Scerri and Fisher

Essays in the Philosophy of Chemistry

Scerri, chap. 6 :

The Changing Views of a Philosopher of Chemistry on the Question of Reduction

MA Philosophy of science (Spring 2017)

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08.03.2017

INTRODUCTION

• Entanglement between the rise of the non-reductionist view on chemistry and the birth of the philosophy of chemistry.

• Scerri: from anti-reductionism (1999) to reductionism (2016).

• Given the conclusion of this paper (chemistry is reducible to physics), we can question the philosophy of chemistry itself.

Plan:

1) Introduction to the "biggest idea of chemistry": the periodic table of elements. Madelung rule, exceptions, etc.

2) Scerri's view on reductionism. Comments and critics.

The Periodic System

• One of the major discoveries in all of modern science, the most influential one in chemistry.

• Discovered on "purely chemical grounds" and then (partly) explained by quantum mechanics.

→ "Purely chemical"? Supposes clear disconnection with physics.

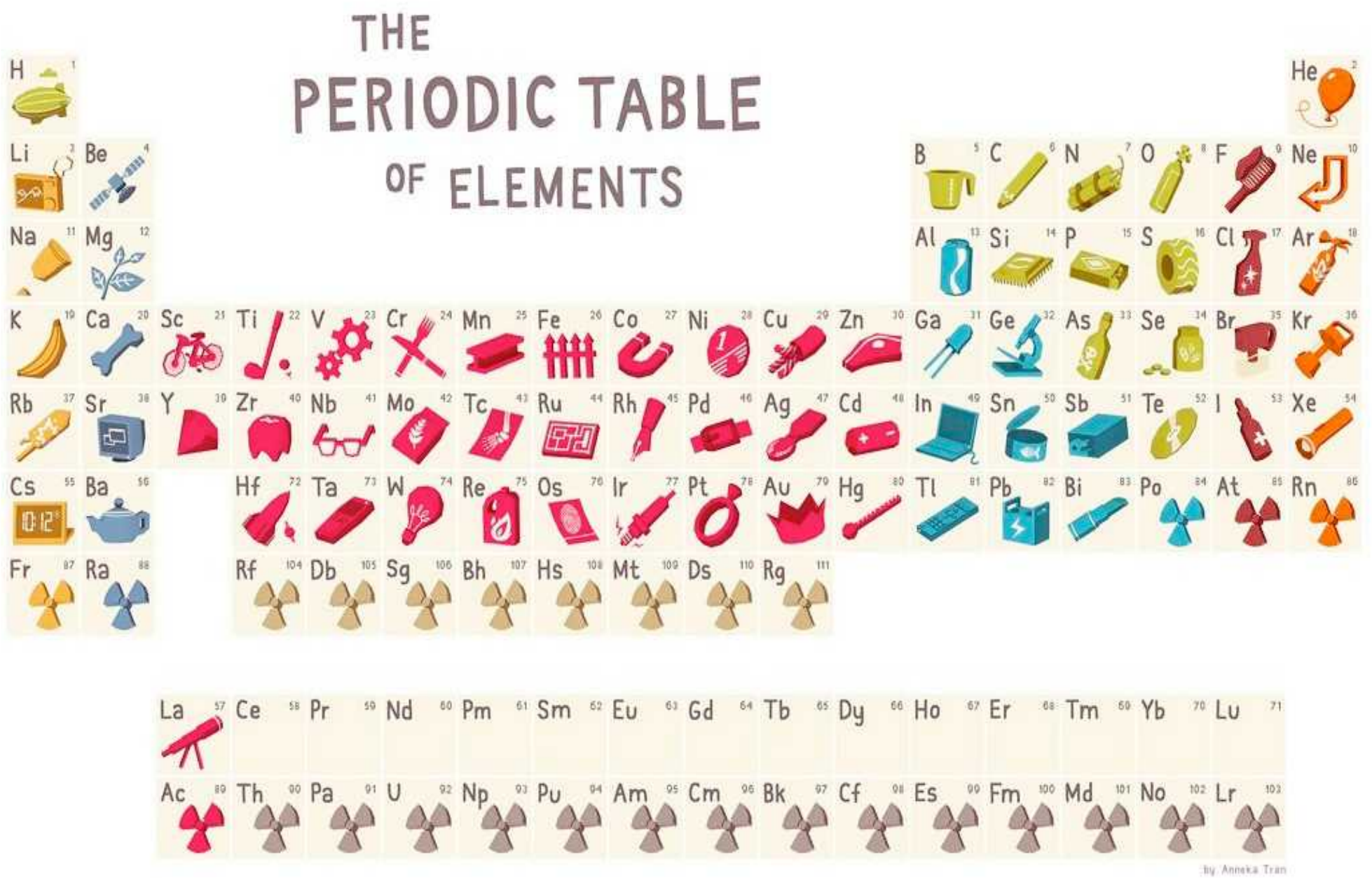
→ To what does it refer?

"*I saw in a dream a table where all elements fell into place as required. Awakening, I immediately wrote it down on a piece of paper, only in one place did a correction later seem necessary.*" [Mendeleev, as quoted by Inostrantzev].

