Modern Physics (PHY 251)
Lecture 25

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• The time independent Schroedinger equation – potential well in 3 dim

Textbook: Sections 6.8 (last lecture), 7.2 - 7.3 -7.4-7.8 (derivations, optional)
Sect. 7.5, 7.6, 7.7
The Time Independent Schroedinger Equation Solutions: the square well potential

Coulomb vs Square Well potential
Particle confinement in Quantum Mechanics results in a discrete (quantized) spectrum of energies.

Exercise:
Determine a normalization constant C, using the normalization condition of the wavefunction. Answer: 

\[ C = \sqrt{\frac{2}{a}} \]
The infinite square well potential - solutions of the Schrödinger equation and their interpretations.

The first four eigenfunctions (blue) and probability functions (red) for the infinite square-well potential problem. (The amplitudes of each function are arbitrarily scaled to give the same maximum amplitude.)

\[
\Psi_n(x, t = 0) = \psi_n(x) = \sqrt{\frac{2}{a}} \sin \left( \frac{n\pi}{a} x \right)
\]

\[
P_n(x, t) = \frac{2}{a} \sin^2 \left( \frac{n\pi}{a} x \right)
\]

\[
\bar{x} = \frac{a}{2} \quad \text{average position}
\]

\[
\bar{p} = 0 \quad \text{average momentum}
\]

Exercise (practice example):
Calculate the average position and average momentum for a given n-state.
The infinite square well potential - solutions of the Schroedinger equation and their interpretations.

The first few eigenvalues of an infinite square potential:

\[ E_n = \frac{n^2 \hbar^2}{8ma^2} \]

\[ n = \pm 1, \pm 2, \pm 3, \ldots \]
Quantum Mechanics in Three Dimensions (Cartesian coordinates)
Quantum Mechanics in Three Dimensions

- **Schroedinger equation in 1-dimension**
  
  - Time dependent
    
    \[- \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x,t) + V(x,t) \Psi(x,t) = i\hbar \frac{\partial}{\partial t} \Psi(x,t)\]
  
  - Time independent
    
    \[- \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V(x) \psi(x) = E \psi(x)\]
    
    \[\Psi(x,t) = \psi(x)e^{-i\omega t}, \quad \omega = E / \hbar\]

- **Schroedinger equation in 3-dimensions**

  \[\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \text{Laplacian}\]

  - Time dependent
    
    \[- \frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r},t) + V(\vec{r},t) \Psi(\vec{r},t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r},t)\]

  - Time independent
    
    \[- \frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r})\]
    
    \[\Psi(\vec{r},t) = \psi(\vec{r})e^{-i\omega t}, \quad \omega = E / \hbar\]
Particle in a 3-dimensional Box

Classically:
a particle would rattle around inside such a box

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

\[ V(\vec{r}) = 0 \text{ for } 0 < x, y, z < L \]

\[ V(\vec{r}) = \infty \text{ for } x, y, z \leq 0, \ x, y, z \geq L \]

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) = -\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \psi(\vec{r}) = E\psi(\vec{r}) \]

Spacial wave function separable:

\[ \psi(\vec{r}) = \psi(x, y, z) = \psi_1(x)\psi_2(y)\psi_3(z) \]
Particle in a 3-dimensional Box

\[-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) = -\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \psi(\vec{r}) = E \psi(\vec{r}) \quad \psi(\vec{r}) = \psi(x, y, z) = \psi_1(x)\psi_2(y)\psi_3(z)\]

\[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_1(x)\psi_2(y)\psi_3(z) - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} \psi_1(x)\psi_2(y)\psi_3(z) - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} \psi_1(x)\psi_2(y)\psi_3(z) =
\]

\[= E \psi_1(x)\psi_2(y)\psi_3(z)\]

\[-\frac{\hbar^2}{2m} \frac{1}{\psi_1(x)} \frac{\partial^2 \psi_1(x)}{\partial x^2} - \frac{\hbar^2}{2m} \frac{1}{\psi_2(y)} \frac{\partial^2 \psi_2(y)}{\partial y^2} - \frac{\hbar^2}{2m} \frac{1}{\psi_3(z)} \frac{\partial^2 \psi_3(z)}{\partial z^2} = E \]

\[-\frac{\hbar^2}{2m} \frac{1}{\psi_1(x)} \frac{\partial^2 \psi_1(x)}{\partial x^2} = E_1 \quad E_1 + E_2 + E_3 = E \]

\[-\frac{\hbar^2}{2m} \frac{1}{\psi_2(y)} \frac{\partial^2 \psi_2(y)}{\partial y^2} = E_2 \quad E_1, E_2, E_3 – separation constants \]

\[-\frac{\hbar^2}{2m} \frac{1}{\psi_3(z)} \frac{\partial^2 \psi_3(z)}{\partial z^2} = E_3 \quad \text{(represent energy of motion along Cartesian axes } x, y, z)\]

We solved this type of equations before …..
Particle confinement in Quantum Mechanics results in a discrete (quantized) spectrum of energies.

