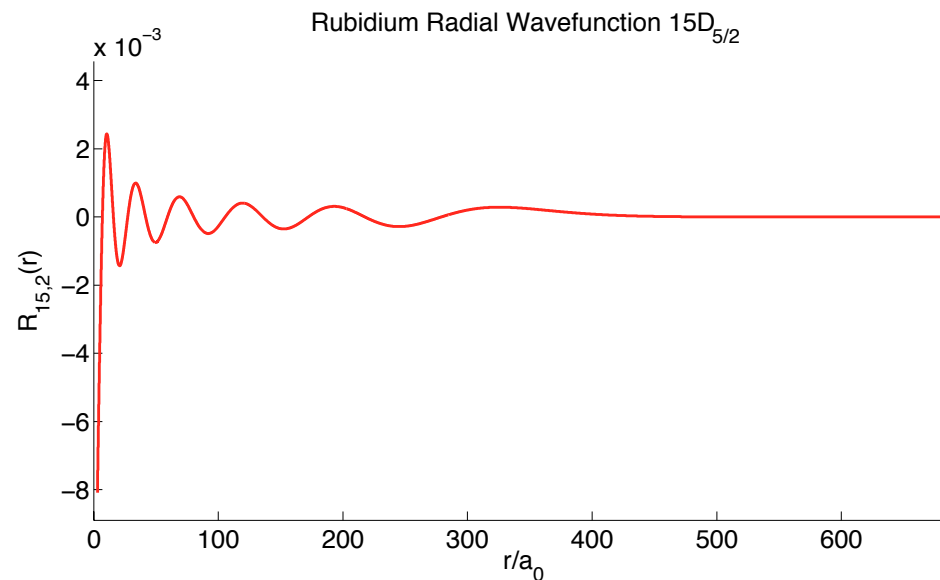


Calculation of Rydberg wavefunctions



A: Calculation of Rydberg wavefunctions:

Calculation of the Radial matrix elements needed for two reasons:

- (i) Calculation of Rubidium dipole moments and Rydberg atom interactions
- (ii) Calculation of Stark shift

B: Stark Shift Calculations

Hydrogen Schrödinger equation

$$\left[- \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{L}^2}{r^2} \right) + V(r) \right] \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$$

Angular dependence means wavefunction is separable $\Psi(r, \theta, \phi) = R(r)Y_\ell^{m_\ell}(\theta, \phi)$

Radial Schrödinger equation becomes

$$\left[- \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\ell(\ell+1)}{r^2} + V(r) \right] R(r) = E R(r)$$

Inserting Coulomb potential $V(r) = -1/r$ due to proton in core gives analytical solutions

$$R_{n\ell}(r) = 2^{\ell+1} n^{-2-\ell} \sqrt{\frac{(-1-\ell+n)!}{(\ell+n)!}} r^\ell e^{-\frac{r}{n}} L_{n-\ell-1}^{2\ell+1} \left(\frac{2r}{n} \right)$$

$$E = -\frac{1}{2n^2}$$

The Numerov equation is defined as a second order ODE of the form:

$$\frac{d^2 X}{dx^2} = g(x)X$$

To solve for X taking a linear increment in x by step size h a Taylor expansion of $X(x-h)$, $X(x+h)$ is taken and the terms kept up to $\mathcal{O}(h^6)$

If $X(x-h)$ and $X(x)$ are known, calculate $X(x+h)$ using:

$$X(x+h) = \frac{[2 + 10h^2g(x)/12] X(x) - [1 - h^2g(x-h)/12] X(x-h)}{[1 - h^2g(x+h)/12]} + \mathcal{O}(h^6)$$

If the Radial wave equations are transformed into the Numerov form we can solve radial wavefunctions numerically

Real benefit in being able to define arbitrary $g(x)$ - will work with any model potential

Two transformations used to calculate Radial wavefunctions:

(A) Square-root scaling [1]

$$x = \sqrt{r}$$

$$X(x) = Rr^{3/4}$$

$$g(x) = -8 - 8Ex^2 + \frac{(2\ell + \frac{1}{2})(2\ell + \frac{3}{2})}{x^2}$$

(B) Logarithmic scaling [2]

$$x = \ln(r)$$

$$X(x) = R\sqrt{r}$$

$$g(x) = 2e^{2x} \left(-\frac{1}{r} - E \right) + \left(\ell + \frac{1}{2} \right)^2$$

