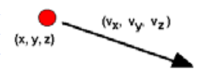
Physical Chemistry

Lecture 10

Mathematics of Quantum Mechanics

Classical mechanics and states

- In mechanics, one describes
  - Where particles are
  - Where particles are going subject to forces
- The state of a system is completely defined by the positions and momenta of all particles -- the trajectories
- Everything is absolutely determined by forces and initial conditions



$$v(t) = v(0) + \frac{1}{m}\int_0^t F(t')dt'$$

$$r(t) = r(0) + \int_0^t v(t')dt'$$

Hamiltonian mechanics

- Newton's mechanics (which most of you learned in physics) does not show clearly the connection to quantum mechanics
- Hamiltonian mechanics (developed by Sir William Rowan Hamilton) is convenient and shows the connection
- Hamiltonian function
  - Energy as a function of position and momentum of particles
  - Emphasizes the importance of energy, rather than forces, in classical mechanics

Finding the Hamiltonian function of a system

- Express energy as a function of momenta and co-ordinates only
- Example: A particle in a Morse potential along the x direction of a co-ordinate system

$$V_{Morse}(x) = D_e\left[1-\exp\left(-\beta(x-x_e)\right)\right]^2$$

$$\begin{aligned} H &= T + V \\ &= \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + D_e\left[1-\exp\left(-\beta(x-x_e)\right)\right]^2 \end{aligned}$$

Hamilton's canonical equations

- Canonical equations give the equations of motion of a conservative system

$$\frac{\partial H}{\partial p_k} = \frac{dx_k}{dt} \quad \text{and} \quad \frac{\partial H}{\partial x_k} = -\frac{dp_k}{dt}$$

- Change of a parameter defined in terms of the Poisson bracket

$$\frac{dA}{dt} = \{A, H\} = \sum_k\left(\frac{\partial A}{\partial x_k}\frac{\partial H}{\partial p_k} - \frac{\partial A}{\partial p_k}\frac{\partial H}{\partial x_k}\right)$$

Example Hamiltonian problem

- Particle in gravitational field along the z direction
- Kinetic energy ≡ $p^2/2m$
- Potential energy ≡ mgz

$$\begin{aligned} H &= K.E. + P.E. \\ &= \frac{p_x^2 + p_y^2 + p_z^2}{2m} + mgz \end{aligned}$$

- Canonical equations give equations of motion directly
  - Equations for x and z motion shown
  - Equation for y motion similar to x motion
- Equations for trajectories can be solved directly by integration of these equations
  - Equivalent to Newton's method
  - More general, and more useful in complex systems

$$\frac{\partial H}{\partial p_z} = \frac{dz}{dt} = \frac{p_z}{m}$$

$$\frac{\partial H}{\partial z} = -\frac{dp_z}{dt} = mg$$

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

$$\frac{\partial H}{\partial x} = -\frac{dp_x}{dt} = 0$$

Conserved quantities

- Quantities that do not change in time are conserved
- Example from the gravitational-field problem

$$\frac{dp_x}{dt} = 0 \Rightarrow p_x \text{ is a conserved quantity}$$

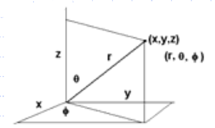
$$\frac{dp_y}{dt} = 0 \Rightarrow p_y \text{ is a conserved quantity}$$

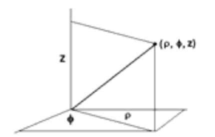
$$\frac{dp_z}{dt} \neq 0 \Rightarrow p_z \text{ is not conserved}$$

- Also called constants of motion

Co-ordinate systems

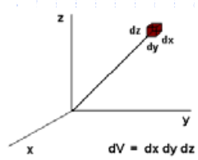
- Positions defined relative to a co-ordinate system
  - Cartesian co-ordinates
    - (x, y, z)
  - Spherical polar co-ordinates
    - (r, θ, ϕ)
  - Cylindrical co-ordinates
    - (ρ, ϕ, z)
  - Confocal elliptical co-ordinates
    - (μ, ν, ϕ)



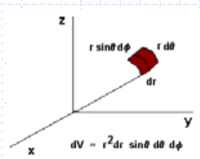


Volume elements for integration

- In the cartesian representation
  - dV = dx dy dz
  - All space
    - $-\infty \le x \le \infty$
    - $-\infty \le y \le \infty$
    - $-\infty \le z \le \infty$



- In the spherical polar representation
  - $dV = r^2 dr \sin\theta d\theta\, d\phi$
  - All space
    - $0 \le r \le \infty$
    - $0 \le \theta \le \pi$
    - $0 \le \phi \le 2\pi$



Vectors and scalars

- Scalar
  - A quantity having magnitude only
- Vector
  - A quantity having magnitude and direction
- Functions
  - Scalar function -- f(x, y, z)
  - Vector function treated as three scalar functions:

$$\mathbf{V}(x,y,z) = V_x(x,y,z)\mathbf{i} + V_y(x,y,z)\mathbf{j} + V_z(x,y,z)\mathbf{k}$$

Vector algebra

- Two vectors are equal if the corresponding components are equal.
- The sum of two vectors is a vector with elements that are sums of corresponding elements.

$$\mathbf{C} = \mathbf{A} + \mathbf{B} \Leftrightarrow c_i = a_i + b_i$$

- The difference of two vectors is defined analogously.

$$\mathbf{C} = \mathbf{A} - \mathbf{B} \Leftrightarrow c_i = a_i - b_i$$

Vector multiplication

- Dot product (scalar or inner product)

$$A \bullet B = \sum_i a_i b_i$$

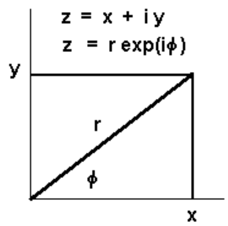
- Cross product (vector or outer product)

$$\mathbf{C} = \mathbf{A} \times \mathbf{B} \Leftrightarrow c_i = \varepsilon_{ijk}\left(a_j b_k - a_k b_j\right)$$

- Division of vectors is not defined.

Complex numbers and functions

- *z* represents a quantity like a two-dimensional vector
- Uses the imaginary number
  $$i = \sqrt{-1}$$
- Expressed as either
  - The real (x) and imaginary (y) parts
  - The magnitude (r) and phase (ϕ)
- Can depend on other variables
  - Complex functions



$$z(t) = x(t) + i\,y(t) = r(t)\exp(i\phi(t))$$

Summary

- Hamiltonian functions are constructed to describe the energy of a system
  - Once known, one can find equations of motion from the Hamiltonian function of a conservative system
- Constants of motion are conserved quantities
- Different co-ordinate systems describe the same system
  - Choose the co-ordinate system to define a problem so that it simplifies the mathematics
  - Integration requires volume elements for each type of co-ordinate system
- Algebra of vectors
  - Sums and differences
  - Two different kinds of products