Radiative and non-radiative transitions

Radiative

bound—bound

absorption

spontaneous emission

stimulated emission

bound—free: photoionization

free—bound: radiative recombination

fluorescence / Auger effect

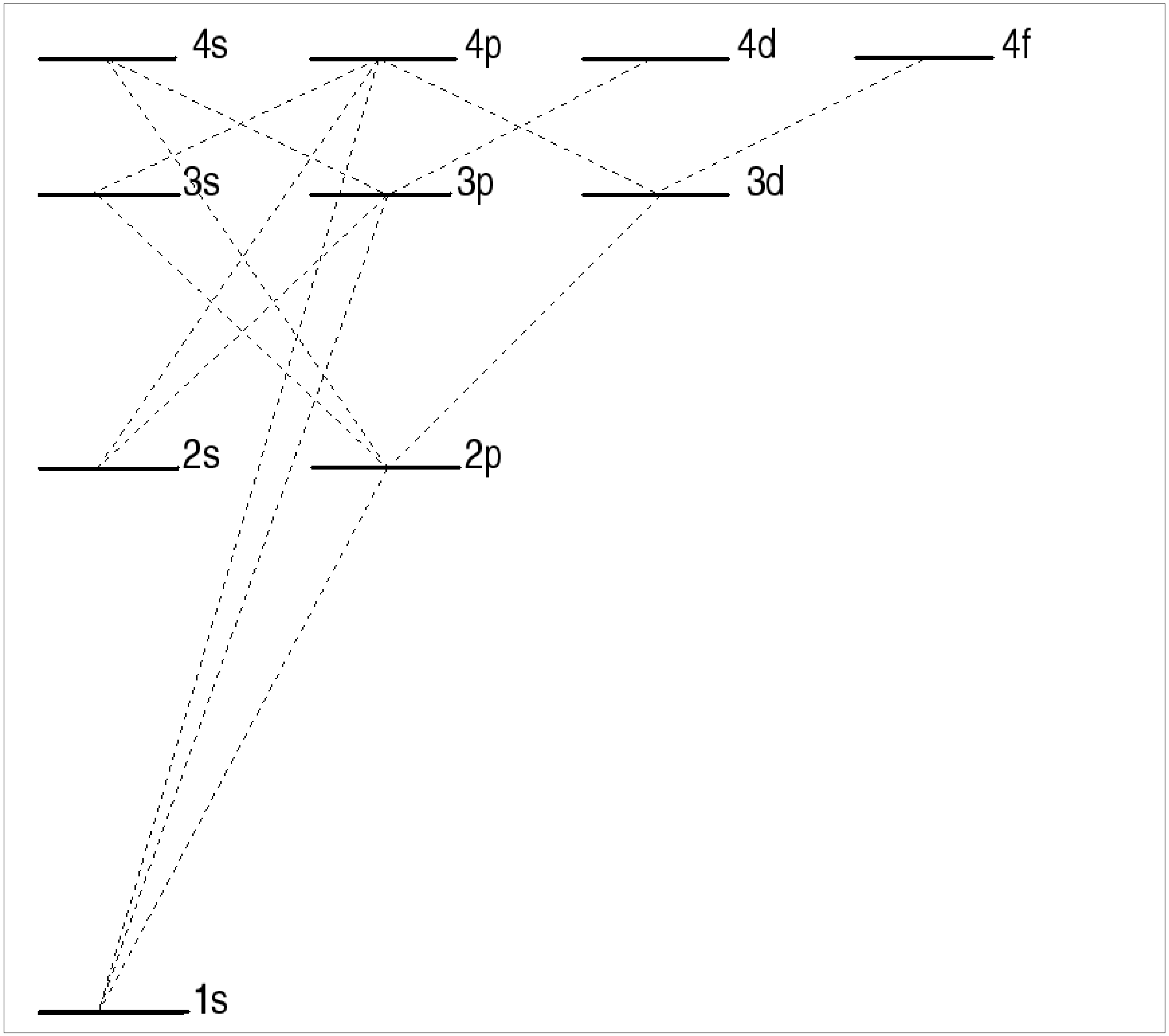
Collisional

excitation

deexcitation

collisional ionization/recombination

Reminder – energy levels



Hydrogen

Radiative transitions

Bound – bound transitions: Einstein coefficients

1. **Spontaneous emission**

   A_{ul} = transition probability per unit time for spontaneous emission (sec^{-1})

