

Mathematical methods in quantum mechanics

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Contents

1 The Schrödinger equation for a particle in a potential	4
1.1 The Schrödinger equation	4
1.2 Observables and expectation values	5
1.3 The Ehrenfest theorem	6
1.4 Momentum	7
1.5 Free propagation	8
1.6 Stationary states	10
1.7 The hydrogen atom	11
1.8 Exercises	13
2 A very quick tour of spectral theory	14
2.1 Self-adjointness and spectrum of bounded operators	15
2.2 Projection-valued measures and orthogonally-resolved operators	18
2.3 Functional calculus	21
2.4 The spectral theorem	22
2.5 Unbounded operators	23
2.6 Schrödinger operators $-\frac{1}{2}\Delta + V$	25
2.7 The Schrödinger equation	27
2.8 Bound states	28
2.9 Exercises	29
3 Postulates of quantum mechanics	30
3.1 Quantum states	30
3.2 Observables	30
3.3 Time evolution	34
4 Symmetries	36
4.1 Symmetries of a quantum system	36
4.2 Discrete symmetries	37
4.3 Continuous symmetries	37
4.4 Translations	38
4.5 Rotations	38

5 Numerical simulation of the time-dependent Schrödinger equation	40
5.1 Smoothness	40
5.2 Fourier approximation	42
5.3 Space discretization: the spectral method	43
5.4 Implementation: fast Fourier transforms and the pseudospectral method	44
5.5 Time discretization	45
5.6 Exercises	48
6 Variational methods for the time-independent Schrödinger equation	49
6.1 The Galerkin method	49
6.2 Application: the H_2^+ molecule and the chemical bond	49
6.3 Exercises	52
7 Time-independent perturbation theory	53
7.1 Perturbation theory	53
7.2 Application: electron in an electric field	55
7.3 Exercises	57
8 Time-dependent perturbation theory	58
8.1 Time-dependent Hamiltonians: the Dyson series	58
8.2 Linear response	59
8.3 Application: absorption spectrum of hydrogen	60
8.4 Other approximation methods	61
8.5 Exercises	61
9 Many-body quantum mechanics and applications	62
9.1 Tensor products of Hilbert space	62
9.2 Many-body quantum mechanics	63
9.3 The many-body electronic Hamiltonian	64
9.4 Non-interacting electrons	64
9.5 Chemistry and spin	65
9.6 The interacting N -body problem	66
9.7 Quantum information and computing	68

Foreword

This document contains the lecture notes for a course given at the graduate (M2) level in mathematics at Université Paris-Saclay. The goal of the course is to introduce students to quantum mechanics and to some of the mathematical tools used.

We will adopt an axiomatic approach, and will not discuss important physical aspects such as the interpretations of quantum mechanics, orders of magnitudes, simplified classical models, solutions of exactly solvable quantum systems, or the historical development of the field. Rather, we will present the equations of practical relevance to the study of matter, and deduce some of their properties rigorously, from first principles. Along the way, we will develop a number of mathematical tools, whose applicability goes beyond quantum mechanics to various domains of applied mathematics. This makes the contents of the course almost orthogonal to those of a first course in quantum mechanics: it is designed to be of interest to both people with and without prior exposure to quantum mechanics.

The equations of quantum mechanics are practically intractable for all but the simplest systems. Accordingly, we will not focus too much on exact results and analytical solutions, and will mostly focus on **approximation methods** (perturbation theory, numerical methods...), with an eye towards their **mathematical justification** (mathematical and numerical analysis) and the quantification of their errors. Many of the examples in this course will be taken from the field of quantum chemistry. In particular, we will use these methods to explain from first principles some features of chemistry (the shell structure of atoms, chemical bonding, polarizability and light absorption/absorption). The field of mathematical methods in quantum mechanics is huge, and we aim for variety more than completeness. We only consider “classical” quantum mechanics of finitely many particles and leave out topics such as the study of solids (which involve infinitely many particles) or of fields (whose classical description involves infinitely many degrees of freedom).

To go beyond the material in this course, the interested reader can consult for instance the following textbooks, from more mathematical to more physical

- [1] by Lewin, in French, available online, covers spectral theory with applications to quantum mechanics
- [2] by Gustafson and Sigal, covering quantum mechanics at a level ranging from mathematically rigorous to semi-rigorous
- [3] Feynman’s classic exposition of quantum mechanics, from the physical point of view

More specific lecture notes include for instance (again from more mathematical to more physical) those by Frederic Schuller, Christopher Beem and David Tong, all available online. Finally, research-level references include the book series [4] (mathematical physics), the reviews [5] and [6] (numerical methods for electronic structure), and the textbook [7] (electronic structure of solids).

1 The Schrödinger equation for a particle in a potential

In this section, we introduce the Schrödinger equation for the specific system of a single particle of mass 1 moving in \mathbb{R}^d in a potential energy function $V : \mathbb{R}^d \rightarrow \mathbb{R}$, according to the classical Newton equation

$$\ddot{x} = -\nabla V(x). \quad (1.1)$$

Some examples are the harmonic oscillator $V(x) = \frac{1}{2}|x|^2$, the pendulum $V(x) = 1 - \cos(x)$ and the electrostatic (or gravitational) potential $V(x) = -\frac{1}{|x|}$. The motion of a particle in a potential is only an example of the more general theory, but gives important intuition into its principles and some of its applications. It will serve as our main example to motivate the abstract formalism of quantum theory that we will describe in later sections. We will use in this whole document the system of atomic units, where most physical constants (the mass and charge of the electron, the reduced Planck constant \hbar and the vacuum permittivity $4\pi\varepsilon_0$) are all equal to 1.

1.1 The Schrödinger equation

In classical mechanics, the state of the particle is encoded in its position x and its velocity \dot{x} , or, equivalently, its momentum¹ $p = \dot{x}$ (recall we took $m = 1$). The motion is given by the Newton equation (1.1), which can be rewritten in the Hamiltonian form

$$\dot{x} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial x} \quad (1.2)$$

with the Hamiltonian (total energy)

$$H(x, p) = \frac{|p|^2}{2} + V(x). \quad (1.3)$$

In quantum mechanics, the state of the particle is encoded in a **wavefunction** $\psi : \mathbb{R}^d \rightarrow \mathbb{C}$. $|\psi(x)|^2$ describes the probability density of finding the particle at the point $x \in \mathbb{R}^d$. Therefore, we must have

$$\int_{\mathbb{R}^d} |\psi(x)|^2 dx = \|\psi\|_{L^2(\mathbb{R}^d, \mathbb{C})}^2 = 1. \quad (1.4)$$

The wavefunction satisfies the **Schrödinger equation**

$$i\frac{\partial\psi}{\partial t}(x, t) = -\frac{1}{2}(\Delta\psi)(x, t) + V(x)\psi(x, t) \quad (1.5)$$

Here, Δ is the usual Laplace operator (sum of second partial derivatives with respect to all the space dimensions). We do not attempt to derive this equation, but rather explore some of its consequences. We will write the equation in the condensed form

$$i\partial_t\psi = H\psi, \quad (1.6)$$

¹For the francophone reader, we recall the following particularly confusing “faux-amis”: momentum = “quantité de mouvement” or “moment linéaire”; angular momentum = “moment cinétique” or “moment angulaire”

where H is the **Hamiltonian operator**

$$H = -\frac{1}{2}\Delta + V. \quad (1.7)$$

Here, by an abuse of language, we identify the function V with the multiplication operator V given by $(V\psi)(x) = V(x)\psi(x)$. The Hamiltonian operator is not an operator in the usual sense of bounded (or continuous) linear maps on a Banach space to itself: we will discuss this in Section 2 with the notion of unbounded operators and domains. For now, we will do formal manipulations without too much pretense at mathematical rigor, but all these computations will be made rigorous later.

1.2 Observables and expectation values

From the interpretation of the square modulus of the wavefunction as a probability, it follows that the average position of the particle is given by $\int_{\mathbb{R}^d} x|\psi(x)|^2 dx$. It is instructive to rewrite this as

$$\int_{\mathbb{R}^d} x|\psi(x)|^2 dx = \langle \psi | x \psi \rangle. \quad (1.8)$$

Here, again, x denotes the multiplication operator² by x . The inner product is the standard $L^2(\mathbb{R}^d, \mathbb{C})$ sesquilinear inner product

$$\langle \psi | \phi \rangle = \int_{\mathbb{R}^d} \overline{\psi(x)} \phi(x) dx. \quad (1.9)$$

In quantum mechanics it is customary to use vertical bars instead of commas, and to have the inner product conjugate on the left. This enables the “Dirac notation”, which splits the bracket $\langle \psi | \phi \rangle$ into conceptually separate objects, the “ket” $|\phi\rangle$ (which is simply a notation for ϕ , a vector in $L^2(\mathbb{R}^d, \mathbb{C})$) and the “bra” $\langle \psi |$ (a notation for the linear form given by $\phi \mapsto \langle \psi | \phi \rangle$). This is nothing but a notational pun, but one which is sometimes convenient. For instance the orthogonal projector on ψ is written compactly as

$$|\psi\rangle\langle\psi| = \psi\langle\psi|\cdot\rangle \quad (1.10)$$

The notation $\langle \psi | x \psi \rangle$ emphasizes the role of x as a multiplication operator, from (a subset of) $L^2(\mathbb{R}^d)$ to $L^2(\mathbb{R}^d)$, given (with some abuse of notation) by $(x\psi)(x) = x\psi(x)$. More generally, for an operator A on $L^2(\mathbb{R}^d, \mathbb{C})$, we will consider the quantity

$$\langle \psi | A \psi \rangle_{L^2(\mathbb{R}^d, \mathbb{C})}, \quad (1.11)$$

to be interpreted later as the **expectation value** of the **observable** A in the state ψ . In order for this quadratic form to have physical meaning, we want it to be real for all ψ . This implies³ that A has to be **formally self-adjoint**, i.e.

$$\langle \psi | A \phi \rangle = \langle A \psi | \phi \rangle \quad (1.12)$$

²When $d > 1$, this is a vector of operators, but this poses no notational difficulty.

³Exercise: show this in finite dimension: if $\langle x | Ax \rangle \in \mathbb{R}$ for all $x \in \mathbb{C}^N$, then A is Hermitian ($A^* = \overline{A^T}$). Hint: use the decomposition $A = \frac{1}{2}(A + A^*) + \frac{1}{2}(A - A^*)$, then show that if a matrix B is such that $\langle x | Bx \rangle = 0$ for all $x \in \mathbb{C}^N$, then $B = 0$.

for all $\psi, \phi \in L^2(\mathbb{R}^d, \mathbb{C})$ (or, rather, those ψ and ϕ that make this expression well-defined). Clearly, the operator x is formally self-adjoint, since $\int_{\mathbb{R}^d} \overline{\psi(x)} x \phi(x) dx = \int_{\mathbb{R}^d} x \overline{\psi(x)} \phi(x) dx$.

Similarly, the operators appearing in quantum mechanics are formally *self-adjoint*. For instance, for the Hamiltonian, we have (whenever ψ, ϕ are smooth and compactly supported, for instance)

$$\langle \psi | H \phi \rangle = -\frac{1}{2} \int_{\mathbb{R}^d} \overline{\psi(x)} (\Delta \phi)(x) dx + \int_{\mathbb{R}^d} V(x) \overline{\psi(x)} \phi(x) dx \quad (1.13)$$

$$= \frac{1}{2} \int_{\mathbb{R}^d} \overline{\nabla \psi(x)} \cdot \nabla \phi(x) dx + \int_{\mathbb{R}^d} V(x) \overline{\psi(x)} \phi(x) dx \quad (1.14)$$

$$= -\frac{1}{2} \int_{\mathbb{R}^d} \overline{\Delta \psi(x)} \phi(x) dx + \int_{\mathbb{R}^d} V(x) \overline{\psi(x)} \phi(x) dx \quad (1.15)$$

$$= \langle H\psi | \phi \rangle \quad (1.16)$$

In fact, as we will see in Section 3, to each physical observable classical quantity of the system (i.e. functions of phase space $A(x, p)$) is associated a quantum observable, a formally self-adjoint operator on $L^2(\mathbb{R}^d, \mathbb{C})$ (and vice versa). Self-adjointness is a very powerful property; for instance, in finite dimensions, every self-adjoint operator (Hermitian matrix) is diagonalizable in an orthogonal basis with real spectrum. Formally, self-adjoint operators are in a one-to-one correspondance with real quadratic forms, enabling for instance the identification $\int_{\mathbb{R}^d} x |\psi(x)|^2 dx = \langle \psi | x \psi \rangle$ that we used above.

1.3 The Ehrenfest theorem

If A is any self-adjoint operator, we can compute using the Schrödinger equation

$$\frac{d}{dt} \langle \psi | A \psi \rangle = \langle \partial_t \psi | A \psi \rangle + \langle \psi | A \partial_t \psi \rangle \quad (1.17)$$

$$= i \langle H \psi | A \psi \rangle - i \langle \psi | A H \psi \rangle \quad (1.18)$$

$$= \langle \psi | i(HA - AH)\psi \rangle \quad (1.19)$$

$$= \langle \psi | i[H, A]\psi \rangle \quad (1.20)$$

where we have introduced the **commutator** $[A, B] = AB - BA$, and where it is easy to check that $i[A, B]$ is formally self-adjoint when A and B are. This is known as the **Ehrenfest theorem**: the time derivative of the expectation value of an observable A is the expectation value of another observable $i[H, A]$. Let us apply this powerful identity to some operators

- $A = I$, the identity operator. Since $i[H, I] = 0$, it follows that $\langle \psi | I \psi \rangle$, the square L^2 norm of ψ , is constant in time, which is good news for the consistency of the theory (since we said that states have to be normalized to 1).
- $A = H$. We also have $i[H, H] = 0$, so that $\langle \psi | H \psi \rangle$ is constant in time. This will be interpreted as the average total energy, which is constant as in classical mechanics⁴.
- $A = x$. We then have (exercise)

$$i[H, x] = i[-\frac{1}{2}\Delta, x] = -i\nabla. \quad (1.21)$$

⁴Dissipative motion, such as that of a particle subject to a force not deriving from a potential energy, and for which the total energy decreases rather than stays constant, is not compatible with the standard version of quantum mechanics; the environment (to which energy is transferred) has to be modeled explicitly.

This important operator is called the **momentum operator**

$$p = -i\nabla. \quad (1.22)$$

- $A = p$. We then have (exercise)

$$i[H, p] = -\nabla V, \quad (1.23)$$

where by ∇V we mean the multiplication operator by the function ∇V (not to be confused with the composition of the operator ∇ and the multiplication operator V).

We have used the self-adjointness of H in the derivation of the Ehrenfest theorem. If we do not assume self-adjointness, we get $\frac{d}{dt}\|\psi\|^2 = \langle\psi|i(H - H^*)\psi\rangle$, which shows that H being self-adjoint is a sufficient and necessary condition for norm preservation.

1.4 Momentum

The newly introduced operator $p = -i\nabla$ satisfies the classical-looking equations

$$\frac{d}{dt}\langle\psi|x\psi\rangle = \langle\psi|p\psi\rangle, \quad \frac{d}{dt}\langle\psi|p\psi\rangle = \langle\psi|(-\nabla V)\psi\rangle \quad (1.24)$$

so that it is very tempting to see p as the quantum observable representing the classical momentum; the laws of classical physics $\dot{x} = p, \dot{p} = -\nabla V(x)$ are then satisfied “on average”. This is all the more tempting that we have

$$H = \frac{1}{2}|p|^2 + V, \quad (1.25)$$

formally equivalent to the classical total energy $\frac{1}{2}|p|^2 + V(x)$.

We will take the convention

$$\psi(x) = \frac{1}{(2\pi)^{d/2}} \int_{\mathbb{R}^d} e^{ik\cdot x} \widehat{\psi}(k) dk, \quad \widehat{\psi}(k) = \frac{1}{(2\pi)^{d/2}} \int_{\mathbb{R}^d} e^{-ik\cdot x} \psi(x) dx \quad (1.26)$$

for the Fourier transform, a unitary isomorphism on $L^2(\mathbb{R}^d, \mathbb{C})$. With this, we have

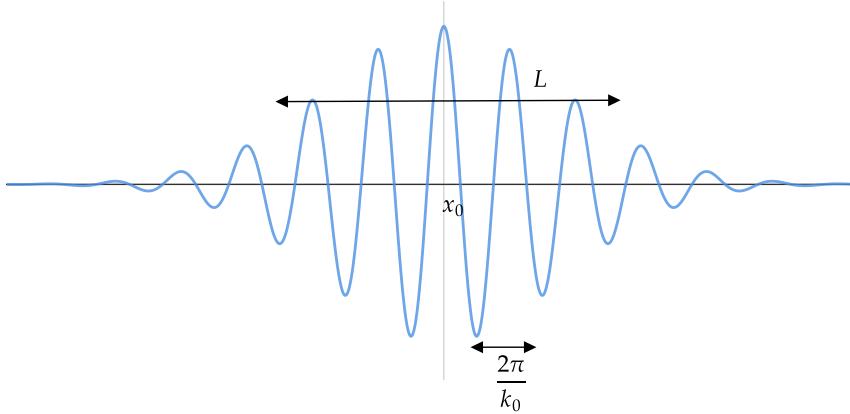
$$\langle\psi|p\psi\rangle = \int_{\mathbb{R}^d} k |\widehat{\psi}(k)|^2 dk \quad (1.27)$$

so that $|\widehat{\psi}(k)|^2$ is nothing but the probability density of finding the particle with momentum k .

Example 1.1 (Wavepackets). Consider a smooth and decaying even function $\chi : \mathbb{R} \rightarrow \mathbb{R}^+$ (for instance, a Gaussian), normalized such that $\|\chi\|_{L^2} = 1$, and let

$$\psi(x) = e^{ik_0 x} L^{-d/2} \chi\left(\frac{x - x_0}{L}\right) \quad (1.28)$$

This is a plane wave with spatial period $2\pi/k_0$, modulated (multiplied) by an enveloppe centered at x_0 , of width L and height $L^{-d/2}$. Its L^2 norm is always 1.



It is straightforward to compute (exercise) that the average position of the particle is

$$\langle \psi | x \psi \rangle = \int_{\mathbb{R}^d} x |\psi(x)|^2 dx = x_0, \quad (1.29)$$

and its standard deviation is $\sqrt{\langle \psi | (x - x_0)^2 \psi \rangle} \propto L$.

Using the standard rules for the Fourier transform of a translation and a dilation, we see that the Fourier transform of ψ is given by

$$\hat{\psi}(k) = e^{ix_0(k-k_0)} L^{d/2} \hat{\chi}(L(k-k_0)) \quad (1.30)$$

which is now a plane wave of period (in frequency space) $2\pi/x_0$, modulated by an enveloppe centered at k_0 , of width $1/L$ and height $L^{d/2}$. The average momentum is

$$\langle \psi | p \psi \rangle = \int_{\mathbb{R}^d} k |\hat{\psi}(k)|^2 dk = k_0, \quad (1.31)$$

and its standard deviation is $\sqrt{\langle \psi | (p - k_0)^2 \psi \rangle} \propto 1/L$. This is an instance of the Heisenberg uncertainty principle: the more accurately the position of a particle is known, the less accurately its momentum is known.

1.5 Free propagation

When $V = 0$, the time evolution can be solved using the Fourier transform. If ψ satisfies $i\partial_t \psi = -\frac{1}{2}\Delta \psi$, then its Fourier transform satisfies $i\partial_t \hat{\psi} = \frac{1}{2}|k|^2 \hat{\psi}$, so that

$$\hat{\psi}(k, t) = e^{-i\frac{|k|^2}{2}t} \hat{\psi}(k, 0). \quad (1.32)$$

This identifies the Schrödinger equation as a wave equation: each Fourier mode (plane wave) evolves with a phase velocity $v_{\text{ph}}(k) = \frac{|k|^2}{2}$, and therefore a group velocity⁵ $v_{\text{gr}}(k) = \nabla v_p(k) = k$.

⁵Recall that, in a wave

$$\psi(x, t) = \int_{\mathbb{R}^d} e^{i(k \cdot x - \omega(k)t)} f(k) dk, \quad (1.33)$$

Example 1.2 (Propagation of a wavepacket). Consider free propagation with a particular initial condition ψ_0 given by the Gaussian wavepacket of the previous example

$$\psi_0(x) = e^{ik_0x} \chi\left(\frac{x - x_0}{L_0}\right). \quad (1.34)$$

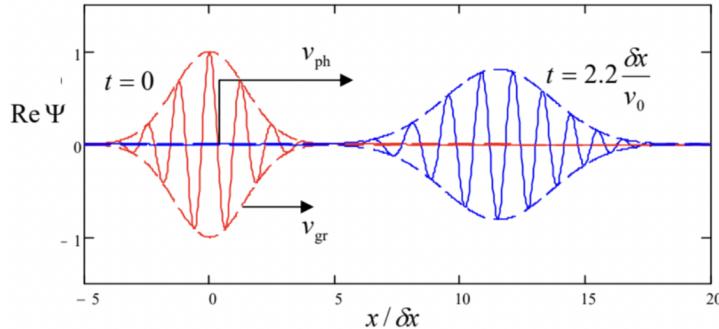
We have seen that

$$\langle \psi_0 | x \psi_0 \rangle = x_0, \quad \langle \psi_0 | p \psi_0 \rangle = k_0. \quad (1.35)$$

and from the Ehrenfest theorem (with $V = 0$) it therefore follows that

$$\langle \psi_t | x \psi_t \rangle = x_0 + tk_0, \quad \langle \psi_t | p \psi_t \rangle = k_0, \quad (1.36)$$

which shows that the wavepacket propagates in a straight line at velocity k_0 . In fact, when χ is a Gaussian, since Fourier transforms of Gaussians are Gaussians, and since the time evolution of a Gaussian is also a Gaussian, an explicit but painful computation using the Fourier transform shows that $|\psi(x, t)|^2$ is proportional to $e^{-\frac{(x-(x_0+k_0t))^2}{L(t)^2}}$ with $L(t) = L_0 \sqrt{1 + (\frac{t}{2L_0})^2}$: the wavepacket additionally broadens as it propagates; this is characteristic of *dispersive* equations with a non-constant group velocity.



Picture from [https://phys.libretexts.org/Bookshelves/Quantum_Mechanics/Essential_Graduate_Physics_-_Quantum_Mechanics_\(Likharev\)](https://phys.libretexts.org/Bookshelves/Quantum_Mechanics/Essential_Graduate_Physics_-_Quantum_Mechanics_(Likharev))

In the case with a nonzero potential, there are generally no analytic solutions available, and even the average motion is hard to predict. One case where the dynamics is clearer is when ψ is localized near a point x_t at a length scale small compared to those of the variations of V . Then, it is reasonable to assume that

$$\frac{d}{dt} \langle \psi | p \psi \rangle = - \int_{\mathbb{R}^d} (\nabla V(x)) |\psi(x)|^2 dx \approx -\nabla V(x_t) \quad (1.37)$$

and the quantum dynamics then tracks closely the classical one (at least, until the wave packet broadens sufficiently that the approximation is not valid anymore). This is what is meant by wave-particle duality: the wave functions have aspects of a wave and aspects of a particle, depending on

$\frac{\omega(k)}{k}$ is the phase velocity (the velocity at which the crests and troughs propagate), and $\nabla \omega(k)$ is the group velocity (the velocity at which the envelope propagates). These concepts are well-defined when f is strongly peaked around a particular wavevector, in which case the solution resembles a plane wave.

the regime. The quantum-classical connection can be made more precise using semiclassical theory, which we will not pursue here.

1.6 Stationary states

We have seen that the Schrödinger equation is able to encode wave propagation. It also supports another class of solutions, stationary states. Naively one might think that stationary states are obtained by solving $i\partial_t\psi = 0$, i.e. $H\psi = 0$, but this is too restrictive, as any solution of the **time-independent Schrödinger equation**

$$H\psi = \lambda\psi \quad (1.38)$$

yields a dynamical solution of the Schrödinger equation $e^{-i\lambda t}\psi$. Phase changes do not affect the physical properties, since $\langle e^{-i\lambda t}\psi | A e^{-i\lambda t}\psi \rangle = \langle \psi | A\psi \rangle$ for any observable A . Therefore, we refer to solutions of (1.38) as **stationary states**. Mathematically, this is an (infinite-dimensional) eigenvalue problem. The eigenvalue λ is interpreted as an energy (we will see later why). The stationary states are variously referred to as stationary states, eigenvectors, eigenfunctions or eigenstates.

Example 1.3 (Particle in a box). Consider a particle confined in an interval $[0, L]$, modeled by Dirichlet boundary conditions $\psi(0) = \psi(L) = 0$. We can solve $-\frac{1}{2}\psi'' = \lambda\psi$ explicitly as

$$\psi_n(x) = \alpha \sin\left(\frac{\pi n}{L}x\right), \text{ with } \lambda_n = \frac{1}{2}\left(\frac{\pi n}{L}\right)^2 \quad (1.39)$$

for any $n \in \mathbb{N}$, with arbitrary prefactors $\alpha \in \mathbb{C}$. The eigenvalues are **discrete** and correspond to localized stationary states, called **bound states**. These form standing wave patterns analogous to the modes of vibration of a string, which have no immediate analogy with the classical motion of a single particle. This **quantification** of the possible energies is one of the most striking features of the theory, and gave its original name to quantum theory (from the use of the word “quantum” to mean the minimal amount of something).

