# Plasma Atomic Physics

- Designation of charge states

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ionization degree | 0+, | 1+, | 2+, | 3+, | …. Z+ | | |
| Atom Y | YI | YII, | YIII, | YIV | | | |
| Carbon C (Z=6) | CI, | CII, | CIII, | CIV, | CV, | CVI, | CVII |
| Isoelectronic series | C-like, | B-like, | Be-like, | Li-like, | He-like, | H-like, | nucleus |

- Atomic states
  - Ground state
  - Excited states (resonance states – 1 electron from outer shell excited to higher shell)
  - Autoionization states (bound states with energy higher than ionization potential – electron excited from inner shell or more excited electrons) – spontaneous non-radiative transition to continuum possible

- Units – cgs units

radius normalized on Bohr radius $a_0$ ($a_0 = \hbar^2 / m e^2 = 0.529177 \times 10^{-8}$ cm)

energy in units Rydberg 1 Ry =1 $R_\infty = e^2/2a_0$ = 13.6058 eV = 109737.3 cm$^{-1}$

# Solution of Schrödinger equation

- Time-independent Schrödinger equation

$$\mathrm{H}\Psi^k\left(\vec{r}\right)=E^k\Psi^k\left(\vec{r}\right)$$

$$\Psi^k\left(\vec{r}\right)=\sum_b y_b^k\psi_b$$

Wave function $\psi_b$ is a function of one-electron states $\varphi_j$

$$\psi_b=f(\varphi_1,\ \varphi_2,\ \ldots,\ \varphi_N)$$

Wave function has to be antisymmetric with respect to exchange of any 2 electrons

$$\psi_{b1}=\varphi_1\left(\vec{r}_1\right)\varphi_2\left(\vec{r}_2\right)=-\psi_{b2}=-\varphi_1\left(\vec{r}_2\right)\varphi_2\left(\vec{r}_1\right)$$

Wave functions have to be orthonormal

$$\left\langle\varphi_i\middle|\varphi_j\right\rangle=\delta_{ij}\qquad\left\langle\psi_i\middle|\psi_j\right\rangle=\delta_{ij}\qquad\left\langle\Psi\middle|\Psi'\right\rangle=\delta_{\Psi\Psi'}$$

# Atom (ion) with 1 electron

- Schrödinger equation $\mathrm{H}\varphi = \mathrm{E}\varphi$

$$\mathrm{H} = -\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\sin\theta}\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + V(r)$$

$$\mathrm{H} = \frac{p^2}{2m} + V(r) = \frac{p_r^2}{2m} + \frac{\mathrm{L}^2}{2mr^2} - \frac{2Za_0}{r}$$

$a_0$ – Bohr radius

- Solution $\varphi(\vec{r}) = \varphi_{nlm_lm_s}(\vec{r}) = \frac{1}{r}P_{nl}(r)\cdot Y_{lm_l}(\theta,\varphi)\cdot\sigma_{m_s}(s_z)$ ,

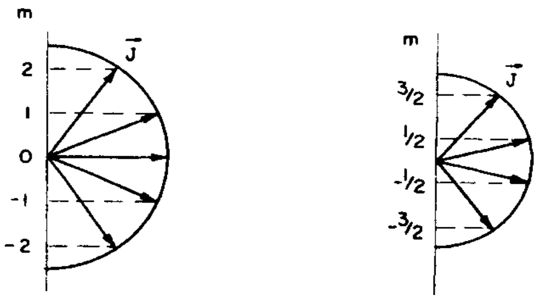
  where n = 1, 2, …- principle quantum number, $l = 0, 1, \ldots, n-1$ characterizes orbital angular momentum, $m_l = -l, -l+1, \ldots, l-1, l$ is orientation of angular momentum and $m_s = -½, +½$ is spin angular momentum orientation

- Operators of angular momentum ($L^2$, $L_z$, $S^2$, $S_z$, $J^2$, $J_z$)

  $J^2 = J\cdot J = J_x^2 + J_y^2 + J_z^2$ - eigenvalues $j(j+1)$ - j=0, ½, 1, 3/2, 2,…

  $J_z$ – eigenvalues *m* (m = -j, -j+1, -j+2,…,j-1,j)

# Orbital and spin angular momentum



*Semiclassical picture for J = 2, 3/2*

- **Eigenfunctions** of operators $L^2$, $L_z$ of orbital angular momentum

$$Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\cdot\Phi_m(\phi) = (-1)^{(m+|m|)/2}\left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)e^{im\phi}$$

- Spherical harmonics are orthonormal

$$\langle Y_{lm}|Y_{l'm'}\rangle \equiv \int_0^{2\pi}\int_0^{\pi} Y_{lm}^{*}Y_{l'm'}\sin\theta\, d\theta\, d\phi = \delta_{ll'}\delta_{mm'}$$

$$|Y_{lm}(\theta,\phi)|^2 = |\Theta_{lm}(\theta)|^2$$

Sum over *m* -spherically symmetric electron density $\sum_{m=-l}^{l} |Y_{lm}(\theta,\phi)|^2 = \frac{2l+1}{4\pi}$

**- Nomenclature of orbital angular momentum**

s (*l* = 0) p (1) d (2) f(3) g(4) h(5) i(6) k(7) l(8) m(9)

- **Electron spin** – electron has internal angular momentum j = ½ (z component $m_s$ = - ½, ½), eigenfunctions $\sigma_{m_s}(s_z) \equiv \delta_{m_s s_z}$ and

$$\langle\sigma_{m_s}(s_z)|\sigma_{m_s'}(s_z)\rangle = \delta_{m_s m_s'} \qquad \langle Y_{lm_l}\sigma_{m_s}|Y_{l'm_l'}\sigma_{m'_s}\rangle = \delta_{ll'}\delta_{m_l m_l'}\delta_{m_s m'_s}$$

