

I think this is the correct interpretation of the fact that ~~Ψ~~ for example $\Psi_a(v_1) \Psi_a(v_2)$ just isn't in the symmetrized wave function.

↳ but maybe other argument is needed. No, it seems right.

How could one cause a collapse to one electron in a state?
For inner electrons the right projectile — a fast electron or X-ray maybe.

12) ATOMS

a) — Hartree & Hartree-Fock and other many-body methods allow us to understand atoms i.e., atomic structure — how forces and QM make them what they are.

5-298)

One key point is that neutral atoms are rather stable.

— One may ask why?

— Many aspects, but one is that Nature has wrapped up a ^{tight} lump of positive charge in the nucleus bound by the nuclear force.

$$r_{\text{nucleus}} \approx r_0 A^{1/3} \quad \text{for } A \geq 20$$

RMS

charge
radius,

$$r_0 = 1.2 - 1.5 \text{ fm}$$

$$1 \text{ fm} = 10^{-15} \text{ m}$$

No hard edge - there's a probability density that declines to zero

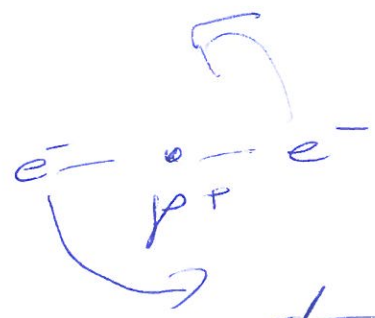
as $r \rightarrow \infty$

The nucleus of charge Ze can obviously tightly ~~bound~~ bind charge of $-e$

(i.e., one electron)

but it can bond tightly up
to $-Ze$ and even
beyond to negative ions.

A crude classical picture shows
how



angular momentum
keeps from
collapse
— but in QM also
the uncertainty Principle

So arrangement not just
amounts of ~~charge~~ +ve & -ve
change is important.

since $l=0$
(or s
states
exist)
too.

On a grander scale consider
a lump of metal.

It stays tightly bound
& even if badly non-neutral.
— They don't just fall
apart if they lose or gain

5-300) a few electrons

b) Atomic size scale

- it is much bigger than nuclear scale which $\sim 1 \text{ fm}$
- but again no hard edge.
- there's a probability density for electrons that declines to zero as $r \rightarrow \infty$.
- Various characteristic radii can be define.

A basic one is the Bohr radius

$$a_{\text{Bohr}} = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = \frac{\hbar}{m_e c \alpha} = \frac{\lambda_c}{2\pi\alpha} = .529177... \text{ \AA}$$

$$\left[\begin{aligned} \alpha &= \frac{e^2}{4\pi\epsilon_0 (\hbar c)} && \text{is the fine structure constant.} \\ &\hat{=} \frac{1}{137} && \text{- The dimensionless strength of the electromagnetic force} \end{aligned} \right]$$

~~where~~
and $\lambda_c = \frac{h}{m_e c}$

is the electron Compton wavelength

The Bohr radius follows from the exact solution of H-atom in infinite-mass nucleus approximation.

depression

It would interesting to have general approximate derivation of the characteristic atomic radius — but it takes a few steps

i) Virial Theorem (Gr-190)

Consider observable $\sum_i \mathbf{r}_i \cdot \mathbf{p}_i$ and general time evolution equation

$$\frac{d\langle Q \rangle}{dt} = \frac{i}{\hbar} \langle [H, Q] \rangle + \left\langle \frac{\partial Q}{\partial t} \right\rangle \quad (\text{Gr-117})$$

5-302

$$\frac{d\langle \underline{r} \cdot \underline{p} \rangle}{dt} = \frac{1}{\hbar} \langle i[H, \underline{r} \cdot \underline{p}] \rangle + 0$$

$$[H, \underline{r} \cdot \underline{p}] = [T, \underline{r} \cdot \underline{p}] + [V, \underline{r} \cdot \underline{p}]$$

$$= \frac{-\hbar^2}{2m} \frac{\rho^2}{\rho x_i \rho x_i} x_j p_j + V \underline{r} \cdot \underline{p}$$

