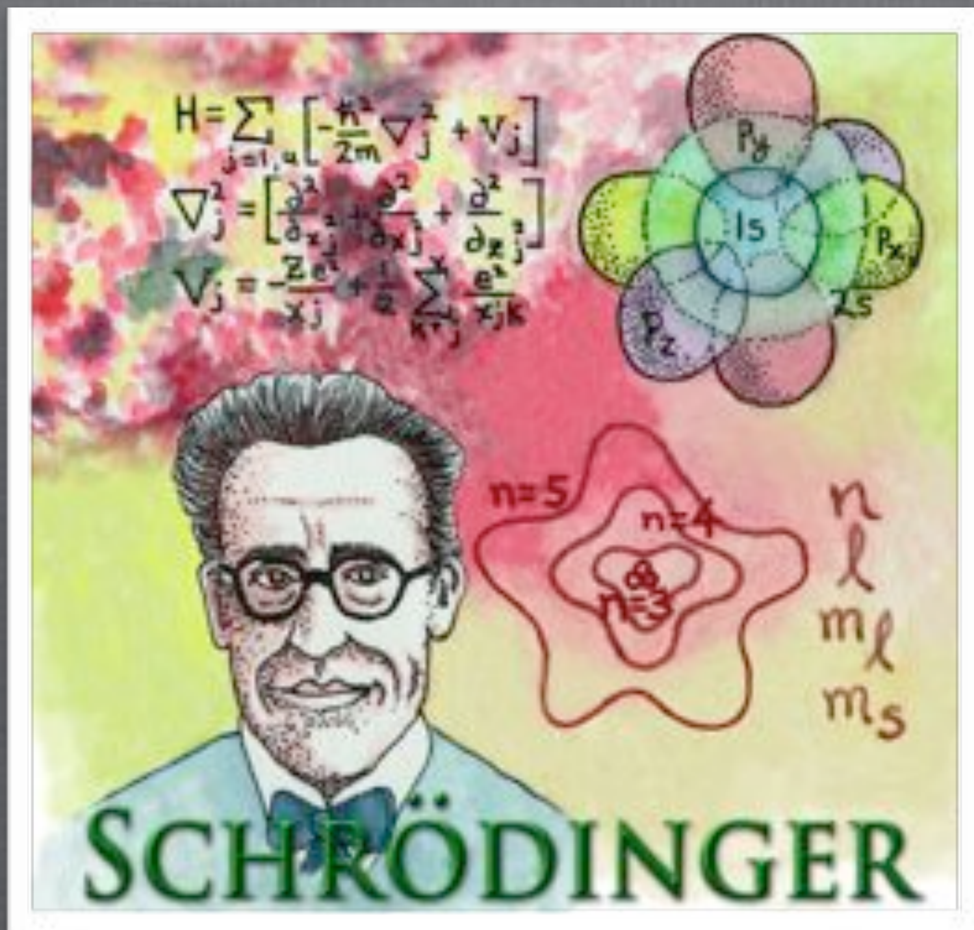
Quantum Numbers

Making Sense of Electron Structure

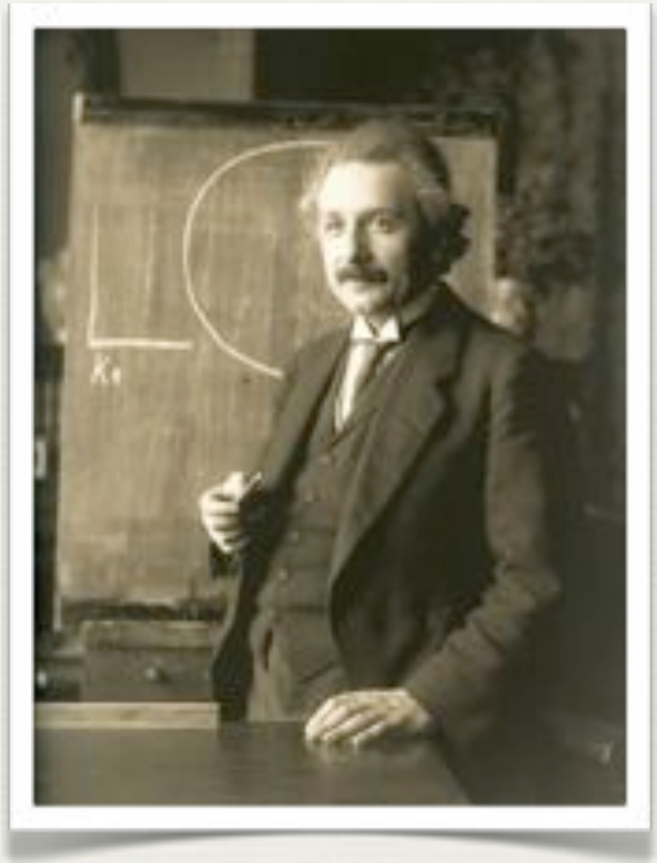


by David V. Black

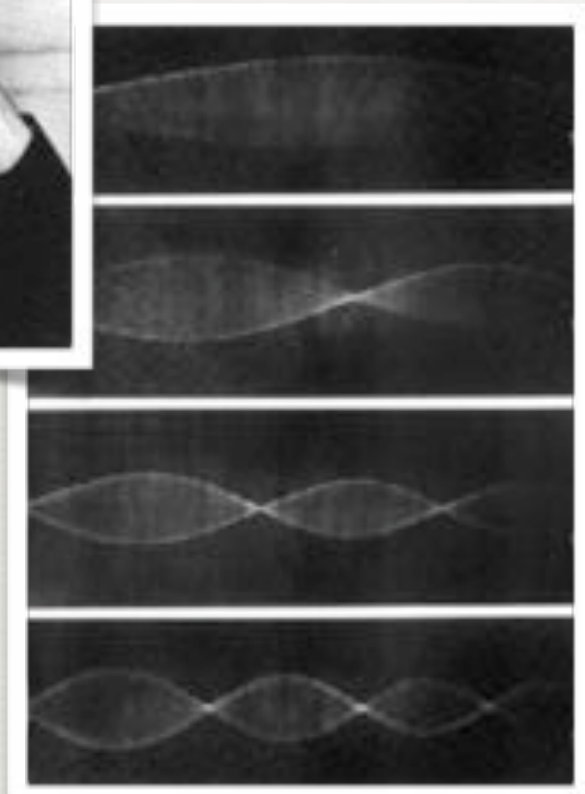
- This presentation was put together by David V. Black, chemistry teacher at Walden School of Liberal Arts in Provo, Utah.
- Feel free to use this however you like: add to it, pass it on, etc. Just give me the credit I so richly deserve . . .

Particles and Waves

- Einstein's 1905 paper on the photoelectric effect demonstrated that photons act as particles.
- For electrons to be knocked off of a semiconductor such as silicon, the incoming light must be in the form of particles or packets of energy (photons).



DE BROGLIE

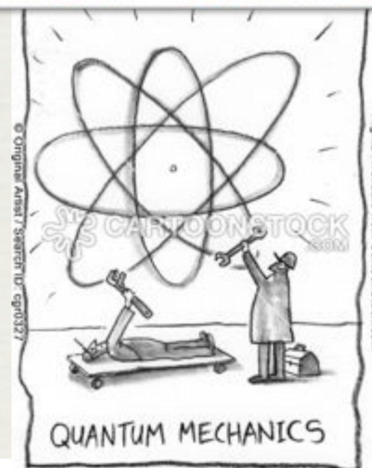


- Experiments by Louis de Broglie and others showed that electrons also act as waves (a single electron can be split through two slits to create interference patterns).
- Certain areas reinforce to create standing waves, other areas cancel each other out (null zones).
- The electrons move continuously, but the standing wave patterns remain stable.

Uncertainty – Get Used to It!

- Werner Heisenberg proposed what is now called the Uncertainty Principle: any two complimentary properties of subatomic particles (such as position or momentum) can't be determined simultaneously.
- OK. Sure. So . . . what does that mean?

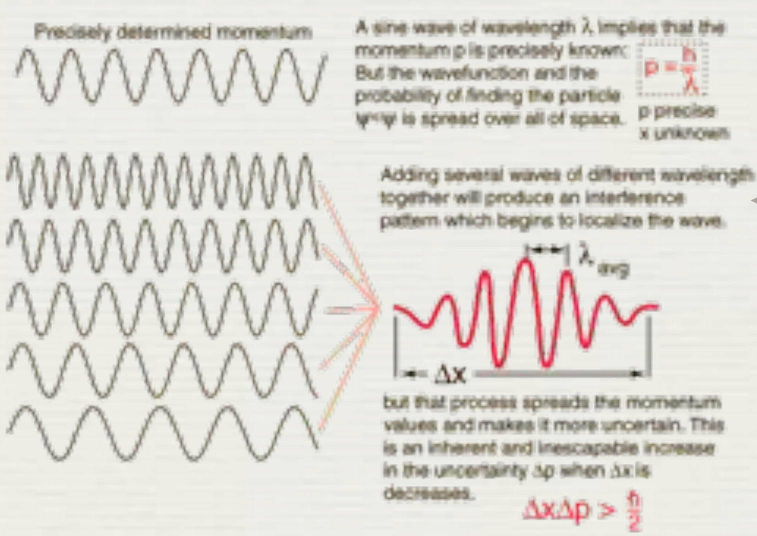
$$\Delta\chi\Delta\rho \geq \frac{\hbar}{2}$$



The Technical Stuff

$$
\begin{aligned}
\langle f|g\rangle - \langle g|f\rangle &= \int_{-\infty}^{\infty} \psi^*(x)\, x \cdot \left(-i\hbar \frac{d}{dx}\right) \psi(x)\, dx \\
&\quad - \int_{-\infty}^{\infty} \psi^*(x) \left(-i\hbar \frac{d}{dx}\right) \cdot x\, \psi(x) dx \\
&= i\hbar \cdot \int_{-\infty}^{\infty} \psi^*(x) \left[\left(-x \cdot \frac{d\psi(x)}{dx}\right) + \frac{d(x\psi(x))}{dx}\right] dx \\
&= i\hbar \cdot \int_{-\infty}^{\infty} \psi^*(x) \left[\left(-x \cdot \frac{d\psi(x)}{dx}\right) + \psi(x) + \left(x \cdot \frac{d\psi(x)}{dx}\right)\right] dx \\
&= i\hbar \cdot \int_{-\infty}^{\infty} \psi^*(x)\psi(x)\, dx \\
&= i\hbar \cdot \int_{-\infty}^{\infty} |\psi(x)|^2 dx \\
&= i\hbar
\end{aligned}
$$

