

Harmonic Oscillator

$$V = \frac{1}{2} K x^2 \quad \Rightarrow \quad F = -Kx$$

K is called the force constant.

The classical oscillation frequency is $\omega = \left(\frac{K}{m}\right)^{1/2}$ where $\omega = 2\pi\nu$

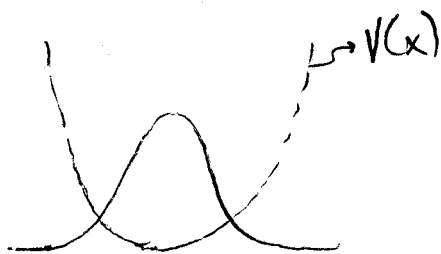
In terms of ω , the potential energy is $V = \frac{1}{2} m \omega^2 x^2$

Hence we need to solve the Schrodinger equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2} m \omega^2 x^2 \psi = E \psi$$

$$\text{or } \frac{\partial^2 \psi}{\partial x^2} = \left(\frac{m^2 \omega^2}{\hbar^2} x^2 - \frac{2mE}{\hbar^2} \right) \psi$$

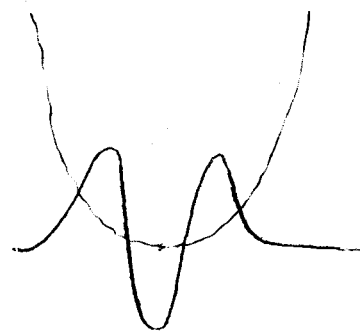
Recalling the particle in a 1d box, our stationary states must look roughly like:



ground state
0 nodes



1st excited state
1 node



2nd excited state
2 nodes

By inspection, seems reasonable to try a Gaussian function for the ground state.

Try $\psi_0 = e^{-\alpha x^2}$ (ignoring normalization constants)

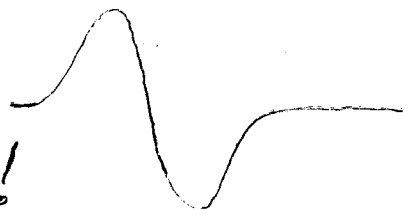
Taking 2nd derivative, get $(4\alpha^2 x^2 - 2\alpha) e^{-\alpha x^2} = \left(\frac{m^2 \omega^2}{\hbar^2} x^2 - \frac{2mE}{\hbar^2} \right) e^{-\alpha x^2}$

Equating gives $4\alpha^2 = \frac{m^2 \omega^2}{\hbar^2}$ and $2\alpha = \frac{2mE}{\hbar^2}$.

$\Rightarrow \alpha = \frac{m\omega}{2\hbar}$ and $E = \frac{\hbar^2 \alpha}{m}$

which yields $\frac{1}{2} \hbar \omega = E = \frac{1}{2} \hbar \omega$ zero point energy

Now go for 1st excited state
Looks like $x e^{-\alpha x^2}$ by inspection!



Taking the 2nd derivative of $\psi_1 = x e^{-\alpha x^2}$ gives

$(4\alpha^2 x^2 - 6\alpha) x e^{-\alpha x^2} = \left(\frac{m^2 \omega^2}{\hbar^2} x^2 - \frac{2mE}{\hbar^2} \right) x e^{-\alpha x^2}$

Again, this works provided that $4\alpha^2 = \frac{m^2 \omega^2}{\hbar^2}$ and $6\alpha = \frac{2mE}{\hbar^2}$

$\Rightarrow E = \frac{3}{2} \hbar \omega$

Feeling ambitious, we will try $\Psi_n = x^n e^{-\alpha x^2}$

Taking 2nd derivatives gives

$$\begin{aligned} & [4\alpha^2 x^2 - 2(2n+1)\alpha + n(n-1)x^{-2}] x^n e^{-\alpha x^2} \\ &= \left[\frac{m^2 \omega^2}{\hbar^2} x^2 - \frac{2mE}{\hbar^2} \right] x^n e^{-\alpha x^2} \end{aligned}$$

① Equate x^2 terms $\Rightarrow 4\alpha^2 = \frac{m^2 \omega^2}{\hbar^2} \Rightarrow \alpha = \frac{m\omega}{2\hbar}$

② Equate constant term $\Rightarrow 2(2n+1)\alpha = \frac{2mE}{\hbar^2}$
 $\Rightarrow E = \frac{(2n+1)\hbar^2 \alpha}{m} = (2n+1) \frac{1}{2} \hbar \omega$

$\boxed{E_n = (n + 1/2) \hbar \omega = E_n}$ harmonic oscillator energies

③ "leftover" x^{-2} term vanishes if $n=0$ or $n=1$.

