

A Rydberg atom can be any atom. The (only) condition is that one electron is excited to a high principal quantum number n . This is equivalent to an atom with exaggerated properties, as we will see later.

The energy of a Rydberg atom state (n, l, m) for the field free situation (no external fields) is given by

$$E_{n\ell m} = E_{0\ell} - \frac{hRy}{(n-\delta_\ell)^2}$$

with $E_{0\ell}$ the ionization energy of the corresponding l -levels and $Ry = 10973731.568508 \text{ m}^{-1}$ the Rydberg constant and δ_ℓ the quantum defect.

The equation was generalised from empirically found equations, describing for $(\delta_\ell = 0)$ by Johannes Rydberg

the absorption wavelengths of H, e.g. Balmer (1875): $\lambda = \frac{6n^2}{n^2-4}$

For Hydrogen all the l -states are degenerated and they have no quantum defect $\delta_\ell = 0 \forall l \in \{0, \dots, n-1\}$.

Obv. $E_{00} = 0$ results in the well known Energy for the Hydrogen atom:

$$E_{n(lm)}^H = -\frac{E_{RY}}{n^2}, \quad E_{RY} \approx 13.6 \text{ eV} \quad (1)$$

non-H For all other atoms $\delta_\ell \neq 0$ and $\forall l \in \{0, \dots, n-1\}$ and $\delta_\ell \neq \delta_{\ell'}$ and also $E_{0\ell} \neq E_{0\ell'}$

This is due to the effect of the core electrons, as we will see later. For examples (plot) of these spectra see Slide of presentation.

2. Exaggerated properties of Rydberg atoms

Rydberg atom properties are determined mainly by the electron far away from the core. In the following we will derive (motivate) the following scaling laws of atomic properties that will scale with n .

E_{∞} in atomic units:

- electron mass: $m_e = 9.1 \cdot 10^{-31} \text{ kg}$ length: a_0 Bohr radius: $= 0.529 \text{ \AA}$
- charge: $e = 1.6 \cdot 10^{-19} \text{ C}$ Velocity (of first Bohr orbit): $= 2.19 \cdot 10^8 \text{ cm/s}$
- Energy: $2E_H = 27.2 \text{ eV}$ Electric field (of first orbit): $= 5.14 \cdot 10^9 \text{ V/cm}$

The Rydberg properties:

- Energy levels: $W = -\frac{Ry}{2(n-\delta_\ell)^2} \propto \frac{1}{n^2}$ Ionization field: $F_I \propto n^4$
- Trans. frequencies: $\frac{dW}{dn} \propto \frac{1}{n^3}$ Lifetimes $\tau_{\text{theo}} \propto n^3$
- Dipole moments: $\langle \vec{r} \rangle \propto n^2$ (transition) $\langle \vec{d} \rangle \propto n^2$ (electric) $\tau_{\text{ex-m}} \propto n^5$

and others ...

Literature: Gallegher: Rydberg atoms (book)

(a) Energy (m_p, m_e, n, l, m)
 We consider a Rydberg atom and an electron orbiting



central potential $V(r) = V(r)$

The Schrödinger equation is: $(-\frac{\nabla^2}{2} - V(r))\psi = E\psi$

Separation of variables $\psi = R(r)\Theta(\vartheta)\Phi(\varphi)$ results in

on angular part: $\frac{1}{\sin\vartheta} \partial_{\vartheta}(\sin\vartheta \partial_{\vartheta}) + \frac{1}{\sin^2\vartheta} \partial_{\varphi}^2 \chi_{lm}(\vartheta, \varphi) = -\frac{l(l+1)}{2} \chi_{lm}$

