

## Lessons from previous lecture

1. In order to explain the “ultra violet catastrophe”, the temperature dependence of heat capacity, and the characteristics of the photoelectron effect, it was necessary to introduce some new ideas to supplement the classic view of electromagnetic radiation as a purely wave function. The recognition that emission and absorption of light were quantized led to the development of quantum theory, and the recognition of the dual nature of electromagnetic radiation, - both wave-like and particle-like behavior.
2. Because the transitions leading to emission or absorption of photons involved changes in energy levels in atoms and molecules, an understanding of the interaction of light required extension of the ideas of quantum theory to the structure of atoms and molecules.
3. De Broglie’s recognition that all matter showed wave-like properties was confirmed for the electron by observations of diffraction.
4. The emission lines of hydrogen, as seen in the Balmer series (and later extensions to wider regions of the spectrum) provided an important clue. Any theory of atomic structure had to explain why the light emitted was constrained to narrow lines, and why they were spaced as observed. The positions in the spectrum represent discrete energies for the transitions between electronic states leading to emission.
5. This led to the Bohr model of the H-atom, which successfully explained the Balmer series by constraining the transitions to quantized changes.

# Bohr's explanation for H-emission lines

## The Bohr atom model and formula

The picture of an atom given by the Rutherford experiment was of a very compact nucleus surrounded by a large volume occupied by the electrons; the latter determines the volume seen by light or chemical reactivity. This was similar in general design to the solar system, giving rise to the idea that the electrons might be orbiting a central nucleus. Bohr took this idea, and applied the classical reasoning of planetary theory to it, but with a quantized twist. He calculated the energy of the system by balancing the kinetic energy of the electron in orbit (the centrifugal force) against the attractive energy of the coulombic interaction between the positively charged nucleus and the negatively charged electron. The twist was the use of quantized energy levels.

The force due to coulombic attraction is given by:  $f = \frac{Ze^2}{4\pi\epsilon_0 r^2}$

(Z is charge of nucleus; r is radius of orbit; e is electron charge;  $\epsilon_0$  is permittivity)

The force due to classical kinetic energy is given by:  $f = \frac{m_e v^2}{r}$  ( $m_e$  is electron mass)

Equating these two forces we have 
$$\frac{m_e v^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

At this point we have a classical description of the forces in the system.

If we write the energy of the electron we need the sum of the two energy terms due to these forces:

$$E = \frac{1}{2}m_e v^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

Substituting the force terms we get the following classical expression for the energy of the electron:

$$E = \frac{1}{2}m_e v^2 - m_e v^2 = -\frac{1}{2}m_e v^2$$

The hydrogen emission lines were taken to represent the changes in energy due to transitions between energy levels in the excited H-atoms. A successful description of the energy level of the electron had to account for the curious spacing of the Balmer (and other) series. Bohr found he could achieve this by the simple expedient of imposing the condition of quantized energy levels; the angular momentum of the electron was restricted to values given by:

$$m_e v r = n \frac{h}{2\pi} \quad n = 1, 2, 3, \dots$$

where  $h$  is Planck's constant.

The energy of the electron was  $E_n = -\frac{m_e e^4}{8h^2 \epsilon_0^2} \frac{1}{n^2}$   $n = 1, 2, 3, \dots$

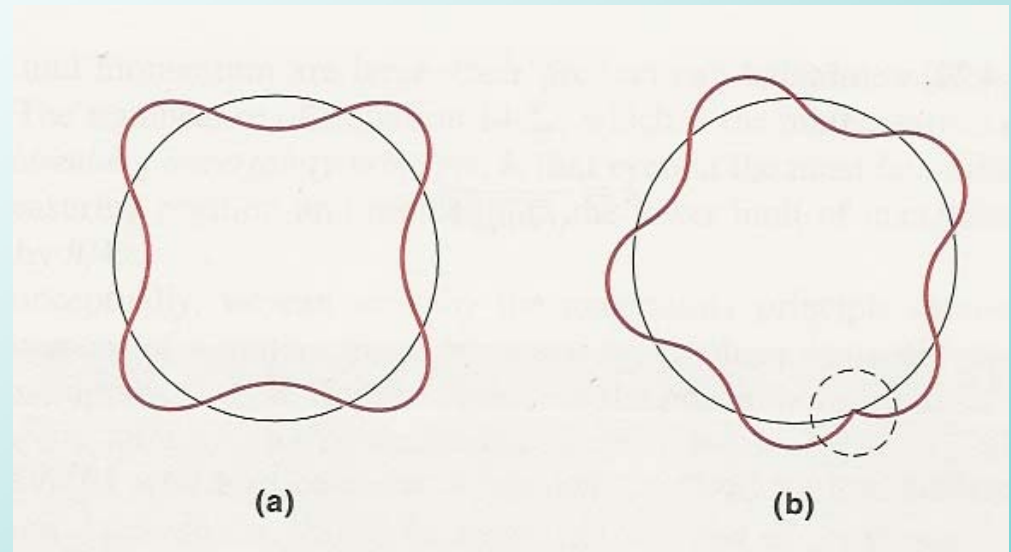
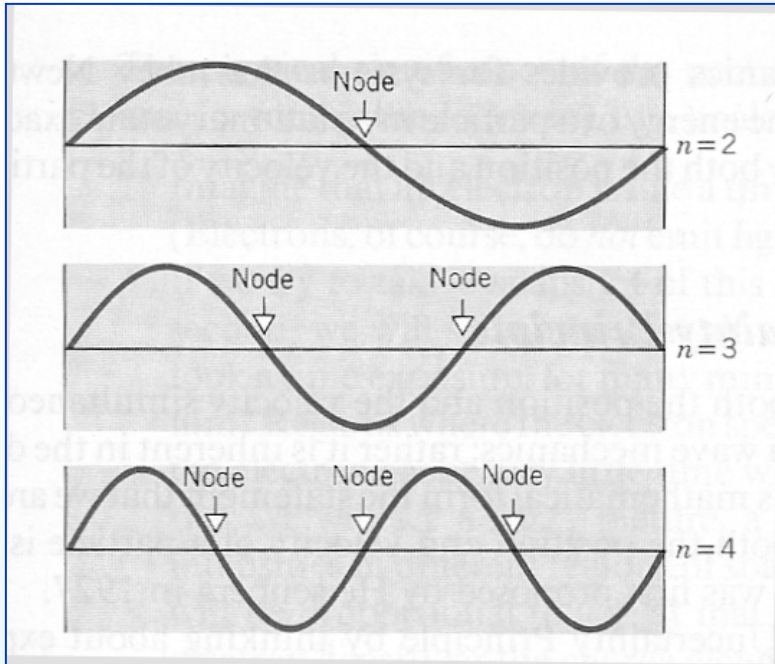
Applying this quantized restriction, he found that the changes in energy level were given by

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{\Delta E}{hc} = \left( \frac{m_e Z^2 e^4}{8h^3 c \epsilon_0^2} \right) \left( \frac{1}{n_L^2} - \frac{1}{n_H^2} \right) = \mathfrak{R} \left( \frac{1}{n_L^2} - \frac{1}{n_H^2} \right)$$

This is identical to the equation for the spacing of the H emission lines.

