

## Quantum Theory and Chemistry

Up to now we have been concerned with the “macroscopic” description of chemical systems and reactions. However, our entire *understanding* of what is going on — of the patterns of properties and reactive behaviour of elements & compounds, and the most incisive methods used for identifying elements and molecular compounds — is based on a mathematical molecular theory which has little direct connection to our personal experience of the physical world. Much of the rest of this course will be concerned with developing an understanding and familiarity with the basis of this “quantum theory”.

### The Origins of Quantum Theory

In the late 19<sup>th</sup> century, many people thought that physics was almost complete. The combination of Newton’s laws and Lagrange’s formulation for classical mechanics, Maxwell’s laws for wave behaviour (including light), and the (still young) atomic theory seemed to explain most observed phenomena. In particular:

**The Atomic Theory** of matter was generally accepted: all matter is made up of atoms whose sizes and masses were fairly well known.

**The Kinetic Theory of Gases** (based on an ordinary classical mechanics description of gases, seen as freely moving atoms or molecules) had predicted/explained the empirically determined ideal gas law  $PV = nRT$

**The Periodic Table** for ordering the atoms in a way grouped those with similar types of properties in a single column had been successfully developed ... although the *reason* for the periodicity of the properties *was not yet understood*.

**Electrons were “known”** to be tiny charged particles, much smaller than atoms, which behaved as ordinary classical particles (mini billiard balls) of known mass and charge

**Light** was generally accepted to be a kind of wave phenomenon (like sound or water waves) of known speed, and most of its properties were quantitatively explained by Maxwell’s equations of electromagnetism.

Indded, the world seemed (to some people) to be so well understood that at the opening of the new physics building at the University of Chigago in 1894, the famous physicist A.A. Michelson (Nobel prize in physics, 1907) announced

*“The more important fundamental laws and facts of physical science have all been discovered, and these are now so firmly established that the possibility of their ever being supplanted in consequence of new discoveries is exceedingly remote ... Our future discoveries must be looked for in the sixth place of decimals.”*

**However ...** a handful of troublesome experimental observations could not be explained within the above framework, and accommodating them led to a revolution on our understanding of the physical world.

**Problem #1:** *light sometimes behaves like (a stream of) particles!*

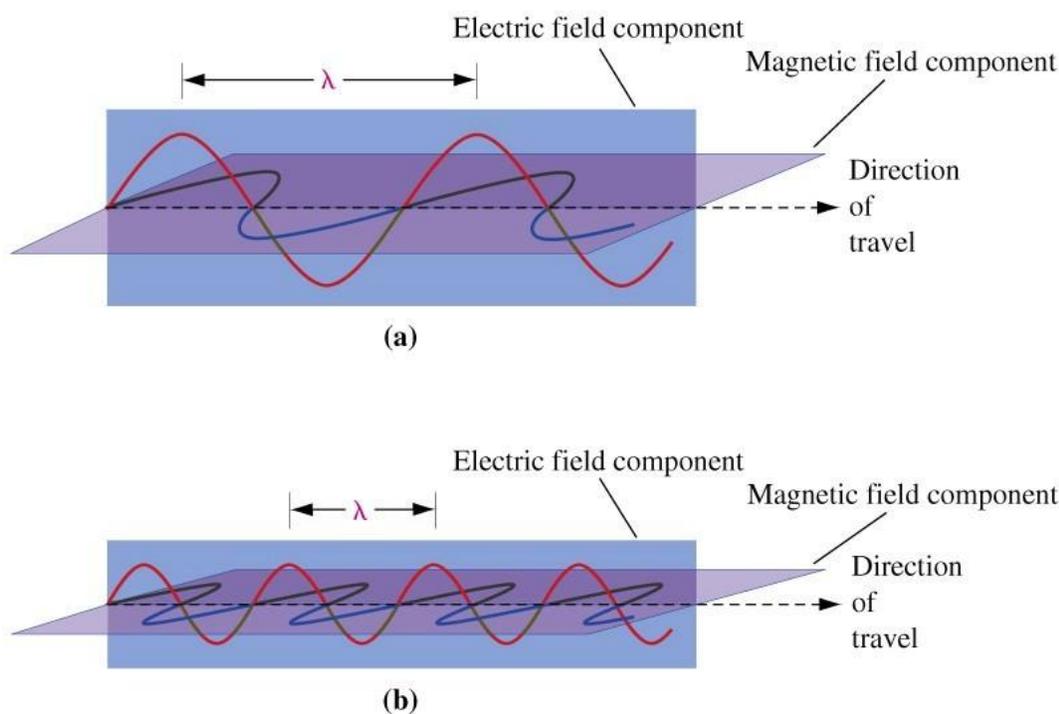
**Problem #2:** *the internal energies of atoms & molecules appear to be “quantized”, and moving electrons and atoms (& molecules) sometimes show wave-like properties!*

## What does it mean to say that *light is a wave phenomenon* ?

Think about waves on water or sound waves: they travel through space and have properties

- velocity or speed  $v$  [m/s]
- amplitude
- wavelength  $\lambda$  [m]
- frequency  $\nu$  [s<sup>-1</sup>]

Light consists of electric & magnetic fields oscillating in a concerted manner at right angles to one another, and propagating through space at speed  $c$ .



Three defining properties of any wave phenomenon are interrelated by the equation

$$\begin{aligned} \{\text{speed [m/s]}\} &= \{\text{frequency [s}^{-1}\text{]}\} \times \{\text{wavelength [m]}\} \\ v \text{ [m/s]} &= \nu \text{ [s}^{-1}\text{]} \times \lambda \text{ [m]} \end{aligned}$$

while the amplitude of a wave defines its intensity, or the energy it carries (e.g., water waves eroding a cliff, sound waves damaging your eardrums).

**Exercise 1.** The speed of sound in dry air at STP is 331.45 m/s. The musical note ‘A’ has a frequency of 440 [s<sup>-1</sup>].

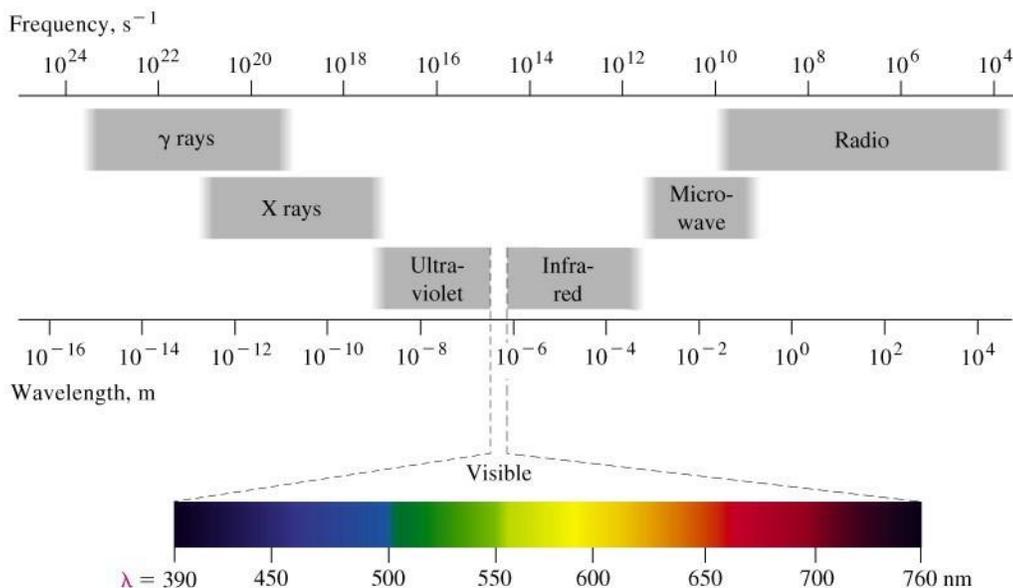
- What is the wavelength of a sound wave at that frequency?
- The speed of sound in water is 1497 m/s. What is the wavelength of an A note there?

**For light:**

- the speed (in a vacuum) is one of the constants of nature

$$v_{\text{light}} \equiv c = 2.997\,924\,58 \times 10^8 \text{ [m/s]}$$

- the frequency (or wavelength) of light defines the property we commonly call “colour”.



for yellow light  $\lambda \approx 550 \text{ [nm]}$  so  $\nu =$

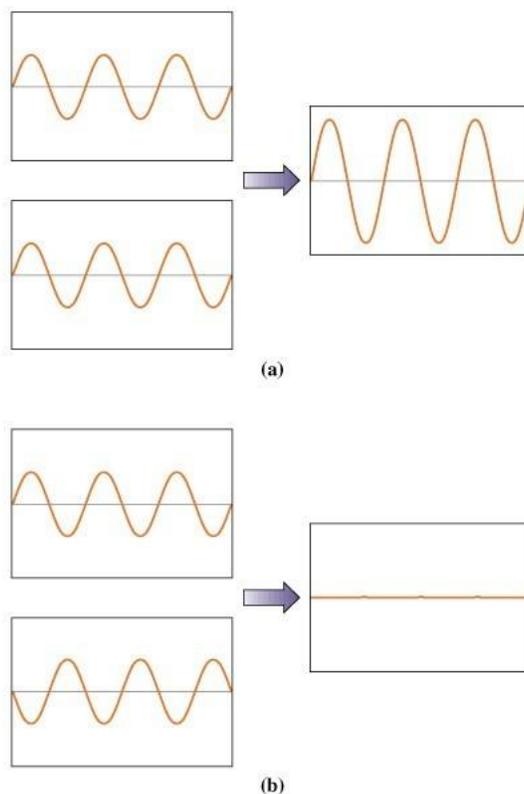
for blue light  $\lambda \approx 425 \text{ [nm]}$  so  $\nu =$

for red light  $\lambda \approx 700 \text{ [nm]}$  so  $\nu =$

**Interference effects:**

If two waves of the same frequency simultaneously pass through the same region of space,

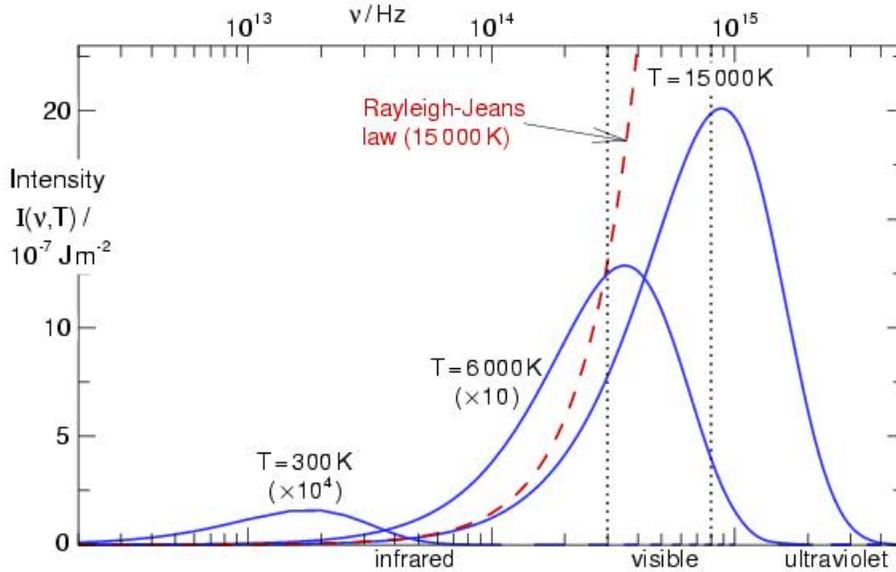
- if they are “in phase” get ‘constructive interference’
  - a resulting wave whose amplitude is the sum of those for the two waves.
- if “out of phase”, get ‘destructive interference’
  - a resulting wave of small or negligible amplitude since the two waves cancel one another out.
- occurs for light, just as for sound or water waves.



