第四章　力学量用算符表示

§4.1 算符及其运算　Operator

4.1.1 基本的和导出的力学量算符

在量子力学里，力学量用算符来代表。

算符就是可以作用于波函数把它变成另一个函数的运算。

此后代表力学量 F 的算符将记做 $\hat{F}$ 。量子力学中基本的力学量算符是：

坐标算符 $\hat{\vec{r}}=\vec{r}$，也就是 $\hat{x}=x,\ \hat{y}=y,\ \hat{z}=z,$

动量算符 $\hat{\vec{p}}=-\mathrm{i}\hbar\nabla$，也就是 $\hat{p}_x=-\mathrm{i}\hbar\dfrac{\partial}{\partial x},\ \hat{p}_y=-\mathrm{i}\hbar\dfrac{\partial}{\partial y},\ \hat{p}_z=-\mathrm{i}\hbar\dfrac{\partial}{\partial z},$

这意思是说：

$$\hat{x}\psi=x\psi,\ \hat{y}\psi=y\psi,\ \hat{z}\psi=z\psi,$$

$$\hat{p}_x\psi=-\mathrm{i}\hbar\frac{\partial\psi}{\partial x},\ \hat{p}_y\psi=-\mathrm{i}\hbar\frac{\partial\psi}{\partial y},\ \hat{p}_z\psi=-\mathrm{i}\hbar\frac{\partial\psi}{\partial z}.$$

其它的力学量算符按下列规则来构成：若在经典力学中力学量 F 用坐标和动量表出的关系式是

$$F=f(\vec{r},\vec{p}),$$

（ f 代表一个函数关系），那么 F 所对应的算符就是：

$$\hat{F}=f(\hat{\vec{r}},\hat{\vec{p}})=f(\vec{r},-\mathrm{i}\hbar\nabla),$$

其中 f 是同样的函数关系。据此可以定义粒子的 Hamiltonian 算符和轨道角动量算符。

更准确地说，上面所定义的算符应该称作是“坐标表象”中的算符。

用算符来代替经典力学中的力学量，是把经典力学“量子化”的重要步骤。但是在量子力学中有一些量是没有经典力学的对应物的，比如宇称和自旋角动量，那时我们就要直接从量子力学的分析出发来引进它们的算符。　parity

4.1.2 线性算符

在量子力学中考虑的力学量（又称可观察量）算符大都是**线性算符**（只有时间反演算符是例外）。线性算符的定义是：若算符 $\hat{F}$ 满足

$$\hat{F}(c_1\psi_1+c_2\psi_2)=c_1(\hat{F}\psi_1)+c_2(\hat{F}\psi_2),$$

其中 c_1, c_2 是复常数，则 $\hat{F}$ 称为线性算符。这个线性性质和态叠加原理相容。

根据前面的法则，坐标算符 $\hat{\vec{r}}=\vec{r}$ 对波函数的作用就是直接相乘，这显然是一个线性算符，微分算符也显然是线性算符，所以它们的函数通常也是线性算符。

4.1.3 算符的运算和厄密(Hermitian)算符

算符的基本运算是相加和相乘，定义为

$$(\hat{F}+\hat{G})\psi=\hat{F}\psi+\hat{G}\psi,\quad(\forall\psi)$$

$$(\hat{F}\hat{G})\psi=\hat{F}(\hat{G}\psi).\quad(\forall\psi)$$

算符的加-乘混合运算满足分配律，即

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

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

常数 c 也可以看作是算符，满足

$$(c\hat{F})\psi=(\hat{F}c)\psi=c(\hat{F}\psi).\quad(\forall\psi)$$

算符的相等定义为：若

$$\hat{F}\psi=\hat{G}\psi,\quad(\forall\psi)$$

则

$$\hat{F}=\hat{G}.$$

单位算符 $\hat{I}$ 定义为

$$\hat{I}\psi=\psi,\quad(\forall\psi)$$

所以

$$\hat{I}\hat{F}=\hat{F}\hat{I}=\hat{F}.\quad(\forall\hat{F})$$

所以 $\hat{I}$ 也经常被简写为1。

由于算符的基本运算是加和乘，所以只有在特定的情形下“算符的函数”才有意义。第一种情形是坐标算符 $\hat{r}$ 的函数 $\hat{V}(\hat{r})$，它在坐标表象中就是 $V(\vec{r})$，其函数形式一般不受限制。第二种情形是这个算符函数是一个多项式或者可以表为收敛的幂级数。一个常用的例子是指数函数 $\mathrm{e}^{\hat{O}}$，它定义为

$$\mathrm{e}^{\hat{O}}=\sum_{n=0}^{\infty}\frac{1}{n!}\hat{O}^n.$$

由此不难验证，比如

$$\mathrm{e}^{a(d/dx)}\psi(x)=\sum_{n=0}^{\infty}\frac{a^n}{n!}\frac{d^n\psi}{dx^n}=\psi(x+a).$$

而像 $1/\hat{O}\equiv\hat{O}^{-1}$（逆算符）这样的函数，对于一般的算符而言只在 $\hat{O}$ 可逆的情况下才有意义。

由一个算符 $\hat{F}$ 还可以产生它的一些伴生算符。在量子力学里最常用的是 $\hat{F}$ 的**厄密(Hermitian)共轭算符**，记为 $\hat{F}^\dagger$，定义为：若

$$\int\psi^*(\hat{F}\phi)\,d\tau=\int(\hat{F}^\dagger\psi)^*\phi\,d\tau,\quad(\forall\psi,\phi)$$

则 $\hat{F}^\dagger$ 称为 $\hat{F}$ 的 Hermitian 共轭算符。要注意：乘积算符的 Hermitian 共轭是它的因子算符的 Hermitian 共轭按**相反次序排列**的乘积，即是

$$(\hat{F}\hat{G})^\dagger=\hat{G}^\dagger\hat{F}^\dagger.$$

若算符 $\hat{F}$ 满足

$$\hat{F}^\dagger=\hat{F},$$

也就是说

$$\int\psi^*(\hat{F}\phi)\,d\tau=\int(\hat{F}\psi)^*\phi\,d\tau,\quad(\forall\psi,\phi)$$

那么 $\hat{F}$ 称为自厄密共轭算符，简称为 Hermitian（厄密的）算符。Hermitian 算符是量子力学中最重要的算符。其他的一些伴生算符，例如复共轭算符，转置算符等等，今后用得不多。

4.1.4 算符的对易关系

算符的相乘与普通乘法的最大区别是：算符相乘的结果可能与乘的次序有关，也就是说，算符的乘积一般说是不满足交换律的。

定义：表达式

$$[\hat{F},\hat{G}]\equiv\hat{F}\hat{G}-\hat{G}\hat{F}$$

对易的

称为 $\hat{F}$ 和 $\hat{G}$ 的**对易括号**或**对易子**（commutator）。在 $[\hat{F},\hat{G}]=0$ 时，称 $\hat{F}$ 和 $\hat{G}$ **对易**，否则称为**不对易**。对易也就是可以交换位置。我们将会看到，算符所满足的对易关系是算符的基本的、极为重要的量子力学性质。

以后经常需要进行对易括号的运算，以便从已知的对易括号导出新的对易括号。对易括号的基本性质是：

(1) 对易括号是交换反对称的，即

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

(2) 对易括号是线性的，即

$$[\hat{A}+\hat{B},\hat{C}]=[\hat{A},\hat{C}]+[\hat{B},\hat{C}],$$
$$[\hat{A},\hat{B}+\hat{C}]=[\hat{A},\hat{B}]+[\hat{A},\hat{C}],$$
$$[c\hat{A},\hat{B}]=[\hat{A},c\hat{B}]=c[\hat{A},\hat{B}].$$

(3) 算符乘积的对易括号可以按照下述法则来展开：

$$[\hat{A}\hat{B},\hat{C}]=\hat{A}[\hat{B},\hat{C}]+[\hat{A},\hat{C}]\hat{B},$$
$$[\hat{A},\hat{B}\hat{C}]=\hat{B}[\hat{A},\hat{C}]+[\hat{A},\hat{B}]\hat{C}.$$

以第一式为例证明如下。

$$[\hat{A}\hat{B},\hat{C}]=\hat{A}\hat{B}\hat{C}-\hat{C}\hat{A}\hat{B}=\hat{A}\hat{B}\hat{C}-\hat{A}\hat{C}\hat{B}+\hat{A}\hat{C}\hat{B}-\hat{C}\hat{A}\hat{B}$$
$$=\hat{A}(\hat{B}\hat{C}-\hat{C}\hat{B})+(\hat{A}\hat{C}-\hat{C}\hat{A})\hat{B}=\hat{A}[\hat{B},\hat{C}]+[\hat{A},\hat{C}]\hat{B}.\ \blacksquare$$

(4) 对易括号满足 Jacobi 恒等式

$$[\hat{A},[\hat{B},\hat{C}]]+[\hat{B},[\hat{C},\hat{A}]]+[\hat{C},[\hat{A},\hat{B}]]=0.$$

(5) 量子力学的基本对易括号是

$$[\hat{x}_i,\hat{x}_j]=0,$$
$$[\hat{p}_i,\hat{p}_j]=0,$$
$$[\hat{p}_i,\hat{x}_j]=-\mathrm{i}\hbar\delta_{ij}=-[\hat{x}_i,\hat{p}_j],$$

其中 $i=1,2,3$ 分别代表 x,y,z，δ_{ij} 的定义是

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

称为 Kronecker 符号。第一个基本对易括号的正确性是一目了然的。第二个基本对易括号利用了“混合偏导数与求导的次序无关”的法则，即

$$\frac{\partial^2\psi}{\partial x_i\partial x_j}=\frac{\partial^2\psi}{\partial x_j\partial x_i}.$$

第三个基本对易括号的证明如下：

$$[\hat{p}_i,\hat{x}_j]\psi=\hat{p}_i\hat{x}_j\psi-\hat{x}_j\hat{p}_i\psi=-\mathrm{i}\hbar\left(\frac{\partial(x_j\psi)}{\partial x_i}-x_j\frac{\partial\psi}{\partial x_i}\right)$$
$$=-\mathrm{i}\hbar\left(\delta_{ij}\psi+x_j\frac{\partial\psi}{\partial x_i}-x_j\frac{\partial\psi}{\partial x_i}\right)=-\mathrm{i}\hbar\delta_{ij}\psi.\ \blacksquare$$

利用上面给出的基本对易括号和对易括号的运算法则，我们又不难证明：若 $\hat{F}=F(\hat{x},\hat{p}_x)$，则

$$[\hat{x},\hat{F}]=\mathrm{i}\hbar\frac{\partial F}{\partial p_x},\quad [\hat{p}_x,\hat{F}]=-\mathrm{i}\hbar\frac{\partial F}{\partial x},$$

以及对于 y 和 z 的类似式子，以及角动量算符的对易关系

$$[\hat{L}_x,\hat{L}_y]=\mathrm{i}\hbar\hat{L}_z,\quad [\hat{L}_y,\hat{L}_z]=\mathrm{i}\hbar\hat{L}_x,\quad [\hat{L}_z,\hat{L}_x]=\mathrm{i}\hbar\hat{L}_y,$$

