Quantum Mechanics & Atomic Structure (Chapter 11)

Quantum mechanics: Microscopic theory of light & matter at molecular scale and smaller.

Atoms and radiation (light) have both wave-like and particle-like properties.

Wave theory of light: light waves interfere

Wavelength (nm, cm or m)

Propagation in x-direction $\rightarrow$

Velocity of wave: $v = \nu \lambda$

$\nu = \text{frequency of wave (Hz } \text{ or } \text{s}^{-1})$

In vacuum: $v = c = 3.00 \times 10^8 \text{ m s}^{-1}$.

Wave number $= \# \text{ of wavelengths per cm}: \tilde{\nu} = 1/\lambda \text{ (units cm}^{-1})$
Wave theory of light: light waves interfere

Constructive interference

Destructive interference
Wave theory of light: Electromagnetic waves

Light has electric and magnetic component.
**Quantum Mechanics & Atomic Structure (Chapter 11)**

**Wave theory of light: Electromagnetic waves**

**Different wavelengths/frequencies of light:**

<table>
<thead>
<tr>
<th>Wavelength/nm</th>
<th>Frequency/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-3}$</td>
<td>$10^{20}$</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>$10^{18}$</td>
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<tr>
<td>$10$</td>
<td>$10^{16}$</td>
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<td>$10^{6}$</td>
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<tr>
<td>$10^{13}$</td>
<td>$10^{4}$</td>
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</tbody>
</table>

- Gamma rays
- X rays
- Ultraviolet
- Visible
- Infrared
- Microwave
- Radio waves
Quantum Mechanics & Atomic Structure (Chapter 11)

Particle theory of light: Photoelectric effect

![Diagram of photoelectric effect with graph showing kinetic energy of ejected electron vs. frequency.](image)
Quantum Mechanics & Atomic Structure (Chapter 11)

Particle theory of light: Photoelectric effect

Observations:

1. Below threshold frequency, $\nu_0$, no electrons ejected.

2. If $\nu > \nu_0$, kinetic energy of electrons is proportional to $\nu$.

Einstein explained observations by assuming light is made up of particles, photons, each with energy $h\nu$.

$h = \text{Planck’s constant} = 6.626 \times 10^{-34} \text{ J s.}$
Example: The color of chlorophyll is due to its absorption of blue light of $\lambda = 435$ nm and red light of $\lambda = 680$ nm. What is the energy absorbed by chlorophyll if struck by 1 mole of photons of these wavelengths?
Bohr’s theory of hydrogen (H) emission spectrum: Light emitted by hot gas of H atoms was observed to have specific wavelengths (or frequencies). Frequencies fit to a formula:

Frequency of emitted light:

$$\nu = cR_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$R_H = \text{Rydberg constant} = 109,737 \text{ cm}^{-1} \quad c = \text{speed of light}$$

$$n_i, n_f \text{ are integers}: \text{Bohr interpreted them as quantum numbers corresponding to initial and final states of H atom.}$$

Formula often expressed in terms of wave number:

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$
Bohr’s theory of hydrogen (H) emission spectrum:

Particle (atom) has quantized energy levels. Energy changes by emission of light at a specific frequency, $\nu$.

$\Delta E = \text{change in energy of atom} = \text{energy of photon (} h \nu \text{)}$

Atom changes energy from $E_2$ to $E_1$ corresponds to emission of photon of frequency $\nu = (E_2 - E_1)/h$. 
Bohr’s theory of hydrogen (H) emission spectrum:

Assume electron (mass $m_e$) orbits nucleus with radius $r$:

Assume angular momentum of electron is quantized:

$$m_e vr = \frac{nh}{2\pi} \quad n = 1, 2, 3, \ldots$$

Balance of forces:

Centrifugal force

Electrostatic force

$$\frac{m_e V^2}{r} = \frac{e^2}{4\pi \varepsilon_0 r^2}$$

e = charge on electron

$\varepsilon_0$ = permittivity of free space
Bohr’s theory of hydrogen (H) emission spectrum:

Assume angular momentum of electron is quantized:

\[ m_e v_r = \frac{nh}{2\pi} \quad n = 1, 2, 3, \ldots \]

Balance of forces:

\[
\frac{m_e v^2}{r} = \frac{e^2}{4\pi \varepsilon_0 r^2}
\]

\( e = \) charge on electron \quad \varepsilon_0 = \) permittivity of free space

Squaring angular momentum:

\[ m_e^2 v^2 r^2 = \frac{n^2 h^2}{4\pi^2} \]

