

# The Shape of the Periodic Table

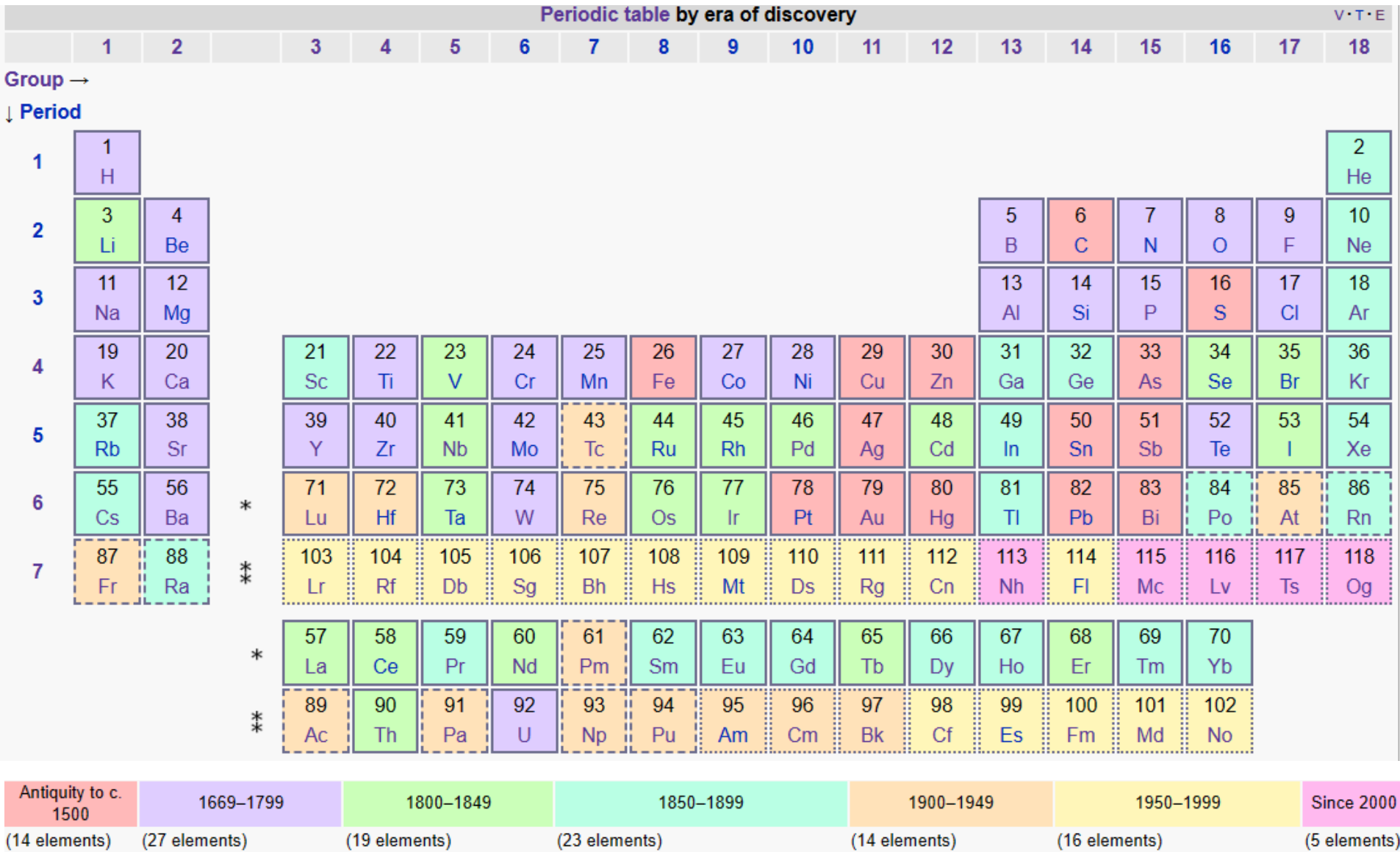
Gavin Jared Bala  
23 February 2022

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	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
Period 5	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
Period 6	55 Cs	56 Ba	* 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
Period 7	87 Fr	88 Ra	* 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			* 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		
			* 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		

# Just a thing to keep in mind

- The two great monuments of early 20<sup>th</sup> century physics are GR and QM
- The mathematical foundations of general relativity were found in the 19<sup>th</sup> century by B. Riemann.
- Quantum mechanics *could* similarly have been found in the 19<sup>th</sup> century: it is a very natural thing to get if you generalise probability theory to allow negative probabilities. (See Scott Aaronson's lecture <https://www.scottaaronson.com/democritus/lec9.html>)
- However, it wasn't

# If you've heard of an element, it was probably discovered very early



# The Schrödinger equation

- $$-\frac{\hbar}{2M} \nabla^2 \psi - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E\psi$$
- $\hbar$  = Planck constant,  $M$  = electron mass,  $\epsilon_0$  = vacuum permittivity,  $Z$  = atomic number,  $r$  = distance to nucleus,  $E$  = energy,  $\psi$  = wavefunction
- Solves using spherical polars
- You get it from a Coulomb potential (see the second term on the LHS!)

# The Schrödinger equation

- $E = E_n = -\frac{\hbar^2 Z^2}{2Ma^2} \cdot \frac{1}{n^2}$
- $n =$  principal quantum number,  $a = \frac{4\pi\epsilon_0\hbar^2}{Me^2}$  Bohr radius
- Corresponding wave function  
$$\psi = \psi_{n,l,m}(r, \theta, \phi) = f_{n,l}(r)e^{-\frac{Zr}{an}}Y_{l,m}(\theta, \phi)$$
- $f_{n,l}$  generalised Laguerre polynomials (degree  $n - 1$ )
- $Y_{l,m}$  spherical harmonics


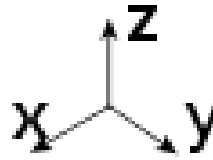












# The four quantum numbers

- $n$  the principal quantum number
- $l \in \{0, 1, \dots, n - 1\}$  the azimuthal quantum number
- $m \in \{-l, -l + 1, \dots, l\}$  the magnetic quantum number
- $s$  (electron spin can be up or down, by Pauli's exclusion principle) – this is a bit of a cheat that you have to tack on. (The proper way to add it is to include relativity, but then you have to solve the Dirac equation instead)

# Spectroscopic notation

- Usually letters are used for the values of  $l$ :
- $l = 0$ :  $s$  for **s**harp
- $l = 1$ :  $p$  for **p**rincipal
- $l = 2$ :  $d$  for **d**iffuse
- $l = 3$ :  $f$  for **f**undamental
- Beyond that it goes alphabetically:  $g, h, i, \dots$
- A choice of  $n$  gives a **shell**, a choice of  $(n, l)$  a **subshell**, and a choice of  $(n, l, m)$  an **orbital**



$l$ :		$P_l^m(\cos\theta) \cos(m\varphi)$							$P_l^{ m }(\cos\theta) \sin( m \varphi)$						
0	<b>s</b>														
1	<b>p</b>														
2	<b>d</b>														
3	<b>f</b>														
4	<b>g</b>														
5	<b>h</b>														
6	<b>i</b>														
	$m$ :	6	5	4	3	2	1	0	-1	-2	-3	-4	-5	-6	

# Filling up the states by $n$

- $2 \times 1^2 = 2$ : H-He
- $2 \times 2^2 = 8$ : Li-Ne
- $2 \times 3^2 = 18$ : Na-Ni?
- $2 \times 4^2 = 32$ : Cu-Nd??
- $2 \times 5^2 = 50$ : Pm-Ds???
- Firstly, nickel coins don't disappear in a puff of logic
- We also have degeneracy problems (which state with a given  $n$  fills first?), but the fact that the order is certainly not by  $n$  past Ar is a more pertinent question
- (By the way,  $Z = 0$  the free neutron is not an element – to be a *chemical* element you need to have *chemistry*, which means you need to have *electrons*)

# The real ordering by $n + l$

- States fill in order of increasing  $n + l$
- When two states have the same value of  $n + l$ , the one with smaller  $n$  fills first
- Largest energy gaps occur just before each new value of  $n$
- The periodic table lists elements in this order (mostly – we'll come back to where it sometimes does not)!
- $1s \ll 2s < 2p \ll 3s < 3p \ll 4s < 3d < 4p \ll 5s < 4d < 5p \ll 6s < 4f < 5d < 6p \ll 7s < 5f < 6d < 7p \ll 8s < 5g < \dots$



Erwin Madelung  
(1881-1972)  
found it first  
1926

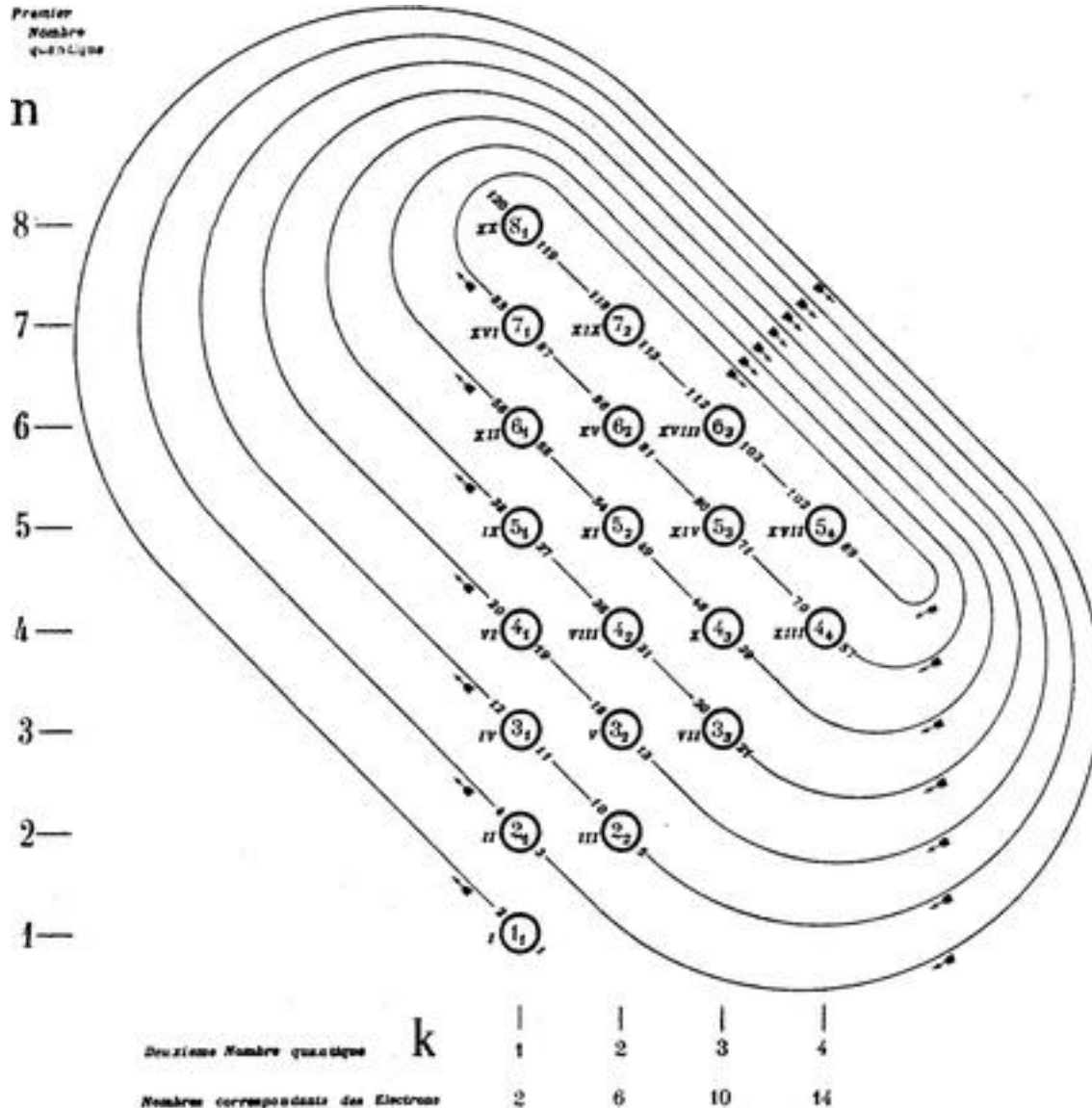


Vladimir Karapetoff  
(1876-1948)  
published it first  
1930



Vsevolod Klechkovsky  
(1900-1972)  
explained it first  
1961

# Charles Janet (1849-1932)



*Concordance de l'arrangement quantique de base des électrons planétaires des atomes avec la classification scalariforme hélicoïdale des éléments chimiques. Beauvais Imprimerie Départementale de l'Oise, Beauvais (1930)*

