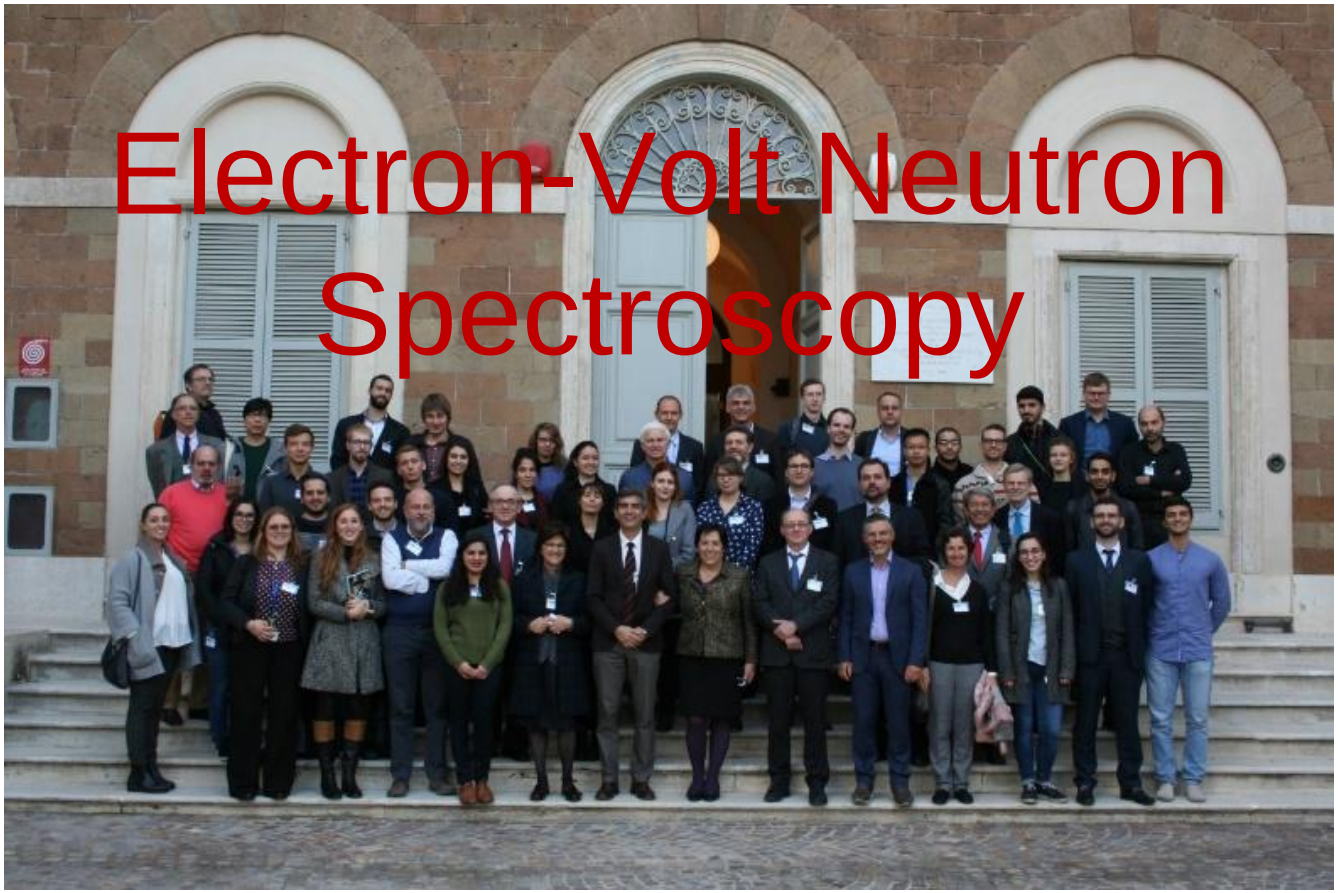
Science & Technology Facilities Council
ISIS

Electron-Volt Neutron Spectroscopy

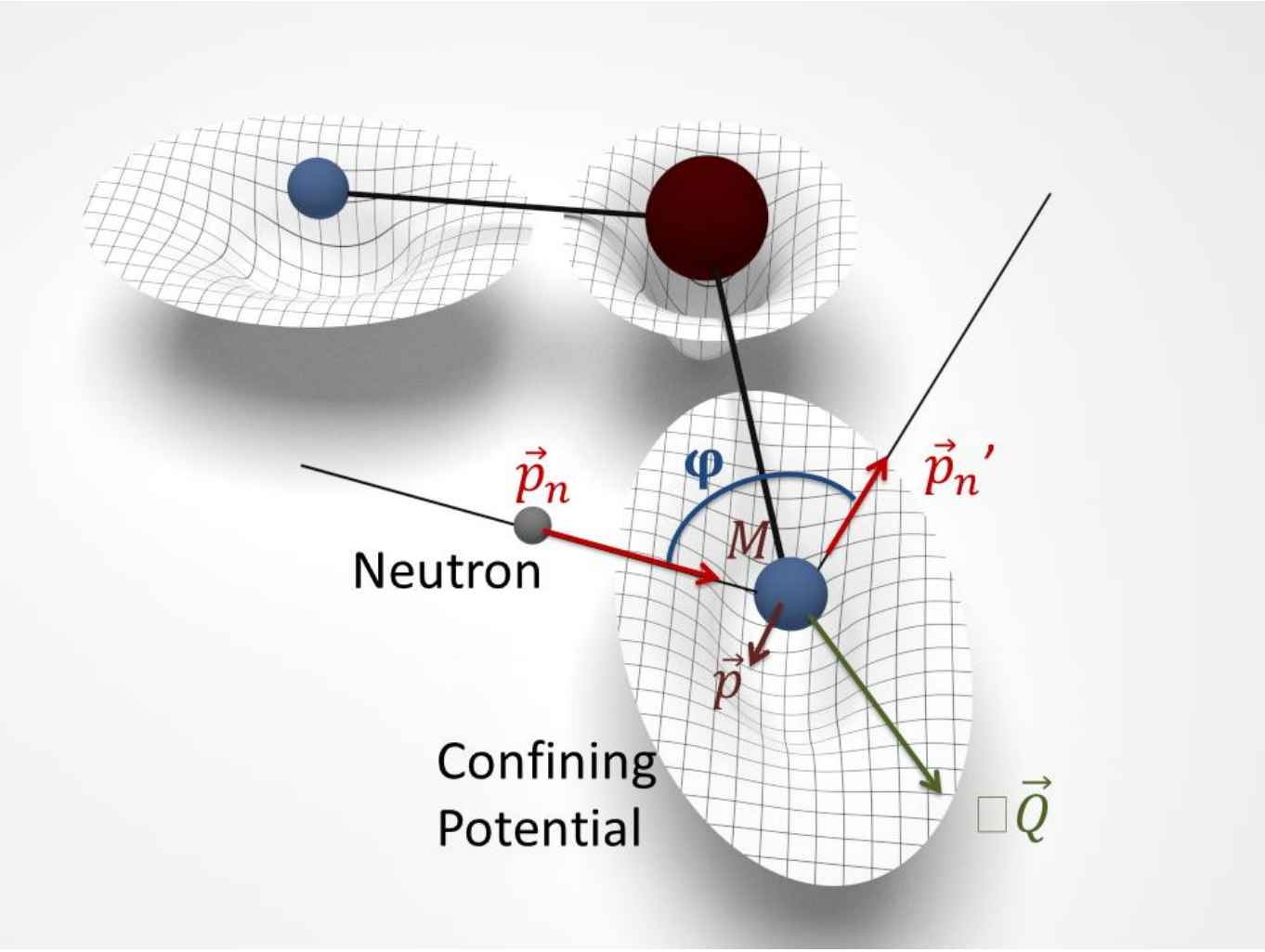


Giovanni Romanelli, Ph.D

Neutrons for Chemistry and Materials Science Applications

Ettore Majorana Foundation and Centre For Scientific Culture – 7th July 2018

Science

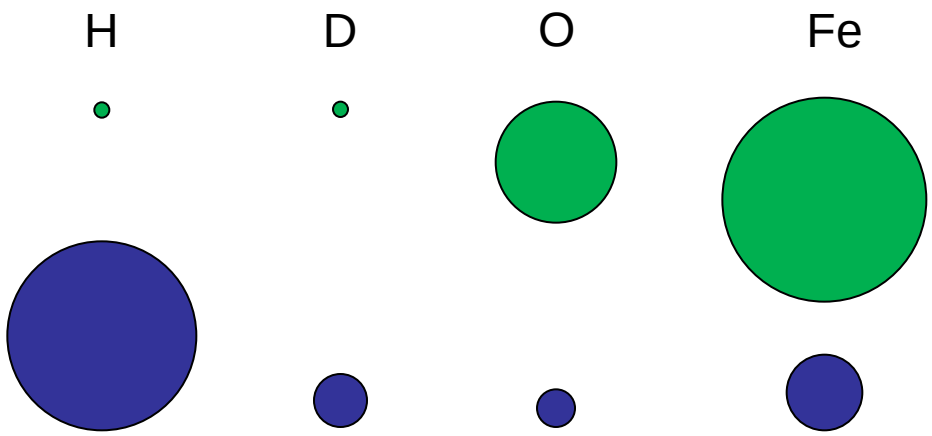


Neutron cross sections

The measured interaction between neutrons and matter is expressed by several parameters, depending on the process and the experimental conditions.

Scattering XS / Nucleus	Coherent [barn]	Incoherent [barn]	Total [barn]
Hydrogen	1.7	80.3	82.0
Deuterium	5.6	2.0	7.6
Oxygen	4.2	0.0	4.2
Iron	11.2	0.4	11.6

Coherent scattering probes global properties, incoherent scattering probes single-particle modes. The total scattering cross section probes everything.



X-ray

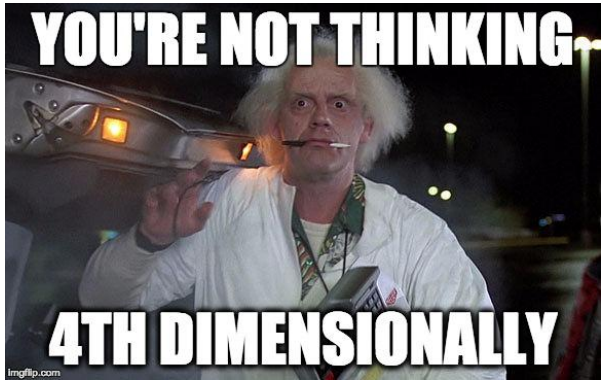
Scattering cross section

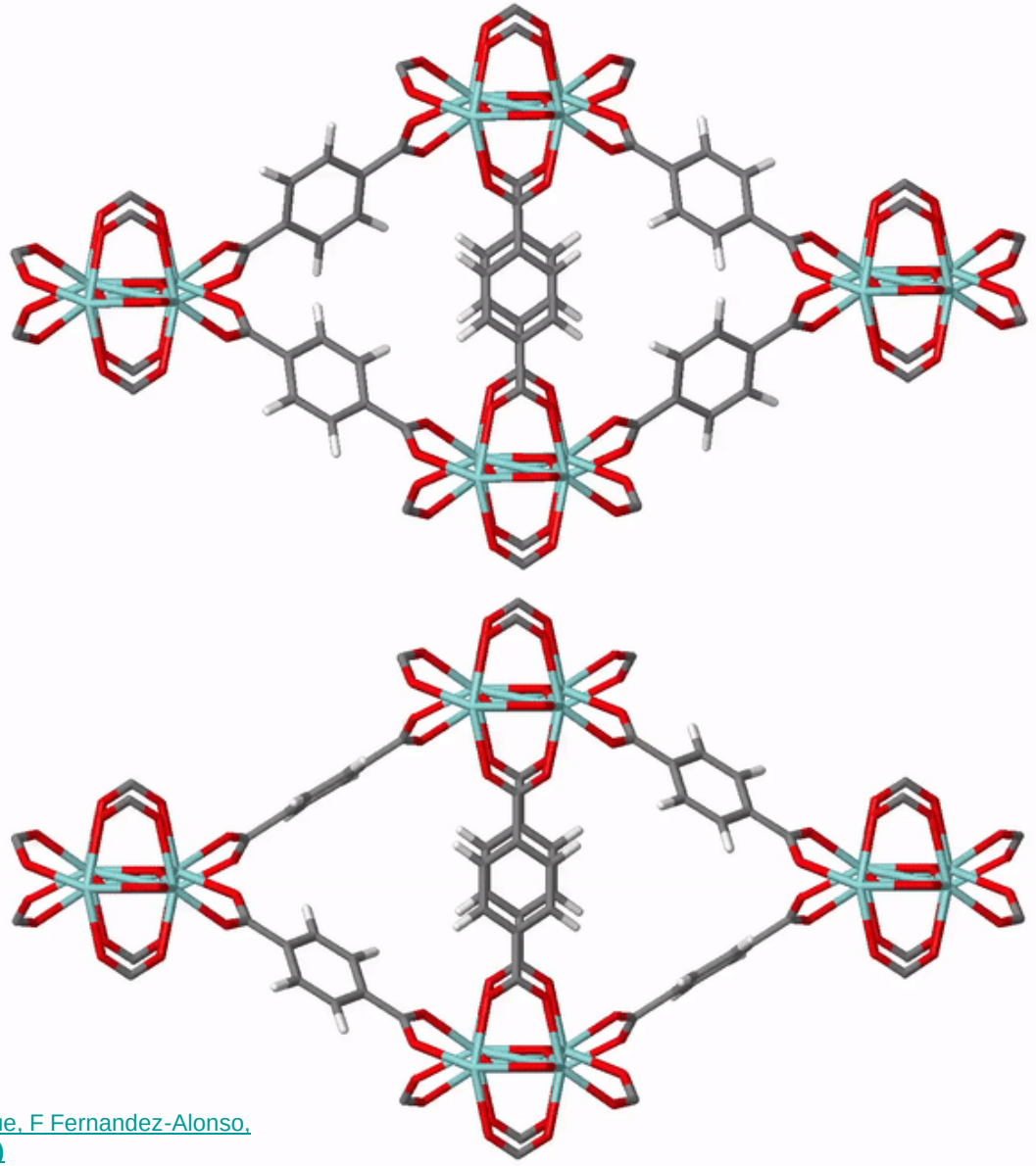
Neutrons

Neutron energy transfer

Neutron scattering techniques can show “where atoms are” and “what atoms do” – Nobel prize to Shull and Brockhouse.

To know “what atoms do” we need to add a new dimensions.

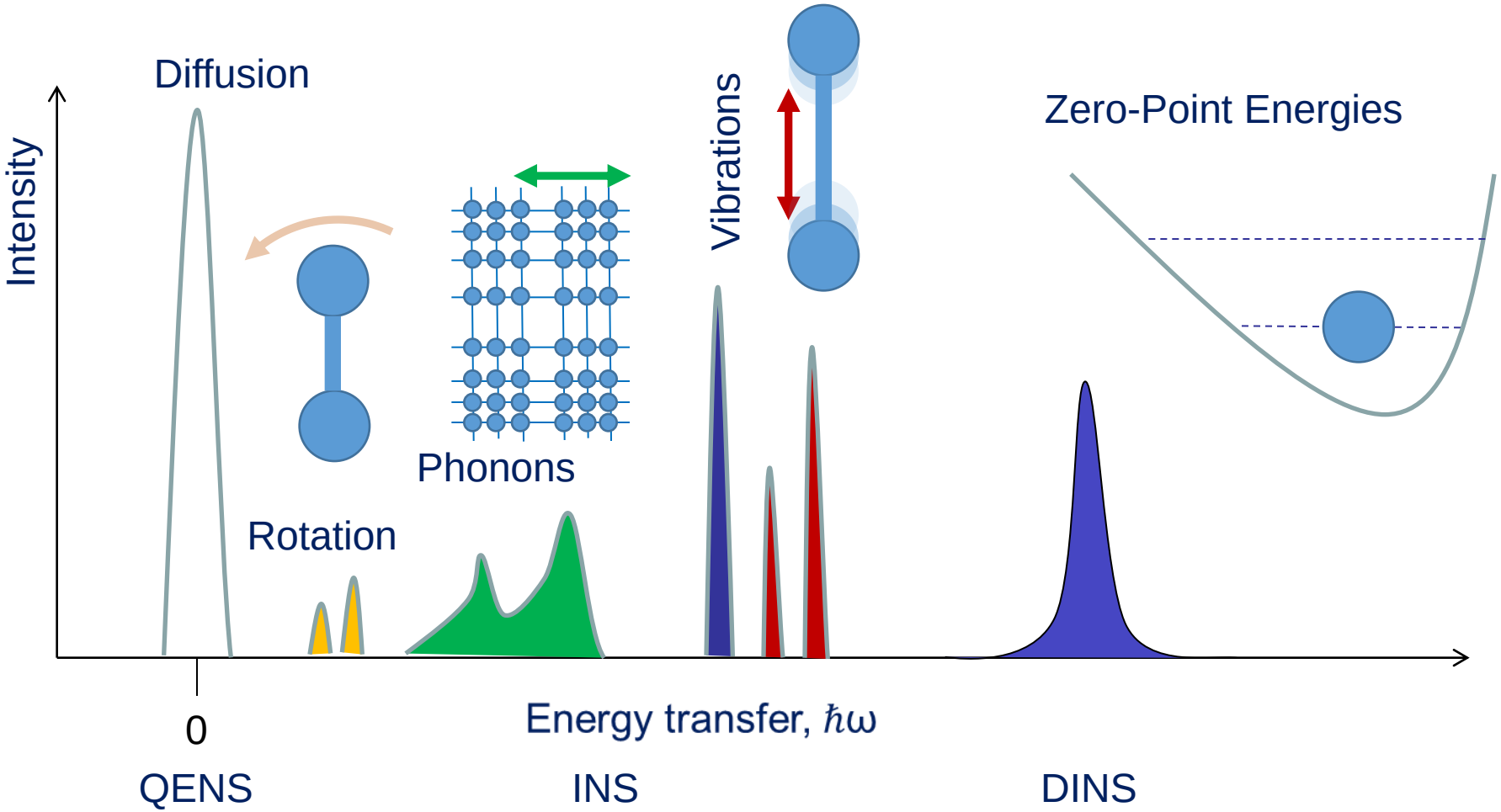




M Ryder, B Van de Voorde, B Civalleri, T Bennett, S Mukhopadhyay, G Cinque, F Fernandez-Alonso, D De Vos, S Rudić, and Jin-Chong Tan; **Phys. Rev. Lett. 118, 255502 (2017)**

Inelastic neutron scattering probes different motions and processes depending on the magnitude of the energy transfer.

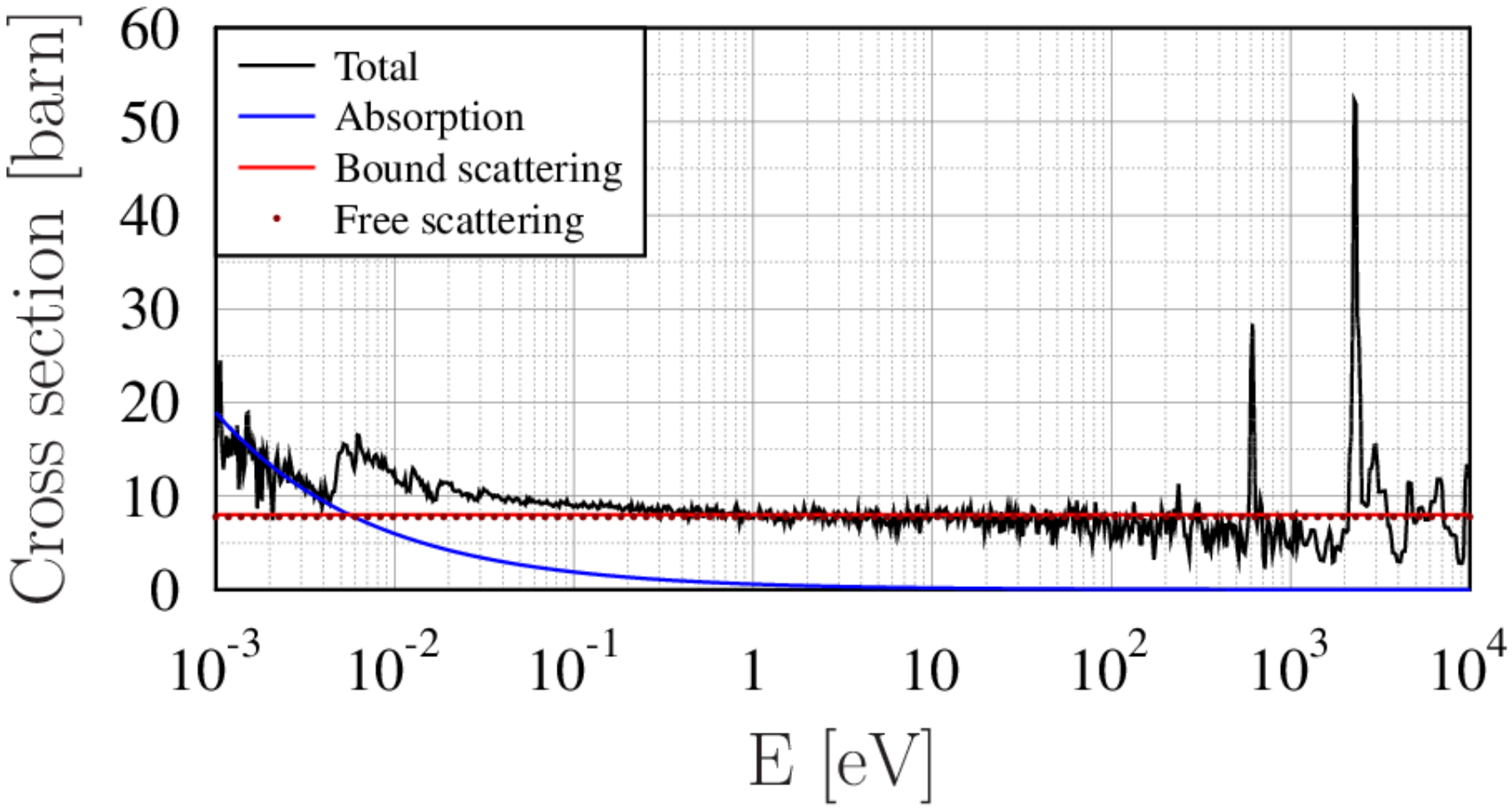
$$Q\Delta x \sim \frac{1}{2} \qquad \omega\Delta t \sim \frac{1}{2}$$



