Atomic physics simulations

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Motivation and content

- Emission and absorption spectroscopy are very important methods of plasma diagnostics plasma
- High-temperature plasmas are intense sources of EUV emission suitable for various applications
- Both for diagnostics interpretation and for source optimization computer modelling of atomic physics necessary
- Content
  - Atomic structure and basic transition processes – semi-relativistic and fully relativistic models
  - Calculations of populations of atomic states
  - Spectral parameters and spectra synthesis
  - Radiative transfer

Atomic structure calculations

- Solution of quantum mechanics equations for wavefunctions usually with additional calculations of basic transition probabilities for bound states, continuum processes are either included or calculated by additional programs
- Two basic approaches
  - **Classical non-relativistic Schrödinger** equation with relativistic corrections
    Codes – Cowan code, CATS code (Los Alamos), CIV3, SUPERSTRUCTURE, MCHF (MultiConfiguration Hartree-Fock), MCDF (MultiConfiguration Dirac-Fock), ATOM (integrated package)
  - **Fully relativistic Dirac equation**
    Codes – HULLAC, SZ, **FAC** (Flexible atomic code)

Classical approach

- Schrödinger equation - atom with 1 electron - $H\varphi = E\varphi$

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

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

a_0 – Bohr radius

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

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

3rd term – mass-velocity term (relativistic electron mass)
4th Darwin term – relativistic non-localizability
5th spin-orbital term – splitting of energy levels with $l \neq 0$

Multielectron atoms (ions)

- **Hamiltonian**

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

mass-velocity and Darwin terms omitted – only level shift after solving

- 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 permutations

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

- Base functions – eigenfunctions J^2 and J_z

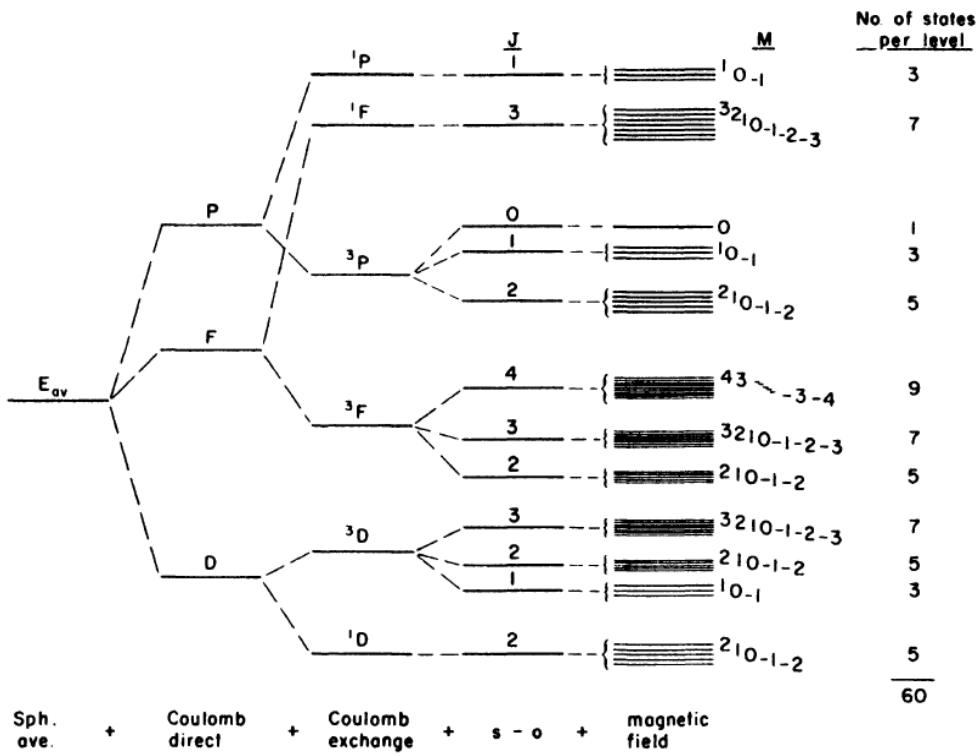
$$\mathbf{J} = \sum_{i=1}^{N} (\boldsymbol{l}_i + \boldsymbol{s}_i)$$

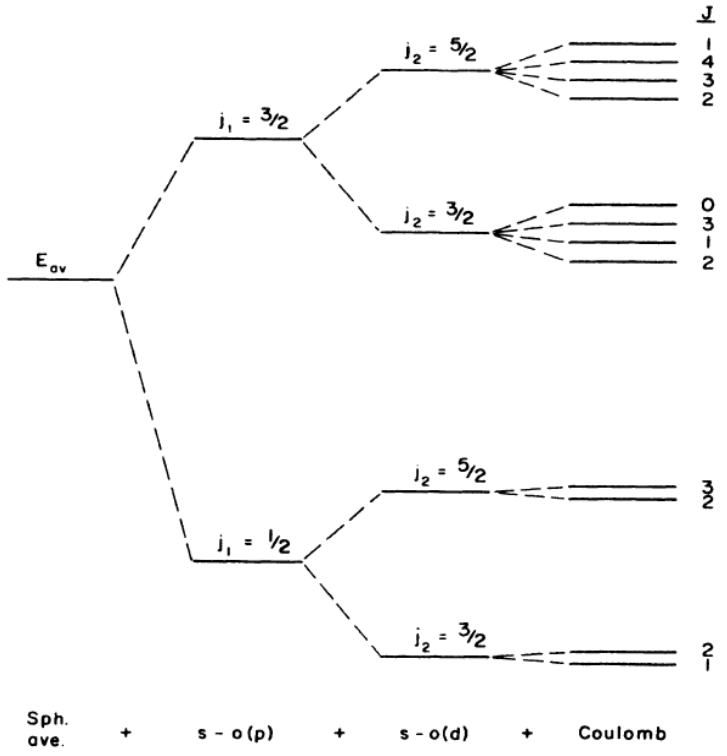
- Equivalent electrons - same *nl* – *w* electrons in subshell $(nl)^w$
- Closed subshells *k* (s^2, p^6, d^{10}, f^{14}, ..,) have $L_k = S_k = J_k = 0$

