Quantum Mechanics and Atomic Physics

Lecture 10:
Virial Theorem, etc

+ The Harmonic Oscillator: Part I

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

Prof. Eva Halkiadakis
Orthogonality

- **Theorem**: Eigenfunctions with different eigenvalues are orthogonal.

- Consider a set of wavefunctions satisfying S.E. for some potential $V(x)$

- Then orthogonality states:

\[
\int_{-\infty}^{\infty} \psi_k^* \psi_n \, dx = 0 \quad \text{for} \quad k \neq n \quad \text{and} \quad E_k \neq E_n
\]

- In other words, if any two members of the set obey the above integral constraint, they constitute an orthogonal set of wavefunctions.

- Let’s prove this…
Proof: Orthogonality Theorem

\[-\frac{\hbar^2}{2m} \frac{d^2 \psi_n}{dx^2} + V \psi_n = E_n \psi_n\]

\[-\frac{\hbar^2}{2m} \frac{d^2 \psi_k}{dx^2} + V \psi_k = E_k \psi_k\]

\[\rightarrow \text{ take complex conjugate:}\]

\[\Rightarrow -\frac{\hbar^2}{2m} \frac{d^2 \psi_k^*}{dx^2} + V \psi_k^* = E_k \psi_k^*\]

\[\Rightarrow \text{ Multiply by } \psi_k^*\]

\[\Rightarrow \text{ Multiply 1st eqn by } \psi_k^*\]

\[\Rightarrow \text{ Subtract:}\]

\[-\frac{\hbar^2}{2m} \left( \psi_k^* \frac{d^2 \psi_n}{dx^2} - \psi_n \frac{d^2 \psi_k^*}{dx^2} \right) + V \left( \psi_k^* \psi_n - \psi_n \psi_k^* \right) = 0\]

\[= (E_n - E_k) \psi_k^* \psi_n\]
Proof, con’t

\[ \Rightarrow \frac{d}{dx} \left( \psi_k^* \frac{d \psi_n}{dx} \right) = \psi_k^* \frac{d^2 \psi_n}{dx^2} + \frac{d \psi_k^*}{dx} \frac{d \psi_n}{dx} \]

and

\[ \frac{d}{dx} \left( \psi_n \frac{d \psi_k^*}{dx} \right) = \psi_n \frac{d^2 \psi_k^*}{dx^2} + \frac{d \psi_n}{dx} \frac{d \psi_k^*}{dx} \]

Take diff:

\[ \frac{d}{dx} \left( \psi_k^* \frac{d \psi_n}{dx} - \psi_n \frac{d \psi_k^*}{dx} \right) = \psi_k^* \frac{d^2 \psi_n}{dx^2} - \psi_n \frac{d^2 \psi_k^*}{dx^2} \]
Theorem is proven
Orthonormality

In addition, if each individual member of the set of wavefunctions is normalized, they constitute an orthonormal set:

\[\text{If } n \neq k, \quad E_n - E_k = 0\]
and integral need not be 0.

If \( \psi_n \) are normalized:

\[\int_{-\infty}^{\infty} \psi_n^* \psi_n \, dx = 1\]

\[\int_{-\infty}^{\infty} \psi_k^* \psi_n \, dx = \langle \psi_k^* | \psi_n \rangle = \delta_{kn}\]

\[\delta_{kn} = \begin{cases} 1 & (k = n) \\ 0 & (\text{otherwise}) \end{cases}\]

Kronecker delta
Degenerate Eigenfunctions

- If \( n \neq k \), but \( E_n = E_k \), then we say that the eigenfunctions are **degenerate**.

- Since \( E_n - E_k = 0 \), the integral need not be zero.

- But it turns out that we can always obtain another set of \( \Psi \)’s, linear combinations of the originals, such that the new \( \Psi \)’s are orthogonal.
Principle of Superposition

- **Any linear combination of solutions to the S.E. is also a solution**
- For example, particle in infinite square well can be in a superposition of states:

\[ \psi = c_1 \Psi_1 + c_2 \Psi_2 \]

- Is this \( \Psi \) an eigenstate of energy?

\[ E_0 \psi = c_1 E_0 \Psi_1 + c_2 E_0 \Psi_2 \]

\[ = c_1 E_1 \Psi_1 + c_2 E_2 \Psi_2 \]

\[ \neq \text{(const)} \Psi \]

Because \( E_1 \neq E_2 \).

