A Quick Review Classical Mechanical Systems and Phase Space

Newton's equations of motion are differential equations in Cartesian coordinates which are specified with knowledge of the force / potential energy

$$m\frac{d^2 x(t)}{dt^2} = F_x\big(x(t)\big) = -\frac{\partial U\big(x(t)\big)}{\partial x}$$

Potential energy of the particle

Total force on particle: depends on the position of the particle at time t: $\{x(t)\}$.

In vector form:

$$m\frac{d^2 \mathbf{r}(t)}{dt^2} = \mathbf{F}\big(\mathbf{r}(t)\big) = -\vec{\nabla} U\big(\mathbf{r}(t)\big)$$

One-dimensional motion under constant gravitational force

Newton's second law for a mass m moving in a constant gravitation force $F_y = mg$:
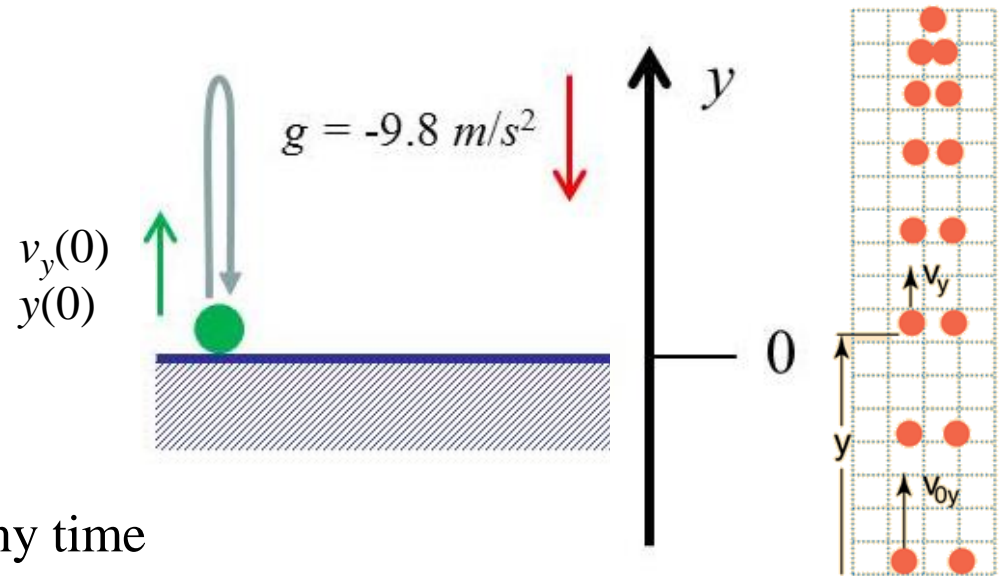
$$m\frac{d^2 y(t)}{dt^2} = F_y = mg$$

Initial conditions:
At $t = 0$, $\qquad y = y(0)$ & $v_y = v_y(0)$

Solution (by integrating twice):

$$y(t) = y(0) + v_y(0)t + \tfrac{1}{2}gt^2$$

$$v_y(t) = v_y(0) + gt$$

$v_y(0)$
$y(0)$

$g = -9.8 \ m/s^2$

y

0

Mechanical energy of the system at any time

$$E(t) = \tfrac{1}{2}mv_y(t)^2 - mgy(t)$$

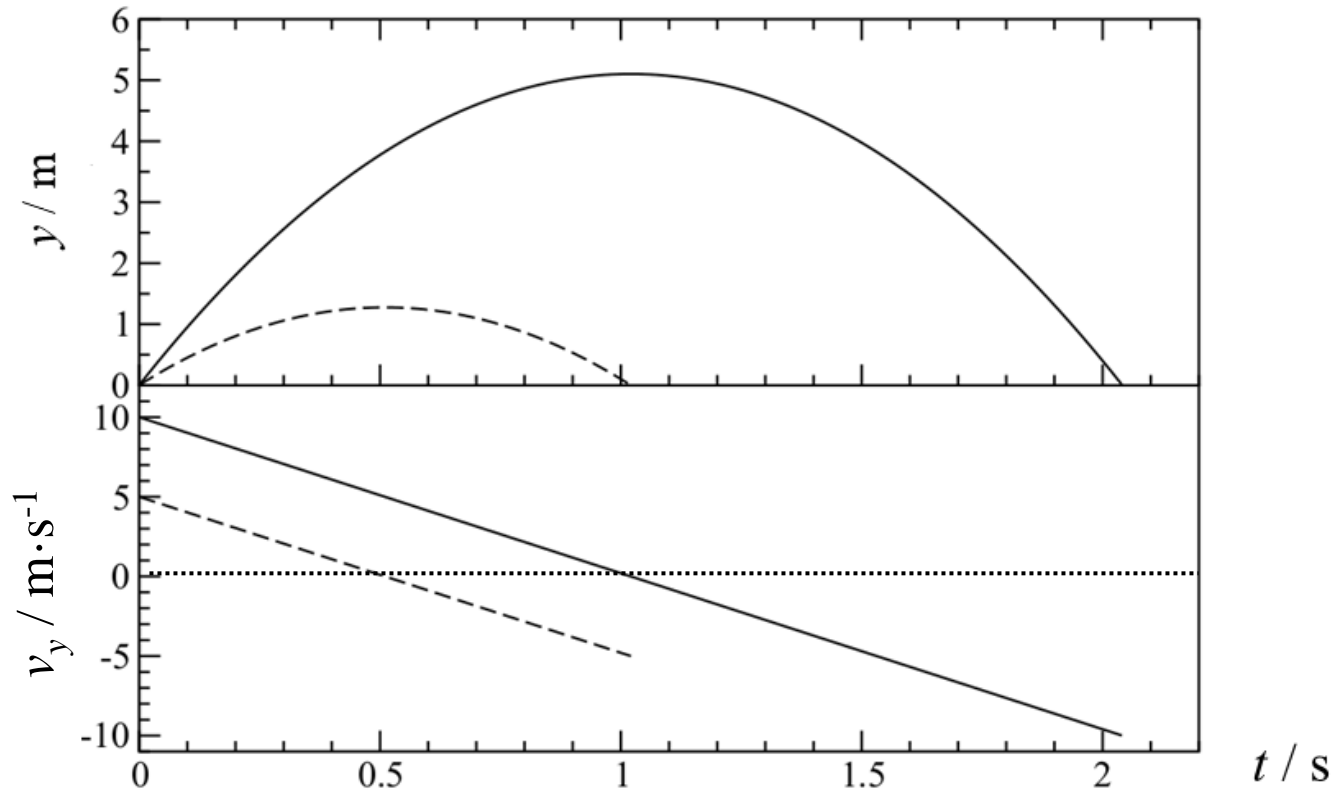$$= \tfrac{1}{2}m[v_y(0) + gt]^2 - mg\left[y(0) + v_y(0)t + \tfrac{1}{2}gt^2 \right]$$

$$= \tfrac{1}{2}mv_y^2(0) - mgy(0) = E(0) = \text{Constant}$$

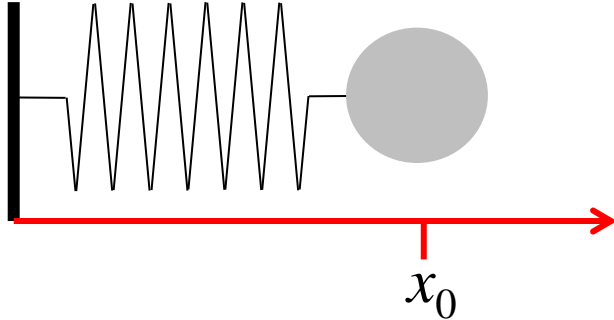# Trajectory of one-dimensional motion under constant gravitational force

Solution with two different initial conditions (what are they?)

