Lecture 18

Mar. 31, 2015

Announcement

Course webpage
http://highenergy.phys.ttu.edu/~slee/2402/

Textbook
Modern Physics, 2/E
Randall Harris, University of California, Davis
©2006 • Addison-Wesley • Cloth, 656 pp
Published 07/26/2007 • Instock

HW5 (due 3/31)
15, 18, 24, 28, 36
Quiz 2 (4/9)

Chapter. 7
QM in 3-dims & Hydrogen Atom

Outline:
• The Schrödinger Eq. in 3-Dimensions
• The 3D Infinite Well
• Energy Quantization & Spectral Lines in Hydrogen
• The Schrödinger Eq. for a Central Force
• Angular Behavior in a Central Force
• The Hydrogen Atom
• Radial Probability
• Hydrogen-like Atoms

Schedule

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<th>Saturday</th>
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<td>[Quiz.2: Ch.6/7]</td>
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<td>4/28</td>
<td>[No class]</td>
<td>5/9 Final Exam 4:300 - 7:00pm</td>
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<td>5/5</td>
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Note.1: Term paper presentation (10 min. = 8+2 (Q&A))
Note.2: Term paper due (S/S)
Schrodinger Equation in 3 Dimensions

\[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(x, y, z, t) + U(x, y, z)\Psi(x, y, z, t) = i\hbar \frac{\partial}{\partial t} \Psi(x, y, z, t) \]

**Kinetic Energy term**

Adopt the generic symbol from vector calculus

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

Bold face, \( \textit{r} \) : Cartesian (x,y,z) or Spherical Polar (r,θ,φ)

Schrödinger eq \( \nrightarrow \) coordinate-independent form

Stationary States in a 3-D Box

**“Factorization”**

\[ \psi(x, y, z) = F(x)G(y)H(z) \]

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

or

\[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) + U(x, y, z)\psi(x, y, z) = \frac{E}{3m/\hbar^2} \psi(x, y, z) \]

Stationary States in a 3-D Box

A particle bound in a box-shaped region by infinitely high potential well

\[ U(r) = \begin{cases} 0 & 0 < x < L_x, 0 < y < L_y, 0 < z < L_z \, \text{otherwise} \\ \infty & \text{otherwise} \end{cases} \]

The simplest 3-D bound system is infinite well!!

\[ \psi(x, y, z) = F(x)G(y)H(z) \]

\[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2 F}{\partial x^2} + \frac{\partial^2 G}{\partial y^2} + \frac{\partial^2 H}{\partial z^2} \right) + U(x, y, z)FGH = \frac{E}{FGH} \]

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

\[ f(x) \quad f(y) \quad f(z) \quad f(x,y,z) \]

… multiplying both side by \(-2m/\hbar^2\)
**Separation Done!!**

Each term should be “Constant”

\[
\frac{d^2F(x)}{dx^2} = C_x F(x), \quad \frac{d^2G(y)}{dy^2} = C_y G(y), \quad \frac{d^2H(z)}{dz^2} = C_z H(z),
\]

and

\[C_x + C_y + C_z = -\frac{2mE}{\hbar^2}\]

**Things now look rather familiar**

\[
\frac{d^2F(x)}{dx^2} = C_x F(x), \quad \frac{d^2G(y)}{dy^2} = C_y G(y), \quad \frac{d^2H(z)}{dz^2} = C_z H(z),
\]

and

\[C_x + C_y + C_z = -\frac{2mE}{\hbar^2}\]

The mathematical solution to the “x-equation" is thus

\[
\frac{d^2F(x)}{dx^2} = -k_x^2 F(x) \implies F(x) = A \sin k_x x + B \cos k_x x
\]

**Region I (0 < x < L)**

Since \(U(x) = 0\) here, the time-independent Schrödinger equation (4-8) is

\[
-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad \text{or} \quad \frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \psi(x)
\]

For convenience, let us make the following definition (which we very soon see is a wave number, thus the symbol):

\[
k = \sqrt{\frac{2mE}{\hbar^2}}
\]

Thus,

\[
\frac{d^2\psi(x)}{dx^2} = -k^2 \psi(x)
\]

\[F(L_x) = 0 \implies A \sin k_x L_x = 0 \implies k_x L_x = n_x \pi\]

**nx, ny, nz = Quantum Number**
Stationary States in a 3-D Box

The Solution

\[ \psi_{nx,ny,nz}(x, y, z) = A \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z} \]

Stationary States in a 3-D Box

Solution

\[ \psi_{nx,ny,nz}(x, y, z) = A \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z} \]

\[ E_{nx,ny,nz} = \frac{(n_x^2 \frac{L_x^2}{\hbar^2} + n_y^2 \frac{L_y^2}{\hbar^2} + n_z^2 \frac{L_z^2}{\hbar^2})}{2m} \]

example: \( L_x = 1, L_y = 2, L_z = 3 \)

The lowest energy (\( n_x=1, n_y=1, n_z=1 \))

\[ E_{1,1,1} = \left( \frac{1^2}{1^2} + \frac{1^2}{2^2} + \frac{1^2}{3^2} \right) \frac{\pi^2 \hbar^2}{2m} = \frac{49 \pi^2 \hbar^2}{72m} \]