## Planck's Radiation Law, and the Quantization of Light Energy

Every hot object or material (e.g., the sun, the earth, a light bulb filament, a furnace) gives off light with a distribution of frequencies (*its "emission spectrum"*), and the intensity as a function of wavelength is *exactly* the same function for every object/material at a particular temperature. This intensity distribution is known as the "*black body*" spectrum for that temperature.

Before 1900, the most sophisticated theory known, the 'Rayleigh-Jeans' theory, predicted that the intensity at a particular frequency  $\nu$  increases as the square of the frequency:  $I(\nu) \propto \nu^2$ . This agreed with experiment at low frequencies, but it also made the absurd prediction that the intensity increased without limit as the frequency got higher (a prediction called the "ultraviolet catastrophe").



Planck re-worked the 'classical' theory, but with one extra mathematical trick: he assumed that the energy emitted/absorbed by a black body came in tiny increments or "quanta" whose magnitude depended on the frequency:  $\delta E_\nu = h\nu$  [i.e.,  $h$  was initially originally introduced as a tiny arbitrary scaling constant, as a mathematical way of forcing all energy increments to be small]. These tiny increments were introduced, just as in calculus we introduce tiny increments  $dx$ , perform some algebra, and then take the limit of the resulting expression as  $dx \rightarrow 0$ .

The resulting derivation gave something very different than the classical expression,

$$I(\nu, T) = \frac{8\pi^3}{h^2 c^3} (\delta E_\nu)^3 \left( \frac{1}{e^{\delta E_\nu/kT} - 1} \right) = \frac{8\pi^3 \nu^3}{c^3} \left( \frac{h}{e^{h\nu/kT} - 1} \right)$$

and the shape of this distribution function happened to agree *exactly* with experiment. However, on taking the limit as  $h \rightarrow 0$ , this expression collapses to the classical Rayleigh-Jeans result, and good agreement with the experimental distribution is only obtained if  $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ .

Planck was initially reluctant to attribute any physical significance to his mathematical 'trick', but he eventually concluded that the light energy emitted/absorbed by material objects *truly must be quantized*, consisting of tiny increments or quanta of magnitude  $\delta E_\nu = h\nu$ .

[ *How much of this Planck stuff do you really need to know ... ??* ]

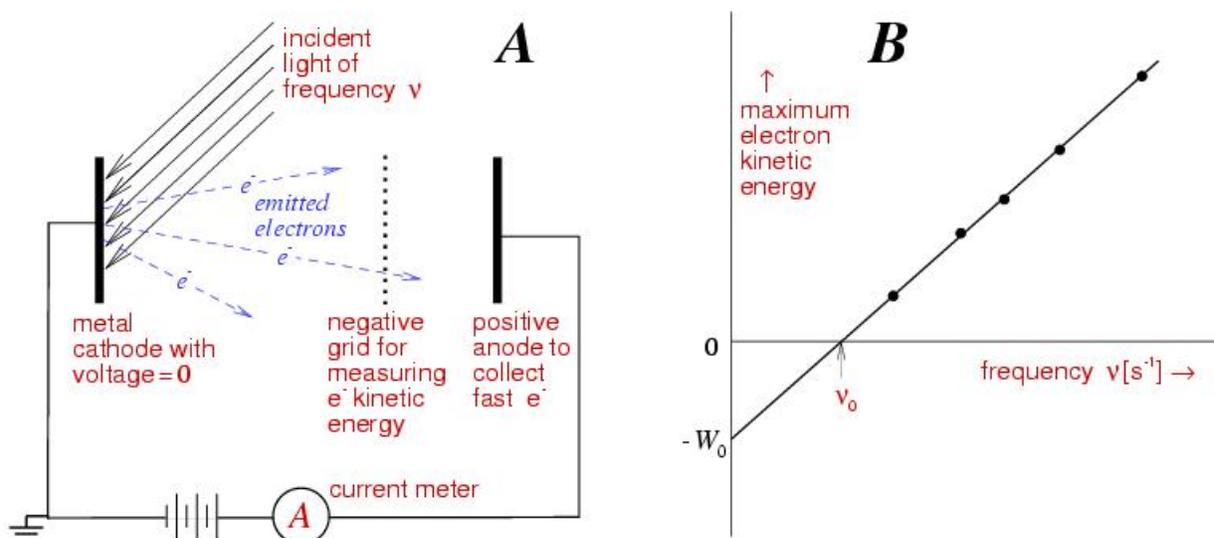
## Einstein & the Photoelectric Effect

Since 1888 it had been known that light shining on the surface of certain metals could cause electrons to be ejected. This *photoelectric effect* is the basis of many everyday electronic devices.

According to the wave theory of light, this must occur by “erosion”, like water waves eating away at a cliff: the higher the waves (i.e., the bigger their intensity or amplitude), the faster the erosion and the greater the energy of motion (kinetic energy) of the rocks washed away from the cliff.

However, this erosion-like theory is contradicted by the four experimental observations:

- For light frequencies below a certain threshold (which is different for different metals), no electrons are ejected *no matter how intense the light*.
- The number of emitted electrons does increase with the intensity of the light, but their maximum kinetic energy does not.
- The maximum kinetic energy of the ejected electrons depends *only* on the frequency  $\nu$  of the light; it increases linearly with  $\nu$ .
- There is no time lag between the arrival of the light beam and the ejection of the first electron.



**Einstein**, in 1905, argued that all this is explained if we assume simply that the energy associated with light of a given frequency  $\nu$  [ $\text{s}^{-2}$ ] come in bundles or “quanta” whose size scales linearly with the frequency:  $\delta E_\nu = h \times \nu$ , where  $h$  is a constant. [At that time, and for some years to come, people did not recognize the relationship between Einstein’s explanation and Planck’s result, and it was not clear initially that the scaling constant (here called  $h$ ) in the two explanations was the same!]

Einstein’s theory suggested that the maximum kinetic energy of the ejected electrons would be

$$\text{KE}_{\text{max}} = \frac{1}{2} m_e (v_{\text{max}})^2 = h\nu - |W_0| = h\nu - h\nu_0 = h(\nu - \nu_0)$$

Plotting measured  $\text{KE}_{\text{max}}$  values *vs.*  $\nu$ , experimentally find that the slope  $h$  has the same value as the scaling constant determined by fitting the Planck equation to the experimental black body intensity distribution function:  $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ .

### Conclusion.

Since it carries its energy in tiny bundles or quanta, light has particle-like properties.

**Clincher:** experiments by Compton in 1923 showed that when light is scattered from (i.e., “bounces off”) electrons, the electrons recoiled as if the light had a momentum of  $p = p_\lambda = h/\lambda$  !

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**Exercise 2.** What are the “photon” energies associated with (a) yellow light ( $\lambda = 550$  nm), (b) blue light ( $\lambda = 425$  nm), (c) red light ( $\lambda = 700$  nm)?

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**Exercise 3.** Metallic potassium K has a work function of 2.30 eV. Would a photoelectric occur using (a) yellow light, (b) blue light, or (c) red light of wavelength used in Ex. 2? If *YES*, what is  $v_{\max}$  [m/s] for the associated ejected electrons?

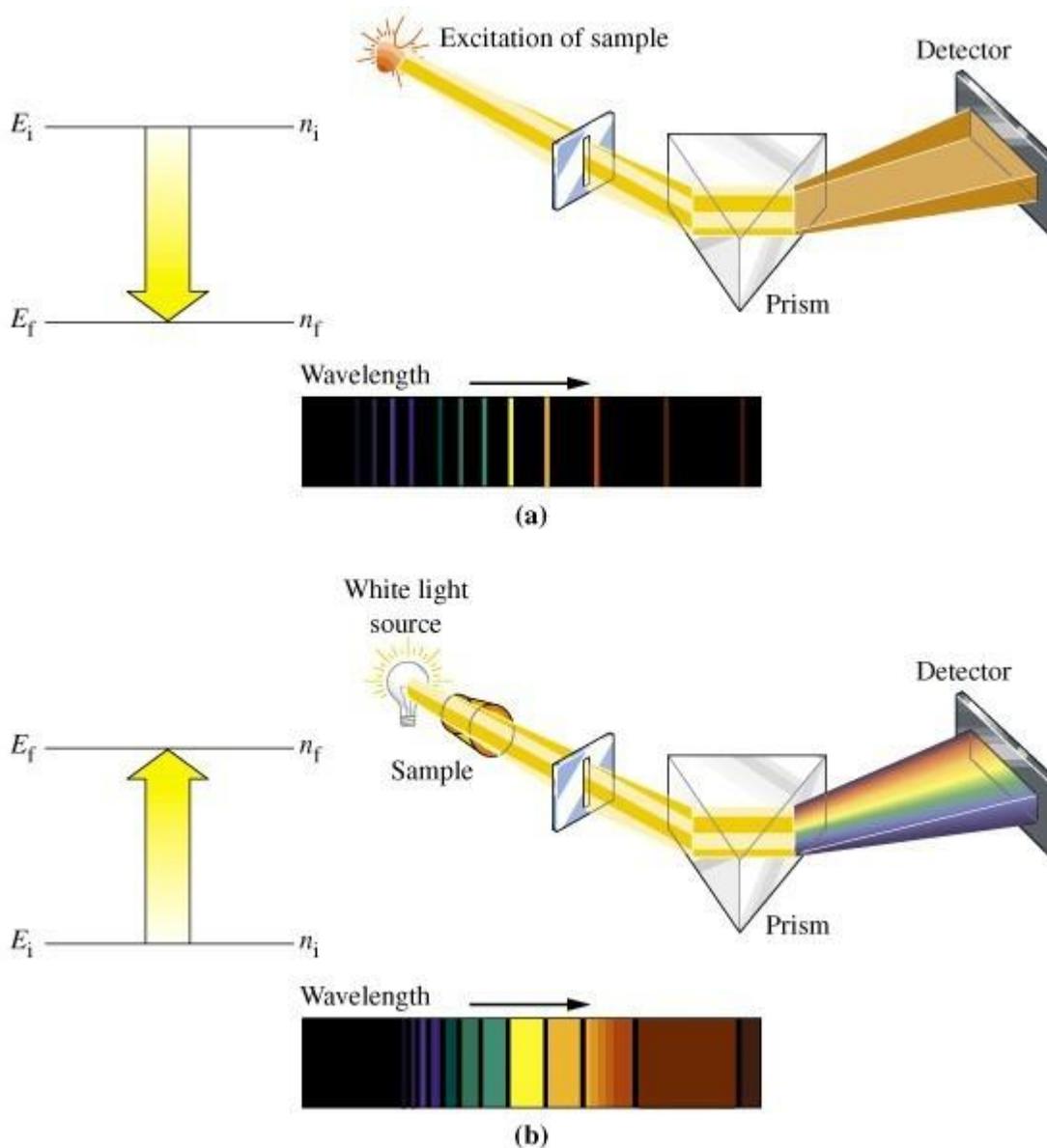
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**Exercise 4.** Experiments on metallic indium (In) tell us that the threshold frequency for observing the photoelectric effect corresponds to  $\nu_0 = 9.96 \times 10^{14} \text{ s}^{-1}$ . What is the maximum velocity (in m/s) of the electrons ejected when In is subjected to UV light of frequency  $\nu = 3.5 \times 10^{15} \text{ s}^{-1}$ ?

