Lectures on Rydberg atoms and cold Rydberg atoms

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- What’s a Rydberg atomic state?
  A highly electonically excited state, meaning with a high principal quantum number.

- What does that mean?
- What are its properties?

- We start with the simplest atom: the hydrogen atom

- But first
  - Who was Mr. Rydberg?
  - Why Rydberg lectures?

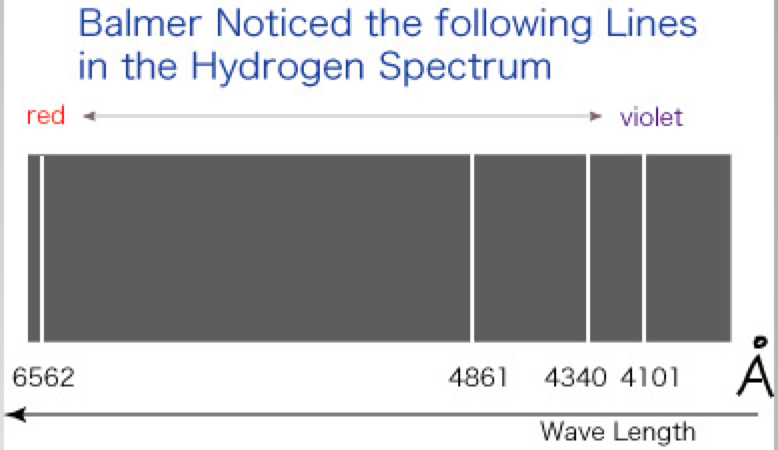
Introduction

- 1885 J. Balmer: regularities of series of the emission lines of the hydrogen with the empirical formula

$$\nu_{ab} = R\left(\frac{1}{n_a^2} - \frac{1}{n_b^2}\right) \quad ; \; n_a = 2 \;\; , \;\; n_b = 3, 4...$$

$$R = 109737.31 \text{ cm}^{-1} \simeq 30 \times 109737.31 \text{ GHz}$$

$$R = 13.6 \text{ eV} \;\; \text{is the Rydberg constant}$$



- 1890 J.R. Rydberg shows that other atoms (especially the alkalis) present similar regularities in their spectra corresponding to differences of terms

$$T_n = R\frac{1}{(n+\alpha)^2}$$

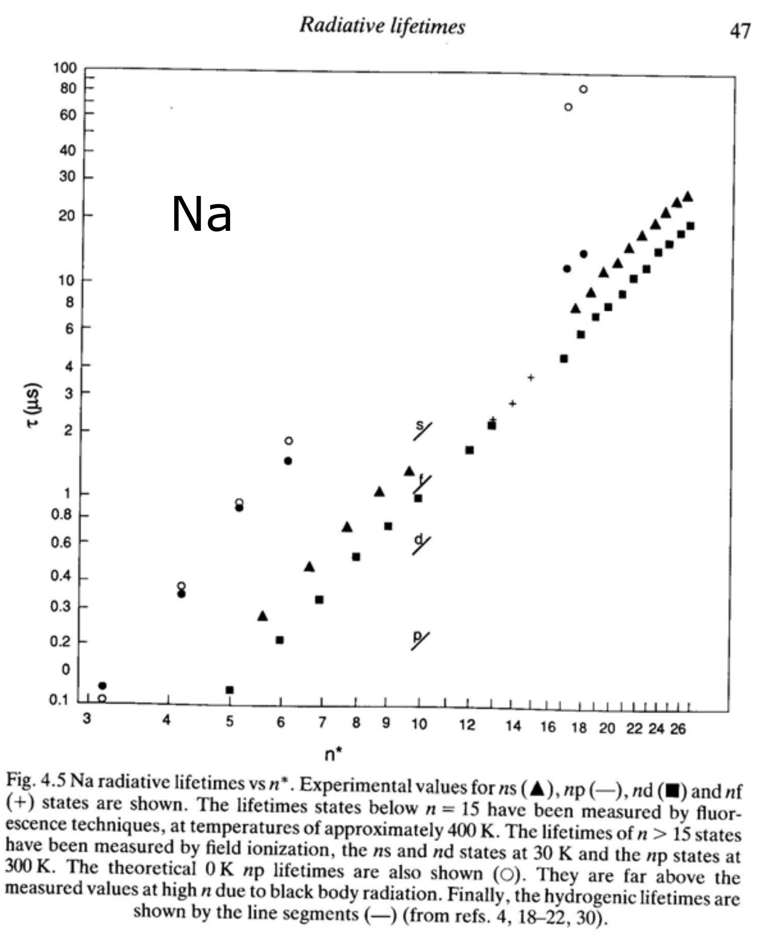
Johannes Robert Rydberg
Swedish physicist

- It looks old physics
- Yes, but it is a very rich Physics.
- All atomic physics, atom light interaction can be learned with Rydberg atoms.
- More Rydberg atoms have exaggerated properties and allow to realize extreme situations laboratories.
- Experimentally they are easily created by laser excitation and detected by electric field ionization.
- They allow to isolate clean physical situation, and to study many fundamental effects.
- Finally cold Rydberg atoms have recently open a new field of research very fascinating, with possible various applications making excitation of Rydberg atoms an efficient tool for quantum engineering or for quantum simulations or novel situations (ultracold plasmas).

Why lectures about Rydberg atoms?

Interests and motivations

- Selectively excited by tunable lasers
- Exaggerated properties
  - Huge size: $n^2 a_0$
  - Long lifetime: scale as n^3
  - …
- Sensitive to external fields (electric, magnetic or electromagnetic fields, blackbody radiation…)
  - Selective electric field ionization as $n^{-4}/16$ a.u. (*$n=30$, 400V/cm; $n=100$, 3V/cm*)
  - …
- To simulate extreme physical situations or « gedanken » experiments (non destructive measurement of the presence of one photon in a cavity)



Radiative lifetimes 47

Fig. 4.5 Na radiative lifetimes vs n^*. Experimental values for ns (▲), np (—), nd (■) and nf (+) states are shown. The lifetimes states below $n = 15$ have been measured by fluorescence techniques, at temperatures of approximately 400 K. The lifetimes of $n > 15$ states have been measured by field ionization, the ns and nd states at 30 K and the np states at 300 K. The theoretical 0 K np lifetimes are also shown (○). They are far above the measured values at high n due to black body radiation. Finally, the hydrogenic lifetimes are shown by the line segments (—) (from refs. 4, 18–22, 30).

- Rydberg atoms by Thomas F. Gallagher (Lectures IFRAF at laboratoire Aimé Cotton)
- Quantum mechanics of one- and two-electron atoms (Bethe and Salpeter)
- Quantum mechanics books (Landau and Lifchitz, Messiah, Cohen-Tannoudji et al., Basdevant and Dalibard, …)
- MQDT (Ch. Jungen, Molecular applications of quantum defect theory)
- Review articles

A few references

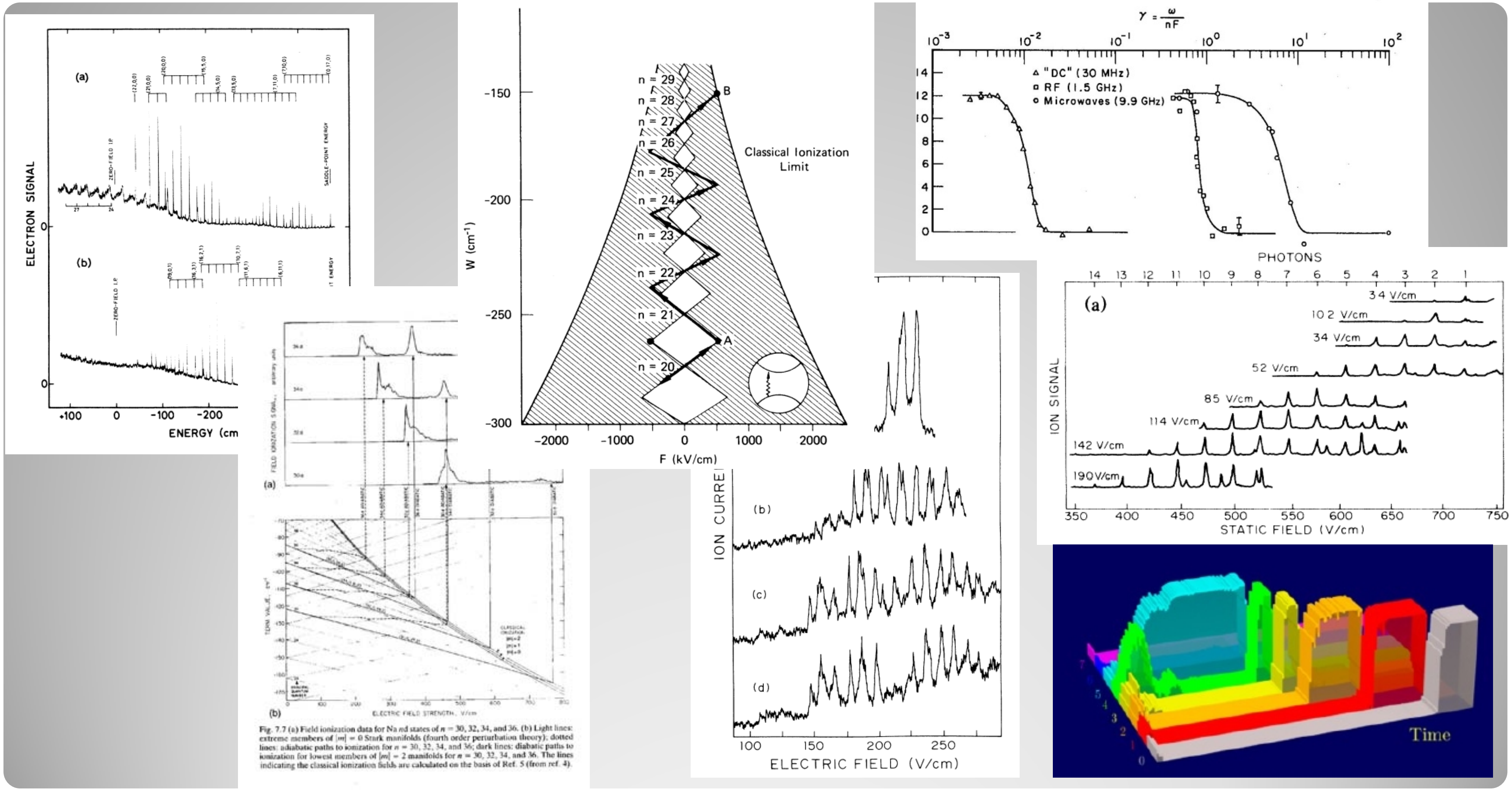


Fig. 7.7 (a) Field ionization data for Na nd states of n = 30, 32, 34, and 36. (b) Light lines: extreme members of |m| = 0 Stark manifolds (fourth order perturbation theory); dotted lines: adiabatic paths to ionization for n = 30, 32, 34, and 36; dark lines: diabatic paths to ionization for lowest members of |m| = 2 manifolds for n = 30, 32, 34, and 36. The lines indicating the classical ionization fields are calculated on the basis of Ref. 5 (from ref. 4).

A few examples

Rydberg atoms in electric field? From static field to quantum field

Photoionization of H in static field, electric field ionization, microwave ionization, multiphoton transition, microwave assisted collisions, Rydberg atoms in cavity

Recall on the hydrogen atom

An anytically solvable quantum system

They are not many (harmonic oscillator, hydrogen atom in an electric field, ~negative molecular ion of hydrogen)

We can show that the equation of the 3D harmonic oscillator are the same as the hydrogen atom one

A separable system with a lot of very interesting symmetries

I am going to recall the hydrogen atom. It can be borrowing. I go fast, do not hesitate to interrupt me!

To separate internal (relative) and external (barycentric) coordinates

Hydrogen atom

- A simple system: one proton (1) + one electron (2)

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} - \frac{1}{4\pi\varepsilon_0}\frac{q^2}{|\overrightarrow{r}_1 - \overrightarrow{r}_2|}$$

- Change of coordinates: internal (relative) and external (motion) degrees of freedom

$$\begin{aligned} \vec{R} &= \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{M} \\ \vec{P} &= \vec{p}_1 + \vec{p}_2 \end{aligned}$$

$$H = \frac{P^2}{2M} + \frac{p^2}{2\mu} - \frac{1}{4\pi\varepsilon_0}\frac{q^2}{r} = H_{CM} + H_{rel}$$

$$M = m_1 + m_2 \sim m_2 \qquad \mu = m_1 m_2 / M \sim m_1$$

$$\begin{aligned} \vec{r} &= \vec{r}_1 - \vec{r}_2 \\ \vec{p} &= \frac{m_2\vec{p}_1 - m_1\vec{p}_2}{M} \end{aligned}$$

$$\left[\hat{X}_j, \hat{P}_k\right] = i\hbar\delta_{jk} \quad , \quad \left[\hat{x}_j, \hat{p}_k\right] = i\hbar\delta_{jk} \quad , \quad \left[\hat{X}_j, \hat{p}_k\right] = 0 \quad , \quad \left[\hat{x}_j, \hat{P}_k\right] = 0$$

$$\left[\widehat{H}_{CM}, \widehat{H}_{rel} = 0\right]$$

Separable system in spherical coordinates

We will see further it is also possible with parabolic coordinates

Schrödinger equation of a separable system (ECOC)

- Spherical coordinates

$$\left[-\frac{\hbar^2}{2\mu}\Delta-\frac{e^2}{r}\right]\Psi\left(\vec{r}\right)=E\Psi\left(\vec{r}\right)$$

$$\frac{q^2}{4\pi\varepsilon_0}=e^2$$

- Laplacian operator

$$\Delta=\frac{1}{r}\frac{\partial^2}{\partial r^2}r-\frac{1}{r^2\hbar^2}L^2$$

- Kinetic orbital momentum

$$L_z=\frac{\hbar}{i}\frac{\partial}{\partial\varphi}$$

$$L^2=-\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

$$\left[H,L_z\right]=\left[H,L^2\right]=\left[L^2,L_Z\right]=0$$

States of the hydrogen atom

E_{nl} , l , m $(-l<m<l)$

- Wave functions

$$\Psi\left(\overrightarrow{r}\right) = R_{n,l}\left(r\right) Y_{l,m}\left(\theta,\varphi\right)$$

- Spherical harmonic

$$\begin{aligned} L^2 Y_{l,m}\left(\theta,\varphi\right) &= l\left(l+1\right)\hbar^2 Y_{l,m}\left(\theta,\varphi\right) \\ L_Z Y_{l,m}\left(\theta,\varphi\right) &= m\hbar Y_{l,m}\left(\theta,\varphi\right) \end{aligned}$$

- Radial wave function

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{l\left(l+1\right)\hbar^2}{2\mu r^2} - \frac{e^2}{r}\right] R_{n,l}\left(r\right) = E_{n,l} R_{n,l}\left(r\right)$$

- Atomic units (a.u.)

$$E_{Hartree} = \frac{e^2}{a_0} = \frac{\mu e^4}{\hbar^2} = \alpha^2 \mu c^2 \sim 2 \times 13.6 \text{ eV}$$

$$a_0 = \frac{\hbar^2}{\mu e^2} = \frac{1}{\alpha}\frac{\hbar}{\mu c} \sim 0.52917 \text{ nm}$$

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

$$\left[-\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{l\left(l+1\right)}{r^2} - \frac{2}{r}\right] R_{n,l}\left(r\right) = 2E_{n,l} R_{n,l}\left(r\right)$$

Spherical harmonics

$l=0$ $$Y_{0,0}(\theta,\varphi)=\frac{1}{\sqrt{4\pi}}$$

$l=1$ $$Y_{1,1}(\theta,\varphi)=-\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$$

$$Y_{1,0}(\theta,\varphi)=\sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_{1,-1}(\theta,\varphi)=\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$$

$l=2$ $$Y_{2,2}(\theta,\varphi)=\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\varphi}$$

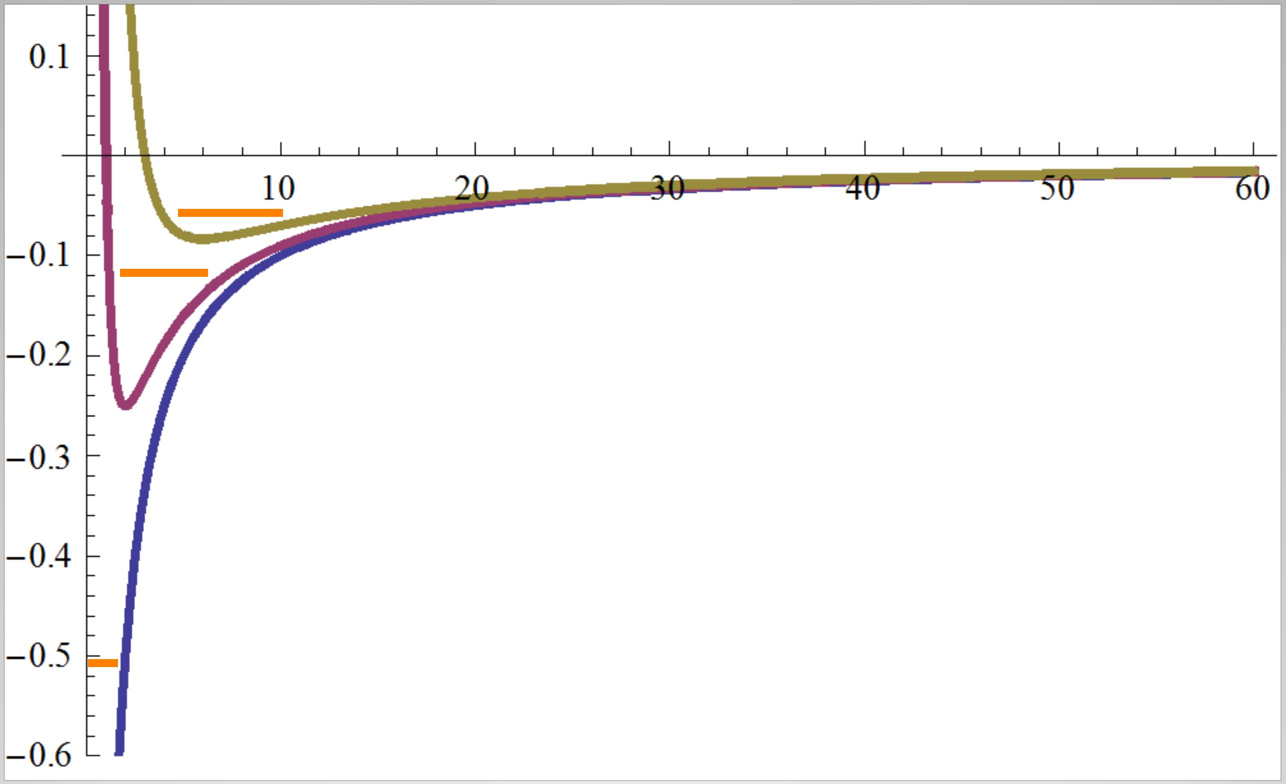
$$Y_{2,1}(\theta,\varphi)=-\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\varphi}$$

$$Y_{2,0}(\theta,\varphi)=\sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta-1\right)$$

$$Y_{2,-1}(\theta,\varphi)=\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\varphi}$$

$$Y_{2,-2}(\theta,\varphi)=\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\varphi}$$

- Atomic units



Potentials for *l*=0, 1 and 2

- Solutions of the Schrödinger equation

$$\left[-\frac{1}{r}\frac{\partial^2}{\partial r^2}r+\frac{l\left(l+1\right)}{r^2}-\frac{2}{r}\right]R_{n,l}\left(r\right)=2E_{n,l}R_{n,l}\left(r\right)$$

$$u_{n,l}\left(r\right)=r\ \ R_{n,l}\left(r\right)$$

$$\left[-\frac{\partial^2}{\partial r^2}+\frac{l\left(l+1\right)}{r^2}-\frac{2}{r}\right]u_{n,l}\left(r\right)=2E_{n,l}u_{n,l}\left(r\right)$$

$$u_{n,l}\left(r\right)=\exp\left(-\gamma r\right)r^{l+1}Q_l\left(r\right),\ \text{with}\ \gamma=\sqrt{-2E_{n,l}}$$

$$\left[-\frac{\partial^2}{\partial r^2}-\frac{2}{r}+2\left(\gamma\frac{\partial}{\partial r}+\gamma\frac{\left(l+1\right)}{r}-\frac{\left(l+1\right)}{r}\frac{\partial}{\partial r}\right)\right]Q_{,l}\left(r\right)=0$$

Radial wave function of hydrogen states (1)

Radial wave function of hydrogen states (2)

- Kummer differential equation $z = 2\gamma r$

$$\left[z\frac{\partial^2}{\partial z^2} + (2l+2-z)\frac{\partial}{\partial z} - \left(l+1-\gamma^{-1}\right)\right] Q_l(z) = 0$$

$$Q_l(z) = A\ {}_1F_1\left(l+1-\gamma^{-1}; 2l+2; z\right)$$

- Confluent hypergeometric function

$${}_1F_1(a;c;z) = 1 + \frac{a}{c}\frac{z}{1!} + \frac{a(a+1)}{c(c+1)}\frac{z^2}{2!} + \ldots + \frac{a(a+1)\ldots(a+\nu-1)}{c(c+1)\ldots(c+\nu-1)}\frac{z^\nu}{\nu!} + \ldots$$

- The normalization implies to limit the degree of the polynomial, which means $a = l+1-\gamma^{-1} < 0$

$$\gamma^{-1} = n' + l + 1 = n$$

Radial wave function of hydrogen states (3)

- Bound states of the hydrogen

$$R_{n,l}\left(r\right)=\frac{1}{(2l+1)!}\sqrt{\frac{(n+l)!}{2n\left(n-l-1\right)!}}\left(2n\right)^{l+3/2}\exp\left(-r/n\right)r^{l}\ {}_{1}F_{1}\left(l+1-n;2l+2;z\right)$$