- So it is **not** an eigenstate of energy.
- The measurement will yield either \( E_1 \) or \( E_2 \), though not with equal probability.
- *The system need not be in an eigenstate* - the superposition state \( \Psi \) “collapses” into one of the eigenstates when one makes a measurement to determine which state the system is actually in.

We covered this in lectures 3 & 4!
A Time-Dependent Wave-Packet

- See Reed Section 4.8 for a very nice example:

\[ \Psi^2 = \alpha^2 \Psi_1^2 + \beta^2 \Psi_2^2 + 2 \alpha \beta \Psi_1 \Psi_2 \cos[(\omega_1 - \omega_2)t] \]

\( \Psi^2 \) oscillates!

\[ \omega T = 2\pi \]

\[ T = \frac{2\pi}{\omega_1 - \omega_2} = \frac{2\pi}{(E_1 - E_2)} = \frac{1}{(E_1 - E_2)} \]

Since \( \Psi_1 \) and \( \Psi_2 \) are orthogonal and \( E_1 \neq E_2 \)

\[ \langle X \rangle = \alpha^2 \int (x \Psi_1^2) \, dx + \beta^2 \int (x \Psi_2^2) \, dx + 2 \alpha \beta \int (x \Psi_1 \Psi_2) \cos[(\omega_1 - \omega_2)t] \, dx \]

This term doesn’t vanish! \( \rightarrow \) superposition of states

Illustrates concept of a traveling wave and the principle of superposition.
Theorem

If $\Psi$ is in an eigenstates of $Q_{op}$ with eigenvalue $\lambda$, then $<Q> = \lambda$ and $\Delta Q = 0$.

So, $\lambda$ is the only value we’ll observe for $Q$!

Proof:

\[
\bar{Q} = <Q> = \int \psi^* Q_{op} \psi \, dx = \int \psi^* \lambda \psi \, dx
\]

\[
\Rightarrow \quad <Q> = \lambda \int \psi^* \psi \, dx = \lambda
\]

\[
\bar{Q}^2 = <Q^2> = \int \psi^* Q_{op} (Q_{op}) \psi \, dx = \int \psi^* Q_{op} \psi \, dx
\]

\[
= \lambda \int \psi^* Q_{op} \psi \, dx = \lambda \int \psi^* \psi \, dx
\]

\[
= \lambda^2 \int \psi^* \psi \, dx = \lambda^2
\]

\[
\Delta Q = \sqrt{<Q^2> - <Q>^2} = \sqrt{\lambda^2 - \lambda^2} = 0
\]

No uncertainty! Observe $\lambda$ only.
The Virial Theorem (VT) is an expression that relates the expectation values of the KE$_{op}$ and PE$_{op}$ for any potential.

Suppose operator A is time-independent

$$[A, H_{op}]\psi = A_{\psi} (H_{op} \psi) - H_{op} (A_{\psi} \psi)$$

$$= i\hbar \left[ A \frac{\partial \psi}{\partial t} - \frac{\partial}{\partial t} (A \psi) \right]$$

$$= i\hbar \left[ A \frac{\partial \psi}{\partial t} - A \frac{\partial \psi}{\partial t} \right] = 0$$

In VT, A is defined as:

$$A = \frac{\partial}{\partial t} \psi$$

Section 4.9 in Reed goes through the proof of the VT in great detail which gives:

$$\Rightarrow 2 \langle KE \rangle = \langle \vec{p} \cdot \vec{D} V \rangle \quad \text{for any potential} \, V$$
Example: VT using a radial potential

\[ V(r) = \frac{k}{r} \]

\[ \nabla V = \left( \frac{\partial V}{\partial r} \right) \hat{r} = n \kappa r^{n-1} \hat{r} \]

\[ \hat{r} \cdot \nabla V = (r \hat{r}) \cdot (n \kappa r^{n-1}) \hat{r} = n \kappa r^n = n V \]

\[ \Rightarrow 2 \langle kE \rangle = n \langle V \rangle \]
The Classical Harmonic Oscillator

