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

Yuri Ralchenko

National Institute of Standards and Technology

Gaithersburg, MD 20899, USA

National Institute of Standards and Technology

Why is atomic structure important for plasmas?

Most of the relevant physics is inside this matrix element

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

final state

interaction operator

initial state

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

NIST
National Institute of Standards and Technology

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, HAS, YR,…

Units

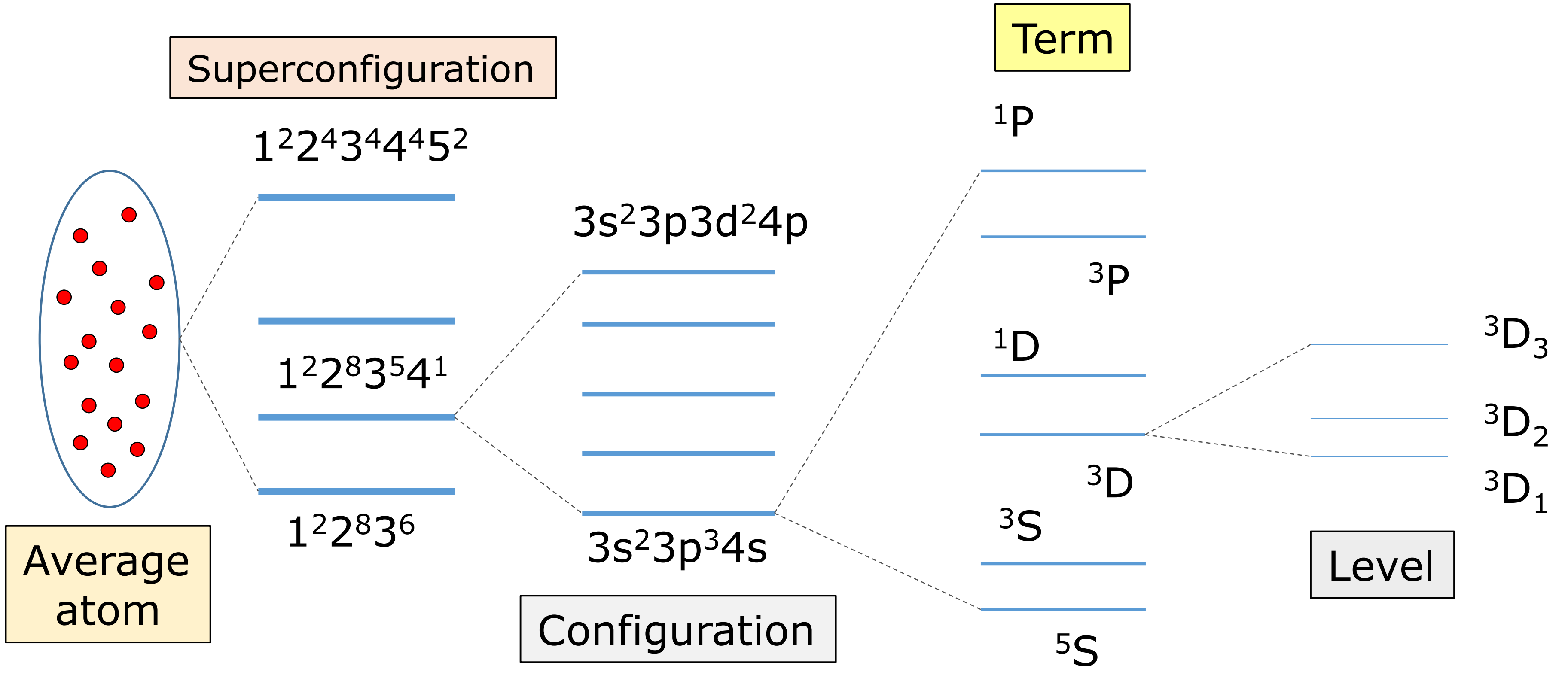
- Energy
  - 1 Ry = 13.61 eV = 109 737 cm^{-1} (ionization energy of H)
  - 1 eV = 8065.5447 cm^{-1}
- Length
  - $a_0 = 5.29 \cdot 10^{-9}$ cm = 0.529 Å (radius of H atom)
- Area (cross section)
  - $\pi a_0^2 = 8.8 \cdot 10^{-17}$ cm^2 (area of H atom)

- **New SI: 2018**

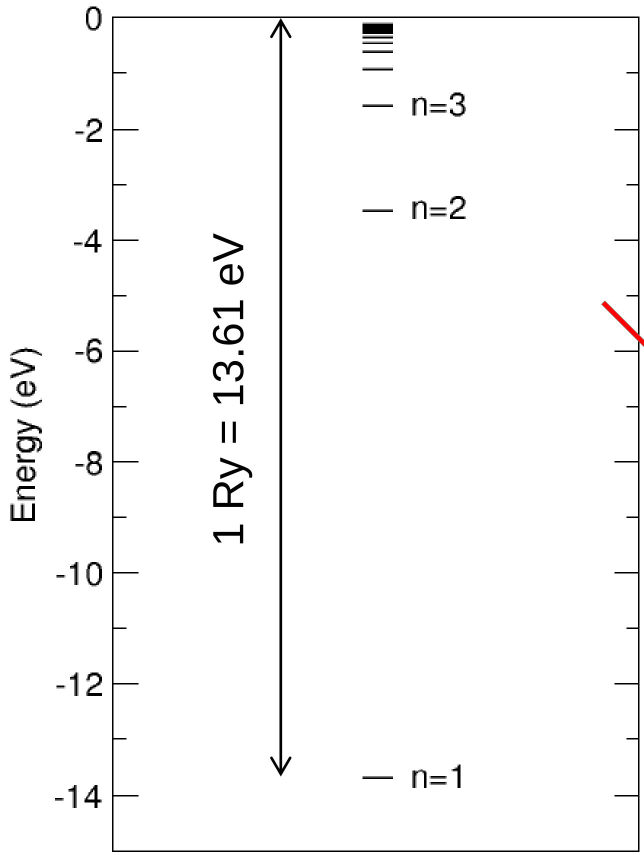
http://physics.nist.gov/cuu/Units/

NIST National Institute of Standards and Technology

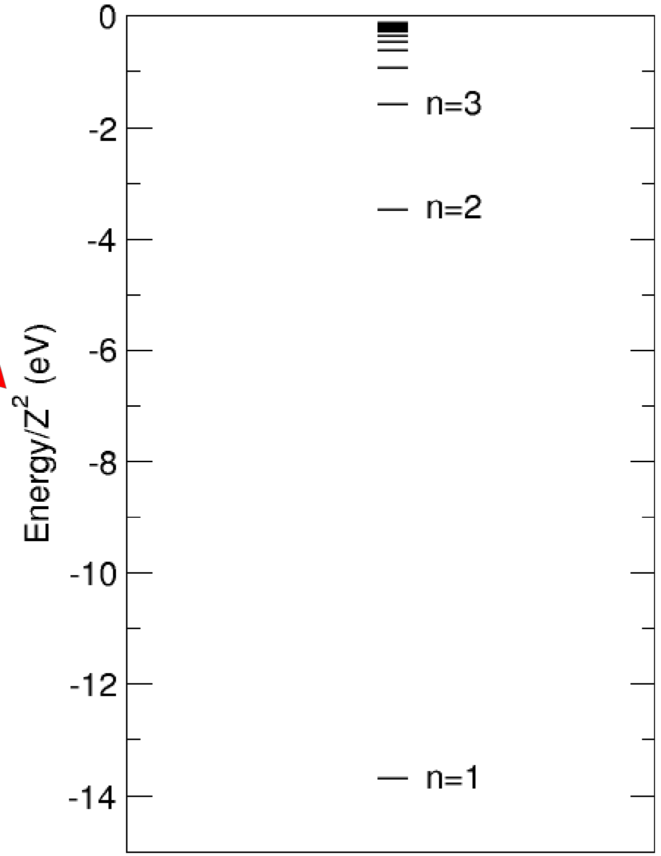
16-electron ion (S-like)



Thank you Nature, for Hydrogen and H-like ions



Hydrogen atom



H-like ion

Radius: $a_n \sim \frac{n^2}{Z}$

Energy:

$$E_n = -\frac{Z^2 Ry}{n^2}$$

There's no hydrogen atom for plasmas…

Exact quantum numbers for general atomic states

- Total angular momentum
- Parity = $(-1)^{\sum_i l_i}$

- Everything else (*L*,*S*,…) is **not exact**!

Complex atoms (non-relativistic)

We (generally) 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 cannot be solved exactly…

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* $\Phi(\gamma_j LS)$ (accounting also for antisymmetry): ***n,l***
- Assume that the *atomic state function* is a linear combination of CSFs: $\Psi(\gamma LS) = \sum_j^M c_j \Phi(\gamma_j LS)$
- Solve Schrodinger eq for mixing coefficients:
  - $(\hat{H} - E\hat{I})\hat{c} = 0, H_{ij} = \langle \Phi(\gamma_i LS) | H | \Phi(\gamma_j LS) \rangle$
- Include other effects (perturbation theory)

NIST
National Institute of Standards and Technology

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)

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

NIST
National Institute of Standards and Technology

Relativistic notations

	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$
	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

Atomic Structure Methods and Codes

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

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

Z_c-scaling of one-electron energies

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

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

$$E = E_0 \boldsymbol{Z_c^2} + E_1 \boldsymbol{Z_c} + E_2 + E_3 \boldsymbol{Z_c^{-1}} + \ldots$$

