Computations of electron-molecule collisions : Prototype case of H_2^+ + e reactions

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Joint ICTP-IAEA Workshop on Fusion Plasma Modelling using Atomic and Molecular Data
23 - 27 January 2012 ICTP Trieste, Italy.

Outline

Lecture 1 : Monday 23 January 2012, 11:15 – 12:00

1. General introduction
2. MQDT and R-matrix approaches in atomic physics
3. Atomic data

Lecture 2 : Thursday 26 January 2012, 08:30 – 10:00

1. Electron-molecular ion collisions : H_2^+ prototype
2. The halfium model
3. Molecular data : Results for H_2
4. Further systems (HeH+, LiH, alkali dimers, …)

Computations of electron-molecule collisions : Lecture 1

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Outline (Lecture 1)

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1. General introduction
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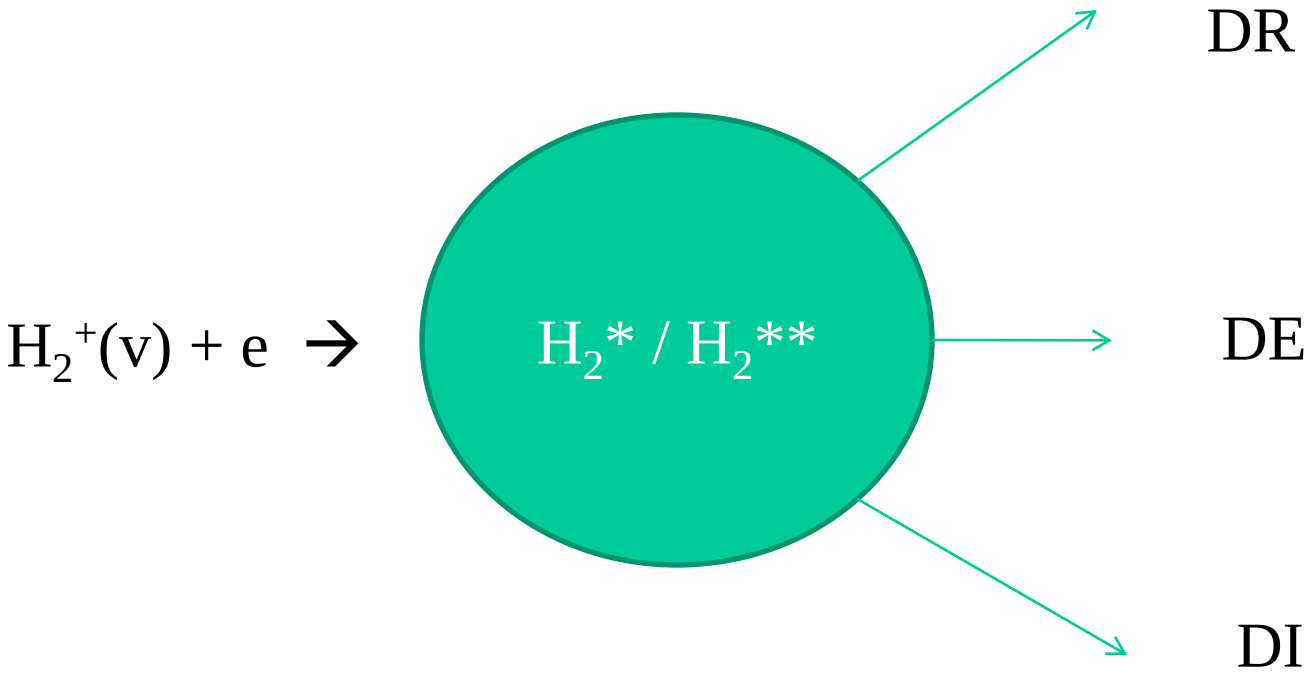
3. Atomic data

Hydrogen molecular ion reactions

- $H_2^+(v)+e \rightarrow H_2^+(v)+e$ (elastic collision)
- $H_2^+(v)+e \rightarrow H_2^+(v')+e$ (inelastic collision $v'>v$)
- $H_2^+(v)+e \rightarrow H_2^+(v')+e$ (superelastic collision $v'<v$)
- $H_2^+(v)+e \rightarrow H+H$ (DR)
- $H_2^+(v)+e \rightarrow H^++H+e$ (DE)
- $H_2^+(v)+e \rightarrow H^++H^+ +2e$ (DI)

Hydrogen molecular ion reactions



Need for *ab initio* characterization of excited and doubly-excited molecular hydrogen

Back to basics

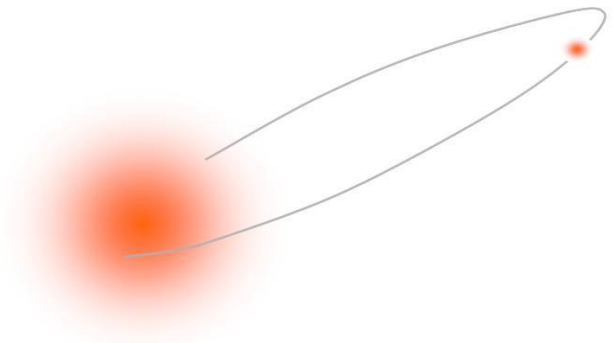
- Hydrogen atom :
  - The non-relativistic Schrödinger equation is exactly solvable
  - The wavefunctions can be factorized

$$H\Psi(\vec{r}) = E\Psi(\vec{r})$$

$$H = -\frac{1}{2}\Delta + V(r)$$

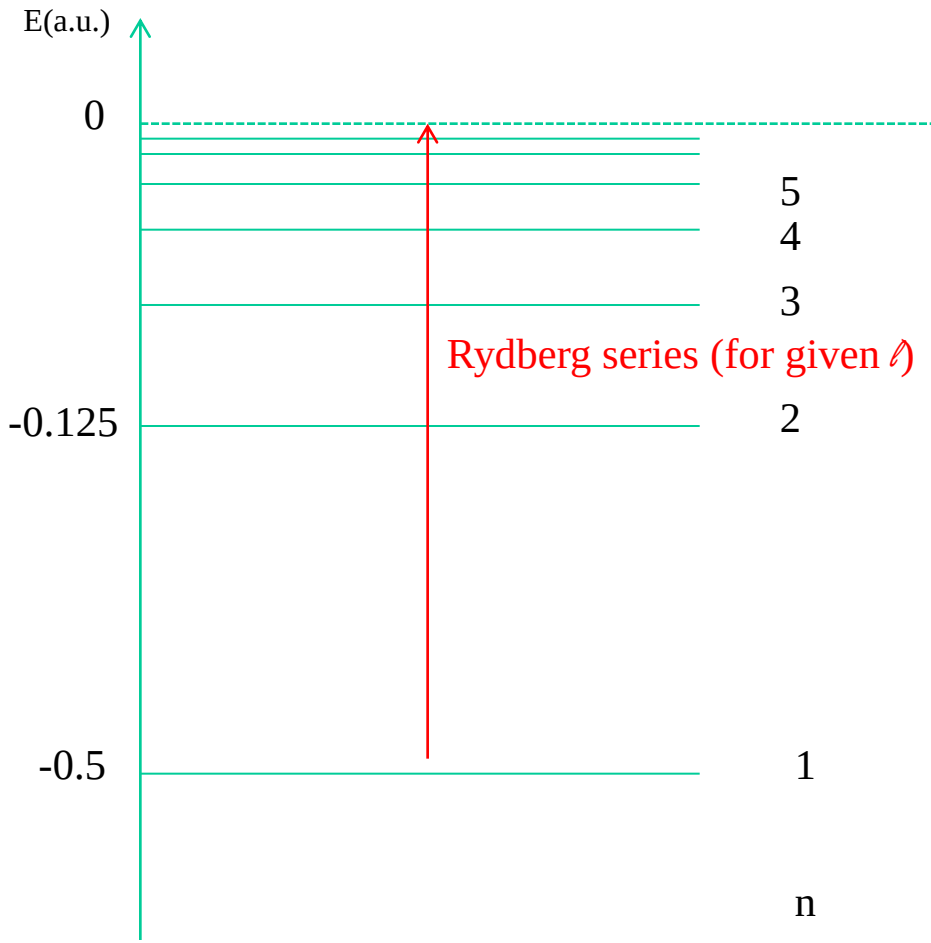
$$V(r) = -\frac{1}{r}$$

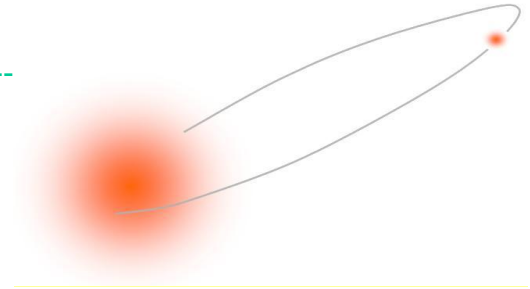
$$\Psi_{n\ell m}(\vec{r}) = \frac{1}{r}u_{n\ell}(r)Y_{\ell}^{m}(\theta,\varphi)$$



