

Research based online course:

”Atomic and Molecular Astrophysics and Spectroscopy with Computational workshops on R-matrix and SUPERSTRUCTURE Codes I”

**- PROF. SULTANA N. NAHAR,
PROF. ANIL K. PRADHAN**

Astronomy Department, Ohio State University, USA

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

May 4 30, 2024

Support: OSU-AMU STEM ER Center, AMU, OSU, OSC

SPECTRAL LINES & RYDBERG FORMULA

Transition of states: Hydrogen spectral line - Photon emitted or absorbed is of energy (Rydberg formula)

$$\Delta\mathcal{E}_{n,n'} = \frac{1}{\lambda} = \mathcal{R}_H \left[\frac{1}{n^2} - \frac{1}{n'^2} \right] \quad (n' > n), \quad (1)$$

where $\mathcal{R}_H = 109,677.576 / \text{cm} = 1/911.76 / \text{\AA}$ is the Rydberg constant. Energy in wavelength in Ångström units:

$$\lambda = \frac{911.76 \text{ \AA}}{\Delta E / \text{Ry}}. \quad (2)$$

• $\Delta\mathcal{E}_{n,n'}$ yields series of spectral lines,

$$\mathcal{R}_H \left[1 - \frac{1}{n'^2} \right], \quad n' = 2, 3, 4, \dots \quad \text{Lyman (Ly)}$$