As $L \rightarrow \infty$, the spectrum (here, the set of eigenvalues) densifies, and approaches a continuous spectrum $[0, +\infty)$. For an infinite interval, the solutions are more conveniently labelled as the plane waves e^{ikx} , $k \in \mathbb{R}$ (rather than the less elementary sine solutions, which can be expressed as sums of two plane waves). These are not in $L^2(\mathbb{R}, \mathbb{C})$, since $\int_{\mathbb{R}} |e^{ikx}|^2 = +\infty$, and therefore do not correspond to a quantum mechanical state. However, they can be localized by a broad wavepacket $e^{ikx}e^{-\frac{1}{2}\left(\frac{x}{\sigma_0}\right)^2}$ with σ_0 large, yielding a normalizable state that approximates a plane wave. Under the time-dependent Schrödinger equation, the wavepacket then moves with momentum k . The plane waves are accordingly called **scattering states**, because of their tendency to *scatter* (move away to infinity).

Stationary states offer a powerful way to solve the time-dependent Schrödinger equation. Indeed, if

$$\psi(0) = \sum_{n=1}^N c_n \psi_n \quad (1.40)$$

for some set of coefficients c_n , and where the ψ_n are a set of eigenfunctions of H ($H\psi_n = \lambda_n\psi_n$), then the solution of the Schrödinger equation $i\partial_t\psi = H\psi$ with initial condition $\psi(0)$ is given by

$$\psi(t) = \sum_{n=1}^N c_n e^{-i\lambda_n t} \psi_n. \quad (1.41)$$

The question then becomes: can all initial states $\psi \in L^2(\mathbb{R}^d)$ be decomposed on a set of eigenfunctions of H ? If $L^2(\mathbb{R}^d)$ was finite-dimensional, the answer would be yes, by the spectral theorem applied to the Hermitian matrix H . In infinite dimensions, things are more subtle; we will investigate this in Section 2.

1.7 The hydrogen atom

We finish this section by computing the stationary states of our first realistic model: the simplest atom, hydrogen. Historically, the study of atoms was one of the key drivers in the discovery of quantum mechanics. The elegant explanation in 1926 of the quantification of physical quantities (such as the absorption spectrum of light by atoms) as being a consequences of fundamental postulates rather than ad-hoc quantification rules (the Bohr model, 1913) provided one of the clearest arguments in favor of quantum mechanics.

The hydrogen atom is composed of one electron, one proton and one neutron. Treated quantum-mechanically, they form a three-body problem, which we will not discuss until Section 9. However, since the proton and neutron are so much more massive than the electron (about 2000 times), it is reasonable to consider the nucleus (proton plus neutron) as a point particle, and treat only the electron with quantum mechanics (the “Born-Oppenheimer approximation”). The potential $V(x)$ results from the electrostatic interaction of the electron and the proton. Since these two particles have opposite charge, they attract, and, in atomic units, we have

$$V(x) = -\frac{1}{|x|}. \quad (1.42)$$

The Newton equation with this potential, $\ddot{x} = -\frac{x}{|x|^3}$, is exactly the same as the one encountered in the problem of determining the motion of a body (such as the earth) under the gravitational influence of a more massive one (such as the sun). Recall that these classical trajectories come in two types. When the energy $\frac{|p|^2}{2} + V(x)$ is negative, the trajectory is elliptic, resulting in periodic motion (the first body is “bound” to the second one); when it is positive, the trajectory is hyperbolic (the trajectory of the first body is deflected, or “scattered”, by the second).

Ignoring spin (which we will encounter later), the time-independent Schrödinger equation is $H\psi = \lambda\psi$, with

$$H = -\frac{1}{2}\Delta + V. \quad (1.43)$$

This turns out to be one of very few examples of exactly solvable models in quantum mechanics. This is essentially because of radial symmetry, which allows one to use the very powerful technique of separation of variables, writing eigenfunctions as a product of a radial and an angular part; the mathematical justification will be given in Section 4. The bound states⁶ can then be found in

⁶There are also uncountably many scattering states at every energy $\lambda \geq 0$.

spherical coordinates in the form (see [1, 3])

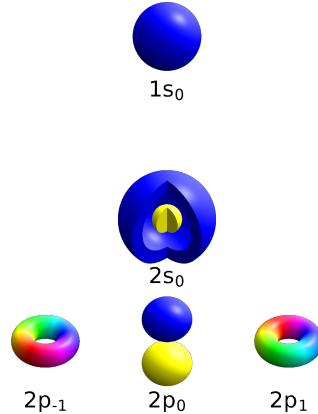
$$\psi_{n\ell m}(r, \theta, \phi) = e^{-r} R_{n\ell}(r) Y_{\ell m}(\theta, \phi), \quad \lambda_n = -\frac{1}{2n^2}. \quad (1.44)$$

In this expression the quantum numbers n, ℓ and m satisfy $n \in \{1, 2, \dots\}$, $\ell \in \{0, 1, \dots, n-1\}$ and $m \in \{-\ell, -\ell+1, \dots, \ell-1, \ell\}$. The functions $Y_{\ell m}$ are the spherical harmonics, which oscillate more and more as ℓ is increased⁷. The radial part $R_{n\ell}$ is a polynomial which has $n-\ell-1$ roots, and therefore oscillates more and more as n is increased; for $n=1, \ell=0$, the **ground state** (state of lowest energy) $\psi_{100}(r, \theta, \phi)$ is simply proportional to e^{-r} .

Conventionally, in chemistry these orbitals are labelled using the index n , followed by a letter corresponding to ℓ , in the “spdfg” order (s for $\ell=0$, p for $\ell=1$, etc). In order, the orbitals are

- 1s ($n=1, \ell=0$, multiplicity 1)
- 2s ($n=2, \ell=0$, multiplicity 1)
- 2p ($n=2, \ell=1$, multiplicity 3)
- 3s ($n=3, \ell=0$, multiplicity 1)
- etc.

The degeneracy (multiplicity) d_n of the n -th energy level λ_n is $d_1=1$ for $n=1$, $d_2=4$ for $n=2$, $d_3=9$ for $n=3$, etc. This is crucial in understanding the periodic table of elements, which we will come back to in Section 9.



The 1s, 2s and 2p orbitals of hydrogen, representing the isosurfaces (surfaces of constant $|\psi(x)|$), colored according to the phase of $\psi(x)$.

Picture from https://commons.wikimedia.org/wiki/File:Atomic_orbitals_n1234_m-eigenstates.png

The bound states are discrete (“quantized”), in contrast to the continuous family of elliptic orbits of classical mechanics. In particular, there is a well-defined lowest energy state, the ground state, in which the electron will be “usually” found in nature at rest⁸. This is contrast with classical mechanics, for which the electron can have an arbitrarily negative energy.

⁷The spherical harmonics are eigenfunctions of the Laplace-Beltrami operator, the restriction of the Laplacian to the sphere. They are the analogue in dimension 3 of the $e^{i\ell\theta}$ functions in polar coordinates in 2 dimensions.

⁸This might seem surprising, given that the Schrödinger is reversible: indeed, left alone, a system will *not* revert towards its ground state purely by the Schrödinger dynamics. However, quantum systems usually interact (hopefully relatively weakly) with their environment. For instance, the hydrogen atom left in an excited state $\lambda_2 > \lambda_{\text{gs}}$ will interact with the electromagnetic field, and decay to its ground state λ_{gs} , stimulating the electromagnetic field in the process (emitting a photon of frequency $\lambda_2 - \lambda_{\text{gs}}$). This is known as spontaneous emission. Modeling it requires the quantum theory of the electromagnetic field. This is the object of quantum field theory, which is outside the scope of these notes.

1.8 Exercises

1. Check that $[x, p] = i$. Show that this commutation relation cannot be realized in finite dimensions, i.e., when x and p are both hermitian matrices on a finite-dimensional space (hint: take the trace).
2. Write the solution of the Schrödinger equation $i\partial_t\psi = -\Delta\psi, \psi(x, t=0) = \psi_0(x)$ as a convolution $\psi = G_t * \psi_0$ (hint: take Fourier transforms and use the Fourier transform of a Gaussian). Identify the Green function (“propagator”) G_t . Deduce that, in 1D, there is $C > 0$ such that

$$\sup_{x \in \mathbb{R}} |\psi(x, t)| \leq \frac{C}{t} \int_{\mathbb{R}} |\psi(x, 0)| dx. \quad (1.45)$$

Interpret. Why does this tell you when combined with the preservation of total probability $\int_{\mathbb{R}} |\psi(x)|^2 dx = 1$?

3. Show that the magnetic Hamiltonian

$$H\psi = \frac{1}{2}(-i\nabla + A)^2 = \frac{1}{2} \left(-\Delta + \sum_{i=1}^3 A_i(x)p_i + |A(x)|^2 \right) \quad (1.46)$$

is formally self-adjoint with $A : \mathbb{R}^3 \rightarrow \mathbb{R}^3$ sufficiently nice and satisfying $\text{div}(A) = 0$. Show that, if ψ evolves with this Hamiltonian,

$$\frac{d}{dt} \langle \psi | x \psi \rangle = \langle \psi | (p + A) \psi \rangle. \quad (1.47)$$

Summary

The Schrödinger equation presents characteristics both of a wave (propagation, dispersion) and a particle (satisfying the Newton equations “on average”). Its mathematical study is facilitated by the operator formalism, whereby physical observables are associated with formally self-adjoint operators. Important operators are the position x , the momentum $p = -i\nabla$ and the Hamiltonian $-\frac{1}{2}\Delta + V$. The stationary states of a Schrödinger Hamiltonian $-\frac{1}{2}\Delta + V$ include localized bound states, typically with quantified energies, and delocalized scattering states, typically with continuous energies. The hydrogen atom $-\frac{1}{2}\Delta - \frac{1}{|x|}$ supports both bound states (for $\lambda < 0$) and scattering states (for $\lambda > 0$).

2 A very quick tour of spectral theory

Spectral theory is concerned with the extension of the concepts of eigenvalues and eigenvectors in the infinite-dimensional setting. We will focus on the self-adjoint case (analogue of finite-dimensional Hermitian matrices), of relevance to quantum mechanics. There also exists a richer (and much more complicated) spectral theory of non-self-adjoint operators, which we will ignore completely. In particular, several of the definitions we give are specific to the self-adjoint case.

The spectral theory of self-adjoint operators is a beautiful topic in analysis, with links with several branches of mathematics (linear algebra, geometry, functional analysis, complex analysis, measure theory...), and which deserves a much more thorough treatment than we have time for. We will only focus on the basic definitions and results, without giving full proofs. We will endeavor to atone for this by giving at least broad outlines of proofs as well as examples. We recommend to the francophone reader the textbook [1]; another good option in English is [8].

The finite-dimensional spectral theory is contained in the spectral theorem: every Hermitian matrix is diagonalizable in an orthogonal basis of eigenvectors, with real spectrum. We now seek extensions of this theory to the infinite-dimensional case.

Example 2.1 (“Continuous eigendecomposition”). As a motivation, consider the operator $-i\nabla = -i\frac{d}{dx}$ on \mathbb{R} , a fundamental operator that we have encountered as the momentum operator. As we have seen, this operator is formally self-adjoint on the Hilbert space $L^2(\mathbb{R}, \mathbb{C})$, in the sense that

$$\langle \psi | (-i\nabla) \phi \rangle = -i \int_{\mathbb{R}} \bar{\psi} \phi' = \int_{\mathbb{R}} \overline{(-i\psi')} \phi = \int_{\mathbb{R}} \langle (-i\nabla)\psi | \phi \rangle \quad (2.1)$$

for all $\psi, \phi \in C_c^\infty(\mathbb{R})$ (smooth compactly supported functions). However, it is not a linear map from $L^2(\mathbb{R})$ to itself, but rather from (say) $H^1(\mathbb{R})$ to $L^2(\mathbb{R})$. Second, even if it was defined as a linear map, it has no eigenfunctions in $L^2(\mathbb{R})$. Indeed, all solutions of $(-i\nabla)\psi = \lambda\psi$ are either oscillatory (plane waves, when λ is real) or exponentially growing at either $+\infty$ or $-\infty$ (when λ is in $\mathbb{C} \setminus \mathbb{R}$); neither are localized. Nevertheless, the Fourier transform

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \hat{\psi}(k) e^{ikx} dk, \quad \hat{\psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \psi(x) e^{-ikx} dx \quad (2.2)$$

is, formally, very similar to the decomposition of the vector ψ on a set of “eigenvectors” e^{ikx} , satisfying

$$(-i\nabla)e^{ikx} = k e^{ikx}. \quad (2.3)$$

Compared to the finite-dimensional case, the “eigenvectors” are not in the Hilbert space $L^2(\mathbb{R})$, and they are indexed by a continuous rather than a discrete label. The sum is also only over plane waves (those that have a real eigenvalue $\lambda = k$), not the exponentially growing eigenvectors. The mathematical difference between these two types of solutions of $(-i\nabla)\psi = \lambda\psi$ is that the plane waves can be relatively easily combined to give localized objects through the Fourier transform, while it is much harder to do with the exponentially growing solutions.

In the example above, there are two separate difficulties. First, the fact that there exists useful

objects that look like eigenvectors but that are not in the Hilbert space and are typically indexed by a continuous label; second, the fact that many formally self-adjoint operators of interest are not defined as linear maps on a single Hilbert space. These two difficulties are in fact orthogonal:

Example 2.2 (Unbounded operators with discrete spectrum, bounded operators with continuous spectrum). The map defined by $(Au)_n = nu_n$, for instance from the compactly supported sequences in $\ell^2(\mathbb{Z})$ to $\ell^2(\mathbb{Z})$, is not a linear map on $\ell^2(\mathbb{Z})$, but has very well-defined set of discrete eigenvectors and eigenvalues, forming a Hilbert basis. On the other hand, the map defined on $\ell^2(\mathbb{Z})$ by $(Au)_n = (-i)(u_{n+1} - u_{n-1})$ is a bounded linear map on $\ell^2(\mathbb{Z})$, but has a “continuous eigendecomposition” as above given by the Fourier transform (from $\ell^2(\mathbb{Z})$ to $L^2([-\pi, \pi])$).

The objective of spectral theory is to provide a unified framework to discuss eigendecompositions in infinite dimensions. We will start by considering the case of bounded linear operators, and will finish by a discussion of unbounded operators. The case of bounded linear operators will be illustrated with two fundamental examples: finite-dimensional operators, and the **multiplication operator** V on an interval I acting on functions of $L^2(I)$ by

$$(V\psi)(x) = V(x)\psi(x), \quad (2.4)$$

where $V : I \rightarrow \mathbb{R}$ is a continuous and bounded function on \bar{I} . Multiplication operators are important in themselves, and also because multiplication operators are dual to translational-invariant operators (which includes convolutions as well as constant-coefficient differential operators) by the Fourier transform.

2.1 Self-adjointness and spectrum of bounded operators

Recall that a linear map $A : \mathcal{H} \rightarrow \mathcal{H}$ on a Hilbert space \mathcal{H} is bounded if there is $C > 0$ such that $\|A\psi\| \leq C\|\psi\|$ for all $\psi \in \mathcal{H}$. Bounded linear maps are also called bounded operators.

Definition 2.3 (Self-adjointness). The adjoint A^* of a bounded operator A is defined as the unique operator such that

$$\langle A^*\psi | \phi \rangle = \langle \psi | A\phi \rangle \quad (2.5)$$

for all $\psi, \phi \in \mathcal{H}$. A bounded operator A is **self-adjoint** if $A^* = A$.

The existence and uniqueness of A^* is ensured by the Riesz representation theorem. In finite dimension, an operator is self-adjoint if and only if its representation in an orthogonal basis is Hermitian, i.e. $A_{ij} = \overline{A_{ji}}$ (exercise).

In the same way as in finite dimension, λ is an **eigenvalue** of A if there is a nonzero $\psi \in \mathcal{H}$ such that $A\psi = \lambda\psi$. In contrast to the finite dimensional case, however, this definition is too restrictive to allow for a satisfactory theory.

Example 2.4 (Absence of eigenvalues of the multiplication operator). Consider the case of the multiplication operator V . It is clearly self-adjoint on $L^2(I)$. Furthermore, $V\psi = \lambda\psi$ implies that $\psi = 0$ whenever $V(x) \neq \lambda$. Therefore, for a generic V (for instance, $V(x) = \cos(x)$) the set of eigenvalues is empty (unless V is equal to λ on a set of non-empty measure, in which case λ is an eigenvalue of infinite multiplicity).

However, not all non-eigenvalues are equal: formally, the Dirac mass δ_y at y satisfies $V\delta_y = V(y)\delta_y$, and therefore $V(y)$ is an “almost-eigenvalue”, in a way that values λ for which $V^{-1}(\lambda) = \emptyset$ are not.

Since there are self-adjoint operators without eigenvalues, we need a weaker notion of spectrum if we are to ever state a spectral theorem. In the previous example, Diracs are not in \mathcal{H} , but can be approximated by elements in \mathcal{H} . Therefore, a reasonable definition is

Definition 2.5. The **spectrum** $\sigma(A)$ of a bounded self-adjoint operator on \mathcal{H} is the set of $\lambda \in \mathbb{C}$ such that there exists a sequence $\psi_n \in \mathcal{H}$ with

$$\|\psi_n\| = 1 \quad (2.6)$$

$$\|A\psi_n - \lambda\psi_n\| \rightarrow 0 \quad (2.7)$$

The set of eigenvalues is called the **point spectrum** $\sigma_p(A)$, clearly a subset of $\sigma(A)$. The set $\sigma_c(A) = \sigma(A) \setminus \sigma_p(A)$ is called the **continuous spectrum**.

We caution the reader that this definition is only valid for self-adjoint operators. There are several other definitions and refinements of the notion of the spectrum; this particular one suffices for our purposes⁹.

Theorem 2.6. Let A be a bounded self-adjoint operator. Then,

1. $\sigma(A) \subset \mathbb{R}$.
2. $\sigma(A)$ is the set of λ such that $A - \lambda$ is not invertible¹⁰.
3. $\sigma(A)$ is closed.
4. $\sigma(A)$ is bounded.

Proof. 1. If there is a sequence ψ_n satisfying $\|\psi_n\| = 1, (A - \lambda)\psi_n \rightarrow 0$, then taking inner products with ψ_n we get

$$\langle \psi_n | A\psi_n \rangle - \lambda \rightarrow 0. \quad (2.8)$$

Since $\langle \psi_n | A\psi_n \rangle \in \mathbb{R}$, λ is real.

⁹For non-self-adjoint operators, the spectrum is defined as the set of λ such that $A - \lambda$ is not invertible, which we will see below is equivalent to our definition in the self-adjoint case. There is also an additional notion of residual spectrum. Finally, for self-adjoint operators, there is also a separate measure-theoretic partitioning of the spectrum as pure point, absolutely continuous and singular.

¹⁰A bounded linear operator is invertible if it is bijective. Recall from the bounded inverse theorem that an invertible bounded linear operator on a Hilbert space (in fact, even on a Banach space) has a bounded inverse.

2. We first show the easy direction $\sigma(A) \subset \{\lambda, A - \lambda \text{ not invertible}\}$. Let $\lambda \in \sigma(A)$. If $A - \lambda$ is invertible, then, because $(A - \lambda)^{-1}$ is continuous, $\psi_n = (A - \lambda)^{-1}(A - \lambda)\psi_n \rightarrow 0$, a contradiction.

We now show $\{\lambda, A - \lambda \text{ not invertible}\} \subset \sigma(A)$. Assume that there are no sequences satisfying (2.6-2.7); this implies that there is $c > 0$ such that

$$\|(A - \lambda)\psi\| \geq c\|\psi\| \quad (2.9)$$

for all $\psi \in \mathcal{H}$, so that $A - \lambda$ is injective. We show that it is surjective by showing that $\text{Ran}(A - \lambda)$ is closed and dense.

To prove that $\text{Ran}(A - \lambda)$ is closed, we use

$$\|\psi_n - \psi_m\| \leq \frac{1}{c}\|(A - \lambda)(\psi_n - \psi_m)\| \quad (2.10)$$

to show that, if $(A - \lambda)\psi_n$ is a sequence in $\text{Ran}(A - \lambda)$ converging to some $\phi \in \mathcal{H}$, then ψ_n is Cauchy and therefore converges to some ψ ; by continuity we deduce that $(A - \lambda)\psi = \phi$ and therefore that $\phi \in \text{Ran}(A - \lambda)$.

To prove that $\text{Ran}(A - \lambda)$ is dense, we apply the equality¹¹

$$\text{Ran}(B)^\perp = \ker(B^*), \quad (2.11)$$

valid for any bounded operator B to $B = A - \lambda$. Passing to the orthogonal, we get

$$\overline{\text{Ran}(A - \lambda)} = \ker(A - \bar{\lambda})^\perp \quad (2.12)$$

If $\lambda \in \mathbb{R}$, the proof is finished because $A - \lambda$ is injective, so that $\text{Ran}(A - \lambda)$ is dense. If $\lambda \in \mathbb{C} \setminus \mathbb{R}$, we have to show that $A - \bar{\lambda}$ is injective. This is clear if A is real (so that if $A\psi_n - \lambda\psi_n \rightarrow 0$, $A\bar{\psi}_n - \bar{\lambda}\bar{\psi}_n \rightarrow 0$), but for general A we need to use the separate argument

$$|\langle \psi | (\bar{\lambda} - A)\psi \rangle| = \sqrt{\langle \psi | (\text{Re } \lambda - A)\psi \rangle^2 + (\text{Im } \lambda)^2 \|\psi\|^2} \geq |\text{Im}(\lambda)|\|\psi\|^2. \quad (2.13)$$

3. If A is invertible, then the Neumann series¹²

$$(A + B)^{-1} = (A(1 + A^{-1}B))^{-1} \quad (2.14)$$

$$= (1 - A^{-1}B + A^{-1}BA^{-1}B + \dots)A^{-1} \quad (2.15)$$

$$= A^{-1} - A^{-1}BA^{-1} + A^{-1}BA^{-1}BA^{-1} + \dots \quad (2.16)$$

converges for $\|B\| < 1/\|A^{-1}\|$. Therefore, if $\lambda \notin \sigma(A)$, the operator $\mu - A = (\lambda - A) + (\mu - \lambda)$ is invertible for μ close enough to λ .

4. The Neumann series $(\lambda - A)^{-1} = \lambda^{-1} + \lambda^{-2}A + \dots$ converges for $|\lambda| > \|A\|$

□

¹¹This is one version of the Fredholm alternative. In finite dimensions, this says that for $Bx = b$ to have a solution when B is not invertible, b must belong to the orthogonal of $\ker(B^*)$. In other words, when a linear combinations of lines makes the left-hand side zero for all x ($y \in \ker(B^*)$), it must also yield zero when applied to b ($\langle y | b \rangle = 0$).

¹²Recall that for A a bounded operator on a Banach space with $\|A\| < 1$, $1 - A$ is invertible, with the Neumann series $(1 - A)^{-1} = 1 + A + A^2 + \dots$ converging normally (for the norm topology of bounded operators on a Banach space)

Example 2.7 (Spectrum of the multiplication operator). In the case of the multiplication operator on an interval of \mathbb{R} , we can take for ψ_n a function localized in a region of size $1/n$ around any point y , for instance

$$\psi_n(x) = C\sqrt{n}\chi(n(x-y)), \quad (2.17)$$

where χ is a localized function (for instance, a Gaussian), and C is chosen so that $\|\psi_n\| = 1$ for all $n \in \mathbb{N}$. Standard arguments (change of variable plus dominated convergence) show that $\|V\psi_n - V(y)\psi_n\| \rightarrow 0$, so that $V(y) \in \sigma(V)$. On the other hand, when λ is at finite distance of $V(\mathbb{R})$, the operator of multiplication by $1/(V - \lambda)$ is bounded, and therefore $\lambda \notin \sigma(V)$. It follows that the spectrum of V is the closure of its range (as we have seen in Example 2.4, whether that spectrum is point spectrum or continuous spectrum is more involved).

This example gives some intuition to the notion of spectrum. The point spectrum is the set of eigenvalues associated with eigenvectors in \mathcal{H} (“bound” or “normalizable” in quantum mechanics). The continuous spectrum is the set of almost-eigenvalues, associated with almost-eigenvectors (“scattering” or “non-normalizable” in quantum mechanics): objects that are not in \mathcal{H} , whose mathematical existence is tricky to define in general, but that can be approximated by sequences of vectors in \mathcal{H} . This is the case of the Dirac delta distribution in this example; we will see when we discuss unbounded operators that the same role is played by plane waves for differential operators.