$$E_n = -\frac{1}{2n^2}(a.u.)$$

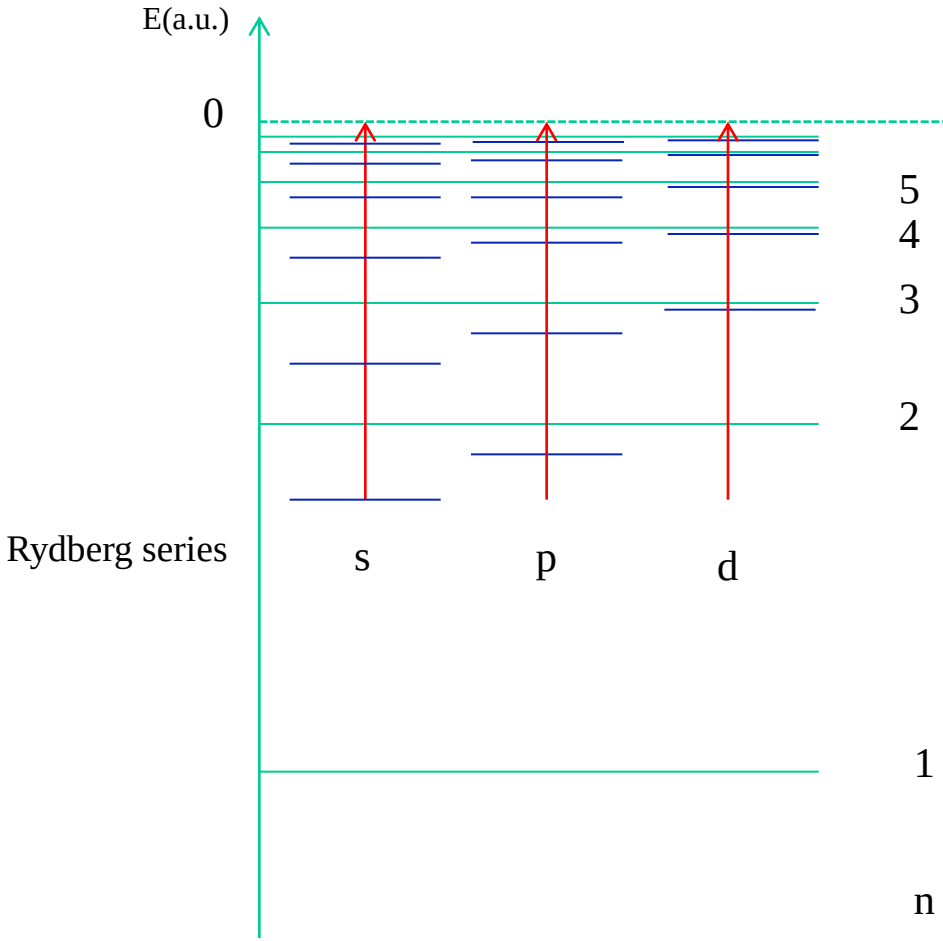
Hydrogen atom spectrum

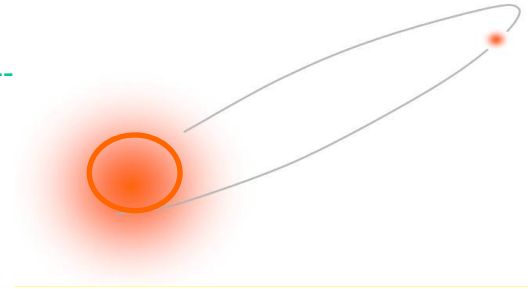




$$E_n = -\frac{1}{2n^2}(a.u.)$$

Alkali atom spectrum





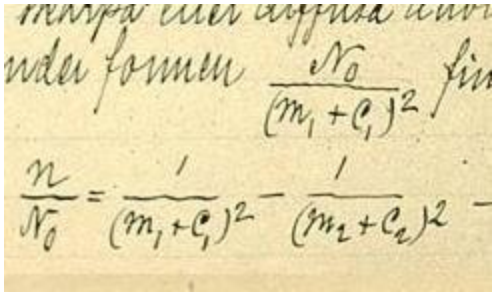
$$E_n = -\frac{1}{2(n-\delta_\ell)^2}(a.u.)$$