2. **Absorption**

   $B_{lu}J$ = transition probability per unit time for absorption

   $$\bar{J} \equiv \int_0^\infty J_\nu \phi(\nu) d\nu; \qquad \int_0^\infty \phi(\nu) d\nu = 1$$ - line profile

3. **Stimulated emission**

   $B_{ul}J$ = transition probability per unit time for stimulated emission

Relations between Einstein coefficients:

$$g_l B_{lu} = g_u B_{ul}$$ (transitions between levels 1 and 2 have to balance)

$$A_{ul} = \frac{2h\nu^3}{c^2} B_{ul}$$ g_l, g_u – statistical weights of the levels involved,

e.g., $g = 2J + 1$

Einstein coefficients

Quantum mechanical calculations of transition probabilities

$$w_{if}=\frac{4\pi^2 e^2}{m^2 c}\frac{J(\omega_{if})}{\omega_{if}^2}\left|\left\langle f\left|\exp(i\,\boldsymbol{k}\cdot\boldsymbol{r})\;\boldsymbol{l}\cdot\sum\nabla_j\right|i\right\rangle\right|^2$$ probability of transition

$$\exp(i\,\boldsymbol{k}\cdot\boldsymbol{r})=1+i\,\boldsymbol{k}\cdot\boldsymbol{r}+\frac{1}{2}(i\,\boldsymbol{k}\cdot\boldsymbol{r})^2+\cdots$$

$\exp(i\,\boldsymbol{k}\cdot\boldsymbol{r})\approx 1 \Rightarrow$ dipole transition; higher orders: electric quadrupole, magnetic dipole, etc ...

in the dipole approximation:

$$\langle w_{if}\rangle=\frac{1}{2}B_{if}J(\omega_{if})=\frac{4\pi^2}{3c\hbar^2}|d_{if}^2|J(\omega_{if})$$

$$|d_{if}^2|=|(d_x)_{if}|^2+|(d_y)_{if}|^2+|(d_z)_{if}|^2$$

$\boldsymbol{d}\equiv e\sum_j \boldsymbol{r}_j$ -- dipole operator

$$|(d_x)_{if}|^2=|\langle f|e\,\boldsymbol{x}|i\rangle|^2$$

hence

$$B_{ul}=\frac{8\pi^2|d_{ul}|^2}{3c\hbar^2} \qquad A_{ul}=\frac{64\pi^4\nu^3}{3hc^3}|d_{ul}|^2$$

For degenerate states:

$$A_{ul}=\frac{64\pi^4\nu_{ul}^3}{3hc^3}\frac{1}{g_u}\sum|d_{ul}|^2$$ where the sum is over all substates of the lower and upper levels

Oscillator strength

Absorption

classically:

$$\sigma_{tot} = \frac{\pi e^2}{mc} = B_{lu}^{classic} \frac{h\nu_{lu}}{4\pi}$$

$$B_{lu}^{classic} = \frac{4\pi^2 e^2}{h\nu_{lu} mc}$$

$\longrightarrow$

$$B_{lu} = \frac{4\pi^2 e^2}{h\nu_{ul} m c} f_{lu}$$

$$f_{lu} = \frac{2m}{3\hbar^2 g_l e^2} (E_u - E_l) \sum |d_{lu}|^2$$

f – oscillator strength – quantum correction to the classical value of *B*

Emission

$$B_{ul} = \frac{4\pi^2 e^2}{h\nu_{lu} m c} f_{ul} \quad \Rightarrow \quad g_l f_{lu} = g_u f_{ul}$$

Oscillator strength for emission are *negative*

$$g_u A_{ul} = -\frac{8\pi^2 e^2 \nu_{ul}^2}{m c^3} g_u f_{ul} = \frac{8\pi^2 e^2 \nu_{ul}^2}{m c^3} g_l f_{lu}$$

Natural line width

Energy levels are somewhat broadened as a result of of Heisenberg's "uncertainty principle". Finite life-time of a level means some spread in energy,

Level lifetime,

$$\Delta t \sim 1/A_{21} \equiv 1/\gamma \qquad \Delta E \, \Delta t \sim \hbar$$

transition,

$$E(t) \sim \sin(2\pi \nu_0 t + \phi_0) e^{-\gamma t/2}$$

hence profile in frequency space (Fourier transform)

$$\phi(\nu) = \frac{\gamma/4\pi^2}{(\nu - \nu_0)^2 + (\gamma/4\pi)^2}$$

Long-lived levels give very narrow lines (e.g. H 21 cm line)