2.2 Projection-valued measures and orthogonally-resolved operators

The spectral theorem for finite-dimensional self-adjoint operators states that, if A is self-adjoint, then there is a set of orthonormal eigenvectors ϕ_n with associated eigenvalues λ_n such that $A\phi_n = \lambda_n\phi_n$ for all $n = 1, \dots, N$. It follows that, for all $\psi \in \mathcal{H}$,

$$A\psi = A \sum_{n=1}^N \langle \phi_n | \psi \rangle \phi_n = \sum_{n=1}^N \langle \phi_n | \psi \rangle \lambda_n \phi_n. \quad (2.18)$$

A common way of rewriting this in quantum mechanics is

$$A = \sum_{n=1}^N \lambda_n |\phi_n\rangle\langle\phi_n| \quad (2.19)$$

Recall that using Dirac’s notation, $\langle \phi_n |$ is the linear form $\psi \mapsto \langle \phi_n | \psi \rangle$, so that $|\phi_n\rangle\langle\phi_n|$ is nothing but a notation for the orthogonal projector on $\text{Span}(\phi_n)$.

For self-adjoint operators on infinite-dimensional Hilbert spaces, the situation is more complicated, and sums may have to be replaced by integrals in the presence of continuous spectrum. A way to formalize this is with the notion of projector-valued measures.

Recall that, like in finite dimensions, an orthogonal projector on \mathcal{H} is a bounded self-adjoint operator A such that $A^2 = A$. A (real-valued) measure on \mathbb{R} is a non-negative map μ from the Borel sets (the countable unions, countable intersections and relative complements of open sets) to the extended real line $\mathbb{R}^+ \cup \{+\infty\}$ such that $\mu(\emptyset) = 0$ and $\mu(\cup_{\alpha=1}^{\infty} E_{\alpha}) = \sum_{\alpha=1}^{\infty} \mu(E_{\alpha})$ for all countable collections of pairwise disjoint Borel sets $\{E_k\}_{k=1}^{\infty}$.

Definition 2.8. A **projection-valued measure** P is a map from the Borel sets to the orthogonal projections on \mathcal{H} such that $P(\mathbb{R}) = 1$ (the identity on \mathcal{H}) and such that, for every $\psi, \phi \in \mathcal{H}$, the mapping $E \rightarrow \langle \psi | P(E) \phi \rangle$ is a complex measure on \mathbb{R} (the positive and negative parts of the real and imaginary parts are measures).

This implies in particular that, if E_1 and E_2 are disjoint Borel sets, $P(E_1) + P(E_2) = P(E_1 \cup E_2)$.

Although measures μ are defined in “integral form”, as mappings from Borel sets to reals, they are often easier to specify in the “differential form”. For instance, the measure $d\mu(x) = 3\delta_2(x)dx + e^{-x^2}dx$ is a notation for $\mu(E) = 3\mathbf{1}(2 \in E) + \int_E e^{-x^2}dx$. In the same way, projection-valued measures are also often more easily specified in differential form.

Example 2.9 (Examples of projection-valued measures).

- In finite dimension, if $A = \sum_{n=1}^N \lambda_n |\phi_n\rangle\langle\phi_n|$, then

$$P(E) = \sum_{n=1}^N \mathbf{1}(\lambda_n \in E) |\phi_n\rangle\langle\phi_n| \quad (2.20)$$

defines a projection-valued measure, written in differential form as

$$dP(\lambda) = \sum_{n=1}^N \delta_{\lambda_n}(\lambda) d\lambda |\phi_n\rangle\langle\phi_n| \quad (2.21)$$

- The formula

$$(P(E)\phi)(x) = \phi(x) \mathbf{1}(x \in E) \quad (2.22)$$

defines a projection-valued measure on $\mathcal{H} = L^2(I)$, written in differential form as

$$(dP(y)\phi)(x) = \delta_y(x) \phi(x) d\lambda = \delta_y(x) \phi(y) dy. \quad (2.23)$$

In the physics literature, this is often written as

$$dP(y) = |\delta_y\rangle\langle\delta_y| dy. \quad (2.24)$$

This should be understood as simply a notation for (2.22).

Given a simple function (in the measure-theoretic sense)

$$f(k) = \sum_{\alpha=1}^M f_\alpha \mathbf{1}(k \in E_\alpha), \quad (2.25)$$

where $f_\alpha \in \mathbb{R}$ and E_α are disjoint Borel sets in a measurable space X , we can define $\int_X f(k) dP(k)$

as the operator

$$\int_X f(k) dP(k) = \sum_{\alpha=1}^M f_\alpha P(E_\alpha). \quad (2.26)$$

It turns out that by the same approximation arguments used to define the Lebesgue integral, one can define the operator $\int_X f(k) dP(k)$ for *all bounded measurable functions* f . These operators are said to be **orthogonally resolved** (their action is simply given by the scalar $f(k)$ on each of the “continuously orthogonal spaces” spaces $dP(k)$).

Example 2.10 (Orthogonal resolutions of finite-dimensional and multiplication operators).

- Consider a finite-dimensional self-adjoint operator $A = \sum_{n=1}^N \lambda_n |\phi_n\rangle\langle\phi_n|$ on \mathbb{C}^N , and set as in (2.21) $dP(\lambda) = \sum_{n=1}^N \delta_{\lambda_n}(\lambda) d\lambda |\phi_n\rangle\langle\phi_n|$. Then, following the definitions, we obtain

$$\int_{\mathbb{R}} \lambda dP(\lambda) = \sum_{n=1}^N \lambda_n |\phi_n\rangle\langle\phi_n| = A. \quad (2.27)$$

- Consider a simple function $V(x) = \sum_{\alpha=1}^M V_\alpha \mathbf{1}(x \in E_\alpha)$, and set as in (2.22) $(P(E)\phi)(x) = \phi(x) \mathbf{1}(x \in E)$. Then, following the definitions,

$$\left[\left(\int_I V(y) dP(y) \right) \phi \right] (x) = \sum_{\alpha=1}^M V_\alpha \mathbf{1}(x \in E_\alpha) \phi(x) = V(x) \phi(x), \quad (2.28)$$

which identifies $\int_I V(y) dP(y)$ as the multiplication operator by the function V :

$$V = \int_I V(y) dP(y), \quad (2.29)$$

often written in the physics literature as $V = \int_I V(y) |\delta_y\rangle\langle\delta_y| dy$, again using the notation of (2.24). Passing to the limit, this is true for any bounded measurable function V .

Consider an orthogonally-resolved operator $\int_X f(k) dP(k)$. Set now for any Borel set E of \mathbb{R}

$$Q(E) = \int_X \mathbf{1}(f(k) \in E) dP(k). \quad (2.30)$$

It can be seen that

$$\int_X f(k) dP(k) = \int_{\mathbb{R}} \lambda dQ(\lambda). \quad (2.31)$$

Operators of the form $\int_{\mathbb{R}} \lambda dQ(\lambda)$ are said to be **spectrally resolved**.

In differential form, the transition from orthogonal to spectral resolution is simply a change of variables: formally, if $dP(k) = g(k) dk$, (and when X is an Euclidean space), the co-area formula

gives

$$\int_X f(k) dP(k) = \int_{\mathbb{R}} \lambda \underbrace{\left(\int_{\{k \in X, f(k) = \lambda\}} \frac{1}{|\nabla f(k)|} g(k) d\sigma(k) \right)}_{dQ(\lambda)} d\lambda, \quad (2.32)$$

where $d\sigma(k)$ is the Hausdorff measure on $f^{-1}(\lambda)$, although this formula is harder to justify mathematically in the general case.

Intuitively, $dQ(\lambda)$ looks like it projects onto the “almost-eigenvectors” associated with the “almost-eigenvalue” λ . This intuition is interesting but incomplete. First, almost-eigenvectors have no natural normalization, and therefore cannot be used directly to write $dQ(\lambda)$. Second, the two operators A for instance and A^2 have the same almost-eigenvectors but are different operators that cannot have the same $dQ(\lambda)$.

Example 2.11 (Spectral resolution of the multiplication operator). We have seen that the multiplication operator was orthogonally resolved onto its almost eigenvectors: in the notation of Example 2.9,

$$V = \int_I V(y) |\delta_y\rangle \langle \delta_y|. \quad (2.33)$$

When for instance $V^{-1}(\lambda)$ is a discrete set for all λ , we have

$$V = \int_{\mathbb{R}} \lambda \left(\sum_{y \in I, V(y)=\lambda} \frac{1}{|V'(y)|} |\delta_y\rangle \langle \delta_y| \right) d\lambda. \quad (2.34)$$

so that $dP(\lambda)$ does project onto the almost-eigenvectors $\{|\delta_y\rangle, V(y) = \lambda\}$, but with a normalizing factor $\frac{1}{|V'(y)|}$. This factor is understood physically as a *density of states*: since the image by V of an infinitesimal volume dy centered at y has measure $d\lambda = |V'(y)|dy$, the “amount of states in x space” in an infinitesimal window $d\lambda$ in λ space is given by $\frac{1}{|V'(y)|} d\lambda$.

2.3 Functional calculus

In the finite-dimensional case, for a self-adjoint operator

$$A = \sum_{n=1}^N \lambda_n |v_n\rangle \langle v_n|, \quad (2.35)$$

and a function f , it is reasonable to define

$$f(A) = \sum_{n=1}^N f(\lambda_n) |\phi_n\rangle \langle \phi_n|. \quad (2.36)$$

This agrees with the notations for polynomials and inverses of operators.

In the infinite-dimensional case, similarly, for a bounded measurable function f and an orthogonally resolved operator

$$A = \int_X g(k) dP(k), \quad (2.37)$$

it is reasonable to define

$$f(A) = \int_X f(g(k)) dP(k). \quad (2.38)$$

Again, this agrees with the usual definitions when f is a polynomial or a rational function. This definition does not depend on the particular orthogonal resolution, and has all the nice properties that can naturally be expected (for instance, $(f \circ g)(A) = f(g(A))$).

2.4 The spectral theorem

We have seen that several operators of interest can be orthogonally resolved, and then spectrally resolved. The spectral theorem states that *all* self-adjoint operator can be spectrally resolved:¹³

Theorem 2.12 (Spectral theorem, projection-valued measure version). Let A be a bounded self-adjoint operator. Then there is a projection-valued measure Q such that

$$A = \int_{\mathbb{R}} \lambda dQ(\lambda). \quad (2.39)$$

Extremely rough sketch of proof. There are many proofs of the spectral theorem, and we sketch one of them, which proceeds by defining the functional calculus for measurable functions.

For any bounded self-adjoint operator and polynomial p , we define $p(A)$ in the usual way. Since any continuous function on an interval can be approximated uniformly by polynomials, one can define $f(A)$ for any continuous function f . Now, for any $\psi \in \mathcal{H}$, the mapping

$$f \mapsto \langle \psi | f(A) \psi \rangle \quad (2.40)$$

defines a bounded positive linear map from the set of continuous compactly supported functions on \mathbb{R} . From the Riesz-Markov theorem, it follows that there is a measure $\mu_{\psi,A}$ on \mathbb{R} such that

$$\langle \psi | f(A) \psi \rangle = \int_{\mathbb{R}} f(\lambda) d\mu_{\psi,A}(\lambda). \quad (2.41)$$

This formula allows us to define $\langle \psi | f(A) \psi \rangle$ for any *measurable* bounded function f , not simply continuous. By polarization, we can define $\langle \phi | f(A) \psi \rangle$, and by the Riesz representation theorem we can define $f(A)\psi$. Then, we set for any Borel set E

$$Q(E) = \chi_E(A) \quad (2.42)$$

with χ_E the characteristic function of the Borel set E . It is then relatively straightforward to check that $A = \int_{\mathbb{R}} \lambda dQ(\lambda)$. □

¹³This is not the only formulation of the spectral theorem in infinite dimension; another is to say that any self-adjoint operator is unitarily equivalent to a multiplication operator. We refer to courses on spectral theory for this.

2.5 Unbounded operators

We now look at unbounded operators; the main example will be various forms of the Laplacian.

Definition 2.13. An **unbounded operator** $(A, D(A))$ on a Hilbert space \mathcal{H} is a linear map from a dense subset $D(A)$ of \mathcal{H} (called its domain) to \mathcal{H} . A is **symmetric** if, for all $\psi, \phi \in D(A)$, $\langle A\psi | \phi \rangle = \langle \psi | A\phi \rangle$.

The terminology “unbounded operator” is confusing but unfortunately standard: unbounded operators are not “operators” in the usual sense of linear maps from \mathcal{H} to \mathcal{H} , and are not to be confused with unbounded linear maps from \mathcal{H} to \mathcal{H} . The terminology “symmetry” is also unfortunate, since symmetric operators in finite dimension correspond to Hermitian matrices (and not complex symmetric matrices). Note that symmetry is still with respect to the inner product of the underlying \mathcal{H} , not that of $D(A)$ if it happens to be a Hilbert of its own; to make this explicit we sometimes say that “ A is self-adjoint on \mathcal{H} with domain $D(A)$ ”. Finally, when the domain is clear, unbounded operators are often denoted by an abuse of notation only by A .

As before, the spectrum of A is the set of points $\lambda \in \mathbb{C}$ such that $A - \lambda$ is not invertible (as an operator from $D(A)$ to \mathcal{H}); in particular, the spectrum depends on the choice of $D(A)$.

Example 2.14 (Various unbounded operator realizations of the Laplacian). The Laplacian on an interval $(0, 1)$ can be seen as an unbounded operator on $\mathcal{H} = L^2(0, 1)$ with several different domains, differing in boundary conditions:

- (a) $H^2(0, 1)$ (no boundary condition). The point spectrum is the whole of \mathbb{C} (the equation $\psi'' = \lambda\psi$ has solutions in $H^2(0, 1)$ for all λ). This operator is not symmetric (the boundary terms in the integration by parts do not vanish).
- (b) $H^2(0, 1) \cap H_0^1(0, 1)$ (Dirichlet boundary condition). The spectrum is purely discrete and is the set $\{-(\pi n)^2, n \in \mathbb{Z}, n \neq 0\}$. This operator is symmetric.
- (c) $C_c^\infty(0, 1)$ (functions with a compact support inside $(0, 1)$, a very strong boundary condition). The spectrum is purely continuous and is the whole of \mathbb{C} (the equation $\psi'' = \lambda\psi$ has no solutions in $C_c^\infty(0, 1)$, but the solutions of $\psi'' - \lambda\psi = f$ for $f \in L^2$ are not in $C_c^\infty(0, 1)$). This operator is symmetric.

As we see in this example, the symmetry of an operator does not ensure that its spectrum is real, or prevent assorted pathologies. As we will see later, it is also not sufficient to ensure the well-posedness of the Schrödinger equation $i\partial_t\psi = A\psi$ ((a) breaks uniqueness, (c) breaks existence). The better notion is that of self-adjointness:

Definition 2.15. A symmetric unbounded operator A is **self-adjoint** if its spectrum is real.

Self-adjointness is a very deep and important concept, and as such there are many equivalent definitions, with textbooks on spectral theory often using another one. This definition is the most relevant for our purposes, as in quantum mechanics the spectrum will be identified with the possible results of a physical measurement. Mathematically, as the examples above show, self-adjointness encodes the need for additional information besides simply the action of the operator

(such as boundary conditions) to ensure the well-posedness of various equations (either static, like $(A - \lambda)\psi = f$, or dynamic, like $i\partial_t\psi = A\psi$).

Example 2.16 (Spectrum of the self-adjoint realizations of the Laplacian). The Laplacian on an interval is not self-adjoint with domain $C_c^\infty(0, 1)$, but is with domain $H^2(0, 1) \cap H_0^1(0, 1)$. It is also self-adjoint with the domains corresponding to Neumann boundary conditions $\psi'(0) = \psi'(L) = 0$ and periodic boundary conditions $\psi(0) = \psi(L), \psi'(0) = \psi'(L)$. In all cases, the spectrum is discrete and easily obtained explicitly.

Example 2.17 (Momentum and Laplacian on the line). The operator $-i\nabla$ is self-adjoint on $L^2(\mathbb{R})$ with domain $H^1(\mathbb{R})$. The Laplacian on the whole real line \mathbb{R} is self-adjoint on $L^2(\mathbb{R})$ with domain $H^2(\mathbb{R})$.

These operators are dual to multiplication operators in the Fourier domain, in the sense that, if $U : L^2(\mathbb{R}, \mathbb{C}) \rightarrow L^2(\mathbb{R}, \mathbb{C})$ is the unitary Fourier transform, then $-i\nabla = U^*kU$, where k is the multiplication operator by the dependent variable. It follows that $\sigma(-i\nabla) = \sigma(k)$, which was computed in example 2.7 to be \mathbb{R} . It is also instructive to identify explicitly the approximate eigenvectors: we used in example 2.7 the sequence

$$\phi_n(k) = C\sqrt{n}\chi(n(k - k_0)) \quad (2.43)$$

which concentrates on k_0 . It follows that the appropriate test functions here are the inverse Fourier transforms

$$\psi_n(x) = (U^*\phi_n)(x) = \frac{C}{\sqrt{n}}\check{\chi}\left(\frac{x}{n}\right)e^{ik_0x} \quad (2.44)$$

with $\check{\chi}$ the inverse Fourier transform of χ . This is a wavepacket, of the type encountered in Example 1.2; when n is large this approximates the plane wave e^{ik_0x} . It can be checked directly that these satisfy $(-i\nabla)\psi_n - k_0\psi_n \rightarrow 0$. This explains why in the motivational example 2.1 we considered the plane waves e^{ik_0x} as appropriate ‘‘almost eigenvectors’’ only when $k_0 \in \mathbb{R}$: while these plane waves can be approximated by sequences ψ_n satisfying $\|\psi_n\| = 1, (-i\nabla)\psi_n - k_0\psi_n \rightarrow 0$, the exponentially growing functions e^{ik_0x} with $k_0 \in \mathbb{C} \setminus \mathbb{R}$ cannot.

Most of the properties of bounded self-adjoint operators, such as the properties of the spectrum (Theorem 2.6) and the spectral theorem (Theorem 2.12), remain valid for unbounded self-adjoint operators. Functional calculus can also be extended to unbounded operators; in this case the domain of $f(A)$ is the set of ψ such that $\int_{\mathbb{R}} f(\lambda)|dQ(\lambda)\psi|^2 < \infty$.

Example 2.18 (Spectral resolution of the momentum operator). We have $-i\nabla = U^*kU$. Since furthermore by the extension to the unbounded case of Example 2.9 on the orthogonal resolution of the multiplication operator we have (always using the abuse of notation that k is the multiplication operator by the dependent variable)

$$k = \int_{\mathbb{R}} kdP(k) \quad (2.45)$$

with P defined in (2.22), we have

$$-i\nabla = \int_{\mathbb{R}} k d\tilde{P}(k), \quad (2.46)$$

with $\tilde{P}(E) = U^* P(E) U$. Explicitly,

$$\widehat{\tilde{P}(E)\phi}(k) = \mathbf{1}(k \in E) \widehat{\phi}(k) \quad (2.47)$$

$$(\tilde{P}(E)\phi)(x) = \frac{1}{2\pi} \int_{\mathbb{R}} \mathbf{1}(k \in E) e^{ikx} \left(\int_{\mathbb{R}} e^{-iky} \phi(y) dy \right) dk. \quad (2.48)$$

In differential form, this gives (again, purely formally)

$$(d\tilde{P}(k)\phi)(x) = \frac{1}{2\pi} e^{ikx} \left(\int_{\mathbb{R}} e^{-iky} \phi(y) dy \right) dk \quad (2.49)$$

$$d\tilde{P}(k) = \frac{1}{2\pi} |e^{ikx}\rangle \langle e^{ikx}| dk. \quad (2.50)$$

This can also be computed more directly: since the (distributional) inverse Fourier transform of the Dirac δ_k is $\frac{1}{\sqrt{2\pi}} e^{ikx}$, we have, formally,

$$-i\nabla = U^* k U = \int_{\mathbb{R}} k U^* |\delta_k\rangle \langle \delta_k| U dk = \int_{\mathbb{R}} k \frac{1}{2\pi} |e^{ikx}\rangle \langle e^{ikx}| dk. \quad (2.51)$$

Example 2.19 (Spectral resolution of the Laplacian). By the functional calculus, the Laplacian has orthogonal resolution $-\Delta = \int_{\mathbb{R}} k^2 d\tilde{P}(k)$ with the same \tilde{P} as above. The spectral resolution can be constructed as in (2.30). In this case, we can also compute explicitly

$$-\Delta = \int_{\mathbb{R}} k^2 \underbrace{\frac{1}{2\pi} |e^{ikx}\rangle \langle e^{ikx}|}_{d\tilde{P}(k)} dk = \int_{\mathbb{R}^+} \lambda \underbrace{\frac{1}{2\pi} \frac{1}{2\sqrt{\lambda}} \left(|e^{i\sqrt{\lambda}x}\rangle \langle e^{i\sqrt{\lambda}x}| + |e^{-i\sqrt{\lambda}x}\rangle \langle e^{-i\sqrt{\lambda}x}| \right)}_{dQ(\lambda)} d\lambda. \quad (2.52)$$

In higher dimensions, $dQ(\lambda)$ involves an integral of projections onto the plane waves of energy $k^2 = \lambda$.

2.6 Schrödinger operators $-\frac{1}{2}\Delta + V$

From the previous section it follows that, if V is a bounded function from \mathbb{R}^d to \mathbb{R} , then the operator $-\frac{1}{2}\Delta + V$ is self-adjoint on $L^2(\mathbb{R}^d)$ with domain $H^2(\mathbb{R}^d)$. The assumption of boundedness of V turns out to be too restrictive to accomodate some potentials of physical interest, such as the Coulomb potential $V(x) = -\frac{1}{|x|}$. In this type of cases, the following criterion is useful:

Theorem 2.20 (Rellich-Kato). Let A be a self-adjoint unbounded operator on its domain $D(A)$, and B be a symmetric unbounded operator with domain $D(A)$. B is said to be relatively bounded

by A with bound c if there is $C > 0$ such that

$$\|B\psi\| \leq c\|A\psi\| + C\|\psi\| \quad (2.53)$$

for all $\psi \in D(A)$. If B is relatively bounded with bound $c < 1$, then $A + B$ is self-adjoint with domain $D(A)$.

Example 2.21. The multiplication operator by x is relatively bounded by x^2 (because $|x| \leq (1+x^2)/2$), and the momentum operator $-i\nabla$ is relatively bounded by $-\Delta$ (because it reduces to x and x^2 through a Fourier transform).

Example 2.22. The multiplication operator by $V(x) = -1/|x|$ (Coulomb potential) is relatively bounded by $-\Delta$. Indeed, because this potential is locally in L^2 , we can write $V = V_1 + V_2$ where V_1 is bounded and V_2 is in L^2 with arbitrary small norm. Then, we have

$$\|V_2\psi\|_{L^2} \leq \|V_2\|_{L^2}\|\psi\|_{L^\infty} \leq C\|V_2\|_{L^2}\|\psi\|_{H^2} \leq C'\|V_2\|_{L^2}(\|\psi\|_{L^2} + \|\Delta\psi\|_{L^2})$$

To prove the Rellich-Kato theorem, it is useful to use the following self-adjointness criterion

Lemma 2.23. Let A be a symmetric unbounded operator. If there are two points z_\pm in the strict upper and lower complex plane respectively such that $z_\pm - A$ is invertible, then A is self-adjoint.

This criterion is weaker than the one used above, because it is sufficient to check invertibility of $z - A$ for only two values of z , not for all $z \in \mathbb{C}$; in particular, one can take z to be very large, which is often useful.

Proof. If $z - A$ is invertible, then we have $\|(z - A)^{-1}\| \leq 1/|\text{Im } z|$ (see the proof of Theorem 2.6). By the resolvent equality

$$w - A = (z - A) + (w - z) = (z - A)(1 + (w - z)(z - A)^{-1}) \quad (2.54)$$

it follows that $w - A$ is invertible for w in a disc of center z and radius $|\text{Im}(z)|$. The result follows. \square

We can then prove the Rellich-Kato theorem 2.20:

Proof of Theorem 2.20. We have for all $\mu \neq 0$

$$A + B + i\mu = (1 + B(A + i\mu)^{-1})(A + i\mu). \quad (2.55)$$

Now, for all $\psi \in \mathcal{H}$,

$$\|B(A + i\mu)^{-1}\psi\| \leq c\|A(A + i\mu)^{-1}\psi\| + C\|(A + i\mu)^{-1}\psi\| \leq \left(c + \frac{C}{\mu}\right)\|\psi\| \quad (2.56)$$

where we have used $\|(A + i\mu)^{-1}\| \leq 1/\mu$ (see (2.13)), and $\|A(A + i\mu)^{-1}\| \leq 1$ because of the inequality

$$\|(A + i\mu)\phi\|^2 = \|A\phi\|^2 + \mu^2\|\phi\|^2 \geq \|A\phi\|^2 \quad (2.57)$$

for all $\phi \in D(A)$. It follows that $A + B + i\mu$ is invertible for μ large enough. \square

This method is not sufficient to treat the case of other interesting operators like $-\frac{1}{2}\Delta + |x|^2$, or $-\frac{1}{2}\Delta + x$, which are not self-adjoint (or indeed, defined) with domain $H^2(\mathbb{R}^d)$. It is still possible to define such self-adjoint extensions, in the first case by the theory of Friedrichs extensions, in the second by a time-dependent method.