$$y(t) = y(0) + v_y(0)t + \frac{1}{2}gt^2$$

$$v_y(t) = v_y(0) + gt$$

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Position-dependent forces: Harmonic oscillator

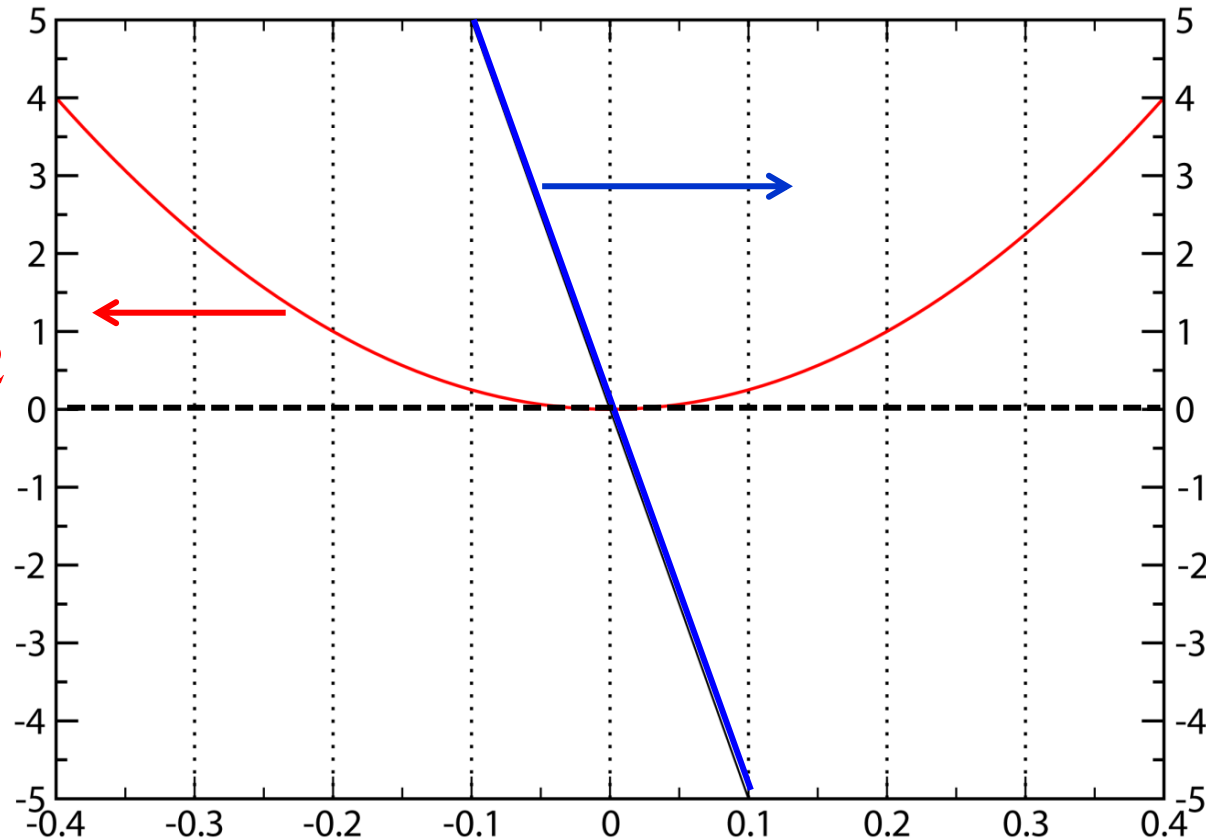Hooke's law

$$\begin{cases} F(x) = -k(x - x_0) \\ U(x) = \frac{1}{2}k(x - x_0)^2 \end{cases}$$

- Force always opposes the displacement
- Potential energy is symmetric with respect to compression and expansion
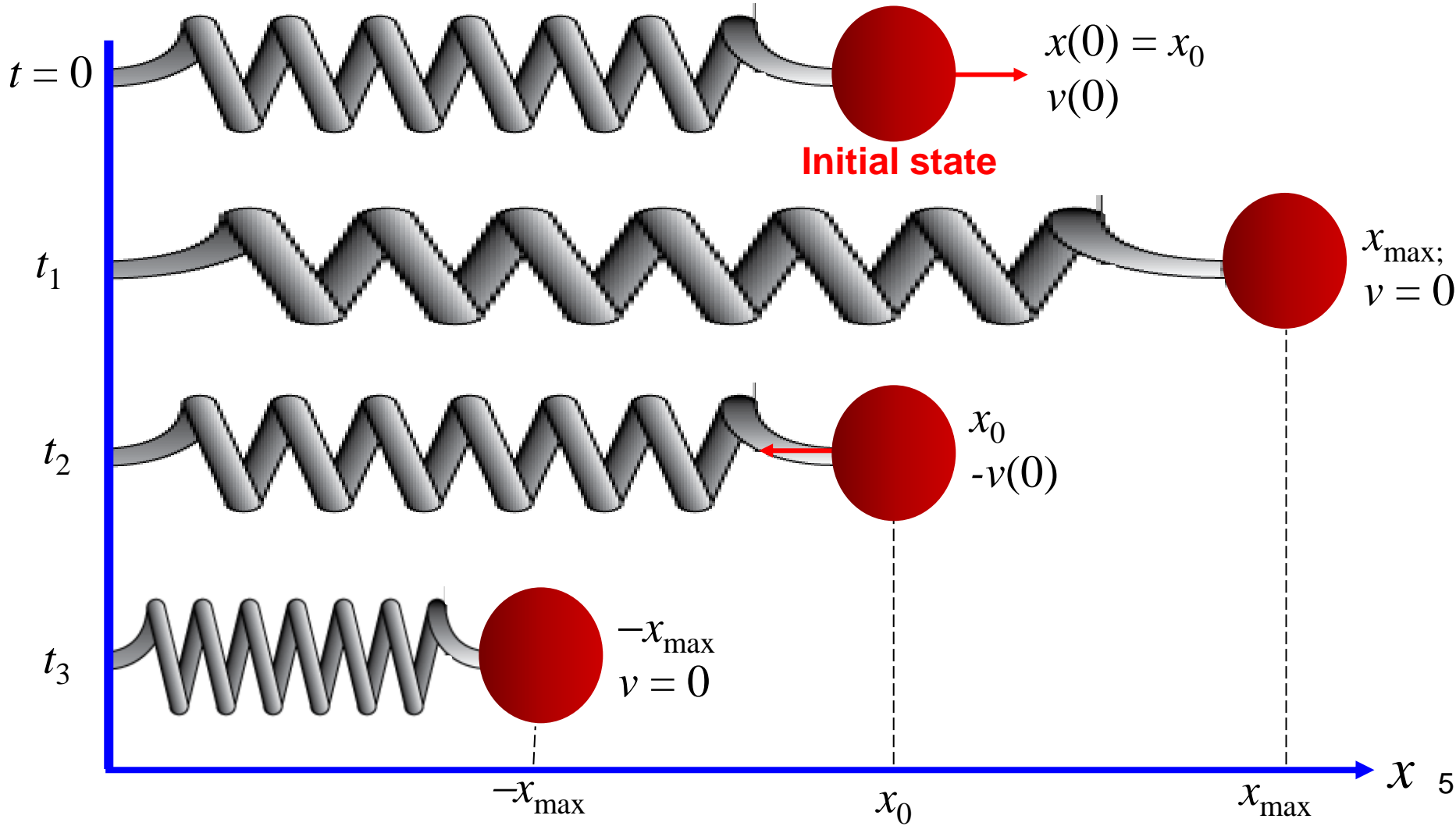
x_0

$U = k(x-x_0)^2/2$

$F = -k(x-x_0)$

$\xi = (x-x_0)$ [displacement]

