6.1 SPECTROSCOPY AND SCATTERING AS PROBES OF MATTER

Much of our information on the structure of atoms (and indeed of matter generally) comes from experiments that are categorized as "spectroscopy" with radiation as the probe, or as "scattering" in which particle projectiles are the tools for examination. It is advantageous to show the parallels between these methods by discussing them together.

In this section we use the term "electron" to represent a generic projectile in scattering experiments, but much of what we discuss also applies when the incident particles are ions or neutral atoms. We are here using the "atom" to represent a generic, massive particle that has internal degrees of freedom; thus the "atom" almost always stands for "atom or molecule" and could apply to either projectile or target.

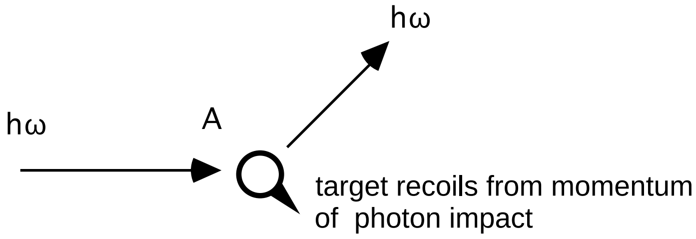
The photons of most interest to us are quanta of electromagnetic radiation in the range between VLF radio waves (10^4 Hz) to X-rays (10^{20} Hz, below the threshold for pair production). Moreover, our focus is on phenomena in which electron energies are well below 100 keV, so relativistic effects enter our discussion in only a minor way.

Inelastic scattering can occur only if the incoming projectile has enough energy to excite one of the states of the target. Thus, for example, thermal energy scattering processes involving atomic helium (first excited state near 20 eV) are wholly elastic. But heavier atoms, and especially molecules, have numerous low-lying excited states and so are likely to undergo inelastic processes.

Elastic Processes

PHOTONS: Rayleigh Scattering

Rayleigh scattering is an elastic process in which the photon scatters with minimal coupling to the internal degrees of freedom of the target. This interaction between the incident radiation and blob of charge (the atomic electrons) is conceptualized without particular regard for the particular properties of the atom.

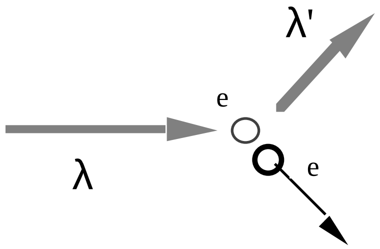


$$\hbar\omega + A \xrightarrow[\textit{elastic}]{} \hbar\omega + A$$

Fig 6.1.1 Rayleigh scattering.

PHOTONS: Compton Effect

A photon has momentum h/λ that enters into the description of radiative interactions. A photon, if elastically scattered from a target, transfers some of its momentum to the target and this shows up as longer wavelength in the scattered photon. This effect is quite small when photons of visible light scatter from massive atoms. However when X-rays are incident, it appears that scattering is from essentially free electrons within the target material (to first order, the electron's binding to the parent atom is a negligibly small). This wavelength shift (first seen by A.H. Compton in 1923) is called the Compton effect.



$$\Delta\lambda = \underbrace{\left(\frac{h}{mc}\right)}_{\text{"Compton wavelength"}} (1-\cos\vartheta)$$

Fig 6.1.2 Electron recoil diminishes photon energy in Compton Effect

The Compton wavelength shift $\Delta\lambda$ depends on the photon scattering angle θ. The shift is expressed in units of the *Compton wavelength* λ_C=(h/mc).which is the wavelength of the photon that has an energy equal to the rest mass the electron.

ELECTRONS: Simple elastic scattering

Electron scattering resembles the Rayleigh scattering of photons, but the momentum transfer is usually more significant. The simple elastic interaction between a blob of charge (the atomic electrons and their nucleus) and the incident electron, is conceptualized without particular regard for the internal degrees of freedom of the atom. The probability for scattering, expressed as a cross section as a function of scattering angle and incident electron energy, depends on the size and shape of the atomic charge distribution.

COMMENT: Unifying The Views Of Electron And Photon Scattering

Electromagnetic coupling governs the collisional interaction between a target atom and an electron projectile The coupling strength is specified by the magnitude of the fundamental charges in both projectile and target. But how can we unify this view with our concept of scattering photons, given that photons have zero charge?

An observer on the atom can describe the effect of the incoming electron as creating a electric field pulse with a duration of (atomic diameter)/(electron velocity) $\approx 10^{-17}$ sec. This pulse, Fourier analyzed, can then be regarded as a shower of photons. over a wide range of frequencies around 10^{+17} Hz. Photon density, as we have seen, relates to $|\mathbf{E}|^2$ so it is this photon-associated field (whether monochromatic from a laser, or broad band form the incoming electron) that couples to charges within the target.

Resonance Scattering

Elastic Resonance Scattering

The scattering process becomes more intricate (and the cross sections become much larger) when the incoming projectile (photon or electron) has an energy that closely matches the excitation energy of one of the target's internal degrees of freedom. Resonance scattering is the name of the process in which the target, absorbing energy from the incoming projectile, goes to an excited state, remains there for a short while, and then de-excites, giving the energy to an outgoing projectile of the same sort, for example in the elastic resonant process:

$$\mathbf{e} + \mathbf{A} \rightarrow (\mathbf{A}^*) \rightarrow \mathbf{A} + \mathbf{e}, \qquad \text{or the inelastic} \qquad \mathbf{e} + \mathbf{A} \rightarrow (\mathbf{A}^{**}) \rightarrow \mathbf{A}^* + \mathbf{e}$$

Elastic resonance scattering conserves energy as does a simple elastic process: Aside from effects of momentum transfer (very small in most cases that interest us here) the incoming and outgoing projectiles have the same energy E. However the internal structure of the target plays a large role and resonance scattering is typically seen as a peak in plot of scattering probability *vs*. incoming projectile energy, the peak occurring when the projectile energy is near to the energy difference ΔE(A-A') between the ground and excited states. .

