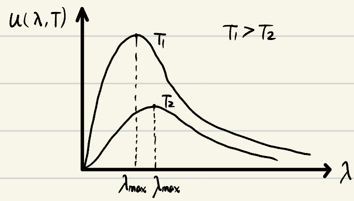
Quantum Mechanics

Lecture Notes

Chapter 1 量力溯源

Kirchhoff th. $\dfrac{r(\nu,T)}{\alpha(\nu,T)} = \dfrac{c}{4} u(\nu,T)$ for black body $\alpha(\nu,T)=1 \Rightarrow r(\nu,T)=u(\nu,T)$



Explaination :

1) Stefan-Boltzmann : $J = \int u(\nu,T)d\nu \propto T^4$

Optical Pressure $p = \frac{1}{3}\varepsilon$ $\quad TdS = du + pdV = Vd\varepsilon + \frac{4}{3}\varepsilon dV$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\frac{4}{3}\varepsilon$$

Maxwell $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \Rightarrow \frac{1}{3}\frac{\partial \varepsilon}{\partial T} = \frac{4}{3}\frac{\varepsilon}{T}$ hence $\varepsilon \propto T^4$

2) Wien $u(\nu,T) = g(\nu)\,\overline{\varepsilon}(\nu,T)$ $\quad g(\nu)$ 为 $\nu \sim \nu+d\nu$ 单位体积电磁波模式数

$\overline{\varepsilon}(\nu,T)$ 每个模式谐振子的平均能量

for 1-Dim $L = n\frac{\lambda}{2}$, $\lambda = \frac{2\pi}{k}$, $k = \frac{n\pi}{L}$

$0 \sim k_m$ $\quad N_m = \dfrac{k_m}{\frac{\pi}{L}}$ $\quad k = \frac{2\pi\nu}{c}$

for 3-Dim ……

第二章 量子力学的基本理论框架

基本公设：

1、系统状态由量子态描述，其满足态叠加原理

2、力学量(可观测量)由算符表示

3.（关于测量）力学量算符的可能测值为其本征值，测量得到某本征值有一定几率，其取值与对应的本征态与系统量子态相关

4. 动力学演化满足 Schrödinger eq.　$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \underbrace{\hat{H}}_{\text{能量算符}}|\psi\rangle$

5. 粒子的全同性

1. 引入量子态概念的必要性（例：波粒二象性 wave and particle duality）

a. 光的本质　　概率正比于 $|E(\vec{r},t)|^2$

b. 物质波 ⟶ 推广到一切微观粒子

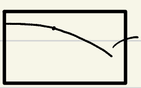
c. Heisenberg 不确定性关系

讨论：轨道的概念

i) 氢原子基态 $E_g \sim -13.6eV$，$\Delta p \sim \sqrt{2mE_g}$，$\Delta x \geq \frac{\hbar}{2\Delta p} = \frac{\hbar}{2\sqrt{2mE_g}} \sim 2.6\times10^{-11}m$

原子尺度 $\sim 10^{-10}m$　} 无法在原子尺度中讨论电子的位置

ii) Wilson 云室



雾滴尺寸 $\sim 10^{-6}m$

$\Delta x \sim 10^{-6}m$

$\Delta p \geq \frac{\hbar}{2\Delta x} \Rightarrow \Delta E \geq \frac{\hbar^2}{4\Delta x^2}\frac{1}{2m} \sim 9\times10^{-9}eV$（相较于高能粒子的能量，非常小）

2. 量子态与算符

b. 用算符表示可观测量　Dirac notation　$|\psi\rangle$，$\hat{A}$

a. 摒弃经典概念用量子态这一抽象概念描述.

3. 态叠加原理与测量

如 $|\psi_m\rangle$ 为系统可能的状态，则其线性叠加 $\sum_m c_m|\psi_m\rangle$ 亦为系统可能状态

$\{c_1, c_2, \cdots, c_m\}$ 为复数. 它表示具有 $|\psi_m\rangle$ 态性质的相对几率为 $|c_m|^2$

例: $|\psi_m\rangle$ 有确定的能量 E_m (能量本征态), 当系统处于 $|\psi\rangle=\sum_m c_m|\psi_m\rangle$ 时, 所有可能的能量测值为 $\{E_1,E_2,\cdots,E_n\}$,
其中测得能量值为 E_m 的几率 $\frac{|c_m|^2}{\sum_i|c_i|^2}$, 测量后, $|\psi\rangle$ 量子态塌缩成为 $|\psi_m\rangle$

例: 连续谱 $|\psi\rangle=\int d^3r\,\overset{\text{波函数}}{\psi(r)}\,\overset{\text{位置本征态}}{|r\rangle}$, 测量 $|r\rangle$ 位置, 得到 $r\to r+d^3r$ 中的几率为 $\frac{|\psi(r)|^2}{\int d^3r|\psi(r)|^2}$

例: 光的偏振 电磁波的电矢量 $E_x\cos(kz-\omega t)\vec{e}_x+E_y\cos(kz-\omega t+\varphi)\vec{e}_y$

$$=\tilde{E}_0\left[\vec{\varepsilon}_p\frac{e^{i(kz-\omega t)}}{2}+c.c.\right]\qquad \cos\theta\sim\frac{E_x}{\sqrt{E_x^2+E_y^2}}$$

设 $\varphi=\frac{\pi}{2}$, 则 $\vec{\varepsilon}_p\propto\cos\theta\,\vec{e}_x+i\sin\theta\,\vec{e}_y$

对于经典光, 检偏器 ($\vec{e}_x$) 测得的光强 $I_0\cos^2\theta$

对于单光子, 可能测值 $\begin{cases}0 & \sin^2\theta\\ 1 & \cos^2\theta\end{cases}$ 本征值 $|\psi\rangle=\cos\theta|\leftrightarrow\rangle+i\sin\theta|\updownarrow\rangle$ 测量改变了微观体系的状态

$\wr$

$\alpha|\nearrow\rangle+\beta|\nwarrow\rangle$

讨论 i) $|\psi\rangle$ 与 $c|\psi\rangle$ 表示同一量子态

ii) 展开系数 c_m、$\psi(r)$ 本身不可测量, 只可测得模方

iii) 同一量子态具有不同态叠加形式

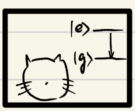
例. 基于态叠加的干涉实验

经典波有 $I=|E|^2=|E_1+E_2e^{i\varphi(r)}|^2=|E_1|^2+|E_2|^2+2|E_1||E_2|\cos\varphi(r)$

量子态 $|\psi\rangle=\frac{\sqrt{2}}{2}|\psi_1\rangle+\frac{\sqrt{2}}{2}|\psi_2\rangle\Rightarrow\frac{\sqrt{2}}{2}\int d^3r[\psi_1(r)+\psi_2(r)]|r\rangle$

几率: $\frac{1}{2}|\psi_1(r)+\psi_2(r)|^2=\frac{1}{2}(|\psi_1|^2+|\psi_2|^2+\psi_1^*\psi_2+\psi_2^*\psi_1)$ 干涉项

4. 干涉实验讨论

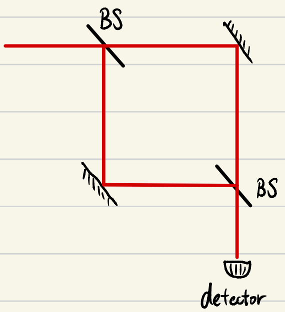


$\frac{\sqrt{2}}{2}(|e,alive\rangle+|g,dead\rangle)$ 经典与量子的界限? ～ 经典几率与量子几率大有不同

$$\begin{cases}\frac{\sqrt{2}}{2}(|\leftrightarrow\rangle+|\updownarrow\rangle) & \text{叠加态}\\ \begin{cases}\frac{1}{2}\leftrightarrow\\ \frac{1}{2}\updownarrow\end{cases} & \text{塌缩}\end{cases}$$

两者不同!!!

5. Wheeler 实验



BS 加入可以影响时间之前的光子

⇒ 量子叠加态有非定域性(包括时间)

d. EPR Paradox (1935)

A　　B　类空间隔

A与B的总动量与相对位置已知

① 测A的位置，则B的位置确定
② 测A的动量，则B的动量确定

亦可在不扰动B的情况下分别测出B的坐标与分量 ⇒ x, p为B的不依赖于测量的客观实在

→ Heisenberg 不确定性原理矛盾

e. 隐变量理论　Bohm 1952

存在经典意义上的(客观实在)隐变量

f. 实在论

Copenhagen 测量之前，经典性质的实在无意义

5. 波函数的讨论

a. 态叠加原理

Born 的几率解释：坐标空间中的态叠加原理，即将 $|\psi\rangle$ 用 $\{|r\rangle\}$ 展开，展开系数为波函数

同理，可将 $|\psi\rangle$ 用 $\{|p\rangle\}$ 展开

量子态 ↓ 表象 ↓

$|\psi\rangle = \sum_n C_n |\psi_n\rangle \Longrightarrow \{|\psi_n\rangle\}$

$|\psi\rangle = \int d^3r\, \psi(r) |r\rangle \Longrightarrow \{|r\rangle\}$，粒子在 $r \to r+d^3r$ 上出现概率 $|\psi(r)|^2$

归一化 $\int d^3r |\psi(r)|^2 = 1$

$|\psi\rangle = \int d^3p\, \varphi(p) |p\rangle \Longrightarrow \{|p\rangle\}$，粒子在 $p \to p+d^3p$ 概率 $|\varphi(p)|^2$

归一化 $\int d^3p |\varphi(p)|^2 = 1$

Fourier Transformation

$$\psi(r) = \frac{1}{(2\pi\hbar)^{3/2}} \int \varphi(p) e^{i\vec{p}\cdot\vec{r}/\hbar} d^3p \qquad \text{with } \vec{p} = \hbar\vec{k}$$

$$\varphi(p) = \frac{1}{(2\pi\hbar)^{3/2}} \int \psi(r) e^{-i\vec{p}\cdot\vec{r}/\hbar} d^3r$$

计算例(归一化)：

$$\int \varphi^*(p)\varphi(p) d^3p = \frac{1}{(2\pi\hbar)^3} \int d^3p\, d^3r\, d^3r'\, \psi^*(r)\psi(r') e^{-i\vec{p}\cdot(\vec{r}-\vec{r}')/\hbar}$$

$$= \int d^3r\, d^3r'\, \psi^*(r)\psi(r')\delta(r-r') \quad \text{with } \boxed{\delta(\vec{r}-\vec{r}') = \frac{1}{(2\pi\hbar)^3}\int e^{i\vec{p}\cdot(\vec{r}-\vec{r}')/\hbar} d^3p}$$

$$= \int d^3r\, \psi^*(r)\psi(r)$$

$$\boxed{\vec{p}\, e^{-i\vec{p}\cdot\vec{r}/\hbar} = i\hbar\nabla_{r'} e^{-i\vec{p}\cdot\vec{r}'/\hbar}}$$

6、测量与测量的期望值

位置期望值：$\bar{r} = \int d^3r |\psi(r)|^2 r$

动量期望值：

$$\bar{p} = \int d^3p |\varphi(p)|^2 p = \frac{1}{(2\pi\hbar)^3} \int d^3p\, d^3r\, d^3r'\, \psi^*(\vec{r})\psi(\vec{r}') e^{i\vec{p}\cdot(\vec{r}-\vec{r}')/\hbar}\, \vec{p}$$

$$= \frac{1}{(2\pi\hbar)^3} \int d^3p\, d^3r\, \psi^*(\vec{r}) e^{i\vec{p}\cdot\vec{r}/\hbar} \int d^3r'\, \psi(\vec{r}')\, i\hbar\nabla_{r'} e^{-i\vec{p}\cdot\vec{r}'/\hbar}$$

$$\overset{\text{intergrate by parts}}{=} \frac{1}{(2\pi\hbar)^3} \int d^3p\, d^3r\, \psi^*(\vec{r}) e^{i\vec{p}\cdot\vec{r}/\hbar} \int d^3r'\, e^{-i\vec{p}\cdot\vec{r}'/\hbar} \left[-i\hbar\nabla_{r'}\psi(r')\right]$$

$$= \int d^3r\, d^3r'\, \delta(r-r')\, \psi^*(r) (-i\hbar\nabla_{r'}) \psi(r')$$

$$= \int d^3r\, \psi^*(r) -i\hbar\nabla_{r'} \psi(r)$$

第三章 量子力学的初步描述

1. 量子态

量子数

a. $|\psi\rangle$ ket矢 满足态叠加原理的所有可能态 $\{|\psi\rangle\}$ 组成的复矢量空间为态空间 (Hilbert Space)

