Outline

- Definition/History
- Requirements/Basic limitations
- Experimental method
- Hyperfine interactions
- Examples. \textit{Lots} of examples...
Rudolf Ludwig Mössbauer
Nobel Prize in Physics, 1961

Prize motivation: "for his researches concerning the resonance absorption of gamma radiation and his discovery in this connection of the effect which bears his name."

It was his doctoral research project.
Resonant absorption

When an ensemble of atoms emit photons, several factors affect the observed distribution of energy:

The lifetime of the level(s) sets the “natural linewidth”

\[ \Gamma = \frac{\hbar}{\tau} \quad 10^{-4} - 10^{-8} \text{ eV} \]

Doppler broadening due to atomic motion

\[ \Delta E = E_\gamma \frac{v}{c} \quad 10^{-2} - 1 \text{ eV} \]

Recoil

\[ E_R = \frac{\hbar^2 k^2}{2M} = \frac{E_\gamma^2}{2Mc^2} \quad 10^{-2} - 10^2 \text{ eV} \]
Achieving resonant absorption in optical transitions is easy
In $^{191}$Ir the thermal and recoil effects are comparable

Modify the overlap either by compensating for $E_R$ or by changing the temperature

Rudolf L. Mössbauer
Hyperfine Interactions 126 (2000) 1–12
Fig. 4. Temperature dependence of the absorption. Relative intensity change $\Delta I/I$ in comparison with that of a non-resonant absorber.
Recoil-free emission in a solid matrix

In a zero-phonon event, the recoil momentum is taken up by the entire (massive) crystal with no energy transfer, so the photon emerges with its unperturbed energy and linewidth.
The doppler shift is used only to scan across the natural linewidth of the transition, and not to compensate for recoil – there is none.

Mössbauer tried to bury the result in a fairly obscure german-language journal in an attempt to buy himself more time to work on the effect.

This failed. Utterly
What can you do with a highly monochromatic beam of 10keV–100keV photons?

- Nuclear physics
- Fundamental physics
- Materials
Tests of General Relativity
Tests of Special Relativity
Second-order Doppler shift

\[ \Delta \omega = -\left( \frac{\omega}{2c^2} \right) \times \langle v^2 \rangle \]

FIG. 1. Fractional shift of energy of 14.4-kev gamma-ray absorption of Fe$^{67}$ vs absolute temperature of the metal. The solid line is derived from assuming a Debye temperature of 420°K.
Tests of Special Relativity
Transverse Doppler effect I

MEASUREMENT OF THE RED SHIFT IN AN ACCELERATED SYSTEM USING THE MÖSBAUER EFFECT IN Fe⁵⁷

Atomic Energy Research Establishment, Harwell, England
(Received January 27, 1960)

30,000 rpm

FIG. 1. Schematic diagram of the experimental equipment.

FIG. 2. Comparison of the calculated curve with experimental points. The statistical errors of each point are indicated. The curve was calculated from the parameters given in the text.
Tests of Special Relativity
Transverse Doppler effect II

THE
Physical Review
A journal of experimental and theoretical physics established by E. L. Nichols in 1893

Second Series, Vol. 129, No. 6
15 March 1963

Measurement of the Transverse Doppler Effect in an Accelerated System

Walter Kundt
Department of Physics, Purdue University, Lafayette, Indiana
(Received 15 October 1962; revised manuscript received 4 December 1962)

Fig. 1. Scale drawing of the rotor. The transducer shown was actually turned 90° so that the longer side of the 3×8 mm source was parallel to the axis of rotation.

Consistent within 1.1%

Fig. 6. Comparison of the experimental points with the theoretically expected transverse Doppler shift. The shift in units of the linear Doppler velocity is plotted against the velocity $R_A \omega$ of the absorber. The statistical error corresponds to the radius of the circles.
No discussion of the early fundamental studies enabled by the Mössbauer effect would be complete without this ground-breaking 1968 paper from Nature...

**Possibility of Investigating Movement in a Group of Ants by the Mössbauer Effect**

*NATURE. VOL. 217, JANUARY 6, 1968 96*

T. Bonchev  
I. Vassilev  
T. Sapundzhiev  
M. Evtimov

Faculty of Physics and the Faculty of Biology, Sofia University, Bulgaria.