## De Broglie's extension of Bohr's model.

The Bohr mechanism for explaining the H-emission spectrum, and hence the allowed energy levels of the electron in the H-atom in its excited states, was a triumph, but it didn't explain why the electrons were constrained to particular orbits; it was descriptive rather than explanatory. With the demonstration of the wave-nature of the electron through de Broglie's postulate, and the diffraction of the electron, an explanation could be offered. If the electron is a wave, then its ability to fit an orbit must be constrained by the condition that it is a standing wave.



In this case, assuming a simple sine wave, the relation between the radius of the orbit and the wavelength of the electron is given by the circumference and the wavelength  $2\pi r = n\lambda$ ,  $n = 1, 2, 3, \dots$

Substituting for  $\lambda$  from the de Broglie relationship we get

$$2\pi r = n \frac{h}{m_e v}$$

Rearrangement gives Bohr's equation, and explains the occupancy.

$$m_e v r = n \frac{h}{2\pi} \quad n = 1, 2, 3, \dots$$

# The Schrödinger equation

The refinement of the **Bohr** model by **de Broglie** paved the way for the more formal description by **Schrödinger**. The concepts behind the new treatment were essentially the same as developed in the preceding slides. What Schrödinger added was a more powerful formalism for the description of the wave function. Unfortunately, this involves some elegant math, - a thing of beauty to the physicist, but perhaps not to the biologist. Fortunately, we don't need to understand the math in detail to appreciate the results, so the approach here will be non-mathematical.

It will help to appreciate a few points:

1. So far we have dealt with simple waves, - effectively sine waves constrained by the need to form a standing wave. This is appropriate for a circular orbit. However, the new approach made it possible to describe wave functions that were three-dimensional, and more complex in shape, while maintaining the constraints required by quantization, and the need to form a “standing wave”.
2. In this context, the kinetic and potential energy terms of the Bohr equation are retained, but it was necessary to recognize that the values will depend in a more complicated way on the “shape” of the wave function.

3. **Heisenberg** had introduced his **Uncertainty Principle**, which showed that the momentum and position of the electron could not be determined simultaneously with certainty. Schrödinger therefore used a term related to the probability of the electron occupying a particular volume.
4. In the context of the constraint of a “standing wave”, this made it possible to make the expression time-independent. Hence the time-independent Schrödinger equation.

The Schrödinger equation for H-like atoms has the following form:

$$E\psi = -\frac{h^2}{8\pi^2m}\nabla^2\psi + \frac{Ze^2}{4\pi\epsilon_0r}\psi$$

## The Schrödinger equation

The Schrödinger equation for H-like atoms has the following form:

$$E\psi = -\frac{\hbar^2}{8\pi^2m}\nabla^2\psi + \frac{Ze^2}{4\pi\epsilon_0r}\psi$$

Let's compare this to the classical expression for the energy of the electron:

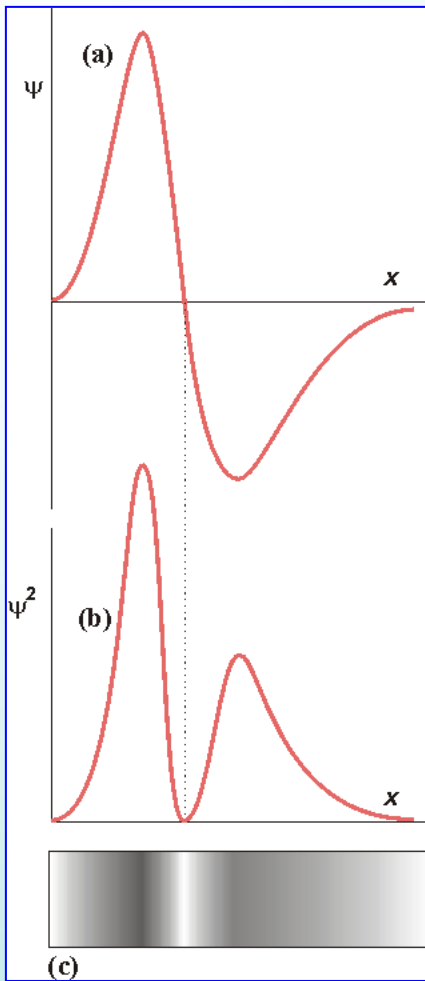
$$E = \frac{1}{2}m_e v^2 - \frac{Ze^2}{4\pi\epsilon_0r}$$

The similarity arises from the need to consider the two balancing forces that determine the electron energy, - the kinetic term (the “centrifugal force” if we consider a planetary model), and the constraining electrostatic term for the potential energy. The first term on the right (the kinetic term) is now quantized, and all terms are modified by the wave function,  $\psi$ .

What is  $\psi$ , and what is that odd symbol,  $\nabla^2$ ?



$$E\psi = -\frac{\hbar^2}{8\pi^2m}\nabla^2\psi + \frac{Ze^2}{4\pi\epsilon_0r}\psi$$



It's difficult to form a solid picture of what  $\psi$  represents, but  $\psi^2$  is easier to grasp; it represents the probability of finding the electron at a particular point in space. This is more formally described by the Born approximation, which, for a one-dimensional system, states that the probability of finding the particle between  $x$  and  $x + \delta x$  is proportional to  $\psi^2 \delta x$ . In three dimensions the probability is proportional to  $\psi^2 \delta V$ .

The term  $\psi^2$  is a probability density, and we get the probability by multiplying the density by the volume of the region of interest.

Examples of a particular wave function,  $\psi$ , in one-dimension, and its square,  $\psi^2$ , plotted against distance are shown on the left. Note that for  $\psi^2$ , all values are positive even when  $\psi$  goes negative. The shaded bar at the bottom is gray-scale encoded to show probability.

The odd symbol,  $\nabla^2$  (pronounced del-squared) is a Laplace operator. In the one-dimensional case,  $\nabla^2$  is superfluous. When we deal with a real system, we have three dimensions to worry about, - in the case of the H-atom and more complex 3-D systems we need to generalize the equation for three-dimensions.

In the one-dimensional case (particle-in-a-box treatment), the term  $\nabla^2 \psi$  is replaced by the second derivative of  $\psi$  with distance,

$$\frac{d^2\psi}{dx^2}$$

For the three dimensional case, in its simplest form as applied to Cartesian coordinates,  $\nabla^2$  is an abbreviation for the term

$$\nabla^2 = \left( \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right)$$

It tells us that we have to perform the second derivative operation on the wave function in a three dimensional coordinate system. It takes a more complicated appearance for other coordinate systems, but serves the same function.

Because trigonometric functions provide a rich field for investigation of potential wave functions,  $\nabla^2$  is often used in the context of spherical polar coordinates.

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right)$$

## The energy operators

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + U(x) \psi = E \psi$$

As noted above, the three operators on  $\psi$  all have energy units. They can be expressed in various forms, which makes for some confusion, but basically they represent the same energies as appear in the classical equation. The form of the equation above is that usually presented (this is just the previous equation rearranged). The Table below shows the equation for the 1-D case in different forms.

kinetic energy + potential energy = total energy

$$T_x \psi + U(x) \psi = E \psi$$

$$\frac{p_x^2}{2m} \psi + U(x) \psi = E \psi$$

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

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi = E \psi$$

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

To cut the clutter, Planck's constant,  $h$ , has been replaced by  $\hbar$ , defined by  $\hbar = h/2\pi$ .

