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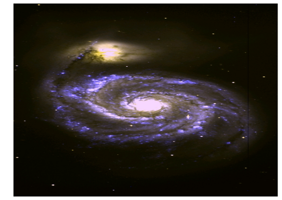
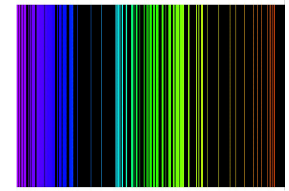

Research based online course:

"Atomic and Molecular Astrophysics and Spectroscopy with Computational workshops on R-matrix and SUPERSTRUCTURE Codes II"

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A.P.J. Abdul Kalam STEM-ER Center
(Indo-US collaboration)

- Organized under the Indo-US STEM Education and Research Center of OSU-AMU, AMU, Aligarh, India, & OSU, Columbus, USA

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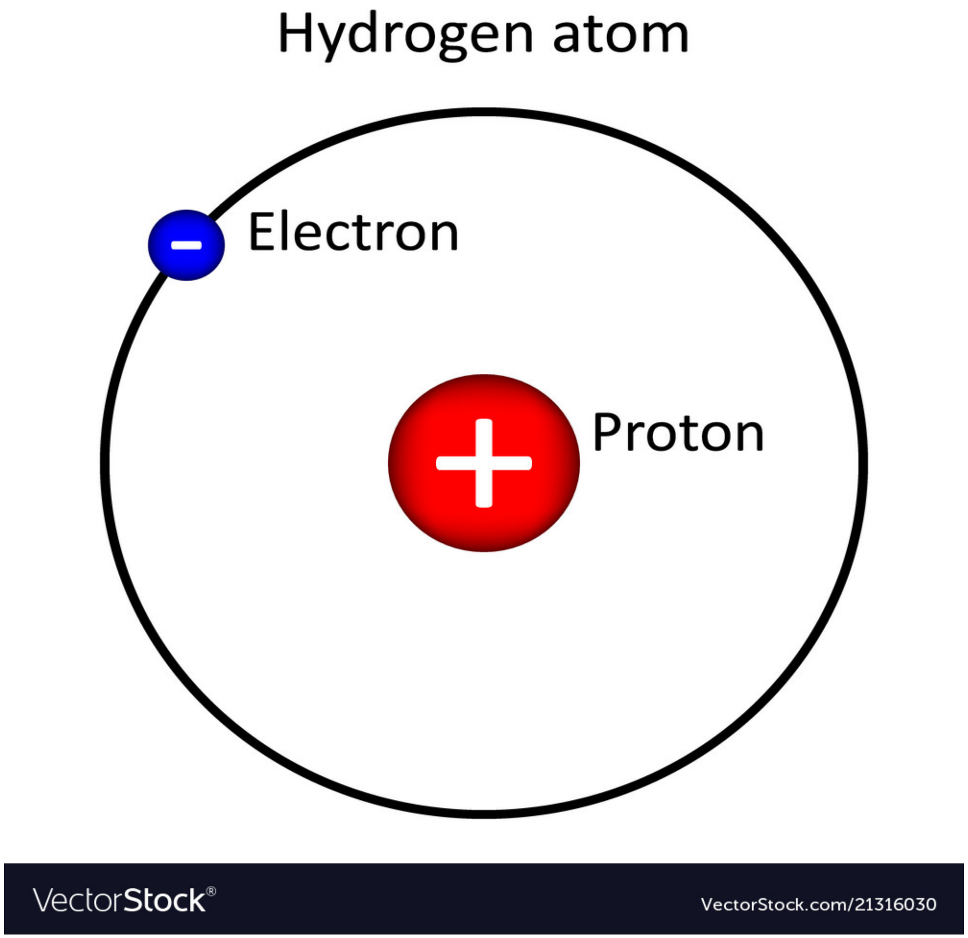
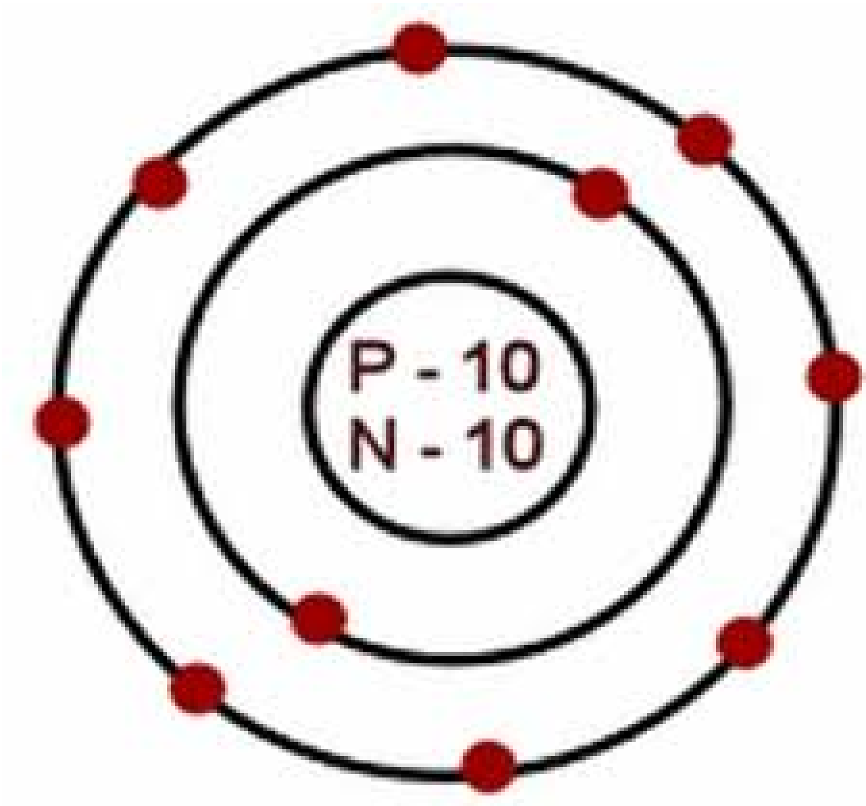
SINGLE & MULTI-ELECTRON ATOMS





- 1-electron: KE + Nuclear Potential
- $>$ 1-electron: KE + Nuclear Potential + Electron-Electron potential
- Complexity starts with Electron-Electron interaction which does not have a center point.

MULTI-ELECTRON ATOM

A many-electron system requires to sum over (i) all one-electron operators, that is KE & attractive nuclear Z/r potential, (ii) two-electron Coulomb repulsion potentials

$$\mathbf{H}\Psi = [H_0 + H_1]\Psi, \tag{1}$$

$$H_0 = \sum_{i=1}^{N}\left[-\nabla_i^2 - \frac{2Z}{r_i}\right], H_1 = \sum_{j<i}\frac{2}{r_{ij}} \tag{2}$$

$$H = \sum_i f_i + \sum_{j\neq i} g_{ij} \equiv F + G \tag{3}$$

• H_0: one-body term, stronger, H_1: two-body term, weaker, can be treated perturbatively

• Start with a trial wave function Ψ^{t} in some parametric form, Slater Type Orbitals

$$\mathbf{P}_{\mathbf{nl}}^{\mathrm{STO}}(\mathbf{r}) = \mathbf{r}^{\mathbf{l+1}}\mathbf{e}^{-\mathbf{ar}}$$

• The lowest energy state: most stable - the ground state

• A trial function should satisfy variational principle that through optimization an upper bound of energy eigenvalue is obtained in the Schrödinger equation.

MULTI-ELECTRON SYSTEM CONFIGURATIONS

- **Determination of Configuration - Arranging electrons in to various orbitals - 1s, 2s, 2p, 3s, 3p**
- **nl orbitals fill up normally up to, 1s - 3p, Ar ($3p^6$)**
- **No particular rule applies for the ground configurations or lowest energy state beyond Ar**
- **For large n all subshells exist, but they become excited states as higher orbitals may become lower states. Ex. For elements beyond Ar, e.g. K (Z=19) and Ca (Z=20), 4s fills up instead of 3d. Two general rules:**

- Rule 1': A *subshell which gives lower* $(n+\ell)$ *value is filled in first* [K, Ca: $(n+\ell) = 4$ with 4s, but $= 5$ with 3d]

- Rule 2': For the same $(n+\ell)$, higher ℓ is filled up first. Ex: Fe-group elements from Sc to Zn $(Z = 21 - 30)$ - 3d fills up after 4s instead of 4p as they have $(n+\ell) = 5$

- **However, for configuration with Z $>$ Fe (Z=26), $(n+\ell)$-first rule deviates, & no particular rule is followed as states are mixed with overlapped wavefunctions**
- **Size: H-radius - a_o He (2) is the smallest element, and Fr (87) is the largest - protons reduce the size**

ANGULAR MOMENTA (L, S, J) COUPLINGS

• Total L and S angular momenta may couple differently for the total angular momentum J - depends on Z

• Multi-electron elements may be divided as, 'light' ($Z \leq 18$) and 'heavy' ($Z > 18$) (although not precise)

• LS coupling (lower Z): Vector summation of orbital and spin angular momenta is done separately. Ex: 2 electrons

$L = |L_2 - L_1|, \ldots, |L_2 + L_1|$, L Multiplicity = 2L+1

$S = |S_2 - S_1|, \ldots, |S_2 + S_1|$, S Multiplicity = 2S+1

Then the *total angular momentum quantum numbers*:

$J = |L - S|, \ldots, |L + S|$, J Multiplicity = 2J+1

• The symmetry of the state: $^{(2S+1)}L^{\pi}$(LS), $^{(2S+1)}L^{\pi}_{J}$ or $J\pi$

• The J-values $\rightarrow$ fine structure levels. Each LS term can have several fine structure J levels (example below)

Ex: Consider configuration: nsn'p - what are the states $^{(2S+1)}L^{\pi}_{J}$?

ns electron: $l=0=L_1$, $s=1/2=S_1$, n'p electron: $l=1=L_2$, $s=1/2=S_2$

nsn'p: $L = |0 \pm 1| = 1$, $S=|\frac{1}{2} \pm \frac{1}{2}| = 0,1$, $2S+1 = 1,3$,

$\pi = (-1)^{\sum_i l_i} = (-1)^{0+1} = -1$ odd, LS states are: $^1P^o, ^3P^o$

$J= |S \pm L|$: $^1P^o$: J=1, $^3P^o$: J= 0,1,2. $^{(2S+1)}L^{\pi}_{J}$: $^1P^o_1$, $^3P^o_0$, $^3P^o_1$, $^3P^o_2$

ANGULAR MOMENTA COUPLINGS

Assignment: Find fine structure levels of ^5D

• **Coulomb force between an electron and nucleus becomes stronger for large Z and highly charged ions and can increase the velocity of the electron to relativistic level. Angular coupling changes to LSJ coupling to JJ coupling**

• **Intermediate or *LSJ* coupling (typically $19 \leq$ Z ≤ 40): Consideration of full relativistic effects is not necessary**

• **Add all l_i and s_i, except for the last interacting electron, separately, then add the last electron as follows:**

$$\mathbf{J_1} = |\sum_{\mathbf{i}} \mathbf{l_i} + \sum_{\mathbf{i}} \mathbf{s_i}|, \qquad \mathbf{K} = \mathbf{J_1} + \mathbf{l}, \quad \mathbf{J} = \mathbf{K} + \mathbf{s}\,,$$

K is a quantum number.