One-dimensional motion under position-dependent forces: Harmonic oscillator

Newton's second law

$$m\frac{d^2x}{dt^2} = F_x = -k(x - x_0)$$

change variable to displacement ξ $\implies$ $\dfrac{d^2\xi}{dt^2} + \dfrac{k}{m}\xi = 0$

$t = 0$

$x(0) = x_0$
$v(0)$

Initial state

t_1

$x_{\max};$
$v = 0$

t_2

x_0
$-v(0)$

t_3

$-x_{\max}$
$v = 0$

$-x_{\max}$ $\quad$ x_0 $\quad$ $x_{\max}$ $\quad$ x $\;$ 5

One-dimensional harmonic oscillator: Analytical solution

- Define $\quad \omega = \sqrt{k/m} \qquad \dfrac{d^2\xi}{dt^2} + \omega^2\xi = 0$

- Second-order differential equation with constant coefficients
- The **general solution** of this equation: (check by substitution)

Displacement

$$\xi(t) = A\sin(\omega t + \varphi)$$

Amplitude   **Phase**

Velocity

$$\dfrac{d\xi(t)}{dt} = v_\xi(t) = A\omega\cos(\omega t + \varphi)$$

Period of motion τ is determined by the condition $\quad \xi(t) = \xi(t+\tau)$

$$\tau = \dfrac{2\pi}{\omega} = 2\pi\sqrt{\dfrac{m}{k}}$$

Frequency of motion $\quad \nu = 1/\tau$

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The specific solution depends on initial conditions

General solution

$$\xi(t) = A\sin(\omega t + \phi)$$
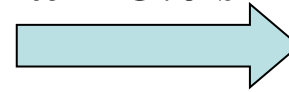
$$v_\xi(t) = A\omega\cos(\omega t + \phi)$$

Apply initial conditions

$$\xi(0) = 0.0 \; m$$

$$v_\xi(0) = 1.0 \; m/s$$

$$\omega = 5.0 \; s^{-1}$$

Specific solution

$$\xi(t) = 0.2\sin(5t)$$

$$v_\xi(t) = \cos(5t)$$

$v_\xi(t) \; / \; m \cdot s^{-1}$

$\xi(t) \; / \; m$

Legend:
— $\xi(t)$
— $v(t)$

$t \; / \; s$
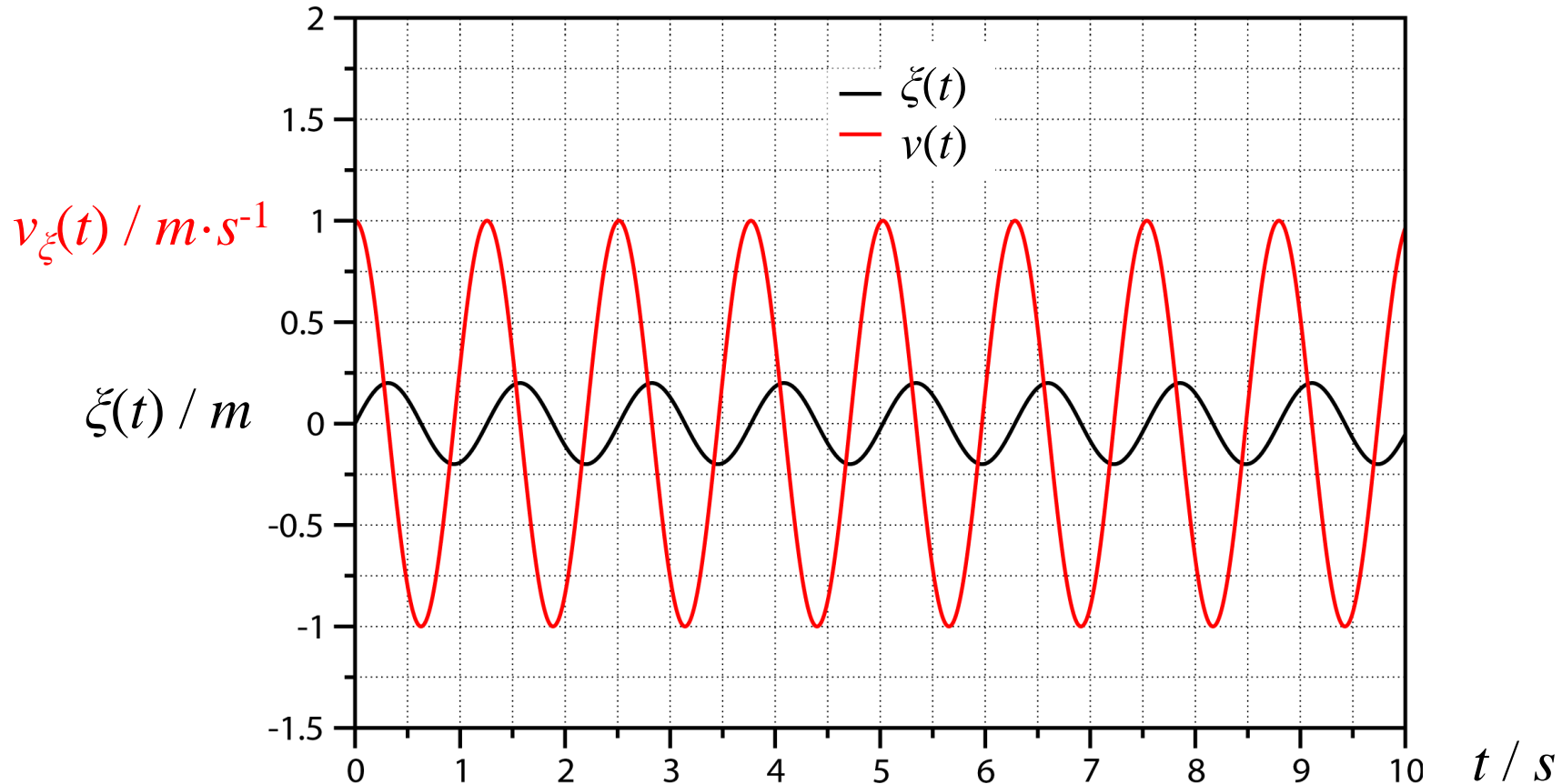
Energy of the harmonic oscillator is determined by the initial conditions

$$E(t) = \frac{1}{2}mv_\xi^2(t) + \frac{1}{2}k\xi^2(t) = \frac{1}{2}kA^2$$

The Lagrangian approach to classical mechanics

We define the Lagrangian in terms of coordinates, **r**, and conjugate velocities, $\mathbf{v} = \dot{\mathbf{r}}$

$$L(\{\mathbf{r}_i, \mathbf{v}_i\}) = K - U = \sum_i \frac{1}{2} m_i v_i^2 - U(\{\mathbf{r}_i\}) = \sum_i \frac{1}{2} m_i \dot{r}_i^2 - U(\{\mathbf{r}_i\})$$

- In the Lagrangian approach, velocity is an independent variable
- Force is eliminated in favor of potential energy

The Euler – Lagrange equations of motion are equivalent to Newton's second law

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{r}}_i}\right) - \frac{\partial L}{\partial \mathbf{r}_i} = 0 \quad \Longrightarrow \quad \frac{d}{dt}\left(\frac{\partial \frac{1}{2} m \dot{\mathbf{r}}_i \cdot \dot{\mathbf{r}}_i}{\partial \dot{\mathbf{r}}_i}\right) - \frac{\partial U(\{\mathbf{r}\})}{\partial \mathbf{r}_i} = 0 \Rightarrow \frac{d(m\dot{\mathbf{r}}_i)}{dt} - F_i(\{\mathbf{r}\}) = 0$$

Example: $L = \frac{1}{2} m\dot{x}^2 - \frac{1}{2} kx^2$ $\Longrightarrow$ $\frac{d}{dt}\left(m\dot{x}\right) + kx = 0$

What has been achieved?

