第一章 量子力学基础

The Foundation of Quantum Mechanics

§1.1 量子力学算符

Operators in quantum mechanics

可观测力学量

- 经典力学 —函数

$$h=\frac{1}{2}gt^2 \qquad F=-kx \qquad E=\frac{1}{2}mv^2$$

- 量子力学 —算符

$$\hat{H} \qquad \hat{M}^2 \qquad \hat{M}_z$$

1.1.1 算符 Operator

- 算符简单地说是一种规则，用它，我们能够从某一给出的函数求出另外的相应函数。算符可用抑扬符(^)表示。

例: 如$\hat{D}$是将一个函数对x微分的算符

$$\hat{D}f(x) = f'(x)$$

$$\hat{D}\left(x^2 + 3e^x\right) = 2x + 3e^x$$

运算	算符	对sin$x$的作用结果
乘以常数c	c	$c\sin x$
取其平方根	$\sqrt{}$	$\sqrt{\sin x}$
对x求导数	d/dx	$\cos x$
对x求积分	$\int(\quad)dx$	$-\cos x$
加以x	$x+$	$x+\sin x$

- **算符的相等**

若$\hat{A}, \hat{B}$ 两个算符对所有函数f，都有 $\hat{A}f = \hat{B}f$ 就说

$\hat{A}$与$\hat{B}$相等： $\hat{A} = \hat{B}$

- **算符的加减**

$$(\hat{A} \pm \hat{B}) f \equiv \hat{A}f \pm \hat{B}f$$

例： $\hat{D} \equiv d/dx$

$$(\hat{D} + \hat{3})(x^3 - 5) \equiv \hat{D}(x^3 - 5) + 3(x^3 - 5) = 3x^2 + 3x^3 - 5$$

- **算符的乘法**：用下式定义两个算符的积

$$\hat{A}\hat{B}f \equiv \hat{A}(\hat{B}f)$$

例： $\hat{3}\hat{D}f(x) = \hat{3}\left[\hat{D}f(x)\right] = \hat{3}f'(x) = 3f'(x)$

例： $\hat{D}\hat{x}f(x)=\dfrac{d}{dx}[xf(x)]=f(x)+xf'(x)$

$\hat{x}\hat{D}f(x)=xf'(x)$

$$\left.\begin{array}{l}\hat{D}\hat{x}f(x)=\dfrac{d}{dx}[xf(x)]=f(x)+xf'(x)\\ \hat{x}\hat{D}f(x)=xf'(x)\end{array}\right\}\ \hat{D}\hat{x}=\hat{I}+\hat{x}\hat{D}$$

$\hat{I}$(乘以1)为单位算符(*unit operator*)

$\hat{0}$ (乘以0)为零算符或空算符(*null operator*)

一般情况下, $\hat{A}\hat{B}$ 与 $\hat{B}\hat{A}$ 是不同的算符

- **算符的平方** $\hat{A}^2=\hat{A}\hat{A}$

例： $\hat{D}^2f(x)=\hat{D}(\hat{D}f)=\hat{D}f'=f''=\dfrac{d^2}{dx^2}f(x)$

$$\hat{D}^2=\frac{d^2}{dx^2}$$

- 算符服从乘法**结合律**

$$\hat{A}(\hat{B}\hat{C}) \equiv (\hat{A}\hat{B})\hat{C}$$

例： $\hat{A} = d/dx,\ \hat{B} = \hat{x},\ \hat{C} = \hat{3}$

$$\hat{A}\hat{B} = \hat{D}\hat{x} = 1 + \hat{x}\hat{D} \quad \hat{B}\hat{C} = 3\hat{x}$$

$$[(\hat{A}\hat{B})\hat{C}]f = (1 + \hat{x}\hat{D})3f = 3f + 3xf'$$

$$[\hat{A}(\hat{B}\hat{C})]f = \hat{D}(3xf) = 3f + 3xf'$$

- 算符乘法一般**不**符合乘法**交换律**
- 定义**对易子(commutator)** $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$

若 $\hat{A}\hat{B} = \hat{B}\hat{A}$, 则 $[\hat{A}, \hat{B}] = 0$ 称 $\hat{A}$与$\hat{B}$ 对易(commute)

若 $\hat{A}\hat{B} \neq \hat{B}\hat{A}$ 称 $\hat{A}$与$\hat{B}$ 不对易

例：

$$\left[\hat{3},\frac{d}{dx}\right]=\hat{3}\frac{d}{dx}-\frac{d}{dx}\hat{3}=0$$

3与d/dx对易

例： $\hat{A}=\hat{p}_i=-i\hbar\frac{\partial}{\partial q_i}$, $\hat{B}=\hat{q}_j=q_j$

$$\hat{A}\hat{B}\psi=\hat{p}_i\hat{q}_j\psi=-i\hbar\frac{\partial}{\partial q_i}(q_j\psi)=-i\hbar\left(\delta_{ij}\psi+q_j\frac{\partial\psi}{\partial q_i}\right)$$

$$\hat{B}\hat{A}\psi=\hat{q}_j\hat{p}_i\psi=-i\hbar q_j\frac{\partial\psi}{\partial q_i}$$

