

CHE 1031: General Chemistry I



6. Electronic structure & periodic properties of elements

6.1: Electromagnetic energy

6.2: The Bohr model

- *Line spectra equations and calculations [sidebar]*

6.3: The development of quantum theory

- *Equations describing aspects of qm [sidebar]*

6.4: Electronic structure of atoms (electron configuration)

6.5: Periodic variations in elemental properties [sidebar]

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6. Electronic structure, periodic properties



6.1: Electromagnetic energy

- Explain the basic behavior of waves, including travelling & standing waves
- Describe the wave nature of light
- *Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength & energy*
- Distinguish between line and continuous emission spectra
- Describe the particle nature of light

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Thinking about light: a quick history

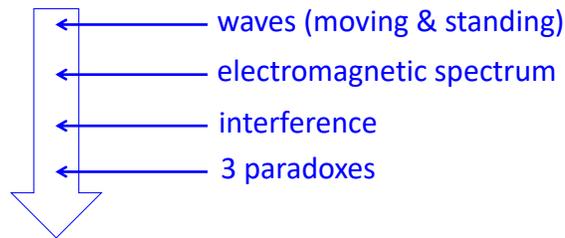


Newton: *light is corpuscular: tiny particles traveling at very high speed*

Huygens: *light is waves traveling through 'luminiferous aether'*

Young: *definitely waves rather than particles*

Maxell: *light is the visible part of the huge spectrum of electromagnetic radiation*



Today? *Wave-particle duality*

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Waves



Wave: (traveling waves) *oscillation or periodic movement that can transport energy from one point in space to another*

- A shaken rope
- Ripples caused by a pebble thrown into a pond
- Thunder (waves of sound)
- 'the wave' by a crowd of people

Kinetic energy is transferred through matter, along the wave, though the matter doesn't move.

<https://www.youtube.com/watch?v=bpojDpZ4m7Y>



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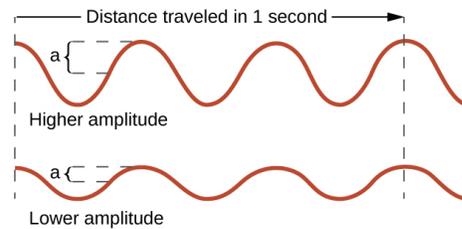
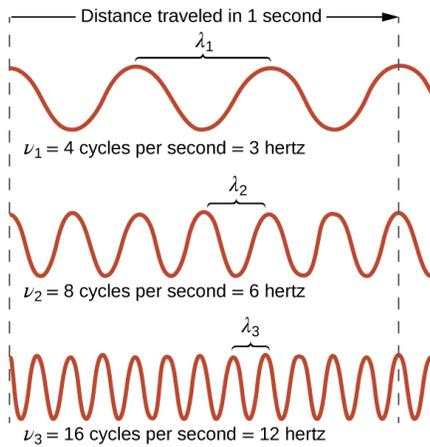
Describing waves



Wavelength (λ): trough-to-trough or peak-to-peak distance

Frequency (ν): number of cycles per unit time (Hz = cycles/s)

Amplitude: (half) height of waves from origin to peak or trough

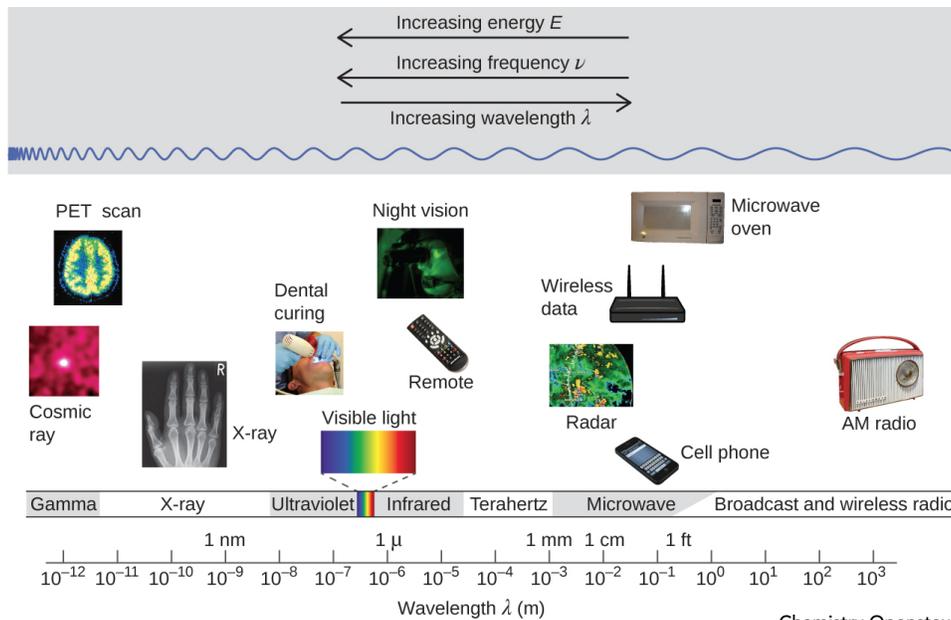


Speed of electromagnetic radiation in a vacuum:

$$c = 2.998 \text{ E}8 \text{ m/s} = (\lambda)(\nu)$$

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Electromagnetic spectrum



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Determining ν & λ of radiation



A sodium streetlight gives off yellow light with a λ of 589 nm.

What is the frequency of the light?

(a)

$$c = (\lambda)(\nu) \rightarrow \nu = \frac{c}{\lambda}$$

$$\nu = \frac{2.998 \text{ E}8 \text{ m}}{1 \text{ s}} \frac{1 \text{ E}9 \text{ nm}}{1 \text{ m}} \frac{1}{589 \text{ nm}} = 5.09 \text{ E}14/\text{s}$$

A common US cell phone frequency is 850 MHz.

What is the wavelength of these radio waves?

(b)

$$c = (\lambda)(\nu) \rightarrow \lambda = \frac{c}{\nu}$$

$$\lambda = \frac{2.998 \text{ E}8 \text{ m}}{1 \text{ s}} \frac{1 \text{ E}9 \text{ nm}}{1 \text{ m}} \frac{1 \text{ s}}{8.50 \text{ E}8} = 3.53 \text{ E}8 \text{ nm} = 0.352 \text{ m}$$

.....*sidebar*.....

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Interference patterns

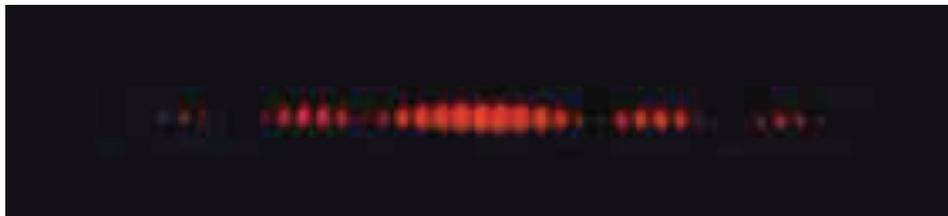


Interference patterns arise when light passes through two narrow slits placed about a λ apart.

- Light forms two new wave as it passes through the slit.
- The two waves collide and interfere either:
 - Constructively or;
 - Destructively.

Red = constructive interference = in-phase peaks adding

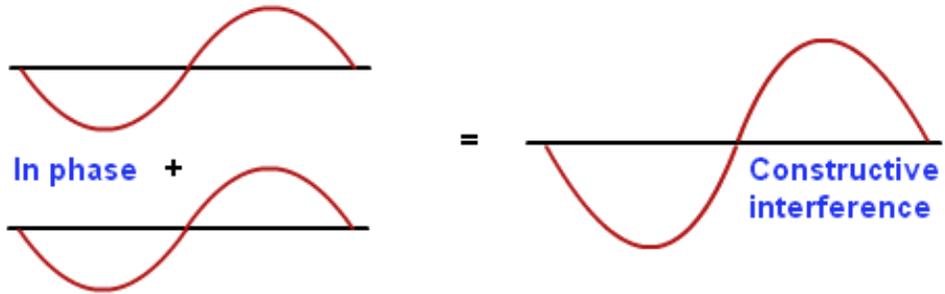
Black = destructive interference = out-of-phase peaks adding



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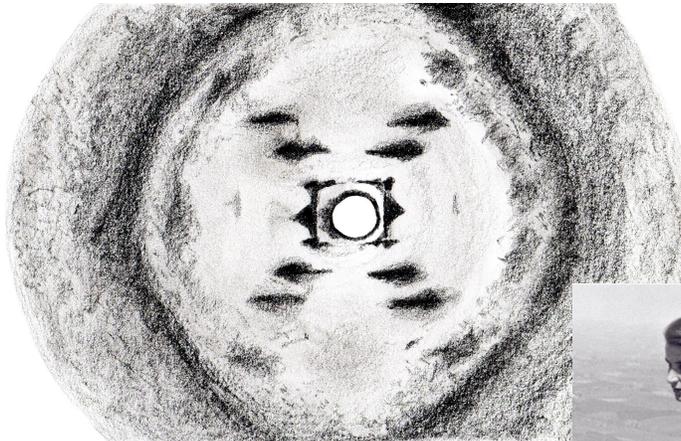
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Visualizing interference



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Interference ~ diffraction



<https://www.youtube.com/watch?v=y0v2rZvNU2c>

<https://rampages.us/teclerh/2016/02/29/rosalind-franklin/>

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Standing waves: 1D



Standing waves don't move but remain fixed in place; one-dimensional

- Only **integer number** (n) of (half) waves can form.
- **Nodes** (places where no motion occurs form $(n-1)$).



