# Science and Technology

## Atomic Theory, Chemical Bonding, Chemical Compounds, and Chemical Warfare

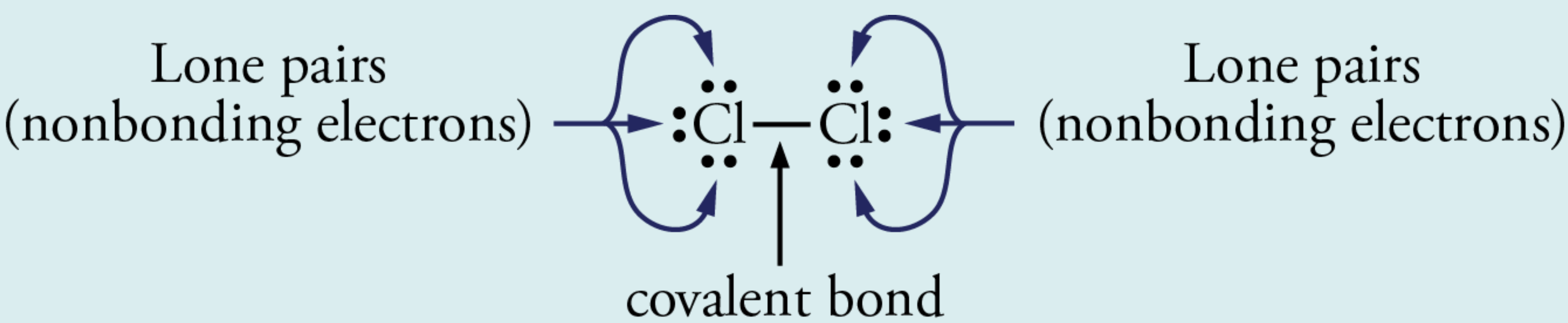
By Mark Bishop

One doesn't discover new lands without consenting to lose sight of the shore for a very long time.

Andre Gide
French Novelist and Essayist

# Our Goals…to get a glimpse at

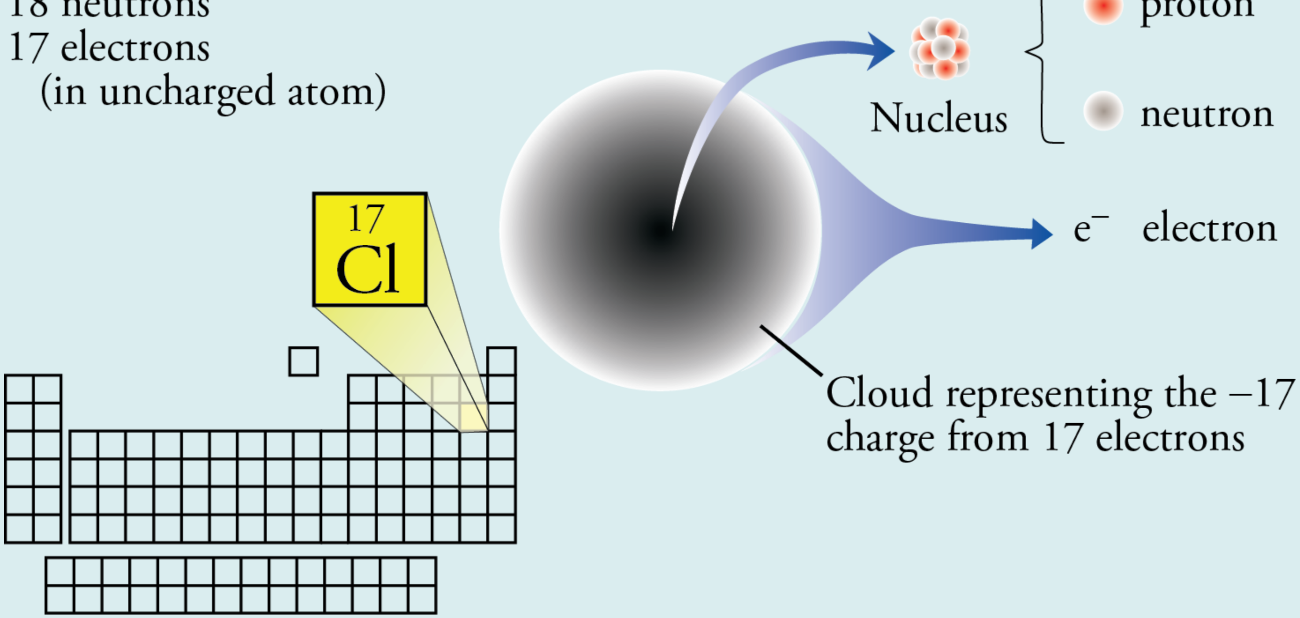
- What humans can and cannot understand
- One way that we can describe things that at some level, we cannot understand
- Get some background, such as a better understanding of atoms and energy
- To understand ***Lewis structures***, such as the Lewis structure of chlorine, the first chemical weapon used in the modern era and one of the most recently used.



# A Chlorine-35 Atom

Chlorine-35 atom

17 protons
18 neutrons
17 electrons
(in uncharged atom)




| | Particle | Charge | Mass |
|---|---|---|---|
| | proton | +1 | 1.00728 u ($1.6726 \times 10^{-24}$ g) |
| | neutron | 0 | 1.00867 u ($1.6750 \times 10^{-24}$ g) |
| $e^-$ | electron | −1 | 0.000549 u ($9.1096 \times 10^{-28}$ g) |

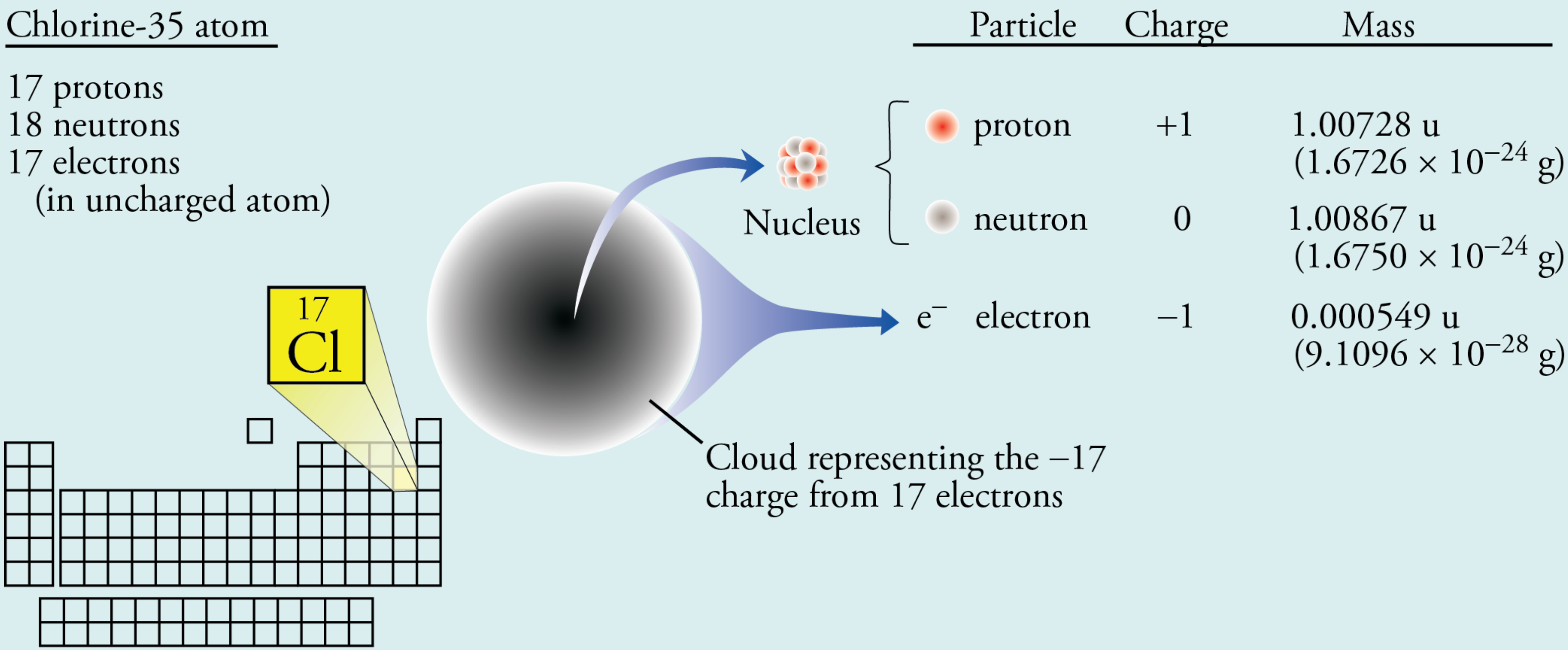
# Barrier to our understanding

- Everyone agrees that there’s a limit to Maverick’s understanding.
- We too have a barrier to our understanding, and there are many things that are beyond that barrier.

# What do we know about mass?

- Standard definition: a measure of the amount of matter in an object.
- Only some particles have it.
- It’s the characteristic of matter that leads to gravitational attraction between objects with mass.
- The greater the masses of the objects attracting each other, the stronger the force of gravitational attraction.
- The greater the distance between the centers of the objects, the weaker the force.
- Mass can be converted into energy, and energy can be converted into mass.

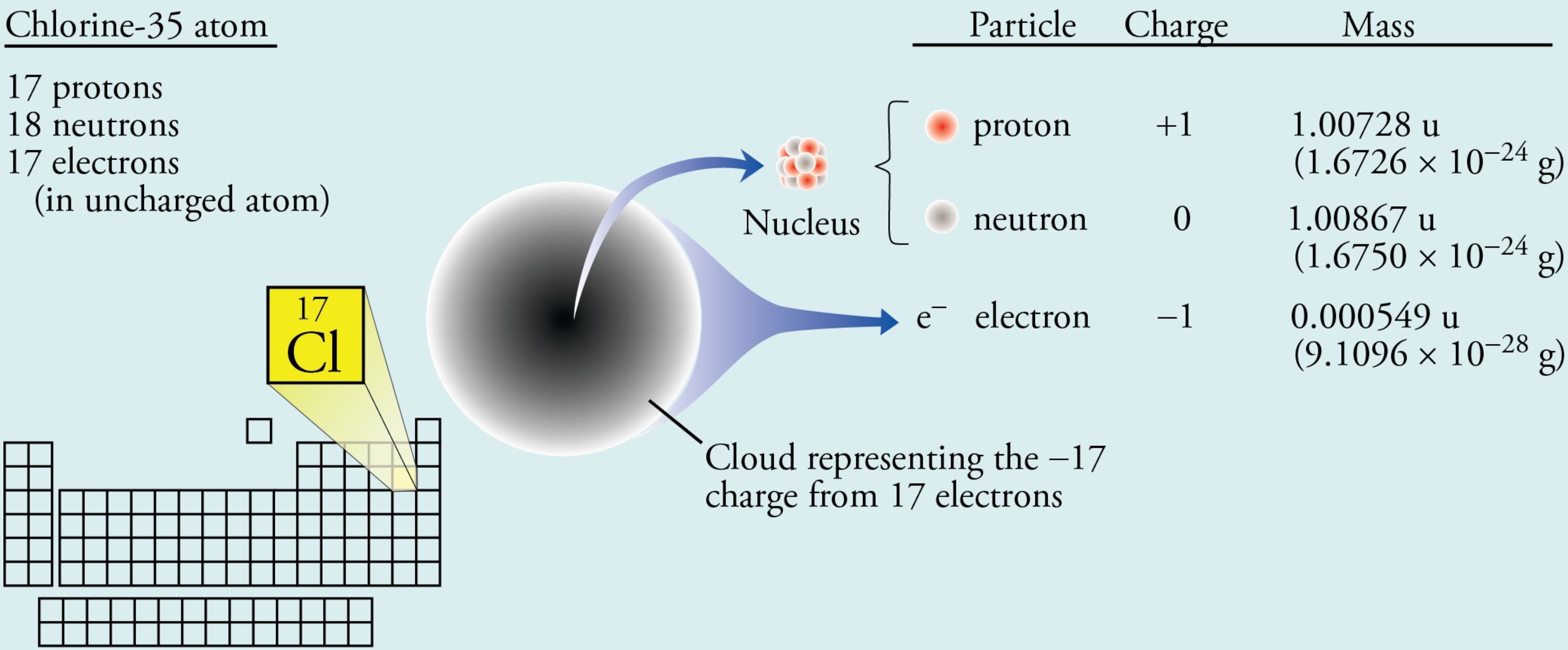
# A Chlorine-35 Atom



# What do we know about charge?

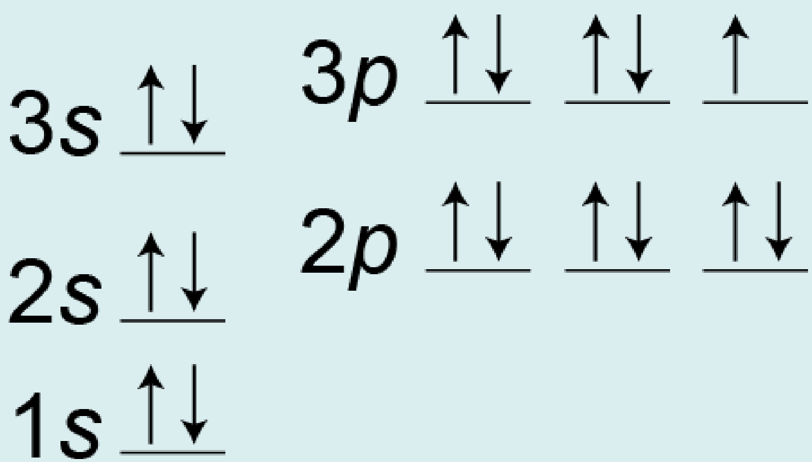
- Only some particles have it.
- There are two types of charge, plus and minus.
- It’s the characteristic of matter that leads to electromagnetic forces due to passing photons back and forth.
- Like charges repel.
- Opposite charges attract.
- The closer the charges, the stronger the force.
- The higher the charges, the stronger the force.

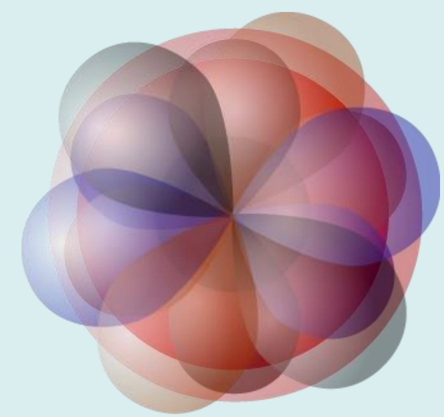
# A Chlorine-35 Atom



# Chlorine's 17 Electrons

- The next time you see this, it will make sense.



# 3 Physics “Trust Me’s”

- **“Trust Me’s” that lie at the basis of our description of the electron**
  - All matter has both particle and wave character.
  - The less massive the particle, the more important its wave character.
  - The electron has a very low mass, low enough to have significant wave character.

# A Problem

- **Problem:** We have a barrier to our understanding, and things with significant wave character are to some degree outside that barrier. This means that the behavior of electrons is non-intuitive.

# How We Solve the Problem

- One way we have been able to “describe” things outside our barrier of understanding is through mathematics.
- We describe things outside our barrier of understanding with mathematical equations, we solve the equations, we drag the results back under our barrier, and we apply them to things we do understand.
- If this helps us explain things or predict things, we assume we are on the right track.

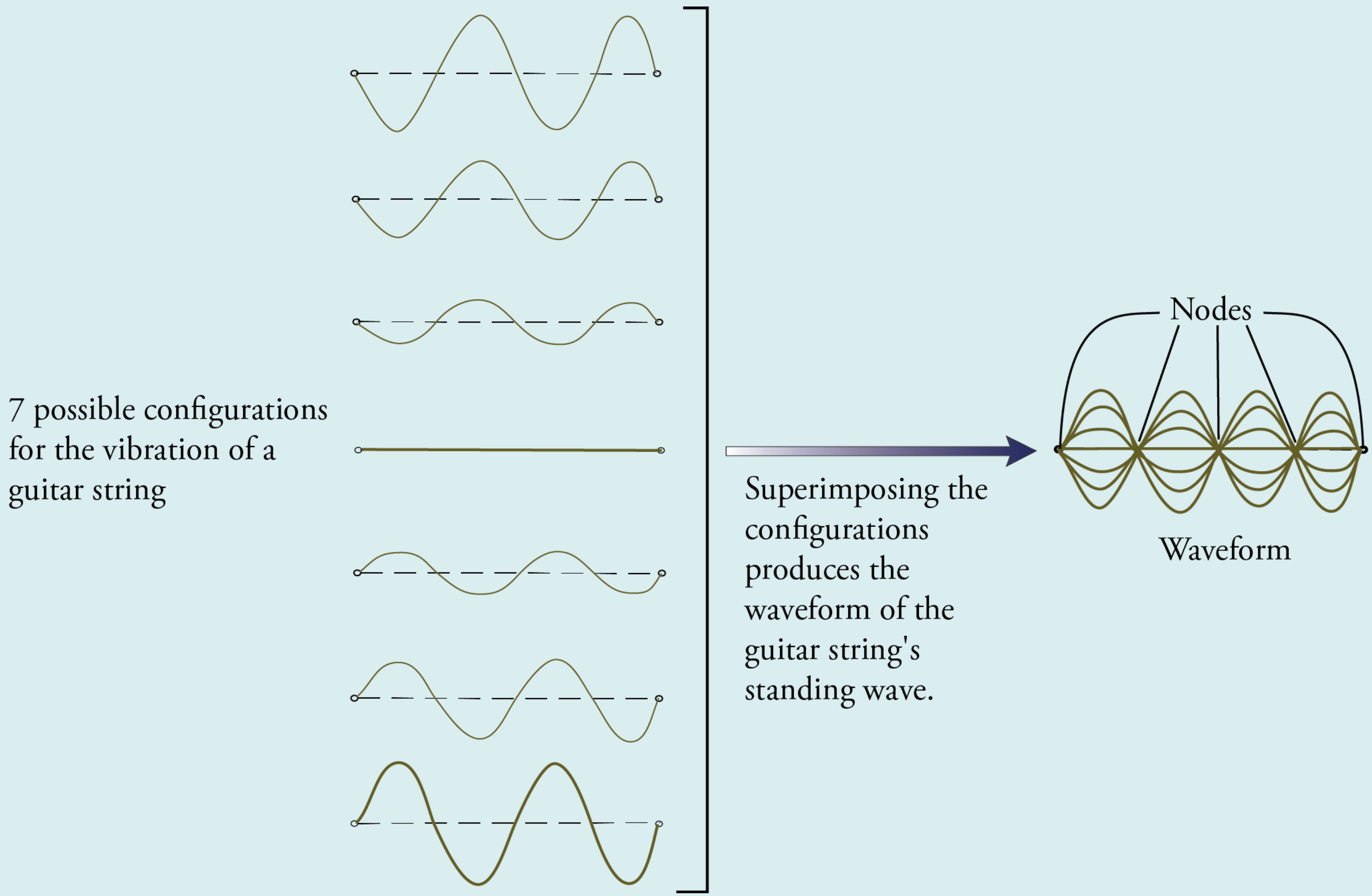
# Strangeness of Tiny Particles

- Things become very strange in the realm of the very, very small.
- One element of this strangeness is that we lose the possibility of being able to predict with certainty where small particles are going to be and how they are moving.
- Thus we shift from talking about where tiny things will be to where they will probably be.