Radiative transitions

Permitted (allowed) transitions: dipole matrix element does not vanish

Semi-forbidden transitions: dipole transitions but with a change of spin

Forbidden transitions: dipole matrix element vanishes (may be possible at higher orders)

Selection rules

$$\exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) = 1 + i\,\boldsymbol{k}\cdot\boldsymbol{r} + \cdots$$

Selection rules for discrete transitions

		Electric dipole (E1) ("allowed")	Magnetic dipole (M1) ("forbidden")	Electric quadrupole (E2) ("forbidden")
Rigorous rules	1.	$\Delta J = 0, \pm 1$ (except $0 \nleftrightarrow 0$)	$\Delta J = 0, \pm 1$ (except $0 \nleftrightarrow 0$)	$\Delta J = 0, \pm 1, \pm 2$ (except $0 \nleftrightarrow 0$, $1/2 \nleftrightarrow 1/2$, $0 \nleftrightarrow 1$)
	2.	$\Delta M = 0, \pm 1$ (except $0 \nleftrightarrow 0$ when $\Delta J = 0$)	$\Delta M = 0, \pm 1$ (except $0 \nleftrightarrow 0$ when $\Delta J = 0$)	$\Delta M = 0, \pm 1, \pm 2$
	3.	Parity change	No parity change	No parity change
With negligible configuration interaction	4.	One electron jumping, with $\Delta l = \pm 1$, Δn arbitrary	No change in electron configuration; i.e., for all electrons, $\Delta l = 0$, $\Delta n = 0$	*No* change in electron configuration; *or* one electron jumping with $\Delta l = 0, \pm 2$, Δn arbitrary
For *LS* coupling only	5.	$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
	6.	$\Delta L = 0, \pm 1$ (except $0 \nleftrightarrow 0$)	$\Delta L = 0$ $\Delta J = \pm 1$	$\Delta L = 0, \pm 1, \pm 2$ (except $0 \nleftrightarrow 0$, $0 \nleftrightarrow 1$)

Transitions with spin “flip”

