Schrödinger Representation – Schrödinger Equation

Time dependent Schrödinger Equation

\[ i\hbar \frac{\partial \Phi(x, y, z, t)}{\partial t} = H(x, y, z, t)\Phi(x, y, z, t) \]

Developed through analogy to Maxwell’s equations and knowledge of the Bohr model of the H atom.

\[ H_{\text{classical}} = \frac{p^2}{2m} + V \]

Sum of kinetic energy and potential energy.

Q.M.

\[ H = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad \text{one dimension} \]

\[ H = \frac{-\hbar^2}{2m} \nabla^2 + V(x, y, z) \quad \text{three dimensions} \]

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

The potential, \( V \), makes one problem different from another  

H atom, harmonic oscillator.

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Getting the Time Independent Schrödinger Equation

\( \Phi(x, y, z, t) \quad \text{wavefunction} \)

\[ i\hbar \frac{\partial}{\partial t} \Phi(x, y, z, t) = H(x, y, z, t)\Phi(x, y, z, t) \]

If the energy is independent of time \( \rightarrow H(x, y, z) \)

Try solution

\( \Phi(x, y, z, t) = \phi(x, y, z)F(t) \quad \text{product of spatial function and time function} \)

Then

\[ i\hbar \frac{\partial}{\partial t} \phi(x, y, z)F(t) = H(x, y, z)\phi(x, y, z)F(t) \]

\[ i \hbar \phi(x, y, z) \frac{\partial}{\partial t} F(t) = F(t)H(x, y, z)\phi(x, y, z) \quad \text{divide through by} \quad \Phi = \phi F \]

independent of \( t \)  \quad \text{independent of} \quad x, y, z

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\[
\frac{i\hbar}{F(t)} \frac{dF(t)}{dt} = \frac{H(x, y, z) \phi(x, y, z)}{\phi(x, y, z)}
\]

depends only on \(t\)
depends only on \(x, y, z\)

Can only be true for any \(x, y, z, t\) if both sides equal a constant.

Changing \(t\) on the left doesn’t change the value on the right.
Changing \(x, y, z\) on right doesn’t change value on left.

\[
\frac{i\hbar}{F} \frac{dF}{dt} = E = \frac{H \phi}{\phi}
\]

Equal constant
Both sides equal a constant, $E$.

$$\frac{i \hbar}{F} \frac{dF}{dt} = E = \frac{H \phi}{\phi}$$

$$H(x, y, z)\phi(x, y, z) = E \phi(x, y, z)$$

Energy eigenvalue problem – time independent Schrödinger Equation

$H$ is energy operator.

Operate on $\phi$ get $\phi$ back times a number.

$\phi$'s are energy eigenkets; eigenfunctions; wavefunctions.

$E \rightarrow$ Energy Eigenvalues

Observable values of energy
**Time Dependent Equation**  \( (H \text{ time independent}) \)

\[
i\hbar \frac{dF(t)}{dt} = E \frac{F(t)}{F(t)}
\]

\[
i\hbar \frac{dF(t)}{dt} = E F(t)
\]

\[
\frac{dF(t)}{F(t)} = \frac{-i}{\hbar} E dt. \quad \text{Integrate both sides}
\]

\[
\ln F = -\frac{iEt}{\hbar} + C \quad \text{Take initial condition at } t = 0, \ F = 1, \text{ then } C = 0.
\]

\[
F(t) = e^{-iEt/\hbar} = e^{-i\omega t}
\]

**Time dependent part of wavefunction for time independent Hamiltonian.**

**Time dependent phase factor used in wave packet problem.**
Total wavefunction for time independent Hamiltonian.

$$\Phi_E(x, y, z, t) = \phi_E(x, y, z)e^{-iEt/\hbar}$$

$E$ – energy (observable) that labels state.

Normalization

$$\langle \Phi_E | \Phi_E \rangle = \int \Phi^*_E \Phi_E d\tau = \int \phi^*_E e^{+iEt/\hbar} \phi_E e^{-iEt/\hbar} d\tau = \int \phi^*_E \phi_E d\tau$$

Total wavefunction is normalized if time independent part is normalized.

Expectation value of time independent operator $S$.

$$\langle S \rangle = \langle \Phi | S | \Phi \rangle = \int \Phi^*_E S \Phi_E d\tau = \int \phi^*_E e^{iEt/\hbar} S \phi_E e^{-iEt/\hbar} d\tau$$

$S$ does not depend on $t$, $e^{-iEt/\hbar}$ can be brought to other side of $S$.  

$$\langle \Phi | S | \Phi \rangle = \int \phi^*_E S \phi_E d\tau$$

Expectation value is time independent and depends only on the time independent part of the wavefunction.
Equation of motion of the Expectation Value in the Schrödinger Representation

Expectation value of operator representing observable for state $|S\rangle$

$$\langle A \rangle = \langle S | A | S \rangle$$

example - momentum $\langle P \rangle = \langle S | P | S \rangle$

In Schrödinger representation, operators don’t change in time.

