

Radiative transitions

Classical and quantum theories of radiative
Absorption and emission.

Selection rules of transitions.

Physical mechanism of changes in lineshape
Observed in atomic spectroscopy.

Classical theories of radiating dipoles

- Developed before modern quantum theory.
- The atom can be described as electrons bound to the nucleus with springs:



- Strength of spring – force between the electrons and the nucleus.

This give a resonance frequency

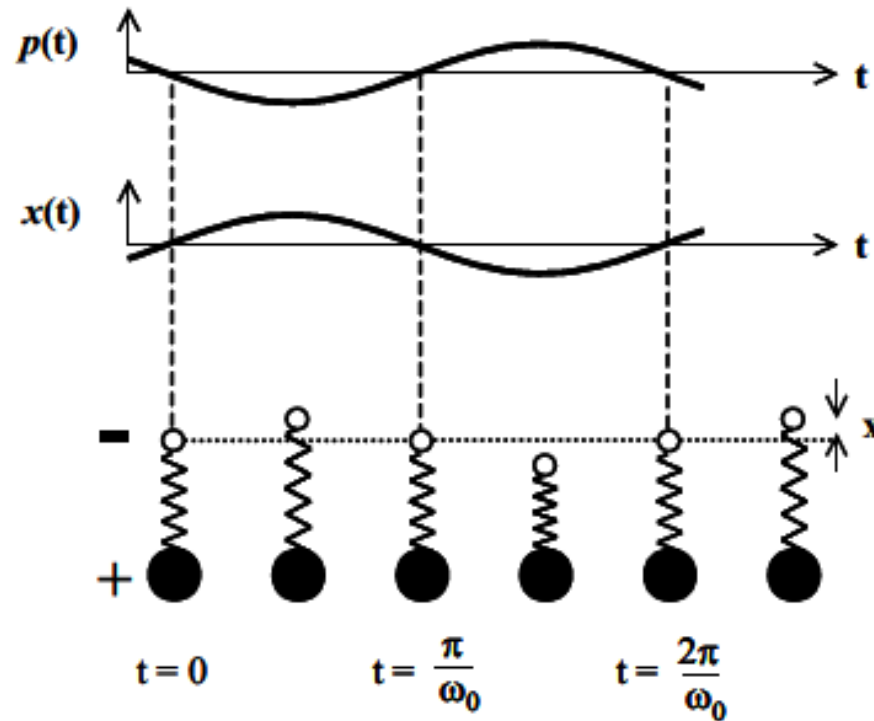
$$f = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

The spring constants might be different and every atom will have several resonance frequencies.

The nucleus is heavy, the electrons are lighter. The fluctuating positions of the electrons – create a fluctuating electric dipole.

The classical picture

- The vibration of an electron creates oscillating dipoles



The electric dipole:

Two opposite charges separated by a distance d .

$$p=qd.$$

The time dependence of p : $p(t)=-ex(t)$.

Related to electron motion.

Oscillating dipole emits electro magnetic radiation.

A molecule excited vibration emits light in frequency f .

Incoming light in f will excite the vibration.

Main problem: Several frequencies for a hydrogen atom

Quantum theory of radiative transitions

- Can explain intensities.
- Quantum theory gives quantized states, and the resonance frequencies are determined by:

$$h\nu = E_2 - E_1$$

- Transition rates determined by the Fermi golden rule:

$$W_{12} = \frac{2\pi}{\hbar} |M_{12}|^2 g(h\nu)$$

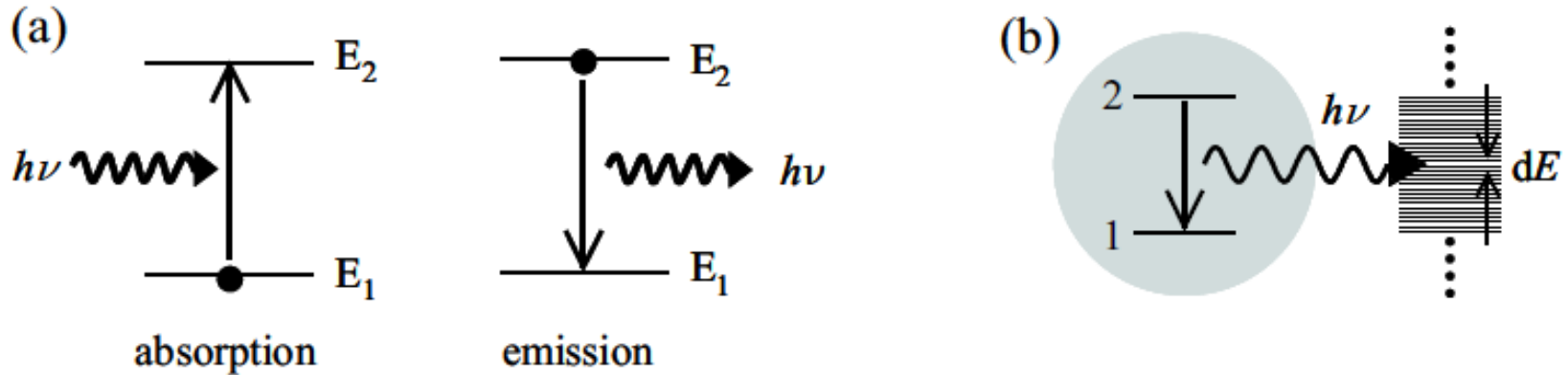
The golden rule formula:

- $g(h\nu)$ is the density of states. M_{12} is the matrix element for the transition:

$$M_{12} = \int \psi_2^*(\mathbf{r}) H'(\mathbf{r}) \psi_1(\mathbf{r}) d^3r$$

- $H'(\mathbf{r})$ – the perturbation – related to the interaction between the atom and the electromagnetic radiation.
- E1 the electric dipole interaction are the strongest one
- $g(h\nu)dE$ # of final states in a volume.

Electric dipole (E1) transitions



Interaction energy between the dipole and an electric field is:

$$E = -\mathbf{p} \cdot \boldsymbol{\mathcal{E}}.$$

The electric dipole perturbation is:

$$H' = +e\mathbf{r} \cdot \boldsymbol{\mathcal{E}}$$

$$H' = e(x\mathcal{E}_x + y\mathcal{E}_y + z\mathcal{E}_z)$$

The matrix elements of the transition:

$$M_{12} \propto \int \psi_1 x \psi_2 d^3 r \quad x\text{-polarized light}$$

$$M_{12} \propto \int \psi_1 y \psi_2 d^3 r \quad y\text{-polarized light}$$

$$M_{12} \propto \int \psi_1 z \psi_2 d^3 r \quad z\text{-polarized light}$$

- They are called the dipole moments
- Why electric dipole transitions lead to the emission of light?

The time dependent Schrodinger eqn:

$$\hat{H}(\mathbf{r})\Psi(\mathbf{r}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t),$$

- $H(\mathbf{r})$ is the Hamiltonian:
- The solutions are:

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{-iEt/\hbar}$$

$\psi(\mathbf{r})$ satisfies the time independent eqn.:

$$\hat{H}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

During the transition between E_1 and E_2 the system is in a superposition of states.

- The mixed wave function:

$$\begin{aligned}\Psi(\mathbf{r}, t) &= c_1 \Psi_1(\mathbf{r}, t) + c_2 \Psi_2(\mathbf{r}, t) \\ &= c_1 \psi_1(\mathbf{r}) e^{-iE_1 t/\hbar} + c_2 \psi_2(\mathbf{r}) e^{-iE_2 t/\hbar}\end{aligned}$$

- The expectation value of the position of the electron:

$$\langle x \rangle = \int \Psi^* x \Psi d^3 r .$$

Substitution:

- Gives:

$$\begin{aligned}\langle x \rangle &= c_1^* c_1 \int \psi_1^* x \psi_1 d^3 r + c_2^* c_2 \int \psi_2^* x \psi_2 d^3 r \\ &+ c_1^* c_2 e^{-i(E_2 - E_1)t/\hbar} \int \psi_1^* x \psi_2 d^3 r \\ &\quad + c_2^* c_1 e^{-i(E_1 - E_2)t/\hbar} \int \psi_2^* x \psi_1 d^3 r\end{aligned}$$

The electron wavepacket oscillates in an angular frequency of: $(E_2 - E_1)/\hbar$.