# Radial part of the wave function

- Radial equation – bound state $P_{nl}(0) = P_{nl}(\infty) = 0$

$$\left[ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2Z}{r} \right] P_{nl}(r) = EP_{nl}(r)$$

- Substitution $\rho = 2Zr/n\,,\quad E = -Z^2/n^2$

$$\left[ \frac{d^2}{d\rho^2} - \frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2} \right] P_{nl} = 0$$

- Analytic solution

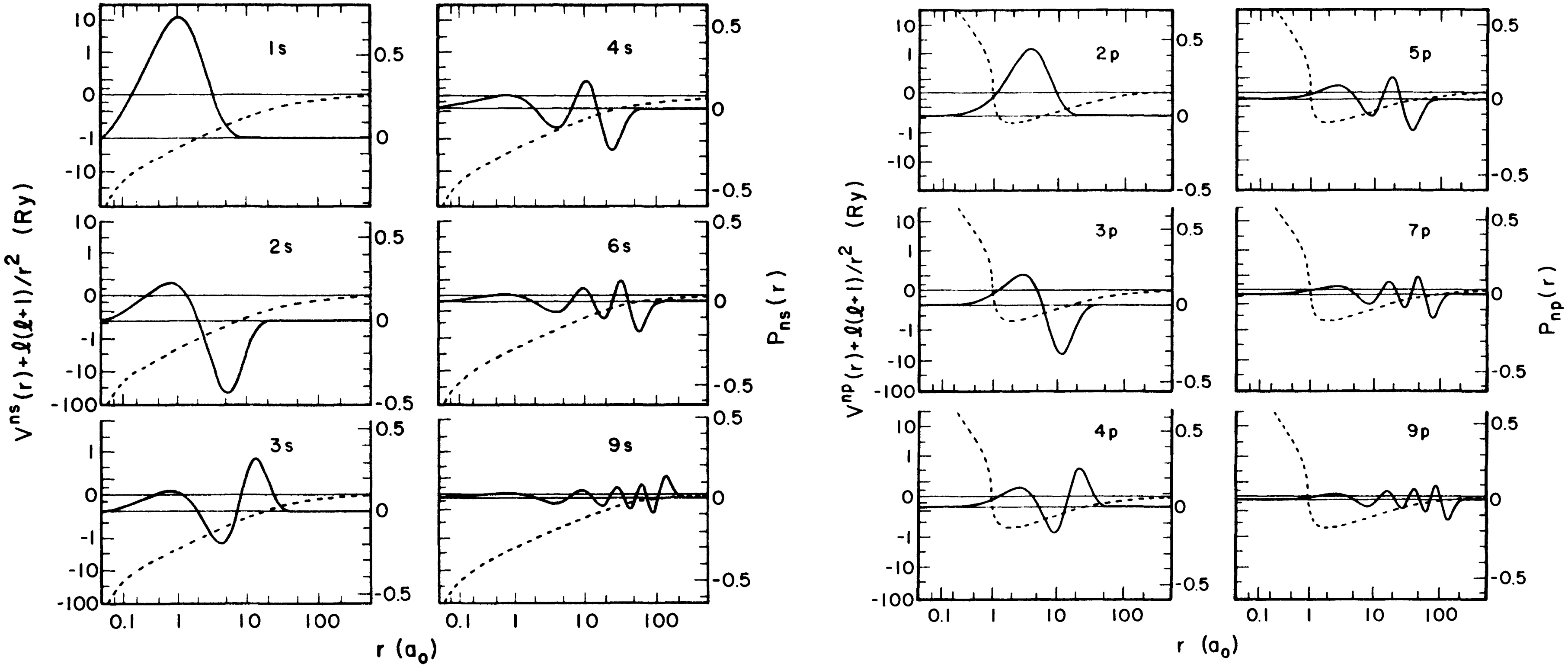
$$P_{nl}(r) = -\left[ \frac{Z(n-l-1)!}{n^2[(n+l)!]^3} \right]^{1/2} \rho^{l+1} e^{-\rho/2} L_{n+l}^{2l+1}(\rho)$$

where the associate Laguerre polynomial is

$$L_{n+l}^{2l+1}(\rho) = -[(n+l)!]^2 \sum_{k=0}^{n-l-1} \frac{(-\rho)^k}{k!(n-l-1-k)!(2l+1+k)!}$$

phase convention used $P_{nl}(r) > 0\,,\quad r \rightarrow 0$

# Radial part of wave function



Radial wave functions (full line) and effective potential (dotted) for the lowest *s* and *p* states

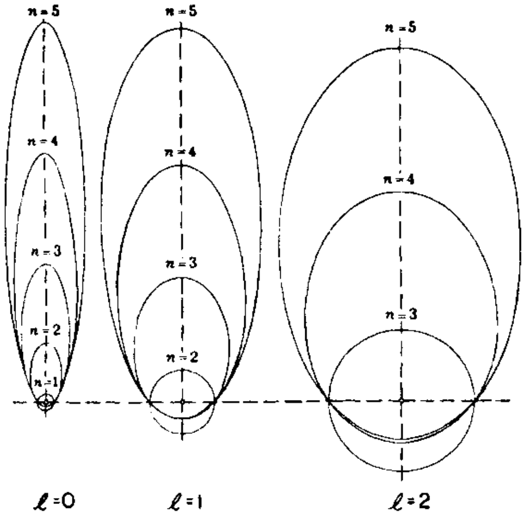
- Number of nodes (zeros) is *n*-*l*-1, number of extremes is *n*-*l*
- For atoms with more than 1 electron, potential *V* has no simply expressible form and analytic solution cannot be found
- Numerical solution – E is iterated for given number of nodes

