Lasers
PH 645/ OSE 645/ EE 613
Summer 2010 Section 1: T/Th 2:45- 4:45 PM
Engineering Building 240

John D. Williams, Ph.D.
Department of Electrical and Computer Engineering
406 Optics Building - UAHuntsville, Huntsville, AL 35899
Ph. (256) 824-2898  email: williams@eng.uah.edu
Office Hours: Tues/Thurs 2-3PM
Chapter 4: Radiative Transitions and Emission Linewidth

- Decay of Excited States
- Emission Broadening and Linewidth due to Radiative Decay
- Additional Emission-Broadening Processes
- Quantum Description of Radiating Atoms

Chapter 4 Homework: 1, 3, 4, 5, 6, 7, 12, 14

Cambridge University Press, 2004

All figures presented from this point on were taken directly from (unless otherwise cited): W.T. Silfvast, laser Fundamentals 2nd ed., Cambridge University Press, 2004.
Radiative Decay of Excited States from Isolated Atoms

- Start with the following assumptions:
- A collection of identical atoms exist in some physical state. All of the atoms present are in their respective ground states.
- Assume a pulse of energy is applied to the system excites many of the atoms to a single excited state, $u$.
- We define the populations density of atoms in the system at state $u$ as $N_u$.
- If we measure $N_u$ over time after the pulse was applied, then we find that $N_u$ decreases exponentially.
- Thus, after the pulse is applied, atoms in the system will tend to return to their ground states.
Radiative Decay of Excited States from Isolated Atoms

- This reduction in energy generally occurs in two ways:
  - Inelastic scattering of atoms leading to momentum transfer and loss
  - Isolated atoms that do not scatter but instead radiate light from into the system in order to reduce their energy states from $E_u - E_1$

- For optical systems, we are primarily concerned with radiative energy transfer which we define as **spontaneous emission**
- Each of the photons radiated by spontaneous emission has a frequency and wavelength:
  $$\nu_{ul} = (E_u - E_1)/h$$
  $$\lambda_{ul} = c/\eta \nu_{ul}, \text{ where } \eta \text{ is the index of refraction of the medium,}$$

- The simplest equation used to model the change in population density is
  $$\frac{dN_u}{dt} = -A_{ul} N_u \quad \Rightarrow \quad N_u = N_u^0 e^{-A_{ul} t}$$

- Where $A_{ul}$ is the inverse of the time constant, $\tau$, associated with the decay
Radiative Decay of Excited States from Isolated Atoms

A more general form of the solution in which the u state is allowed to decay to multiple different energy levels can be written as

\[
\frac{dN_u}{dt} = -(A_{ui} + A_{uj} + A_{uk} + \cdots) N_u = - \left( \sum_i A_{ui} \right) N_u
\]

\[
N_u = N_u^0 \exp \left\{ - \left( \sum_i A_{ui} \right) t \right\}
\]

\[
\tau_u = \frac{1}{\sum_i A_{ui}}
\]

Cd Laser involves the change in quantum number of two electrons (4d⁹5s² → 4d¹⁰5p)

This leads to a much smaller transition probability than a single state change.
Radiative Decay of Excited States from Isolated Atoms

\[ \frac{dN_u}{dt} = -(A_{ui} + A_{uj} + A_{uk} + \cdots) N_u = -\left( \sum_i A_{ui} \right) N_u \]

\[ \tau_u = \frac{1}{\sum_i A_{ui}} \]

\[ \tau_u = \frac{1}{(259 + 2.55 + 13.9 + 3.45 + 33.9 + 6.39} \]

\[ \text{HeNe laser quantum states (2p}^55\text{s} \rightarrow 2\text{p}^6) \]

Single state transition leads to high probability function and shorter time constant
Simplified Equation for Transition Probability

- Includes absorption oscillator strength, $f_{lu}$, wavelength, and statistical degeneracy of the upper and lower states (chapter 3)

$$A_{ul} = \frac{10^{-4}(f_{lu})}{1.5(g_u/g_l)\lambda^2_{ul}}$$

Derived later from QM

- The oscillator strength is unique for each spectral transition. In general though:

$$f_{lu} \leq 1$$

- For most radiative transitions:

$$f_{lu} \ll 1$$

- For most laser transitions:

$$0.1 > f_{lu} > 0.01$$

- Solid state and ruby laser transitions:

$$10^{-4} \text{ to } 10^{-5}$$
Classical Model of a Radiating Oscillator

\[ m_e \frac{d^2 x}{dt^2} + kx = 0 \quad \Rightarrow \quad x = x_0 e^{-i\omega_0 t} \]

\[ \omega_0 = \left( \frac{k}{m_e} \right)^{1/2} = 2\pi v_0 \]

From the Bohr model \( k = 4\pi^2 v_0^2 m_e \)

\[ E_T = \frac{1}{2} kx_0^2 = 2\pi^2 v_0^2 m_e x_0^2 \]

Power loss due to emission provides drag

\[ P_R = -\frac{dE_T}{dt} = \frac{16\pi^3 v_0^4 (e x_0)^2}{3\varepsilon_0 c^3} = \frac{\omega_0^4 (e x_0)^2}{3\pi\varepsilon_0 c^3} = -\gamma_0 E_T \]

\[ E_T = E_T^0 e^{-\gamma_0 t} = E_T^0 e^{-t/\tau_0} \quad \tau_0 = 1/\gamma_0 \]

\[ m_e \frac{d^2 x}{dt^2} + m_e \gamma_0 \frac{dx}{dt} + 4\pi^2 v_0^2 m_e x = 0 \]
Nonradiative Decay (inelastic collisions)