Time dependence contained in wavefunction.

Want Q.M. equivalent of
time derivative of a classical dynamical variable.

$$\begin{align*}
P &\longrightarrow \hat{P} \\
\dot{P} = \frac{\partial P}{\partial t} &\Rightarrow \text{ want Q.M. operator equivalent of time derivative}
\end{align*}$$

Definition: The time derivative of the operator $\hat{A}$, i.e., $\hat{A}$ is defined to mean an operator whose expectation in any state $|S\rangle$ is the time derivative of the expectation of the operator $\hat{A}$. 

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Want to find
\[
\frac{d \langle A \rangle}{dt} = \frac{\partial}{\partial t} \langle S | A | S \rangle
\]

Use \( H |S\rangle = i \hbar \frac{\partial}{\partial t} |S\rangle \)  

time dependent Schrödinger equation.

\[
\frac{\partial}{\partial t} \langle S | A | S \rangle = \left( \frac{\partial}{\partial t} \langle S | A \langle S \rangle + \langle S | A \frac{\partial}{\partial t} | S \rangle\right)
\]
product rule

\[
\text{time independent – derivative is zero}
\]

Use the complex conjugate of the Schrödinger equation  
\( \langle S | H = -i \hbar \frac{\partial}{\partial t} \langle S | \). \)

Then \( \left( \frac{\partial}{\partial t} \langle S | = \frac{i}{\hbar} \langle S | H \right) \), and from the Schrödinger equation (operate to left)

\[
\frac{\partial}{\partial t} |S\rangle = -\frac{i}{\hbar} H |S\rangle
\]
From Schrödinger eq.

\[
\frac{\partial}{\partial t} \langle S | A | S \rangle = \frac{i}{\hbar} \left[ \langle S | H A | S \rangle - \langle S | A H | S \rangle \right]
\]
From complex conjugate of Schrödinger eq.
Therefore

\[ \frac{d}{dt} \langle A \rangle = \frac{i}{\hbar} \langle S | H A - A H | S \rangle = \frac{i}{\hbar} [H, A] \]

This is the commutator of $HA$.

\[ \dot{A} = \frac{i}{\hbar} [H, A] \]

The operator representing the time derivative of an observable is $i/\hbar$ times the commutator of $H$ with the observable.
Solving the time independent Schrödinger equation

The free particle

momentum problem

\[ \hat{P} \hat{P} = \hat{p} \hat{P} \]

\[ \psi_p(x) = \frac{1}{\sqrt{2\pi}} e^{ikx} \quad p = \hbar k \quad k = p/\hbar \]

Free particle Hamiltonian – no potential – \( V = 0 \).

\[ \hat{H} = \frac{\hat{P}^2}{2m} \]

Commutator of \( \hat{H} \) with \( \hat{P} \)

\[ [\hat{P}, \hat{H}] = \frac{\hat{P}^3}{2m} - \frac{\hat{P}^3}{2m} = 0 \quad \hat{P}^3 |S\rangle = \hat{P} \hat{P} \hat{P} |S\rangle \]

\( \hat{P} \) and \( \hat{H} \) commute \( \rightarrow \) Simultaneous Eigenfunctions.
Free particle energy eigenvalue problem

\[ \hat{H} | P \rangle = E | P \rangle \]

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \]

Use momentum eigenkets.

\[ \hat{H} | P \rangle = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \left( \frac{1}{\sqrt{2\pi}} e^{ikx} \right) \]

\[ = -\frac{\hbar^2}{\sqrt{2\pi} 2m} (ik)^2 e^{ikx} \]

\[ = \frac{\hbar^2 k^2}{2m} \left( \frac{1}{\sqrt{2\pi}} e^{ikx} \right) \]

\[ = \frac{p^2}{2m} | P \rangle \]

energy eigenvalues

Therefore, \[ E = \frac{p^2}{2m} \] Energy same as classical result.
Particle in a One Dimensional Box

Particle inside box. Can’t get out because of impenetrable walls.

Classically → $E$ is continuous. $E$ can be zero. One D racquet ball court.

Q.M. → $\Delta x \Delta p \geq \hbar/2$  $E$ can’t be zero.

$H \left| \varphi \right\rangle = E \left| \varphi \right\rangle$  Energy eigenvalue problem

Schrödinger Equation

$$-\frac{\hbar^2}{2m} \frac{d^2 \varphi(x)}{dx^2} + V(x) \varphi(x) = E \varphi(x)$$

$V(x) = 0 \quad |x| < b$

$V(x) = \infty \quad |x| \geq b$
For $|x| < b$

$$-\frac{\hbar^2}{2m} \frac{d^2 \varphi(x)}{dx^2} = E \varphi(x)$$

Want to solve differential Equation, but solution must be physically acceptable.