其中

$$\hat{L}_x=\hat{y}\hat{p}_z-\hat{z}\hat{p}_y,\quad \hat{L}_y=\hat{z}\hat{p}_x-\hat{x}\hat{p}_z,\quad \hat{L}_z=\hat{x}\hat{p}_y-\hat{y}\hat{p}_x,$$

和

$$[L^2,\hat{L}_x]=[L^2,\hat{L}_y]=[L^2,\hat{L}_z]=0,$$

其中

$$L^2=\hat{L}_x{}^2+\hat{L}_y{}^2+\hat{L}_z{}^2.$$

§4.2 Hermitian 算符的主要性质

4.2.1 算符的本征方程

定义：设 $\hat{F}$ 是一个算符，则

$$\hat{F}\psi_\lambda = \lambda\psi_\lambda$$

称为 $\hat{F}$ 的**本征方程**，λ 称为**本征值**，ψ_λ 称为 $\hat{F}$ 的属于 λ 的**本征函数**，或**本征态**。

定义：若 ψ 是归一的，则

$$\overline{(\Delta F)^2} \equiv \overline{(\hat{F}-\bar{F})^2} \equiv \int \psi^*(\hat{F}-\bar{F})^2\psi d\tau \quad \left(\bar{F} \equiv \int \psi^*\hat{F}\psi d\tau\right)$$ 涨落与涨落现象

称为量 F 在态 ψ 上的**均方偏差**，也称**涨落**。

定理：若算符 $\hat{F}$ 是 Hermitian 算符，则且仅当 ψ 是 $\hat{F}$ 的本征态时 F 在态 ψ 上的涨落 $=0$，即

$$\overline{(\Delta F)^2} = 0.$$

证明：若 $\hat{F}$ 是 Hermitian 算符，则 $\hat{F}-\bar{F}$ 也是 Hermitian 算符（$\bar{F}$ 必是实数，证明见后），所以对任何态 ψ 有

$$\overline{(\Delta F)^2} \equiv \int \psi^*(\hat{F}-\bar{F})^2\psi d\tau = \int \left((\hat{F}-\bar{F})\psi\right)^* \left((\hat{F}-\bar{F})\psi\right) d\tau = \int \left|(\hat{F}-\bar{F})\psi\right|^2 d\tau \geq 0,$$

而当且仅当 $(\hat{F}-\bar{F})\psi = 0$ 时上式的“=”号成立。∎

定理：若算符 $\hat{F}$ 是 Hermitian 算符，则当 ψ 是 $\hat{F}$ 的本征态时，

$$\delta\bar{F}_\psi / \delta\psi = 0,$$

其中 $\bar{F}_\psi$ 是 $\hat{F}$ 在 ψ 上的平均值，$\delta\psi$ 是 ψ 的变分，这意味着 ψ 是 $\bar{F}_\psi$ 的局部极大值点或者极小值点或者鞍点。证明从略。

关于本征值和本征函数的物理意义，量子力学的基本假设是：算符 $\hat{F}$ 的**本征值集** $\{\lambda\}$ 就是力学量 F 的**测量值集**；$\hat{F}$ 的本征函数 ψ_λ 代表力学量 F 有**确定值** λ 的量子状态。

4.2.2 Hermitian 算符的本征值

定理：Hermitian 算符的本征值都是实数。

证明：本征方程是

$$\hat{F}\psi_\lambda = \lambda\psi_\lambda,$$

所以

$$(\hat{F}\psi_\lambda)^* = \lambda^*(\psi_\lambda)^*,$$

在 Hermitian 算符的定义式 $\int \psi^*(\hat{F}\phi)d\tau = \int (\hat{F}\psi)^*\phi d\tau$ 中让 $\psi = \phi = \psi_\lambda$，那么

$$\int (\psi_\lambda)^*(\hat{F}\psi_\lambda)d\tau = \int (\hat{F}\psi_\lambda)^*\psi_\lambda d\tau,$$

也就是

$$\lambda\int |\psi_\lambda|^2 d\tau = \lambda^*\int |\psi_\lambda|^2 d\tau,$$

而

$$\int |\psi_\lambda|^2 d\tau \neq 0,$$

所以

$$\lambda = \lambda^*. \text{ ∎}$$

定理的推论：Hermitian 算符的平均值（期望值）必是实数。

由于这个定理，我们要求所有的物理量（或称可观察量）的算符都是 Hermitian 算符。不难证明：坐标算符和动量算符都是 Hermitian 算符。以 $\hat{p}_x$ 为例，其 Hermitian 性证明如下。

$$\int_{-\infty}^{+\infty} \psi^*(\hat{p}_x\phi)\, dx = -i\hbar\int_{-\infty}^{+\infty} \psi^* \frac{\partial\phi}{\partial x} dx = -i\hbar(\psi^*\phi)\Big|_{-\infty}^{+\infty} + i\hbar\int_{-\infty}^{+\infty} \frac{\partial\psi^*}{\partial x}\phi\, dx = \int_{-\infty}^{+\infty} (\hat{p}_x\psi)^*\phi\, dx. \text{ ∎}$$

这里用到了分部积分法则和 $\psi\big|_{\pm\infty} = \varphi\big|_{\pm\infty} = 0$。

在一定条件下，坐标算符和动量算符的函数也是 Hermitian 算符。例如，若 $\hat{F}$ 和 $\hat{G}$ 都是 Hermitian 算符而且 $\hat{F}\hat{G}=\hat{G}\hat{F}$，那么 $\hat{F}\hat{G}$ 也是 Hermitian 算符。因此，角动量算符是 Hermitian 算符。

但是反过来说，任意地构造的 Hermitian 算符并不一定代表物理量。

4.2.3 本征函数系的正交性

定义：若两个函数 ψ_1 和 ψ_2 满足

$$\int \psi_1^* \psi_2 \, d\tau = 0,$$

则称它们是**正交**的。

正交性定理：同一个 Hermitian 算符的属于不同本征值的本征函数必是彼此正交的。

证明：设 Hermitian 算符 $\hat{F}$ 有两个本征函数 ϕ_1 和 ϕ_2，分别属于本征值 λ_1 和 λ_2 且 $\lambda_1 \neq \lambda_2$，那么

$$\hat{F}\psi_1 = \lambda_1 \psi_1,$$
$$\hat{F}\psi_2 = \lambda_2 \psi_2,$$

所以

$$\int \psi_1^* (\hat{F}\psi_2) \, d\tau = \lambda_2 \int \psi_1^* \psi_2 \, d\tau$$
$$= \int (\hat{F}\psi_1)^* \psi_2 \, d\tau = \lambda_1 \int \psi_1^* \psi_2 \, d\tau,$$

由于 $\lambda_1 \neq \lambda_2$，所以

$$\int \psi_1^* \psi_2 \, d\tau = 0. \quad \blacksquare$$

注意：这个定理的结论与 $\hat{F}$ 的本征值谱是分立（离散）谱还是连续谱无关。

彼此“正交”的几何意义就是彼此垂直。

如果 $\hat{F}$ 的本征值谱是非简并的和离散的，本征值为 $\{\lambda_1, \lambda_2, \cdots\}$，本征函数为 $\{\phi_1, \phi_2, \cdots\}$，那么波函数是平方可积的（证明从略），因而可以有限地归一化，所以我们有

$$\int \phi_k^* \phi_l \, d\tau = \delta_{kl}, \quad (k, l = 1, 2, \cdots)$$

其中

$$\delta_{kl} = \begin{cases} 0, & k \neq l \\ 1. & k = l \end{cases}$$

这称为函数系 $\{\phi_k, \ k = 1, 2, \cdots\}$ 的正交归一关系，或**正交归一性**。

为简单起见，以下记

$$\int \psi^* \phi \, d\tau \equiv (\psi, \phi),$$

并称之为 ψ 和 ϕ 的**内积**。它的主要性质有：

$$(\psi, \psi) \geq 0,$$

其中当且仅当 $\psi = 0$ 时 $=$ 号成立，

$$(c_1\psi_1 + c_2\psi_2, \phi) = c_1^*(\psi_1, \phi) + c_2^*(\psi_2, \phi),$$
$$(\psi, c_1\phi_1 + c_2\phi_2) = c_1(\psi, \phi_1) + c_2(\psi, \phi_2),$$
$$(\psi, \phi)^* = (\phi, \psi).$$

这样，函数系 $\{\phi_k\}$ 的正交归一性就可以写为

$$(\phi_k, \phi_l) = \delta_{kl},$$

而算符的 Hermitian 共轭的定义可以写为

$$(\phi, \hat{F}\psi) = (\hat{F}^\dagger \phi, \psi), \quad (\forall \phi, \psi)$$

所以 Hermitian 算符就定义为

$$(\phi, \hat{F}\psi) = (\hat{F}\phi, \psi). \quad (\forall \phi, \psi)$$

如果 $\hat{F}$ 的本征值谱是连续的，那么本征函数就不是平方可积的。这时候，本征函数系可以按 δ 函数归一化（以后再做说明）。

4.2.4 简并情形 共同本征函数

如果出现一个本征值有若干个线性独立的本征函数（即简并）的情形，那么正交性定理不能保证同一个本征值的不同本征函数是彼此正交的。但是不难证明，经过对本征函数进行适当的重新组合，可以使它们仍然是彼此正交的，例如线性代数里的施密特(Schmidt)正交化程序。

但是在量子力学里，我们有一个更加“物理”的办法来解决简并本征函数的正交性，那就是考虑**同时本征函数**。

定理：若 $[\hat{F},\hat{G}]=0$ 即 $\hat{F}\hat{G}=\hat{G}\hat{F}$，则 $\hat{F}$ 和 $\hat{G}$ 可以有同时（共同）本征函数，也就是存在函数 ϕ 使得 $\hat{F}\phi=\lambda\phi$ 和 $\hat{G}\phi=\mu\phi$（λ 和 μ 是常数）同时成立（证明从略）。

这个定理很容易推广到多个算符的情形。假如我们有一系列算符 $\{\hat{F},\hat{G},\hat{H},\cdots\}$，它们**两两对易**，即满足 $[\hat{F},\hat{G}]=[\hat{F},\hat{H}]=[\hat{G},\hat{H}]=\cdots=0$，那么它们就可以有同时本征函数，即存在 ϕ 使得 $\hat{F}\phi=\lambda\phi$，$\hat{G}\phi=\mu\phi$，$\hat{H}\phi=\kappa\phi$ 同时成立，其中 λ,μ,κ 是常数。