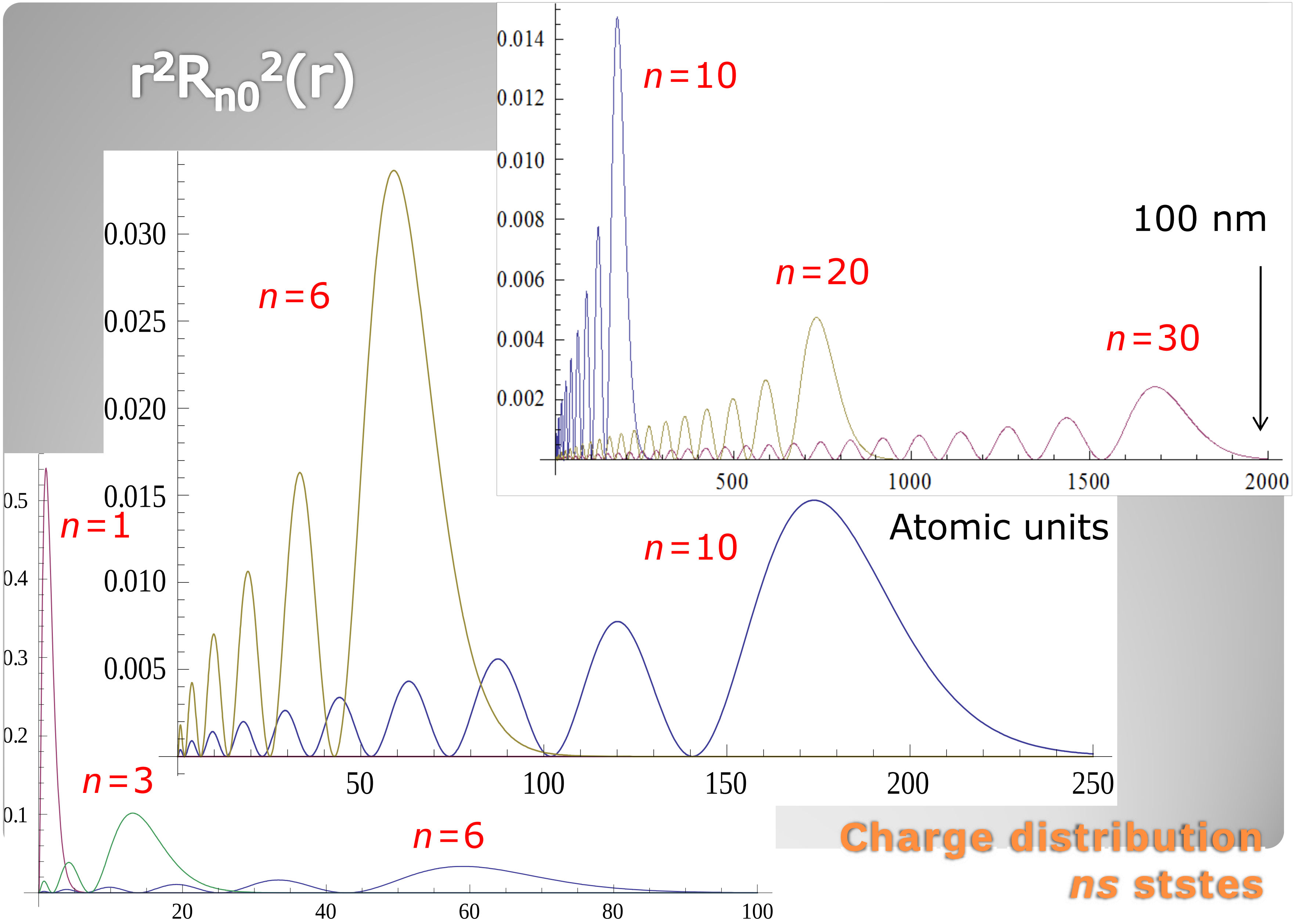
- With Laguerre polynomials

$$L_{p}^{q}\left(z\right)=\frac{(p+q)!}{p!q!}\ {}_{1}F_{1}\left(-p;q+1;z\right)$$

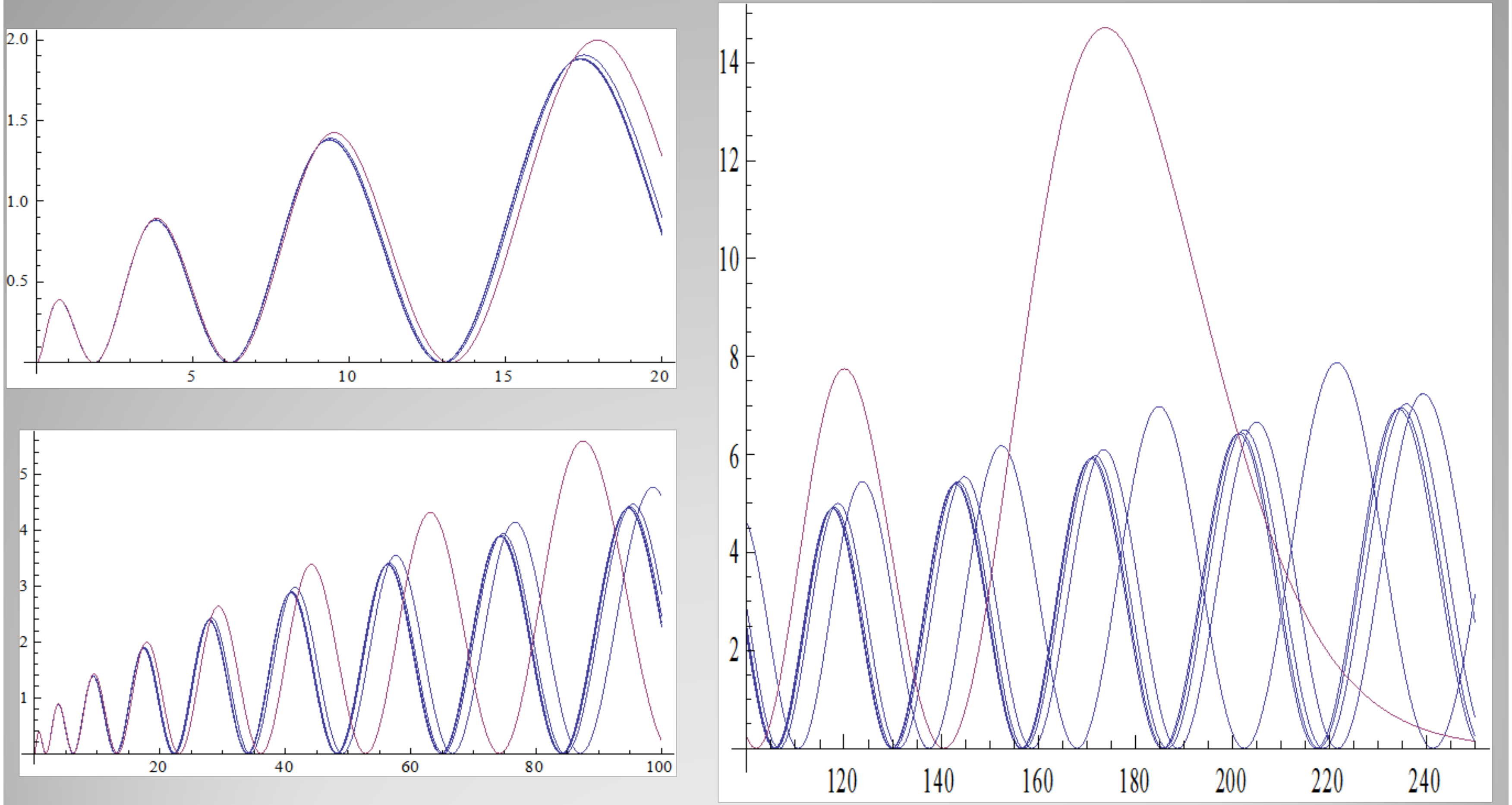
$$R_{n,l}\left(r\right)=\sqrt{\frac{(n-l-1)!}{2n\left(n+l\right)!}}\left(2n\right)^{l+3/2}\exp\left(-r/n\right)r^{l}\ L_{n-l-1}^{2l+1}\left(2r/n\right)$$

- Quantum numbers: *n,l (l=0,1…,n-1),m (-l<m<l)* Energy $E_{nl}=1/(2n^2)$

$r^2R_{n0}^2(r)$

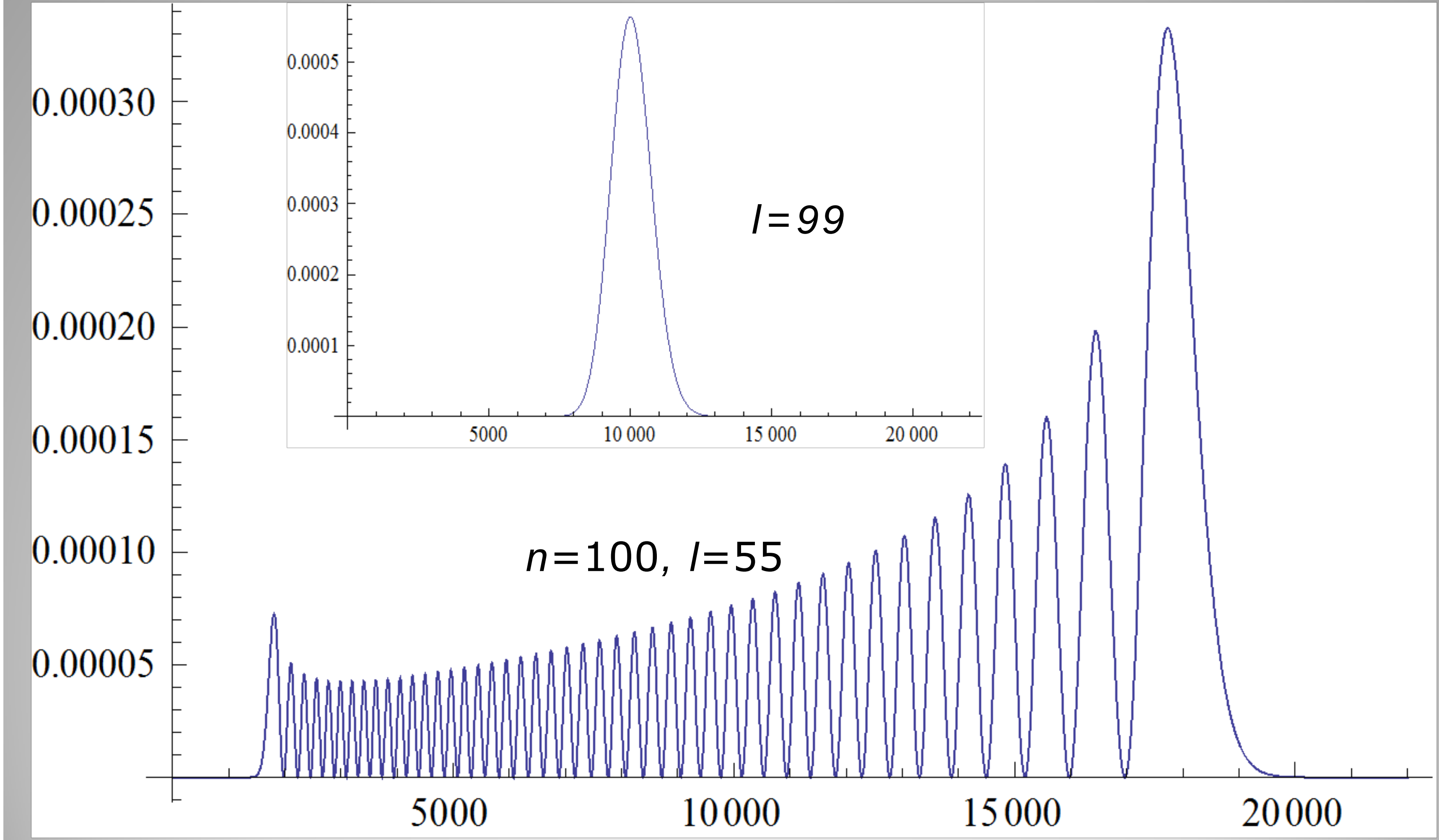


Charge distribution
***ns* ststes**



Internal nodes (charge density x n^3)
ns states, *n*=10,20,40,60,80,100

Charge distribution



Useful formula

$$\frac{s+1}{n^2}\langle r^s\rangle-(2s+1)a\langle r^{s-1}\rangle+\frac{s}{4}\left[(2l+1)^2-s^2\right]a^2\langle r^{s-2}\rangle=0\ ;\ \ (s>-2l-1)$$

$$\langle nl|r|n(l-1)\rangle=\frac{3}{2}n\sqrt{n^2-l^2}$$

$$\left\langle\frac{1}{r}\right\rangle=\frac{1}{n^2}$$

$$\left\langle\frac{1}{r^2}\right\rangle=\frac{1}{n^3(l+1/2)}$$

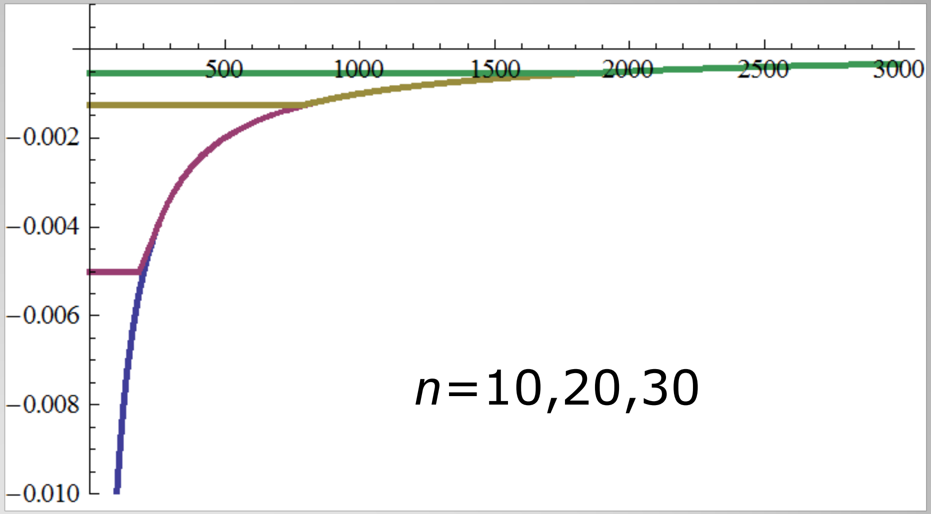
$$\left\langle\frac{1}{r^3}\right\rangle=\frac{1}{n^3(l+1)(l+1/2)l}$$

$$\langle r\rangle=\frac{1}{2}\left(3n^2-l(l+1)\right)$$

$$\langle r^2\rangle=\frac{n^2}{2}\left(5n^2+1-3l(l+1)\right)$$

Properties of Rydberg atoms

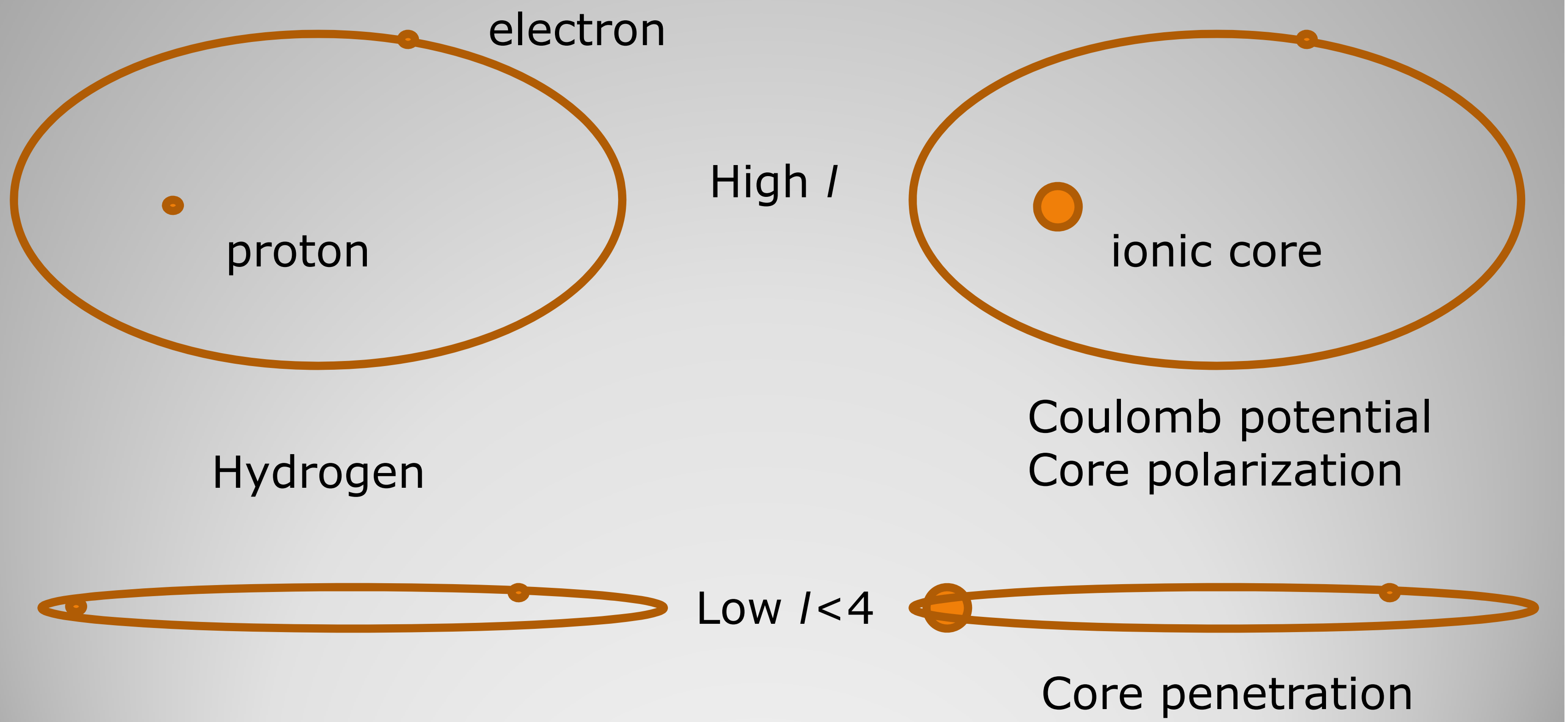
- High *n*, $E_{nl}=0.5n^{-2}$ a.u.
- Close to the ionization limit
- $n=30$, $E\sim15$ meV
- Classical outer turning point n^2 a.u.
- Large size $<r(s)>\sim1.5\ n^2$ a.u.
$n=30$, ~70 nm
- Long lifetime as n^3



$$\boxed{A_{n'l',nl} = \frac{4e^2\omega^3_{nl,n'l'}}{3\hbar c^3}\frac{l_{\max}}{(2l+1)}\left|\langle n'l'|r|nl\rangle\right|^2}$$

Other atoms

Introduction du défaut quantique



electron

proton

High l

ionic core

Hydrogen

Coulomb potential
Core polarization

Low $l<4$

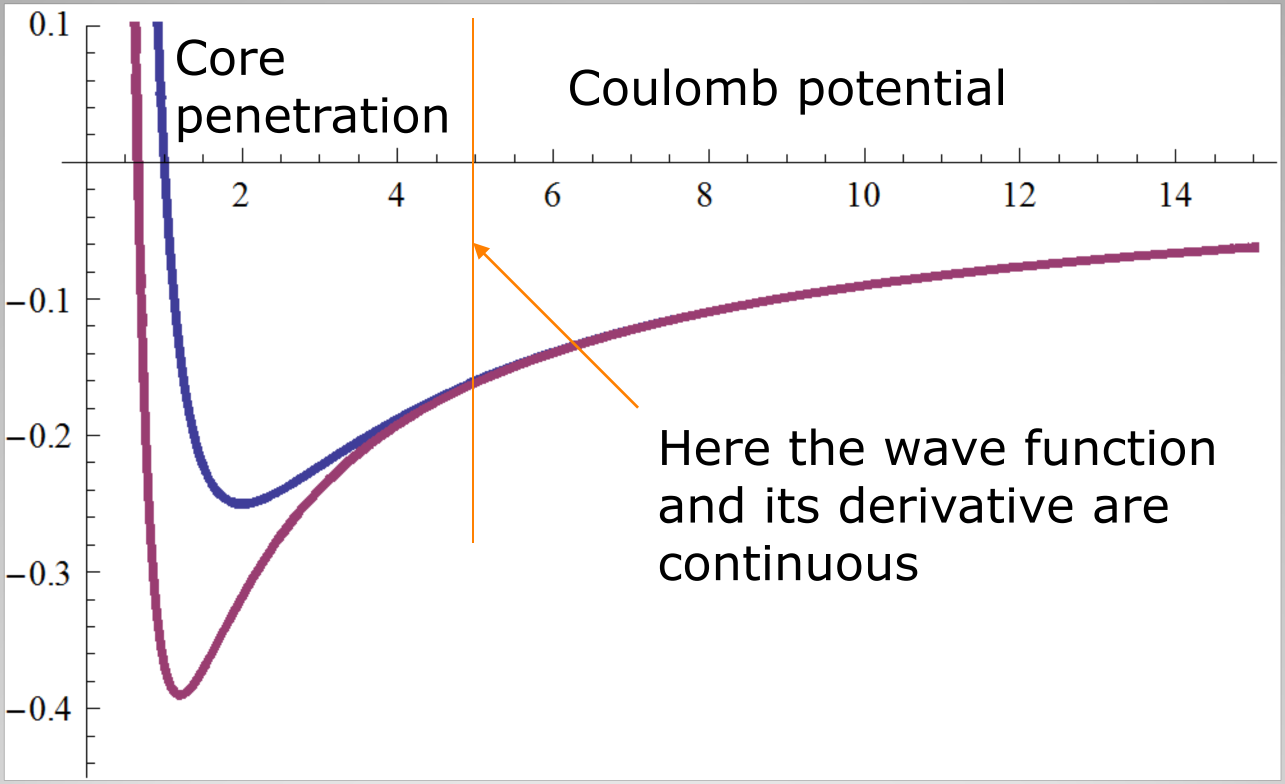
Core penetration

Other atoms (non hydrogen)

Quantum defect theory (δ_l): $n \rightarrow n^* = n - \delta_l$; $E = R_y/n^{*2}$

$\delta_l > 0.01$ for low l

Other atoms



Core penetration

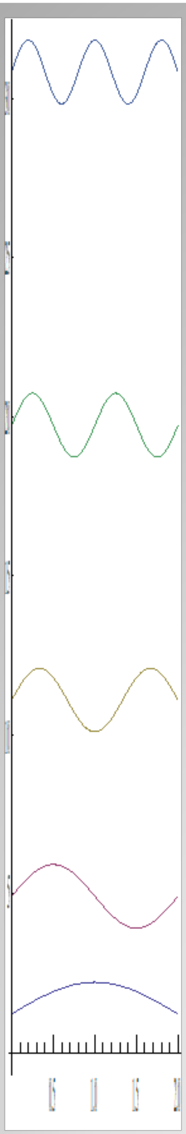
Coulomb potential

Here the wave function and its derivative are continuous

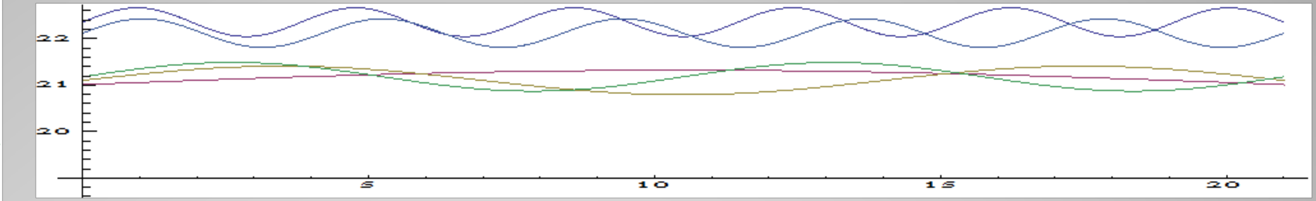
We know the solutions for the Coulomb part
Generally we do not know the inner part of the potential

A simpler problem

2-square well



$n_1=1,2,3,4,5$
$n_2=1,2,3,10,11$



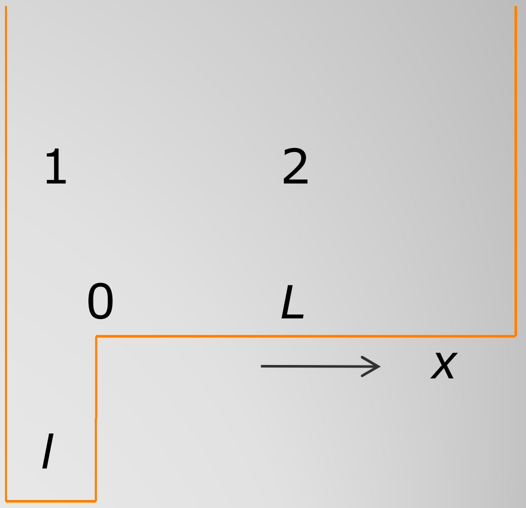
$$\psi_1(x)=A\sqrt{\frac{2}{l}}\sin\left(\frac{\pi n_1}{l}(x+l)\right)$$

