Classical Mechanics

Classical mechanics adequately describes the macroscopic world.
For example. hockey pucks, cars, satellites

It fails miserably for microscopic systems, such as electrons.

Then why study classical mechanics in a quantum chemistry course?

Quantum theory is much more understandable based on knowledge of older classical mechanics.

For example, many fundamental concepts and principles of quantum mechanics are directly obtained from analogous classical ideas. In some limiting cases, such as very small energy-level spacing, quantum and classical descriptions are mathematically identical.

BUT … Some quantum mechanical concepts have no classical analogues.

Useful classical ideas to cover:

a) Newton's 2nd law forms the foundation of classical mechanics.

b) Classical equations of motion derived from classical mechanics.

c) Hamilton's formulation of classical mechanics. It turns out that Hamilton's formulation has useful analogs in quantum mechanics.

For example, the "**Hamiltonian operator**" occurs in the famous Schrödinger equation of quantum mechanics. The reason it is called the Hamiltonian operator is because of its analogy to classical mechanics.

Mechanics

Mechanics is the analysis of the motion of objects.

Equations of motion

Differential equations that prescribe the motion of a particle or system are called the equations of motion.

Newton's Second Law

Equation of motion that relates the external force on a body to the change in motion it causes the body.

$$\vec{F} = m\vec{a}$$

Acceleration of the particle caused by the application of the force.

external or applied force on a body.

mass of the body or particle.

$$\vec{F} = m\vec{a}$$

$\vec{F}, \vec{a}$ are vectors with magnitude + direction.
often represented in bold type, $\boldsymbol{F}$, $\boldsymbol{a}$

m scalar with magnitude only.

$$\vec{a} = \frac{\mathrm{d}^2\vec{r}}{\mathrm{d}t^2}$$

$\vec{r}$ = position vector

t = time

$$\vec{a} = \ddot{\vec{r}}$$

$$\vec{v} = \dot{\vec{r}}$$

Dot notation for time derivatives.

Newton's Equation of motion

$$F_x = ma_x \qquad \text{(in one-dimension)}$$

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

If we know $\boldsymbol{F}$, then Newton's equation of motion can be used to solve for x as a function of time, $x(t)$.

Newton's equation of motion is a **differential equation**, which can be solved for $x(t)$.

$$F_x = m\frac{d^2x(t)}{dt^2} \quad \Longrightarrow \quad x(t)$$

The function $x(t)$ then tells us everything we need to know about the object's motion in time and space.

Classical Linear Momentum

Recall the definition of linear momentum (as opposed to angular momentum)

$$\vec{p} = m\vec{v}$$

in 1-Dimension:

$$p_x(t) = m\dot{x}(t) = mv_x(t) = m\frac{dx(t)}{dt}$$

Once we know $x(t)$, we can also specify the momentum, $p_x(t)$.

In classical mechanics we can exactly specify the position and momentum of a system.

Oddly enough, we can't do this in quantum mechanics.

(more on this later)

Classical Kinetic Energy

Recall that the classical definition of kinetic energy is given by:

$$T = \frac{1}{2} m \left|\vec{\mathrm{v}}\right|^2$$

for one particle

We will use the symbol T for the kinetic energy.

More generally, the kinetic energy is defined in terms of the linear momentum as:

$$T = \frac{\left|\vec{p}\right|^2}{2m} = \frac{\vec{p} \bullet \vec{p}}{2m}$$

scalar or dot-product

$$= \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

If the kinetic energy of a system made up of one particle is given by:

$$T = \frac{\vec{p} \cdot \vec{p}}{2m}$$

The total kinetic energy for a many particle system is given by the sum:

$$T_{\text{tot}} = \sum_{i=1}^{N} T_i = \sum_{i=1}^{N} \frac{\vec{p}_i \cdot \vec{p}_i}{2m_i}$$

where the index i runs over all of the particles.

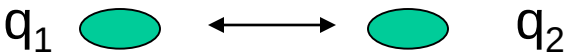
The above is true whether the particles interact or not.

Conservative Systems and Potential Energy

Many problems in chemistry and physics involve "***conservative systems***" where ***the total energy is constant in time***.

