Lecture 4: The alkalis

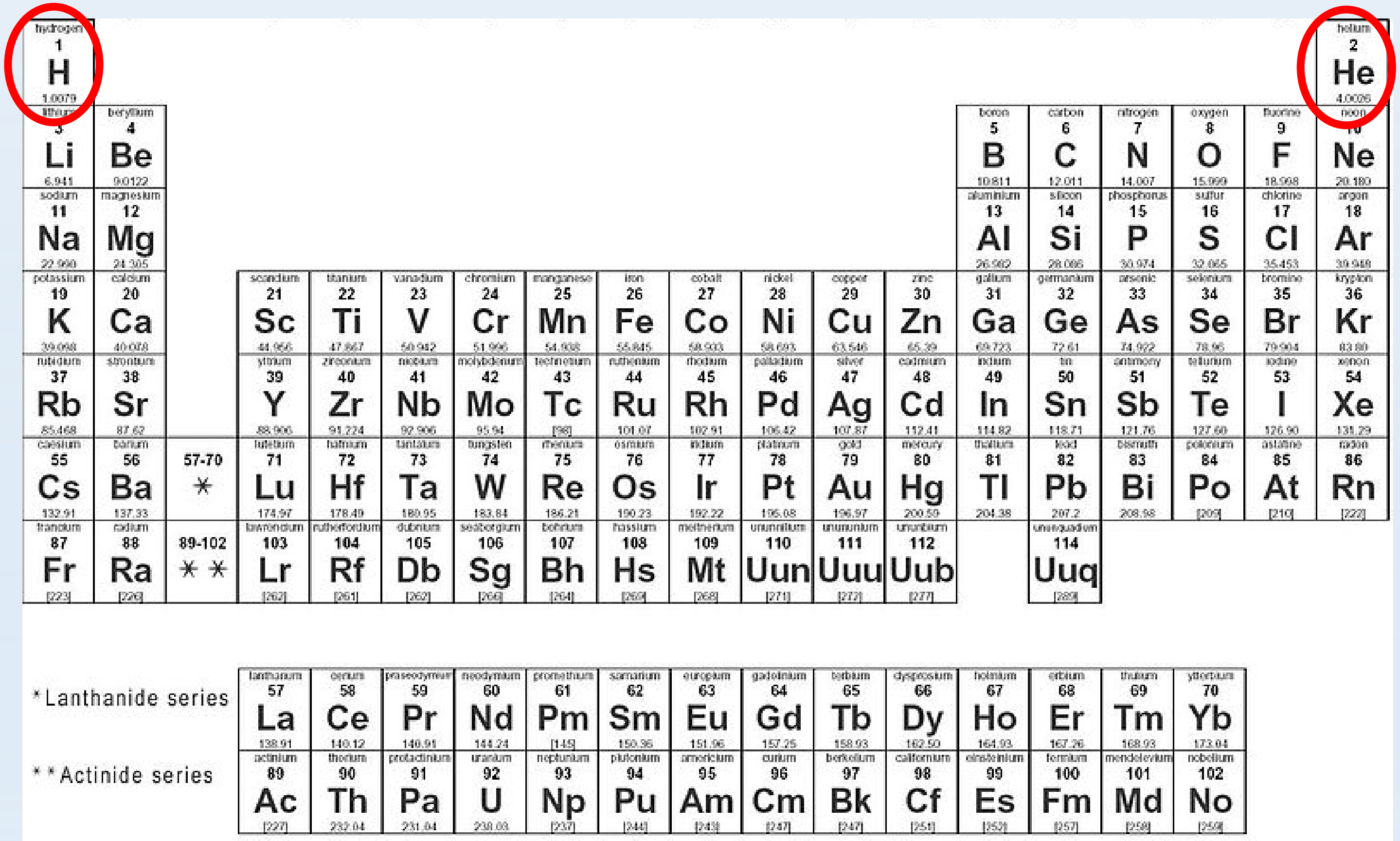
Readings: Foot Chapter 4

Last time: charge screening and energy structure in helium
spin configurations in multi-electron atoms

This time: back to ``single''-electron atoms w/ the alkalis

- unpaired valence electrons
- due to screening from filled inner sub-shell structure, the relevant low-energy (eV-scale) excitations will all be of the valence electron

The alkalis



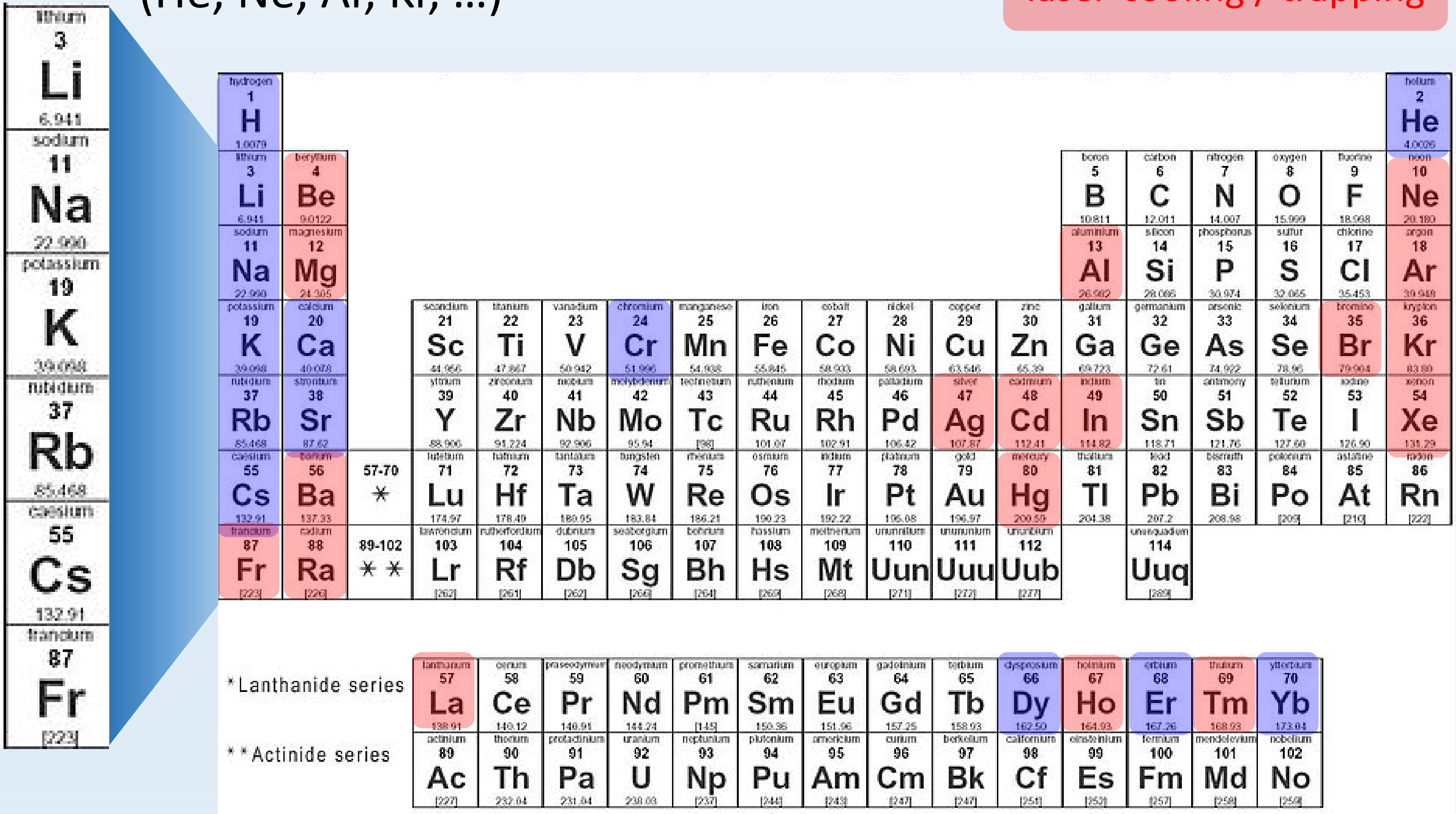
hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				
* Lanthanide series			lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04		
* * Actinide series			actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]		

The alkalis

~ add one electron to the inert gases (He, Ne, Ar, Kr, …)

🟦 quantum degeneracy

🟥 laser-cooling / trapping



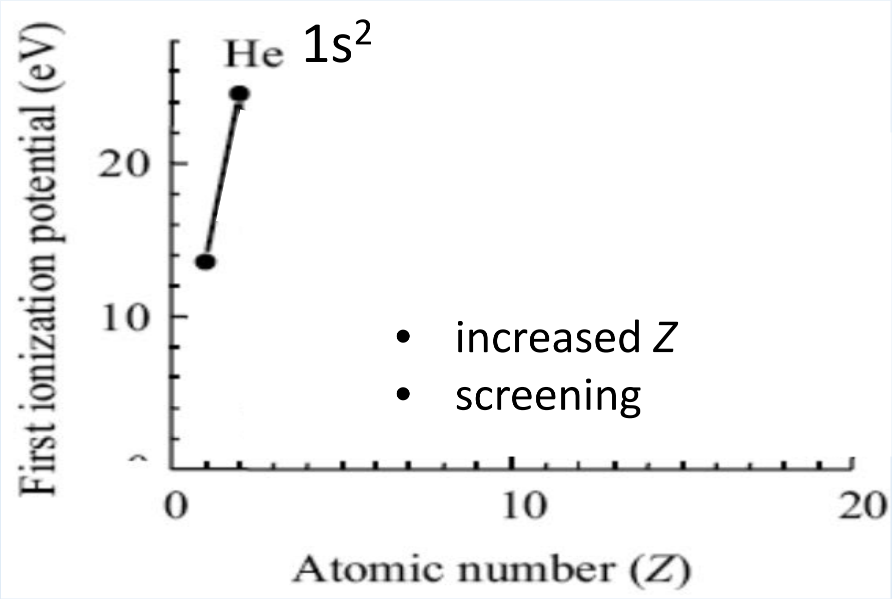
lithium 3 Li 6.941
sodium 11 Na 22.990
potassium 19 K 39.098
rubidium 37 Rb 85.468
caesium 55 Cs 132.91
francium 87 Fr [223]

🟦 1 H																		🟦 2 He
🟦 3 Li	🟥 4 Be												5 B	6 C	7 N	8 O	9 F	🟥 10 Ne
🟦 11 Na	🟥 12 Mg												🟥 13 Al	14 Si	15 P	16 S	17 Cl	🟥 18 Ar
🟦 19 K	🟦 20 Ca		21 Sc	22 Ti	23 V	🟦 24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	🟥 35 Br	🟥 36 Kr
🟦 37 Rb	🟦 38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	🟥 47 Ag	🟥 48 Cd	🟥 49 In	50 Sn	51 Sb	52 Te	53 I	🟥 54 Xe
🟦 55 Cs	🟥 56 Ba	57-70 *	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	🟥 80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
🟥 87 Fr	🟥 88 Ra	89-102 * *	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub		114 Uuq				

* Lanthanide series	🟥 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	🟦 66 Dy	🟥 67 Ho	🟦 68 Er	🟥 69 Tm	🟦 70 Yb
* * Actinide series	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

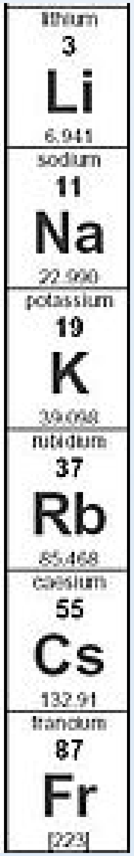
Screening in the alkalis

How do the electron’s fill up?



