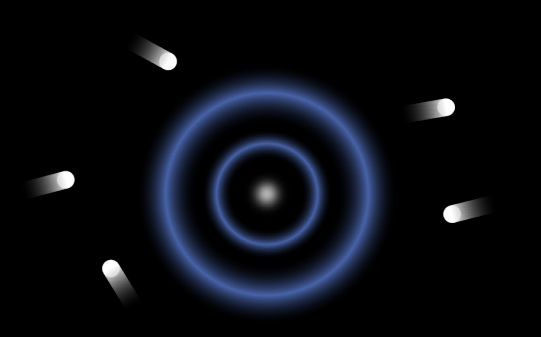


Notes on quantum mechanics



Mathematical foundations

Field (Körper): a set \mathbb{K} is a field when an addition $\mathbb{K} \times \mathbb{K} \rightarrow \mathbb{K}, (x, y) \rightarrow x + y$ and multiplication $\mathbb{K} \times \mathbb{K} \rightarrow \mathbb{K}, (x, y) \rightarrow xy$ can be defined in such a way that both operations are associative, commutative and there are neuter and inverse elements. (Examples: $\mathbb{R}, \mathbb{Q}, \mathbb{C}$).

Group: a group is a set G with an operation \circ , such that a) \circ is associative [$a \circ (b \circ c) = (a \circ b) \circ c$], b) there is a neutral element $\forall a \in G$ such that $e \circ a = a \circ e = a$, c) $\forall a \in G$ there is an inverse element a^{-1} such that $a^{-1} \circ a = a \circ a^{-1} = e$. The group is also *Abelian* if $a \circ b = b \circ a$ (commutativity). Examples of groups: $(\mathbb{C}, +)$, $(\mathbb{R} \setminus \{0\}, \cdot)$

Vector space: a set V is a vector space over a field \mathbb{K} if there is an addition $V \times V \rightarrow V : (x, y) \rightarrow x + y$ and a scalar multiplication $\mathbb{K} \times V : (\lambda, x) \rightarrow \lambda x$. The scalar multiplication should satisfy: a) $\lambda(x + y) = \lambda x + \lambda y$; b) $(\lambda + \mu)x = \lambda x + \mu x$; c) $(\lambda\mu)x = \lambda(\mu x)$; d) $1x = x$, for all $\lambda, \mu \in \mathbb{K}$ and $x, y \in V$.

Linear independence: The vectors ψ_1, ψ_2, \dots are linearly independent when the equation $\sum c_n \psi_n = 0$ only has the trivial solution $c_1 = c_2 = \dots = 0$. The maximum number of linearly independent vectors is called the *dimension* of the vector space.

Basis and coordinates: there are linearly independent vectors $\{e_1, e_2, \dots\} \subset V$ for which each vector $v \in V$ can be written as a linear combination of basis vectors: $v = \sum_i x_i e_i$. There is always a bijective transformation between two given bases. The x_i are the coordinates of the vector, usually written as a column vector (or transposed row vector to save space). Example: polynomials $f(X)$ can form a vector space; for the polynomial $f(X) = 1 + 2X + 3X^2$, the coordinates in the basis $\{1, X, X^2\}$ are $(1, 2, 3)^T$, but in the basis $\{1, 1 + X, 1 + X + X^2\}$, they are $(-1, -1, 3)^T$.

Metric: a metric on a set X is a map $d : X \times X \rightarrow \mathbb{R}$ such that a) is positive definite, $d(x, y) \geq 0$ (it is zero when $x = y$); b) symmetric, $d(x, y) = d(y, x)$; c) satisfies the triangle inequality $d(x, z) \leq d(x, y) + d(y, z)$, for $x, y \in X$ (going from x to z with a detour in y is longer than going directly).

Norm: a norm over a real or complex vector field V is a map $\|\cdot\| : V \rightarrow \mathbb{R}, v \rightarrow \|v\|$ such that its a) positive definite, b) homogeneous, $\|\lambda x\| = |\lambda| \|x\|$; c) satisfies the triangle inequality. There are many possible (equivalent) norms that can be defined in a vector space. Example: the Euclidean norm of a n -dimensional vector space $\|x\| = \sqrt{|x_1|^2 + |x_2|^2 + \dots + |x_n|^2}$ (L2 norm).

Matrix: arrangement of $M \times N$ numbers of a field \mathbb{K} , ordered in M rows and N columns. Matrices also form a vector space \mathcal{M}_{MN} over \mathbb{K} , with element-wise sum and multiplication with scalars,

$$+ : \mathcal{M}_{MN} \times \mathcal{M}_{MN} \rightarrow \mathcal{M}_{MN}, (\mathbf{A}, \mathbf{B}) \rightarrow (a_{ij} + b_{ij})$$

$$\cdot : \mathbb{K} \times \mathcal{M}_{MN} \rightarrow \mathcal{M}_{MN}, (\lambda, \mathbf{A}) \rightarrow (\lambda a_{ij})$$

and a matrix multiplication $\mathcal{M}_{LM} \times \mathcal{M}_{MN} \rightarrow \mathcal{M}_{LN}, (\mathbf{A}, \mathbf{B}) \rightarrow \mathbf{AB} = (\sum_i a_{ij} b_{jk})$. Matrix multiplication a) is associative, $(\mathbf{AB})\mathbf{C} = \mathbf{A}(\mathbf{BC})$; b) is right distributive $(\mathbf{A} + \mathbf{B})\mathbf{C} = \mathbf{AC} + \mathbf{BC}$; c) is left distributive $\mathbf{A}(\mathbf{B} + \mathbf{C}) = \mathbf{AB} + \mathbf{AC}$; d) has a neutral element, the identity matrix $\mathbf{I} = (\delta_{ij})$, such that $\mathbf{AI} = \mathbf{IA} = \mathbf{A}$; e) in general, is non-commutative. The transpose of a matrix exchanges rows and columns, and its rules are a) $(\mathbf{AB})^T = \mathbf{B}^T \mathbf{A}^T$; b) $(\mathbf{A} + \mathbf{B})^T = \mathbf{A}^T + \mathbf{B}^T$; c) $(\mathbf{A}^T)^T = \mathbf{A}$.