Cowan code

- R. D. Cowan, The theory of atomic structure and spectra, Univ. California Press 1981
- Updated version – CATS code (part of LANL atomic suite)
- Semirelativistic (non-relativistic model with relativistic corrections)
- First – RCN code calculates radial wavefunctions and radial integrals for configuration $(\mathrm{n}_1 l_1)^{\mathrm{w1}}\ (\mathrm{n}_2 l_2)^{\mathrm{w2}}\ \ldots.(\mathrm{n}_\mathrm{q} l_q)^{\mathrm{wq}}$, and configuration average energy calculated
- Difficulties due to Pauli exclusion in angular coupling of equivalent electrons in antisymmetric base functions solved by recoupling via method of fractional parentage
- Several up to many configurations have to be calculated simultaneously to include configuration interaction, scaling factors (0.85 – 0.9) used in radial integrals in Hamiltonian

Diagrams of energy states



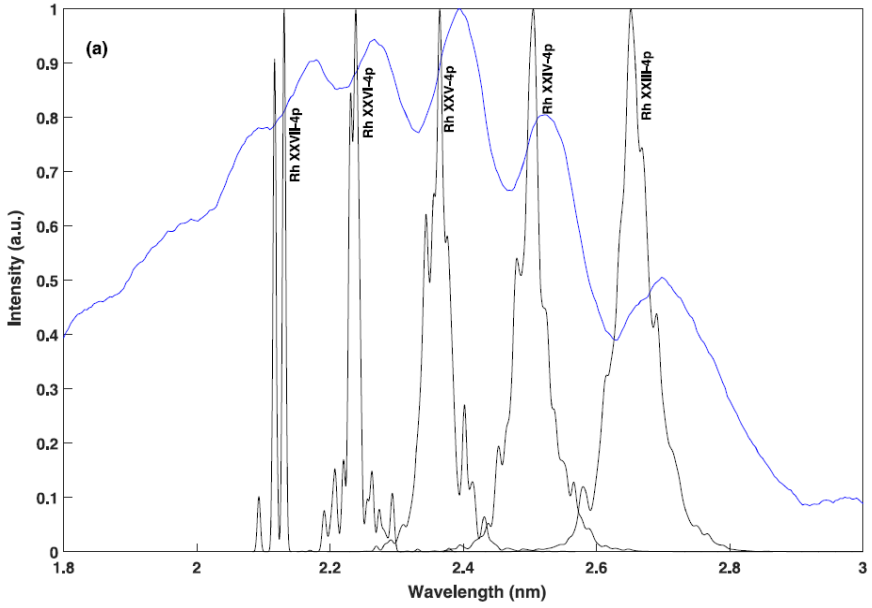


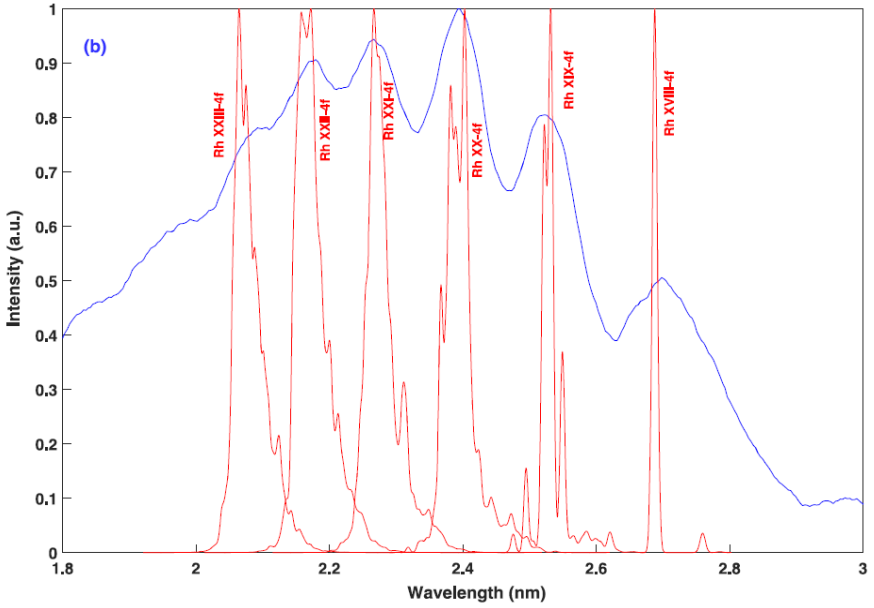
Scheme of splitting of energy levels of ***pd*** configuration in conditions of **LS** coupling starting from averaged E_{av} and gradually adding large Coulomb interaction, spin-orbit interaction and external magnetic field