$$- \left(-\frac{\hbar^2}{2m} x_j p_j \frac{\rho^2}{\rho x_i \rho x_i} \right) - \underline{r} \cdot \underline{p} V$$

$$= \cancel{\frac{\hbar^2}{2m} \left(\frac{\rho^2}{\rho x_i} \right)}$$

$$= \cancel{\frac{\hbar^2}{2m} \left[\dots \right]}$$

using general Leibniz rule

$$= -\frac{\hbar^2}{2m} \left(\frac{\hbar}{i} \right) \left(0 + 2 \delta_{ij} \frac{\rho}{\rho x_i \rho x_j} + x_j \frac{\rho^3}{\rho x_i \rho x_j \rho x_j} \right)$$

$$- x_j \frac{\rho^3}{\rho x_i \rho x_i \rho x_j}$$

$$+ \frac{\hbar}{i} \left(V x_i \frac{\rho}{\rho x_i} - x_i \left(\frac{\rho V}{\rho x_i} \right) - x_i V \frac{\rho}{\rho x_i} \right)$$

$$= \frac{\hbar}{i} 2T + \frac{\hbar}{i} (-x_i) \frac{\rho V}{\rho x_i}$$

$$= \frac{\hbar}{i} [2T - \psi \cdot \nabla V]$$

(5-303)

$$\therefore \frac{d\langle \psi \cdot p \rangle}{dt} = 2\langle T \rangle - \langle \psi \cdot \nabla V \rangle$$

If we have the special case
of a stationary state,

$$\langle \psi \cdot p \rangle = \int \psi^* e^{+iEt/\hbar} \psi \cdot p \psi e^{-iEt/\hbar} dV$$

= Constant
independent
of time.

and

$$2\langle T \rangle = \langle \psi \cdot \nabla V \rangle \quad (\text{Gr-190})$$

$$\text{or} \quad \langle T \rangle = \frac{1}{2} \langle \psi \cdot \nabla V \rangle$$

(there is a classical
analogy that
eludes me
at the
moment)

$$\text{If } V = V_0 \left(\frac{r}{r_0} \right)^n$$

9 { No arbitrary
constants added
on.

5-304)

then $\hat{r} \cdot \nabla V$

$$= \frac{r}{r_0} \left(\frac{\partial V}{\partial r} \hat{r}, 0 \hat{\theta}, 0 \hat{\phi} \right)$$

$$= r \hat{r} \cdot V_0 \frac{r^{q-1}}{r_0^q} \hat{r}$$

$$= V_0 \frac{r^q}{r_0^q}$$

$$= \frac{q}{q} V \quad \text{which is valid even if } q=0$$

In this special case

$$\langle T \rangle = \frac{q}{2} \langle V \rangle$$

If $q=2$ as for 3-d harmonic oscillator

$$\langle T \rangle = \langle V \rangle$$

If $q=-1$ as for an inverse-square law force

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle$$

In a crude approximation

$$\langle T \rangle = \frac{1}{2} \langle \dot{r} \cdot \nabla V \rangle$$

gives to

$$|\langle T \rangle| \approx \frac{1}{2} \frac{v_{ch}}{\Delta v_{ch}} |\langle V \rangle|$$

v_{ch}
and
 Δv_{ch}
for
potential

actually
 $\langle T \rangle \geq 0$
always

and often $|\langle T \rangle| \approx |\langle V \rangle|$

which is true for
power law potentials.

ii) Now we quantize

$\frac{1}{2} \langle V \rangle \approx$ ~~scribble~~ $\langle T \rangle = \frac{\langle p^2 \rangle}{2m}$

$$\approx \frac{\sigma_p^2}{2m}$$

$$\sigma_{p_i}^2 \approx \frac{2m |\langle V \rangle|}{3 \cdot 2}$$

$$\approx \frac{3 \sigma_{p_i}^2}{2m}$$

ith
coordinate

Now $\sigma_{x_i}^2 \sigma_{p_i}^2 \geq \left(\frac{\hbar}{2}\right)^2$ (Gr - III)
Heisenberg

$$\sigma_{x_i}^2 \frac{m}{3} |\langle V \rangle| \approx \left(\frac{\hbar}{2}\right)^2$$