If $n > 1$, this term can always be balanced by adding terms of lower order to $x^n e^{-\alpha x^2}$.

ie $x^{n-2} e^{-\alpha x^2}$, $x^{n-4} e^{-\alpha x^2}$, ...

Then the lowest order terms cancel in a chainwise manner.

ie Mix in $\beta x^{n-2} e^{-\alpha x^2}$ to get rid of the x^{-2} term, then must mix in $\gamma x^{n-4} e^{-\alpha x^2}$ to get rid of the leftover terms from $\beta x^{n-2} e^{-\alpha x^2}$, etc.

Can stop at $x^{n-n} e^{-\alpha x^2}$ ie does terminate

these modifications do not affect the energy.

Conclusion

Harmonic oscillator has energies

$$E_n = (n + 1/2)\hbar\omega, \quad n \in \mathbb{Z} \geq 0.$$

with corresponding wave functions

$$\Psi_n = (x^n + ?x^{n-2} + ?x^{n-4} + \dots) e^{-\alpha x^2} \quad \alpha = \frac{m\omega}{2\hbar}$$

ie degree n polynomial times a Gaussian

The missing coefficients can be determined by "orthogonality" of states (later on)

Some general properties of stationary states

Arguably the most useful tool in integral calculus is integration by parts.

$$\int_a^b u dv = uv \Big|_a^b - \int_a^b v du \quad \text{or} \quad \int_a^b u \frac{\partial v}{\partial x} dx = uv \Big|_a^b - \int_a^b v \frac{\partial u}{\partial x} dx$$

In quantum theory, generally the $uv \Big|_a^b$ term is either zero at ~~a and b~~ the boundaries a and b or is identical at a and b , so that we can always ignore it $\Rightarrow uv \Big|_a^b = 0$.

Hence the quantum integration by parts equation is

$$\int_a^b u dv = - \int_a^b v du$$

Two integrations by parts gives

$$\int_a^b u \frac{\partial^2 v}{\partial x^2} dx = \int_a^b v \frac{\partial^2 u}{\partial x^2} dx$$

α in 3d, $\int_a^b u \nabla^2 v = \int_a^b v \nabla^2 u$

① The energies E_n in the Schrodinger time indep. eq.

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n + V \psi_n = E_n \psi_n$$

are real, even though ψ_n may be complex.

Proof: Multiply through by ψ_n^* and integrate to get

$$-\frac{\hbar^2}{2m} \underbrace{\int \psi_n^* \nabla^2 \psi_n}_{\int \psi_n \nabla^2 \psi_n^*} + \underbrace{\int \psi_n^* V \psi_n}_{\text{clearly real}} = E_n \underbrace{\int \psi_n^* \psi_n}_{\text{clearly real}}$$

But $\int \psi_n^* \nabla^2 \psi_n$ and $\int \psi_n \nabla^2 \psi_n^*$ are complex conjugates and since they are also equal, they must be real (imaginary parts are zero)

$\Rightarrow E_n$ is real.

② Different stationary states are "orthogonal" to each other
 i.e. $\int \psi_n \cdot \psi_m^* = 0$ if $m \neq n$.

Proof Write down the TISE for ψ_n and the complex conjugate of this equation for ψ_m .

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n + V \psi_n = E_n \psi_n \quad \textcircled{1}$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_m^* + V \psi_m^* = E_m \psi_m^* \quad \textcircled{2}$$

always real

Multiply ① by ψ_m^* and integrate
 Multiply ② by ψ_n and integrate

Get
$$\boxed{-\frac{\hbar^2}{2m} \int \psi_m^* \nabla^2 \psi_n} + \int \psi_m^* V \psi_n = E_n \int \psi_m^* \psi_n$$

and
$$\boxed{-\frac{\hbar^2}{2m} \int \psi_n \nabla^2 \psi_m^*} + \int \psi_m^* V \psi_n = E_m \int \psi_m^* \psi_n$$

↓
↓
 equal equal

Subtracting, we get $(E_n - E_m) \int \psi_n \psi_m^* = 0$

If $n \neq m$, $E_n \neq E_m \Rightarrow \int \psi_n \psi_m^* = 0$ for $n \neq m$.