Substituting for \( v^2 \):

\[
\frac{m_e n^2 h^2}{4\pi^2 m_e^2 r^3} = \frac{e^2}{4\pi \varepsilon_0 r^2}
\]

Rearrange and solve for \( r \):

\[ r_n = n^2 r_1 \]

\[ r_1 = \frac{h^2 \varepsilon_0}{\pi m_e e^2} = 0.529 \text{ Å} \]

\[ 1 \text{ Å} = 1 \times 10^{-10} m \]
Bohr’s theory of hydrogen (H) emission spectrum:

\[ r_n = n^2 r_1 \]
\[ r_1 = \frac{\hbar^2 \varepsilon_0}{\pi m_e e^2} = 0.529 \text{ Å} \]
\[ 1 \text{ Å} = 1 \times 10^{-10} m \]

What is the energy, \( E_n \), for quantum number \( n \)? \((n = 1, 2, 3 \ldots)\)

Energy:
\[ E_n = \frac{m_e v^2}{2} - \frac{e^2}{4\pi\varepsilon_0 r} = -\frac{e^2}{8\pi\varepsilon_0 r} \] (using balance of forces)

Substituting for \( r_n \):
\[ E_n = -\frac{m_e e^4}{8\hbar^2 \varepsilon_0^2} \frac{1}{n^2} \quad n = 1, 2, 3, \ldots \]

\( E_n < 0 \), since energy of bound atom is lower than that of free electron and proton \((E = 0)\).

\[ \tilde{\nu} = \frac{\Delta E}{hc} = \frac{m_e e^4}{8ch^3 \varepsilon_0^2} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \]

\( R_H = 109,737 \text{ cm}^{-1} \)
Bohr’s model of H atom

Energy levels:

\[ E_n = -\frac{m_e e^4}{8\hbar^2 \varepsilon_0} \frac{1}{n^2} \quad n = 1, 2, 3, \ldots \]

\( E_n < 0 \), since energy of bound atom is lower than that of free electron and proton \((E = 0)\).

Photon emitted when there is transition from higher to lower energy level:

\[ \Delta E = E_1 - E_2 = -\frac{m_e e^4}{8\hbar^2 \varepsilon_0} \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = -\frac{3}{4} \left( \frac{m_e e^4}{8\hbar^2 \varepsilon_0} \right) \]

Frequency of emitted photon:

\[ \nu = \frac{\Delta E}{h} = \frac{3}{4} \frac{m_e e^4}{8\hbar^3 \varepsilon_0} \]
Bohr’s model of H atom

Photon emitted when there is transition from higher to lower energy level:

\[ \Delta E = E_1 - E_2 = -\frac{m_e e^4}{8\hbar^2 \varepsilon_0^2} \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = -\frac{3}{4} \left( \frac{m_e e^4}{8\hbar^2 \varepsilon_0^2} \right) \]

Frequency of emitted photon:

\[ \nu = \frac{\Delta E}{\hbar} = \frac{3}{4} \frac{m_e e^4}{8\hbar^3 \varepsilon_0^2} \]

\[ \frac{m_e e^4}{8\hbar^3 \varepsilon_0^2} = 3.3 \times 10^{15} \text{ s}^{-1} \quad \rightarrow \quad \nu = \frac{3}{4} \left( 3.3 \times 10^{15} \text{ s}^{-1} \right) = 2.5 \times 10^{15} \text{ s}^{-1} \quad (\text{Hz}) \]

In wave numbers:

\[ \tilde{\nu} = \frac{\nu}{c} = \frac{2.5 \times 10^{15} \text{ s}^{-1}}{3.0 \times 10^{10} \text{ cm/s}} = 82,303 \text{ cm}^{-1} \]

Wave length:

\[ \lambda = \frac{1}{\tilde{\nu}} = 1.21 \times 10^{-5} \text{ cm} = 121 \text{ nm} \]

Ultraviolet region
de Broglie Postulate: Matter has wave-like properties

Energy of photon: \( E = h \nu \)    Momentum of photon: \( p = E / c \)

Then: \( p = h \nu / c = h / \lambda \)  **Suppose this also holds for matter.**

Then wavelength associated with particle, such as electron:

\[
\lambda = h / p = h / mv
\]

\( m = \text{mass of particle} \quad \nu = \text{velocity} \)

Example: What is \( \lambda \) for electron moving at \( \nu = 100 \text{ m s}^{-1} \)?
\( m_e = 9.109 \times 10^{-31} \text{ kg.} \)
Electron microscope: practical application of wave-like property of electron

**Human eye:** Objects closer than \( \approx 0.2 \text{ mm} \) cannot be seen as separate objects.

**Light microscope:** Objects closer than \( \approx \) shortest wavelength of visible light cannot be resolved, so \(< 400 \text{ nm} \) invisible.

