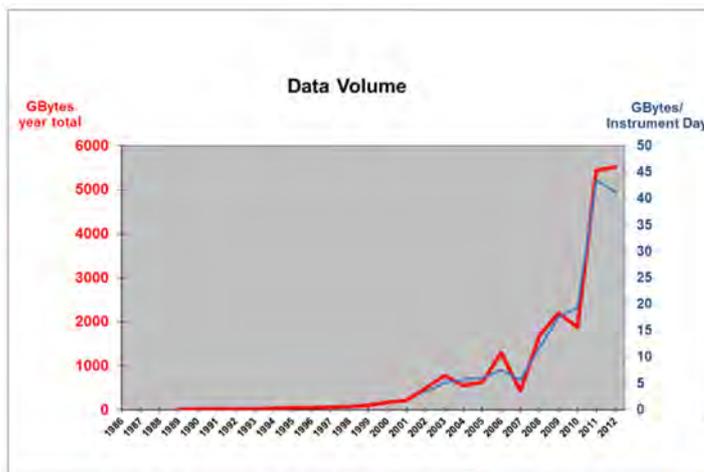
Sectional view showing Chopper Disk Guard And guide sections 5 & 6.



## The “Tertiary” Instrument: Data Mining & Analysis

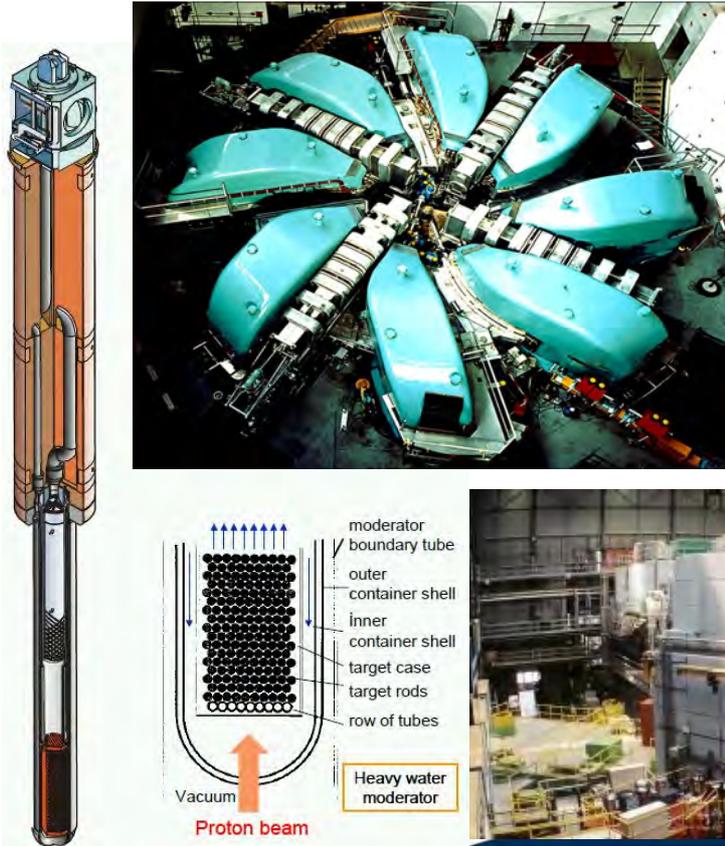


- Multi-dimensional data sets (5d and above!).
- New data collection paradigms, e.g., event mode.
- Extensive use of distributed computing & computer modelling.





# Other Large-Scale Facilities: SINQ at PSI



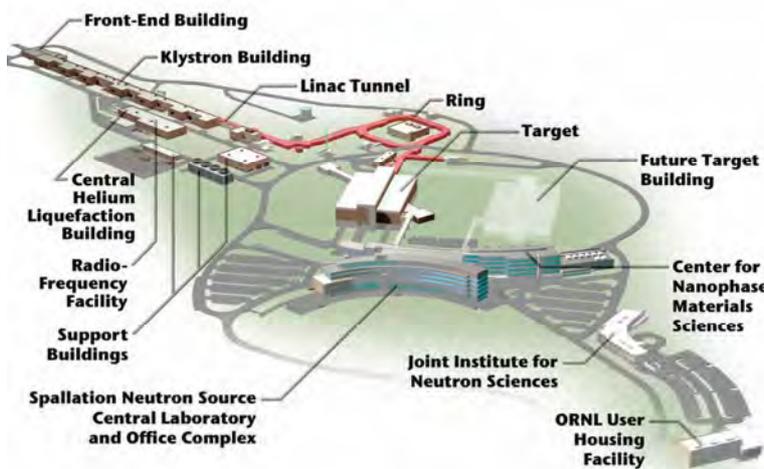
*Operating since 1990s in Switzerland.*

*Proton cyclotron*

*590 MeV, 2 mA, 1.2 MW*

*The exception: continuous neutron beams (reactor-like).*

# Other Large-scale Facilities: SNS at Oak Ridge



*Operational in USA since 2005*

*ISIS 'bigger sister'*

*LINAC (350m) + ring (250 m)*

*1 GeV H<sup>+</sup> superconducting LINAC  
185 MeV (first of its kind).*

*Compressor ring to achieve tight 700 ns pulses.*

*Liquid Hg target.*

*Currently operating at 1.4 MW*

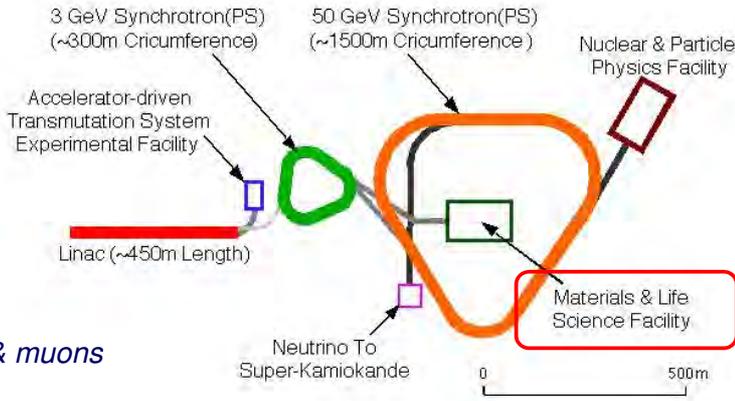
*Second Target (ISIS-like) planned*



# Other Large-scale Facilities: MLF at J-PARC



Liquid Hg target



Neutrons & muons

Short-pulse like ISIS and SNS

High Intensity Proton Accelerator Project

1 MW+

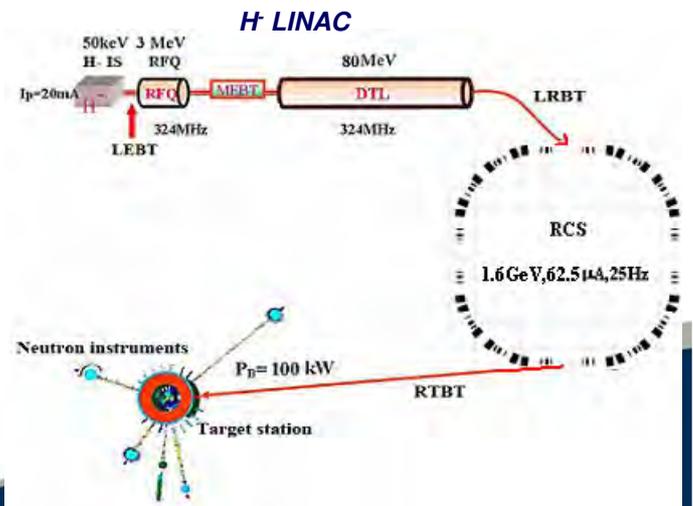
# Under Construction: CSNS in China



Very similar conceptually to ISIS

100 kW at 25 Hz, upgradable to 500 kW

Construction started 2011, aiming for completion early 2018.





# RANS: RIKEN Accelerator Neutron Source



*Be target: direct nuclear reaction (not spallation per se).*

*Very compact: 15 m long, 2 m wide (size of a neutron instrument at a large facility)*

*Sufficient flux for a number of applications in non-destructive testing of materials, neutronics R&D.*

<http://rans.riken.jp/en/rans.html>



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## Closer to Home

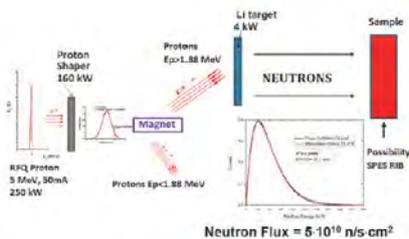


Beam Test Facility  
(DAFNE e<sup>-</sup> LINAC, Frascati)

*Planned for use in materials science*

Frascati Neutron Generator  
(ENEA, D acc, 14 MeV, 10<sup>11</sup> n/s)

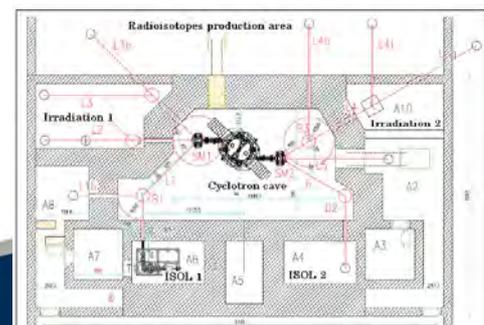
*Devoted to fusion research*



SPES, LENOS  
(Legnaro, up to 10<sup>14</sup> n/s)

*Irradiation & nuclear physics*

*Planned*

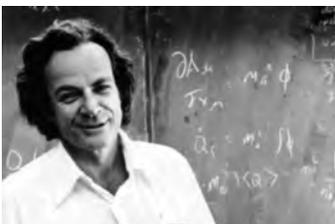
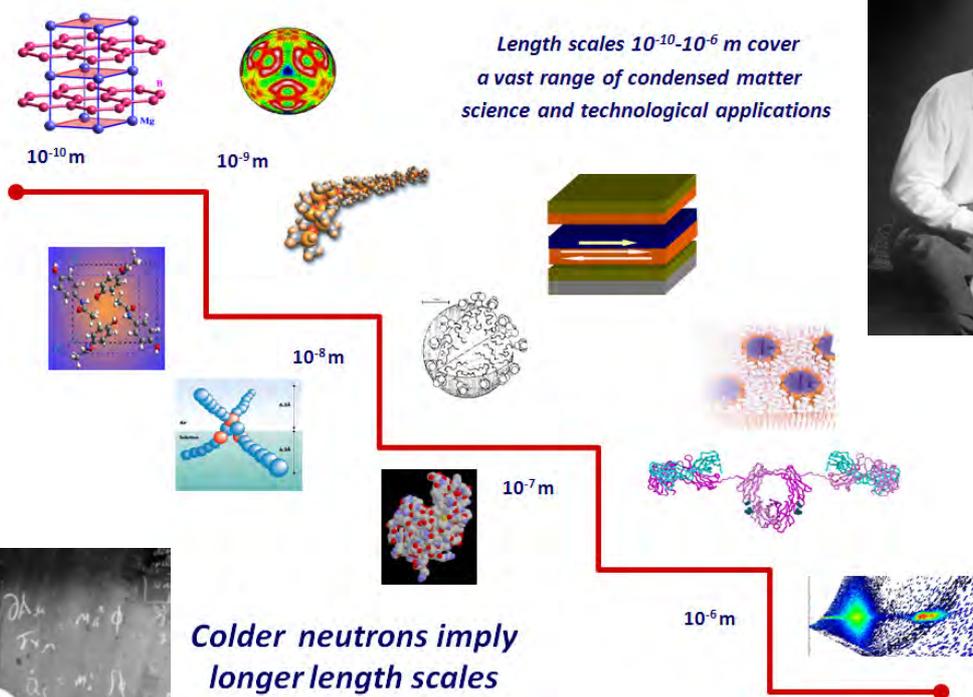


# Challenges & Opportunities



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There is Plenty of Room at the Bottom – *RP Feynman*



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# The Evolutionary Way

ISIS (UK): hot (1984) & cold (2008)



PSI (Switzerland): warm, cold & ultracold



LENS (USA): cold/ultracold

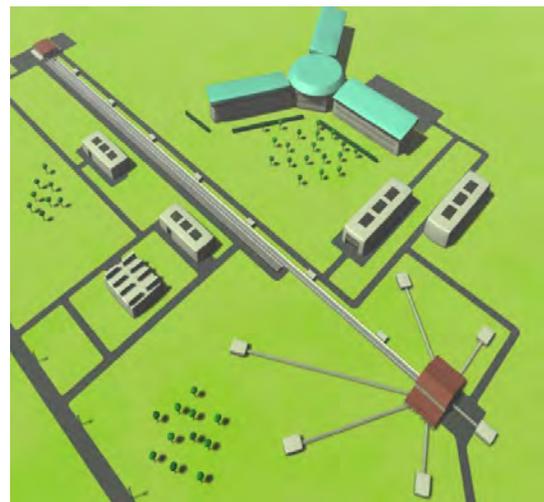


SNS (US): hot (2007) & cold (under consideration)

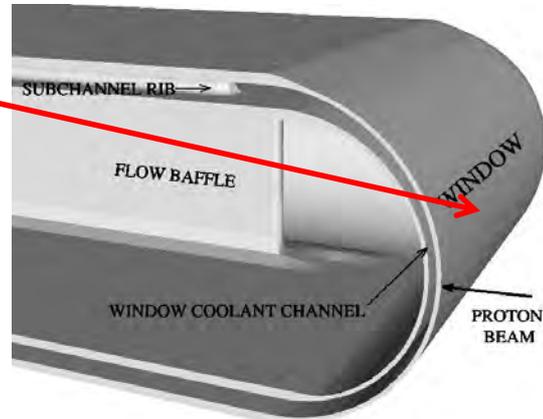
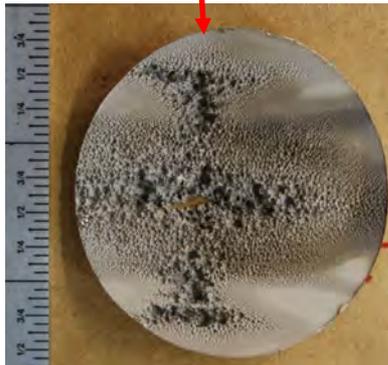
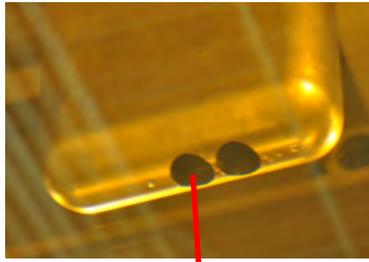


## Beyond Evolution: ESS

- Intense spallation source optimised for cold neutrons.
- Specification: 5 MW, 2.8 msec pulses (H Linac).
- Target station with up to 40 instruments (typical length 200 m).
- Complementary to short-pulse sources (JPARC, SNS, ISIS).
- Large investment, in construction phase (Lund Sweden).
- Challenges:
  - Power dissipation at 5MW: latest solution is a rotating tungsten target.
  - Instrument concepts largely untested to fully exploit 'long pulse.'



# Liquid Mercury Targets and the Challenge of MW Sources



*Ramping up power above 1 MW has been a challenge, requiring extensive R&D (He bubbling to avoid cavitation, etc)*



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## Emerging (Hybrid) Concepts



<http://myrrha.sckcen.be/>

*Construction envisaged 2017-2021*

*Full operations 2025*

**960 M€**

*Fast-neutron reactor 50-100 MW<sub>th</sub>*

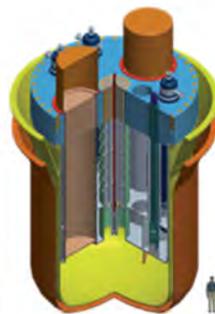
*600 MeV, 4 mA ADS (SC proton LINAC)*

*Spallation target + multiplying MOX core.*

*Transmutation & radioactive waste.*

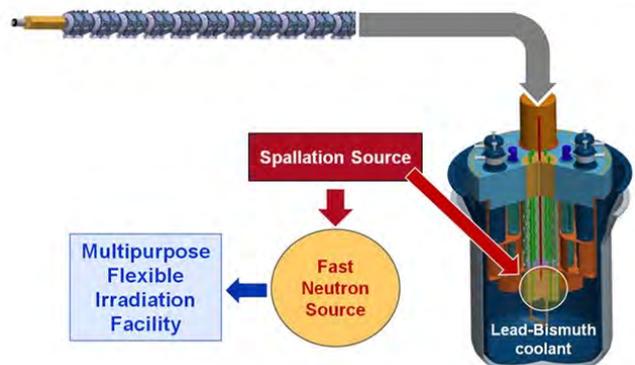
*Replaces BR2 isotope reactor.*

*Plans for a similar facility by JAEA (Japan)*



**Accelerator**  
(600 MeV - 4 mA proton)

**Reactor**  
• Subcritical mode (65 -100 MWth)  
• Critical mode (~100 MWth)



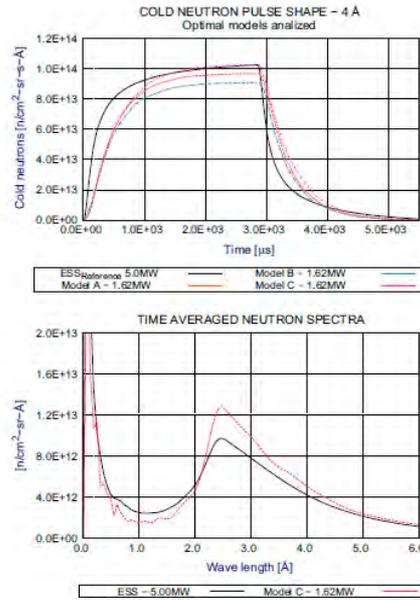
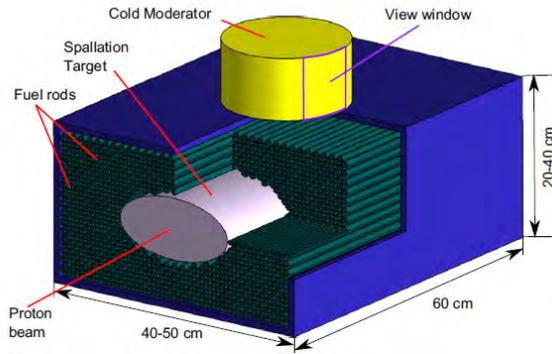
# ADS-based Neutron Facilities

Nuclear Instruments and Methods in Physics Research A 767 (2014) 176–187

Basic concept for an accelerator-driven subcritical system to be used as a long-pulse neutron source for Condensed Matter research

R. Vivanco<sup>a,b,\*</sup>, A. Ghigino<sup>a,b</sup>, J.P. de Vicente<sup>a,b</sup>, F. Sordo<sup>a,b</sup>, S. Terrón<sup>a,b</sup>, M. Magán<sup>a,b</sup>, J.M. Perlado<sup>b</sup>, F.J. Bermejo<sup>c</sup>

<sup>a</sup> ESS-BILBAO, Parque Tecnológico Bizkaia, Leizaola Bidea, Edificio 207 B Barrika Baja, 48160 Derio, Spain  
<sup>b</sup> Instituto de Física Nuclear - UPM, ETS Ingenieros Industriales, C/ José Gutiérrez Abascal, 2, 28006 Madrid Spain  
<sup>c</sup> Instituto de Estructura de la Materia, IEM-CSIC, Consejo Superior de Investigaciones Científicas, Serrano 123, 28006 Madrid, Spain



Neutron pulse shape metrics for different ADS configurations. Neutrons between 4 Å on cold moderator surface.