uncertainty
principle

5-306

Maybe $\Delta V_{ch}^2 \approx 3 e^2$

$$\Delta V_{ch}^2 \left(\frac{m}{3}\right) | \langle V \rangle | \approx \left(\frac{\hbar}{2}\right)^2$$

for the bound state,

$$\Delta V_{ch}^2 \approx \frac{\hbar^2}{\frac{m}{3} | \langle V \rangle |}$$

$$\Delta V_{ch} \geq \frac{\hbar}{\sqrt{\frac{m}{3} | \langle V \rangle |}}$$

For a ~~Hydrogen~~ hydrogenic Coulomb force

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$| \langle V \rangle | \leq \frac{Ze^2}{4\pi\epsilon_0 \Delta V_{ch}}$$

$$\Delta V_{ch}^2 \approx \frac{\hbar^2}{\frac{m}{3} \frac{Ze^2}{4\pi\epsilon_0 \Delta V_{ch}}}$$

$$\Delta V_{ch} \approx \frac{4\pi\epsilon_0 \hbar^2}{\left(\frac{m}{3}\right) Ze^2} = \frac{a_{Bohr}}{\left(\frac{1}{3}\right) Z}$$

Given the crudity
of our approximations
the $\frac{1}{Z}$ factor is
insignificant.

The smallest state is given by
the equality, and so

- lowest energy
state
- most
tightly
bound

$$\Delta V_{ch} \approx \frac{4\pi\epsilon_0\hbar^2}{\mu Z e^2} = \frac{a_{\text{Bohr}}}{Z}$$

This confirms that the
innermost shell of an atom
should order

$$\Delta V_{ch} \sim \frac{a_{\text{Bohr}}}{Z}$$

{ In electrons
are packed
in.

and the outermost ~~unbound~~
electron that is screened
from the nucleus by
~~then~~ $-(Z-1)e$ of charge,
should have $\Delta V_{ch} \sim a_{\text{Bohr}}$

5-308

Our crude argument suggests that atomic radii (however defined) should not vary strongly

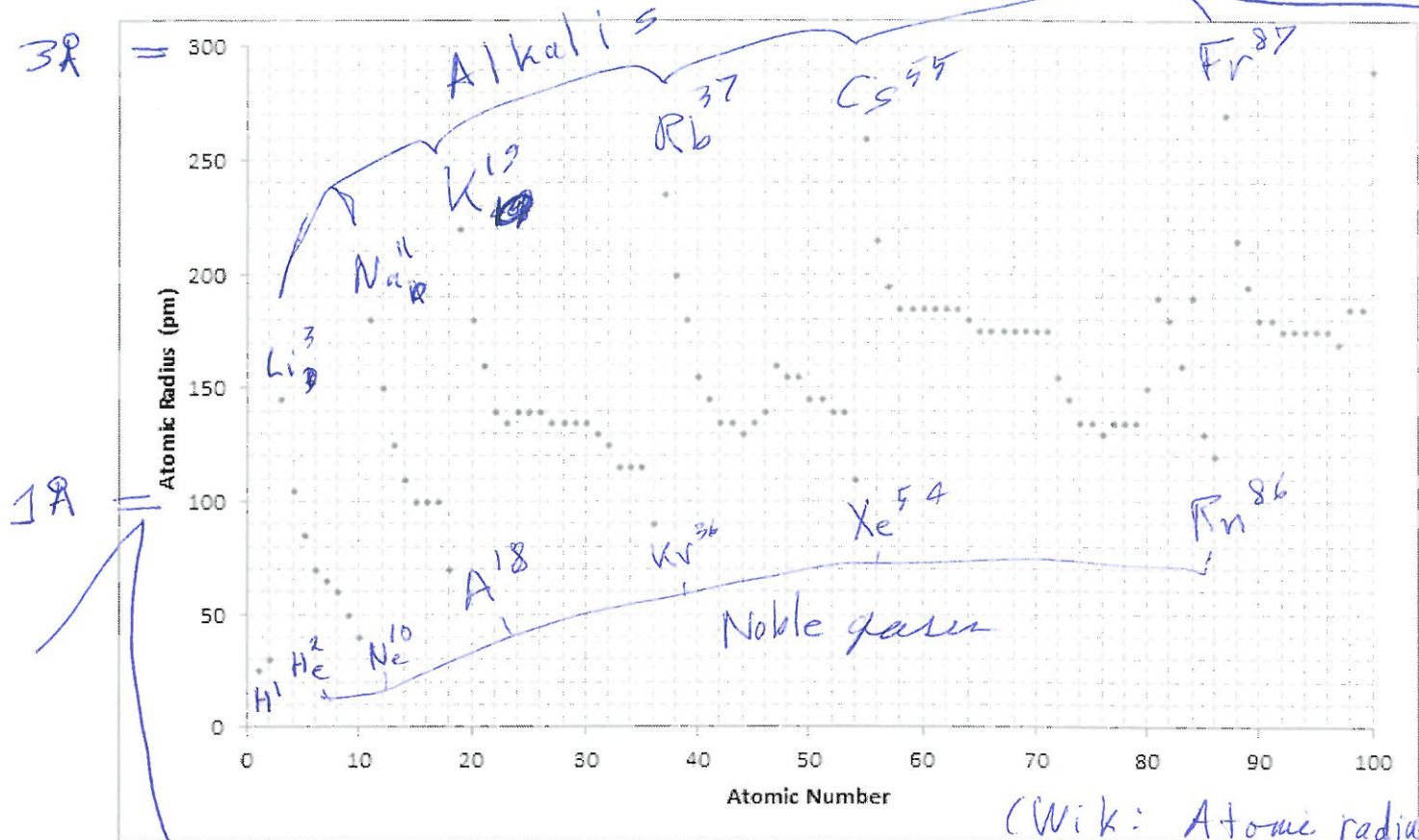
— bigger atoms have more electrons, but the higher nuclear charge compacts them.