δ_ℓ : quantum defect

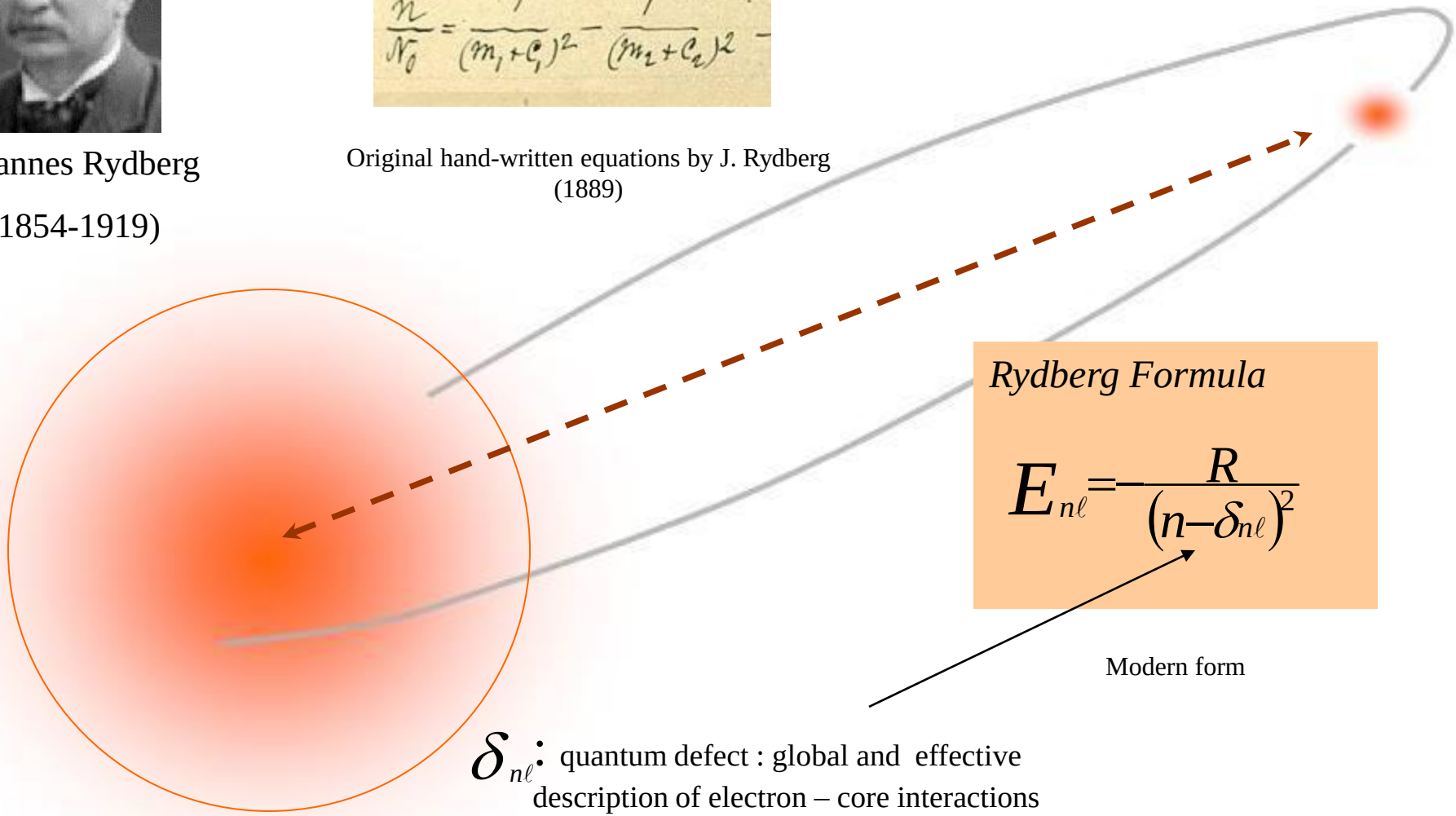
Rydberg Quantum Defects

Johannes Rydberg

(1854-1919)



Original hand-written equations by J. Rydberg (1889)



Rydberg Formula

$$E_{n\ell} = -\frac{R}{(n-\delta_{n\ell})^2}$$

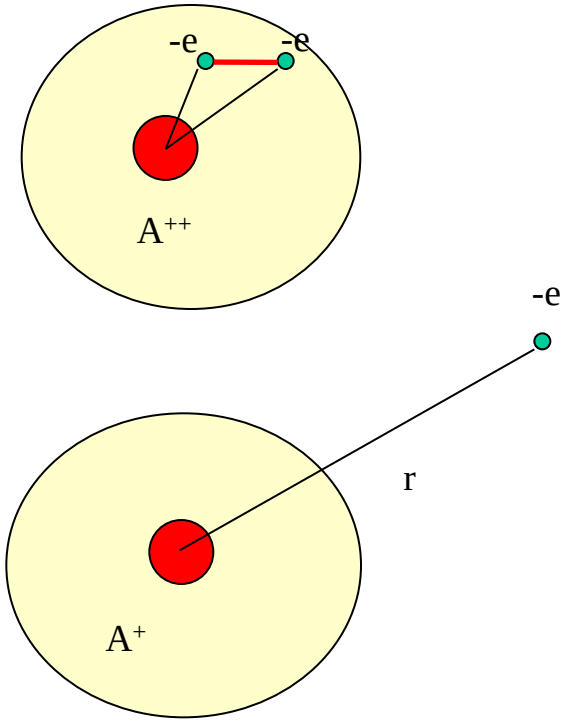
Modern form

$\delta_{n\ell}$: quantum defect : global and effective description of electron – core interactions

Central potential

Bielectronic correlation :

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} P_{\ell}(\cos\theta)\frac{r_{<}^{k}}{r_{>}^{k+1}}$$



Central potential V(r)

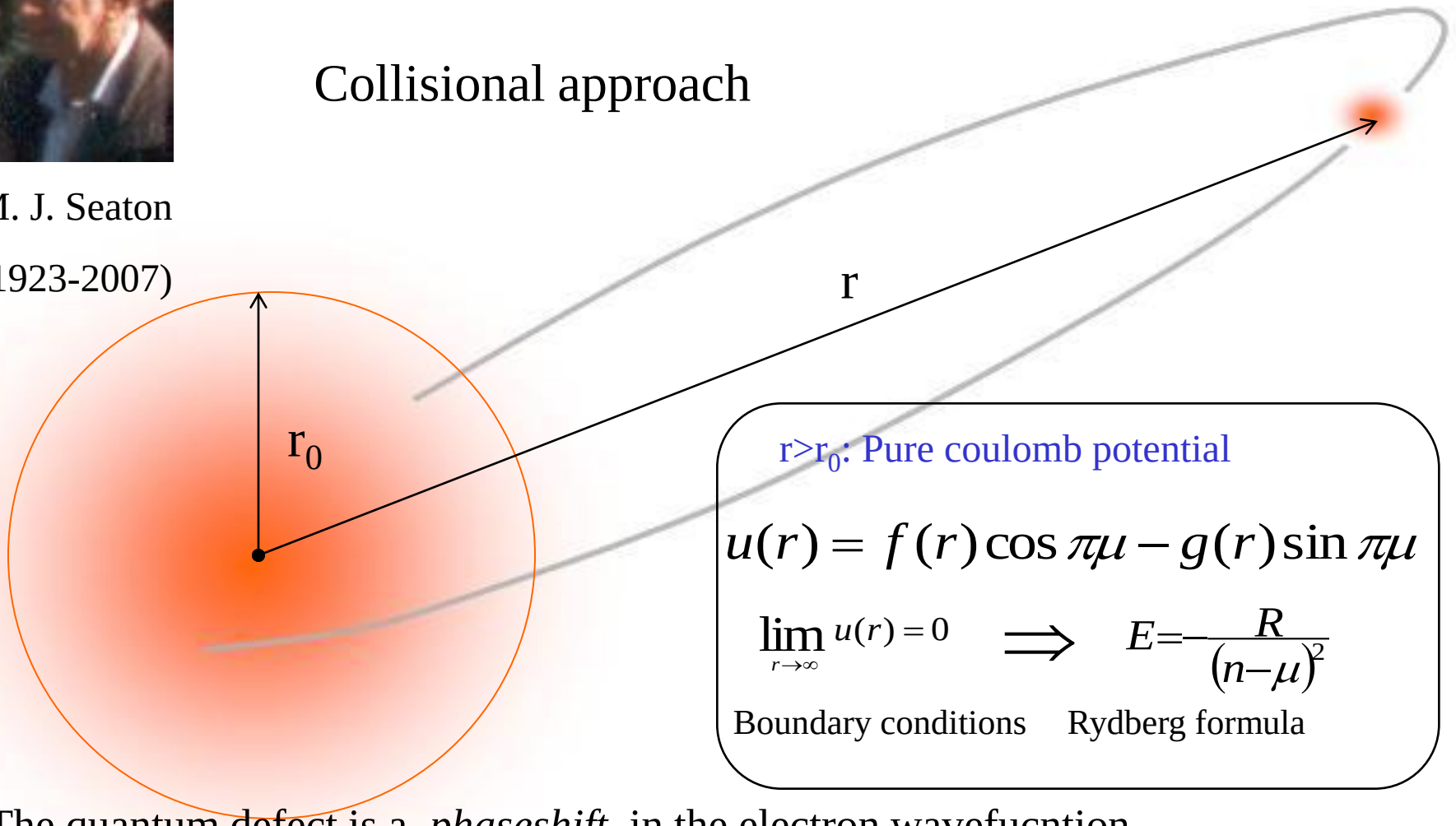
$$V(r) = -\frac{1}{r} + \frac{B}{r^2} \Rightarrow \mu \cong \frac{B}{\ell + 1}$$

Quantum Defect Theory

M. J. Seaton

(1923-2007)

Collisional approach



$r > r_0$: Pure coulomb potential

$$u(r) = f(r)\cos\pi\mu - g(r)\sin\pi\mu$$

$$\lim_{r\to\infty} u(r) = 0 \quad \Longrightarrow \quad E = -\frac{R}{(n-\mu)^2}$$

Boundary conditions Rydberg formula

The quantum defect is a *phaseshift* in the electron wavefucntion

Coulomb functions

Coulomb functions are solutions of radial Schrödinger equation in pure Coulomb potential :

$$\left[-\frac{d^2}{dr^2}-\frac{2}{r}+\frac{\ell(\ell+1)}{r^2}\right]u(r)=Eu(r)$$