同时本征函数所描写的就是几个力学量同时有确定值的状态。 简并/退化， degenrate

这样，如果算符 $\hat{F}$ 的本征值 λ 有简并，我们就再引进另一个算符 $\hat{G}$，满足 $[\hat{F},\hat{G}]=0$，并求出 $\hat{F}$ 和 $\hat{G}$ 的同时本征函数。如果对于 $\hat{F}$ 简并的同时本征函数对于 $\hat{G}$ 不再是简并的（即分属于 $\hat{G}$ 的不同的本征值），那么正交性定理就保证了它们是正交的。但也有可能 $\hat{F}$ 和 $\hat{G}$ 的同时本征函数仍然有简并，那么我们就再引进第三个算符例如 $\hat{H}$，满足 $[\hat{F},\hat{G}]=[\hat{F},\hat{H}]=[\hat{G},\hat{H}]=0$，并求出 $\hat{F},\hat{G},\hat{H}$ 的同时本征函数，如此等等，直到所有的简并完全去除为止。这时，是一组（而不是一个）量子数例如 $(n,l,m,\cdots)$ 完全确定了一个量子态（即一个同时本征函数）。如果这些量子数都是分立量子数，那么这些同时本征函数的正交归一关系就是

$$(\phi_{nlm},\phi_{n'l'm'})=\delta_{nn'}\delta_{ll'}\delta_{mm'}.$$

4.2.5 力学量的完备集

某个力学量有简并本征函数的这种情形，多半出现在多自由度体系中。例如，在三维空间中运动的粒子的自由度数是 3，这时候只用一个力学量来描写粒子的状态显然是不够的。

定义：对于一个量子力学系统，一组彼此函数独立而又两两对易，并且完全去除简并的力学量的集合，称为它的**完备力学量集**。

完备力学量集里所包含的力学量的数目，通常是在经典力学的自由度数之外，再加上一些具有纯量子力学起源的自由度，例如宇称，自旋，或者一些内部自由度（例如同位旋）。

完备力学量集的选择不是唯一的。例如对于一个在三维空间中运动的无自旋粒子（不管它受到什么势场的作用），完备力学量集可以选为 $\{\hat{x},\hat{y},\hat{z}\}$，也可以选为 $\{\hat{p}_x,\hat{p}_y,\hat{p}_z\}$。但是，更经常的做法是让完备力学量集里包含系统的 Hamiltonian $\hat{H}$，这样的完备力学量集称为**完备守恒量集**（关于这样称呼的道理以后再解释）。

4.2.6 一般力学量的测量几率

根据完备力学量集的定义和态叠加原理，完备力学量集的全体算符的同时本征函数构成了表示该系统的量子状态的**正交归一完备基底**，也就是说，系统的任何状态都可以展开为这些状态的线性组合。

以离散本征值的情况为例，把完备力学量集的同时本征态记为 ψ_k，其中 k 代表一个**量子数组**，那么 $\{\psi_k\}$ 的正交归一关系是

$$(\psi_k,\psi_{k'})=\delta_{kk'},$$

而任何状态 ψ 都可以展开为

$$\psi=\sum_k a_k\psi_k.$$

由于

$$(\psi_{k'},\psi)=\sum_k a_k(\psi_{k'},\psi_k)=\sum_k a_k\delta_{k'k}=a_{k'},$$

所以 ψ 的展开式的系数就是

$$a_k=(\psi_k,\psi),$$

而 $|a_k|^2$ 代表了在状态 ψ 中包含状态 ψ_k 的几率，也就是在状态 ψ 下测量完备力学量集的各力学量，得

到ψ_k所对应的那些本征值的几率。这就是波函数的几率解释的一般表述。现在ψ的归一化就体现为

$$(\psi,\psi)=\sum_k|a_k|^2=1.$$

但是，严格说起来，能够写$\psi=\Sigma a_k\psi_k$的前提条件是函数系$\{\psi_k\}$必须是**完备**的。函数系的完备性是一个比较复杂的问题。在一个比较强的意义下，若函数系$\{u_n(x)\}$满足　　完备性 complete

$$\sum_n u_n(x)u_n^*(x')=\delta(x-x'),$$

那么这个函数系是（强）完备的。我们将不对此进行更深入的探讨，只是有时会引用这个完备性条件。从物理上说，函数系的完备性尽管很重要，物理学家却经常不是在最严格的意义上使用这个概念，只把它理解为函数系中的函数已经“足够多”了。

4.2.7 不确定关系的准确形式

如果$[\hat{F},\hat{G}]\neq 0$，那么通常来说力学量F和G不能同时有确定值。比如$[\hat{x},\hat{p}_x]=\mathrm{i}\hbar$，而从粒子波动性的实验中我们又看到了$\Delta x\cdot\Delta p_x\approx\hbar$，所以这二者必然是有联系的。下面就从$[\hat{F},\hat{G}]\neq 0$导出$F$和$G$的不确定关系的准确描写。

定义偏差算符为：

$$\Delta\hat{F}=\hat{F}-\overline{F},\quad(\overline{F}\text{ 是 }\hat{F}\text{ 的平均值})$$

那么

$$\overline{\Delta\hat{F}}=\overline{(\hat{F}-\overline{F})}=\overline{F}-\overline{F}=0,$$

$$\overline{(\Delta\hat{F})^2}=\overline{(\hat{F}-\overline{F})^2}=\overline{(\hat{F}^2-2\hat{F}\overline{F}+\overline{F}^2)}=\overline{\hat{F}^2}-2\overline{F}\cdot\overline{F}+\overline{F}^2=\overline{F^2}-\overline{F}^2.$$

$\overline{(\Delta\hat{F})^2}$这个量（均方偏差）就描写了力学量$\hat{F}$的测量值的偏差程度。如果$[\hat{F},\hat{G}]=\mathrm{i}\hat{C}\neq 0$，那么$\overline{(\Delta\hat{F})^2}$和$\overline{(\Delta\hat{G})^2}$有什么关系？计算方法如下。

引入

$$I(\xi)=\int\left|(\xi\Delta\hat{F}-\mathrm{i}\Delta\hat{G})\psi\right|^2 d\tau,$$

其中ξ是一个实参数，所以我们必有

$$I(\xi)\geq 0.$$

另一方面，由于$\hat{F}$和$\hat{G}$都是 Hermitian 算符，所以

$$\begin{aligned}
I(\xi)&=\left(\xi\Delta\hat{F}\psi-\mathrm{i}\Delta\hat{G}\psi,\ \xi\Delta\hat{F}\psi-\mathrm{i}\Delta\hat{G}\psi\right)\\
&=\xi^2\left(\Delta\hat{F}\psi,\ \Delta\hat{F}\psi\right)-\mathrm{i}\xi\left(\Delta\hat{F}\psi,\ \Delta\hat{G}\psi\right)+\mathrm{i}\xi\left(\Delta\hat{G}\psi,\ \Delta\hat{F}\psi\right)+\left(\Delta\hat{G}\psi,\ \Delta\hat{G}\psi\right)\\
&=\xi^2\left(\psi,(\Delta\hat{F})^2\psi\right)-\mathrm{i}\xi\left(\psi,(\Delta\hat{F}\Delta\hat{G})\psi\right)+\mathrm{i}\xi\left(\psi,(\Delta\hat{G}\Delta\hat{F})\psi\right)+\left(\psi,(\Delta\hat{G})^2\psi\right)\\
&=\xi^2\left(\psi,(\Delta\hat{F})^2\psi\right)-\mathrm{i}\xi\left(\psi,[\Delta\hat{F},\Delta\hat{G}]\psi\right)+\left(\psi,(\Delta\hat{G})^2\psi\right)\\
&=\xi^2\left(\psi,(\Delta\hat{F})^2\psi\right)-\mathrm{i}\xi\left(\psi,[\hat{F},\hat{G}]\psi\right)+\left(\psi,(\Delta\hat{G})^2\psi\right)\\
&=\overline{(\Delta\hat{F})^2}\ \xi^2-\mathrm{i}\overline{[\hat{F},\hat{G}]}\ \xi+\overline{(\Delta\hat{G})^2}.
\end{aligned}$$

其中注意

$$[\Delta\hat{F},\Delta\hat{G}]=[\hat{F}-\overline{F},\hat{G}-\overline{G}]=[\hat{F},\hat{G}].$$

根据二次三项式的判别式的性质，在$I(\xi)\geq 0$时必有

$$\overline{(\Delta\hat{F})^2}\cdot\overline{(\Delta\hat{G})^2}\geq\frac{1}{4}\overline{(-\mathrm{i}[\hat{F},\hat{G}])}^2=\frac{1}{4}\overline{\hat{C}}^2.$$

这就是准确的 Heisenberg 不确定关系。在数学上它称为 Schwarz 不等式。

对于$[\hat{x},\hat{p}_x]=\mathrm{i}\hbar$有$\hat{C}=\hbar$，所以

$$\overline{(\Delta\hat{x})^2}\cdot\overline{(\Delta\hat{p}_x)^2}\geq\frac{\hbar^2}{4}.$$

也有时记

$$\delta x\equiv\sqrt{\overline{(\Delta\hat{x})^2}},\quad \delta p_x\equiv\sqrt{\overline{(\Delta\hat{p}_x)^2}},$$

称为均方根偏差，那么，

$$\delta x\cdot\delta p_x\geq\frac{\hbar}{2}.$$

对于某些量子状态，上面那些不等式中的≥号恰好取＝号，这样的状态通常称为“最小测不准态”。

应用不确定关系的一个例子：谐振子系统的零点能。现在

$$\hat{H}=\frac{1}{2m}\hat{p}^2+\frac{1}{2}m\omega^2\hat{x}^2,$$

所以，

$$\overline{E}=\frac{1}{2m}\overline{\hat{p}^2}+\frac{1}{2}m\omega^2\overline{\hat{x}^2}.$$

不难证明：对于谐振子的能量本征态，$\overline{p}=\overline{x}=0$，所以 $\overline{\hat{p}^2}=\overline{(\Delta\hat{p})^2}$，$\overline{\hat{x}^2}=\overline{(\Delta\hat{x})^2}$，

$$\overline{E}=\frac{1}{2m}\overline{(\Delta\hat{p})^2}+\frac{1}{2}m\omega^2\overline{(\Delta\hat{x})^2}.$$

假设只考虑“最小测不准态”，那么就有

$$\overline{(\Delta\hat{x})^2}\cdot\overline{(\Delta\hat{p})^2}=\frac{\hbar^2}{4}.$$

求 $\overline{E}$ 在这个约束条件下的极小值，可设

$$f=\frac{1}{2m}\overline{(\Delta\hat{p})^2}+\frac{1}{2}m\omega^2\overline{(\Delta\hat{x})^2}+\kappa\left(\overline{(\Delta\hat{x})^2}\cdot\overline{(\Delta\hat{p})^2}-\frac{\hbar^2}{4}\right),$$

其中 κ 是 Lagrange 待定乘子，然后求 f 的无条件极值，结果是：极值点出现在

$$\overline{(\Delta\hat{x})^2}=\frac{\hbar}{2m\omega},\quad \overline{(\Delta\hat{p})^2}=\frac{m\hbar\omega}{2},$$

