Quantum Mechanics and Atomic Physics

Lecture 13:

The S.E. in 3D

http://www.physics.rutgers.edu/ugrad/361

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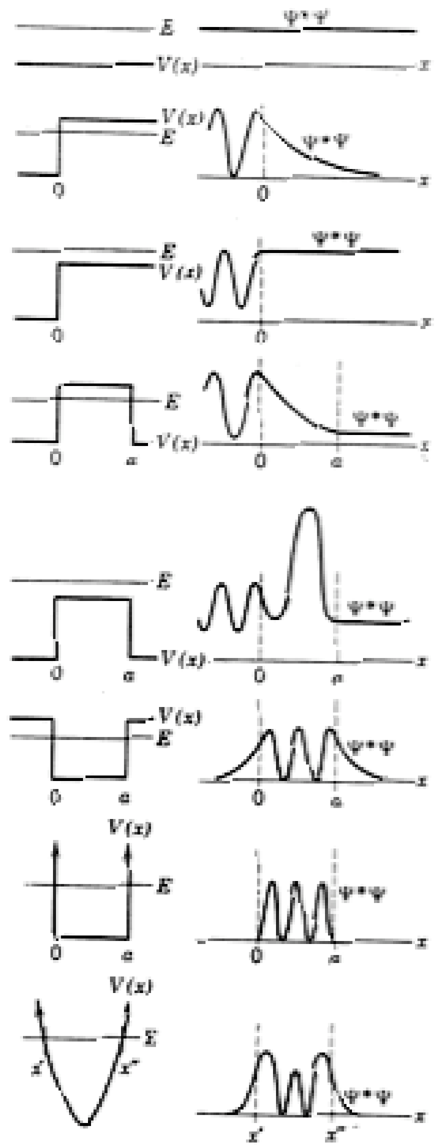
- Until now we considered S.E. in only 1D

- To examine truly realistic problems we need to consider solutions to S.E. in 3D

Table 6-2. A Summary of the Systems Studied in Chapter 6

Name of System	Physical Example	Potential and Total Energies	Probability Density	Significant Feature
Zero potential	Proton in beam from cyclotron			Results used for other systems
Step potential (energy below top)	Conduction electron near surface of metal			Penetration of excluded region
Step potential (energy above top)	Neutron trying to escape nucleus			Partial reflection at potential discontinuity
Barrier potential (energy below top)	α particle trying to escape Coloumb barrier			Tunneling
Barrier potential (energy above top)	Electron scattering from negatively ionized atom			No reflection at certain energies
Finite square well potential	Neutron bound in nucleus			Energy quantization
Infinite square well potential	Molecule strictly confined to box			Approximation to finite square well
Simple harmonic oscillator potential	Atom of vibrating diatomic molecule			Zero-point energy



Eisberg & Resnick

The S.E. in 3D

- S.E.:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(x,y,z)\psi = E\psi$$

or

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

- The Laplacian:

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

- Our first application will be the 3D analog of the infinite square well….

“Particle in a box”

$V=0$ inside box so $0 \le x \le a$
$0 \le y \le b$
$0 \le z \le c$

$V = \infty$ outside box

$\Rightarrow \psi = 0$ outside box

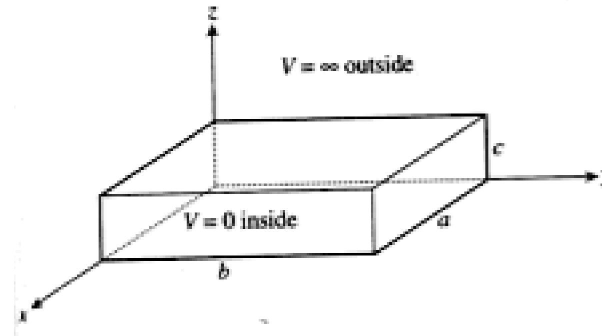


FIGURE 6.1 Infinite potential box.

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- Inside the box:

$\Rightarrow$ Inside box:

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

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

$$-\frac{\hbar^2}{2m}\left(YZ\frac{\partial^2}{\partial x^2}X + XZ\frac{\partial^2}{\partial y^2}Y + XY\frac{\partial^2}{\partial z^2}Z\right) = E \cdot XYZ$$

Particle in a box, con't

- Replace the partial derivatives with ordinary derivatives
- Divide through by Ψ=XYZ

$$-\frac{\hbar^2}{2m}\left(YZ\frac{\partial^2}{\partial x^2}X + XZ\frac{\partial^2}{\partial y^2}Y + XY\frac{\partial^2}{\partial z^2}Z\right) = E\cdot XYZ$$

$$\frac{\partial^2}{\partial x^2} \downarrow \frac{d^2}{dx^2} \qquad \frac{\partial^2}{\partial y^2} \downarrow \frac{d^2}{dy^2} \qquad \frac{\partial^2}{\partial z^2} \downarrow \frac{d^2}{dz^2}$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{d^2}{dx^2}X + \frac{1}{Y}\frac{d^2}{dy^2}Y + \frac{1}{Z}\frac{d^2}{dz^2}Z\right) = E$$

- Each term in the brackets on the left hand side is a function of only one coordinate.
- The right hand side is a constant.
- Therefore, each term must be separately a constant.

