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Neutrons for Condensed Matter Research: Fundamentals and Applications

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Neutrons for Condensed Matter Research: Fundamentals and Applications

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This series of three lectures were first given in February 2014 as part of the university course *Applicazioni della Fisica dei Neutroni* at the Università degli Study di Milano-Bicocca, Italy. It provides an up-to-date introduction to the use of neutrons in condensed matter research. To this end, it takes account of recent advances in neutron production and experimental techniques over the past two decades, and put these in the context of current scientific trends. The first lecture provides a general overview, including a survey of the merits and strengths of the technique, a comparison with other probes such as X-rays, and a first dive into the general formalism to calculate neutron-scattering cross sections. The second lecture is devoted to the conceptual and mathematical framework underpinning neutron-scattering experiments to probe structure and motion in solids, liquids, and gases, from stochastic and relaxation processes responsible for the transport properties of technological materials, all the way up to the use of epithermal neutrons to investigate disordered matter and nuclear quantum dynamics. The third and closing lecture takes a more detailed look at neutron-matter interactions, with particular emphasis on their dependence on unpaired electron density (magnetism) as well as nuclear spin. All throughout, key concepts are illustrated by reference to recent work on phenomena of technological relevance including gas storage and sequestration in nanoporous materials, ionic conduction and charge storage, chemical catalysis, and quantum matter.

The use of neutrons to probe the microscopic underpinnings of the materials world around us dates back to the 1940s and 1950s, shortly after the development of nuclear reactors. Since then, neutron-scattering techniques have matured into a robust and increasingly versatile toolkit across a plethora of scientific disciplines including physics, chemistry, biology, and engineering. The primary objective of the lectures included in this report is to provide a reasonably self-contained introduction to the use of neutrons as a condensed-matter probe. These lectures were first presented in February 2014 as part of the university course *Applicazioni della Fisica dei Neutroni* at the Department of Physics, Università degli Study di Milano-Bicocca, Italy. Course materials have been taken from a recent thematic volume on neutron scattering,[1] the current undergraduate curriculum at Oxford University,[2] and recent research carried out primarily at the ISIS Facility[3] and, in particular, the ISIS Molecular Spectroscopy instrument suite.[4,5] The primary audience in mind are advanced (i.e., last-year) undergraduate or graduate students in physics or chemistry with an interest in understanding the merits and strengths of neutron scattering and how the technique might be applied to specific research areas or interests. Each lecture has been designed to last up to two hours (including ample time for discussion), and the entire series could be delivered quite comfortably over a period of one week. 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 and Formalism) may be subdivided into two distinct parts. The first one starts by discussing the main properties of the neutron and includes a brief historical survey of neutron production, culminating with the advent of last-generation, accelerator-driven neutron facilities across the globe in the past decade. Basic observables such as total and differential cross sections are introduced from the outset, with immediate applications to both nuclear and magnetic scattering in topical areas such as hydrogen storage[6] and quantum phase transitions.[7] As a means of stimulating a more detailed discussion in subsequent lectures, we present the fundamental machinery underpinning both structural and spectroscopic measurements, including quantitative estimates of count rates in typical neutron-scattering experiments. We also take the opportunity to provide a comparison between neutron scattering and other techniques such as X-ray scattering, optical spectroscopy, or nuclear magnetic resonance. This discussion is wrapped up by a list of the main *pro et contra* of neutron scattering. In this context, we note the absence of compact neutron sources analogous to lab-based X-ray or optical equipment, an important area for further research and development in the years to come. The second part of this lecture goes back to the foundations of neutron scattering, and adopts 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. Such a rate is evaluated using Fermi's Golden Rule and generalized to include the exchange of energy between neutron and target. These considerations lead us to the *master formula* connecting the double differential cross section (or DDCS) with a sum of transition probabilities. The *master formula* is then evaluated for the case of nuclear scattering by an extended ensemble of atoms. 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. This approach also provides a convenient platform to illustrate the decoupling between nuclear parameters (scattering lengths) and the intrinsic spatial and temporal correlations of the system. The concepts of coherent and incoherent scattering naturally follow 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 succint definition of a solid.

Lecture II (Canonical Solids and Beyond) starts with a group discussion of solids. An operational definition of a so-called *canonical solid* is offered as a *physical system in which each atom has a well-defined (and fixed) equilibrium position over the duration of the measurement.* Such a definition includes disordered materials such as metastable states of matter (i.e., glasses), of certain relevance to much present-day neutron research. It excludes quantum solids like helium where intrinsic quantum-mechanical delocalization of individual atoms is present from the outset. It also excludes certain types of systems (typically classed as solids) where atoms can undergo translational diffusion (i.e., the anode and cathode materials in your mobile phone). Most importantly, such a definition of a *canonical solid* stresses the importance of time-dependent properties (dynamics) in establishing the character of scattering observables. Armed with this definition, 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[8] and incoherent[9] 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 target audience. To fill this gap, reference is given to an extensive compilation of inelastic neutron-scattering data.[10] We also take the opportunity to explain the direct link between inelastic neutron-scattering data and state-of-the-art computational modelling techniques,[11,12] as well as recent applications in chemical catalysis[13–15] and molecular[16–20] and macromolecular[21–25] intercalation in nanoporous and layered materials. In a brief detour, we also explain the possibility of exploring spectral line widths to access excitation lifetimes[26] as well as free and hindered rotations as in the case of molecular hydrogen.[17] This latter case also represents a departure from purely harmonic behaviour, and requires revisiting the main assumptions associated with the harmonic approximation in the derivation of the dynamic structure factor. Formally speaking, moving beyond the 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) differential cross sections. This approach constitutes the essence of so-called *total scattering techniques*, as illustrated by the classic example of liquid argon[27] as well as a more recent example involving the solvation of palladium ions in aqueous solution.[28] For a compilation of neutron data for disordered materials, the reader is also referred to Ref. 29. 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,[30,31] hydrogen-storage materials[32] or ferroelectrics,[33] not to forget requisite and parallel developments and advances in instrumentation (see Refs. 34–37 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.[38] 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 solid-state diffusion is finally introduced in the context of recent studies on proton conductors.[39]

Lecture III (Neutron Scattering is All About Spin) takes a detailed look at the interactions arising from the fermionic nature of the neutron. For the case of neutron-electron interactions, the *master formula* is revisited to introduce magnetic interaction operators, and an analogous procedure to that followed for nuclear scattering is followed in order to express the DDCS in terms of spatio-temporal correlations for electronic and nuclear spins. Given the more intricate nature of the neutron-electron interaction potential (including its directional dependence relative to the scattering vector), extensive recourse is made to formal comparisons with nuclear scattering where applicable (e.g., the paramagnetic solid and incoherent nuclear scattering). This approach is particularly useful for the case of inelastic scattering, given the parallels which might be drawn between magnons and phonons. The formalism is further illustrated via direct recourse to recent examples in superconductivity,[40] magnon lifetimes in model magnetic materials,[41] and magnetic clusters.[42] A consideration of the spin properties of the neutron leads naturally to a discussion of the use of polarized neutrons. Both nuclear and magnetic cases are treated in detail. In the case of nuclear scattering, such a discussion enables a sound physical understanding of coherent vs incoherent neutron scattering, as well as a powerful means of exploring strategies to separate these two distinct contributions in the laboratory,[43] or the use of nuclear-spin alignment to alter the scattering response of specific elements.[44,45] In the magnetic case, we explore in some detail selection rules associated with spin-flip vs non-spin-flip channels as well as experimental strategies to isolate magnetic and nuclear scattering, of particular relevance to ferromagnetic long-range order. These concepts are illustrated via explicit reference to recent studies on spin-ices[46] and antiferromagnetic heavy-fermion systems.[47] The last few minutes of this final lecture serve as a recap of the current state-of-the-art in the context of current and next-generation neutron facilities, as well as a reminder that 27 February 1932 was the day when it all started,[48] a breakthrough that was to be followed by seminal contributions by *i ragazzi di Via Panisperna*.[49]

In closing these introductory remarks, I wish to thank Prof G Gorini for the invitation to join his group at the Department of Physics, Università degli Study di Milano-Bicocca as part of the *Erasmus Docenti* exchange program. I am also indebted to Drs D di Martino, E Perelli-Cippo, and M Tardocchi for their hospitality and enjoyable discussions during my stay in Milano.

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[4] ISIS Molecular Spectroscopy Group: `http://www.isis.stfc.ac.uk/groups/molecular-spectroscopy/`

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Neutrons for Condensed Matter Research

Lecture I: Fundamentals and Formalism

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ISIS

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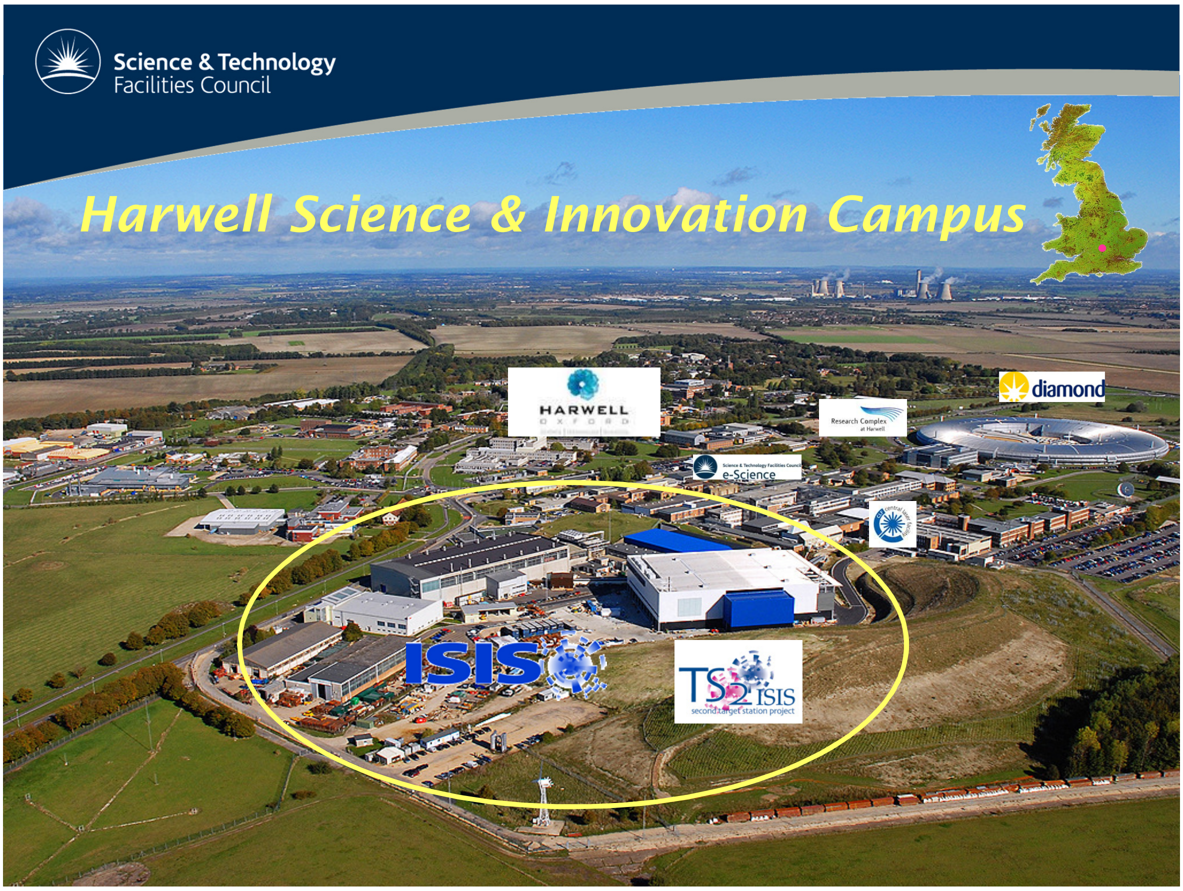
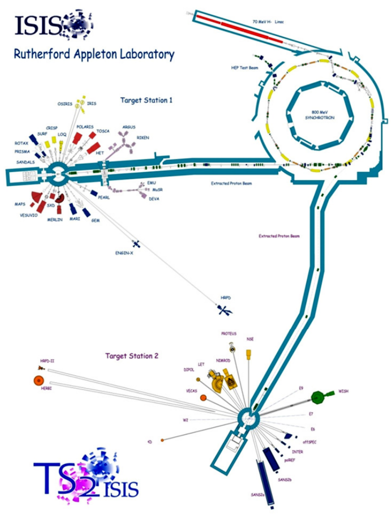


ISIS Pulsed Neutron and Muon Source

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*

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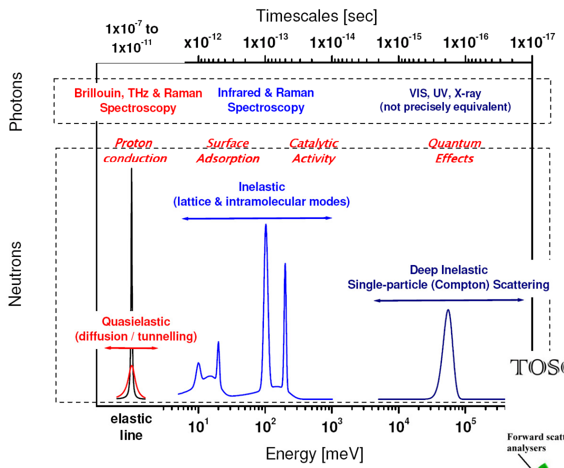
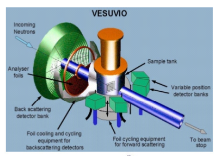
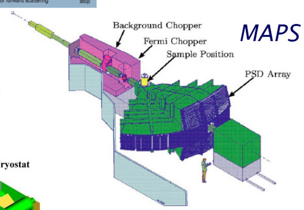
Molecular Dynamics and Spectroscopy at ISIS



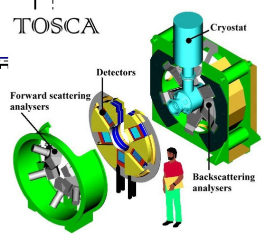


Simultaneous high-resolution diffraction

High energies

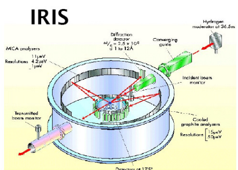


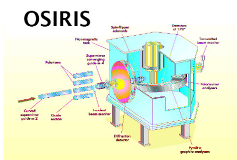
MAPS



Widest spectral range in the World

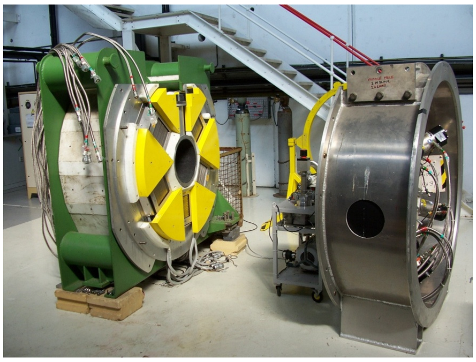
Intermediate energies (infrared, Raman)





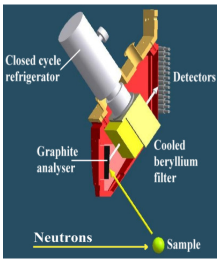
Low energy (Brillouin, THz)

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 cm^{-1}.

TOSCA was ⅔ 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 in Firenze

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

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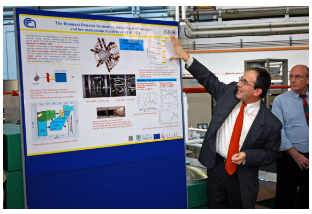
Fast Neutrons and Italy

VESUVIO is a unique neutron spectrometer, with incident energies orders of magnitude higher than any other neutron instrument. Deep inelastic neutron scattering measurements on VESUVO 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.

EUROPEAN COMMISSION

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Outline [today]

- *Lecture I: Fundamentals and Formalism.*
- Lecture II: Canonical Solids and Beyond.
- Lecture III: Neutron Scattering is All about Spin.

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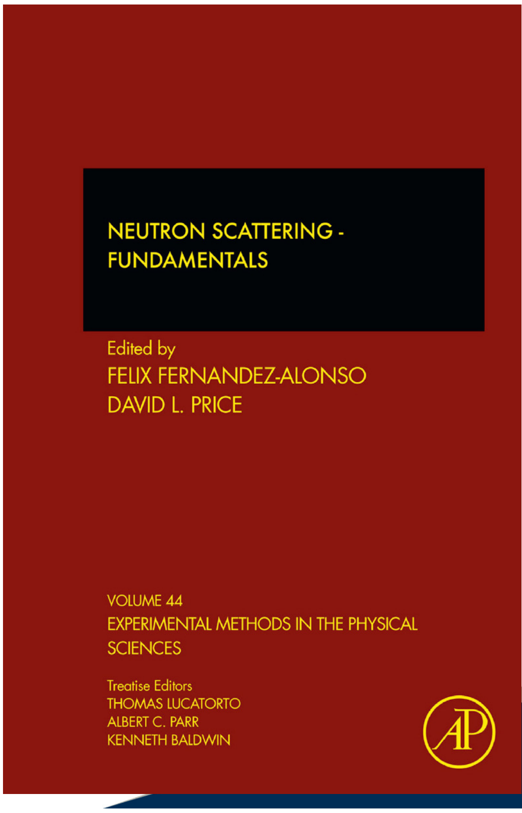
For more …



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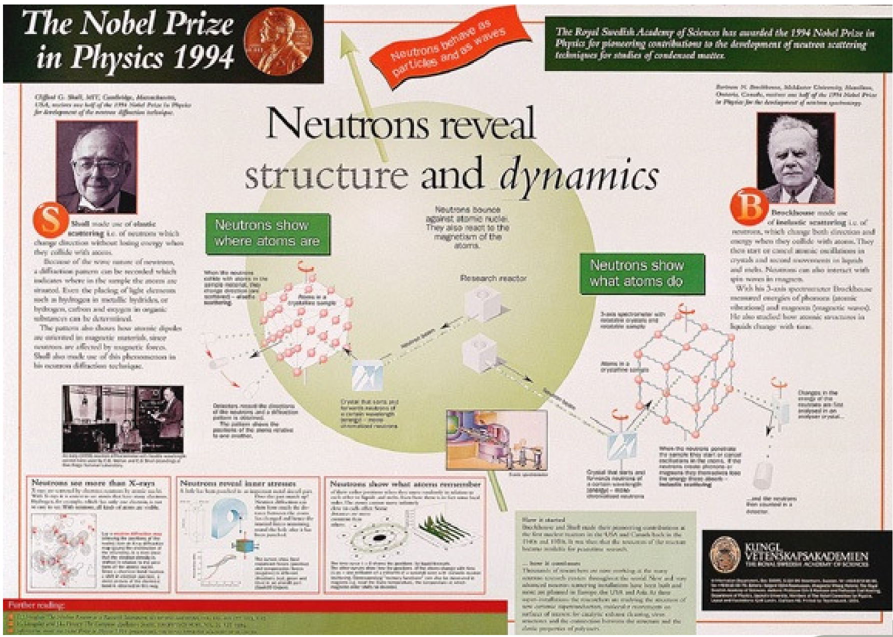
Neutron Science: Achievements



Neutrons can tell us ***where atoms are*** (structure)
and ***what atoms do*** (dynamics)

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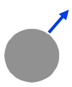
"Neutral Protons" as Condensed Matter Probes

Neutron



- Mass 1 amu
- Spin ½
- 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 δ-like (s-wave scattering).
- Spin magnetic dipole moment ~$1.9\mu_N$
- Stable lifetime ~15 min

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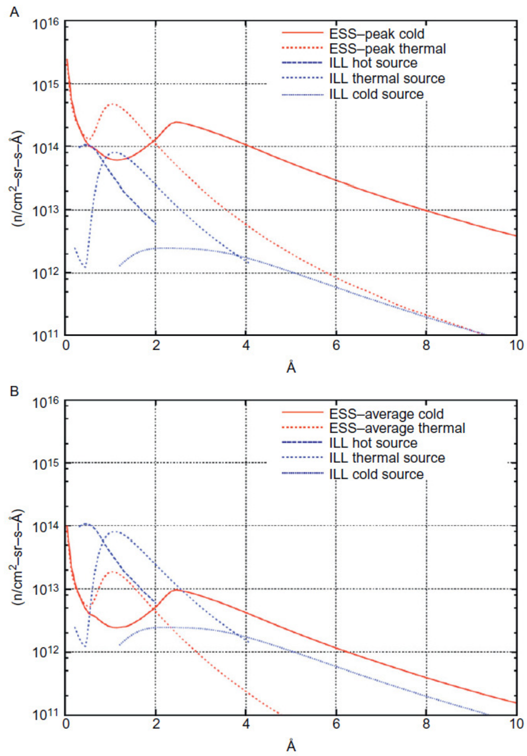
“Neutral Protons” as Condensed Matter Probes

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

Properties of the Neutron at Selected Kinetic Energies

Quantity	Unit	Definition	Ultracold	Cold	Thermal	Epithermal
Energy E_n	meV [a]		2.5×10^{-4}	1	25	1000
Temperature T	K	E_n/k_B	2.9×10^{-3}	12	290	12,000
Wavelength λ_n [b]	Å	$h/(2m_nE_n)^{1/2}$	570	9.0	1.8	0.29
Wave vector k_n [c]	$Å^{-1}$	$(2m_nE_n)^{1/2}/\hbar$	0.011	0.7	3.5	22
Velocity v_n [d]	$m\ s^{-1}$	$(2E_n/m_n)^{1/2}$	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.
[a] *1 meV = 1.6022×10^{-22} J, the amount of energy necessary to move an electron against a potential difference of one millivolt (1 mV).*
[b] *λ_n (Å) = 9.0446 [E_n (meV)]$^{-1/2}$.*
[c] *k_n ($Å^{-1}$) = 0.69469 [E_n (meV)]$^{1/2}$.*
[d] *v_n (m s^{-1}) = 437.39 [E_n (meV)]$^{1/2}$.*



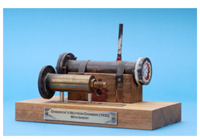
Reactor and Accelerator-based Neutron Sources

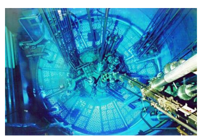
Reactor-based source:

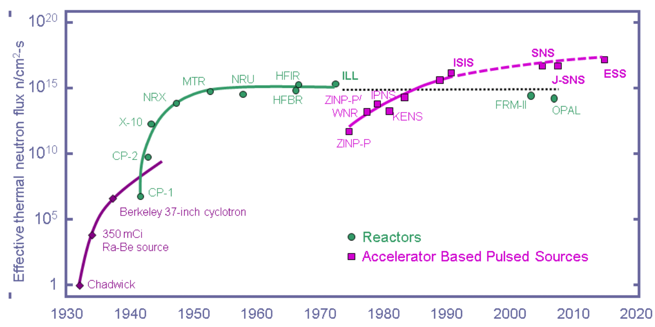
- Neutrons produced by fission reactions
- Continuous neutron beam
- 1 neutron/fission .