• ***jj* coupling (typically for Z >40): When relativistic effect is more prominent, the total J is obtained from sum of individual electron total angular momentum j_i from its angular & spin angular momenta:**

$$\mathbf{j_i} = \mathbf{l_i} + \mathbf{s_i}, \quad \mathbf{J} = \sum_{\mathbf{i}} \mathbf{j_i}, \tag{4}$$

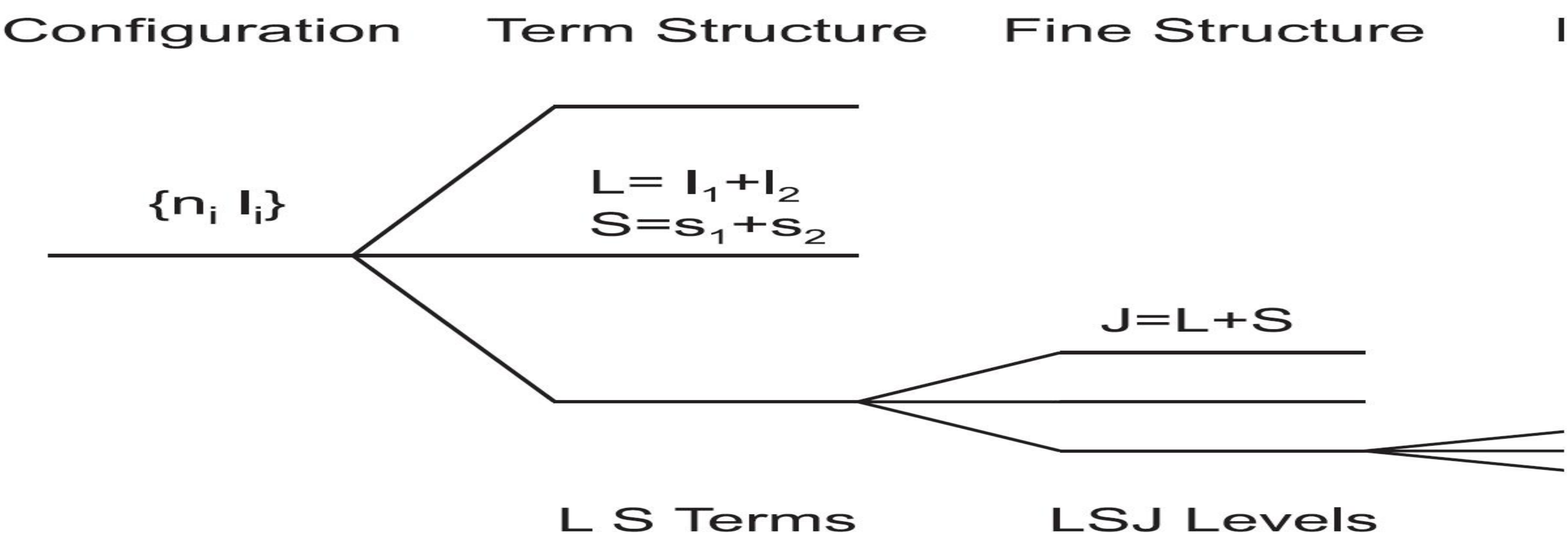
ANGULAR MOMENTA COUPLINGS

For any 2 electrons, J ranges from $|\mathbf{j_1 + j_2}|$ to $|\mathbf{j_1 - j_2}|$

- **States designation= $(j_i j_2)_J$**

Ex; (pd) configuration- .$p\ :\ j_1(1 \pm 1/2)$=1/2, 3/2, and $d : j_2(2 \pm 1/2)$=3/2, 5/2. The states are:
.$(1/2\ 3/2)_{2,1}$, $(1/2\ 5/2)_{3,2}$, .$(3/2\ 3/2)_{3,2,1,0}$, $(3/2\ 5/2)_{4,3,2,1}$

- **Hyperfine structure:** **Form when fine structure levels J split further via vector addition with nuclear spin I $\rightarrow$ quantum state $J + I = F$**



- **LS term energy can be calculated from its fine structure components using**

$$\mathbf{E(LS)} = \frac{\sum_{\mathbf{J}}(\mathbf{2J+1})\mathbf{E(J)}}{\sum_{\mathbf{J}}(\mathbf{2J+1})}$$

NON-EQUIVALENT & EQUIVALENT ELECTRON STATES

- **Number of valence electrons in the outer orbit: $> 1 \rightarrow$ Equivalent electron state**

$= 1 \rightarrow$ Non-equivalent electron state

- **Non-equivalent electron states: All possible states the vectorial sum allows. Ex. States of 3-electron configuration: nsn′pn″d:**

$$ns\; n'\mathbf{p}\; (^1P^o)\; n''\mathbf{d} \longrightarrow {}^2P^o,\; {}^2D^o,\; {}^2F^o$$
$$ns\; n'\mathbf{p}\; (^3P^o)\; n''\mathbf{d} \longrightarrow {}^{(2,4)}(P, D, F)^o\,.$$

- **Equivalent electron state: Less number of LS states.**

Ex: configuration, np^2. If the configuration is npn'p, 6 possible states are: ^{1,3}S, ^{1,3}P, ^{1,3}D. However, for n=n', Pauli exclusion principle will eliminate some -reducing 6 to 3 states, ^{1}S, ^{3}P, ^{1}D, as follows

- **p electron: Possible m_l and m_s values**

m_l = 1, 0, -1; m_s = 1/2, -1/2 (spin up and down)

p electron: Six possible states or designation:

m_l m_s: 1^+= 1 1/2, 0^+= 0 1/2, -1^+= -1 1/2, (spin up)

1^-= 1 -1/2, 0^-= 0 -1/2, -1^-= -1 -1/2 (spin down)

Vector addition for two p-electrons: L $= |1\pm1|$**=0,1,2, S** $= |1/2\pm1/2|$**=0,1**
Arrange the p-states, from 1^+**= 1 1/2 to** -1^-**= -1 -1/2, such that no two electron have the same state (Pauli exclusion principle)**

$M_L = \sum_i m_l = \mathbf{0},\pm1,\pm2$**;** $M_S = \sum_i m_s = \mathbf{0},\pm1$

Possible combinations of np^2

M_S/	M_L= 2	1	0	-1	-2
0	1^+1^-	1^+0^-	1^+-1^-	-1^+0^-	-1^+-1^-
1		1^+0^+	1^+-1^+	-1^+0^+	
0		1^-0^+	1^--1^+	-1^-0^+	
-1		1^-0^-	1^--1^-	-1^-0^-	
0			0^+0^-		

- ^1D**: The highest value of** $M_L = |2|$ **associates only with** M_S **= 0, & hence can only be** ^1D**.** ^1D **includes all 5 entries of** M_L**= 0,±1,±2**
- ^3P**: Next highest value of** $M_L = |1|$ **associates with 3** M_S **= 0,±1 belong to** ^3P **and takes out the 9 entries**
- ^1S**: The single remaining entry with** M_L**=0 and** M_S **= 0 corresponds to** ^1S
- **Following similar method, we can find that for np**^{3}**:** $^4S^o$, $^2D^o$, $^2P^o$

Ahmad's (Landau and liftshiz) (L+S) EVEN RULE FOR nl^2 ATOMIC STATES According to the rule, the nl^2 states with even values of the total (L+S) will survive, that is, will satisfy Pauli exclusion principle.

- For the last example, np^2, the even values are $^1S,^3P,^1D$
- For example, consider two equivalent electrons configuration nd^2. For two non-equivalent $ndn'd$ electrons, total $S = |s_1 \pm s_2| = 0, 1$ and total $L =]L_1 \pm L_2| = 0, 1, 2, 3, 4$.

Hence all possible states are ^{1,3}S, ^{1,3}P, ^{1,3}D, ^{1,3}F, ^{1,3}G. Following the rule for even values of the total (L+S), the surviving equivalent electron states are ^{1}S, ^{3}P, ^{1}D, ^{3}F, and ^{1}G.

- This rule is simpler than Breit scheme for 2 equivalent electron sates.

For f^2, $l = 3$, m_l=-3,-2,...,3, $m_s = \pm 1/2$, instead of 14 non-equivalent states, they will form 7 LS states, $^1(S, D, G, I)$, $^3(P, F, H)$.

HUND'S RULES FOR ATOMIC STATES

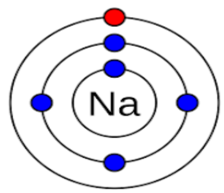
- It governs the energy positions of states from spin multiplicity (2S + 1), orbital L, total J angular momenta
- **S-rule:** An LS term with the highest spin multiplicity (2S + 1) $\rightarrow$ lowest in energy - relates to exchange effect where electrons with like spin spatially avoid one another Ex: np^3 ($^4S^o$, $^2D^o$, $^2P^o$) for N I, P I: ground state is $^4S^o$
- **L-rule:** States of the same (2S+1), larger total L lies lower, again due to less electron repulsion Ex: np^3 above, D > P. $^2D^o$ term lies lower than the $^2P^o$
- **J-rule:** For fine-structure levels L+S =J

- For < half-filled subshells, the lowest J -level lies lowest
- For > half-filled, the highest J -level lies lowest in energy

Ex: Both C with ground configuration $1s^22s^22p^2$ (< half filled p-orbital) and O with $1s^22s^22p^4$ (> half-filled) have the same ground state ^3P. ^3P has 3 fine structure levels with J = 0,1,2. Since C has < half filled p-orbital, the order of fine-structure energy levels is: J = 0,1,2 giving the ground level $^3P_0$. Similarly, for O, the order is J =2, 1,0 and the ground level is $^3P_2$.

