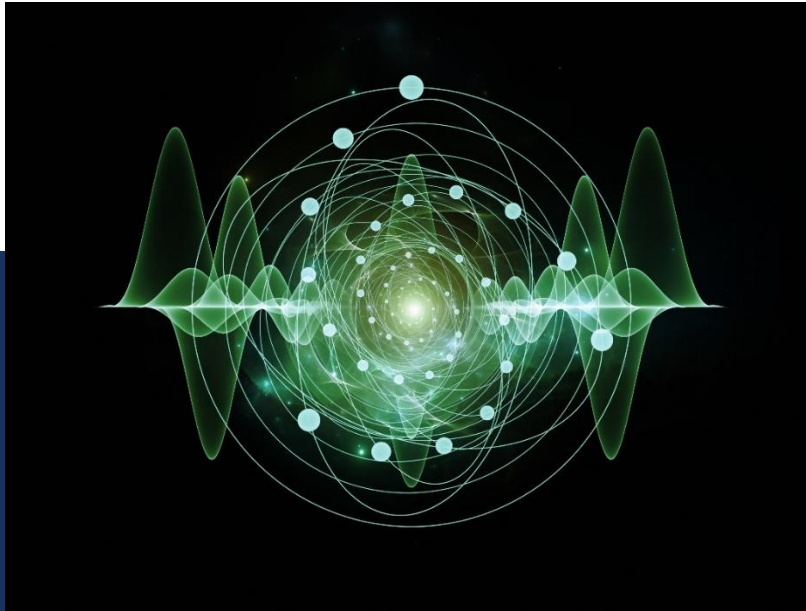


INTRODUCTION TO QUANTUM MECHANICS



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Adapted from course materials by MIT open courseware, UCSC, BYU, Stanford and Oxford

OUTLINE

- Schrödinger equation
- Some exact solutions
- The Variational Method
- Other Details

AN EQUATION FOR MATTER WAVES?

De Broglie postulated that every particles has an associated wave of wavelength:

$$\lambda = h / p$$

Wave nature of matter confirmed by electron diffraction studies *etc* (see earlier).

To describe matter on the very small scale, the scientist Erwin Schrödinger discovered a differential equation with latter came to be called the *Schrödinger equation* and its solution called the *wavefunction*, Ψ .

What is the form of the *Schrödinger equation* ?

POSTULATES OF QUANTUM MECHANICS

1. Associated with any particle moving in a conservative field of force is a wave function which determines everything that can be known about the system.
2. With every physical observable q there is associated an operator Q , which when operating upon the wavefunction associated with a definite value of that observable will yield that value times the wavefunction.
3. Any operator Q associated with a physically measurable property q will be Hermitian.
4. For a system described by a given wavefunction, the expectation value of any property q can be found by performing the expectation value integral with respect to that wavefunction.
5. The set of eigenfunctions of operator Q will form a complete set of linearly independent functions.

THE TIME-DEPENDENT SCHRÖDINGER EQUATION



$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x,t)\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

TDSE

Points of note:

1. The TDSE is one of the postulates of quantum mechanics. Though the SE cannot be derived, **it has been shown to be consistent with all experiments.**
2. SE is first order with respect to *time* (cf. classical wave equation).
3. SE involves the complex number i and so its *solutions are essentially complex*. This is different from classical waves where complex numbers are used imply for convenience – see later.

LHS of TDSE can be written as:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x,t) \Psi = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t) \right) \Psi = \hat{H} \Psi$$

where \hat{H} is called the **Hamiltonian operator** which is the differential operator that represents the **total energy** of the particle.

Thus

$$\hat{H} = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) = \frac{\hat{p}_x^2}{2m} + \hat{V}(x)$$

where the **momentum operator** is

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

Thus shorthand for TDSE is:

$$\hat{H} \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Since for a particle in a potential $V(x,t)$ The energy is

$$E = \frac{p^2}{2m} + V(x,t)$$

LHS involves variation of ψ with t while RHS involves variation of ψ with x . Hence look for a separated solution:

$$\Psi(x, t) = \psi(x)T(t)$$

Suppose the potential is independent of time i.e. $V(x, t) = V(x)$ then TDSE is:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi$$

$$\text{then } -\frac{\hbar^2}{2m} T \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi T = i\hbar \psi \frac{\partial T}{\partial t}$$

$$\text{Now divide by } \psi T: -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{\partial^2 \psi}{\partial x^2} + V(x) = i\hbar \frac{1}{T} \frac{\partial T}{\partial t}$$

LHS depends only upon x , RHS only on t . True for all x and t so both sides must equal a constant, E (E = separation constant).

Thus we have:

$$i\hbar \frac{1}{T} \frac{\partial T}{\partial t} = E$$
$$-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{\partial^2 \psi}{\partial x^2} + V(x) = E$$

THE TIME-INDEPENDENT SCHRÖDINGER EQUATION

Solving the time equation: $i\hbar \frac{1}{T} \frac{dT}{dt} = E \Rightarrow \frac{dT}{T} = -\frac{iE}{\hbar} dt \Rightarrow T(t) = Ae^{-iEt/\hbar}$

This is exactly like a wave $e^{-i\omega t}$ with $E = \hbar\omega$. Therefore $T(t)$ depends upon the energy E .

To find out what the energy actually is we must solve the space part of the problem....

The space equation becomes
$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi \quad \text{or} \quad \hat{H}\psi = E\psi$$

This is the **time independent Schrödinger equation (TISE)** .

The TISE can often be very difficult to solve – it depends upon $V(x)$!

