转动和平移

轨道角动量

球谐函数

三维空间的转动

空间平移

时间平移

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回顾：力学量对应的算符是厄米算符

- 可测物理量的所有本征值都是实数
  →力学量对应的算符是厄米算符

- 定理：同一力学量的不同本征值对应的本征矢正交

$$\left.\begin{array}{l}\mathbf{A}|\alpha\rangle=\alpha|\alpha\rangle \\ \mathbf{A}|\beta\rangle=\beta|\beta\rangle\end{array}\right\} \Rightarrow \langle\alpha|\mathbf{A}|\beta\rangle=\alpha\langle\alpha|\beta\rangle=\beta\langle\alpha|\beta\rangle$$

$$\Rightarrow(\alpha-\beta)\langle\alpha|\beta\rangle=0 \Rightarrow \langle\alpha|\beta\rangle=0$$

- 定理：力学量的所有本征矢，构成态空间的完备基

（谱分解定理）下列条件等价：
1. 算符是规范的（$\hat{A}^{\dagger}\hat{A}=\hat{A}\hat{A}^{\dagger}$）
2. 算符的本征矢构成正交完备基（规范基、标准基）
3. 算符在某组正交完备基下是对角化的

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轨道角动量

$$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} = -i\hbar\vec{r} \times \nabla$$

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

角动量的对易关系

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$$
$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$$
$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$
$$[\hat{L}_j, \hat{L}_k] = i\hbar\varepsilon_{jkl}\hat{L}_l$$

定理：对易的两个厄密算符，有共同本征矢且本征矢完备

- 角动量的三个分量互相不对易，所以没有共同本征矢
- 只有一个分量可以有确定值
- 与经典物理学不同，“角动量矢量”是不存在的
- 海森堡不确定关系与上一定理给出同样结论

$$\boldsymbol{AB} = \boldsymbol{BA}$$
$$\boldsymbol{A}|a,j\rangle = a|a,j\rangle$$
$$\boldsymbol{AB}|a,j\rangle = \boldsymbol{BA}|a,j\rangle = a\boldsymbol{B}|a,j\rangle$$
$$\Rightarrow \boldsymbol{B}|a,j\rangle \equiv \sum_k c_{jk}\,|a,j\rangle$$

$\boldsymbol{B}$是分块矩阵

在$\boldsymbol{A}$的特征子空间将$\boldsymbol{B}$对角化

角动量的模长

模长的平方

$$\hat{\vec{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = \sum_k \hat{L}_k \hat{L}_k$$

$$\hat{\vec{L}}^2 = -\hbar^2 \left\{ (x^2+y^2)\frac{\partial^2}{\partial z^2} + (y^2+z^2)\frac{\partial^2}{\partial x^2} + (z^2+x^2)\frac{\partial^2}{\partial y^2} - 2xy\frac{\partial^2}{\partial x \partial y} - 2yz\frac{\partial^2}{\partial y \partial z} - 2zx\frac{\partial^2}{\partial z \partial x} - 2x\frac{\partial}{\partial x} - 2y\frac{\partial}{\partial y} - 2z\frac{\partial}{\partial z} \right\}$$

$$\left[\hat{\vec{L}}^2, \hat{L}_j\right] = \left[\hat{L}_k\hat{L}_k, \hat{L}_j\right] = \left[\hat{L}_k, \hat{L}_j\right]\hat{L}_k + \hat{L}_k\left[\hat{L}_k, \hat{L}_j\right] = i\hbar\varepsilon_{kjl}\hat{L}_l\hat{L}_k + i\hbar\varepsilon_{kjl}\hat{L}_k\hat{L}_l = i\hbar\varepsilon_{kjl}\hat{L}_l\hat{L}_k - i\hbar\varepsilon_{ljk}\hat{L}_k\hat{L}_l = 0$$

$$\boxed{\left[\hat{\vec{L}}^2, \hat{L}_x\right] = 0, \quad \left[\hat{\vec{L}}^2, \hat{L}_y\right] = 0, \quad \left[\hat{\vec{L}}^2, \hat{L}_z\right] = 0}$$