ENERGIES OF MULTI-ELECTRON SYSTEM & QUANTUM DEFECT

- **The energy formula of a multi-electron system is similar to that of H-like ions, but accounts for the screening effect on the valence electron by the core ion electrons**
- **The outer electron sees an *effective charge* $\mathbf{z = Z - N + 1}$, N = no of electrons**
- **Departure from a pure Coulomb form effectively *reduces* the principal quantum numbers n in the energy formula as**



$$\mathbf{E(nl) = \frac{z^2}{(n - \mu)^2}}$$

where $\mu \geq 0$ = *quantum defect*

- **The amount of screening (μ) depends on the orbital angular momentum ℓ. μ is a constant for each ℓ. We can write,**

$$\mathbf{E(nl) = \frac{z^2}{(n - \mu_\ell)^2}}$$

- **Excited energy levels described by the Rydberg formula $\rightarrow$ "Rydberg levels"**
- $\mu_{\mathrm{s}} > \mu_{\mathrm{p}} > \mu_{\mathrm{d}} \ldots$

ENERGIES OF MULTI-ELECTRON SYSTEM & QUANTUM DEFECT

- For light elements, such as C, with increasing l the valence electron sees a constant Coulomb potential. Hence $\mu_\ell \approx 0$ for any $\ell \geq f$, that is, there is no departure from n an f-electron onwards
- For heavier elements, e.g. Fe, f-orbitals may be occupied causing screening effect for the f-electron. Hence, the $\mu \approx 0$ for $\ell > f$
- Formula holds for all atoms & ions when the outer electron is in high-n state, i. e. sufficiently far away from inner electrons to experience only the residual charge z
- It can be used to obtain energy of any large n-level up to series limit at $\mathrm{n} = \infty$ for any given l
- Define $\nu \equiv \mathrm{n} - \mu =$ *effective quantum number*

$$\mathbf{E_n} = -\frac{\mathbf{z}^2}{\nu^2}$$

As $\mathrm{n} \to \infty$, $E \to 0$ & the bound electron becomes free

- ν increases approximately by unity. However, it is often a decimal number

HARTREE-FOCK EQUATION
(AAS: Pradhan and Nahar 2011)

Optimize Schrodinger equation, $H\Psi = E\Psi$ for minimum E,

$$\delta\langle\Psi|H|\Psi\rangle = 0,$$

- **E is stationary to the variations of the spin-orbitals, ψ_i is subject to N^2 orthogonality conditions (N= number of electrons). Introduce Lagrange multipliers λ_{IJ} such that**

$$\delta E - \sum_k \sum_l \lambda_{kl}\,\delta\langle\psi_k|\psi_l\rangle = 0$$

There are N^2 number of λ_{IJ} values

- **Matrix of Lagrange multiplier λ_{kl} is diagonal with elements $E_k\delta_{kl}$, that is,**

$$\delta E - \sum_k E_k \delta\langle\psi_k|\psi_k\rangle = 0.$$

- **Since each electron moves in a potential created by all other electrons, construct the potential $V(r_i)$ for the i^{th} electron *self-consistently* $\rightarrow$ self-consistent iterative scheme of Hartree-Fock equations**
- **$H_1(r_1)$ depends on $\psi(r_2)$, implying $\psi(r_2)$ must be known before solving $H_1(r_1)$. Hence a trial $\psi(r_2)$ is adopted to obtain $\psi(r_1)$ using the variational criterion**

HARTREE-FOCK EQUATION

• Since the form of $\psi(\mathbf{r_1})$ and $\psi(\mathbf{r_2})$ are identical, the new $\psi(\mathbf{r_2})$ is used again to obtain $\psi(\mathbf{r_1})$. This continues until the desired accuracy is attained. The scheme is often called Hartree-Fock Self-Consistent Field method.

• Hartree approx: total atomic wavefunction - product of one-electron spin orbitals

$$\psi_{n,l,m_l,m_s}(r,\theta,\phi,m_s) = \prod_{i=1}^{N} \psi_{n_i,\ell_i,m_{\ell_i},m_{s_i}} \tag{5}$$

• But this lacks anti-symmetrization - manifestation of Pauli principle that wavefunction changes sign on electron exchange of position

• Fock introduced anti-symmetrization, through the determinant form, to Hartree method → Hartree-Fock method

Ex: He atom:

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\left[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)\right]$$

This can be written in determinant form:

HARTREE-FOCK EQUATION

He wavefunction is then:

$$\mathbf{\Psi} = \frac{\mathbf{1}}{\sqrt{\mathbf{2}}} \begin{vmatrix} \psi_{\mathbf{1}}(\mathbf{1}) & \psi_1(2) \\ \psi_2(1) & \psi_2(2) \end{vmatrix} \tag{6}$$

$\mathbf{\Psi}$ vanishes if coordinates of both electrons are the same

• The N-electron wavefunction in the determinant representation

$$\mathbf{\Psi} = \frac{\mathbf{1}}{\sqrt{\mathbf{N}}} \begin{vmatrix} \psi_{\mathbf{1}}(\mathbf{1}) & \psi_1(2) & \dots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \dots & \psi_2(N) \\ \dots & \dots & \dots & \dots \\ \psi_N(1) & \psi_N(2) & \dots & \psi_N(N) \end{vmatrix} \tag{7}$$

This is called the *Slater determinant.* Substitution in Hartree-Fock equation gives set of one-electron radial equations,

$$\left[-\nabla_{\mathrm{i}}^2 - \frac{\mathbf{2Z}}{\mathbf{r_i}}\right] \mathbf{u_k}(\mathbf{r_i}) + \left[\sum_{\mathrm{l}} \int \mathbf{u_l^*}(\mathbf{r_j}) \frac{\mathbf{2}}{\mathbf{r_{ij}}} \mathbf{u_l}(\mathbf{r_j}) \mathbf{dr_j}\right] \mathbf{u_k}(\mathbf{r_i}) \tag{8}$$
$$- \sum_{\mathrm{l}} \delta_{\mathrm{m_L^k, m_L^l}} \left[\int \mathbf{u_l^*}(\mathbf{r_j}) \frac{\mathbf{2}}{\mathbf{r_{ij}}} \mathbf{u_k}(\mathbf{r_j}) \mathbf{dr_j}\right] \mathbf{u_l}(\mathbf{r_i}) = \mathbf{E_k u_k}(\mathbf{r_i}) \,.$$

1st term= 1-body term or configuration energy, 2nd term= Direct (or Coulomb) term, 3rd term= Exchange term. • The total energy is

$$\mathbf{E}[\mathbf{\Psi}] = \sum_{\mathrm{i}} \mathbf{I_i} + \frac{\mathbf{1}}{\mathbf{2}} \sum_{\mathrm{i}} \sum_{\mathrm{j}} [\mathbf{J_{ij}} - \mathbf{K_{ij}}]. \tag{9}$$

Central Field Approximation for a Multi-Electron System

• It was difficult to compute wavefunctions and energies in Hartree-Fock approximation until powerful computers arrived. Central field approximation was widely used (in many cases still now) for them.
• H_1 consists of non-central forces between electrons which contains a large spherically symmetric component
• We assume that each electron is acted upon by the averaged charge distribution of all the other electrons and construct a potential energy function $V(r_i)$ with one-electron operator. When summed over all electrons, this charge distribution is spherically symmetric and is a good approximation to actual potential. Neglecting non-radial part,

$$\mathbf{H} = \mathbf{H_0} + \mathbf{H_1} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m}\nabla_i^2 - \sum_{i=1}^{N} \frac{e^2 Z}{r_i} + \left\langle \sum_{i \neq j}^{N} \frac{e^2}{r_{ij}} \right\rangle$$

Write $V(r)$ which depends only on r as,

$$\mathbf{V}(\mathbf{r}) = -\sum_{i=1}^{N} \frac{e^2 Z}{r_i} + \left\langle \sum_{i \neq j}^{N} \frac{e^2}{r_{ij}} \right\rangle . \tag{10}$$

A short range exchange potential with spherical charge distribution is often added to it. • $V(r)$ is the *central-field potential* with boundary conditions

$$\mathbf{V}(\mathbf{r}) = -\frac{\mathbf{Z}}{\mathbf{r}} \quad \text{if } r \to 0, \; = -\frac{z}{r} \text{ if } \mathbf{r} \to \infty \tag{11}$$

THOMAS-FERMI-DIRAC-AMALDI (TFDA) APPROXIMATION

- **One most useful procedure:**
- **Treats electrons as Fermi sea: Electrons, constrained by Pauli exclusion principle, fill in cells up to a highest Fermi level of momentum $p = p_{\mathrm{F}}$ at T=0**
- **As T rises, electrons are excited out of the Fermi sea close to the 'surface' levels & approach a Maxwellian distribution $\rightarrow$ spatial density of electrons:**

$$\rho = \frac{(\mathbf{4}/\mathbf{3})\pi \mathbf{p}_{\mathrm{F}}^{\mathbf{3}}}{\mathbf{h}^{\mathbf{3}}/\mathbf{2}}$$

- **Based on quantum statistics, the TFDA model gives a continuous function $\phi(x)$ such that the potential is**

$$\mathbf{V}(\mathbf{r}) = \frac{\mathcal{Z}_{\mathrm{eff}}(\lambda_{\mathbf{nl}}, \mathbf{r})}{\mathbf{r}} = -\frac{\mathbf{Z}}{\mathbf{r}}\phi(\mathbf{x}),$$

where

$$\phi(\mathbf{x}) = \mathrm{e}^{-\mathbf{Zr}/\mathbf{2}} + \lambda_{\mathbf{nl}}(\mathbf{1} - \mathrm{e}^{-\mathbf{Zr}/\mathbf{2}}),\ \ \mathbf{x} = \frac{\mathbf{r}}{\mu},$$

$$\mu = \mathbf{0.8853}\left(\frac{\mathbf{N}}{\mathbf{N-1}}\right)^{\mathbf{2}/\mathbf{3}}\mathbf{Z}^{-\mathbf{1}/\mathbf{3}} = \textbf{constant.}$$