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The Lagrangian approach to classical mechanics

The Euler – Lagrange equations of motion are valid for all coordinate systems

- Starting with Cartesian coordinates, we can convert L to any convenient coordinate system (spherical, cylindrical, etc.)

$$L(\{\mathbf{r}_i, \dot{\mathbf{r}}_i\}) = K - U = \sum_i \frac{1}{2} m_i \dot{r}_i^2 - U(\{\mathbf{r}_i\})$$

$$L\{\mathbf{q}_i; \dot{\mathbf{q}}_i\} = K - U = \sum_i \frac{m_i}{2} \dot{\mathbf{q}}_i \cdot \dot{\mathbf{q}}_i - U(\{\mathbf{q}_i\})$$

- The Euler – Lagrange equations are valid in all coordinate systems

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{q}}_i} \right) - \frac{\partial L}{\partial \mathbf{q}_i} = 0$$

The Hamiltonian approach to classical mechanics

Define a momentum corresponding to a velocity
$$\mathbf{p}_i = \frac{\partial L}{\partial \dot{\mathbf{q}}_i}$$

Try this with Cartesian coordinates

The Hamiltonian function in terms of coordinates and conjugate momenta

$$H(\mathbf{p}_i, \mathbf{q}_i) = \sum_i \dot{\mathbf{q}}_i \mathbf{p}_i - L(\dot{\mathbf{q}}_i, \mathbf{q}_i) = K(\{\mathbf{p}_i\}) + U(\{\mathbf{q}_i\})$$

- The Hamiltonian function represents the energy of the system
- In the Hamiltonian approach, the positions and conjugate momenta are considered independent variables

Example:
$$p = \frac{\partial \left(\frac{m}{2} \dot{x}^2 - \frac{k}{2} x^2 \right)}{\partial \dot{x}} \implies H = \frac{p_\xi^2}{2m} + \frac{1}{2} k \xi^2$$

The Hamiltonian equations of motion:
$$\begin{cases} \dot{\mathbf{q}}_i = \dfrac{\partial H}{\partial \mathbf{p}_i} \\ \dot{\mathbf{p}}_i = -\dfrac{\partial H}{\partial \mathbf{q}_i} \end{cases}$$

Lagrangian and Hamiltonian formulations are better suited for theoretical developments (see quantum mechanics, relativity, statistical mechanics, chaotic systems, …)

The Hamiltonian approach and phase space: Harmonic oscillator

The momentum for the harmonic oscillator is defined as, $\quad p_\xi = \dfrac{\partial L}{\partial \dot{\xi}} = m\dot{x}$

The Hamiltonian is therefore, $\qquad H = \dfrac{p_\xi^2}{2m} + \dfrac{1}{2}k\xi^2$

Hamilton's equations of motion are,

$$\begin{cases} \dot{\xi} = \dfrac{p_\xi}{m} \\ \dot{p}_\xi = -k\xi \end{cases}$$

- These two equations may be solved separately to give the time variation of the coordinates and momentum, as given in Slide 6.

- The structure of the Hamiltonian equations gives direct insight into the dynamical nature of the motion. Eliminating time between the two equations gives the "phase space trajectory",

$$\begin{cases} d\xi = \dfrac{p_\xi}{m}dt \\ dp_\xi = -k\xi dt \end{cases} \Rightarrow p_\xi dp_\xi = -km\xi d\xi \Rightarrow p_\xi^2 + mk\xi^2 = const.$$

Application of Hamilton's approach: Phase space trajectory

Hamilton's equations of motion for a mass moving under constant gravitation force:
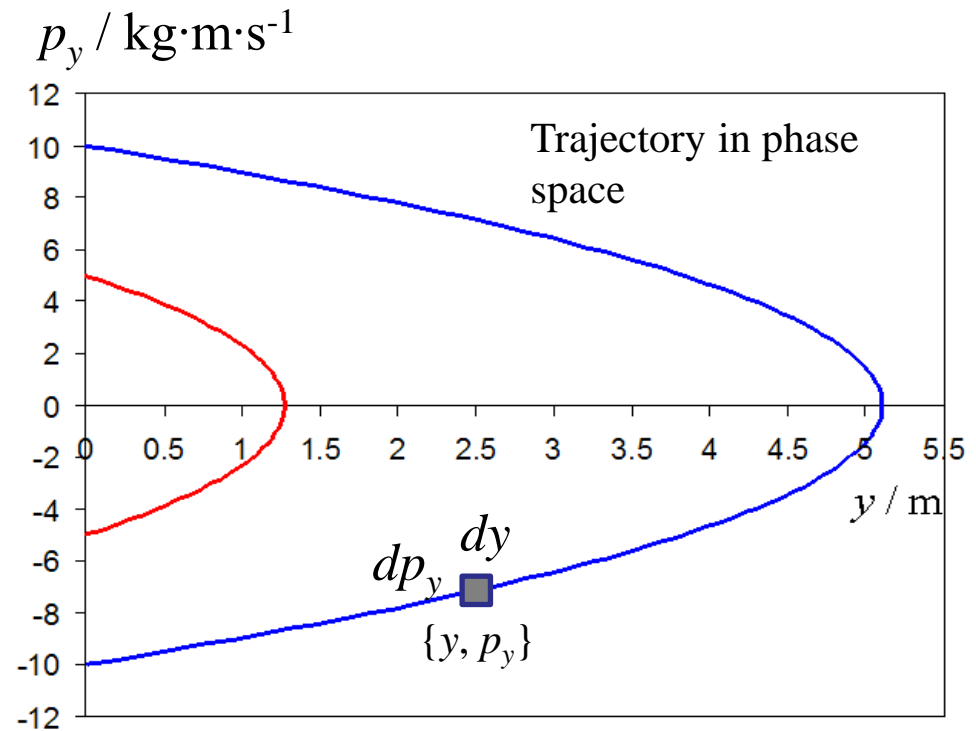
$$\begin{cases} \dot{y} = \dfrac{\partial H}{\partial p_y} \\[2mm] \dot{p}_y = -\dfrac{\partial H}{\partial y} \end{cases} \Rightarrow \begin{cases} dy = \dfrac{p_y}{m}\, dt \\[2mm] dp_y = mg\, dt \end{cases}$$

Eliminating time from the solution:

$$p_y\, dp_y = m^2 g\, dy \Rightarrow$$

$$\tfrac{1}{2} p_y^2(t) - \tfrac{1}{2} p_y^2(0) = m^2 g y(t) - m^2 g y(0)$$

- For one-dimensional motion of a single particle, the phase space has two dimensions: $\{y, p_y\}$.