运算：$c|\alpha\rangle = |\alpha\rangle c$，$|\alpha\rangle$ 与 $c|\alpha\rangle$ 代表同一量子态

b. $\langle\psi|$ bra矢 定义为与 $|\psi\rangle$ 共轭的矢量 由所有 $\{\langle\psi|\}$ 构成的复空间为态空间的共轭空间 (dual)

运算：$c\langle\psi| = \langle\psi|c$

$(|\psi\rangle)^\dagger = \langle\psi|$ $\quad (\langle\psi|)^\dagger = |\psi\rangle$ $\quad (c|\psi\rangle)^\dagger = \langle\psi|c^*$ $\quad (c_1|\psi_1\rangle + c_2|\psi_2\rangle + \cdots + c_n|\psi_n\rangle)^\dagger = \langle\psi_1|c_1^* + \cdots + \langle\psi_n|c_n^*$

c. 内积 $\langle\alpha|\beta\rangle \longrightarrow$ Complex Number 要求 (i) $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^*$

(ii) $\langle\alpha|\alpha\rangle \geq 0$，如 $\langle\alpha|\alpha\rangle = 0$，则 α 为空态 Null

d. 直积 $|\alpha\rangle \otimes |\beta\rangle = |\alpha\rangle|\beta\rangle = |\alpha,\beta\rangle$ ~ 两个独立的状态拼接到一起

e.g.: Schwartz ineq. $|\langle\alpha|\beta\rangle| \leq \sqrt{\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle}$

Profe：$(\langle\alpha| + \langle\beta|\lambda^*)(|\alpha\rangle + \lambda|\beta\rangle) \geq 0$，令 $\lambda = -\dfrac{\langle\beta|\alpha\rangle}{\langle\beta|\beta\rangle}$

$$\Rightarrow \langle\alpha|\alpha\rangle - \frac{\langle\beta|\alpha\rangle}{\langle\beta|\beta\rangle}\langle\alpha|\beta\rangle - \frac{\langle\alpha|\beta\rangle}{\langle\beta|\beta\rangle}\langle\beta|\alpha\rangle + \frac{\langle\beta|\alpha\rangle\langle\alpha|\beta\rangle}{|\langle\beta|\beta\rangle|^2}\langle\beta|\beta\rangle \geq 0$$

$$\Rightarrow \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq \langle\alpha|\beta\rangle\langle\beta|\alpha\rangle$$

$$\Rightarrow \sqrt{\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle} \geq |\langle\alpha|\beta\rangle| \quad \text{Q.E.D.}$$

2. Operator

定义为作用在ket矢上的变换，可理解为矩阵，$\hat{A}|\psi\rangle = |\varphi\rangle$

Linear Operator，力学量算符均为线性算符

Indentical Operator $\hat{I}|\psi\rangle = |\psi\rangle$

对任意态 $|\psi\rangle$ 和 $|\varphi\rangle$，有 $\langle\varphi|\hat{A}|\psi\rangle = \langle\varphi|\hat{B}|\psi\rangle$，则 $\hat{A} = \hat{B}$

算符的积：$\hat{A}\hat{B}|\psi\rangle = \hat{A}(\hat{B}|\psi\rangle)$ $\quad \hat{A}\hat{B}\hat{C} = (\hat{A}\hat{B})\hat{C} = \hat{A}(\hat{B}\hat{C})$

基本对易关系（1-Dim）：$\boxed{[\hat{x},\hat{p}]=\hat{x}\hat{p}-\hat{p}\hat{x}=i\hbar}$

基本假设

形式推导：$\hat{x}\hat{p}|\psi\rangle \Rightarrow \hat{x}\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x)$

$\hat{p}\hat{x}|\psi\rangle \Rightarrow \left(-i\hbar\frac{\partial}{\partial x}\right)(x\psi(x)) = -i\hbar\psi - i\hbar x\frac{\partial\psi}{\partial x}$ $\Bigg\}\Rightarrow [x,-i\hbar\frac{\partial}{\partial x}]\psi = i\hbar\psi$

同理可推得 $[\hat{x},\hat{p}_y]=0$，故一般的三维对易关系为 $[\hat{x}_\alpha,\hat{p}_\beta]=i\hbar\delta_{\alpha\beta}$

以及 $[\hat{x}_\alpha,\hat{x}_\beta]=0$，$[\hat{p}_\alpha,\hat{p}_\beta]=0$

对易关系 $[\hat{A},\hat{B}]=\hat{A}\hat{B}-\hat{B}\hat{A}$，$\{\hat{A},\hat{B}\}=\hat{A}\hat{B}+\hat{B}\hat{A}$

则有 $[\hat{A},\hat{B}\pm\hat{C}]=[\hat{A},\hat{B}]\pm[\hat{A},\hat{C}]$　　类似于线性

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

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

例：角动量算符的对易关系　$\boxed{\hat{\vec{l}}=\hat{\vec{r}}\times\hat{\vec{p}}}$，（此处 $\hat{\vec{p}}=\hat{p}_x\vec{e}_x+\hat{p}_y\vec{e}_y+\hat{p}_z\vec{e}_z$）

$$\Rightarrow\begin{cases}\hat{l}_x=\hat{y}\hat{p}_z-\hat{z}\hat{p}_y\\ \hat{l}_y=\hat{z}\hat{p}_x-\hat{x}\hat{p}_z\\ \hat{l}_z=\hat{x}\hat{p}_y-\hat{y}\hat{p}_x\end{cases}\Rightarrow \hat{l}_i=\varepsilon_{ijk}\hat{x}_j\hat{p}_k$$

容易得到 $[\hat{l}_x,\hat{x}]=0$，

$[\hat{l}_x,\hat{y}]=[\hat{y}\hat{p}_z-\hat{z}\hat{p}_y,\hat{y}]=[\hat{y}\hat{p}_z,\hat{y}]-[\hat{z}\hat{p}_y,\hat{y}]=-\hat{z}[\hat{p}_y,\hat{y}]=i\hbar\hat{z}$

$[\hat{l}_i,\hat{x}_j]=[\varepsilon_{ikl}\hat{x}_k\hat{p}_l,\hat{x}_j]=\varepsilon_{ikl}\hat{x}_k[\hat{p}_l,\hat{x}_j]=-i\hbar\varepsilon_{ikj}\hat{x}_k=i\hbar\varepsilon_{ijk}\hat{x}_k$

同理也有 $[\hat{l}_i,\hat{p}_j]=i\hbar\varepsilon_{ijk}\hat{p}_k$，$[\hat{l}_i,\hat{l}_j]=i\hbar\varepsilon_{ijk}\hat{l}_k$，$[\hat{l}_i,\hat{x}^2]=[\hat{l}_i,\hat{p}^2]=[\hat{l}_i,\hat{l}^2]=0$

定义 $\hat{l}_\pm=\hat{l}_x\pm i\hat{l}_y$，$[\hat{l}_z,\hat{l}_\pm]=\pm\hbar\hat{l}_\pm$

算符的逆　$\hat{A}|\psi\rangle=|\varphi\rangle$，则定义 $\hat{A}^{-1}$，$\hat{A}^{-1}|\varphi\rangle=|\psi\rangle$　$(\hat{A}\hat{B})^{-1}=\hat{B}^{-1}\hat{A}^{-1}$

算符的幂　$\hat{A}^n=\underbrace{\hat{A}\cdots\cdots\hat{A}}_{n个}$，可以定义 $e^{\alpha\hat{A}}=\sum_{n=0}^{\infty}\frac{\hat{A}^n\alpha^n}{n!}$

$$\frac{d}{d\alpha}(e^{\alpha\hat{A}})=\sum_n\frac{1}{n!}n\alpha^{n-1}\hat{A}^n=e^{\alpha\hat{A}}\hat{A}\xrightarrow[\text{利用对易换位置}]{[\hat{A}^n,\hat{A}]=0}\hat{A}e^{\alpha\hat{A}}$$

常用公式小结

1. $[\hat{A}, f(\hat{B})] = [\hat{A},\hat{B}] f'(\hat{B})$ when $[\hat{A},[\hat{A},\hat{B}]]=0$

一些常用的结果:
1. $[\hat{A},\hat{B}^n] = n[\hat{A},\hat{B}]\hat{B}^{n-1}, [\hat{A}, e^{\lambda\hat{B}}] = \lambda[\hat{A},\hat{B}]e^{\lambda B}$
2. $[\hat{x}, F(\hat{p})] = i\hbar F'(\hat{p}), [\hat{p}, G(\hat{x})] = -i\hbar G'(\hat{x})$

2. Baker Hausdorff eq. $e^{\lambda\hat{A}}\hat{B}e^{-\lambda\hat{A}} = \sum_{n=0}^{\infty}\frac{\lambda^n \hat{C}_n}{n!}$

3. Glauber eq. $e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}e^{-\frac{1}{2}[\hat{A},\hat{B}]}$ when $[\hat{A},[\hat{A},\hat{B}]]=[\hat{B},[\hat{A},\hat{B}]]=0$

e.g. $e^{\alpha\hat{a}^\dagger-\alpha^*\hat{a}} = e^{\alpha\hat{a}^\dagger}e^{-\alpha^*\hat{a}}e^{-\frac{1}{2}|\alpha|^2}$

算符与bra矢的作用 算符可以从右边作用于bra矢上，其结果亦为bra矢

$(\langle\varphi|\hat{A})^\dagger = \hat{A}^\dagger|\varphi\rangle$ or $\langle\varphi|\hat{A}^\dagger = (\hat{A}^\dagger|\varphi\rangle)^\dagger$

thus $\langle\varphi|\hat{A}^\dagger|\psi\rangle = \langle\varphi|(\langle\psi|\hat{A})^\dagger = \langle\psi|\hat{A}|\varphi\rangle^*$ using $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^*$

Similarly $\langle\varphi|(\hat{A}^\dagger)^\dagger|\psi\rangle = \langle\psi|\hat{A}^\dagger|\varphi\rangle^* = \langle\varphi|\hat{A}|\psi\rangle \Rightarrow (\hat{A}^\dagger)^\dagger = \hat{A}$, $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$

对于一个简单的复数 $\langle\varphi|\hat{A}|\psi\rangle^{\dagger} = \langle\psi|\hat{A}^\dagger|\varphi\rangle = \langle\varphi|\hat{A}|\psi\rangle^{*}$

外积 $|\alpha\rangle\langle\beta|$ 本质为算符, with $(|\alpha\rangle\langle\beta|)^\dagger = |\beta\rangle\langle\alpha|$

3. Hermitian 厄米算符

def: $\hat{A}^\dagger = \hat{A}$

$\hat{A}$可在本征基下展开成

$\hat{A} = \sum_i A_i|i\rangle\langle i|$, A_i为本征值

本征值和本征态

a. 算符的本征问题 $\hat{A}|\psi_n\rangle = \underbrace{a_n}_{本征值}\underbrace{|\psi_n\rangle}_{本征态}$, then we get $\{a_n\}$ $\{|\psi_n\rangle\}$

b. 厄米算符的本征值为实数，且对应不同本征值的本征态相互正交 ← if $\langle\alpha|\beta\rangle=0$, then $|\alpha\rangle|\beta\rangle$ is orthogonal