- Combined decay for both radiative and collision processes
  \[ N_u = N_u^0 e^{-\gamma_u t} \]
  \[ \gamma_u = \gamma_u^{\text{rad}} + \gamma_u^{\text{coll}} \]

- Decay rate for phonon processes that occur in all types of media:
  \[ \gamma_u^{\text{coll}} = \frac{1}{T_1^u} \]

- The total time constant for atomic transition from an excited state to a lower state is more accurately described by:
  \[ \tau_u = \frac{1}{\gamma_u} = \frac{1}{\gamma_u^{\text{rad}} + \gamma_u^{\text{coll}}} \]

- For Gasses, collisions occur more often as more kinetic energy is placed into the system, thereby increasing the orbital energies

- HeNe laser has a decay rate of
  \[ \gamma_u^{\text{coll}} = 7.5 \times 10^6 \text{ s}^{-1} \text{-Torr (He)} \]
Characteristic frequency of radiating atoms

\[ \omega_0 = \Delta E/\hbar \text{ or } \nu_0 = \Delta E/\hbar \]

The energy associated with the system:

\[ E(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E(t) e^{i\omega t} dt. \]

where \( \tau_0 = 2/\gamma_0 \)

\[ E(\omega) = \frac{E_0}{\sqrt{2\pi}} \int_{0}^{\infty} e^{i(\omega - \omega_0) + i\gamma_0/2} t \, dt \]

\[ = -\frac{E_0}{\sqrt{2\pi}} \frac{1}{i[(\omega - \omega_0) + i\gamma_0/2]} \cdot \gamma_0/\omega \ll 1 \]

Lorentzian Distribution defining Homogeneous broadening

\[ I(\omega) = I_0 \frac{\gamma_0/2\pi}{[(\omega - \omega_0)^2 + \gamma_0^2/4]} \]

\[ I_0 = \int_{0}^{\infty} I(\omega) \, d\omega \]

Find \( \Delta \omega_{\text{FWHM}} \) by taking \( I \) at \( \omega_0 \)

\[ I(\omega_0) = \frac{1}{2} I_o \frac{\gamma_0 / 2\pi}{(\omega_0^2 - \omega_0^2) - \gamma_0^4 / 4} \]

\[ I(\omega) = \left( \frac{1}{2} \right) \left( \frac{2}{\pi\gamma_0} \right) I_0 \]

\[ \Delta \omega_{\text{FWHM}} = 2(\omega - \omega_0) = \gamma_0 = 1/\tau_0 = 2\pi\Delta v_C \]
Quantum Theory of Emission Broadening

- Using the uncertainty principle
  \[ \Delta E \cdot \Delta t \approx \hbar = \frac{\hbar}{2\pi} \]

- The energy level \( u \) will have an uncertainty
  \[ \Delta E_u = \frac{\hbar}{\tau_u} = \hbar \gamma_u = \hbar \sum_i A_{ui} \]

- The energy level \( l \) will have an uncertainty
  \[ \Delta E_l = \frac{\hbar}{\tau_l} = \hbar \gamma_l = \hbar \sum_j A_{lj} \]

- The total effective energy of the two levels is
  \[ \Delta E_T = \Delta E_u + \Delta E_l = \hbar (\gamma_u + \gamma_l) = \hbar \left( \sum_i A_{ui} + \sum_j A_{lj} \right) \]
  \[ \Delta E_T = \hbar \Delta \omega_{ul} = \frac{\hbar}{2\pi} \cdot 2\pi \Delta \nu_{ul} = \hbar \Delta \nu_{ul} \]
  \[ \hbar \left( \sum_i A_{ui} + \sum_j A_{lj} \right) = \hbar \Delta \nu_{ul} \]
Quantum Theory of Emission Broadening

- To solve for the intensity we simply calculate the solution in terms of decay rate

\[ \Delta \nu_{ul}^N = \frac{\sum_i A_{ui} + \sum_j A_{lj}}{2\pi} \]

\[ \gamma_{ul}^T = \gamma_u + \gamma_l \]

\[ \gamma_{ul}^T = 2\pi \Delta \nu_{ul}^N = \sum_i A_{ui} + \sum_j A_{lj} \]

Lorentzian Distribution defining
Homogeneous broadening

\[ I(\omega) = I_0 \frac{\gamma_{ul}^T/2\pi}{(\omega - \omega_0)^2 + (\gamma_{ul}^T/2)^2} \]

\[ I(v) = I_0 \frac{\gamma_{ul}^T/4\pi^2}{(v - v_0)^2 + (\gamma_{ul}^T/4\pi)^2} \]

In terms of angular frequency

In terms of frequency
Broadening Processes due Nonradiative Decay

- Collisional decay rates due to the upper and lower quantum state

\[ \gamma_2^u = 1/T_2^u \]
\[ \gamma_2^l = 1/T_2^l \]

- Energy change associated with collisional decay rates is equal to the change in detectable light frequency

\[ \hbar(\gamma_u + \gamma_l) = \hbar \gamma_{ul}^T = \frac{\hbar}{2\pi} \gamma_{ul}^T = \hbar \Delta \nu_{ul} \]

Frequency broadening due to radiative and elastic scattering

\[ \Delta \nu_{ul} = \frac{1}{2\pi} \left[ \left( \sum_i A_{ui} + \sum_j A_{lj} \right) + \frac{1}{T_1^u} + \frac{1}{T_1^l} \right] \]
\[ = \Delta \nu_{ul}^N + \frac{1}{2\pi} \left( \frac{1}{T_1^u} + \frac{1}{T_1^l} \right). \]

