Supplemental Material for MD computer experiment

at the Advanced Lab in Physical Chemistry

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Contents

§1   Remote access of lab computers

1.1   TAU Computation Center help-desk pages

1.1.1   UNIX

http://www.tau.ac.il/cc/helpdesk/unix/unix.html

¶1.1.1.1   Secure shell `-- ssh`

`ssh USER@HOST`

Log in to HOST as USER. Type `exit` to log out and return to the terminal to the local shell.

For example, to log in to host "`orenstein101-00`" as "`stud1`"

```
ssh stud1@orenstein101-00
```

¶1.1.1.2   Secure copy – `scp`

```
scp file1 file2 ...  USER@HOST:PATH
```

Copy files from local directory to directory PATH on HOST, relative to USER's home directory on HOST.

For example, to copy the file "`/home/inon/data/output.txt`" to the *preexisting* directory "`md`" of user "inon" on the host "gp":

```
scp ~/data/output.txt inon@gp:md/
```

1.1.2   SSL via VPN

`http://www.tau.ac.il/cc/helpdesk/communication/sslvpn/sslvpn.html`

1.2   Ethernet IP and domain names

- To get the host name, type "`echo $HOSTNAME`".

- To get the ethernet (eth0) IP, type " `/sbin/ifconfig -a | grep "132.66.144." --color`".

- To get the domain name pointer, type "`host <IP>`".

host name	OS	eth0 IP	domain name pointer
localhost.localdomain	CentOS	132.66.144.51	orenstein101-00.tau.ac.il
studentlab	RHEL 7	132.66.144.97	–

1.3   Logging in via "gate"

From any ssh terminal:

```
# ssh <TAU_USERNAME>@gate.tau.ac.il
```

```
Host key not found from the list of known hosts.  !!  If host key is new or changed,
ssh1 protocol is vulnerable to an !!  attack known as false-split, which makes it relativel
easy to !!  hijack the connection without the attack being detected.  It is !!  highly
advisable to turn StrictHostKeyChecking to "yes" and !!  manually copy host keys to known_h
Are you sure you want to continue connecting (yes/no)?
```

```
# yes
```

```
Host 'gate' added to the list of known hosts.

TAU_USERNAME@gate's password:

# <TAU_PASSWORD>

Welcome to gate.

The following commands can be used:  telnet, ssh, ssh1, ssh2, rlogin.

(gate)>ssh stud1@orenstein101-00

stud1@orenstein101-00's password:

# alpc-md

\[stud1@localhost ~]$ \
```

conversely,

```
(gate)>ssh stud1@132.66.144.97

stud1@132.66.144.97's password:

# alpc-md

[stud1@studentlab stud1]$
```

§2   Credits

1. Professor Abraham Nitzan

2. Dr. Israel Schek

3. Joel Calev

4. Dr. Hani Yaakobi

5. Dr. Jasmine Meroz

6. Tal Kachman

7. Inon Sharony

Part I

Stochastic simulation

§3   Central Limit Theorem

We define the residual with respect to some realization of a random variable, r_j, and the first moment of the distribution of that variable, M_1:

$$\Delta r_j \equiv r_j - M_1$$

and the average over n samples is

$$\frac{1}{n} \sum_{j=1}^{n} \Delta r_j \equiv \langle \Delta r \rangle_n = \langle r - M_1 \rangle_n = \langle r \rangle_n - M_1$$

the relative error is

$$\eta_n \equiv \frac{\langle r \rangle_n - M_1}{M_1} = \frac{\langle \Delta r \rangle_n}{M_1}$$

The central limit theorem (CLT) states that for any set of samples $\{r_j\}$ which are independently generated from a distribution which is identical for all the $\{r_j\}$, and is known to have some finite mean (M_1) and variance $\left(\sigma^2 \equiv M_2 - M_1^2\right)$, **the set of *averages* of samples taken from that distributions should be distributed normally**:

$$\lim_{n \to \infty} \sqrt{n} \left(\frac{1}{n} \sum_{j=1}^{n} (r_j - M_1) \right) = \lim_{n \to \infty} \sqrt{n} \langle \Delta r \rangle_n \sim N \left(\mu = 0, \sigma = \sqrt{M_2 - M_1^2} \right)$$

meaning that the variable $X \equiv \lim_{n \to \infty} \sqrt{n} \langle \Delta r \rangle_n$ is normally distributed with zero mean and variance $M_2 - M_1^2$. We can also define the variable Y, such that

$$Y \equiv \lim_{n \to \infty} \frac{\langle \Delta r \rangle_n}{\sqrt{M_2 - M_1^2}} \sim N \left(0, \frac{1}{\sqrt{n}} \right)$$

i.e. $Y \equiv \lim_{n \to \infty} \langle \Delta r \rangle_n / \sqrt{M_2 - M_1^2}$ is distributed according to the normal distribution with a standard deviation that decreases as the inverse square root of the sample size: $\sigma = \frac{1}{\sqrt{N}}$.

