Chapter I.
Quantum vs. Classical Dynamics

`chap:intro`

In this introductory chapter we recapitulate basic elements of quantum mechanics, emphasizing relationships with classical mechanics and preparing for the later chapters in a reasonably self-contained way. There are, of course, many texts where this material is presented more extensively and from different viewpoints. To name but a few, we mention the gentle mathematically-minded introduction by Thaller (2000), the complementary but visually equally appealing physical approach by Brandt & Dahmen (2001), the substantial brief text by Gustafson & Sigal (2003) from the mathematical physics point of view and the outreaching book by Tannor (2007) with a time-dependent, chemical physics perspective. There are the monumental classic treatises by Messiah (1962) and Cohen-Tannoudji, Diu & Laloë (1977), and the historical milestones left behind by Dirac (1930) and von Neumann (1932).

I.1 A First Look

To enter the stage, we begin by formulating the equations of motion of one (or several) particles in classical and quantum mechanics. We consider a particle of mass m in a conservative force field, which is the negative gradient of a potential $V(x)$, $x \in \mathbb{R}^3$.

I.1.1 Classical Mechanics

In classical dynamics, the state of the particle at any time t is characterized by its *position* $q(t) \in \mathbb{R}^3$ and *momentum* $p(t) \in \mathbb{R}^3$. It changes in time according to the Newtonian equations of motion

$$m\ddot{q} = -\nabla V(q)\,, \qquad p = m\dot{q}\,,$$

where the dots denote differentiation with respect to time t ($\dot{} = d/dt$). This can equivalently be written as a first-order system of ordinary differential equations,

$$\begin{aligned} \dot{q} &= \frac{p}{m} \\ \dot{p} &= -\nabla V(q)\,. \end{aligned} \tag{1.1}$$

`I:newton-pq`

With the *Hamiltonian function*

Schr“”odinger equation

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

(here $|p|^2 = p \cdot p$ is the squared Euclidean norm), which represents the total energy as the sum of the kinetic energy $T(p)$ and the potential energy $V(q)$, the differential equations become Hamilton's canonical equations of motion

$$\begin{aligned} \dot{q} &= \frac{\partial H}{\partial p}(q,p) \\ \dot{p} &= -\frac{\partial H}{\partial q}(q,p)\,. \end{aligned} \tag{1.2}$$

`I:hamil`

The formalism extends in a straightforward way to a system of N particles of masses $m_1, \dots, m_N$, with the position vector $q = (q_1, \dots, q_N)^T \in \mathbb{R}^{3N}$ and the momentum vector $p = (p_1, \dots, p_N)^T \in \mathbb{R}^{3N}$ collecting the positions and momenta of the particles. The kinetic energy is then given as the sum of the kinetic energies of the particles, $T(p) = \sum_{n=1}^{N} |p_n|^2/(2m_n)$, and the potential $V(q) = V(q_1, \dots, q_N)$ depends on the positions of all the particles and characterizes their interaction. The potential might in addition also depend on time to describe phenomena in a time-varying environment. Adding one more particle has the consequence of adding six *dependent* variables $(q_{N+1}(t), p_{N+1}(t))$ to the system of ordinary differential equations. Computations with millions, even billions of particles are routinely done in classical molecular dynamics simulations.

I.1.2 Quantum Mechanics

In quantum mechanics, the state at time t is described by the complex-valued *wave function* $\psi(x,t)$, depending on $x \in \mathbb{R}^3$ in the case of a single particle. Motivated by de Broglie's hypothesis of a particle-wave duality of matter, Schrödinger (1926) postulated the evolution equation that has since been recognized as the fundamental law for describing non-relativistic particles in physics and chemistry:

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi\,. \tag{1.3}$$

`I:schroed-eq`

Here, $i = \sqrt{-1}$ is the imaginary unit, and $\hbar$ is Planck's constant which has the physical dimension of an action, that is, energy divided by frequency or momentum times length. Its value is $\hbar = 1.0546 \cdot 10^{-34}$ Joule·sec. The *Hamiltonian operator* H on the right-hand side is the sum

$$H = T + V \tag{1.4}$$

`I:HTV`

of the kinetic energy operator T and the potential V. Here,

$$T\psi = -\frac{\hbar^2}{2m}\Delta\psi = \frac{p \cdot p}{2m}\psi \tag{1.5}$$

`I:T`

with the Laplacian $\Delta = \nabla \cdot \nabla$ (the divergence and gradient are with respect to the spatial variable x). With the *momentum operator* $p = -i\hbar\nabla$, the expression of the kinetic energy looks formally the same as in classical mechanics. On the other hand, the potential simply acts as a multiplication operator: $\big(V\psi\big)(x) = V(x)\psi(x)$. The Schrödinger equation (1.3) is thus a partial differential equation of first order in time and second order in space.

The usual *statistical interpretation* of quantum mechanics, due to Born (1926), views $|\psi(\cdot,t)|^2$ as a probability density for the position of the particle: the probability of the particle to be located within a volume $\Omega \subset \mathbb{R}^3$ at time t, equals $\int_\Omega |\psi(x,t)|^2\,dx$. Moreover, the squared absolute value of the Fourier transform of the wave function is interpreted as the probability density for the momentum of the particle.

The formalism again extends directly to several particles. As in the classical case, the multi-particle Hamiltonian is constructed as the sum of the kinetic energies of the single particles and a potential accounting for external forces and interaction. The Hamiltonian operator now acts on a wave function $\psi(x_1,\ldots,x_N,t)$ depending on the spatial coordinates corresponding to each of the N particles. Its squared absolute value represents the joint probability density of particles 1 to N to be at $(x_1,\ldots,x_N)$ at time t. The multi-particle wave function is a high-dimensional object: adding one more particle yields another three *independent* variables! Computations with direct finite-difference discretizations of Schrödinger's equation are out of reach for more than two or three particles.