# Orbits and relativistic corrections

- Hamiltonian with relativistic corrections

$$H = -\nabla^2 + V - \frac{\alpha^2}{4}(E - V)^2 - \frac{\alpha^2}{4}\left(\frac{dV}{dr}\right)\frac{\partial}{\partial r} + \frac{\alpha^2}{2}\frac{1}{r}\left(\frac{dV}{dr}\right)(\boldsymbol{l}\cdot\mathbf{s})$$

  where fine structure constant $\alpha = \frac{e^2}{\hbar c} = \frac{\hbar}{mca_o} = \frac{1}{137.036}$
  - 3rd term – result of relativistic change in mass of electron (mass-velocity term)
  - 4th Darwin term – relativistic non-localizability
  - 5. spin-orbital term – magnetic interaction of spin and orbital magnetic moments



Elliptic Bohr-Sommerfeld orbits for hydrogen atom

- Mass-velocity and Darwin terms → only shift of level energies
- Spin-orbit coupling leads to splitting of energy levels with $l \neq 0$

Operator $\boldsymbol{l}.\boldsymbol{s} = \frac{1}{2}(\boldsymbol{j}^2 - \boldsymbol{l}^2 - \boldsymbol{s}^2)$ – eigenvalues $X \equiv \frac{1}{2}[j(j+1) - l(l+1) - s(s+1)]$

and shift $E_{so} = \alpha^2 Z X\langle r^{-3}\rangle = (1 - \delta_{l0})\frac{\alpha^2 Z^4}{n^3 l(l+1)(2l+1)}[j(j+1) - l(l+1) - s(s+1)]$ **Ry**

where [] = $l$ for j = $l + \frac{1}{2}$ and [] = $-(l+1)$ for j = $l - \frac{1}{2}$

# Complex atoms

- Hamiltonian

$$\mathbf{H} = \mathbf{H}_{\text{kin}} + \mathbf{H}_{\text{elec-nucl}} + \mathbf{H}_{\text{elec-elec}} + \mathbf{H}_{\text{s-o}} = -\sum_i \nabla_i^2 - \sum_i \frac{2Z}{r_i} + \sum_{i>j}\sum \frac{2}{r_{ij}} + \sum_i \xi_i(r_i)(\boldsymbol{l}_i \cdot \mathbf{s}_i)$$

(mass-velocity and Darwin terms omitted – only energy shift after solving)

- Solution is a linear combination of functions $\Psi_b$

$$\Psi^k(\vec{r}) = \sum_b y_b^k \Psi_b \quad , \quad \langle \Psi_b | \Psi_{b'} \rangle = \delta_{bb'}$$

- System of linear equations is solved (M base functions)

$$\sum_{b'=1}^{M} H_{bb'} y_{b'}^k = E^k y_b^k \, , \quad H_{bb'} = \langle \Psi_b | \mathrm{H} | \Psi_{b'} \rangle$$ energies $E^k$ – eigenvalues

- Base functions composed of single-particle wave functions - antisymmetric

$$\Psi = (N!)^{-1/2} \sum_P (-1)^p \varphi_1(\mathbf{r}_{j_1}) \varphi_2(\mathbf{r}_{j_2}) \varphi_3(\mathbf{r}_{j_3}) \cdots \varphi_N(\mathbf{r}_{j_N})$$

sum over all permutations

- Base functions – eigenfunctions of total $J^2$ and $J_z$ -

$$\mathbf{J} = \sum_{i=1}^{N} (\boldsymbol{l}_i + \mathbf{s}_i)$$

- Equivalent electrons - same *nl* – *w* electrons in subshell $(nl)^w$
- Closed subshells *k* ($s^2$, $p^6$, $d^{10}$, $f^{14}$, ..,) have $L_k = S_k = J_k = 0$
- Example Ne I $1s^2 2s^2 2p^5 3s$ usually denoted Ne I $2p^5 3s$ (closed omitted)

# Detailed structure of energy states

- First – radial wave function and average energy of configuration
- Then energy splitting inside one configuration (angular momenta coupling)

– Coupling of 2 angular momenta $j_1, m_1$ and $j_2$, $m_2$ not commutative, coupled

$$|j_1 j_2 jm\rangle = \sum_{m_1=-j_1}^{j_1} C(j_1 j_2 m_1, m - m_1; jm) |j_1 j_2 m_1, m - m_1\rangle = (-1)^{j_1+j_2-j} |j_2 j_1 jm\rangle$$

is eigenfunction of 4 operators $J_1^2$, $J_2^2$, $J^2 = (J_1 + J_2)^2$, $J_z = J_{1z} + J_{2z}$
C() are Glebsch-Gordon coefficients

– Coupling of 3 angular momenta more complicated (not associative)