Radiative broadening
Broadening Processes due to Dephasing

- Decay rate observed determined by the average time observed between phase–interrupting atomic collisions
  
  \[ \gamma_2^u = 1/T_2^u \]
  
  \[ \gamma_2^l = 1/T_2^l \]

- Typically the time constants associated with the upper and lower state are the same, thus

  \[ \gamma_2^u + \gamma_2^l = 2/T_2 \]

Frequency broadening due to radiative, elastic scattering, and dephasing

\[ \Delta \nu_{ul}^H = \frac{\gamma_{ul}^T}{2\pi} = \frac{1}{2\pi} \left[ \left( \sum_i A_{ui} + \sum_j A_{lj} \right) + \frac{1}{T_1^u} + \frac{1}{T_1^l} + \frac{2}{T_2} \right] \]
Figure 4-10 Broadening of atomic energy levels of an atom within a crystal matrix resulting from the phonon-assisted "collisions" of that atom with the surrounding atoms of the crystal for the case of $T_1$ broadening.

$\Delta E_u = \hbar \left( \frac{1}{T_1} \right)$

$\Delta E_l = \hbar \left( \frac{1}{T'_1} \right)$

Atomic levels  Phonom-assisted broadening  Effective levels in crystal matrix
Amorphous Crystal Broadening Processes

- Collisional decay rates due to the upper and lower quantum state
  \[ \gamma_2^u = \frac{1}{T_2^u} \]
  \[ \gamma_2^l = \frac{1}{T_2^l} \]

- Energy change associated with collisional decay rates is equal to the change in detectable light frequency
  \[ \hbar (\gamma_u + \gamma_l) = \hbar \gamma_{ul}^T = \frac{\hbar}{2\pi} \gamma_{ul}^T = \hbar \Delta \nu_{ul} \]

Frequency broadening due to radiative and elastic scattering

\[ \Delta \nu_{ul} = \frac{1}{2\pi} \left[ \left( \sum_i A_{ui} + \sum_j A_{lj} \right) + \frac{1}{T_1^u} + \frac{1}{T_1^l} \right] \]

\[ = \Delta \nu_{ul}^N + \frac{1}{2\pi} \left( \frac{1}{T_1^u} + \frac{1}{T_1^l} \right) \]

Radiative broadening
Doppler Broadening Processes in Gases

- Common process observed in gas lasers with large atomic mobility
- Doppler effect on wave velocity w.r.t a stationary observer
  \[ \nu = \left(1 + \frac{v}{c}\right)v_0 \] (moving toward the observer);
  \[ \nu = \left(1 - \frac{v}{c}\right)v_0 \] (moving away from the observer)
- Average thermal velocity of an atom of mass \( M \)
  \[ \bar{v} = \sqrt{\frac{8kT}{M\pi}} \]
- Probability function for an atom to move at velocity, \( v \)
  \[ P(v_x, v_y, v_z) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\frac{M}{2kT}(v_x^2 + v_y^2 + v_z^2)\right\} dv_x \, dv_y \, dv_z. \]
- The probability that a transition frequency between \( \nu \) and \( \nu + d\nu \) will occur is therefore
  \[ G(\nu) \, d\nu = \left(\frac{M}{2\pi kT}\right)^{3/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left\{-\left(\frac{M}{2kT}\right)(v_x^2 + v_y^2 + v_z^2)\right\} dv_x \, dv_y \, dv_z \]
  \[ \exp\left\{-\left(\frac{M}{2kT}\right)\left(\frac{c^2}{v_0^2}\right)(\nu - \nu_0)^2\right\} \left(\frac{c}{v_0}\right) d\nu. \]
  \[ G(\nu) = \frac{c}{v_0} \left(\frac{M}{2\pi kT}\right)^{1/2} \exp\left\{-\left(\frac{M}{2kT}\right)\left(\frac{c^2}{v_0^2}\right)(\nu - \nu_0)^2\right\} \]

Figure 4-12 Shape of a Doppler-broadened emission line, indicating the natural emission linewidths of individual atoms radiating while traveling in various directions.
Doppler Broadening Processes in Gases

- Broadening Distribution function

\[ G(v) = \frac{c}{v_0} \left( \frac{M}{2\pi kT} \right)^{1/2} \exp \left\{ -\left( \frac{M}{2kT} \right) \left( \frac{c^2}{v_0^2} \right) (v - v_0)^2 \right\} \]

- Normalized intensity:

\[ \int_0^\infty I(v) \, dv = I_0 \]

- Doppler width:

\[ \Delta v_D = 2v_0 \sqrt{\frac{2(\ln 2)kT}{Mc^2}} = (7.16 \times 10^{-7})v_0 \sqrt{\frac{T}{M_N}} \]

- Yielding the reduced form:

\[ I(v) = \frac{2(\ln 2)^{1/2}}{\pi^{1/2} \Delta v_D} I_0 \exp \left\{ -\left[ \frac{4(\ln 2)(v - v_0)^2}{(\Delta v_D)^2} \right] \right\} \]

