Molecular quantum dynamics

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CONTENTS

I. INTRODUCTION

A. Electronic structure and quantum dynamics

The large field of quantum chemistry can be conveniently divided into the subfields studying the electronic structure of molecules and molecular quantum dynamics. This division is far from precise because the two subfields are closely related, in particular thanks to the feasibility and increasing popularity of the "on-the-fly" quantum dynamics calculations relying on highly accurate electronic structure methods.

Knowing the **electronic structure** basically means solving the **time-independent Schrödinger equation** (**TISE**)

$$H\psi = E\psi \tag{1.1}$$

for the electrons in the molecule. (Here H is the electronic Hamiltonian at a given nuclear configuration, ψ is an electronic eigenfunction and E the corresponding eigenvalue of energy.) The hierarchy of electronic structure methods starts with the very accurate but computationally demanding wave function based *ab initio* methods or the density functional theory (**DFT**), continuing with the semi-empirical methods, and ending with the molecular mechanics force fields, which are the least accurate but computationally the most efficient. In this course, we will assume that the difficult electronic structure problem has been solved, i.e., that the Born-Oppenheimer **potential energy surfaces** (**PES**s) and possibly also the electric-dipole, nonadiabatic, and spin-orbit couplings are known. The molecular **quantum dynamics** then studies the solution of the **time-dependent Schrödinger equation** (**TDSE**)

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{1.2}$$

for the nuclei. [Here ψ is the nuclear wavefunction and H is the nuclear Hamiltonian, which contains the potential energy term depending on the solution of the electronic TISE (1.1).] The motion of nuclei can often be treated by classical molecular dynamics but in many situations the nuclear quantum effects are important. This is the case, e.g., in spectroscopy, in reactions involving hydrogen transfer, at low temperatures, etc. If the PESs are strongly coupled, one has to solve the molecular TDSE for electrons and nuclei simultaneously, and again quantum dynamics plays an important role.

In this course, we will study the TDSE from several perspectives:

1) exact methods of solution,

2) approximate and numerical methods of solution,

3) applications, and

4) mathematical formalism.

The three main areas that we will consider are

1) real-time quantum dynamics,

2) semiclassical approximation, and

3) imaginary-time quantum dynamics (i.e., quantum thermodynamics).

Let us demonstrate these three areas by three applications.

B. Photoabsorption spectrum by real-time quantum dynamics

The calculation of vibrationally resolved electronic spectra is a nontrivial problem in quantum chemistry. We will learn a useful procedure that employs quantum dynamics, and therefore, follows closely what happens at the microscopic level.

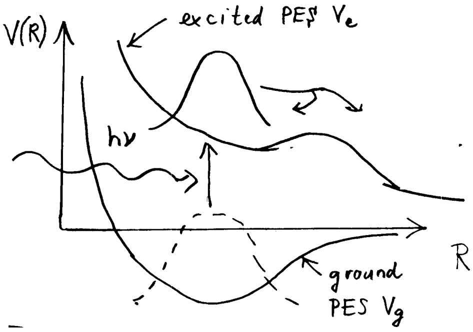

FIG. 1. Photoabsorption.

Postponing the details to a later chapter, let us summarize the procedure for evaluating the photoabsorption spectrum of a diatomic molecule here (see Fig. 1):

The initial state $|\psi(0)\rangle$ is the vibrational ground state of the electronic ground PES V_g,

$$H_g|\psi(0)\rangle = E_{g,0}|\psi(0)\rangle, \tag{1.3}$$

where the ground-state Hamiltonian $H_g = T + V_g$ and T is the kinetic energy operator. An interaction with light induces a transition to the excited electronic PES V_e. Assuming a **Franck-Condon transition**, **Condon approximation**, and **time-dependent perturbation theory**, we can use the **sudden approximation** which implies that the initial state on the excited surface is the exact image of the original state $|\psi(0)\rangle$. This state was a stationary state of V_g, but is no longer a stationary state on the excited PES. It will evolve under the quantum dynamics of V_e, according to the TDSE

$$i\hbar\frac{d|\psi(t)\rangle}{dt} = H_e|\psi(t)\rangle. \tag{1.4}$$

We will soon learn various methods for solving this equation, but for now, we can write its solution, i.e., the time-evolved state, formally as

$$|\psi(t)\rangle = e^{-iH_e t/\hbar}|\psi(0)\rangle. \tag{1.5}$$

The recurrences of the quantum dynamics are conveniently measured by the **autocorrelation function**

$$C(t) = \langle\psi(0)|\psi(t)\rangle, \tag{1.6}$$

equal to the overlap of the initial and time-evolved states (see Fig. 2).

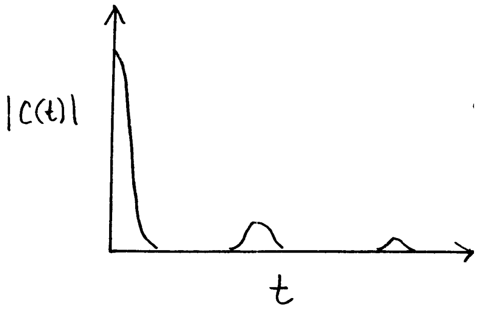

FIG. 2. Autocorrelation function.

Finally, the **photoabsorption spectrum** $\sigma(\omega)$ can be computed, up to a prefactor, as the Fourier transform of the autocorrelation function,

$$\sigma(\omega) = \frac{2\pi\omega}{3\hbar c}\int_{-\infty}^{\infty} C(t)\, e^{i\omega t}\, dt, \tag{1.7}$$

(see Fig. 3).

This approach has several advantages over the direct (i.e., time-independent) calculation of spectra:

1) The time-dependent approach makes the concept of a spectrum intuitive by relating the spectrum to the dynamics of the nuclear wavepacket.

2) The knowledge of the vibrational eigenstates of V_g and V_e, which would require a very difficult calculation, is not needed. This is a big advantage especially for polyatomic molecules.

3) A single quantum dynamics calculation gives the full spectrum. In particular, the use of approximate quantum dynamics methods makes the calculation of a spectrum very simple.

C. Semiclassical dynamics

1. *Bohr model of the hydrogen atom*

The semiclassical approximation which is now often wrongly considered a domain of specialists was born before the discovery of the Schrödinger equation. The simplest example of a semiclassical approximation is the **old quantum theory**, represented by the **Bohr model** of the hydrogen atom.

In this model, the electron is considered to move in circles around the proton (Fig. 4). (Strictly speaking, the motion is circular only if the angular momentum is zero. If the angular momentum is nonzero, the electron moves on elliptic orbits, but for simplicity, we shall not consider that here. A slightly more general version of Bohr-Sommerfeld quantization rules, described in a later chapter, can be still used.) The electron is further assumed to have wavelike properties with a wavelength

$$\lambda_{\mathrm{dB}} = h/p, \tag{1.8}$$

called **de Broglie wavelength.** The **Bohr-Sommerfeld quantization rules** state that the electron moves about the nucleus in circles whose circumference must equal an integer multiple of the de Broglie wavelength:

$$n\lambda_{\mathrm{dB}} = 2\pi r. \tag{1.9}$$

Finally, the "classical" part in the semiclassical approximation states that the **centripetal force** of the circular motion is given by the attractive **Coulomb force**,

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}. \tag{1.10}$$

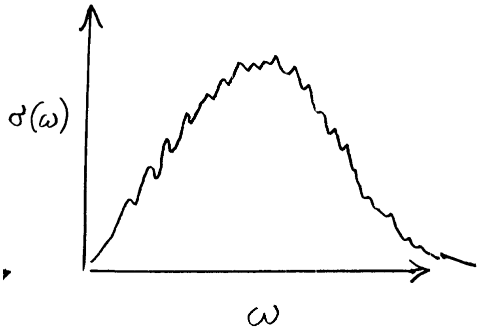

FIG. 3. Photoabsorption spectrum.

Equations (1.8) and (1.9) together yield

$$nh = 2\pi r p \tag{1.11}$$

and Eq. (1.10) can be written as

$$\frac{p^2}{m} = \frac{e^2}{4\pi\varepsilon_0 r}. \tag{1.12}$$

Substituting p from Eq. (1.11) into Eq. (1.12) gives

$$r = \frac{n^2 h^2 \varepsilon_0}{\pi m e^2} = n^2 a_0, \tag{1.13}$$

where $a_0 \approx 0.529\,\text{Å}$ is the **Bohr radius**. Now we can also compute the energy, which is

$$E_n = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r} = -\frac{e^2}{8\pi\varepsilon_0 r} = -\frac{1}{n^2}\frac{me^4}{8h^2\varepsilon_o^2} = -\frac{R_E}{n^2} \tag{1.14}$$

where $R_E \approx 13.6\,\text{eV}$ is the **Rydberg energy**. As the atomic unit of energy, one usually takes 1 **Hartree** $= 2R_E \approx 27.2\,\text{eV}$.

Comments:

1) The above approach is completely semiclassical: it only uses classical trajectories and never employs the Schrödinger equation.

2) The semiclassical hydrogen energies agree *precisely* with the exact quantum energies. This is rather lucky. In general, semiclassical methods can be very accurate, but they are hardly ever exact. The reason that the semiclassical energies are exact is deep and is connected to the **superintegrability** of the Coulomb problem.

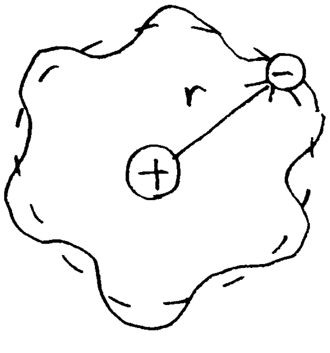

FIG. 4. Bohr model of the hydrogen atom.

Later, we will also discuss more advanced semiclassical methods. However, they all share the basic idea that the wavefunction can be written as a superposition of complex terms, each of which can be computed from classical quantities only. E.g., in the simplest case of two semiclassical (**SC**) contributions, the wave function would be

$$\psi_{\mathrm{SC}}(q,t) = \psi_1 + \psi_2 = A_1(q,t)e^{iS_1(q,t)/\hbar} + A_2(q,t)e^{iS_2(q,t)/\hbar}, \tag{1.15}$$

where the phase of the jth term, $S_j/\hbar$, is determined by the classical **action** S_j along a classical trajectory j. Both A_j and S_j are real numbers.

Consider again a photoabsorption problem, e.g., of the I_2 molecule (see Fig. 5), and assume the Franck-Condon vertical transition. One would often like to know the **radial distribution function** of the iodine molecule in the bound excited electronic state (see Fig. 6). Since the initial state $\psi(q,0)$ is not a stationary state, the wave function of I_2 will evolve after the excitation.

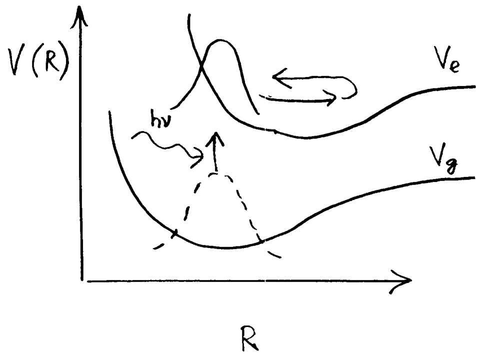

FIG. 5. Absorption of I_2.

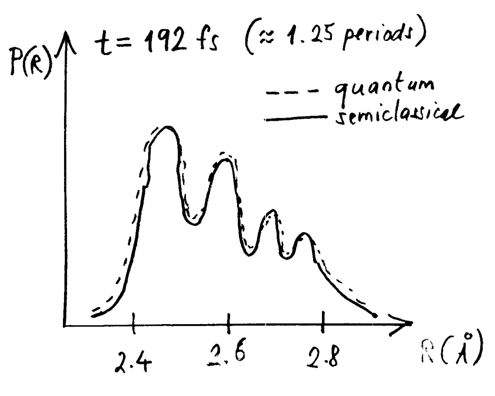

FIG. 6. Radial distribution function of I_2.

As the excited surface is bound, the wavepacket will oscillate. However, because the PES is anharmonic, the different components of the wavepacket will oscillate with different frequencies.

Instead of solving the TDSE exactly, one can use the semiclassical approximation and apply it to the various components of the wavepacket. For the sake of argument, let us make a huge oversimplification and assume that the wave packet consists of only two components, a slow component ψ_1 and a fast component ψ_2. The radial distribution function $P(R)$ is the probability density at a bond length R and can be computed from the wavefunction (1.15), here a function of R only, as its probability density

$$P(R) = |\psi(R)|^2 \approx |\psi_{\mathrm{SC}}(R)|^2 = A_1^2 + A_2^2 + 2A_1A_2 \cos\left[\left(S_1 - S_2\right)/\hbar\right].$$

Note the cosine term in the above equation: this term accounts qualitatively for the oscillations in the experimentally observed radial distribution function. This cosine term describes **interference** between the fast and slow components of the wavepacket. Just think of what happens at time when the faster component bounces from the right turning point and starts moving left while the slower component still moves to the right. The semiclassical approach can qualitatively and often quantitatively describe not only interference, but also **tunneling**, **zero point energy**, and other quantum effects.

D. Quantum effects on thermodynamic properties via quantum dynamics in imaginary time: thermal energy of a diatomic molecule

An important part of physical chemistry is the study of thermodynamic properties such as thermal energies, enthalpies, free energies, heat capacities, thermal rate constants, etc. In **statistical mechanics**, it is shown that any equilibrium thermodynamic property can be derived from the **partition function**,

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} \tag{1.16}$$

where $\beta := 1/k_B T$ is the inverse temperature scaled with the Boltzmann constant. For example, it is easy to show that the average **thermal energy**, defined as

$$\langle E \rangle := \frac{1}{Z} \sum_{n=0}^{\infty} E_n e^{-\beta E_n}, \tag{1.17}$$

can be obtained from the partition function using the relation

$$\langle E \rangle = -\frac{\partial \log Z(\beta)}{\partial \beta}. \tag{1.18}$$

If the partition function is computed classically, one obtains only the classical thermal energy. If the partition function is computed quantum-mechanically, one obtains the full quantum thermal energy.

The reason why we discuss thermodynamics in a course on quantum dynamics is because of the analogy

$$e^{-\beta E} \leftrightarrow e^{-iHt/\hbar} \tag{1.19}$$

between the Boltzmann factor and the exponential in the formal solution (1.5) of the TDSE. While on the left we have a real exponential and on the right a complex exponential, there are similarities in the solutions of these two problems. Defining

$$\tau := -i\hbar\beta, \tag{1.20}$$

the Boltzmann factor $\exp(-\beta H)$ becomes $\exp(-iH\tau/\hbar)$. Because of this, the quantum thermodynamics can and often is interpreted as the **quantum dynamics in imaginary time**. For now, you do not need to understand the analogy beyond the similarity of the equations.

Let us now consider the thermal energy of the vibrational motion of a diatomic molecule. For simplicity, we will assume that the vibrations are harmonic and uncoupled from the rotations. I.e., we will consider the vibrational Hamiltonian of the **simple harmonic oscillator** (**SHO**),

$$H(q,p) = \frac{p^2}{2\mu} + \frac{1}{2}kq^2, \tag{1.21}$$

where μ is the reduced mass and $q = R - R_{\text{eq}}$ is the extension of the bond length from equilibrium.

1. Classical thermal energy obtained from the equipartition theorem and from the classical molecular dynamics

First, we can compute the classical thermal energy by the **equipartition theorem** which states that every quadratic term in the Hamiltonian gives a contribution $k_BT/2$ to the thermal energy. For the SHO, this gives

$$\langle E\rangle_{\text{CL}} = 2 \times \frac{1}{2}k_BT = k_BT. \tag{1.22}$$

In more complicated systems, the equipartition theorem cannot be used and instead one uses **molecular dynamics**. In molecular dynamics, thermodynamic properties are computed by a dynamics simulation with a thermostat keeping constant temperature. In case of the thermal energy, the molecular dynamics evaluates numerically the integral,

$$\langle E\rangle_{\text{CL}} = \frac{1}{Z_{\text{CL}}}h^{-n}\int d^nq\int d^np\, H(q,p)\, e^{-\beta H(q,p)}, \tag{1.23}$$

where

$$Z_{\mathrm{CL}} = h^{-n} \int d^n q \int d^n p \, e^{-\beta H(q,p)} \tag{1.24}$$

is the classical partition function. Basically, the molecular dynamics consists of running a classical trajectory that explores the whole available phase space and evaluates the energy at each point along the trajectory (see Fig. 7).

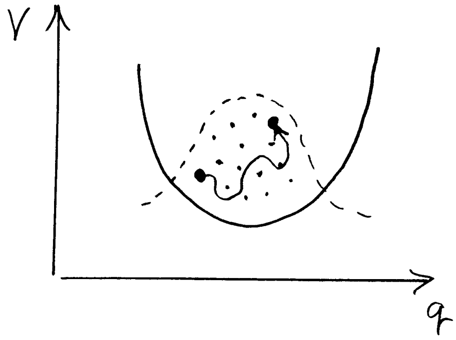

FIG. 7. Molecular dynamics in a simple harmonic oscillator.

The arithmetic average of the energy values along the trajectory can be shown to equal the phase space average energy (1.23).

Exercise 1 ***(Molecular dynamics by pen and paper)*** *Obtain the thermal energy for the SHO by evaluating the integrals (1.23)-(1.24) analytically. Does the result agree with the result obtained by the equipartition theorem?*

2. Quantum thermal energy obtained from the partition function and from the path integral molecular dynamics

The quantum thermal energy for the SHO can also be obtained analytically. Recall that the energy levels are

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right). \tag{1.25}$$

First, we get an analytical expression for the partition function: Defining $x := \exp(-\beta\hbar\omega)$, we have

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} = x^{1/2} \sum_{n=0}^{\infty} x^n = x^{1/2} \frac{1}{1-x} = \frac{1}{x^{-1/2} - x^{1/2}} \\ &= \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} = \frac{1}{2\sinh\frac{\beta\hbar\omega}{2}}. \end{aligned} \tag{1.26}$$

Now we can substitute the result for Z into the general expression (1.18) and find

$$\langle E\rangle_{\mathrm{QM}} = \frac{\hbar\omega/2}{\tanh\frac{\beta\hbar\omega}{2}}. \tag{1.27}$$

Exercise 2 *Show that the exact quantum result for thermal energy reduces to:*

1) the zero point energy $E_0 = \frac{\hbar\omega}{2}$ *for low temperatures* $T \rightarrow 0\,\mathrm{K}$ *and*

2) the classical energy $\langle E\rangle_{CL} = k_B T$ *for high temperatures* $T \rightarrow \infty$*.*

As in the classical case, the quantum thermal energy cannot be computed analytically for most molecules. However, there is an efficient generalization of the classical molecular dynamics, called **path integral molecular dynamics** (PIMD) which makes such a calculation possible for general systems. The PIMD takes into account anharmonicity, zero-point energy, coupling of vibrations and rotations, and correctly quantizes the nuclear motion.

Simply put, each atom in a molecule is replaced by P replicas (artificial atoms) which are connected with artificial harmonic bonds that correspond to the quantization of nuclear energy (see Fig. 8). For $P = 1$ one obtains classical thermodynamics and can perform usual molecular dynamics. For $P \rightarrow \infty$ one obtains the exact quantum thermodynamics. However, in practice, the nuclear quantum effects can be described adequately by a finite and relatively small value of P. E.g., at room temperature a sufficient value is $P = 4$ for heavy atoms like oxygen and $P = 32$ for hydrogen. If our diatomic molecule were H_2 at room temperature, we would obtain an artificial molecule consisting of $2 \times 32 = 64$ atoms. The quantum thermodynamics of the H_2 molecule is in PIMD replaced by the classical thermodynamics (i.e., classical molecular dynamics) of this so-called "ring polymer" consisting of 64 atoms.

E. Operators and observables

Recall that in quantum mechanics, a **state** of a mechanical system is represented by a **vector** in a complex Hilbert space and physical **observables** are represented by **linear operators** acting on these vectors. One often employs a specific representation, such as the **position representation**, in which the state is represented by a **wavefunction**. Below is a table containing several observables together with corresponding operators and the effect on the wavefunction $\psi(q, t)$ in position representation.

Observable	Operator	Effect on the wavefunction
position	$\hat{q}$	$q\,\psi(q,t)$
momentum	$\hat{p}$	$\frac{\hbar}{i}\nabla\psi(q,t)$
potential energy	$\hat{V} = V(\hat{q})$	$V(q)\,\psi(q,t)$
kinetic energy	$\hat{T} = \frac{\hat{p}^2}{2m}$	$-\frac{\hbar^2}{2m}\nabla^2\psi(q,t)$
Hamiltonian	$\hat{H} = \hat{T} + \hat{V}$	$-\frac{\hbar^2}{2m}\nabla^2\psi(q,t) + V(q)\,\psi(q,t)$

F. Dirac notation

It is often convenient to employ the **Dirac notation**, which simplifies expressions for expectation values of observables, overlaps of states, and the change of representation. In the Dirac notation, a vector in the Hilbert space is represented by a **ket** $|\psi(t)\rangle$, whereas a vector in the dual space (i.e., a linear form on the Hilbert space) is denoted by a **bra** $\langle\psi(t)|$. Note that there is only time dependence but no position dependence because both the ket and bra are independent of

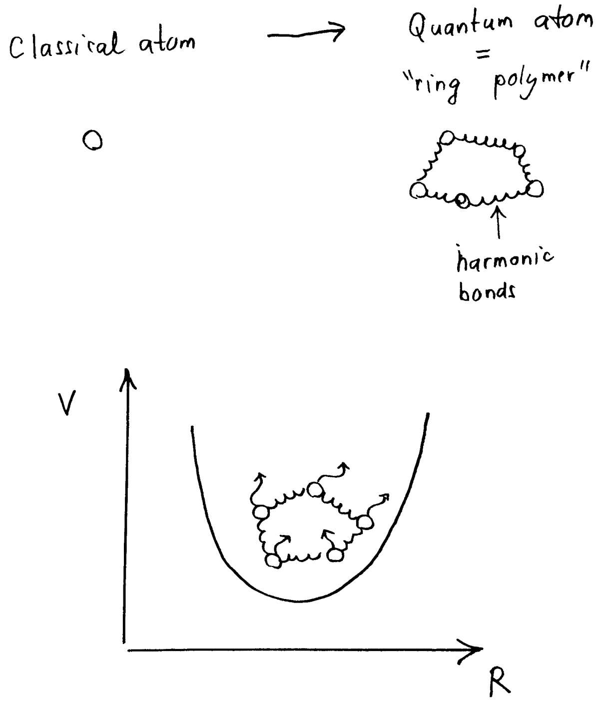

FIG. 8. Path integral molecular dynamics in a simple harmonic oscillator.

representation. E.g., the TDSE, written in the wavefunction form as

$$i\hbar\frac{\partial}{\partial t}\psi(q,t) = -\frac{\hbar^2}{2m}\nabla^2\psi(q,t) + V(q)\,\psi(q,t), \tag{1.28}$$

is simplified in the Dirac notation to the representation-independent expression

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle, \tag{1.29}$$

$$\hat{H} = \frac{\hat{p}^2}{2m} + V\left(\hat{q}\right). \tag{1.30}$$

Let us summarize the basic quantum-mechanical notions in the Dirac notation and compare them to the wavefunction form.

An **overlap** of states ψ and φ (i.e., their **inner product**) is denoted by $\langle\psi|\varphi\rangle$ and satisfies

$$\langle\psi|\varphi\rangle = \int \psi(q)^*\varphi(q)dq. \tag{1.31}$$

An **expectation value** of an operator $\hat{A}$ in the state ψ is denoted by $\langle A\rangle$ or, more precisely, by $\langle A\rangle_\psi$. If the operator $\hat{A} \equiv A(\hat{q})$ is independent of momentum $\hat{p}$, then

$$\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle = \int \psi(q)^*A(q)\psi(q)dq. \tag{1.32}$$

If $\hat{A} \equiv A(\hat{p})$ is independent of position $\hat{q}$, then

$$\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle = \int \psi(q)^*A\left(\frac{\hbar}{i}\frac{\partial}{\partial q}\right)\psi(q)dq. \tag{1.33}$$

A wave function $\psi(q)$ in **position representation** is written as

$$\langle q|\psi\rangle = \psi(q), \tag{1.34}$$

while the same state ψ in **momentum representation** would be written as

$$\langle p|\psi\rangle = \psi(p). \tag{1.35}$$

The eigenvector of the position operator $\hat{q}$ with eigenvalue q' is called the **position state**, denoted by $|q'\rangle$, and satisfies

$$\hat{q}|q'\rangle = q'|q'\rangle. \tag{1.36}$$

Similarly, the **momentum state** $|p'\rangle$ satisfies

$$\hat{p}|p'\rangle = p'|p'\rangle. \tag{1.37}$$

The momentum state is often called a **plane wave**.

A separable Hilbert space has an at most countable **orthonormal basis**, the vectors of which are denoted by $\varphi_n(q)$ in the wavefunction form and simply by $|n\rangle$ using the Dirac notation ($n \in \mathbb{N}$). An orthonormality condition means that different vectors are **orthogonal**, i.e., $\langle n|m\rangle = 0$ for $n \neq m$ and that each vector is **normalized**, i.e., has a unit **norm** $\|n\| := \langle n|n\rangle^{1/2} = 1$. The orthonormality condition is expressed compactly as

$$\langle n|m\rangle = \delta_{nm}, \tag{1.38}$$

where δ_{nm} is the **Kronecker delta** symbol:

$$\delta_{nm} = \begin{cases} 0 & \text{for } n \neq m \\ 1 & \text{for } n = m \end{cases}.$$

This was a **discrete basis**, but one sometimes encounters a **continuous basis**, such as the basis of position eigenstates, in which the overlap of two basis states satisfies

$$\langle q'|q''\rangle = \delta(q' - q'') \tag{1.39}$$

where $\delta(q)$ is the **Dirac delta function**. The “Dirac delta function” is, in fact, not a function, but rather a **distribution**. Roughly speaking, its value is zero for all $q \neq 0$ while $\delta(0) = \infty$ and its integral is given by

$$\int_{-\infty}^{\infty} \delta(q)dq = 1. \tag{1.40}$$

More precisely, it is defined by the following relation satisfied by any “test” function f:

$$\int_{-\infty}^{\infty} f(q - q')\delta(q')dq' = f(q). \tag{1.41}$$

Since an orthonormal basis is a complete orthonormal set, we can obtain the following relation, called a **resolution of identity**, which expresses the identity operator Id as a sum or integral and is extremely useful in derivations:

$$\mathrm{Id} = \sum_n |n\rangle\langle n| = \int dq|q\rangle\langle q| = \int dp|p\rangle\langle p|. \tag{1.42}$$

Using the above, we can already write a position state $|q'\rangle$ in position representation,

$$\psi_{q'}(q) = \langle q|q'\rangle = \delta(q - q'). \tag{1.43}$$

The plane wave $|p'\rangle$ in position representation is an exponential (you have seen this in a basic course on quantum mechanics by solving the Schrödinger equation for the **free particle**),

$$\psi_{p'}(q) = \langle q|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{iqp'/\hbar}. \tag{1.44}$$

Example 3 *Using the above rules in Dirac notation, we can derive the transformation of a position representation wavefunction to the momentum representation:*

$$\psi(p) = \langle p|\psi\rangle = \int dq\, \langle p|q\rangle\, \langle q|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int dq\, e^{-iqp/\hbar}\, \psi(q). \tag{1.45}$$

In other words, the momentum wavefunction is obtained by ***Fourier transforming*** *the position wavefunction.*

Details: The first equality is the momentum representation expression (1.35), the second equality uses the resolution of identity (1.42). Finally, the third equality uses the complex conjugate of the plane wave in position representation (1.44) and the position representation expression (1.34).

II. EXACT METHODS TO SOLVE THE TDSE

Now we are ready to present the first exact methods of solution of the TDSE.

A. Basis set solution of the TDSE: Time-independent H

First, we will describe the basis set solution of the TDSE with the time-independent Hamiltonian H.

Claim 4 *The general solution of the TDSE with a time-independent Hamiltonian H satisfying the initial condition $\psi(q,0) = \psi_0(q)$ is*

$$\psi\left(q,t\right) = \sum_n c_n \varphi_n(q) e^{-iE_n t/\hbar}, \tag{2.1}$$

where $\varphi_n(q)$ is the eigenfunction of H with eigenvalue E_n and the constant coefficient c_n is given by

$$c_n = \langle n|\psi_0\rangle = \int \varphi_n^*(q)\psi_0(q)dq. \tag{2.2}$$

Proof.

1. *Particular solution by separation of variables*

First, we consider **particular solutions** that can be written as a product

$$\psi(q,t) = \varphi(q)f(t) \tag{2.3}$$

of a function $\varphi(q)$ of position and a function $f(t)$ of time. We shall solve for $\varphi(q)$ and $f(t)$ by the method of **separation of variables**. The substitution of the product ansatz (2.3) into the TDSE (1.28) gives

$$i\hbar\varphi(q)\frac{d}{dt}f(t) = f(t)H\varphi(q), \tag{2.4}$$

$$\frac{i\hbar df(t)/dt}{f(t)} = \frac{H\varphi(q)}{\varphi(q)}, \tag{2.5}$$

where the second equation was obtained by dividing the first one by $\psi(q,t)$. Note that the left-hand side (LHS) of Eq. (2.5) is a function of time only whereas the right-hand side (RHS) is a function of position only. The only way that a function of t can equal a function of q is if both functions are constant, i.e., independent of t and independent of q. With a bit of foresight, we denote this "separation" constant E and conclude that the two functions $f(t)$ and $\varphi(q)$ must satisfy the equations

$$H\varphi(q) = E\varphi(q), \tag{2.6}$$

$$i\hbar\frac{df(t)}{dt} = Ef(t). \tag{2.7}$$

The first equation (2.6) above is nothing but the time-independent Schrödinger equation (1.1) in the position representation. Its general solutions are the **eigenfunctions** $\varphi_n(q)$ with **eigenvalues** called **eigenenergies** E_n. As the Hamiltonian is a Hermitian operator, the eigenenergies are real and the eigenfunctions can be taken to be orthonormal as in Eq. (1.38). In fact, if the eigenfunctions φ_n are normalized, they form an orthonormal basis of the Hilbert space.

2. *General solution*

As the TDSE in position representation is a linear **partial differential equation** (**PDE**), its general solution can be obtained as a superposition of the particular solutions (2.1). The coefficients c_n can be found from the initial conditions. At time $t = 0$, we must have

$$\psi(q,0) = \sum_n c_n\varphi_n(q) = \psi_0(q). \tag{2.8}$$

Multiplying on the left by $\varphi_m(q)^*$, integrating over q yields

$$\sum_n c_n \int \varphi_m(q)^*\varphi_n(q)dq = \int \varphi_m(q)^*\psi_0(q)dq. \tag{2.9}$$

Recalling the orthonormality $\langle m|n\rangle = \delta_{mn}$ on the LHS gives the result (2.2), completing the proof.□

Strictly speaking, one typically needs an infinite basis $|n\rangle$ of the Hilbert space for the claim to be true. In practice, the full basis is replaced with a truncated, finite **basis set**. The claim then provides an optimal solution of the TDSE within the subspace of the full Hilbert space spanned by the finite basis set. This method is know in mathematics as the **Galerkin method**.

The solution (2.1) is expressed as a linear combination of stationary states, each of which has a time dependence of different frequency. As we shall see later, this difference between frequencies is precisely what gives rise to time dependence in quantum dynamics.

B. Basis set solution of the TDSE: Time-dependent H

Now we assume that the Hamiltonian is time-dependent. In general, a time-dependent Hamiltonian $H(t)$ can be written as a sum

$$H(t) = H_0 + V(t), \tag{2.10}$$

where H_0 is a time-independent component and $V(t)$ is the time-dependent component. This splitting is very useful in describing interaction of atoms or molecules with the electromagnetic field, where H_0 is the time-independent **molecular Hamiltonian** and $V(t)$ the **interaction of the molecule with the field** (e.g., the field of a laser).

