

Rydberg atoms

part 1

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Content

- Part 1: Rydberg atoms
- Part 2: 2 typical (beam) experiments

References

- T. Gallagher: Rydberg atoms

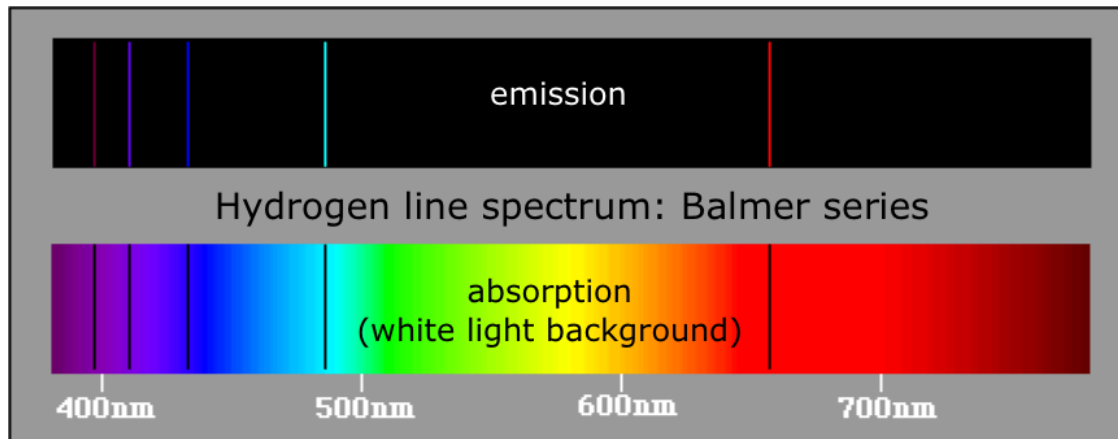
Introduction – What is „Rydberg“?

- Rydberg atoms are (any) atoms in state with high principal quantum number n .
- Rydberg atoms are (any) atoms with exaggerated properties

 *equivalent!*

Introduction – How was it found?

- In 1885: Balmer series:
 - Visible absorption wavelengths of H:



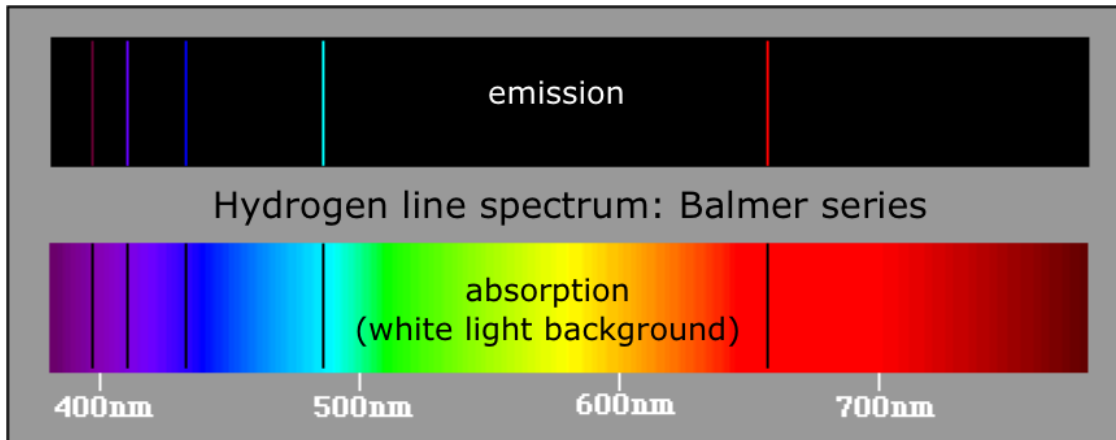
$$\lambda = \frac{bn^2}{n^2 - 4}$$

- Other series discovered by Lyman, Brackett, Paschen, ...

- Summarized by Johannes Rydberg: $\tilde{\nu} = \tilde{\nu}_{\infty} - \frac{Ry}{n^2}$

Introduction – Generalization

- In 1885: Balmer series:
 - Visible absorption wavelengths of H:



$$\lambda = \frac{bn^2}{n^2 - 4}$$

- Other series discovered by Lyman, Brackett, Paschen, ...

- Quantum Defect was found for other atoms: $\tilde{\nu} = \tilde{\nu}_\infty - \frac{Ry}{(n - \delta_l)^2}$

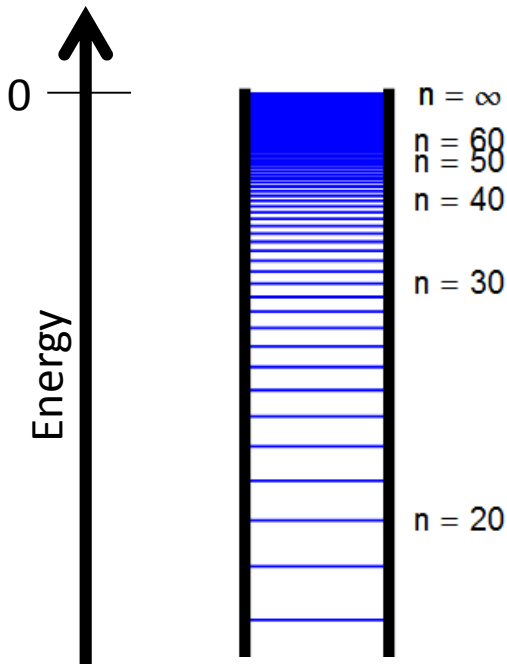
Introduction – Rydberg atom?

- Energy follows Rydberg formula:

Hydrogen

$$E = E_{\infty} - \frac{hRy}{(n - \delta_l)^2}$$

$E_{\infty} = 0$
 $hRy = 13.6 \text{ eV}$
 $\delta_l = 0$



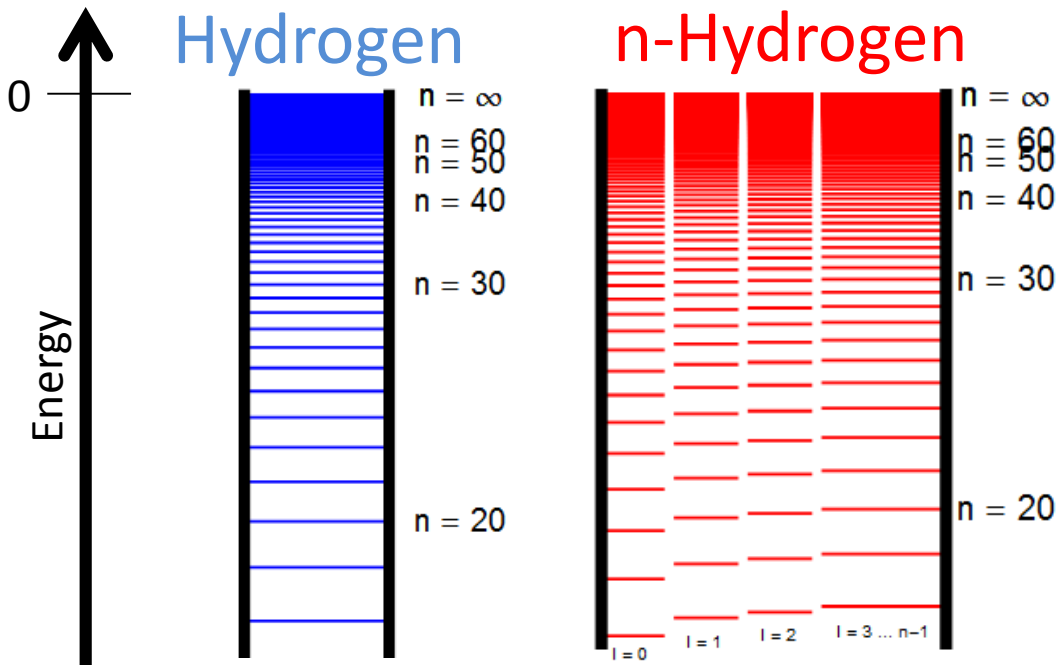
Quantum Defect?