### Doppler versus Natural Broadening

<table>
<thead>
<tr>
<th>Laser species</th>
<th>( \lambda ) (nm)</th>
<th>( f )</th>
<th>( A ) (s(^{-1}))</th>
<th>( \Delta v_N ) (Hz)</th>
<th>( \Delta v_D ) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon (He–Ne)</td>
<td>632.8</td>
<td>0.012</td>
<td>( 3.4 \times 10^6 )</td>
<td>( 1.4 \times 10^7 )</td>
<td>( 1.5 \times 10^9 )</td>
</tr>
<tr>
<td>Argon ion</td>
<td>488.0</td>
<td>0.418</td>
<td>( 7.8 \times 10^7 )</td>
<td>( 4.5 \times 10^8 )</td>
<td>( 2.7 \times 10^9 )</td>
</tr>
<tr>
<td>Cadmium (He–Cd)</td>
<td>441.6</td>
<td>0.006</td>
<td>( 1.4 \times 10^6 )</td>
<td>( 4.5 \times 10^7 )</td>
<td>( 1.1 \times 10^9 )</td>
</tr>
<tr>
<td>Copper</td>
<td>510.5</td>
<td>0.005</td>
<td>( 2.0 \times 10^6 )</td>
<td>( 3.6 \times 10^5 )</td>
<td>( 2.3 \times 10^9 )</td>
</tr>
</tbody>
</table>

Notice that Doppler broadening is significantly larger than natural broadening.
Voigt Lineshape Profile

- Assume a process in which the natural (homogeneous) broadening and the Doppler (inhomogeneous) broadening are comparable.
- In such cases, the line profile shows a combination of these effects because the statistical variation in velocity of different subgroups of atoms in the system provide different Doppler shifts.
- To express the sum of these peaks and the overall line broadening we develop the Voigt profile.
- First, one defines the Doppler parameter as $\Delta = (4\pi v_0/c)(2kT/M)^{1/2}$.
- Beam intensity is then developed in terms of the ratio of the decay rate over the Doppler parameter.

$$I\left(\nu - \nu_0, \frac{\gamma_{ul}}{\Delta}\right) = I_0 \int_{0}^{\infty} \frac{1/\pi^{3/2}}{(\nu - \nu_0)^2 + (\gamma_{ul}/4\pi)^2} \left(\frac{\gamma_{ul}}{\Delta}\right) \exp\left\{ -\left(\frac{16\pi^2}{\Delta^2}\right)(\nu_0 - \nu_0')^2\right\} d\nu'_0$$

- The Voigt profile itself is not an analytical expression. It can however be numerically tabulated.
Voigt Lineshape Profile

• Assume a process in which the natural (homogeneous) broadening and the Doppler (inhomogeneous) broadening are comparable

• In such cases, the line profile shows a combination of these effects b/c the statistical variation in velocity of different subgroups of atoms in the system provide different Doppler shifts

• To express the sum of these peaks and the overall line broadening we develop the Voigt profile

• First one Defines the Doppler parameter as \( \Delta = (4\pi v_0/c)(2kT/M)^{1/2} \)

• Beam intensity is then developed in terms of the ratio of the decay rate over the Doppler parameter

\[
I\left(\nu_0 - \nu, \frac{\gamma_{ul}}{\Delta}\right) = I_0 \int_0^\infty \frac{1/\pi^{3/2}}{(\nu - \nu'_0)^2 + \left(\frac{\gamma_{ul}}{\Delta}\right)^2} \left\{ \exp\left(-\frac{16\pi^2}{\Delta^2}(\nu'_0 - \nu_0)^2\right) \right\} \, d\nu'_0
\]

• The Voigt profile itself is an error function and as such, is not an analytical expression. It can however be numerically tabulated
Broadening in Gases Due to Isotope Shifts

• Broadening is also observed from the presence of isotopes in a gas mixture
• Isotopes are atoms of a particular element with a different neutron value, thus altering the effective mass of the atom, but not its charge
• Examples of isotope percentages in He-Ne gas lasers
  
  99.0008% He$^4$ (2 neutrons) and 0.00013% He$^3$ (1 neutron)
  90.8% Ne$^{20}$ (10 neutrons), 0.26% Ne$^{21}$ (11 neutrons), and 8.9% Ne$^{22}$ (12 neutrons)

• The change in effective mass leads to slight changes in the energy states as expressed in our review of quantum mechanics
• The resulting change in spectral line width is referred to as the isotope shift

![Figure 4-14 Shape of emission line for the 632.8-nm transition of the helium-neon laser, showing the contributions from two different isotopes associated with a naturally occurring mixture of neon](image)
A second example is the He-Cd gas laser operating at 441.6 nm

Isotopes ranging from Cd\textsuperscript{106} to Cd\textsuperscript{116}

Figure 4-15(a) Emission lineshapes of the various isotopes of the cadmium 441.6-nm laser transition from a naturally occurring isotopic mixture
Comparing Various Types of Line Broadening

- **Homogeneous Broadening** (population density depends on quantum states)

  \[ A_{ul}(v) = \frac{\gamma_{ul}^T/4\pi^2}{(v - v_0)^2 + (\gamma_{ul}^T/4\pi)^2} A_{ul} \quad \text{Transition probability depends on velocity and quantum states} \]

  \[ N_u A_{ul}(v) = \frac{\gamma_{ul}^T/4\pi^2}{(v - v_0)^2 + (\gamma_{ul}^T/4\pi)^2} N_u A_{ul} \]

  \[ N_u A_{ul}(v = v_0) \Delta \nu h v_{ul} = \frac{\gamma_{ul}^T/4\pi^2}{\gamma_{ul}^2/16\pi^2} N_u A_{ul} \Delta \nu h v_{ul} \quad \text{Broadening at the resonant frequency} \]

  \[ = \frac{4}{\gamma_{ul}} N_u A_{ul} \Delta \nu h v_{ul} \]