Claim 5 *The general solution of the TDSE with the time-dependent Hamiltonian (2.10) and initial condition* $\psi(q,0) = \psi_0(q)$ *is*

$$\psi\left(q,t\right) = \sum_n c_n(t)\varphi_n(q)e^{-iE_nt/\hbar}, \tag{2.11}$$

where φ_n *and* E_n *are the eigenfunctions and eigenenergies of* H_0*. The time-dependent expansion coefficients are the solutions of the system of* ***ordinary differential equations (ODEs)***

$$\dot{c}_m(t) = -\frac{i}{\hbar}\sum_n e^{i\omega_{mn}t}V_{mn}(t)c_n(t) \tag{2.12}$$

with initial conditions $c_n(0) = \langle n|\psi_0\rangle$ *. In Eq. (2.12), the transition frequency* ω_{mn} *is defined as*

$$\omega_{mn} := \frac{E_m - E_n}{\hbar}, \tag{2.13}$$

and V_{mn} *is the matrix element*

$$V_{mn}(t) = \langle m|V(t)|n\rangle\,. \tag{2.14}$$

Proof: Expression (2.11) is an ansatz to be substituted into the TDSE (1.28), which is justified by the fact that $\varphi_n(q)$ forms a complete set in the Hilbert space and so any permissible function $\psi(q,t)$ can be written in the form (2.11). Upon substitution, one obtains

$$i\hbar \sum_n \left(\dot{c}_n(t) - \frac{i}{\hbar} E_n c_n(t) \right) \varphi_n(q) e^{-iE_n t/\hbar} = \sum_n c_n(t) \left(E_n + V(q,t) \right) \varphi_n(q) e^{-iE_n t/\hbar}, \tag{2.15}$$

$$i\hbar \sum_n \dot{c}_n(t) \varphi_n(q) e^{-iE_n t/\hbar} = \sum_n c_n(t) V(q,t) \varphi_n(q) e^{-iE_n t/\hbar},$$

where the terms containing a factor E_n have cancelled between the left- and right-hand sides. Multiplication by $\varphi_m(q)^*$ and integration over q yield

$$i\hbar \sum_n \dot{c}_n(t) e^{-iE_n t/\hbar} \langle m|n\rangle = \sum_n c_n(t) V_{mn}(t) e^{-iE_n t/\hbar}. \tag{2.16}$$

Since $\langle m|n\rangle = \delta_{mn}$, multiplication by $\exp(iE_m t/\hbar)$ gives the ODE (2.12). The initial conditions are obtained in the same way as in the previous case, completing the proof.□

We have converted the TDSE into a system of linear ODEs for the expansion coefficients c_n. This system can be solved numerically and sometimes even analytically. In general, it is a much simpler problem, especially if only few eigenstates are coupled by the time-dependent potential. In practice, the initial state is often an eigenstate $|m\rangle$ of H_0, so $c_n(0) = \delta_{nm}$. E.g., in spectroscopy it is often the vibrational eigenstate of the electronic ground state of a molecule. The time-dependent electromagnetic field induces transitions to other vibrational states (in **infrared spectroscopy**) or even to other electronic states (in **electronic spectroscopy**).

C. Nonorthogonal, time-dependent basis set solution of the TDSE with a time-dependent Hamiltonian

Let us generalize the previous two methods as much as possible. The goal is to find the quantum state $|\psi(t)\rangle$ that solves the TDSE

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle \tag{2.17}$$

with the initial condition

$$|\psi(0)\rangle = |\psi_0\rangle. \tag{2.18}$$

In this section, both the Hamiltonian *and* the basis can be time-dependent. Moreover, the basis may be nonorthogonal. Most cases in the literature can be obtained as special cases of the general result that we derive below.

We seek a solution in the form

$$|\psi(t)\rangle = \sum_n c_n(t)|n(t)\rangle, \tag{2.19}$$

where $|n(t)\rangle$ is a possibly nonorthogonal, time-dependent basis with the **overlap matrix**

$$S_{kn}(t) := \langle k(t)|n(t)\rangle. \tag{2.20}$$

One usually assumes that the basis states are normalized, i.e.,

$$S_{nn}(t) = 1,$$

but this assumption is not needed for what follows.

In order that $|\psi(t)\rangle$ satisfy the initial condition (2.18), the coefficients $c_n(t)$ must satisfy the coupled initial conditions

$$\sum_n S_{kn}(0)c_n(0) = \langle k(0)|\psi_0\rangle\,, \tag{2.21}$$

which can be shown by projecting the ansatz (2.19) onto a bra vector $\langle k(0)|$.

Inserting the ansatz (2.19) into the TDSE (2.17) and projecting onto the bra vector $\langle k|$ yield an equivalent system of linear ODEs for the coefficients $c_n(t)$:

$$i\hbar\sum_n S_{kn}(t)\dot{c}_n(t) = \sum_n \left(H_{kn}(t) - i\hbar D_{kn}(t)\right)c_n(t), \tag{2.22}$$

where

$$H_{kn}(t) = \langle k(t)|\hat{H}(t)|n(t)\rangle \tag{2.23}$$

is the time-dependent **Hamiltonian matrix element** in our time-dependent basis and

$$D_{kn}(t) := \langle k(t)|\dot{n}(t)\rangle \tag{2.24}$$

is the **nonadiabatic coupling matrix**. This matrix describes the coupling between states $|k(t)\rangle$ and $|n(t)\rangle$ due to the time dependence of the basis.

In matrix notation, equation (2.22) becomes

$$i\hbar\mathbf{S}(t)\dot{\mathbf{c}}(t) = \left(\mathbf{H}(t) - i\hbar\mathbf{D}(t)\right)\mathbf{c}(t). \tag{2.25}$$

This very general result contains seven special cases, which are obtained by all possible combinations of the following three assumptions:

1) A **time-independent basis** satisfies

$$|\dot{n}(t)\rangle = 0, \tag{2.26}$$

implying that the nonadiabatic coupling matrix vanishes and that the overlap matrix is time-independent, i.e.,

$$\mathbf{D}(t) = \mathbf{0} \text{ and } \mathbf{S}(t) = \mathbf{S}. \tag{2.27}$$

2) An **orthonormal basis** is defined by

$$\mathbf{S}(t) = \mathbf{1}. \tag{2.28}$$

3) A **time-independent Hamiltonian** means that

$$\hat{H}(t) = \hat{H}. \tag{2.29}$$

In the case of time-dependent Hamiltonians $\hat{H}(t)$, two special orthonormal bases are useful:

i) If $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$, where $\hat{H}_0$ is a time-independent component, it is often useful to solve the problem using the time-independent eigenbasis of $\hat{H}_0$. In fact, this is what we did in the previous section.

ii) The time-dependent instantaneous eigenbasis of a time-dependent Hamiltonian $\hat{H}(t)$, i.e., a basis defined by the eigenvalue equation

$$\hat{H}(t)|n(t)\rangle = E_n(t)|n(t)\rangle \tag{2.30}$$

and depending continuously on time t. This basis is called the **adiabatic basis**.

D. Time-dependence in QM (See Tannor)

Stationary state, wave packet, expectation value

E. Free-particle wave packet (See Tannor)

particular solution

$$\psi(q,t) = e^{i(kq-\omega t)}$$

$$p = \hbar k, \quad E = \hbar\omega, \quad \omega(k) = \frac{\hbar k^2}{2m}$$

de Broglie relation, Einstein relation, dispersion relation, phase velocity, group velocity

general solution

$$\psi(q,t) = \frac{1}{\sqrt{2\pi}} \int a(k) e^{i(kq - \hbar k^2 t/2m)} dk$$

How to find $a(k)$?

center of the wavepacket, dispersion of the wavepacket

III. GAUSSIAN WAVE PACKET

Note that I use a different convention for α than Tannor, in order to simplify various equations and to extract dependence on $\hbar$, and—if necessary—include the normalization factor in γ.

A Gaussian wavepacket is a wavefunction whose position dependence is a complex Gaussian function

$$\psi(x) = \exp\left\{ \frac{i}{\hbar} \left[\frac{1}{2}\alpha\,(x-q)^2 + p(x-q) + \gamma \right] \right\} \tag{3.1}$$

with real parameters q and p and complex parameters α and γ. As we shall see below, q and p specify the position and momentum of the center of the wavepacket, α controls the width and position-momentum correlation, and γ determines the phase and normalization of the wavepacket. In order that the wavefunction be normalizable, it is necessary that $\operatorname{Im}\alpha > 0$. The norm of the Gaussian (3.1) is then

$$\|\psi\| = e^{-\operatorname{Im}\gamma/\hbar} \left(\pi\hbar/\operatorname{Im}\alpha\right)^{1/4}, \tag{3.2}$$

which follows from the simple calculation

$$\begin{aligned} \|\psi\|^2 = \langle\psi|\psi\rangle = \int_{-\infty}^{\infty} |\psi\,(x)|^2\, dx &= \int_{-\infty}^{\infty} \exp\left\{ -\frac{1}{\hbar} \left[\operatorname{Im}\alpha\,(x-q)^2 + 2\operatorname{Im}\gamma \right] \right\} dx \\ &= \left(\frac{\pi\hbar}{\operatorname{Im}\alpha} \right)^{1/2} e^{-2\operatorname{Im}\gamma/\hbar}. \end{aligned} \tag{3.3}$$

where we have used the standard Gaussian integral

$$\int_{-\infty}^{\infty} \exp\left(-ax^2 + bx + c\right) dx = \sqrt{\frac{\pi}{a}} \exp\left(\frac{b^2}{4a} + c \right), \tag{3.4}$$

valid for complex numbers a, b, c with $\operatorname{Re} a > 0$. Equation (3.2) implies that the Gaussian wavepacket (3.1) is normalized if

$$\gamma = \operatorname{Re}\gamma + i\frac{\hbar}{4} \ln\left(\pi\hbar/\operatorname{Im}\alpha\right), \tag{3.5}$$

where $\operatorname{Re}\gamma$ is arbitrary.

Gaussian wavepackets play a very special role in quantum mechanics for the following reason: if the potential energy function is at most quadratic, i.e., if

$$V(x) = ax^2 + bx + c, \tag{3.6}$$

then a Gaussian wavepacket retains the Gaussian form (3.1) for all times. Moreover, a Gaussian wavefunction is localized both in position and momentum, so it is as close as it gets to the classical situation, where one can determine position and momentum simultaneously.

A. General properties of a Gaussian wavepacket

In the lecture, I showed that the **center** of the Gaussian wavepacket, defined as the expectation value of position and momentum operators, was simply given as

$$\langle \hat{x} \rangle = q \quad \text{and} \quad \langle \hat{p} \rangle = p. \tag{3.7}$$

The **width** of a wavepacket is measured by the uncertainties Δx and Δp of the position and momentum. The **uncertainty** ΔA for a general Hermitian operator $\hat{A}$ is defined as the root mean squared

$$\Delta A := \langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle^{1/2} = (\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2)^{1/2}. \tag{3.8}$$

For a Gaussian wavepacket, the position and momentum uncertainties are

$$\Delta x = \sqrt{\frac{\hbar}{2 \operatorname{Im} \alpha}} \quad \text{and} \quad \Delta p = |\alpha| \sqrt{\frac{\hbar}{2 \operatorname{Im} \alpha}}. \tag{3.9}$$

Note that these satisfy

$$\Delta x \Delta p = \frac{\hbar}{2} \frac{|\alpha|}{\operatorname{Im} \alpha} \geq \frac{\hbar}{2} \tag{3.10}$$

because $|\alpha| \geq \operatorname{Im}\alpha$. This proves the **Heisenberg uncertainty relation** $\Delta x \Delta p \geq \hbar/2$ for the special case of Gaussian wavepackets. Moreover, since $|\alpha| = \operatorname{Im}\alpha$ if and only if α is purely imaginary, we can conclude that the inequality becomes equality $\Delta x \Delta p = \hbar/2$ for Gaussian wavepackets with purely imaginary α, which are, therefore, called **minimum uncertainty wavepackets**.

B. Gaussian free particle ($V = 0$)

Let the initial wavefunction at $t = 0$ have zero position and momentum ($q_0 = p_0 = 0$), i.e.,

$$\psi(x, 0) = \exp\left[\frac{i}{\hbar}\left(\frac{1}{2}\alpha_0 x^2 + \gamma_0\right)\right]. \tag{3.11}$$

As I have shown in the lecture, the wavefunction at time t will be

$$\psi(x,t) = \sqrt{\frac{\alpha_t}{\alpha_0}} \exp\left[\frac{i}{\hbar}\left(\frac{1}{2}\alpha_t x^2 + \gamma_0\right)\right] = \exp\left[\frac{i}{\hbar}\left(\frac{1}{2}\alpha_t x^2 + \gamma_t\right)\right], \tag{3.12}$$

where

$$\alpha_t = \frac{\alpha_0}{1 + t\alpha_0/m}, \tag{3.13}$$

$$\gamma_t = \gamma_0 + i\frac{\hbar}{2}\ln(1 + \alpha_0 t/m), \tag{3.14}$$

and where in the last step of Eq. (3.12), we have absorbed the prefactor $\sqrt{\alpha_t/\alpha_0}$ into γ_t. This shows that the free particle Gaussian wavepacket indeed remains a Gaussian of the form (3.1). In contrast to classical mechanics, where a free particle with zero initial momentum simply remains at the initial position, in quantum mechanics the uncertainty in position changes with time. For purely imaginary α_0, the wavepacket **spreads** with increasing time—the expectation value of position remains constant, but the uncertainty Δx of position increases with time.

C. Gaussian wavepacket in a harmonic oscillator

Now let us turn to the Gaussian wavepacket (3.1) in a simple harmonic oscillator potential

$$V(x) = \frac{1}{2}m\omega^2 x^2. \tag{3.15}$$

We will show that the **ansatz**

$$\psi(x,t) = \exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\alpha_t\left(x - q_t\right)^2 + p_t(x - q_t) + \gamma_t\right]\right\} \tag{3.16}$$

solves the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi + \frac{1}{2}m\omega^2 x^2\psi \tag{3.17}$$

for the simple harmonic oscillator exactly.

We start by evaluating the partial derivatives of $\psi(x,t)$:

$$\frac{\partial\psi}{\partial x} = \frac{i}{\hbar}\left[\alpha_t\left(x - q_t\right) + p_t\right]\psi, \tag{3.18}$$

$$\frac{\partial^2\psi}{\partial x^2} = \left\{\left(\frac{i}{\hbar}\right)^2\left[\alpha_t\left(x - q_t\right) + p_t\right]^2 + \frac{i}{\hbar}\alpha_t\right\}\psi, \tag{3.19}$$

$$\frac{\partial\psi}{\partial t} = \frac{i}{\hbar}\left\{\frac{1}{2}\dot{\alpha}_t\left(x - q_t\right)^2 - \dot{q}_t\left[\alpha_t\left(x - q_t\right) + p_t\right] + \dot{p}_t(x - q_t) + \dot{\gamma}_t\right\}\psi. \tag{3.20}$$

Next, we substitute these derivatives into the TDSE (3.17). Because this *partial* differential equation must hold at all values of x, we separately look at different powers of $(x-q_t)$ and the prefactor of each power will give us a separate equation for the parameters of the Gaussian. Since there are only three powers appearing, namely $(x-q_t)^0$, $(x-q_t)^1$, and $(x-q_t)^2$, we find three complex *ordinary* differential equations for the parameters. The zeroth power gives an equation for $\dot{\gamma}_t$, whereas the second power gives an equation for $\dot{\alpha}_t$. The first power mixes equations for $\dot{q}_t$ and $\dot{p}_t$, but because q_t and p_t are real, by taking real and imaginary part of the equation we can obtain two real ordinary differential equations. In summary, we find that the partial differential TDSE is equivalent to the system of four ordinary differential equations (of which the first and last are complex, while the second and third are real):

$$\dot{\alpha}_t = -\alpha_t^2/m - m\omega^2, \tag{3.21}$$

$$\dot{p}_t = -m\omega^2 q_t, \tag{3.22}$$

$$\dot{q}_t = p_t/m, \tag{3.23}$$

$$\dot{\gamma}_t = \frac{p_t^2}{2m} - \frac{1}{2}m\omega^2 q_t^2 + \frac{i\hbar}{2m}\alpha_t. \tag{3.24}$$

Before solving these equations analytically, let us discuss their meaning: While the equation for $\dot{q}_t$ is the relation between classical velocity ($\dot{q}_t$) and momentum (p_t), the equation for $\dot{p}_t$ can be rewritten as **Newton's equation of motion**

$$\dot{p}_t = -V'(q_t) \tag{3.25}$$

for the simple harmonic oscillator potential (3.15). This implies that in the simple harmonic oscillator, the center (q_t, p_t) of a Gaussian wavepacket follows classical equations of motion! Those familiar with **Lagrangian mechanics** (which will be covered in the next lecture) will recognize that the first two terms in Eq. (3.24) for $\dot{\gamma}_t$ are nothing but the Lagrangian $L(q_t, \dot{q}_t)$ itself! Recall that the **Lagrangian** is defined as the difference between kinetic and potential energies,

$$L(q, \dot{q}) = T(\dot{q}) - V(q), \tag{3.26}$$

where

$$T(\dot{q}) = \frac{1}{2}m\dot{q}^2 \tag{3.27}$$

is the **kinetic energy** written as a function of velocity [we used the relation (3.23) between p_t and $\dot{q}_t$]. Those familiar with **Hamiltonian mechanics** (which will be covered in the next lecture) will recognize that the equations for $\dot{q}_t$ and $\dot{p}_t$ are also **Hamilton's equation of motion**

$$\dot{p}_t = -\frac{\partial H}{\partial q}(q_t, p_t), \tag{3.28}$$

$$\dot{q}_t = \frac{\partial H}{\partial p}(q_t, p_t) \tag{3.29}$$

for the simple harmonic oscillator Hamiltonian

$$H(q, p) = T(p) + V(q), \tag{3.30}$$

where the kinetic energy $T(p) = p^2/2m$ is expressed in terms of momentum instead of velocity.

Claim. Equations of motion (3.21)-(3.24) for the parameters of a Gaussian wavepacket in a simple harmonic oscillator have the analytical solution

$$q_t = q_0 \cos\omega t + \frac{p_0}{a}\sin\omega t, \tag{3.31}$$

$$p_t = p_0 \cos\omega t - a q_0 \sin\omega t, \tag{3.32}$$

$$\alpha_t = a\frac{\alpha_0\cos\omega t - a\sin\omega t}{a\cos\omega t + \alpha_0 \sin\omega t}, \tag{3.33}$$

$$\gamma_t = \gamma_0 + \frac{1}{2}\left(p_t q_t - p_0 q_0 + i\hbar \ln\frac{z_t}{a}\right), \tag{3.34}$$

where

$$a := m\omega, \tag{3.35}$$

$$z_t := \alpha_0 \sin\omega t + a\cos\omega t. \tag{3.36}$$

Proof. Equations (3.31) and (3.32) can be obtained from the system of linear ordinary differential Eqs. (3.22) and (3.23) by any standard method of solution. One can easily verify the result by differentiation and checking the initial conditions at $t = 0$. In fact, one can prove the claim for α_t and γ_t also by "verification" but let us show in detail how we would obtain the result constructively, if we were not given the answer.

The ordinary differential equation (3.21) can be solved by **separation of variables**:

$$\frac{d\alpha}{\alpha^2 + a^2} = -\frac{1}{m}dt.$$

Integrating both sides from time 0 to t gives

$$\int_{\alpha_0}^{\alpha_t} \frac{d\alpha}{\alpha^2 + a^2} = -\frac{1}{m}\int_0^t dt'$$
$$\frac{1}{a}\arctan\frac{\alpha}{a}\Big|_{\alpha_0}^{\alpha_t} = -\frac{t}{m}.$$

Now we need to invert this equation to obtain α_t explicitly. We do it by first defining $\beta := \alpha/a$:

$$\arctan \beta_t - \arctan \beta_0 = -\omega t.$$

Now let us use an identity for the difference of two arctan functions:

$$\begin{aligned} \arctan \frac{\beta_t - \beta_0}{1 + \beta_t \beta_0} &= -\omega t \\ \frac{\beta_t - \beta_0}{1 + \beta_t \beta_0} &= -\tan \omega t. \end{aligned}$$

Now it is straightforward to obtain β_t in terms of β_0:

$$\beta_t = \frac{\beta_0 - \tan \omega t}{1 + \beta_0 \tan \omega t},$$

which implies directly Eq. (3.33).

To solve Eq. (3.24) for $\dot{\gamma}_t$, we first note that Eq. (3.33) for α_t can be written as

$$\alpha_t = \frac{a}{\omega} \frac{\dot{z}_t}{z_t},$$

where z_t is defined in Eq. (3.36). Also using $p_t = m\dot{q}_t$ and $\dot{p}_t = -m\omega^2 q_t$ [Eqs. (3.23) and (3.22)], we can rewrite Eq. (3.24) as

$$\begin{aligned} \dot{\gamma}_t &= \frac{1}{2} (p_t \dot{q}_t + \dot{p}_t q_t) + \frac{i\hbar}{2} \frac{\dot{z}_t}{z_t} \\ &= \frac{1}{2} \frac{d}{dt} (p_t q_t + i\hbar \ln z_t), \end{aligned}$$

which directly implies the final Eq. (3.34) for γ_t and completes the proof.

Exercise 6 *Analyze the quantum-mechanical motion of a Gaussian wavepacket (3.1) in a linear potential* $V(x) = ax$*. Obtain and solve the equations of motion for parameters* q_t*,* p_t*,* α_t*, and* γ_t *by following the procedure used above for the harmonic oscillator.*

D. Thawed Gaussian approximation (Heller 1975)

Now imagine that the potential $V(x)$ is not harmonic. Solving the TDSE is very difficult in general, but if the initial state is a Gaussian, it is localized and so one may try to approximate the potential energy by the **local harmonic approximation** about the center of the wavepacket:

$$V(x,t) \approx V_{\mathrm{LHA}}(x, q_t) := V(q_t) + V'(q_t)(x - q_t) + \frac{1}{2} V''(q_t)(x - q_t)^2.$$

This is a time-dependent harmonic potential, which depends on time implicitly via the time-dependent center q_t of the Gaussian. So, using our results for the harmonic oscillator, we get immediately (after shifting the minimum):

$$\dot{\alpha}_t = -\alpha_t^2/m - V''(q_t), \tag{3.37}$$

$$\dot{p}_t = -V'(q_t), \tag{3.38}$$

$$\dot{q}_t = p_t/m, \tag{3.39}$$

$$\dot{\gamma}_t = \frac{p_t^2}{2m} - V(q_t) + \frac{i\hbar}{2m}\alpha_t. \tag{3.40}$$

These equations express the **thawed Gaussian approximation**, proposed by Heller in 1975. (The name "thawed" was motivated by the flexible width of the Gaussian, in contrast to the fixed width of a **frozen Gaussian** discussed below.)

In the simple harmonic oscillator potential (3.15), i.e., $V(x) = m\omega^2 x^2/2$, these equations immediately reduce to the *exact* Eqs. (3.21)-(3.24) derived in the previous section for the Gaussian wavepacket in harmonic potential, showing that the thawed Gaussian approximation is exact in *globally* harmonic potentials. For short times, the approximation is accurate in general potentials, but it breaks down at longer times, when **anharmonicity** becomes more important and can even lead to **wavepacket splitting**, which, of course, cannot be captured by a single Gaussian ansatz for the wavefunction.

E. Coherent state of a harmonic oscillator

Consider again a Gaussian in a simple harmonic oscillator. Now imagine that the initial width parameter α_0 satisfies

$$\alpha_0 = ia = im\omega.$$

Quick inspection of Eq. (3.33) for α_t shows that, due to a cancellation between the numerator and denominator,

$$\alpha_t = \alpha_0 = ia.$$

In other words, the width parameter remains constant. Such a special Gaussian wavepacket is called a **coherent state** of the simple harmonic oscillator. It is sometimes called a **frozen Gaussian**, because its width parameter is "frozen". Equations for $\dot{q}_t$ and $\dot{p}_t$ remain the same classical equations, but the equation (3.24) for $\dot{\gamma}_t$ simplifies to

$$\dot{\gamma}_t = \frac{p_t^2}{2m} - \frac{1}{2}m\omega^2 q_t^2 - \frac{1}{2}\hbar\omega = p_t\dot{q}_t - H\left(q_t, p_t\right) - \frac{1}{2}\hbar\omega. \tag{3.41}$$

F. Frozen Gaussian approximation (Heller 1981)

Now assume that the potential is arbitrary and, in particular, not harmonic.

First imagine that you would like to make an even more drastic approximation than the thawed Gaussian approximation and approximate the wavefunction by a "frozen Gaussian", i.e., a Gaussian of a fixed width. Assuming again that the center of the Gaussian is moving classically and inspired by the last form of Eq. (3.41) for $\dot{\gamma}_t$ for a coherent state in a harmonic oscillator, Heller proposed the following equations of motion for the Gaussian parameters:

$$\alpha_t = \alpha_0, \tag{3.42}$$

$$\dot{p}_t = -V'(q_t), \tag{3.43}$$

$$\dot{q}_t = p_t/m, \tag{3.44}$$

$$\dot{\gamma}_t = p_t\dot{q}_t - \langle\psi(t)|\hat{H}|\psi\left(t\right)\rangle, \tag{3.45}$$

where $\psi\left(t\right)$ is the frozen Gaussian parametrized by $\alpha_t = \alpha_0$, q_t, p_t, and γ_t.

In fact, Heller was not interested in making such a drastic approximation, but rather in improving upon the thawed Gaussian approximation. He decided to approximate the wavefunction by a superposition of *several* frozen Gaussians:

$$\psi\left(x,t\right) := \sum_n c_n\psi_n\left(x,t\right). \tag{3.46}$$

Because the thawed Gaussian approximation used only a single Gaussian, it required a flexible width to describe the spreading of the wavepacket. In contrast, the superposition (3.46) of several frozen Gaussians can describe spreading of the wavepacket without needing a flexible width parameter. Indeed, it can describe not only the linear spreading as in the thawed Gaussian approximation, but also the nonlinear spreading and even wavepacket splitting because each frozen Gaussian evolves along its own classical trajectory according to Eqs. (3.42)-(3.45), where each of the parameters α_t, q_t, p_t, γ_t, and $\psi\left(t\right)$ should now also have an index n. This describes the essence of the **frozen Gaussian approximation** proposed by Heller in 1981. [!!! Add a figure.]

IV. REVIEW OF CLASSICAL MOLECULAR DYNAMICS

We have seen that the exact solution of the quantum dynamics of a GWP in a harmonic, linear, or constant potential leads to the equations of motion for the center of the wave packet that are the same as the classical equations of motion. A similar analogy between quantum and classical dynamics appears in many situations. At this point, it is, therefore, useful to review various formulations of classical dynamics.

A. Newtonian mechanics

The oldest formulation of classical dynamics is the Newtonian mechanics, which is based on **Newton's equation of motion** (also known as **Newton's second law**),

$$m\frac{d^2}{dt^2}\mathbf{q} = -\nabla V(\mathbf{q}). \tag{4.1}$$

In a more general form useful in relativistic classical dynamics or in other situations where the mass is not constant, the equation is written as

$$\frac{d\mathbf{p}}{dt} = \mathbf{F}(\mathbf{q}), \tag{4.2}$$

where $\mathbf{F}$ is the **force**.

In Molecular Dynamics, Newton's equation describes the motion of nuclei. In the simplest case, $V(\mathbf{q})$ gives the so-called "molecular mechanics force field." Note that this is a misnomer since $V(\mathbf{q})$ is not a force, but a potential. In *ab initio* molecular dynamics, $V(\mathbf{q})$ is a more sophisticated function of coordinates. E.g., in **Born-Oppenheimer molecular dynamics**, $V(\mathbf{q})$ is given by the expectation value

$$V(\mathbf{q}) = \langle \Psi_{\mathrm{el,g}}(\mathbf{q}) | \hat{H}_{\mathrm{el}}(\mathbf{q}) | \Psi_{\mathrm{el,g}}(\mathbf{q}) \rangle,$$

where $|\Psi_{\mathrm{el,g}}(\mathbf{q})\rangle$ is the ground state of the electronic Hamiltonian (including the nuclear repulsion) $\hat{H}_{\mathrm{el}}(\mathbf{q})$ at nuclear positions $\mathbf{q}$. In other words, $|\Psi_{\mathrm{el,g}}(\mathbf{q})\rangle$ is the ground-state solution of the electronic TISE. In **Ehrenfest dynamics**, on the other hand,

$$V(\mathbf{q}, t) = \langle \Psi_{\mathrm{el}}(\mathbf{q}, t) | \hat{H}_{\mathrm{el}}(\mathbf{q}) | \Psi_{\mathrm{el}}(\mathbf{q}, t) \rangle,$$

where $|\Psi_{\mathrm{el}}(\mathbf{q}, t)\rangle$ is the solution of the TDSE for electrons.

B. Lagrangian mechanics

Lagrangian mechanics is a more general formulation of classical mechanics based on a **variational principle** called the

Principle of Stationary Action (or sometimes the **principle of least action** because for short times, the action is minimized): *Classical trajectory follows a path of stationary action.*

Recall other variational principles such as **Fermat's principle of least time** in geometric optics that can be used to derive, e.g., **Snell's law of refraction**, or the quantum-mechanical **variational principle for energy**,

$$E\left[\Psi\right] := \langle\Psi|\hat{H}|\Psi\rangle \geq E_g,$$

that can be used to find, e.g., the Hartree-Fock electronic ground state. We need

Definition 7 ***Lagrangian*** *is defined as the difference of kinetic and potential energies of a given system expressed in terms of generalized coordinates q and corresponding velocities $\dot{q}$,*

$$L\left(q, \dot{q}, t\right) := T(q, \dot{q}) - V(q, t). \tag{4.3}$$

Action *is defined as the time integral of the Lagrangian along a trajectory,*

$$S\left[q(t)\right] := \int_0^t L(q, \dot{q}, \tau)\, d\tau. \tag{4.4}$$

Theorem 8 ***(the Euler-Lagrange equation of motion)*** *A classical trajectory that satisfies the principle of stationary action also satisfies the equation*

$$\frac{\partial L}{\partial q} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}} = 0. \tag{4.5}$$

Proof: Consider two paths, $q(\tau)$ and $q(\tau)+\delta q(\tau)$ with the same end points, i.e., $\delta q(0) = \delta q(t) = 0$. The first variation of the action is

$$\delta S = S\left[q + \delta q\right] - S\left[q\right] = \int_0^t \left(\frac{\partial L}{\partial q}\delta q + \frac{\partial L}{\partial \dot{q}}\delta \dot{q}\right) d\tau. \tag{4.6}$$

Note that the above equation for δS holds even for a time-dependent Lagrangian because $\partial L/\partial t$ does not appear in the variation. Using $\delta\dot{q} = d(\delta q)/dt$ and integrating by parts leads to

$$\delta S = \int_0^t \left(\frac{\partial L}{\partial q}\delta q + \frac{\partial L}{\partial \dot{q}}\frac{d}{d\tau}\delta q\right) d\tau = \left(\frac{\partial L}{\partial \dot{q}}\delta q\right)\Big|_0^t + \int_0^t \left(\frac{\partial L}{\partial q} - \frac{d}{d\tau}\frac{\partial L}{\partial \dot{q}}\right)\delta q d\tau. \tag{4.7}$$

The first term on the RHS is zero by the boundary conditions. The action will be stationary if its first variation is zero and, therefore, if the integral on the RHS is zero for any variation of the path δq. This can only be satisfied if the Euler-Lagrange (EL) equation (4.5) is satisfied.□

Note that the same Euler–Lagrange equation holds whether or not L depends on time explicitly because $\partial L/\partial t$ does not appear in the variation of δS due to varying δq.