Note that in the last line, the kinetic and potential energy terms have been lumped together into a single operator. This term also has energy units, and is called a Hamiltonian operator,  $\mathcal{H}$ .

The kinetic energy operator,  $T_x$  is shown in classical form,  $T_x = \frac{1}{2} m v^2 = \frac{p_x^2}{2m}$ , and in the quantized form above. The potential energy operator is represented by  $U(x)$ .

## Finding appropriate forms for $\psi$

Solution of the Schrödinger equation involves the second derivative of the wave function,  $\psi$ . There are many solutions that can be found, and the problem is to know which ones are appropriate. We have to recognize constraints that relate to the physical reality of the system. These can be summarized as follows:

1. Acceptable solutions must be *single-valued at all points in space*. This is because there cannot be more than one answer to the question “What is the probability of finding the particle at a particular point in space?”.
2. Similarly,  $\psi$  *must be continuous and finite*. This constraint is necessary to provide the “standing-wave” character of the function.
3. *The total value of  $\psi^2$  summed over all space must be 1*. This is because the particle has to be somewhere, but there’s only one of them.

Because energy levels are quantized, *the wave function can take different forms, depending on the quantum number*.

As we have seen, the different quantum numbers in the Bohr model represented different energy levels for orbitals in the ground state and excited states of the H atom. The effect of this last property has interesting connotations when we consider the shapes of the orbitals defined by the wave function.

## Particle in a box, - the Schrödinger equation in 1-D

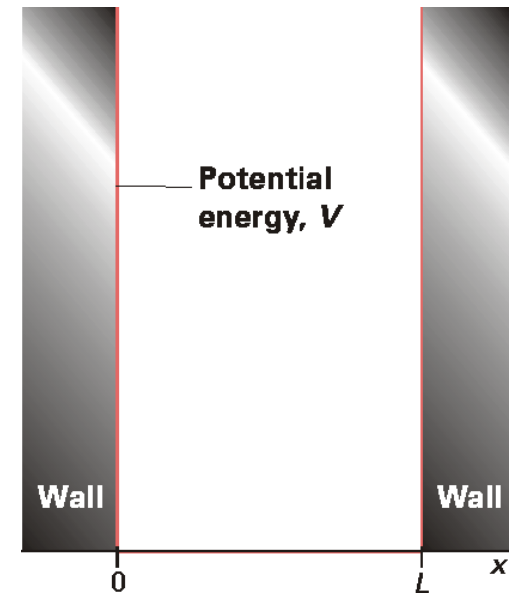
If we constrain our electron to a one-dimensional box, we can simplify things. In 1-D, we don't have to worry about the potential energy term of the planetary model, - the electron is constrained by the walls of the box, not by the attraction of the nucleus, so we only have to worry about the kinetic energy. And we don't have to worry about  $\nabla^2$ , because we're in 1-D. The Schrödinger equation then becomes:

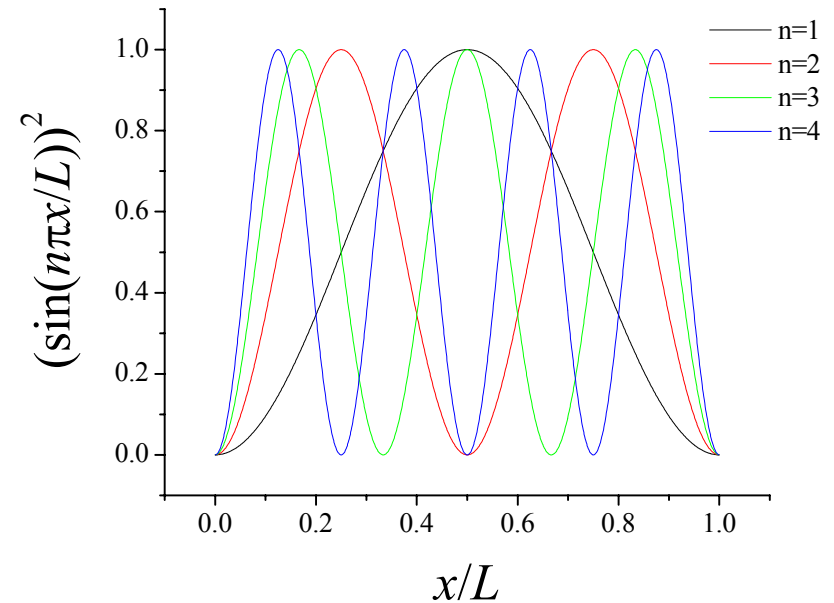
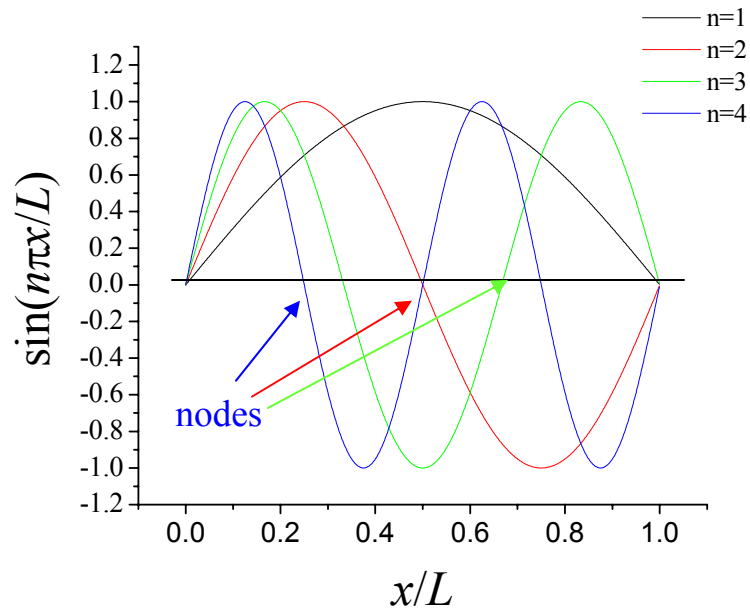
$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi = E \psi$$

To solve this equation, we have to find an appropriate wave function,  $\psi$ . The wavelength of a harmonic oscillator in one-dimension is a sine function, and this provides an appropriate starting point for our search for a wave function. Let's try

$$\psi = A \sin kx$$

where  $x$  is distance. We will take a look at what happens if we set  $k = n\pi/L$ , with  $L$  as the length of our box. Because  $\sin \pi = \sin 2\pi = \sin 3\pi = 0$ , we expect this function to generate a curve that oscillates. In the next slide this function (with  $A = 1$ ) is plotted against distance ( $x$ ) with different values of  $n$ , and with distance scaled to units of  $L$ .





Note that if we change the value of  $n$  in this equation, we change the number of beats per unit distance as measured by the number of times the curve crosses the zero-line at a **node**. The nodes define the distance at which we will form a “standing wave”. At distance  $x=L$ , for  $n = 1$  we have 1 node; for  $n = 2$ , 2 nodes;  $n = 3$ , 3 nodes; etc.

The plot on the right shows the square of the function versus the same distance scale. Each node generates a peak, so there are  $n$  peaks for each curve. The curves are all positive, so (remembering the  $\psi^2$  gives probability) they look suitable.