If all these states are also normalized, they are said to be "orthonormal."

What about degenerate energy levels?

E_n can equal E_m even if $n \neq m$ and the above proof breaks down. But orthogonal states can always be constructed by taking appropriate linear combinations (Gram-Schmitt orthogonalization procedure)

Section 3: general principles of quantum theory

Expectation Values

Recall that $|\Psi(x, y, z, t)|^2$ represents a probability density and that this is meaningful only if Ψ is normalized.

$$\text{ie } \iiint |\Psi(x, y, z, t)|^2 dx dy dz = 1$$

As Ψ evolves with time, is the normalization destroyed?

It is easy to prove that if Ψ is normalized at any particular time t , its normalization is preserved for all time!

Proof: consider the time derivative of the normalization integral

$$\frac{d}{dt} \int \Psi^* \Psi = \int \frac{\partial \Psi^*}{\partial t} \Psi + \int \Psi^* \frac{\partial \Psi}{\partial t}$$

$$\text{We know that } i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \quad (\text{TDSE})$$

$$\Rightarrow \frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m} \nabla^2 \Psi - \frac{i}{\hbar} V\Psi$$

$$\text{and } \frac{\partial \Psi^*}{\partial t} = -\frac{i\hbar}{2m} \nabla^2 \Psi^* + \frac{i}{\hbar} V\Psi^* \quad (\text{taking conjugates})$$

$$\begin{aligned} \text{Hence } \frac{d}{dt} \int \Psi^* \Psi &= -\frac{i\hbar}{2m} \int (\nabla^2 \Psi^*) \Psi + \frac{i}{\hbar} \int V\Psi^* \Psi \\ &+ \frac{i\hbar}{2m} \int \Psi^* \nabla^2 \Psi - \frac{i}{\hbar} \int V\Psi^* \Psi = 0 \end{aligned}$$

Whence $\int \Psi^* \Psi$ is a constant (in time).

(see Math chapter B of Simon and McQuarrie)

Suppose we have a quantity $Q(x, y, z)$ depending only on coordinates (and not on momenta). Since $|\Psi|^2$ is a probability density, $\iiint Q(x, y, z) |\Psi|^2 dx dy dz$ is its average or mean value in the usual probability sense.

ie It is a weighted average with $|\Psi|^2$ being the weight function.

In quantum theory this is generally called the expectation value and is denoted by angular brackets $\langle \cdot \rangle$

ie $\langle Q \rangle \equiv \iiint \Psi^* Q \Psi dx dy dz$

For example, the expectation value of x is

$$\langle x \rangle = \iiint \Psi^* x \Psi dx dy dz$$

and of x^2 is $\langle x^2 \rangle = \iiint \Psi^* x^2 \Psi dx dy dz$

Expectation Value of Momentum

Since $|\Psi|^2$ is a prob. density in spatial coordinates, how do we get information about momentum?

Can get an expression for its expectation value by appealing to the...

Correspondence Principle,

which says Quantum mechanics must reduce to classical mechanics in some way!

We shall require that quantum mechanics reproduce classical mechanics "on average".

In particular, we have in classical mechanics ~~(1d)~~ that

$$p_x = m \frac{dx}{dt}$$

Taking the average (i.e. expectation value) of both sides gives the quantum analog.