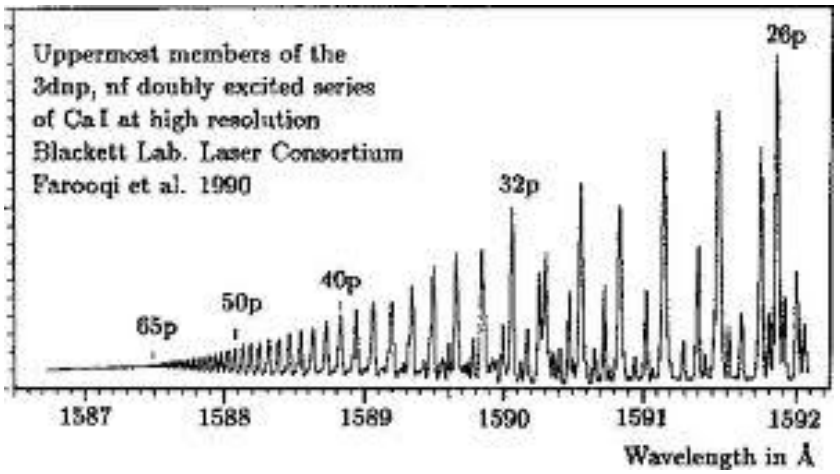
Regular solution $f(r)\propto r^{\ell+1}$

Irregular solution $g(r)\propto r^{-\ell}$

$r\to 0$

The Rydberg formula is analytically derived

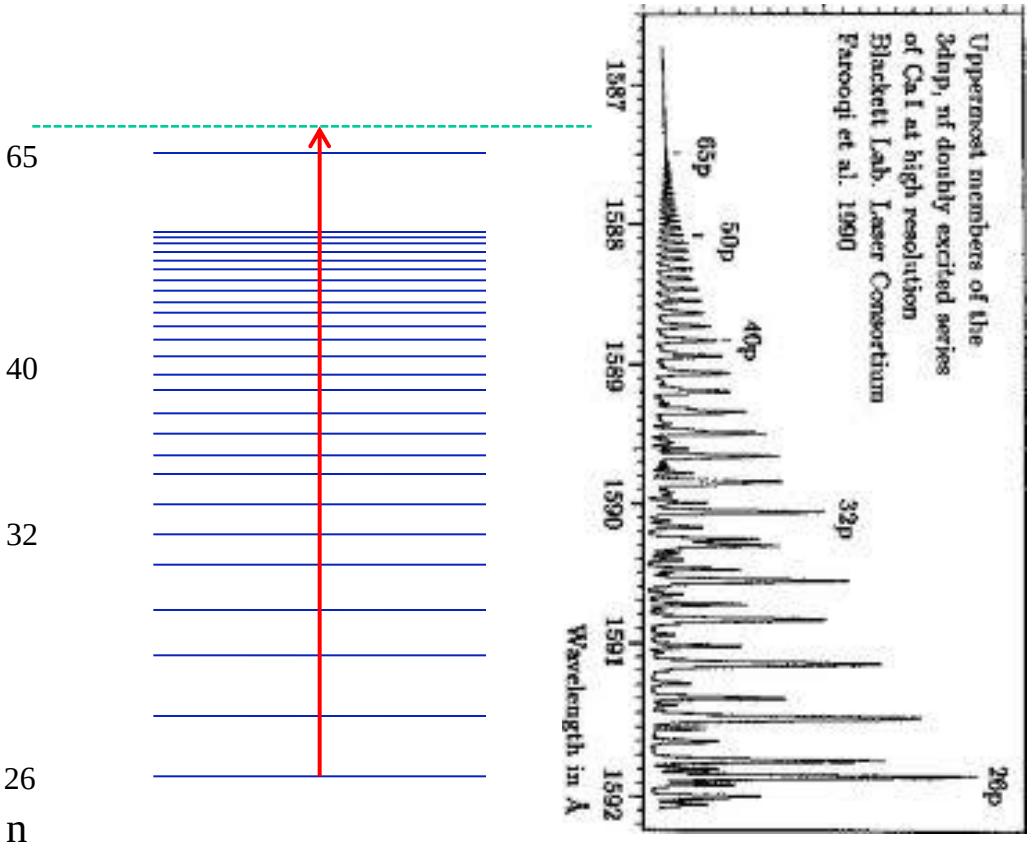
Two-electron atoms spectra



Rydgerg series in calcium spectrum
(Farooqi *et al* 1990)

Two-electron atoms spectra

Rydberg states
are stepstones
towards continuum



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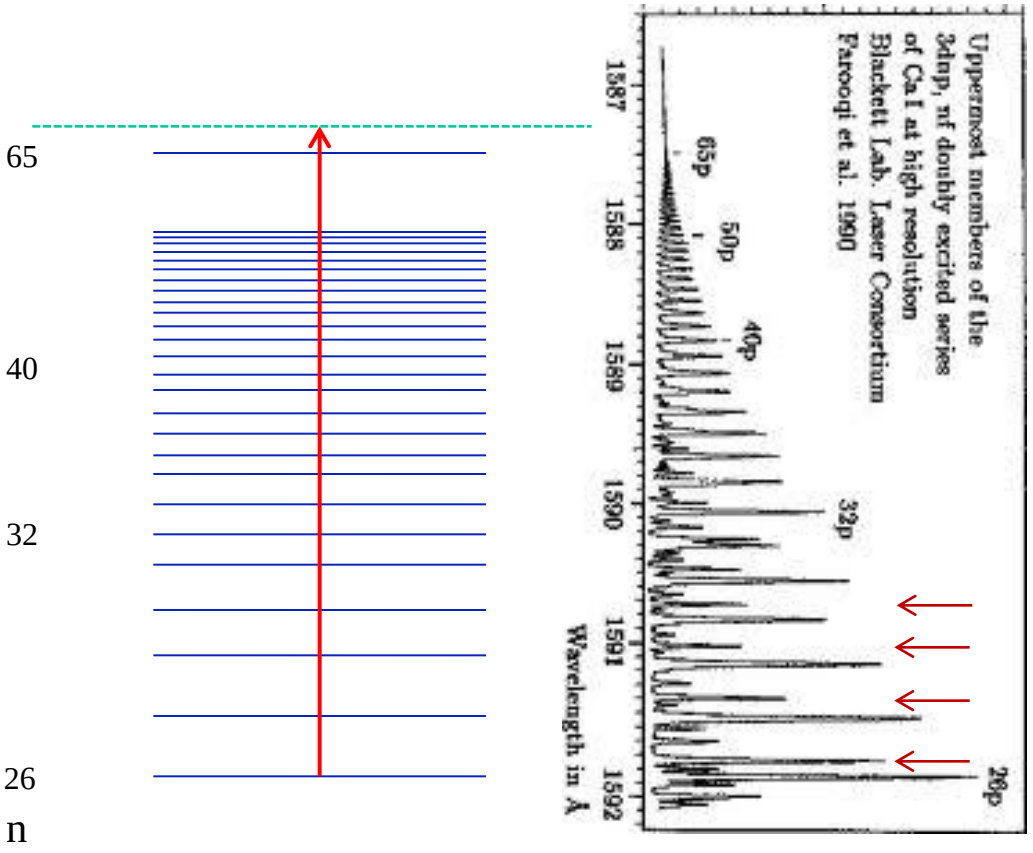
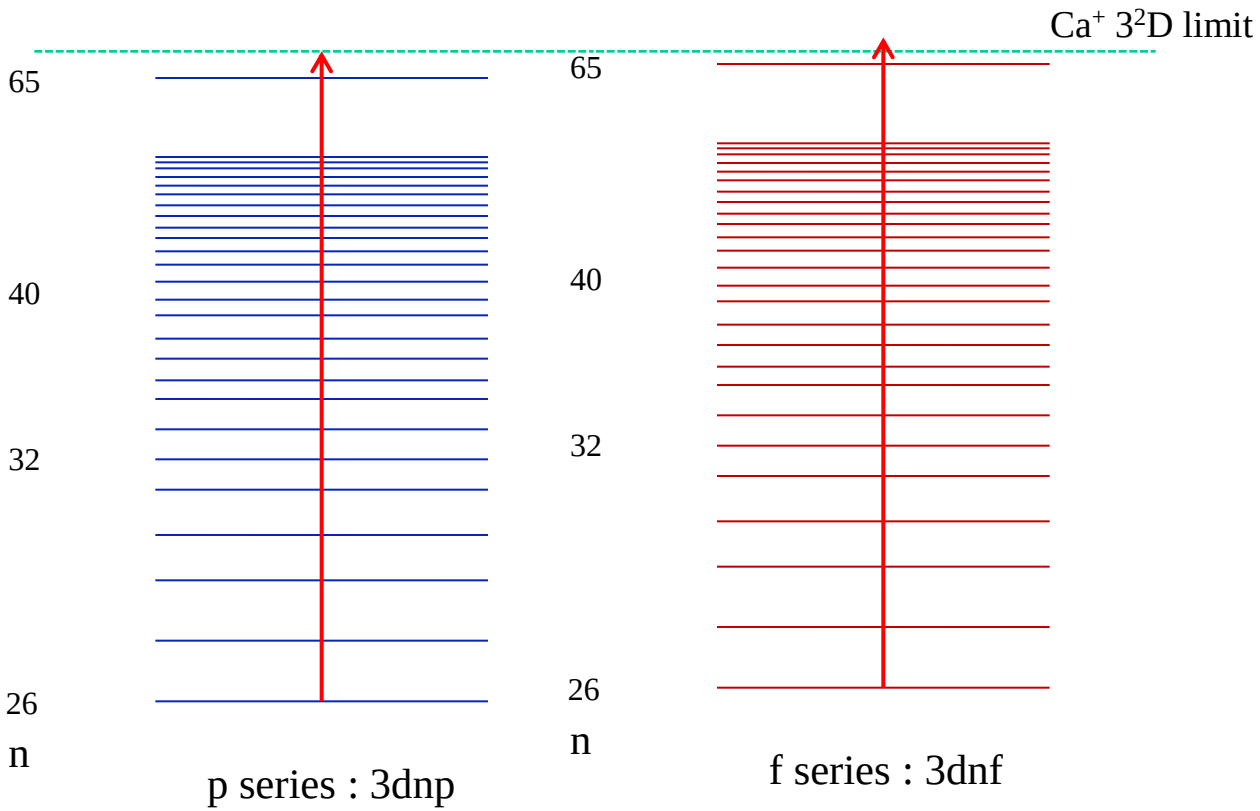