These are systems in which the potential energy, V, of a system of particles depends only on the positions of the particles.

example:



Consider a system of two isolated charged particles. There will be an electrostatic interaction given by:

$$V(\vec{r}_1,\vec{r}_2)=\frac{q_1q_2}{4\pi\varepsilon_o\left|\vec{r}_2-\vec{r}_1\right|}$$

the potential energy of the system in Cartesians is:

$$V(\vec{r}_1,\vec{r}_2)=\frac{q_1q_2}{4\pi\varepsilon_o\sqrt{(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2}}$$

The potential energy of the system depends only on the position of the particles.

Conservative Forces

In a conservative system, where the potential depends only upon the position of the particles, we have a very important relationship:

$$\vec{F} = -\vec{\nabla} V$$

The potential V is a function of the positions only $V(x,y,z)$

A force which satisfies the above is called a "conservative force"

recall:

$$\vec{\nabla} = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$$

'del' is the gradient of the potential, V

The gradient gives the rate of change of the potential with respect to the position of the particle.

Why is this important?

Recall if we know $\boldsymbol{F}$, then we can solve the equations of motion.

Gradient with more than one Particle

$$\vec{F} = -\vec{\nabla} V$$

What if we have a system of more than one particle, like our system of two charged particles (where $k = 1/4\pi\varepsilon_0$)

$$V(x_1, y_1, z_1, x_2, y_2, z_2) = k \frac{q_1 q_2}{\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}}$$

then

$$\vec{F}_i = -\vec{\nabla}_i V(x_1, y_1, z_1, x_2, y_2, z_2)$$

$$\vec{\nabla}_i = \hat{i}\frac{\partial}{\partial x_i} + \hat{j}\frac{\partial}{\partial y_i} + \hat{k}\frac{\partial}{\partial z_i}$$

Back to Conservative Forces

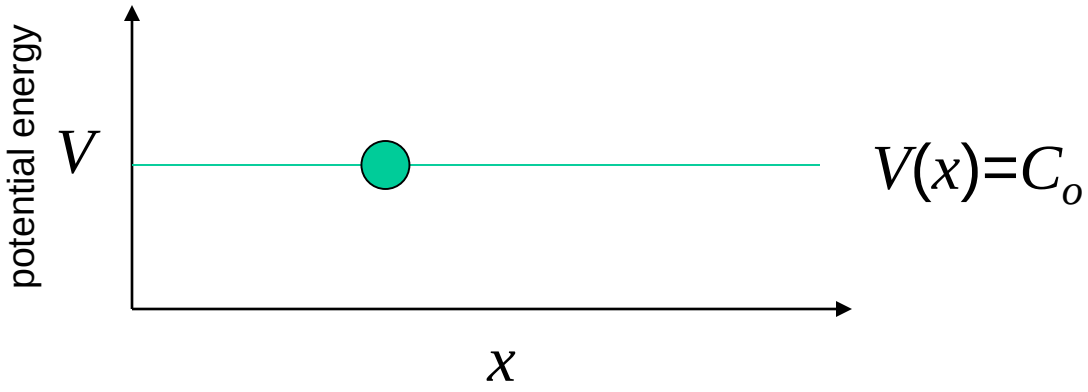
For conservative systems we can derive the force from the potential as:

$$\vec{F} = -\vec{\nabla} V$$

Let's examine this a little more closely from a physical/qualitative point of view.

With our interpretation of the gradient, we are saying that with conservative systems, the value of the force is dependent upon the slope of the potential.

Consider a particle in a uniform potential in the 'x' direction.



There will be no force on the particle due to the potential $V(x)$, because there is no 'favoured' position.

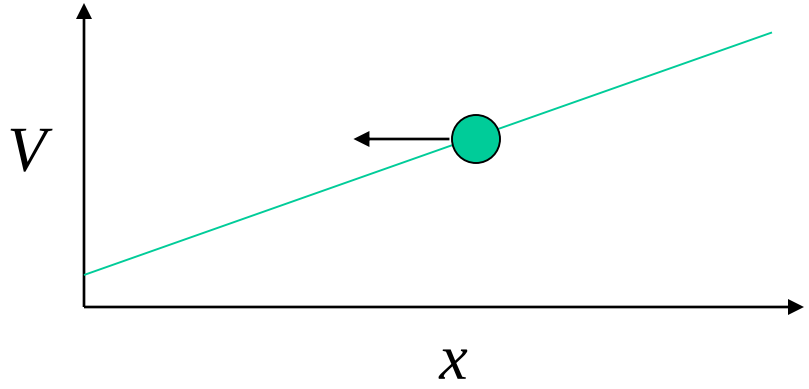
$$F_x = -\frac{\partial V}{\partial x}$$

In the above example, the potential V is constant, so:

$$F_x = -\frac{\partial V}{\partial x} = 0$$

And there is no force on the particle due to the potential.