它对应的 $\overline{E}$ 的极小值是

$$\overline{E}_{\min}=\frac{1}{2}\hbar\omega.$$

这正是谐振子的零点能。我们看到，非零的“零点能”是不确定关系的结果。不难验证：谐振子的基态确实是最小测不准态（但是未必任何系统的基态都是最小测不准态）。

§4.3 动量本征函数的归一化

4.3.1 动量本征函数在无穷空间中的归一化

动量算符是

$$\hat{\vec{p}} = -\mathrm{i}\hbar\nabla,$$

所以它的本征方程是

$$-\mathrm{i}\hbar\nabla\psi_{\vec{p}} = \vec{p}\psi_{\vec{p}},$$

或者

$$\nabla\psi_{\vec{p}} = \mathrm{i}\frac{\vec{p}}{\hbar}\psi_{\vec{p}},$$

其中 $\vec{p}$ 是常数矢量（即是动量的本征值）。按分量写出，这些方程是

$$\begin{cases} \dfrac{\partial\psi}{\partial x} = \mathrm{i}\dfrac{p_x}{\hbar}\psi, \\ \dfrac{\partial\psi}{\partial y} = \mathrm{i}\dfrac{p_y}{\hbar}\psi, \\ \dfrac{\partial\psi}{\partial z} = \mathrm{i}\dfrac{p_z}{\hbar}\psi, \end{cases}$$

也就是说，是彼此对易的 3 个算符 $\{\hat{p}_x, \hat{p}_y, \hat{p}_z\}$ 的同时本征方程。容易发现，这些方程的解（即同时本征函数）是

$$\psi_{\vec{p}}(\vec{r}) = C\,\mathrm{e}^{\mathrm{i}(p_x x + p_y y + p_z z)/\hbar} = C\,\mathrm{e}^{\mathrm{i}\vec{p}\cdot\vec{r}/\hbar},$$

其中 C 是归一化常数。显然，动量本征值 $\vec{p}$ 必须是实矢量，这是因为假如 $\vec{p}$ 有任何虚部（无论多么小），$\psi_{\vec{p}}(\vec{r})$ 就一定会在某个方向的无穷远处趋近于无穷大，就不能满足波函数处处有限的要求了。这从另一个角度证明了动量算符是 Hermitian 算符。我们发现

$$\left|\psi_{\vec{p}}(\vec{r})\right|^2 = |C|^2,$$

它在无穷空间中的积分是发散的，不可能（有限地）归一。所以 $\psi_{\vec{p}}(\vec{r})$ 在无穷空间中的归一化有另外的含义，叫做**按 δ 函数归一化**。

考虑另一个本征函数 $\psi_{\vec{p}'}(\vec{r})$ 并计算交叉积分（或重叠积分）

$$\int_\infty \psi^*_{\vec{p}'}(\vec{r})\psi_{\vec{p}}(\vec{r})\,d^3\vec{r} = |C|^2 \int_\infty \mathrm{e}^{\mathrm{i}(p_x - p'_x)x/\hbar}\,dx \int_\infty \mathrm{e}^{\mathrm{i}(p_y - p'_y)y/\hbar}\,dy \int_\infty \mathrm{e}^{\mathrm{i}(p_z - p'_z)z/\hbar}\,dz,$$

注意到

$$\int_\infty \mathrm{e}^{\mathrm{i}(p_x - p'_x)x/\hbar}\,dx = 2\pi\hbar\,\delta(p_x - p'_x),$$

其中 $\delta(p)$ 是 δ 函数，所以

$$\int_\infty \psi^*_{\vec{p}'}(\vec{r})\psi_{\vec{p}}(\vec{r})\,d^3\vec{r} = |C|^2 (2\pi\hbar)^3 \delta(p_x - p'_x)\delta(p_y - p'_y)\delta(p_z - p'_z).$$

现在取

$$C = \frac{1}{\sqrt{(2\pi\hbar)^3}},$$

也就是

$$\psi_{\vec{p}}(\vec{r}) = \frac{1}{\sqrt{(2\pi\hbar)^3}}\mathrm{e}^{\mathrm{i}\vec{p}\cdot\vec{r}/\hbar},$$

那么就有

$$\int_\infty \psi^*_{\vec{p}'}(\vec{r})\psi_{\vec{p}}(\vec{r})\,d^3\vec{r} = \delta(p_x - p'_x)\delta(p_y - p'_y)\delta(p_z - p'_z) \equiv \delta^3(\vec{p} - \vec{p}'),$$

这就是在无穷大三维空间中按 δ 函数归一化的动量本征函数。在一维空间中，它们化为

$$\psi_p(x)=\frac{1}{\sqrt{2\pi\hbar}}\mathrm{e}^{\mathrm{i}\,px/\hbar},$$

$$\int_\infty \psi^*_{p'}(x)\psi_p(x)dx=\delta(p-p').$$

这样归一化的动量本征函数主要用于计算粒子的动量测量几率。以一维空间的情形为例，坐标表象中的波函数 $\Psi(x,t)$ 可以对动量本征函数 $\psi_p(x)$ 做展开（即进行 Fourier 变换）：

$$\Psi(x,t)=\int_\infty \Phi(p,t)\psi_p(x)dp=\int_\infty \Phi(p,t)\sqrt{\frac{1}{2\pi\hbar}}\,\mathrm{e}^{\mathrm{i}\,px/\hbar}\,dp,$$

其中的系数 $\Phi(p,t)$ 由下式决定：

$$\Phi(p,t)=\int_\infty \Psi(x,t)\psi^*_p(x)dx=\int_\infty \Psi(x,t)\sqrt{\frac{1}{2\pi\hbar}}\,\mathrm{e}^{-\mathrm{i}\,px/\hbar}\,dx,$$

而 $\Phi(p,t)$ 的物理意义是：$|\Phi(p,t)|^2$ 给出动量测量的几率密度。再进一步，如果 $\Psi(x,t)$ 满足 Schrödinger 方程

$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t}=\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)\Psi,$$

那么 $\Phi(p,t)$ 满足下面的方程：

$$\mathrm{i}\hbar\frac{\partial\Phi}{\partial t}=\left(\frac{p^2}{2m}+V\left(\mathrm{i}\hbar\frac{\partial}{\partial p}\right)\right)\Phi.$$

其中 $V(\mathrm{i}\hbar\partial/\partial p)$ 表示在 $V(x)$ 中用 $\mathrm{i}\hbar\partial/\partial p$ 代替 x，这称为动量空间中的 Schrödinger 方程。以上的概念和公式也不难推广到三维空间。在高等量子力学和量子场论中，从坐标空间变换到动量空间是常用的分析方法。

按 δ 函数归一化的方法可以用于任何有连续本征值谱的本征函数系。例如算符 $\hat{x}$ 的本征值谱是连续谱。若记算符 $\hat{x}$ 的本征值为 x_1 ($\in\mathbb{R}$) 的本征函数为 $\psi_{x_1}(x)$，那么它们的正交归一性就是

$$\int_\infty \psi^*_{x_1}(x)\psi_{x_2}(x)dx=\delta(x_1-x_2).$$

显然，$\psi_{x_1}(x)$ 是

$$\psi_{x_1}(x)=\delta(x-x_1),$$

这就是坐标表象中的坐标本征函数。这个结果也不难推广到高维空间。

*4.3.2 动量本征函数的箱归一化

所谓的无穷大空间不是物理的现实空间。实际的物理情况是：问题所涉及的空间虽然很大却仍是有限的，然而这个空间的边界的影响又可以忽略不计。这时可以采用箱归一化的方法。

这里的问题主要是如何处理空间的边界。可以证明：为了保证动量算符是 Hermitian 算符，应该提出**周期性边界条件**。或者从另一个角度来讲，周期性边界条件实际上意味着这个有限的体积可以扩展到无穷，所以边界对内部空间不产生影响。

先以一维空间为例。假设 $x\in[-L/2,\ L/2]$，并且 $\psi_p(x)$ 满足周期性边界条件

$$\psi_p(L/2)=\psi_p(-L/2),$$

其中

$$\psi_p(x)\propto\mathrm{e}^{\mathrm{i}\,px/\hbar}.$$

那么我们首先发现：这时本征值 p 变成离散的了，因为它必须满足

$$\mathrm{e}^{\mathrm{i}\,pL/\hbar}=1,$$

所以

$$\frac{pL}{\hbar}=2n\pi,\quad (n=0,\pm1,\pm2,\cdots)$$

即是

$$p_n = \frac{2n\pi\hbar}{L} = \frac{nh}{L}, \quad (n = 0, \pm 1, \pm 2, \cdots).$$

注意到 de Broglie 关系 $|p| = h/\lambda$，所以 $L = |n|\lambda$，因此上式的意义就是长度 L 必须包含整数个波长。其次，现在我们只需在 $x \in [-L/2,\ L/2]$ 中把波函数归一化，所以

$$\psi_{p_n}(x) = \frac{1}{\sqrt{L}} \mathrm{e}^{\mathrm{i}\, p_n x/\hbar} = \frac{1}{\sqrt{L}} \mathrm{e}^{\mathrm{i}\, 2n\pi x/L},$$

而正交归一条件成为

$$\int_{-L/2}^{L/2} \psi^*_{p_n}(x)\psi_{p_m}(x)\,dx = \delta_{nm}.$$

推广到三维情形，箱归一化的动量本征函数是

$$\psi_{\vec{p}}(\vec{r}) = \frac{1}{L^{3/2}} \mathrm{e}^{\mathrm{i}\, \vec{p}\cdot\vec{r}/\hbar} = \frac{1}{\sqrt{V}} \mathrm{e}^{\mathrm{i}\, \vec{p}\cdot\vec{r}/\hbar}, \quad (V = L^3)$$

其中

$$p_x = \frac{h}{L}n,\ \ p_y = \frac{h}{L}m,\ \ p_z = \frac{h}{L}l, \quad (n, m, l = 0, \pm 1, \pm 2, \cdots)$$

所以

$$\int_V \psi^*_{\vec{p}'}(\vec{r})\psi_{\vec{p}}(\vec{r})\,d^3\vec{r} = \delta_{n'n}\,\delta_{m'm}\,\delta_{l'l}. \quad (V : [-L/2, L/2]^3)$$

在实际的物理问题中，对于凝聚态物理，长度 L 可以取为固体样品的实际尺寸，但是对于原子物理和粒子物理，L 通常是虚拟的，做计算的时候最后还是要让 $L \to \infty$。这时要仔细地处理可观察物理量的定义，使得它们在 $L \to \infty$ 的时候与 L 无关。

动量本征函数的箱归一化有一个直观的物理图像。在动量空间中，动量的本征值都出现在以 h/L 为晶格常数的立方晶格上，这个晶格的晶胞体积（也就是一个量子态平均占有的体积）是 h^3/L^3，而坐标空间的体积是 $V = L^3$，所以一个量子态在相空间（坐标空间和动量空间一起构成的空间）中平均占有的体积是 h^3，或者说，系统在它的相空间中的态密度是 $1/h^3$。这个结论在统计力学中有重要的应用。