# Janet's left-step periodic table

- Each row is one value of  $n + l$
- Well-illustrates the parity difference (secondary periodicity)
- Orbitals in odd rows are kainosymmetric (first of each kind of orbital is smaller than usual because of lack of repulsion from core orbitals with same angular distribution), or have larger nuclear charge because of insertion of new kind of orbital.
- So even rows are more electropositive, prefer higher oxidation states, more metallic, while odd rows differ the other way.
- However, the biggest energy gap happens when a new value of  $n$  appears, so often the table is drawn with the s-block on the left end

	f <sup>1</sup>	f <sup>2</sup>	f <sup>3</sup>	f <sup>4</sup>	f <sup>5</sup>	f <sup>6</sup>	f <sup>7</sup>	f <sup>8</sup>	f <sup>9</sup>	f <sup>10</sup>	f <sup>11</sup>	f <sup>12</sup>	f <sup>13</sup>	f <sup>14</sup>	d <sup>1</sup>	d <sup>2</sup>	d <sup>3</sup>	d <sup>4</sup>	d <sup>5</sup>	d <sup>6</sup>	d <sup>7</sup>	d <sup>8</sup>	d <sup>9</sup>	d <sup>10</sup>	p <sup>1</sup>	p <sup>2</sup>	p <sup>3</sup>	p <sup>4</sup>	p <sup>5</sup>	p <sup>6</sup>	s <sup>1</sup>	s <sup>2</sup>			
	1s																														H	He			
	2s																														Li	Be			
	2p	3s																								B	C	N	O	F	Ne	Na	Mg		
	3p	4s																								Al	Si	P	S	Cl	Ar	K	Ca		
	3d	4p	5s												Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr			
	4d	5p	6s												Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba			
4f	5d	6p	7s	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra
5f	6d	7p	8s	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og	119	120
	f-block														d-block										p-block						s-block				

# THE PERIODIC TABLE OF THE CHEMICAL ELEMENTS

The properties of the elements and their compounds vary periodically with atomic number

Is	IIs												IIIp	IVp	Vp	VIp	VIIp	VIIIp	
1	1 <b>H</b> 1.008	2 <b>He</b> 4.003																	
2	3 <b>Li</b> 6.94	4 <b>Be</b> 9.012											5 <b>B</b> 10.81	6 <b>C</b> 12.01	7 <b>N</b> 14.01	8 <b>O</b> 16.00	9 <b>F</b> 19.00	10 <b>Ne</b> 20.18	
3	11 <b>Na</b> 22.99	12 <b>Mg</b> 24.31	III d	IV d	V d	VI d	VII d	VIII d	IX d	X d	XI d	XII d	13 <b>Al</b> 26.98	14 <b>Si</b> 28.09	15 <b>P</b> 30.97	16 <b>S</b> 32.06	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95	
4	19 <b>K</b> 39.10	20 <b>Ca</b> 40.08	21 <b>Sc</b> 44.96	22 <b>Ti</b> 47.87	23 <b>V</b> 50.95	24 <b>Cr</b> 52.00	25 <b>Mn</b> 54.94	26 <b>Fe</b> 55.85	27 <b>Co</b> 58.93	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.55	30 <b>Zn</b> 65.38	31 <b>Ga</b> 69.72	32 <b>Ge</b> 72.63	33 <b>As</b> 74.92	34 <b>Se</b> 78.97	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80	
5	37 <b>Rb</b> 85.47	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.91	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.91	42 <b>Mo</b> 95.95	43 <b>Tc</b> 96.91	44 <b>Ru</b> 101.1	45 <b>Rh</b> 102.9	46 <b>Pd</b> 106.4	47 <b>Ag</b> 107.9	48 <b>Cd</b> 112.4	49 <b>In</b> 114.8	50 <b>Sn</b> 118.7	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 131.3	
6	55 <b>Cs</b> 132.9	56 <b>Ba</b> 137.3	† 71 <b>Lu</b> 175.0	72 <b>Hf</b> 178.5	73 <b>Ta</b> 181.0	74 <b>W</b> 183.8	75 <b>Re</b> 186.2	76 <b>Os</b> 190.2	77 <b>Ir</b> 192.2	78 <b>Pt</b> 195.1	79 <b>Au</b> 197.0	80 <b>Hg</b> 200.6	81 <b>Tl</b> 204.4	82 <b>Pb</b> 207.2	83 <b>Bi</b> 209.0	84 <b>Po</b> 209.0	85 <b>At</b> 210.0	86 <b>Rn</b> 222.0	
7	87 <b>Fr</b> 223.0	88 <b>Ra</b> 226.0	‡ 103 <b>Lr</b> 266.1	104 <b>Rf</b> 267.1	105 <b>Db</b> 268.1	106 <b>Sg</b> 269.1	107 <b>Bh</b> 270.1	108 <b>Hs</b> 277.2	109 <b>Mt</b> 278.2	110 <b>Ds</b> 281.2	111 <b>Rg</b> 282.2	112 <b>Cn</b> 285.2	113 <b>Nh</b> 286.2	114 <b>Fl</b> 289.2	115 <b>Mc</b> 290.2	116 <b>Lv</b> 293.2	117 <b>Ts</b> 294.2	118 <b>Og</b> 294.2	

s-block
p-block
d-block
f-block

State at 40°C, 1 atm:

**C**

Solid

**C**

Liquid

**C**

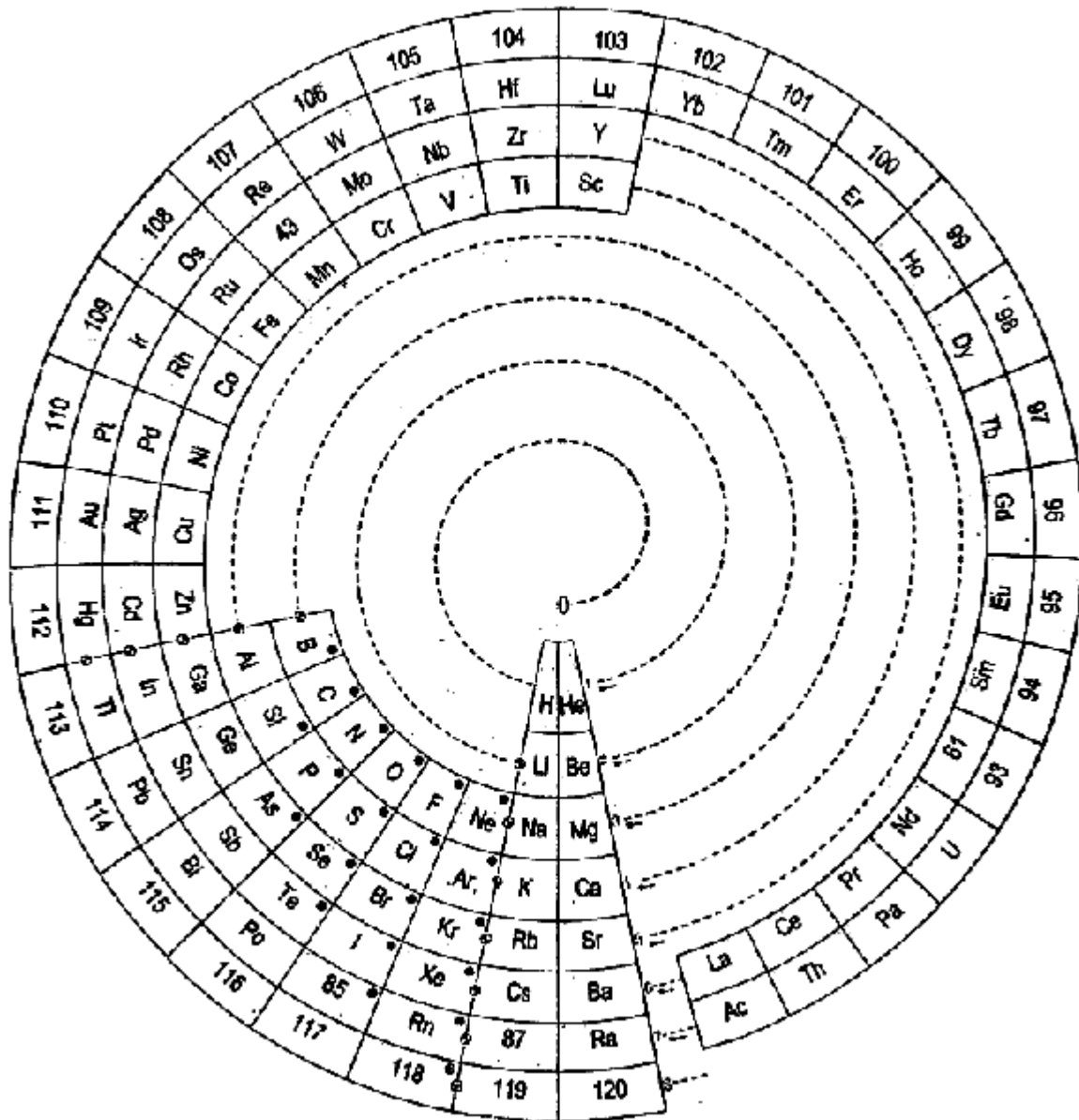
Gas

Atomic number
<b>Symbol</b>
Relative atomic mass

	III f	IV f	V f	VI f	VII f	VIII f	IX f	X f	XI f	XII f	XIII f	XIV f	XV f	XVI f
†	57 <b>La</b> 138.9	58 <b>Ce</b> 140.1	59 <b>Pr</b> 140.9	60 <b>Nd</b> 144.2	61 <b>Pm</b> 144.9	62 <b>Sm</b> 150.4	63 <b>Eu</b> 152.0	64 <b>Gd</b> 157.3	65 <b>Tb</b> 158.9	66 <b>Dy</b> 162.5	67 <b>Ho</b> 164.9	68 <b>Er</b> 167.3	69 <b>Tm</b> 168.9	70 <b>Yb</b> 173.1
‡	89 <b>Ac</b> 227.0	90 <b>Th</b> 232.0	91 <b>Pa</b> 231.0	92 <b>U</b> 238.0	93 <b>Np</b> 237.0	94 <b>Pu</b> 244.1	95 <b>Am</b> 243.1	96 <b>Cm</b> 247.1	97 <b>Bk</b> 247.1	98 <b>Cf</b> 251.1	99 <b>Es</b> 252.1	100 <b>Fm</b> 257.1	101 <b>Md</b> 258.1	102 <b>No</b> 259.1

by G. J. Bala

# The table's really a spiral (Janet 1928)



- Charles Janet, *La Classification Hélicoïdale des Éléments Chimiques*. Beauvais: Imprimerie Départementale de l'Oise. 1928





# Is it perfect?

- If you look at atoms by themselves, not necessarily
- 20 elements have the wrong configuration
- But the excitation energy needed to get the right configuration is always  $< 4$  eV...
- ...and chemical bond energies in practice can go up to 10 eV ( $\text{C}\equiv\text{O}$ ; it's not just nonmetals, Th-O is  $\sim 8$  eV).
- Chemistry is concerned with atoms bonding with each other, not atoms sitting around by themselves filing their metaphorical fingernails
- **We may approximate with a clear conscience!**
- Modern chemical understanding agrees with the mathematics: the orbital that should be filling is always valent.