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Standing waves: 2D



Sand at the nodes of standing waves caused by vibration.



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The 3 paradoxes that led to 'quantum'



In the late 1800s to early 1900s, physicists observed, and struggled to explain, three **paradoxical phenomena**:

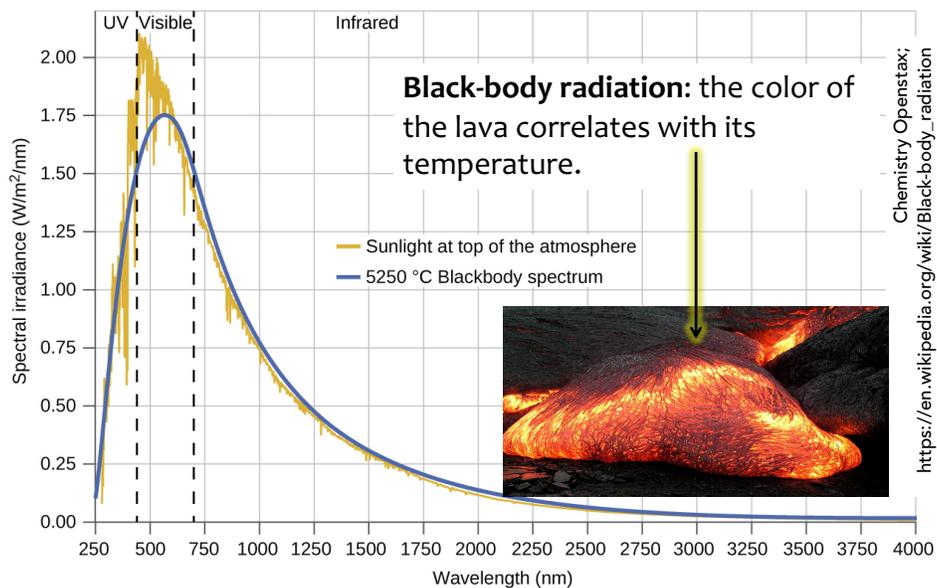
- (1) Black-body radiation;
- (2) Photoelectric effect; &
- (3) Line-spectra.

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(1) Black-body radiation



Note the overlap of the spectra of sunlight & **black-body radiation**.

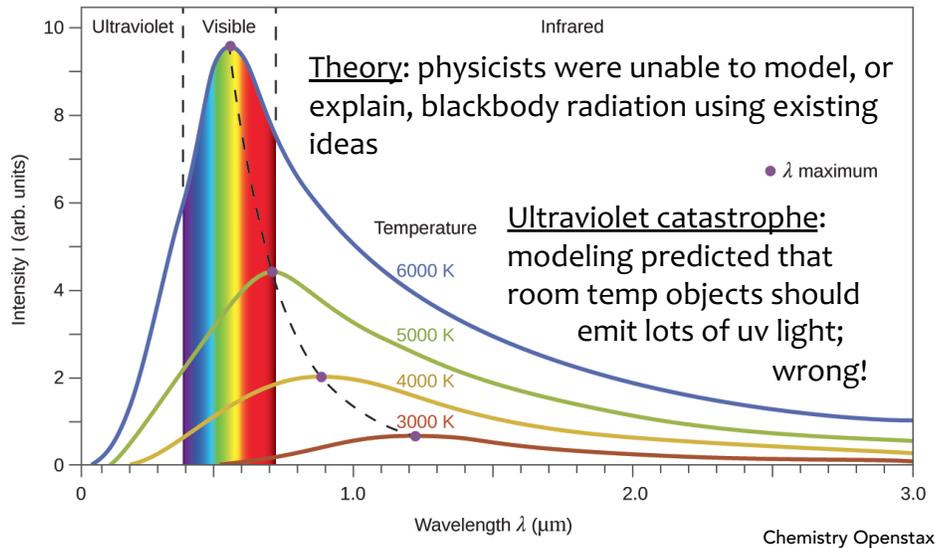


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Black-body observation vs theory



Observation: each temperature corresponds to one peak λ .



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Black-body radiation is also quantum



After years of study, and self-doubt, in 1900, German physicist Max Planck found a theoretical explanation of the black-body phenomenon.

$$E = nh\nu$$

energy (J)

integer

frequency (cycles/s)

Planck's constant (6.626 E-34 J-s)

Two critical points:

- n must be an **integer**; discrete thus **quantum**.
- Quantization of energy is only observed at a very microscopic scale; note the exponent of Planck's constant.

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(2) The photoelectric effect



Photoelectric effect: electrons are ejected from a metal surface if light with a frequency greater than a certain threshold is shined on that surface.

- The light must have more energy than that holding the electrons onto the metal surface to eject them.

Observation:

Frequency matters but intensity does not.

Classic wave theory:

Intensity should matter, frequency should not.



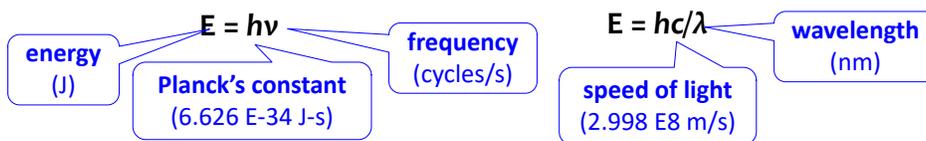
<https://energy.gov/eere/solar/downloads/oak-ridge-visitors-center-solar-array>

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The photoelectric effect is quantum

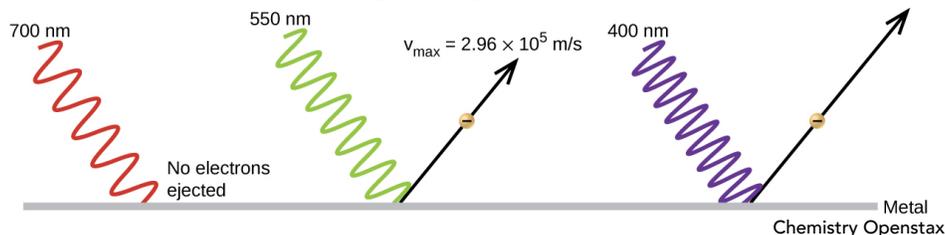


In 1905, Albert Einstein was able to explain the photoelectric effect by applying Planck's work and the concept of quantization.



Here, light behaves like particles (called photons) not as a wave.

- Each photon (greater than threshold ν) can eject one electron from the surface. (ν corresponds to v_{\max} .)
- The more photons (brighter light), the more e- can be ejected.



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So, we can calculate energy of radiation



Neon lights are created by exciting Ne atoms with electricity. If the wavelength of neon light is 640 nm, what is the energy of the photon being emitted by the light?

(c)

$$E = hc/\lambda \quad E = \frac{(6.626 \text{ E-34 J}\cdot\text{s})(2.998 \text{ E8 m/s})}{(640 \text{ nm})(1 \text{ m}/1 \text{ E9 nm})} = 3.10 \text{ E-19 J}$$

Microwaves have a wavelength that heats water molecules in food, but not materials with low water contents.

Microwave frequency is about 3 E9 Hz.

(d)

What is the energy of a microwave photon?

$$E = hv \quad E = (6.626 \text{ E-34 J}\cdot\text{s})(3 \text{ E9 s}) = 2 \text{ E-24 J}$$

.....sidebar.....

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Understanding the photoelectric effect?



Read these statements of the photoelectric effect.

- (a) Identify those that are false.
 (b) Change them to make them true.

(e)

- (1) Increasing the brightness of incoming light increases the kinetic energy of ejected electrons.

False: only if light energy is increased

- (2) Increasing the wavelength of incoming light increases the kinetic energy of ejected electrons.

False: only increasing frequency

- (3) Increasing the brightness of incoming light increases the number of ejected electrons.

True: increasing brightness increases collisions

- (4) Increasing the frequency of incoming light can increase the number of ejected electrons.

True if this increases the number of photons over the threshold frequency

.....sidebar.....

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Try this



Calculate the threshold energy (kJ/mol) of electrons in Al if the lowest frequency for the photoelectric effect is 9.87×10^{14} Hz.

The energy for one photon is given by $E = hf$.