Examples of neutron cross sections

Total cross section of **copper**

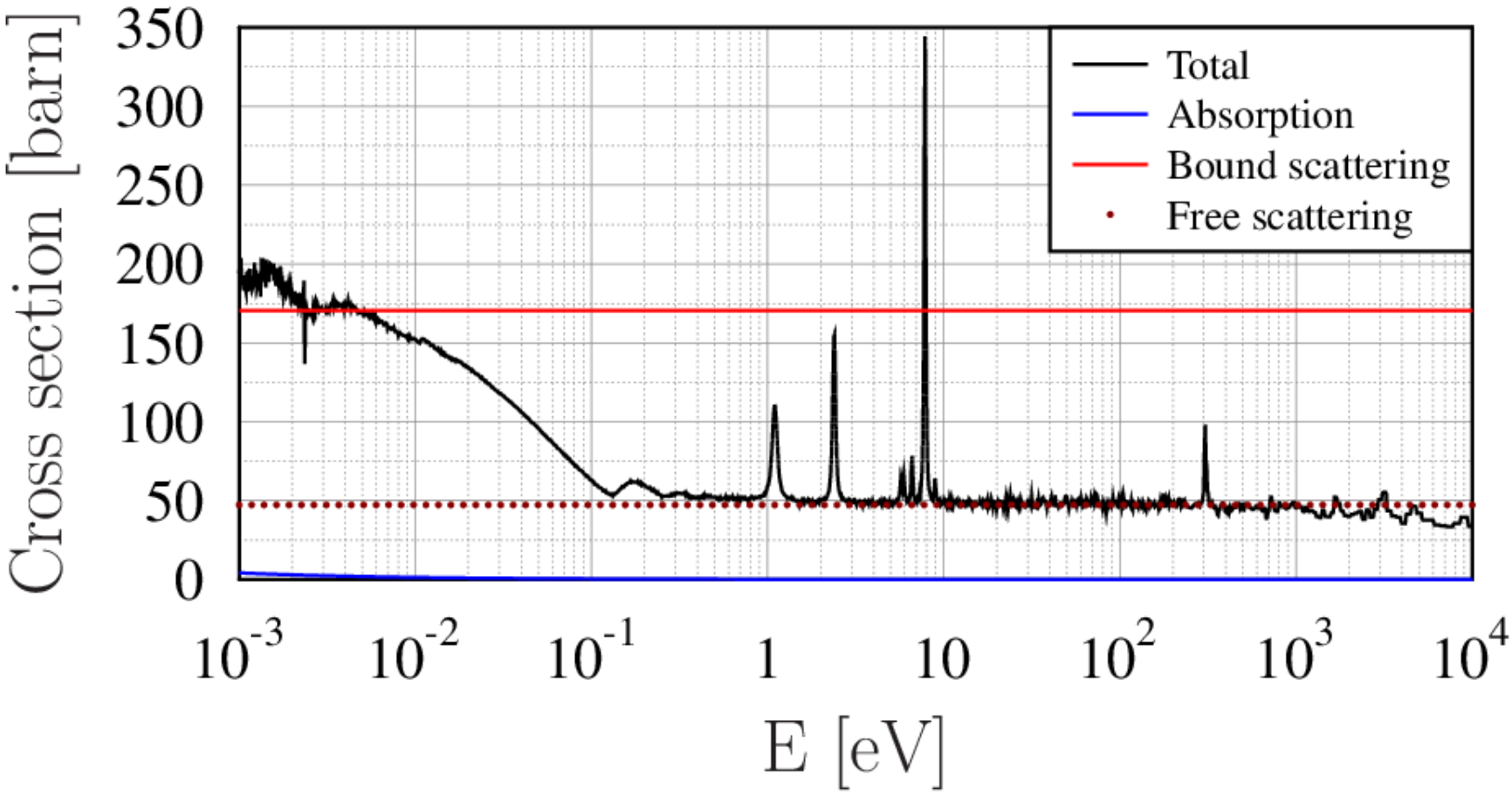
- Bragg edges
- Absorption
- Resonances



Examples of neutron cross sections

Total cross section of **zirconium hydride**

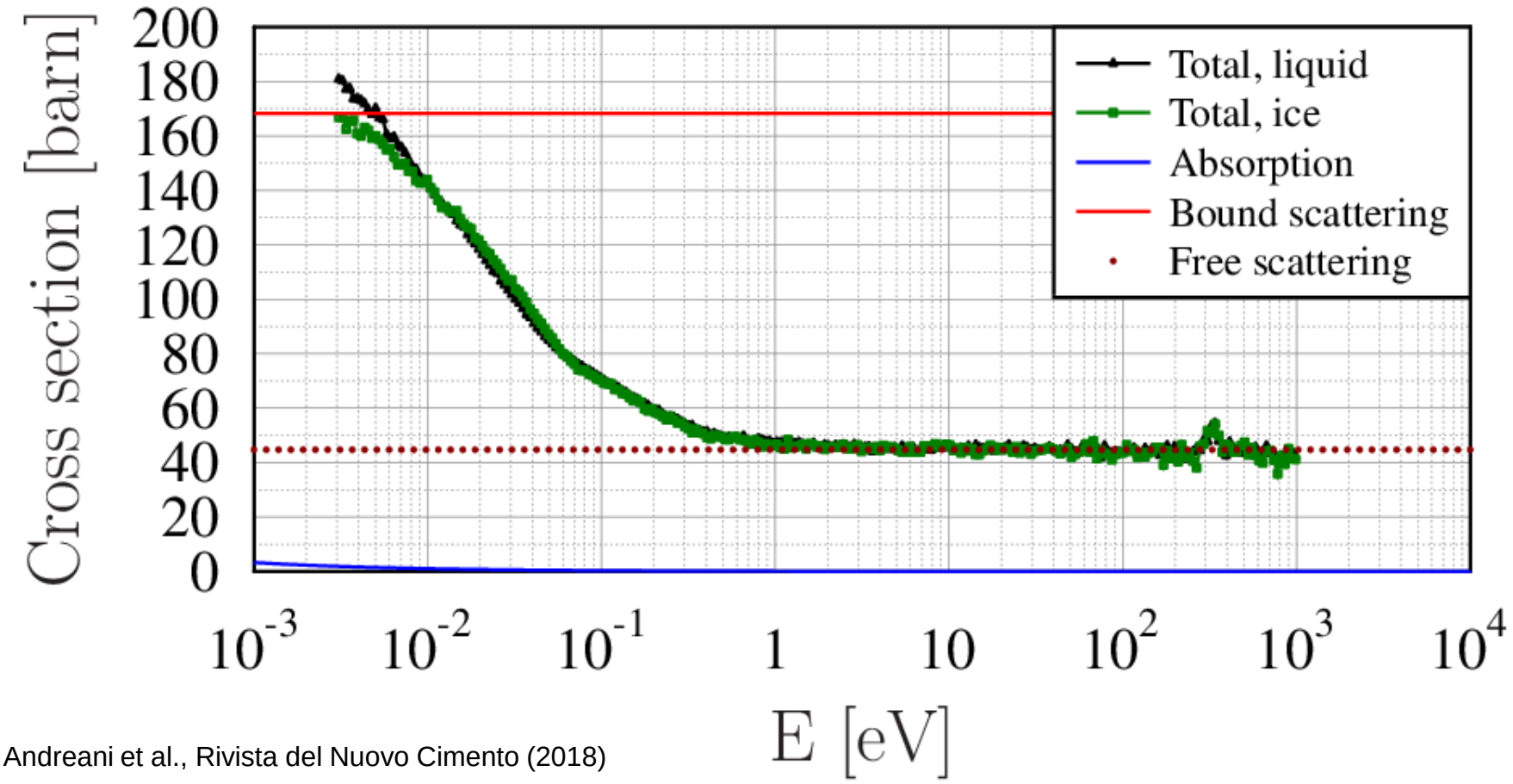
- Phonons
- Resonances (from hafnium impurities)



Examples of neutron cross sections

Total cross section of **dihydrogen monoxide**

- Diffusion
- Vibrations (inter- and intra-molecular)



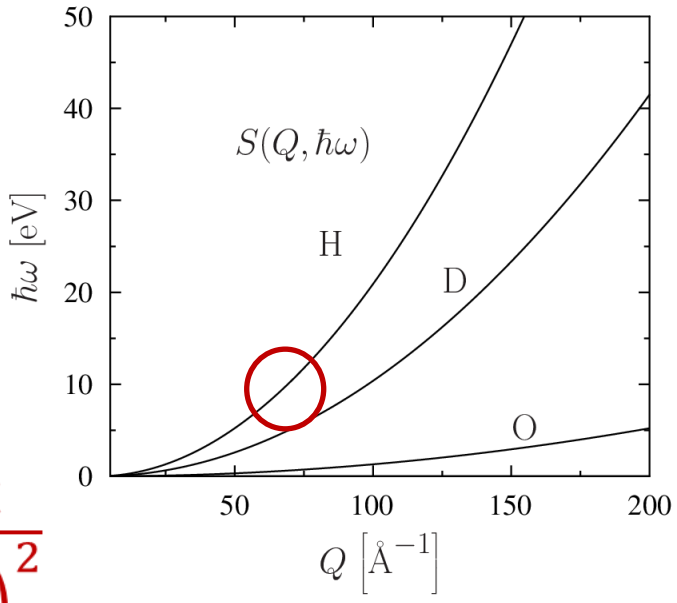
Andreani et al., Rivista del Nuovo Cimento (2018)

Bound and free cross sections

In the **impulse approximation**, struck atoms can recoil freely:

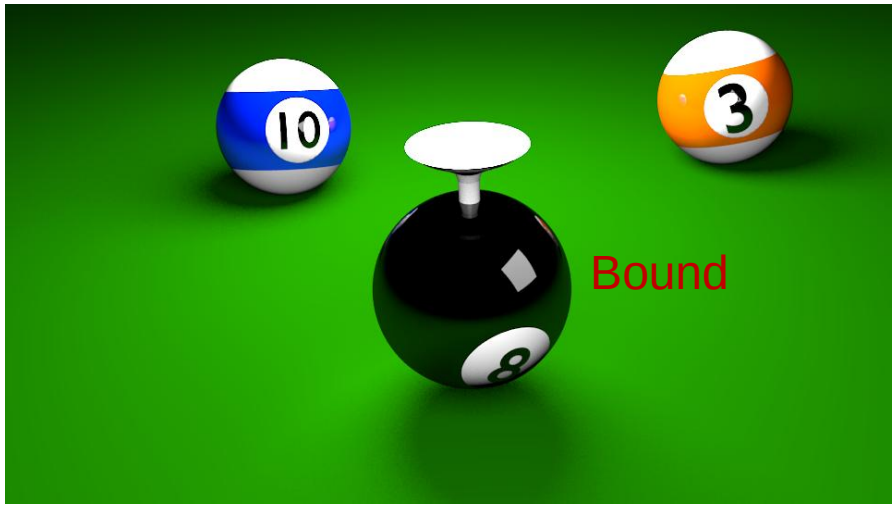
$$E_0 + \frac{p^2}{2M} = E_1 + \frac{p'^2}{2M}$$

$$k_0 + p = k_1 + p'$$



Moving from the lab frame to the centre-of-mass frame, the cross section is reduced by a factor related to the reduced mass.

$$\sigma_{free} = \frac{\sigma_{bound}}{\left(1 + \frac{m}{M}\right)^2}$$

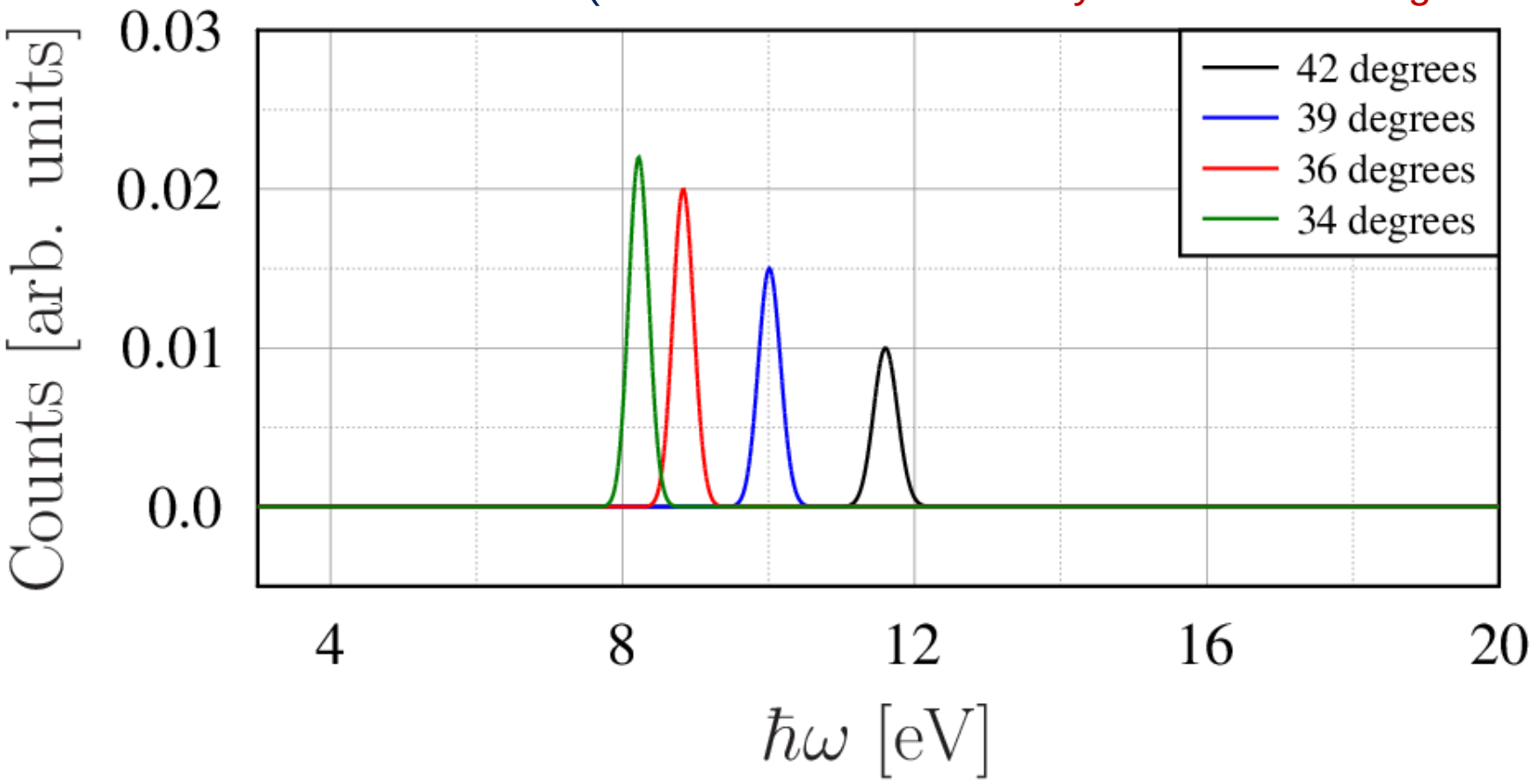


Recoil peaks

$$\langle E_K \rangle = \frac{3}{2} k_B T$$

In measurements at fixed scattering angles (VESUVIO)

- The position of the recoil peak changes with the scattering angle;
- The peak is broadened by the atom kinetic energy (Maxwell-Boltzmann theory of non-interacting atoms?)

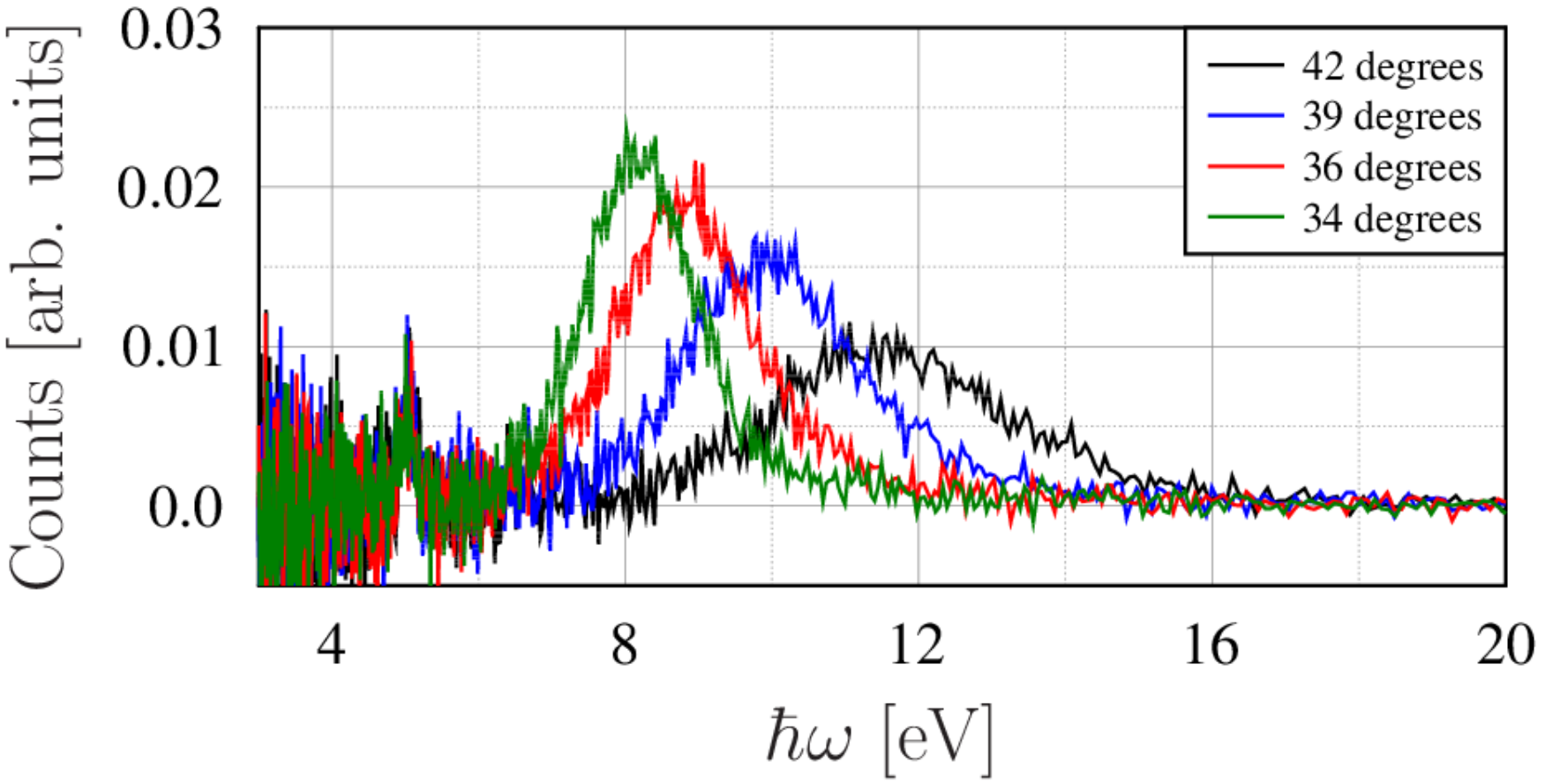


Recoil peaks

In reality, the peaks are broader, especially at very low temperatures (*e.g.*, H_2 at 20K).

$$\langle E_K \rangle \gg \frac{3}{2} k_B T$$

Atoms in condensed-matter systems are affected by **nuclear quantum effects**, *e.g.*, **zero-point energy**.

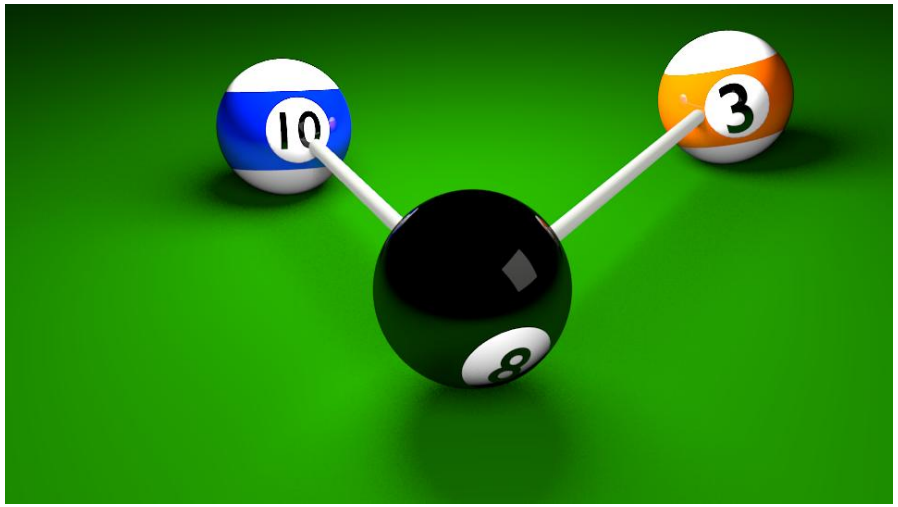


The extra broadening is the result of each atom interacting with its neighbours.

$$k_0 + p = k_1 + p'$$

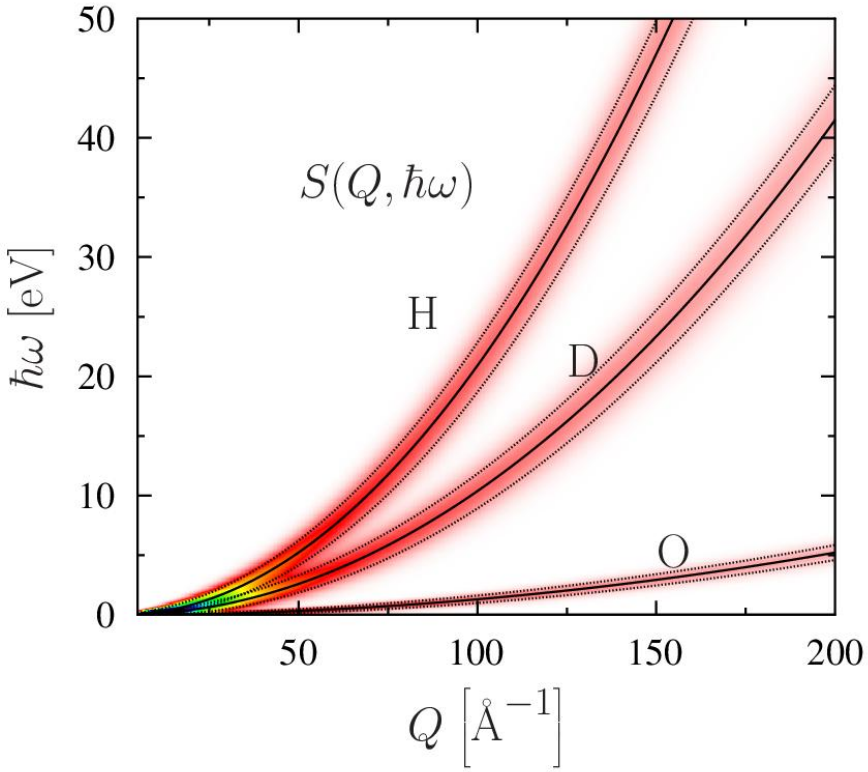
$$E_0 + \frac{p^2}{2M} = E_1 + \frac{p'^2}{2M}$$

Is it safe to exploit the impulse approximation?



Deep inelastic neutron scattering probes the shape of the nuclear momentum distribution.

$$\langle p^2 \rangle = \sigma^2 = \int p^2 n(\boldsymbol{p}) d\boldsymbol{p}$$

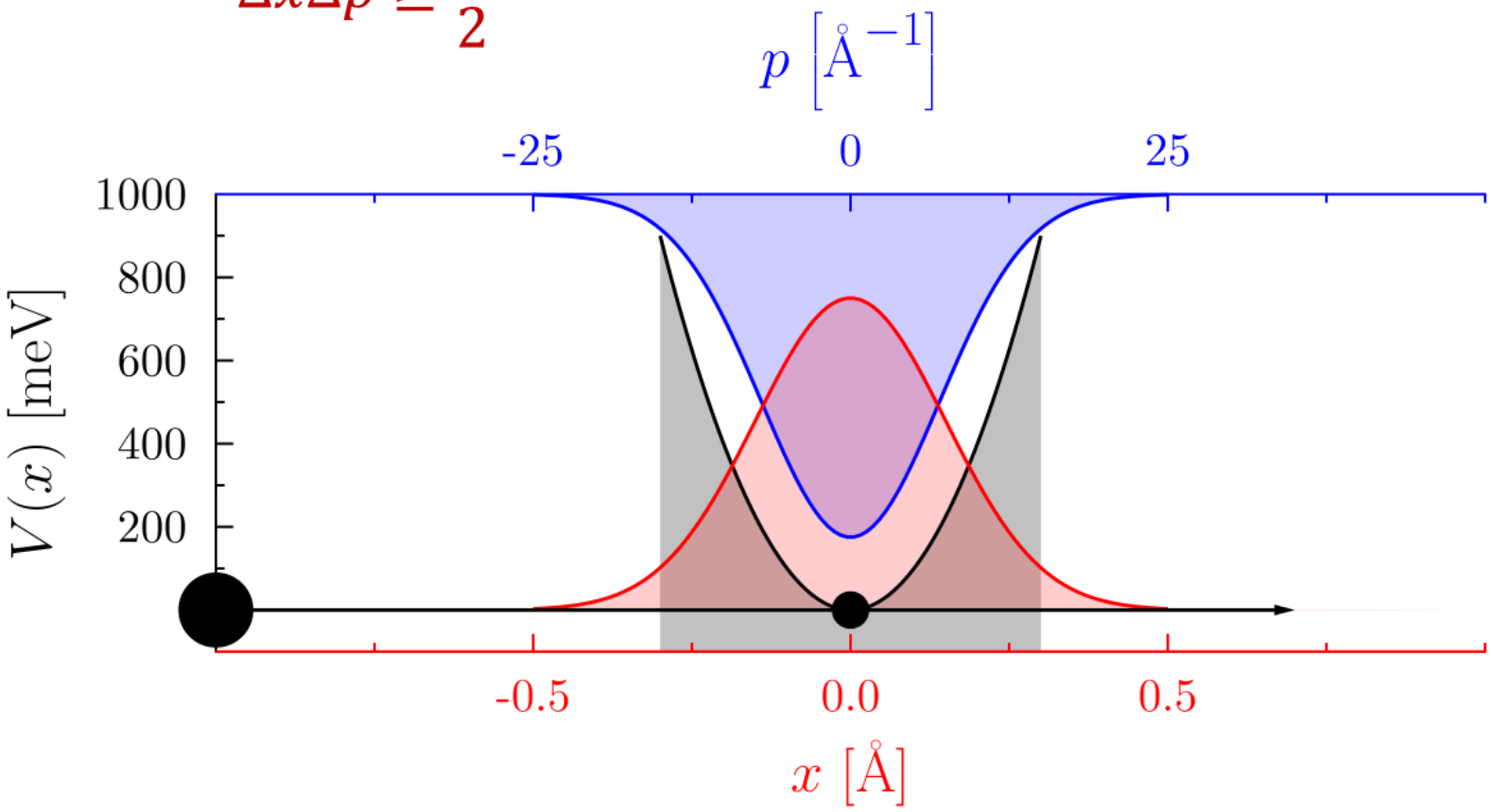


The effect of confinement

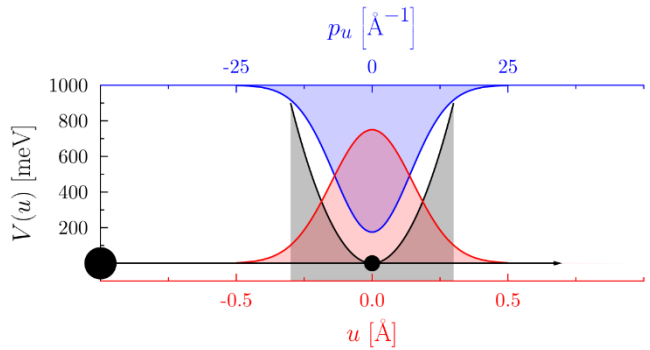
In Schrödinger description of QM, a particle is described by a **wave function**.