$1s^2$

- increased Z
- screening



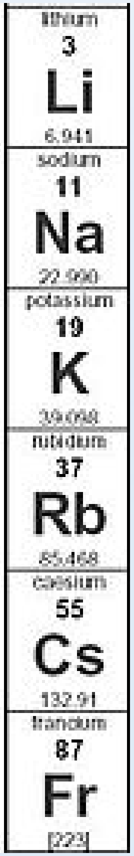
lithium	3	Li	6.941
sodium	11	Na	22.990
potassium	19	K	39.098
rubidium	37	Rb	85.468
caesium	55	Cs	132.91
francium	87	Fr	[223]

We saw that electron screening played a big role for He

Big jump in screening effects as you move up in n or l
(big shift in distance of “next” electron from the nucleus)

Screening in the alkalis

How do the electron’s fill up?



lithium
3
Li
6.941

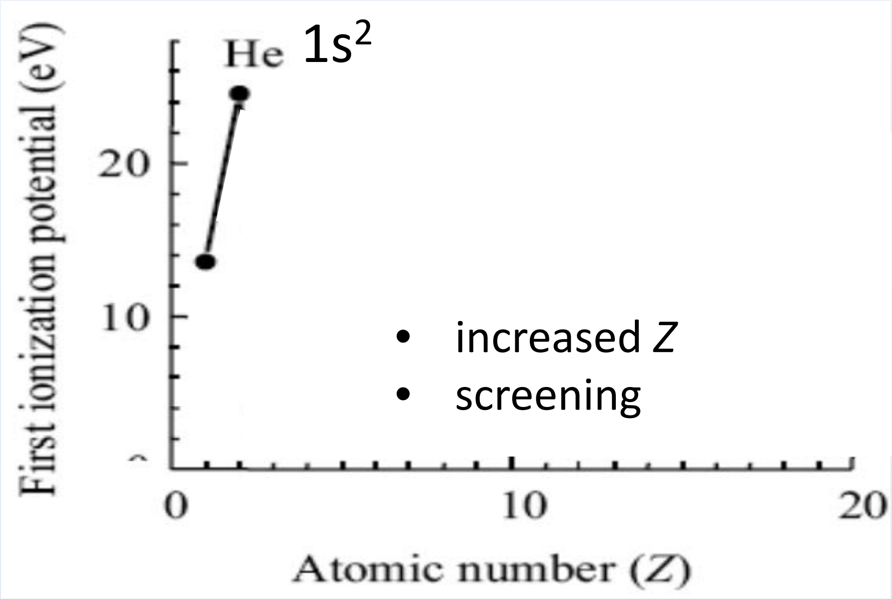
sodium
11
Na
22.990

potassium
19
K
39.098

rubidium
37
Rb
85.468

caesium
55
Cs
132.91

francium
87
Fr
[223]



$1s^2$

- increased *Z*
- screening

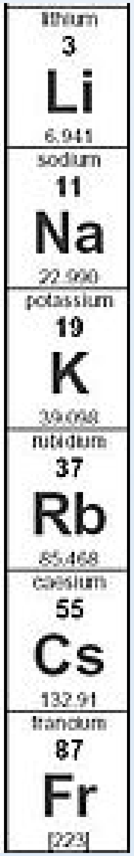
kT << eV, so electrons just fill lowest energy levels

$E_{2s} = E_{2p}$ for hydrogen (1/r potential, E_n ind. of l)

$V(r) \neq \beta/r$ for alkalis (screening, e-e interactions)

Screening in the alkalis

How do the electron’s fill up?



lithium
3
Li
6.941

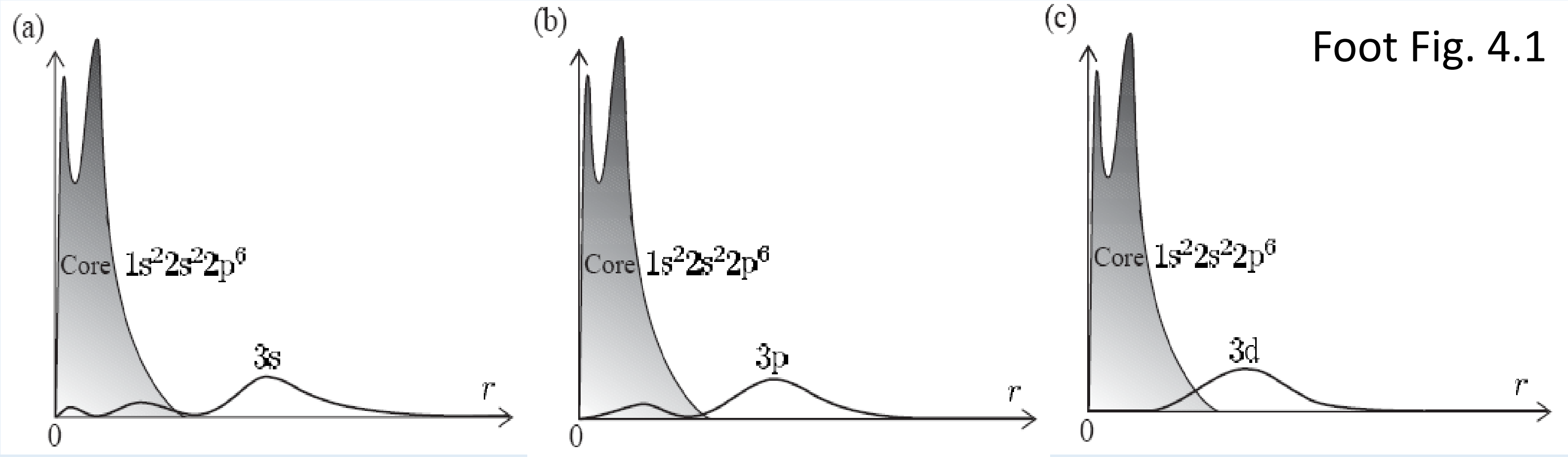
sodium
11
Na
22.990

potassium
19
K
39.098

rubidium
37
Rb
85.468

caesium
55
Cs
132.91

francium
87
Fr
[223]



Foot Fig. 4.1

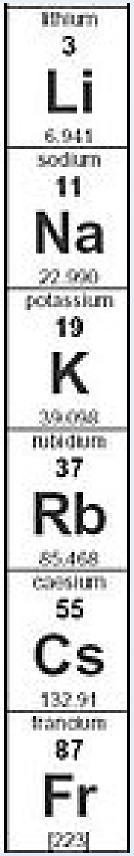
Considering the effects of shielding, which orbital will be most bound (lowest energy)?

a - 3s
b - 3p
c - 3d

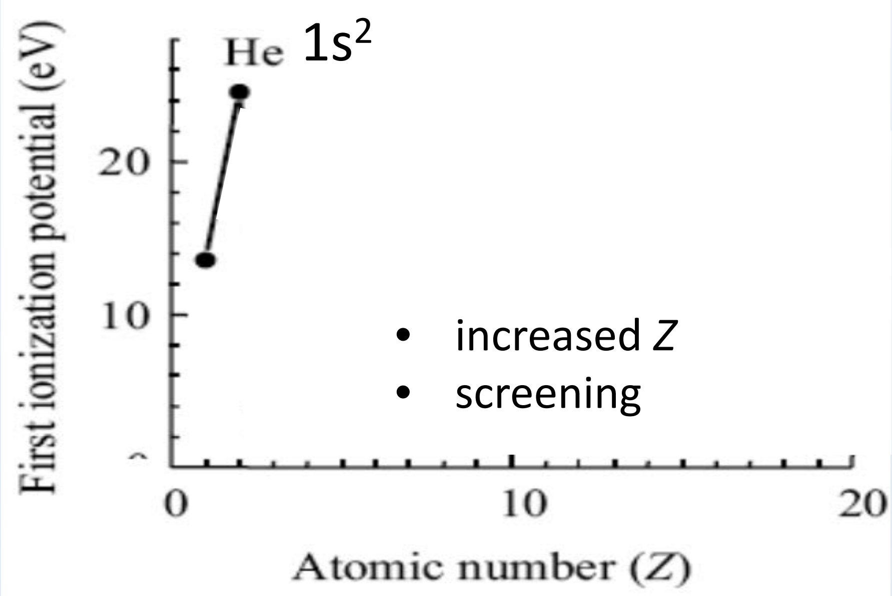
$E_{3s} < E_{3p} < E_{3d}$

Screening in the alkalis

How do the electron’s fill up?