	ESS	Model A	Model B	Model C
Peak (n/cm <sup>2</sup> /Å/sr/s)	10.30 × 10 <sup>13</sup>	9.68 × 10 <sup>13</sup>	9.10 × 10 <sup>13</sup>	10.30 × 10 <sup>13</sup>
Signal (n/cm <sup>2</sup> /Å/sr)	2.54 × 10 <sup>11</sup>	2.26 × 10 <sup>11</sup>	2.13 × 10 <sup>10</sup>	2.37 × 10 <sup>10</sup>
Tail (n/cm <sup>2</sup> /Å/sr)	4.25 × 10 <sup>10</sup>	5.74 × 10 <sup>10</sup>	4.86 × 10 <sup>9</sup>	5.99 × 10 <sup>9</sup>
Signal to tail ratio	5.99	4.25	4.39	3.95
To 50% decrease (µs)	173	393	373	413
To 10% decrease (µs)	1003	1073	1063	1163

Cost effective solution.

Use of fissile fuel (regulatory implications)

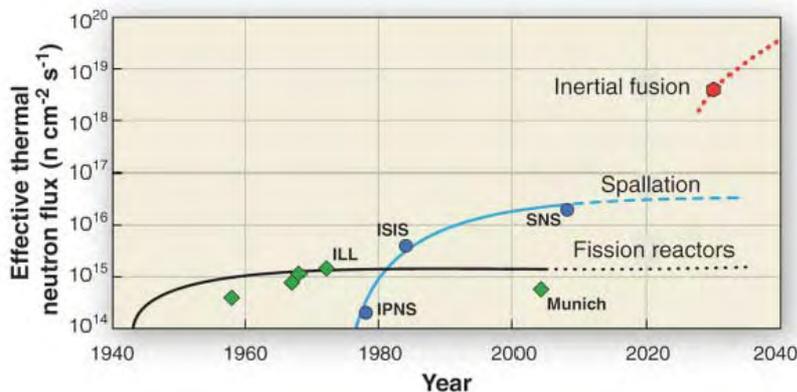
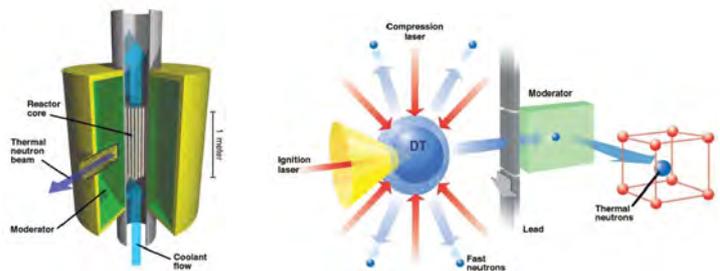
## Beyond Spallation

23 FEBRUARY 2007 VOL 315 SCIENCE

### A Route to the Brightest Possible Neutron Source?

Andrew Taylor,<sup>1</sup> Mike Dume,<sup>1</sup> Steve Bennington,<sup>1</sup> Stuart Ansell,<sup>1</sup> Ian Gardner,<sup>1</sup> Peter Norreys,<sup>1</sup> Tim Broome,<sup>1</sup> David Findlay,<sup>2</sup> Richard Nelmes<sup>2</sup>

We review the potential to develop sources for neutron scattering science and propose that a merger with the rapidly developing field of inertial fusion energy could provide a major step change in performance. In stark contrast to developments in synchrotron and laser science, the past 40 years have seen only a factor of 10 increase in neutron source brightness. With the advent of thermonuclear ignition in the laboratory, coupled to innovative approaches in how this may be achieved, we calculate that a neutron source three orders of magnitude more powerful than any existing facility can be envisaged on a 20- to 30-year time scale. Such a leap in source power would transform neutron scattering science.



Quantum leap in neutron production.

Implementation dependent upon further developments in fusion technology.

# Major Neutron Sources for Condensed Matter Research

## *Accelerator-based*

- Spallation Neutron Source (USA): [neutrons.ornl.gov/facilities/SNS/](http://neutrons.ornl.gov/facilities/SNS/)
- ISIS Pulsed Neutron and Muon Source (UK): [www.isis.rl.ac.uk](http://www.isis.rl.ac.uk)
- Japan Spallation Neutron Source (Japan): [j-parc.jp/MatLife/en/index.html](http://j-parc.jp/MatLife/en/index.html)
- Swiss Spallation Neutron Source (Switzerland): [www.psi.ch/sinq/](http://www.psi.ch/sinq/)
- Los Alamos Neutron Science Centre (USA): [lansce.lanl.gov/](http://lansce.lanl.gov/)
- Low Energy Neutron Source (USA): [www.indiana.edu/~lens/](http://www.indiana.edu/~lens/)
- European Spallation Source (Sweden): [ess-scandinavia.eu/](http://ess-scandinavia.eu/)
- European Spallation Source (Spain): [www.essbilbao.com](http://www.essbilbao.com)
- China Spallation Neutron Source (China): [csns.ihep.ac.cn/english/index.htm](http://csns.ihep.ac.cn/english/index.htm)

## *Reactor-based*

- Institut Laue-Langevin (France): [www.ill.eu/](http://www.ill.eu/)
- NIST Centre for Neutron Research (USA): [www.ncnr.nist.gov/](http://www.ncnr.nist.gov/)
- FRM-II (Germany): [www.frm2.tum.de/en/index.html](http://www.frm2.tum.de/en/index.html)
- Bragg Institute (Australia): [www.ansto.gov.au/research/](http://www.ansto.gov.au/research/)
- High-flux Isotope Reaction (USA): [neutrons.ornl.gov/facilities/HFIR/](http://neutrons.ornl.gov/facilities/HFIR/)
- Laboratoire Léon Brillouin (France): [www-llb.cea.fr/en/](http://www-llb.cea.fr/en/)
- Berlin Neutron Scattering Centre (Germany): [www.helmholtz-berlin.de](http://www.helmholtz-berlin.de)

## *What You Should Remember a Year from Now*

- Thermal neutrons are an exquisite probe of condensed matter.
- Neutrons are hard to produce → need dedicated facilities.
- Accelerator-based neutron sources:
  - Can also produce muons, also a unique probe of condensed matter.
  - Offer higher neutron flux → factors of ~10 justify new facilities.
  - Golden Age for neutron spallation, including compact sources.

**THE FUTURE LOOKS BRIGHT!**



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# This Friday, 83 Years Ago



## Possible Existence of a Neutron

James Chadwick  
*Nature*, p. 312 (Feb. 27, 1932)

It has been shown by Bothe and others that beryllium when bombarded by  $\alpha$ -particles of polonium emits a radiation of great penetrating power, which has been an absorption coefficient in lead of about  $0.3 \text{ (cm)}^{-1}$ . Recently Mme. Curie-Joliot and M. Joliot found, when measuring the ionisation produced by this beryllium radiation in a vessel with a thin window, that the ionisation increased when matter containing hydrogen was placed in front of the window. The effect appeared to be due to the ejection of protons with velocities up to a maximum of nearly  $3 \times 10^9 \text{ cm. per sec.}$  They suggested that the transference of energy to the proton was by a process similar to the Compton effect, and estimated that the beryllium radiation had a quantum energy of  $50 \times 10^6$  electron volts.

I have made some experiments using the valve counter to examine the properties of this radiation excited in beryllium. The valve counter consists of a small ionisation chamber connected to an amplifier, and the sudden production of ions by the entry of a particle, such as a proton or  $\alpha$ -particle, is recorded by the deflexion of an oscillograph. These experiments have shown that the radiation ejects particles from hydrogen, helium, lithium, beryllium, carbon, air, and argon. The particles ejected from hydrogen behave, as regards range and ionising power, like protons with speeds up to about  $3.2 \times 10^9 \text{ cm. per sec.}$  The particles from the other elements have a large ionising power, and appear to be in each case recoil atoms of the elements.

If we ascribe the ejection of the proton to a Compton recoil from a quantum of  $52 \times 10^6$  electron volts, then the nitrogen recoil atom arising by a similar process should have an energy not greater than about 400,000 volts, should produce not more than about 10,000 ions, and have a range in air at N.T.P. of about 1.3 mm. Actually, some of the recoil atoms in nitrogen produce at least 30,000 ions. In collaboration with Dr. Feather, I have observed the recoil atoms in an expansion chamber, and their range, estimated visually, was sometimes as much as 3 mm at N.T.P.

These results, and others I have obtained in the course of the work, are very difficult to explain on the assumption that the radiation from beryllium is a quantum radiation, if energy and momentum are to be conserved in the collisions. The difficulties disappear, however, if it be assumed that the radiation consists of particles of mass 1 and charge 0, or neutrons. The capture of the  $\alpha$ -particle by the  $\text{Be}^9$  nucleus may be supposed to result in the formation of a  $\text{C}^{12}$  nucleus and the emission of the neutron. From the energy relations of this process the velocity of the neutron emitted in the forward direction may well be about  $3 \times 10^9 \text{ cm. per sec.}$  The collisions of the neutron with the atoms through which it passes give rise to the recoil atoms, and the observed energies of the recoil atoms are in fair agreement with this view. Moreover, I have observed that the protons ejected from hydrogen by the radiation emitted in the opposite direction to that of the exciting  $\alpha$ -particle appear to have a much smaller range than those ejected by the forward radiation. This again receives a simple explanation of the neutron hypothesis.

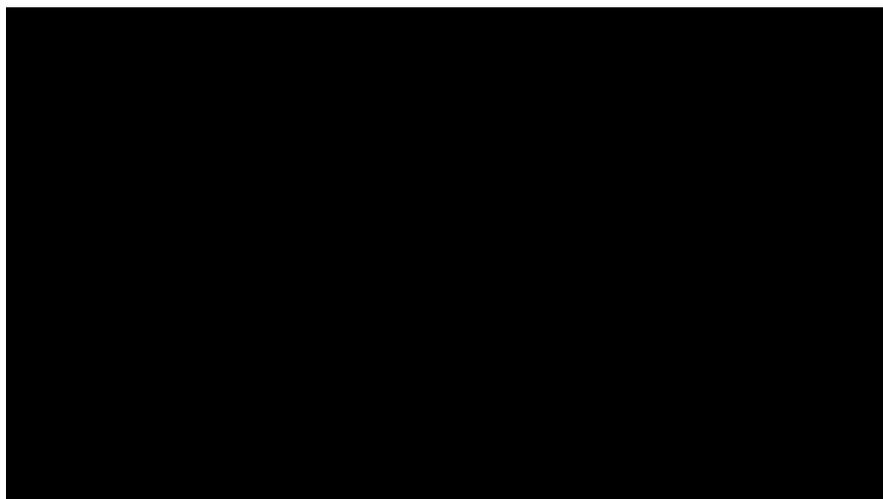
If it be supposed that the radiation consists of quanta, then the capture of the  $\alpha$ -particle by the  $\text{Be}^9$  nucleus will form a  $\text{C}^{13}$  nucleus. The mass defect of  $\text{C}^{13}$  is known with sufficient accuracy to show that the energy of the quantum emitted in this process cannot be greater than about  $14 \times 10^6$  volts. It is difficult to make such a quantum responsible for the effects observed.

It is to be expected that many of the effects of a neutron in passing through matter should resemble those of a quantum of high energy, and it is not easy to reach the final decision between the two hypotheses. Up to the present, all the evidence is in favour of the neutron, while the quantum hypothesis can only be upheld if the conservation of energy and momentum be relinquished at some point.

J. Chadwick.  
Cavendish Laboratory,  
Cambridge, Feb. 17.



## Questions, while we watch



## Come & visit!



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# Lecture IV: First-principles Materials Modelling

## A Primer

*Roma, February 2015*

### Outline [today]

- Fundamentals – ***Why*** neutron scattering
- Applications – ***What*** neutrons can do for you
- Neutron production – ***How neutrons are produced and used***
- First-principles materials modelling – ***The missing link!***

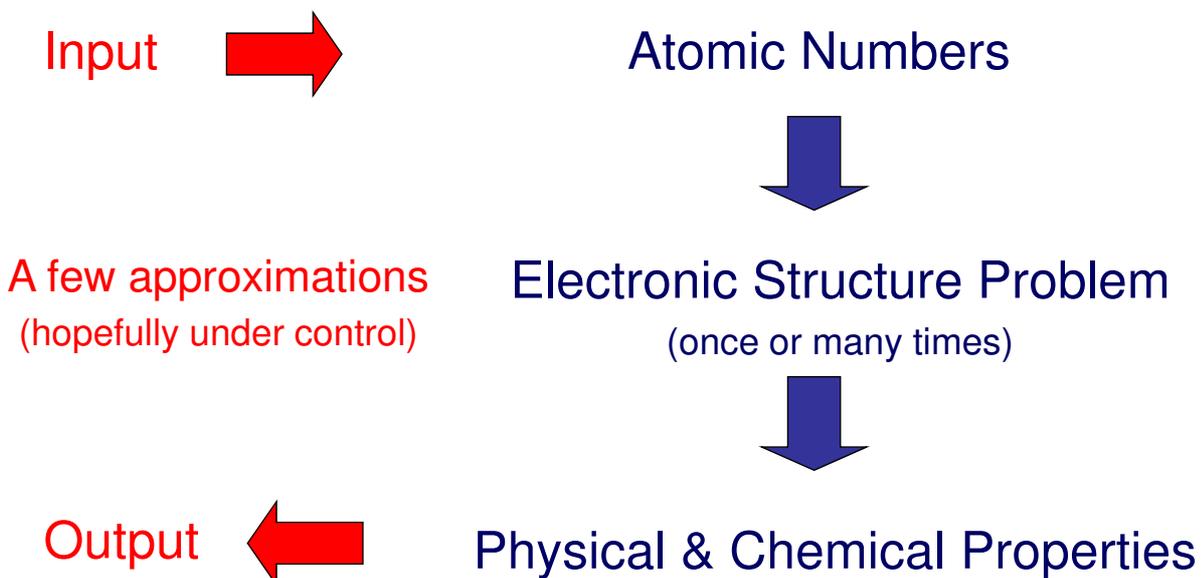
# Outline

- Why should an experimentalist care?
- Electronic structure methods: wavefunction vs. density-based .
- DFT basics, with an emphasis on terminology, some well-known limitations, and implementation of plane-wave methods (easiest to understand).
- Physico-chemical properties and the link to experiment.

*People love jargon. It is so palpable, tangible, visible, audible; it makes so obvious what one has learned; it satisfies the craving for results. It is impressive to the uninitiated. It makes one feels one belongs. Jargon divides People into Us and Them.*

*M. Buber, "I and Thou"*

## The Goal of First-principles (*ab initio*) Calculations



# Why First-principles (*ab initio*) Calculations

- Predictive simulation
  - Accurate calculation of properties from first principles.
  - Model development (structure/property relationships).
  - An integral component of materials design – a full-time job in itself.
- Computational “Experiments”
  - Calculate experimental observables, virtually anything you can measure (*neutron scattering being a very favourable case, as illustrated in Lectures 1 and 2*).
  - Complement experimental data with sophisticated / detailed models.
  - Suggest new experiments.

## Then and Now

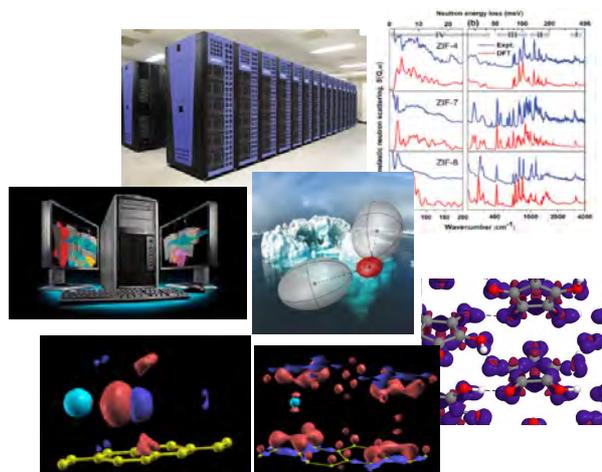
1990s

The ‘Ball-and-stick’ Way



21<sup>st</sup> Century

*In-silico* Neutron Scattering



Software packages have reached a level of sophistication whereby experimentalists can also enter the game (20 years ago, this task was much, much harder).