Wavefunctions integrated inwards with $h=0.01$ starting from $r_s = 2n(n+15)$

Terminate integration at larger of core radius or inner classical turning point

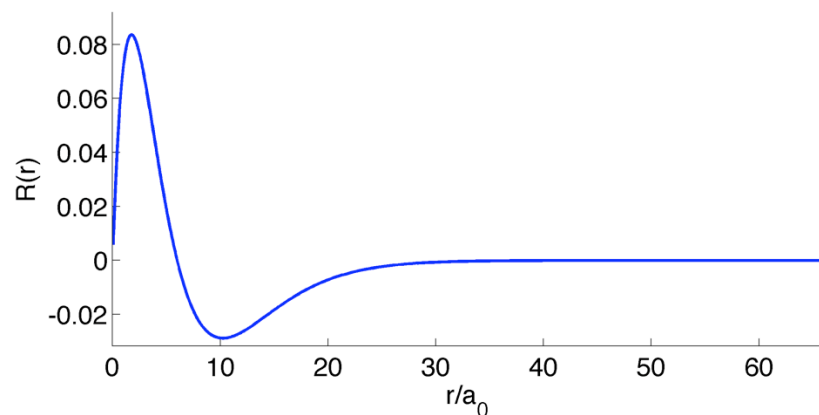
Inward integration allows exponentially decaying solution at large r without the solution becoming unstable at small r

[1] Bhatti *et al.* PRA **24** (1) 161, 1981

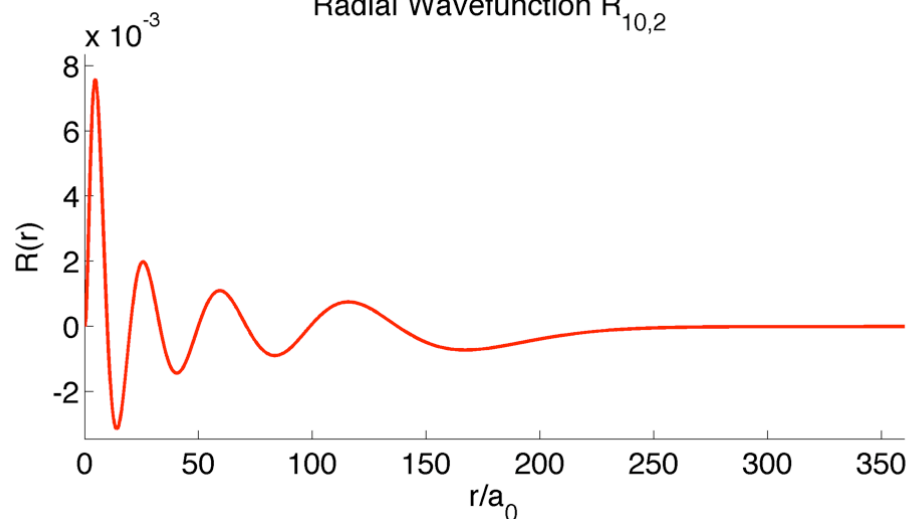
[2] Zimmerman *et al.* PRA **20** (6) 2251, 1979

Comparison of normalised Numerov solution to analytic wavefunctions

Radial Wavefunction $R_{3,1}$



Radial Wavefunction $R_{10,2}$



Both methods reproduce analytic hydrogen wavefunctions - problem going to high n as Laguerre polynomial algorithm for finding analytic solution breaks!

From the normalised wavefunctions it is possible to calculate radial matrix elements

Test numerical solution with analytic result:

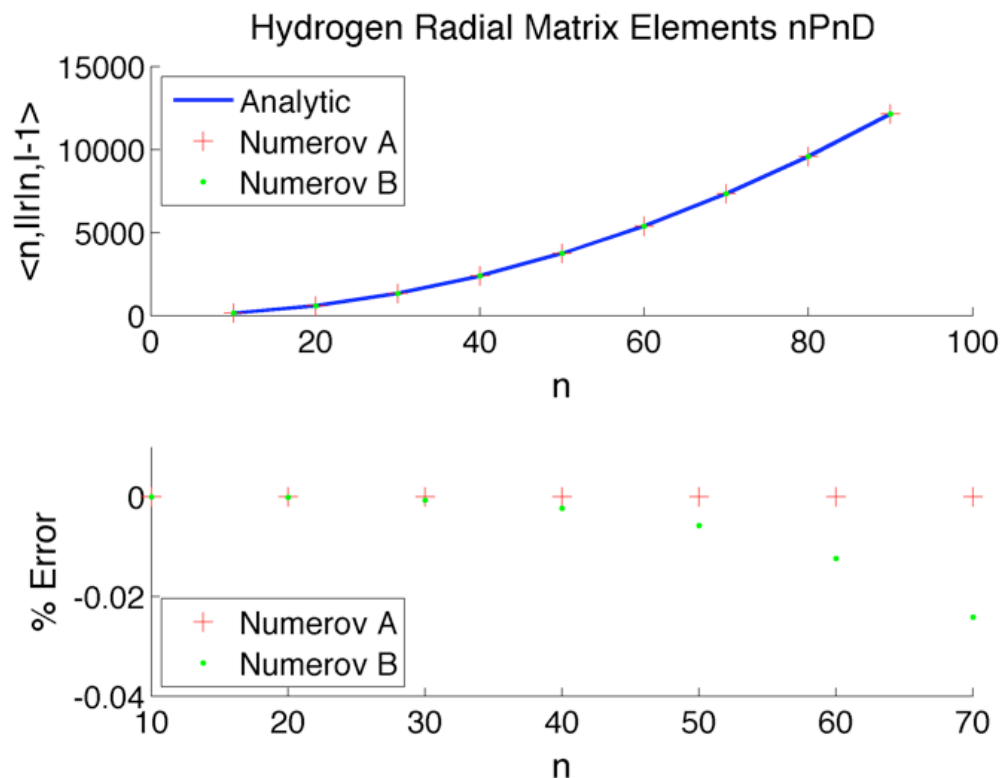
$$\langle n, \ell | r | n, \ell - 1 \rangle = \int_0^\infty R_{n,\ell}(r) r R_{n,\ell-1}(r) r^2 dr = \frac{3}{2} n \sqrt{(n^2 - \ell^2)}$$

Data shows both methods fit the observed matrix elements

Error in method B much higher

Reason is as n increases, wavefunction spreads to higher n where there is a lower point density per oscillation

Use method A



Alkali atoms different from Hydrogen due to finite core size - leads to a modified core potential and quantum defects

Far from core electron sees a Coulomb potential but for low l states need to consider core polarisation ($\sim r^{-4}$) and core penetration, where the electron sees unscreened nuclear charge

From Marinescu *et al.* [3] get model potential of form:

$$V_\ell(r) = -\frac{Z_\ell(r)}{r} - \frac{\alpha_c}{2r^4} \left[1 - e^{-(r/r_c)^6} \right]$$