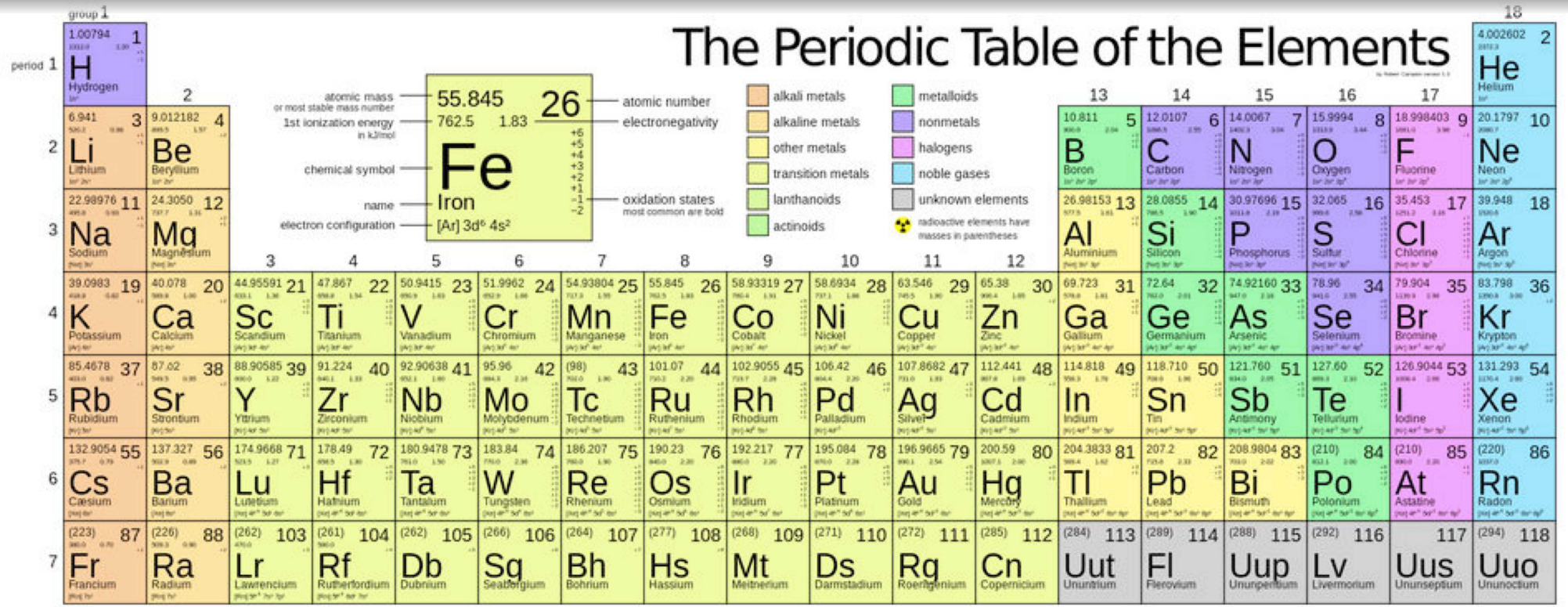
• Skip the historical part.

From the publication of atomic weights by Dalton (1808) to the publication of the periodic table by Mendeleev (1869).

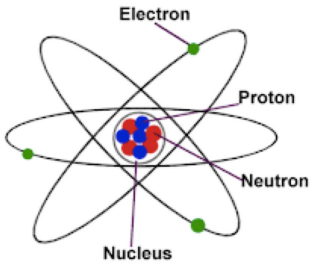
The periodic table of elements



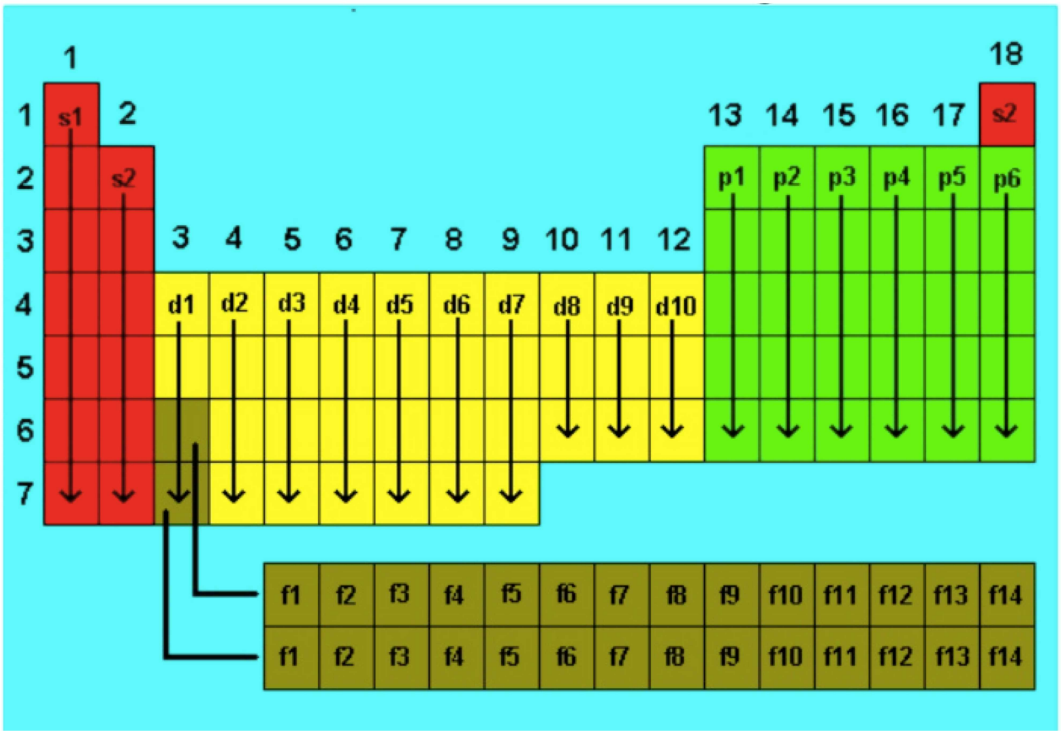
The Periodic Table of Elements

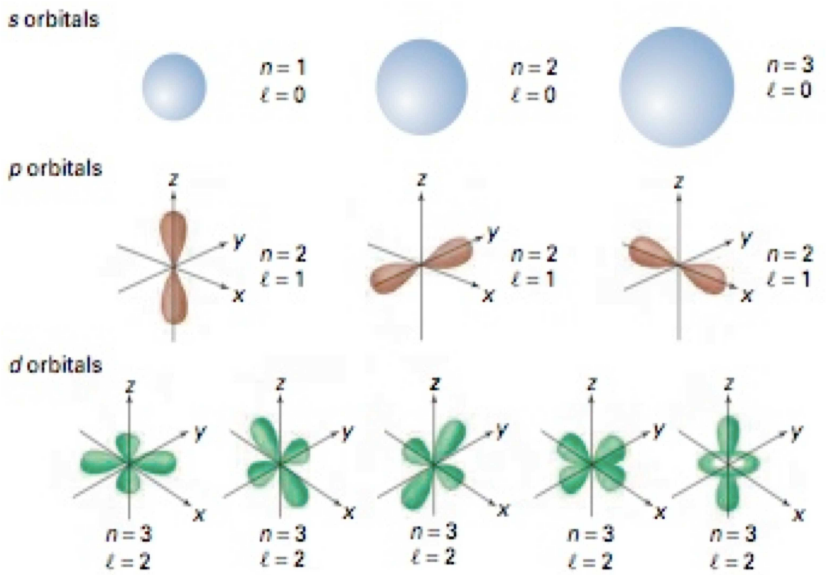


- Atomic number Z: number of protons.



