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:
  ![Hydrogen line spectrum: Balmer series](image)
  \[ \lambda = \frac{bn^2}{n^2 - 4} \]
  - 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:

\[ E = E_\infty - \frac{n \hbar \text{Ry}}{(n - \delta_l)^2} \]

\[ E_\infty = 13.6 \, \text{eV} \]

Hydrogen
Quantum Defect?

- Energy follows Rydberg formula:

\[ E = E_\infty - \frac{h \text{Ry}}{(n - \delta_l)^2} \]

Quantum Defect

Energy

Hydrogen

n-Hydrogen

0

Energy
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

\[ V(r) = -\frac{1}{r} + V_{\text{core}}(r) \]

\[ V(r) \approx -\frac{1}{r} \]

\[ r = r_0 \text{ ion core} \]

Interesting Region
For Rydberg Atoms
(Helium) Energy Structure

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

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

Excentric orbits penetrate into core.
Large deviation from Coulomb.
Large phase shift \( \rightarrow \) large quantum defect
(Helium) Energy Structure

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

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

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

Diagram showing energy levels for different $l$ values, with transitions indicated for $l=0$, $l=1$, and $l>3$ (hydrogenic).
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
  – \( \langle \Psi_f | \vec{d} | \Psi_i \rangle \propto \langle r | l \pm 1 | \cos(\theta) | l \rangle \propto n^2 \)
• Cross Section: \( \sigma \propto \langle r \rangle^2 \propto n^4 \)

\[
W = -\frac{1}{2(n - \delta_i)^2} \quad \frac{dW}{dn} = -\frac{1}{(n - \delta_i)^3}
\]
Stark Effect \[ H\Psi = \left( H_0 + \vec{d}\vec{F} \right)\Psi = E\Psi \]

• 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

\[
W = -\frac{1}{2(n-\delta_l)^2} \quad \frac{dW}{dn} = \frac{1}{(n-\delta_l)^3} \quad \langle \vec{d} \rangle \approx a_0 n^2 \quad \sigma \propto n^4
\]
Cross perfect Runge-Lenz vector conserved

Levels degenerate

Stark Map Hydrogen

Energy levels around 12p
Hydrogen Atom in an electric Field

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

• Energy-Field dependence: Perturbation-Theory

\[
W = -\frac{1}{2n^2} - \frac{3}{2} F(n_1 - n_2) n + \frac{F}{16} n^4 \left(17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19\right) + O(n^5)
\]
Levels not degenerate

Do not cross!
No coulomb-potential

s-type
Stark Map Helium

Energy levels around 12p

Difference from 12p [GHz] vs Electric Field [V/cm]

-4000 0 2000 4000

n=13

k=-11 blue

n=12

k=11 red

n=11
Energy levels around 12p

Inglis-Teller Limit $\alpha n^5$
Rydberg Atom in an electric Field

• When do Rydberg atoms ionize?
  – No field applied

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

• When do Rydberg atoms ionize?
  – No field applied
  – Electric Field applied
  – Classical ionization:
    \[ V = -\frac{1}{r} + F_z \]
    \[ \Rightarrow F_{cl} = \frac{W^2}{4} = \frac{1}{16n^4} \]
  – Valid only for
    • Non-H atoms if F is Increased slowly

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

• When do Rydberg atoms ionize?
  – No field applied
  – Electric Field applied
  – Quasi-Classical ioniz.:

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

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

\[ W = -\frac{1}{2(n-\delta_f)^2} \quad \frac{dW}{dn} = \frac{1}{(n-\delta_f)^3} \quad \langle \vec{d} \rangle \approx a_0n^2 \quad \sigma \propto n^4 \quad F_{IT} \propto n^{-5} \quad F_{cl} \propto \frac{1}{16} n^{-4} \]
(Hydrogen) Atom in an electric Field

• When do Rydberg atoms ionize?
  – No field applied
  – Electric Field applied
  – Quasi-Classical ioniz.:

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

\[
\implies F = \frac{W^2}{4Z_2} \approx \frac{1}{9n^4}
\]

\[
F_b = \frac{2}{9n^4}
\]

\[
F_c = \frac{1}{16n^4}
\]

\[
F_r = \frac{1}{9n^4}
\]

\[
\left\langle \tilde{d}\right\rangle \approx a_0 n^2
\]

\[
\sigma \propto n^4
\]

\[
F_{IT} \propto n^{-5}
\]

\[
F_{cl} \propto \frac{1}{16n^4}
\]
(Hydrogen) Atom in an electric Field

- Blue states
- Red states
- Classic
- Inglis-Teller

Energy/cm$^{-1}$ vs Field / V/cm
Lifetime

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

- From Fermi's golden rule
  - Einstein A coefficient for two states $n, l \rightarrow n', l'$
    
    $$A_{n', l', n, l} = \frac{4e^2 \omega_{n', l', n, l}^3}{3\hbar c^3} \frac{\max(l, l')}{2l + 1} |\langle n'l'|r|nl\rangle|^2$$

- 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)

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

- From Fermi's golden rule
  - Einstein A coefficient for two states $n, l \rightarrow n', l'$
    
    $$A_{n', l', n, l} = \frac{4e^2 \omega_{n', l', n, l}^3}{3\hbar c^3} \frac{\max(l, l')}{2l + 1} |\langle n'l' | r | nl \rangle|^2$$

- 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

---

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

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

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

<table>
<thead>
<tr>
<th>State</th>
<th>Stark State ( (n',l') ) small</th>
<th>Circular state ( (n',l') \approx (n \pm 1, l \pm 1) )</th>
<th>Statistical mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scaling</td>
<td>( n^3 ) (overlap of ( \psi \propto n^{-3/2} ))</td>
<td>( n^5 ) ( \langle r \rangle \propto n^2 )</td>
<td>( n^{4.5} )</td>
</tr>
<tr>
<td>Lifetime</td>
<td>7.2 ( \mu \text{s} )</td>
<td>70 ms</td>
<td>( \approx \text{ms} )</td>
</tr>
</tbody>
</table>

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