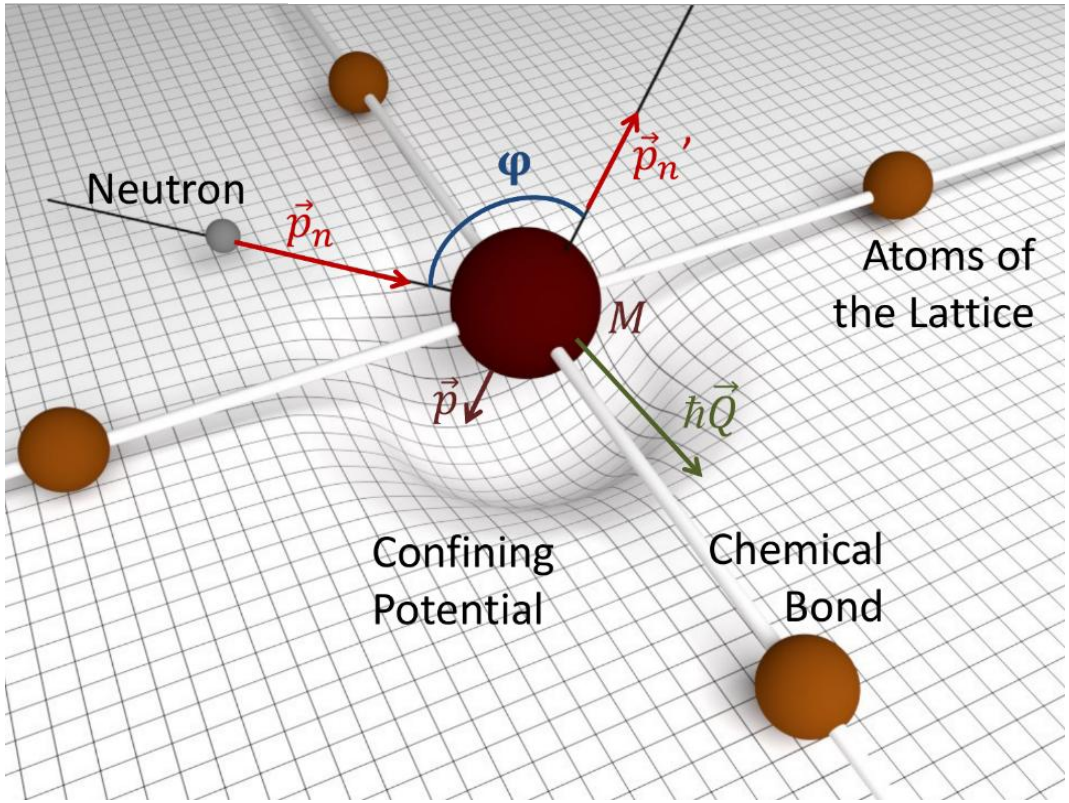
The Fourier transform of the wave function of an atom is related to its **nuclear momentum distribution, n(p)**

$$\Delta x \Delta p \geq \frac{1}{2}$$



Nuclear momentum distributions





In the **incoherent approximation**, we take advantage of the high values of the momentum transfer to study the local single-particle dynamics

$$\Delta t = \frac{1}{\omega} \qquad \Delta x = \frac{1}{Q}$$

In the impulse approximation, we take snapshots of the velocity of the nucleus.

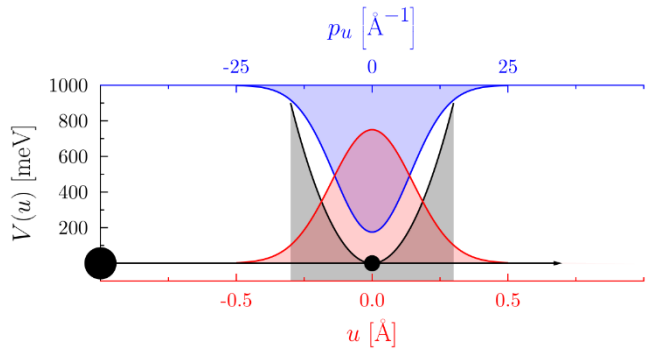
By collecting data from many scattering events, we reconstruct the nuclear momentum distribution.

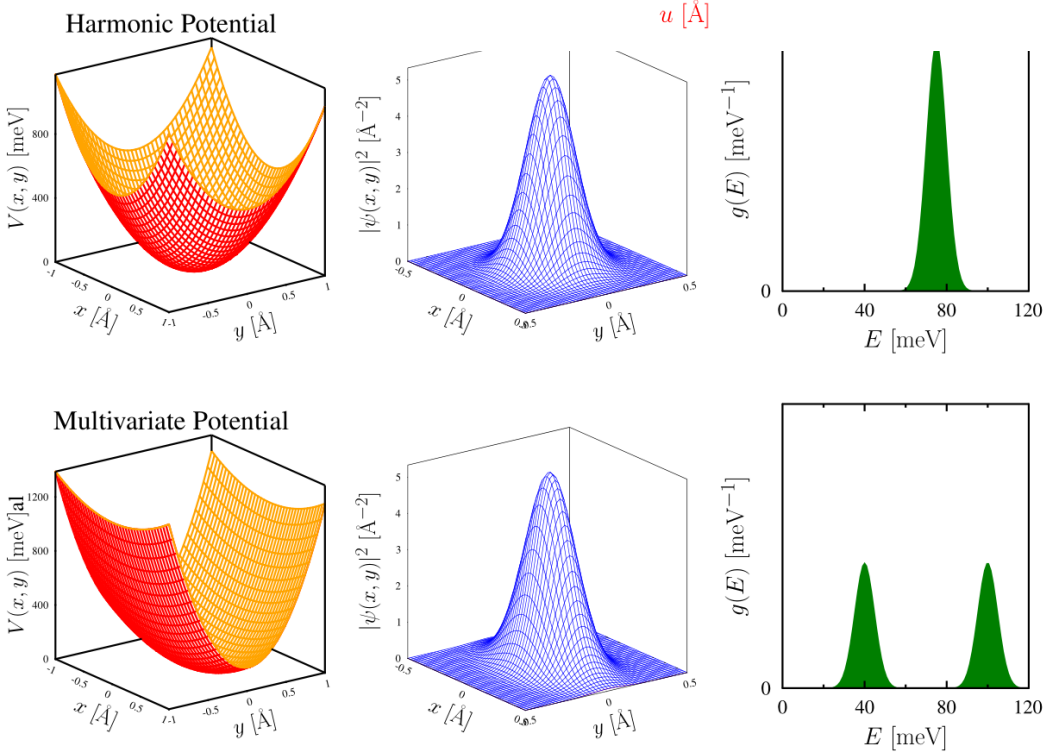
C Andreani, M Krzystyniak, G Romanelli, R Senesi, and F Fernandez-Alonso; Advances in Physics, (2017)

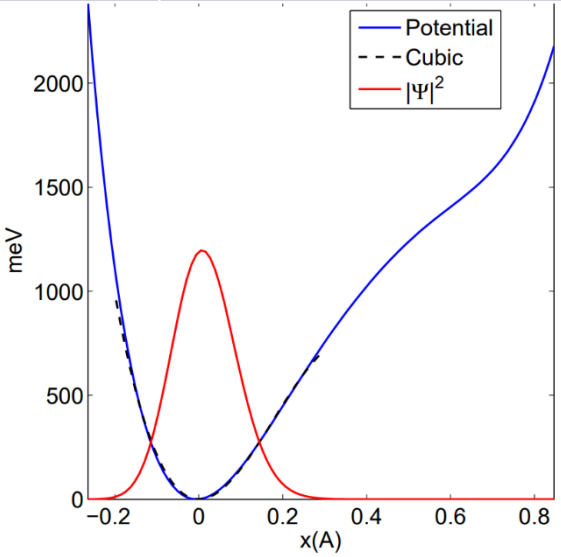
Nuclear momentum distributions

The shape of the potential determines the shape of the nuclear momentum distribution.

Potential	Momentum distribution
Isotropic	Gaussian
Anisotropic	Multivariate
Anharmonic	Gauss-Hermite expansion







C Andreani, R Senesi, M Krzystyniak, G Romanelli, F Fernandez-Alonso; Rivista del Nuovo Cimento, 291-340 (2018)

L Lin, JA Morrone, R Car, and M Parrinello; Phys Rev B 83, 220302(R) (2011)

Neutron Compton profiles

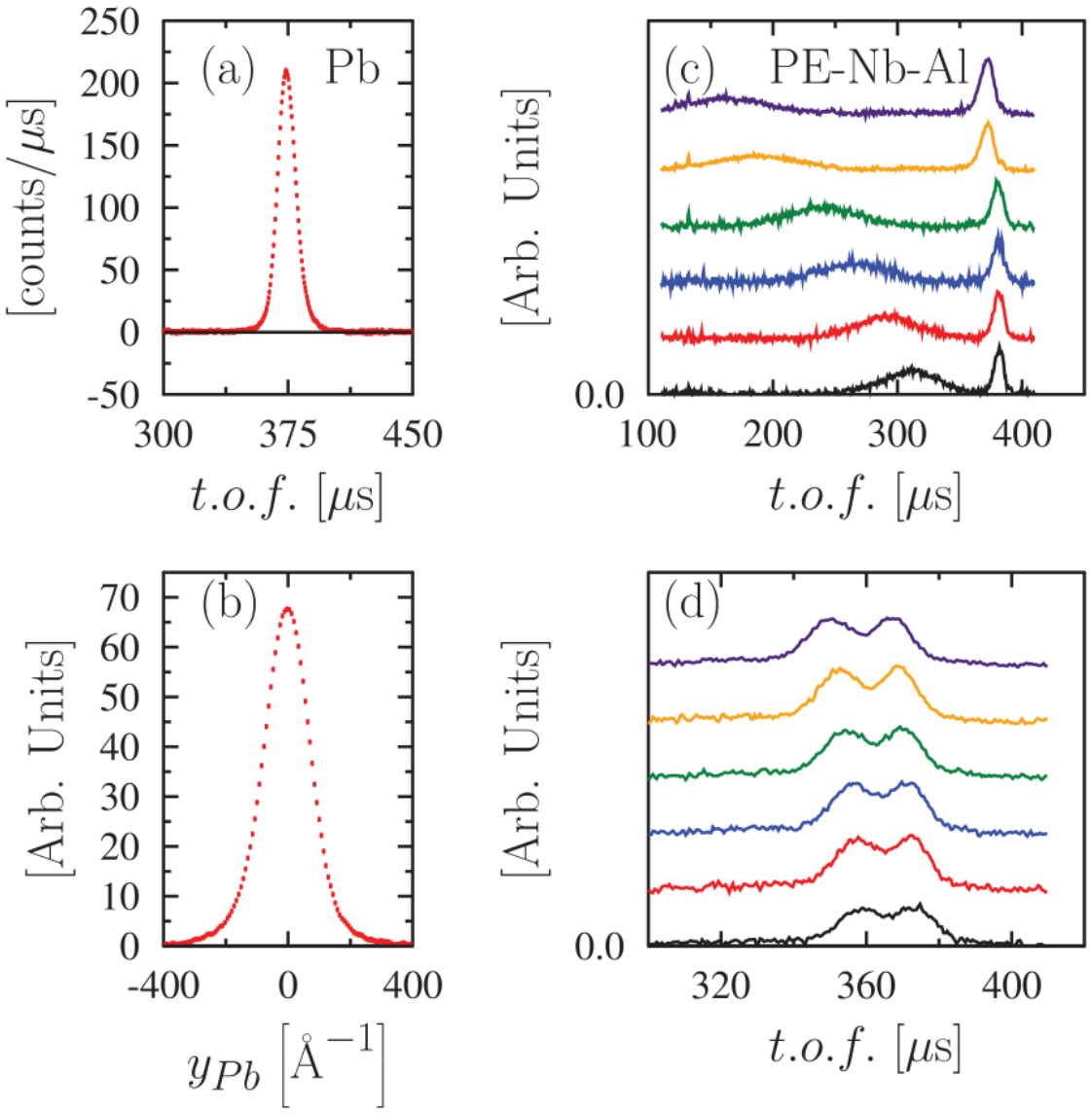
The **West-scaling variable**, *y*, is used to analyse the broadening of the nuclear momentum distribution along the recoil line.

$$y = \frac{M}{\hbar Q}\left(\hbar\omega - \frac{\hbar^2 Q^2}{2M}\right)$$

The variable *y* is interpreted as the value of the nuclear momentum along the neutron momentum transfer.

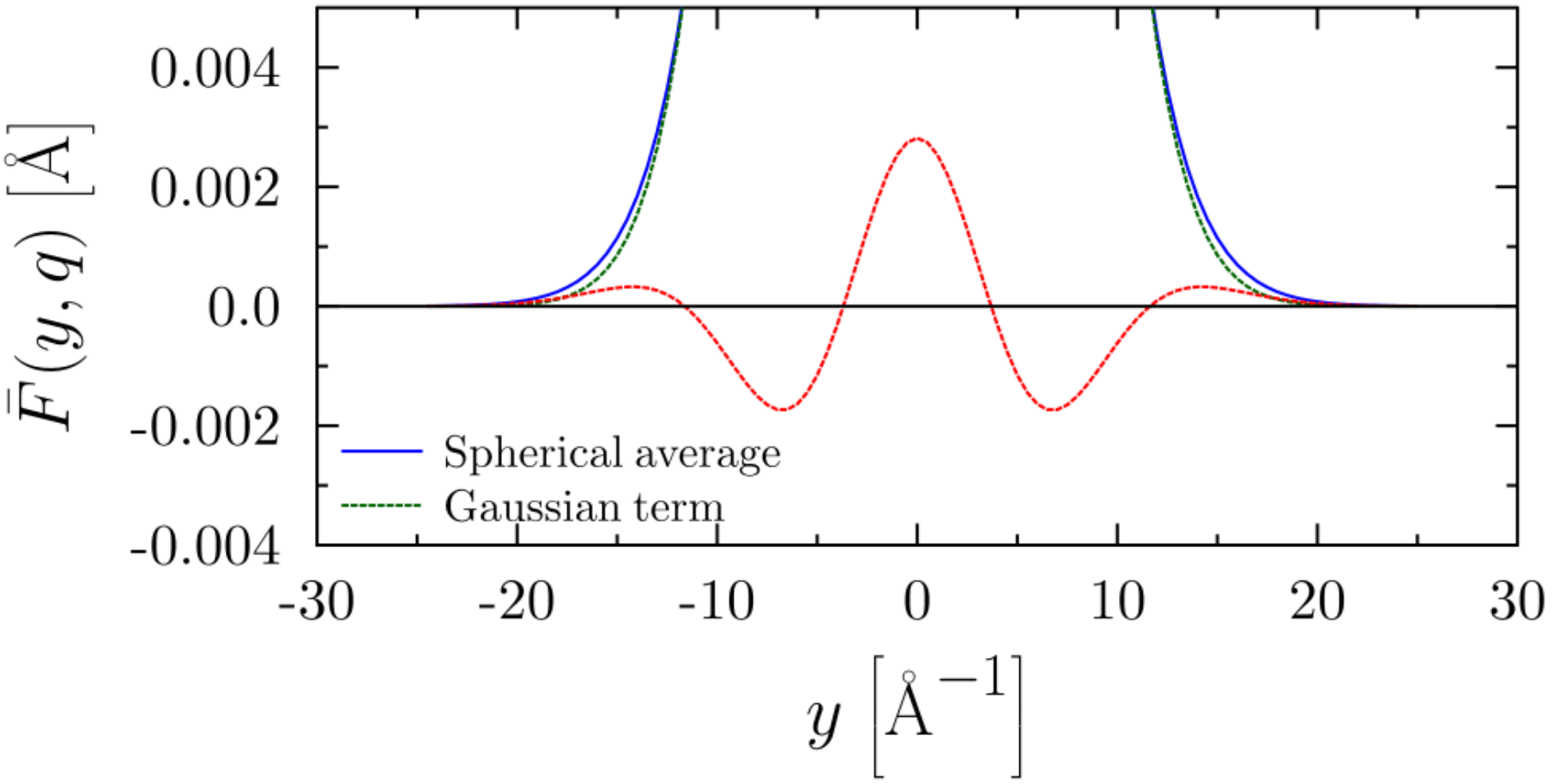
$$y = \boldsymbol{p} \cdot \widehat{\boldsymbol{Q}}$$

The data analysis is performed on the distribution of values of y, referred to as the **neutron Compton profile**.



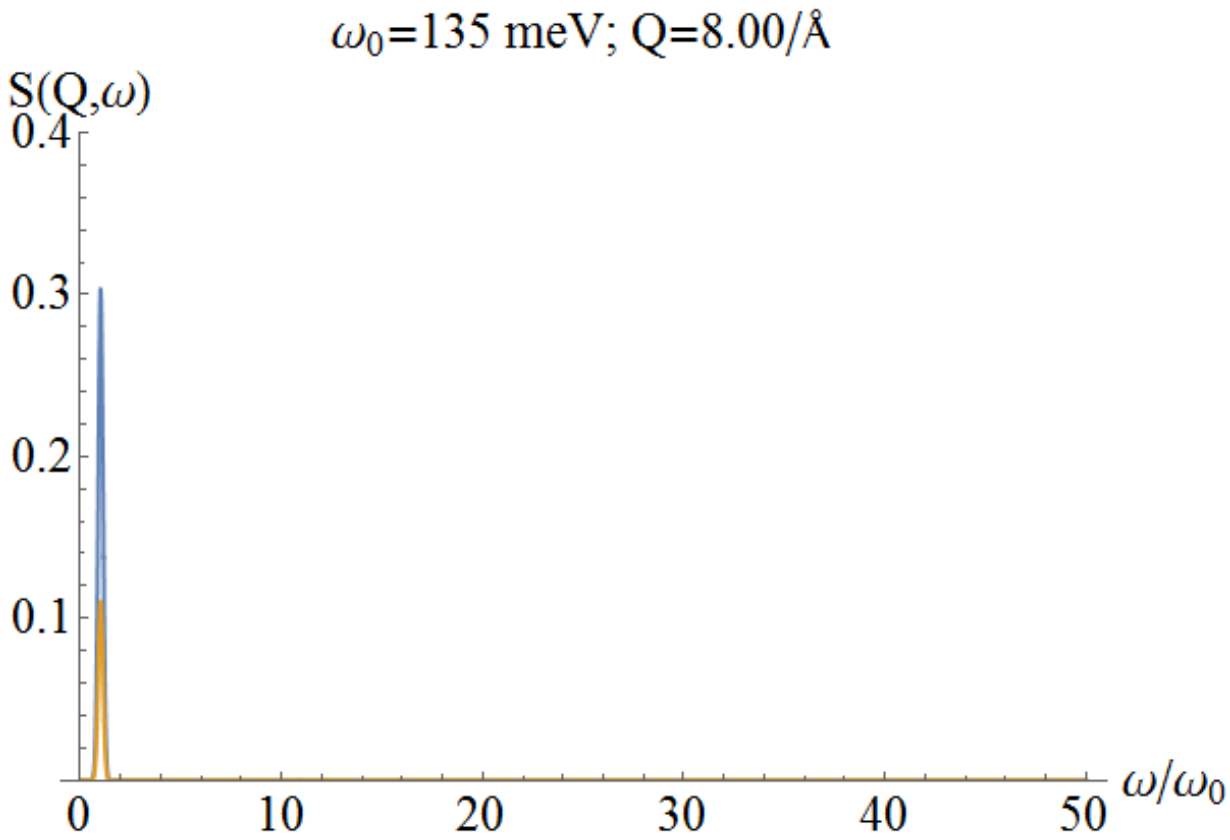
Neutron Compton profiles

When analysing the neutron Compton profile, the difference between isotropic and anisotropic nuclear momentum distributions manifests itself as an oscillation around the peak centre.

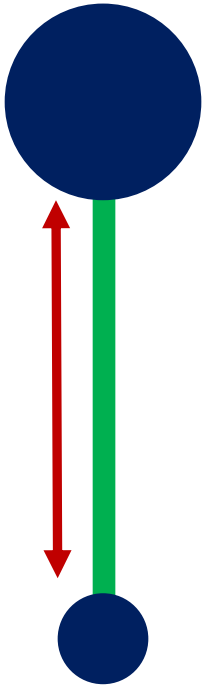


The link to vibrational spectra

The increasing of energy and momentum transfers requires a multi-phonon expansion



In the approximation of a **harmonic potential**, it is possible to relate the vibrational density of states to the width of the nuclear momentum distribution



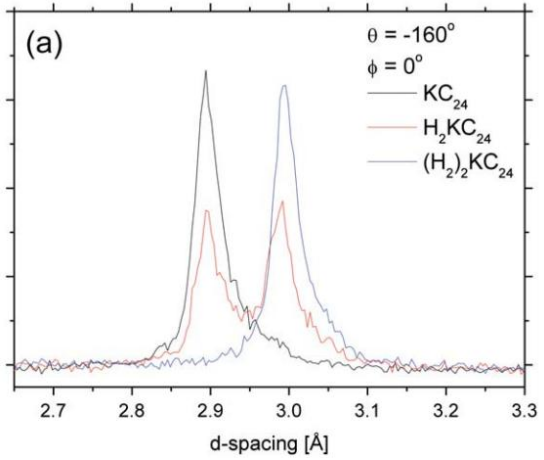
GI Watson; J Phys Cond Matt 8 33 (1996)

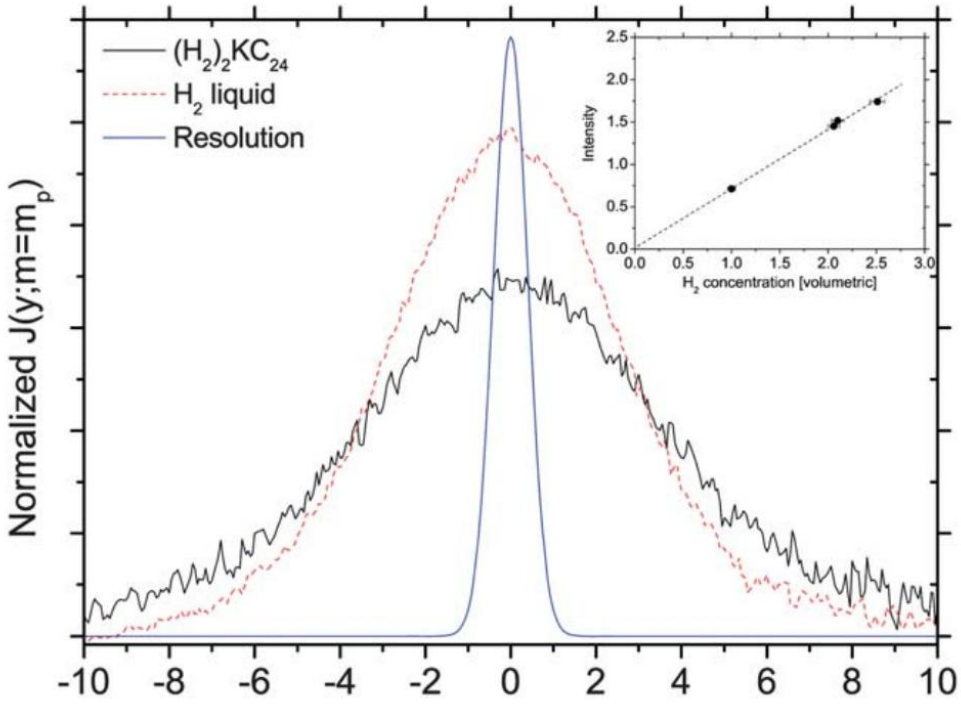
Examples of deep inelastic neutron scattering

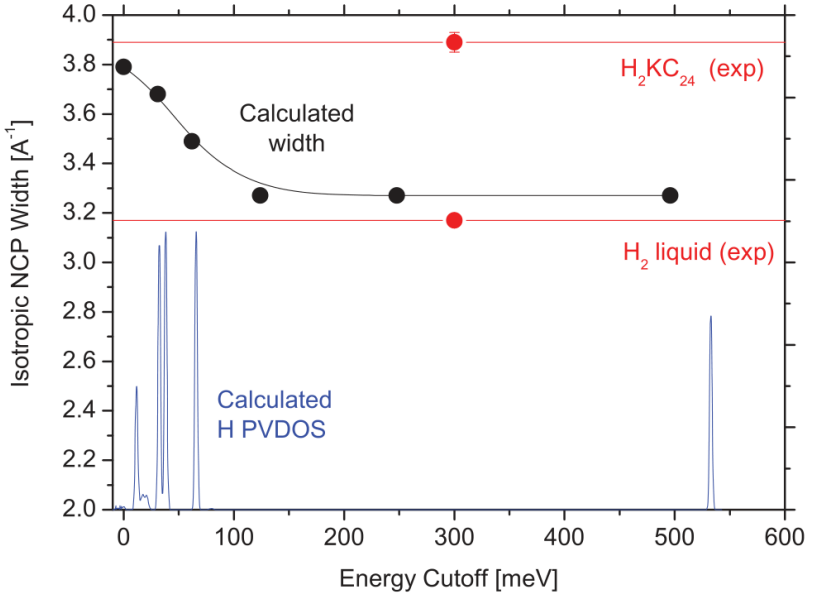
The adsorption, thus confinement, of H_2 in porous media increases its zero-point energy.