- Creating an oscillating electric dipole. and
- light emission.

Selection rules for E_1 transitions:

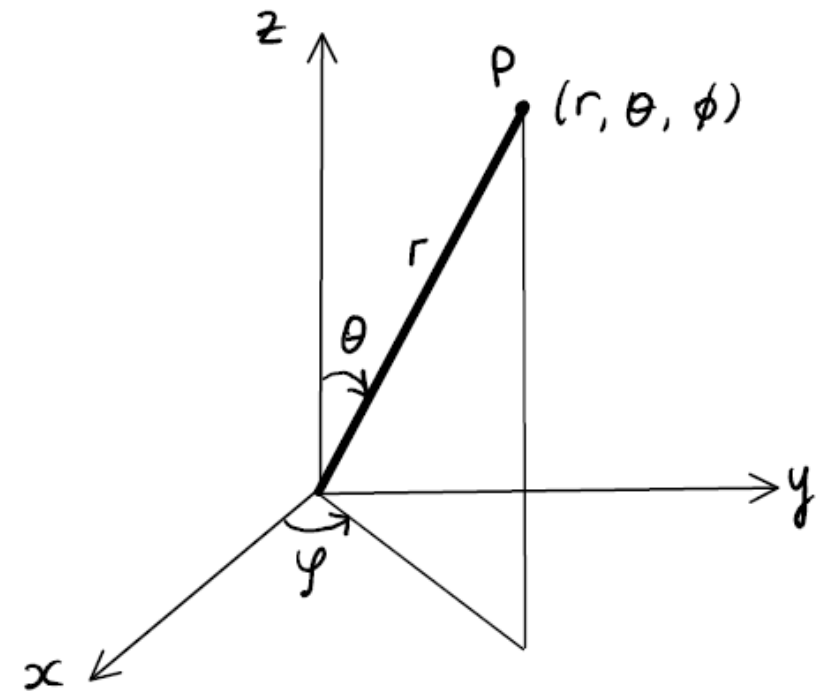
- If these are not fulfilled the matrix elements are zero:

Quantum number	Selection rule	
parity	changes	
l	$\Delta l = \pm 1$	
m	$\Delta m = 0, \pm 1$	unpolarized light
	$\Delta m = 0$	linear polarization $\parallel z$
	$\Delta m = \pm 1$	linear polarization in (x, y) plane
	$\Delta m = +1$	σ^+ circular polarization
	$\Delta m = -1$	σ^- circular polarization
s	$\Delta s = 0$	
m_s	$\Delta m_s = 0$	

Recall:

- The spherical harmonics:

l	m	$Y_{l,m}(\theta, \phi)$
0	0	$\sqrt{\frac{1}{4\pi}}$
1	0	$\sqrt{\frac{3}{4\pi}} \cos \theta$
1	± 1	$\mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$
2	0	$\sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$
2	± 1	$\mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$
2	± 2	$\sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$



Origin of selection rules:

- Parity: Functions might have an odd or even parity:

$$f(-x) = -f(x) \quad f(-x) = f(x)$$

All atomic wave functions have either odd or even parity: $\psi(-r) = \pm\psi(+r)$

Recall (for x): $M_{12} \propto \int \psi_1 x \psi_2 d^3r$

Thus ψ_1 and ψ_2 must have a different parity.