$$\delta_{ij}=\begin{cases}0, & i\neq j\\ 1, & i=j\end{cases}$$

$$\left(\hat{p}_i\hat{q}_j-\hat{q}_j\hat{p}_i\right)\psi=-i\hbar\delta_{ij}\psi$$

$$\left[\hat{p}_i,\hat{q}_j\right]=\hat{p}_i\hat{q}_j-\hat{q}_j\hat{p}_i=-i\hbar\delta_{ij}$$

$$\begin{cases}i=j & \left[\hat{p}_i,\hat{q}_j\right]\neq 0 \quad \text{不对易}\\ i\neq j & \left[\hat{p}_i,\hat{q}_j\right]=0 \quad \text{对易}\end{cases}$$

1.1.2 线性算符(linear operator)

当算符$\hat{A}$具有以下性质时，$\hat{A}$为线性算符

$$\hat{A}[c_1 f + c_2 g] = c_1 \hat{A} f + c_2 \hat{A} g$$

c_1, c_2为常数，f和g为任意函数

根号$\sqrt{\ }$ 不是线性算符

$$\sqrt{c_1 f + c_2 g} \neq c_1 \sqrt{f} + c_2 \sqrt{g}$$

取共轭*也不是线性算符

$$(c_1\psi_1 + c_2\psi_2)^* = c_1^*\psi_1^* + c_2^*\psi_2^* \neq c_1\psi_1^* + c_2\psi_2^*$$

d/dx , $\partial^2/\partial x^2$, $\partial^2/\partial x\partial y$, ∇^2 , $\hat{H}$等是线性算符

- 线性算符满足 $(\hat{A}+\hat{B})\hat{C}=\hat{A}\hat{C}+\hat{B}\hat{C}$

$$\hat{A}(\hat{B}+\hat{C})=\hat{A}\hat{B}+\hat{A}\hat{C}$$

证明： $\hat{A},\hat{B},\hat{C}$ 为线性算符

$$\left[(\hat{A}+\hat{B})\hat{C}\right]f=(\hat{A}+\hat{B})(\hat{C}f)$$

$$=\hat{A}(\hat{C}f)+\hat{B}(\hat{C}f)$$

$$=\hat{A}\hat{C}f+\hat{B}\hat{C}f$$

$$=(\hat{A}\hat{C}+\hat{B}\hat{C})f$$

$$\left[(\hat{A}+\hat{B})\hat{C}\right]f=(\hat{A}\hat{C}+\hat{B}\hat{C})f$$

$$(\hat{A}+\hat{B})\hat{C}=\hat{A}\hat{C}+\hat{B}\hat{C}$$

例： 求算符$d/dx+x$的平方　　设f为任意函数

$$(\hat{D}+\hat{x})^2 f = (\hat{D}+\hat{x})\left[(\hat{D}+\hat{x})f\right]$$

$$= (\hat{D}+\hat{x})(f'+xf)$$

$$= f''+f+xf'+xf'+x^2 f$$

$$= f''+2xf'+(x^2+1)f$$

$$= (\hat{D}^2+2x\hat{D}+x^2+1)f$$

$$(\hat{D}+\hat{x})^2 = \hat{D}^2+2x\hat{D}+x^2+1$$

直接算符运算 $(\hat{D}+\hat{x})^2 = (\hat{D}+\hat{x})(\hat{D}+\hat{x})$

$$= \hat{D}(\hat{D}+\hat{x})+\hat{x}(\hat{D}+\hat{x})$$

$$= \hat{D}^2+\hat{D}\hat{x}+\hat{x}\hat{D}+\hat{x}^2$$

$$= \hat{D}^2+2x\hat{D}+x^2+1$$

1.1.3 本征值、本征函数和本征方程

如果算符$\hat{A}$作用在某个函数ψ等于一常数a乘以ψ

$$\hat{A}\psi = a\psi$$

则称ψ为算符$\hat{A}$的具有**本征值**(eigenvalue)a的**本征函数**(eigenfunction)，上式称为**本征方程**(eigenvalue equation)

例：

$$\frac{d}{dx}e^{ax} = ae^{ax}$$

e^{ax}是算符d/dx的一个本征值为a的本征函数

$$\frac{d}{dx}e^{ax^2} = 2axe^{ax^2}$$

e^{ax^2}不是算符d/dx的本征函数

例： 函数cos(3x+5)是否是算符d^2/dx^2的本征函数，如果是，本征值是多少？

$$\frac{d^2}{dx^2}\cos(3x+5) = \frac{d}{dx}\left[-3\sin(3x+5)\right] = -9\cos(3x+5)$$

例： 求d/dx所有的本征函数和本征值

$$\frac{df(x)}{dx} = kf(x)$$

$$\frac{df}{f} = kdx$$

$$\ln f = kx + 常数$$

$$f = Ce^{kx}$$ 本征值为k

若函数 f 是线性算符$\hat{A}$的本征函数，本征值为a

则cf (c为任意非零的常数)也一定是$\hat{A}$本征值为a的本征函数

1.1.4 厄米算符(Hermitian Operators)