Zero-point energy can be calculated *post hoc* from *ab initio* simulations.

$$\sigma^2 = \frac{2M}{\hbar^2} 3 \int \frac{\hbar\omega}{4} g(\omega) \coth\left(\frac{\hbar\omega}{2k_B T}\right)$$

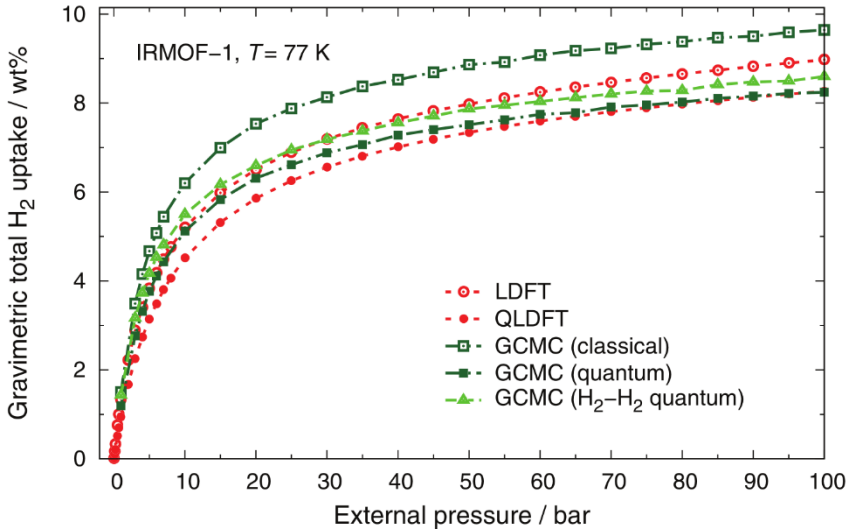


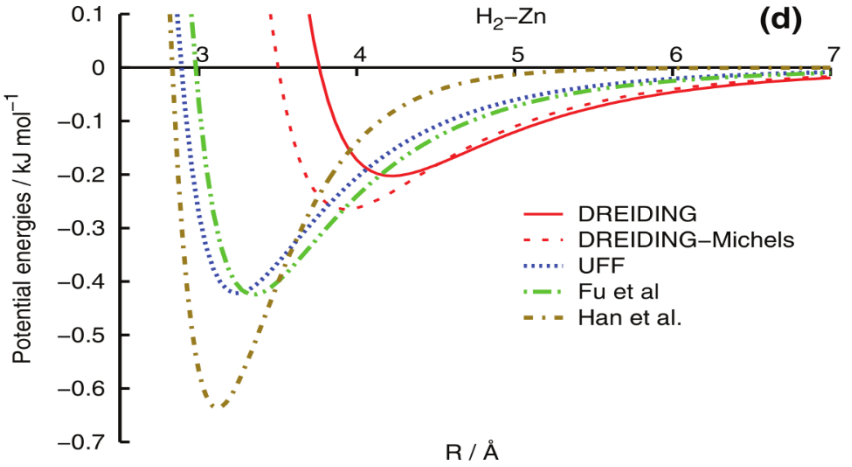




M Krzystyniak, MA Adams, A Lovell, NT Skipper, SM Bennington, J Mayers, and F Fernandez-Alonso; Faraday Discussions 151 (2011)

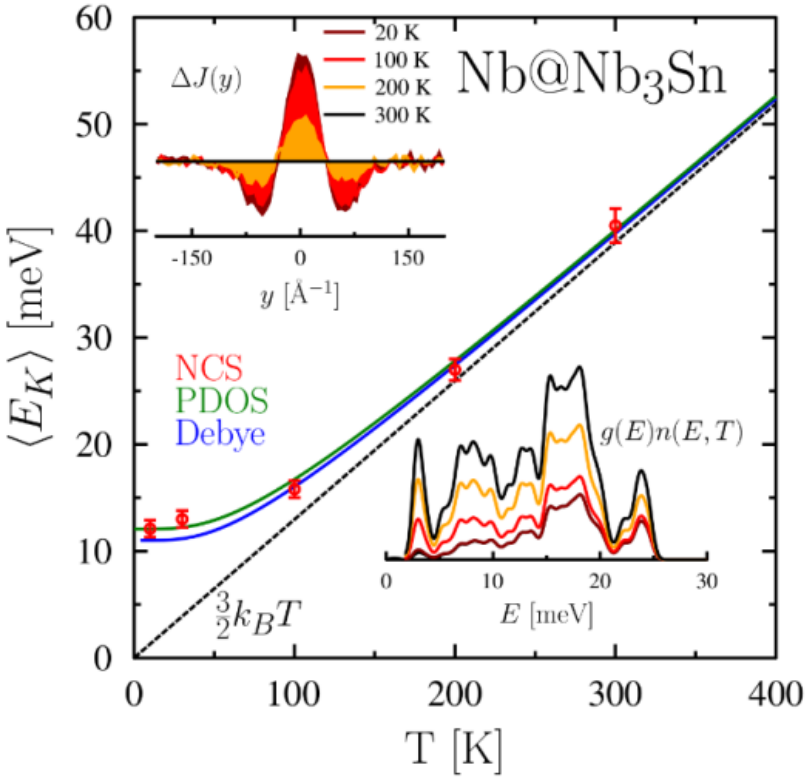
Examples of deep inelastic neutron scattering





M Wahiduzzaman et al., Hydrogen adsorption in metal-organic frameworks: The role of nuclear quantum effects; J. Chem. Phys. 141 064708 (2014)

Romanelli et al., in preparation

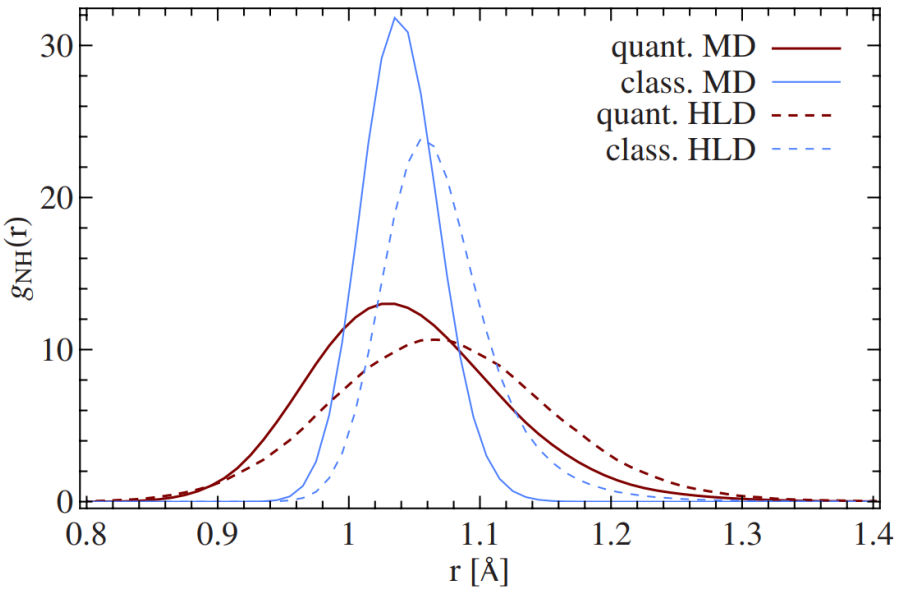


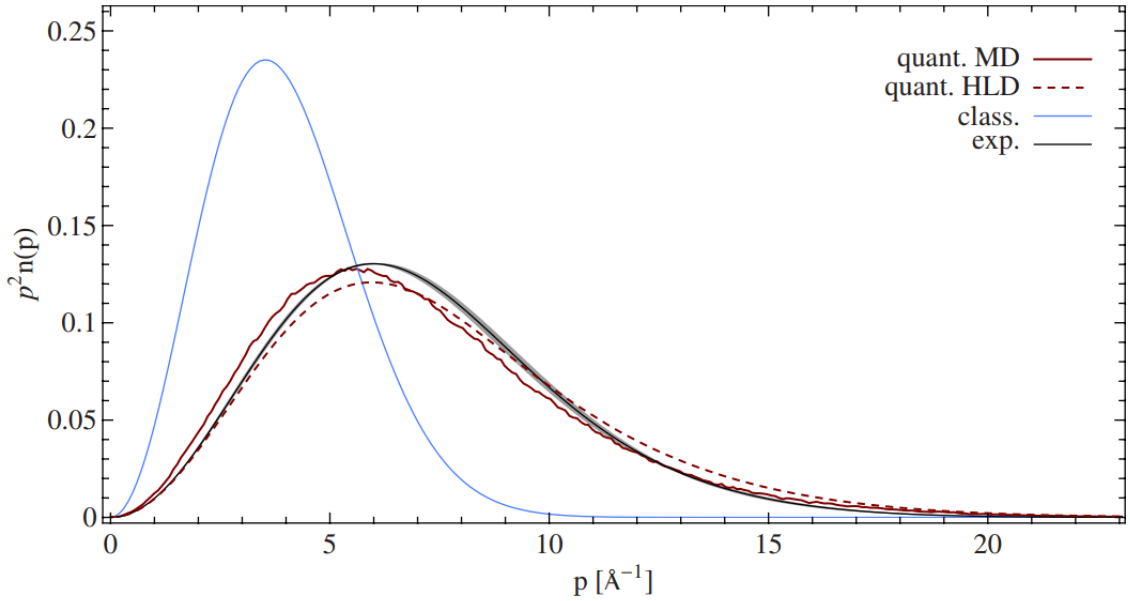
Zero-point energies are important ingredients for the modelling of **superconductors** (above), and the **adsorption of H_2** in porous materials (left).

Examples of deep inelastic neutron scattering

State-of-the-art computer simulations exploit **path integral molecular dynamics.** This implies a theoretical treatment of atoms as delocalised particles.

The *excess* of the kinetic energy from zero-point contributions broadens the momentum distribution as well as structure peaks, as in pair distribution functions.

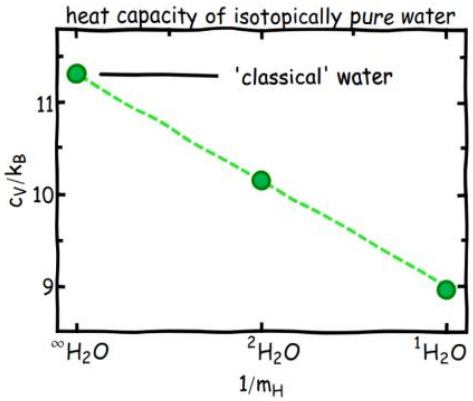


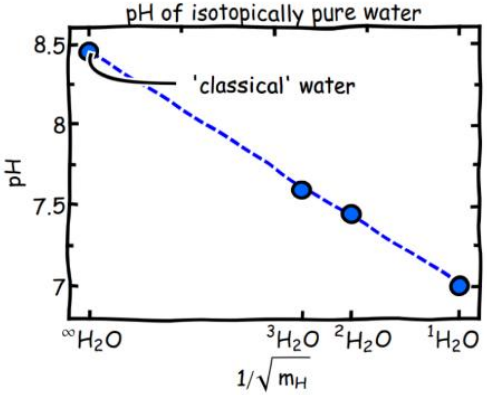


M Ceriotti, G Miceli, A Pietropaolo, D Colognesi, A Nale, M Catti, M Bernasconi, and M Parrinello; **Phys Rev B, 83, 174306 (2010)**

Examples of deep inelastic neutron scattering

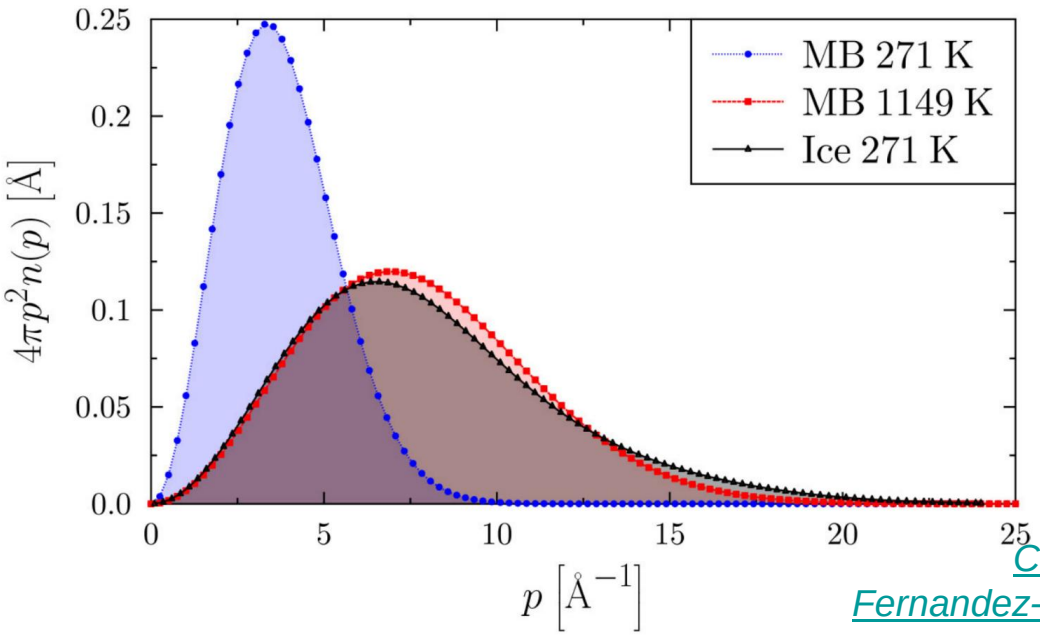
M Ceriotti





An effective temperature, taking into account zero-point motions, is not enough to reproduce the shape of the nuclear momentum distribution of hydrogen in water.

$$n(p) = exp\left(-\frac{p^2}{2Mk_BT^*}\right)$$



One needs to take into account the anisotropy of the potential as well.

$$n(\boldsymbol{p}) = exp\left(-\frac{p_x^2}{2\sigma_x^2} - \frac{p_x^2}{2\sigma_x^2} - \frac{p_x^2}{2\sigma_x^2}\right)$$

D Flammini, A Pietropaolo, R Senesi, C Andreani, and M McBride; J Chem Phys 136 024504 (2012)

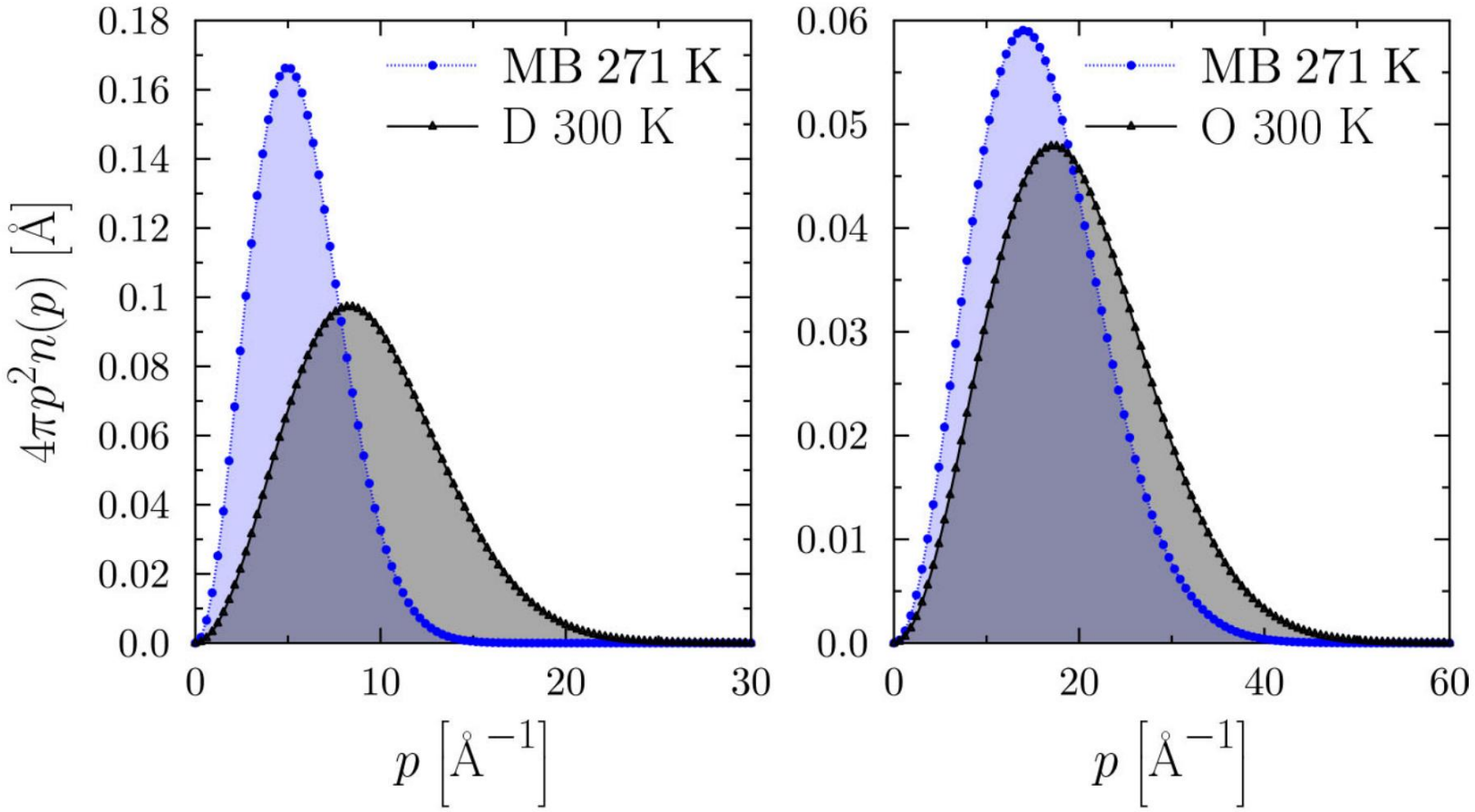
C Andreani, R Senesi, M Krzystyniak, G Romanelli, F Fernandez-Alonso; Rivista del Nuovo Cimento, 291-340 (2018)

Examples of deep inelastic neutron scattering

Nuclear quantum effects are affected by isotopic substitution, with heavier isotopes “less quantum” than lighter ones.

Yet, the mean kinetic energy of oxygen at room temperature is still ca. 50% higher than 3/2kT

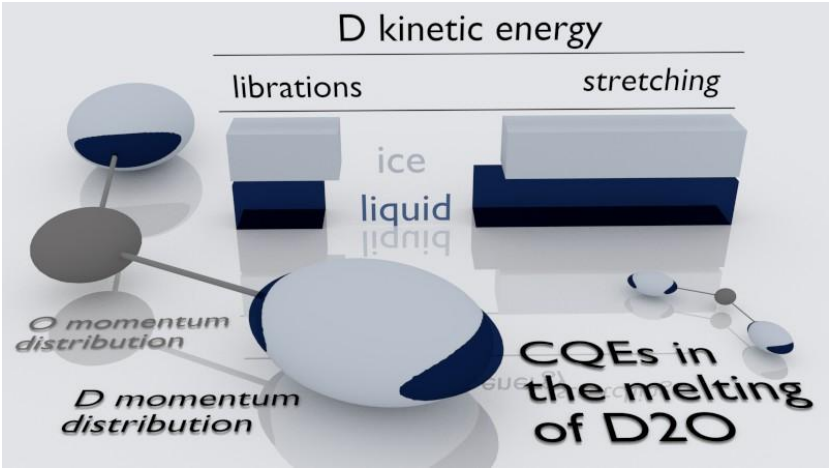
G Romanelli, M Ceriotti, DE Manolopoulos, C Pantalei, R Senesi, and C Andreani; J Phys Chem Lett 4 3251 (2013)

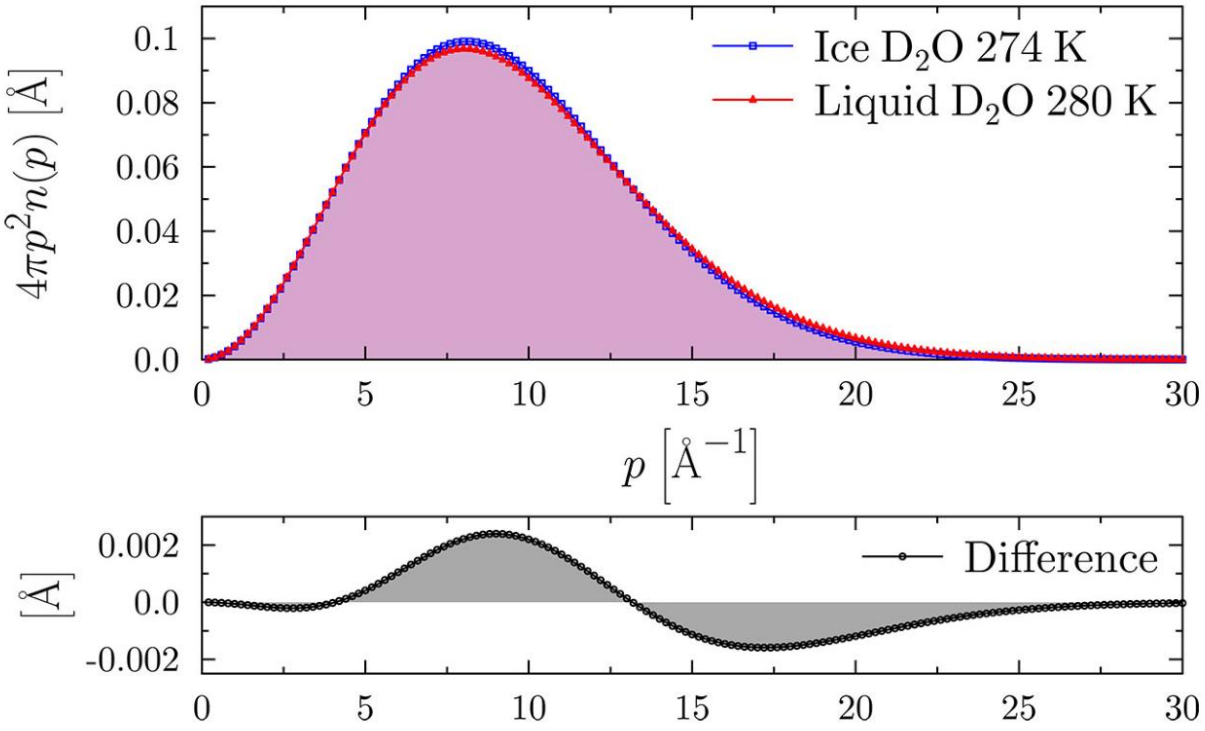


Examples of deep inelastic neutron scattering

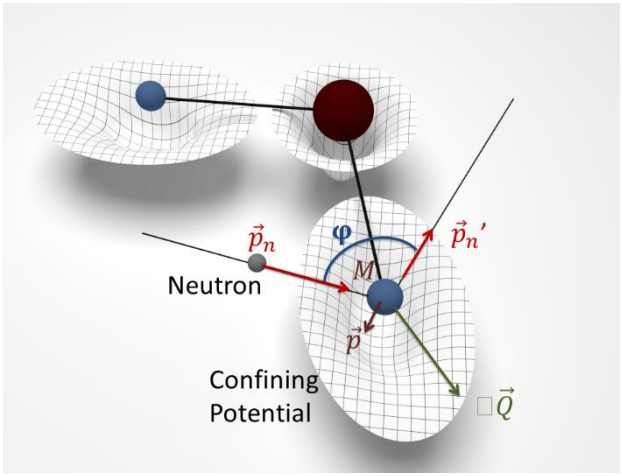
Phase transitions modify the shape of the nuclear momentum distribution.

There are cases, as in the melting of heavy water, where **competing quantum effects** leave the total mean kinetic energy relatively unchanged.





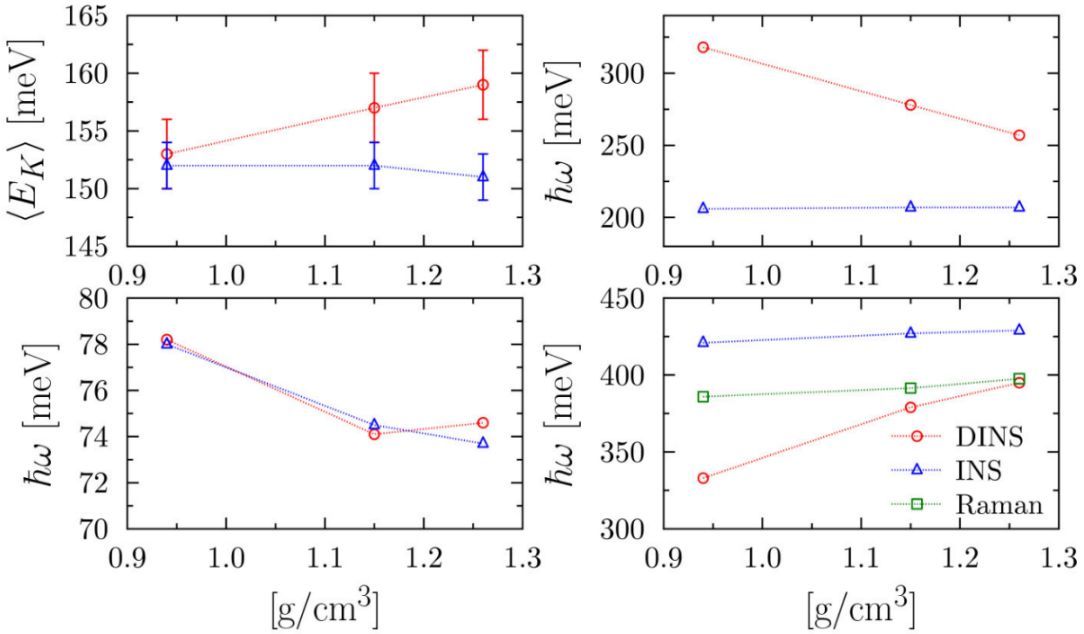
G Romanelli, M Ceriotti, DE Manolopoulos, C Pantalei, R Senesi, and C Andreani; J Phys Chem Lett 4 3251 (2013)

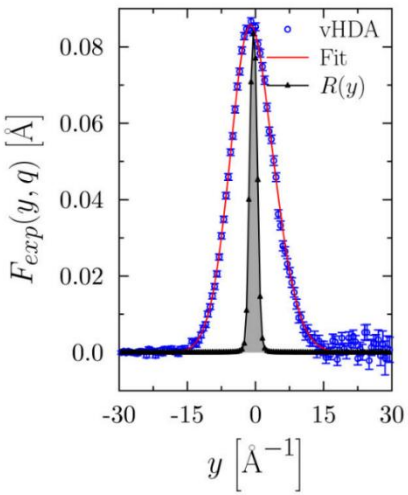


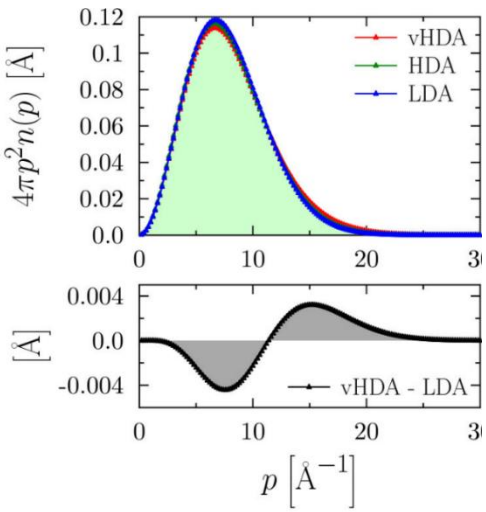
Examples of deep inelastic neutron scattering

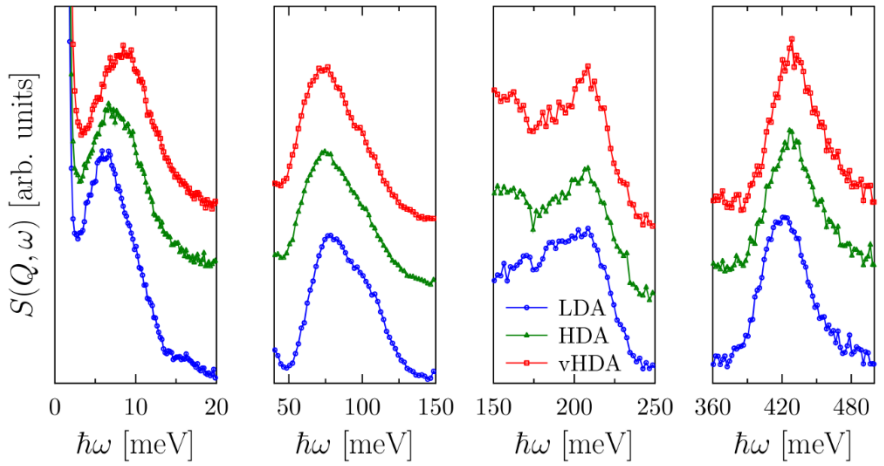
The tackling of disordered systems, as in the case of amorphous ices, can be challenging for computer simulations.