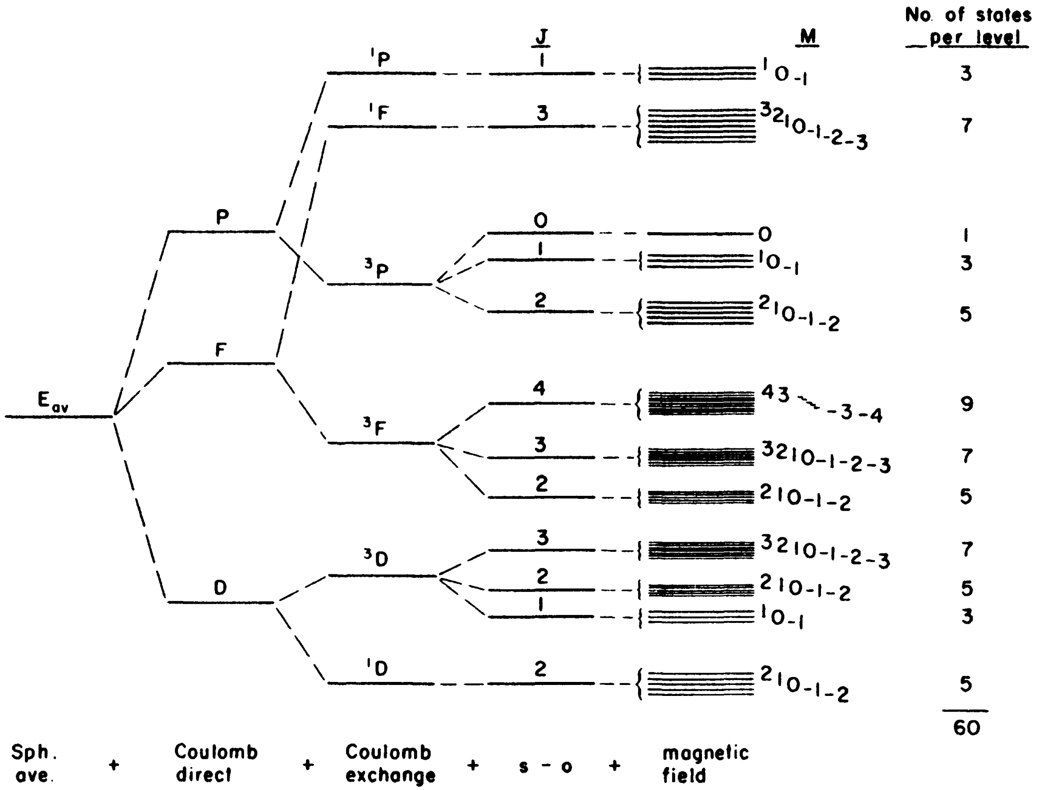
- Coupling schemes

– **LS** coupling (Coulomb repulsion >> spin-orbit interaction)
basic splitting according to $\mathbf{L} = \Sigma_i \, \boldsymbol{l}_i$ and $\mathbf{S} = \Sigma_i \, \boldsymbol{s}_i$, then **L** a **S** are coupled $\mathbf{J} = \mathbf{L} + \mathbf{S}$ to form eigenfunctions of $\mathbf{J}^2$, $\mathbf{J}_z$ – notation $^{2S+1}\mathbf{L}_J$ – 2S+1 - multiplicity, o – odd parity, e.g. $^2\mathrm{P}^{\circ}_{1/2}$

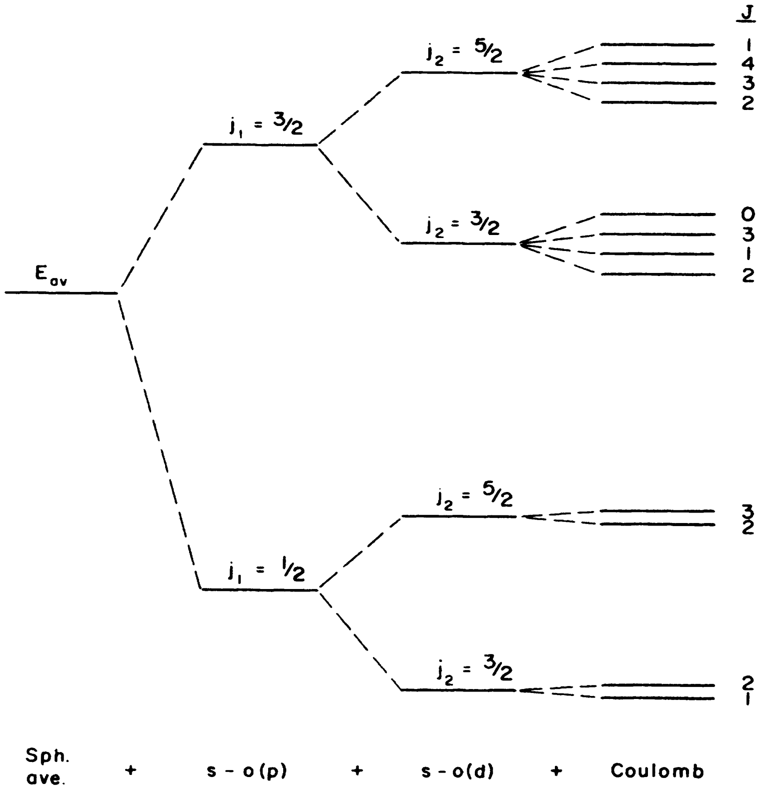
– **jj** coupling (for high Z - spin-orbit interaction >> Coulomb repulsion)
$\boldsymbol{l}_i + \boldsymbol{s}_i = \boldsymbol{j}_i$ , **J** and **M** – sum of $\boldsymbol{j}_i$ – for 2 electrons $[(l_1,s_1)j_1, (l_2,s_2)j_2]JM$

– other coupling schemes (**LK**, j**K**), intermediate coupling

# Diagrams of energy states



Scheme of splitting of energy levels of ***pd*** configuration in conditions of **LS** coupling starting from averaged $E_{av}$ and gradually adding large Coulomb interaction, spin-orbit interaction and external magnetic field



Scheme of energy levels of ***pd*** configuration in conditions of **jj** coupling, 2 strong spin-orbit interactions lead to 4 energies; small splitting due to Coulomb repulsion

# ***Atomic physics of plasma***

Absence of other particles than nuclei and free electrons possible only very low Z

| | |
|---|---|
| ionization degrees | 0+, 1+, …, Z+ |
| atom Y | YI,YII,… |
| carbon C | CI, CII, CIII, |

| CIV, | CV, | CVI, | CVII |
|---|---|---|---|
| Li-like | He-like | H-like | nucleus |