- Energy follows Rydberg formula:

$$E = E_{\infty} - \frac{hRy}{(n - \delta_l)^2}$$

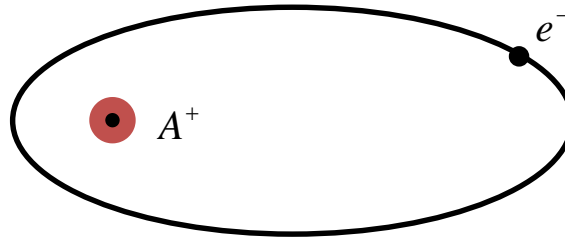
Quantum Defect

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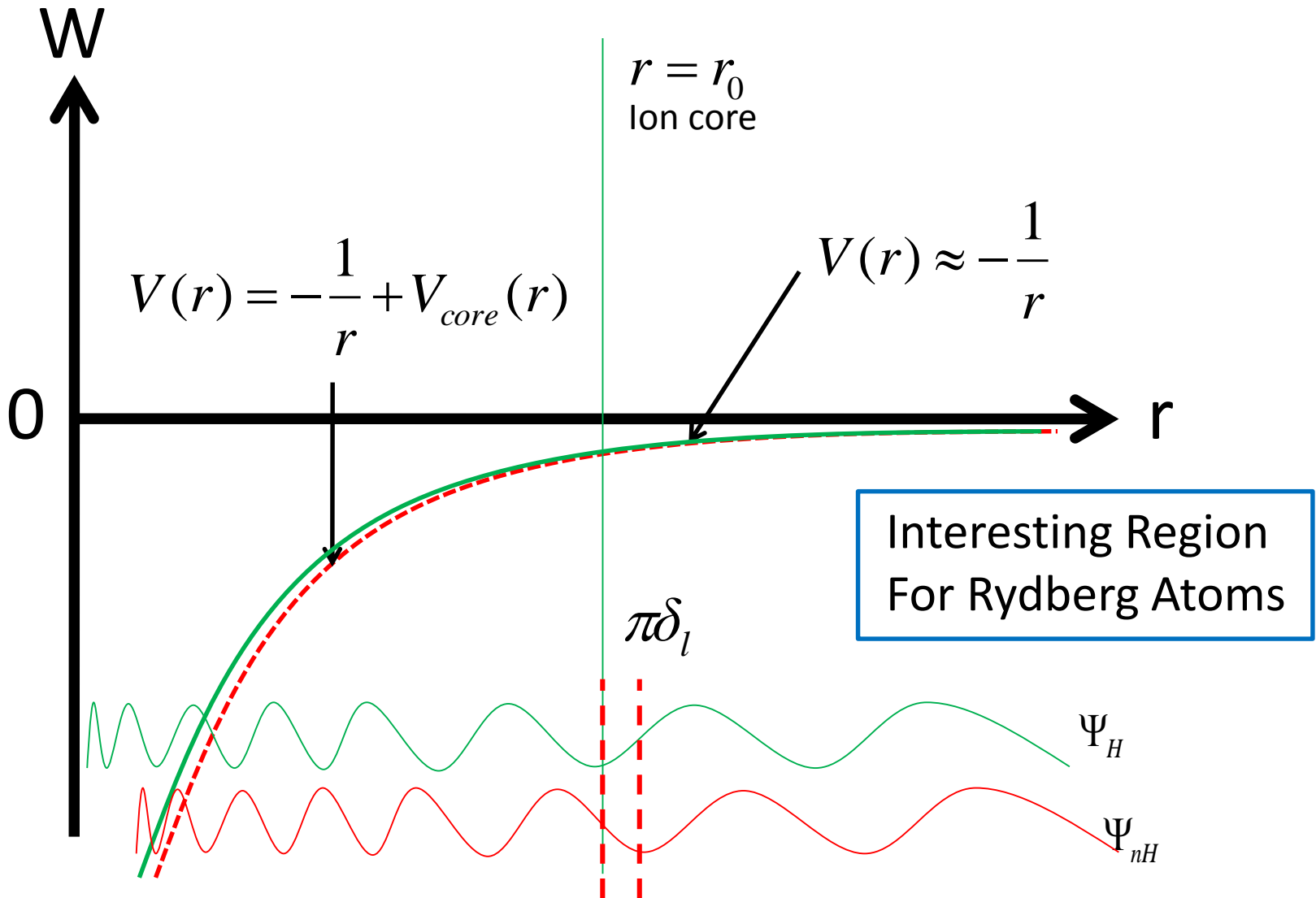
Rydberg Atom Theory

- Rydberg Atom



- Almost like Hydrogen
 - Core with one positive charge
 - One electron
- What is the difference?
 - No difference in angular momentum states

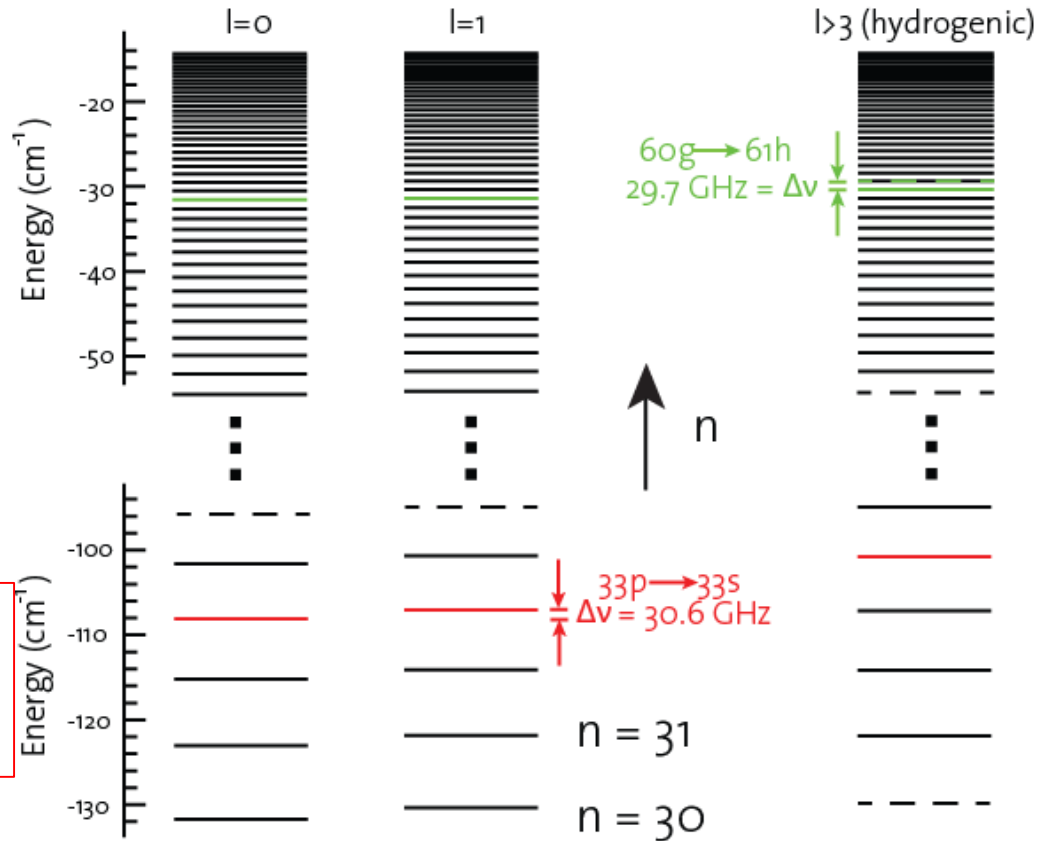
Radial parts-Interesting regions



(Helium) Energy Structure

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

- δ_l usually measured
 - Only large for low l (s,p,d,f)
- He level structure
- δ_l is big for s,p