INTERPRETATION OF Ψ

As mentioned previously the TDSE has solutions that are inherently complex $\Rightarrow \Psi(x,t)$ *cannot* be a physical wave (e.g. electromagnetic waves). Therefore how can $\Psi(x,t)$ relate to real physical measurements on a system?

The Born Interpretation

Probability of finding a particle in a small length dx at position x and time t is equal to

$$\Psi^*(x,t)\Psi(x,t)dx = |\Psi(x,t)|^2 dx = P(x,t)dx$$

The $*$ means complex conjugate: $z = x + iy \rightarrow x - iy$ where $i = \sqrt{-1}$

$\Psi^*\Psi$ is real as required for a probability distribution and is the probability *per unit length* (or volume in 3d).

The Born interpretation therefore calls Ψ the **probability amplitude**, $\Psi^*\Psi (= P(x,t))$ the **probability density** and $\Psi^*\Psi dx$ the **probability**.

Thus if we know $\Psi(x, t)$ (a solution of TDSE), then knowledge of $\Psi^*\Psi dx$ allows the *average* position to be calculated:

$$\bar{x} = \sum_i x_i P(x_i) \delta x$$

In the limit that $\delta x \rightarrow 0$ then the summation becomes:

$$\bar{x} = \langle x \rangle = \int_{-\infty}^{\infty} x P(x) dx = \int_{-\infty}^{\infty} x |\Psi(x, t)|^2 dx$$

The average is also known as the *expectation value* and are very important in quantum mechanics as they provide us with the average values of physical properties because in many cases precise values cannot, even in principle, be determined.

Similarly

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x) dx = \int_{-\infty}^{\infty} x^2 |\Psi(x, t)|^2 dx$$

NORMALISATION

Total probability of finding a particle anywhere must be 1:

$$\int_{-\infty}^{\infty} P(x) dx = \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1$$

This requirement is known as the *Normalisation condition*. (This condition arises because the SE is linear in Ψ and therefore if Ψ is a solution of TDSE then so is $c\Psi$ where c is a constant.)

Hence if original unnormalised wavefunction is $\Psi(x,t)$, then the normalisation integral is:

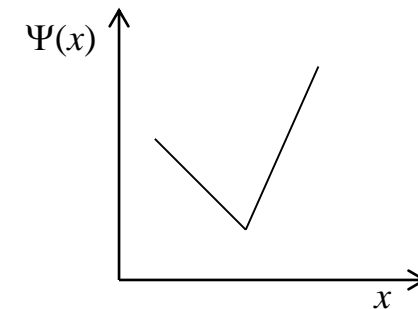
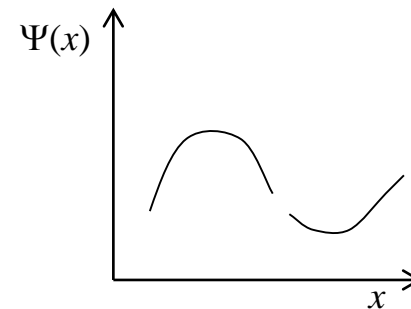
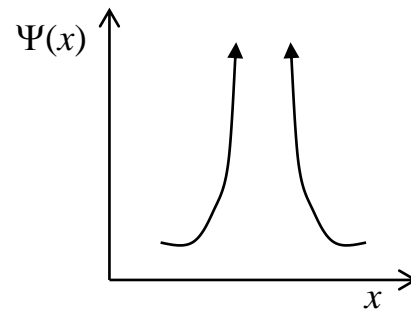
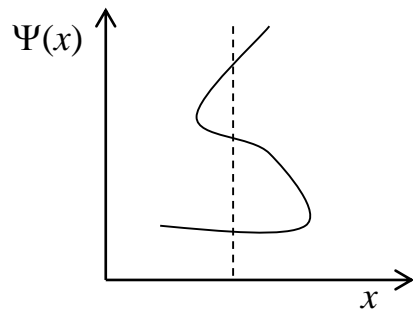
$$N^2 = \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx$$

And the (re-scaled) normalised wavefunction $\Psi_{norm} = (1/N) \Psi$.

BOUNDARY CONDITIONS FOR Ψ

In order for ψ to be a solution of the Schrödinger equation to represent a physically observable system, ψ must satisfy certain constraints:

1. Must be a single-valued function of x and t ;
2. Must be normalisable; This implies that the $\psi \rightarrow 0$ as $x \rightarrow \infty$;
3. $\psi(x)$ must be a continuous function of x ;
4. The *slope* of ψ must be continuous, specifically $d\psi(x)/dx$ must be continuous (except at points where potential is infinite).



STATIONARY STATES

Earlier we saw that even when the potential is independent of time the wavefunction still oscillates in time:

Solution to the full TDSE is: $\Psi(x,t) = \psi(x) T(t) = \psi(x) e^{-iEt/\hbar}$

But probability distribution is *static*:

$$P(x,t) = |\Psi(x,t)|^2 = \psi^*(x) e^{+iEt/\hbar} \psi(x) e^{-iEt/\hbar} = |\psi(x)|^2$$

Thus a solution of the TISE is known as a **Stationary State**.

POSTULATES OF QUANTUM MECHANICS

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3. Any operator Q associated with a physically measurable property q will be Hermitian.
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5. The set of eigenfunctions of operator Q will form a complete set of linearly independent functions.

WHAT OTHER INFORMATION CAN YOU GET FROM ψ ? (AND HOW!)

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

$$\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}.$$

Do the operators work on $\psi^* \psi$, or on ψ , or on ψ^* alone?