$1s^2 2s$



$1s^2$

- increased *Z*
- screening

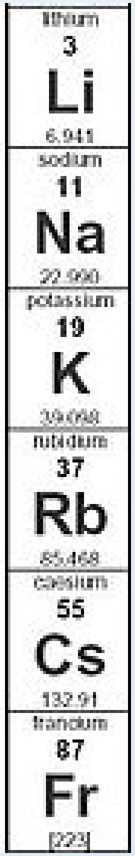
kT << eV, so electrons just fill lowest energy levels

$E_{2s} = E_{2p}$ for hydrogen (1/r potential, E_n ind. of l)

$V(r) \neq \beta/r$ for alkalis (screening, e-e interactions)

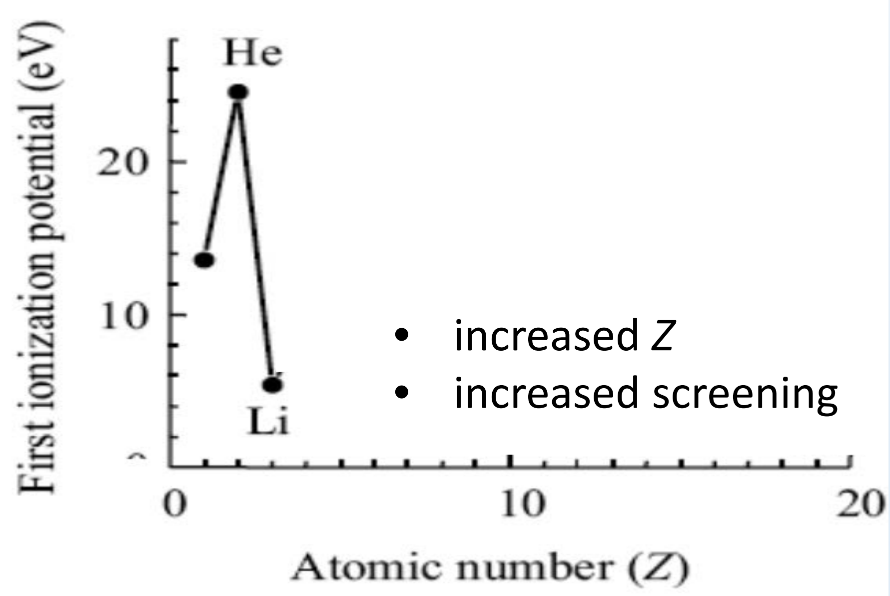
Screening in the alkalis

How do the electron's fill up?



lithium 3 **Li** 6.941
sodium 11 **Na** 22.990
potassium 19 **K** 39.098
rubidium 37 **Rb** 85.468
caesium 55 **Cs** 132.91
francium 87 **Fr** [223]

$1s^2 2s$



- increased *Z*
- increased screening

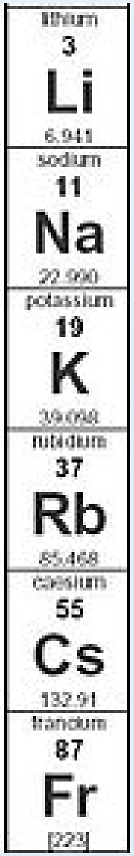
kT << eV, so electrons just fill lowest energy levels

$E_{2s} = E_{2p}$ for hydrogen (1/r potential, E_n ind. of l)

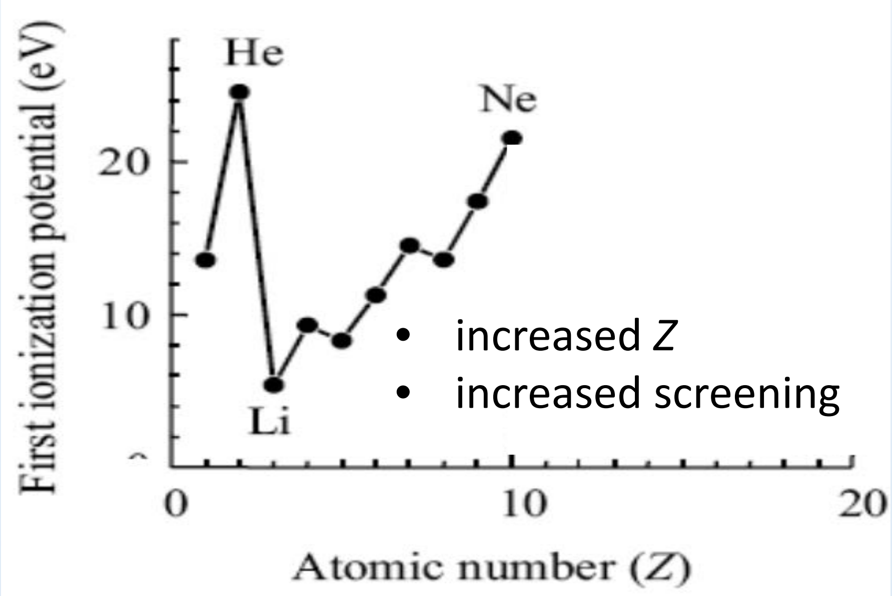
$V(r) \neq \beta/r$ for alkalis (screening, e-e interactions)

Screening in the alkalis

How do the electron's fill up?



$1s^2 2s$



- increased *Z*
- increased screening

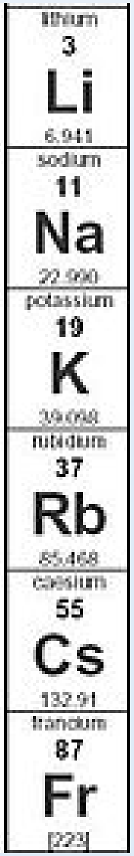
kT << eV, so electrons just fill lowest energy levels

$E_{2s} = E_{2p}$ for hydrogen (1/r potential, E_n ind. of l)

$V(r) \neq \beta/r$ for alkalis (screening, e-e interactions)

Screening in the alkalis

How do the electron’s fill up?



lithium
3
Li
6.941

sodium
11
Na
22.990

potassium
19
K
39.098

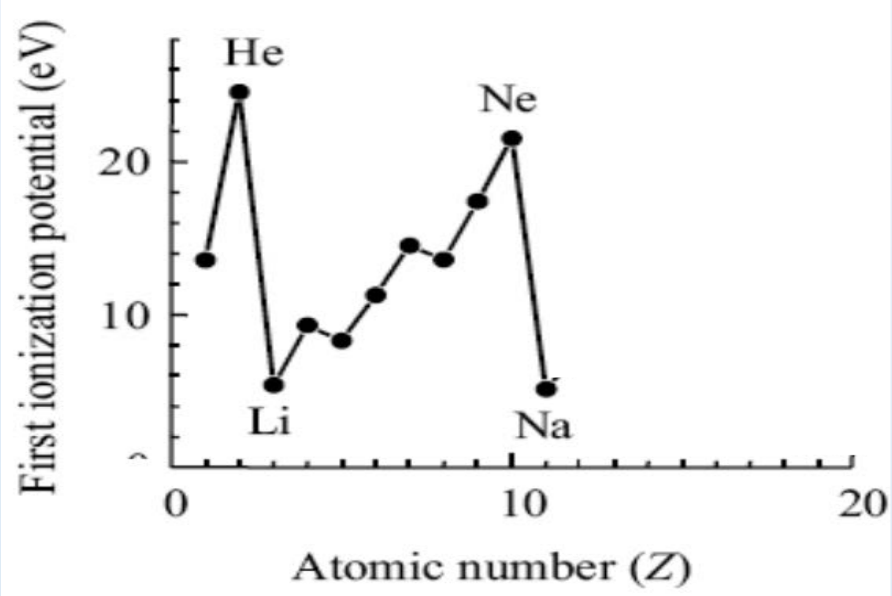
rubidium
37
Rb
85.468

caesium
55
Cs
132.91

francium
87
Fr
[223]

$1s^2 2s$

$1s^2 2s^2 2p^6 3s$



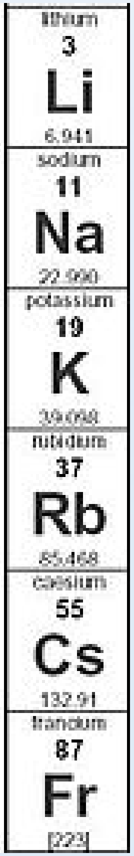
kT << eV, so electrons just fill lowest energy levels

$E_{2s} = E_{2p}$ for hydrogen (1/r potential, E_n ind. of l)

$V(r) \neq \beta/r$ for alkalis (screening, e-e interactions)

Screening in the alkalis

How do the electron's fill up?



lithium
3
Li
6.941

sodium
11
Na
22.990

potassium
19
K
39.098

rubidium
37
Rb
85.468

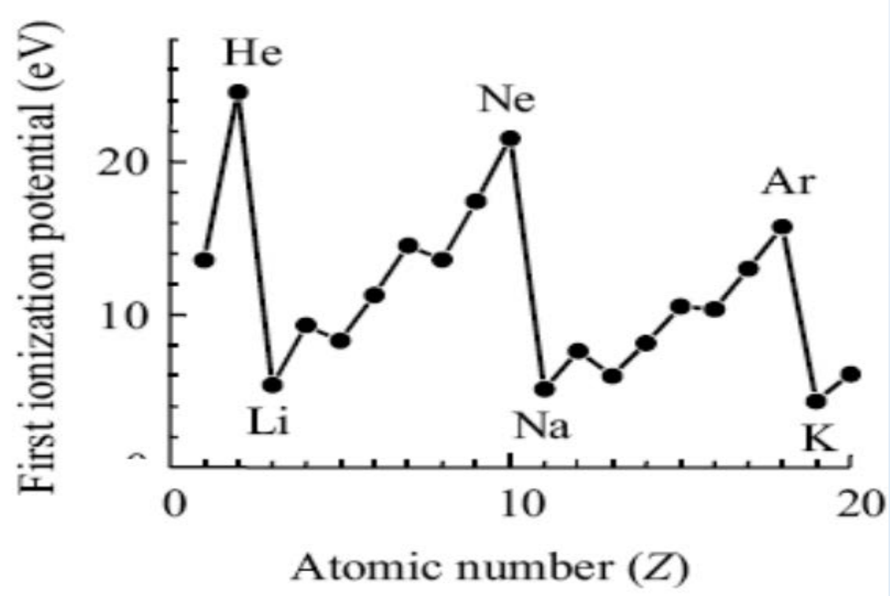
caesium
55
Cs
132.91

francium
87
Fr
[223]

$1s^2 2s$

$1s^2 2s^2 2p^6 3s$

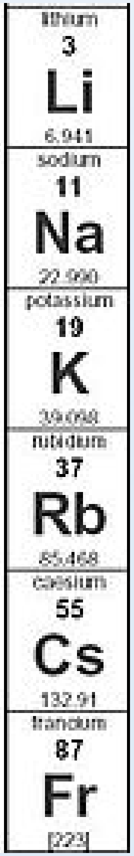
$1s^2 2s^2 2p^6 3s^2 3p^6 4s$



Note: 4s fill before 3d for potassium

Screening in the alkalis

How do the electron's fill up?



