

Quantum Mechanics

- chap0. Operators
 - Hermitian operator
 - Commutator
 - canonical commutation relation
- chap1. Wave function
 - Schrödinger Equation
 - collapse
- chap2. Time-independent Schrödinger equation
 - stationary state
 - One-d infinite potential Well
 - Simple harmonic oscillator
 - Free particle
- chap3. Formalism
 - inner product
 - uncertainty principle
 - Energy-Time uncertainty principle
- QM in 3D
 - Angular Momentum L
 - Spin
 - Spin 1/2
 - Pauli matrices
 - Two-Electron System
- 期末复习
 - 16. 对易和共同本征矢

chapo. Operators

Hermitian operator

Consider an operator \hat{A} and its **Hermitian conjugate** \hat{A}^\dagger satisfies

$$\langle \hat{A}f | g \rangle = \langle f | \hat{A}^\dagger g \rangle$$

Particularly, operators whose Hermitian conjugates are themselves are called **Hermitian operators**

$$\hat{Q} = \hat{Q}^\dagger$$

Commutator

The commutator between two operators is defined as

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

canonical commutation relation

We can easily deduce that $[\hat{x}, \hat{p}] \psi = i\hbar \psi$, where $\hat{x} = x$ and $\hat{p} = -i\hbar \frac{\partial}{\partial x}$, thus

$$[\hat{x}, \hat{p}] = i\hbar \mathbb{I}$$

where \mathbb{I} is the unit operator, sometimes it is 1. The operators whose commutator is not equal to zero is called the canonical commutation relation.

chap1. Wave function

Schrödinger Equation

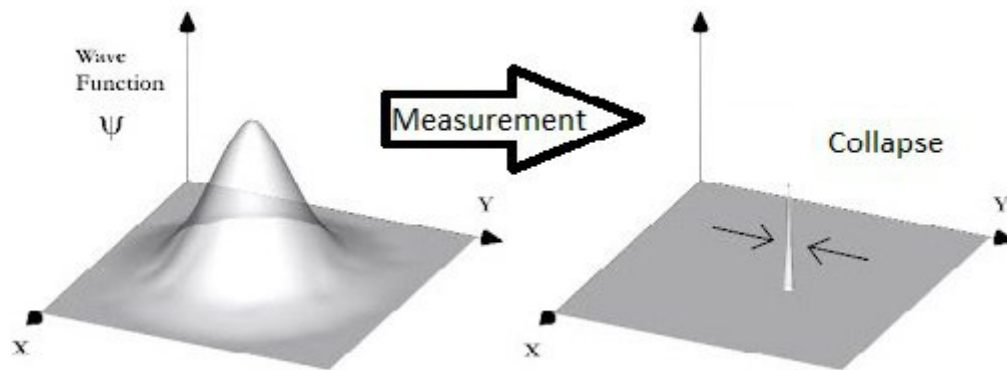
$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi$$

With Hamiltonian $H = \frac{p^2}{2m} + V$, correspondingly, Hamiltonian operator $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V$ with $\hat{p} = -i\hbar \nabla$, it goes

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi$$

collapse

wave function—initially in a superposition of several eigenstates—reduces to a single eigenstate due to the **measurement**



When making a second measurement immediately after the first we will get the same result because of the collapsing. However the wave function spread out again soon.

chap2. Time-independent Schrödinger equation

stationary state

Q: Is there a difference with time-independent states and stationary states in the Schrodinger's equation?

A: If you talk about stationary currents, or stationary states, it means that it is actually moving, there is actually a time dependence (a transport), but you don't see it, because what is transported away is replaced again. So, a stationary current is a current; a time dependence, a charge transport but the current itself is time independent. What flows away flows back again.

The wave function, i.e., the state itself, is time-dependent, i.e. something flows away and is replaced at the other end, so that the overall probability of residence does not change. The probability that the particles can be found in location A is at any time the same in the sense it is stationary but the states themselves are time-dependent. Stationary states are time-dependent!