Take TISE and multiply from left by ψ^* and integrate:

$$\hat{H} \psi_n = E_n \psi_n$$

NB ψ is normalised.

$$\int \psi_n^* \hat{H} \psi_n dx = \int \psi_n^* E_n \psi_n dx = E_n \int \psi_n^* \psi_n dx = E_n$$

Suggest that in order to calculate the *average value* of the physical quantity associated with the QM operator we carry out the following integration:

$$\int \psi_n^* \hat{Q} \psi_n dx = q_n$$

If q is an observable quantity, the operator will be Hermitian and q will be a real number.

POSTULATES OF QUANTUM MECHANICS

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SUPERPOSITION OF EIGENSTATES

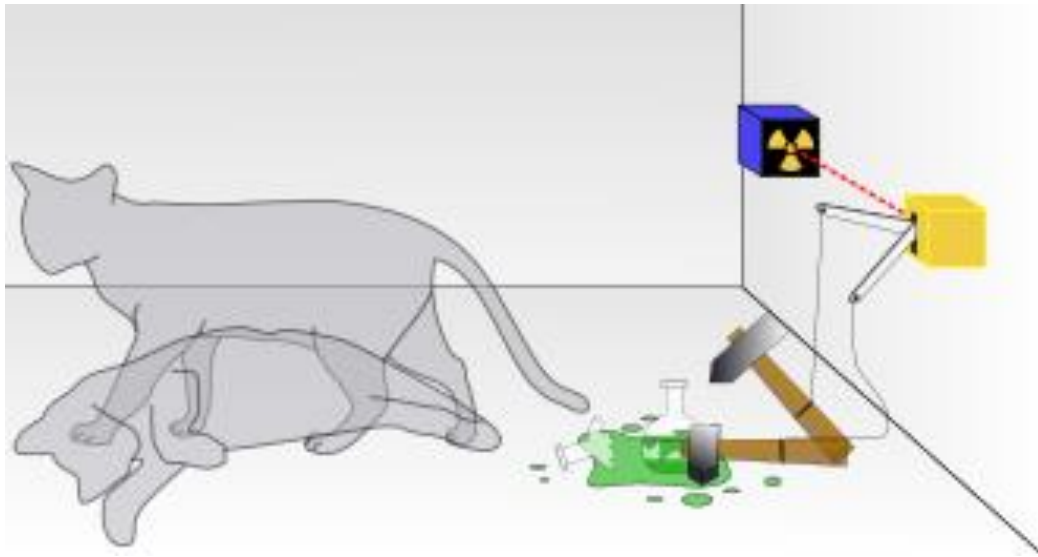
- In any measurement of the observable associated with operator \hat{Q} the only values that will ever be observed are the eigenvalues q , which satisfy the eigenvalue equation

$$\hat{Q}\Psi = q \Psi$$

- This postulate captures the central point of quantum mechanics--the values of dynamical variables can be quantized (although it is still possible to have a continuum of eigenvalues in the case of unbound states). If the system is in an eigenstate of \hat{Q} with eigenvalue q , then any measurement of the quantity Q will yield q .
- Although measurements must always yield an eigenvalue, the state does not have to be an eigenstate of \hat{Q} initially. An arbitrary state can be expanded in the complete set of eigenvectors of \hat{Q} as

$$\Psi = \sum_{i=1}^n c_i \Psi_i$$

SCHRODINGER'S CAT



$$\Psi(x,t) = \frac{1}{\sqrt{2}} (\psi_{dead}(t) + \psi_{alive}(t))$$

MOMENTUM AND ENERGY EXPECTATION VALUES

The expectation value of *momentum* involves the representation of momentum as a **quantum mechanical operator**:

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi(x,t) dx \quad \text{where} \quad \hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}.$$

is the operator for the x component of momentum.

Example: Derive an expression for the average energy of a free particle. $E = \frac{p^2}{2m}$ then $\langle E \rangle = \frac{\langle p^2 \rangle}{2m}$

Since $V = 0$ the **expectation value for energy** for a particle moving in one dimension is

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \Psi(x,t) dx$$

Our definition of the expectation value is one of the postulates of QM

SCHRODINGER EQUATION IS AN EIGENVALUE PROBLEM

General Eigenvalue problem $\mathbf{A}\mathbf{v} = \lambda\mathbf{v}$

The SE $\hat{H}\psi_n = E_n\psi_n$

For a finite representation where 'c' are the coefficients

$$\begin{pmatrix} H_{11} & \cdots & H_{1N} \\ \vdots & \ddots & \vdots \\ H_{N1} & \cdots & H_{NN} \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_N \end{pmatrix} = E_n \begin{pmatrix} c_1 \\ \vdots \\ c_N \end{pmatrix}$$

$H \qquad \psi \qquad E \qquad \psi$

H_{ij}
Are called Matrix Elements

https://en.wikipedia.org/wiki/H%C3%BCckel_method

For simple example

SUMMARY

TDSE:
$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x, t) \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Born interpretation:
$$\Psi^*(x, t) \Psi(x, t) dx = |\Psi(x, t)|^2 dx = P(x, t) dx$$

Normalisation:
$$\int_{-\infty}^{\infty} P(x) dx = \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1$$

TISE:
$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x) \psi = E \psi \quad \text{or} \quad \hat{H} \psi = E \psi$$

$$\Psi(x, t) = \psi(x) T(t) = \psi(x) e^{-iEt/\hbar}$$

Boundary conditions on ψ : single-valued, continuous, normalisable, continuous first derivative.