Received October 31, 1966; revised September 28, 1967.
The glue vapours were toxic to the ants, and the test subjects tended to spray formic acid when handled.

~50 ants in several mesh-based containers at a density of 2.3 ants/cm².
Studying materials
Hyperfine interactions

To be useful in the study of materials, the nuclear energy levels have to be affected by the chemical and magnetic environment of the nucleus.

There are three hyperfine interactions that are relevant to Mössbauer spectroscopy:

- Electric monopole
- Electric quadrupole
- Magnetic dipole
Electric monopole

The nucleus is charged and it is embedded in the electron cloud associated with its host atom.

The interaction with these electrons modifies the energy from that of a point nucleus:

\[ E_c = \frac{Ze^2}{6\varepsilon_0} \left| \psi(0) \right|^2 \left\langle r^2 \right\rangle \]

- s-electron density at the nucleus
- mean-square nuclear radius
In principle, the nucleus can have different sizes in the ground and excited states, and if the chemical environments in the source and sample are different, then the s-electron density at the nuclei can also be different.

\[
v_{res} = \frac{Ze^2c}{6\varepsilon_0 E_\gamma} \left[ \psi_A(0)^2 - \psi_S(0)^2 \right] \left[ \langle r_e^2 \rangle - \langle r_g^2 \rangle \right]
\]

\(s\)-electron densities \hspace{5cm} \text{radii of nuclear states}

Isomer shift
Electric quadrupole

A nucleus with $I > \frac{1}{2}$ will have a quadrupole moment.

An electric field gradient ($e_{fg}$) can lift the degeneracy of the nuclear states and thus split the Mössbauer line.

\[
H_Q = \frac{eQV_{zz}}{4I(2I-1)} \left[ 3\hat{I}_z^2 - \hat{I}^2 + \eta (\hat{I}_x^2 - \hat{I}_y^2) \right]
\]
Electric field gradient

Arises from an asymmetric charge distribution and can come from the atom itself (partially filled shell) or neighbouring atoms.

It is a traceless tensor with components:

\[ V_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j} \]

\[ |V_{zz}| \geq |V_{yy}| \geq |V_{xx}| \]

\[ V_{xx} + V_{yy} + V_{zz} = 0 \]

\[ \eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \]

\( V_{zz} \) and the asymmetry parameter \( \eta \) (0–1) are sufficient to describe it completely.
Magnetic dipole

A magnetic field \( (B_{hf}) \) will lift the degeneracy of any nuclear states that have a magnetic moment \((I > 0)\).

This field could be due to:

- Externally applied field
- Ordered moment on the host atom
- Ordered moment(s) on neighbour(s)
Magnetic dipole

\[ H_M = -\mu \cdot \vec{B}_{hf} = -g_n \mu_N \hat{I} \cdot \vec{B}_{hf} \]
Combined interactions

As the isomer shift just moves the whole pattern left or right (really just changes our “zero”) it combines trivially with the other two effects.

However, the magnetic and quadrupole interactions both move split levels around and their combined action is far from trivial.

If $B_{hf} \approx efg$ and/or $\eta \neq 0$ the problem requires formal solution.
Combined interactions

Furthermore, as both $B_{hf}$ and the $efg$ are vectors, their relative orientation matters (and therefore carries information).
Combined interactions

\[ H = H_M + H_Q = -g_n \mu_N B_{hf} \left[ I_Z \cos \theta + (I_X \cos \phi + I_Y \sin \phi) \sin \theta \right] \\
+ \frac{eQV_{zz}}{4I(2I-1)} \left[ 3I_Z^2 - I + \eta \left( I_X^2 - I_Y^2 \right) \right] \]

Approximations exist for $B_{hf} > efg$, but in general a full diagonalisation of the Hamiltonian is required to get the line positions and intensities right, especially for $\eta \neq 0$. 
Combined interactions

If $B_{hf} \gg efg$ and $\eta=0$, then for the $3/2 \rightarrow 1/2$ transitions the effects are relatively simple, as are the angular effects.

$$\Delta = \frac{eQV_{zz}}{4}(3\cos^2\theta - 1)$$

$\phi$ has no meaning for $\eta=0$
What do I mean by “ordered”?  