根据量子力学基本假设，力学量平均值

$$\bar{A}=\int \Psi^* \hat{A}\Psi d\tau$$

力学量平均值必须是实数

$$\bar{A}=\bar{A}^*$$

$$\bar{A}=\int \Psi^* \hat{A}\Psi d\tau \qquad \bar{A}^*=\int \Psi(\hat{A}\Psi)^* d\tau$$

$$\boxed{\int \Psi^* \hat{A}\Psi d\tau=\int \Psi(\hat{A}\Psi)^* d\tau}$$

对任意品优函数ψ，满足上式的算符$\hat{A}$都是**厄米算符**

对任意品优函数f与g，厄米算符也可以使用下面的定义：

$$\boxed{\int f^* \hat{A} g d\tau=\int g(\hat{A}f)^* d\tau}$$

两个定义是等价的

证明： 设$\psi = f + Cg$　C为任意参数

$$\int \Psi^* \hat{A}\Psi d\tau = \int \Psi (\hat{A}\Psi)^* d\tau$$

$$\int (f+Cg)^* \hat{A}(f+Cg) d\tau = \int (f+Cg)[\hat{A}(f+Cg)]^* d\tau$$

$$\int (f^* + C^* g^*)\hat{A}f d\tau + \int (f^* + C^* g^*)\hat{A}Cg d\tau$$

$$= \int (f+Cg)(\hat{A}f)^* d\tau + \int (f+Cg)(\hat{A}Cg)^* d\tau$$

$$\cancel{\int f^* \hat{A}f d\tau} + C^* \int g^* \hat{A}f d\tau + C\int f^* \hat{A}g d\tau + \cancel{CC^* \int g^* \hat{A}g d\tau}$$

$$= \cancel{\int f(\hat{A}f)^* d\tau} + C\int g(\hat{A}f)^* d\tau + C^* \int f(\hat{A}g)^* d\tau + \cancel{CC^* \int g(\hat{A}g)^* d\tau}$$

C为任意值，　令C=1　$\int g^* \hat{A}f d\tau + \int f^* \hat{A}g d\tau = \int g(\hat{A}f)^* d\tau + \int f(\hat{A}g)^* d\tau$

令C=i　$-\int g^* \hat{A}f d\tau + \int f^* \hat{A}g d\tau = \int g(\hat{A}f)^* d\tau - \int f(\hat{A}g)^* d\tau$

$$\int f^* \hat{A}g d\tau = \int g(\hat{A}f)^* d\tau$$

- **Dirac符号**

量子力学表示积分经常采用Dirac引入的符号，右矢|⟩和左矢⟨|，微观状态可以表示为右矢|ψ⟩，也可以表示为左矢⟨ψ|，|ψ⟩与⟨ψ|互为共轭

$$\hat{A}\psi = a\psi \quad \Longrightarrow \quad \hat{A}|\psi\rangle = a|\psi\rangle$$

$$\int f^* \hat{A} g d\tau = \langle f|\hat{A}|g\rangle \qquad \int g(\hat{A}f)^* d\tau = \langle g|\hat{A}|f\rangle^*$$

$$\int \psi_m^* \hat{A} \psi_n d\tau = \langle \psi_m|\hat{A}|\psi_n\rangle = \langle m|\hat{A}|n\rangle$$

$$\int \psi_m^* \psi_n d\tau = \langle m|n\rangle$$

⟨m|n⟩=0，则称ψ_m与ψ_n相互正交

- **定理：厄米算符本征值一定是实数**

$$\hat{A}\psi = a\psi \Longrightarrow \hat{A}^*\psi^* = a^*\psi^*$$

$$\left.\begin{aligned}&\int \psi^* \hat{A}\psi d\tau = \int \psi^* a\psi d\tau = a\int \psi^*\psi d\tau \\ &\quad \| \text{ 厄米算符定义} \\ &\int \psi(\hat{A}\psi)^* d\tau = \int \psi(a\psi)^* d\tau = a^*\int \psi\psi^* d\tau\end{aligned}\right\} \boldsymbol{a = a^*}$$

Dirac符号 $\int \psi^* \hat{A}\psi d\tau = \langle i|\hat{A}|i\rangle \qquad \int \psi(\hat{A}\psi)^* d\tau = \langle i|\hat{A}|i\rangle^*$

$$\langle i|\hat{A}|i\rangle = \langle i|\hat{A}|i\rangle^*$$

$$\langle i|a|i\rangle = \langle i|a|i\rangle^*$$

$$a\langle i|i\rangle = a^*\langle i|i\rangle^* = a^*\langle i|i\rangle$$

$$(a - a^*)\langle i|i\rangle = 0$$

$$a = a^*$$

1.1.5 厄米算符正交性 Orthogonality

- **定理：厄米算符属于不同本征值的两个函数一定正交**

证明：设ψ_m与ψ_n是厄米算符$\hat{A}$的两个本征函数，a_m和a_n分别是它们的本征值，$a_m \neq a_n$

$$\hat{A}\psi_m = a_m\psi_m \qquad \hat{A}\psi_n = a_n\psi_n$$

$$\hat{A}|m\rangle = a_m|\mathrm{m}\rangle \qquad \hat{A}|n\rangle = a_n|n\rangle$$