**Born Condition on Wavefunction to make physically meaningful.**

1. The wave function must be finite everywhere.
2. The wave function must be single valued.
3. The wave function must be continuous.
4. First derivative of wave function must be continuous.
\[
\frac{d^2 \varphi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \varphi(x)
\]

Second derivative of a function equals a negative constant times the same function.

Functions with this property \(\longrightarrow\) \(\sin\) and \(\cos\).

\[
\frac{d^2 \sin(ax)}{dx^2} = -a^2 \sin(ax)
\]

\[
\frac{d^2 \cos(ax)}{dx^2} = -a^2 \cos(ax)
\]

These are solutions provided

\[
a^2 = \frac{2mE}{\hbar^2}
\]
Solutions with any value of $a$ don’t obey Born conditions.

Well is infinitely deep. Particle has zero probability of being found outside the box.

$$\varphi = 0 \text{ for } |x| \geq b$$

Function as drawn discontinuous at $x = \pm b$

To be an acceptable wavefunction

$$\varphi \Rightarrow \sin \text{ and } \cos \Rightarrow 0 \text{ at } |x| = b$$
\( \varphi \) will vanish at \(|x| = b\) if

\[
a = \frac{n \pi}{2b} \equiv a_n \quad n \text{ is an integer}
\]

\[
\cos a_n x \quad n = 1, 3, 5\ldots
\]

\[
\sin a_n x \quad n = 2, 4, 6\ldots
\]

Integral number of half wavelengths in box. Zero at walls.

Have two conditions for \( a^2 \).

\[
a_n^2 = \frac{n^2 \pi^2}{4b^2} = \frac{2mE}{\hbar^2}
\]

Solve for \( E \).

\[
E_n = \frac{n^2 \pi^2 \hbar^2}{8mb^2} = \frac{n^2 \hbar^2}{8mL^2}
\]

Energy eigenvalues – energy levels, not continuous. 

\( L = 2b \) – length of box.
Energy levels are quantized. Lowest energy not zero.

\[ E_n = \frac{n^2 \pi^2 \hbar^2}{8mb^2} = \frac{n^2 \hbar^2}{8mL^2} \]

\( L = 2b \) – length of box.

\[ \varphi_n(x) = \left(\frac{1}{b}\right)^{\frac{1}{2}} \cos \frac{n\pi x}{2b} \quad |x| \leq b \quad n = 1, 3, 5 \ldots \]

\[ \varphi_n(x) = \left(\frac{1}{b}\right)^{\frac{1}{2}} \sin \frac{n\pi x}{2b} \quad |x| \leq b \quad n = 2, 4, 6 \ldots \]

First few wavefunctions.

Quantization forced by Born conditions (boundary conditions)

Fourth Born condition not met – first derivative not continuous. Physically unrealistic problem because the potential is discontinuous.

Like classical string – has “fundamental” and harmonics.
Anthracene

\[ \pi \text{ electrons – consider “free” in box of length } L. \]

\[ L \approx 6 \, \text{Å} \]

\[ \Delta E = E_2 - E_1 = \frac{3\hbar^2}{8mL^2} \]

\[ m = m_e = 9 \times 10^{-31} \, \text{kg} \]

\[ L = 6 \, \text{Å} = 6 \times 10^{-10} \, \text{m} \]

\[ h = 6.6 \times 10^{-34} \, \text{Js} \]

\[ \Delta E = 5.04 \times 10^{-19} \, \text{J} \]

\[ \Delta E = \hbar \nu \]

\[ \nu = \Delta E / h = 7.64 \times 10^{14} \, \text{Hz} \]

\[ \lambda = c / \nu = 393 \, \text{nm} \quad \text{blue-violet} \]

Experiment \[ \Rightarrow \] 400 nm
Anthracene particularly good agreement.
Other molecules, naphthalene, benzene, agreement much worse.

Important point
Confine a particle with “size” of electron to box size of a molecule
Get energy level separation, light absorption, in visible and UV.

Molecular structure, realistic potential give accurate calculation, but it is the mass and size alone that set scale.

Big molecules absorb in red.
Small molecules absorb in UV.
Particle in a Finite Box – Tunneling and Ionization

Box with finite walls.

Time independent Schrödinger Eq.