The infinite square well potential

\[ \psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) \]

\[ E_n = \frac{n^2 h^2}{8ma^2} , \quad n = 1, 2, 3, \ldots \]

Particle with mass \( m \): e.g. proton or neutron inside a nucleus
Particle in a 3-dimensional Box

\[ \psi_{1,n_1}(x) = C_1 \sin \left( \frac{n_1 \pi x}{L} \right), \quad p_{x,n_1} = n_1 \frac{\pi \hbar}{L}, \quad E_{1,n_1} = n_1^2 \frac{\pi^2 \hbar^2}{2mL^2}, \quad n_1 = 1, 2, 3, \ldots \]

\[ \psi_{2,n_2}(y) = C_2 \sin \left( \frac{n_2 \pi y}{L} \right), \quad p_{y,n_2} = n_2 \frac{\pi \hbar}{L}, \quad E_{2,n_2} = n_2^2 \frac{\pi^2 \hbar^2}{2mL^2}, \quad n_2 = 1, 2, 3, \ldots \]

\[ \psi_{3,n_3}(z) = C_3 \sin \left( \frac{n_3 \pi z}{L} \right), \quad p_{z,n_3} = n_3 \frac{\pi \hbar}{L}, \quad E_{3,n_3} = n_3^2 \frac{\pi^2 \hbar^2}{2mL^2}, \quad n_3 = 1, 2, 3, \ldots \]

\[ \psi_{n_1n_2n_3}(\vec{r}) = \psi_{n_1n_2n_3}(x,y,z) = C_1C_2C_3 \sin \left( \frac{n_1 \pi x}{L} \right) \sin \left( \frac{n_2 \pi y}{L} \right) \sin \left( \frac{n_3 \pi z}{L} \right) \]

A constant \( C \) can be determined from the normalization condition:

\[ \iiint |\psi_{n_1n_2n_3}(x,y,z)|^2 \, dx \, dy \, dz = 1 \quad C = \left( \frac{2}{L} \right)^{3/2} \]

\[ E_{n_1n_2n_3} = E_{n_1} + E_{n_2} + E_{n_3} = \frac{\hbar^2}{8mL^2} \left[ n_1^2 + n_2^2 + n_3^2 \right] \]

Three quantum numbers are needed to specify the quantum condition (three independent degrees of freedom for a particle in space)
Particle in a 3-dimensional Box

\[ E_{n_1n_2n_3} = E_{n_1} + E_{n_2} + E_{n_3} = \frac{\pi^2 \hbar^2}{2mL^2} \left[ n_1^2 + n_2^2 + n_3^2 \right] \]

- **Ground state:** \( n_1 = 1, n_2 = 1, n_3 = 1 \)
  \[ E_{111} = \frac{3\pi^2 \hbar^2}{2mL^2} \]

- **First excited states:** \( n_1 = 2, n_2 = 1, n_3 = 1 \)
  \( n_1 = 1, n_2 = 2, n_3 = 1 \)
  \( n_1 = 1, n_2 = 1, n_3 = 2 \)

  \[ E_{211} = E_{121} = E_{112} = \frac{6\pi^2 \hbar^2}{2mL^2} \]

Degenerate states = different states of the same energy
Particle in a 3-dimensional Box

\[ E_{n_1n_2n_3} = E_{n_1} + E_{n_2} + E_{n_3} = \frac{\pi^2 \hbar^2}{2mL^2} \left[ n_1^2 + n_2^2 + n_3^2 \right] \]

Table 8.1 Quantum Numbers and Degeneracies of the Energy Levels for a Particle Confined to a Cubic Box*

<table>
<thead>
<tr>
<th>(n_1)</th>
<th>(n_2)</th>
<th>(n_3)</th>
<th>(n^2)</th>
<th>Degeneracy</th>
</tr>
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<tr>
<td>1</td>
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<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
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<td>2</td>
<td>1</td>
<td>1</td>
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<td>1</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

*Note: \(n^2 = n_1^2 + n_2^2 + n_3^2\).
Particle in a 3-dimensional Box

\[ E_{n_1n_2n_3} = E_{n_1} + E_{n_2} + E_{n_3} = \frac{\pi^2 \hbar^2}{2mL^2} \left[ n_1^2 + n_2^2 + n_3^2 \right] \]