# All the anomaly energies (from various sources)

<b>Cr</b> ( $3d^5 5s^1 \rightarrow 3d^4 4s^2$ )	<b>Cu</b> ( $3d^{10} 4s^1 \rightarrow 3d^9 4s^2$ )	<b>Nb</b> ( $4d^4 5s^1 \rightarrow 4d^3 5s^2$ )	<b>Mo</b> ( $4d^5 5s^1 \rightarrow 4d^4 5s^2$ )
Exc: 0.96097009 IE: 6.76651	Exc: 1.388948 IE: 7.726380	Exc: 0.141688 IE: 6.75885	Exc: 1.3596041 IE: 7.09243
<b>Ru</b> ( $4d^7 5s^1 \rightarrow 4d^6 5s^2$ )	<b>Rh</b> ( $4d^8 5s^1 \rightarrow 4d^7 5s^2$ )	<b>Pd</b> ( $4d^{10} 5s^0 \rightarrow 4d^8 5s^2$ )	<b>Ag</b> ( $4d^{10} 5s^1 \rightarrow 4d^9 5s^2$ )
Exc: 0.927782 IE: 7.36050	Exc: 1.577460 IE: 7.45890	Exc: 3.1121565 IE: 8.336839	Exc: 3.7495671196 IE: 7.576234
<b>La</b> ( $4f^0 5d^1 \rightarrow 4f^1 5d^0$ )	<b>Ce</b> ( $4f^1 5d^1 \rightarrow 4f^2 5d^0$ )	<b>Gd</b> ( $4f^7 5d^1 \rightarrow 4f^8 5d^0$ )	<b>Pt</b> ( $5d^9 6s^1 \rightarrow 5d^8 6s^2$ )
Exc: 1.884167 IE: 5.5769	Exc: 0.5905018 IE: 5.5386	Exc: 1.3572811 IE: 6.14980	Exc: 0.10212092 IE: 8.95883
<b>Au</b> ( $5d^{10} 6s^1 \rightarrow 5d^9 6s^2$ )	<b>Ac</b> ( $5f^0 6d^1 \rightarrow 5f^1 6d^0$ )	<b>Th</b> ( $5f^0 6d^2 \rightarrow 5f^2 6d^0$ )	<b>Pa</b> ( $5f^2 6d^1 \rightarrow 5f^3 6d^0$ )
Exc: 1.1358412 IE: 9.225554	Exc: 3.873287 IE: 5.380235	Exc: 3.409018576 IE: 6.30670	Exc: 1.6141027 IE: 5.89
<b>U</b> ( $5f^3 6d^1 \rightarrow 5f^4 6d^0$ )	<b>Np</b> ( $5f^4 6d^1 \rightarrow 5f^5 6d^0$ )	<b>Cm</b> ( $5f^7 6d^1 \rightarrow 5f^8 6d^0$ )	<b>Lr</b> ( $6d^0 7p^1 \rightarrow 6d^1 7p^0$ )
Exc: 0.8704575 IE: 6.19405	Exc: 0.3510168 IE: 6.26554	Exc: 0.1505421 IE: 5.99141	Exc: 0.1650 (predicted) IE: 4.96

# Sources

- Data from NIST (elements up to Th), *The Chemistry of the Actinide and Transactinide Elements* (Pa, U, Np, Cm), and S. Fritzsche; C. Z. Dong; F. Koike; A. Uvarov (2007). *The low-lying level structure of atomic lawrencium ( $Z = 103$ ): energies and absorption rates.*, *45(1)*, 107–113. doi:10.1140/epjd/e2007-00136-3 for Lr

# The challenge of Eugen Schwarz

- If you look at the periodic table going from left to right, then  $4s$  fills before  $3d$
- But if you build up a transition metal atom from scratch, then it is the opposite way round!
- $\text{Sc} = [\text{Ar}]3d^14s^2$
- $\text{Sc}^+ = [\text{Ar}]3d^14s^1$
- $\text{Sc}^{2+} = [\text{Ar}]3d^14s^0$
- $\text{Sc}^{3+} = [\text{Ar}]3d^04s^0$

# How big are the differences?

- $\text{Sc} = [\text{Ar}]3d^1 4s^2$
- $\text{Sc}^+ = [\text{Ar}]3d^1 4s^1$ , but  $[\text{Ar}]3d^0 4s^2$  is only at 1.455 eV
- $\text{Sc}^{2+} = [\text{Ar}]3d^1 4s^0$ , but  $[\text{Ar}]3d^0 4s^1$  is only at 3.166 eV
- For titanium I'd agree,  $\text{Ti}^{2+}$  needs 12.729 eV to be  $[\text{Ar}]3d^0 4s^2$ . But still,  $[\text{Ar}]3d^1 4s^1$  (losing one 4s and one 3d) is only 4.719 eV
- It then becomes a huge energy difference even for the very first step.

# Why this is irrelevant

- This is not comparing like with like.
- $4s$  does fill before  $3d$  when it comes to neutral atoms
- The “bare-ion sequence” would have us consider the K isoelectronic sequence  $K^0$ ,  $Ca^+$ ,  $Sc^{2+}$ ,  $Ti^{3+}$ ,  $V^{4+}$ ,  $Cr^{5+}$  ...
- No one claimed that the  $(n + l, n)$  rule applies for highly charged ions (such charges are not *truly* found in chemistry due to strong ligand-to-metal charge transfer) – see the later derivation: the Coulomb potential is valid at short and long (Rydberg) distances, but not in the middle of the electron cloud due to repulsion!
- Did you know that  $Pu^{6+}$  as a bare ion is  $[Hg]6p^5 5f^3$ ? (But it never uses the  $6p$  electrons for real chemistry.)

# T. Titze's potential

- $$U_{\mu}(r) = -\frac{2v}{r^2 R^2 \left[ \left(\frac{r}{R}\right)^{\mu} + \left(\frac{R}{r}\right)^{\mu} \right]^2}$$
- $\mu, v, R$  constant parameters.
- (In the case  $\mu = 1$ , this is James Clerk Maxwell's *fish-eye potential*, useful in optics)
- This is an *approximate* solution to the Thomas-Fermi model (basically, see the electron cloud as a degenerate Fermi-Dirac fluid in hydrostatic equilibrium between electrostatic forces and the pressure gradient)
- You can see why I don't have a slide on that



# The observation of Yu. N. Demkov and V. N. Ostrovsky (1971)

- If the quantisation condition

$$v = v_N = R^2 \mu^2 \left( N + \frac{1}{2\mu} \right) \left( N + \frac{1}{2\mu} - 1 \right)$$

- is satisfied, with  $N = n + (\mu^{-1} - 1)l$ , then this equation can be solved analytically with regular solutions decreasing at infinity!
- The case we care about is clearly  $\mu = \frac{1}{2}$ .
- If you choose  $R$  such that  $\frac{2v_N}{R^3} = Z_N$ , then we recover the Coulomb potential as  $r \rightarrow 0$ .
- This is why highly charged atoms act like hydrogen.

# The solution

$$\psi_{n,l,m} = \left(\frac{r}{R}\right)^l \left[ \left(\frac{r}{R}\right)^{2\mu} + 1 \right]^{-\frac{2l+1}{2\mu}} C_{n-l-1}^{\frac{2l+1}{2\mu} + \frac{1}{2}} \left( \frac{R^{2\mu} - r^{2\mu}}{R^{2\mu} + r^{2\mu}} \right) Y_{l,m}(\theta, \phi)$$

- The  $C_n^\alpha$  are the **Gegenbauer polynomials** which solve the differential equation

$$(1 - x^2)y'' - (2\alpha + 1)xy' + n(n + 2\alpha)y = 0$$

- They satisfy the recurrence

$$C_0^\alpha(x) = 1$$

$$C_1^\alpha(x) = 2\alpha x$$

$$C_n^\alpha(x) = \frac{1}{n} [2x(n + \alpha - 1)C_{n-1}^\alpha(x) + (n + 2\alpha - 2)C_{n-2}^\alpha(x)]$$

# At last, the rule derived

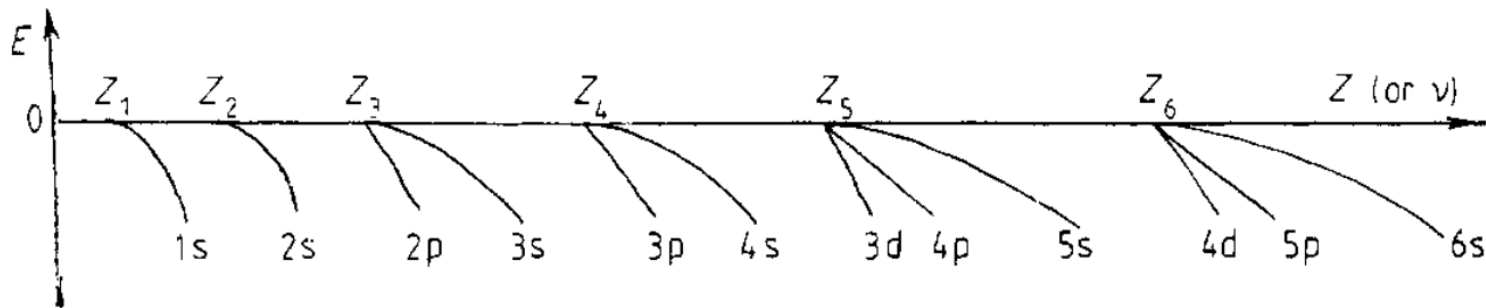
- We suppose  $\mu = \frac{1}{2}$ .
- For each value of  $N = n + l$ , the zero-energy states that arise from choosing the relevant  $v_N$  form precisely the states of that  $n + l$  value.
- As we increase  $v$  beyond that, those states become bound, until the next set of states pass through zero energy at  $v_{N+1}$ .
- **This recovers the first part of the rule.**

# ...well, partially

- You need to do more work to get the second and third parts of the rule, but it likewise follows from this solution.
- It is all done in Demkov and Ostrovsky's 1971 paper using perturbation theory to account for the difference between the potential for  $Z$  and that for  $Z_N$ . One gets the **second part** of the rule, that energies of states increase with increasing  $n$ .
- Moreover the perturbations are largest for the  $s$  orbitals where  $l = 0$ , so much so that their energies are raised to approach that of the next  $n + l$  value, giving the **third part** of the rule.

# Plotting energies!

- V. N. Ostrovsky (1981), *Dynamic symmetry of atomic potential*. Journal of Physics B: Atomic and Molecular Physics, 14(23)



**Figure 1.** A schematic plot of the energy levels in potential (4) as a function of potential strength  $\nu$ .

# A heuristic argument

- William Wiswesser (1945) gave a nice heuristic argument for the second part that you can teach kids in their first chemistry class without drowning them in calculus.
- Essentially, electrons in lower- $n$  orbitals experience a higher effective nuclear charge, as they spend more time in closer vicinity to the nucleus, and should be expected to have lower energies.

# A small issue regarding this potential

- By Bertrand's theorem, the *only* force laws that guarantee stable systems (where launching a body at less than some escape velocity always brings you to a closed orbit in a 2-body problem) are proportional to  $r$  (classical Hooke's law, QM spherical oscillator) or  $r^{-2}$  (classical gravitation/Coulomb, QM Schrödinger atom).
- Classically there is a conserved quantity; in QM you have operators commuting with the Hamiltonian, that form a Lie algebra
- This potential is not of either form. This is aggravating because the rule really suggests that there is some kind of force law, but Bertrand says there cannot be one...

# The 118-Fold Way

- There is still some further work going on to understand this further, even though Demkov and Ostrovsky already showed some kind of consistency with QM.
- The idea is like the Eightfold Way in physics: just as families of baryons are treated as simply different states of one quantum system, so all chemical elements should somehow be treated as one



# A sequence of Lie groups

- Transformations between elements are given by a Lie group (a group that is also a differentiable manifold), and the periodic table arises by breaking it into a chain of subgroups.
- In fact one needs to *generalise* the notion of Lie group, as the symmetry break from hydrogenic atoms to the situation with the Madelung rule (coming from interelectronic repulsion) creates a nonlinearity.
- You can read more in Thyssen and Ceulemann's textbook *Shattered Symmetry* and their chapter in *Mendeleev to Oganesson*.