$\left\{\hat{\vec{L}}^2, \hat{L}_z\right\}$对易，故有共同特征矢，且共同特征矢正交完备

$$\hat{\vec{L}}^2|\alpha,\beta\rangle = \alpha|\alpha,\beta\rangle$$
$$\hat{L}_z|\alpha,\beta\rangle = \beta|\alpha,\beta\rangle$$

以共同特征矢为标准基，$\hat{\vec{L}}^2, \hat{L}_z$都是对角矩阵（即可以同时对角化）

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球坐标系下的算符

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$
$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$
$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$\begin{cases} \dfrac{\partial}{\partial x} = \sin\theta\cos\varphi\dfrac{\partial}{\partial r} + \dfrac{1}{r}\cos\theta\cos\varphi\dfrac{\partial}{\partial\theta} - \dfrac{1}{r}\csc\theta\sin\varphi\dfrac{\partial}{\partial\varphi} \\ \dfrac{\partial}{\partial y} = \sin\theta\sin\varphi\dfrac{\partial}{\partial r} + \dfrac{1}{r}\cos\theta\cos\varphi\dfrac{\partial}{\partial\theta} + \dfrac{1}{r}\csc\theta\cos\varphi\dfrac{\partial}{\partial\varphi} \\ \dfrac{\partial}{\partial z} = \cos\theta\dfrac{\partial}{\partial r} - \dfrac{1}{r}\sin\theta\dfrac{\partial}{\partial\theta} \end{cases}$$

$$\hat{L}_x = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)$$
$$\hat{L}_y = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)$$
$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

$$\hat{\vec{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$
$$= -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}$$

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角动量算符$\hat{\vec{L}}^2, \hat{L}_z$的共同本征态

$$\hat{L}_z \Phi(\varphi) = \lambda \Phi(\varphi)$$

$$\Updownarrow$$

$$-i\hbar \frac{\partial}{\partial \varphi} \Phi(\varphi) = \lambda \Phi(\varphi) \Longrightarrow \Phi_{m_l}(\varphi) = \frac{1}{\sqrt{2\pi}} e^{i m_l \varphi}, m_l \in \mathbb{Z}$$

此即氢原子解中得到的方程：

$$\frac{d^2}{d\varphi^2} \Phi(\varphi) + m_l^2 \Phi(\varphi) = 0$$

$$\hat{\vec{L}}^2 Y(\theta, \varphi) = \alpha Y(\theta, \varphi)$$

$$\Updownarrow$$

$$-\hbar^2 \left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \varphi^2} \right\} Y(\theta, \varphi) = \alpha Y(\theta, \varphi)$$

$$\Downarrow$$

$$Y(\theta, \varphi) = \Theta(\theta) \Phi(\varphi)$$

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角动量本征态是球谐函数

$$-\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\big(\Theta(\theta)\Phi(\varphi)\big)}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\big(\Theta(\theta)\Phi(\varphi)\big)}{\partial\varphi^2}\right\}=\alpha\Theta(\theta)\Phi(\varphi)$$

$$\frac{d^2}{d\varphi^2}\Phi(\varphi)+m_l^2\Phi(\varphi)=0 \qquad -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{m_l^2}{\sin^2\theta}\Theta=\frac{\alpha}{\hbar^2}\Theta$$

即前面得到的方程

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{m_l^2}{\sin^2\theta}\Theta=l(l+1)\Theta$$

$$\boxed{\begin{gathered}\hat{\vec{L}}^2Y_{lm}(\theta,\varphi)=l(l+1)\hbar^2Y_{lm}(\theta,\varphi)\\ \hat{L}_zY_{lm}(\theta,\varphi)=m\hbar Y_{lm}(\theta,\varphi)\\ l=0,1,2,\cdots;m=-l,-l+1,\cdots,+l\end{gathered}}$$