So we have a suggestion that all atoms have a size scale of order

$$\sim a_{\text{Bohr}} \sim 1 \text{ \AA}$$

and this turns out to be case.

5-309



(Wik: Atomic radius)
also Baym-452

Calculated radii (Wik)

but the definition is not specified.

error = $\pm 5 \text{ pm} = \pm .05 \text{ \AA}$

— Maybe where electron probability density starts to decline exponentially?

By most definitions of atomic radius, isolated atoms have

r in range

.3 Å to 3 Å.

(Wik Atomic radius)

~~But~~ so factor of 10

But in Volume the size range is a factor of $\sim 10^3 = 1000$

5-310)

13) Electronic Configuration of Atoms

→ This is the specification of the single-particle states that make up the ground state of an atom ~~and~~ in the common way of speaking ~~are the lowest energy~~ ~~and~~ these states are occupied by ~~electrons~~ ^(which we must adopt) one electron each.

→ actually all electrons are in superpositions of states

but it is true that the each state only occurs once in the product states that are summed to create the ground state.

too long
- long
to say
all the
time.

The lowest energy single-particle states are all occupied to create the ground state.

~~and this~~

— The Pauli exclusion principle forbids multiple occupancy of single-particle states and so the electrons cannot all bunch into the lowest energy state as bosons could.

↳ this is $n=0, l=0, m=0$
 $m_s=0$
 — If spinless electrons ~~bosons~~ all compacted into this lowest energy state, ^{very} atoms would all be tightly bound & spherically symmetric.
 — Chemistry might be impossible

\$-312

The specification terminology & designations
are traditional and best
exhibited by building up the
Periodic Table

periodic trend
is one reason for
name. (Wik)

period is also
another name for
now in this context.

First note single-particle state
energy increasing with
principal quantum number n
(Just as for Hydrogenic
atom)

~~Second~~ $n = 1, 2, 3, 4, 5, 6, 7$

— Each n specifies a shell.

— the shells have traditional
letters too which (for some
reason) are

$n = 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7$

Shell
designations

K L M N O P Q

↑
as
high
as we
need

(Allen-92)

Each shell as n subshells 5-313

(which some books like Baym - 451 call ~~shells~~ these shells)

These are distinguished by angular quantum number l

$$l = 0, 1, 2, 3, \dots, n-1$$

+ traditional symbols

$l = 0$	1	2	3	4	5	6
s	p	d	f	g	h	i

because $n=7$ is highest $l \leq 6$ in fact in nature no more.