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

Other coupling schemes (**LK**, j**K**), intermediate coupling

Spectral identification using Cowan code

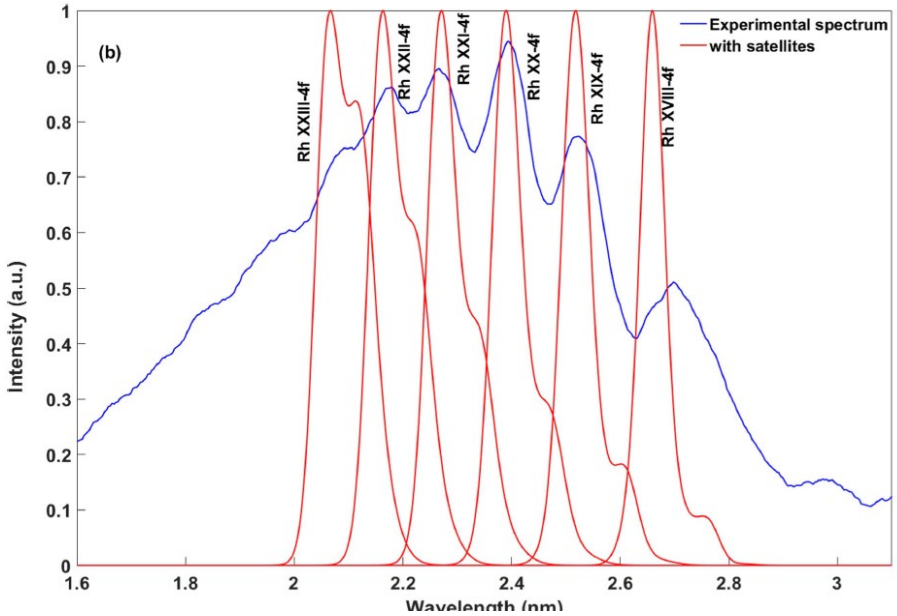




Emission spectrum from bulk Rh target irradiated by fs laser pulse (65 fs FWHM, 4.5 mJ, 3×10^{15} W/cm^2) at KFE FJFI

R. Lokasani, E. Barte,..., J. Limpouch, J. Phys. B **50** (2017) 145001

Our simple calculations - max Z_{av}=19 reached 1-2 ps after laser pulse, fast electrons enhance population of 22+



FAC (flexible atomic code)

- Fully relativistic code (M. F. Gu, Can. J. Phys. (2008) 675) solving Dirac equation – publicly available, open source
- Comprehensive package for computation of various atomic data – energy levels; radiative transition; collisional excitation; ionization by electron impact, photoionization, autoionization; and their inverse processes radiative recombination and dielectronic capture
- Integrates various atomic processes within a single theoretical framework, ensure the self-consistency between different parts
- Provide a uniform flexible and easy-to-use user interface for accessing all computational tasks

Solution of the Dirac equation

- Basic states Φ_ν – antisymmetric combinations of 1 electron Dirac spinors
  $\chi_{\kappa m}$ spin-angular function,
  $\kappa = (l - j)(2j + 1)$ - relativistic angular quantum number

$$\varphi_{n\kappa m} = \frac{1}{r}\begin{pmatrix} P_{n\kappa}(r)\,\chi_{\kappa m}(\theta,\phi,\sigma) \\ i\,Q_{n\kappa}(r)\,\chi_{-\kappa m}(\theta,\phi,\sigma) \end{pmatrix}$$

- Approximate atomic states – mixing coefficients b_ν via diagonalizing Hamiltonian

$$\psi = \sum_\nu b_\nu \Phi_\nu$$

- Hamiltonian matrix calculated from 1 electron radial orbitals

$$H = \sum_{i=1}^{N} H_{\mathrm{D}}(i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

- Potential - nuclear potential + interaction (spherical averaged potential due to bound electrons + exchange interaction), expression explicitly excluding self-interaction is used
- Self-consistent iteration to find radial orbitals $P_{n\kappa}$, $Q_{n\kappa}$

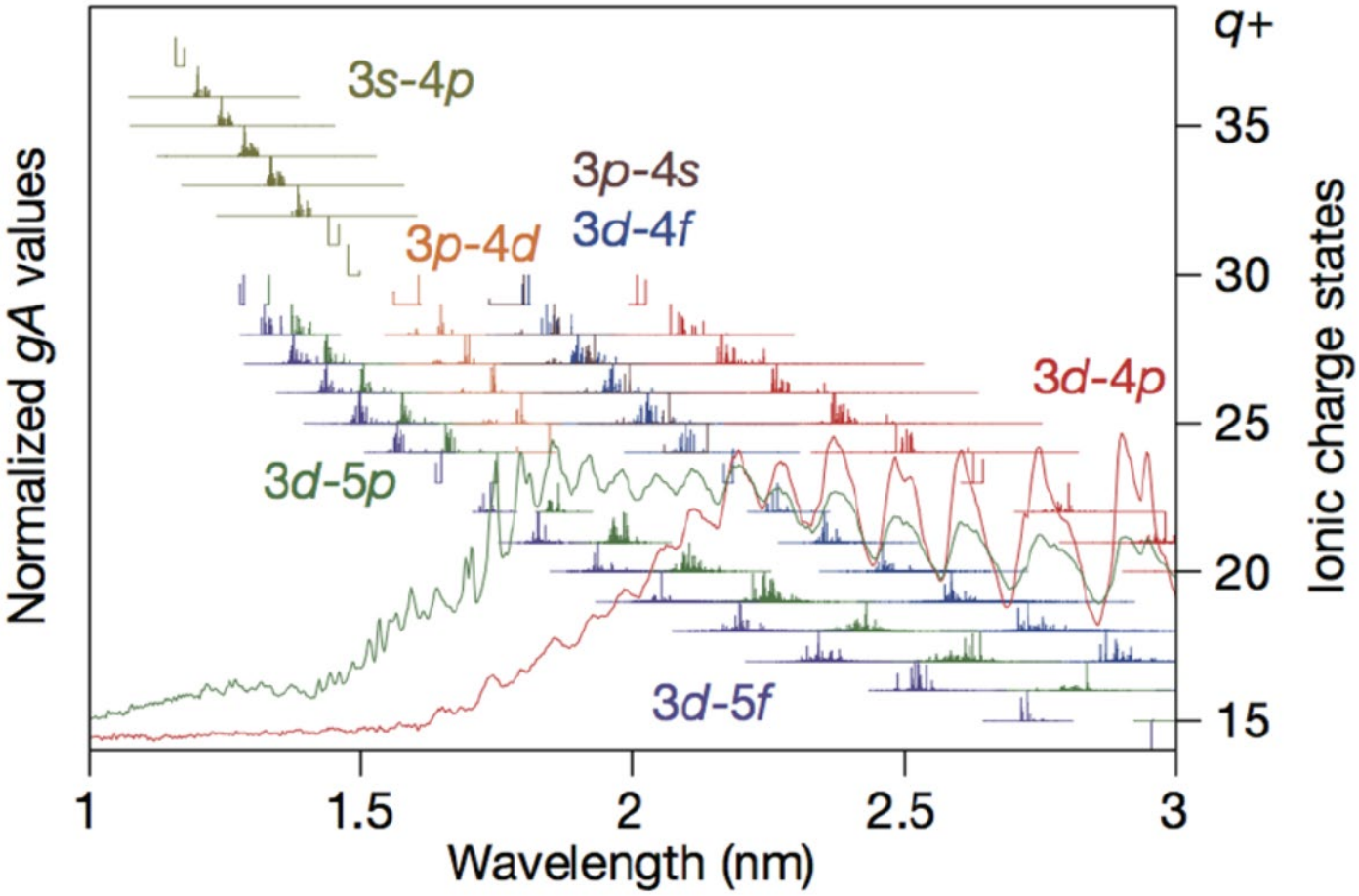
Angular part and radiative transition rates