### THE PRIMARY AIM OF THIS PRIMER:

- **Appreciate what is going on “under the hood,” and the associated benefits.**
- **Encourage you to get your hands dirty : the more you do, the more you know.**

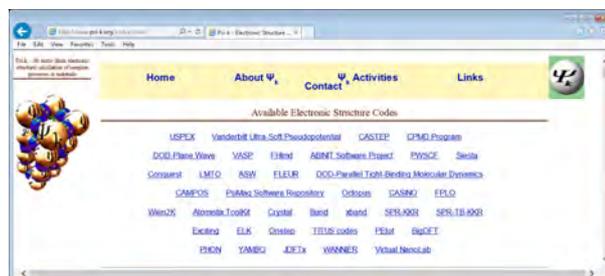
# What Is Out There at the Moment

[dft.sandia.gov/Quest/DFT\\_codes.html](http://dft.sandia.gov/Quest/DFT_codes.html)

## DFT production codes

- Periodic codes (principally)
  - Local orbital basis codes
    - QUEST; [SeqQuest](#) - gaussian basis pseudopotential code
    - SIESTA - numerical atom-centered basis pseudopotential code
    - CRYSTAL - gaussian basis all-electron code
    - AIMPRO
    - FHI-AIMS - (commercial license) full potential, all-electron, numerical orbitals
    - FPLQ
    - OpenMX - GPL - numerical atom-centered basis PP code (Ozaki group)
  - All-electron (augmented methods) codes
    - ELK - GPL - FP-LAPW (one branch from the [old EXCITING code](#))
    - EXCITING - FP-LAPW, focus on excited state properties (TDDFT, MBPT) [license not apparent on website, probably open source] (another branch from the [old EXCITING code](#))
    - FLEUR - "freely available" - FLAPW code
    - RSP1 - "Open Source" - FP-LMTO
    - WIEN2k - modest fee - full potential LAPW
  - Plane wave and related (real space, wavelet, etc.) methods
    - VASP
    - CASTEP
    - CPMD
    - ABINIT - GPL
    - BigDFT - GPL - wavelets
    - Quantum-Espresso (formerly PWscf) - GPL
    - PEtot - GPL
    - DACAPO - GPL
    - Socorro - GPL
    - JDFTx formerly known as DFT++ - GPL
    - Paratec
    - PARSEC - GPL - real space, pseudopotential
    - CP2K - GPL (mixed basis DFT)
    - GPAW - GPL - real-space multigrid PAW code
    - SPHINX
    - QBOX - GPL - plane wave pseudopotential, large parallel

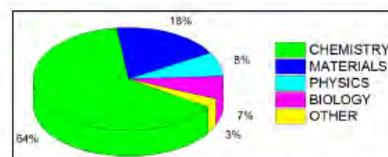
[www.psi-k.org](http://www.psi-k.org)



Examples shown today have used

**CASTEP, VASP, and CRISTAL**

## Where We Are Heading To



Usage of TOSCA by scientific discipline.

### TOSCA International Beamline Review

S Rudic, AJ Ramirez-Cuesta, SF Parker, F Fernandez-Alonso, RS Pinna, G Gorini, CG Salzmann, SE McLain, NT Skipper

December 2013

### The present

Recent advances in materials modelling have been at the heart of the success of TOSCA, with over half of its publications involving some form of modelling. The degree of sophistication of these methods has evolved from empirical ball-and-springs models to *ab initio* calculations of isolated molecules and, latterly, periodic DFT calculations across the entire Brillouin zone as well as the full inclusion of nuclear quantum effects. Such

### The future

large (*i.e.*, >10+), then replacing some of the forward-scattering analysers with these high-flux modules is advantageous, at a cost of ca. £200k.

Data acquisition is vital but so is its analysis. For systems with long-range order, TOSCA instrument scientists have been carrying-out state-of-the-art analysis for several years. There is a clear need to extend this paradigm to disordered materials, a task we intend to pursue primarily via scientific collaborations.

Both research areas targeted for growth (gas and charge storage) attempt to study hydrogenous and non-hydrogenous components simultaneously. While neutrons are ideal for hydrogen, they are less so for other elements. This challenge can be overcome by the use of

**Successes: periodic systems, phonon-based calculations.**

**Challenges: disordered media (catalysis, energy, liquids)**

# For More, in the Context of Neutron Scattering

Science & Technology Facilities Council  
Technical Report  
RAL-TR-2014-002

Science & Technology Facilities Council  
Technical Report  
RAL-TR-2012-016

Science & Technology Facilities Council  
Technical Report  
RAL-TR-2013-014

Science & Technology Facilities Council  
Technical Report  
RAL-TR-2014-017

Density Functional Theory for Experimentalists: A Four-Lecture Primer  
F Fernandez-Alonso  
January 2014

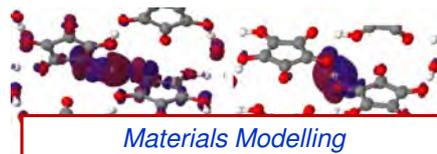
SCARF Annual Report 2011-2012  
P Oliver (ed)  
October 2012

SCARF Annual Report 2012-2013  
D Ross (ed)  
December 2013

SCARF Annual Report 2013-2014  
Version: 1.0  
D Ross (ed)  
November 2014

[epubs.stfc.ac.uk](http://epubs.stfc.ac.uk)

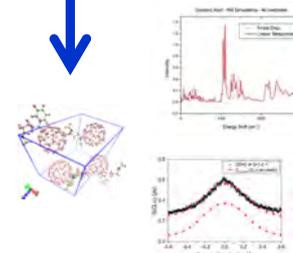
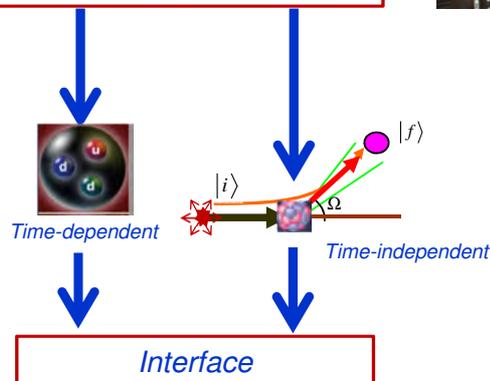
## In-Silico Neutron Scattering: The Basic Idea



*To fully exploit neutron data.*

*Model selection using neutron spectroscopic data.*

*Plenty of opportunities ahead.*

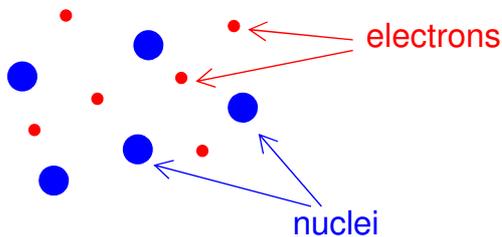


*Experiment-driven model selection*

*Detailed model analysis (CDA, ELF, TD-AIM, ...)*

# Back to Square One: The Schrodinger Equation

Any material can be boiled down to a collection of electrons and nuclei



Obeying the celebrated (time-independent & non-relativistic) Schrödinger equation

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

$$\hat{H} \Psi(\{r_i\}, \{R_j\}) = E \Psi(\{r_i\}, \{R_j\})$$

Where electronic and nuclear variables include BOTH spatial coordinates and spin.

The Hamiltonian operator describes the total energy of the collection in the absence of external fields

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{N-N} + \hat{V}_{N-e} + \hat{V}_{e-e}$$

Including both kinetic and potential (Coulomb) energy terms

$$\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_j^{alle} \nabla_j^2 = -\frac{\hbar^2}{2m_e} \sum_j^{alle} \frac{\partial^2}{\partial r_j^2}$$

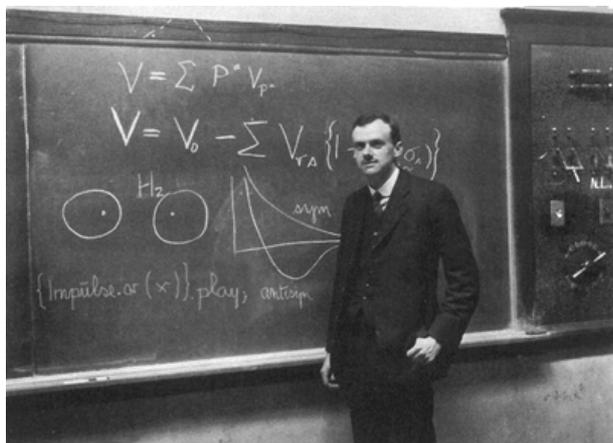
$$\hat{V}_{NN} = \frac{e^2}{4\pi\epsilon_0} \sum_i^{allN} \sum_{j>i}^{allN} \frac{Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}$$

$$\hat{T}_N = -\frac{\hbar^2}{2} \sum_i^{allN} \frac{\nabla_i^2}{m_i} = -\frac{\hbar^2}{2} \sum_i^{allN} \frac{1}{m_i} \frac{\partial^2}{\partial R_i^2}$$

$$\hat{V}_{Ne} = -\frac{e^2}{4\pi\epsilon_0} \sum_i^{allN} \sum_j^{alle} \frac{Z_i}{|\vec{R}_i - \vec{r}_j|}$$

$$\hat{V}_{ee} = \frac{e^2}{4\pi\epsilon_0} \sum_i^{alle} \sum_{j>i}^{alle} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Formally, this solves the problem (!)



*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.*

PAM Dirac (1929)

*Nobody understands quantum mechanics*

RP Feynman



REALITY CHECK: with the exception of the H atom, the SE equation is a many-body problem (thus, unsolvable).

***DEFINITELY, WE NEED APPROXIMATIONS***

## Important Properties of the Total Wavefunction

- Wavefunction must be physical, e.g., normalizable (particles must be somewhere in space).
- Symmetric/Antisymmetric with respect to exchange of fermions/bosons (Pauli exclusion principle).
  - Most important case is the electron (antisymmetric).
  - Other examples include H (antisymm) or D (symm).
- Pauli Principle for electrons implies these are correlated regardless of other interactions (Coulomb repulsion) since

$$\Psi(\dots, r_1, \dots, r_1, \dots) = 0$$

# Understanding What All This Means

- Our goal: solve SE for the many-body wavefunction  $\psi$ .
- This object is a highly dimensional object and thus exceedingly complex:
  - $3N_e$  electron spatial coordinates.
  - $N_e$  electron spin coordinates.
  - $3N_N$  nuclear spatial coordinates (ignoring nuclear spin).
- Let's work out some numbers for a "simple" molecule such as benzene ( $C_6H_6$ ).

## The Benzene Wavefunction

- Total of 12 nuclei and 42 electrons.
- Dimensionality of  $\psi$  in Cartesian space is  $3 \cdot (12+42) = 162$ .
- Removing translations and rotations of the whole system (6 DOFs) does not help much:  $162-6=156$  (but still practicable)
- MUCH WORSE for the ELECTRONIC problem:  $42!$  distinct permutations or  $\sim 10^{51}$  terms.
- How BIG is this number?

## Unsurmountable Practicalities

- Try to store  $\sim 10^{+51}$  terms as a numerical object for a SINGLE point in coordinate space (not much after all!!!).
- Just keeping modest single precision (4 bytes per number), a typical 2 Gb/cm<sup>2</sup> storage capacity would require a surface of  $\sim 10^{+42}$  Km<sup>2</sup>.
- For comparison, the Earth's surface is  $\sim 10^{+9}$  Km<sup>2</sup>.

THE PROMISED WISDOM HIDDEN IN THE SE IS NOT READILY ACCESSIBLE IF ONE LOOKS AT  $\psi$ .

**WE MUST MAKE DO WITH MUCH, MUCH LESS ...**

*Mathematically speaking, we are dealing with a problem like that of the "travelling salesman," still far from being solved due to its rather horrible size scaling (see K. Delvin, The Millennium Problems, Ch. 3).*

## The Born-Oppenheimer Approximation (or the "Dog-Fly" Problem)

$$\hat{H} \Psi(\{r_i\}, \{R_j\}) = E \Psi(\{r_i\}, \{R_j\})$$

- $m_N > 1800m_e$  thus nuclei move far more slowly than electrons (e.g., the dog vs. the fly).
- Electrons (the fly) thus follow nucleus (the dog) instantaneously.
- Mathematically one writes

$$\Psi(\{r_i\}, \{R_j\}) = \Psi_N(\{R_j\}) \Psi_e(\{r_i\})$$

- where electronic wavefunction only depends "parametrically" on nuclear coordinates.
- Procedure: "clamp" nuclei in place and solve the "electronic problem" (or forget about the dog!)

$$\hat{H} \Psi_e(\{r_i\}) = E \Psi_e(\{r_i\})$$

# The Electronic Problem

(or the “Fly” Problem)

$$\hat{H} \Psi_e(\{r_i\}) = E \Psi_e(\{r_i\})$$

Nuclear-only terms are either zero or constant  $\hat{H} = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee}$

$$\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_j^{all e} \nabla_j^2 = -\frac{\hbar^2}{2m_e} \sum_j^{all e} \frac{\partial^2}{\partial r_j^2}$$

Electronic kinetic energy

$$\hat{V}_{ee} = \frac{e^2}{4\pi\epsilon_0} \sum_i^{all e} \sum_{j>i}^{all e} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Electron-electron repulsion

$$\hat{V}_{Ne} = -\frac{e^2}{4\pi\epsilon_0} \sum_i^{all N} \sum_j^{all e} \frac{Z_i}{|\vec{R}_i - \vec{r}_j|}$$

“External” potential

Thus the EXTERNAL POTENTIAL (nuclear structure) and the number of electrons (chemical makeup) determine the problem (within the BO approx).

**THIS OBSERVATION IS IMPORTANT TO LAY THE FOUNDATIONS OF DFT**

## Physico-chemical Properties

- Structure problem: find nuclear coordinates for which the TOTAL energy is a minimum (the so-called ground-state energy, includes what electrons are doing).
- Once ground-state structure has been found, other properties follow, e.g., band structure, phonons, dielectric constant, dipole moment, polarizability, etc.
- To achieve the above, total wavefunction  $\psi$  needs to be obtained by solving the SE (almost always involving BO approx).

$$\hat{H} \Psi(\{r_i\}, \{R_j\}) = E \Psi(\{r_i\}, \{R_j\})$$

# Time-dependent Properties (Molecular Dynamics)

- Choose a starting configuration, compute its total energy, as well as forces acting on ions.
- Propagate in time:
  - Use Newton's equations of motion to compute positions of ions after a short period of time.
  - Solve electronic problem, recompute ionic forces and so on.
  - This approach avoids the use of force fields (great advantage).

*Question: for which ions may this approach fail?*

## Tackling the Electronic Problem

- USE OF FINITE "BASIS SETS" centered around each nucleus (e.g., start with atomic orbitals): choice of basis becomes a crucial point of departure but a hard one to control if not careful.
- Electron motion is highly correlated (we face a complicated many-body problem).
  - Those electrons with same spin are "kept away" by antisymmetry requirements from Pauli Exclusion Principle (also called "exchange correlation" or "Fermi correlation").
  - Those with same spin are kept away due to repulsion (Coulomb correlation).
  - In practice we can only hope to do this APPROXIMATELY.

# Wavefunction-based Electronic Structure Methods

- Simplest method of practical use: Hartree Fock (1950s)
- What is done (& assumed) in HF:
  - Electronic wavefunction is an antisymmetric combination of one-electron orbitals (so-called Slater determinant).
  - Replace exact Hamiltonian by that of a set of non-interacting electrons where each moves in an average field (Mean-field Theory).
  - One-electron “orbitals” obey a set of COUPLED differential equations, whose solution must be obtained ITERATIVELY (so-called SCF or “self-consistent-field” method).

Hartree-Fock and SCF: also important to understand DFT, thus we need to delve a bit into the details.

## The Hartree-Fock Method

Wavefunction is a “Slater determinant” of “spin-orbitals”

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(r_1) & \chi_2(r_1) & \cdot & \chi_N(r_1) \\ \chi_1(r_2) & \chi_2(r_2) & \cdot & \chi_N(r_2) \\ \cdot & \cdot & \cdot & \cdot \\ \chi_1(r_N) & \chi_2(r_N) & \cdot & \chi_N(r_N) \end{vmatrix}$$

“Spin-orbitals” contain both spatial and spin wavefunctions  $\chi_i = \phi_i \alpha$

Simple example: two-electron system (the H<sub>2</sub> molecule)

$$\Psi_{HF}(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(r_1) & \chi_2(r_1) \\ \chi_1(r_2) & \chi_2(r_2) \end{vmatrix} = \chi_1(r_1)\chi_2(r_2) - \chi_1(r_2)\chi_2(r_1) = -\Psi_{HF}(r_2, r_1)$$

Need second term to satisfy antisymmetry requirement (first term is not enough)

# The Hartree-Fock Method for Solving SE Equation

“Slater determinant” is our one-electron guess for

$$\hat{H} \Psi_{HF}(\{r_i\}) = E \Psi_{HF}(\{r_i\})$$

Variational Principle:  $E = \langle \Psi | \hat{H} | \Psi \rangle \geq E_0$

To use this principle we vary spin orbitals to minimize E

Hartree-Fock Energy:  $E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle$

## The Hartree-Fock Method in Some Detail

Seek to solve:  $E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle$

Which for a Slater-type electronic wavefunction gives:

$$E_{HF} = \sum_{i=1}^N \langle \chi_i | \hat{h}_i | \chi_i \rangle + \frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \sum_{i=1}^N \sum_{j=1}^N \left\{ \langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_j \chi_i \rangle \right\}$$

One-electron  
operator

Coulomb

Exchange

*Self-interaction  
cancels out exactly (i=j)*

$$\hat{h}_i = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_j^{\text{all nuclei}} \frac{Z_j}{r_{ij}}$$

$$\langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_i \chi_j \rangle = \int \chi_i^*(r_1) \chi_j^*(r_2) \frac{1}{|r_1 - r_2|} \chi_i(r_1) \chi_j(r_2) dr_1 dr_2$$

$$\langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_j \chi_i \rangle = \int \chi_i^*(r_1) \chi_j^*(r_2) \frac{1}{|r_1 - r_2|} \chi_j(r_2) \chi_i(r_1) dr_1 dr_2$$

# The Hartree-Fock Equations

Apply Variational Theorem & use orthogonality of spin orbitals

$$E_{HF} = \sum_{i=1}^N \langle \chi_i | \hat{h}_i | \chi_i \rangle + \frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \sum_{i=1}^N \sum_{j=1}^N \left\{ \langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_j \chi_i \rangle \right\}$$

and  $\langle \chi_i | \chi_j \rangle = \delta_{ij}$

To obtain a set of equations for each spin orbital

$$\left[ \hat{h}_i + \hat{V}_{HF} \right] \chi_i = \epsilon_i \chi_i \quad \text{with} \quad \hat{V}_{HF} = \sum_{k=1}^{alle} \hat{J}_k - \hat{K}_k$$

Coulomb  $\left[ \hat{J}_k(r_1) \right] \chi_i(r_1) = \left[ \int \chi_k^*(r_2) \chi_k(r_2) \frac{1}{r_{12}} dr_2 \right] \chi_i(r_1)$

Exchange  $\left[ \hat{K}_k(r_1) \right] \chi_i(r_1) = \left[ \int \chi_k^*(r_2) \chi_i(r_2) \frac{1}{r_{12}} dr_2 \right] \chi_k(r_1)$

## The Coulomb and Exchange Terms

Coulomb term related to electronic density

$$\left[ \hat{J}_k(r_1) \right] \chi_i(r_1) = \left[ \int \chi_k^*(r_2) \chi_k(r_2) \frac{1}{r_{12}} dr_2 \right] \chi_i(r_1)$$

$$\sum_{k=1}^{alle} \hat{J}_k = \sum_{k=1}^{alle} \int \chi_k^*(r_2) \chi_k(r_2) \frac{1}{r_{12}} dr_2 = \int \frac{\rho(r_2)}{r_{12}} dr_2$$

Exchange term leads to NON-LOCAL EXCHANGE POTENTIAL

$$-\sum_{k=1}^{alle} \left[ \hat{K}_k(r_1) \right] \chi_i(r_1) = -\int \sum_{k=1}^{alle} \frac{\chi_k^*(r_2) \chi_k(r_1)}{r_{12}} \chi_i(r_2) dr_2 = \int v_X(r_1, r_2) \chi_i(r_2) dr_2$$

Such that

$$\left[ \hat{h}_i + \int \rho(r_2) \frac{1}{r_{12}} dr_2 \right] \chi_i + \int v_X(r_1, r_2) \chi_i(r_2) dr_2 = \epsilon_i \chi_i$$

Hartree term (electron density is important)

exchange potential (hard bit)

# Hartree Fock Recap

HF orbitals obey:

$$\left[ \hat{h}_i + \int \frac{\rho(r_2)}{r_{12}} dr_2 \right] \chi_i + \int v_X(r_1, r_2) \chi_i(r_2) dr_2 = \epsilon_i \chi_i$$

HF one-electron spin orbitals describe a non-interacting system under the influence of a mean-field potential made up of a Coulomb term and a NON-LOCAL exchange potential.