2.7 The Schrödinger equation

Consider now the Schrödinger equation

$$i\partial_t\psi = H\psi, \quad \psi(0) = \psi_0, \quad (2.58)$$

where H is a (potentially unbounded) self-adjoint operator. When H is bounded, one can use the standard Cauchy-Lipschitz theorem (which is valid in any Banach space), or even simply define the operator e^{-iHt} by means of its power series, and check that $e^{-iHt}\psi_0$ is the unique solution. When H is unbounded, the well-posedness of this equation is by no means obvious; for instance recall that the backwards heat equation $\partial_t u = -\Delta u$ is not well-posed in general. However, the Schrödinger equation is always well-posed:

Theorem 2.24. The equation (2.58) with $\psi_0 \in D(H)$ admits a unique strong solution (i.e. a continuously differentiable mapping $t \mapsto \psi(t)$ satisfying (2.58)) given by

$$\psi(t) = e^{-iHt}\psi_0, \quad (2.59)$$

where e^{-iHt} is defined by the functional calculus¹⁴.

The proof depends on the fact that the **propagator** $U(t) = e^{-iHt}$ maps the domain $D(H)$ to itself (which would not be the case for the backwards heat equation). It is also unitary: $U(t)^* = U(t)^{-1}$ and so $\|\psi(t)\| = \|\psi_0\|^{15}$.

This gives even more motivation for the notion of self-adjointness, as opposed to merely symmetry. For instance, the Laplacian with domain $H^2((0, 1))$ violates uniqueness, while the Laplacian with domain $C_c^\infty((0, 1))$ violates existence. There is even a converse of sorts to this theorem:

Theorem 2.25 (Stone). If U is a strongly continuous unitary group (i.e. a mapping from \mathbb{R} to the unitary operators on \mathcal{H} , such that $U(t+s) = U(t)U(s)$ for all $t, s \in \mathbb{R}$, and such that, for all $\psi \in \mathcal{H}$, $t \mapsto U(t)\psi$ is continuous), then there is a self-adjoint operator H such that $U(t) = e^{-iHt}$.

¹⁴When $\psi_0 \in \mathcal{H}$ but is not in $D(H)$, then $\psi(t) = e^{-iHt}\psi_0$ still makes sense, because e^{-iHt} is a bounded operator which can be defined on the whole of \mathcal{H} . In this case, $\psi(t)$ is the unique weak solution, i.e. the only solution of $i\frac{d}{dt}\langle\phi|\psi\rangle = \langle H\phi|\psi\rangle$ for all $\phi \in D(H)$.

¹⁵Note that unitarity was already formally obtained in Section (1) using the Ehrenfest theorem

Rough sketch of proof. Formally,

$$H\psi = \lim_{t \rightarrow 0^+} \frac{U(t) - 1}{-it} \psi. \quad (2.60)$$

We define $D(H)$ as the domain on which the expression above makes sense. This is dense because it contains all the $\int_{\mathbb{R}} \psi(t)U(t)dt$ for $f \in \mathbb{C}_c^\infty(\mathbb{R})$. The operator H defined on $D(H)$ is symmetric. By Lemma 2.23, it is self-adjoint since $\frac{1}{z-H}$ can be computed from the propagator U (for instance, when $\text{Im}(z) > 0$, $\frac{1}{z-H} = -i \int_0^\infty U(t)e^{izt}dt$). \square

2.8 Bound states

Eigenvectors, i.e. solutions of the **time-independent Schrödinger equation**

$$H\psi = \lambda\psi \quad (2.61)$$

in $D(H)$ have the time evolution $e^{-i\lambda t}\psi$: as we will see, these are stationary states (their physical properties are unchanged, even though the wavefunction itself is time-dependent). In quantum mechanics, they are called **bound states**, the term “bound” referring to the fact that they stay in a localized region of space (in contrast to the “scattering states”, which we termed “almost eigenvectors” above, like plane waves, that are not localized).

Where are the bound states of an operator of the form $-\frac{1}{2}\Delta + V$? When V tends to zero at infinity, it is often possible to show that the continuous spectrum of $-\frac{1}{2}\Delta + V$ stays \mathbb{R}^{+} ¹⁶; however, the presence of the potential can create **bound states** (negative eigenvalues).



Typical spectrum of a Schrödinger operator $-\Delta + V$ with V localized,
with discrete negative and continuous positive spectrum.

In order to make this precise it is useful to state

Theorem 2.26 (Variational principle, Courant-Fischer min-max formula). Let H be a self-adjoint operator. Then,

$$\inf \sigma(H) = \inf_{\psi \in D(H)} \frac{\langle \psi | H \psi \rangle}{\langle \psi | \psi \rangle}. \quad (2.62)$$

¹⁶This is not trivial, and we very briefly sketch the ideas of the proof. First, if V tends to zero at infinity, then $V(-\Delta + 1)^{-1}$ is a compact operator (because its integral kernel is proportional to $V(x) \frac{e^{-|x-y|}}{|x-y|}$, a continuous, localized function of two variables, and well-behaved integral operators are compact). Now take a sequence ψ_n of norm 1 that satisfies $(-\Delta - \lambda)\psi_n \rightarrow 0$ for $\lambda > 0$. It turns out that such a sequence converges weakly to zero. Then, we have $(-\Delta + V - \lambda)\psi_n = (-\Delta - \lambda + V(-\Delta - 1)^{-1}(-\Delta - \lambda + 1 - \lambda))\psi_n \rightarrow 0$, so that $R^+ \subset \sigma(H)$. More detailed statements follow from the notion of the essential spectrum (a refinement of the notion of continuous spectrum), see [1, section 5.4], and the absence of embedded eigenvalues in the continuous spectrum (a more delicate issue, which requires a stronger decay of V to establish).

If λ_1 is the smallest eigenvalue below any continuous spectrum, then this infimum is attained at an eigenvector associated with λ_1 . If furthermore the lowest N eigenvalues (counted with multiplicity) are below any continuous spectrum, then

$$\lambda_N = \min_{E \subset \mathcal{H}, \dim(E)=N} \max_{\psi \in E} \frac{\langle \psi | H \psi \rangle}{\langle \psi | \psi \rangle}. \quad (2.63)$$

where the min is taken over all vector subspaces of \mathcal{H} .

Example 2.27. Consider the operator $H_\mu = -\frac{1}{2}\Delta + \mu V$ on $L^2(\mathbb{R})$, where V is a fixed non-positive, continuous and decaying to zero function. Then, if ψ is any localized state (for instance, a Gaussian),

$$\frac{\langle \psi | H_\mu \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\frac{1}{2} \int_{\mathbb{R}} |\psi'(x)|^2 dx + \int_{\mathbb{R}} V(x) |\psi(x)|^2 dx}{\int_{\mathbb{R}} |\psi(x)|^2 dx} = A + \mu B \quad (2.64)$$

with $B < 0$. This shows that sufficiently attractive potentials create bound states.

Generically, an operator of the form $-\frac{1}{2}\Delta + V$ with V smooth and decaying to zero will have a continuous spectrum \mathbb{R}^+ , and possibly negative bound states. The ground state (lowest bound state) is obtained by minimizing the competition between the kinetic energy term $\frac{1}{2} \int_{\mathbb{R}} |\psi'(x)|^2 dx$ (which tends to make ψ as delocalized as possible) and the potential energy $\int_{\mathbb{R}} V(x) |\psi(x)|^2 dx$ (which tends to make ψ concentrated on the minima of V).

2.9 Exercises

- Let $A : \ell^2(\mathbb{Z}) \rightarrow \ell^2(\mathbb{Z})$ be given by

$$(Au)_n = u_{n+1} + u_{n-1}. \quad (2.65)$$

Show that A is bounded and self-adjoint. Show that there are no eigenvectors in $\ell^2(\mathbb{Z})$. By exhibiting “almost eigenvectors” of the form e^{ikn} , show that $[-2, 2]$ belongs to the spectrum of A . Using an appropriate form of the Fourier transform, show that $A - \lambda$ is invertible when $\lambda \notin [-2, 2]$. Conclude.

Summary

The spectrum of bounded self-adjoint infinite-dimensional operator can contain both point spectrum (eigenvalues) and continuous spectrum (“almost-eigenvalues” formally associated with eigenvectors not in \mathcal{H} , but which can be approximated by elements of \mathcal{H}). The spectral theorem generalizes to self-adjoint operators, and gives a decomposition on a (possibly continuous) set of eigenspaces, formalized by the notion of projector-valued measures. This allows for a definition of the functional calculus (functions of operators), and in particular solve the Schrödinger equation. In the unbounded case, care has to be taken to select an appropriate domain (often corresponding to boundary conditions) to ensure self-adjointness; once this is done, much of the theory of bounded operators carries through.

3 Postulates of quantum mechanics

We now discuss the general postulates describing an isolated quantum system, generalizing from the special case of a single particle seen in Section 1, and using the language of spectral theory developed in Section 2. In our examples we focus on single-body quantum systems; there is an additional postulate for many-body systems, which we will explore in Section 9.

3.1 Quantum states

We first define quantum states, or **pure states**¹⁷:

Postulate 1: The state of a system is completely determined by its wavefunction ψ , a normalized element ($\|\psi\| = 1$) of a separable¹⁸ complex Hilbert space \mathcal{H} . Two wavefunctions differing only by a phase factor (i.e. $\psi' = e^{i\theta}\psi$ with $\theta \in \mathbb{R}$) represent the same quantum state.

Technically, this makes quantum states *rays*, elements of the complex projective Hilbert space (the quotient space of \mathcal{H} by the equivalence relation that $\psi \sim \phi$ if $\psi = \alpha\phi$ for some $\alpha \in \mathbb{C}$).

Example 3.1. The simplest nontrivial Hilbert space is \mathbb{C}^2 (there is only one physical state in the Hilbert space \mathbb{C}). There are four degrees of freedom in \mathbb{C}^2 , but the normalization constraint and the phase equivalence remove one each, and therefore the Hilbert space \mathbb{C}^2 has only two physical degrees of freedom. The explicit representation $(\cos(\theta/2), e^{i\phi} \sin(\theta/2))$ with $\theta \in [0, 2\pi]$, $\phi \in [0, \pi]$ (fixing the phase degree of freedom by imposing that the first component is real and positive) identifies it topologically as a sphere, the “Bloch sphere”. This models **qubits**, the basic object of quantum information and an effective model of many physical phenomena. In particular, an electron’s spin (as we will see later) can be modeled as a qubit.

The Hilbert space corresponding to a particle moving in d -dimensional space is $L^2(\mathbb{R}^d, \mathbb{C})$. Another example is that of an electron jumping from site to site in a d -dimensional lattice, modeled by the Hilbert space $\ell^2(\mathbb{Z}^d, \mathbb{C})$.

3.2 Observables

Postulate 2: To each physical observable a there corresponds a (possibly unbounded) self-adjoint operator A on \mathcal{H} . When the physical quantity a is measured in the state ψ , the result is a random variable, defined by

$$\mathbb{P}(\text{value of } a \text{ in state } \psi \in E) = \|Q_A(E)\psi\|^2 \quad (3.1)$$

for each Borel set E , where $Q_A(E)$ is the spectral projection-valued measure defined by the spectral theorem. After a measurement, the state of the system is $\psi = Q_A(E)\psi/\|Q_A(E)\psi\|$.

¹⁷A more general formulation of quantum mechanics also allows for *mixed states*, which are statistical mixtures of the above pure states; this is useful for statistical quantum mechanics, and for describing open systems. We will not discuss mixed states in these notes.

¹⁸Recall that a Hilbert space is separable if it has a countable Hilbert basis (an orthonormal basis which span a dense subset of the Hilbert space). All commonly encountered Hilbert spaces (such as $\ell^2(\mathbb{Z})$ or $L^2(\mathbb{R}^d)$) are separable.

Remember that if the Hilbert space is finite-dimensional and if A has orthonormal eigenvectors v_n and eigenvalues λ_n , then $Q_A(E) = \sum_{\lambda_n \in E} |v_n\rangle\langle v_n|$. In particular, the result of the measurement is necessarily an element of the spectrum, and the probability of a particular result λ_n is $|\langle v_n|\psi\rangle|^2$ (assuming a simple eigenvalue). Another useful result is that the expectation value is

$$\mathbb{E}(\text{value of } a \text{ in state } \psi) = \sum_n \lambda_n |\langle v_n|\psi\rangle|^2 = \langle \psi | A \psi \rangle \quad (3.2)$$

Moments of the probability distribution can be found from similar expressions; for instance,

$$\text{Var}(\text{value of } a \text{ in state } \psi) = \langle \psi | A^2 \psi \rangle - \langle \psi | A \psi \rangle^2 \quad (3.3)$$

This is a very unintuitive postulate, and contains much of the complexity of quantum mechanics. It has for instance the following consequences

- The result of a measure is random, and cannot be predicted from the knowledge of ψ alone. However, its probability distribution is completely determined by ψ .
- Measuring a system changes its state.
- Measuring a quantity a then a again immediately afterwards gives the same result the second time. However, measuring a quantity a , then a quantity b , then a again does *not* necessarily give the same result for a the second time (since Q_A and Q_B do not necessarily commute).
- For some physically continuous observables (such as the energy), the result of a measure can be discrete (the consequence that gave its name to *quantum* mechanics).

It is not very clear what “measure” means in general, and this gives rise to various philosophical paradoxes. We adopt a “shut up and calculate” approach, and the meaning of measurement has to be discussed on a case by case basis.

Example 3.2. Consider the spin of an electron, modeled by the qubit state space \mathbb{C}^2 . Physically, this is an internal degree of freedom, identified with an intrinsic angular momentum (the electron is “spinning on itself”). The classical observables are the angular momentum on an axis $\omega = (\omega_1, \omega_2, \omega_3)$. The corresponding quantum observable is

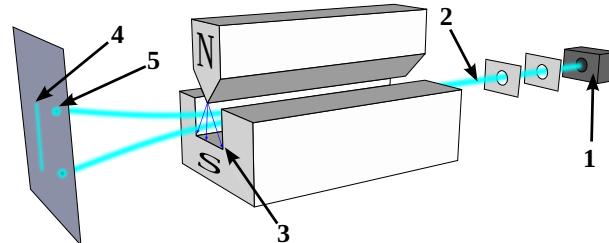
$$S = \omega \cdot \sigma = \sum_{i=1}^3 \omega_i \sigma_i, \quad (3.4)$$

with the Pauli matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (3.5)$$

(physically, electrons have spin 1/2 and there is an extra factor 1/2, which we ignore here).

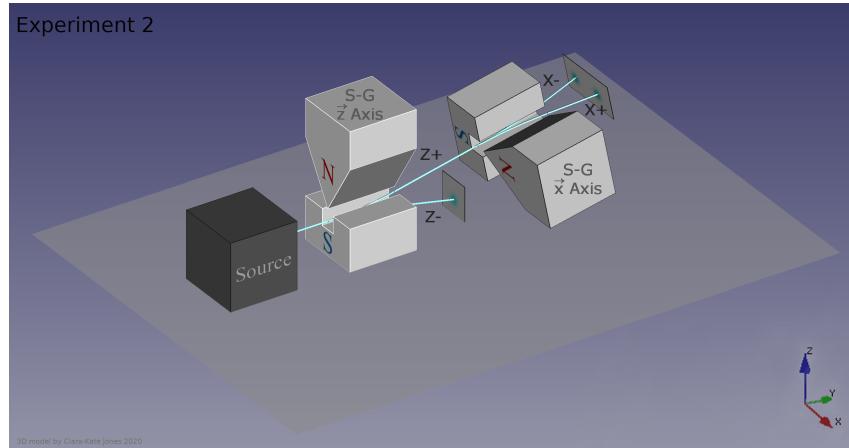
“Measuring” the spin of an electron can be done for instance in the Stern-Gerlach experiment.



In this experiment¹⁹ one produces a beam of electrons (2), a priori with no specific spin orientation. Then one makes them go through a magnet that produces an inhomogeneous magnetic field in the z direction (3). This field deflects electrons upwards if they have positive angular momentum in the direction z , and downwards if they have negative angular momentum. The electrons are collected on a screen (5), where they are observed to only arrive at two specific locations. See <https://toutestquantique.fr/en/spin/> for an animation.

Let us suppose that the system is in the state (a, b) , with $|a|^2 + |b|^2 = 1$, and measure the orientation along the z axis, corresponding to the observable σ_3 . This matrix has orthonormal eigenvectors $v_1 = (1, 0)$ with eigenvalue $\lambda_1 = 1$, and $v_2 = (0, 1)$ with eigenvalue $\lambda_2 = -1$, so that $P_{\sigma_3}(E) = \sum_{\lambda_n \in E} |v_n\rangle\langle v_n|$. The result of the measure is therefore 1 with probability $\|v_1\rangle\langle v_1|\psi\|^2 = |\langle v_1|\psi\rangle|^2 = |a|^2$, and -1 with probability $|b|^2$. Counterintuitively, the angular momentum along the z axis (and in fact along any axis) can only take the value ± 1 .

The state $(1, 0)$ has angular momentum in the z direction equal to 1. For $(0, 1)$ it is -1 . For $\frac{1}{\sqrt{2}}$ it is 1 or -1 with probability $1/2$ each; this is not known until measured. However, once measured, the system is in the state $(a/|a|, 0)$ (if 1 was measured) or $(0, b/|b|)$ (if -1 was). Now, measure immediately after the angular momentum along the x axis. A similar computation (the diagonalization of σ_1) shows that the result is $+1$ exactly half the time, and -1 half the time, whatever a and b , and whatever the result of the first measure of σ_3 . Making a measurement along the z axis made the state maximally indeterminate along the x axis.



This can be observed by combining two sequential Stern-Gerlach experiments oriented differently.

Example 3.3. A particle moving in d -dimensional space is modeled by the Hilbert space $\mathcal{H} = L^2(\mathbb{R}^d, \mathbb{C})$, and the observable corresponding to its position is the vector of operators $x = (x_1, \dots, x_d)$. For instance, in one dimension, the probability that the particle is found in the Borel set E is

$$\mathbb{P}(\text{value of } x \text{ in state } \psi \in E) = \|Q_x(E)\psi\|^2 = \int_E |\psi(x)|^2, \quad (3.6)$$

¹⁹Pictures from the Wikipedia page on the Stern-Gerlach experiment.

where we have used the expression of $Q_x(E)$ derived in Example 2.10. We recover the interpretation of $|\psi(x)|^2$ as a probability density. Similarly, with $p = -i\nabla$ the momentum operator introduced before, the probability density of finding the particle at momentum k is $|\hat{\psi}(k)|^2$ (see Example 2.18).

To obtain the operator corresponding to general functions of phase space $a(x, p)$, one uses the ‘‘correspondence principle’’ (or ‘‘quantization’’), which replaces occurrences of the position and momentum variables by the corresponding operators. For instance, the classical energy $E(x, p) = \frac{1}{2}|p|^2 + V(x)$ (a function on phase space $\mathbb{R}^{2d} \rightarrow \mathbb{R}$) becomes the quantum Hamiltonian $H = \frac{1}{2}|p|^2 + V$ (a self-adjoint operator on $L^2(\mathbb{R}^d)$), where $p = -i\nabla$ and V is interpreted as a multiplication operator. Note that this correspondence is ambiguous in general: for instance, since the operators x and $-i\nabla$ do not commute, what is the operator corresponding to the physical operator $x \cdot p$? Fortunately, for most observables of physical interest, this is not an issue²⁰. For instance, in three dimensions the angular momentum in the z direction is $xp_y - yp_x$ in classical mechanics, and becomes

$$L_z = x(-i\partial_y) - y(-i\partial_x), \quad (3.7)$$

with similar expressions for L_x and L_y . Since x and $-i\partial_y$ commute, there is no ambiguity in defining this expression.

One of the most famous consequences of this postulate is the uncertainty principle:

Proposition 3.4 (Heisenberg uncertainty principle). Let A and B be two bounded self-adjoint operators and $\psi \in \mathcal{H}$ with norm 1, then

$$\text{Var}(\text{value of } A \text{ in state } \psi) \text{Var}(\text{value of } B \text{ in state } \psi) \geq \frac{1}{4}\langle\psi|i[A, B]\psi\rangle^2 \quad (3.8)$$

Proof. Using the fact that scalars commute with all operators,

$$\langle\psi|i[A, B]\psi\rangle = \left\langle\psi|i\left[A - \langle\psi|A\psi\rangle, B - \langle\psi|B\psi\rangle\right]\psi\right\rangle \quad (3.9)$$

$$= -2\text{Im}\left\langle(A - \langle\psi|A\psi\rangle)\psi\middle|(B - \langle\psi|B\psi\rangle)\psi\right\rangle \quad (3.10)$$

and the result follows by the Cauchy-Schwarz inequality. \square

This extends to unbounded operators, but the statement is more complicated because of domain issues.

Example 3.5. We computed in chapter 1 that, for a particle on the line, $[x, p] = i$, so that the product of the uncertainties in the measurement of x and p can never be smaller than $1/2$. Explicitly:

$$\text{Var}(|\psi|^2)\text{Var}(|\hat{\psi}|^2) \geq \frac{1}{4}, \quad (3.11)$$

²⁰There are various ‘‘quantization rules’’, such as the Weyl quantization, which map functions of phase space to self-adjoint operators; all these rules coincide in the classical limit $\hbar \rightarrow 0$.

where $\text{Var}(\rho) = \int_{\mathbb{R}} (x - (\int_{\mathbb{R}} x \rho(x) dx))^2 \rho(x) dx$ is the variance of a probability density. This is a quantitative version of the qualitative observation in Fourier theory that the more a function is concentrated in real space, the more its Fourier transform is delocalized, and vice versa.

3.3 Time evolution

Postulate 3: If a system is at time $t = 0$ in state ψ_0 , then its time evolution is given by the Schrödinger equation

$$i\partial_t \psi = H\psi, \quad (3.12)$$

where the Hamiltonian H is the self-adjoint operator corresponding to the total energy.

If the system is under the influence of a time-dependent forcing (for instance, an external force or magnetic field), the Schrödinger equation becomes $i\partial_t \psi = H(t)\psi$ with a time-dependent Hamiltonian $H(t)$.

Besides the example of the free propagation of a particle seen previously, it is instructive to consider finite-dimensional systems:

Example 3.6. Consider a qubit ($\mathcal{H} = \mathbb{C}^2$) with Hamiltonian

$$H = \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \quad (3.13)$$

The eigenvalues are $\lambda_{\pm} = \pm 1$, with eigenvectors $v_{\pm} = \frac{1}{\sqrt{2}}(1, \pm 1)$. The time evolution is given by

$$e^{-itH} = \sum_{\sigma \in \{+, -\}} e^{-it\lambda_{\sigma}} |v_{\sigma}\rangle \langle v_{\sigma}| \quad (3.14)$$

If for instance $\psi_0 = (1, 0)$, then $\psi(t) = (e^{-it}(1, 1) + e^{it}(1, -1))/2 = (\cos t, -\sin(t))$. The probability of measuring +1 with the observable $\sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ is $\cos(t)$.

Example 3.7. Consider a particle in a potential V which decays at infinity, such as for instance a potential well $V(x) = -E$ for $x \in [-L, L]$, 0 otherwise. Consider a classical particle in such a potential, started inside the well with an initial velocity $v > 0$. The classical motion is easily obtained from conservation of energy: if $v^2/2 > E$, the particle goes through the barrier and then moves at constant speed $2\sqrt{v^2/2 - E}$. If not, it bounces back and forth between the walls at $\pm L$. Quantum mechanically, as we have seen in Example 2.27, the operator $H = -\frac{1}{2}\Delta + V$ has continuous spectrum \mathbb{R}^+ , plus possibly bound states with negative energy. The bound states correspond to the particle bouncing back and forth inside the well (but, since the bound states are not compactly supported, spilling outside the well as well). The continuous spectrum supports the propagation of waves corresponding to particles moving outside the well.

Summary

Each isolated quantum system is modeled by a complex Hilbert space, with states being normalized elements of this space, defined up to a phase. Observables are represented by self-adjoint operators on this Hilbert space, with the spectral theorem providing the probability distribution of measurements; Heisenberg uncertainty relations are obtained as a corollary. There is a particular operator, the Hamiltonian, that determines the dynamics through the Schrödinger equations. Apart from the particle seen in Section 1, an important example is the qubit, modeled by state space \mathbb{C}^2 .

4 Symmetries

4.1 Symmetries of a quantum system

In general, solving either the time-dependent or time-independent Schrödinger equation is a hard problem. In certain cases, it is possible to find explicit solutions, or reductions to simpler problems. This is usually because of underlying physical symmetries. In general, the systematic use of symmetries is a fundamental tool in theoretical physics. For our purposes, a **symmetry** of a system in a transformation of the state space of a quantum system that leaves its dynamics and properties invariant²¹. It is one of the fundamental results of quantum mechanics (Wigner's theorem) that any symmetry (defined in a precise sense) s can be represented by a unitary (or anti-unitary, but we will not consider that case here) operator $U_s : \mathcal{H} \rightarrow \mathcal{H}$.

Symmetries have a group structure: the identity is a symmetry, symmetries can be reversed, and the composition of two symmetries is again a symmetry. This group structure is simply implemented by the group structure of unitary operators (if s and s' are two symmetries, then $U_{sos'} = U_s U_{s'}$). If U is a symmetry of a time-independent system with Hamiltonian H and if the symmetry leaves the dynamics invariant, then

$$e^{-itH} U \psi_0 = U e^{-itH} \psi_0$$

for all states ψ_0 (we will omit considerations about unbounded operators in this section for simplicity, but this creates no additional difficulty). Differentiating this equality at $t = 0$, we get

$$[H, U] = 0.$$

In the case of a point particle (state space $\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C})$), a spatial symmetry is an affine transformation of space $x \mapsto R(x) = Ax + b$ with A an orthogonal matrix, represented by the unitary

$$(U\psi)(x) = \psi(R^{-1}(x))$$

If the particle evolves in a potential V , then we can check from the commutation relation that R is a symmetry of the system if $V(x) = V(R(x))$ for all x .