**Table 8.1 Quantum Numbers and Degeneracies of the Energy Levels for a Particle Confined to a Cubic Box**

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<th>Degeneracy</th>
</tr>
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<td>1</td>
<td>3</td>
<td>None</td>
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<td>6</td>
<td></td>
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<td>2</td>
<td>1</td>
<td>6</td>
<td></td>
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<td>1</td>
<td>1</td>
<td>6</td>
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<td>2</td>
<td>9</td>
<td>Threefold</td>
</tr>
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<td>2</td>
<td>1</td>
<td>9</td>
<td>Threefold</td>
</tr>
<tr>
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<td>1</td>
<td>3</td>
<td>11</td>
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<tr>
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<td>3</td>
<td>1</td>
<td>11</td>
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</tr>
<tr>
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<td>1</td>
<td>1</td>
<td>11</td>
<td></td>
</tr>
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<td>2</td>
<td>2</td>
<td>2</td>
<td>12</td>
<td>None</td>
</tr>
</tbody>
</table>

*Note: \(n^2 = n_1^2 + n_2^2 + n_3^2\).*
Particle in a 3-dimensional Box

Figure 8.4: Probability density (unnormalized) for a particle in a box: (a) ground state, \(|\Psi_{111}|^2\); (b) and (c) first excited states, \(|\Psi_{211}|^2\) and \(|\Psi_{121}|^2\). Plots are for \(|\Psi|^2\) in the plane \(z = \frac{1}{2}L\). In this plane, \(|\Psi_{112}|^2\) (not shown) is indistinguishable from \(|\Psi_{111}|^2\).

\[
\psi_{n_1n_2n_3}(\vec{r}) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_1\pi}{L}x\right) \sin\left(\frac{n_2\pi}{L}y\right) \sin\left(\frac{n_3\pi}{L}z\right)
\]

\(n_3 = 1, \ z = L/2\)
Extra material

How to find the most or least likely location of a particle (maximum or minimum probability)

Maxima and Minima of Functions of Two Variables

Locate relative maxima, minima and saddle points of functions of two variables. Several examples with detailed solutions are presented. 3-Dimensional graphs of functions are shown to confirm the existence of these points. More on Optimization Problems with Functions of Two Variables in this web site.

**Theorem**

Let $f$ be a function with two variables with continuous second order partial derivatives $f_{xx}$, $f_{yy}$ and $f_{xy}$ at a critical point $(a,b)$. Let

$$D = f_{xx}(a,b) f_{yy}(a,b) - f_{xy}^2(a,b)$$

a. If $D > 0$ and $f_{xx}(a,b) > 0$, then $f$ has a relative minimum at $(a,b)$.

b. If $D > 0$ and $f_{xx}(a,b) < 0$, then $f$ has a relative maximum at $(a,b)$.

c. If $D < 0$, then $f$ has a saddle point at $(a,b)$.

d. If $D = 0$, then no conclusion can be drawn.

http://www.analyzemath.com/calculus/multivariable/maxima_minima.html
Next:
Quantum Mechanics in Three Dimensions
(Spherical Coordinates)

Central Forces $V(r) = V(r)$

Example: Coulomb force in Hydrogen atom
Time Independent Schroedinger equation in 3-dimensions

\[ \Psi(\vec{r},t) = \psi(\vec{r})e^{-i\omega t}, \quad \omega = E / \hbar \]

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

- **Cartesian coordinates:**
  \[ \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \]
  \[ \psi(\vec{r}) = \psi(x,y,z) = \psi_1(x)\psi_2(y)\psi_3(z) \]

- **Spherical coordinates:**
  \[ \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \]

**Solution: wave function (central forces, V=V(r))**

\[ \psi(\vec{r}) = R(r)\Theta(\theta)\Phi(\phi) \]
Atomic Hydrogen and Hydrogen-Like Ions

Hydrogen atom:
1 proton + 1 electron

Hydrogen Like ions:
Z protons + A-Z neutrons + 1 electron

\[ Z = 1 \]

\[ Z > 1 \]

\[ V(r) = - \frac{kZe^2}{r} \]

Coulomb potential

3 quantum numbers describing electron’s state
(2 in addition to \( n \) quantum number from the Bohr model)

Examples:
- He\(^+\)
- Li\(^{2+}\)
Central Forces: \( V = V(r) \)

\[ \psi(\vec{r}) = R(r) \Theta(\theta) \Phi(\phi) \]

\[ \Theta(\theta) \Phi(\phi) = Y_{l}^{m_l}(\theta, \phi) \]

**Spherical harmonics**

**A well defined function**

\( l = 0, 1, 2, \ldots, n-1 \)

\(-l \leq m_l \leq l\)

\( l \) – orbital quantum number

\( m_l \) - magnetic quantum number

\[ \Psi_{nlm_l}(\vec{r}, t) \]

**Note:** Spherical harmonics: the same solution for all central forces, \( R(r) \) radial function (solution) depends on the functional form of the potential.