We therefore expect that a sample of given size, n, of averages of the variables $\{r_j\}$ will be distributed normally with mean M_1 and standard deviation $\sqrt{\left(M_2 - M_1^2\right)/n}$. Note that as n tends to infinity, the average of averages tends to M_1 with ever decreasing deviation, so that in the limit $n \to \infty$ the average of averages is

M_1 with probability 1. Note that for finite n, this convergence is not necessarily monotonous.

and we can write Welch's t-test as

$$t_n = \frac{\left| \langle r \rangle_N - M_1 \right|}{\sqrt{\frac{\langle r^2 \rangle_n - \langle r \rangle_n^2}{n} + \frac{M_2 - M_1^2}{n}}}$$

This is a measure of the accuracy of the measurement. We expect $\lim_{n \to \infty} t_n = 1$.

- If $t > 1$ we say the measurement yields lower accuracy (and higher precision) than was expected.

- If $t < 1$ we say the measurement yields lower precision (and higher accuracy) than was expected.

3.1 Distribution of higher moments

The law of large numbers also requires higher moments to converge to those of the generating distribution, but there is no CLT which restricts the rate of convergence (as opposed to the inverse-square-root law for the first moment). We can say, however, that higher moments generally converge more slowly.

§4 Advanced terms in probability

4.1 Probability generating function

For a discrete random variable n, which can take any of the values of the non-negative integers ($n \in \{0, 1, \ldots, \infty\}$), the probability generating function $G_n(z)$ is

$$G_n(z) \quad \equiv \quad \langle z^n \rangle = \sum_{n=0}^{\infty} P(n) z^n$$

And by equating the series expansions of both sides, we get the reverse transform:

$$P(n) = \left[\frac{1}{n!} \frac{d^n}{d^n z} G_n(z) \right]_{z=0}$$

Sometimes the probability generating function, $G_n(z)$, is more concise than the probability mass function[1], $P(n)$. For example:

---

[1]The probability mass function of a discrete variable is the equivalent of the probability density function for a continuous variable.

$$P_{\text{constant}}(n = c) \equiv 1 \quad \Leftrightarrow \quad G_{n=c}(z) = z^c$$

$$P_{\text{binomial}}(n = k, p) \equiv \begin{pmatrix} n \\ k \end{pmatrix} p^k (1-p)^{n-k} \quad \Leftrightarrow \quad G_{B(n=k,p)}(z) = [(1-p)+pz]^k$$

$$P_{\text{Poisson}}(n, \lambda) \equiv \frac{\lambda^n e^{-n}}{n!} \quad \Leftrightarrow \quad G_{\text{Pois}(n,\lambda)}(z) = e^{\lambda(z-1)}$$

4.2   Moment generating function

The moment generating function, $M_x(k)$, of a random variable x is defined as:

$$M_x(k) \equiv \left\langle e^{kx} \right\rangle = \left\langle \sum_{n=0}^{\infty} \frac{k^n}{n!} x^n \right\rangle = 1 + k m_1 + \frac{k^2}{2} m_2 + \ldots + \frac{k^n}{n!} m_n + \ldots$$

by which we can get the n-th moment:

$$m_n \equiv \langle x^n \rangle = \left[\frac{d^n}{dk^n} M_x(k) \right]_{k=0}$$

4.2.1   Probability characteristic function

For a random variable, x, the characteristic function is

$$\varphi_x(k) \equiv \left\langle e^{ikx} \right\rangle = 1 + ik m_1 - \frac{k^2}{2} m_2 + \ldots + i^n \frac{k^n}{n!} m_n + \ldots$$

The characteristic function can also be written in terms of the moment generating function:

$$\varphi_x(k) = M_x(ik)$$

$$m_n \equiv \langle x^n \rangle = \left[\frac{d^n}{dk^n} M_x(k) \right]_{k=0} = \left[\frac{d^n}{dk^n} \varphi_x(-ik) \right]_{k=0} = \left[i^{-n} \frac{d^n}{dk^n} \varphi_x(k) \right]_{k=0}$$

4.3   Cumulant generating function

The cumulants, κ_n, of a random variable, x, are an alternative way to describe the distribution (sometimes better than using moments), and defined via the cumulant generating function:

$$g_x(k) \equiv \ln\left(\left\langle e^{kx}\right\rangle\right) = \sum_{n=1}^{\infty}\frac{k^n}{n!}\kappa_n$$

$$M_x(k) = \left\langle e^{kx}\right\rangle = e^{g_x(k)}$$

$$
\begin{aligned}
g_x(k) = \ln\left(\left\langle e^{kx}\right\rangle\right) &= -\sum_{n=1}^{\infty}\frac{1}{n}\left(1-\left\langle e^{kx}\right\rangle\right)^n \\
&= -\sum_{n=1}^{\infty}\frac{1}{n}\left(-\sum_{j=1}^{\infty}\frac{k^j}{j!}m_j\right)^n \\
&= m_1 k + \left(m_2 - m_1^2\right)\frac{k^2}{2} + \left(m_3 - 3m_2 m_1 + 2m_1^3\right)\frac{k^3}{6} + \ldots \\
\kappa_1 \equiv \mu &\equiv m_1 \equiv \langle x\rangle_c = \langle x\rangle \\
\kappa_2 \equiv \sigma^2 &\equiv m_2 - m_1^2 \equiv \left\langle x^2\right\rangle_c \neq \left\langle x^2\right\rangle = m_2 \\
&\vdots \\
\kappa_n &= \left[\frac{d^n}{dk^n}g(k)\right]_{k=0} \equiv \langle x^n\rangle_c \neq \langle x^n\rangle = m_n
\end{aligned}
$$

Note that, for example for the second power, the cumulant (the variance of a random variable) sometimes carries information of greater physical meaning than the moment (the RMS value of that variable).