non-relativistic

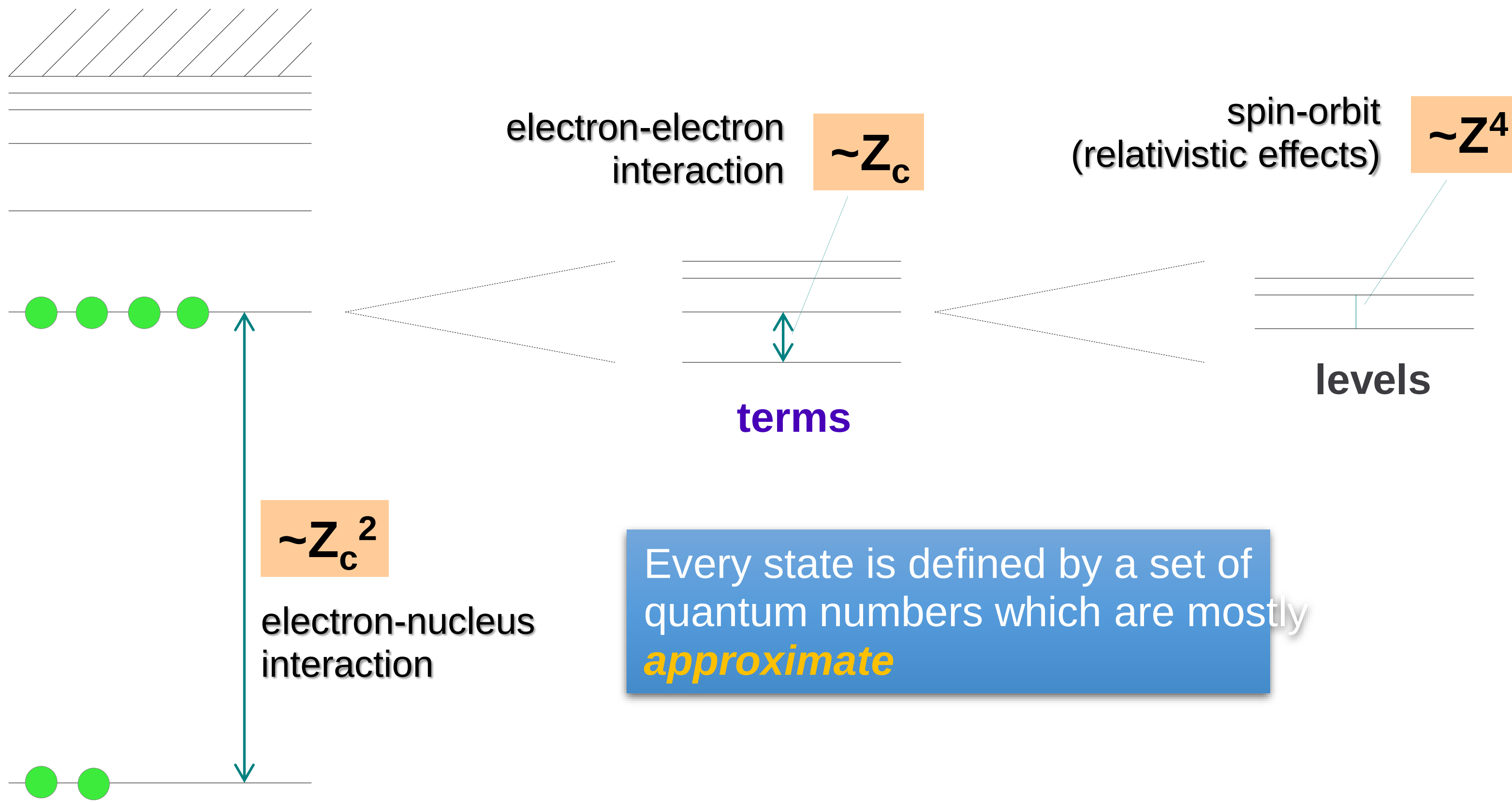
$$E_0 = -\frac{1}{n^2}$$ hydrogenic term

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

Of course, relativistic effects slightly modify this dependence but the general trend remains valid

NIST National Institute of Standards and Technology

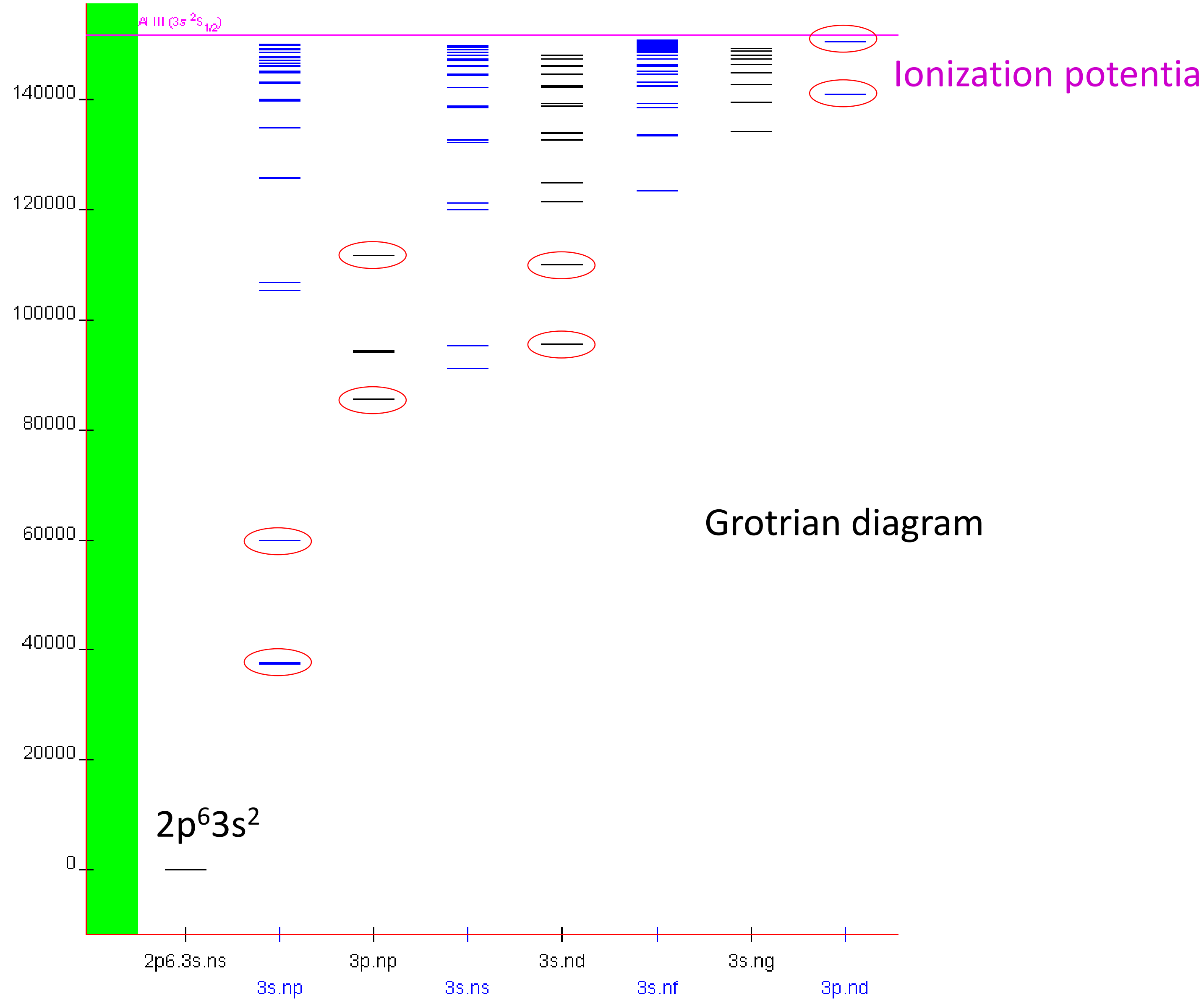
Energy structure of an ion



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

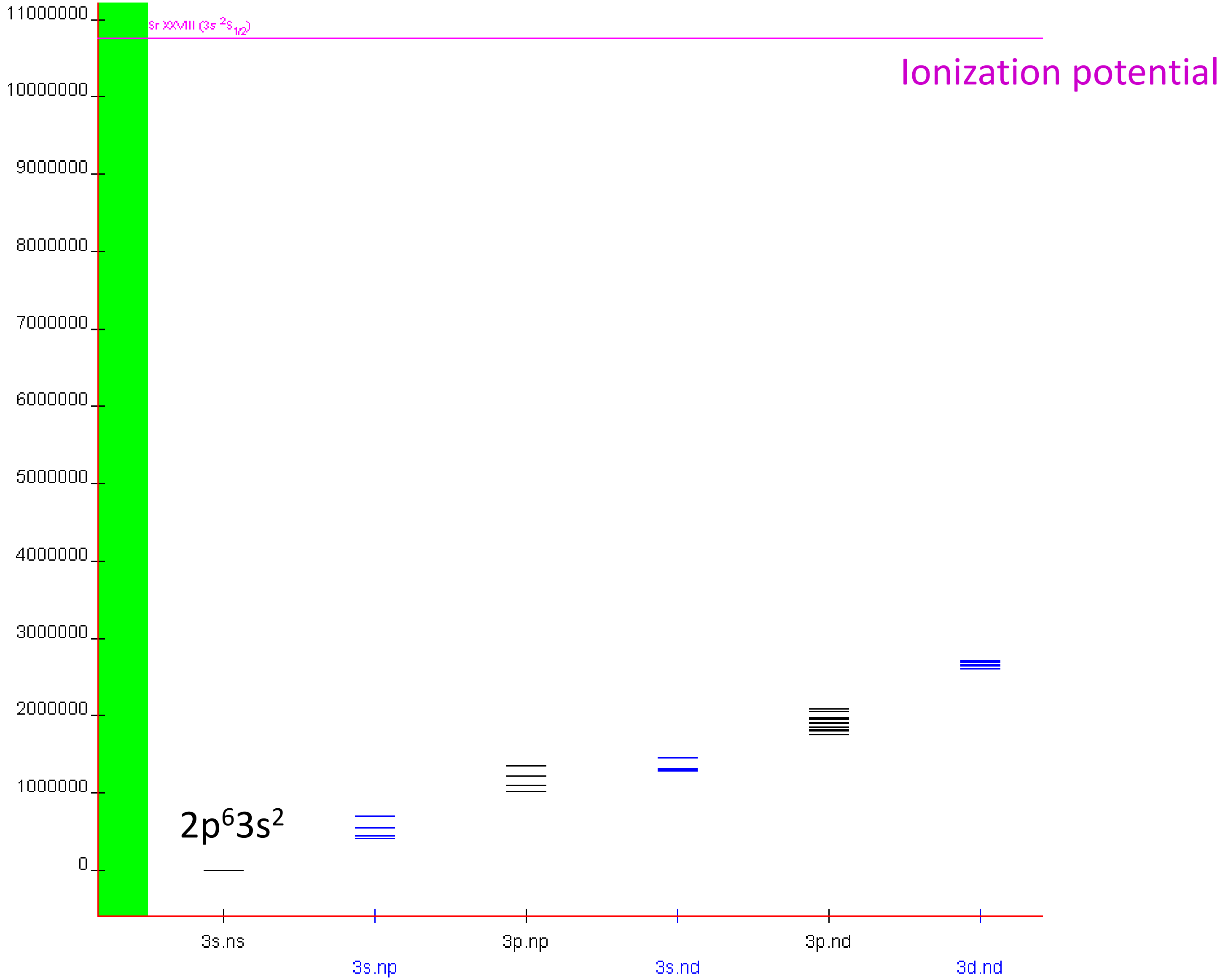
Electrons are grouped into shells *nl*
(K *n*=1, L *n*=2, M *n*=3,...)
producing **configurations (or even superconfigurations)**