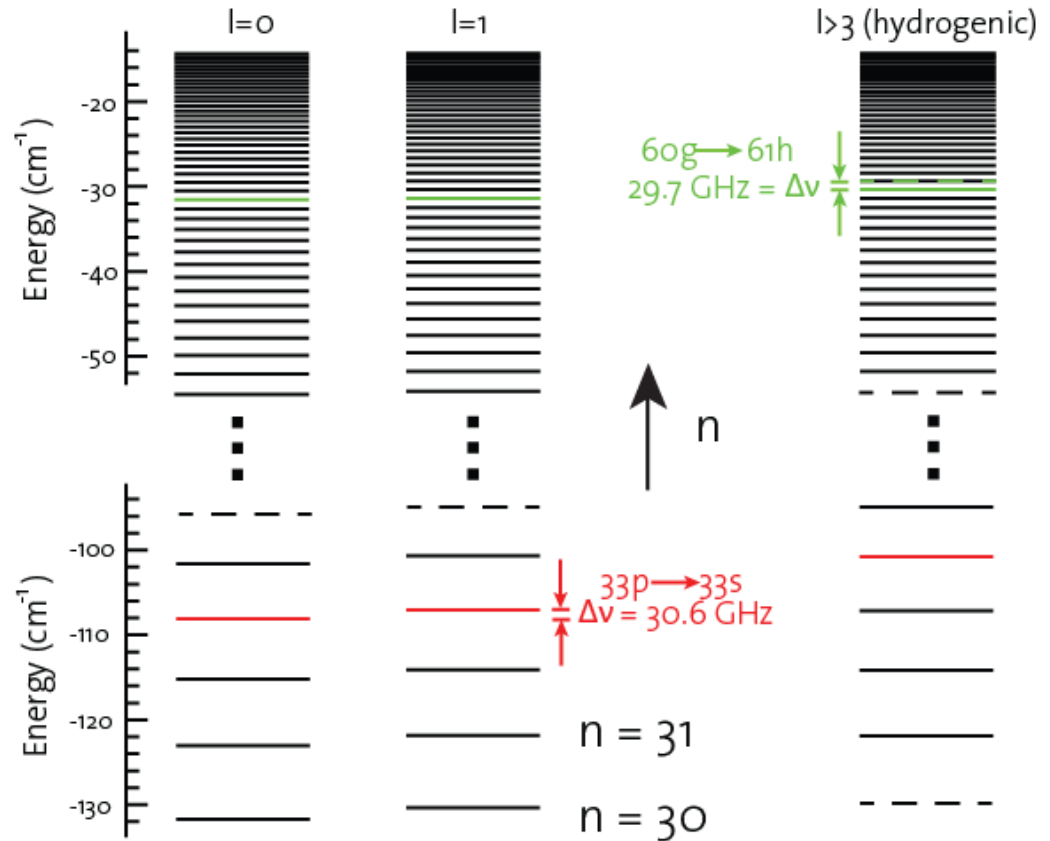
Excentric orbits penetrate into core.
 Large deviation from Coulomb.
 Large phase shift \rightarrow large quantum defect

(Helium) Energy Structure

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

- δ_l usually measured
 - Only large for low l (s,p,d,f)
- He level structure
- δ_l is big for s,p

$$\frac{dW}{dn} = \frac{1}{(n - \delta_l)^3}$$



Electric Dipole Moment

- Electron most of the time far away from core
 - Strong electric dipole: $\vec{d} = e\vec{r}$
 - Proportional to transition matrix element
$$\langle \Psi_f | \vec{d} | \Psi_i \rangle = e \langle \Psi_f | \vec{r} | \Psi_i \rangle = e \langle \Psi_f | r \cos(\theta) | \Psi_i \rangle$$
- We find electric Dipole Moment
 - $\langle \Psi_f | \vec{d} | \Psi_i \rangle \propto \langle r \rangle \langle l \pm 1 | \cos(\theta) | l \rangle \propto n^2$
- Cross Section: $\sigma \propto \langle r \rangle^2 \propto n^4$

$W = -\frac{1}{2(n-\delta_l)^2}$	$\frac{dW}{dn} = \frac{1}{(n-\delta_l)^3}$
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Stark Effect $H\Psi = (H_0 + \vec{d}\vec{F})\Psi = E\Psi$

- For non-Hydrogenic Atom (e.g. Helium)
 - „Exact“ solution by numeric diagonalization of

$$\langle \Psi_f | H | \Psi_i \rangle = \langle \Psi_f | H_0 | \Psi_i \rangle + \langle \Psi_f | \vec{d} | \Psi_i \rangle \vec{F}$$

in undisturbed (standard) basis (\tilde{n}, l, m)