- **Inhomogeneous Broadening** (population density depends on velocity)

  \[ N_u(v) = 2 \sqrt{\frac{\ln 2}{\pi}} \frac{1}{\Delta \nu_D} N_u \exp\left\{ - \left[ \frac{4 \ln 2 (v - v_0)^2}{\Delta \nu_D^2} \right] \right\} \]

  \[ N_u(v) A_{ul} = 2 \sqrt{\frac{\ln 2}{\pi}} \frac{1}{\Delta \nu_D} N_u \exp\left\{ - \left[ \frac{4 \ln 2 (v - v_0)^2}{\Delta \nu_D^2} \right] \right\} N_u A_{ul} \]

  \[ N_u(v = v_0) A_{ul} \Delta \nu h v_{ul} = 2 \left( \frac{\ln 2}{\pi} \right)^{1/2} \frac{1}{\Delta \nu_D} N_u A_{ul} \Delta \nu h v_{ul} \quad \text{Broadening at the resonant frequency} \]
Relative Power Ratios at Resonance

- The ratio of power due to broadening at resonance of both homogenous and inhomogeneous broadening is

\[ N_u A_{ul}(\nu = \nu_0) \Delta \nu h \nu_{ul} = \frac{4}{\gamma_{ul}} N_u A_{ul} \Delta \nu h \nu_{ul} \]

\[ N_u (\nu = \nu_0) A_{ul} \Delta \nu h \nu_{ul} = 2 \left( \frac{\ln 2}{\pi} \right)^{1/2} \frac{1}{\Delta \nu_D} N_u A_{ul} \Delta \nu h \nu_{ul} \]

\[ P_{\text{ratio}} = \frac{2(\pi)^{1/2} \Delta \nu_D}{(\ln 2)^{1/2} \gamma_{ul}} = \frac{2(\pi)^{1/2} \Delta \nu_D}{(\ln 2)^{1/2} 2\pi \Delta \nu_H} \]

\[ = \frac{1}{(\pi \ln 2)^{1/2}} \frac{\Delta \nu_D}{\Delta \nu_H} = 0.68 \frac{\Delta \nu_D}{\Delta \nu_H}, \]

For the case where \( \Delta \nu_D \ll \Delta \nu_H \), we can ignore Doppler broadening.
<table>
<thead>
<tr>
<th>Type of broadening</th>
<th>Nature of broadening</th>
<th>Special features</th>
</tr>
</thead>
</table>
| Natural           | \( \Delta E_T = \Delta E_u + \Delta E_l, \)  
                  | \( h\Delta \nu^N_{ul} = h(\Delta \nu_u + \Delta \nu_l) = h\left(\frac{A_u}{2\pi} + \frac{A_l}{2\pi}\right), \)  
                  | Determines the minimum emission linewidth of a radiating transition. It involves decay rates of both the upper and lower levels. It is homogeneous with a Lorentzian profile.  
                  | \( \Delta \nu^N_{ul} = \frac{1}{2\pi}\left[\sum_i A_{ui} + \sum_j A_{lj}\right]. \)  |
| \( T_1 \)       | \( T_{1}^{u,l} \) are the decay times of levels \( u \) and \( l \) due to outside disturbances;  
                  | \( \Delta \nu_{T_1} = \frac{1}{2\pi}\left[\frac{1}{T_1^u} + \frac{1}{T_1^l}\right]. \)  
                  | Both \( T_1 \) and \( T_2 \) determine the increased broadening on a transition from level \( u \) to level \( l \) due to outside influences, if \( T_1 \) and/or \( T_2 \gtrsim 1/(2\pi\Delta \nu^N) \). We cannot determine which form is dominant in a given instance merely by measuring the broadening. \( T_2 \) broadening is less detrimental because it does not destroy population; however, it still reduces the laser gain because of the increased broadening. Both are homogeneous with a Lorentzian profile.  
                  | It will be relevant only if \( \Delta \nu_{T_1} \gtrsim \Delta \nu^N. \)  |
| \( T_2 \)       | \( T_2 \) is the average phase interruption time of level \( u \) or \( l \) for outside disturbances. It usually occurs equally for levels \( u \) and \( l \). Therefore,  
                  | \( \Delta \nu_{T_2} = \frac{1}{2\pi}\left[\frac{2}{T_2}\right]. \)  
                  | It will be relevant only if \( \Delta \nu_{T_2} \gtrsim \Delta \nu^N. \)  |
Doppler

\[ \Delta v_D = 2\nu_0 \sqrt{\frac{2(\ln 2)kT}{Mc^2}}. \]

It will be relevant only if \( \Delta v_D \gtrsim \Delta v^N \).

This is due entirely to the motion of atoms; it has nothing to do with decay rates or phase interruptions. Each atom still radiates with its own natural width. The total Doppler width is the sum of the shifted natural emission widths of all the atoms.

Isotope

If there is more than one isotope present, each isotope behaves independently and has its own broadening (usually Doppler). The linewidth and shape are determined by the sum of the emissions from each isotope. It is relevant only if the isotope shift is significant compared to linewidths of individual isotopes.

This is essentially a sum of separate emitters that have slight shifts in frequency. The overall emission envelope is therefore an unusually shaped sum of many separate Doppler widths.
Quantum Solution for Line Broadening

• Consider a two coherent quantum states in which a transition occurs:

$$\Psi^* \Psi = C_1^* C_1 \psi_1^* \psi_1 + C_2^* C_2 \psi_2^* \psi_2$$

$$+ C_1^* C_2 \psi_1^* \psi_2 e^{-i\omega_2 t} + C_2^* C_1 \psi_2^* \psi_1 e^{i\omega_2 t}$$

$$\omega_{21} = \frac{E_2 - E_1}{\hbar} \quad \text{or} \quad \nu_{21} = \frac{E_2 - E_1}{\hbar}.$$

• Furthermore, we restrict the states such that only an allowable transition will occur. Such allowed transitions depend on the angular momentum and the parity of the states.

