Chapter 1

Basics

We start with some important background material in classical and quantum mechanics.

1.1 Classical mechanics

Lagrangian mechanics

Compared to Newtonian mechanics, Lagrangian mechanics has the advantage that we can use arbitrary sets of generalised coordinates to describe our system and our fundamental equations always have the same form. Let us denote the coordinates by $q_1, q_2, \ldots, q_n$ and assemble them into a vector $\boldsymbol{q}$. Then the motion of the system is described by the function $\boldsymbol{q}(t)$. We now need the Lagrangian which the difference of the kinetic energy T and the potential energy U expressed as a function of $\boldsymbol{q}$, $\dot{\boldsymbol{q}}$, and time,

$$L(\boldsymbol{q}, \dot{\boldsymbol{q}}, t) = T - U.$$

Then the equations of motion are

$$\frac{\partial L}{\partial q_\alpha} = \frac{d}{dt}\frac{\partial L}{\partial \dot{q}_\alpha} \,.$$

To give an interpretation of the Lagrange equations we define the action of a trajectory (followed between times t_1 and t_2) as

$$S[\boldsymbol{q}] = \int_{t_1}^{t_2} L(\boldsymbol{q}(t), \dot{\boldsymbol{q}}(t), t) dt.$$

Here the square brackets highlight that the argument of S is a function. Now one can show that the Lagrange equations are equivalent to demanding that $S[\boldsymbol{q}]$ is stationary w.r.t. variations of the function $\boldsymbol{q}(t)$ that preserve the boundary conditions, i.e., the values of $\boldsymbol{q}(t)$ at $t = t_1$ and $t = t_2$.

Hamiltonian mechanics

Hamiltonian mechanics is formulated in phase space, i.e., the fundamental variables are $\boldsymbol{q}$ and the momenta defined by

$$\boldsymbol{p} = \frac{\partial L}{\partial \dot{\boldsymbol{q}}} \, .$$

Instead of the Lagrangian we consider the Hamiltonian

$$H(\boldsymbol{q}, \boldsymbol{p}, t) = \boldsymbol{p} \cdot \dot{\boldsymbol{q}} - L \, .$$

The corresponding equations of motion are

$$\dot{q}_\alpha = \frac{\partial H}{\partial p_\alpha}, \qquad \dot{p}_\alpha = -\frac{\partial H}{\partial q_\alpha}.$$

1.2 Quantum mechanics

In quantum mechanics the variables q_α, p_α are replaced by operators $\hat{q}_\alpha, \hat{p}_\alpha$ acting on wavefunctions. In position representation the operator $\hat{q}_\alpha$ simply amounts to multiplication of the wavefunction with its parameter q_α and the momentum operator is $\hat{p}_\alpha = \frac{\hbar}{i}\frac{\partial}{\partial q_\alpha}$. The dynamics of the wavefunctions is then given by the Schrödinger equation

$$\hat{H}\psi(\boldsymbol{q}, t) = i\hbar \frac{\partial}{\partial t}\psi(\boldsymbol{q}, t)$$

where the quantum mechanical Hamiltonian is obtained from the classical Hamiltonian by replacing all q's and p's by operators. As we will usually use Cartesian coordinates we will replace $\boldsymbol{q}$ by $\boldsymbol{r}$ from now on.

We now go on to highlight some aspects of quantum mechanics that will be important for this course.

Bra-ket notation

In bra-ket or Dirac notation wavefunctions $\psi(\boldsymbol{r})$ are denoted by "kets" $|\psi\rangle$. The scalar product of two wavefunctions $\phi(\boldsymbol{r})$ and $\psi(\boldsymbol{r})$ is then denoted by

$$\int_{\mathbb{R}^n} \phi^*(\boldsymbol{r})\psi(\boldsymbol{r}) d^n r = \langle\phi|\psi\rangle.$$

I.e. the "bra" $\langle\phi|$ applied to a wavefunction indicates multiplication with the complex conjugate of the $\phi(\boldsymbol{r})$ and subsequent integration.

When dealing with eigenstates in bra-ket notation, one sometimes writes the corresponding eigenvalue in the bracket.