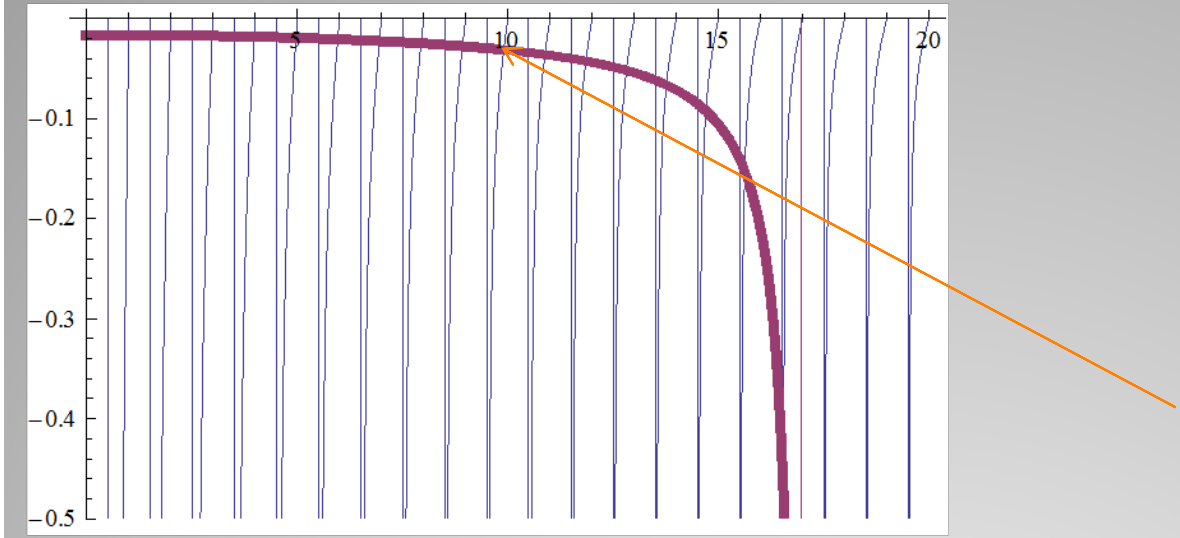
$$\psi_2(x)=B\sqrt{\frac{2}{L}}\sin\left(\frac{\pi n_2}{L}(x-L)\right)$$

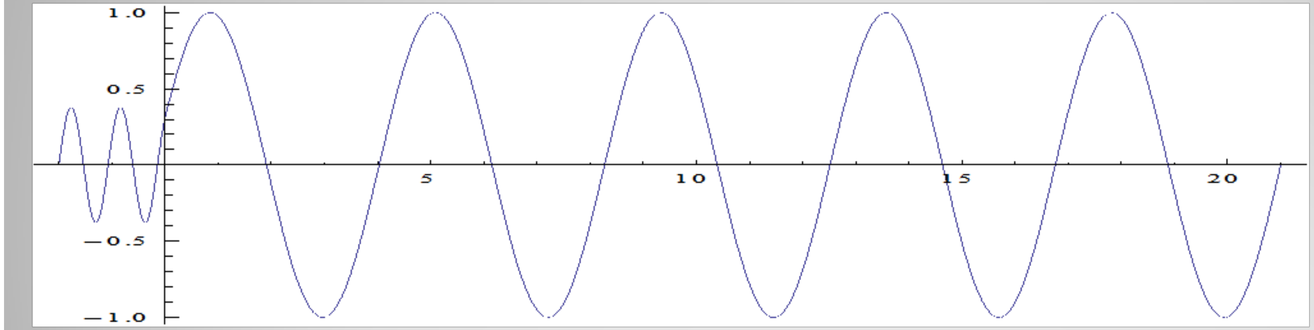
$$\psi_1(l)=\psi_2(l)\quad\text{and}\quad\psi_1'(l)=\psi_2'(l)$$

$$\frac{l}{n_1}\tan(\pi n_1)=-\frac{L}{n_2}\tan(\pi n_2)$$

$$\left(\frac{\pi n_1}{l}\right)^2-\left(\frac{\pi n_0}{l}\right)^2=\left(\frac{\pi n_2}{L}\right)^2$$







n_2=10, n*=9.9 Double-square well

Coulombian potential

Regular « *f* » and irregular « g » two independant solutions
The radial wave function is a linear superposition of *f* ang *g*

The determination of the energy levels depend on the asymptotic behavior of the radial wave function

Regular and irregular functions

- In the region where V=-1/r it has two solutions, which depend on W, ℓ, and r.
- We define the effective quantum number *ν* to parameterize the energy using $W = \dfrac{-1}{2\nu^2}$
- The solutions are: $u(r) = f(\nu, \ell, r)$

  $$u(r) = g(\nu, \ell, r)$$
- In the classically allowed region f and g are oscillatory, like sine and cosine
- For small *r:* $f \propto r^{\ell+1}$

  $$g \propto r^{-\ell}$$

Asymptotic forms

- Bound states

$$W=\frac{-1}{2\nu^2}<0 \qquad \underline{f_{\nu l}(r)\approx u(\nu,l).\sin(\pi\nu)-v(\nu,l).\exp(i\pi\nu)}$$

$$\underline{g_{\nu l}(r)\approx -u(\nu,l).\cos(\pi\nu)+v(\nu,l).\exp\left(i\pi\left(\nu+1/2\right)\right)}$$

$$u(\nu,l)=(-1)^l.\pi^{-1}.\nu^{1/2}.(2.r/\nu)^{-\nu}.e^{r/\nu}.\left[\Gamma(\nu-l).\Gamma(\nu+l+1)\right]^{1/2}$$

$$v(\nu,l)=(-1)^l.\nu^{1/2}.(2.r/\nu)^{\nu}.e^{-r/\nu}.\left[\Gamma(\nu-l).\Gamma(\nu+l+1)\right]^{1/2}$$

$$u(\nu,l).v(\nu,l)=\nu/\pi$$

- For hydrogen, for which $V=-1/r$ everywhere, only the f wave is allowed, so that the wave function does not blow up at $r=0$. Consequently, ν must be an integer, n.

Quantum defect

- For an alkali atom the *r*=0 boundary condition does not apply, and the *r*=∞ boundary condition can be met with a combination of *f* and *g* waves.

$$\rho(r) = f(r)\cos\tau - g(r)\sin\tau$$

- Phase-shifted by τ

$$r \to \infty$$

$$\rho(r) = u(r)\sin\pi\nu\cos\tau + u(r)\cos\pi\nu\sin\tau$$

- This must vanish as r→∞, which occurs if

$$\pi\nu + \tau = n\pi$$

$$\nu = n - \tau/\pi = n - \delta$$

- We obtain the energy relation

$$W = \frac{-1}{2(n-\delta)^2}$$

- The phase-shift is independent of the Rydberg states

Another approach

A few elements of the quantum defect approach (1)

- We have to treat the problem

$$\frac{d^2}{dR^2}y(R)+\frac{2\mu}{\hbar^2}[E-V(R)]y(R)=0$$

- We want two solutions (see Messiah)

$$f(R) \;=\; \alpha(R)\sin\left[\varphi(R)\right] \qquad g(R) \;=\; -\alpha(R)\cos\left[\varphi(R)\right]$$

- The Wronskien is constant

$$W(f,g)=fg'-gf'=1 \qquad W(f,g)=\alpha^2(R)\frac{d\varphi}{dR}(R)=1$$

- We have the relation phase/amplitude

$$\varphi(R)=\int_0^R\frac{dR'}{\alpha^2(R')}$$

A few elements of the quantum defect approach (2)

- The amplitude is solution of

$$\frac{d^2}{dR^2}\alpha(R) + \frac{2\mu}{\hbar^2}[E - V(R)]\alpha(R) = \frac{1}{\alpha^3(R)}$$

- Close channel $\varepsilon = -\kappa^2 = \frac{2\mu}{\hbar^2}\left(E - V(\infty)\right) < 0$, *R* large

(classically forbiden).The amplitude and the phase are

$$\alpha(R) \underset{R\to\infty}{\sim} \frac{1}{(\kappa)^{1/2}} e^{+\kappa R}$$

$$\varphi(R) = \nu(\epsilon) - \int_R^\infty \frac{dR'}{\alpha^2(R')}$$

$$\nu(\epsilon) = \int_0^\infty \frac{dR'}{\alpha^2(R')}$$

$$\varphi(R) \underset{R\to\infty}{\sim} \nu(\epsilon) - \frac{1}{2}e^{-2\kappa R}$$

The Coulomb wave functions of the close channel are

$$f(R) \underset{R\to\infty}{\sim} \frac{1}{(\kappa)^{1/2}} e^{+\kappa R} \sin\left[\nu(\epsilon) - \frac{1}{2} e^{-2\kappa R}\right]$$

$$g(R) \underset{R\to\infty}{\sim} -\frac{1}{(\kappa)^{1/2}} e^{+\kappa R} \cos\left[\nu(\epsilon) - \frac{1}{2} e^{-2\kappa R}\right]$$

$$f(R) \underset{R\to\infty}{\sim} \frac{1}{(\kappa)^{1/2}} \left(e^{+\kappa R} \ \sin\nu(\epsilon) - \frac{1}{2} e^{-\kappa R} \ \cos\nu(\epsilon)\right)$$

$$g(R) \underset{R\to\infty}{\sim} -\frac{1}{(\kappa)^{1/2}} \left(e^{+\kappa R} \ \cos\nu(\epsilon) + \frac{1}{2} e^{-\kappa R} \ \sin\nu(\epsilon)\right)$$

Two independant functions

- ν(ε) is the accumulated phase.
- $\varphi(R) = \int_0^R \frac{dR'}{\alpha^2(R')}$ does not change (versus the energy) in the non coulombian part of the potential.
- ν(ε) is the key parameter. For the normalization of the wave functions, we need ν(ε) be a multiple of π for suppressing the exponential term.
- ν(ε)/ π is equivalent to the principal quantum number. It is the effective quantum number.

A few elements of the quantum defect approach (3)

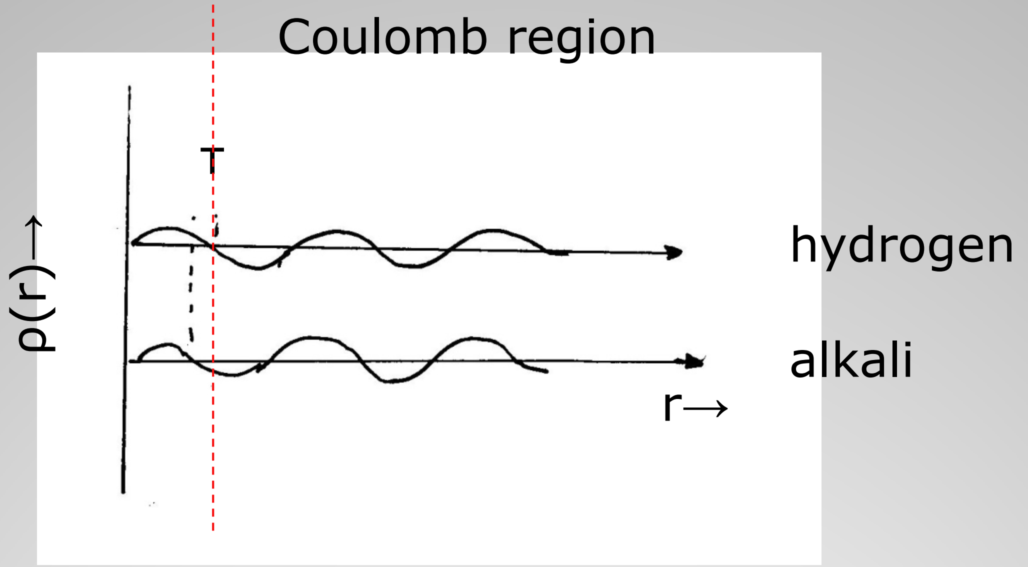
- The wave function is a linear superposition of *f* and *g*

$$\boxed{\begin{aligned} &u_{nl}(R) = \cos(\pi\mu) f(R) - \sin(\pi\mu) g(R) \\ &n = \nu/\pi + \mu \end{aligned}}$$

- See Fano PRA2, 353 (1970)

Quantum defect μ/π

- Radial wavefunctions for hydrogen and an alkali atom



- The alkali radial function oscillates more rapidly at small r (core peneration) producing a phase shifted wave in the coulomb region.

Interpretation

La Grenouille qui se veut faire aussi grosse que le Boeuf
Une grenouille vit un boeuf
Qui lui sembla de belle taille.
Elle, qui n'était pas grosse en tout comme un oeuf,
Envieuse, s'étend, et s'enfle, et se travaille,
Pour égaler l'animal en grosseur,
Disant : « Regardez bien, ma soeur ;
Est-ce assez ? dites-moi ; n' y suis-je point encore ?
- Nenni. - M' y voici donc ? - Point du tout. - M' y voilà ?
- Vous n'en approchez point. » La chétive pécore
S'enfla si bien qu'elle creva.
Le monde est plein de gens qui ne sont pas plus sages :
Tout bourgeois veut bâtir comme les grands seigneurs,
Tout petit prince a des ambassadeurs,
Tout marquis veut avoir des pages.

Jean de Lafontaine (1621 – 1695)

n =200 000 ! Very sentitive to any perturbation

$$\left\langle r^{s}\right\rangle \approx n^{2s}$$

$$\left\langle \frac{1}{r^{s}}\right\rangle \approx n^{-3} \quad (s \geq 2)$$

$$\left\langle n\middle|r^{-s}\middle|n'\right\rangle \approx (nn')^{-3/2}$$

$$\left\langle n\middle|r\middle|n'\right\rangle \approx n^{2}\,\mathrm{sin}\,c\big(\pi(n-n')\big)$$

$$\left\langle n\middle|r\middle|g\right\rangle \approx n^{-3/2}$$

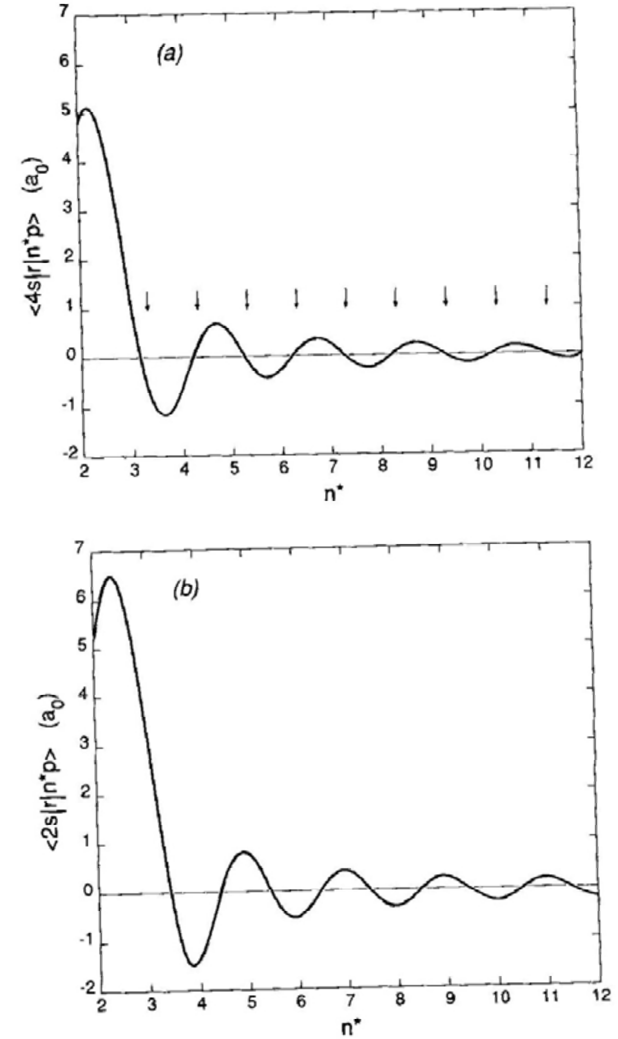
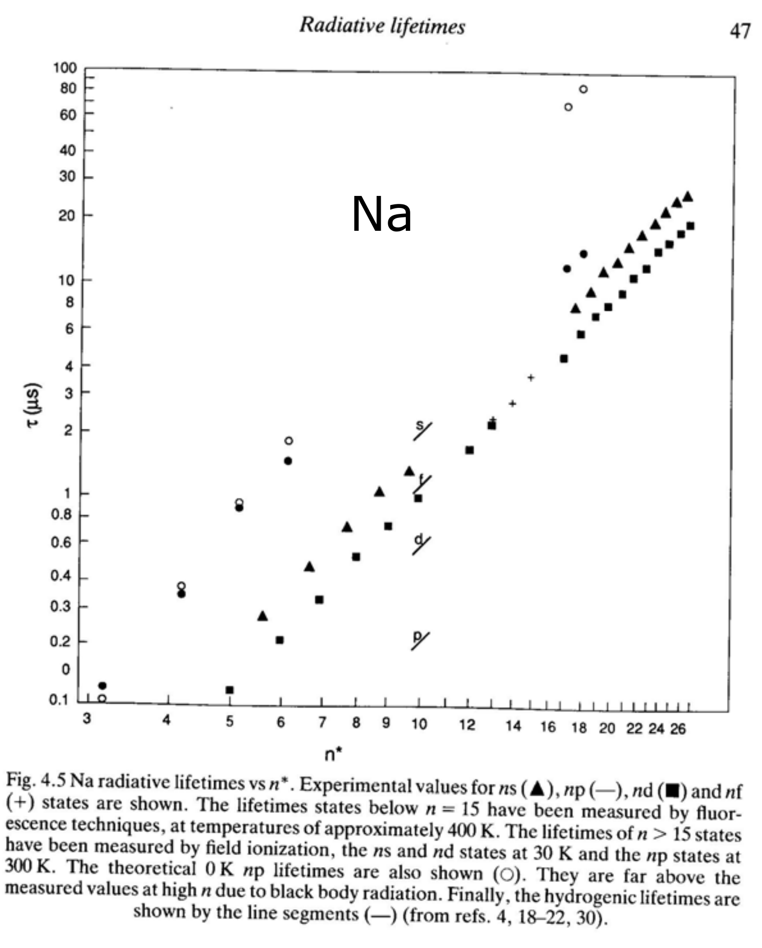


Fig. 4.2 (a) Radial matrix element of the K 4s → n^*p transition with n* a continous variable. The quantum defect of the 4s state is 2.23. The quantum defects of the np states are 1.71, so the np states fall at the locations shown by the arrows near where the matrix element crosses zero. (b) H 2s–n^*p radial matrix element as a function of n^*. Note that the maximum amplitudes of the matrix element occur at integer values of n^*.

Properties of Rydberg atoms

Property	scaling	n=20 value
Binding energy	$-1/n^2$	-274 cm^{-1}
Energy Spacing	$1/n^3$	27.3 cm^{-1}
Orbital radius	n^2	400 Å
Dipole matrix elements ($\Delta n=0$)	n^2	400 ea_0
Geometric cross section	n^4	160,000 Å^2
Radiative lifetime (low ℓ)	n^3	10 μs
Radiative lifetime (ℓ=n)	n^5	1 ms
Stark avoided crossings	$1/n^4$	1 cm^{-1}
Polarizability	n^7	10^8 Å^3
Van der Waals interaction	n^{11}	

Long lifetimes



Radiative lifetimes 47

Fig. 4.5 Na radiative lifetimes vs n^*. Experimental values for *n*s (▲), *n*p (—), *n*d (■) and *n*f (+) states are shown. The lifetimes states below $n = 15$ have been measured by fluorescence techniques, at temperatures of approximately 400 K. The lifetimes of $n > 15$ states have been measured by field ionization, the *n*s and *n*d states at 30 K and the *n*p states at 300 K. The theoretical 0 K *n*p lifetimes are also shown (○). They are far above the measured values at high *n* due to black body radiation. Finally, the hydrogenic lifetimes are shown by the line segments (—) (from refs. 4, 18–22, 30).

Experiments with Rydberg atoms (not cold atoms)

Atomic beams
Laser excitation
Detection through selective field ionization

Rydberg levels Na and H

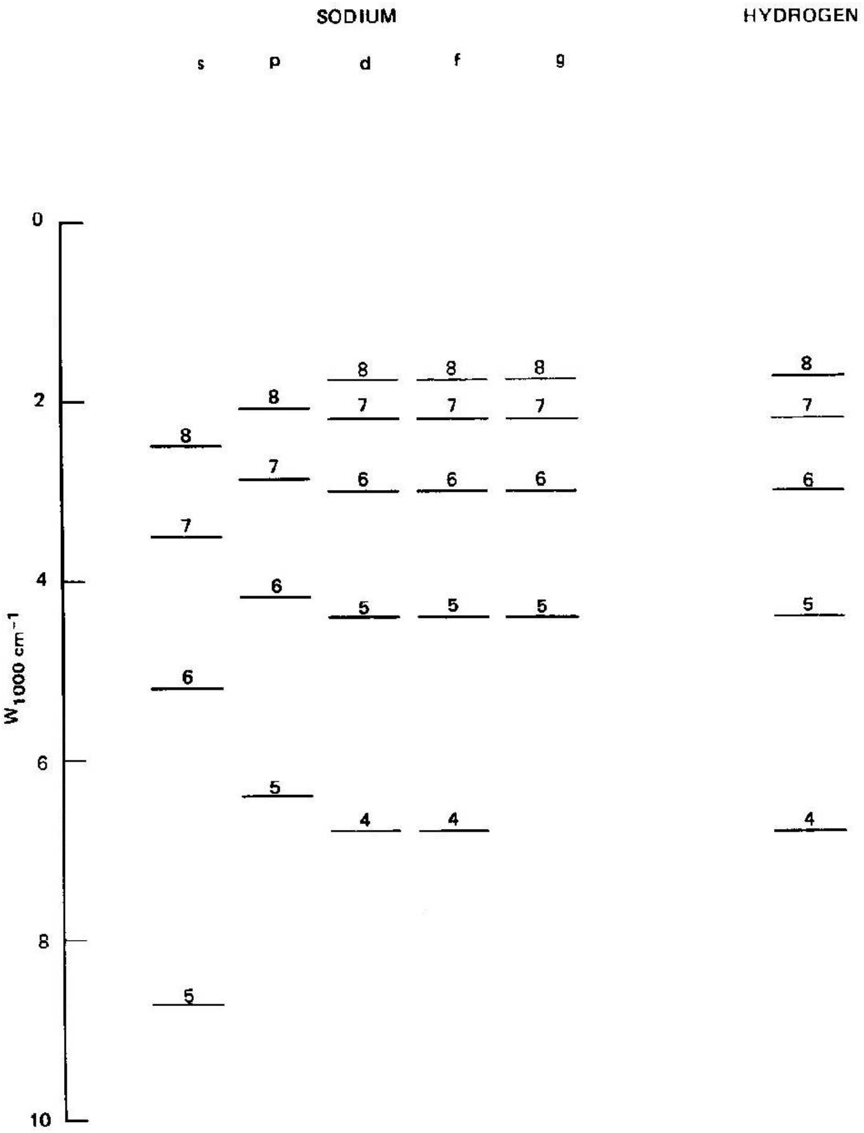


Fig. 2.2 Energy level diagram for H and Na (from ref. 1).