Now consider a potential that is not constant:



$$V(x) = Ax + B$$

In this case, by moving to smaller x, the potential will decrease. As a result of the potential there will be a force that pushes the particle toward a position of lower potential.

$$F_x = -\frac{\partial V}{\partial x} = -\frac{\partial V(x)}{\partial x} = -\frac{\partial (Ax + B)}{\partial x} = -A$$

The stronger the steeper the potential, the larger the gradient and the stronger the force.

Conservation of Total Energy

Many problems in chemistry and physics involve conservative systems where the total energy is constant in time. Let's define the total energy of particle to be the sum of its kinetic and potential energy:

$$E = T + V$$

We can show that the total energy (kinetic plus potential energy) of a conserved system is a constant of motion or invariant in time for a one dimensional system.

$$\frac{d(T+V)}{dt} = 0$$

Conservative Systems - Summary

In this course we will usually be dealing with “conservative systems” where the total energy is constant in time.

Here, the potential energy of the system depends only on the position of the particles. (It is not time-dependant or dependent on the velocity of the particles.)

When the potential depends only on the position of the particles, we have the following important relationship:

$$F_x = -\frac{\partial V}{\partial x} \qquad \vec{F} = -\vec{\nabla} V$$

With an expression for the force, $\boldsymbol{F}$, we can use this to complete Newton’s Second Law and solve for the motion of the system.

Hamilton's Formulation of Classical Mechanics

The "Hamiltonian" formulation of classical mechanics is useful for discussing quantum mechanics.

Practical difficulties can arise with applying Newton's equation of motion:

$$\vec{F} = m\vec{a}$$

These are vector quantities that depend on the choice of coordinate system, so Newton's equations change when the coordinate system changes.

For example, representation of the acceleration vector in polar spherical coordinates is quite formidable:

$$F_r = m\left(\frac{d^2r}{dt^2} - r\left(\frac{d\theta}{dt}\right)^2 - r\sin\theta\left(\frac{d\phi}{dt}\right)^2\right) \qquad F_\theta = m\left(\frac{d^2\theta}{dt^2} + 2\left(\frac{dr}{dt}\right)\left(\frac{d\phi}{dt}\right) - r\sin\theta\cos\theta\left(\frac{d\phi}{dt}\right)^2\right)$$

$$F_\phi = m\left(r\sin\theta\frac{d^2\phi}{dt^2} + 2\sin\theta\left(\frac{dr}{dt}\right)\left(\frac{d\phi}{dt}\right) - r\cos\theta\left(\frac{d\theta}{dt}\right)\left(\frac{d\phi}{dt}\right)\right)$$

Hamilton's Formulation of Classical Mechanics

In 1834 Hamilton reformulated classical mechanics by developing equations of motion in terms of a scalar function instead of the vector $\boldsymbol{F}$.

The scalar function denoted by H is called the **Hamiltonian function** of a system.

For a conservative system the Hamiltonian function is simply:

$$H = T + V$$

To discuss Hamilton's formulation of classical mechanics, we express T in terms of the momentum and not velocity.

$$T = \frac{1}{2} m\vec{\mathrm{v}}^2 = \frac{1}{2m}\vec{p}^{\,2} = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

Thus, $$H = T(p_x, p_y, p_z) + V(x, y, z)$$

Hamilton's equations of motion for a one-dimensional system:

$$\frac{\partial H}{\partial p_x} = \frac{\mathrm{d}x}{\mathrm{d}t} = \dot{x} \qquad \frac{\partial H}{\partial x} = -\frac{\mathrm{d}p_x}{\mathrm{d}t} = -\dot{p}_x$$

Simultaneous solution of the two differential equations, will yield the trajectory of the system, $x(t)$.

How does this compare to Newton's Second Law?

