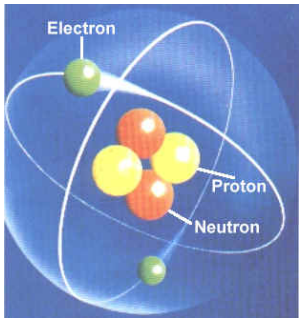
LUNDS UNIVERSITET

Spectroscopy on Atoms and selection rules

I - What is an atom? Modeling ?



- **N-electrons bound to a nucleus (Z)**

$$H_{n-e} = \sum_{i=1\ldots N} -\frac{\hbar^2}{2m}\nabla^2_{\vec{r}_i} - \frac{Ze^2}{4\pi\varepsilon_o r_i}$$

- **N-electrons in interactions**

$$H_{e-e} = \sum_{i<j=1\ldots N} \frac{e^2}{4\pi\varepsilon_o r_{ij}}$$

- **N-electron atom wave function** $\Psi(q_1 \ldots q_N)$ **with** $q_i = \{\vec{r}_i, \sigma_i\}$ **satisfies**

$$H\left|\Psi(q_1 \ldots q_N)\right\rangle = E\left|\Psi(q_1 \ldots q_N)\right\rangle$$
$$\Leftrightarrow \left[H_{e-n} + H_{e-e}\right]\left|\Psi(q_1 \ldots q_N)\right\rangle = E\left|\Psi(q_1 \ldots q_N)\right\rangle$$

Step 1: Independent-particle model – no spin

- **Lets introduce the spherically symmetric potential** $V(r)$

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + S(r) \quad \textbf{with} \quad \begin{cases} V(r) \to -\dfrac{Ze^2}{4\pi\varepsilon_0 r} & r \to 0 \\ V(r) \to -\dfrac{(Z-N+1)e^2}{4\pi\varepsilon_0 r} & r \to \infty \end{cases}$$

Screening of the nucleus

- **Re-writing the total Hamiltonian**

$$H = H_{e-n} + H_{e-e} + \sum_{i=1\ldots N} V(r_i) - \sum_{i=1\ldots N} V(r_i)$$

$$\Rightarrow \quad H = H_{central} + H_{non\,central}$$

$$H_{central} = \sum_{i=1\ldots N} -\frac{\hbar^2}{2m}\nabla^2_{\vec{r}_i} + V(r_i) \qquad H_{non\,central} = H_{e-e} - \sum_{i=1\ldots N} S(r_i)$$

Step 1: Independent-particle model – no spin

- **The Schrodinger equation for the central field is separable in N equations**

$$H_{central}\left|\Psi_{central}(\vec{r}_1 \ldots \vec{r}_N)\right\rangle = E_{central}\left|\Psi_{central}(\vec{r}_1 \ldots \vec{r}_N)\right\rangle$$

since all particles are independent

$$\left|\Psi_{central}(\vec{r}_1 \ldots \vec{r}_N)\right\rangle = \left|u_{\alpha_1}(\vec{r}_1)\right\rangle \otimes \left|u_{\beta_2}(\vec{r}_2)\right\rangle \ldots \otimes \left|u_{\nu_N}(\vec{r}_N)\right\rangle$$

Set of good quantum numbers

- **Schrodinger equation in a central field for the electron *i***

$$\left(-\frac{\hbar^2}{2m}\nabla^2_{\vec{r}_i} - V(r_i)\right)\left|u_{n_i l_i m_{l_i}}(\vec{r}_i)\right\rangle = E_{n_i l_i}\left|u_{n_i l_i m_{l_i}}(\vec{r}_i)\right\rangle$$

with the "natural" solution

$$\left|u_{n_i l_i m_{l_i}}(\vec{r}_i)\right\rangle = \left|R_{n_i l_i}(r_i)\right\rangle \otimes \left|Y_{l_i m_{l_i}}(\theta_i, \varphi_i)\right\rangle$$

The radial part is not the solution of the hydrogen.
The different l-states are not degenerate

Step 1: Independent-particle model

- **Spin and the Pauli exclusion principle**

  Electron are fermions of spin ½, so that the wave function $\Psi(q_1 \ldots q_N)$ must be anti symmetric in the spatial an spin coordinates q_i of the electrons

- **Building up a wave function for N electrons – Slater determinants**

$$\left|\Psi_{central}(q_1 \ldots q_N)\right\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) & \ldots & u_\nu(q_1) \\ u_\alpha(q_2) & u_\beta(q_2) & \ldots & u_\nu(q2) \\ \ldots & \ldots & \ldots & \ldots \\ u_\alpha(q_N) & u_\alpha(q_1) & \ldots & u_\nu(q_N) \end{vmatrix}$$

with $\left|u_{n_i l_i m_{l_i} m_{s_i}}(q_i)\right\rangle = \left|R_{n_i l_i}(r_i)\right\rangle \otimes \left|Y_{l_i m_{l_i}}(\theta_i, \varphi_i)\right\rangle \otimes \left|\chi_{1/2, m_{s_i}}\right\rangle$

Step 1: Independent-particle model

- **Basis set to describe an electronic state – LS representation**

$$\begin{cases} \vec{L} = \sum_{i=1 \ldots N} \vec{l}_i \\ \vec{S} = \sum_{i=1 \ldots N} \vec{s}_i \end{cases}$$