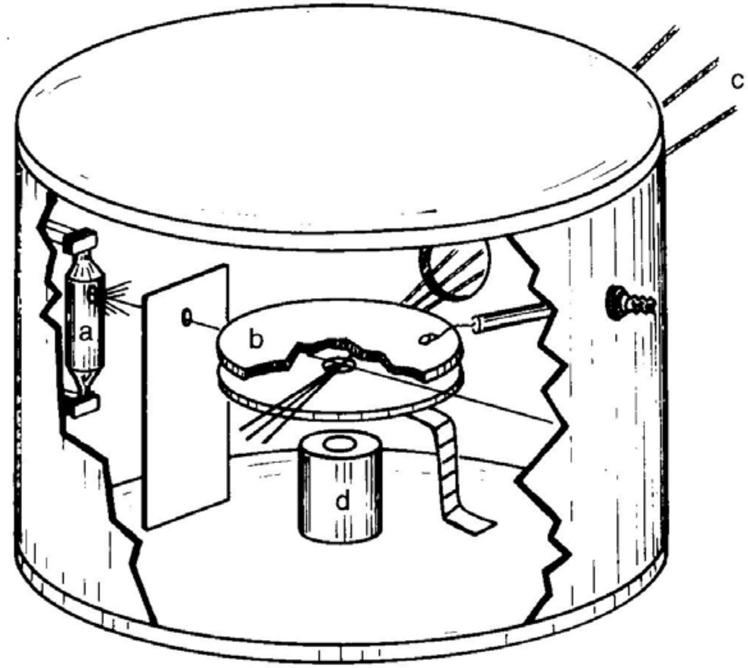


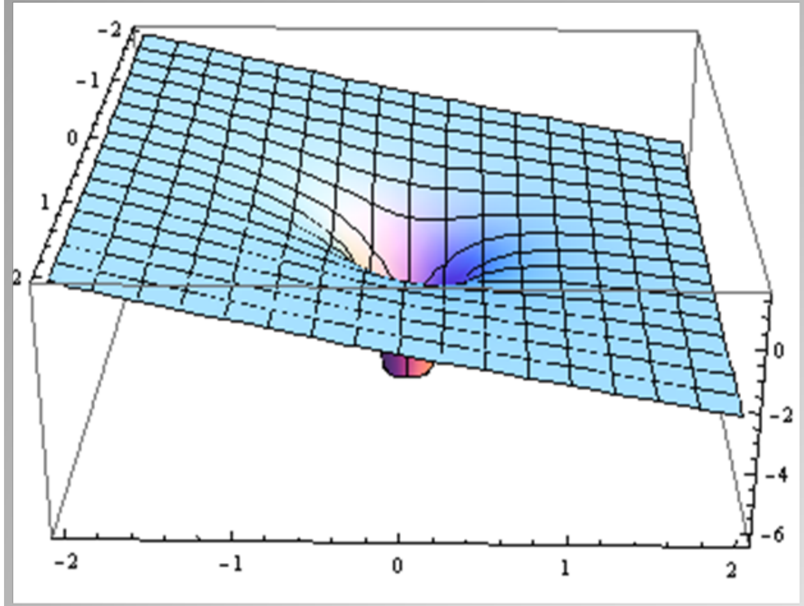
Fig. 3.4 Apparatus for the study of Rydberg states of alkali metal atoms: a, the atomic beam source; b, the electric field plates; c, the pulsed laser beams; and d, the electron multiplier (from ref. 21).

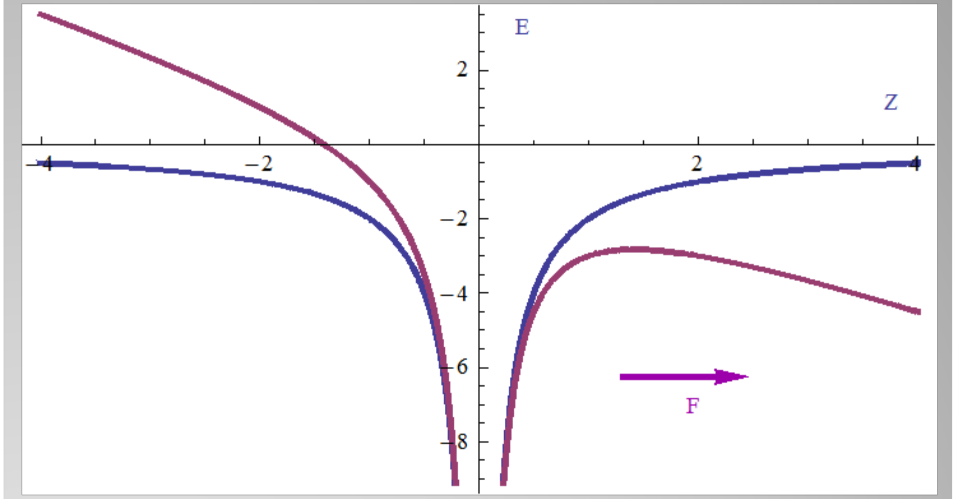
Kleppner *et al.*

Rydberg experiment apparatus

Low density 10^{10} cm^{-3}

High sensivity of the detection





Detection by selective field ionization

Classical ionization limit

u.a.= 5.14 10^9 V/cm

n=30 ; F= 400 V/cm

$$-\frac{2}{z}-2Fz=-\frac{1}{2n^2}$$

$$z^2=F$$

$$F=\frac{1}{16n^4}u.a.$$

Laser excitation below and above the ionization limit

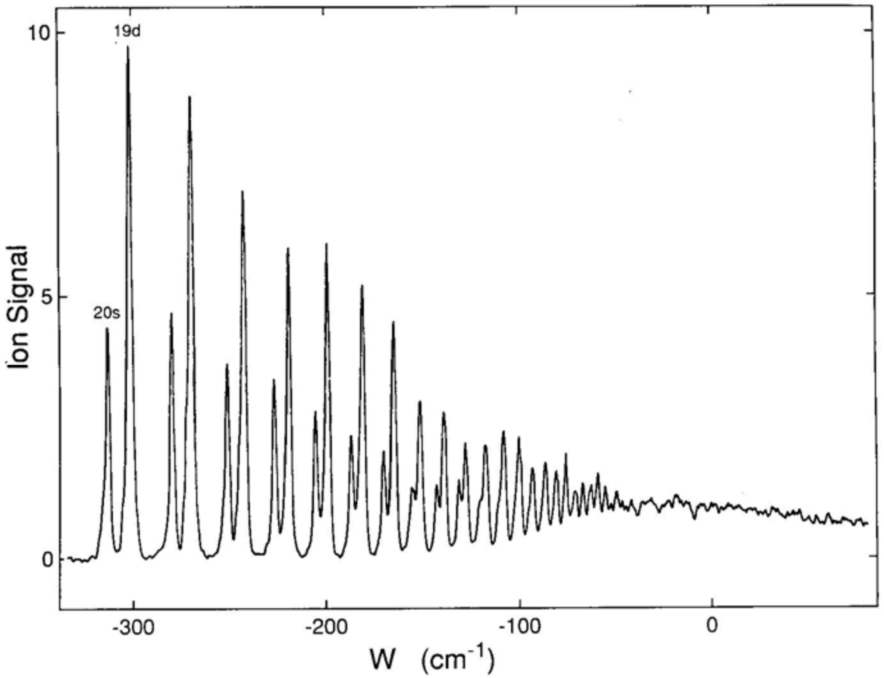
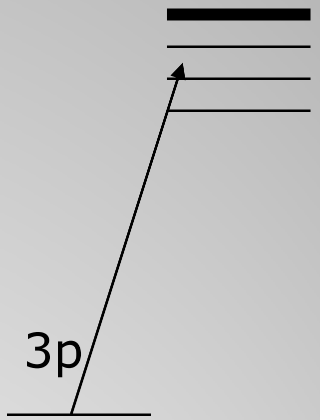


Fig. 3.3 Excitation spectrum of the Na *n*s and *n*d states from the Na $3p_{3/2}$ state (from ref. 19).



Laser excitation of Rydberg atoms

Recalls: dipole approximation,
rotating wave approximation

Is the dipole approximation valid for Rydberg atoms?

Two-level system

Perturbative calculation
Rotating-wave approximation

Appendice

Electric dipole approximation
Laser excitation of a two-level system

$$\vec{A}(z,t) = A_0 \vec{e}_x \sin\left(\omega t - kz + \varphi\right)$$

$$\vec{E}(z,t) = -\frac{\partial \vec{A}(z,t)}{\partial t} = E_0 \vec{e}_x \cos\left(\omega t - kz + \varphi\right) \quad ; \quad E_0 = -\omega A_0$$

$$\vec{E}(z,t) = \vec{\nabla} \times \vec{A}(z,t) = B_0 \vec{e}_y \cos\left(\omega t - kz + \varphi\right) \quad ; \quad B_0 = -A_0 \left(\vec{k} \times \vec{e}_x\right)$$

Semi-classical approach

Electromagnetic field (jauge de Coulomb)

example of a linear polarization

Laser-atom interaction W_I

$$\hat{H} = \frac{1}{2m}\left[\hat{\vec{p}} - q\vec{A}(\hat{\vec{r}},t)\right]^2 + V(\hat{r}) - \frac{q}{m}\hat{\vec{S}}.\vec{B}(\hat{\vec{r}},t)$$

jauge de Coulomb : $\vec{\nabla}.\vec{A}(\hat{\vec{r}},t) = 0$ $\left[\vec{A}(\hat{\vec{r}},t),\hat{\vec{p}}\right] = i\hbar\vec{\nabla}.\vec{A}(\hat{\vec{r}},t) = 0$

$$\hat{W}(t) = -\frac{q}{m}\hat{\vec{p}}.\vec{A}(\hat{\vec{r}},t) - \frac{q}{m}\hat{\vec{S}}.\vec{B}(\hat{\vec{r}},t) + \frac{q^2}{2m}A^2(\hat{\vec{r}},t)$$

$$\begin{aligned}\hat{W}_I(t) &= -\frac{q}{m}\hat{\vec{p}}.\vec{A}(\hat{\vec{r}},t)\\ \hat{W}_{II}(t) &= -\frac{q}{m}\hat{\vec{S}}.\vec{B}(\hat{\vec{r}},t)\end{aligned} \quad \frac{W_{II}}{W_I} \approx \frac{\frac{q}{m}SB}{\frac{q}{m}pA} \approx \frac{\hbar k}{p} \approx \frac{a_0}{\lambda} << 1$$

$$\hat{W}_I(t) = -\frac{q}{m}\hat{\vec{p}}.\vec{A}(\hat{z},t) = -\frac{q}{m}\hat{p}_x\left[A_0 e^{ik\hat{z}}e^{-i\omega t} + c.c.\right]$$

$$e^{\pm ik\hat{z}} = 1 \pm ik\hat{z} - \frac{1}{2}\, k^2 \hat{z}^2 \; \ldots$$

$$\hat{W}_I(t) = \hat{W}_{DE}(t) = -\frac{qE_0}{m\omega}\hat{p}_x \;\; \sin\omega t$$

$$\widehat{W}'_{DE}(t) = -\hat{\vec{D}}.\vec{E}(t) = -qE_0\hat{x}\cos\omega t$$

$$\begin{aligned}
\vec{A}\left(\vec{r},t\right) &= -\frac{E_0}{\omega}\;\vec{e}_x\;\;\sin\left(\omega t - kz\right)\\
U\left(\vec{r},t\right) &= 0
\end{aligned}$$

$$\begin{aligned}
\vec{A}'\left(\vec{r},t\right) &= \vec{A}\left(\vec{r},t\right) + \vec{\nabla}\chi\left(\vec{r},t\right) = \frac{E_0}{\omega}\;\vec{e}_x\;\;\left[-\sin\left(\omega t - kz\right) + \sin(\omega t)\right]\\
U'\left(\vec{r},t\right) &= U\left(\vec{r},t\right) - \frac{\partial\chi\left(\vec{r},t\right)}{\partial t} = -\;xE_0\;\;\cos(\omega t)
\end{aligned}$$

Dipole approximation

The electron sees the same e.m. field the ionic core (λ>> <r> ~ n^2)

Jauge de Coulomb et jauge de Goppert Mayer

Two forms for the interaction hamiltonian

En jauge de Coulomb, l'hamiltonien s'écrivait :

$$\hat{H} = \frac{1}{2m}\left[\hat{\vec{p}} - q\vec{A}(0,t)\right]^2 + V(\hat{r})$$

Dans la nouvelle jauge, l'hamiltonien devient :

$$\hat{H} = \frac{1}{2m}\left[\hat{\vec{p}} - q\vec{A}'(0,t)\right]^2 + V(\hat{r}) - qU'(\hat{\vec{r}},t)$$

Soit :

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{r}) - q\hat{x}E_0\ \cos(\omega t) = \hat{H}_0 + \hat{W}'_{DE}(t)$$

où $\hat{W}'_{DE}\left(\widehat{\vec{r}},t\right) = -\ qU'\left(\widehat{\vec{r}},t\right) = -\ q\hat{x}E_0\ \cos(\omega t)$

qui est la forme le plus souvent usuelle de l'hamiltonien.

$$\hat{W}(t) = \hat{W}_I(t) = -\frac{q}{m}\hat{\vec{p}}.\vec{A}(\hat{z},t) = -\frac{q}{m}\hat{p}_z\left[A_0 e^{ikx} e^{-i\omega t} + c.c.\right]$$

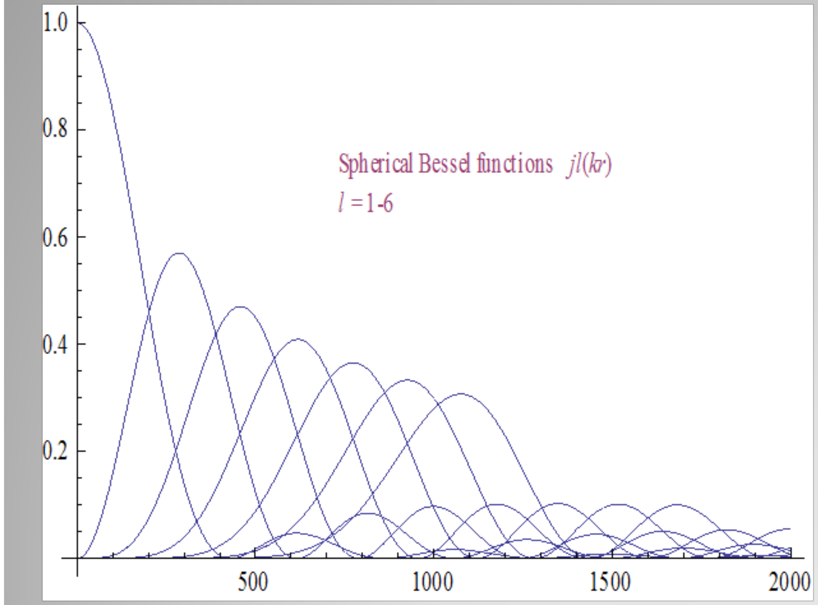
$$e^{i\vec{k}.\vec{r}} = \sum_{l=0}^{\infty}(2l+1)\, i^l j_l(kr)\, P_l(\cos(\theta)) = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{+l} i^l j_l(kr)\, Y_l^{m*}(\theta_k,\varphi_k)\, Y_l^m(\theta_r,\varphi_r)$$

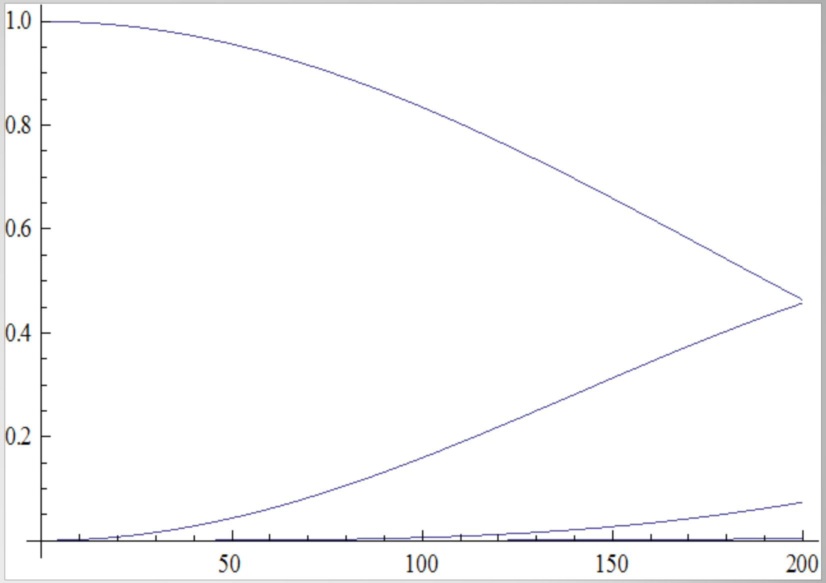
$$\begin{aligned}
\left\langle np\left|-\frac{q}{m}\hat{p}_x A_0 e^{ik\hat{z}}\right|1s\right\rangle &= \left\langle np\left|-\frac{q}{m}\hat{p}_z A_0 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{+l} i^l j_l(kr)\, Y_l^{m*}(\pi/2,0)\, Y_l^m(\theta_r,\varphi_r)\right|1s\right\rangle \\
&= \left\langle np\left|-\frac{q}{m} A_0 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{+l} i^l j_l(kr)\, Y_l^{m*}(\pi/2,0)\, Y_l^m(\theta_r,\varphi_r)\cos\theta_r\frac{\partial}{\partial r}\right|1s\right\rangle \\
&= \left\langle np\left|-\frac{q}{m} A_0 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{+l} i^l j_l(kr)\, Y_l^{m*}(\pi/2,0)\, Y_l^m(\theta_r,\varphi_r)\, Y_1^0(\theta_r,\varphi_r)\frac{\partial}{\partial r}\right|1s\right\rangle
\end{aligned}$$

Validity of the electric dipole approximation

Validiy of the Goppert Mayer jauge for Rydberg atoms

Depends on the overlppi,g between the initial state and the different spherical Bessel functions *$j_l(kr)$*





Overlapping between initial wave function and $j_l(kr)$

$kr<<1$, only $j_1(kr)$ needs to be considered
The Goppert Mayer approximation is valid
This wil not be true for the photoionization of Rydberg atoms

Stark effect

$$W_{Stark} = \frac{3}{2} n^2 E$$

$$W_{Stark}(MHz) = 1.72 n^2 E(V/cm)$$

$$n = 30$$

$$W_{Stark}(GHz) = 1.5 E(V/cm)$$

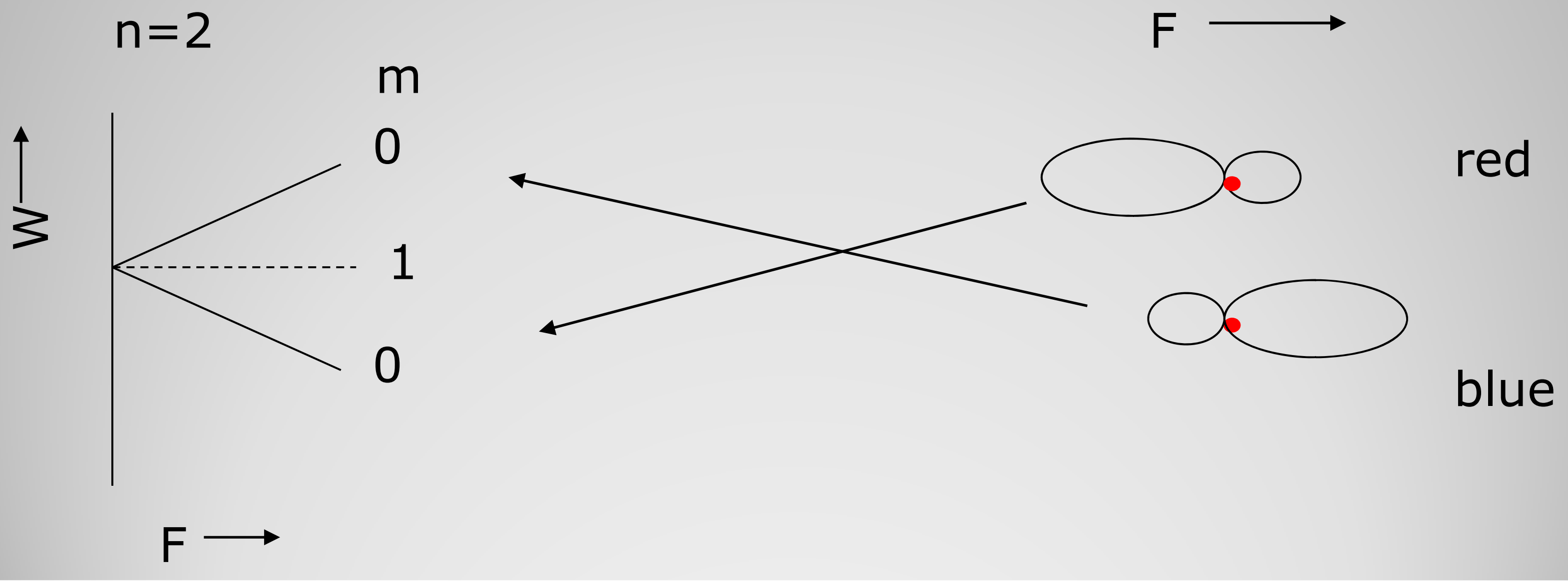
A analytically solvable problem
in the case of the hydrogen atom

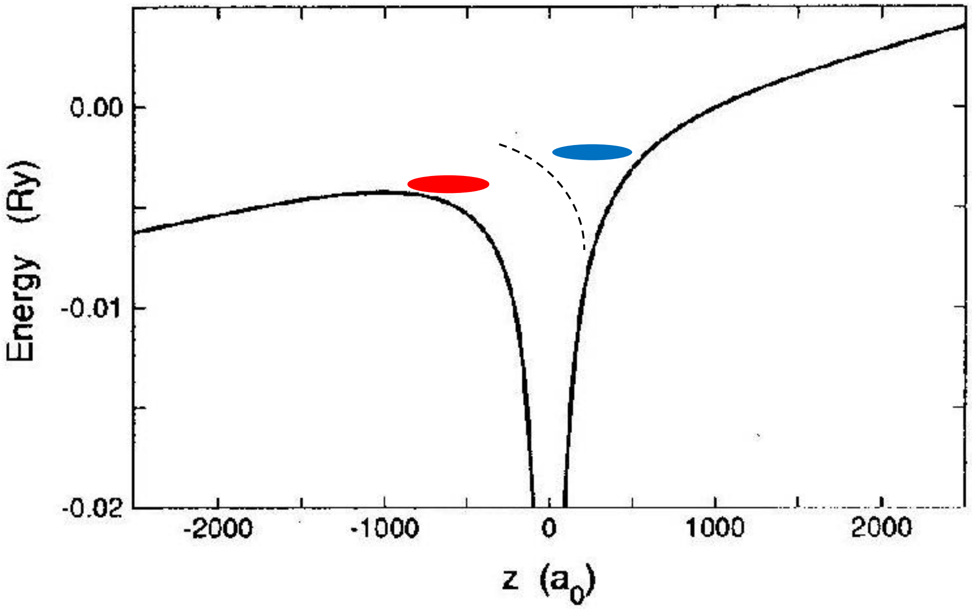
Electric field allows to tune the level
to induce permanent huge dipole
to field ionize the level
by using moderate electric field