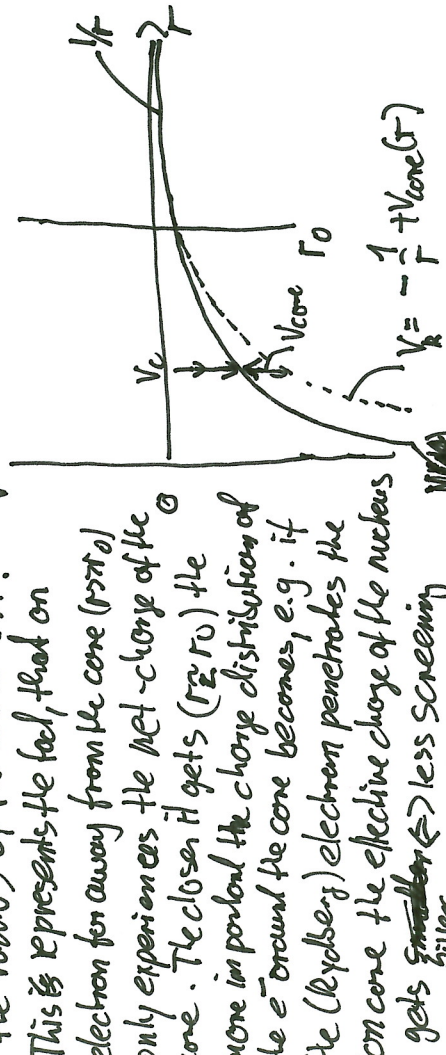
with the solution $\chi_{lm}(\vartheta, \varphi) = \frac{(l-m)!}{(l+m)!} \frac{1}{\sqrt{4\pi}} P_m^l(\cos\vartheta) e^{im\varphi}$

which is the same for all atoms, since the potential only depends on r

- a radial part: $\partial_r^2 + [2E - 2V(r) - \frac{l(l+1)}{r^2}] R = 0$ (2)

The solutions to this problem are determined by the potential V . We consider a potential that is Coulomb-like

for big radii $r > r_0$ and unknown for $r \leq r_0$, where r_0 is the radius of the ion core A^+ .



This represents the fact, that an electron far away from the core (with r_0) only experiences the net-charge of the core. The closer it gets ($r \approx r_0$) the more it penetrates the charge distribution of the e^- around the core becomes, e.g. if the (Rydberg) electron penetrates the ion core the effective charge of the nucleus gets smaller \Leftrightarrow less screening

A Rydberg atom spends most of its time far away from the core (\Rightarrow) its probability distribution is centered far away and is thus only affected by the core, if it has a non-vanishing $\langle l(r) \rangle$ for $r \leq r_0$. This is true for the low l -states (s, p, d, ...).
 which means that we would find an eccentric "Kepler-like orbit" for the low l -states and almost a circular one for the high l -states if we solve the time-dependent Schrödinger equation.

The solutions for (2) are $\begin{cases} f: \text{regular Coulomb function } \propto r^{l+1} \\ g: \text{irregular Coulomb function } \propto r^{-l-1} \end{cases}$
 Since it is a second order diff. equation they are not linearly dependent.

$W > 0$: for an unbound electron scattering (off the ion-core) the solutions are (of course!) oscillatory $\sim \sin(\frac{2\pi r}{k})$

$f = (\frac{2}{k\pi})^{1/2} \sin(kr - \pi l/2 + \frac{1}{k} \ln(2kr) + \sigma_l)$

$g = -(\frac{2}{k\pi})^{1/2} \cos(kr - \pi l/2 + \frac{1}{k} \ln(2kr) + \sigma_l)$

with $k = \sqrt{2W}$, $\sigma_l = \arg(\Gamma(l + i\sqrt{2W}))$ the Coulomb phase by assumption: $V(r) = -\frac{1}{r}$

Therefore we know (from the structure of the equation and in analogy to the hydrogen atom) that we can parameterize our energy of bound states as $W = -\frac{1}{2n^2}$ with an a-priori undetermined quantum number $\tilde{n}(W, l)$.

Now we rewrite f, g in terms of the (linearly independent) set of increasing (u) and decreasing (v) exponential functions as a normalized superposition.