$\left|\gamma n l m l' L S M_L M_S\right\rangle$

Electronic configuration
Close shell electrons

Total spin momentum

Electronic configuration
Open shell electrons

Total orbital angular momentum

$$Parity = \prod_i (-1)^{l_i}$$

- **Russel-Saunders notation**

$$\left|\gamma n l m l' \left[{}^{2S+1}L_J\right]\right\rangle$$

Step 2: Beyond the independent-particle model

- **Apply a perturbation W on the operator H_0** $\quad H_0\left|\varphi_n^0\right\rangle = E_n^0\left|\varphi_n^0\right\rangle$

First order

$$\begin{cases} \left|\varphi_n^1\right\rangle = \left|\varphi_n^0\right\rangle + \sum_{p\neq n} \dfrac{\left|\left\langle\varphi_p^0\left|W\right|\varphi_n^0\right\rangle\right|^2}{E_n^0 - E_p^0}\left|\varphi_p^0\right\rangle \\ E_n^1 = E_n^0 + \left\langle\varphi_n\left|W\right|\varphi_n\right\rangle \end{cases}$$

Second order is required if $\quad \Delta E_{p,n}^0 = E_p^0 - E_n^0 \approx \left\langle\varphi_p\left|W\right|\varphi_n\right\rangle$

- **To be considered in the Hamiltonian**

$$H_{non\,central} = H_{e-e} - \sum_{i=1\ldots N} S(r_i)$$

Electronic correlation ($\propto Z^2$)

$$H_{SO} = \frac{1}{2(mc)^2}\sum_{i=1\ldots N}\frac{1}{r_i}\frac{dV(r_i)}{dr_i}\vec{l}_i.\vec{s}_i$$

Spin orbit ($\propto Z^4$)

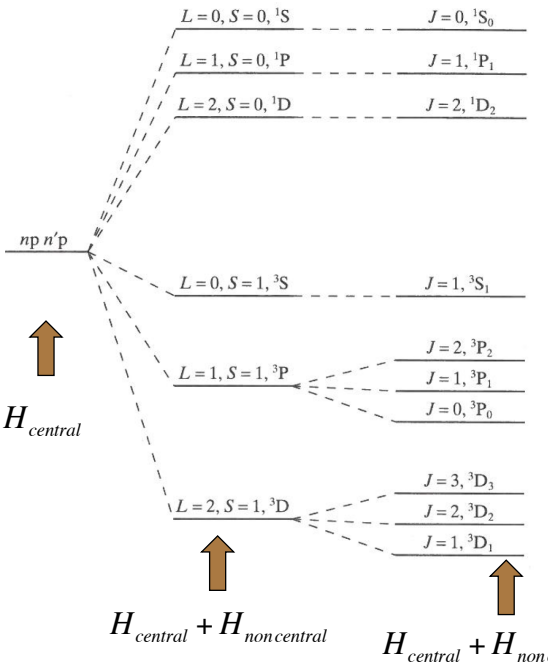
and more terms…

Step 2: Beyond the independent-particle model

	$H_{non\,central} >> H_{SO}$	$H_{SO} >> H_{non\,central}$
First perturbation	$H = H_{central} + H_{non\,central}$ $\left[H,\vec{L}\right] = \left[H,\vec{S}\right] = 0$ ➡ **LS - coupling**	$H = H_{central} + H_{SO}$ $\left[H,\vec{J}\right] = 0$ ➡ **JJ - coupling**
Second perturbation	$H + H_{SO}$ $\left[H,\vec{J}\right] = 0$	$H + H_{non\,central}$ $\left[H,\vec{J}\right] = 0$
Dipole Selection rules	$\Delta J = 0,\pm 1$ *with* $J_i = J_f = 0$ *forbidden* $\Delta S = 0$ $\Delta L = 0,\pm 1$ *with* $L_i = L_f = 0$ *forbidden*	$\Delta j = 0,\pm 1$ *with* $j_i = j_f = 0$ *forbidden*

Step 2: Beyond the independent-particle model

Fine structure with LS-coupling

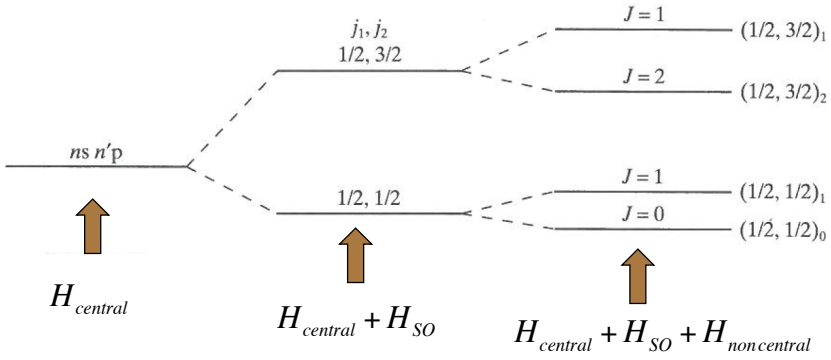


[Hund's rule](#)

1. the term with the largest possible value of S for a given configuration has the lowest energy; the energy of the other terms increases with decreasing S
2. For a given value of S, the term having the maximum possible value of L has the lowest energy

