I. ATOMIC ENERGY LEVELS

Atoms and molecules emit electromagnetic radiation or photons when the electrons or nuclei undergo transitions between various energy levels of the atomic or molecular system. Detailed theory of radiation requires quantum electrodynamics to fully describe the interaction between materials and electromagnetic radiation, so it will not be detailed in this lecture. However, a small set of rules will be discussed to allow the study of the basic physics of radiation.

First we will consider the interaction between electrons in the bound states of atoms and electromagnetic radiation. Atoms emit electromagnetic radiation or photons when their bound electrons undergo transitions between various energy levels of atomic system. Each atomic system has its unique energy levels determined by the electromagnetic interaction among various bound electrons and nucleus.

Calculation of atomic energy levels requires solving a Schrödinger equation for a many particle system (nucleus and electrons) and there is no exact solution available except for the simplest atomic system, i.e., the hydrogen atom. Many approximation methods were developed to calculate the atomic energy levels, currently, the energy levels of many atomic systems are identified and tabulated in the form of Grotrian diagram. One way to designate the various energy levels in the Grotrian diagram is called LS (also known as Russell-Saunders) coupling. However, it should be noted that the LS coupling scheme does not necessarily specify each energy level uniquely, thus one should be careful about using LS coupling scheme. According to the LS coupling scheme, each state is denoted by its orbital angular momentum and the spin state along with each electron’s configuration state.

For example, the ground state neutral helium described by LS coupling scheme is \((1s)^2 \, ^1S_0\). \((1s)^2\) denotes that two electrons occupy the 1s state, and \(^1S_0\) is the spectroscopy term where the superscript 1 denotes the net spin state is singlet, S denotes that
the total orbital angular momentum is 0, and the subscript 0 denotes that the total angular momentum is 0 (J=L+S=0).

Another example: the ground state neutral carbon and oxygen described by LS coupling scheme are (1s)²(2s)²(2p)³ ³P₀ and (1s)²(2s)²(2p)³ ³P₂. Here we have 2 electrons in the 1s state, 2 electrons in the 2s state, and 2 or 4 electrons in the 2p state. In addition, the net spin state is triplet (superscript 3), the orbital angular momentum state is P (angular momentum quantum number is 1) and the total angular momentum state is 0 or 2 (for less than half filled orbital, J=L-S=0; for half filled orbital or more than half-filled orbital, J=L+S= 1 + 1 =2).

In summary, the designation of atomic energy levels can be done using the spectroscopic designation of an atomic state:

\[ X \, I \, n^{2S+1}L_J \]

where X is the element symbol,

I is the ionization state (I: not ionized, II singly ionized, II: doubly ionized, etc.),

n is the principal quantum number,

2S+1 is the multiplicity (S=0: singlet; S=½: doublet; S=1: triplet, etc),

L is the total orbital angular momentum (S, P, D, F, G for L = 0, 1,2,3,4), and

J = L + S is the total electronic angular momentum.

The atomic energy levels of Na is shown in Fig. 1 as an example.

II. ATOMIC COLLISIONS

In a homogeneous plasma, energetic electrons undergo collision with the neutrals to generate excited neutrals, atoms, free radicals, ions, and additional electrons. These electron collision processes make the plasma chemistry complex and interesting. Due to the large mass difference, the electron-particle collision can be viewed as an elastic collision process, as shown in Fig. 2. Several other electron-atom collision processes are listed:

1. Excitation processes
   a) Electron impact ionization (Fig. 3):
Electrons with sufficient energy can remove an electron from an atom and produce one extra electron and an ion. This extra electron can again be accelerated to gain enough energy and ionize another atom. This multiplication process leads to a continuous generation of ionized species and the plasma is sustained. The ionization processes generally have the highest energy barriers, on the order of 10 eV.

b) Electron impact excitation (Fig. 4):
\[ e^- + A \rightarrow e^- + A^* \]
Electrons with sufficient energy can also excite the electrons of an atom from the lower energy level to a higher energy level. This process produces an excited neutral species whose chemical reactivity towards the surface could be quite different from the ground state atoms. The threshold energy needed to produce excited species can vary greatly, depending on the molecule and the type of excitation.