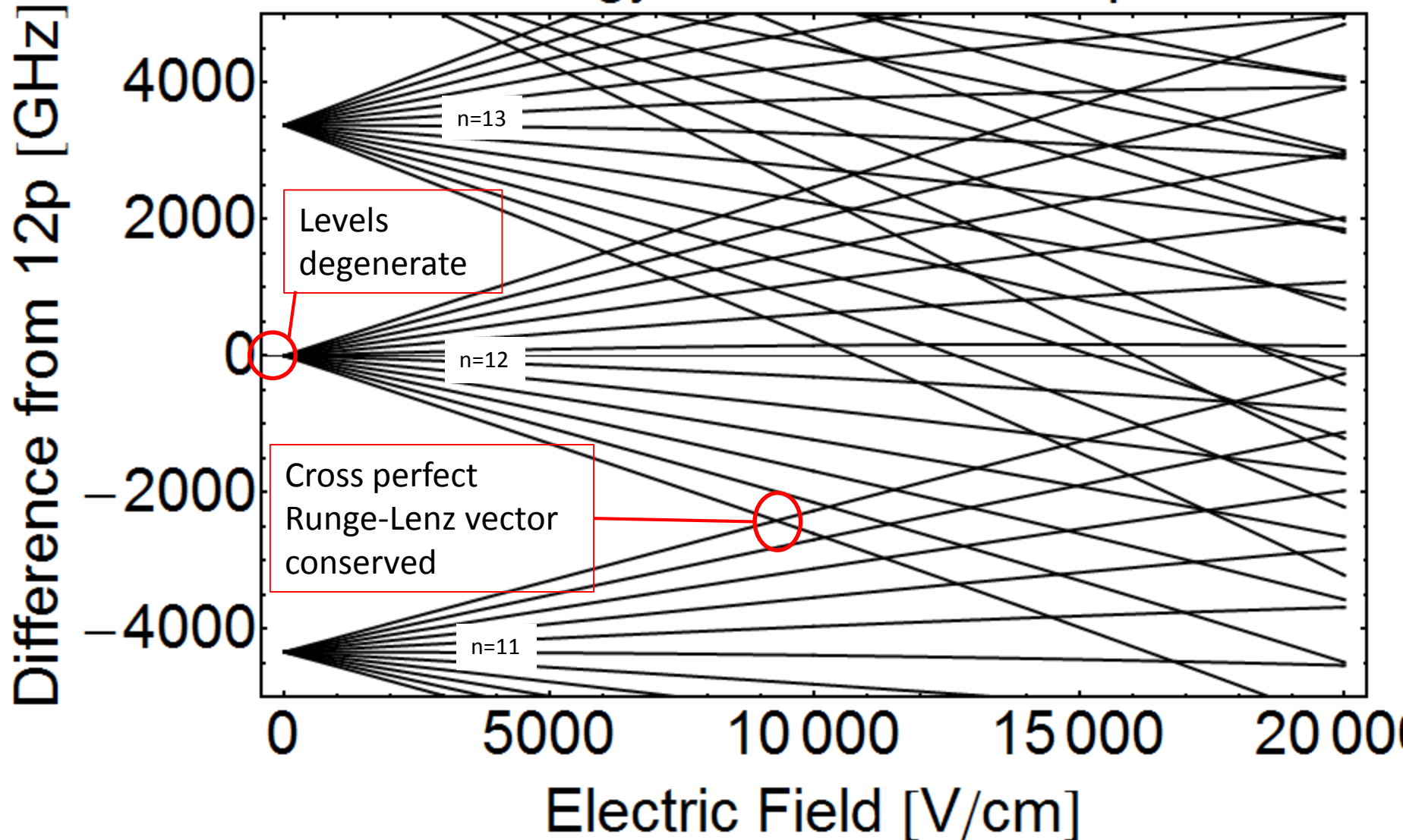
$$W = -\frac{1}{2(n - \delta_l)^2}$$

Numerov

$W = -\frac{1}{2(n - \delta_l)^2}$	$\frac{dW}{dn} = \frac{1}{(n - \delta_l)^3}$	$\langle \vec{d} \rangle \approx a_0 n^2$	$\sigma \propto n^4$
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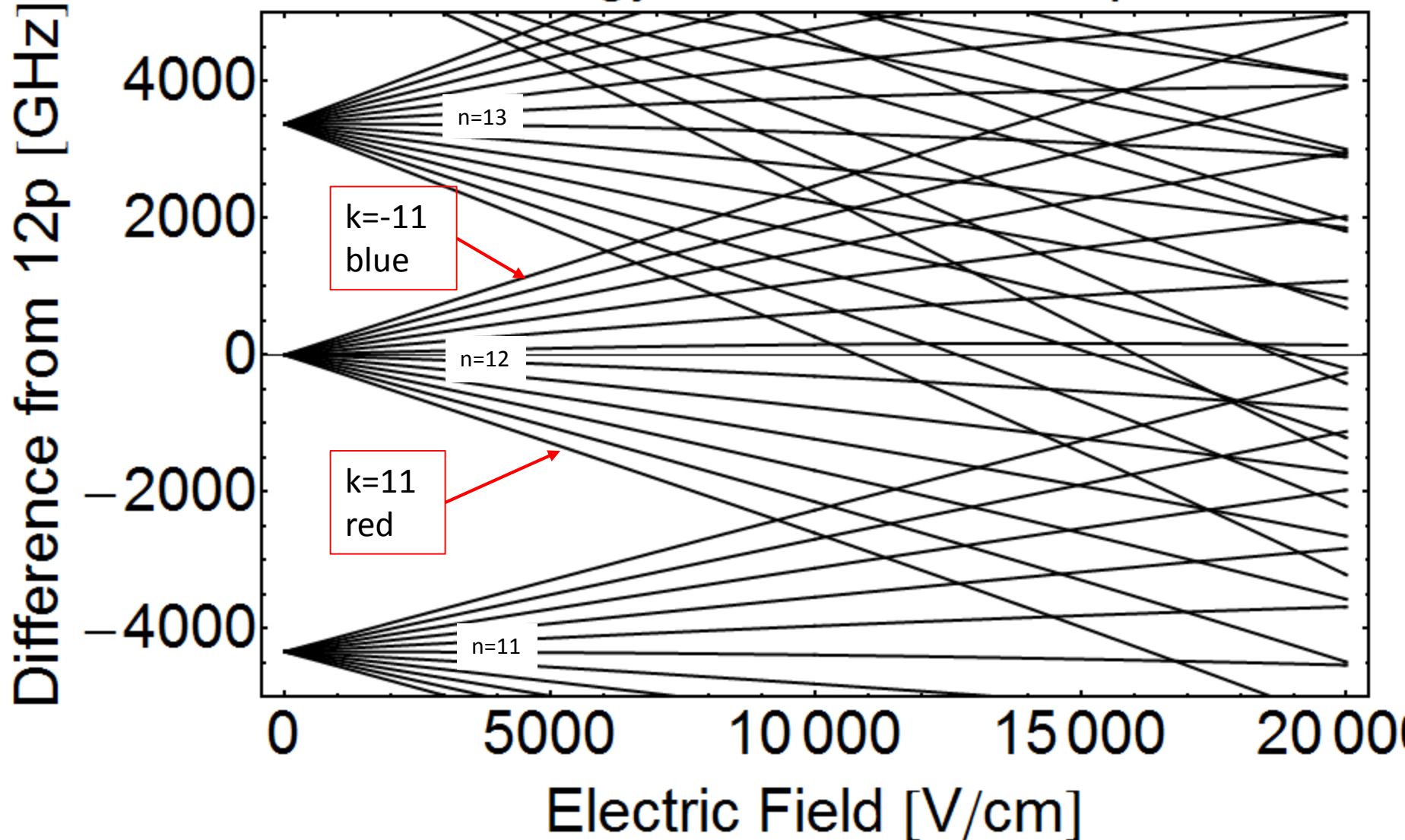
Stark Map Hydrogen