Mg-like Al II: *3l3l'*



NIST
National Institute of Standards and Technology

Mg-like Sr XXVII: *3l3l'*



NIST
National Institute of Standards and Technology

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

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

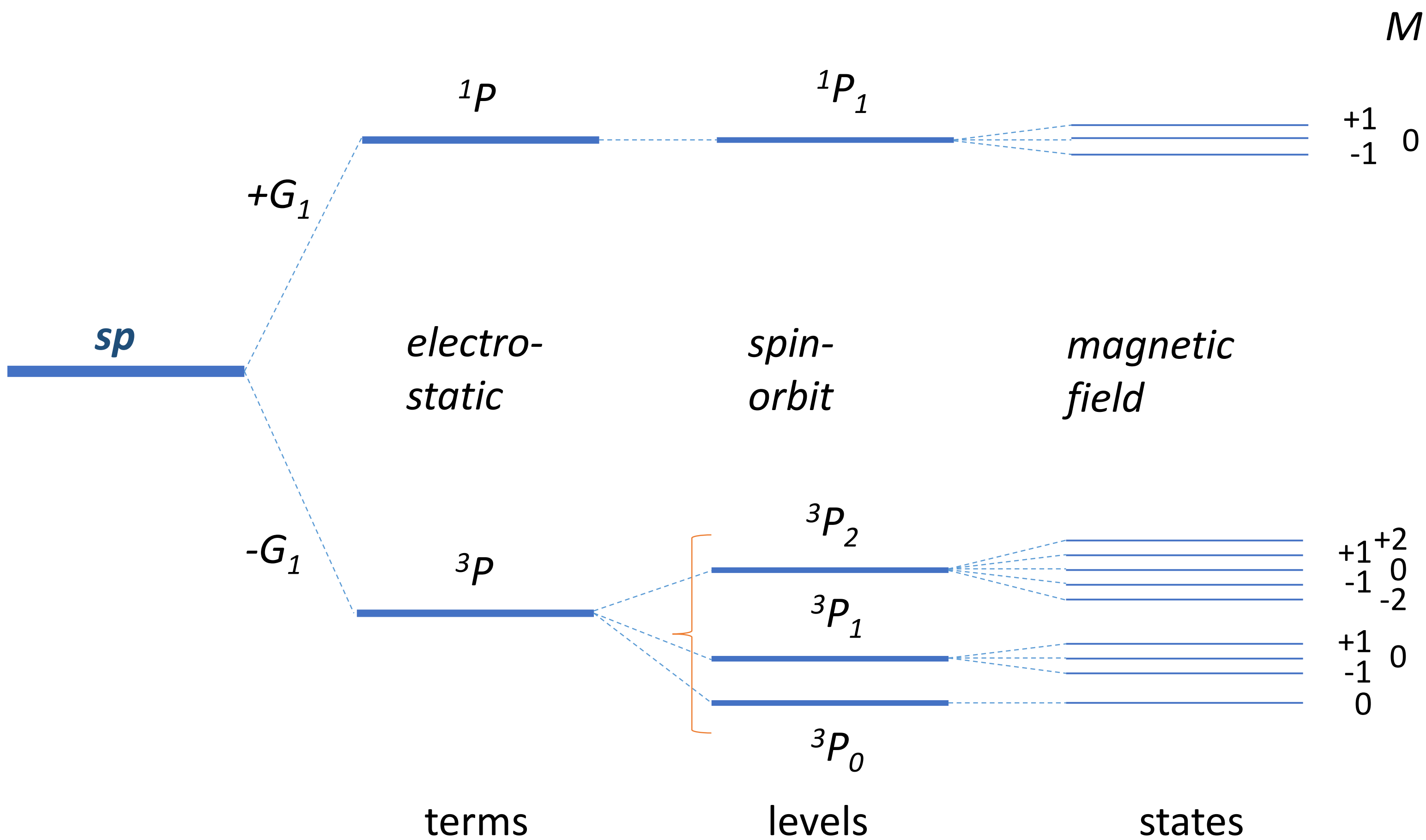
$\tilde{Z}$: effective nuclear charge (for penetrating orbits) = ***Z-n*** for *np* orbitals

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

Types of coupling

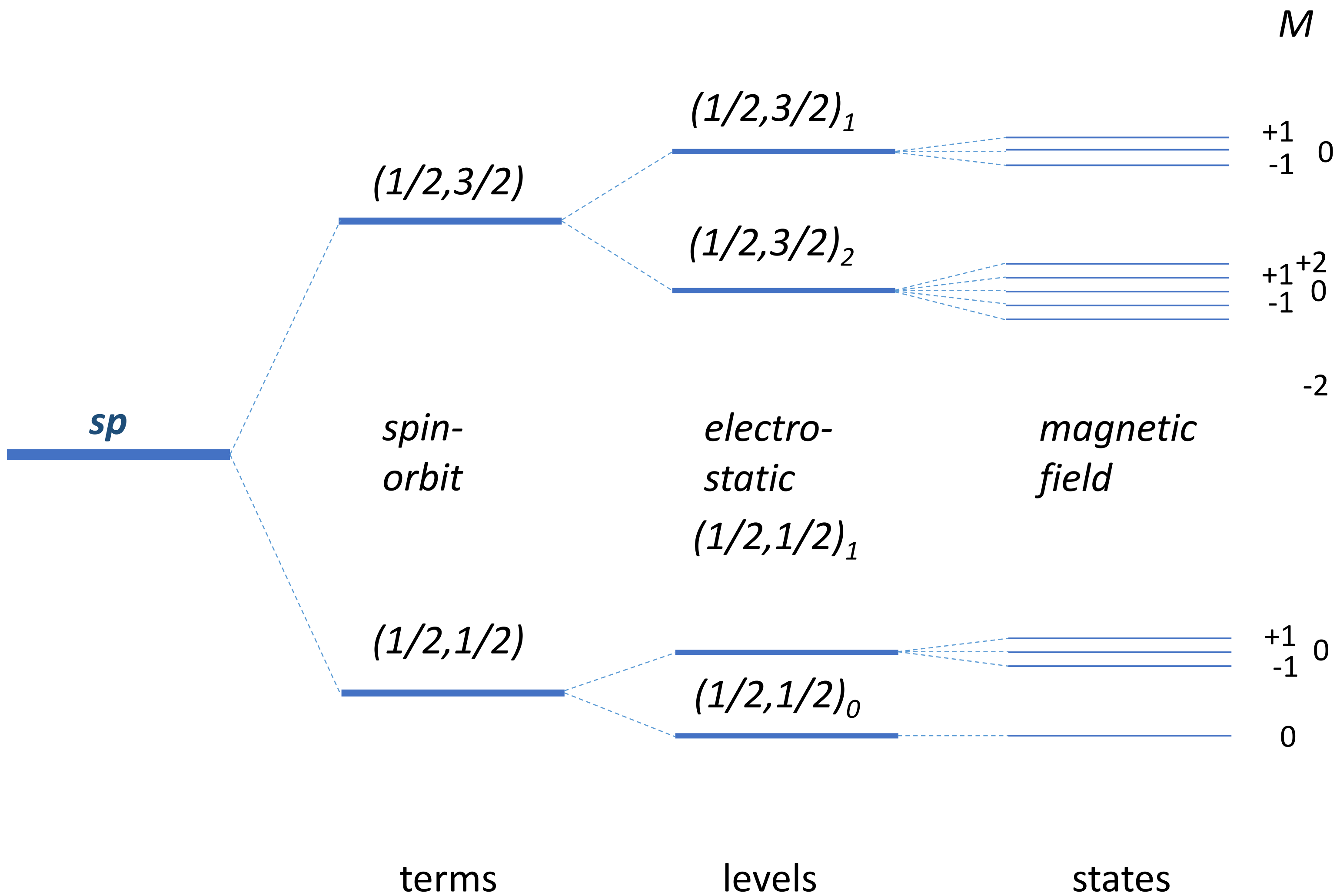
- **LS coupling**: *electron-electron* » *spin-orbit*
  - light elements $\vec{L} = \vec{l}_1 + \vec{l}_2 + \ldots, \quad \vec{S} = \vec{s}_1 + \vec{s}_2 + \ldots, \quad \vec{J} = \vec{L} + \vec{S}$
- **jj coupling**: *spin-orbit* » *electron-electron*
  - heavy elements $\vec{j}_1 = \vec{l}_1 + \vec{s}_1,\ \vec{j}_2 = \vec{l}_2 + \vec{s}_2, \ldots \quad \vec{J} = \vec{j}_1 + \vec{j}_2 + \ldots$
  - *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 stronger
- Other types of couplings exist

Configuration *sp: LS* coupling (*LSJ*)



NIST
National Institute of Standards and Technology

Configuration *sp: jj* coupling



National Institute of Standards and Technology

Intermediate coupling for *sl*:

Non-central: $E(LS) = \sum_k f_k F_k + \sum_k f_k G_k$

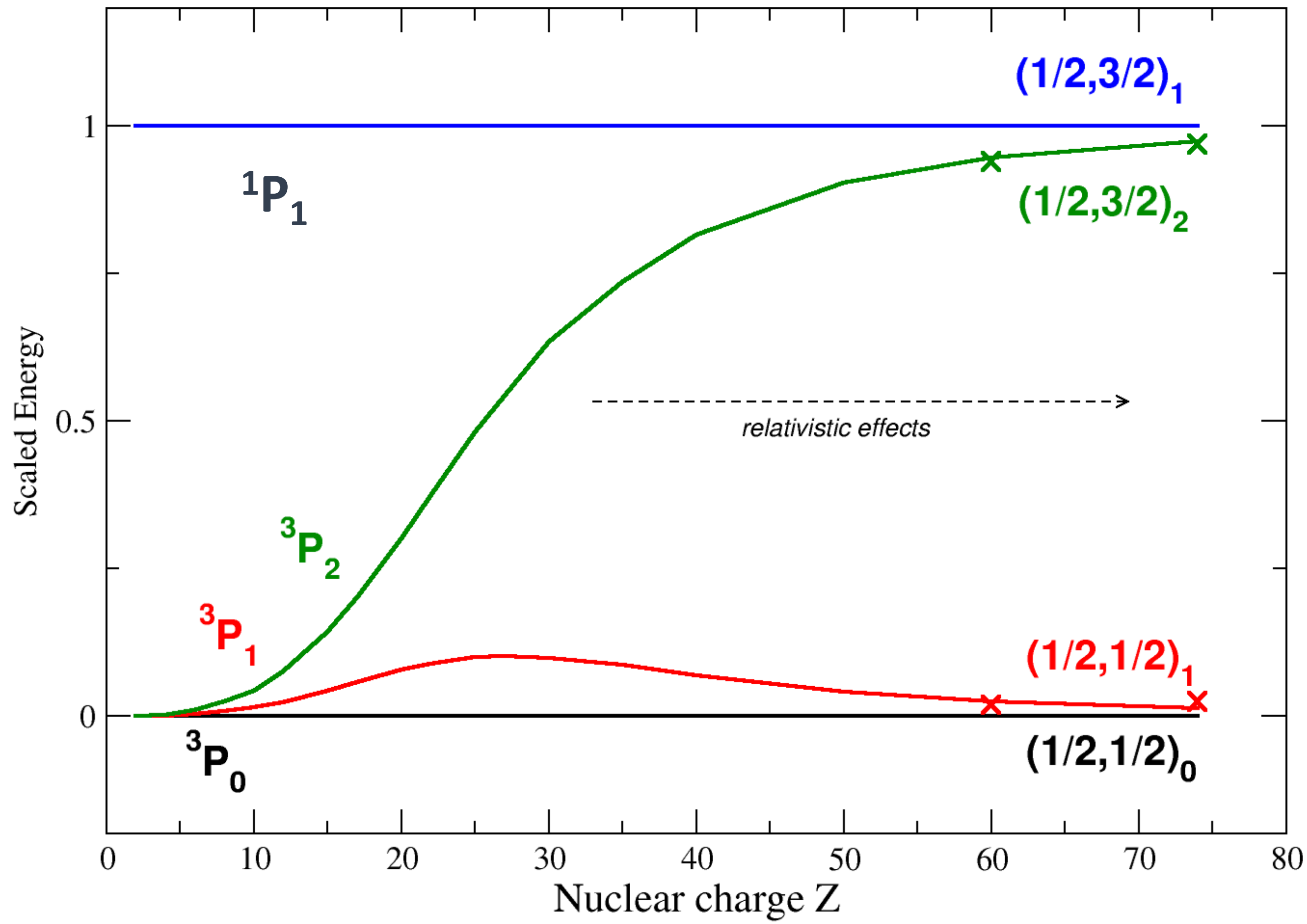
$F_k(nl,n'l')$: direct Coulomb (*ll* interactions)
$G_k(nl,n'l')$: exchange Coulomb (*ss* interactions)

$$^3L_{l+1} \quad = F_0 - G_l + \tfrac{1}{2} l \zeta_{nl}$$

$$\left.\begin{array}{l} ^1L_l \\ ^3L_l \end{array}\right\} = F_0 - \tfrac{1}{4}\zeta_{nl} \pm \sqrt{\left(G_l + \frac{1}{4}\zeta_{nl}\right)^2 + \frac{1}{4} l(l+1)\zeta_{nl}^2}$$