Expectation value of operator $\hat{\Omega}$:
$$\int_{-\infty}^{\infty} \Psi^*(x, t) \hat{\Omega} \Psi(x, t) dx$$

EXACT SOLUTIONS

- Free particle
- Particle in a Box
- Simple Harmonic Oscillator
- Hydrogen atom

Free Particle

A point mass m is allowed to move freely

$$V(x) = 0$$

$$E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi$$

Solution

$$\psi = e^{-ikx}$$

$$k = \frac{\sqrt{2mE}}{\hbar}$$

Any Positive E is allowable

Note
$$\int_{-\infty}^{\infty} P(x) dx = \int_{-\infty}^{\infty} e^{+ikx} e^{-ikx} dx = \int_{-\infty}^{\infty} dx$$

Particle in a Box

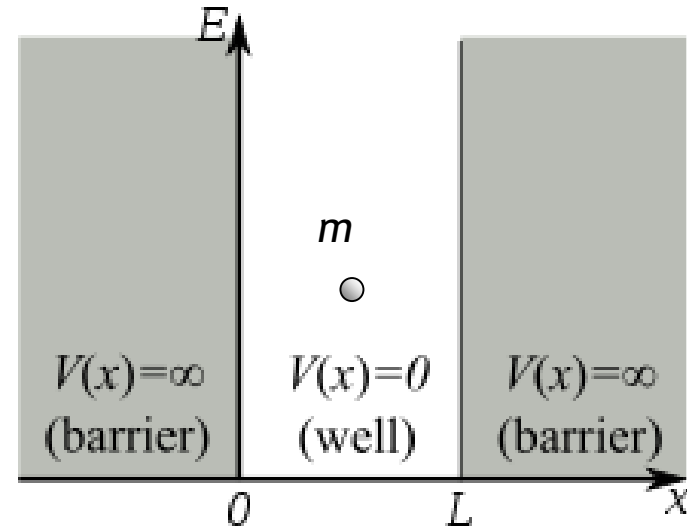
A point mass m constrained to move between two impenetrable walls a distance L apart

for $(x \leq 0, x \geq L)$

$$V(x) = \infty$$

$$E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi + (\infty)\psi$$

➡ $\psi = 0$



for $(0 < x < L)$

$$V(x) = 0$$

$$E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi$$

WE WILL HAVE MULTIPLE SOLUTIONS FOR ψ ,
SO WE INTRODUCE LABEL n

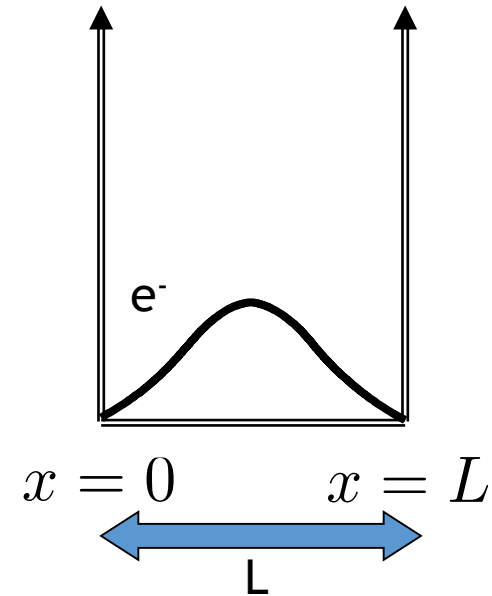
➡ $\psi(0) = \psi(L) = 0$ ψ IS CONTINUOUS

for $(0 < x < L) : V(x) = 0$

$$E_n \psi_n = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_n}{\partial x^2}$$

REWRITE AS:

WE WILL HAVE
MULTIPLE SOLUTIONS
FOR ψ ,
SO WE INTRODUCE
LABEL n



$$\frac{\partial^2 \psi_n}{\partial x^2} + k_n^2 \psi_n = 0 \quad \text{WHERE} \quad k_n^2 = \frac{2mE_n}{\hbar^2}$$

GENERAL SOLUTION:

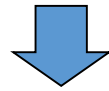
$$\psi_n(x) = A \sin k_n x + B \cos k_n x \quad \text{OR} \quad \psi_n = C_1 e^{jk_n x} + C_2 e^{-jk_n x}$$