p_y / kg·m·s^{-1}

Trajectory in phase space

y / m

dp_y $\quad dy$

$\{y, p_y\}$

Phase space trajectory does not explicitly include time

- The phase space trajectory gives all dynamical information at different times.
- Initial conditions (the energy) determine which specific trajectory passes through a point in phase space.
- All of phase space is covered by trajectories since energy can vary continuously.
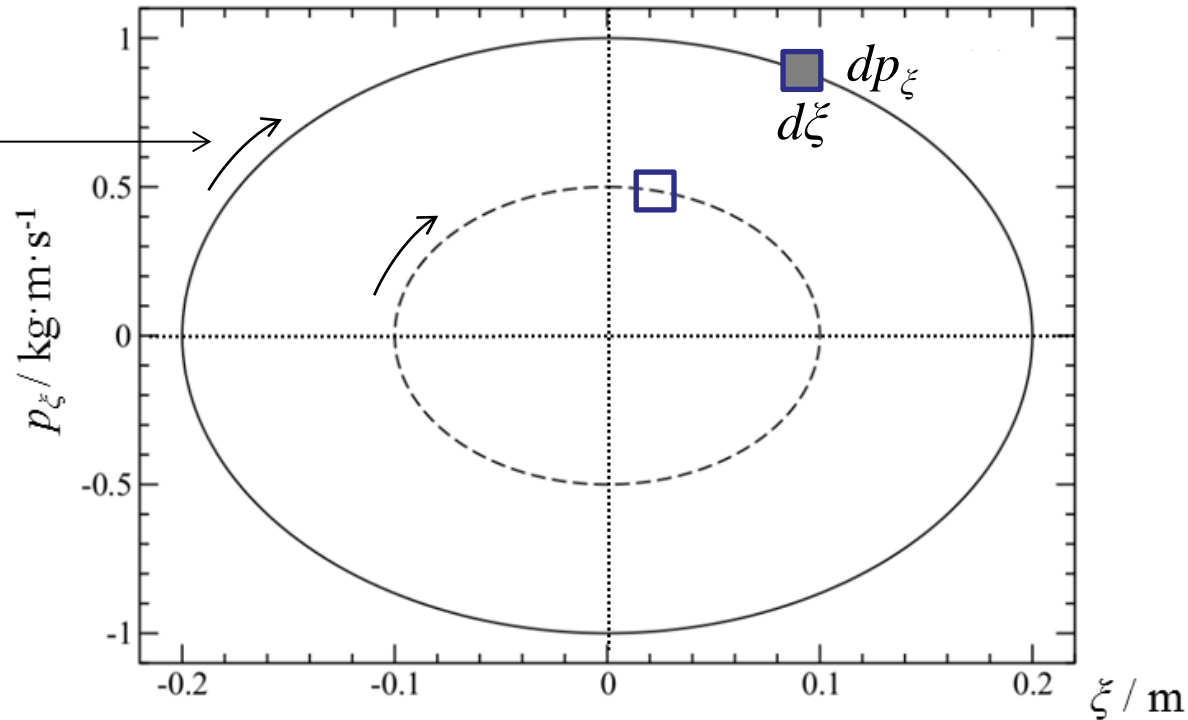- Each point in phase space defines the "state" of a system

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Phase space trajectory for the harmonic oscillator

The phase space trajectory

$$p_\xi(t)^2 + \frac{2mE_0}{A^2}\xi(t)^2 = 1$$

- Direction of motion on the trajectory with time
- Time does not explicitly appear in the phase space representation

- The "**state**" in phase space is determined by the volume element around the point $\{\xi, p_\xi\}$
- The collection of states on a phase space trajectory all have the same energy
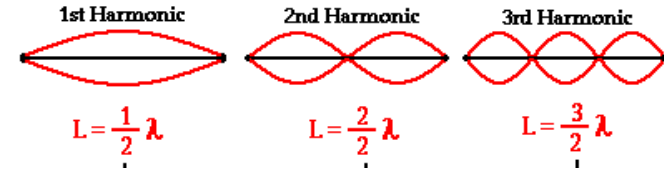- All points in phase space belong to a unique trajectory

Saman Alavi–2022

Quantum mechanics was developed by analogy with the classical wave equation (Schrödinger, 1923)

1st Harmonic $L = \frac{1}{2}\lambda$

2nd Harmonic $L = \frac{2}{2}\lambda$

3rd Harmonic $L = \frac{3}{2}\lambda$
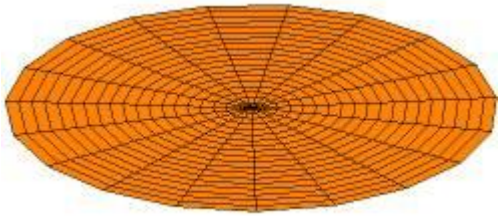
Drum skin with stationary boundary conditions
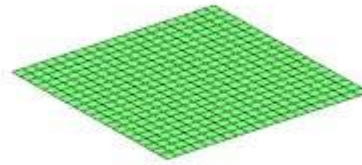
Square membrane with stationary boundary conditions

String confined between two stationary points

Classical wave equation

The "field" which carries the wave

$$\frac{\partial^2 \Psi(x,y,z,t)}{\partial t^2} = c^2 \left[\frac{\partial^2 \Psi(x,y,z,t)}{\partial x^2} + \frac{\partial^2 \Psi(x,y,z,t)}{\partial y^2} + \frac{\partial^2 \Psi(x,y,z,t)}{\partial z^2} \right]$$

$$= c^2 \nabla^2 \Psi(x,y,z,t) \quad \longleftarrow \quad \text{Curvature of the field}$$

Solution by separation of variables $\Psi(x,y,z,t) = \psi(x,y,z)T(t)$

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When the wave has a single frequency, the wave equation simplifies to the "Helmholtz equation"

$$\nabla^2 \psi(x, y, z) + \left(\frac{2\pi}{\lambda}\right)^2 \psi(x, y, z) = 0$$

- Stationary waves have nodes at the boundaries
- The stable waves are "quantized" to satisfy the boundary conditions
- Classically, the energy of the wave depends on the amplitude:
    All energies are possible!

Quantum mechanical time-independent Schrödinger equation is derived by applying de Broglie hypothesis to matter waves

$$\nabla^2 \psi_{n_x, n_y, n_z}(x, y, z) + \frac{2m}{\hbar^2}\left[\varepsilon_{n_x, n_y, n_z} - U(x, y, z)\right]\psi_{n_x, n_y, n_z}(x, y, z) = 0$$

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Quantum mechanical treatment of simple systems: The time-independent Schrödinger equation

Solving the time-independent Schrödinger equation gives allowed stationary quantum states ("wave functions") in a system. For a one-particle, three dimensional system:

$$\left[\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + U(x, y, z) \right]\psi_{n_x, n_y, n_z} = \varepsilon_{n_x, n_y, n_z}\psi_{n_x, n_y, n_z}$$

States characterized by the wave function ψ_{n_x, n_y, n_z} are obtained

Only discrete energies $\varepsilon_{n_x, n_y, n_z}$ are allowed

- The time-independent Schrödinger equation is a "wave equation" which gives all possible stable (stationary waves) for a given system
- It's development uses the classical wave equation and the de Broglie idea that matter can be described by particles and waves, the same way as light

Knowing the state (wave function) does not give exact knowledge of the position and momentum of the object in the quantum mechanical system. The best we can do is to predict these quantities within a minimum uncertainty.

Quantum mechanical particle in a box (ideal gas) system: Spacing of energy levels and degeneracy

Potential energy for particle in a three-dimensional cubic box model:

$$U(x, y, z) = \begin{cases} = 0 & \text{for } 0 \le x < L; \ 0 \le y < L; \ 0 \le z < L \\ = \infty & \text{elsewhere} \end{cases}$$
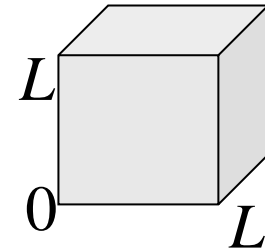
Stationary wave function of particle in a three-dimensional cubic box:

$$\psi_{n_x,n_y,n_z} = A_{n_x,n_y,n_z} \sin(n_x \pi x / L) \sin(n_y \pi y / L) \sin(n_z \pi z / L)$$

Allowed quantized energy levels of particle in a three-dimensional cubic box:

$$\varepsilon_{n_x,n_y,n_z}(1,V) = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{h^2}{8mV^{2/3}}\left(n_x^2 + n_y^2 + n_z^2\right)$$

-For small confinement volumes, the gaps between energy levels for different combinations of n_i are large (quantum dots)
- For large volume (a typical gas), the energy levels are very closely spaced