(f)

$$E = (6.626 \times 10^{-34} \text{ J}\cdot\text{s})(9.87 \times 10^{14} \text{ s}^{-1}) = 6.54 \times 10^{-19} \text{ J}$$

$$\frac{6.54 \times 10^{-19} \text{ J}}{1 \text{ photon}} \times \frac{6.02 \times 10^{23} \text{ photons}}{1 \text{ mole}} = 3.94 \times 10^5 \text{ J/mol}$$

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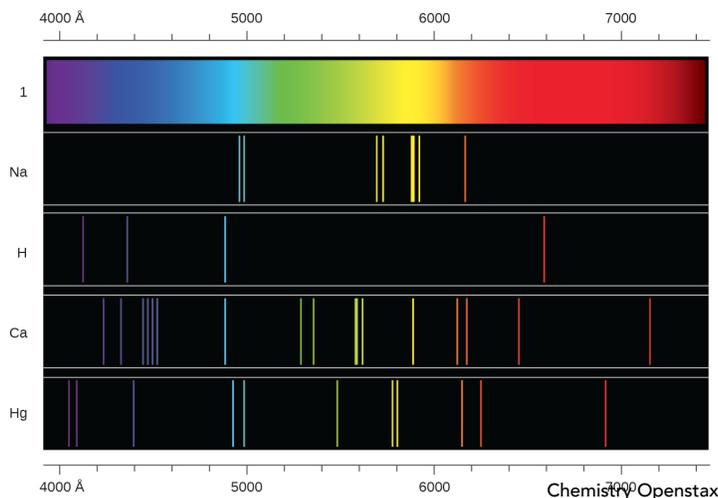
(3) Line spectra



When matter is heated sufficiently it will radiate excess energy as light; as photons. The sun is a mixture of many elements, and sunlight is a continuous spectrum of wavelengths.

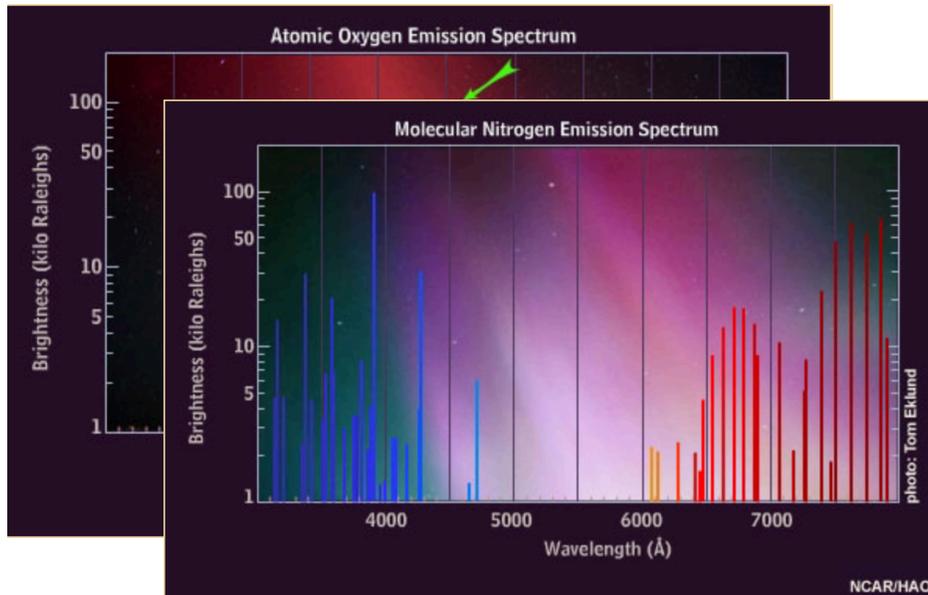
Heating, or excitation, of a single element produces **line spectra** at discrete & characteristic wavelengths.

∴ quantum



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(3) Line spectra of the aurora borealis



https://www.windows2universe.org/earth/Magnetosphere/tour/tour_earth_magnetosphere_09.html

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Can you?



- (1) Explain the difference between waves and particles and define critical characteristics of each?
- (2) Describe the phenomena of wave interference and standing waves?
- (3) List and describe the three phenomena that demonstrate that Newtonian physics isn't able to explain the behavior of light and subatomic particles?
- (4) Use equations provided to calculate basic parameters of waves, light, electrons and atoms?

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6. Electronic structure, periodic properties



6.2: The Bohr model

- Describe the Bohr model of the hydrogen atom
- *Use the Rydberg equation to calculate energies of light emitted or absorbed by hydrogen atoms*

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Paradox of the planetary model



Rutherford & Nagaoka's **planetary or nuclear model** of the atom had a tiny & dense central nucleus surrounded by electrons.

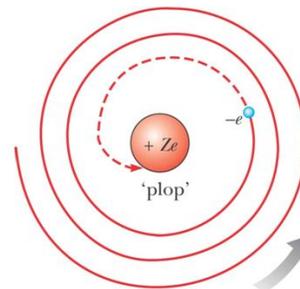
Electrostatic potential should govern the physics of the atom, and cause the electron to adopt an elliptical orbit around the nucleus.

Classical physics would then predict that:

- (1) The electron should be accelerating in order to stay in motion; &
- (2) The electron should emit electromagnetic radiation as it accelerates.

Paradox?

Neither prediction is observed!



<http://slideplayer.com/slide/257194/1/images/8/2-+Early+Models+of+the+Atom.jpg>

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Bohr's model



1913: Niels Bohr attempted to resolve the paradox by applying Planck & Einstein's **quantum work** to the atom.

New predictions:

- (1) Because their energies were quantized, electrons orbiting the nucleus wouldn't emit energy.
- (2) If their energy level were increased by input of energy, electrons would experience a temporary increase in energy level and then emit energy as a photon when they returned to their original energy level.

Energy absorbed or emitted:

$$|\Delta E| = |E_f - E_i| = h\nu = hc/\lambda \quad \text{where } E_f \text{ \& } E_i = \text{final \& initial orbital energies}$$

Quantized energy of electrons:

$$E_n = \frac{k}{n^2} \quad \text{where } n = \text{integer}$$

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Bohr's model agreed with Rydberg's



Johannes Rydberg built on the earlier work of Johann Balmer to mathematically describe elemental line spectra:

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{where } n \text{ are integers } (n_1 < n_2)$$

$R_\infty = \text{Rydberg's constant}$
 $= 1.097 \text{ E7/m}$

Bohr substituted in quantum terms:

$$\Delta E = k \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = \frac{hc}{\lambda} \quad \frac{1}{\lambda} = \frac{k}{hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

.....sidebar.....

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Calculating energy & wavelength



What is the energy (J) and the wavelength (m) of the line in the spectrum of H that represents the movement of an e- from a Bohr orbit of $n = 4$ to the orbit of $n = 6$?

g

Where do we see this in the electromagnetic spectrum?

$$\Delta E = E_1 - E_2 = 2.179 \text{ E-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Delta E = E_1 - E_2 = 2.179 \text{ E-18} \left(\frac{1}{4^2} - \frac{1}{6^2} \right) = (2.179 \text{ E-18})(0.0625 - 0.0278) = 7.561 \text{ E-20 J}$$

+ energy indicates excitation

$$\lambda = \frac{hc}{E} = \frac{(6.626 \text{ E-34 J-s})(2.998 \text{ E8 m/s})}{7.561 \text{ E-20 J}} = 2.627 \text{ E-6 m infrared} = 2627 \text{ nm}$$

sidebar

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Try this



What is the energy (J) and the wavelength (m) of the photon produced when an electron falls from the $n = 5$ to the $n = 3$ level in a He^{+1} ion ($Z = 2$)?

h

$$\Delta E = E_1 - E_2 = 2.179 \text{ E-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Delta E = E_1 - E_2 = 2.179 \text{ E-18} \left(\frac{1}{5^2} - \frac{1}{3^2} \right) = -1.547 \text{ E-19 J}$$

- energy indicates fall back

$$\lambda = \frac{hc}{E} = \frac{(6.626 \text{ E-34 J-s})(2.998 \text{ E8 m/s})}{-1.547 \text{ E-19 J}} = 1.284 \text{ E-6 m} = 1284 \text{ nm so infrared}$$

sidebar

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Bohr's model of the H atom



All matter finds its lowest energy state called the **ground state**.

For H, and other one-electron atoms like He⁺¹, Li⁺², Be⁺³, **energy**:

$$E_n = \frac{-kZ^2}{n^2} \quad \text{where } Z = \text{nuclear charge (atomic number)}$$

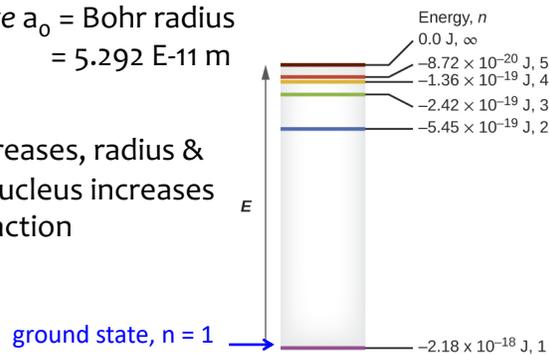
$$k = 2.179 \text{ E-18 J}$$

Radius of the orbit of H-like atoms:

$$r = \frac{n^2}{Z} (a_0) \quad \text{where } a_0 = \text{Bohr radius}$$

$$= 5.292 \text{ E-11 m}$$

As n (e- energy) increases, radius & distance from the nucleus increases & electrostatic attraction decreases.