To note:

- Electronic density plays a role from the outset.
- HF is a mean-field theory and thus breaks down very quickly:  $F_2$  is not a molecule, metallic state does not exist, ...
- Errors in HF approach are due to absence of electron correlation.

## Wavefunction-based Methods Beyond Hartree-Fock

- Better approximations (so-called “correlated methods”) exist but at a very high computational cost due to unfavourable scaling (e.g., need a sum of Slater determinants or “configurations,” or use of perturbation theory).
- Some examples are: MP2, CISD, CCSD, MRCI which scale as  $N^x$  where  $x > 5$  [1]. Be aware of these when reading the literature (they are quite common and useful to benchmark DFT calculations).
- Some problems:
  - Very flexible descriptions of wavefunction required – hard work.
  - A more expensive calculation or basis set does not guarantee better results (uncontrolled cancellation of errors, BSSEs, etc).
  - Case-by-case exploration is typically the norm.
  - ***Extension to large systems (a solid) of practical interest clearly beyond our reach now and in the foreseeable future.***

[1] For an excellent account, see: A Szabo & NS Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, 1989).

*Is it, however, necessary to solve the SE and determine the wavefunction in order to compute the ground-state energy?*

*To what extent can we avoid it?*

*In a sense, the SE equation is quite misleading as it invites us to pay close attention to the wavefunction*

$$\hat{H} \Psi(\{r_i\}, \{R_j\}) = E \Psi(\{r_i\}, \{R_j\})$$

# The Two Theorems that Changed Everything [1]

## Theorem 1

The external potential  $V_{Ne}$  is **uniquely** determined by the density. The total energy is a unique functional of the electron density (written  $E[n]$ ).

$$\hat{V}_{Ne} = -\frac{e^2}{4\pi\epsilon_0} \sum_i^{all N} \sum_j^{alle} \frac{Z_i}{|\vec{R}_i - \vec{r}_j|}$$

## Theorem 2

The density which minimizes the energy corresponds to the **ground-state density** and the minimum energy is the ground state energy (yet another Variational Principle).

*In other words, there is a universal functional  $E[n]$  which can be minimised to obtain the exact **ground state density** and energy.*

[1] Hohenberg & Kohn, Phys. Rev. B 136, 864 (1964).

## What is a Functional?

- We are all familiar with functions, whereby one establishes a map or rule between one set of numbers and another, e.g.,  $y=f(x)$ .
- A functional extends this concept to create a map between a set of functions and a set of numbers, denoted  $y=F[f(x)]$ .
- In the context of DFT,  $y=E$  (the energy) and  $f(x)=n$  (the electronic density).
- In fact, you have all been dealing with functionals for quite a while (e.g., definite integrals)

$$F[g] = \int_a^b g(x) dx$$

where specification of an integrable function  $g(x)$  produces a number defined in terms of the constants  $a$  and  $b$ .

# The Energy Functional

Electronic SE  $\hat{H} \Psi_e(\{r_i\}) = E \Psi_e(\{r_i\})$

Electronic Hamiltonian  $\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{Ne}$

Conventionally  $\hat{V}_{Ne} = \hat{V}_{ext}$  to emphasize its “external” character in the electronic problem

Total energy is given by  $E[n] = T[n] + E_{ee}[n] + E_{ext}[n]$

From SE equation, “external” part follows

$$E_{ext}[n] = \int \hat{V}_{ext} n(r) dr \quad \text{with} \quad \hat{V}_{ext} = -\frac{e^2}{4\pi\epsilon_0} \sum_i^{all N} \sum_j^{alle} \frac{Z_i}{|\vec{R}_i - \vec{r}_j|}$$

**Kinetic and electron-electron functionals are a priori unknown.**

Need to approximate them intelligently.

## The Kohn-Sham Approach [1]

First (and most popular) way to approximate unknown functionals.

Essence: introduce a *fictitious* system of N non-interacting electrons described by a single determinant (Slater-type) wavefunction in N “orbitals”. **FORMALLY IDENTICAL TO HARTREE-FOCK.**

In this non-interacting system, both kinetic energy and electron density can be obtained exactly from the orbitals.

$$\hat{T}_s = -\frac{\hbar^2}{2m_e} \sum_j^{alle} \langle \phi_j | \nabla^2 | \phi_j \rangle \quad \text{Note: this KE is fictitious}$$

$$\rho(r) = \sum_j^{alle} |\phi_j|^2 \quad \text{Note: this construction immediately ensures that it is “legal” (obeys Pauli Exclusion Principle)}$$

[1] Kohn & Sham, Phys. Rev. A 140, 1133 (1965).

Recall expression for Hartree-Fock energy

$$E_{HF} = \sum_{i=1}^N \langle \chi_i | \hat{h}_i | \chi_i \rangle + \frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \sum_{i=1}^N \sum_{j=1}^N \left\{ \left\langle \chi_i \chi_j \left| \frac{1}{r_{12}} \right| \chi_i \chi_j \right\rangle - \left\langle \chi_i \chi_j \left| \frac{1}{r_{12}} \right| \chi_j \chi_i \right\rangle \right\}$$

Coulomb term is related to densities      Exchange is not

We thus treat Coulomb correlation separately (it is an important term)

$$E_H[n] = \frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \int \frac{n(r_1)n(r_2)}{r_{12}} dr_1 dr_2$$

“Hartree” term

And the energy functional  $E[n]$  is rewritten as

$$E[n] = T_s[n] + E_H[n] + E_{ext}[n] + E_{XC}[n]$$

where we have introduced the “exchange-correlation” functional  $E_{XC}$

$$E_{XC}[n] = [T[n] - T_s[n]] + [E_{ee}[n] - E_H[n]]$$

(“exchange-correlation” is somewhat of a misnomer, but never mind)

## What is $E_{XC}$ ?

$$E_{XC}[n] = [T[n] - T_s[n]] + [E_{ee}[n] - E_H[n]]$$

The exchange correlation functional is the error made when using

- A non-interacting kinetic energy term.
- Assuming that electron-electron interactions are classical (no exchange).

IT CONTAINS ALL REMAINING UNCERTAINTIES

With this functional for the total energy in terms of the electronic density we can now

- Apply the Variational Theorem.
- Use the KS orbitals which minimise the total energy to construct the electronic density  $n$ .
- Formally identical to the HF approach where the non-local exchange potential is replaced by a local exchange-correlation potential.

# The Kohn-Sham Equations

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + \hat{V}_{ext} + \int \frac{n(r_2)}{r_{12}} dr_2 + \hat{V}_{XC} \right] \phi_i = \epsilon_i \phi_i$$

where  $V_{XC}$  is a local potential defined as the functional derivative of  $E_{XC}$  wrt to the density.

$$\hat{V}_{XC} = \frac{\delta E_{XC}[n]}{\delta n}$$

KS Equations are solved iteratively until self-consistency is reached.

The procedure does not involve approximations, EXCEPT for the precise form of  $E_{XC}$ .

Conversely, if we knew  $E_{XC}[n]$ , we could solve for the exact ground-state energy and density EXACTLY, FOR ANY SYSTEM .

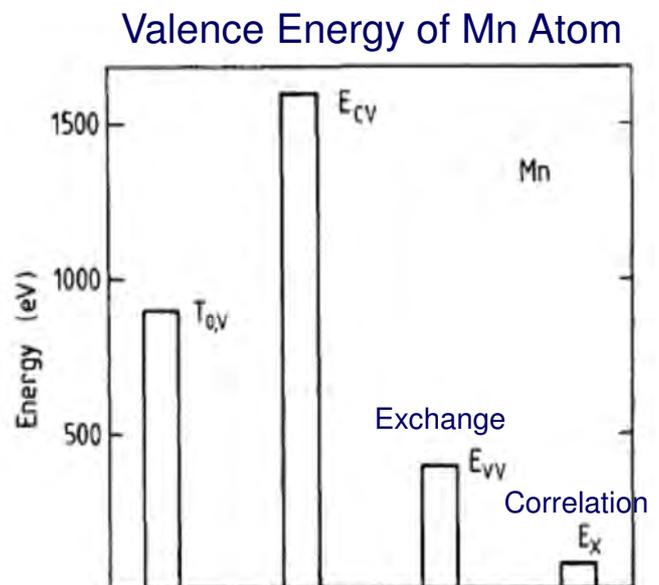
**THE KS Equations ARE AT THE HEART OF ALL DFT CODES**

## Hierarchy of Contributions to the Total Energy

*Our ignorance about how to solve SE appears to have been swept into a single term  $E_{XC}$  accounting for the hard bits (e.g., electron exchange and correlation).*

Does this help?

- Exchange is small, correlation even smaller.
- Thus, a smart choice in most cases.
- A reasonable approx to  $E_{XC}$  is likely to provide a good description of total energy.



Courtesy of Dr K Refson

# Remarks on DFT and KS Equations

- Correspondence between electron density and energy of the real vs. non-interacting system is ONLY EXACT if the exact functional is known.
- In this sense, KS Method is EMPIRICAL: need to guess  $E_{XC}$ .
  - We do not know it.
  - We do not know even know how to systematically approach it.
- However
  - We can work it out in a number of systems for which solutions are known.
  - From this, we can have good approximations to the functional.
  - And use it in an UNBIASED & PREDICTIVE manner.
- Computational cost: traditionally it has been  $N^3$  but recent progress is making it drop towards  $N$  (can do larger systems).

## Functionals: The Uniform Electron Gas

Collection of  $N$  electrons in a uniformly positive background (to keep things neutral).

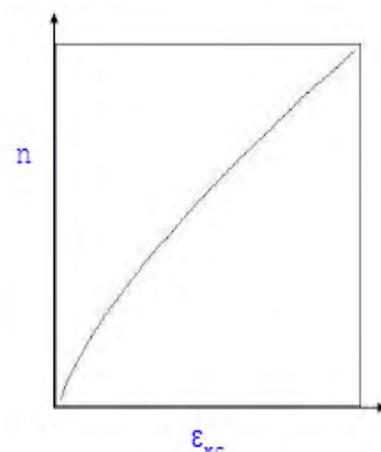
It is an old problem (uniform electron gas):

- Kinetic energy, Thomas & Fermi (1927).
- Exchange, Dirac (1930).
- Coulomb part (numerical, QMC [1])

KE and X terms suggest an ansatz for  $E_{XC}$  in inhomogeneous (real) systems as an integral over a **local function of the charge density**.

$$E_{XC}[n] = \int n(r) \varepsilon_{XC}(n(r)) dr$$

$$T[n] = C_{KE} \int n^{\frac{5}{4}}(r) dr$$
$$E_x[n] = -C_x \int n^{\frac{3}{4}}(r) dr$$



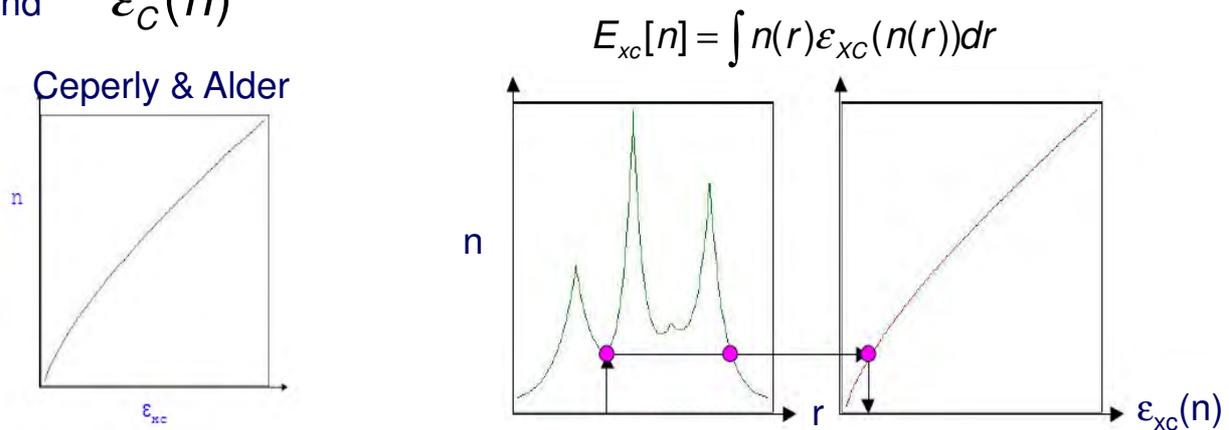
# Functionals: The Local Density Approximation

Simplest approximation: at every point in space, use the value of the density that the uniform gas would have (LDA).

$\epsilon_{xc}(n)$  can then be taken as a sum of exchange and Coulomb correlation terms

$$\epsilon_{XC}(n) = \epsilon_X(n) + \epsilon_C(n) \quad \text{with} \quad \epsilon_X(n) = -C_X n^{\frac{1}{3}} \quad (\text{Dirac})$$

and  $\epsilon_C(n)$



## How Good is the LDA?

ORIGINAL PREDICTION (Kohn & Sham 1965): *"We do not expect an accurate description of chemical bonding."*

Extensive computational experimentation in the past 30+ years shows **REMARKABLE SUCCESS:**

- Good description of covalent, metallic, and ionic bonds.
- Not adequate for:
  - Hydrogen bonds (relatively weak).
  - Van der Waals interaction (London dispersion): but this is a problem with DFT in general.

Common problems:

- Energy differences between very different structures.
- Binding energies are typically OVERESTIMATED.
- Energy barriers for diffusion/chemical reactions can be very small.

# Functionals Beyond LDA: GGA

LDA is the zeroth approximation to the density (sort of a 80-for-20 answer).

To go beyond, need to account for the spatial variation of the density.

Generalized Gradient Approximation (GGA) is the most popular of these approaches.

GGA functional is of the form:

$$E_{xc}[n] = \int n(r) \varepsilon_{xc}(n, \nabla n) dr$$

Approximations are made separately for Exchange & Coulomb terms, usually involving empirical parameters from fits to large sets of accurate calculations on atoms. Some examples are:

- Coulomb: LYP (1988), PW91 (1991), P86 (1986) ...
- Exchange: BPW91, BLYP, ...

# Functionals Beyond GGA: Meta-GGA

Simply, include the second derivatives in your description

$$E_{xc}[n] = \int n(r) \varepsilon_{xc}(n, \nabla n, \nabla^2 n, \tau) dr$$

where  $\tau$  is the “kinetic energy density”

$$\tau = \frac{1}{2} \sum_i |\nabla \phi_i|^2$$

# Hybrid Functionals

If electron-electron interactions are switched off from the problem, one recovers the Hartree-Fock answer.

The above suggests that the GGA functional can be used to improve our ansatz for the exact exchange-correlation functional.

A reasonable, first-order approximation is given by

$$E_{xc}[n] = \alpha E_{HF} + \beta E_{xc}^{GGA}$$

With  $\alpha$  and  $\beta$  determined by reference to exact results (e.g., fit to a data set including ionization potentials, proton affinities, total energies).

B3LYP is the most popular one (particularly amongst chemists): binding energies, geometries, and frequencies are systematically improved with respect to GGA.

## The Kohn-Sham Equations (Recap)

Single-particle equations: 
$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + \hat{V}_{eff} \right] \phi_i = \epsilon_i \phi_i$$

Effective potential:

$$\hat{V}_{eff} = \hat{V}_{ext} + \hat{V}_H + \hat{V}_{XC}$$

External potential: 
$$-\frac{e^2}{4\pi\epsilon_0} \sum_i^{all N} \sum_j^{all e} \frac{Z_j}{|\vec{R}_i - \vec{r}_j|}$$

Hartree term: 
$$\int \frac{n(r_2)}{r_{12}} dr_2$$

Exchange-correlation  
The big unknown:  
LDA, GGA, meta-GGA, ...

Single-particle orbitals can *always* be represented in a convenient BASIS SET.

# Basis Sets

- The traditional choice: start with atomic orbitals, so-called “LCAO basis” (linear combination of atomic orbitals).
  - It makes “physical sense.”
  - Expected to describe well core electrons (those not participating in chemical bonding).
  - But it is an ARBITRARY choice after all.
- Mathematically, we can use ANY complete (orthonormal) basis set as starting point.
- For solid-state problems with translational invariance (well-defined  $k$ ), **PLANE WAVES** are a convenient choice.