根据厄米算符定义

$$\langle m|\hat{A}|n\rangle = \langle n|\hat{A}|m\rangle^*$$

$$\langle m|a_n|n\rangle = \langle n|a_m|m\rangle^*$$

$$a_n\langle m|n\rangle = a_m^*\langle n|m\rangle^* = a_m^*\langle m|n\rangle = a_m\langle m|n\rangle$$

$$(a_m - a_n)\langle m|n\rangle = 0 \xrightarrow{a_m \neq a_n} \langle m|n\rangle = 0$$

- **简并本征函数正交化**

厄米算符$\hat{A}$有两个或两个以上本征函数$\psi_{n1}, \psi_{n2}, \cdots, \psi_{nf}$具有相同的本征值$a_n$，称$a_n$是**$f$重简并**的($f$-fold degenerate)。

如$\psi_{n1}, \psi_{n2}, \cdots, \psi_{nf}$不相互正交，可以把这$f$个函数重新组合成$f$个新函数$\Phi_{nj}$，使这些函数相互正交。

$$\Phi_{nj} = \sum_{i=1}^{f} c_{ji}\psi_{ni} \quad (j = 1, 2, \cdots f)$$

$\hat{A}f = af$；$\hat{A}g = ag$；$\langle f | g \rangle \neq 0$

设$\varphi_1 = f \quad \varphi_2 = g + cf$

$\langle \varphi_1 | \varphi_2 \rangle = \langle f | g + cf \rangle = \langle f | g \rangle + c\langle f | f \rangle = 0$

Schmidt正交化
(orthogonalization)

$$c = \frac{-\langle f | g \rangle}{\langle f | f \rangle} = \frac{-\int f^* g d\tau}{\int f^* f d\tau}$$

虽然不能保证简并的本征函数是正交的，但可以用正交化方法将其转换为正交的，一般未加说明时默认为正交的。

1.1.6 厄米算符本征函数的完备性

厄米算符本征函数构成一个正交归一完备集(complete set)

设$\{\Phi_n(x)\}$是某一个厄米算符的正交归一的集合

正交归一完备集的重要性在于任何函数$f(x)$可以对变数x的全部区域(a, b)展开为下列级数

$$f(x)=\sum_i c_i \Phi(x)_i \qquad i=1,2,\ldots$$

用$\Phi_n^*(x)$乘等式两端，并在x的全部区域(a,b)积分

$$\int_a^b \Phi_n^*(x) f(x) dx=\sum_i c_i \int_a^b \Phi_n^*(x) \Phi(x)_i dx=\sum_i c_i \delta_{ni}=c_n$$

- **定理：如果两个线性算符$\hat{A}$和$\hat{C}$具有相同的本征函数完备集，则这两个算符$\hat{A}$和$\hat{C}$一定对易。**

证明：设$\hat{A}$和$\hat{C}$具有相同的本征函数完备集为φ_i，$\hat{A}\varphi_i = s_i\varphi_i$，$\hat{C}\varphi_i = t_i\varphi_i$，$f$为满足边界条件的任意函数。

$$f = \sum_i c_i\varphi_i \qquad (\hat{A}\hat{C} - \hat{C}\hat{A})f = (\hat{A}\hat{C} - \hat{C}\hat{A})\sum_i c_i\varphi_i$$

$$= \sum_i c_i(\hat{A}\hat{C} - \hat{C}\hat{A})\varphi_i$$

$$= \sum_i c_i\left[\hat{A}\left(\hat{C}\varphi_i\right) - \hat{C}\left(\hat{A}\varphi_i\right)\right]$$

$$= \sum_i c_i\left(\hat{A}t_i\varphi_i - \hat{C}s_i\varphi_i\right)$$

$$= \sum_i c_i\left(s_it_i\varphi_i - t_is_i\varphi_i\right)$$

$$= 0$$

注意：必须是相同的本征函数完备集而非相同的本征函数

- **定理：如果线性厄米算符$\hat{A}$和$\hat{C}$对易，一定可以找到$\hat{A}$和$\hat{C}$的一套相同的本征函数完备集。**

证明：设$\hat{C}$的本征函数为φ_i，$\hat{C}\varphi_i = c_i\varphi_i$，

$$\hat{A}\hat{C}\varphi_i = \hat{A}c_i\varphi_i$$

$\hat{A}$和$\hat{C}$对易 ⇓ **$\hat{A}$是线性算符**

$$\hat{C}\hat{A}\varphi_i = c_i\hat{A}\varphi_i$$

$\hat{A}\varphi_i$是算符$\hat{C}$的具有与本征函数φ_i相同本征值t_i的本征函数，若$\hat{C}$的本征值t_i是**非简并**的，任一给定的本征值对应且仅对应于一个线性独立的本征函数，必然有 $\hat{A}\varphi_i = a_i\varphi_i$