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Try this



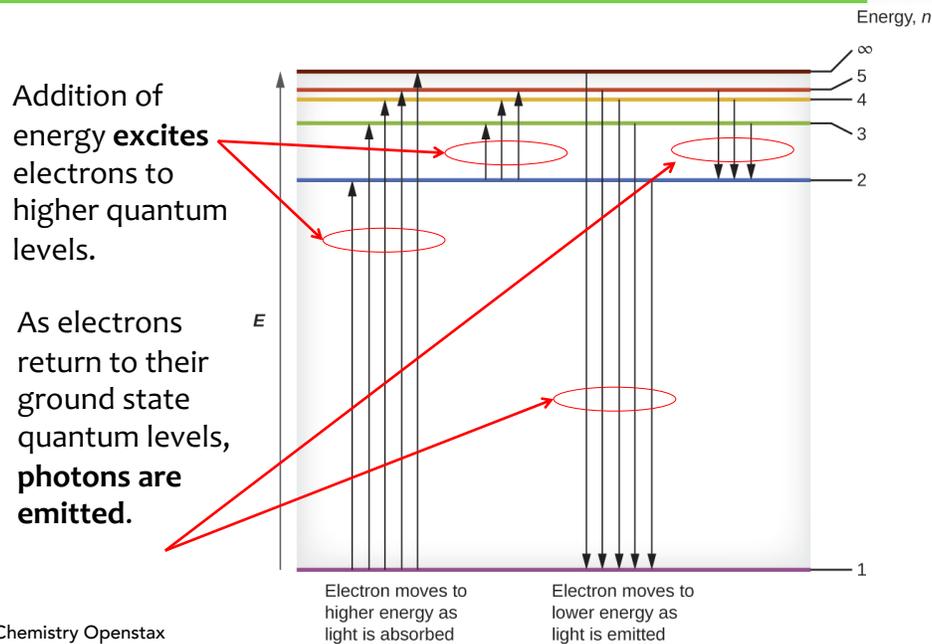
What is the radius, in angstroms, of the orbital of an electron with $n = 4$ in a hydrogen atom?



$$r = \frac{n^2}{Z} (a_0) = \frac{4^2}{1} (5.292 \text{ E-11 m}) = \frac{8.467 \text{ E-10 m}}{1 \text{ m}} \frac{1 \text{ E10 } \text{Å}}{1 \text{ m}} = 8.46 \text{ Å}$$

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Excitation & emission of photons



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Ultimately, Bohr's model failed



While Bohr's model worked for H it **failed** for other atoms, even He with 2 electrons. **Why?**

- The orbits of electrons around the nucleus were still based on classical Newtonian physics.
- Microscopic matter, like atoms and electrons, cannot be described by Newtonian physics.

Bohr's model did make progress:

- Energies of electrons are quantized.
- Electrons' energy increases with increasing distance from the nucleus.
- Discrete line spectra result from quantized electron energies

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Can you?



- (1) Describe the paradox and fatal flaw of the planetary model of the atom?
- (2) Use Bohr's equation to calculate energy of electrons, photons they absorb or emit, and the distance of electrons from the nucleus of atoms? [sidebar]
- (3) Understand why Bohr's model wasn't sufficient to explain the nature of the atom? [sidebar]
- (4) Understand what Bohr did get right?

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6. Electronic structure, periodic properties



6.3: Development of quantum theory

- Extend the concept of wave-particle duality observed in electromagnetic radiation to matter.
- Understand the general idea of the quantum mechanical description of electrons in the atom and that it uses the notion of 3D wave functions, or orbitals, to define the distribution of probability to find an electron in space.
- List & describe traits of the four quantum numbers that form the basis for completely specifying the state of an electron in an atom.

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de Broglie: electrons as waves?



By the 1920s it was clear that microscopic matter didn't behave according to Newtonian physics.

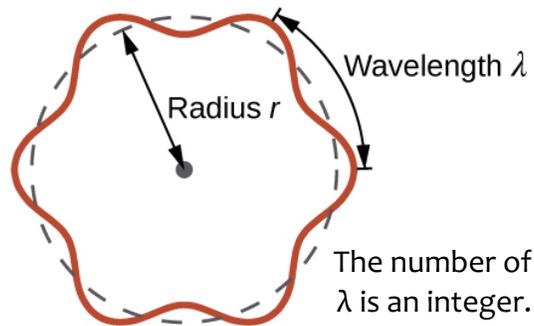
In 1925, Louis de Broglie ('debroy') wondered whether, since electromagnetic energy can act like particles as well as waves, could electrons, a submicroscopic particle, behave like waves?

de Broglie wavelength characteristic of particles & bodies:

$$\lambda = \frac{h}{mv} = \frac{h}{P}$$

where v = velocity (m/s),
 P = linear momentum

de Broglie considered the electron to be a **standing wave**.



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de Broglie: electrons as waves?



de Broglie wavelength characteristic of particles & bodies:

$$\lambda = \frac{h}{mv} = \frac{h}{P}$$

For a circular orbit: $2\pi r = n\lambda$ where n is an integer

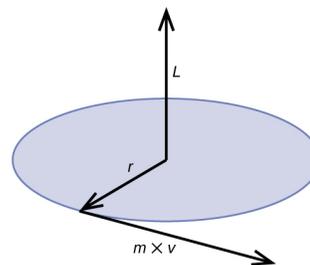
Substitute: $2\pi r = n\lambda = \frac{nh}{P} = \frac{nh}{mv} = \frac{nh}{mvr} = \frac{nh}{L}$

So, the quantized angular momentum ...

$$L = \frac{nh}{2\pi} = n\hbar \quad (\hbar = h/2\pi)$$

... isn't classical angular momentum:

$$L = rp = rmv$$



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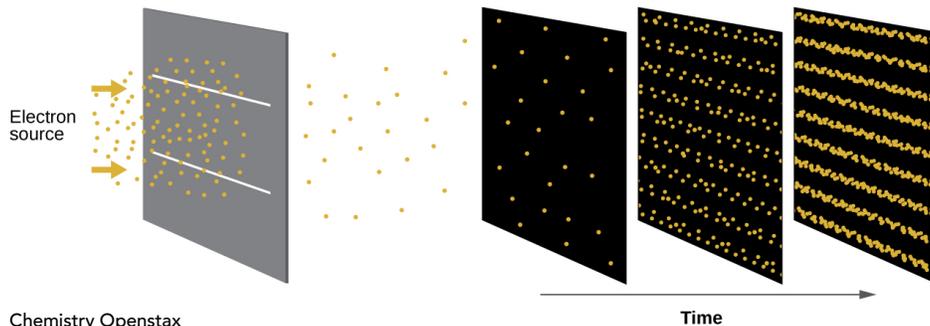
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Proof of electron's wave behavior?



Soon after de Broglie's mathematical demonstration of wave-like behavior of electrons, **Davisson & Germer** at Bell labs found proof (1927).

- Young's double slit experiment, but shooting electrons through slits created from lattices of nickel atoms.
- Observed: interference patterns, thus waves = particle-wave duality



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Calculating the wavelength of electrons



Use de Broglie's equation to calculate the wavelength of an electron traveling at $1.000 \text{ E}7 \text{ m/s}$ if it has a mass of $9.109 \text{ E-}28 \text{ g}$.

$$\lambda = \frac{h}{mv} = \frac{6.626 \text{ E-}34 \text{ J-s}}{(9.109 \text{ E-}28 \text{ g})(1.000 \text{ E}7 \text{ m/s})}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \text{ E-}34 \text{ kg-m}^2/\text{s}}{(9.109 \text{ E-}31 \text{ kg})(1.000 \text{ E}7 \text{ m/s})}$$

$J = \text{kg-m}^2/\text{s}^2$
 $g \rightarrow \text{kg}$

$$\lambda = 7.274 \text{ E-}11 \text{ m}$$

.....sidebar.....

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Try this



Calculate the wavelength of a softball with a mass of 100 g traveling at a velocity of 35 m/s, assuming that it acts as a particle. So, use de Broglie's equation.

k

$$\lambda = \frac{h}{mv} = \frac{6.626 \text{ E-34 J-s}}{(100 \text{ g})(35 \text{ m/s})}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \text{ E-34 kg-m}^2/\text{s}}{(0.100 \text{ kg})(35 \text{ m/s})}$$

$$\lambda = 1.9 \text{ E-34 m}$$

$$J = \text{kg-m}^2/\text{s}^2$$

$$g \rightarrow \text{kg}$$

.....sidebar.....

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Uncertainty at microscopic scale,



Heisenberg found that measuring phenomena at the subatomic scale was difficult and different.

- **Heisenberg uncertainty principle:** *it is fundamentally impossible to determine, simultaneously & exactly, both the momentum and the position of a particle.*

$$(\Delta x)(\Delta p_x) = (\Delta x)(m\Delta v) \geq \frac{\hbar}{2}$$

A particle of mass (m) is traveling in the direction x with velocity (v) & momentum (px). The product of the particle's uncertainty of position (Δx) and uncertainty of momentum (Δpx) must be greater than $\hbar/2$. Where \hbar is $h/2\pi$, h being Planck's constant.