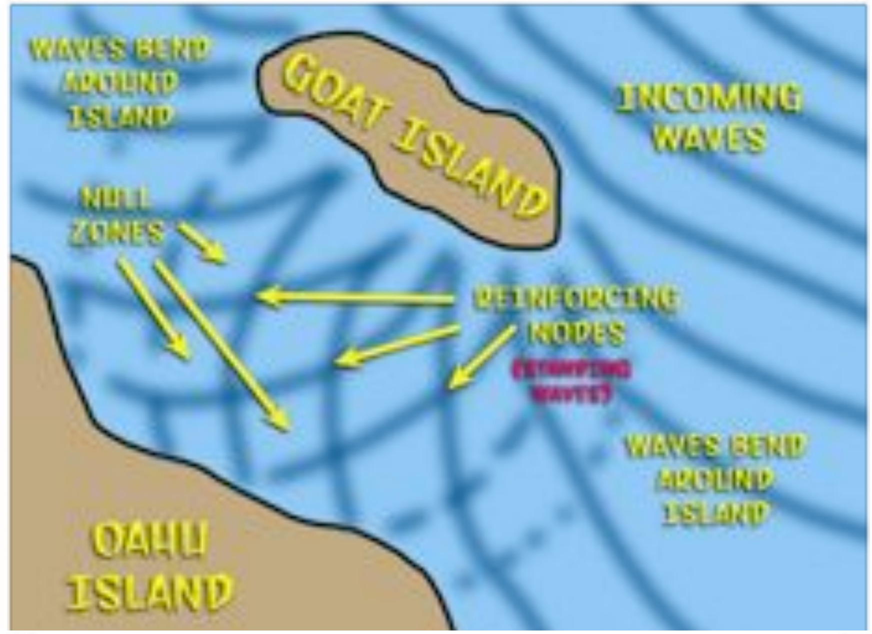
Please memorize this by Monday



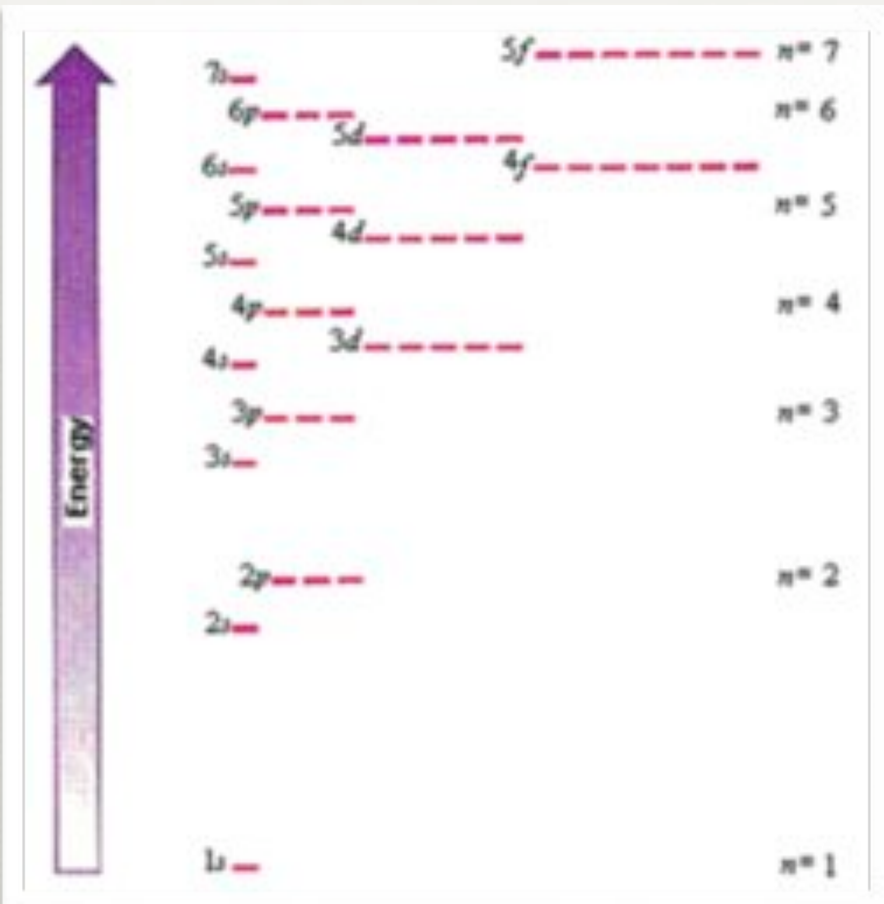
- Since particles are also waves, many quantum wavelengths combined create interference patterns that add up in some places, cancel out in others, creating a “locality” for the particle.
- It’s really about probability: the waves go everywhere, but they are found in some places more often than others.

Standing Waves

- An example of standing waves: Goat Island, Hawaii
- Waves are bent around the island both directions, then meet behind the island to create stable standing wave nodes.



EXPLAINS QUANTA



- Planck's observation that only certain energy levels (***quanta***) are available for an electron in an atom, and that electrons can leap from level to level without passing through the space in between, can only be explained if electrons act as waves.

THE NUMBERS

- Schrödinger's Quantum Mechanics equations provide a set of four numbers for the allowable energy levels of electrons in an atom.
- These describe the regions where electrons are most likely to be found (a probability of 90% or more).
- According to the Pauli Exclusion Principle, no two electrons in the same atom can have the same set of quantum numbers. In other words, each electron has unique energy.

- ***n*** is the principle quantum number, representing the electron's distance from the nucleus (its radius).
- ***l*** is the energy provided by the electron's angular momentum.
- ***m**ₗ* is the energy of the electron's magnetic field created by its angular momentum.
- ***m**ₛ* is the magnetic component created by the electron's spin.

Rules for Allowable Combinations of Quantum Numbers

- The three quantum numbers (n, l, and m) that describe an orbital must be integers.
- "n" cannot be zero. "n" = 1, 2, 3, 4...
- "l" can be any integer between zero and (n-1).

  e.g. If $n = 4$, l can be 0, 1, 2, or 3.

- "m" can be any integer between -l and +l.

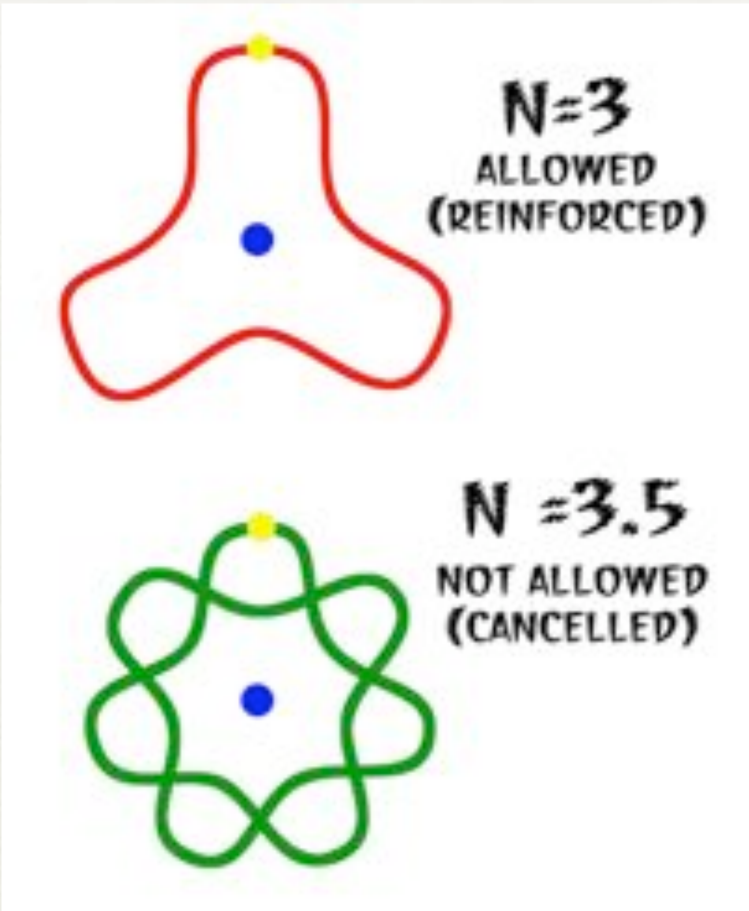
  e.g. If $l = 2$, m can be -2, -1, 0, 1, or 2.

- "s" is arbitrarily assigned as $+\frac{1}{2}$ or $-\frac{1}{2}$, but for any one subshell (n, l, m combination), there can only be one of each.