Our choice of wave function looks pretty good, - it has the sorts of property we're looking for. We now need to plug it into our Schrödinger equation to see if it satisfies all the constraints. Chang has a nice account of how to do this, which we will summarize here. Starting with  $\psi = A \sin kx$ , the critical steps are:

1. Find the second derivative of this function (it's given by  $-k^2 \psi$ )
2. Substitute  $\psi$  from this into the Schrödinger equation to find that  $k = \left( \frac{8\pi^2 mE}{h^2} \right)^{\frac{1}{2}}$ , and that, by back substitution,  $\psi = A \sin \left( \frac{8\pi^2 mE}{h^2} \right)^{\frac{1}{2}} x$ .
3. Satisfy the boundary condition that  $\psi$  is zero at the walls. As we saw in previous slides,  $\sin n\pi = 0$ , so this is satisfied when  $x = 0$  or  $L$ , the length of our box.

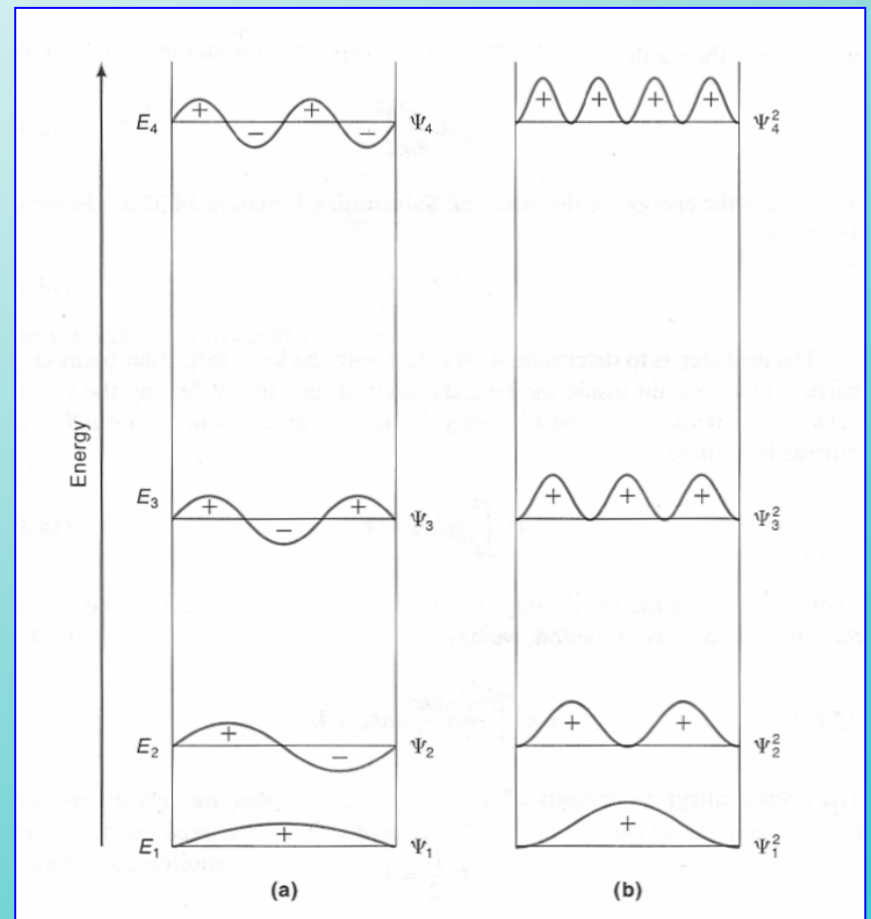
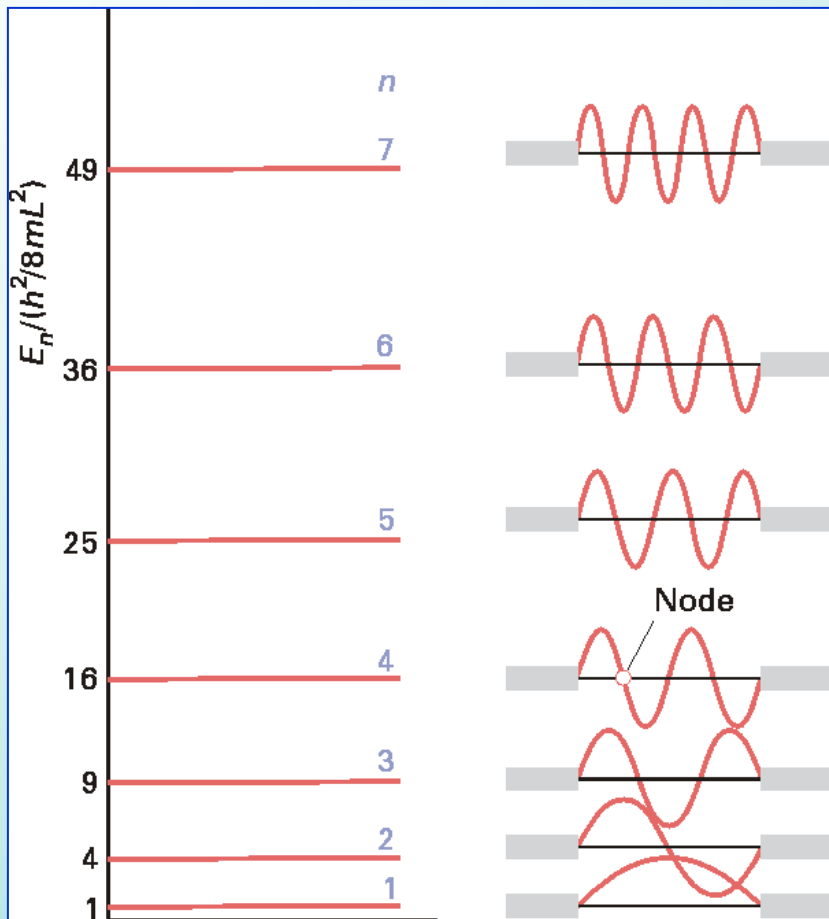
From this, our function can work if  $\left( \frac{8\pi^2 mE}{h^2} \right)^{\frac{1}{2}} = \frac{n\pi}{L}$  ( $n$  is integer). Then by back substitution,

$$\psi_n = A \sin \frac{n\pi}{L} x \quad \text{and} \quad E_n = \frac{n^2 h^2}{8mL^2}$$

4. Satisfy the constraint that the probability is 1. For this we need to adjust the amplitude of our sine wave, using the factor  $A$ . Tables of integrals give us a *normalization constant* such that  $A = \sqrt{\frac{2}{L}}$ . We finally end up with:

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$$

We have already seen plots of this function, and a version is shown on the left below, in the context of energy levels. We can now say that the energy of an electron in a one-dimensional box has different levels that are quantized, and that at each level the wave function,  $\psi$ , is a sine wave, with the number of nodes equal to the quantum number. The probability is given by  $\psi^2$ , and this is shown in the right panel below.