lithium
3
Li
6.941

sodium
11
Na
22.990

potassium
19
K
39.098

rubidium
37
Rb
85.468

caesium
55
Cs
132.91

francium
87
Fr
[223]

$1s^2 2s$

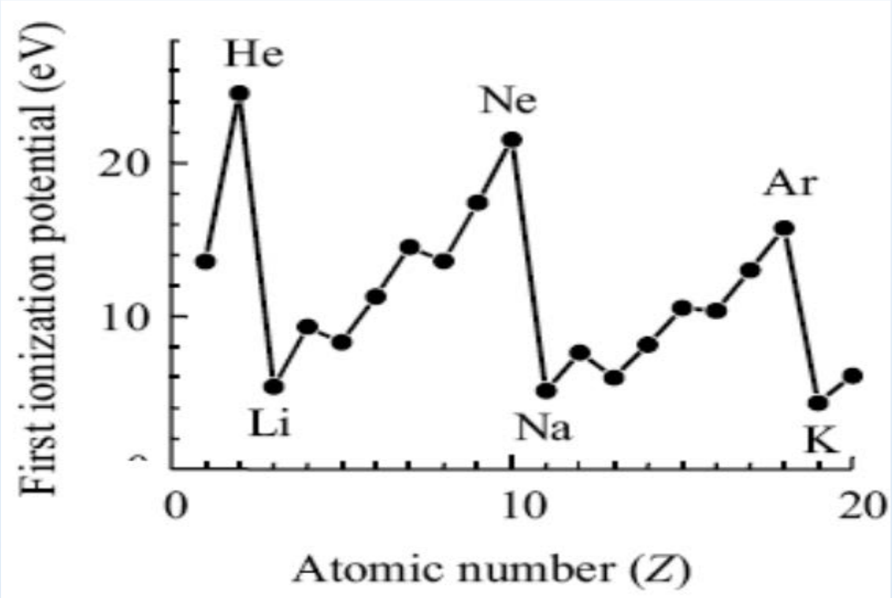
$1s^2 2s^2 2p^6 3s$

$1s^2 2s^2 2p^6 3s^2 3p^6 4s$

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s$

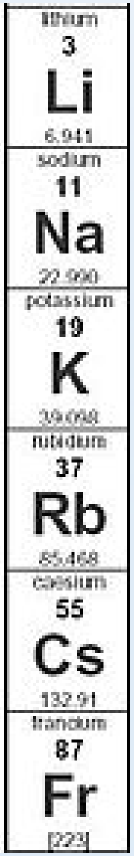
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s$

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^{10} 6s^2 6s^6 7s$



Screening in the alkalis

Some general considerations



lithium	3	Li	6.941
sodium	11	Na	22.990
potassium	19	K	39.098
rubidium	37	Rb	85.468
caesium	55	Cs	132.91
francium	87	Fr	[223]

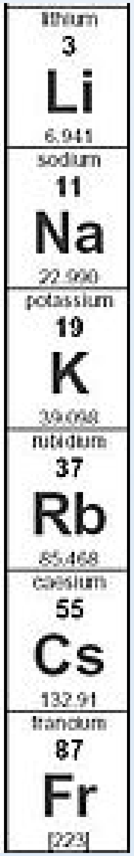
$1s^2 2s$

$1s^2 2s^2 2p^6 3s$

It’s pretty easy to rip the valence electron away, these elements can be a bit hard to handle

Screening in the alkalis

Some general considerations



lithium	3	Li	6.941
sodium	11	Na	22.990
potassium	19	K	39.098
rubidium	37	Rb	85.468
caesium	55	Cs	132.91
francium	87	Fr	[223]

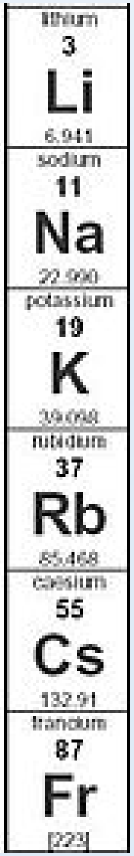
$1s^22s$

$1s^22s^22p^63s$

It's pretty easy to rip the valence electron away, these elements can be a bit hard to handle

Screening in the alkalis

Some general considerations



lithium
3
Li
6.941

sodium
11
Na
22.990

potassium
19
K
39.098

rubidium
37
Rb
85.468

caesium
55
Cs
132.91

francium
87
Fr
[223]

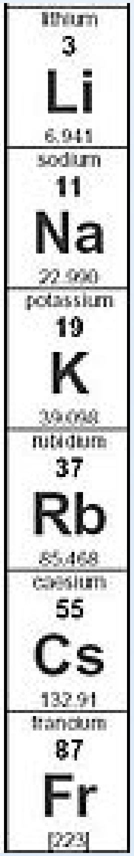
$1s^2 2s$

$1s^2 2s^2 2p^6 3s$

It’s pretty easy to rip the valence electron away, these elements can be a bit hard to handle

Screening in the alkalis

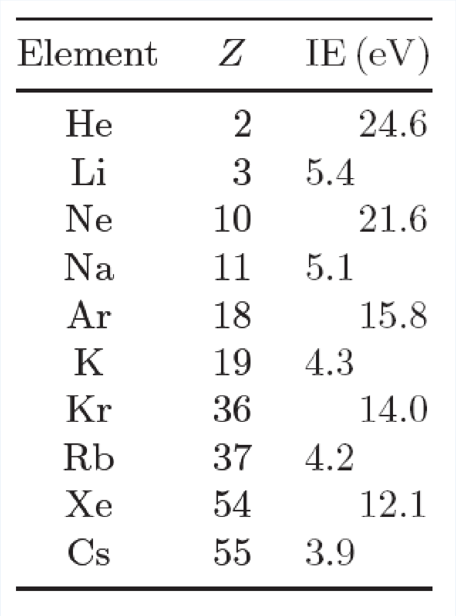
Some general considerations



lithium 3 **Li** 6.941
sodium 11 **Na** 22.990
potassium 19 **K** 39.098
rubidium 37 **Rb** 85.468
caesium 55 **Cs** 132.91
francium 87 **Fr** [223]

$1s^22s$

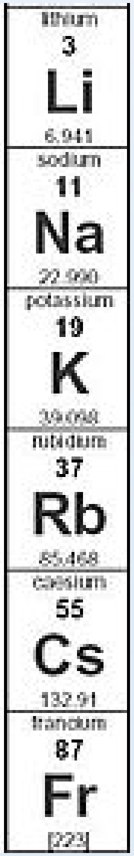
$1s^22s^22p^63s$



Element	Z	IE (eV)
He	2	24.6
Li	3	5.4
Ne	10	21.6
Na	11	5.1
Ar	18	15.8
K	19	4.3
Kr	36	14.0
Rb	37	4.2
Xe	54	12.1
Cs	55	3.9

Screening in the alkalis

Some general considerations



$1s^2 2s$

$1s^2 2s^2 2p^6 3s$

Why not $3s \rightarrow 3d$?

Why not $3s \rightarrow 4s$?

Element	Z	IE (eV)
He	2	24.6
Li	3	5.4
Ne	10	21.6
Na	11	5.1
Ar	18	15.8
K	19	4.3
Kr	36	14.0
Rb	37	4.2
Xe	54	12.1
Cs	55	3.9

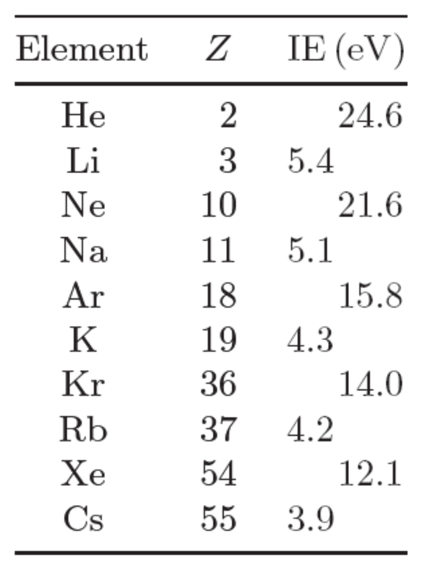
It'll cost wayyy more energy to excite inner-shell electrons than the valence electrons. We'll mostly just care about excitations like:

Na: $\underline{1s^2 2s^2 2p^6}3s \rightarrow \underline{1s^2 2s^2 2p^6}3p$, $\underline{1s^2 2s^2 2p^6}4p$, etc.

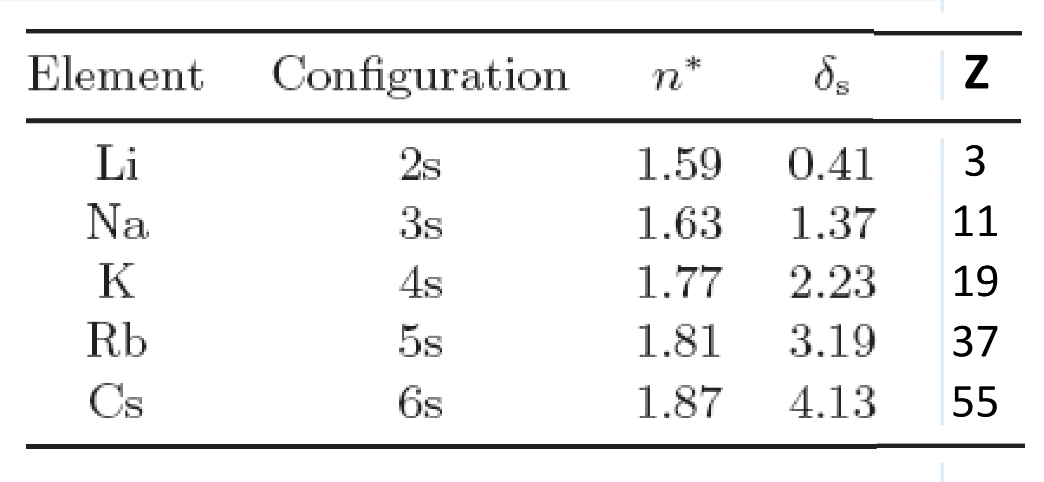
Quantum defects in the alkali metals

An empirical way to parameterize the effects of shielding

$$E_{nl} = \frac{hcR_\infty}{\left(n-\delta_l\right)^2} = -\frac{13.6\,\mathrm{eV}}{\left(n^*\right)^2}$$