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

Under Construction or Planned

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Units, units, units

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

Common Quantities Used to Denote Energy or Energy Transfer

Quantity	Definition	Value at $E = 1$ meV
Radian frequency ω	$E/\hbar$	1.5193×10^{12} rad s^{-1}
Frequency ν	E/h	0.24180×10^{12} Hz $= 0.24180$ THz
Spectroscopic wave number (or kayser) $\tilde{\nu}$	E/hc	8.0655 cm^{-1}
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

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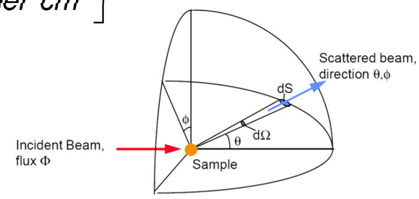
Basic Observables: Scattering Cross Sections

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

This is what we can measure:

(1) Transmission experiment:

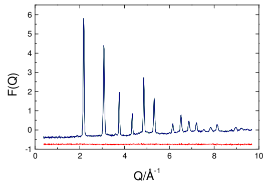


Cross sections also depend on polarisation of incident & scattered neutron.

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

(2) Diffraction experiment:

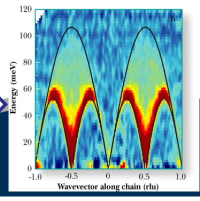
$$\frac{\partial\sigma}{\partial\Omega} = \frac{[\textit{scattered neutrons into } \partial\Omega]}{\Phi\,\partial\Omega}$$



Diffraction pattern (crystallography)

(3) Spectroscopy experiment:

$$\frac{\partial\sigma}{\partial\Omega\partial E_f} = \frac{[\textit{scattered neutrons into } \partial\Omega \,\&\, \partial E_f]}{\Phi\,\partial\Omega\partial E_f}$$



"Dynamic" Diffraction pattern

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A Neutron-scattering Experiment

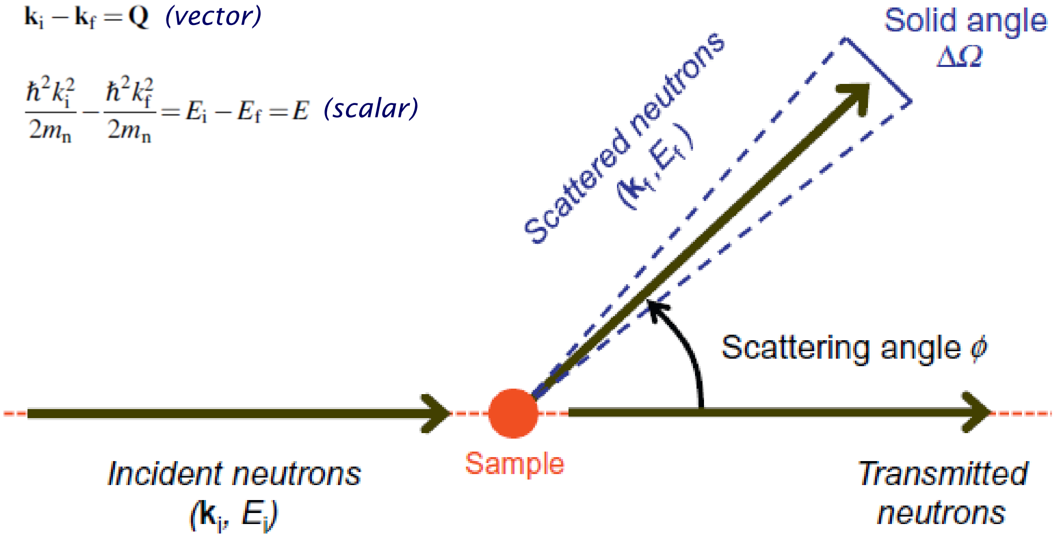
Count rate:

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

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)*

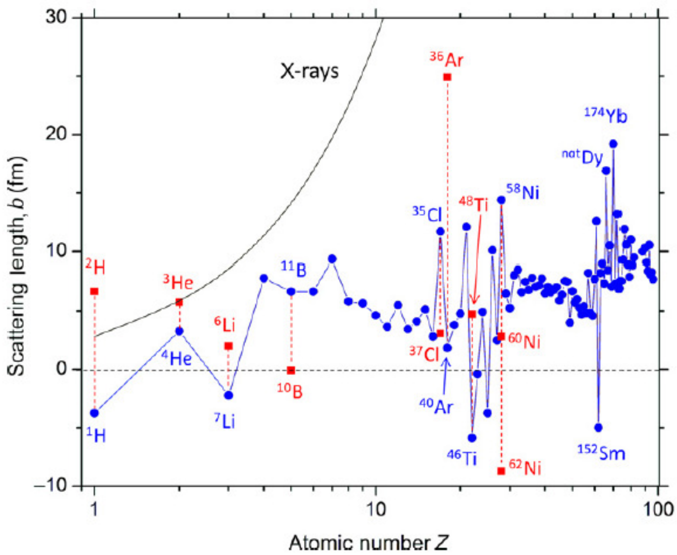


Nuclear Scattering

- 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 fm^2 = 10^{-28} m^2.
- These are tabulated extensively – more later.

Identical & noninteracting nuclei

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



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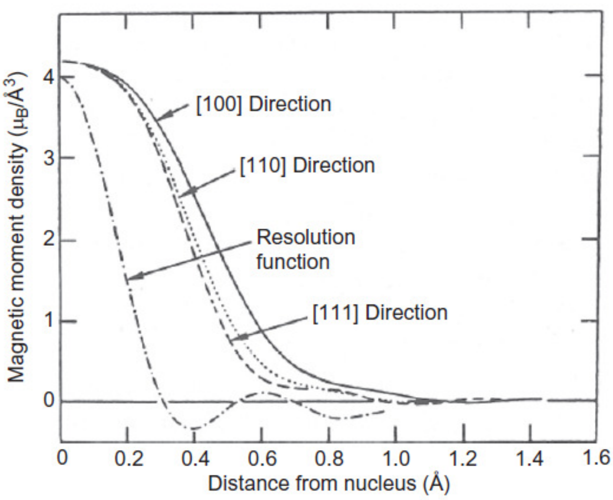
Electron and Nuclear Spins

- Scattering length γr_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).

Ensemble of randomly oriented spins (paramagnet):

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



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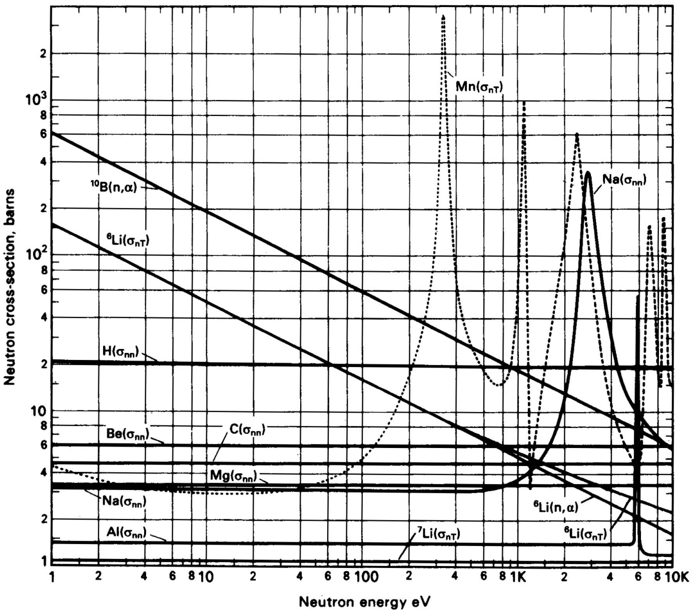
Beyond Thermal Neutron Scattering: Nuclear Absorption and Resonances

- 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.



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Absorption:
Elements to Watch Out for …

Absorption Cross Sections for Nuclides That Have Significant Charged-Particle Reactions with Thermal Neutrons (Cross Sections in Barns)

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

Quite useful for neutronics.

Can you think why?

Resonance Scattering: Elements to Watch For …

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

Radiative-Capture Cross Sections and Resonance Energies of Naturally Occurring Nuclides Having (n,γ) Resonances at Thermal Neutron Energies

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

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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:

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

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

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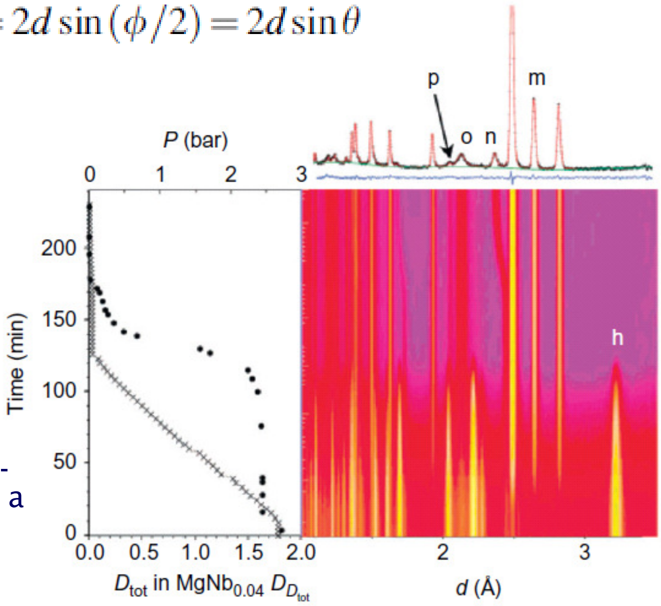
Structure: Example

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

- 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.



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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

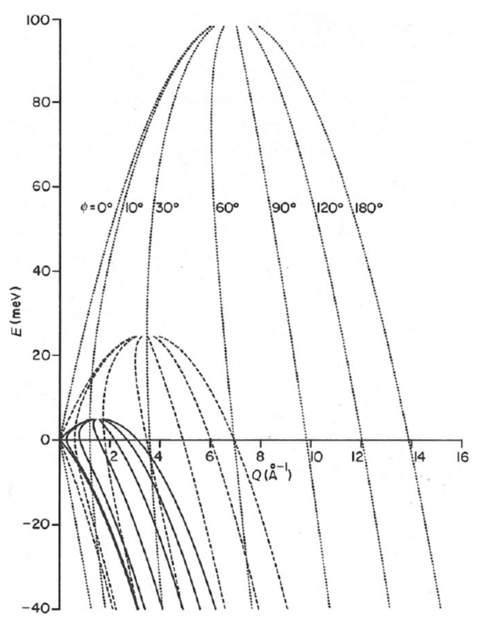
Conservation laws:

$\mathbf{k}_{\mathrm{i}} - \mathbf{k}_{\mathrm{f}} = \mathbf{Q}$ *(vector)*

$\frac{\hbar^2 k_{\mathrm{i}}^2}{2m_{\mathrm{n}}} - \frac{\hbar^2 k_{\mathrm{f}}^2}{2m_{\mathrm{n}}} = E_{\mathrm{i}} - E_{\mathrm{f}} = E$ *(scalar)*

$$k_{\mathrm{i}}^2 - 2k_{\mathrm{i}}k_{\mathrm{f}}\cos\phi + k_{\mathrm{f}}^2 = Q^2$$

$$2\left[1 - (1 - E/E_{\mathrm{i}})^{1/2}\cos\phi\right] - E/E_{\mathrm{i}} = Q^2/k_{\mathrm{i}}^2$$



Observables:

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

$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \int_{-\infty}^{E_0} \frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E_{\mathrm{f}}}\mathrm{d}E$ *Total scattering*

$\sigma_{\mathrm{t}} = \int_{4\pi} \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\mathrm{d}\Omega$ *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).

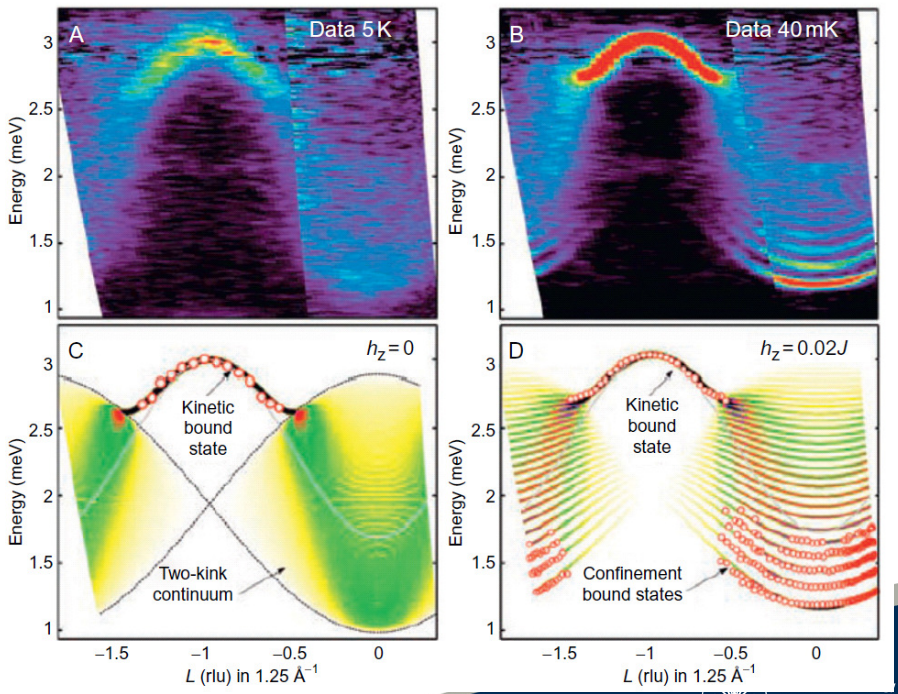
- Strictly speaking, thermal neutrons can only undergo elastic (s-wave) scattering in the scattering (centre-of-mass) frame.

- The condensed-matter scientist always refers to scattering in the laboratory frame (typically with target at rest).

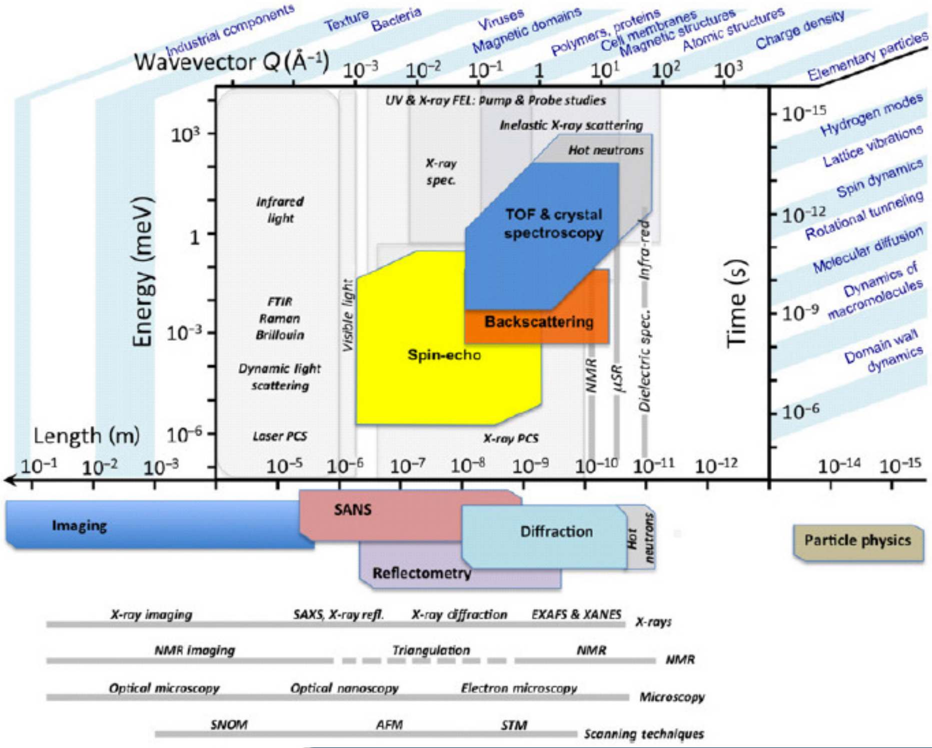
- In lab frame, two types of thermal neutron scattering:
    - "Elastic": velocity of neutron does not change.
    - "Inelastic": velocity of neutron changes due to atomic motions (a Doppler shift).

Keep this in mind, to avoid confusion

Example



The Power of Inelastic Neutron Scattering



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).

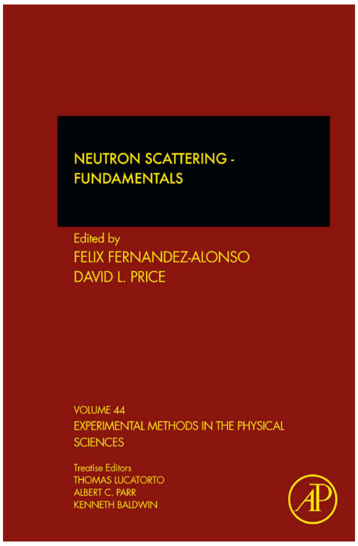
• Dielectric spectroscopy: very wide time range, no information on spatial scales, hard to interpret.

• Computer simulation: highly complementary to neutron scattering, a real synergy.