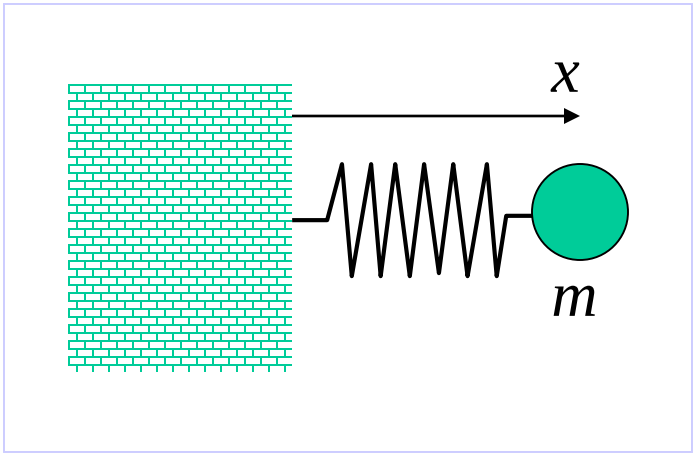
$$F = m\frac{d^2x(t)}{dt^2}$$

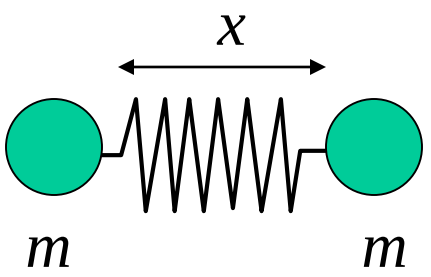
- Newton's equation of motion in one-dimension is a single 2nd order differential equation.
- Hamilton's equations of motion in one-dimension are two, 1st order differential equation.

Hamiltonian Description of the Classical Harmonic Oscillator

Apply Hamilton's equations of motion to a **Harmonic Oscillator**.

e.g.





can serve as a model for a vibrating diatomic molecule.

Note: The potential energy of the system is given by the position only.

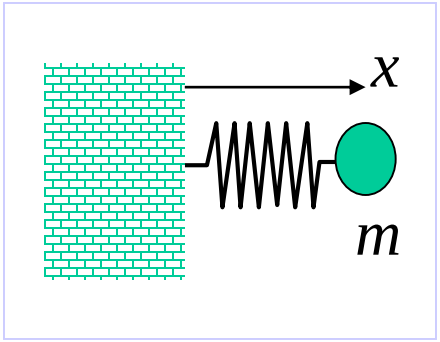
$$V(x) = \frac{1}{2}k(x - x_o)^2$$

x_o = equilibrium position of the spring (resting position)

k is the spring constant. The larger the k the stiffer the spring.

Apply the Hamiltonian equations of motion and solve for $x(t)$.

$$\frac{\partial H}{\partial p} = \frac{\mathrm{d}x}{\mathrm{d}t} \qquad \frac{\partial H}{\partial x} = -\frac{\mathrm{d}p}{\mathrm{d}t}$$



The classical equation for the motion of a harmonic oscillator has mathematical solutions of the form:

$$x(t) = R_o + A\sin(\omega t) + B\cos(\omega t)$$

with

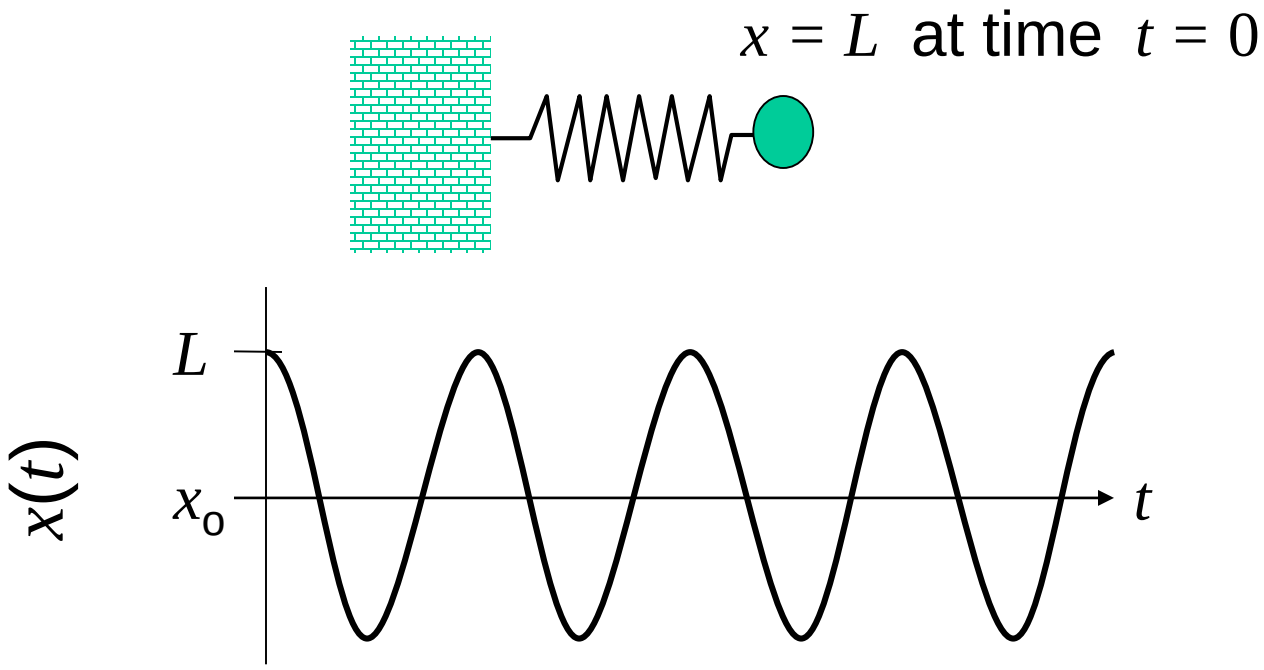
$$\omega = \sqrt{\frac{k}{m}}$$

A and B are constants to be determined from the initial conditions. For example the position and velocity of the mass at time zero.

- As expected the motion is oscillatory.
- For a given spring, we can stretch the system to ‘any’ length and provide the system with energy in a continuous manner.

not the same in quantum mechanics!

- If the mass starts from a stand-still, the mass will never go beyond that point, termed the classical turning point.



not the same in quantum mechanics!

We will see a quantum mechanical analogue of the Hamiltonian Function. Further, these conservation laws used here carry over into quantum mechanics.

Generalized coordinates and Hamilton's equations of Motion

The advantages of Hamilton's formulation of classical mechanics are not always apparent when Cartesian coordinates are used.

It turns out that Hamilton's equations of motion are the same no matter what choice of coordinate system we use, so any convenient coordinate system can be adopted.

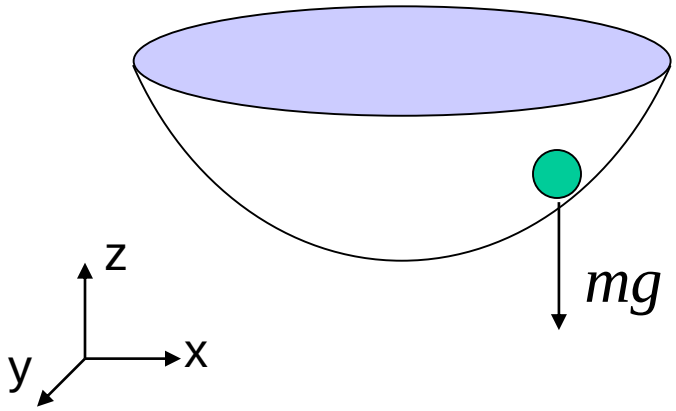
Let q_k = the generalized coordinate

p_k = conjugate momentum pair of q_k

Time derivatives give the generalized velocities $\dot{q}_k$

Note: p_k and $\dot{q}_k$ are **not** linear momentum or velocity unless q_k is a Cartesian coordinate.

Consider a particle sliding on the inside of a frictionless hemispherical bowl of radius R, subject to gravity.



The motion takes place on the surface of the bowl and therefore is constrained so that:

$$x^2 + y^2 + z^2 = R^2$$

One useful set of generalized coordinates for this problem would be the following:

$$q_1 = \frac{x}{R} \qquad q_2 = \frac{y}{R} \qquad q_3 = \frac{z}{R}$$

$$p_1 = m\dot{q}_1 \qquad p_2 = m\dot{q}_2 \qquad p_3 = m\dot{q}_3$$

The Hamiltonian of the system is then given in terms of these generalized coordinates and their conjugate momenta.

$$H = T(q_1, q_2, q_3 \ldots q_{3N}; p_1, p_2, p_3 \ldots p_{3N}) + V(q_1, q_2, q_3 \ldots q_{3N})$$

With these generalized coordinates and momenta, the Hamiltonian equations of motion are:

$$\frac{\partial H}{\partial p_k} = \frac{\mathrm{d}q_k}{\mathrm{d}t} \qquad \frac{\partial H}{\partial q_k} = -\frac{\mathrm{d}p_k}{\mathrm{d}t}$$

$k = 1,2,3 \ldots 3N$

N = number of particles

Notice that this is the same form as in Cartesian coordinates.

Having the flexibility to use any convenient coordinate system is very important for both interpretation and solving the equations of motion.