Part II. Fundamentals of Atomic Spectroscopy
Chapter 4. Introduction to Atomic Structure and Atomic Spectra

1. Overall Atomic Spectroscopy consists of the following aspects:

(1) Quantum Mechanics Fundamentals

(2) Theory of Atomic Structure

[Energy Eigenvalues and Eigenstates of Single Atom]

$\Rightarrow$ Resonance central frequency (Wavelength λ_0) of spectral line.

(3) Theory of Radiative Transitions

[Transition Probability and Selection Rules of Single Atom]

$\Rightarrow$ Intensity (partially), Polarization, and Distribution Direction of spectral line

(4) Theory of Statistical Interaction of an ensemble of atoms with radiation [Quantum Statistical Behavior of an ensemble of atoms]

$\Rightarrow$ Shape, Width, Intensity of spectral Line.

(5) Applications of atomic Spectroscopy.

2. Spectral lines are produced by different processes, e.g., resonant radiative transitions (absorption, stimulated and spontaneous emissions); Scattering, etc.

Recorded spectral Line
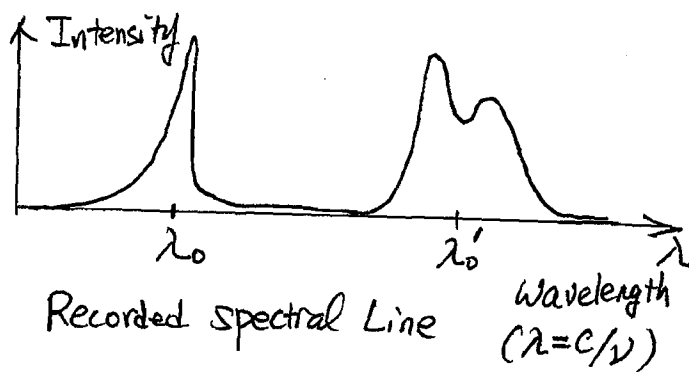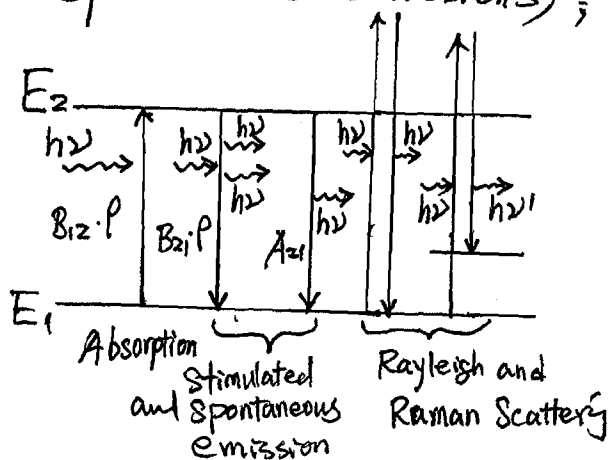
Wavelength $(\lambda = c/\nu)$

3. What parameters do we care about a spectral line?

— There are three major "Characteristic" parameters:

(1) Resonance central frequency (wavelength λ_0) of a spectral line

* The central frequency is determined by the energy difference between the two energy levels where the transition (real) occurs:

$$\nu_0 = \frac{E_2 - E_1}{h} \quad \text{(for real transition)}$$

For scattering case (virtual transition),

$$\nu_0 = \nu_L + \Delta\nu, \quad \text{where} \quad \Delta\nu = \frac{E_3 - E_1}{h}$$

ν_L is the incident light frequency, $\Delta\nu$ is the frequency shift, and ν_0 is the scattered light frequency.

* Deriving the central frequency is to derive the atom energy eigenvalues and eigenstate. This can only be addressed by the "theory of atomic structure" — totally determined by Quantum Physics (Quantum Mechanics and Quantum Electro-Dynamics QED).

* The fundamental approach is to solve the energy eigen-value equation (i.e., the stationary-state Schrödinger equation) of single atom to derive eigenvalues $\{E_n\}$:

$$\hat{H}\,|\psi\rangle = E\,|\psi\rangle, \qquad \hat{H} = \frac{\hat{p}^2}{2m} + \hat{V},$$

where $\hat{H}$ is the atom Hamiltonian operator, $|\psi\rangle$ is $\hat{H}$'s eigenstate, E is the corresponding eigenvalue.

Thus, central frequency $\nu_0 = (E_m - E_n)/h$

or $\omega_0 = (E_m - E_n)/\hbar$.

(2) Intensity, Polarization, and Distribution Direction of a spectral line

* Polarization, distribution direction, and Intensity (partially) are determined by the transition probability and selection rules of the single atom transition corresponding to the spectral line. Intensity is further determined by the statistical interaction of an ensemble of atoms with radiation.

* The single atom transition probability and selection rules are to deal with the interaction of a single atom with radiation field. This is addressed by the "theory of radiative transitions" — determined by Quantum Electro-Dynamics (QED): Quantized Atom interacting with an quantized radiation field.