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

Foundations of Neutron Scattering

DCS and Fermi's Golden Rule

$$\left(\frac{d\sigma}{d\Omega}\right)_{\mathbf{k}_i\sigma_i\tau_i\to\mathbf{k}_f\sigma_f\tau_f} = \frac{1}{N\Phi\Delta\Omega} W_{\mathbf{k}_i\sigma_i\tau_i\to\mathbf{k}_f\sigma_f\tau_f}$$

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

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

W evaluated using Fermi's Golden Rule:

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

Rate = Transition Probability x 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

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

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

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

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

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Master Formula for the DDCS

DDCS from previous slide:

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E_\mathrm{f}}\right)_{\mathbf{k}_\mathrm{i}\sigma_\mathrm{i}\tau_\mathrm{i}\to\mathbf{k}_\mathrm{f}\sigma_\mathrm{f}\tau_\mathrm{f}} = \left(\frac{1}{N}\right)\frac{k_\mathrm{f}}{k_\mathrm{i}}\left(\frac{m_\mathrm{n}V_0}{2\pi\hbar^2}\right)^2 |\langle\mathbf{k}_\mathrm{f}\sigma_\mathrm{f}\tau_\mathrm{f}|V|\mathbf{k}_\mathrm{i}\sigma_\mathrm{i}\tau_\mathrm{i}\rangle|^2\delta(E+E_{\tau_\mathrm{i}}-E_{\tau_\mathrm{f}})$$

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:

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E_\mathrm{f}}\right)_{\mathbf{k}_\mathrm{i}\to\mathbf{k}_\mathrm{f}} = \left(\frac{1}{N}\right)\frac{k_\mathrm{f}}{k_\mathrm{i}}\left(\frac{m_\mathrm{n}V_0}{2\pi\hbar^2}\right)^2 \sum_{\tau_\mathrm{i}\sigma_\mathrm{i}} p_{\tau_\mathrm{i}}p_{\sigma_\mathrm{i}}\sum_{\tau_\mathrm{f}\sigma_\mathrm{f}}|\langle\mathbf{k}_\mathrm{f}\sigma_\mathrm{f}\tau_\mathrm{f}|V|\mathbf{k}_\mathrm{i}\sigma_\mathrm{i}\tau_\mathrm{i}\rangle|^2\delta(E+E_{\tau_\mathrm{i}}-E_{\tau_\mathrm{f}})$$

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

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Application to Nuclear Scattering

Interaction with single nucleus described by a Fermi pseudopotential

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

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:

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m_\mathrm{n}}\sum_j b_j\delta(r-R_j)$$

And bra-ket in Master Formula:

$$\langle k_\mathrm{f}|V|k_\mathrm{i}\rangle = \frac{2\pi\hbar^2}{m_\mathrm{n}V_0}\sum_j b_j\int \mathrm{e}^{-\mathrm{i}\mathbf{k}_\mathrm{f}\cdot\mathbf{r}}\delta(\mathbf{r}-\mathbf{R}_j)\mathrm{e}^{\mathrm{i}\mathbf{k}_\mathrm{i}\cdot\mathbf{r}}\mathrm{d}\mathbf{r} = \frac{2\pi\hbar^2}{m_\mathrm{n}}\sum_j b_j \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_j}$$

with $\mathbf{Q}=\mathbf{k}_\mathrm{i}-\mathbf{k}_\mathrm{f}$

And a Master Formula of the form:

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E_\mathrm{f}} = \left(\frac{1}{N}\right)\frac{k_\mathrm{f}}{k_\mathrm{i}}\sum_{\tau_\mathrm{i}\sigma_\mathrm{i}} p_{\tau_\mathrm{i}}p_{\sigma_\mathrm{i}}\left|\sum_{\tau_\mathrm{f}\sigma_\mathrm{f}}\sum_j b_j\langle\sigma_\mathrm{f}\tau_\mathrm{f}|\mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_j}|\langle\sigma_\mathrm{i}\tau_\mathrm{i}\rangle\right|^2\delta(E+E_{\tau_\mathrm{i}}-E_{\tau_\mathrm{f}})$$

For unpolarized neutron beams:

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

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

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

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

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

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

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):

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

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

Nuclear Physics

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

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 …

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

$$\overline{b_j^* b_{j'}}=\begin{cases}\overline{b_d^*}\,\overline{b_{d'}}, & j\neq j',\\ \left|\overline{b_d^2}\right|, & j=j',\end{cases}$$

$$\overline{b_j^* b_{j'}}=\overline{b_d^*}\,\overline{b_{d'}}+\left(\left|\overline{b_d^2}\right|-\left|\overline{b_d}\right|^2\right)\delta_{jj'}\delta_{dd'}$$

DDCS is then the sum of TWO distinct terms

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

$$=\frac{1}{N}\left(\frac{k_f}{k_i}\right)\sum_{dd'}\overline{b_d^*}\,\overline{b_{d'}}\sum_{j\in d,j'\in d'}S_{jj'}(\mathbf{Q},E)+\frac{1}{N}\left(\frac{k_f}{k_i}\right)\sum_{d}\left(\left|\overline{b_d^2}\right|-\left|\overline{b_d}\right|^2\right)\sum_{j\in d}S_{jj}(\mathbf{Q},E)$$

Atom pairs (coherent)

Individual atoms (incoherent)

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Coherent and Incoherent Cross Sections

$$\sigma_c^d=4\pi\left|\overline{b_d}\right|^2\text{ (coherent cross section)},$$
$$\sigma_i^d=4\pi\left[\left|\overline{b_d^2}\right|-\left|\overline{b_d}\right|^2\right]\text{ (incoherent cross section)}$$

Can be regarded as properties of a given element

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

$\sigma_c^d/4\pi$

For same atom type

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Bound Scattering Lengths and Cross Sections of the Elements and Their Isotopes

Element	Z	A	$I(\pi)$	c_a	$\overline{b}$	b^+	b^-	b_i	σ_c	σ_i	σ_s	σ_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)
^{1}H		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)
^{2}H		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)
^{3}H		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)
^{3}He		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)
^{4}He		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)
^{6}Li		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)

- 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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^{149}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)
^{150}Sm		150	0(+)	7.38	14.0(3.0)	0	25.0 (11.0)	0	25.0 (11.0)	104.0 (4.0)
^{152}Sm		152	0(+)	26.75	−5.0(6)	0	3.1(8)	0	3.1(8)	206.0 (6.0)
^{154}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)
^{151}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)
^{153}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)
^{152}Gd		152	0(+)	0.2	10.0(3.0)E	0	13.0 (8.0)	0	13.0 (8.0)	735.0 (20.0)
^{154}Gd		154	0(+)	2.18	10.0(3.0)E	0	13.0 (8.0)	0	13.0 (8.0)	85.0 (12.0)
^{155}Gd	*	155	3/2(−)	14.8	13.8(3) − 17.0(1)i	±5.(5.) − 13.16(9)i	40.8(4)	25.0(6.0)	66.0 (6.0)	61100.0 (400.0)
^{156}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

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	σ_i	σ_i (spin)	σ_i (isotope)	σ_i (isotope)/σ_i
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

Coherent dynamic structure factor (or 'scattering function')

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

Incoherent counterpart

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

DDCS in its most general form

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E_{\mathrm{f}}}=\frac{k_{\mathrm{f}}}{k_{\mathrm{i}}}\left(\sum_{dd'}\left[c_d^{1/2}c_{d'}^{1/2}\bar{b}_d^{*}\bar{b}_{d'}\right]S_{\mathrm{c}}^{dd'}(\mathbf{Q},E)+\sum_{d}\left[c_d\frac{\sigma_i^d}{4\pi}\right]S_{dd}(\mathbf{Q},E)\right)$$

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Intermediate Scattering Functions

Intermediate scattering function

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

DDCS probes S(Q,E)

ISFs can be probed directly via spin-echo methods.

Self-intermediate scattering function

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

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

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

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

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Next Lecture

Canonical Solids and Beyond (emphasis on inelastic scattering and chemical/molecular systems).

To think about: what is a solid for you?

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Extras for *Lecture I*

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Nuclear Scattering in some Detail (I)

Two-body collision neutron-nucleus collision: $\psi(\mathbf{r}) = \exp(ikz) + \frac{e^{i\mathbf{kr}}}{r} f(\mathbf{k})$

Formally, scattering amplitude given by: $f(\mathbf{k}) = -\frac{m_n}{2\pi\hbar^2}\int e^{-i\mathbf{k}\cdot\mathbf{r}'} U(r')\psi(\mathbf{r}')d\mathbf{r}'$

Thermal neutron scattering is all s-wave (J=0) $\mathbf{k}\cdot\mathbf{r}' \ll 1$

$f(k) = -b + ikb^2 + O(k^2)$ and $|kb| \approx 10^{-4}$ therefore $f(k) = -b$

a complex number $b = b' - ib''$

And the effective potential can be written as $U(r) = \frac{2\pi\hbar^2 b}{m_n}\delta(r)$

Fermi pseudopotential

The DCS is then given by

$$\frac{d\sigma}{d\Omega} = |f(\mathbf{k})|^2 \Rightarrow \frac{d\sigma}{d\Omega} = |b|^2\left(1 - 2kb''\right)$$

k-terms beyond linear neglected

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Nuclear Scattering in some Detail (II)

$\frac{d\sigma}{d\Omega} = |b|^2\left(1 - 2kb''\right)$ can be used to calculate total cross sections

Total: $\sigma_t = \sigma_s + \sigma_a$ and $\sigma_t = \frac{4\pi}{k}\mathrm{Im}[f(\mathbf{k})]_{\theta=0} \Rightarrow \sigma_t = \frac{4\pi}{k}b'' + 4\pi\left(b'^2 - b''^2\right)$

Scattering (integration of DCS over all angles): $\sigma_s = 4\pi|b|^2\left(1 - 2kb''\right)$

Absorption (total-scattering): $\sigma_a = \frac{4\pi}{k}b''\left|1 - 2kb''\right|$

kb" term typically neglected (of order 10^{-4}) and therefore

$$\sigma_s = 4\pi|b|^2$$

$$\sigma_a = \frac{4\pi}{k}b''$$

'1/v Law' for absorption

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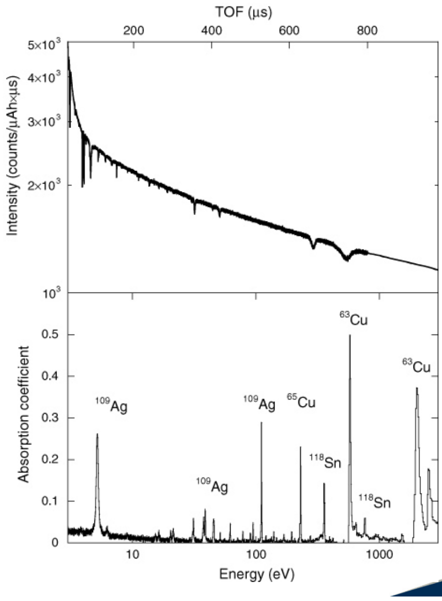
Resonant Neutron Scattering

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.

Neutrons for Condensed Matter Research

Lecture II: Canonical Solids and Beyond

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Milano, Feb 2014

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Outline [today]

- Lecture I: Fundamentals and Formalism.
- *Lecture II: Canonical Solids and Beyond.*
- Lecture III: Neutron Scattering is All about Spin.

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What is a solid?

(discussion)

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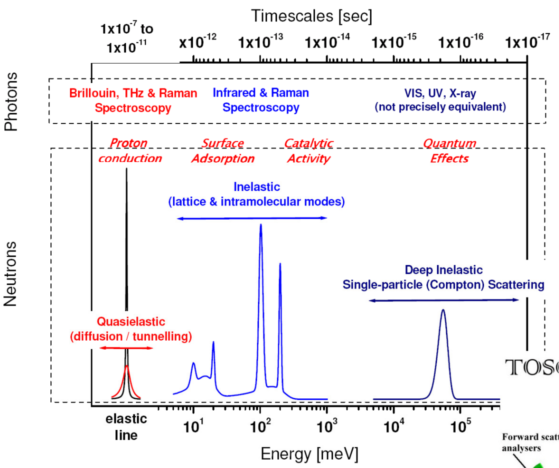
Solids, An Operational Definition

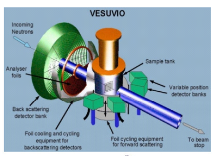
A solid is a physical system in which each atom has a well-defined (and fixed) equilibrium position over the duration of the measurement.

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

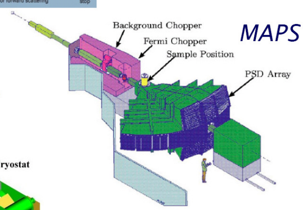
This definition excludes:
- Quantum solids (Helium).
- The battery on your mobile phone: materials where atoms or ions undergo translational diffusion.

Molecular Dynamics and Spectroscopy at ISIS



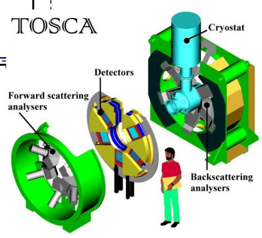


Simultaneous high-resolution diffraction

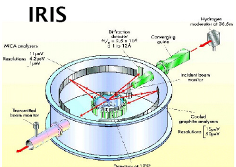


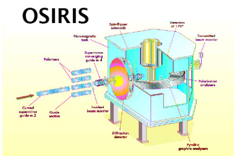
MAPS

High energies



Intermediate energies (infrared, Raman)

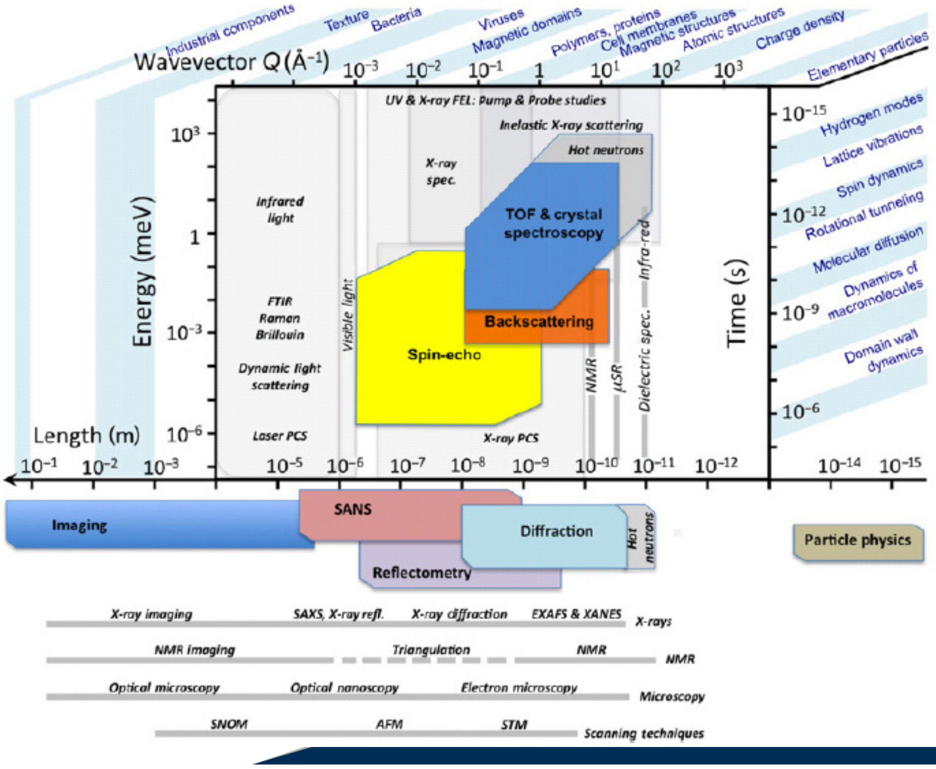




Low energy (Brillouin, THz)

Widest spectral range in the World

The Power of Inelastic Neutron Scattering



Scattering Functions For a Solid

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

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

Recall definition of scattering function from previous lecture:

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

Coherent and incoherent (self) are then given by

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

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

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

Harmonic displacement vectors (second quantization picture):

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

Mode polarization vectors for jth atom

Eigenvalues of dynamical mtx:

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

With force constants:

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

Quantum harmonic oscillator implies:

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

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

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

Debye-Waller Factor for Harmonic Vibrations

For a given atom, sum over all polarization vectors:

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

With a a Bose population factor:

$$\left\langle n_k\right\rangle = \frac{1}{\mathrm{e}^{\hbar\omega_k/k_\mathrm{B}T} - 1}$$

Simplest (and most commonly used) case: angular average

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

defined in terms of a mean-square displacement.

(used for example in the study of proteins)

Purely Elastic Scattering (Coherent)

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

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

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

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)

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

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

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

Gives (note Dirac-delta in time):

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

And energy integration gives *average Debye-Waller Factor*

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

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Purely Elastic Scattering in Ordered Solids

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

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

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

Bragg peaks

The *elastic coherent differential scattering cross* section

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

unit-cell structure factor

The *incoherent scattering cross* section

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

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Inelastic (One-Phonon) Scattering

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

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

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

Scattering function now depends implicitly on time via displacement terms

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

Also note quadratic Q dependence within brackets.

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Harmonic (Coherent) Case

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

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

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

with $E_k=\hbar\omega_k$

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

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Harmonic (Incoherent) Case

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

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

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: $\mathbf{e}_{\mathbf{d}}^{k}=\frac{1}{N_{\mathrm{c}}^{1/2}}\sum_{\mathbf{q}}\mathbf{e}_{\mathbf{d}}^{k}(\mathbf{q})\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{l}}$

Leading to an additional momentum-transfer condition

$$S_{\mathrm{c},+1}^{\mathbf{dd}'}(\mathbf{Q},E)=\frac{1}{2N_{\mathrm{c}}}(2\pi)^{3}\mathrm{e}^{-[W_{\mathbf{d}}(\mathbf{Q})+W_{\mathbf{d}'}(\mathbf{Q})]}\sum_{\mathbf{q}k}\frac{\hbar^{2}\left(\mathbf{Q}\cdot\mathbf{e}_{\mathbf{d}}^{k}(\mathbf{q})\right)^{*}\left(\mathbf{Q}\cdot\mathbf{e}_{\mathbf{d}'}^{k}(\mathbf{q})\right)}{(M_{\mathbf{d}}M_{\mathbf{d}'})^{1/2}E_{k}(\mathbf{q})}\times$$
$$\times\mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot(\mathbf{d}'-\mathbf{d})}\langle n_{\mathbf{q}k}+1\rangle\sum_{\boldsymbol{\tau}}\delta(\mathbf{Q}-\mathbf{q}-\boldsymbol{\tau})\delta(E-E_{k}(\mathbf{q}))$$

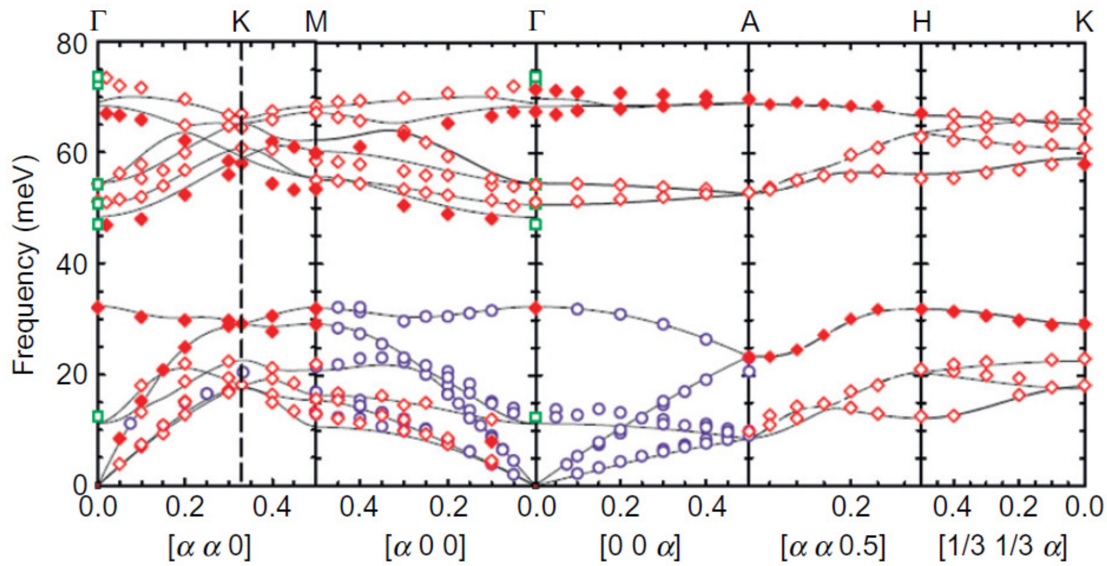
And DDCS

$$\left(\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\Omega\mathrm{d}E_{\mathrm{f}}}\right)_{\mathrm{c},+1}=\frac{k_{\mathrm{f}}}{k_{\mathrm{i}}}\left[\frac{(2\pi)^{3}}{2N_{\mathrm{c}}v_{0}}\right]\sum_{\boldsymbol{\tau}}\sum_{\mathbf{q}k}|F_{1}(\mathbf{Q},\mathbf{q}k)|^{2}\frac{\hbar^{2}\langle n_{\mathbf{q}k}+1\rangle}{E_{k}(\mathbf{q})}$$
$$\delta(\mathbf{Q}-\mathbf{q}-\boldsymbol{\tau})\delta(E-E_{k}(\mathbf{q})),$$

One-phonon structure factor $F_{1}(\mathbf{Q},\mathbf{q}k)=\sum_{\mathbf{d}}\frac{\bar{b}_{\mathbf{d}}}{M_{\mathbf{d}}^{1/2}}\mathrm{e}^{-W_{\mathbf{d}}(\mathbf{Q})}\mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{d}}[\mathbf{Q}\cdot\mathbf{e}_{\mathbf{d}}^{k}(\mathbf{q})]$

Phonon Dispersion Relations

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



Zinc oxide

Incoherent Case

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

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):*

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega \mathrm{d}E_\mathrm{f}}\right)_{\mathrm{i},+1} = \frac{k_\mathrm{f}}{k_\mathrm{i}}\sum_{\mathbf{d}}\frac{3}{2}\frac{\sigma_i^\mathbf{d}}{4\pi}\mathrm{e}^{-2W_\mathbf{d}(\mathbf{Q})}\frac{\hbar^2\overline{\left|\mathbf{Q}\cdot\mathbf{e}_\mathbf{d}^k(\mathbf{q})\right|^2}}{M_\mathbf{d}E}\langle n+1\rangle Z(E)$$

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

Incoherent Case for a Single Mass

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

Extensively used for hydrogen-containing systems.

