Today:
- Rest of the 3D rigid box
- The Hydrogen atom

Final Exam is on Wednesday, Dec. 14, 1:30pm-4pm in G1B20 (our classroom).
Allowed materials: One letter paper-sized, handwritten cheat-sheet and a calculator. (No cell-phones, PCs, textbooks, BBQs etc.)

Exam format: Similar to Exam 1-3 (all bubble; emphasis on understanding concepts)

Review: “Particle in rigid 3D box”

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

\(V(x,y,z) = 0\) inside; \(\infty\) outside.
Separation of variables approach:

\(\psi(x,y,z) = X(x)Y(y)Z(z)\)

Solutions:
\(X(x) = A \cdot \sin \frac{n\pi}{a} \cdot x, \quad k = n \cdot \frac{\pi}{a}, \quad E_x = \frac{\pi^2 \hbar^2}{2ma^2}, \quad n = 1,2,3,\ldots\)

And the total energy is:
\(E = E_x + E_y + E_z\)

Or for a cube \((a=b=c)\):
\(E = E_0(n_x^2 + n_y^2 + n_z^2), \quad E_0 = \frac{\pi^2 \hbar^2}{2ma^2}\)

2D box: Square of the wave function for \(n_x=n_y=1\)

2D box: Square of the wave function of selected excited states

Degeneracy
Sometimes, there are several solutions with the exact same energy. Such solutions are called ‘degenerate’.

<table>
<thead>
<tr>
<th>((n_x, n_y, n_z))</th>
<th>(E = E_0(n_x^2 + n_y^2 + n_z^2))</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>((222))</td>
<td>(12E_0)</td>
<td>1</td>
</tr>
<tr>
<td>((113)) or ((311))</td>
<td>(11E_0)</td>
<td>3</td>
</tr>
<tr>
<td>((122)) or ((212))</td>
<td>(9E_0)</td>
<td>3</td>
</tr>
<tr>
<td>((112)) or ((121))</td>
<td>(6E_0)</td>
<td>3</td>
</tr>
<tr>
<td>((111))</td>
<td>(3E_0)</td>
<td>1</td>
</tr>
</tbody>
</table>

Degeneracy of 1 means “non-degenerate”

\(E = 0\)

Q1:
The ground state energy of the 2D box of size \(L \times L\) is \(2E_0\), where \(E_0 = \frac{\pi^2 \hbar^2}{2mL^2}\) is the ground state energy of a 1D box of size \(L\).

\(E = E_0(n_x^2 + n_y^2)\)

What is the energy of the 1st excited state of this 2D box?

a) \(3E_0\)
b) \(4E_0\)
c) \(5E_0\)
d) \(8E_0\)
Q2: Imagine a 3D cubic box of sides \( L \times L \times L \). What is the degeneracy of the ground state and the first excited state?

Degeneracy of ground state

- Degeneracy of 1st excited state

a) 1, 1
b) 3, 1
c) 1, 3
d) 3, 3
e) 0, 3

\[ E = E_0 \left( n_x^2 + n_y^2 + n_z^2 \right) \]

\[ (\text{Coulomb potential; no time dependence}) \]

**Review Models of the Atom**

- Thomson – Plum Pudding
  - Why? Known that negative charges can be removed from atom.
  - Problem: Rutherford showed nucleus is hard core.

- Rutherford – Solar System
  - Why? Scattering showed hard core.
  - Problem: electrons should spiral into nucleus in \( \sim 10^{-11} \) sec.

- Bohr – fixed energy levels
  - Why? Fits to spectral lines of Hydrogen
  - Problem: No reason for fixed energy levels
    - Structure doesn’t fit physics

- deBroglie – electron standing waves
  - Why? Explains fixed energy levels
  - Problem: still only works for Hydrogen.

- Schrödinger – quantum wave functions
  - Why? Explains everything!
  - Problem: None (except that it’s hard to understand)

**What is Schrödinger’s model of the hydrogen atom?**

Electron is cloud of probability whose wave function \( \Psi(x,y,z,t) \) is the solution to the Schrödinger equation:

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

where:

\( V(x,y,z) = -\frac{Zke^2}{r} \)

(\( Z \) is the number of protons in the nucleus)

**Schroedinger’s Solutions for Hydrogen**

If you understand the 1D quantum well (and how we went from 1D to 3D), then it is easy for you to understand Schrödinger’s hydrogen atom!

All that’s really different is the potential \( V(r) \propto \frac{1}{r} \) (Coulomb)

OK. Mathematically it is a bit ‘involved,’ For now, focus on the concept and let someone else do the math for you!