# Adding special relativity

- We've taken a non-relativistic view (so spin is kind of naughtily tacked on to our QM model – it naturally arises with a finite speed of light)
- In the elements we have it causes quantitative but not qualitative differences (energy gaps between orbitals change, but they still participate when you'd think they should)
- This is the reason why sixth-row elements are often different from fifth-row elements – the effects go like  $Z^4$ . (Mercury is liquid!)
- Seventh row should be even weirder – flerovium (the element below lead) should be a liquid metal!

# Spin-orbit coupling

- In relativistic quantum mechanics, you solve the Dirac equation, not the Schrödinger equation
- Spin-orbit coupling:  $s$  and  $l$  are no longer good quantum numbers (they don't correspond to stationary states), but  $j = s + l$  is fine.
- You get orbitals corresponding to half-integers instead of integers – each orbital type is split into stabilised and destabilised types, e.g.  $p_{1/2}$  vs  $p_{3/2}$ ,  $d_{3/2}$  vs  $d_{5/2}$ ... ( $s_{1/2}$  exceptional)
- [Just because you have the same half-integer does not mean you are really degenerate, there is the Lamb shift. But enough for our purposes!]

# Resulting superheavy weirdness

- The large split  $7p_{1/2}$ - $7p_{3/2}$  turns flerovium into an unreactive liquid, and oganesson into a metal like Sn (four valence electrons) – they basically swapped places!
- Nihonium is also quite weird, between two spherical closed shells (like hydrogen actually) – it should be a cross between silver and astatine chemically
- **One-atom-at-a-time chemistry is already possible!**
- In bulk, maybe wait for multiple nuclear explosions like Orion, or more powerful reactor pulses

- White, H. E (1931). Pictorial Representations of the Dirac Electron Cloud for Hydrogen-Like Atoms. Physical Review, 38(3), 513–520.

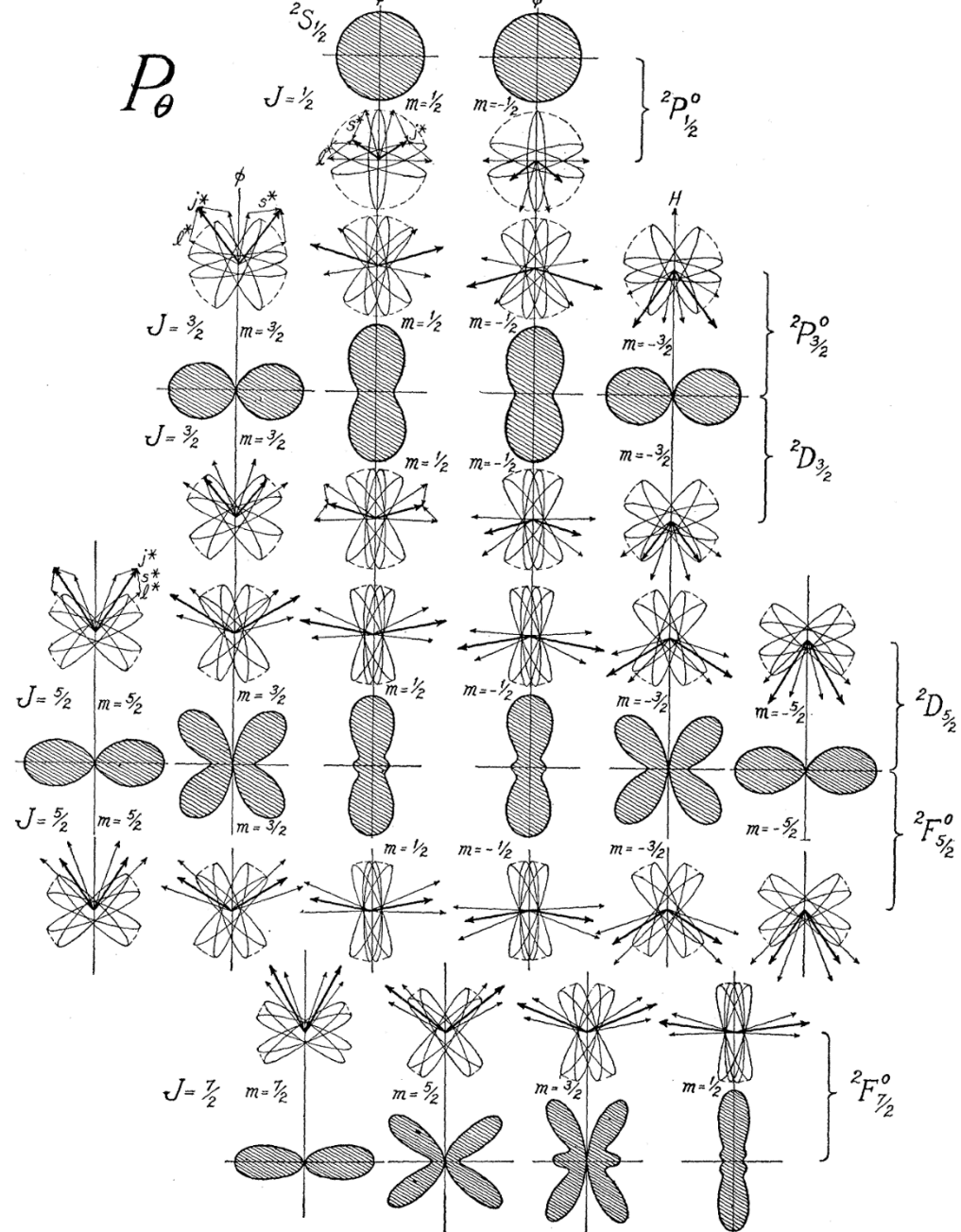
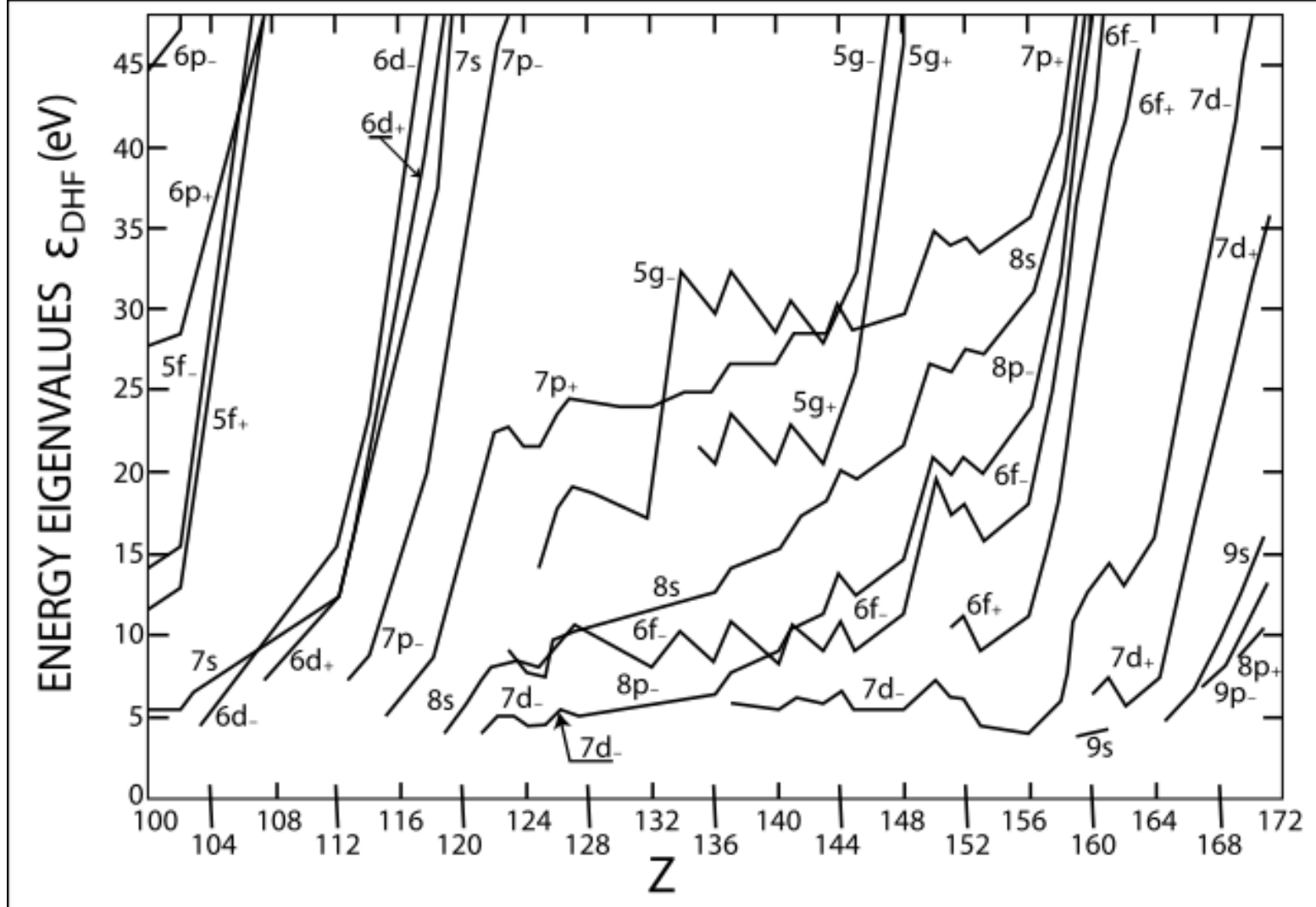


Fig. 2. The angular factor,  $P_\theta$ , of the probability density  $\Psi\Psi^*$  plotted in angular coordinates. Above and below the quantum mechanical electron distributions the corresponding classical electron orbits are shown oriented in each case according to the model  $l^*$ ,  $s^*$ ,  $j^*$  and  $m$ .

# Does the periodic table break down?

- At  $Z = 139$  the system finally breaks
- But we are still only at  $Z = 118$  (Og) and the atoms are getting uselessly unstable anyway
- In fact, the only real problem is that  $5g$  stays open till probably 142 (not 138); then  $6f, 7d, 8p$  follow as normal! So in a certain sense  $n + l$  is still mostly correct!
- (Though the  $5g$  to  $6f$  transition needs further study.)



