Atomic structure, radiation, collisions: what's in it for plasmas?..

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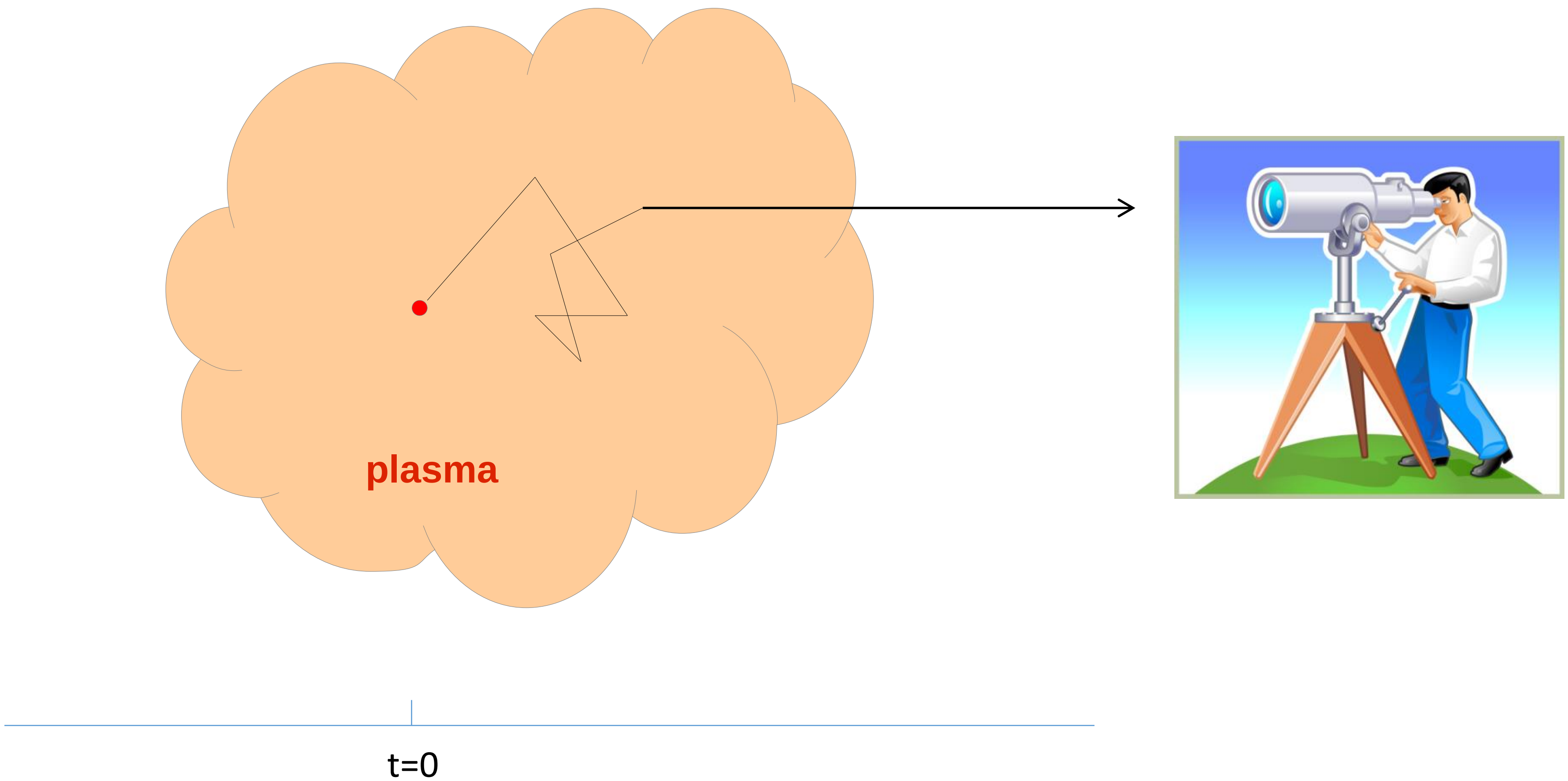
The story of a photon



Questions to ask

- Why was the photon created?
- Who created the photon?
- What was the probability for the photon to be created?
- How does the plasma environment affect photon creation?
- How did the photon propagate in the plasma?
- What has changed when the photon was recorded?
- ……………

Why is atomic structure important for plasmas?

Most of the relevant physics is inside this matrix element

$$\langle \Psi_f(a', b', c', \ldots) | \hat{\mathrm{O}} | \Psi_i(a, b, c, \ldots) \rangle$$

final state

interaction operator

initial state

- Wavelengths
- Energies
- Transition probabilities (radiative and non-radiative)
- Collisional cross sections
- …

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A Few Textbooks on APP

- H.R. Griem
  - Plasma Spectroscopy (1964)
  - Principles of Plasma Spectroscopy (1997)
- R.D. Cowan
  - Theory of Atomic Structure and Spectra (1981)
- V.P. Shevelko and L.A. Vainshtein
  - Atomic Physics for Hot Plasmas (1993)
- D. Salzmann
  - Atomic Physics in Hot Plasmas (1998)
- T. Fujimoto
  - Plasma Spectroscopy (2004)
- H.-J. Kunze
  - Introduction to Plasma Spectroscopy (2009)
- J. Bauche, C. Bauche-Arnoult, O. Peyrusse
  - Atomic Properties in Hot Plasmas (2015)
- Modern Methods in Collisional-Radiative Modeling of Plasmas (2016)
  - HKC, CJF, YR,…

Units

- Energy
  - 1 Ry = 13.61 eV = 109 737 cm^{-1} (ionization energy of H)
  - 1 eV = 8065.5447 cm^{-1}
- Length
  - $a_0 = 5.29 \cdot 10^{-9}$ cm = 0.529 Å (radius of H atom)
- Area (cross section)
  - $\pi a_0^2 = 8.8 \cdot 10^{-17}$ cm^2 (area of H atom)

- New SI (redefinition of base units): May 20 2019

http://physics.nist.gov/cuu/Units/

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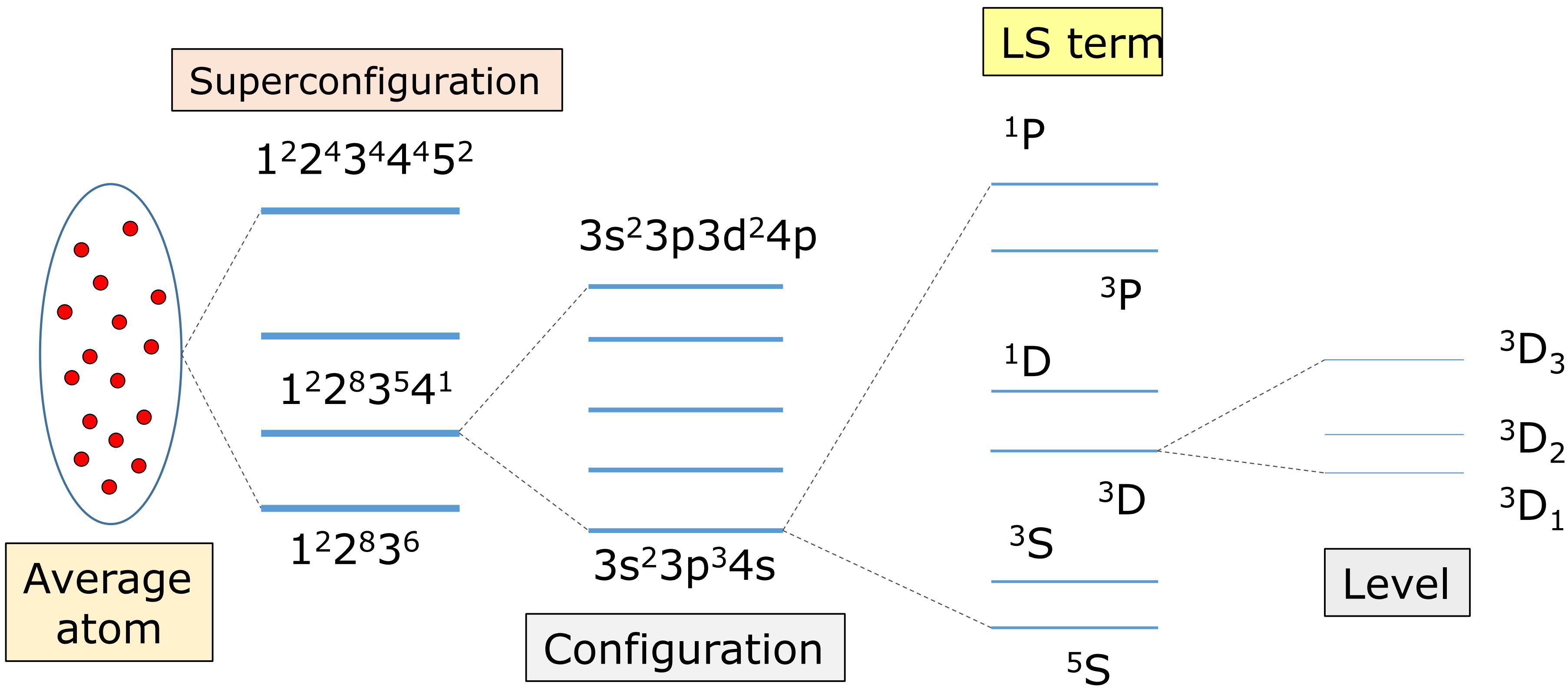
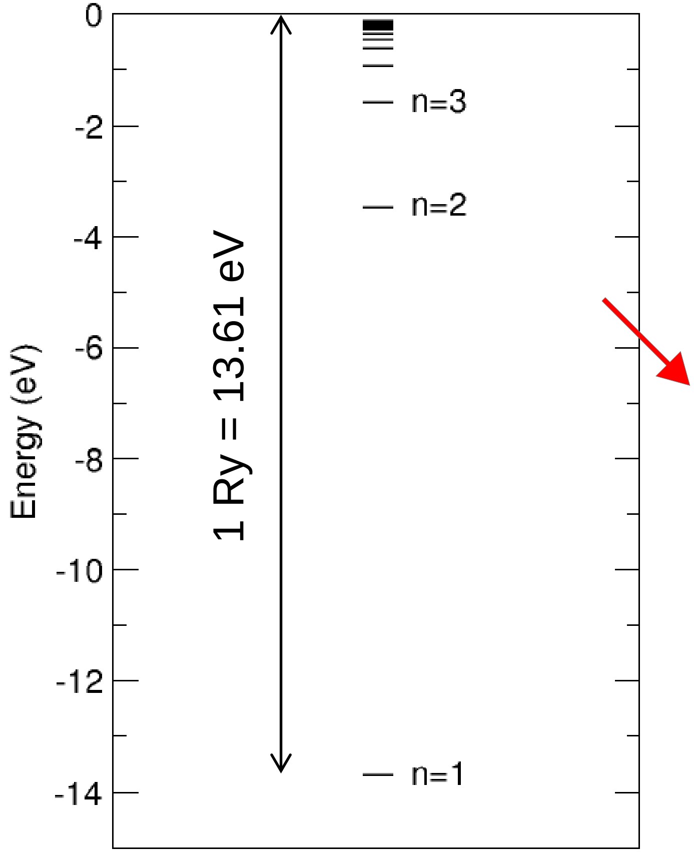
What kind of atomic data is of importance for spectroscopic diagnostics of plasmas?

- Wavelengths of spectral lines
- Line/level identifications
- Level energies
- Transition probabilities (radiative and non-radiative processes)
- Collisional cross sections and rate coefficients
- Spectral line shapes and widths

16-electron ion (S-like): how to describe its atomic structure?..



Hydrogen and H-like ions



Hydrogen atom

Each atomic state (wavefunction) is characterized by a set of quantum numbers

- Generally speaking, only two are exact for an isolated atom:
  - Total angular momentum *J*
  - Parity = $(-1)^{\sum_i l_i}$ (but: *weak interactions*!)
- They are the consequences of conservation laws
  - Noether theorem (1915)
- Everything else (total L, total S,…) is not exact!

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Complex atoms (non-relativistic)

We know all important interactions:

$$H = H_{kin} + H_{elec-nucl} + H_{elec-elec} + H_{s-o} + \ldots$$

$$= -\sum_i \frac{1}{2}\nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i>j} \frac{1}{r_{ij}} + \sum_i \frac{1}{2}\xi_i(r_i)(\boldsymbol{l_i} \cdot \boldsymbol{s_i}) + \ldots$$

$$H\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) = E\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$$

The Schrödinger equation for multi-electron atoms cannot be solved exactly…

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Standard procedure

- Use central-field approximation to approximate the effects of the Coulomb repulsion among the electrons:
  - $H \approx H_0 = \sum_i^N \left(-\frac{1}{2}\nabla_i^2 \ -\frac{Z}{r_i} + V(r_i) \right)$
- Properly choose the potential V(r)
- Find configuration state functions $\Phi\left(\gamma_j LS\right)$ (accounting also for antisymmetry): n,l
- Assume that the atomic state function is a linear combination of CSFs: $\Psi(\gamma LS) = \sum_j^M c_j \Phi\left(\gamma_j LS\right)$
- Solve Schrodinger equation for mixing coefficients:
  - $\left(\widehat{H} - E\hat{I}\right)\hat{c} = 0, H_{ij} = \left\langle \Phi(\gamma_i LS) \middle| H \middle| \Phi\left(\gamma_j LS\right) \right\rangle$
- Include other effects (perturbation theory)…and live happily!

Relativistic atomic structure: heavy and not so heavy ions

$$H_{DC} = \sum_i (c\,\boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i + V_{nuc}(r_i) + \beta_i c^2) + \sum_{i>j} \frac{1}{r_{ij}}$$

Dirac-Coulomb Hamiltonian

$\boldsymbol{p} \equiv -i\boldsymbol{\nabla}$ electron momentum operator

$\boldsymbol{\alpha}, \beta$ 4x4 Dirac matrices

$V_{nuc}(r)$ extended nuclear charge distribution

Transverse photons (magnetic interactions and retardation effects):

$$H_{TP} = -\sum_{j>i} \left[\frac{\alpha_i \cdot \alpha_j \cos(\omega_{ij} r_{ij}/c)}{r_{ij}} + (\boldsymbol{\alpha}_i \cdot \boldsymbol{\nabla}_i)(\boldsymbol{\alpha}_j \cdot \boldsymbol{\nabla}_j) \frac{\cos(\omega_{ij} r_{ij}/c) - 1}{\omega_{ij}^2 r_{ij}/c^2} \right]$$

QED effects: self energy (SE), vacuum polarization (VP)

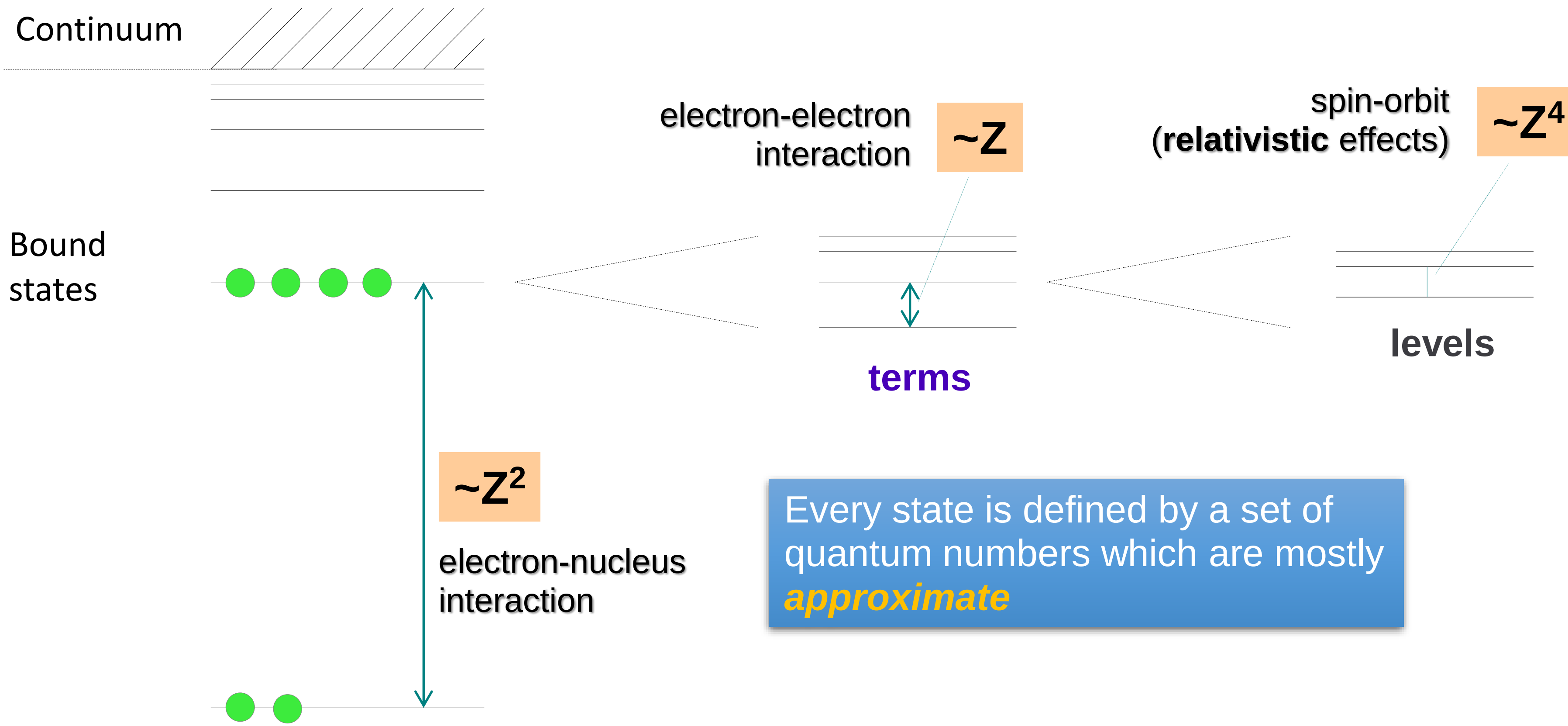
$$\boxed{H_{DCB+QED} = H_{DC} + H_{TP} + H_{SE} + H_{VP}}$$

Relativistic notations

$$l_{\pm} \rightarrow j = l \pm 1/2$$

	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$
	s	p_-	p_+	d_-	d_+	f_-	f_+
l	0	1	1	2	2	3	3
j	½	½	3/2	3/2	5/2	5/2	7/2

Energy structure of an ion



Every state is defined by a set of quantum numbers which are mostly ***approximate***

Electrons are grouped into shells *nl*
(K *n*=1, L *n*=2, M *n*=3,...)
producing **configurations (or even superconfigurations)**

Z-scaling of electron energies

$$H = \sum_i \left(\frac{p_i^2}{2} - \frac{Z}{r_i} \right) + \sum_{i>j} \frac{1}{r_{ij}}$$

Kinetic+nuclear

electrons

New variables $\rho_i = Z r_i, \tilde{p}_i = p_i / Z$ lead to:

$$H = Z^2 \sum_i \left(\frac{\tilde{p}_i^2}{2} - \frac{1}{\rho_i} \right) + Z \sum_{i>j} \frac{1}{\rho_{ij}} = Z^2 (H_0 + Z^{-1} V)$$

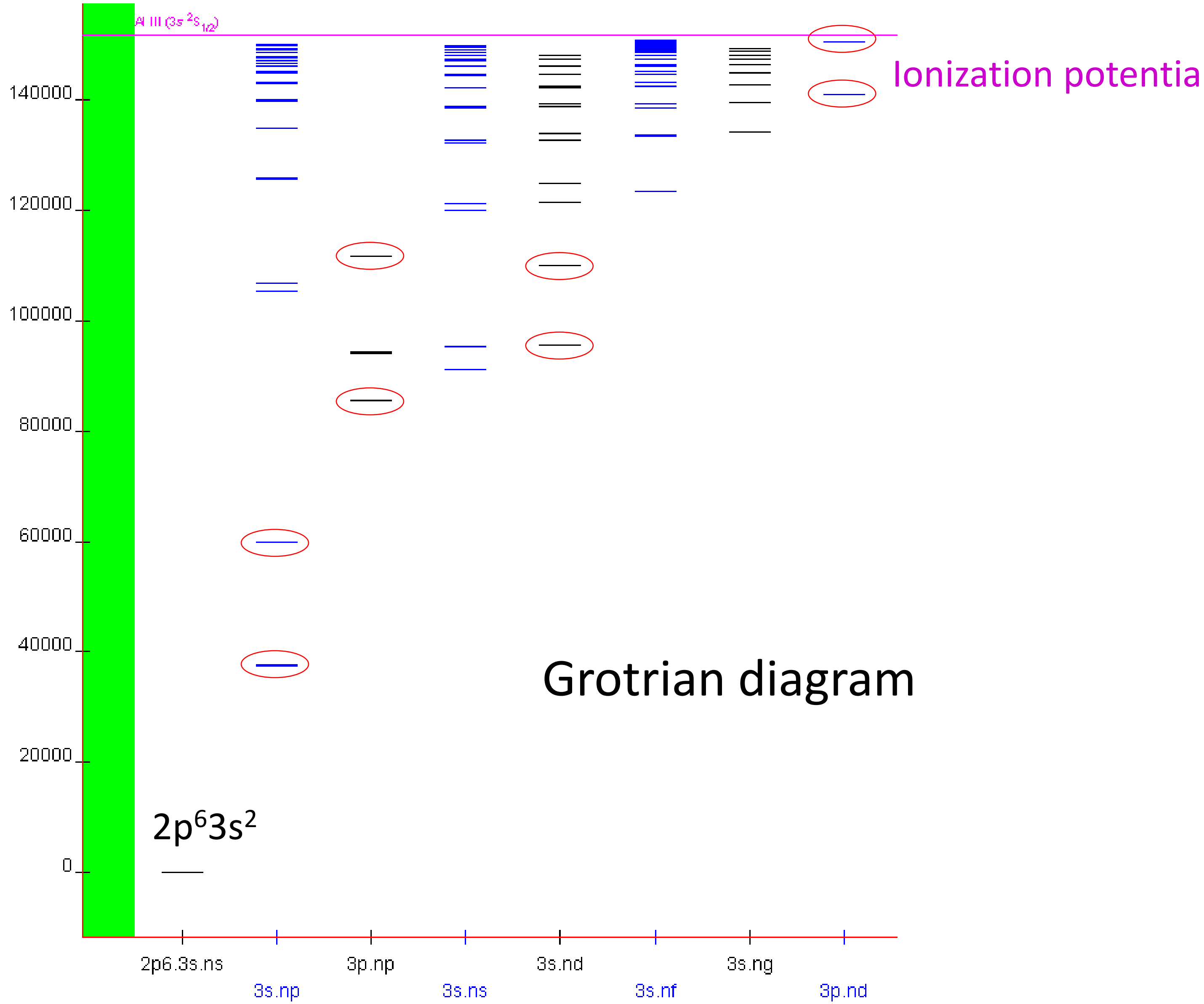
$$H\psi = E\psi \Rightarrow (H_0 + Z^{-1} V)\psi = (Z^{-2} E)\psi$$

$$E = Z^2 (E_0 + Z^{-1} E_1 + Z^{-2} E_2 + \cdots)$$

$$E_0 = -\frac{1}{n^2}$$

Therefore, for high Z the energy structure looks more and more H-like!