Some excited atoms have very long lifetimes (~1-10 msec) because the selection rules forbid its relaxation to the ground state. These excited atoms are thus called *metastables*. All noble gases have metastable states.

c) Electron impact dissociation of diatomic molecules (A₂) (Fig. 5):
\[ e^- + A_2 \rightarrow e^- + A + A \]
Electrons with sufficient energy can also break the chemical bonds of a molecule and produce atomic species. These atomic species could gain enough energy and be at a higher energy level than the ground state atoms. Dissociative processes usually have lower threshold energies than ionization processes. Dissociative threshold energies vary from 0 to above 10 eV, depending upon the strength of the bond that is broken and the mechanism by which the process occurs.

This process is mostly responsible for the production of chemically active radicals in most of the plasmas.

d) Electron metastable ionization (Fig. 6):
Electrons with sufficient energy can also remove an electron from a metastable atom and produce one extra electron and an ion. Since the metastable atom is already excited, less energy is required here to ionize the atom.

e) Metastable-neutral ionization (Fig. 7):
\[ \text{A}^* + \text{B} \rightarrow \text{A} + \text{e}^- + \text{B}^+ \]

Metastable atom can collide with a neutral and ionize it if the ionization energy of the neutral (B) is less than the excitation energy of the metastable (A*). This is also called the Penning Ionization process.

2. Relaxation and Recombination Processes

a) De-excitation (Fig. 8):
\[ \text{A}^* \rightarrow \text{A} + \text{hv} \]

The excited states of atoms are usually unstable and the electron configuration can soon return to its original ground state, accompanied by the emission of a photon with a specific energy that equals the energy difference between the two quantum levels.

b) Electron-ion recombination (Fig. 9):
\[ \text{e}^- + \text{A}^+ + \text{A} \rightarrow \text{A}^* + \text{A} \]

For electron-ion recombination, a third-body must be involved to conserve the energy and momentum conservation. Abundant neutral species or reactor walls are ideal third-bodies. This recombination process typically results in excited neutrals.

c) Radiative recombination (Fig. 10):
\[ \text{e}^- + \text{A}^+ \rightarrow \text{A} + \text{hv} \]

Photon can also be generated during the coalescence process of recombination. This is also a three-body recombination process, since the two-body coalescence is highly unlikely from the standpoint of energy and momentum conservations.

d) Electron attachment (Fig. 11):
\[ \text{e}^- + \text{A} \rightarrow \text{A}^- \]
Electron can attach to an electronegative atom to form a negative ion, for example, a halogen atom or an oxygen atom. Complex gas molecules such as SF$_6$ can also undergo dissociative attachment to form negative SF$_5^-$ ions. This could also be a three-body recombination process.

e) Ion-ion recombination (Fig. 12):

\[ A^+ + A^- \rightarrow A + A \]

With negative ions generated, positive ions and negative ions can collide with finite (usually small) probabilities. In ion-ion recombination, one electron transfers and two neutrals are formed.

### III. ELASTIC COLLISIONS

1. **Coulomb collisions**

   In general, collisions between ion-ion, ion-electron, and electron-electron are all Coulombic collision. The coulomb potential is:

   \[ U(r) = \frac{q_1 q_2}{4 \pi \varepsilon_0 r} \]  

   (1)

   Following the derivation above, the differential collision cross-section can be determined to be:

   \[ I(v_R, \phi) = b_0^2 \frac{b_0}{4 \sin^2 \frac{\phi}{2}} \]  

   (2)

   Note: this is the Rutherford Back Scattering (RBS) cross-section where $b_0$ is the distance of the closest approach.

   \[ b_0 = \frac{q_1 q_2}{4 \pi \varepsilon_0 W_R} = \frac{Z_1 Z_2 e^2}{4 \pi \varepsilon_0 \left( \frac{1}{2} m_v v_R^2 \right)} \]  

   (3)

   From this analysis, Coulombic scattering could lead to a single large-angle scattering (less likely) or cause a series of small-angle scatterings.