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} = E_x$$

$$-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2} = E_y$$

$$-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2Z}{dz^2} = E_z$$

$$E = E_x + E_y + E_z$$

- E_x, E_y and E_z are **separation constants**
- Let's divide through by -2m/hbar^2

$$\Rightarrow \quad \frac{1}{X}\frac{d^2}{dx^2}X + \frac{1}{Y}\frac{d^2}{dy^2}Y + \frac{1}{Z}\frac{d^2}{dz^2}Z = -\frac{2m}{\hbar^2}E$$

So,

$$\frac{1}{X}\frac{d^2X}{dx^2} = -k_x^2, \quad \frac{1}{Y}\frac{d^2Y}{dy^2} = -k_y^2, \quad \frac{1}{Z}\frac{d^2Z}{dz^2} = -k_z^2$$

$$\text{So,} \quad k_x^2 + k_y^2 + k_z^2 = \frac{2mE}{\hbar^2} = \frac{2m}{\hbar^2}(E_x + E_y + E_z)$$

- So, the solutions are:

$$X(x) = A_x \sin k_x x + B_x \cos k_x x$$
$$Y(y) = A_y \sin k_y y + B_y \cos k_y y$$
$$Z(z) = A_z \sin k_z z + B_z \cos k_z z$$

- Continuity @ 0: $X(0) = Y(0) = Z(0) = 0$

So, $B_x = B_y = B_z = 0$

$$\Rightarrow \quad X(x) = A_x \sin k_x x$$
$$Y(y) = A_y \sin k_y y$$
$$Z(z) = A_z \sin k_z z$$

- Continuity @ a, b, c: $X(a) = Y(b) = Z(c) = 0$

$$\Rightarrow \quad k_x a = n_x \pi, \quad k_y b = n_y \pi,$$
$$k_z c = n_z \pi$$

- The total wavefunction is:

$$\psi(x,y,z) = XYZ = A \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi}{b} y \sin\frac{n_z \pi}{c} z$$

$$n_x = 1, 2, 3, \ldots \quad , n_y = 1, 2, 3, \ldots \quad , n_z = 1, 2, 3, \ldots$$

- The constants of normalization A_x A_y A_z are absorbed into one constant A.

- What about energy quantization?

since $k_x^2 + k_y^2 + k_z^2 = \frac{2m}{\hbar^2} E$

and $k_x = \frac{n_x \pi}{a}$, $k_y = \frac{n_y \pi}{b}$, $k_z = \frac{n_z \pi}{c}$

$$\Rightarrow \quad E = \frac{\pi^2 \hbar^2}{2m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right]$$

- Quantization of Energy!

- Normalization requires a triple integral:

- Normalization:

$$\int_0^a \int_0^b \int_0^c A^2 \sin^2 \frac{n_x \pi x}{a} \sin^2 \frac{n_y \pi y}{b} \sin^2 \frac{n_z \pi z}{c} \, dx\, dy\, dz = 1$$

$$A^2 \cdot \frac{a}{2} \cdot \frac{b}{2} \cdot \frac{c}{2} = 1$$

$$A = \sqrt{\frac{8}{abc}} = \sqrt{\frac{8}{V}}$$

Volume of box $= V = a \cdot b \cdot c$.

Wavefunction

- To plot the 3D wavefunction on a 2D piece of paper is tough.
- Let's instead look at the 2D wavefunction
  - $\Psi(x,y)$ for $(a,b)=(1,1)$ and $(n_x,n_y)=(5,2)$
  - Amplitude set to 1 for convenience
  - There are 5 and 2 maxima in the x and y direction, respectively

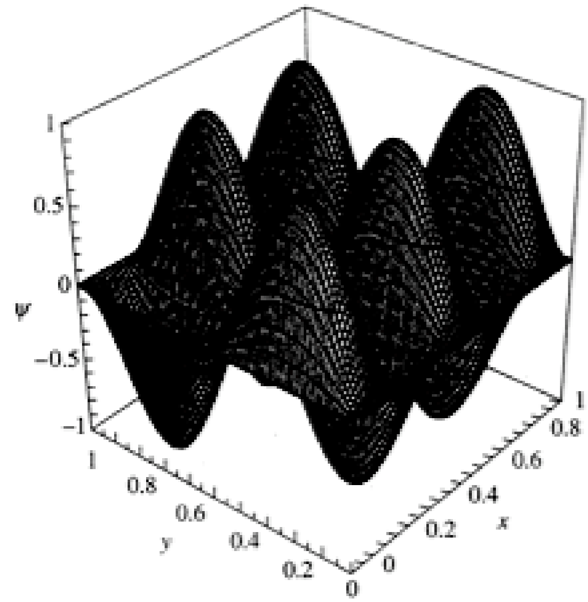

FIGURE 6.2 Two-dimensional infinite-well wavefunction with $(n_x, n_y) = (5, 2)$.