Rydgerg series in calcium spectrum
(Farooqi *et al* 1990)

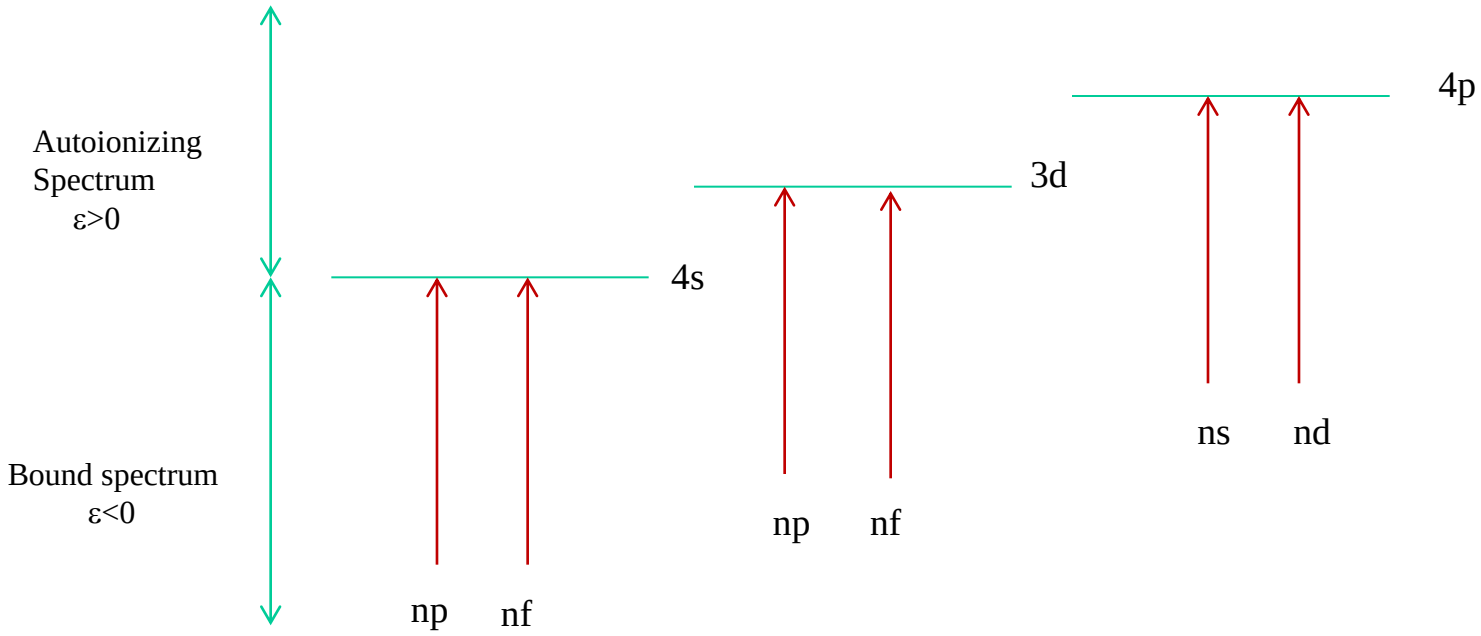
Two-electron atoms spectra

Two interacting Rydberg series converging to the same limit



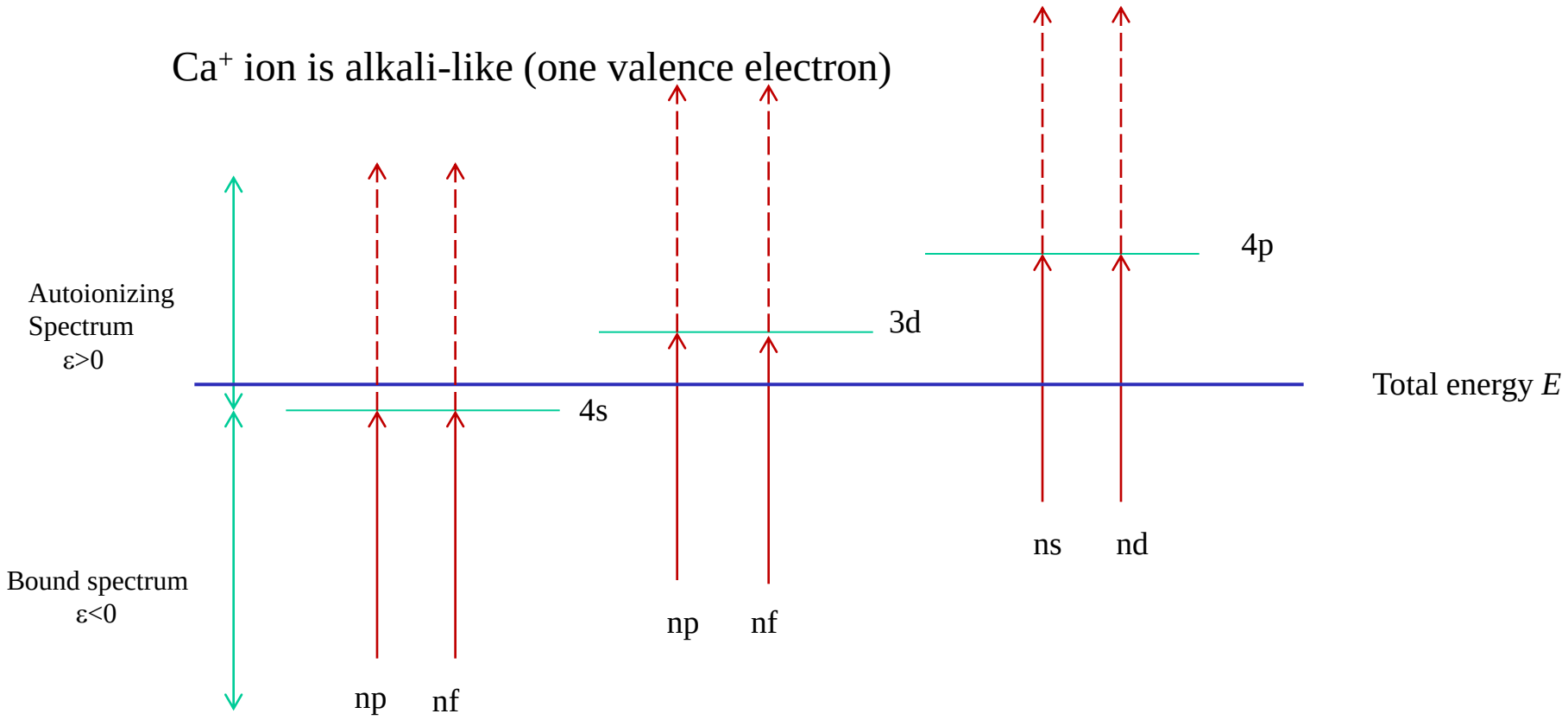
Channels

Ca^+ ion is alkali-like (one valence electron)