Energy levels around 12p



Stark Map Hydrogen

Energy levels around 12p



Hydrogen Atom in an electric Field

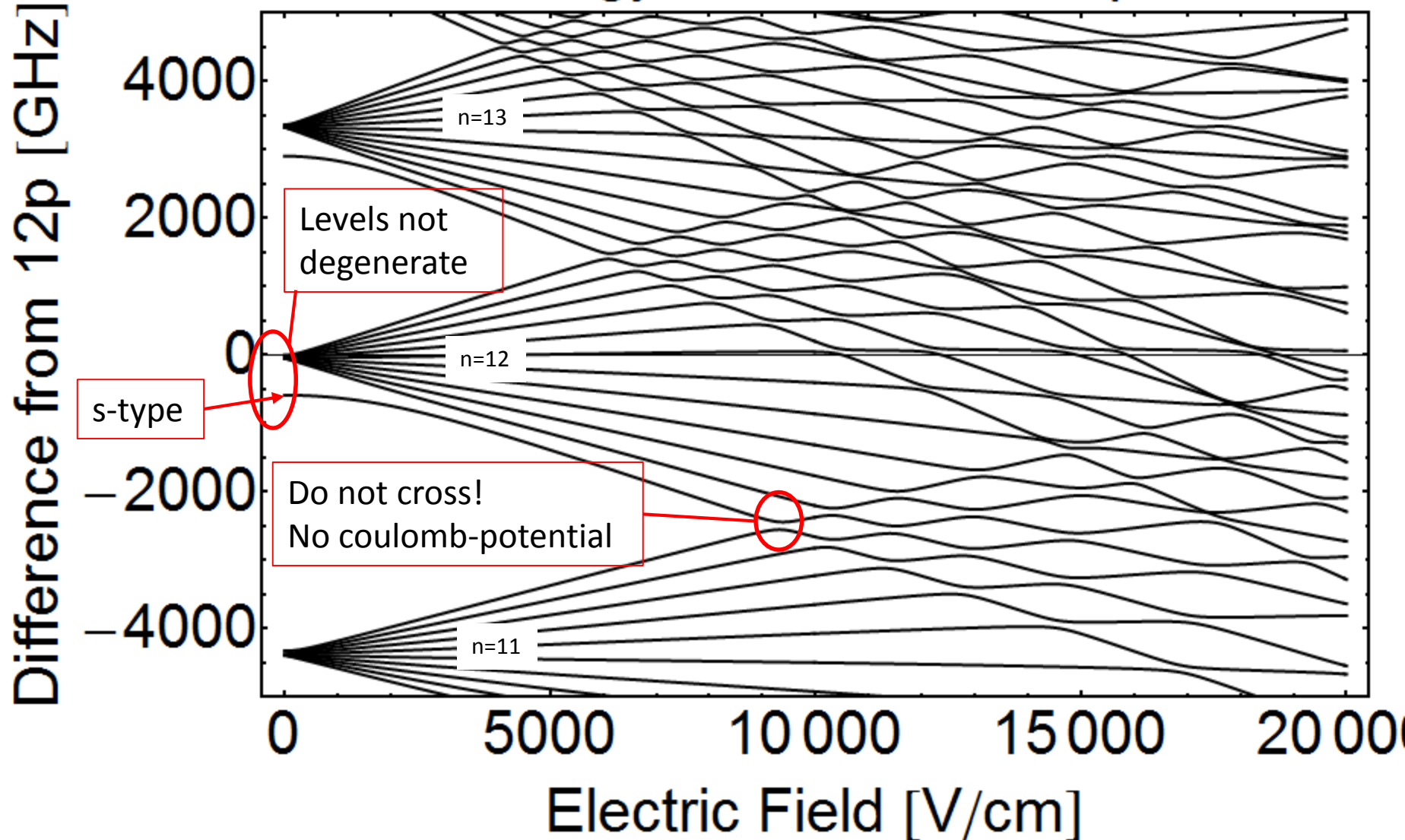
- Rydberg Atoms very sensitive to electric fields
 - Solve: $H\Psi = (H_0 + \vec{d}\vec{F})\Psi = E\Psi$ in parabolic coordinates

- Energy-Field dependence: Perturbation-Theory

$$W = -\frac{1}{2n^2} - \frac{3}{2} F \underbrace{(n_1 - n_2)}_k n + \frac{F}{16} n^4 \left(17n^2 - 3 \underbrace{(n_1 - n_2)^2}_k - 9m^2 + 19 \right) + O(n^5)$$