* The fundamental approach is to solve the time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi\rangle$$

using QM and QED to derive selection rules and transition probability for single atom interaction with radiation field. The spectral line polarization, direction, and partial intensity are then inferred from these results.
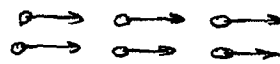
(3) Shape, Width, and Intensity of a spectral line.

* In reality, it is very rare to deal with single atom spectral line, especially in remote sensing area. Usually we deal with a large number of atoms, and the spectral line is also an assemble effect of the atom ensemble. Thus, the shape, width and Intensity of measured line are determined by not only the shape, width, and transition probability of a single atom, but also the statistical results of the ensemble of atoms, in which there are also interactions among atoms.

In other words, the shape, width and intensity of a spectral line are the overall contribution results from the ensemble, not just a single atom.

* For example, each single atom has the natural linewidth, determined by the uncertainty principle $\Delta E \cdot \Delta t \geq \hbar/2$. However, the Doppler linewidth is a result of many atoms in an ensemble. Atoms collide with each other and form Maxwellian distribution. For single atom, there is no Doppler width (1st order).
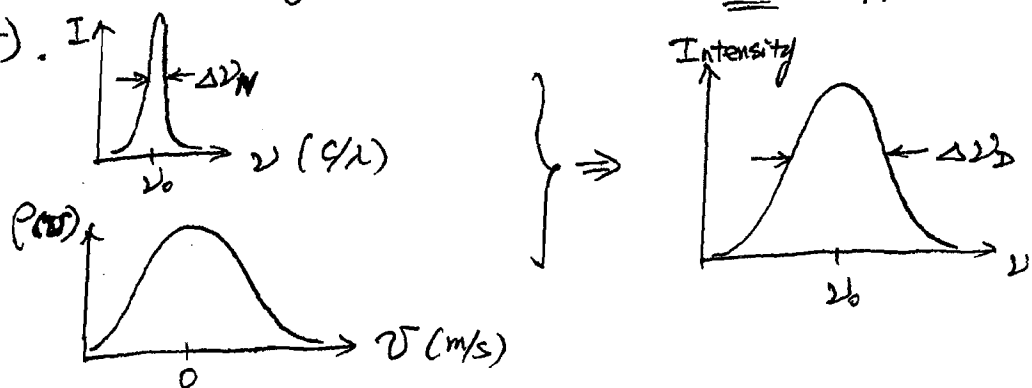
If an ensemble consists of many atoms but no interactions among them, e.g. atomic beam, then there is also no Doppler width.
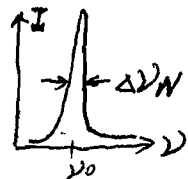
* Although the state of a single atom is perfectly determined by the Schrödinger equation, We usually have incomplete information of a system consisting of a large number of atoms. For this case, Statistical mechanics comes into the picture — Quantum Statistical Mechanics !

Classical Physics	Quantum Physics
Single Particle 　Newton Equations 　$\Rightarrow$ determining the 　behavior of single particle 　$\Rightarrow$ Classical Mechanics	Single Atom 　Schrödinger Equation 　$\Rightarrow$ determing the state 　evolution of single atom 　$\Rightarrow$ Quantum Mechanics
Many Particles (Ensemble) 　$\Rightarrow$ Statistical Mechanics 　distribution functions	Many atoms (ensemble) 　with many states 　$\Rightarrow$ Quantum Statistical 　　Mechanics 　density matrix

* There are three ways to address spectral lineshape issues.

A. Classical Theory: electric dipole makg harmonic or damped harmonic
　　　　　　　　　　　　or forced oscillation

electric
field : $E(t) \xrightarrow[\text{transform}]{\text{Fourier}} g(\nu)$

providg a physical picture, but not accurate, and cannot explain many complicated phenomena (qualitatively)

B. Semiclassical theory: interaction between atom and radiation

$\begin{cases} \text{atom — Quantum Mechanics} \\ \text{radiation — EM waves (classical)} \end{cases}$

For pure ensemble of atoms (i.e., all atoms are in the same state, no interaction between them), then the state of the ensemble can be described by the state wave function of single atom. Then we can solve the Schrödinger equation for this state to derive spectral results.

For mixed ensemble of atoms [i.e., atoms are in different states — a statistical mixture of states (different from the superposition of states)], then it is impossible to write a Schrödinger equation for this system (because we cannot write $|\psi\rangle = P_1 |\psi_1\rangle + P_2 |\psi_2\rangle$ — superposition). We have to use statistical method to solve the problem — the density matrix method.

The semiclassical theory can solve most of the problems. But it cannot explain spontaneous emission.

C. Full Quantum-Mechanics Theory (QED)

$\begin{cases} \text{atom} & - \text{Quantized energy structure} \\ \text{radiation} & - \text{Quantized radiation field} \end{cases}$

We use density matrix to solve problems of all.