Corresponding wave function:

\[ \psi_{1,1,1}(x, y, z) = A \sin \frac{\pi x}{L_x} \sin \frac{\pi y}{2} \sin \frac{\pi z}{3} \]

Suppose the box is as symmetric as possible (i.e. Cube)

\[ L_x = L_y = L_z = L \]

\[ E_{nx,ny,nz} = \frac{(n_x^2 \frac{L^2}{\hbar^2} + n_y^2 \frac{L^2}{\hbar^2} + n_z^2 \frac{L^2}{\hbar^2})}{2mL^2} \]

\[ \psi_{1,1,1} = A \sin \frac{3\pi x}{L} \sin \frac{3\pi y}{L} \sin \frac{3\pi z}{L} \]

\[ \psi_{5,1,1} = A \sin \frac{5\pi x}{L} \sin \frac{1\pi y}{L} \sin \frac{1\pi z}{L} \]

\[ \psi_{1,5,1} = A \sin \frac{1\pi x}{L} \sin \frac{5\pi y}{L} \sin \frac{1\pi z}{L} \]

\[ \psi_{1,1,5} = A \sin \frac{1\pi x}{L} \sin \frac{1\pi y}{L} \sin \frac{5\pi z}{L} \]
Sets of Q.N. for many allowed energies in the 3-D well

<table>
<thead>
<tr>
<th>( n_x, n_y, n_z )</th>
<th>( E_{n_x, n_y, n_z} )</th>
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<tbody>
<tr>
<td>1, 1, 1</td>
<td>3</td>
</tr>
<tr>
<td>2, 1, 1</td>
<td>6</td>
</tr>
<tr>
<td>1, 2, 1</td>
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<td>1, 1, 2</td>
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<td>2, 1, 2</td>
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<td>2, 2, 1</td>
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<tr>
<td>3, 1, 1</td>
<td>11</td>
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<tr>
<td>1, 3, 1</td>
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<tr>
<td>1, 1, 3</td>
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<td>2, 2, 2</td>
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<td>1, 2, 3</td>
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<td>2, 1, 3</td>
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<td>1, 3, 2</td>
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<td>3, 1, 2</td>
<td>14</td>
</tr>
<tr>
<td>3, 2, 1</td>
<td>14</td>
</tr>
</tbody>
</table>

These correspond to unique sets of Q.N. e.g. (111), (222)

E27 results from 4 different sets of Q.N.

Same E, but each sets of Q.N. corresponds to different wave function!!

\[ |\psi_{1,2,1}|^2 \]

\[ |\psi_{2,1,1}|^2 \]

\[ |\psi_{1,1,2}|^2 \]

Sets of Q.N.

Degeneracy in a cubic infinite well –

Equal E but different states

\[ |\psi_{1,2,1}|^2 \]

\[ |\psi_{2,1,1}|^2 \]

\[ |\psi_{1,1,2}|^2 \]

Degeneracy in a cubic infinite well –

Equal E but different states

So, E27 is said to be 4-fold degenerate!! & E3, E12 \( \rightarrow \) Nondegenerate!!

Such coincidence, different wave function having the same E, is called “degeneracy”

Toward the Hydrogen Atom

P.E. Well

\[ E = 0 \]

\[ U(r) \rightarrow (-) \text{ infinity } @ r = 0 \]

\[ U(r) \rightarrow \text{ zero } @ r = (+) \text{ infinity} \]
To calculate Prob., (e.g. normalization integral), we need the expression for the infinitesimal Volume element dV in spherical polar coordinates:

$$dV = (rd\theta)(r\sin\theta d\phi)(dr)$$

**Spherical Polar Coordinate system**

- $r$ = radius
- $\theta$ = polar angle b/w r and z-axis
- $\phi$ = azimuthal angle b/w x-axis and projection of r in x-y planes

**Cartesian-polar conversions**

$$\begin{align*}
  x &= r \sin \theta \cos \phi \\
  y &= r \sin \theta \sin \phi \\
  z &= r \cos \theta
\end{align*}$$

Best choice: *Cartesian-polar conversions* for simplicity.

**Toward the Hydrogen Atom**

Electron’s P.E. depends only on $r$; $u(r) = u(r)$

i.e. Not $(\theta, \phi)$

The force is necessarily along the radial direction and is known as a “central force”.

**Toward the Hydrogen Atom: Schrödinger equation in Spherical Polar Coordinates**

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

$$-\frac{\hbar^2}{2m} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \csc \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \csc^2 \theta \frac{\partial^2}{\partial \phi^2} \right] \psi(r, \theta, \phi) + U(r, \theta, \phi) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

(6-10)

$$\begin{align*}
  \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \csc \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \csc^2 \theta \frac{\partial^2}{\partial \phi^2} \psi(r, \theta, \phi) \\
  = -r^2 \frac{2m(E - U(r))}{\hbar^2} \psi(r, \theta, \phi)
\end{align*}$$