### Table 8.3 The Spherical Harmonics \( Y_{l}^{m_l}(\theta, \phi) \)

<table>
<thead>
<tr>
<th>( Y_{l}^{m_l}(\theta, \phi) )</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Y_{0}^{0} )</td>
<td>( \frac{1}{2\sqrt{\pi}} )</td>
</tr>
<tr>
<td>( Y_{1}^{0} )</td>
<td>( \frac{1}{2} \sqrt{\frac{3}{\pi}} \cdot \cos \theta )</td>
</tr>
<tr>
<td>( Y_{1}^{\pm 1} )</td>
<td>( \pm \frac{1}{2} \sqrt{\frac{3}{4\pi}} \cdot \sin \theta \cdot e^{\pm i\phi} )</td>
</tr>
<tr>
<td>( Y_{2}^{0} )</td>
<td>( \frac{1}{4} \sqrt{\frac{5}{\pi}} \cdot (3 \cos^2 \theta - 1) )</td>
</tr>
<tr>
<td>( Y_{2}^{\pm 1} )</td>
<td>( \pm \frac{1}{2} \sqrt{\frac{15}{4\pi}} \cdot \sin \theta \cdot \cos \theta \cdot e^{\pm i\phi} )</td>
</tr>
<tr>
<td>( Y_{2}^{\pm 2} )</td>
<td>( \frac{1}{4} \sqrt{\frac{15}{2\pi}} \cdot \sin^2 \theta \cdot e^{\pm 2i\phi} )</td>
</tr>
<tr>
<td>( Y_{3}^{0} )</td>
<td>( \frac{1}{4} \sqrt{\frac{7}{\pi}} \cdot (5 \cos^3 \theta - 3 \cos \theta) )</td>
</tr>
<tr>
<td>( Y_{3}^{\pm 1} )</td>
<td>( \pm \frac{1}{8} \sqrt{\frac{21}{\pi}} \cdot \sin \theta \cdot (5 \cos^2 \theta - 1) \cdot e^{\pm i\phi} )</td>
</tr>
<tr>
<td>( Y_{3}^{\pm 2} )</td>
<td>( \frac{1}{4} \sqrt{\frac{105}{2\pi}} \cdot \sin^2 \theta \cdot \cos \theta \cdot e^{\pm 2i\phi} )</td>
</tr>
<tr>
<td>( Y_{3}^{\pm 3} )</td>
<td>( \pm \frac{1}{8} \sqrt{\frac{35}{\pi}} \cdot \sin^3 \theta \cdot e^{\pm 3i\phi} )</td>
</tr>
</tbody>
</table>

The normalization is such that the integral of \( |Y_{l}^{m_l}|^2 \) over the surface of a sphere with unit radius is 1.
Physics interpretation of $l$ and $m_l$ quantum numbers

$\Theta(\theta)\Phi(\phi) = Y^m_l(\theta,\phi)$ – spherical harmonics

$l, m_l$ – quantum numbers for angular momentum only

\begin{align*}
L^2\Psi_{nlm}^l &= l(l+1)\hbar^2\Psi_{nlm}^l & l = 0,1,2,... \text{ n-1} \\
L_z\Psi_{nlm}^l &= m_l\hbar\Psi_{nlm}^l & m_l = 0,\pm 1,\pm 2,...,\pm l
\end{align*}

\textbf{Figure 8.7} (a) The allowed projections of the orbital angular momentum for the case $\ell = 2$. (b) From a three-dimensional perspective, the orbital angular momentum vector $\mathbf{L}$ lies on the surface of a cone. The fuzzy character of $L_x$ and $L_y$ is depicted by allowing $\mathbf{L}$ to precess about the $z$-axis, so that $L_x$ and $L_y$ change continually while $L_z$ maintains the fixed value $m_l\hbar$. 
Orbital Angular Momentum Operators and their Eigenvalues

\[ \vec{L} = \vec{r} \times \vec{p} \]

\[
L_x = yp_z - zp_y \quad L_{x,op} = yp_{z,op} - zp_{y,op} = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)
\]

\[
L_y = zp_x - xp_z \quad L_{y,op} = zp_{x,op} - xp_{z,op} = -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)
\]

\[
L_z = xp_y - yp_x \quad L_{z,op} = xp_{y,op} - yp_{x,op} = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)
\]

\[ L_{op}^2 = L_{x,op}^2 + L_{y,op}^2 + L_{z,op}^2 \]
Orbital Angular Momentum Operators and their Eigenvalues

Spherical coordinates:

\[ \vec{L} = \vec{r} \times \vec{p} \]

\[ L_{x,op} = i\hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \]

\[ L_{y,op} = i\hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \]

\[ L_{z,op} = -i\hbar \frac{\partial}{\partial \phi} \]

\[ L_{op}^2 = -\hbar^2 \left[ \frac{\partial}{\sin \theta \partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \]
The **Hydrogen-like atom** constitutes the central force problem