2. **Polarization scattering**

   With a point charge, $q_o$, approaches an atom whose atomic radius is $a$ with a point positive charge of $q$ and a uniform negative charge cloud $-q$, ...
the point charge can polarize the atom by displacing the uniform charge cloud through quasistatic interactions. The induced electric field due to a small displacement, $d$, around the center of the atom is:

$$E_{\text{ind}} = -\frac{qd}{4\pi\epsilon_0 a^3}$$  

(4)

The induced dipole is therefore:

$$P_{\text{ind}} = qd = \frac{q_o a^3}{r^2}$$  

(5)

The attractive potential due to the incoming charge $q_o$ is:

$$U(r) = -\frac{q_o^2 a^3}{8\pi\epsilon_0 r^4}$$  

(6)

The polarizability in this simple atomic model is: $\alpha_p = a^3$, and the relative polarizability is:

$$\alpha_R = \frac{\alpha_p}{a_o^3}$$  

(7)

Table 1 summarizes the relative polarizability of several atomic species. Note again that $a_o$ is the Bohr radius.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\alpha_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>4.5</td>
</tr>
<tr>
<td>C</td>
<td>12</td>
</tr>
<tr>
<td>N</td>
<td>7.5</td>
</tr>
<tr>
<td>O</td>
<td>5.4</td>
</tr>
<tr>
<td>Ar</td>
<td>11</td>
</tr>
<tr>
<td>CCl4</td>
<td>69</td>
</tr>
<tr>
<td>CF4</td>
<td>19</td>
</tr>
<tr>
<td>CO</td>
<td>13</td>
</tr>
<tr>
<td>CO2</td>
<td>17</td>
</tr>
<tr>
<td>Cl2</td>
<td>31</td>
</tr>
<tr>
<td>H2O</td>
<td>9.8</td>
</tr>
<tr>
<td>NH3</td>
<td>14.8</td>
</tr>
<tr>
<td>O2</td>
<td>10.6</td>
</tr>
<tr>
<td>SF6</td>
<td>30</td>
</tr>
</tbody>
</table>

If the impact parameter, $h$ is small enough, i.e., smaller than the critical impact parameter, $h_L$, the particle will be captured by the atom during this type of collision. This critical impact parameter is:

$$h_L = \left(\frac{\alpha_p q_o^2}{\nu_R^2 \pi \epsilon_0 m_R}\right)^{\frac{1}{2}}$$  

(8)

$$m_R = \frac{m_1 m_2}{m_1 + m_2}$$  

(9)

$$\nu_R = |v_1 - v_2|$$  

(10)

The Langevin or capture cross-section can thus be determined as:

$$\sigma_L = \pi h_L^2$$  

(11)

IV. INELASTIC COLLISIONS

1. Constraints on electronic transitions

Atoms emit electromagnetic radiation (photons) when the electrons undergo transitions between various energy levels. Since the typically radiation time is on the order of 1 ns, much shorter than the characteristic time between collisions,
which are on the order of 100 ns, the excited states will generally be de-excited by electric dipole radiation rather than by collision.

However, not every transition occurs as frequently as others do. The most frequent transition between various energy levels is the electric dipole transition and the following conditions should be satisfied for the electric dipole transition. The general rule of thumb includes:

**Energy conservation**: the energy of emitted radiation (photons) should be equal to the energy difference between the upper energy level and the lower energy level, \( h\nu = E_i - E_j \), where \( h \) is the Planck's constant, \( \nu \) is the frequency of the emitted photon, \( E_i \) is the energy of the upper level the electron occupies prior to the transition, and \( E_j \) is the energy of the lower level the electron occupies after the transition.