Proposition 9 *For the kinetic energy* $T = \frac{1}{2}m\dot{\mathbf{q}}^2$ *and potential energy* $V(\mathbf{q})$*, the Euler-Lagrange equation is equivalent to Newton's equation.*

Proof: This so-called **standard Lagrangian** is

$$L(\mathbf{q}, \dot{\mathbf{q}}) = \frac{1}{2}m\dot{\mathbf{q}}^2 - V(\mathbf{q}). \tag{4.8}$$

The appropriate derivatives are

$$\begin{aligned} \frac{\partial L}{\partial \mathbf{q}} &= -\nabla V(\mathbf{q}), \\ \frac{\partial L}{\partial \dot{\mathbf{q}}} &= m\dot{\mathbf{q}}, \\ \frac{d}{dt}\frac{\partial L}{\partial \dot{\mathbf{q}}} &= m\ddot{\mathbf{q}}, \end{aligned}$$

and so the Euler-Lagrange equation becomes

$$-\nabla V(\mathbf{q}) - m\ddot{\mathbf{q}} = 0, \tag{4.9}$$

which is precisely Newton's equation of motion (4.1).□

C. Hamiltonian mechanics

Another generalization of Newtonian mechanics is the Hamiltonian mechanics. In modern chemistry curricula, students often encounter the Hamiltonian only in the quantum setting, which is a pity as this quantity plays an important role already in classical mechanics. We will not develop the formalism in detail but instead show several main results, in particular that Newton's equation emerges again as a special case.

One starts by defining the **canonical momentum**,

$$p := \frac{\partial L(q, \dot{q}, t)}{\partial \dot{q}}. \tag{4.10}$$

The **Hamiltonian function** (or the **energy**) is the **Legendre transform** of the Lagrangian, expressed as a function of q and p,

$$H(q, p, t) := \dot{q}p - L(q, \dot{q}, t). \tag{4.11}$$

A technical but important detail is that in order for the Legendre transform to exist, one must have $\det(\frac{\partial^2 L}{\partial \dot{q}_i \partial \dot{q}_j}) \neq 0$.

Proposition 10 ***(Hamilton's equations of motion)*** *The coordinates and momenta satisfy the following equations of motion:*

$$\dot{q} = \frac{\partial H}{\partial p} \quad \text{and} \quad \dot{p} = -\frac{\partial H}{\partial q}. \tag{4.12}$$

Moreover, $\partial H/\partial t = -\partial L/\partial t$.

Proof. The differential of the Hamiltonian is

$$\begin{aligned} dH = d(\dot{q}p - L) &= \dot{q}dp + pd\dot{q} - \frac{\partial L}{\partial q}dq - \frac{\partial L}{\partial \dot{q}}d\dot{q} - \frac{\partial L}{\partial t}dt \\ &= \dot{q}dp - \frac{\partial L}{\partial q}dq - \frac{\partial L}{\partial t}dt, \end{aligned} \tag{4.13}$$

where the second and fourth terms in the last expression on the first line cancel due to the definition (4.10) of a canonical momentum. The differential of the Hamiltonian, considered as a general function of three variables q, p, and t, can be also written as

$$dH = \frac{\partial H}{\partial q}dq + \frac{\partial H}{\partial p}dp + \frac{\partial H}{\partial t}dt. \tag{4.14}$$

Equating the corresponding terms of Eqs. (4.13) and (4.14), associated, respectively, with dq, dp, and dt, yields Hamilton's equations

$$\frac{\partial H}{\partial q} = -\frac{\partial L}{\partial q} = -\frac{d}{dt}\frac{\partial L}{\partial \dot{q}} = -\dot{p}, \tag{4.15}$$

$$\frac{\partial H}{\partial p} = \dot{q} \tag{4.16}$$

as well as an expression for $\partial H/\partial t$:

$$\frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}.$$

In the proof (4.15) of Hamilton's equation for $\dot{p}$, we also used the Euler-Lagrange equation and the definition of canonical momentum.□

A general dynamical system that satisfies Hamilton's equations is called a **Hamiltonian system**. The importance of the Hamiltonian function goes far beyond determining the equations of motion: the value of the Hamiltonian gives the **energy of the system**. Let us, therefore, prove the law of conservation of energy.

Proposition 11 ***(Conservation of energy)*** *An* ***autonomous*** *Hamiltonian system (i.e., a Hamiltonian system whose Hamiltonian does not explicitly depend on time) conserves energy along each trajectory.*

Proof. This is a simple calculation:

$$\frac{dH(q(t),p(t))}{dt} = \frac{\partial H}{\partial q}\dot{q} + \frac{\partial H}{\partial p}\dot{p} = \frac{\partial H}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial H}{\partial p}\frac{\partial H}{\partial q} = 0.\square$$

As an example, let us consider the standard Lagrangian (4.8),

$$L(\mathbf{q}, \dot{\mathbf{q}}) = \frac{1}{2}m\dot{\mathbf{q}}^2 - V(\mathbf{q}).$$

The canonical momentum (4.10) and Hamiltonian (4.11) are

$$\begin{aligned} \mathbf{p} &= \frac{\partial}{\partial \dot{\mathbf{q}}}\left(\frac{1}{2}m\dot{\mathbf{q}}^2\right) = m\dot{\mathbf{q}}, \\ H(\mathbf{q},\mathbf{p}) &= m\dot{\mathbf{q}}^2 - \frac{1}{2}m\dot{\mathbf{q}}^2 + V(\mathbf{q}) = \frac{1}{2}m\dot{\mathbf{q}}^2 + V(\mathbf{q}) \\ &= \frac{1}{2m}\mathbf{p}^2 + V(\mathbf{q}). \end{aligned}$$

The first result is Newton's *definition of momentum* and the second is the **standard Hamiltonian**. Finally, Hamilton's equations (4.12) become

$$\dot{\mathbf{q}} = \frac{\mathbf{p}}{m} \quad \text{and} \quad \dot{\mathbf{p}} = -\frac{\partial V(\mathbf{q})}{\partial \mathbf{q}}.$$

The first equation is again Newton's definition of momentum, while the second equation is Newton's law. Substituting the definition of $\mathbf{p}$ into the second equation yields the Euler-Lagrange equation (4.9) for the standard Lagrangian:

$$m\ddot{\mathbf{q}} = -\frac{\partial V(\mathbf{q})}{\partial \mathbf{q}}.$$

D. Application: Lagrangian and Hamiltonian in a central field

Chemical examples of systems with a central field include two famous two-body problems: a **diatomic molecule**, where the two bodies are the two atoms, and a **hydrogen atom**, where the two bodies are a proton and an electron. When analyzing the hydrogen atom, the mass of the proton is often assumed to be infinite in comparison with the mass of the electron. Below, we present a more accurate solution, which does not assume that one mass is much larger than the other. What we must do first is removing the center-of-mass (COM) motion in both cases (see the Exercise below).

After removing the COM motion, the kinetic and potential energies are

$$T = \frac{1}{2}\mu\dot{\mathbf{r}}^2 \quad \text{and } V = V(r) \tag{4.17}$$

where

$$\mu := \frac{m_1 m_2}{m_1 + m_2} \tag{4.18}$$

is the **reduced mass**, $\mathbf{r}$ is the radius vector from one atom to the other (or from proton to the electron in the H atom, see Fig. [!!! Add figure.]) and $r = \|\mathbf{r}\|$ is the bond length. In an arbitrary central field, angular momentum is conserved, and so the motion occurs in a plane, which is proven in most classical mechanics textbooks. Hence $\mathbf{r}$ is a two-dimensional vector that can be written as the product of its length $r = |\mathbf{r}|$ and a unit vector $\hat{\mathbf{r}}$ with the same direction:

$$\mathbf{r} = r\hat{\mathbf{r}}. \tag{4.19}$$

Differentiating $\mathbf{r}$ with respect to time yields

$$\dot{\mathbf{r}} = \dot{r}\hat{\mathbf{r}} + r\frac{d}{dt}\hat{\mathbf{r}} = \dot{r}\hat{\mathbf{r}} + r\dot{\varphi}\hat{\boldsymbol{\varphi}}, \text{ and} \tag{4.20}$$

$$\dot{\mathbf{r}}^2 = \dot{r}^2 + r^2\dot{\varphi}^2, \tag{4.21}$$

where φ is the polar angle, $\hat{\boldsymbol{\varphi}}$ is a unit vector pointing in the direction of increasing φ, and where we used the following relations:

$$\frac{d}{dt}\hat{\mathbf{r}} = \dot{\varphi}\hat{\boldsymbol{\varphi}}, \quad \hat{\mathbf{r}}\cdot\hat{\mathbf{r}} = \hat{\boldsymbol{\varphi}}\cdot\hat{\boldsymbol{\varphi}} = 1, \quad \text{and} \quad \hat{\mathbf{r}}\cdot\hat{\boldsymbol{\varphi}} = 0. \tag{4.22}$$

In particular, $\hat{\mathbf{r}}$ and $\hat{\boldsymbol{\varphi}}$ are orthonormal vectors. Remember that the hat ^ here denotes unit vectors and *not* operators.

Now we can find the Lagrangian,

$$L(r, \varphi, \dot{r}, \dot{\varphi}) = T - V = \frac{1}{2}\mu(\dot{r}^2 + r^2\dot{\varphi}^2) - V(r), \tag{4.23}$$

and the Euler-Lagrange equations of motion,

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{r}} = \frac{\partial L}{\partial r} \Rightarrow \mu\ddot{r} = \mu r\dot{\varphi}^2 - V'(r), \tag{4.24}$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{\varphi}} = \frac{\partial L}{\partial \varphi} \Rightarrow \frac{d}{dt}\left(\mu r^2\dot{\varphi}\right) = 0. \tag{4.25}$$

The second equation is nothing else but the conservation of the magnitude of angular momentum

$$\mathcal{L} = I\omega = \mu r^2\dot{\varphi} = \text{const}\,. \tag{4.26}$$

Using this result, we can rewrite the first Euler-Lagrange equation as

$$\mu\ddot{r} = -V'_{\text{eff}}(r), \tag{4.27}$$

where the **effective potential**

$$V_{\text{eff}}(r) := V(r) + V_{\text{centr}}(r) \tag{4.28}$$

also includes the **centrifugal potential**

$$V_{\text{centr}}(r) := \frac{\mathcal{L}^2}{2\mu r^2}. \tag{4.29}$$

The canonical momenta are

$$p_r := \frac{\partial L}{\partial \dot{r}} = \mu \dot{r}, \tag{4.30}$$

$$p_\varphi := \frac{\partial L}{\partial \dot{\varphi}} = \mu r^2 \dot{\varphi}. \tag{4.31}$$

Note that p_φ, the canonical momentum conjugate to the angle φ, is nothing else but the angular momentum $\mathcal{L}$!

Now we can find the Hamiltonian in polar coordinates,

$$\begin{aligned} H(r, \varphi, p_r, p_\varphi) &= p_r \dot{r} + p_\varphi \dot{\varphi} - L = \frac{1}{2}\mu(\dot{r}^2 + r^2\dot{\varphi}^2) + V(r) \\ &= \frac{p_r^2}{2\mu} + \frac{p_\varphi^2}{2\mu r^2} + V(r) = \frac{p_r^2}{2\mu} + V_{\text{eff}}(r), \end{aligned} \tag{4.32}$$

and associated Hamilton's equations:

$$\dot{r} = \frac{p_r}{\mu}, \tag{4.33}$$

$$\dot{p}_r = \frac{p_\varphi^2}{\mu r^3} - V'(r), \tag{4.34}$$

$$\dot{\varphi} = \frac{p_\varphi}{\mu r^2}, \tag{4.35}$$

$$\dot{p}_\varphi = 0. \tag{4.36}$$

Note that the third equation is the definition of angular momentum p_φ, the last equation represents the conservation of the angular momentum, $p_\varphi = \text{const} = \mathcal{L}$, and we can use this constant value in the second and third equations. The first and second equations together give the Euler-Lagrange equation for the radial motion.

The above example showed the straightforward nature of the Lagrangian or Hamiltonian formalism. The angle and angular momentum are a pair of **conjugate variables** in the same way as position and momentum. In Lagrangian and Hamiltonian formalisms, one does not care which **generalized coordinates** are used. In contrast, in Newtonian mechanics, angles and angular momenta must be treated very differently than position and momentum and one must be much more careful not to make a mistake, especially if the system becomes more complicated.

[!!! To add:]

nondiagonal Hamiltonian for photodissociation of CO_2 (bond lengths coordinates)

$$R_1 = x_3 - x_2 \quad \text{and} \quad R_2 = x_2 - x_3$$

Jacobi coordinates: How are they defined for atoms A, B, C?

E. *Hamilton-Jacobi theory (not required)

First, let us allow the endpoints of the trajectory to vary, i.e., $\delta q\,(0) \neq 0$ and $\delta q\,(t) \neq 0$. Recall that in the derivation (4.7) of the Euler-Lagrange equations, we used an integration by parts, in which the boundary term was zero because we assumed that the endpoints were fixed. For a more general variation of the trajectory, where the endpoints can vary, the action can be stationary only if the Euler-Lagrange equations hold and, in addition, the boundary term is zero,

$$\left.\left(\frac{\partial L}{\partial \dot{q}}\delta q\right)\right|_0^t = 0. \tag{4.37}$$

Assuming that the Euler-Lagrange equations hold, the variation of the action is

$$\delta S = \left.\left(\frac{\partial L}{\partial \dot{\mathbf{q}}} \cdot \delta \mathbf{q}\right)\right|_0^t = \mathbf{p}\,(t) \cdot \delta \mathbf{q}\,(t) - \mathbf{p}\,(0) \cdot \delta \mathbf{q}\,(0)\,. \tag{4.38}$$

If the action is considered as the function of the the initial coordinate $\mathbf{q}_0 = \mathbf{q}(0)$, final coordinate $\mathbf{q} = \mathbf{q}(t)$, and time t, then the above equation implies that

$$\frac{\partial S}{\partial \mathbf{q}} = \mathbf{p} \quad \text{and} \quad \frac{\partial S}{\partial \mathbf{q}_0} = -\mathbf{p}_0, \tag{4.39}$$

where $\mathbf{p} = \mathbf{p}(t)$ and $\mathbf{p}_0 = \mathbf{p}(0)$. Now recall that the Lagrangian is the total time derivative of the action,

$$L = \frac{dS}{dt} = \frac{\partial S}{\partial t} + \frac{\partial S}{\partial \mathbf{q}} \cdot \dot{\mathbf{q}} = \frac{\partial S}{\partial t} + \mathbf{p} \cdot \dot{\mathbf{q}}, \tag{4.40}$$

and that the Hamiltonian is the Legendre transform of the Lagrangian,

$$H = \mathbf{p} \cdot \dot{\mathbf{q}} - L. \tag{4.41}$$

Hence

$$H = -\frac{\partial S}{\partial t}. \tag{4.42}$$

Because $H \equiv H\,(\mathbf{q}, \mathbf{p}, t)$, we obtain a partial differential equation (PDE) for $S(\mathbf{q}, \mathbf{q}_0, t)$:

$$H\left(\mathbf{q}, \frac{\partial S}{\partial \mathbf{q}}, t\right) = -\frac{\partial S}{\partial t}. \tag{4.43}$$

This is the **Hamilton-Jacobi equation**, which is equivalent to Hamilton's equations and forms the basis of **Hamilton-Jacobi theory**.

F. *Derivation of Hamilton's equations from the variational principle (not required)

Hamilton's equations can be derived directly from the variational principle, if the Lagrangian is considered as a function of q, p, $\dot{q}$, and $\dot{p}$. Because the Hamiltonian is the Legendre transform of the Lagrangian, the Lagrangian is also the Legendre transform of the Hamiltonian:

$$L \equiv L\left(q, p, \dot{q}, \dot{p}\right) = p \cdot \dot{q} - H\left(q, p\right). \tag{4.44}$$

Now let us consider the variation of the action integral

$$S = \int_0^t L\left(q, p, \dot{q}, \dot{p}\right) d\tau. \tag{4.45}$$

Because $L(q, p, \dot{q}, \dot{p})$ from Eq. (4.44) does not depend on $\dot{p}$, the first variation of action is

$$\begin{aligned} \delta S &= \int_0^t \left(\frac{\partial L}{\partial q}\delta q + \frac{\partial L}{\partial \dot{q}}\delta \dot{q} + \frac{\partial L}{\partial p}\delta p\right) d\tau \\ &= \int_0^t \left[-\frac{\partial H}{\partial q}\delta q + p\delta\dot{q} + \left(\dot{q} - \frac{\partial H}{\partial p}\right)\delta p\right] d\tau \\ &= \int_0^t \left[\left(-\frac{\partial H}{\partial q} - \dot{p}\right)\delta q(\tau) + \left(\dot{q} - \frac{\partial H}{\partial p}\right)\delta p(\tau)\right] d\tau, \end{aligned} \tag{4.46}$$

where, in the last row, we used again the fact that $\delta\dot{q} = d\left(\delta q\right)/dt$ and that the boundary term in the integration by parts was zero because the endpoints were assumed to be fixed $[\delta q(0) = \delta q(t) = \delta p(0) = \delta p(t) = 0]$.

Because the action must be stationary for arbitrary variations $\delta q(\tau)$ and $\delta p\left(\tau\right)$, the prefactors of these variations in the integrand must be zero. These are exactly Hamilton's equations

$$\dot{p} = -\frac{\partial H}{\partial q} \quad \text{and} \quad \dot{q} = \frac{\partial H}{\partial p}. \tag{4.47}$$

G. Phase space, phase portrait, and Liouville's theorem

Imagine that you are given the coordinates $\mathbf{r}_0 = (x_0, y_0, z_0)$ of a particle at time $t = 0$ and that you know exactly the force $\mathbf{F}(\mathbf{r})$ that acts on the particle at any position $\mathbf{r}$ in space. Can you predict the position of the particle at all times $t > 0$? No, because you do not know its initial velocity or momentum. This is intuitively obvious and mathematically it follows because Lagrange equations of motion are second-order differential equations, so their solution requires initial values of both positions $\mathbf{q}\left(0\right)$ and their first derivatives (velocities) $\dot{\mathbf{q}}\left(0\right)$. As for Hamilton's equations of motion, which are only first-order, you only need initial values of the variables, but now the variables include not only the positions $\mathbf{q}$ but also momenta $\mathbf{p}$. To sum up, if there are D degrees of freedom, you need $2D$ initial data in both cases: D positions and either D velocities or D momenta.

From now on, let us focus on Hamiltonian mechanics, where the trajectory at time t is specified by a D-dimensional coordinate vector $\mathbf{q}(t)$ in the D-dimensional **coordinate space** and a D-dimensional momentum vector $\mathbf{p}(t)$. Together $\mathbf{q}$ and $\mathbf{p}$ form a $2D$-dimensional vector in a $2D$-dimensional **phase space** (see Fig. 9 for $D = 1$ and $D = 3$).

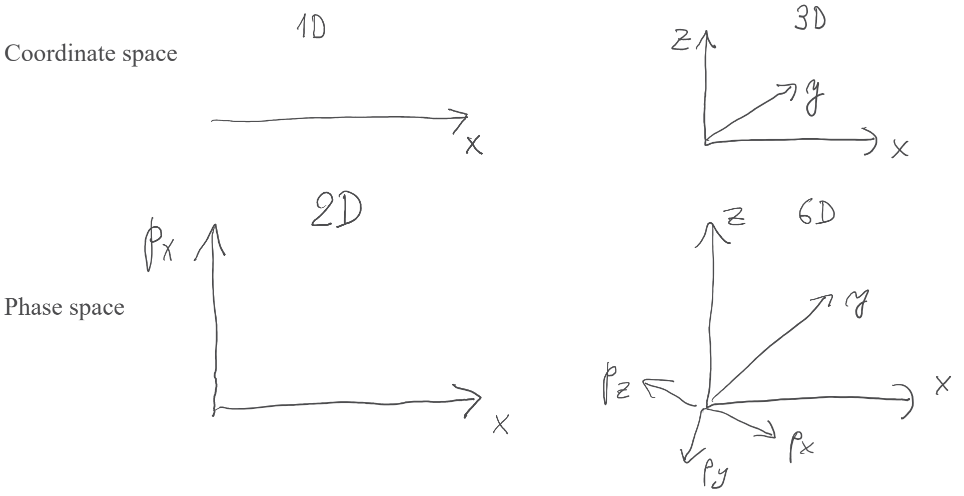

FIG. 9. Coordinate space and phase space for systems with one and three degrees of freedom.

In contrast to initial "coordinate-space coordinates" $\mathbf{q}$, initial phase-space coordinates $(\mathbf{q}, \mathbf{p})$ specify the trajectory $(\mathbf{q}_t, \mathbf{p}_t) \equiv (\mathbf{q}(t), \mathbf{p}(t))$ completely. Different initial conditions lead to different types of trajectories and a **phase portrait** of all topologically different trajectories provides useful information about the dynamics of a system. Let us look at several one-dimensional examples:

For a **free particle**, $V(q) = 0$, the momentum is conserved, $p_t = p_0$, and there are three types of trajectories (see Fig. 10). Those with positive momenta are depicted as horizontal, right-pointing lines $(q_t, p_t) = (q_0 + p_0 t/m, p_0)$ in the phase portrait. Those with zero momentum correspond to separate points $(q_t, p_t) = (q_0, 0)$ and those with negative momenta are depicted as horizontal, left-pointing lines. In the theories of elasticity and dynamical systems, the phase portrait just described is referred to as a **shear**. In chemical physics, examples of a free particle are the **translational motion** of a molecule of an ideal gas between collisions or a **rotation of a rigid molecule** (here $q := \phi$ and $p := \mathcal{L}$, where $\mathcal{L}$ is the angular momentum).

In a **harmonic oscillator**, $V(q) = \frac{1}{2}kq^2$. Because the energy is conserved along a classical

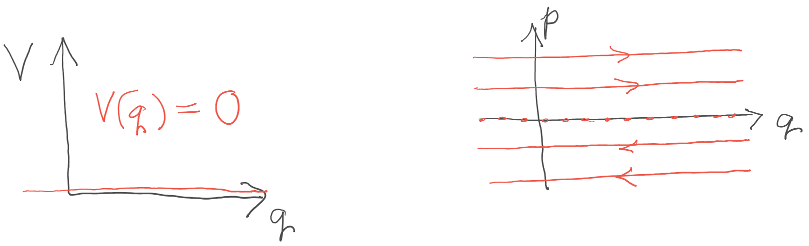

FIG. 10. Phase portrait of a free particle.

trajectory, i.e.,

$$\frac{1}{2m}p_t^2 + \frac{1}{2}kq_t^2 = \mathrm{const} = E,$$

almost every trajectory moves clockwise along an ellipse in phase space (see Fig. 11). The only exception is the **fixed point** at $q = p = 0$, for which $q_t = p_t = 0$. (Such a trajectory is called a fixed point because neither the position nor momentum changes with time.) As you know, in chemical physics the harmonic oscillator arises as a model of **molecular vibrations** for small displacements from the equilibrium.

Finally, let us find the phase portrait of a **mathematical pendulum**, which describes approximately **hindered rotation** in molecules, such as the rotation of a methyl group about the C-C axis in ethane. Potential energy of a pendulum of mass m and length l displaced by an angle ϕ from the vertical axis is

$$V(\phi) = -mgl\cos\phi.$$

Now more types of trajectories appear (see Fig. 12): First, as in the harmonic oscillator, for $E = 0$ there are **stable fixed points** at the minimum of the potential at $(\phi = 2n\pi, \mathcal{L} = 0)$, $n \in \mathbb{Z}$. (A fixed point is said to be "stable" if, for sufficiently small displacements, the motion remains in the vicinity of the fixed point for all times.) For $0 < E < mgl$, the pendulum performs oscillations with amplitude $|\phi_{\max}| < \pi$, exactly as in a pendulum clock; in phase space, these oscillations appear as **periodic orbits** (i.e., trajectories, for which there is a time T such that $\phi_T = \phi_0$ and $\mathcal{L}_T = \mathcal{L}_0$),

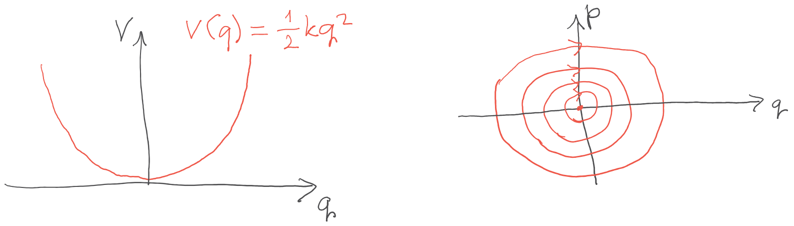

FIG. 11. Phase portrait of a harmonic oscillator.

traversed clockwise. Because they are similar to but not quite the same as vibrations in a harmonic oscillator, such trajectories are called **librations**. For $E > mgl$, the pendulum does not stop at its highest point, but keeps winding about its support so that the angle ϕ either increases to ∞ (if $\mathcal{L} > 0$) or decreases to $-\infty$ (if $\mathcal{L} < 0$). Such motions are called **hindered rotations** because they are similar to free rotations but are hindered by the gravitational potential energy. Finally, if the energy is exactly $E = mgl$, there are two types of trajectories: **unstable fixed points** at $(\phi = (2n+1)\pi, \mathcal{L} = 0)$, $n \in \mathbb{Z}$, and trajectories that connect different unstable fixed points to each other. These trajectories are called **separatrices** because they separate two topologically different families of motion (here hindered rotations and librations). In the pendulum, each separatrix corresponds to a special infinitesimal displacement from an unstable fixed point that results in a very slow but accelerating fall to the minimum of the potential, followed by a decelerated rise to the top of the pendulum; the whole process takes an infinite time.

So far, we have considered individual trajectories. Let us consider what happens to a region of phase space corresponding to the initial conditions of a whole ensemble of classical trajectories. The **phase space volume**, i.e., a volume of a bounded region R of phase space, is measured by the integral

$$V := \int_R d^{2D}V,$$

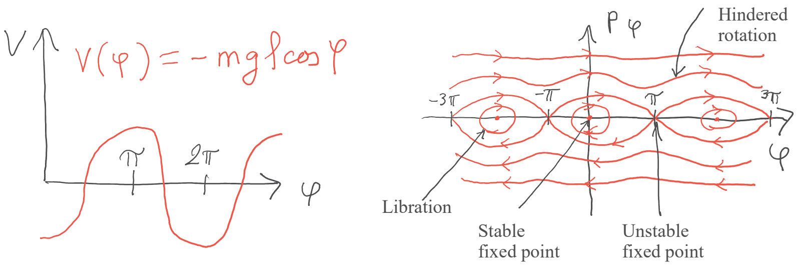

FIG. 12. Phase portrait of a pendulum.

where the **volume element** $d^{2D}V$ is the product of $2D$ position and momentum factors:

$$d^{2D}V = dq_1 dp_1 \cdots dq_D dp_D.$$

Theorem 12 ***(Liouville's theorem)*** *The volume of a phase-space region evolved with Hamilton's equations is conserved.*

Proof. Let us define a $2D$-component phase-space vector $\mathbf{x}$ by

$$\mathbf{x} \equiv (x_1, x_2, \ldots, x_{2D}) := (q_1, p_1, \ldots, q_D, p_D)\,.$$

Using this notation, Hamilton's equations can be rewritten as a nonlinear ordinary differential equation

$$\frac{d\mathbf{x}}{dt} = \mathbf{F}(\mathbf{x}) \tag{4.48}$$

whose solutions are trajectories tangent to a $2D$-component vector field

$$\mathbf{F} := \left(\frac{\partial H}{\partial p_1}, -\frac{\partial H}{\partial q_1}, \ldots, \frac{\partial H}{\partial p_D}, -\frac{\partial H}{\partial q_D}\right).$$

Recall that a **divergence** of a general vector $\mathbf{A}$ is defined as the following sum of the partial derivatives of its components:

$$\mathrm{div}\,\mathbf{A} := \nabla \cdot \mathbf{A} = \sum_{j=1}^{2D} \frac{\partial A_j}{\partial x_j}.$$

The proof of Liouville's theorem is completed by noticing that the vector field $\mathbf{F}$ has zero divergence,

$$\begin{aligned}\operatorname{div}\mathbf{F} &= \frac{\partial}{\partial q_1}\frac{\partial H}{\partial p_1} + \frac{\partial}{\partial p_1}\left(-\frac{\partial H}{\partial q_1}\right) + \cdots + \frac{\partial}{\partial q_D}\frac{\partial H}{\partial p_D} + \frac{\partial}{\partial p_D}\left(-\frac{\partial H}{\partial q_D}\right) \\ &= \left(\frac{\partial^2 H}{\partial q_1 \partial p_1} - \frac{\partial^2 H}{\partial p_1 \partial q_1}\right) + \cdots + \left(\frac{\partial^2 H}{\partial q_D \partial p_D} - \frac{\partial^2 H}{\partial p_D \partial q_D}\right) = 0 + \cdots + 0 = 0,\end{aligned}$$

and by invoking a general theorem from the real analysis of several variables stating that the solution of the vector nonlinear differential equation (4.48) conserves volume if the divergence of $\mathbf{F}$ is zero. □

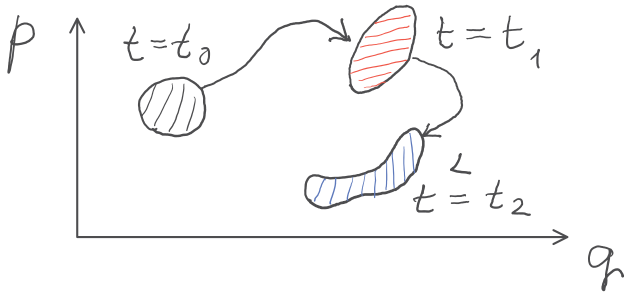

FIG. 13. Conservation of phase-space volume implied by Liouville's theorem. While the coordinate-space and momentum-space volumes change, the phase-space volume is constant—here reflected in the equal areas of the shaded phase-space regions at times t_0, t_1, and t_2.

V. CONNECTIONS BETWEEN QUANTUM AND CLASSICAL MECHANICS

A. Commutator

The **commutator** $[\hat{A}, \hat{B}] := \hat{A}\hat{B} - \hat{B}\hat{A}$ of two quantum-mechanical operators is an important concept in quantum mechanics. Let $\hat{A}$, $\hat{B}$, $\hat{C}$ be operators, and λ a complex number.

Exercise 13 *Show that the commutator is*

1) ***skew-symmetric:***

$$[\hat{B}, \hat{A}] = -[\hat{A}, \hat{B}], \tag{5.1}$$

2) ***bilinear:***

$$[\lambda\hat{A}, \hat{B}] = \lambda[\hat{A}, \hat{B}], \tag{5.2}$$

$$[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}], \tag{5.3}$$

3) and satisfies the ***Jacobi identity:***

$$[\hat{A},[\hat{B},\hat{C}]]+[\hat{B},[\hat{C},\hat{A}]]+[\hat{C},[\hat{A},\hat{B}]]=0. \tag{5.4}$$

These three conditions express that the set of operators together with addition and commutator form a ***Lie algebra****.*

Exercise 14 *Show that a commutator $[\hat{A},\cdot]$ with a fixed operator $\hat{A}$ (i.e., the mapping $[\hat{A},\cdot]:\hat{B}\mapsto[\hat{A},\hat{B}]$) satisfies the* ***Leibniz rule***

$$[\hat{A},\hat{B}\hat{C}]=\hat{B}[\hat{A},\hat{C}]+[\hat{A},\hat{B}]\hat{C}. \tag{5.5}$$

The name comes from an analogy with the Leibniz rule for a derivative of a product, where the linear mapping is $d(\cdot)/dx : f\mapsto df/dx$:

$$\frac{d}{dx}(fg)=f\frac{dg}{dx}+\frac{df}{dx}g.$$

Mathematicians, therefore, call a linear mapping that satisfies the Leibniz rule a **derivation** on the associative algebra of operators with the usual multiplication of operators, $\hat{A}\hat{B}$. (In an **associative algebra**, the product $\hat{A}\hat{B}$ must be again bilinear, but the associative law replaces the Jacobi identity of the Lie algebra. The product does not have to be symmetric or skew-symmetric.) A set that is both an associative algebra (with respect to $\cdot$ operation) and Lie algebra (with respect to $[\cdot,\cdot]$), and, in addition, satisfies the Leibniz rule, is called a **Poisson algebra**.