Within the harmonic approximation, one can obtain an estimate of the mean kinetic energy from inelastic neutron scattering.





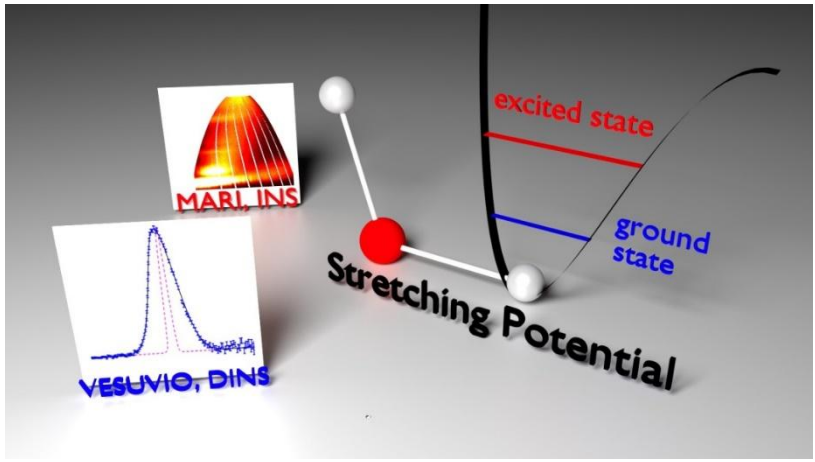


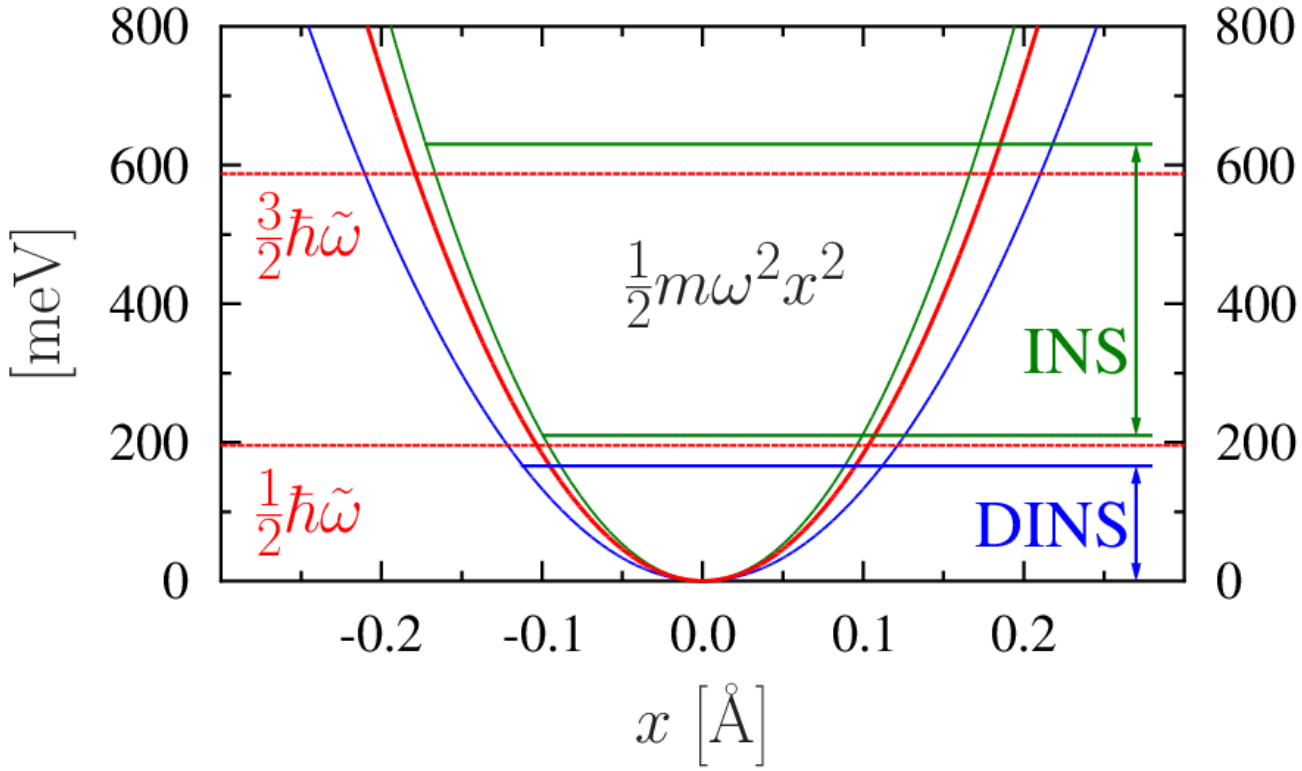


A Parmentier, JJ Shephard, G Romanelli, R Senesi, CG Salzmann, and C Andreani; *J. Phys. Chem. Lett.*, *6*, 11, 2038 (2015)

Examples of deep inelastic neutron scattering

From the comparison of inelastic and deep-inelastic neutron scattering results, one can estimate the anharmonicity constant of the local potential.

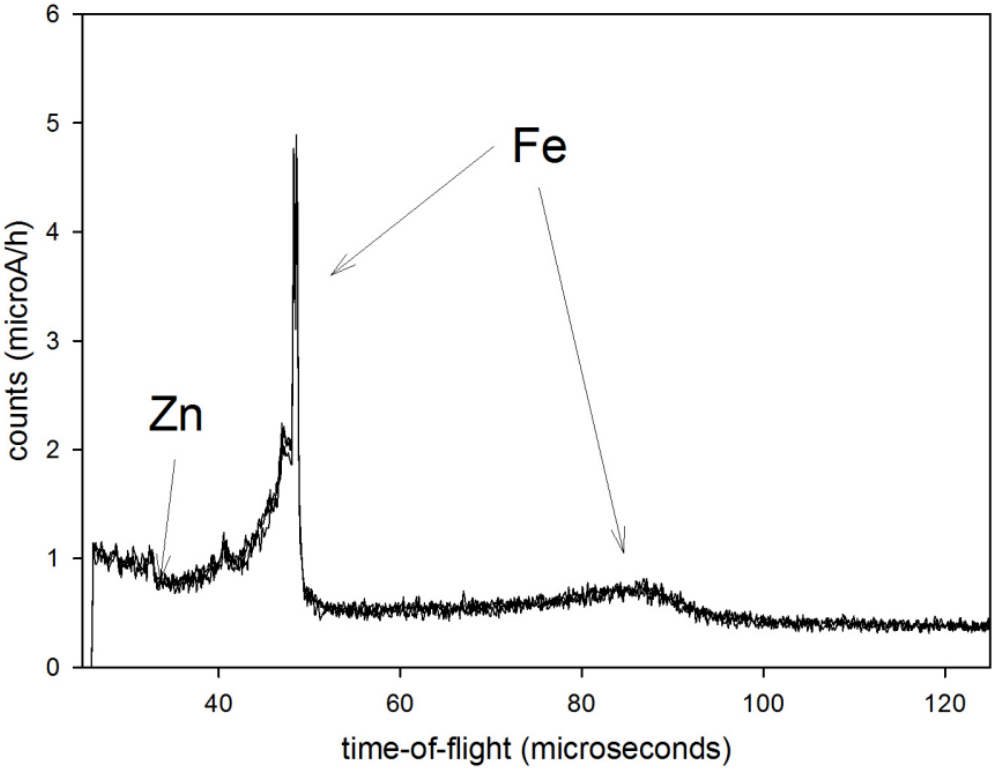


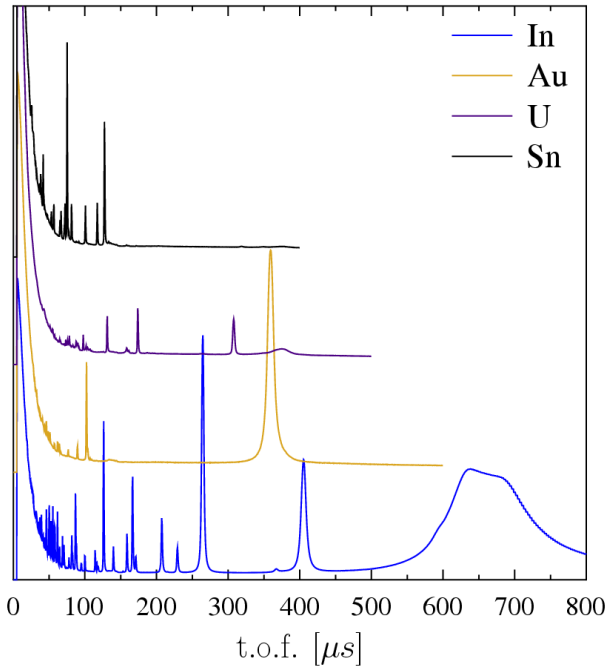


A Parmentier, JJ Shephard, G Romanelli, R Senesi, CG Salzmann, and C Andreani; *J. Phys. Chem. Lett.*, *6*, 11, 2038 (2015)

Neutron resonance capture analysis at INES (ISIS)

Neutron resonance capture analysis is an electron-volt neutron spectroscopy whereby a neutron is resonantly absorbed by a nuclide and emits prompt gamma radiation.





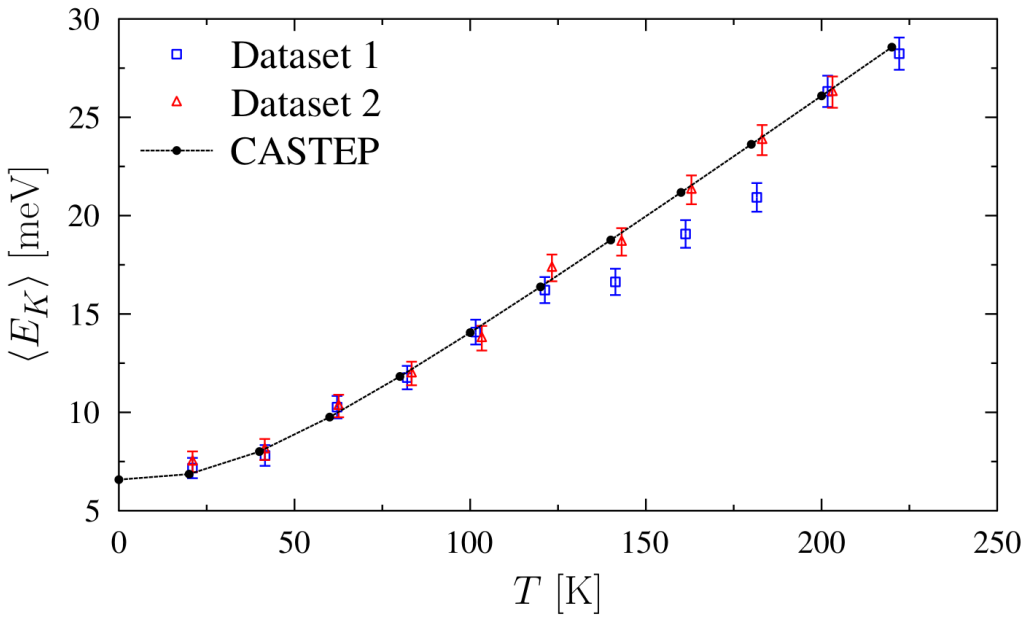
G Romanelli et al, in preparation

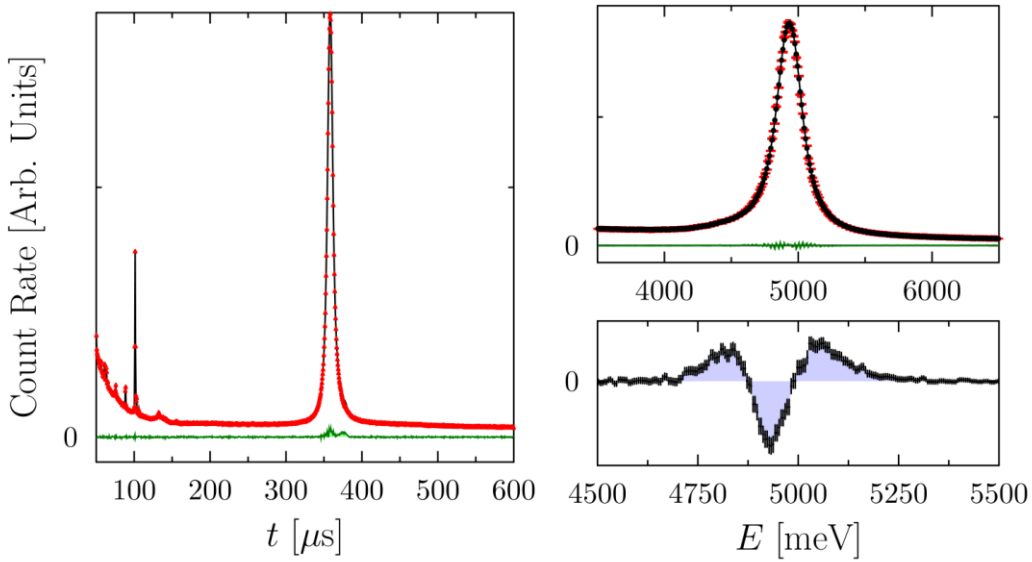
D Di Martino, M Bellanova, E Perelli Cippo, R. Felicetti, A. Scherillo, J Kelleher, Z Kise and G Gorini; JINST 13 C05009 (2018)

Neutron resonance capture analysis at VESUVIO

One can exploit neutron resonance capture analysis to measure the **Doppler broadening** of the gamma emission peak caused by the nuclear mean kinetic energy.

Considering the intensities of nuclear resonance cross sections, in the order of **thousands of barn**, on can measure small samples or low concentrations of nuclides, and perform (relatively) fast measurements.





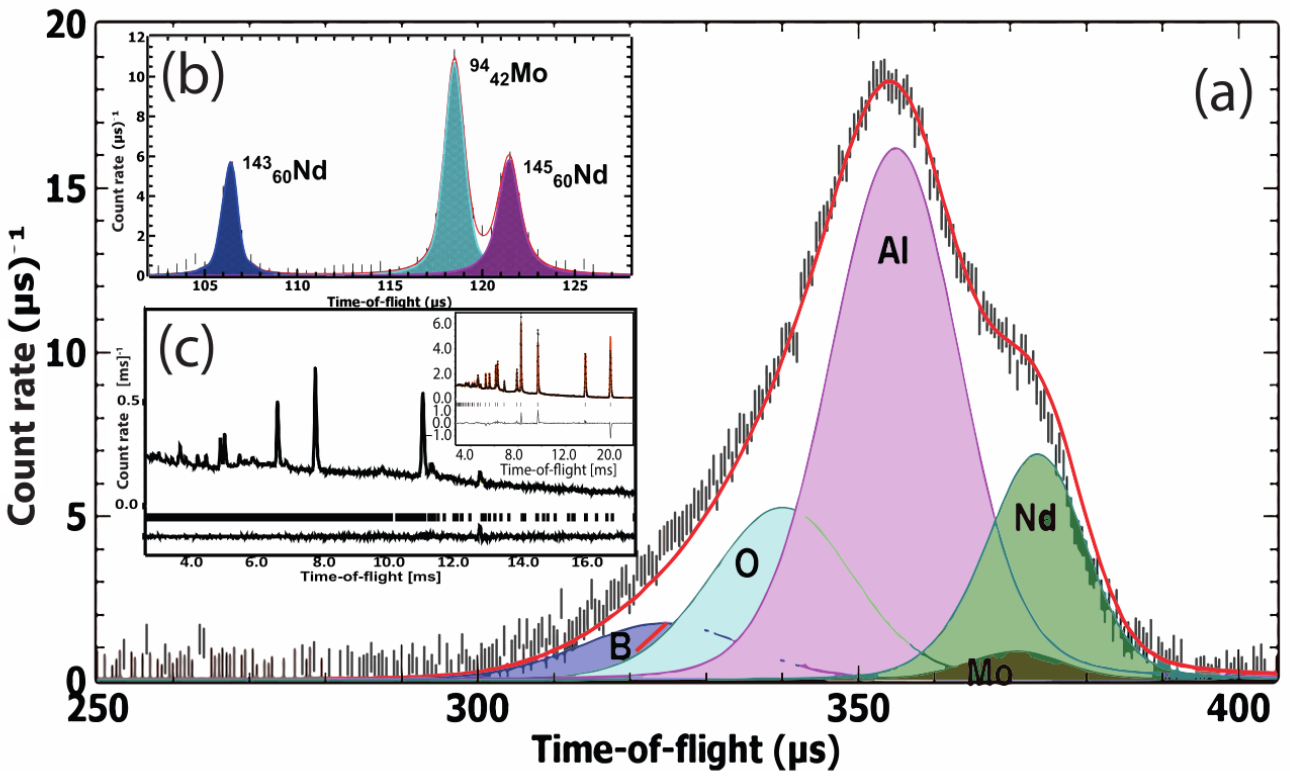
J Mayers, G Baciocco, and A Hannon; N Inst Meth A 275 453 (1989)

H Postma and P Schillebeeckx (2006) Neutron Resonance Capture and Transmission Analysis (John Wiley & Sons, Ltd) ISBN 9780470027318

G Romanelli, M Krzystyniak, and F Fernandez-Alonso; J Phys Conf Ser (2018)

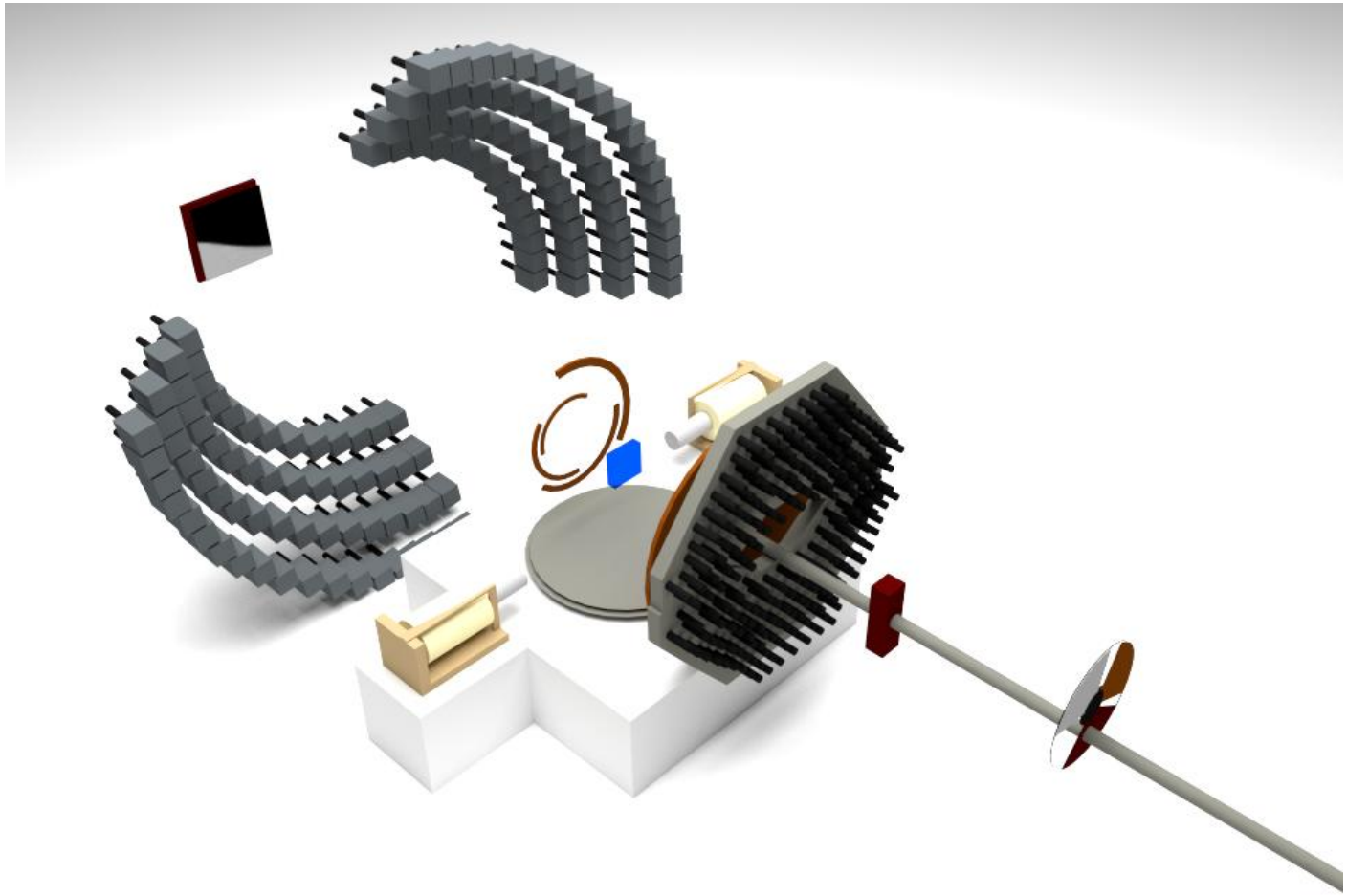
Neutron resonance capture analysis at VESUVIO

Neutron resonance capture analysis and deep inelastic neutron scattering allow for **mass-selective neutron spectroscopy**, whereby the nuclear momentum distributions of several atoms in the system are accessed at the same time.

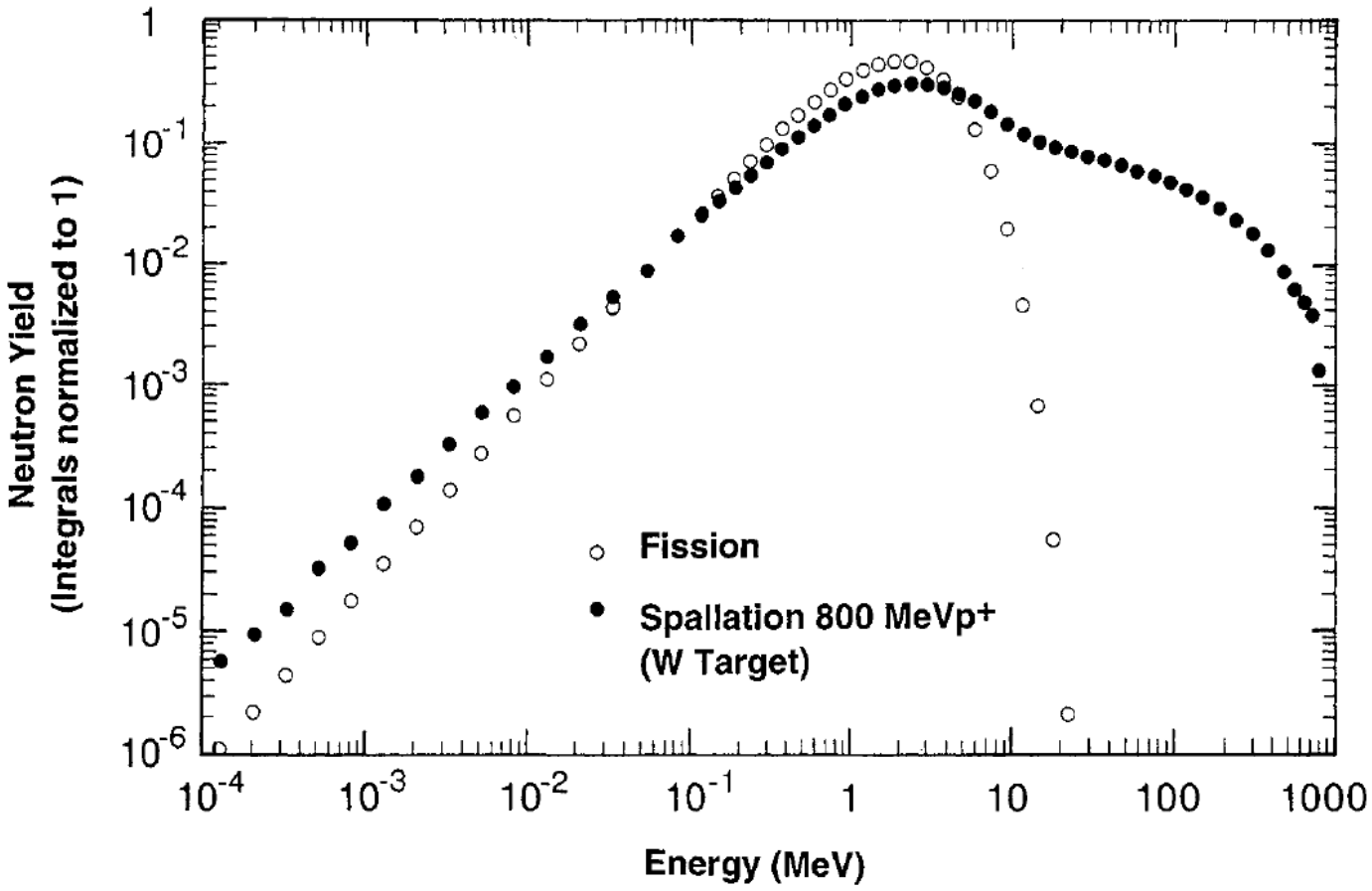


M Krzystyniak, G Romanelli, M Fabian, M Gutmann, G Festa, L Arcidiacono, M Gigg, K Druzbicki, C Andreani, R Senesi, and F Fernandez-Alonso; J Phys Conf Ser 1021 012026 (2018)

Instrumentation



The higher maximum energy of neutrons produced at **spallation sources** increases the flux of epithermal neutrons at the sample position.