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Getting the uncertainty principle?



We measure an electron's position and find the uncertainty of position (Δx) is 1 pm, about 1% of the diameter of a H atom. What's the uncertainty of the electron's momentum? 1

$$(\Delta x)(\Delta p_x) = (\Delta x)(m\Delta v) \geq \frac{\hbar}{2} \rightarrow \Delta p_x = m\Delta v = \frac{h}{2(\Delta x)}$$

$$\Delta p_x = m\Delta v = \frac{h}{2(\Delta x)} = \frac{1.055 \text{ E-34 J}}{(2)(1 \text{ pm})}$$

$J = \text{kg}\cdot\text{m}^2/\text{s}^2$
pm \rightarrow m

$$\Delta p_x = m\Delta v = \frac{h}{2(\Delta x)} = \frac{1.055 \text{ E-34 kg}\cdot\text{m}^2/\text{s}}{(2)(1 \text{ E-12 m})} = 5 \text{ E-23 kg m/s}$$

This uncertainty of momentum is small, but remember that electrons are small, 9.1 E-31 kg each.

- H's uncertainty affects the microscopic, not macroscopic!

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Quantum mechanical model



Schrodinger & Born used math to wrap together & unify the work of Bohr, de Broglie & Heisenberg and create what is now called **quantum mechanics**, the best current model of the atom.

- Electrons are particles..
- ... whose probable location in space is best represented by a 3D stationary wave or **wavefunction** (ψ).
- ψ^2 is the probability of the location of a quantum particle in space.

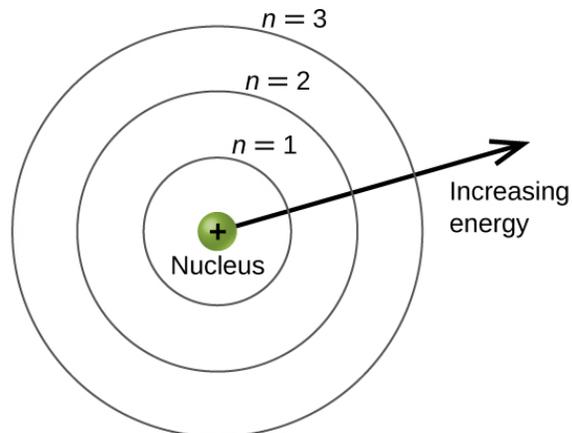
$$\hat{H}\psi = E\psi$$

Where \hat{H} is the Hamiltonian operator representing the energy of the quantum particle, ψ is the wavefunction of the particle & E is the energy of the particle.

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Understanding the qm model of the atom

- (1) Electrons exist only at **discrete quantum energy levels** and not in between them.
- Principle quantum number (n) = 1, 2, 3...



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Understanding the qm model of the atom

- (2) Energy can **boost** electrons to a higher n , but they will fall back to their assigned n , releasing energy as a **photon**.

The energy required to change an electron's principle quantum number:

$$\begin{aligned}\Delta E &= E_f - E_i \\ &= -2.18 \text{ E-18} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{ J}\end{aligned}$$

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Understanding the qm model of the atom

(3) **Orbitals** are regions of the atom in which electrons (0,1,2) most probably reside.

The **angular momentum number (l)** is an integer that describes the shape of an orbital.

- Orbitals with the same l value form a **subshell**.

$l = 0 \rightarrow$ s orbitals

$l = 1 \rightarrow$ p orbitals

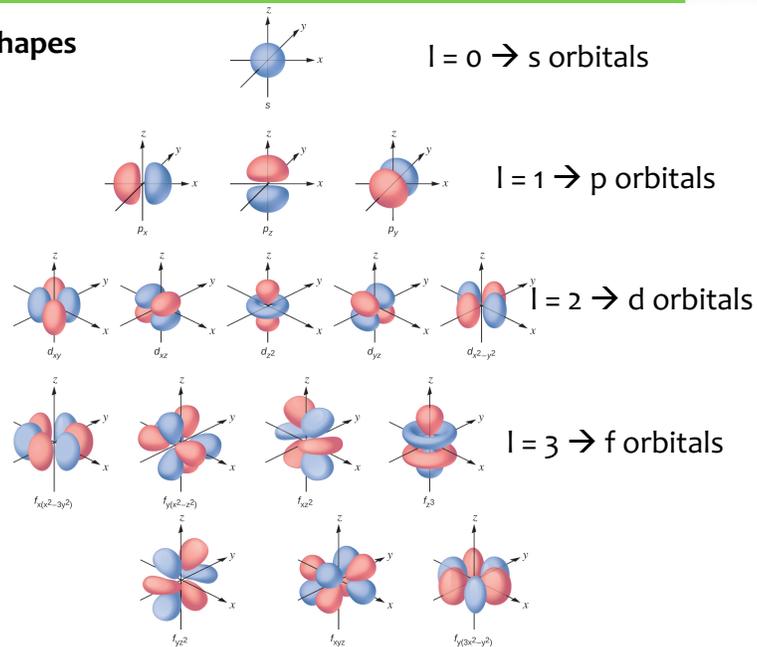
$l = 2 \rightarrow$ d orbitals

etc.,.

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Understanding the qm model of the atom

(3) **Orbital shapes**

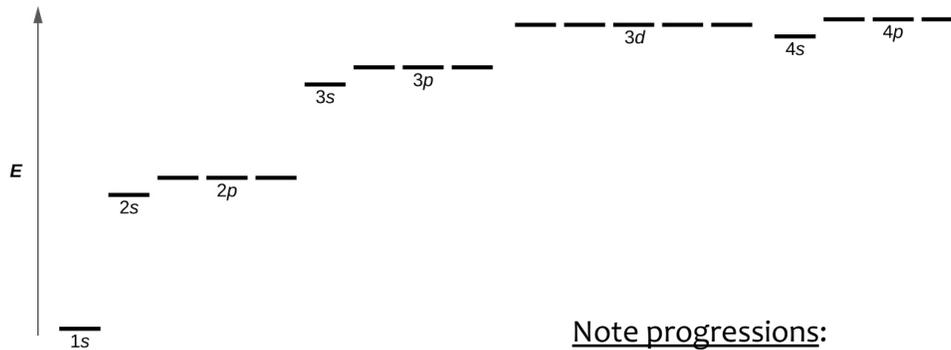


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Understanding the qm model of the atom

(3) **Orbital** energy levels (filling order or aufbau)



Note progressions:

- $1 < 2 < 3$
- $1s \rightarrow 2s, p \rightarrow 3s, p, d$
- $s < p < d$

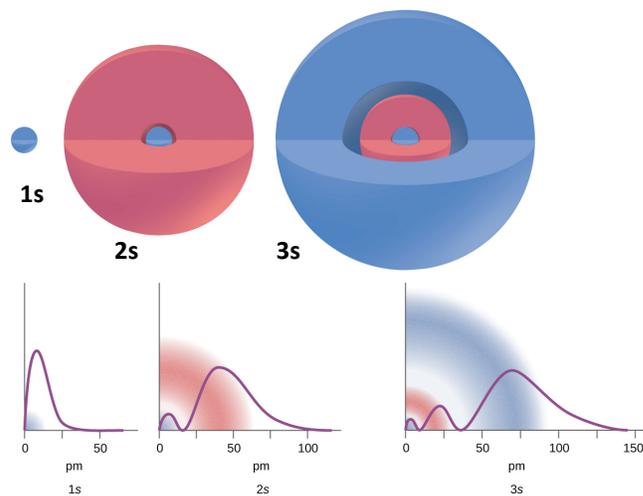
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Understanding the qm model of the atom

(4) Radial **nodes** are regions of the atom in which the probability of finding electrons (ψ) is zero

- The **number of nodes** = $n - l - 1$



So, # nodes:

$$1s = 1 - 0 - 1 = 0$$

$$2s = 2 - 0 - 1 = 1$$

$$3s = 3 - 0 - 1 = 2$$

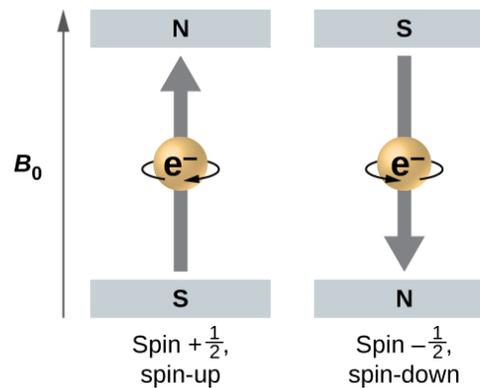
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Understanding the qm model of the atom

(5) Spin quantum number (m_s)

- **Pauli's exclusion principle:** no two electrons in an atom can have the same value for all quantum numbers.
- So, if two electrons occupy the same orbital, same orientation, in the same principle energy level, they must have opposite spin.



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Try this

Consider the $n = 4$ principle energy level (or shell) of an atom.

