Quantum Mechanics  Study Notes → GRE Review  9/11/07

Schrödinger equation: \[ i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V \psi \]

→ in Newton mechanics we solve 2nd order differential equation \( F = m \ddot{x} \) to find \( x(t) \)

→ In QM, given potential \( V \) we solve this partial differential equation to find \( \psi \).

Wave function Formalism:

→ So what can we do with wave function \( \psi(x,t) \)?

\[ \int |\psi|^2 dx = \text{probability of occupation between } a \& b \]

\[ \text{conditions} \Rightarrow \text{Obviously must be normalized} \]

\[ \int_{-\infty}^{\infty} |\psi|^2 dx = 1 \]

→ Square integrable (i.e. can't have discontinuities)

* Note: Wave function can be complex so: \( |\psi|^2 = \psi^* \psi \)
i.e. multiply \( \psi \) by its complex conjugate (inner product)

Position, Momentum & Expectation Value

\[ x \rightarrow x \quad p \rightarrow -i\hbar \frac{\partial}{\partial x} \quad \text{Expectation Value (average)} \]

\[ \langle x \rangle = \int x |\psi|^2 dx \]

\[ \langle p \rangle = -i\hbar \int \frac{\partial |\psi|^2}{\partial x} dx \]

Time Independent

→ Assume time dependence & position dependence are separable

\[ \Psi(x,t) = \Psi(x) \Phi(t) \]

→ Plug into Schröd., separate out using \( E \), separation constant:

result: \( \Phi(t) = e^{-\frac{\hbar E}{\hbar t}} \) and we have time independent

\[ -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V \psi(x) = E \psi(x) \]

Note: Hamiltonian \(\hat{H} = \frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\)

→ So full solutions are \( \Psi(x,t) = \psi(x) e^{-\frac{\hbar E}{\hbar t}} \)

or more generally: \( \sum c_n \psi_n e^{-\frac{\hbar E_n}{\hbar t}} \psi_n \)
**Operator Formalism** (Eigenvectors, Eigenvalues, Stationary States)

→ If you took Lin Algebra you know about linear operators, matrices, eigenvectors, etc...

→ When we solve the Time Independent Schröd equation, we are solving an Eigenvector equation:

\[ \mathbf{H}\psi = E\psi \]

the solutions to this equation are the eigenvectors or eigenstates of the Hamiltonian

⇒ Eigenstates of \( \mathcal{H} \) have constant \( E \) and are stationary!

⇒ Any wavefunction state can be represented as a linear combo of states:

\[ \Psi(x,t) = \sum C_n \Psi_n e^{iEt/\hbar} \]

**Measurement**

→ Here is the big point:

• You have \( \Psi(x,t) \) which can be expanded in terms of the eigenstates of a certain operator (Energy (Hamiltonian), \( p, x \), angular momentum...)

Ex: \( \Psi(x,t) = c_1 \Psi_1(x) e^{-iEt/\hbar} + c_2 \Psi_2(x) e^{-iEt/\hbar} \)

Note: \( c_1^2 + c_2^2 = 1 \) Why? (consider normalization requirement)

• When you measure a quantity (for example \( E \)) the system will collapse randomly to an eigenstate which it has in its wavefunction, with the prob determined by "how much" of the coeff in front of that eigenstate.

Ex: in above the system will collapse to either \( \Psi_1 \) or \( \Psi_2 \) with prob \( c_1^2 \) or \( c_2^2 \) respectively.

• It will stay there for decoy to an e losing all information of the state before.

⇒ simultaneously observables...
Examples of Solving Schröd: \( \infty \) square well

\[ V = 0 \quad 0 < x < a, \quad V = \infty \quad \text{elsewhere} \]

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

\[ \Rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi \quad k = \sqrt{2mE}/\hbar \]

"wavevector" \quad \text{"standard 2nd order Diff Eq"}

\[ \psi(x) = A \sin kx + B \cos kx \]

\[ \text{use boundary conditions to solve:} \]

\[ E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2}{2a^2} \quad \psi_n(x) = \frac{\sqrt{2}}{\sqrt{a}} \sin \left( \frac{n\pi}{a} x \right) \]

\( n = 1, 2, 3, \ldots \)

\[ \psi(x,t) = \sum_{n=1}^{\infty} C_n \sqrt{\frac{2}{a}} \sin \left( \frac{n\pi}{a} x \right) e^{-i \frac{\pi^2}{4a^2} t} \]

\[ \text{General Solution} \]

**Note** \quad **Fourier Series**

\[ |C_n|^2 \text{ is probability of measuring energy } E_n \]

\[ \langle H \rangle = \sum_{n=1}^{\infty} |C_n|^2 E_n \]

\[ \text{average energy} \]
Additional Solutions: Harmonic Oscillator (Quantum That Is!)