**Selection Rules**: during the electric dipole transition, the following changes for angular momentum state need to occur:

- Change in the orbital angular momentum state: \( \Delta L = 0, \pm 1 \)
  
  (0 is not allowed for a transition involving only one electron)

- Change in the spin angular momentum state: \( \Delta S = 0 \)

- Change in the total angular momentum state: \( \Delta J = 0, \pm 1 \)
  (except that \( J=0 \) to \( J=0 \) transition is strictly forbidden).

From the selection rule, the energy levels of He, can be shown divided into singlet (para-helium) and triplet (ortho-helium) states, since the transitions between them are forbidden. Since \( L=0 \rightarrow L=0 \) is forbidden, the \( 2^1S \) and \( 2^3S \) states are metastables (Fig. 14). A more detailed Grotrian diagram is included at the end of this section.

It is noted that the selection rules are not perfect, unlike energy conservation. For example, the very intense mercury resonance line at 253.7 nm is due to the transition from \( ^3P_1 \rightarrow ^1S_0 \).

If the above two conditions are satisfied, the electrons can spontaneously undergo transition from the upper energy level, \( i \), to the lower energy level, \( j \), with a certain probability per unit time. This

![Fig. 14. Atomic energy levels of He, showing the division into singlet and triplet states.](image)
probability is called the transition probability for spontaneous emission (also known as Einstein A coefficient) and can be easily found in the literature for many transitions. For example, the transition probability of hydrogen atom between 2p state and 1s state is $6.28 \times 10^8$ sec$^{-1}$.

### 2. Identification of atomic spectra

Based on the above discussion, we can now understand the essential features of atomic spectrum and obtain some useful information about the plasma system. As shown in Fig. 15, atomic spectrum usually consists of a number of very sharp lines on the constant background. When the spectrum is measured, the first task is to identify every emission line in the spectrum. This is done by comparing the wavelength of the emission lines with the energy differences between two electronic levels using the published spectral data base (NIST database). It is noted that in some cases even this first step is not very straightforward and requires additional consideration. Once this step is completed, we can have at least two (maybe more) very useful information about the plasma. They are:

- Identification of existing atomic species in the plasma.
- Identification of certain excited atomic states and their density in the plasma.

Later, we will learn how to use the information to understand the plasma state.

Light emission is a major characteristic of plasmas. To emit the light, the atoms in the plasma have to be in the excited states. There are two different ways to excite the atoms in the plasma to the excited states. The first one is to use the kinetic energy of the particles in the plasma (in particular electrons) and to transfer this energy to the atoms in the ground state (or another excited state) by collision. This process is called collisional excitation. The second process is to use the energy of the photons and to transfer their energy to the atoms by absorption of photons. This process is called radiative excitation. In most plasma systems, the frequency of the radiative excitation is much smaller than the collisional excitation, thus can be neglected.

Note again that it is not very easy to excite the
Fig. 16. Ionization cross-section of noble gases.

Fig. 17. Excitation cross-section of electrons in hydrogen.

The energy required for this excitation is fairly large. For example, in hydrogen atom, a minimum energy of 10.2 eV is required to move the electron from the ground state (1s) to the lowest excited state (2p) from which atom can emit the photons. An ionization process requires more energy than the excitation process (for example, the ionization potential of hydrogen is 13.6 eV). The ionization cross-sections of several noble gases and the excitation cross-section for H are shown in Fig. 17 and Fig. 18 as examples.

Once the atoms in the plasma are excited above the ground state, it will eventually be de-excited to the ground state. There are three different ways to de-excite the atoms in the plasma. The first one is the spontaneous emission when the electron in the excited level makes a transition to the ground level or another excited level without any external influence. As briefly mentioned earlier, the time scale for this de-excitation is very short if the transition is electric dipole transition, on the order of $10^{-8}$ sec to $10^{-7}$ sec. In this case, the energy conservation is satisfied by emitting the photon whose energy is equal to the energy difference between the initial state and the final state. In many plasma systems, this is the most important de-excitation mechanism. On the other hand, the electron in the excited level also makes a transition if there are other photons around the excited atoms. This process is called stimulated emission. Though the stimulated emission is the key element for the laser, in most plasma systems, the stimulated emission can be neglected. The third process for the de-excitation is the inverse process of the collisional excitation and is called collisional de-excitation. In collisional de-excitation, the colliding particles will gain energy from the excited atoms into their kinetic energy. The importance of collisional de-excitation is a function of plasma density and electron temperature and it varies for various excited states.