若c_i为**n重简并的**， $\hat{A}\varphi_i$必然是对应于本征值c_i的n个线性独立的本征函数的某一线性组合。取n个线性独立的本征函数进行适当的线性组合必可以构成$\hat{C}$的另一个n个线性独立的本征函数，这就是$\hat{A}$的本征函数(证明略)

- **定理：如果f_i和f_j是厄米算符$\hat{A}$具有不同本征值a_i和a_j ($a_i \neq a_j$)的本征函数，$\hat{C}$是与$\hat{A}$对易的线性算符，则$\langle i|\hat{C}|j\rangle=0$**

证明：

如果a_i是非简并的，从上一个定理可知f_i同样是$\hat{C}$的本征函数

$$\hat{C} f_i = c_i f_i$$

$$\langle i|\hat{C}|j\rangle = c_i\langle i|j\rangle = 0$$

如果a_i是n级简并的， $\hat{A}f_k = a_i f_k$ ($k=1,\ldots n$)

$$\hat{C}f_i = \sum_{k=1}^{n} c_k f_k$$

$$\langle i|\hat{C}|j\rangle = \langle i|\hat{C}j\rangle = \left\langle f_i \middle| \sum_{k=1}^{n} c_k f_k \right\rangle = \sum_{k=1}^{n} c_k \langle i|j\rangle = 0$$

§1.2 量子力学公设

The Postulates of Quantum Mechanics

1.2.1 公设 I 状态与波函数

Postulate I States and wavefunctions

- 微观体系的运动状态可用一个坐标和时间的函数$\Psi(q, t)$来描述，$\Psi(q, t)$是体系中所有粒子的坐标$q_1, q_2, \ldots, q_f$与时间t的函数，$f = 3N$为体系的空间自由度，N为体系所包含的微粒数，这个函数叫**状态函数或波函数**(state function or wave function)，它决定着体系的全部可观测的性质

- $\Psi^*\Psi\, d\tau$ ($|\Psi|^2 d\tau$)表示在时间t，发现体系在f维微体积内的**概率**，即在时间t，q_1在q_1与q_1+dq_1, q_2在q_2与q_2+dq_2 , …, q_f在q_f与q_f+dq_f之间的概率。

- 如体系可观测性质不随时间改变，则该体系处于**定态**(time-independent), 描述这种状态的波函数称为**定态波函数**

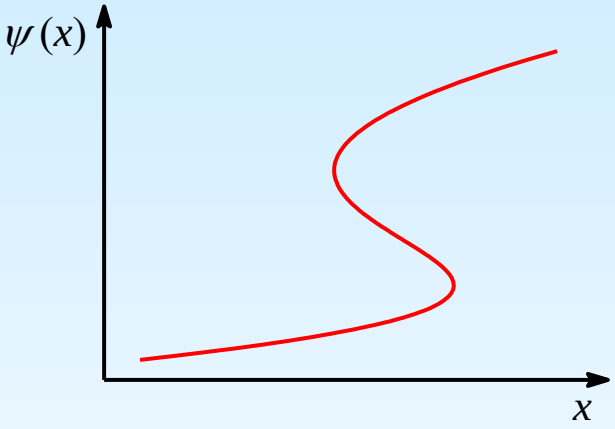
$$\Psi(q,t)=e^{-iEt/\hbar}\psi(q)$$

ψ可用来描述不含时的状态

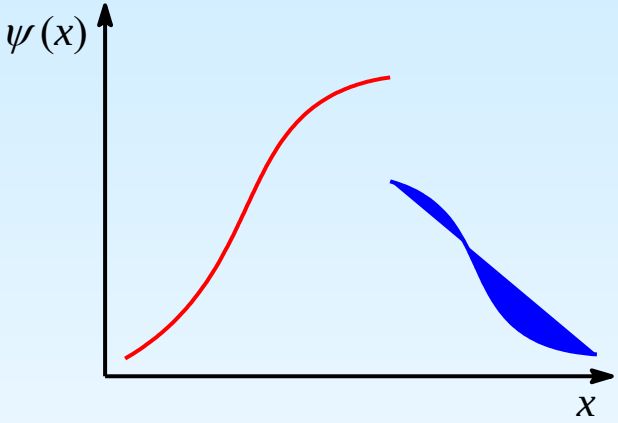
- 为保证状态函数Ψ有明确的物理意义，它必须在变数变化的全部区域内满足三个条件，即Ψ必须是单值的，连续的和平方可积的（对连续谱状态，略去平方可积条件），满足上述条件的波函数称为**合格波函数**或**品优波函数**(well-behaved function)