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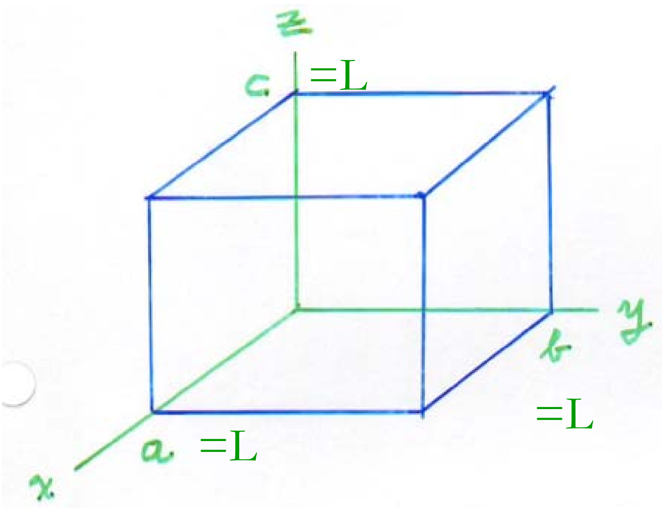
Special case: A cubical box

- a=b=c=L

$$E = \frac{\pi^2 \hbar^2}{2mL^2}\left[n_x^2 + n_y^2 + n_z^2\right]$$



- Ground state has:

Ground state: $n_x = n_y = n_z = 1$

$$E_{111} = \frac{\pi^2 \hbar^2}{2mL^2}\left(1^2 + 1^2 + 1^2\right) = \frac{3\pi^2 \hbar^2}{2mL^2}$$

Energy Degeneracy

- New feature of a 3D box compared to a 1D potential well:
  - Can have the <u>same</u> energy for more than one quantum state
  - This is known as **degeneracy**
- For example:

$$(n_x, n_y, n_z) = (2,1,1)$$

or

$$(1,2,1)$$

or

$$(1,1,2)$$

$$E_{211} = E_{121} = E_{112} = \frac{\pi^2 \hbar^2}{2mL^2}(4+1+1)$$

$$= 6\frac{\pi^2 \hbar^2}{2mL^2}$$

Energy Degeneracy, con't

- What about the eigenfunctions?
  - The eigenfunctions are different!

$$\left.\begin{aligned}
\psi_{211} &= \sqrt{\frac{8}{L^3}}\ \sin\frac{2\pi x}{L}\ \sin\frac{\pi y}{L}\ \sin\frac{\pi z}{L} \\
\psi_{121} &= \sqrt{\frac{8}{L^3}}\ \sin\frac{\pi x}{L}\ \sin\frac{2\pi y}{L}\ \sin\frac{\pi z}{L} \\
\psi_{112} &= \sqrt{\frac{8}{L^3}}\ \sin\frac{\pi x}{L}\ \sin\frac{\pi y}{L}\ \sin\frac{2\pi z}{L}
\end{aligned}\right\}\ \text{not the } \underline{\text{same}}$$

Example

- Suppose the particle in the box is a proton and the box has nuclear dimensions.
- What is the ground state energy E_{111}?
  - $m=1.67\text{x}10^{-27}$kg
  - $L=10^{-14}$m

Ground state energy:

$$E_{111} = \frac{3\pi^2\hbar^2}{2mL^2} = 6.15\ \text{MeV}$$

- This is very typical of nuclear binding energies!