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## Spectroscopy, Quantization and the Bohr Atom

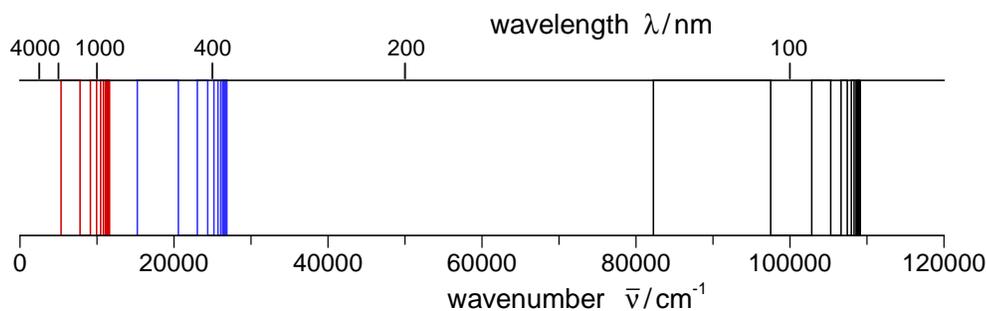
Our experience in the world shows us that different objects and materials have different colours (i.e., they emit/absorb light of different frequency ranges). By the late 1800's, experiments dispersing the light absorbed or emitted by molecular species (e.g., with a prism) had found that such 'spectra' did not consist of light with a continuous range of frequencies, but rather of particular patterns of discrete 'lines' (particular frequencies or wavelengths) which were characteristic of the particular absorbing/emitting material. By 1900 it was clear that all atoms or molecules only absorbed or emitted light at certain discrete frequencies (i.e., colours), *but nobody had any idea why this was so!*



By 1910, the acceptance of the Planck/Einstein idea that light energy was quantized ( $\delta E_\nu = h\nu$ ) led to the realization that the existence of such discrete spectra implied that the allowed energy levels of atoms and molecules must also be discrete, and had energy spacing patterns which were unique for each species. *However, nobody could explain why!*

**"Spectroscopy"** is the science associated with determining exactly what patterns of colours of light a given molecular substance absorbs or emits, and explaining the origin of those patterns.

Since it is the simplest of the elements, atomic hydrogen was the most carefully studied, since it might be expected to be the easiest to be understood. Its spectrum consists of groups of lines, each of which seemed to be converging to a limit.



The group of lines in the visible region of the spectrum was the easiest to observe, and hence the most thoroughly studied. In 1883 Swiss schoolteacher Johannes Balmer showed that the wavelengths of all the ‘lines’ in that group were *precisely* explained by the expression

$$\lambda = \mathbb{B} \frac{n^2}{n^2 - 4}$$

in which  $n$  is an integer  $> 2$  and  $\mathbb{B}$  a constant. Some years later Swedish physicist R. Rydberg constant showed that inverting and generalizing Balmer’s equation gave an expression which worked for *all* of the observed H atom spectral lines:

$$\bar{\nu} \equiv \frac{1}{\lambda} = \mathbb{A}_H \left( \frac{1}{(n_2)^2} - \frac{1}{(n_1)^2} \right)$$

in which  $n_1$  and  $n_2$  are both integers with  $n_1 > n_2 \geq 1$ , and the constant  $\mathbb{A}_H = 1.09737 \times 10^7 \text{ m}^{-1}$ . The “Balmer series” corresponds to the special case of  $n_2 = 2$ .

The perfect agreement with experiment provided by these elegantly simple mathematical formulae were an immense triumph of mathematical intuition, but as Bohr later said, they were considered at the time to be

*... as the lovely patterns on the wings of butterflies; their beauty may be admired, but they are not supposed to reveal any fundamental physical laws.*

**Exercise 5.** Comparing the Balmer and Rydberg expression, what is the value of Balmer’s constant  $\mathbb{B}$ ?

**Exercise 6.** The set of H-atom spectral lines at shortest wavelength, the Lyman series, are associated with  $n_2 = 1$  in the Rydberg formula. What are the value of  $n_1$ , the wavelength, and the photon energy (in J) associated with the very lowest and very highest energy lines in the Lyman series?

## Neils Bohr & the Hydrogen(ic) Atom

The first (apparently) successful ‘model’ to explain the pattern of lines in the H-atom spectrum was presented in 1916 by Neils Bohr. Drawing upon the nuclear model of the atom proposed by Rutherford in 1911 and the Planck/Einstein energy quantization of radiation, Bohr rationalized the atomic emission spectra of hydrogen in terms of a model which combined conventional classical mechanics with an *ad hoc* quantization postulate.

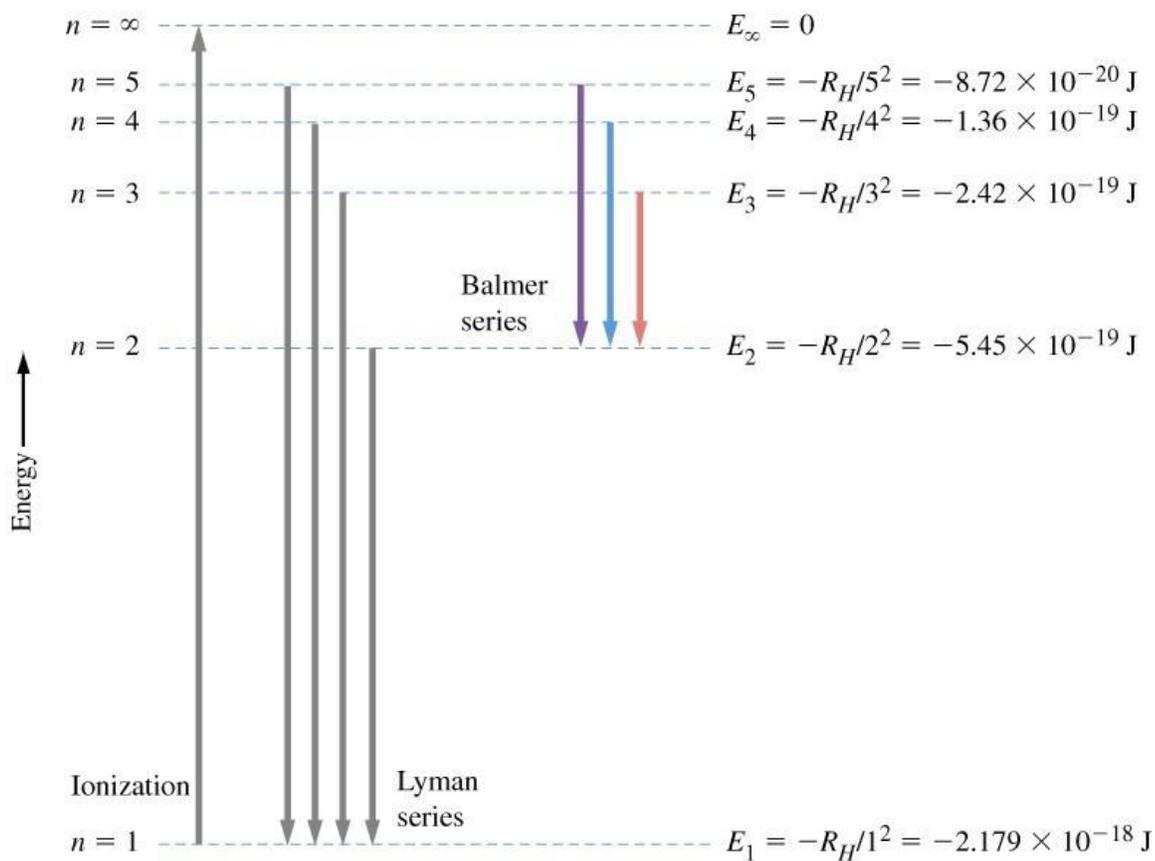
- He started from a mechanical picture in which the electron moved in a circular orbit, with the classical centrifugal force away from the nucleus exactly balanced by the Coulomb attraction between the two opposite charges.
- However, classical electromagnetic theory showed that an orbiting charge (such as the electron) would spontaneously radiate, lose energy, and spiral into the nucleus. Bohr took care of this immutable physical law by simply ignoring it, and assuming that the electron was in some sort of “stationary state” in which the classical electrodynamics rules governing radiation by a moving charge simply did not apply.
- He then added a critical “quantization” postulate, that the angular momentum of electrons in his “stationary states” were associated with integer multiples of the quantity  $h\dot{\theta}/2\pi$ , where  $\dot{\theta}$  is the classical angular speed of the orbiting electron (with units radians per second).
- Finally, he then introduced his famous *correspondence principle*, which asserted that *for orbits with very large radii, the quantum results must merge and agree with the results of classical electrodynamics*. This constraint yielded a value for the proportionality constant relating the energies of the stationary states to the quantity  $h\dot{\theta}/2\pi$ , and then yielded the level energy expression (where  $\hbar \equiv h/2\pi$ ):

$$E_n = - \frac{(e^2/4\pi\epsilon_0)^2 \mu}{2\hbar^2} \frac{1}{n^2} = - \frac{(e^2/4\pi\epsilon_0)}{2a_0} \frac{1}{n^2} = - 2.179 \times 10^{-18} \frac{1}{n^2} = - \frac{\mathbb{R}_H}{n^2}$$

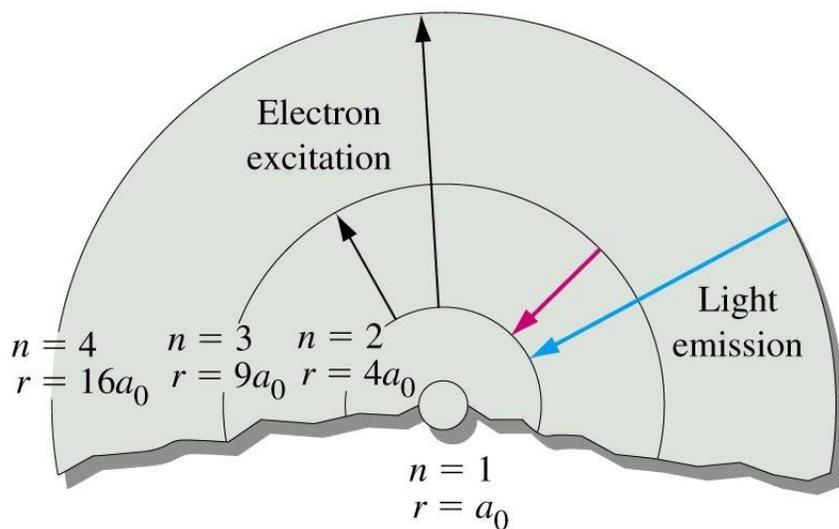
in which  $a_0 = \hbar^2/\mu(e^2/4\pi\epsilon_0)$  is the radius of the innermost orbit in a H atom, and

$$\mu \equiv \left[ \frac{1}{m_e} + \frac{1}{m_{\text{nucleus}}} \right]^{-1} = \left[ \frac{1}{m_e} + \frac{1}{m_{\text{proton}}} \right]^{-1} \approx m_e$$

**Exercise 7.** How is the constant  $\mathbb{R}_H$  in Bohr’s expression related to the constant  $\mathbb{A}_H$  which Rydberg determined from a fit to experimental data?