- Classical mechanics examples
  - Mass on a spring
  - Mass swinging as a simple pendulum

- These examples all correspond to a situation where we have a linear restoring force:
  \[ F = -kx \quad -\infty \leq x \leq \infty \]

- And the harmonic oscillator potential is then:
  \[ V(x) = -\int F(x) \, dx = \int kx \, dx = \frac{1}{2}kx^2 + C \]
The S.E. for the harmonic oscillator potential

\[ V(x) = \frac{1}{2} k x^2 \quad \text{for all } x \]

\[ f(x) = -\frac{dV}{dx} = -k x \]

- S.E.:
  \[ -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} k x^2 \psi = E \psi \]

- Angular Frequency of oscillator:
  \[ \omega = \sqrt{\frac{\hbar}{m}} \Rightarrow \hbar = m \omega^2 \]

- So,
  \[ \frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2} \psi - \frac{m^2 \omega^2}{\hbar^2} x^2 \psi = 0 \]
Let’s define: \( \xi = a \chi \)

and

\[ \alpha = \sqrt{\frac{m\omega}{\hbar}}, \quad \beta = \frac{2mE}{\hbar^2} \]

Think of \( \xi \) as a dimensionless measure of \( x \)

So:

\[ \frac{d^4}{dx^4} = \frac{d^4}{d\xi^4} \frac{d\xi}{dx} = \alpha \frac{d^4}{d\xi^4} \]

\[ \frac{d^2}{dx^2} = \alpha \frac{d}{dx} \left( \frac{d^4}{d\xi^4} \right) = \alpha \frac{d^2}{d\xi^2} \frac{d\xi}{dx} = \alpha^2 \frac{d^2}{d\xi^2} \]

Insert back into S.E. ....
S.E. of H.O., con’t

\[ \alpha^2 \frac{d^2 \psi}{d \xi^2} + (\beta - \alpha^4 (\frac{\xi}{\alpha})^2) \psi = 0 \]

\[ \alpha^2 \frac{d^2 \psi}{d \xi^2} + (\beta - \alpha^4 (\frac{\xi}{\alpha})^2) \psi = 0 \]

\[ \frac{d^2 \psi}{d \xi^2} + (\frac{\beta}{\alpha^2} - \xi^2) \psi = 0 \]

- Let’s define:

\[ \lambda = \frac{\beta}{\alpha^2} = \frac{2mE}{\hbar^2} \cdot \frac{\hbar}{m\omega} = \frac{2}{\hbar\omega} E \]

\[ \varepsilon = \frac{2}{\hbar\omega} \implies \lambda = \varepsilon E \]

- Think of \( \lambda \) as a dimensionless measure of \( E \)
Finally we have:

\[ \Rightarrow \frac{d^2\psi}{d\xi^2} + (\lambda - \xi^2)\psi = 0 \]

This is called Weber’s Differential Equation
Dimensional Analysis

- Let’s check that $\xi$ is a dimensionless measure of $x$

$$\xi = \alpha x$$

$[\alpha]_{\text{units}} = m^{-1}$

Let’s check:

$$\alpha = \sqrt{\frac{mw}{th}} = \left( \frac{mk}{k^2} \right)^{\frac{1}{2}}$$

$m^{-1} = \left[ \frac{kg \cdot N}{m} \cdot \frac{1}{(J \cdot s)^2} \right]^{\frac{1}{2}}$

$m^{-1} = \left[ \frac{kg \cdot kg \cdot m/s^2 \cdot kg^2 m^2 / s^4 \cdot s^2}{kg^2 m^2 / s^4} \right]^{\frac{1}{2}}$