Graphical Representation of Allowable Combinations of Quantum Numbers

Shell n	Subshell l	Subshell Notation	Orientation m	Number of Orbitals
1	0	1s	0	1
2	0	2s	0	1
	1	2p	-1 0 +1	3
3	0	3s	0	1
	1	3p	-1 0 +1	3
	2	3d	-2 -1 0 +1 +2	5
4	0	4s	0	1
	1	4p	-1 0 +1	3
	2	4d	-2 -1 0 +1 +2	5
	3	4f	-3 -2 -1 0 +1 +2 +3	7

THE PRINCIPLE NUMBER

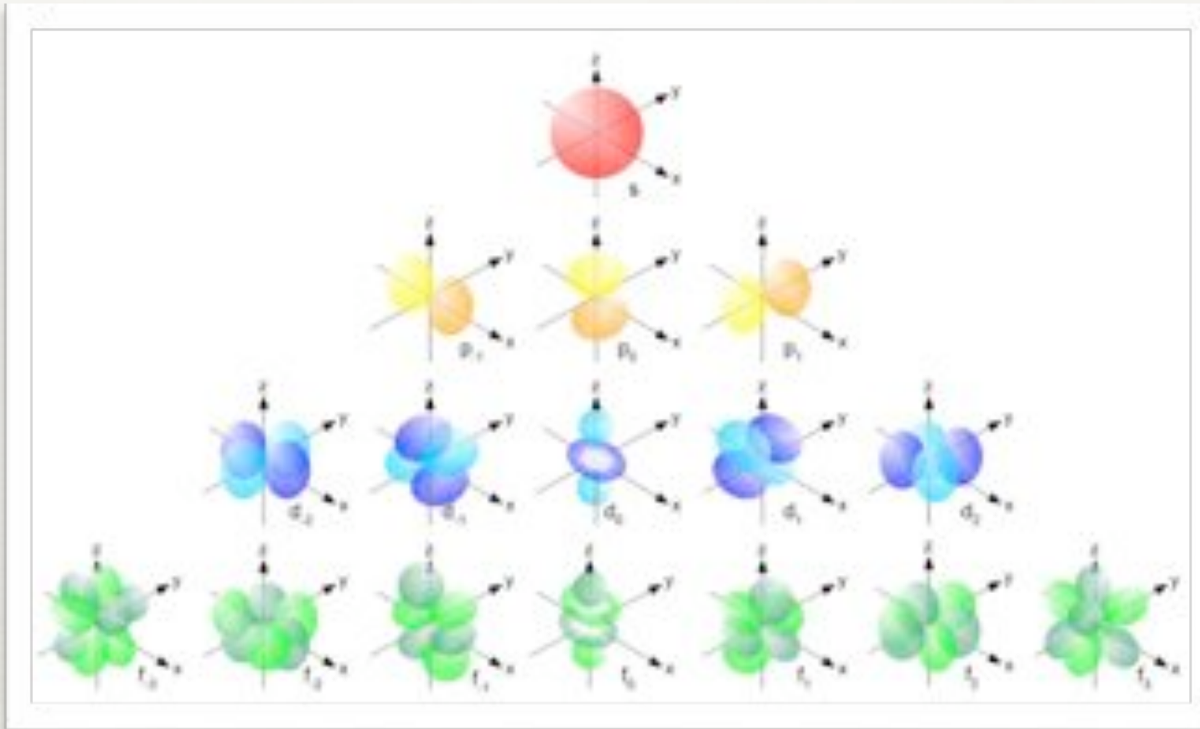


- The values that ***n*** can have are only positive integers (***n*** = 1, 2, 3, 4, etc.).
- ***n*** represents the number of wavelengths of the electron as it travels around the nucleus. The higher the value of ***n***, the more wavelengths and the further out it is (higher energy).
- For integer values, the waves reinforce. For non-integer values, such as ***n*** = 3.5, the waves interfere with each other and cancel out.

ANGULAR MOMENTUM QUANTUM NUMBER

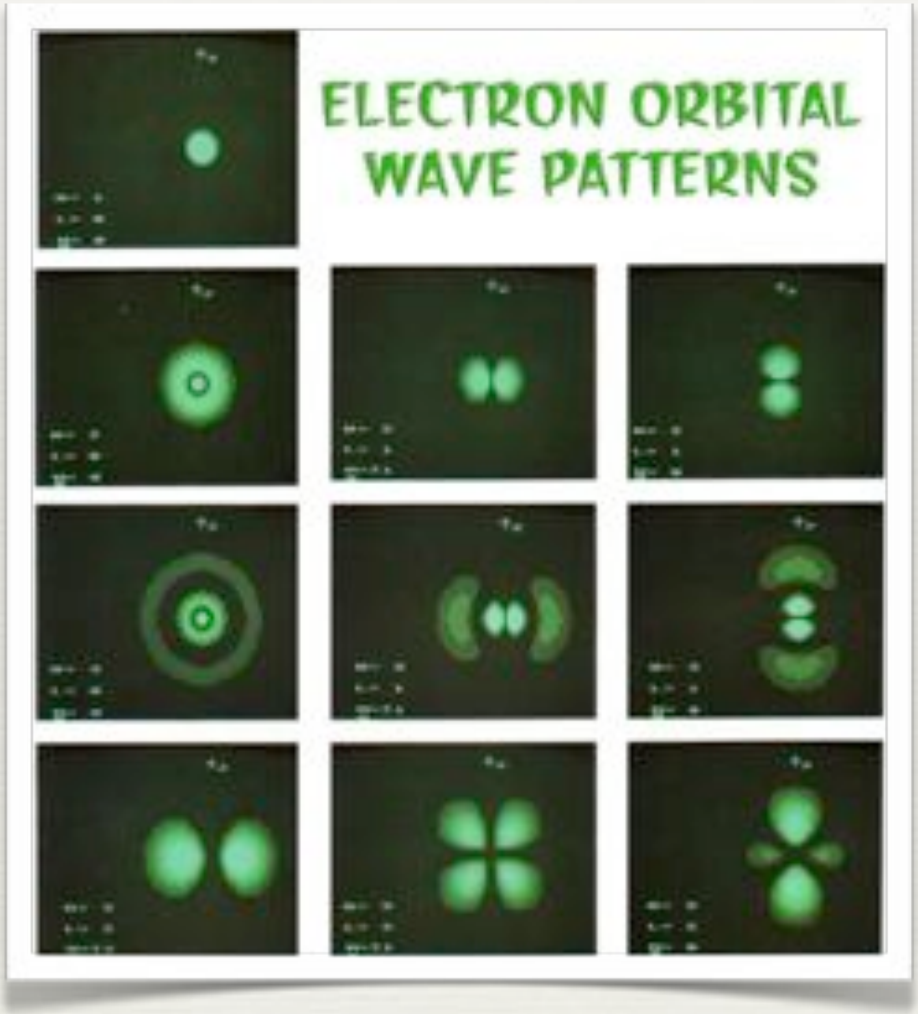
- The second quantum number, ***l***, represents the angular momentum of the electron as it travels around the nucleus. It is also called the ***subshell*** or ***orbital*** number.
- It can have the values of 0 through ***n***-1. For example, if n = 3, then ***l*** can have the values of 0, 1, and 2.
- For ***l*** = 0, the orbital is called ***s***; for ***l*** = 1, it is called ***p***; for ***l*** = 2, it is called ***d***, and for ***l*** = 3, it is called ***f***. If there were higher values for ***l*** (no atom has these yet), they would be ***g***, ***h***, ***i***, etc.

ORBITAL SHAPES



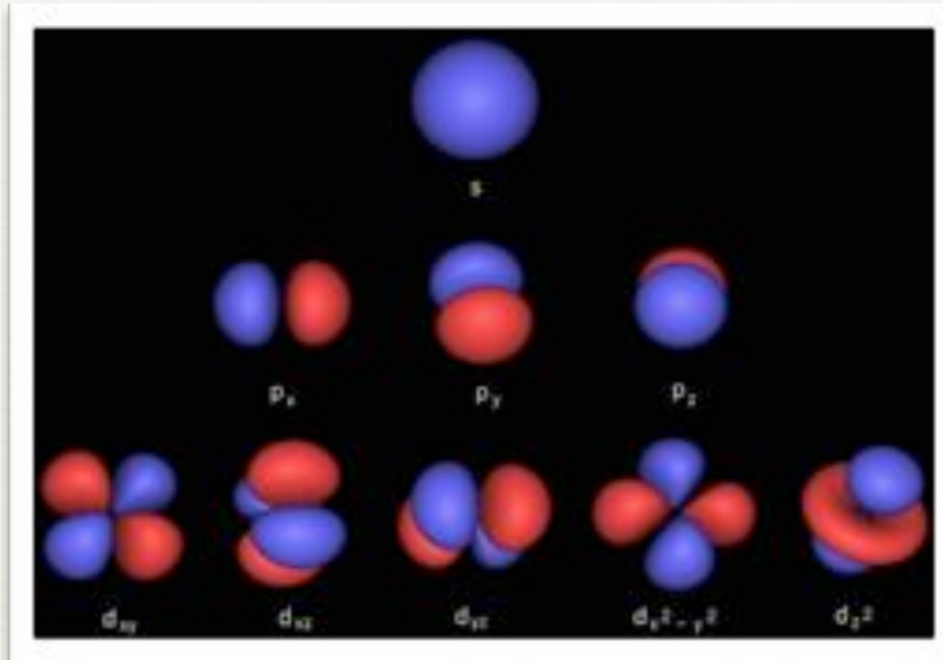
- Since standing waves can't exactly be said to "orbit" around anything, the areas where the electrons are most likely to be found (> 90%) are called ***orbitals***.
- ***s*** orbitals are fuzzy spheres, ***p*** orbitals are shaped like barbells or dumbbells for weightlifting, ***d*** orbitals are shaped like cloverleaves (except one suborbital), and ***f*** orbitals are double cloverleaves (except one suborbital).

PROBABILITY REGIONS

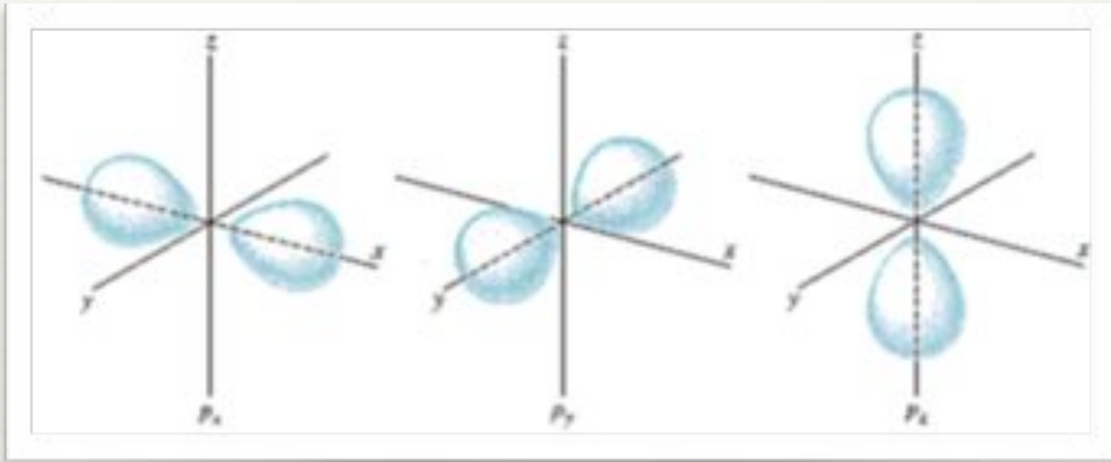


- These shapes represent regions of highest electron density, where the electrons are most likely to be found.
- The shapes not only come out of the equations, but using magnetic resonance, we can get a "picture" of the orbitals.