The wave function of a Hydrogen-like atom is given by:

\[
\Psi_{nlm_i}(\vec{r},t) = \psi_{nlm_i}(\vec{r})e^{i\omega t} = R_{nl}(r)Y_{l}^{m_i}(\theta,\phi)e^{i\omega t}
\]

The wave function of a Hydrogen-like atom is given by:

\[
\Psi_{nlm_i}(\vec{r},t) = \psi_{nlm_i}(\vec{r})e^{i\omega t} = R_{nl}(r)Y_{l}^{m_i}(\theta,\phi)e^{i\omega t}
\]

\[
\psi_{nlm_i}(\vec{r}) = \frac{2Z}{a_0n} \left( \frac{n-l-1}{2n[(n+l)!]} \right)^{\frac{3}{2}} \frac{r}{a_0n} \left( \frac{2Zr}{a_0n} \right)^{l+1} Y_{l}^{m_i}(\theta,\phi) e^{i\omega t}
\]

where

\[
a_0 = \frac{\hbar^2}{meke^2} = 0.529 \text{ Å}
\]

Bohr radius

**Electron is in a state described by three quantum numbers n, l and m_i**

Wave function expression for **reference only**, use tables instead (see next page)

Wave function: $\Psi_{nlm} (\mathbf{r}, t) = \psi_{nlm} (\mathbf{r}) e^{i\omega t} = R_{nl}(r) Y_{l}^{m_l} (\theta, \phi) e^{i\omega t}$

Electron is in a state described by three quantum numbers $n$, $l$ and $m_l$

Table 8.3 The Spherical Harmonics $Y_{\ell}^{m_l}(\theta, \phi)$

| $Y_{0}^{0}$ | $= \frac{1}{2\sqrt{\pi}}$ |
| $Y_{1}^{0}$ | $= \frac{1}{2} \sqrt{\frac{3}{\pi}} \cdot \cos \theta$ |
| $Y_{1}^{\pm 1}$ | $= \pm \frac{1}{2} \sqrt{\frac{3}{2\pi}} \cdot \sin \theta \cdot e^{\pm i\phi}$ |
| $Y_{2}^{0}$ | $= \frac{1}{4} \sqrt{\frac{5}{\pi}} \cdot (3 \cos^2 \theta - 1)$ |
| $Y_{2}^{\pm 1}$ | $= \pm \frac{1}{2} \sqrt{\frac{15}{2\pi}} \cdot \sin \theta \cdot \cos \theta \cdot e^{\pm i\phi}$ |
| $Y_{2}^{\pm 2}$ | $= \frac{1}{4} \sqrt{\frac{15}{2\pi}} \cdot \sin^2 \theta \cdot e^{\pm 2i\phi}$ |
| $Y_{3}^{0}$ | $= \frac{1}{4} \sqrt{\frac{7}{\pi}} \cdot (5 \cos^3 \theta - 3 \cos \theta)$ |
| $Y_{3}^{\pm 1}$ | $= \pm \frac{1}{8} \sqrt{\frac{21}{\pi}} \cdot \sin \theta \cdot (5 \cos^2 \theta - 1) \cdot e^{\pm i\phi}$ |
| $Y_{3}^{\pm 2}$ | $= \frac{1}{4} \sqrt{\frac{105}{2\pi}} \cdot \sin^2 \theta \cdot \cos \theta \cdot e^{\pm 2i\phi}$ |
| $Y_{3}^{\pm 3}$ | $= \pm \frac{1}{8} \sqrt{\frac{35}{\pi}} \cdot \sin^3 \theta \cdot e^{\pm 3i\phi}$ |

Table 8.4 The Radial Wavefunctions $R_{n\ell}(r)$ of Hydrogen-like Atoms for $n = 1, 2, \text{ and } 3$

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\ell$</th>
<th>$R_{n\ell}(r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>$\left( \frac{Z}{a_0} \right)^{3/2} \cdot 2 e^{-Zr/a_0}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\left( \frac{Z}{2a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$\left( \frac{Z}{2a_0} \right)^{3/2} \frac{Zr}{\sqrt{3} a_0} e^{-Zr/2a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\left( \frac{Z}{3a_0} \right)^{3/2} \cdot 2 \left[ 1 - \frac{2Zr}{3 a_0} + \frac{2}{27} \left( \frac{Zr}{a_0} \right)^2 \right] e^{-Zr/3a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$\left( \frac{Z}{3a_0} \right)^{3/2} \frac{4\sqrt{2}}{3} \frac{Zr}{a_0} \left( 1 - \frac{Zr}{6 a_0} \right) e^{-Zr/3a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>$\left( \frac{Z}{3a_0} \right)^{3/2} \frac{2\sqrt{2}}{27\sqrt{5}} \left( \frac{Zr}{a_0} \right)^2 e^{-Zr/3a_0}$</td>
</tr>
</tbody>
</table>