The delta "function"

Definition. The "function" $\delta(\boldsymbol{r})$ is informally defined as follows:

- It vanishes for $\boldsymbol{r} \neq 0$.
- It diverges at $\boldsymbol{r} = 0$.
- If we integrate over it multiplied with a different function $f(\boldsymbol{r})$ we get

$$\int_{\mathbb{R}^n} f(\boldsymbol{r})\delta(\boldsymbol{r})d^n r = f(0).$$

These properties also imply $\int f(\boldsymbol{r})\delta(\boldsymbol{r}-\boldsymbol{r}')d^n r = f(\boldsymbol{r}')$. A mathematically respectable way of defining delta "functions" is based on the theory of distributions[1] however it is convenient to work with them as with usual functions.

Position eigenfunctions. $\delta(\boldsymbol{r})$ can be interpreted as a wavefunction. As it is nonvanishing only for $\boldsymbol{r} = 0$ a particle with this wavefunction is localised as the origin. In other words, $\delta(\boldsymbol{r})$ is an eigenfunction of the position operator with eigenvalue zero.

Similarly $\delta(\boldsymbol{r}-\boldsymbol{r}')$ is nonvanishing only for $\boldsymbol{r} = \boldsymbol{r}'$ and forms an eigenfunction of the position operator with eigenvalue $\boldsymbol{r}'$.[2] It can also be written as the ket $|\boldsymbol{r}'\rangle$.

We note that the position eigenfunctions are a bit different from other eigenfunctions as they are distributions rather than proper functions, and there is one for every possible $\boldsymbol{r}$ so they do not form a discrete set parametrised by integers. One consequence of this is that they cannot be normalised to have $\langle \boldsymbol{r}|\boldsymbol{r}\rangle = 1$.

[1] Remark (not examinable). Distributions are mappings from a space of test functions $\mathcal{F}$ to $\mathbb{R}$. One often uses

$$\mathcal{F} = \{f \in C^\infty(\mathbb{R}^n) : (1+|\boldsymbol{r}|^2)^k f(\boldsymbol{r}) \text{ is bounded for all } k \in \mathbb{N}\}.$$

Functions $g : \mathbb{R}^n \to \mathbb{R}$ give rise to distributions

$$\begin{aligned} &D_g : \mathcal{F} \to \mathbb{R} \\ &D_g[f] = \int_{\mathbb{R}^n} f(\boldsymbol{r})g(\boldsymbol{r})d^n r \in \mathbb{R} \end{aligned} \tag{1.1}$$

where $f \in \mathcal{F}$. The δ-distribution maps each function $f \in \mathcal{F}$ to its value at zero

$$\begin{aligned} &D_\delta : \mathcal{F} \to \mathbb{R} \\ &D_\delta[f] = f(0)\ . \end{aligned}$$

We now use the following notation motivated by (1.1)

$$D_\delta[f] = \int_{\mathbb{R}^n} f(\boldsymbol{r})\delta(\boldsymbol{r})d^n r\ .$$

We thus work with the δ-distribution as we would work with a function.

[2] To see this formally, first for one dimensional systems, we note that an eigenfunction of the position operator with eigenvalue r' has to satisfy

$$\hat{r}\psi(r) = r'\psi(r).$$

This is solved by $\psi(r) = \delta(r-r')$ as

$$\hat{r}\delta(r-r') = r\delta(r-r') = r'\delta(r-r')\ .$$

Here the second equality is trivially correct if $r = r'$. It is also correct if $r \neq r'$ as in that case $\delta(r-r') = 0$. The same argument can be used for vector valued $\boldsymbol{r}$.