I.2 The Free Schrödinger Equation

`sect:free`

In the absence of a potential, for $V = 0$, the Schrödinger equation (1.3) becomes

$$i\hbar\frac{\partial\psi}{\partial t}(x,t) = -\frac{\hbar^2}{2m}\Delta\psi(x,t)\,, \qquad x\in\mathbb{R}^d,\ t\in\mathbb{R}\,. \tag{2.1}$$

`I:free`

I.2.1 Dispersion Relation

Einstein's equation

$$E = \hbar\omega \tag{2.2}$$

`I:Einstein`

relates the energy of emitted electrons to the frequency of incident light in the photoelectric effect, which is explained by light quanta showing the particle nature of light (Einstein 1905). It was hypothesised by de Broglie (1924) that particle-wave duality should exist also for matter, and the energy relation (2.2) should be basic also for matter waves. As we will see in a moment, Equation (2.1) can be understood as resulting from an effort to reconcile (2.2) with the classical expression for the energy of a free particle with mass m and momentum p,

$$E = \frac{|p|^2}{2m}\,, \tag{2.3}$$

`I:Eclass`

for solutions of a linear evolution equation

$$\frac{\partial \psi}{\partial t} = P(\partial_x)\psi\,, \qquad x \in \mathbb{R}^d,\ t \in \mathbb{R}\,,$$

with some (possibly pseudo-) differential operator $P(\partial_x)$. A plane wave $e^{i(k\cdot x - \omega t)}$ with wave vector k and angular frequency ω is a solution of this equation if ω satisfies the *dispersion relation*

$$\omega = \omega(k) = iP(ik)\,.$$

Clearly, knowing the dispersion relation is tantamount to knowing the evolution equation with operator $P(\partial_x)$.

In relating (2.2) and (2.3), it is assumed that the momentum should be

$$p = mv\,, \tag{2.4}$$

`I:pmv`

where the velocity is taken to be the *group velocity*

$$v = \frac{\partial \omega}{\partial k}\,, \tag{2.5}$$

`I:vg`

which is the velocity of the envelope of a localized wave packet (Hamilton 1839, Rayleigh 1877; see also Sect. I.2.3 below) and thus represents the particle velocity. With the relations (2.4)–(2.5), the equality of the energies (2.2) and (2.3) becomes the condition $\hbar\omega = \frac{1}{2}m|\partial\omega/\partial k|^2$, which is satisfied for the dispersion relation of the free Schrödinger equation (2.1),

$$\hbar\omega = \frac{\hbar^2}{2m}\,|k|^2\,. \tag{2.6}$$

`I:disp`

With (2.4)–(2.5), this further yields de Broglie's relation

$$p = \hbar k\,, \tag{2.7}$$

`I:broglie`

which together with (2.2) expresses the plane wave as $e^{i(k\cdot x - \omega t)} = e^{\frac{i}{\hbar}(p\cdot x - Et)}$. The equality of the energies (2.2) and (2.3) is then the dispersion relation (2.6) of the Schrödinger equation.

I.2.2 Solution by Fourier Transformation

`subsec:fourier`

We consider (2.1) together with the initial condition

$$\psi(x,0) = \psi_0(x)\,, \qquad x \in \mathbb{R}^d. \tag{2.8}$$

`I:init`

To concur with the interpretation of $|\psi_0|^2$ as a probability density, we assume that ψ_0 has unit L^2 norm:

$$\|\psi_0\|^2 = \int_{\mathbb{R}^d} |\psi_0(x)|^2 \, dx = 1\,. \qquad (2.9) \quad \boxed{\texttt{I:init-norm}}$$

This initial-value problem is solved using Fourier transforms. We begin by recalling the necessary prerequisites; see, e.g., Katznelson (1976), Chap. VI, or Reed & Simon (1975), Chap. IX. For convenience, in the following we choose physical units such that

$$\hbar = 1.$$

Fourier Transform. Let $\mathcal{S}$ denote the Schwartz space of rapidly decaying smooth functions, that is, of arbitrarily differentiable complex-valued functions on $\mathbb{R}^d$ which, together with all their partial derivatives, decay faster than the inverse of any polynomial as $|x| \to \infty$. For a Schwartz function $\varphi \in \mathcal{S}$, the Fourier transform $\widehat{\varphi} = \mathcal{F}\varphi$ given by

$$\widehat{\varphi}(k) = \frac{1}{(2\pi)^{d/2}} \int_{\mathbb{R}^d} e^{-ik\cdot x}\, \varphi(x)\, dx\,, \qquad k \in \mathbb{R}^d, \qquad (2.10) \quad \boxed{\texttt{I:fourier}}$$

is again a Schwartz function. There is the inversion formula

$$\varphi(x) = \frac{1}{(2\pi)^{d/2}} \int_{\mathbb{R}^d} e^{ik\cdot x}\, \widehat{\varphi}(k)\, dk\,, \qquad x \in \mathbb{R}^d, \qquad (2.11) \quad \boxed{\texttt{I:inv-fourier}}$$

and the Plancherel formula relating the L^2 norms of φ and $\widehat{\varphi}$,

$$\|\varphi\| = \|\widehat{\varphi}\|\,. \qquad (2.12) \quad \boxed{\texttt{I:plancherel}}$$

The Fourier transform changes partial derivatives into multiplication by the Fourier variable:

$$-i\widehat{\partial_j \varphi}(k) = k_j \widehat{\varphi}(k)\,, \qquad (2.13) \quad \boxed{\texttt{I:fourier-diff}}$$

and hence the negative Laplacian is transformed into multiplication by the squared Euclidean norm $|k|^2 = k_1^2 + \cdots + k_d^2$:

$$-\widehat{\Delta\varphi}(k) = |k|^2 \widehat{\varphi}(k)\,. \qquad (2.14) \quad \boxed{\texttt{I:fourier-lap}}$$

By density or duality, the above formulas are extended to appropriate larger spaces of functions or distributions.

