

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

— There are three major "Characteristic" Parameters:

(1) Resonance central frequency (wavelength  $\lambda_0$ ) of a spectral line

\* The central frequency is determined by the energy difference between the ~~to~~ 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),

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

$\nu_L$  is the incident light frequency,  $\Delta\nu$  is the frequency shift, and  $\nu_0$  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 Electrodynamics QED).

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

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

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

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

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

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

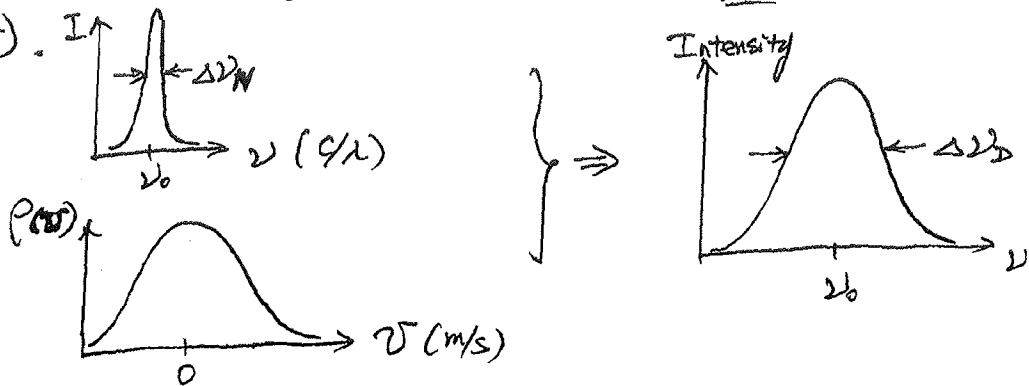
- \* Polarization, distribution direction, and Intensity (partially) are determined by the transition probability and selection rules of the single atom transition corresponding to the spectral line. Intensity is further determined by the statistical interaction of an ensemble of atoms with radiation.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

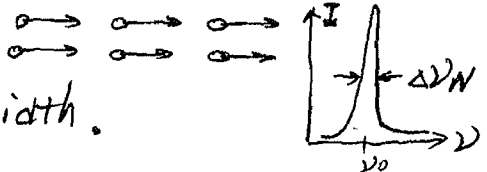
\* In reality, it is very rare to deal with single atom spectral line, especially in remote sensing area. Usually we deal with a large number of atoms, and the spectral line is also an assemble effect of the atom ensemble. Thus, the shape, width and Intensity of measured line are determined by not only 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 ⇒ determining the behavior of single particle ⇒ Classical Mechanics	Single Atom Schrödinger Equation ⇒ determining the state evolution of single atom ⇒ Quantum Mechanics
Many Particles (Ensemble) ⇒ Statistical Mechanics distribution functions	Many atoms (ensemble) with many states ⇒ Quantum Statistical Mechanics density matrix

\* There are three ways to address spectral lineshape issues.

A. Classical Theory: electric dipole making harmonic or damped harmonic or forced oscillations

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

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

B. Semiclassical theory: interaction between atom and radiation

- { atom — Quantum Mechanics
- { radiation — EM waves (classical)

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)

$\left\{ \begin{array}{l} \text{atom — Quantized energy structure} \\ \text{radiation — Quantized radiation field} \end{array} \right.$

