QUANTUM CHEMISTRY -I

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Basics of Quantum Mechanics
- Why Quantum Physics? -

- Classical mechanics (Newton's mechanics) and Maxwell's equations (electromagnetics theory) can explain MACROSCOPIC phenomena such as motion of billiard balls or rockets.

- Quantum mechanics is used to explain microscopic phenomena such as photon-atom scattering and flow of the electrons in a semiconductor.

- QUANTUM MECHANICS is a collection of postulates based on a huge number of experimental observations.

- The differences between the classical and quantum mechanics can be understood by examining both
  - The classical point of view
  - The quantum point of view
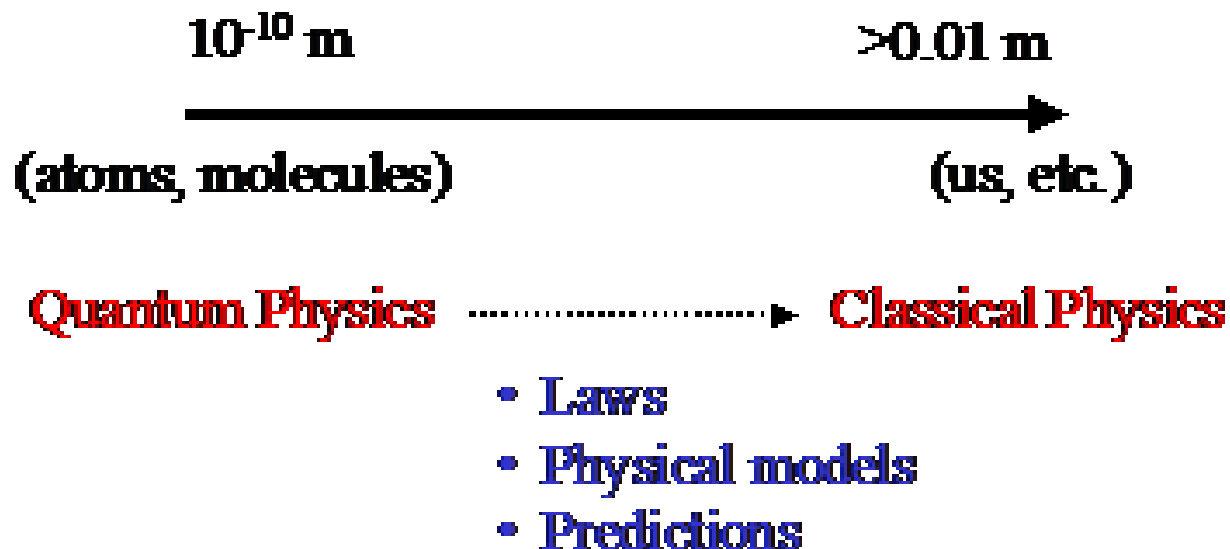
Basics of Quantum Mechanics
- Classical Point of View -

- In Newtonian mechanics, the laws are written in terms of PARTICLE TRAJECTORIES.

- A PARTICLE is an indivisible mass point object that has a variety of properties that can be measured, which we call observables. The observables specify the state of the particle (position and momentum).

- A SYSTEM is a collection of particles, which interact among themselves via internal forces, and can also interact with the outside world via external forces. The STATE OF A SYSTEM is a collection of the states of the particles that comprise the system.

- All properties of a particle can be known to infinite precision.

- **Conclusions:**
  - TRAJECTORY ➔ state descriptor of Newtonian physics,
  - EVOLUTION OF THE STATE ➔ Use Newton's second law
  - PRINCIPLE OF CAUSALITY ➔ Two identical systems with the same initial conditions, subject to the same measurement will yield the same result.

Basics of Quantum Mechanics
- The Correspondence Principle -

When Quantum physics is applied to macroscopic systems, it must reduce to the classical physics. Therefore, the nonclassical phenomena, such as uncertainty and duality, must become undetectable. Niels Bohr codified this requirement into his Correspondence principle:

10^{-10} m   >0.01 m

→

(atoms, molecules)   (us, etc.)

Quantum Physics ....▶ Classical Physics

- Laws
- Physical models
- Predictions

Basics of Quantum Mechanics
- Particle-Wave Duality -

- Waves as particles:

  - Max Plank work on black-body radiation, in which he assumed that the molecules of the cavity walls, described using a simple oscillator model, can only exchange energy in quantized units.

  - 1905 Einstein proposed that the energy in an electromagnetic field is not spread out over a spherical wavefront, but instead is localized in individual clumbs - quanta. Each quantum of frequency n travels through space with speed of light, carrying a discrete amount of energy and momentum =photon => used to explain the photoelectric effect, later to be confirmed by the x-ray experiments of Compton.

- Particles as waves

  - Double-slit experiment, in which instead of using a light source, one uses the electron gun. The electrons are diffracted by the slit and then interfere in the region between the diaphragm and the detector.

  - Aharonov-Bohm effect

Basics of Quantum Mechanics
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Basics of Quantum Mechanics
- Heisenberg Uncertainty Principle -

- One cannot unambiguously specify the values of particle's position and its momentum for a microscopic particle, i.e.

$$\Delta x(t_0) \cdot \Delta p_x(t_0) \geq \frac{1}{2}\frac{h}{2\pi}$$

- Position and momentum are, therefore, considered as incompatible variables.

- The Heisenberg uncertainty principle strikes at the very heart of the classical physics => the particle trajectory.

Postulates of Quantum Mechanics

Basics of Quantum Mechanics
- What is Quantum Mechanics? -

- Quantum Mechanics is nothing more but linear algebra and Hilbert spaces

- What makes quantum mechanics quantum mechanics is the physical interpretation of the results that are obtained

Basics of Quantum Mechanics
- First Postulate of Quantum Mechanics -

Quantum physicists are interested in all kinds of physical systems (photons, conduction electrons in metals and semiconductors, atoms, etc.). State of these rather diverse systems are represented by the same type of functions ➔ STATE FUNCTIONS.

First postulate of Quantum mechanics:

Every physically-realizable state of the system is described in quantum mechanics by a state function ψ that contains all accessible physical information about the system in that state.

- **Physically realizable states** ➔ states that can be studied in laboratory
- **Accesible information** ➔ the information we can extract from the wavefunction
- **State function** ➔ function of position, momentum, energy that is spatially localized.

Basics of Quantum Mechanics
- Second Postulate of Quantum Mechanics -

If a system is in a quantum state represented by a wavefunction ψ, then

$$PdV = |\psi|^2 \, dV$$

is the probability that in a position measurement at time *t* the particle will be detected in the infinitesimal volume d*V*.

Note:

$$|\psi(x,t)|^2$$ ➜ position and time probability density

The importance of normalization follows from the Born interpretation of the state function as a position probability amplitude. According to the second postulate of quantum mechanics, the integrated probability density can be interpreted as a probability that in a position measurement at time t, we will find the particle anywhere in space.

Basics of Quantum Mechanics
- Third Postulate of Quantum Mechanics -

Third Postulate:

Every observable in quantum mechanics is represented by an operator which is used to obtain physical information about the observable from the state function. For an observable that is represented in classical physics by a function $Q(x,p)$, the corresponding operator is $Q(\hat{x}, \hat{p})$.

Observable	Operator
Position	$\hat{x}$
Momentum	$\hat{p} = \dfrac{\hbar}{i} \dfrac{\partial}{\partial x}$
Energy	$E = \dfrac{\hat{p}^2}{2m} + V(\hat{x}) = -\dfrac{\hbar^2}{2m} \dfrac{\partial^2}{\partial x^2} + V(x)$

Basics of Quantum Mechanics
More on Operators

➢ An operator is an instruction, a symbol which tells us to perform one or more mathematical acts on a function, say $f(x)$. The essential point is that they act on a function.

➢ Operators act on everything to the right, unless the action is constrained by brackets.

➢ Addition and subtraction rule for operators:

$$\left(\hat{Q}_1 \pm \hat{Q}_2\right)f(x) = \hat{Q}_1 f(x) \pm \hat{Q}_2 f(x)$$

➢ The product of two operators implies succesive operation:

$$\hat{Q}_1\hat{Q}_2 f(x) = \hat{Q}_1\left[\hat{Q}_2 f(x)\right]$$

➢ The product of two operators is a third operator:

$$\hat{Q}_3 = \hat{Q}_1\hat{Q}_2$$

➢ Two operators commute if they obey the simple operator expression:

$$\left[\hat{Q}_1,\hat{Q}_2\right] = \hat{Q}_1\hat{Q}_2 - \hat{Q}_2\hat{Q}_1 = 0 \quad \Rightarrow \quad \hat{Q}_1\hat{Q}_2 = \hat{Q}_2\hat{Q}_1$$

Basics of Quantum Mechanics
- More on Operators -

The requirement for two operators to be commuting operators is a very important one in quantum mechanics and it means that we can simultaneously measure the observables represented with these two operators. The non-commutivity of the position and the momentum operators (the inability to simultaneously determine particles position and its momentum) is represented with the Heisenberg uncertainty principle, which in mathematical form is expressed as:

and can be

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2} = \frac{1}{2}\left|\langle[\widehat{x}, \widehat{p}]\rangle\right|$$

rvables.

Wavefunctions

- Given any set S of system states (mutually distinguishable, or not),

- A quantum state vector can also be translated to a ***wavefunction*** $\Psi : S \rightarrow \mathbf{C}$, giving, for each state $s \in S$, **the amplitude $\Psi(s)$** of that state.

  – When s is another state vector, and the real state is t, then $\Psi(s)$ is just $s^{\dagger}t.$

  – Ψ is called a *wavefunction* because its time evolution obeys an equation (Schrödinger's equation) which has the form of a ***wave equation*** when S ranges over a space of *positional* states.