where the radial charge is given by

$$Z_\ell(r) = 1 + (Z - 1)e^{-a_1 r} - r(a_3 + a_4 r)e^{-a_2 r}$$

In addition need to add fine structure potential

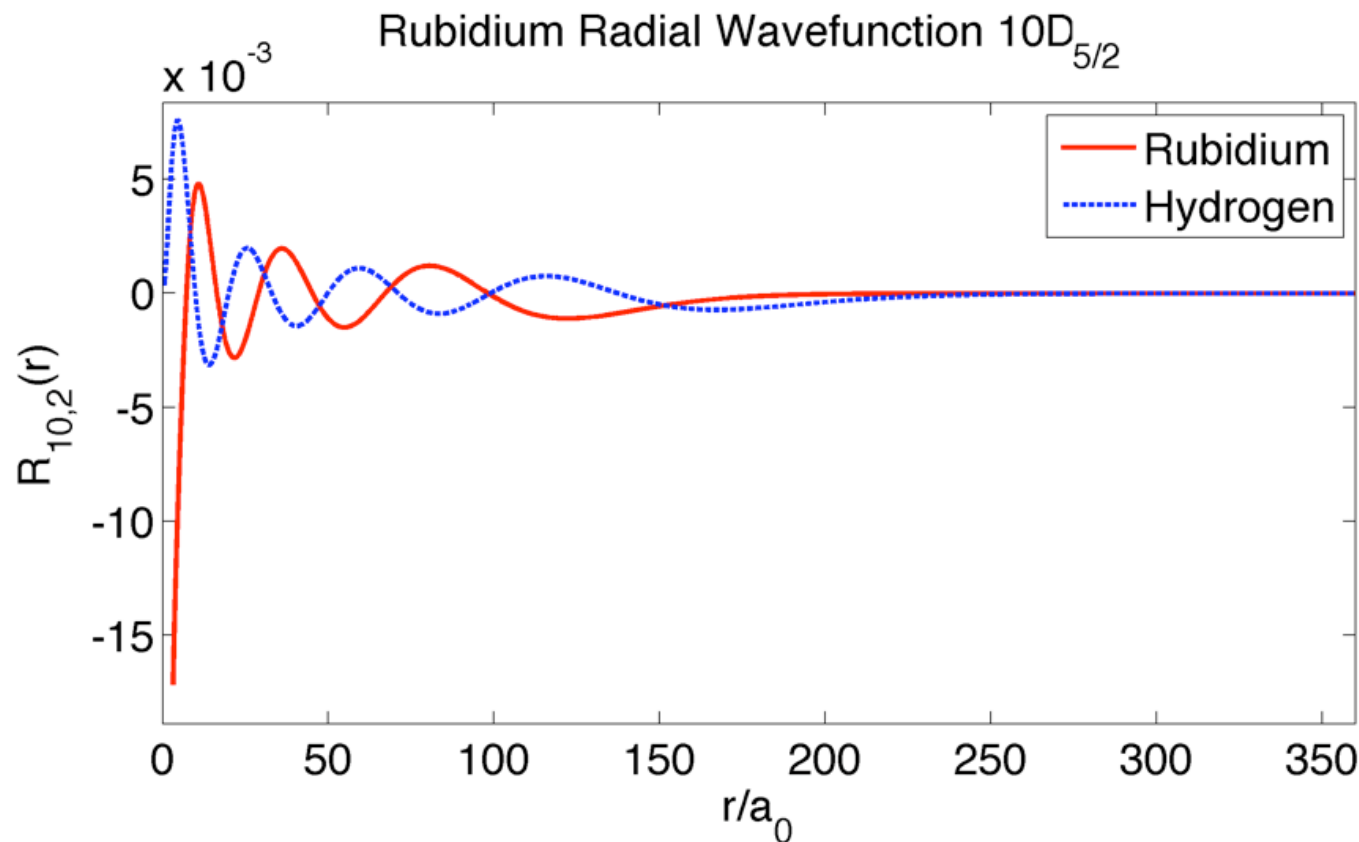
$$V_{\text{fs}}(r) = \frac{1}{2} \frac{\alpha^2}{r^3} \vec{L} \cdot \vec{S}$$

Total potential $V(r) = V_{\text{fs}}(r) + V_\ell(r)$

[3] Z Marinescu *et al.* PRA **49** (2) 982, 1994

Taking quantum defects from [4] (nS,P,D) and [5] (nF) and transforming potential for Numerov method now have Rubidium radial wavefunctions

Comparison with hydrogen wavefunction shows phase shift due to quantum defects



Main purpose of wavefunction code was to generate matrix elements for calculating Stark shifts and dipole-dipole interactions

Need comparison with other work to check accuracy of matrix elements:

Matrix Element	My Value	Quoted Value	Ref	% Difference
$\langle 46d_{5/2} r 48p_{3/2} \rangle$	1551 a_0	1548 a_0	[7]	0.2
$\langle 46d_{5/2} r 44f_{7/2} \rangle$	1586 a_0	1587 a_0	[7]	0.06
$\langle 46d_{5/2} r 47p_{3/2} \rangle$	2708 a_0	2709 a_0	[7]	0.04
$\langle 46d_{5/2} r 45f_{7/2} \rangle$	2694 a_0	2694 a_0	[7]	-
$\langle 50d_{5/2} r 52p_{3/2} \rangle$	1844 a_0	1840 a_0	[8]	0.2
$\langle 50d_{5/2} r 48f_{7/2} \rangle$	1893 a_0	1893 a_0	[8]	-
$\langle 35d_{5/2} r 37p_{3/2} \rangle$	877 a_0	875 a_0	[8]	0.2
$\langle 35d_{5/2} r 33f_{7/2} \rangle$	882 a_0	882 a_0	[8]	-
$\langle 50d_{5/2} r 52p_{3/2} \rangle$	2565 a_0	2563 a_0	[9]	0.08
$\langle 50d_{5/2} r 52p_{3/2} \rangle$	2596 a_0	2594 a_0	[9]	0.08

Still need to check nsnp matrix elements. Discrepancy in ndnp most probably due to different core potential being used - sufficiently accurate for my purposes.