For a given symmetry e.g. $^1P^o$ compatible with the Hamiltonian

Channels

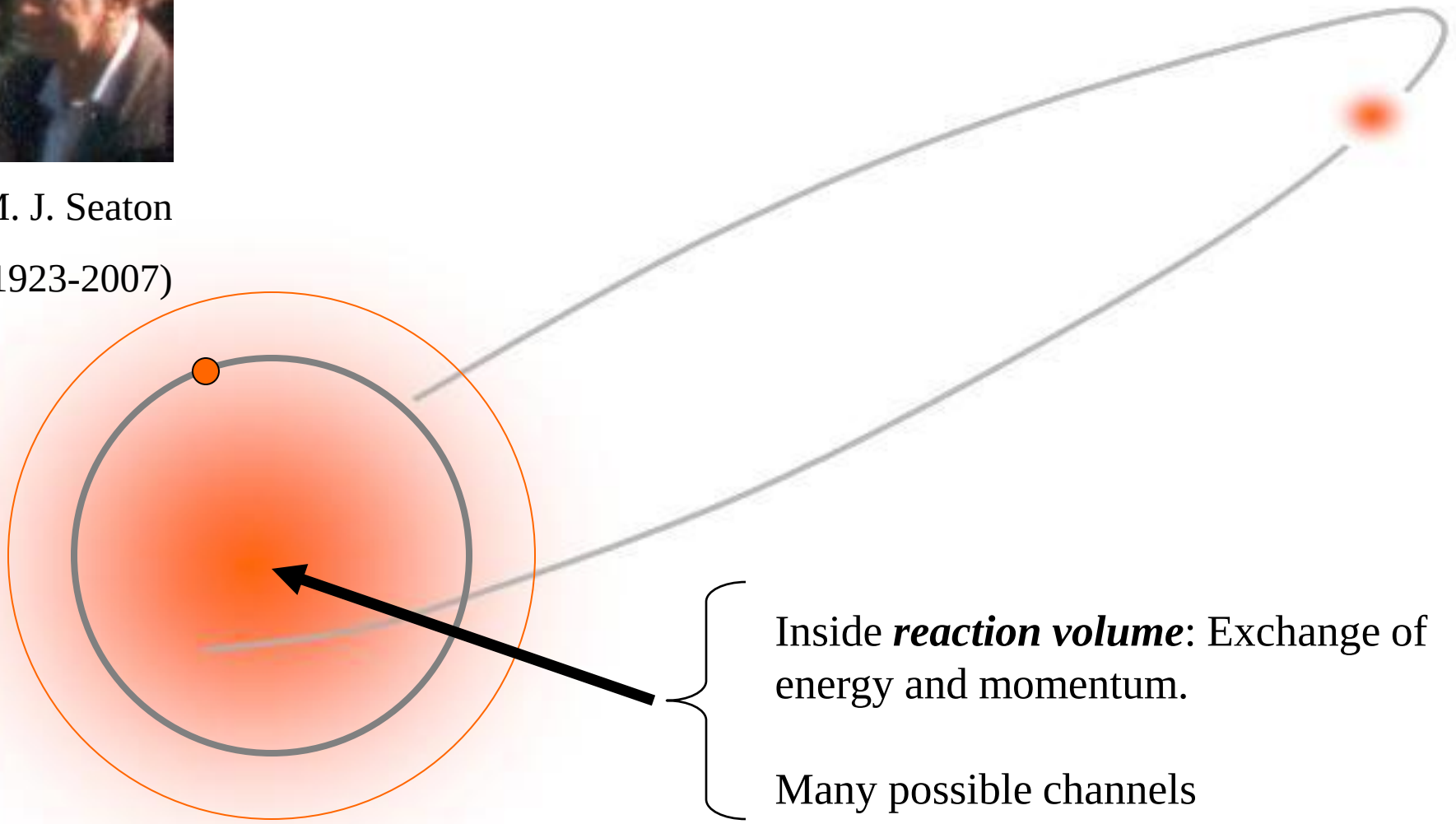


For a given symmetry e.g. $^1P^o$ compatible with the Hamiltonian

Quantum Defect Theory: multichannel case

M. J. Seaton

(1923-2007)



Inside ***reaction volume***: Exchange of energy and momentum.