• Close examination of the interaction between bound states is performed through the use of a dipole matrix element, $M_{ul}$, defined as

$$M_{ul} = \langle e \mathbf{r} \rangle = \int \psi_u^* e \mathbf{r} \psi_l dV$$

$$\mathbf{r} = x \hat{i} + y \hat{j} + z \hat{k}$$

$e \mathbf{r}$ is the electric dipole moment of the electron-proton system. It can also be taken as the Hamiltonian operator acting on state $u$ to achieve state $l$.
Electric Dipole Transition Probability

- The QM expression for radiated power per atom as equated to our classical model is:

\[ P_R = \frac{dE}{dt} = A_{ul} \hbar \nu_{ul} = \frac{16\pi^3 \nu_{ul}^4 (e\chi_0)^2}{3\varepsilon_0 c^3} \]

- If we replace the classical dipole moment with the dipole matrix element, then

\[ A_{ul} = \frac{16\pi^3 \nu_{ul}^3 M_{ul}^2}{3\hbar \varepsilon_0 c^3} = \frac{\omega_{ul}^3 M_{ul}^2}{3\pi \hbar \varepsilon_0 c^3} \]

- The decay rate can be further evaluated in terms of oscillator strength as

\[ A_{ul} = \frac{e^2 \omega_{ul}^2}{2\pi \varepsilon_0 m_e c^3} \left( \frac{g_i}{g_u} \right) f_{iu} = \frac{2\pi e^2 \nu_{ul}^2}{\varepsilon_0 m_e c^3} \left( \frac{g_i}{g_u} \right) f_{iu} = \frac{2\pi e^2}{\varepsilon_0 m_e c^2 \chi_{ul}^2} \left( \frac{g_i}{g_u} \right) f_{iu} \]

- Where \( f_{iu} \) is called the absorption oscillator strength of the transition. Likewise, the emission oscillator strength \( f_{ul} \) will be equal to the negative of the absorption oscillator times the ratio of the degeneracies of each state

\[ f_{ul} = -\frac{g_i}{g_u} f_{iu} \]

- Furthermore, by definition, the sum of all the oscillator strengths in a system must be 1

\[ \sum_{i<u} f_{ui} + \sum_{k>u} f_{uk} = 1 \]

Thomas–Kuhn–Reiche sum rule
Selection Rules for Electric Dipole Transitions in Atoms with a Single Electron in an Unfilled Shell

- One can obtain the probability of the electric dipole matrix element as:

\[ M_{ul}^2 = e^2 (X^2 + Y^2 + Z^2) \]

- using

\[
X = \int \int \int \psi_u^*(n', l', m') \cdot x \cdot \psi_l(n, l, m) \ dV
\]

\[
= \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{n'l'm'}^* r \sin \theta \cos \phi \psi_{nlm} r^2 \sin \theta \ d\theta \ d\phi \ dr
\]

\[
Y = \int \int \int \psi_u^*(n', l', m') \cdot y \cdot \psi_l(n, l, m) \ dV
\]

\[
= \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{n'l'm'}^* r \sin \theta \sin \phi \psi_{nlm} r^2 \sin \theta \ d\theta \ d\phi \ dr;
\]

\[
Z = \int \int \int \psi_u^*(n', l', m') \cdot z \cdot \psi_l(n, l, m) \ dV
\]

\[
= \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{n'l'm'}^* r \cos \theta \psi_{nlm} r^2 \sin \theta \ d\theta \ d\phi \ dr.
\]
Let us break this solution down further by evaluating only the X term:

\[
X = \int \psi_\nu^*(n', l', m') \cdot x \cdot \psi_\lambda(n, l, m) \, dV
\]

\[
= \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{n'l'm'}^* r \sin \theta \cos \phi \psi_{nlm} r^2 \sin \theta \, d\theta \, d\phi \, dr
\]

\[
X = C_{n', l', m'}^* C_{n, l, m} \left( \int_0^\infty R_{n'l'} r R_{nl} r^2 \, dr \right)
\]

\[
\times \left[ \int_0^\pi P_{l'}^{m'}(\cos \theta) \sin \theta P_l^m(\cos \theta) \sin \theta \, d\theta \right]
\]

\[
\times \left( \int_0^{2\pi} e^{-im'\phi} \cos \phi e^{im\phi} \, d\phi \right).
\]

where

\[
\cos \phi = \frac{1}{2} (e^{i\theta} + e^{-i\theta})
\]

and knowing that

\[
\frac{1}{2} \int_0^{2\pi} \left[ e^{i(m-m'+1)\phi} + e^{i(m-m'-1)\phi} \right] d\phi = \begin{cases} \pi & \text{if } m' = m \pm 1, \\ 0 & \text{otherwise.} \end{cases}
\]
Let us also apply the occurring mathematical relation:

\[ \sin \theta P_{l'}^{m-1}(\cos \theta) = \frac{P_{l'+1}^{m}(\cos \theta) - P_{l'-1}^{m}(\cos \theta)}{2l' + 1} \]

where

\[ \int_{0}^{\pi} P_{l'}^{m \pm 1} \sin \theta P_{l}^{m} \sin \theta \, d\theta = 0 \quad \text{unless} \quad l' = l \pm 1 \]

Let us also state that there exist no restrictions on the R integral if \( l' = l \pm 1 \)

Furthermore, if we carried out the evaluation of the Z2 integral, then we would also find that the dipole matrix element is allowed only \( m' = m \) or \( \Delta m = 0 \)