Vector space of functions. The set of wave functions forms a complex vector space \mathcal{H} . If ψ, ϕ are vectors (wave functions) and c, d are complex numbers, then the linear combination $c\psi + d\phi$ is also in \mathcal{H} (superposition principle). There is a null element.

Scalar product in function vector space: $\langle \phi, \psi \rangle = \int d^3x \phi^*(\mathbf{x})\psi(\mathbf{x})$. This is the continuous and complex analogy to the discrete scalar product $\langle \vec{a}, \vec{b} \rangle = \sum_i a_i b_i$ in real space. The norm of the function vector space is then $\|\psi\|^2 = \langle \psi, \psi \rangle$.

Hilbert space: a (complete metric) vector space with a scalar product. One can define an isomorphism between functions (wave mechanics) and matrices (matrix mechanics) as basis for the Hilbert space. A full definition of a Hilbert space requires the definition of a Cauchy sequence.

Addition of Hilbert spaces: two Hilbert spaces can be added as $\mathcal{H}_1 \oplus \mathcal{H}_2$. A vector in the new space is the sum of the vectors in each space, and the basis vectors are united in a bigger set. Example: (anti)symmetrization of wave functions for two particles.

Tensor product of two Hilbert spaces: two Hilbert spaces can form a new Hilbert space $\mathcal{U} \otimes \mathcal{V}$. The basis of the two spaces are combined with the tensor product, and the vectors of the new space are developed in terms of the new basis.

Linear operators: an operator \hat{A} is linear when $\hat{A}(c\phi + d\psi) = c\hat{A}\phi + d\hat{A}\psi$, for c, d complex and ϕ, ψ vectors in Hilbert space.

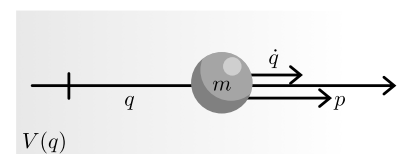
Commutators: for many operators, $\hat{A}(\hat{B}\psi) \neq \hat{B}(\hat{A}\psi)$. Then, the non-commutative part is characterized by an antisymmetric commutator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = -[\hat{B}, \hat{A}]$. The correspondence principle or first quantization implies that the Poisson brackets for of classical mechanics become commutators in quantum mechanics: $\{F, G\} \rightarrow \frac{i}{\hbar}[\hat{F}, \hat{G}]$.

Adjoint of an operator: defined through $\langle \phi, \hat{A}\psi \rangle = \langle \hat{A}^\dagger \phi, \psi \rangle$, or in Dirac notation, $\langle \phi | \hat{A} | \psi \rangle = \langle \psi | \hat{A}^\dagger | \phi \rangle^*$. In matrix representation, \hat{A} is transposed and the complex conjugate applied. The vector $|\psi\rangle$ is called a *ket*, and $\langle \psi |$ is called a *bra*. Bras are the dual vector space of adjoint vectors to kets, such that $\langle \phi | \psi \rangle^* = \langle \psi | \phi \rangle$.

Hermitic operators: typically defined when $\hat{A} = \hat{A}^\dagger$, i.e., when they are self-adjoint: $\langle \phi | \hat{A} | \psi \rangle = \langle \psi | \hat{A} | \phi \rangle^*$. Physically-relevant quantities are obtained through the application of Hermitic operators. Warning: depending on the definition region, not all hermitic operators have a self-adjoint development: for example, for non-bound states, there are no discrete basis vectors \implies the vector space cannot be normed.

From classical to quantum mechanics

Newton's equations: a particle in unidimensional motion along a coordinate q in a potential $V(q)$ has a trajectory $q(t)$ determined by the equation of motion $m\ddot{q} = -\frac{\partial V}{\partial q}$, under the initial conditions $q(t_0)$ and $\dot{q}(t_0)$.



Lagrangian formulation: the same particle has a Lagrangian $L(q, \dot{q}) = T - V = \frac{1}{2}m\dot{q}^2 - V(q)$, forming the action $W = \int_{t_0}^{t_1} d\tau L(q(\tau), \dot{q}(\tau))$. Minimizing the action ($\delta W = 0$) with the boundary conditions $\delta q(t_0) = \delta q(t_1) = 0$, one obtains the Euler-Lagrange equation $\frac{d}{dt} \frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q} = 0$. Introducing the Lagrangian, one obtains Newton's equations of motion.

Noether's theorem: if a system has a continuous symmetry property, then there are corresponding quantities whose values are conserved in time. If the Lagrangian doesn't depend on a given coordinate (=ignorable coordinate), then the corresponding generalized momentum is conserved in time.