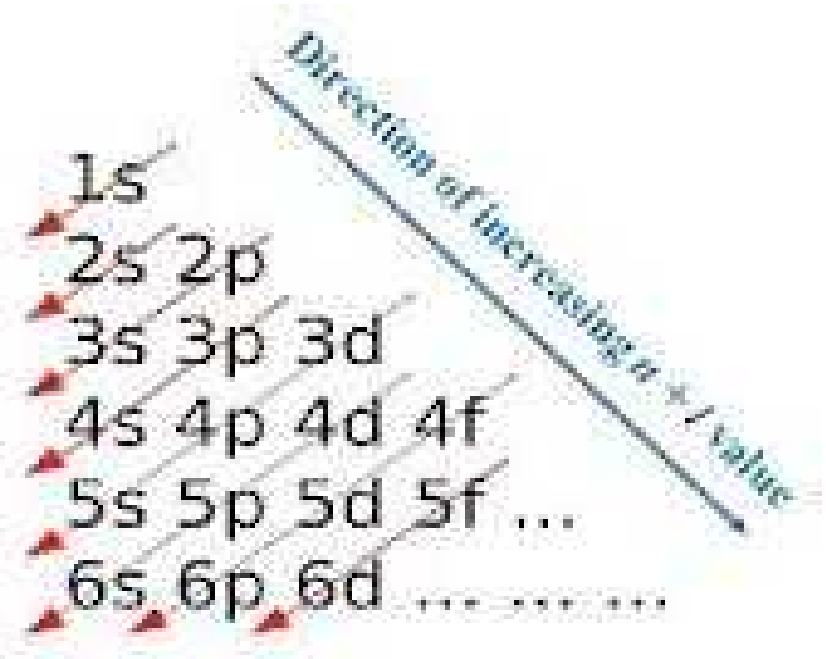
Periodic Table and Electronic Configuration

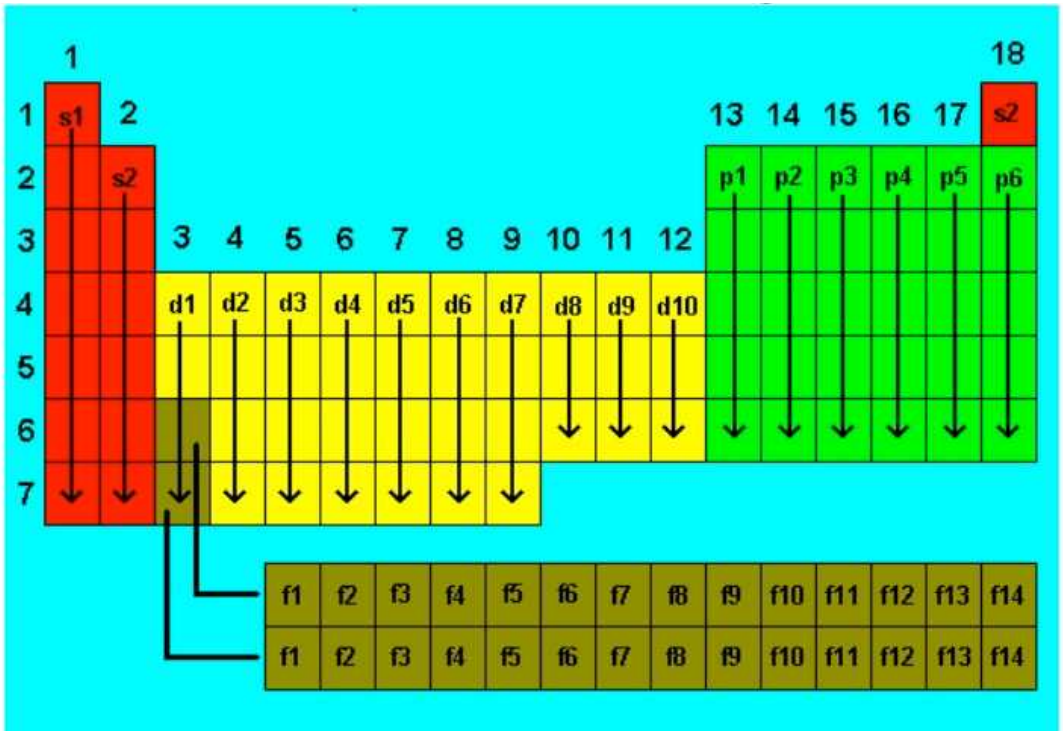




- Chemical properties are determined by the electronic configuration.
- Each line corresponds to one electron shell, given by the main quantum number *n*. In the fundamental state, n varies between 1 and 7, so one have 7 periods (7 lines).
- Each line is divided into blocs, corresponding to the atomic orbital, given by the azimuthal quantum number *l* (column).
- There are 4 different types of atomic orbitals, called s, p, d and f.
  s can contain 2 electrons, p 6 electrons, d 10 electrons and f 14 electrons.
  Note that He should be just above Berylium (but it is also a noble gas).

The Madelung rule (or Klechkowski rule)





Period number versus length of the sequence: unexplained!?

• **Fact:** the lengths of all periods (starting from the second) repeat in terms of their length.

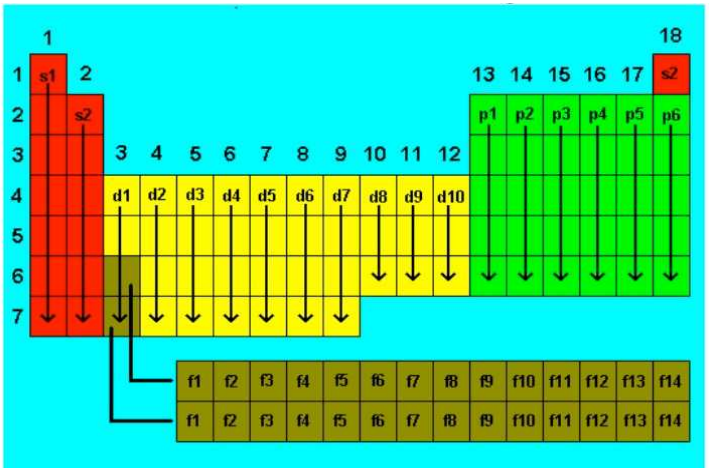
• More than a repetition: the period number determines the length of the sequence:

$$L_n = 1/8[2n+3+(-1)^n]^2$$

• Why #(2s+1p)=#(3s+2p)? Or why $L_2=L_3$?