- Hamiltonian matrix elements expanded into sum – each term is product of radial and angular part
- Racah algebra used to calculate angular part, initial and final basis states must be **recoupled**; the used **new algorithm** recouples creation and annihilation operators (max. 2+2) instead of basis states and extends Racah algebra to the quasi-spin space
- **Radiative transition rates** – single multipole approximation (interference between different multipoles omitted)
  Line strength of transition $S_{fi} = \left| < \psi_f || O_M^L || \psi_i > \right|^2$
  O_M^L multipole operator
- Radial part of single-electron multipole operator is sufficiently accurate in non-relativistic limit (with exception of M_1 transitions)

Electron impact excitation and ionization

- **Excitation (EIE)** - independent excitation channels assumed (1st Born approx)
- Relativistic distorted wave (DW) approximation used for calculations of free orbitals (more realistic potential)
- Angular and radial integrals are completely factorized
- Detailed cross-sections between magnetic sublevels of lower and upper states may be calculated in FAC (needed when aligned excitation produces polarized line emission)
- Ionization **(EII)** – Coulomb-Born exchange approximation is used in FAC for radial integrals
- Angular factors involving free electron are simplified via Racah decoupling formula

Spectral identification using FAC code



Emission spectra of bulk Mo target irradiate by Nd-laser 8.5×10^{13} W/cm^2 – red 1064 nm, 150 ps; green 532 nm, 130 ps. Normalized gA values calculated by FAC code for ionization degrees 15+ - 35+.
R. Lokasani, H. Kawasaki, …, J. Limpouch, Opt. Express **27** (2019) 33351

Atomic level populations and spectra

- **Simple models**
  - **Coronal equilibrium** – low density plasmas, radiative processes dominate over collisional processes, small radiation spectral intensity – collisional de-excitation << photo-de-excitation; dielectronic and 3-body recombination << photorecombination; analytic calculation of populations feasible
  - **LTE** (local thermodynamic equilibrium) – dense plasmas, equilibrium populations of atomic states though radiation not in equilibrium, collisional processes must dominate
- **Collisional-radiative model**
  - Rate equation solved for populations of atomic states; rate equations can be solved in principle for any known spectral radiation intensity I_ν
  - Optically thin plasma – simplest, $I_\nu = 0$, no spatial populations coupling
  - Self-consistent spectral intensity can be calculated via radiative transport, simplified methods (e.g. escape factors) are often used
  - Principle of detailed balancing used for rates of inverse processes

Atomic level populations

- **Set of atomic states**
  - Populations can be calculated individually or for groups of states coupled together (e.g. equilibrium assumed inside one group) – degree of detail may differ for various ionization states
  - For each ionization state – ground state, many resonance excitation states, autoionization states, multiply-excited autoionization states
  - Continuum lowering in dense plasmas – states above threshold either cease to exist or population probability is strongly decreased
- **Computing of populations**
  - Either temporal evolution of populations is solved or stationary populations are found by setting time derivatives = 0
  - Matrix of transitions is block-diagonal, transition is possible only between states of neighboring ionization states
  - Populations in each Lagrangian cell governed by a set of ordinary differential equations

Spectral characteristics and synthesis

- Emissivities can be calculated when populations are known
- Spectral line widths and shapes must known for calculation of opacities and spectral intensities
- Spectral lines and recombination edges are mainly broadened by natural, Stark (electron impact and quasi-static ion) and Doppler broadening
- Basic line profiles – Lorentz, Gaussian and Voigt (convolution of previous), often line splitting has to be taken into account

Examples of codes

- **FLYCHK** with web access via NIST
  - Simple, easy-to-use zero-dimensional (homogenous plasma of given width), evolved from RATION and FLY codes for K-shell spectroscopy
  - Either steady-state LTE and non-LTE populations on temperature and density grid or evolution for input history of density and temperatures and initial populations
  - Possibilities - two-electron temperatures, ion temperature different from electron one, mixtures (other element only as source of free electrons)
  - It uses original FLY and HULLAC data for H-, He- and Li-like ions for $Z<27$, screened hydrogenic model for other ions
  - The basic aim is improve accuracy of K-shell spectroscopy, not to provide tool for spectroscopy of ions with more electrons
  - 25 states for H-like ion (n=1…25), He-like (n=1…22), 4 states only for n=2 (1s2s ^{1}S, 1s2s ^{3}S, 1s2p ^{1}P, 1s2p ^{3}P), + 6 autoionization states (2l2l'), Li-like ion – states ($1s^2$) 2s,2p,3s,…,5g and coupled state for n=6,..,10, 6 autoionization states (1s2l2l'), Be-like – ground + 8 excited resonance states, 8 autoionization doubly excited states, 9 autoionization states with 1 electron excited from K shell