Hamiltonian formulation: the generalized momentum is $p = \partial L / \partial \dot{q}$, with which one builds the Hamiltonian with a Legendre transformation $H(q, p) = p \dot{q}(p) - L(q, \dot{q}(p))$. The goal is to change variables $\dot{q} \rightarrow p$. Now, the equations of motion are two coupled first-order differential equations:

$$\dot{p} = -\frac{\partial H}{\partial q}; \dot{q} = \frac{\partial H}{\partial p}.$$

Poisson's brackets: for functions $A(p, q)$ and $B(p, q)$, the Poisson bracket is defined as

$$\{A, B\}_P = \frac{\partial A}{\partial q} \frac{\partial B}{\partial p} - \frac{\partial A}{\partial p} \frac{\partial B}{\partial q}. \text{ Examples: } \{p, p\}_P = \{q, q\}_P = 0, \{q, p\}_P = 1.$$

Hamiltonian and energy: if the Hamiltonian doesn't depend on time, $\frac{dH}{dt} = \frac{\partial H}{\partial t} + \{H, H\}_P = 0$.

Heisenberg's fundamental quantization: $\{A, B\}_P \rightarrow \frac{1}{i\hbar} [\hat{A}, \hat{B}]$ (dynamical quantities become operators). For position and momentum, $[\hat{q}, \hat{p}] = i\hbar$.

Definitions in quantum mechanics

States and probabilities: the state of a quantum system is described by a vector $|\Psi\rangle$ in Hilbert space. The probability density is, in wave function and position representation, $|\psi(x)^* \psi(x)|$, such that

$$\langle \Psi | \Psi \rangle = \|\Psi\|^2 = \int_{-\infty}^{\infty} |\Psi^*(x) \Psi(x)| dx = 1 \text{ (the probability of finding the system somewhere is 1).}$$

Expectation (mean) value of a quantity: $O = \langle \Psi | \hat{O} | \Psi \rangle$

Eigenvalues and eigenstates: $|\Psi\rangle$ is an eigenstate and O is an eigenvalue of the operator \hat{O} , if $\hat{O} |\Psi\rangle = O |\Psi\rangle$. The eigenstates of a self-adjoint operator form a basis of the Hilbert space.

Uncertainty principle: $|\Psi\rangle$ cannot be the simultaneous eigenstate of two non-commuting operators \hat{A}, \hat{B} . Then, the associated uncertainties to the measurements in both quantities are

$$\Delta A \Delta B \geq \frac{1}{2} \left| \langle \Psi | [\hat{A}, \hat{B}] | \Psi \rangle \right|. \text{ Example: } \Delta p \Delta q \geq \hbar/2.$$

Position representation: position operator: $\hat{q} |q\rangle = q |q\rangle$, with normalization $\langle q' | q \rangle = \delta(q - q')$.

Completeness relation: $1 = \int dq |q\rangle \langle q|$. The Schrödinger wave function is the projection of the state in position or coordinate representation: $\psi(q) = \langle q | \Psi \rangle$. (Convention of norm. factor only in p)

Momentum representation: momentum operator: $\hat{p} |p\rangle = p |p\rangle$, with chosen normalization

$\langle p' | p \rangle = 2\pi \hbar \delta(p - p')$. Completeness relation: $1 = \int \frac{dp}{2\pi \hbar} |p\rangle \langle p|$. Coordinate representation of the momentum eigenstate: $\langle q | p \rangle = e^{ipq/\hbar} \implies$ satisfaction of uncertainty principle, Fourier transform. (Convention of norm. factor only in p)

Time evolution of an operator: $i\hbar \frac{d\hat{O}}{dt} = [\hat{O}, \hat{H}]$, with time-independent state vectors, and a time evolution operator $\hat{U}(t, t_0) = e^{-i\hat{H}(t-t_0)/\hbar}$.

Simple quantum systems

Schrödinger equation. 4D position of a particle: $(x_\mu) = (-ct, \vec{r})$. 4D energy-momentum: $(p_\mu) = (-E/c, \vec{p})$. With the first quantization (commutator) one can deduce that $(p_\mu) = -i\hbar(\partial_\mu) = -i\hbar(-1/c \partial_t, \nabla)$, with which one can see $\hat{E} = i\hbar \partial_t$. [Verif. of commutator for space in 1D:

$[x, \hat{p}_x]\psi = -i\hbar x \partial_x \psi + i\hbar \partial_x(x\psi) = i\hbar\psi$. The Hamiltonian describes the total energy of the system, which means $\hat{E}\Psi(\mathbf{x}, t) = \hat{H}\Psi(\mathbf{x}, t)$ (*time-dependent Schrödinger equation*), with $\hat{E} = i\hbar\partial_t$ and $\hat{H} = \hat{\mathbf{p}}^2/(2m) = -\hbar^2/(2m)\nabla^2$.

Wave mechanics of the free particle: a solution of the Schrödinger equation for a free particle is a plane wave: $\psi(t, \mathbf{x}) = A \exp\left[-\frac{i}{\hbar}(Et - \mathbf{p} \cdot \mathbf{x})\right] = A \exp\left[\frac{i}{\hbar}p_\mu x^\mu\right]$. One can also start with this plane wave solution (De Broglie waves, experimentally obtained) and build the operators with it. The superposition of those waves forms a full solution: $\psi(t, \mathbf{x}) = \kappa \int_{\mathbb{R}^3} \tilde{\psi}(\mathbf{k}) e^{i(\mathbf{p} \cdot \mathbf{x} - \omega t)} d^3k = \kappa \int_{\mathbb{R}^3} \tilde{\psi}(t, \mathbf{p}) e^{i\mathbf{p} \cdot \mathbf{x}/\hbar} d^3p$, with $\tilde{\psi}(t, \mathbf{p}) = e^{-iEt/\hbar} \tilde{\psi}(0, \mathbf{p})$. Then, we have that the wave function in position space is the Fourier transform of the wave function in momentum space, and vice versa: $\tilde{\psi}(t, \mathbf{p}) = \kappa' \int_{\mathbb{R}^3} \psi(t, \mathbf{x}) e^{-i\mathbf{p} \cdot \mathbf{x}/\hbar} d^3x$. The constants κ and κ' can be selected in several ways, e.g., symmetrically: $\kappa = \kappa' = (2\pi\hbar)^{-d/2}$ for d dimensions. For a free particle, the initial wave function is a free parameter. The Fourier transform automatically satisfies the uncertainty principle.