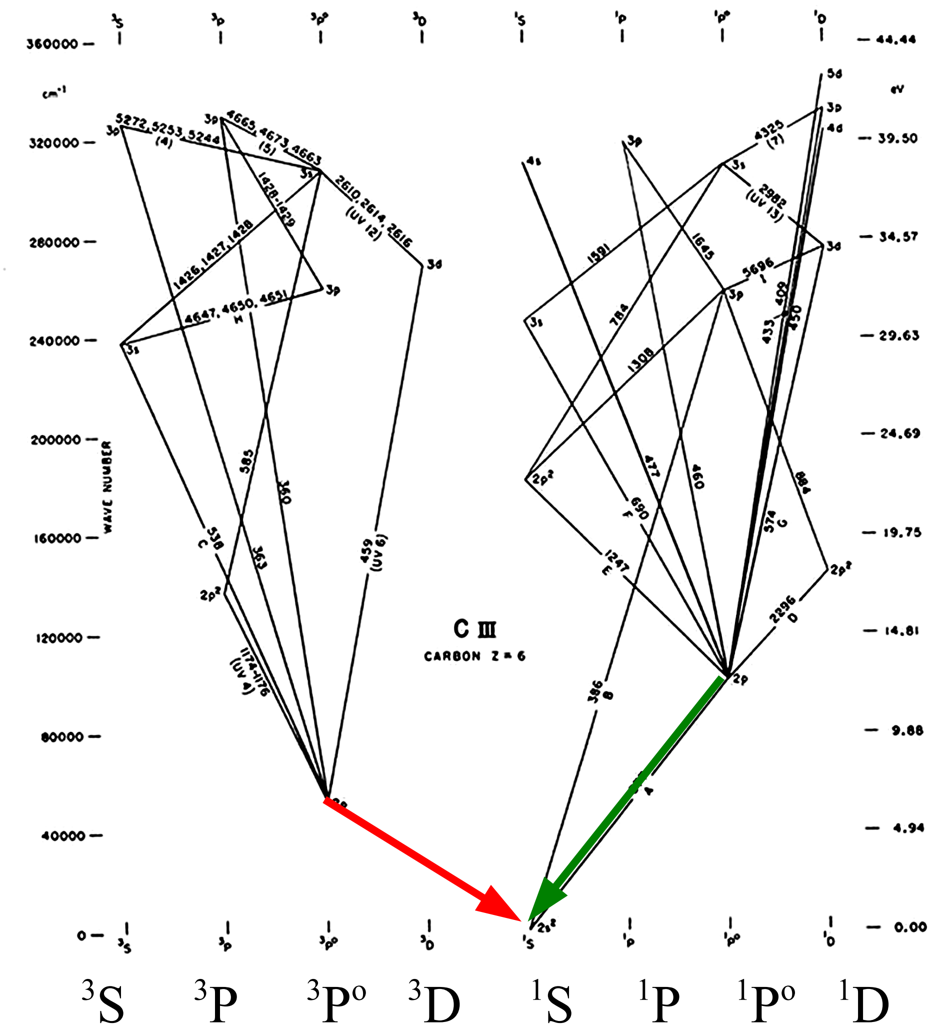
Intercombination (semi-forbidden) lines

Grotrian diagram

CIII] 1909 Å, 6.50 eV   ($2s2p \rightarrow 2s^2$)

The first few **C III Energy Levels**

Energy (eV)	**Configuration**	**J**	**L**	**S**	**Notes**
0.0	$1s^2\,2s^2\,{}^1S_0$	0	0	0	ground-state
6.492690	$1s^2\,2s\,({}^2S_0)\,2p\;{}^3P^o{}_0$	0	1	1	transition to ground completely forbidden (since J=0<->0 transition not allowed)
6.495627	$1s^2\,2s\,({}^2S_0)\,2p\;{}^3P^o{}_1$	1	1	1	transition to ground semi-forbidden Electric Dipole (E1) (since Delta-S=0)
6.502615	$1s^2\,2s\,({}^2S_0)\,2p\;{}^3P^o{}_2$	2	1	1	transition to ground "forbidden" Magnetic Quadrupole (M2)
12.69004	$1s^2\,2s\,({}^2S_0)\,2p\;{}^1P^o{}_1$	1	1	1	transition to ground allowed electric-dipole (E1)



The He-like ions line triplet

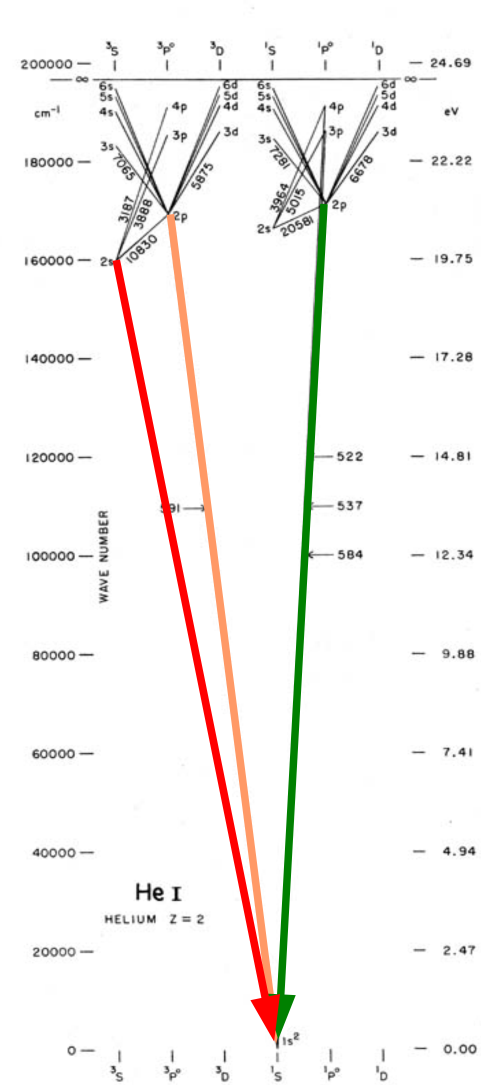
Ground state: $1s^2\ ^1S_0$

$1s2p\ ^1P_1$ – permitted (resonance) line (ΔL=1, ΔS=0, ΔJ=1)

$1s2p\ ^3P_1$ – intercombination (ΔL=1, ΔS=1, ΔJ=1)