Examples include

- Translations in space (example: free particle with zero potential), represented by \mathbb{R}^3
- Rotations around a center (example: the hydrogen atom), represented by $\text{SO}(3)$
- Rotations around one axis (example: the H_2 molecule), represented by $\text{SO}(2) = S(1)$
- Translations along vectors with integer coordinates (example: an electron in a crystal), represented by \mathbb{Z}^3
- Reflection by a plane (example: the H_2O molecule), represented by $\{1, -1\}$

Symmetries can be *continuous* (depend on continuous parameters, as in the first two examples) or *discrete* (as in the last two examples).

²¹There is one important symmetry, the time invariance symmetry, which is not a transformation of the state space but rather encoded in the equations of motion, and is not part of our discussion here. In more advanced relativistic theories, time and space symmetries are treated on an equal footing.

4.2 Discrete symmetries

Recall that two operators that commute preserve each other's invariant subspaces: if $[H, U] = 0$ and μ is an eigenvalue of U with eigenspace E , then, for all $\psi \in E$, $UH\psi = HU\psi = \mu H\psi$, so that $H\psi \in E$. Furthermore, if H is self-adjoint, for all $\psi \in E^\perp, \phi \in E$, $\langle \phi, H\psi \rangle = \langle H\phi, \psi \rangle = 0$. What this means is that, in the decomposition $\mathcal{H} = E \oplus E^\perp$,

$$H = \begin{pmatrix} H_{EE} & 0 \\ 0 & H_{E^\perp E^\perp} \end{pmatrix}$$

with $H_{EE} : E \rightarrow E$, $H_{E^\perp E^\perp} : E^\perp \rightarrow E^\perp$. To solve the eigenproblem for H , we therefore only need to solve the eigenproblem for H_{EE} and $H_{E^\perp E^\perp}$, which are of reduced size and therefore easier to solve.

As an example, consider the operator $H = -\frac{1}{2}\Delta + V$, with V even. Clearly, this operator is invariant by the parity symmetry $(U\psi)(x) = \psi(-x)$. The operator U has two eigenspaces: the even functions (eigenvalue 1) and the odd (eigenvalue -1). Therefore, we can look for eigenvectors as being either even or odd, which simplifies the resolution²².

When there are multiple symmetries that commute between themselves, one can restrict H to common eigenspaces of all the symmetries. The larger the symmetry group, the smaller the blocks of H , and the simpler their resolution. When symmetries do not commute, this process is not straightforward, and relies on the possible representations of the group. Representation theory is therefore an important tool to understand the properties (in particular, spectroscopic properties) of molecules.

4.3 Continuous symmetries

Continuous symmetries such as translations (\mathbb{R}^3) or rotations ($SO(3)$) form a **Lie group**: a group that also has a compatible continuous structure (a manifold). Lie groups are often better studied through their Lie algebra, the tangent space at the identity of the Lie group. Here, assume that there is a smooth family $U(\alpha), \alpha \in \mathbb{R}$ of symmetries, with $U(0) = 1$. Then, we can differentiate the equality $[H, U(\alpha)] = 0$ at $\alpha = 0$ and obtain

$$[H, G] = 0,$$

where

$$G = i \frac{dU}{d\alpha}(0)$$

The factor of i is chosen so that G is self-adjoint²³; indeed, differentiating $U(\alpha)^*U(\alpha) = 1$, we get $G^* = G$. The operator G is called the **generator** of the symmetry group, because if $U(\alpha)$ respects the group structure, $U(\alpha + \beta) = U(\alpha)U(\beta)$, it can be checked that $U(\alpha) = e^{-i\alpha G}$. When the group is indexed by several parameters, there are different generators for each direction.

²²This is not to say that *every* eigenvector is either even or odd; if ψ_1 even and ψ_2 odd both happen to be eigenvectors of H with the *same* eigenvalue, then $\psi_1 + \psi_2$ is also an eigenvector of H which is neither even nor odd.

²³If $U(\alpha)$ is C^1 in the topology of bounded operators, then G is well-defined and bounded. It turns out that this is too restrictive to discuss most interesting examples where G is unbounded, so one has to be more careful here, but we keep the discussion at a formal level.

Since G is self-adjoint, it corresponds to an observable. The relation $[H, G] = 0$, together with the Ehrenfest theorem, means that $\langle \psi(t) | G | \psi(t) \rangle$ is constant in time. This is the powerful and very general **Noether's theorem**: to each continuous symmetry there corresponds a conserved quantity²⁴.

4.4 Translations

Consider translations along an axis e , $(U(\alpha)\psi)(x) = \psi(x - \alpha e)$. The generator is

$$T_e = -i \sum_{j=1}^3 e_j \partial_j = p \cdot e,$$

where we recognize the **momentum** operator $p = -i\nabla$. This simply says that in translation-invariant systems, momentum is preserved (first Newton law: with no external force, speed is constant).

We can apply the same philosophy as before to diagonalize H ²⁵. As we saw before, the momentum operator (in 1D, for simplicity) has spectrum \mathbb{R} , with generalized eigenbasis given by the plane waves e^{ikx} . Furthermore, each plane wave e^{ikx} has its own eigenvalue k . Therefore, He^{ikx} must be proportional to e^{ikx} , say $He^{ikx} = \hat{f}(k)e^{ikx}$. This means that $\widehat{H\psi}(k) = \hat{f}(k)\widehat{\psi}(k)$: H is diagonalized by the Fourier transform. The symmetry group is so rich that the blocks of H are of size 1, and do not need further diagonalization²⁶.

Example of translation-invariant operators include differential operators with constant coefficients (such as $H = -\frac{1}{2}\Delta$, the Hamiltonian of a free particle) and convolutions, which are indeed diagonalized by the Fourier transform²⁷.

4.5 Rotations

Consider first the two-dimensional case. In polar coordinates, rotations are given by

$$(U(\alpha)\psi)(r, \theta) = \psi(r, \theta - \alpha)$$

Their generator is therefore

$$L = -i\partial_\theta = -i(x\partial_y - y\partial_x) = x \times p$$

²⁴This also holds in classical mechanics, following essentially the same process with Poisson brackets instead of commutators.

²⁵The mathematical justification is more involved because these are not eigenvectors but generalized eigenvectors, but typically in these matters it is simplest to not worry and do things formally, and find ad-hoc ways to prove the desired result once it is known.

²⁶By contrast, if we take the less rich group of translations by integers \mathbb{Z}^d , one can check that the common eigenspaces are Bloch waves $e^{ikx}u(x)$ with u \mathbb{Z}^d -periodic: this is still an infinite-dimensional space, but much smaller than the full space.

²⁷Formally, *all* reasonable translation-invariant operators on $L^2(\mathbb{R}^d)$, including differential operators, are convolutions, in a generalized sense. Indeed, by the Schwartz kernel theorem, any reasonable operator (continuous from test functions to distributions) can be written formally as $(A\psi)(x) = \int A(x, y)\psi(y)dy$, where $A(x, y)$ is a distribution over $(\mathbb{R}^d)^2$ and the integral is taken in the sense of distributions. For instance, $A\psi = \psi'$ is given by the kernel $A(x, y) = \delta'(x - y)$. A being translation invariant means that $A(x, y) = f(x - y)$ for some f , therefore a convolution.

In classical mechanics, $L = x \times p = x_1 p_2 - x_2 p_1$ is the **angular momentum**: a rotationally-invariant system has constant angular momentum.

The eigenstates of the angular momentum operator satisfy $-i\partial_\theta\psi = \mu\phi$, so are of the form $\psi(r, \theta) = f(r)e^{i\mu\phi}$. Clearly, μ has to be an integer, so the spectrum of $x \times p$ is \mathbb{Z} .

For instance, if $H = -\frac{1}{2}\Delta + V$ with V a radial function, this means that we can seek eigenvectors in the form above. Plugging back into the equation, the function f then satisfies

$$-\frac{1}{2} \left(f'' + \frac{1}{r} f' + \frac{\mu^2}{r^2} f \right) = \lambda f$$

Therefore, one has just to solve for this one-dimensional equation for all values of $\mu \in \mathbb{Z}$ to get the full spectrum of H .

In the 3-dimensional case, things are more complicated, because the group $\text{SO}(3)$ is not commutative. This means that the generators of rotations along the 3 dimensions

$$L_j = (x \times p)_j$$

(this notation means that for instance $L_3 = x_1 p_2 - x_2 p_1$) do not commute between themselves and do not admit a common basis of eigenstates. The usual way out is to diagonalize the operators $L^2 = \sum_{j=1}^3 L_j^2$ and L_3 , which turn out to commute, resulting in a basis of common eigenstates $f(r)Y_{\ell m}$, $\ell = 0, 1, \dots, m = -\ell, \dots, \ell$ satisfying

$$L^2 f(r)Y_{\ell m} = \ell(\ell+1)f(r)Y_{\ell m}, \quad L_3 f(r)Y_{\ell m} = m f(r)Y_{\ell m}$$

The resolution of the time-dependent Schrödinger then boils down to a one-dimensional equation for f , for each ℓ, m (see Section 1.7).

Finally, note that the commutativity properties of the Lie group imply some properties of the generators, *irrespective of their representation*. For instance, it can be shown in all generality that, if L is the generator of *any* representation of the rotations (not necessarily on $L^2(\mathbb{R}^3, \mathbb{C})$), then $L \times L = iL$ (e.g. $L_1 L_2 - L_2 L_1 = iL_3$, etc), which turns out implies very rigid constraints on the spectrum of L . This is important for the discussion of more general types of operators of angular momentum type, such as spin.

Summary

Spatial symmetries act on the Hilbert space of a quantum system as unitary transformations. They allow for a reduction in complexity by reducing the time-independent Schrödinger equation to one on a smaller subspace of \mathcal{H} . Continuous symmetries give rise to conserved quantities through their generator, with the momentum being the generator of translations and angular momentum the generator of rotations.

5 Numerical simulation of the time-dependent Schrödinger equation

In this section, we will consider the following problem: solve the Schrödinger equation

$$i\partial_t\psi = -\frac{1}{2}\partial_{xx}\psi + V(x)\psi, \quad \psi(x, 0) = \psi_0(x) \quad (5.1)$$

on the real line. In this section we will assume that V and ψ_0 are 2π -periodic, so that ψ stays periodic for all times (exercise). This problem is a prototype of more involved problems in numerical quantum mechanics, and displays a number of interesting features. Equation (5.1) can be thought of as a truncated version of the same equation posed on the whole space. Some applications, such as the modeling of crystals, also yield Schrödinger equations that are directly periodic. We present here the one-dimensional case, but the extension of the theory to multiple dimensions is immediate.

Many methods can be used to discretize and solve numerically (5.1). We will focus here on the (pseudo)spectral Fourier method in space, and a splitting technique in time, which are particularly well-suited to this type of problems.

5.1 Smoothness

We first study the smoothness of the solution of (5.1). We will quantify it using the Sobolev space

$$H_{\text{per}}^s = \{\psi \in H_{\text{loc}}^s, \psi \text{ is } 2\pi\text{-periodic}\}. \quad (5.2)$$

with natural norm

$$\|\psi\|_{H_{\text{per}}^s}^2 = \sum_{k=0}^s \int_0^{2\pi} |\psi^{(k)}(x)|^2 dx \quad (5.3)$$

and associated inner product. We will use the Fourier conventions

$$c_n(\psi) = \langle e_n | \psi \rangle = \frac{1}{\sqrt{2\pi}} \int_0^{2\pi} \psi(x) e^{-inx} dx \quad (5.4)$$

$$\psi(x) = \sum_{n \in \mathbb{Z}} c_n(\psi) e_n(x) = \frac{1}{\sqrt{2\pi}} \sum_{n \in \mathbb{Z}} c_n(\psi) e^{inx} \quad (5.5)$$

with

$$e_n(x) = \frac{1}{\sqrt{2\pi}} e^{inx} \quad (5.6)$$

the orthonormal Fourier modes, a Hilbert basis of $L^2((0, 2\pi), \mathbb{C})$.

From $c_n(\psi') = -inc_n(\psi)$ and the Parseval theorem it follows that

$$\|\psi\|_{H_{\text{per}}^s}^2 \simeq \sum_{n \in \mathbb{Z}} (1 + n^2)^s |c_n(\psi)|^2 \quad (5.7)$$

where \simeq means that both expressions define equivalent norms.

From the results in Section 2 it follows that, if $V(x)$ is continuous, $H = -\frac{1}{2}\partial_{xx} + V$ is self-adjoint on L^2_{per} with domain H^2_{per} . The equation (5.1) therefore has a unique solution $\psi(t)$ in H^2_{per} for $\psi_0 \in H^2_{\text{per}}$, given by $e^{-iHt}\psi_0$. More regularity can be obtained if V is smooth. To show this, we

will use the Duhamel formula, a fundamental tool for the study of time-dependent equations. It is nothing but an extension of the variation of the constant formula. We present the general formula in the bounded case, and will perform the extension to the unbounded case on a case-by-case basis.

Theorem 5.1 (Duhamel's formula). Let A be a bounded operator on \mathcal{H} , $f \in C^0(\mathbb{R}, \mathcal{H})$ and $\psi_0 \in \mathcal{H}$. Then the solution of

$$i\partial_t \psi = A\psi + f(t), \quad \psi(0) = \psi_0 \quad (5.8)$$

is given by

$$\psi(t) = e^{-iAt}\psi_0 - i \int_0^t e^{-iA(t-t')} f(t') dt'. \quad (5.9)$$

In particular, if B is another bounded operator on \mathcal{H} , $\psi : C^1([0, T], \mathcal{H})$ solves

$$i\partial_t \psi = A\psi + B\psi, \quad \psi(0) = \psi_0 \quad (5.10)$$

if and only if it solves

$$\psi(t) = e^{-iAt}\psi_0 - i \int_0^t e^{-iA(t-t')} B\psi(t') dt'. \quad (5.11)$$

Proof. Like in the variation of the constant method, set

$$\psi(t) = e^{-iAt}\phi(t). \quad (5.12)$$

Differentiating, we obtain

$$i\partial_t \phi = e^{iAt}f(t) \quad (5.13)$$

and we obtain the result by solving this trivial differential equation and plugging it back into (5.12). \square

This enables us to show smoothness:

Theorem 5.2. If for $s \geq 2$ $\psi_0 \in H_{\text{per}}^s$ and V is s times continuously differentiable, then the solution $\psi(t)$ of (5.1) is in $C^0([0, T], H_{\text{per}}^s)$ for all $T > 0$.

Proof. We interpret the Duhamel formula

$$\psi(t) = e^{-it(-\frac{1}{2}\partial_{xx})}\psi_0 - i \int_0^t e^{-i(t-t')(-\frac{1}{2}\partial_{xx})}V\psi(t') dt'. \quad (5.14)$$

as a linear equation

$$(1 + K)\psi = e^{-it(-\frac{1}{2}\partial_{xx})}\psi_0 \quad (5.15)$$

for ψ in the space $C^0((0, T), H_{\text{per}}^s)$, with

$$(K\psi)(t) = i \int_0^t e^{-i(t-t')(-\frac{1}{2}\partial_{xx})} V\psi(t') dt'. \quad (5.16)$$

Since $e^{-i(t-t')(-\frac{1}{2}\partial_{xx})}$ and V both preserve H_{per}^s ,

$$\|K\|_{C^0((0,T),H_{\text{per}}^s)} \leq t \sup_{x \in \mathbb{R}, k \in \{0, \dots, s\}} |V^{(k)}(x)|. \quad (5.17)$$

By Neumann series, the equation (5.15) has a unique solution for t smaller than a constant that depends only on V . We can then continue this solution up to arbitrary times. Once the solution has been obtained, it is easy to check that it is also in $C^1([0, T], H_{\text{per}}^{s-2})$ for all $T > 0$, and that it is a solution of (5.1). The result follows by uniqueness. \square

5.2 Fourier approximation

Consider now the space

$$X_N = \text{Span}(e_n, |n| \leq N) \quad (5.18)$$

of functions supported on the low-frequency Fourier modes. Let P_N be the projector on X_N : explicitly,

$$P_N = \sum_{|n| \leq N} |e_n\rangle \langle e_n|. \quad (5.19)$$

We quantify the error of best approximation of any given function ψ in this basis:

Theorem 5.3. For all $s \geq 0$, there is $C > 0$ such that, for all $\psi \in H_{\text{per}}^s$, $N \geq 1$,

$$\|\psi - P_N \psi\|_{L_{\text{per}}^2} \leq \frac{C}{N^s} \|\psi\|_{H_{\text{per}}^s} \quad (5.20)$$

Proof.

$$\|\psi - P_N \psi\|_{L_{\text{per}}^2}^2 = \frac{1}{2\pi} \sum_{|n| > N} |c_n(\psi)|^2 \quad (5.21)$$

$$\leq \frac{1}{2\pi N^{2s}} \sum_{|n| > N} |n|^{2s} |c_n(\psi)|^2 \quad (5.22)$$

$$\leq \frac{C}{N^{2s}} \|\psi\|_{H_{\text{per}}^s}^2 \quad (5.23)$$

\square

If ψ is C_{per}^∞ , its approximation by its N first Fourier modes converges faster than any inverse polynomial in N . More is in fact true: if ψ is analytic, the error decays exponentially²⁸. The Fourier approximation of smooth and periodic functions is therefore usually very efficient.

From the two previous results, it follows that $\psi(t)$ can be very well approximated by a truncated Fourier series $P_N \psi(t)$. It is therefore reasonable to attempt to discretize the equation on this finite-dimensional space.

5.3 Space discretization: the spectral method

In the spectral method to solve (5.1), we seek an approximation $\psi_N(t) \in X_N$ of the solution $\psi(t)$ of

$$i\partial_t \psi = H\psi, \psi(0) = \psi_0. \quad (5.25)$$

Of course, if $\psi_0 \in X_N$, the solution of (5.25) does not belong to X_N in general. To obtain an evolution equation for $\psi_N(t)$, we use a Galerkin scheme²⁹ and project (5.1) on X_N to obtain

$$i\partial_t \psi_N = P_N H P_N \psi_N, \quad \psi_N(0) = P_N \psi_0 \quad (5.26)$$

where $H = -\frac{1}{2}\partial_{xx} + V$. This is a finite-dimensional equation, with a unique solution.

Theorem 5.4. If V is s times continuously differentiable and $\psi_0 \in H_{\text{per}}^s$, then, for all $T > 0$ there is C_T such that, for all $N \geq 1$, $t \in [0, T]$,

$$\|\psi_N(t) - \psi(t)\| \leq \frac{C_T}{N^{s-2}} \quad (5.27)$$

Proof. Let $e(t) = \psi_N(t) - \psi(t)$. We have $e(0) = P_N \psi_0 - \psi_0$ and

$$i\partial_t e = P_N H P_N \psi_N - H\psi \quad (5.28)$$

$$= P_N H P_N e - (H - P_N H P_N)\psi \quad (5.29)$$

Using Duhamel's formula, we get

$$e(t) = e^{-itP_N H P_N} e(0) - i \int_0^t e^{-i(t-t')P_N H P_N} (H - P_N H P_N)\psi(t') dt' \quad (5.30)$$

and from the approximation Theorem 5.3 we get

$$\|e(t)\| \leq \frac{C}{N^s} + t \sup_{t' \in [0, t]} \|(H - P_N H P_N)\psi(t')\|. \quad (5.31)$$

²⁸Sketch of proof: using a contour deformation, write

$$c_n(\psi) = \frac{1}{\sqrt{2\pi}} \int_0^{2\pi} \psi(x) e^{-inx} dx = \frac{1}{\sqrt{2\pi}} \int_0^{2\pi} \psi(x+iy) e^{-in(x+y)} dx, \quad (5.24)$$

picking y positive or negative depending on the sign of n .

²⁹The Galerkin method is sometimes presented using the weak formulation of the equation, with bilinear forms. This is mainly because in the usual finite element method, we use basis functions that are not necessarily in the domain of the operator, such as piecewise polynomials to solve the Laplace equation. Here, we do not encounter this difficulty and adopt a simpler presentation, but both formulations are equivalent.

for some constant C . Set $Q_N = 1 - P_N$, and split orthogonally H on X_N and X_N^\perp :

$$H - P_N H P_N = \begin{pmatrix} 0 & 0 \\ 0 & Q_N(-\frac{1}{2}\partial_{xx})Q_N \end{pmatrix} + \begin{pmatrix} 0 & P_N V Q_N \\ Q_N V P_N & Q_N V Q_N \end{pmatrix} \quad (5.32)$$

so that, using that P_N and ∂_{xx} commute,

$$\|(H - P_N H P_N)\psi\| \leq \frac{1}{2}\|Q_N \partial_{xx} Q_N \psi\| + \|Q_N V P_N \psi\| + \|Q_N V Q_N \psi\| + \|P_N V Q_N \psi\| \quad (5.33)$$

$$\leq \frac{1}{2}\|Q_N \partial_{xx} \psi\| + \|Q_N V P_N \psi\| + 2 \left(\sup_{x \in \mathbb{R}} |V(x)| \right) \|Q_N \psi\| \quad (5.34)$$

Since $\partial_{xx}\psi$, $V P_N \psi$ and ψ are in H_{per}^{s-2} uniformly in $t \in [0, T]$, the result follows from Theorem 5.3. \square

The proof presented here is simple but suboptimal, as our bound for the error is of order $N^{-(s-2)}$, while the error of best approximation (i.e. $\|\psi - P_N \psi\|$) is of order N^{-s} . Obtaining a sharper error bound requires a more detailed analysis (see [9]).

Note that the scheme of proof is the same as for many methods in numerical analysis (for instance, the analysis of integration methods for ordinary differential equations). One sets up an equation (5.29) for the error, which is of the same type as the equation being solved (a Schrödinger evolution equation), but has an added consistency error (here, $(H - P_N H P_N)\psi$) as source term. One then uses two ingredients: the stability of the equation to external perturbations (here, guaranteed by the preservation of the L^2 norm by the dynamics) and the smallness of the consistency (or truncation) error. This is the mantra of numerical analysis: stability + consistency = convergence.

5.4 Implementation: fast Fourier transforms and the pseudospectral method

Let us now compute the matrix representation H_N of the linear map $P_N H P_N$ in the orthonormal basis $e_n, n = -N, \dots, N$:

$$(H_N)_{mn} = \langle e_m | P_N H P_N e_n \rangle = \langle e_m | H e_n \rangle = \frac{1}{2}n^2 \delta_{mn} + \frac{1}{2\pi} \int_0^{2\pi} V(x) e^{i(n-m)x} dx. \quad (5.35)$$

The kinetic energy term (Laplacian) is diagonal and easily handled. The potential energy term has the property that H_{mn} is only a function of $m - n$. This means that matrix-vector products Hc are discrete convolutions:

$$(V_N c)_m = \sum_{n=-N}^N v_{m-n} c_n \quad (5.36)$$

where $v_k = \frac{1}{2\pi} \int_0^{2\pi} V(x) e^{-ikx} dx$.

Naive convolutions get relatively expensive for large N (scaling as $O(N^2)$) and are not easily handled (for instance, there is no easy way to compute exponentials of V_N). However, there is a very intuitive way of computing an approximation to $(V_N c)_m$: perform the inverse discrete Fourier transform to get the values of $\psi(x) = \sum_{n=-N}^N c_n e_n(x)$ on a uniform grid $x_i = \frac{2\pi i}{2N+1}, i = 0, \dots, 2N$, multiply these values by $V(x_i)$ to obtain the values of $V\psi$ on the grid, then take the discrete

Fourier transform to obtain approximate values of the Fourier coefficients of $V\psi$. This method, known as the pseudospectral method, is not equivalent to the spectral method, because the last step is an approximation (the Fourier coefficients of $V\psi$ are not determined by the values on the grid). However, it is often almost as accurate as the spectral method. It is much more efficient, since applying V_N to a vector can now be done in $O(N \log N)$ thanks to the fast Fourier transform.

To understand why the pseudospectral is so accurate, one can notice that it is (formally) exactly the spectral method applied to the *sampled* potential

$$\tilde{V}(x) = \sum_{i \in \mathbb{Z}} V(x_i) \delta_{x_i}(x).$$

Computing the Fourier coefficients of \tilde{V} can be done by expanding the Dirac comb $\sum_{i \in \mathbb{Z}} \delta_{x_i}$ in Fourier series (as in the proof of the Shannon sampling theorem, for instance), with the result that

$$c_n(\tilde{V}) = \sum_{m \in (2N+1)\mathbb{Z}} c_{n+m}(V),$$

i.e. the Fourier coefficients of \tilde{V} are the periodization, with period $2N + 1$, of those of V . If the Fourier coefficients of V decay quickly, it follows that, for N large, the Fourier coefficients of \tilde{V} in the range of interest $[-2N, 2N]$ (see (5.36)) are very close to those of V ³⁰.