§4.4 角动量算符的本征值和本征态

4.4.1 角动量算符的球坐标表示

轨道角动量算符的定义是：

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

即是

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

它们满足对易关系

$$[\hat{L}_x,\hat{L}_y]=\mathrm{i}\hbar\hat{L}_z,\quad [\hat{L}_y,\hat{L}_z]=\mathrm{i}\hbar\hat{L}_x,\quad [\hat{L}_z,\hat{L}_x]=\mathrm{i}\hbar\hat{L}_y,$$

或简记为

$$[\hat{L}_i,\hat{L}_j]=\mathrm{i}\hbar\varepsilon_{ijk}\hat{L}_k,\ (i,j,k=x,y,z=1,2,3)$$

其中 ε_{ijk} 是“完全反对称三阶单位张量”，它的非零分量是

$$\varepsilon_{123}=\varepsilon_{231}=\varepsilon_{312}=-\varepsilon_{321}=-\varepsilon_{213}=-\varepsilon_{132}=1,$$

此外定义

$$L^2\equiv\vec{L}^2=\hat{L}_x{}^2+\hat{L}_y{}^2+\hat{L}_z{}^2,$$

那么就有

$$[L^2,\hat{L}_x]=[L^2,\hat{L}_y]=[L^2,\hat{L}_z]=0.$$

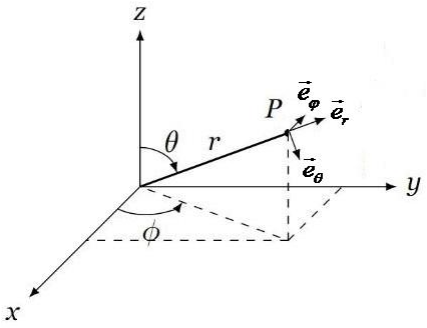
所以，这些算符的完备集是 L^2 以及 $\hat{L}_x,\hat{L}_y,\hat{L}_z$ 之中的某一个，通常选为 $\hat{L}_z$。我们的任务是求解 L^2 和 $\hat{L}_z$ 的同时本征方程（注意：这和动量算符的情况完全不同）。

这些方程更便于从直角坐标系 (x,y,z) 转入球坐标系 (r,θ,φ) 求解。这个变换是

$$x=r\sin\theta\cos\varphi,\quad y=r\sin\theta\sin\varphi,\quad z=r\cos\theta,$$

其中

$$r\in[0,\infty),\quad \theta\in[0,\pi],\quad \varphi\in[0,2\pi),$$



那么，

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

$$L^2=-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right].$$

注意：它们与 r 无关。目前暂时用不到 $\hat{L}_x$ 和 $\hat{L}_y$ 的表达式。

4.4.2 $\hat{L}_z$ 的本征值和本征函数

记 $\hat{L}_z$ 的本征值为 $m\hbar$，本征函数为 $\psi_m(\varphi)$，则本征方程是：

$$\hat{L}_z\psi_m=m\hbar\psi_m,$$

即是：

$$\frac{d\psi_m}{d\varphi}=\mathrm{i}m\psi_m(\varphi),$$

所以 $\psi_m(\varphi)=C\,\mathrm{e}^{\mathrm{i}m\varphi}$。由波函数的单值性，必须有：

$$\psi_m(\varphi+2\pi)=\psi_m(\varphi),$$

所以

$$m=0,\pm1,\pm2,\cdots$$

归一化条件 $\int_0^{2\pi}|\psi_m(\varphi)|^2d\varphi=1$ 导致 $C=1/\sqrt{2\pi}$，所以

$$\psi_m(\varphi)=\frac{1}{\sqrt{2\pi}}\mathrm{e}^{\mathrm{i}m\varphi}.$$

这些本征函数可以用于求解平面转子问题。

注。这里出现了量子数 $m\in\mathbb{Z}$ (整数集)的情形，其数学原因是圆周 S^1 的第一同伦群是 $\mathbb{Z}$，所以 m 在本质上是一个拓扑量子数，数学上称为第一 Chern（陈省身）数，物理上称为绕数(winding number)。

4.4.3 L^2 的本征值和本征函数

L^2 的本征函数是 (θ,φ) 的函数，记为 $Y(\theta,\varphi)$，本征值记为 $\lambda\hbar^2$，则本征方程是

$$L^2Y=\lambda\hbar^2Y,$$

即是

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

我们要求 $Y(\theta,\varphi)$ 同时是 $\hat{L}_z$ 的本征函数，这个要求等价于 $Y(\theta,\varphi)$ 是一个分离变量的解，也就是

$$Y(\theta,\varphi)=P(\theta)\mathrm{e}^{\mathrm{i}m\varphi},$$

因而 $P(\theta)$ 满足：

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)-\frac{m^2}{\sin^2\theta}P(\theta)=-\lambda P(\theta).$$

通常引入

$$w=\cos\theta,\quad w\in[-1,+1],$$

则方程成为：

$$\frac{d}{dw}\left((1-w^2)\frac{dP}{dw}\right)+\left(\lambda-\frac{m^2}{1-w^2}\right)P(w)=0.$$

这个方程称为连带(associated)（又称缔合）勒让德(Legendre)方程。$w=\pm1$ 是这个方程的奇点，所以，除非 λ 取某些特定值，方程的解会在 $w=\pm1$ 处变成无穷大。λ 的这些允许值是：

$$\lambda=l(l+1),\quad l=|m|,|m|+1,\cdots$$

我们把对应的解记为 $P_l^m(w)$，所以 $P_l^m(w)$ 满足方程

$$\frac{d}{dw}\left((1-w^2)\frac{dP_l^m}{dw}\right)+\left(l(l+1)-\frac{m^2}{1-w^2}\right)P_l^m(w)=0.$$

特别是，当 $m=0$ 时，$P_l(w)\equiv P_l^{m=0}(w)$ 满足：

$$\frac{d}{dw}\left((1-w^2)\frac{dP_l}{dw}\right)+l(l+1)\,P_l(w)=0.$$

这个方程称为 Legendre 方程，它的解 $P_l(w)$ 是 w 的 l 阶多项式，称为 **Legendre 多项式**，定义为

$$P_l(w)=\frac{1}{2^l\,l!}\frac{d^l}{dw^l}(w^2-1)^l.$$

直接求导就不难验证 $P_l(w)$ 满足 Legendre 方程。$P_l(w)$ 还有如下的母函数（生成函数）展开式：

$$\frac{1}{\sqrt{1-2wx+x^2}}=\sum_{l=0}^{\infty}P_l(w)\,x^l.\quad(0<x<1,\ -1\le w\le1)$$

头三阶 Legendre 多项式是

$$P_0(w)=1,$$
$$P_1(w)=w,$$
$$P_2(w)=\frac{1}{2}(3w^2-1).$$

连带 Legendre 方程的解 $P_l^m(w)$ 称为连带 Legendre 函数，定义为

$$P_l^m(w)=\frac{1}{2^l l!}(1-w^2)^{m/2}\frac{d^{l+m}}{dw^{l+m}}(w^2-1)^l.\quad (m=l,\ l-1,\cdots,-l)$$

事实上，在 $m>0$ 的时候，

$$P_l^m(w)=(1-w^2)^{m/2}\frac{d^m}{dw^m}P_l(w),$$

而 $P_l^{-m}(w)$ 和 $P_l^m(w)$ 只有常数因子的差别：

$$P_l^{-m}(w)=(-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(w).$$

例如 $P_1^m(w)\ \ (m=1,0,-1)$ 是

$$P_1^1(w)=\sqrt{1-w^2},\quad P_1^0(w)=w,\quad P_1^{-1}(w)=-\frac{1}{2}\sqrt{1-w^2},$$

换为变量 θ 的表达式就是

$$P_1^1(\cos\theta)=\sin\theta,\quad P_1^0(\cos\theta)=\cos\theta,\quad P_1^{-1}(w)=-\frac{1}{2}\sin\theta.$$

综上所述，轨道角动量的本征函数是

$$Y_{lm}(\theta,\varphi)=N_{lm}P_l^m(\cos\theta)\mathrm{e}^{\mathrm{i}m\varphi},$$

其中本征值 l,m 的取值范围是

$$l=0,1,2\cdots,\quad m=l,\ l-1,\cdots,-l.$$

N_{lm} 是归一化常数，使

$$\int Y_{lm}^*(\theta,\varphi)Y_{lm}(\theta,\varphi)\,d\Omega=1,\quad (d\Omega=\sin\theta\,d\theta\,d\varphi)$$

结果是（关于 N_{lm} 的相位的选择以后再解释）

$$N_{lm}=(-1)^m\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}},$$

最后得

$$Y_{lm}(\theta,\varphi)=(-1)^m\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)\mathrm{e}^{\mathrm{i}m\varphi}.$$

$Y_{lm}(\theta,\varphi)$ 称为**球谐函数**，l 称为**角量子数**，m 称为**磁量子数**。采用原子物理的术语，$l=0,1,2,3$ 的状态分别称为 S, P, D, F 态，$l=4,5,6,\cdots$ 的状态按字母表的顺序依次称为 G, H, I,$\cdots$ 态。对于指定的 l，有 $2l+1$ 个不同的 m 值，这就是 $\vec{L}^2$ 的本征值 $l(l+1)\hbar^2$ 的简并度。$l=0$ 和 $l=1$ 的球谐函数是：

$$Y_{00}=\sqrt{\frac{1}{4\pi}},$$

$$Y_{10}=\sqrt{\frac{3}{4\pi}}\cos\theta,\quad Y_{1,\pm1}=\mp\sqrt{\frac{3}{8\pi}}\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\varphi}.$$

注意到 $Y_{1m}\ (m=0,\pm1)$ 也可以写为 $Y_{10}=\sqrt{\frac{3}{4\pi}}\hat{z},\ Y_{1,\pm1}=\mp\sqrt{\frac{3}{8\pi}}(\hat{x}\pm\mathrm{i}\hat{y})\ \left(\hat{x},\hat{y},\hat{z}\equiv\frac{x}{r},\frac{y}{r},\frac{z}{r}\right)$，所以

$$Y_{1x}\equiv\frac{1}{\sqrt{2}}(-Y_{1,1}+Y_{1,-1})=\sqrt{\frac{3}{4\pi}}\hat{x},\ Y_{1y}\equiv\frac{\mathrm{i}}{\sqrt{2}}(Y_{1,1}+Y_{1,-1})=\sqrt{\frac{3}{4\pi}}\hat{y},\ Y_{1z}\equiv Y_{10}=\sqrt{\frac{3}{4\pi}}\hat{z}.$$

这表明，3 个 1 阶球谐函数实际上就是单位矢径 $\hat{r}\equiv\vec{r}/r$ 的 3 个分量。

4.4.4 球谐函数的基本性质

(1) $Y_{lm}(\theta,\varphi)$ 是 L^2 和 $\hat{L}_z$ 的同时本征函数：

$$\begin{cases} L^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}, & (l = 0, 1, 2, \cdots) \\ \hat{L}_z Y_{lm} = m\hbar Y_{lm}. & (m = l, l-1, \cdots, -l) \end{cases}$$