Why #(4s+3d+4p)=#(5s+4d+5p)? Or why $L_4=L_5$?

...



• **Reference: [Kryachko 2007]?**

→ "A formula offered in 1951 by Tomkeieff" [Kryachko 2007].

"I believed I showed that" this formula had not been derived from quantum mechanics.

→ Where? Not in [Scerri 2009].

Failures of the Madelung rule → non-reductionism ?

- **The "lack of fundamental status of the Madelung rule"**

The Madelung rule (for ordering the sequence of orbitals: 1s, 2s, 2p, 3s, etc...) works only for the case of metals in the s-block.

Given this lack, is the reduction still be expected?

Conclusion:

"*My previous ardent claims that the periodic system has bot been fully reduced to quantum mechanics because of a lack of derivation of the n+l rule has therefore fallen by the wayside. Mea culpa. I was wrong.*" [Scerri 2016].

→ "*Differing views on reduction are briefly reviewed and a suggestion is made for a working definition of 'approximate reduction'. […] I conclude that chemistry has not even been approximately reduced.*" [Scerri 1999].

- **Anomalous configuration**

20 elements do not follow the Madelung rule in that they have anomalous configuration: the most exterior orbital does not possess a s^2 configuration.

This anomaly can be used for claiming the periodic table has not been reduced to quantum mechanics.

But, QM + experimental data give an explanation.

Scerri's view on reductionism

• **First arguments** (given in the introduction):
– Number of practitioners (in chemistry),
– "big ideas" (in chemistry),
– Complexity (in biology).

• **Chemistry versus physics**, more precisely, vs QM.
– Has lived in the shadow of physics since the beginning of the XXth.
– Reduction expected once QM achieved. Cf. the quote of Dirac, famous among philosophers of chemistry.

→ Presupposes chemistry expressed in mathematical language.

1. Compare to biology.

2. The situation has not always been the same:
"Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry.... if mathematical analysis should ever hold a prominent place in chemistry—an aberration which is happily almost impossible—it would occasion a rapid and widespread degeneration of that science."
[Comte 1830]

First critic: about the failures of the Madelung rule.

- **The "lack of fundamental status of the Madelung rule"**

The Madelung rule (for ordering the sequence of orbitals: 1s, 2s, 2p, 3s, etc...) works only for the case of metals in the s-block.

→ Consider Oxygen. According to the Madelung rule: $2s^2 2p^4$. That is correct!

→ What about Hund's rules (1927)?
Reduce the energy due to spin interactions in the same orbital (instead of $6s^2$ one have $6s^1 4f^1$). Explained by QM!

→ Some doubts about the paper of Wang...

• "*Some authors insist that "still nobody has deduced the n+l rule from the principles of quantum mechanics"* Scerri (2004), *while others present quantum justification of the rule* (Demkov and Ostrovsky, 1971; Ostrovsky, 1981, 2001) *that was not ever disputed.*" [Ostrovsky 2005]

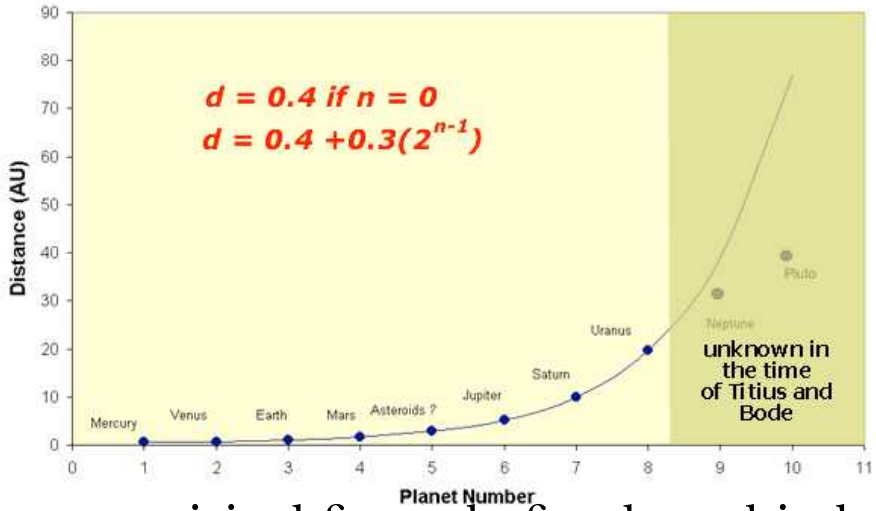
• "*For multielectron atoms the angular momentum coupling schemes, Slater determinants and methods of calculations (such as Hartree–Fock and configuration interaction) are briefly covered. This standard quantum theoretical technique is capable of treating any ground state atom, and thus reproducing periodic variation with the atomic number Z of atomic properties (such as ionization potential). This is of course an outstanding achievement of quantum mechanics. However, some researchers could be not fully satisfied by the fact that the Periodic System arises in such an approach from piecewise calculations for individual atoms, while an overview of the System structure is not provided.*" [Ostrovsky 2005]

The argument for reductionism

• Non-reductionism because no deduction from first principle of quantum mechanics.
(Remember that concerning the rules governing the periodic table, this claim is controversial).

→ What the difference with the Titius-Bode law? Or the Dermott law?

• The Titius–Bode law is an hypothesis that the bodies in some orbital systems, including the Sun's, orbit at semi-major axes in a function of planetary sequence. The hypothesis correctly anticipated the orbits of Ceres and Uranus, but failed as a predictor of Neptune's orbit.



• The Dermott law is an empirical formula for the orbital period of major satellites orbiting planets in the Solar System.

The argument for reductionism

- Similar case?

1) No explanation of the Titius-Bode law in terms of Newton's law...