We can also see the pseudospectral method dually, taking as the primary unknown the values of ψ on an equispaced grid, like in the finite difference method. The Laplacian operator is then approximated by computing the discrete Fourier transform, multiplying by n^2 and transforming back.

5.5 Time discretization

We now turn to the time discretization of the finite-dimensional evolution equation

$$i\partial_t c = H_N c, \tag{5.37}$$

the finite-dimensional representation of $i\partial_t \psi_N = P_N H P_N \psi_N$ in the orthonormal basis of the e_n . Of course, the solution can simply be obtained by computing a matrix exponential. There are drawbacks to this approach: first, it is not applicable to time-dependent Hamiltonians $H_N(t)$, and second, it is expensive, requiring a full diagonalization of H_N . For this reason, numerical integration methods are often preferred.

Explicit integration methods are not very efficient since $P_N H P_N$ has eigenvalues of order N^2 , so that the equation is very stiffly oscillating. This requires taking timesteps of the order of $1/N^2$ (an instance of a Courant–Friedrichs–Lewy condition, or CFL). An alternative is implicit methods, which do not suffer from a CFL condition but requires solving a nontrivial linear system. Both methods also have the drawback that they do not necessarily preserve the structure of the equation, such as the conservation of the L^2 norm and of the energy. There is however another class

³⁰A detailed analysis is out of the scope of this course, but can be found for instance in [10, 9]. The proper spectral method is however sometimes desirable, for instance because it preserves the symmetries of the solution better than the pseudospectral method, or because it is strictly variational, which ensures for instance approximations of eigenvalues from above. In this case, one uses the fact that it is possible to reformulate exactly the matrix-vector products (5.36) as cyclic convolutions of larger vectors by extending the input with zeros to avoid boundary effects (zero-padding).

of integrators that are particularly suited to Schrödinger equations (and to Hamiltonian systems in general): splitting methods. The simplest method is based on the Lie-Trotter formula³¹

Theorem 5.5. Let A and B be bounded operators. Then

$$e^{A+B} = \lim_{n \rightarrow \infty} \left(e^{A/n} e^{B/n} \right)^n \quad (5.38)$$

Proof. As $n \rightarrow \infty$, we have from direct expansion of the power series

$$e^{A/n} e^{B/n} = 1 + \frac{A+B}{n} + O\left(\frac{1}{n^2}\right) \quad (5.39)$$

$$\log\left(e^{A/n} e^{B/n}\right) = \frac{A+B}{n} + O\left(\frac{1}{n^2}\right) \quad (5.40)$$

$$\left(e^{A/n} e^{B/n} \right)^n = e^{A+B+O(\frac{1}{n})} = e^{A+B} + O\left(\frac{1}{n}\right) \quad (5.41)$$

where the O is in the sense of bounded operators. \square

This proof also shows that the error is $O(\frac{1}{n})$. Higher-order approximations exist (such as the Strang splitting).

Then, to approximate the solution of

$$i\partial_t \psi = (H_0 + H_1)\psi, \quad (5.42)$$

on $[0, T]$ with timestep

$$\Delta t = \frac{T}{M}, \quad (5.43)$$

we use the recurrence relation

$$\psi_{n+1} = e^{-i\Delta t H_0} e^{-i\Delta t H_1} \psi_n, \quad (5.44)$$

to obtain an estimate ψ_n of $\psi(t_n)$ at time $t_n = n\Delta t$. This means that, for each timestep, one solves (“propagates”) exactly the equation first with H_1 turned off, then with H_0 turned off.

It might at first glance look like nothing much is gained compared to a simple forward Euler discretization, but the main interest of the splitting method is to preserve some of the structure of the original equation by expressing the solution e^{-iHt} as a composition of elementary unitary operations. This means for instance that the L^2 norm is automatically preserved. This is in contrast with most integration schemes, such as the forward or backward Euler method. Consider for instance the scalar equation $i\dot{x} = \lambda x$ for $\lambda \in \mathbb{R}$. The forward Euler solution at time $t_n = \Delta tn$ is

$$x^{\text{FE}}(t_n) = (1 - i\lambda\Delta t)^n x(0) \quad (5.45)$$

$$|x^{\text{FE}}(t_n)| = \left(\sqrt{1 + \lambda^2 \Delta t^2} \right)^n |x(0)| \quad (5.46)$$

³¹Also called by various names, including Suzuki and Kato.

For any value of $\lambda \neq 0$, the forward Euler solution at time T will be significantly greater than 1 (explode), unless $M\lambda^2\Delta t^2 \ll 1$, i.e. $\Delta t \ll \frac{1}{\lambda^2}$ (assuming T to be order 1). Similarly, the backward Euler will implode under the same condition.

With the forward Euler scheme, when integrating the discrete Schrödinger equation $i\partial_t\psi = H\psi$, this means that Δt will have to be smaller than the inverse square of the largest eigenvalue of H (otherwise, the solution will be dominated by an exploding mode). When H arises from the discretization of the Schrödinger equation, the largest eigenvalue is typically of the order of the inverse square of the spatial linear grid size Δx , which results in a very severe restriction on possible timesteps. This in particular means that the combined discretization scheme (in space and time) may not converge even if Δt and Δx both go to zero (they have to go to zero in such a way that the explosion issue is absent): this is a Courant-Friedrichs-Lowy (CFL) condition.

By contrast, the splitting method is free of a CFL condition. To see this, let $\psi(t)$ be the solution of $i\partial_t\psi = (H_0 + H_1)\psi$, and

$$\psi_n = (e^{-iH_0T/M} e^{-iH_1T/M})^n \psi(0), \quad (5.47)$$

an approximation to $\psi(t_n)$. Following the classical method for proving convergence of integration scheme, we set $e_n = \psi_n - \psi(t_n)$, and write

$$e_{n+1} = \psi_{n+1} - \psi(t_{n+1}) \quad (5.48)$$

$$= (e^{-iH_0T/M} e^{-iH_1T/M})\psi_n - e^{-i(H_0+H_1)T/M}\psi(t_n) \quad (5.49)$$

$$= (e^{-iH_0T/M} e^{-iH_1T/M})e_n + \left(e^{-iH_0T/M} e^{-iH_1T/M} - e^{-i(H_0+H_1)T/M} \right) \psi(t_n) \quad (5.50)$$

$$\|e_{n+1}\| \leq \|e_n\| + \left\| \left(e^{-iH_0T/M} e^{-iH_1T/M} - e^{-i(H_0+H_1)T/M} \right) \psi(t_n) \right\| \quad (5.51)$$

$$\|e_n\| \leq \sum_{k=0}^{n-1} \left\| \left(e^{-iH_0T/M} e^{-iH_1T/M} - e^{-i(H_0+H_1)T/M} \right) \psi(t_n) \right\| \quad (5.52)$$

The quantity $\left\| \left(e^{-iH_0T/M} e^{-iH_1T/M} - e^{-i(H_0+H_1)T/M} \right) \psi(t_n) \right\|$ is known as the truncation error, and the last step (a particularly degenerate case of the Gronwall lemma) expresses *stability*, i.e. the fact that truncations errors at each step only accumulate without amplification. This would not be the case with the forward Euler method for instance, because $e^{-iH_0T/M} e^{-iH_1T/M}$ would be replaced by $1 - i\Delta t(H_0 + H_1)$, which has norm larger than 1. Combining this with estimates on the truncation error (based on the spatial smoothness of $\psi(t)$) would yield convergence without a CFL condition.

Splitting methods are particularly easy to implement when the Hamiltonian can be split in two simple parts (in the sense that one can compute propagators for each term explicitly). This is the case for the pseudospectral (but not the spectral) method, where the propagator of both the kinetic energy term (diagonal in reciprocal space) and the potential energy term (diagonal in real space) are easily computed. The final resulting scheme is: at each timestep,

- Propagate the potential energy term (by applying a factor $e^{-i\Delta t V(x_n)}$ to each $\psi(x_n)$)
- Take a fast Fourier transform to obtain approximations to the Fourier coefficients of ψ
- Propagate the kinetic energy term (by applying a factor $e^{-i\Delta t \frac{k^2}{2}}$ to the Fourier coefficients)
- Take an inverse fast Fourier transform to come back to real space

5.6 Exercises

1. Consider the equation

$$i\partial_t \psi_k = \psi_{k+1} + \psi_{k-1}, \quad (5.53)$$

posed in $\ell^2(\mathbb{Z})$, with an initial condition with compact support. Redo the analysis of this chapter to prove an error bound analogous to Theorem 5.4 for the truncation of ψ to the space $X_N = \{\psi \in \ell^2(\mathbb{Z}), \psi_k = 0 \text{ for } |k| > N\}$. You can use the weighted norm $\ell_s^2 = \{\psi \in \ell^2(\mathbb{Z}), \sum(1 + |k|)^{2s}|\psi_k|^2 < \infty\}$, and use an appropriate version of the Fourier transform to prove that this space is preserved by the evolution.

Summary

The Schrödinger equation with a smooth periodic potential is very efficiently approximated by a Galerkin method in the Fourier basis (spectral method), with convergence faster than any inverse polynomial in the truncation parameter. Time integration is efficiently performed by a splitting method, which guarantees a reasonable long-time behavior and is free of a CFL condition. In practice, the spectral method is often approximated by the pseudospectral method, which is similar in accuracy but allows the efficient fast Fourier transform method to be used.

6 Variational methods for the time-independent Schrödinger equation

We have seen how to solve the time-dependent Schrödinger numerically. We now turn to the time-independent case.

6.1 The Galerkin method

We have seen in the previous section that the Galerkin method for an operator H in an approximation space X_N with orthonormal basis e_n constructed the matrix

$$(H_N)_{mn} = \langle e_m | H e_n \rangle \quad (6.1)$$

and solved the Schrödinger equation $i\partial_t c = H_N c$. In the same spirit, this method can also be used to find approximations of solutions of the time-independent Schrödinger equation $H\psi = \lambda\psi$ simply by solving the eigenvalue equation for the matrix H_N :

$$H_N \psi_N^{(i)} = \lambda_N^{(i)} \psi_N^{(i)}. \quad (6.2)$$

Similarly to the time-dependent case, one can show smoothness results on eigenvectors, and corresponding error bounds on their numerical approximations [11]. The crucial ingredient is the existence of a **gap**: one can prove that $\text{Span}(\psi_N^{(i)})$ converges to $\text{Span}(\psi^{(i)})$ (in an appropriate sense) provided that $\lambda^{(i-1)} < \lambda^{(i)} < \lambda^{(i+1)}$, where the eigenvalues $\lambda^{(i)}$ of H are ordered in ascending order.

The spectral method can also be understood as a variational approximation of the eigenvalues; for instance, for the lowest eigenvalue $\lambda_N^{(1)}$ of H_N , we have

$$\lambda_N^{(1)} = \min_{\psi \in X_N, \|\psi\|=1} \langle \psi | H_N \psi \rangle \geq \min_{\psi \in X, \|\psi\|=1} \langle \psi | H \psi \rangle = \lambda^{(1)} \quad (6.3)$$

which shows that $\lambda_N^{(1)}$ overestimates the true eigenvalue $\lambda^{(1)}$.

6.2 Application: the H_2^+ molecule and the chemical bond

The Galerkin method is not only numerical. Consider the H_2^+ molecule, composed of a single electron and two nuclei, positioned at 0 and at $R \in \mathbb{R}^3$. Since there is only one electron, this is the simplest molecule possible, and remains (in the Born-Oppenheimer approximation where nuclei are modeled classically) a one-body problem. The electronic Hamiltonian is

$$H_R = -\frac{1}{2} \Delta - \frac{1}{|x|} - \frac{1}{|x-R|}. \quad (6.4)$$

The total energy at rest (with the electron in its ground state) is given by

$$E(R) = \frac{1}{|R|} + \lambda_{\min}(H_R), \quad (6.5)$$

where $\frac{1}{|R|}$ originates from the (classical) nucleus-nucleus Coulomb interaction, and $\lambda_{\min}(H_R)$ is the lowest eigenvalue (ground state) of H_R . Physically, the molecule H_2^+ is stable (it is commonly found in space). This means that we expect the curve $E(R)$ to have a minimum at finite $|R|$; if it had a minimum at $|R| = \infty$ it would mean that the molecule would not be stable, but rather be found

naturally $H^+ + H$. In this section, we will explain theoretically why this molecule should be stable, i.e. why a bond naturally forms. This is a simple prototype of covalent bonding in chemistry.

How can we compute $\lambda_{\min}(H_R)$? This is a complicated three-dimensional partial differential equation without radial symmetry, and is therefore hard to solve³². However, we can approximate the solution for R large, using the fact that we know how to solve the hydrogen atom explicitly (see Section 1.7). Let $\psi_{\text{gs}}(x)$ be the ground state of the Hamiltonian $-\frac{1}{2}\Delta - \frac{1}{|x|}$ (the 1s orbital, a radial and exponentially decaying function), normalized in L^2 and taken to be real, and λ_{gs} the associated eigenvalue. Then, we can expect the ground state of H_R for R large to have something to do with $\psi_1(x) = \psi_{\text{gs}}(x)$ and $\psi_2(x) = \psi_{\text{gs}}(x - R)$. By symmetry, we should not expect the ground state to be either one of these, but rather a linear combination. In chemistry this is called the LCAO method (“Linear Combination Of Atomic Orbitals”); mathematically, it is the Galerkin method in the subspace $\text{Span}(\psi_1, \psi_2)$.

To use the methodology in the previous sections, we would have to first get an orthonormal basis of this subspace, form the matrix of the Hamiltonian inside this basis and diagonalize it to get an approximation to the eigenvalues and eigenvectors of H_R . We can however bypass the orthonormalization by solving instead a generalized eigenvalue problem in the non-orthogonal basis (ψ_1, ψ_2) . We start from the variational principle

$$\min_{\psi \in \text{Span}(\psi_1, \psi_2), \|\psi\|=1} \langle \psi | H_R \psi \rangle \quad (6.6)$$

for the lowest eigenvalue. Let $\psi = c_1\psi_1 + c_2\psi_2$. We then have

$$\langle \psi | H_R \psi \rangle = c^T A c, \quad \|\psi\|^2 = c^T B c, \quad (6.7)$$

where A and B are the 2×2 Hamiltonian (in mechanics, stiffness) and overlap (in mechanics, mass) matrices, given by

$$A_{ij} = \langle \psi_i | H_R \psi_j \rangle, \quad B_{ij} = \langle \psi_i | \psi_j \rangle. \quad (6.8)$$

We can then solve

$$\min_{c \in \mathbb{R}^2, c^T B c = 1} c^T A c \quad (6.9)$$

analytically by applying the method of Lagrange multipliers. We obtain the generalized eigenvalue problem (note that we could also have obtained this directly by expanding ψ in ψ_1 and ψ_2 , and testing the equality $H\psi = \lambda\psi$ with ψ_1 and ψ_2)

$$Ac = \lambda Bc. \quad (6.10)$$

We now compute these matrices. From the L^2 normalization, the fact that ψ_{gs} is an eigenvector of $-\frac{1}{2}\Delta - \frac{1}{|x|}$ and the symmetries of the problem, we get

$$A = \begin{pmatrix} \lambda_{\text{gs}} - a_1 & -a_2 \\ -a_2 & \lambda_{\text{gs}} - a_1 \end{pmatrix} \quad (6.11)$$

³²Actually it turns out that it can be solved exactly using a coordinate system adapted to the particular symmetry of the problem (prolate spheroidal coordinates), but the solution method is complicated and does not extend to more complex systems.

and

$$B = \begin{pmatrix} 1 & b \\ b & 1 \end{pmatrix} \quad (6.12)$$

where

$$b = \langle \psi_1 | \psi_2 \rangle, \quad a_1 = \langle \psi_1 | \left(\frac{1}{|x - R|} \right) \psi_1 \rangle, \quad a_2 = -\lambda_{\text{gs}} b + \langle \psi_1 | \left(\frac{1}{|x - R|} \right) \psi_2 \rangle. \quad (6.13)$$

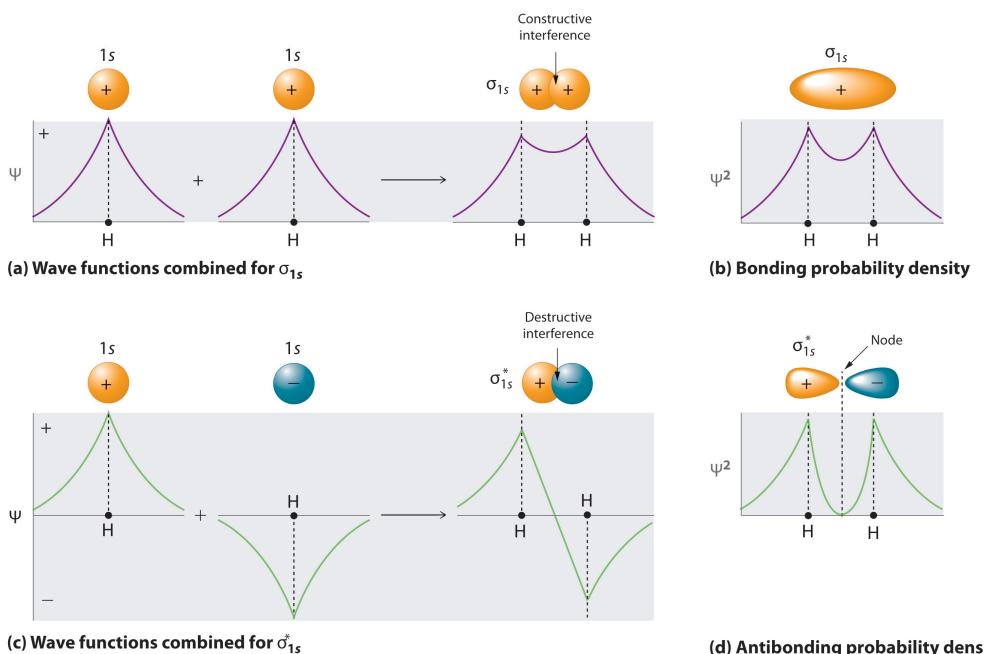
These quantities are all positive, and go to zero with $|R|$. Even without numerical values, we can see directly that the eigenvectors of $Ac = \lambda Bx$ are $c_{\pm} = (1, \pm 1)$. The eigenvalues are easily found to be

$$\lambda_{\pm} = \frac{\lambda_{\text{gs}} - a_1 \mp a_2}{1 \pm b}. \quad (6.14)$$

Expanding to first order in (a_1, a_2, b) , we get

$$\lambda_{\pm} = \lambda_{\text{gs}} - a_1 \mp a_2 \mp \lambda_{\text{gs}} b = \lambda_{\text{gs}} - \langle \psi_1 | \left(\frac{1}{|x - R|} \right) \psi_1 \rangle \mp \langle \psi_1 | \left(\frac{1}{|x - R|} \right) \psi_2 \rangle \quad (6.15)$$

It is now clear that $\lambda_+ < \lambda_-$, so that the ground state in the Galerkin approximation is (proportional to) the **bonding orbital** $\psi_1 + \psi_2$. Plotting the density $|\psi_1 + \psi_2|^2$, we see that compared to the **anti-bonding orbital** $\psi_1 - \psi_2$, the bonding orbital has more probability density in the region between the two atoms. On average, it makes the electrons closer to both nuclei (the electron is “shared” between the two atoms), minimizing the energy.



Picture from https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/

We have seen that the electronic ground state was an bonding orbital, which resulted in an energy smaller than λ_{gs} by an exponentially small amount in $|R|$. Coming back to the expression of the total energy $E(R)$ defined in (6.5), we get the approximation

$$E(R) \approx \frac{1}{|R|} + \lambda_+ (|R|) \quad (6.16)$$

$$\approx \lambda_{\text{gs}} + \frac{1}{|R|} - \langle \psi_1 | \left(\frac{1}{|x-R|} \right) \psi_1 \rangle - \langle \psi_1 | \left(\frac{1}{|x-R|} \right) \psi_2 \rangle. \quad (6.17)$$

A more careful analysis³³ shows that $E(R) < \lambda_{\text{gs}}$ when $|R|$ is large. This shows **chemical bonding**: the energy of the H_2^+ is minimized at some finite bond length R .

Although the above picture is plausible, it is still unclear what the error committed by the Galerkin approximation is. Because of the variational character of the Galerkin method, we know that the exact ground state energy is below λ_- , but we do not know how much. Here, a more detailed analysis shows that the true ground state is within about $O(e^{-2L})$ of the LCAO approximation³⁴.

6.3 Exercises

1. Show without computation that the lowest eigenvalue of

$$A = \begin{pmatrix} 1 & 2 \\ 2 & 3 \end{pmatrix} \quad (6.20)$$

is smaller than 1.

Summary

The Galerkin method can be used to obtain approximations (from above) to eigenvalues of Schrödinger operators. The Galerkin basis can be numerical (finite element, Fourier basis...) or physically inspired (exact solutions of approximate problems). The LCAO method (Galerkin with atomic orbitals as basis) gives a qualitatively accurate picture of chemical bonding.

³³For this we can use Newton's shell theorem, which says that the gravitational potential created by a spherically symmetric mass distribution outside its support is equal to that created by a point charge at the center of equal mass (this itself is proven from the Poisson equation $-\Delta V = 4\pi\rho$ and the divergence theorem). Then, interpreting $\langle \psi_1 | \left(\frac{1}{|x-R|} \right) \psi_1 \rangle$ as the potential created by the mass distribution $|\psi_1|^2$ at the point R , we see that

$$\frac{1}{|R|} - \langle \psi_1 | \left(\frac{1}{|x-R|} \right) \psi_1 \rangle = \frac{1}{|R|} \left(1 - \int_{|x|<|R|} |\psi_1(x)|^2 dx \right) - \int_{|x|>|R|} \frac{|\psi_1(x)|^2}{|x-R|} dx, \quad (6.18)$$

which turns out to decay like a polynomial in $|R|$ times $e^{-2|R|}$; the other ("exchange") negative term decays like e^{-R} and therefore dominates at large R .

³⁴This is by no means trivial to prove. One first splits the space along $X = \text{Span}(\psi_1, \psi_2)$ and its orthogonal complement X^\perp , yielding

$$H = \begin{pmatrix} H_{XX} & H_{XX^\perp} \\ H_{X^\perp X} & H_{X^\perp X^\perp} \end{pmatrix}. \quad (6.19)$$

The off-diagonal terms H_{XX^\perp} involve the product of the potential of the atom at R and of the orbital ψ_1 , and are therefore about $O(e^{-L})$. If $\psi \in X^\perp$, then, writing $\psi = \chi\psi + (1-\chi)\psi$, where ψ is a smooth function localized on the half-space centered at $R/2$ and containing the atom at 0, one can show that $\langle \psi | H \psi \rangle$ is well above λ_\pm . One can then apply perturbation theory, developed in Section 7.

7 Time-independent perturbation theory

Consider a Hamiltonian $H(\varepsilon) = H^{(0)} + \varepsilon H^{(1)}$, with ε small. What can we say about the spectrum of $H(\varepsilon)$? We focus here on the bound states (the study of the continuous spectrum is the topic of scattering theory, which is more involved). Assume that there is a bound state $H^{(0)}\psi^{(0)} = \lambda^{(0)}\psi^{(0)}$. Since $\psi^{(0)}$ is only defined up to scaling, we fix $\|\psi^{(0)}\| = 1$. We assume that $\lambda^{(0)}$ is simple³⁵.

7.1 Perturbation theory

Formal perturbation theory Let us consider the finite-dimensional case for simplicity. We first apply formal perturbation theory: assume that

$$H(\varepsilon)\psi(\varepsilon) = \lambda(\varepsilon)\psi(\varepsilon) \quad (7.1)$$

with ψ and λ analytic in ε . We can then expand:

$$\psi(\varepsilon) = \psi^{(0)} + \varepsilon\psi^{(1)} + \dots \quad \lambda(\varepsilon) = \lambda^{(0)} + \varepsilon\lambda^{(1)} + \dots \quad (7.2)$$

Expanding the equation (7.1) to order 0 just gives us $H^{(0)}\psi^{(0)} = \lambda^{(0)}\psi^{(0)}$, which we assumed. To first order, we get

$$(H^{(0)} - \lambda^{(0)})\psi^{(1)} = -(H^{(1)}\psi^{(0)} - \lambda^{(1)}\psi^{(0)}) \quad (7.3)$$

This is a linear equation for $\psi^{(1)}$, but the operator $H^{(0)} - \lambda^{(0)}$ is singular, with nullspace $\text{Span}(\psi^{(0)})$. From a spectral decomposition it is easy to see that this system has either no solution if $\langle\psi^{(0)}|H^{(1)}\psi^{(0)} - \lambda^{(1)}\psi^{(0)}\rangle \neq 0$, or infinitely many (up to the addition of a multiple of $\psi^{(0)}$) if it is 0. This shows that, necessarily,

$$\lambda^{(1)} = \langle\psi^{(0)}|H^{(1)}\psi^{(0)}\rangle. \quad (7.4)$$

This is our first important result, known as the **Hellman-Feynman theorem**. It states that, in order to know the first-order correction to an eigenvalue, it is only necessary to know the corresponding eigenvector (and not any other eigenvectors, or the first-order correction to ψ). Then, the first-order equation (7.3) has infinitely many solutions; this is not surprising, as ψ is only determined up to a normalization and a phase. To obtain a unique solution, we set

$$\langle\psi^{(0)}|\psi^{(1)}\rangle = 0. \quad (7.5)$$

The vanishing of the real part ensures that $\|\psi(\varepsilon)\| = 1 + \varepsilon\text{Re}\langle\psi^{(0)}|\psi^{(1)}\rangle + \dots$ is 1 to first order. Imposing the vanishing of the imaginary part is a way to fix the phase (or **gauge**), an instance of parallel transport. This condition together with (7.3) uniquely defines $\psi^{(1)}$.