One-d infinite potential Well

consider the potential

$$V(x) = \begin{cases} 0 & 0 < x < a \\ \infty & \text{otherwise} \end{cases}$$

Simple harmonic oscillator

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2$$

The time-independent Schrodinger equation (TISE) goes

$$\frac{1}{2m} [\hat{p}^2 + (m\omega x)^2] \psi = E\psi$$

Ladder operators

$$\hat{a}_{\pm} \equiv \frac{1}{\sqrt{2m\hbar\omega}} (\mp i\hat{p} + m\omega x)$$

The \hat{a}_+ is called **raising operator**, while \hat{a}_- is **lowering operator**, and obviously ~~they are the complex conjugates of each other. $i\hat{p}$ is actually a real operator, as $\hat{p} = -i\hbar\nabla$.~~ However, they are the Hermitian conjugates of each other. \hat{a}_- is sometimes written as \hat{a} , and thus \hat{a}_+ can be written as \hat{a}^\dagger

$$\hat{a}_- \hat{a}_+ = \frac{1}{2m\hbar\omega} [\hat{p}^2 + (m\omega x)^2] - \frac{i}{2\hbar} [\hat{x}, \hat{p}] = \frac{\hat{H}}{\hbar\omega} + \frac{1}{2}$$

The second step is according to canonical commutation relation that suggest $[\hat{x}, \hat{p}] = i\hbar$. And $\hat{a}_+ \hat{a}_- = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2}$, so their commutator can be calculated to be 1

$$[\hat{a}_-, \hat{a}_+] = \hat{a}_- \hat{a}_+ - \hat{a}_+ \hat{a}_- = 1$$

So we can rewrite the Hamiltonian by ladder operators

$$\hat{H} = \hbar\omega(\hat{a}_- \hat{a}_+ - \frac{1}{2}) \quad \text{or} \quad \hat{H} = \hbar\omega(\hat{a}_+ \hat{a}_- + \frac{1}{2})$$

With these two formulas, we are now going to prove that $\hat{a}_- \psi$ is a solution to the TISE with energy $E - \hbar\omega$, which is $\hat{H}(\hat{a}_- \psi) = (E - \hbar\omega)(\hat{a}_- \psi)$:

$$\begin{aligned} \hat{H}(\hat{a}_- \psi) &= \hbar\omega \left(\hat{a}_- \hat{a}_+ - \frac{1}{2} \right) (\hat{a}_- \psi) = \hbar\omega \hat{a}_- \left(\hat{a}_+ \hat{a}_- - \frac{1}{2} \right) \psi \\ &= \hat{a}_- \left[\hbar\omega \left(\hat{a}_- \hat{a}_+ - 1 - \frac{1}{2} \right) \psi \right] = \hat{a}_- (\hat{H} - \hbar\omega) \psi = \hat{a}_- (E - \hbar\omega) \psi \\ &= (E - \hbar\omega) (\hat{a}_- \psi) \end{aligned}$$

Similarly, $\hat{H}(\hat{a}_+ \psi) = (E + \hbar\omega)(\hat{a}_+ \psi)$ is also established, and those are why they are called *ladder operators*.

If we use lowering operator \hat{a}_- on ψ multiple times, we end up with TISE with energy 0 and cannot use it anymore, which is to say, $\exists \psi_0$ makes that there is no state whose wavefunction is $\hat{a}_- \psi_0$, as a result, its wavefunction can't be normalized for it is 0 everywhere, i.e.

$$\hat{a}_- \psi_0 = 0$$

Here ψ_0 is ground state, which can be obtained by solving the above equation, with

$\hat{a}_- = \frac{1}{2m\hbar\omega}(i\hat{p} + m\omega x)$ and $\hat{p} = -i\hbar\frac{\partial}{\partial x}$, the equation goes

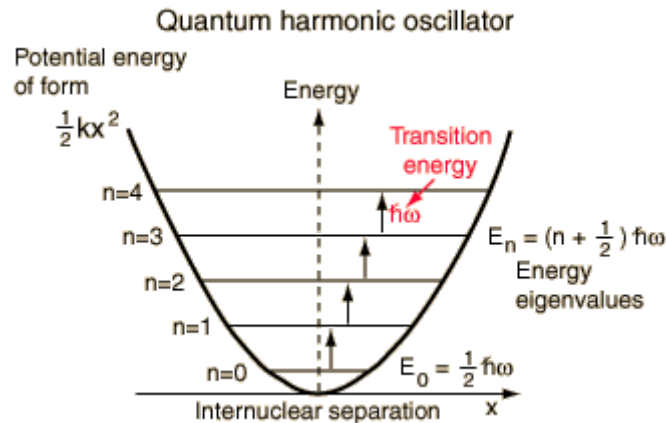
$$\frac{1}{2m\hbar\omega} \left(\hbar\frac{\partial}{\partial x} + m\omega x \right) \psi_0 = 0$$

Solve the equation and introduce the normalization condition ($\int |\psi_0|^2 dx = 1$), we can get the ground state