Stationary-state Schrödinger equation with potential: $\hat{H} = \hat{T} + \hat{V} = -\hbar^2/(2m)\nabla^2 + V(\mathbf{x})$
 $\implies E\psi(\mathbf{x}) = -\hbar^2/(2m)\nabla^2\psi(\mathbf{x}) + V(\mathbf{x})\psi(\mathbf{x})$

Particle in an infinite well: potential: $V(\mathbf{x}) = \begin{cases} 0, & 0 < x < a; 0 < y < b; 0 < z < c \\ \infty, & \text{elsewhere} \end{cases}$

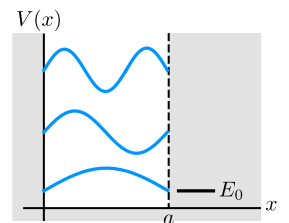
Inside of the box, the Schrödinger equation is the same as the free particle, and it can be reduced by separation of variables (Ansatz: $\psi(x, y, z) = \psi(x)\psi(y)\psi(z)$) into $\partial_i^2\psi(x_i) + k_i^2\psi(x_i) = 0$, which has solutions $\psi_i(x_i) = A_i \sin(k_i x_i + \delta_i)$, or $\psi(\mathbf{x}) = A \sin(k_1 x + \delta_1) \sin(k_2 y + \delta_2) \sin(k_3 z + \delta_3)$ (standing waves, bound states). The constants δ_i are determined by the boundary conditions

$\psi(0, y, z) = \psi(x, 0, z) = \psi(x, y, 0) = 0 \implies \delta_i = 0$ and

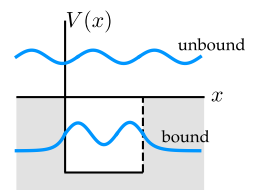
$\psi(a, y, z) = \psi(x, b, z) = \psi(x, y, c) = 0 \implies k_i = n_i \pi / L_i$, where $L_i = a, b, c$ and n_i are *quantum numbers*, i.e., non-zero integers for which the wave function exists (several possible solutions). The constant A is

determined by normalization: $1 = \int_0^a \psi_1^* \psi_1 dx \int_0^b \psi_2^* \psi_2 dy \int_0^c \psi_3^* \psi_3 dz \implies |A| = \sqrt{8/(abc)}$. With the full

solution, the energy is $E_{n_1 n_2 n_3} = \frac{\hbar^2}{2m} [(n_1 \pi/a)^2 + (n_2 \pi/b)^2 + (n_3 \pi/c)^2]$. The minimum energy for which there is a non-trivial solution is $E_0 = \hbar^2 \pi^2 / (2m)$, and it is called the *ground state*.

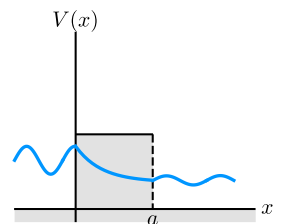


Finite well, atoms: the Schrödinger equation has sinusoidal solution inside of the well for $-V_0 < E < 0$; outside, the solution is a vanishing exponential: the state is bound. For $E > 0$, the solution is a combination of sine waves: it's unbound. In atoms, the proton creates an electrostatic potential well for the electrons. The energy required for an electron to go from a bound state to the minimum unbound state is the *ionization energy*. In bound states of an atom, the electron can jump to a higher energy level by absorbing a photon that has an energy $\Delta E = h\nu$, and it can jump to a lower energy level by emitting a photon with that energy. The collection of all the energy transitions forms an *spectrum* (both absorption and emission form spectra).

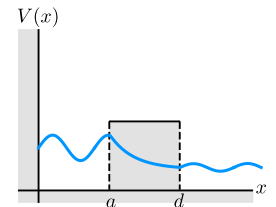


Quantum tunneling: with a 1D finite potential wall, the Schrödinger equation has a sinusoidal solution for the regions with $V = 0$ (free particle), and an exponential decrease inside the wall. An incoming free particle from the left of the wall is partially reflected, and partially transmitted through the wall (although with exponential decay), emerging as a free particle again beyond the wall (with lower amplitude). The probability of finding the particle across the wall is not zero \implies quantum tunneling. The transmission coefficient (amplitude of transmitted wave) is

$T(E) \propto e^{-2a\sqrt{2m(V_0 - E)/\hbar}}$, for low energy levels.



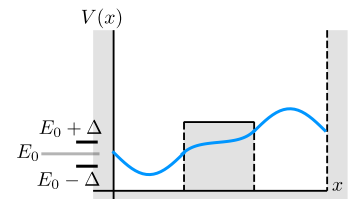
Alpha decay: in an atomic nucleus, the potential is roughly constant (residual attractive strong force). Outside of the nucleus, the Coulomb potential dominates (decreases with $\propto r^{-2}$). In between, there is a potential barrier. In heavy nuclei ($> \text{Ni}$), an α particle (He nucleus = two protons + two neutrons) can tunnel out of the nucleus. The heavy nucleus is therefore not fully stable and it can decay into a lighter isotope and the emission of an alpha particle.