USE BOUNDARY CONDITIONS TO DETERMINE COEFFICIENTS A and B

$$\longrightarrow k_n L = n\pi$$

$$\longrightarrow B = 0 \text{ since } \psi(0) = 0$$

NORMALIZE THE INTEGRAL OF PROBABILITY TO 1

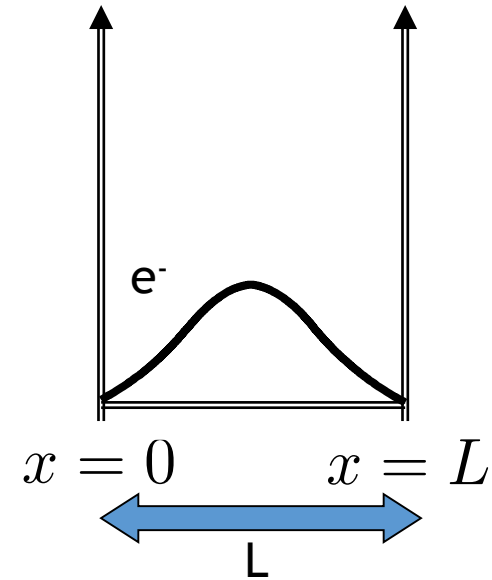


$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

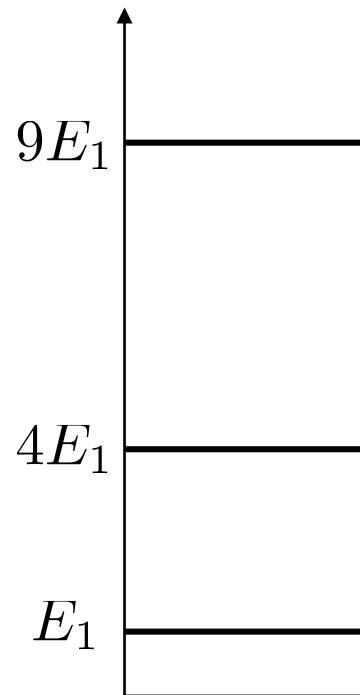
$$k_n^2 = \frac{2mE_n}{\hbar^2}$$

$$\longrightarrow E_n = n^2 E_1$$

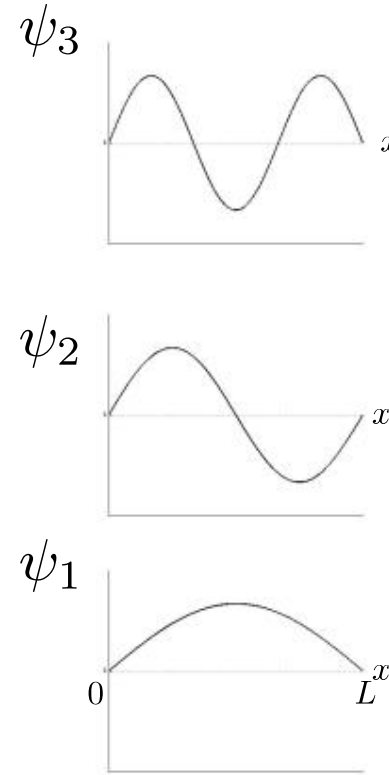
$$E_1 = \frac{\hbar^2 k_1^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2}$$



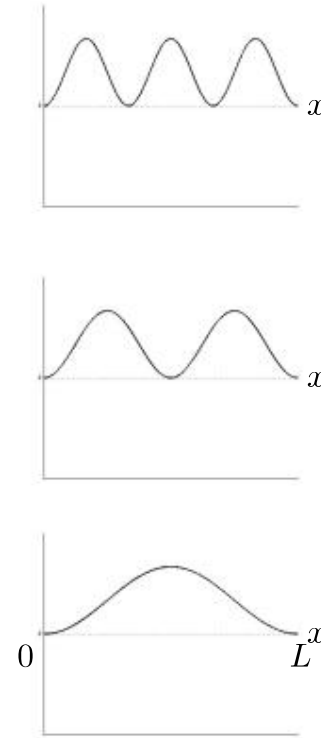
EIGENENERGIES for 1-D BOX



EIGENSTATES for 1-D BOX



PROBABILITY DENSITIES



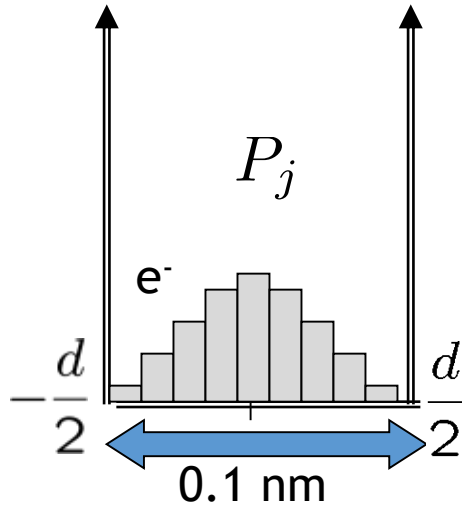
$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