$1s2s\ ^3S_1$ – forbidden (magnetic dipole) (ΔL=0, ΔS=1, ΔJ=1)

$1s2p\ ^3P_2$ – magnetic quadrupole (ΔL=1, ΔS=1, ΔJ=2)



$^3S\ ^3P^o\ ^3D\ ^1S\ ^1P^o\ ^1D$

Forbidden lines

Example: [OIII] 5007 Å line

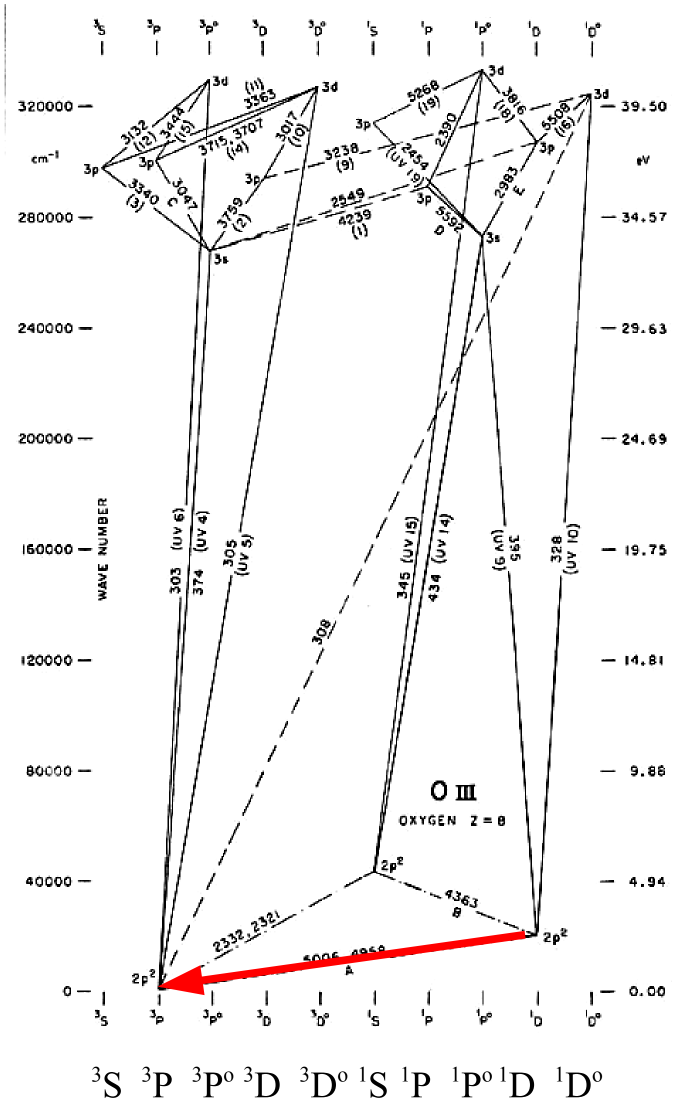
configuration: $2s^2\,2p^2 \leftrightarrow 2s^2\,2p^2$

line components:

4931 Å $\quad {}^3P_0 - {}^1D_2$, E2 $\quad \Delta L=1, \Delta S=1, \Delta J=2$

4959 Å $\quad {}^3P_1 - {}^1D_2$, M1, E2 $\quad \Delta L=1, \Delta S=1, \Delta J=1$

5007 Å, $\quad {}^3P_2 - {}^1D_2$, M1, E2 $\quad \Delta L=1, \Delta S=1, \Delta J=0$



Strictly forbidden transitions

Matrix element vanishes to all perturbational orders.

Example: Lyα radiative decay of hydrogen: 2*s* to 1*s* – two spherically symmetric wave functions.

Possibilities:

collisional shifting 2*s*→2*p*, then 2*p*→1*s*. A = 6.2×10^{8} s^{-1}

two-photon process: $\nu+\nu'=\nu_{21}$ A = 8.2 s^{-1}

2-photon dominates if $n<10^{4}$ cm^{-3}.