$Y_{lm}(\theta,\varphi)$是$\hat{\vec{L}}^2$和$\hat{L}_z$的共同本征态

$Y_{lm}(\theta,\varphi)$是球面平方可积函数的正交完备基
可能出现在任何三维空间的问题中

l:轨道量子数，m:磁量子数

球谐函数 Spherical Harmonics

l	m	$Y_{lm}(\theta,\varphi)$	$r^l Y_{lm}(\theta,\varphi)$
0	0	$Y_{0,0}(\theta,\varphi)=\frac{1}{\sqrt{4\pi}}$	$Y_{0,0}=\frac{1}{\sqrt{4\pi}}$
1	0	$Y_{1,0}(\theta,\varphi)=\sqrt{\frac{3}{8\pi}}\cos\theta$	$rY_{1,0}=\sqrt{\frac{3}{8\pi}}z$
	±1	$Y_{1,\pm1}(\theta,\varphi)=\mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\varphi}$	$rY_{1,\pm1}=\mp\sqrt{\frac{3}{8\pi}}(x+iy)$
2	0	$Y_{2,0}(\theta,\varphi)=\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$	$r^2Y_{2,0}=\sqrt{\frac{5}{16\pi}}(2z^2-x^2-y^2)$
	±1	$Y_{2,\pm1}(\theta,\varphi)=\mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{\pm i\varphi}$	$r^2Y_{2,\pm1}=\mp\sqrt{\frac{15}{8\pi}}(x\pm iy)z$
	±2	$Y_{2,\pm2}(\theta,\varphi)=\mp\sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\varphi}$	$r^2Y_{2,\pm2}=\mp\sqrt{\frac{15}{32\pi}}(x\pm iy)^2$
3	0	$Y_{3,0}(\theta,\varphi)=\sqrt{\frac{7}{16\pi}}(5\cos^3\theta-3\cos\theta)$	$r^3Y_{3,0}=\sqrt{\frac{7}{16\pi}}[2z^3-3(x^2+y^2)z]$
	±1	$Y_{3,\pm1}(\theta,\varphi)=\mp\sqrt{\frac{21}{64\pi}}\sin\theta\,(5\cos^2\theta-1)e^{\pm i\varphi}$	$r^3Y_{3,\pm1}=\mp\sqrt{\frac{21}{64\pi}}(x\pm iy)(4z^2-x^2-y^2)$
	±2	$Y_{3,\pm2}(\theta,\varphi)=\sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\varphi}$	$r^3Y_{3,\pm2}=\sqrt{\frac{105}{32\pi}}(x\pm iy)^2 z$
	±3	$Y_{3,\pm3}(\theta,\varphi)=\mp\sqrt{\frac{35}{64\pi}}\sin^3\theta\, e^{\pm 3i\varphi}$	$r^3Y_{3,\pm3}=\mp\sqrt{\frac{35}{64\pi}}(x\pm iy)^3$

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例

- 某一时刻的波函数

$$\psi(\vec{r}) = f(r)\left(1 + \frac{z}{r} + \frac{z^2}{r^2}\right)$$

- 测量角动量$\vec{L}^2, L_z$

测量是向仪器本征态的投影

用$(\vec{L}^2, L_z)$的共同本征态展开波函数，

$$\psi \propto \sqrt{4\pi}Y_{00} + \sqrt{\frac{8\pi}{3}}Y_{10} + \left(\frac{1}{3}\sqrt{\frac{16\pi}{5}}Y_{20} + \frac{1}{3}\sqrt{4\pi}Y_{00}\right)$$

$$\propto 4\sqrt{5}Y_{00} + \sqrt{30}Y_{10} + 2Y_{20}$$

根据统计解释：

L_z必然是$0\hbar$;

$\vec{L}^2$可能是（1）$0\hbar^2$，$p = \frac{40}{57}$;　（2）$2\hbar^2$，$p = \frac{5}{19}$;　（2）$6\hbar^2$，$p = \frac{2}{57}$

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角动量在氢原子中守恒

$$\frac{d\hat{A}}{dt} = \frac{\partial \hat{A}}{\partial t} + \frac{1}{i\hbar}[\hat{A}, \hat{H}]$$

$$\frac{\partial \hat{L}_j}{\partial t} = 0$$

哈密顿算符

$$\hat{H} = \frac{\hat{\vec{p}}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}$$