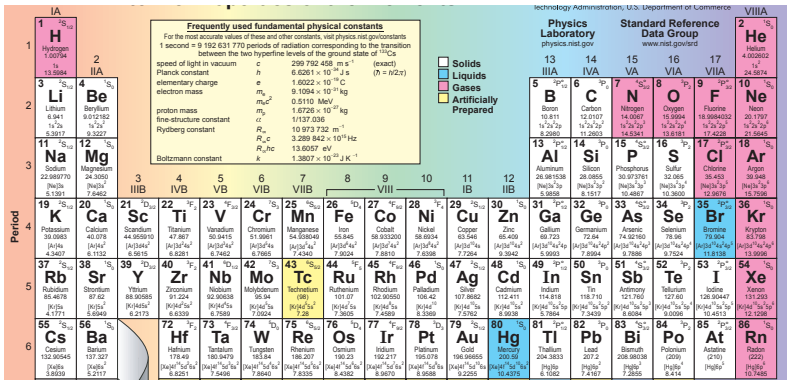
Step 2: Beyond the independent-particle model

Fine structure with JJ-coupling



Summary

- Define a basis to describe the **electronic structure**
  - simple model : independent-particle model
- Use this basis to describe the **fine structure**
  - more sophisticated model including electron correlations, relativistic term
  - coupling scheme informs on the interactions



II - Experimental manifestation

V. Schmidt, Rep. Prog. Phys. **55**, 1483 (1992)

Absorption Cross sections

$$\sigma_a = \sum_{\text{all } nlj} \{\sigma^+ + \sigma^{+*} + \sigma^{++} + \ldots\}$$

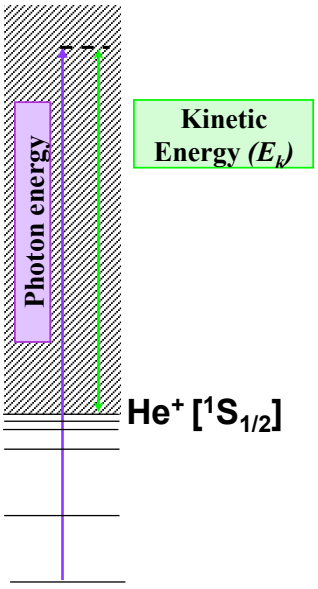
Main transitions: single ionization cross section (σ^+) for different shells

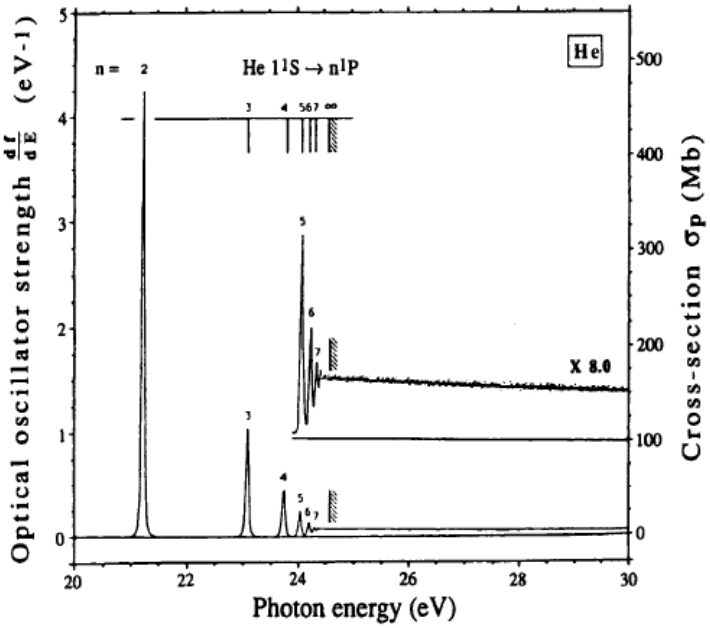
Satellite transitions: many electron processes – mainly two electrons
double excitation (σ^{**}), ionization and excitation (σ^{+*}-discrete satellites)
double ionization (σ^{++}- continuous satellites)

$$\sigma_a = \sigma_{ionization} + \sigma_{fluorescence} (+\sigma_{dissociation})$$