For a hydrogenic atom, the subshell states are all degenerate (i.e., have the same energy)

9-314

But in ~~fact~~ general atoms
energy of state increases
with l

Handwaving reason

— the larger l , the more
of the probability of state
is at larger radius
and is ~~less~~ more
screened from nucleus
and thus less tightly
bound (Baym-453)

Handwaving
~~since~~ since
it doesn't
seem like
~~an~~ a full
argument
one needs
some argument
about Y_{lm} shapes
did say.

That energy increases with l
makes the filling of the
lowest states (or ~~the~~ orbitals)
tricky since it sets
up a competition of n and l 's
as we'll ~~see~~ see.

For inner filled ^{subshells} ~~shells~~ (5-3/4)

the orbitals of common
 n, l are all degenerate
(or nearly so anyways)

↳ these are distinguished
by $\begin{pmatrix} m \\ m_s \end{pmatrix}$ quantum numbers

m is z -component of
angular momentum

m_s is spin quantum number

What sets z direction
for an atom?

This is unspeakable.

My guess is maybe some part
or present external magnetic
field collapses overall wavefunction
to orientated relative to it.

— Probably fluctuating in dense environments,
(but no textbooks delve into this obvious point.)

5-356

Resistant energy

The ~~unfilled~~ outer subshell takes special consideration as we will see.



closed

All

~~full~~ subshells that are not the

outermost subshell

are rather inert

chemically and magnetically



their total angular momentum quantum number $J=0$

their total ^{orbital} angular quantum number $L=0$

their total spin quantum number $S=0$

Capitals used for totals

eigen
function
numbers
capitals

I think they give a spherically symmetric electron probability density — to high approximation anyway

Proof? Baym - 456 states

$J, L, S = 0$ and

the proof is unspeakable.

(5-317)

— but I imagine you

construct a joint $J_{op}^2, L_{op}^2, S_{op}^2$
observables ^{for a subshell} and show that
the eigenvalues are all zero.

What if the outermost
(highest energy) subshell
is closed?

If it is p subshell

or the $n=1, s$ subshell,

then the atom is chemically
rather inert \rightarrow it's
a noble gas.

Other atoms that have
an outermost closed subshell
are not chemically inert

5-318)

even though they must be rather spherically symmetric in electron density.

There must be something about the change from p subshell to d subshell that requires a big jump in energy.

Something about the shape of the Y_{2m} 's, $Y_{2,0}$, $Y_{2,2}$, $Y_{2,-2}$, $Y_{2,1}$, $Y_{2,-1}$, for p and d .

I don't think this point is unspeakable. Some textbook must say why — just not the ones I've looked at

Periodic table run thru

5-319

<u>element</u>	<u>Z</u>	<u>Configuration</u>
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H	1	(1s) ↑ ↑ n=1 l=0
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He	2	(1s) ² } Not a power but indication of 2 electrons in the 1s subshell.
----	---	--

Now $n=1$

doesn't have

$l=2$ or p orbitals, and

so the jump to the next

Z is to the $n=2$ shell with a large increase in energy.

So it makes sense that

He is a noble gas,

— highly unreactive and tightly bound.

— it and all noble gases can form ionic molecules (WIK)

— Ar, Kr, Xe, Rn can form neutral molecules (WIK)

5-320

- all noble gases ~~form~~
are reactive enough
to form liquids & solids
at low enough T and
high enough pressure