Solution via Fourier Transformation. Formally taking Fourier transforms with respect to the spatial variable x in (2.1) yields decoupled ordinary differential equations parametrized by the dual variable k:

$$i\frac{\partial\widehat{\psi}}{\partial t}(k,t) = \frac{|k|^2}{2m}\, \widehat{\psi}(k,t)\,, \qquad k \in \mathbb{R}^d,$$

which are solved by

$$\widehat{\psi}(k,t) = e^{-i\frac{|k|^2}{2m}t}\,\widehat{\psi}_0(k)\,. \tag{2.15}$$

I:psi-hat

Obviously, $|\widehat{\psi}(k,t)|^2 = |\psi_0(k)|^2$ for all k and t. We note that for initial data in the Schwartz space, $\psi_0 \in \mathcal{S}$, we have $\widehat{\psi}_0 \in \mathcal{S}$ and thus further $\widehat{\psi}(\cdot,t) \in \mathcal{S}$ for all real t. The function obtained by the inverse Fourier transform (2.11),

$$\psi(x,t) = \frac{1}{(2\pi)^{d/2}} \int_{\mathbb{R}^d} e^{i(k\cdot x - \frac{|k|^2}{2m}t)}\,\widehat{\psi}_0(k)\,dk\,, \tag{2.16}$$

I:psi-free

is thus again a Schwartz function, and by the above transform rules, this function is verified to be a solution to (2.1)-(2.8). We have unit L^2 norm

$$\|\psi(\cdot,t)\|^2 = 1 \qquad \text{for all } t \tag{2.17}$$

I:psi-norm

by the Plancherel formula, by (2.15) and condition (2.9), so that $|\psi(\cdot,t)|^2$ remains a probability density for all times.

The Free-Evolution Operator. With the kinetic energy operator $T = -\frac{1}{2m}\Delta$, we use the notation

$$\psi(\cdot,t) = \psi(t) =: e^{-itT}\psi_0\,.$$

This defines the evolution operator

$$e^{-itT} : \mathcal{S} \to \mathcal{S}.$$

By (2.17) and because the Schwartz space $\mathcal{S}$ is dense in the Hilbert space L^2 of square-integrable functions, we can extend the operator to a norm-preserving operator

$$e^{-itT} : L^2 \to L^2,$$

and we consider $e^{-itT}\psi_0$ for arbitrary $\psi_0 \in L^2$ as a generalized solution to the free Schrödinger equation (2.1) with initial state (2.8).

I.2.3 Propagation of Wave Packets with Large Mass

sec:wavepacket

We consider the free Schrödinger equation (2.1) with $\hbar = 1$, and as initial state a wave packet

$$\psi_0(x) = e^{ip\cdot x}\,a(x) \qquad \text{with} \quad a \in \mathcal{S},\ p \in \mathbb{R}^d, \tag{2.18}$$

I:wavepacket

where we are particularly interested in p of large norm, so that a highly oscillatory complex exponential is modulated by the smooth, rapidly decaying function $a(x)$. We show that the following holds for the solution of (2.1), uniformly in $p \in \mathbb{R}^d$ as the mass $m \to \infty$:

$$\psi(x,t) = e^{ip\cdot\left(x - \frac{p}{2m}t\right)}\,a\Big(x - \frac{p}{m}t\Big) + O\Big(\frac{t}{m}\Big)\,. \tag{2.19}$$

I:large-m

Here we note the *phase velocity* $p/(2m)$ in the argument of the exponential and the *group velocity* $v = p/m$ in the argument of a, and

$$|\psi(x,t)|^2 \approx |\psi_0(x-vt)|^2\,,$$

which describes uniform straight motion of the envelope with the group velocity v. Heavy particles thus show approximately classical behaviour.

Proof of (2.19): We start from formula (2.16) for $\psi(x,t)$ and note that $\widehat{\psi}_0(k) = \widehat{a}(k-p)$. We decompose $|k|^2 = |k-p+p|^2 = |p|^2 + 2(k-p)\cdot p + |k-p|^2$ and substitute the integration variable k for $k-p$ to obtain

$$\psi(x,t) = e^{ip\cdot x}\, e^{-i\frac{|p|^2}{2m}t}\, \frac{1}{(2\pi)^{d/2}} \int_{\mathbb{R}^d} e^{ik\cdot x}\, e^{-ik\cdot\frac{p}{m}t}\, e^{-i\frac{|k|^2}{2m}t}\, \widehat{a}(k)\, dk\,.$$

With the relation $e^{-i\frac{|k|^2}{2m}t} = 1 + O(|k|^2\frac{t}{m})$, we obtain with the inverse Fourier transform formula

$$\begin{aligned}\psi(x,t) &= e^{ip\cdot x - i\frac{|p|^2}{2m}t}\, \frac{1}{(2\pi)^{d/2}} \int_{\mathbb{R}^d} e^{ik\cdot(x-\frac{p}{m}t)}\, \widehat{a}(k)\, dk + O\Big(\frac{t}{m}\Big) \\ &= e^{ip\cdot x - i\frac{|p|^2}{2m}t}\, a\Big(x - \frac{p}{m}t\Big) + O\Big(\frac{t}{m}\Big)\,,\end{aligned}$$

where the constant in the O-symbol is $C = \int_{\mathbb{R}^d} |k|^2 |\widehat{a}(k)|\, dk$. □

I.3 The Schrödinger Equation with a Potential

We now turn to the Schrödinger equation (1.3) with a real-valued potential $V(x)$, $x \in \mathbb{R}^d$,

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\Delta\psi + V\psi. \qquad (3.1)$$

`I:schroed-V`

For convenience we choose again units with $\hbar = 1$, as we will usually do when we treat mathematical rather than physical questions.