## Plane Waves

For a given electronic orbital

$$\phi_i(\vec{r}) = \int \phi_i(\vec{k}) e^{i\vec{k}\cdot\vec{r}} d\vec{r} \quad \text{where } \phi_i(k) \text{ is the Fourier transform of } \phi_i(r).$$

Very familiar expression to many, e.g., diffraction, image or signal processing, or FT-IR if  $r$  is replaced by *time* ...

Fourier transformation is computationally efficient (FFT algorithms).

Also, certain operations are easier to do in  $k/r$  space.

In addition, for a periodic system:

$$\phi_{i,k}(r) = u_{i,k}(r) e^{ik\cdot r}$$

BLOCH's THEOREM

$u(r)$  has periodicity of unit cell

# Plane Waves: How Many?

Plane-wave basis functions are of the form:

$$\phi_{i,k}(r) = \sum_{\mathbf{G}} u_{i,k}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})r} \quad \text{for reciprocal lattice vectors } \mathbf{G}, \mathbf{k} \text{ spanning 1st Brillouin zone.}$$

E.g.,  $\phi_{i,k}(\mathbf{G})$  is the  $\mathbf{k}$  component of the  $i^{\text{th}}$  electronic orbital.

$u_{i,k}(\mathbf{G})$  are simply expansion coefficients (constants).

In principle, we need an infinite number of terms.

**PLANE-WAVE ENERGY CUTOFF (a convergence parameter)**

$$E_{\text{cutoff}} \geq \frac{\hbar^2 (k^2 + G^2)}{2m_e} \quad \text{or length scale:} \quad \lambda_{\text{cutoff}} = \frac{h}{\sqrt{2m_e E_{\text{cutoff}}}}$$

## The Performance of DFT Functionals

“Functional Design:” two schools of thought

- Puristic: use the properties of the functional to determine its form and shape (including parameters).
- Pragmatic: come up with a functional form, introduce lots of parameters to be fitted against experimental data or accurate calculations (empirical).

**THIS IS A USEFUL DISTINCTION IN ASSESSING PERFORMANCE FOR A PARTICULAR PROBLEM.**

Characteristics of some popular functionals:

- BLYP, PBE, PKZB: virtually “ab-initio.”
- HCTH, VS98: heavily parameterised (large molecular training sets).

Some tabulations/benchmarks:

- Kurth, Perdew & Blaha, *Int. J. Quantum Chemistry* 75, 889 (1999).
- Adamo, Ernzerhof & Scuseria, *J. Chem. Phys.* 112, 2643 (2000).

# DFT Functionals: Benchmarking (I)

TABLE I  
Exchange energies ( $-E_x$  in hartree) for some spherically symmetric atoms.<sup>a</sup>

	$E_x^{\text{exact}}$	$E_x^{\text{LSD}}$	$E_x^{\text{PBE}}$	$E_x^{\text{PW92}}$	$E_x^{\text{BLYP}}$	$E_x^{\text{HCTH}}$	$E_x^{\text{PKZB}}$	$E_x^{\text{VGN}}$	$E_x^{\text{THH}}$
H	0.3125	0.2680	0.3059	0.3112	0.3068	0.3055	0.3081	0.3148	0.3120
He	1.0258	0.8840	1.0138	1.0313	1.0255	1.0069	1.0302	1.0399	1.0302
Li	1.7807	1.5379	1.7572	1.7876	1.7754	1.7454	1.7692	1.7893	1.7652
Be	2.6658	2.3124	2.6358	2.6601	2.6578	2.6114	2.6482	2.6579	2.6707
B	3.6044	5.9008	6.5521	6.8252	6.5961	6.5145	6.5255	6.5968	6.6045
Ne	12.1050	11.0335	12.0667	12.1599	12.1376	12.0114	11.9514	12.1404	12.1260
Na	14.0131	12.7859	13.9506	14.0528	14.0304	13.9009	13.8115	14.0374	14.0177
Mg	15.9884	14.6117	15.9147	16.0260	16.0005	15.8596	15.7448	15.9967	15.9862
P	22.8341	20.7951	22.5028	22.6221	22.6221	22.5016	22.2475	22.6365	22.8089
Ar	30.1747	27.8632	29.9961	30.1484	30.1535	30.0751	29.6437	30.1918	30.1429
Kr	93.8330	88.6245	93.4257	93.6645	93.8721	95.1602	92.2849	94.8248	93.8407
Xe	179.0835	170.5660	178.2450	178.5649	179.0427	183.2130	176.2574	181.8907	179.0836
mean (in %)	—	9.6	0.3	0.2	0.2	1.4	1.3	0.5	0.1

<sup>a</sup>All functionals were evaluated with self-consistent exchange-only OEP orbitals and densities [47]. Exact values,  $E_x^{\text{exact}}$ , were obtained by evaluating Eq. (11) with these orbitals. The "mean" is the mean absolute value of the relative error.

Mean absolute value of the average error

- LDA overbinds by 20-30%
- GGA: significant improvements.
- Highly parameterized HCTH a bit better than PBE and BLYP.
- Meta-GGA: 2-3% error (3-5 kcal/mol, thus "chemical" accuracy)
- Maximum errors can be large (30-40 kcal/mol for "difficult systems").

- LDA or GGA bond lengths in solids at the few % level.
- Heavily parameterised functionals biased towards isolated molecules (training sets).
- Lightly parameterized functionals are more transferable.
- Bulk modulus and vib freq.: GGA (~10%) better than LDA. VG98 > PBE-GGA.

TABLE VIII  
Equilibrium unit cell volumes  $V_0$  (in bohr<sup>3</sup>) for bulk solids, using self-consistent LSD- $\alpha$  orbitals and densities for LSD, and self-consistent PBE-GGA- $\alpha$  orbitals and densities for the other functionals.<sup>a</sup>

Solid	$V_0^{\text{LSD}}$	$V_0^{\text{PBE}}$	$V_0^{\text{PW92}}$	$V_0^{\text{BLYP}}$	$V_0^{\text{HCTH}}$	$V_0^{\text{PKZB}}$	$V_0^{\text{VGN}}$	$V_0^{\text{THH}}$	$V_0^{\text{exact}}$
Na	255.4	224.4	249.8	267.8	250.1	275.6	272.0	271.0	229.1
NaCl	302.7	275.1	313.1	336.3	324.3	353.6	342.5	340.0	321.0
Al	112.1	105.6	111.2	113.3	115.5	108.4	109.3	108.0	106.0
Si	279.0	296.2	276.3	282.1	285.6	278.9	274.5	280.4	296.1
Ge	305.8	301.4	322.1	331.0	343.1	328.8	314.6	318.8	318.1
GeAs	304.9	298.3	320.5	350.2	340.1	329.0	314.0	319.4	315.8
Cu	78.7	73.5	80.6	89.5	85.7	82.5	78.5	79.9	82.7
W	106.5	104.0	108.8	110.2	112.7	108.1	107.1	108.1	106.9
Fe	78.5	70.5	78.7	78.1	80.3	—	75.9	77.0	—
Pd	99.3	95.5	103.2	106.1	110.1	104.3	100.9	102.9	110.0
Pt	101.3	97.7	105.7	107.3	112.4	104.4	103.0	104.0	110.2
Au	112.8	111.8	121.1	124.8	131.0	123.5	117.6	120.6	120.8
mean (in %)	—	4.8	3.6	6.0	8.0	6.3	2.6	3.8	6.1

<sup>a</sup>The calculations were done with the WIEN code [48]. The experimental values are from Fyfe [49] for most of the solids, [113] for Pd, and [60] for Pt and Au. For Fe, the HCTH and VGN energies oscillate near the minimum.

# DFT Functionals: Benchmarking (II)

TABLE I Electronic atomization energies (in kcal/mol) for the molecules in the extended G2 set (Refs. 38-40). The MP2/6-31G(d) geometries of Refs. 38-40 and 6-311+G(3d,2p) basis sets are used.

Molecule	Exp.	PBE <sup>a</sup>	PBE1PBE <sup>b</sup>	MGGA
LiH	57.8	-4.5	-5.1	1.3
BeH	49.8	1.8	4.0	3.7
CH	83.8	1.0	-0.6	1.8
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	190.0	4.3	3.7	2.7
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	180.7	3.0	3.1	0.7
CH <sub>3</sub>	306.6	3.4	1.8	3.8
CH <sub>4</sub>	419.2	0.9	-1.3	2.9
NH	83.5	5.0	1.7	3.6
NH <sub>2</sub>	151.5	7.2	1.7	5.7
NH <sub>3</sub>	297.5	4.6	-2.4	2.3
OH	106.4	3.6	-0.7	1.7
H <sub>2</sub> O	232.2	2.2	-5.2	-1.7
HF	140.8	1.3	-4.1	-2.1
SiH <sub>2</sub> ( <sup>3</sup> A <sub>1</sub> )	151.3	-2.7	-4.2	4.3
SiH <sub>2</sub> ( <sup>1</sup> B <sub>1</sub> )	131.2	1.8	1.5	8.3
SiH <sub>4</sub>	225.1	-2.0	-1.7	8.3
SiH <sub>3</sub>	221.4	-7.3	-4.3	6.5
PH <sub>3</sub>	152.9	1.9	0.5	7.2
PH <sub>2</sub>	241.8	-2.3	-3.9	5.9
SH <sub>2</sub>	182.4	-0.3	-2.4	4.2
HCl	106.3	1.1	-1.1	3.3
Li <sub>2</sub>	24.4	-4.0	-4.8	-0.5
LiF	137.5	1.7	-5.3	-8.2
C <sub>2</sub> H <sub>2</sub>	405.3	9.7	-1.3	-3.1
C <sub>2</sub> H <sub>4</sub>	562.6	9.2	1.3	-0.1
C <sub>2</sub> H <sub>6</sub>	710.8	6.1	1.3	0.8
CN	180.9	14.8	-2.6	0.5
HCN	312.6	13.7	-3.2	0.4
CO	259.3	10.3	-3.8	-1.8
HCO	278.7	17.3	2.1	3.9
H <sub>2</sub> CO	373.6	13.1	-0.7	1.4
H <sub>2</sub> COH	211.9	8.8	-1.5	-1.4
N <sub>2</sub>	228.6	13.9	-5.8	1.1
N <sub>2</sub> H <sub>4</sub>	437.8	15.5	0.4	2.7

TABLE III Bond lengths (Å) for diatomic molecules in the G2-1 set (Ref. 42). All values are computed using 6-311G(d,p) basis sets.

Molecule	PBE	PBE1PBE	MGGA	Exp.
H <sub>2</sub>	0.749	0.745	0.750	0.741
LiH	1.604	1.597	1.634	1.595
BeH	1.355	1.347	1.372	1.343
CH	1.140	1.126	1.150	1.120
NH	1.053	1.040	1.060	1.045
OH	0.983	0.971	0.986	0.971
HF	0.928	0.916	0.928	0.917
Li <sub>2</sub>	2.734	2.752	2.781	2.670
LiF	1.569	1.559	1.592	1.564
CN	1.177	1.163	1.186	1.172
CO	1.138	1.125	1.146	1.128
N <sub>2</sub>	1.105	1.093	1.113	1.098
NO	1.160	1.143	1.167	1.151
O <sub>2</sub>	1.221	1.194	1.225	1.207
F <sub>2</sub>	1.420	1.401	1.434	1.417

Unfortunately, the geometries and frequencies calculated with the meta-GGA are worse than PBE and PBE hybrid results.

Useful rule of thumb: *GGA is always a good starting point (but always check!). But before delving into the unknown ...*

- Be aware of common features of a particular functional.
- If possible, compare to experiment.

# DFT Functionals: Some Suggestions

- LDA:
  - Covalent systems.
  - Simple metals.
- GGA:
  - Molecules.
  - Hydrogen-bonded materials.
  - Highly varying electronic densities (d and f orbitals).
  - Complex metals.
  - Most magnetic systems.
- Non-local sX / empirical LDA+U Band gaps (with care).
  - Complex magnetic systems.

***PLEASE NOTE: VdW materials not listed***

## Advantages of DFT

- It is quite forgiving to the uninitiated or non-dedicated person (e.g., an experimentalist):
  - Choice of functional largely determines quality of calculation
  - Parameters: relatively few; easy to ascertain convergence.
- Good scaling with system size (particularly with plane-wave basis sets).
- Allows calculations on large systems (particularly if periodic; more next lecture)
- Large data base to compare with / benchmark your calculation (first thing to do is to check the literature for similar systems; DFT publication rate at present +10,000 papers/year).

***Efficient & unbiased tool to model materials properties.***

# What is missing in DFT?

- Van der Waals interactions (mutual electronic polarization due to induced-dipole-induced-dipole interactions): very weak. These are not included in ANY existing approximation to  $E_{xc}$ .  
**VERY CAREFUL WITH MOLECULAR SOLIDS AND SOFT MATERIALS (e.g., graphite)**
- Excited states:
  - DFT, as explained today, is a ground-state theory.
  - Time-dependent DFT can overcome this limitation (in its infancy but watch out for progress in this area)
- Non-adiabatic processes (breakdown of the BE approx; a universal limitation):
  - Non-radiative electronic transitions.
  - Jahn-Teller systems (symmetry forces electron-nuclear coupling).
  - Superconductivity (electron-phonon coupling)
- Self-interaction problem: each electron lives in field created by all electrons, including itself (need so-called SIC-DFT methods). This is not a problem in HF Theory where cancellation is exact.
- Still hard: extended magnetism & associated magnetic excitations (magnons).

## From Energies to Properties: Geometry Optimization

- All our work so far assumed a given structure (e.g., as obtained from experimental data), for which we can calculate the electronic problem (single-point-energy calculation).
- However, the DFT ground state does not necessarily correspond to the true ground state, e.g., this ground state will also change with the level of theory (and convergence parameters).
- Thus, it is likely we have been doing calculations on a strained sample!
- The way out of this problem:
  - Calculate electronic energy for an initial (guess) structure.
  - Modify ionic positions (and/or unit-cell parameters).
  - Recalculate energy.
  - Iterate till minimum is found (usually closest minimum, not necessarily the absolute minimum).
- Agreement with experiment is typically on the order of a percent or better.

## Geometry Optimization: What One Gets

- Cell dimensions, bond lengths & angles
- Which structure is most stable (phase diagrams)
- Bulk moduli & elastic constants.
- A gateway to materials' properties: phonons, dielectric constants, etc on the GROUND-STATE structure.

## Geometry Optimization: How It Works

- Within the Born-Oppenheimer approximation (frozen nuclei), need to find global energy minimum dictated by geometry of ions → *Multidimensional optimization Problem*.

How to do it:

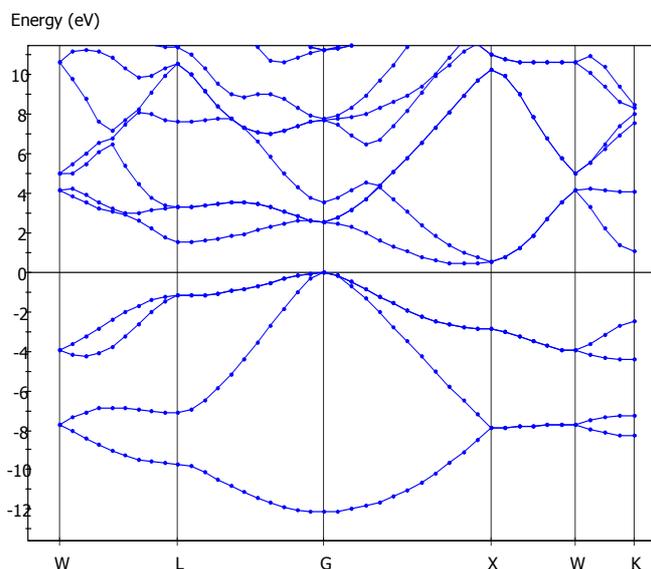
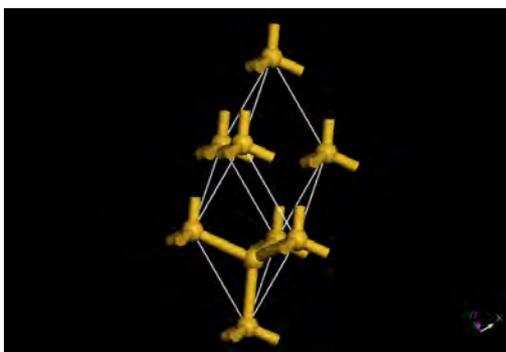
- Simplest approach: Steepest-descent Methods.
- More sophisticated: Damped Molecular Dynamics, Conjugate Gradients, BFGS.
- Caveat: all of above will find minima, but not necessarily the ABSOLUTE minimum. Always need to check for this (and this might not be easy).

# Properties, at Last

With a properly converged structure we can now access ground-state properties such as:

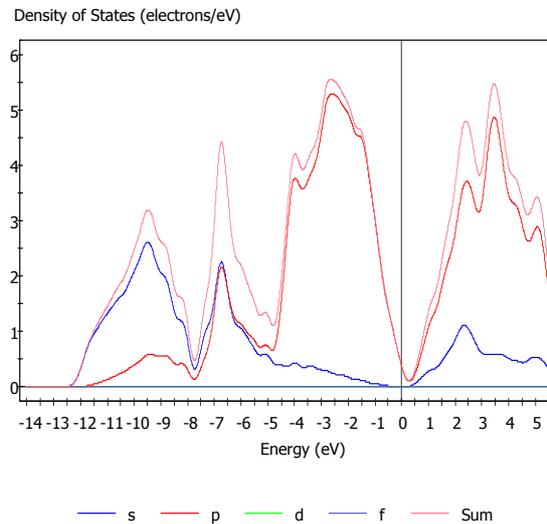
- Electronic band structure (and density of states).
- Optical properties (refractive index, dielectric constants).
- Phonons (dispersion & density of states).
- IR spectra.
- NMR spectra.
- Thermodynamic properties.
- Even STM profiles (which I have not tried myself in detail but looks interesting).