Li $Z = 3$

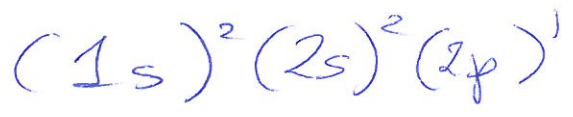


Be $Z = 4$



↗
outermost
subshell is closed
but Beryllium is still
very reactive

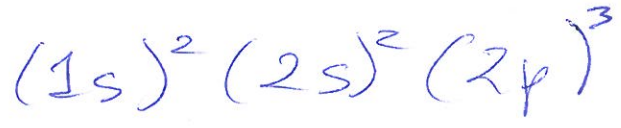
B $Z = 5$



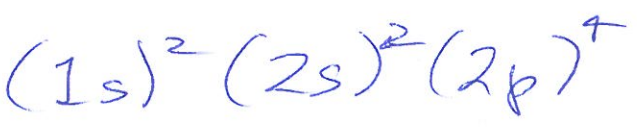
C $Z = 6$



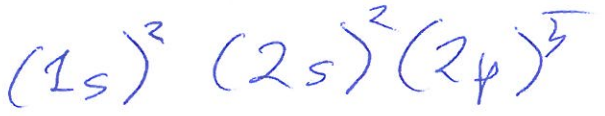
N $Z = 7$



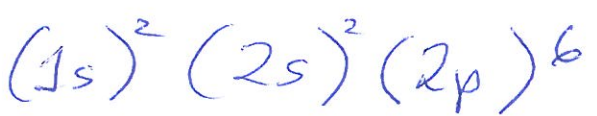
O $Z = 8$



F $Z = 9$



Ne $Z = 10$



Now one might logically think the next electron would go into the $n=2$

5-32

$n=2$ has no d states and so we must make a big jump in energy to $n=3$

Na	$Z=11$	$(\text{Ne})(3s)^1$	closed outer shell But still very reactive
Mg	$Z=12$	$(\text{Ne})(3s)^2$	
Al	$Z=13$	$(\text{Ne})(3s)^2(3p)^1$	
Si	$Z=14$	$(\text{Ne})(3s)^2(3p)^2$	
P	$Z=15$	$(\text{Ne})(3s)^2(3p)^3$	
S	$Z=16$	$(\text{Ne})(3s)^2(3p)^4$	
Cl	$Z=17$	$(\text{Ne})(3s)^2(3p)^5$	
Ar	$Z=18$	$(\text{Ne})(3s)^2(3p)^6$	

Now at this point the next electron should ~~go to the~~ ^{print a} _{facie}

5-322)

go into the 3d subshell.

But for whatever reason } lots of
the energy jump to } screening
the 3d subshell
is so large

that the 4s subshell
has a lower energy

↳ But still so high that
Ar is a noble gas

K.	Z=19	(Ar)(4s)	{ closed outer subshell But Not inert
Ca	Z=20	(Ar)(4s) ²	
Sc	Z=21	(Ar)(4s) ² (3d)	

Now the 3d subshell
starts getting ~~full~~
filled
— it outcompetes the 4p
subshell.

~~For~~

5-323

In forming the periodic table it was found ~~or~~ useful to end each row with a noble gas and begin on with the filling of an s subshell

1	H							He	
2	Li	Be		B	C	N	O	F	Ne
3	Na	Mg		Al	Si	P	S	Cl	Ar

We only need 8 columns for the first 3 rows.

But in the 4th row we start filling the (3d) subshell

→ d is $l = 2$
and so has $2(2l+1) = 10$ orbitals.

So the idea is to stick them in between where the (4s) subshell fills and the (4p) starts to fill.

5-324

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	H																		He
2	Li	Be											B	C	N	O	F		Ne
3	Na	Mg											Al	Si	P	S	Cl		Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe					Ga	Ge	As	Se	Br		Kr
			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn							

filling 4f shell

and no history decided
on an 18 column periodic table.

This works fine for now too.

One fills the (5s) subshell (2 electrons)

then the (4d) subshell (10 electrons)

then the 5p subshell (8 electrons)

ending on Xe with

configuration $(Kr)(5s)^2(4d)^{10}(5p)^6$

But $n=4$ has $l=0, 1, 2, 3$
s p d f

so when does the 4f subshell

get filled?

5-325

In the 6th row.

But that means
we'd need more
columns
an f shell has

$$2(2 \cdot 3 + 1) = 14 \text{ orbitals.}$$

So if in the 6th row we go
~~we fill (5s)~~

Cs	$z = 55$	$(Xe)(6s)$	
Ba	$z = 56$	$(Xe)(6s)^2$	
{	Ld	$z = 57$	$(Xe)(6s)^2(5d)$
	Ce	$z = 58$	$(Xe)(6s)^2(5d)(4f)$
{	Lu	$z = 71$	$(Xe)(6s)^2(5d)(4f)^{14}$

→ rare earths or Lanthanides

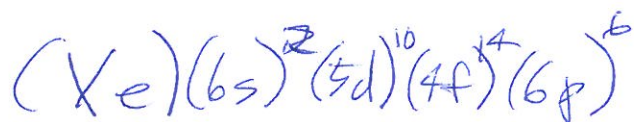
then finish filling the (5d) ~~shell~~ subshell
then finish filling the (6p) subshell

5-326

and end the row with

Rn

$Z = 86$



~~★~~

But we don't make
the periodic table 32
columns wide,

— we jump from La⁵⁷
to Hf⁷²

and stick the Lanthanides
below in a separate
little row.