$f = u(\tilde{n}, l, r) \sin(\pi \tilde{n}) - v(\tilde{n}, l, r) e^{\pi i \tilde{n}}$
 $g = -u(\tilde{n}, l, r) \cos(\pi \tilde{n}) - v(\tilde{n}, l, r) e^{\pi i (\tilde{n} + 1/2)}$ with $u \rightarrow \infty (r \rightarrow \infty)$ and $v \rightarrow 0 (r \rightarrow \infty)$

We obtain the energy of the system now through straight-forward application of boundary conditions for $S(r) = a + b \cdot g$

- Hydrogen: 1) $\psi < \infty$ ($r \rightarrow 0$)
 2) $\psi = 0$ ($r \rightarrow \infty$)

Since, as we have seen before, $g \propto r^{-l}$ ($r \rightarrow \infty$) $\Rightarrow b = 0$ which means we are left with the regular Coulomb function f !

$$f = u(\vec{n}, \varphi, r) \sin(\pi \vec{n}) - v(\vec{n}, \varphi, r) e^{-\pi \vec{n}}$$

Application of the second boundary condition results in

$$\sin(\pi \vec{n}) = 0 \quad \forall \vec{n} \Rightarrow \vec{n} \in \mathcal{N} \Rightarrow \vec{n} = n$$

and we obtain $W = -\frac{1}{2n^2}$, $n \in \mathcal{N}$, the well known result!

- Non-H: 1) $\psi = 0$ ($r \rightarrow \infty$) clean $e^{-Hydrogen}$
 2) $r > r_0$: ψ_{NH} shifted in phase w.r.t. ψ_H

To 2) since for $r > r_0$ we are in a Coulomb potential there cannot be other solutions to the Schrödinger Equations. This can also be seen in the fact that the number of nodes in the wavefunction needs to be conserved for a given energy \Rightarrow the Coulomb potential can only "stretch" the wavefunction for $r > r_0$.

This means: phase shift

$$2) \Rightarrow \psi_{NH} = f \cos(\varphi) - g \sin(\varphi) \quad (\text{a,b parametrized by phase shift})$$

$$\Rightarrow \cos(\varphi) \sin(\pi \vec{n}) + g \sin(\varphi) \cos(\pi \vec{n}) = 0$$

$$\Leftrightarrow \pi \vec{n} + \varphi = n\pi \Rightarrow \vec{n} = (n - \frac{\varphi}{\pi}) = n - \delta_e$$

and we obtain $W = -\frac{1}{2\vec{n}^2} = -\frac{1}{2(n - \delta_e)^2}$

This means that the quantum defect δ_e is exp. the phase shift w.r.t. to the Hydrogen that an electron experiences when it enters the ion core (gets close to the nucleus). Akin to the dynamics deviate from a perturbed $1/r$ -potential! This small effect at the ion core is only big for trajectories that pass by the core (excited trajectories) namely for the ones with low quantum number l or small centrifugal force. Nonetheless it can have big influences on other effects, e.g. the Stark effect; since the Runge-Lenz-vector is not conserved in a potential other than $1/r \propto r^{-1}$! This leads to an effective interaction of the states!

We determined now the first scaling law $W \propto -\frac{1}{2(n - \delta_e)^2}$

The difference in two (consecutive) states of same l but different n follows trivially $\frac{dW}{dn} \propto \frac{1}{n^3} + O(n^{-5})$

3) Dipole Moment

The electron spends most of the time separated from the core which results in a big dipole $\vec{d} = e\vec{r}$ that aligns with the external electric field.

Since the electron is loosely bound it a dipole is also induced which is characterized by the polarizability α .