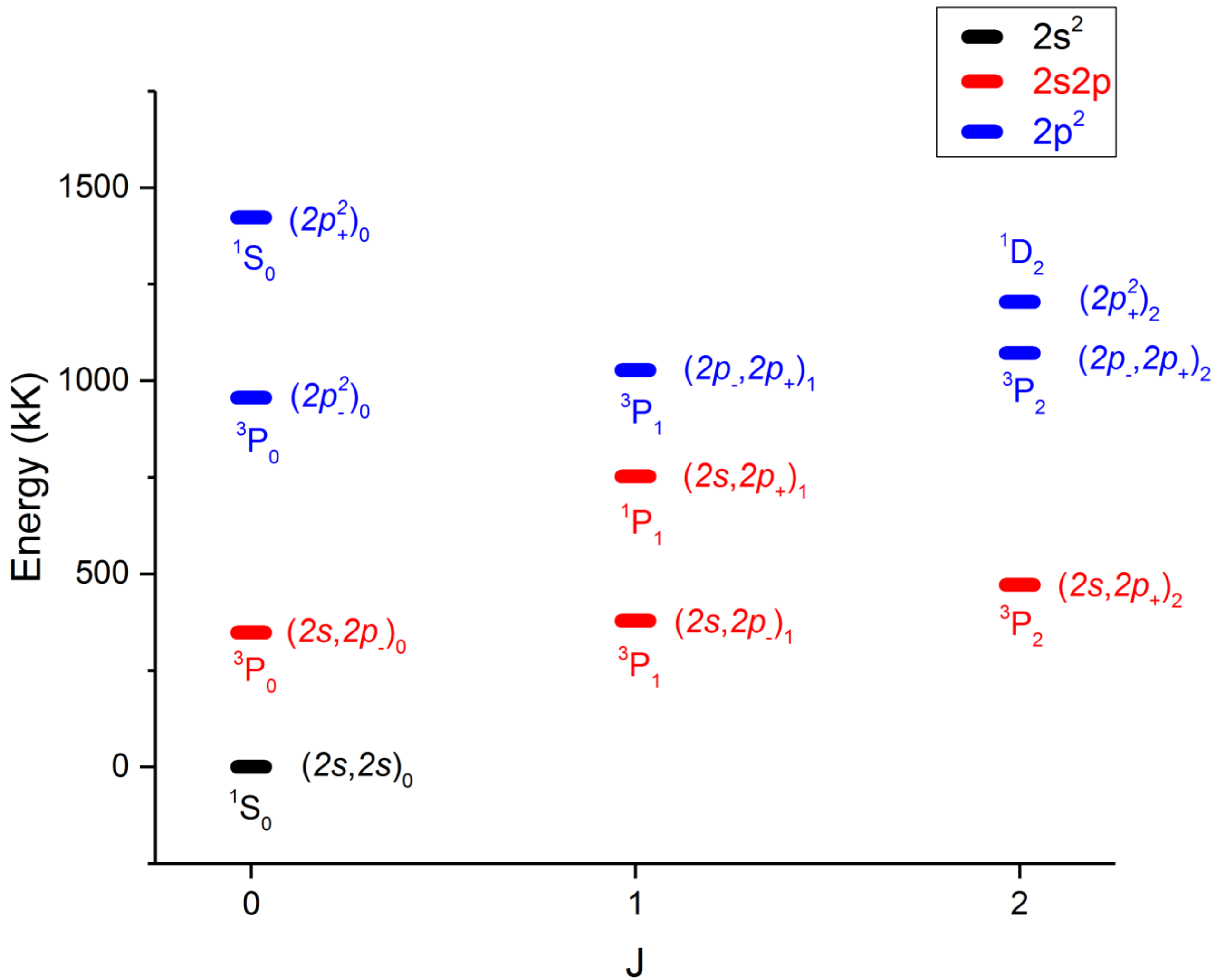
$$^3L_{l-1} \quad = F_0 - G_l - \tfrac{1}{2}(l+1)\zeta_{nl}$$

From LS to jj: 1*s*2*p* in He-like ions



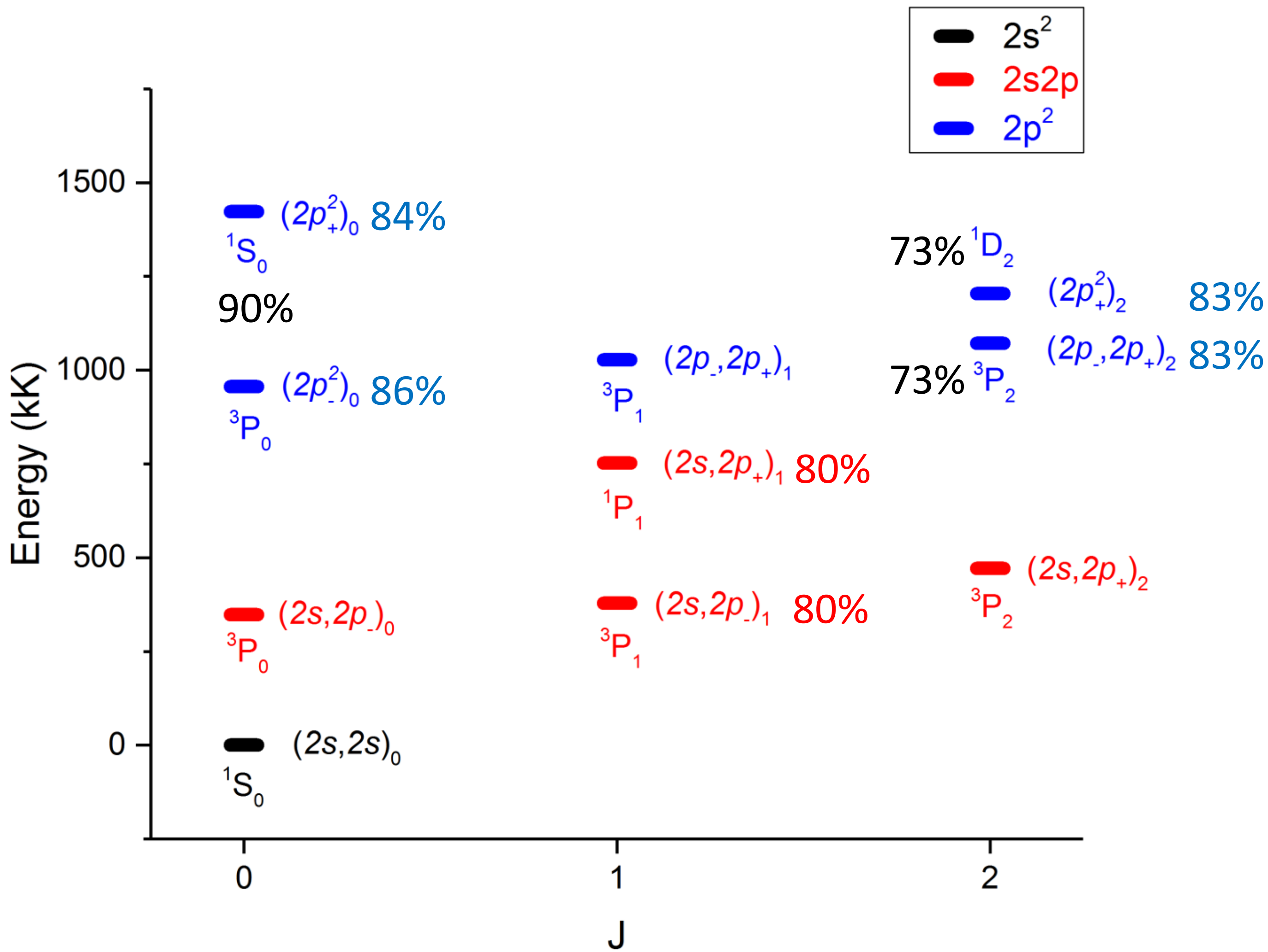
National Institute of Standards and Technology