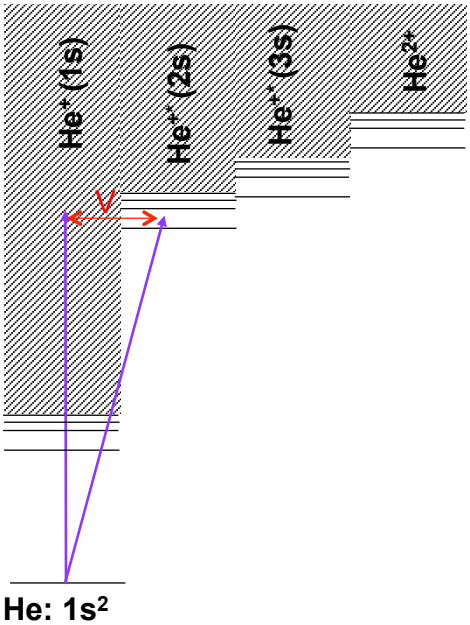
Photo-absorption / Photo-Ionization

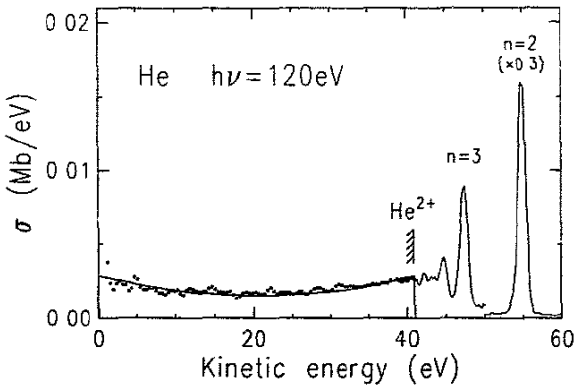
$He + h\nu \rightarrow He^{+(*)}\,[^1S_{1/2}] + e^-(\text{"p"})$



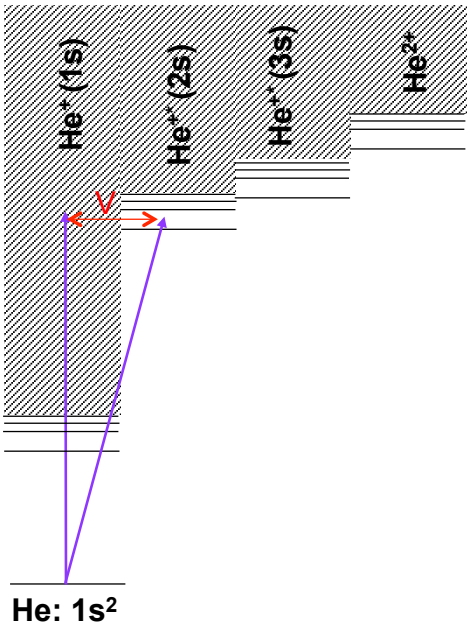


Total cross section / partial cross- section





Total cross section / partial cross- section



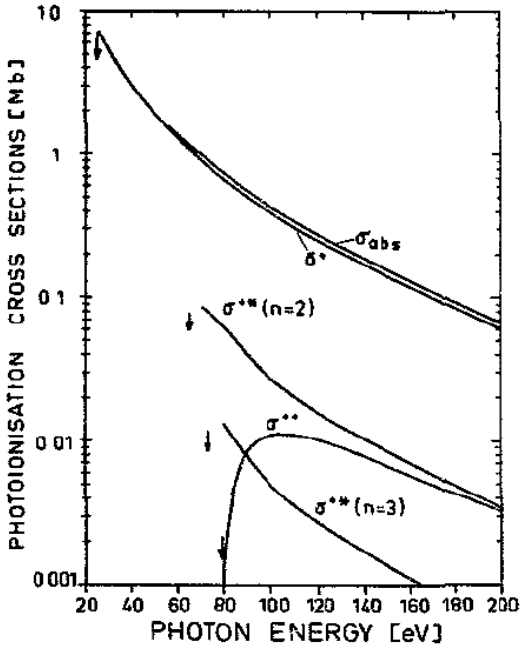
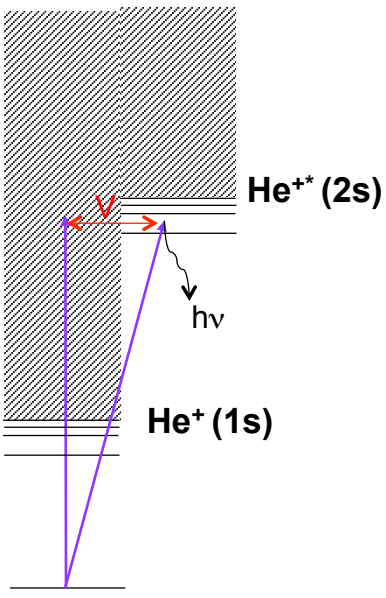
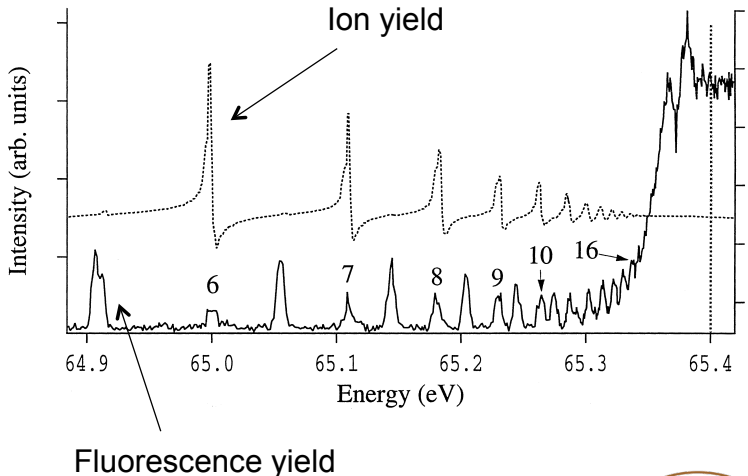