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

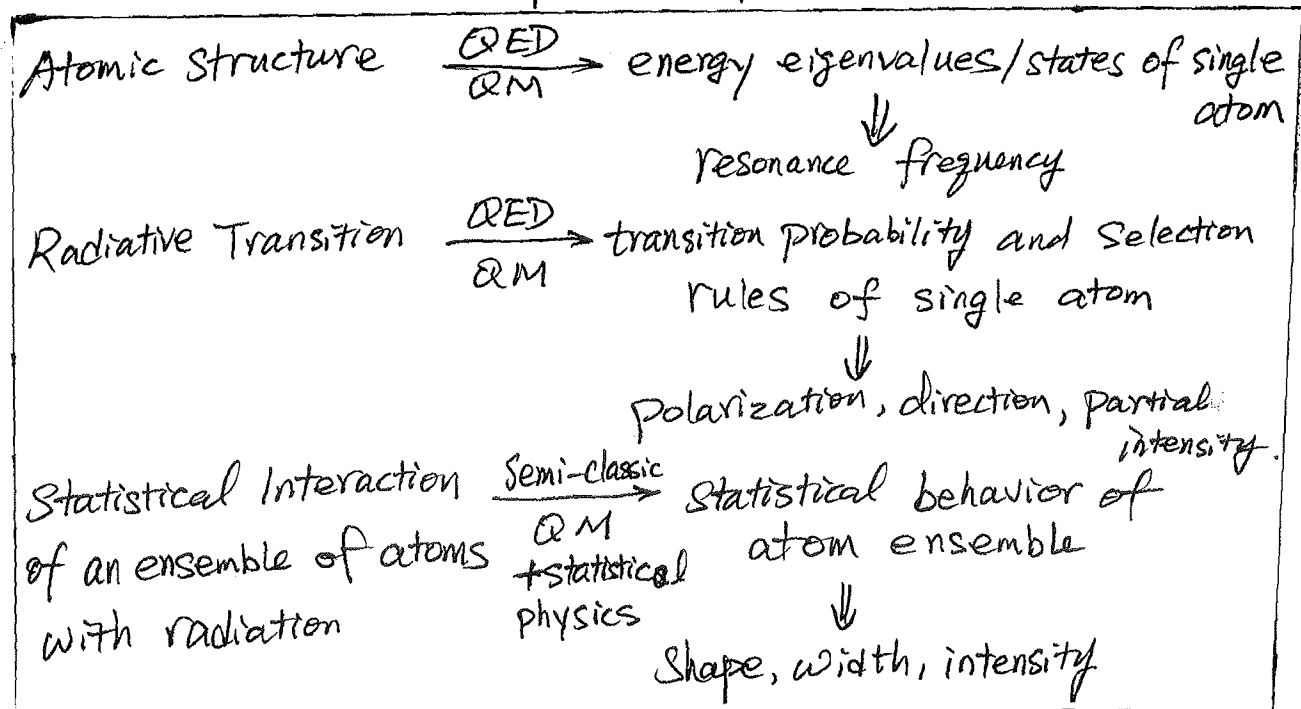
Assume  $|\psi_1\rangle, |\psi_2\rangle$  are two orthonormal eigenstates with  $a_1$  and  $a_2$  eigenvalues for operator  $\hat{A}$ .

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  $|\psi'\rangle$  state, but cannot be both.

\*\* In summary of Atomic Spectroscopy



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, Springer, 2003. (Shape and Width)

# Chapter 5. Atomic Structure

18.

## §5.1. Atomic Structure Overview

(1) The main clue is to solve stationary-state Schrödinger equation of a single atom (i.e., the eigenvalue equation of  $\hat{H}$ ) to derive energy eigenvalues and eigenstates:

$$\hat{H} |\psi\rangle = E |\psi\rangle.$$

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \hat{V} = \text{Kinetic Energy} + \text{Potential Energy}$$

All these operators in the eigenvalue equation are independent of time. ( $\mu$  is the reduced mass  $\mu = \frac{mM}{m+M}$ )

(2)  $\hat{V}$  is determined by interactions: inside an atom and interactions between atom and external field (Static, independent of time) if any.

\* When  $\hat{V}$  changes, the energy eigenvalues will change  $\rightarrow$  the shift of energy levels or the removal of degeneracy of the energy levels.

(3) We have very limited ability to solve the stationary-state Schrödinger equation analytically. Only when  $\hat{V}$  is in a simple format, e.g.,  $\hat{V} \propto \frac{1}{r}$ , it is possible to solve the equation analytically, e.g. hydrogen atom when only consider Coulomb force between the nucleus and the single electron.

(4) For most of other cases, not only we can't solve the equation analytically, but also can't even numerically. Approximation methods have to be used to get an approximate solution. The most common approach

is the perturbation theory, in particular, time-independent perturbation theory for solving the  $\hat{H}$  eigenvalue equation.

(5) The main idea of perturbation theory is to solve the equation for the major force, e.g., the Coulomb force between nucleus and electron, and produce the main energy levels, denoted by the principal quantum number  $n$ . And then consider the other minor force (e.g., spin-orbit coupling) as a perturbation to the main energy levels, so the equation can be simplified and approximated, and solutions approximate can be derived. The results are to place a correction to the main levels, depending on different states. Different states may experience different corrections, i.e., different shift of energy, thus, some degeneracy can be removed.

(6) Interactions to be considered in atomic structure theory:  
Let's consider the simplest atom -  ${}^1\text{H}$ .

① Electrostatic Interaction between the nucleus and the electron (Coulomb force) forming main energy levels with quantum number  $n, l, m_l$  (but  $l, m_l$  are degenerate)  
degeneracy =  $n^2$ .