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

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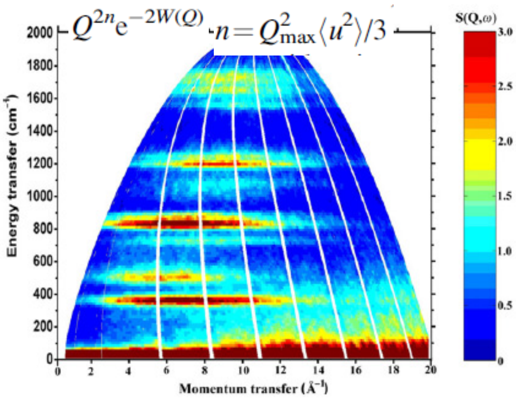
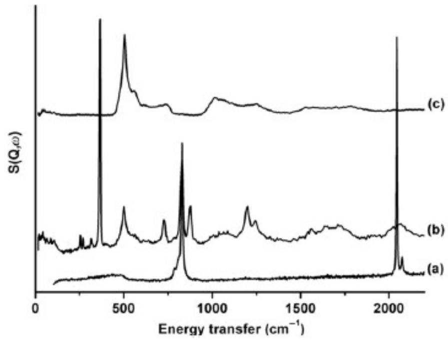
Incoherent Inelastic Neutron Scattering





For many more examples, see INS database

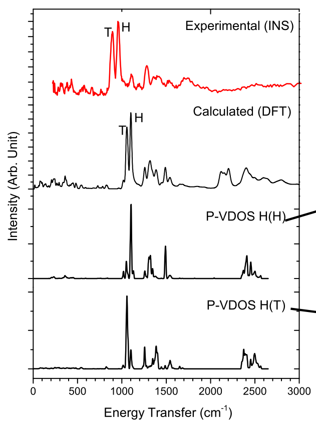
http://wwwisis2.isis.rl.ac.uk/INSdatabase/

Data collected on TOSCA at ISIS

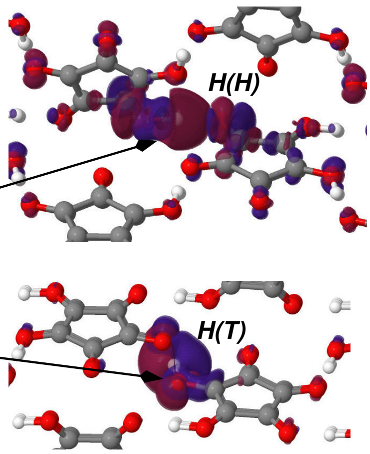
In-silico Neutron Spectroscopy

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.

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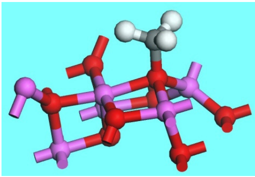
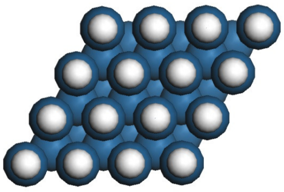
Chemical Catalysis

Methyl Chloride Synthesis

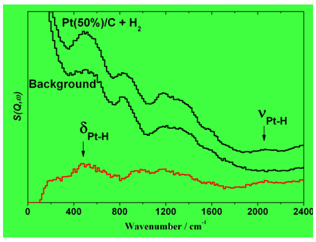


Neutron results: £4M cost saving to industrial partner.

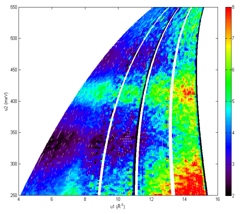


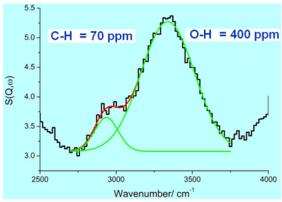
First observation of on-top hydrogen on an industrial Pt fuel-cell catalyst.
Catalysis Today, 114 (2006) 418.

Fuel Cells



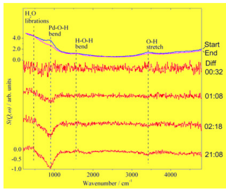
Dry Reforming of Methane

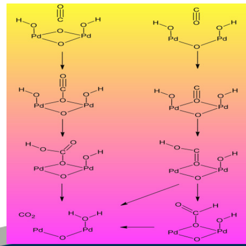




Quantitation of hydroxyl and adsorbed hydrocarbon
Phys Chem Chem Phys 12 (2010) 3102.

Operando Neutron Studies





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

Research Complex at Harwell
UCL
Cardiff University Prifysgol Caerdydd
Keele University
University of Glasgow
EPSRC Engineering and Physical Sciences Research Council
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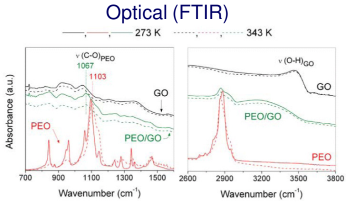
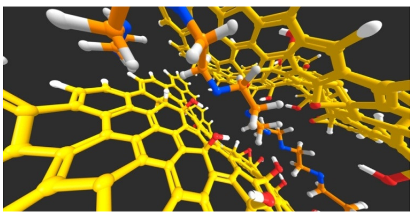
Carbon-based Nanomaterials

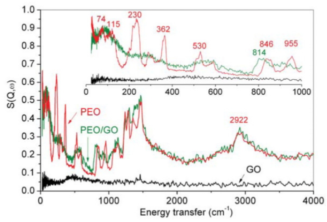
Macromolecules

Optical (FTIR)



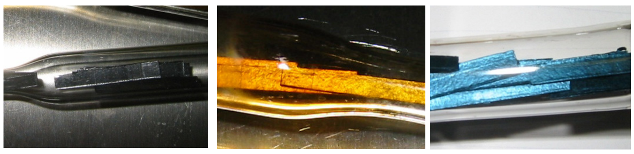


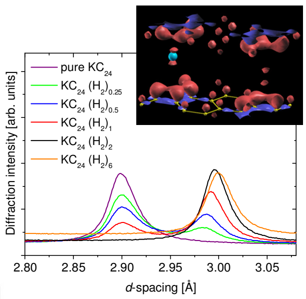
Intercalate conformation: only with neutrons

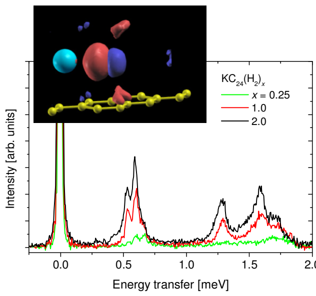


Soft Matter Comm **7** 7173 (2011).
ACS Macro Lett **1** 550 (2012).
Macromolecules **45** 3137 (2012).
Carbon **50** 5232 (2012).

Atoms and Molecules







Properties can be controlled by molecular uptake
Access to both structure & motions of adsorbate and lattice.

Faraday Disc **151** 95-115 (2011)
J Chem Phys **129** 224701 (2009)
Phys Rev Lett **101** 126101 (2008)

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UCL
Universidad del País Vasco Euskal Herriko Unibertsitatea
LCN London Centre for Nanotechnology
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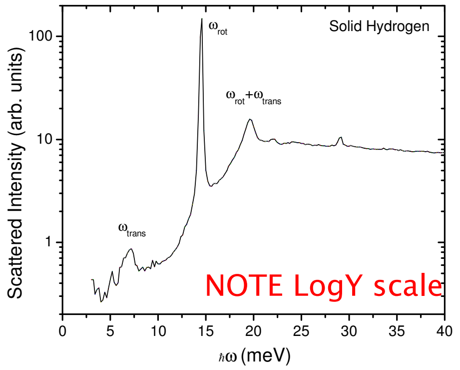
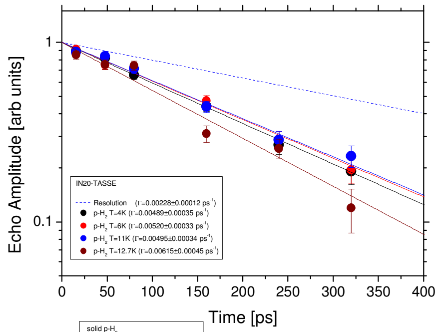
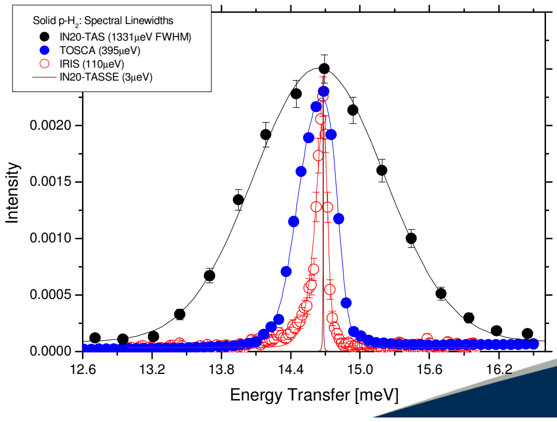
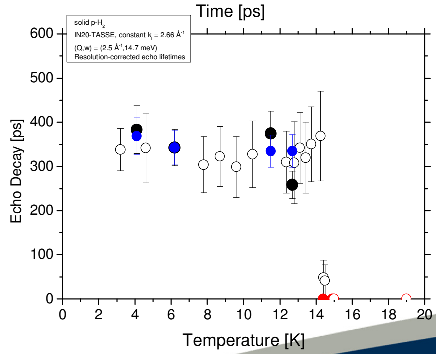
Beyond Line Positions: Spectral Linewidths









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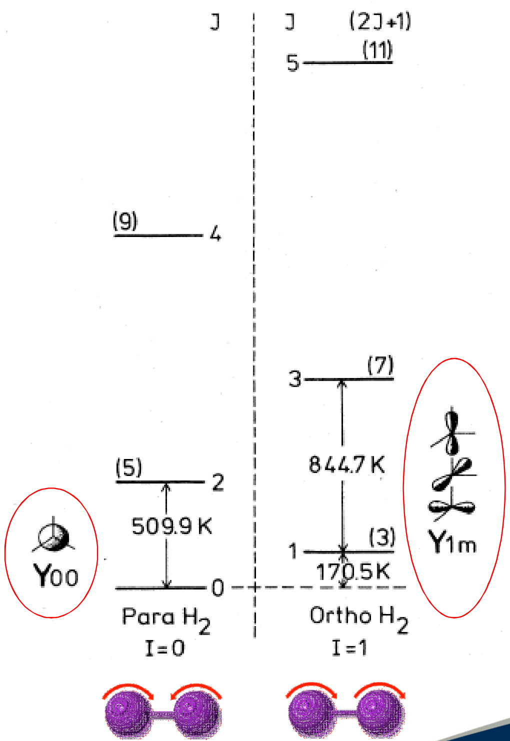
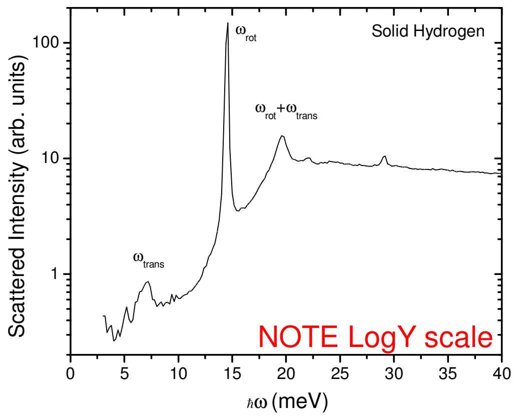
Beyond Vibrations: Molecular Hydrogen





- (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.

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Rotational Levels in Presence of Angular Potential

Free diatomic rotor

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

Additional hindering potential

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

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

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

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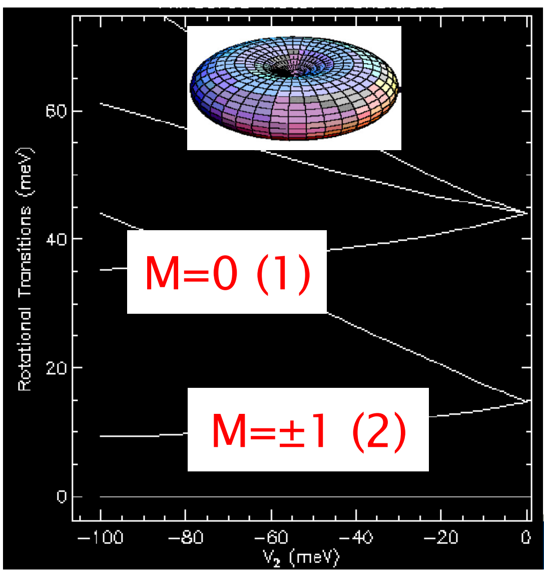
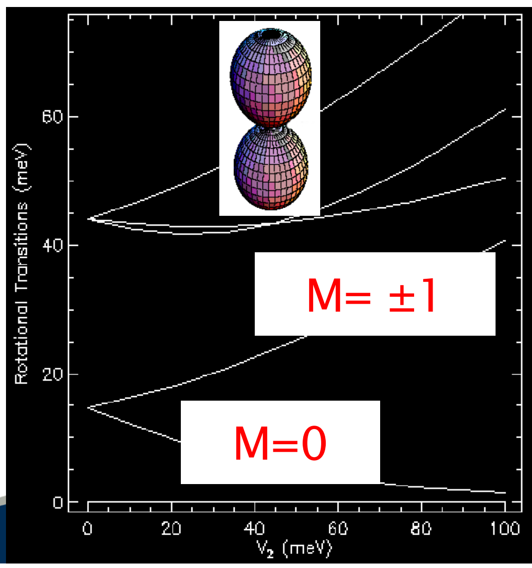
Pinning H_2 along an Axis or a Plane

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

Free Rotation on Plane



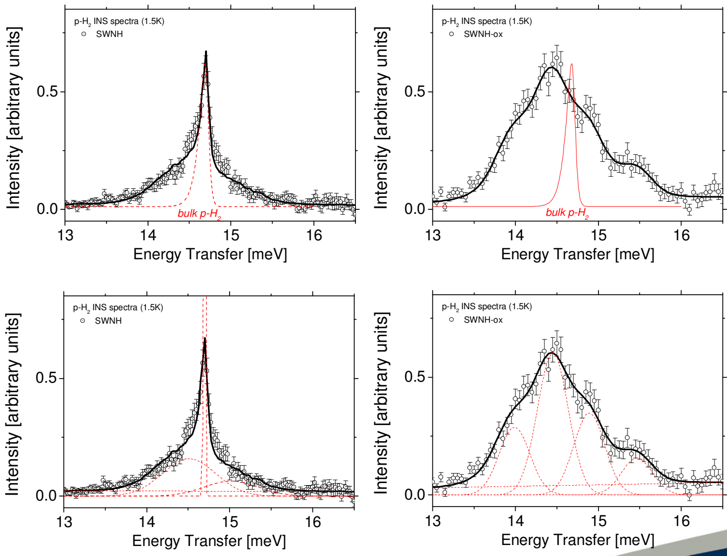
Libration along axis



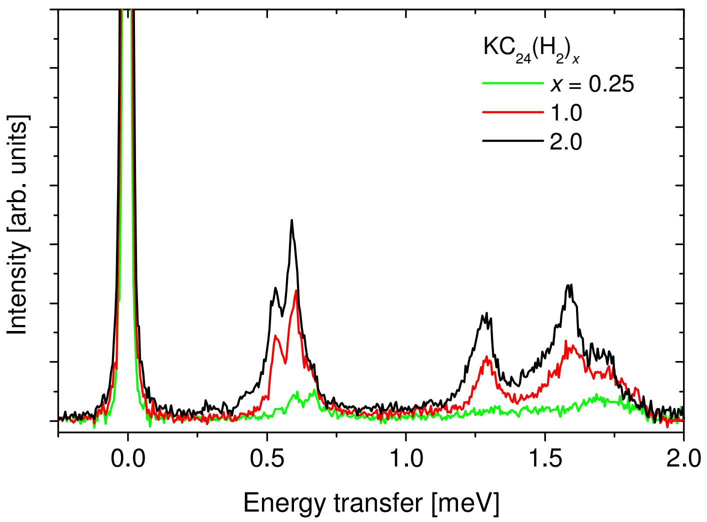
Hydrogen Spectra in Carbon Nanohorns

Closed Tips (exohedral adsorption)

Open Tips (tube filling)



K-GIC Hydrogen Uptake: Neutron Spectroscopy



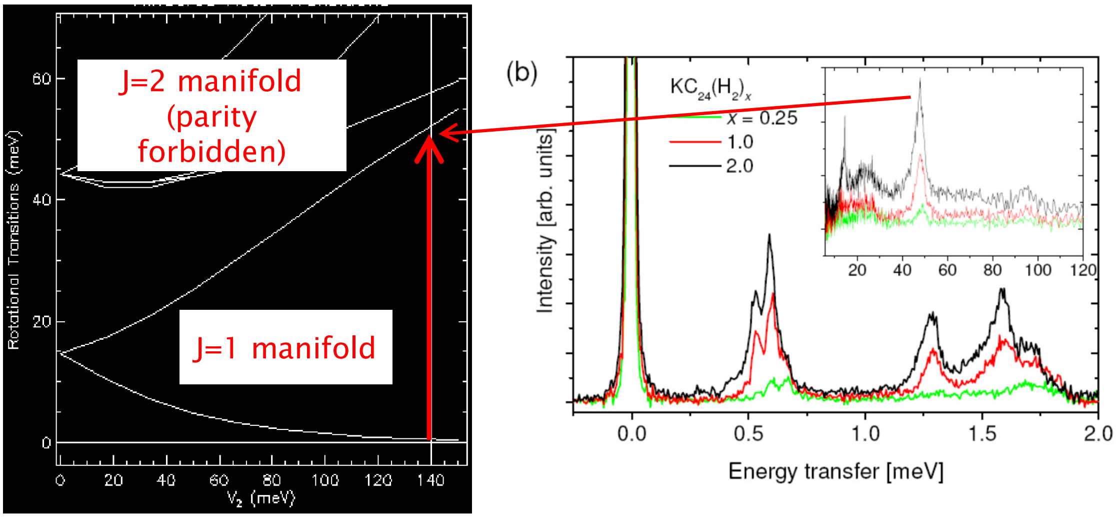
–"Tunnelling" bandhead at very low energies: strong pinning about an axis, not a plane (V_Θ~140 meV).

– Features >1.0 meV are combination bands (libron+phonon).

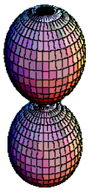
– Only evidence for single site adsorption.

If assignment is correct then expect M=±1 levels at circa 50 meV (separate experiment).

Higher Energy Transfers to Confirm Assignment



Thus, H_2 is 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:

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

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

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

Van Hove Correlation Functions

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

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

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

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

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

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

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

Pair Distribution Functions

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

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 $$G_{\mathrm{s}}^{d}(\mathbf{r},0) = \delta(\mathbf{r})$$

From which we define structure factors as energy integrals of S(Q,E)

$$S^{dd'}(\mathbf{Q}) = \int_{-\infty}^{\infty} S_{\mathrm{c}}^{dd'}(\mathbf{Q},E)\mathrm{d}E = I^{dd'}(\mathbf{Q},0)$$

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

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

coherent

$$\int_{-\infty}^{\infty} S_{\mathrm{i}}^{d}(\mathbf{Q},E)\mathrm{d}E = I_{\mathrm{s}}^{d}(\mathbf{Q},0) = 1$$ *incoherent*

Total Scattering

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

Structure factors sought after in a so-called 'total-scattering experiment'

Relationship between differential cross section (measured) and structure factors

$$\left.\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right|_{\mathbf{Q}} = \int_{-\infty\atop \text{const.}\mathbf{Q}}^{E_\mathrm{i}} \frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E_\mathrm{f}}\mathrm{d}E_\mathrm{f} \approx \sum_{dd'} c_d^{1/2}c_{d'}^{1/2}\overline{b_d^* b_{d'}}S^{dd'}(\mathbf{Q}) + \sum_d c_d\frac{\sigma_i^d}{4\pi}$$
$$= \sum_{dd'} c_d^{1/2}c_{d'}^{1/2}\overline{b_d^* b_{d'}}\left[S^{dd'}(\mathbf{Q}) - \delta_{dd'}\right] + \sum_d c_d\frac{\sigma^d}{4\pi},$$

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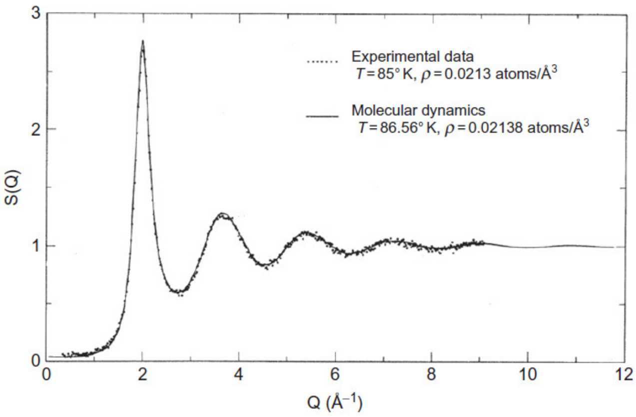
Neutron Diffraction on Disordered Matter

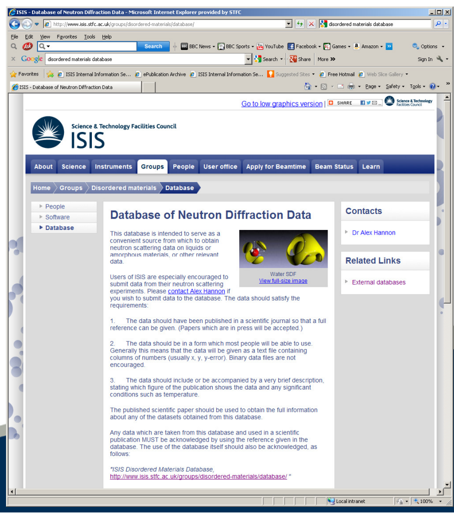
$$S^{dd'}(\mathbf{Q}) = \int_{-\infty}^{\infty} S_c^{dd'}(\mathbf{Q},E)\mathrm{d}E = I^{dd'}(\mathbf{Q},0)$$

Information on instantaneous (ensemble-averaged) positions

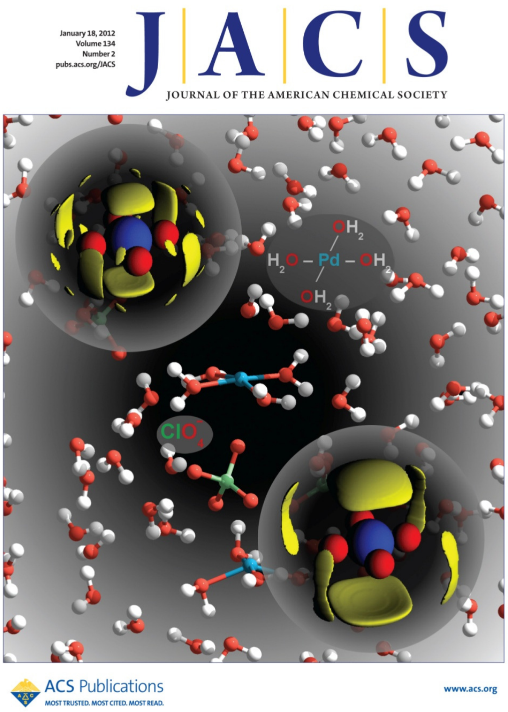


For many more examples, see disordered materials database

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



Heavy Metals in Solution: From Catalysis to Pharmacy



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

Daniel T. Bowron,† Elizabeth C. Beret,†,‡,∥ Eloisa Martin-Zamora,§ Alan K. Soper,† and Enrique Sánchez Marcos*,‡

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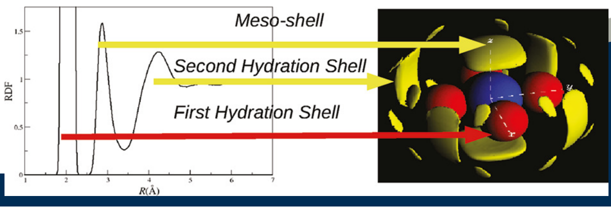
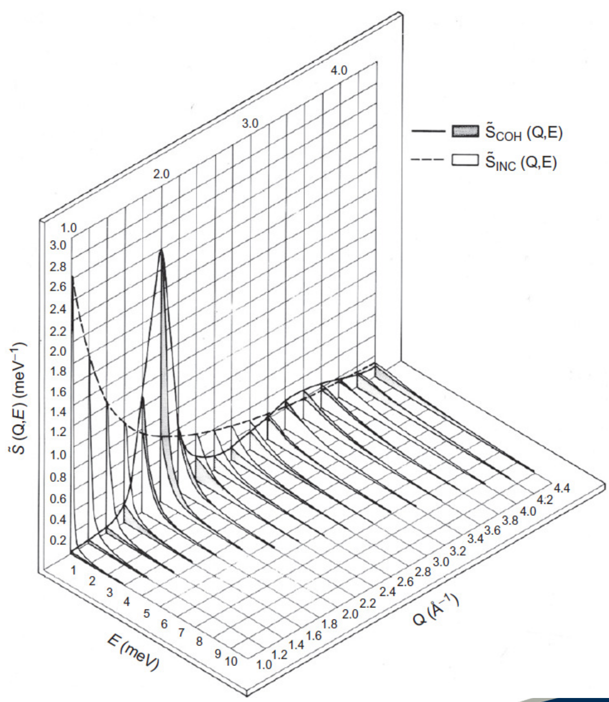
- *Solution structure of Pt(II) and Pd(II) ions of relevance to homogeneous catalysis and pharmacological activity of drugs.*
- *Pd-O axial coordination related to reactivity.*
- *What neutrons (with X-rays) tell us:*
  - *It is located between 1st and 2nd hydration shells*
  - *Strong competition between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

$$\int_{-\infty}^{\infty} S_{\mathrm{i}}^{d}(\mathbf{Q},E)\mathrm{d}E = I_{\mathrm{s}}^{d}(\mathbf{Q},0) = 1$$

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

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

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Properties of the Dynamic Structure Factor

It is real (as any observable):

$$S_{\mathrm{c}}^{dd'}(\mathbf{Q},E)=S_{\mathrm{c}}^{dd'}*(\mathbf{Q},E),$$
$$S_{\mathrm{i}}^{d}(\mathbf{Q},E)=S_{\mathrm{i}}^{d}*(\mathbf{Q},E).$$

Must satify detailed balance:

$$S_{\mathrm{c}}^{dd'}(\mathbf{Q},E)=\mathrm{e}^{E/k_{\mathrm{B}}T}S_{\mathrm{c}}^{dd'}(-\mathbf{Q},-E),$$
$$S_{\mathrm{i}}^{d}(\mathbf{Q},E)=\mathrm{e}^{E/k_{\mathrm{B}}T}S_{\mathrm{i}}^{d}(-\mathbf{Q},-E).$$

Transition probabilities are same in either direction

Zeroth moment: $\int_{-\infty}^{\infty} S_{\mathrm{c}}^{dd'}(\mathbf{Q},E)\mathrm{d}E=S^{dd'}(\mathbf{Q})$ and $\int_{-\infty}^{\infty} S_{\mathrm{i}}^{d}(\mathbf{Q},E)\mathrm{d}E=1$

First moment: $\int_{-\infty}^{\infty} S_{\mathrm{c}}^{dd'}(\mathbf{Q},E)E\ \mathrm{d}E=\frac{\hbar^2Q^2}{2M_d}\delta_{dd'}$ and $\int_{-\infty}^{\infty} S_{\mathrm{i}}^{d}(\mathbf{Q},E)E\ \mathrm{d}E=\frac{\hbar^2Q^2}{2M_d}$

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

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Total Scattering and Static Approximation

For energy changes in system are much smaller than the incident energy:

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E_{\mathrm{f}}}=\frac{1}{N}\frac{k_{\mathrm{f}}}{k_{\mathrm{i}}}\sum_{\tau_{\mathrm{i}}}p_{\tau_{\mathrm{i}}}\left|\sum_{\tau_{\mathrm{f}}}\sum_{j}b_j\langle\tau_{\mathrm{f}}|\mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_j}|\tau_{\mathrm{i}}\rangle\right|^2\delta(E+E_{\tau_{\mathrm{i}}}-E_{\tau_{\mathrm{f}}})$$

$\delta(E)$

And the differential cross section:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}=\int_{-\infty}^{E_{\mathrm{i}}}\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E_{\mathrm{f}}}\mathrm{d}E_{\mathrm{f}}=\frac{1}{N}\sum_{\tau_i}p_{\tau_i}\sum_{j\in d,j'\in d'}\overline{b_j^*b_{j'}}\left\langle\mathrm{e}^{-i\mathbf{Q}_0\cdot(\mathbf{R}_{j'}-\mathbf{R}_j)}\right\rangle$$
$$=\sum_{dd'}c_d^{1/2}c_{d'}^{1/2}\overline{b_d^*b_{d'}}S^{dd'}(\mathbf{Q}_0)+\sum_d c_d\frac{\sigma_{\mathrm{i}}^d}{4\pi}.$$

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

Good approximation for $E_{\mathrm{i}}\gg\hbar^2Q^2/2M$ and $k_{\mathrm{i}}\gg Q/A^{1/2}$

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:

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

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

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

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

Impulse approximation
(measures momentum distribution)

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

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

All three satisfied

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Neutron Compton Scattering

Measured Compton profile:

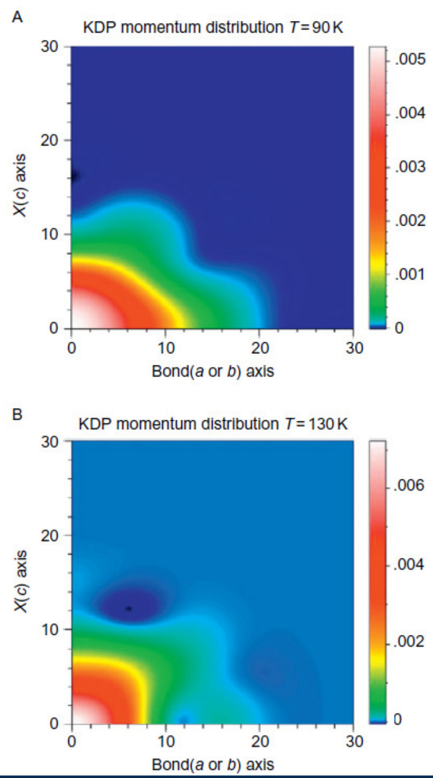
$$J\left(\hat{\mathbf{Q}},y\right) = \hbar\int n(\mathbf{p})\delta\left(\hbar y - \mathbf{p}\cdot\hat{\mathbf{Q}}\right)d\mathbf{p}$$

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

Beyond Structure:
Nuclear Quantum Dynamics on VESUVIO

PHYSICAL REVIEW B 82, 174306 (2010)

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

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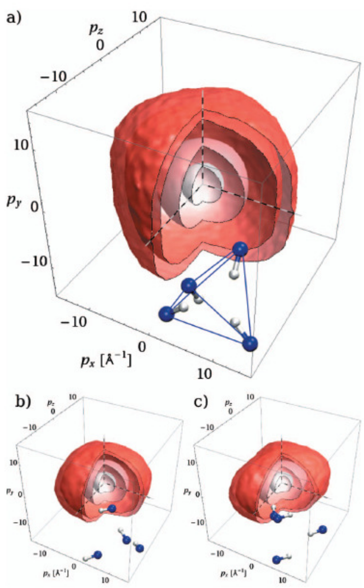

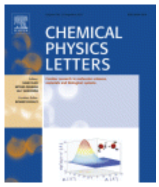

Chemical Physics Letters 518 (2011) 1–6

FRONTIERS ARTICLE

Ground state proton dynamics in stable phases of water

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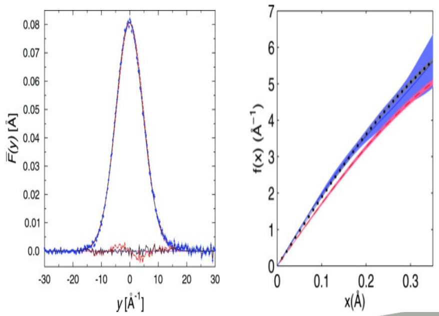
- *Direct acccess to proton momentum distributions with neutrons.*
- *Quantum effects essential to explain material properties.*
- *Extension to other masses of technological interest (e..g., Li, O).*



ETH Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

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Fast-neutron Detector Development

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Stochastic Diffusion & Relaxation

No well-defined equilibrium sites – use Van Hove formalism

Translational diffusion:

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

Gaussian Approximation

Mean-square displacement:

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

Intermediate scattering function:

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

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

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 $\gamma(t) = Dt,$ ⇒ $S_i(\mathbf{Q},E) = \frac{1}{\pi}\frac{\hbar DQ^2}{E^2 + (\hbar DQ^2)^2}$

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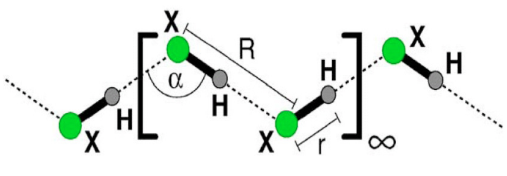
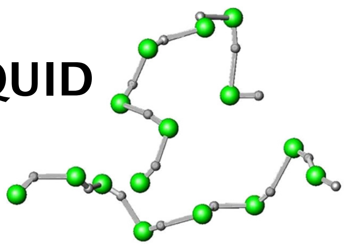
Stochastic Motions in the Simplest Hydrogen-bonded Liquid



SOLID

LIQUID



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

- Quintessential H-bonded liquid.
  - Linear geometry (R_{HF} = 0.94 Å).
  - Strongest hydrogen bond (~250 meV).
- Abundant theoretical and simulation studies.
- Very few experiments (very aggressive material)

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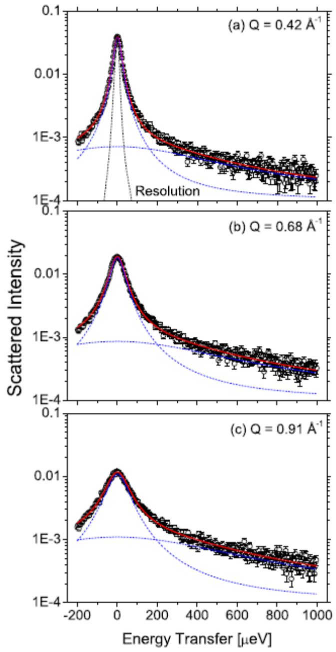
Dynamics of Liquids: Hydrogen Fluoride

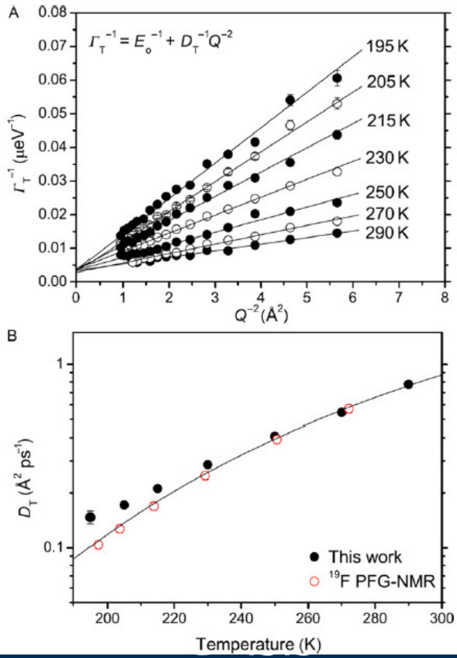
'Quasielastic' data



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

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

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

Internal rotations:

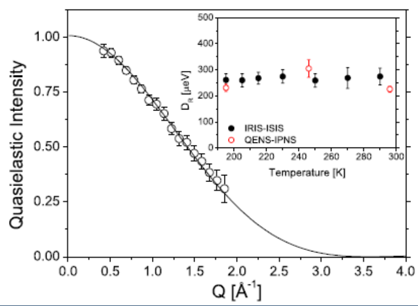
$$S_R(Q,E)=j_0^2(QR)\delta(E)+\sum_{l>0}(2l+1)j_l^2(QR)\left[\frac{1}{\pi}\frac{l(l+1)\Gamma_R}{E^2+(l(l+1)\Gamma_R)^2}\right]$$

Total (incoherent) dynamic structure factor:

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

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

Simultaneous information on molecular shape and motions



What Happens When Translations are Frozen?

$$S_{\mathrm{i}}(Q,E)=\mathrm{e}^{-Q^2\langle u^2\rangle/3}\left\{\begin{array}{l} j_0^2(QR)\left[\dfrac{1}{\pi}\dfrac{\Gamma_{\mathrm{T}}(Q)}{E^2+\Gamma_{\mathrm{T}}(Q)^2}\right]+ \\ +\sum\limits_{l>0}(2l+1)j_l^2(QR)\left[\dfrac{1}{\pi}\dfrac{\Gamma_{\mathrm{RT}}(l;Q)}{E^2+\Gamma_{\mathrm{RT}}^2(l;Q)}\right]\end{array}\right\}$$

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Frozen Translations

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

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

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?

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Disordered Solids
(important applications to proton, ionic conductors)

Basic picture: discontinuous jumps across sites.

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

with jump-distance d and residence time τ

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

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

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

For a cubic lattice with lattice parameter *a*
$$\Gamma(\mathbf{Q})=\frac{\hbar}{3\tau}\left(3-\cos Q_x a-\cos Q_y a-\cos Q_z a\right)$$

And at low Q
$$\Gamma(Q)=\hbar\frac{Q^2a^2}{6\tau}\equiv\hbar DQ^2$$

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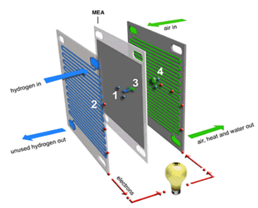
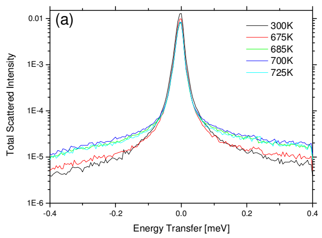
Energy Research: Fuel Cells & Battery Materials

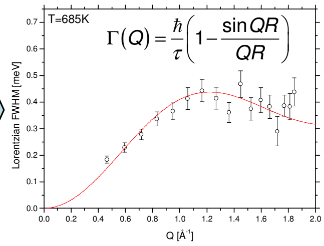


$LaSrCoO_3H_{0.7}$: transition metal oxide with a high H concentration.

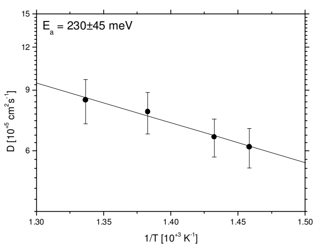
Neutron Spectra

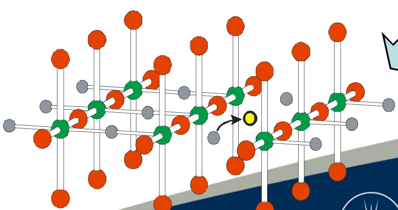


Hydride Diffusion



Energetics of Diffusion





Hopping mechanism

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

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Next Lecture

Neutron Scattering is All about Spin

To think about: neutrons have spin, electrons and many nuclei have spin. Consider how these might interact, and what information they might provide.