The second characteristic function is that of the cumulants instead of that of the moments:

$$h_x(k) \equiv g_k(-ik) = \sum_{n=1}^{\infty}\frac{k^n}{n!}\kappa_n = \ln\left(\left\langle e^{ikx}\right\rangle\right) = ik\mu - \frac{k^2}{2}\sigma^2 + \ldots + \frac{(ik)^n}{n!}\kappa_n + \ldots$$

4.3.1   Cumulants and moments

$$
\begin{aligned}
\sum_{n=0}^{\infty}\frac{k^n}{n!}m^n = M_x(k) &= e^{g(k)} = \exp\left(\sum_{n=1}^{\infty}\frac{k^n}{n!}\kappa_n\right) \\
\kappa_n &= m_n - \sum_{k=1}^{n-1}\binom{n-1}{k-1}\kappa_k m_{n-k}
\end{aligned}
$$

4.4 Physical significance

While the probability of a certain event occurring (zeroth moment), or any higher moment, can be measured indirectly in a lab, the probability density is not physically accessible. The best we can do is draw histograms and take the limit of an ever smaller bin size.

A distribution for which some moment is ill defined, mathematically, will still yield a value for the laboratory measurement of such a variable, but the mathematical regression from probability to density might not be valid.

§5 Choosing time-step length and simulation duration

5.1 Sampling rate

From the Nyquist-Shannon sampling theorem, we know that in order to correctly depict the time evolution of our system, we need to make sure our sampling frequency is higher than the system Nyquist frequency (twice the highest intrinsic frequency in the system).

$$1/dt > 2\max\left(\{v_i\}\right)$$

Conversely, the time between consecutive samples should be shorter than any intrinsic time scale in the system:

$$dt < \frac{1}{2}\min\left(\{\tau_i\}\right)$$

An alternative approach, in order to keep the time-step big enough to manage long simulation durations (e.g. if there are unavoidably large differences between intrinsic system time-scales), is to remove higher frequencies from the system. This can be done prior to the simulation, for instance by grouping smaller components of the system (usually using constraints or unified atoms). If this is done after the simulation, it is called anti-aliasing.

5.2 Noise

In case our system is involved in some random processes, this is even worse. From the central limit theorem, we know that the S/N ratio of a random signal improves (i.e. increases) as $\sqrt{N}$, where N is the number of

measurement samples. Hence, in order to get an order of magnitude signal to noise ratio (S/N or SNR), we need $\sqrt{N} = 10 \Rightarrow N = 100$ samples. Therefore,

$$1/dt \geq 100 \times \max \left(\{v_i\}_{i \in \text{random processes}} \right)$$

5.3   Coarse graining

Given a signal with exponential decay life-time, γ, and oscillatory noise with a high frequency, Ω:

$$f(t) = \cos(\Omega t) \exp(-\gamma t)$$

If we can find a time length, τ, such that $\Omega^{-1} \ll \tau \ll \gamma^{-1}$,

$$
\begin{aligned}
\widetilde{f_\tau}(t) &\equiv \frac{1}{\tau} \int_{t-\tau/2}^{t+\tau/2} dt' \, f(t') \\
&= \frac{1}{\tau} \int_{t-\tau/2}^{t+\tau/2} dt' \cos(\Omega t') \exp(-\gamma t') \\
\lim_{\gamma/\Omega \to 0} \widetilde{f_\tau}(t) &= \lim_{\gamma/\Omega \to 0} \frac{1}{\tau} \int_{t-\tau/2}^{t+\tau/2} dt' \cos(\Omega t') \times \int_{t-\tau/2}^{t+\tau/2} dt' \exp(-\gamma t') \\
&= \lim_{\gamma/\Omega \to 0} \frac{1}{\tau} \left[\frac{\sin(\Omega t')}{\Omega} \right]_{t-\tau/2}^{t+\tau/2} \times \left[\frac{\exp(-\gamma t')}{-\gamma} \right]_{t-\tau/2}^{t+\tau/2} \\
&= \lim_{\gamma/\Omega \to 0} \frac{1}{\tau} \left[\delta(\Omega t) \right]_{t-\tau/2}^{t+\tau/2} \times \left[\frac{\exp(-\gamma t')}{-\gamma} \right]_{t-\tau/2}^{t+\tau/2} \\
&= \frac{1}{\tau} \frac{\exp(-\gamma t)\exp(-\gamma\tau/2) - \exp(-\gamma t)\exp(\gamma\tau/2)}{-\gamma} \\
&= \frac{\sin(\gamma\tau)}{\gamma\tau} \exp(-\gamma t) \\
\lim_{\gamma\tau \to 0} \lim_{\gamma/\Omega \to 0} \widetilde{f_\tau}(t) &= \exp(-\gamma t)
\end{aligned}
$$

Here we used the $\text{sinc}(x)$ representation of the Dirac delta: $\lim_{x \to 0} \sin(x)/x = \delta(x)$, but this principle can be applied to any suitable signal, $f(t)$.