$$P(x) = |\psi(x)|^2 dx = \frac{2}{L} \sin^2 \frac{n\pi x}{L} dx$$

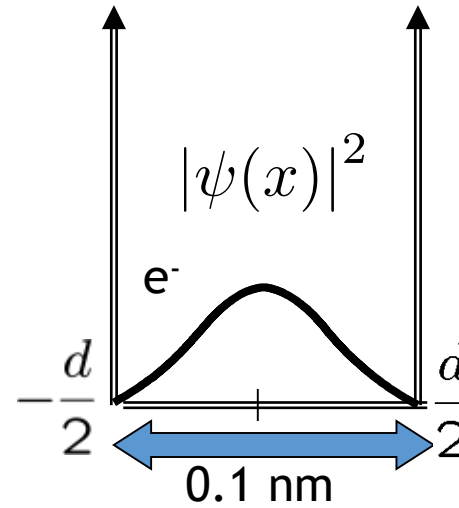
Expectation Values

$$\langle x \rangle = \sum_{j=-\infty}^{\infty} x P_j$$

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\psi|^2 dx$$



$$\langle x \rangle = 0$$



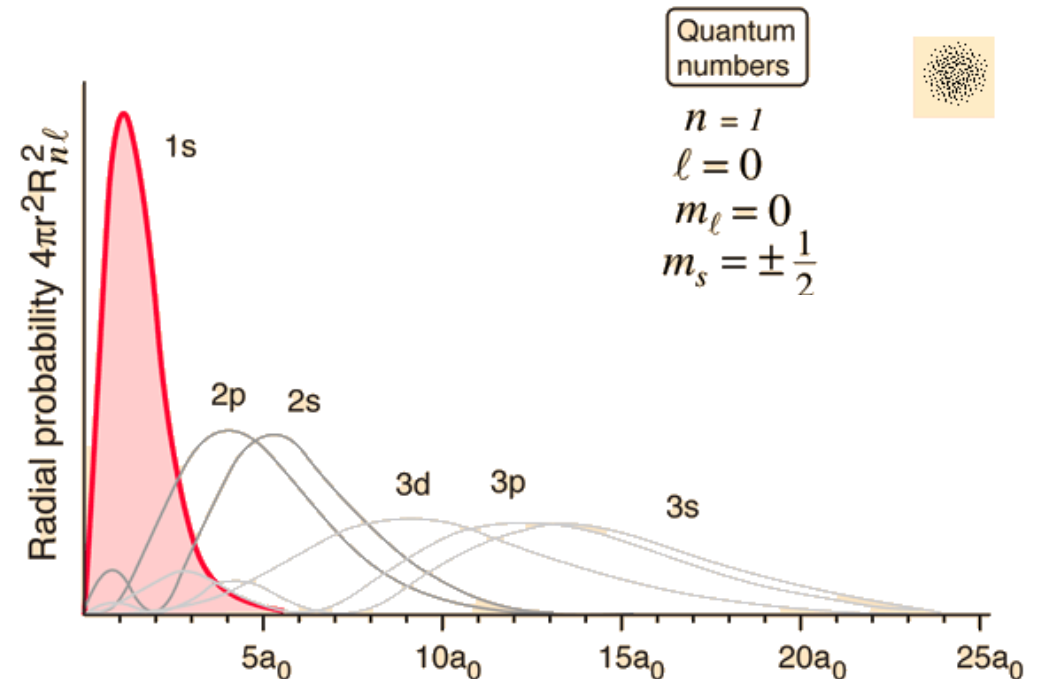
$$\langle x \rangle = 0$$

Hydrogen atom

Table 7.1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0^2} e^{-r/3a_0}$

$$H = -\frac{\hbar^2}{2m_\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$



BRA-KET NOTATION

- Introduced by Dirac in 1939
- It uses a convenient notation to define functions and inner products of functions.

Denote a ket as $|\phi\rangle$ Which is a function (can think of as a quantum state or eigenstate)

Also $|\beta\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle$ Is a valid ket

Denote a bra as $\langle\gamma|$ This is not a ket, and does not belong in ket space. $|\phi\rangle + \langle\gamma|$ Has no meaning!

For every ket $|\phi\rangle$ there is a bra $\langle\phi|$ which is said to be the dual of ket $|\phi\rangle$

$$\text{Also } |\beta\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \Leftrightarrow c_1^* \langle\phi_1| + c_2^* \langle\phi_2| = \langle\beta|$$

where \Leftrightarrow signifies a dual correspondence. This is an anti-linear relation.

BRA-KET NOTATION

- Inner product $\langle \psi | \phi \rangle$ represents a complex number that is equal to the value of the inner product of the ket

Note $\langle \psi | \phi \rangle = \langle \phi | \psi \rangle^*$ Results in a number

- Outer product $X = |\alpha\rangle\langle\beta|$ We can construct $X|\psi\rangle = |\alpha\rangle\langle\beta|\psi\rangle = c|\alpha\rangle$

BRA-KET NOTATION

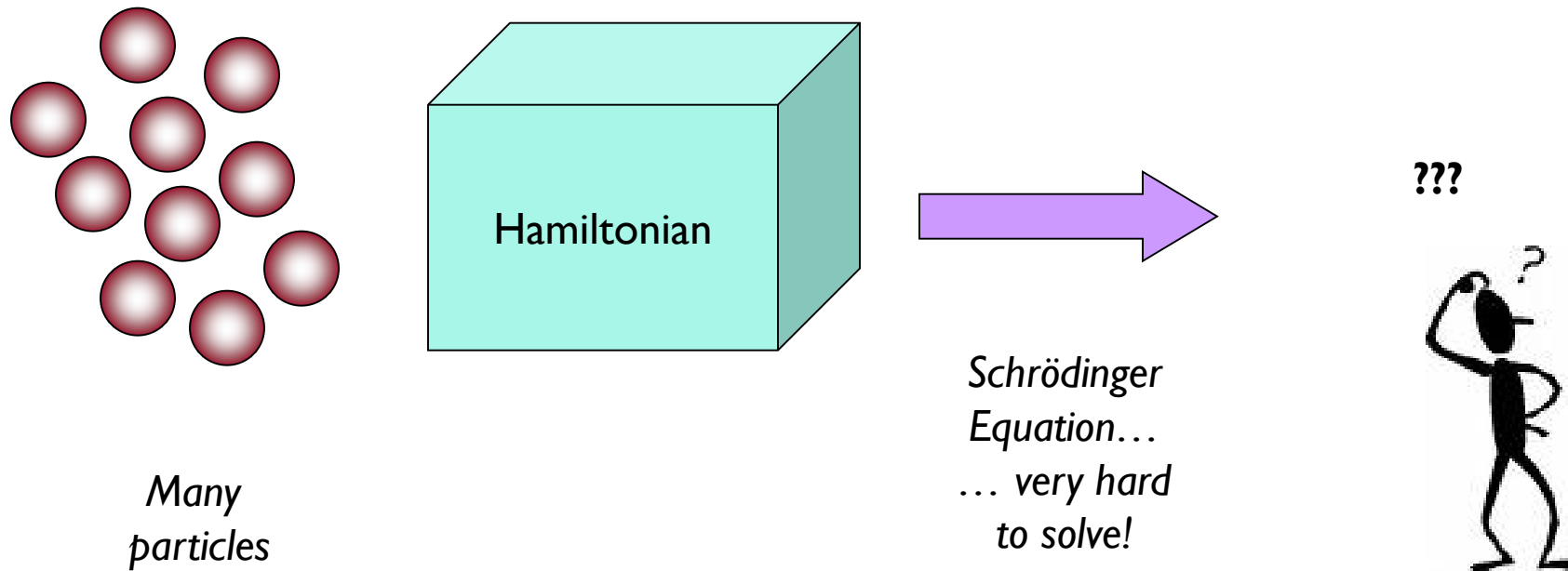
- The completeness relation is given as
$$\sum_k |a_k\rangle\langle a_k| = I$$