The expectation value of $\langle \vec{d} \rangle = e \langle \vec{r} \rangle$

which means that $\langle \vec{r} \rangle \propto \langle r \rangle \langle \cos \vartheta \rangle \propto n^2$ independent of n , couples neighbours e -states

\Rightarrow First order Stark shift $E = E_0 + \langle \vec{d} | \vec{E} | \vec{d} \rangle$

We can derive further properties from the scaling of $\langle n, l, m | \vec{r} | n, l, m \rangle$ e.g. $\langle r \rangle \sim \sum_{n', l', m'} \langle n', l', m' | \vec{r} | n, l, m \rangle / \Delta E_{n', l', m'}$

(4) External electric fields

External electric fields are the best way to manipulate Rydberg atoms (DC or AC) because of their large dipole moment.

For an "exact" solution one needs to diagonalize the Stark Hamiltonian:

$$H_S = H_0 + \vec{d} \cdot \vec{F}$$

H_0 : unperturbed atomic Hamiltonian
 \vec{d} : Dipole moment
 \vec{F} : electric field

(3)

The best way is to simply diagonalize the matrix

$$\langle \psi_f | H_S | \psi_i \rangle = \langle \psi_f | H_0 | \psi_i \rangle + \langle \psi_f | \vec{d} | \psi_i \rangle \cdot \vec{F}$$

$$\langle \psi_f | H_0 | \psi_i \rangle = \begin{cases} W = \frac{1}{2pr_{fe}} & \text{for } f=i \\ 0 & \text{otherwise} \end{cases}$$

Therefore we label states now according to their l, m field-free situation $|\psi\rangle = |W, l, m\rangle$

The part we still have to determine is $\langle W, l, m | F_z | W', l', m' \rangle$ since F_z is on quantization axis and $d = ez$:

$$\langle W, l, m | F_z | W', l', m' \rangle = \delta_{l, m} \delta_{l', m'} F \langle l, m | \cos \theta | l', m' \rangle = \left(\frac{l^2 - m^2}{2l(l-1)} \right)^{1/2}$$

$$\langle l, m | \cos \theta | l-1, m \rangle = \left(\frac{l^2 - m^2}{(2l-1)(2l+1)} \right)^{1/2}$$

For the radial part $\langle W, l | r | W', l' \rangle$ we have to integrate the radial function. This can be done using Numerov's algorithm, which solves equations from the form $\frac{d^2 X}{dx^2} + q(x)X = 0$ by integration from $x(r) = \infty$.

The radial wavefunction couples only l and $l \pm 1$ and is thus off-diagonal. The transition can be done straight forward.

Another property that can be derived from $\langle n, l, m | z | n', l', m' \rangle \propto n^2$ is the collisional cross section scaling like n^2 .

$\langle n, l, m | z | n', l', m' \rangle \propto n^4$

A strong dipole influences another dipole with its field.

Consider a pair of atoms initially in states $|n, l, m\rangle = |4, 2, 2\rangle$

The dipole interaction potential is

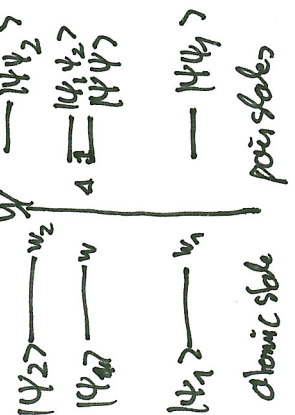
$$V(\vec{r}) = \frac{d_1 d_2}{r^3} - \frac{3(d_1 \cdot \vec{r})(d_2 \cdot \vec{r})}{r^5}$$

where $d_i, i \in \{1, 2\}$ can be seen as the transition dipole moment to states N_i :

In a two atom basis we have thus $|\psi\rangle = |4, 2, 2\rangle$ coupled to $|\psi_1\rangle = |4, 2, 2\rangle$ by $V(\vec{r})$