- Fricke, Burkhard (1975). Superheavy elements: a prediction of their chemical and physical properties. *Recent Impact of Physics on Inorganic Chemistry. Structure and Bonding. Vol. 21. pp. 89–144.*

# ПЕРИОДИЧЕСКАЯ СИСТЕМА ХИМИЧЕСКИХ ЭЛЕМЕНТОВ Д. И. МЕНДЕЛЕЕВА

Свойства атомов химических элементов, а также состав и свойства их соединений находятся в периодической зависимости от заряда атомных ядер

	I A																VIII A				
	1																18				
1	1,00794 <b>1 H</b> ВОДОРОД															4,00260 <b>2 He</b> Гелий					
2	6,941 <b>3 Li</b> Литий															9,01218 <b>4 Be</b> Бериллий					
3	22,9898 <b>11 Na</b> Натрий															24,3050 <b>12 Mg</b> Магний					
4	39,0983 <b>19 K</b> Калий															40,078 <b>20 Ca</b> Кальций					
5	85,4678 <b>37 Rb</b> Рубидий															87,62 <b>38 Sr</b> Стронций					
6	132,905 <b>55 Cs</b> Цезий															137,327 <b>56 Ba</b> Барий					
7	[223] <b>87 Fr</b> Франций															[226] <b>88 Ra</b> Радий					
8	<b>119</b>															<b>120</b>					

101,07 <b>44 Ru</b> Рутений	— Атомная масса
— Атомный номер и химический символ	
— Название элемента	

III B	IV B	V B	VI B	VII B	VIII B		IB	II B	
3	4	5	6	7	8	9	10	11	12
44,9559 <b>21 Sc</b> Скандий	47,867 <b>22 Ti</b> Титан	50,9415 <b>23 V</b> Ванадий	51,9961 <b>24 Cr</b> Хром	54,9380 <b>25 Mn</b> Марганец	55,845 <b>26 Fe</b> Железо	58,9332 <b>27 Co</b> Кобальт	58,6934 <b>28 Ni</b> Никель	63,546 <b>29 Cu</b> Медь	65,38 <b>30 Zn</b> Цинк
88,9058 <b>39 Y</b> Иттрий	91,224 <b>40 Zr</b> Цирконий	92,9064 <b>41 Nb</b> Ниобий	95,96 <b>42 Mo</b> Молибден	[98] <b>43 Tc</b> Технеций	101,07 <b>44 Ru</b> Рутений	102,905 <b>45 Rh</b> Родий	106,42 <b>46 Pd</b> Палладий	107,868 <b>47 Ag</b> Серебро	112,411 <b>48 Cd</b> Кадмий
174,967 <b>71 Lu</b> Лютеций	178,49 <b>72 Hf</b> Гафний	180,948 <b>73 Ta</b> Тантал	183,84 <b>74 W</b> Вольфрам	186,207 <b>75 Re</b> Рений	190,23 <b>76 Os</b> Осмий	192,217 <b>77 Ir</b> Иридий	195,084 <b>78 Pt</b> Платина	196,967 <b>79 Au</b> Золото	200,59 <b>80 Hg</b> Ртуть
[223] <b>87 Fr</b> Франций	[226] <b>88 Ra</b> Радий	[262] <b>103 Lr</b> Лоренций	[267] <b>104 Rf</b> Резерфордий	[270] <b>105 Db</b> Дубний	[271] <b>106 Sg</b> Сборний	[274] <b>107 Bh</b> Борний	[277] <b>108 Hs</b> Хассий	[278] <b>109 Mt</b> Митчерий	[281] <b>110 Ds</b> Дармштадтий
[281] <b>111 Rg</b> Рентгий	[285] <b>112 Cn</b> Коперничий	[286] <b>113 Uut</b>	[289] <b>114 Uuq</b>	[289] <b>115 Uup</b>	[293] <b>116 Uuh</b>	[294] <b>117 Uus</b>	[294] <b>118 Uuo</b>		

138,905 <b>57 La</b> Лантан	140,116 <b>58 Ce</b> Церий	140,908 <b>59 Pr</b> Прометий	144,242 <b>60 Nd</b> Неодим	[145] <b>61 Pm</b> Прометий	150,36 <b>62 Sm</b> Самарий	151,964 <b>63 Eu</b> Европий	157,25 <b>64 Gd</b> Гадолиний	158,925 <b>65 Tb</b> Тербий	162,500 <b>66 Dy</b> Диспрозий	164,930 <b>67 Ho</b> Гольмий	167,259 <b>68 Er</b> Эрбий	168,934 <b>69 Tm</b> Тулий	173,054 <b>70 Yb</b> Иттербий
[227] <b>89 Ac</b> Актиний	232,038 <b>90 Th</b> Торий	231,036 <b>91 Pa</b> Протактиний	238,029 <b>92 U</b> Уран	[237] <b>93 Np</b> Нептуний	[244] <b>94 Pu</b> Плутоний	[243] <b>95 Am</b> Америций	[247] <b>96 Cm</b> Кюрий	[247] <b>97 Bk</b> Берклий	[251] <b>98 Cf</b> Калифорний	[252] <b>99 Es</b> Эйнштейний	[257] <b>100 Fm</b> Фермий	[258] <b>101 Md</b> Менделеев	[259] <b>102 No</b> Нобелий

121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138
139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156



# This is a self-imposed problem

- Anyway, nature does not seem to have elements that high in the first place. Probably spontaneous fission happens before such high  $Z$  is reached in the wild. (Though, Przybylski's star is suspicious...)
- Very weird things may happen that high – it's possible that quark matter is the stable state for baryonic matter at high  $A$ , not binding them into hadrons!
- Something like how van der Waals merges into metallic bonding – compare similar structures of bromine, iodine, gallium, or clusters of mercury atoms. One loses the idea of discrete molecules.
- Or maybe they don't even last long enough to grab an electronic cloud. Who knows right now.

# The group 3 problem

- Everyone's favourite flame war

21
<b>Sc</b>
44.96
39
<b>Y</b>
88.91
71
<b>Lu</b>
175.0
103
<b>Lr</b>
266.1

21
<b>Sc</b>
44.96
39
<b>Y</b>
88.91

21
<b>Sc</b>
44.96
39
<b>Y</b>
88.91
57
<b>La</b>
138.9
89
<b>Ac</b>
227.0

- The middle one is a compromise attempt, but shows a fencepost error (15 *f*-elements when there should be 14)
- It also has multiple elements (La-Lu, Ac-Lr) all sharing the same place...

# What does the rule say?

- According to the  $(n + l, n)$  rule, the  $4f$  orbitals should fill ( $Z = 57-70$ ) before the  $5d$  ( $Z = 71-80$ )
- This immediately settles Sc, Y, Lu, Lr as group 3.
- Confirmed by theoretical modelling of bonding: La and Ac can use their  $f$  orbitals for chemistry, but Lu and Lr cannot. (Known from coordination numbers and symmetry –  $f$  orbitals must be invoked in the linear combinations for La and Ac. Basically, there's no other way to get extreme high coordination numbers or cubic molecular geometry.)

# The first long table

- Alfred Werner (1866-1919) got it right in 1905!



-																-		-									
H																He		4									
1.008																											
Li										Be		B	C	N	O	F	Ne										
7.03										9.1		11	12	14.04	16.00	19	20										
Na										Mg		Al	Si	P	S	Cl	A										
23.05										24.36		27.1	28.4	31.0	32.06	35.45	39.9										
K	Ca											Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.10	40.1											44.1	48.1	51.2	52.1	55.0	55.9	59.0	58.7	63.6	65.4	70	72	75.0	79.1	79.96	81.12
Rb	Sr											Y	Zr	Nb	Mo	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	J	X	
85.4	87.6											89.0	90.7	94	96.0	101.7	103.6	106	107.93	112.4	114	118.5	120	127.6	126.96	128	
Cs	Ba	La	Ce	Nd	Pr	Sa	Eu	Gd	Tb	Ho	Er	Tu	Yb	Ta	W	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi				
133	137.4	139	140	143.6	140.5	150.3	151.79	156	160	162	166	171	173.0	183	184.0	191	193.0	194.8	197.2	200.3	204.1	206.9	208.5				
Ra	La	Th				U					Ac								Pb	Bi	Te						
226	?	232.5				238.5					?								?	?	?						

# A zombie mistake

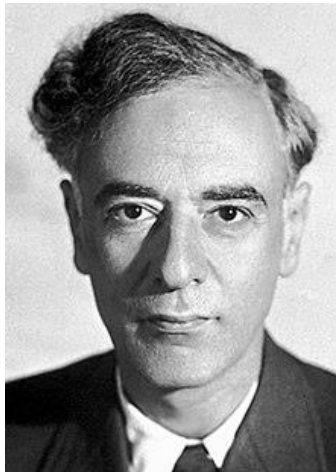


- Friedrich Hund (1896-1997) thought that one  $5d$  electron would fill first, then fourteen  $4f$ , before the  $5d$  continued – because he thought that rare earths only have three valence electrons and that  $4f$  isn't valence
- Turns out, that's all wrong (though it was a good guess for 1927)
- Most of the lanthanide and actinide atoms do not have a  $d$  electron and show exactly the configuration you would expect from the  $(n + l, n)$  rule!
- In any case, energy differences between configurations of  $d$  and  $f$  elements are very low (you can excite them with visible photons i.e. by shining a light on them, or more obviously by chemistry)
- Unfortunately, almost no one noticed when the corrected measurements were made
- Don't be too harsh, he got most of the rest right – but arguments from gas-phase configurations belong to a bygone era

# Landau and Lifshitz did notice

† In books on chemistry, lutetium is also usually placed with the rare-earth elements. This, however, is incorrect, since the  $4f$  shell is complete in lutetium; it must therefore be placed in the platinum group, as in Table 4.

- *Quantum Mechanics: Non-Relativistic Theory*, p. 257 (1948, translation of 1959)



Lev Landau  
(1908-1968)



Evgeny Lifshitz  
(1915-1985)

# 近藤 淳 Jun Kondō

## (1930-2022)



- Noted that La is superconducting at standard pressure, but *not* Sc, Y, Lu

When the band becomes broader,  $T_c$  is lower than that given by this equation. Thus we see that the interband interaction enhances superconductivity when a sharp and dense empty band lies near the Fermi level.

Now it is quite possible that this situation is encountered in lanthanum. This shows a marked increase of the magnetic susceptibility<sup>11)</sup> and the Knight shift<sup>12)</sup> with decreasing temperature. Besides, its electronic heat is large.<sup>13)</sup> From these facts, the  $f$ -bands of lanthanum are supposedly very close to or overlapping the Fermi level. Then it is quite naturally understood by introducing the interband interaction that lanthanum has a high superconducting transition temperature ( $\sim 5^\circ\text{K}$ ), whereas scandium and yttrium are not superconducting

- Kondō, Jun (January 1963). "Superconductivity in Transition Metals". *Progress of Theoretical Physics*. 29 (1): 1–9. doi:10.1143/PTP.29.1.

# Putting two and two together

- Hamilton, David C. (1965). *Position of Lanthanum in the Periodic Table*. *American Journal of Physics*, 33(8), 637-42. doi:10.1119/1.19720

Li 3	Be 4									
Na 11	Mg 12									
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79
Fr 87	Ra 88	Ac 89	104	105						

Ce 58	Pr 59		Lu 71
Th 90	Pa 91		Lw 103

Li 3	Be 4									
Na 11	Mg 12									
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47
Cs 55	Ba 56	Lu 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79
Fr 87	Ra 88	Lw 103	104	105						

La 57	Ce 58		Yb 70
Ac 89	Th 90		No 102





# Good things are worth doing twice

## IUPAC 1988 report (*New notations in the periodic table*)

436

INORGANIC CHEMISTRY DIVISION

### THE ELEMENTS OF THE SCANDIUM GROUP

In the "Red Book" which will appear in 1988 the same arrangement was chosen for the elements of the scandium group as in the periodic table as originally proposed by CNIC and subsequently published by VCH Verlagsgesellschaft, Weinheim.

It is a compromise. According to the electron configurations of the elements, the scandium group consists of the elements

Sc, Y, Lu, Lr.

This was pointed out as early as 1959 by L.D. Landau (ref. 20) and later by other authors (ref. 13, 14, 20 to 25). Most periodic tables in textbooks and classrooms, however, list Sc, Y, La, and Ac as elements of the scandium group and designate the elements Ce to Lu and Th to Lr as lanthanides and actinides, respectively. The historical background for this arrangement is given in a paper by W.B. Jensen (ref. 21). Based upon their electronic configurations and their chemical and physical properties, the elements La to Yb and Ac to No should be inserted between barium and lutetium and between radium and lawrencium or for practical reasons be listed at the bottom of the table. The series La to Yb and Ac to No then, however, cannot be named correctly as lanthanides and actinides since they contain the elements lanthanum and actinium and not only elements similar to lanthanum and actinium as is purported by the ending -ide (or -oid according to an earlier IUPAC recommendation).

# Good things are worth doing twice

## IUPAC 2021 report (*Provisional report on Discussions on Group 3 in the Periodic Table*)

representation masks somewhat. This difference is far more apparent if the periodic table is displayed in an even more expanded 32-column format which incorporates the f-block into the main body of the table.