(2) $Y_{lm}(\theta,\varphi)$ 是正交归一的：

$$\int Y^*_{l'm'}(\theta,\varphi) Y_{lm}(\theta,\varphi) d\Omega = \delta_{l'l}\delta_{m'm}.$$

(3) 空间反射变换 $\vec{r} \to -\vec{r}$ $(x \to -x,\ y \to -y,\ z \to -z)$ 在球坐标系 (r,θ,φ) 中成为

$$r \to r,\ \ \theta \to \pi - \theta,\ \ \varphi \to \pi + \varphi .$$

当 $\theta \to \pi - \theta$ 时 $w \to -w$，利用 $P_l^m(-w) = (-1)^{l+m} P_l^m(w)$ 和 $Y_{lm}(\theta,\varphi)$ 的表达式，不难发现

$$Y_{lm}(\pi - \theta, \pi + \varphi) = (-1)^l Y_{lm}(\theta,\varphi),$$

所以，$Y_{lm}(\theta,\varphi)$ 的宇称是 $(-1)^l$。

(4) 球谐函数 $Y_{lm}(\theta,\varphi)$ 是单位球面（$r = 1$）上的完备函数系，也就是说，以 (θ,φ) 为变量的任何函数都可以展开为 $Y_{lm}(\theta,\varphi)$ 的线性组合。

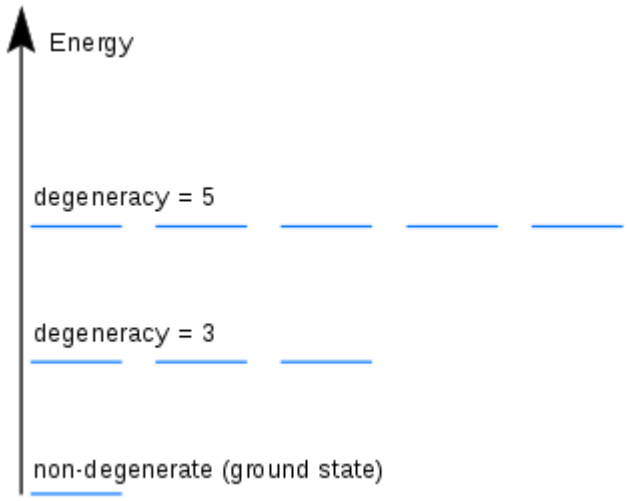
在经典力学里动量和角动量都是矢量，二者的区别只是动量是极矢量而角动量是轴矢量。但是在量子力学里动量和角动量的区别要大得多。请思考一下这些区别都有哪些？

Degenerate energy levels

In quantum mechanics, an energy level is **degenerate** if it corresponds to two or more different measurable states of a quantum system. Conversely, two or more different states of a quantum mechanical system are said to be degenerate if they give the same value of energy upon measurement. The number of different states corresponding to a particular energy level is known as the degree of degeneracy of the level. It is represented mathematically by the Hamiltonian for the system having more than one linearly independent eigenstate with the same energy eigenvalue.[1]:p. 48 When this is the case, energy alone is not enough to characterize what state the system is in, and other quantum numbers are needed to characterize the exact state when distinction is desired. In classical mechanics, this can be understood in terms of different possible trajectories corresponding to the same energy.

Degeneracy plays a fundamental role in quantum statistical mechanics. For an N-particle system in three dimensions, a single energy level may correspond to several different wave functions or energy states. These degenerate states at the same level are all equally probable of being filled. The number of such states gives the degeneracy of a particular energy level.

Contents



Degenerate states in a quantum system

Mathematics

The possible states of a quantum mechanical system may be treated mathematically as abstract vectors in a separable, complex Hilbert space, while the observables may be represented by linear Hermitian operators acting upon them. By selecting a suitable basis, the components of these vectors and the matrix elements of the operators in that basis may be determined. If A is a $N \times N$ matrix, X a non-zero vector, and λ is a scalar, such that $\boldsymbol{AX = \lambda X}$, then the scalar λ is said to be an eigenvalue of A and the vector X is said to be the eigenvector corresponding to λ. Together with the zero vector, the set of all eigenvectors corresponding to a given eigenvalue λ form a subspace of $\mathbb{C}^n$, which is called the **eigenspace** of λ. An eigenvalue λ which corresponds to two or more different linearly independent eigenvectors is said to be **degenerate**, i.e., $\boldsymbol{AX_1 = \lambda X_1}$ and $\boldsymbol{AX_2 = \lambda X_2}$, where $\boldsymbol{X_1}$ and $\boldsymbol{X_2}$ are linearly independent eigenvectors. The dimension of the eigenspace corresponding to that eigenvalue is known as its **degree of degeneracy**, which can be finite or infinite. An eigenvalue is said to be non-degenerate if its eigenspace is one-dimensional.

The eigenvalues of the matrices representing physical observables in quantum mechanics give the measurable values of these observables while the eigenstates corresponding to these eigenvalues give the possible states in which the system may be found, upon measurement. The measurable values of the energy of a quantum system are given by the eigenvalues of the Hamiltonian operator, while its eigenstates give the possible energy states of the system. A value of energy is said to be degenerate if there exist at least two linearly independent energy states associated with it. Moreover, any linear combination of two or more degenerate eigenstates is also an eigenstate of the Hamiltonian operator corresponding to the same energy eigenvalue. This clearly follows from the fact that the eigenspace of the energy value eigenvalue λ is a subspace (being the kernel of the Hamiltonian minus λ times the identity), hence is closed under linear combinations.

> **Proof of the above theorem.**[2]:p. 52
>
> If $\hat{\boldsymbol{H}}$ represents the Hamiltonian operator and $|\boldsymbol{\psi_1}\rangle$ and $|\boldsymbol{\psi_2}\rangle$ are two eigenstates corresponding to the same eigenvalue E, then
>
> $$\hat{\boldsymbol{H}}|\boldsymbol{\psi_1}\rangle = \boldsymbol{E}|\boldsymbol{\psi_1}\rangle$$
>
> $$\hat{\boldsymbol{H}}|\boldsymbol{\psi_2}\rangle = \boldsymbol{E}|\boldsymbol{\psi_2}\rangle$$

Let $|\psi\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle$, where c_1 and c_2 are complex(in general) constants, be any linear combination of $|\psi_1\rangle$ and $|\psi_2\rangle$. Then,

$$\begin{aligned}\hat{H}|\psi\rangle &= \hat{H}(c_1|\psi_1\rangle + c_2|\psi_2\rangle)\\ &= c_1\hat{H}|\psi_1\rangle + c_2\hat{H}|\psi_2\rangle\\ &= E(c_1|\psi_1\rangle + c_2|\psi_2\rangle)\\ &= E|\psi\rangle\end{aligned}$$

which shows that $|\psi\rangle$ is an eigenstate of $\hat{H}$ with the same eigenvalue E.

Effect of degeneracy on the measurement of energy

In the absence of degeneracy, if a measured value of energy of a quantum system is determined, the corresponding state of the system is assumed to be known, since only one eigenstate corresponds to each energy eigenvalue. However, if the Hamiltonian $\hat{H}$ has a degenerate eigenvalue E_n of degree g_n, the eigenstates associated with it form a vector subspace of dimension g_n. In such a case, several final states can be possibly associated with the same result E_n, all of which are linear combinations of the g_n orthonormal eigenvectors $|E_{n,i}\rangle$.

In this case, the probability that the energy value measured for a system in the state $|\psi\rangle$ will yield the value E_n is given by the sum of the probabilities of finding the system in each of the states in this basis, i.e.

$$P(E_n) = \sum_{i=1}^{g_n} |\langle E_{n,i}|\psi\rangle|^2$$

Degeneracy in different dimensions

This section intends to illustrate the existence of degenerate energy levels in quantum systems studied in different dimensions. The study of one and two-dimensional systems aids the conceptual understanding of more complex systems.

Degeneracy in one dimension

In several cases, analytic results can be obtained more easily in the study of one-dimensional systems. For a quantum particle with a wave function $|\psi\rangle$ moving in a one-dimensional potential $V(x)$, the time-independent Schrödinger equation can be written as

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

Since this is an ordinary differential equation, there are two independent eigenfunctions for a given energy E at most, so that the degree of degeneracy never exceeds two. It can be proven that in one dimension, there are no degenerate bound states for normalizable wave functions. A sufficient condition on a piecewise continuous

potential V and the energy E is the existence of two real numbers M, x_0 with $M \neq 0$ such that $\forall x > x_0$ we have $V(x) - E \geq M^2$.[3] In particular, V is bounded below in this criterion.

Proof of the above theorem.

Considering a one-dimensional quantum system in a potential $V(x)$ with degenerate states $|\psi_1\rangle$ and $|\psi_2\rangle$ corresponding to the same energy eigenvalue E, writing the time-independent Schrödinger equation for the system:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} + V\psi_1 = E\psi_1$$
$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + V\psi_2 = E\psi_2$$

Multiplying the first equation by ψ_2 and the second by ψ_1 and subtracting one from the other, we get:

$$\psi_1\frac{d^2}{dx^2}\psi_2 - \psi_2\frac{d^2}{dx^2}\psi_1 = 0$$

Integrating both sides

$$\psi_1\frac{d\psi_2}{dx} - \psi_2\frac{d\psi_1}{dx} = \text{constant}$$

In case of well-defined and normalizable wave functions, the above constant vanishes, provided both the wave functions vanish at at least one point, and we find: $\psi_1(x) = c\psi_2(x)$ where c is, in general, a complex constant. For bound state eigenfunctions (which tend to zero as $x \to \infty$), and assuming V and E satisfy the condition given above, it can be shown[3] that also the first derivative of the wave function approaches zero in the limit $x \to \infty$, so that the above constant is zero and we have no degeneracy.

Degeneracy in two-dimensional quantum systems

Two-dimensional quantum systems exist in all three states of matter and much of the variety seen in three dimensional matter can be created in two dimensions. Real two-dimensional materials are made of monoatomic layers on the surface of solids. Some examples of two-dimensional electron systems achieved experimentally include MOSFET, two-dimensional superlattices of Helium, Neon, Argon, Xenon etc. and surface of liquid Helium. The presence of degenerate energy levels is studied in the cases of particle in a box and two-dimensional harmonic oscillator, which act as useful mathematical models for several real world systems.

Particle in a rectangular plane

Consider a free particle in a plane of dimensions L_x and L_y in a plane of impenetrable walls. The time-independent Schrödinger equation for this system with wave function $|\psi\rangle$ can be written as

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)=E\psi$$

The permitted energy values are

$$E_{n_x,n_y}=\frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}\right)$$

The normalized wave function is

$$\psi_{n_x,n_y}(x,y)=\frac{2}{\sqrt{L_xL_y}}\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right)$$

where $n_x, n_y = 1, 2, 3...$

So, quantum numbers n_x and n_y are required to describe the energy eigenvalues and the lowest energy of the system is given by

$$E_{1,1}=\pi^2\frac{\hbar^2}{2m}\left(\frac{1}{L_x^2}+\frac{1}{L_y^2}\right)$$

For some commensurate ratios of the two lengths L_x and L_y, certain pairs of states are degenerate. If $L_x/L_y = p/q$, where p and q are integers, the states (n_x, n_y) and $(pn_y/q, qn_x/p)$ have the same energy and so are degenerate to each other.