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar} x^2}$$

We simply apply the raising operator (repeatedly) to generate the excited states, increasing the energy by $\hbar\omega$ with each step

$$\psi_n = \frac{1}{\sqrt{n!}} (\hat{a}_+)^n \psi_0, \quad \text{with} \quad E_n = \left(n + \frac{1}{2}\right) \hbar\omega$$



How we determined coefficient:

$$\langle \hat{a}_+ \psi | \hat{a}_+ \psi \rangle = \langle \psi | \hat{a}_- \hat{a}_+ \psi \rangle = \left(\frac{E}{\hbar\omega} + \frac{1}{2} \right) \langle \psi | \psi \rangle = (n + 1) \langle \psi | \psi \rangle$$

here we used $E = (n + 1/2)\hbar\omega$ and $\langle\psi_n|\psi_n\rangle = \langle\psi_{n+1}|\psi_{n+1}\rangle = 1$ (normalization). Similarly

$$\langle\hat{a}_-\psi|\hat{a}_-\psi\rangle = n\langle\psi|\psi\rangle$$

So, we get those two formulas:

$$\hat{a}_+\psi_n = \sqrt{n+1}\psi_{n+1} \quad \hat{a}_-\psi_n = \sqrt{n}\psi_{n-1}$$

Free particle

chap3. Formalism

inner product

- conjugate symmetric(共轭对称)

$$\langle f|g\rangle = \langle g|f\rangle^\dagger$$

- conjugate linear(共轭线性)

$$\begin{cases} \langle af|g\rangle = a^\dagger \langle f|g\rangle & \langle f|bg\rangle = b \langle f|g\rangle \\ \langle af_1 + bf_2|g\rangle = a^\dagger \langle f_1|g\rangle + b^\dagger \langle f_2|g\rangle \\ \langle f|ag_1 + bg_2\rangle = a \langle f|g_1\rangle + b \langle f|g_2\rangle \end{cases}$$

- The inner product of an element with itself is positive definite

$$\langle f|f\rangle \begin{cases} > 0 & x \neq 0 \\ = 0 & x = 0 \end{cases}$$

uncertainty principle

In QM, the **uncertainty** σ of an observable \hat{O} is its variance.

$$\sigma^2 = \langle(\hat{O} - \langle\hat{O}\rangle)^2\rangle = \langle O^2\rangle - \langle O\rangle^2$$

consider a wave function ψ satisfies $\langle\hat{x}\rangle = 0, \langle\hat{p}\rangle = 0$, as a result,

$$\begin{cases} \sigma_p^2 = \langle\hat{p}^2\rangle - \langle\hat{p}\rangle^2 = \langle\hat{p}^2\rangle = \langle\psi|\hat{p}^2\psi\rangle \\ \sigma_x^2 = \langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2 = \langle\hat{x}^2\rangle = \langle\psi|\hat{x}^2\psi\rangle \end{cases}$$

Next consider a one-parameter ($s \in \mathbb{R}$) family of states $\Psi_s = (\hat{p} - is\hat{x})\psi$. Because every wave function lives in **Hilbert space**, Ψ_s satisfies

$$\langle \Psi_s | \Psi_s \rangle = \langle (\hat{p} - is\hat{x})\psi | (\hat{p} - is\hat{x})\psi \rangle \geq 0$$

Obviously, $(\hat{p} - is\hat{x})^\dagger = (\hat{p} + is\hat{x})$, hence

$$\langle \Psi_s | \Psi_s \rangle = \langle \psi | (\hat{p} + is\hat{x})(\hat{p} - is\hat{x})\psi \rangle = \langle \psi | (\hat{p}^2 + is[\hat{x}, \hat{p}] + s^2\hat{x}^2)\psi \rangle \geq 0$$

with $[\hat{x}, \hat{p}] = i\hbar$, we get

$$\langle \psi | (\hat{p}^2 - s\hbar + s^2\hat{x}^2)\psi \rangle \geq 0 \rightarrow \sigma_p^2 - s\hbar + s^2\sigma_x^2 \geq 0$$

This is a quadratic equation for s , to greater than or equal to 0, it satisfies

$$\hbar^2 - 4\sigma_x^2\sigma_p^2 \leq 0$$

After transposition and taking square root, it goes the form of **Heisenberg uncertainty relation**

$$\sigma_x\sigma_p \geq \frac{\hbar}{2}$$

Energy-Time uncertainty principle

Generalized Ehrenfest theorem

$$\frac{d}{dt}\langle Q \rangle = \frac{i}{\hbar}\langle [\hat{H}, \hat{Q}] \rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle$$