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

\[V(x) = 0 \quad |x| < b\]

\[V(x) = V \quad |x| \geq b\]

Inside Box  \( V = 0 \)

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

Second derivative of function equals negative constant times same function.

\[\frac{d^2 \varphi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \varphi(x)\]

Solutions – sin and cos.
Solutions inside box

\[ \varphi(x) = q_1 \sin\sqrt{\frac{2mE}{\hbar^2}} x \]

or

\[ \varphi(x) = q_2 \cos\sqrt{\frac{2mE}{\hbar^2}} x \]

Outside Box

Two cases: Bound states, \( E < V \)

Unbound states, \( E > V \)

Bound States

Second derivative of function equals positive constant times same function.

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

Not oscillatory.
Try solutions

\( \exp(\pm ax) \) \quad \Rightarrow \quad \frac{d^2 e^{\pm ax}}{dx^2} = a^2 e^{\pm ax} \quad \text{Second derivative of function equals positive constant times same function.}

Then, solutions outside the box

\[ \varphi(x) = e^{\pm \left[ \frac{2m(V-E)}{\hbar^2} \right]^{1/2} x} \quad |x| \geq b \]

Solutions must obey Born Conditions

\( \varphi(x) \) can’t blow up as \( |x| \to \infty \) \quad Therefore,

\( \varphi(x) = r_1 e^{-\left[ \frac{2m(V-E)}{\hbar^2} \right]^{1/2} x} \quad x \geq b \quad \text{Outside box} \quad \rightarrow \quad \text{exp. decays} \)

\( \varphi(x) = r_2 e^{+\left[ \frac{2m(V-E)}{\hbar^2} \right]^{1/2} x} \quad x \leq -b \quad \text{Inside box} \quad \rightarrow \quad \text{oscillatory} \)
Outside box → exp. decays
Inside box → oscillatory

The wavefunction and its first derivative continuous at walls – Born Conditions.

Expanded view

For a finite distance into the material finite probability of finding particle.

Classically forbidden region $V > E.$

probability → 0
Tunneling - Qualitative Discussion

Classically forbidden region.

Wavefunction not zero at far side of wall.

Probability of finding particle finite outside box.

A particle placed inside of box with not enough energy to go over the wall can Tunnel Through the Wall.

Formula derived in book: \[ e^{-2d \left[ \frac{2m(V-E)}{\hbar^2} \right]^{1/2}} \]

Ratio probs - outside vs. inside edges of wall.

<table>
<thead>
<tr>
<th>Wall thickness (d)</th>
<th>1 Å</th>
<th>10 Å</th>
<th>100 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>probability ratio</td>
<td>0.68</td>
<td>0.02</td>
<td>3 \times 10^{-17}</td>
</tr>
</tbody>
</table>

mass = m_e

\[ E = 1000 \text{ cm}^{-1} \]

\[ V = 2000 \text{ cm}^{-1} \]
Chemical Reaction

not enough energy to go over barrier

Temperature dependence of some chemical reactions shows too much product at low T. \( V > kT \).

Decay of probability in classically forbidden region for parabolic potential.

\( e^{-\lambda} \)

\[
\lambda = d \left( \frac{2mV}{\hbar^2} \right)^{1/2}
\]

light particles tunnel

tunneling parameter
distance mass barrier height

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Methyl groups rotate even at very low T.
Unbound States and Ionization

If $E > V$ - unbound states

Inside the box (between $-b$ and $b$)

$V = 0$

$\varphi(x) = q_1 \sin \sqrt{\frac{2mE}{\hbar^2}}x$

$\varphi(x) = q_2 \cos \sqrt{\frac{2mE}{\hbar^2}}x$

Solutions oscillatory

$E$ large enough - ionization

Outside the box ($x > |b|$)

$E > V$

$\varphi(x) = s_1 \sin \sqrt{\frac{2m(E-V)}{\hbar^2}}x$

$\varphi(x) = s_2 \cos \sqrt{\frac{2m(E-V)}{\hbar^2}}x$

Solutions oscillatory

$d^2 \varphi(x) = -\frac{2m(E-V)}{\hbar^2} \varphi(x)$
To solve (numerically)
Wavefunction and first derivative equal at walls, for example at $x = b$

$$q_1 \sin \sqrt{\frac{2mE}{\hbar^2}} b = s_1 \sin \sqrt{\frac{2m(E-V)}{\hbar^2}} b$$

In limit
$$E \gg V$$
$$(E - V) \approx E$$

$\therefore \ q_1 = s_1$

Wavefunction has equal amplitude everywhere.
For $E >> V$

$$\varphi(x) = \sin \sqrt{\frac{2mE}{\hbar^2}} x$$ for all $x$

As if there is no wall.

Continuous range of energies - free particle

Particle has been ionized.

$$\sqrt{\frac{2mE}{\hbar^2}} = \sqrt{\frac{2mp^2}{2m\hbar^2}} = \sqrt{\frac{\hbar^2k^2}{\hbar^2}} = k$$

$$\varphi(x) = \sin k x$$ Free particle wavefunction
In real world potential barriers are finite.