In Bohr's model, the radius of the orbit associated with quantum number  $n$  is  $r_n = n^2 a_0$



Generalizing Bohr's result to the cases of  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{B}^{3+}$ , ... etc., one electron atoms with nuclear charges of  $+Ze$  for  $Z = 2, 3, 4, \dots$  etc., yields

$$E_n^{(Z)} = -2.17987 \times 10^{-18} \frac{Z^2}{n^2}$$

**Exercise 8.** What are the wavelengths of the three lowest energy transitions in the Balmer-like ( $n_2 = 2$ ) spectrum of  $\text{Li}^{2+}$ ? How are the radii of the orbits in  $\text{Li}^{2+}$  related to those in an H atom?

### ***Problems !***

The Bohr model was an amazing result for its time: it accurately explained the observed spectroscopic properties of atomic hydrogen and of all one-electron atomic ions in terms of a simple physical model based on well understood and accepted electrical and mechanical laws ... *plus with two key ad hoc additional assumptions!* This seemed to justify the observation that atoms and molecules appeared to have only discrete allowed internal energies.

However ...

- The Bohr model did not work for molecules or for atoms with more than one electron, and no-one could devise an extension of the model which would!
- No fundamental justification could be devised for the two *ad hoc postulates*:
  - that the orbital angular momentum could only change by increments of  $\hbar$
  - that one could simply ignore the laws of electromagnetism which predict that a charged particle moving in a circular orbit would spontaneously radiate

## More trouble ... two bits of Quantum Weirdness:

### I. *Moving Particles as Waves: de Broglie's Hypothesis*

By the 1920's it was fully accepted that the energy carried by light was quantized in increments  $\delta E_\nu = h\nu$ , and Compton's experiments (see p.5 of these notes) showed that "photons" of light would "recoil" on collisions as if they carried a momentum of  $p_\lambda = h/\lambda$ . Thus, the fact that light had both particle-like and wave-like properties was seeping into general acceptance. Also, in spite of its shortcomings, Bohr's theory seemed to confirm that energy levels in atoms and molecules also were quantized.

This led Prince Louis-Victor de Broglie to base his 1924 PhD thesis on the question

*Since light can be described as a wave with characteristics of a particle, shouldn't matter (made up of particles) also possess wave characteristics?*

Although there was (at the time) no evidence to support it, this arbitrary and seemingly crazy hypothesis received an almost tolerant reception, at least in part because it was quickly picked up by Einstein who announced that de Broglie "had lifted the corner of a great veil". Using intuitive reasoning based on the (by then) accepted fundamental wave-particle dual nature of light, de Broglie argued that a particle of mass  $m$  moving with velocity  $v$  would show wave-like properties, and be characterized by what is known now as its "de Broglie wavelength"

$$\lambda = \lambda_p = \frac{h}{mv} = \frac{h}{p}$$

in which  $p = mv$  is the particle momentum. This prediction implies that beams of particles should display the full range of properties predicted by the classical theory of wave motion, including reflection, diffraction, and constructive and destructive interference.

This hypothesis was confirmed experimentally in 1927, when George Thomson in the UK and Clinton Davisson and Lester Germer in the USA reported experiments which showed that beams of fast electrons reflecting off metal crystals did indeed show exactly the same diffraction properties as X-rays (very high frequency light). Today we know that all atomic particles, electrons, neutrons and protons, as well as whole atoms and molecules, possess wave-like as well as ordinary particle properties (such as mass). Indeed, in principle moving trucks in a column on a highway would have wave-like properties! However, the theory of wave-particle duality also predicts that in the limit of extremely large quantum numbers or extremely small de Broglie wavelength, the wave-like properties of matter become indistinguishable from our normal classical mechanical experience for material objects. Thus, one should not expect their wave-like properties to mitigate the effects of standing in the middle of the road in front of an fleet of oncoming transport trucks.

**Exercise 9.** What is the de Broglie wavelength of

- an  $\text{H}_2(\text{g})$  molecule at  $25^\circ\text{C}$ ?
- R.J. Le Roy (mass  $\approx 70$  kg) on HiWay 401 at 120 km/hr?

## II. *How accurately can we know what we know?* Heisenberg's Uncertainty Principle

In 1925 Werner Heisenberg presented a matrix algebra description of molecular systems which explain energy quantization (... if you can accept that his matrix “operators” and “eigenvalues” could actually represent things in the real physical world). Manipulation of his matrix operators gave rise to a famous result, now widely quoted and accepted, which many still find hard to accept.

We rely on light (composed of photons) to observe particles. Very small particles such as electrons may interact with the photons and change speed or position as a consequence of our observation. The implications of this were first perceived by Heisenberg, who stated:

*It is impossible to make simultaneous and exact measurements of both the position and momentum of a particle.*

Hence position and momentum are “*uncertain*”. Since de Broglie’s hypothesis allows us to treat microscopic particles as waves, we have to leave behind a deterministic (i.e., definite) view of small-particle behaviour, and resort to a statistical view based on probabilities. Heisenberg’s uncertainty principle is part of this new view. Mathematically, the uncertainty principle can be expressed as

$$\Delta p \Delta x \geq h/4\pi$$

where  $\Delta p$  is the uncertainty in momentum and  $\Delta x$  is the uncertainty in position.

An analogous equation which has more direct implications for spectroscopic observables is

$$\Delta E \Delta t \geq h/4\pi$$

where the uncertainties are in energy ( $E$ ) and time ( $t$ ). In the context of spectroscopy, this time uncertainty is the natural lifetime of a state whose population decays exponentially due to some natural process, and the associated energy uncertainty  $\Delta E$  is the half width of observed spectral lines involving that level.

This presents a quandary: If these uncertainties are an inevitable part of measurement of microscopic systems, how do we define *anything* to do with precise values of position or momentum of particles in quantum atomic and molecular systems? The answer is that instead of a definite view in terms of particles and absolute certainties (since a particle of defined size must be *somewhere*), we resort to the wave description, statistical measures and probabilities.

[While introduced here as a matter of ‘culture’, we do not make quantitative use of these bits of “quantum weirdness” in the following ...]

## Schrödinger's Wave Mechanics

Bohr's theory gave us a quantum "mechanics", since it basically superimposed quantization (of the angular momentum) onto a standard "mechanical" description of the system. While it *did* provide the first ever quantitative explanation of atomic spectra, the fact that even after strenuous effort it could not be extended beyond the case of a one-electron atom indicated that it was a dead end. The "matrix mechanics" which Heisenberg introduced in 1925 seemed in principle more general, but its abstractness and mathematical complexity made it quite intimidating. An alternate approach introduced in 1926 by Erwin Schrödinger proved to be much more intuitively accessible, and provides the basis of molecular quantum mechanics we think of it today.

By 1926, in spite of the absence of any proof, many leading physicists had accepted de Broglie's hypothesis that particles would have wave-like behaviour. Using analogies to optics and shrewd generalizations of classical wave theory (as for a vibrating string, for waves in water, or for sound) Schrödinger proposed (i.e., guessed!) a wave-like differential equation to describe the motion of atomic particles.

If we mathematically separate off the time-dependent part of Schrödinger's equation, for a system consisting of a single particle of mass  $m$  moving in one dimension along the  $x$  axis, subject to a potential energy field  $V(x)$ , the Schrödinger's resulting *differential equation* is

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x) \psi(x) = E \psi(x)$$

in which the "wave function"  $\psi(x)$  is the solution of the differential equation, the special function for which

$$\left(-\frac{\hbar^2}{2m}\right) \times \{\text{second derivative of } \psi(x)\} + V(x) \times \psi(x) = \{\text{system energy}\} \times \psi(x)$$

The allowed discrete energies of the system are the special values of  $E = E_n$  for which this equation can be satisfied, and the associated special functions  $\psi_n(x)$  define the probability of finding the particle at position  $x$ , which probability is proportional to  $|\psi(x)|^2$ .

[*Aside: ... but what is a differential equation ?* ]

### **But how does this give quantization ?**

Consider a case in which the particle is trapped inside a 1-D "box" extending from  $x = 0$  to  $x = L$ , defined by the fact that inside the box (for  $0 \leq x \leq L$ )  $V(x) = 0$ , and outside the box (for  $x < 0$  or  $x > L$ )  $V(x) = \infty$ .

For the particle inside the box, rearranging the Schrödinger equation gives us

$$\frac{d^2 \psi(x)}{dx^2} = -\left(\frac{2mE}{\hbar^2}\right) \psi(x) = -k^2 \psi(x)$$

where we define  $k = \sqrt{2mE/\hbar^2}$ .

This is one differential equation for which you *all* know the solution! What is the function whose second derivative is minus a constant times the function itself?

## What is a Differential Equation ?

This differential equation solution has the general form  $\psi(x) = A \sin(kx) + B \cos(kx)$   
 However, since the particle is trapped inside the box

- $\psi(x) = 0$  outside the box
- and if  $\psi(x)$  is to be a “continuous” mathematical function, necessarily:  
 $\psi(x=0) = 0$  and  
 $\psi(x=L) = 0$  (see figure  $\rightarrow$ )

Playing with the math shows this these conditions are only satisfied if

$$kL = \sqrt{2mE/\hbar^2} L = n\pi$$

or (rearranging)

$$E = E_n = \left( \frac{\hbar^2 \pi^2}{2m L^2} \right) n^2$$

In other words the only solutions which both satisfy our differential equation and satisfy the condition that the particle remain “trapped in the box” occur for discrete separated level energies  $E_n$ , when the integer  $n$  is the number of “loops” of the oscillating wave function inside the box.

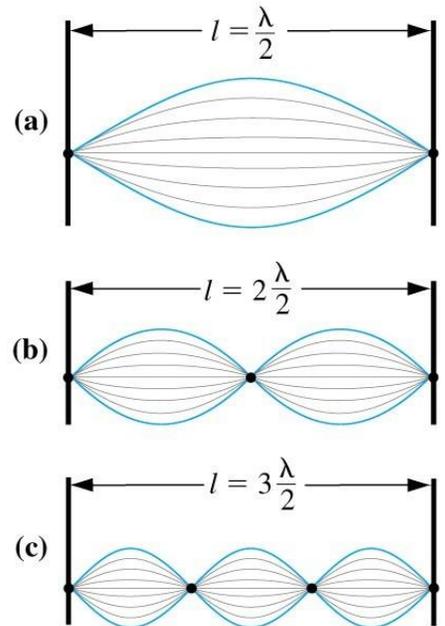
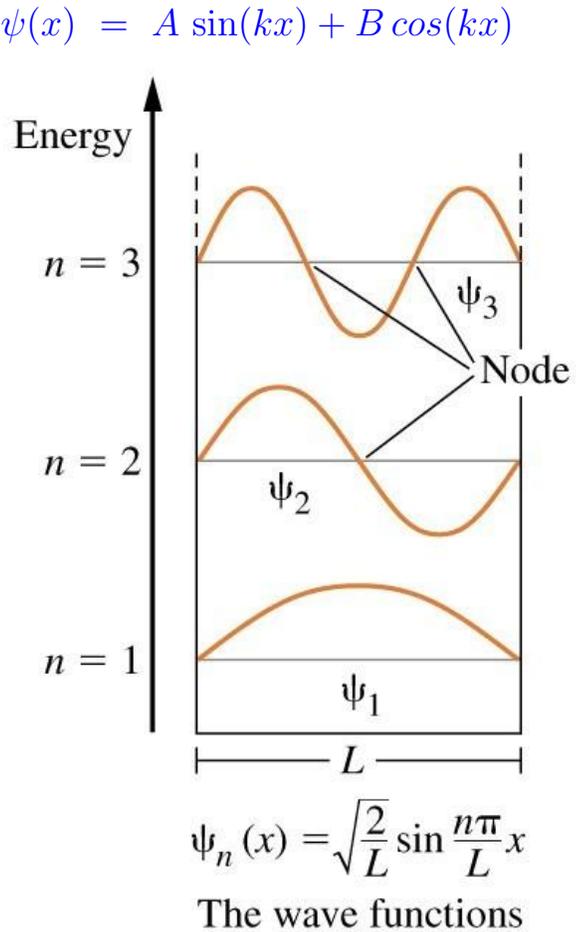
The only difference between these results and the case of the radial motion for an electron in the H atom is that instead of a potential function with two rigid vertical walls, in the H atom the confining potential is the Coulomb potential for the attraction of a positive and negative charge. While the math is somewhat messier (!!), the wavefunction solutions are qualitatively the same.