# Applying the Schrödinger equation to the hydrogen atom

Chang also has a succinct account of this, but starts off with a form of the equation which is unfamiliar. Our general equation is:

$$-\frac{\hbar^2}{8\pi^2 m} \nabla^2 \psi + \frac{e^2}{4\pi\epsilon_0 r} \psi = E \psi$$

To get it into Chang's form, we abbreviate

the potential energy term:

$$\frac{e^2}{4\pi\epsilon_0 r} = V,$$

and rewrite the equation.

$$-\frac{\hbar^2}{8\pi^2 m} \nabla^2 \psi + V \psi = E \psi$$

Then we bring all terms to one side,

and rearrange them.

$$\nabla^2 \psi + \frac{8\pi^2 m}{\hbar^2} (E - V) \psi = 0$$

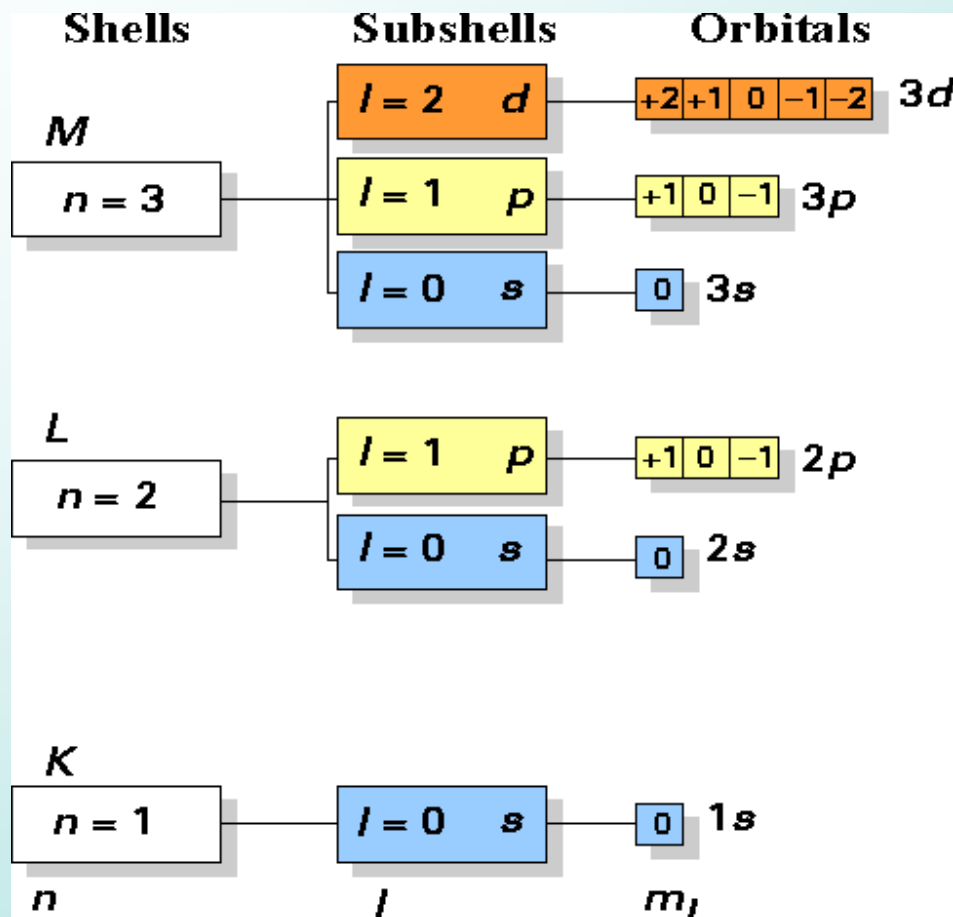
This is Chang's (14.39).

Then we substitute into the leftmost term using  $\nabla^2$  in its spherical polar coordinate form, and put back the unabbreviated potential function.

$$\frac{\partial^2 \psi}{dr^2} + \frac{2\partial \psi}{r\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 m}{\hbar^2} \left( E - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi = 0$$

As Chang says: "Fortunately, this fearsome-looking equation has already been solved, so we need be concerned only with the result."

The solutions are given in Chang in a form appropriate for the spherical polar coordinates chosen. The solutions requires that we use three quantum numbers to describe each energy level. The nomenclature for these is not very helpful.



The three quantum numbers are:

$n$ , the principal quantum number;

$l$ , the angular momentum quantum number\*;

$m_l$ , the magnetic quantum number.

$$n = 1, 2, 3, \dots, n$$

$$l = 0, 1, 2, \dots, (n-1)$$

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

The resulting orbitals are grouped into subshells and shells, as nicely summarized on the left.

\*Note that Chang also calls this the azimuthal quantum number.

The solutions of the equation give the energy of the electrons in the orbitals, and their distribution in space. The energy of the electron is given by:

$$E_n = -\frac{m_e e^4}{8h^2 \epsilon_0^2} \frac{1}{n^2} \quad n = 1, 2, 3, \dots$$

Not surprisingly (because it worked), this is the same as the equation Bohr developed to account for the emission lines for the H-atom.

Where have the  $l$  and  $m_l$  quantum numbers gone?

Chang presents the above equation without explanation, but the answer is straightforward. All three quantum numbers characterize the electron **distribution**, but for any shell, all the wave functions use the same value for radius. The radius enters into the energy through the potential energy function, - the coulombic force holding the electron to the nucleus, which depends only on  $r$ , and is spherically symmetrical. Since this balances the centrifugal energy represented by the angular momentum of the electron, all electrons in the shell have the same potential energy function, determined by  $n$ , as in the Bohr equation.

This simple case applies only to the H-atom.

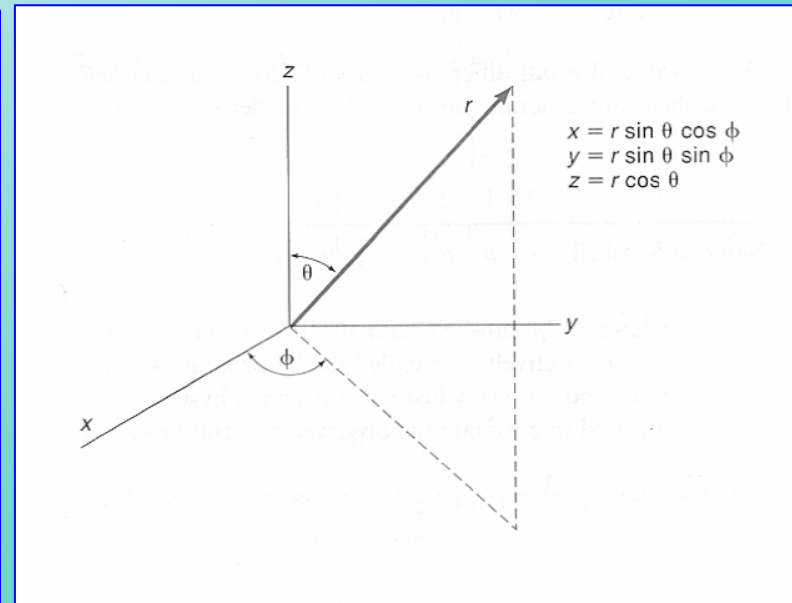
Because  $n$  uniquely determines the energy, the value of  $E$  for a particular  $n$  is called its characteristic energy, or **eigenvalue**. The wave function for a particular  $n$  is called the characteristic wave function, or **eigenfunction**.

The relation between  $\psi$  and probability of distribution depends on the quantum number. Choice of polar coordinates gives  $\psi$  as a function of  $r$ ,  $\theta$ , and  $\phi$ , so that

$$\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

The terms on the right are called the radial part, ( $R(r)$ ), and the angular part, ( $\Theta(\theta)\Phi(\phi)$ ), of this expression. As the equation shows, the radial part is dependent on  $r$ , so we can think of  $n$  as characterizing the distance dependence, with each shell having a different radius. The solution for each orbital differs (see Chang), depending on the values of the quantum numbers. For orbitals with  $l$  and  $m$  equal to zero, the solution depends only on  $r$ , the radius. As a consequence, these orbits are spherical.