Stark effect of the hydrogen atom

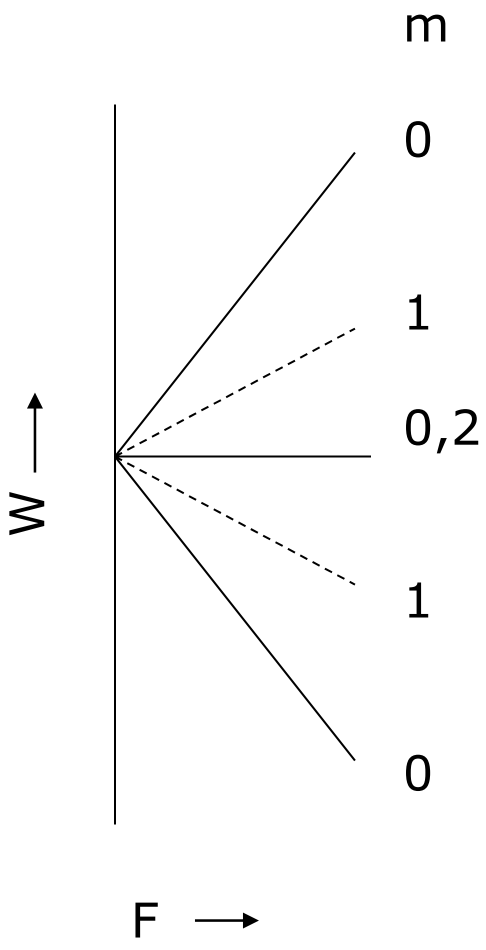
- For an electric field *F* in the direction *z*, the hamiltonian is modified by the quantity: $\boxed{-qFz}$
- Case n=2: 4 levels, only the *s* and *p* (m=0) levels are coupled by the electric field *F* as

$$\boxed{\left\langle 2p, m=0 \middle| -qFz \middle| 2s \right\rangle = \frac{-qF}{\sqrt{3}} \left\langle 2p \middle| r \middle| 2s \right\rangle = -3qFa}$$




0.00
-0.01
-0.02
Energy (Ry)
-2000
-1000
0
1000
2000
z (a_0)

n=3, m=0,1,2

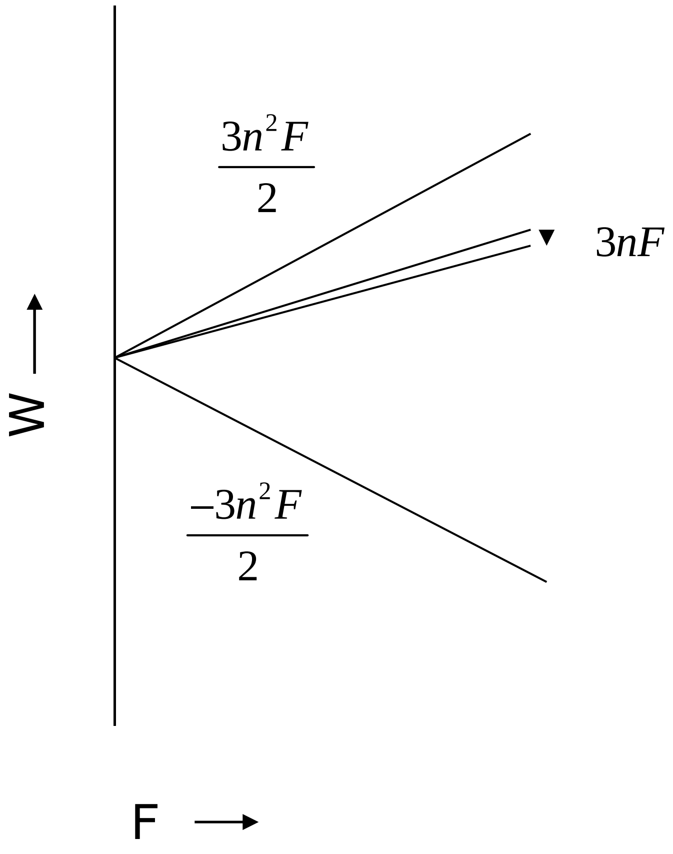


Levels of even and odd m are interleaved.

Levels of even m are degenerate

Levels of odd n are degenerate

High n



Levels of even and odd m
are interleaved.

Total energy span $3n^2$ F

Energy between adjacent Stark
states of the same m 3nF

The distribution of an ℓ state over the Stark states

$$\langle nn_1m|n\ell m\rangle = \sqrt{\frac{2}{n}}(-1)^{\ell}P_{\ell m}(\frac{2n_1-n}{n})$$

$$\langle nn_1 0|n00\rangle = \frac{1}{\sqrt{n}}$$

The ns states are spread evenly over
The m=0 Stark states.

The np states are shown at right.

m

0

1

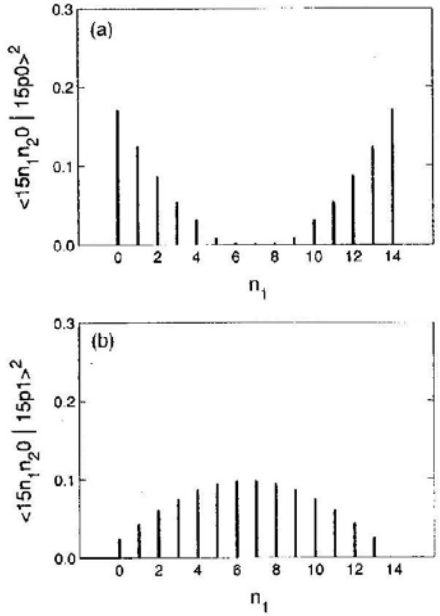


Fig. 8.1 Squared transformation coefficients from the $n = 15$ parabolic 15 n_1n_2m states to spherical 15p states for (a) $m = 0$ and (b) $m = 1$. Note that the 15p state is concentrated in the edges of the $m = 0$ Stark manifold but at the center of the $m = 1$ manifold.

There is always the 1/√n scaling.

Hydrogen atom with parabolic coordinates

- Parabolic coordinates

$$x=\sqrt{\xi\eta}\cos\varphi,\quad y=\sqrt{\xi\eta}\sin\varphi,\quad z=\frac{1}{2}(\xi-\eta),$$

$$r=\frac{1}{2}(\xi+\eta),\quad \xi=r+z,\quad \eta=r-z,\quad \varphi=\arctan\frac{x}{y}$$

$$\frac{d}{d\xi}\left(\xi\frac{df_1(\xi)}{d\xi}\right)+\left[\frac{E}{2}\xi-\frac{m^2}{4\xi^2}+\beta_1\right]f_1(\xi)=0$$

$$\frac{d}{d\eta}\left(\eta\frac{df_2(\eta)}{d\eta}\right)+\left[\frac{E}{2}\eta-\frac{m^2}{4\eta^2}+\beta_2\right]f_2(\eta)=0$$

$$\beta_1+\beta_2=1$$

$$\psi = f_1(\xi)\, f_2(\eta)\, e^{im\varphi}$$

$$f_1(\xi) = e^{-\xi/2n}\left(\frac{\xi}{n}\right)^{|m|/2} {}_1F_1\left(-n_1, |m|+1, \frac{\xi}{n}\right)$$

$$n = n_1 + n_2 + |m| + 1 \qquad \left(\beta_{1(2)}\right) = \frac{1}{n}\left(n_{1(2)} + \frac{|m|+1}{2}\right)$$

$$\vec{A} = \frac{\vec{p}\times\vec{L} + \vec{L}\times\vec{p}}{2m} - e^2\,\frac{\vec{r}}{r}$$

$$\left[H_0, \vec{L}\right] = \left[H_0, \vec{A}\right] = 0 \;\; ; \;\; A_z\psi = \frac{n_2 - n_1}{n} e^2 \psi$$

$$\left[A_i, A_j\right] = -\frac{2i\hbar}{m}\varepsilon_{ijk} H_0 L_k \;\; ; \;\; \left[L_i, A_j\right] = i\hbar\varepsilon_{ijk} A_k$$

Solutions

New quantum numbers, Runge Lenz vector

$$\langle n_1,n_2,m|z|n_1',n_2',m\rangle = \frac{3}{2}n(n_1-n_2)\delta_{n_1n_1'}a$$

$$= -\frac{3}{2}n^2\frac{a}{e^2}\langle n_1,n_2,m|A_z|n_1',n_2',m\rangle$$

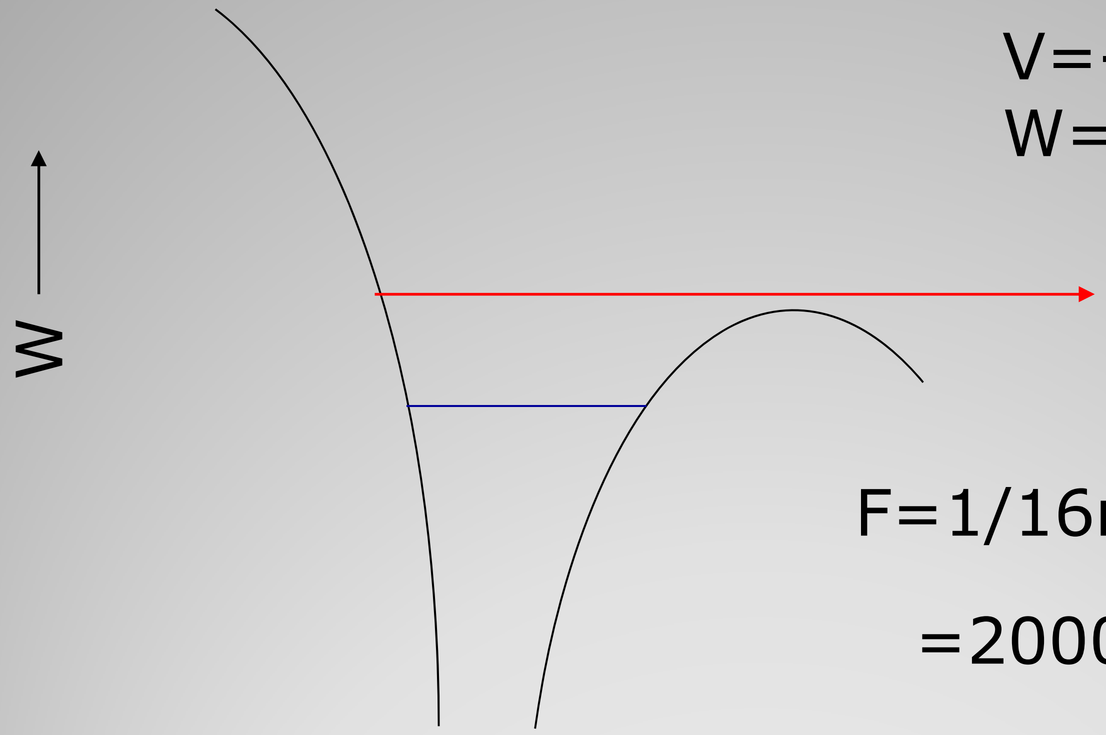
$$\vec{r} = \frac{3}{4W}\vec{A}$$

$$\boxed{\Delta W^{(1)}_{n_1,n_2} = -\frac{3qa_0F}{2}n(n_1-n_2) = \frac{3F}{2}n(n_1-n_2) \quad \text{(a.u.)}}$$

For the manifold n

Stark effect: perturbation theory

Detection by field Ionization



$V=-1/r-Ez$

$W=-1/2n^2$

$F=1/16n^4$

$=2000$ V/cm @ $n=20$

Hydrogen n=15 m=0 Stark states

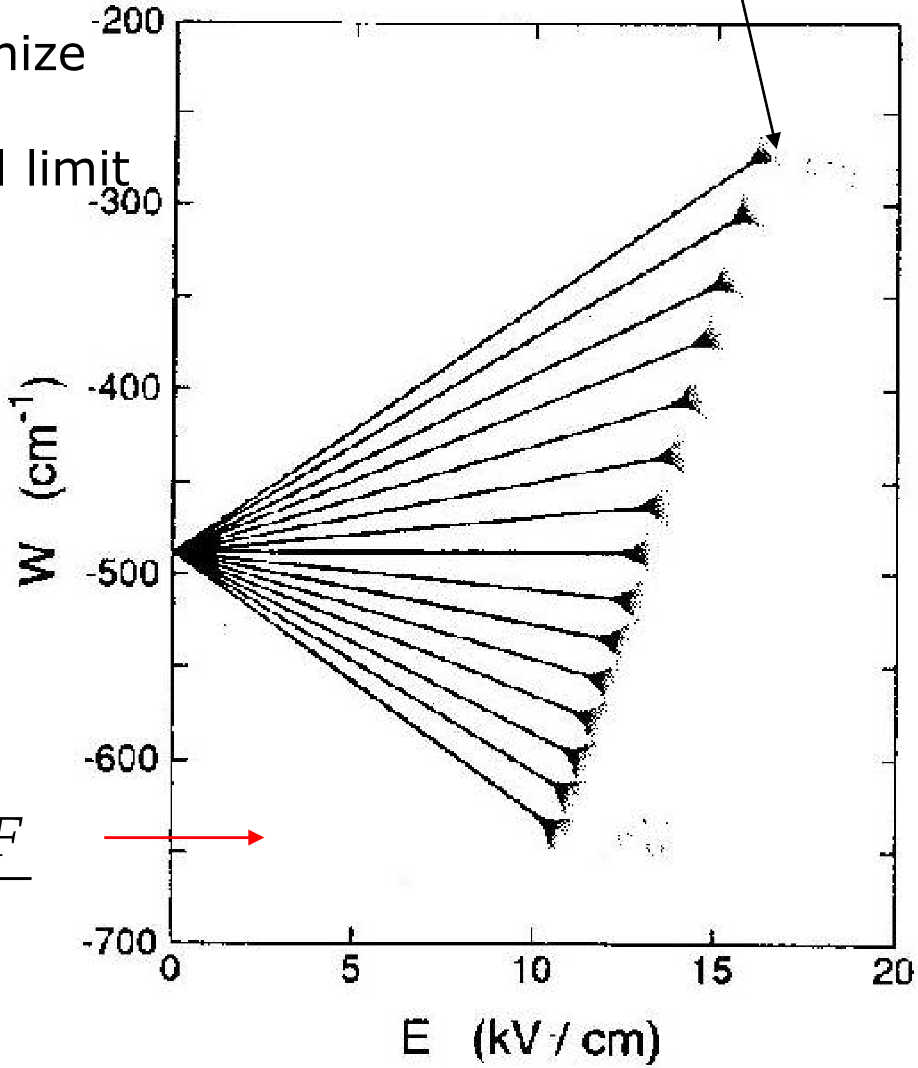
The blue states are harder to ionize

Red states ionize at the classical limit
 F=1/16n^4

$$F = \frac{1}{9n^4}$$

$$F = \frac{1}{16n'^4}$$

$$\frac{-1}{2n'^2} = \frac{-1}{2n^2} - \frac{3n^2F}{2}$$



Field ionization
1µs

Why is it so hard to ionize the blue states?

$$\frac{d}{d\xi}\left(\xi\frac{df_1(\xi)}{d\xi}\right)+\left[\frac{E}{2}\xi-\frac{m^2}{4\xi^2}+\beta_1-\frac{F}{4}\xi^2\right]f_1(\xi)=0$$

$$\frac{d}{d\eta}\left(\eta\frac{df_2(\eta)}{d\eta}\right)+\left[\frac{E}{2}\eta-\frac{m^2}{4\eta^2}+\beta_2+\frac{F}{4}\xi^2\right]f_2(\eta)=0$$

$$\beta_1+\beta_2=1$$

$$f_{1(\text{or }2)}\left(\xi(\text{or }\eta)\right)=\chi_{1(\text{or }2)}\left(\xi(\text{or }\eta)\right)/\sqrt{\xi(\text{or }\eta)}$$

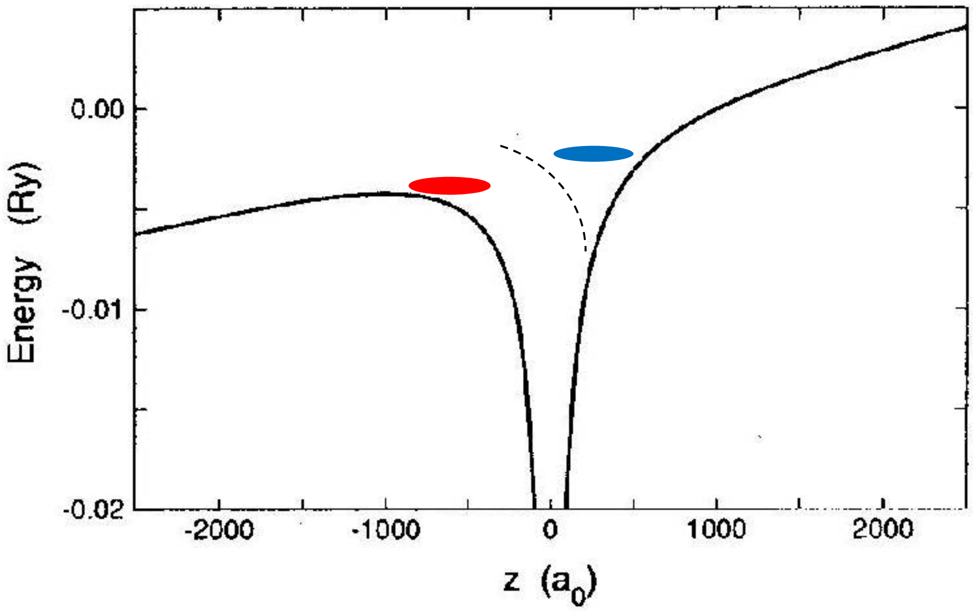
$$\frac{d^2}{d\xi(\text{or }\eta)^2}\chi_{1(\text{or }2)}\left(\xi(\text{or }\eta)\right)+\frac{\chi_{1(\text{or }2)}}{2}\left(\xi(\text{or }\eta)\right)\left[W-V\left(\xi(\text{or }\eta)\right)\right]$$

$$V(\xi)=2\left(-\frac{\beta_1}{\xi}+\frac{m^2-1}{4\xi^2}+\frac{F}{4}\xi\right)$$

$$V(\eta)=2\left(-\frac{\beta_2}{\eta}+\frac{m^2-1}{4\eta^2}-\frac{F}{4}\eta\right)$$

A separable system: hydrogen atom in electric field *F*

They are held on the wrong side of the atom by a barrier analogous to a centrifugal barrier.



The ionization fields of all the n=31 levels

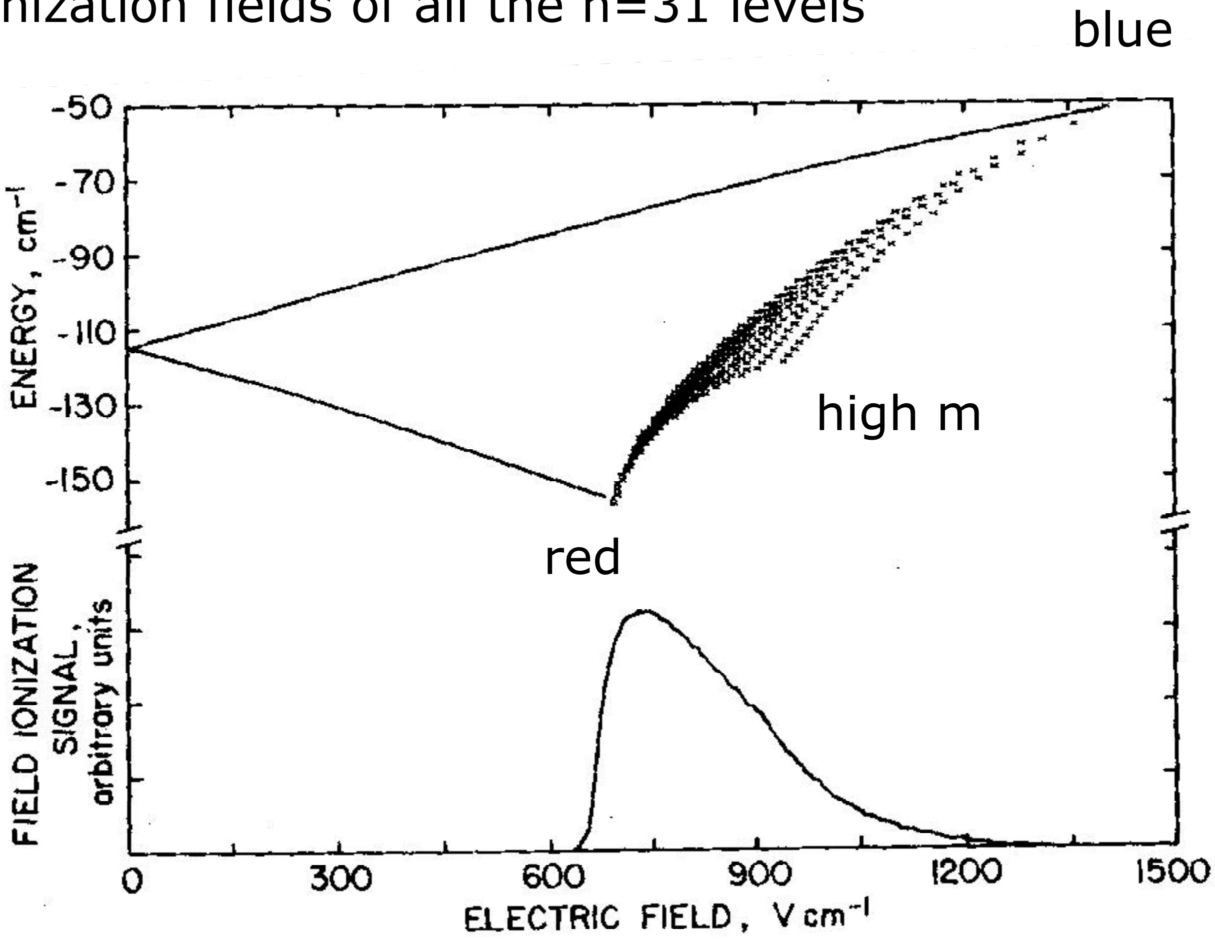
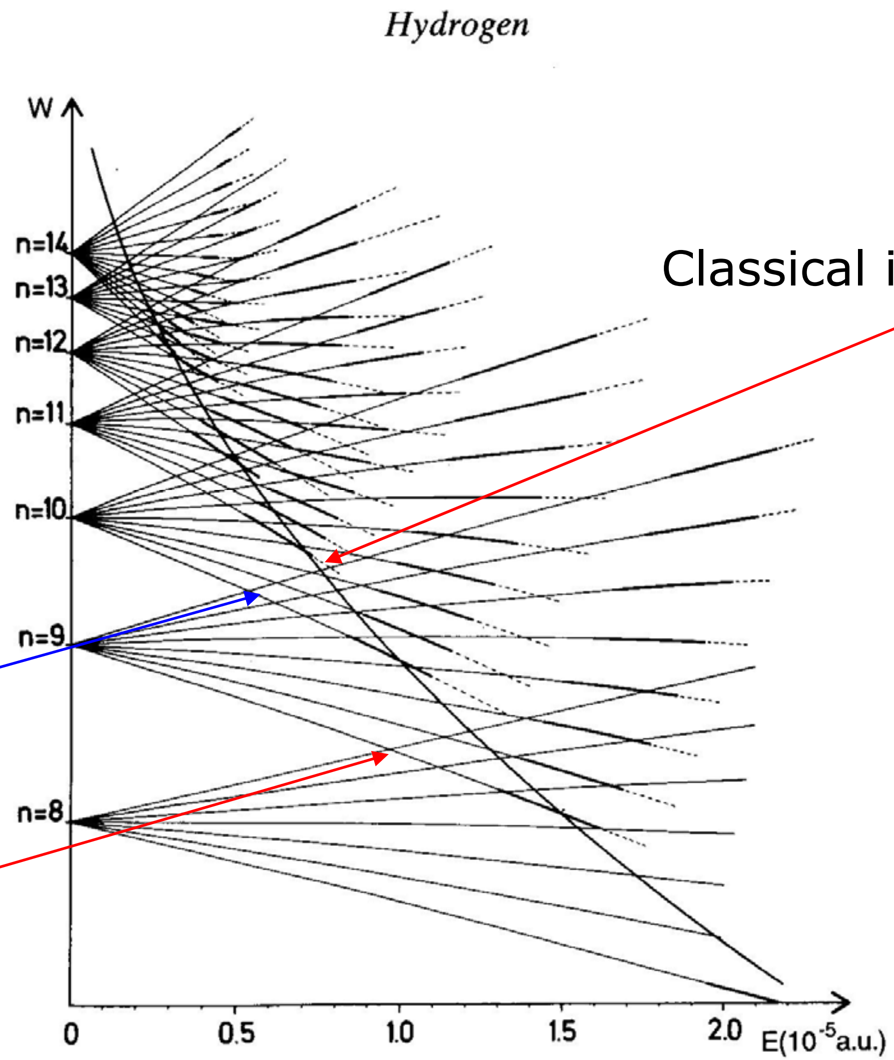


Fig. 6.10 Calculated SFI profile for diabatic ionization of the H like $|m| \geq 3$ states. Top, extreme members of the $n = 31$, $|m| = 3$ Stark manifold. The crosses represent the points at which each $|m| \geq 3$ Stark state achieves an ionization rate of 10^9 s^{-1}. Bottom, calculated SFI profile for diabatic ionization of a mixture containing equal numbers of atoms in each $|m| \geq 3$ Stark level for $n = 31$ at a slew rate of 10^9 V/cm s. (from ref. 26).