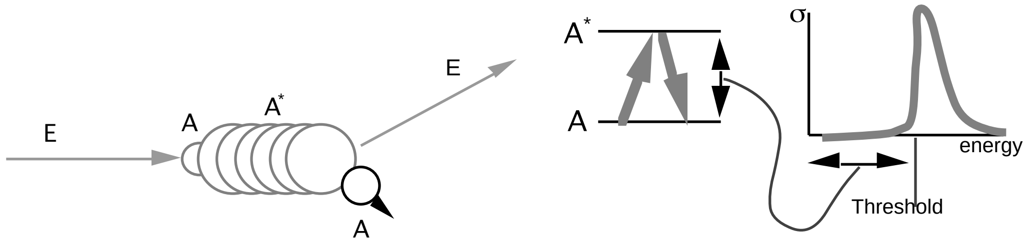


Fig. 6.1.3 Elastic Resonance Scattering Process

$$\hbar\omega + A \longrightarrow (A^*) \longrightarrow A + \hbar\omega$$

The resonance scattering has a significant probability when the incoming energy is a close match for one of the energy level differences of the atom.

> In the simplest instances, the process is regarded as an absorption of the energy to create the excited atomic state A* which subsequently de-excites, giving the energy (less the loss from momentum transfer) to an identical outgoing photon/particle.
>
> Sometime this heuristic, step-wise picture is not adequate. For example, if the atom has two closely-spaced excited states A* and A** at the appropriate energy, there are interference effects that arise from indistinguishable paths
>
> $$[\mathbf{h}\nu + \mathbf{A} \rightarrow (\mathbf{A}^*) \rightarrow \mathbf{A} + \mathbf{h}\nu] \quad \text{and} \quad [\mathbf{h}\nu + \mathbf{A} \rightarrow (\mathbf{A}^{**}) \rightarrow \mathbf{A} + \mathbf{h}\nu]$$
>
> leading to the same event. This interference in photon resonance scattering, conceptually similar to two-slit interference, was discovered at the University of Michigan in 1960 by Colgrove, Franken, Sands, and Lewis. It is the basis of the powerful technique of Level Crossing Spectroscopy.

Electron-Atom Resonance Scattering: Elastic and Inelastic

The electron resonance scattering process has a significant probability when the incoming electron energy is a close match for one of the energy level differences between the ground state of the atomic target and the excited state of the target atom's negative ion. The process is regarded as the formation of a temporary bound state of the incident electron to the neutral atom thereby creating a short-lived, excited negative ion; this excited ion then decays a short time later by emission of an electron .

> The electron may leave with an energy equal to the original with the atom returning to its ground state. This is an essentially elastic process.
>
> The electron may leave with an energy lower than the impact energy and the atom may be left in an excited state that will later decay in some manner.. This is obviously an inelastic scattering process.

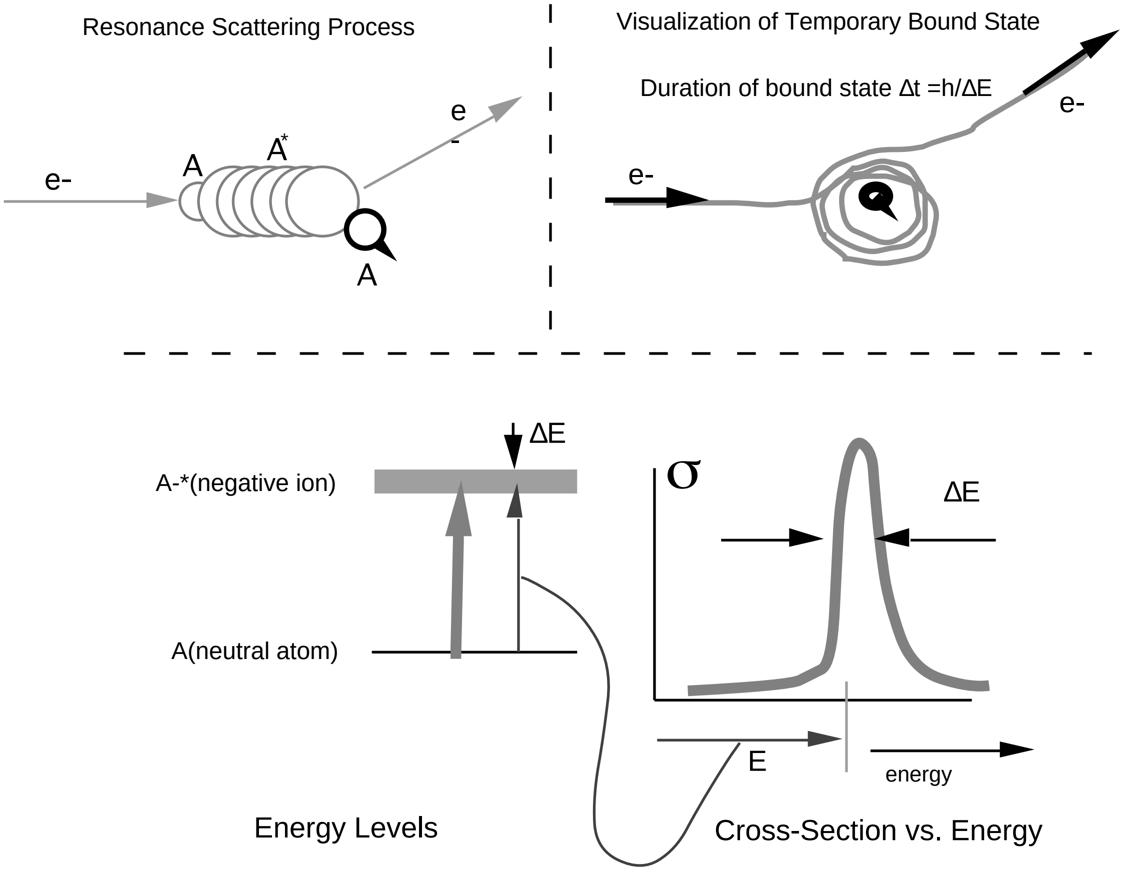


Fig 6.1.4 Electron Resonance Scattering: Formation of Temporary Bound State of Negative Ion

Resonance scattering occurs only if the incoming electron having enough energy to excite the atomic ion state. As one would expect from the Heisenberg uncertainty principle, the width of the scattering resonance ΔE depends inversely on the lifetime Δt of the negative ion state.

Inelastic Processes

Resonance absorption

Resonance absorption is a process in which the energy and momentum of the photon is simply absorbed by the atom and we observe the final state of the atom as A*. We can regard this as the first step of a resonance absorption where, for some reason, the atom does not de-excite before the measurements are done. In the long term, of course the atom will de-excite in some manner, perhaps by collision or by radiative decay.