For non-zero  $l$ , and for  $m$  quantum numbers, the “shape” of the orbit is not spherical, and the wave function is determined by  $x$ ,  $y$  and  $z$ , the parameters of its position in Cartesian space. For example, of the four electrons in the  $L$  shell, one has  $l = 0$ , and hence  $m$  is also zero, and the orbital is spherical. The other three are arranged along the  $x$ ,  $y$ , and  $z$  axes, and are not spherical.



The Table on the right shows wave functions, in  $x$ ,  $y$  and  $z$  coordinates, for hydrogenic atoms (H, He<sup>+</sup>, Li<sup>2+</sup>, etc., - atoms with only 1 electron;  $Z$  is the atomic number, giving the charge of the nucleus).

Chang has a more complete set of values with the radial and angular parts shown separately.

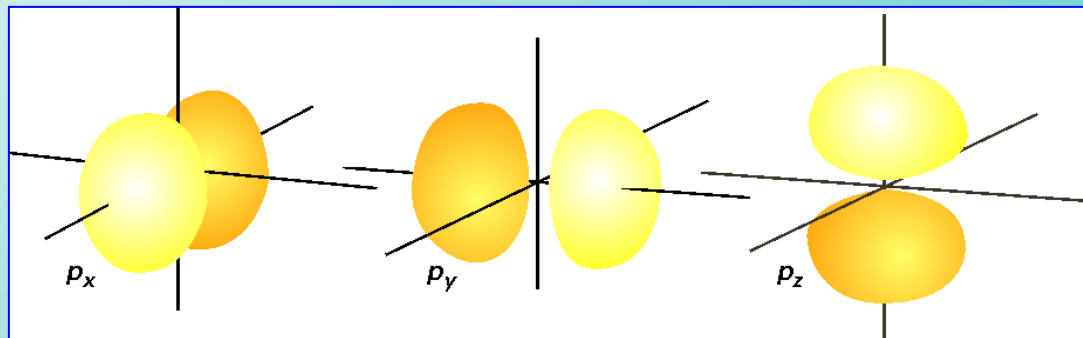
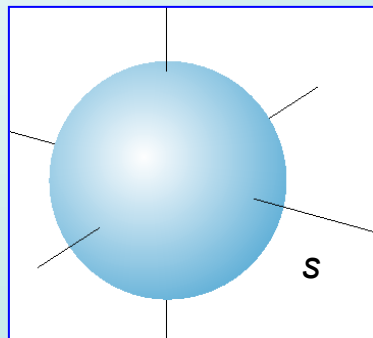
The Figures below show the “shapes” (boundary surfaces) of the corresponding orbitals.

**Table 9.4** Hydrogenic wavefunctions\*

$n$	$l$	$m$	
1	0	0	$\psi(1s) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi(2s) = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	$\psi(2p_z) = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{5/2} (z) e^{-Zr/2a_0}$
2	1	$\pm 1$	$\psi(2p_x) = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{5/2} (x) e^{-Zr/2a_0}$
			$\psi(2p_y) = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{5/2} (y) e^{-Zr/2a_0}$

\*  $z = r \cos \theta$   
 $x = r \sin \theta \cos \phi$   
 $y = r \sin \theta \sin \phi$   
 $r^2 = x^2 + y^2 + z^2$

$a_0 = \text{Bohr radius} = \frac{\hbar^2}{me^2}$   
 $= 0.529 \text{ \AA} = 5.29 \times 10^{-2} \text{ nm}$   
 $Z = \text{charge on nucleus}$



from Tinoco, Sauer and Wang,  
Physical Chemistry

from Atkins, The Elements of  
Physical Chemistry

The subshells are named  $s$ ,  $p$ ,  $d$ ,  $f$ ,  $g$ , and  $h$  for electrons with  $l = 0, 1, 2, 3, 4$  and  $5$ .

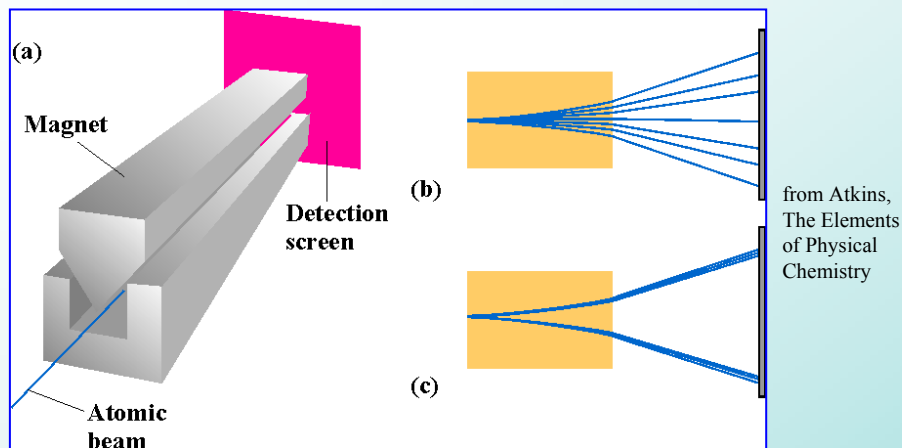
## Magnetic properties of the atom

We have skipped over the relation between  $\psi$  and the boundary surface, as represented by the “shapes” in the previous slide. Chang has a discussion of the radial distribution function,  $4\pi r^2 \psi^2$ , which provides a picture of the total probability of finding an electron in a spherical shell, but the pictures show enough information for our further discussion.

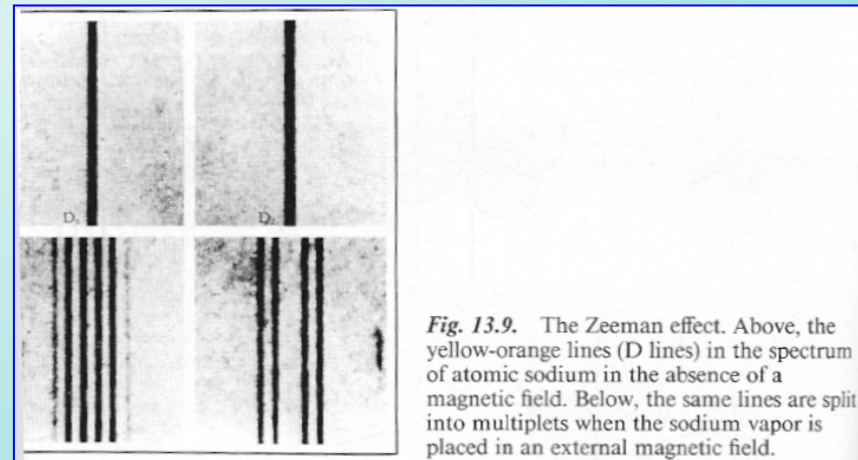
Does the Schrödinger equation provide a complete description?

No. The Schrödinger equation did not account for experimental results showing that some electron energy levels could be split by a magnetic field, - the **Zeeman** effect.