Transition rates: bound – bound, hydrogen

A simple case: Hydrogen

$$h\nu = Ry(n^{-2} - n'^{-2}) \qquad Ry \equiv \frac{e^2}{(2a_0)} = 13.6\,eV$$

Bound-bound transitions

Lyman-α transition: $g f = \frac{2^{14}}{3^9} = 0.83 \qquad A_{21} = 5\times 10^8\,s^{-1}$

other Lyman series: $g_1 f_{1n} = \frac{2^9 n^5 (n-1)^{2n-4}}{3(n+1)^{2n+4}}; \qquad n \gg 1 \quad \Rightarrow \quad g_1 f_{1n} \sim \frac{1}{n^3}$

Absorption: $B_{12} = 8.3\,A_{21} = 4.2\times 10^9\,s^{-1}$

Absorption cross section (at the line center, assuming the natural line width only):

$$\sigma_\nu = B_{12}\frac{h\nu}{4\pi}\phi(\nu) \approx 10^{-11}\,cm^2$$

Transition rates: bound – bound

Number of absorptions:

$$n_i R_{ij} = n_i B_{ij} \int \phi_\nu J_\nu \, d\nu \equiv n_i B_{ij} \bar{J}_{ij} = n_i 4\pi \alpha_{ij} \frac{\bar{J}_{ij}}{h\nu} = n_i 4\pi \int \alpha_{ij}(\nu) \frac{J_\nu}{h\nu} \, d\nu$$

$$\alpha_{ij} \equiv \sigma_\nu$$

Number of stimulated emissions:

$$n_j B_{ji} \int \phi_\nu J_\nu \, d\nu = n_j B_{ji} \bar{J}_{ij} = n_j \frac{g_i}{g_j} B_{ij} \bar{J}_{ij} = n_j 4\pi \frac{g_i}{g_j} \alpha_{ij} \frac{\bar{J}_{ij}}{h\nu}$$

Number of spontaneous emissions:

$$n_j A_{ji} \int \phi_\nu \, d\nu = n_j \frac{2h\nu_{ij}^3}{c^2} B_{ji} = n_j \frac{2h\nu_{ij}^3}{c^2} 4\pi \frac{g_i}{g_j} \frac{\alpha_{ij}}{4\pi}$$

Transition rates: bound – free

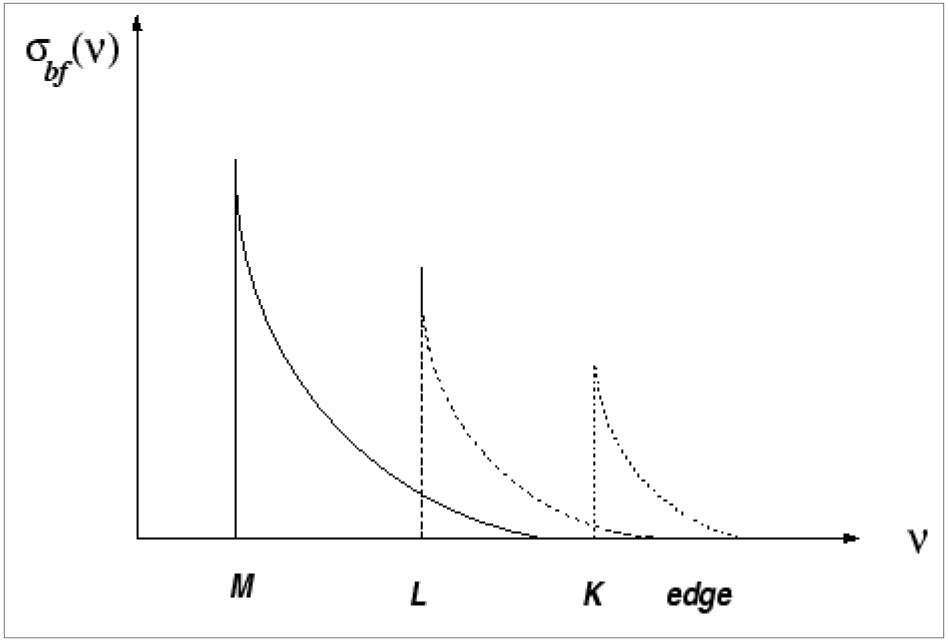
Bound-free transitions (photoionization)