What happens when we take more than one n state into account?

Luc Koenig and Bachelier



Classical ionization limit

Levels cross

Inglis Teller field

$$F = \frac{1}{3n^5}$$

The blue states really are more stable!

Photoexcitation of hydrogen from n=2 states in a field F=5714 V/cm
Classical ionization limit at -440 cm^{-1}

red

blue

m

0

1

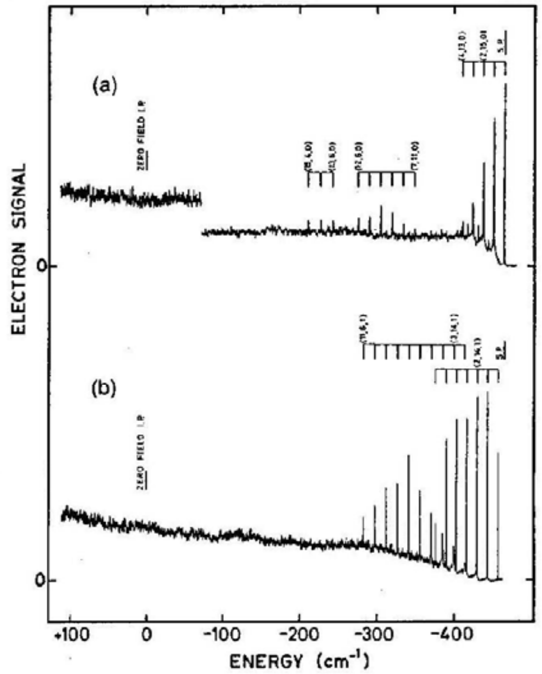


Fig. 8.9 Observed spectrum from the red $n = 2$, $n_1 = 0$, $m = 0$ Stark state in a field of 5714 V/cm with (a) π and (b) σ polarization of the second laser. Note the sharp onset of the continuous spectrum (from ref. 15).

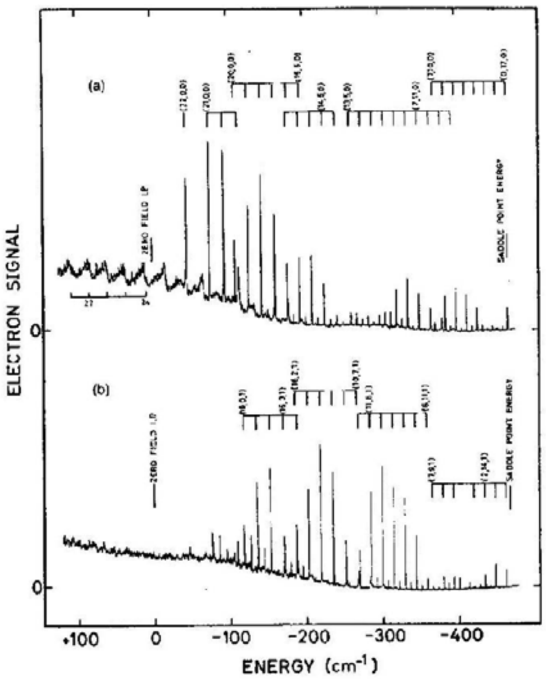


Fig. 8.10 Observed spectrum from the blue H $n = 2$, $n_1 = 1$, $m = 0$ Stark state in a field of 5714 V/cm with (a) π polarization and (b) σ polarization of the second laser. Note the progression from the extreme blue Stark states to the strong field mixing resonances (from ref. 15).

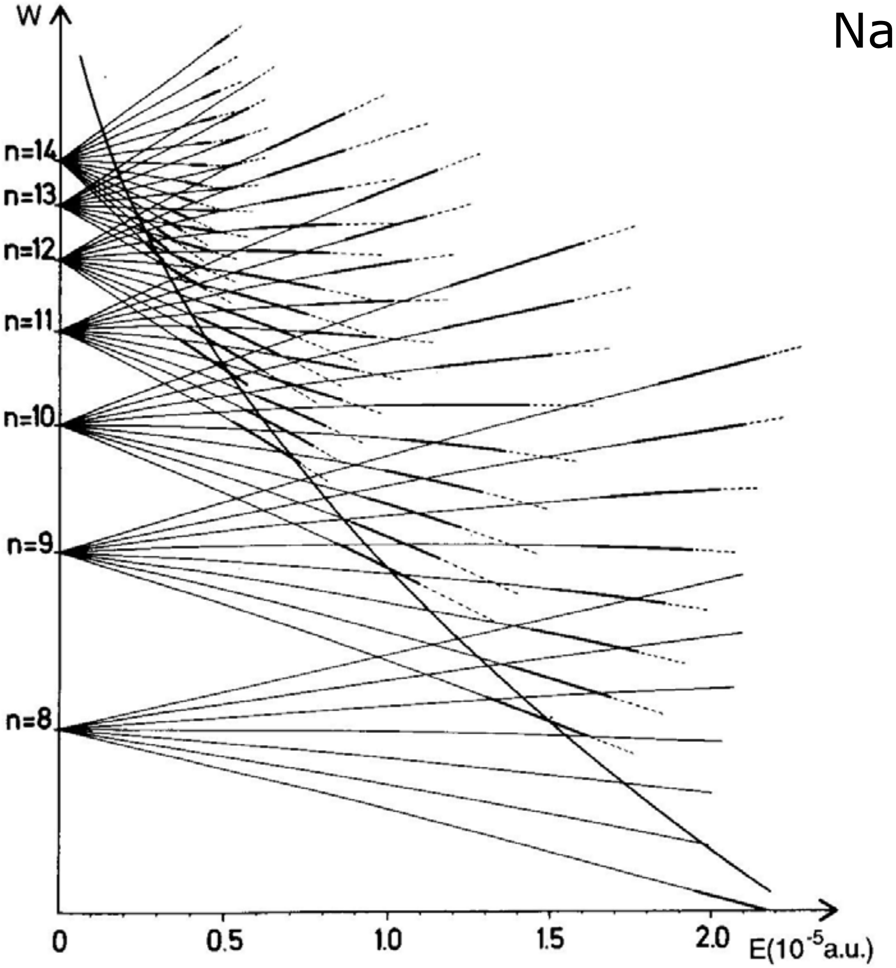
Rottke and Welge

Stark effect for other atoms (case of alkali)

High m only degenerate high ℓ states- hydrogen like
Low m states are different
Consider Na as an example

Hydrogen

Na m>2



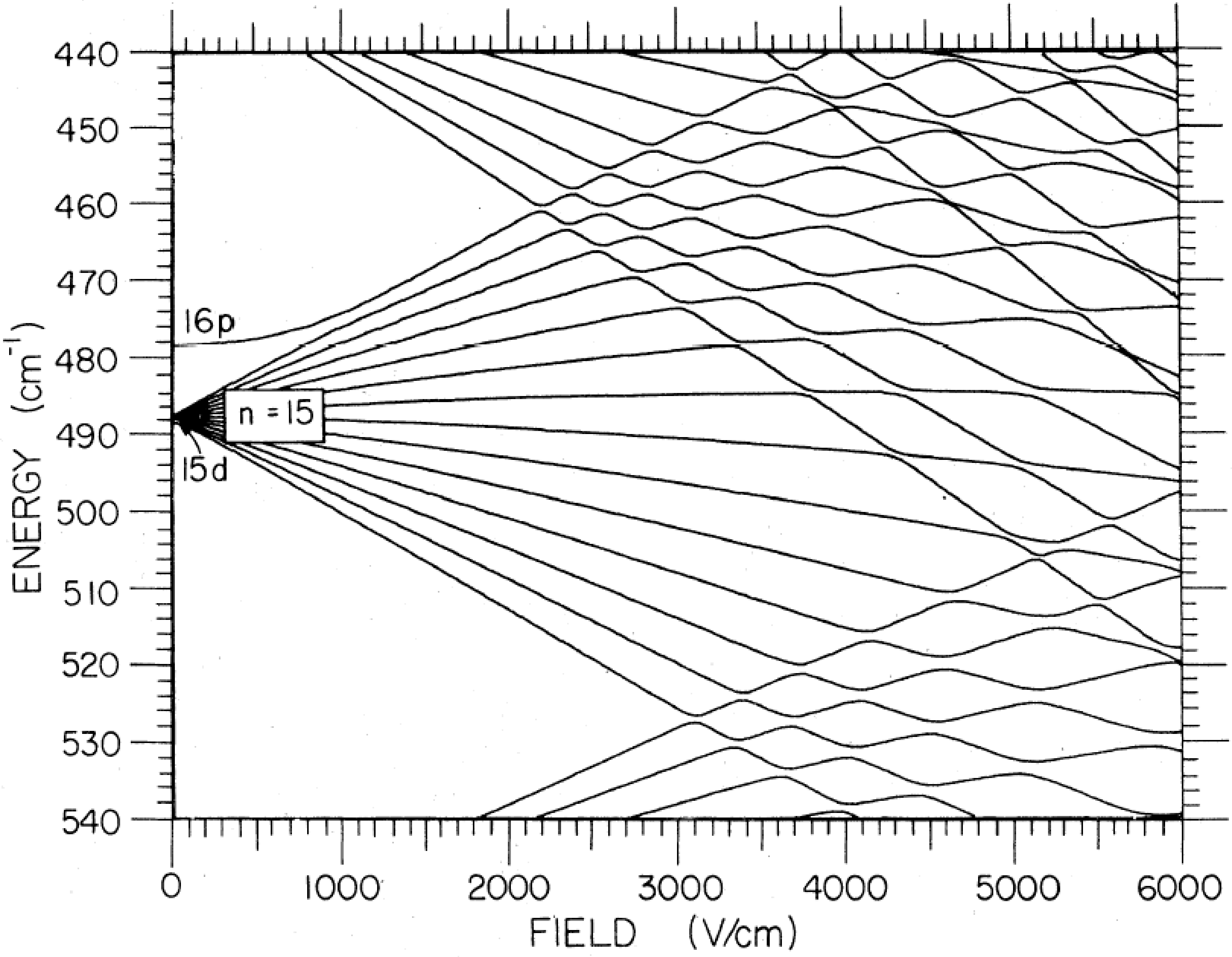


FIG. 10. Sodium, $|m| = 1$.

Kleppner et al

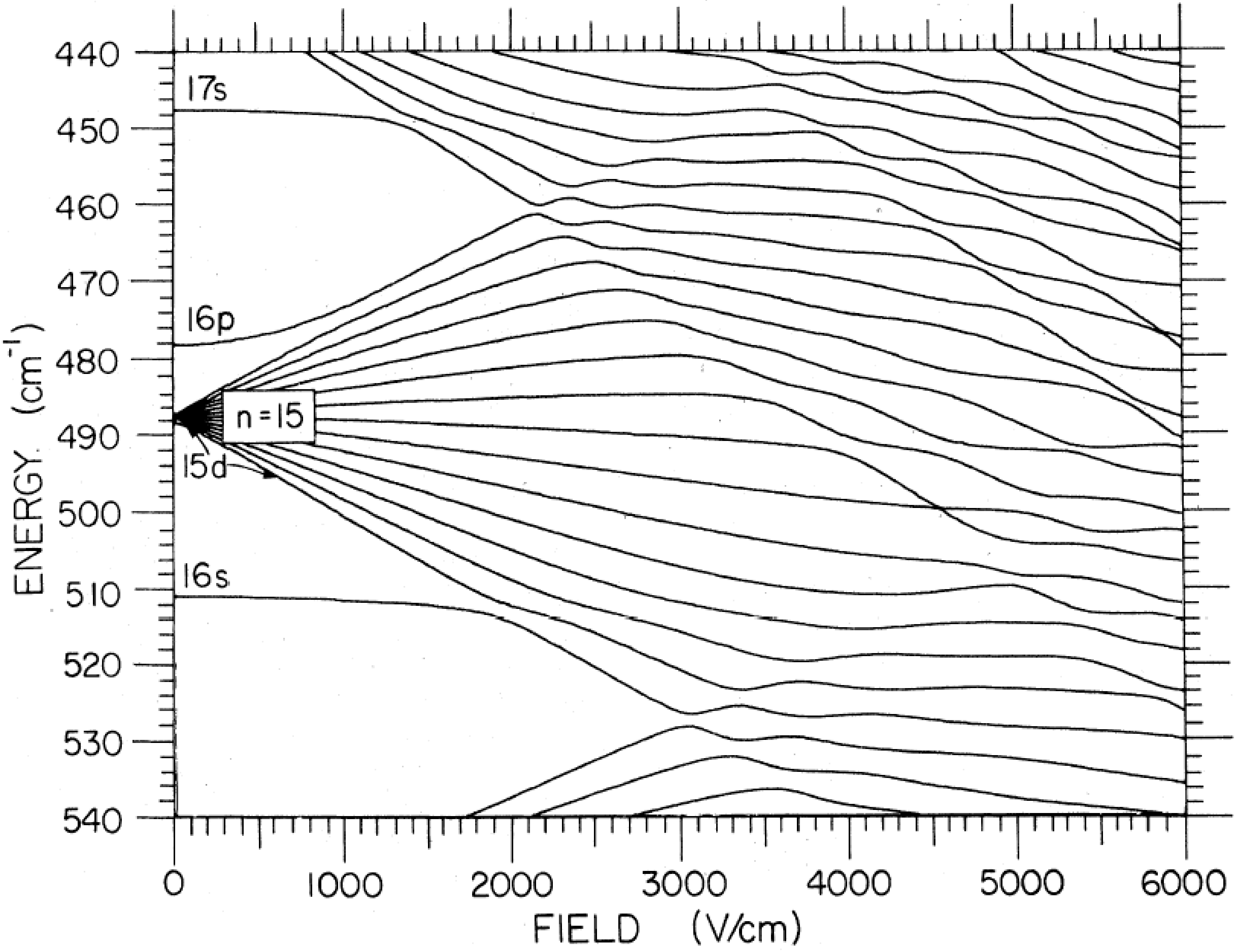
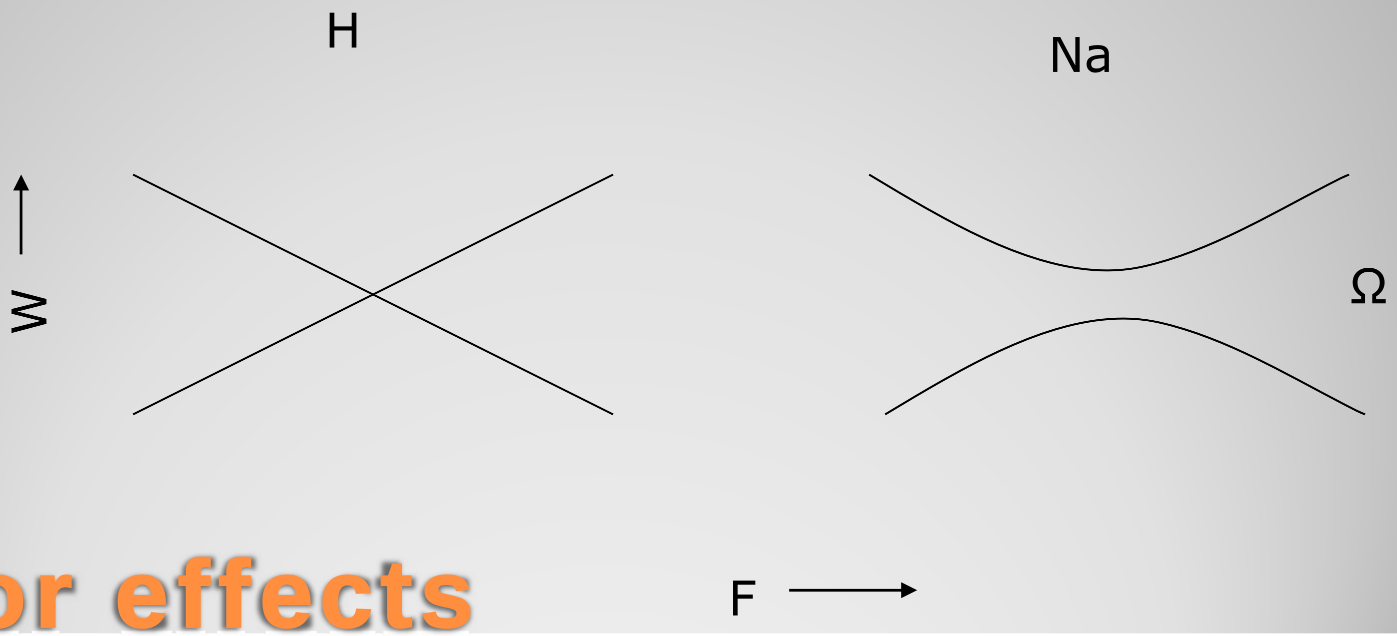


FIG. 11. Sodium, $m = 0$.

Kleppner et al

Major effects

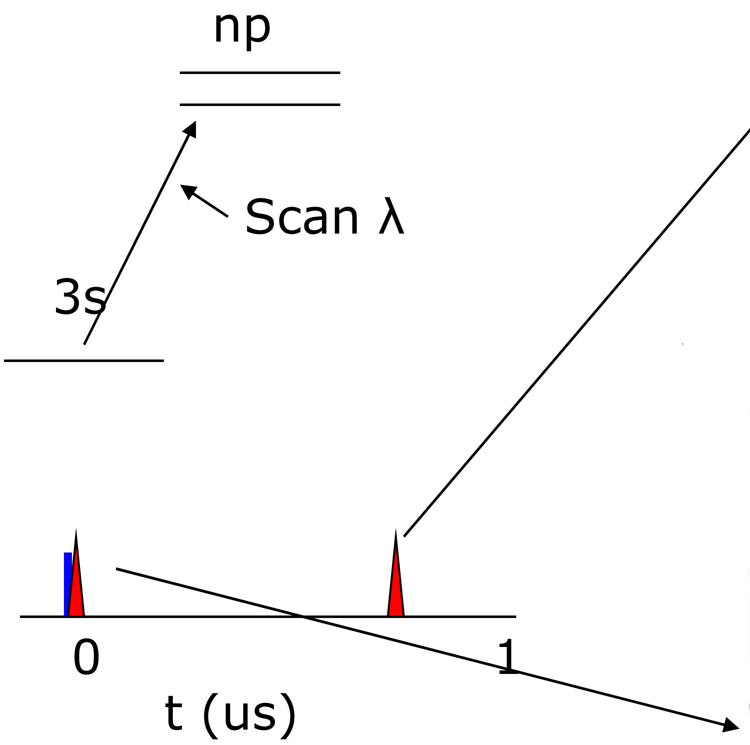
- Curvature at zero field (quadratic behavior)
- Level crossings in hydrogen above the Inglis Teller field ($F=1/3n^5$) become avoided crossings due to the core coupling of the red and blue states.



The connection of the red blue coupling to the quantum defect. Haroche et al.

$$\Omega = \langle n, blue | V_{core} | n+1, red \rangle$$
$$= \langle n, blue | ns \rangle \langle ns | V_{core} | n+1s \rangle \langle n+1s | n+1, red \rangle$$
$$= (1/\sqrt{n})(\delta_s / n^3)(1/\sqrt{n+1})$$
$$= \delta_s / n^4$$

Avoided crossings scale as $1/n^4$



Ionization in alkalis the Li excitation spectra Kleppner et al

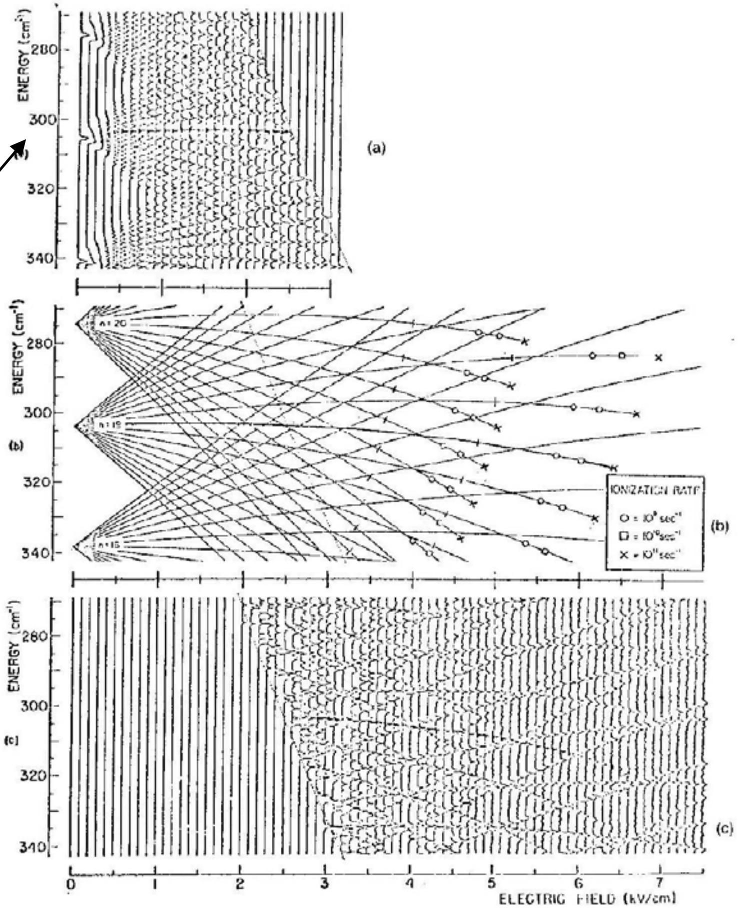
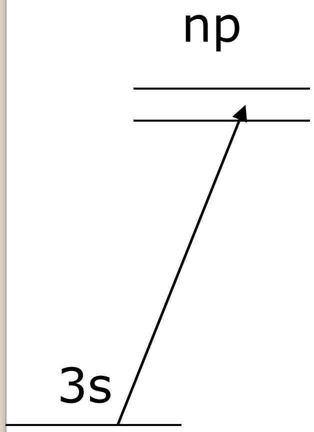


Fig. 6.17 Tunnelling and saddle point ionization in Li. (a) Experimental map of the energy levels of Li $|m| = 1$ states in a static field. The horizontal peaks arise from ions collected after laser excitation. Energy is measured relative to the one-electron ionization limit. Disappearance of a level with increasing field indicates that the ionization rates exceed $3 \times 10^5\ s^{-1}$. The dotted line is the classical ionization limit given by Eqs. (6.35) and (6.36). One state has been emphasized by shading. (b) Energy levels for H ($n = 18$–20, $|m| = 1$) according to fourth order perturbation theory. Levels from nearby terms are omitted for clarity. Symbols used to denote the ionization rate are defined in the key. The tick mark indicates the field where the ionization rate equals the spontaneous radiative rate. (c) Experimental map as in (a) except that the collection method is sensitive only to states whose ionization rate exceeds $3 \times 10^5\ s^{-1}$. At high fields, the levels broaden into the continuum in agreement with tunnelling theory for H (from ref. 32).