This type of analysis leads to a simple set of selection rules obtained while ignoring electron spin that indicate that transitions can occur only if \( \Delta l = \pm 1 \) and \( \Delta m = \pm 1 \) or 0

\[ \Delta l = \pm 1, \]
\[ \Delta s = 0, \]
\[ \Delta j = \pm 1 \text{ or } 0 \quad \text{but} \quad j = 0 \rightarrow j = 0, \]
\[ \Delta m_j = \pm 1 \text{ or } 0 \quad \text{but} \quad m_j = 0 \rightarrow m_j = 0 \quad \text{if} \ \Delta j = 0 \]
Example of Selection Rule Determination Using the Full QM Solution

- Transition probability for the Hydrogen atom from
  
  \[
  n = 2, \ l = 1, \ m = +1 \ (2p^2P_{3/2}^o)
  \]
  
  to
  
  \[
  n = 1, \ l = 0, \ m = 0 \ (1s^2S_{1/2})
  \]

- Then obtain the oscillator strength and the radiative time of the upper level

\[
2p^2P_{3/2}^o \ (2, \ 1, \ +1) \Rightarrow \psi_u^{2,1,+1} = \frac{1}{8\pi^{1/2}a_H^{5/2}} re^{-r/2a_H} \sin \theta e^{i\phi}
\]

\[
1s^2S_{1/2} \ (1, \ 0, \ 0) \Rightarrow \psi_l^{1,0,0} = \frac{1}{\pi^{1/2}a_H^{3/2}} e^{-r/a_H}
\]

\[
A_{ul}(2p_{+1} \rightarrow 1s) \frac{\omega_{21}^3}{3\pi\varepsilon_0\hbar c^3} \left| \int \psi_u^{2,1,+1}e^r\psi_l^{1,0,0} \ dV \right|^2
\]

\[
r = x\hat{i} + y\hat{j} + z\hat{k}
\]

\[
x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta
\]

\[
dV = r^2 \sin \theta \, dr \, d\theta \, d\phi
\]
Example of Selection Rule Determination Using the Full QM Solution

\[
\int |\psi_u^* e^r \psi_1| dV = M_{ul}^2 = e^2 \left[ \int |\psi_u^* x \psi_1| dV \right]^2 + \int |\psi_u^* y \psi_1| dV \right]^2 + \int |\psi_u^* z \psi_1| dV \right]^2 \]

\[X = \int \psi_u^* x \psi_1 dV\]

\[= \int \frac{1}{8\pi^{1/2} a_H^{5/2}} r e^{-r/2 a_H} \sin \theta e^{-i\phi} r \sin \theta \cos \phi \frac{1}{\pi^{1/2} a_H^{3/2}} e^{-r/2 a_H} r^2 \sin \theta \sin \theta \, dr \, d\theta \, d\phi\]

\[= \frac{1}{8\pi a_H^4} \int \int \int r^4 e^{-3r/2 a_H} \, dr \, (\cos^2 \theta - 1) \, d(\cos \theta) \, e^{-i\phi} \left( \frac{e^{i\phi} + e^{-i\phi}}{2} \right) \, d\phi\]

\[= \frac{1}{8\pi a_H^4} \int_0^\infty r^4 e^{-3r/2 a_H} \, dr \int_0^\pi (\cos^2 \theta - 1) \, d(\cos \theta) \int_0^{2\pi} \frac{1 + e^{-2i\phi}}{2} \, d\phi\]

\[= 4 \left( \frac{2}{3} \right)^5 a_H.\]

\[\int \psi_u^* y \psi_1 dV = \frac{4}{i} \left( \frac{2}{3} \right)^5 a_H \quad \text{and} \quad \int \psi_u^* z \psi_1 dV = 0.\]
Example of Selection Rule Determination Using the Full QM Solution

\[ M_{ul}^2 = \left| \int \psi_u^* \mathbf{r} \psi_l \, dV \right|^2 = e^2 \left[ \left| 4 \left( \frac{2}{3} \right)^5 a_H \right|^2 + \left| \frac{4}{i} \left( \frac{2}{3} \right)^5 a_H \right|^2 + |0|^2 \right] \]

\[ = \left[ 4^2 \left( \frac{2}{3} \right)^{10} a_H^2 + 4^2 \left( \frac{2}{3} \right)^{10} a_H^2 \right] = 32 \left( \frac{2}{3} \right)^{10} e^2 a_H^2. \]

\[ A_{ul} (2p_{+1} \rightarrow 1s) = \frac{\omega_{ul}^3}{3\pi\varepsilon_0 \hbar c^3} 32 \left( \frac{2}{3} \right)^{10} e^2 a_H^2 = 6.2 \times 10^8 \text{ s}^{-1} \]

Now consider the degeneracy probabilities: n = 2 had 3 p states for spin up and spin down
n = 1 had 1 s state for spin up or spin down

Probability of the upper p state: J = L+S = 1+1/2 \quad g_{2p} = 2J+1 = 5+1 = 6
Probability of being in an upper n state: \quad g_{2s} = 2

\[ A(2 \rightarrow 1) = (6/8)(6.2 \times 10^8 \text{ s}^{-1}) = 4.7 \times 10^8 \text{ s}^{-1} \]

Combined upper state probabilities: g_2 = 8
Probability for the lower state: J = L+S = \frac{1}{2} \quad g_1 = 2J+1 = 2

\[ \lambda_{21} = 1.2157 \times 10^{-7} \text{ m}, \quad g_2 = 8, \quad \text{and} \quad g_1 = 2 \quad \Rightarrow \quad f_{12} = (1.5 \times 10^4) \left( \frac{g_2}{g_1} \right)^2 \lambda_{21}^2 A_{21} \]

\[ f_{12} = 0.416 \]
Selection Rules for Radiative Transitions Transition Involving Atoms with More than One Electron in an Unfilled Shell