Be-like Fe XXIII: n=2 levels



NIST
National Institute of Standards and Technology

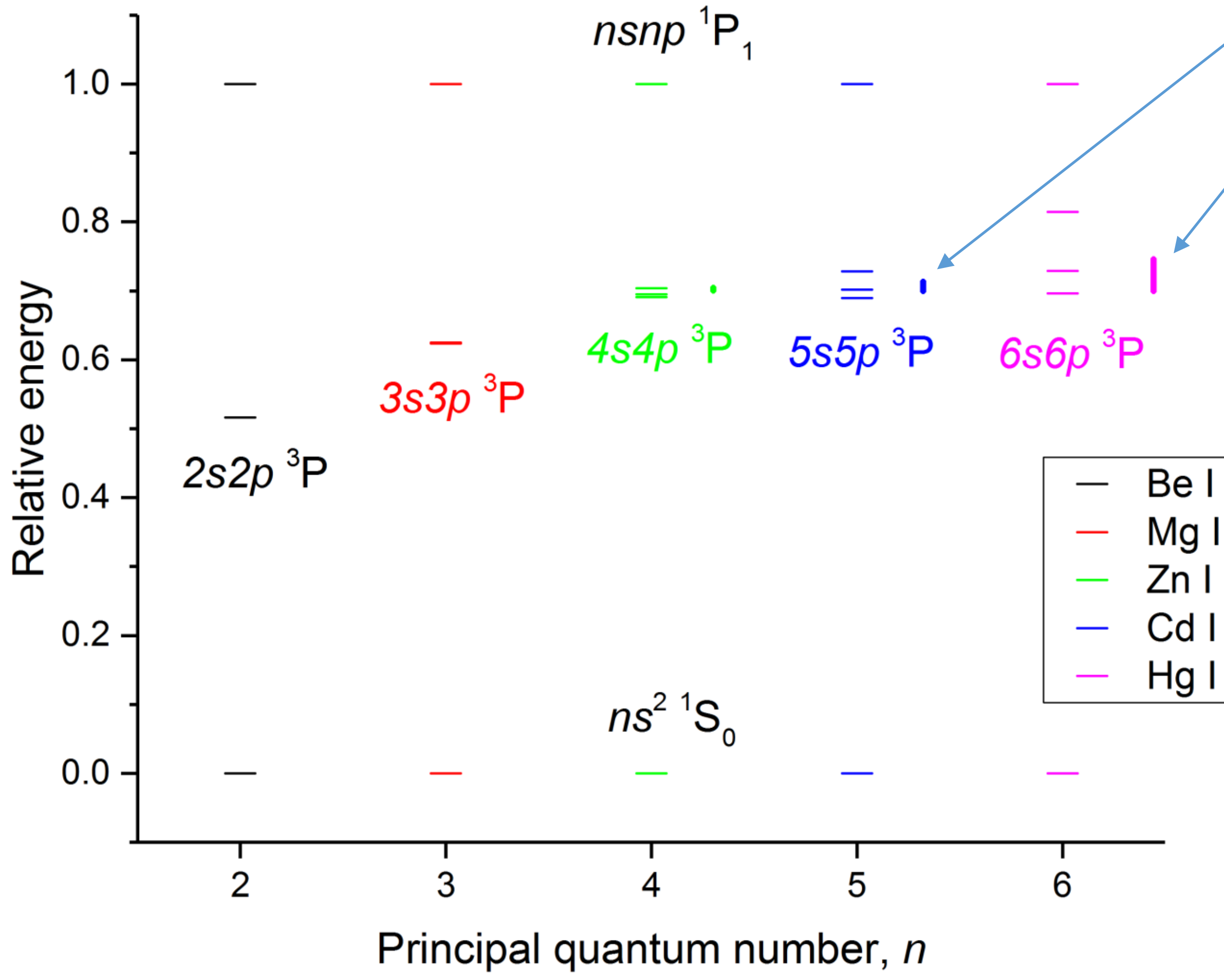
Be-like Fe XXIII: n=2 levels



Spin-orbit interaction does depend on nuclear charge!

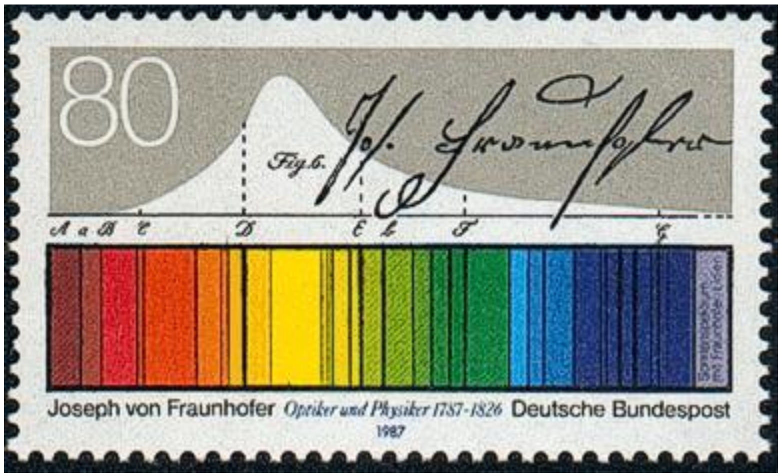
$$\zeta_{nl} = \frac{Ry\ \alpha^2\ Z_c^2 \tilde{Z}^2}{n^{*3}\ l\ (l+1/2)\ (l+1)}$$

Lande formula

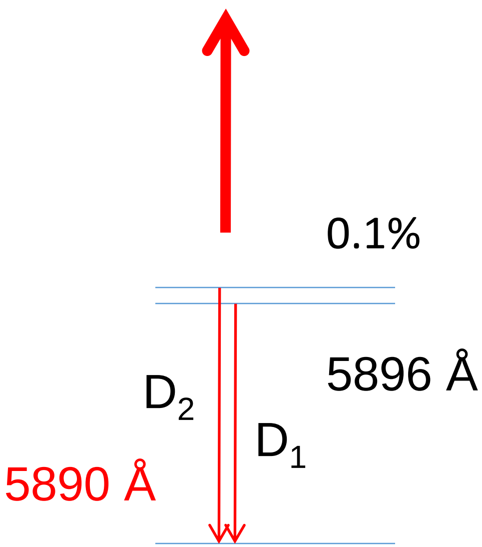


NIST
National Institute of Standards and Technology

Na-like doublet in highly-charged ions

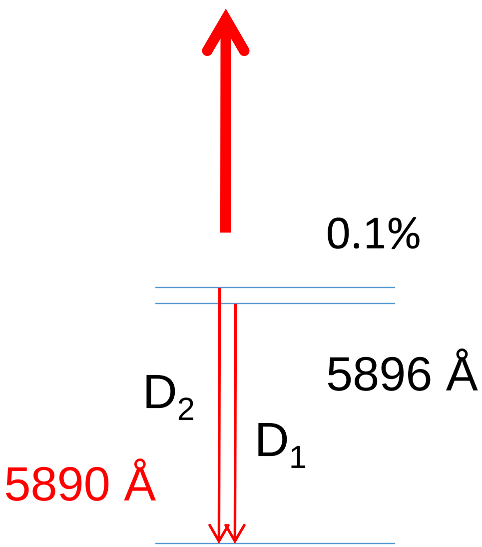


Fraunhofer absorption lines in the solar spectrum

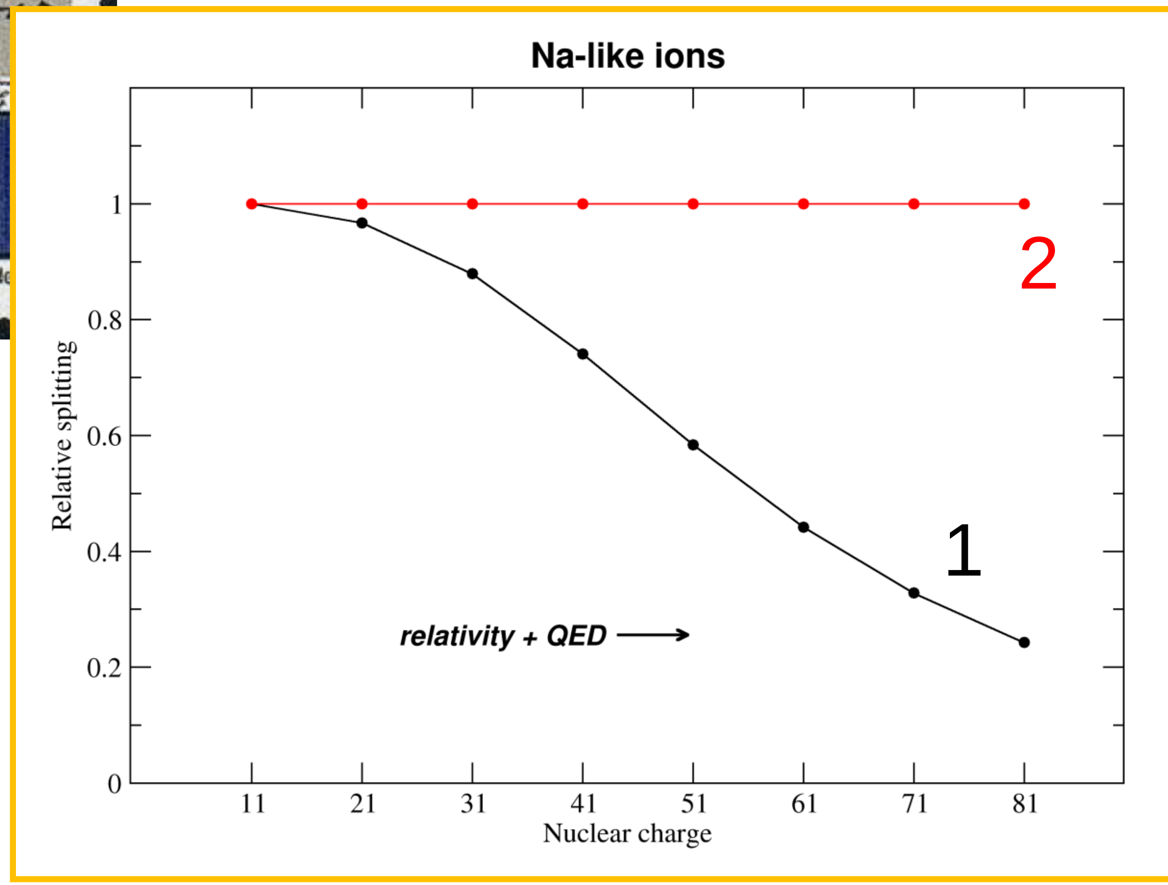


National Institute of Standards and Technology

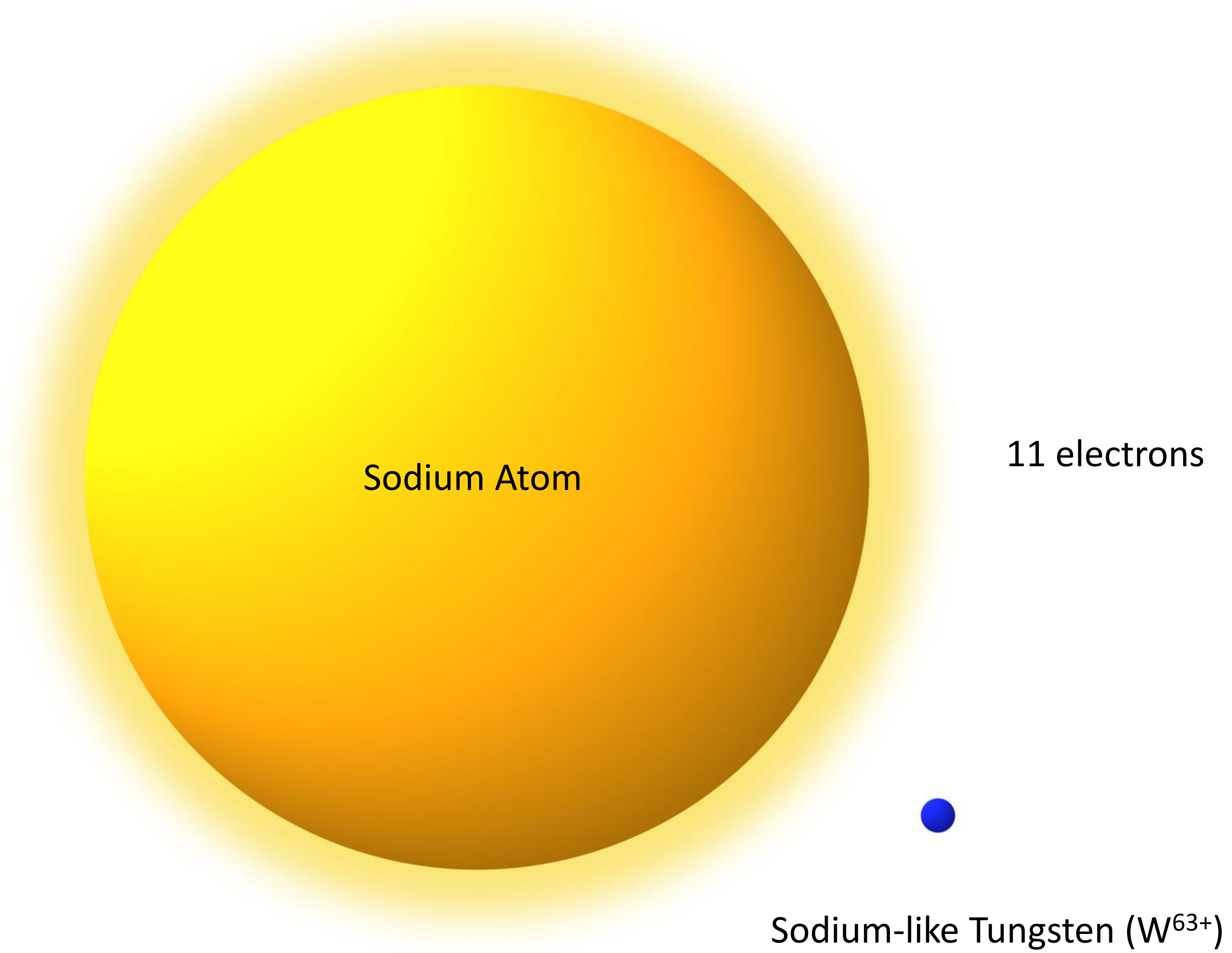
Na-like doublet in highly-charged ions: 3s-3p