QM in 3D

Angular Momentum L

Commutation relations of angular momentum **L**

$$[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k$$

eigenvalues of operators ($[L^2, L_z] = 0$, where $L_z = -i\hbar\frac{\partial}{\partial\phi}$)

$$H\psi = E\psi \quad L^2\psi = \hbar^2 l(l+1)\psi \quad L_z\psi = \hbar m\psi$$

Spin

Commutation relations of intrinsic angular momentum **S**

$$[\hat{S}_i, \hat{S}_j] = i\hbar\epsilon_{ijk}\hat{S}_k$$

eigenvalues of operators ($[S^2, S_z] = 0$, where $S_z =$)

$$S^2 |s\ m\rangle = \hbar^2 s(s+1) |s\ m\rangle \quad S_z |s\ m\rangle = \hbar m |s\ m\rangle$$

the spin s is a special and imutable number for any given particle.

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots; \quad m = -s, -s+1, \dots, s-1, s$$

Spin 1/2

$s = 1/2$ is the spin of the particles that make up ordinary matter (protons, neutrons, and electrons). When $s = 1/2$, there are two cases, namely $m = \pm 1/2$

$$|\frac{1}{2} \ \frac{1}{2}\rangle \rightarrow \mathcal{X}_+ \quad |\frac{1}{2} \ -\frac{1}{2}\rangle \rightarrow \mathcal{X}_-$$

Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k$$

Two-Electron System

consider two electrons that spin 1/2

- uncoupled representation(非耦合表象), using $|s_1\ m_1\ s_2\ m_2\rangle$

$$\text{span}\{|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle\}$$

- coupled representation $|S\ M\ s_1\ m_1\rangle$

$$\text{span}\{|1\ 1\rangle, |1\ -1\rangle, |1\ 0\rangle, |0\ 0\rangle\}$$

to transform:

$$\begin{cases} |1\ 1\rangle &= |\uparrow\uparrow\rangle \\ |1\ -1\rangle &= |\downarrow\downarrow\rangle \\ |1\ 0\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |0\ 0\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \end{cases}$$

期末复习

来自于bilibili@Jusuchan7投稿视频「量子力学基础知识」BV1mb4y1s7Wg

16. 对易和共同本征矢

命题1: 如果两个算符 \hat{A} 和 \hat{B} commute, i.e. $[\hat{A}, \hat{B}] = 0$ 即 $\hat{A}\hat{B} = \hat{B}\hat{A}$, 而且 ψ 是 \hat{A} 的一个本征矢 **eigenvector**, 则 $\hat{B}\psi$ 也是 \hat{A} 的一个本征矢, 且本征值 eigenvalue 相同。

• **proof:**

$$\hat{A}(\hat{B}\psi) = \hat{A}\hat{B}\psi = \hat{B}\hat{A}\psi = \hat{B}a\psi = a\hat{B}\psi$$

1. 推论1: 若 a 是 \hat{A} 的非简并的本征值 **nondegenerate eigenvalue**, 则 ψ 也是 \hat{B} 的一个本征矢。

proof: 若非简并, 则不存在 ψ' 使 $\hat{A}\psi' = a\psi'$, 所以 \hat{A} 的所有本征矢都可以用 ψ 表示 (若是 generate 则是 ψ 和 ψ 的线性组合 combination)。所以 $\hat{B}\psi$ 也能用 ψ 表示, 即存在一个常数 b , 使得 $\hat{B}\psi = b\psi$

2. 推论2: 若 a 是 \hat{A} 的简并的本征值 **degenerate eigenvalue**, 则 $\hat{B}\psi$ 存在于 \hat{A} 对应本征值 a 的 eigensubspace 本征子空间 ϵ_a 中

proof: 若简并, 则存在 $|\psi_n\rangle$, 可以张成一个本征子空间, 每个本征矢都存在于这个空间中, 所以 $\hat{B}\psi$ 也存在于本征子空间中。

定理2: 如果两个算符 \hat{A} 和 \hat{B} commute, 且 ψ_1 和 ψ_2 是 \hat{A} 的两个本征矢, 且对应不同的本征值。则 $\langle\psi_1, \hat{B}\psi_2\rangle = 0$

- **proof:** 根据命题1, $\hat{B}\psi_2$ 也是 \hat{A} 的本征矢, 且对应的本征值等于 ψ_2 对应的本征值。根据不同本征值的本征矢的正交性 orthogonality 可以知道 ψ_1 和 $\hat{B}\psi_2$ 的内积等于0。