Population Kinetics Modeling

Rate equations are solved for level population distributions for given plasma conditions

$$\frac{dn_i}{dt} = -n_i \sum_{j \neq i}^{N\max} W_{ij} + \sum_{j \neq i}^{N\max} n_j W_{ji}$$

$$W_{ij} = B_{ij}\overline{J_{ij}} + n_e C_{ij} + \beta_{ij} + n_e \gamma_{ij}$$

$$W_{ji} = A_{ij} + B_{ji}\overline{J_{ji}} + n_e D_{ji} + n_e(\alpha_{ji}^{RR} + \alpha_{ji}^{DR}) + n_e^2 \delta_{ij}$$

B_{ij} Stimulated absorption

C_{ij} Collisional excitation

γ_{ij} Collisional ionization

β_{ij} Photoionization (+st. recom)

A_{ij} Spontaneous emission

B_{ij} Stimulated emission

D_{ij} Collisional deexcitation

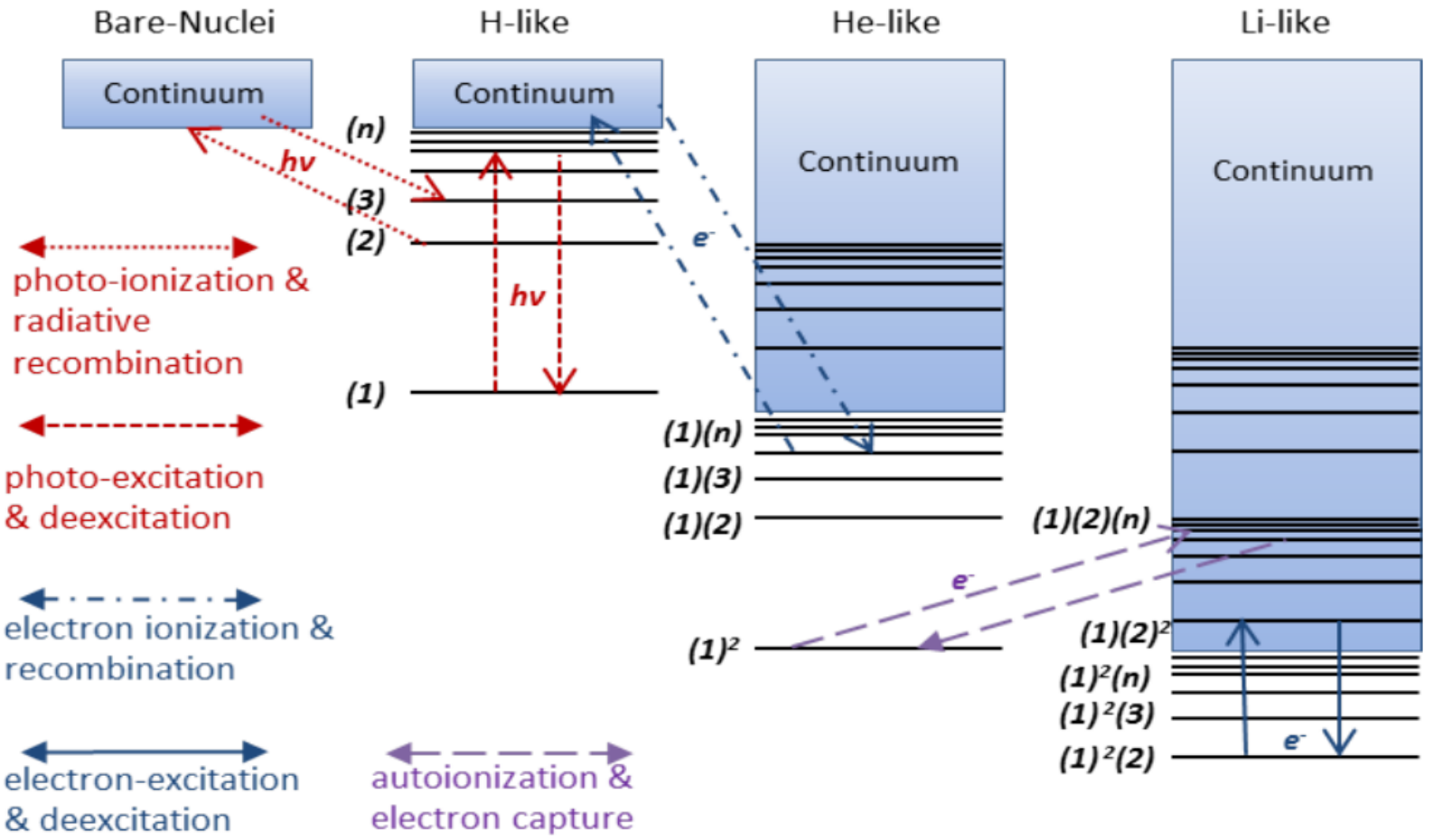
a_{ij}^{DR} Dielectronic recombination

a_{ij}^{RR} Radiative recombination