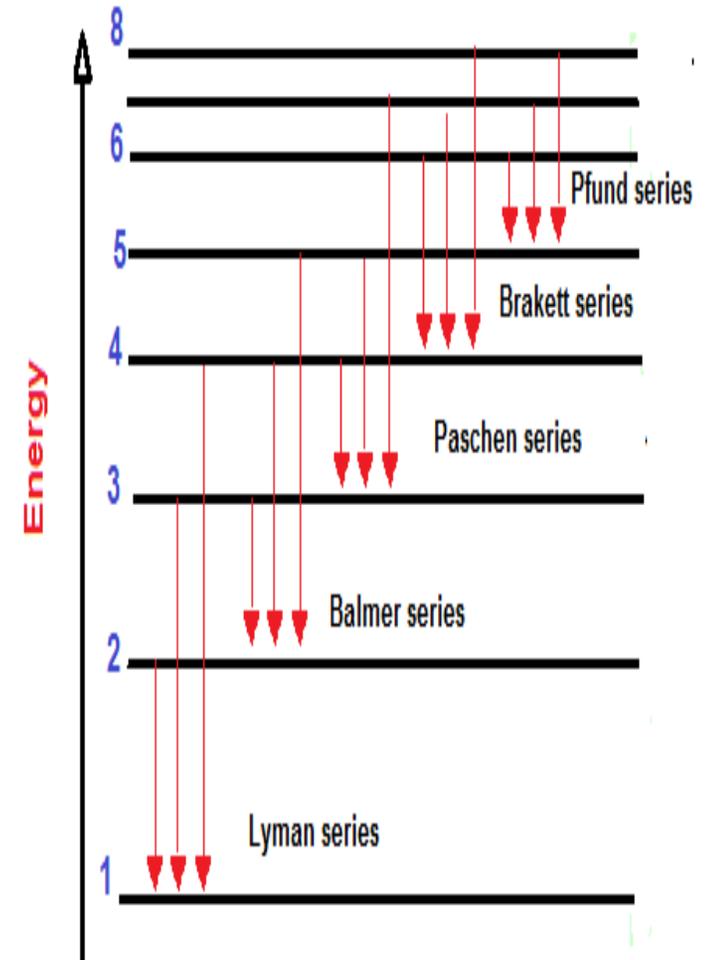
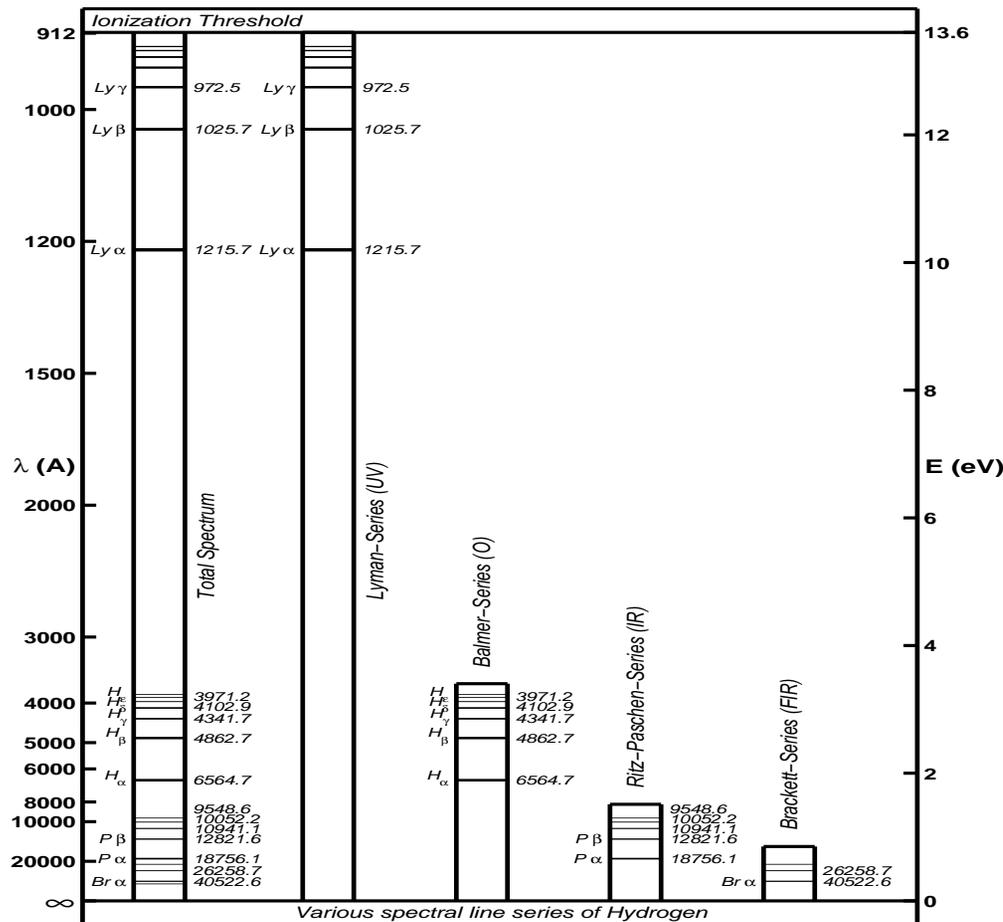
$$\mathcal{R}_H \left[\frac{1}{2^2} - \frac{1}{n'^2} \right], \quad n' = 3, 4, 5, \dots \quad \text{Balmer (Ba)}$$

$$\mathcal{R}_H \left[\frac{1}{3^2} - \frac{1}{n'^2} \right], \quad n' = 4, 5, 6, \dots \quad \text{Paschen (Pa)}$$

$$\mathcal{R}_H \left[\frac{1}{4^2} - \frac{1}{n'^2} \right], \quad n' = 5, 6, 7, \dots \quad \text{Brackett (Br)}$$

$$\mathcal{R}_H \left[\frac{1}{5^2} - \frac{1}{n'^2} \right], \quad n' = 6, 7, 8, \dots \quad \text{Pfund (Pf)}$$

HYDROGEN SPECTRUM & EI



- Lyman series: 1215 – 912 Å (Far ultra-violet FUV), Balmer series: 6564 – 3646 Å (Optical O & Near UV), Paschen series: 18751 – 8204 Å (Near IR NIR), Brackett series: Far IR (FIR)
- For each series, Δn sequence is defined with α , β , γ , δ , etc.,
Ex: Lyman series: Ly α (1215.67 Å), Ly β (1025.72 Å), Ly γ (972.537 Å...), Ly $_{\infty}$ (911.76 Å)
- Ly α - (1s-2p) is "the resonance line"