The normalization is such that the integral of $|Y_{\ell}^{m_l}|^2$ over the surface of a sphere with unit radius is 1.
The **Hydrogen-like atom** constitutes the central force problem

\[ \Psi(\vec{r}, t) = \psi(\vec{r}) e^{i\omega t} = R_n l(r) Y_l^m(\theta, \phi) e^{i\omega t} \]

Electron is in a state described by three quantum numbers \( n, l \) and \( m_l \)

Use tables

\[ a_0 = \frac{\hbar^2}{m_e k e^2} = 0.529 \, \text{Å} \]

Bohr radius

\[ E_n = -\frac{k e^2}{2a_0} \left( \frac{Z^2}{n^2} \right) \quad n = 1, 2, 3, \ldots \]

Ground state:

\[ E_1 = -\frac{k e^2}{2a_0} Z^2 = -(13.6 \, \text{eV}) Z^2 \]

**Important!**

- \( n \) principal quantum number
- \( l = 0, 1, 2, \ldots, (n-1) \) orbital quantum number
- \(-l \leq m_l \leq l\) magnetic quantum number

For hydrogen-like atoms the quantum numbers \( n, l(l+1) \) and \( m_l \) are associated with the “sharp” observables \( E, L^2 \) and \( L_z \)
Spectroscopic notation (chemistry):

- States with the same quantum number $n$ form a **shell**
- Shells are identified by letters K,L,M,… which designate the states for which $n=1,2,3,…$.
- States which have the same value of both $n$ and $l$ form a **subshell**
- The letters s,p,d,f,… are used to designate the states for which $l=0,1,2,3,…$

\[
\begin{align*}
n & = 1, 2, 3, \ldots \\
l & = 0, 1, 2, \ldots, (n - 1) \\
-l & \leq m_l \leq l \\
n, l, m_l & \text{ – integers}
\end{align*}
\]

<table>
<thead>
<tr>
<th>$n$</th>
<th>Shell Symbol</th>
<th>$\ell$</th>
<th>Shell Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K</td>
<td>0</td>
<td>s</td>
</tr>
<tr>
<td>2</td>
<td>L</td>
<td>1</td>
<td>p</td>
</tr>
<tr>
<td>3</td>
<td>M</td>
<td>2</td>
<td>d</td>
</tr>
<tr>
<td>4</td>
<td>N</td>
<td>3</td>
<td>f</td>
</tr>
<tr>
<td>5</td>
<td>O</td>
<td>4</td>
<td>g</td>
</tr>
<tr>
<td>6</td>
<td>P</td>
<td>5</td>
<td>h</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>


Practice @ home: Find

Z=1:

The lowest order wave functions are

<table>
<thead>
<tr>
<th>n</th>
<th>ℓ</th>
<th>m</th>
<th>$\Phi_m(\phi)$</th>
<th>$\Theta_{lm}(\theta)$</th>
<th>$R_{nl}(r)$</th>
<th>$\Psi_{nlm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>$\frac{1}{\sqrt{\pi a_o^3}}e^{-r/a_o}$</td>
<td>$\frac{1}{\sqrt{\pi a_o^3}}e^{-r/a_o}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2s</td>
<td>$\frac{1}{\sqrt{\pi a_o^3}}e^{-r/a_o}$</td>
<td>$\frac{1}{\sqrt{\pi a_o^3}}e^{-r/a_o}$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>2p</td>
<td>$\frac{1}{\sqrt{\pi a_o^3}}e^{-r/a_o}$</td>
<td>$\frac{1}{\sqrt{\pi a_o^3}}e^{-r/a_o}$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>±1</td>
<td>2</td>
<td>2p</td>
<td>$\frac{1}{\sqrt{\pi a_o^3}}e^{-r/a_o}$</td>
<td>$\frac{1}{\sqrt{\pi a_o^3}}e^{-r/a_o}$</td>
</tr>
</tbody>
</table>
(assumption: no spin)

Examples:

1. If \( n=1 \), then
   • \( l=0 \), and \( m_l =0 \)

2. If \( n=2 \), then
   • \( l=0 \), and \( m_l =0 \)
   • \( l=1 \), and \( m_l = -1,0,1 \)

3. If \( n=3 \), then
   • \( l=0 \), and \( m_l =0 \)
   • \( l=1 \), and \( m_l = -1,0,1 \)
   • \( l=2 \), and \( m_l = -2, -1,0,1,2 \)

and so on (n=1,2, .... Infinity)

In general, for a particle there are \( n^2 \) possible states. Every state is characterized by a set of 3 quantum numbers (\( n,l \) and \( m_l \))