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Neutrons for Condensed Matter Research

Lecture III: Neutron Scattering is All About Spin

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Outline [today]

- Lecture I: Fundamentals and Formalism.
- Lecture II: Canonical Solids and Beyond (emphasis on inelastic scattering and chemical/molecular systems).
- *Lecture III: Neutron Scattering is All about Spin.*

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Magnetic Scattering

Recall *Master Formula* in Lecture I:

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

So far we have worked with nuclear interactions: $\frac{2\pi\hbar^2}{m_n} b_{\sigma\tau}\delta(\mathbf{r}-\mathbf{R})$

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

Neutron-electron-spin interaction potential:

$$V(\mathbf{r}) = -(2\gamma\mu_N\mu_B)\sigma\cdot\left(\nabla\times\left(\frac{\mathbf{s}\times\hat{\mathbf{r}}}{r^2}\right)+\frac{\mathbf{p}\times\hat{\mathbf{r}}}{\hbar r^2}\right)$$

with $\gamma = -1.913$

Neutron and electron spins present from outset

Plug back into *Master Formula* …

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Magnetic Master Formula

"Spatial" or "orbital" matrix elements

$$\langle \mathbf{k}_\mathrm{f}|V|\mathbf{k}_\mathrm{i}\rangle = 8\pi(\gamma\mu_\mathrm{N}\mu_\mathrm{B})\sigma\cdot\mathbf{D}_\perp(\mathbf{k}_\mathrm{i}-\mathbf{k}_\mathrm{f}) \qquad \mathbf{D}_\perp(\mathbf{Q}) = \sum_j \left(\hat{\mathbf{Q}}\times\left(\mathbf{s}_j\times\hat{\mathbf{Q}}\right)+\frac{i}{\hbar Q}\mathbf{p}\times\hat{\mathbf{Q}}\right)e^{i\mathbf{Q}\cdot\mathbf{r}_j}$$

Magnetic interaction operator

"Spin" matrix elements (unpolarized case) $\sum_{\sigma_\mathrm{i}} p_{\sigma_\mathrm{i}} \sum_{\sigma_\mathrm{f}} \left|\langle\sigma_\mathrm{f}|\sigma_\alpha\sigma_\beta|\sigma_\mathrm{i}\rangle\right|^2 = \delta_{\alpha\beta}$

Master Formula becomes:

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E_\mathrm{f}} = \frac{1}{N_\mathrm{m}}\left(\frac{k_\mathrm{f}}{k_\mathrm{i}}\right)(\gamma r_0)^2 \sum_\alpha \sum_{\tau_\mathrm{i}} p_{\tau_\mathrm{i}} \sum_{\tau_\mathrm{f}} \langle\tau_\mathrm{i}|\mathbf{D}^+_{\perp\alpha}|\tau_\mathrm{f}\rangle\langle\tau_\mathrm{f}|\mathbf{D}_{\perp\alpha}|\tau_\mathrm{i}\rangle\delta(E+E_{\tau_\mathrm{i}}-E_{\tau_\mathrm{f}})$$

$r_0 = \frac{e^2}{4\pi\varepsilon_0 m_e c^2} = 2.8179\mathrm{fm}$ *Classical electron radius*

Same order as nuclear interactions (recall Lecture I)

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Real-Time Representation

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E_\mathrm{f}} = \frac{1}{N_\mathrm{m}}\left(\frac{k_\mathrm{f}}{k_\mathrm{i}}\right)(\gamma r_0)^2 \sum_\alpha \sum_{\tau_\mathrm{i}} p_{\tau_\mathrm{i}} \sum_{\tau_\mathrm{f}} \langle\tau_\mathrm{i}|\mathbf{D}^+_{\perp\alpha}|\tau_\mathrm{f}\rangle\langle\tau_\mathrm{f}|\mathbf{D}_{\perp\alpha}|\tau_\mathrm{i}\rangle\delta(E+E_{\tau_\mathrm{i}}-E_{\tau_\mathrm{f}})$$

$$\Downarrow$$

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E_\mathrm{f}} = \frac{1}{N_\mathrm{m}}\left(\frac{k_\mathrm{f}}{k_\mathrm{i}}\right)(\gamma r_0)^2 \sum_\alpha \frac{1}{2\pi\hbar}\int \langle\mathbf{D}_{\perp\alpha}(-\mathbf{Q},0)\mathbf{D}_{\perp\alpha}(\mathbf{Q},t)\rangle e^{-iEt/\hbar}\mathrm{d}t$$

Compare with nuclear case

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

$4\pi(\gamma r_0)^2 = 3.652\ \mathrm{b}$ *Characteristic magnetic cross section*

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Magnetic Interaction Operators

$\mathbf{D}_\perp(\mathbf{Q},t)$ can be viewed as projections of a generalized operator **D** on a plane ***perpendicular*** to the scattering vector **Q**

$$\mathbf{D}_\perp = \hat{\mathbf{Q}} \times \mathbf{D} \times \hat{\mathbf{Q}} = \mathbf{D} - \left(\mathbf{D}\cdot\hat{\mathbf{Q}}\right)\left(\hat{\mathbf{Q}}\right)$$

And *D* is related to the Fourier transform of the magnetization

$$\mathbf{D}(\mathbf{Q},t) = -\frac{\mathbf{M}(\mathbf{Q},t)}{2\mu_\mathrm{B}} = -\frac{1}{2\mu_\mathrm{B}}\int \mathbf{M}(\mathbf{r},t)e^{i\mathbf{Q}\cdot\mathbf{r}}d\mathbf{r}$$

Using the above tensorial properties, we can then write the DDCS as

$$\frac{d^2\sigma}{d\Omega dE_\mathrm{f}} = \frac{1}{N_\mathrm{m}}\left(\frac{k_\mathrm{f}}{k_\mathrm{i}}\right)(\gamma r_0)^2\sum_{\alpha\beta}\left(\delta_{\alpha\beta} - \hat{Q}_\alpha\hat{Q}_\beta\right)\frac{1}{2\pi\hbar}\int\langle D_\alpha(-\mathbf{Q},0)D_\beta(\mathbf{Q},t)\rangle e^{-iEt/\hbar}dt$$

DDCS related to magnetic fluctuations, analogous to nuclear case

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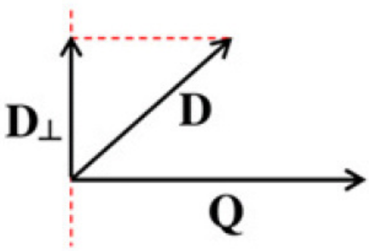
Directional Properties of Magnetic DDCS

$$\frac{d^2\sigma}{d\Omega dE_\mathrm{f}} = \frac{1}{N_\mathrm{m}}\left(\frac{k_\mathrm{f}}{k_\mathrm{i}}\right)(\gamma r_0)^2\sum_{\alpha\beta}\left(\delta_{\alpha\beta} - \hat{Q}_\alpha\hat{Q}_\beta\right)\frac{1}{2\pi\hbar}\int\langle D_\alpha(-\mathbf{Q},0)D_\beta(\mathbf{Q},t)\rangle e^{-iEt/\hbar}dt$$

$$1-\left(\hat{\mathbf{Q}}\cdot\hat{\eta}\right)^2$$



Tensorial term ‘picks out’ magnetization components orthogonal to **Q**

This relationship makes it possible to deduce the magnetic moment in a crystalline materials relative to a given crystallographic orientation

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Evaluation of Magnetic Interaction Operator

Very much dependent on nature of magnetic electrons.

Example: atom-centered electrons of intrinsic and orbital spins **s** and **l**

$$\mathbf{D}(\mathbf{Q},t)=\sum_j \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_j}\sum_{n\in j}\mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{r}_n}(\mathbf{s}_n+\mathbf{l}_n)$$

If electrons obey Russell-Saunders (LS) coupling:

$$\mathbf{D}(\mathbf{Q},t)=\sum_j f_j(\mathbf{Q})\boldsymbol{\mu}_j(t)\mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_j(t)}$$ with magnetic moment $\boldsymbol{\mu}_j=\frac{1}{2}g_j\mathbf{S}_j$

And magnetic form factor $f_j(\mathbf{Q})$

LS coupling $f(\mathbf{Q})=\frac{g_S}{g}\bar{j}_0(\mathbf{Q})+\frac{g_L}{g}[\bar{j}_0(\mathbf{Q})+\bar{j}_2(\mathbf{Q})]$ with $\bar{j}_n(\mathbf{Q})=\int j_n(Qr)|\psi(r)|^2\mathrm{d}\mathbf{r}$

Form factor tells us about electronic wavefunction

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Evaluation of Magnetic DDCS

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E_\mathrm{f}}=\frac{1}{N_\mathrm{m}}\left(\frac{k_\mathrm{f}}{k_\mathrm{i}}\right)(\gamma r_0)^2\sum_{\alpha\beta}\left(\delta_{\alpha\beta}-\hat{Q}_\alpha\hat{Q}_\beta\right)\sum_{jj'}f_j^*(\mathbf{Q})f_{j'}(\mathbf{Q})\times$$
$$\times\frac{1}{2\pi\hbar}\int\left\langle\mu_{j\alpha}(0)\mu_{j'\beta}(t)\right\rangle\left\langle\mathrm{e}^{-\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_j(0)}\mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_{j'}(t)}\right\rangle\mathrm{e}^{-\mathrm{i}Et/\hbar}\mathrm{d}t,$$

Assumes separation of nuclear and electronic motions

To be contrasted again with nuclear analogue (Lecture I)

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

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Magnetic DDCS for Random Spins

Case of a paramagnetic solid at zero magnetic field

Absence of spin correlations implies $\langle \mu_{j\alpha}(0)\mu_{j'\beta}(t)\rangle = \left\langle \mu_{j\alpha}(0)^2 \right\rangle \delta_{jj'}\delta_{\alpha\beta} = \frac{1}{12} g_j^2 S_j(S_j+1)\delta_{jj'}\delta_{\alpha\beta}$

Recalling $\sum_{\alpha\beta}\left(\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta\right) = 2$

With a DDCS $$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N_m}\left(\frac{k_f}{k_i}\right)(\gamma r_0)^2 \sum_j |f_j(Q)|^2 \frac{1}{6} g_j^2 S_j(S_j+1)\frac{1}{2\pi\hbar}\int \left\langle e^{-i\mathbf{Q}\cdot\mathbf{R}_j(0)} e^{i\mathbf{Q}\cdot\mathbf{R}_j(t)} \right\rangle e^{-iEt/\hbar} dt$$

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

With a Q-dependent effective cross section $$4\pi(\gamma r_0)^2 |f_j(Q)|^2 \frac{1}{6} g_j^2 S_j(S_j+1)$$

Elastic Scattering from Spin Order

Magnetic DDCS $$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N_m}\left(\frac{k_f}{k_i}\right)(\gamma r_0)^2 \sum_\alpha \frac{1}{2\pi\hbar}\int \langle \mathbf{D}_{\perp\alpha}(-\mathbf{Q},0)\mathbf{D}_{\perp\alpha}(\mathbf{Q},t)\rangle e^{-iEt/\hbar} dt$$

Static magnetic order implies no implicit time (energy) dependence, that is, purely elastic scattering

$$\left(\frac{d\sigma}{d\Omega}\right)_{el} = \frac{1}{N_m}(\gamma r_0)^2 |\langle \mathbf{D}_\perp(\mathbf{Q})\rangle|^2$$

Periodic magnetic structure (non-Bravais) $\mathbf{R}_j(t) = \mathbf{l} + \mathbf{d} + \mathbf{u}_j(t)$

And magnetic interaction operator $\mathbf{D}(\mathbf{Q},t) = \sum_j f_j(\mathbf{Q})\boldsymbol{\mu}_j(t) e^{i\mathbf{Q}\cdot\mathbf{R}_j(t)}$ becomes

$$\langle \mathbf{D}(\mathbf{Q})\rangle = \sum_l \sum_d f_d(\mathbf{Q})\langle \mu_d\rangle e^{i\mathbf{Q}\cdot(\mathbf{l}+\mathbf{d})} e^{-W_d(\mathbf{Q})} = \frac{1}{|\gamma r_0|}\sum_{\mathbf{l}} \mathbf{F}_M(\mathbf{Q}) e^{i\mathbf{Q}\cdot\mathbf{l}}$$

Magnetic Unit-cell Structure Factor

$$\mathbf{F}_\mathrm{M}(\mathbf{Q}) = |\gamma r_0| \sum_d f_d(\mathbf{Q}) \langle \mu_d \rangle e^{i\mathbf{Q}\cdot\mathbf{d}} e^{-W_d(\mathbf{Q})}$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{el}} = \frac{1}{N_\mathrm{m}} (\gamma r_0)^2 |\langle \mathbf{D}_\perp(\mathbf{Q}) \rangle|^2 \quad \Rightarrow \quad \left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{el}} = \frac{1}{N_\mathrm{m}} \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}_\mathrm{M}} \delta(\mathbf{Q} - \boldsymbol{\tau}_\mathrm{M}) |\mathbf{F}_{\mathrm{M}\perp}(\boldsymbol{\tau}_\mathrm{M})|^2$$

Magnetic Bragg condition

$$\mathbf{F}_{\mathrm{M}\perp} = \hat{\mathbf{Q}} \times \mathbf{F}_\mathrm{M} \times \hat{\mathbf{Q}}$$

Magnetic structure factor

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Spin Dynamics

Time-dependent fluctuations of the embodied in DDCS, and recall that

$$\frac{d^2\sigma}{d\Omega dE_\mathrm{f}} = \frac{1}{N_\mathrm{m}} \left(\frac{k_\mathrm{f}}{k_\mathrm{i}}\right) (\gamma r_0)^2 \sum_{\alpha\beta} \left(\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta\right) \sum_{jj'} f_j^*(\mathbf{Q}) f_{j'}(\mathbf{Q}) \times$$
$$\times \frac{1}{2\pi\hbar} \int \langle \mu_{j\alpha}(0) \mu_{j'\beta}(t) \rangle \left\langle e^{-i\mathbf{Q}\cdot\mathbf{R}_j(0)} e^{i\mathbf{Q}\cdot\mathbf{R}_{j'}(t)} \right\rangle e^{-iEt/\hbar} dt$$

DDCS contains two types of correlation functions, which can be recast in terms of time-independent and time-dependent terms:

$$J_{jj'}^{\alpha\beta}(t) \equiv \langle \mu_{j\alpha}(0) \mu_{j'\beta}(t) \rangle = J_{jj'}^{\alpha\beta}(\infty) + \widetilde{J}_{jj'}^{\alpha\beta}(t),$$
$$I_{jj'}(Q,t) = \langle e^{-iQ\cdot R_j(0)} e^{iQ\cdot R_{j'}(t)} \rangle = I_{jj'}(\mathbf{Q},\infty) + \widetilde{I}_{jj'}(\mathbf{Q},t)$$

Such that integral in DDCS can be written as

$$\int \left[J_{jj'}^{\alpha\beta}(\infty) + \widetilde{J}_{jj'}^{\alpha\beta}(t)\right] \left[I_{jj'}(\mathbf{Q},\infty) + \widetilde{I}_{jj'}(\mathbf{Q},t)\right] e^{-iEt/\hbar} dt$$

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Spin Dynamics

$$\int \left[J_{jj'}^{\alpha\beta}(\infty) + \tilde{J}_{jj'}^{\alpha\beta}(t) \right] \left[I_{jj'}(\mathbf{Q},\infty) + \tilde{I}_{jj'}(\mathbf{Q},t) \right] \mathrm{e}^{-\mathrm{i}Et/\hbar} \mathrm{d}t$$

Physical meaning of each component:

$J_{jj'}^{\alpha\beta}(\infty) I_{jj'}(\mathbf{Q},\infty)$	Purely elastic scattering, discussed earlier
$J_{jj'}^{\alpha\beta}(\infty) I_{jj'}(\mathbf{Q},t)$	Magneto-vibrational term (same energy dependence as vibrational nuclear scattering, interaction is through magnetic potential)
$J_{jj'}^{\alpha\beta}(t) I_{jj'}(\mathbf{Q},\infty)$	Responsible for inelastic magnetic scattering

Fourth term?

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Inelastic Magnetic Scattering with Long-range Order

A solid obeying long-range order $\mathbf{j} = \mathbf{l} + \mathbf{d}$

The magnetic DDCS can be written

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega \mathrm{d}E_\mathrm{f}} = \frac{1}{N_\mathrm{m}} \left(\frac{k_\mathrm{f}}{k_\mathrm{i}}\right) \frac{(\gamma r_0)^2}{4\pi\mu_\mathrm{B}^2} \sum_{\alpha\beta} \left(\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta\right) \left(1 - \mathrm{e}^{-E/k_\mathrm{B}T}\right)^{-1}$$
$$\sum_{dd'} \mathrm{e}^{-[W_d(\mathbf{Q}) + W_{d'}(\mathbf{Q})]} \left(\chi''\right)_{\alpha\beta}^{dd'} (\mathbf{Q}, E),$$

Where we have introduced the imaginary part of a generalized susceptibility

$$(\chi'')_{\alpha\beta}^{\mathbf{dd'}}(\mathbf{Q},E) = 4\pi\mu_\mathrm{B}^2 f_\mathbf{d}^*(\mathbf{Q}) f_{\mathbf{d'}}(\mathbf{Q}) \left(1 - \mathrm{e}^{-E/k_\mathrm{B}T}\right)$$
$$\times \sum_{\mathbf{l}} \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot(\mathbf{l}+\mathbf{d'}-\mathbf{d})} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \langle \mu_{\mathbf{0d}\alpha}(0) \mu_{\mathbf{ld'}\beta}(t) \rangle \mathrm{e}^{-\mathrm{i}Et/\hbar} \mathrm{d}t$$

Susceptibility is the magnetic analogue of the dynamic structure factor

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Spin Waves (or ‘Magnetic Phonons’)

Spin-waves: collective excitations arising from long-range magnetic order. The quantum of excitation is the ‘magnon’

Physical picture: sinusoidal deviations of spin components along a particular direction.