The orbital quantum number l

- Parity of spherical harmonics: $(-1)^l$.
- Δl has to be odd.
- Actually the rule is: $\Delta l = \pm 1$. Can be observed performing the matrix element calculation.
- **Recall:** Angular momentum of photon can be $\pm \hbar$ (light with circular polarization).
- Thus absorption and emission of photons can be only if $\Delta l = \pm 1$

The magnetic quantum # m :

- **Recall:** The dipole moment of the transition:

$$M_{12} \propto \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \Psi_{n',l',m'}^* r \Psi_{n,l,m} r^2 \sin \theta \, dr d\theta d\phi$$

- Consider the Φ part alone:

$$M_{12} \propto \int_0^{2\pi} e^{-im'\phi} r e^{im\phi} d\phi$$

- **Recall:** $\Psi_{n,l,m}(r, \theta, \phi) \propto e^{im\phi}$.

- For z polarized light: $z = r \cos \theta$. $m' = m$

$$M_{12} \propto \int_0^{2\pi} e^{-im'\phi} z e^{im\phi} d\phi \propto \int_0^{2\pi} e^{-im'\phi} \cdot 1 \cdot e^{im\phi} d\phi,$$

The other dipole moments:

Light polarized in the x and y directions:

$$M_{12} \propto \int_0^{2\pi} e^{-im'\phi} x e^{im\phi} d\phi \propto \int_0^{2\pi} e^{-im'\phi} \cdot e^{\pm i\phi} \cdot e^{im\phi} d\phi$$

Recall $x = r \sin \theta \cos \phi = r \sin \theta \frac{1}{2} (e^{+i\phi} + e^{-i\phi})$.

M_{12} will not be 0 if: $m' - m = \pm 1$.

Similar for y

Higher order transitions:

- It is possible to have two transitions one after the other. For example: First $3s \rightarrow 2p$, and afterwards $2p \rightarrow 1s$.

Other possible transitions are magnetic and quadrupole transitions with different selection rules. For example parity is conserved.

A third possibility a strong perturbation.

Radiative lifetimes

- Spontaneous emission of atom in the excited state (state #2).
- The rate in which it returns to ground state (state #1):

$$\frac{dN_2}{dt} = -AN_2$$

- A is the Einstein coefficient of spontaneous emission.

$$N_2(t) = N_2(0) \exp(-At)$$

- The solution:

$$= N_2(0) \exp(-t/\tau)$$

$$\tau = \frac{1}{A}$$

Value of A depends on transition

- Allowed and forbidden transition:

Transition	Einstein A coefficient	Radiative lifetime
E1 allowed	$10^8 - 10^9 \text{ s}^{-1}$	1 – 10 ns
E1 forbidden (M1 or E2)	$10^3 - 10^6 \text{ s}^{-1}$	1 μs – 1 ms

- Radiative transition of magnetic and quadrupole transitions – micro and milli seconds.

The width and shape of spectral lines

- Emitted radiation not monochromatic.
- At the peak center: $h\nu_0 = (E_2 - E_1)$
- The shape function is normalized:

$$\int_0^{\infty} g(\nu) d\nu = 1$$

$\Delta\nu$, Full width at half maximum

- Different types of broadening mechanism – leads to Gaussian and Lorentzian lineshapes.

Homogeneous and inhomogeneous broadening:

In a gas of atoms, broadening occurs due to 3 main processes:

- natural broadening,
- collision broadening,
- Doppler broadening.

Natural and collision broadening are homogenous. All atoms are affected in the same way.

Doppler broadening – atoms are affected by different velocities. – Also in solids.

Natural Broadening:

- Spontaneous emission – the population decays exponentially: Each atom will emit a photon with frequency: $\omega_0 = (E_2 - E_1)/\hbar$
- The intensity will decay exponentially

$$I(t) = I(0) \exp(-t/\tau)$$

Time dependent electric fields:

$$t < 0 : \quad \mathcal{E}(t) = 0,$$

$$t \geq 0 : \quad \mathcal{E}(t) = \mathcal{E}_0 e^{i\omega_0 t} e^{-t/2\tau}$$

Factor of 2 because:

(It is related to power). $I(t) \propto \mathcal{E}(t)^2$

Frequency spectrum of the burst:

- Fourier transform:

$$\mathcal{E}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \mathcal{E}(t) e^{i\omega t} dt$$