② Electron Spin and Angular momentum coupling

An electron orbiting around a nucleus  $\rightarrow$  current in a circle  $\Rightarrow$  magnetic moment: orbital angular momentum

An electron has spin  $\Rightarrow$  spin magnetic moment  $\Rightarrow$   
spin angular momentum



The electron's orbital and spin angular momentum can have magnetic interaction: the coupling between spin and orbit  
 $\Rightarrow$  main energy levels split, shift, ~~and~~ partially remove degeneracy  
 $\Rightarrow$  fine structure of energy levels.  $\vec{L} + \vec{S} = \vec{J}$

### ③ Nuclear influence:

a). Nuclear spin angular momentum coupling with electron total angular momentum  $\vec{J} + \vec{I} = \vec{F}$   
 $\Rightarrow$  hyperfine structure

b). neutrons in nucleus affect mass and volume  
 $\Rightarrow$  isotope shift of energy levels.  
 e.g.,  $^1\text{H}$ ,  $^2\text{D}$ ,  $^3\text{T}$  (neutrons: 0, 1, 2)

### ④ External field: static electric and magnetic field

magnetic: Zeeman effect  $\Rightarrow$  energy levels split and shift

Electric: Stark effect  $\rightarrow$  energy level split and shift.

Let's consider when an atom has more than one electron:

### ⑤ Electron-Electron Interactions:

(e.g.,  $^2\text{He}$ )

a). Electrostatic interaction between electrons:

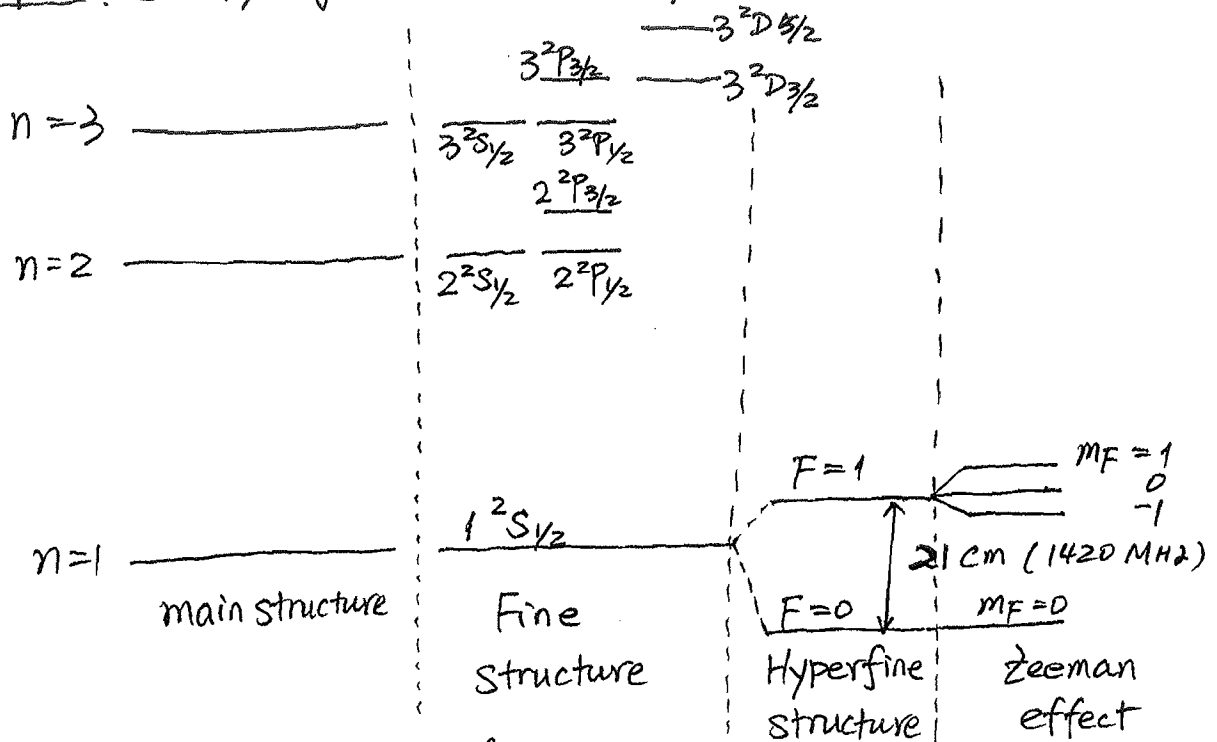
{ Central Field part  
 { non-central Field part

b). Magnetic interaction between electron magnetic moments:

{ one electron spin coupling with another electron orbital angular momentum  
 { Spin-spin electron angular momentum coupling.

The electron-electron interactions are much stronger than nuclear influence. So for multielectron atoms, we usually consider e-e interactions before considering nuclear influences.

Examples, ① Hydrogen atomic energy levels:



② Na atomic energy levels:

