1.VO, 7.10.2008, 16^{00}, SEM 101 C

1. From Classical to Quantum Dynamics

1.1 Classical Mechanics

Newton's Second Law:

"Mutationem motus proportionalem esse vi motrici impressae, et fieri secundum lineam rectam qua vis illa imprimitur"

$$\vec{F} = m \cdot \vec{a} = m\dot{\vec{v}} = m\ddot{\vec{q}}$$

Notation: $F = m \cdot a = m\ddot{q}$ (no "$\rightarrow$")

Definition of momentum p

$$p = m\dot{q}$$ (q... position, $\dot{q}$... velocity, $\ddot{q}$... acceleration)

Assume F... force field, $F = -\nabla V(q)$

$$\dot{q} = \frac{p}{m}$$
$$\dot{p} = -\nabla V(q)$$

Define Hamiltonian

$$H(q,p) = T(p) + V(q), \quad T(p) = \frac{|p|^2}{2m} \rightsquigarrow$$

$$\dot{q} = \frac{\partial H}{\partial p}(q,p)$$
$$\dot{p} = -\frac{\partial H}{\partial q}(q,p)$$

Remark: Straight forward extension to f particles

1.2 Conserved Quantities (of the exact flow)

Consider a Hamiltonian system

$$\begin{aligned} \dot{p}(t) &= -H_q(p,q) \\ \dot{q}(t) &= H_p(p,q) \end{aligned} \quad :\Longleftrightarrow: \quad \dot{y}(t) = F(y(t)) \qquad (1)$$

A "<u>first integral</u>" is a function $I(y)$ s.t.

$$I'(y)\,F(y) = 0$$

for all functions y. In particular, this implies

$$I(y(t)) \equiv \text{const} \quad \forall \text{ solutions } y(t) \text{ of } (1)$$

Also called "<u>invariant</u>", "<u>conserved quantity</u>", "<u>constant of motion</u>"

For a Hamiltonian system: H is conserved:

$$\frac{d}{dt} H(p(t), q(t)) = \frac{\partial H}{\partial p}\dot{p} + \frac{\partial H}{\partial q}\dot{q} = H_p(-H_q) + H_q H_p = 0$$

1.3 Ex: <u>Molecular Dynamics</u>

Consider a system of N particles interacting pairwise with potential forces which depend on the distances of the particles $\rightsquigarrow$ Hamiltonian system with

$$H(p,q) = \frac{1}{2}\sum_{i=1}^{N} \frac{1}{m_i} p_i^T p_i + \sum_{i=2}^{N}\sum_{j=1}^{i-1} V_{ij}(\| q_i - q_j \|)$$

q_i ... position of i-th particle

p_i ... momentum – " –

V_{ij} ... interaction potential

Equations of Motion

$$\dot{q}_i = \frac{1}{m_i} p_i$$

$$\dot{p}_i = \sum_{j=1}^{N} v_{ij} (q_i - q_j) \quad , v_{ij} = v_{ji} = - V'_{ij}(r_{ij}) / r_{ij} ,$$

$$r_{ij} := \| q_i - q_j \| , \; v_{ii} = 0$$

Linear Momentum $p := \sum_{i=1}^{N} p_i$

is conserved:

$$\frac{d}{dt} \sum_{i=1}^{N} p_i = \sum_{i=1}^{N} \sum_{j=1}^{N} v_{ij} (q_i - q_j) = 0$$

Angular Momentum $L := \sum_{i=1}^{N} q_i \times p_i$

is conserved:

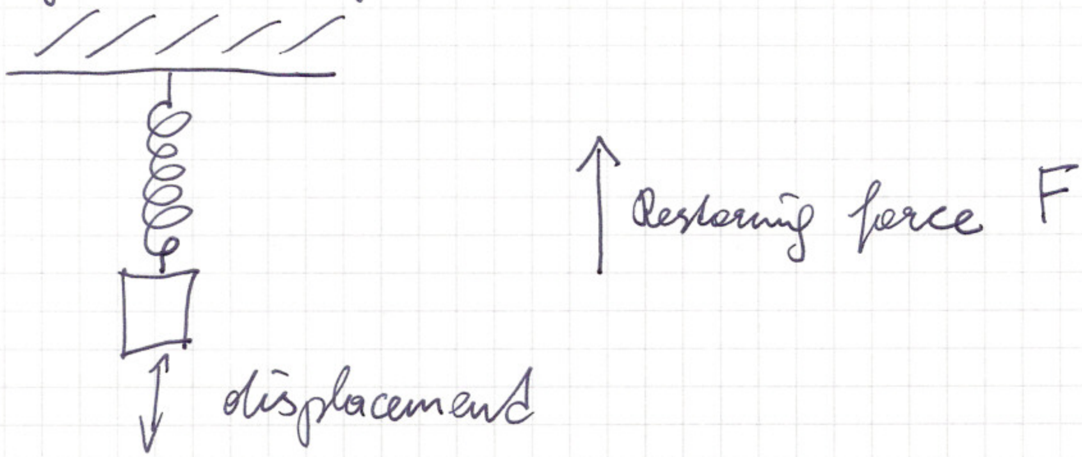
$$\frac{d}{dt} \sum_{i=1}^{N} q_i \times p_i = \underbrace{\sum_{i=1}^{N} \frac{1}{m_i} p_i \times p_i}_{= 0} + \sum_{i=1}^{N} \sum_{j=1}^{N} q_i \times v_{ij} (q_i - q_j)$$

$$= - \sum_{i=1}^{N} \sum_{j=1}^{N} q_i \times (v_{ij} q_j) = 0$$

since $q_i \times q_i = 0$, $q_i \times q_j = - q_j \times q_i$

1.4 Ex: Classical Harmonic Oscillator

Spring-Mass system



Hooke's law: Restoring force proportional to displacement, i.e.

$$F = -x$$

Newton's second law $\quad F = ma = m\ddot{x} \quad \rightsquigarrow$

$$m\ddot{x} + x = 0$$

First order formulation

$$\dot{u} = v = H_v(u,v) = \frac{\partial H}{\partial v}(u,v)$$

$$\dot{v} = -\frac{1}{m}u = -H_u(u,v) = -\frac{\partial H}{\partial u}(u,v),$$

$$H(u,v) = \frac{1}{2}\left(\frac{1}{m}u^2 + v^2\right)$$

Recall: Hamiltonian is conserved!

Remark: Exact solution $x(t) = A \cdot \sin\left(\sqrt{\frac{1}{m}}\, t + \delta\right)$

1.5 "Geometric Numerical Integration"

Numerical solution method which preserves structural properties of the exact flow, e.g. conserves invariants

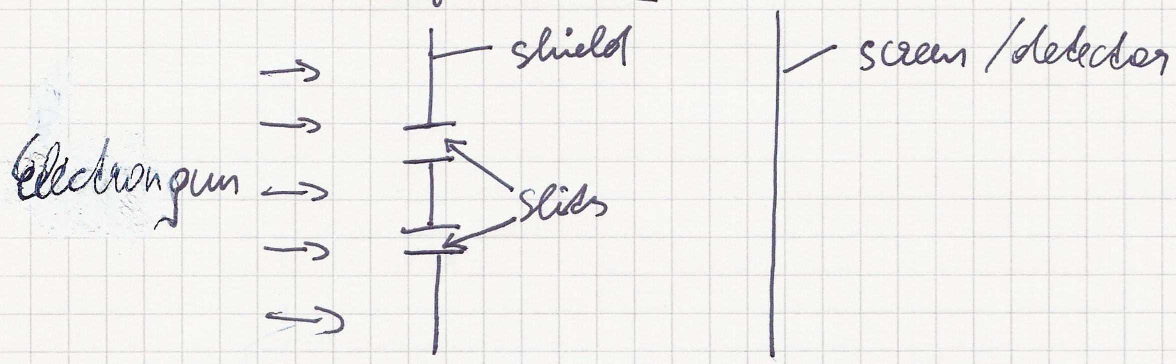
<u>Thm</u>: All explicit & implicit Runge-Kutta methods conserve linear invariants, e.g. <u>linear momentum</u>

<u>Thm</u>: <u>Gauss methods</u> (collocation at Gaussian points, a subset of implicit RK methods) conserve quadratic invariants, e.g. <u>angular momentum</u>

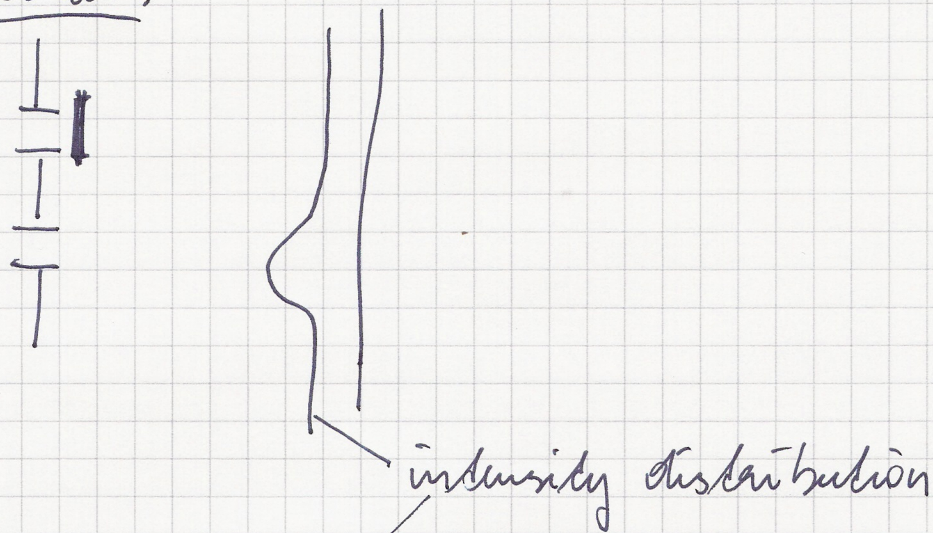
<u>Proofs</u>: See [8 , p. 95, Thm. 1.5] and [8 , p. 97, Thm. 2.1]

1.6 Quantum Dynamics

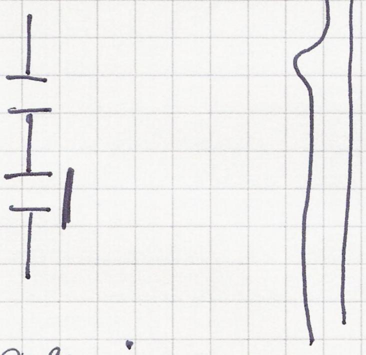
Double Slit Experiment



First slit blocked:

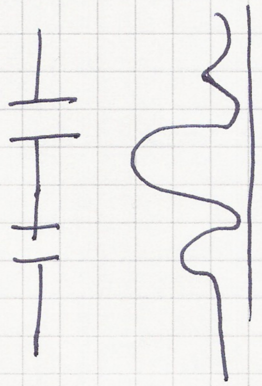


Second slit blocked:



Both slits open:

Interference!



Conclusions from double-slit experiment:

1.) Matter behaves in a random way

2.) Matter exhibits wave-like properties

In quantum mechanics, the state of a particle is described by a complex-valued function

$$\psi = \psi(x,t) \quad , x \in \mathbb{R}^3, \ t \in \mathbb{R}$$

"<u>wave function</u>"

From the properties above, ψ should satisfy:

1.) $|\psi(\cdot,t)|^2$ is a probability distribution for the particle's position, i.e. probability that particle is in a region $\Omega \subseteq \mathbb{R}^3$ is

$$\int_\Omega |\psi(x,t)|^2 \, dx$$

Normalization for probability distribution:

$$\int_{\mathbb{R}^3} |\psi(x,t)|^2 \, dx = 1$$

2.) ψ satisfies some type of wave equation

Further physically sensible properties:

3.) <u>Causality</u>: The initial state $\psi(\cdot,t_0)$ should determine the state $\psi(\cdot,t)$ $\forall \, t > t_0$

4.) <u>Superposition principle</u>: If ψ and ϕ are evolutions of states, then $\alpha\psi + \beta\phi$ (α, β constants) should also describe the evolution of a state

5.) <u>Correspondence principle</u>: In "every day situation" (macroscopic systems), quantum mechanics should be close to classical mechanics

<u>Heuristics for derivation of TDSE</u>

3.) $\Rightarrow$ DE which is first order in time, $\dot{\psi} = A\psi$

4.) $\Rightarrow$ A ... linear operator

<u>Recall classical mechanics</u>

S ... classical action ("action" describes evolution of a physical system over time)

Hamilton-Jacobi equation

$$\dot{S} = -H(x, \nabla_x S) \qquad (1)$$

with, $H(q,p) = \frac{|p|^2}{2m} + V(q)$

This is a fundamental equation of classical mechanics.