δ_{ij} Collisional recombination

H. K. Chung, Introduction to FLYCHK code, presentation at ICTP Trieste 2019

Atomic processes included in FLYCHK



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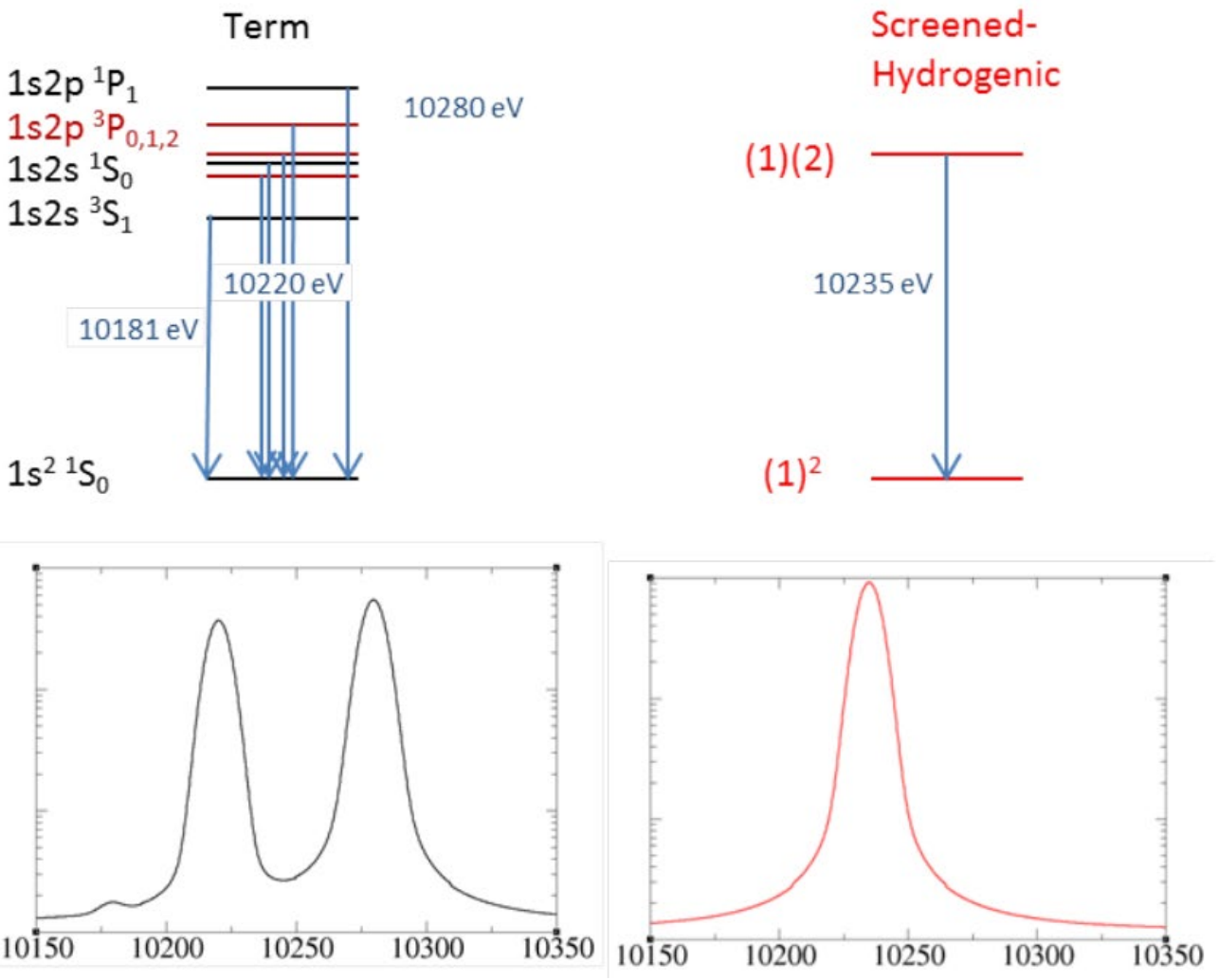
FLYSPEC uses detailed (H, He, Li-like) and Super Transition Array for spectra



H. K. Chung, Introduction to FLYCHK code, presentation at ICTP Trieste 2019

Data Types for Spectroscopic Model

Z < 27 H, He and Li	FLY model
Z > 27 H, He and Li	HULLAC data (term levels up to n=4)
Be-like and lower charge states	Super Transition Array (STA) made with Configurations (jj) 1s, 2s, $2p^-$, $2p^+$, 3s, $3p^-$, $3p^+$, $3d^-$, $3d^+$, Up to n=6

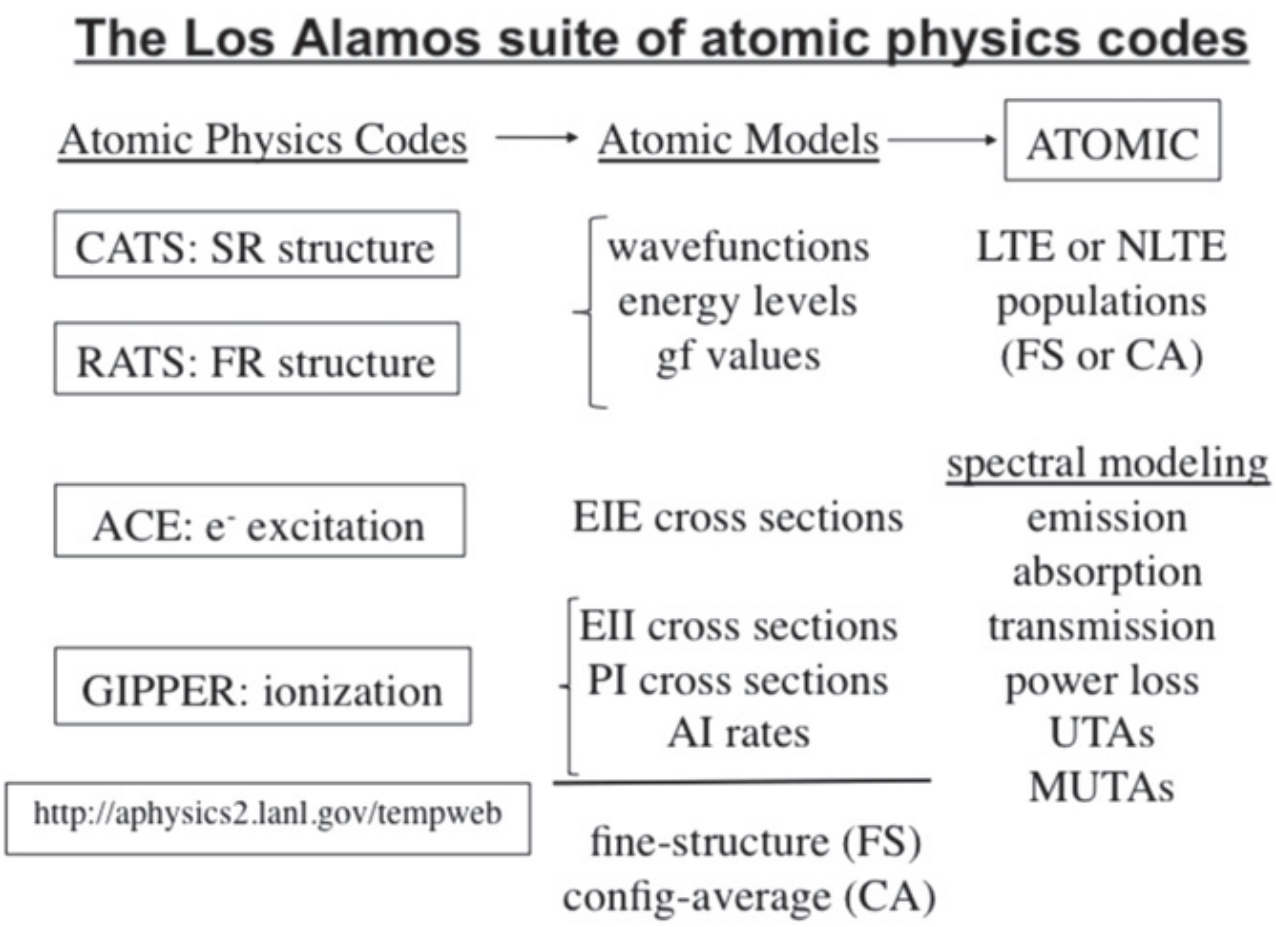
Stark broadening included only for H-, He- and Li-like ions