Many possible channels

Quantum Defect Theory: multichannel case

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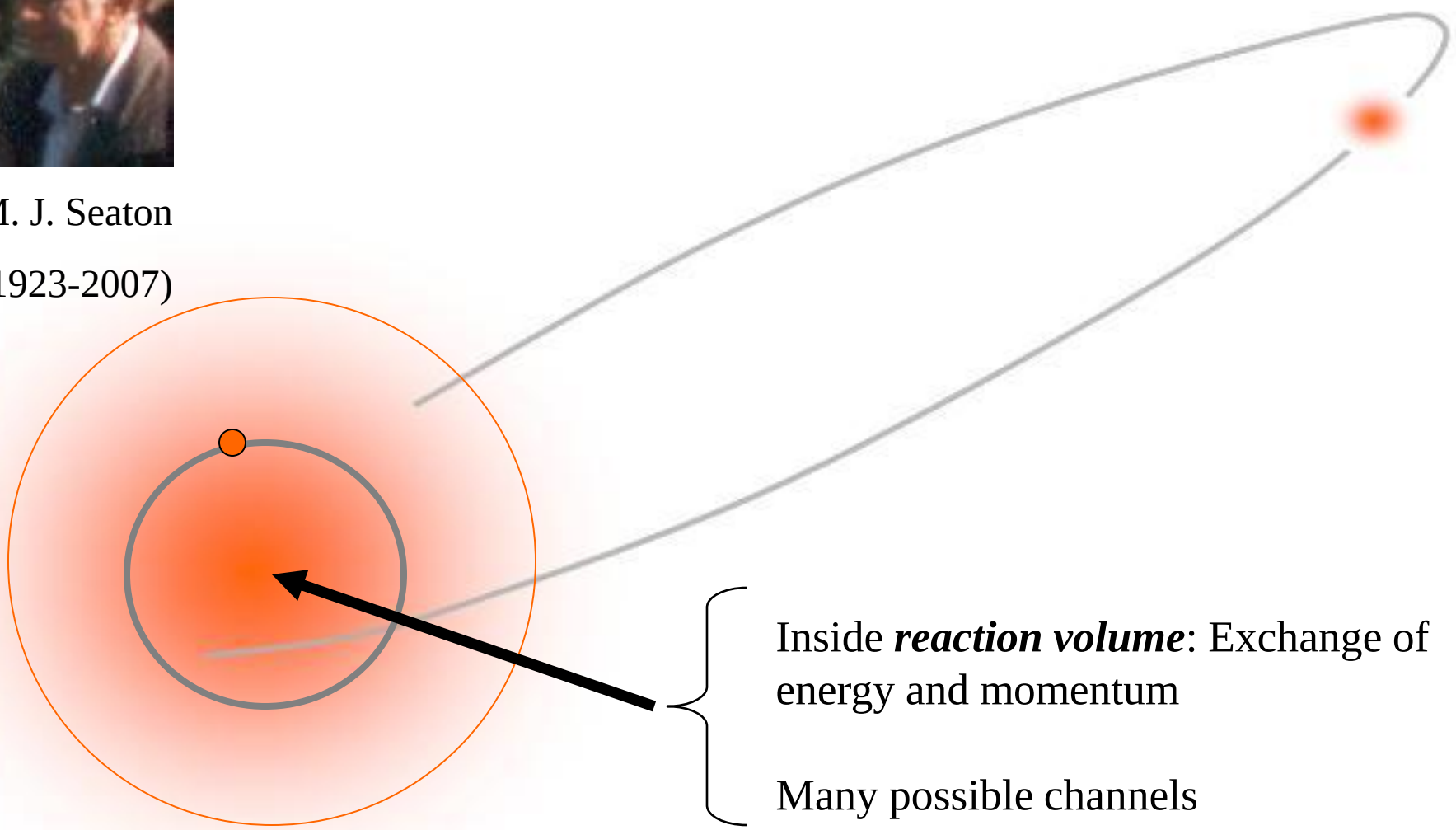

Quantum Defect Theory: multichannel case

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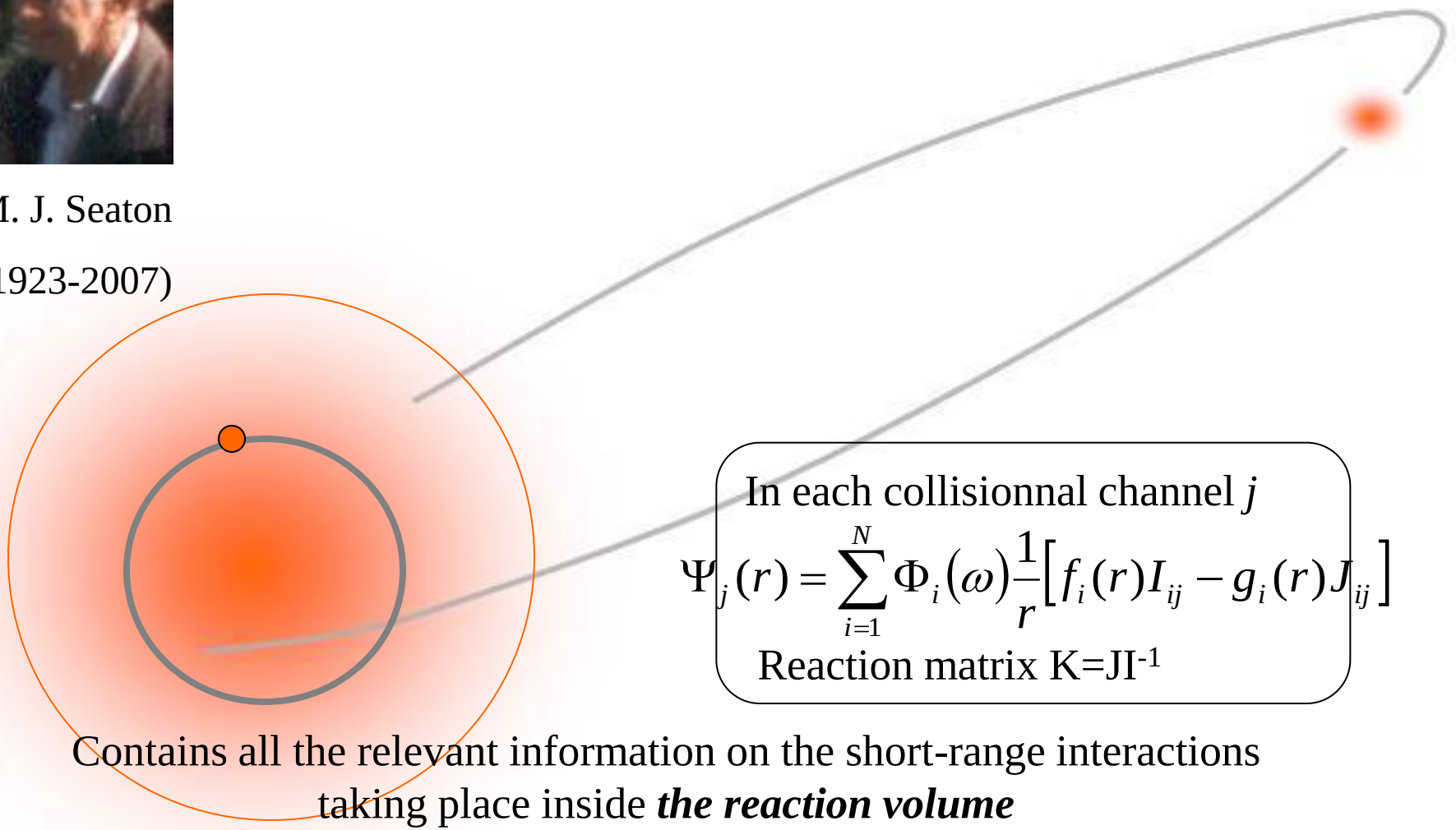


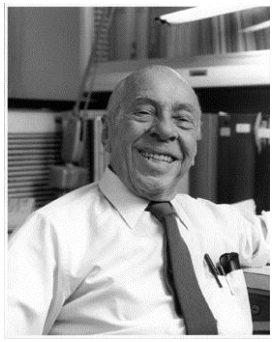
In each collisionnal channel j

$$\Psi_j(r) = \sum_{i=1}^{N} \Phi_i(\omega) \frac{1}{r} \left[f_i(r) I_{ij} - g_i(r) J_{ij} \right]$$

Reaction matrix $K = JI^{-1}$

Contains all the relevant information on the short-range interactions taking place inside ***the reaction volume***

Eigenchannel approach

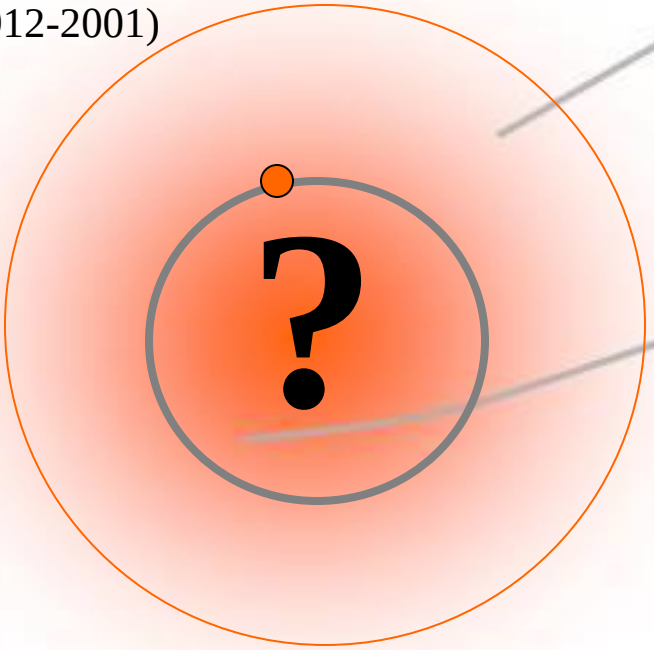


Ugo Fano

(1912-2001)