Particle in a square box

In this case, the dimensions of the box $L_x = L_y = L$ and the energy eigenvalues are given by

$$E_{n_x,n_y}=\frac{\pi^2\hbar^2}{2mL^2}(n_x^2+n_y^2)$$

Since n_x and n_y can be interchanged without changing the energy, each energy level has a degeneracy of at least two when n_x and n_y are different. Degenerate states are also obtained when the sum of squares of quantum numbers corresponding to different energy levels are the same. For example, the three states (n_x = 7, n_y = 1), (n_x = 1, n_y = 7) and (n_x = n_y = 5) all have $E = 50\frac{\pi^2\hbar^2}{2mL^2}$ and constitute a degenerate set.

Degrees of degeneracy of different energy levels for a particle in a square box:

n_x	n_y	$E\left(\frac{\hbar^2\pi^2}{2mL^2}\right)$	Degeneracy
1	1	2	1
2 1	1 2	5 5	2
2	2	8	1
3 1	1 3	10 10	2
3 2	2 3	13 13	2
4 1	1 4	17 17	2
3	3	18	1

Particle in a cubical box

In this case, the dimensions of the box $L_x = L_y = L_z = L$ and the energy eigenvalues depend on three quantum numbers.

$$E_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

Since n_x, n_y and n_z can be interchanged without changing the energy, each energy level has a degeneracy of at least three when the three quantum numbers are not all equal.

Finding a unique eigenbasis in case of degeneracy

If two operators $\hat{A}$ and $\hat{B}$ commute, i.e. $[\hat{A}, \hat{B}] = 0$, then for every eigenvector $|\psi\rangle$ of $\hat{A}$, $\hat{B}|\psi\rangle$ is also an eigenvector of $\hat{A}$ with the same eigenvalue. However, if this eigenvalue, say λ, is degenerate, it can be said that $\hat{B}|\psi\rangle$ belongs to the eigenspace E_λ of $\hat{A}$, which is said to be globally invariant under the action of $\hat{B}$.

For two commuting observables *A* and *B*, one can construct an orthonormal basis of the state space with eigenvectors common to the two operators. However, λ is a degenerate eigenvalue of $\hat{A}$, then it is an eigensubspace of $\hat{A}$ that is invariant under the action of $\hat{B}$, so the representation of $\hat{B}$ in the eigenbasis of $\hat{A}$ is not a diagonal but a block diagonal matrix, i.e. the degenerate eigenvectors of $\hat{A}$ are not, in general, eigenvectors of $\hat{B}$. However, it is always possible to choose, in every degenerate eigensubspace of $\hat{A}$, a basis of eigenvectors common to $\hat{A}$ and $\hat{B}$.

Choosing a complete set of commuting observables

If a given observable *A* is non-degenerate, there exists a unique basis formed by its eigenvectors. On the other hand, if one or several eigenvalues of $\hat{A}$ are degenerate, specifying an eigenvalue is not sufficient to characterize a basis vector. If, by choosing an observable $\hat{B}$, which commutes with $\hat{A}$, it is possible to construct an orthonormal basis of eigenvectors common to $\hat{A}$ and $\hat{B}$, which is unique, for each of the possible pairs of eigenvalues {a,b}, then $\hat{A}$ and $\hat{B}$ are said to form a complete set of commuting observables. However,

if a unique set of eigenvectors can still not be specified, for at least one of the pairs of eigenvalues, a third observable $\hat{C}$, which commutes with both $\hat{A}$ and $\hat{B}$ can be found such that the three form a complete set of commuting observables.

It follows that the eigenfunctions of the Hamiltonian of a quantum system with a common energy value must be labelled by giving some additional information, which can be done by choosing an operator that commutes with the Hamiltonian. These additional labels required naming of a unique energy eigenfunction and are usually related to the constants of motion of the system.

Degenerate energy eigenstates and the parity operator

The parity operator is defined by its action in the $|r\rangle$ representation of changing r to -r, i.e.

$$\langle r|P|\psi\rangle = \psi(-r)$$

The eigenvalues of P can be shown to be limited to ± 1, which are both degenerate eigenvalues in an infinite-dimensional state space. An eigenvector of P with eigenvalue +1 is said to be even, while that with eigenvalue −1 is said to be odd.

Now, an even operator $\hat{A}$ is one that satisfies,

$$\tilde{A} = P\hat{A}P$$
$$[P, \hat{A}] = 0$$

while an odd operator $\hat{B}$ is one that satisfies

$$P\hat{B} + \hat{B}P = 0$$

Since the square of the momentum operator $\hat{P}^2$ is even, if the potential V(r) is even, the Hamiltonian $\hat{H}$ is said to be an even operator. In that case, if each of its eigenvalues are non-degenerate, each eigenvector is necessarily an eigenstate of P, and therefore it is possible to look for the eigenstates of $\hat{H}$ among even and odd states. However, if one of the energy eigenstates has no definite parity, it can be asserted that the corresponding eigenvalue is degenerate, and $P|\psi\rangle$ is an eigenvector of $\hat{H}$ with the same eigenvalue as $|\psi\rangle$.

Degeneracy and symmetry

The physical origin of degeneracy in a quantum-mechanical system is often the presence of some symmetry in the system. Studying the symmetry of a quantum system can, in some cases, enable us to find the energy levels and degeneracies without solving the Schrödinger equation, hence reducing effort.

Mathematically, the relation of degeneracy with symmetry can be clarified as follows. Consider a symmetry operation associated with a unitary operator S. Under such an operation, the new Hamiltonian is related to the original Hamiltonian by a similarity transformation generated by the operator S, such that $H' = SHS^{-1} = SHS^{\dagger}$, since S is unitary. If the Hamiltonian remains unchanged under the transformation operation S, we have

$$SHS^{\dagger} = H$$
$$SHS^{-1} = H$$
$$HS = SH$$
$$[S, H] = 0$$

Now, if $|\alpha\rangle$ is an energy eigenstate,

$$H|\alpha\rangle = E|\alpha\rangle$$

where E is the corresponding energy eigenvalue.

$$HS|\alpha\rangle = SH|\alpha\rangle = SE|\alpha\rangle = ES|\alpha\rangle$$

which means that $S|\alpha\rangle$ is also an energy eigenstate with the same eigenvalue E. If the two states $|\alpha\rangle$ and $S|\alpha\rangle$ are linearly independent (i.e. physically distinct), they are therefore degenerate.

In cases where S is characterized by a continuous parameter ϵ, all states of the form $S(\epsilon)|\alpha\rangle$ have the same energy eigenvalue.

Symmetry group of the Hamiltonian

The set of all operators which commute with the Hamiltonian of a quantum system are said to form the symmetry group of the Hamiltonian. The commutators of the generators of this group determine the algebra of the group. An n-dimensional representation of the Symmetry group preserves the multiplication table of the symmetry operators. The possible degeneracies of the Hamiltonian with a particular symmetry group are given by the dimensionalities of the irreducible representations of the group. The eigenfunctions corresponding to a n-fold degenerate eigenvalue form a basis for a n-dimensional irreducible representation of the Symmetry group of the Hamiltonian.

Types of degeneracy

Degeneracies in a quantum system can be systematic or accidental in nature.

Systematic or essential degeneracy

This is also called a geometrical or normal degeneracy and arises due to the presence of some kind of symmetry in the system under consideration, i.e. the invariance of the Hamiltonian under a certain operation, as described above. The representation obtained from a normal degeneracy is irreducible and the corresponding eigenfunctions form a basis for this representation.

Accidental degeneracy

It is a type of degeneracy resulting from some special features of the system or the functional form of the potential under consideration, and is related possibly to a hidden dynamical symmetry in the system.[4] It also results in conserved quantities, which are often not easy to identify. Accidental symmetries lead to these additional degeneracies in the discrete energy spectrum. An accidental degeneracy can be due to the fact that the group of the Hamiltonian is not complete. These degeneracies are connected to the existence of bound orbits in classical Physics.

Examples: Coulomb and Harmonic Oscillator potentials

For a particle in a central $1/r$ potential, the Laplace–Runge–Lenz vector is a conserved quantity resulting from an accidental degeneracy, in addition to the conservation of angular momentum due to rotational invariance.

For a particle moving on a cone under the influence of $1/r$ and r^2 potentials, centred at the tip of the cone, the conserved quantities corresponding to accidental symmetry will be two components of an equivalent of the Runge-Lenz vector, in addition to one component of the angular momentum vector. These quantities generate SU(2) symmetry for both potentials.

Example: Particle in a constant magnetic field

A particle moving under the influence of a constant magnetic field, undergoing cyclotron motion on a circular orbit is another important example of an accidental symmetry. The symmetry multiplets in this case are the Landau levels which are infinitely degenerate.

Examples

The hydrogen atom

In atomic physics, the bound states of an electron in a hydrogen atom show us useful examples of degeneracy. In this case, the Hamiltonian commutes with the total orbital angular momentum $\hat{L^2}$, its component along the z-direction, $\hat{L_z}$, total spin angular momentum $\hat{S^2}$ and its z-component $\hat{S_z}$. The quantum numbers corresponding to these operators are l, m_l, s (always 1/2 for an electron) and m_s respectively.

The energy levels in the hydrogen atom depend only on the principal quantum number n. For a given n, all the states corresponding to $l = 0, \ldots, n-1$ have the same energy and are degenerate. Similarly for given values of n and l, the $(2l+1)$, states with $m_l = -l, \ldots, l$ are degenerate. The degree of degeneracy of the energy level E_n is therefore : $\sum_{l=0}^{n-1}(2l+1) = n^2$, which is doubled if the spin degeneracy is included.[1]:p. 267f

The degeneracy with respect to m_l is an essential degeneracy which is present for any central potential, and arises from the absence of a preferred spatial direction. The degeneracy with respect to l is often described as an accidental degeneracy, but it can be explained in terms of special symmetries of the Schrödinger equation which are only valid for the hydrogen atom in which the potential energy is given by Coulomb's law.[1]:p. 267f

Isotropic three-dimensional harmonic oscillator

It is a spinless particle of mass m moving in three-dimensional space, subject to a central force whose absolute value is proportional to the distance of the particle from the centre of force.

$$F = -kr$$

It is said to be isotropic since the potential $V(r)$ acting on it is rotationally invariant, i.e. : $V(r) = 1/2(m\omega^2 r^2)$

where ω is the angular frequency given by $\sqrt{k/m}$.