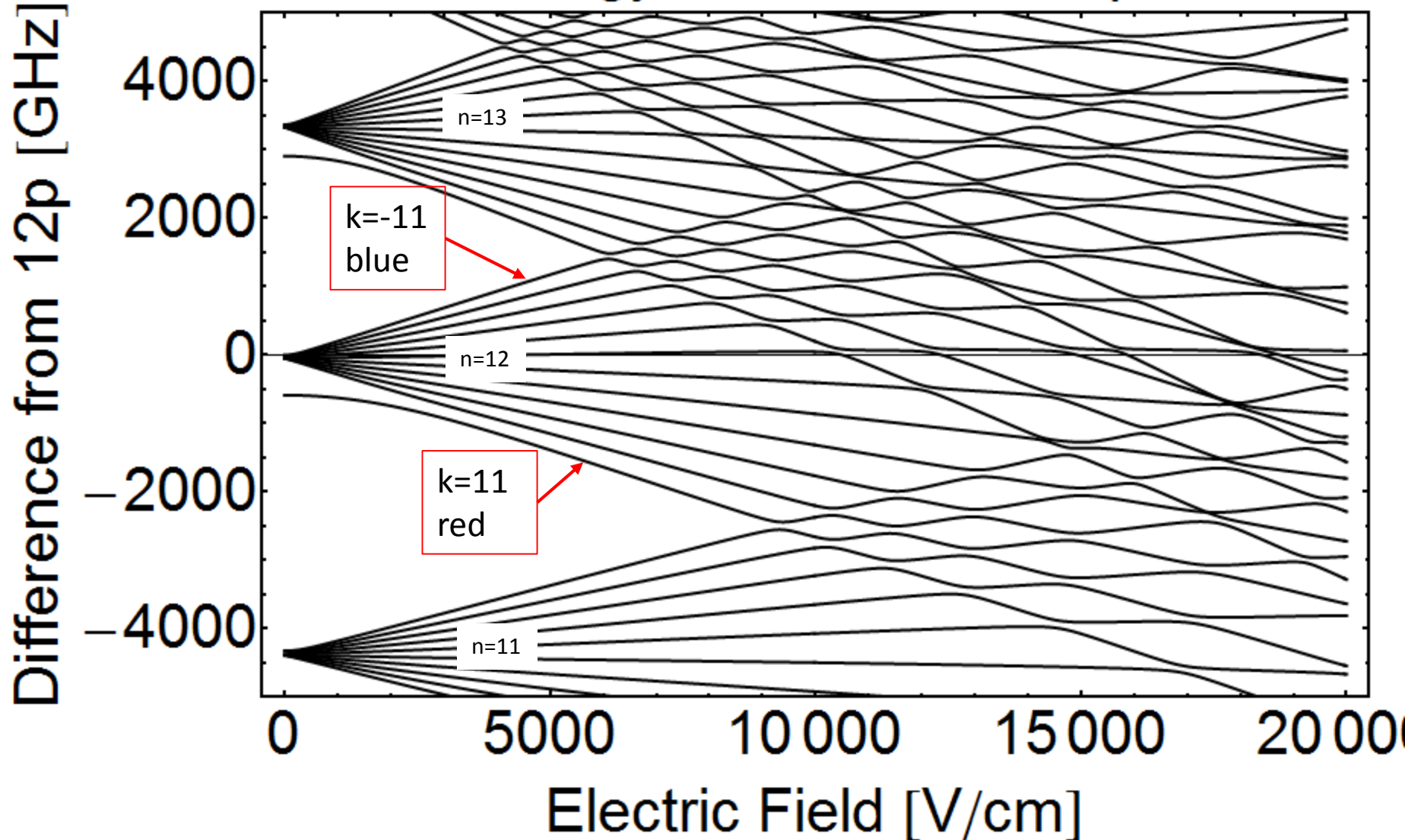
Stark Map Helium

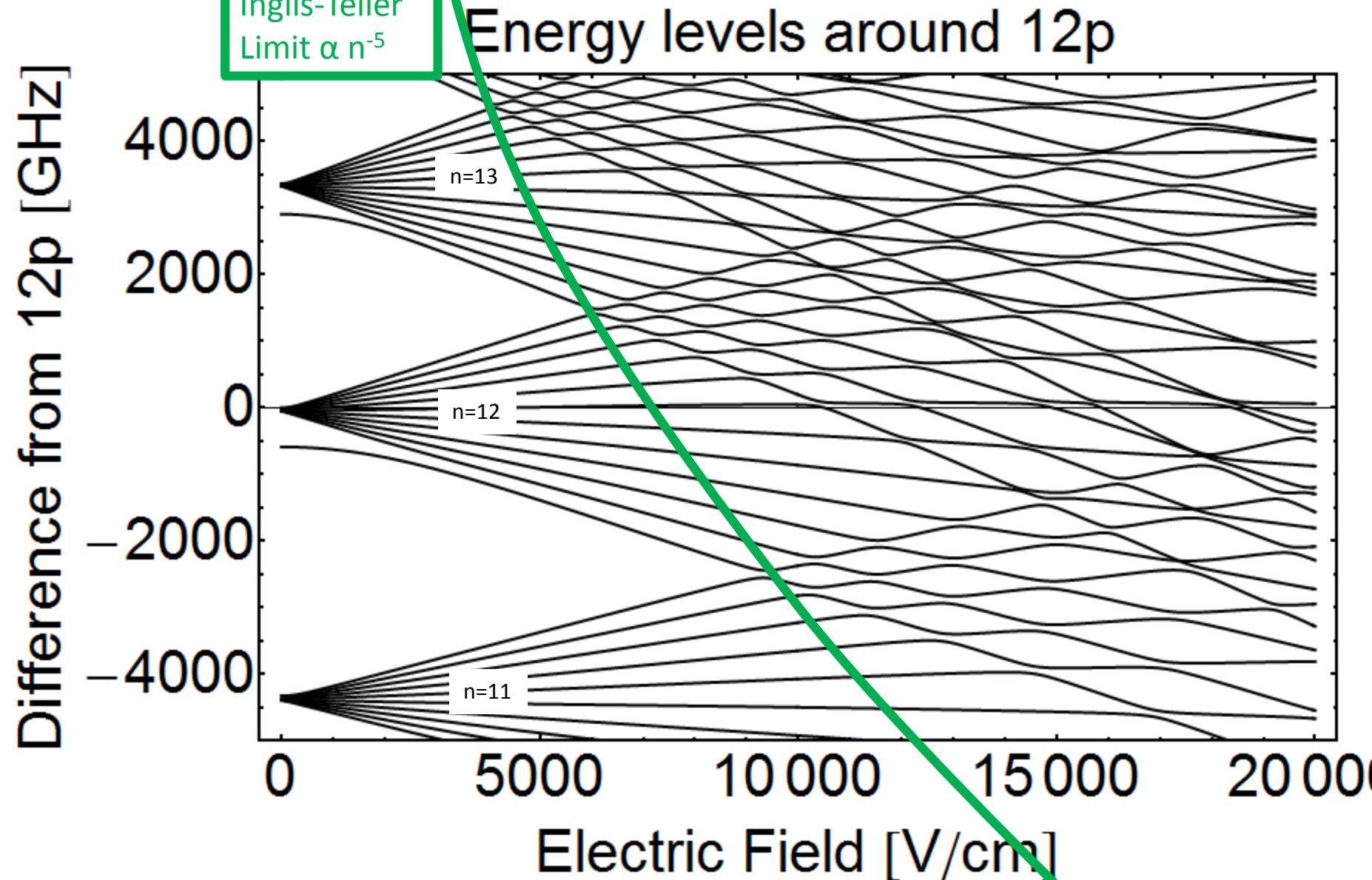
Energy levels around 12p



Stark Map Helium

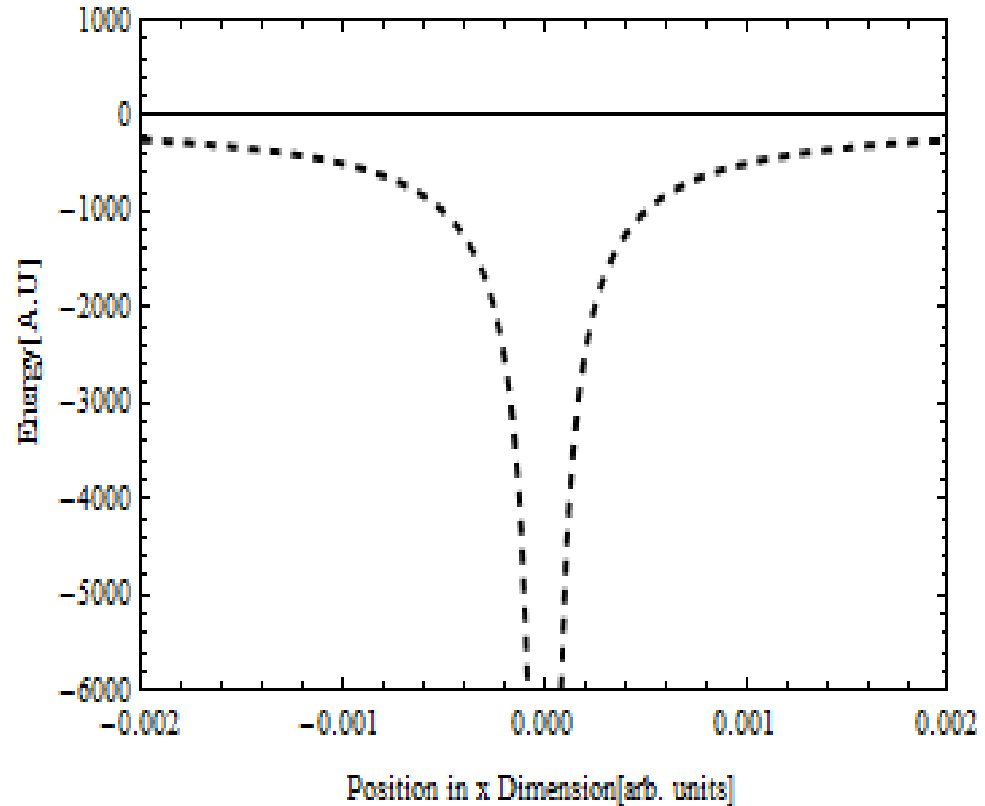
Energy levels around 12p





Rydberg Atom in an electric Field

- When do Rydberg atoms ionize?
 - No field applied



$W = -\frac{1}{2(n-\delta_l)^2}$	$\frac{dW}{dn} = \frac{1}{(n-\delta_l)^3}$	$\langle \vec{d} \rangle \approx a_0 n^2$	$\sigma \propto n^4$	$F_{IT} \propto n^{-5}$
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Rydberg Atom in an electric Field

- When do Rydberg atoms ionize?

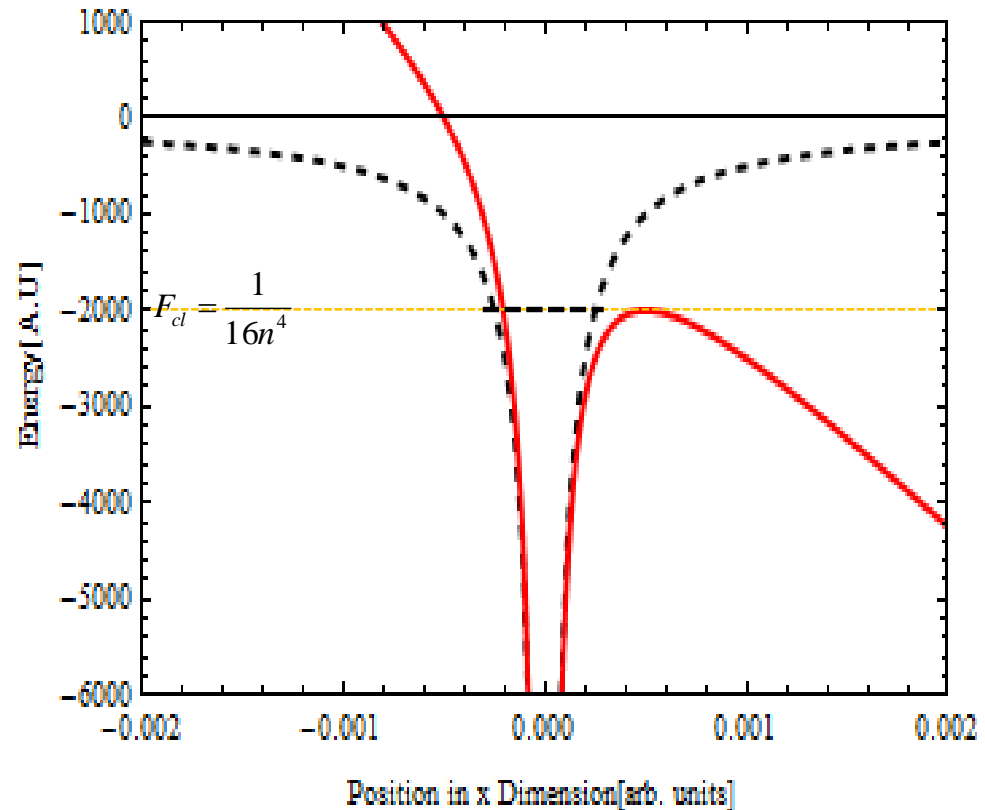
- No field applied
- Electric Field applied
- Classical ionization:

$$V = -\frac{1}{r} + Fz$$

$$\Rightarrow F_{cl} = \frac{W^2}{4} = \frac{1}{16n^4}$$

- Valid only for

- Non-H atoms if F is increased slowly



$W = -\frac{1}{2(n-\delta_l)^2}$	$\frac{dW}{dn} = \frac{1}{(n-\delta_l)^3}$	$\langle \vec{d} \rangle \approx a_0 n^2$	$\sigma \propto n^4$	$F_{IT} \propto n^{-5}$
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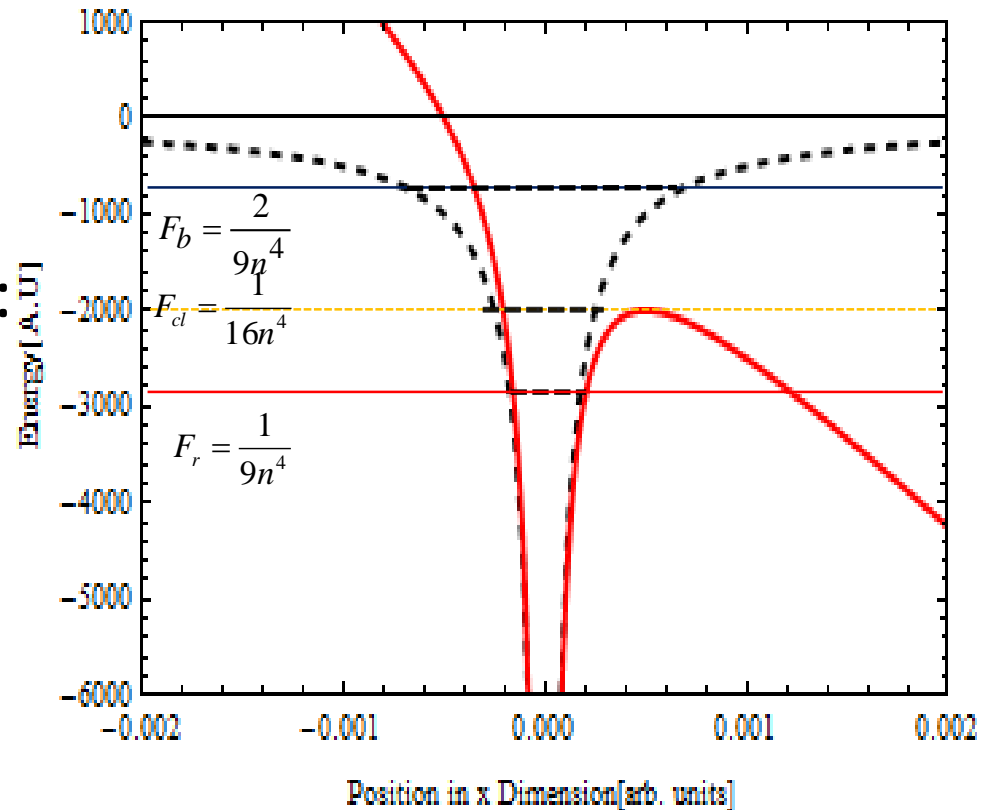
(Hydrogen) Atom in an electric Field

- When do Rydberg atoms ionize?

- No field applied
- Electric Field applied
- Quasi-Classical ioniz.:

$$V(\eta) = 2 \left(-\frac{Z_2}{\eta} + \frac{m^2 - 1}{4\eta^2} - \frac{F\eta}{4} \right)$$

$$\Rightarrow F = \frac{W^2}{4Z_2}$$



$W = -\frac{1}{2(n-\delta_l)^2}$	$\frac{dW}{dn} = \frac{1}{(n-\delta_l)^3}$	$\langle \vec{d} \rangle \approx a_0 n^2$	$\sigma \propto n^4$	$F_{IT} \propto n^{-5}$	$F_{cl} \propto \frac{1}{16} n^{-4}$
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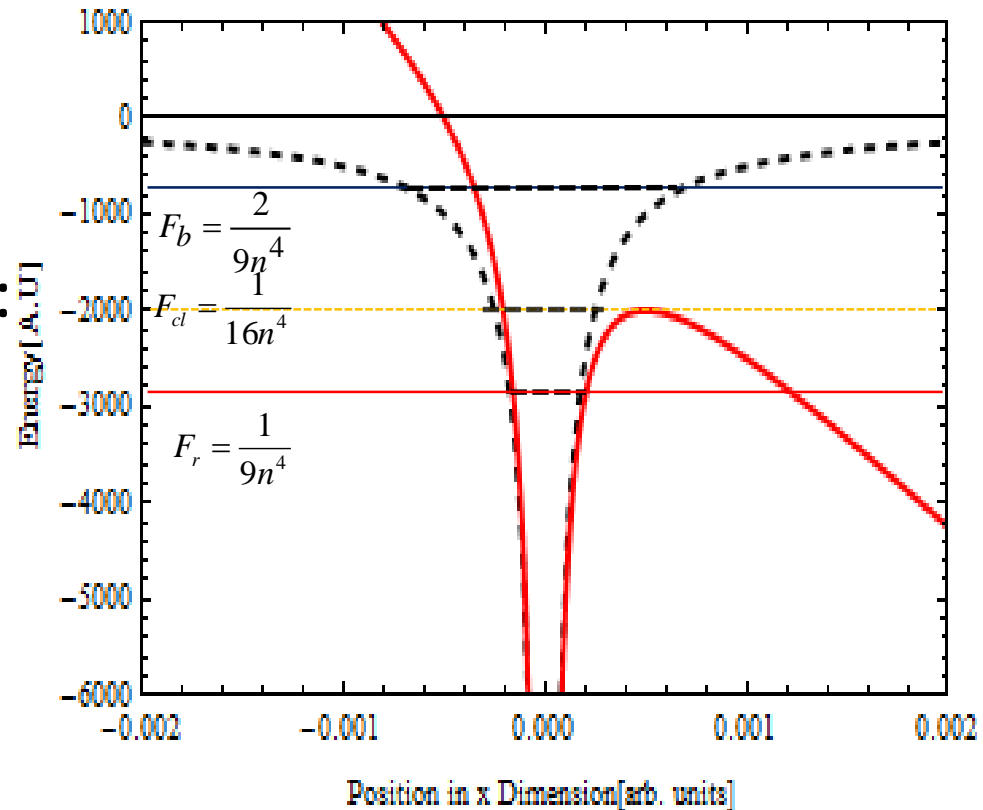
(Hydrogen) Atom in an electric Field

- When do Rydberg atoms ionize?