• The QM selection rules for multi-electron atoms in terms of their orbital angular momentum description quantum numbers: \( L, S, \) and \( J \)

\[
\Delta l = \pm 1 \quad \text{for the changing electron (change in parity)},
\]
\[
\Delta S = 0, \quad \Delta L = 0, \pm 1,
\]
\[
\Delta J = 0, \pm 1 \quad \text{but} \quad J = 0 \rightarrow J = 0,
\]
\[
\Delta M_J = 0, \pm 1 \quad \text{but} \quad M_J = 0 \rightarrow M_J = 0 \text{ if } \Delta J = 0,
\]

• Most cases ignore the \( \Delta M \) rule and only use \( L, S, \) and \( J \) when considering LS coupling

• Note higher order transitions can occur due to quadrupole functions in which \( \Delta L = \pm 2 \)
• Such transitions due exist with decay rates 4-6 orders of magnitude longer than dipole interactions and are present in some laser systems, however ....
Wave functions of various states possess even or odd symmetry.
States with odd angular momentum quantum number (L) are said to have odd parity
States with even angular momentum quantum number (L) are even parity
The overlap integral between two states A and B will only have a nonzero value if A and B have the same parity.

\[ \int \psi^*(A)\psi(B) \, dV \]

This effect is noted in the previous selection rules by requiring \( \Delta l = \pm 1 \) and thereby requiring the electron involved in the transition must change parity.
Energy level parity is determined by the number of electrons having odd parity

\[ l = 1, 3, 5, \ldots \]
\[ p, f, h, \ldots \]

If there are an even number of odd parity electrons, then the energy level has even parity
- Example: An unfilled shell 2p or \((2p)^3\) or 4f would have odd parity
- Example: \((2p)^2, 4(f)^4, 2p4f\) have even parity
Odd parity can be denoted by a superscript o in the upper right corner

\[ ^3P_1^o \quad \text{or} \quad ^1D_2^o \]
\[ 2p^2P_{3/2}^o \rightarrow 1s^2S_{1/2} \]
Defining Orbital Angular Momentum States

<table>
<thead>
<tr>
<th>Principal number</th>
<th>symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>orbital</td>
<td>$l$</td>
<td>integer up to $(n - 1)$</td>
</tr>
<tr>
<td>magnetic</td>
<td>$m_l$</td>
<td>integer from $-l$ to $+l$</td>
</tr>
<tr>
<td>spin</td>
<td>$m_s$</td>
<td>$\pm 1/2$</td>
</tr>
</tbody>
</table>

Table 4.1: Quantum numbers for electrons in atoms.

<table>
<thead>
<tr>
<th>Shell</th>
<th>$n$</th>
<th>$l$</th>
<th>$m_l$</th>
<th>$m_s$</th>
<th>$N_{shell}$</th>
<th>$N_{accum}$</th>
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<tbody>
<tr>
<td>1s</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>$\pm 1/2$</td>
<td>2</td>
<td>2</td>
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<tr>
<td>2s</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>$\pm 1/2$</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>2p</td>
<td>2</td>
<td>1</td>
<td>$-1, 0, +1$</td>
<td>$\pm 1/2$</td>
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<td>10</td>
</tr>
<tr>
<td>3s</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>$\pm 1/2$</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>3p</td>
<td>3</td>
<td>1</td>
<td>$-1, 0, +1$</td>
<td>$\pm 1/2$</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>4s</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>$\pm 1/2$</td>
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<td>20</td>
</tr>
<tr>
<td>3d</td>
<td>3</td>
<td>2</td>
<td>$-2, -1, 0, +1, +2$</td>
<td>$\pm 1/2$</td>
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<td>30</td>
</tr>
<tr>
<td>4p</td>
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<td>1</td>
<td>$-1, 0, +1$</td>
<td>$\pm 1/2$</td>
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<td>36</td>
</tr>
<tr>
<td>5s</td>
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<td>0</td>
<td>0</td>
<td>$\pm 1/2$</td>
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<td>38</td>
</tr>
<tr>
<td>4d</td>
<td>4</td>
<td>2</td>
<td>$-2, -1, 0, +1, +2$</td>
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<td>48</td>
</tr>
<tr>
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<td>$-1, 0, +1$</td>
<td>$\pm 1/2$</td>
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<td>54</td>
</tr>
<tr>
<td>6s</td>
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<td>0</td>
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<tr>
<td>4f</td>
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<td>$-3, -2, -1, 0, +1, +2, +3$</td>
<td>$\pm 1/2$</td>
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</tr>
<tr>
<td>5d</td>
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<td>0</td>
<td>0</td>
<td>$\pm 1/2$</td>
<td>2</td>
<td>88</td>
</tr>
</tbody>
</table>

**LS coupling** $2S + 1L_J$

1. The parity of the wave function must change.
2. $\Delta l = \pm 1$ for the electron that jumps between shells.
3. $\Delta L = 0, \pm 1$, but $L = 0 \rightarrow 0$ is forbidden.
4. $\Delta J = 0, \pm 1$, but $J = 0 \rightarrow 0$ is forbidden.
5. $\Delta S = 0$.

- S implies $L = 0$, D implies $L = 2$
- P implies $L = 1$, F implies $L = 3$

Note: These solutions provide the angular momentum states for a given $n$ value. One must still solve Schrödinger's equation for the atom in question to obtain the various constants required to solve for the energies related to each orbital configuration.