Compare the above result with the solution of the classical wave equation for vibrations of a string.

*What is the physical significance of the wave function  $\psi(x)$  ?*

Max Born said ...

Schrödinger said ...



The discussion about what the wavefunction  $\psi$  really meant got rather heated, and some of the great figures of the early quantum physics too things rather personally. For example ...

On October 12 1925, Werner Heisenberg (uncertainty principle, Nobel Prize in Physics, 1932) wrote to Wolfgang Pauli (exclusion principle, Nobel Prize in Physics, 1945):

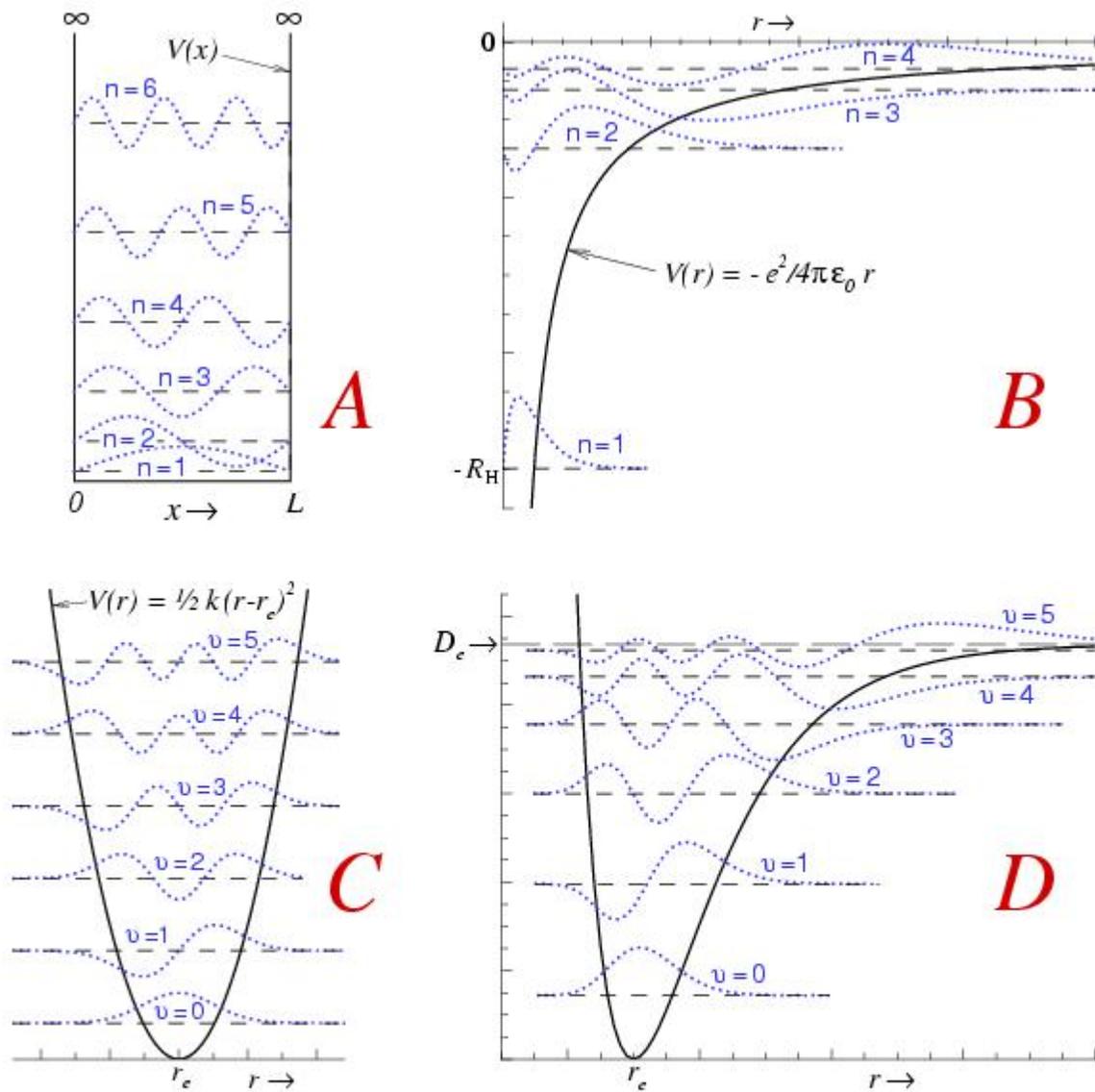
*“With respect to both of your last letters I must preach you a sermon, and beg your pardon for proceeding in Bavarian:*

*It is really a pigsty that you cannot stop indulging in a slanging match. Your eternal reviling of Copenhagen and Göttingen (i.e., of the ‘probabilistic’ interpretation of QM) is a shrieking scandal. You will have to allow that, in any case, we are not seeking to ruin physics out of malicious intent. When you reproach us that we are such big donkeys that we have never produced anything new in physics, it may well be true. But then, you are also an equally big jackass because you have not accomplished it either ..... (The dots denote a curse of about two-minutes duration!).*

*Do not think badly of me and many greetings.”*

On June 8 1926, Werner Heisenberg again wrote to Wolfgang Pauli :

*“The more I think about the physical part of the Schrödinger theory, the more detestable I find it. What Schrödinger writes about visualization makes scarcely any sense; in other words, I think it is shit. The greatest result of his theory is the calculation of matrix elements.”*



Level energies and wavefunctions for 1-D “particle-in-a-box” systems associated with differently shaped potential energy functions. In all cases:

- the allowed solutions correspond to particular discrete energies
- the energy increases with the number of wavefunction loops
- at higher energies, the wavefunction solutions oscillate more rapidly
- the number of wavefunction loops gives us a quantum number labeling for the levels.

The particular pattern of level energy spacings depends on the shape of the potential energy function binding the particle. For the H-atom (Case B), doing the (somewhat more complicated) math gives us (for a single electron and a nucleus with charge  $+Ze$ )

$$E_n = - \frac{(e^2/4\pi\epsilon_0)^2 \mu}{2 \hbar^2} \frac{Z^2}{n^2} = - \frac{(e^2/4\pi\epsilon_0)}{2 a_0} \frac{Z^2}{n^2} = - 2.17987 \times 10^{-18} \frac{Z^2}{n^2} \text{ [J]}$$

This is *exactly* the same expression obtained by Bohr! However ...

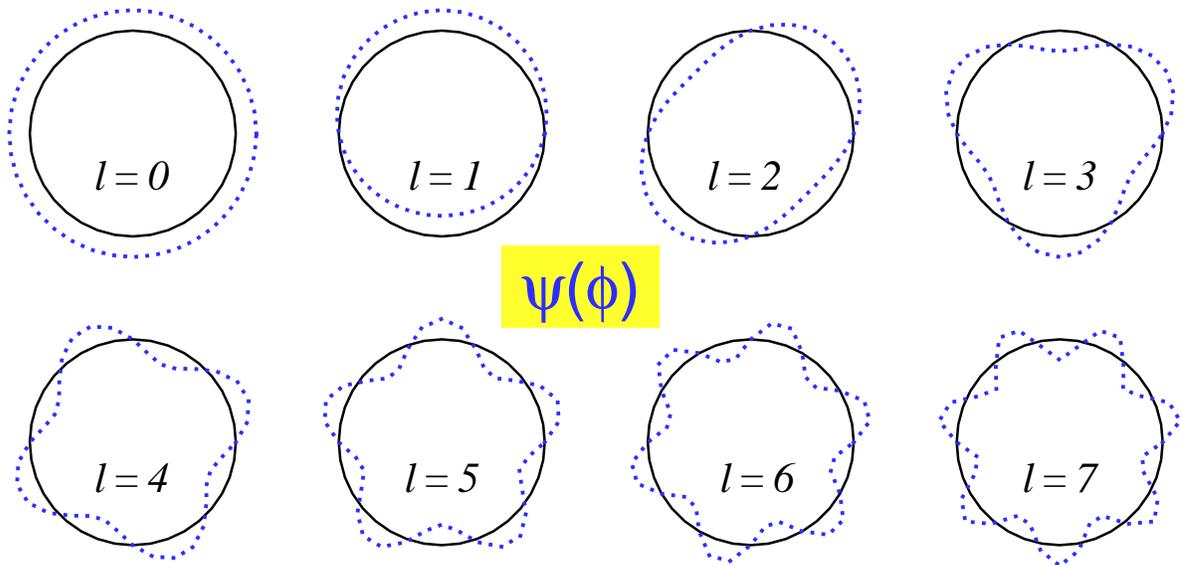
- For Schrödinger, quantization is not an *ad hoc* postulate; rather, it simple falls out on applying “boundary conditions” to the differential equation!
- Schrödinger’s description *does not assume* that the electron is a classical particle in an orbit, so *there is no prediction* that the electron should spontaneously emit radiation, lost energy, and spiral into the nucleus.
- While the Bohr theory *only* works for a one-electron hydrogen(ic) atom, Schrödinger’s “wave mechanics” works for *all* atomic and molecular systems [though the mathematical complexity and computational effort escalate with the numbers of electrons & nuclei!].

While the above discussion has been framed in terms of a description of the 1-D radial behaviour of an electron or linear stretching of a molecular bond. However, it applies equally well to orbital or rotational motion,

For an electron in a 1-D circular domain of radius  $r$ , valid solutions of the Schrödinger equation are only possible if

$$E = E_\ell = \left( \frac{\hbar^2}{2mr^2} \right) \ell^2 \quad \text{and} \quad \psi_\ell(\phi) = \sqrt{\frac{1}{2\pi}} \sin \phi, \quad \text{for} \quad \ell = 0, 1, 2, 3, \dots$$

In the diagram below: the wavefunction is the dotted curve which is drawn to lie outside the ring when it has (algebraic) positive values and inside the ring for negative values.



Once again:

- the allowed solutions correspond to particular discrete energies
- the energy increases with the number of wavefunction loops
- at higher energies, the wavefunction solutions oscillate more rapidly
- the number of wavefunction loops gives us a quantum number labeling for the levels.