Mg-like Al II: 3*l*3*l*'



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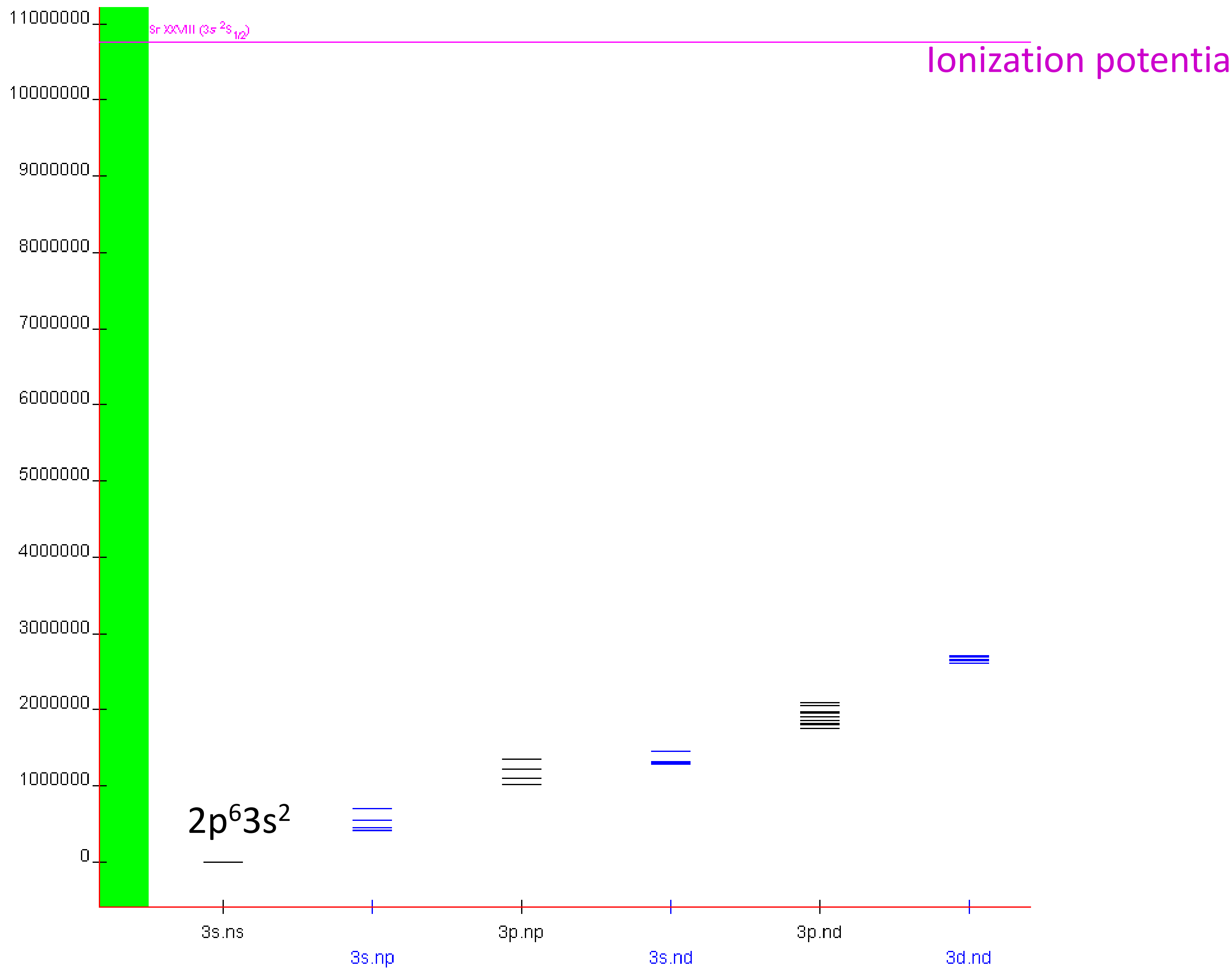
Mg-like Sr XXVII: 3*l*3*l*'



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Importance of Z_c

Spectroscopic charge: **Z_c= ion charge + 1** (H I, Ar XV…)

This is the charge that is seen by the outermost (valence) electron

Isoelectronic sequences: ions with the same number of electrons

- Li I, Be II, B III,…

It is often useful to consider variation of atomic parameters along isoelectronic sequences

Spin-orbit interaction

Hydrogenic ion:

$$\zeta_{nl} = \frac{Ry\,\alpha^2\,Z^4}{n^3\,l\,(l+1/2)\,(l+1)}$$

Semi-theoretical Lande formula:

$$\zeta_{nl} = \frac{Ry\,\alpha^2\,Z_c^2\tilde{Z}^2}{n^{*3}\,l\,(l+1/2)\,(l+1)}$$

n*: effective n

$$I = \frac{Ry\,Z_c^2}{n^{*2}}$$

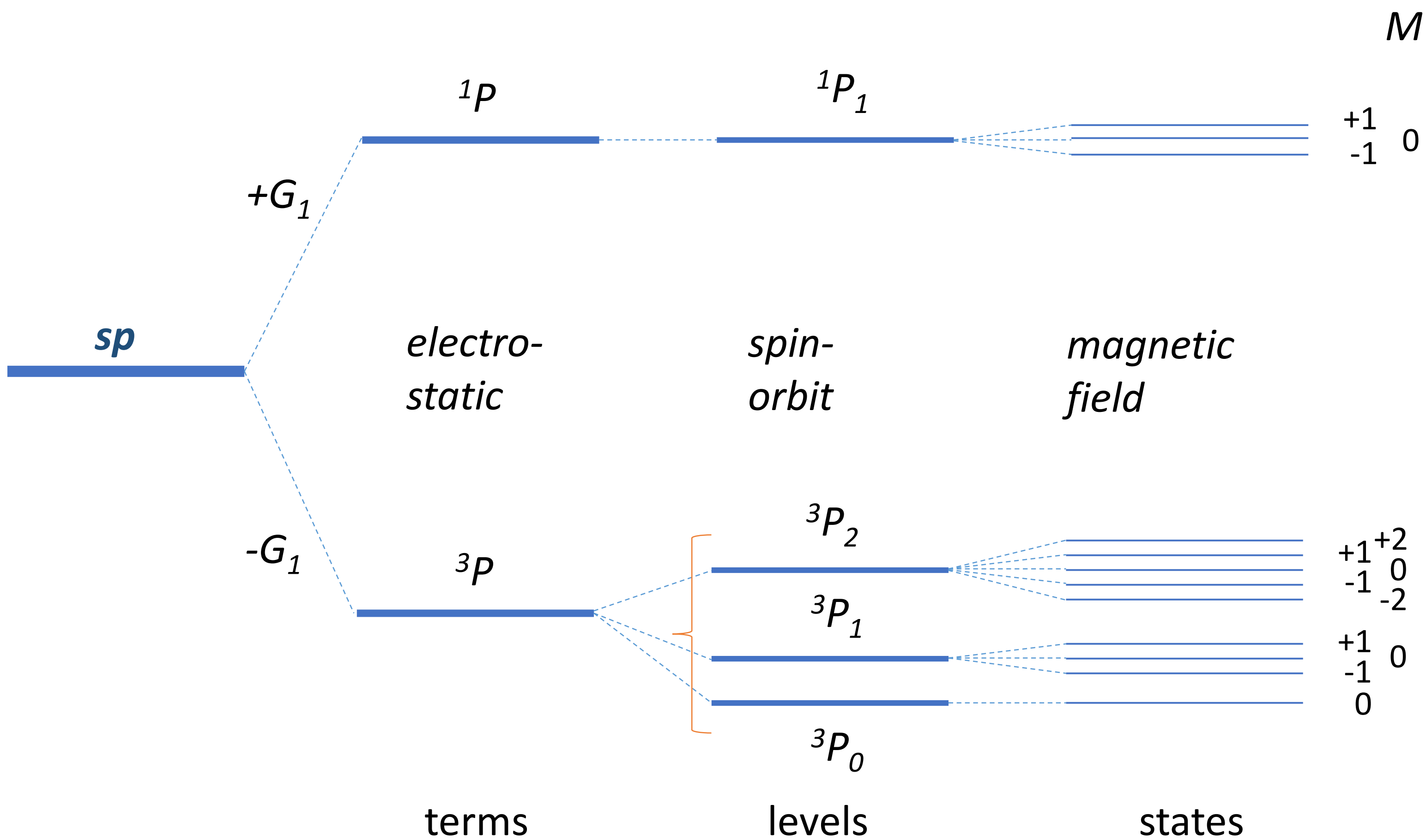
$\tilde{Z}$: effective nuclear charge (for penetrating orbits) = ***Z-n*** for *np* orbitals

$$H = -\sum_i \frac{1}{2}\nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i>j} \frac{1}{r_{ij}} + \sum_i \frac{1}{2}\xi_i(r_i)(\boldsymbol{l_i}\cdot\boldsymbol{s_i}) + \ \ldots$$

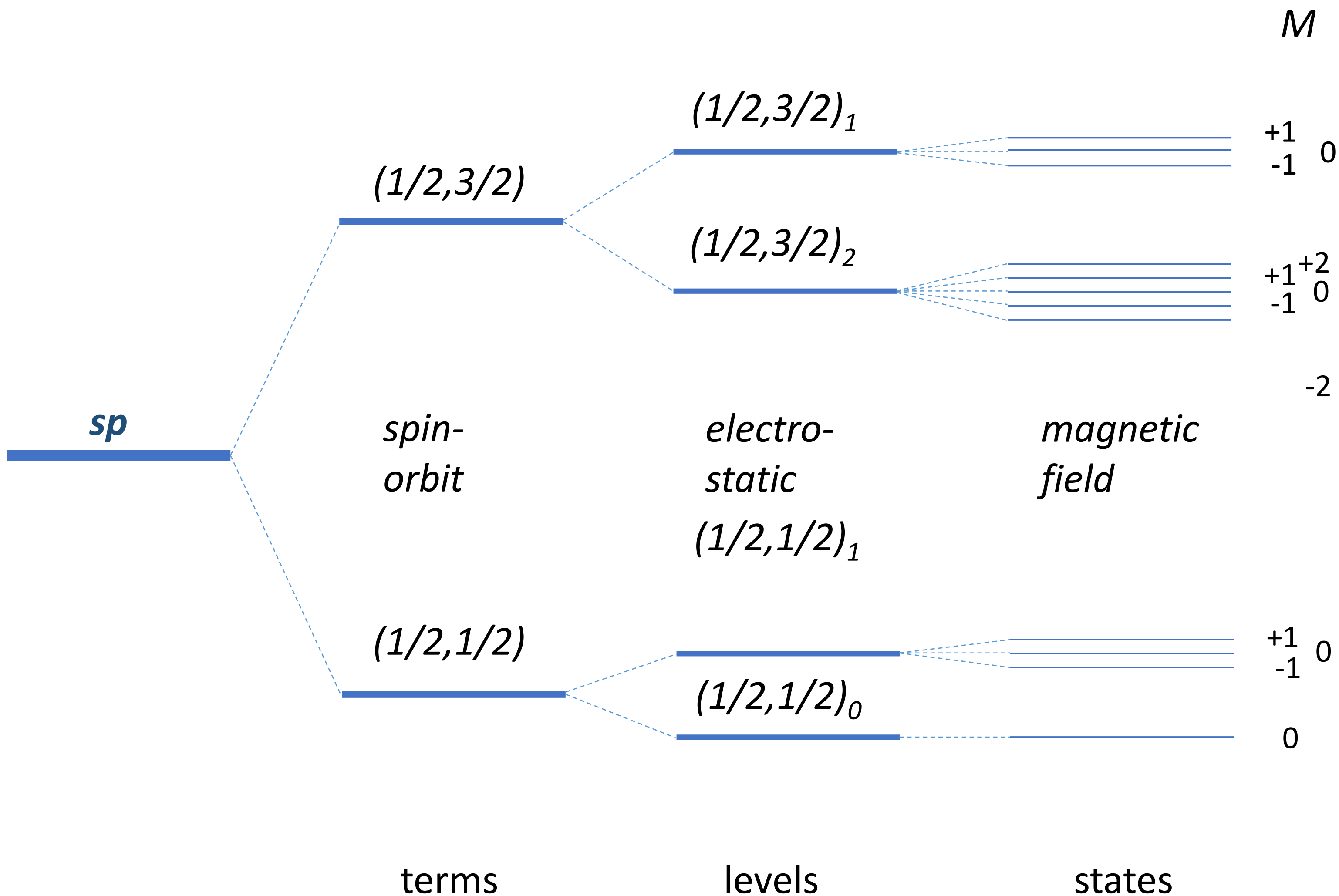
Types of coupling

- LS coupling: electron-electron » spin-orbit
  - light elements $\vec{L} = \vec{l}_1 + \vec{l}_2 + \ldots, \quad \vec{S} = \vec{s}_1 + \vec{s}_2 + \ldots, \quad \vec{J} = \vec{L} + \vec{S}$
- jj coupling: spin-orbit » electron-electron
  - heavy elements $\vec{j}_1 = \vec{l}_1 + \vec{s}_1,\ \vec{j}_2 = \vec{l}_2 + \vec{s}_2,\ \ldots \quad \vec{J} = \vec{j}_1 + \vec{j}_2 + \ldots$
  - 2s2p: $(2s_{1/2},2p_{1/2})$ or (2s,2p-)
  - $3d^5$: $((3d_-^{\,3})_{5/2},(3d_+^{\,2})_2)_{3/2}$
- *Intermediate coupling*: neither is overwhelmingly strong
- Other types of couplings exist

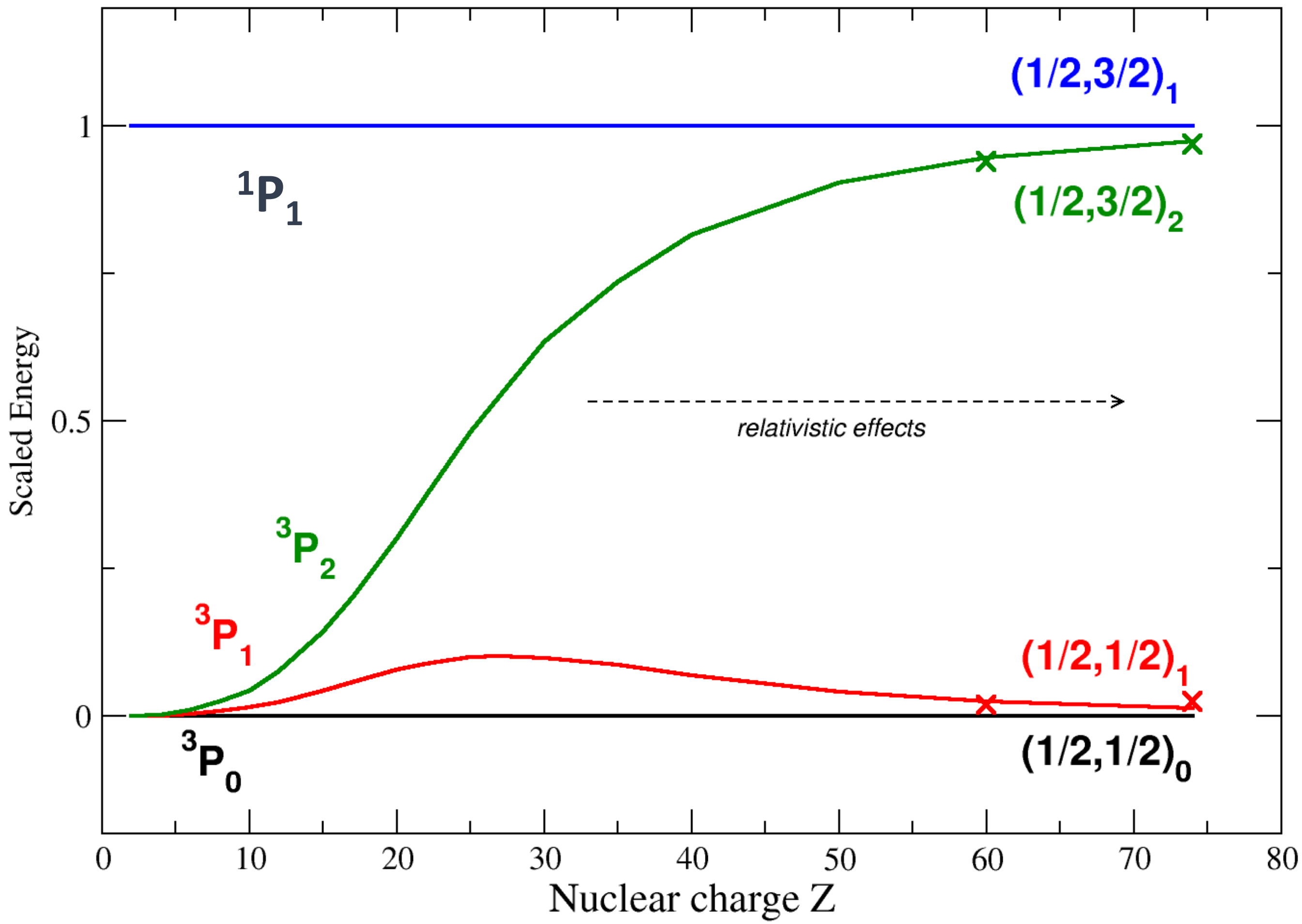
Configuration *sp*: LS coupling (LSJ)



Configuration sp: jj coupling



From LS to jj: 1s2p in He-like ions



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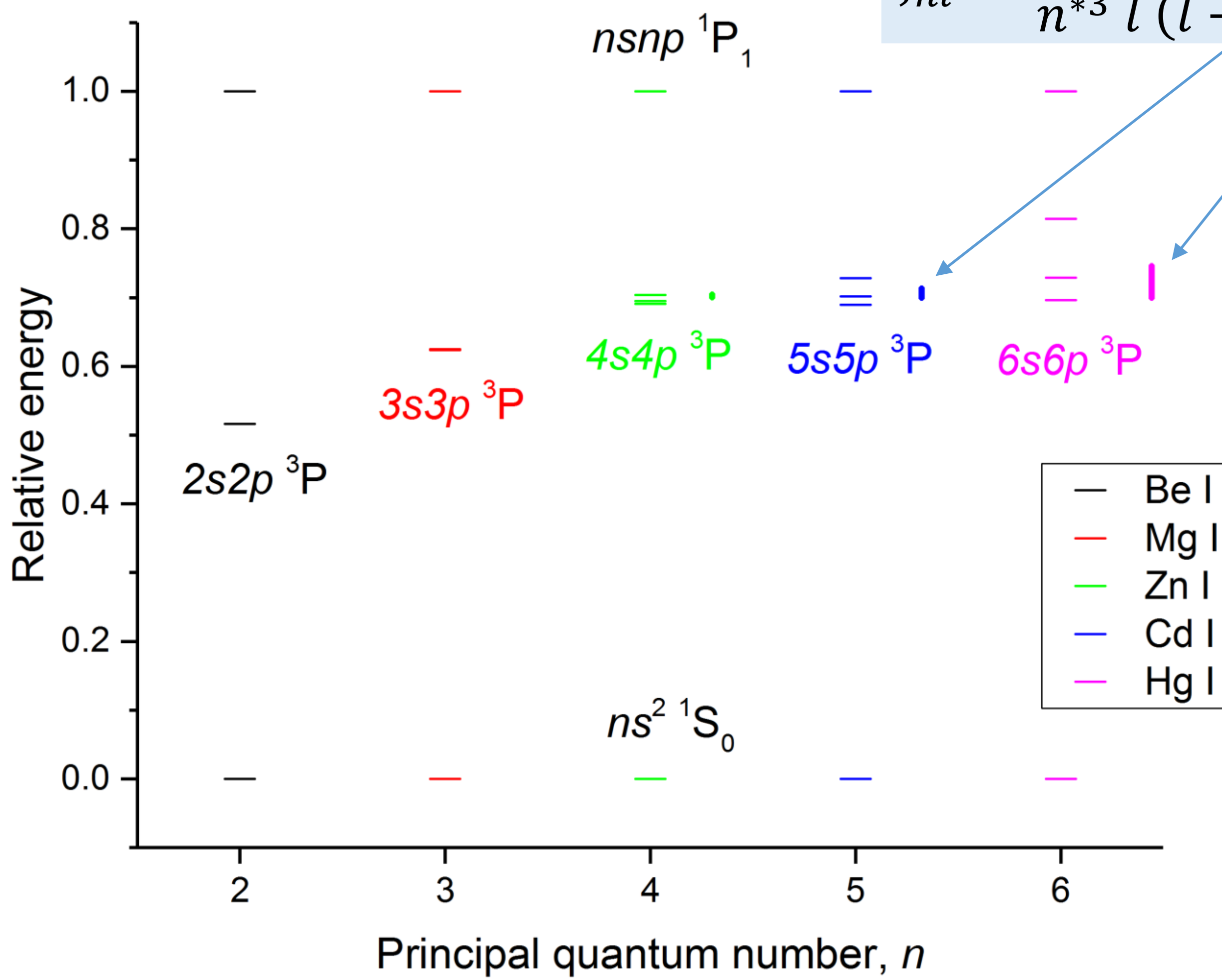
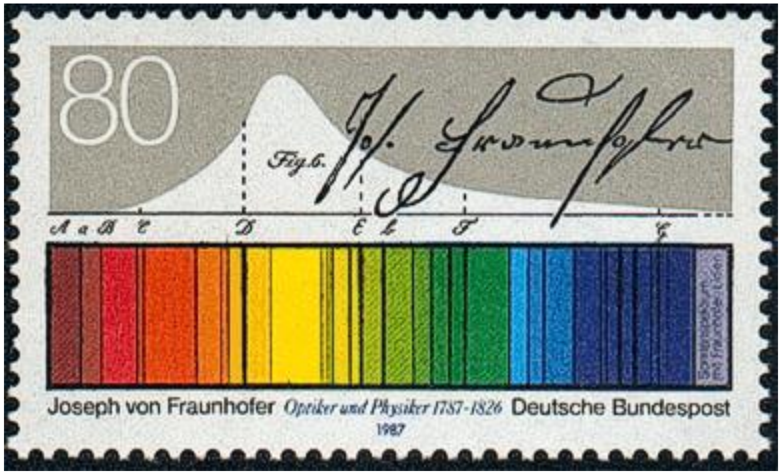
Spin-orbit interaction does depend on nuclear charge!

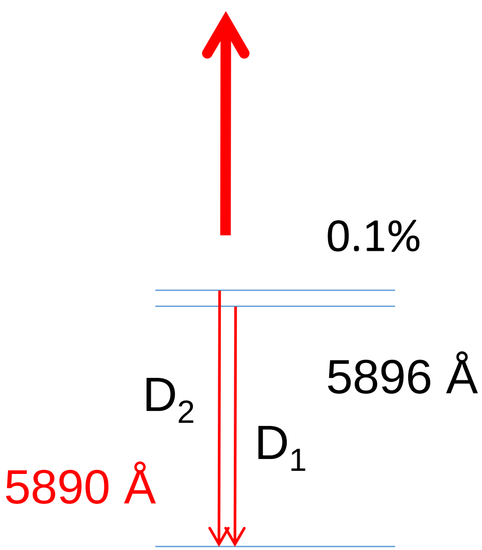
$$\zeta_{nl} = \frac{Ry\,\alpha^2\,Z_c^2\tilde{Z}^2}{n^{*3}\,l\,(l+1/2)\,(l+1)}$$

Lande formula



Na-like doublet: from neutral to HCI





Fraunhofer absorption lines in the solar spectrum

D1: $3s_{1/2} - 3p_{1/2}$

D2: $3s_{1/2} - 3p_{3/2}$

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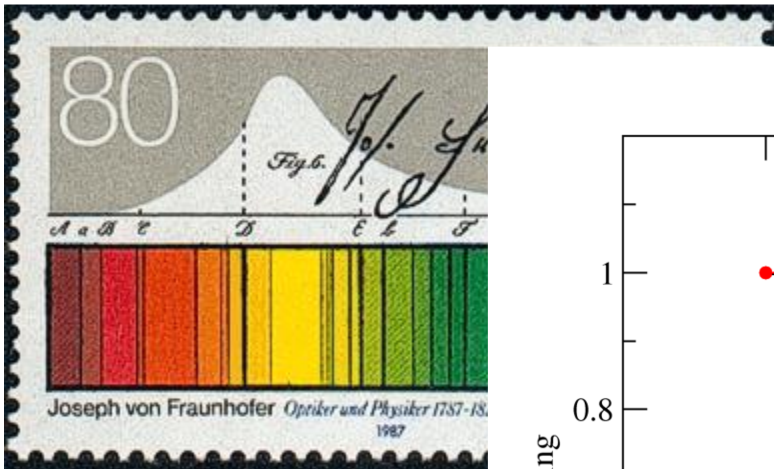
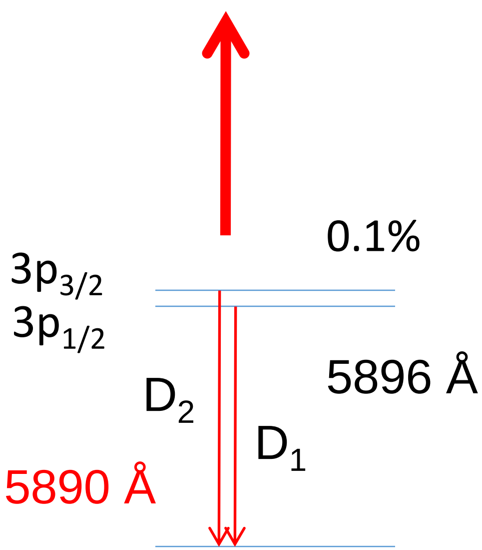
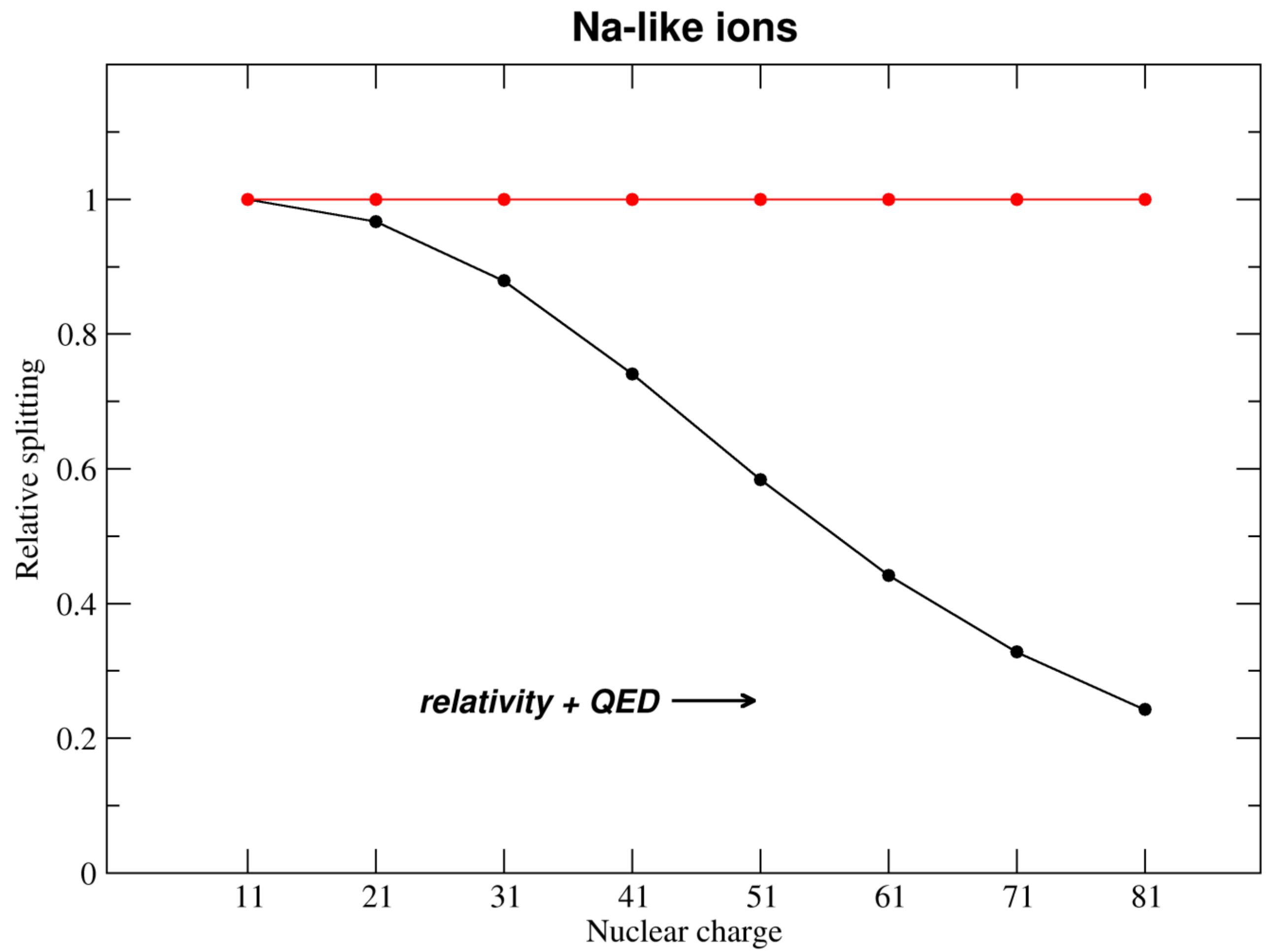
Na-like doublet: from neutral to HCI