5.3.1   Fourier transform and low band pass filtering

$$
\begin{aligned}
\hat{f}_t(\omega) &\equiv \frac{1}{2\pi} \int_0^\infty f(t) e^{i\omega t} dt \\
&\propto \delta(\Omega \pm \omega) + \delta(\omega - i\gamma)
\end{aligned}
$$

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Low band pass filter with frequency $\omega_0 : (\gamma < \omega_0 < \Omega)$

$$
\begin{aligned}
\hat{f}_t\left(\omega < \omega_0\right) &= \delta\left(\omega - i\gamma\right) \\
f_{\omega < \omega_0}\left(t\right) &= \int_{-\infty}^{\infty} \delta\left(\omega - i\gamma\right) e^{-i\omega t}\, dt \\
&= \exp\left(-\gamma t\right)
\end{aligned}
$$

Part II

Numerical solution of Newton's equations of motion

§6 Error propagation in the velocity Verlet algorithm

6.1 Local error

$$
\begin{aligned}
x\left(t + dt\right) &= x\left(t\right) + \dot{x}\left(t\right)\Delta t + \frac{1}{2}\ddot{x}\left(t\right)\left(\Delta t\right)^2 + O\left[\left(\Delta t\right)^4\right] \\
\dot{x}\left(t + dt\right) &= \dot{x}\left(t\right) + \frac{1}{2}\left\{\ddot{x}\left(t\right) + \ddot{x}\left(t + \Delta t\right)\right\}\left(\Delta t\right)^2 + O\left[\left(\Delta t\right)^2\right] \\
E &= \frac{m}{2}\dot{x}^2 + \frac{k}{2}x^2 \\
\Delta E &\gtrsim \sqrt{\left[\left(\Delta t\right)^2\right]^2 + \left[\left(\Delta t\right)^2\right]^2} \sim O\left[\left(\Delta t\right)^2\right]
\end{aligned}
$$

6.2 Global error

$$
\lim_{n \to \infty} \Delta x\left(t + n\Delta t\right) \sim \lim_{n \to \infty} \Delta \dot{x}\left(t + n\Delta t\right) \sim O\left[\left(\Delta t\right)^2\right]
$$

$$
\begin{aligned}
\Delta E &\sim O\left[\left(\Delta t\right)^2\right] \\
\frac{\Delta E\left(\Delta t\right)}{\Delta E\left(\sqrt{10}\Delta t\right)} &\sim \frac{1}{10}
\end{aligned}
$$

to get an order of magnitude more accurate energy, the time step needs to be shortened by a factor of more

than 3.

6.3   Example: Harmonic Oscillator

$$H = \frac{m}{2}\dot{x}^2 + \frac{m}{2}\omega_0^2 x^2 \Rightarrow x(t) \propto \exp(i\omega_0 t)$$

$$dt < t_0/2 = (2\pi/\omega_0)/2 \approx 12.6/\omega_0$$

almost ten samples per oscillation period.

§7   Reduced units

Reduced units, also known as dimensionless quantities, are used to make sure we work with quantities as close as possible to 1. Working with number which are very large, very small, or with a mixture of large and small numbers is a sure way to get numerical errors. The standard single precision variables the computer works with keep numbers with up to 7 significant figures (in floating-point decimal notation). Therefore, an operation such as addition or subtraction of two numbers which are more than 7 orders of magnitude apart will fail, as the result of the operation is smaller than machine error allows:

$$(a + \varepsilon) - a \overset{?}{=} \varepsilon$$

$$(1000.000 + 0.001499999) - 1000.000 = (1000.001) - 1000.000 = 0.001$$

in the previous example, we've incurred a relative error of almost 50%, which is completely unacceptable. If we continue adding and subtracting more numbers, the error incurred will only continue to increase.

We now look at examples of reduced units for the classical harmonic oscillator.

7.1   System parameters

Given the oscillator mass (m) and spring constant (k):

$$
\begin{aligned}
m &= m_0 m^* \\
k &= k_0 k^* \\
\omega &= \omega_0 \omega^* = \sqrt{k_0/m_0}\,\omega^* \\
t &= t_0 t^* = (2\pi/\omega_0)\,t^*
\end{aligned}
$$

Note that the mass may be given via the masses of the two particles attached on either end of the spring, in which case we first need to calculate the reduced mass (not related to reduced units):

$$
\mu = \mu_0 \mu^* = \left(\frac{m_1 m_2}{m_1 + m_2} \right) \mu^* = \left(\frac{1}{1/m_1 + 1/m_2} \right) \mu^*
$$

§8   Checks for week 2 program (numeric solution of HO)

8.1   Good coding practice

1. Don't start coding without a plan.

2. Whenever possible, break your code up into smaller subroutines, in order to be able to edit and test each unit independently (unit testing).