## Silicon: Primitive Cell, LDA Approximation



# Silicon: Electronic Density of States

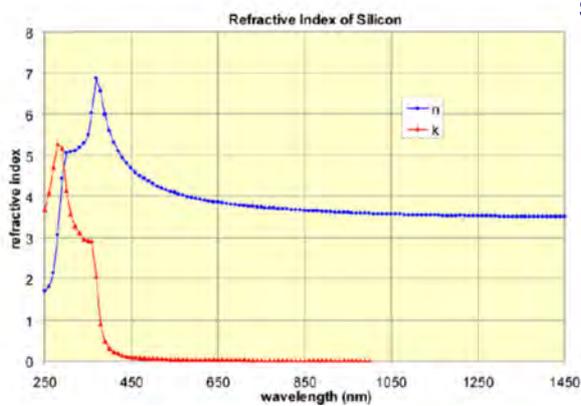
Can also calculate partial DOS (s, p, d, f bands in a solid).



# LDA Silicon: Optical Properties

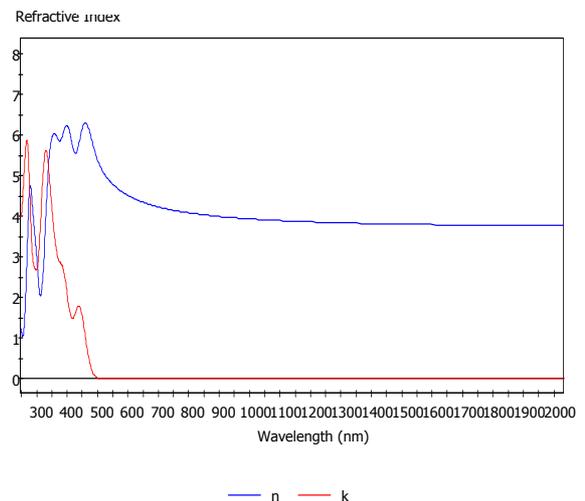
## Literature

Access to reflectivity, absorption, refractive index, dielectric properties, conductivity for polarized, unpolarized and polycrystalline systems.



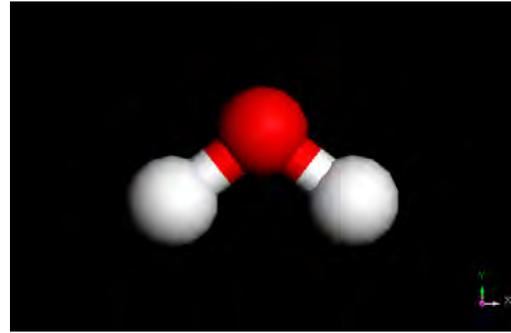
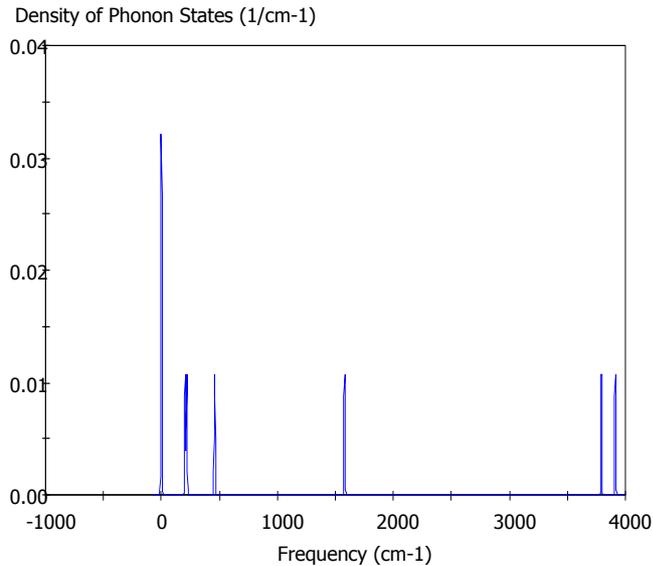
From: MA Green & MJ Keevers, "Optical Properties of Intrinsic Silicon at 300K", *Progress in Photovoltaics Research and Applications*, Vol. 3, pp. 189-192, 1995.

## LDA Silicon



# Vibrational Spectra (Density of States)

CASTEP Density of Phonon States



## Intramolecular modes (cm<sup>-1</sup>)

Mode	GGA-PBE	Literature
Bend	1579	1594
Symm OH stretch	3794	3657
Asymm OH stretch	3913	3755

[1] P. F. Bernath, *The spectroscopy of water vapour: Experiment, theory and applications*, *Phys. Chem. Chem. Phys.* 4, 1501 (2002). Also see <http://www.lsbu.ac.uk/water/vibrat.html> (very comprehensive!)

## Phonon Calculations in a Bit More Detail

- Total energy (electronic + nuclear) is central quantity
  - And it is a function of nuclear positions about the equilibrium geometry.
  - At equilibrium first derivatives (forces) are zero.
  - In the harmonic approximation, only second derivatives exist.
  - Knowledge of 2<sup>nd</sup> derivative matrix (Hessian) provides us with
    - » Normal-mode frequencies (directly accessible from experiment).
    - » Eigenvectors (experiment can only provide partial projections).
- Three common methods:
  - “Frozen-phonon.”
  - Finite displacement.
  - Supercell method.

# Finite Displacement

- What is done:
  - Execute small displacements, one ion at a time.
  - Use single-point energy calculations to evaluate forces on every ion.
  - Compute derivative of force wrt displacement to get second derivatives and associated frequencies.
- Remarks:
  - Only need 6 energy calculations per ion – why?
  - General method (but can take advantage of symmetry as well).

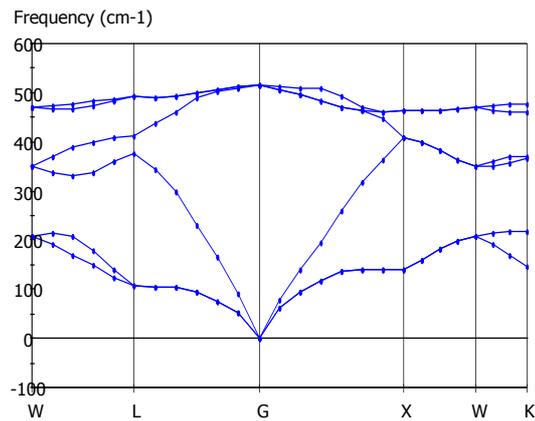
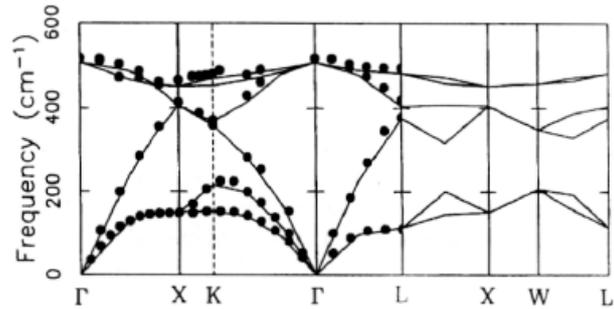
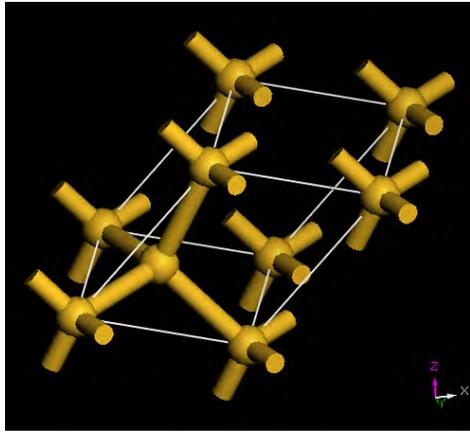
## From Phonons to Thermodynamic Properties

Once phonon dispersion relations are known (supercell or interpolation methods), Free Energy can be calculated as an integral over  $k$

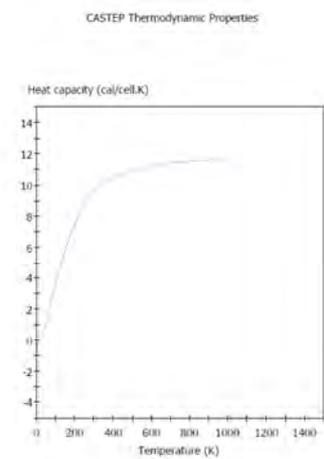
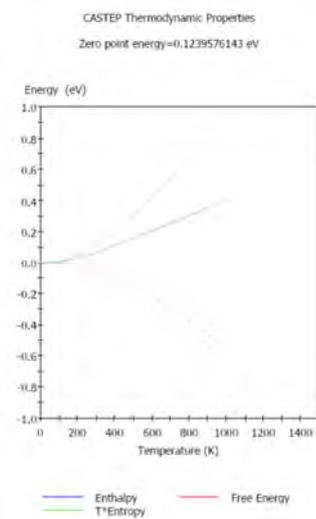
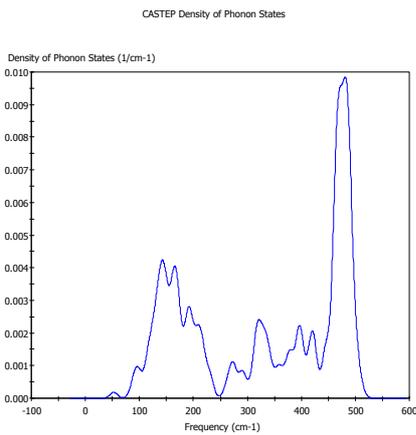
$$A(T) = E + k_B T \sum_k \log \left[ 2 \sinh \frac{\hbar \omega(k)}{2k_B T} \right]$$

*Beware: electronic part is not calculated as function of  $T$ .*

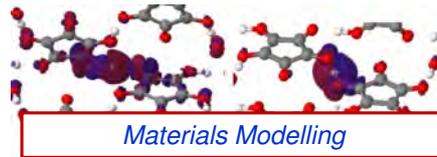
# Periodic Solids and Phonon Dispersion: Silicon



## Silicon: Phonon DOS and Thermodynamics



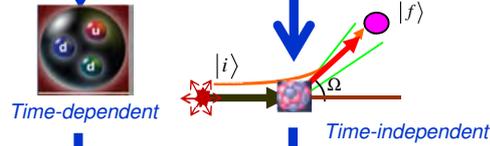
# In-Silico Neutron Scattering



To fully exploit neutron data.

Model selection using neutron spectroscopic data.

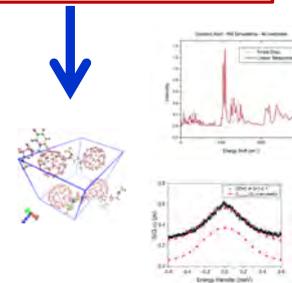
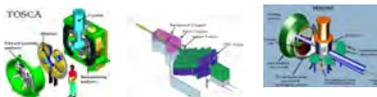
Plenty of opportunities ahead.



Interface



Experiments

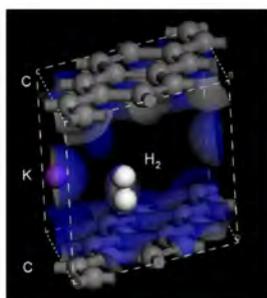
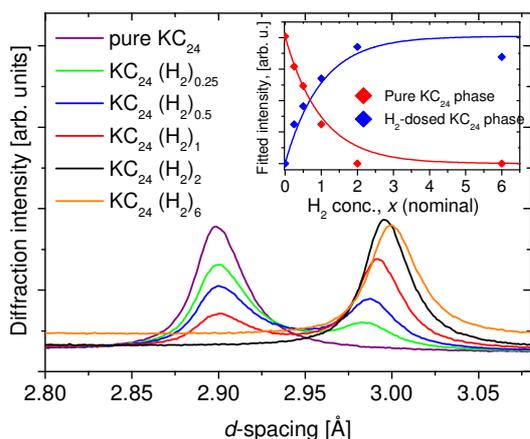


## Some Neutron Observables Amenable to Calculation

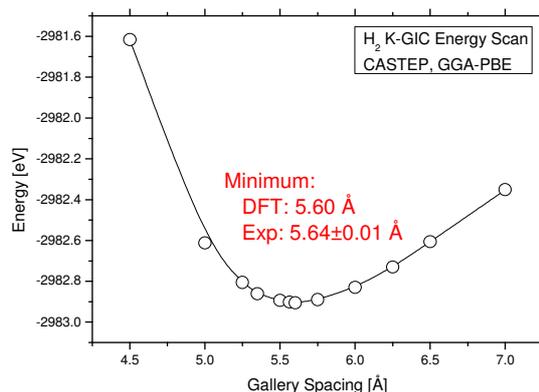
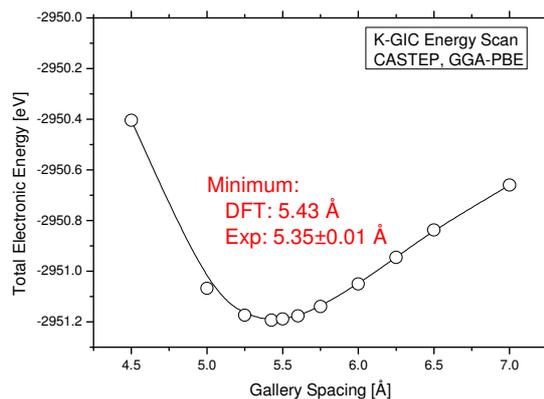
(back to Lectures 1 and 2)

# Simplest Neutron Observable: Regular & Time-averaged Structure

## Neutron Diffraction



- DFT can reproduce experimental data *quantitatively*.
- Significant expansion of graphite c-axis is significant



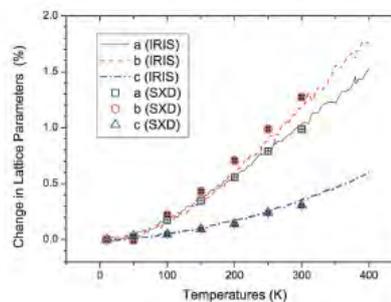
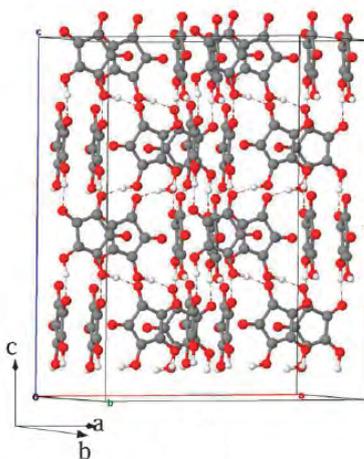
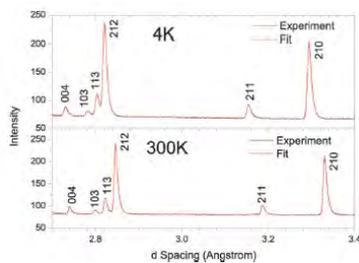
## More Complex Materials



Cite this: *Phys. Chem. Chem. Phys.*, 2014, 16, 26234

### Hydrogen-bond structure and anharmonicity in croconic acid

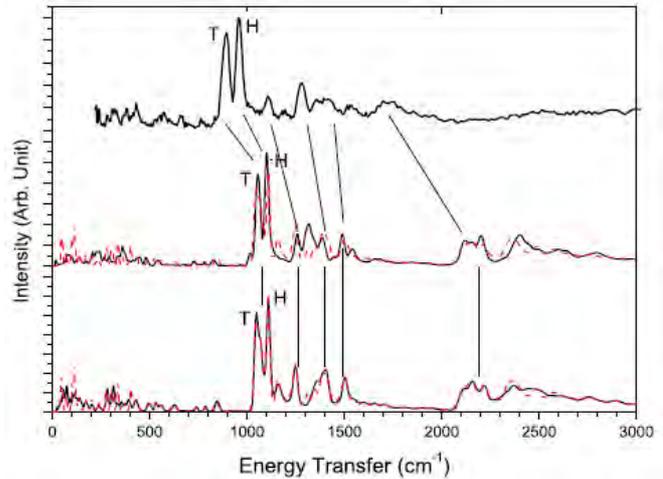
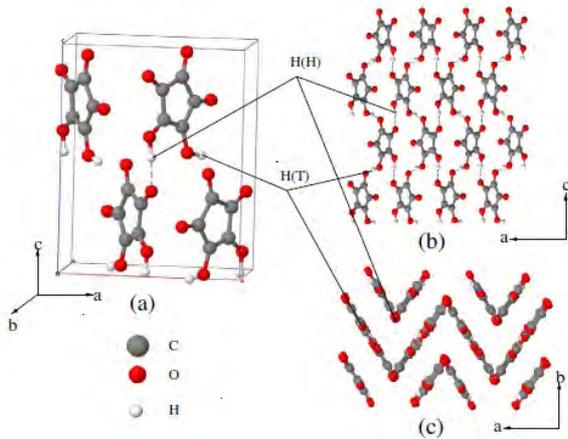
Sanghamitra Mukhopadhyay,<sup>a,b</sup> Matthias Gutmann<sup>a</sup> and Felix Fernandez-Alonso<sup>a,c</sup>



Parameters	10 K		100 K		200 K		300 K	
	ND	Calculated	ND	Calculated	ND	Calculated	ND	Calculated
O-H(H)	1.008 (±1.4)	1.040 (3.2%)	1.008 (±2.0)	1.0392 (3.1%)	0.997 (±2.5)	1.0380 (4.1%)	1.000 (±2.3)	1.0369 (3.7%)
O-H(T)	1.005 (±2.4)	1.044 (3.9%)	1.005 (±2.0)	1.0434 (3.8%)	1.010 (±2.6)	1.0420 (3.2%)	1.002 (±2.5)	1.0408 (3.9%)
O...H(H)	1.604 (±1.4)	1.476 (8.0%)	1.604 (±1.9)	1.4799 (7.7%)	1.617 (±2.5)	1.4865 (8.1%)	1.631 (±2.4)	1.4930 (8.5%)
O...H(T)	1.611 (±1.4)	1.531 (5.0%)	1.611 (±2.1)	1.5400 (4.4%)	1.619 (±2.6)	1.5406 (4.8%)	1.639 (±2.3)	1.5473 (5.6%)
O...O(H)	2.594 (±1.1)	2.517 (3.0%)	2.599 (±1.7)	2.5204 (3.0%)	2.601 (±2.5)	2.5255 (2.9%)	2.617 (±2.1)	2.5305 (3.3%)
O...O(T)	2.612 (±1.1)	2.553 (2.2%)	2.610 (±1.7)	2.5555 (2.1%)	2.622 (±2.5)	2.5610 (2.3%)	2.633 (±2.1)	2.5665 (2.5%)

# Neutron Observables: Vibrations in Solids

$$\left( \frac{d^2 \sigma}{d\Omega dE_f} \right)_{i,+1} = \frac{k_f}{k_i} \left( \frac{\hbar^2 Q^2}{2M} \right) e^{-2W(Q)} \frac{\langle n+1 \rangle}{E} Z(E)$$



Extensively used for hydrogen-containing systems.