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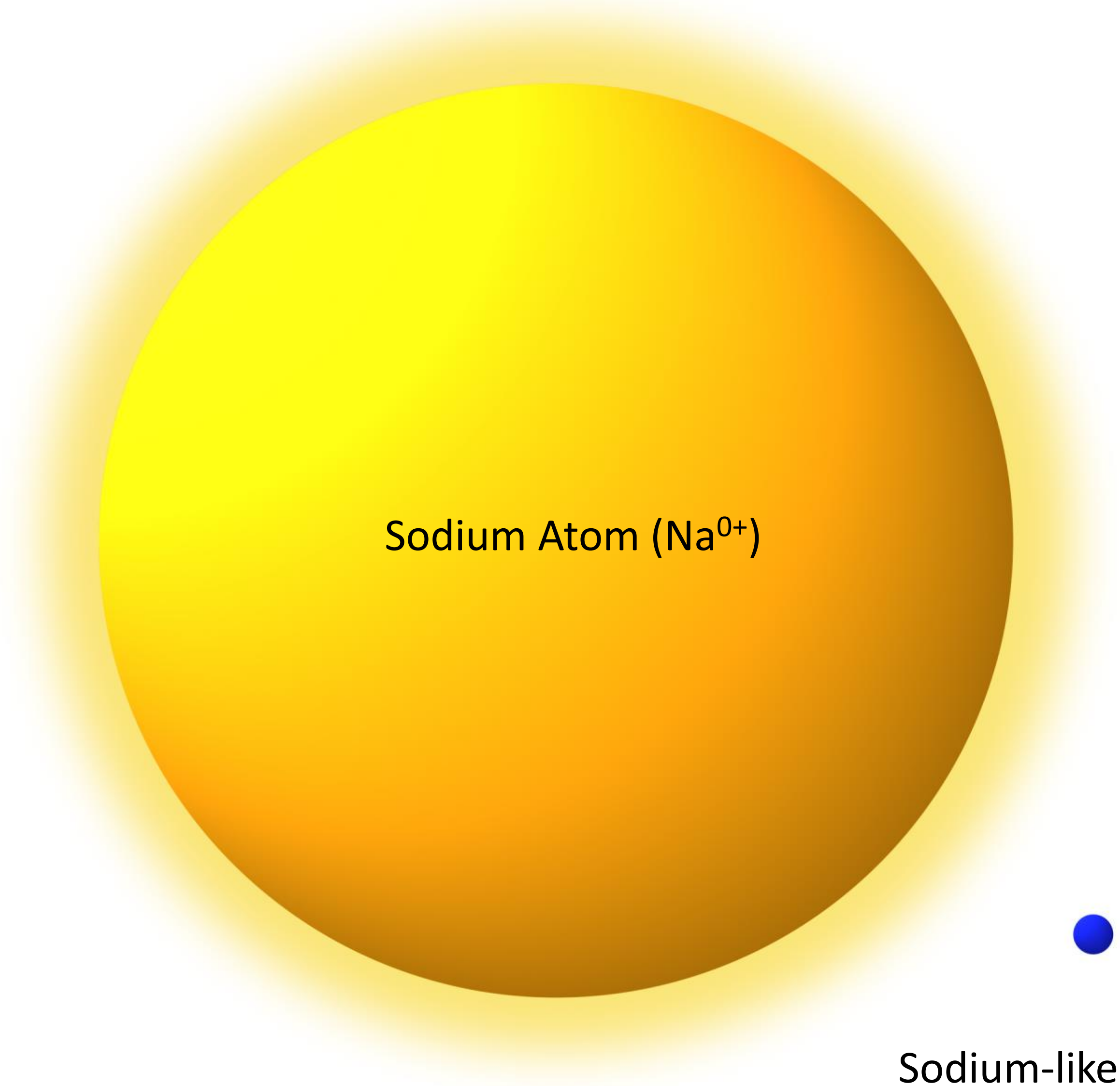
Little Ions With a Big Charge



11 electrons

Sodium-like Tungsten (W^{63+})

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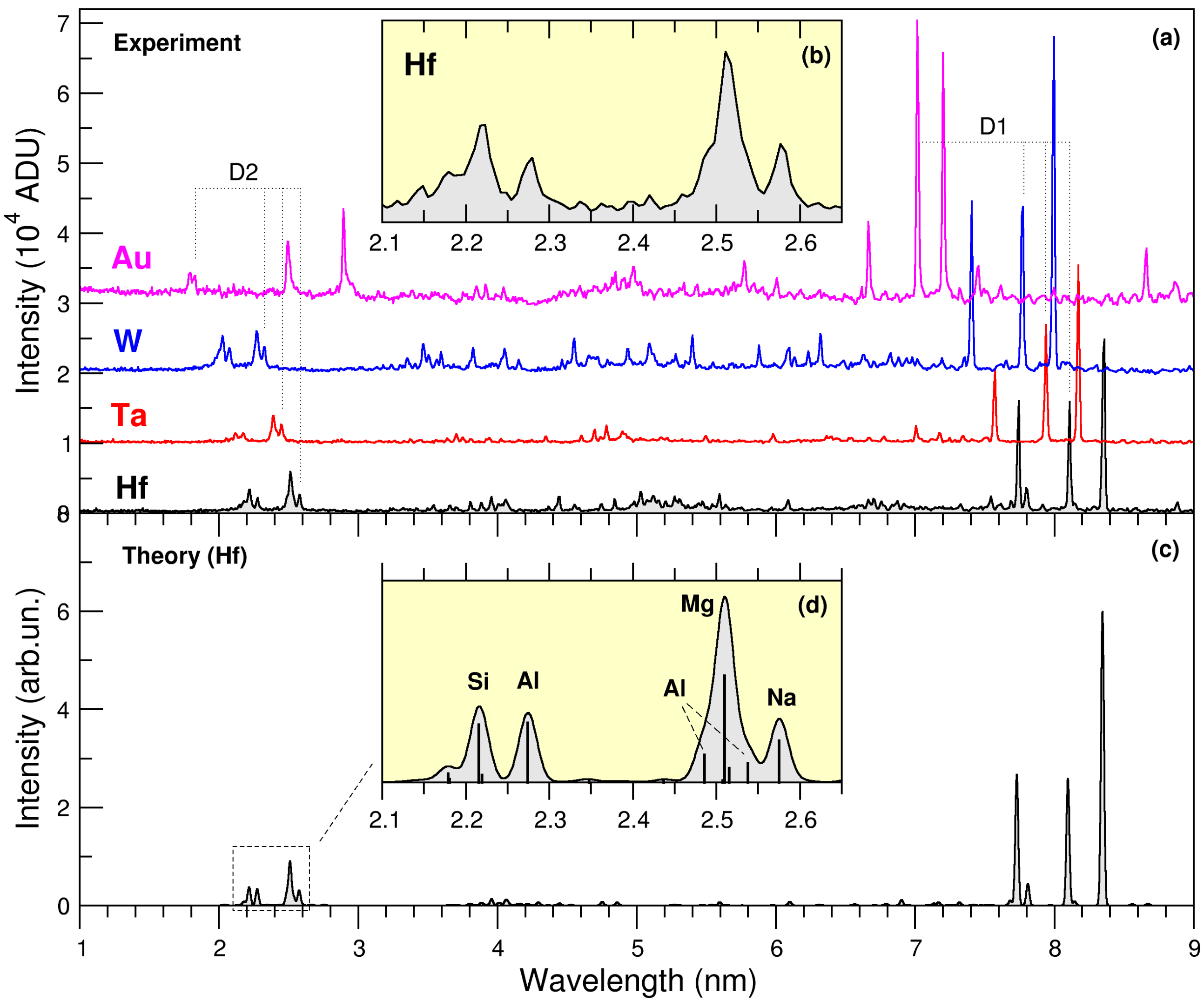
D-doublet in Na-like W, Hf, Ta, and Au



J.D. Gillaspy et al, *Phys. Rev. A* **80**, 010501 (2009)

State mixing in intermediate coupling

$$|\Psi(a,b,c,\ldots)\rangle = \alpha\cdot\Psi_1(a,b,c,\ldots) + \beta\cdot\Psi_2(a,b,c,\ldots) + \gamma\cdot\Psi_3(a,b,c,\ldots) + \ldots$$

expansion coefficients

He-like Na^{9+}: $1s2p\ {}^3P_1 = 0.999\ {}^3P + 0.032\ {}^1P$
He-like Fe^{24+}: $1s2p\ {}^3P_1 = 0.960\ {}^3P + 0.281\ {}^1P$
He-like Mo^{40+}: $1s2p\ {}^3P_1 = 0.874\ {}^3P + 0.486\ {}^1P$

Very, VERY important for radiative transitions!!!

Hund's rules (equivalent electrons, LS)

- **Largest *S*** has the lowest energy
- **Largest *L*** with the same *S* has the lowest energy
- For atoms with less-than half-filled shells, **lowest *J*** has lowest energy

C I

Configuration	Term	J	Level (cm^{-1})	Reference
$2s^22p^2$	^3P	0	0.00	L7288
		1	16.40	
		2	43.40	
$2s^22p^2$	^1D	2	10 192.63	
$2s^22p^2$	^1S	0	21 648.01	
$2s2p^3$	$^5S°$	2	33 735.20	
$2s^22p3s$	$^3P°$	0	60 333.43	
		1	60 352.63	
		2	60 393.14	
$2s^22p3s$	$^1P°$	1	61 981.82	
$2s2p^3$	$^3D°$	3	64 086.92	
		1	64 089.85	
		2	64 090.95	

O I

Configuration	Term	J	Level (cm^{-1})
$2s^22p^4$	^3P	2	0.000
		1	158.265
		0	226.977
$2s^22p^4$	^1D	2	15 867.862
$2s^22p^4$	^1S	0	33 792.583

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Superconfigurations

Motivation: for very complex atoms (ions) not only the **number of levels** is overwhelmingly large, but also the **number of configurations**

Example:

$1s^2 2s^2 2p^5 3s$
$1s^2 2s^2 2p^5 3p$
$1s^2 2s^2 2p^5 3d$
$1s^2 2s 2p^6 3s$
$1s^2 2s 2p^6 3p$
$1s^2 2s 2p^6 3d$

→

different *n*'s

$(1s)^2(2s2p)^7(3s3p3d)^1 \equiv (1)^2(2)^7(3)^1$

BUT: $(1s)^2(2s2p)^7(3s3p3d4s4p4d4f)^1$

Instead of producing millions or billions of lines, SCs are used to calculate Super Transition Arrays → Statistical methods

See J. Bauche et al's book (2015)

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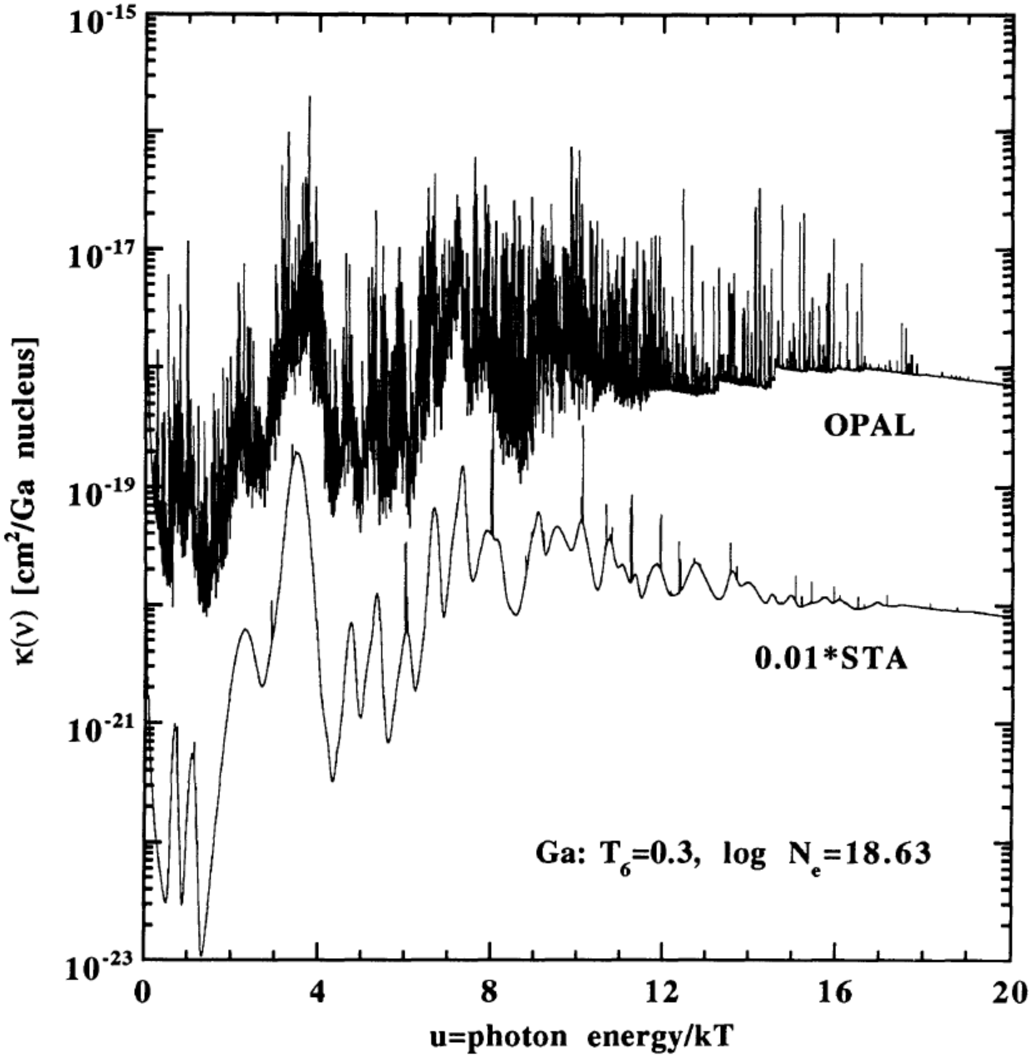
Superconfigurations vs. detailed level accounting



Ga: photoabsorption cross section

Iglesias et al (1995)

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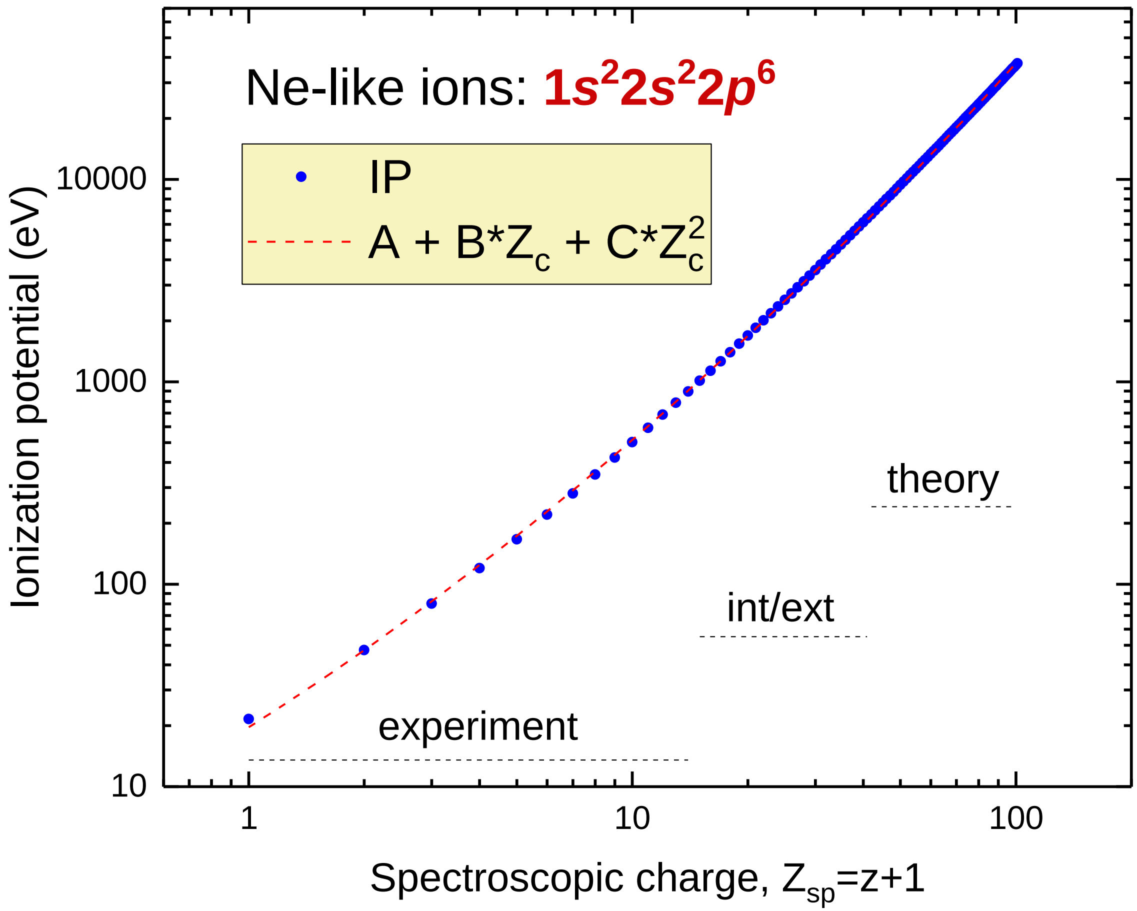
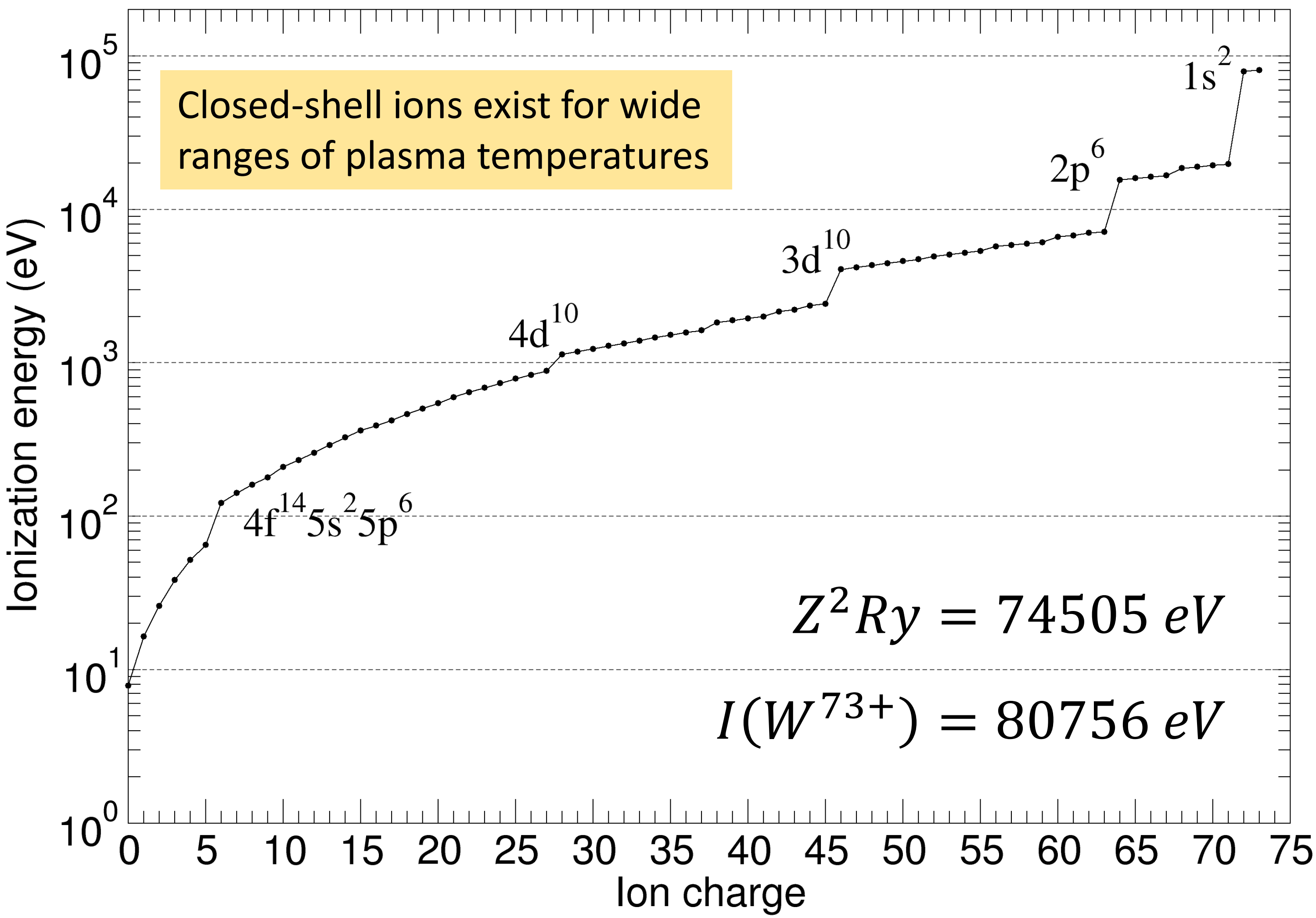
Ionization potentials

- IPs are directly connected with ionization distributions in plasmas
- Most often are determined from Rydberg series



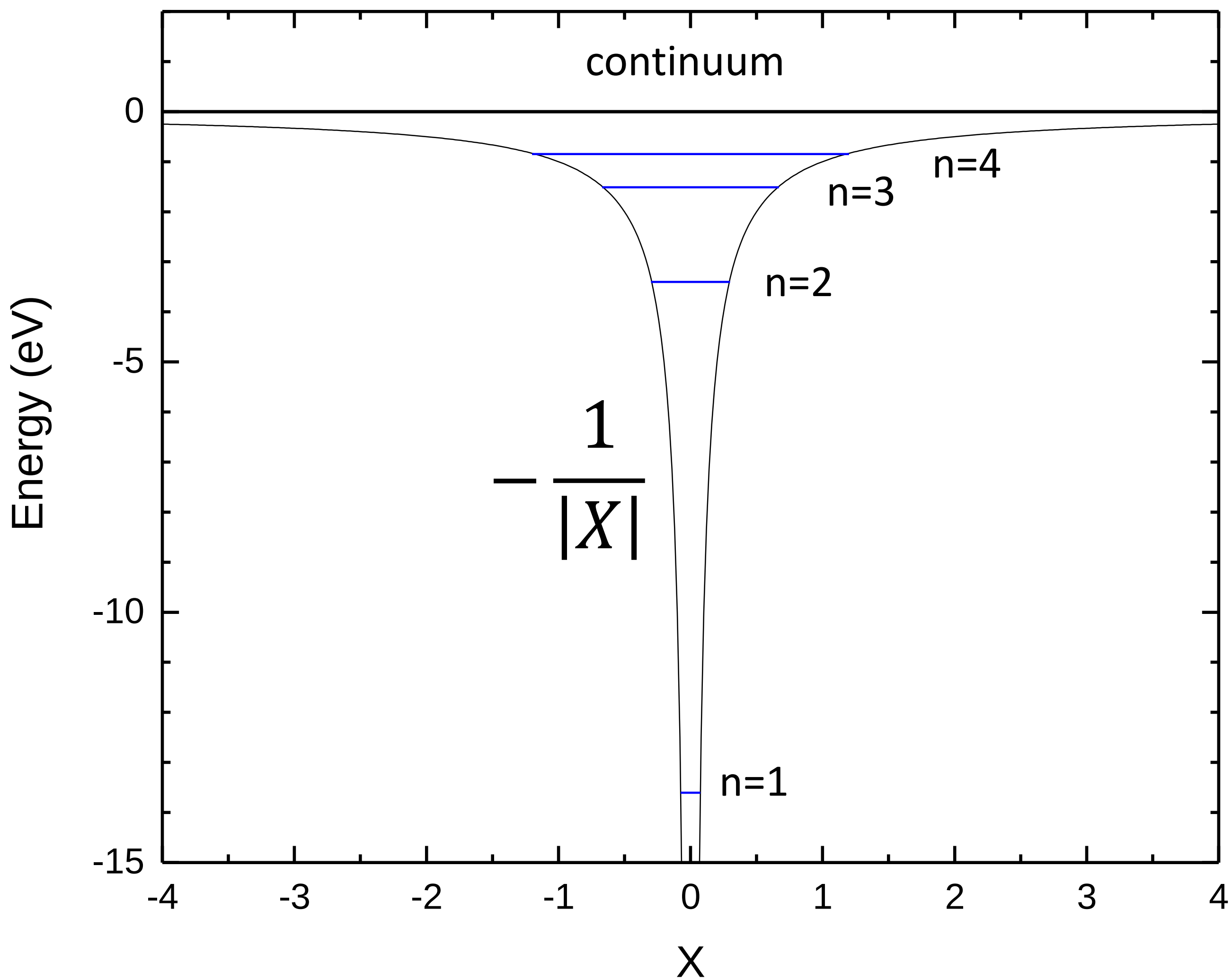
Ionization potentials of W ions



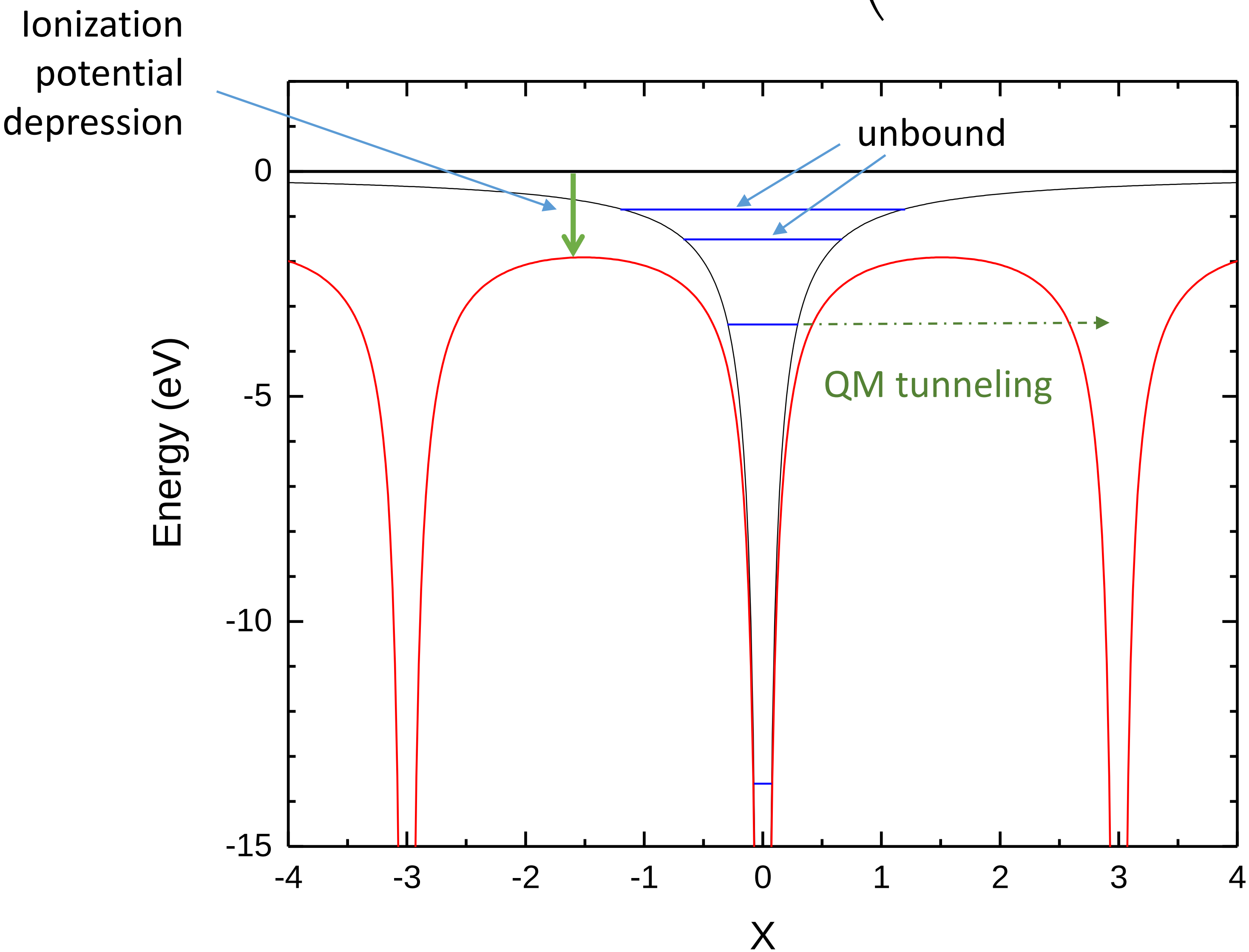
Ionization potential: constant?..