Mössbauer spectroscopy is extremely “short sighted”. We only measure changes in the nuclear energy levels, and they really only respond to the 1-s electrons of the host atom. Changes in the host atom (valence, moment...) have significant impacts. The first neighbours are also seen, but less so.

For magnetism, this means that the host state dominates and the nature of the order is irrelevant: Ferromagnetic, antiferromagnetic, spin glass, they all look the same!

The moments need to be “static” but not “organised”.

Some definitions...

- **FM**: All spins are aligned in the same direction.
- **AF**: Every other spin is opposite in direction.
- **FI**: Half of the spins are aligned, but not all in the same direction.
- **SG**: The spins are randomly oriented without any specific pattern.
Impact of these interactions on the $^{57}\text{Fe}$ transition.
How big are the changes?

• Going from Fe$^{2+}$ to Fe$^{3+}$ changes the energy of the emitted $\gamma$ by about $10^{-7}$ eV (about one part in $10^{11}$) – this is a very small effect!

• There is no detector we can build that can even begin to resolve such small changes, so we have to rely on the nuclei to do the work:

Resonant absorption
Mössbauer Spectroscopy

- Uses *recoilless emission* and absorption of $\gamma$-photons by nuclei
- Nucleus *must* be bound in a solid so that momentum-conserving recoil does not modify the $\gamma$ energy
- Maximum useful $\gamma$ energy is about 100 keV as recoil is unavoidable above this energy

- Nuclear $\gamma$s are *extremely* monochromatic ($1:10^{12}$ is typical)
- This allows us to exploit the hyperfine interactions between a nucleus and its atomic environment to study a solid
Tuning $\gamma$ energies

- Nuclei do not come with knobs to adjust the emission energy
- Fortunately, the hyperfine interactions that we use have very little impact on the transition energies
- Sweep the $\gamma$ energy by Doppler shifting it
- Required velocities are a few, to a few 10’s of mm/s (hence the odd axes on Mössbauer plots)
Conventional absorption spectroscopy

- Shine the monochromatic beam of $\gamma$’s through the sample
- Monitor the transmission as a function of energy (Doppler velocity)
- Where the incoming energy matches a transition in the sample, resonant absorption occurs and the transmitted intensity is reduced
- Collect the pattern, fit, interpret
- Repeat as necessary
Accessible isotopes

- Need the isotope to exist naturally ($^{237}$Np)
- $8 \text{ kev} < E_\gamma < 100 \text{ kev}$
- Need a convenient parent isotope ($^{55}$Mn)
- Element needs to be “interesting” ($^{83}$Kr)

$^{57}$Fe is the isotope of choice

- Magnetism
- Metallurgy
- Chemistry
- Biology
- Geology...
$^{57}\text{Fe Mössbauer}$
Instant Mössbauer
Accessible isotopes

Mössbauer Spectroscopy Periodic Table

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Number of publications
- N > 1000
- 100 < N < 1000
- 10 < N < 100
- N < 10
- Silent

Mössbauer Effect Data Center
Tel: (828) 251-6617 Fax: (828) 251-1719 Email: medc@unca.edu Web: www.unca.edu/medc

Commercial sources
Room temperature work
What is wrong with the others?

• Typically they have short-lived parents, so commercial sources are not available

• Higher $\gamma$-energies means that the $f$-factor at room temperature is effectively zero and both source and sample must be cooled
Loss of signal from recoil at higher energies is a serious problem.

In many ways the 103keV transition in $^{153}$Eu is quite attractive (efficient decay, lots of activity from the 47-hr $^{153}$Sm source) but the f-factor is terrible and the resolution is not as good as that provided by the 21.6keV transition in $^{151}$Eu. However, the count rates for $^{151}$Eu are poor at best.
Conventional Mössbauer

- Done in transmission mode
- Resonance is detected by loss of transmitted intensity
- Need about 20mg of Fe (for $^{57}$Fe)
- Easily adapted to work in magnetic fields or at low temperatures
- Almost all Mössbauer resonances can be used in this mode
Typical spectrometer components