**Electrons:** Not hard to have electrons with \( \lambda \ll 400 \text{ nm} \).

\[
\lambda = \frac{h}{m_e v} \quad \lambda \text{ small if } v \text{ large.}
\]

Accelerate electrons to large \( v \) in electrostatic field:

kinetic energy of electrons = \( m_e v^2/2 = \) energy of field = \( eV \)

\( e = \) charge on electron = \( 1.602 \times 10^{-19} \text{ C} \)

**Velocity of electron:** \( v = \sqrt{\frac{2eV}{m_e}} \)  ---> **Wavelength:** \( \lambda = \frac{h}{\sqrt{2m_e eV}} \)

Example: What is \( \lambda \) for electron accelerated by 1000 \( V \)?
Heisenberg Uncertainty Principle

\( \Delta x = \) uncertainty in knowledge of position of particle.

\( \Delta p = \) uncertainty in knowledge of momentum of particle.

Heisenberg: \[ \Delta x \Delta p \geq \frac{h}{4\pi} \]

If we know \( \Delta x \) is small, \( \Delta p \geq \frac{h}{4\pi \Delta x} \) is large.

Rough argument: We cannot know position of particle better than \( \lambda \) of light we use to “see” it. So \( \Delta x \approx \lambda \). While “seeing” particle, some momentum is transferred to it, \( \Delta p \approx h/\lambda \). This means at best: \( \Delta x \Delta p \approx h \).

Example: Radius of lowest energy orbit of H atom = 0.529 Å. Assuming we know the position of the electron in this orbit to accuracy of 1% of radius, what is uncertainty in its velocity?
Heisenberg Uncertainty Principle

$\Delta x =$ uncertainty in knowledge of position of particle.

$\Delta p =$ uncertainty in knowledge of momentum of particle.

Heisenberg: $\Delta x \Delta p \geq \frac{h}{4\pi}$

Also energy-time uncertainty: $\Delta E \Delta t \geq \frac{h}{4\pi}$

$\Delta E =$ uncertainty in particle’s energy.

$\Delta t =$ time during which we observe particle.

We can only know a particle’s energy exactly, $\Delta E \to 0$, if we observe it for infinitely long time.
Schrödinger Equation: Wave Equation for Matter

In one-dimension (x-direction): Time-independent equation:

\[
\frac{-\hbar^2}{8\pi^2m} \frac{d^2\Psi}{dx^2} + V\Psi = E\Psi \quad \text{E = total energy of particle}
\]

\( V = \text{potential energy, } m = \text{particle’s mass, } \hbar = \text{Planck’s constant} \)

\( \Psi(x) = \text{wave function for particle} \)

Classical Mechanics: kinetic energy + potential energy = E

\[
\frac{-\hbar^2}{8\pi^2m} \frac{d^2}{dx^2}
\]

Associate \( \frac{-\hbar^2}{8\pi^2m} \frac{d^2}{dx^2} \) with kinetic energy.

\( E = \text{energy of system (particle), found by solving equation with appropriate boundary conditions} \).
Schrödinger Equation: Wave Equation for Matter

What is wave function?

$\Psi(x)$ is in general a complex function (contains $i = \sqrt{-1}$)

$|\Psi|^2(x)$ is real and represents probability density: probability of finding particle between $x$ and $x + dx$ is $|\Psi|^2(x)dx$

Three restrictions on meaningful wave function:

1. $\Psi(x)$ must be single valued at any $x$, because we can have only 1 probability $|\Psi|^2(x)$, at point $x$. Cannot have:

2. $\Psi(x)$ must be finite at any $x$, since probability $|\Psi|^2(x)$ is finite.

3. $\Psi(x)$ must be smooth and continuous. Cannot have:
**Schrödinger Equation: Example**

*Polyenes*: molecules with delocalized $\pi$ electrons; play critical role in vision and photosynthesis.

In polyene, C-C bonds alternate with C=C bonds. Simplest polyene is butadiene: $H_2C = CH - CH = CH_2$. Butadiene has 4 $\pi$ electrons.

**What is the electronic spectrum of a polyene?**

We assume:
1. Polyene is linear
2. Electrons move freely in polyene and hit “wall” at the ends.
3. Each electron moves independently of others.