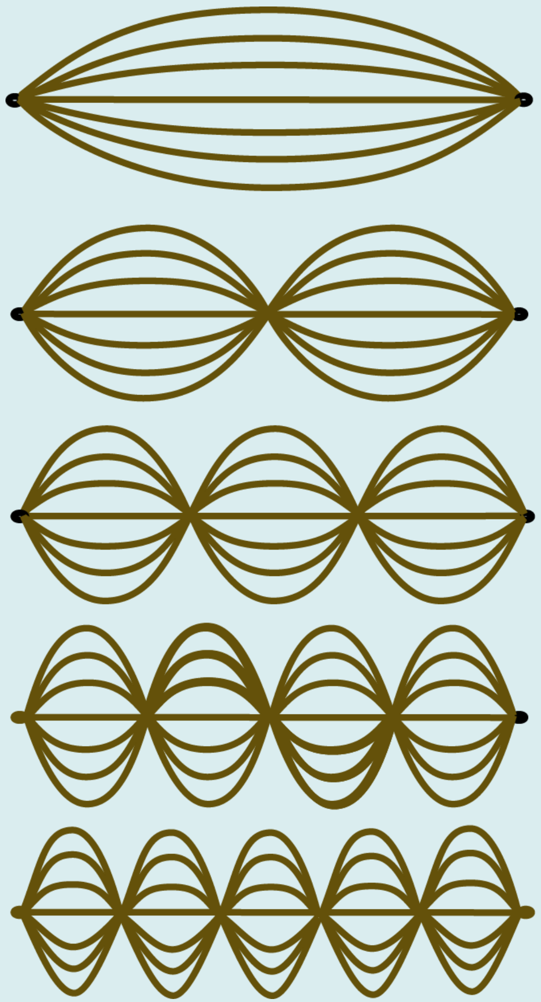
# Ways to deal with Complexity and Uncertainty

- **Analogies** In order to communicate something of the nature of the electron, scientists often use analogies. For example, in some ways, electrons are *like* vibrating guitar strings.
- **Probabilities** In order to accommodate the uncertainty of the electron's position and motion, we refer to where the electron *probably is* within the atom instead of where it definitely is.

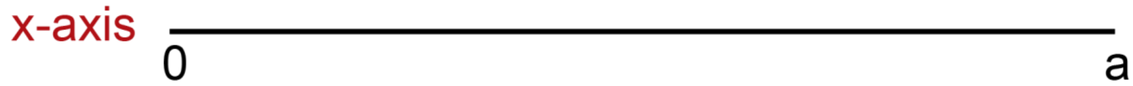
# Guitar String Waveform



# Allowed Vibrations for a Guitar String

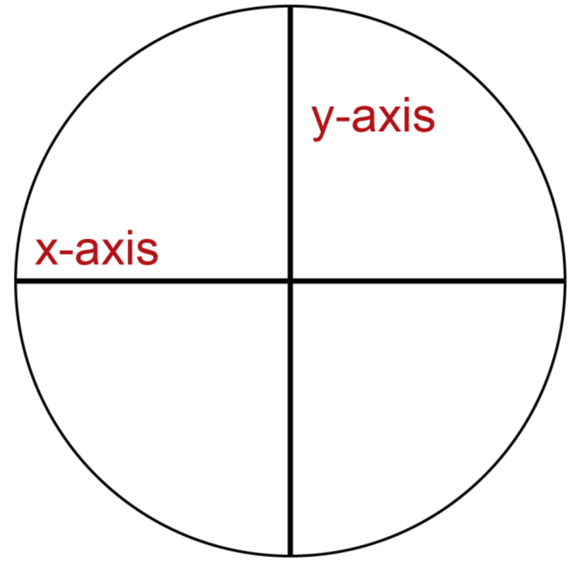


# Dimensions

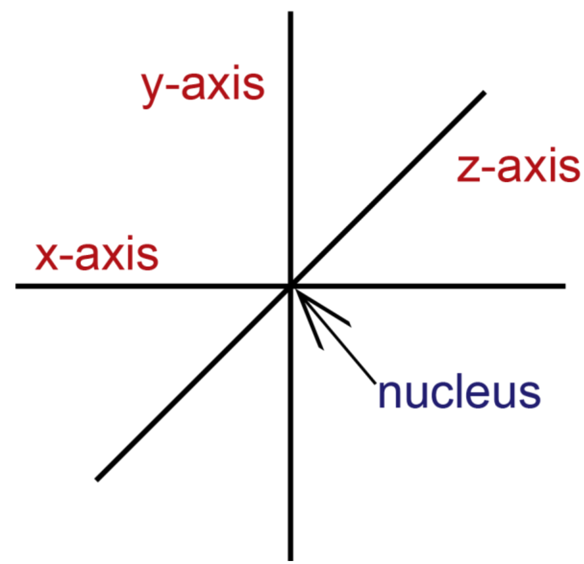



Guitar String

Drumhead




Electron for hydrogen



# Equation for Guitar String

$$A_x = A_o \sin \frac{n\pi x}{a}$$

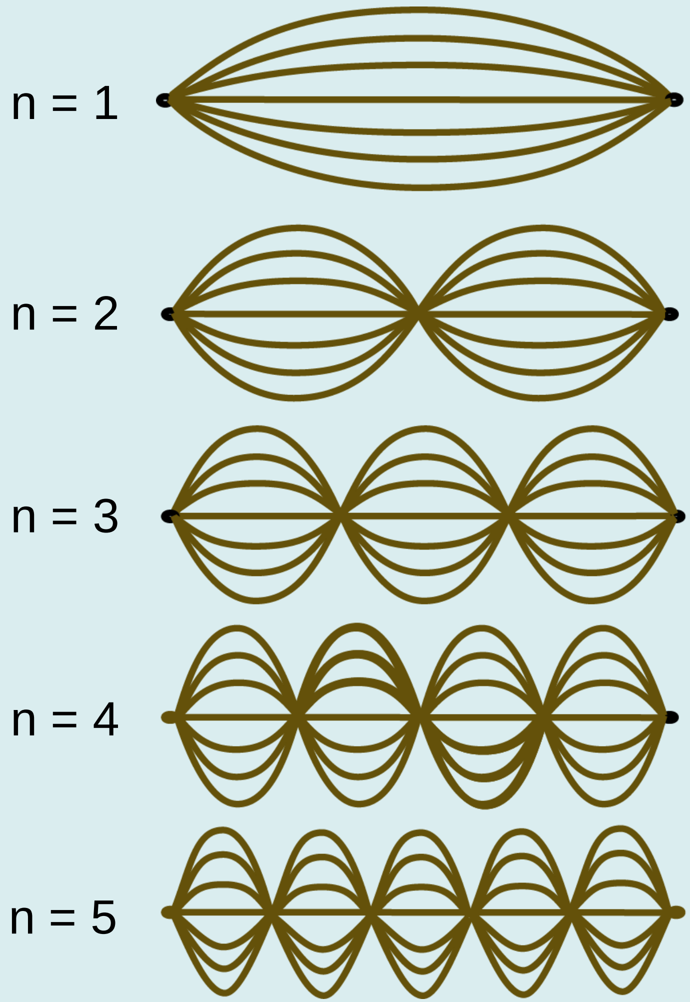
x-axis

0 a

Guitar String

- $A_x$ = the amplitude at position x
- $A_o$ = the maximum amplitude at any point on the string
- n = 1, 2, 3, ...
- x = the position along the string
- a = the total length of the string

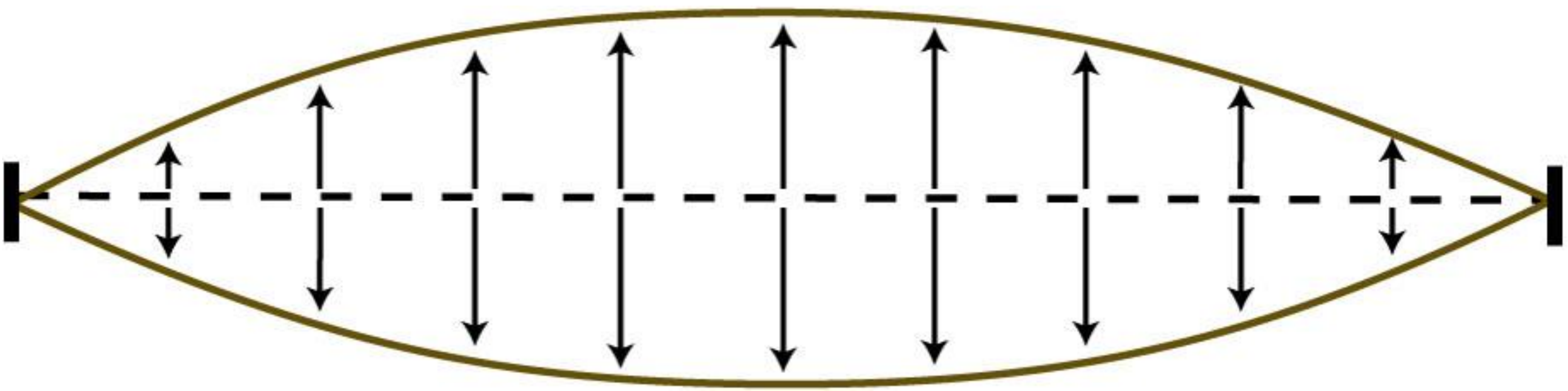
# Allowed Vibrations for a Guitar String



# Guitar String Waveform 1

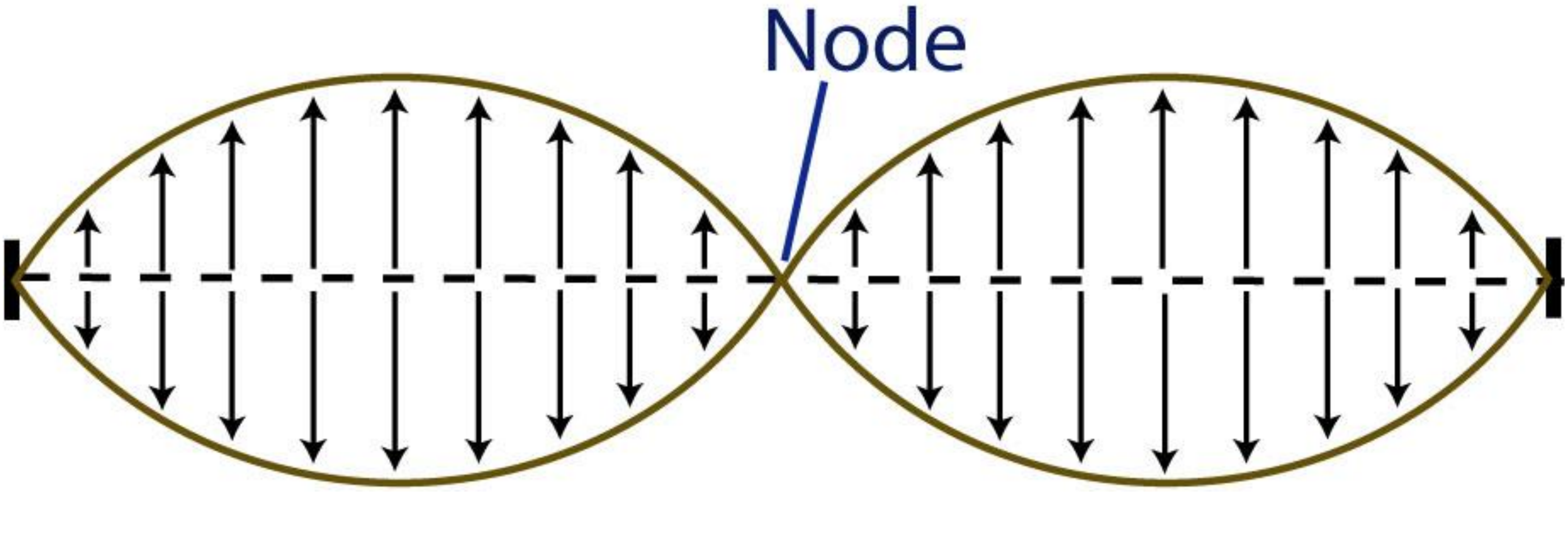
$$A_x = A_o \sin \frac{n\pi x}{a}$$

$$A_x = A_o \sin \frac{\pi x}{a}$$



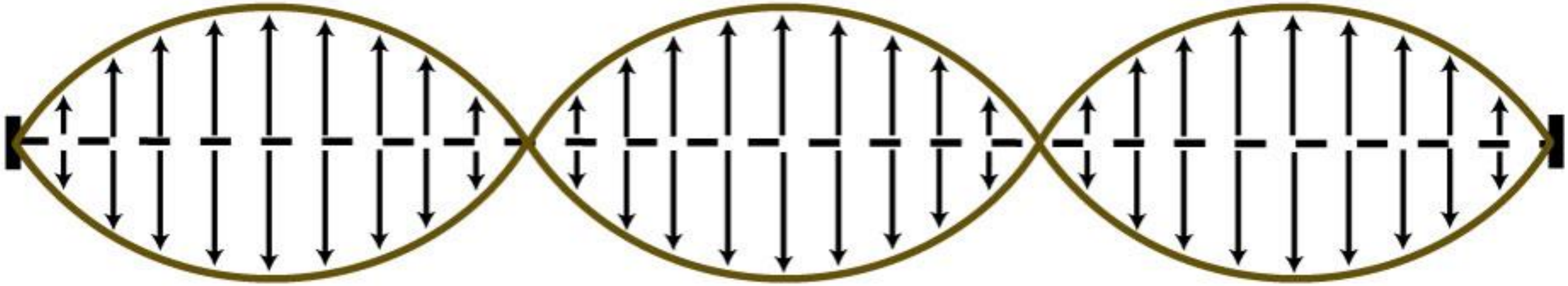
# Guitar String Waveform 2

$$A_x = A_o \sin \frac{2\pi x}{a}$$

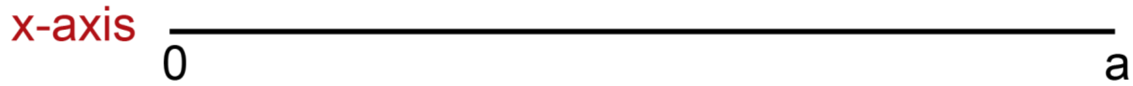


# Guitar String Waveform 3

$$A_x = A_o \sin \frac{3\pi x}{a}$$

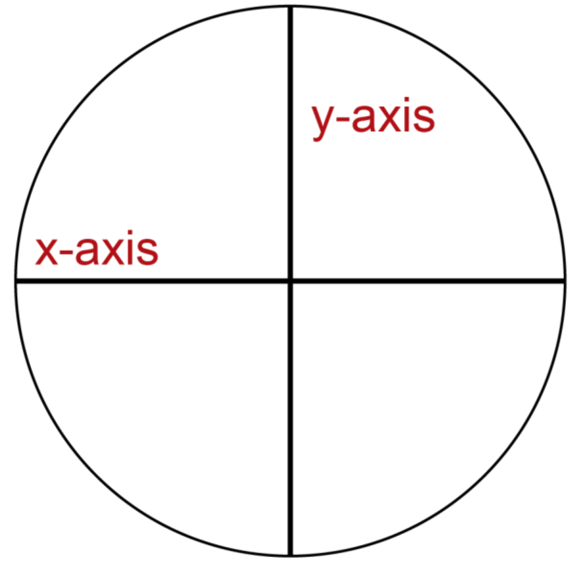


# Dimensions

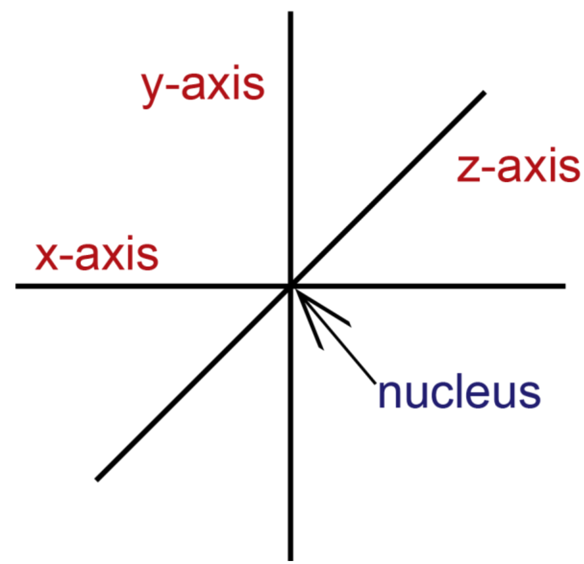



Guitar String

Drumhead




Electron for hydrogen

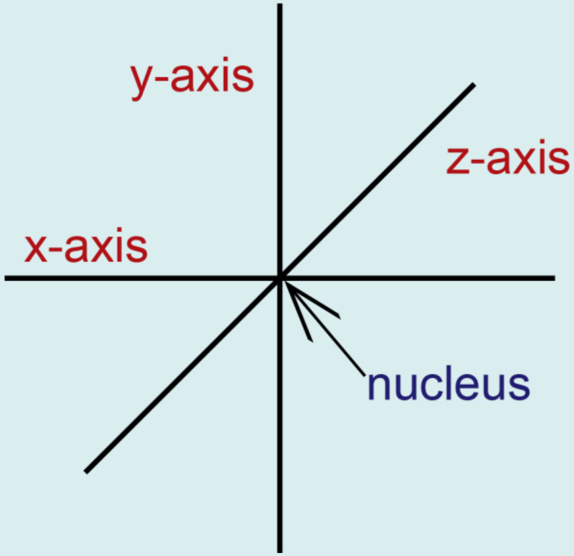


# Determination of the Allowed Electron Waveforms

- **Step 1:** Set up the general form of the wave equation that describes the electron in a hydrogen atom. We call this equation the wave function and the values calculated from the wave equation are represented by $\Psi$.

$$\Psi_{x,y,z} = f(x,y,z)$$

Electron for hydrogen



# Determination of the Allowed Electron Waveforms

- **Step 2:** Determine the forms of the general equation that fit the boundary conditions. Each equation has its own set of three quantum numbers. For example,