$$\langle p_x \rangle = m \frac{d}{dt} \langle x \rangle$$

Work out the RHS:

$$\frac{d}{dt} \langle x \rangle = \frac{d}{dt} \int \psi^* x \psi = \int \frac{\partial \psi^*}{\partial t} x \psi + \int \psi^* x \frac{\partial \psi}{\partial t} \quad (\text{product rule})$$

$$= \underbrace{-\frac{i\hbar}{2m} \int \frac{\partial^2 \psi^*}{\partial x^2} x \psi}_{\text{circled}} + \underbrace{\frac{i}{\hbar} \int V \psi^* x \psi}_{\text{circled}} \rightarrow 0$$

$$+ \frac{i\hbar}{2m} \int \psi^* x \frac{\partial^2 \psi}{\partial x^2} - \frac{i}{\hbar} \int V \psi^* x \psi$$

use previous expressions for $\frac{\partial \psi}{\partial t}$ $\frac{\partial \psi^*}{\partial t}$

→ apply integration by parts twice $\int \frac{\partial^2 \psi^*}{\partial x^2} x \psi = \int \psi^* \frac{\partial^2}{\partial x^2} (x \psi)$

$$= \int \psi^* \left(2 \frac{\partial \psi}{\partial x} + x \frac{\partial^2 \psi}{\partial x^2} \right)$$

This yields $\frac{d}{dt} \langle x \rangle = -\frac{i\hbar}{2m} \int \psi^* \left(2 \frac{\partial \psi}{\partial x} + x \frac{\partial^2 \psi}{\partial x^2} \right) + \frac{i\hbar}{2m} \int \psi^* x \frac{\partial^2 \psi}{\partial x^2}$

$$= -\frac{i\hbar}{m} \int \psi^* \frac{\partial \psi}{\partial x}$$

Multiplying by m , we finally obtain

$$\boxed{\langle p_x \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x}}$$

What about $\langle p_x^2 \rangle$? An important classical formula

involving p_x^2 is $\frac{p_x^2}{2m} + V = \text{constant}$ (conservation of energy in a 1d system) (*) (label)

Take the TDSE $-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = i\hbar \frac{\partial \psi}{\partial t}$

and multiply both sides by ψ^* and integrate

$$-\frac{\hbar^2}{2m} \int \psi^* \frac{\partial^2 \psi}{\partial x^2} + \int \psi^* V \psi = i\hbar \int \psi^* \frac{\partial \psi}{\partial t}$$

The 2nd term is just $\langle V \rangle$.

The RHS can be handled using the general solution

$$\psi = \sum_{n=-\infty}^{\infty} c_n \psi_n e^{-iE_n t/\hbar} \text{ where } \psi_n \text{ are the stationary states.}$$

$$\text{then } \psi^* = \sum_k c_k^* \psi_k^* e^{iE_k t/\hbar} \text{ and}$$

$$\frac{\partial \psi}{\partial t} = \sum_l (-\frac{iE_l}{\hbar}) c_l \psi_l e^{-iE_l t/\hbar}$$

$$\text{therefore } i\hbar \int \psi^* \frac{\partial \psi}{\partial t} = \sum_k \sum_l c_k^* c_l E_l e^{i(E_k - E_l)t/\hbar} \int \psi_k^* \psi_l$$

But $\int \psi_k^* \psi_l = \delta_{k,l}$ by orthonormality, so ^{> Kronecker delta}

$$\Rightarrow \sum_n |c_n|^2 E_n = \boxed{\text{constant}} \text{ is not a function of time}$$

thus we have shown that $-\frac{\hbar^2}{2m} \int \psi^* \frac{\partial^2 \psi}{\partial x^2} + \langle V \rangle = \text{constant}$ for all time-dep. ψ

Comparing with (*) and applying the correspondence principle, we

$$\text{deduce that } \langle p_x^2 \rangle = -\hbar^2 \int \psi^* \frac{\partial^2 \psi}{\partial x^2}$$

Quantum Operators

We have just deduced that, in 1d,

$$\langle p_x \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} \quad \text{and} \quad \langle p_x^2 \rangle = -\hbar^2 \int \psi^* \frac{\partial^2 \psi}{\partial x^2}$$

If we now define a momentum operator by

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad \text{where the "hat" denotes an operator,}$$

then we can write

$$\begin{aligned} \langle p_x \rangle &= \int \psi^* \hat{p}_x \psi \\ \langle p_x^2 \rangle &= \int \psi^* \hat{p}_x^2 \psi \end{aligned}$$

where \hat{p}_x^2 means $\hat{p}_x \hat{p}_x \Rightarrow$ apply the operator twice