The emission spectrum will be:

$$I(\omega) \propto |\mathcal{E}(\omega)|^2 \propto \frac{1}{(\omega - \omega_0)^2 + (1/2\tau)^2}$$

The normalized lineshape function:

$$g(\nu) = \frac{\Delta\nu}{2\pi} \frac{1}{(\nu - \nu_0)^2 + (\Delta\nu/2)^2}$$

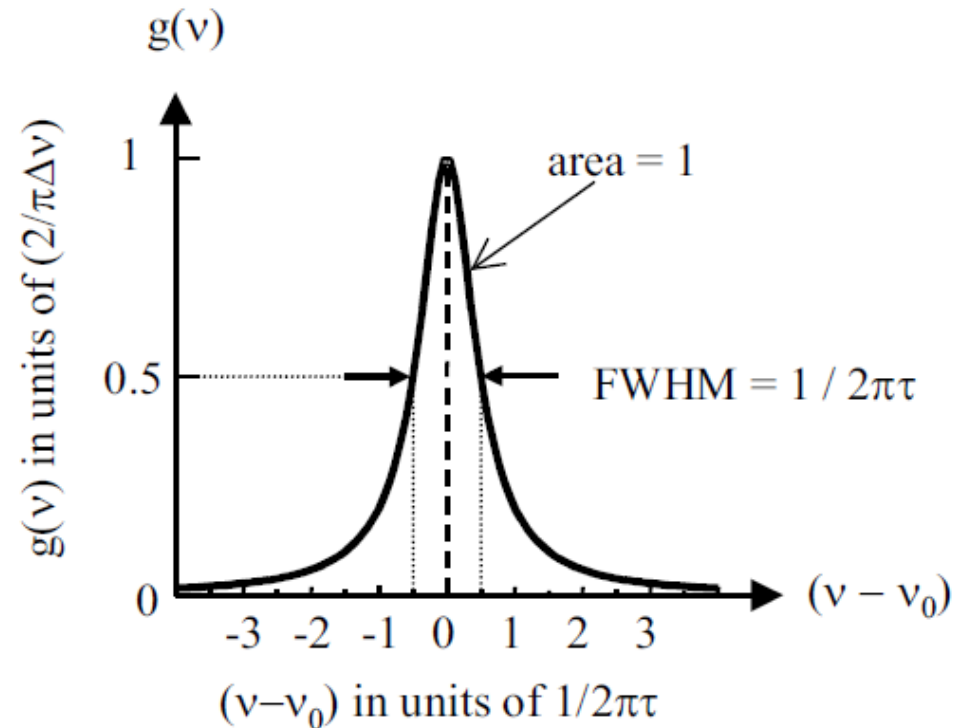
Full width at half maximum:

- This is a Lorentzian.

$$\Delta\nu = \frac{1}{2\pi\tau} \quad \Delta\nu \cdot \tau = \frac{1}{2\pi}$$

- Multiplying by h:

$$\Delta E \cdot \tau = h/2\pi$$



- Time energy uncertainty principle.