- IP is a function of plasma conditions
- High-lying states are no longer bound due to interactions with neighboring atoms, ions, and electrons
- Orbit radius in H I: where is n=300,000?

Isolated atom



Stewart-Pyatt: $\Delta I \approx 2.2 \cdot 10^{-7} \frac{z}{r_i} \left(\left(1 + \left(\frac{r_d}{r_i} \right)^3 \right)^{2/3} - \left(\frac{r_d}{r_i} \right)^2 \right)$ (eV)



Atomic Structure Methods and Codes

- Coulomb approximation (Bates-Damgaard)
- Thomas-Fermi (**SUPERSTRUCTURE**, **AUTOSTRUCTURE**)
- Single-configuration Hartree-Fock (self-consistent field)
  - **Cowan's code (LANL)**
- Model potential (including relativistic)
  - **HULLAC**, **FAC**
- Multiconfiguration non-relativistic HF (**http://nlte.nist.gov/MCHF**)
- Multiconfiguration Dirac-(Hartree)-Fock (**MCDF or MCDHF**)
  - **GRASP2K** (**http://nlte.nist.gov/MCHF**)
  - **Desclaux's code**
- Various perturbation theory methods (MBPT, RMBPT)
- B-splines

http://plasma-gate.weizmann.ac.il/directories/free-software/

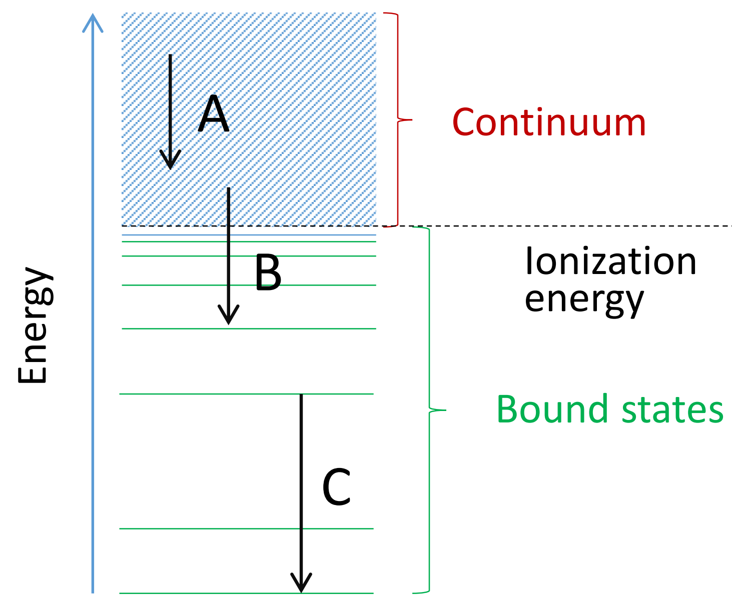
Atomic Structure & Spectra Databases

- (Reasonably) Extensive list
  - http://plasma-gate.weizmann.ac.il/directories/databases/
- Evaluated and recommended data
  - NIST Atomic Spectra Database http://physics.nist.gov/asd
    - Level energies, ionization potentials, spectral lines, transition probabilities
- Other data collections
  - VALD (Sweden)
  - SPECTR-W3 (Russia)
  - CAMDB (China)
  - CHIANTI (USA/UK/…)
  - Kurucz databases (USA)
  - GENIE (IAEA)
  - …

Now to radiative processes…

Three major sources of photons

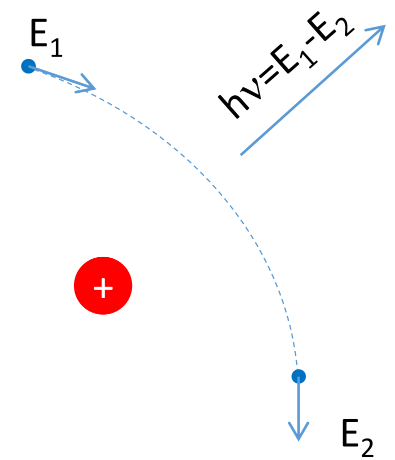
- Free-free transitions (bremsstrahlung)
  - $A^{z+} + e \rightarrow A^{z+} + e + h\nu$
- Free-bound transitions (radiative recombination)
  - $A^{z+} + e \rightarrow A^{(z-1)+} + h\nu$
- Bound-bound transitions
  - $A_j^{z+} \rightarrow A_i^{z+} + h\nu$



.Bremsstrahlung (free-free)

- Calculation is straightforward for Maxwellian electrons off bare nuclei of Z:

$$\varepsilon_{\lambda}^{ff}(\lambda)=\frac{32\sqrt{\pi}\,c(\alpha a_0)^3 Ry}{3\sqrt{3}} N_Z N_e Z^2\left(\frac{Ry}{T_e}\right)^{1/2}\frac{1}{\lambda^2}e^{-\frac{hc}{\lambda T_e}}G^{ff}(T_e,\lambda)$$



- Total power loss

$$\varepsilon^{ff}=4.51\times10^{-45}Z^2\left(\frac{T_e}{Ry}\right)^{1/2}N_z N_e\left[\frac{W}{sr\cdot cm^3}\right]$$

- Multicomponent plasma:

$$\varepsilon_{\lambda}^{ff}(\lambda)=z_{eff}\,\varepsilon_{\lambda}^{ff}(\lambda)[H];\quad z_{eff}=\frac{1}{N_e}\sum_{i,z}z_i^2N_z^i=\frac{\sum_{i,z}z_i^2N_z^i}{\sum_{i,z}z_iN_z^i}$$

Dominant at longer wavelengths

Maximum emission at $\lambda_{\max}=\dfrac{620\ nm}{T_e[eV]}$

Bremsstrahlung (cont'd)

$$\varepsilon(\lambda)d\lambda = \varepsilon(\omega)d\omega \qquad \omega = \frac{2\pi c}{\lambda}$$

$$\varepsilon_{\omega}^{ff}(\omega) = \frac{64c(\alpha a_0)^3 Ry}{3c\sqrt{3\pi}} N_Z N_e Z^2 \left(\frac{Ry}{T_e}\right)^{1/2} e^{-\frac{\hbar\omega}{T_e}} G^{ff}(T_e, \omega)$$

$$\varepsilon_{\omega}^{ff}(E) \approx Ae^{-\frac{E}{T_e}}$$

Spectral Line Intensity

Upper state density (cm^{-3})

Einstein coefficient or transition probability (s^{-1})

strongly depends on plasma conditions

$$I_{ij} = N_j \cdot A_{ij} \cdot E_{ij}$$

(*almost*) purely atomic parameters

Energy emitted due to a specific transition from a unit volume per unit time

Photon energy (erg)

BB Radiative transitions

- Classical rate of loss of energy: **dE/dt ~ |a|^2**, and decay rate ~ **|r|^2** for harmonic oscillator

- Quantum treatment: $\left\langle \Psi_f \middle| \vec{\nabla} \cdot \vec{a}\, e^{i\vec{k}\vec{r}} \middle| \Psi_i \right\rangle$
  - $e^{ikr} = 1 + ikr + \ldots \approx 1$ (**electric dipole or E1 = allowed**)
  - Velocity form: $\left\langle \Psi_f \middle| \nabla \middle| \Psi_i \right\rangle$
  - Length form: $\left\langle \Psi_f \middle| r \middle| \Psi_i \right\rangle$

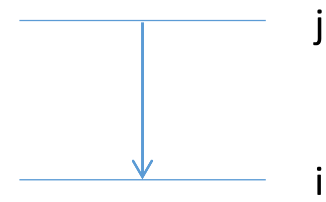
must be equal for an exact wavefunction (*good test!*)

QUESTION:

Why would a STATIONARY excited state of the atomic Hamiltonian not live forever but rather experience a radiative decay to a lower state?..

S, f, and A (1)

- Line strength
  - Symmetric w/r to initial-final



$$S_{ji} = \left| \langle i \| r \| j \rangle \right|^2 = S_{ij}$$

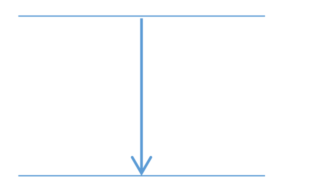
- Oscillator strength (**absorption** or emission)
  - $g_j f_{ij} = g_i f_{ji}$ ($g_j = 2J_j+1$); dimensionless
  - Typical values for strong lines: ~ **0.1-1**

$$f_{ij} = \frac{1}{3g_i} \frac{\Delta E}{Ry} S$$

S, f, and A (2)

- Transition probability (or Einstein coefficient)

$$A_{ji} = 4.3 \cdot 10^{7} \frac{g_i}{g_j} \left(\Delta E[eV]\right)^2 f_{ij} [s^{-1}]$$



- Typical values for neutrals: ~10^8-10^9 s^{-1}

$$A_{ji} = \frac{2h\nu^3}{c^2} B_{ji},\ g_j B_{ji} = g_i B_{ij}$$

Lifetime: $\tau_j = 1/\Sigma_i A_{ji}$

H I:	4.7e8 (1-2)
	5.6e7 (1-3)
He I:	1.8e9 ($1s^2$-1s2p)
	5.7e8 ($1s^2$-1s3p)

Selection rules and Z-scaling

Fundamental law:
parity and J do not change

Before:	P_j	$\vec{J}_j$
After:	$P_i \cdot P_{ph}$	$\vec{J}_i + \vec{J}_{ph}$

$P_{ph} = -1$
$J_{ph}(E1) = 1$

Exact selection rules:
$P_j = - P_i$
$|\Delta J| \leq 1,\ 0 \not\rightarrow 0\ (J_j + J_i \geq 1)$

Approximate selection rules (for LS coupling):
$\Delta S = 0,\ |\Delta L| \leq 1,\ 0 \not\rightarrow 0$

Intercombination transitions: $\Delta S \neq 0$
$2s^2\ {}^1S_0 - 2s2p\ {}^3P_1$

Selection rules and Z-scaling

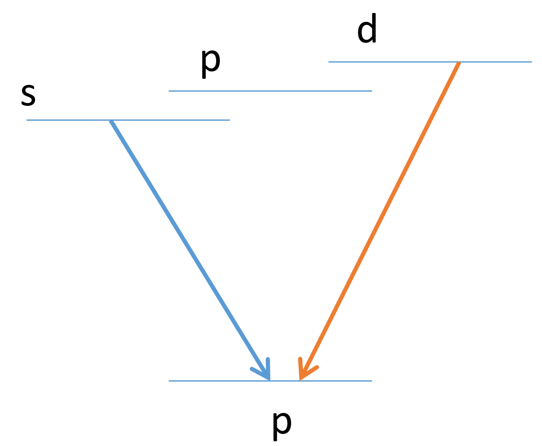
- $\Delta n \neq 0$
  - $r \propto Z^{-1} \Rightarrow S \propto Z^{-2}$
  - $\Delta E \propto Z^2 \Rightarrow f \propto Z^0$
  - $A \propto Z^4$

$$S_{ji} = \left| \langle i \| r \| j \rangle \right|^2 = S_{ij}$$

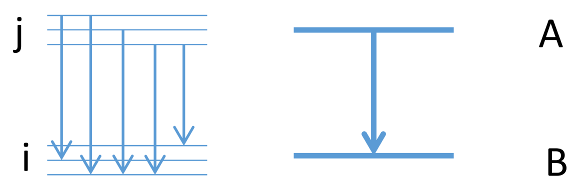
- $\Delta n = 0$
  - $r \propto Z^{-1} \Rightarrow S \propto Z^{-2}$
  - $\Delta E \propto Z \Rightarrow f \propto Z^{-1}$
  - $A \propto Z$

Some useful info

- "Left" is stronger than "right"
  - $f(\Delta l = -1) > f(\Delta l = +1)$
  - He I
    - $f(1s2p\ ^1P_1 - 1s3s\ ^1S_0) = 0.049$
    - $f(1s2p\ ^1P_1 - 1s3d\ ^1D_2) = 0.71$



- Level grouping
  - Average over initial states
  - Sum over final states
  - Example: from levels to terms
  - Any physical parameter



$$\alpha_{BA} = \sum_i \frac{\sum_j g_j \alpha_{ij}}{\sum_j g_j}$$

Principal quantum number n

- n-dependence for *f*:

$$f\left(n_1 \to n_2\right) \approx \frac{32}{3\pi\sqrt{3}}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)^{-3}\frac{1}{n_1^5}\frac{1}{n_2^3}$$

$$f\left(\Delta n = 1\right) \approx \frac{4}{3\pi\sqrt{3}}n \approx 0.245n$$

$$f\left(n_2 >> n_1\right) \propto \frac{1}{n_2^3}$$

- n-dependence for A

$$\boxed{A\left(n_2 >> n_1\right) \propto \frac{1}{n_2^3}}$$

- Total radiative rate from a specific n

$$A_Z\left(n\right) \approx 1.6\times 10^{10}\,\frac{Z^4}{n^{9/2}}$$

Mixing effects

He-like Na^{9+}: $1s2p\ ^3P_1 = 0.999\ ^3P + 0.032\ ^1P$

He-like Fe^{24+}: $1s2p\ ^3P_1 = 0.960\ ^3P + 0.281\ ^1P$

He-like Mo^{40+}: $1s2p\ ^3P_1 = 0.874\ ^3P + 0.486\ ^1P$

Z	$1s^2\ ^1S_0$ - $1s2p\ ^1P_1$	$1s^2\ ^1S_0$ - $1s2p\ ^3P_1$
2	1.8(9)	1.8(2)
11	1.3(13)	1.4(10)
26	4.6(14)	4.4(13)
42	2.6(15)	9.0(14)
54	6.7(15)	3.0(15)
74	2.2(16)	1.2(16)

Quick estimates of A

$$A_{ji} = 4.3 \cdot 10^{7} \frac{g_i}{g_j} \left(\Delta E \left[eV \right] \right)^2 f_{ij} [s^{-1}]$$

Calculate **A(Fe^{24+} 1s^2 $^1S_0$ - 1s2p $^1P_1$)** if ***f*****(O^{6+} 1s^2 $^1S_0$ - 1s2p $^1P_1$)** = 0.7

NIST ASD: **$4.6 \cdot 10^{14}$** s^{-1} (<10%)

Forbidden transitions (high multipoles)

- QED: En, Mn (n=1, 2,…)
- E1/M1 dipole, E2/M2 quadrupole, E3/M3 octupole,…
- Selection rules
  - $P_j \cdot P_i$
    - +1 for M1, E2, M3,…
    - -1 for E1, M2, E3,…
  - $J_{ph}(En/Mn) = n$
- M3 and E3 were measured!

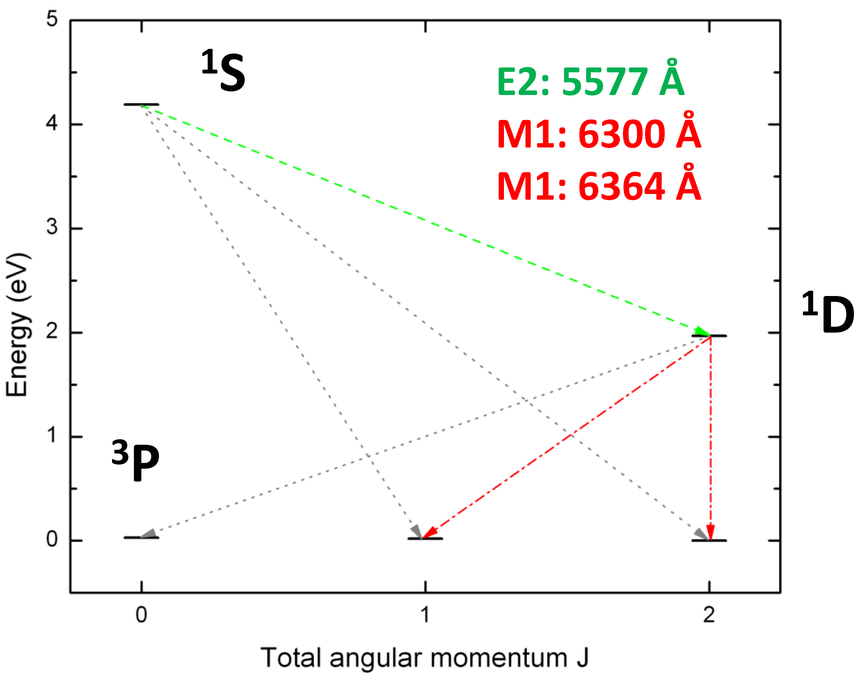
- Magnetic dipole (M1)
  - Stronger within the same configuration/term
  - $\mathbf{A} \propto \mathbf{Z^6}$ or stronger
  - Same parity, $|\Delta J| \leq 1$, $J_j + J_i \geq 1$
- Electric quadrupole (E2)
  - Stronger between configurations/terms
  - $\mathbf{A} \propto \mathbf{Z^6}$ or stronger
  - Same parity, $|\Delta J| \leq 2$, $J_j + J_i \geq 2$

Generally weak…

Aurora borealis

Forbidden transitions: auroras

O I $2p^4$



Wavelength	Transition	A(s^{-1})
2958	$^1S_0$-$^3P_2$	E2: 2.42(-4)
2972	$^1S_0$-$^3P_1$	M1: 7.54(-2)
5577	$^1\mathbf{S_0}$-$^1\mathbf{D_2}$	**E2: 1.26(+0)**
6300	$^1\mathbf{D_2}$-$^3\mathbf{P_2}$	**M1: 5.63(-3)**
6300	$^1D_2$-$^3P_2$	E2: 2.11(-5)
6364	$^1\mathbf{D_2}$-$^3\mathbf{P_1}$	**M1: 1.82(-3)**
6364	$^1D_2$-$^3P_1$	E2: 3.39(-6)
6392	$^1D_2$-$^3P_0$	E2: 8.60(-7)

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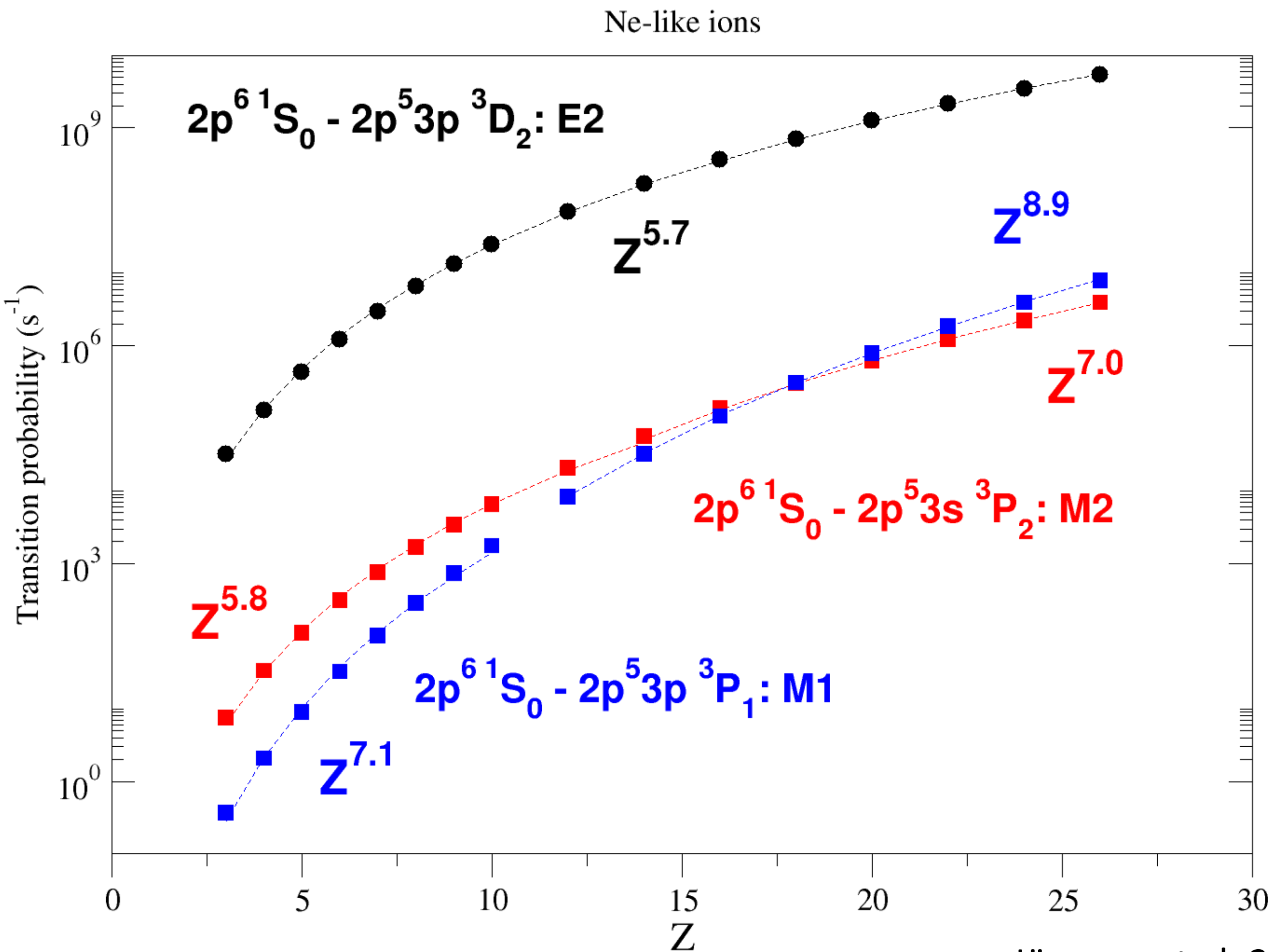
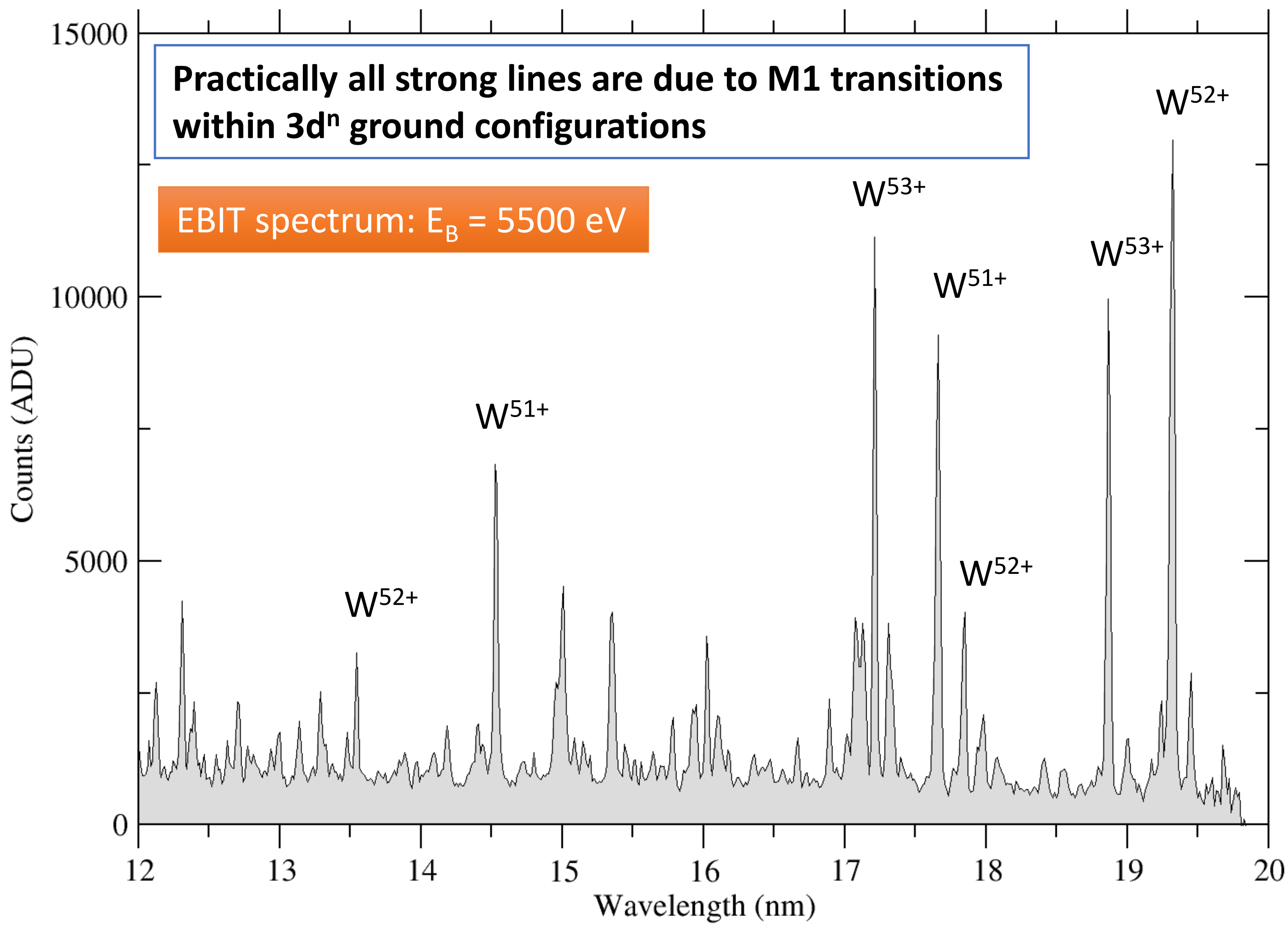
Scaling in Ne-like ions