ASTROPHYSICAL SPECTROSCOPY: IDENTIFICATION OF LINES

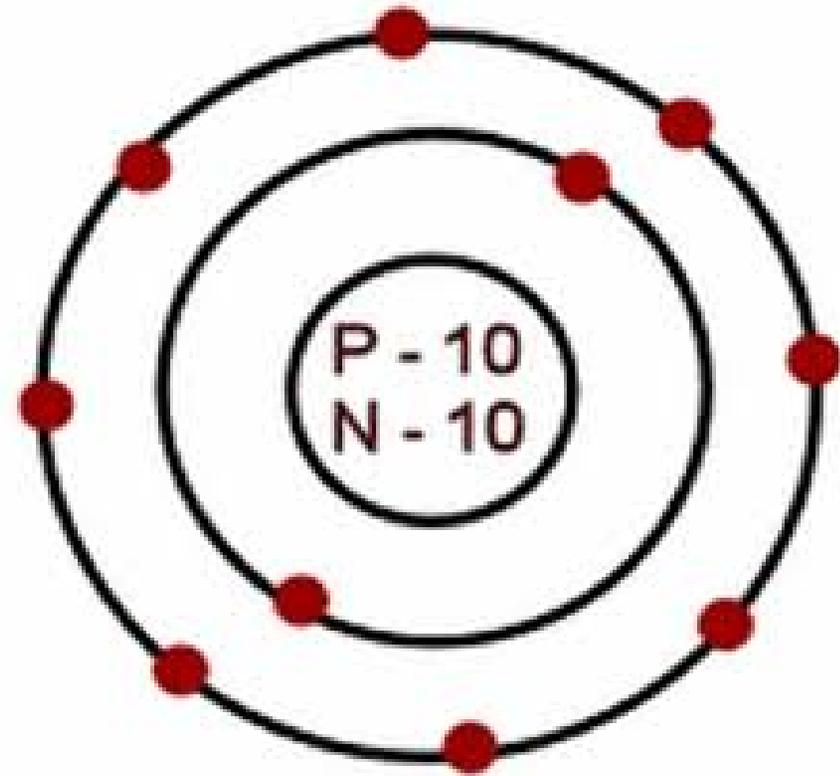
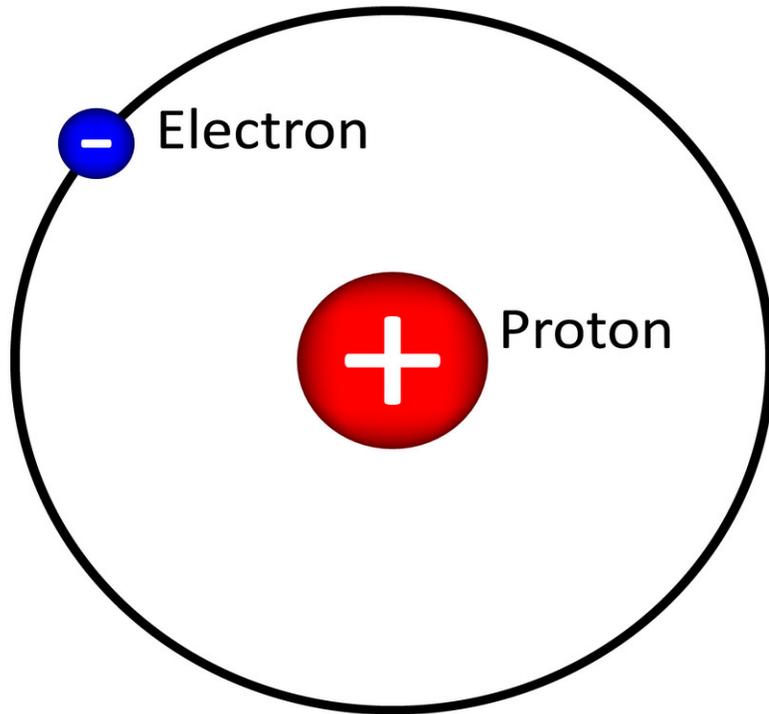
- We study atoms and ions experimentally and theoretically and determine the atomic energies and transition lines with their energies, mainly in wavelengths, and make them publicly available by publications and data tables, such as, the National Institute of Standards and Technology (NIST) in the USA
- Each atomic system has its own set of energies and transitions. But lines can form at the same wavelength by two different atomic species which we call blend. In such case we need some additional information
- Through ground- or space-based telescopes, we take the spectrum of an astronomical object and clean out the noise introduced by the observing equipment - data reduction
- We match the observed lines with those pre-existing lines and identify the element that produced those lines.
- Existence of an observed line depends on the atomic processes of photo-excitation, electron-ion excitation, photoionization, electron-ion recombination which can occur in empty space or in a plasma environment. In pure atomic physics, theoretical or experimental, lines are studied independent of the environment. These can go in model where plasma effects on the lines are incorporated.
- Observation of a sharp line typically indicates thin and cool plasma not affecting the atomic system