To find wavelength of light polyene absorbs, we calculate energy levels of $\pi$ electron.
Schrödinger Equation: Example

What is the electronic spectrum of a polyene?

We assume:
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To find wavelength of light polyene absorbs, we calculate energy levels of $\pi$ electron.

Schrödinger Equation:

We seek $E$ and $\Psi(x)$ (wave function) for particle.
**Particle in a box**

Potential, $V$

- $V = \infty$
- $V = 0$

$L = \text{length of polyene}$

Particle (electron) free to move anywhere in box, where $V = 0$.

**Schrödinger Equation**:

$$\frac{-h^2}{8\pi^2m} \frac{d^2\Psi}{dx^2} + V\Psi = E\Psi$$

We seek $E$ and $\Psi(x)$ (wave function) for particle.

**Boundary conditions**: Particle cannot be outside the box. At boundary, probability of finding particle = 0.

$$\Rightarrow \quad \Psi^2(x = 0) = \Psi^2(x = L) = 0, \quad \text{or} \quad \Psi(0) = \Psi(L) = 0$$

Start with a general form for $\Psi(x)$:

$$\Psi(x) = A\sin(kx) + B\cos(kx) \quad A, B, k = \text{constants}$$
Particle in a box

Boundary conditions: Particle cannot be outside the box. At boundary, probability of finding particle = 0.

\[ \Psi^2(x = 0) = \Psi^2(x = L) = 0, \quad \text{or} \quad \Psi(0) = \Psi(L) = 0 \]

Start with a general form for \( \Psi(x) \):

\[ \Psi(x) = Asin(kx) + Bcos(kx) \quad A, B, k = \text{constants} \]

\( x = 0 \): \( \Psi(0) = 0 = Asin(k0) + Bcos(k0) = B \)

So \( B \) must be 0. Then \( \Psi(x) = Asin(kx) \)

\( x = L \): \( \Psi(L) = 0 = Asin(kL) \)

Then \( kL = n\pi \quad n = 1, 2, ... \)  
So: \( k = \frac{n\pi}{L} \quad n = 1, 2, ... \)

And: \( \Psi(x) = Asin(kx) = Asin(n\pi x/L) \quad n = 1, 2, 3, ... \)
Particle in a box

Then $kL = n\pi$, $n = 1, 2, \ldots$. So: $k = n\pi/L$, $n = 1, 2, \ldots$

And: $\Psi(x) = A\sin(kx) = A\sin(n\pi x/L)$, $n = 1, 2, 3, \ldots$

What is $A$? Particle must be in box, so $\int_0^L \psi^2(x)dx = 1$

Solving for $A$: $A = \sqrt{2/L}$

Then wave function for each state $n$:

$\Psi_n(x) = \sqrt{2/L} \sin(n\pi x/L)$, $n = 1, 2, 3, \ldots$

To find energy levels, use Schrödinger Equation:

Inside box, $V = 0$: $\frac{-\hbar^2}{8\pi^2 m} \frac{d^2\Psi}{dx^2} = E\Psi$
Particle in a box

Then wave function for each state \( n \):

\[
\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad n = 1, 2, 3, \ldots
\]

To find energy levels, use Schrödinger Equation:

Inside box, \( V = 0 \):

\[
\frac{-\hbar^2}{8\pi^2 m} \frac{d^2\Psi}{dx^2} = E\Psi
\]

Then:

\[
\frac{n^2\hbar^2}{8mL^2} \left(\sin\left(\frac{n\pi x}{L}\right)\right) = E \sin\left(\frac{n\pi x}{L}\right)
\]

Energy level for each state \( n \):

\[
E_n = \frac{n^2\hbar^2}{8mL^2}, \quad n = 1, 2, 3, \ldots
\]
Particle-in-box solutions:

1. Lowest energy of particle (“ground state energy”):
   \[ E_1 = \frac{\hbar^2}{8mL^2} \neq 0 \]. We get classical energy minimum (0) with large particle mass, \( m \), or length of box, \( L \).

2. \( \Psi(x) \) can be + or -, but \( \Psi^2(x) \) is always positive, since it is a probability.

3. Energy levels are quantized. This is always the case for bound states, which are restricted in space.

**Node**: point where \( \Psi(x) = 0 \): no possibility of finding particle at node.
Spectra of Polyenes:

Consider butadiene: \( \text{H}_2\text{C} = \text{CH} - \text{CH} = \text{CH}_2 \) 4 \( \pi \) electrons

Energy levels: \( E_n = \frac{n^2\hbar^2}{8mL^2} \) \( m \) = mass of electron
\( L \) = length of polyene

We have 4 electrons, each with “spin” up or down. What are the two lowest energy states of butadiene?