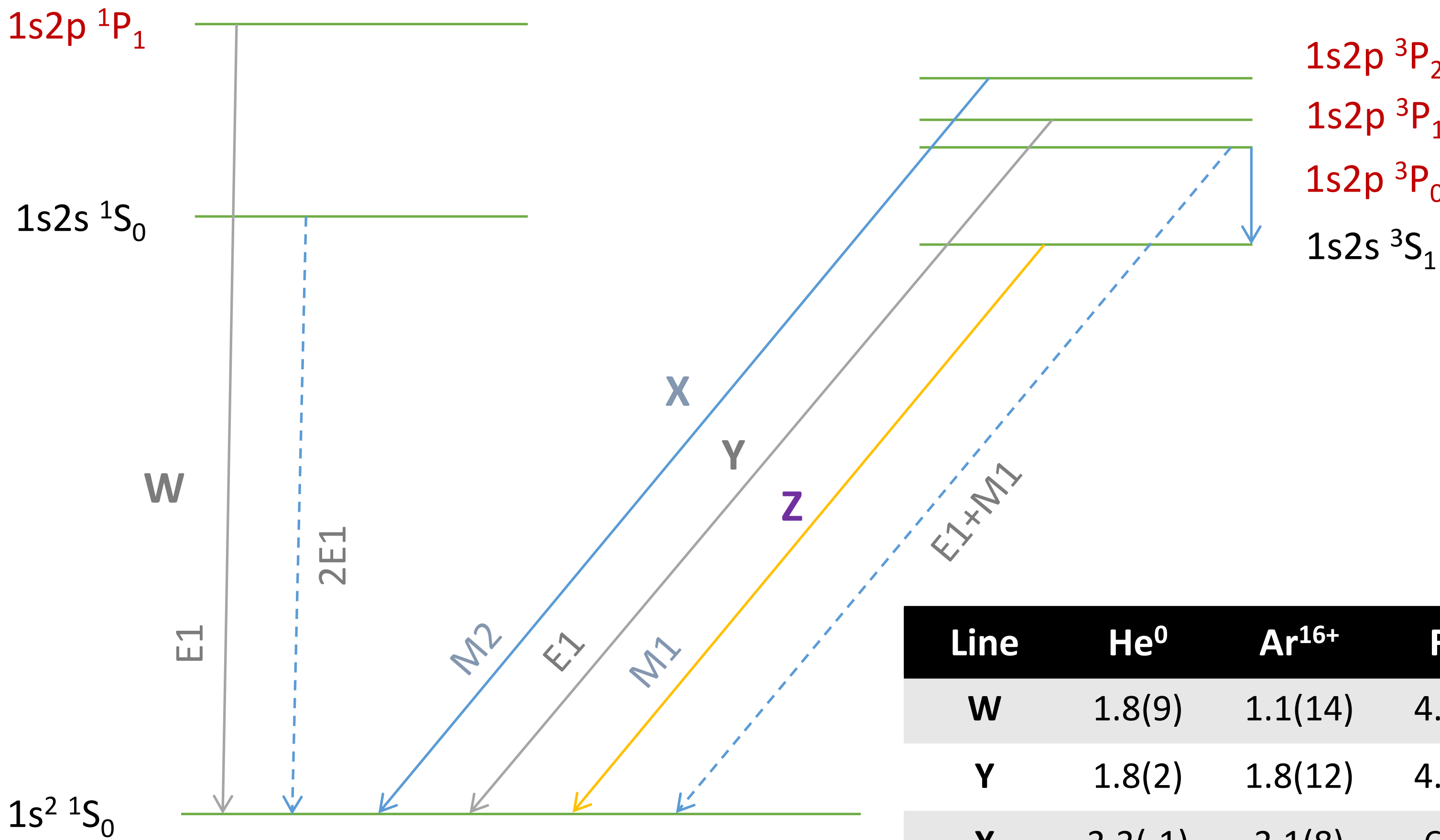
Jönsson et al, 2011

Forbidden transitions: highly-charged W

A ~ 10^4-10^6 s^{-1}



He-like Ar Levels and Lines



Line	He^0	Ar^{16+}	Fe^{25+}	Kr^{34+}
W	1.8(9)	1.1(14)	4.6(14)	1.5(15)
Y	1.8(2)	1.8(12)	4.4(13)	3.9(14)
X	3.3(-1)	3.1(8)	6.5(9)	9.3(10)
Z	1.3(-4)	4.8(6)	2.1(8)	5.8(9)

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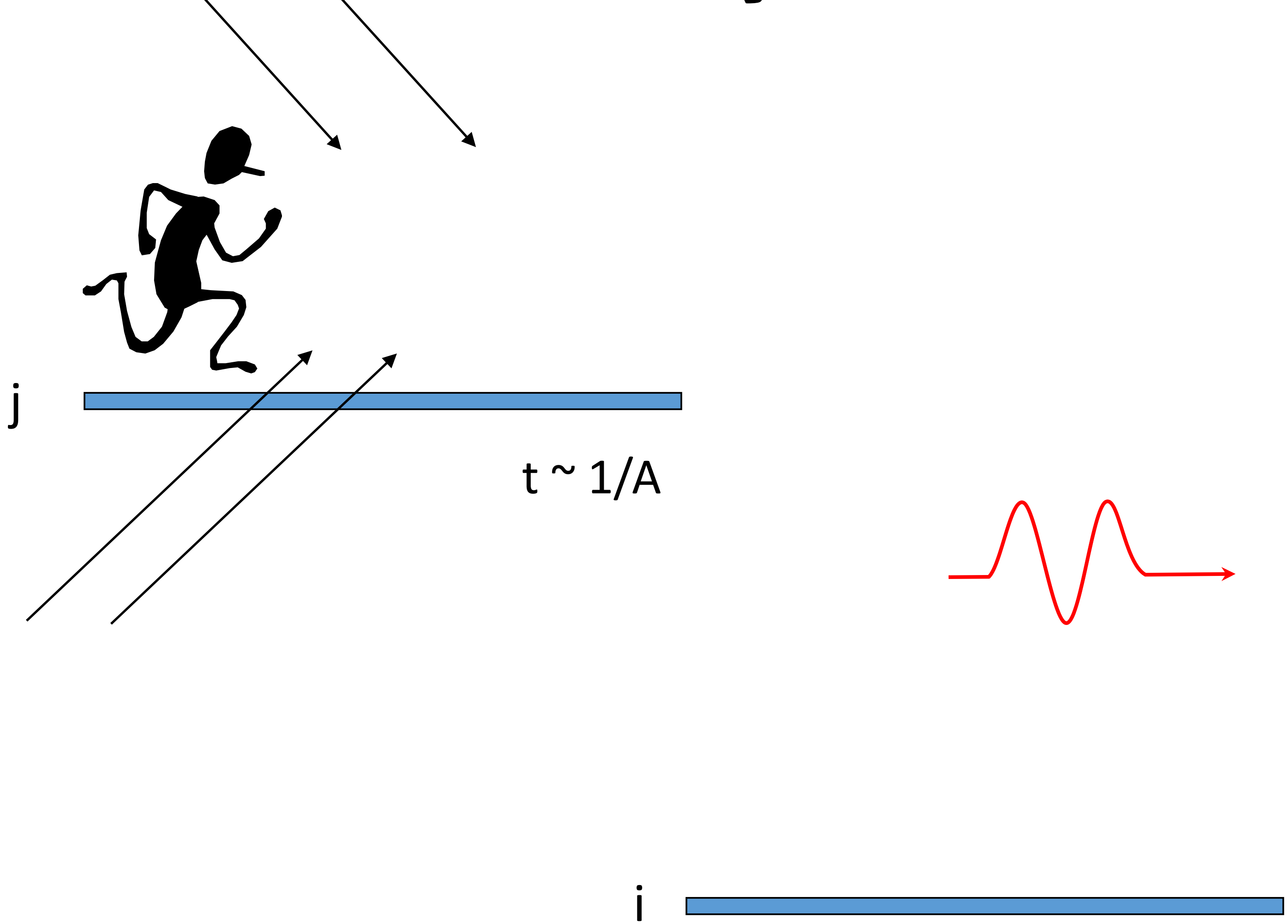
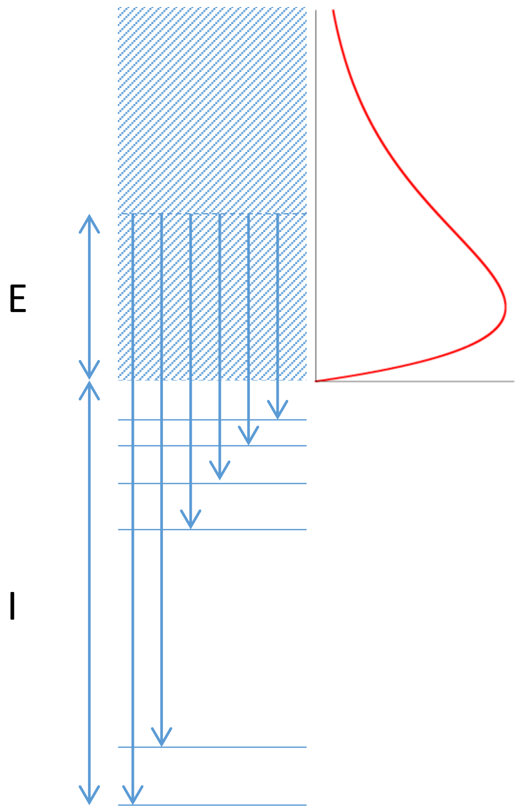
Z-scaling of A's

- **W**[E1]: $A(1s^2\ {}^1S_0 - 1s2p\ {}^1P_1) \propto Z^4$
  - $\Delta J = 1$, $P_1 * P_2 = -1$, $\Delta S = 0$
- **Y**[E1]: $A(1s2\ {}^1S_0 - 1s2p\ {}^3P_1)$
  - $\Delta J = 1$, $P_1 * P_2 = -1$, $\Delta S = 1$
  - $\propto Z^{10}$ for low Z
  - $\propto Z^8$ for large Z
  - $\propto Z^4$ for very large Z
- **X**[M2]: $A(1s^2\ {}^1S_0 - 1s2p\ {}^3P_2) \propto Z^8$
  - $\Delta J = 2$, $P_1 * P_2 = -1$, $\Delta S = 1$
- **Z**[M1]: $A(1s^2\ {}^1S_0 - 1s2s\ {}^3S_1) \propto Z^{10}$
  - $\Delta J = 1$, $P_1 * P_2 = -1$, $\Delta S = 1$

Why are the forbidden lines sensitive to density?



Radiative Recombination

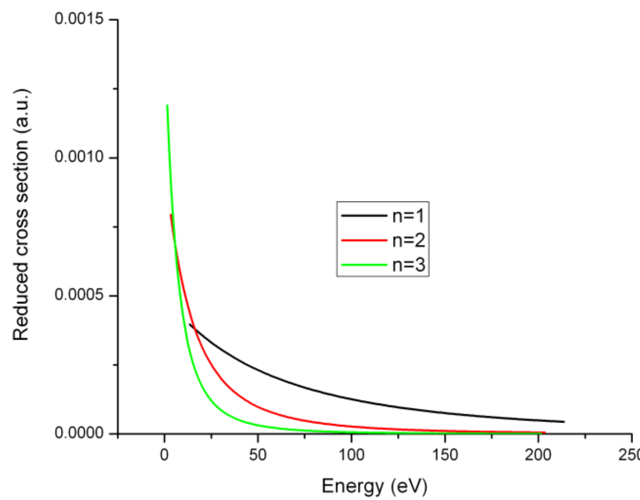


$$A^{Z+} + e \rightarrow A^{(Z-1)} + h\nu$$ (inverse of photoionization)

$$h\nu = E + I$$

Semiclassical Kramers cross section: $$\sigma_{Kr}(E) = \frac{64\alpha}{3\sqrt{3}} \frac{Z^4}{n^5} \left(\frac{Ry}{E+I} \right)^3 \pi a_0^2$$

Quantummechanical cross section: $$\sigma_{ph}(E) = \sigma_{Kr}(E) \cdot G_n^{bf}(E)$$

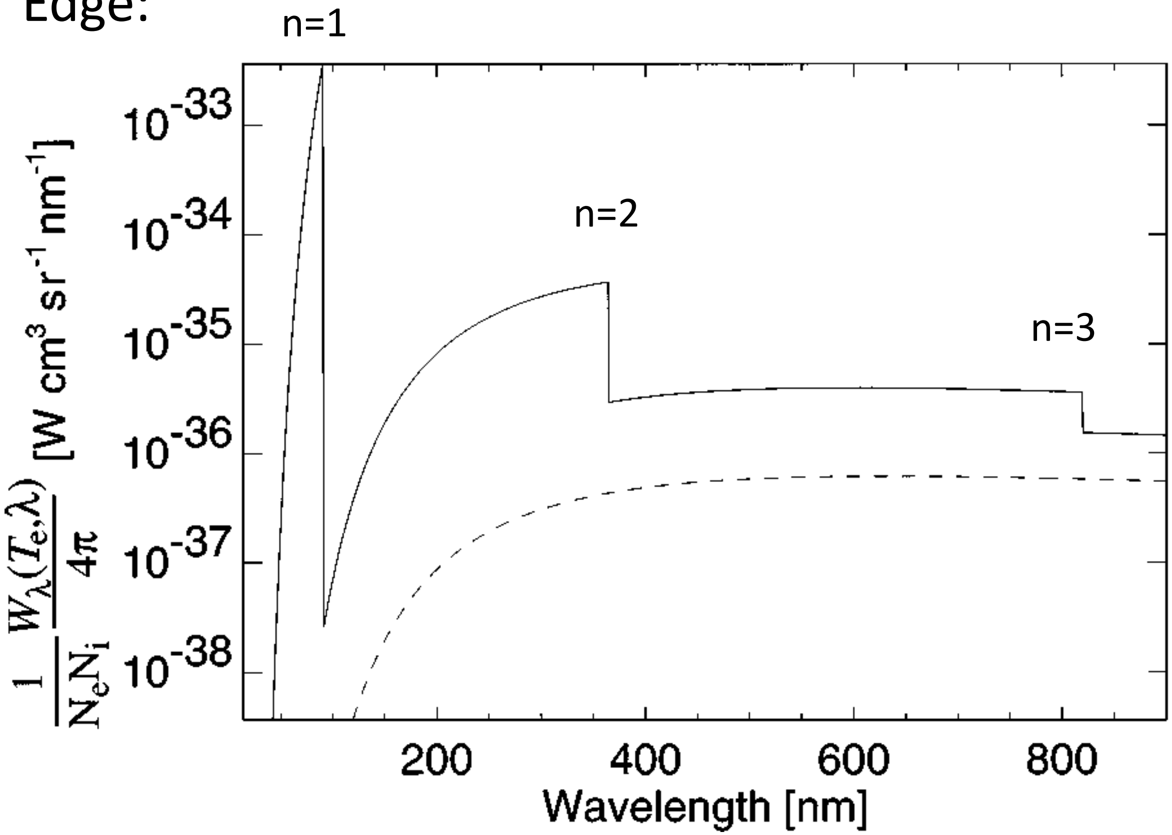


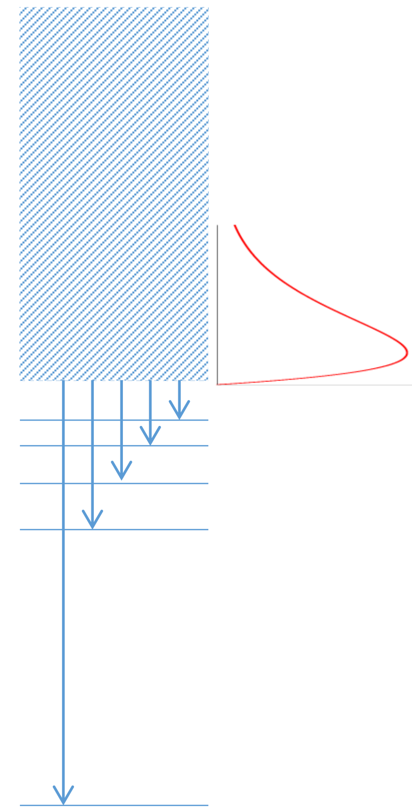
Cross section Z-scaling:

$$\sigma\left(\frac{h\nu}{Z^2}\right) \propto \frac{1}{Z^2}$$

FF+BF at Alcator C-mod: 1 eV, H

Edge:

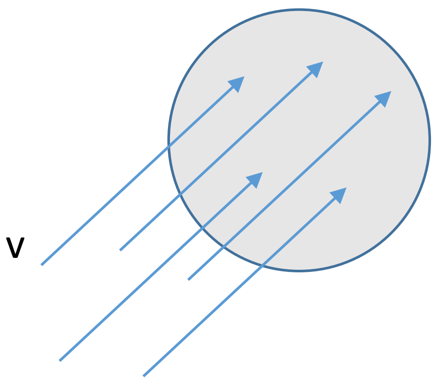




Lumma et al (1997)

Collisions in plasmas

- More than one particle: collisions!
- Elastic, inelastic



Number of collisions per unit time:

projectile_density[1/cm^3] *
velocity[cm/s] *
effective_area[cm^2]

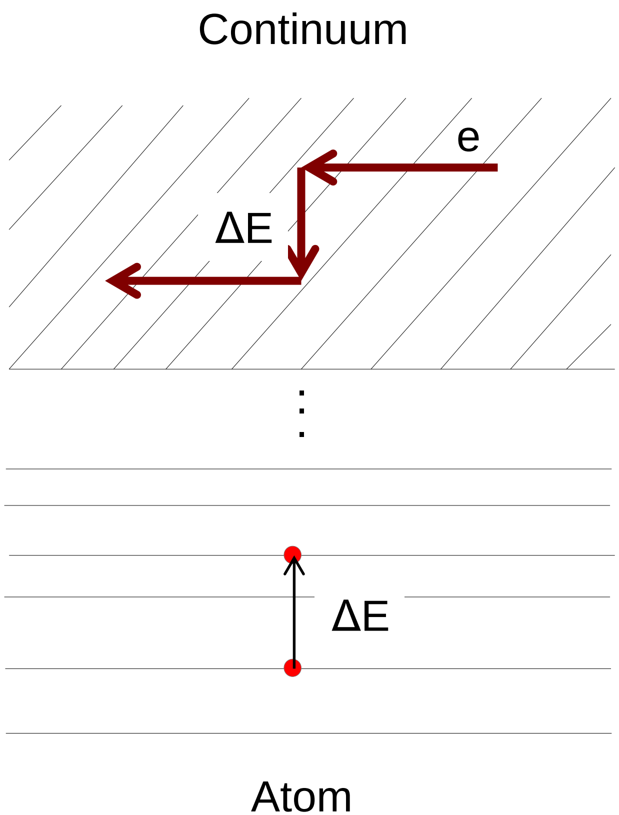
[1/s]

Equilibrium plasma: $T_e = T_A$

$$\frac{v_e}{v_A} = \sqrt{\frac{M}{m_e}}$$

Electrons are much faster!

Collision (excitation)



Main ***binary*** quantity: cross section **σ(E)** [**cm²**]

Effective area for a particular process

$$\sigma(E) = \int |f(E,\theta,\phi)|^2 \, d\Omega$$

f is the scattering amplitude

Process rate in plasmas:

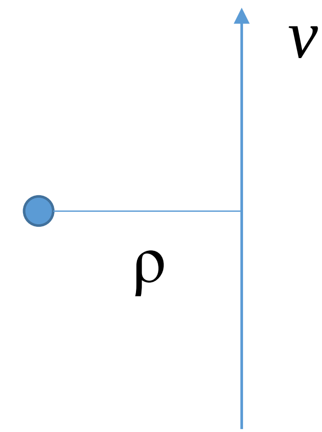
$$R[s^{-1}] = N\underbrace{\langle\sigma v\rangle}_{\text{rate coefficient}} \equiv N \int_{E_{min}}^{E_{max}} \sigma(E) \cdot v \cdot f(E) dE$$

Physics is here!

Basic Parameters

- Cross sections are *probabilities*
  - Classically:

$$\sigma(\Delta E, E) = \int_0^\infty P(\Delta E, E, \rho) \cdot 2\pi\rho d\rho$$



- Typical values for atomic cross sections
  - $a_0 \sim 5\cdot10^{-9}$ cm $\Rightarrow \pi a_0^{\,2} \sim$ **10^{-16} cm^2**
- Collision strength **Ω** (dimensionless, *on the order of unity*):

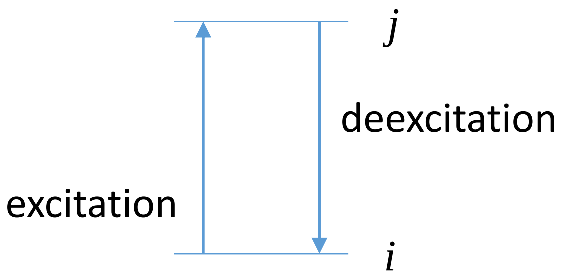
$$\sigma_{ij}(E) = \pi a_0^2 \frac{Ry}{g_j E} \Omega_{ij}(E)$$

  - Ratio of cross section to the de Broglie wavelength squared
  - Symmetric w/r to initial and final states

Direct and inverse

- Quantum mechanics tells us that characteristics of direct and inverse processes are related

ΔE is the excitation threshold



$$\Omega_{ij}(E+\Delta E)=\Omega_{ji}(E)$$

Klein-Rosseland formula:

$$g_i(E+\Delta E)\sigma_{exc}(E+\Delta E)=g_j E\sigma_{dxc}(E)$$

$$\boxed{A(i)+e\leftrightarrow A(j)+e}$$

Rates: $\boxed{g_i\langle\sigma v\rangle_{exc}=g_j\langle\sigma v\rangle_{dxc}\cdot e^{-\Delta E/T}}$

Milne formula for photoionization/photorecombination: $\hbar\omega=E+I_Z$

$$\boxed{A+h\nu\leftrightarrow A^{+}+e}$$

$$g_z\sigma_{ph}(\hbar\omega)=\frac{2mc^2}{\hbar^2\omega^2}g_{z+1}\sigma_{rr}(E)$$

Types of transitions for excitation

- Optically(dipole)-allowed
  - $P \cdot P' = -1$ (different parity)
  - $|\Delta l| = 1$
  - $\Delta S = 0$
  - $\sigma(E \to \infty) \sim \ln(E)/E$
- Optically(dipole)-forbidden
  - $\Delta S = 0$
  - $\sigma(E \to \infty) \sim 1/E$
- Spin-forbidden (EXCHANGE! Coulomb does not change spin…)
  - $\Delta S \neq 0$
  - $\sigma(E \to \infty) \sim 1/E^3$

Examples in He I:

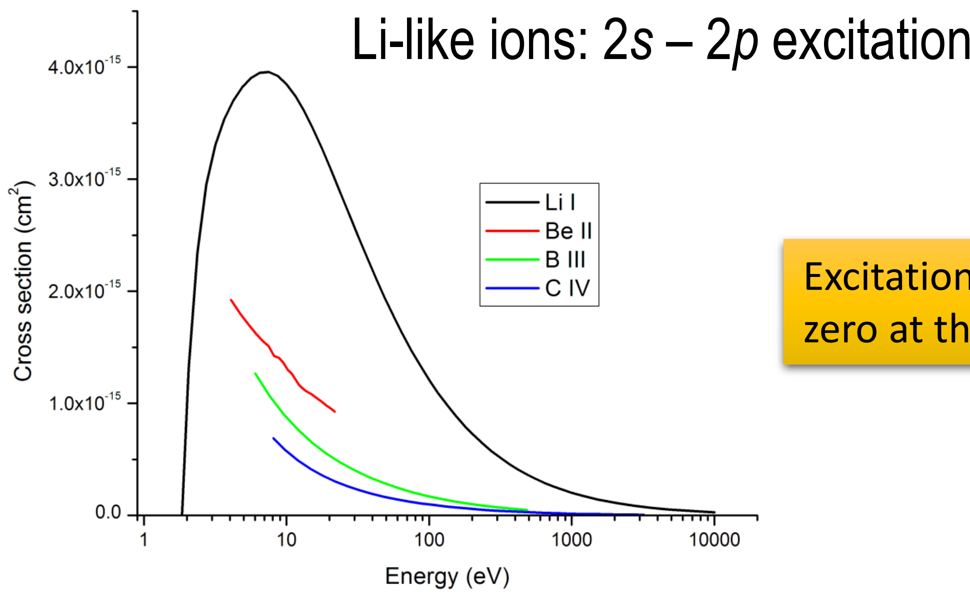
$1s^2\ ^1S \to 1s2p\ ^1P$
$1s2p\ ^3P \to 1s4d\ ^3D$