ASTROPHYSICAL SPECTROSCOPY: PLASMA EFFECTS ON LINES

- The intensity of the observed line depends on
 - population of transitional levels which can be caused by the atomic processes, and
 - environmental factors such as density and temperature of the plasmaTo study these, we need plasma modeling using the pure atomic data
- The width of a line of an atomic system can be broadened mainly by three factors in the dense and high temperature plasma:
 - Collisional broadening when low level excitation energy is added to the line by electron impact
 - Doppler broadening when the atomic species moving fast in the plasma
 - Stark broadening when the surrounding close-by ions affecting the atomic system by their electromagnetic field which can reduce the ionization energy and lower the levels.
- Line broadening means when spectral lines are broaden and continuum broadening means when the spectral background shows the effect such as due to dissolving photoionization resonances or weak bound-bound transition
- When single lines are observed, they can be simulated by broadening theoretical spectra with a gaussian profile. It does not depend on the temperature and density of the plasmas

SINGLE & MULTI-ELECTRON ATOMS

Hydrogen atom



- 1-electron: $KE + \text{Nuclear Potential}$
- > 1 -electron: $KE + \text{Nuclear Potential} + \text{Electron-Electron potential}$
- 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

$$\mathbf{H}\Psi = [H_0 + H_1]\Psi, \quad (3)$$

$$H_0 = \sum_{i=1}^N \left[-\nabla_i^2 - \frac{2Z}{r_i} \right], H_1 = \sum_{j<i} \frac{2}{r_{ij}} \quad (4)$$

$$H = \sum_i f_i + \sum_{j \neq i} g_{ij} \equiv F + G \quad (5)$$

- 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

$$P_{nl}^{\text{STO}}(\mathbf{r}) = r^{l+1} e^{-ar}$$

- **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 $(n+l)$ value is filled in first [K, Ca: $(n+l) = 4$ with 4s, but $= 5$ with 3d]
 - **Rule 2'**: For the same $(n+l)$, 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 $(n+l) = 5$
- However, for configuration with $Z > Fe$ ($Z=26$), $(n+l)$ -first rule deviates, & no particular rule is followed as states are mixed with overlapped wavefunctions
- **Size: H-radius - a_0** 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

$$L = |L_2 - L_1|, \dots, |L_2 + L_1|, \text{ L Multiplicity} = 2L+1$$

$$S = |S_2 - S_1|, \dots, |S_2 + S_1|, \text{ S Multiplicity} = 2S+1$$

Then the *total angular momentum quantum numbers*:

$$J = |L - S|, \dots, |L + S|, \text{ J Multiplicity} = 2J+1$$

- The symmetry of the state: $(2S+1)L^\pi(LS)$, $(2S+1)L_J^\pi$ or J^π

- 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 $(2S+1)L_J^\pi$?

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

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

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

$$J = |S \pm L|: {}^1P^0: J=1, {}^3P^0: J=0, 1, 2. (2S+1)L_J^\pi: {}^1P_1^0, {}^3P_0^0, {}^3P_1^0, {}^3P_2^0$$

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 $19 \leq Z \leq 40$):

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:

$$\mathbf{J}_1 = \left| \sum_i \mathbf{l}_i + \sum_i \mathbf{s}_i \right|, \quad \mathbf{K} = \mathbf{J}_1 + \mathbf{l}, \quad \mathbf{J} = \mathbf{K} + \mathbf{s},$$

\mathbf{K} is a quantum number.