Which can be used to change from one 'basis' type of function to another

For real-space this looks like $\langle x|\psi\rangle = \psi(x)$

$$\langle\psi|\phi\rangle = \sum_k \langle\psi|x_k\rangle\langle x_k|\phi\rangle = \int_{all\ space} \psi^*(\vec{x})\phi(\vec{x})dx$$

Techniques to solve for the allowed energies



VARIATIONAL PRINCIPLE

$$E_{gs} \leq \langle \psi | H | \psi \rangle$$

*Ground
state*

*Expectation value
on any normalized
function ψ*

Works with **ANY** normalized wavefunction !!!!!
(must meet boundary conditions)

VARIATIONAL PRINCIPLE: METHOD

- Define your system, and the Hamiltonian H
- Pick a normalized wave function ψ
- Calculate $\langle \psi | H | \psi \rangle$
- Minimize $\langle \psi | H | \psi \rangle$
- You get an estimate of ground state energy

$$E_{gs} \leq \langle \psi | H | \psi \rangle_{\min}$$

A mean value is always higher than the lowest value !

VARIATIONAL PRINCIPLE: FIRST EXCITED STATE

$$E_{fe} \leq \langle \psi_{\perp} | H | \psi_{\perp} \rangle$$

*First
excited
state*

*Expectation value
on a normalized function ψ
normal to ground state*

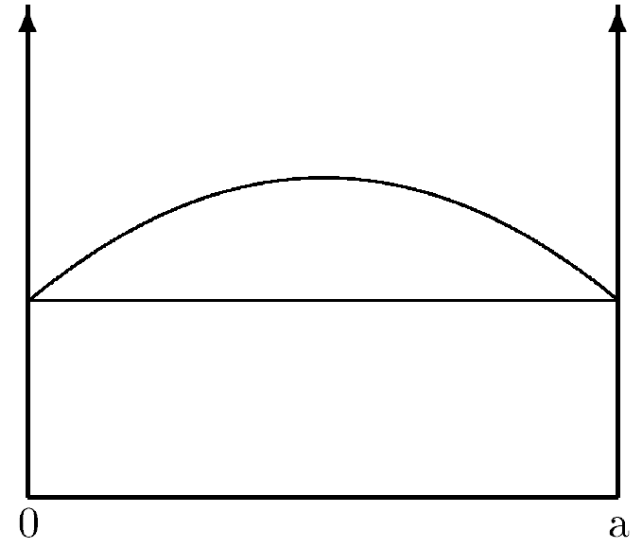
Must find a state orthogonal to the ground state

VARIATIONAL PRINCIPLE: PARTICLE IN A BOX

Trial function: $\tilde{\psi} = x(a - x)$

Norm: $\langle \tilde{\psi} | \tilde{\psi} \rangle = \int_0^a x^2 (a - x)^2 dx = \frac{a^5}{30}$

$$\begin{aligned} \langle \tilde{\psi} | \mathcal{H} | \tilde{\psi} \rangle &= -\frac{\hbar^2}{2m} \int_0^a x(a - x) \frac{d^2}{dx^2} x(a - x) dx \\ &= \frac{\hbar^2}{2m} \frac{a^3}{3}, \end{aligned}$$



Variational Energy: $\tilde{E} = \langle \mathcal{H} \rangle = \frac{10\hbar^2}{2ma^2}$

Exact energy: $E_1 = \frac{\hbar^2 \pi^2}{2m a^2}$

Overestimates by a factor: $\frac{10}{\pi^2} = 1.013$

HELIUM ATOM

Ground State of the He Atom – 1s State

Neglecting nuclear motion

$$\underline{H} = -\frac{\hbar^2}{2m_0}\nabla_1^2 - \frac{\hbar^2}{2m_0}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

kinetic energies attraction of electrons to nucleus electron – electron repulsion

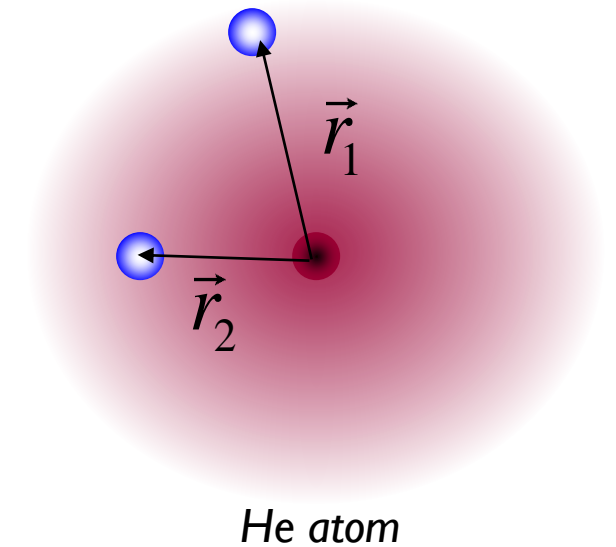
1 - electron 1

2 - electron 2

r_1 - distance of 1 to nucleus

r_2 - distance of 2 to nucleus

r_{12} - distance between two electrons



Hamiltonian for He:

$$H = -\frac{\hbar^2}{2m}(\vec{\nabla}_1^2 + \vec{\nabla}_2^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}},$$

$$r_{12} \equiv |\vec{r}_1 - \vec{r}_2|$$

Trial Wavefunction:

$$\psi(\vec{r}_1, \vec{r}_2, Z) = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}$$