Pauli exclusion principle: no 2 electrons occupy same state.

Energy level, \( n \)

\[
\begin{array}{c}
\text{Energy} \\
1 \\
2 \\
3 \\
\end{array}
\]

Lowest energy for 4 electrons

Next lowest energy

Lowest energy transition takes electron from \( n = 2 \) to \( n = 3 \).
Spectra of Polyenes

In general, for polyene with N carbon atoms, there are $N\pi$ electrons.

**Lowest energy:** Fill lowest $N/2$ levels.

**Lowest energy transition:** Electron in level $N/2 \rightarrow N/2 + 1$

**Energy change for transition:**

$$\Delta E = \frac{(N/2 + 1)^2 h^2}{8mL^2} - \frac{(N/2)^2 h^2}{8mL^2} = (N + 1) \frac{h^2}{8mL^2}$$

What is wavelength of light absorbed in this transition?

$$\Delta E = h\nu = \frac{hc}{\lambda} \quad \Rightarrow \quad \lambda = \frac{hc}{\Delta E} = \frac{8mL^2c}{h(N + 1)}$$

Consider butadiene (N=4): What is wavelength of photon absorbed for transition?

Need L: 2 C=C bonds (each 1.35 Å), 1 C-C bond (1.54 Å), 2 “ends” (radius of C atom is $\approx 0.77$ Å).
Spectra of Polyenes

Consider butadiene (N=4): What is wavelength of photon absorbed for transition?

Need L: 2 C=C bonds (each 1.35 Å), 1 C-C bond (1.54 Å), 2 “ends” (radius of C atom is ≈ 0.77 Å).

\[ L = 2 \times 1.35 \text{ Å} + 1 \times 1.54 \text{ Å} + 2 \times 0.77 \text{ Å} = 5.78 \text{ Å}. \]

\[ \lambda = \frac{8mL^2c}{h(N + 1)} = \frac{8(9.11 \times 10^{-31} \text{ kg})(5.78 \times 10^{-10} \text{ m})^2(3.00 \times 10^8 \text{ m/s})}{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(4 + 1)} \]

\[ \lambda = 2.20 \times 10^{-7} \text{ m} = 220 \text{ nm} \]

Experimental result is 217 nm! (UV light)
Schrödinger Equation for Hydrogen Atom

In 3-dimensions:
\[ -\frac{\hbar^2}{8\pi^2 m_e} \left( \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V(x,y,z)\Psi = E\Psi(x,y,z) \]

\( r = \text{distance of electron from proton} = (x^2 + y^2 + z^2)^{1/2} \).

\( V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \)

Express Schrödinger equation in spherical polar coordinates:

\[ x = r \sin \theta \cos \varphi \]
\[ y = r \sin \theta \sin \varphi \]
\[ z = r \cos \theta \]

In spherical polar coordinates: \( \Psi(r, \theta, \varphi) = R(r)\Theta(\theta)\Phi(\varphi) \)
Schrödinger Equation for Hydrogen Atom

In spherical polar coordinates: \( \Psi(r, \theta, \varphi) = R(r)\Theta(\theta)\Phi(\varphi) \)

3 quantum numbers arise from solving Schrödinger equation:

- \( n \) = principal quantum number.
- \( l \) = angular momentum quantum number.
- \( m_l \) = magnetic quantum number; determines orientation of wave function in space.

What are possible values of \( n \), \( l \) and \( m_l \)?

- \( n = 1, 2, 3, \ldots \) establishes energy of atom, as in Bohr model.
- For given \( n \), \( l = 0, 1, 2, \ldots, n-1 \) so \( n \) different values of \( l \).
- For given \( l \), \( m_l = -l, -l + 1, \ldots, 0, \ldots, l - 1, l \) so \( 2l + 1 \) values.

Example: \( n = 2 \), \( l = 0 \) or \( 1 \)

- \( l = 0 \) \( m_l = 0 \)
- \( l = 1 \) \( m_l = -1, 0, +1 \)
Schrödinger Equation for Hydrogen Atom

\( n = 1, 2, 3, \ldots \) establishes energy of atom, as in Bohr model.

For given \( n, \ell = 0, 1, 2, \ldots, n-1 \) so \( n \) different values of \( \ell \).