$\Psi_{1s} = f_{1s}(x,y,z)$ with 1,0,0 for quantum numbers

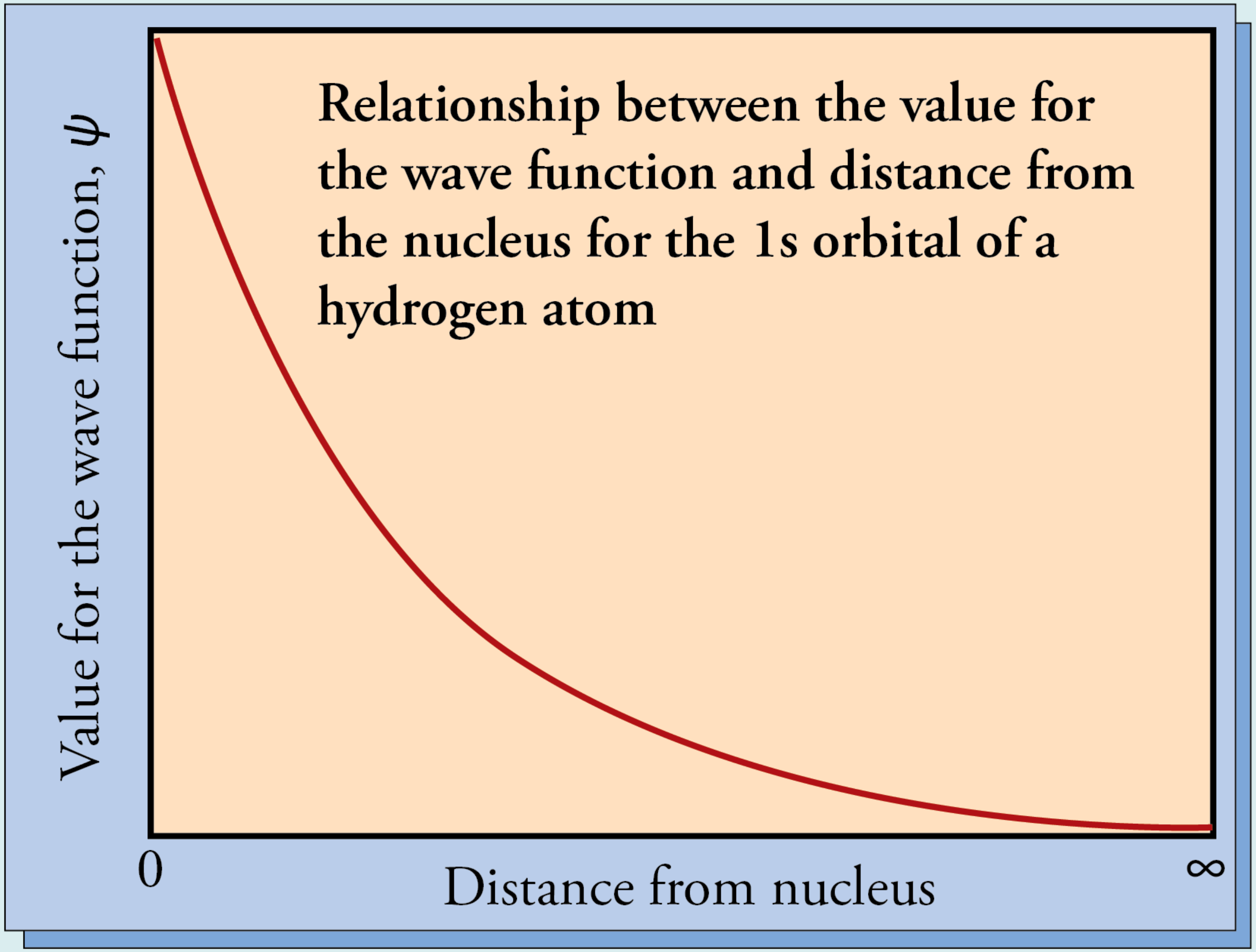
$\Psi_{2s} = f_{2s}(x,y,z)$ with 2,0,0 for quantum numbers

$\Psi_{2p} = f_{2p}(x,y,z)$ with 2,1,1 or 2,1,0
or 2,1,−1 for quantum numbers

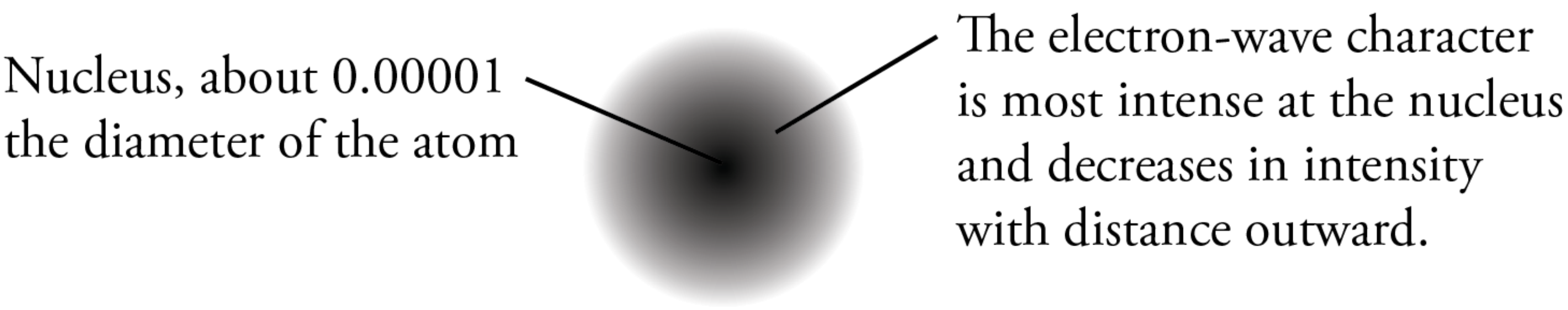
# Determination of the Allowed Electron Waveforms (cont.)

- **Step 3:** Use the specific form of the wave equation to do a series of repetitive calculations to get values for many different positions outside the nucleus. Each position is represented in the equation by different x, y, and z coordinates.
- **Step 4:** We ask our computer to summarize the values calculated in two ways.

# Graph for 1s electron (1,0,0)



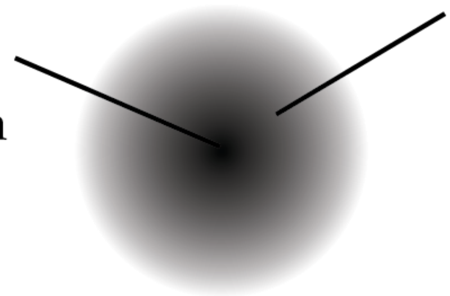
# Waveform for 1s Electron (1,0,0)



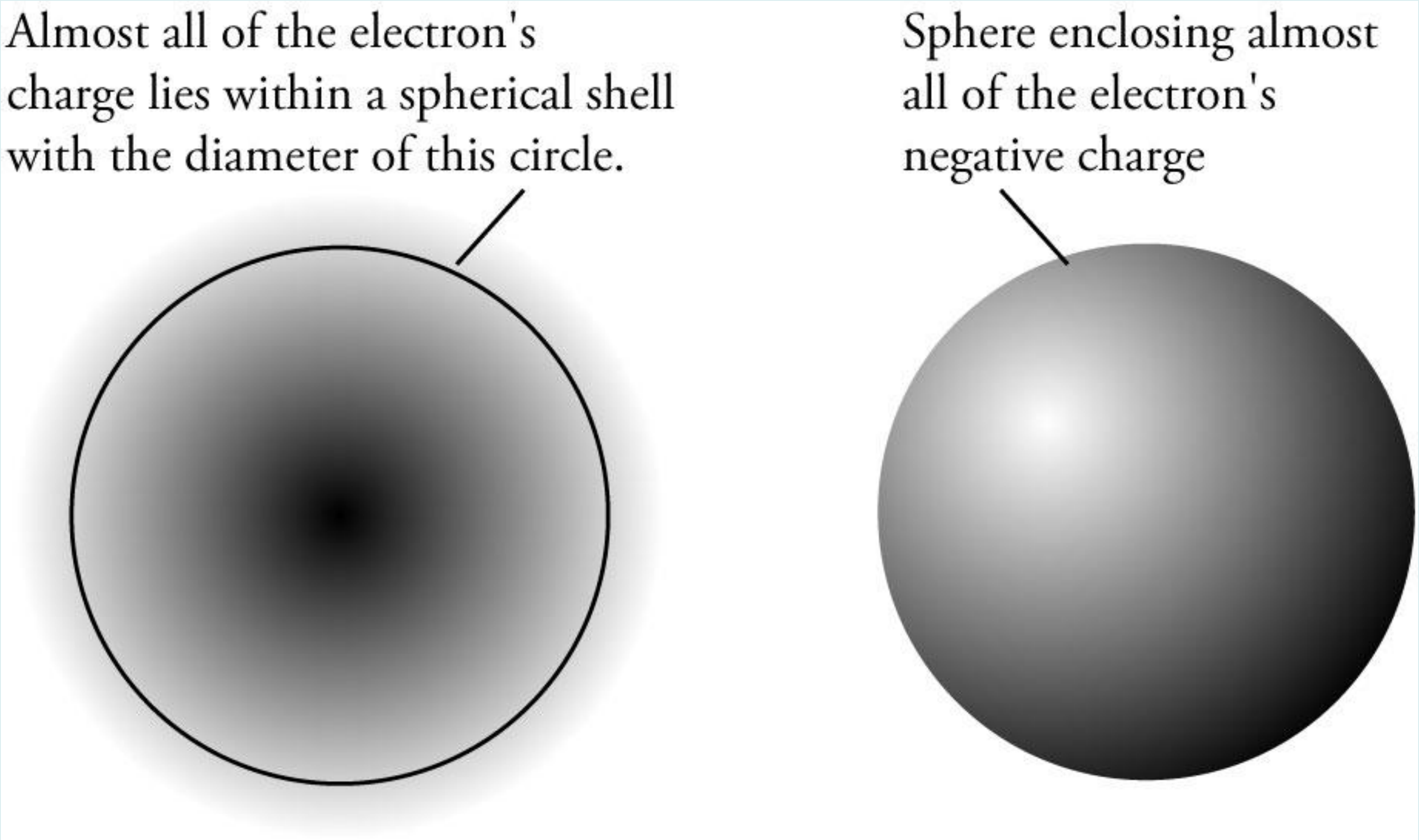
# Particle Interpretation of 1*s* Orbital

A multiple exposure picture of the electron in a 1*s* orbital of a hydrogen atom might look like this.

# “Just give up approach”



# 1s Orbital

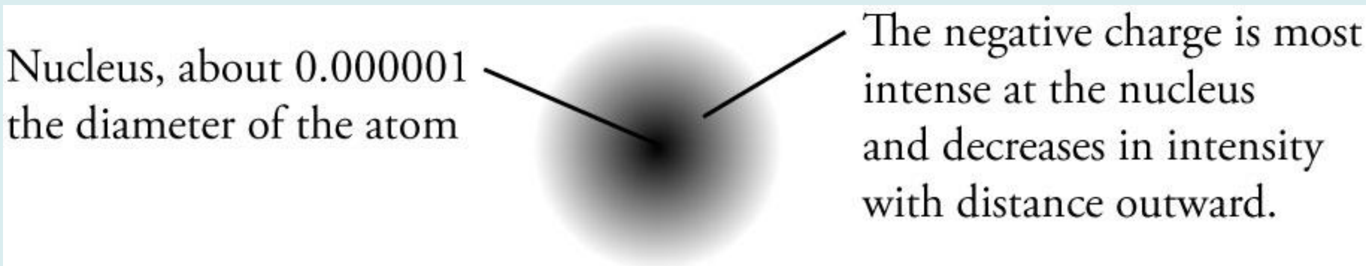

Almost all of the electron's charge lies within a spherical shell with the diameter of this circle.
Sphere enclosing almost all of the electron's negative charge

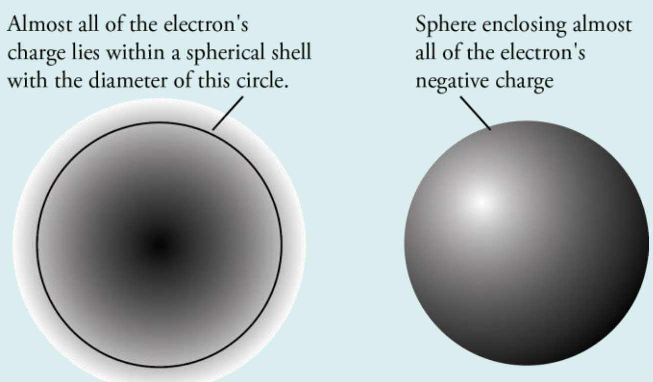
# Here's what we know

- Everything has both particle and wave character, the less massive the particle the more important the wave character is, and electrons are small enough to have significant wave character.
- We don't intuitively understand waves, and therefore, we don't understand electrons, but we can describe the one electron of a hydrogen atom with 3-D wave mathematics.
- There's a general form of the wave equation and specific forms of the general wave equation, and each specific form has a unique set of allowed quantum numbers (1,0,0 or 2,0,0 etc.).
- When we ask the computer to create an image that summarizes the results of repetitive calculations with one specific form of the general wave equation, the computer provides a 3-D image.

# Here’s what we know

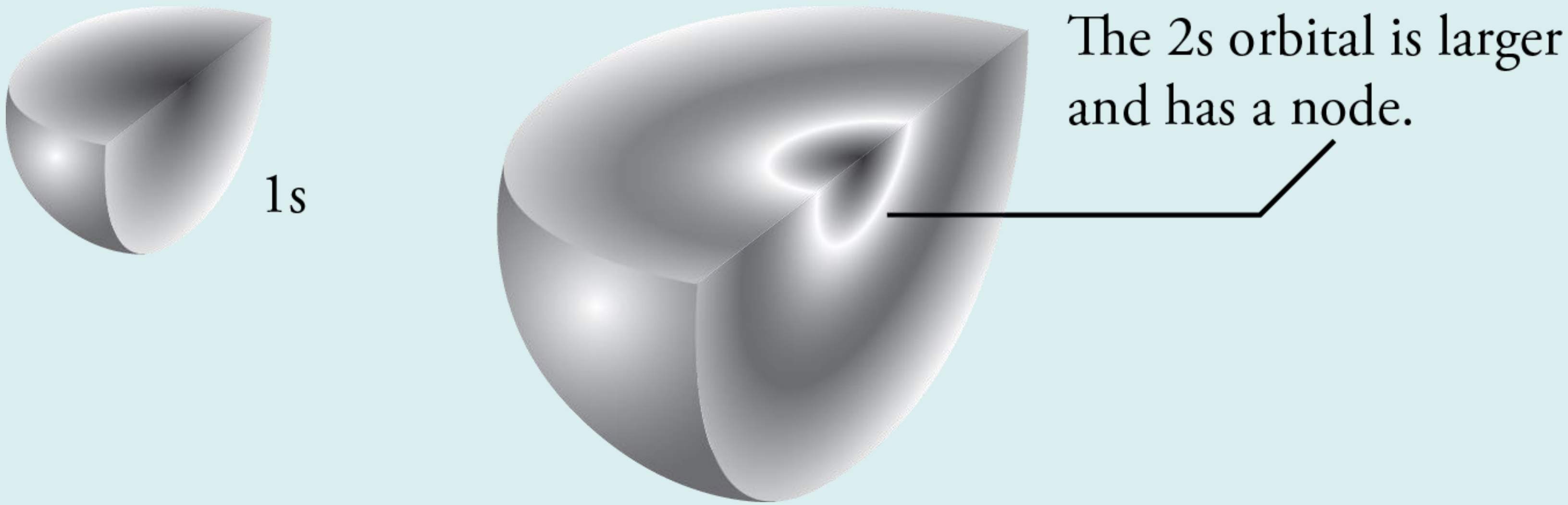
- We call these orbitals, and we choose to think that they describe the distribution of negative charge around the nucleus.



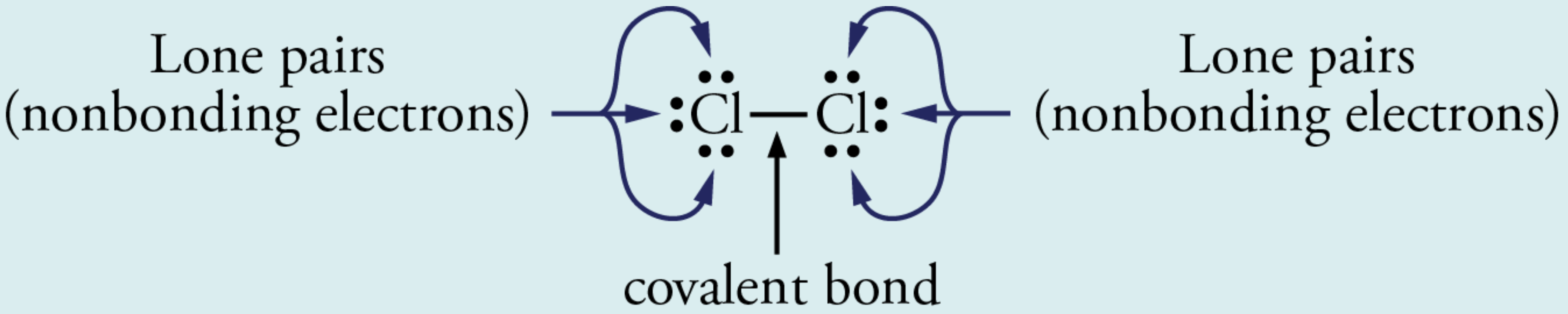

- Each specific form of the general wave equation provides a different image with different sizes and shapes.

# Cutaway of 1s and 2*s* (2,0,0) Orbitals



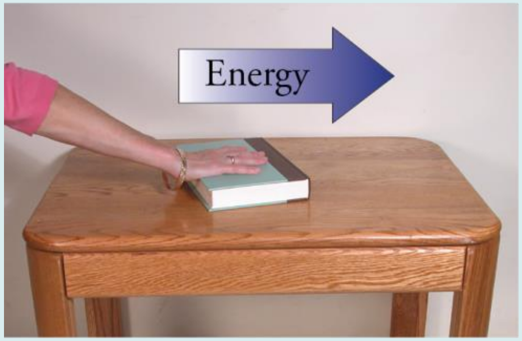
# Lewis Structures

- ***Lewis structures*** represent molecules using element symbols, lines for bonds, and dots for lone pairs.
- The halogens, including chlorine, usually form one covalent bond and three lone pairs. When pure, they are composed of diatomic molecules. For example, chlorine is $Cl_2$.

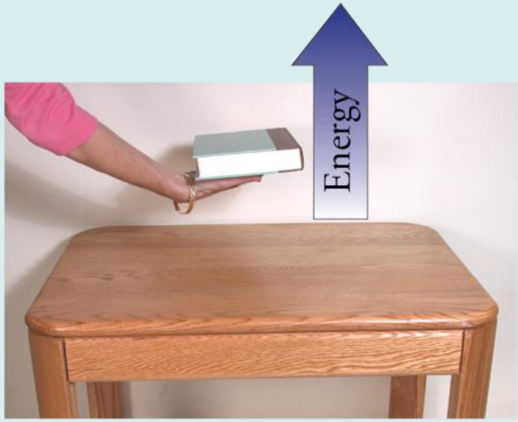


# Energy

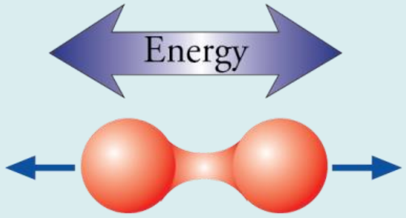
- **Energy** = the capacity to do work
- **Work**, in this context, may be defined as what is done to move an object against some sort of resistance.




Energy is required to push a book across a table and overcome the resistance to movement due to friction.




Energy is required to lift a book and overcome the resistance to movement due to gravity.