Profe: $\hat{A}|\psi_n\rangle = A_n|\psi_n\rangle \Rightarrow$ $\langle\psi_m|\hat{A}|\psi_n\rangle$ $\nearrow A_n\langle\psi_m|\psi_n\rangle$

非简并的

$\langle\psi_m|\hat{A} = \langle\psi_m|A_m^* \Rightarrow$ $\searrow A_m^*\langle\psi_m|\psi_n\rangle$

thus $(A_n - A_m^*)\langle\psi_m|\psi_n\rangle$, if $m=n$, then $A_n - A_n^* = 0 \Rightarrow A_n \in \mathbb{R}$

if $m\neq n$, & $A_m \neq A_n$, then $\langle\psi_m|\psi_n\rangle = 0$, Orthogonal

c. 厄米算符的归一化，非简并本征态集合构成对应态空间的一组正交完备基

正交归一性: $\langle\psi_m|\psi_n\rangle = \delta_{mn}$ 完备性: $\sum_n|\psi_n\rangle\langle\psi_n| = \hat{I}$

对任意态 $|\psi\rangle = \sum_n C_n|\psi_n\rangle \Rightarrow \langle\psi_m|\psi\rangle = C_m$

$|\psi\rangle = \sum_n C_n|\psi_n\rangle = \sum_n\langle\psi_n|\psi\rangle|\psi_n\rangle = \left(\sum_n|\psi_n\rangle\langle\psi_n|\right)|\psi\rangle$

*对于连续基的情况 $\langle r|r'\rangle=\delta(r-r')$, $\int d^3r\,|r\rangle\langle r|=\hat{I}$

$|\psi\rangle=\int d^3r\,\psi(r)|r\rangle$ $\langle r'|\psi\rangle=\int d^3r\,\psi(r)\langle r'|r\rangle=\psi(r')$

then $\langle\psi|\psi\rangle=\langle\psi|\left(\sum_n|\psi_n\rangle\langle\psi_n|\right)|\psi\rangle=\sum_n C_nC_n^*=1$

$\quad\quad\quad\quad\quad\quad\quad\quad \parallel \langle\psi|\left(\int d^3r\,|r\rangle\langle r|\right)|\psi\rangle=\int d^3r\,\psi(r)\psi^*(r)=1$

with $\hat{A}|\psi_n\rangle=A_n|\psi_n\rangle$ $\quad$ equivalent to $\hat{I}$

$$\bar{A}=\sum_n|C_n^2|A_n=\sum_n A_n\langle\psi|\psi_n\rangle\langle\psi_n|\psi\rangle=\sum_n\langle\psi|\left(A_n|\psi_n\rangle\right)\langle\psi_n|\psi\rangle=\sum_n\langle\psi|\hat{A}\left(|\psi_n\rangle\langle\psi_n|\right)|\psi\rangle=\langle\psi|\hat{A}|\psi\rangle$$

d. 厄米算符的性质

i) 于任意量子态下，Hermition 期望值为实数

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

ii) 于任意量子态下，期望值为实数的 Operator 为 Hermition

Profe：取 $|\psi\rangle=|\psi_1\rangle+c|\psi_2\rangle$，则 $\langle\psi|=\langle\psi_1|+\langle\psi_2|c^*$，

$\bar{A}=\langle\psi|\hat{A}|\psi\rangle=\bar{A}^*=\langle\psi|\hat{A}|\psi\rangle^*$，并取 $c=1\,\&\,i$，可得 $\langle\psi_1|\hat{A}|\psi_2\rangle=\langle\psi_1|\hat{A}^\dagger|\psi_2\rangle$ 即 $\hat{A}=\hat{A}^\dagger$

例：$\hat{p}_x$ 的本征态

$$\hat{p}_x|p_x\rangle=p_x|p_x\rangle\Rightarrow -i\hbar\frac{\partial}{\partial x}\varphi_{p_x}(x)=p_x\varphi_{p_x}(x)\Rightarrow\varphi_{p_x}=\frac{1}{\sqrt{2\pi\hbar}}e^{ip_xx/\hbar}$$

4. 简谐振子的代数算法

a. 一维谐振子的能量本征问题

$$H\xlongequal[\text{one-dim}]{\text{for}}\frac{p^2}{2m}+\frac{1}{2}m\omega^2x^2\sim\hat{H}=\frac{\hat{p}^2}{2m}+\frac{1}{2}m\omega^2\hat{x}^2$$

定义算符 $\begin{cases}\hat{a}=\frac{1}{\sqrt{2}}\left(\sqrt{\frac{m\omega}{\hbar}}\hat{x}+\frac{i}{\sqrt{m\omega\hbar}}\hat{p}\right)\\ \hat{a}^\dagger=\frac{1}{\sqrt{2}}\left(\sqrt{\frac{m\omega}{\hbar}}\hat{x}-\frac{i}{\sqrt{m\omega\hbar}}\hat{p}\right)\end{cases}\Rightarrow\begin{cases}\hat{x}=\sqrt{\frac{\hbar}{2m\omega}}(\hat{a}+\hat{a}^\dagger)\\ \hat{p}=-i\sqrt{\frac{m\omega\hbar}{2}}(\hat{a}-\hat{a}^\dagger)\end{cases}$

$\boxed{\begin{matrix}\hat{a}\neq\hat{a}^\dagger\\ \hat{x}=\hat{x}^\dagger\\ \hat{p}=\hat{p}^\dagger\end{matrix}}$ ，由 $[\hat{x},\hat{p}]=i\hbar$

推得 $[\hat{a},\hat{a}^\dagger]=1$

$\hookrightarrow\hat{H}=\hbar\omega\left(\underline{\hat{a}^\dagger\hat{a}}+\frac{1}{2}\right)=\hbar\omega\left(\frac{1}{2}+\underline{\hat{N}}\right)$

粒子数 Operator

此处 $\boxed{\hat{N}=\hat{a}^\dagger\hat{a}}$，设 $\hat{N}|n\rangle=n|n\rangle$ (fake 态)，则 $\hat{H}|n\rangle=\underbrace{\left(n+\frac{1}{2}\right)\hbar\omega}_{\text{能量本征值}}\underbrace{|n\rangle}_{\text{能量本征态}}$

$[\hat{N},\hat{a}]=[\hat{a}^\dagger\hat{a},\hat{a}]=-\hat{a}$, $[\hat{N},\hat{a}^\dagger]=[\hat{a}^\dagger\hat{a},\hat{a}^\dagger]=\hat{a}^\dagger$

$$\begin{cases}\hat{N}\hat{a}^\dagger|n\rangle=(\hat{a}^\dagger\hat{N}+\hat{a}^\dagger)|n\rangle=(n+1)\hat{a}^\dagger|n\rangle\Rightarrow\hat{a}^\dagger|n\rangle=c|n+1\rangle\\ \hat{N}\hat{a}|n\rangle=(\hat{a}\hat{N}-\hat{a})|n\rangle=(n-1)\hat{a}|n\rangle\Rightarrow\hat{a}|n\rangle=d|n-1\rangle\end{cases}$$

$\langle n|\hat{a}^+\hat{a}|n\rangle = \langle n-1|d^*d|n-1\rangle = |d|^2 = \langle n|n|n\rangle = n$ 取 $d=\sqrt{n}$

$\langle n|\hat{a}\hat{a}^+|n\rangle = |c|^2 = n+1$ 取 $|c| = \sqrt{n+1}$

$$\Rightarrow \begin{cases} \hat{a}^+|n\rangle = \sqrt{n+1}\,|n+1\rangle \\ \hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle \end{cases}$$

连续地把 a 作用于 $|n\rangle$ 上，同时 $n=\langle n|\hat{a}^+\hat{a}|n\rangle \geq 0$，设存在 n 的下限记为 n_0

if $n_0 = 0$ ✓, then n is positive integer

if $0<n_0<1$, then $\hat{a}|n_0\rangle = \sqrt{n_0}\,|n_0-1\rangle$, $\hat{N}\hat{a}|n_0\rangle = (n_0-1)\,\hat{a}|n_0\rangle$ is impossible

$(\langle n_0|\hat{a}^+\hat{a}^+)(\hat{a}\hat{a}|n_0\rangle) = (\langle n_0|\hat{a}^+)\hat{N}(\hat{a}|n_0\rangle)$

$= n_0 - 1 < 0$，违背了正定性

then $\begin{cases} \hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle \\ \hat{a}|n-1\rangle = \sqrt{n-1}\,|n-2\rangle \\ \vdots \\ \hat{a}|1\rangle = |0\rangle \\ \hat{a}|0\rangle = 0 \end{cases}$

能谱 $\hat{H}|n\rangle = E_n|n\rangle$, $E_n = (n+\frac{1}{2})\hbar\omega$, $n = 0,1,2,\cdots$ (离散化的)

粒子数

对于 $n=0$，$E_0 = \frac{1}{2}\hbar\omega$ 为真空能，来源于测不准(量子涨落) ~ Dark Energy?

对于 fock 态，$|n\rangle = \frac{(\hat{a}^+)^n}{\sqrt{n!}}|0\rangle$，
$\begin{cases} \hat{x}|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n}\,|n-1\rangle + \sqrt{n+1}\,|n+1\rangle\right) \\ \hat{p}|n\rangle = -i\sqrt{\frac{m\omega\hbar}{2}}\left(\sqrt{n}\,|n-1\rangle - \sqrt{n+1}\,|n+1\rangle\right) \end{cases}$

$\Rightarrow \langle n|\hat{x}|n\rangle = 0$, $\langle n|\hat{p}|n\rangle = 0$, $\langle n|\hat{x}^2|n\rangle \neq 0$, $\langle n|\hat{p}^2|n\rangle \neq 0$. $\Delta x \Delta p = (n+\frac{1}{2})\hbar$

b. fock 态的波函数

出发点：$\langle \hat{x}|\hat{a}|0\rangle = 0 \Rightarrow \langle x|(\hat{x}+\frac{i}{m\omega}\hat{p})|0\rangle = 0 \xRightarrow[\hat{x}\to x]{\hat{p}\to -i\hbar\frac{\partial}{\partial x}} (x+\frac{\hbar}{m\omega}\frac{\partial}{\partial x})\varphi_0(x) = 0$，其中 $\varphi_0(x) = \langle x|0\rangle$

解得 $\varphi_0(x) = \frac{1}{\pi^{1/4}\sqrt{x_0}}e^{-\frac{1}{2}(\frac{x}{x_0})^2}$，其中 $x_0 = \sqrt{\hbar/m\omega}$ 为特征长度.