H. K. Chung, Introduction to FLYCHK code, presentation at ICTP Trieste 2019

Examples of codes

- **Prism suite of codes**
  - PrismSpec, Spec3D, fluid code Helios with detailed spectroscopic analysis and spectra synthesis
  - Commercial codes – very expensive, 20 k$/year (> 10 k$ for universities), limited information for user about model details
  - Spectroscopy of low Z elements up to Kr (Z = 36)
  - Detailed set of atomic states – separate states for different orbital numbers *l*, also more autoionization states
  - Relatively accurate line shape calculations
  - Difficulties in post-processing other fluid code by Spec3D
- **Cretin** (H. A. Scott, LLNL)
  - very efficient code for radiative transport in lines in various geometries
  - can be obtained on request, but only with simple testing atomic data
  - user has to prepare atomic data according to manual provided by the author

Examples of codes - continued



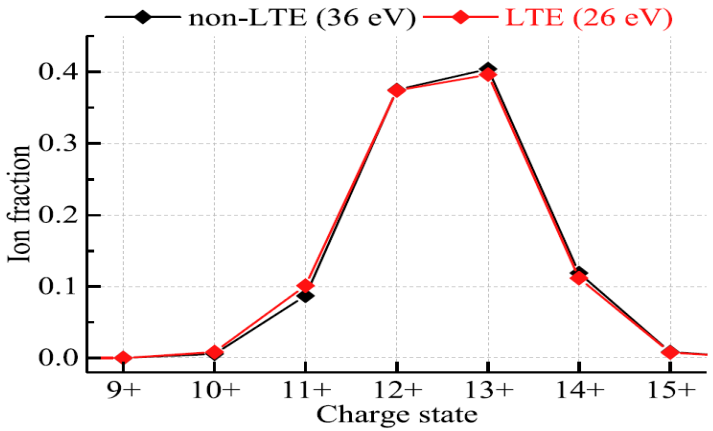
CATS, RATS, ACE and GIPPER codes produce fundamental atomic physics data that are processed by ATOMIC, which calculates populations for plasmas under local thermodynamic equilibrium (LTE) or non-LTE (NLTE) conditions, as well as a variety of spectral quantities. MUTA – mixed unresolved transition array

Tin emission for EUV lithography

Configuration set adopted for calculations of emission from Sn droplet target using LANL suite