[7] Li *et al.* PRL **94** (17) 173001, 2005

[8] Li *et al.* Eur. Phys. J. D **40** (1) 2006

[9] Gaëtan *et al.* Nature Physics 2009

In an electric field eigenvalues are no longer bare state eigenvalues but eigenvalues of the Stark matrix:

$$\hat{\mathcal{H}}_{\text{Stark}} = \hat{\mathcal{H}}_{\text{atom}} + E\hat{z}$$

For 'low' fields shifts can be calculated from static polarisability α_0 :

$$\Delta W = -\frac{1}{2}\alpha_0 E^2$$

In 'high' fields get avoided crossings - perturbation theory doesn't work.

High/Low fields depends on S/P/D state and n.

Generate the Stark map for Rubidium Rydberg states using fine-structure Stark couplings: [Zimmerman *et al.* PRA 20 (6) 2251 (1979)]

$$\begin{aligned} \langle n, \ell, j, m_j | Ez | n', \ell', j', m'_j \rangle &= \delta_{m_j, m'_j} \delta_{\ell, \ell' \pm 1} E \langle n, \ell | r | n', \ell' \rangle \\ &\times \sum_{m_\ell = m_j \pm \frac{1}{2}} \langle \ell, \frac{1}{2}, m_\ell, m_j - m_\ell | j, m_j \rangle \langle \ell', \frac{1}{2}, m_\ell, m_j - m_\ell | j', m_j \rangle \langle \ell, m_\ell | \cos \theta | \ell', m_\ell \rangle \end{aligned}$$

Electric field selection rules couple $|m_j|$ states

Generate Stark maps by diagonalising Stark matrix:

$$\mathcal{H} = \begin{pmatrix} W_1 & 0 & 0 \\ 0 & W_2 & 0 \\ 0 & 0 & W_3 \end{pmatrix} + E \begin{pmatrix} 0 & \langle 1|z|2 \rangle & \langle 1|z|3 \rangle \\ \langle 1|z|2 \rangle & 0 & \langle 2|z|3 \rangle \\ \langle 1|z|3 \rangle & \langle 2|z|3 \rangle & 0 \end{pmatrix}.$$

For each $|m_j|$ manifold need $\Delta n = \pm 5$, $\ell \leq 20$ and $j = \ell \pm s$ - results in very large basis set.

Method 1: MATLAB Implementation

- Bottleneck in finding Stark couplings - simplified by using analytic radial wavefunctions for $\ell > 4$ [see Bautista-Moedano, Apeiron 13(1)]
- Creation and diagonalisation of $n = 40$ took 2 days on Mamamku