One of the pillars of quantum mechanics is the expression for the commutator of the position and momentum operators:

$$[\hat{q},\hat{p}]=i\hbar. \tag{5.6}$$

Exercise 15 *Using the Leibniz rule, show that if functions $f(q)$ and $g(p)$ can be expanded in power series of their arguments, then*

$$[\hat{q},f(\hat{q})]=0 \quad \textit{and} \quad [\hat{q},g(\hat{p})]=i\hbar\frac{d}{dp}g(\hat{p}), \tag{5.7}$$

$$[\hat{p},g(\hat{p})]=0 \quad \textit{and} \quad [\hat{p},f(\hat{q})]=-i\hbar\frac{d}{dq}f(\hat{q}). \tag{5.8}$$

B. Ehrenfest theorem

Recall that the **expectation value** $\langle A\rangle$ of operator $\hat{A}$ in the state $|\psi\rangle$ is defined as

$$\langle A\rangle := \langle\psi|\hat{A}|\psi\rangle.$$

If it is useful to keep the information about the state, in which the expectation value is evaluated, we use the more detailed notation $\langle A\rangle_\psi$. Sometimes, if the operator in the brackets is a more complicated expression, it is also useful to keep the hat on the operator. To sum up, the following four expressions are equivalent:

$$\langle A\rangle = \langle A\rangle_\psi = \langle \hat{A}\rangle = \langle \hat{A}\rangle_\psi .$$

Theorem 16 ***(Ehrenfest)*** *If the quantum state $|\psi(t)\rangle$ evolves according to the TDSE with a Hamiltonian operator*

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

then the expectation values of position and momentum evolve according to the following equations:

$$\frac{d\left\langle q\right\rangle}{dt} = \frac{\langle p\rangle}{m}, \tag{5.9}$$

$$\frac{d\left\langle p\right\rangle}{dt} = -\left\langle\frac{\partial V}{\partial q}\right\rangle . \tag{5.10}$$

Note that equations for $\langle q\rangle$ and $\langle p\rangle$ are very similar to Hamilton's equations of motion, except that, in general, $\langle -\partial V/\partial q\rangle \neq -\partial V(\langle q\rangle)/\partial q$. To prove the Ehrenfest theorem, we will employ the following

Lemma 17 *Expectation value of a general operator $\hat{A}$ evolves as*

$$\frac{d\langle\hat{A}\rangle}{dt} = \langle \partial\hat{A}/\partial t\rangle + \frac{1}{i\hbar}\langle[\hat{A},\hat{H}]\rangle . \tag{5.11}$$

In particular, if the operator $\hat{A}$ does not explicitly depend on time (i.e., $\partial\hat{A}/\partial t = 0$), then

$$\frac{d\langle\hat{A}\rangle}{dt} = \frac{1}{i\hbar}\langle[\hat{A},\hat{H}]\rangle . \tag{5.12}$$

Proof of lemma. Using the Leibniz rule and the fact that $|\psi\rangle$ satisfies the TDSE (i.e., $i\hbar|\dot{\psi}\rangle = \hat{H}|\psi\rangle$ as well as $-i\hbar\langle\dot{\psi}| = \langle\psi|\hat{H}|$), the time derivative of the expectation value $\langle\hat{A}\rangle = \langle\psi(t)|\hat{A}(t)|\psi(t)\rangle$ is expanded as

$$\begin{aligned}\frac{d\langle\hat{A}\rangle}{dt} &= \langle\dot{\psi}|\hat{A}|\psi\rangle + \langle\psi|\partial\hat{A}/\partial t|\psi\rangle + \langle\psi|\hat{A}|\dot{\psi}\rangle \\ &= -\frac{1}{i\hbar}\langle\psi|\hat{H}\hat{A}|\psi\rangle + \langle\partial\hat{A}/\partial t\rangle + \frac{1}{i\hbar}\langle\psi|\hat{A}\hat{H}|\psi\rangle \\ &= \langle\partial\hat{A}/\partial t\rangle + \frac{1}{i\hbar}\langle\psi|(\hat{A}\hat{H} - \hat{H}\hat{A})|\psi\rangle .\square \end{aligned} \tag{5.13}$$

Proof of theorem. To prove Eqs. (5.9) and (5.10), we apply the lemma to the position and momentum operators. For $\hat{A} = \hat{q}$, we need to evaluate the commutator of position with Hamiltonian:

$$[\hat{q}, \hat{H}] = \frac{1}{2m}[\hat{q}, \hat{p}^2] = \frac{1}{2m}\left([\hat{q}, \hat{p}]\hat{p} + \hat{p}[\hat{q}, \hat{p}]\right) = \frac{1}{2m}(i\hbar\hat{p} + \hat{p}i\hbar) = i\hbar\frac{\hat{p}}{m}, \tag{5.14}$$

where we have used the fact that $\hat{q}$ commutes with $V(\hat{q})$ [this is relation (5.7) applied to $f(q) = V(q)$], together with properties (5.5) and (5.6). The lemma then yields Eq. (5.9). Likewise, for $\hat{A} = \hat{p}$, we need the commutator of momentum with Hamiltonian,

$$[\hat{p}, \hat{H}] = [\hat{p}, V(\hat{q})] = -i\hbar\frac{\partial}{\partial q}V(\hat{q}), \tag{5.15}$$

which follows from property (5.8) applied to $f(q) = V(q)$ and $g(p) = p^2/(2m)$. The lemma then yields Eq. (5.10).□

Note that the equations of the Ehrenfest theorem would be simpler to solve if Eq. (5.10) were replaced with $d\langle p\rangle/dt = -\partial V(\langle q\rangle)/\partial q$. Then the expectation values of q and p would follow classical trajectories. To see when this would happen, let us expand $V'(q)$ about $\langle q\rangle$:

$$V'(q) = V'(\langle q\rangle) + (q - \langle q\rangle)V''(\langle q\rangle) + \frac{1}{2}(q - \langle q\rangle)^2 V'''(\langle q\rangle) + \cdots . \tag{5.16}$$

Taking the expectation value yields

$$\langle V'(q)\rangle = V'(\langle q\rangle) + \frac{1}{2}\langle(q - \langle q\rangle)^2\rangle V'''(\langle q\rangle) + \cdots . \tag{5.17}$$

Now if $V(q) = aq^2 + bq + c$, i.e., if the potential is at most quadratic, then $V^{(n)} = 0$ for $n \geq 3$, so $\langle V'(q)\rangle = V'(\langle q\rangle)$. In this case, Eq. (5.10) becomes Hamilton's equation

$$\frac{d\langle p\rangle}{dt} = -\frac{\partial V(\langle q\rangle)}{\partial q} \qquad (V \text{ at most quadratic}), \tag{5.18}$$

and $\langle q\rangle$ and $\langle p\rangle$ evolve classically. We saw this simplification when we studied the Gaussian wavepacket in the free space [$V(q) = c$], in a harmonic oscillator [$V(q) = aq^2$], or in a linear potential [$V(q) = bq$]—in all these situations the potential energy was a special case of the general quadratic polynomial $V(q) = aq^2 + bq + c$.

C. Poisson bracket

Let us explore the analogy between classical and quantum evolution further and consider the time dependence of a classical quantity $f(q, p, t)$, which depends both on phase space coordinates and time.

Proposition 18 *If $q\left(t\right)$ and $p\left(t\right)$ denote the phase space coordinates of a classical trajectory of a Hamiltonian $H\left(q,p\right)$, then the change of the quantity $f(q,p,t)$ along this trajectory satisfies the equation*

$$\frac{df}{dt}=\frac{\partial f}{\partial t}+\{f,H\}, \tag{5.19}$$

where the symbol $\{f,g\}$ is called the ***Poisson bracket*** *of quantities f and g and is defined as*

$$\{f,g\}:=\frac{\partial f}{\partial q}\frac{\partial g}{\partial p}-\frac{\partial f}{\partial p}\frac{\partial g}{\partial q}. \tag{5.20}$$

Proof. The change of f along a classical trajectory is found by taking the total derivative with respect to time,

$$\frac{df}{dt}=\frac{\partial f}{\partial t}+\frac{\partial f}{\partial q}\frac{dq}{dt}+\frac{\partial f}{\partial p}\frac{dp}{dt}=\frac{\partial f}{\partial t}+\frac{\partial f}{\partial q}\frac{\partial H}{\partial p}-\frac{\partial f}{\partial p}\frac{\partial H}{\partial q}=\frac{\partial f}{\partial t}+\{f,H\}, \tag{5.21}$$

where we have used Hamilton's equations (4.12) in the second equality and the definition of the Poisson bracket in the third equality.□

Because the proposition holds for any function $f\left(q,p,t\right)$, it can be applied, in particular, to position $[f\left(q,p,t\right)=q]$ and momentum $[f\left(q,p,t\right)=p]$, resulting in a simpler and more symmetric form of **Hamilton's equations of motion**:

$$\frac{dq}{dt}=\{q,H\}\quad\text{and}\quad\frac{dp}{dt}=\{p,H\}. \tag{5.22}$$

To verify explicitly that the new form agrees with the standard form (4.12) of Hamilton's equations, note that

$$\{q,H\}=\frac{\partial q}{\partial q}\frac{\partial H}{\partial p}-\frac{\partial q}{\partial p}\frac{\partial H}{\partial q}=1\cdot\frac{\partial H}{\partial p}-0\cdot\frac{\partial H}{\partial q}=\frac{\partial H}{\partial p}, \tag{5.23}$$

$$\{p,H\}=\frac{\partial p}{\partial q}\frac{\partial H}{\partial p}-\frac{\partial p}{\partial p}\frac{\partial H}{\partial q}=0\cdot\frac{\partial H}{\partial p}-1\cdot\frac{\partial H}{\partial q}=-\frac{\partial H}{\partial q}. \tag{5.24}$$

The Poisson bracket has many other intriguing properties, most of which are analogous to the properties of the quantum-mechanical commutator. Remarkably, classical quantities together with the Poisson bracket also form a **Lie algebra,** and together with both multiplication and Poisson bracket, they form a **Poisson algebra**. Indeed, this feature of the Poisson bracket gave the Poisson algebra its name! There is, nevertheless, a crucial difference between the commutator $[\hat{A},\hat{B}]=\hat{A}\hat{B}-\hat{B}\hat{A}$, which is defined directly from multiplication of operators, and the Poisson bracket $\{f,g\}$, which requires differentiation—because the multiplication of functions is commutative, a simple commutator $fg-gf$ is always zero and would not yield anything interesting.

Exercise 19 *Show that the Poisson bracket is skew-symmetric, bilinear, and satisfies both the Jacobi identity and the Leibniz rule. In other words, if* f, g, h *are real functions and* λ *a real number, show that:*

$$\{f, g\} = -\{g, f\} \quad \textit{(skew-symmetry)} \tag{5.25}$$

$$\{\lambda f, g\} = \lambda\{f, g\} \quad \textit{(bilinearity 1: homogeneity)} \tag{5.26}$$

$$\{f, g + h\} = \{f, g\} + \{f, h\} \quad \textit{(bilinearity 2: additivity)} \tag{5.27}$$

$$\{f, \{g, h\}\} + \{g, \{h, f\}\} + \{h, \{f, g\}\} = 0 \quad \textit{(Jacobi identity)} \tag{5.28}$$

$$\{f, gh\} = \{f, g\}h + g\{f, h\} \quad \textit{(Leibniz rule)} \tag{5.29}$$

The skew-symmetry of the Poisson bracket implies immediately that $\{f, f\} = 0$ for any $f(q, p, t)$. Applying this property and the proposition to $f(q, p, t) = H(q, p)$ provides an alternative, trivial proof of the **law of conservation of energy** for autonomous systems, i.e., systems with $\partial H/\partial t = 0$:

$$\frac{dH}{dt} = \{H, H\} = 0. \tag{5.30}$$

Exercise 20 *If* $f \equiv f(q, p, t)$*, show that Poisson brackets with position and momentum satisfy*

$$\{q, p\} = 1, \tag{5.31}$$

$$\{p, f\} = -\frac{\partial f}{\partial q}, \tag{5.32}$$

$$\{q, f\} = \frac{\partial f}{\partial p}. \tag{5.33}$$

A quantity f is said to be a **constant of motion** or an **integral of motion** if $f = \text{const}$ along the trajectory $(q(t), p(t))$. Because this is equivalent to the requirement that $df/dt = 0$ along the trajectory, f is a constant of motion if and only if

$$0 = \frac{\partial f}{\partial t} + \{f, H\} \qquad (f \text{ an integral of motion}). \tag{5.34}$$

In particular, if f does not depend on time explicitly ($\partial f/\partial t = 0$), then f is a constant of motion if and only if $\{f, H\} = 0$.

If we have two constants of motion, there is an interesting recipe for constructing other, sometimes independent constants of motion:

Proposition 21 *If both* f *and* g *are integrals of motion, then so is their Poisson bracket:*

$$\frac{df}{dt} = \frac{dg}{dt} = 0 \Rightarrow \frac{d\{f, g\}}{dt} = 0. \tag{5.35}$$

Proof.

$$\begin{aligned}\frac{d}{dt}\{f,g\} &\overset{(5.19)}{=} \frac{\partial}{\partial t}\{f,g\}+\{\{f,g\},H\} \overset{(5.28)}{=} \left\{\frac{\partial f}{\partial t},g\right\}+\left\{f,\frac{\partial g}{\partial t}\right\}-\{\{g,H\},f\}-\{\{H,f\},g\} \\ &\overset{(5.27),\,(5.25)}{=} \left\{\frac{\partial f}{\partial t}+\{f,H\},g\right\}+\left\{f,\frac{\partial g}{\partial t}+\{g,H\}\right\} \overset{(5.19)}{=} \left\{\frac{df}{dt},g\right\}+\left\{f,\frac{dg}{dt}\right\} \\ &= \{0,g\}+\{f,0\} \overset{(5.26)}{=} 0. \end{aligned} \tag{5.36}$$

D. Conservation of probability and energy in quantum mechanics

The lemma [see Eq. (5.12)] employed to prove the Ehrenfest theorem has other important consequences. In particular, this lemma implies that the time-dependent Schrödinger equation conserves the norm of a quantum state as well as its energy:

Proposition 22 *Let $|\psi(t)\rangle$ solve the TDSE with a possibly time-dependent Hamiltonian $\hat{H}(t)$.*

*1) (**Conservation of norm**) The norm of a quantum state is independent of time:*

$$\|\psi(t)\| = \|\psi(0)\|. \tag{5.37}$$

In other words, probability is conserved by the TDSE.

*2) (**Conservation of energy**) If the Hamiltonian is time-independent (i.e., if $\partial H/\partial t = 0$) then the expectation value of energy is conserved:*

$$\langle\hat{H}\rangle_{\psi(t)} = \langle\hat{H}\rangle_{\psi(0)}. \tag{5.38}$$

Proof. From the definition of the norm of the state ψ we have

$$\|\psi(t)\|^2 = \langle\psi(t)|\psi(t)\rangle = \langle\psi(t)|\hat{1}|\psi(t)\rangle,$$

where we have inserted the identity operator $\hat{1}$, which is, obviously, time-independent and commutes with the Hamiltonian $\hat{H}(t)$. Using the lemma for $\hat{A}=\hat{1}$, we have

$$\frac{d}{dt}\|\psi(t)\|^2 = \frac{d}{dt}\langle\hat{1}\rangle = \frac{1}{i\hbar}\langle[\hat{1},\hat{H}(t)]\rangle = 0.$$

Conservation of energy for time-independent Hamiltonians follows from the same lemma applied to $\hat{A}=\hat{H}$:

$$\frac{d}{dt}\langle\hat{H}\rangle = \frac{1}{i\hbar}\langle[\hat{H},\hat{H}]\rangle = 0 \tag{5.39}$$

because the Hamiltonian commutes with itself.□

It is important to point out the analogy between the conservation of probability and Liouville's theorem, which asserts the conservation of phase-space volume, and the analogy between the laws of conservation of energy in quantum and classical mechanics—notice the similarity of the proofs using the Poisson bracket [Eq. (5.30)] and the commutator [Eq. (5.39)].

E. Bohr-Sommerfeld quantization rules

Let us put what we have learned about phase space to use in quantum mechanics. Indeed, the approach that we shall use to "**quantize**" the harmonic oscillator was the approach used in "**old quantum theory**" to quantize the hydrogen atom before Erwin Schrödinger derived his equation.

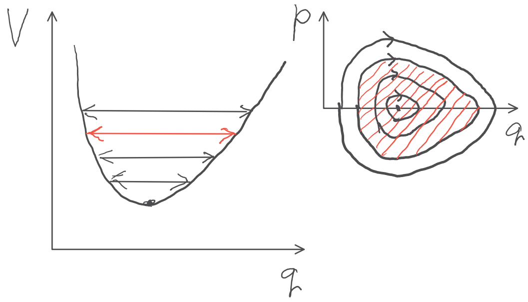

FIG. 14. Potential energy and phase portrait of a one-dimensional bound system. Bohr-Sommerfeld quantization rules state that the only allowed states are those represented by periodic orbits encircling an area that is an integer multiple of the Planck constant.

Let us consider a one-dimensional system with a two-dimensional phase space. We assume that the system is **bound**, i.e., that its trajectories do not escape to infinity. In one spatial dimension, this implies that each trajectory bounces back and forth between two **turning points** (see Fig. 14). In phase space, such trajectories will form **periodic orbits**, i.e., loops topologically equivalent to a circle. According to **Bohr-Sommerfeld quantization** rules, the only quantum-mechanically allowed states of the system are those described by a periodic orbit encircling a phase-space region whose area is an integer multiple of Planck's constant h (not $\hbar$). These rules were the basis of the above-mentioned "old quantum theory," which is now recognized as a **semiclassical approximation** to quantum mechanics. The phase-space area I encircled by the periodic orbit is computed as

$$I := \oint p dq$$

and called an **action**.

[*Remark*: Action I has the same physical dimension as the action S defined in the principle of least action, but it is a somewhat different quantity, which is easy to see from the following calculation. The action S along a trajectory that loops once about a periodic orbit is

$$S(T) = \int_0^T L(q_t, \dot{q}_t)\, dt = \int_0^T [p_t \dot{q}_t - H(q_t, p_t)]\, dt = \int_0^T (p_t \dot{q}_t - E)\, dt = \oint p dq - ET = I - ET, \tag{5.40}$$

where T is the period of the periodic orbit and where we have used the conservation of energy along the trajectory $[H(q_t, p_t) = E]$, definition of velocity ($\dot{q} = dq/dt$), and the periodic-orbit property $q(T) = q(0)$. Note that it does not matter where on the periodic orbit the trajectory starts as long as the trajectory loops once but fully about the orbit.]

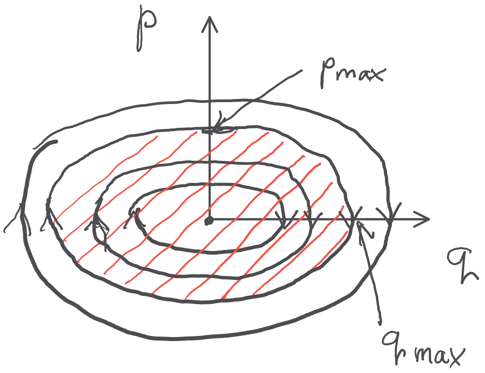

FIG. 15. Phase portrait of a harmonic oscillator. Bohr-Sommerfeld quantization rules state that the red-shaded area of the ellipse with semiaxes $q_{\max}$ and $p_{\max}$ must be an integer multiple of the Planck constant: $\pi q_{\max} p_{\max} = nh$.

Let us apply the **Bohr-Sommerfeld quantization rule**, which states that

$$I = nh, \quad n \in \mathbb{N}, \tag{5.41}$$

to the harmonic oscillator, in which each trajectory forms an ellipse (see Fig. 15)

$$E = \frac{p^2}{2m} + \frac{1}{2} k q^2$$

in phase space. By considering $p = 0$ and $q = 0$, respectively, we find that this ellipse has semiaxes

$$q_{\max} = \sqrt{2E/k} \quad \text{and} \quad p_{\max} = \sqrt{2mE}. \tag{5.42}$$

Because an ellipse with semiaxes a and b has an area πab, the action of our trajectory is

$$I = \pi q_{\max} p_{\max} = 2\pi E \sqrt{m/k} = 2\pi \frac{E}{\omega} = TE,$$

where $\omega = \sqrt{k/m}$ is the angular frequency and $T = 2\pi/\omega$ is the period, which—in a harmonic oscillator—does not depend on the amplitude $q_{\max}$. Applying the Bohr-Sommerfeld rule tells us that

$$I = 2\pi \frac{E}{\omega} = nh,$$

and therefore, the only allowed energies should be

$$E_n = n \frac{h}{2\pi} \omega = n\hbar\omega.$$

Comparing this result with the well-known exact quantum energies $E_n = (n + 1/2)\,\hbar\omega$ of a harmonic oscillator, we realize that there is a shift of $\hbar\omega/2$ due to the **zero-point vibrational energy**. Still, the result of Bohr-Sommerfeld quantization rules is rather impressive because it completely avoids an explicit solution of the Schrödinger equation. I should mention that the Bohr-Sommerfeld rules yield the *exact* quantum-mechanical energies of the hydrogen atom (without the fine structure, of course), which we have seen indirectly in the first chapter, and that, since the original statement by Bohr and Sommerfeld, their rules have been refined so that one can predict the correction of 1/2 that must be added to n even in the harmonic oscillator.

[*Historical note*: The reason why these refined rules give exact results for both the harmonic oscillator and the Coulomb problem are rather deep and are connected to the exceptional nature of the potentials r^2 and r^{-1}. In three dimensions ($D = 3$), both of these systems are **superintegrable**, which means that they have $2D - 1$ independent constants of motion. In celestial mechanics, **Newton's gravitational law** is also described by the r^{-1} potential and is the reason why the perihelion (i.e., the point along the orbit at which a planet approaches the Sun the most) does not change over time. A tiny deviation from this, reflected in the observed **precession of the perihelion of Mercury** puzzled astronomers for a long time and was one of the first confirmations of **Einstein's general theory of relativity**, which explained this deviation quantitatively.]

F. Wigner representation of a wave function

1. *Classical probability density*

In classical statistical mechanics, an **average value of an observable** $A(q,p)$ depending both on positions and momenta can be evaluated as the average

$$\langle A \rangle_{\mathrm{cl}} = \int dq \int dp\, A\,(q,p)\, \rho\,(q,p)\,, \tag{5.43}$$

where $\rho(q,p)$ is the **probability density** of the system being located at the phase space point (q,p). In thermal equilibrium, e.g., $\rho(q,p)$ is the classical **Boltzmann distribution**

$$\rho_{\mathrm{B}}(q,p) := e^{-\beta H(q,p)}/Z_{\mathrm{cl}}, \tag{5.44}$$

where $\beta := 1/(k_B T)$ and the division by the **classical partition function**

$$Z_{\mathrm{cl}} := \int dq \int dp\, e^{-\beta H(q,p)} \tag{5.45}$$

guarantees normalization. Being a probability density, the function $\rho(q,p)$ in general satisfies the following conditions:

$$\rho(q,p) \in \mathbb{R}, \tag{5.46}$$

$$\rho(q,p) \geq 0, \tag{5.47}$$

$$\int dq \int dp\, \rho(q,p) = 1, \tag{5.48}$$

$$\int dq\, \rho(q,p) = \rho_p(p), \tag{5.49}$$

$$\int dp\, \rho(q,p) = \rho_q(q). \tag{5.50}$$

In other words, ρ is a normalized nonnegative real-valued function on phase space with a unit phase-space integral. The last two relations express that the integral of ρ over q gives the **marginal probability density** $\rho_p(p)$ for momentum (i.e., probability density for a momentum being p regardless of the position q) and that the integral of ρ over p yields the marginal probability density $\rho_q(q)$ for position.

2. Wigner function

In quantum mechanics, because of the Heisenberg uncertainty principle, it seems impossible to represent a quantum state as a simultaneous function of q and p. Instead, it seems obligatory to use either the position or momentum representation of the wavefunction. Yet, wouldn't it be great if we could define a quantity ρ_W analogous to the classical probability density ρ, which would allow us to compute expectation values of observables by evaluating a phase space integral

$$\langle A \rangle_\psi = \int dq \int dp\, A_W(q,p)\, \rho_W(q,p), \tag{5.51}$$

where A_W is some kind of phase-space representation of the observable A? Indeed, Eugene Wigner invented such a quantity, now called the **Wigner function** (hence the subscript W) and defined it using the integral

$$\rho_W(q,p) := \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\psi(q-s/2)\psi(q+s/2)^* e^{ips/\hbar}ds. \tag{5.52}$$

Alternatively, in Dirac notation,

$$\rho_W(q,p) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\langle q-s/2|\psi\rangle\langle\psi|q+s/2\rangle e^{ips/\hbar}ds. \tag{5.53}$$

Proposition 23 *(**Properties of the Wigner function**) The Wigner function (5.52) satisfies:*

$$\rho_W\,(q,p) \in \mathbb{R}, \tag{5.54}$$

$$\int dq \int dp\,\rho_W\,(q,p) = 1, \tag{5.55}$$

$$\int dq\,\rho_W\,(q,p) = \left|\tilde{\psi}(p)\right|^2, \tag{5.56}$$

$$\int dp\,\rho_W\,(q,p) = |\psi(q)|^2\,. \tag{5.57}$$

In particular, ρ_W is not a probability density because it may be negative. It is, instead, called a **quasiprobability density function**. In contrast, both marginal distributions yield positive probability density functions $|\tilde{\psi}(p)|^2$ and $|\psi(q)|^2$.

Proof. To show that ρ_W is real [Eq. (5.54)], we show that it is equal to its complex conjugate:

$$\begin{aligned}\rho_W\,(q,p)^* &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\psi(q-s/2)^*\psi(q+s/2)e^{-ips/\hbar}ds\\ &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\psi(q+r/2)^*\psi(q-r/2)e^{ipr/\hbar}dr = \rho_W\,(q,p)\,,\end{aligned}$$

where we have changed variables from s to $r := -s$. The normalization (5.55) of the Wigner function follows from Eq. (5.57) because $\psi(q)$ is normalized:

$$\int dq\int dp\,\rho_W\,(q,p) \overset{(5.57)}{=} \int dq\,\left|\psi(q)\right|^2 = 1$$

Proofs of properties (5.56) and (5.57) are left as an exercise.□

3. *Wigner function of a Gaussian wavepacket*

Because a Gaussian wavepacket describes "the most classical" among all possible quantum states and because the Wigner function provides an analogue of the classical probability density, one should have high expectations from the Wigner function of a Gaussian wavepacket (see Fig. 16).

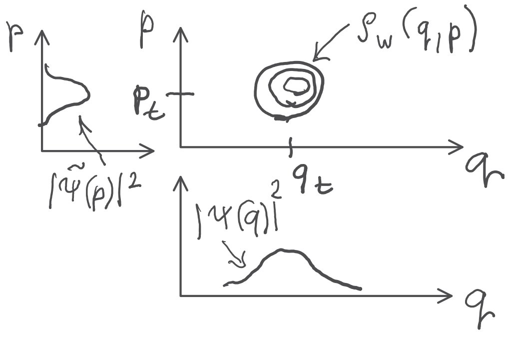

FIG. 16. Contour plot of the Wigner function of a Gaussian wavepacket (here with a purely imaginary α_t). Also shown are the marginal probability densities of position and momentum.

Proposition 24 *The Wigner function of the Gaussian wavepacket (3.16)*

$$\psi(q,t) = \exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\alpha_t (q-q_t)^2 + p_t(q-q_t) + \gamma_t\right]\right\}, \tag{5.58}$$

$$e^{-\operatorname{Im}\gamma_t/\hbar} = (\operatorname{Im}\alpha_t/\pi\hbar)^{1/4}, \tag{5.59}$$

is a phase-space Gaussian

$$\rho_W(q,p,t) = \frac{1}{\pi\hbar}\exp\left\{-\frac{1}{\hbar}\left[\operatorname{Im}\alpha_t (q-q_t)^2 + (p-p_t-\operatorname{Re}\alpha_t (q-q_t))^2/\operatorname{Im}\alpha_t\right]\right\}. \tag{5.60}$$

In particular, if the width parameter α_t is purely imaginary, there is no correlation between position and momentum, and the Wigner function can be factorized as

$$\rho_W(q,p,t) = |\psi(q,t)|^2 |\tilde{\psi}(p,t)|^2, \tag{5.61}$$

where

$$|\psi(q,t)|^2 = \left(\frac{\operatorname{Im}\alpha_t}{\pi\hbar}\right)^{1/2}\exp\left[-\frac{1}{\hbar}\operatorname{Im}\alpha_t (q-q_t)^2\right] \text{ and}$$
$$|\tilde{\psi}(p,t)|^2 = (\pi\hbar\operatorname{Im}\alpha_t)^{-1/2}\exp\left[-\frac{1}{\hbar}(p-p_t)^2/\operatorname{Im}\alpha_t\right].$$

are the probability densities in position and momentum, respectively. In the special case of a coherent state of a harmonic oscillator, $\alpha_t = im\omega$ is a constant imaginary number and

$$\rho_W(q,p,t) = \frac{1}{\pi\hbar}\exp\left\{-\frac{1}{\hbar}\left[m\omega(q-q_t)^2 + \frac{(p-p_t)^2}{m\omega}\right]\right\}. \tag{5.62}$$

Proof. From the definition of the Wigner function, it follows that

$$\rho_W(q,p,t) = \frac{1}{2\pi\hbar}(\operatorname{Im}\alpha_t/\pi\hbar)^{1/2}\int_{-\infty}^{\infty} e^{iF/\hbar} ds, \tag{5.63}$$

where

$$F = i \operatorname{Im} \alpha_t [(q - q_t)^2 + (s/2)^2] + [p - p_t - \operatorname{Re} \alpha_t (q - q_t)] \, s. \tag{5.64}$$

The integral over s is a Gaussian integral with an analytical solution

$$\int_{-\infty}^{\infty} e^{iF/\hbar} ds = \int_{-\infty}^{\infty} \exp\left(-As^2 + iBs + C\right) ds = \sqrt{\frac{\pi}{A}} e^{C - B^2/(4A)}, \tag{5.65}$$

where

$$A := \frac{\operatorname{Im} \alpha_t}{4\hbar}, \quad B := [p - p_t - \operatorname{Re} \alpha_t (q - q_t)] / \hbar, \quad \text{and} \quad C := -\frac{\operatorname{Im} \alpha_t}{\hbar} (q - q_t)^2 . \tag{5.66}$$

Inserting the result (5.65) of the integral over s into Eq. (5.63) and using the definitions (5.66) of A, B, C yields the assertion (5.60).□

4. Time evolution of the Wigner functions of coherent and squeezed states of a harmonic oscillator

Because it provides simultaneous information about position and momentum, the Wigner function yields a more intuitive picture of the time evolution of a quantum state. Figures 17 and 18 contrast the time evolutions of the Wigner function $\rho_W(q)$ and of the position-space density $|\psi(q)|^2$ for a Gaussian wavepacket moving in a harmonic oscillator.

The coherent state has a constant width and, in the q-representation, the density simply moves back and forth between two turning points (see Fig. 17). The contour plot of the Gaussian Wigner function is a circle moving along the trajectory of the wavepacket's center. The position-space density is a marginal probability density obtained from the Wigner function by projecting onto the q-axis; because the Wigner function is a circle of constant radius, the q-spread of the wavepacket is also constant. While both pictures are consistent, the Wigner function visualizes information about q and p simultaneously.

The situation becomes even more interesting for the squeezed state (see Fig. 18). Here the plot of $|\psi(q)|^2$ seems mysterious: not only does the wavepacket move back and forth between the turning points, but, in addition, its width changes magically. In phase space, the change of the width is not magic at all: the contour plot of the Wigner function is now an ellipse, rather than a circle, which again follows rigidly the trajectory of the wavepacket's center. This implies that the ellipse rotates in phase space and that the projection of ρ_W onto the q-axis, giving $|\psi(q)|^2$, changes accordingly, resulting either in narrow but high peaks at $t = T/4$ and $t = 3T/4$ or in wide but small peaks at $t = 0$ and $t = T/2$. You probably heard about the four-dimensional space-time, in which Einstein's theory of relativity becomes simpler than if it is presented in the usual space and time separately. Likewise, many theoretical physicists believe that we live in ten space-time dimensions because the laws of nature become more natural there. Here, we are less ambitious by moving from one spatial dimension to two phase-space dimensions. Still, what seemed magical in position space becomes completely clear in the higher-dimensional phase space: the spread of q is explained by projecting the rotating Wigner function onto the q axis.