Final energy of the electron: $E_f = \hbar\omega - \chi$

Cross section: $\sigma_{bf} \approx \dfrac{(2\alpha)^{9/2}\pi Z^5 c^{7/2}}{3 a_0^{3/2}\omega^{7/2}}$ $\qquad \hbar\omega \gg \chi$

more accurate form: Gaunt factor ≈ 1

$$\sigma_{bf} = \frac{512\pi^7 m e^{10} Z^4}{3\sqrt{3}\,c h^6 n^5}\,\frac{g(\omega, n, l, Z)}{\omega^3}$$



for 1^2S level of H-like ions (Osterbrock 1989):

$$\sigma_{bf} = \frac{A_0}{Z^2}\left(\frac{\nu_1}{\nu}\right)^4 \frac{\exp\left(4 - \frac{4\arctan\epsilon}{\epsilon}\right)}{1-\exp(-2\pi/\epsilon)}, \qquad \nu \geqslant \nu_1 \qquad \epsilon = \sqrt{\frac{\nu}{\nu_1} - 1}$$

$$A_0 = \frac{2^8\pi}{3e^4}\left(\frac{1}{137.0}\right)\pi a_0^2 = 6.30\times10^{-18}\ cm^2 \qquad h\nu_1 = Z^2 h\nu_0 = 13.6\,Z^2\,eV$$

Number of photoionizations: $n_i R_{ik} = n_i 4\pi \displaystyle\int_{\nu_0}^{\infty} \alpha_{ik}(\nu)\frac{J_\nu}{h\nu}\,d\nu$

Transition rates

Radiative recombination – the inverse process to photoionization

k – ion
i – atom

Number of recombinations (spontaneous + stimulated), obtained from the principle of *detailed balance*:

$$n_k\left(R'_{ki,spon}+R'_{ki,stim}\right)\equiv n_k\overline{\left(\frac{n_i}{n_k}\right)}R_{ki}=n_k\overline{\left(\frac{n_i}{n_k}\right)}4\pi\int_{\nu_0}^{\infty}\frac{\alpha_{ik}(\nu)}{h\nu}\left(\frac{2h\nu^3}{c^2}+\bar{J}\right)e^{-h\nu/kT}d\nu \qquad \bar{J}\equiv\int_0^{\infty}\phi_\nu J_\nu d\nu$$

sometimes used: *recombination coefficient*:

$$n_k\left(R'_{ki,spon}+R'_{ki,stim}\right)\equiv n_k n_e\alpha_{RR}(T)$$

Collisional rates: excitation/deexcitation, ionization/three body recombination

Upward rate *i->j,* where *j* is a bound or free state:

$$n_i C_{ij}=n_i n_e\int_{v_0}^{\infty}\sigma_{ij}(v)f(v)v\,dv\equiv n_i n_e q_{ij}(T) \qquad \frac{1}{2}m_e v_0^2=E_0$$ - threshold for the ionization

Downward rates:

in equilibrium: $\overline{n}_i C_{ij}=\overline{n}_j C_{ji}$ hence: $n_j C_{ji}=n_j\overline{(n_i/n_j)}C_{ij}=n_j\overline{(n_i/n_j)}n_e q_{ij}(T)$

Collisional transitions

Autoionization

Doubly excited states - two electrons in excited levels – may have energy higher than the ionization potential of the ion in ground state. Then ***autoionization*** energetically favorable. One electron leaves the ion, the other returns to the ground state.