Method 2: FORTRAN Implementation

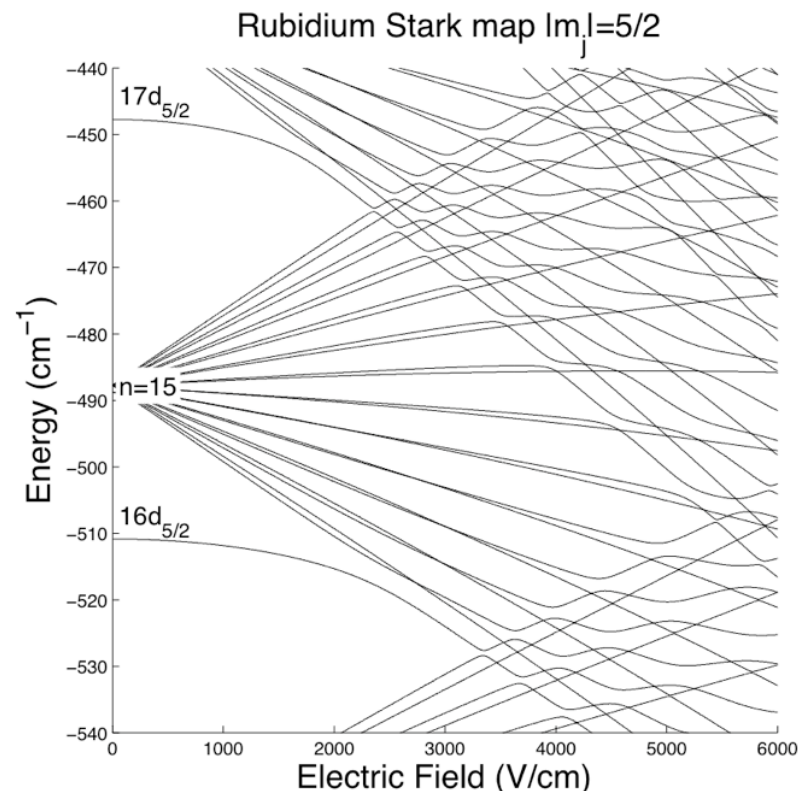
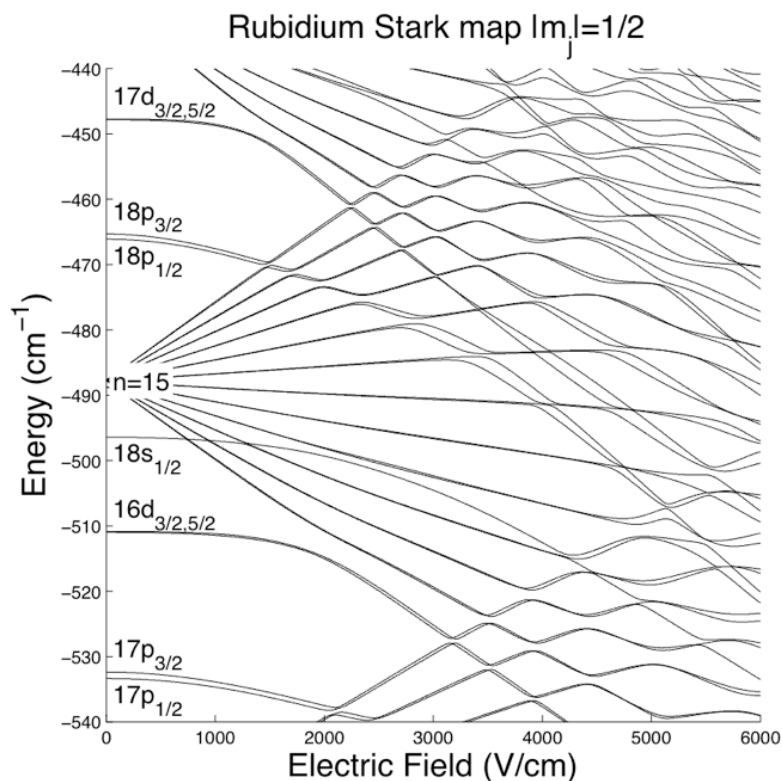
- Learn FORTRAN!
- Evaluate all couplings using Numerov wavefunctions
- Diagonalise using DSYEV algorithm (same as Matlab)
- Code runs in <30s!!

Test 1: reproduce Stark maps for $n=15$ and compare to Zimmerman (1979)

Avoided crossings occur due fine structure mixing of low l states.