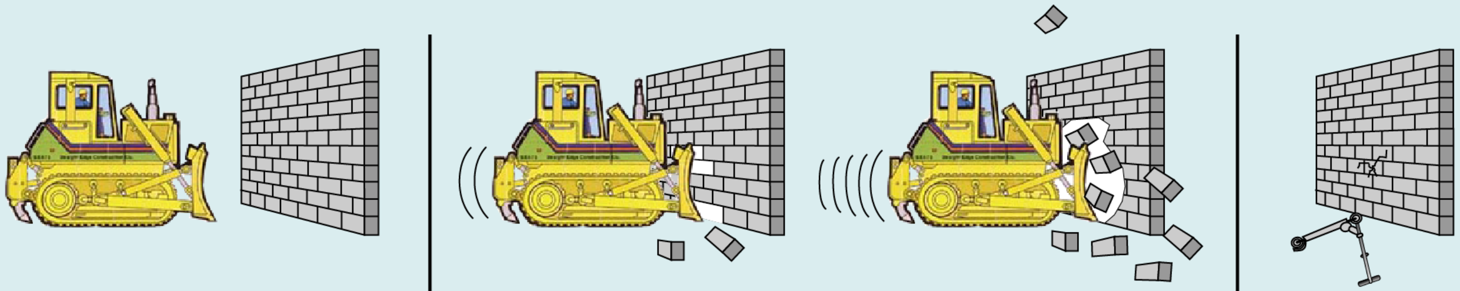

Energy is required to separate two atoms in a molecule and overcome the resistance to movement due to the chemical bond between them.

# Kinetic energy, momentum, force of collisions, and work

- **Kinetic Energy** = the energy of motion = $\frac{1}{2}m\mu^2$. ($m$ = mass, $\mu$ = velocity)
- The force of collisions is proportional to the momentum (mass × velocity, $m\mu$) of the objects colliding.
- Therefore, if two objects are moving at the same velocity, the more massive object will have greater momentum, so it will collide with more force, giving it a greater capacity to do work, and a greater kinetic energy.
- If two objects have the same mass but are moving at different velocities, the faster moving object will have greater momentum, so it will collide with more force, giving it a greater capacity to do work, and a greater kinetic energy.

# Two Types of Energy

- **Kinetic Energy** = the energy of motion = $\frac{1}{2}m\mu^2$



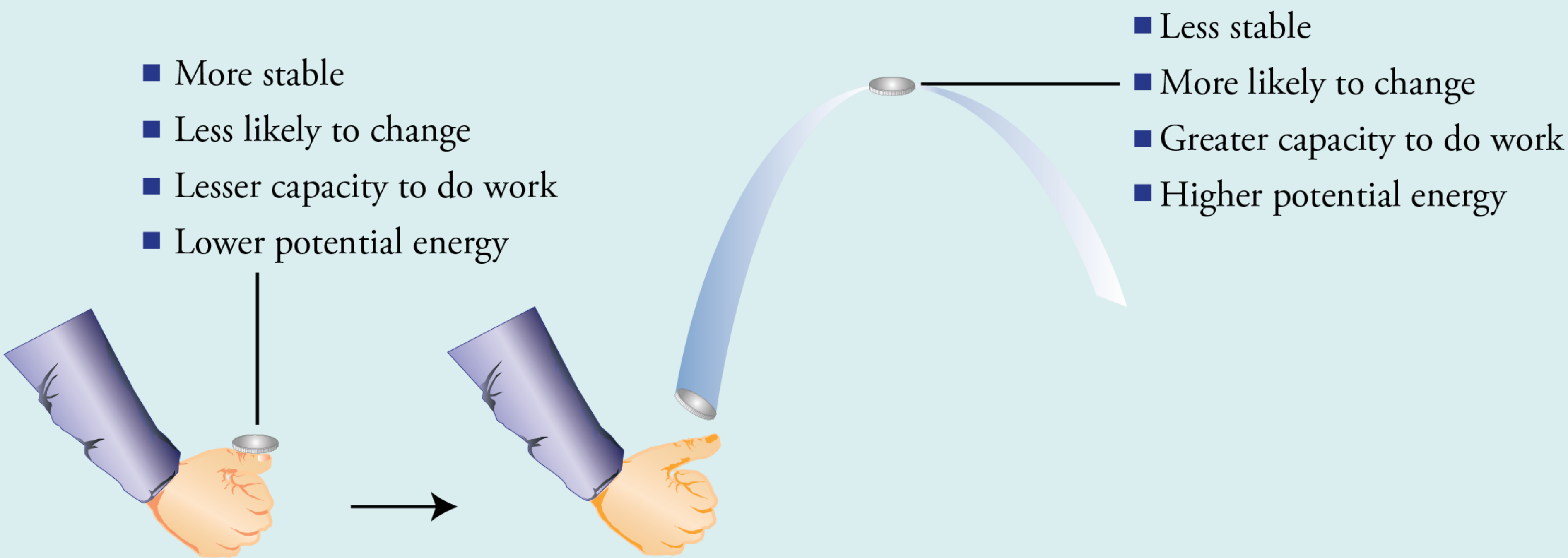
A stationary buldozer does not have the capacity to do the work of moving a wall.

The faster moving bulldozer does more of the work of moving the wall. The faster an object moves, the more work it can do, and the more kinetic energy it has.

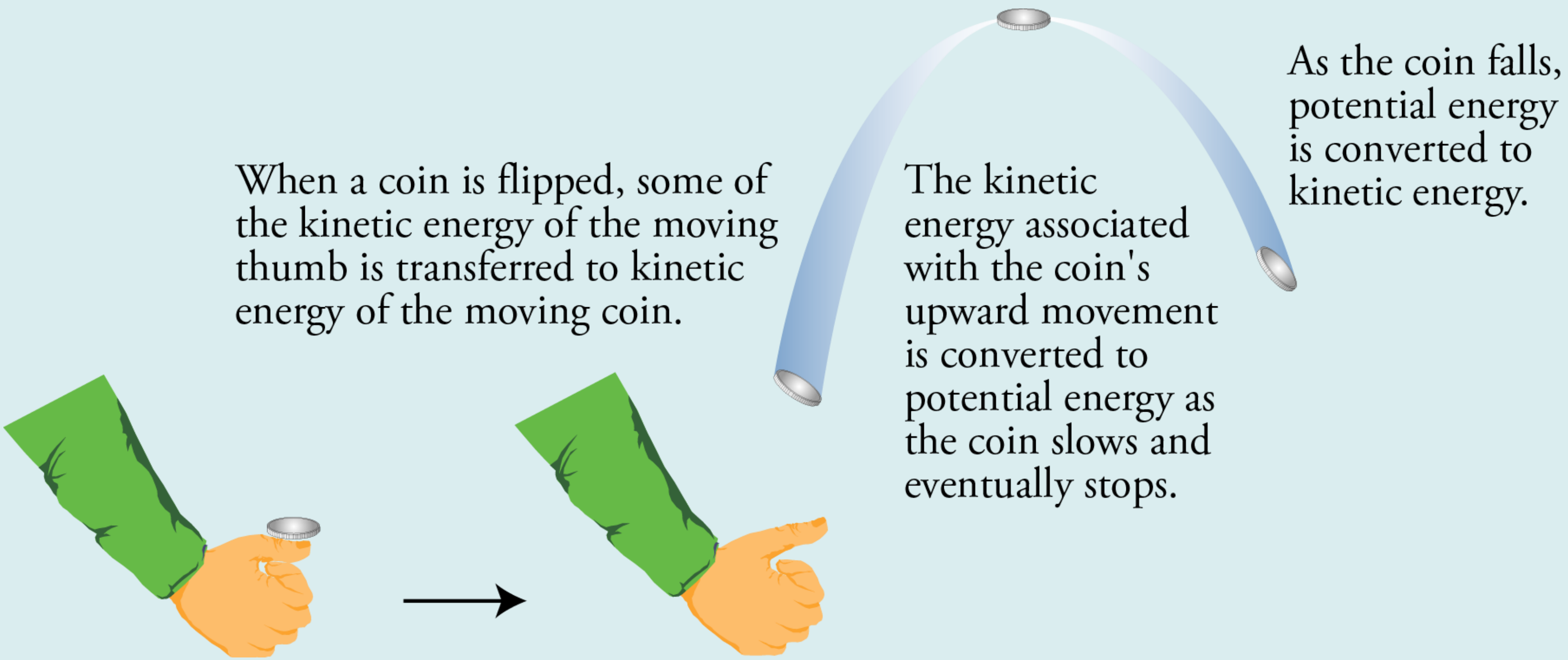
A scooter moving at the same velocity as a bulldozer will do less work and therefore has less energy.

- **Potential Energy** = energy by virtue of position or state

# Coin and Potential Energy



# Law of Conservation of Energy



# Exergonic Change

less stable system $\rightarrow$ more stable

more likely to change $\rightarrow$ less likely to change

greater capacity to do work
$\rightarrow$ lesser capacity to do work

higher PE $\rightarrow$ lower PE + energy

coin in air above hand $\rightarrow$ coin on ground + energy

# Endergonic Change

more stable $\rightarrow$ less stable system

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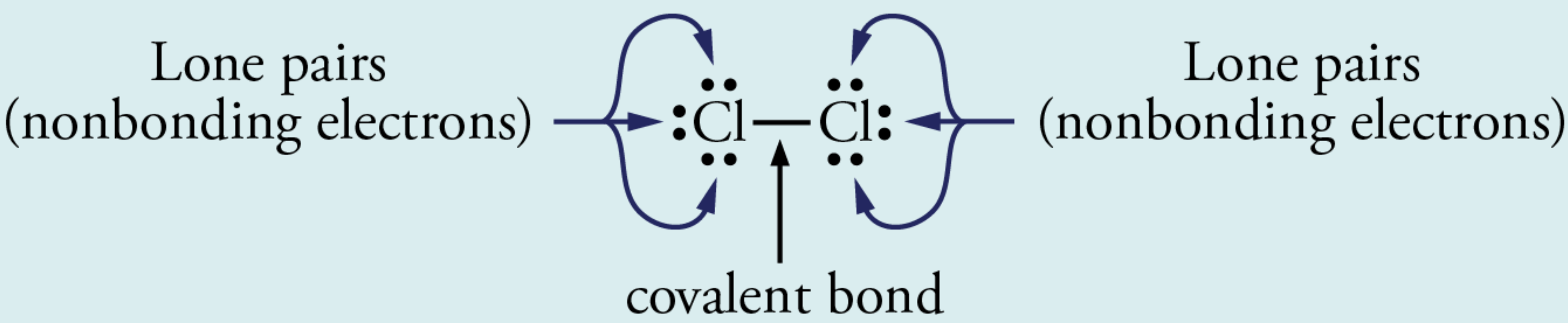
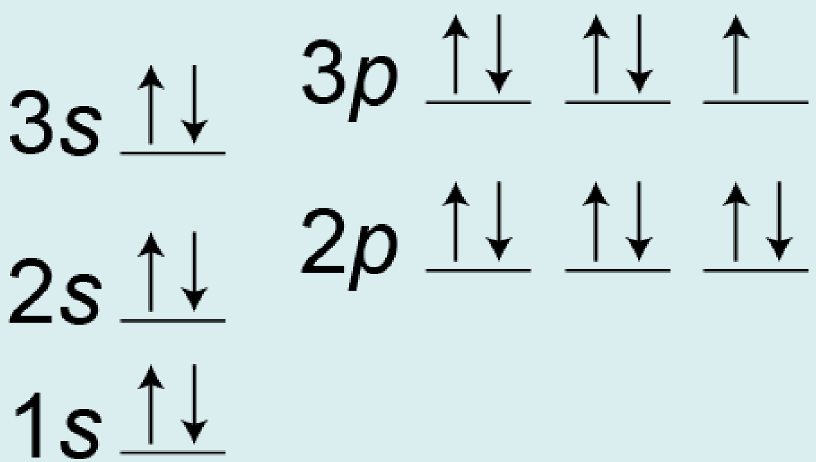
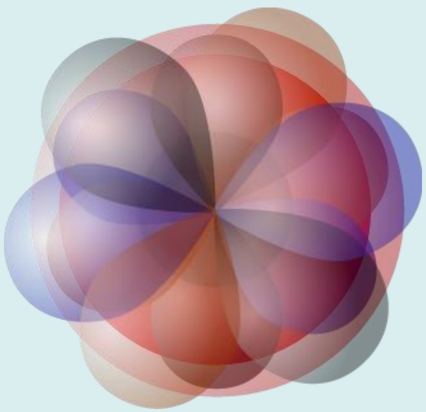


# Chlorine's 17 Electrons

- Orbital Diagram for chlorine



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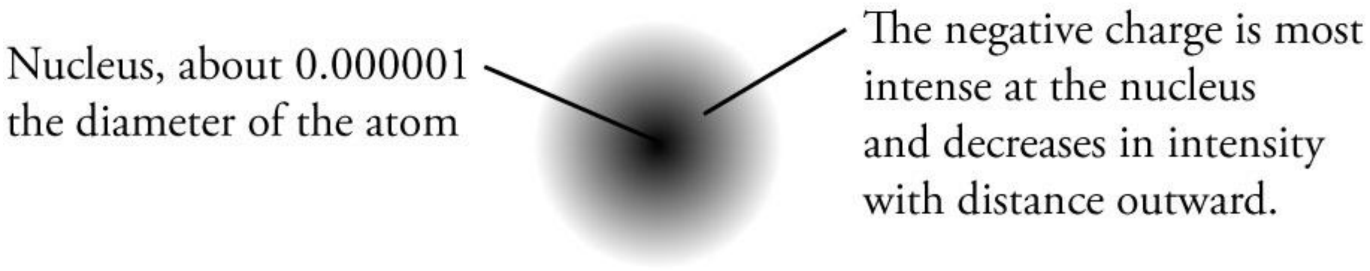
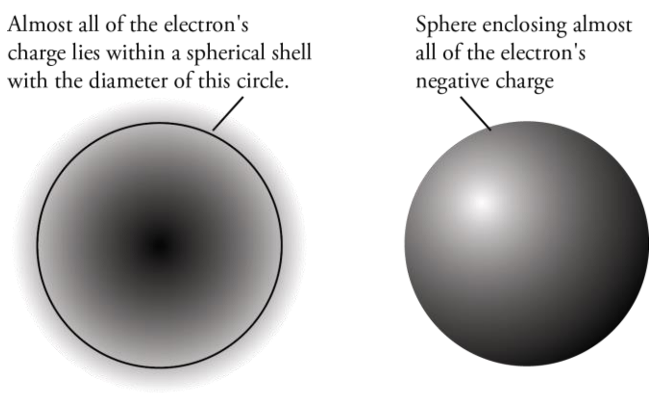
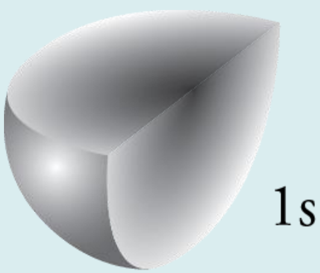


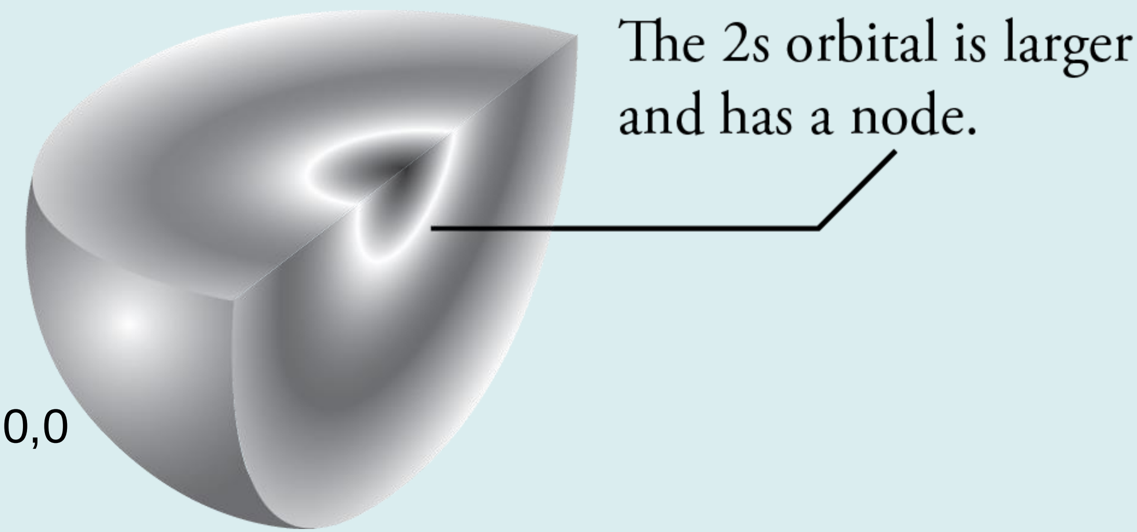

- Each specific form of the general wave equation provides a different image with different sizes and shapes.

# An electron in 2s is less stable and higher PE than an electron in 1s

- Electron in 2s is a greater average distance from the positive nucleus than an electron in the 1s.
- 2s electron less attracted.
- 2s electron is less stable (more likely to change).
- 2s electron is higher potential energy.
- The one electron of hydrogen is more likely to be in the smaller, more stable, and lower PE 1s orbital where it is most strongly attracted to the nucleus.



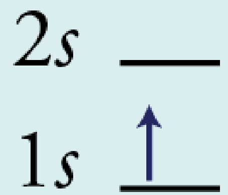

1,0,0



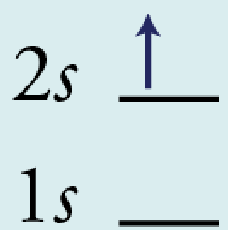

2,0,0

# Ground State and Excited State

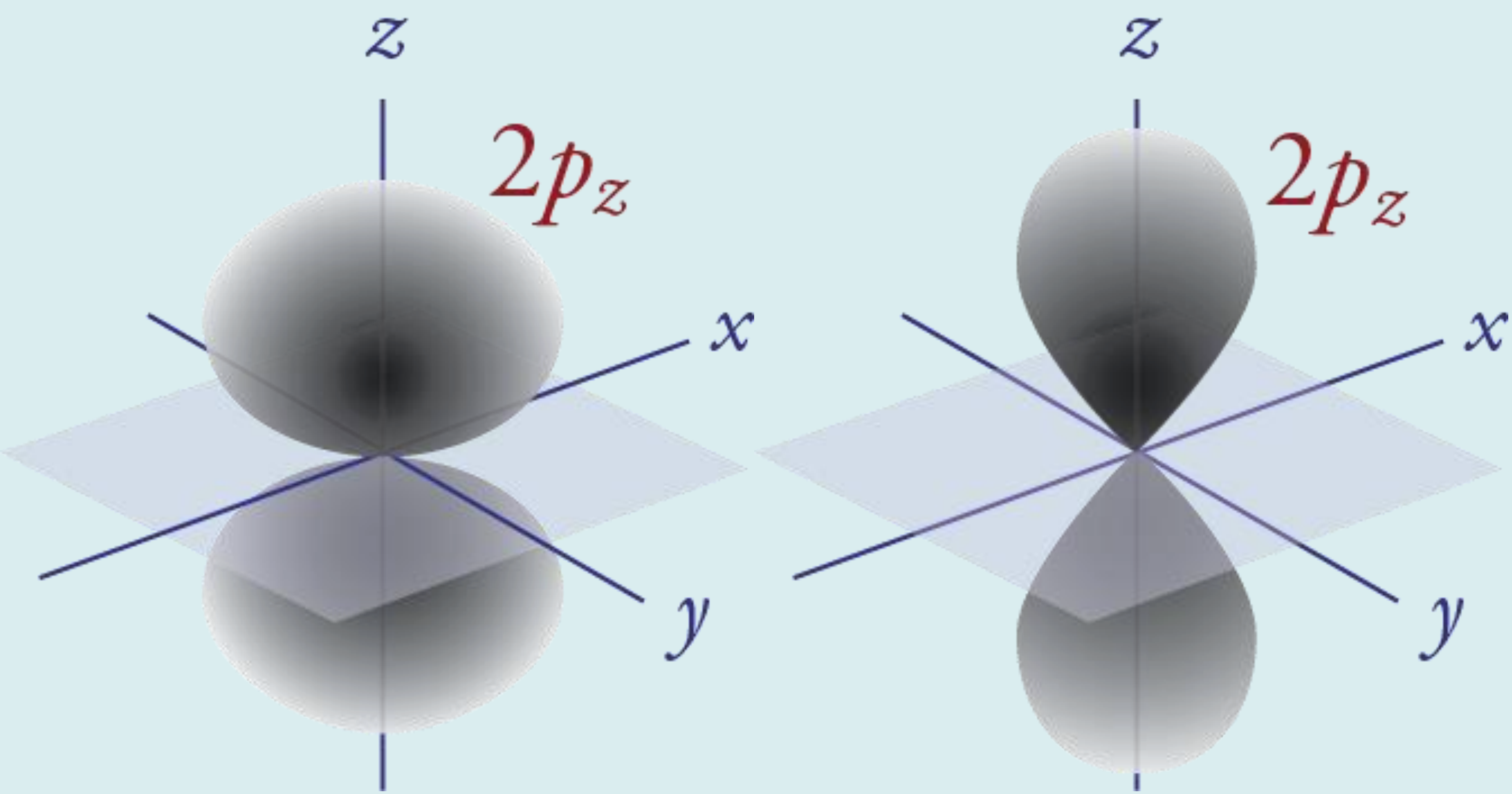
- Hydrogen atoms with their electron in the 1*s* orbital are said to be in their ***ground state***.