## Schematics of energy states

singlet

1s2s $^1S$ L=0 S=0 g=1

triplet

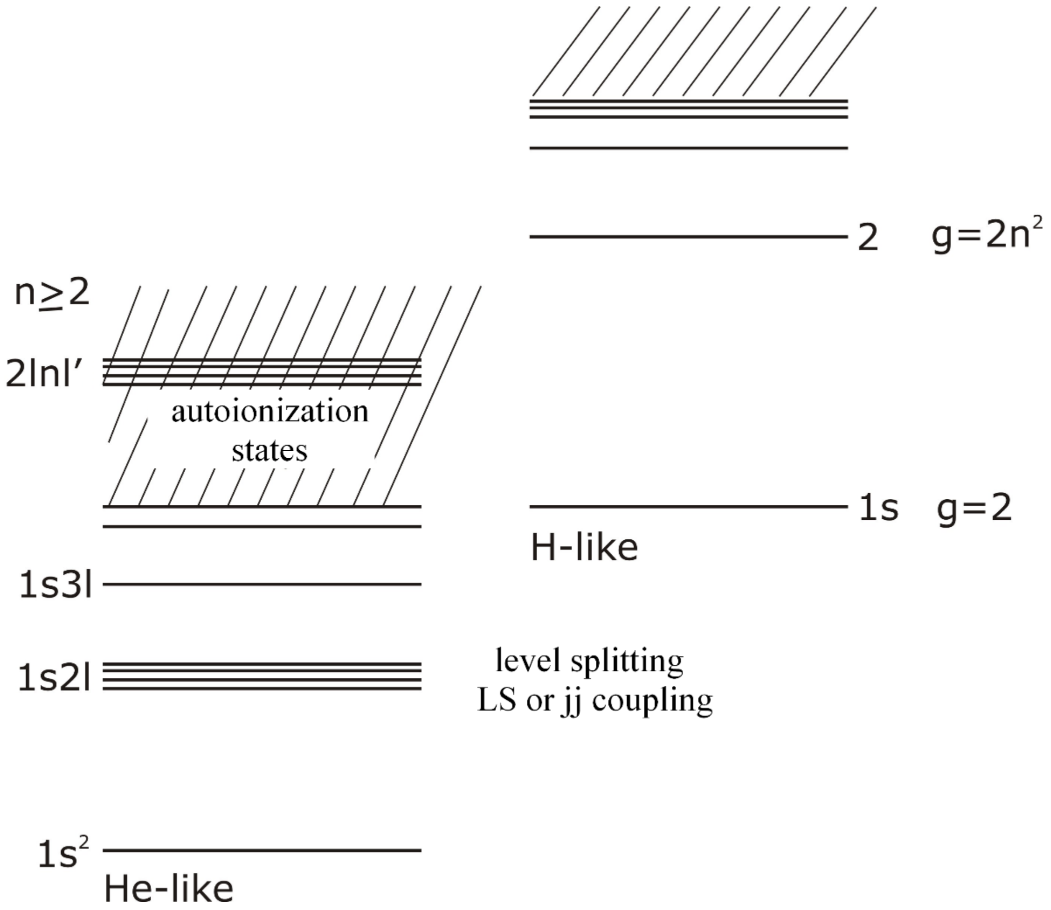
1s2s $^3S$ L=0 S=1 g=3

1s2p$^1P$ L=1 S=0 g=3

1s2p$^3P$ L=1 S=1 g=9

allowed dipole transition to the ground state ΔS=0, ΔL=±1 (0)

LS coupling for low Z; for high Z – relativistic effects=> jj coupling (less restrictions)



## Autoionization states

1. excited > 1 electron
2. excited electron from inner shell e.g. for Li-like 1s2l2l′

Autoionization process $Y^{**} \rightarrow Y^{+} + e^{-}$

Photon energy for transition $Y^{**} \rightarrow Y^{*}$ is near to transition $Y^{+*} \rightarrow Y^{+}$ in once more ionized atom - ***satellite*** to resonance line (satellites important for diagnostics)

## Classification of ions according to electron shells

**K-shell** – H-like, He-like usually ≤ 30 states is enough

**L-shell** – Li-like to Ne-like Li-like ≤ 30 states other ≥ 100 states

Ne-like – relatively simple and well known – collisionally pumped XUV lasers

ground state $1s^2 2s^2 2p^6 \rightarrow 1s^2 2s^2 2p^5 3p$ collisional excitation forbidden optical transition to ground state

inversion with state $1s^2 2s^2 2p^5 3s$, where dipole transition to ground state is allowed

**M-shell** – ≥ $10^3$ states TA – transition arrays (transitions between groups of states) band spectrum – line cannot be resolved in principle

Plasma chemistry – dissociation vibration states interesting for applications

# Atomic processes

## 1. Collisional processes

- if $n_e$ is not small, often ion-electron collisions dominate
- effective collision cross section for process α

$Q^{(\alpha)}$ let flux $\Gamma_1$ flies onto particle 2 $\Gamma_1 = n_1 g$

$$Q^{(\alpha)} = \frac{\text{number of events } \alpha \text{ per 1 s per 1 particle of type 2}}{\Gamma_1}$$