As for phonons, we can write time dependence of ‘spin displacements’ in terms of creation and annihilation operators

$$S_l^x(t)+S_l^y(t)=\left(\frac{2S}{N}\right)^{1/2}\sum_{\mathbf{q}} b(\mathbf{q})\mathrm{e}^{\mathrm{i}[\mathbf{q}\cdot\mathbf{l}-\omega(\mathbf{q})t]},$$

$$S_l^x(t)-S_l^y(t)=\left(\frac{2S}{N}\right)^{1/2}\sum_{\mathbf{q}} b^+(\mathbf{q})\mathrm{e}^{-\mathrm{i}[\mathbf{q}\cdot\mathbf{l}-\omega(\mathbf{q})t]},$$

$$S_l^z(t)=S-\frac{1}{N}\sum_{\mathbf{q}\mathbf{q}'} b(\mathbf{q})b^+(\mathbf{q}')\mathrm{e}^{\mathrm{i}\{(\mathbf{q}'-\mathbf{q})\cdot\mathbf{l}-[\omega(\mathbf{q}')-\omega(\mathbf{q})]t\}}$$

for $\mathrm{H}=-\sum_{ll'} J_{ll'}\,\mathbf{S}_l\cdot\mathbf{S}_{l'}$

and small spin displacements

Spin-wave Hamiltonian of the form

$$H=H^0+\sum_{\mathbf{q}}\hbar\omega(\mathbf{q})b^+(\mathbf{q})b(\mathbf{q})$$

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Spin-wave Susceptibility

Recall

$$(\chi'')_{\alpha\beta}^{\mathbf{dd}'}(\mathbf{Q},E)=4\pi\mu_{\mathrm{B}}^2 f_{\mathbf{d}}^*(\mathbf{Q})f_{\mathbf{d}'}(\mathbf{Q})\left(1-\mathrm{e}^{-E/k_{\mathrm{B}}T}\right)\times\sum_{\mathbf{l}}\mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot(\mathbf{l}+\mathbf{d}'-\mathbf{d})}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\langle\mu_{\mathbf{0d}\alpha}(0)\mu_{\mathbf{ld}'\beta}(t)\rangle\mathrm{e}^{-\mathrm{i}Et/\hbar}\mathrm{d}t$$

For Bravais lattice $\quad \chi''(\mathbf{Q},E)=\pi g^2\mu_{\mathrm{B}}^2\left(1-\mathrm{e}^{-E/k_{\mathrm{B}}T}\right)\sum_{\mathbf{l}}\mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{l}}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\langle S_{0\alpha}(0)S_{l\beta}(t)\rangle\mathrm{e}^{-\mathrm{i}Et/\hbar}\mathrm{d}t.$

Non-zero components of $\langle S_{0\alpha}(0)S_{l\beta}(t)\rangle$

$$\langle S_{0x}(0)S_{lx}(t)\rangle=\langle S_{0y}(0)S_{ly}(t)\rangle=\frac{S}{2N}\sum_{\mathbf{q}}\left[\mathrm{e}^{-\mathrm{i}[\mathbf{q}\cdot\mathbf{l}-\omega(\mathbf{q})t]}\langle n_{\mathbf{q}}+1\rangle+\mathrm{e}^{\mathrm{i}[\mathbf{q}\cdot\mathbf{l}-\omega(\mathbf{q})t]}\langle n_{\mathbf{q}}\rangle\right]$$

$$\langle S_{0x}(0)S_{ly}(t)\rangle=-\langle S_{0y}(0)S_{lx}(t)\rangle=\frac{iS}{2N}\sum_{\mathbf{q}}\left[\mathrm{e}^{-\mathrm{i}[\mathbf{q}\cdot\mathbf{l}-\omega(\mathbf{q})t]}\langle n_{\mathbf{q}}+1\rangle+\mathrm{e}^{\mathrm{i}[\mathbf{q}\cdot\mathbf{l}-\omega(\mathbf{q})t]}\langle n_{\mathbf{q}}\rangle\right]$$

$$\langle S_{0z}(0)S_{lz}(t)\rangle=S^2-\frac{S}{2N}\sum_{\mathbf{q}}\langle n_{\mathbf{q}}\rangle$$

Static term

with Bose population term $\quad \langle n_{\mathbf{q}}\rangle=\dfrac{1}{\exp[\hbar\omega(\mathbf{q})/k_{\mathrm{B}}T]-1}$

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Spin-wave DDCS

Creation

$$\left(\frac{d^2\sigma}{d\Omega dE_f}\right)_{m,+1} = \left(\frac{k_f}{k_i}\right)\frac{(2\pi)^3}{2N_m v_0}(\gamma r_0)^2\left(\frac{g^2 S}{4}\right)\left(1+\hat{Q}_z^2\right)f^2(\mathbf{Q})e^{-2W(\mathbf{Q})}\times$$
$$\times\sum_{\tau\mathbf{q}}\langle n_\mathbf{q}+1\rangle\delta(\mathbf{Q}-\mathbf{q}-\boldsymbol{\tau})\delta[E-\hbar\omega(\mathbf{q})],$$

Destruction

$$\left(\frac{d^2\sigma}{d\Omega dE_f}\right)_{m,-1} = \left(\frac{k_f}{k_i}\right)\frac{(2\pi)^3}{2N_m v_0}(\gamma r_0)^2\left(\frac{g^2 S}{4}\right)\left(1+\hat{Q}_z^2\right)f^2(\mathbf{Q})e^{-2W(\mathbf{Q})}$$
$$\times\sum_{\tau\mathbf{q}}\langle n_\mathbf{q}\rangle\delta(\mathbf{Q}+\mathbf{q}-\boldsymbol{\tau})\delta[E+\hbar\omega(\mathbf{q})],$$

With selection rules $\mathbf{Q}=\boldsymbol{\tau}\pm\mathbf{q},\ E=\hbar\omega(\mathbf{q})$

For comparison, phonon case reads

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

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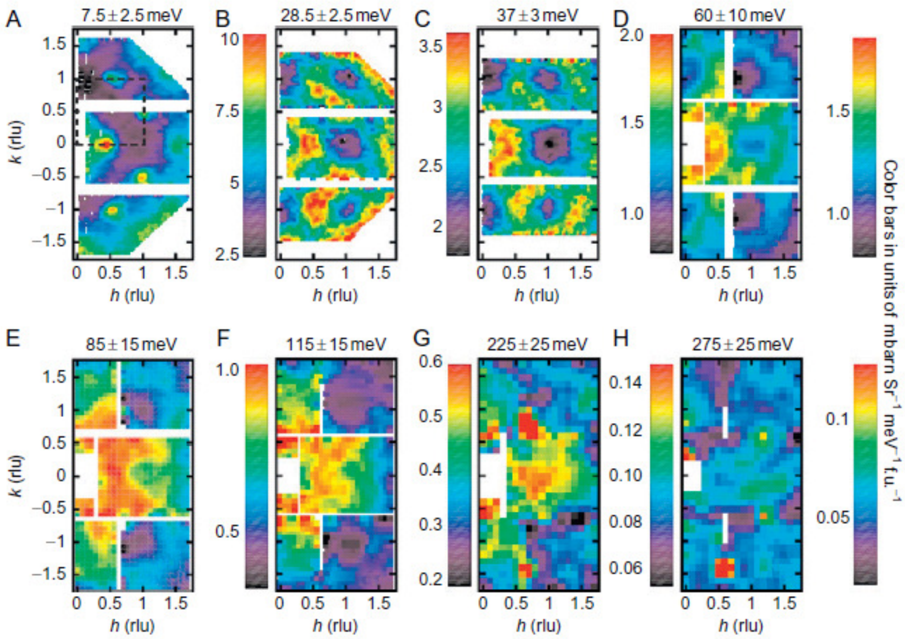
Spin Waves in Superconductors: Dynamic Diffraction



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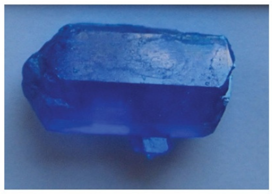
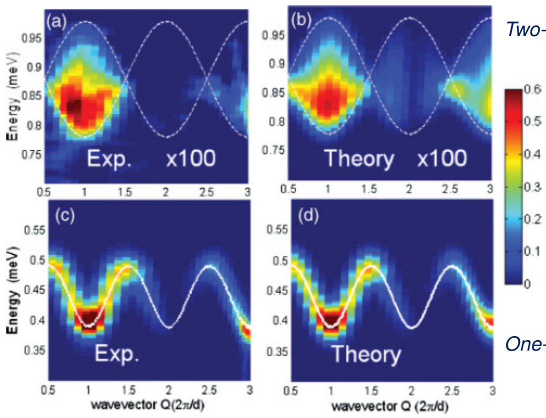
Excitation Lifetimes in Quantum Magnets

Copper Nitrate: a model spin ½ AF Heisenberg Chain



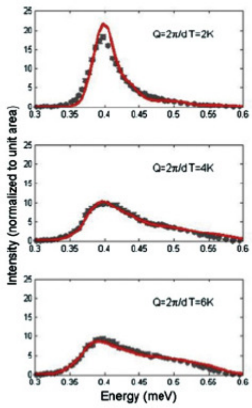
T=120 mK



Two-magnon

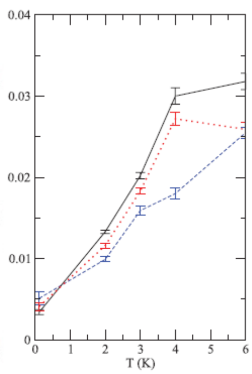
One-magnon

One-magnon line shapes



Lifetimes

Γ(Q)



Extension to 10's of meV

Parametric studies

Phys Rev B ***85*** *014402 (2012)*

Magnetic Clusters (Localized Excitations)

Mn_{12} Acetate (S=10)

$$H = D\left[S_z - \frac{1}{3}S(S+1)\right] + B_4^0 O_4^0 + B_4^4 O_4^4$$

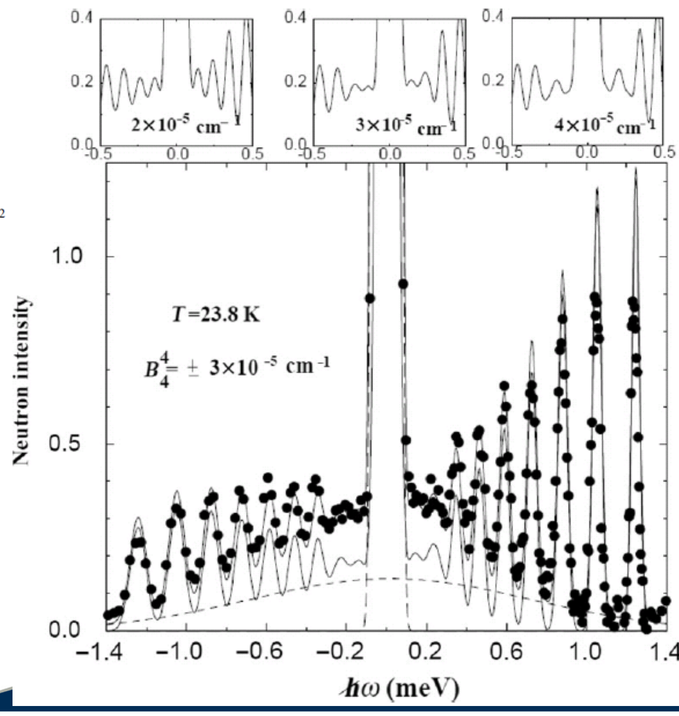
$$O_4^0 = 35S_z^4 - [30S(S+1) - 25]S_z^2 - 6S(S+1) + 3S^2(S+1)^2$$

$$O_4^4 = \frac{1}{2}[S_+^4 + S_-^4]$$

From neutron data:

$$D = -56.7(2)\,\mu\text{eV}$$

$$B_4^0 = -2.89(2)\times 10^{-3}\,\mu\text{eV}$$



Polarized Neutrons and Nuclei

Nuclear scattering lengths depend on relative orientation of incoming neutron spin and intrinsic spin of nucleus:

$$\hat{b}_j = \bar{b}_j + \frac{1}{2} b_{\mathrm{N}j} (\sigma \cdot \mathbf{I}_j)$$

For a single isotope, this dependence is responsible for incoherent scattering

In terms of angular momentum algebra, compound neutron-nucleus systems leads to two distinct states *I*±½ with scattering lengths $b^{\pm}$

$$\bar{b}_j = \frac{1}{2I_j+1}\left[(I_j+1)b_j^+ + I_j b_j^-\right],$$
$$b_{\mathrm{N}j} = \frac{2}{2I_j+1}\left[b_j^+ - b_j^-\right].$$

And can define four possible outcomes for a polarized experiment

non-spin-flip

$$\langle\uparrow|\hat{b}_j|\uparrow\rangle = \bar{b}_j + \frac{1}{2} b_{\mathrm{N}j} I_{jz},$$
$$\langle\downarrow|\hat{b}_j|\downarrow\rangle = \bar{b}_j - \frac{1}{2} b_{\mathrm{N}j} I_{jz},$$

spin-flip

$$\langle\downarrow|\hat{b}_j|\uparrow\rangle = \frac{1}{2} b_{\mathrm{N}j} (I_{jx} + iI_{jy}),$$
$$\langle\uparrow|\hat{b}_j|\downarrow\rangle = \frac{1}{2} b_{\mathrm{N}j} (I_{jx} - iI_{jy}),$$

Coherent vs Incoherent Scattering

Recall definition of cross sections

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

For a single element with randomly distributed isotopes and associated spins

$$\bar{b}_{\mathrm{nsf}} = \sum_a c_a \bar{b}_a = \sum_a \frac{c_a}{2I_a+1}\left[(I_a+1)b_a^+ + I_a b_a^-\right] = \bar{b},$$
$$\bar{b}_{\mathrm{sf}} = 0,$$

Coherent scattering is all nsf

For incoherent scattering, both nsf and sf are possible:

$$\sigma_{\mathrm{i,nsf}} = 4\pi \sum_a c_a \overline{b_a^2} - 4\pi\left(\sum_a c_a \bar{b}_a\right)^2 + \frac{\pi}{3}\sum_a c_a I_a(I_a+1) b_{\mathrm{N}a}^2 = \sigma_{\mathrm{i}} - \sigma_{\mathrm{i,sf}},$$
$$\text{with } \sigma_{\mathrm{i,sf}} = \frac{2\pi}{3}\sum_a c_a I_a(I_a+1) b_{\mathrm{N}a}^2 = \frac{8\pi}{3}\sum_a c_a \frac{I_a(I_a+1)}{(2I_a+1)^2}\left[\bar{b}_a^+ - \bar{b}_a^-\right]^2.$$

Conversely, incoherent scattering requires an intrinsic dependence of scattering length on spin state.

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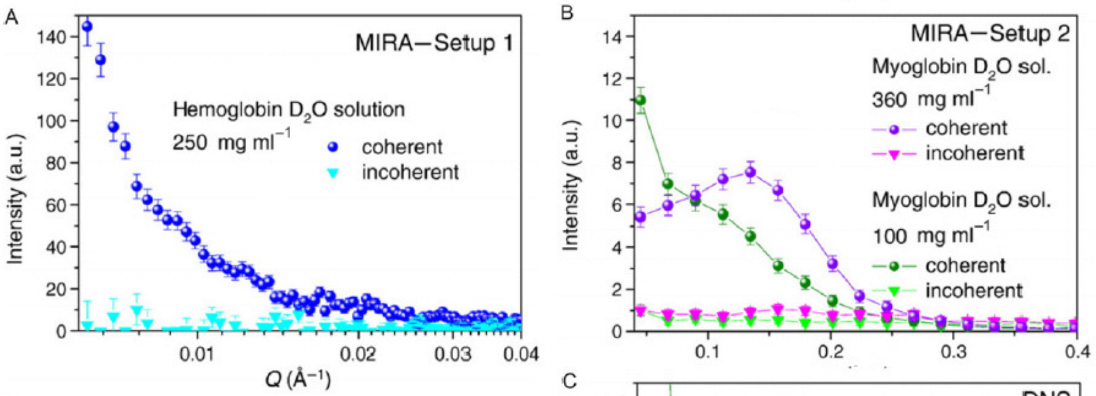
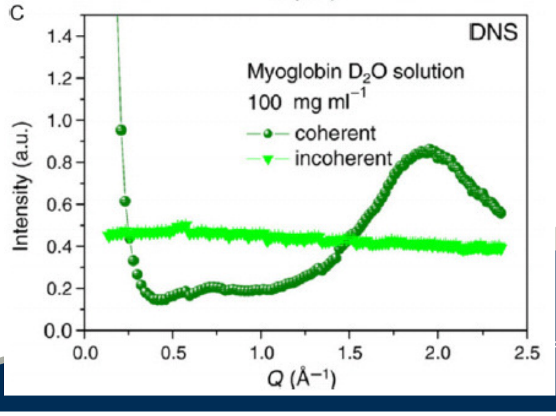
Polarization Analysis – Nuclear Scattering



Incoherent: featureless (see C)

Coherent: sensitive to inter-particle correlations

- A Protein-protein
- B Intramolec helix-helix
- C Solvent-solvent



Neutron and Electron Spins

Recall *Master Formula* and magnetic interaction potential terms

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

$$\langle \mathbf{k}_f|V|\mathbf{k}_i\rangle = 8\pi(\gamma\mu_N\mu_B)\sigma\cdot\mathbf{D}_\perp(\mathbf{k}_i - \mathbf{k}_f)$$

$$\mathbf{D}_\perp(\mathbf{Q}) = \sum_j \left(\hat{\mathbf{Q}}\times\left(\mathbf{s}_j\times\hat{\mathbf{Q}}\right) + \frac{i}{\hbar Q}\mathbf{p}\times\hat{\mathbf{Q}}\right)e^{i\mathbf{Q}\cdot\mathbf{r}_j}$$

Matrix elements relative to spin state of neutron

non-spin-flip $\langle\uparrow|\sigma\cdot\mathbf{D}_\perp|\uparrow\rangle = D_{\perp z},$

$\langle\downarrow|\sigma\cdot\mathbf{D}_\perp|\downarrow\rangle = -D_{\perp z},$

spin-flip $\langle\downarrow|\sigma\cdot\mathbf{D}_\perp|\downarrow\rangle = D_{\perp x} + iD_{\perp y},$

$\langle\uparrow|\sigma\cdot\mathbf{D}_\perp|\downarrow\rangle = D_{\perp x} - iD_{\perp y}.$

Note underlying symmetries (spherical tensors)

Can use these to pick out different components.

Non-spin-flip DDCS

$\langle\uparrow|\sigma\cdot\mathbf{D}_\perp|\uparrow\rangle = D_{\perp z}$ implies $\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N_m}\left(\frac{k_f}{k_i}\right)(\gamma r_0)^2 \sum_{\tau_i} p_{\tau_i} \sum_{\tau_f} |\langle\tau_f|D_{\perp z}|\tau_i\rangle|^2 \delta(E + E_{\tau_i} - E_{\tau_f})$

For a paramagnetic solid, can integrate over energy

$$\left(\frac{d\sigma}{d\Omega}\right)_{nsf} = \frac{1}{N_m}(\gamma r_0)^2 \langle D^+_{\perp z} D_{\perp z}\rangle \Rightarrow \left(\frac{d\sigma}{d\Omega}\right)_{nsf} = \frac{1}{N_m}(\gamma r_0)^2 \sum_j |f_j(Q)|^2 \frac{g_j^2}{12} S_j(S_j+1)\left(1-\hat{Q}_z^2\right)$$

Which also implies that $\left(\frac{d\sigma}{d\Omega}\right)_{sf} = \frac{1}{N_m}(\gamma r_0)^2 \sum_j |f_j(Q)|^2 \frac{g_j^2}{12} S_j(S_j+1)\left(1+\hat{Q}_z^2\right)$

For **Q** parallel to direction of neutron spin, ALL SCATTERING IS SPIN FLIP

For **Q** perpendicular, BOTH CHANNELS ARE EQUAL

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Probing Magnetic Order with Polarized Neutrons

Look at coherent elastic scattering from a collection of magnetic ions

Allow for BOTH nuclear and magnetic scattering. Interaction potential terms look like:

$$\langle\mathbf{k}_f|V|\mathbf{k}_i\rangle_{mag} = \frac{2\pi\hbar^2}{m_n}(\gamma r_0)\sigma\cdot\mathbf{D}_\perp = \frac{2\pi\hbar^2}{m_n}\sum_j \sigma\cdot\mathbf{C}_j e^{i\mathbf{Q}\cdot\mathbf{R}_j} \quad \text{with} \quad \mathbf{C}_j = (\gamma r_0) f_j(\mathbf{Q})\left(\hat{\mathbf{Q}}\times\mu_j\times\hat{\mathbf{Q}}\right)$$

$$\langle\mathbf{k}_f|V|\mathbf{k}_i\rangle_{nucl} = -\frac{2\pi\hbar^2}{m_n}\sum_j \hat{b}_j e^{i\mathbf{Q}\cdot\mathbf{R}_j} \quad \text{with} \quad \hat{b}_j = \bar{b}_j + \frac{1}{2} b_{Nj}(\sigma\cdot\mathbf{I}_j)$$

With cross section

$$\left(\frac{d^2\sigma}{d\Omega dE_f}\right)_{\sigma_i\tau_i\to\sigma_f\tau_f} = \frac{1}{N_m}\left(\frac{k_f}{k_i}\right)\left|\left\langle\sigma_f\tau_f\left|\sum_j(\hat{b}_j + \sigma\cdot\mathbf{C}_j)e^{i\mathbf{Q}\cdot\mathbf{R}_j}\right|\sigma_i\tau_i\right\rangle\right|^2 \delta(E + E_{\tau_i} - E_{\tau_f})$$

For coherent elastic events

$$\left(\frac{d\sigma}{d\Omega}\right)_{\sigma_i\to\sigma_f} = \frac{(2\pi)^3}{v_0}\sum_{\boldsymbol{\tau}} \left|\langle\sigma_f|\hat{F}(\boldsymbol{\tau})|\sigma_i\rangle\right|^2 \delta(\mathbf{Q}-\boldsymbol{\tau}) \qquad \hat{F}(\boldsymbol{\tau}) = \sum_d (\bar{b}_d + \sigma\cdot\mathbf{C}_d) e^{-W_d} e^{i\boldsymbol{\tau}\cdot\mathbf{d}}$$

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Polarization Analysis, Nuclear and Magnetic

Combined nuclear-magnetic form factor $\hat{F}(\boldsymbol{\tau}) = \sum_d (\bar{b}_d + \sigma\cdot\mathbf{C}_d)\mathrm{e}^{-W_d}\mathrm{e}^{\mathrm{i}\boldsymbol{\tau}\cdot\mathbf{d}}$

And for coherent scattering (remenber *nsf* only):

$$\begin{aligned}
\langle\uparrow|\hat{F}|\rangle\uparrow &= F_\mathrm{N} - F_{\mathrm{M}\perp z},\\
\langle\downarrow|\hat{F}|\rangle\downarrow &= F_\mathrm{N} + F_{\mathrm{M}\perp z},\\
\langle\downarrow|\hat{F}|\rangle\uparrow &= -(F_{\mathrm{M}\perp x} + iF_{\mathrm{M}\perp y}),\\
\langle\uparrow|\hat{F}|\rangle\downarrow &= -(F_{\mathrm{M}\perp x} - iF_{\mathrm{M}\perp y}),
\end{aligned}$$

Nuclear form factor $F(\boldsymbol{\tau}) = \sum_\mathbf{d} \bar{b}_\mathbf{d}\mathrm{e}^{-W_\mathbf{d}(\boldsymbol{\tau})}\mathrm{e}^{\mathrm{i}\boldsymbol{\tau}\cdot\mathbf{d}}$

Magnetic form factor $\mathbf{F}_\mathrm{M}(\mathbf{Q}) = |\gamma r_0| \sum_d f_d(\mathbf{Q})\langle\mu_d\rangle\mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{d}}\mathrm{e}^{-W_d(\mathbf{Q})}$

In essence, need to consider a total of three vectors:

- Neutron-spin quantization vector.
- Magnetization of system ($\mathbf{F}_\mathrm{M}$)
- Wave-vector Q (governs orientation of transv. comp of $\mathbf{F}_\mathrm{M}$)

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Common Geometries for Polarized-neutron Exps

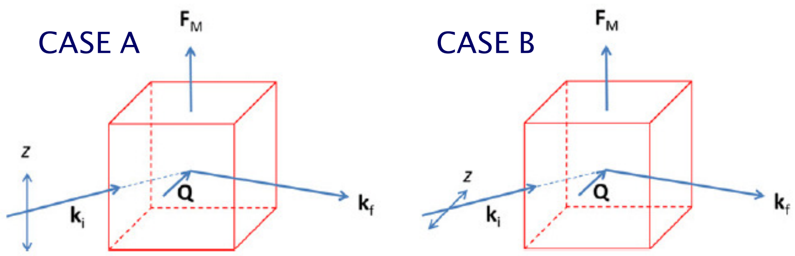
CASE A: z parallel/perpendicular to F/Q: zero spin-flip channel, and flipping ratio (neutron parallel/antiparallel to F) given by

$$r = \left(\frac{F_\mathrm{N} - F_{\mathrm{M}\perp}}{F_\mathrm{N} + F_{\mathrm{M}\perp}}\right)^2 \approx 1 - \frac{4F_{\mathrm{M}\perp}}{F_\mathrm{N}}$$

CASE B: z parallel Q, such that transverse component of F becomes perpendicular to z.