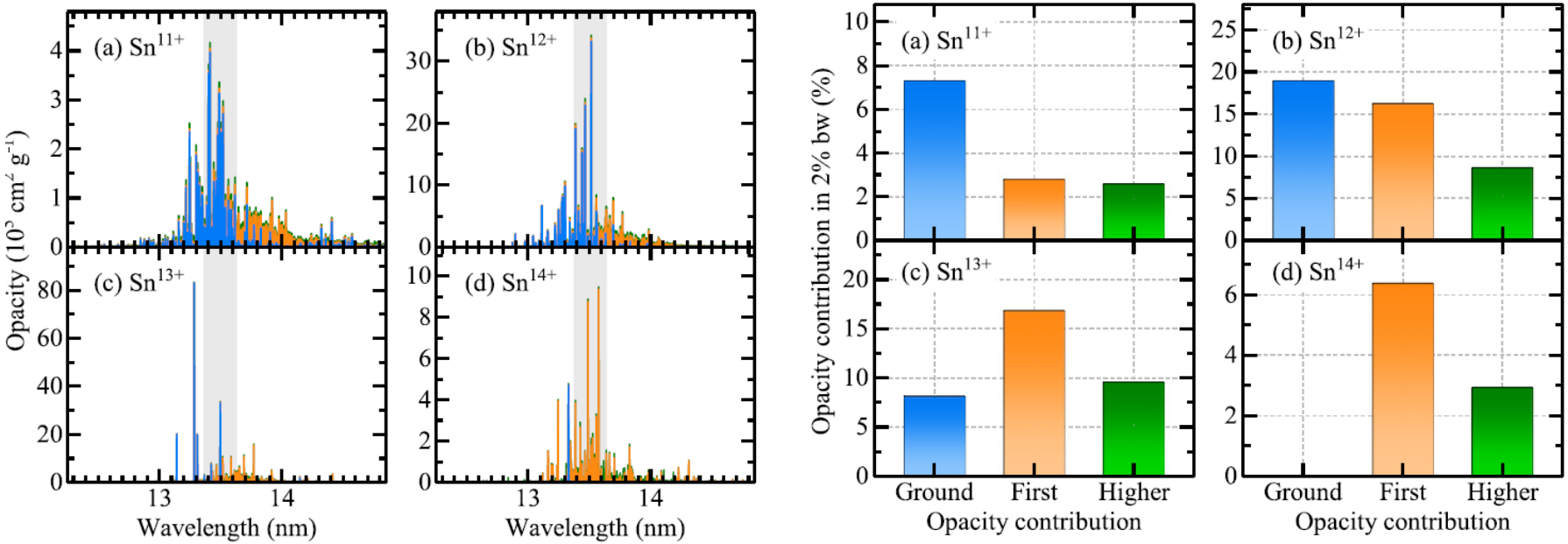
Sn^{12+}	Sn^{14+}
Ground configuration	*Ground configuration*
$4s^2 4p^6 4d^2$	$4s^2 4p^6$
Singly-excited configurations	*Singly-excited configurations*
$4s^2 4p^6 4d + \{4f, 5l\}$	$4s^2 4p^5 + \{4d, 4f, 5l\}$
$4s^2 4p^5 + \{4d^3, 4d^2 4f, 4d^2 5l\}$	$4s^1 4p^6 + \{4d, 4f, 5l\}$
$4s4p^6 + \{4d^3, 4d^2 4f, 4d^2 5l\}$	
Doubly-excited configurations	*Doubly-excited configurations*
$4s^2 4p^6 + \{4f^2, 4f5l, 5s5l, 5p5l', 5d5\tilde{l}, 5f5g\}$	$4s^2 4p^4 + \{4d^2, 4d4f, 4f^2, 4d5l, 4f5l, 5s5l, 5p5l', 5d5f, 5d5g, 5f5g\}$
$4s^2 4p^5 + \{4d4f^2, 4d5s^2, 4d4f5l, 4d5s5p, 4d5s5d\}$	$4s^1 4p^5 + \{4d^2, 4d4f, 4f^2, 4d5l, 4f5l, 5s5l, 5p5l', 5d5f, 5d5g, 5f5g\}$
$4s^2 4p^4 + \{4d^4, 4d^3 4f, 4d^3 5l, 4d^2 4f^2\}$	$4p^6 + \{4d^2, 4d4f, 4d5l, 4f5l\}$
$4s4p^5 4d^4$	
Triply-excited configuration	*Triply-excited configurations*
$4s^2 4p^3 4d^5$	$4s^2 4p^3 4d^3, 4s^2 4p^3 4d^2 4f, 4s4p^4 4d^3, 4s4p^4 4d^2 4f$

66% of the opacity in the industrially-relevant 2% bandwidth centred at 13.5 nm arises from transitions between multiply-excited states. Complex, multiply-excited states necessary for modelling the radiative properties of laser-driven plasma sources of EUV light.



J Sheil et al 2021 J. Phys. B: At. Mol. Opt. Phys. 54 035002

Sn opacities in 2% bw at 13.5 nm



Left: Opacities of the ions Sn^{11+}–Sn^{14+}. Photoabsorption from levels of the ground manifold to singly-excited levels is in blue (‘ground opacity’). The summation of photoabsorption from singly-excited levels to doubly-excited levels (‘first opacity’) and the ground opacity is shown by the line bounding the orange shaded region. The summation of photoabsorption from doubly- and triply-excited levels (‘higher opacity’) shown in green.

Right: Contributions from the ground, first and higher opacities in the 2% bw in Sn^{11+}–Sn^{14+}.

Radiative transport

- Radiation transport plays essential role for high-Z targets
- Radiation transport is described by equation

$$\underbrace{\frac{1}{c}\frac{\partial I_\nu}{\partial t}}_{\approx 0} + \vec{n}\cdot\nabla I_\nu = j_\nu + \sigma_{s\nu}\bar{I}_\nu - \left(k_\nu' + \sigma_{s\nu}\right) I_\nu$$

  where $I_\nu\left(t,\vec{r},\vec{n}\right)$ is the radiation spectral intensity, angular averaged spectral intensity $\bar{I}_\nu = \int I_\nu \,\mathrm{d}\vec{n}/(4\pi)$, k_ν' is the opacity (including stimulated emission), $\sigma_{s\nu}$ is scattering coefficient and the emissivity $j_\nu = k_\nu' I_{\nu p}$
- Energy density $U_\nu = 4\pi\bar{I}_\nu / c$ and energy flux $\vec{S}_\nu = \int \vec{n}\, I_\nu \,\mathrm{d}\vec{n}$
- Radiation transport is solved in multi-group approximation or more simply in one-group (grey) approximation
- Diffusion approximation $\mathrm{div}\,\vec{S}_\nu = c k_\nu'\left(U_{\nu p} - U_\nu\right) \qquad k_\nu'\vec{S}_\nu = -c\nabla U_\nu / 3$
- Transport is diffusive in dense cold target, but is near to free streaming in hot corona (non-local radiative transport)

Summary

- Emission and absorption spectroscopy are very important methods of plasma diagnostics plasma
- High-temperature plasmas are intense sources of EUV emission suitable for various applications
- Both for diagnostics interpretation and for source optimization computer modelling of atomic physics necessary
- Atomic data are calculated via equation of quantum mechanics in semi-relativistic or fully relativistic description
- Atomic data are then used in rate equations for populations of atomic states
- Spectral parameters and synthetic spectra are calculated from known populations, line and edge broadening included

Thank you for attention