$\langle \hat{x}|1\rangle = \langle \hat{x}|\hat{a}^+|0\rangle = \frac{1}{\sqrt{2}x_0}(x - x_0^2\frac{\partial}{\partial x})\varphi_0(x)$

$\vdots$

$\langle \hat{x}|n\rangle = \frac{1}{\pi^{1/4}\sqrt{2^n \cdot n!}}\left(\frac{1}{x_0^{n+\frac{1}{2}}}\right)(x - x_0^2\frac{\partial}{\partial x})^n e^{-\frac{1}{2}(\frac{x}{x_0})^2}$ Hermit 多项式

c. 相干态 Coherent State

Complex Number as $|\alpha\rangle$ is not a Hermitian

$\hat{a}$ 的本征态：$\hat{a}|\alpha\rangle = \alpha|\alpha\rangle \iff \langle\alpha|\hat{a}^+ = \langle\alpha|\alpha^*$

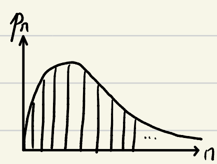
$$\boxed{\{|n\rangle\} \Rightarrow \begin{cases} \langle n|m\rangle = \delta_{mn} \\ \sum_n |n\rangle\langle n| = \hat{I} \end{cases}}$$

i) 相干态用 Fock 态表示 $|\alpha\rangle = \sum_n |n\rangle\langle n|\alpha\rangle$, with $\langle n|\alpha\rangle = \frac{\alpha^n}{\sqrt{n!}}\langle 0|\alpha\rangle$

let $\langle\alpha|\alpha\rangle = 1$, then $1 = \sum_n \langle\alpha|n\rangle\langle n|\alpha\rangle = \sum_n \frac{|\alpha|^{2n}}{n!}|\langle 0|\alpha\rangle|^2 = e^{|\alpha|^2}|\langle 0|\alpha\rangle|^2$

then $\langle 0|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2}$

$\Rightarrow |\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2}\sum_n \frac{\alpha^n}{\sqrt{n!}}|n\rangle$ & $|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2}e^{\alpha\hat{a}^+}|0\rangle$



ii) 粒子数 $\langle\alpha|\hat{N}|\alpha\rangle = \langle\alpha|\hat{a}^+\hat{a}|\alpha\rangle = |\alpha|^2\langle\alpha|\alpha\rangle = |\alpha|^2$ ~ 模方具有观测意义 $= \bar{n}$

$P_n = |\langle n|\alpha\rangle|^2 = e^{-|\alpha|^2}\frac{|\alpha|^{2n}}{n!} = e^{-\bar{n}}\frac{\bar{n}^n}{n!} \sim P(\bar{n})$ Poisson Distribution

iii) 正交归一的完备性能保证吗

$\langle\alpha|\alpha\rangle = 1$, $\langle\alpha|\beta\rangle = \sum_{m,n}\frac{\alpha^{*m}}{\sqrt{m!}}\frac{\beta^n}{\sqrt{n!}}\underbrace{\langle m|n\rangle}_{\delta_{mn}} e^{-\frac{1}{2}|\alpha|^2-\frac{1}{2}|\beta|^2} = \sum_n \frac{(\alpha^*\beta)^n}{n!}e^{-\frac{1}{2}|\alpha|^2-\frac{1}{2}|\beta|^2} = \sum_n e^{\alpha^*\beta-\frac{1}{2}|\alpha|^2-\frac{1}{2}|\beta|^2}$ 不正交

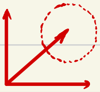
$\int d^2\alpha\,|\alpha\rangle\langle\alpha| = \pi\hat{I}$

复平面上积，令 $\alpha = \rho e^{i\varphi}$ 由 $\int_0^{2\pi}d\varphi\, e^{i\varphi(n-m)} = 2\pi\delta_{mn}$

考虑时间演化算符 $|\psi, t=t_0\rangle = \exp\left(-i\frac{Ht_0}{\hbar}\right)|\psi, t=0\rangle$ for $i\hbar\frac{d}{dt}|\psi\rangle = H|\psi\rangle$

$a^\dagger a|n\rangle = n|n\rangle$ 则 $|\alpha, t=t_0\rangle = e^{-i\frac{\hbar\omega a^\dagger a t_0}{\hbar}}\sum\frac{e^{-|\alpha|^2/2}}{\sqrt{n!}}\alpha^n|n\rangle$ $\Rightarrow \alpha' = \alpha e^{-i\omega t_0}$ (转动)

iv) 相干态下的不确定性关系 定义位置/动量算符



取实 $\hat{x}_1 = \frac{1}{2}(\hat{a}+\hat{a}^\dagger)$, $\langle\alpha|\hat{x}_1|\alpha\rangle = \frac{1}{2}(\alpha+\alpha^*) = Re\,\alpha$

取虚 $\hat{x}_2 = \frac{1}{2i}(\hat{a}-\hat{a}^\dagger)$, $\langle\alpha|\hat{x}_2|\alpha\rangle = \frac{1}{2i}(\alpha-\alpha^*) = Im\,\alpha$

$\hat{x}_1^2 = \frac{1}{4}(\hat{a}^2+\hat{a}^{\dagger 2}+\hat{a}\hat{a}^\dagger+\hat{a}^\dagger\hat{a})$, $\langle\alpha|\hat{x}_1^2|\alpha\rangle = \langle\hat{x}_1^2\rangle_\alpha = \frac{1}{4}(\alpha^2+\alpha^{*2}+2|\alpha|^2+1)$

$= \frac{1}{4}[(\alpha+\alpha^*)^2+1] = (Re\,\alpha)^2+\frac{1}{4}$

$\langle\hat{x}_2^2\rangle_\alpha = -\frac{1}{4}(\alpha^2+\alpha^{*2}-2|\alpha|^2-1) = -\frac{1}{4}[(\alpha-\alpha^*)^2-1] = (Im\,\alpha)^2+\frac{1}{4}$

$\Delta x_1 = \sqrt{\langle\hat{x}_1^2\rangle-\langle\hat{x}_1\rangle_\alpha^2} = \frac{1}{2} = \Delta x_2$, $\Delta x_1\Delta x_2 = \frac{1}{4}$ 最小不确定度

d. 三维谐振子

$$\hat{H} = \sum_{i=x,y,z}\left(\frac{\hat{p}_i^2}{2m}+\frac{1}{2}m\omega^2\hat{r}_i^2\right) \quad [\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ij} \quad [\hat{a}_i, \hat{a}_j^\dagger] = \delta_{ij}$$

$qE\hat{x}$ (电场中附加项)

$$\hat{H} = (\hat{N}_x+\hat{N}_y+\hat{N}_z+\frac{3}{2})\hbar\omega$$

直积 $|n_x\rangle|n_y\rangle|n_z\rangle = |n_x, n_y, n_z\rangle$

简并子空间

$\langle n_x=1, n_y=0|n_x=0, n_y=1\rangle = 0$

$\Rightarrow \langle n_x=1|\otimes\langle n_y=0||n_x=0\rangle\otimes|n_y=1\rangle$

$\Rightarrow 0$

$$E_{n_x,n_y,n_z} = (n_x+n_y+n_z+\frac{3}{2})\hbar\omega, \quad n_x, n_y, n_z = 0, 1, 2, \cdots$$

三份真空能

当 $E = \frac{5}{2}\hbar\omega$ 时, $|100\rangle$ $|010\rangle$ $|001\rangle$ 三态简并

$\hat{H} = \frac{\hat{p}^2}{2m}+\frac{1}{2}m\omega^2\hat{x}^2-qE\hat{x} = \frac{\hat{p}^2}{2m}+\frac{1}{2}m\omega^2(\underbrace{\hat{x}-\frac{qE}{m\omega^2}}_{\hat{x}'})^2-E_0$, 仍有 $[\hat{x}', \hat{p}] = i\hbar$

利用 $[\hat{p}, \hat{x}] = -i\hbar$, 则 $[\hat{p}, \hat{x}^n] = n(-i\hbar)\hat{x}^{n-1}$

$f(\hat{x}) = f(0)+f'(0)\hat{x}+\frac{f''(0)}{2!}\hat{x}^2+\cdots$, 则 $[\hat{p}, f(\hat{x})] = -i\hbar\frac{\partial f(x)}{\partial x}$

第四章 表象representation与表象交换

1 表象与量子态的表达方式

矢量 ～ 量子态

坐标系 ～ 表象

坐标 ～ 量子态表示 ⇒ 矩阵、波函数

2 如何确定表象

$|\psi\rangle=\sum_n \underbrace{C_n}_{\langle\psi_n|\psi\rangle}|\psi_n\rangle$ 用力学量的本征态作为表象的基，可以用本征值为量子数特定基组中的态

Hermitian

a 如$\hat{A}$的本征态非简并 则它构成一组正交归一完备的基

任意态均可用其展开。$|\psi\rangle=\sum_n C_n|A_n\rangle$，且每个均可用$A_n$唯一确定

b $\hat{A}$的本征值存在简并

$\{A_1, A_2, \cdots, A_m \cdots A_m, \cdots A_n\}$

$\{|\psi_1\rangle, |\psi_2\rangle, \cdots, \underbrace{|\psi_{m1}\rangle, \cdots, |\psi_{ms}\rangle}_{s个}, \cdots |\psi_n\rangle\}$

对于简并子空间的正交基与维度

(i) $\hat{A}|\psi_{m\alpha}\rangle=A_m|\psi_{m\alpha}\rangle \quad \alpha=1,2,\cdots,s$

(ii) 构造$\{|\psi_{m\alpha}\rangle\}$两两正交（Schmit 正交化）

(iii) 使所有 $\sum_\alpha C_\alpha|\psi_{m\alpha}\rangle$ 构成$\hat{A}$算符本征值A_m的简并子空间.
$(\alpha=1,2,\cdots,s)$

性质

(i) $\hat{A}\left(\sum_\alpha C_\alpha|\psi_{m\alpha}\rangle\right)=A_m\left(\sum_\alpha C_\alpha|\psi_{m\alpha}\rangle\right)$

(ii) 简并子空间内任意态与本征值不为A_m的本征态正交

(iii) 简并子空间内的任意态均可表示为$\{|\psi_{m\alpha}\rangle\}$的线性叠加

所有$\hat{A}$的本征值为A_m的本征态均属于该子空间

① 如何唯一地确定$\{|\psi_{m\alpha}\rangle\}$？ ⇒ 再引入一力学量$\hat{B}$，其满足$[\hat{A},\hat{B}]=0$，由$\hat{B}$在简并子空间内的本征问题确定一组$\{|\psi_{m\alpha}\rangle\}$

$\begin{cases}\hat{A}|\psi_{m\alpha}\rangle=A_m|\psi_{m\alpha}\rangle \\ \hat{B}|\psi_{m\alpha}\rangle=B_{m\alpha}|\psi_{m\alpha}\rangle\end{cases}$ 共同本征态 $\quad |\psi_{m\alpha}\rangle \Rightarrow |A_m, B_{m\alpha}\rangle$

定理：若$[\hat{A},\hat{B}]=0$，则$\hat{A},\hat{B}$有共同本征态

① 非简并：$0=\langle\psi_n|\hat{A}\hat{B}-\hat{B}\hat{A}|\psi_k\rangle=(A_n-A_k)\langle\psi_n|\hat{B}|\psi_k\rangle \Rightarrow \underbrace{\langle\psi_n|\hat{B}|\psi_k\rangle}=B_n\delta_{nk}$ $\quad \langle\psi_n|\hat{B}|\psi_n\rangle$

$\therefore \hat{B}|\psi_n\rangle=\sum_k|\psi_k\rangle\langle\psi_k|\hat{B}|\psi_n\rangle=\sum_k|\psi_k\rangle B_n\delta_{nk}=B_n|\psi_n\rangle$

② 简并：$\hat{A}(\hat{B}|\psi_{m\alpha}\rangle)=A_m\hat{B}|\psi_{m\alpha}\rangle$ ， $\hat{B}|\psi_{m\alpha}\rangle=\sum_\beta B_{\beta\alpha}|\psi_{m\beta}\rangle$

$|\varphi\rangle=\sum_\alpha C_\alpha|\psi_{m\alpha}\rangle$，$\hat{B}|\varphi\rangle=B|\varphi\rangle \Rightarrow \sum_\alpha \underbrace{B_{\beta\alpha}}_{\langle\psi_{m\beta}|\hat{B}|\psi_{m\alpha}\rangle}C_\alpha=BC_\beta$

$$\begin{pmatrix} B_{\beta1} & B_{\beta2} & \cdots & B_{\beta s}\end{pmatrix}\begin{pmatrix}C_1\\ \vdots \\ C_s\end{pmatrix}=B\begin{pmatrix}\vdots\\ C_\beta \\ \vdots\end{pmatrix}$$

以矩阵的视角看

$\langle\psi_{n'}|\hat{A}|\psi_n\rangle$ $\qquad\qquad$ $\langle\psi_{n'}|\hat{B}|\psi_n\rangle = \langle\psi_n|\hat{B}|\psi_{n'}\rangle^*$

$$\begin{pmatrix} A_1 & & & & 0 \\ & A_2 & & & \\ & & \boxed{\begin{matrix} A_m & 0 \\ 0 & A_m \end{matrix}} & & \\ & & & \ddots & \\ 0 & & & & A_n \end{pmatrix} \qquad \begin{pmatrix} B_1 & & & \\ & B_2 & & \\ & & \boxed{\text{非对角}} & \\ & & & \ddots \\ & & & & B_n \end{pmatrix}$$

厄米矩阵，可对角化为对角阵

$$B_m^{(\alpha)} = B_m^{(\beta)}$$

② 如$\hat{B}$在$\hat{A}$的简并子空间内仍存在简并，找第三个力学量$\hat{C}$，$[\hat{A},\hat{C}]=[\hat{B},\hat{C}]=0$，并在$\hat{B}$的残余子空间内求$\hat{C}$的本征问题，依此类推，直至找到一组两两对易的力学量算符，它们的共同本征态由这些算符的本征值完全确定，则$\{\hat{A},\hat{B},\cdots\}$构成体系的力学量完备集

$$|\psi\rangle = \sum_{\alpha\beta\cdots\gamma} C_{\alpha\beta\cdots\gamma}|\alpha\beta\cdots\gamma\rangle$$

此时$\{|\alpha\beta\cdots\gamma\rangle\}$构成由该力学量完备集所确定的表象的基.