This process does not occur unless there is a very close match between the energy of the incident photon and an energy level difference in the atom.

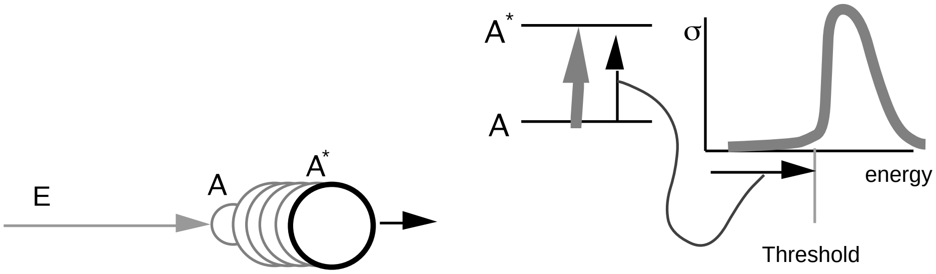


Fig 6.1.5: Resonance absorption

$$\hbar\omega + A \longrightarrow (A^*)$$

Inelastic resonant processes

Inelastic resonant processes are those in which an projectile incident on a target in state A excites a state A** which then decays rapidly to a lower excited state A* that is differs in energy from the original state A. The energy E and the difference E-E' are measured in order to determine the values of the energy levels in the target.

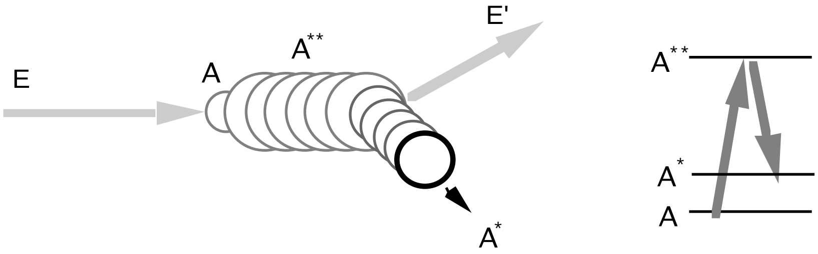


Fig. 6.1.6: Inelastic resonant processes

$$E + A \longrightarrow (A^{**}) \longrightarrow \underbrace{A^*}_{\textit{decays later}} + E'$$

Here the lower excited level A* may itself decay back to the original state A by emission of another photon; alternatively the state A* may persist until it loses its energy in some non-radiative (e.g. collision) process.

Raman Effect as Inelastic resonant process

If optical radiation (photon energy E≈ 2eV, easy to measure) excites a level (A**) in molecule that has numerous sublevels (A_1* A_2* …) just above its ground state, then examination of the scattered visible radiation (Raman spectroscopy) can reveal the structure of the low lying levels.

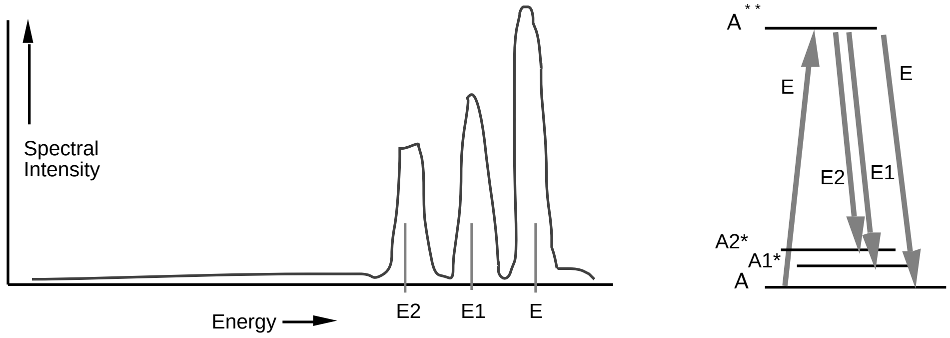


Fig 6.1.7: Raman Spectrum and the associated Energy Level Diagram

The processes are (E+**A**→**A****→$\mathbf{A}_1$* +E_1'), (E+**A**→**A****→$\mathbf{A}_2$* +E_2'), etc., where E1, E2 differ from E only slightly and thus give a good measure of the levels $\mathbf{A}_1$* $\mathbf{A}_2$* ….

If the E1, E2, … photons are only slightly lower in energy than the incident photon of energy E, then all lines (including the resonantly scattered E) will show up on the same spectral scan This is an important method of molecular spectroscopy since the low lying levels are typically ≈0.1 eV above the ground state and are thus hard to measure directly.

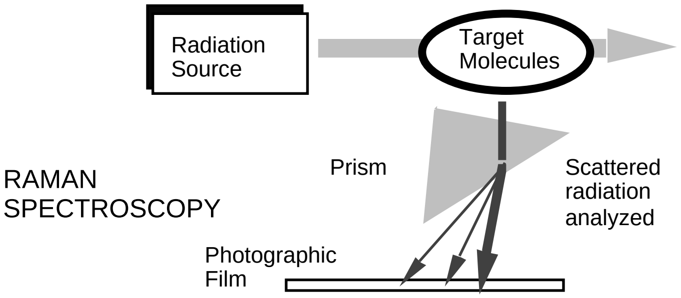


Fig. 6.1.8: The Raman method, originated for the study of molecules with optical spectrometers, has its parallel in the gamma-ray spectroscopy for the study of nuclear energy levels.

Inelastic Electron-Atom Scattering correlated with Optical Spectroscopy: The Franck-Hertz Experiment

The Franck-Hertz experiment is one in which electrons of known, variable energy E are sent into a gas (mercury vapor). The energy E' of the outgoing electrons is measured. The energy loss ΔE is plotted as a function of E, and one finds a pattern that reveals the energy level structure of the mercury atom. The interpretation is aided by doing optical spectroscopy on the collisionally excited gas: Peaks in the ΔE vs. E plot correlate with the onset of appropriate lines in the optical spectrum of radiation emitted from the mercury atoms.