Since the state space of such a particle is the tensor product of the state spaces associated with the individual one-dimensional wave functions, the time-independent Schrödinger equation for such a system is given by-

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+(1/2)m\omega^2(x^2+y^2+z^2)\psi=E\psi$$

So, the energy eigenvalues are $E_{n_x,n_y,n_z}=(n_x+n_y+n_z+3/2)\hbar\omega$

or, $E_n=(n+3/2)\hbar\omega$

where n is a non-negative integer. So, the energy levels are degenerate and the degree of degeneracy is equal to the number of different sets n_x, n_y, n_z satisfying

$$n_x+n_y+n_z=n$$

The degeneracy of the n^{th} state can be found by considering the distribution of n quanta across n_x, n_y and n_z. Having 0 in n_x gives $n+1$ possibilities for distribution across n_y and n_z. Having 1 quanta in n_x gives n possibilities across n_y and n_z and so on. This leads to the general result of $n-n_x+1$ and summing over all n leads to the degernecy of the n^{th} state,

$$\sum_{n_x=0}^{n}(n-n_x+1)=(n+1)(n+2)/2$$

As shown, only the ground state where $n=0$ is non-degenerate (ie, has a degerancy of 1).

Removing degeneracy

The degeneracy in a quantum mechanical system may be removed if the underlying symmetry is broken by an external perturbation. This causes splitting in the degenerate energy levels. This is essentially a splitting of the original irreducible representations into lower-dimensional such representations of the perturbed system.

Mathematically, the splitting due to the application of a small perturbation potential can be calculated using time-independent degenerate perturbation theory. This is an approximation scheme that can be applied to find the solution to the eigenvalue equation for the Hamiltonian H of a quantum system with an applied perturbation, given the solution for the Hamiltonian H_0 for the unperturbed system. It involves expanding the eigenvalues and eigenkets of the Hamiltonian H in a perturbation series. The degenerate eigenstates with a given energy eigenvalue form a vector subspace, but not every basis of eigenstates of this space is a good starting point for perturbation theory, because typically there would not be any eigenstates of the perturbed system near them. The correct basis to choose is one that diagonalizes the perturbation Hamiltonian within the degenerate subspace.

Lifting of degeneracy by first-order degenerate perturbation theory.

Consider an unperturbed Hamiltonian $\hat{H_0}$ and perturbation $\hat{V}$, so that the perturbed Hamiltonian

$$\hat{H}=\hat{H_0}+\hat{V}$$

The perturbed eigenstate, for no degeneracy, is given by-

$$|\psi_0\rangle=|n_0\rangle+\sum_{k\neq 0}V_{k0}/(E_0-E_k)|n_k\rangle$$

The perturbed energy eigenket as well as higher order energy shifts diverge when $E_0 = E_k$, i.e., in the presence of degeneracy in energy levels. Assuming $\hat{H_0}$ possesses N degenerate eigenstates $|m\rangle$ with the same energy eigenvalue E, and also in general some non-degenerate eigenstates. A perturbed eigenstate $|\psi_j\rangle$ can be written as a linear expansion in the unperturbed degenerate eigenstates as-

$$|\psi_j\rangle = \sum_i |m_i\rangle\langle m_i|\psi_j\rangle = \sum_i c_{ji}|m_i\rangle$$
$$[\hat{H_0} + \hat{V}]\psi_j\rangle = [\hat{H_0} + \hat{V}]\sum_i c_{ji}|m_i\rangle = E_j \sum_i c_{ji}|m_i\rangle$$

where E_j refer to the perturbed energy eigenvalues. Since E is a degenerate eigenvalue of $\hat{H_0}$,

$$\sum_i c_{ji}\hat{V}|m_i\rangle = (E_j - E)\sum_i c_{ji}|m_i\rangle = \Delta E_j \sum_i c_{ji}|m_i\rangle$$

Premultiplying by another unperturbed degenerate eigenket $\langle m_k|$ gives-

$$\sum_i c_{ji}[\langle m_k|\hat{V}|m_i\rangle - \delta_{ik}(E_j - E)] = 0$$

This is an eigenvalue problem, and writing $V_{ik} = \langle m_i|\hat{V}|m_k\rangle$, we have-

$$\begin{vmatrix} V_{11} - \Delta E_j & V_{12} & \dots & V_{1N} \\ V_{21} & V_{22} - \Delta E_j & \dots & V_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ V_{N1} & V_{N2} & \dots & V_{NN} - \Delta E_j \end{vmatrix}.$$

The N eigenvalues obtained by solving this equation give the shifts in the degenerate energy level due to the applied perturbation, while the eigenvectors give the perturbed states in the unperturbed degenerate basis $|m\rangle$. To choose the good eigenstates from the beginning, it is useful to find an operator $\hat{V}$ which commutes with the original Hamiltonian $\hat{H_0}$ and has simultaneous eigenstates with it.

Physical examples of removal of degeneracy by a perturbation

Some important examples of physical situations where degenerate energy levels of a quantum system are split by the application of an external perturbation are given below.

Symmetry breaking in two-level systems

A two-level system essentially refers to a physical system having two states whose energies are close together and very different from those of the other states of the system. All calculations for such a system are performed on a two-dimensional subspace of the state space.

If the ground state of a physical system is two-fold degenerate, any coupling between the two corresponding states lowers the energy of the ground state of the system, and makes it more stable.

If E_1 and E_2 are the energy levels of the system, such that $E_1 = E_2 = E$, and the perturbation W is represented in the two-dimensional subspace as the following 2×2 matrix

$$\mathbf{W} = \begin{bmatrix} 0 & W_{12} \\ W_{12}^* & 0 \end{bmatrix}.$$

then the perturbed energies are

$$E_+ = E + |W_{12}|$$
$$E_- = E - |W_{12}|$$

Examples of two-state systems in which the degeneracy in energy states is broken by the presence of off-diagonal terms in the Hamiltonian resulting from an internal interaction due to an inherent property of the system include:

- Benzene, with two possible dispositions of the three double bonds between neighbouring Carbon atoms.
- Ammonia molecule, where the Nitrogen atom can be either above or below the plane defined by the three Hydrogen atoms.
- H_2^+ molecule, in which the electron may be localized around either of the two nuclei.

Fine-structure splitting

The corrections to the Coulomb interaction between the electron and the proton in a Hydrogen atom due to relativistic motion and spin-orbit coupling result in breaking the degeneracy in energy levels for different values of *l* corresponding to a single principal quantum number *n*.

The perturbation Hamiltonian due to relativistic correction is given by

$$H_r = -p^4/8m^3c^2$$

where p is the momentum operator and m is the mass of the electron. The first-order relativistic energy correction in the $|nlm\rangle$ basis is given by

$$E_r = (-1/8m^3c^2)\langle nlm|p^4|nlm\rangle$$

Now $p^4 = 4m^2(H^0 + e^2/r)^2$

$$\begin{aligned} E_r &= (-1/2mc^2)[E_n^2 + 2E_n e^2\langle 1/r\rangle + e^4\langle 1/r^2\rangle] \\ &= (-1/2)mc^2\alpha^4[-3/(4n^4) + 1/n^3(l+1/2)] \end{aligned}$$

where α is the fine structure constant.

The spin-orbit interaction refers to the interaction between the intrinsic magnetic moment of the electron with the magnetic field experienced by it due to the relative motion with the proton. The interaction Hamiltonian is

$$H_{so} = -(e/mc)\vec{m} \cdot \vec{L}/r^3 = [(e^2/(m^2c^2r^3))\vec{S} \cdot \vec{L}]$$

which may be written as

$$H_{so} = (e^2/(4m^2c^2r^3))[\vec{J}^2 - \vec{L}^2 - \vec{S}^2]$$

The first order energy correction in the $|j, m, l, 1/2\rangle$ basis where the perturbation Hamiltonian is diagonal, is given by

$$E_{so} = (\hbar^2 e^2)/(4m^2c^2)[j(j+1) - l(l+1) - 3/4]/((a_0)^3 n^3 (l(l+1/2)(l+1))]$$

where a_0 is the Bohr radius. The total fine-structure energy shift is given by

$$E_{fs} = -(mc^2\alpha^4/(2n^3))[1/(j+1/2) - 3/4n]$$

for $j = l \pm 1/2$.

Zeeman effect

The splitting of the energy levels of an atom when placed in an external magnetic field because of the interaction of the magnetic moment $\vec{m}$ of the atom with the applied field is known as the Zeeman effect.

Taking into consideration the orbital and spin angular momenta, $\vec{L}$ and $\vec{S}$, respectively, of a single electron in the Hydrogen atom, the perturbation Hamiltonian is given by

$$\hat{V} = -(\overrightarrow{m_l} + \overrightarrow{m_s}) \cdot \vec{B}$$

where $m_l = -e\vec{L}/2m$ and $m_s = -e\vec{S}/m$. Thus,

$$\hat{V} = e(\vec{L} + 2\vec{S}) \cdot \vec{B}/2m$$

Now, in case of the weak-field Zeeman effect, when the applied field is weak compared to the internal field, the spin-orbit coupling dominates and $\vec{L}$ and $\vec{S}$ are not separately conserved. The good quantum numbers are *n*, *l*, *j* and m_j, and in this basis, the first order energy correction can be shown to be given by

$E_z = -\mu_B g_j B m_j$, where

$\mu_B = e\hbar/2m$ is called the Bohr Magneton.Thus, depending on the value of m_j, each degenerate energy level splits into several levels.

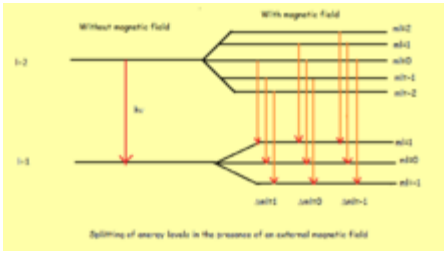
In case of the strong-field Zeeman effect, when the applied field is strong enough, so that the orbital and spin angular momenta decouple, the good quantum numbers are now *n*, *l*, m_l, and m_s. Here, L_z and S_z are conserved, so the perturbation Hamiltonian is given by-

$$\hat{V} = eB(L_z + 2S_z)/2m$$

assuming the magnetic field to be along the *z*-direction. So,

$$\hat{V} = eB(m_l + 2m_s)/2m$$

For each value of m_l, there are two possible values of m_s, $\pm 1/2$.



Lifting of degeneracy by an external magnetic field

Stark effect

The splitting of the energy levels of an atom or molecule when subjected to an external electric field is known as the Stark effect.

For the hydrogen atom, the perturbation Hamiltonian is

$$\hat{H}_s = -|e|Ez$$

if the electric field is chosen along the *z*-direction.

The energy corrections due to the applied field are given by the expectation value of $\hat{H}_s$ in the $|nlm\rangle$ basis. It can be shown by the selection rules that $\langle nlm_l|z|n_1 l_1 m_{l1}\rangle \neq 0$ when $l = l_1 \pm 1$ and $m_l = m_{l1}$.

The degeneracy is lifted only for certain states obeying the selection rules, in the first order. The first-order splitting in the energy levels for the degenerate states $|2,0,0\rangle$ and $|2,1,0\rangle$, both corresponding to $n = 2$, is given by $\Delta E_{2,1,m_l} = \pm|e|(\hbar^2)/(m_e e^2)E$.

See also

- Density of states

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