2) Failure of the Titius-Bode law in our solar system.

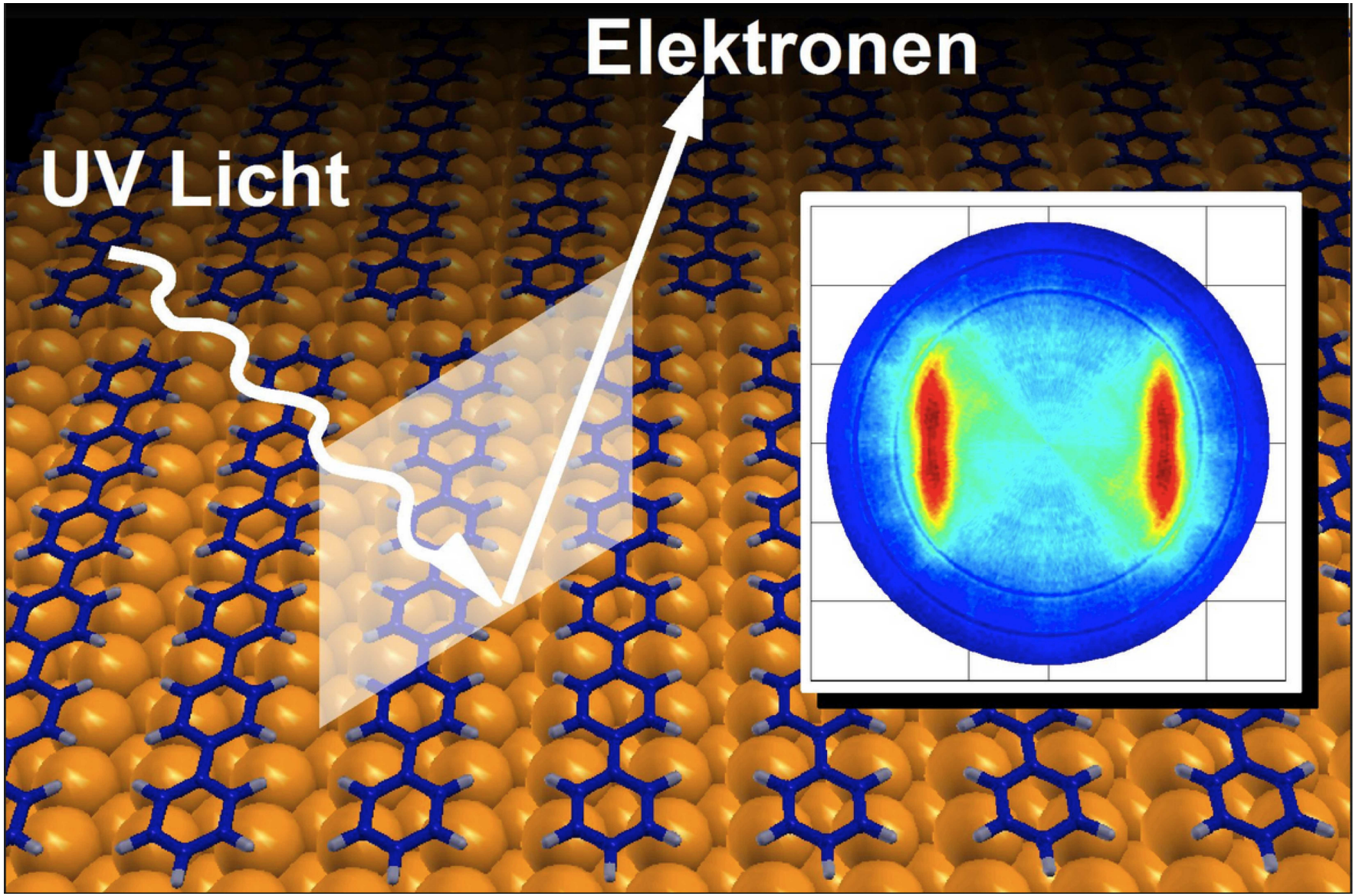
3) Test of the law for exoplanetory solar system applied a generalized Titius–Bode relation to 68 exoplanet systems that contain four or more planets. [Bovaird 2013] shows that 96% of these exoplanet systems adhere to a generalized Titius–Bode relation to a similar or greater extent than the Solar System does.

Also used for predictions of new exoplanets in observed multi-planet systems [Hobson 2017].

- In physics we have relations, rules or laws for which:
  - No deduction from first principle (Titius-Bode's law)
  - Failure in somes cases (Titius-Bode's law)
  - Approximations as mean-field approximations as Hartree-Fock
  - Numerical simulations

- Philosophy of chemistry vs philosophy of kinetic theory, thermodynamics, classic physics, etc.