I.3.1 Self-Adjoint Operators and Existence of Dynamics

The existence of solutions to (3.1) rests on the theory of self-adjoint unbounded operators on a Hilbert space. Let us briefly recall the relevant concepts.

Let $\mathcal{H}$ be a complex Hilbert space with inner product denoted by $\langle\cdot\,|\,\cdot\rangle$. A linear operator $H : D(H) \to \mathcal{H}$, defined on a domain $D(H)$ dense in $\mathcal{H}$, is called *symmetric* if

$$\langle H\psi\,|\,\varphi\rangle = \langle\psi\,|\,H\varphi\rangle \qquad \forall \psi,\varphi \in D(H).$$

The operator is *self-adjoint* if for any $\varphi,\eta \in \mathcal{H}$ the relation

$$\langle H\psi\,|\,\varphi\rangle = \langle\psi\,|\,\eta\rangle \quad \forall\psi \in D(H) \qquad \text{implies} \qquad \varphi \in D(H) \;\text{ and }\; \eta = H\varphi.$$

Every self-adjoint operator is symmetric, but the converse is not true for unbounded operators. Every self-adjoint operator is *closed*: for any sequence (φ_n) in $D(H)$, the convergence $\varphi_n \to \varphi,\ \ H\varphi_n \to \eta$ implies $\varphi \in D(H)$ and $\eta = H\varphi$.

An operator U on $\mathcal{H}$ is *unitary* if it preserves the inner product:

$$\langle U\psi \,|\, U\varphi\rangle = \langle \psi \,|\, \varphi\rangle \qquad \forall \psi, \varphi \in \mathcal{H}.$$

As the following theorem states, for self-adjoint operators H the abstract Schrödinger equation

$$i\frac{d\psi}{dt} = H\psi \tag{3.2}$$

`I:schroed-abstract`

has a unitary evolution.

`:thm:existence`

Theorem 3.1. *Assume that H is a self-adjoint operator on a Hilbert space $\mathcal{H}$. Then, there is a family of unitary operators $e^{-itH},\ t \in \mathbb{R}$, with the following properties:*

1. *The operators e^{-itH} have the group property:*

$$e^{-i(t+s)H} = e^{-itH}\, e^{-isH} \qquad \text{for all } s, t \in \mathbb{R}\,.$$

2. *The mapping $t \mapsto e^{-itH}$ is strongly continuous: for every $\psi_0 \in \mathcal{H}$,*

$$e^{-itH}\psi_0 \to \psi_0 \quad \text{in the } \mathcal{H}\text{-norm as } t \to 0\,.$$

3. *Equation (3.2) with initial value $\psi_0 \in D(H)$ has the solution $\psi(t) = e^{-itH}\psi_0$:*

$$i\frac{d}{dt}e^{-itH}\psi_0 = He^{-itH}\psi_0\,,$$

where the expressions on both sides of the equality sign indeed exist.

Theorem 3.1 can be proved by first noting that it holds for bounded operators, then by approximating H by a sequence of symmetric bounded operators H_n and carefully passing to the limit in the exponentials e^{-itH_n}; see Gustafson & Sigal (2003), Chap. 2. Another proof is based on the spectral theory of self-adjoint operators as developed by von Neumann and put to good use in his mathematical foundations of quantum mechanics (von Neumann, 1932). Based on von Neumann's spectral theory, Theorem 3.1 was given by Stone (1932) who also proves an interesting converse: if $U(t),\ t \in \mathbb{R}$, is a strongly continuous group of unitary operators, then $U(t) = e^{-itH}$ for some self-adjoint operator H.

I.3.2 Potentials Giving Self-Adjoint Operators

In applying Theorem 3.1 to the Schrödinger equation (3.1) on the Hilbert space $\mathcal{H} = L^2(\mathbb{R}^d)$ of square-integrable functions, we need conditions that ensure that the Hamiltonian $H = T + V$ is a self-adjoint operator. While symmetry is easily obtained, showing self-adjointness can be quite subtle.

First we remark that $T = -\frac{1}{2m}\Delta$ is self-adjoint with the domain $D(T) = H^2(\mathbb{R}^d)$, the Sobolev space of functions which together with their generalized partial derivatives up to order 2 are square integrable. (This is shown using Fourier transforms.)

Knowing that T is self-adjoint, what can we say about $T + V$? The following very useful perturbation result is known as the *Kato-Rellich theorem*, see Kato (1980), Sect. V.4.1, Theorem 4.3:

Let T be a self-adjoint operator on a Hilbert space, and V a symmetric operator bounded by $\|V\psi\| \leq a\|\psi\| + b\|T\psi\|$ for all $\psi \in D(T)$, with $b < 1$. Then, $H = T + V$ is self-adjoint with domain $D(H) = D(T)$.

In particular, for $T = -\frac{1}{2m}\Delta$ a bounded potential always gives a self-adjoint Hamiltonian $H = T + V$ with domain $H^2(\mathbb{R}^d)$. A simple criterion that follows from the above result with the Sobolev inequality on $\mathbb{R}^3$, is the following (Kato 1980, Sect. V.5.3): Assume

$$V = V_\infty + V_2 \qquad \text{with} \quad V_\infty \in L^\infty(\mathbb{R}^3),\ V_2 \in L^2(\mathbb{R}^3).$$

Then, $T+V$ is self-adjoint with domain $D(H) = H^2(\mathbb{R}^3)$. For example, this applies to the *Coulomb potential* $V(x) = |x|^{-1}$.