例：一维运动 $\hat{x}$, $\hat{p}_x$都构成力学量完备集 $\quad \hat{x}|x\rangle = x|x\rangle$，$|\psi\rangle = \int dx\, \psi(x)|x\rangle$

例：二维谐振子 $\hat{H} = (\hat{N}_x + \hat{N}_y + 1)\hbar\omega$

③ 量子涨落，不确定性关系及共同本征态

$\langle\psi|\hat{A}|\psi\rangle = \bar{A}$，

涨落 $\Delta A = \sqrt{\langle\psi|(\hat{A}-\bar{A})^2|\psi\rangle}$ $\qquad$ 令 $\Delta A = 0 \Rightarrow \hat{A}|\psi\rangle = \bar{A}|\psi\rangle$

而 $\Delta x\cdot\Delta p = 0 \Rightarrow$ 找不到$\hat{x}$, $\hat{p}$的共同本征态.

不确定性关系

依 Schwartz ineq. $\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2$

构造 $|\alpha\rangle = (\hat{A}-\bar{A})|\psi\rangle$，$|\beta\rangle = (\hat{B}-\bar{B})|\psi\rangle$

则 $\langle\alpha|\alpha\rangle = \Delta A^2$，$\langle\beta|\beta\rangle = \Delta B^2$，$\langle\alpha|\beta\rangle = \langle\psi|\,\frac{1}{2}[\hat{A},\hat{B}] + \frac{1}{2}\{\hat{A}-\bar{A},\hat{B}-\bar{B}\}\,|\psi\rangle$

$[\hat{A},\hat{B}]^\dagger = -[\hat{A},\hat{B}] \leftarrow$ 反厄米算符

$\therefore \langle[\hat{A},\hat{B}]\rangle^* = -\langle[\hat{A},\hat{B}]\rangle \Rightarrow \langle[\hat{A},\hat{B}]\rangle$为纯虚数

$\{\hat{A}-\bar{A},\hat{B}-\bar{B}\}^\dagger = \{\hat{A}-\bar{A},\hat{B}-\bar{B}\} \Rightarrow \langle\{\hat{A}-\bar{A},\hat{B}-\bar{B}\}\rangle$为实数

$$\Rightarrow (\Delta A)^2(\Delta B)^2 \geq \frac{1}{4}\left|\langle[\hat{A},\hat{B}]\rangle\right|^2+\frac{1}{4}\left|\langle\{\hat{A}-\bar{A},\hat{B}-\bar{B}\}\rangle\right|^2$$

$$\Rightarrow (\Delta A)^2(\Delta B)^2 \geq \frac{1}{4}\left|\langle[\hat{A},\hat{B}]\rangle\right|^2 \qquad \Delta A\,\Delta B \geq \frac{1}{2}\left|\langle[\hat{A},\hat{B}]\rangle\right|$$

如 $[\hat{A},\hat{B}]=0$，则 $\Delta A\Delta B$ 同时为零，有共同本征态

$\neq 0$，则 $\Delta A\Delta B$ 在 $\langle[\hat{A},\hat{B}]\rangle=0$，且 $\langle\{\hat{A}-\bar{A},\hat{B}-\bar{B}\}\rangle=0$ 时，可以取零.

3. 分离谱表示（矩阵表象）

性质 (1) 算符在其本征态为基的表象下，其矩阵为对角阵 $\langle\psi_n|\hat{A}|\psi_m\rangle=\delta_{mn}A_m$

(2) 若某算符在某组基矢下的矩阵表示为对角阵，则该组基矢为算符的本征态，其对角元为本征值。 $\hat{A}|\psi_n\rangle=\boxed{\overset{\text{插入完备性关系}}{\sum_m|\psi_m\rangle\langle\psi_m|}}\hat{A}|\psi_n\rangle=A_n|\psi_n\rangle$

(3) 期望值 $\langle\psi|\hat{A}|\psi\rangle=\sum_{mn}\langle\psi\boxed{|\psi_m\rangle\langle\psi_m|}\hat{A}\overset{\text{插入完备性关系}}{\boxed{|\psi_n\rangle\langle\psi_n|}}\psi\rangle=\sum_{mn}C_m^*A_{mn}C_n$

(4) $\hat{A}=\sum_{ij}|\psi_i\rangle\langle\psi_i|\hat{A}|\psi_j\rangle\langle\psi_j|=\sum_{ij}A_{ij}|\psi_i\rangle\langle\psi_j|$

4. 分离谱的表象变换

$\{|\psi_n\rangle\}$ $\quad \langle\psi_n|\psi_m\rangle=\delta_{mn}$, $\quad \sum_n|\psi_n\rangle\langle\psi_n|=\hat{I}$

$\{|\varphi_n\rangle\}$ $\quad \langle\varphi_n|\varphi_m\rangle=\delta_{mn}$, $\quad \sum_n|\varphi_n\rangle\langle\varphi_n|=\hat{I}$

G（旧） F（新）

$$|\psi\rangle=\sum_n C_n|\psi_n\rangle=\sum_\alpha C_\alpha|\varphi_\alpha\rangle$$

$$\Rightarrow \sum_n C_n\langle\varphi_\beta|\psi_n\rangle=C_\beta$$

$$\Rightarrow C_\beta=\sum_n\langle\varphi_\beta|\psi_n\rangle C_n=\sum_n S_{\beta n}C_n$$

thus $\quad (C_\beta)=(S_{\beta n})(C_n)$ $\quad$ ($|\psi_1\rangle\ |\psi_2\rangle\ \cdots\ |\psi_n\rangle$)

$$C^{(F)}=\underset{\text{变换矩阵}}{S}C^{(G)}$$

$$(S^\dagger S)_{mn}=\sum_\beta(S^\dagger)_{m\beta}(S)_{\beta n}=\sum_\beta\langle\psi_m|\varphi_\beta\rangle\langle\varphi_\beta|\psi_n\rangle=\langle\psi_m|\psi_n\rangle=\delta_{mn}$$

即 $S^\dagger S=I=SS^\dagger$ 或 $S^\dagger=S^{-1}$ $\quad$ S为幺正矩阵（Unitary Matrix）其不改变向量的模

因此 $\overset{\langle\psi|\psi\rangle}{(C^{(F)})^\dagger C^{(F)}}=(C^{(G)})^\dagger S^\dagger S\,C^{(G)}=\overset{\langle\varphi|\varphi\rangle}{(C^{(G)})^\dagger C^{(G)}}$

对任意 $\hat{A}$，$A_{\alpha\beta}=\langle\varphi_\alpha|\hat{A}|\varphi_\beta\rangle=\sum_m\sum_n\langle\varphi_\alpha|\psi_m\rangle\langle\psi_m|\hat{A}|\psi_n\rangle\langle\psi_n|\varphi_\beta\rangle=\sum_m\sum_n S_{\alpha m}A_{mn}(S^\dagger)_{\beta n}$

$\Rightarrow \boxed{A^{(F)}=SA^{(G)}S^\dagger}$, $\quad S^\dagger A^{(F)}S=A^{(G)}$

例：$f(\hat{A})=\sum_n\frac{f^{(n)}(0)}{n!}\hat{A}$ $\qquad f^{(F)}=Sf^{(G)}S^\dagger$ $\qquad$ 对比 $C^{(F)}=SC^{(G)}$

$|\psi\rangle=\sum_n C_n|\psi_n\rangle$ $\qquad |\psi\rangle=\sum_\alpha C_\alpha|\varphi\rangle$

5. 连续谱表象 $\{|r\rangle\}$ $\{|p\rangle\}$

a. 坐标表象

$|\psi\rangle = \int d^3r\, \underbrace{\psi(r)}_{\langle r|\psi\rangle} |r\rangle$ 定义 $\langle r|\psi\rangle = \psi(r)$

$\langle\psi| = \int d^3r\, \langle r|\psi^*(r)$ 正交性 $\langle r|r'\rangle = \delta(r-r')$ Dirac-delta fuction

$\langle\varphi|\psi\rangle = \int d^3r\, \varphi^*(r)\psi(r)$ 完备性 $\int d^3r\, |r\rangle\langle r| = \hat{I}$

算符的表示 $\hat{A}|\psi\rangle = \iint d^3r\, d^3r'\, |r\rangle\langle r|\hat{A}|r'\rangle\langle r'|\psi\rangle$

$|\varphi\rangle = \int d^3r\, \varphi(r)|r\rangle$

故 $|\varphi\rangle = \hat{A}|\psi\rangle \Leftrightarrow \varphi(r) = \int d^3r' \langle r|\hat{A}|r'\rangle \psi(r') \Leftrightarrow a_n = \sum_m A_{nm} C_m$

$\langle r|\hat{r}|r'\rangle = r'\delta(r-r')$

$\langle r|V(\hat{r})|r'\rangle = V(r)\delta(r-r')$

$\langle r|\hat{p}|r'\rangle = ?$

一维情况，考察 $\langle x|[\hat{x},\hat{p}]|x'\rangle = i\hbar\langle x|x'\rangle = i\hbar\delta(x-x')$

$\parallel$ $\langle x|\hat{x}\hat{p}-\hat{p}\hat{x}|x'\rangle = (x-x')\langle x|\hat{p}|x'\rangle$

即 $\langle x|\hat{p}|x'\rangle = i\hbar\dfrac{\delta(x-x')}{x-x'} = -i\hbar\dfrac{d}{dx}\delta(x-x')$

三维 $\langle r|\hat{p}|r'\rangle = -i\hbar\nabla_r\delta(r-r')$

$\langle r|A(\hat{p})|r'\rangle = A(-i\hbar\nabla_r)\,\delta(r-r')$

考虑 δ 性质

$\int f(x)\dfrac{d\delta(x)}{dx}dx \xlongequal[\text{by parts}]{\text{integrate}} \cancel{\delta(x)f(x)\Big|_{-\infty}^{+\infty}} - \int \delta(x)f'(x)dx$

thus $-\int \delta(x)f'(x)dx = \int f(x)\delta'(x)dx \Rightarrow -\delta(x)f'(x) = f(x)\delta'(x)$

let $f(x) = x$, then $\delta(x) = -x\delta'(x)$

讨论 (i) $\langle x|\hat{p}|p\rangle = p\langle x|p\rangle$

$\langle x|\hat{p}|p\rangle = \int dx'\langle x|\hat{p}|x'\rangle\langle x'|p\rangle = \int dx'\left[-i\hbar\frac{\partial}{\partial x}\delta(x-x')\right]\langle x'|p\rangle = \int dx'\left[i\hbar\frac{\partial}{\partial x'}\delta(x-x')\right]\langle x'|p\rangle$