This makes sense for cogency.
— a periodic table with
32 columns is unwisely

and also the ~~(4f)~~ ~~electrons~~

4f electrons are rather deep
in the atom
and so the Lanthanides have

$n=4$ has
 $l=0, 1, 2, 3$
 s, p, d, f
so all
 $n=4$ orbitals
are
occupied
before
 $n=5$ goes up
to $l=4$
g
Apparently
no need

for
5g
electrons

rather similar chemistry } 5-327
and don't need their
own columns.

Then finally now ↓

Fr $Z=87$ $(Rn)(7s)$

Ra $Z=88$ $(Rn)(7s)^2$

{ Ac $Z=89$ $(Rn)(7s)^2(6d)$

{ Th $Z=90$ $(Rn)(7s)^2(6d)^2$

{ Pa $Z=91$ $(Rn)(7s)^2(6d)^3$

{ U $Z=92$ $(Rn)(7s)^2(6d)(5f)^3$

{ \vdots \vdots \vdots
{ ~~M~~r $Z=103$ $(Rn)(7s)^2(6d)(5f)^{17}$

3.6 hour half-life

- so it does collect

electrons and has

chemistry - though

poorly known

actinides

5-328)

Ununocium $Z=118$

— current record highest ~~at~~ Z

$t_{1/2} \cong .89 \text{ ms}$ (Wik)

~~and no $t_{1/2}$~~

— and maybe only 304 \uparrow atoms detected.

— so it's elemental and chemical properties are predicted and hardly likely to even come into play much.

$n=6$ has $l=0, 1, 2, 3, 4, 5$
s p d f g h

$n=5$ has $l=0, 1, 2, 3, 4$
s p d f g

Configuration predicted
~~(Rn) (5f)¹⁴ (6d)¹⁰~~
(Rn) (7s)² (6d)¹⁰ (5f)¹⁴ (7p)⁶

ends with a full p shell and so might be a noble gas

but relativistic effects predict it would form a solid under STP

— Not that we are likely to ever have enough to know (Wik)

never come into

now?

to see

(Wik)

So apparently no need for 5g electrons either.

↳ but maybe in the elements I've skipped they turn up.

Up to element D_6^{104} ($t_{1/2} = 28 \text{ h}$)
the half-life is long enough for electrons to gather and if you had enough of the stuff do chemistry.

But Sg^{106}	$t_{1/2} = 1.9 \text{ min}$	Uut^{113}	$t_{1/2} \approx 20 \text{ ns}$
Bh^{107}	$t_{1/2} = 61 \text{ sec}$	Uug^{114}	$t_{1/2} \approx 2.6 \text{ ns}$
Hs^{108}	$t_{1/2} \approx 10 \text{ s}$	Uup^{115}	$t_{1/2} \approx 220 \text{ ns}$
Mt^{109}	$t_{1/2} \approx 8 \text{ s}$	Uub^{116}	$t_{1/2} \approx 60 \text{ ns}$
Ds^{110}	$t_{1/2} \approx 10 \text{ s}$	Uus^{117}	$t_{1/2} = \begin{cases} 78 \text{ ns} \\ 14 \text{ ns} \end{cases}$
Rg^{111}	$t_{1/2} \approx 20 \text{ s}$	Uuo^{118}	$t_{1/2} = .89 \text{ ns}$
Cn^{112}	$t_{1/2} = 30 \text{ s}$		

5-330)

So these live long enough
to gather electrons

if there are any in
the vacuum conditions
in which they are
created.

— one could do spectroscopy
but
chemical reactions would
be tricky.

— their physical/chemical
properties as materials
are mostly predicted
according to Wigner