Lecture 6: Introductory Quantum Theory
  • Wave Equation, Allowed Energies, Wavelengths

Lecture 7: Properties of waves and shapes of electron atomic orbitals
  • Shapes of Waves
  • Representations of Orbitals

Lecture 8: Energies and Orbitals in Many-electron atoms
What does the wave equation tell us?

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = E \psi \]

Solving the wave equation for a particular potential energy function tells us

1. The wavefunction, \( \psi \).
2. A value for the energy, \( E \).

The wavefunction describes the properties of an electron bound by potential energy. But how are the properties of waves described?

We can understand something about the properties of electron waves by looking at waves in other situations.
Energy, Frequency, Wavelength - Worked Example

E.g. Calculate the energy of red light

Referring to the previous diagram, \( \lambda = 750\text{nm} \). The energy is simply

\[
E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{750 \times 10^{-9}} \left( \frac{J \cdot m}{s^2} \right) = 2.65 \times 10^{-19} \text{J}
\]

E.g. Calculate the energy and wavelength of an x-ray of frequency \( 10^{18}\text{s}^{-1} \).

The energy is \( E = h\nu = 6.626 \times 10^{-34} \times 10^{18} \left( J \cdot s \cdot s^{-1} \right) = 6.63 \times 10^{-16} \text{J} \)

and the wavelength is \( \lambda = \frac{c}{\nu} = \frac{3 \times 10^8}{10^{18}} \left( \frac{m \cdot s}{s^2} \right) = 3 \times 10^{-10} \text{m} = 0.3 \text{nm} \)
E.g. What wavelength of light will excite an electron in a hydrogen atom from $n=1$ to $n=3$?

First, calculate the energy difference for $Z = 1$, $n = 3$, $m = 1$

$$\Delta E = -Z^2 E_R \left( \frac{1}{n^2} - \frac{1}{m^2} \right) = -1 \times 2.18 \times 10^{-18} \times \left( \frac{1}{9} - \frac{1}{1} \right) = 1.94 \times 10^{-18} \text{ J}$$

Now, calculate the wavelength corresponding to that energy

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{1.94 \times 10^{-18} \left( \frac{J \text{ s} m \text{ s}^{-1}}{J} \right)} = 1.02 \times 10^{-7} \text{ m}$$

or 102 nm. This wavelength lies in the ultraviolet range.

This is an example of an atomic spectral line, which was part of the early evidence for quantum effects in nature. We will examine these in more detail in Lectures 8 & 9.
Atomic Spectroscopy - Alternative Working

E.g. What wavelength of light will excite an electron in a hydrogen atom from \(n=1\) to \(n=3\)?

First, equate the energy difference for \(Z = 1\), \(n = 3\), \(m = 1\) to the photon energy

\[
\frac{hc}{\lambda} = -Z^2 E_R \left( \frac{1}{n^2} - \frac{1}{m^2} \right)
\]

\[\Rightarrow \lambda = \frac{hc}{Z^2 E_R \left( \frac{1}{n^2} - \frac{1}{m^2} \right)} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{2.18 \times 10^{-18} \times \left( \frac{1}{1} - \frac{1}{9} \right)} = 1.02 \times 10^{-7} m
\]

This alternative is included because it also shows the form of the equation used (empirically) by Moseley in 1913 to fit his x-ray spectral lines (see lecture 5).
Atomic Spectrum of Hydrogen

Quantum mechanics can be used to explain atomic line spectra through these two relationships, which had previously been figured out *empirically*. That atomic *visible* line spectra of hydrogen fall into *series* had been known since Balmer in 1885 showed that they followed the equation

\[ \frac{1}{\lambda} = R \left( \frac{1}{n^2} - \frac{1}{2^2} \right) \]

where \( R = \frac{E_R}{hc} \).

This series describes absorption or emission from hydrogen atoms with electrons in the 3rd, 4th, 5th, etc... energy levels dropping to the 2nd allowed level.