Ansatz for the solution of the governing equation of <u>wave mechanics</u> (whose form we are seeking)

$$\psi(x,t) = a(x,t)e^{iS(x,t)/\hbar} \qquad (2)$$

where S satisfies classical mechanics (1)

S is the <u>phase</u> of the wave. $\hbar \ll 1$ ... Planck's constant $\hbar = 1{,}0547162853 \cdot 10^{-34}$ Js

With ansatz (2):

$$i\hbar\dot\psi = i\hbar\left[\dot a\, e^{iS(x,t)/\hbar} + a e^{iS(x,t)/\hbar}\cdot\frac{i}{\hbar}\dot S\right] =$$

$$= i\hbar\dot a e^{iS/\hbar} - a e^{iS(x,t)/\hbar}\left(-\frac{|\nabla_x S|^2}{2m} - V(x)\right)$$

$$= i\hbar\dot a e^{iS/\hbar} + \cancel{a e^{iS/\hbar}\frac{|\nabla S|^2}{2m}} + \cancel{a e^{iS/\hbar} V}$$

$$\nabla\psi = \nabla a\, e^{iS/\hbar} + \frac{i}{\hbar} a e^{iS/\hbar}\nabla S$$

$$\Delta\psi = \Delta a e^{iS/\hbar} + \nabla a \frac{i}{\hbar} e^{iS/\hbar}\cdot\nabla S + \frac{i}{\hbar}\nabla a e^{iS/\hbar}\cdot\nabla S -$$

$$- \frac{1}{\hbar^2} a e^{iS/\hbar}|\nabla S|^2 + \frac{i}{\hbar} a e^{iS/\hbar}\Delta S$$

$$-\frac{\hbar^2}{2m}\Delta\psi + V\psi = -\frac{\hbar^2}{2m}(\Delta a)e^{iS/\hbar} - \frac{i\hbar}{2m}(\nabla a)e^{iS/\hbar}\cdot\nabla S +$$

$$+ \cancel{\frac{1}{2m} a e^{iS/\hbar}|\nabla S|^2} - \frac{i\hbar}{2m} a e^{iS/\hbar}\Delta S + \cancel{V a e^{iS/\hbar}}$$

$$\underbrace{i\hbar\dot\psi}_{O(1)} + \underbrace{\frac{\hbar^2}{2m}\Delta\psi}_{O(1)} - \underbrace{V\psi}_{O(1)} = \underbrace{i\hbar\dot a e^{iS/\hbar}}_{O(\hbar)} + \underbrace{\frac{\hbar^2}{2m}(\Delta a)e^{iS/\hbar}}_{O(\hbar^2)} + \underbrace{\frac{i\hbar}{m}e^{iS/\hbar}(\nabla a)\cdot(\nabla S)}_{O(\hbar)}$$

$$+ \underbrace{\frac{i\hbar}{2m} a e^{iS/\hbar}\Delta S}_{O(\hbar)}$$

Leading order in $\hbar$ (assuming S, a and their derivatives are $O(1)$)

$$\boxed{i\hbar\dot\psi = -\frac{\hbar^2}{2m}\Delta\psi + V\psi}$$ ... "time-dependent Schrödinger equation"

<u>Atomic units</u>: Rescaling, such that

$\hbar \equiv 1$, elementary charge $e \equiv 1$,
electron mass $m \equiv 1$, Bohr radius of hydrogen atom $a \equiv 1$, i.e. $x \leftarrow x\sqrt{\frac{m}{\hbar}}$ ↝

$$\boxed{i\dot\psi = -\frac{1}{2}\Delta\psi + V\psi} =: H\psi$$

mass: 1 au[mass] = $9.10953 \cdot 10^{-31}$ kg
length: 1 Bohr = $5.28446 \cdot 10^{-11}$ m
time: 1 au[time] = $2.41220 \cdot 10^{-17}$ s
energy: 1 Hartree = $4.37129 \cdot 10^{-18}$ J

Atomic units;

Mass: $1\,\mathrm{au}[\mathrm{mass}] = m = 9.10953 \cdot 10^{-31}\,\mathrm{kg}$

Length: $1\,\mathrm{Bohr} = \frac{\hbar^2}{me^2} = 5.28446 \cdot 10^{-11}\,\mathrm{m}$

Time: $1\,\mathrm{au}[\mathrm{time}] = \hbar^3/me^4 =$
$= 2.41220 \cdot 10^{-17}\,\mathrm{s}$

Energy: $1\,\mathrm{Hartree} = me^4/\hbar^2 =$
$= 4.37189 \cdot 10^{-18}\,\mathrm{J}$