3. Make incremental backups.

4. Comment your code as if the next guy to work on it after you will be seven feet tall, weigh three hundred pounds, and have anger management issues.

5. Be able to insert lines anywhere in the code to print variable values to screen (old school debugging).

8.2   Debugging

1. When debugging, set your compiler to output as many debugging symbols and warning messages as possible, and with no optimization flags. Once your work on the code is done, you can compile it again using the highest optimization setting, for performance.

2. Use can use code analysis tools to check your code for memory leaks, and for allocation and CPU bottlenecks.

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8.3 Quality assurance

1. Solve first three time-steps by hand, and compare $r(t)$ and $v(t)$.

2. Numerical limiting cases:

   (a) Energy drift becomes negligible as the time-step is decreased.

   (b) If center of mass motion is subtracted, check that the center of mass momentum becomes negligible as the time-step is decreased.

   (c) Check periodic boundary conditions, if applied.

3. Physical limiting cases and trivial results:

   (a) Parity – time-reversal symmetry (in a microcannonical ensemble): Starting from $x = x(t)$ and setting $v = -v(t)$, after time t we should reach exactly $x(0), v(0)$.

   (b) Thermal equilibrium self-consistency (in a canonical ensemble): The average kinetic energy per degree of freedom should equal the thermal energy, as calculated for the input bath temperature.

§9   Derivation of velocity Verlet algorithm by Trotter decomposition of the Liouville operator

9.1 Liouville dynamics

The complete time differential of a dynamic variable (in quantum mechanics, an operator) which could be directly dependent on time (e.g. an external field) $X(\mathbf{q}, \mathbf{p}, t)$:

$$\frac{d}{dt}X(\mathbf{q}, \mathbf{p}, t) = \frac{\partial X}{\partial \mathbf{q}}\dot{\mathbf{q}} + \frac{\partial X}{\partial \mathbf{p}}\dot{\mathbf{p}} + \frac{\partial X}{\partial t}$$

Using the Hamilton equations,

$$\frac{d}{dt}X(\mathbf{q}, \mathbf{p}, t) = \frac{\partial X}{\partial \mathbf{q}}\frac{\partial H}{\partial \mathbf{p}} - \frac{\partial X}{\partial \mathbf{p}}\frac{\partial H}{\partial \mathbf{q}} + \frac{\partial X}{\partial t}$$

Rewriting using the Poisson brackets

$$\frac{d}{dt}X(\mathbf{q}, \mathbf{p}, t) = \{X, H\} + \frac{\partial X}{\partial t}$$

This is the Liouville equation, which serves as the origin of the equivalent quantum results – the von Neuman equation and the related Ehrenfest theorem (which deals only with the expectation values of the terms in the equation).

We also replace the Poission brackets with the Liouville operator (or Liouvillian),

$$
\begin{aligned}
\frac{d}{dt} X(\mathbf{q}, \mathbf{p}, t) &= i\mathscr{L}X + \frac{\partial X}{\partial t} \\
\mathscr{L}X &\equiv \frac{1}{i}\{X, H\}
\end{aligned}
$$

Thus, for variables which are not independently dependent on time $\left(\frac{\partial}{\partial t}X(\mathbf{q}, \mathbf{p}) = 0\right)$, we get

$$
\frac{d}{dt} X(t) = i\mathscr{L}X(t)
$$

The solution to which is

$$
X(t) = e^{it\mathscr{L}} X(0)
$$

In other words, the operator which serves as the time-propagator is

$$
U(t) = e^{it\mathscr{L}}
$$

in this role it is also known as the generator of time translation, exactly as $e^{a\frac{\partial}{\partial \mathbf{q}}}$ generates a translation of magnitude a in the direction of coordinate $\mathbf{q}$, for some function $f(\mathbf{q})$:

$$
\mathscr{T}_i(a) f(\mathbf{q}) \equiv e^{a\frac{\partial}{\partial \mathbf{q}}} f(\mathbf{q}) = \sum_{n=1}^{\infty} \frac{a^n}{n!} \frac{\partial^n}{\partial q_i^n} f(\mathbf{q}) = f(\mathbf{q} + a)
$$

Where the last equality is due to the equivalence of the Taylor expansions of the quantities on either side of the equal sign.

9.2   Symplectic integration scheme and Trotter decomposition

In order to propagate X in time, we need to apply the time propagation operator U to X:

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$$X\left(t\right) = U\left(t\right)X\left(0\right) = e^{it\mathscr{L}}X\left(0\right) = \exp\left(t\left\{\frac{\partial H}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{q}} - \frac{\partial H}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{p}}\right\}\right)X\left(0\right) = \exp\left(t\left\{i\mathscr{L}_x + i\mathscr{L}_v\right\}\right)X\left(0\right)$$

In order to apply the exponential operator $e^{it\mathscr{L}}$ to X, we split it into a product of exponential operators, $\prod_j e^{it\mathscr{L}_j}$, each of which is practically applicable. In choosing to perform this procedure canonically, some important properties of the Hamiltonian are conserved. This is known as the symplectic integration scheme for reasons to do with issues in symplectic topology beyond the scope of this text[2].