Note that if \hat{A} and \hat{B} are operators,

$\hat{A}\hat{B}\psi$ means $\hat{A}(\hat{B}\psi)$ i.e. from right to left

like composition of functions i.e. $(f \circ g)(x) = f(g(x))$

An obvious generalization suggests

$$\langle p_x^n \rangle = \int \psi^* \hat{p}_x^n \psi$$

Recall, also, that for powers of x ,

$$\langle x^n \rangle = \int \psi^* x^n \psi$$

All of this can be unified by postulating the following general principle:

The expectation value of any property $Q(x, y, z, p_x, p_y, p_z)$ depending on the coordinates and/or the momenta of the particle is given by

$$\langle Q \rangle = \iiint \Psi^* \hat{Q} \Psi \, dx \, dy \, dz$$

where \hat{Q} is an operator obtained by making the replacements $\hat{x} \rightarrow x, \hat{y} \rightarrow y, \hat{z} \rightarrow z, \hat{p}_x \rightarrow -i\hbar \frac{\partial}{\partial x}, \hat{p}_y \rightarrow -i\hbar \frac{\partial}{\partial y}, \hat{p}_z \rightarrow -i\hbar \frac{\partial}{\partial z}$ in the expression for Q

ex Energy = $\frac{p^2}{2m} + V$ \rightarrow corresponding operator $\hat{p}^2 \rightarrow -\hbar^2 \nabla^2$
 $p^2 = p_x^2 + p_y^2 + p_z^2$

The energy operator is $-\frac{\hbar^2}{2m} \nabla^2 + V = \hat{H} = H$

This operator dominates quantum theory so it is given a special symbol H , called the "Hamiltonian" operator.

Schrodinger's Equations can thus be written succinctly as

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

$\hat{H} \Psi_n = E_n \Psi_n$ time-independent

"Sharpness" of the Q distribution

Now that we can calculate expectation values, we can also calculate standard deviations.

For any property Q, the deviation from the mean value is just $Q - \langle Q \rangle$.

The squared deviation is $(Q - \langle Q \rangle)^2 = Q^2 - 2Q\langle Q \rangle + \langle Q \rangle^2$ and the mean value of this is $\langle Q^2 \rangle - 2\langle Q \rangle^2 + \langle Q \rangle^2 = \langle Q^2 \rangle - \langle Q \rangle^2$

The rms (root mean square) deviation = standard deviation = $\Delta Q = \sqrt{\langle Q^2 \rangle - \langle Q \rangle^2}$

ΔQ is a measure of the "sharpness" of the distribution of Q values in a given ψ . Generally $\Delta Q \neq 0$.

\Rightarrow Q is spread over a range of values. However, ... there are special situations in which Q is not spread out. i.e. $\text{var } Q = 0$.

Eigenfunctions & Eigenvalues

Consider functions ψ satisfying $\hat{Q}\psi = q\psi$ \otimes
i.e. \hat{Q} operating on ψ produces a number q multiplied by ψ .

These ψ 's are called the eigenfunctions of Q and the corresponding numbers q the eigenvalues.

For an eigenfunction of Q ,

$$\langle Q \rangle = \int \Psi^* \hat{Q} \Psi = \int \Psi^* q \Psi = q \int \Psi^* \Psi = q \text{ since } \Psi \text{ normalized.}$$

$$\langle Q^2 \rangle = \int \Psi^* \hat{Q}^2 \Psi = \int \Psi^* q^2 \Psi = q^2$$

$$\text{Hence } \Delta Q = \sqrt{\text{Var } Q} = \sqrt{\langle Q^2 \rangle - \langle Q \rangle^2} = \sqrt{q^2 - q^2} = 0.$$

Thus if Ψ is an eigenfunction of the operator \hat{Q} , the property Q has an absolutely precise value, the eigenvalue q .

Only under these conditions can we have precise, well-defined values of physical properties in quantum theory.

ex stationary states satisfy $\hat{H}\Psi_n = E_n\Psi_n$.

this is an eigenvalue equation.

→ the stationary states are precisely defined with energy E_n , the eigenvalues.

SECTION 4 --- the Central Force Problem

"Central" force : means that the potential energy depends only on the distance r from the origin.