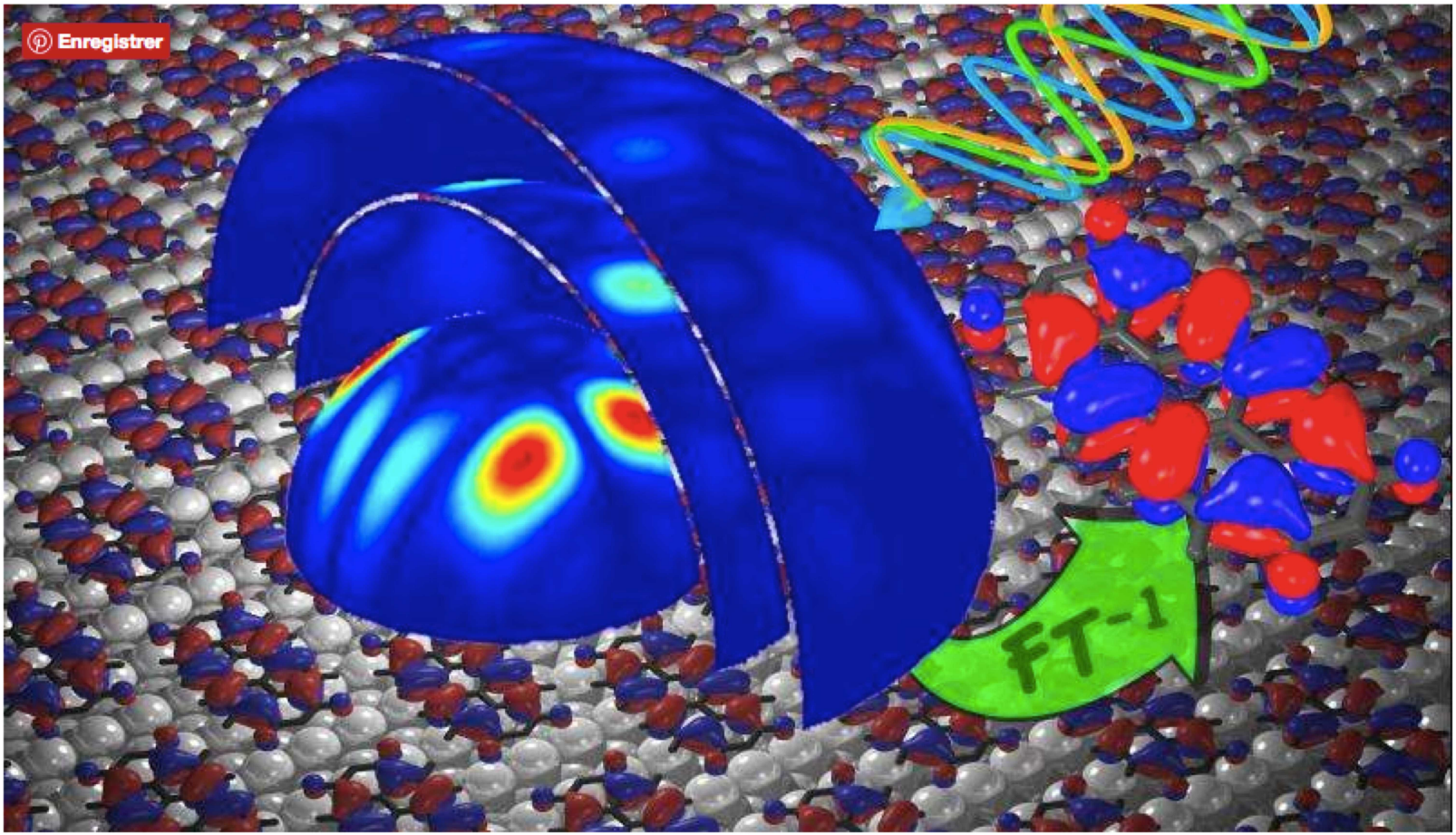
Measure electron orbitals (2009)



Measure electron orbitals in 3-D (2015)

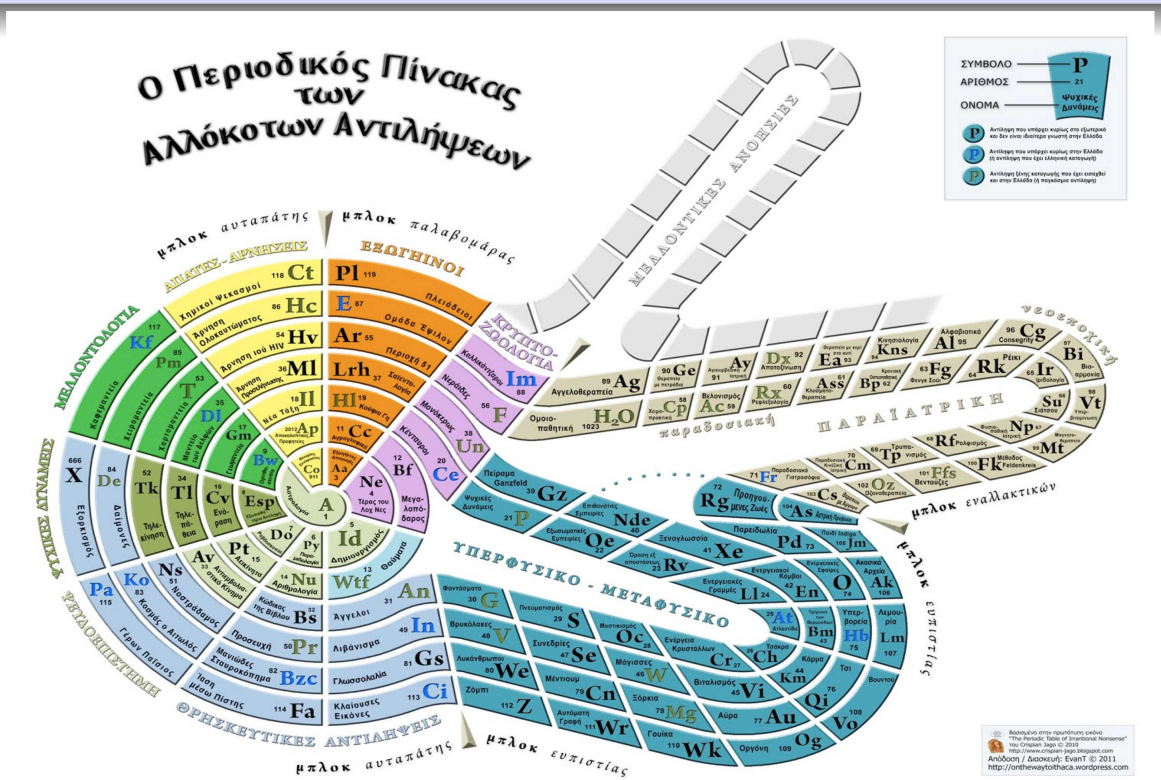
Researchers measure electron orbitals of molecules in 3-D