Photoionization

Photoionization is the microscopic limit of the photoelectric effect as done on a single atom. For this process to occur, the photon energy must exceed the ionization energy (Φ) of the atom. The extra photon energy goes into the kinetic energy of the outgoing electron: $E_{kinetic}=h\nu-\Phi$

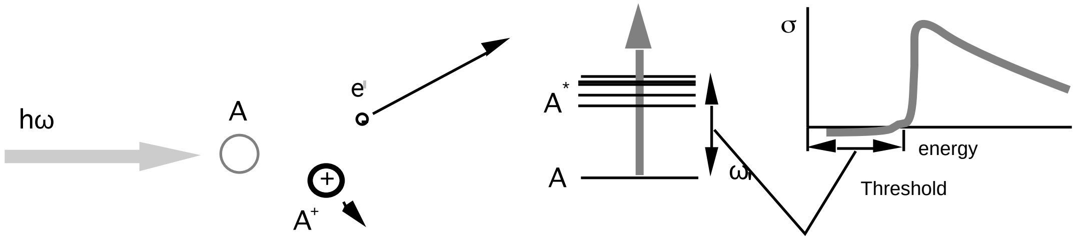


Fig. 6.1.9: Photoionization

$$\hbar\omega + A \longrightarrow A^{+} + e^{-}$$

Multiphoton ionization: It should be mentioned that modern light sources make it feasible to arrange that 2, 3, 4, …20 photons act together to ionize a target atom.

Electron impact ionization $e + A \rightarrow A^{+} + 2e$

Electron impact ionization is an important process:

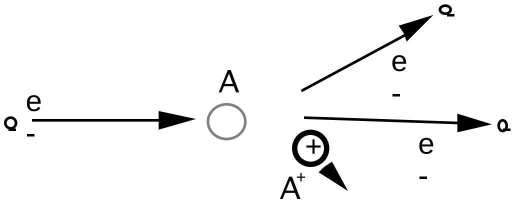


Fig. 6.1.10: Electron Impact Ionization

$$e^{-} + A \longrightarrow A^{+} + 2e^{-}$$

This process may be as simple as having the valence electron of the atom knocked off by the incident electron. On the other hand, if the incident electron has enough energy, it is possible that one of the inner electrons of the atom will be knocked out. If that happens, the atom rearranges itself to fill that inner vacancy, usually with the transition of an outer electron to the inner location. This transition is accompanied by the emission of an energetic photon of well-defined wavelength.

InteractIon of Photons & Electrons with Solids

Projectiles of well defined wavelength may show clear diffraction patterns if they are incident on solids that have a spatial regularity in their structure. This general field, although outside our nominal scope, has interesting connections to our main topic. Notable examples include

Elastic interactions

1. Two-source interference

Two-slit diffraction, reflection from the two surfaces of thin films, and diffraction around the two sides of a thin wire are commonly seen in with visible radiation and are now also measurable with beams of neutral atoms. .

2. N-sources on a plane interference

Ruled diffraction gratings (e.g. the playing surfaces of a compact disc) give striking effects for visible radiation; comparable effects are seen with electrons, neutrons, and neutral atoms.

3. N sources in a volume interference

X-rays are diffracted by the regular array of atoms in a single crystal. This is called "Bragg Scattering". Analogous effects are seen with neutrons. We often regard these as purely elastic processes, but there are interesting diffraction situations where small amounts of energy and momentum are exchanged between the radiation and the solid.

Inelastic interactions

1. Interactions with Surfaces

A clean surface can be given a monolayer coating, and that coating acts like a two-dimensional system upon which experiments can be performed. Scattering of particles or of photons can be inelastic, with discrete energy losses showing the structure of the 2D target system.

2. Interactions with Solids

radiation/particles scattered from a solid (whether from the surface or from the bulk) can undergo discrete shifts to longer wavelengths if the radiation/particles excite internal modes of vibration in the solid. This is analogous to the Raman effect seen when light scatters from individual molecules.

Apparatus & Techniques
for
Spectroscopy And Scattering

When working on theoretical topics, it is a good idea to ask from time to time how experiments are actually done. We list here some topics regarding apparatus and methods because they are so often relevant to the interpretation of quantum mechanics. Some of the most important points will be covered in lecture, but other reference works must be consulted for details.

A. Instrumentation for Scattering Experiments:.

1) Sources :[ions, electrons, positrons ...], both pulsed and continuous

2) Analyzers [momentum, energy, ..] with E and B fields and with timing devices.

3) Targets [thin foil, gas, crossed beam ...] in which single collision processes will dominate.

4) Detectors for ions, electrons, and photons: Photographic emulsions, Particle/photon multiplier, ionizer + mass spectrometer, ionization chamber, scintillation counter, proportional counter, spark chamber, bubble chamber, wire chamber, photographic emulsion ...]

B. Instrumentation for Conventional Spectroscopy:

1) Sources [microwave, IR, visible, uv, X, gamma]

2) Analyzers [tuned circuits (lumped or distributed), resonant cavities, prisms, grating, thin films, crystals]

3) Targets for study of atoms individually [gas or beam]

4) Detectors: mechanism depends on wavelength

a> infra-red detected by heat
b> near IR, visible, uv, soft x-rays photoelectric effect.
c> hard x rays, gamma rays with ionization detectors