If Lu and Lr appear in group 3, as they do in figure 4, the d-block consists of a continuous sequence of 10 elements. On the other hand, if group 3 consists of Sc, Y, La and Ac, as it does in figure 1, the d-block rows now appear to be split in a very uneven fashion (fig 5). For example, in period 6 we find La (considered as a d-block element) followed by a sequence of 14 f-block elements from Ce to Lu followed by a sequence of nine d-block elements from Hf to Hg.

The periodic table that is sometimes labeled as “IUPAC periodic table” as shown in figure 3 avoids assigning the 3<sup>rd</sup> and 4<sup>th</sup> members of group 3 altogether, by simply leaving empty spaces below Sc and Y. As a result, the f-block then appears to contain two rows of 15 elements, and thereby violates the simple one-to-one correspondence between orbital capacity as required by the elementary quantum mechanical account of the periodic table.

The only 18-column table that appears to avoid the drawback in the split of the d-block while also maintaining a 14-element-wide f-block is the one shown in figure 2. Needless to say, the assignment of elements to these blocks is approximate, just as the assignment of

electronic configurations to atoms also represents an approximation. Moreover, one may readily concede that an element such as thorium does not actually possess any f-orbital electrons and yet it is classified as being among the f-block elements in all five of the periodic table representations shown in figures 1 to 5.

A student looking at the table shown in figure 3 is bound to wonder whether there is some scientific reason for making the f-block have a width of 15 elements. Neither a student, nor his/her instructors, would probably realize that the table in question has been designed by practitioners of specialized branch of relativistic quantum mechanics concerned with the properties of super-heavy elements [6]. Such interest-dependence should not, in our view, dictate how the periodic table is presented to the general chemical and scientific community.

Perhaps a compromise could be reached on the table depicted as figure 2 since it achieves three *desiderata*. First, it displays all the elements in order of increasing atomic number. Secondly, it avoids splitting the d-block into two highly uneven portions, and thirdly, it depicts all the blocks of the periodic table in accordance with the underlying quantum mechanical account of the periodic table which calls for 2, 6, 10 and 14 orbitals to occur in the extra-nuclear electron-shells.

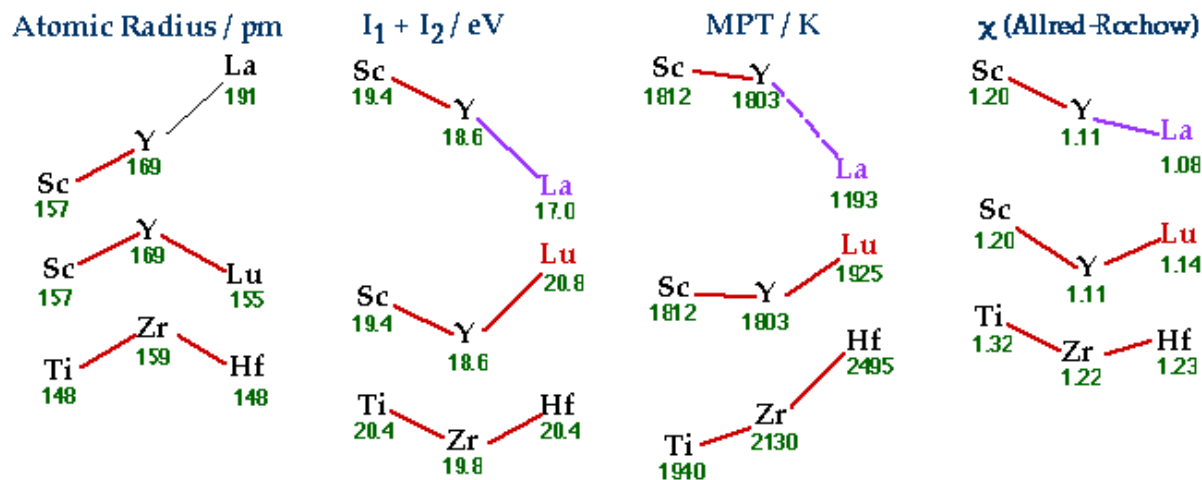
Historical developments have shown that quantum

# Prof. Stephen J. Heyes, Oxford

<http://web.archive.org/web/20130210085720/http://www.chem.ox.ac.uk/icl/heyeyes/lanthact/I5.html>

Some suggestions why **Lu** might best regarded as the **first 5d transition element**.

## • Periodic Trends in Various Properties



## • Structures of **Metal**, Metal Sesquioxide ( $M_2O_3$ ) and Metal Chloride ( $MCl_3$ )

**Similarities for Sc, Y, Lu**

**Differences from La**

# Whither hydrogen and helium?

- If we follow the electron configurations, there is no issue: these fill the  $s$  states (hydrogen  $1s^1$ , helium  $1s^2$ ). Therefore they belong over lithium  $2s^1$  and beryllium  $2s^2$ .
- Yet people are often unwilling to do this, probably because H and He are nonmetals, but Li and Be are strong metals.
- (For H people accept it more, because it does form  $H^+$ , a cornerstone of acid-base chemistry)

# That is irrelevant though



Nitrogen



Phosphorus



Bismuth



Arsenic



Antimony  
All are in group 15...  
As for valence, look one  
column to the right: oxygen  
has no +6, fluorine no +7

# The electronic revolution

- The periodic table as we have it is based firmly on the subshells – which is why some columns start late (there are no transition metals in the first few rows)
- If it were based on stoichiometry, then transition metals would be mixed with main-group elements, because the valences match!

$\text{Na}_2\text{O}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{P}_2\text{O}_5$	$\text{SO}_3$	$\text{Cl}_2\text{O}_7$
$\text{K}_2\text{O}$	$\text{CaO}$	$\text{Sc}_2\text{O}_3$	$\text{TiO}_2$	$\text{V}_2\text{O}_5$	$\text{CrO}_3$	$\text{Mn}_2\text{O}_7$

# Mendeleev's 1871 periodic table

ЕСТЕСТВЕННАЯ СИСТЕМА ЭЛЕМЕНТОВЪ Д. МЕНДЕЛѢЕВА.