Stationary wave function of particle on a 2-dimensional surface:

$$\psi_{2,2} = A_{2,2} \sin(2\pi x / L) \sin(2\pi y / L)$$
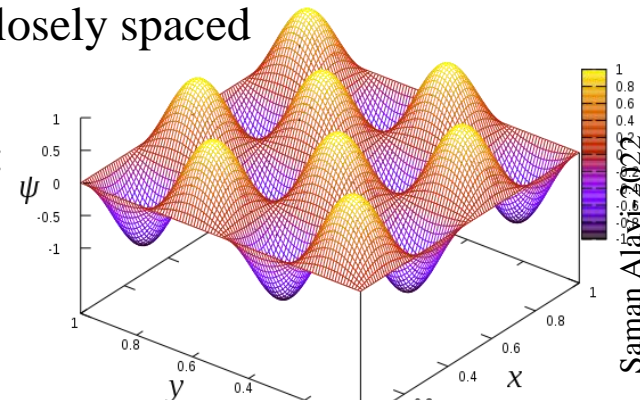
Degeneracy of states of molecules in a 3-dimensional cubic box

Consider the following three states:

$$\psi_{2,1,1} = A_{2,1,1} \sin(2\pi x / L) \sin(\pi y / L) \sin(z\pi / L)$$

$$\psi_{1,2,1} = A_{1,2,1} \sin(\pi x / L) \sin(2\pi y / L) \sin(\pi z / L)$$

$$\psi_{1,1,2} = A_{1,1,2} \sin(\pi x / L) \sin(\pi y / L) \sin(2\pi z / L)$$

They all have an energy of:

$$\varepsilon_{2,1,1}(1,V) = \frac{h^2}{8mV^{2/3}}\left(2^2 + 1^2 + 1^2\right)$$

Degeneracy: Three microstates have the same energy

$$\begin{matrix} (2,1,1) \\ (1,2,1) \\ (1,1,2) \end{matrix} \Leftrightarrow \frac{h^2}{8mV^{2/3}} 6$$

Two non-interacting particles in a three-dimensional cubic box have higher degeneracy:

$$E_{\mathbf{j_1},\mathbf{j_2}}(2,V) = \frac{h^2}{8mV^{2/3}}\left(n_{1x}^2 + n_{1y}^2 + n_{1z}^2 + n_{2x}^2 + n_{2y}^2 + n_{2z}^2\right)$$

Six degenerate microstates: (2,1,1,1,1,1) (1,2,1,1,1,1) (1,1,2,1,1,1)
(1,1,1,2,1,1) (1,1,1,1,2,1) (1,1,1,1,1,2)

Discrete states for the quantum mechanical harmonic oscillator

$$\hat{H}\psi_n = \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right]\psi_n = \varepsilon_n\psi_n$$

Time-independent Schrödinger equation

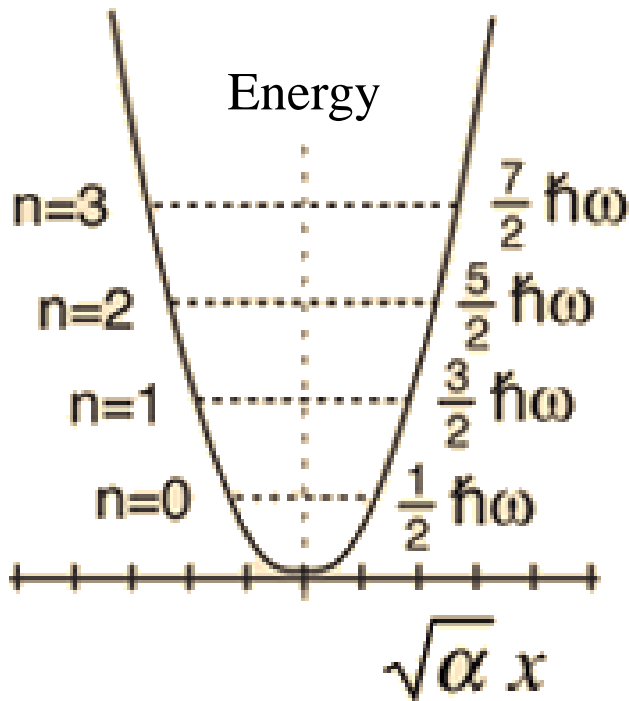The energy of the quantum mechanical harmonic oscillator are quantized.
Only certain energy values are allowed.

$$\varepsilon_n = (n + 1/2)h\nu = (n + 1/2)\hbar\omega$$

The quantum index or quantum number

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

Further reading

Energy

n=3 .... $\frac{7}{2}\hbar\omega$

n=2 .... $\frac{5}{2}\hbar\omega$

n=1 .... $\frac{3}{2}\hbar\omega$

n=0 .... $\frac{1}{2}\hbar\omega$

$\sqrt{\alpha}\,x$

The "state" of the system is represented by a single discrete quantum index i. The state is equivalent to a phase space trajectory with constant energy.

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Discrete states for the quantum mechanical harmonic oscillator

- The wavefunction does not give the exact position and momentum of the object, but rather a probability of observing the object in certain locations

$$\psi_3$$

$$\psi_3^2$$
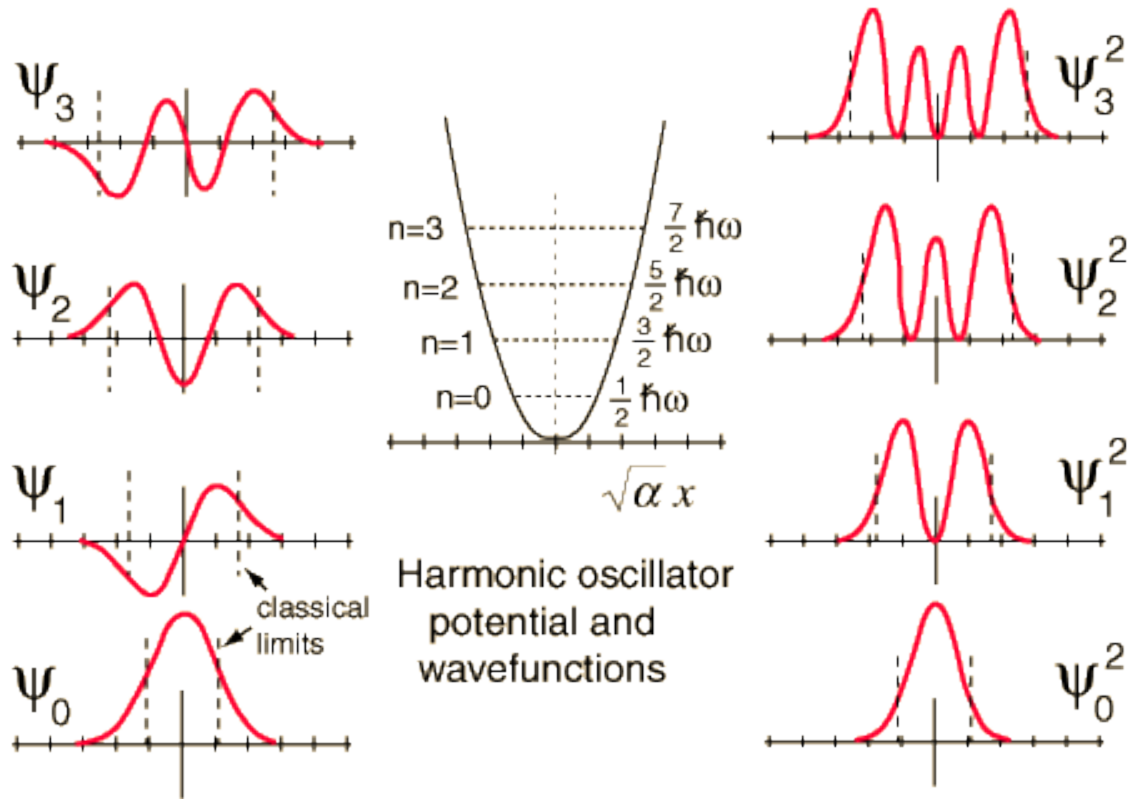
Hermite polynomials

$$\psi_3 = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{3}}\left[2(\sqrt{\alpha}x)^3 - 3\sqrt{\alpha}x)\right]e^{-\alpha x^2/2}$$

$$\psi_2$$

$$\psi_2^2$$

$$\psi_2 = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{2}}\left[2\alpha x^2 - 1\right]e^{-\alpha x^2/2}$$