Element	Z	IE (eV)
He	2	24.6
Li	3	5.4
Ne	10	21.6
Na	11	5.1
Ar	18	15.8
K	19	4.3
Kr	36	14.0
Rb	37	4.2
Xe	54	12.1
Cs	55	3.9

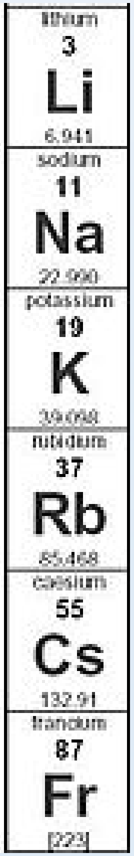


Element	Configuration	n^*	δ_s	**Z**
Li	2s	1.59	0.41	3
Na	3s	1.63	1.37	11
K	4s	1.77	2.23	19
Rb	5s	1.81	3.19	37
Cs	6s	1.87	4.13	55

Pretty remarkable: all ionization energies (and transition energies) are roughly equal despite Z^2 scaling of energies without shielding

Alkalis - wide range of physics to study

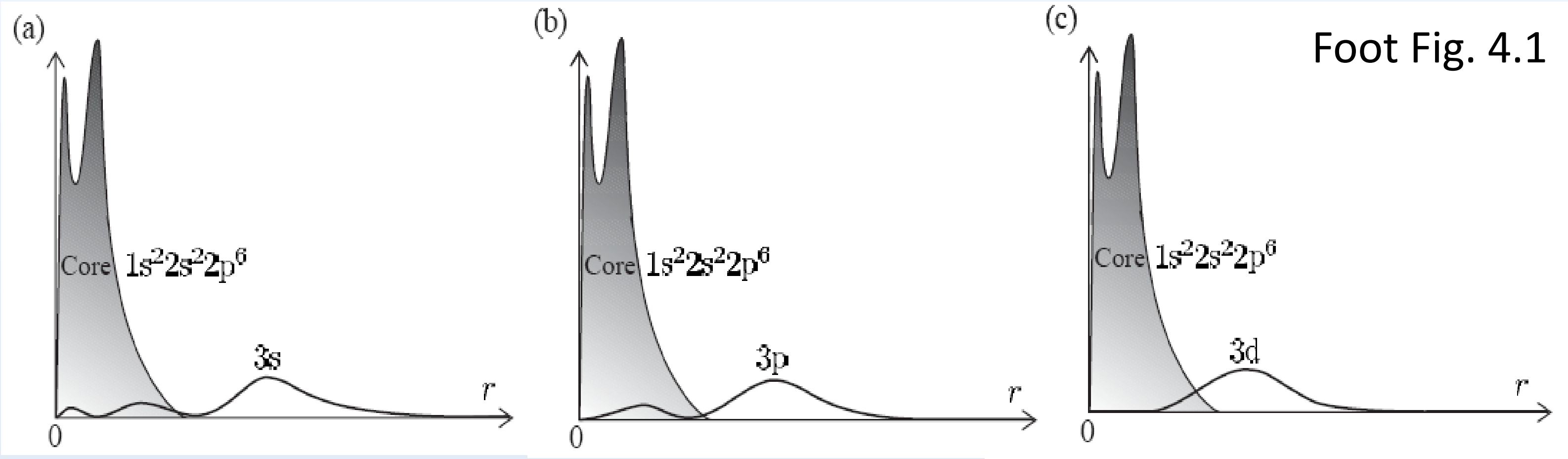
Consequently, transitions in a wide range of species (with very different Z values) can be addressed with roughly the same range of laser wavelengths (within a factor of <2)



Stable isotopes		
$^{6,7}\mathrm{Li}$	lithium 3 Li 6.941	$^{7}\mathrm{Li}$ BEC in 1997, $^{6}\mathrm{Li}$ DFG in 2001 – very light, very broad Feshbach resonances for both the bosonic and fermionic species
$^{23}\mathrm{Na}$	sodium 11 Na 22.990	$^{23}\mathrm{Na}$ BEC in 1995 – stable scattering properties, stable mixtures used to explore spinor physics
$^{39,40,41}\mathrm{K}$	potassium 19 K 39.098	$^{40}\mathrm{K}$ DFG in 1999, $^{39,41}\mathrm{K}$ BECs in early 2000s – fermions, broad feshbach resonances,
$^{85,87}\mathrm{Rb}$	rubidium 37 Rb 85.468	$^{87}\mathrm{Rb}$ BEC in 1995; $^{87}\mathrm{Rb}$ has stable scattering properties, nice Feshbach resonances in $^{85}\mathrm{Rb}$; large spin-orbit splitting allows for state-dependent potentials / Raman-dressing schemes
$^{133}\mathrm{Cs}$	caesium 55 Cs 132.91	BEC in 2002 ; nice Feshbach resonances, mostly unstable in spin mixtures and mixtures with other species
$^{223}\mathrm{Fr}$ (not really)	francium 87 Fr [223]	Laser cooling and magneto-optical trapping for parity nonconservation studies

note that the mass number A = Z + N is written as, e.g., $^{87}\mathrm{Rb}$ for the rubidium isotope with A = 87.
(atomic number Z = # of protons) + (N = # of neutrons).
An odd value of A implies a fermionic isotope for the alkalis (1 “extra” valence electron).

Quantum defect for different orbitals



Foot Fig. 4.1

$$E_{nl} = \frac{hcR_\infty}{(n-\delta_l)^2} = -\frac{13.6\,\mathrm{eV}}{(n^*)^2}$$

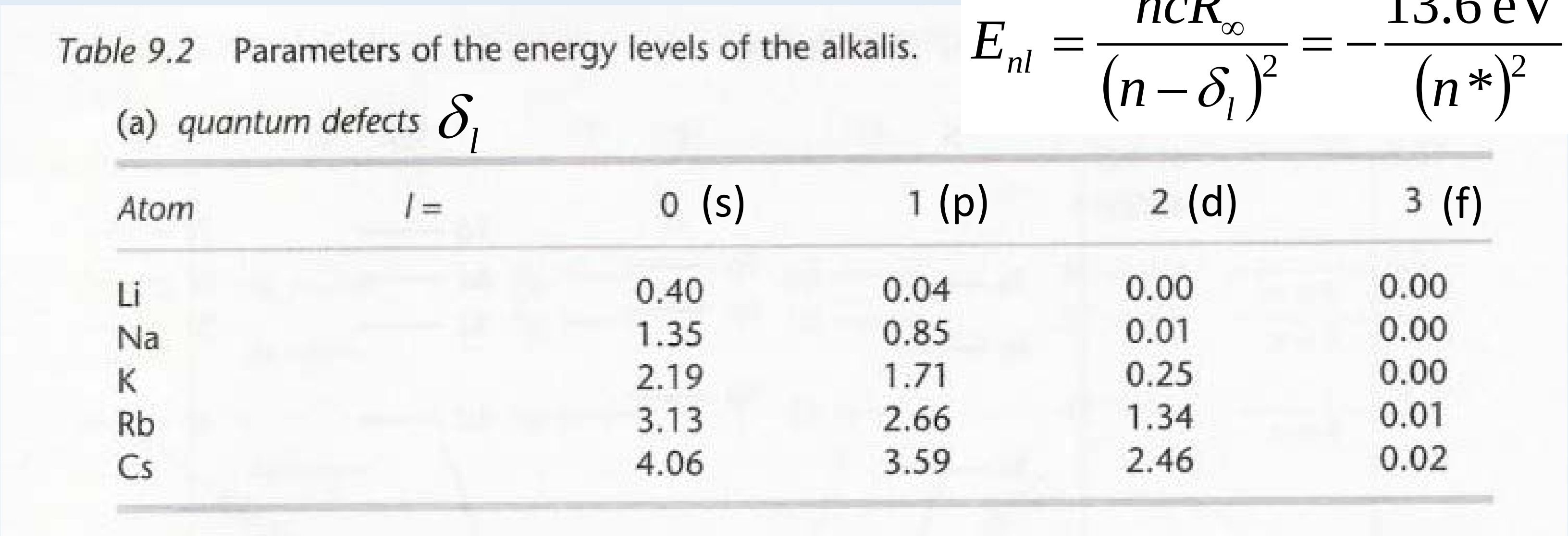


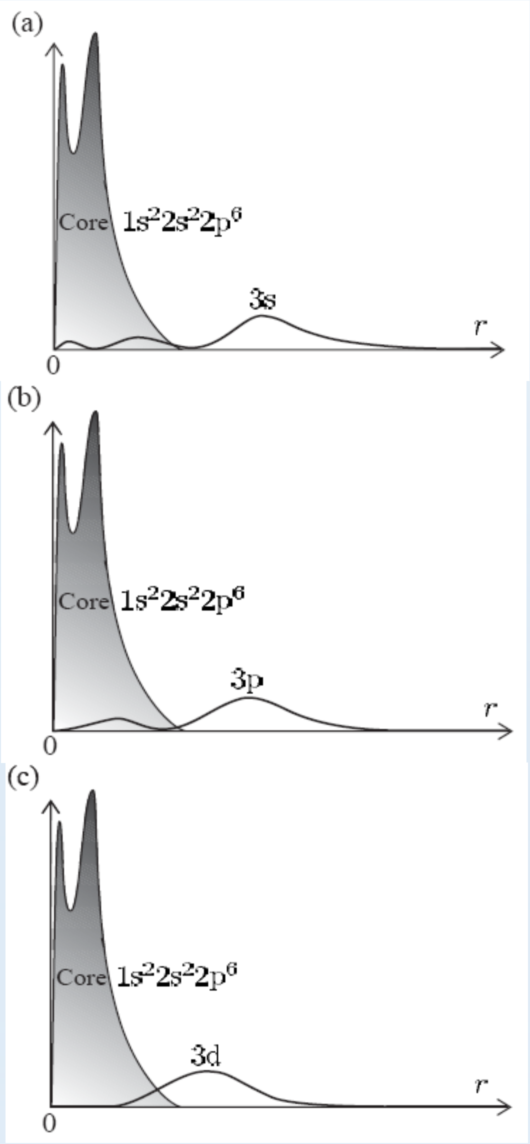
Table 9.2 Parameters of the energy levels of the alkalis.