Note, however, that the form e^{A+B} is not simply equal to $e^A e^B$ for A and B which do not commute (e.g. $A \propto \frac{\partial}{\partial \mathbf{q}}, B \propto \frac{\partial}{\partial \mathbf{p}}$). In this case we should use the Baker–Campbell–Hausdorff formula:

$$e^{A+B} = e^A e^B e^{\frac{1}{2}\{A,B\}} e^{\frac{1}{12}\{A,\{A,B\}\}} e^{-\frac{1}{12}\{B,\{A,B\}\}} \ldots$$

Which, in the case where $\{A,B\}$ commutes with both A and B (the commutator is said to be group theoretically "central"), gives the more concise

$$e^{A+B} = e^A e^B e^{\frac{1}{2}\{A,B\}}$$

However, in our case, the commutator is generally not central[3], and we must resort to using either a cut-off of the BCH formula or an approximation of its result. We use the Trotter expansion[4]:

$$e^{A+B} = \lim_{\Delta \to 0}\left(e^{\frac{\Delta}{2}A}e^{\Delta B}e^{\frac{\Delta}{2}A}\right)^{1/\Delta} \approx \left(e^{\frac{\Delta}{2}A}e^{\Delta B}e^{\frac{\Delta}{2}A}\right)^{1/\Delta} e^{O[\Delta^2]}$$

which in our case would read

$$e^{it\{\mathscr{L}_v + \mathscr{L}_x\}} \approx \left(e^{i\frac{\Delta t}{2}\mathscr{L}_v}e^{\Delta t\mathscr{L}_x}e^{i\frac{\Delta t}{2}\mathscr{L}_v}\right)^{1/\Delta} e^{O[\Delta^2]} = \left(e^{-\frac{\Delta t}{2}\frac{\partial H}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{p}}}e^{\Delta t\frac{\partial H}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{q}}}e^{-\frac{\Delta t}{2}\frac{\partial H}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{p}}}\right)^{1/\Delta} e^{O[\Delta^2]}$$

---

[2] For a discussion of canonical transformations and the symplectic condition in Hamiltonian dynamics, see appendix A of Frenkel & Smit.

[3]

$$\frac{\partial}{\partial \mathbf{q}}\left\{\frac{\partial}{\partial \mathbf{q}},\frac{\partial}{\partial \mathbf{p}}\right\} - \left\{\frac{\partial}{\partial \mathbf{q}},\frac{\partial}{\partial \mathbf{p}}\right\}\frac{\partial}{\partial \mathbf{q}} = \frac{\partial}{\partial \mathbf{q}}\left\{\frac{\partial}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{p}} - \frac{\partial}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{q}}\right\} - \left\{\frac{\partial}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{p}} - \frac{\partial}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{q}}\right\}\frac{\partial}{\partial \mathbf{q}}$$

$$= \frac{\partial}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{p}} - \frac{\partial}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{q}} - \frac{\partial}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{q}} + \frac{\partial}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{q}}$$

$$= \frac{\partial^2}{\partial \mathbf{q}^2}\frac{\partial}{\partial \mathbf{p}} - 2\frac{\partial}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{q}} + \frac{\partial}{\partial \mathbf{p}}\frac{\partial^2}{\partial \mathbf{q}^2} \neq 0$$

[4] H. F. Trotter, Proc. Am. Math. Soc 10 , 545 (1959)

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Note that we have changed $\mathscr{L}_x + \mathscr{L}_v$ to $\mathscr{L}_v + \mathscr{L}_x$. The reason for this will be explained shortly, and since addition is commutative, this is always allowed.

Applying this propagation operator to the initial $X(0)$, i.e. starting from $X(\mathbf{q}(0), \mathbf{p}(0))$ and finishing at $X(\mathbf{q}(\Delta t), \mathbf{p}(\Delta t))$, we conceptually see a a series of three operations (operators act in order from right to left):

1. $e^{-\frac{\Delta t}{2}\frac{\partial H}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{p}}} X(\mathbf{q}(0), \mathbf{p}(0)) = e^{\frac{\Delta t}{2}\mathbf{F}(\mathbf{q}(0))\frac{\partial}{\partial \mathbf{p}}} X(\mathbf{q}(0), \mathbf{p}(0)) = X(\mathbf{q}(0), \mathbf{p}(\frac{\Delta t}{2})) \Rightarrow \mathbf{p}(\frac{\Delta t}{2}) = \mathbf{p}(0) + \frac{\Delta t}{2}\mathbf{F}(\mathbf{q}(0))$

   Update the velocity by half a time-step, according to the forces at the beginning of the time-step.

2. $e^{\Delta t\frac{\partial H}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{q}}} X(\mathbf{q}(0), \mathbf{p}(\frac{\Delta t}{2})) = e^{\Delta t\frac{\mathbf{p}(\Delta t/2)}{m}\frac{\partial}{\partial \mathbf{q}}} X(\mathbf{q}(0), \mathbf{p}(\frac{\Delta t}{2})) = X(\mathbf{q}(\Delta t), \mathbf{p}(\frac{\Delta t}{2})) \Rightarrow \mathbf{q}(\Delta t) = \mathbf{q}(0) + \Delta t\,\mathbf{p}(\frac{\Delta t}{2})/m$

   Update the position by a full time-step, according to the velocities at half the time-step.