Degeneracy increases with E

- It turns out that degeneracy is very common and it increases with E.
- Let's take some examples:

1. 6-fold degeneracy

$$E_{124} = E_{142} = E_{214} = E_{241} = E_{412} = E_{421} = 21\frac{\pi^2\hbar^2}{2mL^2} = 7 \cdot E_{111}$$

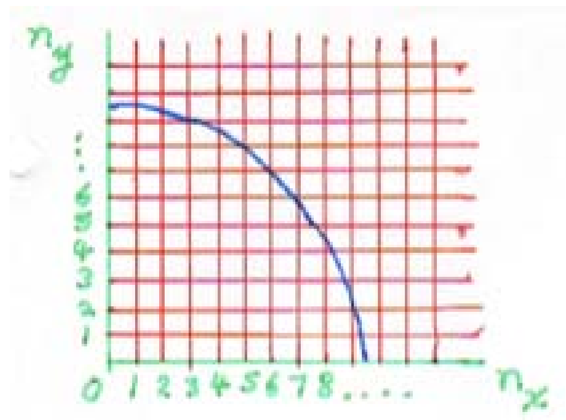
2. 9-fold degeneracy

$$E_{532} = E_{523} = E_{352} = E_{325} = E_{253} = E_{235} = E_{611} = E_{161} = E_{116}$$
$$= 38\frac{\pi^2\hbar^2}{2mL^2} \simeq 13E_{111}$$

Degeneracy increases with E, con't

- To see how degeneracy increases with energy, again let's consider the 2D case:

$$n_x^2 + n_y^2 = \frac{2mL^2 E}{\pi^2 \hbar^2}$$



- Each value of E gives us a circle in the graph of n_x vs n_y.
- If the circle intersects any lattice point, then we have a solution.

- So, # solutions = degeneracy
- And it will be roughly proportional to the circumference of the circle, which is proportional to the radius
- So, $R \propto \sqrt{E}$ and the degeneracy roughly increases as $\sqrt{E}$
- <u>For the 3D lattice:</u>

$$n_x^2 + n_y^2 + n_z^2 = \frac{2mL^2E}{\pi^2\hbar^2}$$

  - Each energy gives us a sphere of radius $R \propto \sqrt{E}$ in the 3D graph of (n_x, n_y, n_z)
  - The degeneracy will be roughly proportional to the surface area of the sphere.
  - So, degeneracy is $\propto R^2 \propto E$
  - In the 3D case, the degeneracy increases roughly linearly with E.

Number of available quantum states

- Q: How many individual quantum states with energies ≤ E are available to the particle?

$$E = \frac{\pi^2 \hbar^2}{2m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right]$$

Divide by E:

$$\Rightarrow \quad 1 = \frac{n_x^2}{\alpha^2} + \frac{n_y^2}{\beta^2} + \frac{n_z^2}{\gamma^2}$$

where:

$$\alpha = \sqrt{\frac{2mEa^2}{\pi^2\hbar^2}}, \quad \beta = \sqrt{\frac{2mEb^2}{\pi^2\hbar^2}}, \quad \gamma = \sqrt{\frac{2mEc^2}{\pi^2\hbar^2}}$$

- This equation describes the surface of a 3D ellipsoid of semi-axes (α,β,γ) along the (n_x, n_y, n_z) axes.

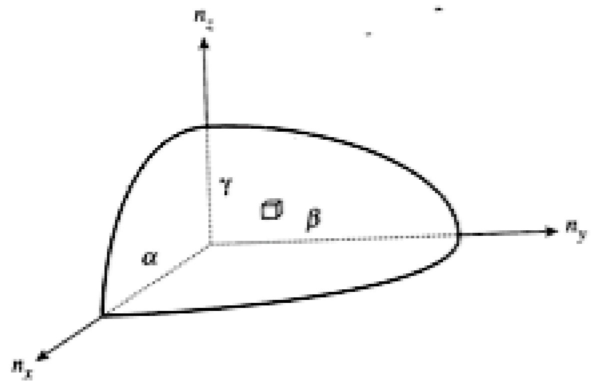


FIGURE 6.3 Positive octant of an ellipsoid of semi-axes (α, β, γ).

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- The volume of the ellipsoid (all 8 octants) is:

$$\left(\frac{4}{3}\pi\right)\alpha\beta\gamma$$

- Divide up into a large number of tiny cubes of volume $\Delta n_x \Delta n_y \Delta n_z$
- Each with $\Delta n_x = \Delta n_y = \Delta n_z = 1$
- Each tiny volume would correspond to a single quantum state (n_x, n_y, n_z)
- The total volume within ellipsoid then represents the number of individual quantum states lying below energy E, N(E):

$$N(E) = \frac{1}{8}\left(\frac{4\pi}{3}\right)\alpha\beta\gamma$$

$$= \frac{\pi}{6}\sqrt{\frac{2mEa^2}{\pi^2\hbar^2}}\sqrt{\frac{2mEb^2}{\pi^2\hbar^2}}\sqrt{\frac{2mEc^2}{\pi^2\hbar^2}}$$

$$\Rightarrow N(E) = \frac{2^{3/2}}{6}\frac{1}{\pi^2} V \frac{m^{3/2}}{\hbar^3} E^{3/2} \quad , \quad V = abc$$

Summary/Announcements

- S.E. in 3D
  - Particle in a box
- Next time: Angular momentum

- Next homework due on Monday Oct 31.