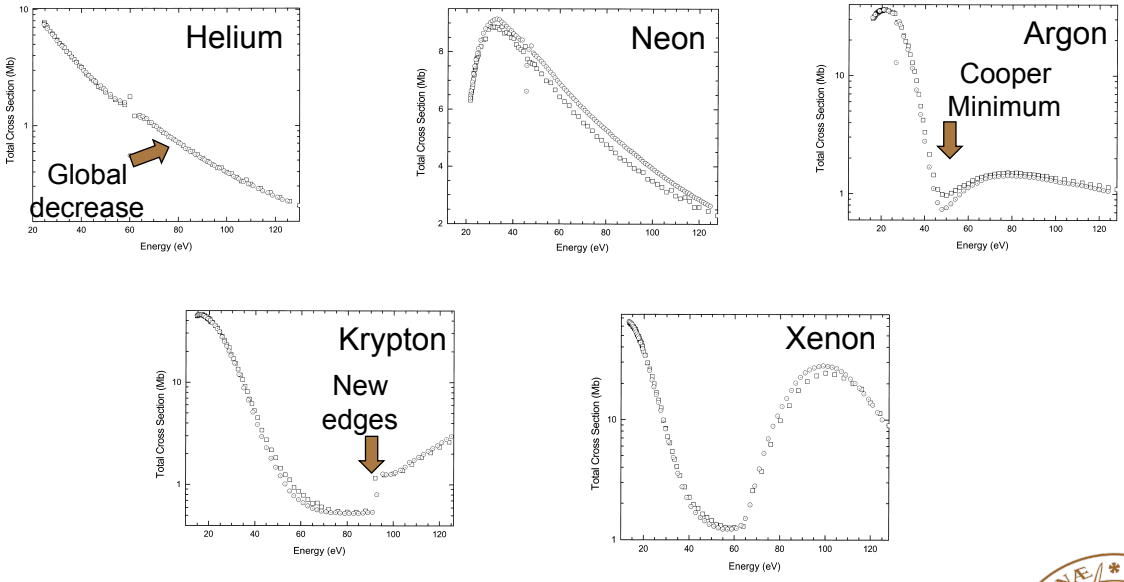
Photo-absorption/ ionization & Fluorescence





Evolution of the cross section

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



Samson *et al*, J. Elec. Spec. Rel. Phenom, **123** ,265 (2002)

Effect of the radial overlap

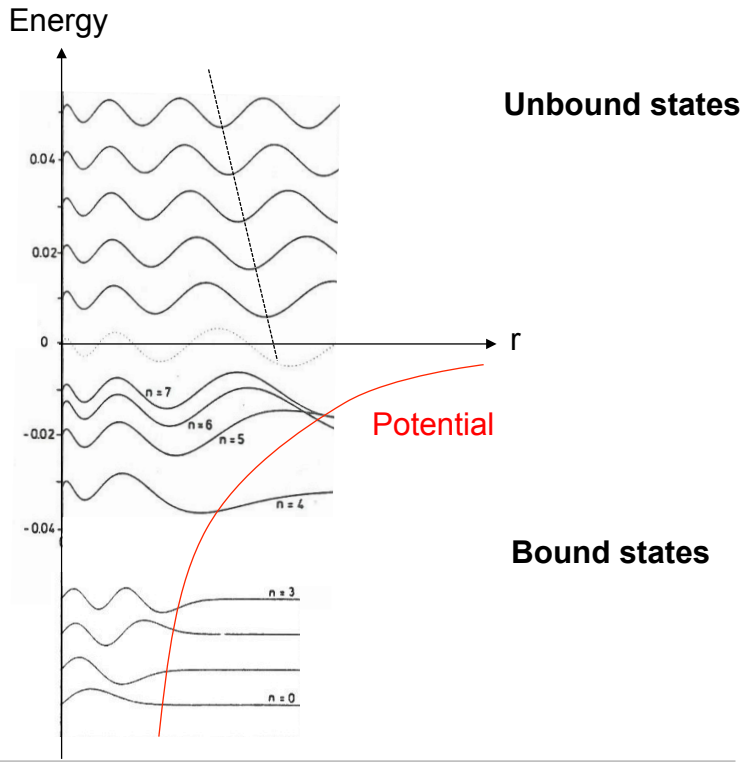
Many electron matrix element
in terms of one electron matrix element

$$D_\gamma = (2j_i+1)^{1/2} i^{-l_\gamma} (-)^{j_i-1/2} e^{i(\sigma_\gamma+\delta_\gamma)} R_{\gamma,nl,j_i} (2j+1)^{1/2} \begin{pmatrix} j & 1 & j_i \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}.$$

Radial overlap

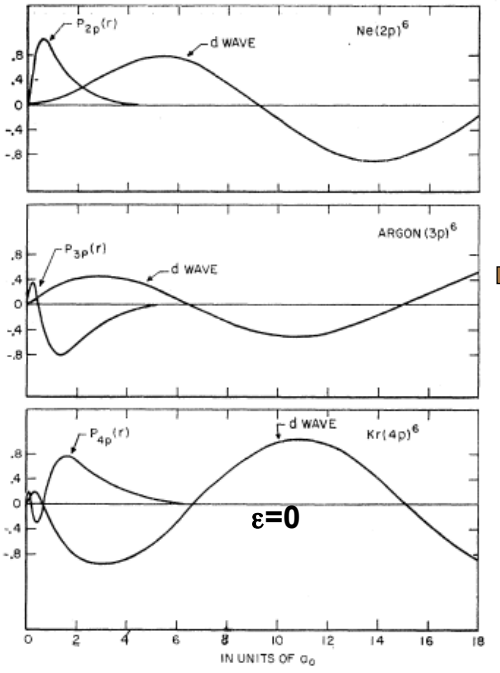
$$R_{\gamma,nl,j_i} = \int_0^\infty P_\gamma(r) r P_{nl,j_i}(r)\, dr$$

