Quatum Mechanics

chap0. Operators

Hermitian opertator

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 Hemitian 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 dedude that $[\hat{x}, \hat{p}]\,\psi = i\hbar\psi$, where $\hat{x} = x$ and $\hat{p} = -i\hbar\dfrac{\partial}{\partial x}$, 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

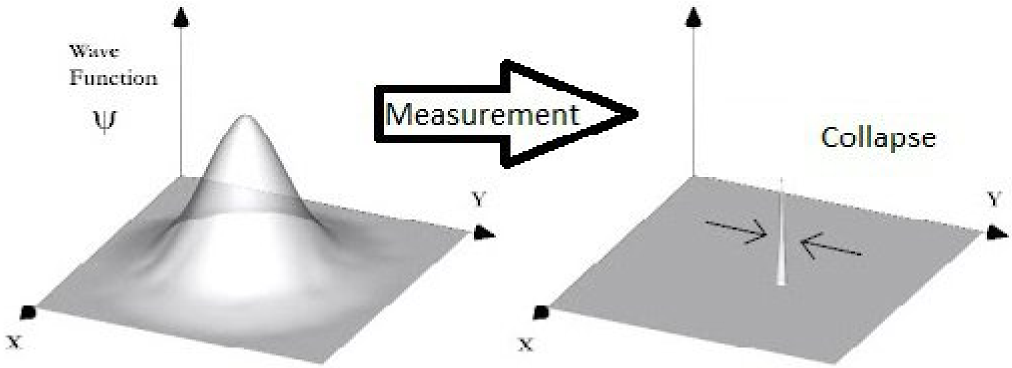
$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$$

With Hamiltonian $H = \dfrac{p^2}{2m} + V$, correspondingly, Hamiltonian operator $\hat{H} = -\dfrac{\hbar^2}{2m}\nabla^2 + V$ 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

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

The time-independent Schrodinger equation (TISE) goes

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

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~~ $\hat{p} = -i\hbar\nabla$. Howvere, they are the Hermitian conjugates of each other. $\hat{a}_-$ is sometimes written as $\hat{a}$, and thus $\hat{a}_+$ can be written as $\hat{a}^\dagger$

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

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

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

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 $\hat{H}(\hat{a}_-\psi) = (E - \hbar\omega)(\hat{a}_-\psi)$:

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

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

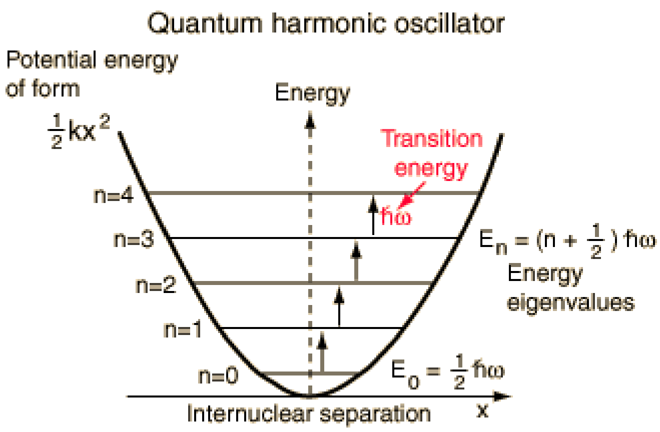
$$\frac{1}{2m\hbar\omega}\left(\hbar\frac{\partial}{\partial x} + m\omega x\right)\psi_0 = 0$$

Solve the equation and introduce the normalization condition ($\int |\psi_0|^2 \mathrm{d}x = 1$), 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

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



How we determinated 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). Simlarly

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

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)

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

- 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 a 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 $\mathbf{L}$

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

eigenvalues of opertators ($[L^2, L_z] = 0$, 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 instrinsic angular momentum $\mathbf{S}$

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

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

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

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

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

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 $\left| s_1\, m_1\, s_2\, m_2 \right\rangle$

$$span\{\left|\uparrow\uparrow\right\rangle, \left|\downarrow\downarrow\right\rangle, \left|\uparrow\downarrow\right\rangle, \left|\downarrow\uparrow\right\rangle\}$$

- coupled represemtation $\left| S\ M\ s_1\ m_1 \right\rangle$

$$span\{\left|1\,1\right\rangle, \left|1\ -1\right\rangle, \left|1\,0\right\rangle, \left|0\,0\right\rangle\}$$

to transform:

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