3. $e^{-\frac{\Delta t}{2}\frac{\partial H}{\partial \mathbf{q}}\frac{\partial}{\partial \mathbf{p}}} X(\mathbf{q}(\Delta t), \mathbf{p}(\frac{\Delta t}{2})) = e^{\frac{\Delta t}{2}\mathbf{F}(\mathbf{q}(\Delta t))\frac{\partial}{\partial \mathbf{p}}} X(\mathbf{q}(\Delta t), \mathbf{p}(\frac{\Delta t}{2})) = X(\mathbf{q}(\Delta t), \mathbf{p}(\Delta t)) \Rightarrow \mathbf{p}(\Delta t) = \mathbf{p}(\frac{\Delta t}{2}) +$
   $\frac{\Delta t}{2}\mathbf{F}(\mathbf{q}(\Delta t)) = \mathbf{p}(0) + \frac{\Delta t}{2}[\mathbf{F}(\mathbf{q}(0)) + \mathbf{F}(\mathbf{q}(\Delta t))]$

   Re-update the velocity by half a time-step, according to the forces at the end of the time-step.

This is the velocity-Verlet algorithm, and we have now finished demonstrating its derivation from the Liouvillian.

The reason we wanted two velocity updating operations and one position updating operation rather than the other way around, is that the higher order derivatives (e.g. velocity) change more quickly over time than the lower derivatives (e.g. position). Therefore, we want more updates to the higher order derivatives.

§10   A result of analytical mechanics: Noether's invariance theorem

10.1   Lagrangian formalism

The action, S, is a functional of the Lagrangian, L:

$$
\begin{aligned}
S[L(q,\dot{q},t)] &\equiv \int L(q(t),\dot{q}(t),t)\,dt \\
L(q,\dot{q},t) &\equiv T(\dot{q}) - V(q,t)
\end{aligned}
$$

- T is the kinetic energy and V is the potential energy.

- A functional maps a function (e.g. $L(q,\dot{q},t)$) to a number (the result of the integral, S, is just a number).

- The generalized coordinate (q) can, in general, be replaced by any number of coordinates, q_i. We'll look at some examples later.

The principle of stationary action (more commonly, though erroneously, known as the principle of least action) states that the trajectory a system will take, $q(t)$, is the one for which the action is stationary, i.e. the functional derivative of the action is zero, $\delta S = 0$. Use of this principle allows us to obtain the equations of motion for the system at hand, known as the Euler-Lagrange equations:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}$$

We can also define p_i, the generalized momentum which is conjugate to the generalized coordinate q_i, and rewrite the Euler-Lagrange equations:

$$\frac{d}{dt}p_i = \frac{\partial L}{\partial q_i}$$
$$p_i \equiv \frac{\partial L}{\partial \dot{q}_i}$$

The Hamiltonian is a defined according to the Legendre transform, $H(q_i, p_i, t) = p_i \cdot \dot{q}_i - L(q_i, \dot{q}_i, t)$, which replaces the use of velocities by the conjugate momenta.

10.2   Noether's invariance theorem

If a system has a continuous symmetry property (i.e. the action has a differentiable symmetry), then there are corresponding quantities whose values are conserved (or constant) throughout the system's motion (i.e. a constant of motion).

It is shown that a translation along the q_i coordinate can be induced using the generator:

$$\mathcal{T}_i(a)f(\mathbf{q}) \equiv e^{a\frac{\partial}{\partial q_i}}f(\mathbf{q}) = \sum_{n=1}^{\infty}\frac{a^n}{n!}\frac{\partial^n}{\partial q_i^n}f(\mathbf{q}) = f(q_1, q_2, \ldots, q_{i-1}, q_i + a, q_{i+1}, \ldots q_N)$$

An infinitesimal perturbation in the system coordinates can be generated using only the first order of the expansion:

$$\lim_{\delta q_i \to 0}f(q_1, \ldots, q_i + \delta q_i, \ldots q_N) = \lim_{\delta q_i \to 0}\left(1 + \delta q_i\frac{\partial}{\partial q_i} + O\left[(\delta q_i)^2\right]\right)f(\mathbf{q})$$

Given an infinitesimal perturbation in the system coordinates and time which keeps the action stationary is defined according to[5],

---

[5]In general, this could be a simultaneous change in any number of the system generalized coordinates, or a mixture of spacial

$$
\begin{aligned}
t &\mapsto t + \delta t \\
q_i &\mapsto q_i + \delta q_i \\
0 = \delta S &= S\left[L\left(q_i + \delta q_i, t + \delta t\right)\right] - S\left[L\left(q_i, t\right)\right]
\end{aligned}
$$

we write these changes in terms of some uniform infinitesimal parameter, ε, and other terms relevant to the particular coordinates involved:

$$
\begin{aligned}
\delta t &= \varepsilon T \\
\delta q_i &= \varepsilon Q_i
\end{aligned}
$$

and the constant of motion is

$$
\left(p_i \cdot \dot{q}_i - L\right) T - p_i \cdot Q_i
$$

10.3 Some examples

10.3.1 A free particle

¶10.3.1.1 Definition of the system Lagrangian

$$
\begin{aligned}
q_i^{\text{Cartersian}} &= \{x, y, z\} \\
T\left(\dot{x}, \dot{y}, \dot{z}\right) &= \frac{1}{2} m\dot{x}^2 + \frac{1}{2} m\dot{y}^2 + \frac{1}{2} m\dot{z}^2 \\
L &= T\left(\dot{x}, \dot{y}, \dot{z}\right)
\end{aligned}
$$

and temporal coordinates.