Schrödinger's Wave Equation

We have a system with states given by (**x**,t) where:

- – **t** is a global time coordinate, and
- – **x** describes $N/3$ particles ($p_1,...,p_{N/3}$) with masses ($m_1,...,m_{N/3}$) in a 3-D Euclidean space,
- – where each p_i is located at coordinates (x_{3i}, x_{3i+1}, x_{3i+2}), and
- – where particles interact with potential energy function $V(\mathbf{x},t)$,

- • the wavefunction $\Psi(\mathbf{x},t)$ obeys the following (2nd-order, linear, partial) differential equation:

Planck
Constant

$$-\frac{\hbar}{2}\left(\sum_{j=0}^{N-1}\frac{1}{m_{\lfloor j/3\rfloor}}\frac{\partial^2}{\partial x_j^2}\Psi(\mathbf{x},t)\right)+V(\mathbf{x},t)=i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x},t)$$

Features of the wave equation

- Particles' *momentum* state ***p*** is encoded implicitly by the particle's wavelength λ: *p=h/λ*

- The *energy* of any state is given by the <u>frequency ν of rotation</u> of the wavefunction in the complex plane: ***E=hν.***

- By simulating this simple equation, one can observe basic quantum phenomena such as:
  - Interference fringes

The Schrödinger Equation

$$\left|\Psi(0)\right\rangle \qquad\qquad\qquad\qquad \left|\Psi(t)\right\rangle$$

- The Schrödinger Equation governs the transformation of an initial *input state* to a final *output state*. It is a prescription for what we want to do to the computer.

$$\left|\Psi(t)\right\rangle = T_\tau \exp\left[i\int_0^t \hat{H}(\tau)d\tau \right] \left|\Psi(0)\right\rangle = \hat{U}(t)\left|\Psi(0)\right\rangle$$

$$\hat{H}(\tau)$$

- is a time-dependent Hermitian matrix of size 2^n called the **Hamiltonian**

$$\hat{U}(t)$$

- is a matrix of size 2^n called the **evolution matrix**,

- Vectors of complex numbers of length 2^n
- T_τ is the time-ordering operator

The Schrödinger Equation

- n is the number of quantum bits (qubits) in the quantum computer

- The function *exp* is the traditional exponential function, but some care must be taken here because the argument is a matrix.
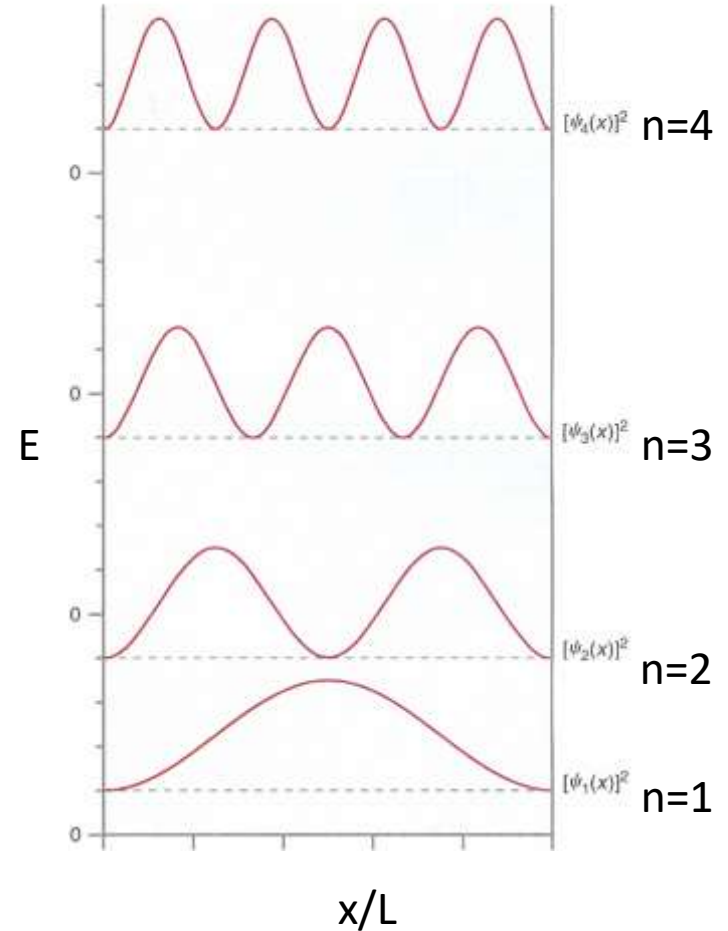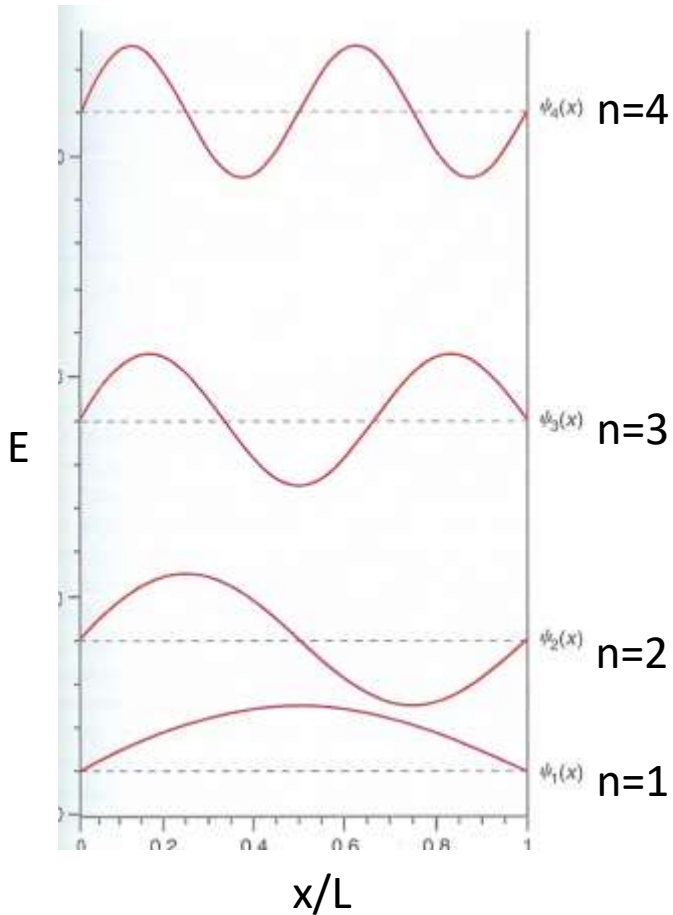
$$\exp[x] = \sum_{n=0}^{\infty} \left(\frac{x^n}{n!} \right)$$

$$\hat{U}(t)$$

- The evolution matrix $\hat{U}(t)$ is the program for the quantum computer. Applying this program to the input state produces the output state $|\Psi(t)\rangle$,which gives us a solution to the problem.
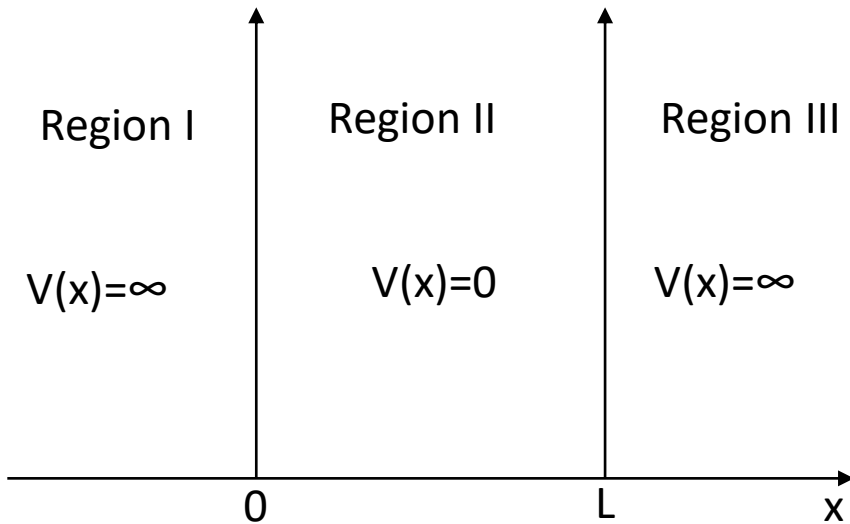
$$\left| \Psi(t) \right\rangle = T_\tau \exp\left[i \int_0^t \hat{H}(\tau) d\tau \right] \left| \Psi(0) \right\rangle = \hat{U}(t) \left| \Psi(0) \right\rangle$$

Particle in a 1-Dimensional Box

$$\psi_{II} = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

Applying the Born Interpretation

$$\left|\psi_{II}\right|^2 = \frac{2}{L}\left(\sin \frac{n\pi x}{L}\right)^2$$

E

$\psi_4(x)$ n=4

$\psi_3(x)$ n=3

$\psi_2(x)$ n=2

$\psi_1(x)$ n=1

x/L

E

$[\psi_4(x)]^2$ n=4

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x/L

Particle in a 1-Dimensional Box

Region I	Region II	Region III
$V(x)=\infty$	$V(x)=0$	$V(x)=\infty$

0   L   X

$V(x)=0$ for $L>x>0$
$V(x)=\infty$ for $x\geq L, x\leq 0$

Classical Physics: The particle can exist anywhere in the box and follow a path in accordance to Newton's Laws.

Quantum Physics: The particle is expressed by a wave function and there are certain areas more likely to contain the particle within the box.

Time Dependent Schrödinger Equation

$$\underbrace{\frac{-\hbar^2}{2m}\frac{d^2\Psi}{dx^2}}_{KE}+\underbrace{V(x)\Psi}_{PE}=\underbrace{E\Psi}_{TE}$$

Wave function is dependent on time and position function:

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

Time Independent Schrödinger Equation

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

Applying boundary conditions:
Region I and III:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+\infty*\psi=E\psi\longrightarrow\left|\psi\right|^2=0$$

Region II:

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

Finding the Wave Function

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

This is similar to the general differential equation:

$$-\frac{d^2\psi(x)}{dx^2} = k^2\psi \qquad\longrightarrow\qquad \psi = A\sin kx + B\cos kx$$

So we can start applying boundary conditions:

x=0 ψ=0
$$0 = A\sin 0k + B\cos 0k \longrightarrow 0 = 0 + B*1 \therefore B = 0$$

x=L ψ=0
$$0 = A\sin kL \quad A \neq 0 \longrightarrow kL = n\pi \quad \text{where n} \neq \quad *$$

Calculating Energy Levels:

$$k^2 = \frac{2mE}{\hbar^2} \longrightarrow E = \frac{k^2\hbar^2}{2m} \longrightarrow E = \frac{k^2h^2}{2m4\pi^2}$$

$$\hbar = \frac{h}{2\pi}$$

$$E = \frac{n^2\pi^2}{L^2}\frac{h^2}{2m4\pi^2} \longrightarrow E = \frac{n^2h^2}{8mL^2}$$

Our new wave function:
$$\psi_{II} = A\sin\frac{n\pi x}{L} \qquad \text{But what is 'A'?}$$

Normalizing wave function:

$$\int_0^L (A\sin kx)^2 dx = 1$$

$$|A|^2 \left[\frac{x}{2} - \frac{\sin 2kx}{4k}\right]_0^L = 1$$

$$|A|^2 \left[\frac{L}{2} - \frac{\sin 2\frac{n\pi}{L}L}{4\frac{n\pi}{L}}\right] = 1$$
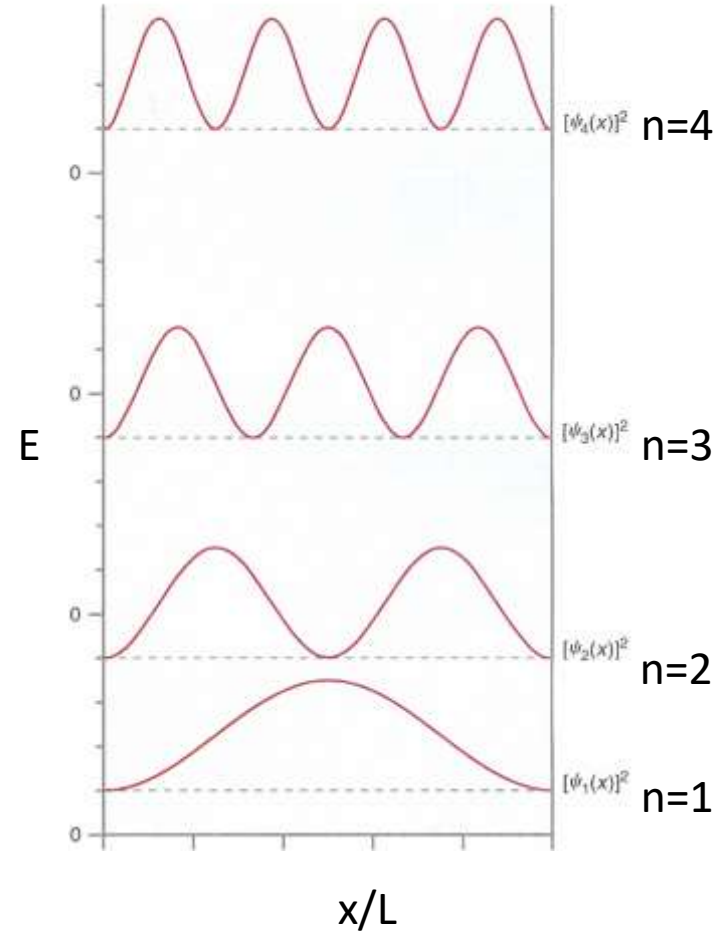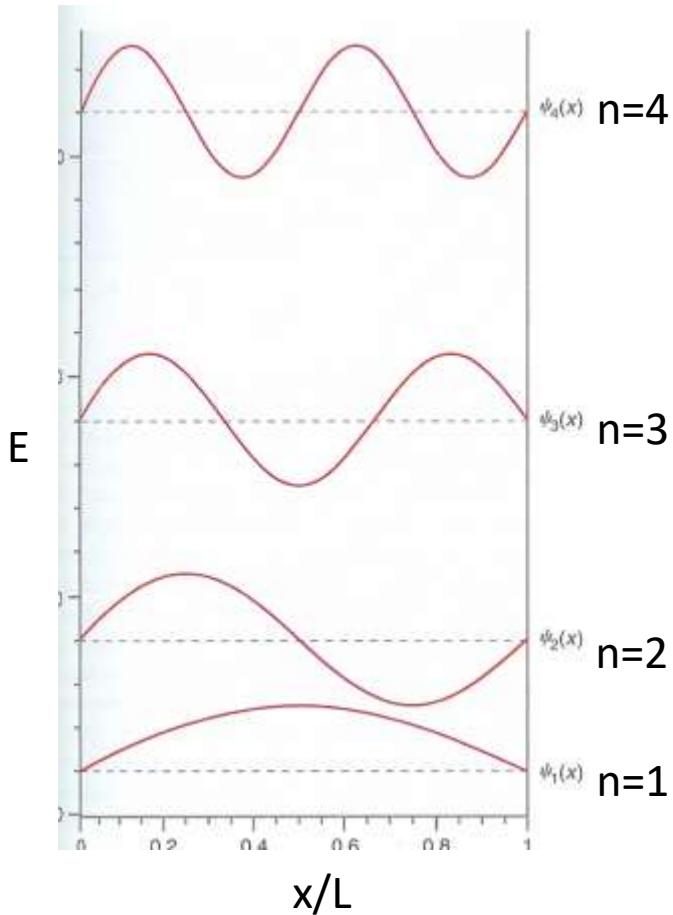
Since n $\neq$ *

$$|A|^2\left(\frac{L}{2}\right) = 1 \longrightarrow |A| = \sqrt{\frac{2}{L}}$$

Our normalized wave function is:

$$\psi_{II} = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

Particle in a 1-Dimensional Box

$$\psi_{II} = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

Applying the
Born Interpretation $\longrightarrow$

$$\left|\psi_{II}\right|^2 = \frac{2}{L}\left(\sin \frac{n\pi x}{L}\right)^2$$

E

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x/L

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x/L

Variational principle

Statement 1:

The complete set of exact eigenfunctions of H define an orthogonal complete basis set for the total space of wave functions.

demonstration:

H is Hermitic. Let be Ψ_a and Ψ_b two normalized wavefunctions (associated with two different values E_a and E_b). We have therefore (due to hermiticity)

$$< \Psi_a |H| \Psi_b > = E_a < \Psi_a | \Psi_b >$$
$$< \Psi_a |H| \Psi_b > = E_b < \Psi_a | \Psi_b >$$

Wherefrom $(E_a - E_b) < \Psi_a | \Psi_b > = 0$

and since $E_a \neq E_b$

$$< \Psi_a | \Psi_b > = 0$$

Consequence:

If so, it is possible to express any function as a linear combination of the exact eigenfunctions, Ψ_t.

Variational principle

The energy associated with Ψ a function is always above that of the eigenfunction of lowest energy: E_0.

Ψ is not a eigenfunction; it is associated with an energy <E> that is an average energy (mean value)

A mean value is always intermediate relative to extreme:
Greater than the smallest!

<E> > E_0

Mean value

- If Ψ_1 and Ψ_2 are associated with the same eigenvalue o:
  $O(a\Psi_1 + b\Psi_2) = o(a\Psi_1 + b\Psi_2)$

- If not $O(a\Psi_1 + b\Psi_2) = o_1(a\Psi_1) + o_2(b\Psi_2)$

we define $<O> = (a^2 o_1 + b^2 o_2)/(a^2 + b^2)$

$$\Psi^* \, \mathbf{O} \, \Psi = \Psi^* \, o \, \Psi$$

o is a multiplying factor

$$\int_\infty (\Psi^* O \Psi) dV = o \int_\infty (\Psi^* \Psi) dV$$

$$o = \frac{\int_\infty (\Psi^* O \Psi) dV}{\int_\infty (\Psi^* \Psi) dV} = \frac{<\Psi | O | \Psi>}{<\Psi | \Psi>}$$

Dirac notations

Variational principle

Statement 2:

The energy associated with Ψ a function is always above that of the eigenfunction of lowest energy: E_0.

Ψ_α and Ψ_β are two eigenfunctions

$< \Psi_\alpha |H| = < \Psi_\alpha | E_\alpha$ and $|H| \Psi_\beta > = E_\beta | \Psi_\beta >$

wherefrom $< \Psi_\alpha |H| \Psi_\beta > = E_\alpha \delta_{\alpha\beta}$

From statement 1, Ψ is a linear combination of Ψ_α s

$$| \Psi_\alpha > = \sum_\alpha c_\alpha | \Psi_\alpha >$$

let multiply the left by $< \Psi_\alpha |$; this leads to only one term $c_\alpha = < \Psi_\alpha | \Psi >$

and similarly $c^*_\alpha = < \Psi | \Psi_\alpha >$

then $| \Psi > = \sum_\alpha < \Psi_\alpha | \Psi > | \Psi_\alpha >$

Variational principle

Ψ_α and Ψ_β are two eigenfunctions
associated to E_α and E_β
From statement 1, Ψ is a linear combination of Ψ_α s

$$| \Psi > = \sum_\alpha c_\alpha | \Psi_\alpha >$$

then

$$< \Psi | \Psi > = \sum_{\alpha,\beta} c_\alpha < \Psi_\alpha | \Psi_\beta > c_\beta$$

$$< \Psi | \Psi > = \sum_\alpha c_\alpha{}^2 < \Psi_\alpha | \Psi_\alpha > = \sum_\alpha c_\alpha{}^2 = 1$$

Variational principle

Statement 2, Demonstration:

$$< \Psi |H| \Psi > = \Sigma_{\alpha,\beta} c_\alpha < \Psi_\alpha |H| \Psi_\beta > c_\beta$$

$$< \Psi |H| \Psi > = \sum_{\alpha,\beta} E_\alpha < \Psi_\alpha | \Psi_\beta > c_\beta$$

$$< \Psi |H| \Psi > = \sum_{\alpha,\beta} E_\alpha \, c_\alpha \, \delta_{\alpha\beta} \, c_\beta$$

$$< \Psi |H| \Psi > = \sum_{\alpha,} E_\alpha \, c_\alpha{}^2 \; {}_> \; \Sigma_{\alpha,} E_0 \, c_\alpha{}^2 = E_0$$

$$E \quad {}_> E_0$$

An non-exact solution has always a higher energy than the lowest exact solution

Operator

- A rule that transforms a given function into another function

A New mathematical tool:
Wave functions and Operators

Each particle may be described by a wave function $Y(x,y,z,t)$, real or complex, having a single value when position (x,y,z) and time (t) are defined.

If it is not time-dependent, it is called stationary.

The expression $Y=Ae^{i(pr-Et)}$ does not represent one molecule but a flow of particles: a plane wave

Operators associated to physical quantities

We cannot use functions (otherwise we would end with classical mechanics)

Any physical quantity is associated with an operator.
An operator O is "the recipe to transform **Y** into **Y**' "
We write: O **Y** = **Y**'
If O **Y** = o**Y** (o is a number, meaning that O does not modify **Y**, just a scaling factor), we say that **Y** is an eigenfunction of O and o is the eigenvalue.
We have solved the wave equation O **Y** = o**Y** by finding simultaneously **Y** and o that satisfy the equation.
o is the measure of O for the particle in the state described by **Y**.

Operator

- Example. Apply the following operators on the given functions:
- (a) Operator d/dx and function x^2.
- (b) Operator d^2/dx^2 and function $4x^2$.
- (c) Operator $(\partial/\partial y)x$ and function xy^2.
- (d) Operator $-i\hbar d/dx$ and function $\exp(-ikx)$.
- (e) Operator $-\hbar^2 d^2/dx^2$ and function $\exp(-ikx)$.

Identifying the operators

Observable	Classical Symbol	Quantum Operator	Operation
position	$\mathbf{r}$	$\hat{r}$	multiply by $\mathbf{r}$
momentum	$\mathbf{p}$	$\hat{p}$	$-i\hbar(\hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z})$
kinetic energy	T	$\hat{T}$	$\frac{-\hbar^2}{2m}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})$
potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	multiply by $V(\mathbf{r})$
total energy	E	$\mathcal{H}$	$\frac{-\hbar^2}{2m}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) + V(\mathbf{r})$
angular momentum	l_x	$\hat{l}_x$	$-i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})$
	l_y	$\hat{l}_y$	$-i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})$
	l_z	$\hat{l}_z$	$-i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$

Linearity

The operators are linear:

$$O\,(a\Psi_1 + b\Psi_1) = O\,(a\Psi_1) + O(\,b\Psi_1)$$

Normalization

An eigenfunction remains an eigenfunction when multiplied by a constant

O($\lambda\Psi$)= o($\lambda\Psi$) thus it is always possible to normalize a finite function

$$\int_{total\_space} \Psi^* \Psi dV = N \ \text{taking} \ \Psi' = \frac{1}{\sqrt{N}} \Psi \ \text{gives} \ \int_{total\_space} \Psi'^* \Psi' dV = 1$$

Dirac notations   <Ψ|Ψ>

Hermitian Operator

- Hermitian operators have two properties that forms the basis of quantum mechanics

(i) Eigen value of a Hermitian operator are real.

(ii) Eigenfunctions of Hermitian operators are orthogonal to each other or can be made orthogonal by taking linear combinations of them.

Hermitian operator

A hermitian operator $\hat{A}$ satisfies

$$\int f^* \hat{A} g dx = \int g(\hat{A}f)^* dx \; ; \text{if } f \text{ and } g \text{ are well behaved}$$

- Prove Operator x is Hermitian.

$$x_{rs} \equiv \int \psi_r^* x \psi_s \, dx = \int \left(\psi_r x^* \psi_s^* \right)^* dx = \int (\psi_s^* x^* \psi_r)^* \, dx \equiv x_{sr}^*$$

Hermitian operator or not ??

$$(i)\,\frac{\partial}{\partial x}$$

$$(ii)\,-i\hbar\,\frac{\partial}{\partial x}$$

$$(iii)\,\frac{\partial^2}{\partial x^2}$$

Eigen function and eigen value

$$f(x) = e^{ikx}$$

Is it eigen function of momentum operator ?

What is eigen value ?

Eigenvalue equation

Eigenvalue equation

    (Operator)(function) = (constant factor)*(same function)

Example: e^{ikx} is an eigenfunction of a operator $\hat{P}_x = -i\hbar\dfrac{\partial}{\partial x}$

    $F(x) = e^{ikx}$

    $= -i\,\hbar\dfrac{\partial}{\partial x}\,e^{ikx}$

$$= -i^2\,\hbar k^2 e^{ikx}$$

$$= \hbar\,k^2 e^{ikx}$$
    Thus e^{ikx} is an eigenfunction

Significance of commutation rules

- The eigenvalue of a Hermitian operator is real.

- A real eigenvalue means that the physical quantity for which the operator stands for can be measured experimentally.

- The eigenvalues of two commuting operators can be computed by using the common set of eigenfunctions.

If the two operators commute, then it is possible to measure the simultaneously the precise value of both the physical quantities for which the operators stand for.

Question: Find commutator of the operators x and p_x

 Is it expected to be a non-zero or zero quantity?

Hint: Heisenberg Uncertainty Principle

Commute or not ??

- Operator x and d/dx

They don't

$$\hat{A} = \hat{x}$$

$$\hat{B} = \frac{d}{dx}$$

$$\hat{A}\,\hat{B}\,f(x) = xf'(x)$$

$$\hat{B}\,\hat{A}\,f(x) = \frac{d}{dx}[xf(x)] = xf'(x) + f(x)$$

$$\left[\hat{A},\hat{B}\right]f(x) = -f(x)$$

$$\left[\hat{A},\hat{B}\right] = -1$$

Mean value theorem

Expectation value in general:

$$\langle a \rangle = \frac{\displaystyle\int_{-\infty}^{\infty} \Psi^*(x)\,\hat{A}\Psi(x)\,dx}{\displaystyle\int_{-\infty}^{\infty} \Psi^*(x)\,\Psi(x)\,dx}$$

$$= \int_{-\infty}^{\infty} \Psi^*(x)\,\hat{A}\Psi(x)\,dx \quad (\text{if normalized})$$

The fourth postulates states what will be measured when large number of identical systems are interrogated one time. Only after large number of measurements will it converge to <a>.

In QM, the act of the measurement causes the system to "collapse" into a single eigenstate and in the absence of an external perturbation it will remain in that eigenstate.

Mean value

- If Ψ_1 and Ψ_2 are associated with the same eigenvalue o: $O(a\Psi_1 + b\Psi_2) = o(a\Psi_1 + b\Psi_2)$
- If not $O(a\Psi_1 + b\Psi_2) = o_1(a\Psi_1) + o_2(b\Psi_2)$

we define $\bar{o} = (a^2 o_1 + b^2 o_2)/(a^2 + b^2)$

$$\Psi^* \, \mathbf{O} \, \Psi = \Psi^* \, o \, \Psi$$

$\underline{o}$ is a multiplying factor

$$\int_\infty (\Psi * O\Psi) dV = o \int_\infty (\Psi * \Psi) dV$$

$$o = \frac{\int_\infty (\Psi * O\Psi) dV}{\int_\infty (\Psi * \Psi) dV} = \frac{<\Psi | O | \Psi>}{<\Psi | \Psi>}$$

Dirac notations

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Sum, product and commutation of operators

$(A+B)\Psi = A\Psi + B\Psi$

$(AB)\Psi = A(B\Psi)$

eigenvalues

wavefunctions

operators

	$y_1 = e^{4x}$	$y_2 = x^2$	$y_3 = 1/x$
d/dx	4	--	--
x3	3	3	3
x d/dx	--	2	-1

Sum, product and commutation of operators

[A,C]=AC-CA$\neq$0

[A,B]=AB-BA=0
[B,C]=BC-CB=0

$$[\mathbf{A,C}]\,(y) = \mathbf{AC}(y)-\mathbf{CA}(y) = \frac{d}{dx}\left[x\frac{dy}{dx}\right] - x\left[\frac{d}{dx}\left(\frac{dy}{dx}\right)\right]$$

$$[\mathbf{A,C}]\,(y) = x\frac{d^2y}{dx^2} + \frac{dy}{dx} - x\frac{d^2y}{dx^2} = \mathbf{A}(y)$$

$$[\mathbf{A,C}] = \mathbf{A}$$

not compatible
operators

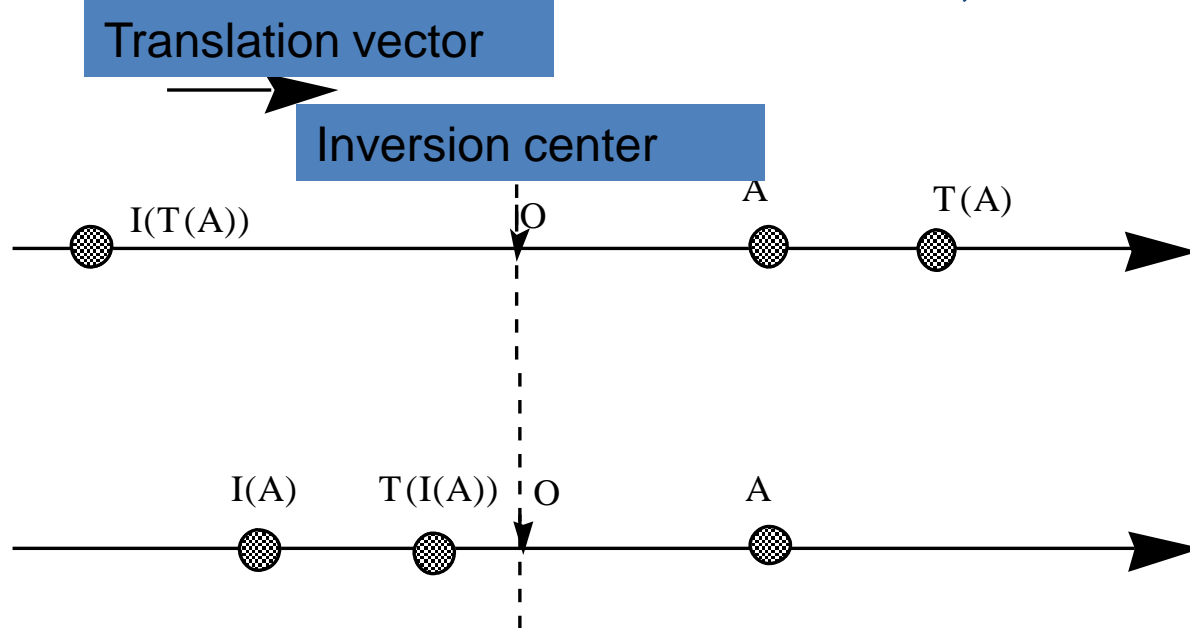|	$y_1 = e^{4x}$	$y_2 = x^2$	$y_3 = 1/x$
A = d/dx	4	--	--
B = x3	3	3	3
C = x d/dx	--	2	-1

x and d/dx do not commute, are incompatible

$$[\![d/dx, x]\!] = d/dx(x\ ) - x(d/dx)$$

$$[\![d/dx, x]\!](y) = \frac{d(xy)}{dx} - x\frac{dy}{dx} = x\frac{dy}{dx} + y - x\frac{dy}{dx} = y$$

$$[\![d/dx, x]\!] = +1$$

Translation and inversion do not commute, are incompatible

Translation vector

Inversion center

I(T(A))   O   A   T(A)

I(A)   T(I(A))   O   A

Momentum and Energy Operators

$$\Psi(r,t) = \Psi(r)\, \Psi(t) = A\, e^{\frac{i}{\hbar}(pr)}\; e^{\frac{i}{\hbar}(-Et)}\; .$$

$$\Psi(r) = A e^{\frac{i}{\hbar}(pr)} \qquad\qquad \Psi(t) = e^{\frac{i}{\hbar}(-Et)}$$

$$\frac{\partial \Psi}{\partial r} = \frac{ip}{\hbar}\, \Psi \quad \text{and} \quad \frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar}\, \Psi$$

$$\text{therefore}\quad \mathbf{p} = \frac{\hbar}{i}\, \frac{\partial}{\partial r} \quad \text{and} \quad \mathbf{E} = i\hbar\, \frac{\partial}{\partial t}$$

Remember during this chapter

Stationary state E=constant

$$\Psi(t) = e^{\frac{i}{\hbar}(-Et)}$$

$$i\hbar\,\frac{\partial \Psi(r,t)}{\partial t} = E\Psi(r,t) = E\Psi(r)\Psi(t)$$

Remember for 3 slides after

Kinetic energy

Classical

$$T = \frac{p^2}{2m}$$

quantum operator

$$\mathbb{P}^2 = \frac{-\hbar^2}{2m} \frac{\partial 2}{\partial_x 2}$$

In 3D :

$$\mathbb{T} = \frac{-\hbar^2}{2m} \left(\frac{\partial 2}{\partial_x 2} + \frac{\partial 2}{\partial_y 2} + \frac{\partial 2}{\partial_z 2} \right) = \frac{-\hbar^2}{2m} \triangle$$

Calling

$$\triangle = \left(\frac{\partial 2}{\partial_x 2} + \frac{\partial 2}{\partial_y 2} + \frac{\partial 2}{\partial_z 2} \right)$$

the laplacian

Pierre Simon, Marquis de Laplace
(1749 -1827)

Correspondence principle angular momentum

Classical expression

Quantum expression

$l_z = xp_y - yp_x$

$$\mathbb{L}_Z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

Quantum-mechanical Operators

Operator name	Symbol	Form	Notes
position (in x direction, for example)	$\hat{\mathbf{x}}$	x	There are also corresponding operators for y, z.
position (three-dimensional, Cartesian coordinates)	$\hat{\mathbf{r}}$	$(x, y, z) \;=\; x\,\vec{x} + y\,\vec{y} + z\,\vec{z}$	
dipole moment (three-dimensional, Cartesian coordinates)	$\hat{\boldsymbol{\mu}}$	$\displaystyle\sum_{j=\text{allatoms}} q_j \mathbf{r}_j$	q is the charge on each atom; **r** is the position of each atom.
dipole moment (one atom in spherical coordinates)	$\hat{\boldsymbol{\mu}}$	$-e\,r\left(\vec{\mathbf{x}}\sin\theta\cos\varphi + \vec{\mathbf{y}}\sin\theta\sin\varphi + \vec{\mathbf{z}}\cos\theta\right)$	
del	∇	$\vec{\mathbf{x}}\dfrac{\partial}{\partial x} + \vec{\mathbf{y}}\dfrac{\partial}{\partial y} + \vec{\mathbf{z}}\dfrac{\partial}{\partial z}$	
Laplacian (three dimensional, Cartesian coordinates)	∇^2	$\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$	
Laplacian (spherical coordinates)	∇^2	$\dfrac{1}{r^2}\left(\dfrac{\partial}{\partial r}\,r^2\,\dfrac{\partial}{\partial r} \;+\; \dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\sin\theta\dfrac{\partial}{\partial\theta} \;+\; \dfrac{1}{\sin^2\theta}\dfrac{\partial^2}{\partial\varphi^2}\right)$	
linear momentum (in x direction, for example)	$\hat{p}_x$	$-i\,\hbar\,\dfrac{\partial}{\partial x}$	There are also corresponding operators for y, z.

linear momentum (3 dimensions)	$\hat{\mathbf{p}}$	$-i\hbar\nabla$	
z-component of angular momentum	$\hat{M}_z$	$-i\hbar\dfrac{\partial}{\partial\varphi}$	
the square of total angular momentum	$\hat{M}^2$	$-\hbar^2\left[\dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\sin\theta\dfrac{\partial}{\partial\theta} + \dfrac{1}{\sin^2\theta}\dfrac{\partial^2}{\partial\varphi^2}\right]$	
electronic angular momentum	$\hat{\mathbf{L}}$	$\vec{x}\,\hat{L}_x + \vec{y}\,\hat{L}_y + \vec{z}\,\hat{L}_z$	Operator has the same form as the angular momentum operator, $\hat{M}$
total energy (Hamiltonian)	$\hat{H}$	$\hat{T} + \hat{V}$	The potential energy (V) depends on the specific system being modeled. Additional energy terms can be added (e.g., interactions with electric or magnetic fields.)
kinetic energy for a single particle (Cartesian coordinates)	$\hat{T}_x$	$\left(\dfrac{-\hbar^2}{2m}\right)\dfrac{\partial^2}{\partial x^2}$	one-dimensional expression
	$\hat{T}$	$\left(\dfrac{-\hbar^2}{2m}\right)\nabla^2$	generalized expression
kinetic energy for a single particle (spherical coordinates)	$\hat{T}$	$\dfrac{-\hbar^2}{2\mu r^2}\left[\dfrac{\partial}{\partial r}r^2\dfrac{\partial}{\partial r} + \dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\sin\theta\dfrac{\partial}{\partial\theta} + \dfrac{1}{\sin^2\theta}\dfrac{\partial^2}{\partial\varphi^2}\right]$	

potential energy for a particle in a box	$\hat{V}$	V = 0 inside box ($0 \le x \le L$) V = ∞ outside box ($x < 0, x > L$)	The box can be extended to 2 or 3 dimensions and the length of the box, L, can be different in each direction.
harmonic oscillator potential	$\hat{V}$	$\dfrac{K}{2}\left(x - x^e\right)^2$	For diatomic molecules; K is the force constant; x^e is the equilibrium bond length.
		$\dfrac{K}{2}\hat{Q}^2$	For polyatomic molecules; $\hat{Q}$ is the operator for the magnitude of the normal coordinate.
Morse (anharmonic) potential	$\hat{V}$	$D_e\left(1 - e^{-\beta x}\right)^2$	where x is the displacement of the oscillator from its equilibrium position, and D_e and β are constants or parameters.
Coulombic potential energy	$\hat{V}$	$\dfrac{q_1 q_2}{4\pi\varepsilon_o r_{12}}$	q is the charge on each particle; r is the distance between particles.
electric field	$\hat{E}$	E	Simple multiplicative operator as long as the field is constant over the area of interaction with the system.
magnetic field	$\hat{B}$	B	Operator is multiplicative and can be written without the caret.

magnetic moment of an electron	$\hat{\boldsymbol{\mu}}_m$	$-\dfrac{e}{2m_e}\,\hat{L}$	
energy of interaction with a magnetic field	$\hat{H}_m$	$-\hat{\boldsymbol{\mu}}_m \bullet \mathbf{B}$	general form
		$\dfrac{e}{2m_e}\,\hat{L}\bullet\mathbf{B}$	the particle is an electron and the magnetic field is directed along the z-axis
		$\dfrac{e\,B_z}{2m_e}\,\hat{L}_z$	
spin orbit interaction	$\hat{H}_{s-o}$	$\lambda\,\hat{\mathbf{S}}\bullet\hat{\mathbf{L}}$	
Coulomb operator	$\hat{J}$	$\hat{J}_j(1)\,\varphi_i(1)\;=\;\left[\displaystyle\int \varphi_i^*(2)\,\dfrac{1}{r_{12}}\,\varphi_i(2)\,d\tau_2\right]\varphi_i(1)$	
Exchange operator	$\hat{K}$	$\hat{K}_j(1)\,\varphi_i(1)\;=\;\left[\displaystyle\int \varphi_j^*(2)\,\dfrac{1}{r_{12}}\,\varphi_i(2)\,d\tau_2\right]\varphi_j(1)$	
Fock operator	$\hat{F}$	$\hat{H}^0 + \displaystyle\sum_{j=1}^{N}\left(2\hat{J}_j - \hat{K}_j\right)$	
		$-\dfrac{\hbar^2}{2m}\nabla^2 - \dfrac{Z\,e^2}{4\pi\varepsilon_0\,r} + \displaystyle\sum_{j=1}^{N}\left(2\hat{J}_j - \hat{K}_j\right)$	

Particle in a 3-D box

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

$$H_x(x)\Psi_x(x) = E_x\Psi_x(x)$$
$$H_y(y)\Psi_y(y) = E_y\Psi_y(y)$$
$$H_z(z)\Psi_z(z) = E_z\Psi_z(z)$$

$$H(x, y, z) = H_x(x) + H_y(y) + H_z(z)$$

$$E = E_x + E_y + E_z$$

$$\Psi(x, y, z) = \Psi_x(x)\Psi_y(y)\Psi_z(z)$$

$$\Psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{2^3}{abc}}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi z}{c}\right)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

Question: An electron is in 1D box of 1nm length. What is the probability of locating the electron between x=0 and x=0.2nm in its lowest energy state?

Question: An electron is in 1D box of 1nm length. What is the probability of locating the electron between x=0 and x=0.2nm in its lowest energy state?

Solution:

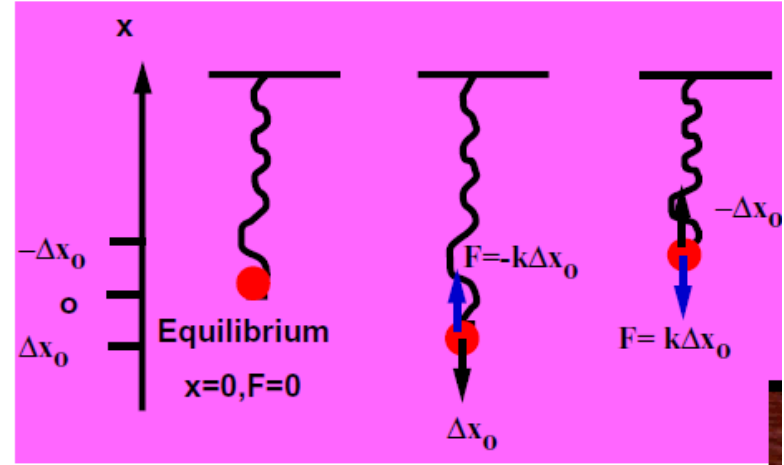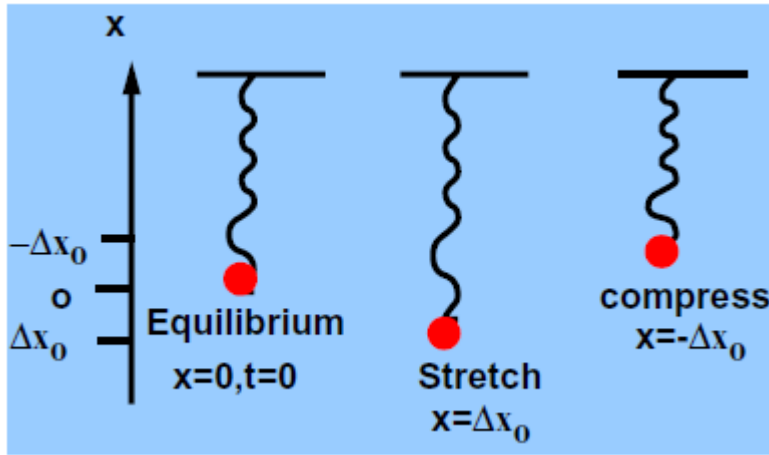$$P(x_1, x_2) = \int_{x_1}^{x_2} |\psi(x)|^2 \, dx$$

$$\int_{x=0 \text{ nm}}^{0.2 \text{ nm}} |\psi_1(x)|^2 \, dx = \overbrace{\frac{2}{1.0 \text{ nm}} \int_{0 \text{ nm}}^{0.2 \text{ nm}} \sin^2\left(\frac{\pi x}{1.0 \text{ nm}}\right) dx}^{n=1, a=1 \text{ nm}}$$

$$\int \sin^2\left(\frac{\pi}{a} x\right) dx = \frac{x}{2} - \frac{\sin(2\pi x/a)}{4\pi/a}\bigg)$$

$$= \frac{2}{1.0 \text{ nm}} \left(\frac{0.2 \text{ nm}}{2} - \frac{\sin(2\pi \times (0.2 \text{ nm})/(1.0 \text{ nm}))}{4\pi/(1.0 \text{ nm})}\right) \approx 0.05$$

Classical Harmonic Oscillator

Let us consider a particle of mass **'m'** attached to a spring

At the beginning at t = o the particle is at equilibrium, that is no force is working at it , F = 0

In general, according to Hooke's Law:

$$F = -k\,x$$

i.e. the force proportional to displacement and pointing in opposite direction and where k is the force constant and x is the displacement.

Classically, a harmonic oscillator is subject to Hooke's law.

Newton's second law says

$$F = ma$$

Therefore,

$$-k\,x = m\,\frac{d^2x}{dt^2}.$$

$$m\,\frac{d^2x}{dt^2} + k\,x = 0.$$

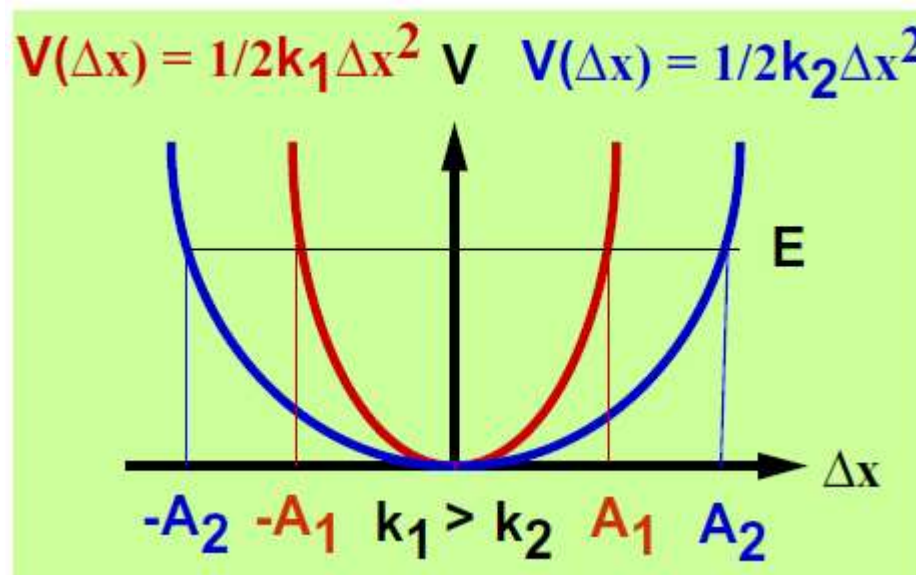The solution to this differential equation is of the form:

$$x(t) = A\sin(wt)$$

where the angular frequency of oscillation is '**ω**' in radians per second

$$\omega = \sqrt{\frac{k}{m}}$$

Also,   **ω = 2πυ**,   where '**υ**' is frequency of oscillation

Potential Energy

$$\int dU = \int -Fdx = \frac{1}{2}kx^2 = \frac{1}{2}kA^2 \sin^2 wt$$

$V(\Delta x) = 1/2k_1\Delta x^2$ v $V(\Delta x) = 1/2k_2\Delta x^2$

$-A_2$ $-A_1$ $k_1 > k_2$ A_1 A_2

➢The **parabolic potential energy V = ½ kx²** *of a harmonic oscillator, where x is* the displacement from equilibrium.

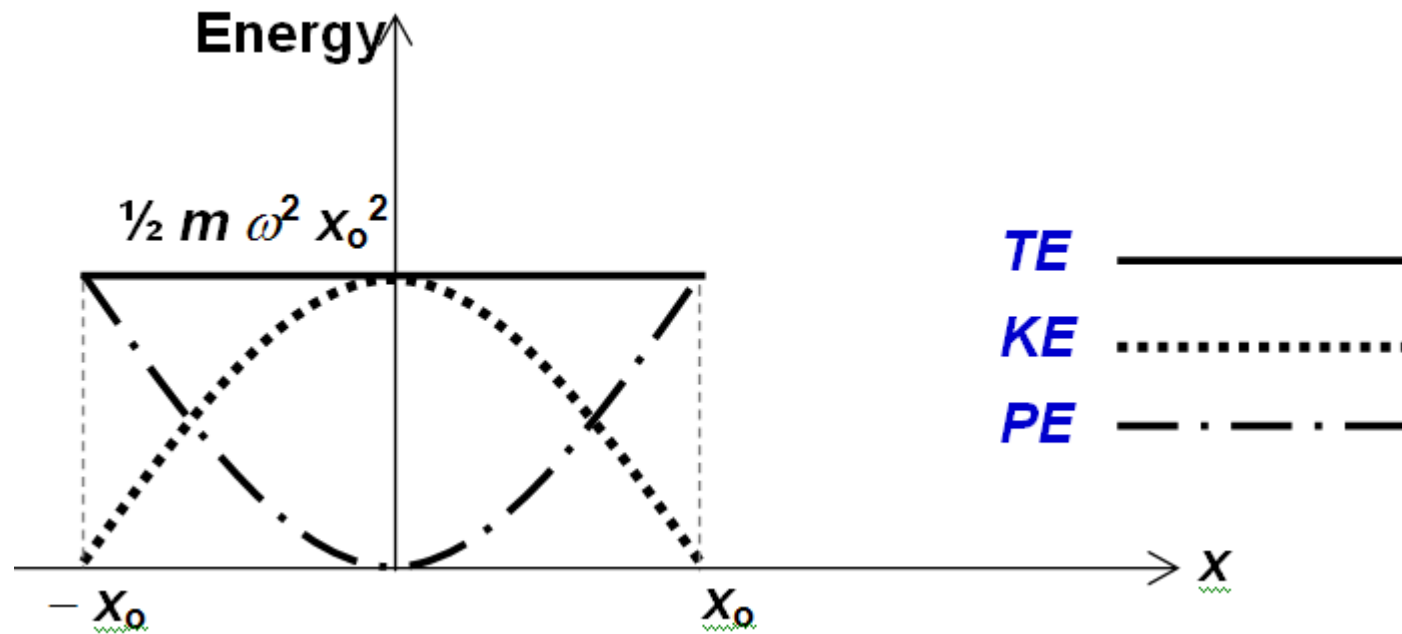➢The **narrowness of the curve depends on the force constant k**: *the larger the* value of *k, the narrower the well.*

Kinetic energy

$$x = A \sin wt$$

$$\frac{dx}{dt} = Aw \cos wt$$

$$K.E. = \frac{1}{2}mv^2 = \frac{1}{2}mA^2w^2 \cos^2 wt$$

Energy in Classical oscillator

$$E = T + V = \tfrac{1}{2}\,kA^2 \quad \text{........ How ????}$$

Total energy is constant i.e. **harmonic oscillator is a conservative system**

Quantum Harmonic Oscillator

In classical physics, the Hamiltonian for a harmonic oscillator is given by:

$$H = \frac{1}{2\mu}p_x^2 + \frac{1}{2}\omega^2\mu x^2 = \frac{1}{2\mu}p_x^2 + \frac{1}{2}kx^2 \text{ with } \omega = \sqrt{k/\mu}$$

where μ denotes the reduced mass:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \text{ (in kg; } m_1 \text{ and } m_2 \text{ are masses for two particles)}$$

The quantum mechanical harmonic oscillator is obtained by replacing the classical position and momentum by the corresponding quantum mechanical operators.

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + 2\pi^2\nu^2\mu x^2 \text{ where } \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Solution of Schrödinger Equation for Quantum Harmonic Oscillator

Thus

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + 2\pi^2 v^2 mx^2$$

$$= -\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2} - \frac{4\pi^2 v^2 m^2}{\hbar^2}x^2\right)$$

$$= -\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2} - \beta^2 x^2\right)$$

$$\text{where } \beta = \frac{2\pi\, v\, m}{\hbar}$$

$$\hat{H}\,\psi(x) = E\psi(x)$$

or

$$-\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2} - \beta^2 x^2\right)\psi(x) = E\psi(x)$$

Thus

$$\frac{d^2\psi(x)}{dx^2} - \beta^2 x^2 \psi(x) = -\frac{2mE}{\hbar^2}\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2} + \left(\frac{2mE}{\hbar^2} - \beta^2 x^2\right)\psi(x) = 0$$

The solution $\psi(x) = \exp(-\frac{\beta}{2}x^2)f(x)$

with $f(x) = \sum\limits_{m=0}^{n=\infty} c_n x^n$

Must satisfy $\psi(-\infty) = \psi(\infty) = 0$.

It is only possible if

$$E = \hbar\varpi\left(\frac{1}{2} + v\right) \quad v = 1, 2, 3, 4...$$

$$f(x) = e^{-\alpha x^2/2} \qquad \text{(gaussian function)}$$

$$\frac{d^2 f(x)}{dx^2} = -\alpha e^{-\alpha x^2/2} + \alpha^2 x^2 e^{-\alpha x^2/2} = -\alpha f(x) + \alpha^2 x^2 f(x)$$

or rewriting, $\qquad \dfrac{d^2 f(x)}{dx^2} + \alpha f(x) - \alpha^2 x^2 f(x) = 0w$

which matches our original diff. eq. if

$$\alpha = \frac{2mE}{\hbar^2} \qquad \text{and} \qquad \alpha^2 = \frac{mk}{\hbar^2}$$

$$\therefore \qquad \boxed{E = \frac{\hbar}{2}\sqrt{\frac{k}{m}}}$$

$$E = \frac{\hbar}{2}\sqrt{\frac{k}{m}}$$

We have found <u>one</u> eigenvalue and eigenfunction

Recall
$$\omega = \sqrt{\frac{k}{m}} \quad \text{or} \quad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$\therefore \quad \boxed{E = \frac{1}{2}\hbar\omega = \frac{1}{2}h\nu}$$

This turns out to be the <u>lowest</u> energy: the "ground" state

Quantum Mechanical Linear Oscillator

$$\psi_n(x) = \left(\frac{\sqrt{\alpha}}{2^n n! \sqrt{\pi}} \right)^{1/2} e^{-\alpha x^2/2} H_n\left(x\sqrt{\alpha}\right)$$

It is interesting to calculate probabilities $P_n(x)$ for finding a harmonically oscillating particle with energy E_n at x; it is easier to work with the coordinate q; for n=0 we have:
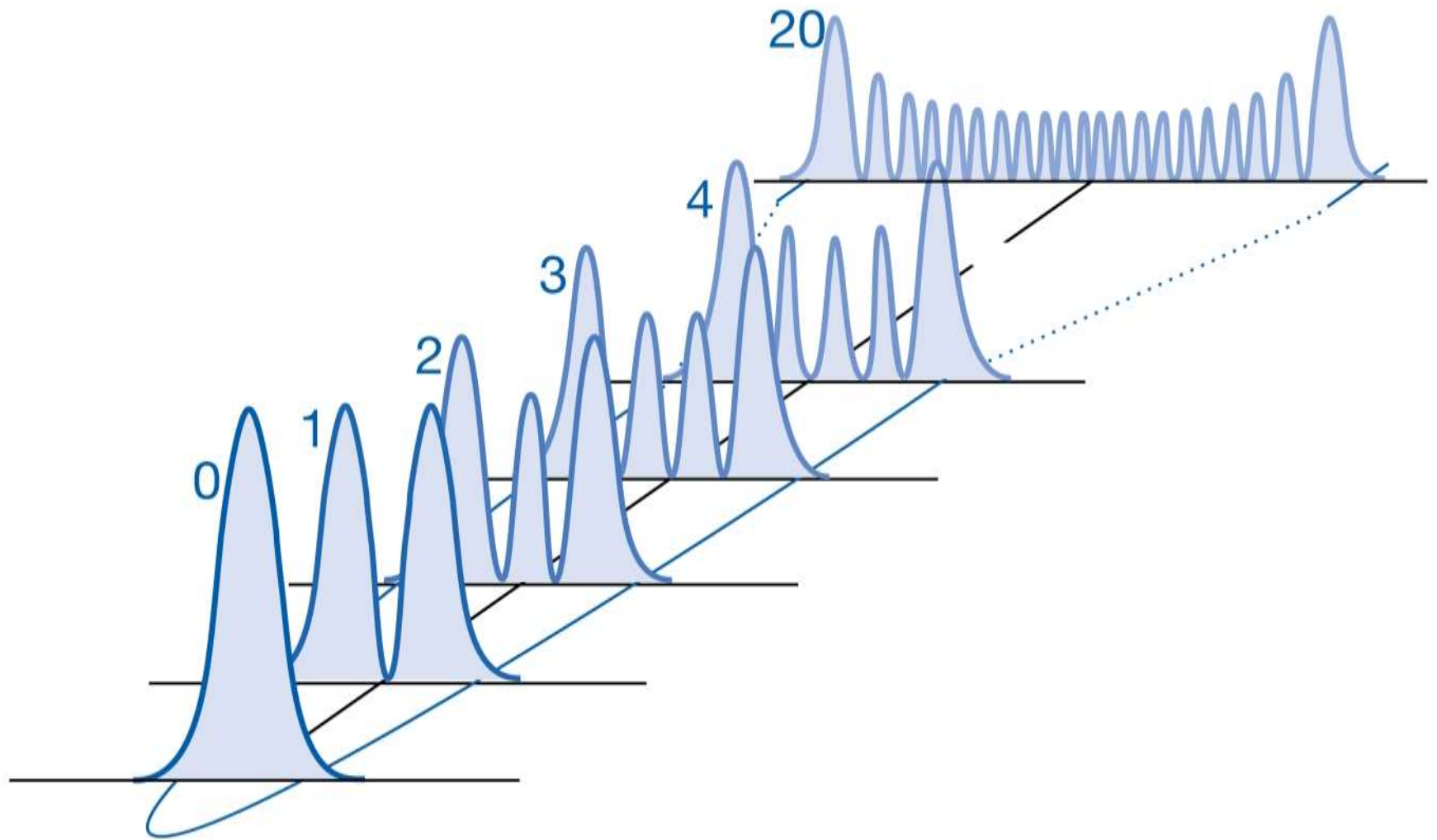
$$\psi_0(q) = A_0 \left(\frac{1}{\sqrt{\pi}} \right)^{1/2} e^{-q^2/2} \Rightarrow P_0(q) = \left|\psi_0(q)\right|^2 \propto \frac{1}{\sqrt{\pi}} e^{-q^2}$$
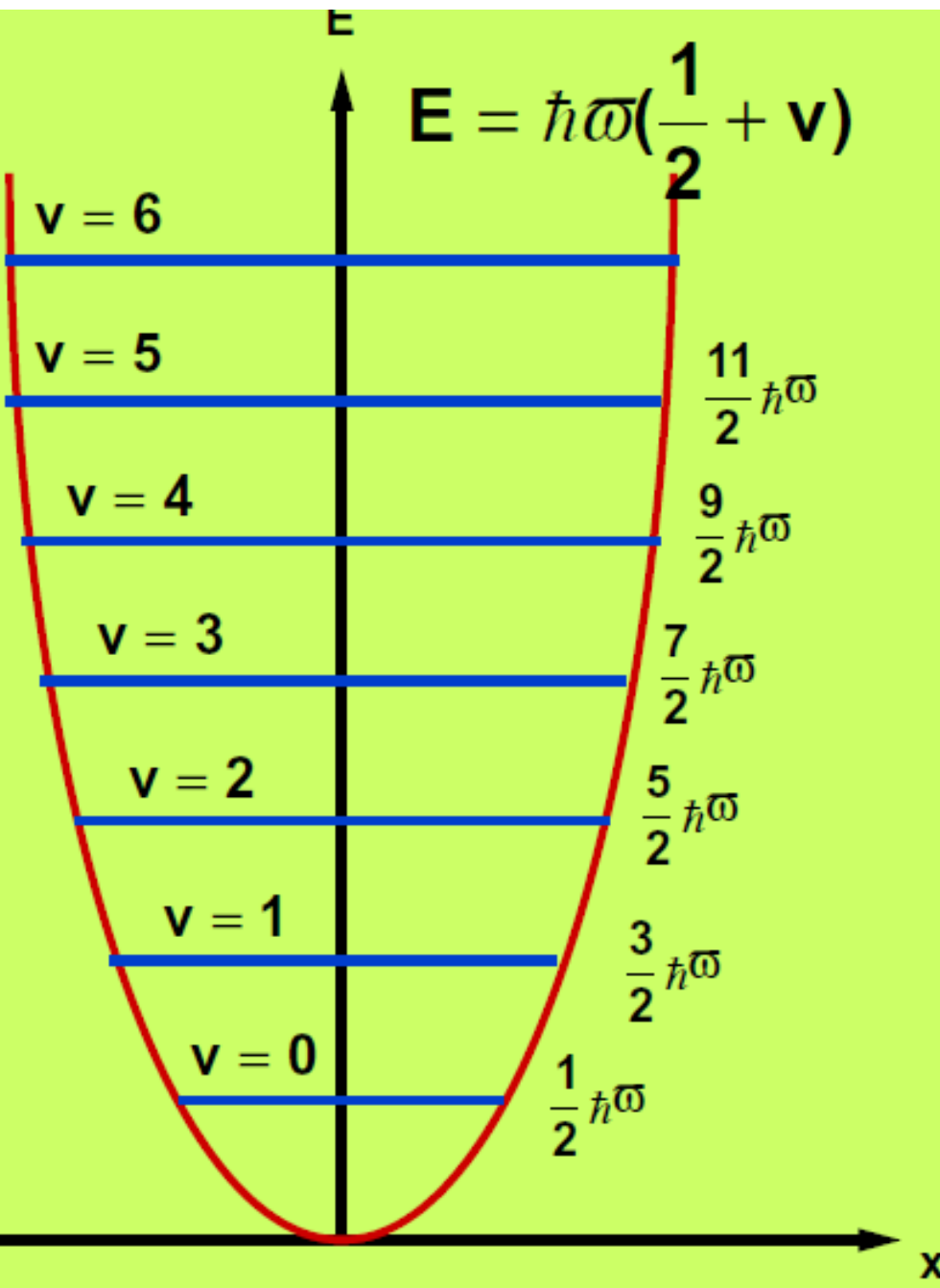
$$\psi_1(q) = A_1 \left(\frac{2}{\sqrt{\pi}} \right)^{1/2} q e^{-q^2/2} \Rightarrow P_1(q) = \left|\psi_1(q)\right|^2 \propto \frac{2q^2}{\sqrt{\pi}} e^{-q^2}$$

$$\psi_2(q) = A_2 \left(\frac{1}{2\sqrt{\pi}} \right)^{1/2} \left(2q^2 - 1\right) e^{-q^2/2} \Rightarrow P_2(q) = \left|\psi_2(q)\right|^2 \propto \frac{\left(2q^2 - 1\right)^2}{2\sqrt{\pi}} e^{-q^2}$$

$$\psi_3(q) = A_3 \left(\frac{1}{3\sqrt{\pi}} \right)^{1/2} \left(2q^3 - 3q\right) e^{-q^2/2} \Rightarrow P_3(q) = \left|\psi_3(q)\right|^2 \propto \frac{\left(2q^3 - 3q\right)^2}{3\sqrt{\pi}} e^{-q^2}$$

Wave functions of the harmonic oscillator

$$E = \hbar\varpi\left(\frac{1}{2} + v\right)$$

v = 6

v = 5 — $\frac{11}{2}\hbar\varpi$

v = 4 — $\frac{9}{2}\hbar\varpi$

v = 3 — $\frac{7}{2}\hbar\varpi$

v = 2 — $\frac{5}{2}\hbar\varpi$

v = 1 — $\frac{3}{2}\hbar\varpi$

v = 0 — $\frac{1}{2}\hbar\varpi$

➤ **Energy levels are equally spaced** with separation of **hυ**

➤ **Energy of ground state is not zero**, unlike in case of classical harmonic oscillator

➤ Energy of ground state is called **zero point energy**

➤ $E_0 = hυ/2$

➤ Zero point energy is in accordance with Heisenberg uncertainty principle

Show harmonic oscillator eigenfunctions obey the uncertainty principle ????

- Harmonic oscillator eigenfunctions obey the uncertainty principle

  Show that probability density for the zero-point level of the harmonic oscillator is in accord with the Heisenberg uncertainty principle.

  To calculate the standard deviation for the x coordinate using equation, we need to calculate $<x>$ and $<x^2>$:

  $$\langle x \rangle = \int_{-\infty}^{\infty} \psi_o{}^* \, x \, \psi_o \, dx = 0$$

  Since the wavefunction is real, $\Psi_o{}^* = \Psi_o$. Since $\Psi_o{}^2$ is an even function and x is an odd function, the integrand is odd and so this integral is zero.

Harmonic oscillator eigenfunctions obey the uncertainty principle

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_0 {}^* x^2 \psi_0 \, dx$$

$$= \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} x^2 \, e^{-\alpha x^2} \, dx$$

$$= \left(\frac{\alpha}{\pi} \right)^{1/2} \left[\frac{1}{2\alpha} \left(\frac{\pi}{\alpha} \right)^{1/2} \right]$$

$$= \frac{1}{2\alpha} = \frac{1}{2} \frac{\hbar}{(\mu k)^{1/2}}$$

Since the integrand function is an even function so this integral is non-vanishing.

Harmonic oscillator eigenfunctions obey the uncertainty principle

To calculate the standard deviation for the p coordinate using equation, we need to calculate $<p>$ and $<p^2>$:

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi_o * \left(-i\hbar \frac{d}{dx} \right) \psi_o \, dx = 0$$

Since Ψ_o is an even function its derivative is an odd function, Therefore the integrand is odd and this integral is zero.

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} \psi_o * \left(-\hbar^2 \frac{d^2}{dx^2} \right) \psi_o \, dx$$

$$= \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2/2} \left(-\hbar^2 \frac{d^2}{dx^2} \right) e^{-\alpha x^2/2} \, dx$$

$$= \hbar^2 \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} (\alpha^2 - \alpha^2 x^2) \, e^{-\alpha x^2} \, dx$$

$$= \hbar^2 \frac{\alpha}{2} = \frac{\hbar}{2} (\mu k)^{1/2}$$

$$\Delta x^2 = \langle x^2 \rangle - \langle x \rangle^2 \qquad \Delta x = \langle x^2 \rangle^{1/2} = \sqrt{\frac{\hbar}{2}} (\mu k)^{-1/4}$$

$$\Delta p^2 = \langle p^2 \rangle - \langle p \rangle^2 \qquad \Delta p = \langle p^2 \rangle^{1/2} = \sqrt{\frac{\hbar}{2}} (\mu k)^{1/4}$$

$$\Delta x \, \Delta p = \hbar/2$$

Angular Momentum Operator

- **L** is important to us because electrons are constantly changing direction (turning) when they are confined to atoms and molecules

- $\hat{\mathbf{L}}$ is a vector operator in quantum mechanics
  - $\hat{L}_x$: operator for projection of **L** on a *x*-axis
  - $\hat{L}_y$: operator for projection of **L** on a *y*-axis
  - $\hat{L}_z$: operator for projection of **L** on a *z*-axis

Angular Momentum Operator

- Just for concreteness $\hat{\mathbf{L}}$ is written in terms of position and momentum operators as:

$$\hat{L}_x = \hat{y}\,\hat{p}_z - \hat{z}\,\hat{p}_y$$

$$\hat{L}_y = \hat{z}\,\hat{p}_x - \hat{x}\,\hat{p}_z \qquad \text{with} \qquad \hat{\mathbf{L}} = \begin{pmatrix} \hat{L}_x \\ \hat{L}_y \\ \hat{L}_z \end{pmatrix}$$

$$\hat{L}_z = \hat{x}\,\hat{p}_y - \hat{y}\,\hat{p}_x$$

Angular Momentum Operators

- Ideally we'd like to know **L** BUT…

$$\left[\hat{L}_x, \hat{L}_y\right] = i\,\hbar\,\hat{L}_z$$

$$\left[\hat{L}_z, \hat{L}_x\right] = i\,\hbar\,\hat{L}_y \qquad \text{One day this will be a lab…}$$

$$\left[\hat{L}_y, \hat{L}_z\right] = i\,\hbar\,\hat{L}_x$$

- $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ don't commute!
- By Heisenberg, we can't measure them simultaneously, so we can't know exactly where and what **L** is!

Angular Momentum Operators

- $\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ does commute with each of $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ individually
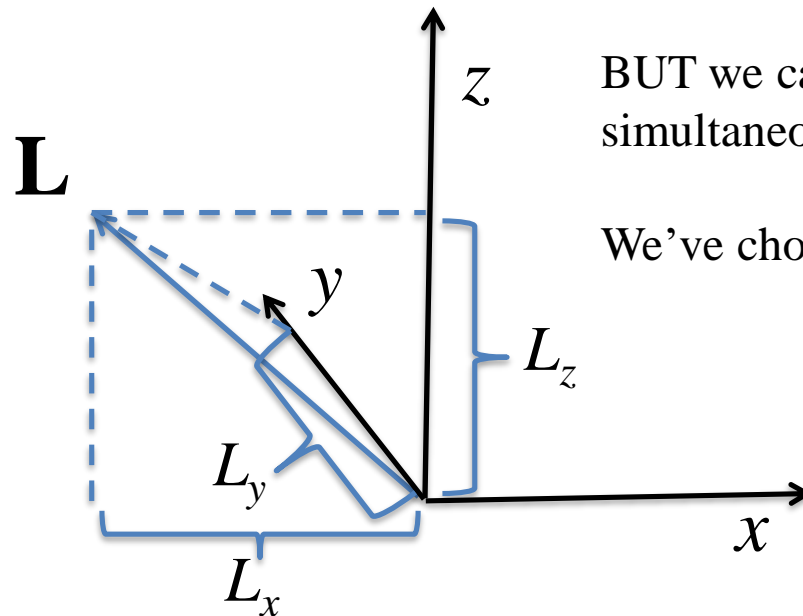
$$\left[\hat{L}^2, \hat{L}_x\right] = 0$$

$$\left[\hat{L}^2, \hat{L}_y\right] = 0$$

$$\left[\hat{L}^2, \hat{L}_z\right] = 0$$

- $\hat{\mathbf{L}}^2$ is the length of **L** squared.
- $\hat{L}_z$ *has the simplest mathematical form*
  - So let's pick the z-axis as our "reference" axis

Angular Momentum Operators

- So we've decided that we will use $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ as a substitute for $\hat{\mathbf{L}}$

  - Because we can simultaneously measure:

    - L^2 the length of **L** squared

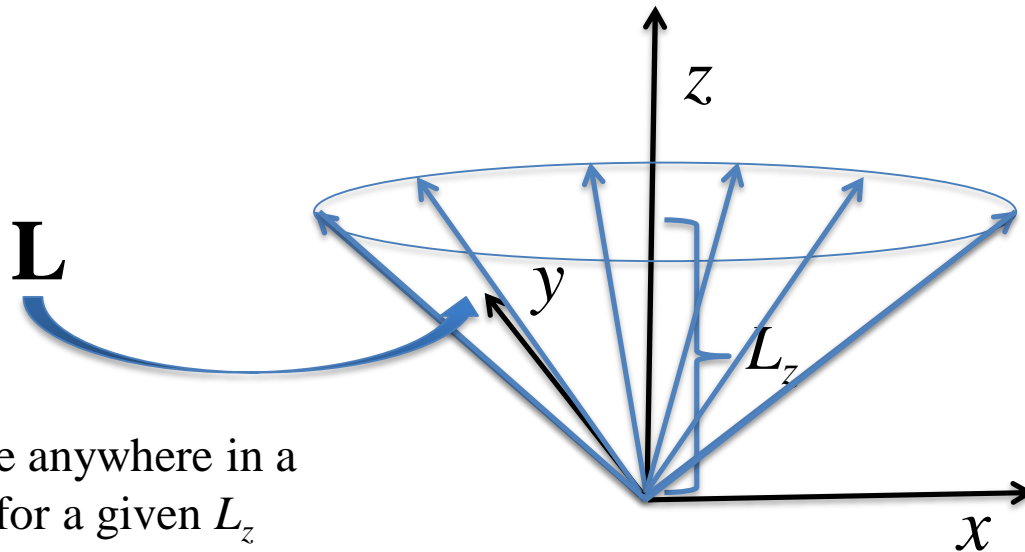   - L_z the projection of **L** on the z-axis

BUT we can't know L_x, L_y and L_z simultaneously!

We've chosen to know only L_z (and L^2)

Angular Momentum Operators

- So we've decided that we will use $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ as a substitute for $\hat{\mathbf{L}}$

  - Because we can simultaneously measure:

    - L^2 the length of **L** squared

    - L_z the projection of **L** on the z-axis

L

can be anywhere in a cone for a given L_z

For different L^2's we'll have different L_z's

So what are the possible $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ eigenvalues and what are their eigenfunctions?

Total Angular Momentum

- The spin-orbit interaction couples the orbital (L) and spin (S) angular momentum to form the total angular momentum (J)
  - The internal magnetic field is determined by L and this acts on the spin magnetic dipole of the electron determined by S so the two angular momenta are not independent

$$\vec{J} = \vec{L} + \vec{S}$$

- The new "good" quantum numbers of the hydrogen atom are n, l, s, j, m_j

Total Angular Momentum

- Coupling of L and S to form J
  - L and S precess around J
  - J precesses around the z axis