MAGNETIC-ANGULAR MOMENTUM QUANTUM NUMBER



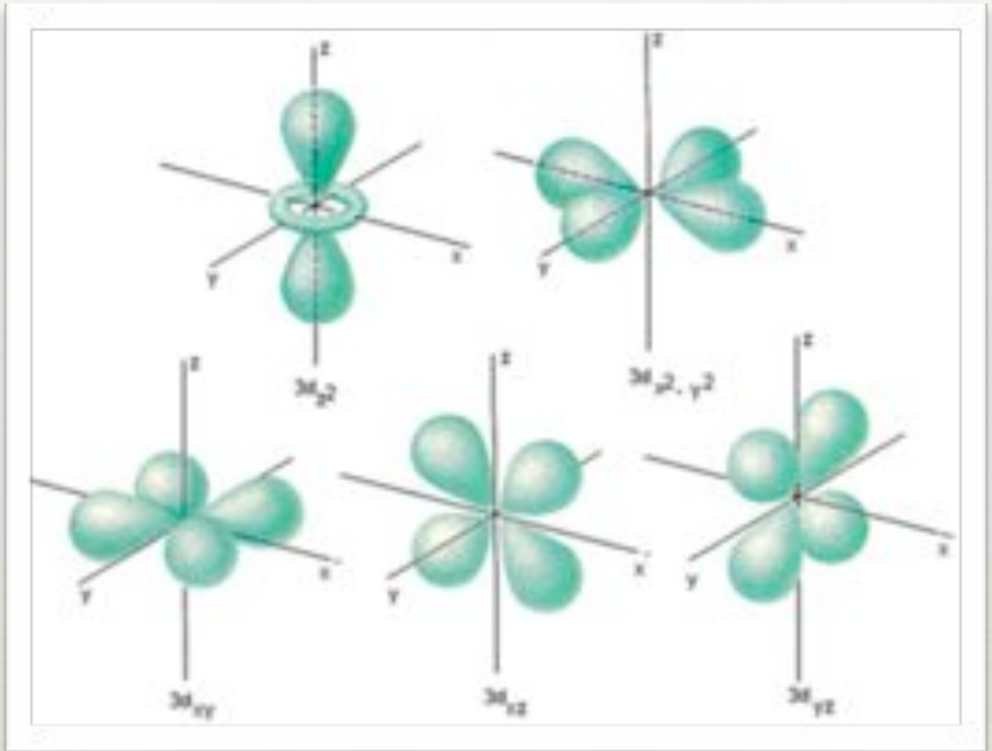
- The third quantum number is $\boldsymbol{m_l}$ (***m*** sub ***l***), which is the energy provided by the magnetic field associated with the electron's angular momentum.
- According to Faraday's Principle, a moving electrical charge (or electron) will produce a magnetic field.
- $\boldsymbol{m_l}$ can have allowable values from -***l*** to +***l***. For example, for ***l*** = 3, $\boldsymbol{m_l}$ can be -3, -2, -1, 0, 1, 2, and 3.



SUB-ORBITALS

- The m_l quantum number is also called the ***suborbital*** number, since it splits the orbitals into various orientations because of magnetic repulsion between electrons.
- The ***p*** orbitals (l = 1) split into three suborbitals, each aligned along one of the coordinate axes and called p_x, p_y, and p_z.
- The total suborbitals for each value of l is $2l + 1$.

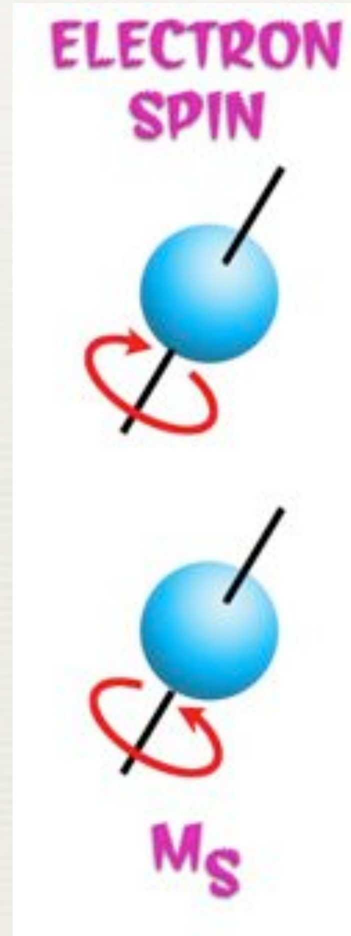
D SUB-ORBITALS



- The d-type orbital splits into five suborbitals (***l*** = 2 and ***ml*** = -2, -1, 0, 1, and 2).
- Four of the suborbitals are shaped like cloverleaves, the final (***ml*** = 0) is a dumbbell with a ring.
- They are aligned as far apart from each other as possible.

SPIN QUANTUM NUMBER

- The fourth quantum number, $\boldsymbol{m_s}$, is the energy provided to the electron by the magnetic field associated with the electron's spin.
- If we show an electron as a spherical particle, it can be said to have a rotational axis and can either rotate clockwise or counter-clockwise.
- These spins are given values of -1/2 and +1/2.

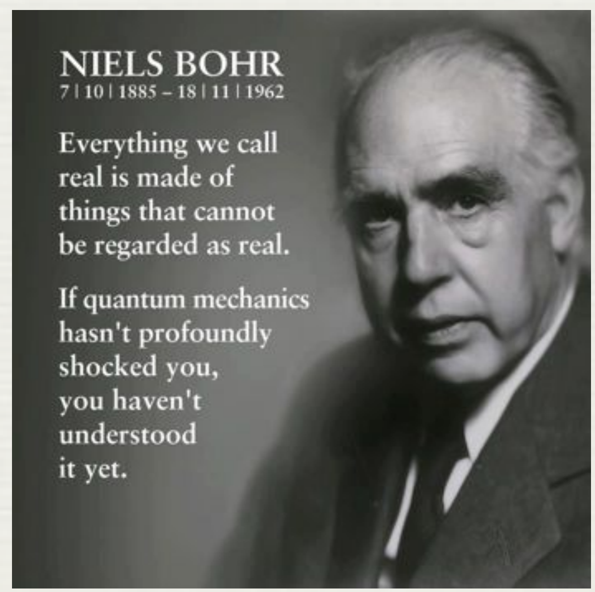


ELECTRON PAIRS

- Although electrons tend to repel each other (having like charges), two electrons can pair up in the same suborbital if they have opposite spins.
- However, according to Hund's Rule, if there are empty suborbitals available, electrons won't pair up unless they have to.

The London Bus Analogy

- Imagine getting on a bus with many levels of benches. The benches have room for two people each.
- You would not want to sit by a stranger if an empty bench was available. But you would rather sit by a stranger than climb to a higher level.
- Electrons fill atoms in just the same way. The benches are the suborbitals (m_l).



ALL THE NUMBERS

- Now that you understand quantum numbers . . . you do, don't you??
- (According to Richard Feynman, no one really understands quantum mechanics)
- Here's a table showing the allowable numbers for each main energy shell (***n***) for ***n*** = 1 to 4:

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  e.g. If *n* = 4, *l* can be 0, 1, 2, or 3.

- "*m*" can be any integer between -*l* and +*l*.

  e.g. If *l* = 2, *m* can be -2, -1, 0, 1, or 2.

- "*s*" is arbitrarily assigned as $+\frac{1}{2}$ or $-\frac{1}{2}$, but for any one subshell (*n*, *l*, *m* combination), there can only be one of each.

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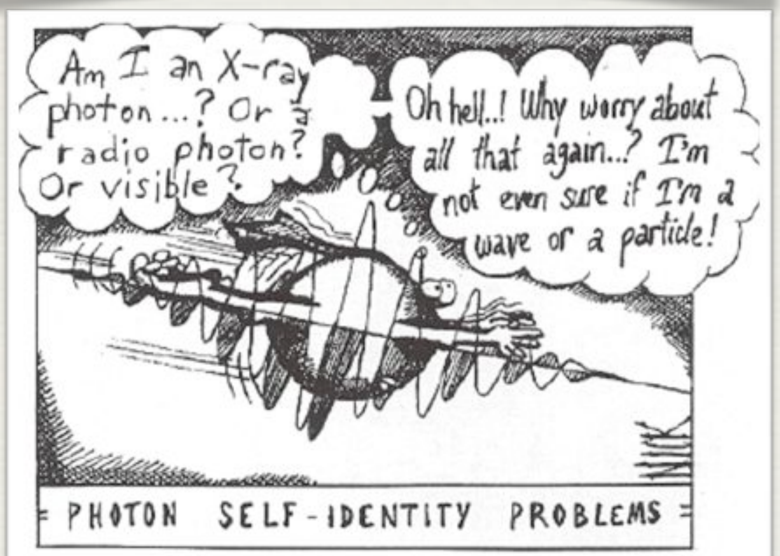
	3	4f	-3 -2 -1 0 +1 +2 +3	7

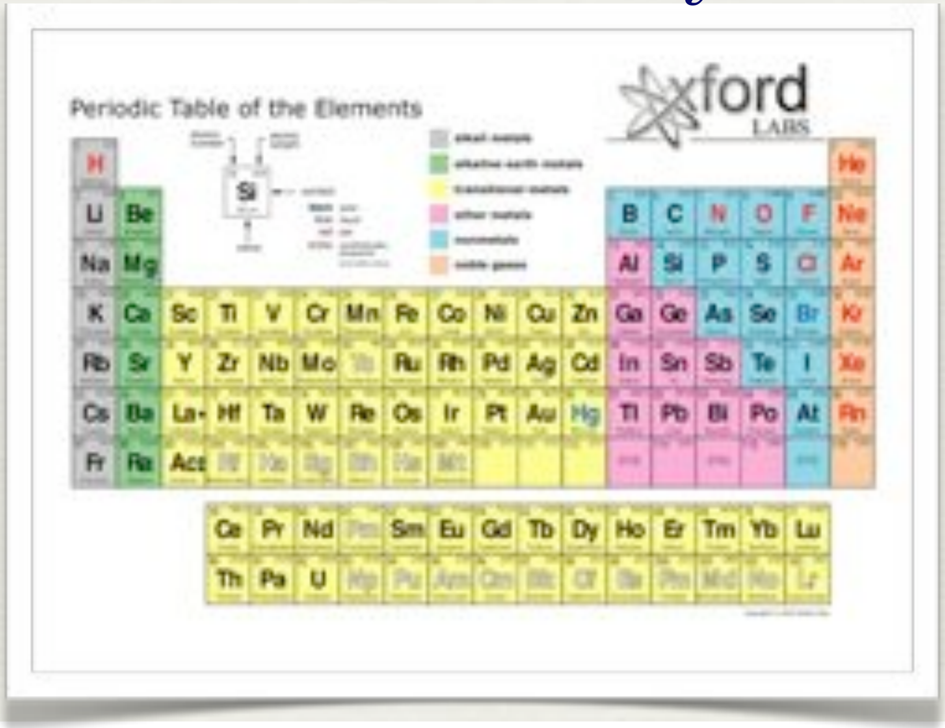
ELECTRONS PER ORBITAL



- About now, you should be having an "Ah hah!" moment: "If two electrons can fill each suborbital," you say to yourself, "Then there can be two electrons in an *s* orbital, six in a ***p***, ten in a ***∂***, and fourteen in an ***f***."
- Either that, or you wish all quantum theorists would pack up and move to Goat Island . . . or better yet, you wish YOU were on Goat Island instead of studying quantum numbers.