Other series occur at higher (*ultraviolet*)

\[ \frac{1}{\lambda} = R \left( \frac{1}{n^2} - \frac{1}{1^2} \right) \]

and at lower energies (*infrared*)

\[ \frac{1}{\lambda} = R \left( \frac{1}{n^2} - \frac{1}{3^2} \right) \]
E.g.1. Waves in one dimension: Waves on a (guitar) string

The guitar string is bounded at each end, and oscillates with a particular frequency. The only waves that can be sustained by a string are those with zero amplitude at each end. These are called nodes.

Amplitude is the magnitude of the displacement from the average position. It can be positive (up) or negative (down).

In other words, the distance between the nodes (half-wavelength) must divide into the total length of the guitar string an integer number of times.

These are known as standing waves or stationary states or normal modes of the string.
E.g.1. Waves in one dimension: Waves on a (guitar) string

The lowest frequency mode, \( L = \frac{\lambda}{2} \), is called the fundamental frequency, \( \nu \), and has nodes only at the ends.

The first harmonic is the next lowest frequency, and has one node at the mid-point: \( L = \lambda \). The frequency is twice that of the fundamental, \( 2\nu \).

The second harmonic has two nodes between the end-points, and its frequency is 3 times the fundamental, \( 3\nu : \lambda = \frac{2L}{3} \).

Etc., etc.

As with all waves, wavelength and frequency are related by \( \lambda = \frac{\text{constant}}{\nu} \).
E.g.2. Waves in two dimensions: Modes of a drumhead

Standing waves can also be generated on a surface or thin membrane. A drumhead has a fixed perimeter, and oscillations on this surface lead to more complicated patterns of displacement and nodes.

First, consider the *fundamental mode* of the membrane. It is analogous to the fundamental of a vibrating string, and the diameter of the drum is $\lambda/2$. The whole drumhead oscillates above and below the plane with an amplitude defined by the maximum displacement.

These waves can be represented as a *contour plot*, or simply as lobes of positive (above the plane) and negative (below the plane) displacement. The fundamental oscillates between positive and negative with a frequency, $\nu$. The whole drum is either + or -.
Mechanics of Waves on a Surface

The *fundamental*.  

Like 1-D waves, the higher-order harmonic oscillations in higher dimensions also have nodes (lines in 2-D) where the drumhead *never* moves.

The nodes are lines in the plane of the circumference of the drum.
Mechanics of Waves on a Surface

Membranes can also generate asymmetric standing waves of various kinds.

In the simplest kind of harmonic the membrane is halved, making a linear node.

In another, it is quartered, giving two linear nodes at right angles.

These normal modes are described mathematically as orthogonal. This simply means that you can’t create one of them by combining any two or more of the others.
Electrons as Waves in Three Dimensions

The wavefunctions that describe electrons are three-dimensional waves. They have similar properties and features as one- and two-dimensional waves. i.e. Positive and negative lobes, and nodes (which are planes in 3-D).

The quantum description of an electron is simply a standing wave in three dimensions.

Like the modes of a drumhead, standing waves or stationary states in 3-D may be spherically symmetric or asymmetric.

We can use a contour plot or lobe representation to describe an electron wave, but it is need simple representations of 3-D waves.
Spherically Symmetric Wavefunctions

The lowest energy \((n=1)\) solution of the wave equation for the hydrogen atom corresponds to one, spherically symmetric, wavefunction. The shape of the wavefunction is described by the equation

\[
\psi(r) = \exp\left(-\frac{r}{\rho}\right)
\]

The wavefunction only depends on distance from the nucleus, \(r\).

The Bohr radius, \(= 0.528\text{Å}\)

\(\psi\) is a maximum at the nucleus.

This wavefunction can be represented as a graph of amplitude versus radial distance from the nucleus.

This wavefunction is called the 1s orbital and corresponds to an energy

\[
E_1 = -E_R = -2.18 \times 10^{-18} \text{ J}
\]
The 1s Orbital

This orbital can be represented as a radial function, or as gradient or contour or simply as a lobe.