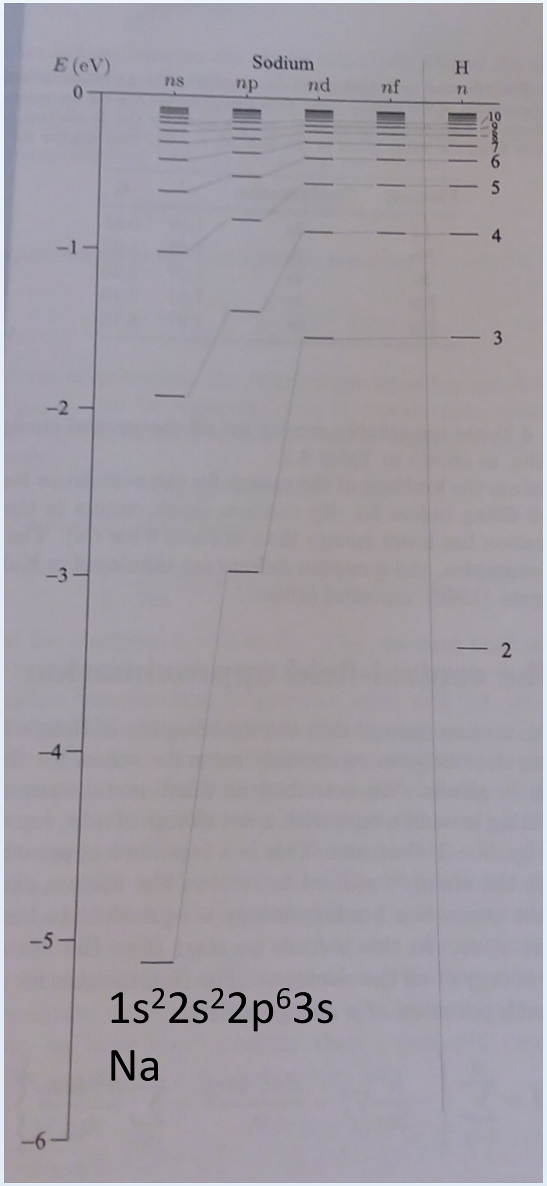
(a) *quantum defects* δ_l

Atom	*l* =	0 (s)	1 (p)	2 (d)	3 (f)
Li		0.40	0.04	0.00	0.00
Na		1.35	0.85	0.01	0.00
K		2.19	1.71	0.25	0.00
Rb		3.13	2.66	1.34	0.01
Cs		4.06	3.59	2.46	0.02

Cs: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s$

Quantum defects in the alkali metals





$1s^22s^22p^63s$

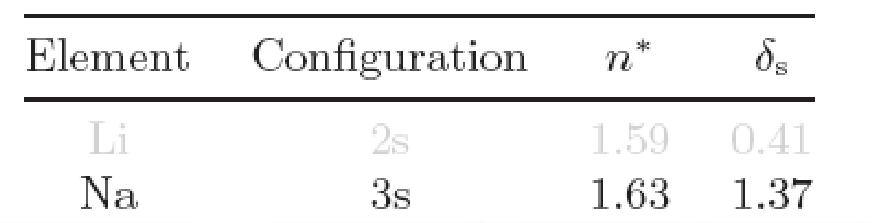
Na

Transition energies (wavelengths)

Recall $E_{2p} - E_{1s} \sim 10.2$ eV for hydrogen, relating to $\lambda_{1\rightarrow 2} \sim 120$ nm

$hc = 1240 \text{ eV nm}$

>> Estimate the wavelength related to the Na 3s → 4p transition

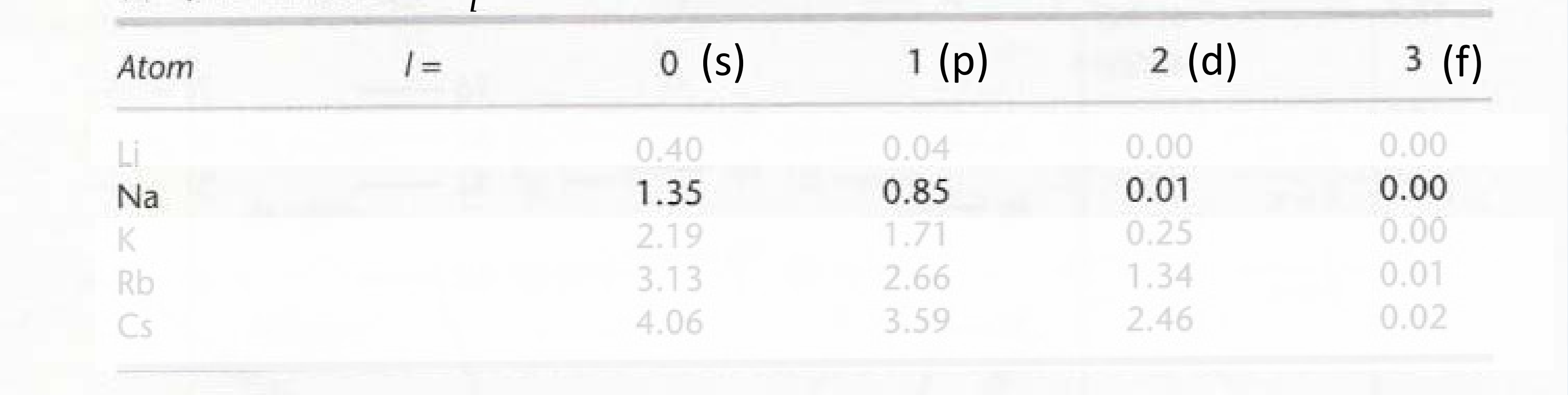


Element	Configuration	n^*	δ_s
Li	2s	1.59	0.41
Na	3s	1.63	1.37

$$E_{nl} = \frac{hcR_\infty}{(n-\delta_l)^2} = -\frac{13.6\text{ eV}}{(n^*)^2}$$

Table 9.2 Parameters of the energy levels of the alkalis.

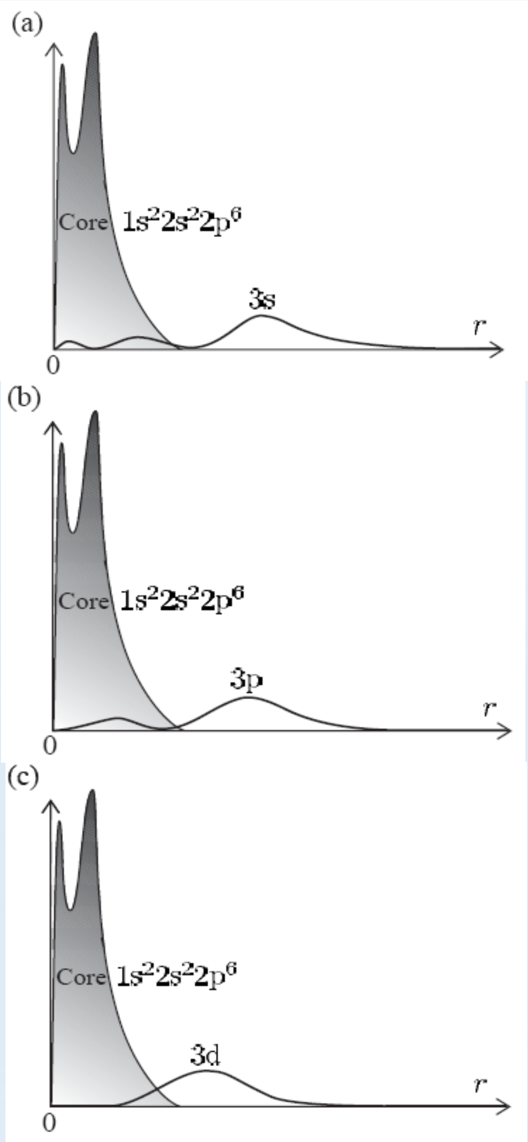
(a) *quantum defects* δ_l



Atom	*l* =	0 (s)	1 (p)	2 (d)	3 (f)
Li		0.40	0.04	0.00	0.00
Na		1.35	0.85	0.01	0.00
K		2.19	1.71	0.25	0.00
Rb		3.13	2.66	1.34	0.01
Cs		4.06	3.59	2.46	0.02

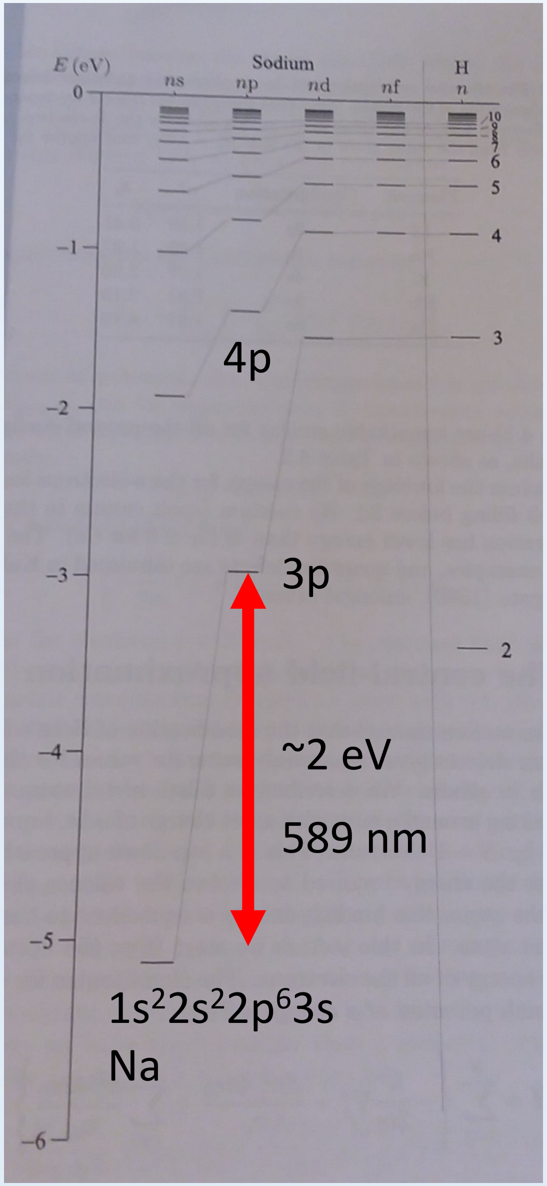
>> Is this the longest wavelength that can be used to excite g.s. sodium?