Perturbations: consider a Hamiltonian with a perturbation $\hat{H} = \hat{H}^0 + \hat{H}^1$ (superindices indicate smaller terms). The states can be developed into a power series $|\psi_n\rangle = |\psi_n^0\rangle + |\psi_n^1\rangle + \dots$, as well as the energy states $E_n = E_n^0 + E_n^1 + \dots$, where n is a quantum number. The perturbed states are chosen to be orthonormal to the unperturbed state, i.e., $\langle \psi_n^0 | \psi_n \rangle = 1 \implies \langle \psi_n^0 | \psi_n^k \rangle = 0$ for $k \neq 0$. The Schrödinger equation is $\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle$. Substituting the series development up to zeroth order (keeping superindices 0,0) we get the unperturbed equation $\hat{H}^0 |\psi_n^0\rangle = E_n^0 |\psi_n^0\rangle$ (for which the solution is known). Keeping up to first order terms (superindices up to 0,1) we get $\hat{H}^0 |\psi_n^1\rangle + \hat{H}^1 |\psi_n^0\rangle = E_n^0 |\psi_n^1\rangle + E_n^1 |\psi_n^0\rangle$. Bra-ing the first order equation with $\langle \psi_n^0 |$ and using orthonormality, one gets the first-order energy correction $E_n^1 = \langle \psi_n^0 | \hat{H}^1 | \psi_n^0 \rangle$.

Degeneration: consider a Hamiltonian \hat{H}^0 that produces energy levels that only depend on one quantum number E_n , but the state contains more than one quantum number, e.g., $|n, l\rangle$. This can happen if \hat{H}^0 contains symmetries, that is, when \hat{H}^0 operates on $|n, l\rangle$, it only brings n out. Then, the energy levels are said to be *degenerate*, because different values of l , i.e., different states that share the same n have the same energy. If now the Hamiltonian is perturbed with \hat{H}^1 , such that it contains an operator \hat{L} that does bring out the other quantum number l , the energy correction will depend on l . Then, the energy levels *split* and the degeneration is broken.

Electrons in a molecule: a double finite potential well can be used as a rudimentary model for the nuclei of a simple molecule. Near each nucleus, the electrons are bound, and the wave function in the simple model looks like a sine function. In the potential barrier, where the electron feels the attraction of both nuclei in opposite directions, there is a combination of exponential functions. Compared to the ground state of the infinite potential well E_0 , the energy levels of the electrons in the lowest energy states in each atom feel a perturbation. The perturbation causes both a positive and negative shift in the energy levels. The ground state energy for the electrons in the molecule can be lower than the ground state energy of individual atoms \implies chemical bond.



Introduction to quantum statistics

Multiple identical particle systems: consider two identical particles with Hilbert spaces \mathcal{H}_1 and \mathcal{H}_2 . The Hilbert space of the system is the tensor product of the components: $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$. The state of the whole system is then based on the tensor product of the components: $|n_1 n_2\rangle = |n_1\rangle \otimes |n_2\rangle$. However, since the particles are identical, the state of the system must not depend on the order of the tensor product of the states of the components. The state of the system should then be a combination of states in different orders. There are two ways of doing this: symmetrization and antisymmetrization. In a symmetric total wave function, $\psi(\xi_1 \xi_2) = \psi(\xi_2 \xi_1)$ (where ξ_i is each particle) and $\psi(\xi_1 \xi_2) = -\psi(\xi_2 \xi_1)$ in an antisymmetric wave function.

Spin: intrinsic angular momentum of a given particle (intrinsic symmetry). Usually represented by vectors, with matrix spin operators. For example, for the spin of an electron, whose quantum number can be either $-1/2$ or $1/2$, one can use $(0,1)^T$ and $(1,0)^T$ as states, and the Pauli matrices as operators.

Bosons: particles such that the collective state is symmetrical: $|n_1 n_2\rangle = \frac{1}{\sqrt{2}} (|n_1\rangle \otimes |n_2\rangle + |n_2\rangle \otimes |n_1\rangle)$.

Here, n represents the quantum number(s) of each particle, and the subindex labels each particle. Examples: photons, α particles (superfluidity of He_4). In general, particles with integer spin.

Fermions and Pauli's exclusion principle: fermions are particles such that the collective state is antisymmetrical: $|n_1 n_2\rangle = \frac{1}{\sqrt{2}} (|n_1\rangle \otimes |n_2\rangle - |n_2\rangle \otimes |n_1\rangle)$. Examples: protons, electrons, neutrons. In general, particles with semi-integer spin. If $n_1 = n_2$, the collective state vanishes. This means that two fermions cannot have the same quantum numbers at the same time (*Pauli's exclusion principle*).

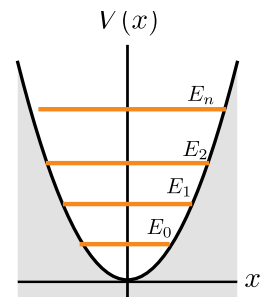
Fermions and atoms: in an atom (simple model: potential well), the Hamiltonian doesn't explicitly depend on the spin \implies the state of two atoms can be factor into the spatial wave functions and the spin vectors. The total state must be antisymmetric, but this can be achieved with either a symmetric space function and antisymmetric spin (same level, different spin), or with an antisymmetric space function and symmetric spin (different level, same spin). In the infinite potential well for example, a maximum of two electrons could be in each energy level. In an atom, there are more quantum numbers per energy level in addition to spin, $|n l m_l\rangle$. If one orderly adds electrons with the minimum energy possible at a time in a central potential like an atom, *electron shells* are formed. These shells form the basis for the periodic table of elements.