THE IMPORTANT PART

- If you've been skimming through this presentation until now, here's the important part: the shape of the periodic table actually depends on these quantum numbers and how electrons fill the orbitals.
- Quantum numbers also explain why different elements have different properties and determine how they react with each other.
- In other words, quantum mechanics explains just about all of chemistry! Not bad for just four numbers.

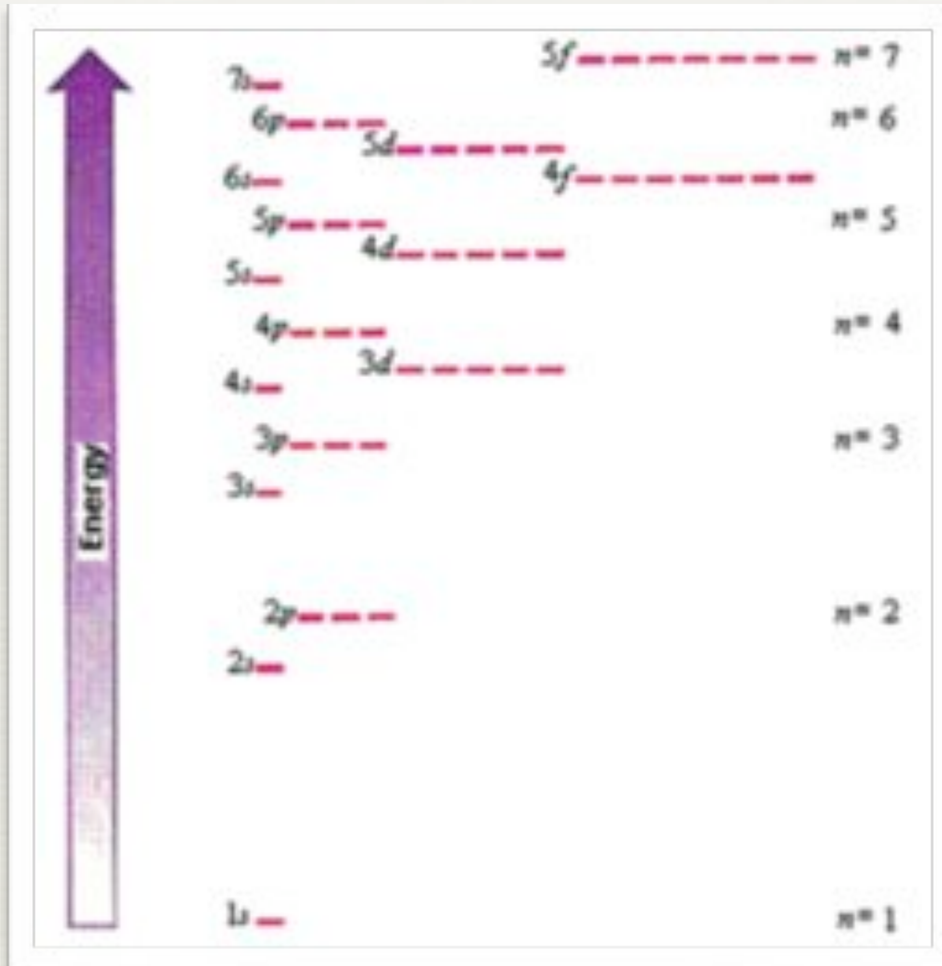


PERIODIC TABLE BLOCKS

- Quantum numbers are represented by the different blocks of elements in the periodic table.
- The two left-most columns represent the *s*-orbital electrons.
- The central ten columns are *d*-orbital electrons.
- The right six columns are the *p*-orbitals.
- The bottom two rows with 14 elements each are the *f*-orbital electrons.

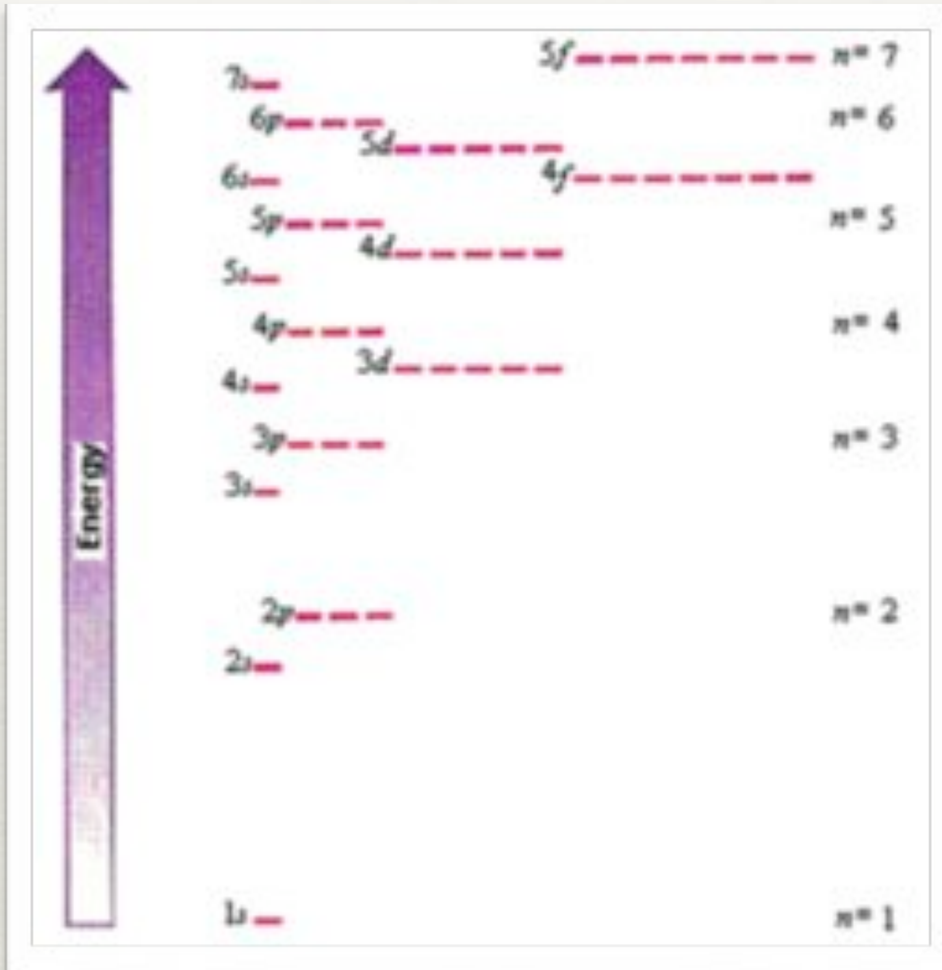
THE AUFBAU PRINCIPLE

- The various energy shells (***n***) fill up with electrons from the lowest levels up.
- This is the Aufbau ("filling up") Principle.
- Since shells split up into orbitals and suborbitals, they overlap each other.

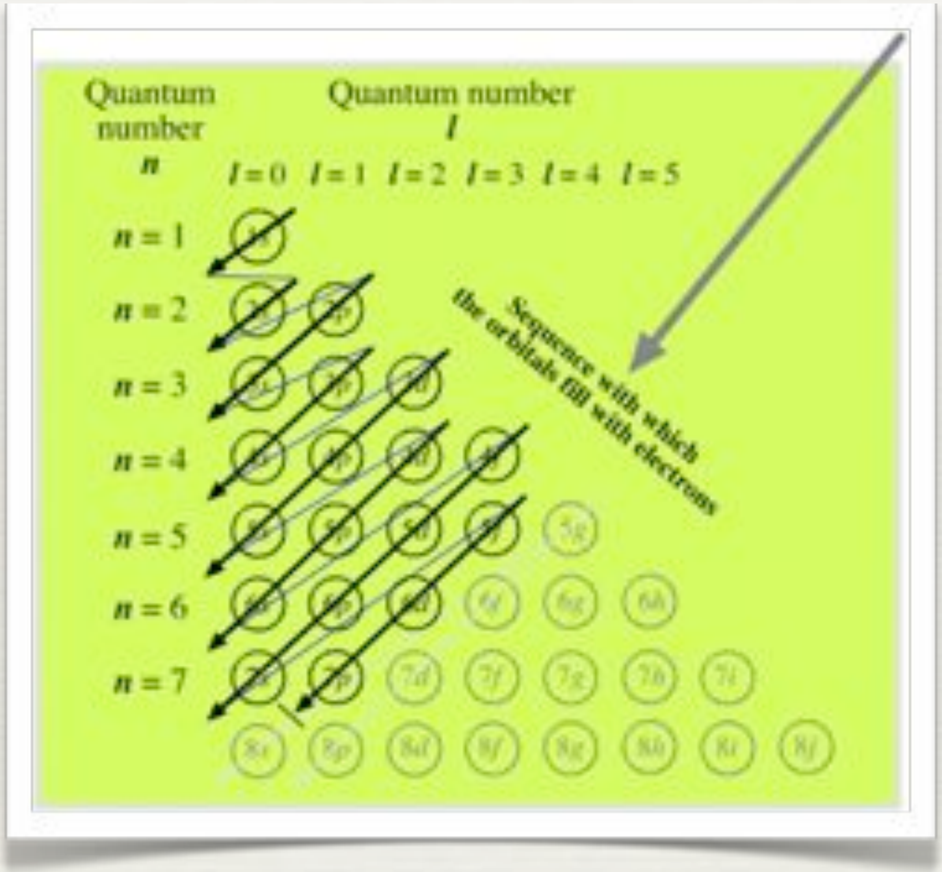


ELECTRON LADDER

- For example, electrons start to fill up the fourth shell (4*s* orbital) before they finish the third shell (3*d* orbital).
- In this electron ladder diagram, each suborbital is represented by a dashed red line.
- Each suborbital can hold two electrons.