a) Global decrease

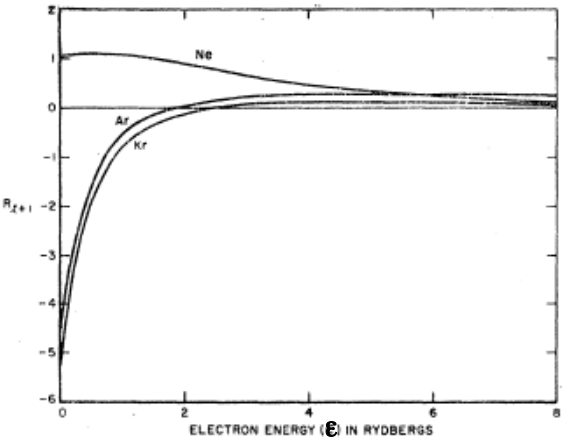


b) Cooper minima

Radial wave function

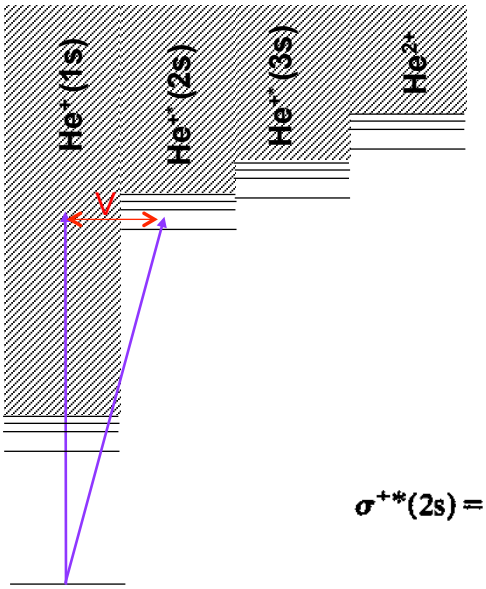


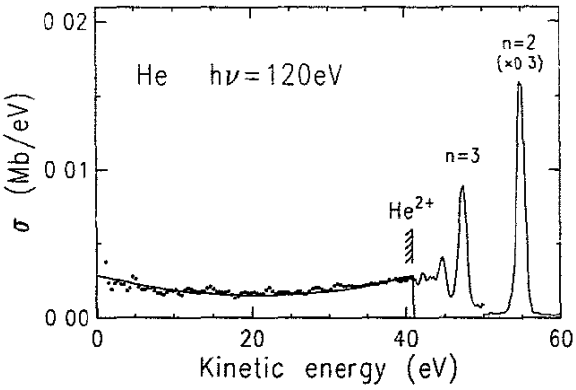
Radial overlap



Cooper, Phys. Rev. **128**, 681 (1962)

Satellites – Shake up



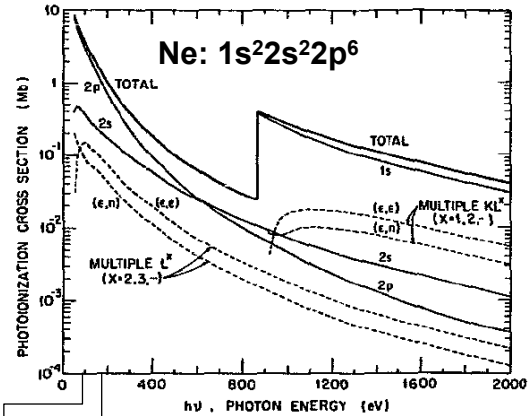


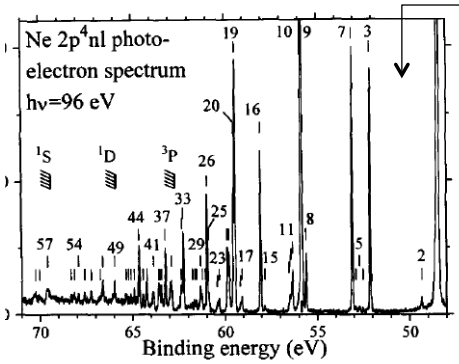
$$\sigma^{+*}(2s) = \frac{4\pi^2}{3}\alpha\omega 2|\langle 2s|1s\rangle|^2 R^2_{ep,1s}$$

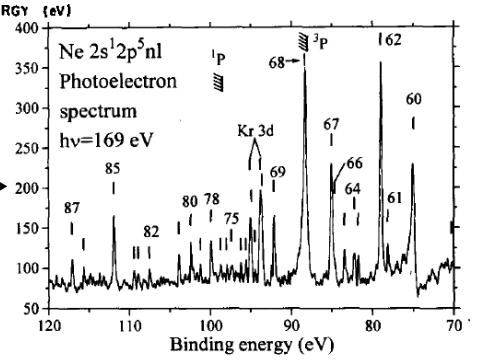
$$\sigma^{+*}(2p) = \frac{4\pi^2}{3}\alpha\omega 2|\langle \varepsilon s|1s\rangle|^2 R^2_{2p,1s}$$