$1s2s\ ^1S \to 1s3s\ ^1S$
$1s2s\ ^3S \to 1s4d\ ^3D$

$1s^2\ ^1S \to 1s2p\ ^3P$
$1s2p\ ^3P \to 1s4d\ ^1D$

Order of cross sections

- *General* order
  - *optically allowed > optically forbidden > spin forbidden*
- OA: long-distance, similar to E1 radiative transitions
- The larger Δ*l*, the smaller cross section



Excitation cross sections for ions are **NOT** zero at the threshold

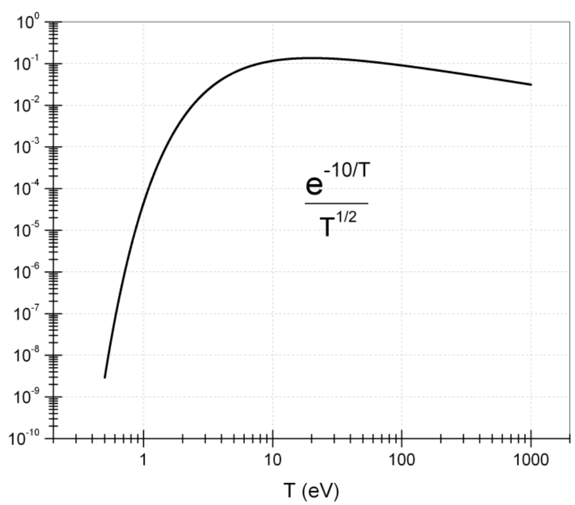
From cross sections to rates

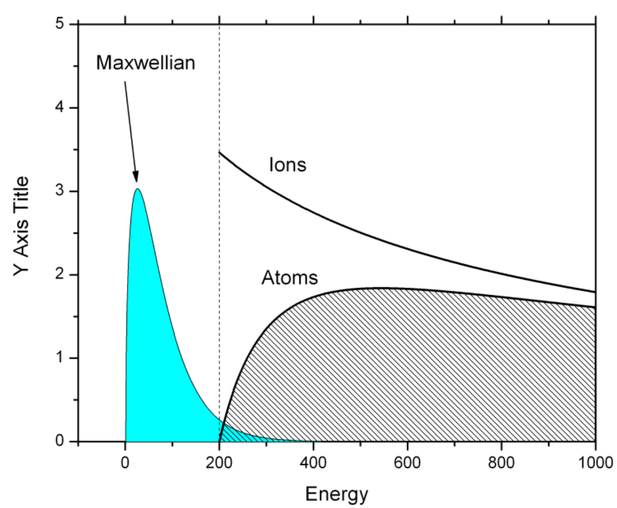
Rate coefficients for an arbitrary energy distribution function

$$\langle \mathrm{v}\sigma \rangle = \int_{E_{min}}^{E_{max}} \mathrm{v} \cdot \sigma(E) \cdot f(E) dE \xrightarrow{Maxw} \left(\frac{8}{\pi m T^3}\right)^{1/2} \int_{\Delta E}^{\infty} E \cdot \sigma(E) \cdot e^{-E/T} dE$$

For $\sigma(E) = A/E$: $\langle v\sigma \rangle \propto \frac{e^{-\frac{\Delta E}{T}}}{\sqrt{T}}$

Often only threshold is important:





Effective collision strength:

$$\gamma(T_e) = \frac{1}{T_e} \int \Omega(E) \exp\left(-\frac{E}{T_e}\right) dE$$

$$R_{ji}(T_e) = \left(\frac{8}{\pi m T_e}\right)^{1/2} \frac{\pi a_0^2}{g_i} Ry \cdot \gamma_{ji}(T_e)$$

van Regemorter-Seaton-Bethe formula

- Optically-allowed excitations

Gaunt factor

$X \equiv E/\Delta E_{ij}$

$$\sigma_{ij}(E) = \pi a_0^2 \frac{8\pi}{\sqrt{3}} \left(\frac{Ry}{\Delta E_{ij}}\right)^2 \frac{g(X)}{X} f_{ij}$$

oscillator strength

$$X \to \infty: \; g(X) \approx \frac{\sqrt{3}}{2\pi} \ln(X) \qquad \sigma(E) \approx \frac{6.51 \cdot 10^{-14}}{(\Delta E[eV])^2} \frac{\ln(X)}{X} f_{ij} \quad [cm^{-2}]$$

"*Recommended*" Gaunt factors:

Atoms:

$$g(\Delta n = 0, X) = \left(0.33 - \frac{0.3}{X} + \frac{0.08}{X^2}\right) \ln(X)$$

$$g(\Delta n \neq 0, X) = \left(\frac{\sqrt{3}}{2\pi} - \frac{0.18}{X}\right) \ln(X)$$

Ions:

$$g(\Delta n = 0, X) = \left(1 - \frac{1}{Z}\right)\left(0.7 + \frac{1}{n}\right)\left[0.6 + \frac{\sqrt{3}}{2\pi} \ln(X)\right]$$

$$g(\Delta n \neq 0, X) = 0.2 (X < 2), \; \frac{\sqrt{3}}{2\pi} \ln(X) \;\; for \; X \geq 2$$

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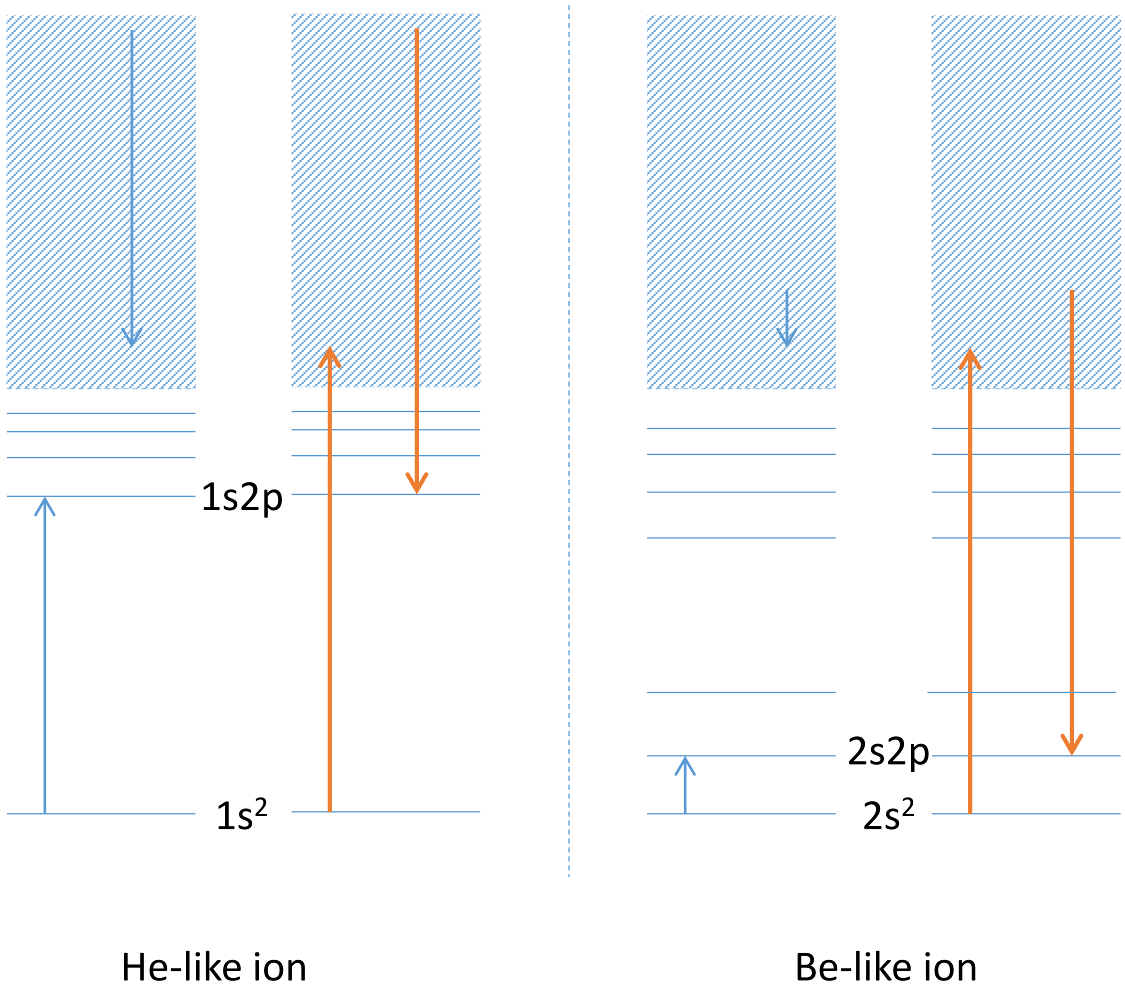
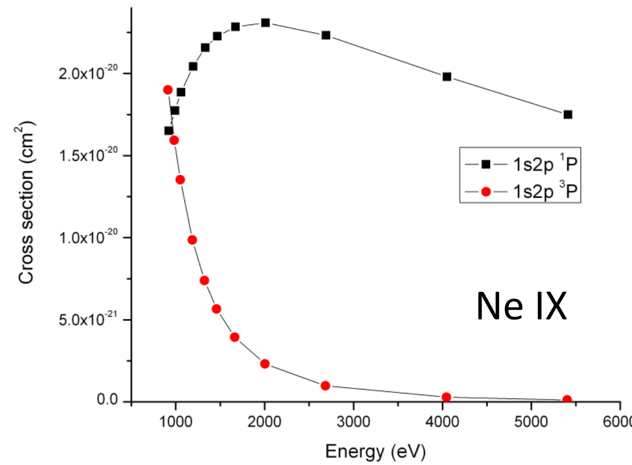
Scaling of Excitations

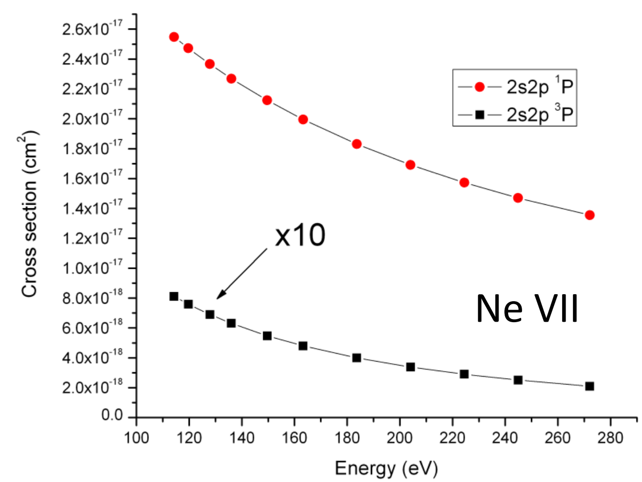
$$\sigma_{ij}(E) \propto \frac{f}{\Delta E_{ij}^2}$$

- n-scaling
  - $\Delta n=1$
    - $f \sim n$, $\Delta E \sim n^{-3}$, $\cancel{\sigma \sim n^7}$, $\boldsymbol{\sigma \sim n^4}$
  - Into high n
    - $f \sim n^{-3}$, $\Delta E \sim n^0$, $\boldsymbol{\sigma \sim n^{-3}}$
- Z-scaling
  - $\Delta n=0$
    - $f \sim Z^{-1}$, $\Delta E \sim Z$, $\boldsymbol{\sigma \sim Z^{-3}}$, $\boldsymbol{\langle \sigma v \rangle \sim Z^{-2}}$
  - $\Delta n \neq 0$
    - $f \sim Z^0$, $\Delta E \sim Z^2$, $\boldsymbol{\sigma \sim Z^{-4}}$, $\boldsymbol{\langle \sigma v \rangle \sim Z^{-3}}$

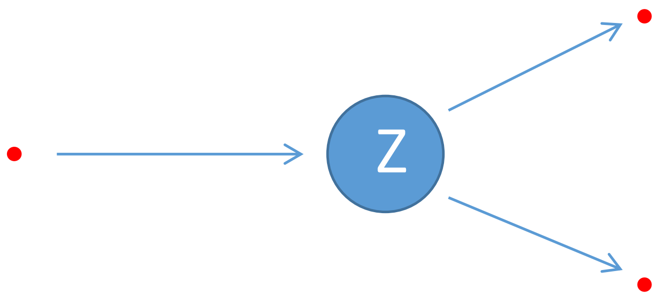
Direct and Exchange (cont'd)



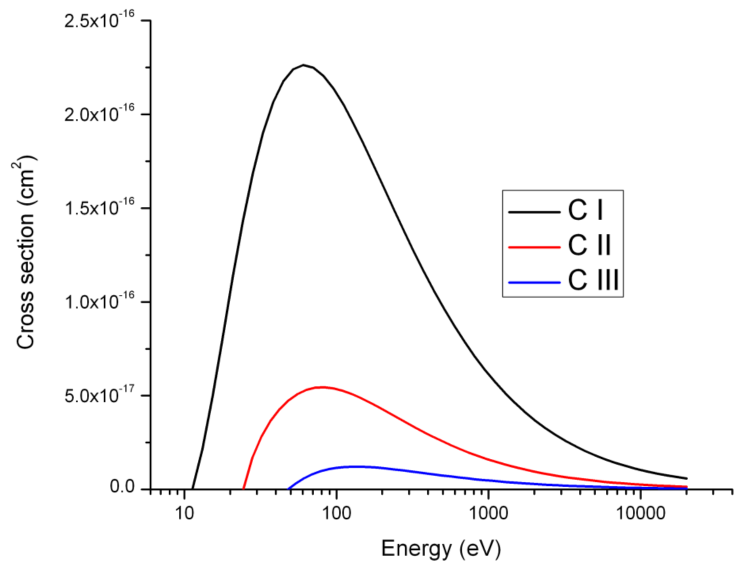




Ionization cross sections



$$A + e \rightarrow A^{+} + e + e$$



Lotz formula:

$$\sigma_{ion}(n, E) = 2.76\,\pi a_0^2 \frac{Ry^2}{I_n} \frac{\ln(E/I_n)}{E} = 2.76\,\pi a_0^2 \frac{n^4}{Z^4} \frac{\ln X}{X}$$

Same theoretical methods as for excitation: Born, Coulomb-Born, DW, CC, CCC, RMPS…

3-Body Recombination

$$\boxed{A + e \leftrightarrow A^{+} + e + e}$$

3-body rate coefficient $\alpha_{Z+1}(T_e)$ from ionization rate coefficient $S_Z(T_e)$:

$$\alpha_{Z+1}(T_e) = \frac{1}{2}\frac{g_z}{g_{z+1}}\left(\frac{2\pi\hbar^2}{m_e T_e}\right)^{3/2} exp\left[\frac{E_z}{T_e}\right] S_Z(T_e)$$

Rates from rate coefficients: $n_e S_Z(T_e)$ but $n_e^2 \alpha_{Z+1}(T_e)$

Likes high-n states; $\alpha(T_e)\sim 1/T_e^{9/2}$

Collisional Methods and Codes

- Plane-wave Born (first order perturbation)
- Coulomb-Born (better for HCI)
- Distorted-wave methods

Perturbative methods

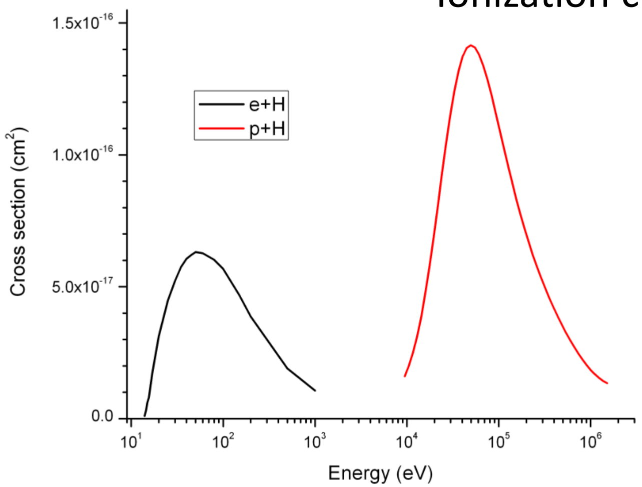
- Close-coupling (CC) methods
  - Convergent CC (CCC)
  - R-matrix (with pseudostates, etc.)
  - B-splines R-matrix
  - Time-Dependent CC
  - …

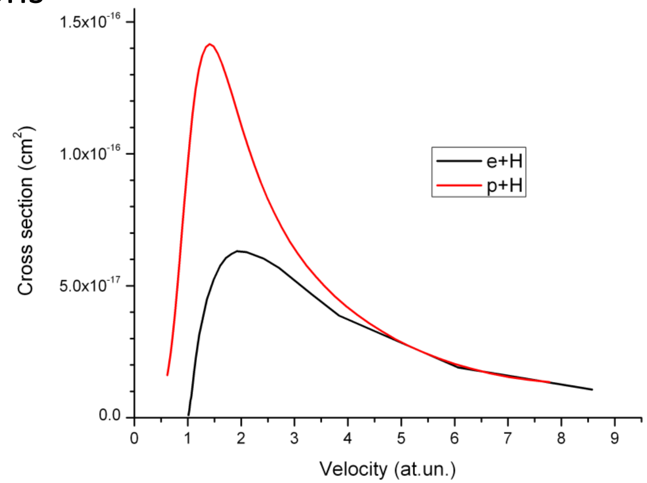
Non-perturbative methods

- Relativistic versions are available

Heavy-particle collisions

Ionization cross sections





In ***thermal*** plasmas electrons are always more important for excitations than heavy particles
Exception: **closely-spaced levels** (e.g., 2s and 2p in H-like ions)

Neutral beams: **E ~ 100-500 keV** $\Rightarrow$ heavy particle collisions are of highest importance

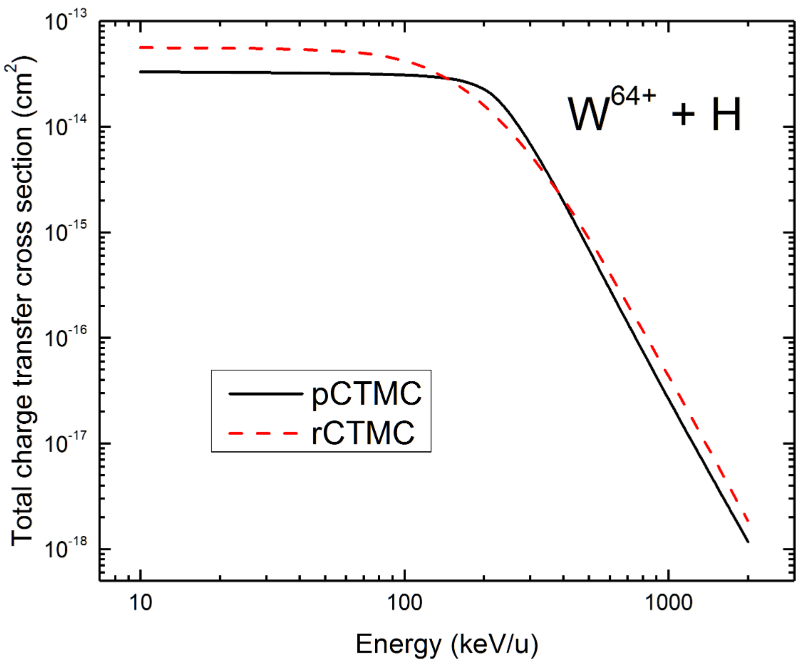
Charge exchange $H + A^{z+} \Rightarrow H^{+} + A^{(z-1)+}(n)$

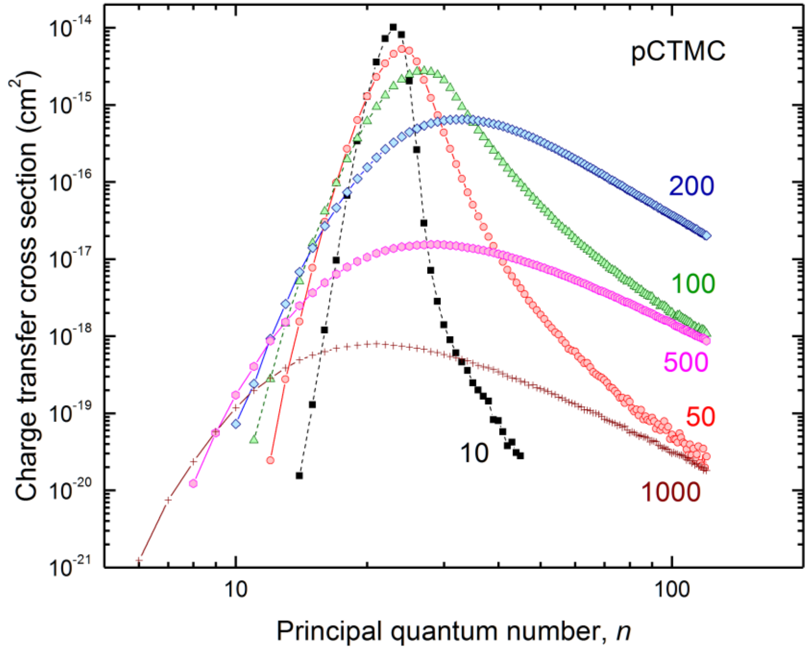
- Very large cross sections **> 10^{-15} cm^2**; $\sigma(Z) \sim Z \cdot 10^{-15}\ cm^2$
- High excited states populated: $n \sim Z^{0.77}$
- Higher l values are preferentially populated but it depends on collision energy and *n*

Neutral beam in ITER: H+W^{64+}

$\sigma(Z) \sim Z \cdot 10^{-15}\ cm^2 = \mathbf{6.4 \cdot 10^{-14}}\ cm^2$

$n \sim Z^{0.77} \approx \mathbf{25}$





Classical Trajectory Monte Carlo (CTMC): two variations

D.R.Schultz and YR, to be published

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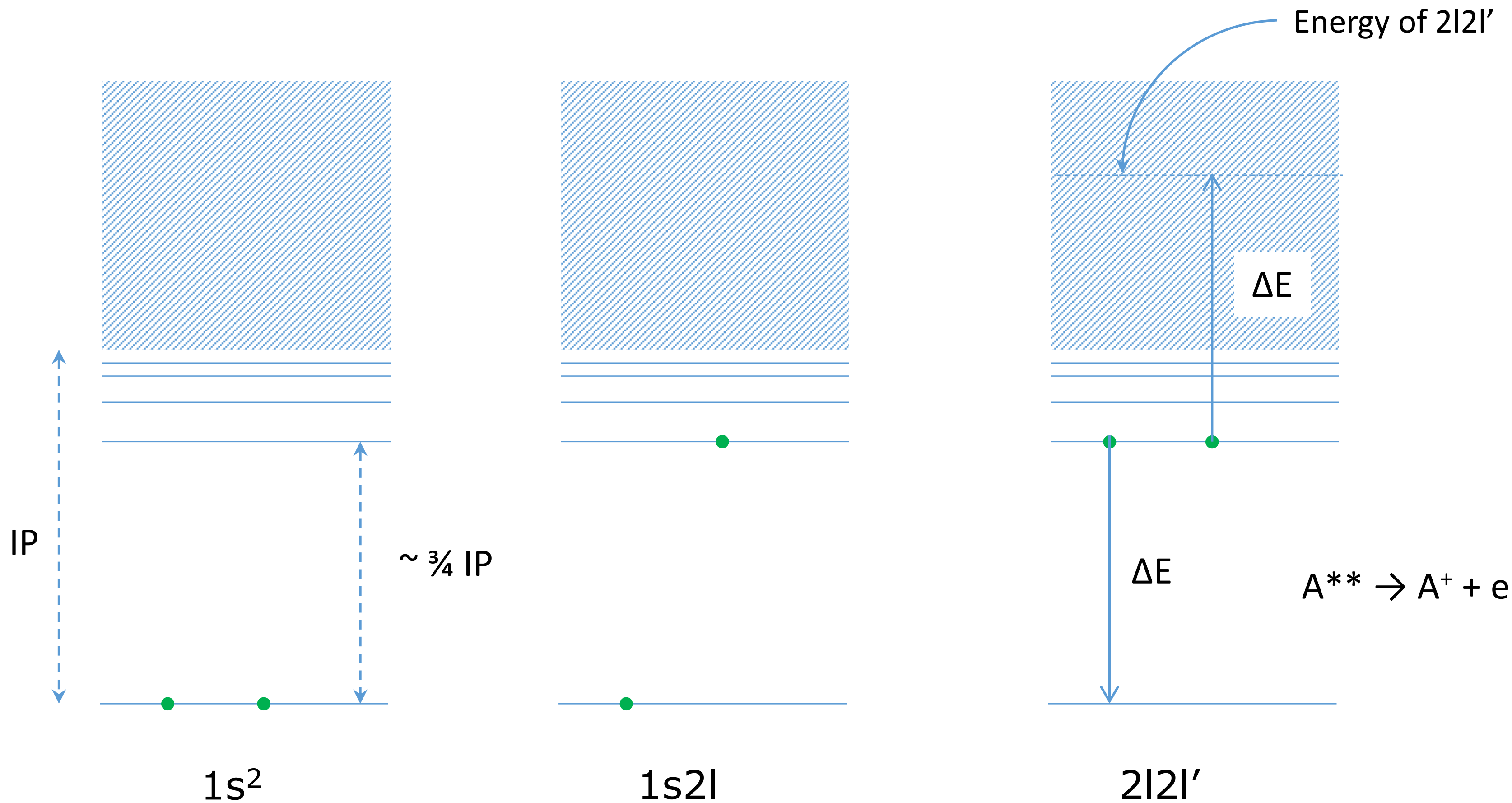
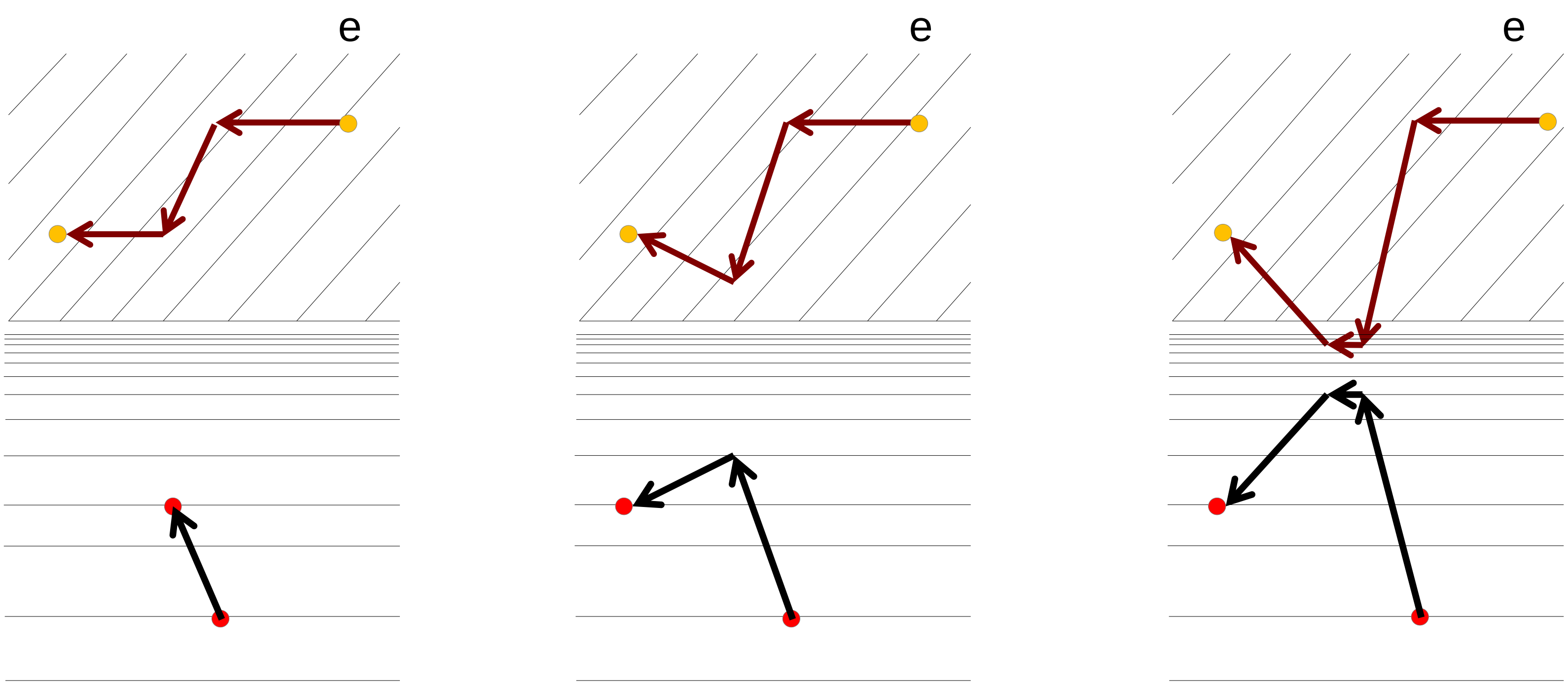
Autoionization

$$A_a = \frac{2\pi}{\hbar}\left|\langle\psi|\hat{H}|\varphi\rangle\right|^2;\ 10^{13}\text{-}10^{14}\ s^{-1}$$