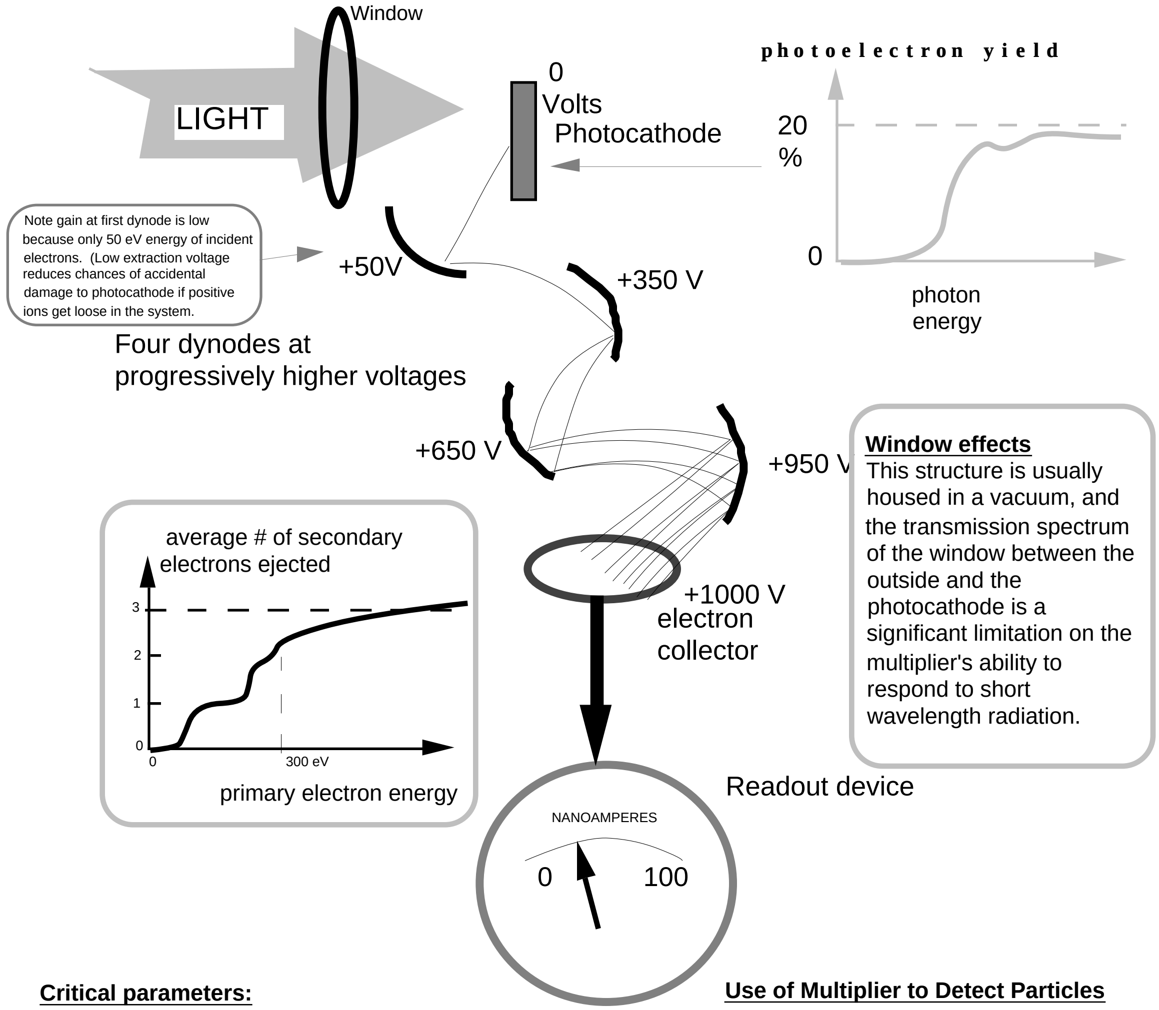
C) Alternative Spectroscopic & Scattering Methods:
Multiple Beam Laser Spectroscopy

Nuclear Magnetic Resonance, Electron Paramagnetic Resonance

Atomic Beams etc. Can be conceptualized as a scattering experiment in which atoms are scattered from photons, with the count of scattered atoms (vs. radiation frequency) comprising the output data.

Classics in the History of Spectroscopy:
a) Emission from flames [Bunsen & Kirchhoff]
b) Absorption in sun's outer layers [Fraunhofer]

The photomultiplier is a paradigmatic detector that is found in various forms in many experiments. An input photon can liberate an electron provided that the photon energy exceeds the work function of the photocathode. The photoelectron, once liberated, is accelerated and produces further secondary electrons as in an avalanche, and the net effect is that the original , feeble photon produces a hugely measurable effect.



Note gain at first dynode is low because only 50 eV energy of incident electrons. (Low extraction voltage reduces chances of accidental damage to photocathode if positive ions get loose in the system.)

Four dynodes at progressively higher voltages

Window effects
This structure is usually housed in a vacuum, and the transmission spectrum of the window between the outside and the photocathode is a significant limitation on the multiplier's ability to respond to short wavelength radiation.

Critical parameters:

Photoelectric threshold and photon-photoelectron efficiency of cathode
(depends on choice of cathode material and condition of cathode surface)

Secondary electron yield of dynodes
(depends on kinetic energy of incoming electron [i.e. on interdynode voltage] and on dynode material and surface condition.)

Use of Multiplier to Detect Particles

The structure described here is also used to detect charged particles (electrons, protons, positive and negative ions) and metastable atoms (e.g. He(2S). The particle to be detected is incident on the cathode, and if it has enough kinetic energy (> 30 eV) or enough metastable state energy (>6 eV) to eject an electron, then the multiplier structure can generate a cascade. A current pulse out of the last dynode is the signature of the arrival of photon (or particle) at the photocathode.

Fig 6.1.11: Operation of a Photomultiplier

6.2 HOW DO WE OBTAIN SPECTRAL LINES?

Spectral lines arise from the emission or absorption of radiation at a relatively well defined frequency . It is assumed that such lines arise when a sample of atoms of a given type undergo transitions between two energy levels. Spectral patterns are interpreted in terms of such energy level diagrams.

Emission Spectra

Simplest source of spectral lines is to have a self-luminous sample and then pass the emitted light through a prism. If the source is merely a hot object, one may get only a broad, thermal distribution of radiation. But if one takes a piece of paper, soaks it in salt water, and then holds this wet paper in a flame, then one sees the strong orange lines of the spectrum of sodium *emitted* from the sample:

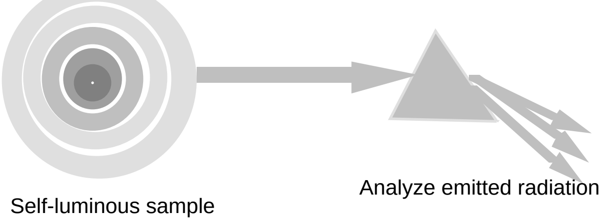


Fig. 6.2.1 Simple emission spectroscopy

Absorption Spectra

It is also possible to have a sample of atoms absorb certain wavelengths and from that deduce properties of the source and of the absorbing atoms:

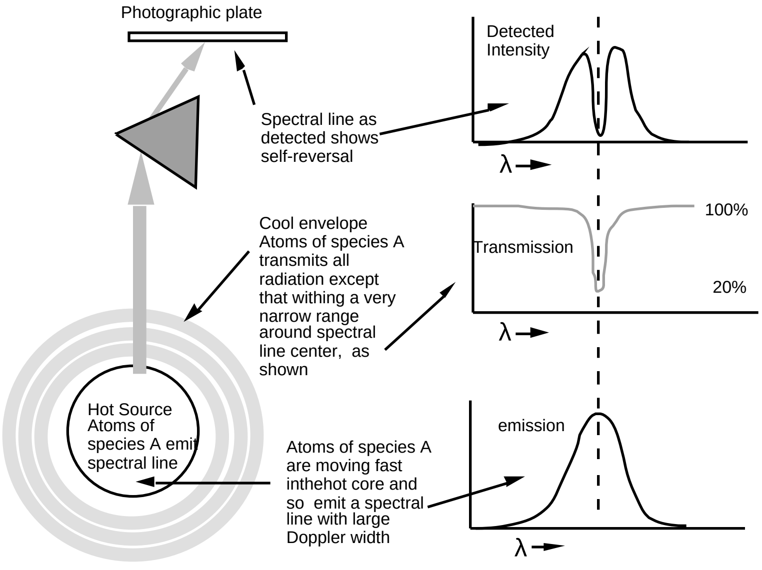


Fig 6.2.2 Simple Absorption Spectroscopy

A hot source, for example the sun, radiates a continuous spectrum with a broad spectrum. The outer regions of the sun are comprised of atoms of the most abundant solar constituents, and these atoms, being in a relatively cooler gas, are more likely to be in their ground state. These atoms in the envelope then absorb, selectively, from the broad spectrum of the core's radiation at wavelengths that are characteristic of the envelope atoms. This is the origin of the Fraunhofer's dark lines in the solar spectrum, first seen in the early 1800's. .

Absorption Spectra

A more controllable method of spectroscopy is to separate the sample cleanly from the source of radiation,

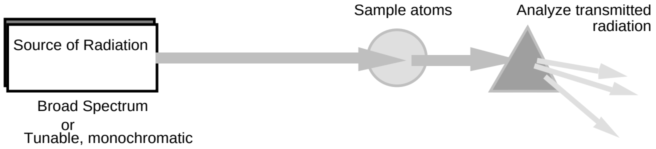


Fig. 6.2.3 Absorption Spectroscopy with radiation source separated from sample

This is a straightforward, frequently used method in which the source of radiation may be broad band (for example a hot object) or narrow band (e.g. a laser) The drawback of this method is that much of the radiation incident on the analyzer has had no interaction with the sample; it just passes through and forms a strong, irrelevant and noisy background signal. The spectral lines are seen as *reductions* in the intensity of detected light at well-defined wavelengths.

Scattering Spectra

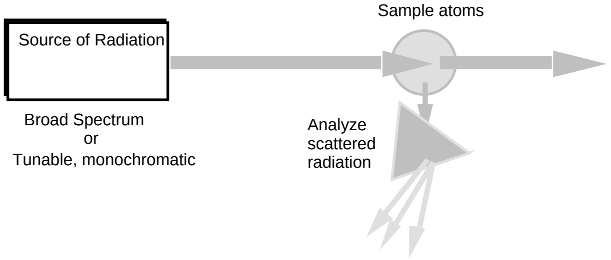


Fig 6.2.4 Spectroscopy of Scattered Light

If light excites a relatively dilute sample of atoms, those atoms usually decay by emitting characteristic radiation in almost all directions. By accepting only scattered light into the analyzer, relatively little of the direct radiation from the source is seen and the interpretation of the spectrum is simplified. The spectral lines are seen as *increases* in the intensity of detected light at well-defined wavelengths.

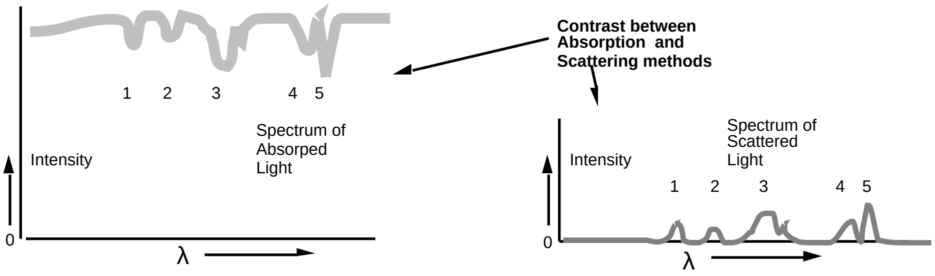
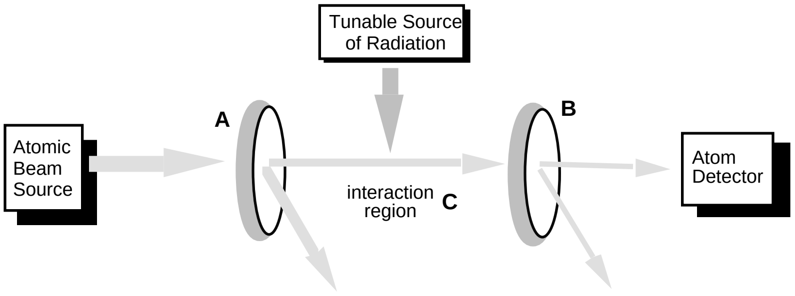


Fig 6.2.5 Contrast between absorption spectrum and scattered light spectrum

Atomic Beam Spectroscopy

Our discussion so far has concentrated on experiments in which the radiation is detected. This is somewhat limiting because individual photons with energies below 1 eV (corresponding to wavelengths in the near infra-red) are hard to detect individually because the photon energy is not sufficiently in excess of the characteristic thermal energy (kT) of the detectors. It is still possible to do spectroscopy with photons of low energy if the total photon flux is large enough to make spectrometer signals usefully large. One can, for example, do nuclear magnetic resonance spectroscopy at MHz frequencies (photons with nanovolt energies) because intense RF sources and dense samples are available. To do spectroscopy at low frequencies with dilute samples requires more technique. A representative method is atomic beam spectroscopy, a method that can work with pico-volt photons on sample densities s low (10^6 atoms/cc) enough so that most would consider them a vacuum.