- Below the classical limit the non zero blue-red matrix elements lead to avoided crossings.
- Above the classical limit the blue states are coupled to rapidly ionizing red states. The blue states ionize by passing to the red states.
- Completely different from hydrogen

Summary

Spectrum of Li from the 3s state (to the p part of the Stark states)



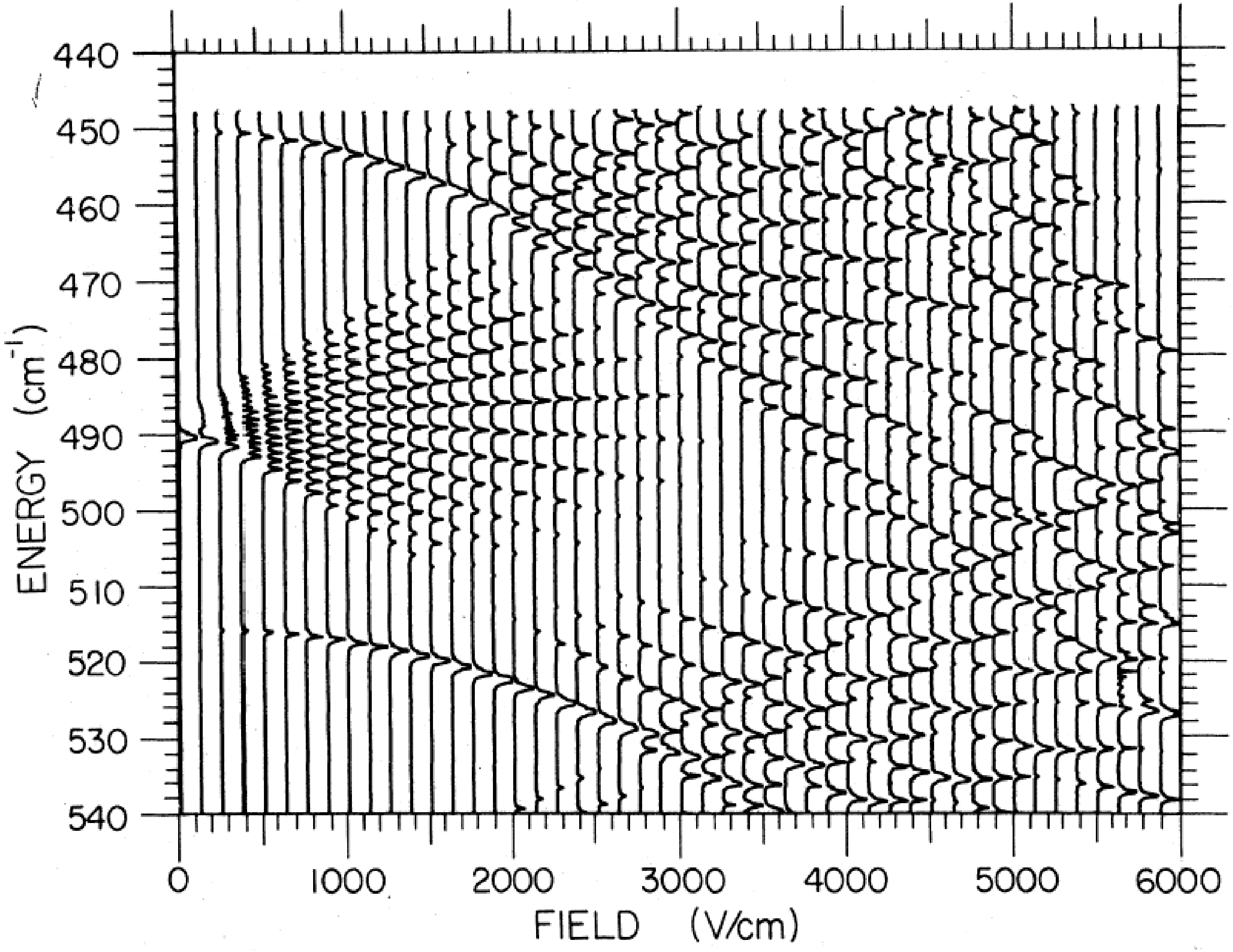
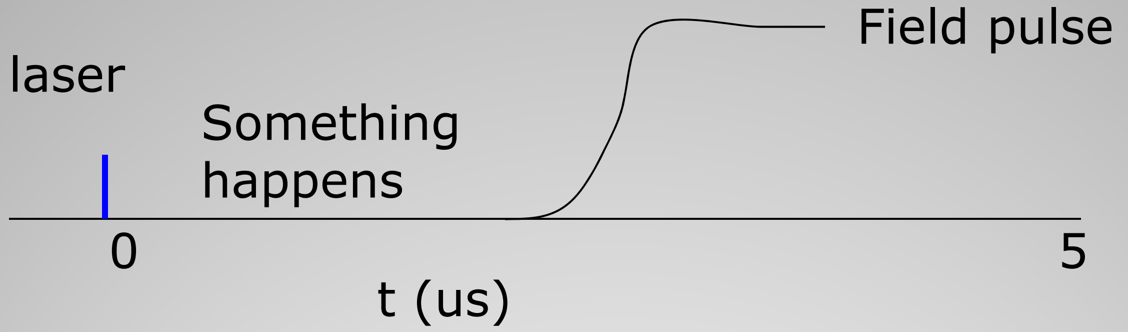


FIG. 7. Lithium, $m = 0$; experimental Stark structure.



laser

Something happens

Field pulse

0

5

t (us)

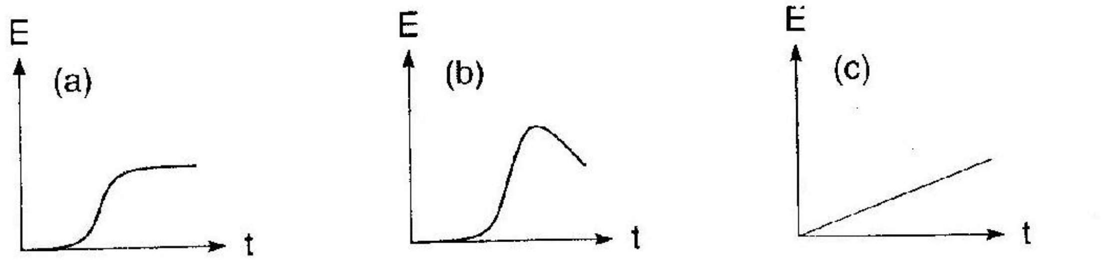
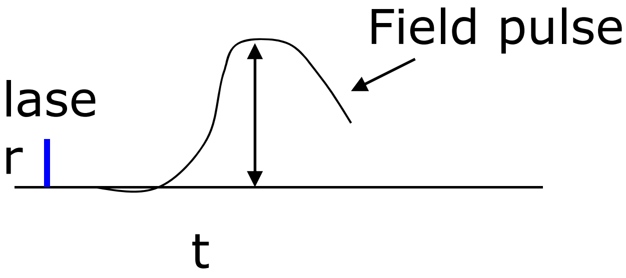


Fig. 7.1 Typical field pulses: (a) a pulse which rises in time to a flat topped pulse; (b) a pulse which rises to a peak then falls quickly ; (c) a linearly rising field.

Field ionization as a useful detection technique

Typically experiments are done in zero or low field and the field ionization is done by a pulse



Field pulse

laser

t

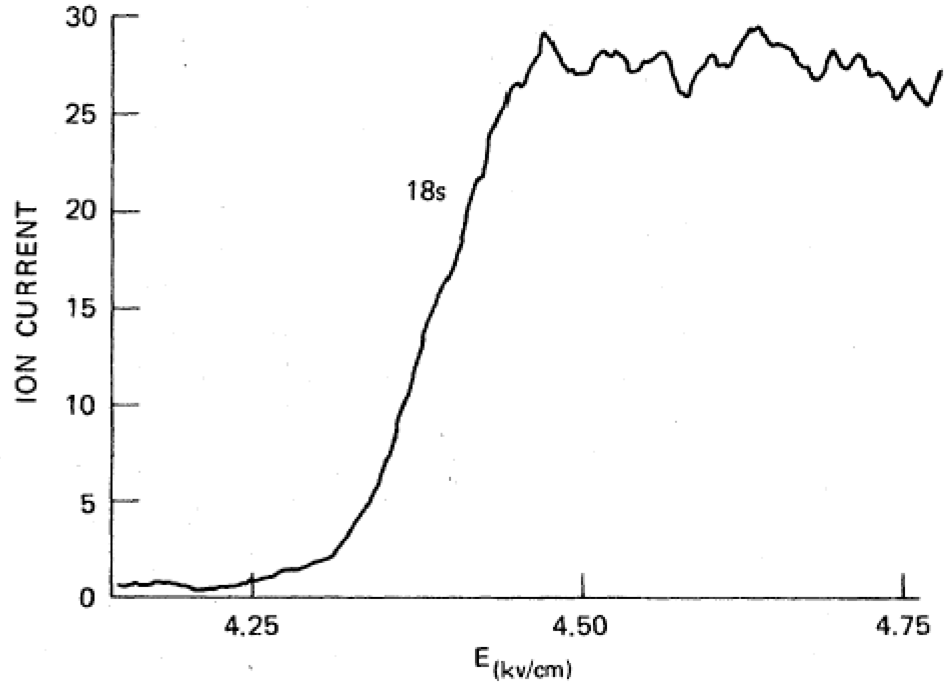


FIG. 3. 18*s* ionization threshold. The field ionization current is plotted vs the peak ionizing field.

Same experiment p states

m

0 1

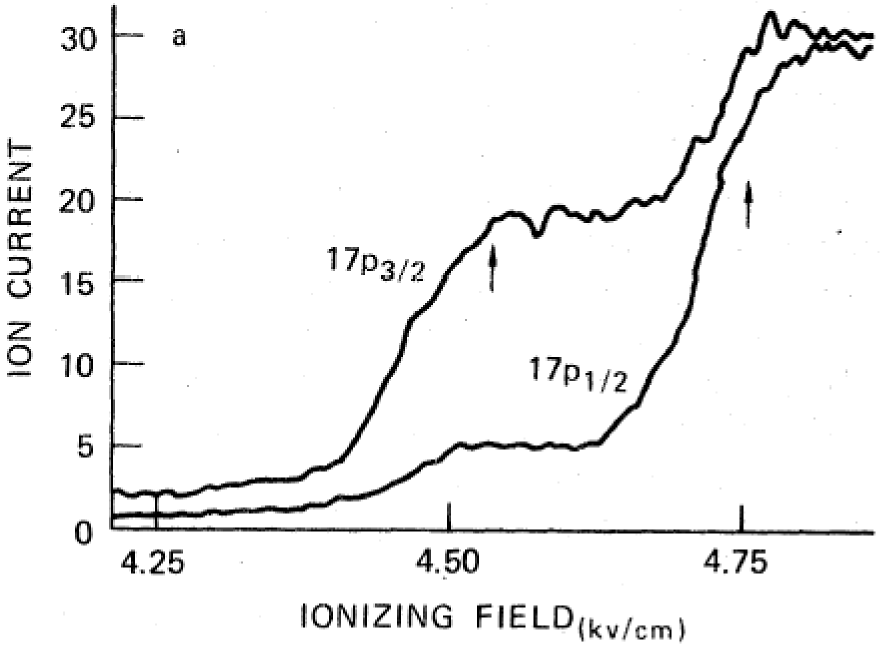


FIG. 4. (a) $17p_{1/2}$ and $17p_{3/2}$ ionization thresholds. The field ionization current is plotted vs the peak ionizing field. (b) The time-resolved signal when the peak

Na 17d

m

0 1 2

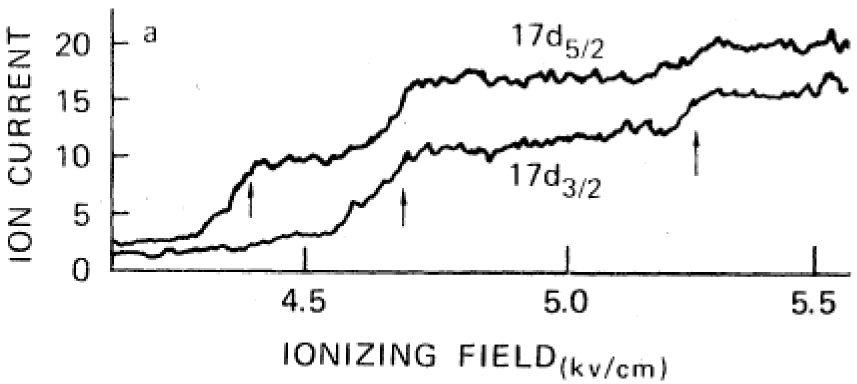


FIG. 5. (a) Experimental traces of the ion current vs peak ionization voltage for the $17d_{3/2}$ and $17d_{5/2}$ states. The approximate locations of the $|m_l|=0,1,$ and 2 thresholds are indicated by arrows. (b), (c), (d) Os-

Resolving states by the time resolution
Oscilloscope traces (200 ns/div)

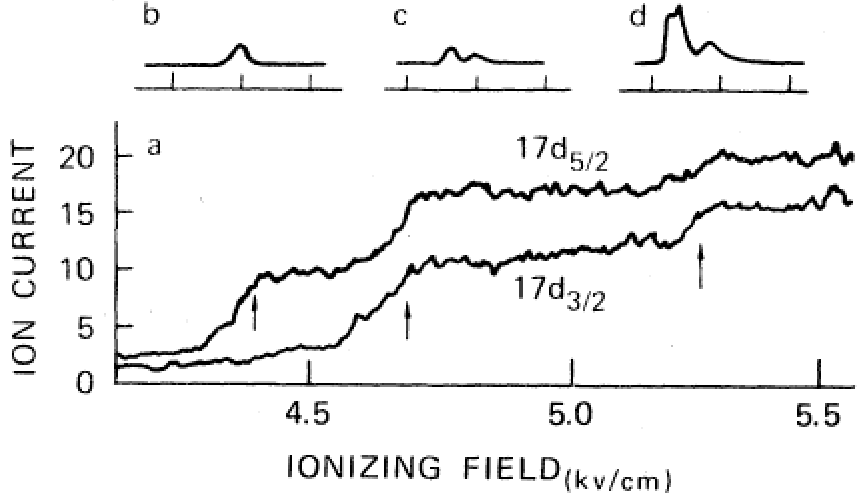
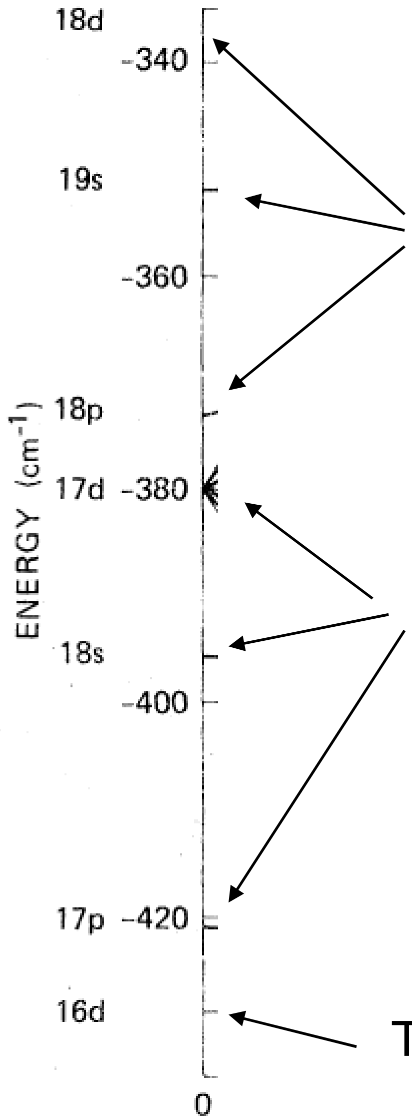


FIG. 5. (a) Experimental traces of the ion current vs peak ionization voltage for the $17d_{3/2}$ and $17d_{5/2}$ states. The approximate locations of the $|m_l|=0,1$, and 2 thresholds are indicated by arrows. (b), (c), (d) Oscilloscope traces of ion signals at different peak ionizing fields. In each case the center time marker corresponds to the peak of the ionizing high-voltage pulse. The horizontal scale is 200 nsec/division. (b) $|m_l|=0$ ion pulse, peak field $=4.58$ kV/cm. (c) $|m_l|=0$ followed by $|m_l|=1$ ion pulse, peak field $=4.98$ kV/cm. (d) $|m_l|=0$ overlapping $|m_l|=1$ followed by $|m_l|=2$ ion pulse, peak field $=5.27$ kV/cm.

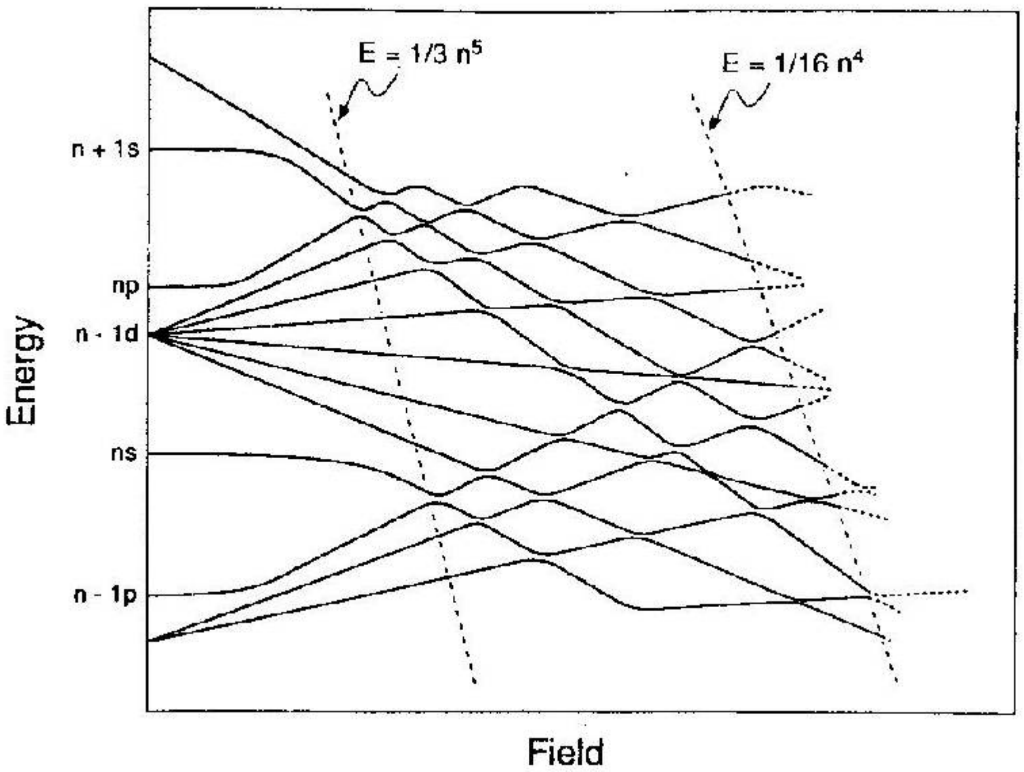


These three ionize at 3.5 kV/cm

These three ionize at 4.3 kV/cm

This one ionizes at 5.5 kV/cm

The atoms follow an adiabatic path to the classical limit, where they ionize (by coupling to a red state)



Criterion for an adiabatic passage

Landau-Zener criterion

$$\frac{dW}{dE} \bullet \frac{dE}{dt} < \Omega^2$$

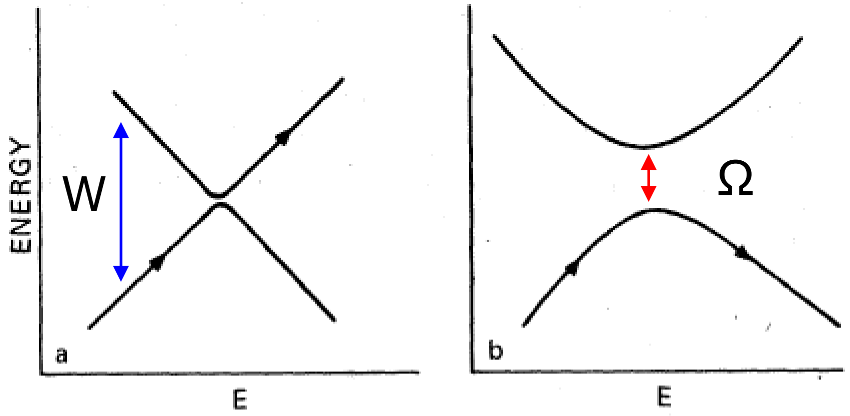
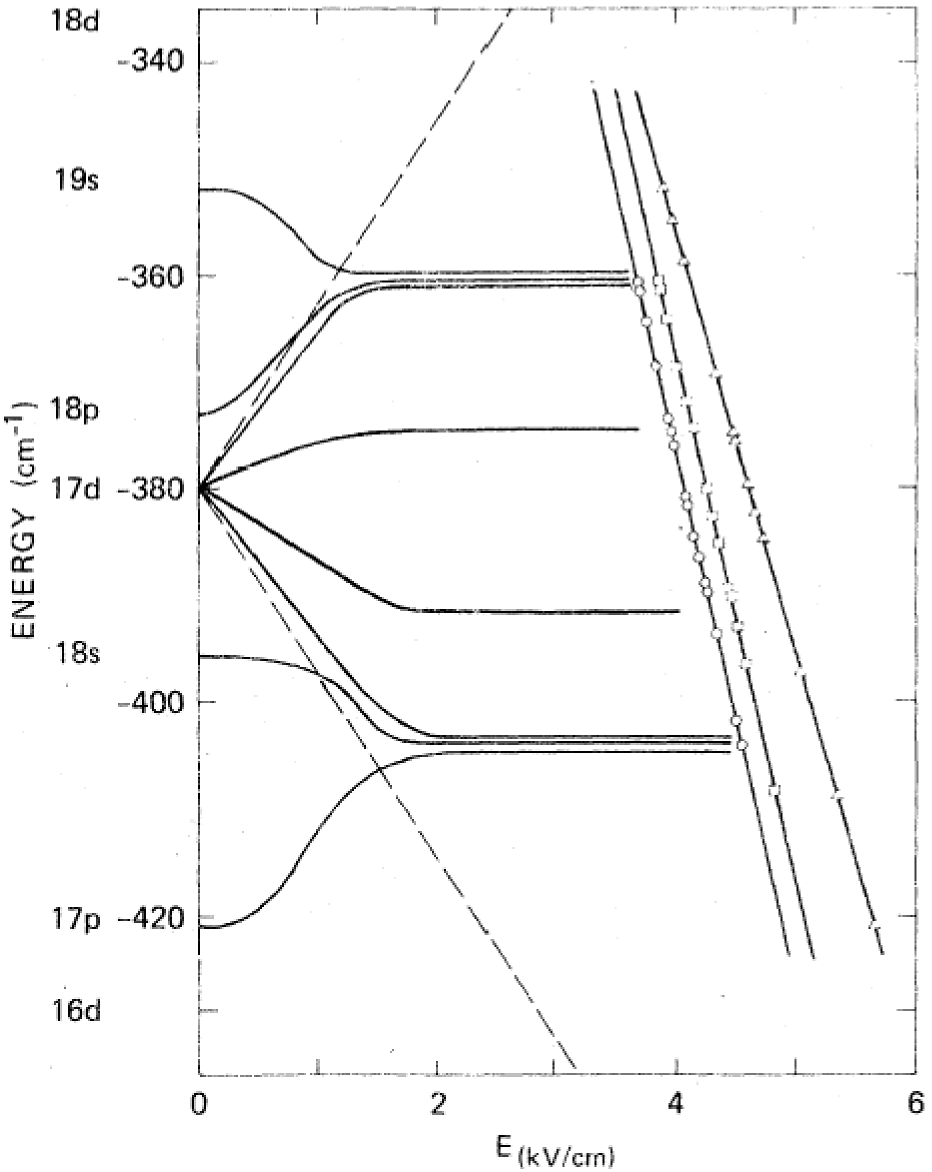


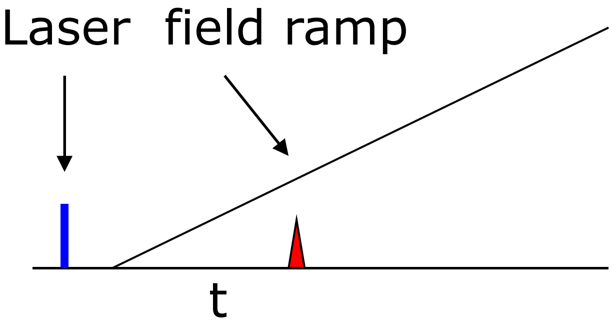
FIG. 7. (a) Plot of the energies of two states as a function of electric field *E* for the case of weak coupling between the states. The energy gap between the two curves is small and as the ionizing field is applied, the atom traverses the crossing diabatically as shown by the arrow, crossing the energy gap. (b) The same for the case of stronger coupling. As the ionizing field is applied, the atom traverses the avoided crossing adiabatically with no level crossing as shown by the arrows.