Number of events / m$^3$s $R_{12}{}^{(\alpha)} = n_1 n_2 g Q_{12}{}^{(\alpha)}(g)$ $\left( R_{11}{}^{(\alpha)} = \frac{1}{2} n_1{}^2 g Q_{11}{}^{(\alpha)}(g) \right)$

$$\left( \frac{dn_2}{dt} \right)^{(\alpha)} = -R_{12}{}^{(\alpha)}$$

… decrease of particle density $n_2$ due to process α

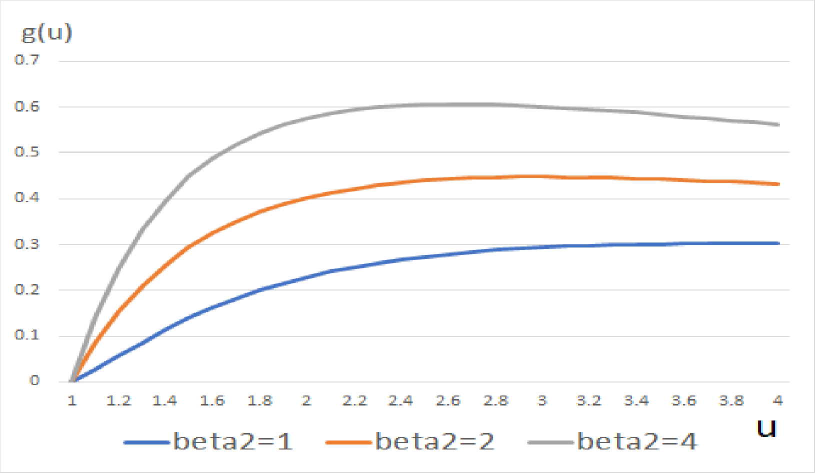
- **Collisional excitation (deexcitation)**

$i^{(k)} + e \rightleftarrows i^{(l)} + e$ $\varepsilon_{kl} = \varepsilon_l - \varepsilon_k$ $\varepsilon \geq \varepsilon_{kl}$ … electron energy threshold

– effective cross section has very similar dependence on $u = \varepsilon / \varepsilon_{kl}$ (for transitions of outer e$^-$ between levels, where dipole transition is allowed)

$$Q^{(k\to l)}(\varepsilon) = 4\pi a_0{}^2 \left(\frac{\varepsilon^H}{\varepsilon_{kl}}\right)^2 f_{kl}\beta_1 g(u)$$

$$g(u) = \frac{u-1}{u^2}\ln\left(\frac{5}{4}\beta_2 u\right)$$



maximum $g$ for $u \sim$ 2-4; for large process has low probability, $\beta_1$, $\beta_2$ constants of order 1

$\varepsilon^H = 13{,}6\ \mathrm{eV}$ hydrogen ionization potential

$a_0 = \dfrac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = 5{,}3\times 10^{-11}\ \mathrm{m}$ Bohr radius (radius of the 1st hydrogen orbital)

$f_{\mathrm{kl}}$ – absorption oscillator strength (characterizes photoexcitation)

$Q \sim \dfrac{1}{\varepsilon_{kl}{}^2}$ collisional processes are fast between near energy levels e.g. between states with the same $n$ (principle quantum number)

energy splitting of states with different $l$ decreases with $n$ - equilibrium inside 1 split level can be ensured by collisions

collisional transition between states, where dipole transition is not allowed may be as fast as for allowed transitions!!! (only the rate cannot be expressed via $f_{kl} \cong 0$)

- **Collisional ionization (three-body recombination)**

$Y + e \rightleftarrows Y^+ + e + e$ $\varepsilon_{k\lambda}$ for ionization from state $k$

(three body recombination → rate ~ $n_i n_e^2$, non-negligible only in dense plasmas)

$u = \dfrac{\varepsilon}{\varepsilon_{k\lambda}}$ $Q^{(k\to\lambda)}(\varepsilon) = 2{,}66\pi a_0{}^2 \left(\dfrac{\varepsilon^H}{\varepsilon_{k\lambda}}\right)^2 \xi_k \beta_1 g(u)$ $\xi_k$ number $e^-$ in outer shell $k$

**Dielectronic recombination** – collision-radiative process

$$Y^+ + e \to Y^{**} \to Y^* + h\nu$$

## *2. Radiative processes*

Transitions between states

bound – bound → line emission

free – bound → continuous emission with boundary (recombination edge)

free – free → bremsstrahlung

- **Bound – bound (photodeexcitation and photoexcitation)**

$i^{(l)} \rightleftarrows i^{(k)} + h\nu$ $h\nu = \varepsilon_l - \varepsilon_k = \varepsilon_{kl}$ $\vec{p}_\nu = \dfrac{h\nu}{c}\vec{\Omega}$ $\vec{\Omega}$ - unit vector

$I_\nu(\vec{\Omega})$ - spectral intensity of emission in unit solid angle $I_\nu(\Omega)d\nu d\vec{\Omega}$

- in vacuum for isotropic electromagnetic field $I_\nu = n_\nu \cdot \dfrac{c}{4\pi} \cdot h\nu$

Photon absorption – number of absorbed photons by non-moving particles of concentration $n_2$ per unit time in unit volume

$$R = \int R_\nu d\nu = n_2 \int \frac{I_\nu\left(\vec{\Omega}\right)}{h\nu} d\nu \cdot Q_\nu d\vec{\Omega}$$

$Q_\nu$ effective cross section for absorption

(for moving particle $\nu$ changes due to Doppler, in rest system $Q_\nu\left(\nu, \vec{\Omega}\right)$)

**Photoexcitation** $k \to l$ $$Q_\nu^{(k\to l)} = \frac{e^2}{4\varepsilon_0 m_e c} f_{kl} \Phi\left(\nu\right)$$

$f_{kl}$ – absorption oscillator strength ($0 < f_{kl} < 1$) ($f_{lk} = -g_k f_{kl} / g_l$ – emission oscil. strength)

$\Phi\left(\nu\right)$ – absorption line shape $\int \Phi\left(\nu\right) d\nu = 1$ emission line shape may differ (often same)

$$I^{kl}\left(\vec{\Omega}\right) = \int I_\nu\left(\vec{\Omega}\right) \Phi\left(\nu\right) d\nu$$