- **jj coupling** (typically for $Z > 40$): When relativistic effect is more prominent, the total \mathbf{J} is obtained from sum of individual electron total angular momentum \mathbf{j}_i from its angular & spin angular momenta:

$$\mathbf{j}_i = \mathbf{l}_i + \mathbf{s}_i, \quad \mathbf{J} = \sum_i \mathbf{j}_i, \quad (6)$$

ANGULAR MOMENTA COUPLINGS

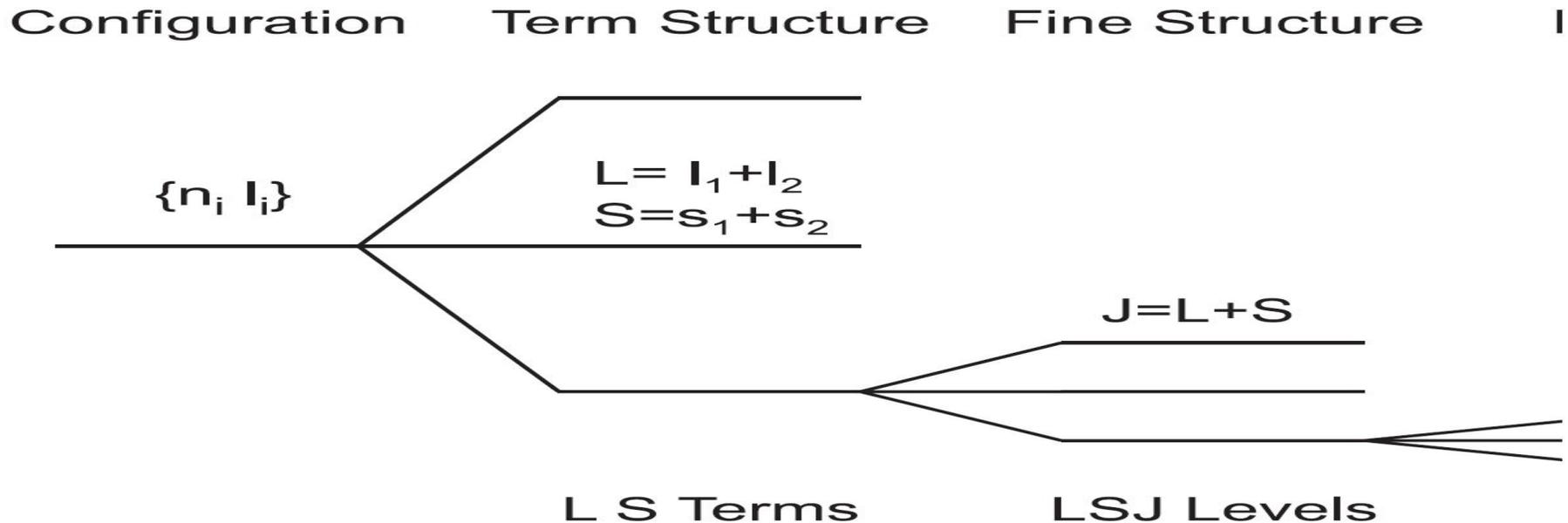
For any 2 electrons, J ranges from $|j_1 + j_2|$ to $|j_1 - j_2|$

- States designation = $(j_1 j_2)_J$

Ex; (pd) configuration- $j_1(1 \pm 1/2) = 1/2, 3/2$, and $j_2(2 \pm 1/2) = 3/2, 5/2$. 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

$$E(\text{LS}) = \frac{\sum_J (2J + 1) E(J)}{\sum_J (2J + 1)}$$

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: $nsn'pn''d$:

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

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

- Equivalent electron state: Less number of LS states.