$\Rightarrow \mathcal{H} = \begin{pmatrix} 0 & V(\vec{r}) \\ V(\vec{r}) & 0 \end{pmatrix}$. If we restrict to the z -axis as \vec{r}

$$V(\vec{r}) \text{ becomes } \frac{d_1 d_2}{r^3} + \frac{d_1 d_2}{r^3} - \frac{2 d_1 d_2}{r^3} = \frac{d_1 d_2}{r^3}$$



and $\Delta = W_1 + W_2 - 2W$

\Rightarrow Eigenvalues of $\mathcal{H} : \lambda = \frac{\Delta \pm \sqrt{\Delta^2 + 4V(\vec{r})^2}}{2}$

atomic state

Short range scaling: $V(r) \propto \Delta \Rightarrow \lambda = \pm V(r) = \frac{C_6}{r^3} \propto n^4$

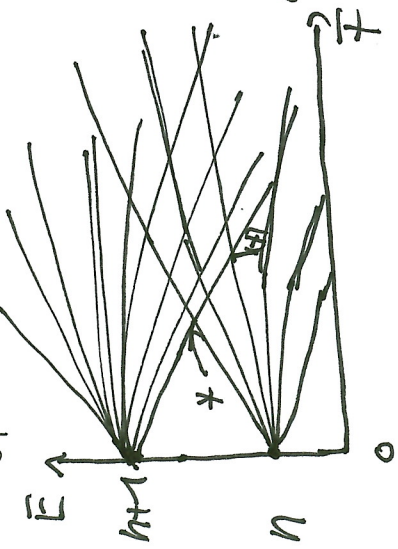
Dipole Interaction!

long range scaling: $V(r) \ll \Delta \Rightarrow \lambda = -\frac{V(r)^2}{\Delta} = -\frac{C_6^2}{r^6} \propto n^{11}$

$n^{-3} \leftarrow$ Energy shift

The transition between the two limits is at $\Delta \approx V(r) \Rightarrow r = \sqrt[6]{\frac{C_6}{\Delta}} \propto n^{7/3}$

v.1 Stark manifolds
From the diagonalization of the Hamiltonian (3) give the following Energy levels for Hydrogen.



We observe:
a) at $F=0$ all the manifolds are degenerate
b) Energies split into n (for manifolds) differential energy levels

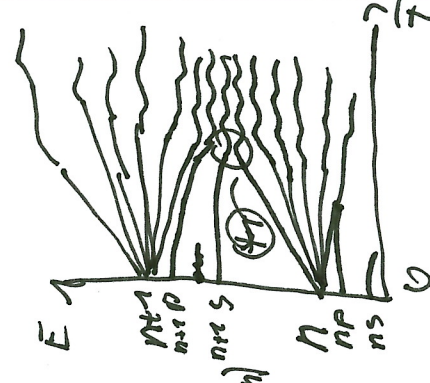
c) The 66 quantum numbers $|nlm\rangle$ are not good anymore for $F>0$, since the l -states mix strongly (due to $\langle W | l^2 | m \rangle$)

We can label the states with $k = n_2 - m_1$, where $n = n_1 + n_2 + |m| + 1$ and therefore $\langle n, n_1, n_2, m | n, l, m \rangle = \sqrt{\frac{2l+1}{2n}} \langle l, m | P_m(z) | l, m \rangle$, $2n_1 - 1 = (n_1 + \frac{|m|+1}{2})$ the states in parabolic coordinates (where the Stark Hamiltonian is separable in m).
Bsp: for $n=13$, the states are labeled $k = -12, \dots, 12$.

d) Two states from different manifolds cross perfectly! see (x)
This means, that a state will always stay in its k -state and not interact with the others! This is only true for H^2 since the electron is always in a perfect $1/r$ potential. Therefore the Runge-Lenz vector is conserved and the state d will never undergo a charge. This is equivalent to the electron moving in a perfect Kepler orbit; always!