The reaction matrix K is diagonal

$$K_{ij}=\sum_{\alpha=1}^{N} U_{i\alpha}\tan\pi\mu_\alpha U^{+}_{\alpha j}$$



$$\Psi_\alpha(r)=\sum_{i=1}^{N}\Phi_i(\omega)U_{i\alpha}\frac{1}{r}[f_i(r)\cos\pi\mu_\alpha-g(r)\sin\pi\mu_\alpha]$$

$$\det|U_{i\alpha}\sin\pi(\nu_i+\mu_\alpha)|=0$$

μ_α: Eigenquantum defect in eigenchannel α

Frame transformation

R-matrix Theory

Eugene Paul Wigner

(1902-1995)

Resonances in nuclear collisions (1947)

Reaction volume

$$\Psi(r)=\sum_{k=1}^{N} c_k y_k$$

The basis functions y_k have the same logarighmic derivative on the reaction surface

$$R_{ij}=\frac{1}{2}\sum_{\lambda}\frac{\gamma_\lambda^i\gamma_\lambda^j}{\mathrm{E}\lambda-E}$$ Wigner matrix

$$K=(f'+R^{-1}f)(g'+R^{-1}g)^{-1}$$

To determine ***the reaction matrix K***, one needs ***Wigner R-matrix***

Variational R-matrix method

Normal logarithmic derivative of the wavefunction Ψ on the reaction surface

$$\Psi + b\frac{\partial\Psi}{\partial n} = 0 \Leftrightarrow b = -\frac{1}{\Psi}\frac{\partial\Psi}{\partial n}$$

Walter Kohn

$$\delta b = 0 \quad \Leftrightarrow \quad \delta E = 0$$

Simple case:

E minimal ⇔ b maximal

$$\tan \pi\mu = \frac{f' + bf}{g' + bg}$$

John W. Rayleigh

(1842-1919)

Variational calculation

Expansion of the wavefunction on the variational basis

$$\Psi(\vec{r}_1,\vec{r}_2)=\sum_k c_k y_k(\vec{r}_1,\vec{r}_2)$$

Kohn variational principle

$$\delta b=0 \Leftrightarrow \frac{\partial b}{\partial c_k}=0$$

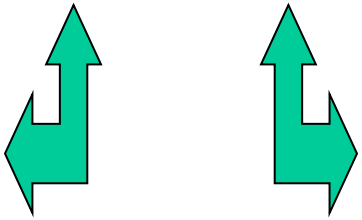
Genaralized eigensystem

$$\Gamma\vec{c}=b\Lambda\vec{c}$$

For each given energy E

$$\Gamma=2(EO-H-L)$$

Interaction matrix



Λ

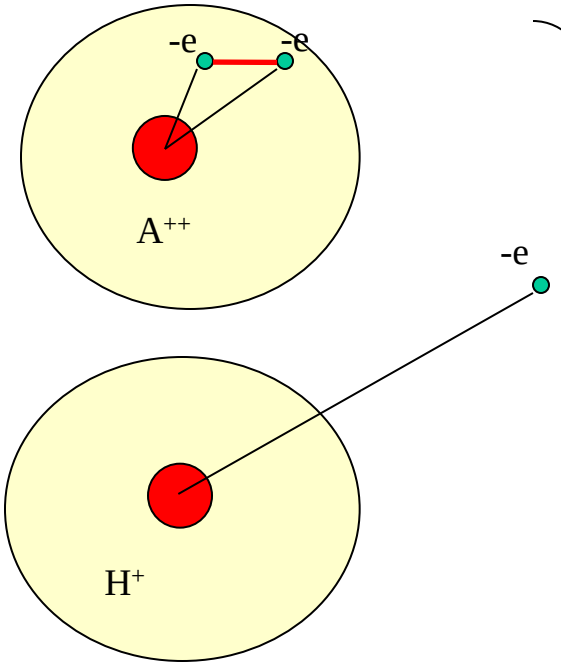
Surface matrix

Ψ_β Solutions havin stationnary logarithmic derivative $\boldsymbol{b}_\beta$ on the reaction surface.

Matching on the reaction surface

• Outside ($r < r_0$)

$$\Psi_\beta = \sum_{i=1}^{N} c_k^\beta y_k$$



•Outside ($r > r_0$)

$$\Psi_\alpha = \sum_{i=1}^{N} \Phi_i(\omega) U_{i\alpha} \frac{1}{r}\left[f_i(r)\cos \pi\mu_\alpha - g(r)\sin \pi\mu_\alpha \right]$$

Projection over the surface harmonics $\Phi_i(\omega)$

Short-range reaction matrix K

$$K_{ij} = \sum_{\alpha=1}^{N} U_{i\alpha} \tan \pi\mu_\alpha U^{+}_{\alpha j}$$

Eigenquantum defects

Quantum defects

- Bound states : below the ionization threshold ($\varepsilon<0$)

Quantization $\det\left|U_{i\alpha}\sin\left(\beta_i+\pi\mu_\alpha\right)\right|=0$ Secular equation

→ Bound states energies

- Resonances : above the ionization threshold ($\varepsilon>0$)

State density $ds(E)=\frac{d}{dE}\sum_\rho \tau_\rho$ Breit-Wigner lorentzian shape

→ Positions and widths of the resonances

Applications in atomic physics

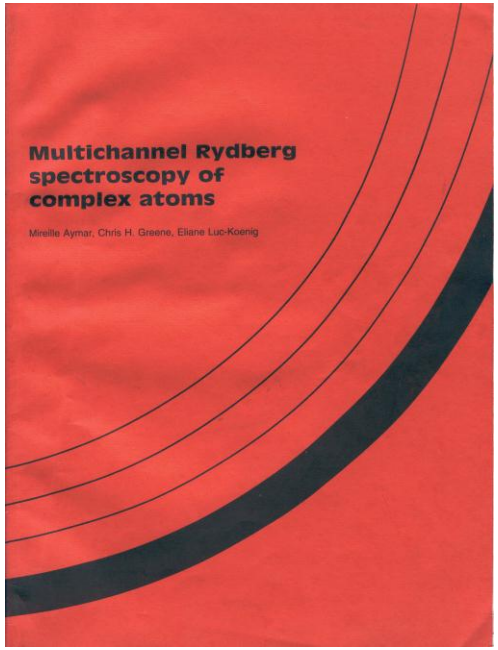
Combination of the multi-channel quantum defect theory and the variational eigenchannel R-matrix (C.H. Greene et M. Aymar)

- Alkaline earth atoms : Be, Mg, Ca, Sr, Ba, Ra

- Energies of bound states for many Rydberg series
- Autoionization widths and branching ratios
- Photoionization cross sections
- Fine and hyperfine structure (frame transformation)
- Angular distributions of photoelectrons
- etc.

Applications in atomic physics

Combination of the multi-channel quantum defect theory and the variational eigenchannel R-matrix (C.H. Greene et M. Aymar)



M. Aymar, C.H. Greene and E. Luc-Koenig,
Rev. Mod. Phys. **68** 1015 (1996)

Conclusion

- Theoretical study of electron-ion collisions at low energy requests a good description of the excited atomic compound
- The combination of Multichannel Quantum Defect Theory and Variational R-matrix method allows for an ab initio investigation of Rydberg and doubly-excited states with a very good agreement with experimental data
- The formalism is potentially generalizable to other systems, in particular to electron-molecular ion collisions
- The latter point will be developed in the second lecture of this course.

Outlook

- Next lecture will focuss on melecular systems
- Prototype system $H_2^+ + e$
- Generalization of the (R-matrix + MQDT) formalism to small diatomic molecules : The halfium model
- Applications and results