## H Atom Wavefunctions and Orbital Shape

The electron in a hydrogen atom can move in 3 dimensions, and the full Schrödinger equation for it is

$$-\frac{\hbar^2}{2m_e} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \psi = E \psi$$

or

$$\left\{ -\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \right\} \psi = E \psi$$

To save clutter we normally write this symbolically as

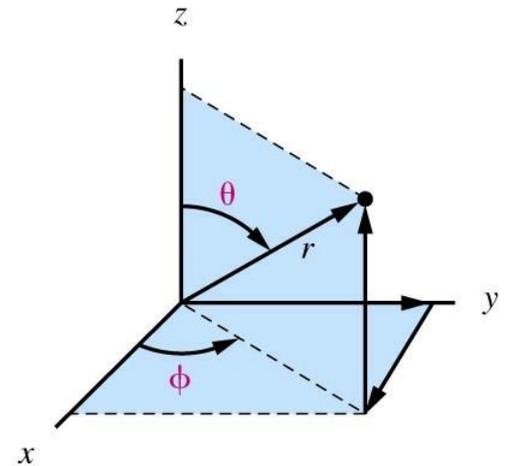
$$H \psi = E \psi$$

Because of the spherical symmetry of an H atom (or *any* atom), this Schrödinger equation is much easier to solve if we replace the “Cartesian”  $(x, y, z)$  coordinates for the position of the electron by the “spherical polar coordinates”  $(r, \theta, \phi)$

Moreover, when we do the math, we find that the wavefunctions may be written as the product of a function of  $r$  times a function of the angles  $\theta$  &  $\phi$ :

$$\psi(r, \theta, \phi) = Y_{l,m}(\theta, \phi) \times R_{n,l}(r)$$

The integer  $n$  here is the same integer  $n$  appearing in the Schrödinger and Bohr H-atom level energy formula,



Spherical polar coordinates

$$x^2 + y^2 + z^2 = r^2$$

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

except that now we can associate its values with the properties of the wavefunction allowed solutions of the Schrödinger equation:

similarly, the value of  $l$  tells us about the angular oscillations of  $\psi(r, \theta, \phi)$ :

while the label  $m$  tells us something about the orientation in space of the regions where the wavefunction goes to zero and changes algebraic sign.

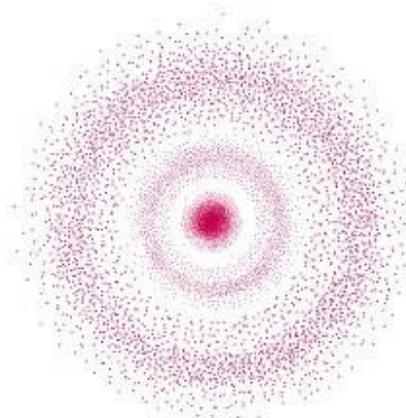
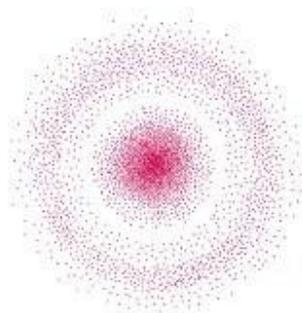
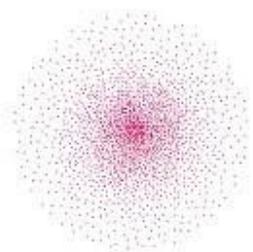
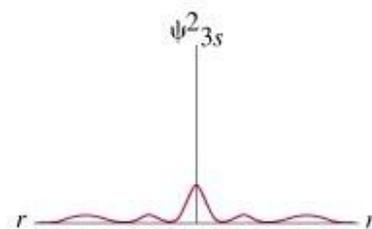
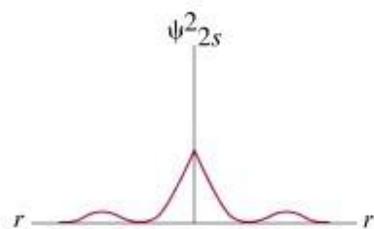
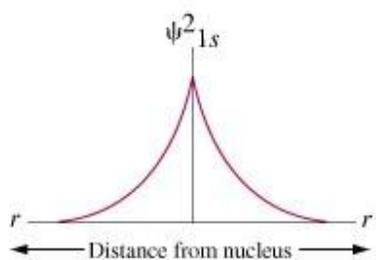
All this information is contained in the mathematical expressions for these wavefunctions.

**Consider cases with  $l = 0$**  (the math tells us that this means  $m = 0$  too).

For this case  $Y_{l,m}(\theta, \phi) = Y_{l,m}(\theta, \phi) = \sqrt{1/2\pi} = \{\text{a constant!}\}$

and defining  $\sigma = \left(\frac{2Z}{n a_0}\right) r$ , for  $n = 1, 2$  and  $3$  we have

$$R_{1,0}(r) = A_{1,0} e^{-\sigma/2} \quad R_{2,0}(r) = A_{2,0} (2 - \sigma) e^{-\sigma/2} \quad R_{3,0}(r) = A_{3,0} (6 - 6\sigma + \sigma^2) e^{-\sigma/2}$$



(a) 1s



(b) 2s



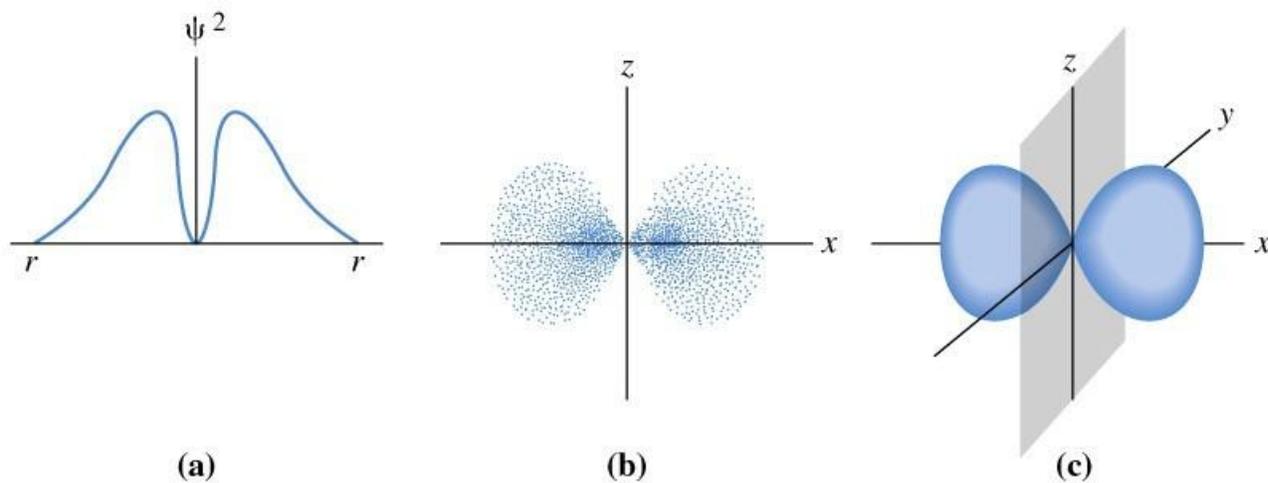
(c) 3s

### Consider cases with $l = 1$ .

The math tells us that this means  $m$  can be -1, 0 or +1, but the solutions we normally draw are the  $m = 0$  solution  $\psi_{p_z} = \psi_{m=0}$  and  $\pm$  linear combinations of the  $m = +1$  and  $-1$  solutions.

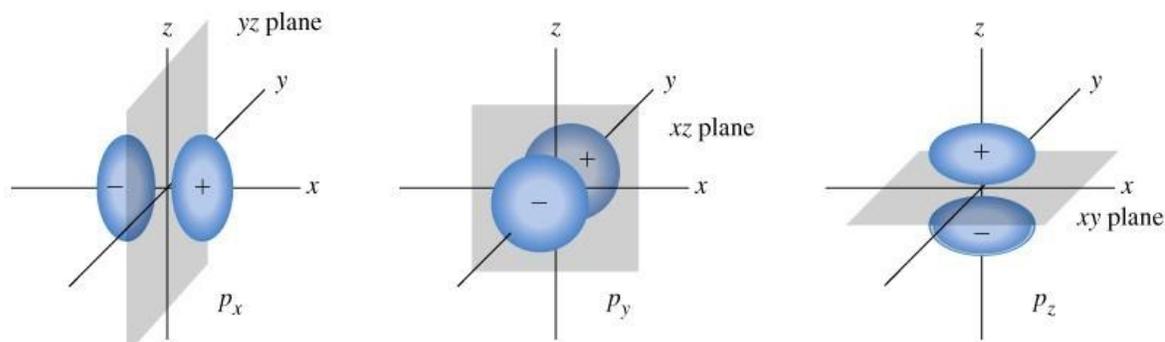
The “ $p_x$  orbital” is the solution with the angular form:  $Y_{p_x}(\theta, \phi) = \sqrt{3/4\pi} \sin \theta \cos \phi$

For  $n = 2$  the radial wavefunction is  $R_{2,1} = A_{2,1} \sigma e^{-\sigma/2}$  and we have



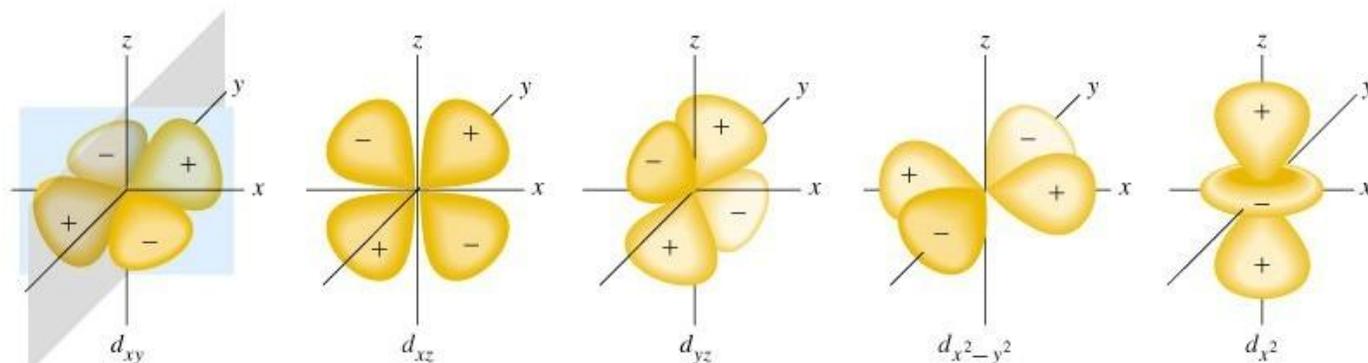
For  $n = 3$  the radial wavefunction is  $R_{3,1} = A_{3,1} \sigma (4 - \sigma) e^{-\sigma/2}$  and we have

For both of these cases we have *exactly one* angular “nodal surface”, and in 3-D space, if we have only one such angular surface, there can exist three and only three possible independent ways of arranging it, and we normally choose to use the ones called  $\phi_{p_x}$ ,  $\phi_{p_y}$  and  $\phi_{p_z}$ , which for  $n = 2$  have the familiar “balloon” shapes:



### Consider cases with $l = 2$ .

The mathematical expressions are more complicated (see Table 9.1 in the text), but the net result is that all possible  $l = 2$  solutions have *exactly two* angular nodal surfaces — and the math shows that there can exist exactly *five* linearly independent ways of arranging those two surfaces in space. For a given value of  $n$  the Bohr/Schrödinger level energy formula tells us that these five solutions all have exactly the same energy, and the ones we normally choose to draw are the ones shown below:



These pictures illustrate the properties of the  $n = 3$  solutions, for which the radial wavefunction has the form:  $R_{3,2}(r) = A_{3,2} \sigma^2 e^{-\sigma/2}$

**Exercise 10:** Sketch the  $d_{xz}$  solution for the cases  $n = 4$  and  $n = 5$  !

### Considering cases with $l = 3$ and larger ...

By analogy with the  $l = 0 - 2$  case:

- The angular wavefunction will have  $l$  nodal surfaces – i.e.,  $l$  regions where the wavefunction goes to zero and changes mathematical sign.
- since the “principle quantum number”

$$n = 1 + \{\text{total no. of angular \& radial nodes}\}$$

a given value of  $l$  is not allowed unless  $n > l$  !