- **波函数和量子数**

①单值性(single-valued)条件—$\Psi^*\Psi$表示粒子出现的概率密度，所以必须是时间和坐标的单值函数

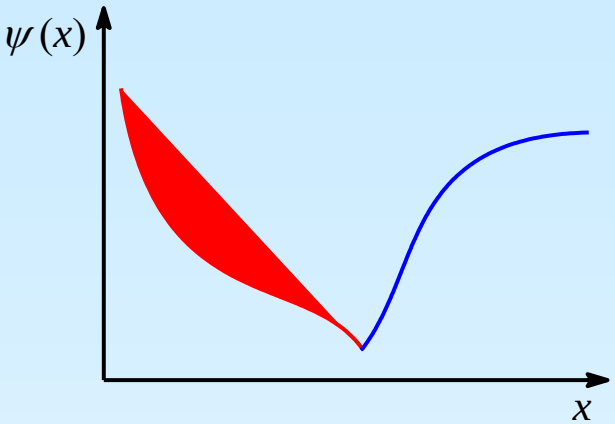


违反单值条件

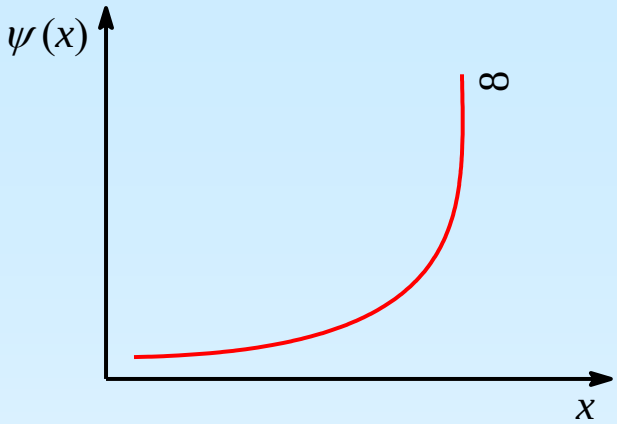


不连续

②连续性(continuous)条件—粒子在空间各处出现的概率密度是连续变化的，因此波函数必须在变数变化的全部区域内是连续的，并且具有连续的一级微商



一阶微商不连续



波函数不是有限的

③平方可积(quadratically integrable)条件—在变数变化的全部区域内，积分 $\int \Psi^* \Psi \, d\tau = C$ 必须是有限的

- **归一性**:一般从物理意义上看，总规定一个粒子在全部空间出现的概率为1。因此通常要求将波函数归一化。

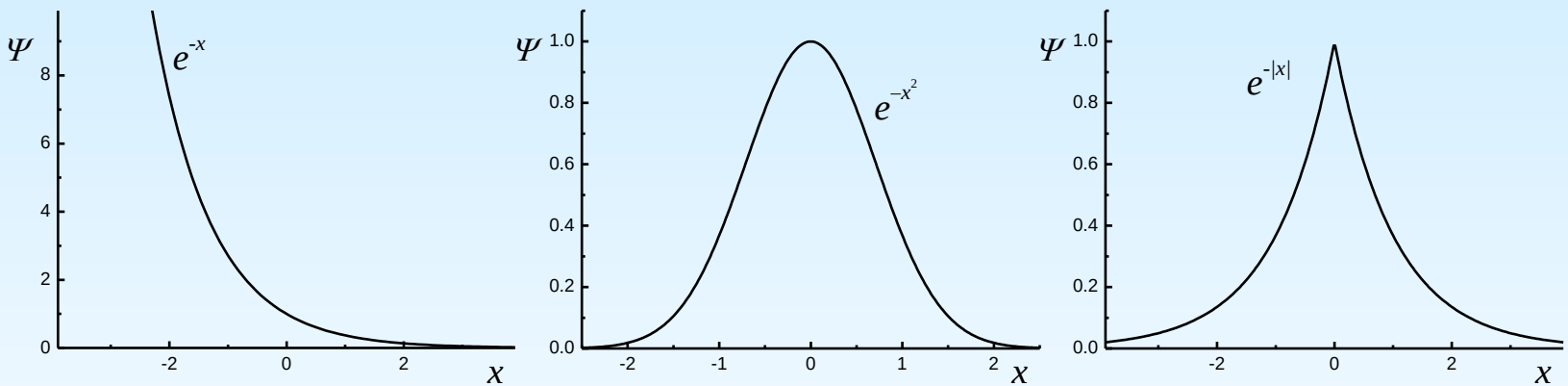
如：$\int \Psi^* \Psi \, d\tau = K$ 则可令 $\Psi' = \frac{1}{\sqrt{K}} \Psi$

$$\int \Psi'^* \Psi' d\tau = \frac{1}{K} \int \Psi^* \Psi \, d\tau = 1$$

$\frac{1}{\sqrt{k}}$ 为归一化系数 (normalization factor)

例： 下面那些函数是品优的?

① e^{-x}； ② e^{-x^2}； ③ $e^{-|x|}$；



① e^{-x}；不是品优函数，当$x \to -\infty$, $e^{-x} \to +\infty$ 不是有限的

② e^{-x^2}；是品优函数

③ $e^{-|x|}$；不是品优函数，当$x = 0$时, 一阶微商不连续

1.2.2 公设 II. 力学量与线性线性厄米算符

Postulate II Physical observable and its corresponding linear hermitian operators

- 对于体系的每个可观测的力学量，有一个对应的**线性厄米算符**。
- 组成力学量算符的规则如下：

①如力学量F是(q, t)的函数，则其算符就是简单地用F表示，即：$\hat{F}(q,t)=F(q,t)$

②如果力学量G是(q, p, t)的函数(p是动量)，则其算符为

$$\hat{G}(q_1,\cdots q_f,p_1,\cdots p_f,t)=\hat{G}\left(q_1,\cdots q_f,-i\hbar\frac{\partial}{\partial q_1},\cdots-i\hbar\frac{\partial}{\partial q_f},t\right)$$