Quantum defects in the alkali metals



n → n' = n transitions are typically in the visible or near-IR

> convenient range for lasers



Solving the many-electron atom

Everything so far has been super empirical, results of experiment

How do you actually tackle the problem for a many-electron atom?

$$H = \sum_i \left[-\frac{\hbar^2}{2m}\vec{\nabla}_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right] + \sum_{i \neq j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

- no analytical solution to this problem

- we’ll walk through one approximate way to treat the effect of many core electrons

Central-field approximation

$$H=\sum_i\left[-\frac{\hbar^2}{2m}\vec{\nabla}_i^2-\frac{Ze^2}{4\pi\varepsilon_0 r_i}\right]+\sum_{i\neq j}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

$$H\approx H_{CF}=\sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m}\vec{\nabla}_i^2+V_{CF}\left(r_i\right)\right]$$

One a V_{CF} is assumed, this problem breaks down into *N* independent single-particle Schrödinger equations.

For the *N* solutions (lowest energy eigenstate wave functions), the total wave function will be of the form

$$\psi_{TOT}=\psi_1\psi_2\psi_3\ldots\psi_N$$

or rather a properly symmetrized version of this (this text goes into more details on the use of Slater determinants to ensure proper w.f. antisymmetrization)

Central-field approximation

$$H = \sum_i \left[-\frac{\hbar^2}{2m} \vec{\nabla}_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right] + \sum_{i \neq j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

$$H \approx H_{CF} = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m} \vec{\nabla}_i^2 + V_{CF}\left(r_i\right) \right]$$

$V_{CF}(r)$ → an effective, spherically symmetric potential that captures

(1) the static Coulomb potential of the nucleus and

(2) an effectively static, spherically symmetric potential due to the total electron charge distribution
(for product states ψ this gives a Hartree term like in the He treatment)

> no longer 1/r potential, so E depends on l

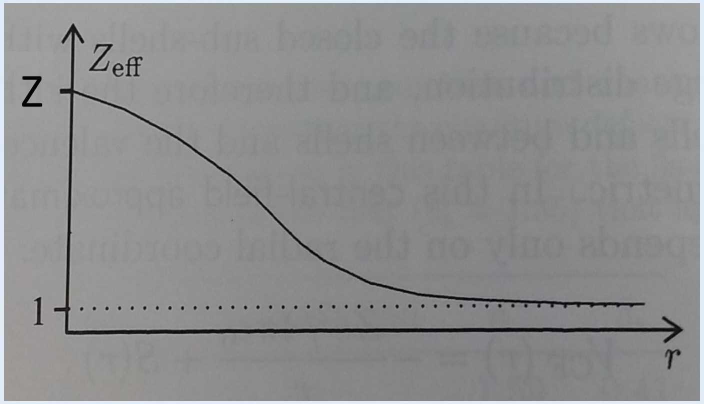
> still spherically symmetric, so E independent of m_l

Central-field approximation

$$H=\sum_{i}\left[-\frac{\hbar^{2}}{2m}\vec{\nabla}_{i}^{2}-\frac{Ze^{2}}{4\pi\varepsilon_{0}r_{i}}\right]+\sum_{i\neq j}\frac{e^{2}}{4\pi\varepsilon_{0}r_{ij}}$$

$$H\approx H_{CF}=\sum_{i=1}^{N}\left[-\frac{\hbar^{2}}{2m}\vec{\nabla}_{i}^{2}+V_{CF}\left(r_{i}\right)\right]$$

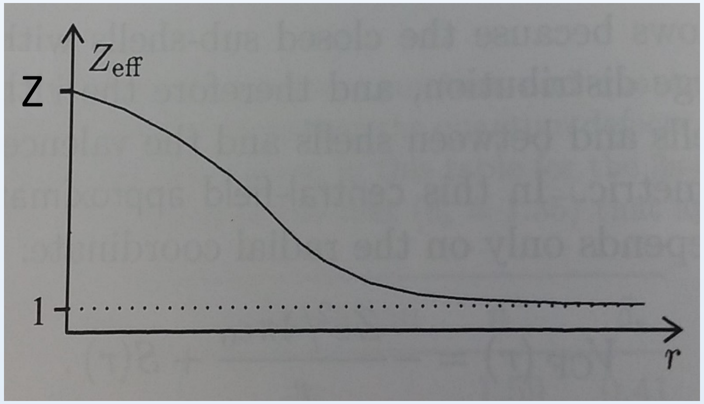
Basically, an effective electric field $\vec{E}_{CF}\left(r\right)=\frac{Z_{eff}\left(r\right)e}{4\pi\varepsilon_{0}r^{2}}\hat{r}$ exists, of the form



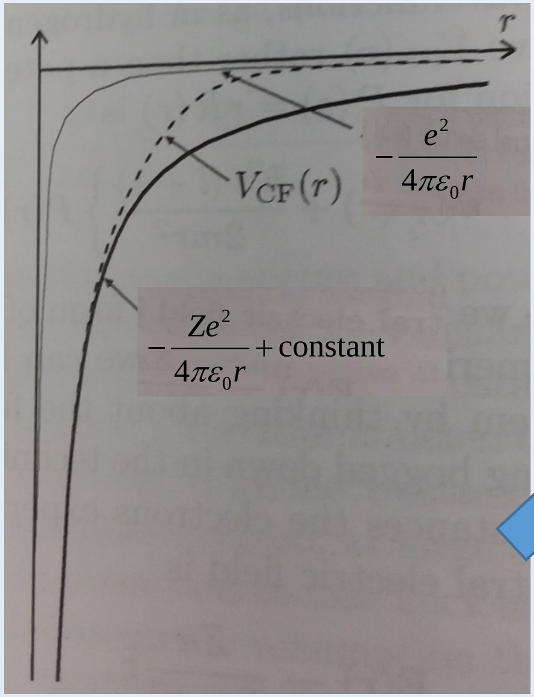
and an electron at distance *r* will experience the potential

$$V_{CF}\left(r\right)=-e\int_{r}^{\infty}E_{CF}\left(r'\right)dr'$$

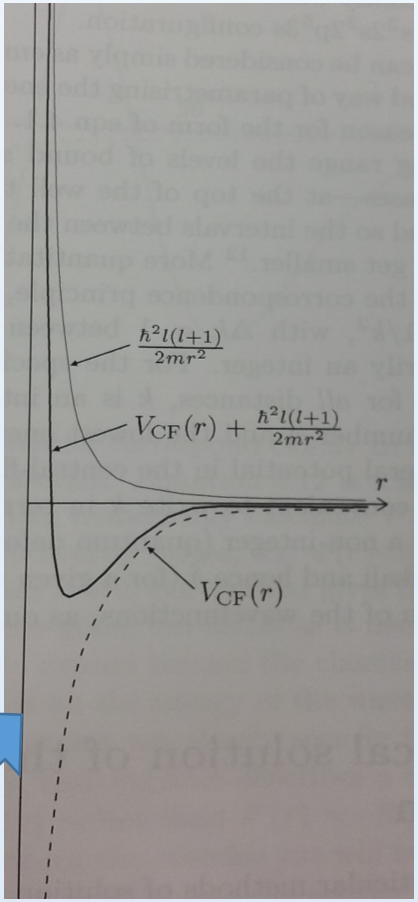
Central-field approximation



$$V_{CF}(r) = -e\int_{r}^{\infty} E_{CF}(r')\,dr'$$



As intuition would suggest, the effective potential is unchanged by screening at small *r*, and looks like a Z = 1 potential at very large *r*



The effect of the centrifugal barrier can also be incorporated for $l \neq 0$ solutions

Solving the many-electron atom

In broad strokes, the basic procedure for obtaining solutions to this problem would look like:

1) Make an initial guess at ψ and V_{CF}

2) Solve the *N* Schrodinger equations (for *N* electrons), respecting the necessary antisymmetric nature of ψ

3) From the new ψ, get a new V_{CF}

4) Iterate

Note: experiments still do the best job at determining state energies (energy differences), up to a part in 10^{18} in some cases

Fine structure in the alkalis

An important result that comes from the central-field approximation

Recall from lecture 2 (hydrogen-like atoms with a 1/r potential), that the fine-structure splitting between states with $j = l + 1/2$ and $j = l - 1/2$ have the form

$$\Delta E_{s-o} = \frac{Z^2\alpha^2}{nl(l+1)} E_{gross}(n) = \frac{Z^4\alpha^4}{n^3 l(l+1)} mc^2$$

For the multi-electron atom, which does not follow a 1/r potential, and where Z_{eff} varies from Z to 1 as a function of r, this takes the modified form (the Landé formula):