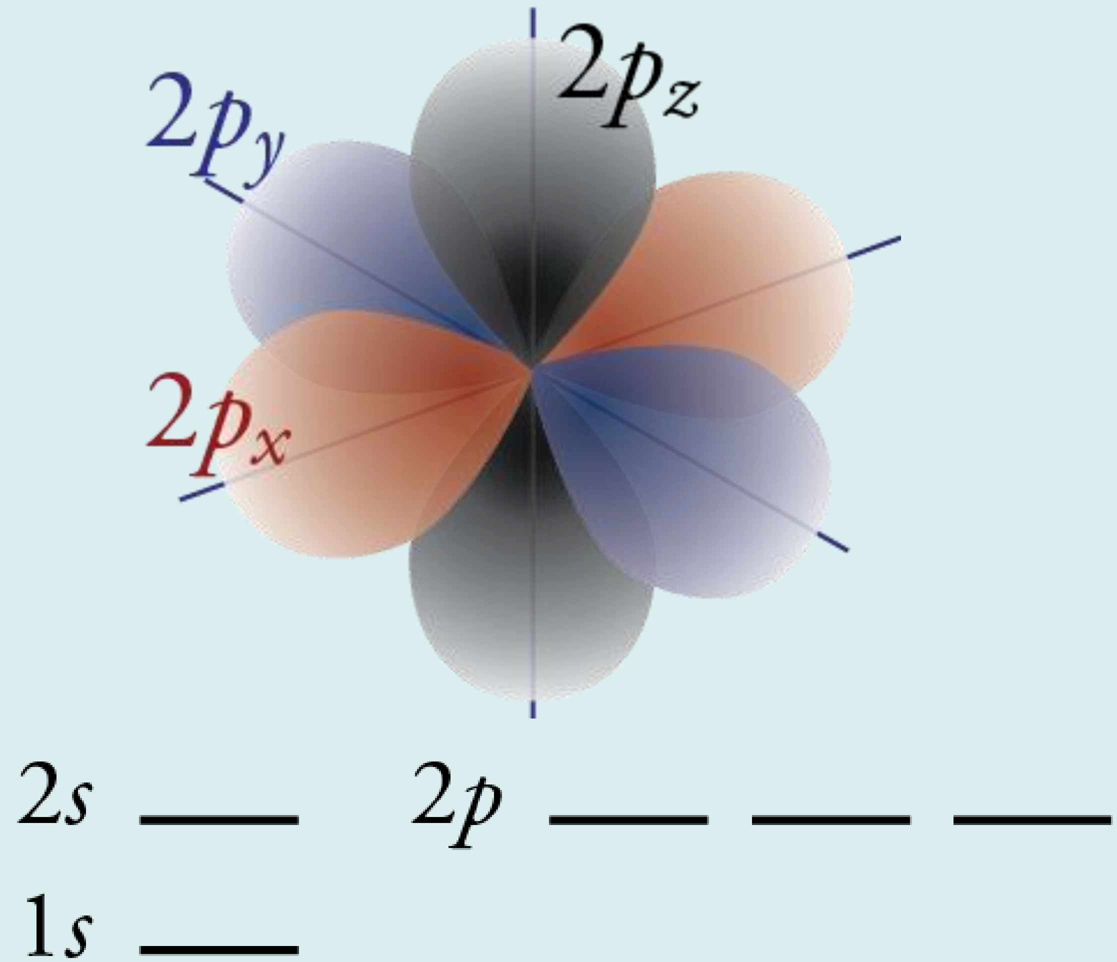

- A hydrogen atom with its electron in the 2*s* orbital is in an ***excited state***.

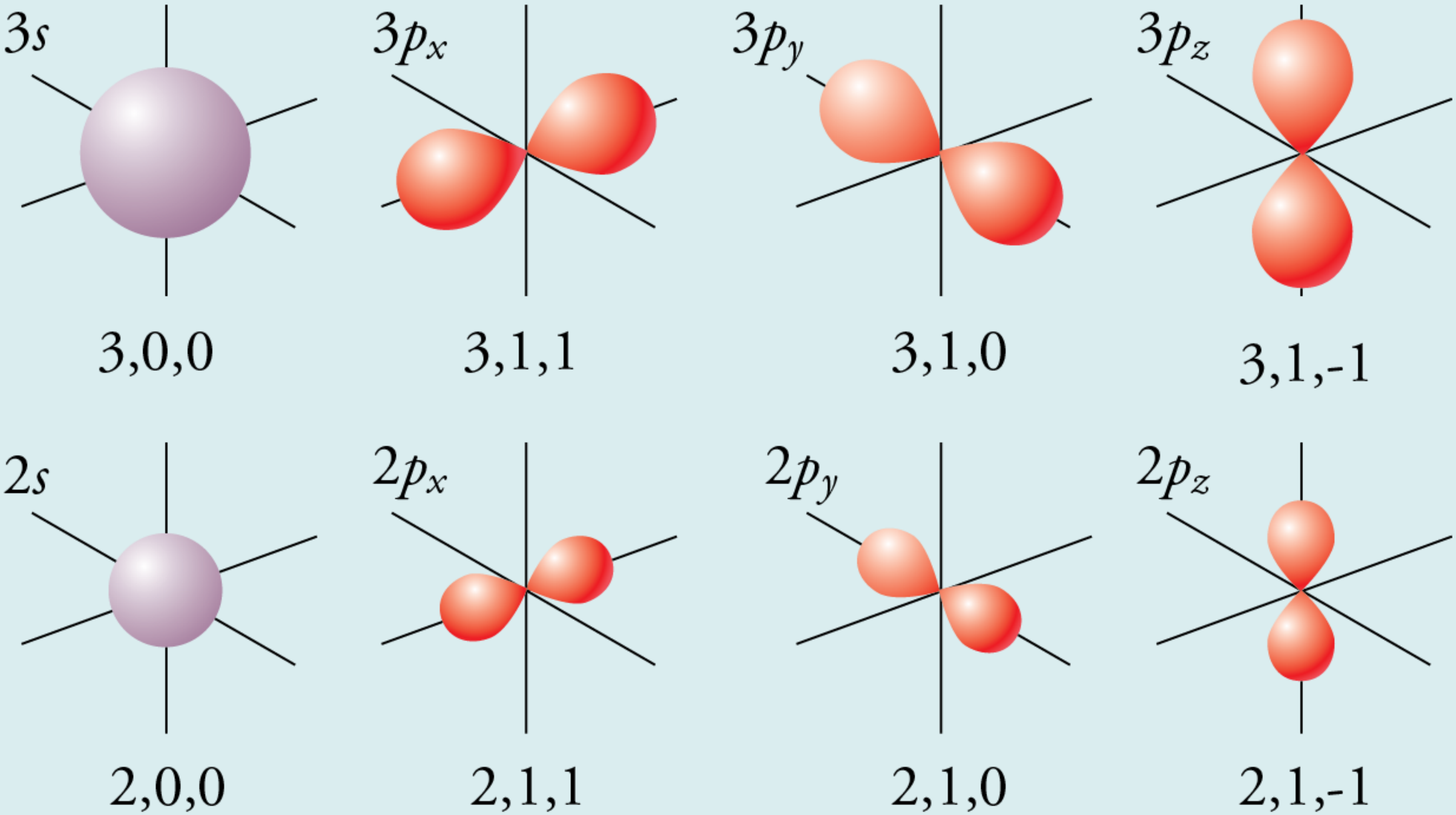


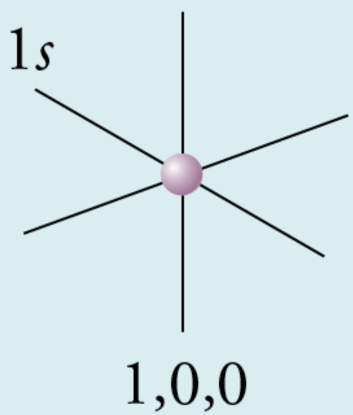
# Realistic and Stylized 2$p_z$ Orbital (2,1,1)



# $2p_x$ (2,1,1),
# $2p_y$ (2,1,0), and
# $2p_z$ (2,1,-1) Orbitals






# Some Allowed Waveforms

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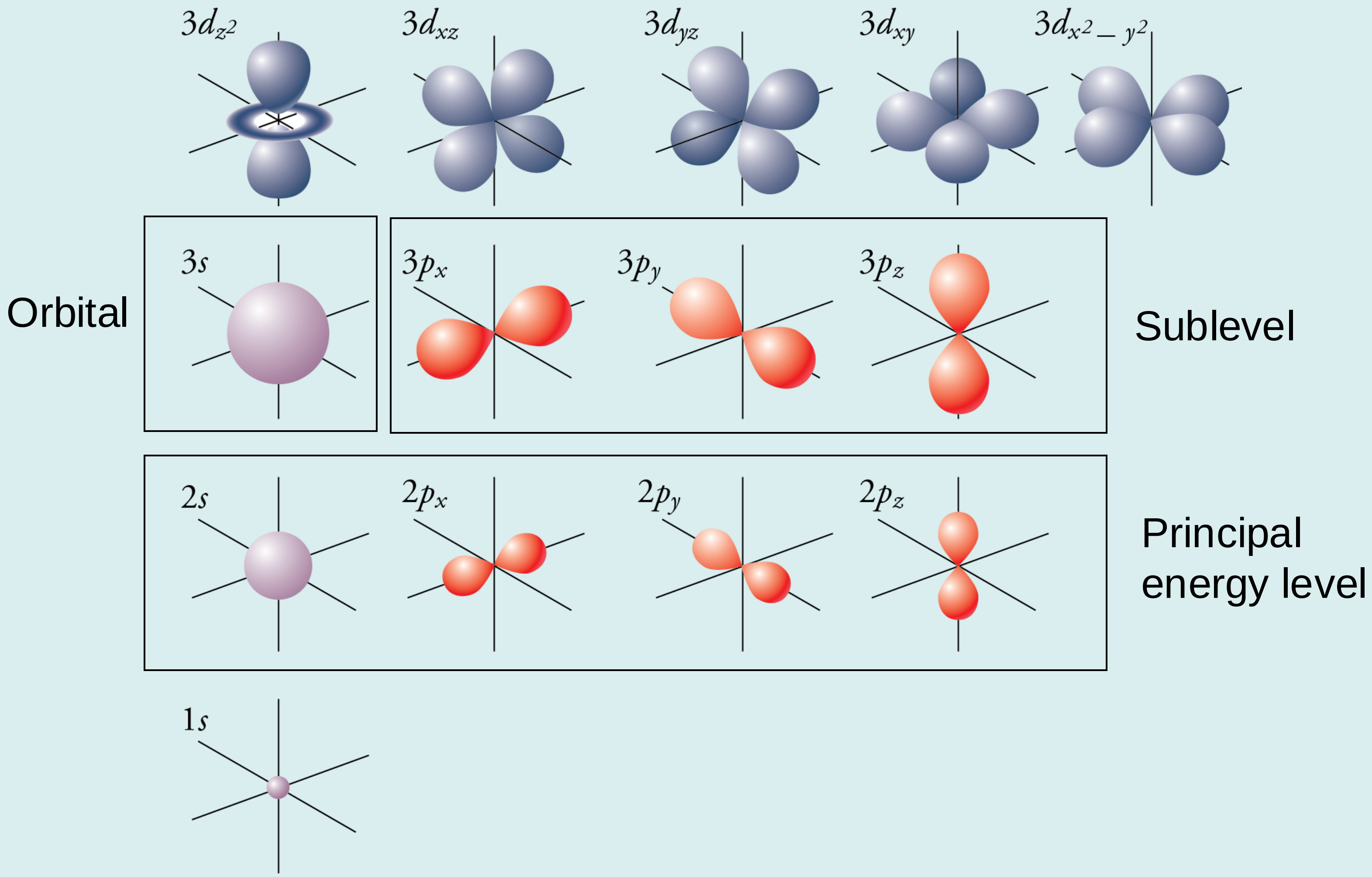
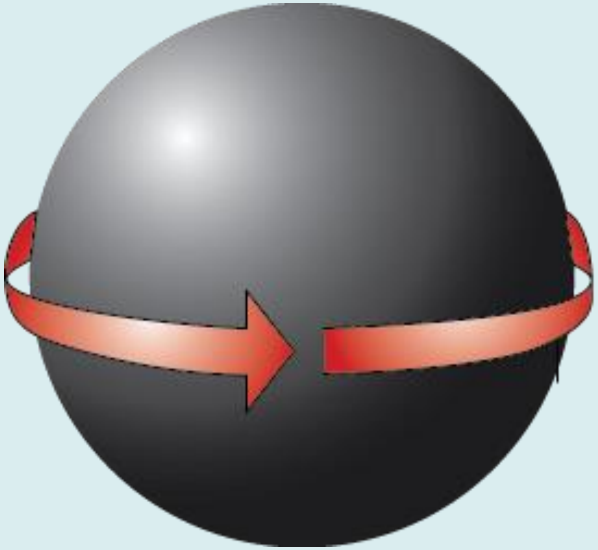


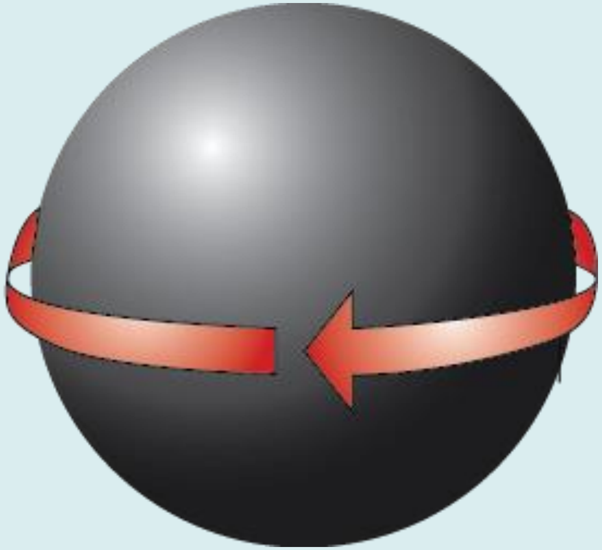
# Quantum Numbers

- The first quantum number identifies the principal energy level, e.g. $n=2$ describes the second principal energy level that includes the 2s and 2p sublevels.
- The first two quantum numbers identify a sublevel, e.g. 3,1 represents the 3p sublevel.
- Three quantum numbers identifies an orbital, e.g. 3,0,0 describes the 3s orbital.
- It takes four quantum numbers to describe an electron.

# Electron Spin



$m_s = +1/2$



$m_s = -1/2$

# Pauli Exclusion Principle

- No two electrons in an atom can have the same unique set of four quantum numbers.
- Electrons in an atom can share up to three of the following…but not all four.
    - Same principal energy level.
    - Same sublevel.
    - Same orbital.
    - Same spin.

# Orbital Diagrams

- Add two electrons (represented by arrows) to each orbital (line) in the order below from the bottom up. The first arrow is pointed up, and the second is pointed down.

*3p* ___ ___ ___

*3s* ___

*2p* ___ ___ ___

*2s* ___

*1s* ___

- When adding electrons to orbitals of the same level, add one electron (arrow) to each orbital first with the same spin (arrows pointing up) before you go back and start pairing them.