$n=3$ $\frac{7}{2}\hbar\omega$

$n=2$ $\frac{5}{2}\hbar\omega$

$n=1$ $\frac{3}{2}\hbar\omega$

$n=0$ $\frac{1}{2}\hbar\omega$

$\sqrt{\alpha}\,x$

$$\psi_1$$

$$\psi_1^2$$

$$\psi_1 = \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{2\alpha}\,xe^{-\alpha x^2/2}$$

classical limits

Harmonic oscillator potential and wavefunctions

$$\psi_0$$

$$\psi_0^2$$

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

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N-molecule states in quantum mechanics

- For the three-dimensional system of *N* atoms, the Schrödinger equation is:

$$\left[\sum_{j=1}^{N} \frac{-\hbar^2}{2m_j} \nabla_j^2 + U\left(\{\mathbf{r}\}\right) \right] \psi_{\mathbf{n}}\left(\{\mathbf{r}\}\right) = E_{\mathbf{n}} \psi_{\mathbf{n}}\left(\{\mathbf{r}\}\right)$$

- The wave function $\psi_{\mathbf{n}}(\{\mathbf{r}\})$ is a function of coordinates:

  $\{\mathbf{r}\} = \{x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N\}$.

- For an *N*-atom quantum system, the state of the system is represented by a discrete quantum index **n**. The index is a compound of all $3N$ dimensions in the system

- The state **n** has a corresponding energy $E_{\mathbf{n}}$

- We may not be able to explicitly determine the state $\psi_{\mathbf{n}}$ and the $E_{\mathbf{n}}$

- We can still say the system is characterized by discrete states

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Molecular motion: Diatomic molecules, separating motions

The total energy for the two atom system is

$$E = T + U = \frac{1}{2}m_1 v_1^2 + \frac{1}{2}m_2 v_2^2 + U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right)$$

The total energy in the center of mass and relative position frame becomes

$$E = T + U = \frac{1}{2}\left(m_1 + m_2\right)v_{cm}^2 + \frac{1}{2}\mu_{12}v_{\mathbf{r}}^2 + U\left(|\mathbf{r}|\right)$$

Changing the relative position to polar coordinates allows separation of vibrational motion (involving changing r) and rotational motion (involving change of θ and ϕ)

$$E = \frac{1}{2}\left(m_1 + m_2\right)\dot{R}_{cm}^2 + \frac{1}{2}\mu_{12}\dot{r}^2 + U(r) + \frac{1}{2}\mu_{12}r^2\dot{\theta}^2 + \frac{1}{2}\mu_{12}r^2\sin^2\theta\dot{\phi}^2$$

$$= E_{trans} + E_{vib} + E_{rot}$$

The energy is broken down to independent contributions from translation of the "molecule" as a whole, and "intramolecular" rotations and vibrations.

A procedure is carried out to show that for polyatomic molecules, the mechanical energy is separated into translational motion of the center of mass and rotational - vibrational intermolecular motions

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Molecular motion: Diatomic molecules

Consider to atoms 1 and 2 interacting with some force which is just a function of the distance between the two atoms, $\mathbf{F}(|\mathbf{r}_1-\mathbf{r}_2|) = \mathbf{F}(r)$

$$\left\{ \begin{array}{l} m_1 \dfrac{d^2\mathbf{r}_1}{dt^2} = F_{12}(|\mathbf{r}_1 - \mathbf{r}_2|) \\[2mm] m_2 \dfrac{d^2\mathbf{r}_2}{dt^2} = F_{21}(|\mathbf{r}_1 - \mathbf{r}_2|) = -F_{12}(|\mathbf{r}_1 - \mathbf{r}_2|) \end{array} \right.$$
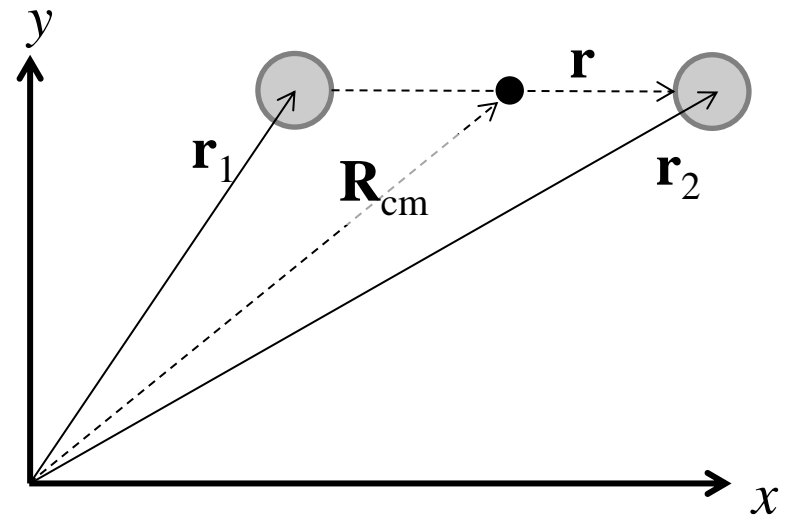
We define the center of mass position, $\mathbf{R}_{cm}$, and relative coordinates, $\mathbf{r}$, as,

$$\left\{ \begin{array}{l} \mathbf{R}_{cm} = \dfrac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \\[3mm] \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \end{array} \right.$$

In terms of these coordinates, the position vectors of the two particles can therefore be written as,

$$\left\{ \begin{array}{l} \mathbf{r}_1 = \mathbf{R}_{cm} + \dfrac{m_2}{m_1 + m_2}\mathbf{r} \\[4mm] \mathbf{r}_2 = \mathbf{R}_{cm} - \dfrac{m_1}{m_1 + m_2}\mathbf{r} \end{array} \right.$$

The second time derivatives of $\mathbf{r}_1$ and $\mathbf{r}_2$ can be written in terms of time derivatives of $\mathbf{R}_{cm}$ and $\mathbf{r}$

Molecular motion: Diatomic molecules, separating motions

Substituting into the equations motion gives two new equations for the center of mass and relative motion:

$$\begin{cases} (m_1 + m_2)\dfrac{d^2\mathbf{R}_{cm}}{dt^2} = 0 \\[3mm] \dfrac{m_1 m_2}{m_1 + m_2}\dfrac{d^2\mathbf{r}}{dt^2} = \mu_{12}\dfrac{d^2\mathbf{r}}{dt^2} = \mathbf{F}(r) \end{cases}$$

In the new coordinate system,
- Motions of the center of mass and relative coordinates are not coupled
- The center of mass moves as a free particle subject to no force
- The relative motion is described by a particle of mass μ_{12} moving under a force $\mathbf{F}(r)$.