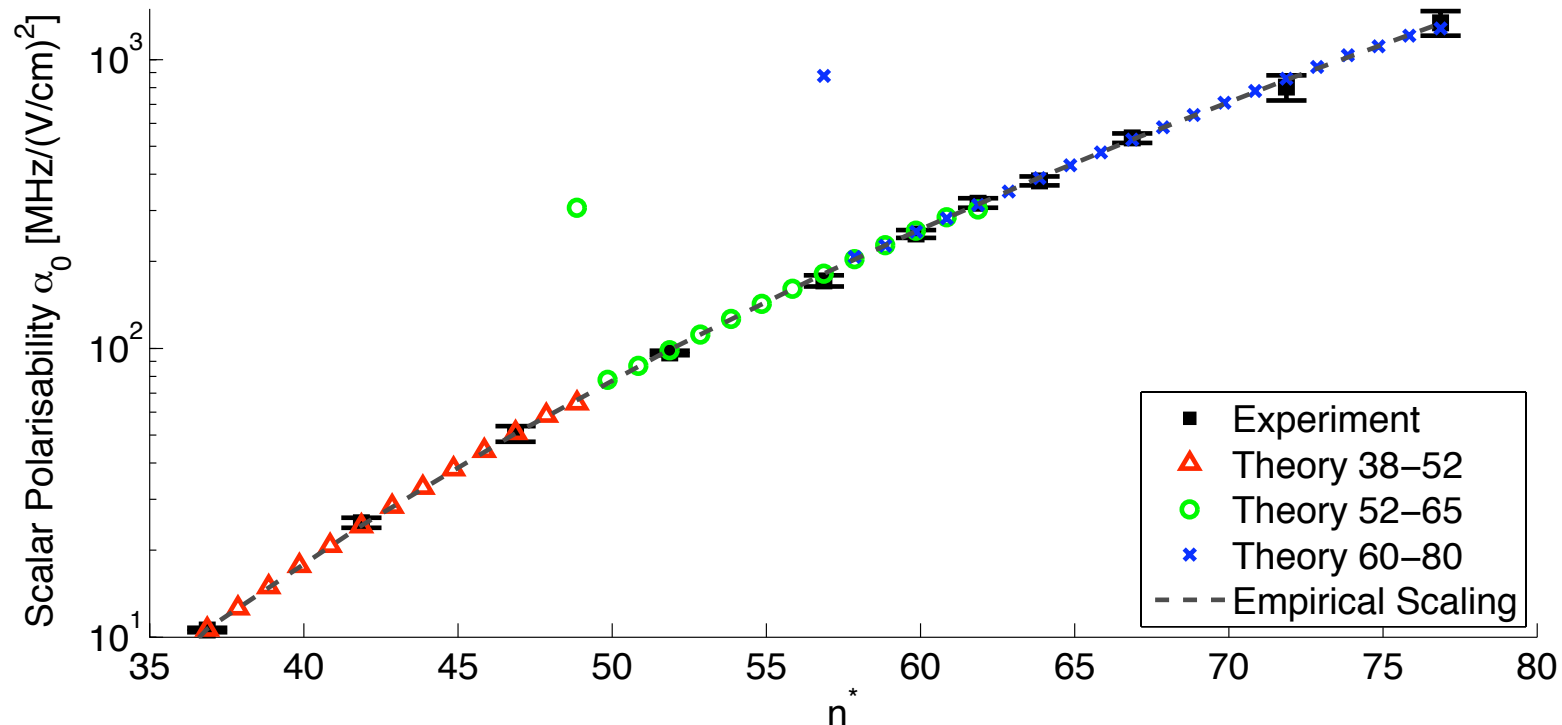
$|m_j| = 5/2$ has two manifolds:

- $|m_j| = 3$ manifold with linear shift from couplings to states of equal energy
- $|m_j| = 2$ manifold with avoided crossings from couplings with states with quantum defect



Test 2: Compare polarisabilities to experimental data from O'Sullivan and Stoicheff
For nS states determined following empirical scaling [PRA 31(4) 2718]

$$\alpha_0 = 2.202 \times 10^{-9} n^{*6} + 5.53 \times 10^{-11} n^{*7}$$



Outliers due to truncated basis set - lowest n state has no negative contribution

Förster defect for a pair of atoms in state $|n\ell j\rangle$ dipole coupled to states $|n'\ell'j'\rangle$ $|n''\ell''j''\rangle$

$$\Delta = W_{|n''\ell''j''\rangle} + W_{|n'\ell'j'\rangle} - 2W_{|n\ell j\rangle}$$

Due to Stark shift can tune into resonance with electric field -
Förster resonance