Relative splitting $3p_{1/2}$-$3p_{3/2}$

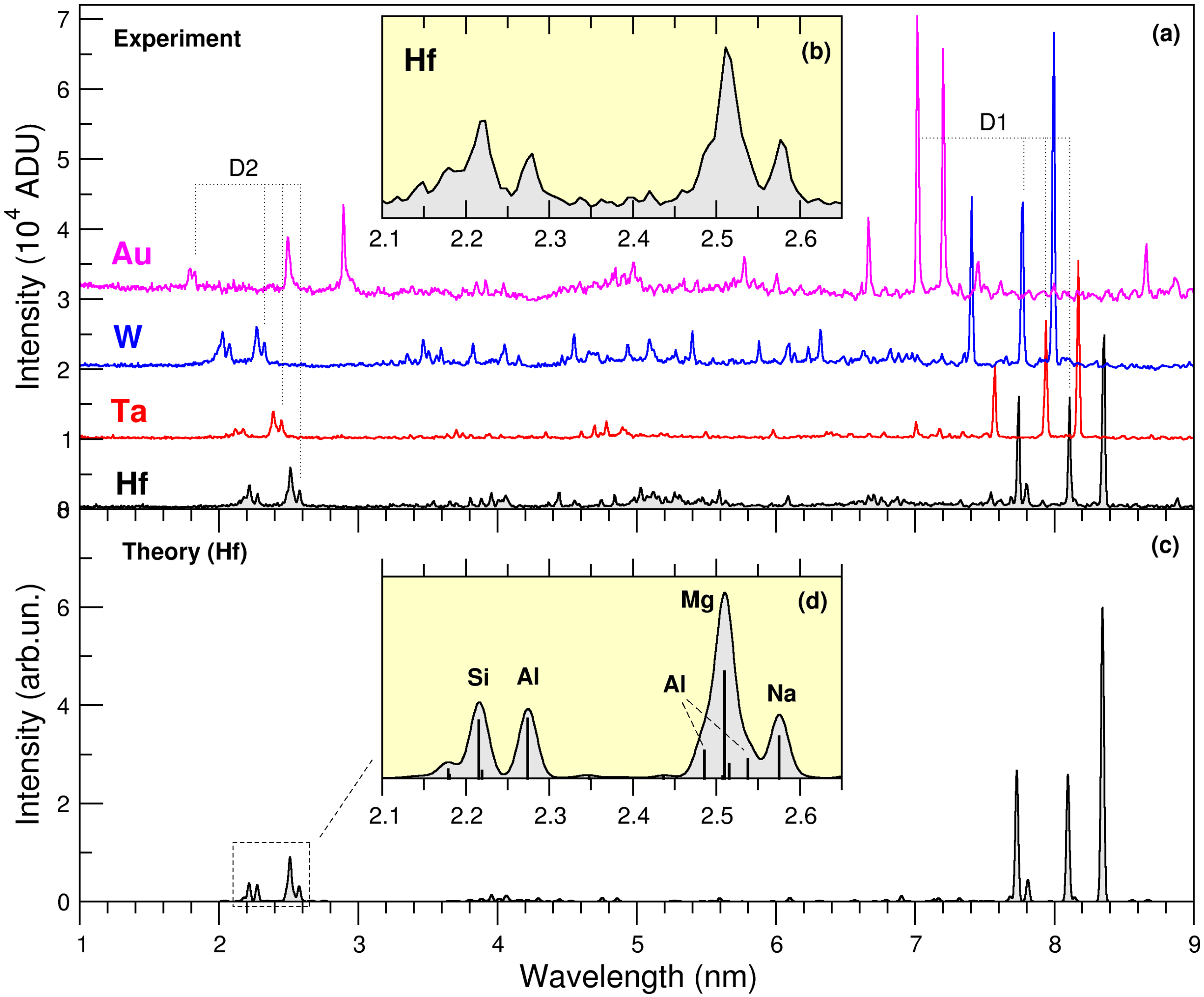


Little Ions With a Big Charge



National Institute of Standards and Technology

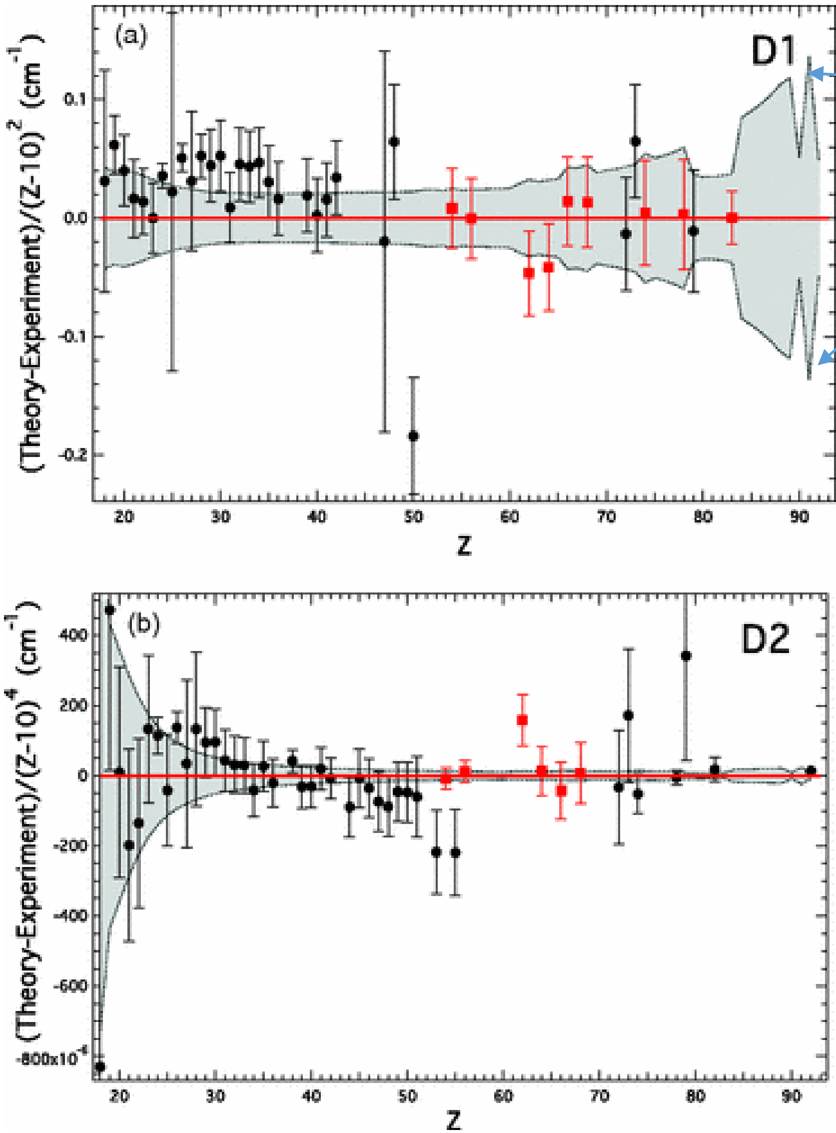
D-doublet in Na-like W, Hf, Ta, and Au



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

National Institute of Standards and Technology

Comparison of transition energies: RMBPT+QED vs experiment



Uncertainties of the most advanced calc

Red points:
NIST EBIT
(electron beam ion trap)

National Institute of Standards and Technology

State mixing in intermediate coupling

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

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

s-o coupling increases with Z $\Rightarrow$
change of coupling scheme

Other types of coupling

- jK coupling
  - **Excited states in neutral noble gases**
  - ***np*⁵*n*'*l***
    - Hole in np^6 with a strong spin-orbit: j_c=1/2 or j_c=3/2
    - $\vec{j_c} + \vec{l} = \vec{K}$
    - $\vec{K} + \vec{s} = \vec{J}$ (total angular momentum)
    - Example: $\boldsymbol{2p^5 3p}$ **in Ne I**
      - j_c=1/2: K=1/2,3/2
        - J=0,1; 1,2
      - j_c=3/2: K=1/2,3/2, 5/2
        - J=0,1; 1,2; 2,3
- If the final s-K interaction is the weakest, then doublets are produced

National Institute of Standards and Technology

Hund's rules (equivalent electrons, LS)

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

C I

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

NIST
National Institute of Standards and Technology

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

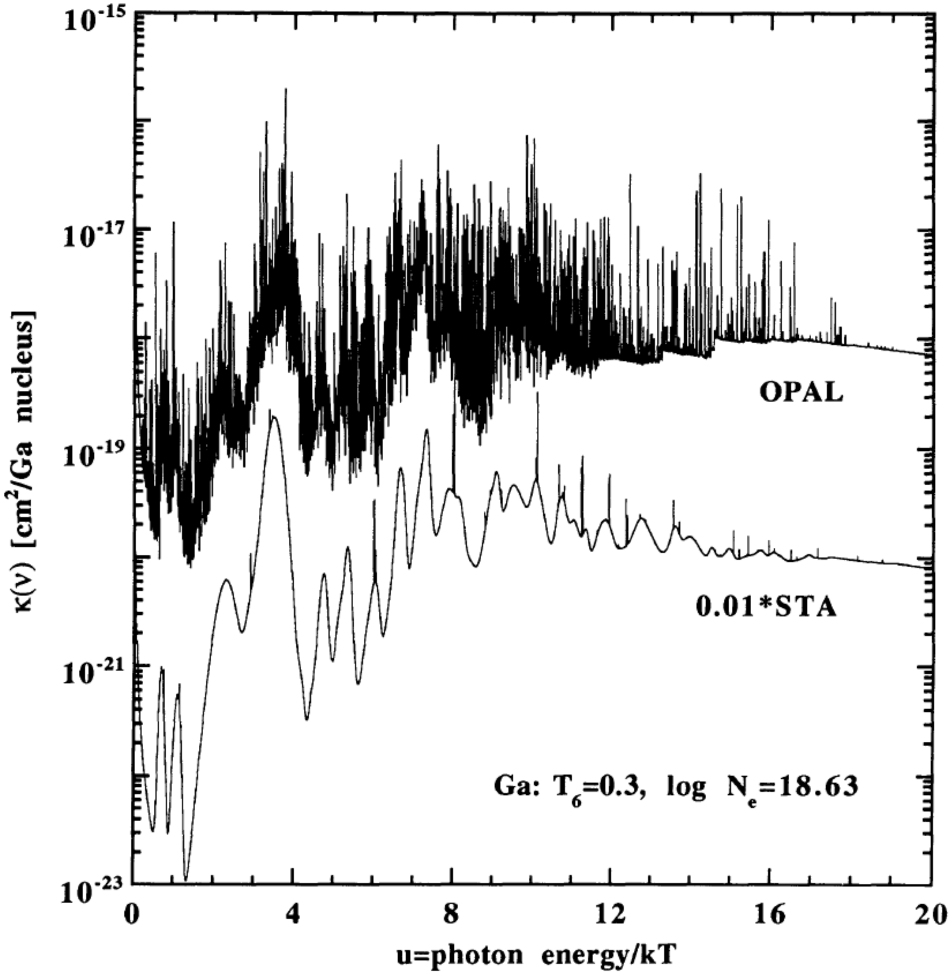
Instead of producing millions or billions of lines, SCs are used to calculate Super Transition Arrays → Statistical methods

FLYCHK, CRETIN!