Rather than Cartesian coordinates $\mathbf{r} \equiv \{x, y, z\}$, the relative motion is described in the polar coordinate system

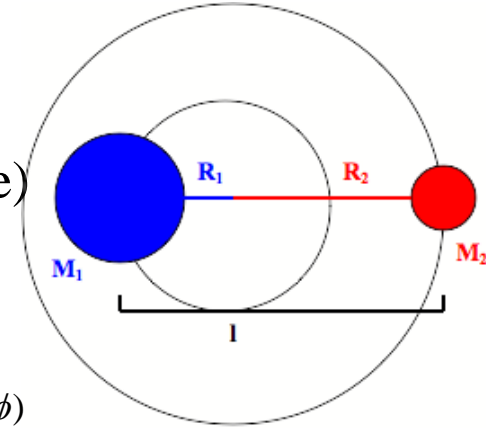$$\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{cases}$$
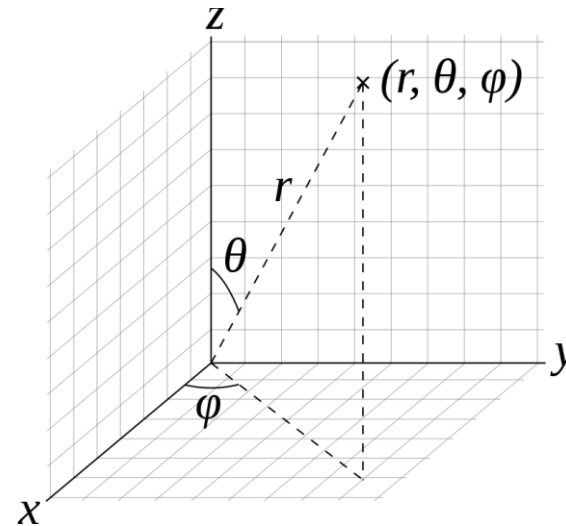
Showing time derivatives with the "dot" notation introduced by Newton: $\implies$

$$\dot{x} = \frac{dx}{dt}$$
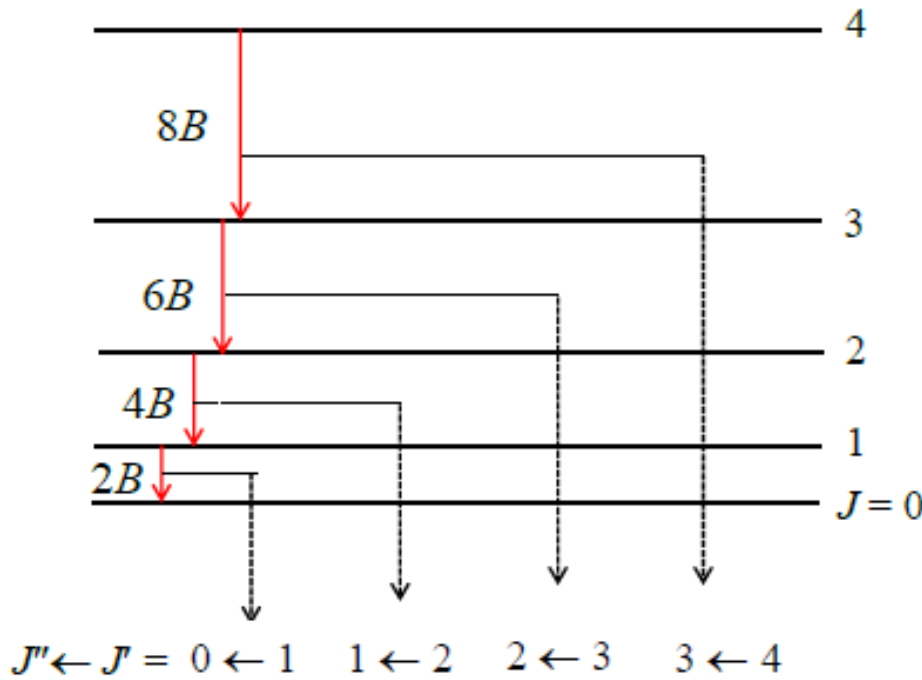
$$\begin{cases} \dot{x} = \dot{r}\sin\theta\cos\phi + r\cos\theta\dot{\theta}\cos\phi - r\cos\theta\sin\phi\dot{\phi} \\ \dot{y} = \dot{r}\sin\theta\sin\phi + r\cos\theta\dot{\theta}\sin\phi - r\cos\theta\cos\phi\dot{\phi} \\ \dot{z} = \dot{r}\cos\theta - r\sin\theta\dot{\theta} \end{cases}$$

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Discrete states for the quantum mechanical "rigid rotor"

- Solving the Schrödinger equation for rotation of a rigid linear molecule;
- The rotation is represented by angular variables θ (polar angle) and ϕ (azimuth);

$$\hat{H}\psi_{J,m(\theta,\phi)} = \frac{-\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi_{J,m(\theta,\phi)} = \varepsilon_J\psi_{J,m(\theta,\phi)}$$

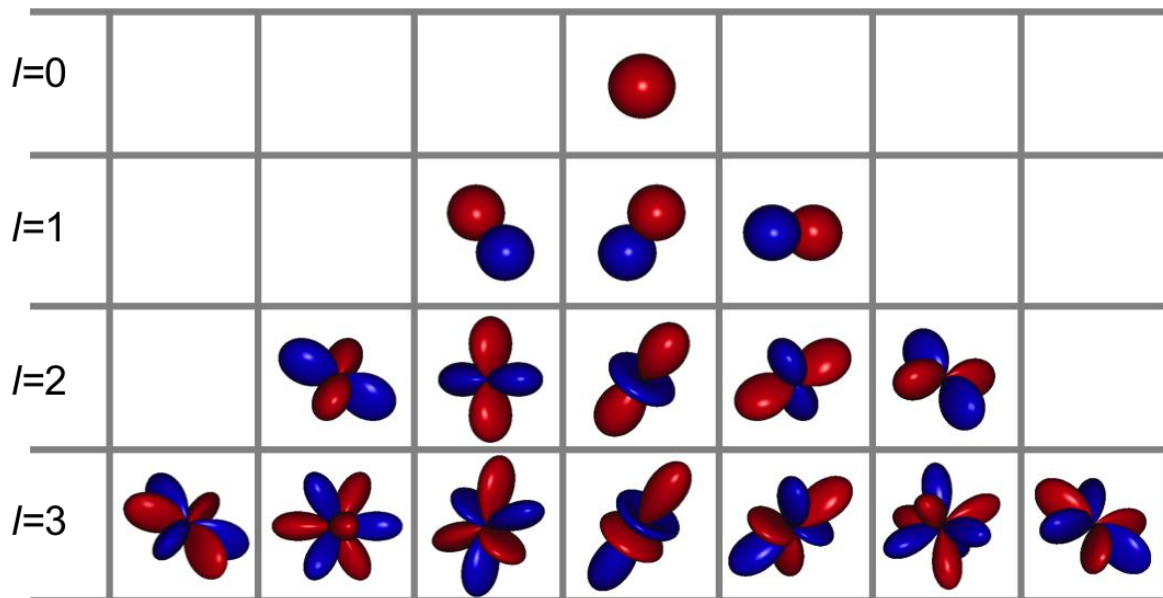The energies of the quantum mechanical rigid rotor are quantized.

$$\varepsilon_J = J(J+1)\frac{\hbar^2}{2I} = J(J+1)hB$$

Rotational quantum number

The rotational energy states have a degeneracy of $2J + 1$.

$$J'' \leftarrow J = 0 \leftarrow 1 \quad 1 \leftarrow 2 \quad 2 \leftarrow 3 \quad 3 \leftarrow 4$$

Discrete states for the quantum mechanical rigid rotor

- The wave functions for the rigid rotor are the spherical harmonics $Y_{J,m}(\theta,\phi)$

Spherical harmonics

$$\psi_{0,0} = \frac{1}{\sqrt{4\pi}}$$

$$\psi_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$\psi_{1,\pm 1} = \sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$$

$$\psi_{2,0} = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)$$

$$\psi_{2,\pm 1} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi}$$

$$\psi_{2,\pm 2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\phi}$$

The rigid rotor wave functions with:
- l = even are symmetric with respect to inversion around the molecule center
- l = odd are antisymmetric with respect to inversion about the molecule center
- Important when applying the Pauli exclusion principle to molecular wave functions