$\xlongequal[\text{by ports}]{\text{integrate}} -i\hbar\frac{\partial}{\partial x}\langle x|p\rangle$

$$\boxed{\frac{1}{2\pi\hbar}\int e^{ip(x-x')/\hbar}dp = \delta(x-x')}$$

thus $-i\hbar\frac{\partial}{\partial x}\langle x|p\rangle = p\langle x|p\rangle \Rightarrow \langle x|p\rangle \propto e^{ipx/\hbar}$, $\langle r|p\rangle \propto e^{i\vec{p}\cdot\vec{r}/\hbar}$

(ii) 归一化?? $\langle r|p\rangle = \dfrac{e^{i\vec{p}\cdot\vec{r}/\hbar}}{(2\pi\hbar)^{3/2}}$ with $\delta(r-r') = \langle r|r'\rangle = \int d\vec{p}^3\, \langle r|p\rangle\langle p|r'\rangle = \frac{1}{(2\pi\hbar)^3}\int e^{i\vec{p}\cdot(\vec{r}-\vec{r}')/\hbar}d\vec{p}^3 = \delta(r-r')$

(iii) $\langle r|\hat{l}|r'\rangle = -i\hbar\,\vec{r}\times\nabla_r\delta(r-r')$ $\langle r|A(\hat{r},\hat{p})|r'\rangle = A(r, -i\hbar\nabla_r)\,\delta(r-r')$

$\langle r|\hat{H}|r'\rangle = \langle r|\frac{\hat{p}^2}{2m}+V(\hat{r})|r'\rangle = -\frac{\hbar^2}{2m}\nabla_r^2\delta(r-r') + V(r)\,\delta(r-r')$

Schrödinger eq. $i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle$

考察 $i\hbar\frac{\partial}{\partial t}\langle r|\psi\rangle = i\hbar\frac{\partial}{\partial t}\psi(r) = \langle r|\hat{H}|\psi\rangle = \int d^3r' \langle r|\hat{H}|r'\rangle \psi(r') = -\frac{\hbar^2}{2m}\nabla_r^2\psi(r) + V(r)\psi(r)$

以及 $\hat{H}|\psi\rangle = E|\psi\rangle \Rightarrow \left[-\frac{\hbar^2}{2m}\nabla_r^2 + V(r)\right]\psi(r) = E\psi(r)$

(iv) 期望值的做法 $\langle\psi|\hat{A}|\psi\rangle = \int d^3r\, \psi^*(r) A(r, -i\hbar\nabla_r)\psi(r)$

b. 动量表象

作用后刚好出一个 $\vec{r}$!!!

$\langle p|\hat{r}|p'\rangle = \iint d^3r d^3r' \langle p|r\rangle\langle r|\hat{r}|r'\rangle\langle r'|p'\rangle = \int d^3r\, r\, \langle p|r\rangle\langle r|p'\rangle = \frac{1}{(2\pi\hbar)^3}\int d^3r\, (i\hbar\nabla_p) e^{-i\vec{p}\cdot\vec{r}/\hbar} e^{i\vec{p}'\cdot\vec{r}/\hbar} = i\hbar\nabla_p\delta(p-p')$

$i\hbar\nabla_r\varphi^*(r) = \left[-i\hbar\nabla_r\varphi(r)\right]^*$

$= \left[\int d^3r' \langle r|\hat{p}|r'\rangle\langle r'|\varphi\rangle\right]^*$

$= \left(\langle r|\hat{p}|\varphi\rangle\right)^* = \left(\hat{p}|\varphi\rangle\right)^\dagger|r\rangle$

(i) $\begin{cases}\langle p|\hat{p}|p'\rangle = p\,\delta(p-p') \\ \langle p|A(\hat{p})|p'\rangle = A(p)\,\delta(p-p')\end{cases}$ $\begin{cases}\langle p|\hat{r}|p'\rangle = i\hbar\nabla_p\delta(p-p') \\ \langle p|A(\hat{r})|p'\rangle = A(i\hbar\nabla_p)\,\delta(p-p')\end{cases}$

(ii) $\hat{p}$ 的厄米性

profe: $\langle\varphi|\hat{p}|\psi\rangle = \int d^3r\, \varphi^*(r)(-i\hbar\nabla_r)\psi(r) = \varphi^*(r)\psi(r)\Big|_{+\infty}^{0} + \int \psi(r)(i\hbar\nabla_r)\varphi^*(r)\, d^3r = 0 + \int \langle r|\psi\rangle \left(\hat{p}|\varphi\rangle\right)^\dagger|r\rangle\, d^3r$

$= \left(\hat{p}|\varphi\rangle\right)^\dagger|\psi\rangle = \langle\varphi|\hat{p}^\dagger|\psi\rangle \Rightarrow \hat{p} = \hat{p}^\dagger$

6. 连续谱的表象变换

$|\psi\rangle = \int d^3r\, \psi(r)|r\rangle = \int d^3p\, \varphi(p)|p\rangle$

$\langle r'| \Longrightarrow \int d^3r\, \psi(r)\langle r'|r\rangle = \int d^3p\, \varphi(p)\langle r'|p\rangle$

$\begin{cases}\psi(r) = \int d^3p\, \varphi(p)\langle r|p\rangle \\ \varphi(p) = \int d^3r\, \psi(r)\langle p|r\rangle\end{cases}$ with $\langle r|p\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\vec{p}\cdot\vec{r}/\hbar}$

$\langle r|\hat{A}|r'\rangle = \int \langle r|p\rangle\langle p|\hat{A}|p'\rangle\langle p'|r'\rangle\, d^3p\, d^3p'$

连续谱 $\Longleftrightarrow$ 分离谱

$|\psi\rangle = \sum_n C_n|\psi_n\rangle$ $\therefore \begin{cases} C_n = \langle\psi_n|\psi\rangle = \int d^3r\, \langle\psi_n|r\rangle\langle r|\psi\rangle = \int d^3r\, \psi_n^*(r)\psi(r) \\ \psi(r) = \langle r|\psi\rangle = \sum_n \langle r|\psi_n\rangle\langle\psi_n|\psi\rangle = \sum_n \psi_n(r) C_n\end{cases}$

以及 $A_{mn} = \langle\psi_m|\hat{A}|\psi_n\rangle = \int d^3r\, d^3r'\, \psi_m^*(r)\langle r|\hat{A}|r'\rangle\psi_n(r')$

关于$\psi_n(r)$的讨论 $\psi_n(r)=\langle r|\psi_n\rangle$

$$\begin{cases}\langle\psi_n|\psi_m\rangle=\delta_{mn} \Rightarrow \int d^3r\, \psi_n^*(r)\psi_m(r)=\delta_{mn}\\ \sum_n|\psi_n\rangle\langle\psi_n|=\hat{I} \Rightarrow \langle r|\left(\sum_n|\psi_n\rangle\langle\psi_n|\right)|r'\rangle=\langle r|r'\rangle\hat{I}=\delta(r-r')\end{cases}$$

$$\underbrace{\sum_n\psi_n(r)\psi_n^*(r')=\delta(r-r')}$$

例：$e^{i\hat{p}a/\hbar}|\psi\rangle$（一维情况），写到坐标表象下：

$$\langle x|e^{i\hat{p}a/\hbar}|\psi\rangle=\int dx'\, e^{i(-i\hbar\frac{\partial}{\partial x})a/\hbar}\delta(x-x')\psi(x')=e^{\frac{\partial}{\partial x}a}\psi(x)=\sum_n\frac{1}{n!}a^n\frac{\partial^n}{\partial x^n}\psi(x)=\psi(x+a)$$

即 $|\psi\rangle\to\psi(x)$ $\quad e^{i\hat{p}a/\hbar}|\psi\rangle\to\psi(x+a)$

第五章 时间演化

a. 时间与空间不同，不做为 Operator，仅为 parameter

b. 之前的态与算符理论仅为~~某一时~~刻的刻画

c. 存在多种等价的描述方式

1. Schrödinger eq:

$i\hbar\frac{\partial}{\partial t}|\psi\rangle=\hat{H}|\psi\rangle$ *公设 *NR

如$|\psi\rangle$为$\hat{H}$本征态，则 $\hat{H}|\psi\rangle=E|\psi\rangle=i\hbar\frac{\partial}{\partial t}|\psi\rangle$，解为 $|\psi\rangle=e^{-iEt/\hbar}|\psi(0)\rangle \Longrightarrow$ 定态 Stationary State

写在坐标表象：$i\hbar\frac{\partial}{\partial t}\psi(r,t)=\left[-\frac{\hbar^2}{2m}\nabla^2+V(r)\right]\psi(r,t)$

Trick：Seperate of Variables $\psi(r,t)=\psi(r)T(t) \Rightarrow \frac{i\hbar}{T(t)}\frac{dT(t)}{dt}=\frac{1}{\psi(r)}\left[-\frac{\hbar^2}{2m}\nabla^2+V(r)\right]\psi(r)\overset{\text{let}}{=\!=}E$

$\Rightarrow T(t)\propto e^{-iEt/\hbar}$, thus $\psi(r,t)=e^{-iEt/\hbar}\psi_E(r)$, with $\left[-\frac{\hbar^2}{2m}\nabla^2+V(r)\right]\psi(r)=E\psi(r)$

任意不含时的力学量在定态下的期望值与测量值的概率分布均不随时变化

证：(1) $\langle\psi_E|\cancel{e^{iEt/\hbar}}\hat{A}\,\cancel{e^{-iEt/\hbar}}|\psi_E\rangle=\langle\psi_E|\hat{A}|\psi_E\rangle$

(2) $\hat{A}|\varphi_n\rangle=A_n|\varphi_n\rangle \qquad \left|\langle\varphi_n|\psi_E\rangle e^{-iEt/\hbar}\right|^2=\left|\langle\varphi_n|\psi_E\rangle\right|^2$

2. 任意态的时间演化

利用 Hermitian的本征态 正交完备(归一)

$\underline{i\hbar\frac{\partial}{\partial t}|\psi\rangle=\hat{H}|\psi\rangle}$ with $\hat{H}|\psi_n\rangle=E|\psi_n\rangle$

thus $|\psi(t)\rangle=\sum_n C_n(t)|\psi_n\rangle \Rightarrow i\hbar\sum_n\frac{\partial}{\partial t}C_n(t)|\psi_n\rangle=\hat{H}\sum_n C_n(t)|\psi_n\rangle=\sum_n C_n(t)E_n|\psi_n\rangle \Rightarrow i\hbar\frac{\partial}{\partial t}C_n(t)=C_n(t)E_n \Rightarrow C_m(t)=e^{-iE_mt/\hbar}C_m(0)$

对于演化 $i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle$

①⇒ $i\hbar\frac{\partial}{\partial t}\psi(r,t) = \left[-\frac{\hbar^2}{2m}\nabla^2+V\right]\psi(r,t)$

特解 $\left[-\frac{\hbar^2}{2m}\nabla^2+V\right]\psi_n(r) = E_n\psi_n(r)$ → 定态波函数 $\xRightarrow{\text{总解}}$ $\psi(r,t) = \sum_n C_n e^{-iE_nt/\hbar}\psi_n(r)$

② $\{|\varphi_\alpha\rangle\}$ $|\psi\rangle = \sum_\alpha C_\alpha|\varphi_\alpha\rangle$