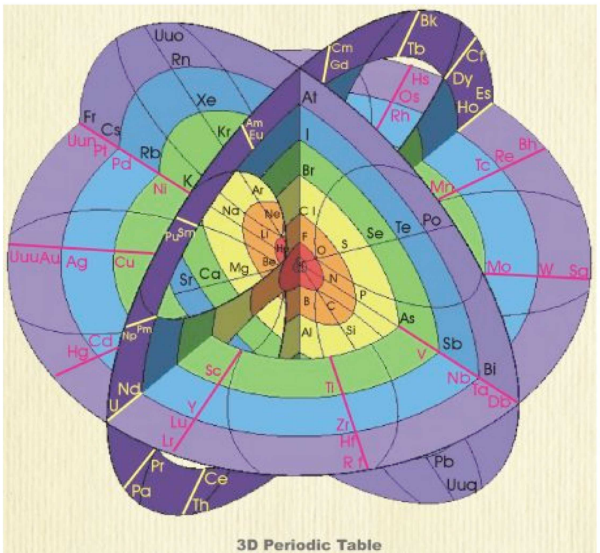
October 5, 2015

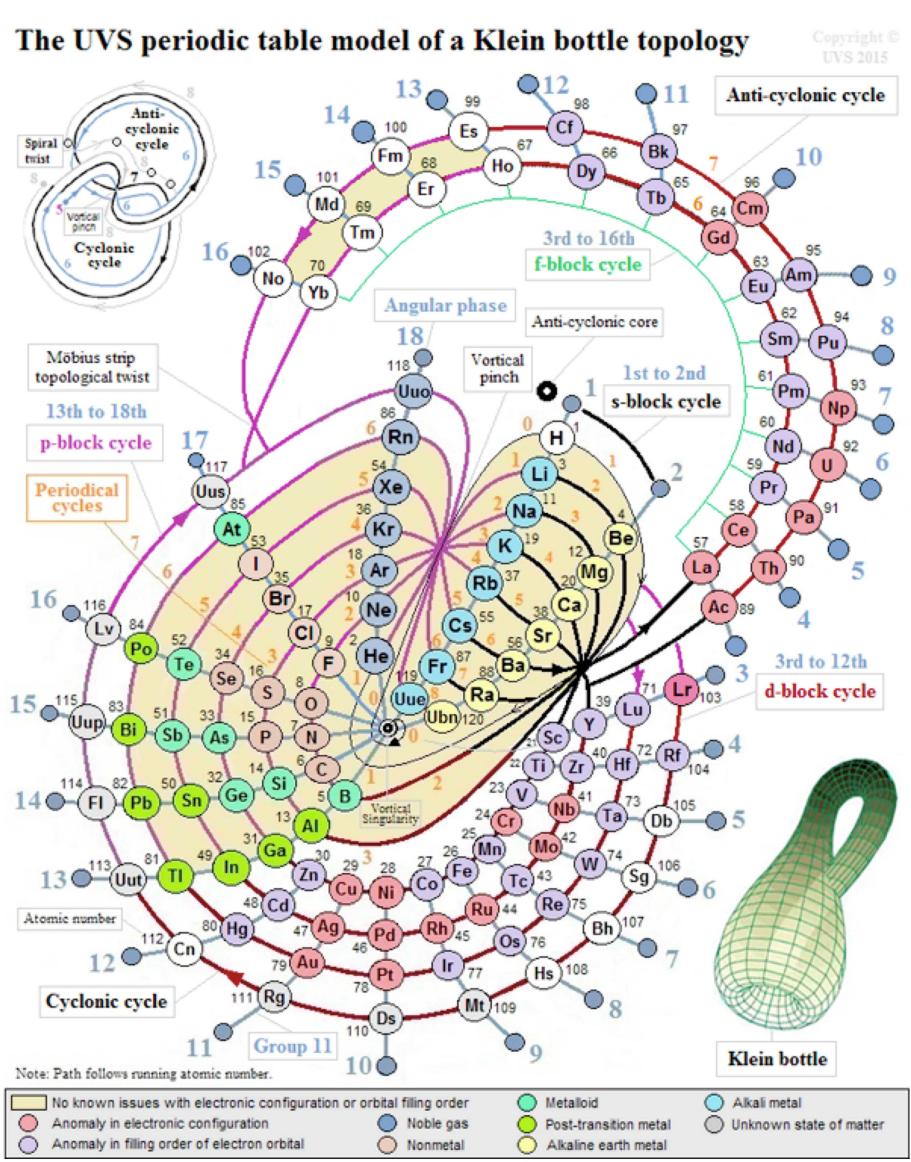


Basic principle of 3D reconstruction by photoelectron spectroscopy: electrons released from the electron shell by photons enable conclusions to be drawn on the orbitals. The three-dimensional structure of the orbital can be reconstructed from experiments at different photon energies. Credit: Forschungszentrum Jülich

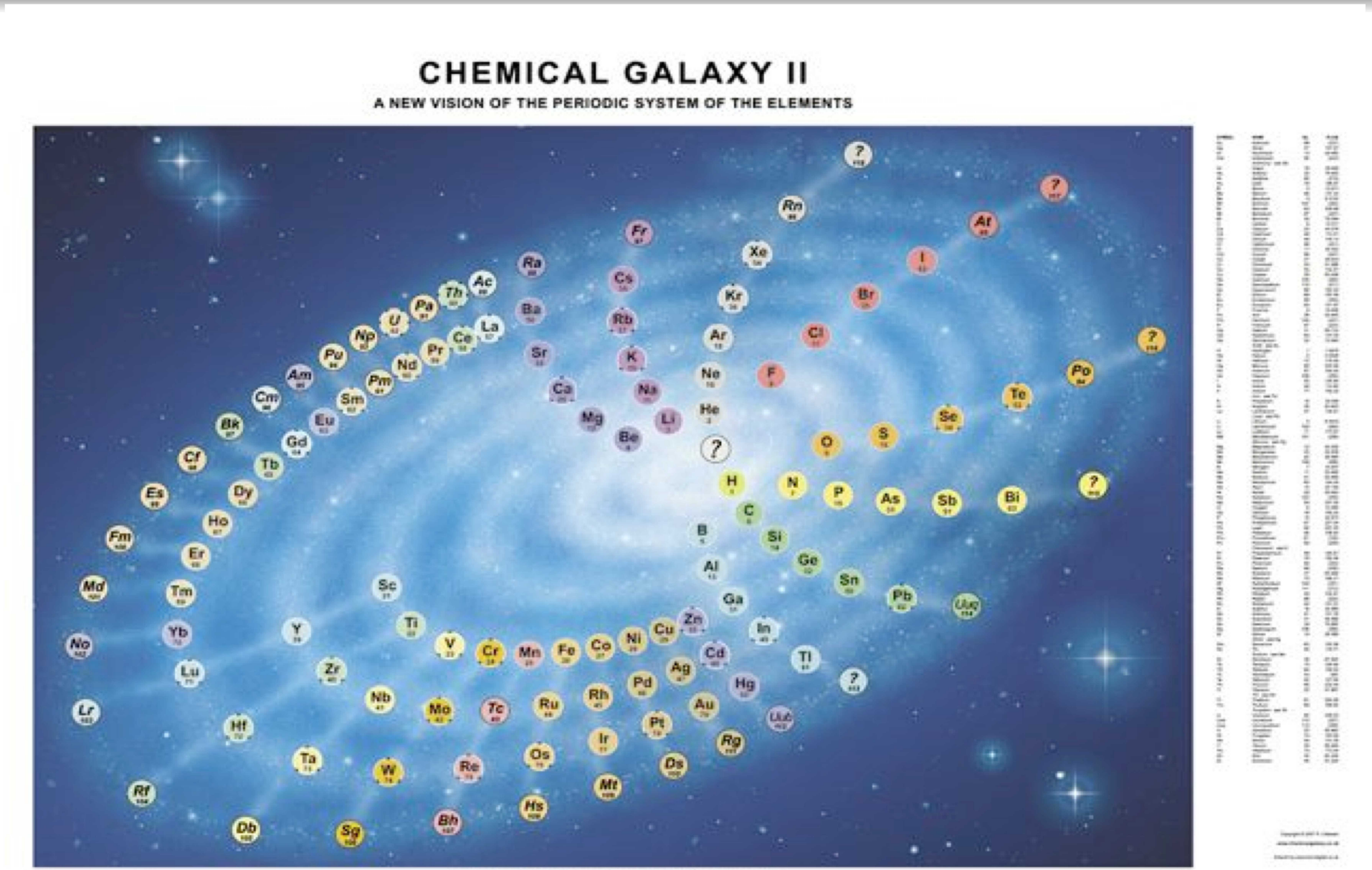
The periodic table of elements: 2D, 3D, etc.