Ex: configuration, np^2 . If the configuration is nnp , 6 possible states are: ${}^1, {}^3S, {}^1, {}^3P, {}^1, {}^3D$. However, for $n=n'$, Pauli exclusion principle will eliminate some -reducing 6 to 3 states, ${}^1S, {}^3P, {}^1D$, 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: $L = |1 \pm 1| = 0, 1, 2$, $S = |1/2 \pm 1/2| = 0, 1$
 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)

$$M_L = \sum_i m_l = 0, \pm 1, \pm 2; \quad M_S = \sum_i m_s = 0, \pm 1$$

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 $M_L = 0, \pm 1, \pm 2$
- 3P : Next highest value of $M_L = |1|$ associates with 3 $M_S = 0, \pm 1$ 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 Lifshitz) (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 $^1, ^3S, ^1, ^3P, ^1, ^3D, ^1, ^3F, ^1, ^3G$. Following the rule for even values of the total (L+S), the surviving equivalent electron states are $^1S, ^3P, ^1D, ^3F$, and 1G .
- This rule is simpler than Breit scheme for 2 equivalent electron states.

For f^2 , $l = 3$, $m_l = -3, -2, \dots, 3$, $m_s = \pm 1/2$, 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 ($^4S^0$, $^2D^0$, $^2P^0$) for N I, P I: ground state is $^4S^0$
- **L-rule:** States of the same ($2S+1$), larger total L lies lower, again due to less electron repulsion
Ex: np^3 above, $D > P$. $^2D^0$ term lies lower than the $^2P^0$
- **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 energyEx: Both C with ground configuration $1s^2 2s^2 2p^2$ ($<$ half filled p-orbital) and O with $1s^2 2s^2 2p^4$ ($>$ 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* $z = Z - N + 1$, $N =$ no of electrons
- Departure from a pure Coulomb form effectively *reduces* the principal quantum numbers n in the energy formula as

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

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,

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

- Excited energy levels described by the Rydberg formula
→ “Rydberg levels”
- $\mu_s > \mu_p > \mu_d \dots$

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 $\mu_l \approx 0$ for any $l \geq f$, 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 $l > f$
- 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 $n = \infty$ for any given l
- Define $\nu \equiv n - \mu = \text{effective quantum number}$

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

As $n \rightarrow \infty$, $E \rightarrow 0$ & 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* → 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

$$\psi_{n,l,m_l,m_s}(\mathbf{r}, \theta, \phi, \mathbf{m}_s) = \prod_{i=1}^N \psi_{n_i, l_i, m_{l_i}, m_{s_i}} \quad (7)$$

- 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 \rightarrow Hartree-Fock method
- Ex: He atom:

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

This can be written in determinant form:

Hartree-Fock Equation

He wavefunction is then:

$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(\mathbf{1}) & \psi_1(\mathbf{2}) \\ \psi_2(\mathbf{1}) & \psi_2(\mathbf{2}) \end{vmatrix} \quad (8)$$

Ψ vanishes if coordinates of both electrons are the same

• The N -electron wavefunction in the determinant representation

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{1}) & \psi_1(\mathbf{2}) & \dots & \psi_1(N) \\ \psi_2(\mathbf{1}) & \psi_2(\mathbf{2}) & \dots & \psi_2(N) \\ \dots & \dots & \dots & \dots \\ \psi_N(\mathbf{1}) & \psi_N(\mathbf{2}) & \dots & \psi_N(N) \end{vmatrix} \quad (9)$$

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

$$\left[-\nabla_i^2 - \frac{2Z}{r_i} \right] u_k(r_i) + \left[\sum_l \int u_l^*(r_j) \frac{2}{r_{ij}} u_l(r_j) dr_j \right] u_k(r_i) - \sum_l \delta_{m_L^k, m_L^l} \left[\int u_l^*(r_j) \frac{2}{r_{ij}} u_k(r_j) dr_j \right] u_l(r_i) = E_k u_k(r_i). \quad (10)$$

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

$$E[\Psi] = \sum_i I_i + \frac{1}{2} \sum_i \sum_j [J_{ij} - K_{ij}]. \quad (11)$$

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,

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

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

$$V(\mathbf{r}) = - \sum_{i=1}^N \frac{e^2 Z}{r_i} + \left\langle \sum_{i \neq j}^N \frac{e^2}{r_{ij}} \right\rangle. \quad (12)$$

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

$$V(\mathbf{r}) = -\frac{Z}{r} \quad \text{if } r \rightarrow 0, \quad = -\frac{Z}{r} \quad \text{if } r \rightarrow \infty \quad (13)$$