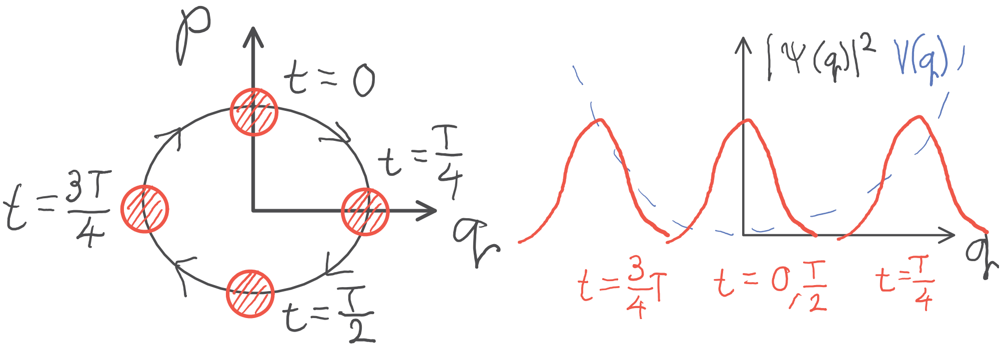

FIG. 17. Time evolution of the Wigner function (left) and corresponding position density (right) of a coherent state of a harmonic oscillator.

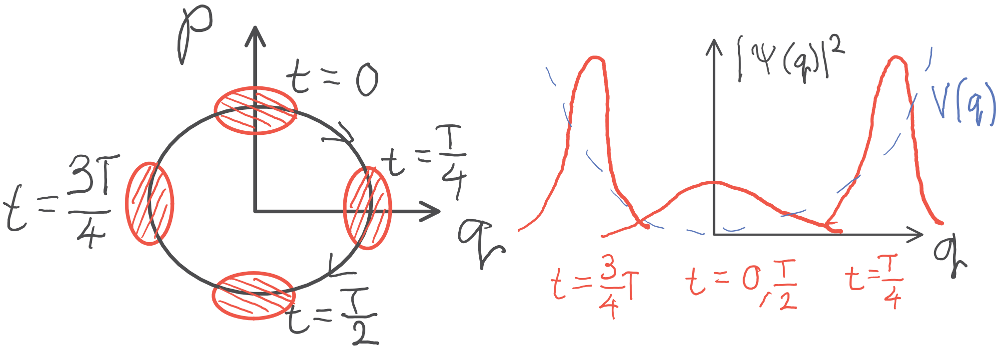

FIG. 18. Time evolution of the Wigner function (left) and corresponding position density (right) of a squeezed state of a harmonic oscillator.

5. *Calculation of expectation values of observables using the Wigner function*

The original motivation for introducing the Wigner function was having a phase space analogue (5.51) of the expression (5.43) for classical expectation values. To reach this goal, one first needs to define a **Wigner transform** A_W of an operator $\hat{A}$ corresponding to a classical observable $A(q,p)$. Indeed, even the question of associating an operator $\hat{A}$ to a classical observable $A(q,p)$ is, in general, nontrivial. The most widely used prescription is called **Weyl quantization**. Without building up the full machinery of the general definition, let us demonstrate the basic issue on the simplest nontrivial example, i.e., an observable qp to which Weyl quantization associates a Hermitian operator $\left(\hat{q}\hat{p}+\hat{p}\hat{q}\right)/2$. In general, the process is "democratic" for all polynomials of q and p in the sense that it gives an equal weight to all possible orderings of the noncommuting operators $\hat{q}$ and $\hat{p}$. Note that the "obvious" and simpler but wrong prescription would associate to the classical observable qp the quantum operator $\hat{q}\hat{p}$, which is not Hermitian, and therefore can have complex eigenvalues, even though both $\hat{q}$ and $\hat{p}$ are Hermitian. The product $\hat{q}\hat{p}$ is not Hermitian because $\hat{q}$ and $\hat{p}$ do not commute:

$$(\hat{q}\hat{p})^{\dagger}=\hat{p}^{\dagger}\hat{q}^{\dagger}=\hat{p}\hat{q}=\hat{q}\hat{p}-i\hbar\neq\hat{q}\hat{p}.$$

For simplicity, we will only consider observables that are sums of observables depending only on position or only on momentum,

$$A(q,p)=Q(q)+P(p), \tag{5.67}$$

and for which the above-mentioned complication does not occur. For such observables, the corresponding operator is the same function of $\hat{q}$ and $\hat{p}$ operators,

$$\hat{A}=\hat{Q}+\hat{P}=Q\left(\hat{q}\right)+P\left(\hat{p}\right),$$

whose Wigner transform is equal to the original phase space function:

$$A_W(q,p)=Q(q)+P(p).$$

Examples of such special observables include the position $[q_W\left(q,p\right)=q]$, momentum $[p_W\left(q,p\right)=p]$, and the standard Hamiltonian $[H_W(q,p)=H(q,p)=p^2/2m+V(q)]$.

Proposition 25 *For an observable (5.67), equal to a sum of a function of* q *and a function of* p*, the quantum expectation value of the corresponding operator* $\hat{A}$ *in a quantum state* ψ *described by a Wigner function* ρ_W *can be computed according to the classical-like Eq. (5.51).*

Proof.

$$\begin{aligned}\langle\hat{A}\rangle=\langle\hat{Q}\rangle+\langle\hat{P}\rangle&=\int dq\,Q\left(q\right)\left|\psi\left(q\right)\right|^2+\int dp\,P\left(p\right)|\tilde{\psi}\left(p\right)|^2\\&=\int dq\,Q\left(q\right)\int dp\,\rho_W\left(q,p\right)+\int dp\,P\left(p\right)\int dq\,\rho_W\left(q,p\right)\\&=\int dq\int dp\,\left[Q\left(q\right)+P\left(p\right)\right]\rho_W\left(q,p\right)=\int dq\int dp\,A_W\left(q,p\right)\,\rho_W\left(q,p\right).\square\end{aligned}$$

VI. APPROXIMATE METHODS TO SOLVE THE TIME-DEPENDENT SCHRÖDINGER EQUATION

There exist only very few systems, for which the TDSE (1.4)

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle \tag{6.1}$$

with a time-dependent Hamiltonian $\hat{H}(t)$ can be solved exactly analytically. When an exact analytical solution does not exist, it is possible to solve the TDSE (6.1) numerically or analytically but approximately. In this chapter, we shall discuss three approximations, which are valid when the change of $\hat{H}(t)$ is (i) fast, (ii) slow, or (iii) small in some sense. In addition, we will describe the variational approximation, which finds the optimal solution to Eq. (6.1) among wavefunctions of a specific form.

A. Sudden approximation

[!!! See also Tannor 1.3: Please do the calculation presented there yourself, as an exercise.]

Sometimes the Hamiltonian $\hat{H}(t)$ changes very quickly (see Fig. 19) from an initial time-independent value $\hat{H}^i$ to a final time-independent value $\hat{H}^f$, and the change is so fast that the quantum state $\psi(t)$ does not have time to adjust (see Fig. 20).

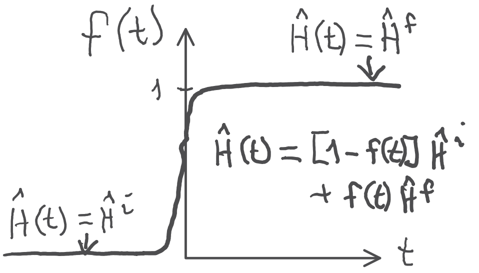

FIG. 19. Fast change of the Hamiltonian required for the validity of the sudden approximation.

For all practical purposes, we can therefore write

$$\hat{H}(t) = \begin{cases} \hat{H}^i, & t < 0 \\ \hat{H}^f, & t > 0 \end{cases}.$$

The **sudden approximation**, mathematically expressed by the equation

$$\lim_{t\to 0^+} \psi(t) = \lim_{t\to 0^-} \psi(t),$$

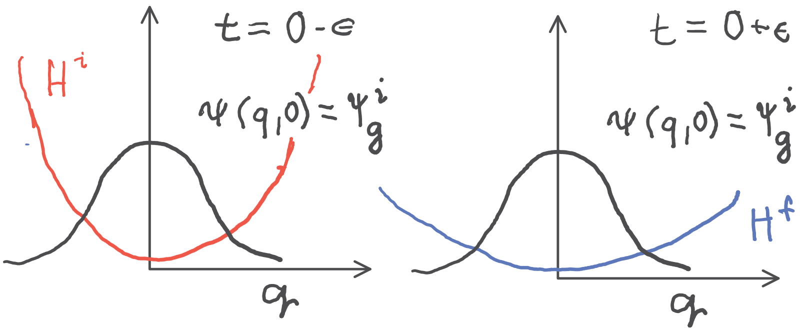

FIG. 20. Sudden approximation applied to the ground state of a harmonic oscillator.

requires that the state of the system do not change during the rapid change of the Hamiltonian. Most frequently encountered situation occurs when the initial state for $t \leq 0$ is a stationary state of $\hat{H}^i$, i.e.,

$$|\psi\,(t)\rangle = |\psi\,(0)\rangle e^{-iE_n^i t/\hbar} \quad \text{for } t < 0.$$

In such a state, expectation values of observables are independent of time. However, even such states give rise to interesting dynamics after the change of the Hamiltonian to $\hat{H}^f$ because the state is now a superposition of the eigenstates of the new Hamiltonian.

The recipe for solving quantum dynamics problems with the sudden approximation is very simple: All one must do is solve the TDSE with the *time-independent* new Hamiltonian $\hat{H}^f$, which can be done using the basis set method. The solution for $t > 0$ is

$$|\psi(t)\rangle = \sum_n c_n e^{-iE_n^f t/\hbar} |\varphi_n\rangle,$$

where E_n^f are the eigenenergies of $\hat{H}^f$ and the coefficients c_n are obtained by expanding the initial state $\psi\,(0)$ in the eigenstates φ_n of $\hat{H}^f$:

$$c_n = \langle \varphi_n | \psi(0) \rangle = \int \varphi_n(q)^* \psi(q,0) dq.$$

The most prominent example of the **sudden approximation** in physical chemistry is the time-dependent description of **Franck-Condon transition** between two electronic states that was already mentioned in the Introduction (compare Figs. 1 and 21). After an absorption of a visible or UV photon, the molecule undergoes a transition between two electronic states. This occurs on the electronic time scale ($\sim$ 1 fs), which is much shorter than a typical time scale of nuclear motion ($\sim$ 10 fs to 100 fs). As a result, the nuclear wavefunction does not have time to adjust during the short electronic excitation and we can solve the problem by simply promoting the initial nuclear wavefunction from the ground to the excited electronic potential energy surface (see Fig. 21).

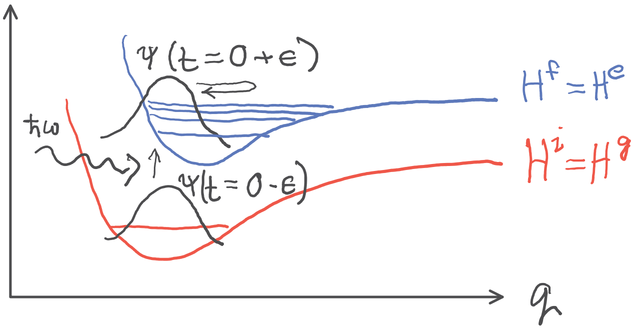

FIG. 21. Sudden approximation applied to the Franck-Condon transition between two electronic states of a molecule. The shape of the wavefunction does not change because we assume the Condon approximation: the transition dipole moment between the ground and excited electronic states is independent of the nuclear coordinate q.

Note: As we shall learn later, there are two further assumptions that give rise to this simplified picture: the electromagnetic interaction cannot be too strong (i.e., the **time-dependent perturbation theory** is valid) and the **transition dipole moment** $\mu_{eg}(q)$ between the excited (e) and ground (g) electronic states should be approximately constant as a function of nuclear coordinates q (this is called the **Condon approximation**):

$$\mu_{eg}(q) \approx \mu_{eg,\mathrm{CA}} = \mathrm{const} \tag{6.2}$$

Yet, if the transition dipole moment depends on nuclear coordinates, there is a simple extension of the sudden approximation: We take for the initial state $\Psi(q,0)$ on the excited-state surface the product of the transition dipole moment and the original state $\psi(q,0)$ on the ground-state surface:

$$\lim_{t\to 0^+} \Psi(q,t) = \mu_{eg}(q) \lim_{t\to 0^-} \psi(q,t) \,. \tag{6.3}$$

This prescription remains valid even if the Condon approximation breaks down. An extreme example is an **electronically forbidden transition**, in which $\mu_{eg}(q_{\mathrm{eq}}) = 0$, which typically happens due to symmetry of the ground and excited electronic states. Here, using the Condon approximation $\mu_{eg}(q) \approx \mu_{eg,\mathrm{CA}} = \mathrm{const} = \mu_{eg}(q_{\mathrm{eq}}) = 0$ would result in no transition and no spectrum. Such transitions, however, can be weakly "**vibronically allowed**" due to the coordinate dependence of the transition dipole moment. The leading coordinate dependence comes from the gradient of μ_{eg} at the equilibrium geometry and gives rise to the **Herzberg–Teller approximation**, in which the transition dipole moment is assumed to depend linearly on the nuclear coordinates:

$$\mu_{eg}(q) \approx \mu_{eg,\mathrm{HT}} = \mu'_{eg}(q_{\mathrm{eq}}) \cdot (q - q_{\mathrm{eq}}). \tag{6.4}$$

An example of an electronically forbidden but vibronically allowed spectrum is the absorption spectrum of benzene, which is associated to the electronic transition $\tilde{A}^1B_{2u} \leftarrow \tilde{X}^1A_{1g}$.

B. Adiabatic approximation

The **adiabatic approximation** is, in a sense, the opposite of the sudden approximation. Here, the time-dependent Hamiltonian $\hat{H}(t)$ changes so *slowly* that the initial state $\psi(t)$ has "all the time it needs to adjust" to the changes in the Hamiltonian. In particular, if $\psi(0)$ is an eigenstate of $\hat{H}(0)$, then the **adiabatic theorem** shows that the exact state $\psi(t)$ at time t will *approximately* remain an eigenstate of $\hat{H}(t)$ at all times. The **adiabatic approximation** consists in assuming that the $\psi(t)$ remains *exactly* an eigenstate of $\hat{H}(t)$. Figure 22 shows an example in which a harmonic potential has a slowly changing force constant. In the limit of very slow change of $\hat{H}(t)$, we would find that if the initial state $\psi(0)$ were the Gaussian ground state of $\hat{H}(0)$, the state at time t would be a (Gaussian) ground state of the instantaneous Hamiltonian $\hat{H}(t)$. Again, this behavior is justified rigorously by the **quantum adiabatic theorem**, which finds estimates on the probability of transitions for slow changes of the Hamiltonian. Roughly speaking, the theorem asserts that the probability of transition goes to zero as the energy gap between states increases and the rate of change of the Hamiltonian decreases. Many textbooks on quantum mechanics claim to provide proofs, which are not proofs in the mathematical sense. Instead of attempting a difficult mathematical proof, let me show you which terms in the TDSE must be neglected to obtain the adiabatic approximation.

In Sec. II C, we solved the TDSE with a time-dependent Hamiltonian in a general, nonorthogonal, time-dependent basis $|n(t)\rangle$. Now we will consider a special case of the **adiabatic basis**,

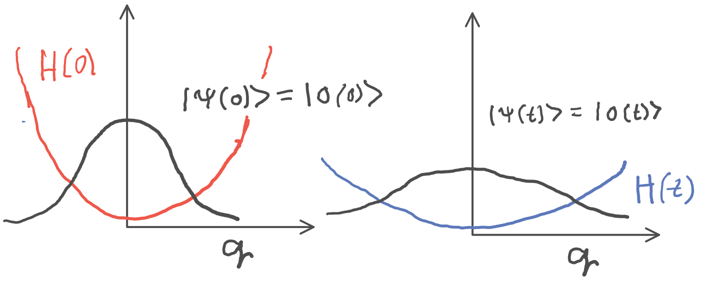

FIG. 22. Adiabatic approximation applied to the ground state of the harmonic oscillator. Assuming that the potential changes slowly, then if $\psi(0)$ is the ground state of $\hat{H}(0)$, $\psi(t)$ will be approximately the ground state of $\hat{H}(t)$ for $t > 0$.

consisting of the instantaneous eigenstates of $\hat{H}(t)$, i.e., a basis $|n(t)\rangle$ that depends continuously on t and is defined by the relation

$$\hat{H}(t)|n(t)\rangle = E_n(t)|n(t)\rangle. \tag{6.5}$$

Note that because eigenstates of a Hermitian operator $\hat{H}(t)$ corresponding to different eigenvalues are orthogonal, we can assume that the basis is in fact orthonormal (if there are degenerate eigenvalues, you can find such a basis by Gramm-Schmidt orthonormalization within each set of eigenstates with the same energy): the overlap matrix

$$S_{kn}(t) := \langle k(t)|n(t)\rangle = \delta_{kn} \tag{6.6}$$

becomes the *identity* and the Hamiltonian matrix

$$H_{kn}(t) = \langle k(t)|\hat{H}(t)|n(t)\rangle = E_n(t)\delta_{kn} \tag{6.7}$$

becomes *diagonal.* Recall that in Sec. II C, we rewrote the general TDSE as [see Eq. (2.25)]

$$i\hbar\mathbf{S}(t)\dot{\mathbf{c}}(t) = (\mathbf{H}(t) - i\hbar\mathbf{D}(t))\,\mathbf{c}(t), \tag{6.8}$$

where

$$D_{kn}(t) := \langle k(t)|\dot{n}(t)\rangle \tag{6.9}$$

is the **nonadiabatic coupling** matrix, depending on the time derivative of the eigenstate $|n(t)\rangle$. In the adiabatic basis, where $\mathbf{S}(t) = \mathrm{Id}$ and $\mathbf{H}(t) = \mathbf{E}(t)$ are both diagonal matrices, this equation reduces to

$$i\hbar\dot{\mathbf{c}}(t) = (\mathbf{E}(t) - i\hbar\mathbf{D}(t))\,\mathbf{c}(t). \tag{6.10}$$

If the change of the Hamiltonian $\hat{H}(t)$ is slow, so will be the change of the eigenstate $|n(t)\rangle$ expressed in the time derivative $|\dot{n}(t)\rangle$. This, in turn, will decrease the nonadiabatic couplings (6.9), which induce transitions between different eigenstates of $\hat{H}(t)$ due to the time dependence of these eigenstates. The adiabatic approximation is then obtained by simply neglecting these nonadiabatic couplings in Eq. (6.10):

$$i\hbar\dot{\mathbf{c}}(t) = \mathbf{E}(t)\mathbf{c}(t). \tag{6.11}$$

Because $\mathbf{E}(t)$ is a diagonal matrix, the system of differential equations for $c_n(t)$ decouples and Eq. (6.11) is equivalent to

$$i\hbar\dot{c}_n(t) = E_n(t)c_n(t) \quad \text{for each } n, \tag{6.12}$$

with a simple solution

$$c_n(t) = c_n\,(0)\,e^{-i\int_0^t E_n(\tau)d\tau/\hbar} \tag{6.13}$$

This implies that

$$|c_n(t)| = |c_n(0)|\,. \tag{6.14}$$

In particular, if $\psi(0)$ is the kth eigenstate of $\hat{H}(0)$, expressed by $c_n(0) = \delta_{kn}$, then $\psi(t)$ will remain the kth eigenstate of $\hat{H}(t)$ for all t: $|c_n(t)| = \delta_{kn}$.

Born-Oppenheimer approximation provides an example of the adiabatic approximation in molecular physics. You may well ask: “Where is the time dependence in the molecular Hamiltonian?” Indeed, H_{mol} is time-independent, but if you view it as a Hamiltonian for electrons depending parametrically on the moving positions of nuclei, you can think of it as a slowly changing time-dependent Hamiltonian for electrons—remember that the much heavier nuclei move much more slowly than the lighter electrons.

C. Time-dependent variational approximation

Let us seek an approximate solution of the time-dependent Schrödinger equation only within a certain subset M of the full Hilbert space $\mathcal{H}$. For example, we could search a solution among wavefunctions $\phi_{\alpha,\beta,\ldots} \in M \subset \mathcal{H}$ that depend on real or complex parameters $\alpha, \beta, \ldots$. The **Dirac-Frenkel time-dependent variational principle** (TDVP) suggests that an optimal solution within the manifold M is the one that satisfies the equation

$$\langle \delta\phi | i\hbar \frac{d}{dt} - \hat{H} | \phi(t) \rangle = 0, \tag{6.15}$$

where $\delta\phi$ is a variation of the solution, i.e., an infinitesimal change of ϕ such that $\phi + \delta\phi$ is still in the approximation manifold M. More precisely, the variation can be written as $\delta\phi = \varepsilon\eta$, where ε is an infinitesimal real number and η is an arbitrary tangent vector to the manifold M at the point $\phi(t)$. See Fig. 23. In particular, $\delta\phi$ does not have to be related to the solution ϕ.

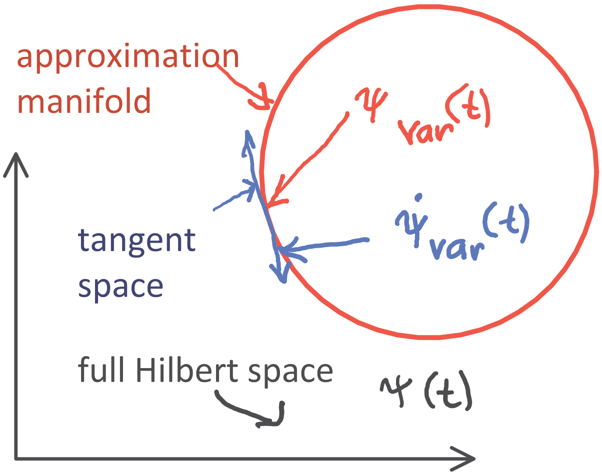

FIG. 23. Schematic representation of the time-dependent variational principle. The exact wavefunction $\psi(t)$ can lie anywhere in the Hilbert space, here represented by the two-dimensional plane. The approximate variational state $\psi_{\mathrm{var}}(t)$ must, at any time t, be a state representable in terms of a certain set of parameters and, therefore, lie in the "approximation manifold".

The application of the TDVP (6.15) to the ansatz $\phi_{\alpha,\beta,\ldots}$ will replace the original time-dependent Schrödinger equation for ϕ with a system of coupled differential equations for the parameters α, β, … In analogy to the time-independent variational principle, well-known from basic courses on quantum mechanics for finding approximately the ground state of $\hat{H}$ as the optimal solution among candidates in a set, the TDVP finds an optimal solution to the TDSE within a manifold of options. In addition to this, the time-dependent variational approximation has several remarkable properties that mimic the properties of the exact solution of the TDSE:

Proposition 26 *$\phi(t)$ obtained by the time-dependent variational principle (6.15) applied to a TDSE with a time-independent Hamiltonian $\hat{H} = \mathrm{const}$ conserves the expectation value of energy.*

Proof. For the proof, it is convenient to rewrite the variational principle (6.15) as

$$\langle \delta\phi | i\hbar \dot{\phi}(t) \rangle = \langle \delta\phi | \hat{H} | \phi(t) \rangle \tag{6.16}$$

Let $\phi(t)$ denote the solution obtained from the time-dependent variational principle. The time derivative of energy satisfies

$$\begin{aligned} \frac{d}{dt}\langle \hat{H} \rangle_{\phi(t)} &= \frac{d}{dt}\langle \phi(t) | \hat{H} | \phi(t) \rangle = \langle \dot{\phi} | \hat{H} | \phi \rangle + \langle \phi | \hat{H} | \dot{\phi} \rangle = 2\,\mathrm{Re}\langle \dot{\phi} | \hat{H} | \phi \rangle \\ &\underset{\text{with } \delta\phi = \varepsilon\dot{\phi}}{\overset{(6.16)}{=}} 2\,\mathrm{Re}\langle \dot{\phi} | i\hbar\dot{\phi} \rangle = 2\hbar\,\mathrm{Re}[i\|\dot{\phi}\|^2] = 0, \end{aligned} \tag{6.17}$$

where we invoked the time independence and Hermitian property of $\hat{H}$, conjugate symmetry of the scalar product, the TDVP (6.16) with a specific choice of $\delta\phi$, namely, $\delta\phi = \varepsilon\dot{\phi}$ (because $\dot{\phi}$ is certainly a tangent vector to the approximation manifold), linearity of the scalar product in the second argument, and the real-valuedness of the norm $\|\dot{\phi}\|$.□

Proposition 27 *Let us assume that $\lambda\phi \in M$ for every $\phi \in M$ and every $\lambda > 0$. (In other words, the approximation manifold contains rays.) Then $\phi(t)$ obtained by the time-dependent variational principle (6.15) conserves the norm of the state.*

Proof. The assumption implies that $\delta\phi = \varepsilon\phi$ is a possible variation. To see this, just take $\lambda = 1 + \varepsilon$. Since both ϕ and $\lambda\phi = (1 + \varepsilon)\phi$ are in the approximation manifold, their infinitesimal difference $\delta\phi = \varepsilon\phi$ is a possible variation. The remainder of the proof of norm conservation is almost identical to the proof of conservation of energy: The square of the norm is time-independent because

$$\begin{aligned} \frac{d}{dt}\|\phi(t)\|^2 &= \frac{d}{dt}\langle \phi(t) | \phi(t) \rangle = \langle \dot{\phi} | \phi \rangle + \langle \phi | \dot{\phi} \rangle = 2\,\mathrm{Re}\langle \phi | \dot{\phi} \rangle \\ &\underset{\text{with } \delta\phi = \varepsilon\phi}{\overset{(6.16)}{=}} 2\,\mathrm{Re}\langle \phi | (i\hbar)^{-1}\hat{H}\phi \rangle = -\frac{2}{\hbar}\,\mathrm{Re}[i\langle \hat{H} \rangle_{\phi(t)}] = 0, \end{aligned} \tag{6.18}$$

where we invoked the TDVP (6.16) now with $\delta\phi = \varepsilon\phi$ and noticed that the expectation value of energy, $\langle \hat{H} \rangle_{\phi(t)}$, is real because Hamiltonian is a Hermitian operator.□

Note that the energy and norm are conserved regardless of how good or bad your variational solution is. If you have very few and poorly chosen parameters, the variational solution can differ greatly from the exact solution of the TDSE, yet the energy and norm are conserved exactly by both solutions.

As for the requirement of the ray property, it is not very restrictive: if the given ansatz, e.g., $\phi_{\alpha,\beta}$ does not have the ray property, it is easy to augment the set of parameters by a prefactor parameter (here to $\phi_{\alpha,\beta,\gamma} := \gamma\phi_{\alpha,\beta}$). The new, augmented ansatz will automatically have the ray property because $\phi_{\alpha,\beta,\gamma} \in M$ implies that

$$\lambda\phi_{\alpha,\beta,\gamma} = \lambda\gamma\phi_{\alpha,\beta} = \phi_{\alpha,\beta,\lambda\gamma} \in M. \tag{6.19}$$

Therefore, the variational principle applied to the augmented ansatz will automatically conserve the norm.

Finally, remember that the variational principle can be applied to time-dependent Hamiltonians $\hat{H}(t)$: then, of course, energy will not be conserved.

1. *Variational Gaussian approximation*

An example of an application of the variational principle is the **variational Gaussian approximation**, where the solution of the TDSE is sought among wavefunctions of the Gaussian form (3.16). One can show that the variational solution is equivalent to solving the following system of ordinary differential equations for the parameters α_t, q_t, p_t, and γ_t:

$$\dot{\alpha}_t = -\alpha_t^2/m - \langle V''(\hat{q})\rangle, \tag{6.20}$$

$$\dot{p}_t = -\langle V'(\hat{q})\rangle, \tag{6.21}$$

$$\dot{q}_t = p_t/m, \tag{6.22}$$

$$\dot{\gamma}_t = \frac{p_t^2}{2m} - \langle V(\hat{q})\rangle + \frac{\hbar\langle V''(\hat{q})\rangle}{4\,\mathrm{Im}\,\alpha_t} + \frac{i\hbar}{2m}\alpha_t, \tag{6.23}$$

where, as usual, $\langle\hat{A}\rangle := \langle\psi(t)|\hat{A}|\psi(t)\rangle$ denotes the expectation value of operator $\hat{A}$ in the state $\psi\,(t)$. The derivation is beyond the scope of the course but notice the similarity with Eqs. (3.37)-(3.40) for the thawed Gaussian approximation. In the first two equations, $V''(q_t)$ and $V'\,(q_t)$ are replaced with $\langle V''\rangle$ and $\langle V'\rangle$, respectively. In a harmonic potential $V\,(q) = \frac{1}{2}kq^2$, the two approximations are equivalent because there

$$\begin{aligned}
\langle V''(\hat{q})\rangle &= V''(q_t),\\
\langle V'(\hat{q})\rangle &= V'(q_t),\\
\langle V(\hat{q})\rangle &= V(q_t) + \frac{\hbar V''(q_t)}{4\,\mathrm{Im}\,\alpha_t}.
\end{aligned}$$

The variational Gaussian approximation uses a variational instead of the classical trajectory, and typically is more accurate than the thawed Gaussian approximation. In particular, the variational Gaussian approximation can qualitatively describe tunneling. However, for general potential energy functions $V(q)$, it is much more expensive to evaluate expectation values $\langle V(\hat{q})\rangle$, $\langle V'(\hat{q})\rangle$, and $\langle V''(\hat{q})\rangle$ than to evaluate $V(q_t)$, $V'(q_t)$, and $V''(q_t)$ at the center of the Gaussian. As a consequence, more computational resources are required to evaluate the variational than the thawed Gaussian approximation.

D. Time-dependent Hartree approximation

The time-dependent Hartree approximation finds the optimal solution of the TDSE for a many-dimensional system among the direct-product states. Here we consider a system consisting of two distinguishable particles and seek the variationally optimal solution of the TDSE in the form of the product

$$\psi(t) = a(t)\varphi_1(t)\varphi_2(t), \tag{6.24}$$

where $\varphi_j(t)$ describes the state of the jth particle and $a(t)$ is a complex number inserted for convenience. Note that each of the two "particles" can be many-dimensional and may even consist of many, possibly indistinguishable, particles. An example is a molecular wavefunction $\psi(t)$, where one "particle", described by φ_1, consists of all nuclei and the other "particle", described by φ_2, consists of all electrons. We assume that all states are normalized, i.e., $\|\psi\| = 1$ and

$$|a| = \|\varphi_1\| = \|\varphi_2\| = 1. \tag{6.25}$$

Obviously, there remains some *gauge freedom* in choosing the phases of a, φ_1, and φ_2, and therefore we fix them by a gauge condition ($j = 1, 2$)

$$\langle\varphi_j|\dot{\varphi}_j\rangle = 0. \tag{6.26}$$

Proposition (**Time-dependent Hartree approximation**). Applying the time-dependent variational principle (TDVP) to the ansatz (6.24) yields an approximate solution, in which the prefactor evolves as

$$a(t) = a(0)e^{-iEt/\hbar}, \tag{6.27}$$

where

$$E := \langle\hat{H}\rangle_\psi = \text{const} \tag{6.28}$$

is the conserved total energy of the system, and the states φ_j satisfy the system

$$i\hbar\dot{\varphi}_j = (\hat{H}_j - E)\varphi_j, \tag{6.29}$$

of two coupled nonlinear Schrödinger equations with mean-field Hamiltonian operators

$$\hat{H}_1 = \langle \varphi_2 | \hat{H} | \varphi_2 \rangle \quad \text{and} \quad \hat{H}_2 = \langle \varphi_1 | \hat{H} | \varphi_1 \rangle, \tag{6.30}$$

acting, respectively, on the first and second particle.