*Direct measure of vibrational density of states, quite unique to neutrons*

# Complex Materials

## Identifying the Role of Terahertz Vibrations in Metal-Organic Frameworks: From Gate-Opening Phenomenon to Shear-Driven Structural Destabilization

Matthew R. Ryder,<sup>1,2,3</sup> Bartolomeo Civalleri,<sup>4</sup> Thomas D. Bennett,<sup>5</sup> Sebastian Henke,<sup>5</sup> Svenmir Rudić,<sup>2</sup> Gianfelice Cinque,<sup>3</sup> Felix Fernandez-Alonso,<sup>2,6</sup> and Jin-Chong Tan<sup>1,7</sup>

<sup>1</sup>Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, United Kingdom  
<sup>2</sup>ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, United Kingdom  
<sup>3</sup>Diamond Light Source, Harwell Campus, Didcot, Oxford OX11 0DE, United Kingdom

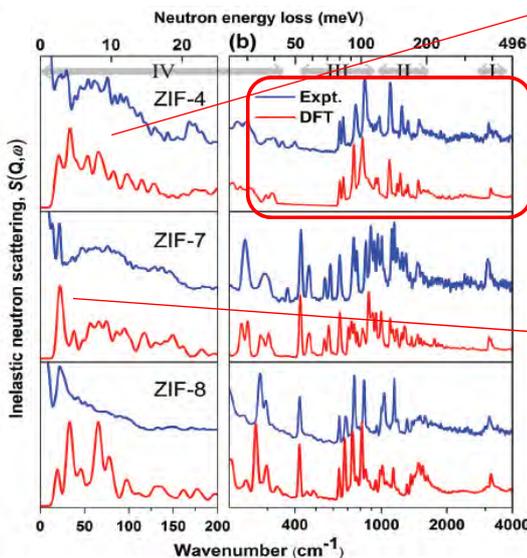
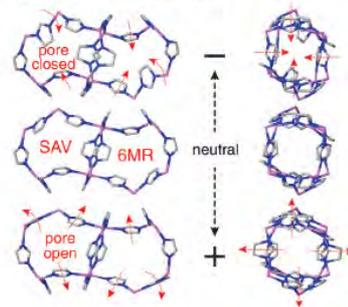
<sup>4</sup>Department of Chemistry, NIS and INSTM Reference Centre, University of Turin, via Pietro Giuria 7, 10125 Torino, Italy

<sup>5</sup>Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB3 0FS, United Kingdom

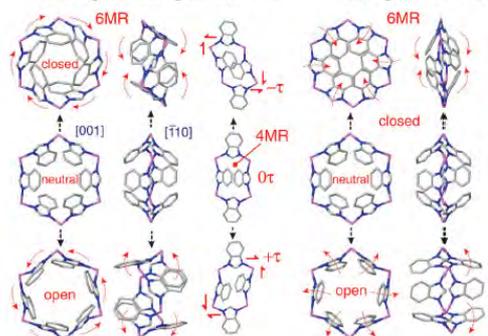
<sup>6</sup>Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

(Received 1 August 2014; published 20 November 2014)

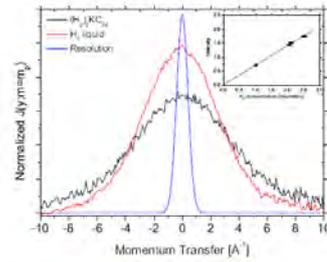
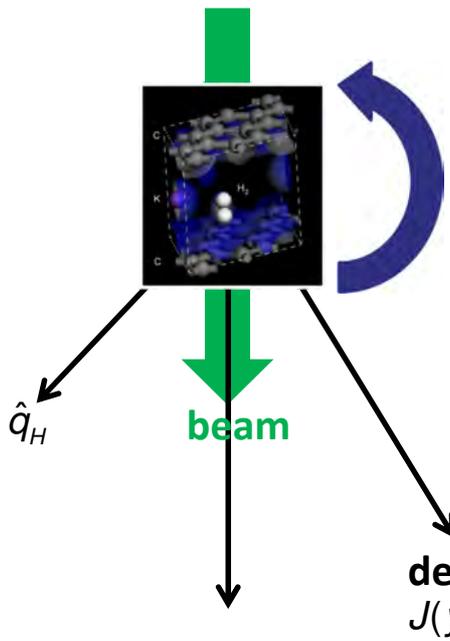
### Gate-opening mechanism at ~1 THz



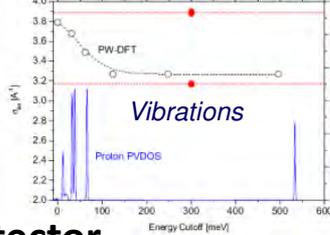
### Breathing & shearing at 0.654 THz



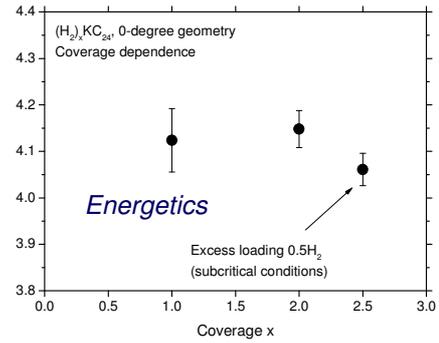
# From Vibrations to Atomic Thermometry



$$\sigma_{\text{inc}}(\hat{q})^2 = \frac{M_s}{N_s h^2} \sum_{\alpha=1}^{N_s} \sum_{\lambda=1}^{N_s} \langle e_{\alpha}(\lambda, \hat{q}) \cdot \hat{q} \rangle^2 \frac{\omega(\lambda, \hat{q})}{2} \coth\left(\frac{\omega(\lambda, \hat{q})}{2k_B T}\right)$$

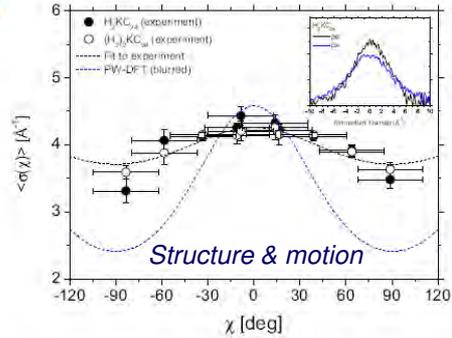


**detector**  
 $J(y; \hat{q})$



*Energetics*

Excess loading 0.5H<sub>2</sub>  
(subcritical conditions)



- Calculations to dissect Compton profiles.
- Access to adsorbate-adsorbate interactions.
- Molecular alignment smeared by NQEs.

Faraday Disc 151 95-115 (2011).  
Phys Rev B 83 134205 (2011).

## Neutron Observables: Coherent Vibrations in Solids

$$S_{\text{c},+1}^{\text{dd}'}(\mathbf{Q}, E) = \frac{1}{2N_c} (2\pi)^3 e^{-[W_d(\mathbf{Q})+W_{d'}(\mathbf{Q})]} \sum_{\mathbf{qk}} \frac{\hbar^2 (\mathbf{Q} \cdot \mathbf{e}_d^k(\mathbf{q}))^* (\mathbf{Q} \cdot \mathbf{e}_{d'}^k(\mathbf{q}))}{(M_d M_{d'})^{1/2} E_k(\mathbf{q})} \times e^{i\mathbf{Q} \cdot (\mathbf{d}' - \mathbf{d})} \langle n_{\mathbf{qk}} + 1 \rangle \sum_{\boldsymbol{\tau}} \delta(\mathbf{Q} - \mathbf{q} - \boldsymbol{\tau}) \delta(E - E_k(\mathbf{q}))$$

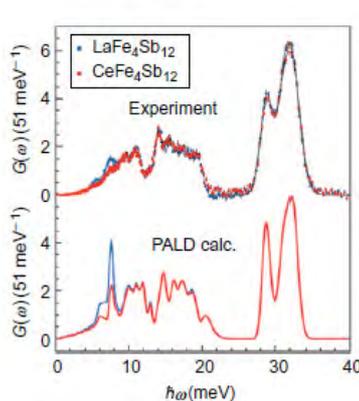
And DDCS

$$\left( \frac{d^2 \sigma}{d\Omega dE_f} \right)_{\text{c},+1} = \frac{k_f}{k_i} \left[ \frac{(2\pi)^3}{2N_c v_0} \right] \sum_{\boldsymbol{\tau}} \sum_{\mathbf{qk}} |F_1(\mathbf{Q}, \mathbf{qk})|^2 \frac{\hbar^2 \langle n_{\mathbf{qk}} + 1 \rangle}{E_k(\mathbf{q})} \delta(\mathbf{Q} - \mathbf{q} - \boldsymbol{\tau}) \delta(E - E_k(\mathbf{q}))$$

$\delta(\mathbf{Q} - \mathbf{q} - \boldsymbol{\tau}) \delta(E - E_k(\mathbf{q}))$ , *One-phonon structure factor*  $F_1(\mathbf{Q}, \mathbf{qk}) = \sum_{\mathbf{d}} \frac{\bar{b}_{\mathbf{d}}}{M_{\mathbf{d}}^{1/2}} e^{-W_{\mathbf{d}}(\mathbf{Q})} e^{i\mathbf{Q} \cdot \mathbf{d}} [\mathbf{Q} \cdot \mathbf{e}_{\mathbf{d}}^k(\mathbf{q})]$

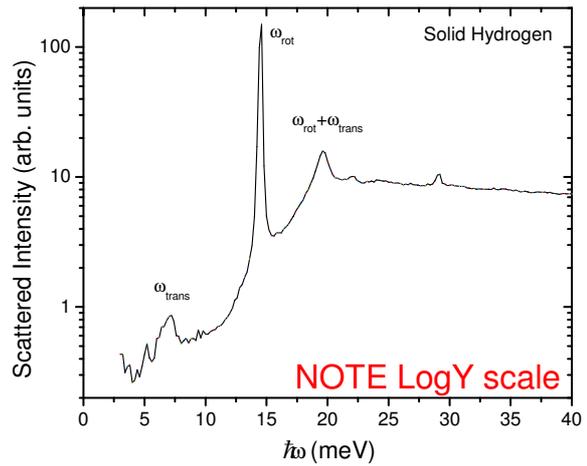
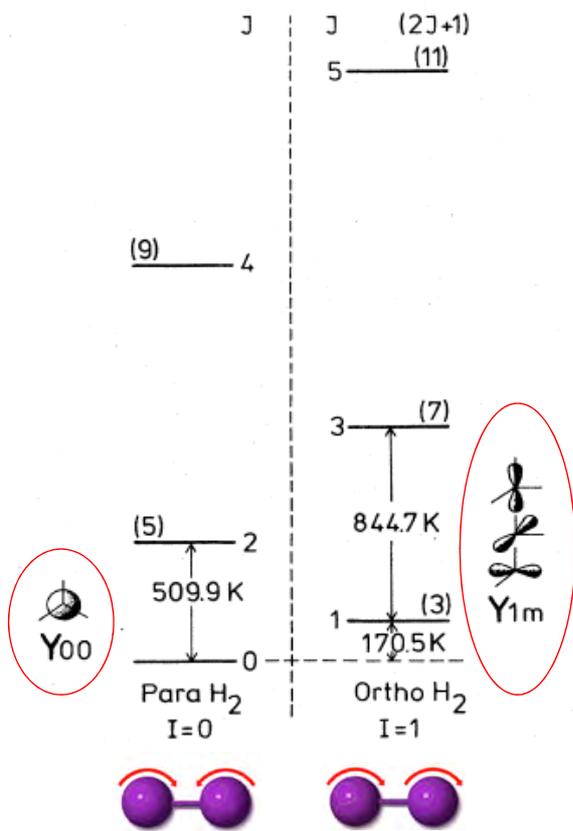
*Low-energy cage modes of heavy atoms in skutterudites.*

*Microscopic understanding of thermoelectrics.*



Koza et al., Nat Mater 7 805(2008).

# Molecular Rotations



- (0→1) rotational transition is purely incoherent & strong (strong for neutrons but optically forbidden)
- M-level splitting of J=1 state is a sensitive probe of local environment.

## Rotational Levels in Presence of Angular Potential

### Free diatomic rotor

$$Y_{JM}(\Theta, \phi) = |JM\rangle \quad \text{with} \quad \langle J'M' | H_{rot} | JM \rangle = B_{rot} J(J+1) \delta_{J',J} \delta_{M',M}$$

### Additional hindering potential

$$H_{total} = H_{rot} + V(\Theta, \phi) \quad \text{with} \quad V(\Theta, \phi) = \sum_{J_v M_v} V_{J_v M_v} Y_{J_v M_v}(\Theta, \phi)$$

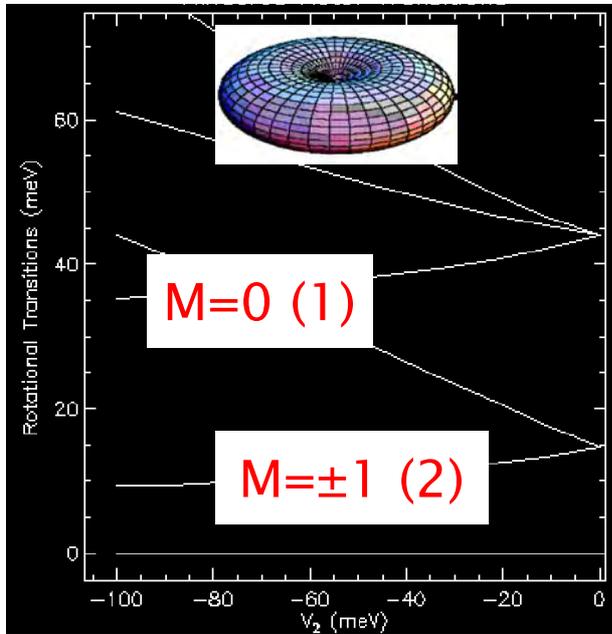
$$\langle J'M' | H_{tot} | JM \rangle = B_{rot} J(J+1) \delta_{J',J} \delta_{M',M} + \sum_{J_v M_v} V_{J_v M_v} \langle J'M' | Y_{J_v M_v}(\Theta, \phi) | JM \rangle$$

$$\langle J'M' | Y_{J_v M_v}(\Theta, \phi) | JM \rangle = (-1)^{M'} \sqrt{\frac{(2J'+1)(2J_v+1)(2J+1)}{4\pi}} \begin{pmatrix} J' & J_v & J \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J' & J_v & J \\ -M' & M_v & M \end{pmatrix}$$

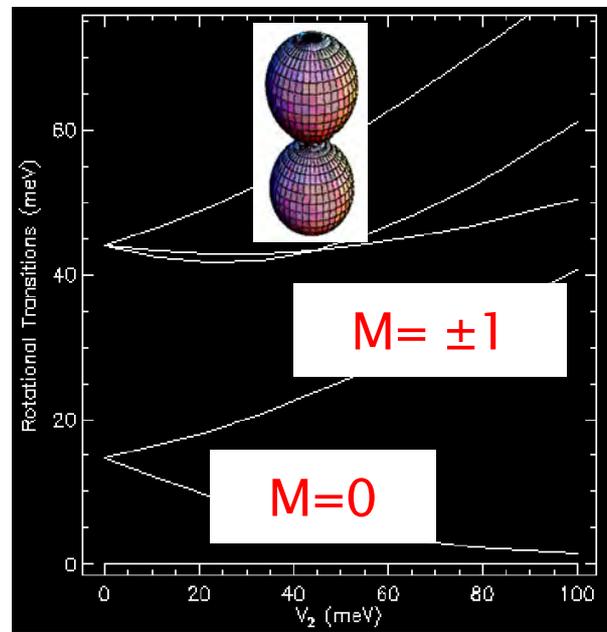
# Pinning H<sub>2</sub> along an Axis or a Plane

Lowest-order term for a homonuclear diatomic:  $V(\Theta, \phi) = V_{\Theta} \sin^2 \Theta$

## Free Rotation on Plane

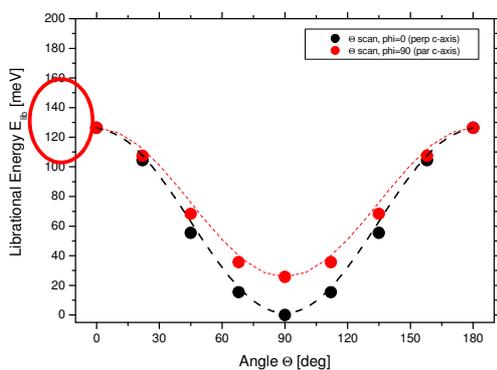
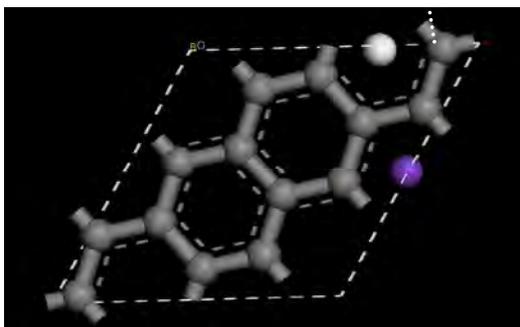