Периодъ 1-й. Периодъ 2-й. Периодъ 3-й. Периодъ 4-й. Периодъ 5-й	Группа I.	Группа II.	Группа III.	Группа IV.	Группа V.	Группа VI.	Группа VII.	Группа VIII. (переходъ къ I)				II=I HX	
	Висшій окиселъ образующій соли: $R^2O$ $H=1$ $H^2O, NH, HCl,$ $H^2N, H^2C, ROH.$	$R^2O^2$ или $RO$	$R^2O^3$	$R^2O^4$ или $RO^2$	$R^2O^5$	$R^2O^6$ или $RO^3$	$R^2O^7$	$R^2O^8$ или $RO^4$					
Типичес. Рядъ	<b>Li=7</b> LiCl, LiOH, Li <sup>2</sup> O. LiX, Li <sup>2</sup> CO <sup>2</sup>	<b>Be=9, 4</b> BeCl <sup>2</sup> ; BeO <sub>2</sub> . Be <sup>2</sup> Al <sup>2</sup> Si <sup>6</sup> O <sup>14</sup> ;	<b>B=11</b> BCl <sup>3</sup> ; B <sup>2</sup> O <sup>3</sup> ; BN. B <sup>2</sup> Na <sup>2</sup> O <sup>2</sup> ; BF <sup>3</sup> ;	<b>C=12</b> CH <sup>4</sup> ; C <sup>2</sup> H <sup>2</sup> ; CO <sup>2</sup> . CO <sub>2</sub> ; CO <sup>2</sup> ; CO <sup>2</sup> M <sup>2</sup>	<b>N=14</b> NH <sup>3</sup> ; NH <sup>4</sup> Cl; N <sup>2</sup> O. NO <sub>2</sub> ; NO <sup>2</sup> M; CNM.	<b>O=16</b> OH; H <sup>2</sup> O; C, O <sup>2</sup> O <sup>2</sup> . OM <sup>2</sup> O <sup>2</sup> R, HOR.	<b>F=19</b> FH, BF <sup>3</sup> ; SiF <sup>4</sup> . CaF <sup>2</sup> ; KF, KHF <sup>2</sup> .	<div style="border: 1px solid black; padding: 5px;">           * Тяго твердое, малорастворимое въ водѣ.            △ Тяго газообразное или летучее.            M=K, Ag.... M<sup>2</sup>=Ca, Pb....            X=Cl, ONO<sup>2</sup>; OH, OM.... X<sup>2</sup>=SO<sup>2</sup>; CO<sup>2</sup>; O, S....         </div>					
Рядъ 1.	<b>Na=23</b> NaCl, NaHO, Na <sup>2</sup> O. Na <sup>2</sup> SO <sup>4</sup> ; Na <sup>2</sup> CO <sup>3</sup>	<b>Mg=24</b> MgCl <sup>2</sup> ; MgO, MgCO <sup>3</sup> . MgSO <sup>4</sup> ; MgNH <sup>4</sup> PO <sup>4</sup> ;	<b>Al=27, 3</b> Al <sup>2</sup> Cl <sup>3</sup> ; Al <sup>2</sup> O <sup>3</sup> . KAIS <sup>2</sup> O <sup>2</sup> 12H <sup>2</sup> O.	<b>Si=28</b> SiH <sup>4</sup> ; SiCl <sup>4</sup> ; SiH <sup>2</sup> F <sup>2</sup> . KAIS <sup>2</sup> O <sup>2</sup> ; SiO <sup>2</sup> ;	<b>P=31</b> PH <sup>3</sup> ; PCl <sup>3</sup> ; PCl <sup>5</sup> . P <sup>2</sup> O <sup>3</sup> ; P <sup>2</sup> O <sup>5</sup> ; Ca <sup>2</sup> P <sup>2</sup> O <sup>7</sup> ;	<b>S=32</b> SH <sup>2</sup> ; SM <sup>2</sup> ; S <sup>2</sup> M <sup>2</sup> . SO <sup>2</sup> ; SO <sup>2</sup> X <sup>2</sup> ; Ba <sup>2</sup> SO <sup>4</sup> ;	<b>Cl=35, 5</b> ClH, ClM, ClCl. ClOH, ClO <sup>2</sup> H, AgCl.						
Рядъ 2.	<b>K=39</b> KCl, KOH, K <sup>2</sup> O. KNO <sup>3</sup> ; K <sup>2</sup> PtCl <sup>6</sup> ; K <sup>2</sup> SIF <sup>6</sup> ;	<b>Ca=40</b> CaSO <sup>4</sup> ; CaOnSiO <sup>2</sup> . CaCl <sup>2</sup> ; CaO, CaCO <sup>3</sup> ;	744—Eh?	<b>Ti=48 (50?)</b> TiCl <sup>3</sup> ; TiO <sup>2</sup> ; Ti <sup>2</sup> O <sup>3</sup> . FeTiO <sup>2</sup> ; TiOSO <sup>4</sup> ;	<b>V=51</b> VOCl <sup>3</sup> ; V <sup>2</sup> O <sup>3</sup> ; VO <sup>2</sup> . Pb <sup>2</sup> V <sup>2</sup> O <sup>7</sup> ; VO <sup>2</sup> ;	<b>Cr=52</b> CrCl <sup>3</sup> ; CrCl <sup>2</sup> ; Cr <sup>2</sup> O <sup>3</sup> . CrO <sup>2</sup> ; K <sup>2</sup> CrO <sup>4</sup> ; Cr <sup>2</sup> O <sup>3</sup> Cl <sup>2</sup> ;	<b>Mn=55</b> MnK <sup>2</sup> O <sup>2</sup> ; MnKO <sup>4</sup> . MnCl <sup>2</sup> ; MnO <sub>2</sub> , MnO <sup>2</sup> ;	<b>Fe=56</b> FeK <sup>2</sup> O <sup>2</sup> ; FeS <sup>2</sup> . FeO, Fe <sup>2</sup> O <sup>3</sup> . FeK <sup>2</sup> Cy <sup>6</sup>	<b>Co=59</b> CoX <sup>2</sup> ; CoX <sup>3</sup> . CoX <sup>2</sup> 5NH <sup>2</sup> . Cok <sup>2</sup> Cy <sup>6</sup>	<b>Ni=59</b> NiX <sup>2</sup> ; NiO. NiSO <sup>4</sup> 6H <sup>2</sup> O. NiK <sup>2</sup> Cy <sup>6</sup>	<b>Cu=63</b> CuX, CuX <sup>2</sup> ; CuH. Cu <sup>2</sup> O, CuO. CuKCy <sup>2</sup>		
Рядъ 3.	<b>Cu=63</b> CuX, CuX <sup>2</sup>	<b>Zn=65</b> ZnCl <sup>2</sup> ; ZnO, ZnCO <sup>3</sup> . ZnSO <sup>4</sup> ; ZnEt <sup>2</sup> ;	768—Ei?	772—Es? 711, EsO <sup>2</sup> ?	<b>As=75</b> AsH <sup>3</sup> ; AsCl <sup>3</sup> ; As <sup>2</sup> O <sup>3</sup> . As <sup>2</sup> O <sup>5</sup> ; As <sup>2</sup> S <sup>5</sup> ;	<b>Se=78</b> SeH <sup>2</sup> ; SeO <sup>2</sup> ; SeO <sup>3</sup> . SeM <sup>2</sup> ; SeM <sup>2</sup> O <sup>3</sup> ;	<b>Br=80</b> BrH, BrM, BrO <sup>2</sup> M, BrAg.						
Рядъ 4.	<b>Rb=85</b> RbCl, RbOH. Rb <sup>2</sup> PtCl <sup>6</sup> ;	<b>Sr=87</b> SrCl <sup>2</sup> ; SrO, SrH <sup>2</sup> O <sup>2</sup> . SrSO <sup>4</sup> ; SrCO <sup>3</sup> ;	788—Yt <sup>2</sup> (92) 7Y <sup>2</sup> O <sup>3</sup> ; YX <sup>2</sup> ?	<b>Zr=90</b> ZrCl <sup>4</sup> ; ZrO <sup>2</sup> ; ZrX <sup>4</sup> .	<b>Nb=94</b> NbCl <sup>5</sup> ; Nb <sup>2</sup> O <sup>5</sup> . Nb <sup>2</sup> O <sup>5</sup> ; NbOK <sup>2</sup> F <sup>2</sup> ;	<b>Mo=96</b> MoCl <sup>5</sup> ; MoS <sup>2</sup> ; MoO <sup>3</sup> . M <sup>2</sup> Mo <sup>2</sup> O <sup>4</sup> ; nMoO <sup>2</sup> ;	100	<b>Ru=104</b> RuO <sup>2</sup> ; RuCl <sup>4</sup> . RuO <sup>3</sup> ; RuCl <sup>5</sup> . RuK <sup>2</sup> Cy <sup>6</sup>	<b>Rh=104</b> RhCl <sup>3</sup> ; RhCl <sup>4</sup> . Rh <sup>2</sup> O <sup>3</sup> ; RhX <sup>2</sup> . RhK <sup>2</sup> Cy <sup>6</sup>	<b>Pd=106</b> PdH, PdO. PdI <sup>2</sup> ; PdCl <sup>2</sup> . PdK <sup>2</sup> Cy <sup>6</sup>	<b>Ag=108</b> AgNO <sup>3</sup> ; AgX. AgCl, Ag <sup>2</sup> O. AgKCy <sup>2</sup>		
Рядъ 5.	<b>Ag=108</b> AgX, AgCl.	<b>Cd=112</b> CdCl <sup>2</sup> ; CdO, CdS. CdSO <sup>4</sup> ;	<b>In=113</b> InCl <sup>3</sup> ; In <sup>2</sup> O <sup>3</sup> ;	<b>Sn=118</b> SnCl <sup>4</sup> ; SnCl <sup>2</sup> ; SnO. SnX <sup>2</sup> ; SnNa <sup>2</sup> O <sup>2</sup> ;	<b>Sb=122</b> SbH <sup>3</sup> ; SbCl <sup>3</sup> ; Sb <sup>2</sup> O <sup>3</sup> . Sb <sup>2</sup> O <sup>5</sup> ; Sb <sup>2</sup> S <sup>5</sup> ; SbOX	<b>Te=125 (128?)</b> TeH <sup>2</sup> ; TeCl <sup>4</sup> ; TeO <sup>2</sup> . TeO <sup>2</sup> M <sup>2</sup> ; TeM <sup>2</sup> ;	<b>I=127</b> IH, IAg, IHO <sup>2</sup> . IHO <sup>2</sup> ; HgI <sup>2</sup> ; KI						
Рядъ 6.	<b>Cs=133</b> CsCl, CsOH. Cs <sup>2</sup> PtCl <sup>6</sup> ;	<b>Ba=137</b> BaCl <sup>2</sup> ; BaH <sup>2</sup> O <sup>2</sup> ; BaO. BaSO <sup>4</sup> ; BaSiF <sup>6</sup> ;	?188—La?—Di?(144) ?La <sup>2</sup> O <sup>3</sup> ; LaX <sup>2</sup> ?	<b>Ce=140 (138?)</b> CeCl <sup>3</sup> ; Ce <sup>2</sup> O <sup>3</sup> ; CeO <sup>2</sup> . CeX <sup>2</sup> ; CeX <sup>3</sup> ; CeK <sup>2</sup> X <sup>2</sup> ;	142	146	148	150	151	152	153		
Рядъ 7.	153	158	160	162	164	166	168						
Рядъ 8.	175	177	?17—Er? <sup>109</sup> ?Er <sup>2</sup> O <sup>3</sup> ; ERX <sup>2</sup> ?	?180—Di?—La(187) ?DIO <sup>2</sup> ; DiX <sup>2</sup> ?	<b>Ta=182</b> TaCl <sup>5</sup> ; Ta <sup>2</sup> O <sup>5</sup> . Tak <sup>2</sup> F <sup>2</sup> ;	<b>W=184</b> WCl <sup>6</sup> ; WCl <sup>5</sup> ; WO <sup>2</sup> . K <sup>2</sup> W <sup>2</sup> O <sup>7</sup> ; nWO <sup>2</sup> ;	190	199?	<b>Os=193</b> OsO <sup>2</sup> ; OsH <sup>2</sup> O <sup>2</sup> . OsCl <sup>3</sup> ; OsCl <sup>4</sup> . OsK <sup>2</sup> Cy <sup>6</sup>	198?	<b>Ir=195</b> K <sup>2</sup> IrCl <sup>6</sup> ; IrCl <sup>3</sup> . IrCl <sup>4</sup> ; Ir <sup>2</sup> O <sup>3</sup> . IrK <sup>2</sup> Cy <sup>6</sup>	<b>Pt=197</b> PtCl <sup>2</sup> BO <sup>2</sup> . PtCl <sup>4</sup> ; Pt <sup>2</sup> X <sup>2</sup> . PtK <sup>2</sup> Cy <sup>6</sup>	<b>Au=197</b> AuCl <sup>3</sup> ; AuCl. Au <sup>2</sup> O <sup>2</sup> ; Au <sup>2</sup> O. AuKCy <sup>2</sup>
Рядъ 9.	<b>Au=197</b> AuX, AuX <sup>2</sup>	<b>Hg=200</b> HgCl <sup>2</sup> ; HgCl <sup>2</sup> ; Hg <sup>2</sup> O. HgO, HgX <sup>2</sup> ; nHgO	<b>Tl=204</b> TlCl <sup>3</sup> ; Tl <sup>2</sup> O, Tl <sup>2</sup> O <sup>2</sup> . Tl <sup>2</sup> SO <sup>4</sup> ; TlCl <sup>3</sup>	<b>Pb=207</b> PbCl <sup>2</sup> ; PbO, PbO <sup>2</sup> . PbEt <sup>2</sup> ; PbSO <sup>4</sup> ; PbK <sup>2</sup> O <sup>2</sup> ;	<b>Bi=208</b> BiCl <sup>3</sup> ; Bi <sup>2</sup> O <sup>3</sup> ; Bi <sup>2</sup> O <sup>5</sup> ; H <sup>2</sup> . BiX <sup>2</sup> ; BiOX, BiNO <sup>2</sup> (HO) <sup>2</sup> ;	210	212						
Рядъ 10.	220	225	227	<b>Th=231</b> ThCl <sup>4</sup> ; ThO <sup>2</sup> . ThX <sup>4</sup> ; Th(SO <sup>4</sup> ) <sup>2</sup> ;	235	<b>U=240</b> UCI <sup>4</sup> ; UO <sup>2</sup> ; UO <sup>2</sup> X <sup>2</sup> . UO <sup>2</sup> M <sup>2</sup> O <sup>2</sup> ;	245	246	248	249	250		



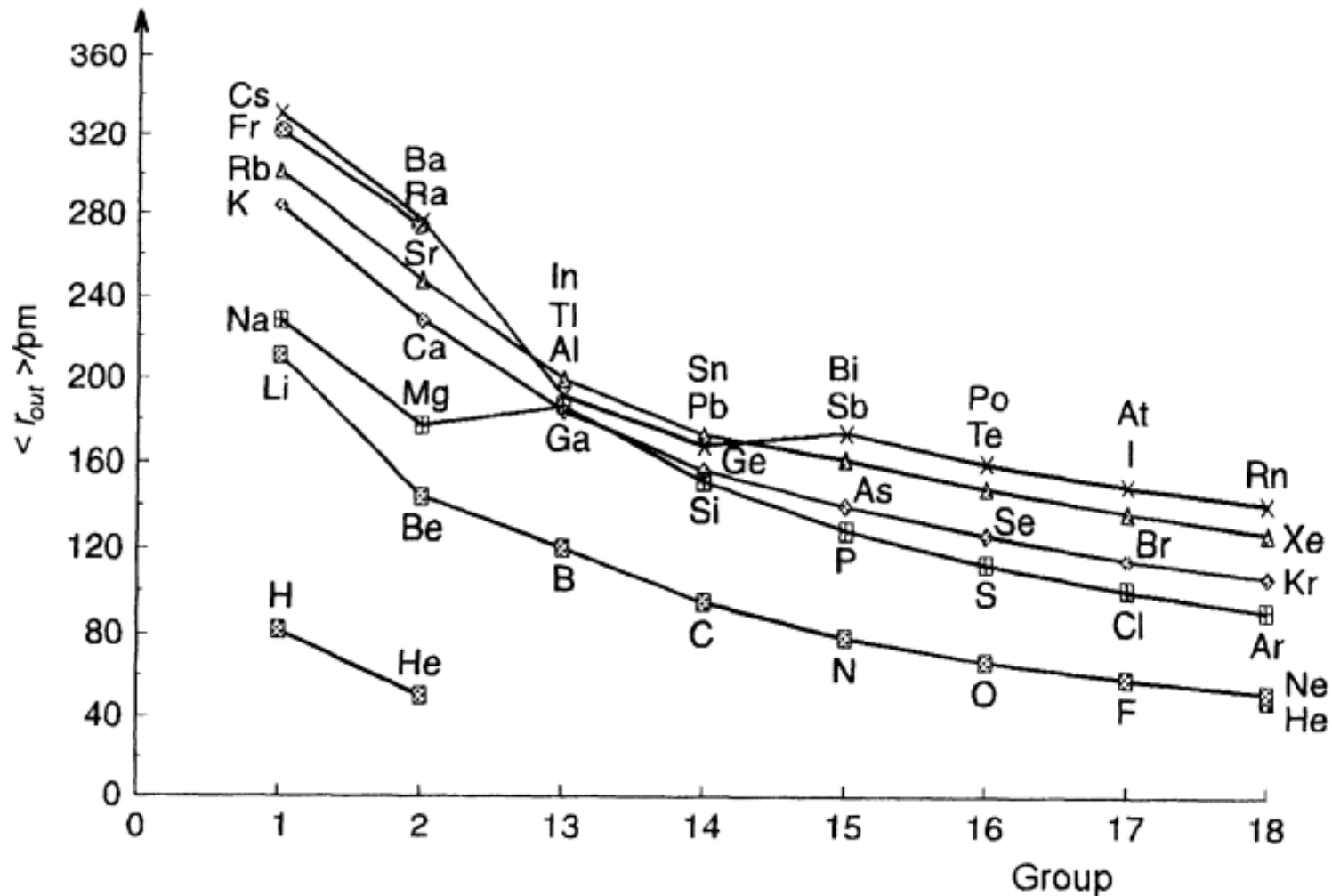
# Three chemical revolutions

- Molar (1770-1790, conservation of mass), molecular (1855-1875, valence and stoichiometry), electric (1904-1924, quantum theory)
- Continuing to put He with the noble gases is not progressing from the molecular level to the electric level!
- Jensen, William B. (1998). *Logic, History, and the Teaching of Chemistry: III. One Chemical Revolution or Three?. Journal of Chemical Education, 75(8), 961–*  
. doi:10.1021/ed075p961

# A superheavy precedent

- Besides, everybody places the heaviest elements on the table anyway, even though nobody has made enough oganesson to do any chemistry yet.
- And even if they did, relativistic effects (remember them?) suggest it'd be more like tin than like a noble gas
- So if you can have a non-noble non-gas in the noble gas column...
- ...and what's the big deal? Helium still ends the row!