前面作业计算过

$$[\hat{L}_j, \hat{\vec{p}}^2] = 0$$

$$\hat{L}_x = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)$$

$$\hat{L}_y = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

$$[\hat{L}_j, 1/r] = 0$$

$$[\hat{L}_j, \hat{H}] = 0$$

$$[\hat{\vec{L}}^2, \hat{H}] = 0$$

$\hat{\vec{L}}^2, \hat{L}_z$是守恒量

$\{\hat{H}, \hat{\vec{L}}^2, \hat{L}_z\}$相互对易，有完备共同本征矢

前面求解氢原子的薛定谔方程时，作了三次分离变量，等价于找到三个相互对易的守恒量

本征态下轨道角动量的空间取向

$Y_{lm}(\theta,\varphi)$是$\hat{\vec{L}}^2$和$\hat{L}_z$的共同本征态
不是$\hat{L}_x$或$\hat{L}_y$的本征态

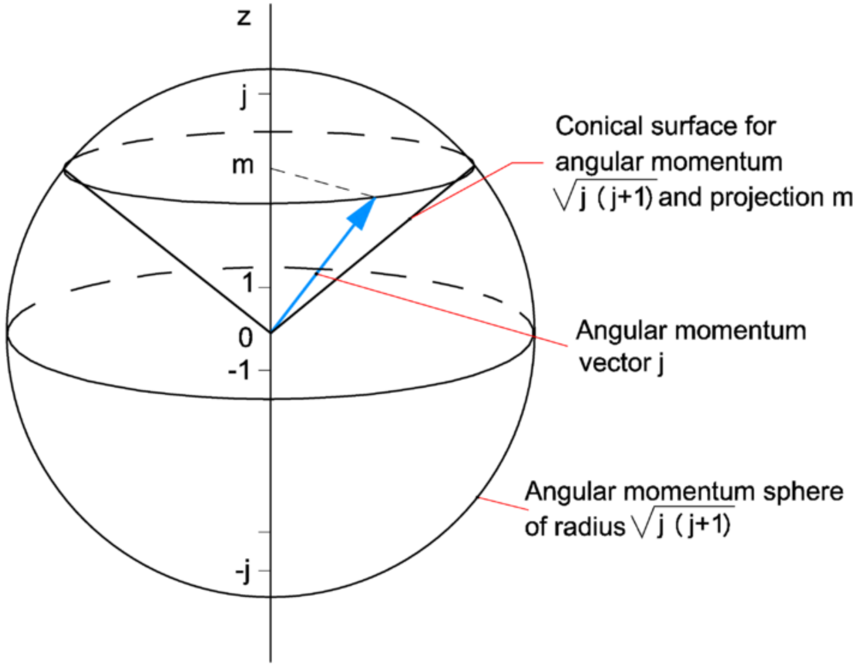
$$\langle L_x\rangle = \int_0^\pi d\cos\theta \int_0^{2\pi} d\varphi\, Y_{lm}^*(\theta,\varphi)\hat{L}_x Y_{lm}(\theta,\varphi) = 0$$

$$\langle L_y\rangle = \cdots = 0$$

$$\langle L_z\rangle = \cdots = m\hbar$$

$$\left\langle\sqrt{\vec{L}^2}\right\rangle = \sqrt{l(l+1)}\hbar$$

易误解的图示



角动量算符是转动的生成元*

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

$$\hat{L}_z f(x,y,z) = \hat{L}_z f(r,\theta,\varphi)(\text{球坐标})$$
$$= -i\hbar\frac{\partial}{\partial\varphi}f(r,\theta,\varphi)$$

$$\frac{i}{\hbar}\hat{L}_z f(r,\theta,\varphi) = \frac{\partial}{\partial\varphi}f(r,\theta,\varphi)$$

$$\boxed{\hat{R}(\vec{\psi}) \overset{\text{def}}{=} e^{-\frac{i}{\hbar}\hat{\vec{L}}\cdot\vec{\psi}}, \qquad \hat{R}f(\vec{r}) = f(R^{-1}\vec{r})}$$

泰勒展开，可证

$$e^{\frac{i}{\hbar}\hat{L}_z\alpha}f(r,\theta,\varphi) = f(r,\theta,\varphi+\alpha)$$