动量算符： $\hat{p}_i = -i\hbar \dfrac{\partial}{\partial q_i}$

$$\begin{cases} \hat{p}_x = -i\hbar \dfrac{\partial}{\partial x} \\ \hat{p}_y = -i\hbar \dfrac{\partial}{\partial y} \\ \hat{p}_z = -i\hbar \dfrac{\partial}{\partial z} \end{cases}$$

例： 在经典力学中，质量为m在势场$V(x, y, z)$中运动的粒子的动能T为

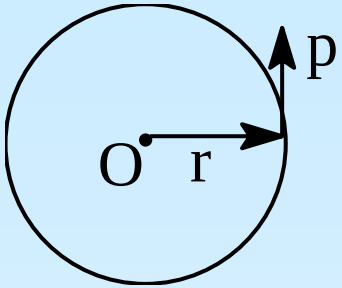
$$T = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

$$\hat{T} = \frac{1}{2m}\left(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2\right) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$E = T + V \qquad \hat{V}(x, y, z) = V(x, y, z)$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z)$$

角动量:



$$\vec{M}=\vec{r}\times\vec{p}=\begin{vmatrix}\vec{i} & \vec{j} & \vec{k}\\ x & y & z\\ p_x & p_y & p_z\end{vmatrix}=\vec{i}(yp_z-zp_y)+\vec{j}(zp_x-xp_z)+\vec{k}(xp_y-yp_x)$$

$$\left.\begin{aligned}M_x&=yp_z-zp_y\\ M_y&=zp_x-xp_z\\ M_z&=xp_y-yp_x\end{aligned}\right\}\Rightarrow$$

$$\hat{M}_x=-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$$

$$\hat{M}_y=-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$$

$$\hat{M}_z=-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$$

角动量平方算符

$$M^2=M_x^2+M_y^2+M_z^2$$

$$\hat{M}^2=-\hbar^2\left[\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)^2+\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)^2+\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)^2\right]$$

1.2.3 公设3. 力学量的本征态和本征值

Postulates 3. Eigenfunctions and eigenvalues of a physical observable

- 如某一力学量A的算符$\hat{A}$作用于某一状态函数$\Psi(q, t)$等于某一常数a乘以$\Psi(q, t)$，即：$\hat{A}\Psi(q, t) = a\Psi(q, t)$，那么，这一微观体系的**力学量$A$在状态$\Psi(q, t)$具有确定的数值$a$**。$a$称$\hat{A}$的**本征值**，$\Psi(q, t)$称$\hat{A}$的**本征态**；
  $\hat{A}\Psi(q, t) = a\Psi(q, t)$称$\hat{A}$的**本征方程**。

1.2.4 公设4. 力学量的平均值

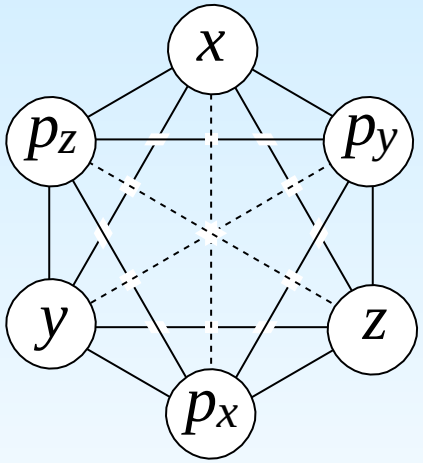
Postulates 4. Average value of a physical observable

- 如$\Psi(q, t)$是一体系在时刻t的归一化的状态函数，则在t时刻某一力学量A的平均值是

$$\overline{A} = \int \Psi^* \hat{A} \Psi d\tau$$

1.2.5 量子力学算符的对易规律

- 体系的两个力学量$\hat{A}$与同时具有确定值的条件是$\hat{A}$与$\hat{C}$对易即$[\hat{A}, \hat{C}]=0$
- 动量算符与坐标算符 $\hat{p}_i = -i\hbar \dfrac{\partial}{\partial q_i}$



$$\left[\hat{p}_i, \hat{q}_j\right] = \hat{p}_i\hat{q}_j - \hat{q}_j\hat{p}_i$$

$$= \left(-i\hbar\partial/\partial q_i\right)\hat{q}_j - \hat{q}_j\left(-i\hbar\partial/\partial q_i\right)$$

$$= \hat{q}_j\left(-i\hbar\partial/\partial q_i\right) - \left(-i\hbar\partial q_j/\partial q_i\right) - \hat{q}_j\left(-i\hbar\partial/\partial q_i\right)$$

$$= i\hbar\delta_{ij}$$

$$\left[\hat{p}_i, \hat{q}_i\right] = -i\hbar$$

海森堡不确定关系式可由此推出

参见《量子化学—基本原理和从头计算法》(上册)