Resonances in excitation

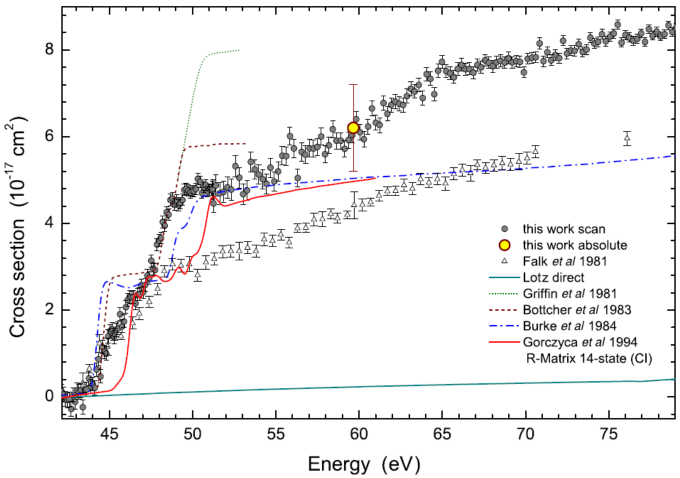


Direct excitation

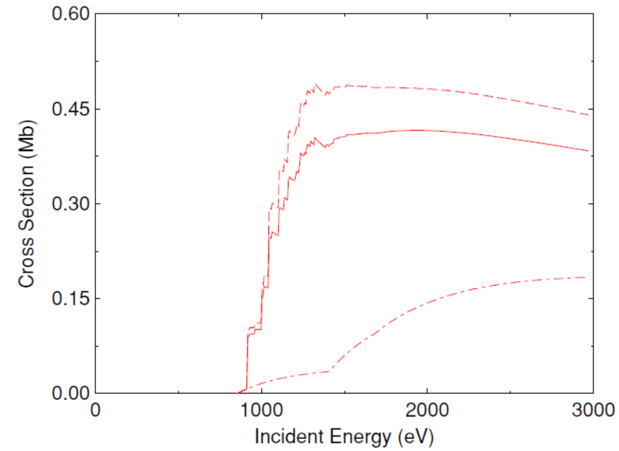
Intermediate states

Intermediate AI states (coupled channels!)

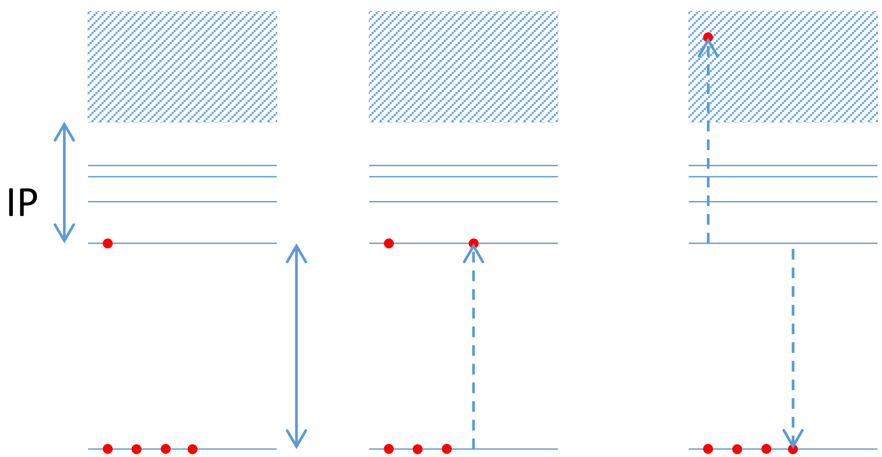
Excitation-Autoionization



3p^{6}3d Ti^{3+}: van Zoest et al, 2004



3s^{2}3p^{6}3d^{10}4s^2 Xe^{24+}: Pindzola et al, 2011

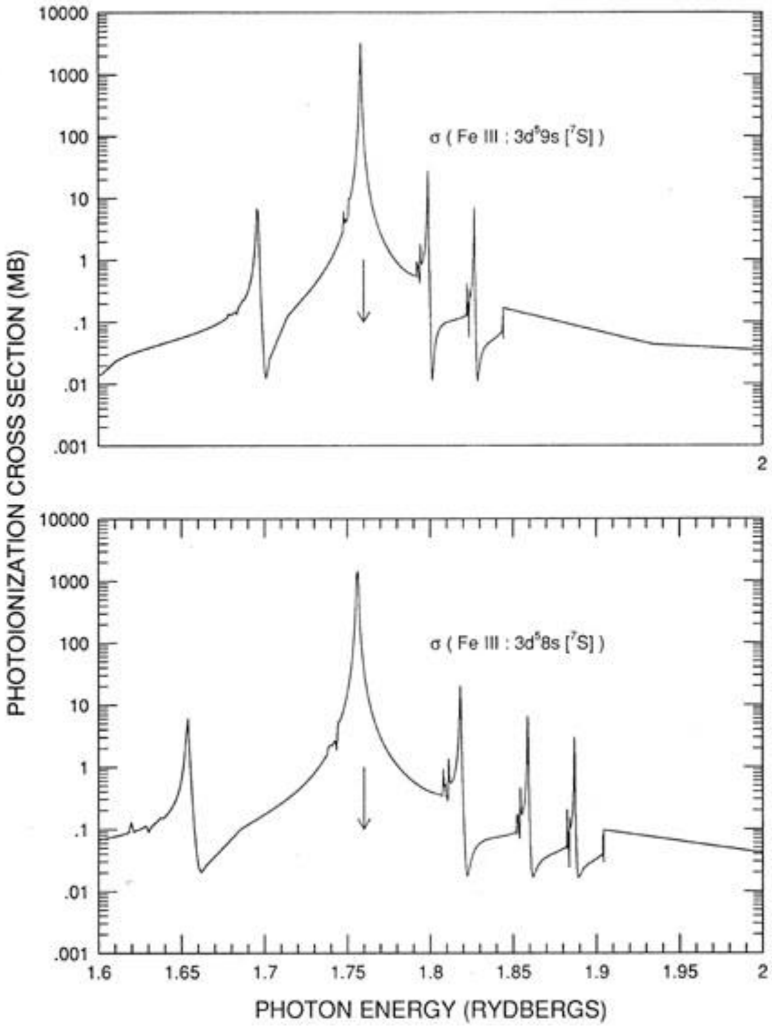


When EA is important:

- few electrons on the outermost shell
- Mid-Z multielectron ions
- …but less important for higher Z (rad!)

EA in ionization cross sections is not required for detailed modeling with AI states!

Resonances in photoionization



Fe III

$3d^5(^6S)ns\ ^7S + h\nu$
$\quad \rightarrow 3d^5\ ^6S$

$3d^5(^6S)ns\ ^7S + h\nu$
$\quad \rightarrow 3d^44p(^4P^o)ns\ ^7P^o$
$\quad \rightarrow 3d^5\ ^6S$

A. Pradhan

Selection rules

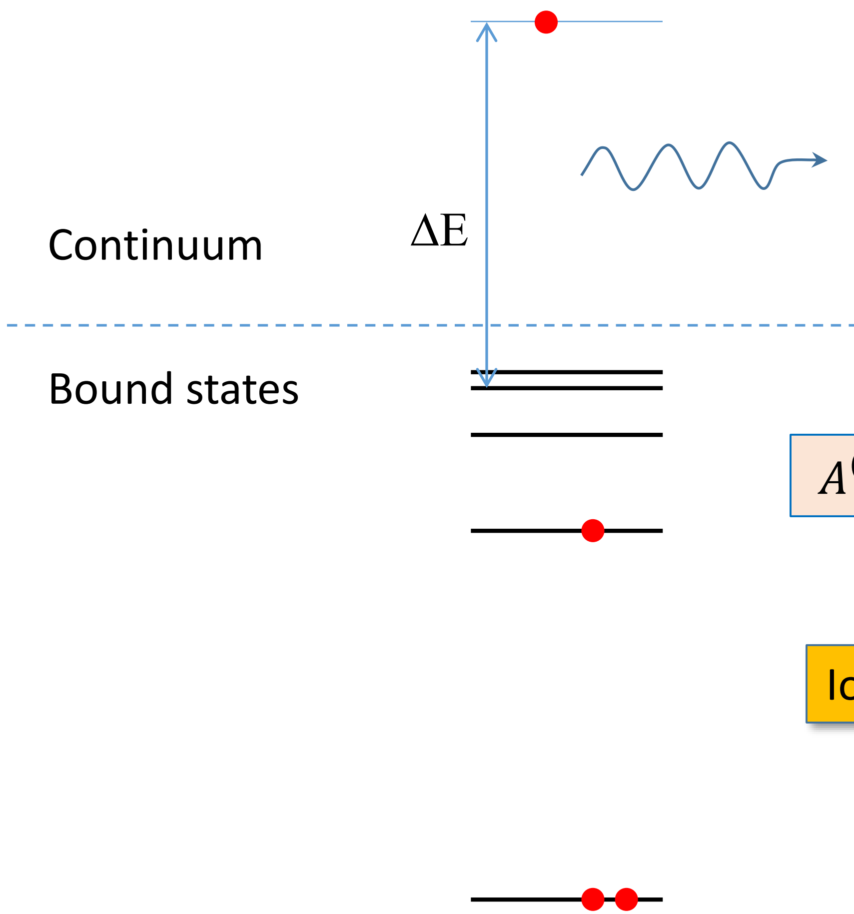
- Examples of AI states: $1s2s^2$, $1s^22pnl$ (high n)
- Same old rule: before = after
- $A^{**} \rightarrow A^{*} + \varepsilon l$
  - Exact: $P_j = P_i$; $\Delta J = 0$
  - Approximate (LS coupling): $\Delta S = 0$, $\Delta L = 0$

- $2p^2\ ^3P \rightarrow 1s + \varepsilon p$: parity/L violation (for LS)!
  - BUT: $\Psi(2p^2\ ^3P_2) = \alpha\Psi(2p^2\ ^3P_2) + \beta\Psi(2p^2\ ^1D_2) + \ldots$
  - and $\Psi(2p^2\ ^3P_0) = \alpha'\Psi(2p^2\ ^3P_0) + \beta'\Psi(2p^2\ ^1S_0) + \ldots$
  - YET: $A_a(2p^2\ ^3P_1)$ is much smaller…

$2p^2$ autoionization probabilities

Level	Ne^{8+}	Fe^{24+}
$^3P_0$	2.2(10)	3.7(12)
$^3P_1$	3.1(8)	1.9(10)
$^3P_2$	6.2(11)	1.1(14)
$^1D_2$	2.7(14)	2.3(14)
$^1S_0$	1.4(13)	3.2(13)

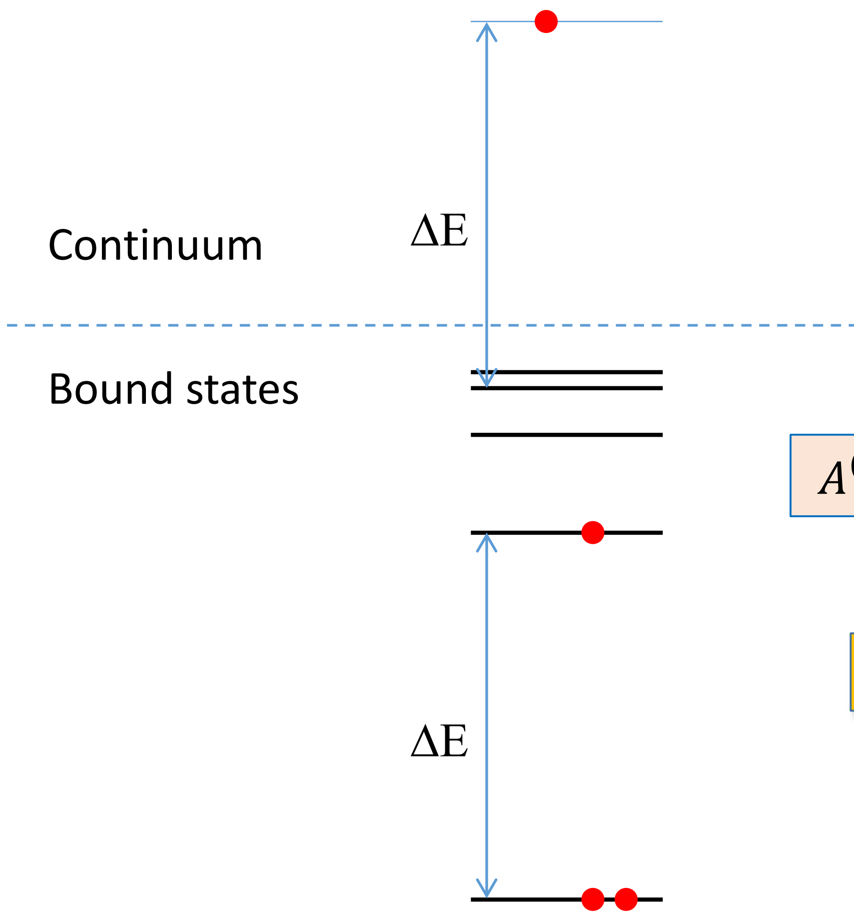
Radiative recombination



$$A^{(Z+1)+} + e \rightarrow A^{Z+} + h\nu$$

Ion recombined

DR step 1: dielectronic capture

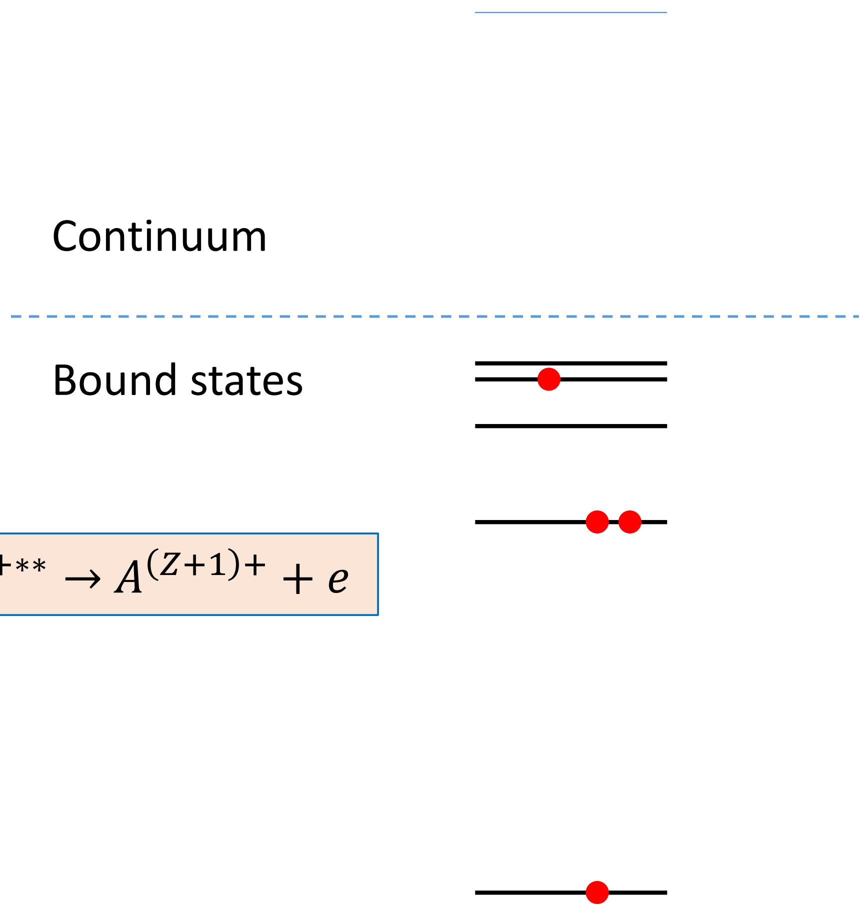


$$A^{(Z+1)+} + e \rightarrow A^{Z+**}$$

Resonant process!

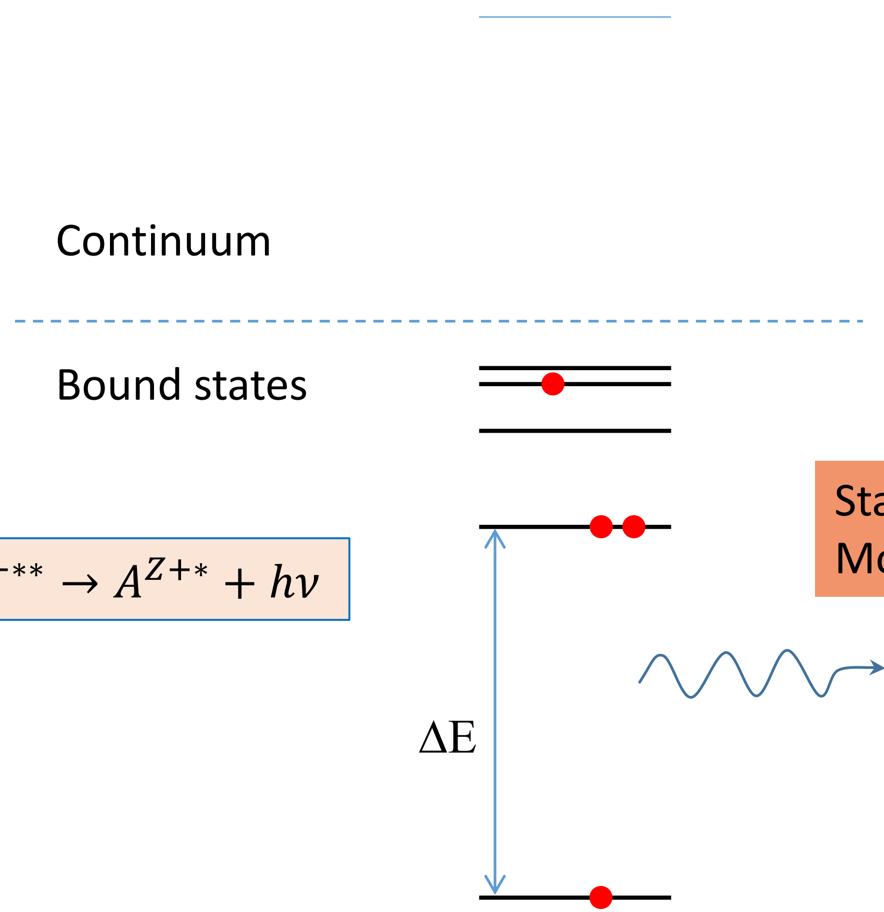
Dielectronic capture + autoionization = no recombination

DC and AI are direct and inverse



$$A^{(Z+1)+} + e \rightarrow A^{Z+**} \rightarrow A^{(Z+1)+} + e$$

DR step 2: radiative stabilization



$$A^{(Z+1)+} + e \rightarrow A^{Z+**} \rightarrow A^{Z+*} + h\nu$$

Stabilizing transition:
Mostly x-rays

Dielectronic Recombination

$$A^{+}+e \xrightarrow{DC} A^{**} \xrightarrow{AI} A^{+}+e$$

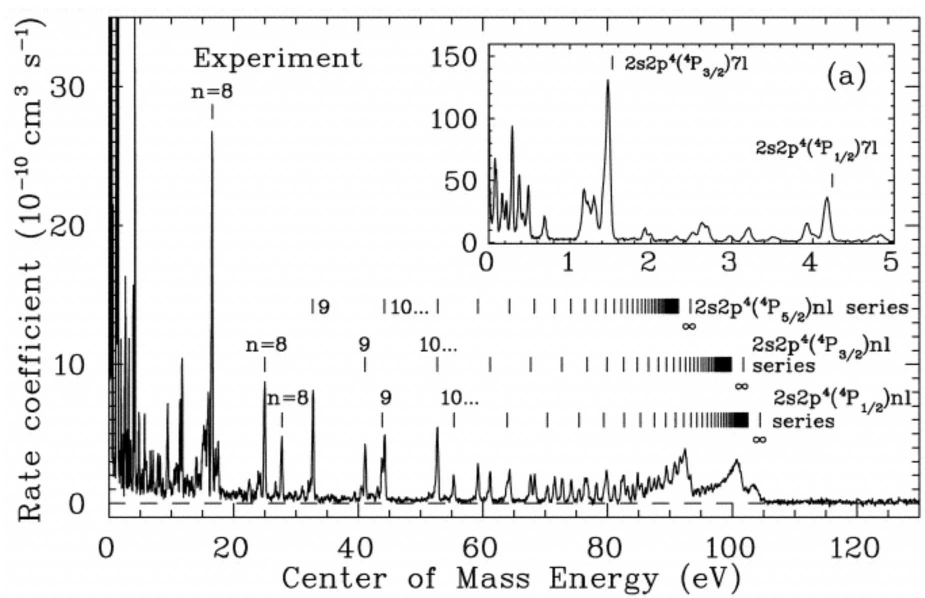
$$A^{**} \xrightarrow{RS} A^{*}+h\nu$$

Example: **Δn=0 for Fe XX 2s²2p³**

$2s^2 2p^3\ {}^4S_{3/2} + e \rightarrow 2s2p^4({}^4P_{5/2})nl$

$2s^2 2p^3\ {}^4S_{3/2} + e \rightarrow 2s2p^4({}^4P_{5/2})nl$

$2s^2 2p^3\ {}^4S_{3/2} + e \rightarrow 2s2p^4({}^4P_{5/2})nl$



$n \geq 7$

Savin et al, 2004

Examples of dielectronic recombination & resonances

He$^+$ + e

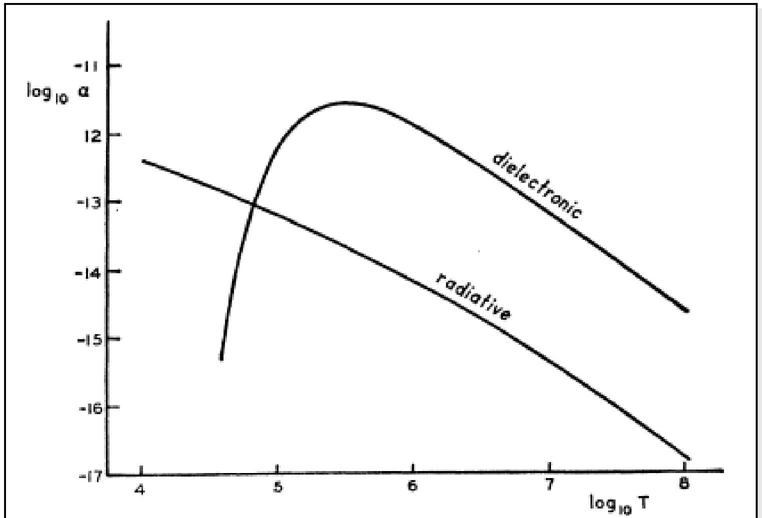
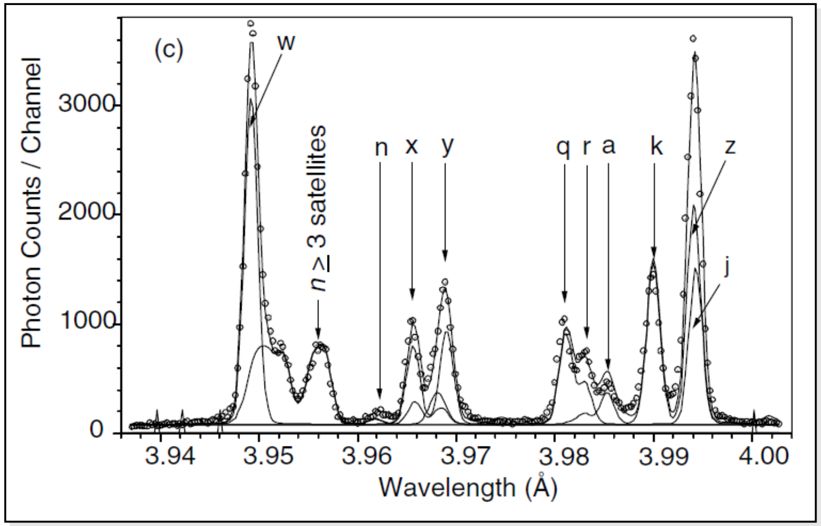