This plot shows the amplitude of the 1s wavefunction, plotted as a function of distance, $r$, away from the nucleus. The maximum amplitude is at the nucleus.

or as gradient or contour

The intensity of the shading indicates the amplitude of the wavefunction, which is a maximum at the nucleus and decreases with increasing $r$. Only 1/4 of the wavefunction is represented here.

or simply as a lobe.

The spherical lobe indicates the sign of the wavefunction, and its radius is an indication of how far the electron extends from the nucleus. (This will be quantified later.)

Note that there are no nodes in the 1s orbital.
Spherically Symmetric Orbitals

Higher energy solutions to the wave equation have more than one wavefunction. Like drums in 2-D, these can be radially symmetrical or not. Higher energy wavefunctions have more nodes (and shorter wavelengths). The nodes of the radially symmetric wavefunctions are the surfaces of spheres.

\[ n=1 \quad 1s \quad n=2 \quad 2s \quad n=3 \quad 3s \quad n=4 \quad 4s \]

The lobe depiction of each of these s orbitals is a sphere, whose radius increases with quantum number \( n \). Nodes are only seen in cross-section.
Boundary Conditions

Unlike a drumhead or a string, an electron is not fixed at its perimeter or ends by a mechanical device. An electron wave is bounded by the potential energy function which is not an abrupt step, but a smooth function. For the hydrogen atom this bounding potential is $V(r) = -\frac{e^2}{r}$.

Higher energy (and higher quantum number) electron wavefunctions extend farther from the nucleus.
Non-spherical orbitals

The Schrödinger equation for the hydrogen atom also has solution wavefunctions that are *not spherically symmetrical*. These are easily seen to be analogous to the asymmetric drumhead modes. The simplest form consists of two lobes separated by a nodal plane, and is denoted a a p-orbital.

There are three (orthogonal) p-orbitals, one with lobes oriented along each of the x-, y-, and z-axes.

The lobe representing the angular dependence of the wavefunctions are described by functions known as *spherical harmonics*.
Orbital Angular Momentum

As we have seen from the de Broglie relation, electrons have both wavelength and momentum. Electrons bound in orbitals also have angular momentum, and this is described by two additional quantum numbers.

Like energy, angular momentum is quantised into discrete values.

- Spherically symmetric (s) orbitals have 0 angular momentum.

- Other orbitals have angular momenta that are integer multiples of $\frac{h}{2\pi}$. This integer is the orbital angular momentum quantum number, $l$.

- $l$ may take on any value between 0 and $n-1$;

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l$</th>
<th>Orbital Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>s orbital</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>s orbital</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>p orbitals</td>
</tr>
</tbody>
</table>

For $n = 1$, $l = 0$ - Only an s orbital.
For $n = 2$, $l = 0$ (s orbital) or 1 (p orbitals)
Orbital Angular Momentum

The *number* of orbitals with angular momentum $lh/2\pi$ is determined by their shape. This also determines the number of orthogonal wavefunctions - such as $p_x$, $p_y$, and $p_z$.

This is characterised by the *magnetic quantum number*, $m$ or $m_l$. $m$ can take any integer value between -$l$ and $l$, and describes the *orientation* of the orbital.

- For $l = 0$, $m = 0$ (one s orbital)
- For $l = 1$, $m = -1$, 0, +1 (three p orbitals)
- For a given $l$, there are always $2l+1$ orbitals

In hydrogen-like (one electron) atoms, the energy of the wavefunction depends only on the principal quantum number, $n$. Thus for $n = 1$, there is one wavefunction (1s), for $n = 2$ there are four *degenerate* wavefunctions - 2s, 2$p_x$, 2$p_y$, 2$p_z$.