1.2.6 公设5. 态随时间变化的Schrödinger方程

Postulates 5. Time Dependent Schrödinger Equation

- 一个未微扰体系的状态随时间的变化是由含时间的Schrödinger方程给出

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

- 能量*E*与时间*t*

$$\hat{E} = i\hbar\partial/\partial t$$

$$\left[\hat{E},t\right] = \hat{E}t - t\hat{E} = i\hbar$$

- 定态Schrödinger方程

如Hamilton算符与时间无关，则设 $\Psi(q,t)=\psi(q)f(t)$

$$\hat{H}\Psi = f(t)\hat{H}\psi(q) = i\hbar\frac{\partial}{\partial t}\Psi = i\hbar\frac{\partial f(t)}{\partial t}\psi(q)$$

$$\frac{\hat{H}\psi(q)}{\psi(q)} = i\hbar\frac{1}{f(t)}\frac{\partial f(t)}{\partial t}$$

令两边均等于E

$$\frac{df(t)}{f(t)} = -\frac{iE}{\hbar}dt \longrightarrow f(t) = Ae^{-iEt/\hbar}$$

$$\hat{H}\psi(q) = E\psi(q)$$ 定态Schrödinger方程

$$\Psi(q,t) = e^{-iEt/\hbar}\psi(q)$$ 定态波函数

§1.3 维里定理 The Virial Theorem

定态Schrödinger方程$\hat{H}\psi = E\psi$，设$\hat{A}$为不含时的线性算符

$$\int \psi^*[\hat{H},\hat{A}]\psi d\tau = \langle\psi|\hat{H}\hat{A}-\hat{A}\hat{H}|\psi\rangle$$

$$= \langle\psi|\hat{H}|\hat{A}\psi\rangle - E\langle\psi|\hat{A}|\psi\rangle$$

$\hat{H}$是厄米算符 $$\langle\psi|\hat{H}|\hat{A}\psi\rangle = \langle\hat{A}\psi|\hat{H}|\psi\rangle^*$$

$$= E^*\langle\hat{A}\psi|\psi\rangle^* = E\langle\psi|\hat{A}|\psi\rangle$$

$$\int \psi^*[\hat{H},\hat{A}]\psi d\tau = 0$$

超维里定理

hypervirial theorem

$$\hat{A} = \sum_i q_i \hat{p}_i = -i\hbar\sum_i q_i \frac{\partial}{\partial q_i}$$

$$\left[\hat{H},\sum_i q_i\hat{p}_i\right] = \sum_i [\hat{H},q_i\hat{p}_i] = \sum_i q_i[\hat{H},\hat{p}_i] + \sum_i [\hat{H},q_i]\hat{p}_i$$

单粒子体系 $\hat{H}=\hat{T}+\hat{V}=\frac{1}{2m}(\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2)+V(x,y,z)$

$$[\hat{H},x]=[\hat{T}+\hat{V},x]=[\hat{T},x]+[V(x,y,z),x]$$

$$=\frac{1}{2m}[\hat{p}_x^2,x]+\frac{1}{2m}[\hat{p}_y^2,x]+\frac{1}{2m}[\hat{p}_z^2,x]$$

$$=\frac{1}{2m}(\hat{p}_x^2x-x\hat{p}_x^2)=-i\hbar\frac{\hat{p}_x}{m}$$

$$[\hat{H},\hat{p}_x]=[\hat{T}+\hat{V},\hat{p}_x]=[\hat{T},\hat{p}_x]+[V(x,y,z),\hat{p}_x]=i\hbar\frac{\partial V}{\partial x}$$

$$\left[\hat{H},\sum_i q_i\hat{p}_i\right]=\sum_i q_i[\hat{H},\hat{p}_i]+\sum_i[\hat{H},q_i]\hat{p}_i$$

$$=i\hbar\sum_i q_i\frac{\partial V}{\partial q_i}-i\hbar\sum_i\frac{\hat{p}_i^2}{m}$$

$$=i\hbar\sum_i q_i\frac{\partial V}{\partial q_i}-2i\hbar\hat{T}$$

$$\left\langle\psi\left|\sum_i q_i\frac{\partial V}{\partial q_i}\right|\psi\right\rangle=2\left\langle\psi\left|\hat{T}\right|\psi\right\rangle=2\left\langle\hat{T}\right\rangle$$

维里定理 virial theorem

维里定理的简化形式

若函数$f(x_1, x_2, \ldots, x_j)$满足 $f(sx_1, sx_2, \ldots, sx_j) = s^n f(x_1, x_2, \ldots, x_j)$，则称$f$为**$n$次齐函数**(homogeneous of degree n)

Euler齐次函数定理 $$\sum_{i=1}^{N} x_i \frac{\partial f}{\partial x_i} = nf$$

若体系的势能V是直角坐标的n次齐函数，则 $\sum_{i=1}^{N} q_i \frac{\partial V}{\partial q_i} = nV$

维里定理简化为

$$2\langle T\rangle = n\langle V\rangle$$

对束缚态，$\langle T\rangle + \langle V\rangle = E$

$$\langle V\rangle = \frac{2E}{n+2} \qquad \langle T\rangle = \frac{nE}{n+2}$$