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 $p = p_F$ at $T=0$
- As T rises, electrons are excited out of the Fermi sea close to the 'surface' levels & approach a Maxwellian distribution
→ spatial density of electrons:

$$\rho = \frac{(4/3)\pi p_F^3}{h^3/2}$$

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

$$V(\mathbf{r}) = \frac{Z_{\text{eff}}(\lambda_{nl}, \mathbf{r})}{r} = -\frac{Z}{r}\phi(\mathbf{x}),$$

where

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

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

THOMAS-FERMI-DIRAC-AMALDI (TFDA) APPROXIMATION

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

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

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

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

- 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 $r \rightarrow 0$ and $r \rightarrow \infty$, 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

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

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

$$\mathbf{a}_1 = \nu \{l(l+1) - \nu(\nu-1)\} \frac{1}{2z}$$

$$\mathbf{a}_{\mathbf{k}} = \mathbf{a}_{\mathbf{k}-1} \nu \{l(l+1) - (\nu-\mathbf{k})(\nu-\mathbf{k}+1)\} \frac{1}{2\mathbf{k}z}$$

and the normalization factor is

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

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 $SL\pi$, with different configurations, interact with one another - configuration interaction. Hence the wavefunction of the $SL\pi$ may be represented by a linear combination of configurations giving the state.
- Example, the ground state of Al I is $[1s^2 2s^2 2p^6] 3s^2 3p$ ($^2P^0$). $^2P^0$ state can also be formed from $3s^2 4p$ ($^2P^0$), $3s 3p 3d$ ($\dots, ^2P^0$), $3p^3$ ($^2P^0$) and so on. These 4 configurations contribute with different amplitudes or mixing coefficients (a_i) to form the four state vectors $^2P^0$ of a 4×4 Hamiltonian matrix. Hence for the optimized energy and wavefunction for each $^2P^0$ state all 4 configurations should be included,

$$\Psi(^2P^0) = \sum_{i=1}^4 a_i \psi[C_i(^2P^0)] = [a_1 \psi(3s^2 3p) + a_2 \psi(3s^2 4p) + a_3 \psi(3p^3) + a_3 \psi(3s 3p 3d)]$$

Relativistic Breit-Pauli Approximation

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

$$\mathbf{H}_{\text{BP}} = \mathbf{H}_{\text{NR}} + \mathbf{H}_{\text{mass}} + \mathbf{H}_{\text{Dar}} + \mathbf{H}_{\text{so}} + \frac{1}{2} \sum_{i \neq j}^N [\mathbf{g}_{ij}(\mathbf{so} + \mathbf{so}') + \mathbf{g}_{ij}(\mathbf{ss}') + \mathbf{g}_{ij}(\mathbf{css}') + \mathbf{g}_{ij}(\mathbf{d}) + \mathbf{g}_{ij}(\mathbf{oo}')]]$$

where the non-relativistic Hamiltonian is

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

the Breit interaction is

$$\mathbf{H}_{\text{B}} = \sum_{i>j} [\mathbf{g}_{ij}(\mathbf{so} + \mathbf{so}') + \mathbf{g}_{ij}(\mathbf{ss}')]]$$

and one-body correction terms are

$$\mathbf{H}_{\text{mass}} = -\frac{\alpha^2}{4} \sum_i \mathbf{p}_i^4, \quad \mathbf{H}_{\text{Dar}} = \frac{\alpha^2}{4} \sum_i \nabla^2 \left(\frac{Z}{r_i} \right), \quad \mathbf{H}_{\text{so}} = \frac{Ze^2 \hbar^2}{2m^2 c^2 r^3} \mathbf{L} \cdot \mathbf{S}$$

Spin-orbit interaction energy: $\mathbf{E}_{\text{SO}} = \frac{1}{2} A \hbar^2 [\mathbf{J}(\mathbf{J} + 1) - \mathbf{L}(\mathbf{L} + 1) - \mathbf{S}(\mathbf{S} + 1)]$
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 $\frac{1}{2} A \hbar^2 j$