- How many subshells?
- How many orbitals in each subshell?
- Orbital l values?
- Orbital m_l values?

1

$n = 4$

- s, p, d, f subshells
- s have one orbital; p have 3 orbitals; d have 5 orbitals; f have 7 orbitals
- s: $l = 0$; p: $l = 1$; d: $l = 2$; f: $l = 3$
- s: $m_l = 0$; p: $m_l = -1, 0, +1$; d: $m_l = -2, -1, 0, +1, +2$; f: $m_l = -3, -2, -1, 0, +1, +2, +3$

52

Try this



Use these quantum numbers to identify subshells.

- (a) $n = 3, l = 1$
- (b) $n = 5, l = 3$
- (c) $n = 2, l = 0$

m

- (a) 3p
- (b) 5f
- (c) 2s

.....*sidebar*.....

53

Try this



What is the maximum number of electrons that can occupy these valence shells. (Ignore core electrons.)

- (a) $n = 2$
- (b) $n = 5$ (through f)

2

- (a) 4 orbitals: $s + 3 \times p = 8$ electrons
- (b) $1s + 3p + 5d + 7f = 16$ orbitals = 32 electrons

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6. Electronic structure, periodic properties



6.4: Electronic structure of atoms (configuration)

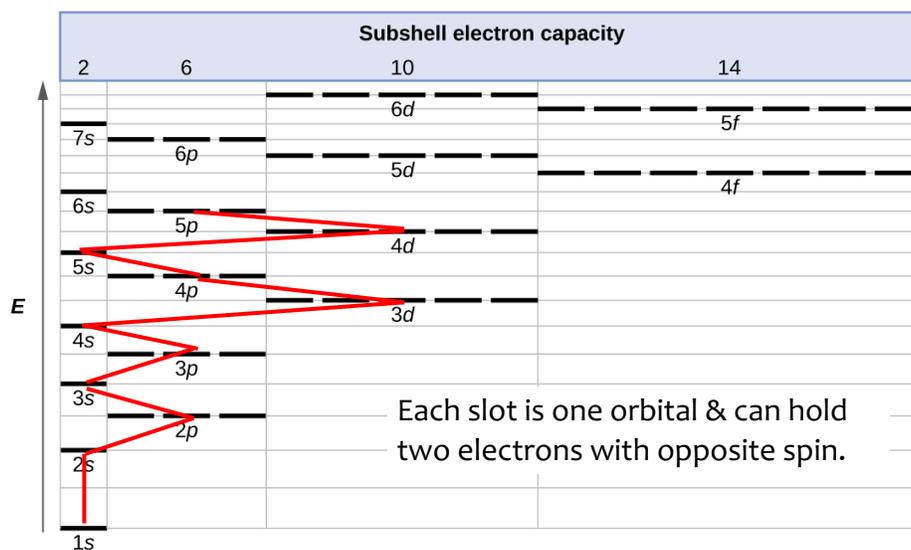
- Derive the predicted, ground-state electron configuration of atoms.
- Identify & explain exceptions to predicted electron configuration of atoms & ions.
- Relate electron configuration to element classification & the periodic table.

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Electrons fill up the energy levels



The filling order (or **aufbau**) determines **electron configuration**.



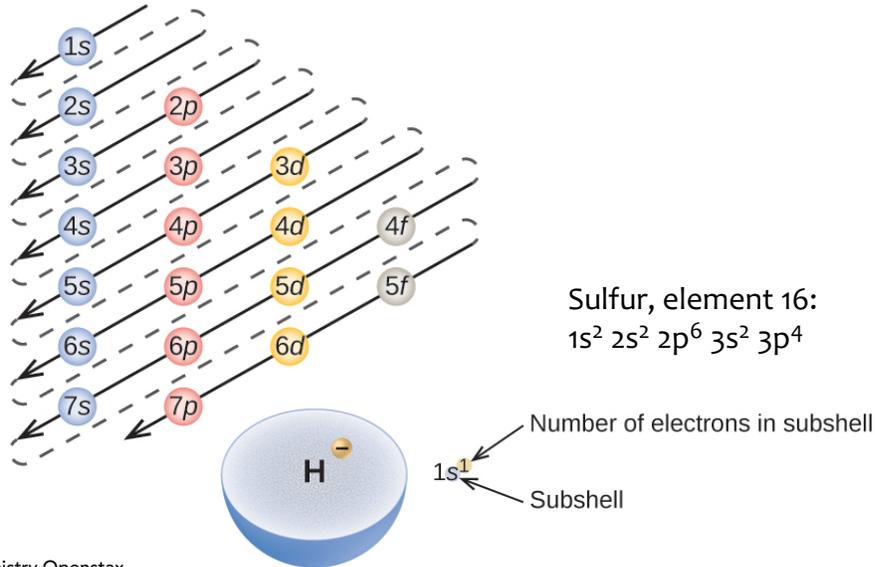
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Order of subshell filling



This 'Christmas tree' diagram shows the order of filling



Sulfur, element 16:
 $1s^2 2s^2 2p^6 3s^2 3p^4$

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Electron configuration & periodic table



Note that **valence electron configuration** is constant within each column (or group). The 'n' increases with each row.

1																	18																																																													
1	H 1s																	He 1s																																																												
2	Li 1s	Be 2s											B 1s	C 2s	N 3s	O 4s	F 5s	Ne 6s																																																												
3	Na 1s	Mg 2s											Al 1s	Si 2s	P 3s	S 4s	Cl 5s	Ar 6s																																																												
4	K 1s	Ca 2s	Sc 3s	Ti 4s	V 5s	Cr 6s	Mn 7s	Fe 8s	Co 9s	Ni 10s	Cu 11s	Zn 12s	Ga 1s	Ge 2s	As 3s	Se 4s	Br 5s	Kr 6s																																																												
5	Rb 1s	Sr 2s	Y 3s	Zr 4s	Nb 5s	Mo 6s	Tc 7s	Ru 8s	Rh 9s	Pd 10s	Ag 11s	Cd 12s	In 1s	Sn 2s	Sb 3s	Te 4s	I 5s	Xe 6s																																																												
6	Cs 1s	Ba 2s	La *1s	Hf 3s	Ta 4s	W 5s	Re 6s	Os 7s	Ir 8s	Pt 9s	Au 10s	Hg 11s	Tl 1s	Pb 2s	Bi 3s	Po 4s	At 5s	Rn 6s																																																												
7	Fr 1s	Ra 2s	Ac **1s	Rf 3s	Db 4s	Sg 5s	Bh 6s	Hs 7s	Mt 8s	Ds 9s	Rg 10s	Cn 11s	Uut 1s	Fl 2s	Uup 3s	Lv 4s	Uus 5s	Uuo 6s																																																												
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td>*</td> <td>Ce 1s</td> <td>Pr 2s</td> <td>Nd 3s</td> <td>Pm 4s</td> <td>Sm 5s</td> <td>Eu 6s</td> <td>Gd 7s</td> <td>Tb 8s</td> <td>Dy 9s</td> <td>Ho 10s</td> <td>Er 11s</td> <td>Tm 12s</td> <td>Yb 13s</td> <td>Lu 14s</td> </tr> <tr> <td colspan="15" style="text-align: center;">4f</td> </tr> <tr> <td>**</td> <td>Th 1s</td> <td>Pa 2s</td> <td>U 3s</td> <td>Np 4s</td> <td>Pu 5s</td> <td>Am 6s</td> <td>Cm 7s</td> <td>Bk 8s</td> <td>Cf 9s</td> <td>Es 10s</td> <td>Fm 11s</td> <td>Md 12s</td> <td>No 13s</td> <td>Lr 14s</td> </tr> <tr> <td colspan="15" style="text-align: center;">5f</td> </tr> </table>																			*	Ce 1s	Pr 2s	Nd 3s	Pm 4s	Sm 5s	Eu 6s	Gd 7s	Tb 8s	Dy 9s	Ho 10s	Er 11s	Tm 12s	Yb 13s	Lu 14s	4f															**	Th 1s	Pa 2s	U 3s	Np 4s	Pu 5s	Am 6s	Cm 7s	Bk 8s	Cf 9s	Es 10s	Fm 11s	Md 12s	No 13s	Lr 14s	5f														
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4f																																																																														
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5f																																																																														

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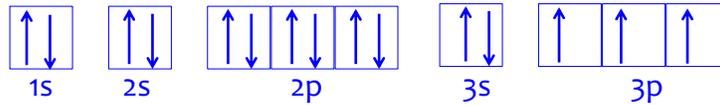
Try these



Draw the box-arrow diagram of the electron configuration of phosphorus.

4

P is element number 15:



Identify the atom from its electron configuration:

5

- (a) $[\text{Ar}]4s^23d^6$
 (b) $[\text{Kr}]5s^24d^{10}5p^6$

- (a) $\text{Ar} = 18 + 2 + 6 = 26$ electrons \rightarrow Fe
 (b) $\text{Kr} = 36 + 2 + 10 + 6 = 54$ electrons \rightarrow Xe

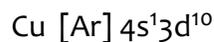
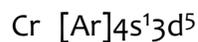
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Transition metals



The electron configuration of transition metals is not as expected.