- No field applied
- Electric Field applied
- Quasi-Classical ioniz.:

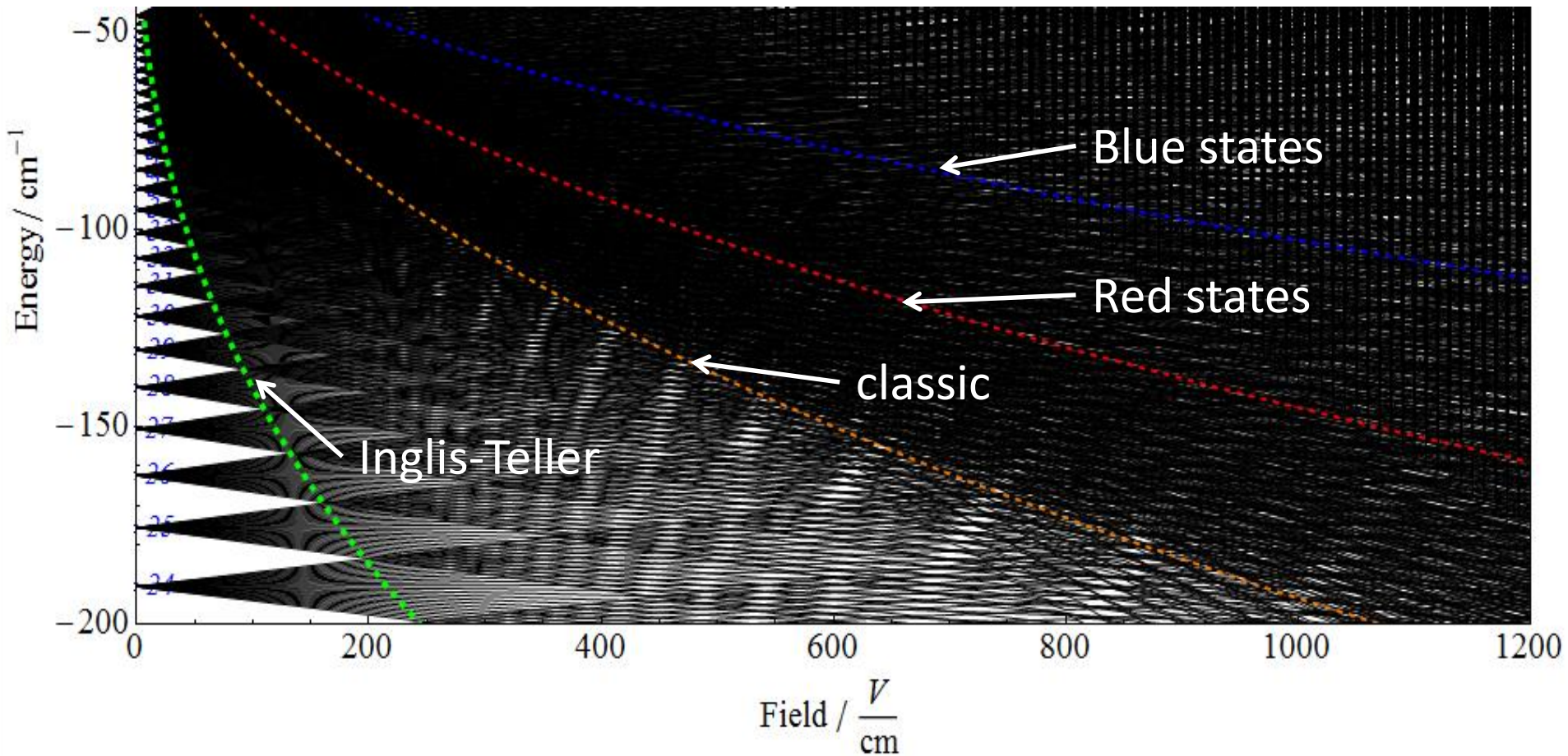
$$V(\eta) = 2 \left(-\frac{Z_2}{\eta} + \frac{m^2 - 1}{4\eta^2} - \frac{F\eta}{4} \right)$$

$$\Rightarrow F = \frac{W^2}{4Z_2} \begin{cases} = \frac{1}{9n^4} & \text{red} \\ \approx \frac{2}{9n^4} & \text{blue} \end{cases}$$



$W = -\frac{1}{2(n-\delta_l)^2}$	$\frac{dW}{dn} = \frac{1}{(n-\delta_l)^3}$	$\langle \vec{d} \rangle \approx a_0 n^2$	$\sigma \propto n^4$	$F_{IT} \propto n^{-5}$	$F_{cl} \propto \frac{1}{16} n^{-4}$
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(Hydrogen) Atom in an electric Field



Lifetime

- From Fermis golden rule

- Einstein A coefficient for two states $n, l \rightarrow n', l'$

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

- Lifetime $\tau_{n,l} = \left(\sum_{n',l' < n,l} A_{n',l',n,l} \right)^{-1}$

$W = -\frac{1}{2(n-\delta_l)^2}$	$\frac{dW}{dn} = \frac{1}{(n-\delta_l)^3}$	$\langle \vec{d} \rangle \approx a_0 n^2$	$\sigma \propto n^4$	$F_{IT} \propto n^{-5}$	$F_{cl} \propto \frac{1}{16} n^{-4}$
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- Lifetime $\tau_{n,l} = \left(\sum_{n',l' < n,l} A_{n',l',n,l} \right)^{-1}$

For $l \approx 0$: $\propto n^{-3/2}$
Overlap of WF

For $l \approx 0$:
Constant (dominated
by decay to GS)

$W = -\frac{1}{2(n-\delta_l)^2}$	$\frac{dW}{dn} = \frac{1}{(n-\delta_l)^3}$	$\langle \vec{d} \rangle \approx a_0 n^2$	$\sigma \propto n^4$	$F_{IT} \propto n^{-5}$	$F_{cl} \propto \frac{1}{16} n^{-4}$	$\tau_{n,0} \propto n^3$
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Lifetime

- From Fermis golden rule

- Einstein A coefficient for two states $n, l \rightarrow n', l'$

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

- Lifetime $\tau_{n,l} = \left(\sum_{n',l' < n,l} A_{n',l',n,l} \right)^{-1}$

For $l \approx n: \propto n^2$
Overlap of WF

For $l \approx n: \propto n^{-3}$
Overlap of WF

$W = -\frac{1}{2(n-\delta_l)^2}$	$\frac{dW}{dn} = \frac{1}{(n-\delta_l)^3}$	$\langle \vec{d} \rangle \approx a_0 n^2$	$\sigma \propto n^4$	$F_{IT} \propto n^{-5}$	$F_{cl} \propto \frac{1}{16} n^{-4}$	$\tau_{n,l} \propto n^3, n^5$
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Lifetime

$$A_{n',l',n,l} = \frac{4e^2 \omega_{n',l',n,l}^3}{3\hbar c^3} \frac{\max(l,l')}{2l+1} \left| \langle n'l' | r | nl \rangle \right|^2 \quad \tau_{n,l} = \left(\sum_{n',l' < n,l} A_{n',l',n,l} \right)^{-1}$$

State	Stark State 60 p (n',l') small	Circular state 60 l=59 m=59 (n',l') ≈ (n±1, l±1)	Statistical mixture
Scaling	n^3 (overlap of $\psi \propto n^{-3/2}$)	n^5 $\langle r \rangle \propto n^2$	$n^{4.5}$
Lifetime	7.2 μs	70 ms	≈ms

$W = -\frac{1}{2(n-\delta_l)^2}$	$\frac{dW}{dn} = \frac{1}{(n-\delta_l)^3}$	$\langle \vec{d} \rangle \approx a_0 n^2$	$\sigma \propto n^4$	$F_{IT} \propto n^{-5}$	$F_{cl} \propto \frac{1}{16} n^{-4}$	$\tau_{n,l} \propto n^3, n^5$
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