<table>
<thead>
<tr>
<th>Quantum Numbers</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>principal quantum number</td>
</tr>
<tr>
<td>( l = 0,1,2,...,(n-1) )</td>
<td>orbital quantum number</td>
</tr>
<tr>
<td>(-l \leq m_l \leq l )</td>
<td>magnetic quantum number</td>
</tr>
</tbody>
</table>
Probability Densities: Hydrogen-like atoms

\[ |\psi_{211}(\vec{r})|^2 \]

\[ |\psi_{310}(\vec{r})|^2 \]

\[ |\psi_{320}(\vec{r})|^2 \]

Symmetric about z-axis

Figure 8.12  (a) The probability density \(|\psi_{211}|^2\) for a hydrogen-like 2\(p\) state. Note the axial symmetry about the z-axis. (b) and (c) The probability densities \(|\psi(\vec{r})|^2\) for several other hydrogen-like states. The electron “cloud” is axially symmetric about the z-axis for all the hydrogen-like states \(\psi_{n\ell m_\ell}(\vec{r})\).
Wave function: $\Psi_{nlm}(\vec{r}, t) = \psi_{nlm}(\vec{r})e^{i\omega t} = R_{nl}(r)Y_{lm}^{m}(\theta, \phi)e^{i\omega t}$

Electron is in a state described by three quantum numbers $n$, $l$ and $m_l$

Table 8.3  The Spherical Harmonics $Y_{\ell}^{m}(\theta, \phi)$

<table>
<thead>
<tr>
<th>$Y_{\ell}^{m}$</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_{0}^{0} = \frac{1}{2\sqrt{\pi}}$</td>
<td></td>
</tr>
<tr>
<td>$Y_{1}^{0} = \frac{1}{2\sqrt{\pi}} \cdot \cos \theta$</td>
<td></td>
</tr>
<tr>
<td>$Y_{1}^{\pm 1} = \frac{1}{2\sqrt{\pi}} \cdot \sin \theta \cdot e^{\pm i\phi}$</td>
<td></td>
</tr>
<tr>
<td>$Y_{2}^{0} = \frac{1}{4\sqrt{\pi}} \cdot (3 \cos^{2}\theta - 1)$</td>
<td></td>
</tr>
<tr>
<td>$Y_{2}^{\pm 1} = \frac{1}{4\sqrt{\pi}} \cdot \sin \theta \cdot \cos \theta \cdot e^{\pm i\phi}$</td>
<td></td>
</tr>
<tr>
<td>$Y_{2}^{\pm 2} = \frac{1}{4\sqrt{\pi}} \cdot \sin^{2}\theta \cdot e^{\pm 2i\phi}$</td>
<td></td>
</tr>
<tr>
<td>$Y_{3}^{0} = \frac{1}{4\sqrt{\pi}} \cdot (5 \cos^{3}\theta - 3 \cos \theta)$</td>
<td></td>
</tr>
<tr>
<td>$Y_{3}^{\pm 1} = \frac{1}{8\sqrt{\pi}} \cdot \sin \theta \cdot (5 \cos^{2}\theta - 1) \cdot e^{\pm i\phi}$</td>
<td></td>
</tr>
<tr>
<td>$Y_{3}^{\pm 2} = \frac{1}{4\sqrt{\pi}} \cdot \sin^{2}\theta \cdot \cos \theta \cdot e^{\pm 2i\phi}$</td>
<td></td>
</tr>
<tr>
<td>$Y_{3}^{\pm 3} = \frac{1}{8\sqrt{\pi}} \cdot \sin^{3}\theta \cdot e^{\pm 3i\phi}$</td>
<td></td>
</tr>
</tbody>
</table>

The normalization is such that the integral of $|Y_{\ell}^{m}|^2$ over the surface of a sphere with unit radius is 1.

Table 8.4  The Radial Wavefunctions $R_{n\ell}(r)$ of Hydrogen-like Atoms for $n = 1, 2, \text{ and } 3$

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\ell$</th>
<th>$R_{n\ell}(r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>$\left( \frac{Z}{a_0} \right)^{3/2} 2e^{-Zr/a_0}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\left( \frac{Z}{2a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right)e^{-Zr/2a_0}$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$\left( \frac{Z}{2a_0} \right)^{3/2} \frac{Zr}{\sqrt{3}a_0}e^{-Zr/2a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\left( \frac{Z}{3a_0} \right)^{3/2} 2 \left[ 1 - \frac{2Zr}{3a_0} + \frac{2}{27} \left( \frac{Zr}{a_0} \right)^2 \right]e^{-Zr/3a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$\left( \frac{Z}{3a_0} \right)^{3/2} \frac{4\sqrt{2}}{3} \frac{Zr}{a_0} \left[ 1 - \frac{Zr}{6a_0} \right]e^{-Zr/3a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>$\left( \frac{Z}{3a_0} \right)^{3/2} \frac{2\sqrt{2}}{27\sqrt{5}} \left( \frac{Zr}{a_0} \right)^2 e^{-Zr/3a_0}$</td>
</tr>
</tbody>
</table>
Probabilities (electron in hydrogen-like atoms)