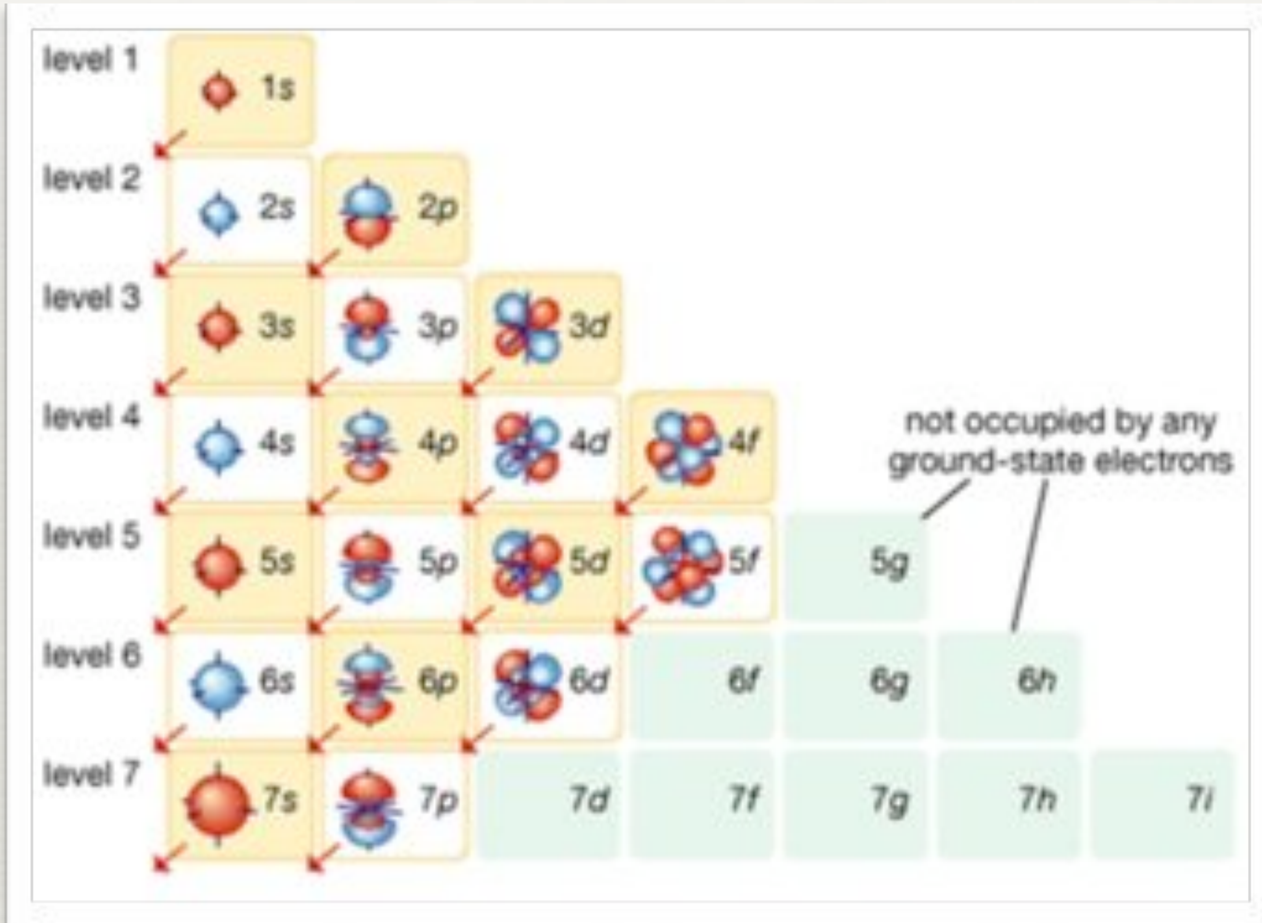
ORBITAL FILLING ORDER



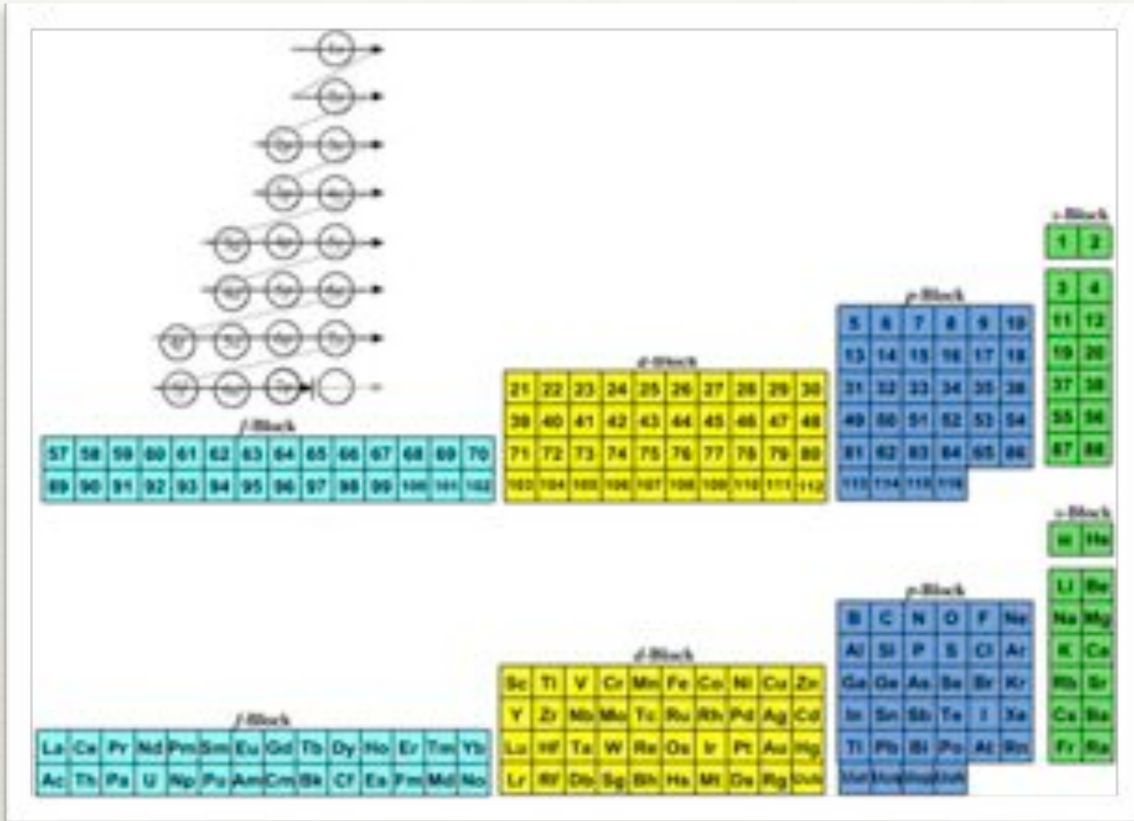
- The order of orbital filling is therefore: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, 5*f*, 6*d*, 7*p* . . . and that's as far as we've gotten.
- The next orbitals should be 8*s*, then 5*g*. We don't know what a *g* orbital would look like.
- Fortunately, there is a pattern to all this, as this diagram shows.

ORBITAL FILLING ORDER

- Here's another version of the same filling diagram:



LEFT-STEP TABLE



- The best way to visualize electron orbital filling as it relates to the Periodic Table is to use the left-step version, invented by Charles Janet in 1928.

- Here, the order of electron orbital filling as it relates to atomic number (and electron number for neutral atoms) is more easily seen.

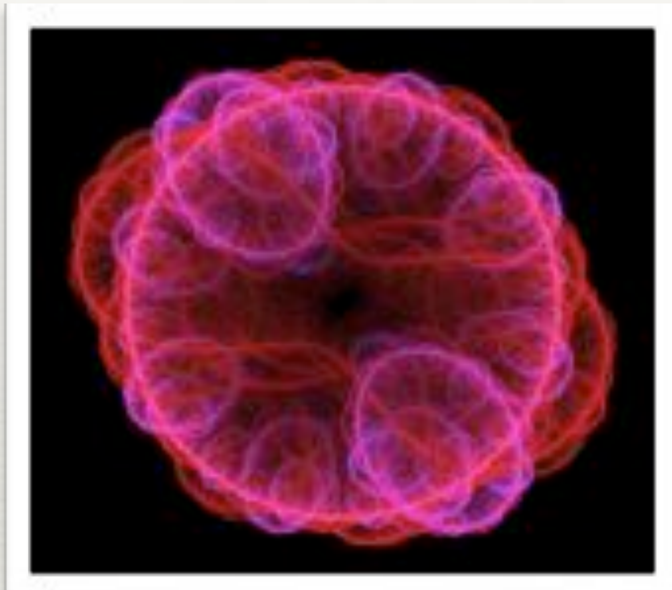
ELECTRON CONFIGURATIONS

- Each element has an electron configuration that represents how many electrons are in each shell and orbital.
- We use a shorthand that looks like this for platinum, for example: [Xe] 6*s*2 4*f*10 5*d*8.
- This means that platinum has the same core electron structure as Xenon (the previous noble gas) plus a full 6*s* orbital, a full 4*f* orbital, and eight electrons in the 5*d* orbital.