⇒ $i\hbar\frac{\partial}{\partial t}C_\alpha = \sum_\beta H_{\alpha\beta}C_\beta$

(i) 如 $\{|\varphi_\alpha\rangle\}$ 为 $\hat{H}$ 的本征态，$\hat{H}_{\alpha\beta} = E_\alpha\delta_{\alpha\beta}$

$i\hbar\frac{\partial}{\partial t}\left(\quad\right) = \left(\qquad\right)\left(\quad\right)$

(ii) 如 $\{|\varphi_\alpha\rangle\}$ 非 $\hat{H}$ 的本征态

3. 时间演化算符

let: $|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle$，代入 $i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle$ ⇒ $\boxed{i\hbar\frac{\partial}{\partial t}\hat{U}(t)}|\psi(0)\rangle = \boxed{\hat{H}\hat{U}(t)}|\psi(0)\rangle$

⇒ $i\hbar\frac{\partial}{\partial t}\hat{U}(t) = \hat{H}\hat{U}(t)$

如 $\hat{H}$ 不显含时，则 $\hat{U}(t) = e^{-i\hat{H}t/\hbar}$ (展开成 $\frac{\partial}{\partial t}\hat{U}(t) = \frac{\partial}{\partial t}\sum_n\frac{1}{n!}\left(\frac{-it}{\hbar}\right)^n\hat{H}^n = -\frac{i}{\hbar}\hat{H}e^{-i\hat{H}t/\hbar} = -\frac{i}{\hbar}\hat{H}\hat{U}(t)$

演化可逆

性质：$\langle\psi(t)|\psi(t)\rangle = \langle\psi(0)|\hat{U}^\dagger\hat{U}|\psi(0)\rangle = \langle\psi(0)|\psi(0)\rangle$ ⇒ $\hat{U}^\dagger\hat{U} = \hat{I}$ ⇒ $|\psi(0)\rangle = \hat{U}^\dagger|\psi(t)\rangle$ ⇒ $\hat{U}\hat{U}^\dagger = \hat{I}$ 幺正

例. 期望值的时间演化，Ehrenfest 定理

$\frac{d}{dt}\langle\psi(t)|\hat{A}|\psi(t)\rangle = \frac{1}{i\hbar}\langle[\hat{A},\hat{H}]\rangle_\psi + \langle\frac{\partial\hat{A}}{\partial t}\rangle_\psi$

由 $\frac{\partial}{\partial t}|\psi(t)\rangle = \frac{1}{i\hbar}\hat{H}|\psi(t)\rangle$，$\frac{\partial}{\partial t}\langle\psi(t)| = -\frac{1}{i\hbar}\langle\psi(t)|\hat{H}$

⇒ $i\hbar\frac{d}{dt}\langle\hat{A}\rangle_\psi = \langle[\hat{A},\hat{H}]\rangle_\psi + i\hbar\langle\frac{\partial\hat{A}}{\partial t}\rangle_\psi$

如 $\hat{H}$ 含时，则形式解 $\hat{U}(t) = \int_0^t\left(-\frac{i}{\hbar}\right)\hat{H}(t')\hat{U}(t')dt' + \underset{\hat{I}}{\hat{U}(0)}$

可迭代求解 $\hat{U}(t) = \hat{I} + \int_0^t\left(-\frac{i}{\hbar}\right)\hat{H}(t')dt' + \int_0^t dt'\int_0^{t'}dt''\,\hat{H}(t')\hat{H}(t'') + \cdots\cdots$

编时算符 ⟶ $T e^{-\frac{i}{\hbar}\int_0^t\hat{H}(t)dt}$

例.在某组基下，体系 $\hat{H}$ 矩阵表示为 $\begin{pmatrix}0 & \frac{A}{2}\\ \frac{A}{2} & 0\end{pmatrix}$，初态为 $\begin{pmatrix}1\\0\end{pmatrix}$，求任意时刻 t 的态

法Ⅰ.(推荐) ① 求 $\hat{H}$ 的本征问题：$E_1 = \frac{A}{2}$，$\frac{\sqrt{2}}{2}\begin{pmatrix}1\\1\end{pmatrix}$

$E_2 = -\frac{A}{2}$，$\frac{\sqrt{2}}{2}\begin{pmatrix}1\\-1\end{pmatrix}$

② 态表示为 $\begin{pmatrix}1\\0\end{pmatrix} = \frac{\sqrt{2}}{2}\left[\frac{\sqrt{2}}{2}\begin{pmatrix}1\\1\end{pmatrix} + \frac{\sqrt{2}}{2}\begin{pmatrix}1\\-1\end{pmatrix}\right]$

③ 演化系数 $\frac{1}{2}e^{-i\frac{At}{2\hbar}}\begin{pmatrix}1\\1\end{pmatrix} + \frac{1}{2}e^{i\frac{At}{2\hbar}}\begin{pmatrix}1\\-1\end{pmatrix} = \begin{pmatrix}\cos\left(\frac{At}{2\hbar}\right)\\ -i\sin\left(\frac{At}{2\hbar}\right)\end{pmatrix}$

法Ⅱ：G 旧基：$\underset{|G_1\rangle}{\frac{\sqrt{2}}{2}\begin{pmatrix}1\\1\end{pmatrix}}$ $\underset{|G_2\rangle}{\frac{\sqrt{2}}{2}\begin{pmatrix}1\\-1\end{pmatrix}}$

F 新基：$\begin{pmatrix}1\\0\end{pmatrix}$ $\begin{pmatrix}0\\1\end{pmatrix}$

S 为从 F→G 的表象变换阵

$S = \begin{array}{cc} |G_1\rangle & |G_2\rangle \end{array}$

$S = \begin{pmatrix}\boxed{\begin{matrix}(1\ 0)\frac{\sqrt{2}}{2}\begin{pmatrix}1\\1\end{pmatrix}\\ (0\ 1)\frac{\sqrt{2}}{2}\begin{pmatrix}1\\1\end{pmatrix}\end{matrix}} & \boxed{\begin{matrix}(1\ 0)\frac{\sqrt{2}}{2}\begin{pmatrix}1\\-1\end{pmatrix}\\ (0\ 1)\frac{\sqrt{2}}{2}\begin{pmatrix}1\\-1\end{pmatrix}\end{matrix}}\end{pmatrix} = \frac{\sqrt{2}}{2}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix}$

用 G：$\hat{H} \longrightarrow \begin{pmatrix}\frac{A}{2} & 0\\ 0 & -\frac{A}{2}\end{pmatrix}$ $A^{(F)} = SA^{(G)}S^\dagger$

幺正变换 $S e^{-i\begin{pmatrix}\frac{A}{2} & 0\\ 0 & -\frac{A}{2}\end{pmatrix}t/\hbar}S^\dagger\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}\cos\frac{At}{2\hbar}\\ -i\sin\frac{At}{2\hbar}\end{pmatrix}$

$\frac{\sqrt{2}}{2}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix}\begin{pmatrix}0 & \frac{A}{2}\\ \frac{A}{2} & 0\end{pmatrix}\frac{\sqrt{2}}{2}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix} = \begin{pmatrix}\frac{A}{2} & 0\\ 0 & -\frac{A}{2}\end{pmatrix}$

$S^\dagger e^{-i\begin{pmatrix}0 & \frac{A}{2}\\ \frac{A}{2} & 0\end{pmatrix}t/\hbar}S = \begin{pmatrix}e^{-i\frac{At}{2\hbar}} & 0\\ 0 & e^{i\frac{At}{2\hbar}}\end{pmatrix}$

依 Ehrenfest 关系 $i\hbar\frac{d}{dt}\langle\hat{A}\rangle_\psi = \langle[\hat{A},\hat{H}]\rangle_\psi + i\hbar\langle\frac{\partial\hat{A}}{\partial t}\rangle_\psi$

守恒量为：不显含时且与 $\hat{H}$ 对易的力学量 $[\hat{A},\hat{H}]=0$

如 $[\hat{A},\hat{H}]=0$，则共同本征态 $\{|\psi_n\rangle\}$ $\{A_n, E_n\}$

4. 三种绘景 picture

a. Schrödinger Picture

$|\psi(t)\rangle$ 含时演化 $i\hbar\frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle$

$\hat{A}$ 不演化

可观测量 $\langle\psi(t)|\hat{A}|\psi(t)\rangle = \bar{A}(t)$

$|c_n|^2 = |\langle\psi_n|\psi(t)\rangle|^2$

b. Heisenberg Picture

态不演化但算符演化的情况

$|\psi(0)\rangle_S = |\psi\rangle_H = \hat{U}^\dagger|\psi(t)\rangle_S$

为保证 $\langle\hat{A}\rangle = \langle\psi|\hat{A}|\psi\rangle$ 不变，$\hat{A}_H = ?$

$\Rightarrow {}_H\langle\psi|\hat{A}_H|\psi\rangle_H = {}_S\langle\psi(t)|\hat{U}\hat{A}_H\hat{U}^\dagger|\psi(t)\rangle_S = {}_S\langle\psi(t)|\hat{A}_S|\psi(t)\rangle_S$

$$\boxed{\Rightarrow\begin{cases}\hat{A}_H = \hat{U}^\dagger\hat{A}_S\hat{U}\\ |\psi\rangle_H = \hat{U}^\dagger|\psi(t)\rangle_S\end{cases}}$$ 完整的 Heisenberg Picture

故 $\boxed{\text{Heisenberg eq.: } \frac{d\hat{A}_H}{dt} = \hat{U}^\dagger\frac{\partial\hat{A}}{\partial t}\hat{U} + \frac{1}{i\hbar}[\hat{A}_H,\hat{H}_H] = \left(\frac{\partial\hat{A}}{\partial t}\right)_H + \frac{1}{i\hbar}[\hat{A}_H,\hat{H}_H]}$

Trick $[\hat{p},V(\hat{x})] = \sum_n\frac{V^{(n)}(0)}{n!}\underbrace{[\hat{p},\hat{x}^n]}_{-i\hbar n\hat{x}^{n-1}} = -i\hbar\sum_n\frac{V^{(n)}(0)}{(n-1)!}\hat{x}^{n-1} = -i\hbar\frac{\partial}{\partial x}V(\hat{x})$

（直接用 $[\hat{p},V(\hat{x})] = [\hat{p},\hat{x}]V'(\hat{x})$ 亦可）

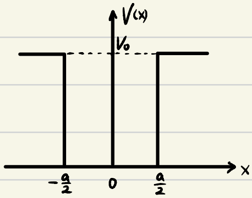
*c. 相互作用绘景

$\hat{H} = \hat{H}_0 + \hat{V}$

定义 $\begin{cases}|\psi(t)\rangle_I = e^{i\hat{H}_0t/\hbar}|\psi(t)\rangle_S = e^{i\hat{H}_0t/\hbar}e^{-i\hat{H}t/\hbar}|\psi(0)\rangle_S\\ \hat{A}_I = e^{i\hat{H}_0t/\hbar}\hat{A}_S e^{-i\hat{H}_0t/\hbar}\end{cases}$

动力学方程 $\begin{cases}i\hbar\frac{d}{dt}\hat{A}_I = [\hat{A}_I,\hat{H}_0] + \left(\frac{\partial\hat{A}}{\partial t}\right)_I\\ i\hbar\frac{d}{dt}|\psi(t)\rangle_I = \hat{V}_I|\psi(t)\rangle_I\end{cases}$ 此处 $\hat{V}_I = e^{i\hat{H}_0t/\hbar}\hat{V}_S e^{-i\hat{H}_0t/\hbar}$