Overlap should be non zero

Total cross section / partial cross- section



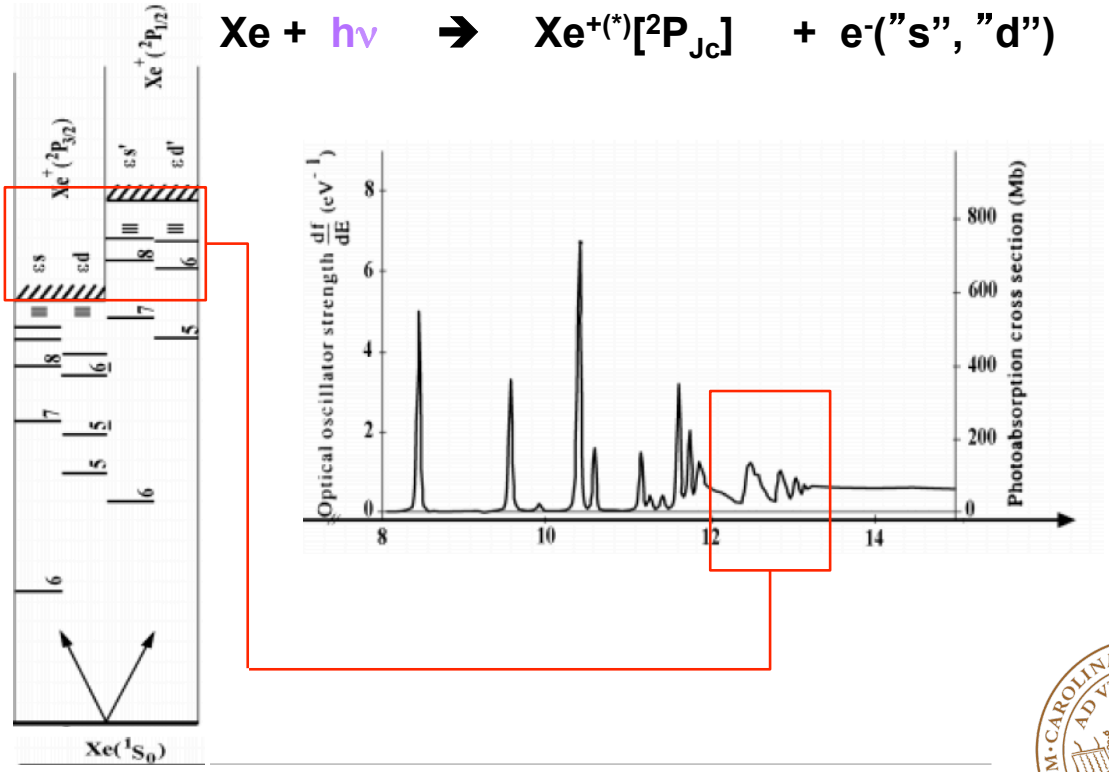




… and some more effects..?..

Photo-absorption / Ionization – two cores

Xe + hν ➔ $Xe^{+(*)}[^2P_{Jc}]$ + e^-(”s”, ”d”)



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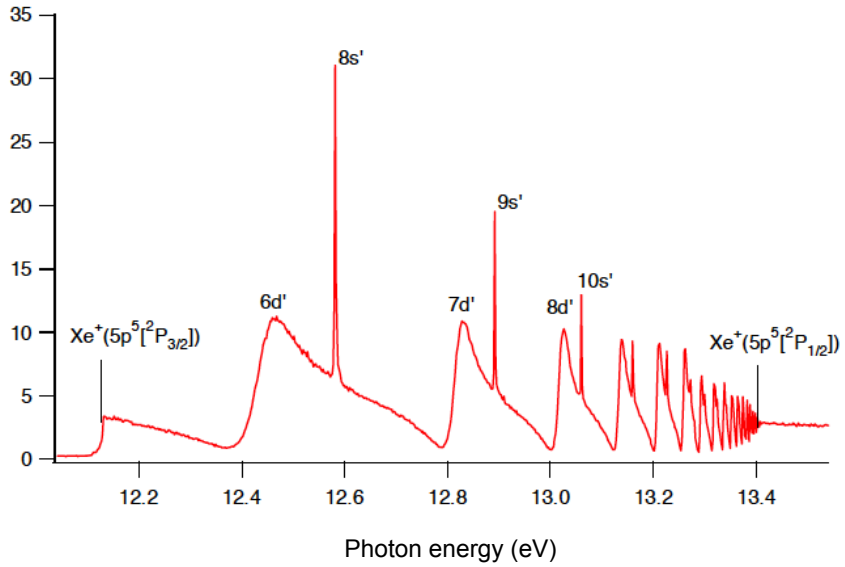
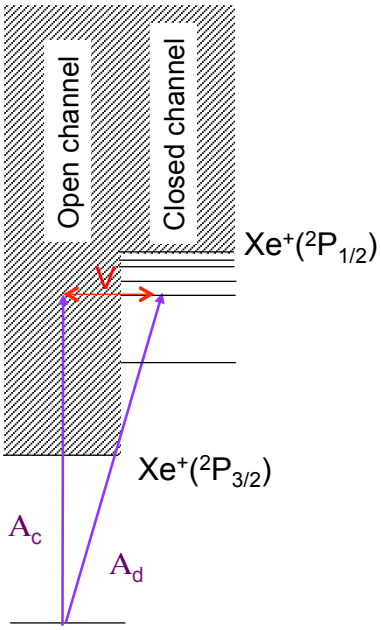
Auto-ionization – two cores