State selector **A** passes only atoms in state |1>

State selector **B** passes only atoms in state |1> (OR only atoms in state |2>)

Fig. 6.2.6 Atomic Beam Spectroscopy

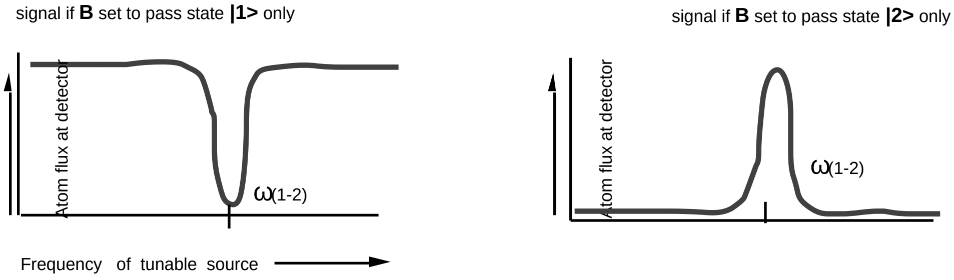


Fig 6.2.7 Spectra from Transmission and Absorption Methods of Atomic Beam Spectroscopy

6.3 WHAT CAN WE LEARN FROM A SPECTRAL LINE?

The motions of charged particles within an atom (or molecule) are governed by the potential V(r) characteristic of that atom, and the best information about the potential comes from the overall pattern of spectral lines radiated as a result of the motion of charges within the atom. We will spend quite a bit of time in explorations of that idea. However in this section we consider briefly what can be learned from a detailed examination of the frequency, width, intensity, and shape of a single line of the spectrum from an atom.

6.3.1 INFORMATION FROM THE LINE INTENSITY

Number of Sources

The intensity of the spectral line (i.e. the number of photons per second at the chosen frequency that enter our spectrometer) depends on

–the number of atoms in the sample,

–the ease which the atoms make the transition between the energy levels associated with that particular spectral line.

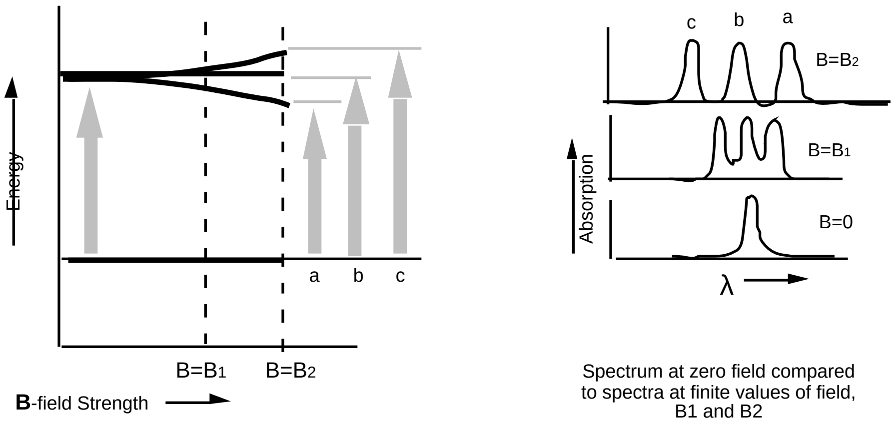
–the population of the relevant energy states.

–the directionality and degree of coherence of the source.

6.3.2 INFORMATION FROM THE LINE FREQUENCY

External field can cause shifts (Stark & Zeeman Effects; Chemical Shifts)

The spectral line frequency is determined by the energy difference between the initial and final levels. A spectral line may be displaced or split if the atom is perturbed by external electric or magnetic fields [Stark effect and Zeeman effect, respectively].



Spectrum at zero field compared to spectra at finite values of field, B1 and B2

Fig. 6.3.1 Zeeman effect on spectral line at zero field and at two finite values of B

The frequency of the line can also be shifted from its nominal value (particularly when the atom is imbedded in a solid host) by the continued, close presence of neighboring atoms . In many instances (particularly in NMR studies of solids) the size of the shift can be used to identify the host and to identify the location of the atom within the host. "Chemical shift" is one of the names associated with this phenomenon.

Directed Velocity can cause shifts (Doppler Effect)

The line frequency may be displaced if the atoms, as an ensemble, are moving with a relatively uniformly speed toward or away from the observer. This is the Doppler effect, and it is used to measure velocities ranging from .01 m/sec [as in Mössbauer spectroscopy] all the way up to the rate at which the edge of the visible universe appears to recede.

In most applications discussed in these pages (except for the deep galactic red shifts) we will find it adequate to write the Doppler shift as:

$$\left|\frac{\Delta\lambda}{\lambda}\right| = \left|\frac{\Delta\omega}{\omega}\right| \approx \left|\frac{v}{c}\right| \qquad (6.3.1)$$

When v/c is not small, one should use the actual relativistic expression for the Doppler shift, (here given in terms of a frequency ratio):

$$\frac{\omega'}{\omega} = 1 \pm \frac{v}{c} + \frac{1}{2}\left(\frac{v}{c}\right)^2 \pm \frac{1}{2}\left(\frac{v}{c}\right)^3 + \cdots \to \frac{\text{perceived from atom moving to/from } (\pm) \text{ observer}}{\text{perceived from stationary atom}} \qquad (6.3.2)$$

Doppler shifted line patterns have the general form shown here:

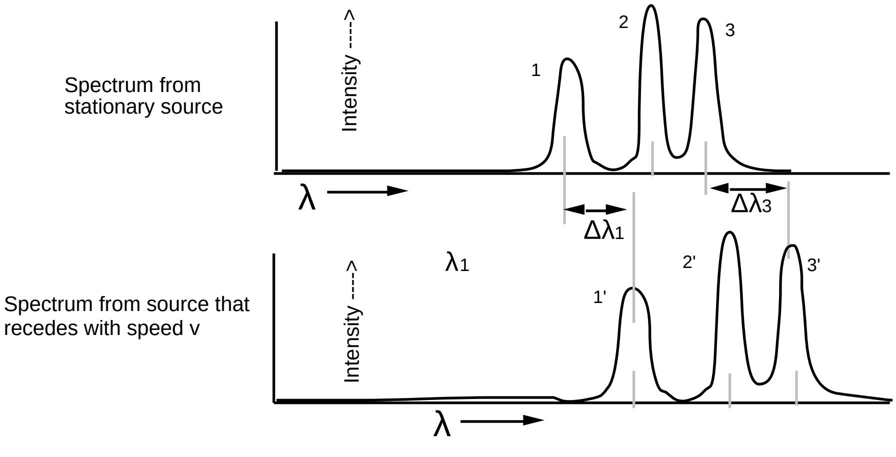


Fig. 6.3.2 Doppler shift: Spectrum from stationary and receding sources

6.3.3 INFORMATION FROM THE LINE WIDTH

Lifetime Broadening:

A sinusoidal oscillation at frequency ω_0 and with a constant amplitude has a single component Fourier representation. If, however, the oscillation dies away exponentially with decay constant γ, then the population of an aggregate of such oscillators decays exponentially ($N(t) = No \times e^{-\gamma t}$ · The spectral distribution of radiation from the aggregate is such that the intensity of the Fourier component at frequency ω has a symmetric distribution with a single maximum at the frequency ω_0:

$$I(\omega) = \frac{\left(\frac{\gamma}{2}\right)^2}{\left[(\omega - \omega_0)^2 + \left(\frac{\gamma}{2}\right)^2\right]} \qquad (6.3.3)$$

This is called a *Lorentzian* distribution

Any excited atomic state has a finite decay rate because it is inevitably coupled to the ambient electromagnetic field. The coupling increases with the cube of the excited state's energy, so that states with excitation energies in excess of 1 eV typically have lifetimes of 10 nanoseconds or less. Because this mode of decay arises from coupling of the atom with the very weak fluctuations that are [almost] always present in what we conventionally call *zero field,* the process is called *spontaneous emission* and the quantity $(1/\gamma)$ is called the *natural lifetime* of the state. And if this is the only inducement to decay, the observed line is said to have its *natural width.*

Collision Broadening:

It sometimes happens that the excited atom in a sample undergoes a collision before it undergoes spontaneous decay. This collision may seriously disturb the clean rhythm of the isolated atom's internal motions with a consequent effect on the spectral purity of the radiation emitted. The width of a spectral line measured from an aggregate of atoms undergoing collisions will increase beyond its natural value if the collision time is less than the state's natural lifetime. Bumps from other atoms and from wall collisions interrupt the otherwise highly-ordered motion of the radiating atom's charge distribution. This is called collision broadening and it increases with the temperature and density of the sample.

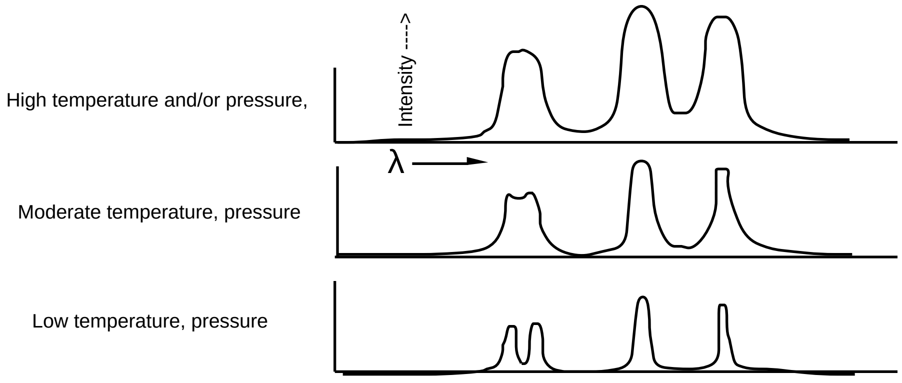


Fig. 6.3.3 Showing broadening of spectral lines as sample density, temperature increase

Doppler Broadening from Thermal Velocities

If the atoms of mass M in the sample are in the form of a hot gas at temperature T, then the typical atom is moving in a random direction with a speed $\langle v_{AVG} \rangle$:

$$\tfrac{1}{2} Mv^2 = \tfrac{3}{2} kT \longrightarrow \langle v \rangle_{AVG} = \sqrt{\frac{3kT}{M}} \tag{6.3.4}$$

The Doppler effect of randomly directed, thermally-distributed velocities leads to blue shifts as well as red shifts, with a resultant *Doppler broadening* of the spectral line:

$$\frac{\Delta\lambda}{\lambda} \approx \frac{\langle v \rangle_{AVG}}{c} = \sqrt{\frac{3kT}{Mc^2}} \tag{6.3.5}$$

A measurement of the Doppler broadening can thus reveal the kinetic temperature of the sample of atoms. For satisfactory thermometry of this sort, it is important that the pressure and temperature of the sample be such that the Doppler broadening dominates both the natural broadening and the collision broadening. Such conditions obtain in many astrophysical situations.

Comment: Spectral Lines reveal Degrees of Freedom

Sometimes line shapes deviate in an asymmetric manner from the ideal Lorentzian, and this can indicate that there are more energy levels involved than one first suspected. This unexpected multiplicity can arise if the atom has more degrees of freedom than originally envisioned. For example, the spectral lines of many elements were found to show fine structure, and this was finally understood to be a consequence of the electron spin's degree of freedom.

Comment: Self-Reversed Spectral Lines

Sometimes a transition between two levels produces a line shape with a pronounced dip in the center. This can arise from a phenomenon called *self-reversal*. This often occurs when one observes an emission line from a source that has a sample of atoms in hot dense center surrounded by an envelope of cooler gas of the same atomic species. The atoms in the center radiate a lineshape that is severely broadened by Doppler and collision effects, but the cool atoms outside have a relatively narrow absorption spectrum because their Doppler and collision effects are less. So the wings of the emission line are transmitted readily through the cool envelope, while the center of the emission line is severely attenuated from absorption by atoms in the envelope.

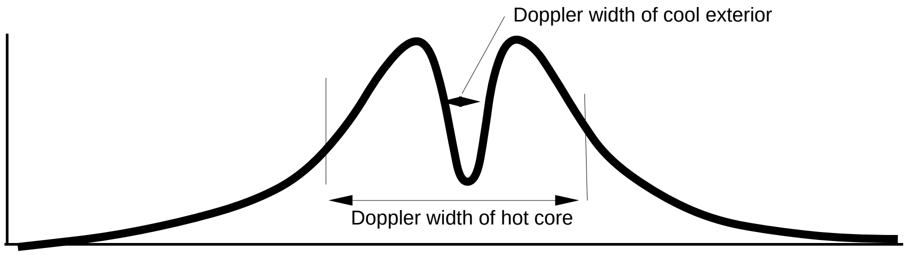


Fig. 6.3.4: Showing typical shape of self-reversed spectral line