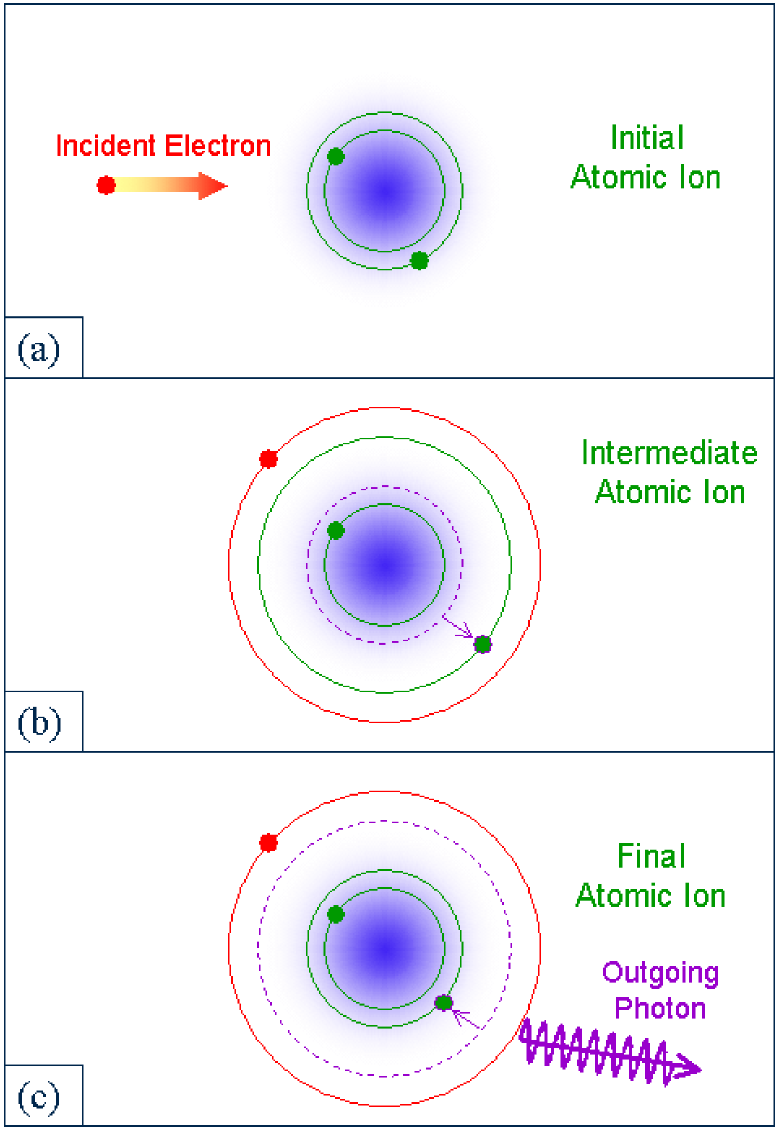
Dielectronic recombination

An ion collides with with an energetic electron: doubly excited state may form. This may *autoionize*, or a *radiative* downward transition can take place, leaving a bound atom with a single excited electron.

$He^0(1s^2) + e \rightarrow He^-(1s\ 2p^2)$

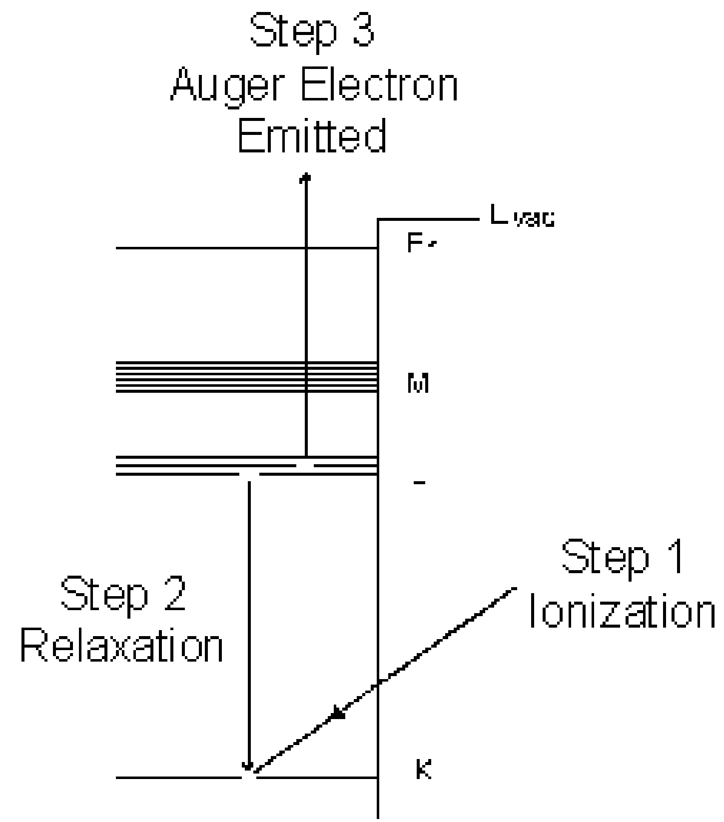
$He^-(1s\ 2p^2) \rightarrow He^0(1s^2\ 2p) + h\upsilon_1$ (satellite line)

$He^-(1s^2\ 2p) \rightarrow He^0(1s^2\ 2s) + h\upsilon_2$



Fluorescence/Auger effect

An electron is removed from an inner (e.g., K) shell and a highly excited ion is formed. This may decay with the emission of a **fluorescent** line (e.g. Kα line). *Or*, the excitation energy may be used to eject a number of electrons (Auger process).



The Auger Process