THOMAS-FERMI-DIRAC-AMALDI (TFDA) APPROXIMATION

- The function $\phi(x)$ is a solution of the potential equation

$$\frac{d^2\phi(x)}{dx^2} = \frac{1}{\sqrt{x}}\phi(x)^{\frac{3}{2}}$$

- The boundary conditions on $\phi(x)$ are

$$\phi(0) = 1, \quad \phi(\infty) = -\frac{Z - N + 1}{Z}.$$

- The one-electron orbitals $P_{nl}(r)$ can be obtained by solving the wave equation

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + 2V(r) + \epsilon_{nl}\right] P_{nl}(r) = 0.$$

- This is similar to the radial equation for the hydrogenic case, with the same boundary conditions on $P_{nl}(r)$ as $r \to 0$ and $r \to \infty$, and $(n - l + 1)$ nodes.
- The second order radial is solved numerically since, unlike the hydrogenic case, there is no general analytic solution.
- It may be solved using an exponentially decaying function appropriate for a bound state, e.g. Whittaker function

THOMAS-FERMI-DIRAC-AMALDI (TFDA) APPROXIMATION

- **The solution is normalized Whittaker function**

$$\mathbf{W}(\mathbf{r}) = \mathrm{e}^{-\mathbf{zr}/\nu} \left(\frac{\mathbf{2zr}}{\nu}\right) \left(\mathbf{1} + \sum_{\mathbf{k=1}}^{\infty} \frac{\mathbf{a_k}}{\mathbf{r^k}}\right) \mathcal{N}$$

where $\nu = \mathbf{z}/\sqrt{\epsilon}$ is the effective quantum number and ϵ is the eigenvalue. The coefficients are

$$\mathbf{a_1} = \nu \, \{\mathbf{l}(\mathbf{l}+\mathbf{1}) - \nu(\nu - \mathbf{1})\} \, \frac{\mathbf{1}}{\mathbf{2z}}$$

$$\mathbf{a_k} = \mathbf{a_{k-1}} \, \nu \, \{\mathbf{l}(\mathbf{l}+\mathbf{1}) - (\nu - \mathbf{k})(\nu - \mathbf{k} + \mathbf{1})\} \, \frac{\mathbf{1}}{\mathbf{2kz}}$$

and the normalization factor is

$$\mathcal{N} = \left\{\frac{\nu^{\mathbf{2}}}{\mathbf{z}} \, \mathbf{\Gamma}(\nu + \mathbf{l} + \mathbf{1}) \, \mathbf{\Gamma}(\nu - \mathbf{1})\right\}^{-\mathbf{1/2}}$$

The one-electron spin orbital functions then assume the familiar hydrogenic form

$$\psi_{\mathbf{n},\ell,\mathbf{m}_\ell,\mathbf{m_s}}(\mathbf{r}, \theta, \phi, \mathbf{m_s}) = \phi(r, \theta, \phi)\zeta_{m_s}$$

THOMAS-FERMI-DIRAC-AMALDI (TFDA) APPROXIMATION

- TFDA orbitals are based on a statistical treatment of the free electron gas, & hence neglect the shell-structure

• However, in practice configuration interaction accounts for much of the discrepancy that might otherwise result.

CONFIGURATION INTERACTION

• **A multi-electron system is described by its configuration and a defined spectroscopic state.**

• **All states of the same SLπ, with different configurations, interact with one another - configuration interaction. Hence the wavefunction of the SLπ may be represented by a linear combination of configurations giving the state.**

• **Example, the ground state of Al I is $[\mathbf{1s^2 2s^2 2p^6}]\mathbf{3s^2 3p}\,(^2\mathbf{P^o})$. $^2\mathbf{P^o}$ state can also be formed from $\mathbf{3s^2 4p}\,(^2\mathbf{P^o})$, 3s3p3d $(\ldots, ^2\mathbf{P^o})$. $\mathbf{3p^3}(^2\mathbf{P^o})$ and so on. These 4 configurations contribute with different amplitudes or mixing coefficients (a_i) to form the four state vectors $^2\mathbf{P^o}$ of a 4×4 Hamiltonian matrix. Hence for the optimized energy and wavefunction for each $^2\mathbf{P^o}$ state all 4 configurations should be included,**

$$\Psi(^2\mathbf{P^o}) = \sum_{i=1}^{4} a_i \psi[C_i(^2\mathbf{P^o})] = \Big[a_1\psi(\mathbf{3s^2 3p}) + a_2\psi(\mathbf{3s^2 4p})$$

$$+\; a_3\psi(\mathbf{3p^3}) + a_3\psi(\mathbf{3s3p3d})\Big]$$

RELATIVISTIC BREIT-PAULI APPROXIMATION

Hamiltonian: For a multi-electron system, the relativistic Breit-Pauli Hamiltonian is:

$$\mathbf{H_{BP} = H_{NR} + H_{mass} + H_{Dar} + H_{so} +}$$

$$\mathbf{\frac{1}{2}\sum_{i\neq j}^{N}[g_{ij}(so + so') + g_{ij}(ss') + g_{ij}(css') + g_{ij}(d) + g_{ij}(oo')]}$$

where the non-relativistic Hamiltonian is

$$\mathbf{H_{NR} = \left[\sum_{i=1}^{N}\left\{-\nabla_i^2 - \frac{2Z}{r_i} + \sum_{j>i}^{N}\frac{2}{r_{ij}}\right\}\right]}$$

the Breit interaction is

$$\mathbf{H_B = \sum_{i>j}[g_{ij}(so + so') + g_{ij}(ss')]}$$

and one-body correction terms are

$\mathbf{H_{mass} = -\frac{\alpha^2}{4}\sum_i p_i^4}$, $\mathbf{H_{Dar} = \frac{\alpha^2}{4}\sum_i \nabla^2\left(\frac{Z}{r_i}\right)}$, $\mathbf{H_{so} = \frac{Ze^2\hbar^2}{2m^2c^2r^3}\sum_i l_i.s_i}$

Spin-orbit interaction energy: $\mathbf{E_{SO} = \frac{1}{2}A\hbar^2[J(J+1) - L(L+1) - S(S+1)]}$ where A is the fine structure splitting constant which is proportional to z as $A \propto \frac{z^4}{n^3}$ and separation between two fine structure levels is given by $\frac{1}{2}A\hbar^2 j$

ATOMIC PROCESSES PRODUCING ASTROPHYSICAL SPECTRA *and* Relevant Atomic Parameters

RADIATIVE PROCESSES:

1. Photoexcitation & De-excitation (bound-bound transition):

$$\mathbf{X^{+Z} + h\nu \rightleftharpoons X^{+Z*}}$$

- **Oscillator Strength (f), Radiative Decay Rate (A-value)**
- **Examples:** **Seen as lines in astrophysical spectra**
- **Determines opacities in astrophysical plasmas**

2. Photoionization (PI) & Radiative Recombination (RR):

$$\mathbf{X^{+Z} + h\nu \rightleftharpoons X^{+Z+1} + e}$$

3. Autoionization (AI) & Dielectronic recombination (DR):

$$e + X^{+Z} \rightleftharpoons (X^{+Z-1})^{**} \rightleftharpoons \begin{cases} e + X^{+Z} & \text{AI} \\ X^{+Z-1} + h\nu & \text{DR} \end{cases}$$

The doubly excited state - "autoionizing state" - introduces resonances

- 2 & 3. **Photoionization Cross Sections (σ_{PI}), Recombination Cross Sections (σ_{RC}) and Rate Coefficients (α_{RC})**

Examples:

- **Photoionization resonances - seen in absorption spectra,**
- **Recombination resonances - seen in emission spectra**

ATOMIC PROCESSES PRODUCING ASTROPHYSICAL SPECTRA

and Relevant Atomic Parameters

• Determine ionization fractions in astrophysical plasmas

COLLISIONAL PROCESSES:

4. Electron-impact excitation (EIE):

$$\mathbf{e + X^{+Z} \rightarrow e' + X^{+Z*} \rightarrow e' + X^{+Z} + h\nu}$$

• Collision Strength (Ω)

• (i) Can go through an intermediate autoionizing state, (ii) gives out a photon as the ion de-excites. Ex. seen as forbidden lines in emission spectra

.5. Electron-impact Ionization:

$$\mathbf{e + X^{+Z} \rightarrow e' + e" + X^{+Z+1}}$$

• Ionization cross section and strength

- It does not involve any photon and hence can not be produce lines. However, it is needed for modeling to determine level populations, ionization fractions etc

6. Hydrogen-impact excitation:

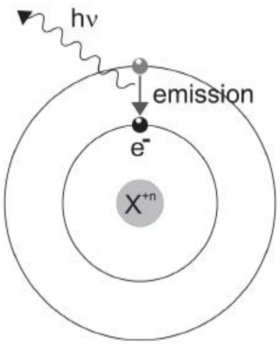
$$\mathbf{H + X^{+Z} \rightarrow H' + X^{+Z*}}$$

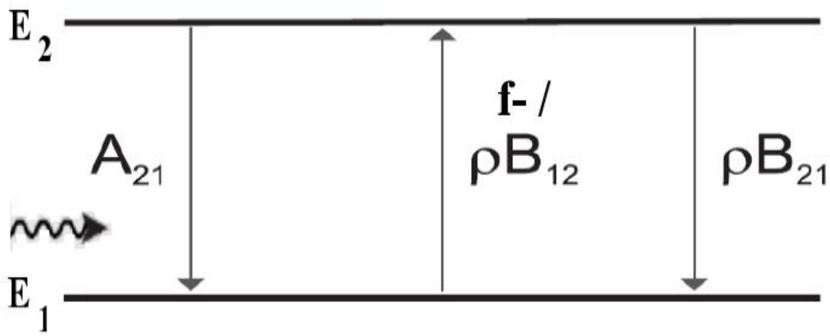
• Excitation rate coefficient and transition rate