An enlightening discussion and a variety of results on the self-adjointness of Schrödinger operators are given in Chapter X of Reed & Simon (1975). Remarkably, self-adjoint extensions always exist for a potential bounded from below (*ibid.*, p. 177), but they need not be unique, and different extensions can correspond to different physics (*ibid.*, p. 145). A unique self-adjoint extension is known to exist for every non-negative continuous *confining* potential, that is, satisfying $V(x) \to \infty$ as $|x| \to \infty$; see Hislop & Sigal (1996).

Later in this text, we will not pay much attention to the subtleties of self-adjointness and, in cases of possible doubt, we simply assume that the potential is such that $H = T + V$ yields a well-defined self-adjoint operator on $L^2(\mathbb{R}^d)$.

I.3.3 Lie–Trotter Product Formula

We have already constructed the free-particle evolution operator e^{-itT} by Fourier transformation, and for the potential we simply have $\big(e^{-itV}\psi\big)(x) = e^{-itV(x)}\psi(x)$. We do *not* have $e^{-i(T+V)} = e^{-itT}\,e^{-itV}$, but there is the following result due to Trotter (1959), whose finite-dimensional version is credited to Lie. See also Reed & Simon (1972), Theorem VIII.30, for precisely this version and a short proof.

`I:thm:trotter` **Theorem 3.2.** *Suppose that T, V, and $H = T + V$ are self-adjoint operators on a Hilbert space $\mathcal{H}$. Then, for every $t \in \mathbb{R}$ and $\varphi \in \mathcal{H}$,*

$$e^{-itH}\varphi = \lim_{n\to\infty}\Big(e^{-itT/n}\,e^{-itV/n}\Big)^n\varphi\,.$$

In view of the strong continuity of e^{-itV}, an equivalent statement is

$$e^{-itH}\varphi = \lim_{n\to\infty}\Big(e^{-itV/(2n)}\, e^{-itT/n}\, e^{-itV/(2n)}\Big)^n \varphi\,.$$

We will encounter the short-time approximation (over a small time step Δt)

$$e^{-i\Delta t H} \approx e^{-i\Delta t V/2}\, e^{-i\Delta t T}\, e^{-i\Delta t V/2}\,, \tag{3.3}$$

`I:strang`

known as *symmetric Trotter splitting* or *Strang splitting*, repeatedly in this text, in various versions and disguises. This is one of the most widely used approximations to the evolution operator in computations.

Relationship with the Störmer–Verlet Method for Classical Mechanics. Consider now a wavepacket as in Sect. I.2.3, $\psi_0(x) = e^{ip\cdot x}a(x)$, where we think of $a(x)$ as being localized near $x = q$. We consider the Taylor expansion of the potential $V(x)$ at q,

$$V(x) = V(q) + \nabla V(q)\cdot(x-q) + Q(x,q)$$

with the quadratic remainder term Q, so that we have

$$e^{-i\frac{\Delta t}{2}V(x)}\psi_0(x) = e^{i(p\cdot q - \frac{\Delta t}{2}V(q))}\, e^{i(p-\frac{\Delta t}{2}\nabla V(q))\cdot(x-q)}\, e^{-i\frac{\Delta t}{2}Q(x,q)}\, a(x)\,. \tag{3.4}$$

`I:exp-V`

Here the first exponential on the right-hand side carries a phase which is modified by $-\frac{\Delta t}{2}V(q)$ over the half-step $\frac{\Delta t}{2}$. In the second exponential, the *momentum* p is shifted to $p - \frac{\Delta t}{2}\nabla V(q)$. We recall that in (2.19) we had a shift from *position* q to $q + \Delta t\, p/m$ for the centre of the wave packet propagated by the free evolution operator $e^{-i\Delta t T}$ in the situation of a large mass m. Combining these formulas for changing momenta and positions as they appear from the composition $e^{-i\Delta t V/2}\, e^{-i\Delta t T}\, e^{-i\Delta t V/2}$ of (3.3), we arrive at the following scheme: starting from q^0, p^0, set

$$\begin{aligned} p^{1/2} &= p^0 - \frac{1}{2}\Delta t\,\nabla V(q^0)\\ q^1 &= q^0 + \Delta t\,\frac{p^{1/2}}{m}\\ p^1 &= p^{1/2} - \frac{1}{2}\Delta t\,\nabla V(q^1)\,. \end{aligned} \tag{3.5}$$

`I:verlet`

This is the *Störmer–Verlet method* for the numerical solution of the Newtonian equations of motion (1.1), which is by far the most widely used numerical integration method in classical molecular dynamics. See Hairer, Lubich & Wanner (2003) for a discussion of this basic numerical method and its remarkable properties. We further note from (2.19) and (3.4) that the overall phase (the term in the exponential that is independent of x) is modified to

$$\phi^1 = \phi^0 + \Delta t\,\frac{|p^{1/2}|^2}{2m} - \frac{1}{2}\Delta t\,\big(V(q^0) + V(q^1)\big),$$

where the increment is a quadrature formula approximation to the classical action integral $\int_0^{\Delta t}\big(\frac{|p(t)|^2}{2m} - V(q(t))\big)\,dt$ along the solution $(q(t),p(t))$ of the classical equations of motion (1.1). We will explore relationships between (3.3) and (3.5) in more depth in Chapter V.

I.4 Averages, Commutators, Uncertainty

We consider again the Schrödinger equation (3.1) with the Hamiltonian $H = T + V$ and look at spatial averages of position, momentum, etc. along the wave function.