In transition metals, valence electrons appear to shift from the lower energy 4s orbital to a half-filled (Cr) or filled (Cu) 3d orbital.

- So, while the energy level of 3d should be above 4s we have to conclude that this shift – a sharing of valence orbitals) increases atomic stability.

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Electron configuration of ions



Ions form when atoms gain or lose electrons and this lowers energy and increases stability.

- Non-transition metals lose the last electrons to fill.
- Transition metals lose s orbital electrons first.

Write the atomic & ionic electron configurations of these elements:

6

- (a) Na $1s^2 2s^2 2p^6 3s^1$ $1s^2 2s^2 2p^6$
- (b) P $1s^2 2s^2 2p^6 3s^2 3p^3$ $1s^2 2s^2 2p^6 3s^2 3p^6$
- (c) Al $1s^2 2s^2 2p^6 3s^2 3p^1$ $1s^2 2s^2 2p^6$
- (d) Fe (+2) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^6$

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Try this



Which ion with a charge of +2 has an electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^5$?

7

Look for the atom that has the total in configuration + 2 = 43
 Tc^{+2}

Which ion with a charge of +3 has an electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^5$?

8

Look for the atom with the configuration total + 3 = 44
 Ru^{+3}

66

Can you?



- (1) Explain Hund's rule and Pauli's principle?
- (2) Describe the order of orbital filling, or aufbau?
- (3) Use box-arrow diagrams, written and abbreviated versions of electron configuration?
- (4) Describe how the electron configuration of transition metals differs from that of main-group elements?
- (5) Understand and describe how the electron configuration of atoms differs from that of ions?

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6. Electronic structure, periodic properties



6.5: Periodic variations in elemental properties

- Describe & explain the observed trends in atomic size, ionization energy, and electron affinity of elements.

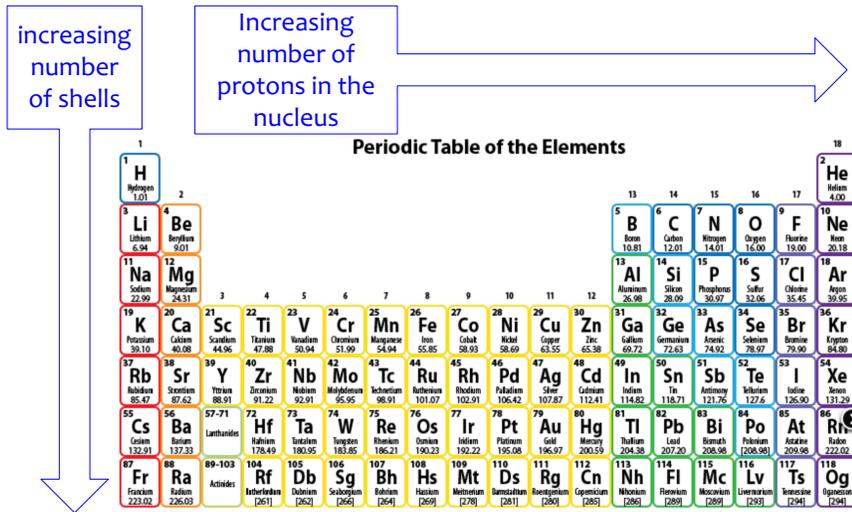
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Which properties vary?



Many atomic properties are governed by these basic changes that occur **across** and **down** the periodic table.



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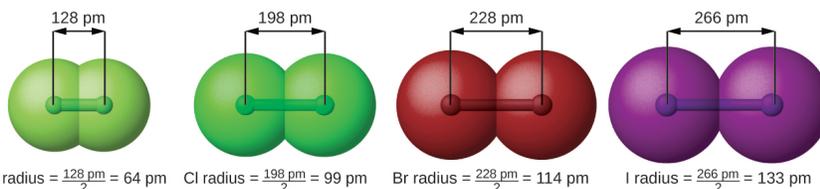
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Covalent radius



Covalent radius: $\frac{1}{2}$ the distance between the nuclei of two identical atoms when they are joined by a covalent bond

Atom	row	Covalent radius (pm)	Nuclear charge
F	2	64	+9
Cl	3	99	+17
Br	4	114	+35
I	5	133	+53
At	6	148	+85



.....sidebar.....

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Covalent radius: trends down & across



So it makes sense that radius increases down columns.

But can you make sense of the trend across rows from left to right?

Periodic Table of the Elements

Period	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

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Covalent radius: trends down & across



So it makes sense that radius increases down columns.

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Periodic Table of the Elements

Period	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

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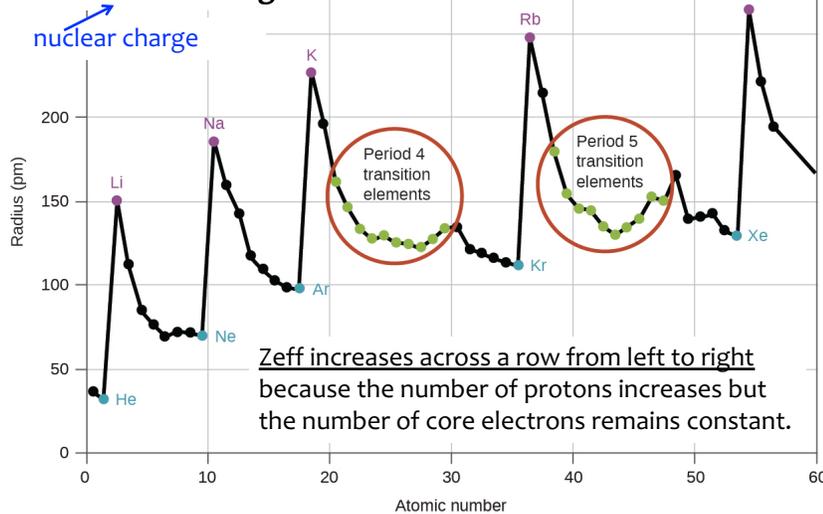
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Effective nuclear charge (Z_{eff})



Effective nuclear charge (Z_{eff}): the 'pull' exerted on electrons by the nucleus

$$Z_{\text{eff}} = Z - \text{shielding} \leftarrow \text{core electrons}$$



.....sidebar.....

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Try this



Arrange these atoms in order of increasing covalent radius by looking at the periodic table: Ge, Fl, Br, Kr.



Ge and Fl are in the same column (IVA) & Ge is above Fl.

- So $\text{Ge} < \text{Fl}$.

Kr, Br & Ge are in the same row. Radius decreases across rows from left to right.

- So $\text{Ge} > \text{Br} > \text{Kr}$.

Putting it all together: $\text{Fl} > \text{Ge} > \text{Br} > \text{Kr}$.

Name an atom whose size is smaller than fluorine.



Atoms in the row above and those to its right (just Ne) are smaller than fluorine.

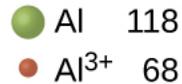
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Ionic radii



Metal atoms generally empty their valence shell when they become cations, so it's clear that the **radii of cations are smaller** than that of the atoms they are formed from.



Nonmetal atoms gain electrons when they become anions, but they don't gain a shell or principle energy level, so why are the **radii of anions greater**?

- Added electrons increase the electrostatic repulsion within the valence shell, causing its electrons to spread out.
- Added electrons cause slight decreases in Z_{eff} .



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Isoelectronic?



Isoelectronic atoms & ions: *have identical valence configurations*

Remember that every atom in the periodic table has a unique valence electron configuration.

But atoms lose or gain electrons to when they **ionize**:

- Metals lose electrons until they share the electron configuration of the noble element in the row above them.
- Nonmetals gain electrons until they share the electron configuration of the noble gas in their row.

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So?



List five ions or atoms that are isoelectronic 'with' nitrogen ion.

9

N^{3-} 's isoelectronic 'family' includes:

O^{2-} , F^{-1} , Ne , Na^{+1} , Mg^{+2} , Al^{+3} .

All have a valence configuration of $1s^2 2s^2 2p^6$.

List four ions or atoms that are isoelectronic 'with' phosphorus ion.

10

P^{3-} 's isoelectronic 'family' includes:

S^{2-} , Cl^{-1} , Ar , K^{+1} , Ca^{+2} , Sc^{+3} .

All have a valence configuration of $[Ne] 3s^2 3p^6$.

.....sidebar.....