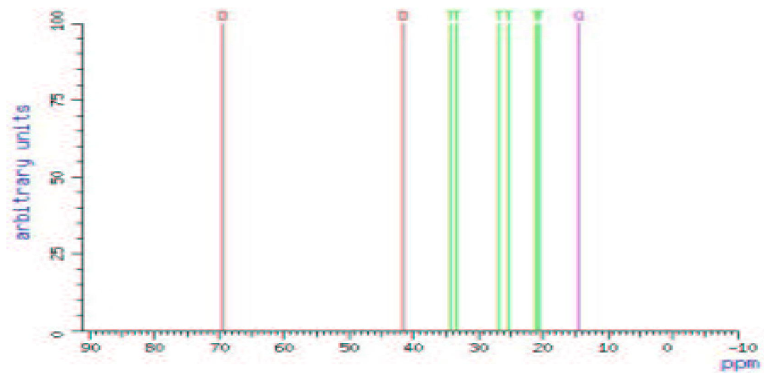
1. "PHOTO-EXCITATION"

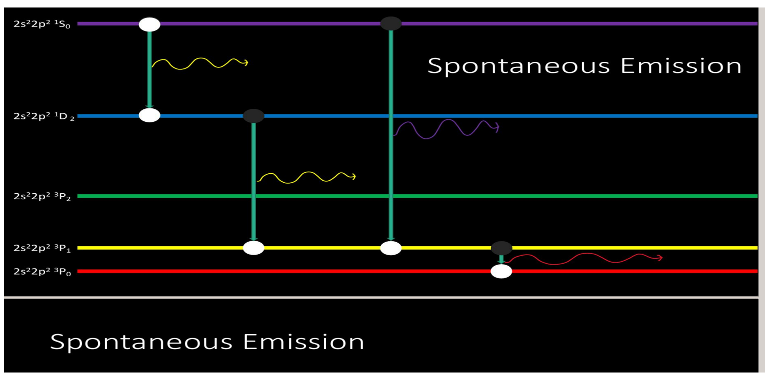
Photo-Excitation & De-excitation:

$$\mathbf{X^{+Z} + h\nu \rightleftharpoons X^{+Z*}}$$









- **Atomic quantities**

B_{12} **- Photo-excitation, Oscillator Strength (**f**)**

A_{21}**- Spontaneous Decay, - Radiative Decay Rate (**A**-value)**

B_{21}**- Stimulated Decay with a radiation field**

- P_{ij}, **transition probability,** $\mathbf{P_{ji} \sim |<j|H'|i>|^2 \sim |<j|A.p|i>|^2}$

$$\mathbf{P_{ij} = 2\pi\frac{c^2}{h^2\nu_{ji}^2}|<j|\frac{e}{mc}\hat{e}.pe^{ik.r}|i>|^2\rho(\nu_{ji}).} \tag{12}$$

TRANSITION MATRIX ELEMENTS WITH A PHOTON

- **1st term:** Dipole operator: $\mathbf{D} = \sum_i \mathbf{r}_i$:
- **Transition matrix for Photo-excitation & Deexcitation:**

$$< \mathbf{\Psi_B}||\mathbf{D}||\mathbf{\Psi_{B'}} >$$

Matrix element is reduced to generalized line strength (length form):

$$\mathbf{S} = \left| \left\langle \Psi_\mathbf{f} \right| \sum_{\mathbf{j=1}}^{\mathbf{N+1}} \mathbf{r_j} \left| \Psi_\mathbf{i} \right\rangle \right|^\mathbf{2} \tag{13}$$

- **There are also "Velocity" & "Acceleration" forms**

Allowed electric dipole (E1) transitions

The oscillator strength (f_{ij}) and radiative decay rate (A_{ji}) for the bound-bound transition are

$$\mathbf{f_{ij}} = \left[\frac{\mathbf{E_{ji}}}{\mathbf{3g_i}}\right]\mathbf{S}, \quad \sigma_\mathbf{PI}(\nu) = \mathbf{8.064}\frac{\mathbf{E_{ij}}}{\mathbf{3g_i}}\mathbf{S}^\mathrm{E1}\ [\mathbf{Mb}],,,$$

$$\mathbf{A_{ji}}(\mathbf{sec}^{-1}) = \left[\mathbf{0.8032} \times \mathbf{10}^{10}\frac{\mathbf{E_{ji}^3}}{\mathbf{3g_j}}\right]\mathbf{S}$$

Selection Rules: Allowed & Forbidden Transitions

Angular momentum integrals introduce the selection rules

General rules: x=type of transtion: For total J,

- **Δ J = $J_2 - J_1$ 0,$\pm$1, ...,$\pm$x ; $J_1 + J_2 \geq$ x , ΔM = 0,$\pm$1, ...,$\pm$x**

For the parity

$\Delta P = (-1)^x \ for \ E_x \ and \ -(-1)^x \ for \ M_x \ transitions$

Allowed: i) Electric Dipole (E1) transitions - a) same-spin (stronger) & intercombination (different spin, relatively weaker) transitions

(Δ J = 0,$\pm$1, Δ L = 0,$\pm$1,$\pm$2; parity changes)

Forbidden:

ii) Electric quadrupole (E2) transitions

(Δ J = 0,$\pm$1,$\pm$2, parity does not change)

iii) Magnetic dipole (M1) transitions

(Δ J = 0,$\pm$1, parity does not change)

iv) Electric octupole (E3) transitions

(Δ J= $\pm$2, $\pm$3, parity changes)

v) Magnetic quadrupole (M2) transitions

(Δ J = $\pm$2, parity changes)

Allowed transitions are much stronger than Forbidden transitions

FORBIDDEN TRANSITIONS

i) Electric quadrupole (E2) transitions (Δ J = 0,$\pm$1,$\pm$2, π - same)

$$\mathbf{A^{E2}_{ji} = 2.6733 \times 10^{3}\frac{E^{5}_{ij}}{g_{j}}S^{E2}(i,j)}\ \mathrm{s}^{-1}, \tag{14}$$

ii) Magnetic dipole (M1) transitions (Δ J = 0,$\pm$1, π - same)

$$\mathbf{A^{M1}_{ji} = 3.5644 \times 10^{4}\frac{E^{3}_{ij}}{g_{j}}S^{M1}(i,j)}\ \mathrm{s}^{-1}, \tag{15}$$

iii) Electric octupole (E3) transitions (Δ J= $\pm$2, $\pm$3, π changes)

$$\mathbf{A^{E3}_{ji} = 1.2050 \times 10^{-3}\frac{E^{7}_{ij}}{g_{j}}S^{E3}(i,j)}\ \mathrm{s}^{-1}, \tag{16}$$

iv) Magnetic quadrupole (M2) transitions (Δ J = $\pm$2, π changes)

$$\mathbf{A^{M2}_{ji} = 2.3727 \times 10^{-2}}\mathrm{s}^{-1}\mathbf{\frac{E^{5}_{ij}}{g_{j}}S^{M2}(i,j)}\,. \tag{17}$$

LIFETIME:

$$\tau_{\mathbf{k}}(\mathbf{s}) = \frac{\mathbf{1}}{\sum_{\mathbf{i}} \mathbf{A_{ki}}(\mathbf{s^{-1}})}.$$

Monochromatic Opacity (κ_ν): $\kappa_\nu(\mathbf{i} \rightarrow \mathbf{j}) = \frac{\pi \mathbf{e^2}}{\mathbf{mc}}\mathbf{N_i f_{ij}}\phi_\nu$

Selection Rules: ALLOWED & FORBIDDEN TRANSITIONS

• E1 transitions are strong and are given the name allowed while E2, E3, ..., M1, M2, ... are much weaker and are referred to as forbidden. However, with higher charges, E2 which varies as z^6 and M1 as z^8 increases faster that E1 which varies as z^2.
• E2 and M1 can become comparable to each other with highly charged ions, as seen in tunsten case.
- The forbidden transitions within the ground ^3P state of highly charged Fe XIV was strong to be observed in solar flare by Edlen. He calculated and found that the flare temperature over million degrees compared to the assumed value of a few thousand degrees. Solar surfact temperature is 5770 K.
- Forbidden lines are denoted by square brackets, e.g. [O III] lines can be transitions among $^3P_{0,1,2}$ levels of the ground configuration.
- Forbidden lines disappear above a certain critical density (typically about 10^8 atoms/cm^3), and so their existence is an indicator of density in interstellar gas.
- Although an intercombination line where the spin changes during transition is a dipole allowed (E1) transition, it is often treated in Astronomy as semi-forbidden line because of the lower transition probability (A-value) compared to same-spin transition. A forbidden line is often denoated by a ket notation, e.g. C III] means an inter-