- For *any* value of  $l$ , there exist exactly  $2l+1$  distinct possible spatial arrangements of those  $l$  angular nodes. In other words, the Schrödinger equation has  $2l+1$  distinct “degenerate” (i.e., having exactly the same energy) spatial solutions for each value of  $l$  !

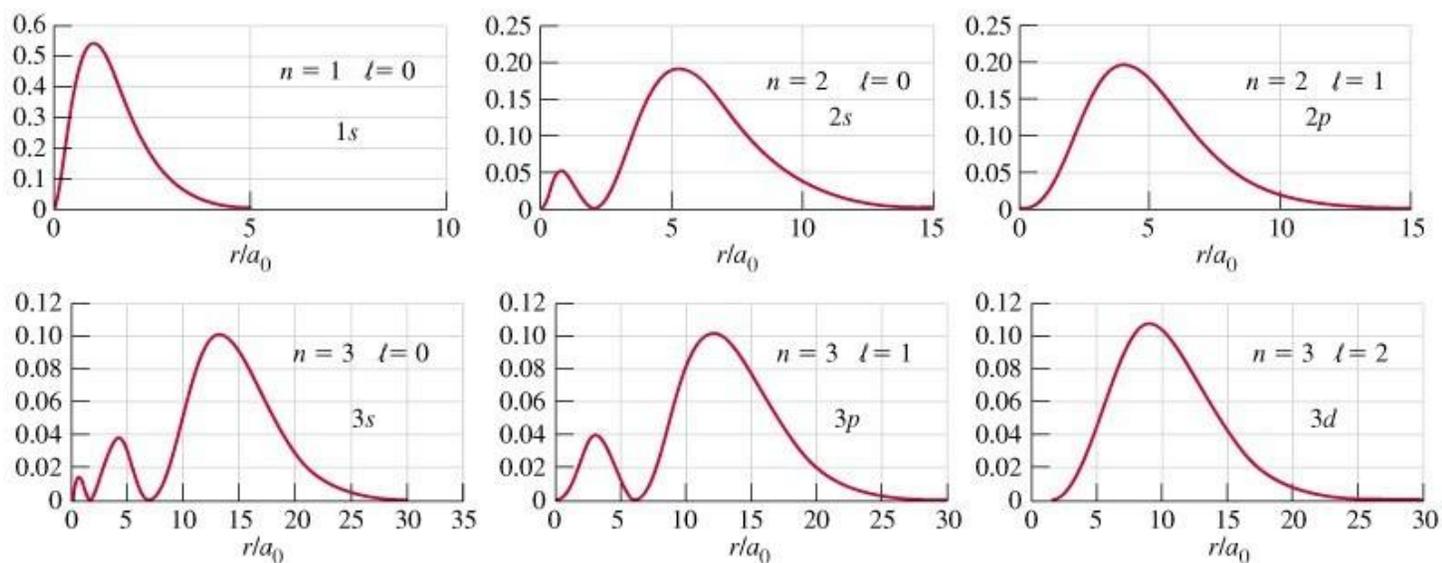
## Radial Electron Densities

Within the conventional probability interpretation of quantum mechanics, the square of the wavefunction  $|\psi_{n,l,m_l,m_s}(x,y,z)|^2$  or  $|\psi_{n,l,m_l,m_s}(r,\theta,\phi)|^2$  tells us the probability of finding an electron labeled with a particular set of quantum numbers at a particular point in space,  $(x,y,z)$  or  $(r,\theta,\phi)$ .

However ... atoms are (roughly) spherical, and we often want to talk about the *total* probability of finding the electron at a given distance from the nucleus. We do that by summing over the probabilities associated with all the bits of space at that particular radius

$$\rho(r) = \int_0^{2\pi} d\phi \left\{ \int_0^\pi d\theta \left[ \sin \theta r^2 |\psi_{n,l,m_l,m_s}(r,\theta,\phi)|^2 \right] \right\}$$

Since *s* orbitals are spherical, their wavefunctions  $\psi$  do not depend on the angles, and we can simply write  $\rho(r) = 4\pi r^2 |\psi(r)|^2$ . For  $l > 0$  orbitals ... the calculus is a bit messier, but we still get simple well defined “radial density functions”:



Note that *all* of these radial density plots go to zero as  $r \rightarrow 0$  (even for the *s* orbitals whose wavefunctions are *not* zero there!), since the total amount of space associated with a given radius  $\propto r^2$  which  $\rightarrow 0$  as  $r \rightarrow 0$ !

### For a given value of $n$ :

- The Bohr/Schrödinger level energy formula tells us that *all possible* solutions for a given value of  $n$  correspond for to *exactly* the same energy.
- Level energy increases  
 $\Rightarrow$  with the *total* number (radial *plus* angular) of wavefunction “nodal surfaces” ( $n - 1$ ).
- For a given value of  $n$ , distinct spatial solutions exist for each of  $l = 0, 1, 2, 3, \dots, l_{\max} = n - 1$ . The common names associated with those different types of orbital shapes are

$l =$	0	1	2	3	4	5	...
name =	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i>	...

For each of these values of  $l$ , there exist  $2l + 1$  distinct spatial solutions.

We sometimes explicitly identify these  $2l + 1$  distinct solutions with  $2l + 1$  possible distinct arrangements of the  $l$  angular nodal surfaces and give them the spatial labels (e.g.,  $p_x, p_y, d_{xz}, d_{x^2-y^2}, \dots$  etc.). Alternately, we sometimes label them with the  $2l + 1$  integer quantum numbers:  $m_l = -l, -l + 1, -l + 2, \dots, l - 1, l$ .

{ *What's the difference between these two types of labels?* }

**Exercise 11:** How many radial nodes are there

- in the  $8g$  orbital ( $n=8, l=4$ ) wavefunction?
- in the  $4h$  orbital wavefunction?

## Electron Spin

As wonderful as the Schrödinger equation is, it doesn't account for everything!

In addition to the spatial properties associated with their orbital wavefunctions, as itemized by the quantum number labels  $n$ ,  $l$  and  $m = m_l$ , electrons (and protons, and neutrons) behave as if they have an inherent magnetic moment, which in a magnetic field can be oriented in two possible ways. We label the quantum states associated with those two possible orientations

$$m_s = +\frac{1}{2} \quad \text{or "spin up", and}$$

$$m_s = -\frac{1}{2} \quad \text{or "spin down".}$$

This inherent property of "spin" applies to all electrons, everywhere, whether they are inside an atom, free in space, or flowing through a metal as electric current.

### *Summarizing ...*

This means that an electron in an atom requires four quantum number labels to identify it:

- $n$

- 
- $l$

- 
- $m_l$

- 
- $m_s$

*Note:* "spin" is very different than the other quantum numbers, as there is no explicit spatial description for the spin component of a wavefunction. Also, no-one has yet devised an extended Schrödinger equation which incorporates spin in a natural way, together with all the other quantum numbers.



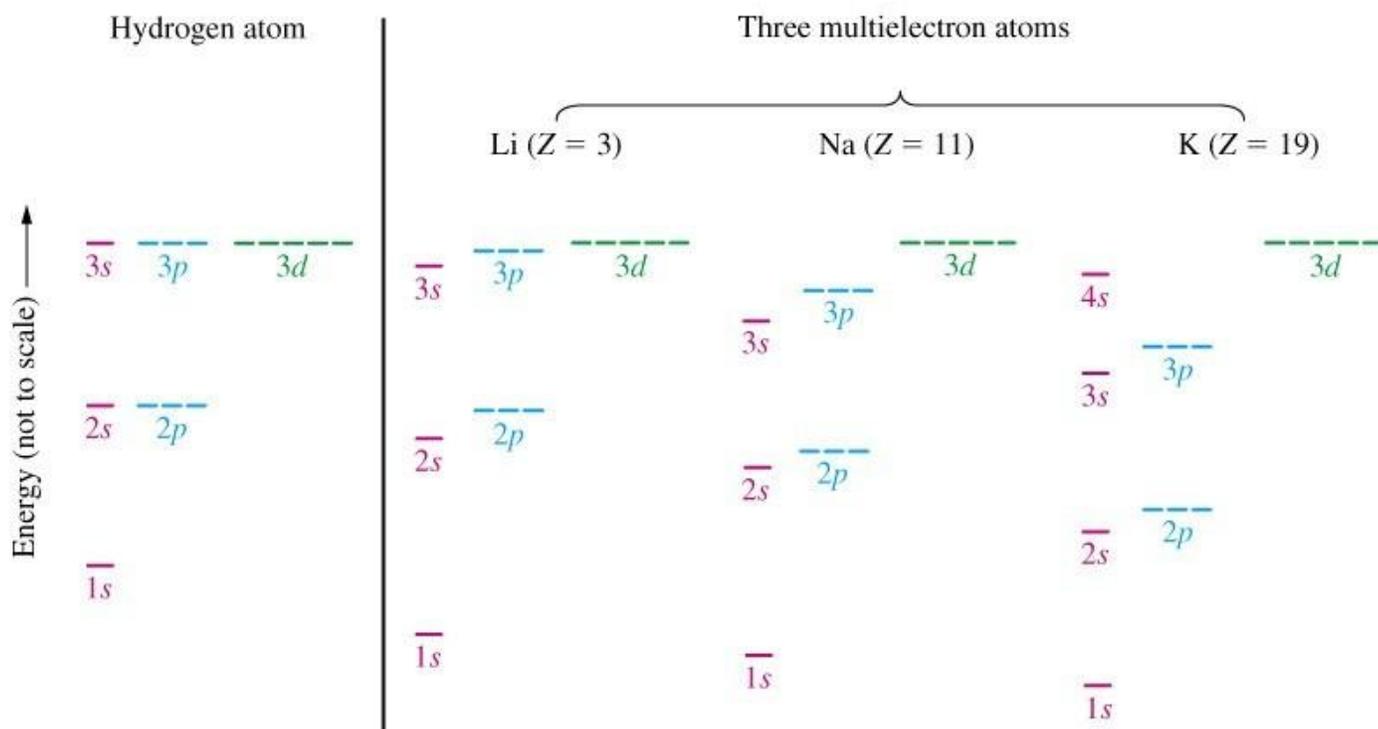
## Many-Electron Atoms

A hydrogenic atom with only one electron, but nuclear charge  $+Ze$  has level energies given exactly by the generalized Bohr/Schrödinger level energy formula which includes the factor  $Z^2$ :

and all states with the same value of  $n$  are *exactly* degenerate (i.e., have exactly the same energy).