I.4.1 Observables and Averages

With the jth position coordinate as multiplication operator, $\big(q_j\psi\big)(x) = x_j\psi(x)$, and a function ψ of unit L^2 norm with $q_j\psi \in L^2$, we associate

$$\langle \psi \,|\, q_j\psi \rangle = \int_{\mathbb{R}^d} x_j \, |\psi(x)|^2 \, dx \,,$$

which represents the jth component of the *position average* of the state ψ.

With the jth component of the momentum operator, $p_j = -i\hbar\,\partial/\partial x_j$, we form (for $\psi \in D(p_j)$ and of unit L^2 norm)

$$\langle \psi \,|\, p_j\psi \rangle = \int_{\mathbb{R}^d} \overline{\psi}(x)\Big(-i\hbar\,\frac{\partial\psi}{\partial x_j}\Big)\, dx = \int_{\mathbb{R}^d} \hbar k_j \, |\widehat{\psi}(k)|^2 \, dk \,,$$

which is the jth component of the *momentum average* of the state ψ. Similarly, we can consider the *total energy* $\langle \psi \,|\, H\psi \rangle$. It is such averages that can be observed experimentally.

Noting that q_j, p_j, H are self-adjoint operators on L^2, more generally we call any self-adjoint operator $A : D(A) \to L^2$ an *observable*, and its *average in the state* ψ (ψ of unit L^2 norm and $\psi \in D(A)$) is written, in varying notations,

$$\langle A \rangle = \langle A \rangle_\psi = \langle \psi \,|\, A \,|\, \psi \rangle = \langle \psi \,|\, A\psi \rangle \,. \tag{4.1}$$

`I:brackets`

I.4.2 Heisenberg Picture and Ehrenfest Theorem

Evolution of Averages and the Heisenberg Picture. We now study how the average $\langle A \rangle(t) = \langle A \rangle_{\psi(t)}$ of an observable A changes in time along a solution $\psi(t) = \psi(\cdot, t)$ of the Schrödinger equation (1.3). Since $\psi(t) = e^{-itH/\hbar}\psi_0$, we have

$$\langle A \rangle_{\psi(t)} = \langle A(t) \rangle_{\psi_0} \qquad \text{with} \quad A(t) = e^{itH/\hbar} A e^{-itH/\hbar} \,. \tag{4.2}$$

`I:heis-pic`

The operator $A(t)$ is said to give the *Heisenberg picture* of the evolution of the observable (after Heisenberg, 1925), as opposed to the Schrödinger picture working with wave functions. For a fixed initial state ψ_0, Eq. (4.2) can be written more briefly as

$$\langle A \rangle(t) = \langle A(t) \rangle \,. \tag{4.3}$$

`I:heis-aver`

Heisenberg Equation. A formal calculation, using $\frac{d}{dt}e^{-itH/\hbar} = \frac{1}{i\hbar}He^{-itH/\hbar} = e^{-itH/\hbar}\frac{1}{i\hbar}H$, yields

$$\frac{dA}{dt}(t) = \frac{1}{i\hbar} e^{itH/\hbar}(-HA + AH)e^{-itH/\hbar}$$

and hence, with the *commutator* $[A, H] = AH - HA$ and with $\dot{} = d/dt$, we have the *Heisenberg equation*

$$\dot{A}(t) = \frac{1}{i\hbar}\,[A(t), H]\,. \tag{4.4}$$

`I:heis-eq`

Remark. Some care is needed in giving a precise meaning to the commutator of unbounded self-adjoint operators, which in general need not exist. We note, however, that for initial states ψ_0 in a domain D which A maps into $D(H)$ and H maps into $D(A)$, the averages of both sides of (4.4) are well-defined and are indeed equal.

Energy Conservation. Since H commutes with itself, we obtain from (4.3) and (4.4) that the total energy is conserved along every solution of the Schrödinger equation:

$$\frac{d}{dt}\langle H\rangle = 0. \tag{4.5}$$

`I:energy-cons`

Formal Analogy with Classical Mechanics. The Heisenberg equation (4.4) shows a close analogy to the corresponding situation in classical mechanics: a real-valued function $F(q, p)$ along a solution $(q(t), p(t))$ of the Hamiltonian equations (1.2) changes according to

$$\frac{d}{dt}F(q(t), p(t)) = \bigl\{F, H\bigr\}(q(t), p(t))$$

with the *Poisson bracket*

$$\bigl\{F, G\bigr\} = \sum_{j=1}^{d}\Bigl(\frac{\partial F}{\partial q_j}\frac{\partial G}{\partial p_j} - \frac{\partial F}{\partial p_j}\frac{\partial G}{\partial q_j}\Bigr)\,,$$

as is seen by the chain rule and using (1.2). Formally thus, one bracket replaces the other in going from classical to quantum mechanics.

We now consider the Heisenberg equations for the position and momentum operators, with components q_j and p_j:

$$\begin{aligned} \dot{q}_j &= \frac{1}{i\hbar}\,[q_j, H] \\ \dot{p}_j &= \frac{1}{i\hbar}\,[p_j, H]\,. \end{aligned}$$

For a Hamiltonian $H = T + V$ with kinetic energy $T = -\frac{\hbar^2}{2m}\,\Delta$ and with a potential $V(x)$ acting as a multiplication operator, we calculate

$$\frac{1}{i\hbar}\,[q_j,H]\psi=\frac{1}{i\hbar}[q_j,T]\psi=-\frac{1}{i\hbar}\sum_{\ell=1}^{d}\frac{\hbar^2}{2m}\,[q_j,\frac{\partial^2}{\partial x_\ell^2}]\,\psi=-\frac{i\hbar}{m}\frac{\partial\psi}{\partial x_j}=\frac{p_j}{m}\,\psi$$

$$\frac{1}{i\hbar}\,[p_j,H]\psi=\frac{1}{i\hbar}[p_j,V]\psi=-\frac{\partial}{\partial x_j}(V\psi)+V\frac{\partial\psi}{\partial x_j}=-\frac{\partial V}{\partial x_j}\psi\,.$$

This gives us equations that look exactly like the classical equations of motion (1.1):

$$\begin{aligned}\dot q &= \frac{p}{m}\\ \dot p &= -\nabla V\,.\end{aligned}\tag{4.6}$$

`I:heis-pq`

Ehrenfest Theorem. When we take averages $\langle\cdot\rangle$ on both sides of (4.6) according to (4.3), then we obtain the result by Ehrenfest (1927) that the position and momentum averages evolve by Newton-like equations. It should be noted, however, that in general

$$\langle\nabla V\rangle\neq\nabla V\big(\langle q\rangle\big)\,,$$

unless the potential is quadratic.