Proof: The overlap of the state ψ with its time derivative

$$\dot{\psi} = \dot{a}\varphi_1\varphi_2 + a\dot{\varphi}_1\varphi_2 + a\varphi_1\dot{\varphi}_2 \tag{6.31}$$

is

$$\langle \psi | \dot{\psi} \rangle = a^*\dot{a} + |a|^2 \left(\langle \varphi_1 | \dot{\varphi}_1 \rangle + \langle \varphi_2 | \dot{\varphi}_2 \rangle \right) = a^*\dot{a} = a^{-1}\dot{a}, \tag{6.32}$$

where we have used the normalization (6.25) and gauge condition (6.26).

Now let us apply the time-dependent variational principle by requiring that the relation

$$\langle \delta\psi | i\hbar \frac{d}{dt} - \hat{H} | \psi \rangle = 0 \tag{6.33}$$

hold for an arbitrary variation $\delta\psi$ of the solution ψ. First, let us assume that $\delta\psi = c\psi$, where c is a complex constant, is an allowed variation. (Recall that this assumption is already needed for norm conservation under the TDVP.) Applying the TDVP (6.33) to this variation and using Eq. (6.32) gives

$$\langle \psi | \hat{H} | \psi \rangle = i\hbar \langle \psi | \dot{\psi} \rangle = i\hbar a^{-1}\dot{a}, \tag{6.34}$$

$$\dot{a} = -\frac{i}{\hbar} \langle \hat{H} \rangle_\psi a. \tag{6.35}$$

Now let us consider two particular variations,

$$\delta\psi_1 = a\,\delta\varphi_1\,\varphi_2 \quad \text{and} \quad \delta\psi_2 = a\,\varphi_1\,\delta\varphi_2, \tag{6.36}$$

each of which varies the state of only one of the two particles. We have

$$\begin{aligned} \langle \delta\psi_j | \dot{\psi} \rangle &= a^*\dot{a}\,\langle \delta\varphi_j | \varphi_j \rangle + |a|^2\,\langle \delta\varphi_j | \dot{\varphi}_j \rangle \\ &= a^{-1}\dot{a}\,\langle \delta\varphi_j | \varphi_j \rangle + \langle \delta\varphi_j | \dot{\varphi}_j \rangle \end{aligned} \tag{6.37}$$

On one hand, applying the TDVP to the variation $\delta\psi_j$ gives

$$\begin{aligned} \langle \delta\psi_j | \hat{H} | \psi \rangle &= i\hbar \langle \delta\psi_j | \dot{\psi} \rangle \\ &= i\hbar a^{-1}\dot{a}\,\langle \delta\varphi_j | \varphi_j \rangle + i\hbar \langle \delta\varphi_j | \dot{\varphi}_j \rangle \\ &= \langle \hat{H} \rangle_\psi \langle \delta\varphi_j | \varphi_j \rangle + i\hbar \langle \delta\varphi_j | \dot{\varphi}_j \rangle, \end{aligned} \tag{6.38}$$

where we have used Eqs. (6.37) and (6.34). On the other hand, recalling the definition (6.36) of the variation $\delta\psi_j$ gives

$$\langle\delta\psi_j|\hat{H}|\psi\rangle = |a|^2 \langle\delta\varphi_j|\hat{H}_j|\varphi_j\rangle = \langle\delta\varphi_j|\hat{H}_j|\varphi_j\rangle, \tag{6.39}$$

where $\hat{H}_j$ is the effective Hamiltonian (6.30) for particle j in the mean field of the other particle. Comparing Eqs. (6.38) and (6.39) and noting that their right-hand sides must be equal for an arbitrary variation $\delta\varphi_j$, we get

$$\langle\hat{H}\rangle_\psi\varphi_j + i\hbar\dot{\varphi}_j = \hat{H}_j\varphi_j. \tag{6.40}$$

Because the TDVP in general conserves the energy [Eq. (6.28)], we can replace $\langle\hat{H}\rangle_\psi$ with E in Eqs. (6.35) and (6.40), and obtain Eqs. (6.27) and (6.29), completing the proof of the proposition.□

Remark: Typically, one uses an alternative parametrization

$$\tilde{a} = ae^{2iEt/\hbar}, \tag{6.41}$$

$$\tilde{\varphi}_j = \varphi_j e^{-iEt/\hbar}. \tag{6.42}$$

The resulting TDH equations are:

$$\tilde{a}(t) = \tilde{a}(0)e^{iEt/\hbar}, \tag{6.43}$$

$$i\hbar\frac{d}{dt}\tilde{\varphi}_j = \hat{H}_j\tilde{\varphi}_j, \tag{6.44}$$

$$\psi = \tilde{a}\tilde{\varphi}_1\tilde{\varphi}_2. \tag{6.45}$$

Note that the differential equations for $\tilde{\varphi}_j$ resemble the standard TDSEs, yet—in contrast to the standard TDSE—they are (a) coupled and (b) nonlinear, due to the dependence of the mean-field Hamiltonian $\hat{H}_j$ on the state.

E. Time-dependent perturbation theory (TDPT, see also Schatz & Ratner)

The next approximate method we shall consider does not assume that the Hamiltonian $H(t)$ changes quickly, as in the sudden approximation, or slowly, as in the adiabatic approximation. In the **time-dependent perturbation theory**, we instead assume that the changes in $H(t)$ are *small*. We will consider that the Hamiltonian operator

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t) \tag{6.46}$$

is a sum of a time-independent Hamiltonian $\hat{H}_0$ and a small "**perturbation**" potential $\hat{V}(t)$. In molecular spectroscopy, one would take $\hat{H}_0$ to be the molecular Hamiltonian and $\hat{V}(t)$ the interaction with the electromagnetic field.

As we know from Sec. II B, the exact solution can be expanded in the basis of eigenstates of $\hat{H}_0$ as

$$|\psi(t)\rangle = \sum_n c_n(t)\,|n\rangle.$$

In Sec. II B, we found that the exact solution of the TDSE with Hamiltonian (6.46) was equivalent to the system (2.12)

$$\dot{c}_k(t) = -\frac{i}{\hbar}\sum_n e^{i\omega_{kn}t} V_{kn}(t)\, c_n(t)\,, \tag{6.47}$$

of ordinary differential equations for the coefficients $c_n(t)$, where $\omega_{kn} := (E_k - E_n)/\hbar$ are the transition frequencies and $V_{kn}(t) := \langle k|\hat{V}(t)|n\rangle$ are the matrix elements of the perturbation. Recall that the typically infinite basis is, in practice, replaced with a truncated, finite basis set. The same truncation is usually performed in the time-dependent perturbation theory, although we will not distinguish between the full basis and finite basis set in the following discussion.

1. *First-order TDPT*

In time-dependent perturbation theory, the perturbation is assumed to be small. As a result, we expect that the coefficients $c_n(t)$ change slowly and that we may replace them, *on the right-hand side of Eq. (6.47) only*, by their values $c_n(0)$ at time $t = 0$. In the **first-order time-dependent perturbation theory**, the system (6.47) becomes

$$\dot{c}_k^{(1)}(t) = -\frac{i}{\hbar}\sum_n e^{i\omega_{kn}t} V_{kn}(t)\, c_n(0)\,, \tag{6.48}$$

which can be solved by integration because the $c_n^{(1)}(t)$ coefficients do not appear on the right-hand side anymore:

$$c_k^{(1)}(t) = c_k(0) - \frac{i}{\hbar}\sum_n c_n(0)\int_0^t e^{i\omega_{kn}\tau} V_{kn}(\tau)\, d\tau. \tag{6.49}$$

In most interesting applications, the initial state is an eigenstate $|m\rangle$ of $\hat{H}_0$, and therefore

$$c_k(0) = \delta_{km}. \tag{6.50}$$

Then the differential equation (6.48) and its solution (6.49) reduce to

$$\dot{c}_k^{(1)}(t) = -\frac{i}{\hbar} e^{i\omega_{km}t} V_{km}(t), \tag{6.51}$$

$$c_k^{(1)}(t) = c_k(0) - \frac{i}{\hbar} \int_0^t e^{i\omega_{km}\tau} V_{km}(\tau)\, d\tau. \tag{6.52}$$

In particular, the **transition probability** from state m to state $k \neq m$ at time t is

$$P_{m\to k}(t) = |c_k^{(1)}(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t V_{km}(\tau) e^{i\omega_{km}\tau} d\tau \right|^2 .$$

2. Higher-order TDPT

This was the *first-order* perturbation theory, but one can go to higher orders by iterating the procedure used for the first order. To start, the **zeroth-order** coefficients are time-independent, given at all times by their initial values:

$$c_k^{(0)}(t) = c_k(0). \tag{6.53}$$

The jth-order time-dependent perturbation theory is obtained, for $j = 1, 2, 3, \ldots$, iteratively from the previous, $(j-1)$th-order, by using the jth order coefficients $c_k^{(j)}(t)$ on the left-hand side of Eq. (6.47) and the $(j-1)$th-order coefficients $c_n^{(j-1)}(t)$ on the right-hand side:

$$\dot{c}_k^{(j)}(t) = -\frac{i}{\hbar} \sum_n e^{i\omega_{kn}t} V_{kn}(t) c_n^{(j-1)}(t). \tag{6.54}$$

These equations are solved iteratively, either analytically—if it is possible—or numerically, on a computer. Finally, it is easy to see that for $j = 1$, Eq. (6.54) for the jth-order TDPT reduces to Eq. (6.48) obtained above for the first-order TDPT.

3. TDPT for a constant potential V

Let us consider the simplest possible application of TDPT, where the perturbation

$$V = \text{const}$$

is constant. More precisely, the perturbation is *turned on* at time $t = 0$ and *turned off* at time $t = T$ at which we evaluate the probability of transition. Switching off the perturbation helps to define rigorously the probability of transition because the stationary states for $t > T$ are then the same as stationary states for $t < 0$.

Assuming, as in Eq. (6.50), that the initial state is the mth eigenstate of $\hat{H}_0$, the first-order TDPT yields (for $k \neq m$)

$$c_k^{(1)}(T) = -\frac{i}{\hbar} V_{km} \int_0^T e^{i\omega_{km}t} dt = -V_{km} \frac{e^{i\omega_{km}T} - 1}{\hbar\omega_{km}},$$

where we were able to evaluate the integral analytically because the perturbation is constant. Hence the probability of transition to level k at time T, when the perturbation is switched off, is

$$\begin{aligned} P_{m\to k}(T) = |c_k^{(1)}(T)|^2 &= |V_{km}|^2 \frac{2[1 - \cos(\omega_{km}T)]}{(\hbar\omega_{km})^2} \\ &= |V_{km}|^2 \frac{\sin^2(\omega_{km}T/2)}{(\hbar\omega_{km}/2)^2} = \left(\frac{|V_{km}|\, T}{\hbar} \frac{\sin x}{x}\right)^2, \end{aligned} \qquad (6.55)$$

where

$$x := \frac{\omega_{km}T}{2} = \frac{(E_k - E_m)T}{2\hbar}$$

is a dimensionless quantity. The transition probability is plotted as a function of E_k in Fig. 24. Its shape is a square of the "sinc" function $(\sin x)/x$, appearing also in diffraction patterns in optics.

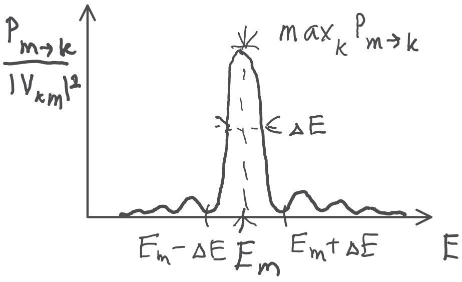

FIG. 24. Probability $P_{m\to k}(T)$ at time T of a transition from a state with energy E_m plotted as a function of the final energy E_k. The probability was obtained by the first-order time-dependent perturbation theory for a constant perturbation V.

Let us discuss expression (6.55) and Fig. 24 in more detail.

(1) Because the function $P_{m\to k}$ is symmetric about the point $E_k = E_m$, probabilities of transition to levels $E_k = E_m + E$ and $E_k = E_m - E$ are the same for any value of E! This is rather remarkable because this implies that a constant perturbation is equally likely to excite and de-excite the system by the same energy.

(2) To find the boundaries of the main, central peak in Fig. 24, we set $x = \pm\pi$, which are the zeros of $(\sin x)/x$ of smallest absolute value. The transition probability decays to zero at the

corresponding values of energy, which are

$$E_k = E_m \pm \frac{2\pi\hbar}{T}.$$

Let us take as the width of the main peak one half of the difference between the two energies E_k at which $P_{m\to k} = 0$, i.e.,

$$\Delta E = 2\pi\hbar/T.$$

As the time T increases, the central peak becomes sharper. The uncertainty in energy thus satisfies the **time-energy uncertainty relation**

$$T\,\Delta E = 2\pi\hbar > \hbar/2.$$

(3) The height of the central, highest peak is

$$\max_k P_{m\to k} = \lim_{x\to 0}\left(\frac{|V_{km}|\,T}{\hbar}\frac{\sin x}{x}\right)^2 = \frac{|V_{km}|^2\,T^2}{\hbar^2}$$

because $\lim_{x\to 0}[(\sin x)/x] = 1$.

(4) The total probability $P_{\text{main peak}}\,(T)$ of transition to levels within the main peak is proportional (not equal!) to the area of this peak. If V_{km} does not change much for energy levels within the first peak, we can estimate $P_{\text{main peak}}\,(T)$ by the area of the main peak, which, in turn, can be estimated by an area of a triangle with base $2\Delta E$ and height $\max_k P_{m\to k}$:

$$A = \Delta E\,\max_k P_{m\to k} = \frac{2\pi\hbar}{T}\frac{|V_{km}|^2\,T^2}{\hbar^2} = \frac{2\pi\,|V_{km}|^2\,T}{\hbar}.$$

Note that this area, and therefore, transition probability increases linearly with time T. The TDPT, therefore, must break down for very long times T when the transition probability predicted by the TDPT would become larger than 1.

4. Fermi's Golden Rule

!!! See Schatz & Ratner:

$$\sum_k P_{m\to k} \approx \frac{\Delta x}{\Delta E}\int_{-\infty}^{\infty} P_{m\to k}(x)dx = \left(\frac{|V_{km}|\,T}{\hbar}\right)^2\int_{-\infty}^{\infty}\frac{\sin^2 x}{x^2}dx = \cdots$$

$$w_T = \frac{P_T}{T} = \frac{2\pi}{\hbar}\rho(E_m)\langle|V_{km}|^2\rangle$$

5. TDPT for a periodic potential $V(t) = U \cos \omega t$

!!! See Schatz & Ratner:

electric dipole approximation

FGR for a periodic potential

$$w_T = \frac{P_T}{T} = \frac{2\pi}{\hbar} \rho(E_m \mp \hbar\omega) \langle |U_{km}|^2 \rangle$$

absorption, stimulated emission, spontaneous emission

*6. *Collision induced excitation of a diatomic molecule [See Schatz & Ratner]*

collision cross section $\sigma_{m \to k}$, microcanonical rate constant $k_{m \to k}(E_0)$, thermal rate constant $k_{m \to k}(T)$

VII. CORRELATION FUNCTIONS AND SPECTRA

Recommended reading: Schatz & Ratner 5.4.1., 5.4.2, 5.4.9; Tannor 6.1.1, 6.1.2, 6.2.1, from sections 6.2.2, 11.6.5, and 11.7.1 only parts that I teach in the lecture are required.

A. Molecular transitions: Franck-Condon factors

electric dipole moment

Franck-Condon overlap

B. Spectrum as a Fourier transform of the autocorrelation function

As we shall see later, within the first-order perturbation theory for the molecule-light interaction, the molecular absorption cross section is exclusively a molecular property and—remarkably—does not depend on the precise properties of the light. We can, therefore, forget the electromagnetic field for the moment and study the "wavepacket spectrum." Let us start with two definitions:

Definition 28 *The **wavepacket autocorrelation function** is a complex-valued function of time, defined as the overlap*

$$C(t) := \langle \psi(0) | \psi(t) \rangle \tag{7.1}$$

of the initial wavepacket with the wavepacket at time t. The wavepacket spectrum is the sum of the squares of the energy components of the wavepacket. More precisely, if

$$|\psi(t)\rangle = \sum_n c_n |n\rangle e^{-iE_n t/\hbar} \tag{7.2}$$

is the wavepacket at time t, then the ***wavepacket spectrum*** *is defined to be the generalized real function of angular frequency ω, given by*

$$\sigma(\omega) := \sum_n |c_n|^2 \delta(\omega - \omega_n), \tag{7.3}$$

where $\omega_n := E_n/\hbar$.

The wavepacket spectrum is a sequence of sharp Dirac delta peaks at frequencies $\omega = \omega_n$ whose intensities are proportional to $|c_n|^2$.

Claim 29 *The wavepacket spectrum is given by the inverse Fourier transform of the wavepacket autocorrelation function:*

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C(t)\, e^{i\omega t} dt. \tag{7.4}$$

Proof. First note that for the wavepacket (7.2), the autocorrelation becomes

$$C(t) = \left(\sum_n c_n^* \langle n|\right) \left(\sum_m c_m |m\rangle e^{-i\omega_m t}\right) = \sum_n c_n^* \sum_m c_m \delta_{nm} e^{-i\omega_m t} = \sum_n |c_n|^2 e^{-i\omega_n t}.$$

The right-hand side of Eq. (7.4) then becomes

$$\frac{1}{2\pi} \int C(t) e^{i\omega t} dt = \frac{1}{2\pi} \sum_n |c_n|^2 \int e^{i(\omega - \omega_n)t} dt = \frac{1}{2\pi} \sum_n |c_n|^2 2\pi \delta(\omega - \omega_n). \square$$

!!! For features of spectra and autocorrelation functions: recurrences, decays, peak spacings, peak widths, see Tannor's book.

Let us consider two representative examples of molecular electronic spectra, which demonstrate the relationship between $C(t)$ and $\sigma(\omega)$:

Figure 25 shows the autocorrelation function and spectrum resulting from **direct photodissociation**, a process in which the electronic excitation promotes the nuclear wavefunction onto an unbound excited potential energy surface, and the wavepacket leaves the Franck-Condon region without ever returning back.

In contrast, Fig. 26 depicts the autocorrelation function and spectrum for a **photoabsorption** to a bound excited state, in which the wavepacket moves forever back and forth between the two turning points. In a one-dimensional harmonic potential, the recurrences are perfect and the spectrum will exhibit a single progression of infinitely sharp peaks.

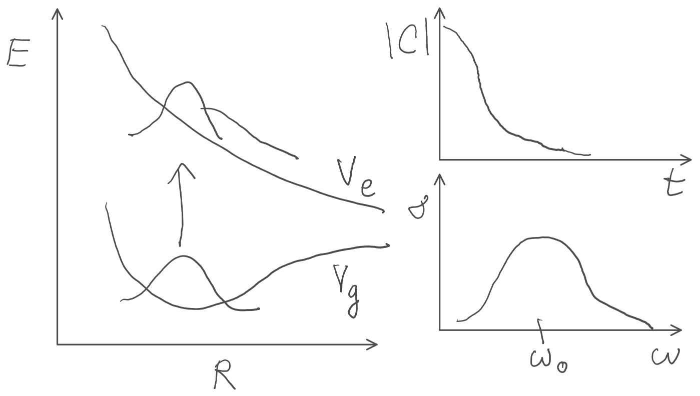

FIG. 25. Direct dissociation and corresponding autocorrelation function and spectrum.

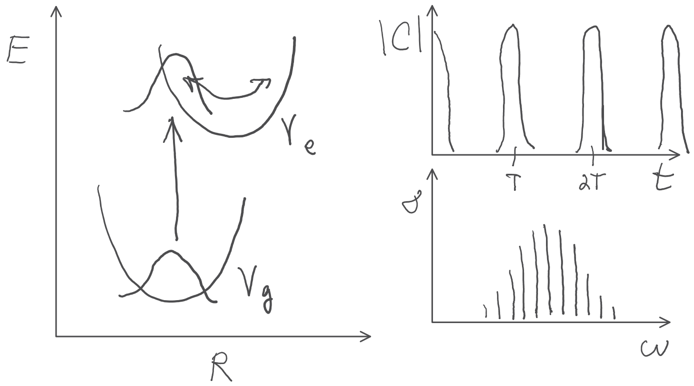

FIG. 26. Electronic absorption into a harmonic bound excited state. Autocorrelation function exhibits a series of perfect recurrences, while the spectrum consists of a single progression of infinitely sharp peaks.

C. Fourier transform

Let us spend a moment discussing the Fourier transform in general.

Definition 30 ***Fourier transform*** *of an integrable function $f(x)$ is a function $\tilde{f}(k)$ defined as*

$$\tilde{f}(k) := \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx. \tag{7.5}$$

Theorem 31 *(**Fourier inversion theorem**) If $\tilde{f}$ is the Fourier transform of f, then*

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{f}(k) e^{+ikx} dk. \tag{7.6}$$

“**Proof**”. Substitution of the definition (7.5) of the Fourier transform into the right-hand side of Eq. (7.6) gives

$$\begin{aligned}\frac{1}{2\pi}\int_{-\infty}^{\infty} dk e^{+ikx}\int_{-\infty}^{\infty} dx' f(x')e^{-ikx'} &= \frac{1}{2\pi}\int_{-\infty}^{\infty} dx' f(x')\int_{-\infty}^{\infty} dk e^{+ik(x-x')}\\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty} dx' f(x')2\pi\delta\left(x-x'\right) = f(x).\square\end{aligned}$$

Warning: There are other common conventions for the Fourier transform: the prefactor may not be $(2\pi)^{-1/2}$ but 1 for the forward and $(2\pi)^{-1}$ for the inverse Fourier transform. Also the signs in the exponents of the forward and inverse Fourier transforms are sometimes switched. Finally, some texts include a prefactor 2π in the exponent, which requires a modification of the prefactor of the integral as well.

We will also say that $f(x)$ and $\tilde{f}(k)$ are Fourier transform pairs and write

$$f(x) \leftrightarrow \tilde{f}(k).$$

An example of a Fourier transform pair is the pair $(\psi(q), a(k))$ of the wavefunction $\psi(q)$ in position representation and wavefunction $a(k)$ in k-representation. Likewise, in the pair $(\sigma(\omega), C(t))$ the wavepacket spectrum $\sigma(\omega)$ and autocorrelation function $C(t)$ are related by the forward and inverse Fourier transforms, albeit using the convention with prefactors 1 and $(2\pi)^{-1}$:

$$\begin{aligned}\int_{-\infty}^{\infty}\sigma(\omega)e^{-i\omega t}d\omega = \int_{-\infty}^{\infty}\sum_n |c_n|^2\,\delta\left(\omega-\omega_n\right)e^{-i\omega t}d\omega &= \sum_n |c_n|^2 e^{-i\omega_n t} = C(t)\\ \sigma(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} C(t)e^{i\omega t}dt.&\end{aligned}$$

In what follows, we shall use the convention from the definition and theorem.

Among the most important Fourier transform pairs are Gaussian ↔ Gaussian, real exponential ↔ Lorentzian, and complex exponential ↔ delta function:

$$\begin{aligned}e^{-\alpha x^2} &\leftrightarrow \frac{1}{\sqrt{2\alpha}}e^{-k^2/4\alpha}, \quad \alpha > 0,\\ e^{-\Gamma|x|} &\leftrightarrow \frac{1}{\sqrt{2\pi}}\frac{2\Gamma}{k^2+\Gamma^2}, \quad \Gamma > 0,\\ \frac{1}{\sqrt{2\pi}}e^{ik_0x} &\leftrightarrow \delta\left(k-k_0\right), \quad k_0 \in \mathbb{R}.\end{aligned}$$

The first two pairs are very important in spectroscopy because they provide a relationship between the damping of autocorrelation and the broadening of peaks in the spectra. The **Doppler broadening** of spectral lines due to the Doppler effect (change in frequency due to the relative motion between the source and detector) is an example of a Gaussian line shape because of the Maxwell distribution of velocities in thermal equilibrium. The **natural broadening** (or **lifetime broadening**), due to a finite lifetime of an excited state (which decays by spontaneous emission), gives rise to exponential decay of the autocorrelation function and to the Lorentzian shape of spectral lines.

D. Properties of the Fourier transform

The Fourier transform has many interesting properties. If $\tilde{f}$ and $\tilde{g}$ are Fourier transforms of f and g, i.e., $f \leftrightarrow \tilde{f}$ and $g \leftrightarrow \tilde{g}$, then the following relationships hold.

1) Linearity ($a, b \in \mathbb{C}$):

$$af(x) + bg(x) \leftrightarrow a\tilde{f}(k) + b\tilde{g}(k)$$

2) Scaling ($a \in \mathbb{R}$, $a \neq 0$):

$$f\left(ax\right) \leftrightarrow \frac{1}{|a|}\tilde{f}\left(\frac{k}{a}\right)$$

3) Even functions of x are transformed into even functions of k, while odd functions are transformed to odd functions:

$$f\left(-x\right) = f(x) \Leftrightarrow \tilde{f}(-k) = \tilde{f}(k),$$
$$f\left(-x\right) = -f(x) \Leftrightarrow \tilde{f}(-k) = -\tilde{f}(k).$$

4) Fourier transform conserves the inner product (**Parseval's theorem**), and therefore also the norm (**Plancherel's theorem**):

$$\langle f, g\rangle = \langle \tilde{f}, \tilde{g}\rangle \quad \text{and} \quad \|f\| = \|\tilde{f}\|.$$

5) Fourier transform converts differentiation into multiplication and vice versa:

$$\frac{d}{dx}f\left(x\right) \leftrightarrow ik\tilde{f}(k) \quad \text{and} \quad xf(x) \leftrightarrow i\frac{d\tilde{f}(k)}{dk}$$

6) (**Convolution theorem**) Fourier transform converts multiplication into convolution and vice versa:

$$\widetilde{f \cdot g} = \frac{1}{\sqrt{2\pi}}\tilde{f} * \tilde{g} \quad \text{and} \quad \widetilde{f * g} = \sqrt{2\pi}\tilde{f}\ \cdot \tilde{g},$$

where the **convolution** of functions f and g is a function $f * g$ defined by

$$f * g(x) := \int_{-\infty}^{\infty} f(y)\, g(x-y)\, dy.$$

"**Proof**". Let us prove only the properties 4, 5, and 6. To prove Parseval's theorem, we use the definition of the inner product and the Fourier transforms of f and g:

$$\begin{aligned}\langle \tilde{f}, \tilde{g}\rangle &= \int dk \tilde{f}(k)^* \tilde{g}(k) = \frac{1}{2\pi}\int dk \int dx' f(x')^* e^{ikx'} \int dx'' g(x'') e^{-ikx''} \\ &= \frac{1}{2\pi}\int dx' f(x')^* \int dx'' g(x'') 2\pi\delta(x'-x'') = \int dx' f(x')^* g(x') = \langle f, g\rangle \,.\end{aligned}$$

Plancherel's theorem follows immediately by setting $g = f$. Assuming that f decays to zero at $\pm\infty$, the Fourier transform of a derivative $df(x)/dx$ can be simplified using an integration by parts:

$$\int e^{-ikx} \frac{d}{dx} f(x)\, dx = -\int f(x) \frac{d}{dx} e^{-ikx} dx = ik \int f(x)\, e^{-ikx} dx,$$

while the Fourier transform of $xf(x)$ is obtained by noticing that $\frac{d}{dk}e^{-ikx} = -ixe^{-ikx}$:

$$\int e^{-ikx} x f(x)\, dx = i\int f(x) \frac{d}{dk} e^{-ikx} dx = i\frac{d}{dk}\int f(x)\, e^{-ikx} dx.$$

As for the convolution theorem, we have

$$\begin{aligned}\widetilde{fg}(k) &= \frac{1}{\sqrt{2\pi}}\int f(x)g(x)e^{-ikx}dx = (2\pi)^{-3/2}\int dx e^{-ikx}\int dk' e^{ik'x}\tilde{f}(k')\int dk'' e^{ik''x}\tilde{g}(k'') \\ &= \frac{1}{\sqrt{2\pi}}\int dk' \tilde{f}(k')\int dk'' \tilde{g}(k'')\delta(k'+k''-k) = \frac{1}{\sqrt{2\pi}}\int dk' \tilde{f}(k')\tilde{g}(k-k') = \frac{1}{\sqrt{2\pi}}\tilde{f} * \tilde{g}.\end{aligned}$$

The proof of the inverse convolution theorem is left as an exercise.

E. Convolution theorem and molecular spectra

Both versions of the convolution theorem are very useful for interpreting molecular spectra. On one hand, if the autocorrelation function $C(t) = C_1(t)C_2(t)$ is a product, then the corresponding spectrum $\sigma(\omega) \propto \sigma_1 * \sigma_2(\omega)$ is proportional to the convolution of the spectra corresponding to the two elementary autocorrelation functions. This is because

$$\sigma \propto \mathcal{F}^{-1}C = \mathcal{F}^{-1}(C_1C_2) \propto \mathcal{F}^{-1}(C_1) * \mathcal{F}^{-1}(C_2) \propto \sigma_1 * \sigma_2.$$

On the other had, if the autocorrelation function $C(t) = C_1 * C_2(t)$ is a convolution, then the spectrum $\sigma(\omega) \propto \sigma_1(\omega)\sigma_2(\omega)$ is proportional to the product of spectra corresponding to the two elementary correlation functions. Figure 27 shows how damping of the recurrences in correlation function C_1 with a damping function C_2 gives rise to the broadening of the spectral peaks. Figure 28, in turn, demonstrates the origin of the spectral envelope (!!! note that the relation between C_2 and σ_2 follows from the **Poisson summation formula**).

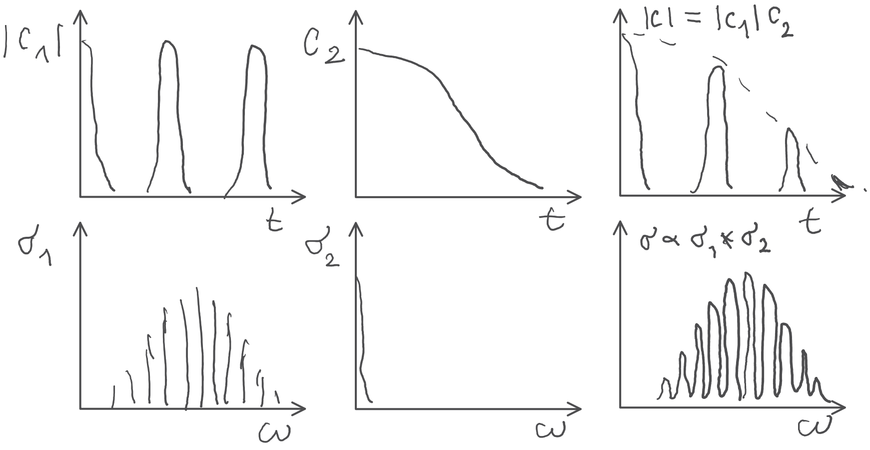

FIG. 27. Convolution theorem and peak broadening. C_1 consists of an infinite series of perfect recurrences giving rise to a spectrum σ_1 with infinitely sharp peaks. C_2 describes the damping of the recurrences and determines the peak broadening.

VIII. NUMERICAL METHODS FOR SOLVING THE TIME-DEPENDENT SCHRÖDINGER EQUATION

!!! discretization of the wave function

discrete Fourier transform (DFT)

fast Fourier transform (FFT)

A. Fourier method

algorithm?

B. Split operator method

algorithm?