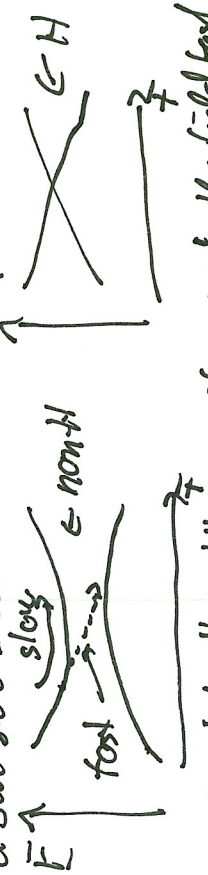
e) If we perturbatively treat the Stark Hamiltonian in the parabolic coordinates we obtain for the Energy: $W = -\frac{1}{2n^2} - \frac{3}{2} F (n_1 - n_2) n + h.v.$
 $\Rightarrow k$ labels the dipole $k > 0 \Rightarrow$ blue states \Rightarrow anti-symmetric position of dipole $k < 0 \Rightarrow$ red states \Rightarrow symmetric position of dipole

FOR NON-H atoms



The electron penetrates the core and experiences a differential $V(r) \neq -1/r$. Therefore two states $|k_1\rangle, |k_2\rangle$ interact, when their energies come close.

2 effects of this:
i) if two states cross they show an avoided crossing, if a blue state becomes a red and v.v.; see (x-1)



\Rightarrow the states "repel". Only if we ramp the field fast enough the state will maintain its blue (red) character.

2) The low l -states have a quadratic Stark effect until they join the manifold.

Before that, the electric field induces a dipole $\Rightarrow d = d(F) \Rightarrow d \propto d(F) \Rightarrow d \propto F^2$.

Stark - effect / polarization until The state will maintain longer in its l -character if mixes with the other l -states (when W is the same) and joins the manifold. In H they all mix directly \Rightarrow only l -states Stark-effect!

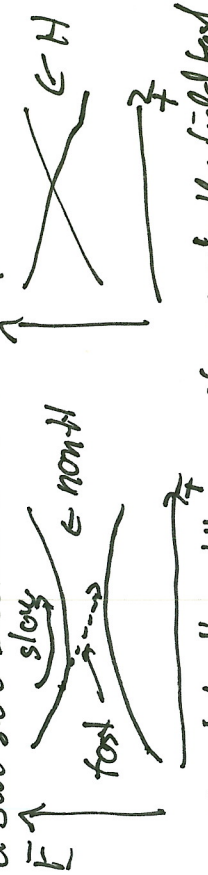
the situation is slightly changed.

- a) Due to F_e the states are not degenerate for $F=0$, although for high l ($l_e \approx 0$) almost.
- b) is similar to Hydrogen
- c) also

d) ~~Problem~~ In all atoms except for H the Runge-Lenz vector is not conserved especially for the low l -states, where the core and experiences a differential $V(r) \neq -1/r$.

Therefore two states $|k_1\rangle, |k_2\rangle$ interact, when their energies come close.

2 effects of this:
i) if two states cross they show an avoided crossing, if a blue state becomes a red and v.v.; see (x-1)



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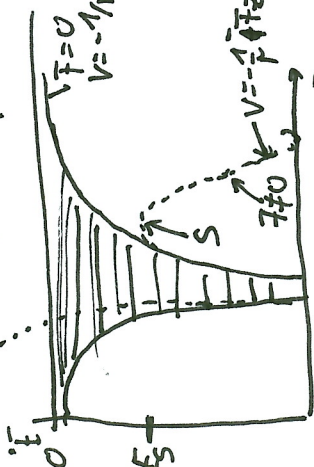
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4.2 Important electric field settings

If we apply one electric field to $V(r)$ in atom $V(r)$ $\rightarrow z, -\frac{1}{r}$ becomes $V(r) \approx -\frac{1}{r} + Fz$ along the field direction (and quantization axis).



Assume we switch on F instantaneously then all the states higher than E_S , the saddle point of the new potential, will now bound anymore. \Rightarrow they ionize.