$m^{-1} = \left( \frac{1}{m^2} \right)^{\frac{1}{2}}$

$m^{-1} = m^{-1} \checkmark$
Dimensional Analysis

- Let’s check that $\lambda$ is a dimensionless measure of $E$

\[
\lambda = \varepsilon E
\]

\[
\varepsilon = \frac{2}{h\omega}
\]

\[
[\varepsilon]_{\text{units}} = \frac{1}{J}
\]

\[
\frac{1}{J} = \frac{1}{J \cdot s \cdot H_3}
\]

\[
= \frac{1}{J \cdot s \cdot s^{-1}}
\]

\[
= \frac{1}{J}
\]

\[\checkmark\]
The Asymptotic Solution

- Let’s solve for $\Psi(\xi)$ and then revert back to $x$.
- First, let’s consider $\Psi$ at large $\xi$, i.e. large $x$
  - $\lambda$ stays finite so:
    \[
    \frac{d^2 \Psi}{d\xi^2} - \xi^2 \Psi = 0 \quad \text{for } \xi \to \pm \infty
    \]
    \[
    \frac{d^2 \Psi}{d\xi^2} \approx \xi^2 \Psi
    \]
  - A general solution is:
    \[
    \Psi = A e^{-\frac{\xi^2}{2}} + B e^{\frac{\xi^2}{2}}
    \]
The Asymptotic Solution, con’t

- Just like finite square well, we want that $\Psi(\xi) \to 0$ as $\xi \to \infty$
  - We establish the **asymptotic form** of the wavefunction
  - So if we require finiteness at $\xi = \infty$, then we must require $B = 0$, so:

$$\Psi(\xi) \approx A e^{-\xi/2} \quad \text{for} \quad \xi \to +\infty$$
For a more general solution, valid at any $\xi$, let’s try

$$\psi(\xi) = H(\xi) e^{-\frac{1}{2} \xi^2}$$

$H(\xi)$:
- is a yet unknown function.
- It must vary more slowly than $\exp(-\frac{\xi^2}{2})$ at large $\xi$. 

The Series Solution
The Series Solution, con’t

- How do we know if this is a valid assumption?
  - We don’t know yet, but let’s see if it works.

\[
\frac{d^2 \psi}{d \xi^2} = \left( \frac{d^2 H}{d \xi^2} - 2 \xi \frac{d H}{d \xi} + (\xi^2 - 1) H \right) e^{-\xi^2/2} \\
\frac{d^2 \psi}{d \xi^2} + (\lambda - \xi^2) \psi = 0
\]

\[
\Rightarrow \left( \frac{d^2 H}{d \xi^2} - 2 \xi \frac{d H}{d \xi} + (\xi^2 - 1) H \right) e^{-\xi^2/2} + (\lambda - \xi^2) H e^{-\xi^2/2} = 0
\]

\[
\frac{d^2 H}{d \xi^2} - 2 \xi \frac{d H}{d \xi} + (\lambda - 1) H = 0
\]
The Series Solution, con’t

Let’s try series solution:

\[ H(\xi) = \sum_{n=0}^{\infty} a_n \xi^n \]

(We omit negative powers since they would blow up at \( x=\xi=0 \))

\[
\frac{dH}{d\xi} = \sum_{n=0}^{\infty} n a_n \xi^{n-1}
\]

\[
\frac{d^2H}{d\xi^2} = \sum_{n=0}^{\infty} n(n-1) a_n \xi^{n-2}
\]
The Series Solution, con’t

Plug back into eqn on p. 24:

\[ \sum_{n=0}^{\infty} n(n-1) a_n \xi^{n-2} - 2 \sum_{n=0}^{\infty} n a_n \xi^n + \sum_{n=0}^{\infty} (\lambda - 1) a_n \xi^n = 0 \]

\[ \sum_{n=0}^{\infty} n(n-1) a_n \xi^{n-2} + \sum_{n=0}^{\infty} (\lambda - 1 - 2\alpha) a_n \xi^n = 0 \]

\[ \sum_{n=0}^{\infty} n(n-1) a_n \xi^{n-2} = 0 + 0 + \sum_{n=2}^{\infty} n(n-1) a_n \xi^{n-2} \]

(n=0)        (n=1)        (since sum makes no contribution due to n(n-1))
We’ll continue this next time....
Summary/Announcements

- Next time: Harmonic Oscillator continued
  - Wavefunctions, probability, raising and lowering operators

- Next homework due on Monday Oct 16.

- Midterm exam Wed. Oct. 25 - it will be closed book – covers chapters 1-5 and related lectures - check website for more information.