($I^{kl}\left(\vec{\Omega}\right) = I_{\nu_{kl}}\left(\vec{\Omega}\right)$ if intensity depends on $\nu$ weakly)

Number of photoexcitations/volume/time $R^{kl} = n_k B_{kl} \overline{I}^{kl}$ where $\overline{I}^{kl} = \int I^{kl}\left(\vec{\Omega}\right) d\Omega$

$$B_{kl} = \frac{e^2}{4\varepsilon_0 m_e c\, h\, \nu_{kl}} f_{kl}$$ Einstein coefficient for absorption

**Stimulated emission** $R^{lk}_{stim} = n_l B_{lk} \overline{I}^{kl}$ $B_{\mathrm{lk}}$ - Einstein coefficient for stimulated emission

**Spontaneous emission** $R^{lk}_{spon} = n_l A_{lk}$ Radiative lifetime $\tau_{lk} = A_{lk}^{-1} \sim \frac{1}{\nu_{kl}^2}$

***Equilibrium for black body*** => relations of Einstein coefficients

In equilibrium – emission must be equal to absorption

Black-body radiation $I_\nu = B_\nu = \frac{2h\nu^3 / c^2}{e^{h\nu/kT} - 1}$ and $n_k = \frac{g_k}{g_l} n_l \mathrm{e}^{h\nu/k_B T}$

$$g_k B_{kl} = g_l B_{lk} \qquad \frac{A_{lk}}{B_{lk}} = \frac{8\pi h\nu_{kl}^3}{c^2} \quad \Rightarrow \quad A_{lk} = \frac{g_k}{g_l} \frac{2\pi e^2 \nu_{kl}^2}{\varepsilon_0 m_l c^3} f_{kl}$$

(for allowed transitions in XUV region with photon energy $\varepsilon_{\mathrm{kl}} \sim$ 1 keV is $\tau_{lk} \geq 10^{-14}\,\mathrm{s}$

for allowed transition in optical region with photon energy $\varepsilon_{\mathrm{kl}} \sim$ 1 eV is $\tau_{lk} \geq 10^{-8}\,\mathrm{s}$ )

**Line shape** (very often $\Phi(\nu)$ emission = $\Phi(\nu)$ absorption)

*1. Natural broadening*

– Consequence of finite radiative lifetime due to spontaneous emission

$\Delta\varepsilon_{lk} \cong h\gamma_{lk}$ state energy width $\gamma_l = \sum_{j<l} A_{lj}$ $\gamma_{lk} \simeq \gamma_l + \gamma_k$

Lorentzian line shape
$$\Phi(\nu) = \frac{1}{\pi} \frac{\gamma_{lk}/4\pi}{(\nu - \nu_{kl})^2 + (\gamma_{lk}/4\pi)^2}$$

*2. Pressure broadening* (consequence of interactions with neighboring particles)

In plasmas with prevalence of charged particles actions of electric fields, thus **Stark** broadening (+ splitting) – sources – collisions with electrons and ion microfields

For neutral particles e.g.. Van der Waals broadening

3. *Doppler broadening* –due to ion thermal motion for Maxwellian distribution function - line shape
$$\Phi(\nu) \sim \exp\left[ -\frac{(\nu - \nu_{kl})^2}{\Delta\nu_D^2 / 4\ln 2} \right]$$

If Lorentz and Doppler broadening simultaneously – **Voigt profile** (convolution)

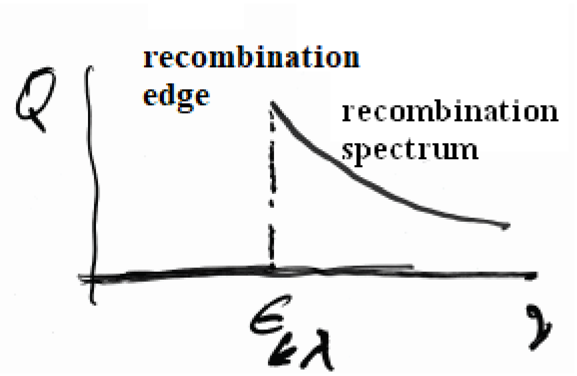
- **Bound – free transitions** (photoionization and photorecombination)

  photoionization from state *k* $h\nu \geq \varepsilon_{k\lambda}$ $Q^{(k\rightarrow\lambda)} \sim \frac{1}{\nu^3}$

  photorecombination emission – source

  $j_\nu \sim e^{-\frac{h\nu-\varepsilon_{k\lambda}}{k_B T_e}}$ for Maxwellian distribution of $e^-$

  coefficient dependent on ion and state $g_{bf}$ (Gaunt factor)



- **Free – free transitions**

  ***bremsstrahlung***

  spectrum near to $\sim e^{-\frac{h\nu}{k_B T_e}}$ total power $P^{ff} \sim Z^2 n_e n_i T_e^{1/2} \bar{g}_{ff}$ Gaunt free-free factor)

Ratio of recombination emission and bremsstrahlung
(for hydrogen atom; *k* is principle quantum number)

$$\frac{P_k^{fb}}{P^{ff}} = \frac{2\varepsilon_{k\lambda}/k}{k_B T_e}$$

for collisional absorption of a photon

$$Q_\nu \sim \frac{n_e Z^2 \bar{g}_{ff}}{\nu^3 v_{Te}}$$

***cyclotron radiation*** – in magnetic fields

emission mainly at the electron cyclotron frequency $\omega_{ce}$, and also at its harmonics

emitted power by an electron $P = \frac{e^2}{4\pi\varepsilon_0}\frac{4\omega_{ce}^2}{3m_e c^2}\frac{8\pi}{3}E_{kin}$ $E_{kin} = m_e v^2/2$