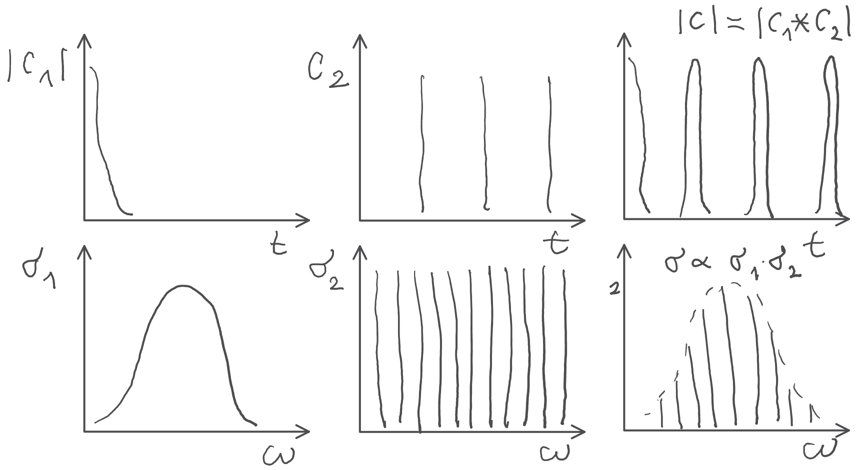

FIG. 28. Convolution theorem and spectral envelope. C_1 is a correlation function of direct dissociation, resulting in a broad spectrum σ_1. C_2 describes an infinite series of very sharp recurrences, which corresponds to an infinite series of equally intense sharp peaks in the spectrum σ_2.

C. *Second-order methods

IX. INTERACTIONS OF MOLECULES WITH ELECTROMAGNETIC FIELD

As mentioned before, interaction of molecules with electromagnetic fields can often be described by the electric dipole approximation. Here, we obtain this form of interaction from a few fundamental principles. We start by deriving the Lagrangian describing the interaction of a charged particle with an electromagnetic field. Remarkably, we can do that almost exclusively by considering only the symmetries of spacetime. We will find that the interaction depends on the scalar potential φ and vector potential $\mathbf{A}$, which we shall relate to the electric and magnetic fields $\mathbf{E}$ and $\mathbf{B}$. From the Lagrangian, we will obtain the well-known expression for the Lorentz force. As an exercise, you will also derive the canonical momentum and Hamiltonian, which is important in the quantum mechanical treatment of the interaction of molecules with light. Finally, by assuming that the wavelength of the electromagnetic field is longer than the size of the molecule, we will obtain the electric dipole approximation.

A. Lagrangian for a particle interacting with electromagnetic field

Our first goal is to obtain the Lagrangian

$$L(\mathbf{x},\mathbf{v},t)=\frac{1}{2}mv^2-e\,\varphi(\mathbf{x},t)+e\,\mathbf{v}\cdot\mathbf{A}(\mathbf{x},t) \tag{9.1}$$

describing the interaction of a charged particle with the electromagnetic field. Here $\mathbf{x}$ and $\mathbf{v}$ are the position and velocity of the particle, e is its charge, while φ and $\mathbf{A}$ are the scalar and vector potentials characterizing the electromagnetic field.

1. Gauge invariance of the Lagrangian

A useful fact from Lagrangian mechanics is that if L and

$$L'=L+\frac{df(q,t)}{dt}, \tag{9.2}$$

are two Lagrangians differing by a total time derivative of a function of coordinates and time, then the two Lagrangians lead to exactly the same equations of motion. In this case, we say that the **Lagrangian is invariant up the gauge term** df/dt.

Proof. The variation of the action corresponding to L',

$$\delta S'=\delta S+\delta\int_0^t\frac{df(q(\tau),\tau)}{d\tau}d\tau=\delta S+\delta f(q(\tau),\tau)|_0^t=\delta S+\left.\frac{\partial f(q(\tau),\tau)}{\partial q}\cdot\delta q(\tau)\right|_0^t=\delta S, \tag{9.3}$$

is the same as the variation of the action corresponding to L, and hence yields the same equations of motion. [The last step follows because the endpoints of the trajectory are fixed: $\delta q(t)=\delta q(0)=0$.]

*2. *Symmetries of nonrelativistic space time*

In nonrelativistic physics, both space and time are homogeneous (i.e., invariant under translations), while space is also isotropic (i.e., invariant under rotation). In addition, **Galileo's principle of relativity** states that the physical laws are the same in all inertial frames moving with constant velocity with respect to each other. The table below expresses relations between the position $\mathbf{x}$, velocity $\mathbf{v}$, and time t in an inertial frame K and the corresponding position $\mathbf{x}'$, velocity $\mathbf{v}'$, and time t' in an inertial frame K' that is related to K by one of the basic symmetries of spacetime.

Symmetry operation	Position	Velocities	Time
Translation	$\mathbf{x}' = \mathbf{x} + \mathbf{a}$	$\mathbf{v}' = \mathbf{v}$	$t' = t$
Time translation	$\mathbf{x}' = \mathbf{x}$	$\mathbf{v}' = \mathbf{v}$	$t' = t + \tau$
Rotation	$\mathbf{x}' = R \cdot \mathbf{x}$	$\mathbf{v}' = R \cdot \mathbf{v}$	$t' = t$
Galilean transformation	$\mathbf{x}' = \mathbf{x} + \mathbf{w}t$	$\mathbf{v}' = \mathbf{v} + \mathbf{w}$	$t' = t$
Space inversion (parity)	$\mathbf{x}' = -\mathbf{x}$	$\mathbf{v}' = -\mathbf{v}$	$t' = t$
Time reversal	$\mathbf{x}' = \mathbf{x}$	$\mathbf{v}' = -\mathbf{v}$	$t' = -t$

In order that the equations of motion be invariant under a symmetry, the Lagrangian $L(\mathbf{x}, \mathbf{v}, t)$ must transform under the transformation of coordinates, velocities, and time into a new Lagrangian

$$L'(\mathbf{x}, \mathbf{v}, t) := L(\mathbf{x}', \mathbf{v}', t') = L(\mathbf{x}, \mathbf{v}, t) + \frac{df(\mathbf{x}, t)}{dt} \tag{9.4}$$

that differs from the original Lagrangian L at most by a total time derivative of a function of coordinates and time. By the chain rule, the total derivative satisfies the relation

$$\frac{df(\mathbf{x}, t)}{dt} = \mathbf{v} \cdot \frac{\partial f(\mathbf{x}, t)}{\partial \mathbf{x}} + \frac{\partial f(\mathbf{x}, t)}{\partial t}. \tag{9.5}$$

3. Lagrangian of the free particle

Have you ever wondered *why* the kinetic energy of a particle is $mv^2/2$? Let us employ the symmetry of spacetime to justify this relation.

In Lagrangian mechanics, a free particle is characterized by its position $\mathbf{x}$, velocity $\mathbf{v}$, and possibly by some other, internal parameters. Since both space and time are homogeneous, the Lagrangian L cannot depend on either $\mathbf{x}$ or t explicitly, and must be a function of $\mathbf{v}$ alone. The isotropy of space implies that L cannot depend on the direction of $\mathbf{v}$ but only on its magnitude v, or equivalently, on its square v^2, i.e., $L \equiv L(v^2)$. Let us use Galileo's principle of relativity and consider another inertial frame K', moving with a velocity $-\mathbf{w}$ with respect to the original inertial frame K. For small relative velocities $\mathbf{w}$, the Lagrangian in the frame K' becomes

$$L' = L(v'^2) = L(v^2) + \frac{dL(v^2)}{dv^2} 2\mathbf{v} \cdot \mathbf{w} + \mathcal{O}(w^2).$$

A total time derivative of a function $f(\mathbf{x}, t)$ is given by $(\partial f/\partial \mathbf{x}) \cdot \mathbf{v} + \partial f/\partial t$, and is always a linear function of $\mathbf{v}$. Therefore, in order that the second term in the above equation be a total time derivative, $dL(v^2)/dv^2$ must be independent of v^2, and we can write

$$L_{\text{free p.}} = \frac{1}{2} m v^2, \tag{9.6}$$

where m is an internal parameter called the **mass** (or **inertial mass**) of the particle. Note that the above Lagrangian satisfies Galileo's principle of relativity for arbitrary, and not necessarily infinitesimal, velocities $\mathbf{w}$, because L' differs from L only by a total derivative of a function of $\mathbf{x}$ and t:

$$L' = \frac{1}{2}mv'^2 = \frac{1}{2}mv^2 + m\mathbf{v}\cdot\mathbf{w} + \frac{1}{2}mw^2 = L + m\mathbf{v}\cdot\mathbf{w} + \frac{1}{2}mw^2 = L + \frac{d}{dt}\left(m\mathbf{x}\cdot\mathbf{w} + \frac{1}{2}mw^2 t\right).$$

Finally, the principle of least action implies that the mass cannot be negative:

$$m > 0.$$

If the mass were negative, the action $S = \int_{t_1}^{t_2} \frac{1}{2}mv^2 dt$ would not be bounded from below for short times for particles moving very quickly from the initial to final position.

4. Lagrangian for a particle interacting with a scalar and vector fields

This Lagrangian can be written as a sum

$$L = L_{\text{free p.}} + L_{\text{p.-scalar}} + L_{\text{p.-vector}} \tag{9.7}$$

of three terms, the first being the Lagrangian (9.6) of a free particle, while the second and third terms describe, respectively, the interactions of the particle with a scalar field φ and vector field $\mathbf{A}$. These Lagrangians are given by

$$L_{\text{p.-scalar}} = -a\,\varphi(\mathbf{x},t), \tag{9.8}$$

$$L_{\text{p.-vector}} = b\,\mathbf{v}\cdot\mathbf{A}(\mathbf{x},t), \tag{9.9}$$

where a and b are properties of the particle and characterize the strength of the coupling to the scalar and vector fields. Note that the signs were chosen for convenience and that the parameters a and b themselves can have either sign.

The two Lagrangians can be again obtained simply from the symmetry of spacetime. The Lagrangian should not depend on the rotation of the coordinate system and so must be a scalar. The scalar field φ is, as the name suggests, already a scalar, and so the simplest interaction is simply proportional to the field at the position of the particle. The interaction with the vector field must be a scalar that depends both on the particle and the field. The simplest such scalar is proportional to the scalar product of the vector field at the position of the particle with the velocity of the particle. (We cannot take the scalar product with the position of the particle because that would violate the homogeneity of space.)

5. *Interaction of a particle with an electromagnetic field*

In the case of interaction of a particle with an electromagnetic field, the coupling constants to the scalar and vector fields are

$$a = e \quad \text{and} \quad b = e,$$

where e is the **electric charge** of the particle. The Lagrangian is, therefore,

$$L = \frac{1}{2}mv^2 - e\,\varphi(\mathbf{x}, t) + e\,\mathbf{v} \cdot \mathbf{A}(\mathbf{x}, t).$$

It is an incredible experimental fact that the coupling constants to the scalar and vector fields are the same: $a = b$, or, equivalently, in other systems of units, such as Gaussian or Lorentz–Heaviside systems, a and b are proportional to each other: $a = bc = e$, where the proportionality constant c is the same for all particles and is the speed of light c. This suggests that the interaction with the scalar and vector fields are rather "reflections" of an interaction with a 4-component vector field in a four-dimensional space. This space turns out to be the Minkowski spacetime of special relativity. Therefore, the fact that $a = b$ for all particles leads to the *unification* of electrostatics and magnetostatics by *electrodynamics*, to the recognition of the *Minkowski space*, and to the *special theory of relativity.*

Now you may well ask: Where do the scalar and vector potentials come from? How are they related to the electric and magnetic fields?

B. Maxwell's equations in terms of the scalar and vector potentials

First, let us recall several vector algebra and vector calculus identities.

1. *Useful vector algebra identities*

Let **A**, **B**, and **C** be vectors in $\mathbb{R}^3$. The scalar and vector products of two vectors, defined, respectively, as

$$\mathbf{A} \cdot \mathbf{B} := A_x B_x + A_y B_y + A_z B_z,$$

$$\mathbf{A} \times \mathbf{B} := \det \begin{pmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{pmatrix},$$

have the following properties:

$$\begin{aligned}
\mathbf{A}\cdot\mathbf{B} &= \mathbf{B}\cdot\mathbf{A},\\
\mathbf{A}\times\mathbf{B} &= -(\mathbf{B}\times\mathbf{A}),\\
\mathbf{A}\cdot(\mathbf{B}\times\mathbf{C}) &= \mathbf{B}\cdot(\mathbf{C}\times\mathbf{A}) = \mathbf{C}\cdot(\mathbf{A}\times\mathbf{B}),\\
\mathbf{A}\cdot(\mathbf{B}\times\mathbf{C}) &= \det\begin{pmatrix} A_x & A_y & A_z\\ B_x & B_y & B_z\\ C_x & C_y & C_z \end{pmatrix},\\
\mathbf{A}\times(\mathbf{B}\times\mathbf{C}) &= \mathbf{B}(\mathbf{A}\cdot\mathbf{C}) - \mathbf{C}(\mathbf{A}\cdot\mathbf{B}),\\
(\mathbf{A}\times\mathbf{B})\cdot(\mathbf{C}\times\mathbf{D}) &= (\mathbf{A}\cdot\mathbf{C})\,(\mathbf{B}\cdot\mathbf{D}) - (\mathbf{A}\cdot\mathbf{D})\,(\mathbf{B}\cdot\mathbf{C})\,.
\end{aligned}$$

2. Useful vector calculus identities

Let $f(\mathbf{x})$ be a scalar field and $\mathbf{A}(\mathbf{x})$, $\mathbf{B}(\mathbf{x})$, $\mathbf{C}(\mathbf{x})$ vector fields on $\mathbb{R}^3$. First, we denote by symbol ∇, called "nabla", the vector

$$\nabla := \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

whose components are partial derivatives with respect to the three Cartesian coordinates. Recall that the scalar field

$$\operatorname{div}\mathbf{A} \equiv \nabla\cdot\mathbf{A} := \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z}$$

is called the **divergence** of the vector field $\mathbf{A}$, the vector field

$$\operatorname{grad} f \equiv \nabla f := \left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z}\right)$$

is called the **gradient** of the scalar field f, and the vector field

$$\operatorname{curl}\mathbf{A} \equiv \nabla\times\mathbf{A} := \left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}, \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}, \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right)$$

is called the **curl** of the vector field $\mathbf{A}$. Finally, one can define the **Laplacian** of either scalar or vector field by

$$\begin{aligned}
\Delta f \equiv \nabla^2 f &:= \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2},\\
\Delta\mathbf{A} \equiv \nabla^2\mathbf{A} &:= \frac{\partial^2 \mathbf{A}}{\partial x^2} + \frac{\partial^2 \mathbf{A}}{\partial y^2} + \frac{\partial^2 \mathbf{A}}{\partial z^2},
\end{aligned}$$

The first derivative operators div, grad, and curl satisfy the following identities:

$$\nabla(fg) = g\,\nabla f + f\,\nabla g, \tag{9.10}$$

$$\nabla\left(\mathbf{A}\cdot\mathbf{B}\right) = \left(\mathbf{A}\cdot\nabla\right)\mathbf{B} + \left(\mathbf{B}\cdot\nabla\right)\mathbf{A} + \mathbf{A}\times\left(\nabla\times\mathbf{B}\right) + \mathbf{B}\times\left(\nabla\times\mathbf{A}\right), \tag{9.11}$$

$$\nabla\cdot(f\mathbf{A}) = \mathbf{A}\cdot\nabla f + f\,(\nabla\cdot\mathbf{A}), \tag{9.12}$$

$$\nabla\cdot(\mathbf{A}\times\mathbf{B}) = (\nabla\times\mathbf{A})\cdot\mathbf{B} - \mathbf{A}\cdot(\nabla\times\mathbf{B}), \tag{9.13}$$

$$\nabla\times(f\mathbf{A}) = (\nabla f)\times\mathbf{A} + f(\nabla\times\mathbf{A}), \tag{9.14}$$

$$\nabla\times(\mathbf{A}\times\mathbf{B}) = \mathbf{A}\,(\nabla\cdot\mathbf{B}) - \mathbf{B}\cdot(\nabla\cdot\mathbf{A}) + (\mathbf{B}\cdot\nabla)\mathbf{A} - (\mathbf{A}\cdot\nabla)\mathbf{B}. \tag{9.15}$$

The second-derivative operators obtained by composing the div, grad, and curl operators satisfy the following identities:

$$\nabla\cdot(\nabla f) = \Delta f \quad \text{or} \quad \operatorname{div}\operatorname{grad} f = \Delta f, \tag{9.16}$$

$$\nabla\cdot(\nabla\times\mathbf{A}) = 0 \quad \text{or} \quad \operatorname{div}\operatorname{curl}\mathbf{A} = 0, \tag{9.17}$$

$$\nabla\times(\nabla f) = 0 \quad \text{or} \quad \operatorname{curl}\operatorname{grad} f = 0, \tag{9.18}$$

$$\nabla\times(\nabla\times\mathbf{A}) = \nabla(\nabla\cdot\mathbf{A}) - \Delta\mathbf{A} \quad \text{or} \quad \operatorname{curl}\operatorname{curl}\mathbf{A} = \operatorname{grad}\operatorname{div}\mathbf{A} - \Delta\mathbf{A}. \tag{9.19}$$

If $\mathbf{A}$ is a vector field, then Eqs. (9.17) and (9.18) imply, respectively, that:

(Property 1) If $\nabla\cdot\mathbf{A} = 0$, then there is a vector field $\mathbf{B}$ such that $\mathbf{A} = \nabla\times\mathbf{B}$.

(Property 2) If $\nabla\times\mathbf{A} = 0$, then there is a scalar field f such that $\mathbf{A} = \nabla f$.

3. Maxwell's equations in terms of $\mathbf{A}$ *and* φ

Recall that the **electric field E** and **magnetic field B** must satisfy their own equations of motion, called **Maxwell's equations**

$$\nabla\cdot\mathbf{E} = \rho/\varepsilon_0, \tag{9.20}$$

$$\nabla\cdot\mathbf{B} = 0, \tag{9.21}$$

$$\nabla\times\mathbf{E} = -\frac{\partial\mathbf{B}}{\partial t}, \tag{9.22}$$

$$\nabla\times\mathbf{B} = \frac{1}{c^2}\frac{\partial\mathbf{E}}{\partial t} + \mu_0\mathbf{j}, \tag{9.23}$$

where ρ is the **charge density**, $\mathbf{j}$ is the **current density**, c is the speed of light, ε_0 and μ_0 are, respectively, the permittivity and permeability of the vacuum, which satisfy the relation $\varepsilon_0\mu_0 = c^{-2}$. Maxwell's equations can be derived by generalizing Lagrangian mechanics from point particles to continuous fields and this can be again done largely by relying on spacetime symmetries. The derivation is, unfortunately, beyond the scope of this course.

Using the Property 1 from the preceding section, Eq. (9.21) implies that **B** can be expressed as a curl of a **vector potential A**:

$$\mathbf{B} = \nabla \times \mathbf{A}. \tag{9.24}$$

Substituting expression (9.24) for **B** into Maxwell's equation (9.22) shows that

$$\nabla \times \left(\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} \right) = 0.$$

Now Property 2 from the previous section implies that

$$\mathbf{E} = -\nabla \varphi - \frac{\partial \mathbf{A}}{\partial t}, \tag{9.25}$$

where φ is a **scalar potential**. **A** and φ are the two fields that showed up earlier when we derived the Lagrangian of a particle interacting with electromagnetic field.

Using Eq. (9.24) for **B** and Eq. (9.25) for **E**, Maxwell's equations (9.20) and (9.23) become

$$\nabla^2 \varphi + \frac{\partial}{\partial t} \left(\nabla \cdot \mathbf{A} \right) = -\rho/\varepsilon_0, \tag{9.26}$$

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} - \nabla \left(\nabla \cdot \mathbf{A} \right) - \frac{1}{c^2} \nabla \frac{\partial \varphi}{\partial t} = -\mu_0 \mathbf{j}, \tag{9.27}$$

where in deriving the last equation relation (9.19) was used.

4. Gauge invariance of electromagnetic fields

The scalar and vector potentials φ and **A** are not defined uniquely. In particular, if one makes a so-called **gauge transformation**

$$\mathbf{A} \mapsto \mathbf{A}' := \mathbf{A} + \nabla \chi(\mathbf{x}, t) \quad \text{and} \quad \varphi \mapsto \varphi' := \varphi - \frac{\partial \chi(\mathbf{x}, t)}{\partial t}, \tag{9.28}$$

where the **gauge function** $\chi(\mathbf{x}, t)$ is an arbitrary function of position and time, the observable fields **E** and **B** remain unchanged. The electric field

$$\mathbf{E}' = -\nabla \varphi' - \frac{\partial \mathbf{A}'}{\partial t} = -\nabla \varphi + \nabla \frac{\partial \chi}{\partial t} - \frac{\partial \mathbf{A}}{\partial t} - \frac{\partial}{\partial t} \nabla \chi = -\nabla \varphi - \frac{\partial \mathbf{A}}{\partial t} = \mathbf{E}$$

is unchanged because of the commutativity of the partial derivatives ($\nabla \frac{\partial \chi}{\partial t} = \frac{\partial}{\partial t} \nabla \chi$). Likewise, the magnetic field is unaffected:

$$\mathbf{B}' = \nabla \times \mathbf{A}' = \nabla \times \mathbf{A} + \nabla \times (\nabla \chi) = \nabla \times \mathbf{A} = \mathbf{B},$$

which follows from relation (9.18). In other words, the electric and magnetic fields **E** and **B** are **gauge invariant**.

5. *Coulomb gauge*

Gauge invariance can be used to simplify Maxwell's equations. In particular, one can impose various additional conditions on the scalar and vector potentials. This is called **gauge fixing**. Among many useful gauges, the one particularly useful for nonrelativistic treatment of molecules is the **Coulomb gauge**, which imposes the condition

$$\nabla \cdot \mathbf{A} = 0 \tag{9.29}$$

on the vector potential. To show that such a gauge is always possible, let us consider a general vector potential $\mathbf{A}$, which does not necessarily satisfy the Coulomb gauge condition (9.29) and set $\mathbf{A}' = \mathbf{A} + \nabla\chi$. Then $\mathbf{A}'$ will satisfy the Coulomb gauge condition if

$$\nabla \cdot \mathbf{A}' = \nabla \cdot \mathbf{A} + \nabla^2\chi,$$

in other words, if χ solves **Poisson's equation**

$$\nabla^2\chi = -\nabla \cdot \mathbf{A},$$

where $\nabla \cdot \mathbf{A}$ is given.

Assuming that $\mathbf{A}$ satisfies the Coulomb gauge condition (9.29), Maxwell's equations (9.26)-(9.27) for φ and $\mathbf{A}$ reduce to **Poisson's equation** for φ and to an **inhomogeneous wave equation** for $\mathbf{A}$:

$$\nabla^2\varphi = -\rho/\varepsilon_0, \tag{9.30}$$

$$\nabla^2\mathbf{A} - \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} = \frac{1}{c^2}\nabla\frac{\partial\varphi}{\partial t} - \mu_0\mathbf{j}. \tag{9.31}$$

C. Derivation of the Lorentz force and gauge invariance of the particle-field interaction

Lagrangian (9.1) for the interaction of a charged particle with electromagnetic field leads to the following Euler-Lagrange equation of motion:

$$m\ddot{\mathbf{x}} = e\left(-\nabla\varphi - \frac{\partial\mathbf{A}}{\partial t} + \mathbf{v}\times(\nabla\times\mathbf{A})\right) = e\left(\mathbf{E} + \mathbf{v}\times\mathbf{B}\right), \tag{9.32}$$

which is nothing else but the second Newton's law $m\ddot{\mathbf{x}} = \mathbf{F}$ with the **Lorentz force**

$$\mathbf{F} = e\left(\mathbf{E} + \mathbf{v}\times\mathbf{B}\right). \tag{9.33}$$

Proof: First, we compute the required derivatives of the Lagrangian:

$$\begin{aligned}
\frac{\partial L}{\partial \mathbf{x}} &= -e\nabla\varphi + e\nabla\left(\mathbf{v}\cdot\mathbf{A}\right) = -e\nabla\varphi + e\left(\left(\mathbf{v}\cdot\nabla\right)\mathbf{A} + \mathbf{v}\times\left(\nabla\times\mathbf{A}\right)\right) \\
\frac{\partial L}{\partial \mathbf{v}} &= m\mathbf{v} + e\mathbf{A} \\
\frac{d}{dt}\frac{\partial L}{\partial \mathbf{v}} &= m\ddot{\mathbf{x}} + e\left(\left(\mathbf{v}\cdot\nabla\right)\mathbf{A} + \frac{\partial \mathbf{A}}{\partial t}\right)
\end{aligned}$$

The first equation follows from the identity (9.11) for the divergence of a scalar product. Equation (9.32) then follows by setting

$$\frac{d}{dt}\frac{\partial L}{\partial \mathbf{v}} = \frac{\partial L}{\partial \mathbf{x}}$$

as usual, subtracting the term $e\left(\left(\mathbf{v}\cdot\nabla\right)\mathbf{A} + \partial\mathbf{A}/\partial t\right)$ from both sides and using the relations (9.25) and (9.24) for electric and magnetic fields in terms of φ and $\mathbf{A}$.□

Note that the Lagrangian (9.1) is invariant up to a gauge term under the gauge transformation (9.28)

$$\mathbf{A}' := \mathbf{A} + \nabla\chi(\mathbf{x},t) \quad \text{and} \quad \varphi' := \varphi - \frac{\partial\chi(\mathbf{x},t)}{\partial t}$$

of the vector and scalar potentials.

Proof:

$$L' := \frac{1}{2}mv^2 - e\varphi' + e\mathbf{v}\cdot\mathbf{A}' = L + e\left(\frac{\partial\chi}{\partial t} + \mathbf{v}\cdot\nabla\chi\right) = L + \frac{d}{dt}\left(e\chi(\mathbf{x},t)\right).\square$$

Because L and L' differ by a total time derivative of a function of position and time, the equation of motion (9.32) containing the Lorentz force (9.33) is exactly invariant under gauge transformations. (This, in fact, follows already from the gauge invariance of **E** and **B** fields.) In summary, the equations of motion for both the particle (Newton's second law with Lorentz force) and for the electromagnetic fields (Maxwell's equations) are invariant under gauge transformations.

Exercise 32 *Derive an analytical expression for the canonical momentum* $\mathbf{p} := \partial L/\partial\mathbf{v}$ *associated to the Lagrangian (9.1) of a particle interacting with electromagnetic field and show that the Hamiltonian is*

$$H(\mathbf{x},\mathbf{p}) = \frac{1}{2m}\left(\mathbf{p} - e\mathbf{A}\right)^2 + e\varphi.$$

Derive Hamilton's equations of motion and show that they are equivalent to Newton's second law with Lorentz force (9.33).

D. Long wavelength and electric dipole approximations

Assuming that the sources of the electromagnetic fields are far away, we can take $\varphi = 0$ in addition to the Coulomb gauge condition $\nabla \cdot \mathbf{A} = 0$. (Because it requires a bit of work, I postpone the justification to the following section.)

Now consider that the wavelength of the electromagnetic field is much longer than the size of the molecule. This is quite well satisfied for not too large molecules and for visible light (wavelength $\sim 500\,\mathrm{nm}$). Then the fields $\mathbf{E}$, $\mathbf{B}$, $\mathbf{A}$ will be almost constant on the scale of the molecule, and, in particular, we can consider the vector potential $\mathbf{A}$ to be a function of time only:

$$\mathbf{A}(\mathbf{x}, t) \approx \mathbf{A}(t).$$

In this **long wavelength approximation**, Lagrangian becomes

$$L(\mathbf{x}, t) = \frac{1}{2} m v^2 + e\mathbf{v} \cdot \mathbf{A}(t).$$

This form of the Lagrangian is said to be in the **velocity gauge**.

Let us make a gauge transformation with

$$\chi(\mathbf{x}, t) = -\mathbf{x} \cdot \mathbf{A}(t),$$

which yields new fields

$$\mathbf{A}' = \mathbf{A} + \nabla\chi = \mathbf{A} - \mathbf{A} = 0 \quad \text{and} \quad \varphi' = \varphi - \frac{\partial \chi}{\partial t} = 0 + \mathbf{x} \cdot \frac{\partial \mathbf{A}(t)}{\partial t} = -\mathbf{x} \cdot \mathbf{E}(t).$$

As a result, the Lagrangian and Hamiltonian in this so-called **length gauge** become

$$\begin{aligned} L' &= \frac{1}{2} m v^2 - e\varphi'(\mathbf{x}, t) = \frac{1}{2} m v^2 + e\mathbf{x} \cdot \mathbf{E}(t) = \frac{1}{2} m v^2 + \boldsymbol{\mu} \cdot \mathbf{E}(t), \\ H' &= \frac{p^2}{2m} + e\varphi'(\mathbf{x}, t) = \frac{p^2}{2m} - \boldsymbol{\mu} \cdot \mathbf{E}(t), \end{aligned}$$

where $\boldsymbol{\mu} = e\mathbf{x}$ is the **electric dipole moment** of the particle. All together, the approximation is called the **electric dipole approximation**.

In a molecule, we need to add the contributions from all electrons and all nuclei and so the interaction potential will be

$$V_{\text{int}} = -\boldsymbol{\mu}_{\text{tot}} \cdot \mathbf{E}(t),$$

where $\boldsymbol{\mu}_{\text{tot}}$ is the sum over electric dipole moments of all electrons and nuclei. For electromagnetic waves, the field in the region of the molecule has the form

$$\mathbf{E}(t) = \mathbf{E}_0 \cos\left(\omega t + \theta\right),$$

and therefore the interaction potential has the form

$$\begin{aligned} V_{\text{int}} &= V_0 \cos\left(\omega t + \theta\right), \\ V_0 &= -\boldsymbol{\mu}_{\text{tot}} \cdot \mathbf{E}_0, \end{aligned}$$

which we used when we discussed the time-dependent perturbation theory with periodic perturbation.

E. *Justification of setting $\varphi = 0$ in the derivation of electric dipole approximation

1. *Weyl gauge*

The **Weyl gauge**, in which $\varphi = 0$, is another useful gauge. It is obtained from arbitrary vector and scalar potentials $\mathbf{A}$ and φ by a gauge transformation with a gauge function

$$\chi(\mathbf{x}, t) := \int_0^t \varphi(\mathbf{x}, \tau) d\tau.$$

The transformed fields are

$$\begin{aligned} \mathbf{A}' &= \mathbf{A} + \nabla\chi = \mathbf{A} + \int_0^t \nabla\varphi(\mathbf{x}, \tau) d\tau, \\ \varphi' &= \varphi - \frac{\partial \chi}{\partial t} = \varphi - \varphi = 0. \end{aligned}$$

As desired, the scalar potential vanishes.

2. *Maxwell's equations for φ and $\mathbf{A}$ in the absence of sources*

In the absence of charges and currents ($\rho = \mathbf{j} = 0$), Maxwell's equations (9.30) and (9.31) for φ and $\mathbf{A}$ in the Coulomb gauge reduce to **vacuum Maxwell's equations**

$$\nabla^2 \varphi = 0, \tag{9.34}$$

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = \frac{1}{c^2} \nabla \frac{\partial \varphi}{\partial t}. \tag{9.35}$$

When we discuss the interaction of electromagnetic fields with a molecule, of course there are charges present, but these charges and currents are not sources of the electromagnetic field. As a result, if the sources of the electromagnetic field are far away from the molecule, we can obtain the scalar and vector fields as well as the electric and magnetic fields by solving the vacuum equations.