The harmonic oscillator

Ladder operators: the Hamiltonian is $\hat{H} = \hat{p}^2/(2m) + m\omega^2\hat{q}^2/2$. One can define an operator $\hat{a} := \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{q} + i\frac{\hat{p}}{m\omega} \right)$, with the adjoint $\hat{a}^\dagger := \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{q} - i\frac{\hat{p}}{m\omega} \right)$, and

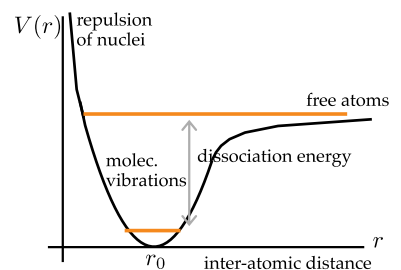
write the position and momentum operators as $\hat{q} = \sqrt{\frac{\hbar}{2m\omega}} (\hat{a} + \hat{a}^\dagger)$ and

$\hat{p} = \frac{1}{i} \sqrt{\frac{\hbar m\omega}{2}} (\hat{a} - \hat{a}^\dagger)$. The commutator is $[\hat{a}, \hat{a}^\dagger] = 1$.



Transformed Hamiltonian, ground state: $\hat{H} = \hbar\omega(\hat{a}^\dagger\hat{a} + \frac{1}{2})$. Then, the Schrödinger equation becomes $\hat{H}|n\rangle = E_n|n\rangle$, with $n = 0, 1, 2, \dots$. The ladder operators shift the energy, raising it, $\hat{H}\hat{a}^\dagger|n\rangle = \hbar\omega(\hat{a}^\dagger\hat{a} + \frac{1}{2})\hat{a}^\dagger|n\rangle = \hbar\omega\hat{a}^\dagger(\hat{a}^\dagger\hat{a} + \frac{3}{2})|n\rangle = (E_n + \hbar\omega)\hat{a}^\dagger|n\rangle$, or lowering it, $\hat{H}\hat{a}|n\rangle = (E_n - \hbar\omega)\hat{a}|n\rangle$. The ground state $|0\rangle$ is the lowest possible energy, so $\hat{a}|0\rangle = 0$, and $E_0 = \frac{1}{2}\hbar\omega$.

Molecular binding and vibrations: as a whole, atoms in a molecule feel both attraction (electrons against nuclei) and repulsion (nuclei against nuclei). In terms of the interatomic distance r , the potential of the system is repulsive when $r \rightarrow 0$, it has a harmonic-oscillator-like well around an optimal value r_0 and it approaches a fixed value when $r \rightarrow \infty$. In the well, the atoms oscillate \implies *molecular vibrations*. The energy needed for the atoms in the molecule to reach the unbound state is called the *dissociation energy*.



Introduction to quantum field theory

Creation and annihilation operators for photons: if one solves the classical electromagnetism equations in a cubic box, and expands in a Fourier series the vector potential, and with it one computes the electromagnetic energy contained within the box $H = \frac{1}{8\pi} \int d^3x (E^2 + B^2)$, one obtains

$H = C_0 \sum_{\vec{k}\sigma} (a_{\vec{k}\sigma}^- a_{\vec{k}\sigma}^{*+} + a_{\vec{k}\sigma}^{*+} a_{\vec{k}\sigma}^-)$ (where a is a plane wave, \vec{k} is the wave vector, σ is the polarization,). This

energy can be identified with the Hamiltonian with the quantum ladder operators (*quantization of the electromagnetic field*) such that $\hat{H} = \sum_{\vec{k}\sigma} \hbar\omega_k \left(\hat{a}_{\vec{k}\sigma}^- \hat{a}_{\vec{k}\sigma}^{*+} + \frac{1}{2} \right)$ (after using the commutation relation). The

result is a collection of photons (quantization of energy), with the operator $\hat{a}_{\vec{k}\sigma}^{*+} \hat{a}_{\vec{k}\sigma}^- |n_{\vec{k}\sigma}\rangle = n_{\vec{k}\sigma} |n_{\vec{k}\sigma}\rangle$ returning the number of photons with a given wave vector and polarization.

Radiation and matter: consider a collection of particles (e.g., electrons, atoms, molecules etc.) with a system Hamiltonian $H_0 = \sum_i \frac{1}{2m_i} p_i^2 + V(\dots x_i \dots x_j \dots)$. When there is interaction with an electromagnetic field that can be described from a vector potential, one can replace $\mathbf{p}_i \rightarrow \mathbf{p}_i - e_i/c \mathbf{A}(\mathbf{x}_i)$ and obtain $H = \sum_i \frac{1}{2m_i} \left| \mathbf{p}_i - \frac{e_i}{c} \mathbf{A}(\mathbf{x}_i) \right|^2 + V + \frac{1}{8\pi} \int d^3x (E^2 + B^2)$, which expanded can be written as $H = H_0 + H_{\text{rad}} + H_I$, where $H_{I,\text{all}} = \sum_i \left[-\frac{e}{m_i c} \mathbf{p}_i \cdot \mathbf{A}(\mathbf{x}_i) + \frac{e^2}{2m_i c^2} A^2(\mathbf{x}_i) \right]$ is the hamiltonian of the interaction between particles and field. Now, the photon field can be introduced in \mathbf{A} in each term, and one obtains for *each* particle $H_I = H' + H''$. The first term contains \mathbf{A} (plane wave) terms proportional to $a_{\vec{k}\sigma} e^{i\vec{k}\cdot\vec{x}} + \text{Adj}$ (Adj = *adjoint*), i.e., only one creation and annihilation operator \implies first order process \implies emission and absorption of radiation. The second term involves the creation and/or annihilation of two photons.