3. A simplified model for emission

To simplify the discussion, we will make a number of assumptions on our plasma system.

1. Plasma density ($n_e$) is uniform throughout the volume.
2. Electron energy distribution is Maxwellian and
3. Our plasmas are made of hypothetical atoms that have only 4 energy levels, ground state, first and second excited state and ionized state.

4. The rate of collisional de-excitations are small compared to the rate of spontaneous emission, thus will be neglected.

5. The system is in steady state.

As shown in Fig. 18, $E_0$, $E_1$, $E_2$, and $E_i$ are the ground state, excited state 1, excited state 2, and the ionized state. $R_1$, and $R_2$ are rate of collisional excitation from the ground state, and $A_{1o}$, $A_{2o}$, and $A_{21}$ are rate of spontaneous emission (Note that they are also called Einstein A coefficient). $R_1$, and $R_2$ can be calculated using the collisional cross-sections:

$$R_1 = n_e n_0 \langle \sigma_1 v \rangle$$

$$R_2 = n_e n_0 \langle \sigma_2 v \rangle$$

Remember $\langle \sigma v \rangle$ is the collision rate averaged over the MBD.

From these rates, the equations governing the density of each state can be determined:

$$\frac{dn_0}{dt} = -n_e n_0 \langle \sigma_1 v \rangle + n_1 A_{1o} + n_2 A_{20}$$

$$\frac{dn_1}{dt} = n_e n_0 \langle \sigma_1 v \rangle + n_2 A_{21} - n_1 A_{10}$$

$$\frac{dn_2}{dt} = n_e n_0 \langle \sigma_2 v \rangle - n_2 (A_{21} + A_{20})$$

In steady state, the time derivatives in the LHS are zero, and we have two independent equations with five unknowns ($n_e$, $n_0$, $n_1$, $n_2$, $T_e$).

From charge quasi-neutrality and particle conservation, we have one more equation:

$$n_e + n_0 + n_1 + n_2 = n_g$$

where $n_g$ is the gas density without the plasma.

During spontaneous emission, the excited state 1 and 2 will emit photons at the following frequencies:

$$h \nu_{10} = E_1 - E_0$$

$$h \nu_{20} = E_2 - E_0$$

$$h \nu_{21} = E_2 - E_1$$

If we can measure the number of photons emitting
at these frequencies, we can then determine the density of excited states \((n_1 \text{ and } n_2)\) independently:

\[
\begin{align*}
\text{# photons at } \nu_{10} &= n_1 A_{10} \cdot \text{volume} \\
\text{# photons at } \nu_{21} &= n_2 A_{20} \cdot \text{volume}
\end{align*}
\]

Now we have three unknowns \((n_e, n_0, T_e)\) for three equations:

\[
\begin{align*}
n_e n_0 < \sigma_1 \nu > + n_2 A_{21} - n_1 A_{10} &= 0 \\
n_e n_0 < \sigma_2 \nu > - n_2 (A_{21} + A_{20}) &= 0 \\
n_e + n_0 + n_1 + n_2 &= n_g
\end{align*}
\]

Therefore \(n_e, n_0, \text{ and } T_e\) can be calculated.

Unfortunately the situation in real systems is very different from this simplified model. Thus, the use of plasma spectroscopy alone may not provide the enough information about the plasma system that we want to know. However, we can still obtain some very valuable information on our plasma system from plasma spectroscopy.
Fig. 19. He Grotrian Diagram