# Periodic Table

| | 1 1A | 2 2A | 3 3B | 4 4B | 5 5B | 6 6B | 7 7B | 8 8B | 9 8B | 10 8B | 11 1B | 12 2B | 13 3A | 14 4A | 15 5A | 16 6A | 17 7A | 18 8A |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | | | 1 H 1.00794 | | | | | | | 2 He 4.0026 |
| 2 | 3 Li 6.941 | 4 Be 9.0122 | | | | | | | | | | | 5 B 10.811 | 6 C 12.011 | 7 N 14.0067 | 8 O 15.9994 | 9 F 18.9984 | 10 Ne 20.1797 |
| 3 | 11 Na 22.9898 | 12 Mg 24.3050 | | | | | | | | | | | 13 Al 26.9815 | 14 Si 28.0855 | 15 P 30.9738 | 16 S 32.066 | 17 Cl 35.4527 | 18 Ar 39.948 |
| 4 | 19 K 39.0983 | 20 Ca 40.078 | 21 Sc 44.9559 | 22 Ti 47.867 | 23 V 50.9415 | 24 Cr 51.9961 | 25 Mn 54.9380 | 26 Fe 55.845 | 27 Co 58.9332 | 28 Ni 58.6934 | 29 Cu 63.546 | 30 Zn 65.39 | 31 Ga 69.723 | 32 Ge 72.61 | 33 As 74.9216 | 34 Se 78.96 | 35 Br 79.904 | 36 Kr 83.80 |
| 5 | 37 Rb 85.4678 | 38 Sr 87.62 | 39 Y 88.9058 | 40 Zr 91.224 | 41 Nb 92.9064 | 42 Mo 95.95 | 43 Tc (98) | 44 Ru 101.07 | 45 Rh 102.9055 | 46 Pd 106.42 | 47 Ag 107.868 | 48 Cd 112.411 | 49 In 114.818 | 50 Sn 118.710 | 51 Sb 121.760 | 52 Te 127.60 | 53 I 126.9045 | 54 Xe 131.29 |
| 6 | 55 Cs 132.9054 | 56 Ba 137.327 | 71 Lu 174.967 | 72 Hf 178.49 | 73 Ta 180.948 | 74 W 183.84 | 75 Re 186.207 | 76 Os 190.23 | 77 Ir 192.22 | 78 Pt 195.08 | 79 Au 196.9665 | 80 Hg 200.59 | 81 Tl 204.38 | 82 Pb 207.2 | 83 Bi 208.9804 | 84 Po (209) | 85 At (210) | 86 Rn (222) |
| 7 | 87 Fr (223) | 88 Ra (226) | 103 Lr (262) | 104 Rf (261) | 105 Db (262) | 106 Sg (266) | 107 Bh (264) | 108 Hs (269) | 109 Mt (268) | 110 Ds (281) | 111 Rg (272) | 112 Cn (285) | 113 Nh (284) | 114 Fl (289) | 115 Mc (288) | 116 Lv (293) | 117 Ts (294) | 118 Og (294) |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 57 La 138.9055 | 58 Ce 140.115 | 59 Pr 140.9076 | 60 Nd 144.24 | 61 Pm (145) | 62 Sm 150.36 | 63 Eu 151.965 | 64 Gd 157.25 | 65 Tb 158.9253 | 66 Dy 162.50 | 67 Ho 164.9303 | 68 Er 167.26 | 69 Tm 168.9342 | 70 Yb 173.04 |
| 7 | 89 Ac (227) | 90 Th 232.0381 | 91 Pa 231.0359 | 92 U 238.0289 | 93 Np (237) | 94 Pu (244) | 95 Am (243) | 96 Cm (247) | 97 Bk (247) | 98 Cf (251) | 99 Es (252) | 100 Fm (257) | 101 Md (258) | 102 No (259) |

# Chlorine's 17 Electrons

- Orbital Diagram for chlorine

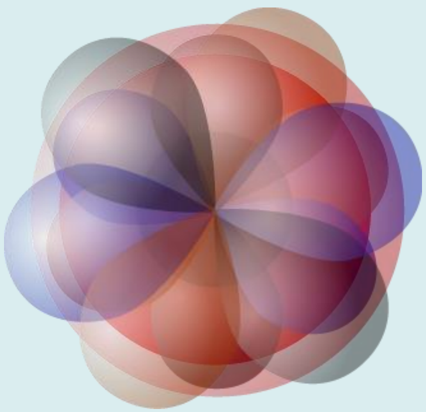
3*p* ↑↓ ↑↓ ↑

2*p* ↑↓ ↑↓ ↑↓

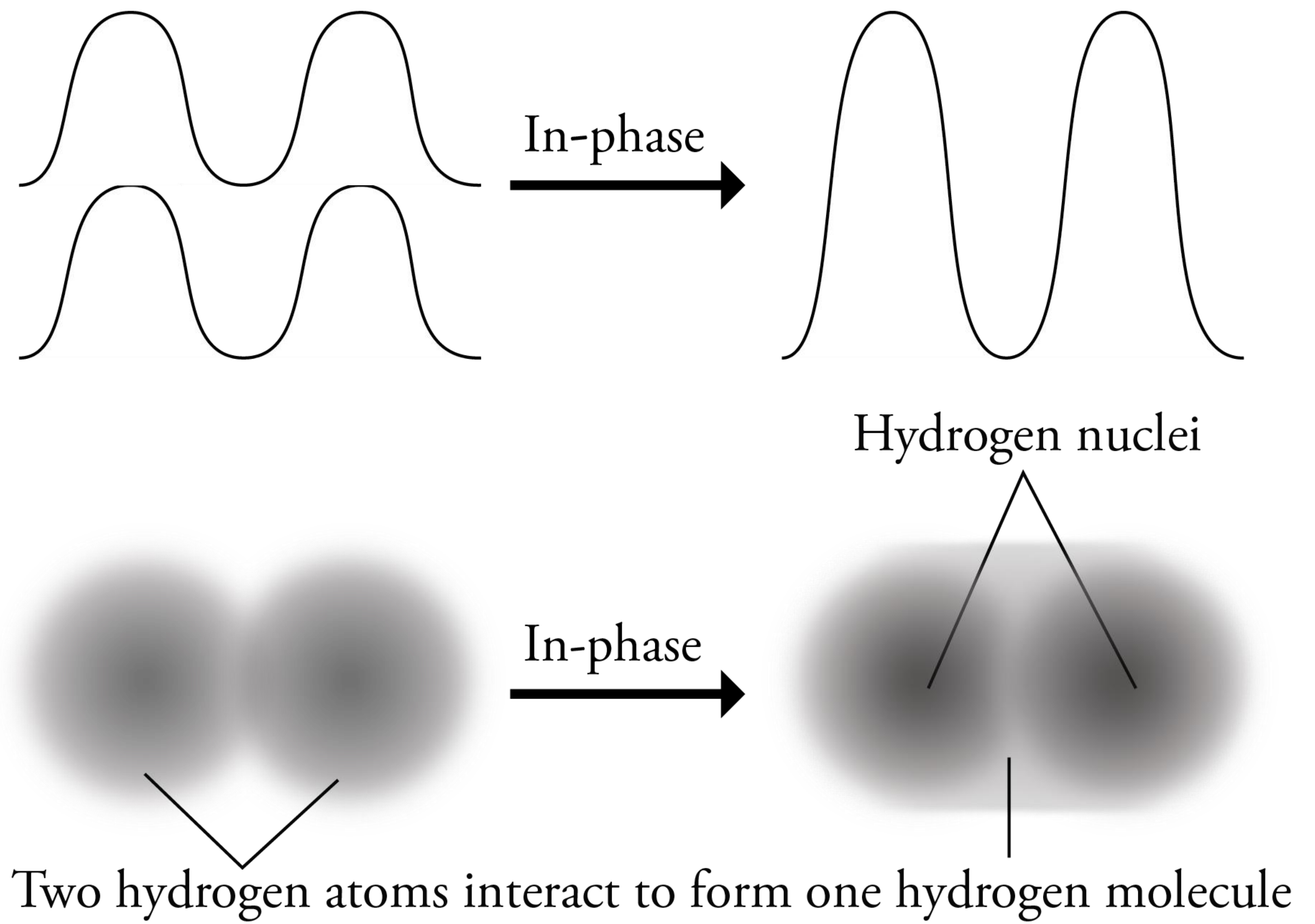
3*s* ↑↓

2*s* ↑↓

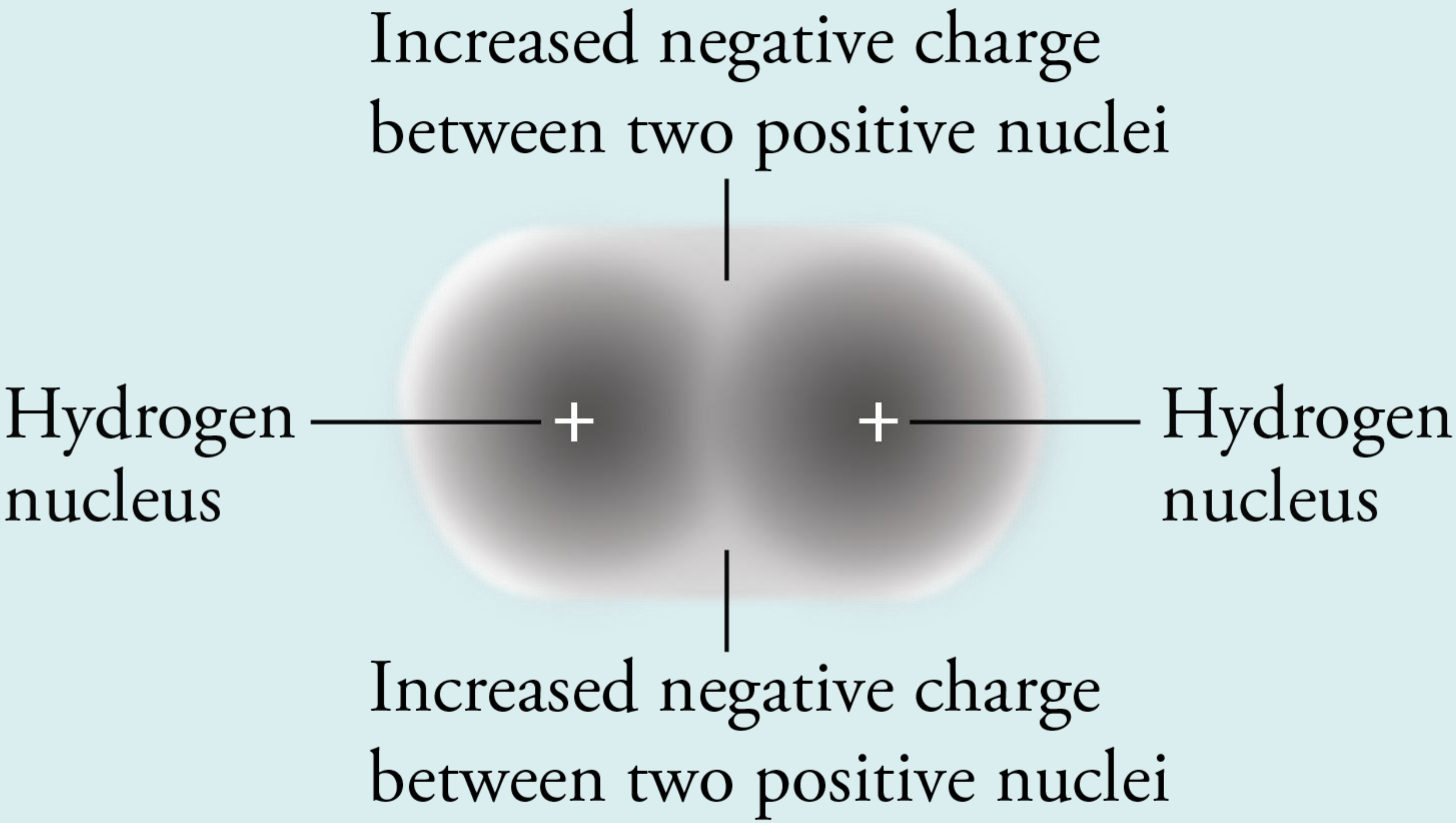
1*s* ↑↓



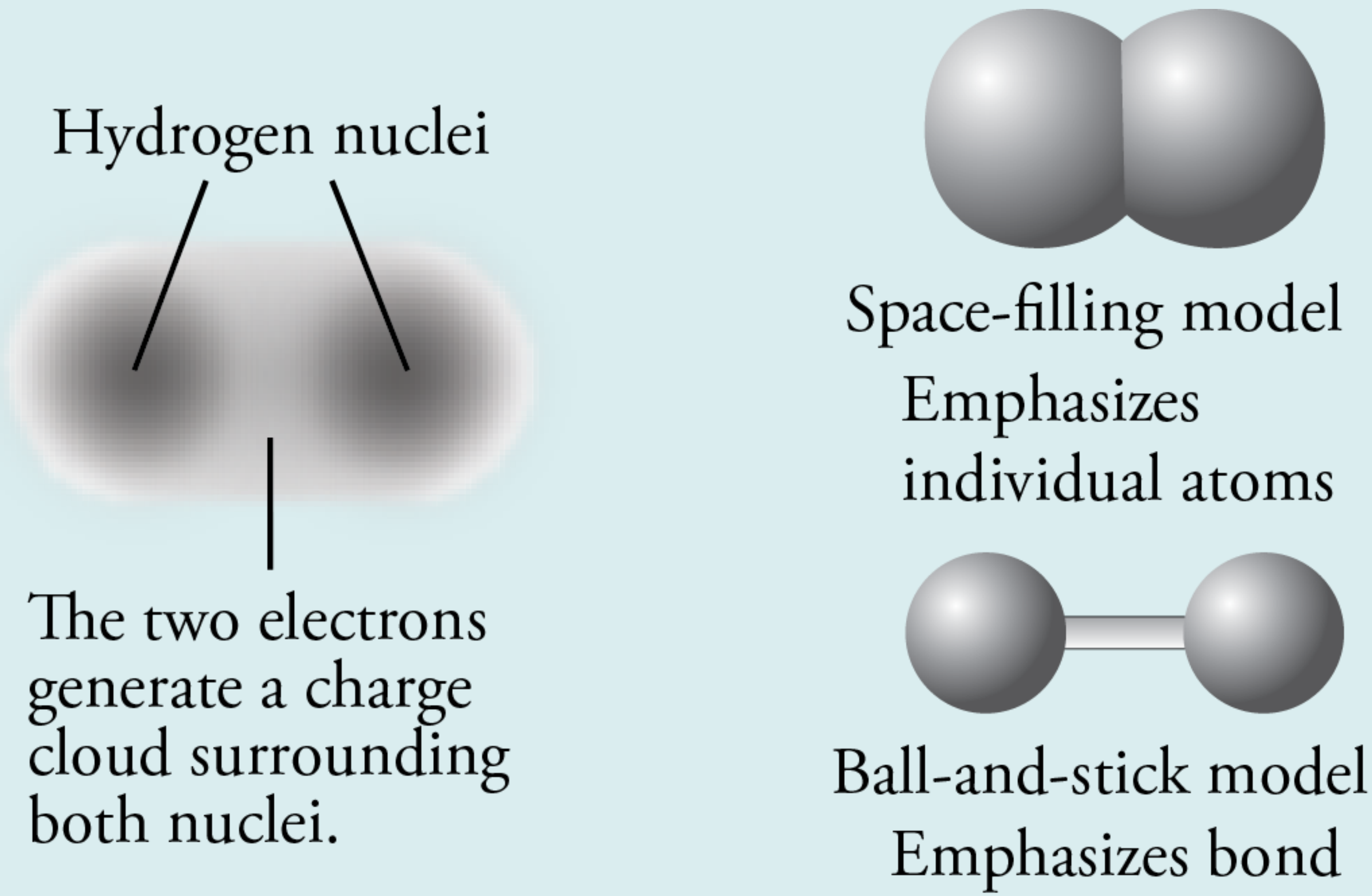
# Covalent Bond Formation



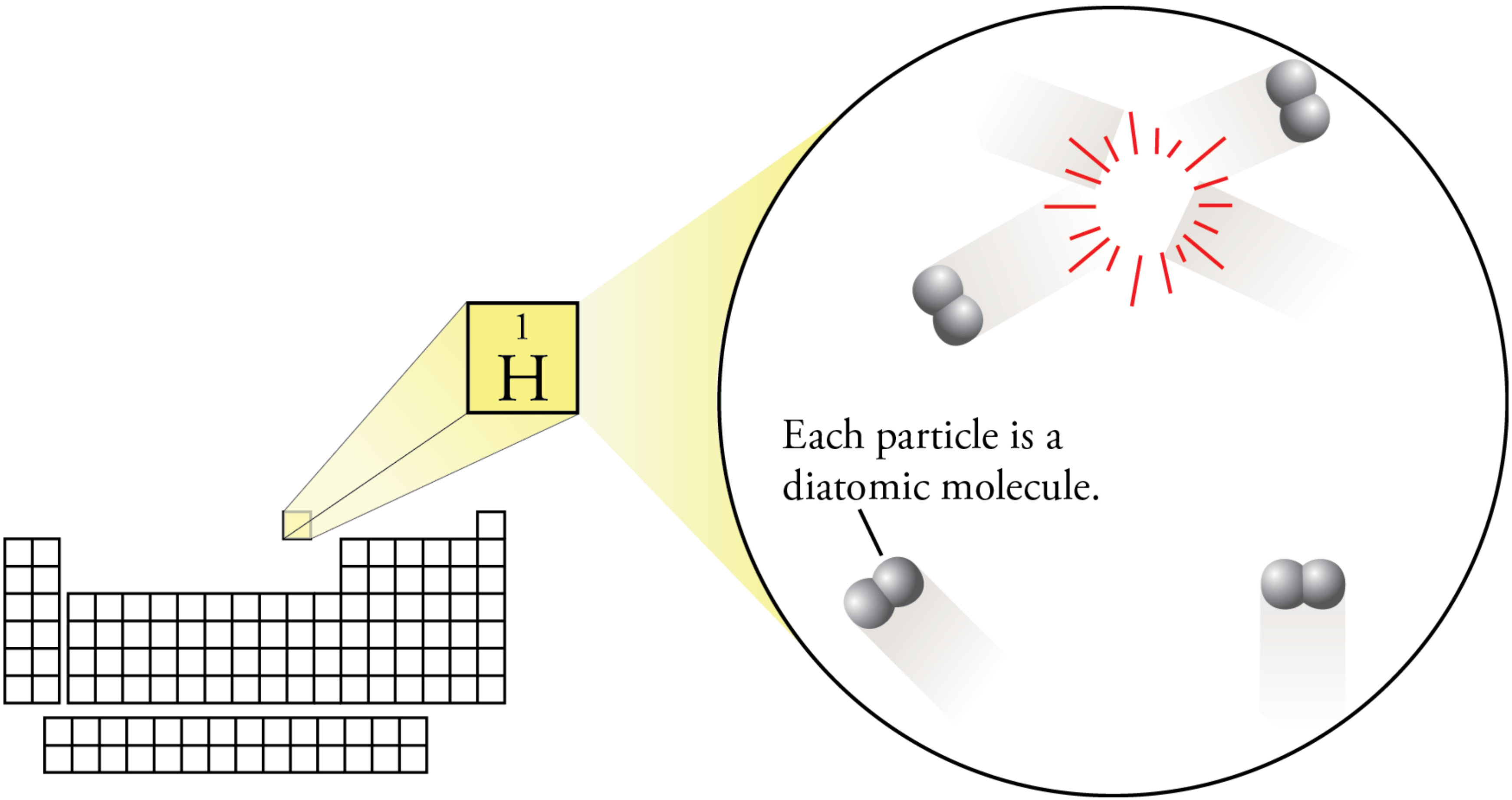
# Covalent Bond Formation



# Hydrogen, $H_2$, Molecule



# Hydrogen Gas, $H_2$



# Description of Gas

- Particles constantly moving in straight-line paths
- About 0.1% of volume occupied by particles…99.9% empty.
- Average distance between particles is about 10 times their diameter.
- No significant attractions or repulsions.
- Constant collisions that lead to changes in direction and velocity.
- Variable volume and shape, due to lack of attractions and a great freedom of motion.

https://preparatorychemistry.com/KMT_Canvas.html

# Assumptions of the Valence-Bond Model for Covalent Bonding

- Only the highest energy electrons participate in bonding.
- Covalent bonds usually form to pair unpaired electrons.

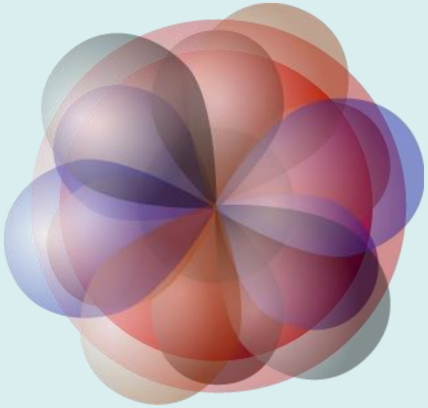
# Chlorine's 17 Electrons

- They are arranged in different energy levels, sublevels, and orbitals. (See Chapter 4 of *An Introduction to Chemistry – Atoms First*)

3*s* ↑↓   3*p* ↑↓ ↑↓ ↑

2*s* ↑↓   2*p* ↑↓ ↑↓ ↑↓

1*s* ↑↓

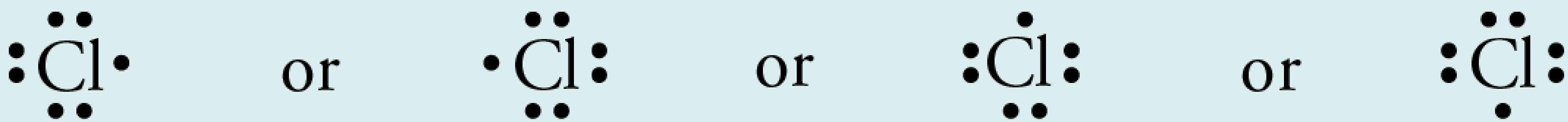


- The seven highest energy electrons have the greatest effect on the chemistry of chlorine. They are called **valence electrons**. They can be described with an electron dot symbol.