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Ionization energies



Ionization energy: *the amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state.*

First ionization energy (IE₁): $X(g) \rightarrow X^{+1}(g) + e^{-}$

Second ionization energy (IE₂): $X^{+1}(g) \rightarrow X^{+2}(g) + e^{-}$

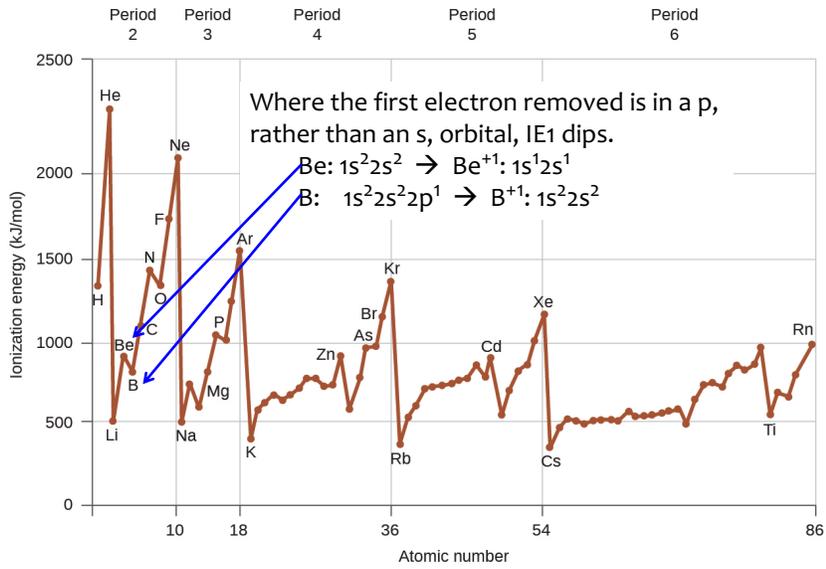
Trends in ionization energies?

- Decrease down a column since electrons further from the nucleus are more loosely held by the nucleus.
- Generally increase across rows as more protons hold electrons more tightly.
 - **But** s electrons are more firmly held than p & d electrons.

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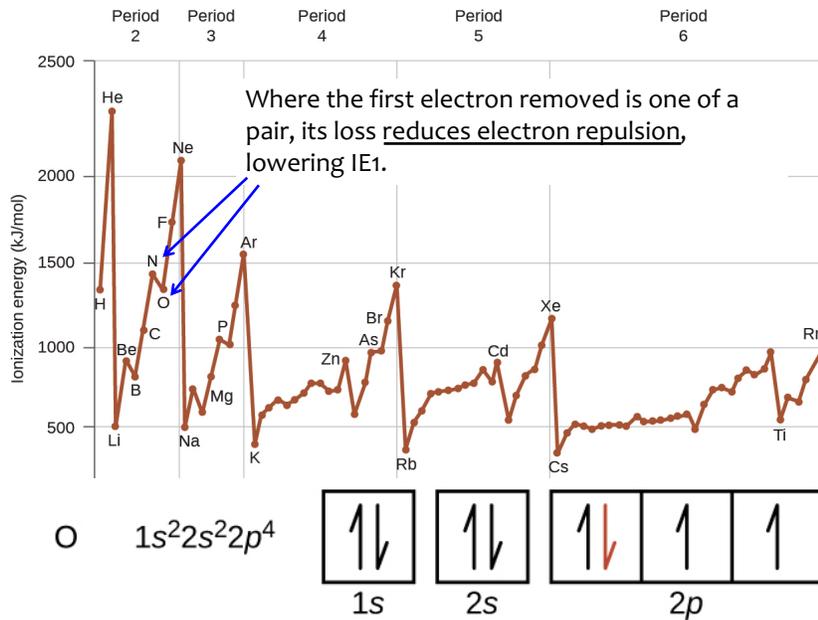
Effect of shape of orbital on IE1



.....sidebar.....

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Effect of half-filled orbitals on IE1



.....sidebar.....

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Effect of increasing positive charge



Each successive ionization of a metal increases the metal's positive charge and thus **each ionization requires more energy**.

- Fewer electrons increase Z_{eff} .

across

element	IE1	IE2	IE3	IE4	IE5	IE6	IE7
K	418.8	3,051.8	4,419.6	5,876.9	7,975.5	9,590.6	11,343.0
Ca	589.8	1,145.4	4,912.4	6,490.6	8,153.0	10,495.7	12,272.9
Sc	633.1	1,235.0	2,388.7	7,090.6	8,842.9	10,679.0	13,315.0
Ga	578.8	1,979.4	2,964.6	6,180.0	8,298.7	10,8793.9	13,594.8
Ge	762.2	1,537.5	3,302.1	4,410.6	9,021.4	NA	NA
As	944.5	1,793.6	2,735.5	4,836.8	6,042.9	12,311.5	N

↓

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81

Try this



Rank the energy required for these ionizations:

- Al IE1 $IE1 = 3p1 \rightarrow 1^{\text{st}} \text{ ve-}$
- Tl IE1 $IE1 = 6p1 \rightarrow 1^{\text{st}} \text{ ve- (further out)}$
- Na IE2 $IE2 = 2p6 \rightarrow \text{core electron}$
- Al IE3 $IE3 = 3s1 \rightarrow 3^{\text{rd}} \text{ ve-}$

q

Valence always easier than core. Each ve- harder.

$Tl \text{ IE1} < Al \text{ IE1} < Al \text{ IE3} < Na \text{ IE2}$

Which has the lowest IE2 value?

r

- O $IE2 = 2p3$
- Po $IE2 = 6s26p4$
- Pb $IE2 = 6s26p2$
- Ba $IE2 = 6s2$
- Ba
- All are ve-.
- Row 6 elements larger so lower IE than O.
- Ba furthest to the left, less p+.

sidebar.....

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Electron affinity



Electron affinity (EA): the energy change required to add an electron to a gaseous atom to form an anion



Trends?

Adding electrons becomes easier when Z_{eff} increases, so EA generally increases from left to right.

Electron Affinity Values for Selected Elements (kJ/mol)

Negative charge indicates release of energy as e⁻ are added, indicating easier addition of electrons. (endothermic)

Period	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1	H -72																	He +20*
2	Li -60	Be +240*											B -23	C -123	N 0	O -141	F -322	Ne -30
3	Na -53	Mg +230*											Al -44	Si -120	P -74	S -20	Cl -348	Ar +35*
4	K -48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga -40*	Ge -115	As -7	Se -195	Br -324	Kr +40*
5	Rb -46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In -40*	Sn -121	Sb -101	Te -190	I -295	Xe +40*
6	Cs -45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl -50	Pb -101	Bi -101	Po -170	At -270*	Rn +40*
7	Fr	Ra																

* Calculated value

83

EA: exceptions to the trend



8A: noble elements have a full shell, so new electrons would have to be added to a new 'n' level

2A: elements have a full s orbital, so new electrons would have to be added to the next level

5A: elements have a half-full p orbital, so new electrons fill a pair, increasing electrostatic repulsion

Electron Affinity Values for Selected Elements (kJ/mol)

Period	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1	H -72																	He +20*
2	Li -60	Be +240*											B -23	C -123	N 0	O -141	F -322	Ne -30
3	Na -53	Mg +230*											Al -44	Si -120	P -74	S -20	Cl -348	Ar +35*
4	K -48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga -40*	Ge -115	As -7	Se -195	Br -324	Kr +40*
5	Rb -46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In -40*	Sn -121	Sb -101	Te -190	I -295	Xe +40*
6	Cs -45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl -50	Pb -101	Bi -101	Po -170	At -270*	Rn +40*
7	Fr	Ra																

* Calculated value

84

Can you?



- (1) List the atomic properties that vary with the table's periodicity?
- (2) Describe, in a basic sense, how each varies down and across the periodic table?
- (3) Where variation depends on electron configuration explain how and why?
- (4) Define the term isoelectronic and identify ions and atoms that fit the bill?

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Key terms



amplitude	Hund's rule	valence shell
angular momentum quantum no. (l)	intensity	wave
atomic orbital	interference pattern	wave-particle duality
Aufbau principle	ionization energy	wavefunction (ψ)
blackbody	isoelectronic	wavelength (λ)
Bohr's model of the hydrogen atom	line spectrum	
continuous spectrum	magnetic quantum number (ml)	
core electron	node	
covalent radius	orbital diagram	
d orbital	p orbital	
effective nuclear charge	Pauli exclusion principle	
electromagnetic radiation	photon	
electromagnetic spectrum	principal quantum number (n)	
electron affinity	quantization	
electron configuration	quantum mechanics	
electron density	quantum number	
excited state	s orbital	
f orbital	shell	
frequency (ν)	spin quantum number (ms)	
ground state	standing wave	
Heisenberg uncertainty principle	subshell	
hertz (Hz)	valence electrons	

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Equations



$$c = \lambda \nu$$

$$E = h\nu = \frac{hc}{\lambda}, \text{ where } h = 6.626 \times 10^{-34} \text{ J s}$$

$$\frac{1}{\lambda} = R_{\infty} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$E_n = -\frac{kZ^2}{n^2}, \quad n = 1, 2, 3, \quad \text{Where:}$$

$$\Delta E = kZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$r = \frac{n^2}{Z} a_0$$

c = the speed of em radiation (light) = 2.998 E8 m/s

λ = wavelength (nm)

ν = frequency (cycles/s = Hz)

E = energy (J)

h = Planck's constant = 6.626 E-34 J-s

R = the Rydberg constant = 1.097 E7 m⁻¹ (1/m)

n = integers or whole numbers

E_n = a quantized energy (J)

k = a constant = 2.179 E-18 J

Z = nuclear charge or atomic number

r = radius of atomic orbits

a_0 = the Bohr radius (5.292 E-11 m)

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