Spin-flip: magnetic
Non-spin-flip: nuclear

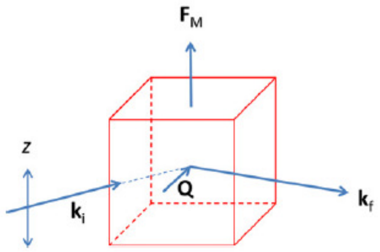
$$\begin{aligned}
\langle\uparrow|\hat{F}|\rangle\uparrow &= F_\mathrm{N} - F_{\mathrm{M}\perp z},\\
\langle\downarrow|\hat{F}|\rangle\downarrow &= F_\mathrm{N} + F_{\mathrm{M}\perp z},\\
\langle\downarrow|\hat{F}|\rangle\uparrow &= -(F_{\mathrm{M}\perp x} + iF_{\mathrm{M}\perp y}),\\
\langle\uparrow|\hat{F}|\rangle\downarrow &= -(F_{\mathrm{M}\perp x} - iF_{\mathrm{M}\perp y}),
\end{aligned}$$



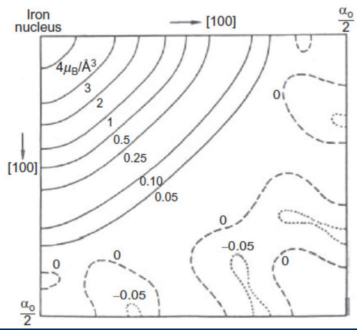
Ferromagnets

- Same nuclear & magnetic unit cells: Bragg peaks in same place.
- Magnetic structure determination:
  - Comparison of data above and below ordering (Curie) temperature.
  - Apply saturating magnetic field along Q, to remove magnetic scattering since transverse component of $\mathbf{F}_M$ becomes zero.
  - Polarized diffraction from single crystals such that

$\mathbf{F}_M \| z \perp \boldsymbol{\tau}$ *such that* $\mathbf{F}_{M\perp} \approx \mathbf{F}_M$ *and measure flipping ratio* $1 - \dfrac{4F_{M\perp}}{F_N}$

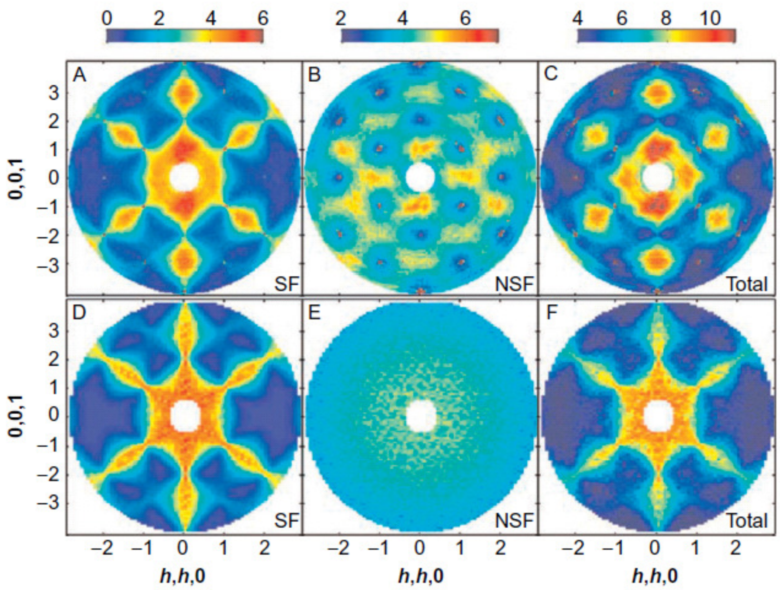


Fourier transform of $\mathbf{F}_M$ gives spin density in unit cell



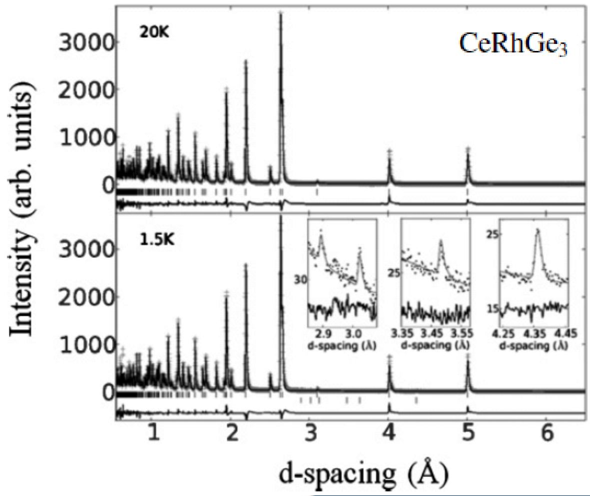
Example: Polarized Neutrons

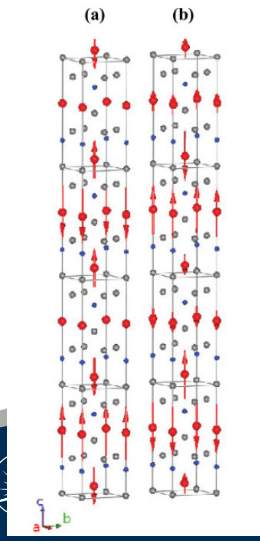
Spin-ice $Ho_2Ti_2O_7$



Antiferromagnets

- Distinct nuclear and magnetic lattices, leading to the presence of purely magnetic Bragg peaks.
- Magnetic structure determination: most antiferromagnetic structures have been determined with unpolarized neutron beams (and often with powder samples)





Nuclear 'Magnetism'

More subtle that electron magnetism: $\mu_N = (m_e/m_p)\mu_B$

Recall interaction with neutron implies: $\mathbf{J} = \mathbf{I} + \frac{1}{2}\sigma$

Two distinct angular-momentum states: $J = I \pm \frac{1}{2}$

And a spin-dependent scattering length: $\hat{b} = \bar{b} + \frac{1}{2} b_N \sigma \cdot \mathbf{I}$

where
$$\bar{b} = \frac{1}{(2I+1)}[(I+1)b^+ + Ib^-],$$
$$b_N = \frac{2}{(2I+1)}[b^+ - b^-],$$

Why Should We Bother?

Alignment of specific nuclear spins in a sample modulates their neutron response. Possibility to extend isotopic substitution experiments to many elements, without the need for isotopic substitution.

The neutronic response of some important species like H_2, CH_4, CH_3 groups rely on the relative alignment of nuclear spins.

Major difficulties: achieving macroscopic nuclear polarizations (at least of a few %) is not a trivial task.

$$\mu_{\mathrm{N}} = (m_{\mathrm{e}}/m_{\mathrm{p}})\mu_{\mathrm{B}}$$

Typically requires high external fields and very low Ts

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Nuclear-spin Correlations

General expression for DCS
$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{1}{N}\left(\sum_j \left\langle |\hat{b}_j|^2 \right\rangle + \sum_{j \neq j'} \left\langle \hat{b}_j \hat{b}_{j'}^{+} \right\rangle \mathrm{e}^{-\mathrm{i}\mathbf{Q}\cdot(\mathbf{R}_j - \mathbf{R}_{j'})}\right)$$

with $\hat{b} = \bar{b} + \frac{1}{2} b_{\mathrm{N}} \sigma \cdot \mathbf{I}$

Write explicitly in terms of AM operators for neutron and nuclei

$$|\hat{b}_j|^2 = \bar{b}^2 + \bar{b} b_{\mathrm{N}} \sigma \cdot \mathbf{I}_j + \frac{1}{4} b_{\mathrm{N}}^2 \left[I(I+1) - \sigma \cdot \mathbf{I}_j \right]$$

$$\hat{b}_j \hat{b}_{j'}^{+} = \bar{b}^2 + \frac{1}{2} \bar{b} b_{\mathrm{N}} \left[\sigma \cdot \mathbf{I}_j + \sigma \cdot \mathbf{I}_{j'} \right] + \frac{1}{4} b_{\mathrm{N}}^2 \left[\mathbf{I}_j \cdot \mathbf{I}_{j'} + i\sigma \cdot (\mathbf{I}_j \times \mathbf{I}_{j'}) \right]$$

This is general expression for spin-dependent DCS

Note that both terms have an explicit dependence on nuclear-spin orientation.

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Nuclear-spin Correlations

Assume no correlation between spin-dependent scattering amplitude of a particle pair and their relative position

$$\frac{d\sigma}{d\Omega} = \frac{1}{N}\left(\sum_j \left\langle |\hat{b}_j|^2 \right\rangle + \sum_{j\neq j'} \left\langle \hat{b}_j \hat{b}_{j'}^+ \right\rangle_{j\neq j'} e^{-i\mathbf{Q}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})}\right)$$

i.e., a single b-pair per particle pair

Define polarization of target (P) and neutron (p) such that correlations are

$$\langle \mathbf{I}_j \cdot \mathbf{I}_{j'} \rangle = \langle \mathbf{I}_j \rangle \cdot \langle \mathbf{I}_{j'} \rangle = P^2 I^2, \quad \langle \mathbf{I}_j \times \mathbf{I}_{j'} \rangle = 0, \quad \langle \sigma \cdot \mathbf{I}_j \rangle = pPI$$

Then $\left\langle |\hat{b}_j|^2 \right\rangle = \overline{b}^2 + \overline{b} b_N pPI + \frac{1}{4} b_N^2 [I(I+1) - pPI]$ and $\left\langle \hat{b}_j \hat{b}_{j'}^+ \right\rangle_{i\neq j} = \overline{b}^2 + \overline{b} b_N pPI + \frac{1}{4} b_N^2 P^2 I^2$

And DCS

$$\frac{d\sigma}{d\Omega} = \frac{1}{4} b_N^2 [I(I+1) - pPI - P^2 I^2] + \left(\overline{b}^2 + \overline{b} b_N pPI + \frac{1}{4} b_N^2 P^2 I^2\right) \frac{1}{N} \sum_{j,j'} e^{-i\mathbf{Q}\cdot(\mathbf{R}_j - \mathbf{R}_{j'})}$$

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Nuclear-spin Correlations

Take one atom per unit cell such that $\frac{1}{N}\sum_{j,j'} e^{-i\mathbf{Q}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})} = \sum_j e^{-i\mathbf{Q}\cdot\mathbf{R}_j}$

And DCS then simplifies to

$$\frac{d\sigma}{d\Omega} = \frac{1}{4} b_N^2 [I(I+1) - pPI - P^2 I^2] + \left(\overline{b}^2 + \overline{b} b_N pPI + \frac{1}{4} b_N^2 P^2 I^2\right) \sum_j e^{-i\mathbf{Q}\cdot\mathbf{R}_j}$$

In terms of scattering cross sections

$$\frac{d\sigma}{d\Omega} = \frac{1}{4\pi}\left(\sigma_i + \sigma_c \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}} \delta(\mathbf{Q} - \boldsymbol{\tau})\right)$$

with $\sigma_i = \pi b_N^2 [I(I+1) - pPI - P^2 I^2]$

$$\sigma_c = 4\pi \left(\overline{b}^2 + \overline{b} b_N pPI + \frac{1}{4} b_N^2 P^2 I^2\right)$$

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Nuclear-spin Correlations – Consequences

For an unpolarized target (P=0), we can write the scattering cross sections as

$$\sigma_i = \pi I(I+1) b_N^2 = 4\pi \frac{I(I+1)}{(2I+1)^2}(b^+ - b^-)^2$$

$$\sigma_c = 4\pi \bar{b}^2 = 4\pi \frac{1}{(2I+1)^2}[(I+1)b^+ + Ib^-]^2$$

as we have presented earlier for polarized neutrons

For a fully polarized target (P=1), incoherent scattering will disappear when both P and p are maximally aligned along the same quantization axis

$$\sigma_i = \pi b_N^2 \left[I(I+1) - pPI - P^2 I^2 \right]$$

And the coherent cross section is maximal

$$\sigma_c = 4\pi \left(\bar{b}^2 + \bar{b} b_N pPI + \frac{1}{4} b_N^2 P^2 I^2 \right)$$

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Nuclear-spin Correlations – General Case

Non-zero correlations between spin orientation and relative position

$$\langle \mathbf{I}_j \cdot \mathbf{I}_{j'} \rangle = \langle \mathbf{I}_j \rangle \cdot \langle \mathbf{I}_{j'} \rangle = P^2 I^2 \quad \Rightarrow \quad \langle \mathbf{I}_d \cdot \mathbf{I}_{d'} \rangle = \langle \mathbf{I}_d \rangle \cdot \langle \mathbf{I}_{d'} \rangle = P_d P_{d'} I^2$$

DCS generalizes to $\frac{d\sigma}{d\Omega} = \frac{1}{4\pi}\left(\sigma_i + \sigma_c \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}} |F(\boldsymbol{\tau})|^2 \delta(\mathbf{Q} - \boldsymbol{\tau}) \right)$

with $\sigma_i = \pi b_N^2 \sum_d \left[I(I+1) - pP_d I - {P_d}^2 I^2 \right]$

$$|F(\boldsymbol{\tau})|^2 = \sum_{d,d'} \left[\bar{b}^2 + \frac{1}{2} \bar{b} b_N p (P_d + P_{d'}) I + \frac{1}{4} b_N^2 P_d P_{d'} I^2 \right] e^{-i\mathbf{Q}\cdot(\mathbf{d}-\mathbf{d}')}$$

Nuclear ‘ferromagnet’: cross sections modulated by P’s, no new peaks.

Nuclear ‘antiferromagnet’: cross sections modulated by P’s, new peaks with DCS

$$\left(\frac{d\sigma}{d\Omega} \right)_m = \frac{(2\pi)^3}{v_m} \frac{1}{4} \sum_{d,d'} b_N^2 P_d P_{d'} I^2 e^{-i\mathbf{Q}\cdot(\mathbf{d}-\mathbf{d}')} \sum_{\boldsymbol{\tau}_m} \delta(\mathbf{Q} - \boldsymbol{\tau}_m)$$

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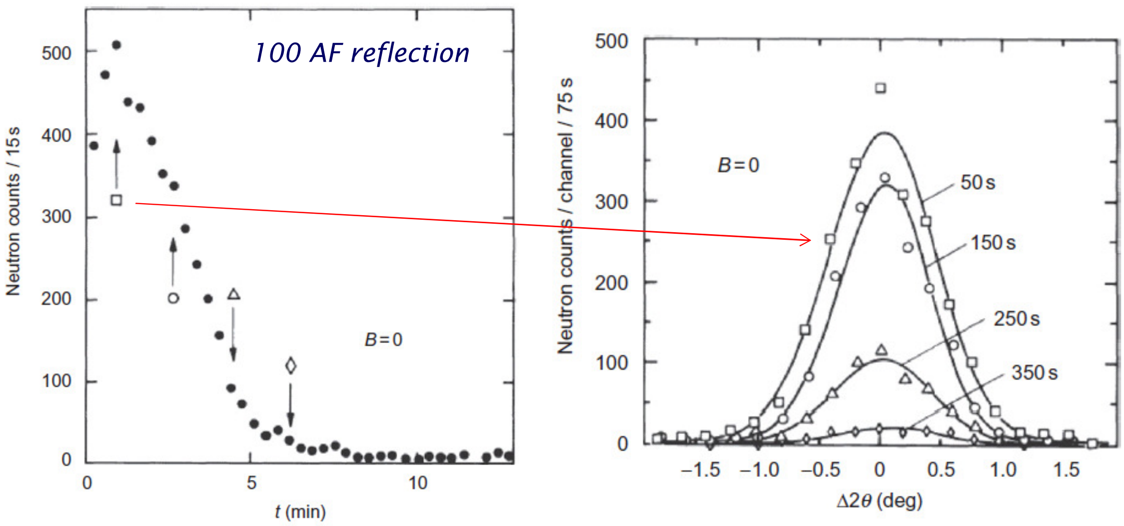
Nuclear Antiferromagnetism in ^{65}Cu



Exciting Prospects, Yet to Be Realized

Chemical Physics Letters 371 (2003) 517–521

NMR-modulated neutron scattering

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Abstract

The possibility of combining NMR with neutron scattering to exploit the spin dependence of the scattering length of a resonant nucleus is investigated. In NMR a π pulse inverts the magnetization of the resonant nuclei; a second π pulse restores the magnetization and the sequence could be repeated. The inverting nuclear spins modulate the scattering of polarized neutrons and could provide information similar to that obtainable through isotope substitution. But unlike isotope substitution, slow conformational changes, like those exhibited by proteins, could in principle be followed using NMR modulation. The modulated intensity will be weak unless enhanced nuclear orientation is used.

Quick Recap

- Lecture I: Fundamentals and Formalism.
- Lecture II: Canonical Solids and Beyond (emphasis on inelastic scattering and chemical/molecular systems).
- Lecture III: Neutron Scattering is All about Spin.

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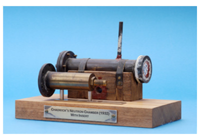
Reactor and Accelerator-based Neutron Sources

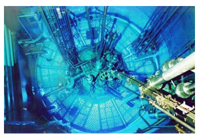
Reactor-based source:

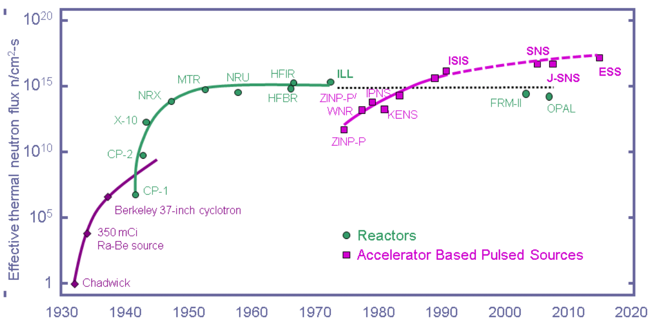
- Neutrons produced by fission reactions
- Continuous neutron beam
- 1 neutron/fission .

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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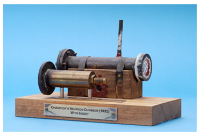
Tomorrow, 82 Years Ago



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 α-particles of polonium emits a radiation of great penetrating power, which has been an absorption coefficient in lead of about 0.3 $(cm)^{-1}$. 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 3×10^9 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 50×10^6 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 α-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 3.2×10^9 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 52×10^6 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 α-particle by the Be^9 nucleus may be supposed to result in the formation of a 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 3×10^9 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 α-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 α-particle by the Be^9 nucleus will form a C^{13} nucleus. The mass defect of C^{13} is known with sufficient accuracy to show that the energy of the quantum emitted in this process cannot be greater than about 14×10^6 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.

The Golden Age of Accelerator-driven Neutron Sources

Operational

Under Construction or Planned

european spallation source

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