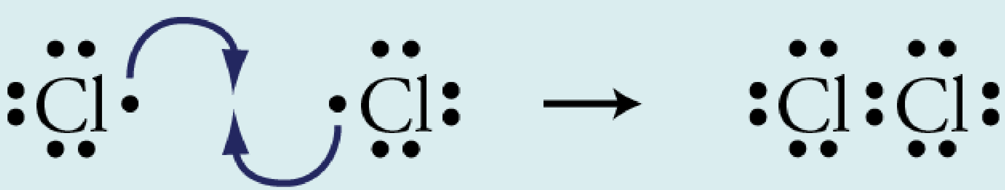
3*s* ↑↓   3*p* ↑↓ ↑↓ ↑

# Chlorine, $Cl_2$

- **Electron-dot symbols** show valence electrons. Cl is in group 7A, so it has 7 valence electrons, leading to 7 dots spread out on the four sides of the symbol.

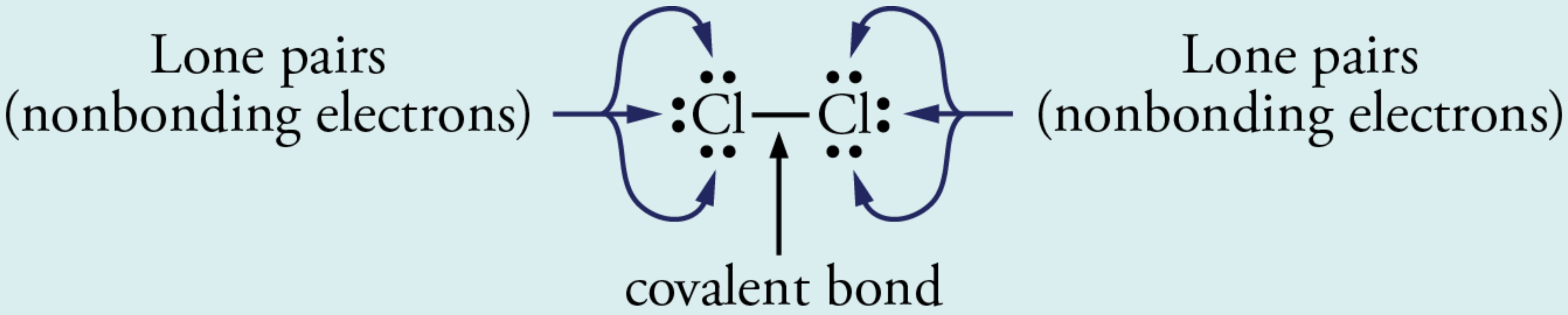



- Nonbonding pairs of valence electrons are called ***lone pairs***.
- The unpaired electrons for each of two chlorine atoms pair to form one covalent bond.

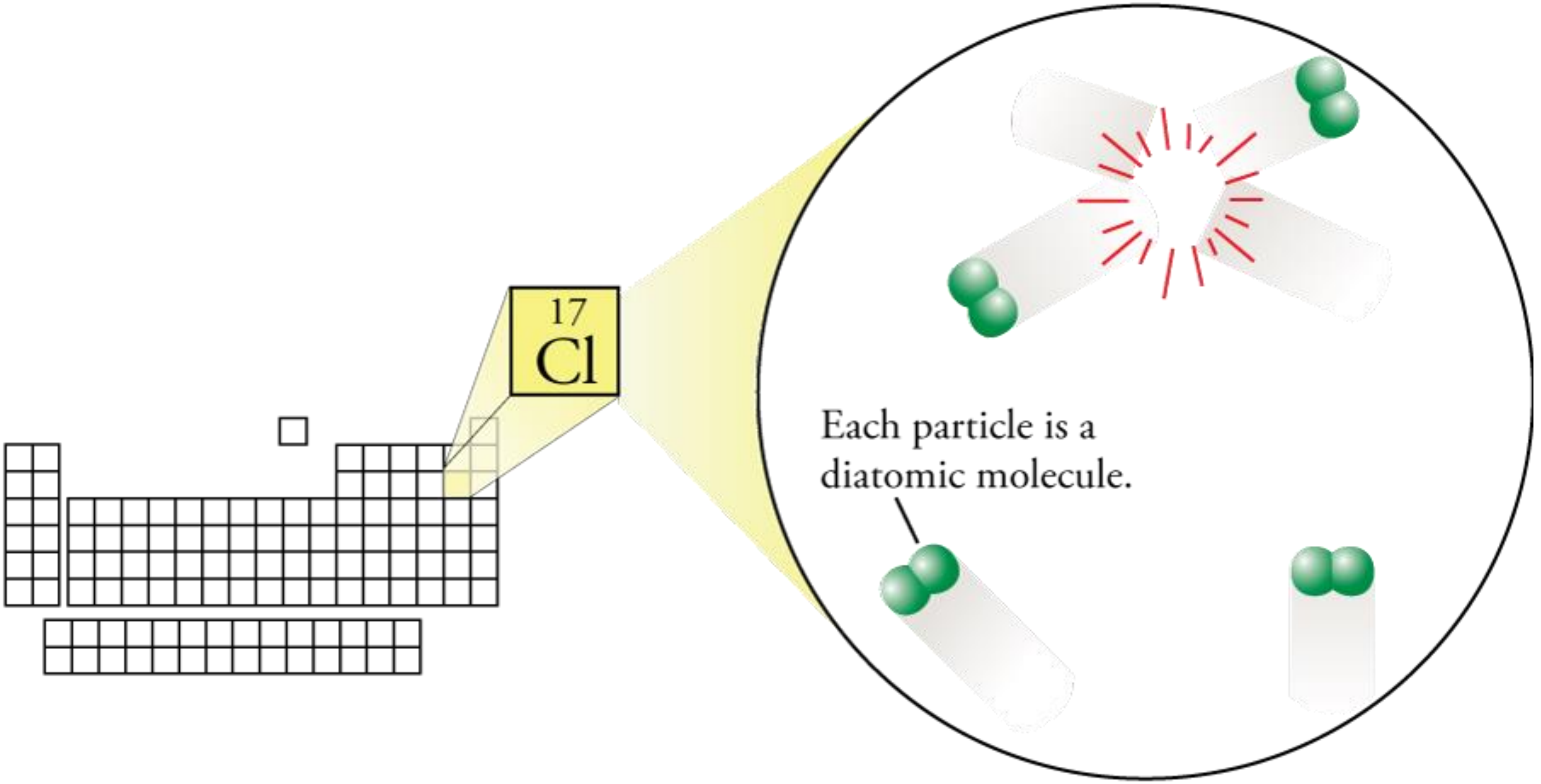


# Lewis Structures

- ***Lewis structures*** represent molecules using element symbols, lines for bonds, and dots for lone pairs.
- The halogens, including chlorine, usually form one covalent bond and three lone pairs. When pure, they are composed of diatomic molecules. For example, chlorine is $Cl_2$.



# Chlorine Gas



# Chlorine Gas

- At room temperature and pressure, chlorine molecules
  - have an average velocity of about 300 m/s or 700 mi/h
  - move about $10^{-8}$ m between collisions
  - and have about $10^{10}$ (10 billion) collisions per second

# Compressed Chlorine

- Chlorine molecules attract each other to some extent, even in the gas form.
- In the gas form, the attractions are too weak to keep the molecules together.
- If you compress chlorine gas, you push the molecules closer together, increasing the strength of these attractions.
- If you compress the gas enough, the attractions become strong enough to cause the chlorine to form a liquid.
- Chlorine is transported as a liquid in pressurized cylinders.

# Fritz Haber

*During peace time a scientist belongs to the world, but during war time he belongs to his country.*

Fritz Haber

- There is a chamber opera called "Haber's Law" which focuses on the life of Fritz Haber and his wife Clara Immerwahr.
- Fritz Haber won the Nobel Prize for chemistry in 1918 for developing a procedure for making ammonia, $NH_3$, from nitrogen, $N_2$, and hydrogen, $H_2$.
- The ammonia could be used to make nitrogen fertilizers or nitrogen explosives.

# Hague Conventions 1899 and 1907

- At The Hague, Netherlands (now one of the major cities hosting the UN, along with New York and Geneva)
- 26 countries, including Germany, signed the 1899 treaty.
- One section outlawed the use of "projectiles the object of which is the diffusion of asphyxiating or deleterious gases."

# Chlorine and WWI

*During peace time a scientist belongs to the world, but during war time he belongs to his country.*

Fritz Haber

- In 1914-15, WWI, which was expected to end quickly, was bogged down in trench warfare, so each side was looking for ways to break through the lines.
- Haber and others suggested loading projectiles with chlorine and shrapnel.
- They thought that they could avoid violating the Hague Convention by putting poison gas ***and shrapnel*** in projectiles, based on the interpretation that the convention banned "projectiles, the ***sole*** object of which is the diffusion of asphyxiating or deleterious gases."

# Chlorine as a Chemical Weapon

- Shortage of artillery shells led to use of chlorine from pressurized gas cylinders.
- Used against French near Ypres (**ee**·pruh), Belgium, April 22, 1915.
- Wind conditions had to be in the correct direction, strong enough to move the gas to the enemy lines, but not too strong to disperse the gas too quickly.

# Chlorine as a Chemical Weapon

- 168 metric tons (megagrams) released from 5730 cylinders
- $Cl_2$ is more dense than air
- 5-ft cloud moved at 4 mph
- Warmed, expanded to 30-ft yellow-green cloud, causing blindness, coughing, nausea, headache, and chest pain
- Created 4-mile gap in Allied line

# Chlorine as a Chemical Weapon

- 600 French and Algerian troops lay blinded and dying.
- Within an hour after the clearing of the gas, the Germans captured two villages, took 2000 prisoners, and confiscated 51 artillery pieces.
- German High Command had not expected the attack to work, so they did not place enough troops in the area to exploit the break in the lines, so Ypres remained in Allied hands.
- German press hailed the new innovation, but in other parts of Europe, the use of chlorine gas was condemned.

# For each Chemical Weapon

- Identify the chemical structure from a line drawing or Lewis structure (For example, I may give you a structure and ask you which of the chemical agents listed above it represents.)
- List examples of its use as a chemical weapon, if any.
- Identify whether it's more likely to be lethal or incapacitating.
- How it can be obtained and the relative difficulty in obtaining it compared to the other chemical weapons
- How it can be dispersed and the relative difficulty of dispersing it.

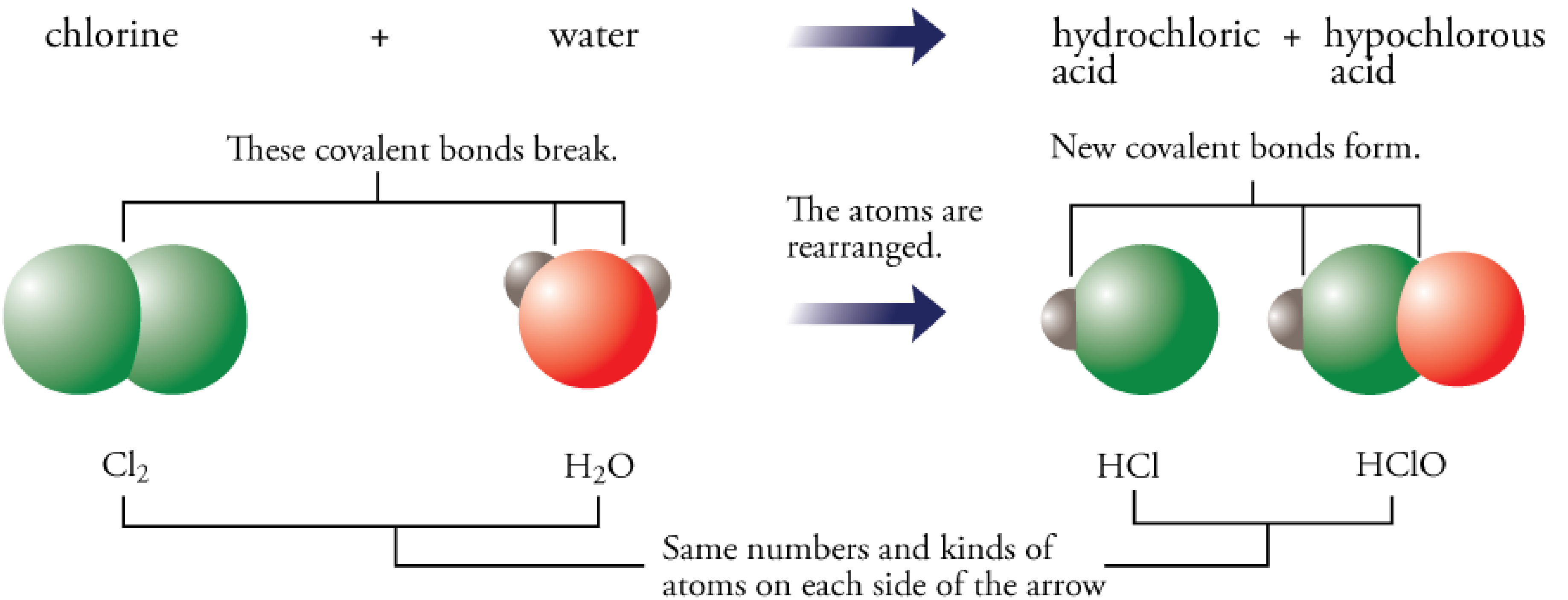
# For each Chemical Weapon

- Whether or not it has uses other than as a chemical weapon.
- Which CWC schedule it's listed on (if any)
- Its physiological effects and the symptoms that arise from them
- Its relative persistence on the ground
- Necessary protective gear
- Treatment for exposure
- How it can be destroyed

# Chemical Reaction

- A ***chemical change*** or ***chemical reaction*** is a process in which one or more pure substances are converted into one or more different pure substances.

# Chemical Reactions - Example



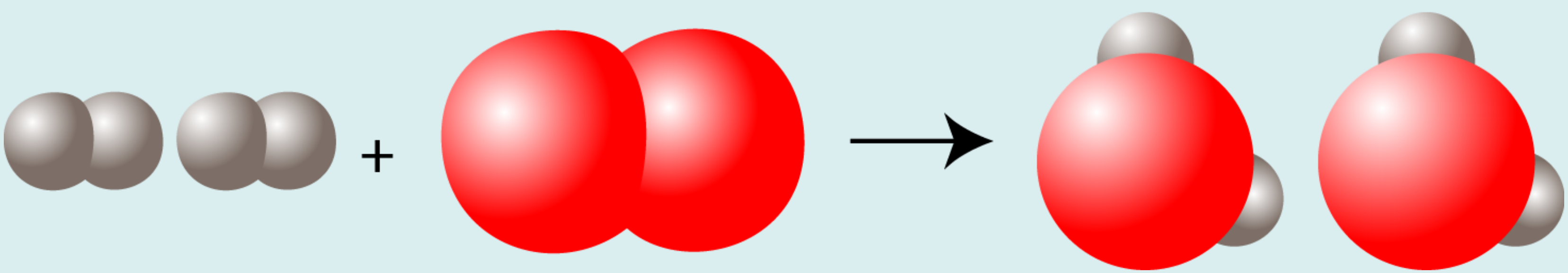
# Chemical Equation Example

Coefficient Coefficient

"goes to"

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

Physical states Physical state



# Chlorine as a Chemical Weapon

- Reacts with water to form hydrochloric acid and hypochlorous acid.

$$Cl_2(g) + H_2O(l) \rightarrow HCl(aq) + HClO(aq)$$

- Death can come from asphyxia due to at least three possible mechanisms
  - May replace oxygen in lungs.
    - Chlorine is more than twice as dense as air.
  - Oxidative injury to the airways and lungs.
  - Fluid build-up in lungs
- Cardiac toxicity leading to cardiac dysfunction.

# Reluctance Overcome by Perceived Necessity

*I must confess that the commission for poisoning the enemy, just as one poisons rats, struck me as it must any other straightforward soldier; it was repulsive to me. If, however, the poison gas were to result in the fall of Ypres, we would win a victory that might decide the entire campaign. In the view of this worthy goal, all personal reservations had to be silent. So onward, do what must be done. War is necessity and knows no exception.*

Berthold von Deimling

Commander of the German XV Army Corps at Ypres

# Personal Protection (Military)

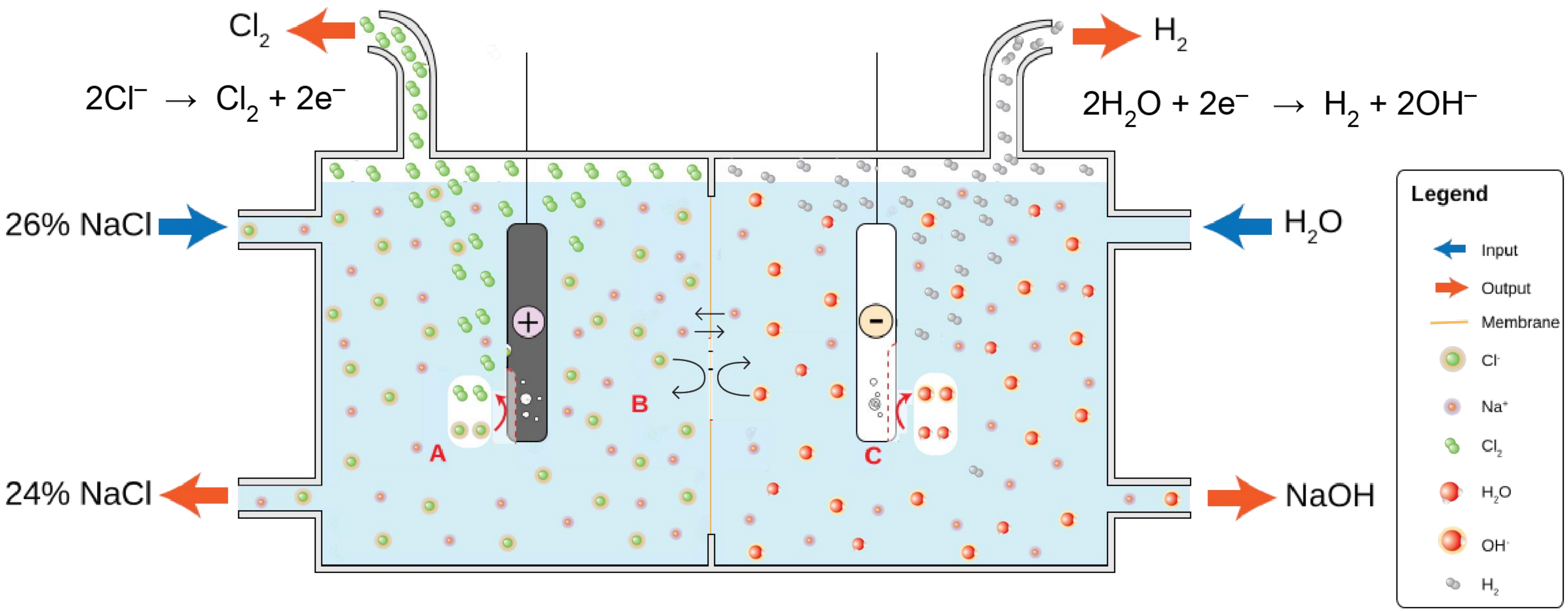

# Ways to Obtain Chlorine, $Cl_2$

- Produce it
- Capture it from production plant
- Divert it during transportation
- Capture it from water treatment plant

# Production of Chlorine

- Relatively easy to make by electrolysis of sodium chloride (table salt) in water

$$2NaCl(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2NaOH(aq)$$



# Chemical and Equipment from Chemical Plant

- From June 2014 to July 2017, the Islamic State held the city of Mosul, Iraq and its surrounding area. This included the University of Mosul and a chemical plant, which provided them with chemicals and equipment to make chemical weapons.
- See *The Evolution of the Islamic State's Chemical Weapons Efforts* by Columb Strack for the Combating Terrorism Center at West Point.

https://ctc.usma.edu/the-evolution-of-the-islamic-states-chemical-weapons-efforts/

# Transportation of Chlorine

- By rail in tank cars


- By highway in cargo tanks and cylinders
- By barge

# Chlorine in Water Treatment Plant

- Commonly in one-ton containers

# Ways to Disperse Chlorine, $Cl_2$, as a CW

- Stationary device, e.g. pressurized gas tanks
- Car or truck bombs
- Drop containers from planes or helicopters that will burst on impact (barrel bombs)
- Roadside bombs
- Projectiles

A 120-millimeter mortar shell struck fortifications at a Kurdish military position near the Mosul Dam, arms experts said, sickening several Kurdish fighters who were nearby.