For concreteness, assume that \mathcal{H} is finite-dimensional, that ψ_1, \dots, ψ_N is an orthonormal eigenbasis of $H^{(0)}$ with eigenvalues λ_n and that we are performing perturbation theory about $\psi^{(0)} = \psi_1$. Expanding (7.3), we get

$$\psi^{(1)} = \sum_{n=2}^N \frac{\langle\psi_n|H^{(1)}\psi_0\rangle}{\lambda_1 - \lambda_n} \psi_n \quad (7.6)$$

³⁵Perturbation theory of non-simple eigenvalues is degenerate, and in that case one has to diagonalize explicitly a reduced Hamiltonian, as we have done in the previous section.

One sees the appearance of **energy denominators** $\lambda_1 - \lambda_n$: the variation of a given eigenvector is influenced more by eigenvectors that are close in eigenvalue than by those that are far.

Progressing in this way, one can derive expressions for ψ and λ at all orders, called the **Rayleigh-Schrödinger** series. For instance, the expression for $\lambda^{(2)}$ is³⁶

$$\lambda^{(2)} = \sum_{n \neq 1} \frac{|\langle \psi_n | H^{(1)} \psi_0 \rangle|^2}{\lambda_1 - \lambda_n} \quad (7.7)$$

Higher-order expressions can also be obtained by expanding (7.1) to higher orders and solving equations of the form $(H^{(0)} - \lambda^{(0)})\psi^{(k)} = r^{(k)}$, but the right-hand side $r^{(k)}$ gets more and more complicated.

Convergence of the series Does the Rayleigh-Schrödinger series converge? To answer this question would require estimating each term $\psi^{(n)}$ and showing that their magnitude decays quickly enough. This is doable but cumbersome, and rather hard to do in infinite dimensions. Fortunately, there is a simpler method using complex-analytic arguments, due to Kato [12].

Theorem 7.1. Let $H^{(0)}$ be self-adjoint, with a simple eigenvalue $\lambda^{(0)}$ isolated in the spectrum of A . Let $H^{(1)}$ be symmetric on the domain of $H^{(0)}$ and $H^{(0)}$ -bounded. Then, for ε small enough, the self-adjoint operator $H(\varepsilon) = H^{(0)} + \varepsilon H^{(1)}$ has an isolated simple eigenvalue $\lambda(\varepsilon)$ with associated eigenvector $\psi(\varepsilon)$, both of which are analytic as a function of ε .

This theorem extends to the case of several eigenvalues; in this case, the object that is analytic is the spectral projector associated to a set of eigenvalues that are isolated from the rest of the spectrum (but not necessarily from each other).

Proof. By the Rellich-Kato theorem 2.20, $H(\varepsilon)$ is self-adjoint of domain $D(H^{(0)})$ for ε small enough. Let C be a circle in the complex plane centered at λ_0 of radius δ , oriented trigonometrically. Pick δ such that C encloses $\lambda^{(0)}$ and no other part of the spectrum of $H^{(0)}$. Consider the operator

$$P(\varepsilon) = \frac{1}{2\pi i} \int_C (z - H(\varepsilon))^{-1} dz. \quad (7.8)$$

Since $\frac{1}{2\pi i} \int_C (z - w)^{-1} dz$ equals 1 if w is inside C and 0 otherwise, by the spectral theorem $P(\varepsilon) = \mathbb{1}(\cdot \in [\lambda_0 - \delta, \lambda_0 + \delta])(H(\varepsilon))$. We can expand the operator $(z - H(\varepsilon))^{-1}$ in Neumann series, for $z \in C$:

$$(z - H(\varepsilon))^{-1} = (z - H^{(0)})^{-1} + \varepsilon(z - H^{(0)})^{-1} H^{(1)} (z - H^{(0)})^{-1} + \dots, \quad (7.9)$$

with the series converging in the topology of bounded operators, and analytic in ε for $|\varepsilon| < \|(z - H^{(0)})^{-1} H^{(1)}\|$. As in the proof of the Rellich-Kato Theorem 2.20, we can show that $(z - H^{(0)})^{-1} H^{(1)}$ is continuous and uniformly bounded in $z \in C$. It follows that $P(\varepsilon)$ is analytic in ε for ε small

³⁶This describes among other things the phenomenon of eigenvalue repulsion: when two eigenvalues are very close together, the second-order variation gets very large, and tends to separate the eigenvalues (analogous to a repulsive force). This tends to make eigenvalues of generic $H(\varepsilon)$ distinct, and eigenvalue crossings “rare”, unless the coupling $\langle \psi_n | \frac{d}{d\varepsilon} H(\varepsilon) \psi_m \rangle$ happens to be zero (for instance, because of a symmetry).

enough (in the topology of bounded operators). This means that its trace is constant and equal to 1, and therefore that there is a simple eigenvalue in $[\lambda_0 - \delta, \lambda_0 + \delta]$.

Let

$$\psi(\varepsilon) = P(\varepsilon)\psi(0), \quad (7.10)$$

which is analytic in the topology of \mathcal{H} , and non-zero for ε small enough. The same computation as above actually shows it is analytic in a stronger topology:

$$(H^{(0)} + \varepsilon H^{(1)})\psi(\varepsilon) = \frac{1}{2\pi i} \int_C (H^{(0)} + \varepsilon H^{(1)})(z - H^{(0)})^{-1} \left(1 + \varepsilon(z - H^{(0)})^{-1} H^{(1)} + \dots\right) \psi(0) dz, \quad (7.11)$$

so that $(H^{(0)} + \varepsilon H^{(1)})\psi(\varepsilon)$ is analytic (in the topology of \mathcal{H}), and the result follows from

$$\lambda(\varepsilon) = \frac{\langle \psi(\varepsilon) | (H^{(0)} + \varepsilon H^{(1)})\psi(\varepsilon) \rangle}{\langle \psi(\varepsilon) | \psi(\varepsilon) \rangle}. \quad (7.12)$$

□

The Rayleigh-Schrödinger power series for $\psi(\varepsilon)$ and $\lambda(\varepsilon)$ therefore has a finite radius of convergence³⁷.

7.2 Application: electron in an electric field

Consider a particle with Hamiltonian

$$H^{(0)} = -\frac{1}{2}\Delta + V \quad (7.14)$$

in its ground state $\psi^{(0)}$ (assumed to be non-degenerate). We submit it to a small potential $\varepsilon V^{(1)}$, with $V^{(1)}$ continuous and bounded, yielding a new ground state

$$H(\varepsilon)\psi(\varepsilon) = (H^{(0)} + \varepsilon V^{(1)})\psi(\varepsilon) = \lambda(\varepsilon)\psi(\varepsilon). \quad (7.15)$$

Rayleigh-Schrödinger perturbation theory is then applicable. Using the Hellman-Feynmann theorem, we get the first order variation

$$\lambda^{(1)} = \langle \psi | V^{(1)} \psi \rangle = \int_{\mathbb{R}^d} V^{(1)}(x) |\psi^{(0)}(x)|^2 dx \quad (7.16)$$

This term can be interpreted as the average classical potential energy of a particle randomly located in space, with probability density $|\psi(x)|^2$. If for concreteness we take $V^{(1)}(x) = -E \cdot x$ (ignoring

³⁷Estimating this radius of convergence is an interesting and non-trivial problem. Since power series converge in discs, the radius of convergence is the radius of the largest disc in the complex plane inside which $\lambda(\varepsilon)$ is a simple eigenvalue. A simple example is the **avoided crossing**

$$H(\varepsilon) = \begin{pmatrix} \delta & \varepsilon \\ \varepsilon & -\delta \end{pmatrix} \quad (7.13)$$

with eigenvalues $\pm\sqrt{\delta^2 + \varepsilon^2}$. The power expansion of this eigenvalue around 0 has a radius of convergence equal to δ , because $H(\pm i\delta)$ has repeated eigenvalues. Therefore, perhaps surprisingly, the investigation of the radius of convergence of the series involves considering *complex* values of ε , even if we are interested only in real values.

for a moment that x is not bounded³⁸), where E is the electrical field, the first-order energy shift $\varepsilon\lambda^{(1)}$ is equal to $-E \cdot d$, where

$$d = \int_{\mathbb{R}^d} x|\psi(x)|^2 dx \quad (7.17)$$

is the permanent dipole moment of the charge distribution $|\psi(x)|^2$. This explains why molecules such as water, possessing a permanent electrostatic dipole, acquire a dipole energy in an electrical field (and therefore tend to orient in the direction of the field).

The ground state of atoms such as the hydrogen atom is radial, and therefore its permanent dipole moment in direction e is zero:

$$\int_{\mathbb{R}^d} (e \cdot x)|\psi_0(x)|^2 dx = 0. \quad (7.18)$$

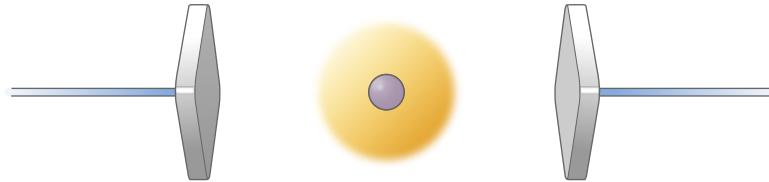
Under the influence of an external field however, an induced dipole is created: the electron reorganizes in response to the applied field, and shifts towards regions of lower potential. This can be computed by solving the equation

$$(H^{(0)} - \lambda^{(0)})\psi^{(1)} = -(V^{(1)}\psi^{(0)} - \lambda^{(1)}\psi^{(0)}), \quad (7.19)$$

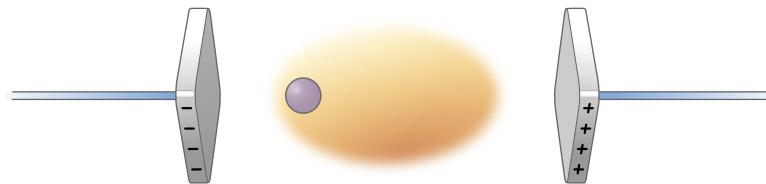
which has a unique solution when supplemented by the orthogonality condition $\langle \psi^{(1)} | \psi_0 \rangle = 0$. The new dipole moment in the direction e can then be computed by

$$d(\varepsilon) = \int_{\mathbb{R}^d} (e \cdot x)|\psi(\varepsilon)(x)|^2 dx = 0 + \varepsilon \int_{\mathbb{R}^d} (e \cdot x)(\overline{\psi^{(0)}(x)}\psi^{(1)}(x) + \overline{\psi^{(1)}(x)}\psi^{(0)}(x))dx + \dots \quad (7.20)$$

The dipole $d(\varepsilon)$ is a bilinear function of e and E , and so there is a 3×3 matrix α such that $d(\varepsilon) = e^T \alpha E$. This is the polarizability tensor α_{ij} , which describes the response in the dipole moment in direction i to a field in direction j . A simple calculation using the positivity of $H^{(0)} - \lambda^{(0)}$ implies that α is negative semidefinite: the electrons move in the same direction as the force $E = -\nabla V$.



³⁸The potential $E \cdot x$ is not relatively bounded by H_0 , and therefore the previous theory is inapplicable. In fact, the operator $H_0 + V_1$ in this case has only continuous spectrum, the notion of ground state is inapplicable and the Rayleigh-Schrödinger series diverges. Dynamically, the particle “leaks out” to regions where the potential V_1 is small by the tunnel effect. The eigenvalue then turns into a **resonance** with a finite lifetime, an object with a well-defined mathematical meaning but which falls outside the scope of this course. Nevertheless, the lifetime is often large enough (it is exponential in $1/\varepsilon$) that it makes physical sense to pretend that the state is bound and to apply perturbation theory blindly. Even the series is not convergent, it is asymptotic to the real part of the resonance energy, and therefore useful in applications.



Polarizability of an atom: the electron cloud deforms in response to an applied external field.

Picture from https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/

7.3 Exercises

- Find the eigenvectors up to first order and eigenvalues up to second order of

$$\begin{pmatrix} 1 + 2\varepsilon & 3 + 4\varepsilon \\ 3 + 4\varepsilon & 5 + 6\varepsilon \end{pmatrix} \quad (7.21)$$

- Using the implicit function theorem, show that there exists a unique solution of the equation $x^{42} - x^3 + 3x^2 - 2x = 1 + \varepsilon$ near $x = 1$ when ε is small. Give its expansion to second order in ε .

Summary

Perturbation theory gives a series expansion for the eigenvalues of slightly perturbed Hamiltonians. Truncating it to first or second-order often allows for physically meaningful results: for instance, first-order perturbation theory explains the interaction between the permanent dipole of a molecule and an electric field, and second-order perturbation theory explains the polarizability (induced dipole) of atoms.

8 Time-dependent perturbation theory

In this section, we develop perturbation theory for the time-dependent Schrödinger with Hamiltonian $H^{(0)} + \varepsilon H^{(1)}(t)$, where ε is small. For simplicity, we will assume in our estimates that $H^{(1)}(t)$ remains bounded for all times.

8.1 Time-dependent Hamiltonians: the Dyson series

We have seen that the equation $i\partial_t \psi = H\psi$ was well-posed whenever H is a self-adjoint operator. When H is time-dependent but bounded, well-posedness is rather easy to establish using standard Cauchy-Lipschitz theory. In the unbounded case, things get more complicated [4], and we will not enter into these subtleties here.

Consider a time-dependent Hamiltonian of the form

$$H(t) = H^{(0)} + \varepsilon H^{(1)}(t). \quad (8.1)$$

Typically, this is the case of a quantum system subject to an external forcing (such as an external electric or magnetic field). Using the Duhamel formula, we get

$$\psi(t) = e^{-itH^{(0)}}\psi_0 - i\varepsilon \int_0^t e^{-i(t-t')H^{(0)}} H^{(1)}(t')\psi(t')dt'. \quad (8.2)$$

This equation is of the form

$$(1 + \varepsilon K)\psi = e^{-itH^{(0)}}\psi_0 \quad (8.3)$$

for $\psi \in C^0([0, T], \mathcal{H})$, and

$$(K\psi)(t) = i \int_0^t e^{-i(t-t')H^{(0)}} H^{(1)}(t')\psi(t')dt' \quad (8.4)$$

For $\varepsilon t \sup_{t' \in \mathbb{R}} \|H^{(1)}(t')\|$ small enough, we have $\varepsilon \|K\|_{X \rightarrow X} < 1$, and we can expand in Neumann series

$$\psi(t) = e^{-itH^{(0)}}\psi_0 \quad (8.5)$$

$$+ (-i\varepsilon) \int_0^t e^{-i(t-t_1)H^{(0)}} H^{(1)}(t_1)e^{-it_1H^{(0)}}\psi_0 dt_1 \quad (8.6)$$

$$+ (-i\varepsilon)^2 \int_0^t \int_0^{t_2} e^{-i(t-t_2)H^{(0)}} H^{(1)}(t_2)e^{-i(t_2-t_1)H^{(0)}} H^{(1)}(t_1)e^{-it_1H^{(0)}}\psi_0 dt_2 dt_1 \quad (8.7)$$

$$+ \dots \quad (8.8)$$

with the series converging in $C^0([0, t], \mathcal{H})$ ³⁹. This remarkable series, the **Dyson series**, has a mechanistic interpretation. The particle starts in state ψ_0 , and propagates with Hamiltonian $H^{(0)}$. At time t_1 , it encounters a scattering event (analogous to a collision), picking up a factor $-i\varepsilon H^{(1)}(t_1)$. It then propagates until the time $t_2 > t_1$, at which it undergoes another scattering event, propagates until time t_3 , etc. The final $\psi(t)$ is a sum over all these possible scenarios.

³⁹Note that this also proves the existence and uniqueness of solutions to the Duhamel form (8.2) of the equation when $H^{(1)}(t)$ is bounded, even if $H^{(0)}$ is not; however, it is then not trivial to see that ψ is a strong solution of $i\partial_t \psi = H\psi$.

8.2 Linear response

We now focus on **linear response**, i.e. the first order in (8.5). We also will assume that ψ_0 is an eigenvector of $H^{(0)}$ (the system is in a stationary state before perturbing it), with eigenvalue λ_0 . We then get

$$\psi(t) = e^{-i\lambda_0 t} \psi_0 - i\varepsilon \int_0^t e^{-i(t-t_1)H^{(0)}} H^{(1)}(t_1) e^{-it_1\lambda_0} \psi_0 dt_1 + O(t^2\varepsilon^2). \quad (8.9)$$

To analyze this formula, let us first assume a finite-dimensional Hamiltonian, with orthonormal eigenvectors $H\psi_n = \lambda_n \psi_n$, for $n \in \{0, \dots, N\}$. Then, we can write this formula as

$$\psi(t) = e^{-i\lambda_0 t} \psi_0 - i\varepsilon \sum_{n=0}^N \psi_n e^{-it\lambda_n} \int_0^t \langle \psi_n | H^{(1)}(t_1) \psi_0 \rangle e^{it_1(\lambda_n - \lambda_0)} dt_1 + O(\varepsilon^2 t^2). \quad (8.10)$$

We see here that the time dependence of $H^{(1)}(t)$ plays an important role. Consider for instance⁴⁰

$$H^{(1)}(t) = e^{-i\omega t} H^{(1)}. \quad (8.11)$$

Then,

$$\psi(t) = e^{-i\lambda_0 t} \psi_0 - i \sum_{n=0}^N \psi_n e^{-it\lambda_n} \langle \psi_n | H^{(1)} \psi_0 \rangle \frac{1}{i(\lambda_n - \lambda_0 - \omega)} (e^{it(\lambda_n - \lambda_0 - \omega)} - 1) + O(\varepsilon^2 t^2) \quad (8.12)$$

with the convention $\frac{e^{t_0}-1}{0} = t$. Simple algebra shows that

$$|\langle \psi_n | \psi(t) \rangle| = \varepsilon \frac{|\langle \psi_n | H^{(1)} \psi_0 \rangle|}{|\lambda_n - \lambda_0 - \omega|} |\sin((\lambda_n - \lambda_0 - \omega)t)| + O(\varepsilon^2 t^2). \quad (8.13)$$

When ω is far from any resonant frequency, i.e. one that matches an energy difference $\lambda_n - \lambda_0$, the components $\langle \psi_n | \psi(t) \rangle$ oscillate at a non-zero frequency, with a normal amplitude. However, when ω is close to an energy difference $\lambda_n - \lambda_0$, the amplitude of the oscillations is large and their period long: the system undergoes a strong **excitation** from state ψ_0 to state ψ_n .

These excitations are analogous to a mechanical system with an external forcing, such as the harmonic oscillator⁴¹

$$\ddot{x} + \omega^2 x = f(t). \quad (8.14)$$

There, there is a strong excitation (mechanical resonance) when $f(t)$ oscillates at frequency $\pm\omega$. To emphasize this analogy, it is useful to write the Schrödinger equation as, to first order,

$$i\partial_t \psi \approx H^{(0)} \psi(t) + \varepsilon H^{(1)}(t) e^{-i\lambda_0 t} \psi_0 + O(\varepsilon^2 t). \quad (8.15)$$

This is the equation of a system oscillatory at frequencies λ_n , forced by a source term $\varepsilon H^{(1)}(t) e^{-i\lambda_0 t} \psi_0$; resonances occur when the frequency of the forcing $H^{(1)}(t)$ is such that $H^{(1)}(t) e^{-i\lambda_0 t} \psi_0$ oscillates

⁴⁰This is not physical because $e^{-i\omega t} H^{(1)}$ is not self-adjoint; however, by linearity, understanding what is happening for $e^{-i\omega t} H^{(1)}$ is enough to reconstruct what is happening for general (real) signals $f(t) H^{(1)}$.

⁴¹The harmonic oscillator is second-order rather than first-order, but this is a minor difference; the equation $i\dot{x} = \omega x + f(t)$ displays the same behavior.

at the frequencies λ_n . In contrast with the mechanical case, the “signal” $H^{(1)}(t)$ is multiplied by a factor $e^{-i\lambda_0 t}$; this is why frequency differences (and not frequencies themselves, as in the mechanical case) are important.

Even though quantum mechanics is linear, the mapping $\varepsilon \mapsto \psi$ is not, and our reasoning is only exact to first order. The longer-time behavior of quantum systems is considerably more complex. For instance, if a simple two-level system (with state space \mathbb{C}^2) with eigenvalues λ_0 and λ_1 is started in the state ψ_0 and excited at the frequency $\lambda_1 - \lambda_0$, it transitions to the state ψ_1 (as described by linear response), but then comes back to ψ_0 for longer times and oscillates back and forth with a period $\frac{2\pi}{\lambda_1 - \lambda_0}$, a phenomenon known as Rabi oscillations.

8.3 Application: absorption spectrum of hydrogen

A physical application of this theory is the absorption spectrum of atoms. Consider the hydrogen atom, with electronic Hamiltonian $H^{(0)} = -\frac{1}{2}\Delta - \frac{1}{|x|}$ and eigenvalues $-\frac{1}{2n^2}$ (see Section 1.7). Assume that the electron is in its ground state, and that we submit the atom to an incident source of light. We can model light by a monochromatic plane wave (and reconstruct more general radiation as a superposition of monochromatic waves), resulting in the time-dependent electric potential

$$H^{(1)}(t) = V_0 \sin(\omega t - k \cdot x) \quad (8.16)$$

with $V_0 \in \mathbb{R}$, $\omega = c|k|$ the frequency and $k \in \mathbb{R}^3$ the wavector. The wavelength $(2\pi/|k|)$ of visible light is in the range of hundreds of nanometers, much larger than the characteristic length scale of the electron in the hydrogen atom (the atomic unit of length, the Bohr, is about 0.05 nanometers). It is therefore reasonable to make the approximation

$$k \cdot x \ll 1, \quad (8.17)$$

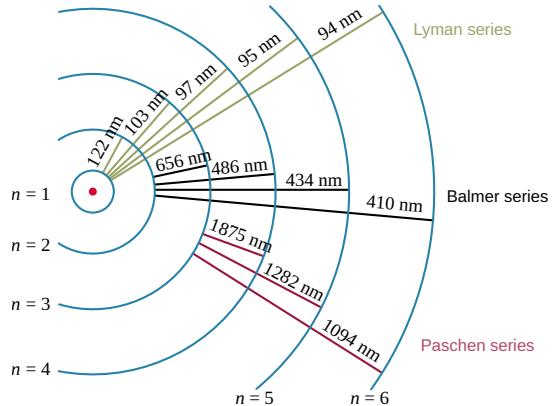
resulting in (ignoring the constant term $\sin(\omega t)$)

$$H^{(1)}(t) \approx V_0 \cos(\omega t) k \cdot x \quad (8.18)$$

By the previous reasoning, we expect a strong reaction of the electron when ω is equal to an energy difference $\lambda_j - \lambda_0$, i.e.

$$\omega = \frac{1}{2} - \frac{1}{2n^2} \quad (8.19)$$

for some $n > 1$. Indeed, this is observed in practice: the absorption spectrum of hydrogen has very sharp peaks at these frequencies. These are called the Lyman series, with frequencies in the ultraviolet range; there are also other types of series at frequencies $\omega = \frac{1}{2n} - \frac{1}{2m}$, $n \neq m$, corresponding to transitions involving excited states. In particular, the Balmer series ($m = 2$, $n > 2$) falls into the visible spectrum.



Hydrogen possible transitions, with associated light wavelength
 Visible light: about 400 (violet) to 800 nm (red).

Picture from https://en.wikipedia.org/wiki/Hydrogen_spectral_series

This process is the basis for instance of astronomical spectroscopy, where one points a telescope at a star and analyzes the frequency content of light to detect the presence of hydrogen (or other chemical elements).

8.4 Other approximation methods

We have here investigated the regime $H(t) = H^{(0)} + \varepsilon H^{(1)}(t)$, where ε is small. This gives an analytic expression for the first-order variation to ψ . As we have seen, this approximation is only valid when $\varepsilon t \|H^{(1)}\|$ is small, and is therefore only applicable for short times; for longer times, perturbation theory is not applicable. Also, in some cases, $H(t)$ is not naturally of the form $H(t) = H^{(0)} + \varepsilon H^{(1)}(t)$.

We have seen before that variational methods (restricting the form of ψ) yielded approximations to the dynamics. Two other approximation methods are the adiabatic regime (when H varies slowly), and the semiclassical regime (when the quantum dynamics approximates the classical one, e.g. when $H = -\varepsilon^2 \Delta + V$ with ε small). Which method is appropriate for a given system depends on the physical regime.

8.5 Exercises

1. Give the series expansion of the solution of $i\partial_t\psi = (E + \varepsilon)\psi$ for $\psi_0 \in \mathbb{C}$. Do the same for $i\partial_t\psi = (E + \varepsilon f(t))\psi$.