I.4.3 Heisenberg Uncertainty Relation

Still in analogy with classical mechanics, position and momentum are *canonically conjugate* observables, which here means that they satisfy (with Kronecker's delta)

$$\frac{1}{i\hbar}\,[q_j,p_k]=\delta_{jk}\,,\tag{4.7}$$

`I:qp-comm`

as is readily verified by a direct calculation of the commutator similar to the one given above. This has an important consequence to which we turn next. We define the *standard deviation* or *width* of an observable A in a state ψ as

$$\varDelta A=\big\langle(A-\langle A\rangle)^2\big\rangle^{1/2}\,,\tag{4.8}$$

`I:dispersion`

where the average is taken with respect to the given state ψ.

Theorem 4.1 (Heisenberg Uncertainty Relation). *The standard deviations of the position and momentum operators satisfy the inequality*

$$\varDelta q_j\,\varDelta p_j\geq\frac{\hbar}{2}\,.\tag{4.9}$$

`I:heis-uncert`

According to Heisenberg (1927), this now world-famous inequality is interpreted as saying that it is impossible to know both the exact position and exact momentum of an object at the same time.

Proof. The result follows from (4.7) and from the *Robertson-Schrödinger relation* which states that for any observables A and B,

$$\varDelta A\,\varDelta B \geq \frac{1}{2}\Big|\big\langle [A,B]\big\rangle\Big|\,. \qquad (4.10)$$ I:rs

This is obtained with the Cauchy-Schwarz inequality and the identity

$$-2\,\mathrm{Im}\,\langle A\psi \,|\, B\psi\rangle = \langle \psi \,|\, i[A,B]\psi\rangle$$

as follows (we may assume $\langle A\rangle = \langle B\rangle = 0$ for ease of notation):

$$\varDelta A\,\varDelta B = \|A\psi\|\cdot\|B\psi\| \geq \big|\langle A\psi \,|\, B\psi\rangle\big| \geq \big|\mathrm{Im}\,\langle A\psi \,|\, B\psi\rangle\big| = \frac{1}{2}\big|\langle i[A,B]\rangle\big|\,. \qquad \square$$

I.5 Many-Body Systems

I.5.1 Distinguishable Particles

Consider first N independent free particles, without any interaction, numbered from $n = 1,\dots,N$. The probability density at time t for particle n to be at position x_n is $|\psi_n(x_n,t)|^2$, the square of the absolute value of the wave function. Since the particles are assumed independent, the joint probability density for particle 1 at $x_1,\dots,$ particle N at x_N is the product $\prod_{n=1}^N |\psi_n(x_n,t)|^2$, which is the squared absolute value of the product wave function $\psi(x_1,\dots,x_N,t) = \prod_{n=1}^N \psi_n(x_n,t)$ that solves the $3N$-dimensional free Schrödinger equation

$$i\hbar\,\frac{\partial\psi}{\partial t} = T\psi \qquad \text{with} \quad T = \sum_{n=1}^{N} T_n\,, \quad T_n = -\frac{\hbar^2}{2m_n}\varDelta_n\,,$$

where $\varDelta_n$ is the Laplacian with respect to the variable x_n. Similarly, if each particle is subjected to an external potential $V_n(x_n)$, then the product wave function solves a Schrödinger equation with a potential that is the sum of the single-particle potentials. With particles interacting via a potential $V(x_1,\dots,x_N)$, however, the solution of the multi-particle Schrödinger equation

$$i\hbar\,\frac{\partial\psi}{\partial t} = H\psi\,, \qquad H = T + V\,, \qquad \psi = \psi(x_1,\dots,x_N,t)\,,$$

is in general no longer in product form. As a rough *approximation* to the high-dimensional wave function we might still look for a function in product form — an old idea realized in the time-dependent *Hartree method* discussed in Chapter II.

I.5.2 Indistinguishable Particles

subsec:indist

When particles cannot be distinguished in their physical properties, such as mass, charge, or spin, the potential remains the same under an exchange of the coordinates of the particles; in the case of identical particles 1 and 2,

$$V(x_2, x_1) = V(x_1, x_2)\,. \tag{5.1}$$

`I:V-exch`

Moreover, the probability density of particle 1 to be at x_1 and particle 2 at x_2 must then remain unaltered under an exchange:

$$|\psi(x_2, x_1, t)|^2 = |\psi(x_1, x_2, t)|^2\,. \tag{5.2}$$

`I:prob-exch`

If $\phi(x_1, x_2, t)$ is *some* solution of the Schrödinger equation, then because of (5.1), so is any linear combination

$$\psi(x_1, x_2, t) = a\,\phi(x_1, x_2, t) + b\,\phi(x_2, x_1, t)\,.$$

Requiring (5.2) yields conditions on the coefficients a, b: $|a|^2 = |b|^2$ and $\overline{a}b = a\overline{b}$, which imply $b^2 = a^2$ and hence

$$b = \pm a\,.$$

We are thus left with two possibilities, symmetry or antisymmetry:

$$\psi(x_2, x_1, t) = \psi(x_1, x_2, t) \qquad \text{(bosons)} \qquad \text{or} \tag{5.3}$$