Deflection of Ag atom beam by a magnetic field



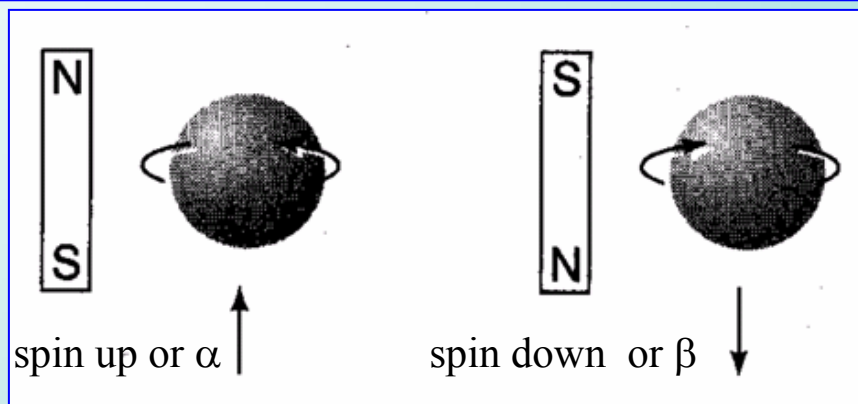
Splitting of Na D-line emission by a magnetic field



At the same time as Schrödinger was developing his approach, both **Heisenberg** and **Dirac** were developing alternative systems of equations. Both explicitly added a fourth dimension to their treatments, in recognition of Einstein's introduction of time as an addition to the three Cartesian coordinates of space. This introduced a fourth quantum number, which we now know as  $m_s$ , the spin quantum number.

## The electron spin quantum number, and Pauli's exclusion principle.

In order to account for the magnetic splitting of atomic lines, it was necessary to understand how the magnetic properties of the electron could be included in the grand scheme of the Schrödinger equation.



Since the electron has a negative charge, it is clear that any electron moving in an orbital should also generate a magnetic field. **Pauli** realized that the problem could be inverted, - why do all atoms not show a magnetic response? The answer he proposed was that electrons normally came in pairs, so that their magnetic effects cancelled out. This would be the case if, in addition to movement in an “orbit”, the electrons were also spinning on their axes. Each electron would then be a magnet. A pair of electrons in the same orbit would cancel out, but **only if they had opposite spins**. More formally, **Pauli's exclusion principle** states that two, but no more than two, electrons can occupy any orbit. As a result, the number of electron orbitals described by the Schrödinger equation was doubled, by adding the fourth quantum number,  $m_s$ , which can have one of two values,  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . It was later realized that this was equivalent to inclusion of the fourth quantum number of Heisenberg's or Dirac's treatments.



With the addition of  $m_s$ , the properties of elements in the Periodic Table could be accounted for. In addition to the atomic number, and the matching of electronic to protonic charge, the reactivities of the elements could be explained in terms of the need to fill the electronic orbitals by sharing electrons, thus explaining the valence properties, and their periodic pattern.

Figure 13.3. Ground Electronic Configurations of the first 18 Elements of the Periodic Table

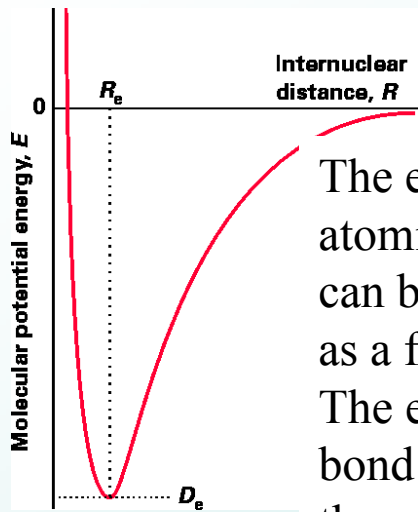
	K Shell		L Shell			M Shell			Electronic Configuration
H	↑								1s
He	↑↓								1s <sup>2</sup>
Li	↑↓	↑							1s <sup>2</sup> 2s
Be	↑↓	↑↓							1s <sup>2</sup> 2s <sup>2</sup>
B	↑↓	↑↓	↑						1s <sup>2</sup> 2s <sup>2</sup> 2p
C	↑↓	↑↓	↑	↑					1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>
N	↑↓	↑↓	↑	↑	↑				1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>
O	↑↓	↑↓	↑↓	↑	↑				1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>
F	↑↓	↑↓	↑↓	↑↓	↑				1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>
Ne	↑↓	↑↓	↑↓	↑↓	↑↓				1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>
Na	↑↓	↑↓	↑↓	↑↓	↑↓	↑			(Ne)3s
Mg	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓			(Ne)3s <sup>2</sup>
Al	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑		(Ne)3s <sup>2</sup> 3p
Si	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	(Ne)3s <sup>2</sup> 3p <sup>2</sup>
P	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	(Ne)3s <sup>2</sup> 3p <sup>3</sup>
S	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	(Ne)3s <sup>2</sup> 3p <sup>4</sup>
Cl	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	(Ne)3s <sup>2</sup> 3p <sup>5</sup>
Ar	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	(Ne)3s <sup>2</sup> 3p <sup>6</sup>
	1s	2s	2p		3s	3p		3d	

Filling of orbital shells, - the building-up (*Aufbau*) principle

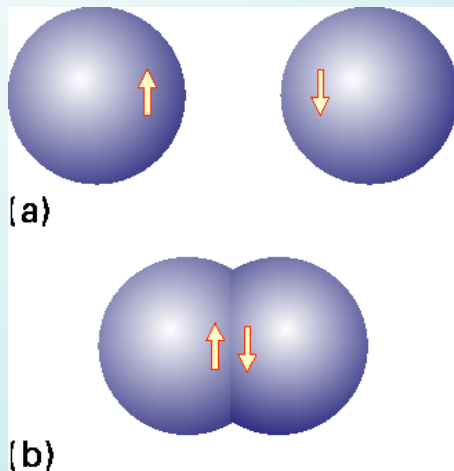
What are the **take-home messages** here?

1. The Schrödinger equation allows us to calculate exactly the distributions of electrons in hydrogen (and hydrogen-like) atoms with a single electron.
2. The orbitals described by solution of the Schrödinger equation are potential orbitals of occupancy of the one electron in a H-atom. It usually sits in 1s.
3. Application of the Schrödinger equation to atoms with more than one electron becomes increasingly intractable. This is because of interactions between the multiple charges of electrons and the nucleus; the many bodies problem cannot be solved exactly.
4. Use of approximations shows that the orbitals in more complicated atoms likely have a similar probability distribution to the those calculated for the H-atom.
5. The orbitals provide insights into (and allow approximate calculations of) the molecular orbitals associated with chemistry.
6. The orbitals provide an explanation for properties seen in the Periodic Table.
7. The solutions explain the spectroscopic properties of atoms and molecules.