$$\Delta E_{s-o} = \frac{Z_i^2 Z_o^2 \alpha^4}{(n*)^3 l(l+1)} mc^2$$

$$Z_i \sim Z$$

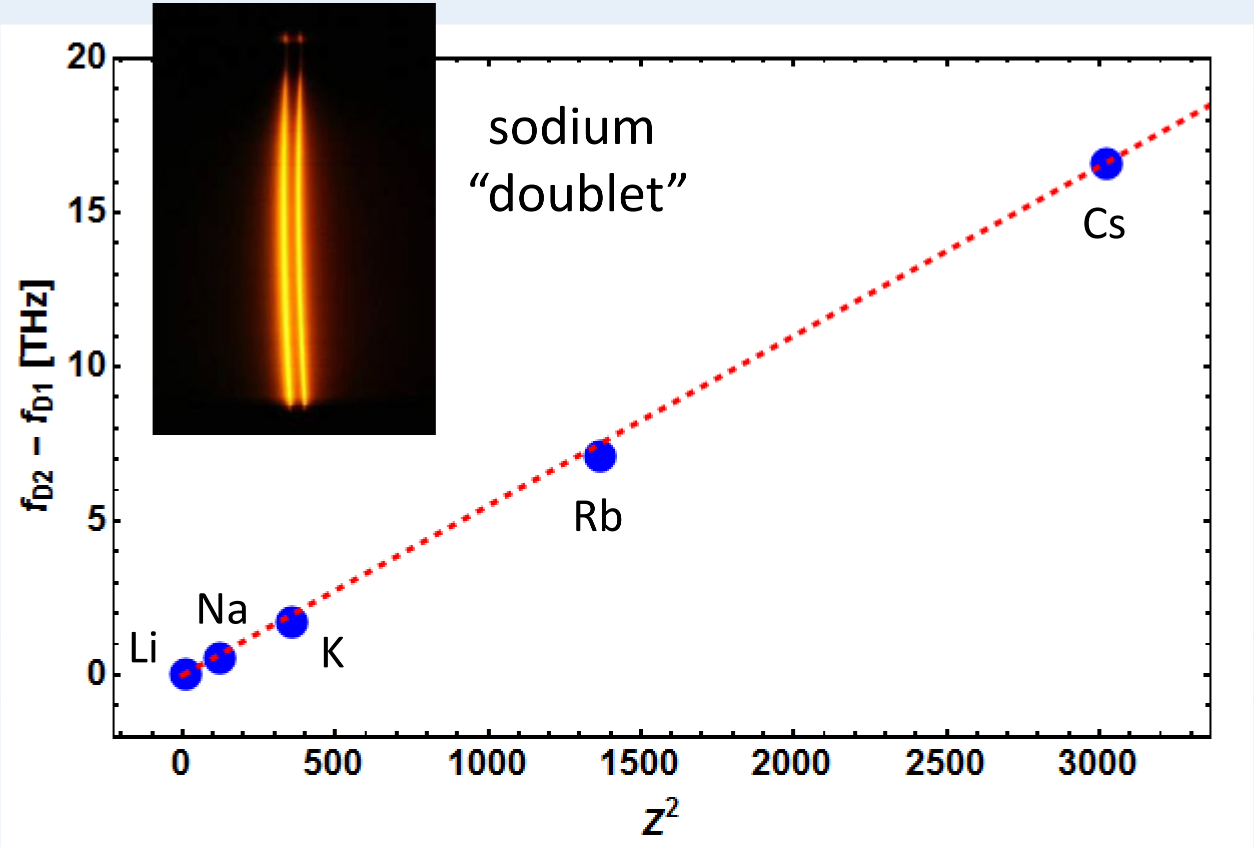
$$Z_o \sim 1$$

Fine structure in the alkalis

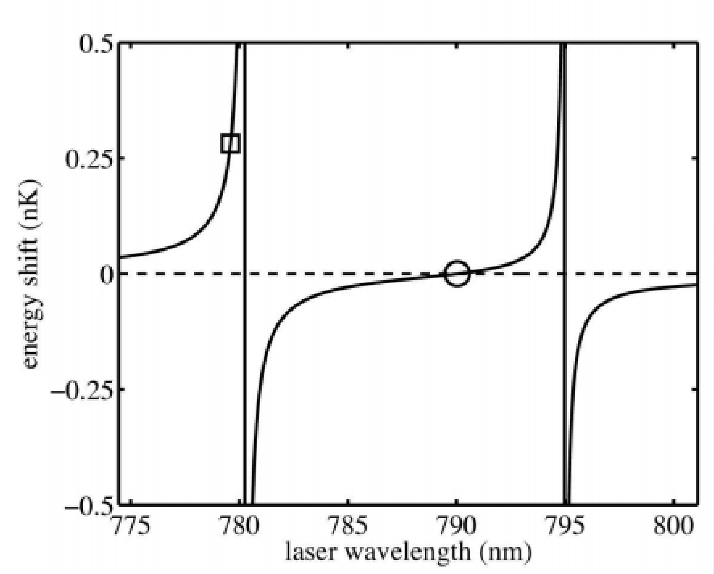
See how well this scaling works $\Delta E_{s-o} \propto Z^2$

	$\Delta E_{s-o} / h$
Li	10.056 GHz
Na	516 GHz
K	1730 GHz
Rb	7123 GHz
Cs	16,610 GHz
Fr	50,562 GHz

Frequency splitting between "D1" and "D2" lines



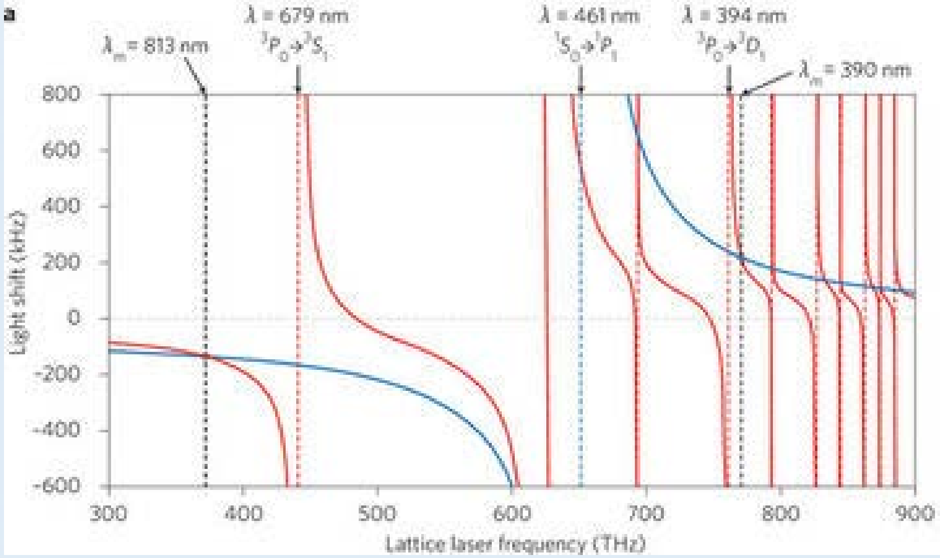
What can this splitting be good for?



Control of polarizability by tuning between D1 and D2 optical transitions

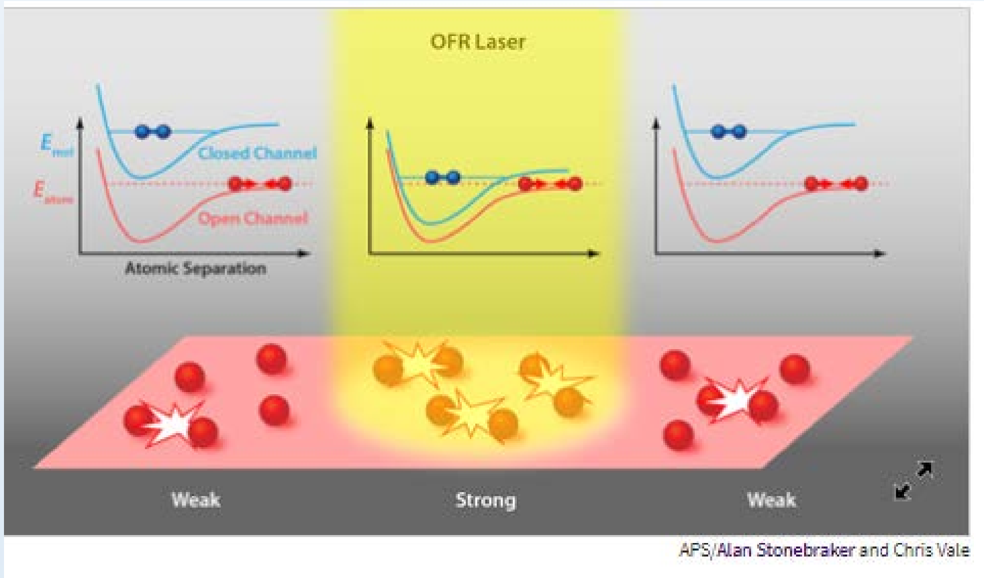
LeBlanc

Polarizability matching in optical atomic clocks



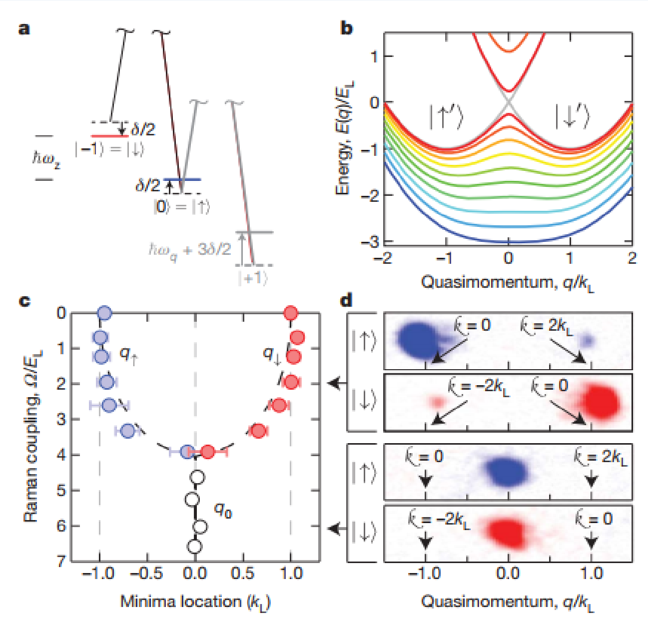
Katori, Ye

Why this splitting matters?

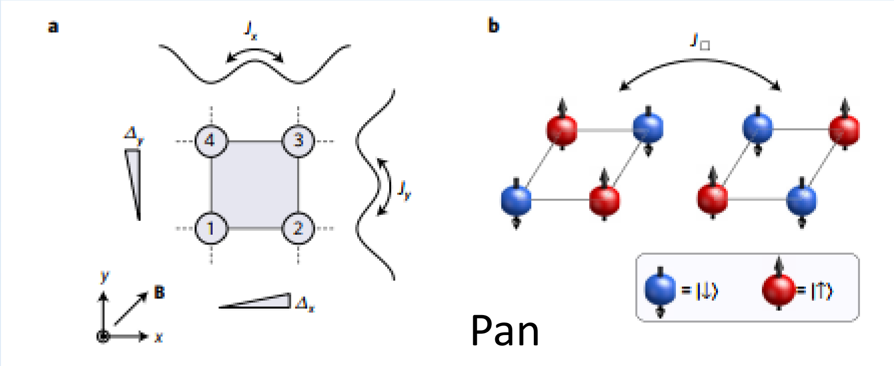


APS/Alan Stonebraker and Chris Vale

Chin



Spielman



Pan

Spin-dependent potentials and Raman-dressing

Fine structure in the alkalis

See how well this scaling works $\Delta E_{s-o} \propto Z^2$