D. In practice, QED conclusion for single atom structure/transition
   + statistical physics

$\Rightarrow$ spectral properties

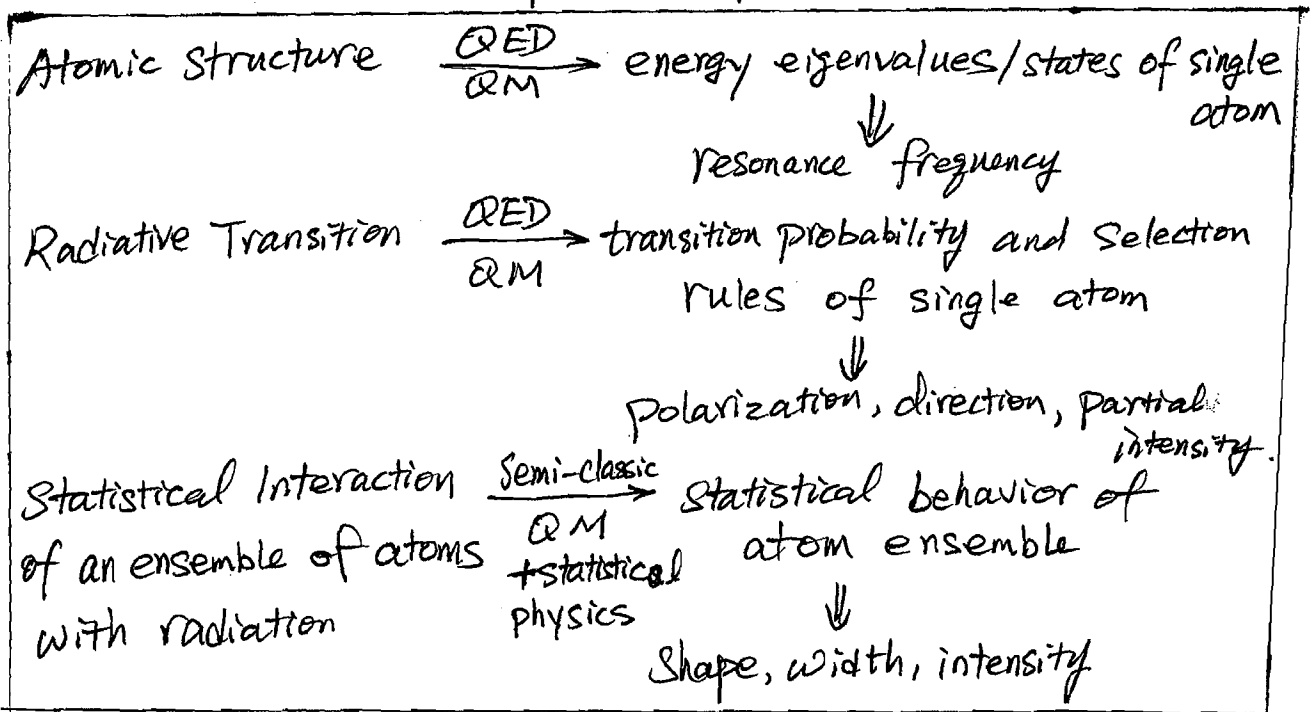> **Statistical mixture of states $\neq$ superposition of states**

Assume $|\psi_1\rangle$, $|\psi_2\rangle$ are two orthonormal eigenstates with a_1 and a_2 eigenvalues for operator $\hat{A}$.

If an atom 1 is in state $|\psi\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle$ (superposition) the atom is indeed in both states at the same time, with measurement results a_1 and a_2 of probabilities $|c_1|^2$, and $|c_2|^2$.

atom 2 is in state $|\psi'\rangle = c_1'|\psi_1\rangle + c_2'|\psi_2\rangle$ (superposition), where $c_1' \neq c_1$, $c_2' \neq c_2$.

If a system consists of atom 1 and atom 2, then we cannot write the overall system state as $|\psi\rangle + |\psi'\rangle$. The system is either in $|\psi\rangle$ or in $|\psi'\rangle$ state, but cannot be both.

** In summary of atomic spectroscopy

Atomic Structure $\xrightarrow{\frac{QED}{QM}}$ energy eigenvalues/states of single atom

$\Downarrow$ resonance frequency

Radiative Transition $\xrightarrow{\frac{QED}{QM}}$ transition probability and selection rules of single atom

$\Downarrow$

Polarization, direction, partial intensity

Statistical Interaction of an ensemble of atoms with radiation $\xrightarrow[\substack{QM \\ +\text{statistical} \\ \text{physics}}]{Semi-classic}$ Statistical behavior of atom ensemble

$\Downarrow$

Shape, width, intensity

Further Reading Books:

1. Condon E.U., and G.H. Shortley, The Theory of Atomic Spectra, Cambridge University Press, 1964 (for Atomic Structure)

2. Sobelman, I.I., Atomic Spectra and Radiative Transitions, Springer – Verlag, 1992. (for structure and transition probability)

3. Demtröder, W, Laser Spectroscopy, Spinger, 2003. (Shape and Width)