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

NIST
National Institute of Standards and Technology

Superconfigurations vs. detailed level accounting



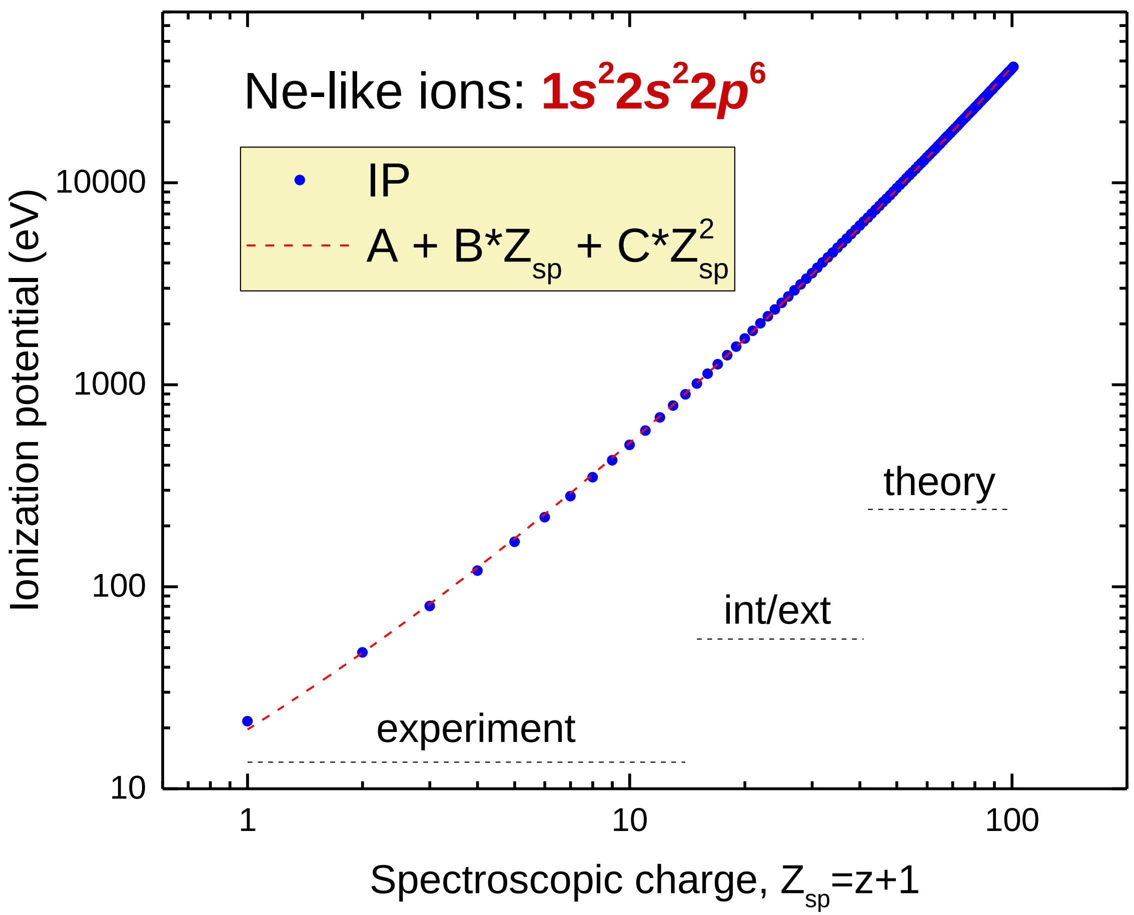
Ga: photoabsorption cross section

Iglesias et al (1995)

NIST
National Institute of Standards and Technology

Ionization potentials

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



Ground state configurations (2004)

Series	Z	Configuration	J
Ru	44	[Kr]$4d^7 5s$	5
	45–118	[Kr]$4d^8$	4
Rh	45	[Kr]$4d^8\ 5s$	9/2
	46–118	[Kr]$4d^9$	5/2
Pd	46–118	[Kr]$4d^{10}$	0
Ag	47–118	[Kr]$4d^{10}5s$	1/2
Cd	48–118	[Kr]$4d^{10}5s^2$	0
In	49–118	[Kr]$4d^{10}5s^2 5p$	1/2
Sn	50–118	[Kr]$4d^{10}5s^2 5p^2$	0
Sb	51–118	[Kr]$4d^{10}5s^2 5p^3$	3/2
Te	52–118	[Kr]$4d^{10}5s^2 5p^4$	2
I	53–118	[Kr]$4d^{10}5s^2 5p^5$	3/2
Xe	54–118	[Kr]$4d^{10}\ 5s^2 5p^6$	0
Cs	55–56	[Xe]$6s$	1/2
	57	[Xe]$5d$	3/2
	58–118	[Xe]$4f$	5/2
Ba	56	[Xe]$6s^2$	0
	57	[Xe]$5d^2$	2
	58–118	[Xe]$4f^2$	4
La	57	[Xe]$5d6s^2$	3/2
	58	[Xe]$4f5d^2$	7/2
	59–118	[Xe]$4f^3$	9/2
Ce	58	[Xe]$4f5d6s^2$	4
	59	[Xe]$4f^3 6s$	4
	60–118	[Xe]$4f^4$	4
Pr	59	[Xe]$4f^3 6s^2$	9/2
	60	[Xe]$4f^4 6s$	7/2
	61–118	**[Xe]$4f^5$**	**5/2**

Series	*Z*	Configuration	*J*
Ru	44	$[Kr]4d^7 5s$	5
	45–118	$[Kr]4d^8$	4
Rh	45	$[Kr]4d^8\ 5s$	9/2
	46–118	$[Kr]4d^9$	5/2
Pd	46–118	$[Kr]4d^{10}$	0
Ag	47–118	$[Kr]4d^{10} 5s$	1/2
Cd	48–118	$[Kr]4d^{10} 5s^2$	0
In	49–118	$[Kr]4d^{10} 5s^2 5p$	1/2
Sn	50–118	$[Kr]4d^{10} 5s^2 5p^2$	0
Sb	51–118	$[Kr]4d^{10} 5s^2 5p^3$	3/2
Te	52–118	$[Kr]4d^{10} 5s^2 5p^4$	2
I	53–118	$[Kr]4d^{10} 5s^2 5p^5$	3/2
Xe	54–118	$[Kr]4d^{10}\ 5s^2 5p^6$	0
Cs	55–56	$[Xe]6s$	1/2
	57	$[Xe]5d$	3/2
	58–118	$[Xe]4f$	5/2
Ba	56	$[Xe]6s^2$	0
	57	$[Xe]5d^2$	2
	58–118	$[Xe]4f^2$	4
La	57	$[Xe]5d6s^2$	3/2
	58	$[Xe]4f5d^2$	7/2
	59–118	$[Xe]4f^3$	9/2
Ce	58	$[Xe]4f5d6s^2$	4
	59	$[Xe]4f^3 6s$	4
	60–118	$[Xe]4f^4$	4
Pr	59	$[Xe]4f^3 6s^2$	9/2
	60	$[Xe]4f^4 6s$	7/2
	61–118	$\mathbf{[Xe]4f^5}$	**5/2**

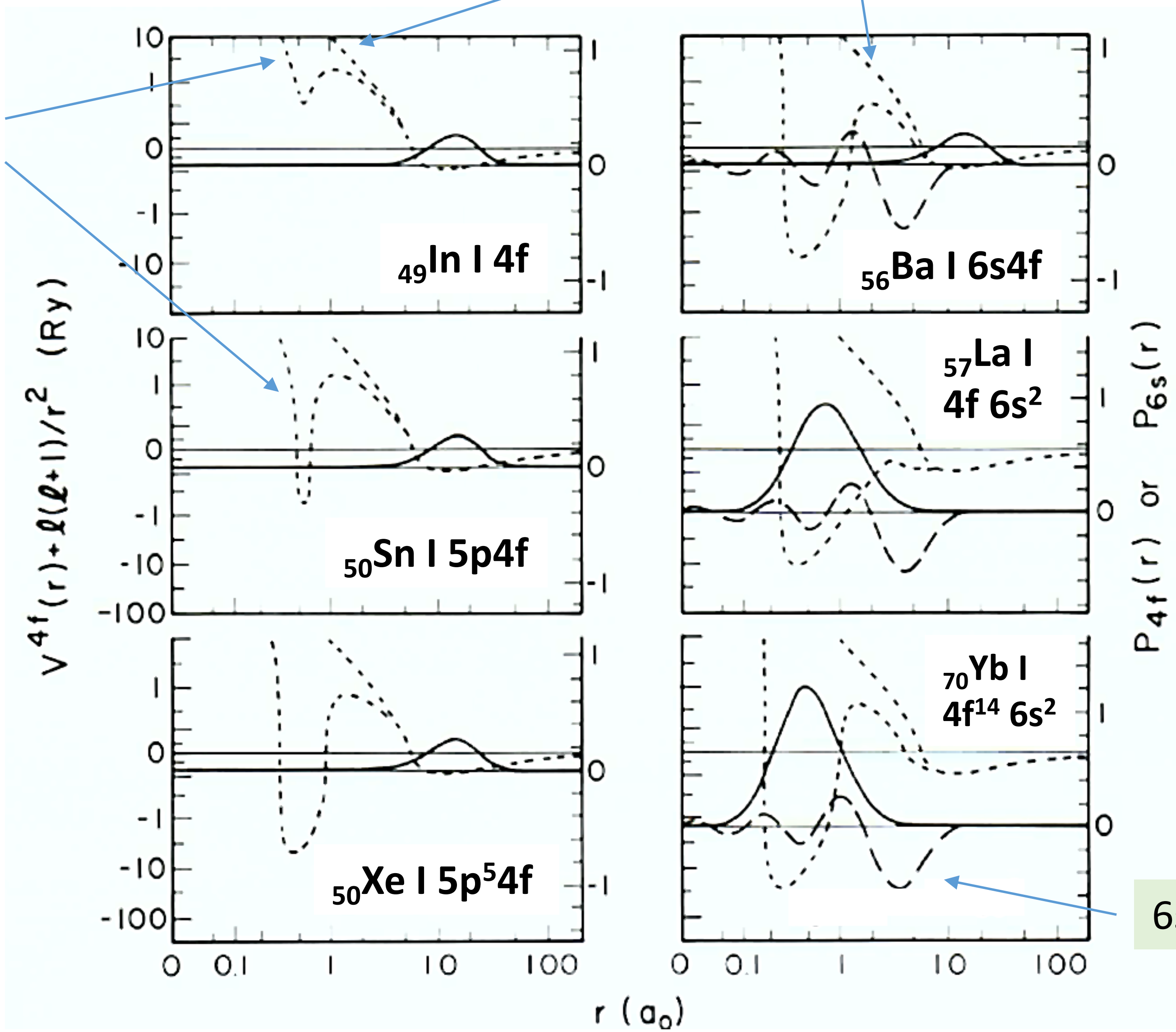
Collapse of f-shells overlooked!