The atoms follow adiabatic paths.
The low ℓ states are trapped between the Stark states.



The passage does not have to be adiabatic Stebbings et al

The avoided crossings decrease as $1/n^4$ So higher n with the same ramped field is adequate



Laser field ramp

t

Time of signal depends on n

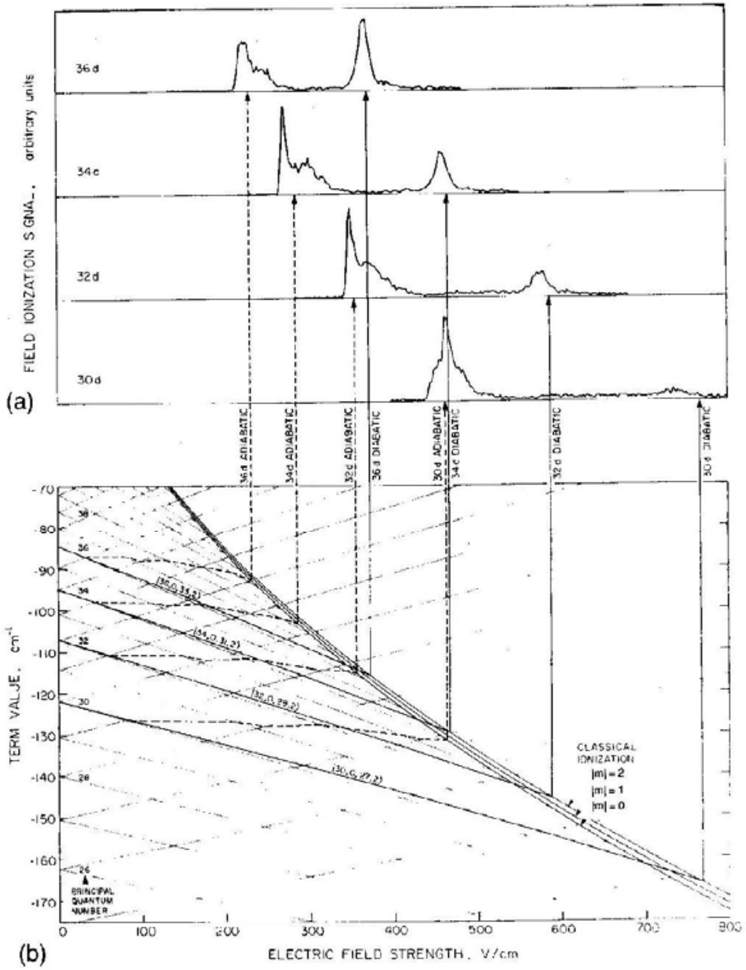
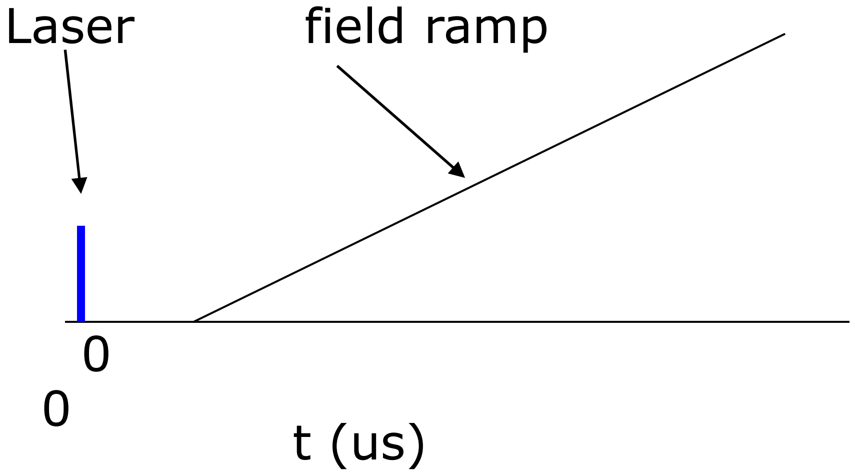
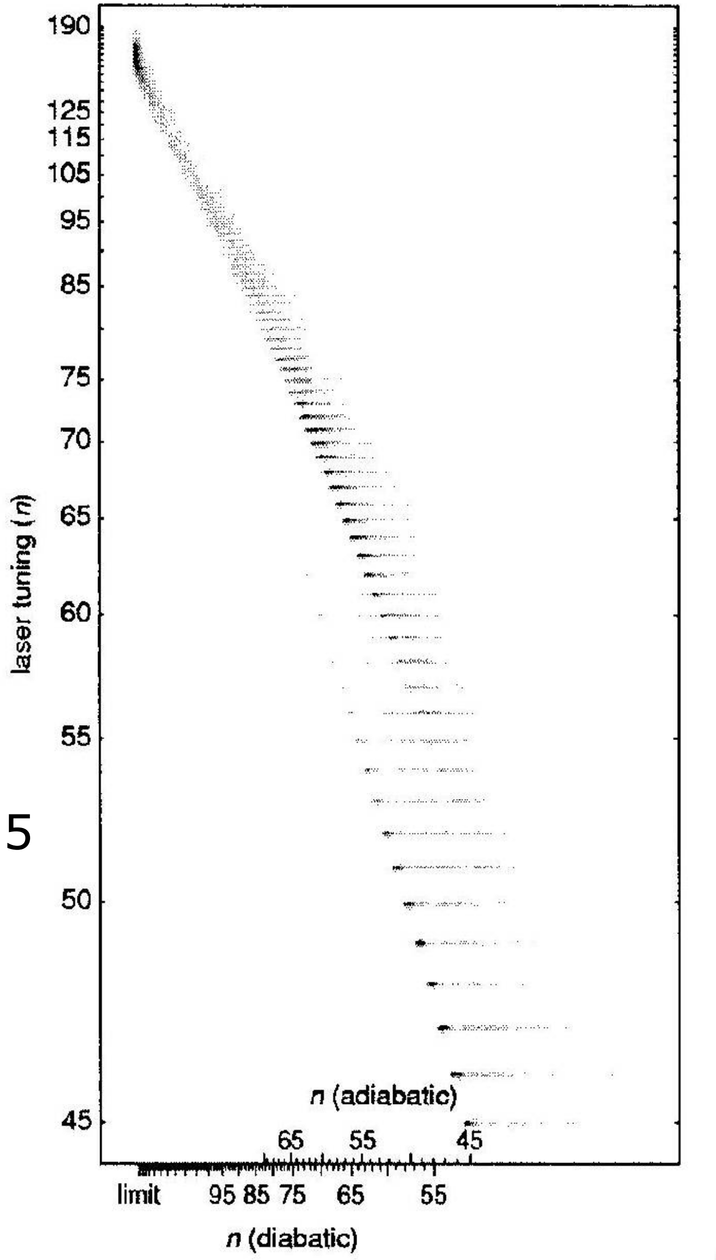


Fig. 7.7 (a) Field ionization data for Na *n*d states of $n = 30, 32, 34$, and 36. (b) Light lines: extreme members of $|m| = 0$ Stark manifolds (fourth order perturbation theory); dotted lines: adiabatic paths to ionization for $n = 30, 32, 34$, and 36; dark lines: diabatic paths to ionization for lowest members of $|m| = 2$ manifolds for $n = 30, 32, 34$, and 36. The lines indicating the classical ionization fields are calculated on the basis of Ref. 5 (from ref. 4).

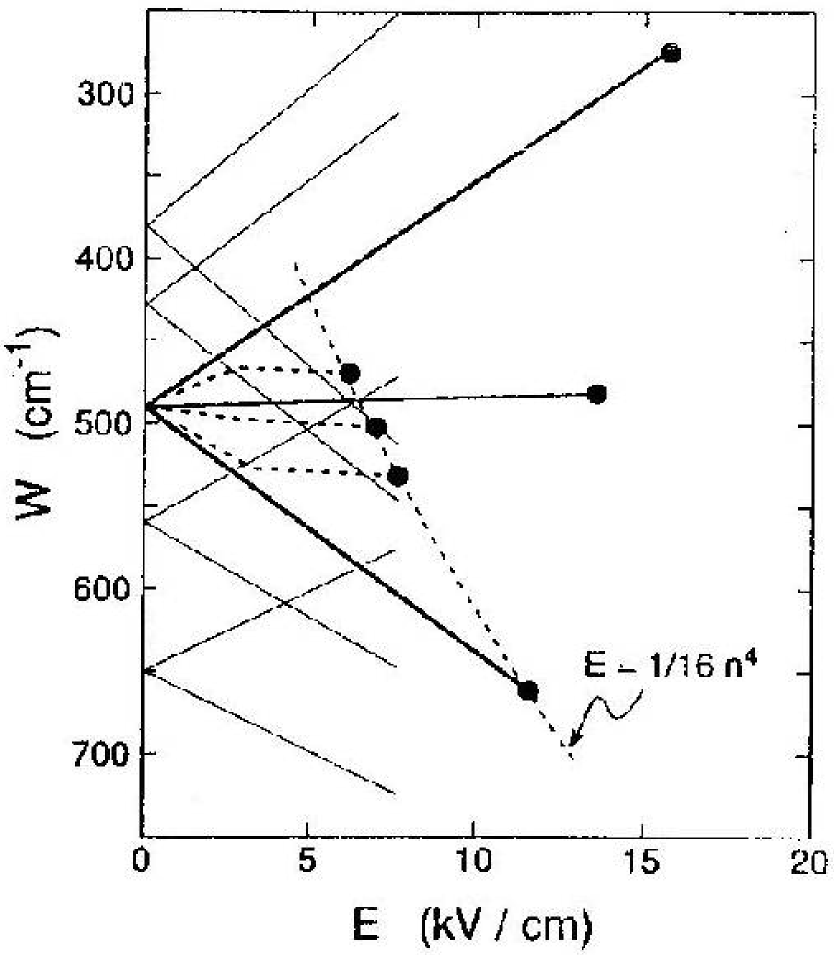
Ionization of Li by a field ramp
Showing the change from adiabatic to diabatic ionization as n goes from 50 to 60.





Noel et al

Field ionization in a nutshell



End Stark effect

The Stark effect allows easy tuning of the energy levels.
Field ionization is an effective tool for the study of Rydberg atoms.

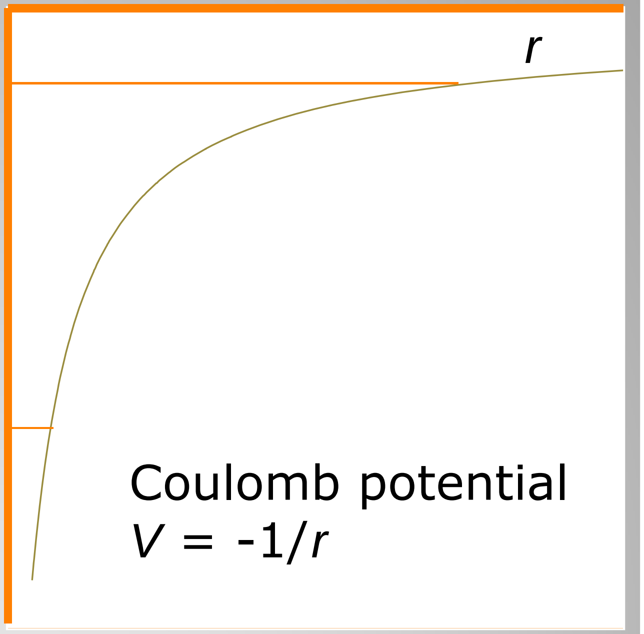
Rydberg states of Hydrogen atom

- Quantum numbers: n, l, m, (l=0,1…,n-1) or (l=s,p,d…), (m=-l…, +l)

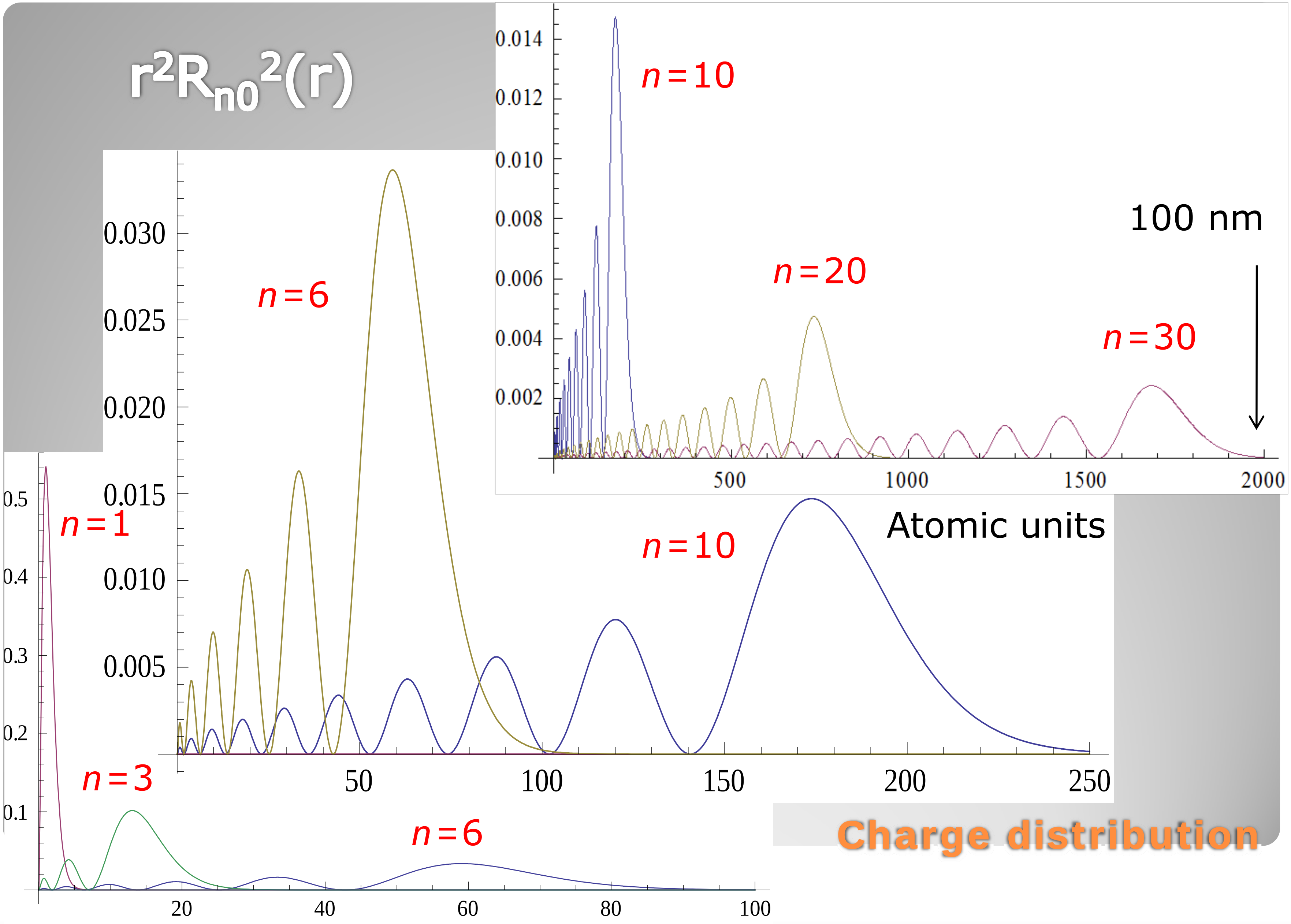
- Wavefunction: $R_{nl}(r)Y_l^m(\theta,\varphi)$
- Energy: $E=R_y/n^2$; Ry=13.6 eV =109737 cm^{-1}

- $\langle r \rangle = (3n^2 - l(l+1))/2$
- $\langle r^2 \rangle = (5n^2 + 1 - 3l(l+1))n^2/2$

- Rydberg state = State with high principal quantum number: n
- Weakly bound orbit: n=30, E=15 meV, $\langle r_s \rangle$=70 nm



$r^2R_{n0}^2(r)$



100 nm

Atomic units

Charge distribution

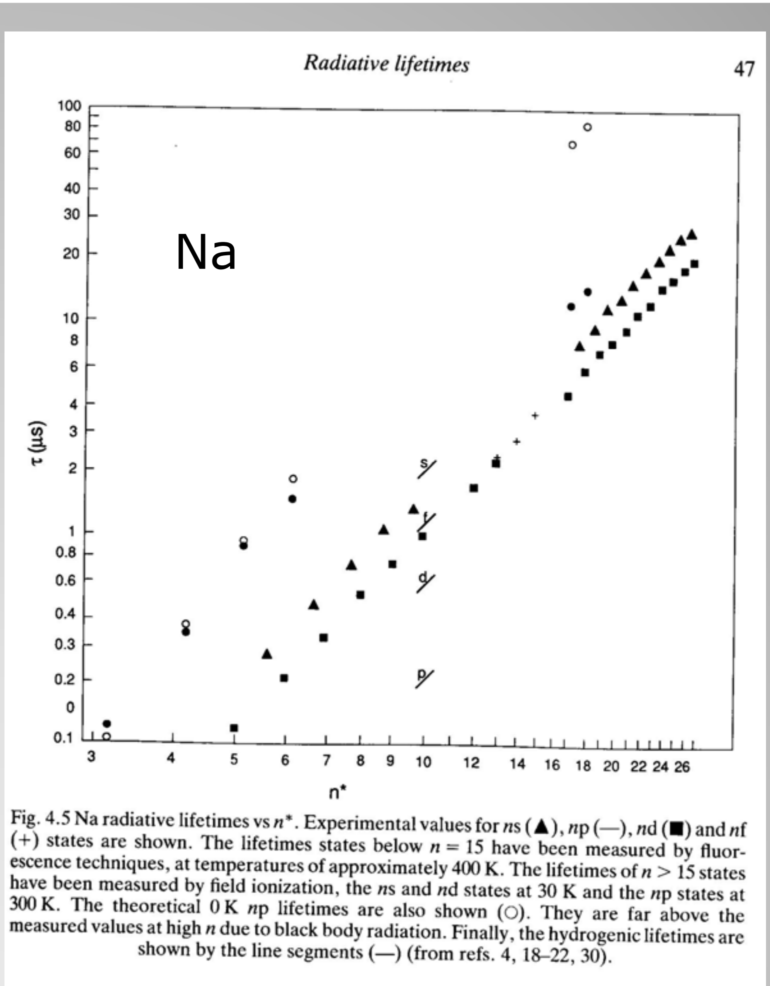
La Grenouille qui se veut faire aussi grosse que le Boeuf
Une grenouille vit un boeuf
Qui lui sembla de belle taille.
Elle, qui n'était pas grosse en tout comme un oeuf,
Envieuse, s'étend, et s'enfle, et se travaille,
Pour égaler l'animal en grosseur,
Disant : « Regardez bien, ma soeur ;
Est-ce assez ? dites-moi ; n' y suis-je point encore ?
- Nenni. - M' y voici donc ? - Point du tout. - M' y voilà ?
- Vous n'en approchez point. » La chétive pécore
S'enfla si bien qu'elle creva.
Le monde est plein de gens qui ne sont pas plus sages :
Tout bourgeois veut bâtir comme les grands seigneurs,
Tout petit prince a des ambassadeurs,
Tout marquis veut avoir des pages.

Jean de Lafontaine (1621 – 1695)

n =200 000 ! Very sentitive to any perturbation

Interests and motivations

- Selectively excited by tunable lasers
- Exaggerated properties
    - Huge size: $n^2 a_0$
    - Long lifetime: scale as n^3
    - …
- Sensitive to external fields (electric, magnetic or electromagnetic fields, blackbody radiation…)
    - Selective electric field ionization as $n^{-4}/16$ a.u. (*n=30, 400V/cm; n=100, 3V/cm*)
    - …
- To simulate extreme physical situations or « gedanken » experiments (non destructive measurement of the presence of one photon in a cavity)



Radiative lifetimes 47

Fig. 4.5 Na radiative lifetimes vs n^*. Experimental values for ns (▲), np (—), nd (■) and nf (+) states are shown. The lifetimes states below $n = 15$ have been measured by fluorescence techniques, at temperatures of approximately 400 K. The lifetimes of $n > 15$ states have been measured by field ionization, the ns and nd states at 30 K and the np states at 300 K. The theoretical 0 K np lifetimes are also shown (○). They are far above the measured values at high n due to black body radiation. Finally, the hydrogenic lifetimes are shown by the line segments (—) (from refs. 4, 18–22, 30).