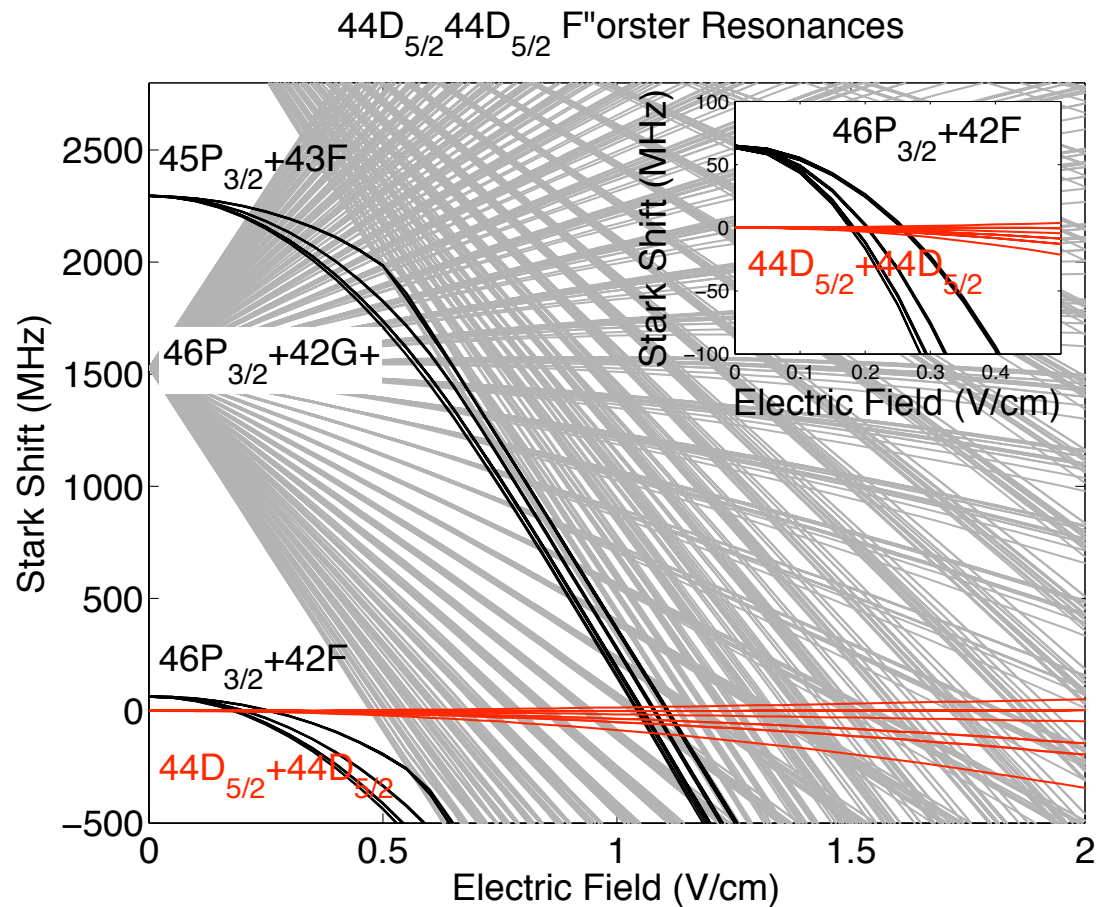
Long range resonant dipole-dipole interaction C_3/R^3

Interested in resonances
 $n \sim 43-50$ along near-resonant
channel

$nD_{5/2}nD_{5/2} \rightarrow (n+2)P_{3/2}(n-2)F_{5/2,7/2}$

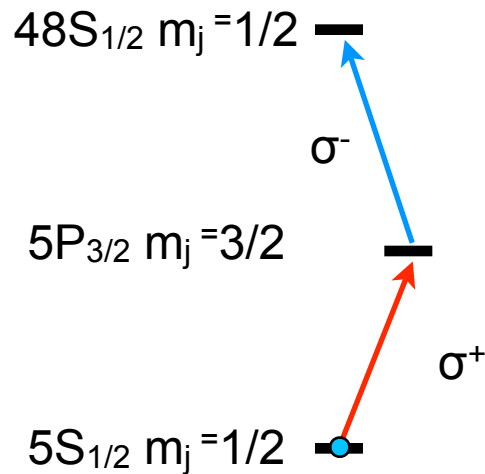
For 44D zero field $\Delta \sim 63$ MHz

Förster resonance at ~ 0.2 V/cm



Need to calibrate electric field plates on MOT chamber using S state Stark shift.

S state allows calibration of polarisation



48S Polarisability $\alpha_0 = 38.4 \text{ MHz}/(\text{V/cm})^2$

Fit data to give calibration from applied field to Electric field in chamber

Stark Shift 48S