Z = variational parameter

Variational Energy:

$$E(Z) = \langle \psi(Z) | H | \psi(Z) \rangle ,$$

$$E_0 \equiv E(Z_{\min}) \qquad E_0 \geq E_g.$$

Solve integral:

$$E(Z) = \left(\frac{Z^3}{\pi a_0^3} \right)^2 \int d^3 r_1 d^3 r_2 e^{-Z(r_1+r_2)/a_0} \times \left[\frac{\hbar^2}{2m} (\vec{\nabla}_1^2 + \vec{\nabla}_2^2) - 2e^2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{r_{12}} \right] e^{-Z(r_1+r_2)/a_0} .$$

Simplification (from Hydrogen atom):

$$\left[\frac{\hbar^2}{2m} (\vec{\nabla}_1^2 + \vec{\nabla}_2^2) - Ze^2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right] e^{-Z(r_1+r_2)/a_0} = (-2Z^2 \text{ Ry}) e^{-Z(r_1+r_2)/a_0} ,$$

$$1 \text{ Ry} = \frac{me^4}{2\hbar^2} = \frac{e^2}{2a_0} \simeq 13.6 \text{ eV} ,$$

Normalization condition:

$$\left(\frac{Z^3}{\pi a_0^3} \right)^2 \int d^3 r_1 d^3 r_2 e^{-2Z(r_1+r_2)/a_0} = 1 ,$$

$$E(Z) = -2 \text{ Ry}(4Z - Z^2) + \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int d^3r_1 d^3r_2 \frac{e^2}{r_{12}} e^{-2Z(r_1+r_2)/a_0} .$$

After integrating: $E(Z) = -2 \text{ Ry} \left[4Z - Z^2 - \frac{5}{8}Z\right] = -2 \text{ Ry} \left[\frac{27}{8}Z - Z^2\right]$

Minimizing: $\frac{dE}{dZ} = -2 \text{ Ry} \left[\frac{27}{8} - 2Z\right] = 0, \quad Z_{\min} = \frac{27}{16} .$

Variational Energy: $E_0 \simeq -77.4 \text{ eV} \quad E_g = -78.98 \text{ eV}$

It can still be improved much further with other trial functions...

ATOMIC UNITS

Atomic units (au or a.u.) form a system of natural units which is especially convenient for atomic physics calculations. There are two different kinds of atomic units, Hartree atomic units and Rydberg atomic units, which differ in the choice of the unit of mass and charge.

$$-\frac{\hbar^2}{2m_e} \nabla^2 \Psi - \frac{e^2}{4\pi\epsilon_0 r} \Psi = E\Psi$$

The following are set to unity for Hartree atomic units

$$\hbar \quad m_e \quad e \quad 1/4\pi\epsilon_0$$

Hartree atomic units

Some physical constants expressed in atomic units

Name	Symbol/Definition	Value in atomic units
speed of light	c	$1/\alpha \approx 137$
classical electron radius	$r_e = \frac{1}{4\pi\epsilon_0} \frac{e^2}{m_e c^2}$	$\alpha^2 \approx 5.32 \times 10^{-5}$
proton mass	m_p	$m_p/m_e \approx 1836$

ATOMIC UNITS

(Hartree atomic units)

Derived atomic units

Dimension	Name	Symbol	Expression	Value in SI units	Value in more common units
length	bohr	a_0	$4\pi\epsilon_0\hbar^2/(m_e e^2) = \hbar/(m_e c\alpha)$	$5.291\,772\,1092(17) \times 10^{-11} \text{ m}^{[6]}$	$0.052\,917\,721\,092(17) \text{ nm}$ $= 0.529\,177\,210\,92(17) \text{ Å}$
energy	hartree	E_h	$m_e e^4 / (4\pi\epsilon_0 \hbar)^2 = \alpha^2 m_e c^2$	$4.359\,744\,17(75) \times 10^{-18} \text{ J}$	$27.211\,385 \text{ eV} =$ $627.509 \text{ kcal}\cdot\text{mol}^{-1}$
time			\hbar/E_h	$2.418\,884\,326\,505(16) \times 10^{-17} \text{ s}$	
velocity			$a_0 E_h / \hbar = \alpha c$	$2.187\,691\,2633(73) \times 10^6 \text{ m}\cdot\text{s}^{-1}$	
force			E_h/a_0	$8.238\,7225(14) \times 10^{-8} \text{ N}$	$82.387 \text{ nN} =$ $51.421 \text{ eV}\cdot\text{Å}^{-1}$
temperature			E_h/k_B	$3.157\,7464(55) \times 10^5 \text{ K}$	
pressure			E_h/a_0^3	$2.942\,1912(19) \times 10^{13} \text{ Pa}$	
electric field			$E_h/(ea_0)$	$5.142\,206\,52(11) \times 10^{11} \text{ V}\cdot\text{m}^{-1}$	$5.142\,206\,52(11) \text{ GV}\cdot\text{cm}^{-1}$ $= 51.422\,0652(11) \text{ V}\cdot\text{Å}^{-1}$
electric potential			E_h/e	$2.721\,138\,505(60) \times 10^1 \text{ V}$	



Questions???

Sources

MIT OpenCourseWare

<http://ocw.mit.edu>

UCSC

<http://scipp.ucsc.edu/~haber/ph216/>

Oxford University

<http://ritchie.chem.ox.ac.uk/teaching.htm>

BYU

<http://www.physics.byu.edu/faculty/chesnel/physics451.aspx>

Stanford

<https://chemistry.stanford.edu/faculty/michael-fayer>