## Transport of radiation

$l$ - path along a ray →

for $\nu >> \frac{\omega_p}{2\pi}$   $v_g \approx c$   $\varepsilon_r \approx 1$

$$\underbrace{\frac{1}{c}\frac{\partial I_\nu}{\partial t}}_{\approx 0} + \frac{\partial I_\nu}{\partial l} = j_\nu - k_\nu I_\nu$$

( $j_\nu$, $k_\nu$ may depend on $\vec{\Omega}$, e.g. due to macroscopic motion of medium)
(scattering is omitted for simplicity)

$L$ – scale length   $k_\nu L << 1$   optically thin medium
$k_\nu L \geq 1$   optically thick medium
for $k_\nu L \to \infty$   $I_\nu \to B_\nu$   blackbody

Photoexcitation, photoionization, stimulated emission => radiation IMPACT on populations

Laboratory plasmas are mostly optically thin (in some cases with an exception of the centers of the most intense emission lines)
Exception - cyclotron emission at the electron cyclotron frequency $\omega_{ce}$ from magnetically confined plasmas (eg tokamak) is optically thick

# Equilibria

## 1. TE (full thermodynamic equilibrium) – matter and radiation in equilibrium

- Radiation = black-body radiation $I_\nu = B_\nu = \dfrac{2h\nu^3/c^2}{e^{h\nu/kT}-1}$ ($T = T_\mathrm{e} = T_\mathrm{i} = T_\mathrm{r}$)
- Equilibrium of excitation states (Boltzmann relation)

$$\frac{n_l}{n_k} = \frac{g_l}{g_k}\,\mathrm{e}^{-\varepsilon_{kl}/k_B T_e} \qquad \text{where } \varepsilon_{kl} = \varepsilon_k - \varepsilon_l$$

Relative population of ground state $\dfrac{n}{n_1} = \sum_{k=1}^{k_\mathrm{max}} \dfrac{n_k}{n_1} = \dfrac{1}{g_1}\sum g_k\,\mathrm{e}^{-\varepsilon_k/k_B T_e} = \dfrac{Z(T)}{g_1}$

Partition function $Z$(T) diverges for $k_\mathrm{max}=\infty$, one has to realize that for very high states is $r_{orbit} \gg \sqrt[3]{1/n_i}$ and such states ***need not be bound*** – these are not states of an isolated ion and are influenced by their neighborhood

***Ionization potential lowering*** $\Delta I$– assumption is often used that states with energy $\varepsilon_k > I - \Delta I$ are not bound for $T_e \ll \varepsilon_2$ is then $Z(T) \simeq g_1$

- Equilibrium of ionization states (chemical equilibrium – Saha equation)

  Equilibrium of $k^{\mathrm{th}}$ state of neutral atom and ground state of one-time ionized ion

  $$\frac{n_e n_1^+}{n_k} = 2\frac{g_1^+}{g_k}\left(\frac{2\pi m_e k_B T_e}{h^2}\right)^{3/2} \mathrm{e}^{-\frac{\varepsilon_{k\lambda}}{k_B T_e}} \qquad \varepsilon_{k\lambda} = \varepsilon_{1\lambda} - \varepsilon_k = I - \varepsilon_k$$

  the same relation holds between any states of $p$-times and $p$+1-times ionized ions
  Similar relations may be written for total populations of ions – here I present for neutrals and one-time ionized ions

  $$\frac{n_e n_i}{n_n} = 2\frac{Z_i}{Z_n}\left(\frac{2\pi m_e k_B T_e}{h^2}\right)^{3/2} \mathrm{e}^{-\frac{I}{k_B T_e}}$$

  where $Z_\mathrm{i}$ and $Z_\mathrm{n}$ are respective partition functions.

- Electrons (and ions) have Maxwellian distributions with respective temperature ($T = T_\mathrm{e} = T_\mathrm{i}$)

2. **LTE (local thermodynamic equilibrium) –** matter in equilibrium, radiation not

There hold - Maxwellian distributions + Boltzmann relations + Saha equations, but radiation **is not** black body radiation (radiation must be in equilibrium at least in the part of the spectrum, where radiative processes have substantial impact on populations!)

LTE always holds when the density is so high that collisional processes dominate over radiative ones (impact of radiative processes on populations is negligible)

3. **Coronal equilibrium (very rarified plasma)**

It is a stationary state, not an equilibrium

Rarified plasma – photodeexcitation >> collisional deexcitation
– photorecombination >> 3-body and dielectronic recombination

Omission of slow processes simplifies calculations of the stationary state significantly

4. **Solving of rate equations**

Equations are solved for populations $n_{\mathrm{pk}}$ ($k^{\mathrm{th}}$ state of p-times ionized ion)

System of ordinary differential equations (stationary state – time derivatives = 0)

Coupling among different parts of the system only due to radiation transport

In approximation of an optically thin system – terms including radiation intensity are omitted, i.e. impact of absorption and stimulated emission is disregarded

## Principle of detailed balancing

Differential reaction rate of ***direct*** and ***inverse processes*** must be equal in equilibrium (invariance with respect to time reversal)

***Differential cross section*** of ***inverse*** process can be thus calculated from ***differential cross section*** of **direct** process and it can be also used ***outside equilibrium***

If additionally, Maxwellian electron distribution holds even outside equilibrium, then the same method can be applied also for ***rate coefficients***

In equilibrium, the rate of collisional excitation = rate of collisional deexcitation and the rate of collisional ionization = rate of three-body recombination

***Rate coefficients*** *of* ***inverse*** process can be calculated from rate coefficients of ***direct*** process and then they can be used ***outside equilibrium***

Similar application of the principle of detailed balancing are the relations between **Einstein coefficients**

(calculation of coefficients from detailed balancing is preferential also for numerical modeling – preserving of equilibrium solution is guaranteed automatically)