结果与坐标系选取无关

$$e^{\frac{i}{\hbar}\hat{L}_z\alpha}f(x,y,z)$$
$$= f(x\cos\alpha - y\sin\alpha, x\sin\alpha + y\cos\alpha, z)$$

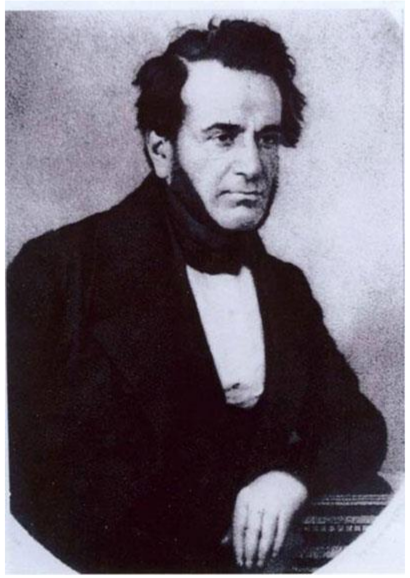
同理$\hat{L}_x, \hat{L}_y$分别是绕x, y轴的转动生成元

氢原子的哈密顿量转动不变，

$$H = \frac{\vec{p}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}$$

所以转动的生成元角动量守恒

转动公式*



Benjamin Olinde Rodrigues
1795–1851
French banker, mathematician, and social reformer

罗德里格斯参数

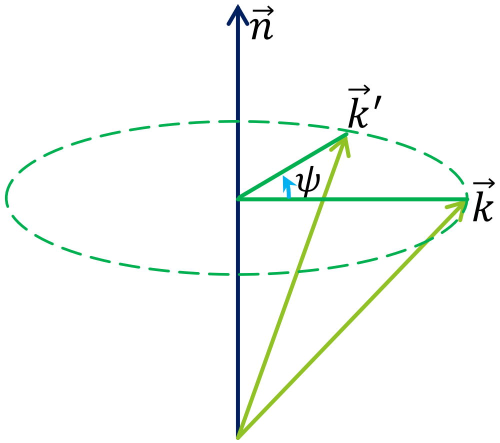
$$\vec{\psi} = \psi \vec{n}$$

$\vec{n}$为转动轴， ψ为转动角

矢量$\vec{k}$转动后成为（推导）

$$\vec{k}' = \vec{k} + (1-\cos\psi)\vec{n}\times\left(\vec{n}\times\vec{k}\right) + \sin\psi\,\vec{n}\times\vec{k}$$

$$\stackrel{\text{def}}{=} R\left(\vec{\psi}\right)\vec{k}$$



其中转动矩阵为

$$R\left(\vec{\psi}\right) = 1 + X_{\vec{n}}^2(1-\cos\psi) + X_{\vec{n}}\sin\psi$$

$$= \begin{pmatrix} n_1^2(1-\cos\psi)+\cos\psi & n_1n_2(1-\cos\psi)-n_3\sin\psi & n_1n_3(1-\cos\psi)+n_2\sin\psi \\ n_1n_2(1-\cos\psi)+n_3\sin\psi & n_2^2(1-\cos\psi)+\cos\psi & n_2n_3(1-\cos\psi)-n_1\sin\psi \\ n_1n_3(1-\cos\psi)-n_2\sin\psi & n_2n_3(1-\cos\psi)+n_1\sin\psi & n_3^2(1-\cos\psi)+\cos\psi \end{pmatrix}$$

量子力学中波函数的转动

$$\hat{R}\left(\vec{\psi}\right)u(\vec{r}) = u\left(R^{-1}\left(\vec{\psi}\right)\vec{r}\right)$$