Ground states change many times along these sequences

4f-orbital collapse

$$-\frac{1}{r}+\frac{l(l+1)}{2r^2}$$

effective potential



6s

Orb	Exp Z
3d	20
4d	38
5d	56
4f	57
5f	90
5g	124(th)

Ground state configurations (2004)

Series	Z	Configuration	J
Ru	44	$[Kr]4d^7 5s$	5
	45–118	$[Kr]4d^8$	4
Rh	45	$[Kr]4d^8\ 5s$	9/2
	46–118	$[Kr]4d^9$	5/2
Pd	46–118	$[Kr]4d^{10}$	0
Ag	47–118	$[Kr]4d^{10}5s$	1/2
Cd	48–118	$[Kr]4d^{10}5s^2$	0
In	49–118	$[Kr]4d^{10}5s^2 5p$	1/2
Sn	50–118	$[Kr]4d^{10}5s^2 5p^2$	0
Sb	51–118	$[Kr]4d^{10}5s^2 5p^3$	3/2
Te	52–118	$[Kr]4d^{10}5s^2 5p^4$	2
I	53–118	$[Kr]4d^{10}5s^2 5p^5$	3/2
Xe	54–118	$[Kr]4d^{10}\ 5s^2 5p^6$	0
Cs	55–56	$[Xe]6s$	1/2
	57	$[Xe]5d$	3/2
	58–118	$[Xe]4f$	5/2
Ba	56	$[Xe]6s^2$	0
	57	$[Xe]5d^2$	2
	58–118	$[Xe]4f^2$	4
La	57	$[Xe]5d6s^2$	3/2
	58	$[Xe]4f5d^2$	7/2
	59–118	$[Xe]4f^3$	9/2
Ce	58	$[Xe]4f5d6s^2$	4
	59	$[Xe]4f^3 6s$	4
	60–118	$[Xe]4f^4$	4
Pr	59	$[Xe]4f^3 6s^2$	9/2
	60	$[Xe]4f^4 6s$	7/2
	61–118	**$[Xe]4f^5$**	**5/2**

We already know:

Higher Z_c, close to H-like!

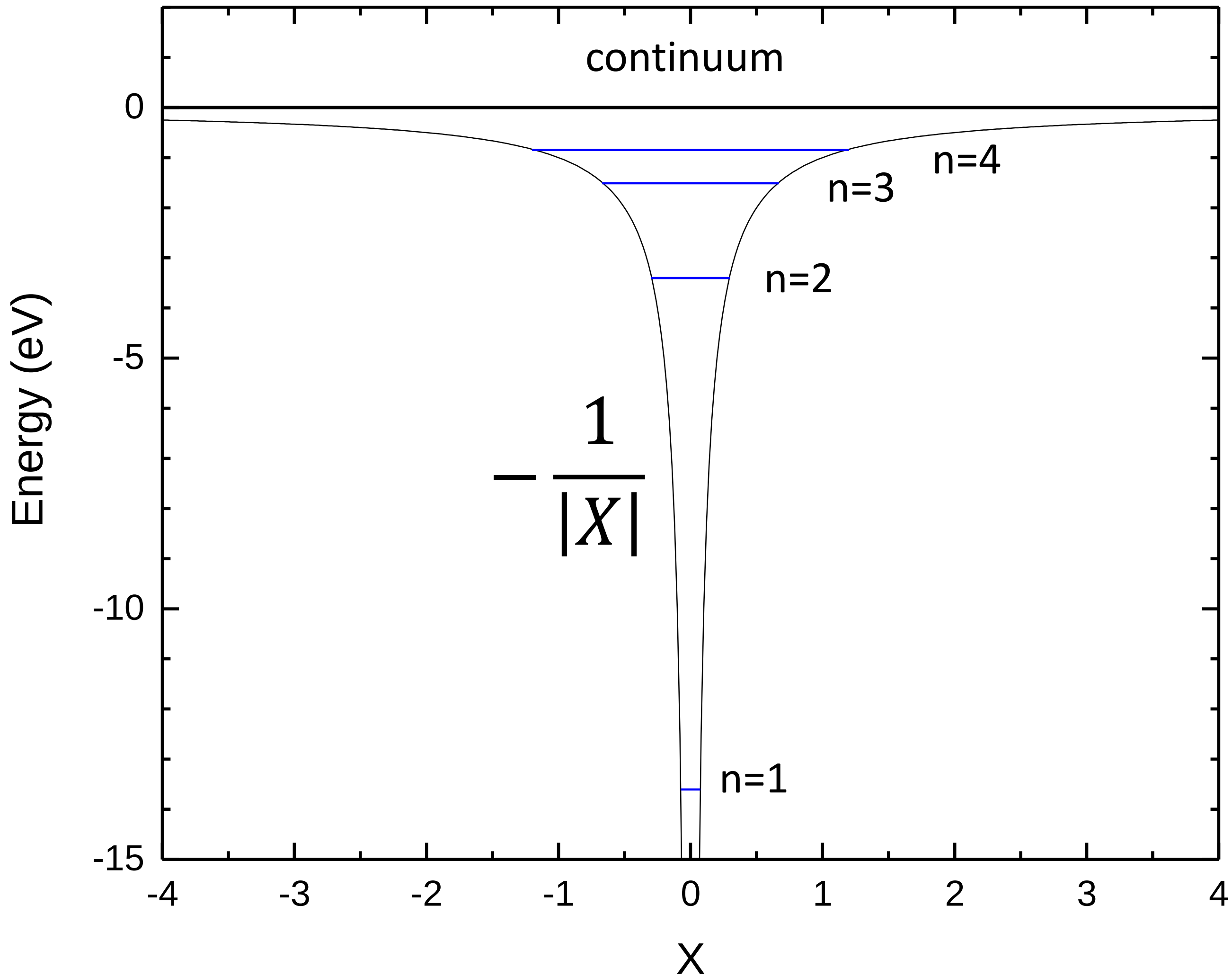
At $Z_c \rightarrow \infty$, $[Xe] \rightarrow 4d^{10}4f^8$!

NIST
National Institute of Standards and Technology

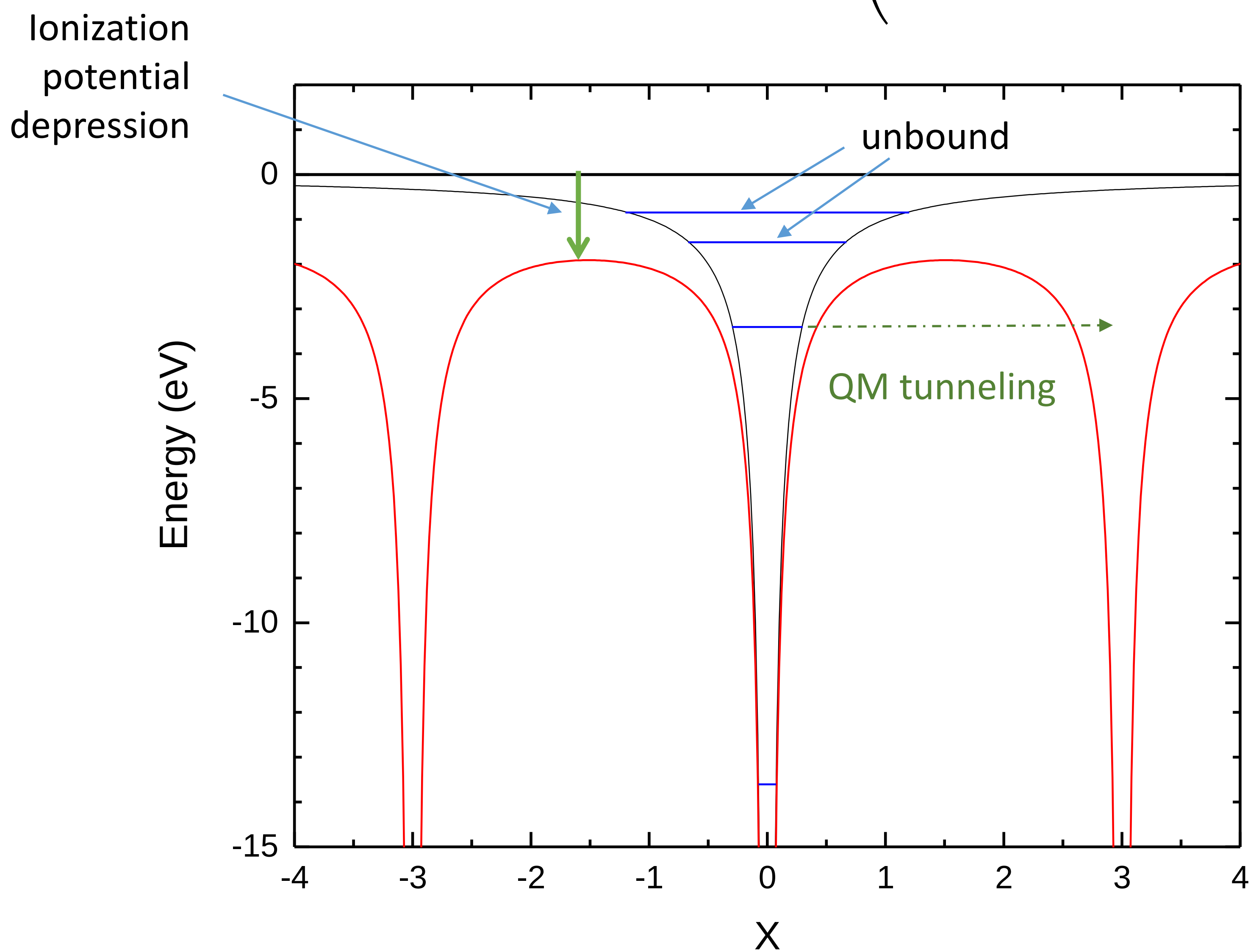
Ionization potential: constant?..

- 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 & Spectra Databases

- 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)
  - …

ASD

- Contents
  - Procedure: evaluation, analysis
- Basic search of energies
  - Units, ascii,
  - Term energies
- Spectral lines
  - Multiplets
  - Grotrian diagrams