\[ V = \frac{1}{2} k x^2 \implies \text{Solution is a bit involved. Cut to the chase:} \]

\[ E_n = (n + \frac{1}{2}) \hbar \omega \]

\[ \psi_n = \left( \frac{m \hbar}{2\pi \hbar} \right)^{\frac{3}{4}} e^{-\frac{m \hbar x^2}{2\pi \hbar}} \]

\[ \psi_0 = \left( \frac{m \hbar}{2\pi \hbar} \right)^{\frac{1}{4}} e^{-\frac{m \hbar x^2}{2\pi \hbar}} \]

Note! Cannot have \( E = 0 \) since \( \text{zero point energy} = E_0 = \frac{1}{2} \hbar \omega \)

\[ \psi(x) = \psi(-x) \implies \text{Note!} \]

\[ n = 0, 1, 3, 5, \ldots, \text{odd} \]

\[ \text{These are odd functions!} \]

Free Particle \( \implies V = 0 \)

\[ -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = E \psi \quad \text{solutions} \rightarrow \psi(x) = A e^{ikx} + B e^{-ikx} \]

\[ +k \rightarrow \text{right moving wave} \quad k = \frac{\sqrt{2mE}}{\hbar} \]

\[ -k \rightarrow \text{left moving wave} \]

\[ \psi(-x) = -\psi(x) \rightarrow \text{cross zero (0, 0)} \]

\[ \psi(x) = Ae^{ikx} + Be^{-ikx} \]

\[ k \rightarrow \text{right moving wave} \]

\[ -k \rightarrow \text{left moving wave} \]

\[ \text{Not a real solution (non-normalizable)} \]

\[ \text{but can have linear combo of different waves to form wavepacket that does normalize.} \]
Barriers \( (\text{i.e. tunneling}) \)

\[ \psi(x) \]

\[ E < V_0 \]

→ Do solution in different zones.
→ Within barrier, if \( E < V_0 \) then solution will have no imaginary part and will just be exponential decay.
→ Outside barrier it is free traveling wave.
→ Use continuity rules at boundaries to link up solution and solve!

\[ \Rightarrow \text{Tunneling! There is Transmission} \]

\[ \text{probability} \propto \text{Energy of particle} \]

\[ \text{and inversely proportional to barrier height.} \]

\[ \text{Also will have Reflected wave.} \]

\[ I = R + T \]
\[ L = \text{incident wave.} \]
3-D Schröd: \( p \rightarrow \frac{\hbar}{i} \nabla - \frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi \)

Use separation of variables \( \Psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \)

\( \phi \rightarrow \text{is easy; has to meet up with itself so must be } 2\pi \text{ periodic} \)

\[ Y_\ell(\phi) = e^{im\phi} \]

\( \Rightarrow \text{Spherical Harmonics (Angular Solutions) are defined} \)

by quantum numbers \( m, \ell \)

\( \rightarrow \text{remember general shapes...} \)

\( \ell = 0 \rightarrow \Theta \text{-symmetric} \)

\( \ell = 1 \rightarrow \Theta \text{-dumbbells} \)

Radial \( \rightarrow \text{Bohr: use potential} \)

\[ V(r) = -\frac{e^2}{4\pi \epsilon_0 r} \]

\( \rightarrow \text{obviously all solutions must be bounded and go to zero as } r \rightarrow \infty \)

Remember: \( \Psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \)

\[ a = \text{Bohr radius} = \frac{4\pi \epsilon_0 h^2}{m e^2} \approx \frac{1}{2} A^{1/3} \]

\[ \text{most probable} \]

\[ \text{distance from center in ground state} \]
Angular Momentum: \( L_x, L_y, L_z \) are incompatible observables but \( L^2 \) does commute with any of them

\[ \Rightarrow \text{Only can know } L^2 \text{ & } L_z \text{ at same time} \]

\[ \text{Note} \quad L_z = \frac{\hbar}{\alpha} \frac{d}{d\phi} \]

→ eigenvalues:
\[ L^2 \rightarrow \hbar^2 (l+\frac{1}{2}) \]
\[ L_z \rightarrow \hbar m \]
\( L^2 \) has values
\[ m = -l, -l+1, \ldots, l-\frac{1}{2}, l \]

→ note \( L_z \) never equals \( L \)

\underline{Spin \ (\frac{1}{2})} \]

\[ S^2 \rightarrow \hbar^2 s(s+1) \quad S_z \rightarrow \hbar m \]
→ for electron can only have
\[ m = \frac{1}{2}, -\frac{1}{2} \]