Summary

The Dyson series gives an approximation to the Schrödinger dynamics induced by a slightly perturbed Hamiltonian. When the perturbing Hamiltonian oscillates at a frequency close to a difference in the eigenvalues of the rest Hamiltonian, a transition between the corresponding states occurs, in a way very similar to mechanical resonances. This explains the absorption of light by atoms at particular frequencies.

9 Many-body quantum mechanics and applications

We have up to now focused on the quantum mechanics of a single particle. We now discuss the mathematical formalism of many-body quantum mechanics, with applications to chemistry.

9.1 Tensor products of Hilbert space

Definition 9.1. Let \mathcal{H}_1 and \mathcal{H}_2 be two separable Hilbert spaces, with Hilbert bases $(e_i)_{i \in B_1}, (f_j)_{j \in B_2}$, with B_1 and B_2 subsets of \mathbb{N} . The **tensor product** $\mathcal{H}_1 \otimes \mathcal{H}_2$ is the Hilbert space obtained by completing

$$\text{Span}(e_i \otimes f_j, i \in B_1, j \in B_2) \quad (9.1)$$

with respect to the inner product defined by

$$\langle u_1 \otimes u_2 | v_1 \otimes v_2 \rangle = \langle u_1 | v_1 \rangle \langle u_2 | v_2 \rangle. \quad (9.2)$$

and extended by bilinearity.

The elementary tensor product $e_i \otimes f_j \in \mathcal{H}_1 \otimes \mathcal{H}_2$ is only a notation for an abstract object, which serves to define the tensor product $\mathcal{H}_1 \otimes \mathcal{H}_2$. It is however often possible to make the tensor space more explicit by identifying it with a known Hilbert space.

Example 9.2. The tensor product of \mathbb{C}^{N_1} and \mathbb{C}^{N_2} has an orthonormal basis $e_i \otimes f_j$, and dimension $N_1 N_2$. It can be identified with the space of complex matrices with the canonical inner product $\langle A, B \rangle = \sum_{mn} A_{mn}^* B_{mn}$, through the identification $(e_i \otimes f_j)_{mn} = \delta_{mi} \delta_{nj}$.

The space $L^2(\Omega) \otimes L^2(\Omega)$ with Ω a subset of \mathbb{R}^d can be identified with $L^2(\Omega^2)$ through the identification of $u_1 \otimes u_2$ with the function $u_1(x)u_2(y)$.

It is useful for quantum mechanics to consider symmetric and antisymmetric versions of the tensor product:

Definition 9.3. The **symmetric** (resp. **antisymmetric**) tensor product $\mathcal{H} \vee \mathcal{H}$ (resp. $\mathcal{H} \wedge \mathcal{H}$) is the subspace of $\mathcal{H} \otimes \mathcal{H}$ of elements that satisfy $Eu = u$ (resp. $Eu = -u$), where E is the exchange operator, defined by $E(u_1 \otimes u_2) = u_2 \otimes u_1$ and extended by linearity.

Example 9.4. $\mathbb{C}^2 \vee \mathbb{C}^2$ is spanned by $e_1 \otimes e_1, e_1 \otimes e_2 + e_2 \otimes e_1$ and $e_2 \otimes e_2$, and has dimension 3. $\mathbb{C}^2 \wedge \mathbb{C}^2$ is spanned by $e_1 \otimes e_2 - e_2 \otimes e_1$ and has dimension 1.

$L^2(\Omega) \vee L^2(\Omega)$ (resp. $L^2(\Omega) \wedge L^2(\Omega)$) is isomorphic to the subspace of $u \in L^2(\Omega^2)$ such that $u(x, y) = u(y, x)$ (resp. $u(x, y) = -u(y, x)$) for almost all x, y .

A few remarks before continuing:

⁴¹We say that two Hilbert spaces can be identified when there is an isometric isomorphism between them.

- All these definitions are associative, i.e. $(H_1 \otimes H_2) \otimes H_3$ is isomorphic to $H_1 \otimes (H_2 \otimes H_3)$, with the same holding for \vee and \wedge .
- The tensor product \otimes can be extended by bilinearity to a bounded linear map $\otimes : \mathcal{H}_1 \times \mathcal{H}_2 \rightarrow \mathcal{H}_1 \otimes \mathcal{H}_2$, and the same holds for \vee and \wedge .
- If A_1 is an operator that acts on \mathcal{H}_1 and A_2 is an operator that acts on \mathcal{H}_2 , we can define the operator $A_1 \otimes A_2$ that acts on $\mathcal{H}_1 \otimes \mathcal{H}_2$ by $(A_1 \otimes A_2)(u_1 \otimes u_2) = (A_1 u_1) \otimes (A_2 u_2)$ and extend by linearity.
- The dimension of tensor product spaces grows rapidly: $\mathbb{C}^N \otimes \cdots \otimes \mathbb{C}^N$ with n repeats has dimension N^n , so that in practice only a very moderate number of repeats n can be treated explicitly.

9.2 Many-body quantum mechanics

Postulate 4: The Hilbert space of a system composed of two **distinguishable subsystems** 1 and 2 with Hilbert spaces \mathcal{H}_1 and \mathcal{H}_2 is $\mathcal{H}_1 \otimes \mathcal{H}_2$. If A_1 is an operator corresponding to an observable on subsystem 1, then $A_1 \otimes 1_{\mathcal{H}_2}$ is the operator corresponding to the same observable on the composite system (and similarly for A_2).

The Hilbert space of a system composed of two identical **bosons** (resp. **fermions**) with Hilbert space \mathcal{H} is $\mathcal{H} \vee \mathcal{H}$ (resp. $\mathcal{H} \wedge \mathcal{H}$).

Example 9.5. Consider a system with two distinct orthogonal states ψ^\pm , and another with possible states ϕ^\pm . Put two such (distinguishable) systems in contact. A valid state for the composite quantum system is for instance the “Bell state”

$$\frac{1}{\sqrt{2}}(\psi^+ \otimes \phi^- + \psi^- \otimes \phi^+) \quad (9.3)$$

If we measure the first system to be in the state ψ^+ (by measuring an observable that distinguishes between the two states), the composite system collapses to the state $\psi^+ \otimes \phi^-$ (exercise), and the second system is necessarily in the state ϕ^- . On the other hand, if we measure the first particle to be in the state ψ^- , the second particle will be in the state ϕ^+ . We say that the particles are **intricated**.

This example shows that it is generally not possible to speak about the state of a subsystem without specifying the state of all other particles, unlike in classical mechanics. This is analogous to several random variables X_1, \dots, X_N in probability theory, where one cannot know the probability distribution of X_1 without knowing that of all the others. The exception is whenever the composite system is in a non-intricated state $\psi \otimes \phi$ (analogous to independent random variables).

It is a fact of nature that elementary particles are either bosons or fermions. For example, photons are bosons, electrons are fermions. The most important consequence of this is that two bosons are able to occupy the same quantum state, while two fermions are not (the state $\psi \otimes \psi$ belongs to $\mathcal{H} \vee \mathcal{H}$, but not to $\mathcal{H} \wedge \mathcal{H}$). For instance, it is possible to have many photons in the same state (as in lasers), but electrons occupy different electronic states in atoms and molecules (**Pauli exclusion principle**). As we will see, this has profound physical repercussions.

9.3 The many-body electronic Hamiltonian

We now consider N electrons in a molecule composed of $M \geq 1$ nuclei at positions $R_m \in \mathbb{R}^3$ and charge $Z_m > 0$. We will consider the nuclei as classical point particles, even though they should be considered as quantum particles in a fuller description⁴².

Still ignoring spin (we will come to it shortly), the state space of an electron is $L^2(\mathbb{R}^3, \mathbb{C})$. The state space of N electrons is therefore identified with (see Example 9.4)

$$L_{\text{as}}^2(\mathbb{R}^{3N}, \mathbb{C}) = \{\psi \in L^2(\mathbb{R}^{3N}, \mathbb{C}) \mid \psi(x_{p(1)}, \dots, x_{p(N)}) = (-1)^{s(p)} \psi(x_1, \dots, x_N), \forall p \in S_N, x \in \mathbb{R}^{3N}\}, \quad (9.4)$$

where S_N is the group of all permutations of $\{1, \dots, N\}$ and $s(p)$ is the signature of a permutation (number of transpositions). In particular this means that for $N = 2$ the probability density $|\psi(x, x)|^2$ of finding two electrons at the same point in space is zero.

The total Hamiltonian is composed of the kinetic energy of the electron, the electron-nuclei Coulomb attraction, and the electron-electron and nuclei-nuclei Coulomb repulsion:

$$H = -\frac{1}{2} \sum_{n=1}^N \Delta_{x_n} - \sum_{n=1}^N \sum_{m=1}^M \frac{Z_m}{|x_n - R_m|} + \frac{1}{2} \sum_{\substack{n \in \{1, \dots, N\} \\ n' \in \{1, \dots, N\} \\ n \neq n'}} \frac{1}{|x_n - x_{n'}|} + \frac{1}{2} \sum_{\substack{m \in \{1, \dots, M\} \\ m' \in \{1, \dots, M\} \\ m \neq m'}} \frac{Z_m Z_{m'}}{|R_m - R_{m'}|} \quad (9.5)$$

where Δ_{x_n} means the Laplacian with respect to the coordinate x_n only.

9.4 Non-interacting electrons

Let us first ignore completely the electron-electron interaction. The last nuclei-nuclei term is a constant, and therefore we will ignore it too. The resulting Hamiltonian is then of the form

$$H = (h \otimes 1 \otimes \dots \otimes 1) + (1 \otimes h \otimes \dots \otimes 1) + \dots + (1 \otimes 1 \otimes \dots \otimes h), \quad (9.6)$$

with the one-electron Hamiltonian

$$h = -\frac{1}{2} \Delta + V_{\text{nucl}}, \quad (9.7)$$

acting on $L^2(\mathbb{R}^3, \mathbb{C})$, and

$$V_{\text{nucl}}(x) = - \sum_{m=1}^M \frac{Z_m}{|x - R_m|}. \quad (9.8)$$

This Hamiltonian does not couple the different electrons, and therefore its eigenstates are easily obtained from those of h ; indeed, when $N = 2$, if ϕ_1 and ϕ_2 are orthonormal eigenfunctions of h with associated eigenvalues λ_1 and λ_2 , it can be seen (exercise) that

$$\frac{1}{\sqrt{2}} (\phi_1(x)\phi_2(y) - \phi_2(x)\phi_1(y)) \quad (9.9)$$

⁴²Physically, it is justified to consider the nuclei as classical particles because they are much more massive than electrons, so that their wavefunction is strongly localized. This is known as the Born-Oppenheimer approximation, and its mathematical justification involves the tools of semiclassical and adiabatic theory [13]

is a normalized eigenvector of H , with eigenvalue $\lambda_1 + \lambda_2$. More generally,

$$\psi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \sum_{p \in S_N} (-1)^{s(p)} \Pi_{n=1, \dots, N} \phi_{p(n)}(x_n), \quad (9.10)$$

is a normalized eigenvector of H in $L^2_{\text{as}}(\mathbb{R}^{3N}, \mathbb{C})$, with eigenvalues $\lambda_1 + \dots + \lambda_N$. Note that this can also be written as a determinant (called a **Slater determinant**)

$$\psi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \det((\phi_n(x_m))_{n=1, \dots, N, m=1, \dots, N}) \quad (9.11)$$

The bound states of H are therefore obtained by selecting N different bound states of h , and adding their eigenvalues, a massive simplification compared to solving the full N -body Schrödinger equation. Clearly, the ground state of the system is therefore the sum of the lowest N eigenvalues of h : one diagonalizes h and fills the energy levels successively by increasing order, as mandated by the Pauli principle. This is known as the Aufbau (from the German “building up”) principle in chemistry.

Consider now an atom of $N = Z$ protons and electrons. The one-electron Hamiltonian is now

$$h = -\frac{1}{2}\Delta - \frac{Z}{|x|}. \quad (9.12)$$

This is simply a scaling of the hydrogen Hamiltonian seen in Section 1.7; the bound state energies are given by $-\frac{Z}{2n^2}$, $n \in \mathbb{N}$, with multiplicity 1, 4, 10, etc.

9.5 Chemistry and spin

According to the theory developed in the previous section, the ground state of Helium for instance ($N = 2$) would be to put one electron in the 1s orbital, and the other in the 2s orbital (or one of the 2p orbitals). This is a shell structure of 1 space in the first shell, 4 in the second, 9 in the third, etc. For instance, since chemistry is largely dictated by the shell structure of atoms, this would predict that hydrogen ($N = 1$, first shell filled) would be chemically similar to boron ($N = 5$, second shell filled). This is not very much not the case in practice (in ambient conditions, hydrogen is a diatomic gas, boron is a solid metalloid). Instead, it is found that helium ($N = 2$) is very similar to Neon ($N = 10$): both are monoatomic noble gases. Similar trends appear in other parts of the periodic table: it appears there is a factor of 2 missing, and that not one but two electrons can occupy the same quantum state. This mysterious factor of two comes from the spin degree of freedom, that we have neglected up until now.

The spin is an intrinsic additional degree of freedom that each electron possesses, with no classical analogue. The spin by itself has two possible states, “spin up” and “spin down”, and is modeled with Hilbert space \mathbb{C}^2 . The state space of one electron, which has both position and spin degrees of freedom, is

$$L^2(\mathbb{R}^3, \mathbb{C}) \otimes \mathbb{C}^2 \simeq L^2(\mathbb{R}^3, \mathbb{C}^2). \quad (9.13)$$

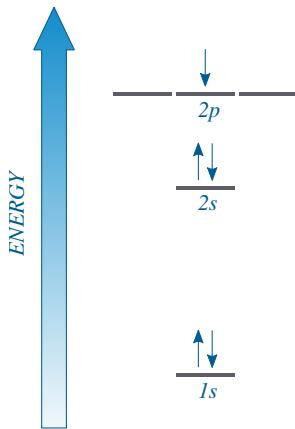
$|\psi(x)_\pm|^2$ gives the probability of finding the electron at position x in the spin state \pm . In the absence of magnetic fields⁴³ or strong relativistic effects, the spin does not interact with the position

⁴³In the presence of a magnetic field, spins tend to align to the direction of the magnetic field. This has many important consequences, and is used for instance in magnetic resonance imaging.

degrees of freedom (the Hamiltonian is such that $(H\psi)_{\pm}$ only depends on ψ_{\pm}), so that a system of N electrons still has the same N -body Hamiltonian (9.5), but now on the state space $\bigwedge_{i=1}^N L^2(\mathbb{R}^3, \mathbb{C}^2)$. This means that the ground state of a system of non-interacting electrons will fill 2 electrons in the lowest energy state (one spin up, and one spin down), 2 electrons in the next lowest, etc.

Spin highlights a non-intuitive structural consequence of quantum mechanics: **extra degrees of freedom have an indirect impact** on the system, simply by the Pauli principle, even if they have no explicit interactions.

The Aufbau principle and the ordering of electron states of the hydrogen atom gives the theoretical basis for the labelling scheme used in chemistry. For instance, boron has 5 electrons, and its electronic structure is given in chemistry textbooks as $1s^2 2s^2 2p^1$: this means 2 electrons on the $1s$ orbital ($n = 1, \ell = 0$, with 2 spaces), 2 electrons on the $2s$ orbital ($n = 2, \ell = 0$, with 2 spaces) and 1 on the $2p$ orbital ($n = 2, \ell = 1$, with 8 spaces).



Electronic structure of Boron $1s^2 2s^2 2p^1$, justified by the Aufbau principle

Picture from https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/

Note that the electronic levels of the hydrogen atom predict an energy of $-\frac{Z}{2n^2}$, and therefore the same energy for the $2s$ and $2p$ orbital, so that the structures $1s^2 2s^2 2p^1$ and $1s^2 2s^1 2p^2$ (for instance) should have the same energy. In chemistry, this degeneracy is settled by Madelung's rule⁴⁴, which states that the ordering of shells is by increasing $n + \ell$, so that the $2s$ has lower energy than the $2p$ orbital. Even worse, the $4s$ orbital ($n = 1, \ell = 0$) has lower energy than the $3d$ orbital ($n = 3, \ell = 2$), directly contradicting the $-\frac{Z}{2n^2}$ result. This discrepancy turns out to be caused by electron-electron interaction, which we have ignored until now.

9.6 The interacting N -body problem

We saw that neglecting electron-electron interaction completely was already able to give a reasonable qualitative description of the electronic structure of atoms, and in particular explains most of their shell structure. However, it is not complete, and electron-electron interaction plays a key role, both qualitative and quantitative, in many processes (one of the the simplest being the Madelung $n + \ell$ rule). The treatment of electron-electron interaction however massively complicates the solution of the N -body problem, which was trivial in the non-interacting case.

⁴⁴Also called Klechkowski's rule, especially in the French literature.

The N -body state space $L^2_{\text{as}}(\mathbb{R}^{3N}, \mathbb{C})$ (ignoring spin once more) is a huge and incomprehensible beast: even if we could compute $\psi(x_1, \dots, x_N)$, simply storing a discretization of it, or plotting it is impossible. In the non-interacting problem, the reduction to N functions of \mathbb{R}^3 instead of one function of \mathbb{R}^{3N} was a massive simplification, and allowed interpretative concepts (such as the chemical notion of orbitals) to be used. This was realized very early on in the history of quantum mechanics: in 1929 already Paul Dirac wrote

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

These “approximate practical methods” became much more practical with the advent of computers, and nowadays a very large variety of approximate methods exist to treat the N -body problem.

Among these methods, probably the simplest is the Hartree-Fock method (1935). Briefly, it is a (non-linear) variational ansatz based on the variational principle (going back to ignoring spin for notational simplicity)

$$\inf_{\psi \in L^2_{\text{as}}(\mathbb{R}^{3N}, \mathbb{C}), \|\psi\|=1} \langle \psi | H \psi \rangle \quad (9.14)$$

for the lowest eigenvalue (ground state) of the many-body Hamiltonian (9.5). Instead of minimizing over the whole (huge) Hilbert space, or a linear subspace (like in the Galerkin method), we restrict to the (non-linear) subset of those many-body wavefunctions that can be written as Slater determinants:

$$\psi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \det((\phi_n(x_m))_{n=1, \dots, N, m=1, \dots, N}) \quad (9.15)$$

with $\langle \phi_n | \phi_m \rangle_{L^2(\mathbb{R}^{3N}, \mathbb{C})} = \delta_{ij}$. We can then compute the energy $\langle \psi | H \psi \rangle$ explicitly as a function of the ϕ_n , which turns out to be:

$$\langle \psi | H \psi \rangle = \underbrace{\sum_{n=1}^N \langle \phi_n | h \phi_n \rangle}_{\text{non-interacting}} + \underbrace{\frac{1}{2} \int_{\mathbb{R}^6} \frac{\rho(x)\rho(y)}{|x-y|} dx dy}_{\text{direct (Hartree)}} - \underbrace{\frac{1}{2} \int_{\mathbb{R}^6} \frac{\sum_{n=1}^N |\phi_n(x)\phi_n(y)|^2}{|x-y|} dx dy}_{\text{exchange (Fock)}}. \quad (9.16)$$

where

$$\rho(x) = \sum_{n=1}^N |\phi_n(x)|^2 \quad (9.17)$$

is the total electronic density. The first term is simply the non-interacting energy of the one-body Hamiltonian $h = -\frac{1}{2}\Delta + V_{\text{nucl}}$; if there was only this term the minimum (which would be exact) would be achieved by taking for ϕ_n the N lowest energy states of h . The Hartree term can be interpreted as the electrostatic energy of electrons in their *own* electric potential. The third (Fock) term has no easy interpretation; note however that for $N = 1$ it compensates the double-counting

Hartree term. With this expression of the energy $\langle \psi | H \psi \rangle$ at hand, we can then minimize it with respect to the orbitals ϕ_n . The first-order optimality conditions are

$$h_\phi \phi_n = \sum_{m=1}^N \lambda_{mn} \phi_m, \quad (9.18)$$

where λ_{mn} is the Lagrange multiplier associated with the constraint $\langle \phi_m | \phi_n \rangle = \delta_{mn}$, and

$$(h_\phi \phi)(x) = -\frac{1}{2} \Delta \phi(x) + V_{\text{nucl}}(x) \phi(x) + \left(\int_{\mathbb{R}^3} \frac{\rho(y)}{|x-y|} dy \right) \phi(x) - \int_{\mathbb{R}^3} \sum_{n=1}^N \frac{\phi_n(x) \overline{\phi_n(y)}}{|x-y|} \phi(y) dy. \quad (9.19)$$

This is a **mean-field** Hamiltonian: each electron is subject to an external potential V_{nucl} , plus a term resulting from the effect of all other electrons. The Hartree term contributes a local electrostatic potential; the last (Fock) term gives rise to a *non-local* (integral) operator.

In practice, the orbitals ϕ_n are discretized on a basis set (a standard Galerkin procedure). The problem (9.18) is then reformulated as a non-linear eigenvalue problem, and can be solved using specialized iterative algorithms. The Hartree-Fock method, and variants like Kohn-Sham density functional theory (DFT, 1965), are very successful at describing quantitatively many molecules and materials, and are extensively used in physics in chemistry⁴⁵. We will not go deeper here; the interested reader is referred to [5, 6, 7].

9.7 Quantum information and computing

We have seen that the state space of a system of N distinguishable qubits, each with state space \mathbb{C}^2 , can be identified with \mathbb{C}^{2^N} . It is conventional to label the one-body states as $|0\rangle = (1, 0)$ and $|1\rangle = (0, 1)$ (this is just notation, and has nothing to do with the numerical values of 0 and 1; in particular, $\| |0\rangle \| = 1$).

The state of classical systems of several bits is given by binary strings like 01001 with $N = 5$. In the quantum case, the state $|01001\rangle = |0\rangle \otimes |1\rangle \otimes |0\rangle \otimes |0\rangle \otimes |1\rangle$ is a valid quantum state, but so are linear combinations like

$$\frac{1}{\sqrt{2}}|01001\rangle - \frac{i}{\sqrt{2}}|10011\rangle, \quad (9.20)$$

resulting in a state space \mathbb{C}^{2^N} . This opens up intriguing possibilities: is it possible to design an experiment that, by setting up the state of a system of N qubits in a specific way, is able to explore the exponentially large state space to perform useful computations on them faster than what would classically be possible? This is the topic of **quantum computing**.

What, according to quantum mechanics, can we do with qubits? Essentially, submit them to an evolution in time, and measure them at the end. This can be formalized using the notion of quantum gates, analogous to classical logical gates. A logical gate operates on one or more bits and sets the output state according to a logical transformation of the input state (encoded by a “truth table”).

⁴⁵The papers describing the theory and implementation of Kohn-Sham DFT are among the most highly cited in all of science. Globally, these simulations occupy about one fourth of all the scientific computing time on supercomputers. About 50 thousand papers per year report results of simulations using DFT.

A quantum gate operates on one or more qubits, and encodes a unitary transformation (which, hopefully, can be realized physically by letting the system evolve with a well-chosen Hamiltonian).

For instance, the NOT logical gate operates on a single qubit and is encoded by the unitary $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$.

However, in contrast to the classical case, not all logical operations are allowed. For instance, it is not possible to set a qubit to be in a particular state (say $|1\rangle$), because this would be encoded by the operation $\begin{pmatrix} 0 & 0 \\ 1 & 1 \end{pmatrix}$, which is not unitary. Similarly, the controlled NOT gate (apply the NOT operation to a qubit if another qubit is 1) is possible, but the AND gate is not (it is not even reversible, so cannot be unitary).

Since the state space of a qubit, \mathbb{C}^2 , is richer than the classical logical values $\{0, 1\}$, it is also possible to perform operations that have no analogues in classical logic, such as the Hadamard gate $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$. A quantum algorithm, like a classical computer circuit, is a succession of gates and the specification of a measurement at the end.

It is not at all obvious that useful computations can result from this, since many primitives of usual computing (some logical operations, but also setting, copying or deleting state) are not expressible as unitary transforms. Nevertheless, extremely clever quantum algorithms are able to yield measurements that, statistically, provide some useful information. The most striking result is probably Shor's algorithm, which uses a number of gates (and therefore a runtime) polynomial in N to find the prime factors of an integer of size $O(2^N)$, with a negligible error rate. This algorithm is highly non-trivial (quantum algorithms look nothing like classical algorithms), and was only discovered in 1994, nearly 70 years after the discovery of quantum mechanics. Even now, only a very small set of interesting problems is known to be solvable efficiently on quantum computers.

The practical realization of quantum algorithms is a herculean engineering task, because of the need to keep qubits entangled with each other, but not with their environment. As of 2023, “quantum supremacy” (building a quantum computer that solves a problem that would be impractically slow to solve with a classical computer) has essentially been achieved, but this is only on specially constructed problems chosen for that purpose. The largest integer ever factored using Shor's algorithm remains 21, and it remains to be seen whether a quantum computer that can solve actually useful problems faster than a classical computer can be constructed.

Summary

The state space of many-body systems is obtained by taking tensor products of Hilbert spaces, possibly including symmetry or antisymmetry constraints in the case of systems of bosons or fermions. Non-interacting systems can be solved easily, but the solution of the full N -body problem is completely out of reach. Approximation methods allow for practical computations of systems with a large number of electrons.

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