*However*, if an atom has *more* than one electron (a “many-electron atom”)

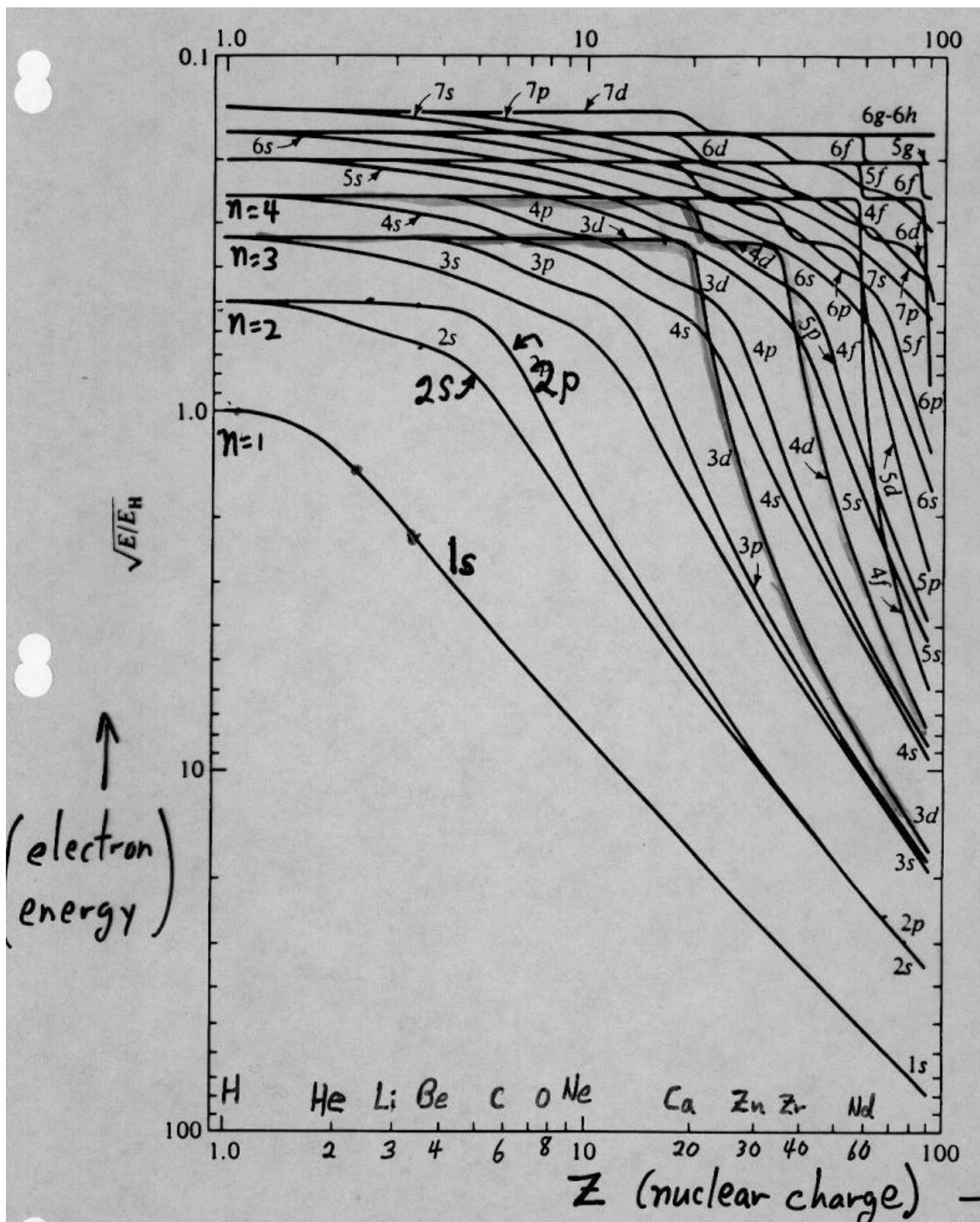
- all the electrons *repel* one another, with the repulsive Coulomb interaction
- each electron partially “shields” the nuclear charge from the others, so that they do not “see” the full  $+Ze$  nuclear charge, making their binding weaker than would be predicted by the generalized Bohr/Schrödinger formula.
- These effects give rise to a splitting of the energies of the  $ns$ ,  $np$ ,  $nd$ , ... etc., sub-orbitals associated with a given value of  $n$ . which splitting increases with  $Z$ .



Within a given shell ( $n$ ) the sub-shell energies increase from  $s \rightarrow p \rightarrow d \rightarrow f \rightarrow \dots$ , etc.

This is easily understood from orbital radial wavefunction/electron density plots, which show that for a given  $n$ , the electron density close to the nucleus decreases as  $l$  increases, so low- $l$  orbitals are *least* shielded, and their energies will be lower!

**Note** that the text's Figure 9.33 (above) showing orbital energy splitting is not really to scale, and a more realistic view is shown below.



Note that while  $n$  becomes an increasingly ambiguous label for characterizing orbital energy in multi-electron atoms, the angular quantum number labels  $l$  and  $m_l$  are still accurate ways of characterizing orbital shape and orientation!

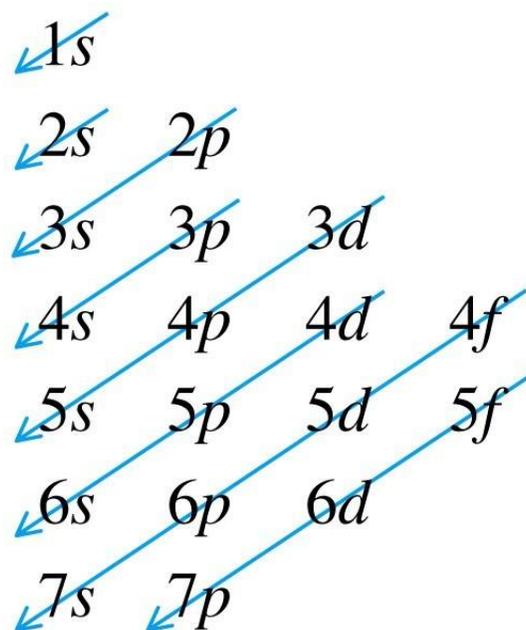
## How are Orbitals Filled in a Multi-Electron Atom?

### 1. The Pauli Exclusion Principle.

*“No two electrons in a system may be in exactly the same state.” or*

*“No two electrons in an atom may have exactly the same values for the four quantum numbers  $n$ ,  $l$ ,  $m_l$  and  $m_s$ .”*

### 2. Electrons normally occupy orbitals in a way which minimizes the total atomic energy; i.e., always fill the lowest available orbital first.



### 3. Hund's Rule

We know each orbital in a sub-shell can hold 2 electrons, one with  $m_s = +\frac{1}{2}$  and one with  $m_s = -\frac{1}{2}$ : i.e.,

Hund's rule requires that: when degenerate sub-orbitals are available (same  $l$  but different  $m_l$ ), *all sub-shells must be half-filled with electrons whose spins point in the same direction before any electrons are allowed to pair up.*

An ***Electron Configuration*** is a label indicating the distribution of electrons in the orbitals of an atom (or molecule).

Sometimes we use the name of the nearest smaller inert gas atom to indicate a configuration full up to its last filled  $np$  sub-shell.

### ***Exceptions to the “normal” Aufbau orbital filling rules***

*Exactly full* or *exactly half-full*  $d$  sub-shells have a very special energy stability which can be enough to over-ride the normal orbital filling rules.

e.g., Cr ( $Z=24$ ) has the configuration:  $[\text{Ar}] 4s^1 3d^5$  and not

Cu ( $Z=29$ ) has the configuration:  $[\text{Ar}] 4s^1 3d^{10}$  and not

Similar sorts of things happen around  $Z=42$  &  $47$ , but with more extreme variations, and again after the filling of the  $6s^2$  sub-shell (after  $Z=56$ ).

Sc:	[Ar]	$\uparrow$					$\uparrow\downarrow$	$[\text{Ar}]3d^14s^2$	
Ti:	[Ar]	$\uparrow$	$\uparrow$				$\uparrow\downarrow$	$[\text{Ar}]3d^24s^2$	
V:	[Ar]	$\uparrow$	$\uparrow$	$\uparrow$			$\uparrow\downarrow$	$[\text{Ar}]3d^34s^2$	
Cr:	[Ar]	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$[\text{Ar}]3d^54s^1$	
Mn:	[Ar]	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$	$[\text{Ar}]3d^54s^2$	
Fe:	[Ar]	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$	$[\text{Ar}]3d^64s^2$	
Co:	[Ar]	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$	$[\text{Ar}]3d^74s^2$	
Ni:	[Ar]	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$	$[\text{Ar}]3d^84s^2$	
Cu:	[Ar]	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$[\text{Ar}]3d^{10}4s^1$	
Zn:	[Ar]	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$[\text{Ar}]3d^{10}4s^2$	
		$3d$					$4s$		

**Valence electrons** are those electrons in the configuration which lie outside the last complete rare gas configuration [excluding fully filled inner  $d$  or  $f$  sub-shells].

## The Periodic Table!

Although the hydrogenic-atom level energy formula clearly breaks down for multi-electron atoms, the hydrogenic classification of the different allowed wave function solutions in terms of

- number of angular nodes  $l$
- number of radial nodes  $n - l - 1$

is still valid, and the similar qualitative chemical and physical properties of elements which Mendeleev had put together in columns in his empirically derived periodic table are now explained by the fact that they have similar “valence electron” structures.

**TABLE 9.2 Electron Configurations of Some Groups of Elements**

Group	Element	Configuration
1	H	$1s^1$
	Li	$[\text{He}]2s^1$
	Na	$[\text{Ne}]3s^1$
	K	$[\text{Ar}]4s^1$
	Rb	$[\text{Kr}]5s^1$
	Cs	$[\text{Xe}]6s^1$
	Fr	$[\text{Rn}]7s^1$
17	F	$[\text{He}]2s^2 2p^5$
	Cl	$[\text{Ne}]3s^2 3p^5$
	Br	$[\text{Ar}]3d^{10} 4s^2 4p^5$
	I	$[\text{Kr}]4d^{10} 5s^2 5p^5$
	At	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^5$
18	He	$1s^2$
	Ne	$[\text{He}]2s^2 2p^6$
	Ar	$[\text{Ne}]3s^2 3p^6$
	Kr	$[\text{Ar}]3d^{10} 4s^2 4p^6$
	Xe	$[\text{Kr}]4d^{10} 5s^2 5p^6$
	Rn	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^6$

In the periodic table:

- groups are
  
- periods are
  
- *s*-block, *p*-block, *d*-block & *f*-block elements are
  
- main group elements are
  
- transition elements are
  
- inner transition elements are

---

**Exercise 12.** Write down the electronic configuration for (a) Tc , (b) Ir , (c) Po .

## Electronic Configurations for Atomic Ions

**Negative ions** (or “anions”) are formed by attaching one (or more) electrons to a neutral atom

- have the same configuration as a neutral atom with that many electrons.

e.g., the configuration for  $\text{Cl}^-$  is  $[\text{Ar}]$  (or  $1s^2 2s^2 2p^6 3s^2 3p_6$ )

the configuration for  $\text{N}^-$  is

**Positive ions** (or “cations”)

The electrons with highest  $n$  are removed first, even if they were not the last subshell filled. For example:

- Fe ( $Z=26$ , 26 electrons) has the configuration:  $[\text{Ar}] 4s^2 3d^6$
- $\text{Fe}^+$  ( $Z=26$ , 25 electrons) has the configuration:
  
- $\text{Fe}^{2+}$  ( $Z=26$ , 24 electrons) has the configuration:
  
- $\text{Fe}^{3+}$  ( $Z=26$ , 23 electrons) has the configuration:
  
- $\text{Fe}^{4+}$  ( $Z=26$ , 22 electrons) has the configuration:

***s*-Block Metal Ions** are formed by losing 1 or 2 electrons to give an “inert gas” (or “noble gas” or “rare gas”)  $np^6$  configuration.

***p*-Block or Transition Metal Ions** sometimes lose enough electrons to leave an ion with a stable  $ns^2$  or  $ns^2(n-1)d^{10}$  configuration (e.g., Al or Ga) configuration ... but for most there are no useful general rules.

**Main Group Non-Metal Ions** are all *p*-block elements, and tend to try to *gain* enough electrons to attain a rare gas configuration: e.g.,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , ... , and  $\text{O}^{2-}$ ,  $\text{S}^{2-}$

**Exercise 13.** Write down the electronic configuration for (a)  $\text{Tc}^{2+}$ , (b)  $\text{Ir}^-$ , (c)  $\text{Po}^+$ .