Spin operators:
\[ S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \]

Pauli Matrices:
\[ \sigma_x \quad \sigma_y \]

So \( S_z \) has eigenvectors
\[ \chi_+ = (\begin{pmatrix} 1 \\ 0 \end{pmatrix}) \rightarrow \text{eigenvalue } \hbar/2 \]
\[ \chi_- = (\begin{pmatrix} 0 \\ 1 \end{pmatrix}) \rightarrow -\hbar/2 \]
Addition of Spins (Multiple particle systems)

\begin{align*}
\text{triplet state: } & \quad s = 1 \\
1s^m \rightarrow & \text{ total spin } m = 1 \\
|11\rangle &= \uparrow \uparrow \\
|10\rangle &= \frac{1}{\sqrt{2}} (\uparrow \downarrow + \downarrow \uparrow) \\
|1-1\rangle &= \downarrow \downarrow
\end{align*}

\begin{align*}
\text{singlet state: } & \quad s = 0 \\
|00\rangle &= \frac{1}{\sqrt{2}} (\uparrow \downarrow - \downarrow \uparrow) \\
\end{align*}

A Little Out of Order...

De Broglie Relation: \[ \beta = \frac{\hbar}{\lambda} \]
\( \Rightarrow \) once \( \lambda \) is on the order of the characteristic length of what you are studying...
\( \Rightarrow \) quantum (wave-like) effects will be evident!!

Heisenberg Relation & Uncertainty

\( \rightarrow \) Important quantity is the variance / Uncertainty

\( \rightarrow \) \( \langle (x - \mu)^2 \rangle = \text{Variance}(x) \) where \( \mu = \langle x \rangle \)

\( \rightarrow \) \( \text{sd} = \sqrt{\langle (x - \mu)^2 \rangle} = \sigma_x \)

\( \text{Nice Relation} \)

\[ \text{Var}(x) = \langle x^2 \rangle - \langle x \rangle^2 \]

Heisenberg characterizes relation between uncertainty of incompatible observables \( x \) & \( p \)

\[ \Delta x \Delta p \geq \frac{\hbar}{2} \quad \Rightarrow \text{Good to know!} \]

also \( \Delta E \Delta E \geq \frac{\hbar}{2} \)

Gaussian wave packet

\( \text{hits min uncertainty: } \sigma_x \sigma_p = \frac{\hbar}{2} \)
Problems & Examples

1. $\psi(x) = \begin{cases} 3 & \text{for } 1 \leq x < 2 \\ 2 & \text{for } 2 \leq x < 3 \\ 1 & \text{for } 3 \leq x \leq 4 \end{cases}$

   - 1a) Find constant $A$ such that $A\psi(x)$ is a valid wavefunction.
   - 1b) What is the probability of finding particle in $2 \leq x \leq 4$.
   - 2c) What is $\langle x \rangle$.

2. A wavefunction is in a mixed state $\psi(x) = c_1\psi_1 + c_2\psi_2$. $A$
   where $\psi_1$ and $\psi_2$ are energy eigenstates with energies $E_1$, $E_2$ respectively. $c_1 = 2$, $c_2 = 3$.
   - What is normalization constant $A$?
   - If energy is measured, what is probability of measuring $E_1$?
   - If $E_1$ is measured, what is $\psi(x)$ now?
   - If $E$ is measured again (after measuring $E_1$) immediately afterwards, what energy will be measured?

3. All physical observables are represented by Hermitian matrices. What is one special property of Hermitian matrices that makes this necessary?

4. Draw a Gaussian which is highly localized. How will it change as time progresses? Will the area underneath it change?

5. Given a Gaussian like wavepacket with wavenumber $k$, what is its width? (estimate)
Problems & Examples 2

6. What is the momentum of a traveling wave with wavevector $\mathbf{e}^{i\mathbf{kx}}$?

7. Ground State of infinite square well from $x=0 \to x=a$.
   Compute expectation value of $x$, $p$, and $x^2$.

8. Plot Cut the harmonic oscillator in half:
   What are the energy levels of this system? (in terms of $\hbar$)

9. A molecule's angular portion of its wavefunction is:
   $\psi(\theta, \phi) = A (10Y_1^0 + 2Y_5^5 + 2Y_5^{-1})$
   where $Y_{lm}^m$ are spherical harmonics.
   $\rightarrow$ What is the value of the constant $A$?
   $\rightarrow$ What is the most probable value of the total angular momentum $\ell$?
   $\rightarrow$ What is the probability of measuring this value?

   Let's suppose you measure $\ell$ and get the most probable value. Immediately afterwards you measure $\ell_\perp$. What do you get?
   $\rightarrow$ What is the expectation value of $\ell^2$?