3. Coulomb-Weyl gauge

In general, Coulomb and Weyl gauges are not compatible. To see that, consider that $\mathbf{A}$ and φ are in Coulomb gauge, i.e., $\nabla \cdot \mathbf{A} = 0$ and let us try to find a gauge function $\chi(\mathbf{x}, t)$ so that $\nabla \cdot \mathbf{A}' = 0$ (Coulomb gauge) and, at the same time, $\varphi' = 0$ (Weyl gauge). The two conditions will be satisfied if

$$\begin{aligned} 0 &= \nabla \cdot \mathbf{A}' = \nabla \cdot (\mathbf{A} + \nabla\chi) = \nabla \cdot \mathbf{A} + \nabla^2\chi = \nabla^2\chi, \\ 0 &= \varphi' = \varphi - \partial\chi/\partial t. \end{aligned}$$

In other words χ must satisfy the Laplace equation and also $\partial\chi/\partial t = \varphi$. However, these conditions are incompatible in general because on one hand, Maxwell's equation (9.30) requires that $\nabla^2\varphi = -\rho/\varepsilon_0$, and, on the other hand, the two conditions imply that

$$\nabla^2\varphi = \nabla^2\frac{\partial\chi}{\partial t} = \frac{\partial}{\partial t}\nabla^2\chi = 0.$$

Hence, in the presence of charge, Weyl and Coulomb gauges are incompatible. However, in the absence of sources ($\rho = 0$), the two gauges are compatible as long as

$$\nabla^2\chi = 0 \quad \text{and} \quad \partial\chi/\partial t = -\varphi.$$

The resulting gauge, in which both

$$\nabla \cdot \mathbf{A} = 0 \quad \text{and} \quad \varphi = 0,$$

is called the **Coulomb-Weyl gauge,** but most often people refer to it simply as the Coulomb gauge. This is the reason why we could start with a Lagrangian, in which $\varphi = 0$ in the derivation of the electric dipole approximation.

4. Electromagnetic waves

In the Coulomb-Weyl gauge, Maxwell's equations for φ and $\mathbf{A}$ in vacuum simplify further to

$$\varphi = 0, \tag{9.36}$$

$$\nabla^2\mathbf{A} - \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} = 0, \tag{9.37}$$

where the only interesting equation is the **wave equation** for the vector potential. Among other solutions, it is solved by the **plane electromagnetic waves**

$$\mathbf{A}(\mathbf{x}, t) = \mathbf{A}_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t + \theta),$$

where **k** is the **wave vector** determining the direction of propagation of the wave, ω is the angular frequency, and θ is an arbitrary phase. The wave vector and angular frequency satisfy the **linear dispersion relation**

$$\omega(k) = ck.$$

Because this relation is linear, the phase and group velocities ($v_p = \omega/k = c$ and $v_g = d\omega/dk = c$) are equal to each other and both are equal to the speed of light. Compare this with the nonlinear dispersion relation

$$\omega(k) = \frac{\hbar k^2}{2m}.$$

satisfied by the Schrödinger free-particle wave in quantum mechanics.

X. PATH INTEGRAL FORMALISM

A. Feynman path integral propagator

As we have seen already on multiple occasions, the time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle \tag{10.1}$$

with a time-independent Hamiltonian $\hat{H}$ has a formal solution

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi(0)\rangle. \tag{10.2}$$

Another way to express the solution is with the so-called quantum propagator. The **quantum propagator** $K(q'', q'; t)$ from point q' to point q'' in time t is defined via the equation

$$\psi(q'', t) = \int K(q'', q'; t)\, \psi(q', 0)\, dq', \tag{10.3}$$

which expresses the propagator as the **integral kernel** transforming the initial wavefunction $\psi(q', 0)$ to the final wavefunction $\psi(q'', t)$. The quantum propagator can be evaluated as the matrix element of the evolution operator in the position representation:

$$K(q'', q'; t) = \langle q''|e^{-i\hat{H}t/\hbar}|q'\rangle, \tag{10.4}$$

which is easily proven by expressing Eq. (10.2) in the position representation, inserting the resolution of identity, and comparing the result with Eq. (10.3):

$$\begin{aligned} \psi(q'', t) &= \langle q''|\psi(t)\rangle = \langle q''|e^{-i\hat{H}t/\hbar}|\psi(0)\rangle \\ &= \int \langle q''|e^{-i\hat{H}t/\hbar}|q'\rangle\langle q'|\psi(0)\rangle dq' = \int \langle q''|e^{-i\hat{H}t/\hbar}|q'\rangle \psi(q', 0)\, dq'. \end{aligned} \tag{10.5}$$

Let us consider several special cases first.

1. Free-particle propagator

In the absence of potential energy ($V = 0$), the Hamiltonian $\hat{H} = \hat{p}^2/(2m)$ is given by the kinetic energy and the propagator can be evaluated exactly. The **free-particle propagator** is

$$\begin{aligned} K_f\left(q'', q'; t\right) &= \langle q''|e^{-i\hat{p}^2 t/(2m\hbar)}|q'\rangle = \int \langle q''|p\rangle\langle p|e^{-i\hat{p}^2 t/(2m\hbar)}|q'\rangle dp \\ &= \int \frac{1}{\sqrt{2\pi\hbar}} e^{iq''p/\hbar} e^{-ip^2 t/(2m\hbar)}\langle p|q'\rangle dp = \frac{1}{2\pi\hbar}\int \exp\left\{\frac{i}{\hbar}\left[-\frac{t}{2m}p^2 + (q''-q')p\right]\right\} dp \\ &= \left(\frac{m}{2\pi i\hbar t}\right)^{1/2} \exp\left[\frac{im\left(q''-q'\right)^2}{2t\hbar}\right], \end{aligned} \tag{10.6}$$

where a Fourier transform of a complex Gaussian was used in the last step. This Fourier transform can be found in tables or derived by "completing the square" in the exponent and using the standard Gaussian integral.

2. Short-time propagator

If the potential is nonzero, but we are only interested in the propagator for short times Δt, we can employ the **Trotter factorization**

$$e^{-i\hat{H}\Delta t/\hbar} = e^{-i\hat{V}\Delta t/\hbar} e^{-i\hat{T}\Delta t/\hbar} + \mathcal{O}(\Delta t^2) \tag{10.7}$$

used in deriving the split-operator algorithm. For short times Δt, the quantum propagator can, therefore, be approximated as

$$K\left(q'', q'; \Delta t\right) = K_{\mathrm{st}}(q'', q'; \Delta t) + \mathcal{O}(\Delta t^2), \tag{10.8}$$

where $K_{\mathrm{st}}(q'', q'; \Delta t)$ is the **short-time propagator**, given by

$$\begin{aligned} K_{\mathrm{st}}(q'', q'; \Delta t) &= \langle q''|e^{-i\hat{V}\Delta t/\hbar} e^{-i\hat{T}\Delta t/\hbar}|q'\rangle = e^{-iV(q'')\Delta t/\hbar}\langle q''|e^{-i\hat{T}\Delta t/\hbar}|q'\rangle \\ &= e^{-iV(q'')\Delta t/\hbar} K_f\left(q'', q'; t\right) = \left(\frac{m}{2\pi i\hbar\Delta t}\right)^{1/2} \exp\left\{\frac{i}{\hbar}\left[\frac{m\left(q''-q'\right)^2}{2\Delta t} - V(q'')\Delta t\right]\right\} \\ &\approx \left(\frac{m}{2\pi i\hbar\Delta t}\right)^{1/2} \exp\left[\frac{i}{\hbar}S(q'', q'; \Delta t)\right]. \end{aligned} \tag{10.9}$$

To obtain the last line, we used a short-time approximation for the classical action:

$$\begin{aligned} S\left(q'', q'; \Delta t\right) &= \int_0^{\Delta t} L(q, \dot{q})dt \approx \Delta t L(q'', v'') = \Delta t\left[\frac{1}{2}m\left(v''\right)^2 - V\left(q''\right)\right] \\ &= \Delta t\left[\frac{1}{2}m\left(\frac{q''-q'}{\Delta t}\right)^2 - V\left(q''\right)\right]. \end{aligned} \tag{10.10}$$

Basically, we approximated the integral by a single term of a Riemann sum and in this single term, employed the value of the integrand at the final endpoint.

A propagator for long (i.e., finite and not infinitesimal) times t and with a nonzero potential V is obtained by composing N times the short-time propagator for time $\Delta t := t/N$:

$$\begin{aligned} K\left(q'', q'; t\right) &= \langle q''|e^{-i\hat{H}t/\hbar}|q'\rangle = \langle q''|(e^{-i\hat{H}\Delta t/\hbar})^N|q'\rangle \\ &= \langle q''|e^{-i\hat{H}\Delta t/\hbar}\int dq_{N-1}|q_{N-1}\rangle\langle q_{N-1}|e^{-i\hat{H}\Delta t/\hbar}\cdots e^{-i\hat{H}\Delta t/\hbar}\int dq_1|q_1\rangle\langle q_1|e^{-i\hat{H}\Delta t/\hbar}|q'\rangle \\ &\approx \left(\frac{m}{2\pi i\hbar\Delta t}\right)^{N/2}\int dq_{N-1}\cdots\int dq_1 \exp\left[\frac{i}{\hbar}\sum_{j=1}^{N}L\left(t_j\right)\Delta t\right], \end{aligned} \tag{10.11}$$

where we inserted $N-1$ resolutions of identity in the second line and used the short-time propagator (10.9) in the third line.

Now let us take the limit $N \to \infty$. Because $\Delta t = t/N \to 0$, the short-time approximation will get better and better. Moreover, the sum in the exponent will turn into an integral

$$\int_0^t L dt = S.$$

Still, the question whether the limit of the infinite product of integrals exists in a rigorous mathematical sense is very difficult and has not been answered fully (to the best of my knowledge). However, Richard Feynman ignored this issue and, by taking the limit, obtained the celebrated **Feynman path integral propagator**

$$K_{\mathrm{PI}}\left(q'', q'; t\right) = \lim_{N\to\infty}\left(\frac{mN}{2\pi i t\hbar}\right)^{N/2}\int dq_1\cdots\int dq_{N-1}e^{iS[q(\tau)]/\hbar} =: \int \mathcal{D}q\left(\tau\right)e^{iS[q(\tau)]/\hbar}, \tag{10.12}$$

in which the third expression defines a short-hand notation for the complicated limit in the second expression.

This integral is complicated for two reasons: first, it is infinite-dimensional and second, it is highly oscillatory. The integral is infinite-dimensional because it integrates over all, classical or nonclassical trajectories leading from q' to q'' in time t. At any time τ such that $0 < \tau < t$, the trajectory can pass through an arbitrary point $q(\tau)$ in space. If this were not complicated enough, each trajectory contributes a complex exponential, the phase of which can change fast when the trajectory changes little.

Despite these complications, the integral is believed to be an exact representation of the quantum propagator, even though this statement has not been proven mathematically. The beauty of the integral lies in the "democracy of trajectories": each trajectory has the same weight and only differs from the other trajectories in the phase. Because of the wildly oscillatory behavior of the phase, this integral is rarely used for numerical applications (there are notable exceptions, such as the work of Nancy Makri); the path integral is mostly used for formal derivations of modern theories of particle physics. It is also an excellent starting point for deriving the **semiclassical approximation** to the quantum propagator: Note that the trajectories that contribute the most to the integral are the trajectories whose phase does not change under infinitesimal perturbations. This happens if the phase and, therefore, the action is stationary, which shows that such trajectories are exactly the classical trajectories derived from the principle of stationary action. This is also one way to derive **classical mechanics** from **quantum mechanics**.

Despite its difficulties in numerical applications to quantum dynamics, the Feynman path integral turns out to be remarkably useful for molecular simulations. However, one must simulate quantum thermodynamics instead of the real-time quantum dynamics.

B. Quantum thermodynamics

There is a beautiful analogy between thermodynamics and quantum dynamics expressed in the duality

$$e^{-\beta E} \leftrightarrow e^{-it\hat{H}/\hbar}.$$

In thermodynamics, the central quantity is the **Boltzmann factor** $\exp(-\beta E)$, which is proportional to the probability at temperature T to be in a state with energy E. [Recall that $\beta := 1/(k_B T)$ denotes the inverse temperature.] In quantum dynamics, the evolution of a quantum state is governed by the **evolution operator** $\exp(-it\hat{H}/\hbar)$. Remembering that the Hamiltonian operator $\hat{H}$ is the quantum-mechanical representation of energy E, we can complete the analogy by identifying β with $it/\hbar$. In other words,

$$e^{-\beta\hat{H}} = e^{-i\tau\hat{H}/\hbar},$$

where we defined the **imaginary time**

$$\tau := -i\beta\hbar.$$

This time is imaginary because both β and $\hbar$ are, of course, real. In conclusion, one can view **quantum thermodynamics** as **quantum dynamics in imaginary time**.

To see how the Feynman path integral can be useful for computing quantum thermodynamic quantities, we will consider a specific example: the calculation of **thermal energy** $E(\beta)$.

1. *Thermal energy from the partition function*

First, let us recall a general thermodynamic relation between the thermal energy $E(\beta)$ and partition function $Q(\beta)$, namely

$$E\left(\beta\right) = -\frac{\partial \ln Q(\beta)}{\partial \beta}. \tag{10.13}$$

This identity is proven as follows:

$$\begin{aligned} E(\beta) := \langle E \rangle &= \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = \frac{1}{Q}\sum_n E_n e^{-\beta E_n} = -\frac{1}{Q}\sum_n \frac{\partial}{\partial \beta} e^{-\beta E_n} \\ &= -\frac{1}{Q}\frac{\partial}{\partial \beta}\sum_n e^{-\beta E_n} = -\frac{1}{Q}\frac{\partial Q}{\partial \beta} = -\frac{\partial \ln Q(\beta)}{\partial \beta}, \end{aligned} \tag{10.14}$$

where we defined the **partition function**

$$Q\left(\beta\right) = \sum_n e^{-\beta E_n} \tag{10.15}$$

as the sum of Boltzmann factors for all energy eigenstates of the system. In the derivation, we used the definition of the thermal energy as the average energy over the Boltzmann distribution.

2. *Partition function as the trace of the Boltzmann operator*

The partition function (10.15) can be rewritten as the trace of the **Boltzmann operator** $e^{-\beta \hat{H}}$:

$$Q\left(\beta\right) = \sum_n \langle n | e^{-\beta \hat{H}} | n \rangle = \mathrm{Tr}(e^{-\beta \hat{H}}). \tag{10.16}$$

This trace, which is a generalization of a matrix trace to operators, can be also expressed in the position representation:

$$Q\left(\beta\right) = \sum_n \langle n | e^{-\beta \hat{H}} \int dq |q\rangle\langle q|n\rangle = \int dq \langle q| \sum_n |n\rangle\langle n| e^{-\beta \hat{H}} |q\rangle = \int dq \langle q| e^{-\beta \hat{H}} |q\rangle. \tag{10.17}$$

In the derivation, we first inserted a resolution of identity in terms of the position basis and then, after exchanging the order of integration and sum, removed another resolution of identity in terms of the energy eigenstates.

3. *Partition function as the trace of the imaginary-time quantum propagator*

The last expression can be rewritten as

$$Q\left(\beta\right) = \int dq K(q, q; -i\beta\hbar), \tag{10.18}$$

which is nothing but the trace of the quantum propagator in imaginary time $-i\beta\hbar$. Because it is a trace, the initial and final positions coincide and, in addition, are integrated over. The last equation is a rigorous statement of the duality between **quantum thermodynamics**, reflected in the partition function on the left-hand side, and **imaginary-time quantum dynamics**, reflected in the propagator on the right-hand side.

4. Path integral representation of the partition function

Now we replace the quantum propagator in the trace (10.18) with its path integral representation (10.12), but will not take the limit $N \to \infty$. Substituting the finite N version of the path integral propagator for $K(q, q; -i\beta\hbar)$ and renaming the variable q as q_N yields the discretized **path-integral representation of the partition function**

$$Q_N(\beta) = \left(\frac{mN}{2\pi\hbar^2\beta}\right)^{N/2} \int dq_1 \cdots \int dq_N \exp\left[-\beta V_{\text{eff}}(q)\right], \tag{10.19}$$

where we defined an **effective potential**

$$V_{\text{eff}}(q) = \frac{mN}{2\hbar^2\beta^2} \sum_{j=1}^{N} (q_j - q_{j-1})^2 + \frac{1}{N} \sum_{j=1}^{N} V(q_j) \tag{10.20}$$

of the so-called **ring polymer** consisting of N monomers of the original system. The exact quantum partition function is obtained in the limit $N \to \infty$ of Eq. (10.19), while the classical partition function is found by taking $N = 1$ (check!).

Exercise 33 *Show that, for $N = 1$, partition function $Q_N(\beta)$ of Eq. (10.19) reduces to the classical partition function*

$$Q_{cl}(\beta) = \frac{1}{2\pi\hbar} \int dq \int dp \exp\left[-\beta H(q, p)\right], \tag{10.21}$$

$$H(q, p) = \frac{p^2}{2m} + V(q). \tag{10.22}$$

We have converted a one-dimensional quantum-mechanical problem to an N-dimensional classical problem because all that remains to do is applying classical thermodynamics to the classical ring polymer described by the effective potential. The first term in V_{eff} arose from the kinetic energy, but now becomes a harmonic bond interaction between adjacent "**beads**" of the ring polymer, while the second term is an arithmetic average over the beads of the original potential V; effectively, each bead feels an N times weaker potential, i.e., V/N. In conclusion, using the discretized path integral, quantum thermodynamics can be also interpreted as the **classical thermodynamics of a ring polymer**. [!!!] In the lecture, I drew figures of the ring polymer in two cases: (a) an atom in an external potential and (b) a diatomic molecule with a two-body interaction.

5. *Practical implementation*

Once we have converted a quantum problem to a classical thermodynamic problem, we can use all the tools available for classical thermodynamic simulations. If we apply classical **molecular dynamics** to the ring polymer, we obtain **path integral molecular dynamics** (PIMD). If we, instead, sample the ring polymer with classical **Monte Carlo** method, we obtain the **path integral Monte Carlo** (PIMC) method. Both PIMD and PIMC can use all the machinery of molecular dynamics and Monte Carlo simulations, and, in addition, many tricks available specifically in the ring polymer case due the special form of the effective potential (10.20).

How is it possible that the real-time Feynman path integral is rather impractical for numerical computations while the quantum thermodynamical version is used so successfully in molecular simulations? The answer lies in the imaginary time! The Boltzmann factor is real and decays rapidly in regions with high effective potential, whereas the complex factor $\exp(iS/\hbar)$ has the same magnitude for each trajectory and also oscillates rapidly.

Nowadays, imaginary-time path integral simulations are easily performed for 1000 atoms, which corresponds to 10^5-dimensional integrals if $N = 100$. At room temperature, it is typically sufficient to take $N = 64$ to 128 for hydrogen or its isotopes, and $N = 8$ to 32 for heavier atoms such as carbon or oxygen.

6. *Sampling weight and estimators*

To find the thermal average of a quantity in classical or path integral molecular dynamics or Monte Carlo simulations, you need to explore the configuration space and sample the quantity of interest using a so-called estimator. More precisely, a thermally averaged quantity $A(\beta)$ is obtained as

$$A(\beta) \approx \langle A_{\mathrm{est}} \rangle_\rho, \tag{10.23}$$

where $\langle A_{\mathrm{est}} \rangle_\rho$, the average obtained in the simulation, is defined as

$$\langle A_{\mathrm{est}} \rangle_\rho := \frac{\int A_{\mathrm{est}}(q)\rho(q)\,dq}{\int \rho(q)\,dq}. \tag{10.24}$$

Here $\rho(q)$ is the **sampling weight** from which the configurations q are sampled and $A_{\text{est}}(q)$ is the so-called **estimator** of the quantity A. In classical Monte Carlo simulations, if the observable $A(q)$ depends only on positions but not on the momenta, the sampling weight can be taken as $\rho(q) = \exp[-\beta V(q)]$ (because the kinetic factor can be evaluated analytically and cancels between the numerator and denominator) and its estimator is simply $A_{\text{est}}(q) = A(q)$, i.e., the quantity itself, expressed as a function of coordinates. If the sampling of positions is done properly, according to the weight $\rho(q)$, then the weighted average (10.24) is equal to the arithmetic average

$$\bar{A} = \lim_{S\to\infty} \frac{1}{S} \sum_{s=1}^{S} A_{\text{est}}(q^{(s)}), \tag{10.25}$$

where S is the number of samples taken and $q^{(s)}$ denotes the coordinates of the sth sample.

In path integral simulations, $q = (q_1, \ldots, q_N)$ denotes the combined coordinates of all beads and the sampling weight is given by

$$\rho_N(q,\beta) = \left(\frac{mN}{2\pi\hbar^2\beta}\right)^{N/2} \exp\left(-\beta V_{\text{eff}}(q)\right). \tag{10.26}$$

7. Thermodynamic estimator for energy

To complete our example, in which we wanted to evaluate the quantum thermal energy of a system, we need to find the estimator for energy. The most straightforward one is obtained by expressing the energy from the path integral representation of the partition function, using the relation (10.13):

$$E_N(\beta) = -\frac{\partial Q_N(\beta)/\partial\beta}{Q_N(\beta)} = \frac{\int E_{\text{th-est}}(q,\beta)\rho_N(q,\beta)dq}{\int \rho_N(q,\beta)dq} = \langle E_{\text{th-est}}(q,\beta)\rangle_{\rho_N(q,\beta)}, \tag{10.27}$$

where the factor $E_{\text{th-est}}(q,\beta)$ is given by

$$E_{\text{th-est}}(q,\beta) = \frac{N}{2\beta} - \frac{mN}{2\hbar^2\beta^2}\sum_{j=1}^{N}(q_j - q_{j-1})^2 + \frac{1}{N}\sum_{j=1}^{N} V(q_j) \tag{10.28}$$

and is called the **thermodynamic estimator for energy**. If you take a large enough N (so that you approach the quantum limit), run a long enough simulation, and evaluate the energy at each ring polymer configuration q using the thermodynamic estimator, then you will eventually converge to the correct quantum thermal energy. However, the convergence will be very slow, especially if you need a large N, because the estimator (10.28) contains the difference between two large positive terms proportional to N, and as you know, the average must be independent of N in the limit of large N (quantum mechanics does not know that we have discretized the path integral).

The difference of large numbers leads to large statistical errors. For a given number of samples, the statistical error of energy will be proportional to N, and therefore, since an error of a Monte Carlo calculation is proportional to $1/\sqrt{S}$, you will have to increase the number S of samples N^2 times to achieve the same level of convergence as for a classical simulation with $N = 1$ bead. This issue is avoided by using the **virial estimator** or even better **centroid virial estimator**. You will derive the virial estimator in an exercise.

XI. INTRODUCTION TO SEMICLASSICAL METHODS

Semiclassical approximation, as its name suggests, provides a bridge between the quantum and classical mechanics. It many ways, semiclassical approximation makes quantum mechanics easier to understand. Before thinking that this approximation is inferior to the exact solution of the Schrödinger equation, one should remember that it was exactly the quantum-classical correspondence that guided Schrödinger in deriving his equation. Moreover, while the wavefunction can be propagated by the Schrödinger equation, the concept of measurement even in quantum mechanics relies on a classical apparatus.

We have already encountered several examples of the semiclassical approximation: the Bohr model of the hydrogen atom, Bohr-Sommerfeld quantization rules

$$\oint p\, dq = nh,$$

as well as the thawed and frozen Gaussian approximations. Yet, the most common semiclassical approximation discussed in quantum-mechanical textbooks is the WKB approximation. While most text only discuss the time-independent, one-dimensional version, we shall present the D-dimensional, time-dependent formulation.

A. Time-dependent WKB approximation

Let us start by writing the wavefunction in the **polar form**, i.e.,

$$\psi(q,t) = A(q,t) \exp\left[\frac{i}{\hbar} S(q,t)\right], \tag{11.1}$$

where both A, S are real functions of position and time. Substituting this ansatz into the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi(q,t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(q,t) + V(q,t)\psi(q,t) \tag{11.2}$$

requires derivatives with respect to both q and t, which we will denote $\partial\psi/\partial q =: \psi'$ and $\partial\psi/\partial t =: \dot{\psi}$:

$$\psi' = \left(A' + \frac{i}{\hbar}AS'\right)e^{iS/\hbar} \quad \text{and} \quad \dot{\psi} = \left(\dot{A} + \frac{i}{\hbar}A\dot{S}\right)e^{iS/\hbar},$$
$$\psi'' = \left[A'' + \frac{i}{\hbar}\left(A'S' + AS''\right) + \left(A' + \frac{i}{\hbar}AS'\right)\frac{i}{\hbar}S'\right]e^{iS/\hbar}.$$

Although the derivation is valid in arbitrary number of dimensions, for the moment, the reader may think that there is only one spatial dimension. Inserting the ansatz (11.1) into the Schrödinger equation (11.2) and dividing both sides by $\exp\left(iS/\hbar\right)$ yields

$$i\hbar\dot{A} - A\dot{S} = -\frac{\hbar^2}{2m}\left[A'' + \frac{i}{\hbar}\left(2A'S' + AS''\right) - \frac{1}{\hbar^2}A\left(S'\right)^2\right] + VA. \tag{11.3}$$

Let us separate the real and imaginary parts of this complex-valued partial differential equation because both parts provide different pieces of information.

The real part, after dividing by A, reads

$$-\dot{S} = \frac{1}{2m}\left(S'\right)^2 + V - \frac{\hbar^2}{2m}\frac{A''}{A}.$$

Recalling the definition of the **probability density** $\rho := |\psi|^2 = A^2$ and reverting to the three-dimensional notation, we can rewrite the last equation as

$$-\frac{\partial S}{\partial t} = \frac{\left(\nabla S\right)^2}{2m} + V + V_{\text{Bohm}}, \tag{11.4}$$

where

$$V_{\text{Bohm}} = -\frac{\hbar^2}{2m}\frac{\nabla^2\rho^{1/2}}{\rho^{1/2}} \tag{11.5}$$

is the so-called **quantum potential** (or **Bohm potential**). Note that if V_{Bohm} were zero, then the equation satisfied by S would be nothing else but the classical **Hamilton-Jacobi equation** (4.43)

$$-\frac{\partial S}{\partial t} = H\left(\mathbf{q}, \mathbf{p}\right)|_{\mathbf{p}=\nabla S}.$$

With nonzero V_{Bohm}, the Hamilton-Jacobi equation is a generalized one, with an effective potential $V + V_{\text{eff}}$.

Now, multiplying with A the imaginary part of Eq. (11.3),

$$\dot{A} + \frac{1}{2m}\left(2A'S' + AS''\right) = 0,$$

yields

$$\frac{1}{2}\frac{\partial}{\partial t}\left(A^2\right) + \frac{1}{2m}\left(A^2S'\right)' = 0.$$

Reverting to the three-dimensional notation and using the definition of ρ, the last equation becomes

$$\frac{\partial}{\partial t}\rho + \nabla \cdot \left(\rho \frac{\nabla S}{m}\right) = 0, \tag{11.6}$$

which can be recognized as the **continuity equation** after acknowledging, as in Eq. (4.39), that $\nabla S = \mathbf{p}$ and interpreting

$$\rho \frac{\nabla S}{m} = \rho \frac{\mathbf{p}}{m} = \rho \mathbf{v} = \mathbf{j}$$

as the **probability density current**.

In conclusion, the time-dependent Schrödinger equation (11.2) is equivalent to the coupled partial differential equations (11.4) and (11.6) for the probability density $\rho(\mathbf{q}, t)$ and "phase" $S(\mathbf{q}, t)$, or equivalently, for $A(\mathbf{q}, t)$ and $S(\mathbf{q}, t)$. These equations are the central components of so-called **Bohmian mechanics**, in which the generalized Hamilton-Jacobi equation is further solved with the method of characteristics, i.e., by running **"quantum" trajectories**—trajectories satisfying Hamilton's equations of motion with the potential $V + V_{\text{Bohm}}$.

Alternatively, one may neglect the quantum potential (11.5) and obtain **semiclassical mechanics**, in which S becomes the **classical action** and ρ becomes the **classical density**. The semiclassical wavefunction,

$$\psi(\mathbf{q}, t) = \sqrt{\rho\,(\mathbf{q}, t)}\, e^{iS(\mathbf{q},t)/\hbar},$$

is composed of purely classical quantities. However, this form only holds for short times. For longer times, one must generalize it to a sum

$$\psi(\mathbf{q}, t) = \sum_j A_j\,(\mathbf{q}, t)\, e^{iS_j(\mathbf{q},t)/\hbar},$$

where each term corresponds to a different classical trajectory contributing to the wavefunction at position $\mathbf{q}$ at time t.

B. *Van Vleck propagator

Quantum propagator

$$\begin{aligned} K(q'', q'; t) &:= \left\langle q'' \left| e^{-iHt/\hbar} \right| q' \right\rangle, \\ \psi(q'', t) &= \int K(q'', q'; t)\, \psi(q', 0)\, dq'. \end{aligned}$$

Van Vleck-Gutzwiller propagator

$$K_{\mathrm{SC}}(q'', q'; t) = (2\pi i\hbar)^{-D/2} \sum_j A_j e^{iS_j/\hbar - i\pi\nu_j/2},$$

$$A_j = \sqrt{\left|\det \frac{\partial^2 S_j}{\partial \mathbf{q}'' \partial \mathbf{q}'}\right|}$$

Van Vleck determinant

Maslov index ν_j

Problems with Van Vleck determinant: root search, singularities

C. *Initial value representation

$$\left(e^{-i\hat{H}t/\hbar}\right)_{\mathrm{IVR}} = (2\pi i\hbar)^{-D/2} \int dq_0 \int dp_0\, A^{-1} e^{iS(q_0,p_0,t)/\hbar} |q_t\rangle\langle q_0|$$

Advantages: Initial value problem, no singularities (become zero)

D. Wigner function

E. *Derivation of the Van Vleck propagator from the Feynman path integral

Appendix A: *Basis set methods to solve the TISE

The goal is to find the quantum state $|\psi\rangle$ that solves the TISE

$$\hat{H}|\psi\rangle = E|\psi\rangle. \tag{A1}$$

Because we are solving the *time-independent* Schrödinger equation, in this section we obviously assume that both the Hamiltonian and the basis are time-independent. On the other hand, we will first consider a general basis that may not be orthogonal. Obviously, we cannot assume that our basis is the eigenbasis of $\hat{H}$, since such an eigenbasis is unknown before we solve the problem—it is formed exactly by the solutions $|\psi\rangle$ that we seek. To simplify various expressions, we shall always use the Dirac notation.

1. Nonorthogonal basis set methods to solve the TISE

We seek a solution in the form

$$|\psi\rangle = \sum_{n=1}^{N} c_n |n\rangle, \tag{A2}$$

where $|n\rangle$ is a nonorthogonal basis with the **overlap matrix**

$$S_{kn} := \langle k|n\rangle. \tag{A3}$$

Usually, one assumes that the basis states are normalized, i.e.,

$$S_{nn} = 1,$$

but this assumption is not needed for what follows.

Substitution of the ansatz (A2) into the TISE (A1) and taking the inner product with $\langle k|$ ("multiplying on the left") gives

$$\sum_n H_{kn} c_n = E \sum_n S_{kn} c_n,$$

where $H_{kn} := \langle k|\hat{H}|n\rangle$ are the **Hamiltonian matrix elements**. The above equation describes a **generalized eigenvalue problem**, which, in matrix notation, reads

$$\mathbf{Hc} = E\,\mathbf{Sc}. \tag{A4}$$

To find the energies E and vectors $\mathbf{c}$, one would have to solve the equation

$$\det(\mathbf{H} - E\mathbf{S}) = 0.$$

If $\mathbf{S}$ is invertible, we can also write

$$\mathbf{S}^{-1}\mathbf{Hc} = E\,\mathbf{c},$$

which is the standard eigenvalue problem for the matrix $\mathbf{S}^{-1}\mathbf{H}$. In this case, $\mathbf{c}$ is an eigenvector of the matrix $\mathbf{S}^{-1}\mathbf{H}$ and to find it, one must solve the secular equation

$$\det(\mathbf{S}^{-1}\mathbf{H} - E\mathbf{1}) = 0,$$

where $\mathbf{1}$ is an N-dimensional identity matrix.

2. Orthonormal basis set methods to solve the TISE

In the special case of an orthonormal basis, the overlap matrix is the identity:

$$S_{kn} = \delta_{kn}, \text{ i.e., } \mathbf{S} = \mathbf{1},$$

and the equation to be solved is the eigenvalue problem

$$\sum_n H_{kn} c_n = E c_n.$$

In matrix notation, this equation reads

$$\mathbf{Hc} = E\mathbf{c},$$

so $\mathbf{c}$ is an eigenvector of the matrix $\mathbf{H}$. To find the eigenvalues E and eigenvectors $\mathbf{c}$, one must solve the secular equation

$$\det(\mathbf{H} - E\mathbf{1}) = 0.$$

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