## Libration along axis



## H<sub>2</sub> Potential Energy Landscape

### Calculation



PRL 101, 126101 (2008) PHYSICAL REVIEW LETTERS week ending 19 SEPTEMBER 2008

### Quantum Delocalization of Molecular Hydrogen in Alkali-Graphite Intercalates

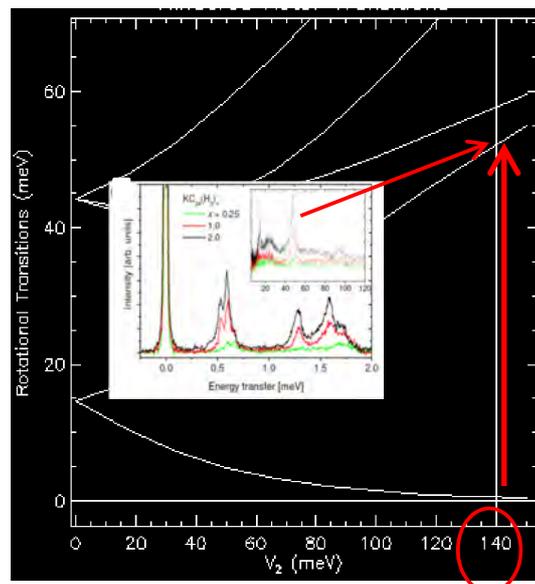
Arthur Lovell,<sup>1\*</sup> Felix Fernandez-Alonso,<sup>1\*</sup> Neal T. Skipper,<sup>2</sup> Keith Refson,<sup>2</sup> Stephen M. Benington,<sup>1\*</sup> and Stewart F. Parker<sup>1</sup>

<sup>1</sup>ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom

<sup>2</sup>Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, United Kingdom

(Received 7 March 2008; published 18 September 2008)

### Experiment



*Orientational potential:*

$$V(\Theta, \phi) = V_{\Theta} \left[ 1 - \left( 1 - \frac{V_{\phi}}{V_{\Theta}} \sin^2 \phi \right) \sin^2 \Theta \right]$$

**Quantitative agreement in barrier height**

# Structure & Dynamics Beyond Vibrations

$$G^{dd'}(\mathbf{r}, t) = \frac{1}{(N_d N_{d'})^{1/2}} \sum_{\substack{j \in d \\ j' \in d'}} \int \langle \delta[\mathbf{r}' - \mathbf{R}_j(0)] \delta[\mathbf{r}' + \mathbf{r} - \mathbf{R}_{j'}(t)] \rangle d\mathbf{r}'$$

Atomic trajectories from MD simulations

$$G_s^d(\mathbf{r}, t) = \frac{1}{N_d} \sum_{j \in d} \int \langle \delta[\mathbf{r}' - \mathbf{R}_j(0)] \delta[\mathbf{r}' + \mathbf{r} - \mathbf{R}_j(t)] \rangle d\mathbf{r}'$$

Intermediate scattering function

$$I^{dd'}(\mathbf{Q}, t) = \frac{1}{(N_d N_{d'})^{1/2}} \sum_{j \in d, j' \in d'} \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_{j'}(t)} \rangle$$

and dynamic structure factors

$$I_s^d(\mathbf{Q}, t) = \frac{1}{N_d} \sum_{j \in d} \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_j(t)} \rangle$$

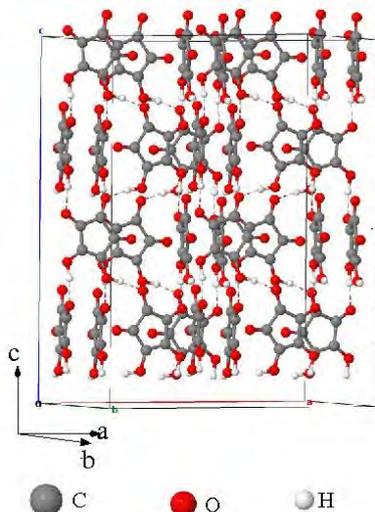
$$S_c^{dd'}(\mathbf{Q}, E) = \frac{1}{(N_d N_{d'})^{1/2}} \sum_{j \in d, j' \in d'} S_{jj'}(\mathbf{Q}, E)$$

$$= \frac{1}{(N_d N_{d'})^{1/2}} \left( \frac{1}{2\pi\hbar} \right) \sum_{j \in d, j' \in d'} \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_{j'}(t)} \rangle e^{-iEt/\hbar} dt$$

$$S_i^d(\mathbf{Q}, E) = \frac{1}{N_d} \sum_{i \in d} S_{ii}(\mathbf{Q}, E) = \frac{1}{N_d} \left( \frac{1}{2\pi\hbar} \right) \sum_{j \in d} \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_j(t)} \rangle e^{-iEt/\hbar} dt$$

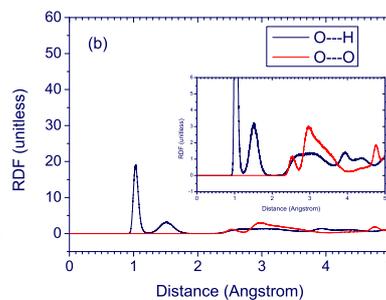
## Molecular Dynamics without Force Fields

Time-dependent structure (movie)



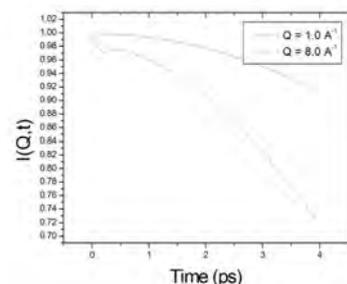
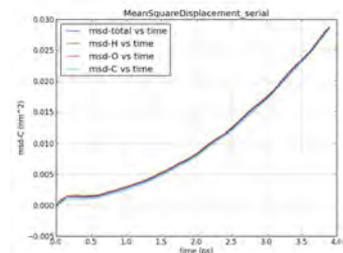
Time-averaged pair correlations

$$g_{i,j}(r) = n_{i,j}(r) / [\rho_j 4\pi r^2 dr]$$



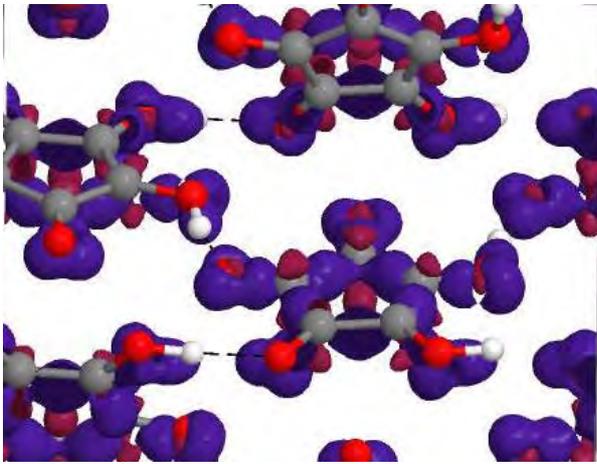
$$\frac{1}{(2\pi)^3} \int [S^{dd'}(\mathbf{Q}) - \delta_{dd'}] e^{-i\mathbf{Q} \cdot \mathbf{r}} d\mathbf{Q} = \left( \frac{N_d}{N_{d'}} \right)^{1/2} \rho^{dd'}(\mathbf{r})$$

Temporal correlations

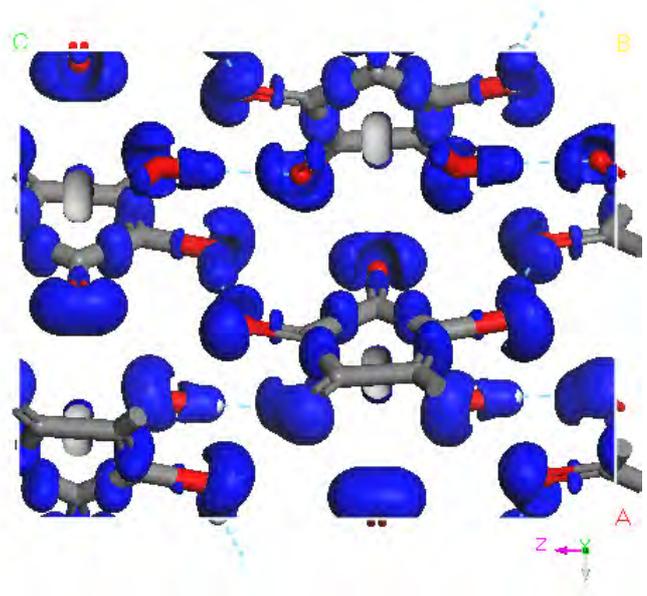


Can you think what we might be missing here?

# Beyond Experimental Observables



*Charge density difference*



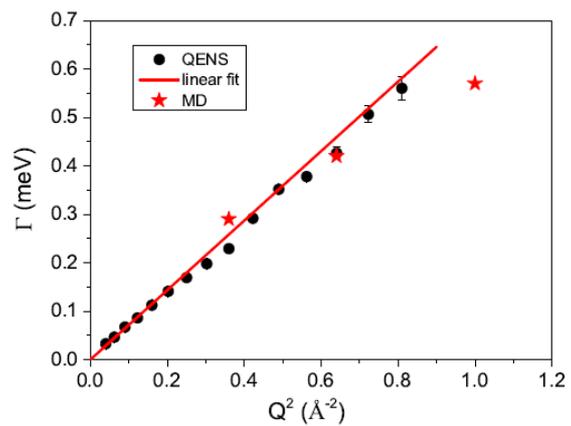
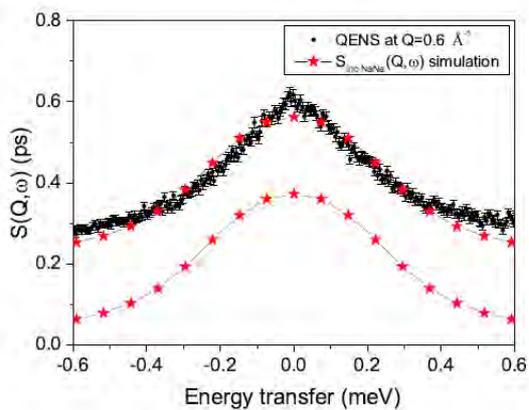
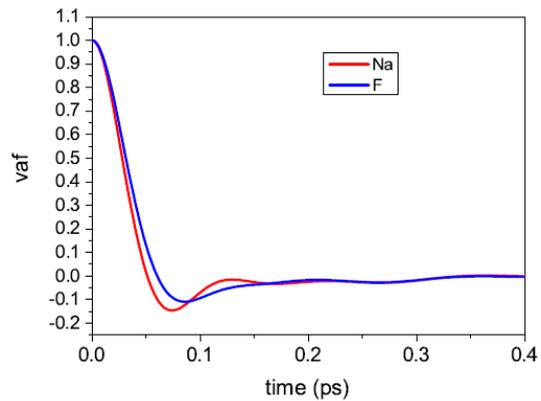
*Electron localization function*

*Bonding analysis*

## Molecular Transport

*From temporal correlations,  
to neutronic response.*

*Model selection & validation*



# Quantum Thermometry: Path Integral Molecular Dynamics

Experiment

$$J(\hat{Q}, y) = \hbar \int n(\mathbf{p}) \delta(\hbar y - \mathbf{p} \cdot \hat{Q}) d\mathbf{p}$$

Calculation

$$n(\mathbf{p}) = \frac{1}{2\pi\hbar^3} \int d\mathbf{r} d\mathbf{r}' e^{i/\hbar(\mathbf{p} \cdot (\mathbf{r} - \mathbf{r}'))} \frac{\rho(\mathbf{r}, \mathbf{r}')}{Z}$$

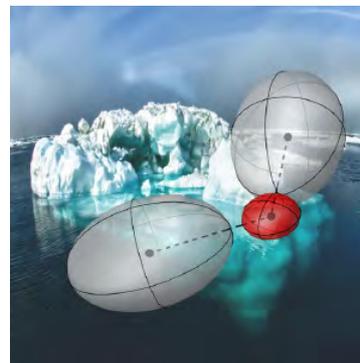
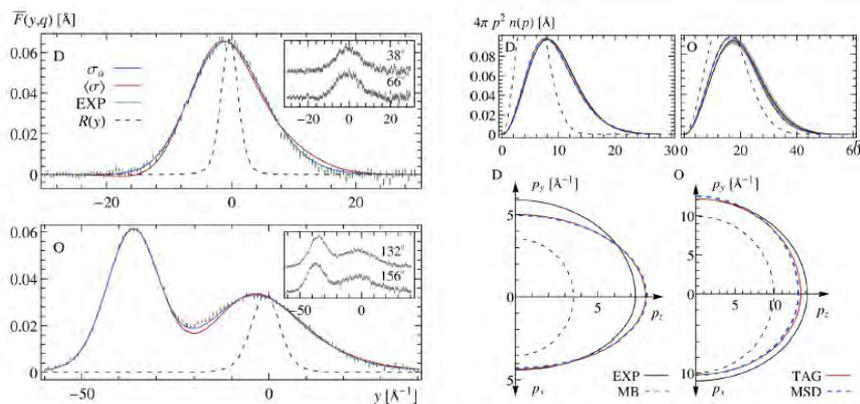
Direct Measurement of Competing Quantum Effects on the Kinetic Energy of Heavy Water upon Melting

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J. Phys. Chem. Lett. 2013, 4, 3251–3256



Direct assessment of nuclear quantum effects in condensed matter.

**NOTE: real-time quantum molecular dynamics still a challenge.**

## Where To Go From Here ...

### Recent:

- J Kohanoff, "Electronic Structure Calculations for Solids & Molecules: Theory & Computational Methods," Cambridge University Press (2006). Relatively concise & quite informative
- RM Martin, "Electronic Structure: Basic Theory and Practical Methods," Cambridge University Press (2004). Comprehensive & extensively documented.

### Useful & Didactical:

- W Koch & MC Holthausen, "A Chemist's Guide to Density Functional Theory," Wiley-VCH (2002). Theory behind DFT covered in some detail; quite some emphasis on isolated molecules (quantum chemical applications).
- AP Sutton, "Electronic Structure of Materials," Oxford Science Publications (1996). Excellent introductory book to the electronic structure of materials.

### A Bit Outdated but Still Authoritative:

- RM Dreizler and EKV Gross, "Density Functional Theory," Springer Verlag (1990).
- RG Parr and W Yang, "Density Functional Theory of Atoms and Molecules," Oxford University Press (1989).
- A Szabo & NS Ostlund, "Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory," McGraw-Hill (1989). The "Bible" of wavefunction-based electronic structure methods (Hartree-Fock and beyond).

**IF YOU ARE AN EXPERIMENTALIST, GOOD IDEA TO TALK TO COMPUTATIONAL SCIENTIST ABOUT YOUR SPECIFIC PROBLEM, TO GET YOU GOING.**

# Recap

- Fundamentals – **Why neutron scattering**
- Applications – **What neutrons can do for you**
- Neutron production – **How neutrons are produced and used**
- First-principles materials modelling – **No longer the missing link!**



## Tomorrow, 83 Years Ago



### Possible Existence of a Neutron

James Chadwick  
*Nature*, p. 312 (Feb. 27, 1932)

It has been shown by Bothe and others that beryllium when bombarded by  $\alpha$ -particles of polonium emits a radiation of great penetrating power, which has been an absorption coefficient in lead of about  $0.3 \text{ (cm)}^{-1}$ . Recently Mme. Curie-Joliot and M. Joliot found, when measuring the ionisation produced by this beryllium radiation in a vessel with a thin window, that the ionisation increased when matter containing hydrogen was placed in front of the window. The effect appeared to be due to the ejection of protons with velocities up to a maximum of nearly  $3 \times 10^9 \text{ cm. per sec.}$  They suggested that the transference of energy to the proton was by a process similar to the Compton effect, and estimated that the beryllium radiation had a quantum energy of  $50 \times 10^6$  electron volts.

I have made some experiments using the valve counter to examine the properties of this radiation excited in beryllium. The valve counter consists of a small ionisation chamber connected to an amplifier, and the sudden production of ions by the entry of a particle, such as a proton or  $\alpha$ -particle, is recorded by the deflexion of an oscillograph. These experiments have shown that the radiation ejects particles from hydrogen, helium, lithium, beryllium, carbon, air, and argon. The particles ejected from hydrogen behave, as regards range and ionising power, like protons with speeds up to about  $3.2 \times 10^9 \text{ cm. per sec.}$  The particles from the other elements have a large ionising power, and appear to be in each case recoil atoms of the elements.

If we ascribe the ejection of the proton to a Compton recoil from a quantum of  $52 \times 10^6$  electron volts, then the nitrogen recoil atom arising by a similar process should have an energy not greater than about 400,000 volts, should produce not more than about 10,000 ions, and have a range in air at N.T.P. of about 1.3 mm. Actually, some of the recoil atoms in nitrogen produce at least 30,000 ions. In collaboration with Dr. Feather, I have observed the recoil atoms in an expansion chamber, and their range, estimated visually, was sometimes as much as 3 mm at N.T.P.

These results, and others I have obtained in the course of the work, are very difficult to explain on the assumption that the radiation from beryllium is a quantum radiation, if energy and momentum are to be conserved in the collisions. The difficulties disappear, however, if it be assumed that the radiation consists of particles of mass 1 and charge 0, or neutrons. The capture of the  $\alpha$ -particle by the  $\text{Be}^9$  nucleus may be supposed to result in the formation of a  $\text{C}^{12}$  nucleus and the emission of the neutron. From the energy relations of this process the velocity of the neutron emitted in the forward direction may well be about  $3 \times 10^9 \text{ cm. per sec.}$  The collisions of the neutron with the atoms through which it passes give rise to the recoil atoms, and the observed energies of the recoil atoms are in fair agreement with this view. Moreover, I have observed that the protons ejected from hydrogen by the radiation emitted in the opposite direction to that of the exciting  $\alpha$ -particle appear to have a much smaller range than those ejected by the forward radiation. This again receives a simple explanation of the neutron hypothesis.

If it be supposed that the radiation consists of quanta, then the capture of the  $\alpha$ -particle by the  $\text{Be}^9$  nucleus will form a  $\text{C}^{13}$  nucleus. The mass defect of  $\text{C}^{13}$  is known with sufficient accuracy to show that the energy of the quantum emitted in this process cannot be greater than about  $14 \times 10^6$  volts. It is difficult to make such a quantum responsible for the effects observed.

It is to be expected that many of the effects of a neutron in passing through matter should resemble those of a quantum of high energy, and it is not easy to reach the final decision between the two hypotheses. Up to the present, all the evidence is in favour of the neutron, while the quantum hypothesis can only be upheld if the conservation of energy and momentum be relinquished at some point.

J. Chadwick,  
Cavendish Laboratory,  
Cambridge, Feb. 17.



*Grazie!*