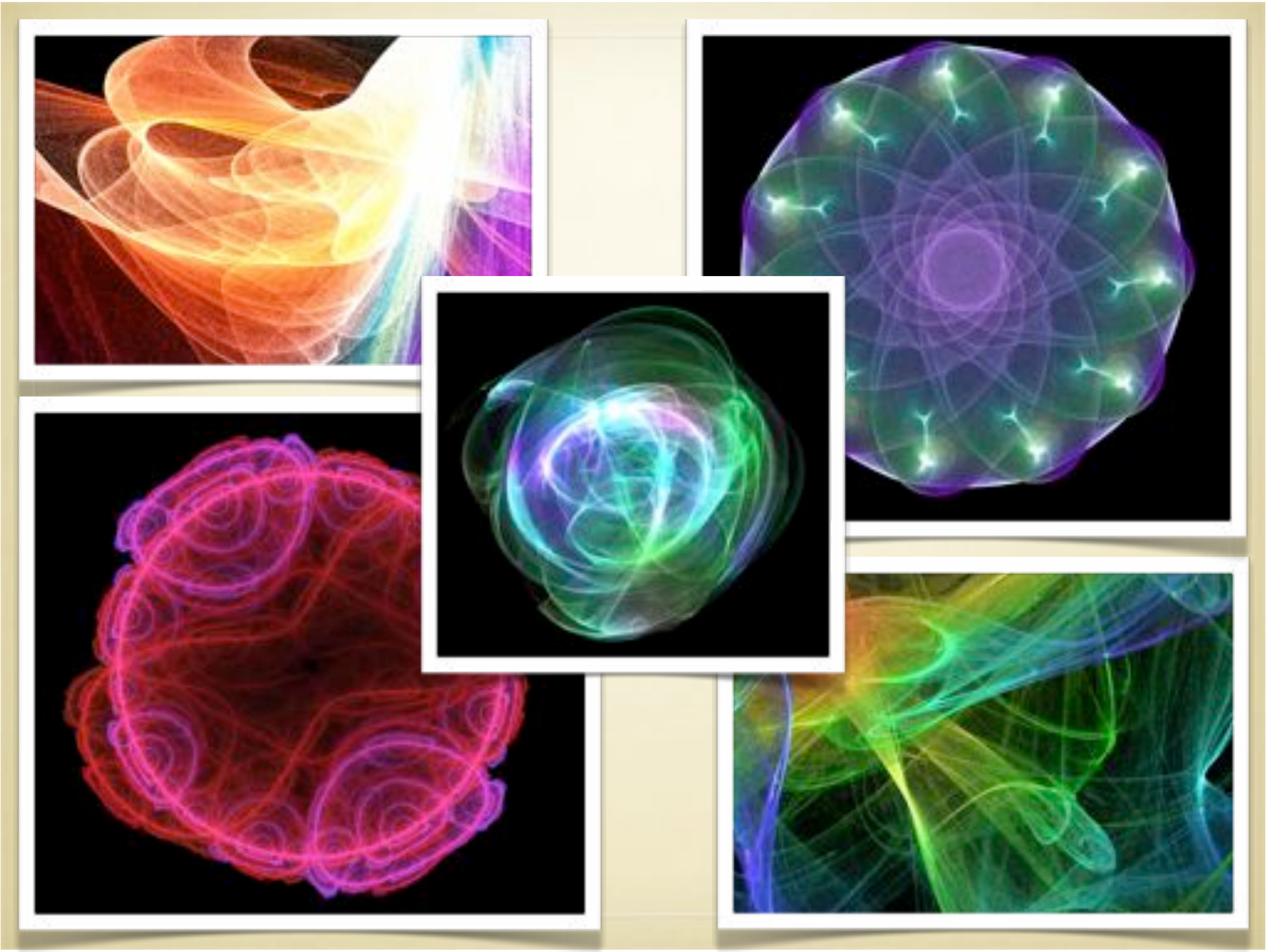
DANCE OF ENERGY

- All of these shells, orbitals, and suborbitals fit inside each other, nestled together in an intricate dance of electrons.
- Electrons absorb energy as atoms are heated up or are struck by photons.
- As they absorb energy, they leap to higher quantum levels (a so-called quantum leap).
- When they drop back to their ground state, they emit very specific wavelengths of light that can be used to identify the elements. And make fireworks . . . .

CRYSTALLIZED ENERGY

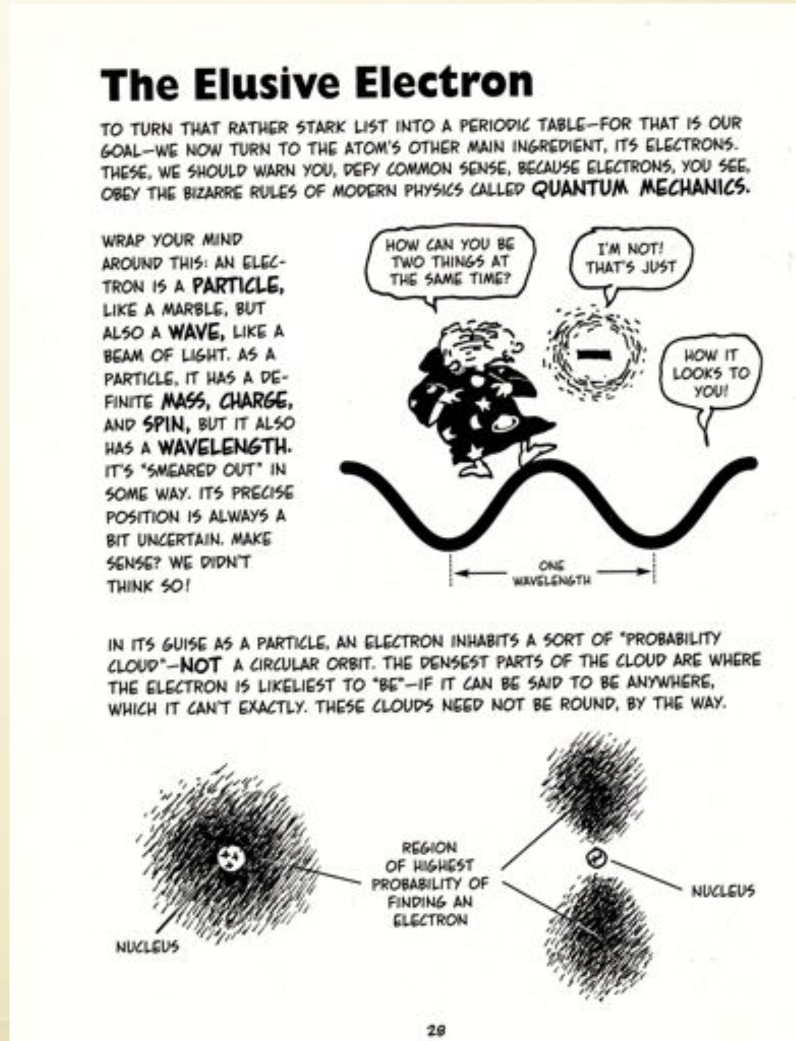


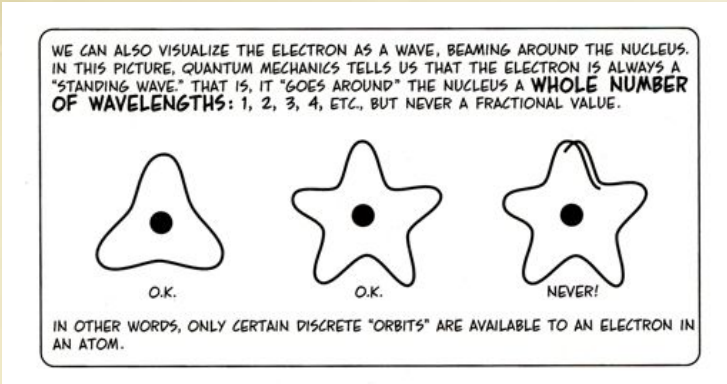
- From Einstein's Special Relativity equation, we understand that energy and matter are two sides of the same coin.
- Matter (including electrons) is really just crystallized energy, a pattern of standing waves (or localized interference) which is predicted by quantum mechanics.
- Just something to think about . . . .

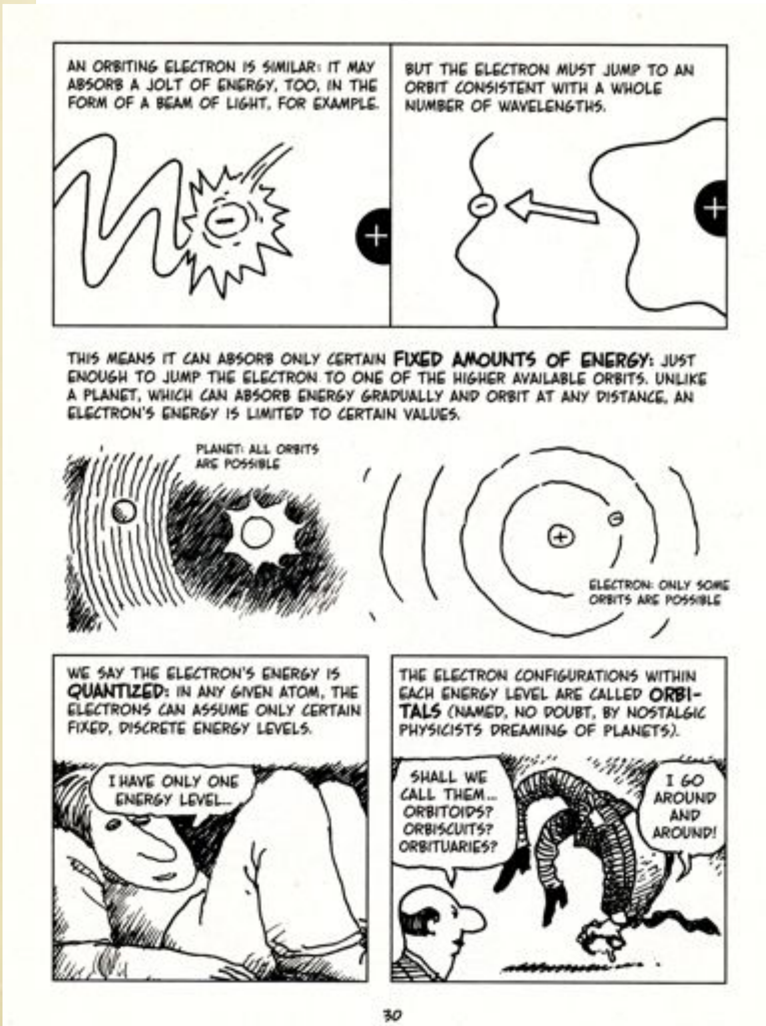


The Cartoon Guide to Chemistry

- Let's look at this another way:
- "The Cartoon Guide to Chemistry" by Larry Gonick and Craig Criddle
- Electrons are particles that are smeared out into waves.