Collision (Pressure) broadening

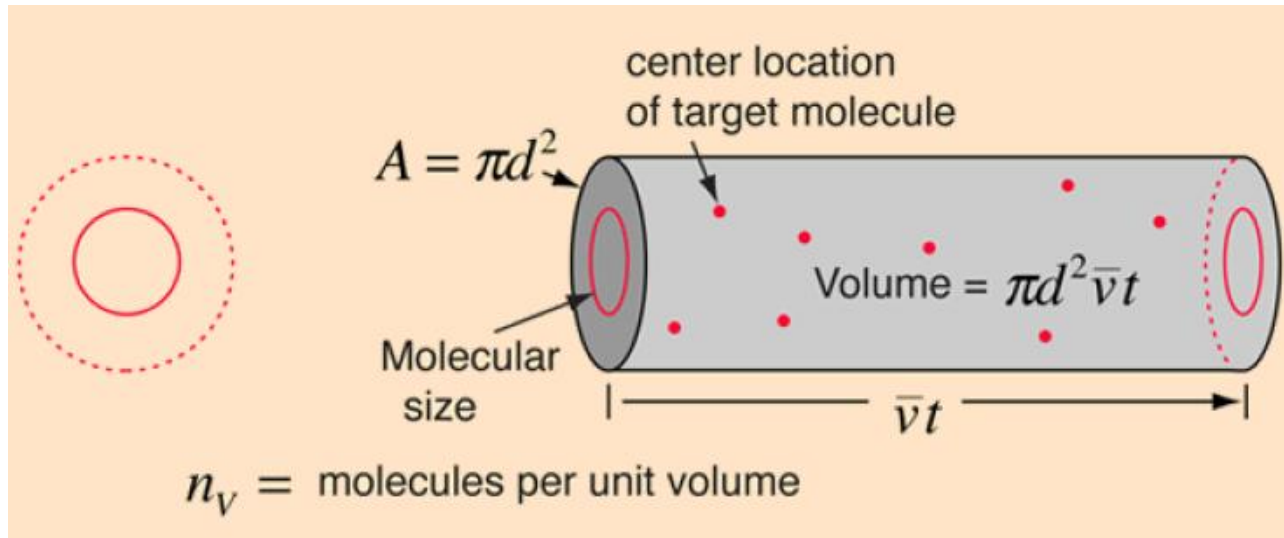
- The collisions of the atoms with the walls and with each other, shortens the lifetime of an excited state.
- Using the connection between the temperature and kinetic energy:

$$v_p = \sqrt{2 \cdot \frac{k_B T}{m}} \quad \bar{v} = \frac{2}{\sqrt{\pi}} v_p = \sqrt{\frac{8}{\pi} \cdot \frac{k_B T}{m}}$$

- But $\bar{v} = \lambda / \tau$. (mean free path, time between collisions).

Mean free path:

- In an ideal gas:



Distance traveled $\bar{v}t$

Mean distance per collision

Mean free path estimate = $\frac{\bar{v}t}{\underbrace{\pi d^2 \bar{v}t}_{\text{Volume of interaction}} n_V} = \frac{1}{\pi d^2 n_V}$

Number of molecules per unit volume

Average time between collisions

- We get

$$\tau = \frac{1}{\pi d^2 n_v} \left(\frac{\pi m}{8 k_B T} \right)^{1/2} \quad n_v = P / k_B T$$

$$\tau = \frac{k_B T}{\pi d^2 P} \left(\frac{\pi m}{8 k_B T} \right)^{1/2} \quad \tau = \frac{1}{\pi d^2 P} \left(\frac{\pi m k_B T}{8} \right)^{1/2}$$

For sodium atoms:

$$\sigma_s \sim \pi r_{\text{atom}}^2 \sim \pi \times (0.2 \text{ nm})^2 = 1.2 \times 10^{-19} \text{ m}^2$$

At ambient conditions:

$$\tau_c \sim 6 \times 10^{-10} \text{ s,}$$

$E = -$

The collision lifetimes are order of magnitude smaller than the radiation lifetime

- D line of sodium has a radiation time of 16ns
- We tend to work with low pressure in discharge lamps for spectroscopy.

Doppler broadening

The linewidth is normally much larger than the radiation linewidth (even without collisions - low pressure).

Neon line at 632.8nm has radiative lineshape of 2.7×10^{-7} Sec. equivalent to 0.54MHz. The observed linewidth is 3 orders of magnitude larger. The lineshape is not Lorentzian.

The reason – Doppler broadening.

Thermal motion of atoms:

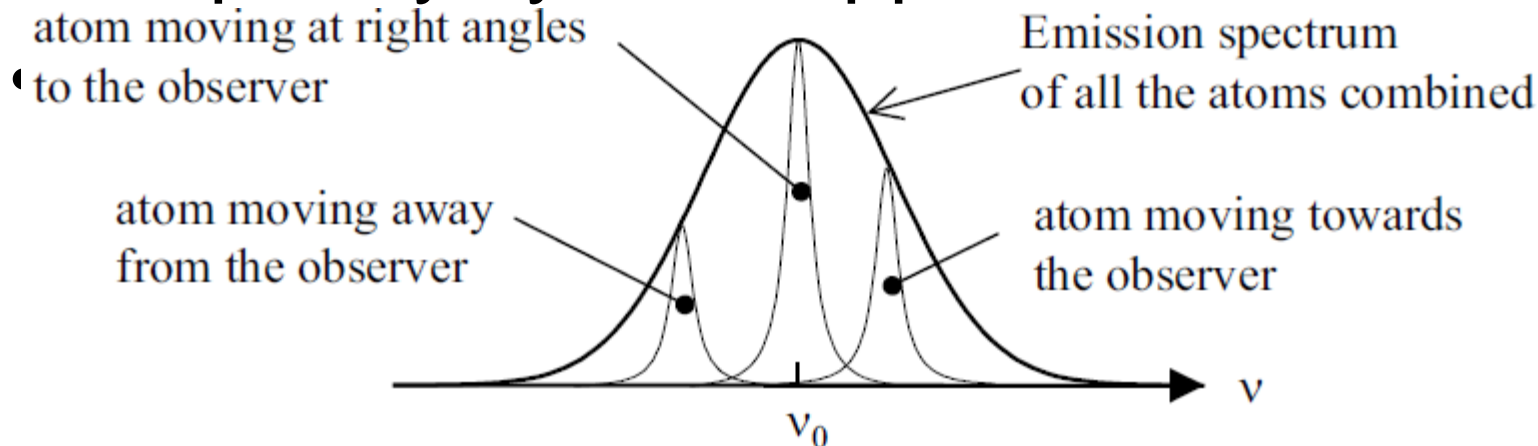
- Average thermal velocity:

$$\frac{1}{2}mv_x^2 = \frac{1}{2}k_B T$$

- Na atom at RT – mass # 23 gives:

$$v_x \sim 330 \text{ ms}^{-1}$$

- The random thermal motion shifts the frequency by the Doppler effect:



An atom that moves in a velocity v_x

- Will have the observed frequency shifted by:

$$\nu = \nu_0 \left(1 \pm \frac{v_x}{c} \right)$$

- The Distribution of the velocities of atoms

$$N(v_x) = N_0 \left(\frac{2k_B T}{\pi m} \right)^{1/2} \exp \left(-\frac{\frac{1}{2} m v_x^2}{k_B T} \right)$$

The distribution of frequencies:

$$N(\nu) = N_0 \left(\frac{2k_B T}{\pi m} \right)^{1/2} \exp \left(-\frac{m c^2 (\nu - \nu_0)^2}{2k_B T \nu_0^2} \right)$$

The observed lineshape:

- We get a Gaussian lineshape.

$$g(\nu) \propto \exp\left(-\frac{mc^2(\nu - \nu_0)^2}{2k_B T \nu_0^2}\right)$$

- With FWHM of:

$$\Delta\nu_D = 2\nu_0 \left(\frac{(2 \ln 2)k_B T}{mc^2}\right)^{1/2} = \frac{2}{\lambda} \left(\frac{(2 \ln 2)k_B T}{m}\right)^{1/2}$$

- **Recall** The Gaussian function and linewidth:

$$f(x) = a e^{-\frac{(x-b)^2}{2c^2}}$$

$$\mathbf{FWHM} = 2\sqrt{2 \ln 2} c \approx 2.35482c.$$

The Doppler linewidth:

- The most significant mechanism in emission spectrum of atoms in gas.
- The linewidth of the neon 632.8nm line is 1.3 GHz.

Atoms in solids:

- Collision and Doppler broadening irrelevant
- Main mechanism: Emission through phonons – non radiative transitions.
- The rate eqn.

$$\frac{dN_2}{dt} = -AN_2 - \frac{N_2}{\tau_{\text{NR}}} = - \left(A + \frac{1}{\tau_{\text{NR}}} \right) N_2 = -\frac{N_2}{\tau}$$

- Life time shortened by:

$$\frac{1}{\tau} = A + \frac{1}{\tau_{\text{NR}}}$$

- Other possibilities inhomogeneous broadening.