¶10.3.1.2   Euler-Lagrange equations of motion

$$
\begin{aligned}
\frac{\partial L}{\partial x} &= 0 \\
\frac{\partial L}{\partial \dot{x}} &= \frac{\partial T}{\partial \dot{x}} = m\dot{x} \equiv p_x
\end{aligned}
$$

$$
\begin{aligned}
\frac{d}{dt}p_i &= \frac{\partial L}{\partial q_i} = 0 \\
\frac{d}{dt}\mathbf{p} = m\frac{d^2}{dt^2}\mathbf{r} &= 0
\end{aligned}
$$

¶10.3.1.3   Continuous symmetries of the action and the corresponding constants of motion

1. Since the time variable does not appear explicitly in the Lagrangian, the action is invariant to time translation: $S[L(t)] = S[L(t + \delta t)]$

$$
\begin{aligned}
T &= 1 \\
\mathbf{Q} &= 0 \\
(\mathbf{p}\cdot\dot{\mathbf{q}} - L)T - \mathbf{p}\cdot\mathbf{Q} &= (\mathbf{p}\cdot\dot{\mathbf{q}} - L) \equiv H
\end{aligned}
$$

   i.e. energy conservation.

2. Since the coordinate do not appear explicitly in the Lagrangian (though their time derivatives do), the action is invariant to spacial translation: $S[L(q_i)] = S[L(q_i + \delta q_i)]$

$$
\begin{aligned}
T &= 0 \\
\mathbf{Q} &= 1 \\
(\mathbf{p}\cdot\dot{\mathbf{q}} - L)T - \mathbf{p}\cdot\mathbf{Q} &= -\mathbf{p}
\end{aligned}
$$

   i.e. linear momentum conservation.

3. The same is true in cylindrical coordinates: $S[r, \theta, z] = S[r, \theta + \delta\theta, z]$

$$
\begin{aligned}
\mathbf{r} = (r, \theta, z) &\mapsto (r, \theta + \delta\theta, z) = \mathbf{r} + \delta\theta \mathbf{e}_\theta = \mathbf{r} + \delta\theta \left(\mathbf{e}_z \times \mathbf{r}\right) \\
T &= 0 \\
\mathbf{Q} &= \mathbf{e}_z \times \mathbf{r} \\
(\mathbf{p} \cdot \dot{\mathbf{q}} - L)T - \mathbf{p} \cdot \mathbf{Q} &= -\mathbf{p} \cdot (\mathbf{e}_z \times \mathbf{r}) = -\mathbf{e}_z \cdot (\mathbf{r} \times \mathbf{p}) \equiv -\mathbf{e}_z \cdot \mathbf{L}
\end{aligned}
$$

where $\mathbf{e}_\theta$ is the unit vector in the tangential direction, and $\mathbf{e}_z$ is the unit vector in the z direction.

We have thus shown that angular momentum, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, in the direction defined by a rotation around the z-axis is also conserved.

4. Note that if time is included with the coordinates as space-time $(q_0 = t)$, as we do in relativistic problems, the previous results give conservation of the four dimensional stress-energy matrix.

10.3.2 A single particle in an external potential

¶10.3.2.1 Definition of the system Lagrangian

$$
\begin{aligned}
q_i^{\text{Cartersian}} &= \{x, y, z\} \\
T(\dot{x}, \dot{y}, \dot{z}) &= \frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\dot{y}^2 + \frac{1}{2}m\dot{z}^2 \\
L &= T(\dot{x}, \dot{y}, \dot{z}) - V(x, y, z)
\end{aligned}
$$

¶10.3.2.2 Euler-Lagrange equations of motion

$$
\begin{aligned}
\frac{\partial L}{\partial x} &= \frac{\partial V}{\partial x} \equiv -F_x \\
\frac{\partial L}{\partial \dot{x}} &= \frac{\partial T}{\partial \dot{x}} = m\dot{x} \equiv p_x
\end{aligned}
$$

$$\frac{d}{dt}p_i = \frac{\partial L}{\partial q_i} = -F_i$$

$$\frac{d}{dt}\mathbf{p} = m\frac{d^2}{dt^2}\mathbf{r} = \mathbf{F}$$

¶10.3.2.3 Continuous symmetries of the action and the corresponding constants of motion

10.3.3 Two particles

$q_i^{\text{Hylleraas}} = \{\mathbf{r}_1 + \mathbf{r}_2, \mathbf{r}_1 - \mathbf{r}_2, |\mathbf{r}_1 - \mathbf{r}_2|\}$

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