\Rightarrow The field F for which n ionizes is called the ionization energy of the state.

To calculate it classically, we realize that the potential at

the saddle point $z_S = \frac{1}{4F}$ is $V = -2\sqrt{F}$

By definition: $V = -2\sqrt{F} \stackrel{!}{=} W \Rightarrow F_I = \frac{W^2}{4} = \frac{1}{4n^4 \cdot 4} = \frac{1}{16n^4} \propto \frac{1}{n^4}$

the classical ionization limit!

All the non-hydrogenic atoms ionize in the limit $F_I = \frac{1}{16n^4} \propto \frac{1}{(n \cdot a_0)^4}$ for $n^* \in (n \pm \frac{1}{2})$ of the close lying manifold and if the field is

switched on slowly (since then they undergo the avoided crossings) For hydrogen and if the field is switched on (infinitely fast) we have to take the Stark effect into account.

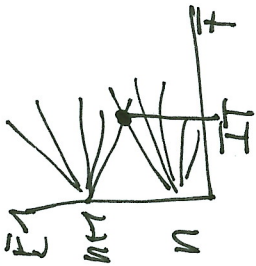
With a similar argument (but in parabolic coordinates) as above we obtain $V \rightarrow \frac{F}{4z_2} - \frac{W}{4z_2}$, where z_2 is now the reduced charge. For the extreme (red) states $z_2 \approx 1$ (\Rightarrow the whole dipole is aligned in the field)

As seen before the $W = -\frac{1}{2n^2} - \frac{3}{2}nE$ ($z_2 n$, for red) = $-\frac{1}{2n^2} - \frac{3}{2}n^2E$

This results in $F_I = \frac{1}{9n^4}$ for the red states, for the blue states $F_I = \frac{2}{9n^4}$ due since they are sitting on the other side of the potential!

There is one more lost electric field setting which is important.

Two distinct manifolds cross at the Inglis-Teller field (IT). For fields $\gg F_{IT} > F_{IT}$ we cannot distinguish the two manifolds anymore; since all states overlap



There holds: $-\frac{1}{2n^2} + \frac{3}{2}n^2F = -\frac{1}{2(n+1)^2} - \frac{3}{2}(n+1)^2F$ for the extreme states $\Rightarrow 0 = 2n-1 - 3n^4(n+1)^2F_{IT} - 3(n+1)^4n^2F_{IT}$

$$\begin{aligned} \text{above} \\ n \gg 1 \end{aligned} \Rightarrow +2n = 3n^6F_{IT} + 3n^6F_{IT} \Rightarrow n = 3n^6F_{IT} \Rightarrow F_{IT} = \frac{1}{3n^5} \propto \frac{1}{n^5}$$

5) lifetime

The lifetime of a Rydberg state $|n, \ell\rangle$ is given by $\tau_{ne} = \left(\sum_{n', \ell', L, n', \ell'} A_{n', \ell', n, \ell} \right)^{-1}$, the inverse sum over lower states of

the Einstein A coefficient $A_{n', \ell', n, \ell} = \frac{4e^2 \omega_{n', \ell', n, \ell}^3}{3\hbar c^3} \frac{\max(\ell, \ell')}{2\ell+1} |\langle n', \ell' | r | n, \ell \rangle|^2$

We see 2 possible n -dependent parts in there

where $\propto \frac{1}{n^3}$ for $\ell \approx n$ and $\langle n', \ell' | r | n, \ell \rangle \propto n^2$ for $\ell = n$

$\propto 1$ for $\ell \approx 0$ and $\langle n', \ell' | r | n, \ell \rangle \propto n^{-3/2}$ for $\ell = 0$

due to the overlap of ℓ in the core.

Therefore for $A \approx 0 \propto n^3$ (F_{IT} for $n=60$)

$\ell \approx n \propto n^9 \cdot n^{-4} = n^5!$ (70ms for $n=60$)