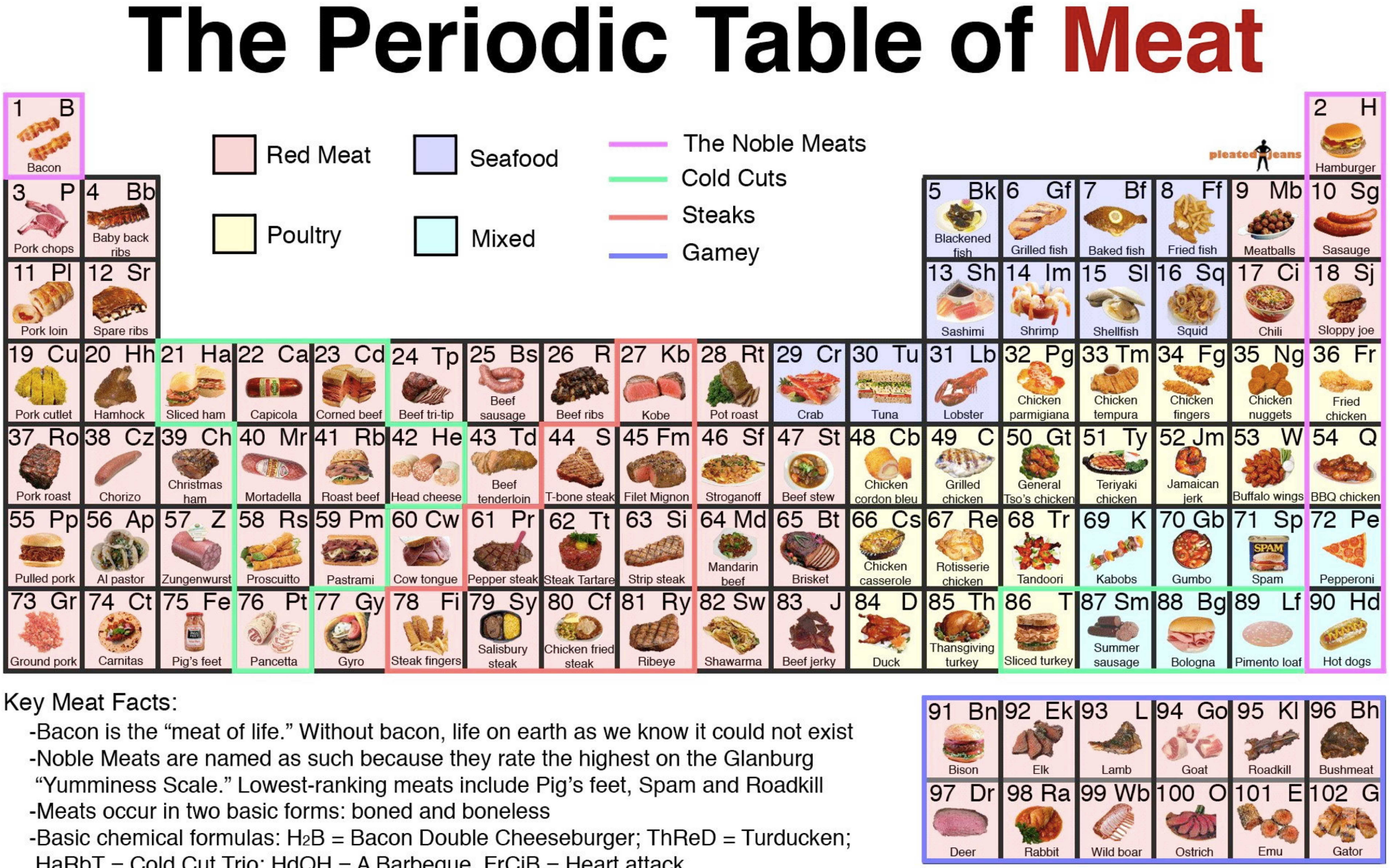




The chemical galaxy: "the role of aesthetically engaging images in drawing non-professionals into the wonder of scientific understanding."



The periodic table of meat



Key Meat Facts:

-Bacon is the "meat of life." Without bacon, life on earth as we know it could not exist

-Noble Meats are named as such because they rate the highest on the Glanburg "Yumminess Scale." Lowest-ranking meats include Pig's feet, Spam and Roadkill

-Meats occur in two basic forms: boned and boneless

-Basic chemical formulas: H_2B = Bacon Double Cheeseburger; ThReD = Turducken; HaRbT = Cold Cut Trio; HdQH = A Barbeque, FrCiB = Heart attack