Auto-ionization – parametrization



Parameterization of the resonance

$$\sigma(E) = \sigma_a \frac{(q+\varepsilon)^2}{1+\varepsilon^2}$$

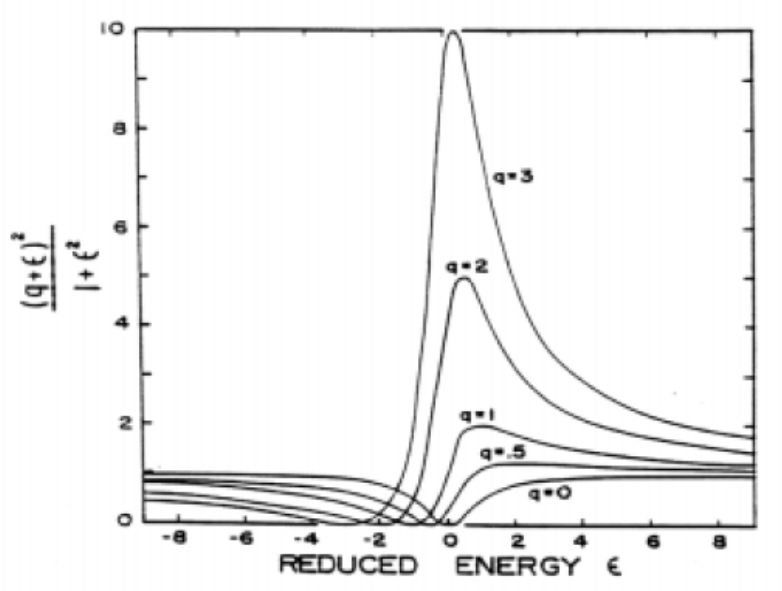
σ_a: is the cross section $\propto |A_c|^2$

q: is the profile index $\propto A_d/(V^*A_c)$

ε: is the reduced energy $(E-E_r)/(\Gamma/2)$

Γ: is resonance width $2\pi|V_E|^2$

Auto-ionization - parametrization



U. Fano, Phys. Rev. **124**, 1866 (1961)

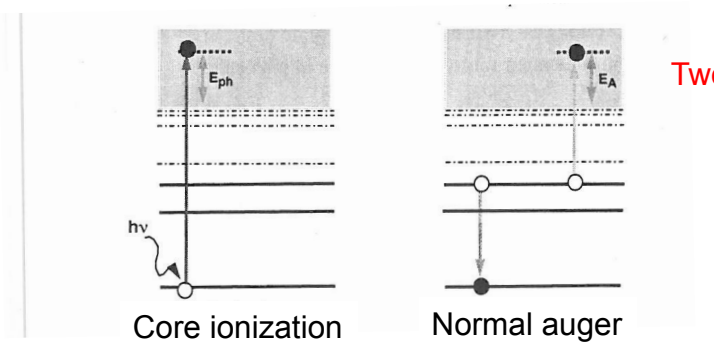
Tips: Rydberg series assignment

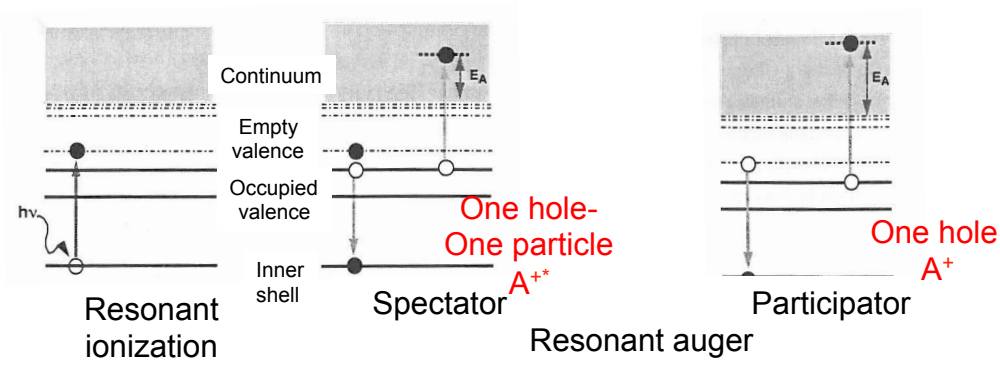
Generalized Rydberg formulae

$$E_n = IP - \frac{R}{(n-\mu)^2} = IP - \frac{R}{n^{*2}}$$

IP: Ionization potential
R: Rydberg constant (109736,86 cm^{-1})
n: principal quantum number, n* effective principal quantum number
μ: quantum defect

Auger


E_{ph}
hν
E_A
Two holes
A^{2+}
Core ionization
Normal auger


Continuum
Empty valence
Occupied valence
Inner shell
hν
E_A
One hole-
One particle
A^{+*}
E_A
One hole
A^+
Resonant ionization
Spectator
Participator
Resonant auger