He-LIKE ION: ALLOWED & FORBIDDEN TRANSITIONS

Diagnostic Lines of He-like Ions: w,x,y,z

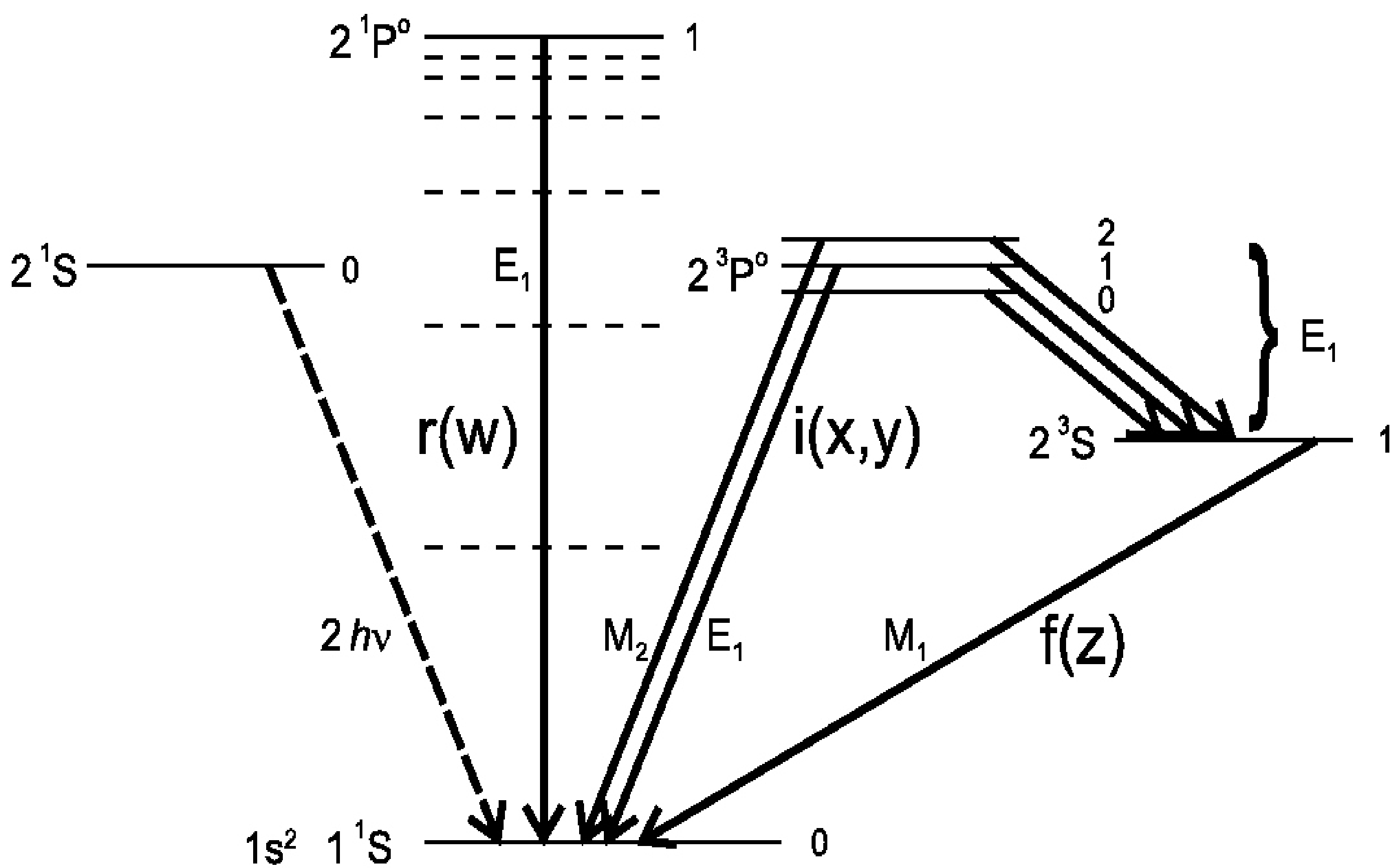
$\mathbf{w(E1): \; 1s2p(^1P^o_1) - 1s^2(^1S_0)}$ **(Allowed Resonant)**

$\mathbf{x(M2): \; 1s2p(^3P^o_2) - 1s^2(^1S_0)}$ **(Forbidden), [He]**

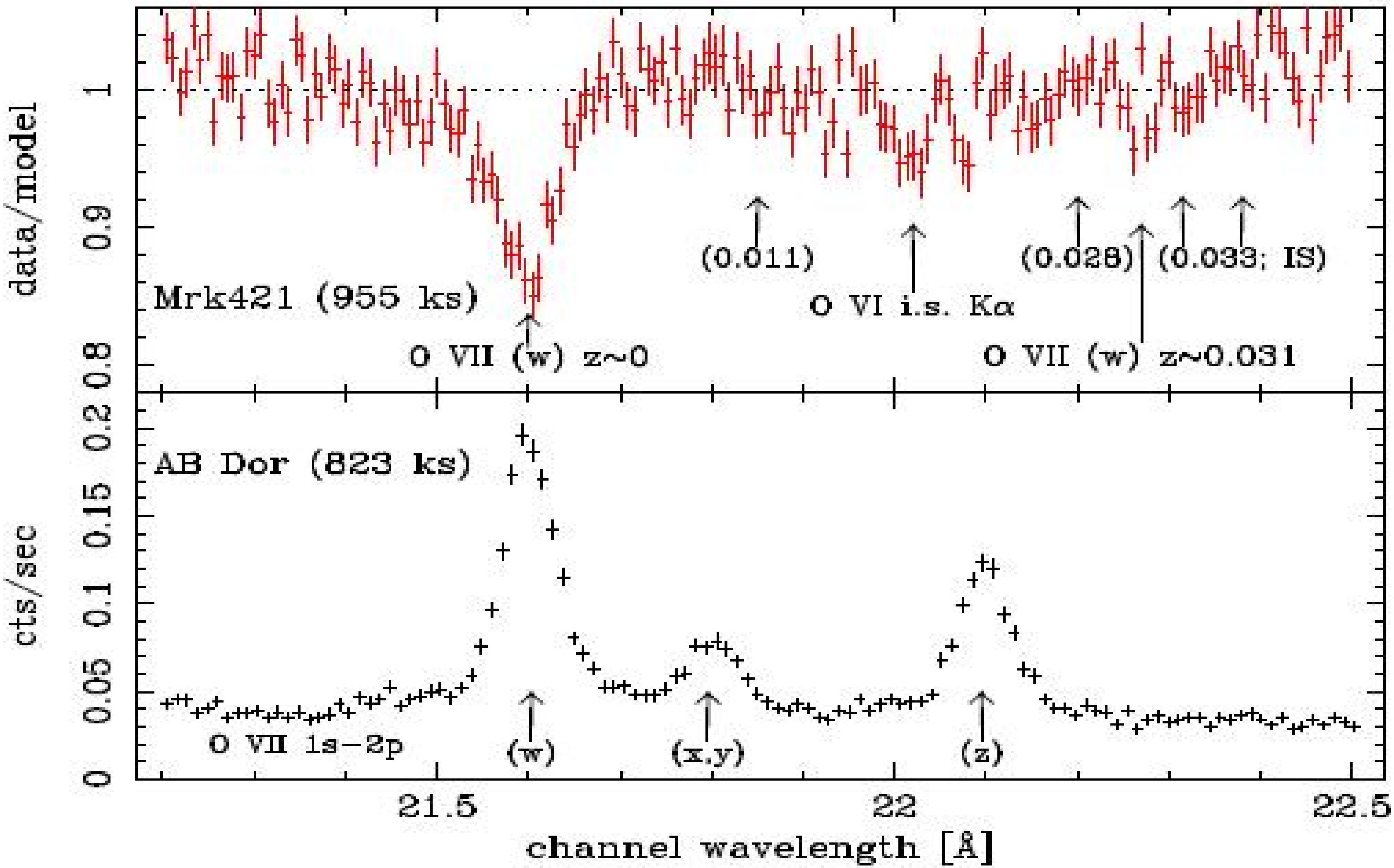
$\mathbf{y(E1): \; 1s2p(^3P^o_1) - 1s^2(^1S_0)}$ **(Intercombination), He]**

$\mathbf{z(M1): \; 1s2s(^3S_1) - 1s^2(^1S_0)}$ **(Forbidden), [He]**

NOTE: 1s-2p are the K_α transitions



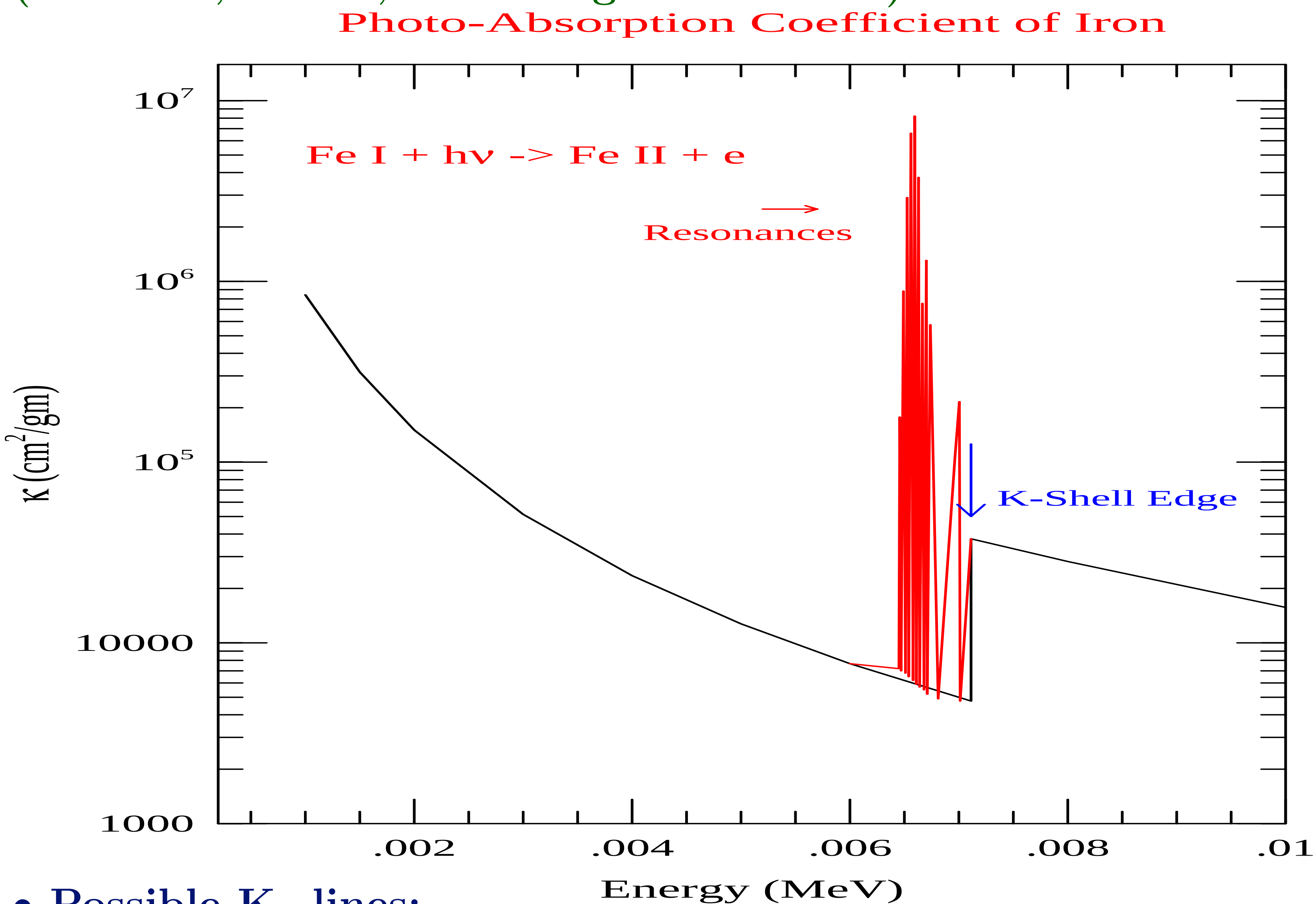
O VII w,x,y,z LINES IN ASTROPHYSICAL SPECTRA