Quantum states or wavefunctions of equal energy are referred to as *degenerate*. 
3p and 3d Orbitals

When \( n = 3 \), then \( l \) can be 0 (one 3s orbital),

\( l = 1 \) (three 3p orbitals)

3p orbitals have the same shape and designation as 2p orbitals (3p\(_x\), 3p\(_y\), 3p\(_z\)), but have an extra spherical node.

or \( l = 2 \) (d-orbitals). 3d orbitals have more lobes than 2p orbitals, and their shape is obviously different.

For d-orbitals, \( m \) may take on five values:

\[
\begin{align*}
 m &= -2 \\
 m &= -1 \\
 m &= 0 \\
 m &= 1 \\
 m &= 2
\end{align*}
\]

3d orbitals have four lobes. The lobes point along pair of axes (d\(_{x^2-y^2}\)), or between axes (d\(_{xy}\), d\(_{xz}\), d\(_{yz}\)) or along the z axis (d\(_{z^2}\); The donut in \( m=0 \) is like two lobes).
Higher $n$ and $l$...

Higher principal quantum numbers and higher orbital angular momentum quantum numbers lead to more nodes and more lobes.

As $l$ increases, the orbitals are denoted s, p, d, f, g, h,...

E.g.

$n = 5 \quad l = 2 \quad m = 0 \quad (5d_z^2)$

$n = 4 \quad l = 3 \quad m = 0 \quad (4f_z^3)$

There are $2x3+1 = 7$ f orbitals, each with 8 lobes.

s, p, d & f are named for historical reasons - g, h,... just continue the alphabet
The Born Hypothesis - Electron Density

Charge (electron) density is proportional to the square of the wavefunction $\psi$. This means that $\psi^2$ is equivalent to the probability of finding an electron at a particular point in space. $\psi^2$ is always positive, so this removes the complication of the sign of the amplitude of the wave. Squaring $\psi$ changes lobe shape slightly, but the general features are the same.

E.g.
- $2p_z$ orbital - same number of lobes and nodes
- $3d_{yz}$ - same number of lobes and nodes
Meaning of the Lobes Representation

Because electrons are not bound within a perimeter, the radial part of all wavefunctions decays \textit{exponentially} towards 0 as \( r \to \infty \).

This means the electron density \textit{also decays exponentially towards 0}, so that there is a finite charge density even at a very large distance from the nucleus. (There is a finite probability of finding an electron at a large distance from the nucleus.)

Lobes are commonly drawn to represent \textit{surfaces of constant probability}. E.g. The surface within which the probability of finding an electron is 95%; Alternatively the surface that contains 95% of the electronic charge density.

The probability is a function of radial distance only, so the size or extent of the lobes varies with probability \textit{but not the shape}.

To see more orbital shapes, check the “Grand Table of Orbitals” on the CHEM1101 web site. You can also download an orbital calculating and rendering program, and calculate different orbitals yourself.
Experimental Observation

Orbital shapes are one of the unexpected predictions of quantum theory. The experimental observable is electron density, which can be obtained from x-ray diffraction experiments on crystals.

The electron density in the $3d_{2}$ orbital of Cu in Cu$_2$O has been measured in this way, with the lobes clearly visible in the results. This provides a powerful confirmation of the predictions of quantum theory. [Nature 401, 49 - 52 (1999)]

http://www.nature.com/cgi-taf/DynaPage.taf?file=/nature/journal/v401/n6748/full/401049a0_r.html
Summary

You should now be able to

- Identify the key features of waves in 1-3 dimensions -- displacement, amplitude, nodes
- Understand the representations of waves as cross-sectional graphs, contour plots and lobe representations
- Explain the meaning of the orbital quantum numbers, $n$, $l$, $m$, and the designation of orbitals as e.g. 1s, 3d, 4p, 4f...
- Recognise the shapes of atomic orbitals in these representations
- Understand how the wavefunction relates to electron charge density
- Explain why the size of the electron increases with energy.

Next Lecture

- Quantum theory
  - Many-electron atoms.
  - Electronic Structure and the Periodic Table.