Nature of Electrons

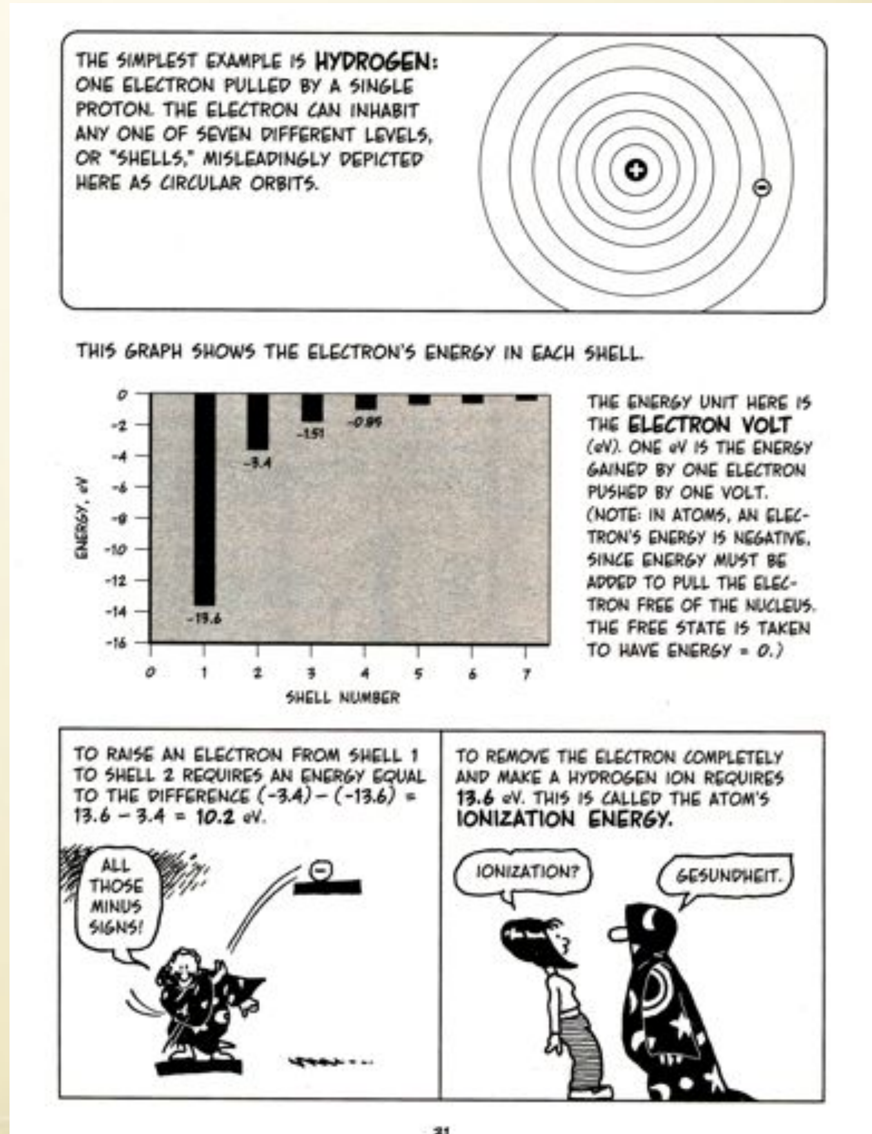
- Electrons are standing wave patterns wrapped around the nucleus of the atom.
- The principle quantum number can only be an integer, because for other values the waves interfere and cancel each other out.
- Think of it as the number of waves that are wrapped around, an example of discrete math.

Energy Levels

•In the hydrogen atom, there are seven possible energy levels.

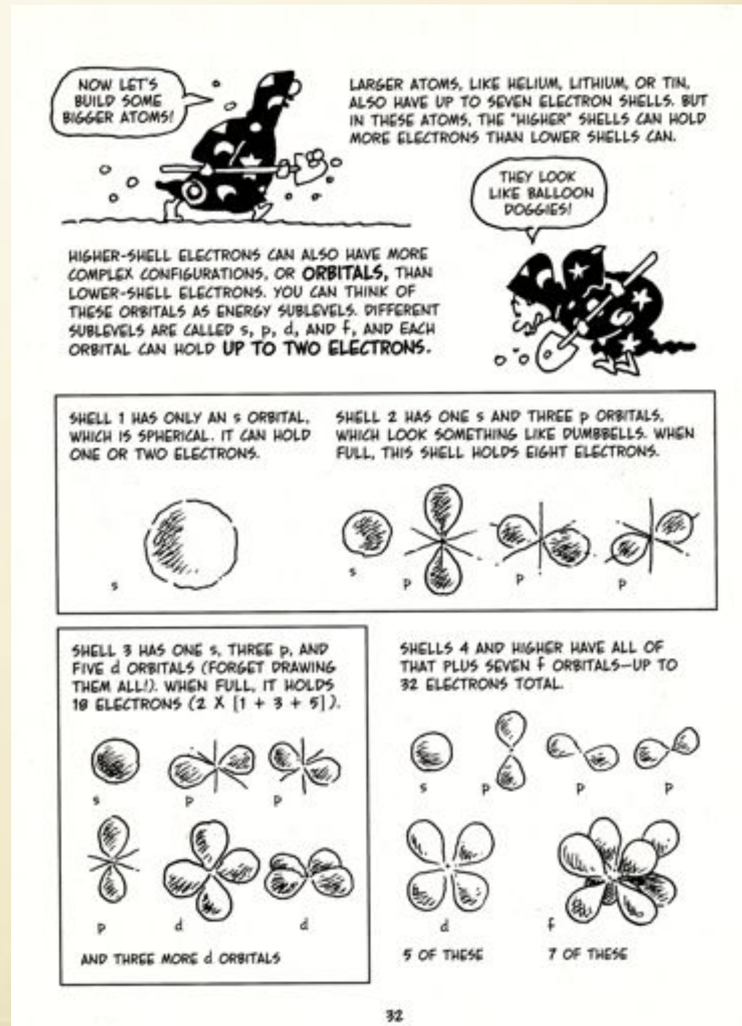
•The energy levels become closer to each other as they get further from the nucleus.

•Since each energy level has many sub-levels, they start to cross over each other.

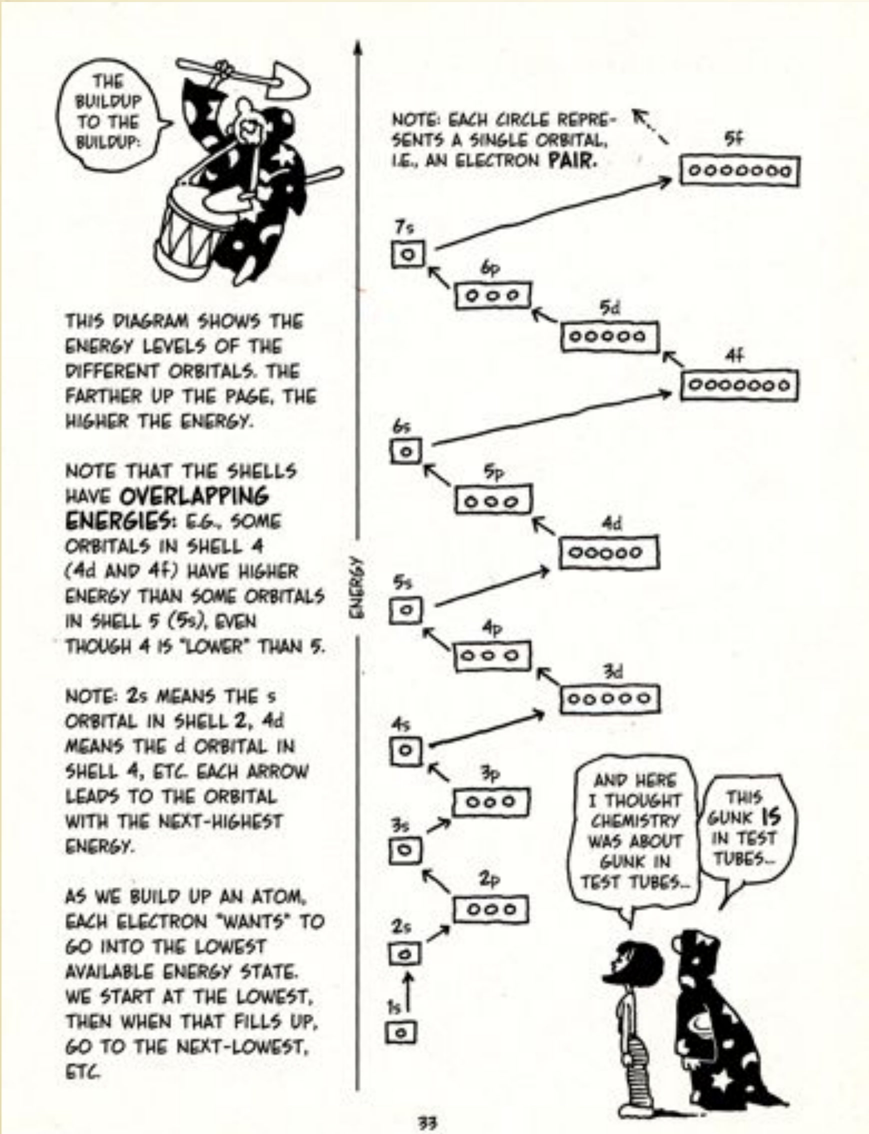


Orbital Shapes

- According to the quantum numbers, each main level has the same number of sublevels as the number of the main level (n = 1 has 1, n = 2 has 2, etc.)
- Each sublevel (orbital) can hold four more electrons than the next lowest orbital type.
- That means that s = 2, p = 6, d = 10, and f = 14.
- Each orbital has its own shape created by the angular momentum of the various electrons in it and their mutual repulsion.



Filling Up the Levels



- The Aufbau and Hund Principles give us rules for how the electrons fill up the various orbitals and levels.
- They don't pair up unless they have to, and they almost always go to the lowest available energy level (orbital).

How This Relates to the Periodic Table

- The various blocks of the periodic table correspond to the numbers of electrons allowed in each orbital as the levels fill up, starting with hydrogen.