- These lines are detected in the X-ray spectra of AB DOR (AB Doradus is a quadruple star system in the constellation Dorado), and of Mrk 421 galaxy by XMM-Newton observatory (Rasmussen et al 2007)

K-α RESONANCES IN Fe PHOTOIONIZATION

(Pradhan, Nahar, Montenegro et al 2009)



- **Possible K_α lines:**

$\mathbf{1s^2 \rightarrow 2p^5, 2p^4, 2p^3, 2p^2, 2p, 2p^-}$

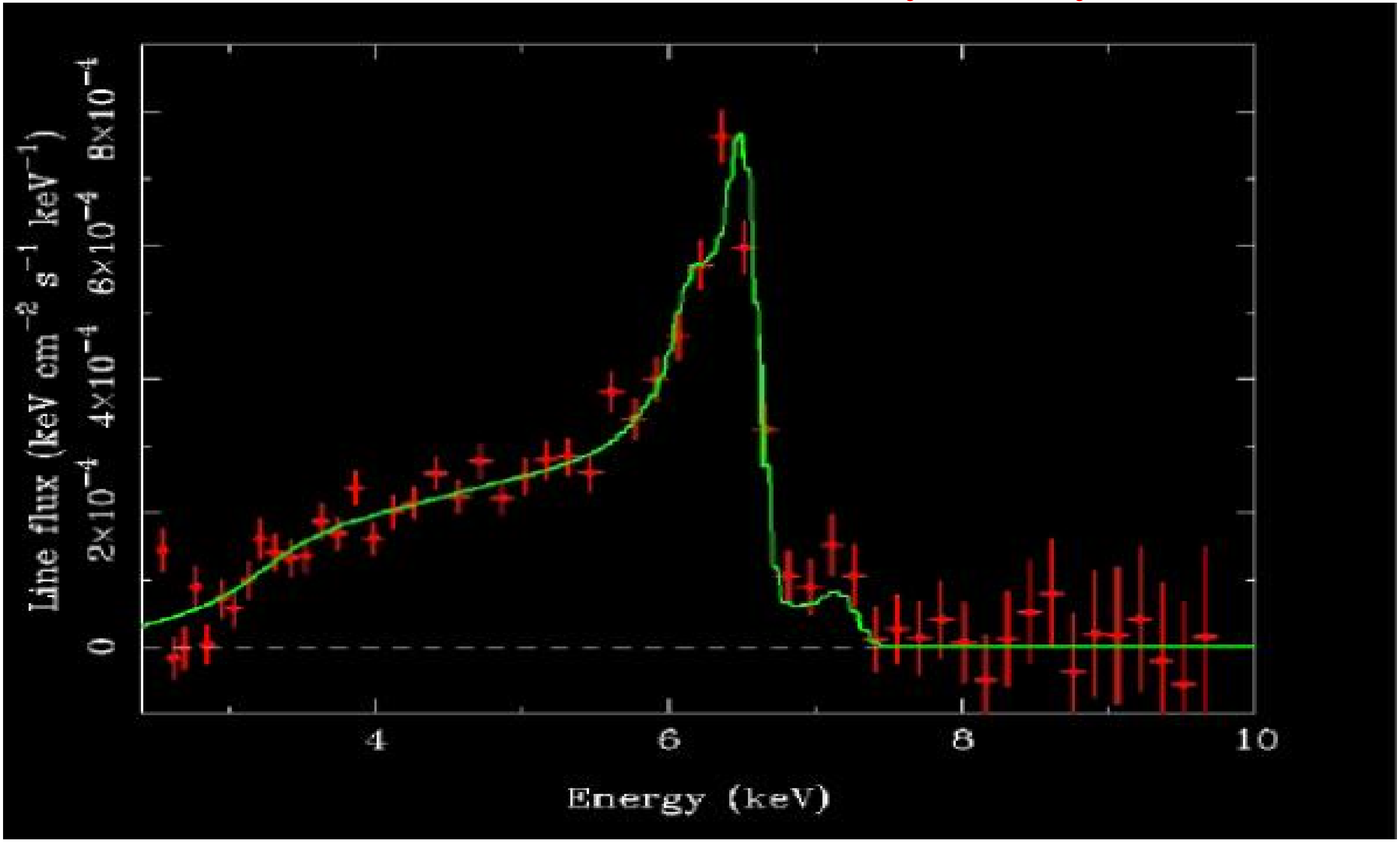
$\mathbf{1s \rightarrow 2p^5, 2p^4, 2p^3, 2p^2, 2p, 2p^-}$

- **There are 112 narrow resonances in the energy range of 6.457 - 7 keV formed due to 1s-2p (K_α) transitions**

X-RAYS FROM A BLACK HOLE - CENTAURUS A GALAXY (Chandra)

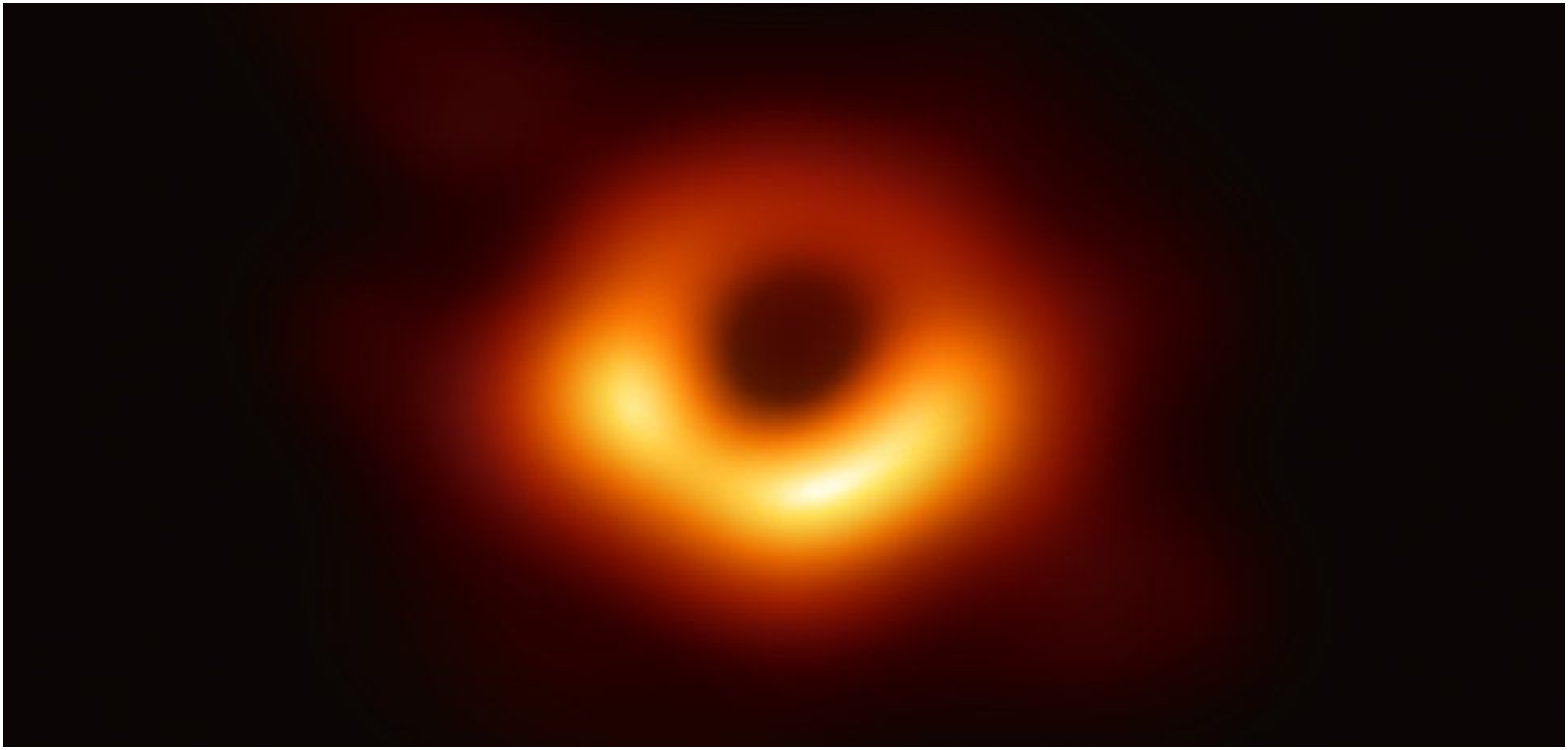
- Photometric image: red - low, green - intermediate, blue - high energy X-rays. Dark green & blue bands - dust lanes that absorb X-rays
  - Blasting from the black hole a jet of a billion solar-masses extending to 13,000 light years

SIGNATURE OF A BLACK HOLE: SeyfertI Gy MCG-6-30-15 6



• The energy range for 1s-2p transitions in Fe = 6.4 - 7 keV. However, the large extension of the lines toward low energy, 3 - 7 keV, indicate that the escaped photons have lost energies in the gravitational force of the black hole. (Illustrated in AAS, Pradhan and Nahar 2011)