Credit
Conflict Armament Research and Sahan Research

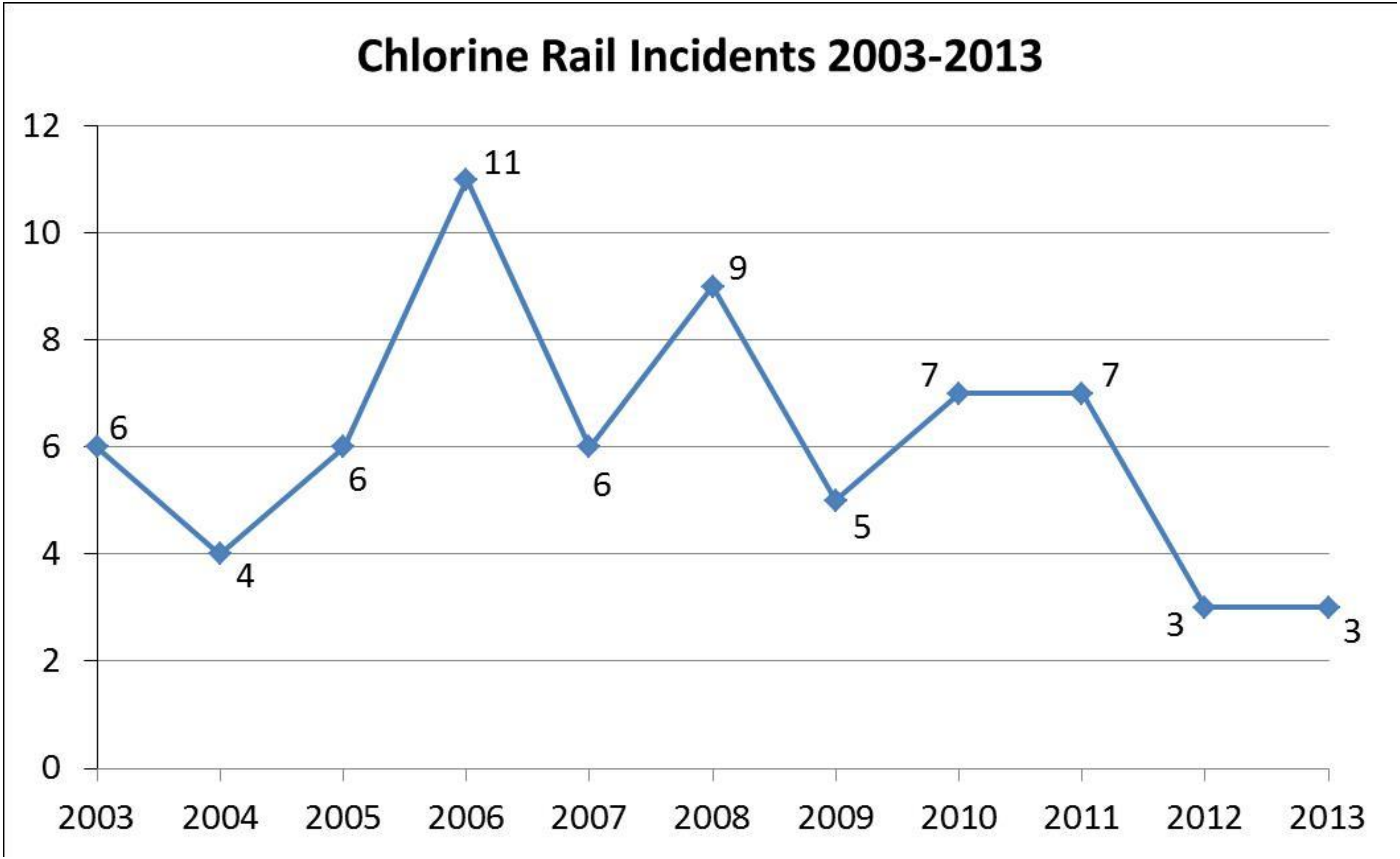
http://www.nytimes.com/2015/07/18/world/middleeast/islamic-state-isis-chemical-weapons-iraq-syria.html

# Chlorine, $Cl_2$, is still a threat today.

- The United States produces approximately *1 billion pounds of chlorine* a year for use in water treatment facilities.
- Potential vulnerability of chlorine-filled rail tank cars, by which chlorine is primarily transported (accident, sabotage)

**Chlorine rail-car derailment, South Carolina, 2005**

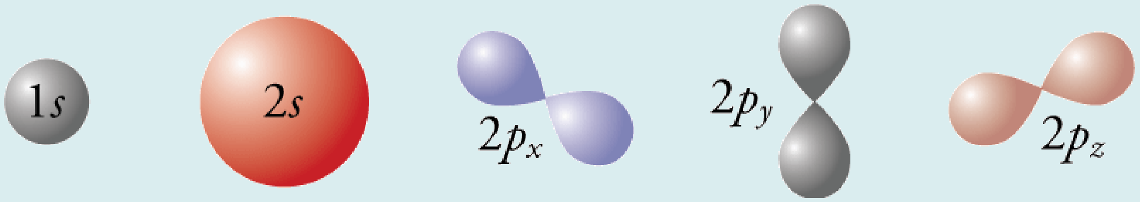
# Chlorine, $Cl_2$, Accidents in U.S.




http://www.chlorineinstitute.org/transportation/incident-statistics.cfm

# Where does the Lewis structure for phosgene, $COCl_2$ come from?

- 3-D wave mathematics for the one electron of hydrogen leads to




- Assume that all other elements have hydrogen-like orbitals.
- Recognize that electrons can have one of only two possible spins.
- Assume that no two electrons in the same atom can be exactly the same.

# For the O in phosgene, $COCl_2$

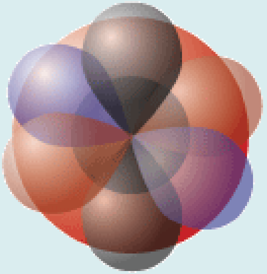
- Leads to orbital diagram of oxygen.

$2s$ ↑↓ $2p$ ↑↓ ↑ ↑

$1s$ ↑↓

O

$1s^2\,2s^2\,2p^4$



- Assume that only the highest energy electrons participate in bonding.

$2s$ ↑↓ $2p$ ↑↓ ↑ ↑

$2s^2\,2p^4$

$\cdot\ddot{\text{O}}\cdot$ (with two lone pairs)

- Assume that covalent bonds form to pair, unpaired electrons.

$-\ddot{\underset{\cdot\cdot}{\text{O}}}-$ or $:\!\text{O}\!=$

# For the C in phosgene, $COCl_2$

Carbon with atomic number 6 has 6 electrons in uncharged atom and 4 valence electrons

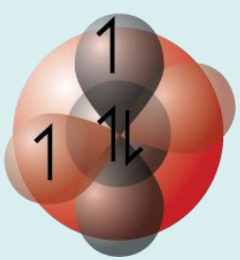
$2p$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\quad}$

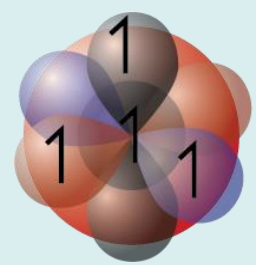
$2s$ $\underline{\uparrow\downarrow}$

$1s$ $\underline{\uparrow\downarrow}$

$2s$ $\underline{\uparrow\downarrow}$ $2p$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\quad}$ $\rightarrow$ $2s$ $\underline{\uparrow}$ $2p$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$

$:\!\underset{\cdot}{C}\cdot$ $\qquad$ $\cdot\overset{\cdot}{\underset{\cdot}{C}}\cdot$

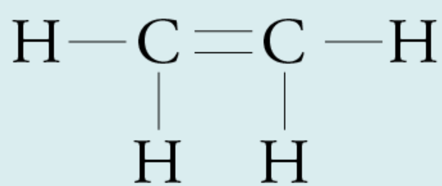




$-\overset{|}{\underset{|}{C}}-$ or $-\underset{|}{C}=$ or $-C\equiv$ or $=C=$

# Carbon – Multiple Bonds

- Carbon atoms can have double or triple bonds. For example, ethene (ethylene), $C_2H_4$, has a double bond.




- Ethyne (acetylene), $C_2H_2$, has a triple bond.

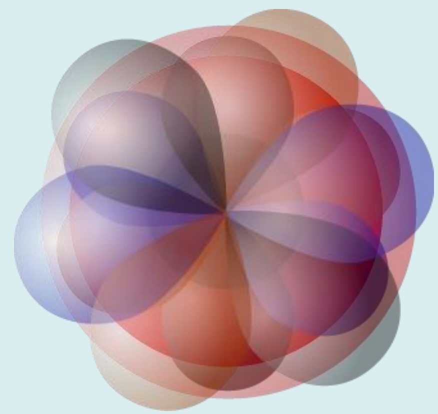
# For the Cl in phosgene, $COCl_2$

Chlorine with atomic number 17 has 17 electrons in uncharged atom and 7 valence electrons

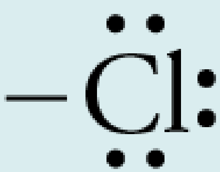
3*s* ↑↓ 3*p* ↑↓ ↑↓ ↑

2*s* ↑↓ 2*p* ↑↓ ↑↓ ↑↓

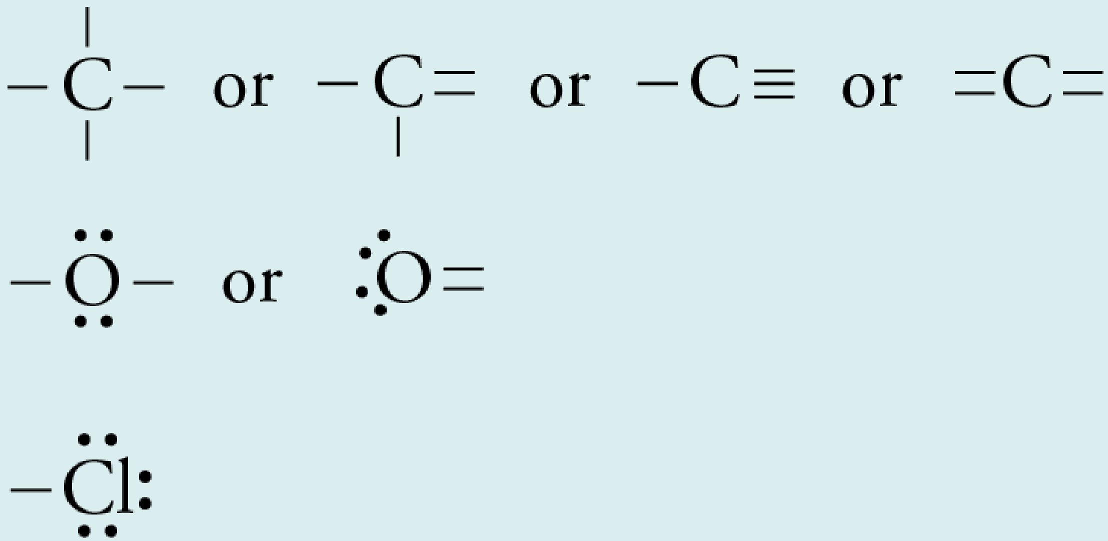
1*s* ↑↓

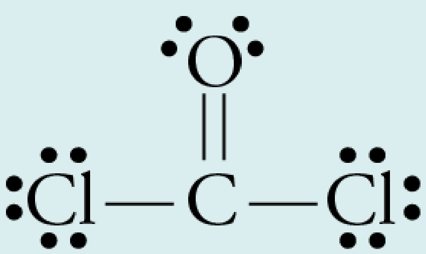


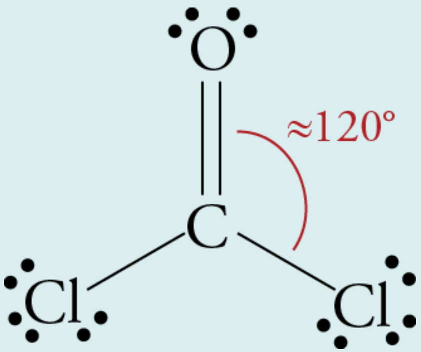
3*s* ↑↓ 3*p* ↑↓ ↑↓ ↑

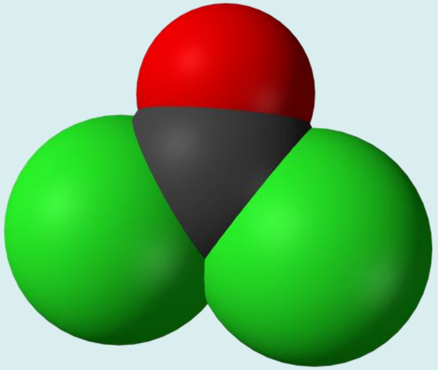


# Phosgene, $COCl_2$







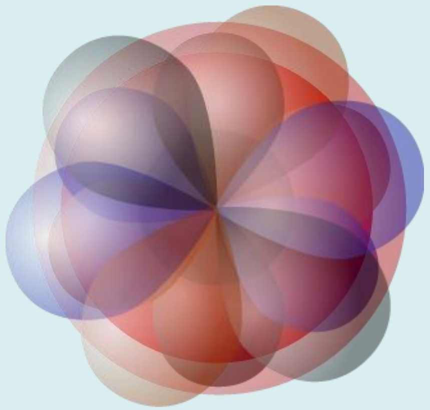



# Sulfur's 16 Electrons

3*s* ↑↓ 3*p* ↑↓ ↑ ↑

2*s* ↑↓ 2*p* ↑↓ ↑↓ ↑↓

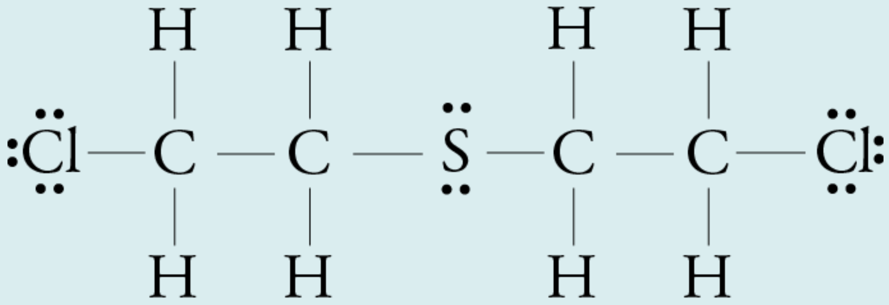
1*s* ↑↓



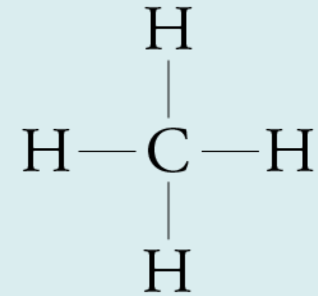
3*s* ↑↓ 3*p* ↑↓ ↑ ↑

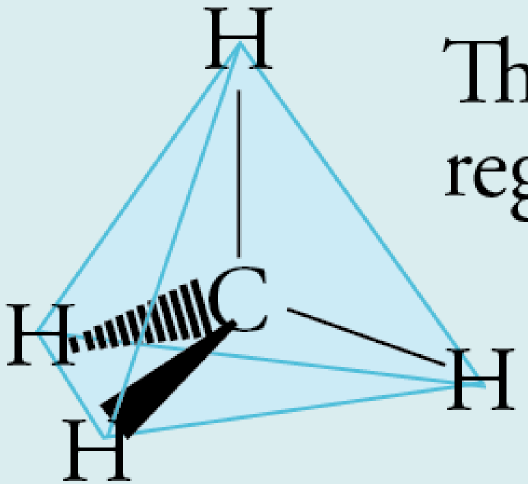
# Compounds with Sulfur

- Sulfur atoms usually form two bonds and two lone pairs. For example, sulfur has two bonds and two lone pairs in the mustard agent $ClCH_2CH_2SCH_2CH_2Cl$.

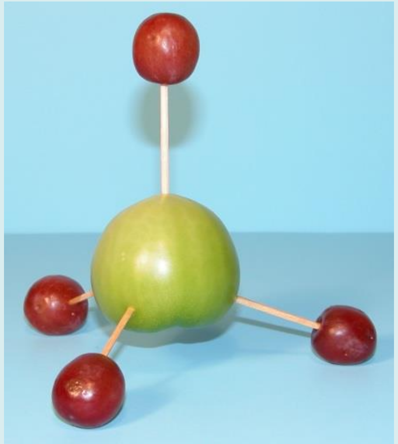


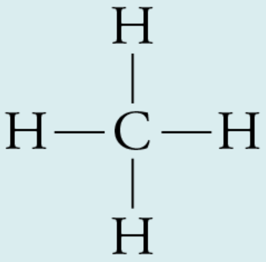
# Methane, $CH_4$



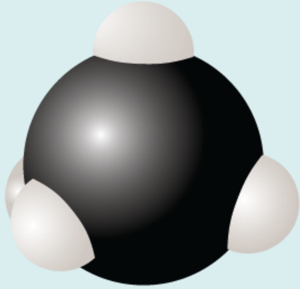


The shaded shape is a regular tetrahedron.

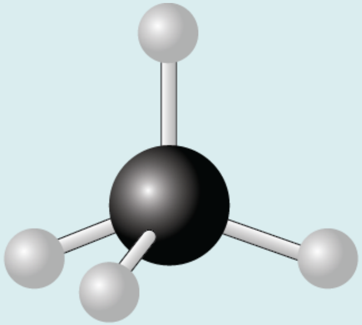




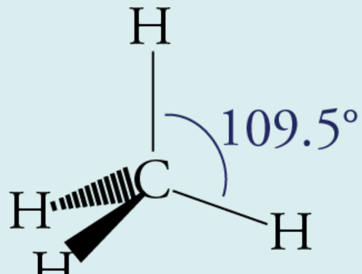
Lewis structure



Space-filling model



Ball-and-stick model




Geometric Sketch

# Compounds with Phosphorus

- Phosphorus atoms usually form three bonds and one lone pair, but they can form five bonds in compounds such as the nerve agent sarin.