State $n,l,m_l$:

- **Wave function:**
  \[
  \Psi_{nlm_l}(\vec{r},t) = \psi_{nlm_l}(\vec{r})e^{i\omega t} = R_{nl}(r)Y_l^{m_l}(\theta,\phi)e^{i\omega t}
  \]

- **Probability density:**
  \[
  P_{nlm_l}(\vec{r},t) = |\Psi_{nlm_l}(\vec{r},t)|^2 = |\psi_{nlm_l}(\vec{r})e^{i\omega t}|^2 = |R_{nl}(r)Y_l^{m_l}(\theta,\phi)|^2
  \]
  \[
  P_{nlm_l}(\vec{r},t)\,dV = |R_{nl}(r)Y_l^{m_l}(\theta,\phi)|^2 r^2 \sin \theta \, dr \, d\theta \, d\phi
  \]
  \[
  \int P_{nlm_l}(\vec{r},t)\,dV = \int |R_{nl}(r)Y_l^{m_l}(\theta,\phi)|^2 r^2 \sin \theta \, dr \, d\theta \, d\phi
  \]

Normalization condition:
\[
\int_{\text{total volume}} P_{nlm_l}(\vec{r},t)\,dV = \int_{0}^{\infty} \int_{0}^{\pi/2} \int_{0}^{2\pi} |R_{nl}(r)Y_l^{m_l}(\theta,\phi)|^2 r^2 \sin \theta \, dr \, d\theta \, d\phi = 1
\]

Radial probability density (see also next slide)

Def: \( P( r) = r^2 |R_{nl}(r)|^2 \)

Average \( r = \int_{0}^{\infty} rP_{nl}(r) \, dr \)

r position where an electron is **most likely** to be found:

Use the following condition: \( dP_{nl}(r)/dr = 0 \)
Example:
Ground state of the hydrogen-like atom

- Ground state: \( n = 1, l = 0, m_l = 0 \)

- Wave function of the electron in the ground state:

\[
\psi_{100}(\vec{r}) = R_{10}(r)Y_0^0(\theta, \phi)
\]

where:
\[
R_{10}(r) = \left( \frac{Z}{a_0} \right)^{3/2} 2e^{-Zr/a_0} \quad \text{and} \quad Y_0^0(\theta, \phi) = \frac{1}{2\sqrt{\pi}}
\]

(from tables)

- **Radial probability density** of the electron in the ground state:

\[
P_{100}(\vec{r}) dV = \left| \psi_{100}(\vec{r}) \right|^2 r^2 \sin\theta dr d\theta d\phi
\]

\[
\int \int \frac{1}{4\pi} \left( \frac{Z}{a_0} \right)^3 4e^{-2Zr/a_0} r^2 dr \sin\theta d\theta d\phi =
\]

\[
= \frac{1}{4\pi} \left( \frac{Z}{a_0} \right)^3 4e^{-2Zr/a_0} r^2 dr 4\pi = \frac{4Z^3}{a_0^3} e^{-2Zr/a_0} r^2 dr
\]

Radial probability density for the electron in ground state
Example:
Ground state \( (n=1, l=0, m_l=0) \) of the hydrogen-like atom

\[
\mathbf{P}(r) = r^2 |\mathbf{R}_{10}(r)|^2
\]
Practice problems (part of exam preparation)

Problem 1
Consider an atomic electron in the l=3 state. Calculate the magnitude $L^2$ of the total angular momentum and the allowed values of $L_z$.

Problem 2
Enumerate all states of the hydrogen atom corresponding to the principal quantum number $n=2$, giving the spectroscopic designation for each. Calculate energies of these states.

Problem 3
How many possible states are there for the
a) $n=3$ level
b) $n=4$ level
of hydrogen?

Problem 4
Calculate the probability that the electron in the ground state of hydrogen will be found outside the first Bohr radius.

Problem 5
Calculate the most probable distance of the electron from the nucleus in the ground state of hydrogen and compare this with the average distance.

Hint: $\int_0^\infty x^n e^{-x} \, dx = n!$
Next/Last lecture:
Spin, Atomic orbital electron configurations

The discovery of the electron spin, S.A. Goudsmit:
https://www.lorentz.leidenuniv.nl/history/spin/goudsmit.html
Final exam:
December 19, 2016 (Monday) 5:30pm-8pm
Place: Javits 102
Material: Lectures 1-25, Practice problems, Recitations, Homeworks

Thank you!