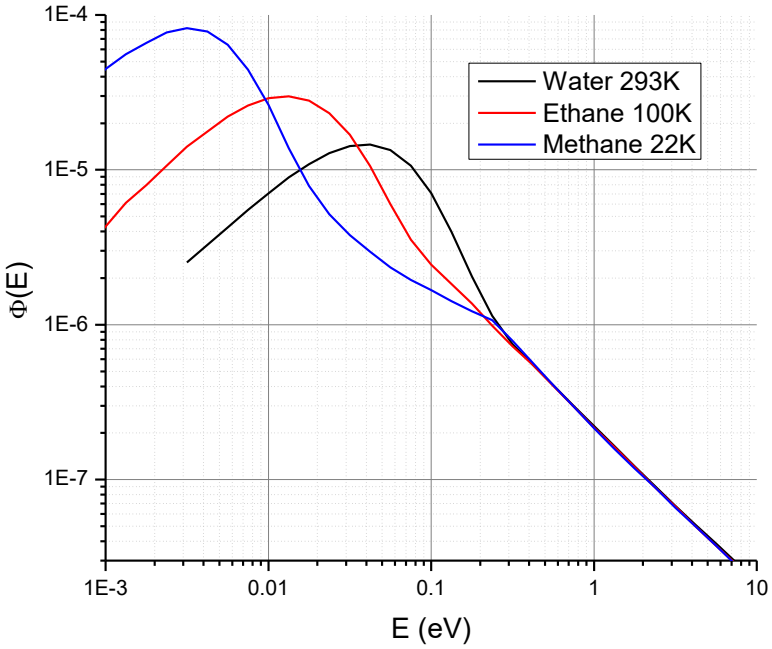


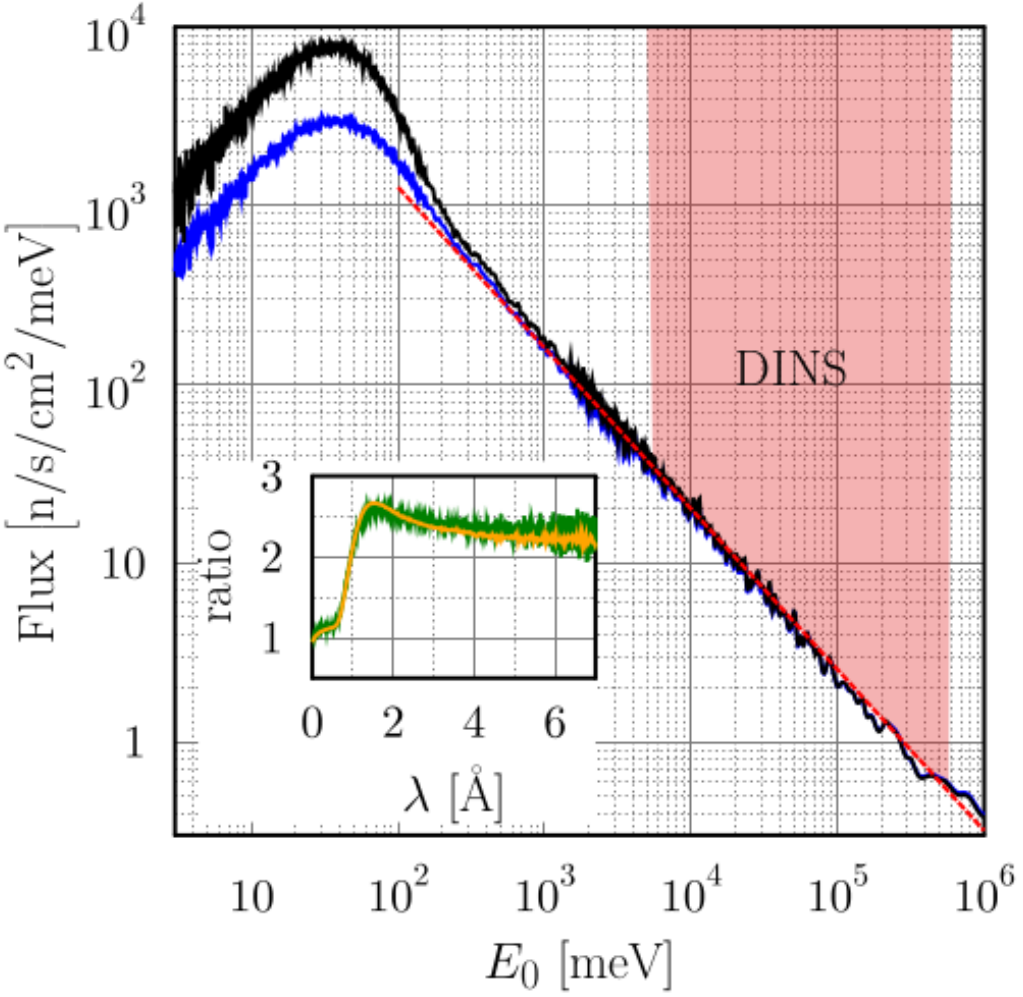
Calculated neutron spectra for fission and spallation.
(G.J. Russell, *ICANS-XI*, Tsukuba 1990)
http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/22/090/22090884.pdf

Epithermal tail

G Romanelli, M Krzystyniak, R Senesi, D Raspino, J Boxall, D Pooley, S Moorby, E Schooneveld, NJ Rhodes, C Andreani and F Fernandez-Alonso; Meas Sci Technol 28 095501 (2017)

The epithermal neutron flux at the sample position is approximately inversely proportional to the incident neutron energy, with no dependence upon the moderating material.





R Granada et al.

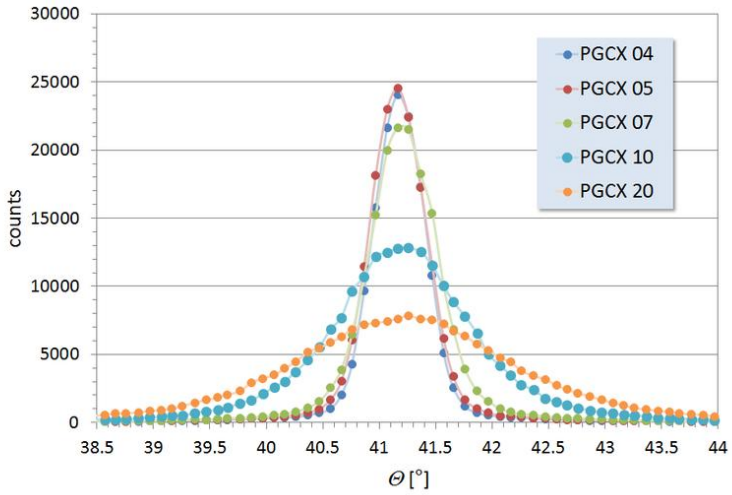
eV energy selection

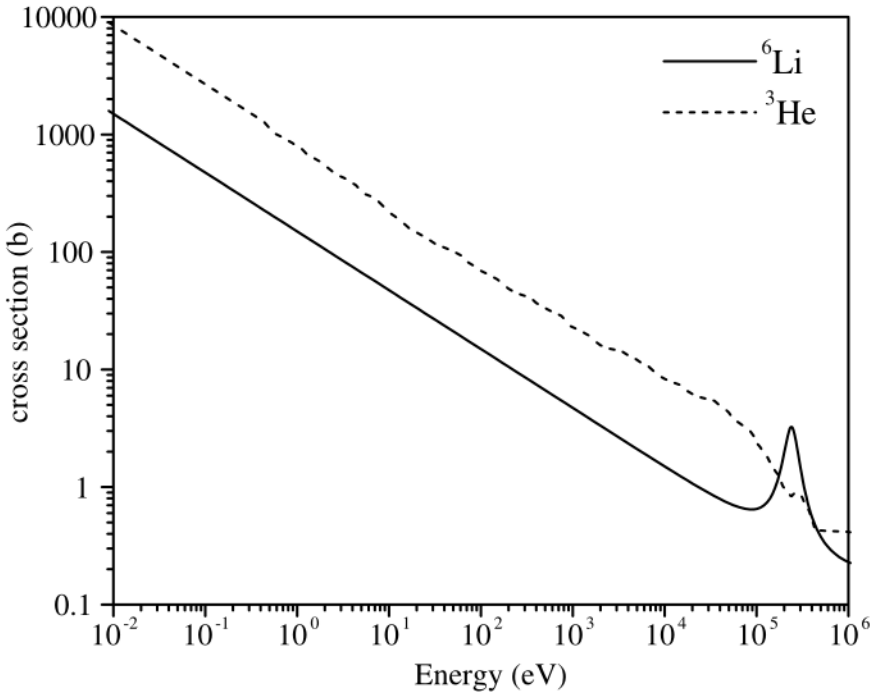
Crystal monochromators and mechanical energy selectors cannot be used for eV neutrons.

It is not possible to measure the neutron energy while detecting it.

Table 1
List of the nuclear reactions useful for neutron detection.

Reaction
$n + {}^{3}\mathrm{He} \rightarrow {}^{3}\mathrm{H} + {}^{1}\mathrm{H} + 0.764\ \mathrm{MeV}$
$n + {}^{6}\mathrm{Li} \rightarrow {}^{4}\mathrm{He} + {}^{3}\mathrm{H} + 4.80\ \mathrm{MeV}$
$n + {}^{10}\mathrm{B} \rightarrow {}^{7}\mathrm{Li}^{*} + {}^{4}\mathrm{He} \rightarrow {}^{7}\mathrm{Li} + {}^{4}\mathrm{He} + \gamma\ (0.480\ \mathrm{MeV}) + 2.3\ \mathrm{MeV}\ (\mathrm{br}\ 0.93)$
$n + {}^{10}\mathrm{B} \rightarrow {}^{7}\mathrm{Li}^{*} + {}^{4}\mathrm{He} \rightarrow {}^{7}\mathrm{Li} + {}^{4}\mathrm{He} + 2.8\ \mathrm{MeV}\ (\mathrm{br}\ 0.07)$
$n + {}^{155}\mathrm{Gd} \rightarrow \mathrm{Gd}^{*} \rightarrow \gamma\text{-rays} \rightarrow \text{conversion } e^{-}$
$n + {}^{157}\mathrm{Gd} \rightarrow \mathrm{Gd}^{*} \rightarrow \gamma\text{-rays} \rightarrow \text{conversion } e^{-}$
$n + {}^{235}\mathrm{U} \rightarrow \text{fission fragments} + 160\ \mathrm{MeV}$
$n + {}^{239}\mathrm{Pu} \rightarrow \text{fission fragments} + 160\ \mathrm{MeV}$





eV energy selection

The resonant foil used should…

- Narrow nuclear width (Decay time)
- Narrow Doppler width (cold temperature)
- Isolated resonance
- Easy to handle;

One can use nuclear resonances so as to select the neutron energy, with the energy of the resonance being isotope specific.

RM Brugger, AD Taylor, CE Olsen, JA Goldstone, and AK Soper; Nucl Inst Meth Phys Res A 221 393 (1984)

Table 1
Some possible resonances for FBS.

Isotope	Natural abundance [%]	Resonance energy (E_R) [eV]	Nuclear width (Γ) [meV]	Doppler broadened width (ΔE_0) [meV]	Peak cross section (temperature) [b (K)]	Foil thickness for 1/e transmission [mm]
^{149}Sm	13.9	0.872	61		2790(300)	0.12
^{240}Pu	–	1.056	33.3	58	112000(300)	0.0018
^{240}Pu	–	–	–	43	139000(77)	0.0015
^{103}Rh	100	1.257	156	178	4081(300)	0.034
^{193}Ir	62.7	1.303	87.3		5830(300)	0.025
^{115}In	95.7	1.457	75		29900(300)	0.0088
^{185}Re	37.4	2.156	57.7		9300(300)	0.016
^{242}Pu	–	2.67	27		35200(300)	0.0058
^{238}Pu	–	2.90	38		1020(300)	0.20
^{169}Tm	100	3.90	108		30100(300)	0.010
^{181}Ta	100	4.28	57		14100(300)	0.013
^{197}Au	100	4.906	139	180	30800(300)	0.0055
^{234}U	–	5.19	29		27500(300)	0.0076
^{236}U	–	5.45	27		15700(300)	0.013
^{238}U	99.3	6.674	27.5	104	7712(300)	0.027
^{238}U	–	–	–	54	12475(77)	0.017
^{238}Pu	–	9.98	42		4200(300)	0.048
^{159}Tb	100	11.14	95		7140(300)	0.045
^{195}Pt	33.8	11.9	127		3120(300)	0.049
^{163}Dy	24.9	16.23	124		2070(300)	0.15
^{186}W	28.6	18.84	337		29800(300)	0.0054
^{238}U	99.3	20.90	34		8510(300)	0.025
^{238}U [a)]	99.3	100	1000			
^{238}U [a)]	99.3	186	1600			

[a)] Window filter instead of resonance filter.

eV energy selection

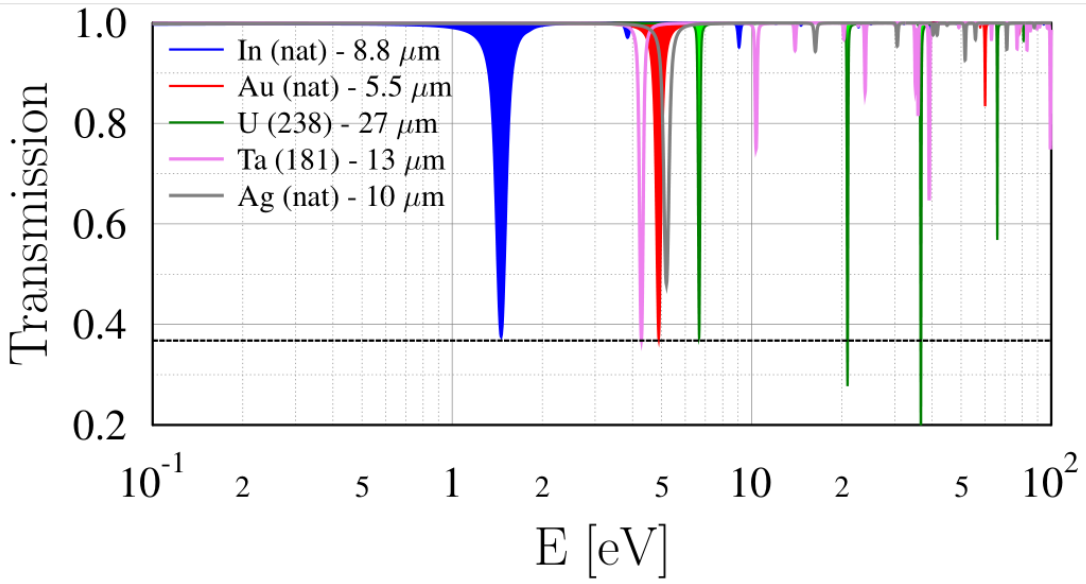
When a resonant material is cycled in the neutron beam, it absorbs part of the neutrons with energies nearby the energy of the resonance(s).

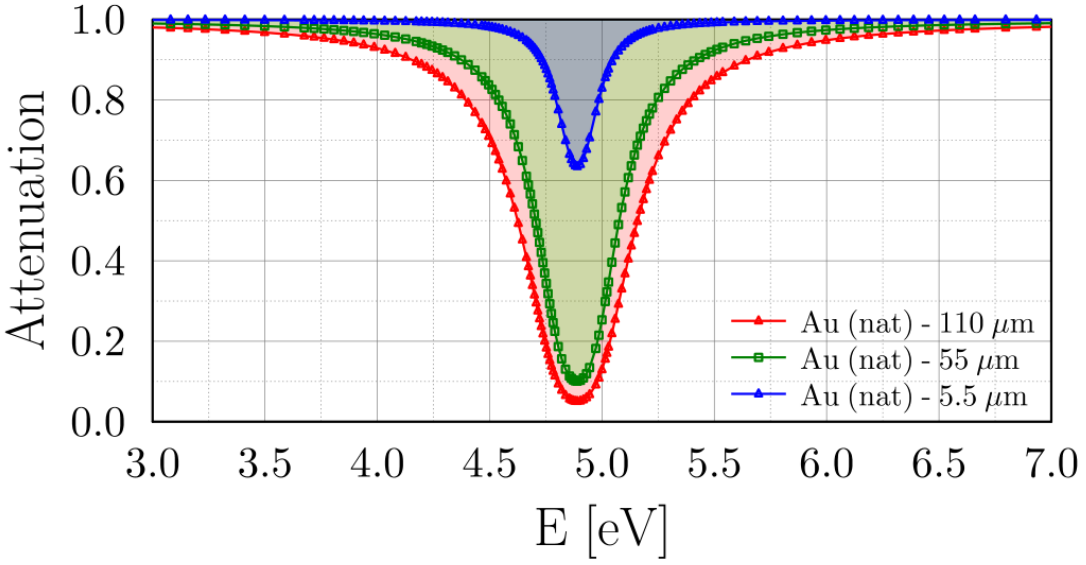
$$T(E) = exp(-n\sigma(E)d)$$

The energy resolution becomes broader when the thickness (d) of the foil is increased.

A rule of thumb is to chose a thickness whereby

$$T(E) = e^{-1}$$

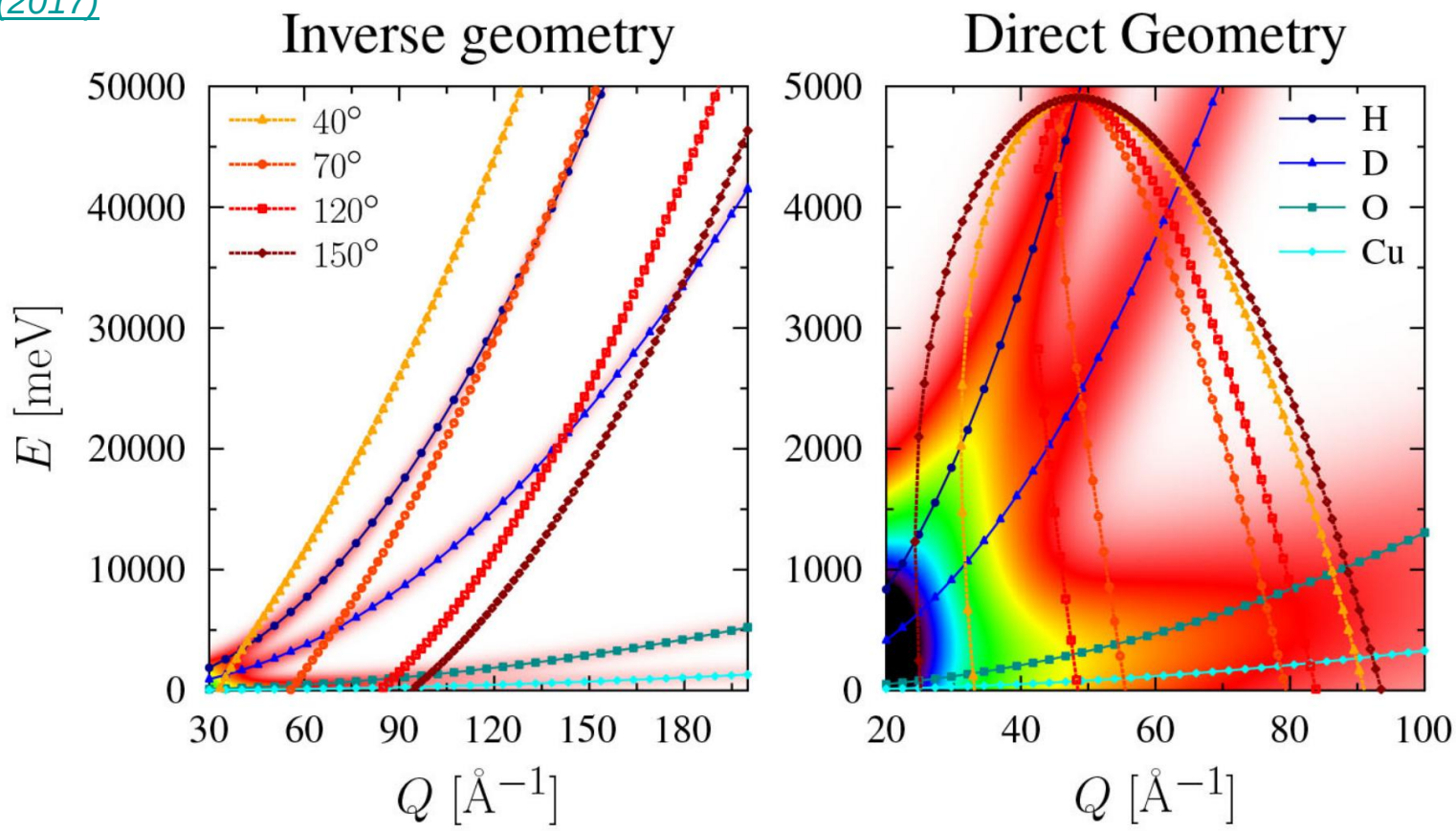




Geometry of eV spectrometers

At pulsed sources, by selecting the initial (final) energy of the neutron with a resonant foil, one can evaluate the final (initial) energy using the time-of-flight technique, thereby obtaining the energy transfer.

C Andreani, M Krzystyniak, G Romanelli, R Senesi, and F Fernandez-Alonso; Advances in Physics, (2017)

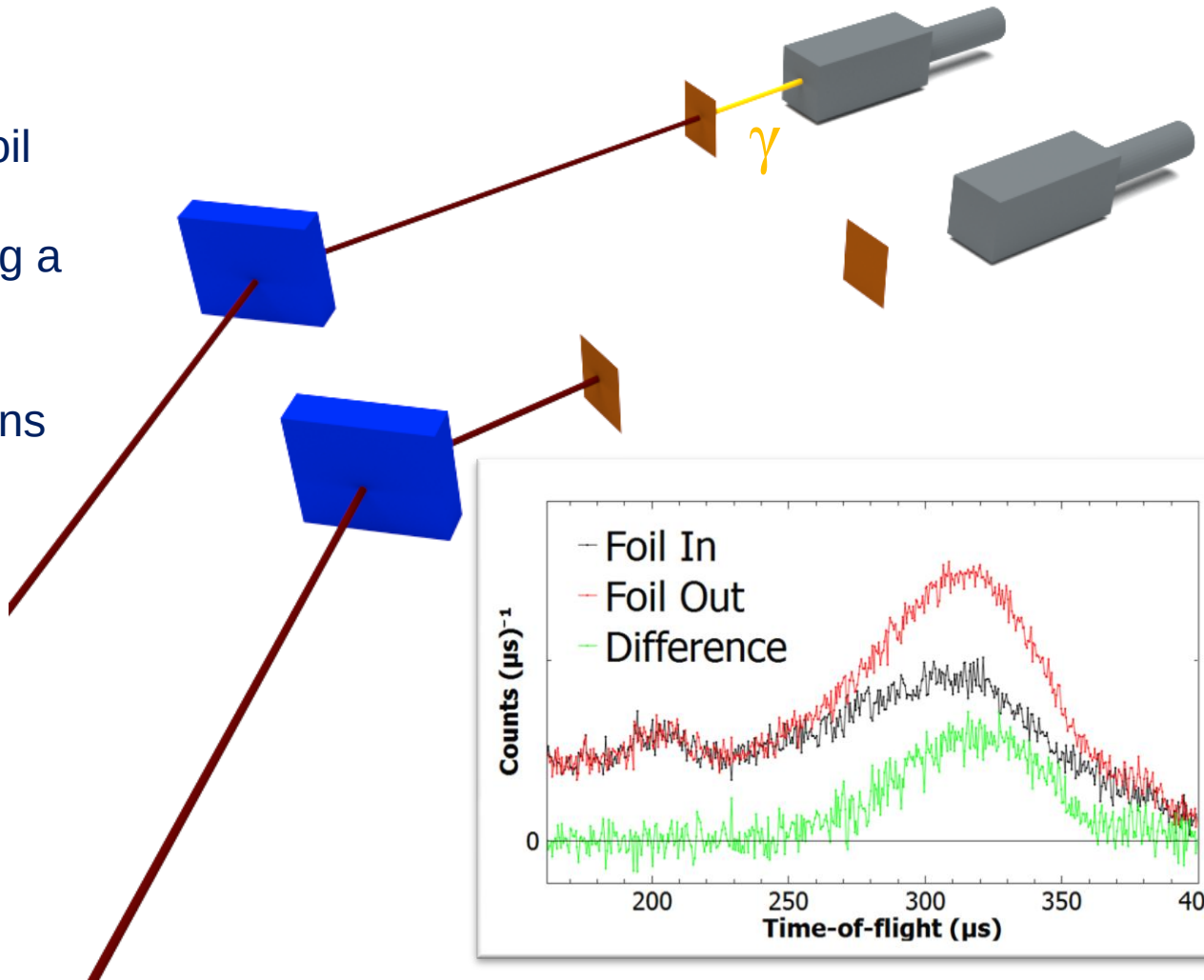


Geometry of eV spectrometers

In a **resonant detector spectrometer**, eV neutrons absorbed by the analyser foil are transformed in prompt-gamma radiation, then detected by a gamma sensitive detector

Emission geometry

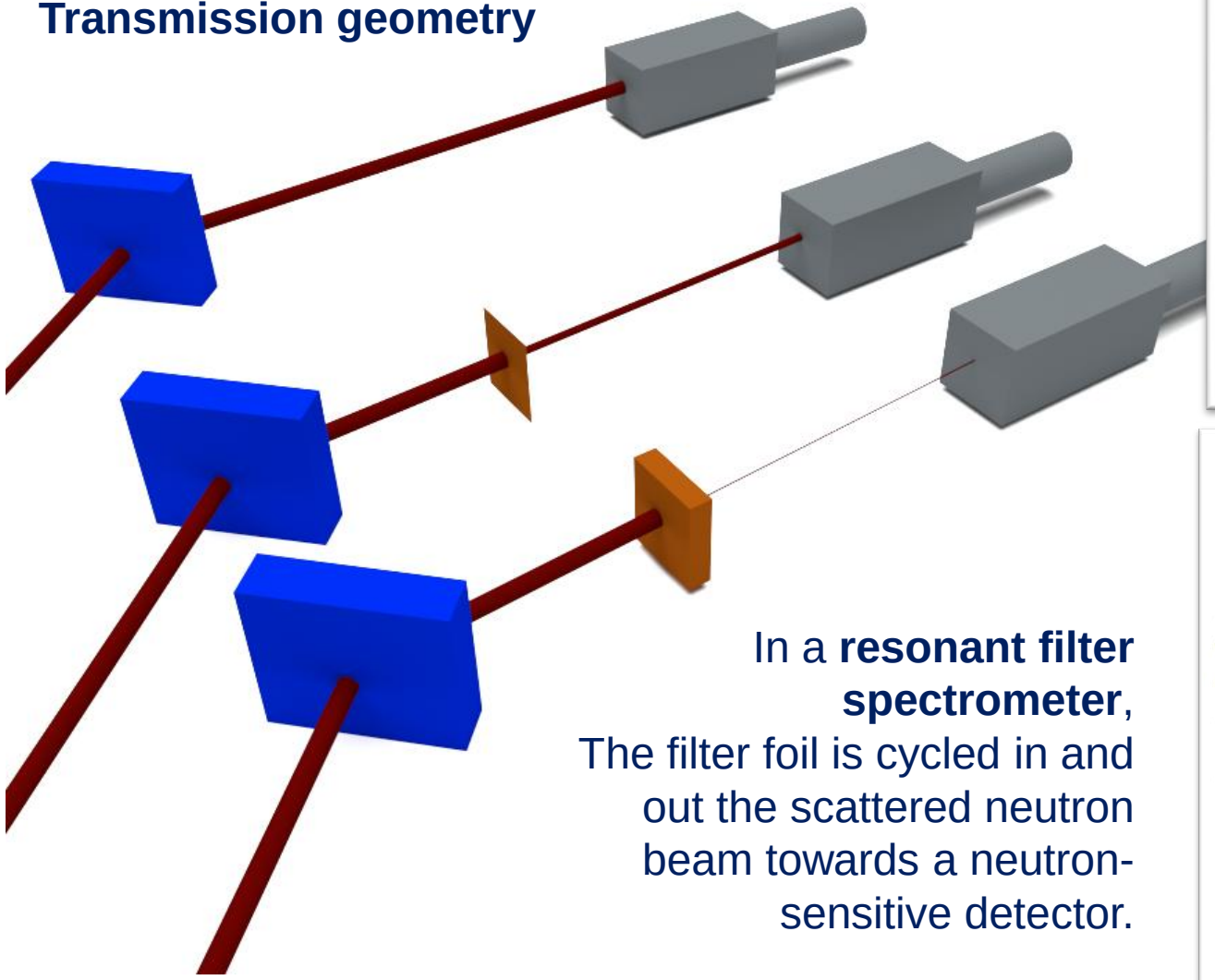
By cycling the analyser foil in and out the scattered neutron beam, then taking a difference of the two spectra, one selects the final energy of the neutrons and removes the environmental gamma background.