`I:boson`

$$\psi(x_2, x_1, t) = -\psi(x_1, x_2, t) \qquad \text{(fermions).} \tag{5.4}$$

`I:fermion`

Remarkably, for one kind of physical particle, always one and the same of the two cases is realized. The two situations lead to very different physical behaviour. It is the antisymmetry (5.4) that is known to hold for electrons, protons and neutrons: these are *fermions*. They obey the *Pauli exclusion principle* (Pauli 1925) which states that like particles cannot simultaneously be in the same quantum state. Note that (5.4) implies

$$\psi(x, x, t) = 0\,,$$

so that two identical fermions cannot be at the same position at the same time.

A product state does not have the antisymmetric behaviour (5.4) but it can be antisymmetrized: with two indistinguishable particles,

$$\psi(x_1, x_2, t) = \frac{1}{\sqrt{2}}\Big(\varphi_1(x_1, t)\varphi_2(x_2, t) - \varphi_1(x_2, t)\varphi_2(x_1, t)\Big)$$

has the required antisymmetry (and vanishes if $\varphi_1(\cdot, t) = \varphi_2(\cdot, t)$, in accordance with the Pauli principle), and so does the *Slater determinant*

$$\psi(x_1, \dots, x_N, t) = \frac{1}{\sqrt{N!}}\ \det\big(\varphi_j(x_n, t)\big)_{j,n=1}^{N} \tag{5.5}$$

`I:slater`

in the case of N identical particles. Approximation of the electronic wave function by Slater determinants of orthogonal orbitals (i.e., single-electron wave functions) φ_j is done in the time-dependent *Hartree–Fock method*, see Chapter II.

It is also of interest to see what is the effect of ignoring antisymmetry in the wave function of well-separated identical fermionic particles. Suppose that $\phi(x_1, x_2, t)$ is a solution of the time-dependent Schrödinger equation which is essentially localized near $(\langle x_1\rangle(t), \langle x_2\rangle(t))$ but which is not antisymmetric. As long as $\langle x_1\rangle(t)$ and

$\langle x_2\rangle(t)$ remain clearly separated (well beyond the widths $\Delta x_1(t)$ and $\Delta x_2(t)$), the antisymmetrization of ϕ does not deviate substantially from ϕ in a neighbourhood of $(\langle x_1\rangle(t), \langle x_2\rangle(t))$, so that the particles can be considered to be distinguishable by their well-separated positions. This observation often justifies ignoring antisymmetry in the treatment of identical *nuclei* of a molecule, for which the above localization and separation condition is usually met in chemistry. On the other hand, for the less localized *electrons* a careful treatment of antisymmetry is essential.

I.5.3 The Molecular Hamiltonian

For a molecule, the Hamiltonian is the sum of the kinetic energy of the nuclei and the electrons, and the potential is the sum of the Coulomb interactions of each pair of particles:

$$H_{\mathrm{mol}} = T + V \qquad \text{with} \quad T = T_N + T_e \quad \text{and} \quad V = V_{NN} + V_{Ne} + V_{ee}\,. \tag{5.6}$$

`I:Hmol`

For N nuclei of masses M_n and electric charges $Z_n e$, with position coordinates $x_n \in \mathbb{R}^3$, and L electrons of mass m and charge $-e$, with coordinates $y_\ell \in \mathbb{R}^3$, the respective kinetic energy operators are

$$T_N = -\sum_{n=1}^{N} \frac{\hbar^2}{2M_n}\,\Delta_{x_n} \qquad T_e = -\sum_{\ell=1}^{L} \frac{\hbar^2}{2m}\,\Delta_{y_\ell}\,,$$

and the potential is the sum of the nucleus-nucleus, nucleus–electron and electron–electron interactions given by

$$V_{NN}(x) = \sum_{1\le k<n\le N} \frac{Z_k\,Z_n\,e^2}{|x_k - x_n|}\,, \qquad V_{Ne}(x,y) = -\sum_{\ell=1}^{L}\sum_{n=1}^{N} \frac{Z_n e^2}{|y_\ell - x_n|}\,,$$
$$V_{ee}(y) = \sum_{1\le j<\ell\le L} \frac{e^2}{|y_j - y_\ell|}\,.$$

It is often convenient to choose *atomic units* where $\hbar = 1$, the elementary charge $e = 1$, the mass of the electron $m = 1$, and the Bohr radius of the hydrogen atom $r = 1$.

The self-adjointness of such Hamiltonian operators, with domain $H^2(\mathbb{R}^{3N+3L})$, has been shown by Kato (1951); see also Reed & Simon (1975), Theorem X.16.

Any attempt to "solve" numerically the molecular Schrödinger equation

$$i\hbar\,\frac{\partial\Psi}{\partial t} = H_{\mathrm{mol}}\,\Psi\,, \qquad \Psi = \Psi(x_1,\dots,x_N,y_1,\dots,y_L,t)$$

faces a variety of severe problems:

- the high dimensionality (even for a small molecule such as CO_2, there are 3 nuclei and 22 electrons, so that Ψ is a function on $\mathbb{R}^{75}$!);

- multiple scales in the system (the mass of the electron is approximately 1/2000 of the mass of a proton);
- highly oscillatory wave functions.

To obtain satisfactory results in spite of these difficulties, one requires a combination of *model reduction*, based on physical insight and/or asymptotic analysis, and *numerical techniques* used on the reduced models that are intermediate between classical and full quantum dynamics. This is the subject of the following chapters.