FIG 1 —He$^+$ + e recombination coefficients α (cm^3 sec^{-1})

A. Burgess, ApJ **139**, 776 (1964)

This work solved the ionization balance problem for solar corona

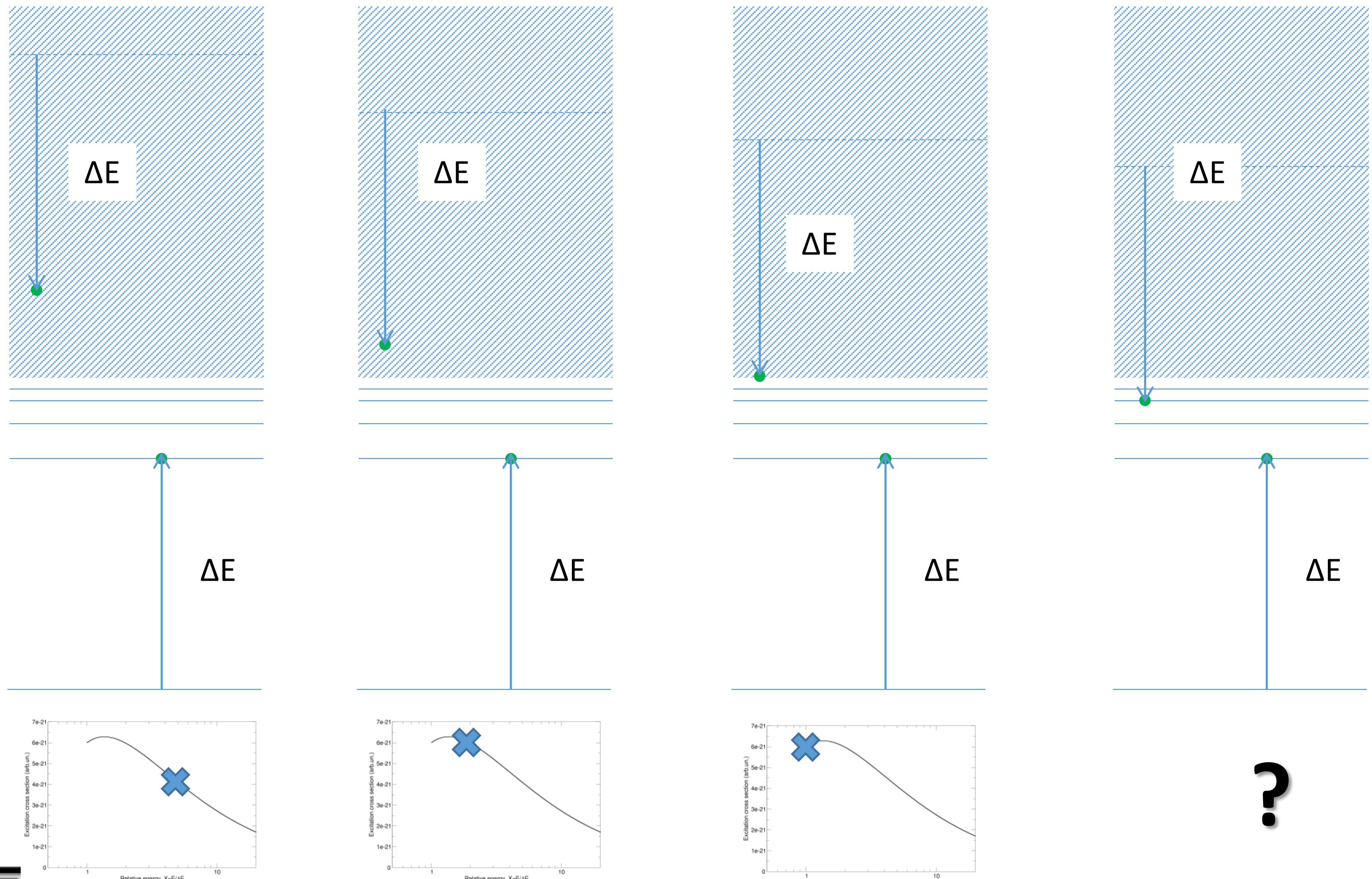
Dielectronic satellites are important for plasma diagnostics (e.g., He- and Li-like ions)



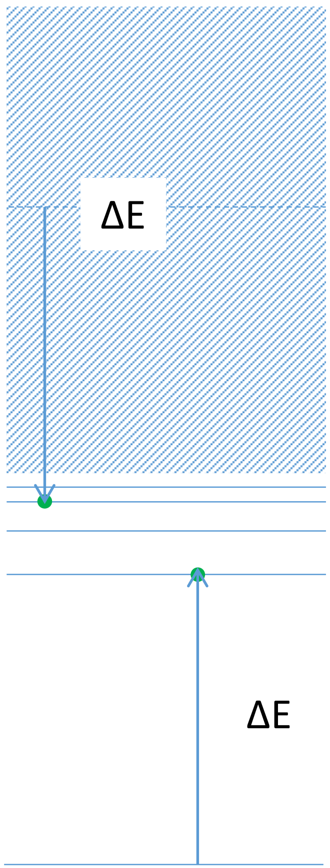
Ar at NSTX, Bitter et al (2004)

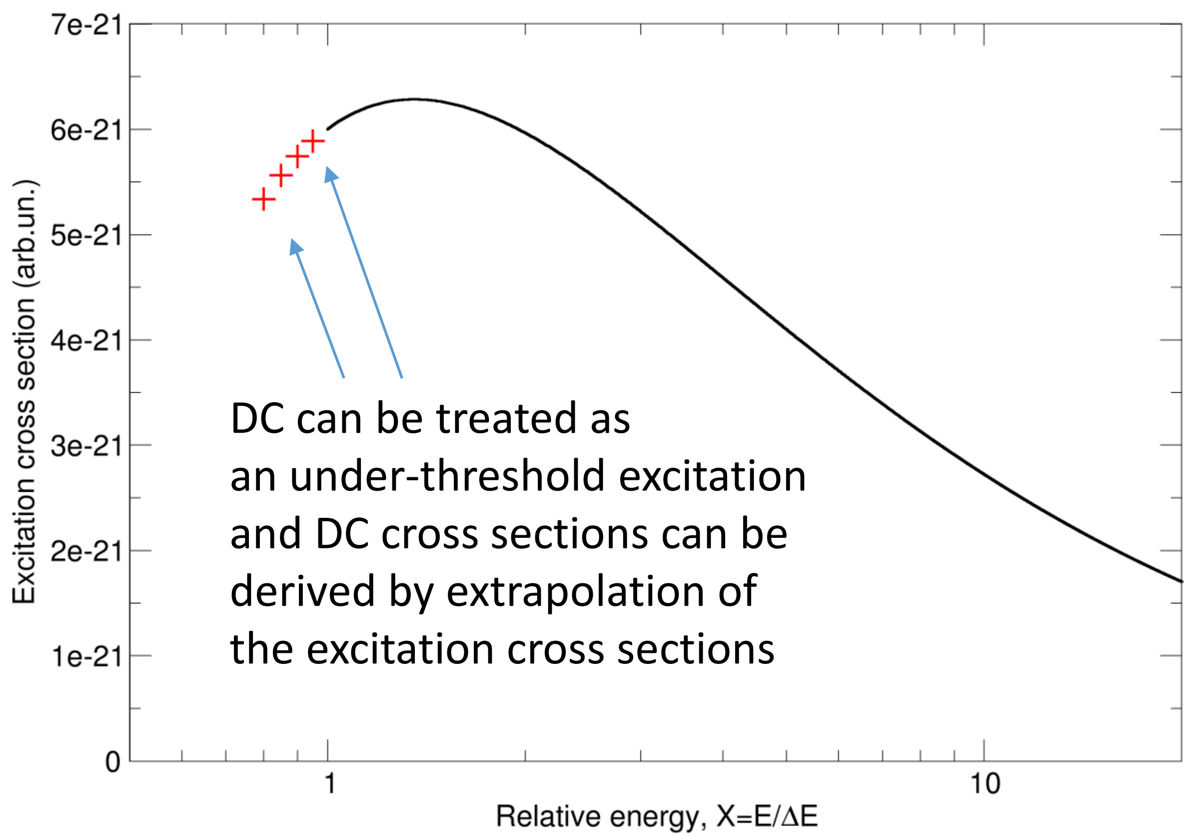
BUT: DR for high-Z multi-electron ions is barely known!

Connection between DC and EXC



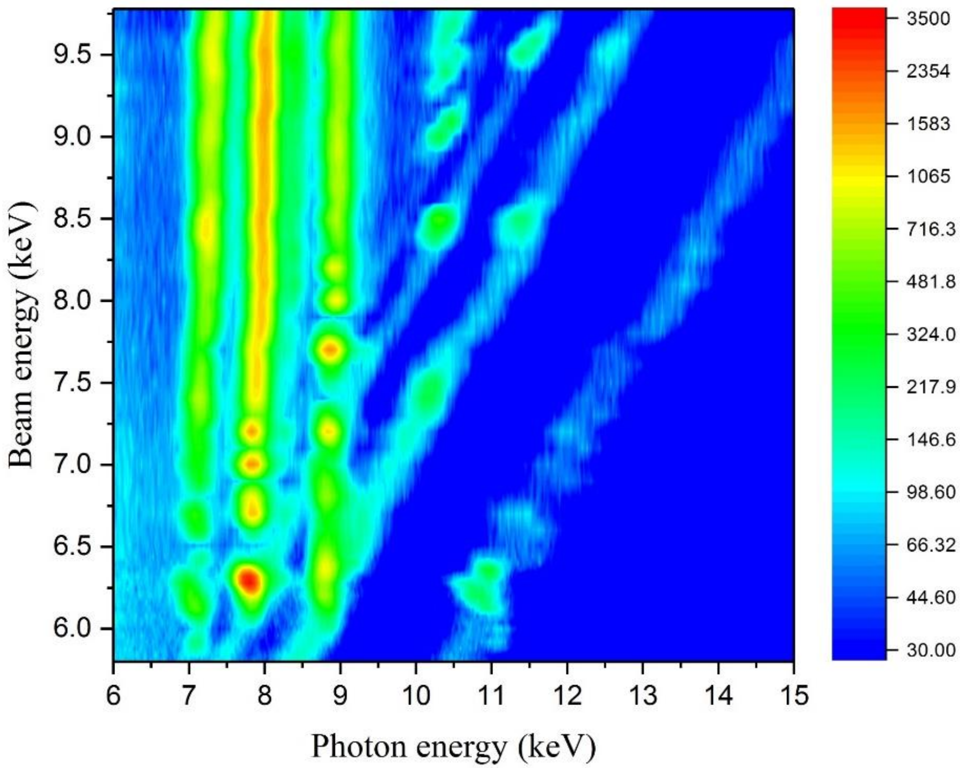
Connection between DC and EXC





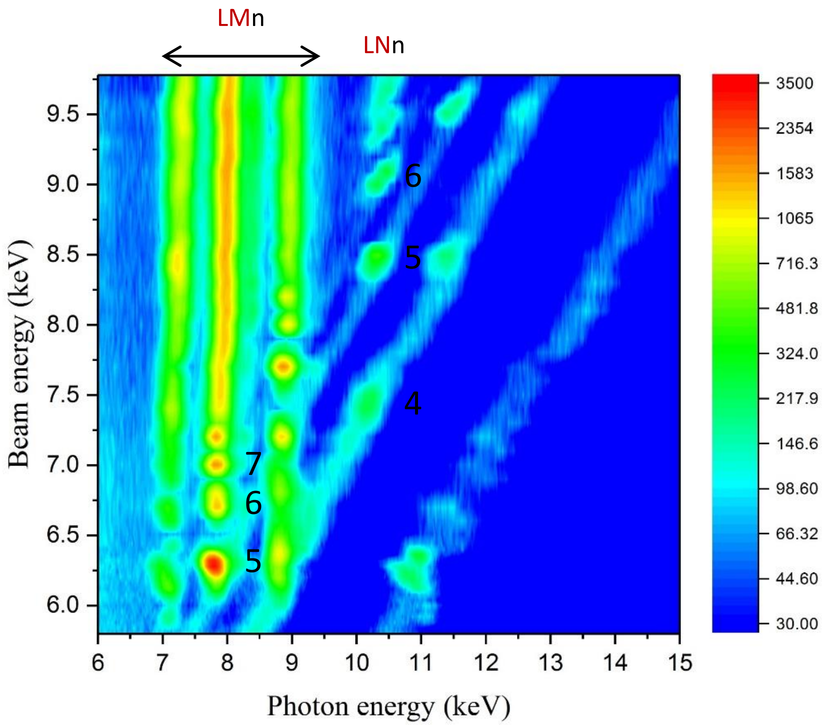
Inner-shell dielectronic resonances in HCI

$$K^2L^8M^k + e \rightarrow K^2L^7M^k nln'l'$$

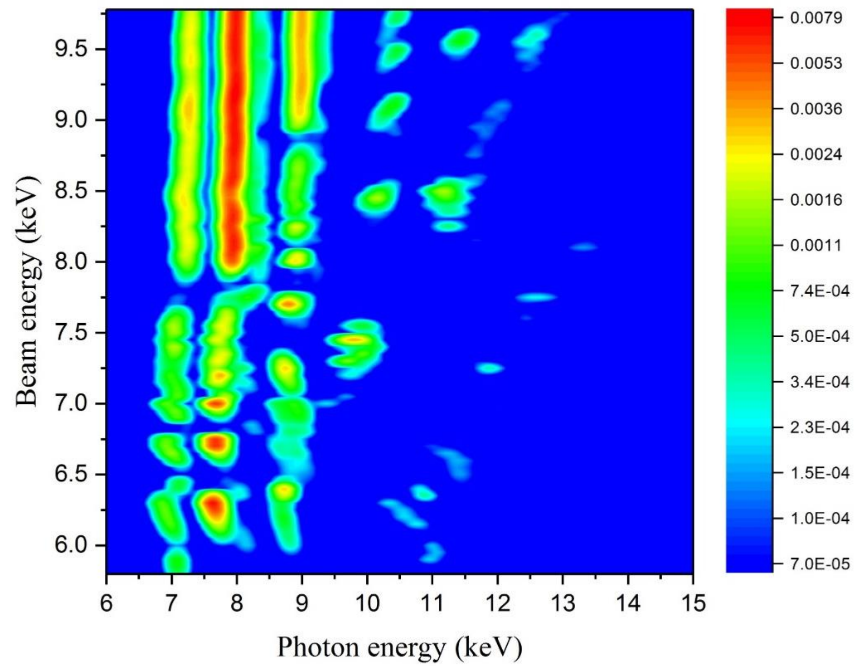


~Yb^{40+}

Experiment



Theory

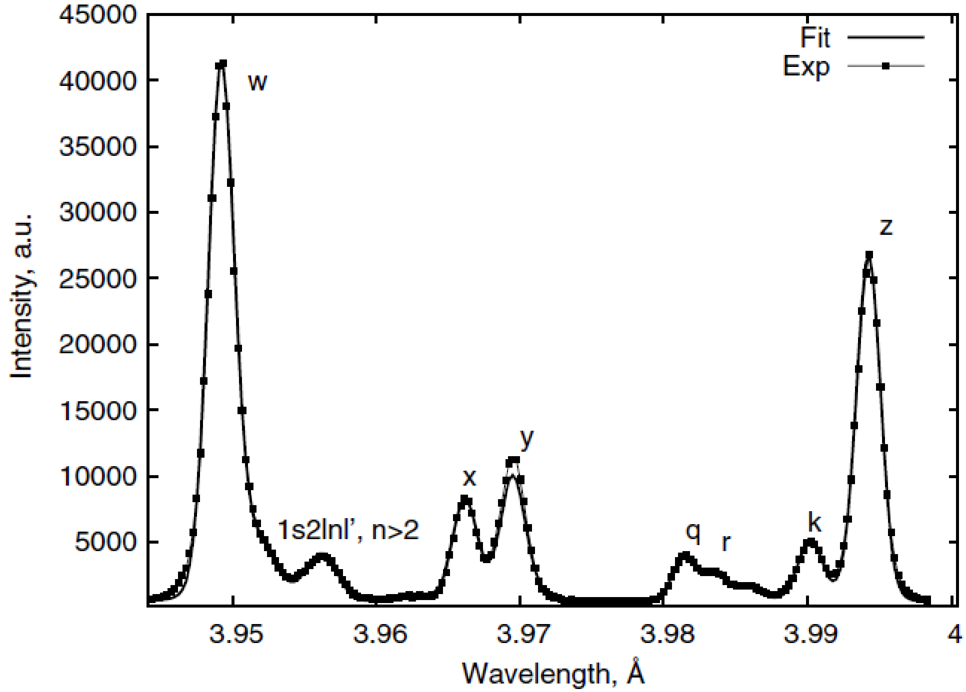


$$1s^2 2s^2 \mathbf{2p^6} 3s^2 3p^m \mathbf{3d^k} + e \longrightarrow 1s^2 2s^2 \mathbf{2p^5} 3s^2 3p^m \mathbf{3d^{k+1} nl}$$

$$1s^2 2s^2 \mathbf{2p^6} 3s^2 3p^m \mathbf{3d^k} + e \longrightarrow 1s^2 2s^2 \mathbf{2p^5} 3s^2 3p^m \mathbf{3d^k 4l nl'}$$

$$1s^2 \mathbf{2s^2} 2p^6 3s^2 3p^m \mathbf{3d^k} + e \longrightarrow 1s^2 \mathbf{2s} 2p^5 3s^2 3p^m \mathbf{3d^{k+1} nl}$$

He-like lines and satellites

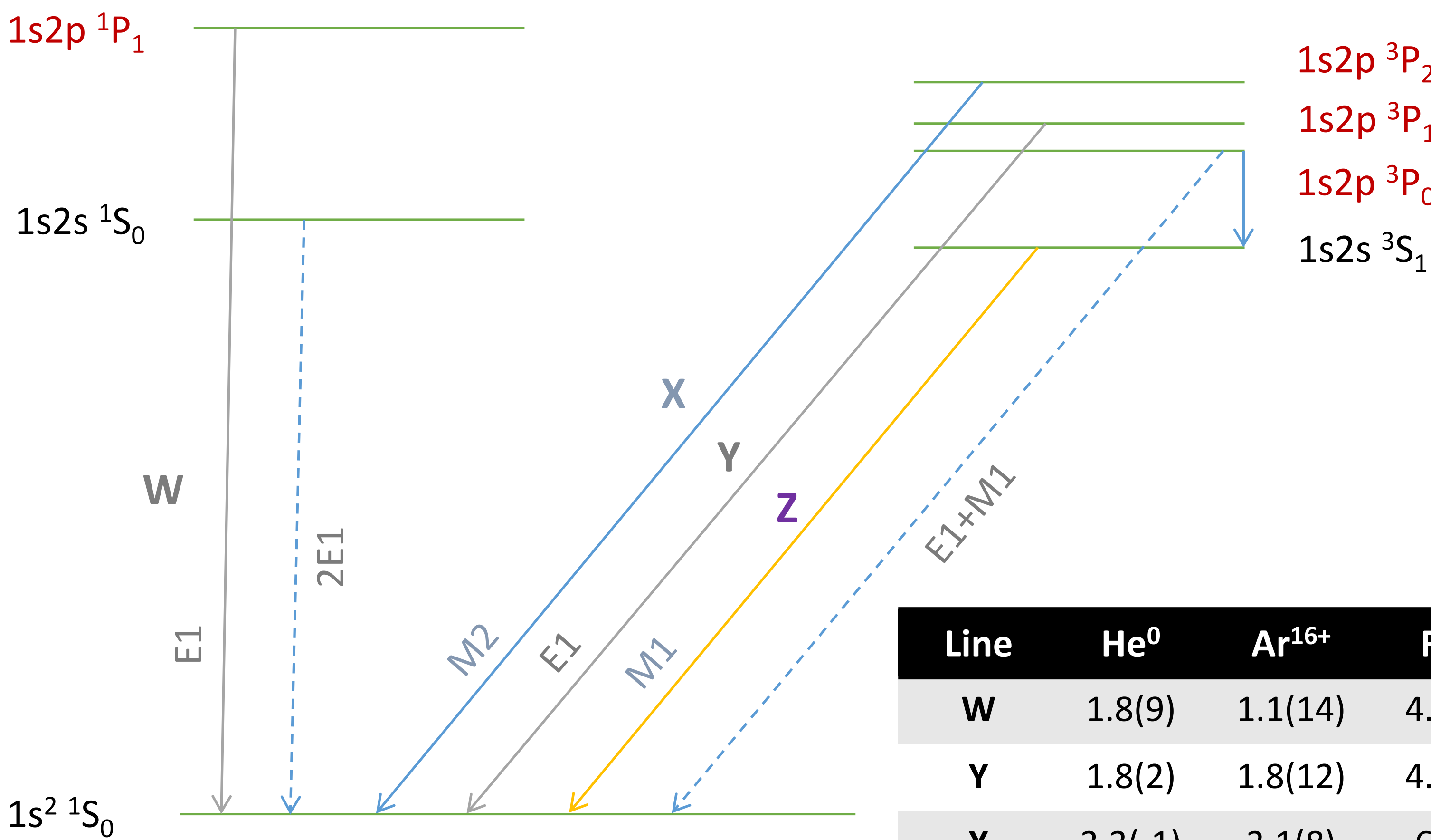


O.Marchuk et al, J Phys B 40, 4403 (2007)

Energy levels in He-like Ar

- Ground state: 1s2 1S0
- Two subsystems of terms
  - Singlets 1snl 1L, J=l (example 1s3d 1D2)
  - Triplets 1snl 3L, J=l-1,l,l+1 (example 1s2p 3P0,1,2)
- Radiative transitions within each subsystem are strong, between systems depend on Z

He-like Ar Levels and Lines



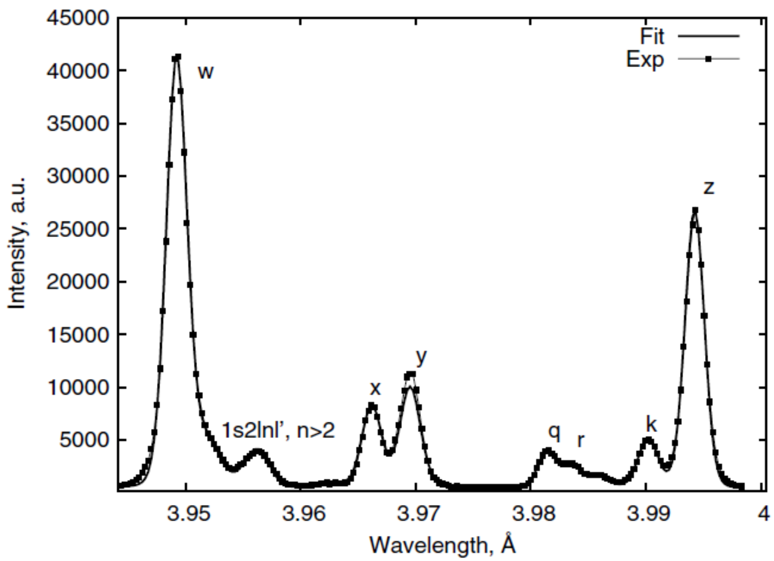
Line	He^0	Ar^{16+}	Fe^{25+}	Kr^{34+}
W	1.8(9)	1.1(14)	4.6(14)	1.5(15)
Y	1.8(2)	1.8(12)	4.4(13)	3.9(14)
X	3.3(-1)	3.1(8)	6.5(9)	9.3(10)
Z	1.3(-4)	4.8(6)	2.1(8)	5.8(9)

National Institute of Standards and Technology

Z-scaling of A's

- **W**[E1]: $A(1s^2\ {}^1S_0 - 1s2p\ {}^1P_1) \propto Z^4$
- **Y**[E1]: $A(1s2\ {}^1S_0 - 1s2p\ {}^3P_1)$
  - $\propto Z^{10}$ for low Z
  - $\propto Z^8$ for large Z
  - $\propto Z^4$ for very large Z
- **X**[M2]: $A(1s^2\ {}^1S_0 - 1s2p\ {}^3P_2) \propto Z^8$
- **Z**[M1]: $A(1s^2\ {}^1S_0 - 1s2s\ {}^3S_1) \propto Z^{10}$

1s2lnl satellites



$$1s^2 + e \leftrightarrow 1s2l2l'$$

- 1l2l2l'
  - $1s2s^2$: $^2S_{1/2}$
  - 1s2s2p:
    - $1s2s2p(^1P)\ ^2P_{1/2,3/2}$
    - $1s2s2p(^3P)\ ^2P_{1/2,3/2}$; $^4P_{1/2,3/2,5/2}$
  - $1s2p^2$
    - $1s2p^2(^1D)\ ^2D_{3/2,5/2}$
    - $1s2p^2(^3P)\ ^2P_{1/2,3/2}$; $^4P_{1/2,3/2,5/2}$
    - $1s2p^2(^1S)\ ^2S_{1/2}$
- 1s2lnl'
  - Closer and closer to W
  - Only 1s2l3l can be reliably resolved
  - Contribute to W line profile