注意算子只能是对态矢的线性变换

满足同态关系：

$$\hat{R}_1\hat{R}_2 f(\vec{r}) \equiv f\left((R_1R_2)^{-1}\vec{r}\right)$$

动量是空间平移的生成元

- 空间平移算符

$$\psi(x-a)=\psi(x)+(-a)\frac{\partial}{\partial x}\psi(x)+\frac{1}{2!}\left(-a\frac{\partial}{\partial x}\right)^2\psi(x)+\cdots$$

$$=\left\{1+\left(-a\frac{\partial}{\partial x}\right)+\frac{1}{2!}\left(-a\frac{\partial}{\partial x}\right)^2+\cdots\right\}\psi(x)$$

$$=e^{-a\frac{\partial}{\partial x}}\psi(x)=e^{-\frac{ia\hat{p}}{\hbar}}\psi(x)$$

$$\hat{T}(a)\stackrel{\text{def}}{=}e^{-\frac{ia\hat{p}}{\hbar}}$$

$$\hat{T}(a)\psi(x)=\psi(x-a)$$

- 空间平移对称性

$$\hat{T}(a)\hat{H}\hat{T}(a)^{-1}=\hat{H}\Rightarrow e^{\frac{a\hat{p}}{i\hbar}}\hat{H}e^{-\frac{a\hat{p}}{i\hbar}}=\hat{H}\xRightarrow{a=\epsilon\to 0}\left(1+\epsilon\frac{1}{i\hbar}\hat{p}\right)\hat{H}\left(1-\epsilon\frac{1}{i\hbar}\hat{p}\right)=\hat{H}$$

$$\Rightarrow[\hat{p},\hat{H}]=0\Rightarrow\frac{d}{dt}\hat{p}=\frac{\partial}{\partial t}\hat{p}+[\hat{p},\hat{H}]=0\Rightarrow\hat{p}\text{守恒}$$

时间演化算符

薛定谔方程

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

引进时间演化算符

$$\psi(t) \stackrel{\text{def}}{=} \hat{U}(t,t_0)\psi(t_0)$$

时间演化算符满足薛定谔方程

$$i\hbar\frac{\partial}{\partial t}\hat{U}(t,t_0)\cancel{\psi(t_0)} = \hat{H}\hat{U}(t,t_0)\cancel{\psi(t_0)}$$

若$\hat{H}$不含时，

$$\hat{U}(t,0) = e^{-\frac{i}{\hbar}\hat{H}t}$$

$$\equiv 1 + \left(-\frac{i}{\hbar}\hat{H}t\right) + \frac{1}{2!}\left(-\frac{i}{\hbar}\hat{H}t\right)^2 + \cdots$$

代入方程可直接检验成立

哈密顿量是时间平移的生成元

类比：控制论中的状态转移矩阵

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含时系统的时间演化算符*

演化算符的薛定谔方程

$$\frac{\partial}{\partial t}\hat{U}(t,0)=\frac{1}{i\hbar}\hat{H}(t)\hat{U}(t,0)$$

取近似

$$\hat{U}(t,0)=1$$

代入薛定谔方程积分，然后迭代得

Dyson级数

$$\begin{aligned}&\hat{U}(t,0)\\&=1+\frac{1}{i\hbar}\int_0^t d\tau_1\hat{H}(\tau_1)\\&+\frac{1}{(i\hbar)^2}\int_0^t d\tau_1\hat{H}(\tau_1)\int_0^{\tau_1} d\tau_2\hat{H}(\tau_2)\\&+\frac{1}{(i\hbar)^3}\int_0^t d\tau_1\hat{H}(\tau_1)\int_0^{\tau_1} d\tau_2\hat{H}(\tau_2)\int_0^{\tau_2} d\tau_3\hat{H}(\tau_3)\\&+\cdots\end{aligned}$$

Freeman J. Dyson 1923–2020
英国数学家、理论物理学家

引进编时乘积算子

$$\mathbf{T}\{\hat{H}(\tau_1)\hat{H}(\tau_2)\}\overset{\text{def}}{=}\begin{cases}\hat{H}(\tau_1)\hat{H}(\tau_2), & \tau_1\geq\tau_2;\\ \hat{H}(\tau_2)\hat{H}(\tau_1), & \tau_1<\tau_2.\end{cases}$$

$$\boxed{\hat{U}(t,0)=\mathbf{T}\left\{\exp\left(\frac{1}{i\hbar}\int_0^t\hat{H}(\tau)d\tau\right)\right\}}$$

类比：控制论中含时系统的状态转移矩阵