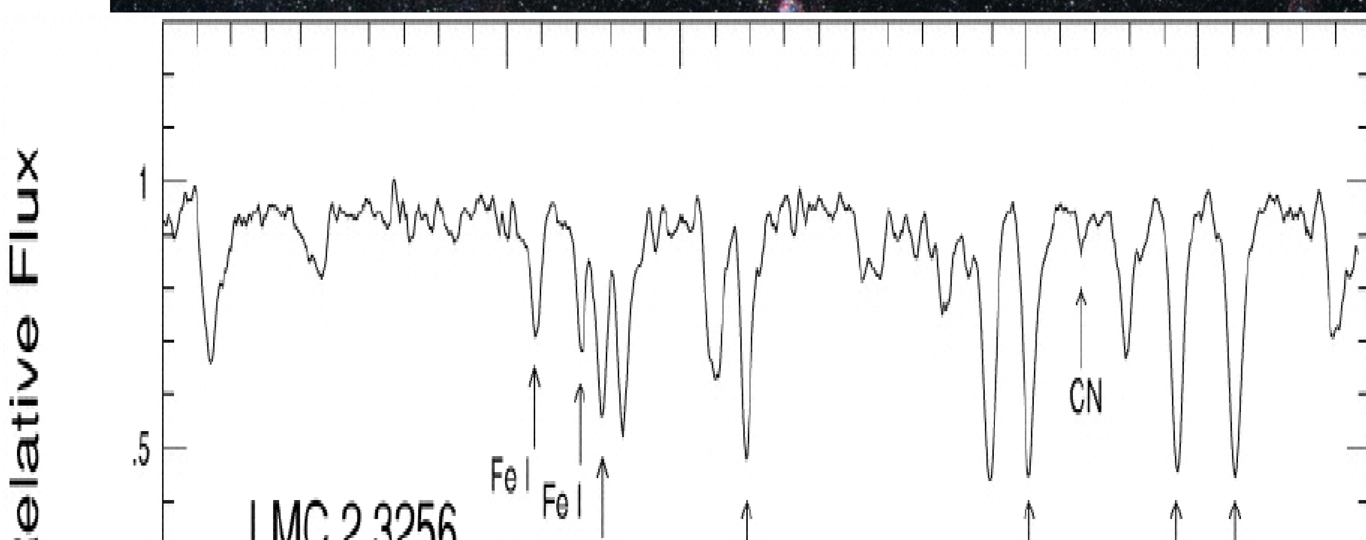
First ever black hole image released, Apr 10, 2019



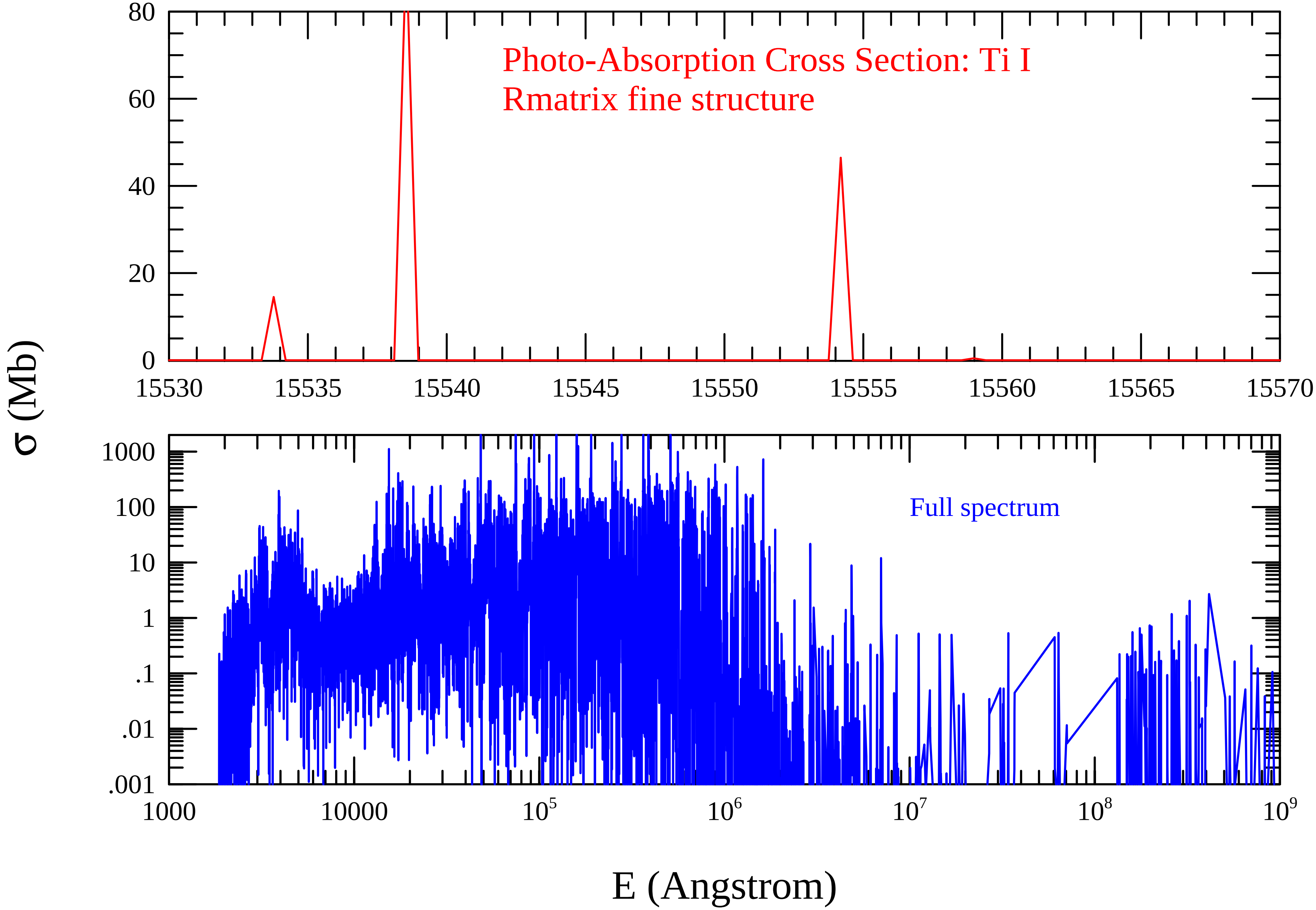
- The first ever image of a black hole, located in a distant galaxy, measures 40 Bkm across - 3M times the size of the Earth - and has been described as ”a monster”. It was composed from photographs by a network of eight ”Event Horizon” telescopes across the world.
- The monster black hole in the center of our Milky Way galaxy: 4M time heavier than our Sun, tracked by the movement of 28 stars circling around it - Nobel prize in 2020

OBSERVATION OF Ti I LINES:

• LMC (Cloud around our Milky Way) 157 ly away, but is a prime target to probe the chemical evolution of stars. • Ti I in LMC Spectra: PHOENIX, Gemini South. • Ti line at 15544 $\AA$.



PREDICTED SPECTRUM OF Ti I: IDENTIFY LINE



- **TOP: lines in 15535 - 15560 indicating the observed line of LMC**
- **Bottom: Total spectrum, number of lines / transitions = 270,423**

SPECTROSCOPY OF LINES IN PLASMAS USING OSCILLATOR STRENGTHS

• For a plasma condition dependent spectrum, the theoretical spectrum can be run through the popularly used astrophysical SME spectra program (a python based program) with temperature and abundances of elements. (check website: https://www.stsci.edu/ valenti/sme.html - valenti and piskunov)

• When two lines, 1 and 2. in an LTE plasma (follow Boltzman-Saha equation) are observed which are originating from the same level but going to different levels, temperature and density dependence for the lines are the same and hence do not enter in the diagnostics. Only ratio of A-values can be used to predict the observed ratio.

level 1 of energy E_1 (in eV) emits a photon of wavelength λ_1 with transition probability A_1 and decaying to the level with statistical weight factor g_1, and level 2 has the similar parameters denoted by subscript 2. The line intensity I ratio of the two lines are given by

$$R = \frac{I_1}{I_2} = \frac{\lambda_2 A_1 g_1}{\lambda_1 A_2 g2} exp\left[-\frac{E_1 - E_2}{KT}\right] \tag{18}$$

where K is the Boltzmann constant, T is the plasma temperature is K, E is the transition energy in eV. The overall number of electron collisions must be high to achieve LTE.

SPECTROSCOPY OF LINES IN PLASMAS

The McWhirter criterion establishes the minimal or limiting value of electron density n_e in cm^{-3} for this purpose.

$$n_e \geq 1.6 \times 10^{12}\sqrt{T}(\Delta E)^3 \tag{19}$$

where T is plasma temperature in Kelvin, and $\Delta E = (E_1 - E_2)$ in eV. The other plasma parameters such as plasma frequency, skin depth and coupling parameter can be related with electron density as

$n_e = 0.124 \times 10^{-9}\omega_e^2$

$n_e = 28.1961 \times 10^{10}\delta^{-2}$

$\Gamma = \frac{q_e^2}{4\pi\epsilon_0 k}\left[\frac{4\pi}{3}\right]^{1/3}\frac{n_e^{1/3}}{T_e}$

In the above equations ω_e, δ, Γ are the plasma frequency, skin depth, and coupling parameter, respectively. Skin depth, δ, is defined as the depth where the current density is just 1/e (about 37%) of the value at the surface; it depends on the frequency of the current and the electrical and magnetic properties of the conductor.

SUPERSTRUCTURE (SS)

The program SUPERSTRUCTURE (SS) calculates number of quantities for atomic structure and atomic processes. The useful ones are the energies of atomic states and transition parameters, such as, oscillator strengths, line strengths, and radiative decay rates or Einstein's A-coefficients. There are a few references for the atomic structure program SUPERSTRUCTURE (SS). The main references are:

1. Eissner, W., Jones, M., Nussbaumer, H. Comput. Phys. Commun. 8, 270 (1974)

2. Eissner, W., Jones, M., Storey P., Nussbaumer, H. Comput. Phys. Commun. (draft 1994)

3. Nahar S.N., Eissner, W., Chen, G.X., Pradhan, A.K., A&A 408, 789 (2003) (transitions of types E2, M1, E3 and M2 by Werner Eissner)

4. Eissner W, in *The Effects of Relativity on Atoms, Molecules, and the Solid State* **(Edited by S. Wilson et al., Plenum Press, New York), p.55 (1991)**

SUPERSTRUCTURE files:

• For your own use, copy files from Sultana's OSC account or download them from her website:
https://www.astronomy.ohio-state.edu/nahar.1/teaching.html#program

• Download files to your laptop: "struct.f", ssinar17, ssout.bp.ar17, sspnl.ar17, runss, rss, and the document. You will upload these files to your workshop or w account

• Check that you can login to you account from a terminal, follow as:

1. Download "putty" from internet to your computer & click on it to open the login window - Or, open a "terminal" on your laptop or from OSC onDemand page

- From the terminal window, log in to your OSC account

2. Type: ssh YourID@owens.osc.edu → to login (Omit "ssh " if you are using putty) and hit the return button

- Please note that after typing each command, you will hit the <return> key