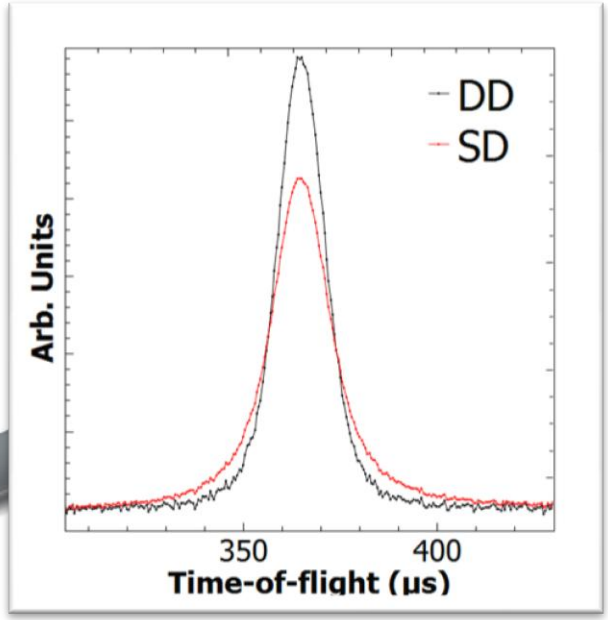


$$t.o.f. = \frac{L_0}{v_0} + \frac{L_1}{v_1}$$

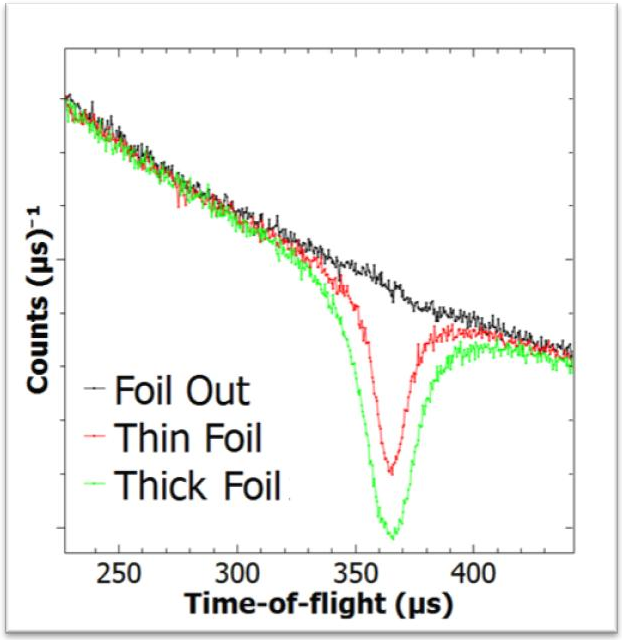
Geometry of eV spectrometers

Transmission geometry



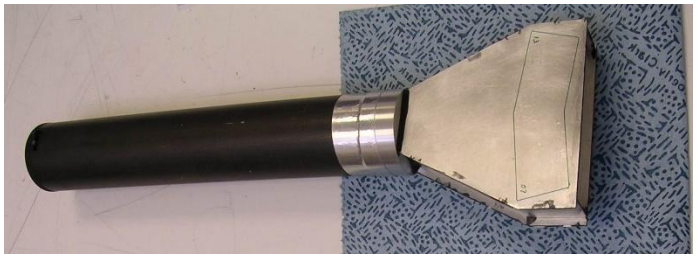


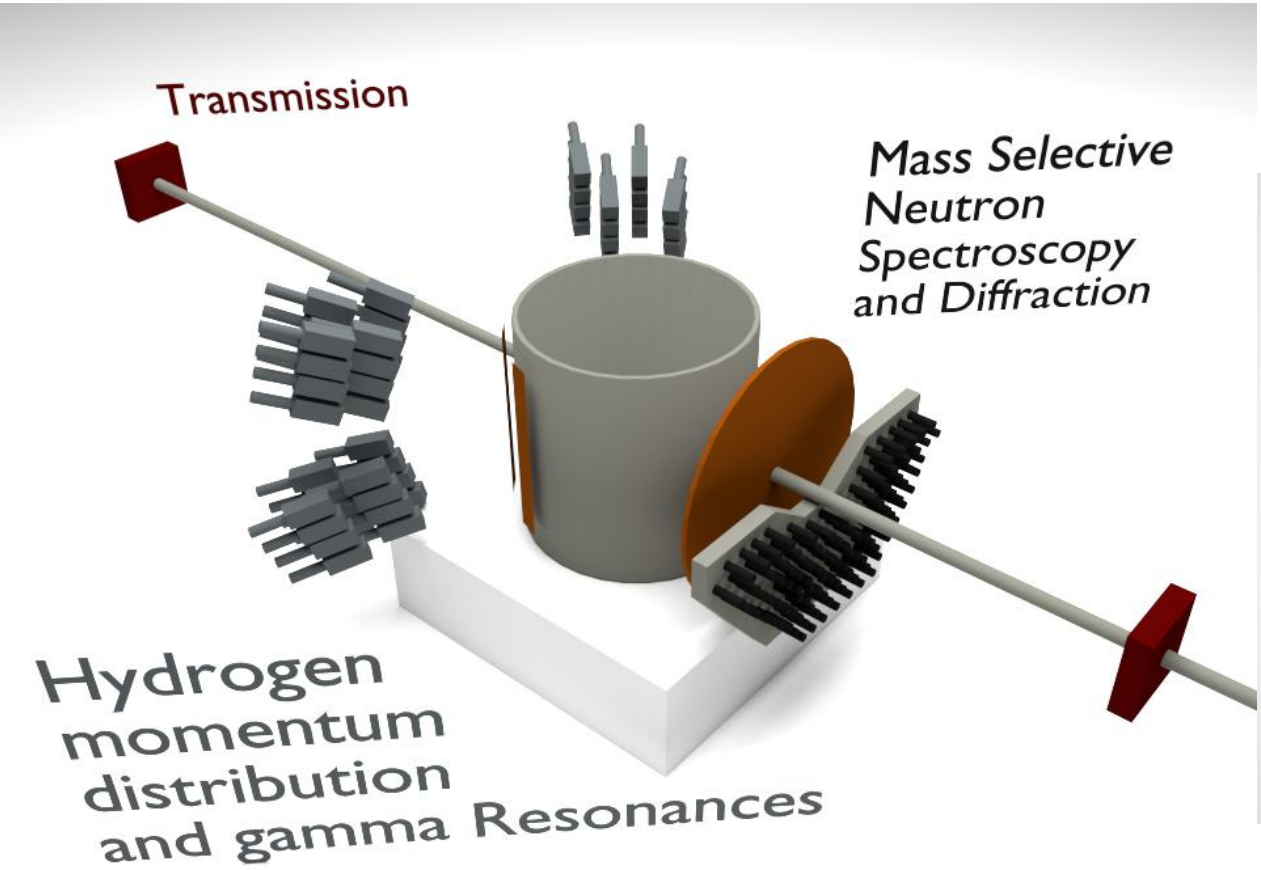
In a **resonant filter spectrometer**, The filter foil is cycled in and out the scattered neutron beam towards a neutron-sensitive detector.

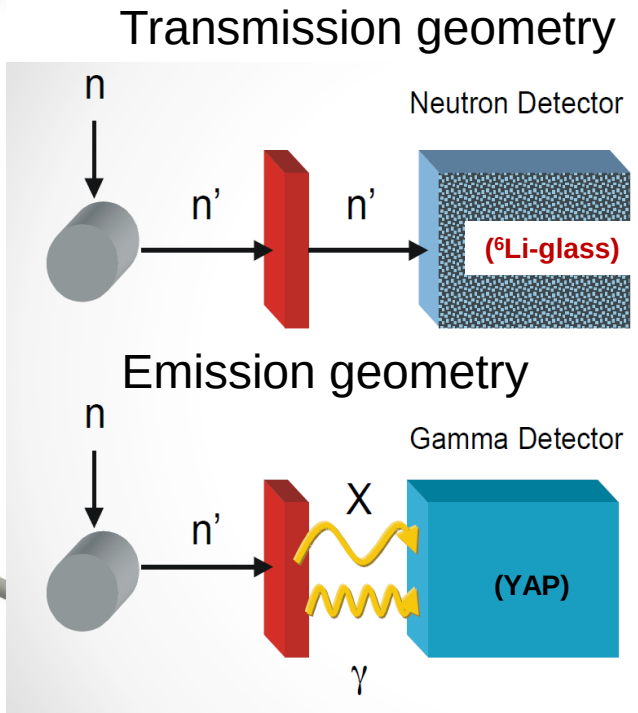


Geometry of eV spectrometers

The **VESUVIO spectrometer**, at the ISIS pulsed neutron and muon source, is an inverted-geometry spectrometer operating in both transmission and emission geometries.







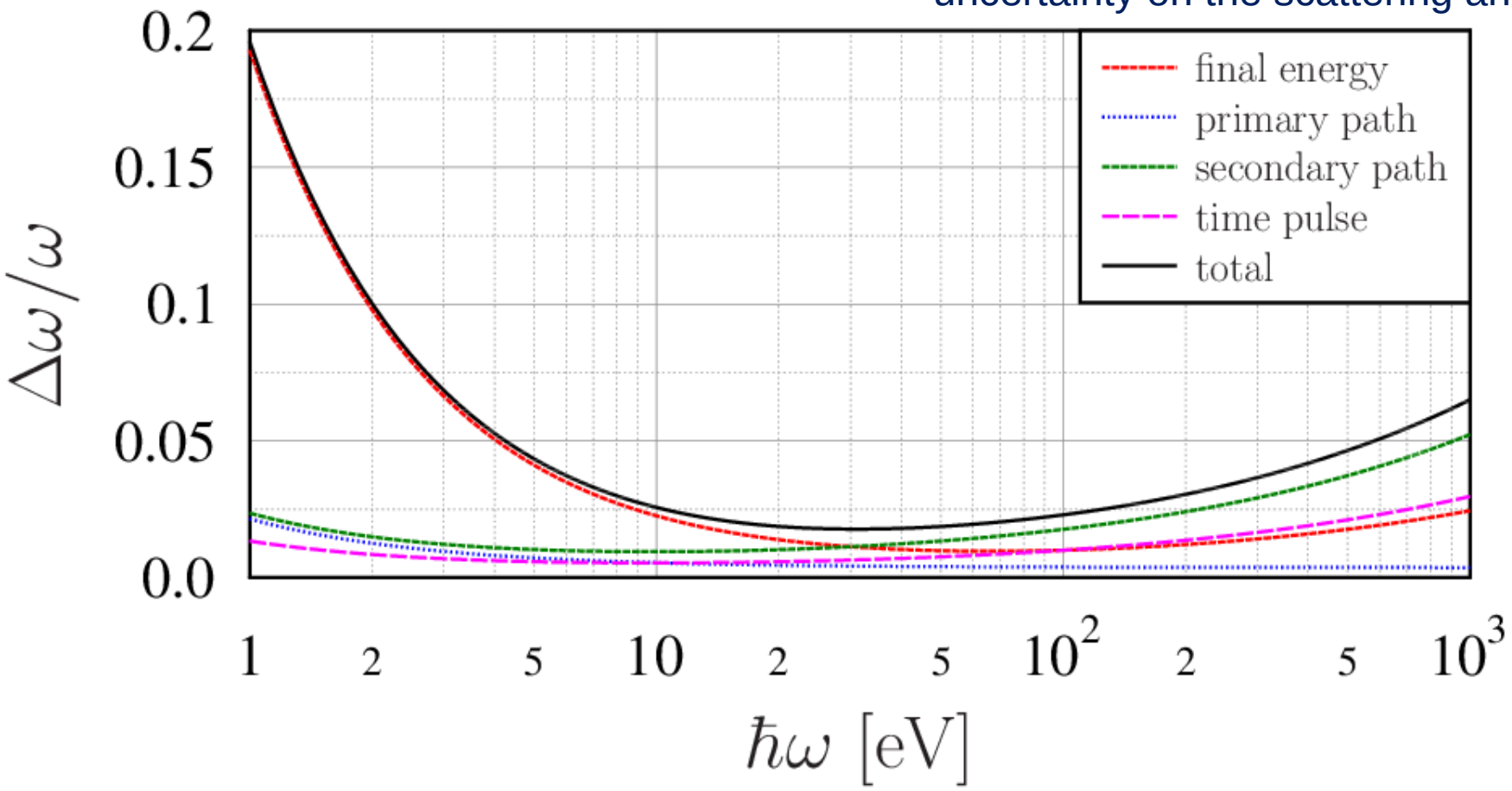
EM Schooneveld

Example of resolution function

The energy-transfer component to the resolution function at an **inverted-geometry** spectrometer is dominated by the contribution from the final energy.

$$y = \frac{M}{\hbar Q}\left(\hbar\omega - \frac{\hbar^2 Q^2}{2M}\right)$$

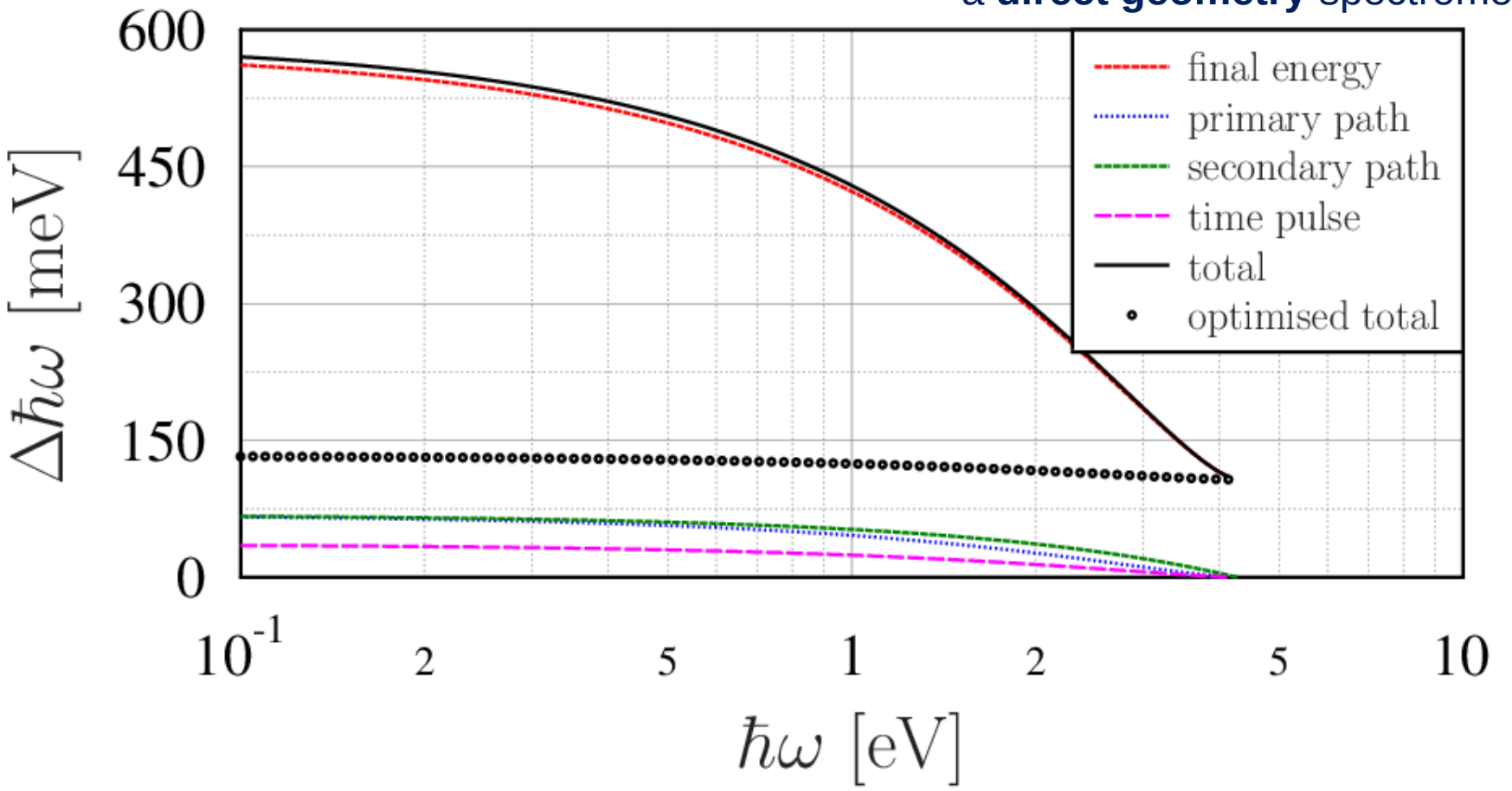
The momentum transfer component is dominated by the uncertainty on the scattering angle.



Example of resolution function

The energy-transfer component is driven by the ratio of the incident and scattered flight paths.

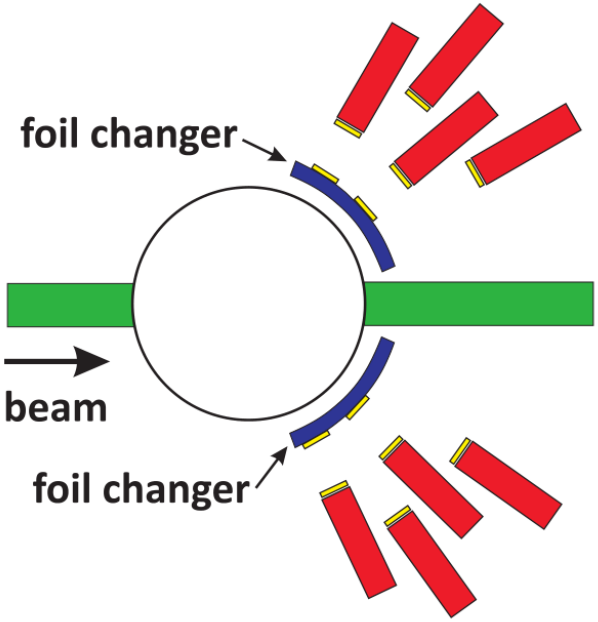
An inverted-geometry spectrometer should have an incident flight path much longer than the scattered one, while the opposite is true in the case of a **direct geometry** spectrometer.

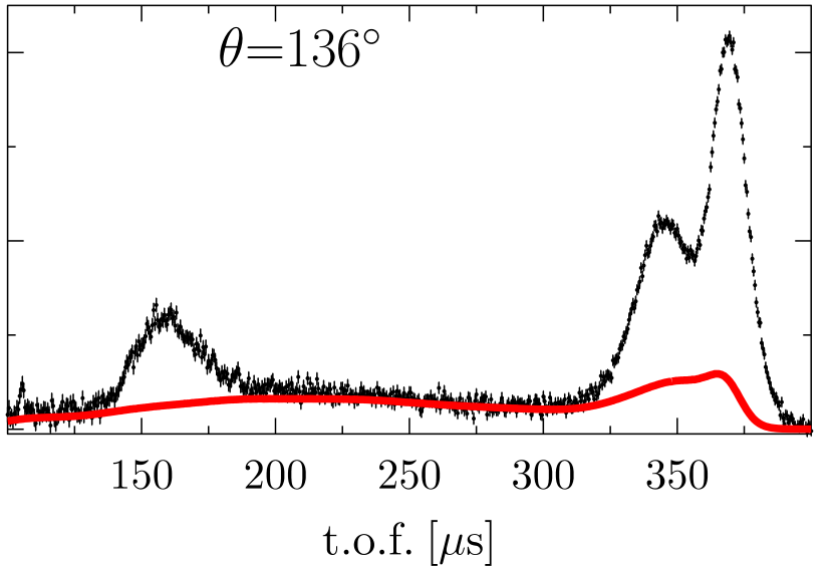


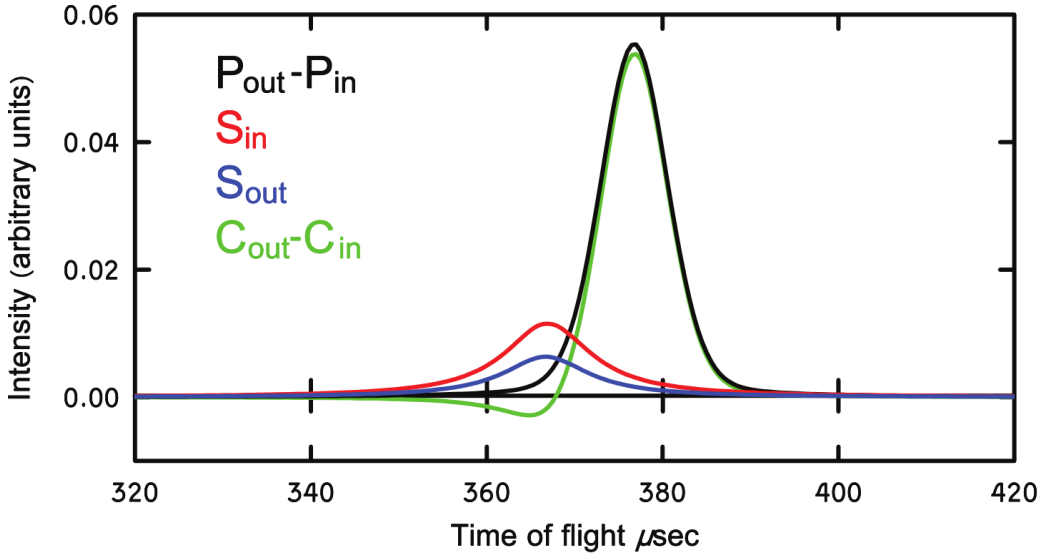
Sample-related backgrounds

A sample-dependent gamma background is generated when the filter foil is cycled in and out the scattering path.

The multiple scattering in deep inelastic neutron scattering can be modelled accurately with MonteCarlo codes, yet it is recommendable to keep the scattering power at about 10%.

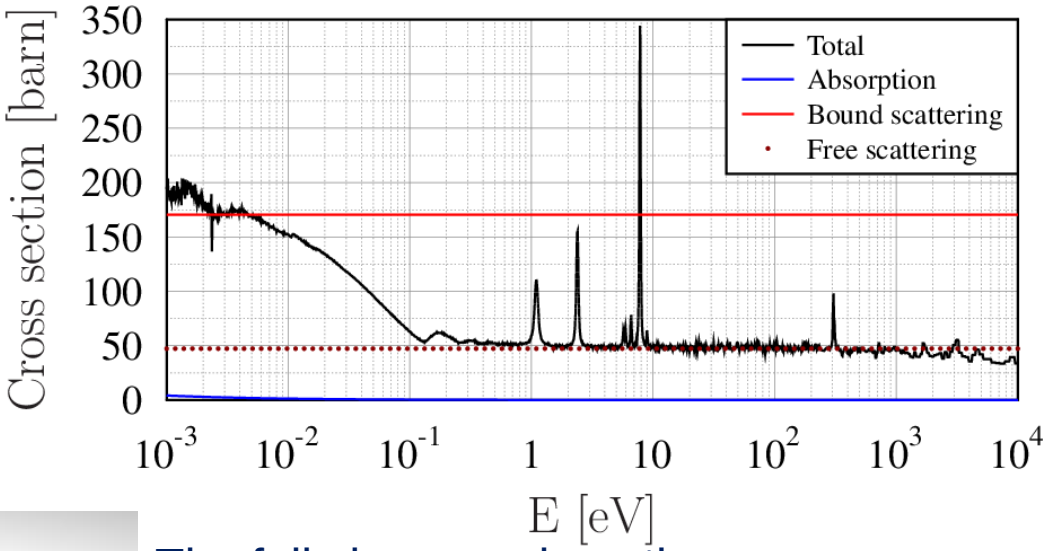


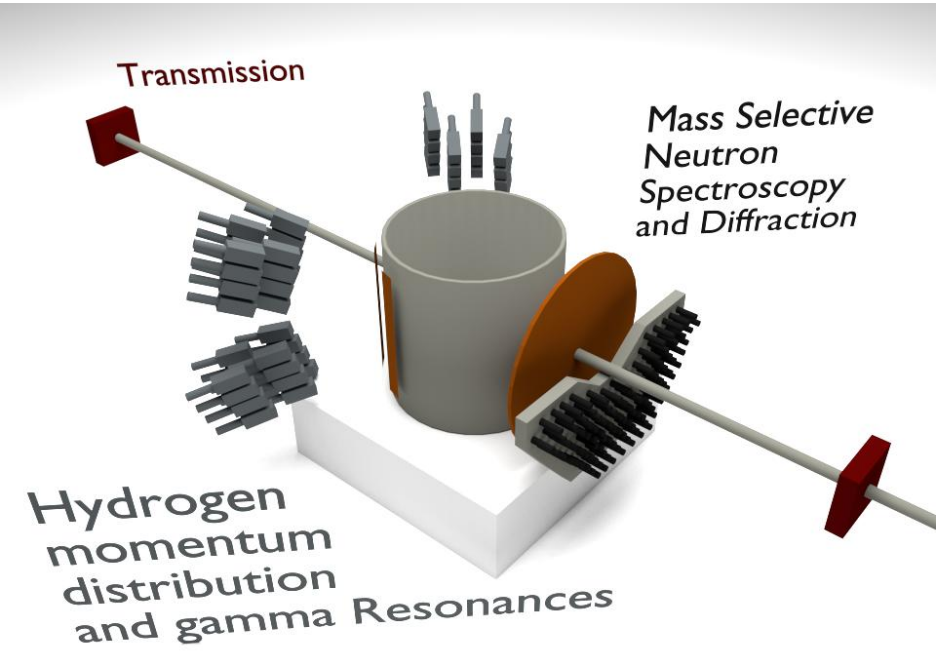




Environmental backgrounds

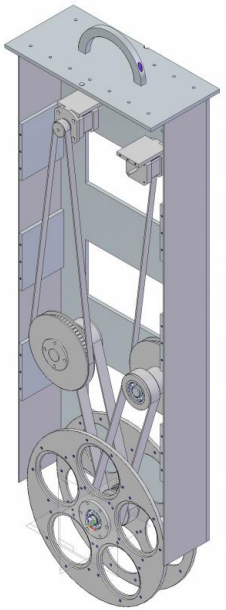
Due to the broad energy range accessed, VESUVIO is a suitable instrument for measurements of neutron cross sections.



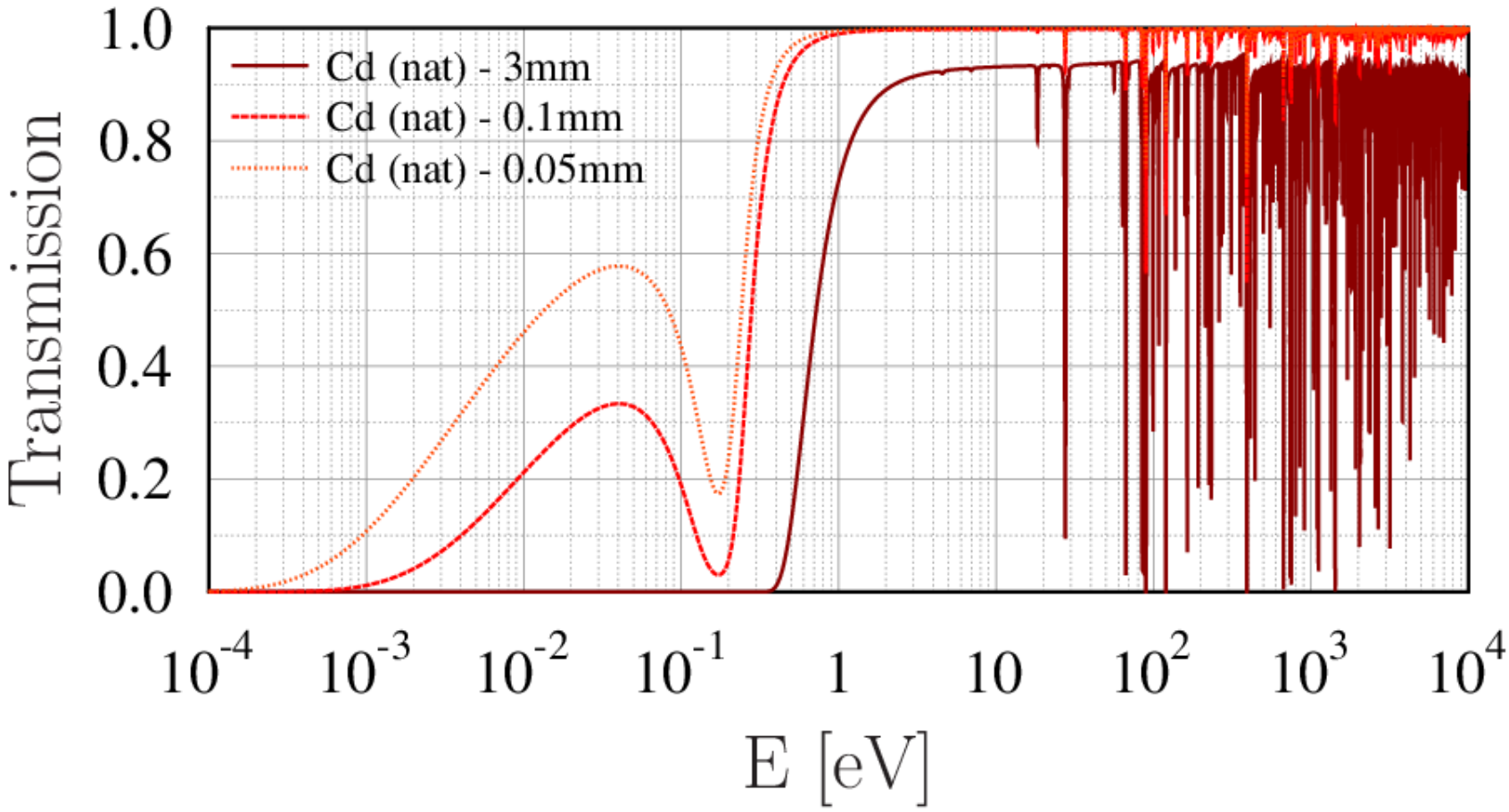


The foil changer along the incident beam (coming soon) will allow:

- The characterisation of the background for transmission;
- The suppression of the gamma background for scattering;
- The test of new foils for direct-geometry spectroscopy.

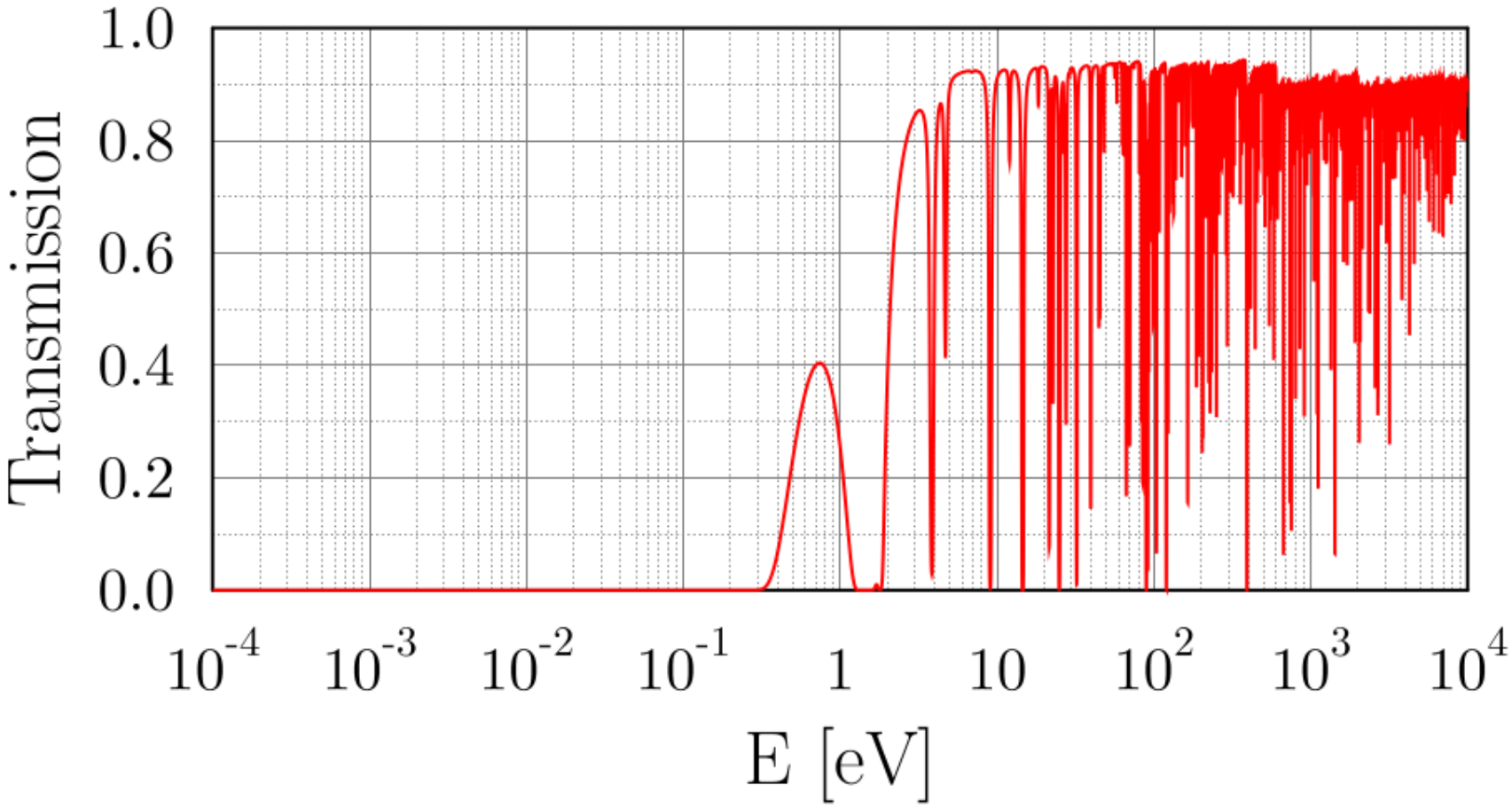


By increasing the thickness of an absorbing material, the sample becomes **back** in specific energy regions, where the number of transmitted neutrons drops to zero.



$$T(E) = exp(-n\sigma(E)d) = \frac{S(E)}{C(E)}$$

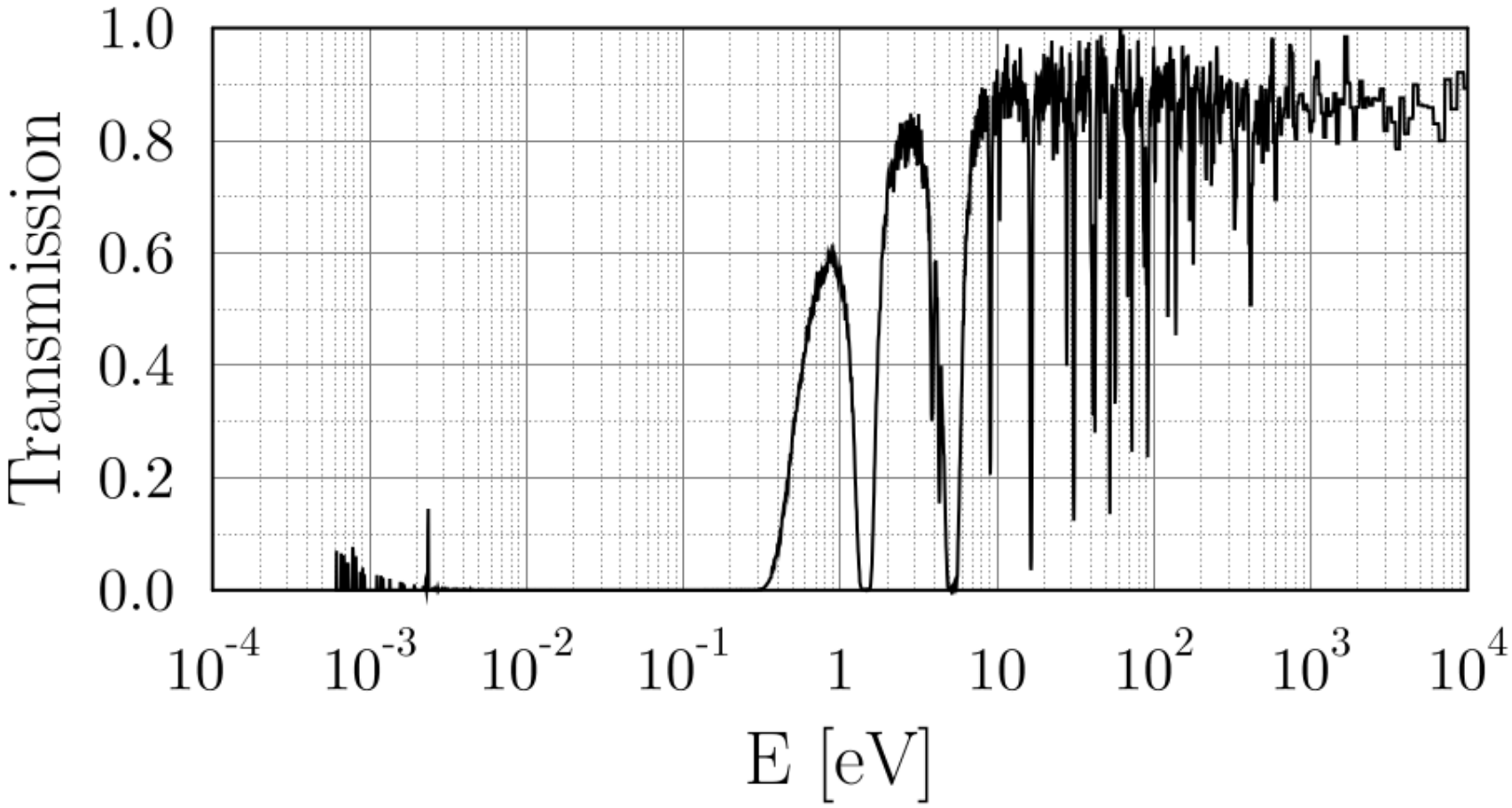
In the case of silver, tungsten, cadmium, or indium with thickness of few millimetres, the neutron transmission in the resonance region should vanish.



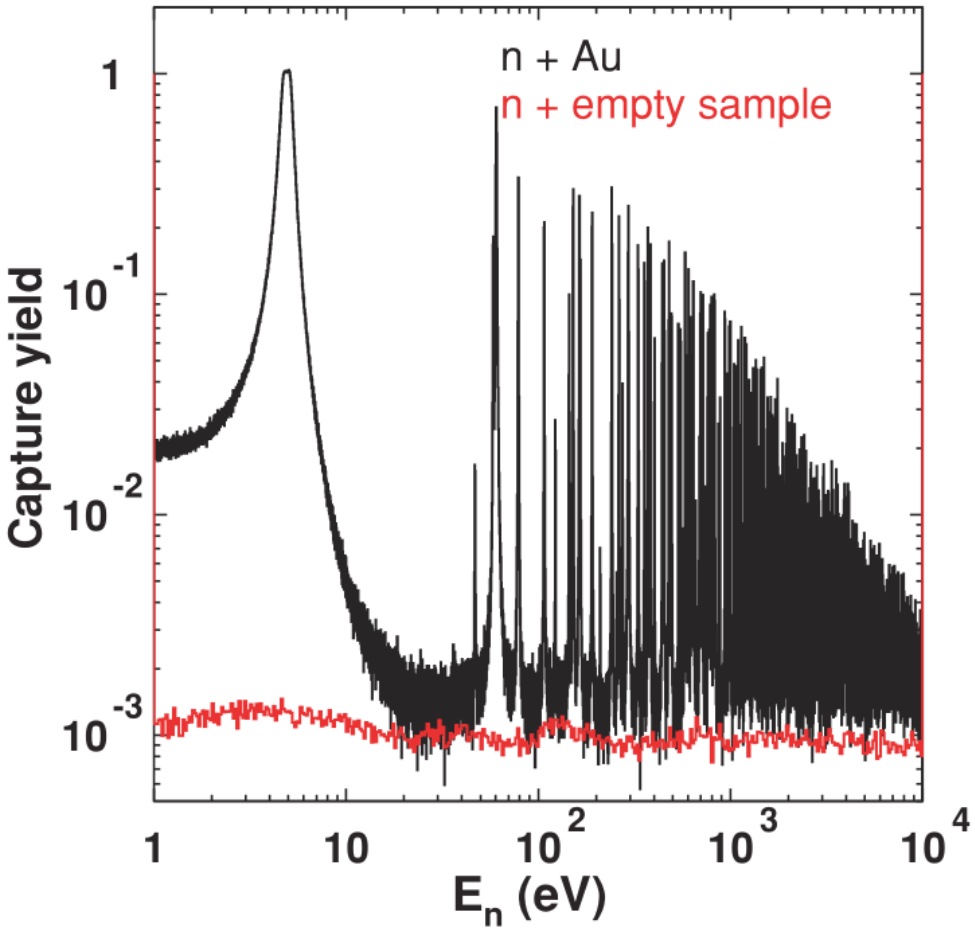
Environmental backgrounds

$$T(E) = exp(-n\sigma(E)d) = \frac{S(E) - B(E)}{C(E) - B(E)}$$

In practice, there is an environmental background that needs to be characterised and subtracted.

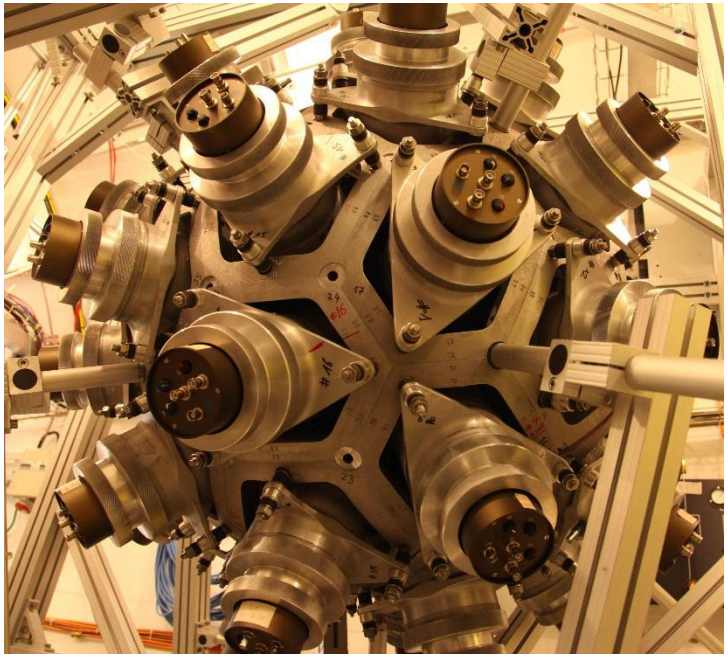


Other electron-Volt spectrometers



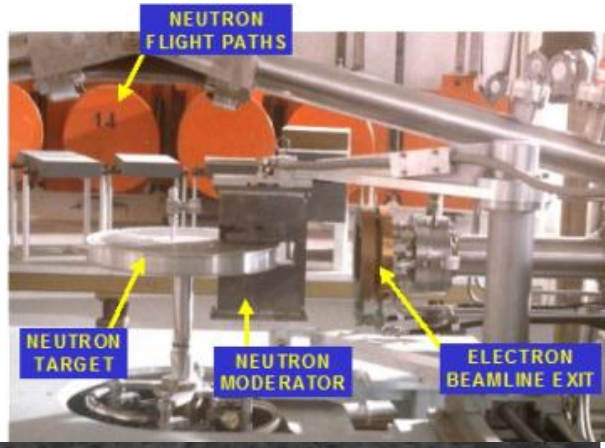
C Massimi and n_TOF Collaboration;
Phys Rev C 81, 044616 (2010)

n_TOF is a 200-meter-long time-of-flight spectrometer at CERN, mainly dedicated for the measurement of neutron cross sections **for nuclear physics** in the energy range from the meV to the GeV.



Other electron-Volt spectrometers

Gelina is the JRC electron linear accelerator in Geel for time-of-flight neutron measurements. The length of the beamlines ranges between 10 and 400 metres, and it is mainly used for nuclear physics.



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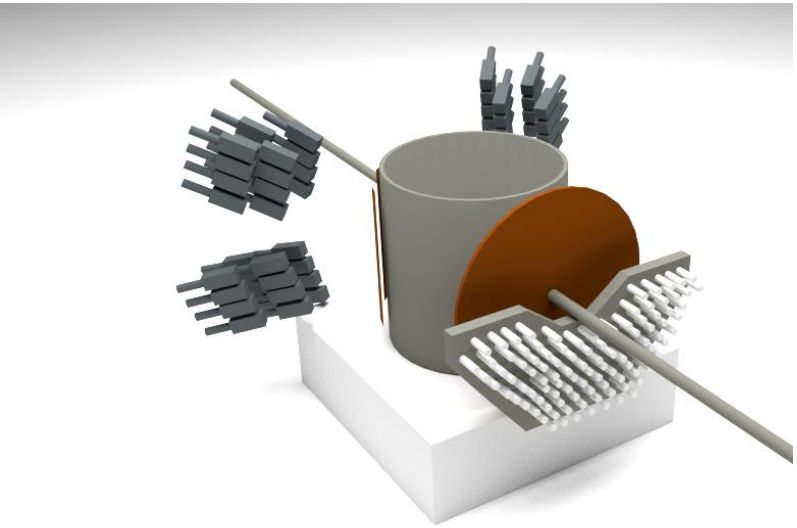
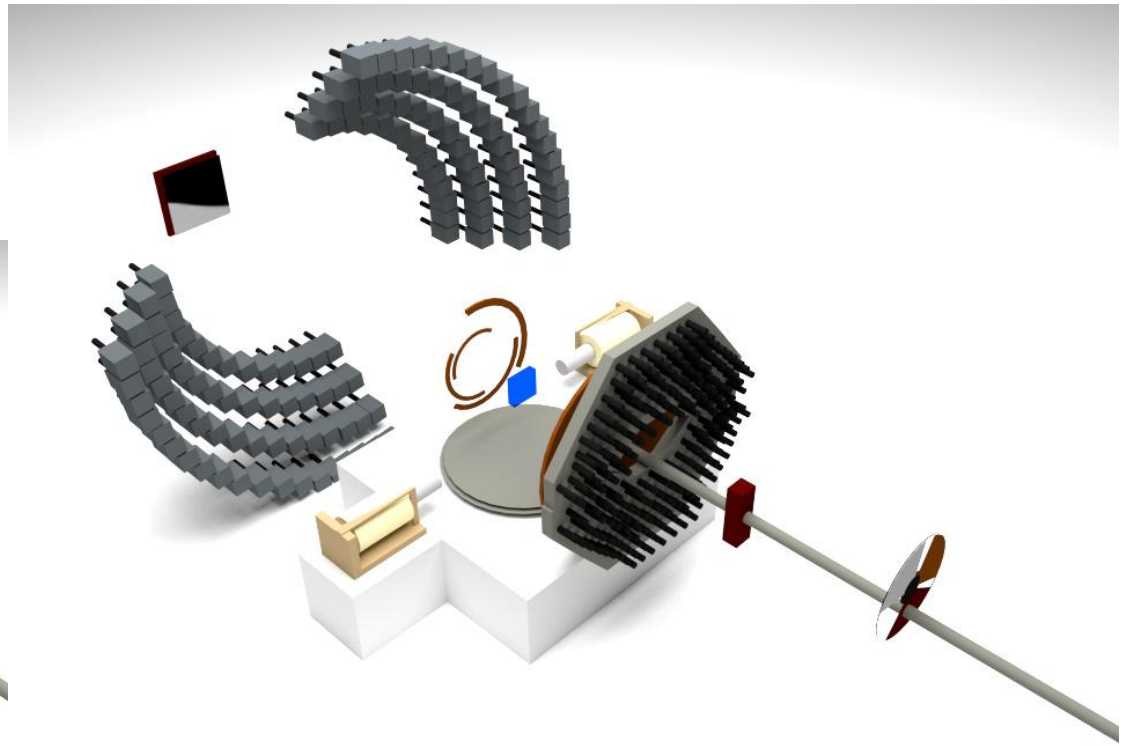
Electron-Volt spectroscopy include unique techniques to characterise the **nuclear quantum effects in condensed-matter systems**.

The technique suffers in the signal-to-background ratios, yet a number of strategies are ready to be used for next-generation electron-Volt neutron spectrometers.

Epithermal neutrons can be used also for elemental analysis and to determine hydrogen uptake levels.





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Thanks