For given \( \ell, m_\ell = -\ell, -\ell + 1, \ldots, 0, \ldots, \ell - 1, \ell \) so \( 2\ell + 1 \) values.

Example: \( n = 2, \ell = 0 \) or 1

\[
\begin{align*}
\ell &= 0 & m_\ell &= 0 \\
\ell &= 1 & m_\ell &= -1, 0, +1
\end{align*}
\]

Terminology:

**Orbital**: Wavefunction specified by values of \( n, \ell, m_\ell \). Orbitals labeled by shell and subshell.

**Shell**: Orbitals with same \( n \) form a shell. \( n = 1 \ 2 \ 3 \ 4 \)

**Subshell**: Orbitals with same \( n \) but different \( \ell \) form subshell. \( \ell = 0 \ 1 \ 2 \ 3 \ 4 \)

Subshell: \( s \ p \ d \ f \ g \)
Schrödinger Equation for Hydrogen Atom

Energy of H atom from Schrödinger equation:

\[ E_n = -\frac{m_e e^4}{8\hbar^2 \varepsilon_0^2} \frac{1}{n^2} \quad n = 1, 2, 3, \ldots \] (same as for Bohr model)

\[ \Psi(r, \theta, \varphi) = R(r)\Theta(\theta)\Phi(\varphi) \] listed in Table 11.2 of text for many orbitals.

Consider first distance of electron from nucleus, \( R(r) \):

\[ 4\pi r^2 R^2(r) = \text{probability of finding electron in spherical shell at } r. \]

Radial distribution function
Radial Distribution Functions for Hydrogen Atom

- Peak at 0.529 Å, Bohr radius
- Node: electron cannot be found here

- $n = 1, l = 0$
- $n = 2, l = 0$
- $n = 2, l = 1$
Angular Wavefunction: Shapes of Orbitals

s orbitals: not dependent on $\theta, \phi$: “spherically symmetric”

p orbitals: equivalent “dumbbell”-shaped orbitals of different orientation.

Each p orbital has same energy: degenerate

Node in $yz$-plane
Node in $xz$-plane
Node in $xy$-plane
Schrödinger Equation for Many-Electron Atoms

Cannot solve Schrödinger eq. exactly for many-electron atom. Wavefunction still labeled by \((n, l, m_l)\).

Electron configurations:

H-atom: Energy depends only on \(n\):

\[ 1s < 2s = 2p < 3s = 3p = 3d < ... \]

Increasing energy

For many-electron atom, energy depends on \(n\) \& \(l\):

\[ 1s < 2s < 2p < 3s < 3p < 4s < 3d < ... \]
What are quantum numbers for atomic ground state?

Filling orbitals:

H atom: electron in 1s orbital. Also spin, \( m_s = -1/2 \) or \(+1/2\).

Quantum numbers of electron \((n, l, m_l, m_s)\):
\[(1, 0, 0, 1/2) \text{ or } (1, 0, 0, -1/2)\]

Pauli Principle: No 2 electrons have the same set of quantum numbers.

He: Ground state is 1s\(^2\). Since 2 spins have opposite sign, no magnetic moment: diamagnetic.

Li: 3 electrons, ground state is 1s\(^2\)2s. Li has 1 valence electron (like H atom).

Valence electrons are in outermost shell (highest \(n\)) of atom; mainly responsible for chemical bonds.
What are quantum numbers for atomic ground state?

C: Ground state is $1s^22s^22p^2$. How are electrons arranged in p orbital?

3 ways to arrange 2 valence electrons in 3 p-orbitals:

\[
\begin{array}{ccc}
\uparrow \downarrow & \_ & \_ \\
2p_x & 2p_y & 2p_z \\
\end{array}
\text{ or } \begin{array}{ccc}
\uparrow \downarrow & \_ & \_ \\
2p_x & 2p_y & 2p_z \\
\end{array}
\text{ or } \begin{array}{ccc}
\_ & \_ & \_ \\
2p_x & 2p_y & 2p_z \\
\end{array}
\]

(All other arrangements are equivalent to these.)

Lowest energy decided by Hund’s rule.

Hund’s Rule: When $>1$ electron enters set of degenerate levels, most likely arrangement is one with greatest number of parallel spins: So for C-atom:

\[
\begin{array}{ccc}
\uparrow \uparrow & \_ & \_ \\
2p_x \hspace{1cm} 2p_y \hspace{1cm} 2p_z \\
\end{array}
\]

C is paramagnetic: 2 unpaired electrons of same spin.