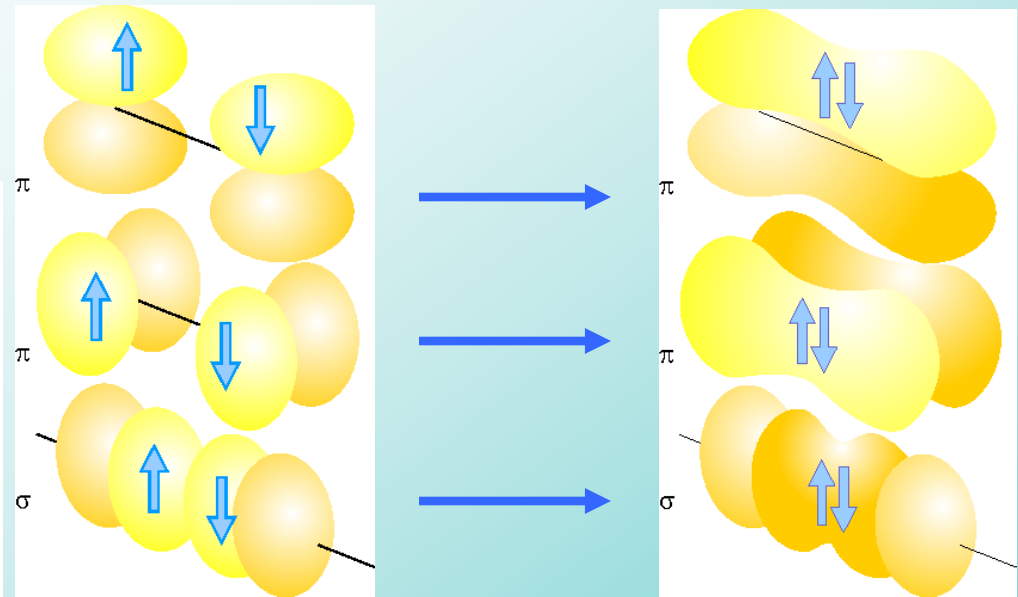
# Molecular orbitals



The energy due to atomic interaction can be calculated as a function of  $R$ . The equilibrium bond length is at the minimum.



$1s$  orbitals of H-atoms coalesce to form a  $\sigma$  bond of  $H_2$ , with cylindrical symmetry

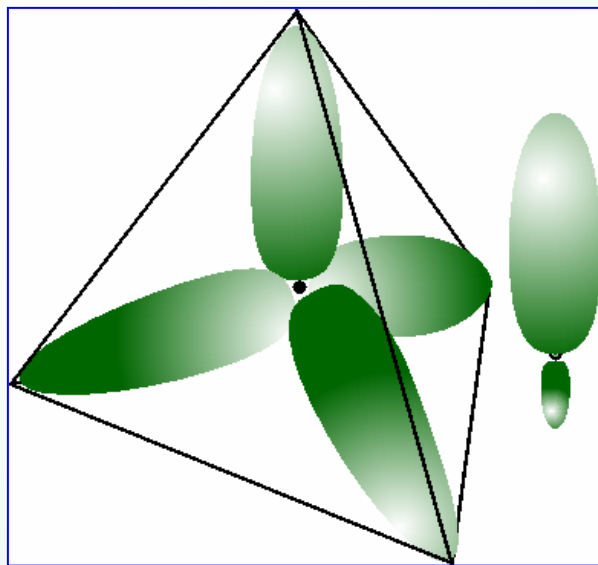


Formation of the bonds in  $N_2$ . The  $2p_z$  orbitals overlap and coalesce into a  $\sigma$  molecular orbital; the  $p_x$  and  $p_y$  orbitals form  $\pi$  orbitals perpendicular to each other.

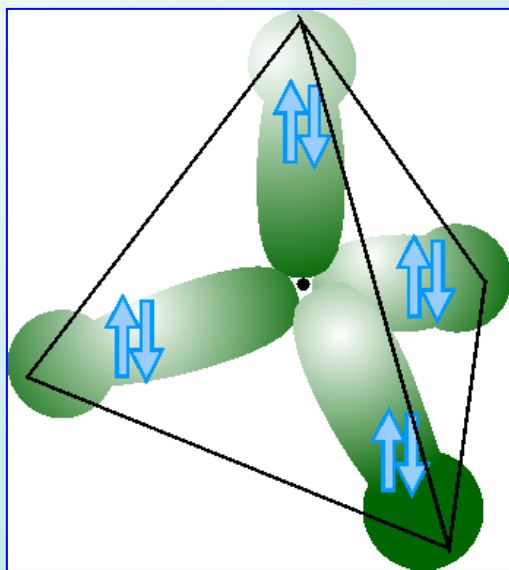
Bond wave functions are formed by summing atomic wave functions. Bonds formed by combining antiparallel spins are favored. For  $H_2$ , the molecular orbital has a lower energy than the atomic orbitals, so is stable.

## Bonds of carbon

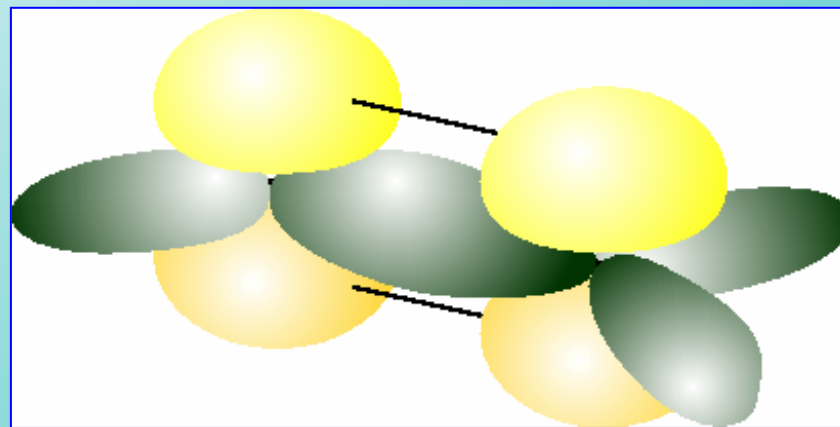
Carbon has one empty, and two 1-electron filled  $2p$  orbitals, giving four valence electrons. In order to explain the symmetrical chemical behavior of molecules like methane, we have to have four identical orbitals in tetrahedral symmetry. In order to provide these, a mixing of orbitals occurs, to give four  $sp^3$  hybrid orbitals (left). This involves promotion of 1  $2s$  electron to the vacant  $2p$  orbital, hence  $sp^3$ .



Figs. from Atkins, The Elements of Physical Chemistry



In methane, each  $sp^3$  forms a  $\sigma$  bond with a  $1s$  atom of H



In ethylene (ethene), the double-bond is made up of a  $\sigma$  and a  $\pi$  bond.

## Take-home message on bonds.

1. Bonding orbitals can take up quite complicated shapes. Extended  $\pi$ -bonding occurs in molecules like cytochromes, chlorophylls, flavins, nucleic acid bases, tryptophan, etc. The electrons in these extended orbitals roam over the entire coordinated  $\pi$  system.
2. Transitions between energy levels in molecules can occur between orbitals of different type. The change in electron distribution results in an electrical **dipole difference** between the ground and excited states, as discussed in the earlier part of the course. When the orbital is asymmetric, as in an extended  $\pi$  system, the excited state can remain in the  $\pi$ -orbital, but will have a different eigenfunction and eigenvalue, and so a different orbital “shape”. This also gives rise to an excited state dipole.
3. Normally, molecular orbitals are at lowest energy when they are filled by two electrons of antiparallel spin. If an electron is removed (for example, by oxidation), or an extra electron added (for example, by reduction), the lone electron is not spin-coupled, and therefore acts as a magnet. The magnetic effect arises from the unpaired spin, and the magnetic dipole results from the angular momentum of the electron in its orbital.