Emission of light by an excited atom: consider an electron in an atom in a high energy state a , such that the state of the system is $|i\rangle = |a\rangle_{\text{atom}} \otimes |\dots n_{\vec{k}\sigma} \dots\rangle_{\text{rad}}$. Now the electron emits a photon by going to a lower energy state, $|f\rangle = |b\rangle_{\text{atom}} \otimes |\dots n_{\vec{k}\sigma} + 1 \dots\rangle_{\text{rad}}$. This is a first order process, so the energy corrections can be found as $\langle f | H' | i \rangle$, for which only a creation operator survives for the radiation field. One can compute the transition probability per unit time as $\propto |\langle f | H' | i \rangle|^2$, and with it, the lifetime of emission. In the case of emission, the presence of the term $n_{\vec{k}\sigma} + 1$ implies that there are two kinds of emission: stimulated and spontaneous (the latter happens when $n_{\vec{k}\sigma} = 0$).

Second quantization of the Schrödinger equation: we can build a Hamiltonian (or Lagrangian) such that, when the equation of motion is computed, we get the Schrödinger equation. We can guess

$$H = \int d^3x \psi^*(\mathbf{x}, t) \left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] \psi(\mathbf{x}, t), \text{ with } \psi(\mathbf{x}, t) = \sum_n b_n(t) \psi_n(\mathbf{x}), \text{ and } \left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] \psi_n = E_n \psi_n.$$

After substitution in the integral, we find $H = \sum_n E_n b_n^* b_n$, similar to the harmonic oscillator. One can

quantize now (*second quantization*) in two ways: a) with the commutation relations $[b_n, b_{n'}] = [b_n^\dagger, b_{n'}^\dagger] = 0$, $[b_n, b_n^\dagger] = \delta_{nn'}$, or with the anticommutation¹ relations $\{b_n, b_{n'}\} = \{b_n^\dagger, b_{n'}^\dagger\} = 0$, $\{b_n, b_n^\dagger\} = \delta_{nn'}$. The first possibility yields bosons and the second one, fermions.

Dirac equation: relativistic equation for fermions: $-\frac{\hbar}{i} \frac{\partial \psi}{\partial t} = \left[\frac{\hbar c}{i} \underline{\alpha} \cdot \underline{\nabla} + \beta m c^2 \right] \psi$, where $\underline{\alpha}, \underline{\beta}$ are the

Dirac matrices. One can form the Hamiltonian $H = \int d^3x \psi^\dagger \left[\frac{\hbar c}{i} \underline{\alpha} \cdot \underline{\nabla} + \beta m c^2 \right] \psi$, with

$\psi = [\psi_1 \ \psi_2 \ \psi_3 \ \psi_4]^T$ and $\psi^\dagger = [\psi_1^\dagger \ \psi_2^\dagger \ \psi_3^\dagger \ \psi_4^\dagger]$ being operators with the second quantization $\{\psi_j(\mathbf{x}, t), \psi_k(\mathbf{x}, t)\} = \{\psi_j^\dagger(\mathbf{x}, t), \psi_k^\dagger(\mathbf{x}, t)\} = 0$, $\{\psi_j(\mathbf{x}, t), \psi_k^\dagger(\mathbf{x}, t)\} = \delta_{jk} \delta(\mathbf{x} - \mathbf{x}')$. The Dirac Hamiltonian has eigenfunctions $\psi_{\vec{p}, \lambda} \propto u_{\vec{p}, \lambda} e^{i\vec{p}\cdot\vec{x}}$, where u are *spinors* and $\lambda = 1, 2, 3, 4$. The eigenvalues are

$$E_{\vec{p}, \lambda} = \pm \sqrt{\hbar^2 c^2 p^2 + m^2 c^4}.$$

Lagrangian: the Dirac equation can also be written as $(i\gamma^\mu \partial_\mu - m)\psi = 0$, where the four Dirac matrices γ^μ satisfy the Clifford algebra $\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = 2g^{\mu\nu}$, such that $\beta = \gamma^0$, $\beta^2 = 1$, $\alpha = \gamma^0 \gamma$. The Lagrange density can be written as $\mathcal{L} = \bar{\psi} (i\gamma^\mu \partial_\mu - m)\psi = i\psi^\dagger \dot{\psi} + i\psi^\dagger \alpha \cdot \nabla \psi - m\psi^\dagger \beta \psi$, where the bar indicates the adjoint spinor $\bar{\psi} = \psi^\dagger \gamma^0$. Introducing the Lagrange density into the (matrix) Euler-Lagrange equations, one obtains the Dirac equation.

¹ An anticommutator is defined as $\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$.

Creation and annihilation of electrons: The separation of time and space states $\psi(\mathbf{x}, t) = \sum_{\vec{p}\lambda} b_{\vec{p}\lambda}(t)\psi_{\vec{p}\lambda}(\vec{x})$

(and adjoint) leads to the creation and annihilation operators for the Dirac field. The operator $b_{\vec{p}\lambda}$ destroys an electron of momentum $\hbar\vec{p}$, and the operator $b_{\vec{p}+\vec{k},\lambda'}^\dagger$ creates an electron of momentum $\hbar(\vec{p} + \vec{k})$. (These operators are quantized in time as creation and annihilation).

Quantum electrodynamics I, introduction: it's the study of the interaction of electrons and photons. The interaction Hamiltonian is constructed by the same procedure as in the Schrödinger case, and leads to

$H_I = -e \sum_{\vec{k}\sigma} \sum_{\vec{p}\lambda} \sum_{\lambda'} \left(\frac{2\pi\hbar c^2}{\Omega\omega_k} \right)^{1/2} \left\{ (\bar{u}_{\vec{p}+\vec{k},\lambda'}\gamma_\mu u_{\vec{k}\sigma\mu} u_{\vec{p},\lambda}) b_{\vec{p}+\vec{k},\lambda'}^\dagger b_{\vec{p}\lambda} a_{\vec{k}\sigma} + \text{HC} \right\}$, where HC stands for hermitian conjugate of the first term in brackets. The terms of H_I can be represented by Feynman diagrams.