# The first-row anomaly (kainosymmetry)



Siekierski and Burgess, *Concise Chemistry of the Elements*

# Electronegativity

- On the most complete scale of A. V. Kulsha and T. A. Kolevich

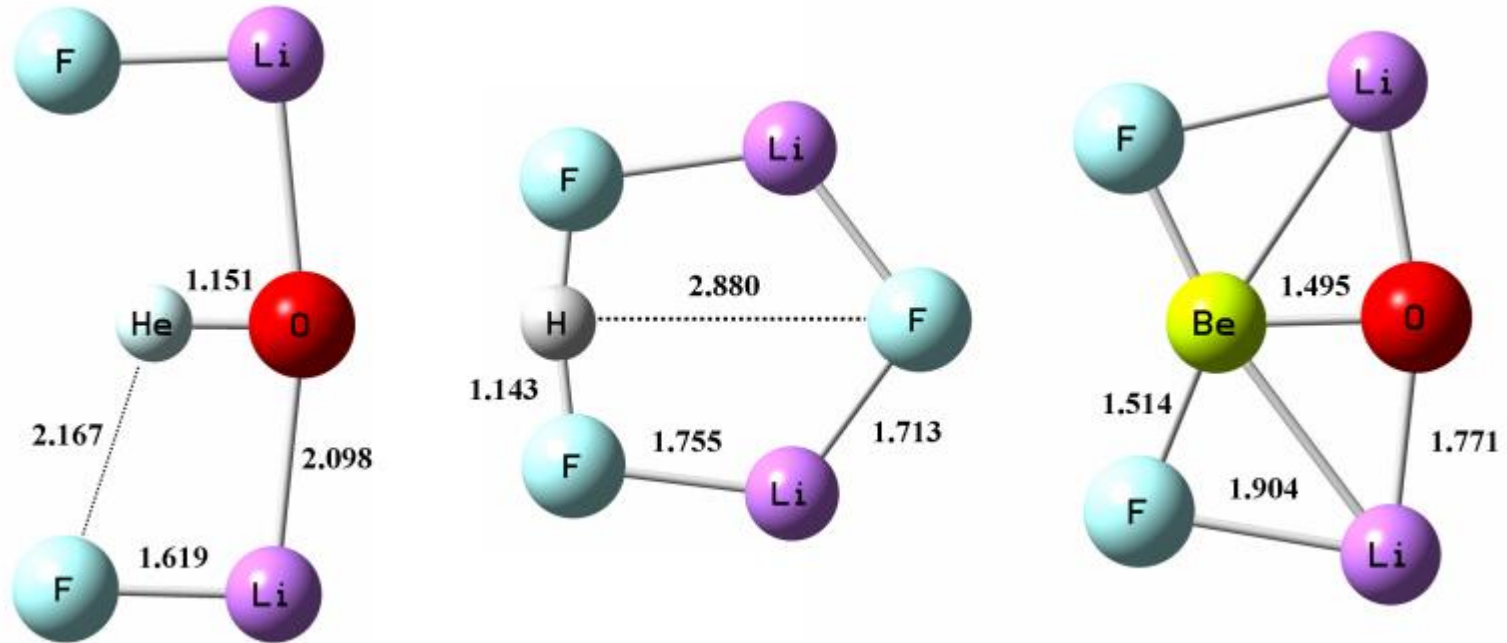
Is	IIs	IIIf	IVf	Vf	VIf	VIIIf	VIIIIf	IXf	Xf	XIf	XIIIf	XIIIIf	XIVf	XVf	XVIIf	IIId	IVd	Vd	VId	VIIId	IXd	Xd	XId	XIIId	IIIp	IVp	Vp	VIp	VIIp	VIIIp	
H 2.20	He 3.20																														
Li 1.00	Be 1.50																								B 2.00	C 2.50	N 3.00	O 3.50	F 4.00	Ne 4.50	
Na 0.90	Mg 1.30																								Al 1.70	Si 1.90	P 2.24	S 2.64	Cl 3.06	Ar 2.94	
K 0.80	Ca 1.10															Sc 1.33	Ti 1.40	V 1.48	Cr 1.56	Mn 1.52	Fe 1.60	Co 1.64	Ni 1.69	Cu 1.77	Zn 1.71	Ga 1.80	Ge 1.96	As 2.22	Se 2.52	Br 2.86	Kr 2.70
Rb 0.77	Sr 1.05															Y 1.28	Zr 1.35	Nb 1.44	Mo 1.53	Tc 1.51	Ru 1.62	Rh 1.68	Pd 1.73	Ag 1.79	Cd 1.66	In 1.74	Sn 1.86	Sb 2.04	Te 2.28	I 2.58	Xe 2.39
Cs 0.70	Ba 0.92	La 1.11	Ce 1.13	Pr 1.14	Nd 1.15	Pm 1.16	Sm 1.17	Eu 1.09	Gd 1.20	Tb 1.21	Dy 1.23	Ho 1.24	Er 1.25	Tm 1.26	Yb 1.19	Lu 1.31	Hf 1.38	Ta 1.46	W 1.54	Re 1.55	Os 1.67	Ir 1.75	Pt 1.84	Au 1.93	Hg 1.81	Tl 1.78	Pb 1.82	Bi 1.88	Po 1.98	At 2.09	Rn 1.94
Fr 0.72	Ra 0.85	Ac 0.97	Th 1.01	Pa 1.04	U 1.06	Np 1.08	Pu 1.12	Am 1.07	Cm 1.18	Bk 1.22	Cf 1.27	Es 1.32	Fm 1.36	Md 1.39	No 1.37	Lr 1.29	Rf 1.34	Db 1.41	Sg 1.49	Bh 1.59	Hs 1.72	Mt 1.83	Ds 1.92	Rg 1.99	Cn 1.91	Nh 1.87	Fl 1.85	Mc 1.57	Lv 1.65	Ts 1.76	Og 1.61

- Similar trends for ionisation energy, electron affinity

# Surprises of noble-gas chemistry!

- A helium compound,  $\text{Na}_2\text{He}$ , is known at high pressure!
- It's actually less noble than neon (which still has no neutral compounds)
- Probably there are some at low pressure too, showing analogy to beryllium (both elements seem to have higher affinity to oxygen than to fluorine). See the theoretical work of Wojciech Grochala
- Isn't most condensed-phase hydrogen and helium metallic anyway? It's stuck down under terrific pressure in the cores of Jupiter and Saturn. When metallised they do have the same valences as Li and Be.

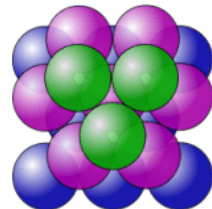
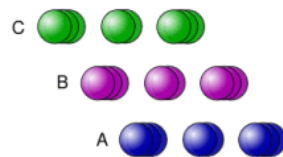
# Metastable helium oxide!



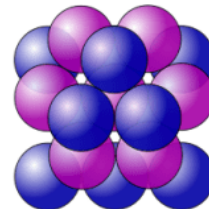
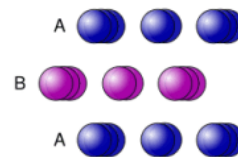
- Grochala, Wojciech (2012). *A metastable He–O bond inside a ferroelectric molecular cavity: (HeO)(LiF)<sub>2</sub>*. *Physical Chemistry Chemical Physics*, 14(43), 14860–. doi:10.1039/c2cp42321

# Crystal structures!

- Most atoms are extremely able mathematicians and found close-packed arrangements to solve Kepler's conjecture
- He, Be, Mg are hexagonal close-packed.
- Ne and Ar are cubic close-packed.
- (Pointed out by M. Kurushkin, 2020)



Cubic Close Packing (CCP)



Hexagonal close packing (HCP)

# Join the helium in group 2 club today!

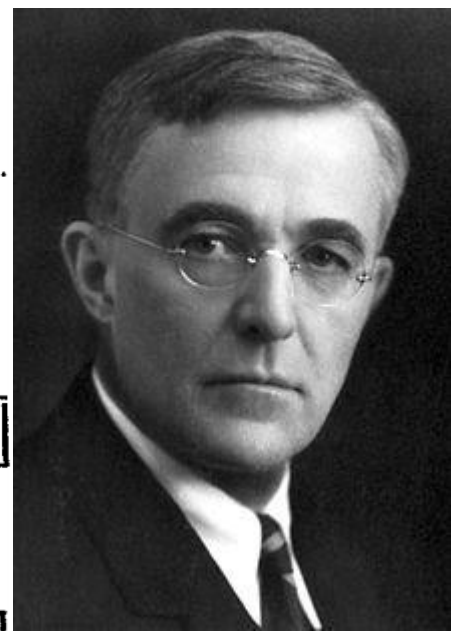
- The  $1s$  vs  $2p$  core shell difference also matters for subsequent elements. Alkali metals break up as Li ( $1s$  core), Na (kainosymmetric  $2p$  core), then much more polarisable K, Rb, Cs
- E.g. when burnt in air, they form  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{KO}_2$ ,  $\text{RbO}_2$ ,  $\text{CsO}_2$ .
- **It's not just about mathematics – it explains a lot about observed chemistry.**
- (And yes, Janet got this one right too. But partially, so did Irving Langmuir in 1919!)



TABLE I.

Classification of the Elements According to the Arrangement of Their Electrons.

Layer.	$N$	$E = 0$	1	2	3	4	5	6	7	8	9	10	
I			H	He									
IIa	2	He	Li	Be	B	C	N	O	F	Ne			
IIb	10	Ne	Na	Mg	Al	Si	P	S	Cl	A			
IIIa	18	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	
			11	12	13	14	15	16	17	18			
IIIa	28	Ni $\beta$	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
IIIb	36	Kr	Rb	Sr	Y	Zr	Cb	Mo	43	Ru	Rh	Pd	
			11	12	13	14	15	16	17	18			
IIIb	46	Pd $\beta$	Ag	Cd	In	Sn	Sb	Te	I	Xe			
IVa	54	Xe	Cs	Ba	La	Ce	Pr	Nd	61	Sa	Eu	Gd	
			11	12	13	14	15	16	17	18			
IVa			Tb	Ho	Dy	Er	Tm	Tm <sub>2</sub>	Yb	Lu			
			14	15	16	17	18	19	20	21	22	23	24
IVa	68	Er $\beta$	Tm $\beta$	Tm <sub>2</sub> $\beta$	Yb $\beta$	Lu $\beta$	Ta	W	75	Os	Ir	Pt	
			25	26	27	28	29	30	31	32			
IVa	78	Pt $\beta$	Au	Hg	Tl	Pb	Bi	RaF	85	Nt			
IVb	86	Nt	87	Ra	Ac	Th	U <sub>x2</sub>	U					



Irving Langmuir  
(1881-1957)