Application of $\langle \boldsymbol{r}'|$. Applying the bra $\langle \boldsymbol{r}'|$ to a quantum state $|\psi\rangle$ simply means to write down the wavefunction at position $\boldsymbol{r}'$ as

$$\langle \boldsymbol{r}'|\psi\rangle = \int \delta(\boldsymbol{r}-\boldsymbol{r}')\psi(\boldsymbol{r})d^n r = \psi(\boldsymbol{r}').$$

Integral representation of the delta function. The delta function can be obtained from the following integral (see problem sheet 1)

$$\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{ipr/\hbar}dp = \delta(r).$$

The analogous formula for $\boldsymbol{r} \in \mathbb{R}^n$ is

$$\frac{1}{(2\pi\hbar)^n}\int_{\mathbb{R}^n} e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}d^n p = \delta(\boldsymbol{r}). \tag{1.2}$$

Resolution of the identity

If the states $|m\rangle$ form a discrete orthonormal basis it was shown in 3rd year Quantum Mechanics that the identity operator can be written as

$$1 = \sum_m |m\rangle\langle m|.$$

We will later need an analogous result for position eigenstates. As these states form a continuous rather than a discrete basis the result for this case involves an integral:

$$1 = \int |\boldsymbol{r}\rangle\langle \boldsymbol{r}|d^n r \tag{1.3}$$

To prove this result we consider matrix elements where the r.h.s. is sandwiched between two arbitrary states $\langle\phi|$ and $|\psi\rangle$. We then have

$$\langle\phi|\left(\int |\boldsymbol{r}\rangle\langle \boldsymbol{r}|d^n r\right)|\psi\rangle = \int \langle\phi|\boldsymbol{r}\rangle\langle \boldsymbol{r}|\psi\rangle d^n r = \int \phi(\boldsymbol{r})^*\psi(\boldsymbol{r})d^n r = \langle\phi|\psi\rangle = \langle\phi|1|\psi\rangle$$

proving our claim.

Time evolution in quantum mechanics

A formal solution of the Schrödinger equation

$$\hat{H}\psi(\boldsymbol{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{r},t)$$

is

$$\psi(\boldsymbol{r},t) = e^{-\frac{i}{\hbar}\hat{H}t}\psi(\boldsymbol{r},0) \tag{1.4}$$

This result is obtained heuristically if we momentarily forget that $\hat{H}$ is an operator and we integrate as if it were, say, a real number. If we want the result to be true for operators we first of all have to define what an exponential of an operator means. We can define such exponentials through the Taylor series of the the exponential, as in

$$e^{-\frac{i}{\hbar}\hat{H}t} = \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{i}{\hbar}\hat{H}t\right)^n .$$

Here $\hat{H}^n$ is the operator obtained by applying $\hat{H}$ n times. $e^{-\frac{i}{\hbar}\hat{H}t}$ is also referred to as the time evolution operator.

Proof: Now we prove (1.4). Using that the derivative of the operator exponential defined above obeys the same rules as the derivative of a usual exponential we get

$$i\hbar\frac{\partial}{\partial t}\left(e^{-\frac{i}{\hbar}\hat{H}t}\psi(\boldsymbol{r},0)\right) = i\hbar\left(-\frac{i}{\hbar}\hat{H}\right)\left(e^{-\frac{i}{\hbar}\hat{H}t}\psi(\boldsymbol{r},0)\right) = \hat{H}\left(e^{-\frac{i}{\hbar}\hat{H}t}\psi(\boldsymbol{r},0)\right)$$

which means that the Schrödinger equation is satisfied. Moreover the claimed formula for $\psi(\boldsymbol{r},t)$ reduces to $\psi(\boldsymbol{r},0)$ if we insert $t=0$.

Propagator. To describe the time evolution of a quantum system it is helpful to consider the propagator, defined by the matrix elements of the time evolution operator,

$$K(\boldsymbol{r}_f,\boldsymbol{r}_0,t) = \langle \boldsymbol{r}_f | e^{-\frac{i}{\hbar}\hat{H}t} | \boldsymbol{r}_0 \rangle.$$

The propagator represents a state starting with $|\boldsymbol{r}_0\rangle$, i.e., a delta function located at $\boldsymbol{r}_0$, at time 0. Then this state evolves according to the Schrödinger equation over a time interval t, as expressed by the time evolution operator $e^{-\frac{i}{\hbar}\hat{H}t}$. Applying $\langle \boldsymbol{r}_f|$ means that we are considering the resulting wavefunction at the position $\boldsymbol{r}_f$.