Quantum electrodynamics II, Lagrangian: Lagrangian density for quantum electrodynamics:

$\mathcal{L} = \mathcal{L}_0^{\text{Dirac}} + \mathcal{L}_0^{\text{em}} + \mathcal{L}_1$, where $\mathcal{L}_0^{\text{Dirac}} = \bar{\psi} \left(\frac{i}{2} \gamma_\mu \overleftrightarrow{\partial}^\mu - m \right) \psi$ (the arrow on top indicates the direction where the operator should be applied), $\mathcal{L}_0^{\text{em}} = -\frac{1}{4} F_{\mu\nu} F^{\mu\nu} - \frac{1}{2} \zeta (\partial_\mu A^\mu)^2$ (the second term is used to fix the gauge), and the interaction term $\mathcal{L}_1 = -e \bar{\psi} \gamma_\mu \psi A^\mu$. (The e.m. coupling is achieved by doing $\partial_\mu \rightarrow \partial_\mu + ieA_\mu$). The idea of quantum electrodynamics is to study the interaction term, for which the second quantization gives $\hat{\mathcal{L}}_1 = -e : \hat{\psi} \gamma_\mu \hat{\psi} \hat{A}^\mu :$ (the colon denotes *time ordering*).

The S-matrix: the scattering matrix \hat{S} describes the probability amplitude from an initial to a final state in a system, due to an interaction: $S_{fi} = \lim \langle \Phi_f | \Psi(t) \rangle = \langle \Phi_f | \hat{S} | \Psi_i \rangle$. It can be computed from a

perturbation series $\hat{S} = \mathbb{1} + \sum_{n=1}^{\infty} \hat{S}^{(n)} = \sum_{n=0}^{\infty} \frac{1}{n!} (-i)^n \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{\infty} dt_n T(\hat{H}_1(t_1) \cdots \hat{H}_1(t_n))$
 $= \sum_{n=0}^{\infty} \frac{1}{n!} (-i)^n \int_{-\infty}^{\infty} d^4x_1 \cdots \int_{-\infty}^{\infty} d^4x_n T(\hat{H}_1(t_1) \cdots \hat{H}_1(t_n))$, where T is the time ordering operator (it orders the operators such that they occur progressively in time). The S-matrix is a kind of time-evolution operator, and it's unitary.

Quantum electrodynamics III, route for calculations: with the Lagrangian one can build the Hamiltonian operator, $\hat{\mathcal{H}}_1 = -\hat{\mathcal{L}}_1$, and with it, one builds the S-matrix, and with it, one can compute, for example, transition probabilities. Note that the second quantization develops the operators in the following way:

$$\hat{\psi}(\vec{x}) = \int \frac{d^3p}{(2\pi)^{3/2}} \sqrt{\frac{m}{E_p}} \sum_s \left(\hat{b}_{\vec{p}s} u(\vec{p}, s) e^{-i\vec{p}\cdot\vec{x}} + \hat{d}_{\vec{p}s}^\dagger v(\vec{p}, s) e^{+i\vec{p}\cdot\vec{x}} \right),$$

$$\hat{\bar{\psi}}(\vec{x}) = \int \frac{d^3p}{(2\pi)^{3/2}} \sqrt{\frac{m}{E_p}} \sum_s \left(\hat{d}_{\vec{p}s} \bar{v}(\vec{p}, s) e^{-i\vec{p}\cdot\vec{x}} + \hat{b}_{\vec{p}s}^\dagger \bar{u}(\vec{p}, s) e^{+i\vec{p}\cdot\vec{x}} \right),$$

$$\hat{A}_\mu(\vec{x}) = \int \frac{d^3k}{\sqrt{(2\pi)^3 2\omega_k}} \sum_\lambda \left(\hat{a}_{\vec{k}\lambda} \epsilon^\mu(\vec{k}, \lambda) e^{-i\vec{k}\cdot\vec{x}} + \hat{a}_{\vec{k}\lambda}^\dagger \epsilon^{*\mu}(\vec{k}, \lambda) e^{+i\vec{k}\cdot\vec{x}} \right), \text{ where the } \hat{b} \text{ are the particle creation/}$$

annihilation operators, \hat{d} are the antiparticle creation/operation operators, and the \hat{a} are the photon creation/annihilation operators, s denotes spin, λ denotes polarization, with the unit spinors/vectors u, v, ϵ in each case.

The S-matrix for processes and Feynman diagrams: In the \hat{S} perturbation series, the $\hat{S}^{(1)}$ terms don't satisfy simultaneously the conservation of momentum and energy, so they can't occur (they can occur with external fields that give/absorb the extra momentum/energy). For scattering processes involving free particles, the higher order terms are needed. The second order scattering operator is

$\hat{S}^{(2)} = \frac{1}{2!} (-ie)^2 \int d^4x_1 d^4x_2 T \left[: \hat{\psi}(\vec{x}_1) \gamma_\mu \hat{\psi}(\vec{x}_1) \hat{A}^\mu(\vec{x}_1) :: \hat{\psi}(\vec{x}_2) \gamma_\nu \hat{\psi}(\vec{x}_2) \hat{A}^\nu(\vec{x}_2) : \right]$. With photons and electrons-positrons, one can compute the interactions: a) Compton scattering at an electron, b) Compton