**Can get rid of time dependence and simplify:**

Equation in 3D, looking for \( \Psi(x,y,z,t) \):

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

Since \( V(x,y,z) \) not function of time:

\[
\Psi(x,y,z,t) = \psi(x,y,z)e^{-iEt/\hbar}
\]

Time independent Schrödinger Equation (analogous to 1D):

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

**Quick note on vector derivatives**

Laplacian (or ‘Laplace operator’) in cartesian coordinates:

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

Same thing! Just different coordinates.

Laplacian in spherical coordinates:

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

3D Schrödinger with Laplacian (coordinate free):

\[
\frac{-\hbar^2}{2m} \nabla^2 \psi(r) + V(r)\psi(r) = E\psi(r)
\]
Since potential is spherically symmetric ($V(r) = -Zke^2/r$), easier to solve w/ spherical coords:

Time-independent Schrödinger eqn. in spherical coordinates:

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

$$\psi(r, \theta, \phi) = R(r) f(\theta) g(\phi) e^{-iEt/\hbar}$$

Using separation of variables:

$$\psi(r, \theta, \phi) = R(r) f(\theta) g(\phi)$$

Once we have $\psi(r, \theta, \phi)$ we also know the time-dependent solution:

$$\Psi(r, \theta, \phi, t) = R(r) f(\theta) g(\phi) e^{-iEt/\hbar}$$

Done!

Q3:

In 1D (electron in a wire):

we got quantization from applying boundary conditions in terms of $x$.

In 3D: have 3 degrees of freedom.

Boundary conditions in terms of $r, \theta, \phi$

What are the boundary conditions on the wave function $\psi$ in $r$?

A. $\psi$ must go to 0 at $r=0$
B. $\psi$ must go to 0 at $r=\infty$
C. $\psi$ at $r=\infty$ must equal to $\psi$ at $r=0$, but value can be non-zero.
D. A and B
E. A, B, and C

Q4:

In 1D (electron in a wire):

Have 1 quantum number ($n$).

Need to specify value of $n$ to know what state electron is in.

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)e^{-iEt/\hbar}$$

In 3D, now have 3 degrees of freedom (ignore spin):

3 sets of boundary conditions in terms of $r, \theta, \phi$

How many quantum numbers are there in 3D?

In other words, how many numbers do you need to specify unique wave function? And why?

a. 1
b. 3
c. 4
d. 6
e. 9

The Hydrogen atom

$\rightarrow$ 3D-Schrödinger with $V(r) = -ke^2/r$

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(r, \theta, \phi) + ke^2 \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

with:

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

Use separation of variables:

$$\psi(r, \theta, \phi) = R(r) f(\theta) g(\phi)$$

Once we have $\psi(r, \theta, \phi)$ we also know the time-dependent solution:

$$\Psi(r, \theta, \phi, t) = R(r) f(\theta) g(\phi) e^{-iEt/\hbar}$$

Done!

Comparing H atom & Infinite Square Well

Infinite Square Well: (1D)

$V(x) = 0$ if $0<x<L$

$$\psi_{n}(x) = \frac{\pi}{2L} \sin\left(\frac{n\pi x}{L}\right)$$

$\Psi_{n}(x,t) = \psi_{n}(x)e^{-iEt/\hbar}$

Energy eigenstates:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

Wave functions:

$$\psi_{n}(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$\Psi_{n}(x,t) = \psi_{n}(x)e^{-iEt/\hbar}$

$V_{\text{ISW}}(x) = \begin{cases} 0 & \text{if } 0<x<L \\ \infty & \text{otherwise} \end{cases}$

Energy eigenstates:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

Wave functions:

$$\psi_{n}(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$\Psi_{n}(x,t) = \psi_{n}(x)e^{-iEt/\hbar}$$

H Atom: (3D)

$V(r) = -\frac{ke^2}{r}$

Energy eigenstates:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

Wave functions:

$$\psi_{n}(r, \theta, \phi) = R_{n}(r)f_{\ell}(\theta)g_{m}(\phi)$$

$$\Psi_{n}(r, \theta, \phi, t) = \psi_{n}(r, \theta, \phi)e^{-iEt/\hbar}$$

$R_{n}(r)$: generalized Laguerre polynomials

$f_{\ell}(\theta)$: spherical harmonic functions

$g_{m}(\phi)$: spherical harmonic functions

$p = \frac{\hbar}{m}$
Answers to clicker questions

Q1: C; nx=1, ny=2 or nx=2 ny=1s
Q2: C
  Ground state = 1,1,1 : E_1 = 3E_0
  1st excited state: 2,1,1 ; 1,2,1 ; 1,1,2 : all same E_2 = 6 E_0
Q3: B
  \psi must be 'normalizable', so needs to go to zero at r=\infty
  (Also makes sense physically: not probable to find electron there)
  NOTE: \psi(0)=const. is sufficient! Probability of finding it around r=0 is proportional to: 4\pi r^2 |\psi|^2.
Q4: B