1. 一维有限深势阱



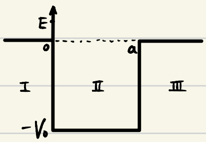
a. $E<V_0$, Bound State

能量本征方程 $\psi''+\frac{2m}{\hbar^2}(E-V(x))\psi=0$

令 $\sqrt{2mE}/\hbar=k_0$, $\sqrt{2m(V_0-E)}/\hbar=\beta$, 即有

$$\begin{cases}\psi''+\frac{2mE}{\hbar^2}\psi=0 & |x|\le a/2 \Rightarrow \psi(x)=\overset{\text{偶宇称}}{A\cos k_0x}+\overset{\text{奇宇称}}{B\sin k_0x}\\ \psi''-\beta^2\psi=0 & |x|\ge a/2 \Rightarrow \psi(x)=Ce^{-\beta|x|}\end{cases}$$

b. $E>V_0$ Scattering



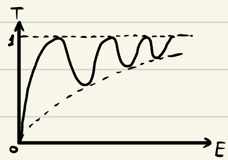
$$\psi(x)=\begin{cases}e^{ikx}+Re^{-ikx} & \text{I} \\ Ae^{ik'x}+Be^{-ik'x} & \text{II} \\ Se^{ikx} & \text{III}\end{cases}\qquad \begin{aligned}k&=\sqrt{2mE}/\hbar\\ k'&=\sqrt{2m(E+V_0)}/\hbar\end{aligned}$$

散射概率 $|R|^2+|S|^2=1$

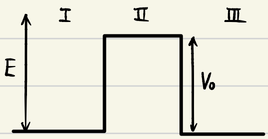
定义透射率 $T=|S|^2=\left[1+\frac{\sin k'a}{4\frac{E}{V}(1+\frac{E}{V})}\right]^{-1}$

当 $E=-V+\frac{n^2\pi^2\hbar^2}{2ma^2}$ → $k'R=n\pi$ (驻波条件)

产生共振透射



c. 方势阱

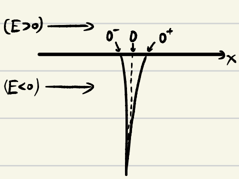


$$\psi(x)=\begin{cases}e^{ikx}+Re^{-ikx} & \text{I} \\ Ae^{ik'x}+Be^{-ik'x} & \text{II} \\ Se^{ikx} & \text{III}\end{cases}\qquad \begin{aligned}k&=\sqrt{2mE}/\hbar\\ k'&=\sqrt{2m(V_0-E)}/\hbar\end{aligned}$$

透射率: $T=|S|^2=\left[1+\frac{1}{\frac{E}{V}(1-\frac{E}{V})}\sinh^2(k'a)\right]^{-1}$

∽ STM 的机制

2. 一维 δ 势阱问题



$V(x)=-\gamma\delta(x)$, $\gamma>0$

Boundary Condition: $\psi'(0^+)-\psi'(0^-)=\frac{2m}{\hbar^2}\psi(0)\int_{0^-}^{0^+}V(x)dx=-\frac{2m}{\hbar^2}\gamma\psi(0)$

对 $x\neq0$, $\psi''+\frac{2mE}{\hbar^2}\psi=0$, 设 $k=\sqrt{2mE}/\hbar$

① $E<0$ (Bound State) 偶宇称 $\psi(x)=\begin{cases}Ae^{-kx}, & x>0\\ Ae^{kx}, & x<0\end{cases}$ $\xRightarrow{B.C.} k=\frac{m\gamma}{\hbar^2}$, $E=-\frac{m\gamma^2}{2\hbar^2}$

奇宇称 $\psi(x)=\begin{cases}Ae^{-kx}, & x>0\\ -Ae^{kx}, & x<0\end{cases}$ ⇒ $A=0$, trivial

3. 一维谐振子

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2x^2\right)\psi(x)=E\psi(x)$$

first step：无量纲化 $\Rightarrow$ 定义 $\alpha=\sqrt{\frac{m\omega}{\hbar}}$，则 $\xi=\alpha x$ 为无量纲的长度

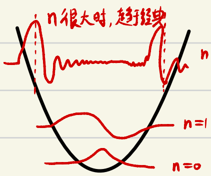
定义 $\lambda=\frac{E}{\frac{1}{2}\hbar\omega}$ 为无量纲的能量

next step：$\Rightarrow \frac{d^2\psi}{d\xi^2}+(\lambda-\xi^2)\psi=0$，with $\xi\to\pm\infty$，$\psi\to 0$ (Bound State) $\psi\sim Ae^{-\frac{1}{2}\xi^2}+Be^{\frac{1}{2}\xi^2}$

令 $\psi=u(\xi)e^{-\frac{1}{2}\xi^2}$，代入原方程即得 $\frac{d^2u}{d\xi^2}-2\xi\frac{du}{d\xi}+(\lambda-1)u=0$ (Hermit eq.)

其解 $H_n(\xi)=(-1)^n e^{\xi^2}\frac{d^n}{d\xi^n}(e^{-\xi^2})$ (Hermit 多项式)

介绍级数解法：$u(\xi)=\sum_{k=0}^{\infty}C_k\xi^k$，$|\xi|<+\infty$，代入可得递推关系为 $C_{k+2}=\frac{2k-\lambda+1}{(k+1)(k+2)}C_k$



为使 $\psi(\xi)|_{\xi\to+\infty}=0$，则 $u(\xi)$ 的级数展开必须被截断，otherwise $C_{k+2}\sim\frac{2}{k}C_k\Rightarrow C_k\sim\frac{1}{(k/2)!}$

$\Rightarrow u=\sum_k\frac{1}{(k/2)!}\xi^k=e^{\xi^2}\Rightarrow\psi=e^{+\frac{1}{2}\xi^2}$ 发散

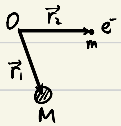
于是截断方式 $\lambda=2k+1$ $\begin{cases}C_0 & \sim 偶数项\\ C_1 & \sim 奇数项\end{cases}$ $\Rightarrow \frac{E}{\frac{1}{2}\hbar\omega}=2k+1\Rightarrow E_n=(n+\frac{1}{2})\hbar\omega$，$n=0,1,2,\cdots\cdots$

$\psi_n(x)=\underset{归一化系数}{N_n}\,e^{-\frac{1}{2}\xi^2}H_n(\xi)$

(推广至 3-Dim，$\psi=\prod\psi_x\psi_y\psi_z$ OR Sphere Cordinate)

$|n_x,n_y,n_z\rangle$

4. 氢原子 (三维中心力场的定态问题)



$$\left[-\frac{\hbar^2}{2M}\nabla_1^2-\frac{\hbar^2}{2m}\nabla_2^2+V(|\vec{r}_1-\vec{r}_2|)\right]\psi(\vec{r}_1,\vec{r}_2)=E\psi(\vec{r}_1,\vec{r}_2)$$

令 $\begin{cases}\vec{R}=\frac{m}{m+M}\vec{r}_2+\frac{M}{m+M}\vec{r}_1\\ \vec{r}=\vec{r}_1-\vec{r}_2\quad(M\gg m)\end{cases}$ 则 $\left[-\frac{\hbar^2}{2(M+m)}\nabla_R^2-\frac{\hbar^2}{2\mu}\nabla_r^2+V(|\vec{r}|)\right]\psi(\vec{R},\vec{r})=E\psi(\vec{R},\vec{r})$

$\mu\sim m$ Born-Oppenheimer 近似

即 R.r 为分离变量，$\psi(\vec{R},\vec{r})=\psi_c(\vec{R})\psi(\vec{r})$，①质心运动为平面波：$-\frac{\hbar^2}{2(M+m)}\nabla_R^2\psi_c(\vec{R})=E_c\psi_c(\vec{R})$

②相对运动为：$\left[-\frac{\hbar^2}{2\overset{\mu}{m}}\nabla^2+V(|\vec{r}|)\right]\psi(\vec{r})=E\psi(\vec{r})$ 球对称问题，辅助有 $\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$

分离变量，令 $\psi(r,\theta,\varphi)=R(r)Y(\theta,\varphi)$，得 $\underbrace{\left\{\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2m}{\hbar^2}[V(r)-E]\right\}}_{(**)}+\underbrace{\frac{1}{Y(\theta,\varphi)}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2Y}{\partial\varphi^2}\right\}}_{(*)}=0$

应有 $(**)=-(*)=l(l+1)$

解 $(*)$，得球谐函数 $Y_l^m(\theta,\varphi)$ $l=0,1,2,\cdots$，$m=-l,-l+1,\cdots,l-1,l$

解 $(**)$，令 $u(r)=rR(r)$，则 $-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2}+\left[V(r)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u(r)=Eu(r)$

下面令 $V(r)=-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$，无量纲化 $\kappa=\sqrt{\frac{-2mE}{\hbar^2}}$，则 $\rho=\kappa r$ 无量纲：$\frac{d^2u}{d\rho^2}-\left[1-\frac{\rho_0}{\rho}+\frac{l(l+1)}{\rho^2}\right]u=0$，$\rho_0=\frac{me^2}{2\pi\varepsilon_0\hbar^2\kappa}$

其渐近行为 $\begin{cases}\rho\to\infty，u''-u=0，u\sim Ae^{-\rho}+Be^{+\rho}\\ \rho\to 0，u''-\frac{l(l+1)}{\rho^2}u=0，u\sim A\rho^{l+1}+B\rho^{-l}\end{cases}$ 令 $u(\rho)=\rho^{l+1}e^{-\rho}v(\rho)$

$\Rightarrow \rho v''+2(l+1-\rho)v'+(\rho_0-2l-2)v=0$

令 $v=\sum_k C_k\rho^k\Rightarrow C_{k+1}=\frac{2(k+l+1)}{(k+1)(k+2l+2)}C_k$，当 $k\to+\infty$ 时，$C_k\sim\frac{2^k}{k!}C_0\Rightarrow v\sim e^{2\rho}$ 则 u 会发散

级数需要截断 $\Rightarrow \rho_0=2(k_{max}+l+1)=2n$，$n=1,2,\cdots$

得到 $E_n = -\frac{\hbar^2 k^2}{2m} = -\frac{\hbar^2}{2ma_0^2}\frac{1}{n^2}$，$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$ 为 Bohr Radius

进而波函数 $v(\rho) = L_{n-l-1}^{2l+1}(2\rho) \to$ 广义 Legendre 多项式

$$\Rightarrow \psi_{nlm}(\vec{r}) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{n-l-1}{2n[(n+l)!]^3}}\, e^{-\frac{r}{na_0}} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) Y_l^m(\theta,\varphi)$$

$= \langle r|nlm\rangle$ $\quad E_n \sim \frac{1}{n^2} \sim |nlm\rangle \Rightarrow E_n$ 有 $\sum_{l=0}^{n-1}(2l+1) = n^2$ 重简并. 考虑 Spin 后为 $2n^2$.

第六章 角动量

1. 轨道角动量

Operator $\hat{\vec{l}} = \hat{\vec{r}} \times \hat{\vec{p}}$ with $[\hat{l}^2, \hat{l}_i] = 0$，$[\hat{l}_i, \hat{l}_j] = i\hbar\varepsilon_{ijk}\hat{l}_k$

$$\begin{cases} \hat{l}^2 Y(\theta,\varphi) = l(l+1)\hbar^2 Y(\theta,\varphi) \\ \hat{l}_z Y(\theta,\varphi) = m\hbar\, Y(\theta,\varphi) \end{cases}$$

球谐函数 $Y_l^m(\theta,\varphi) = (-1)^m \sqrt{\frac{(l-m)!\,(2l+1)}{(l+m)!\; 4\pi}}\, P_l^m(\cos\theta)\, e^{im\varphi}$

在 Dirac 符号下，只需掌握

$$\begin{cases} \hat{l}^2 |l,m\rangle = l(l+1)\hbar^2 |l,m\rangle \\ \hat{l}_z |l,m\rangle = m\hbar\, |l,m\rangle \end{cases}$$

with $Y_l^m(\theta,\varphi) = \langle r|l,m\rangle$

Properties: i) $\langle l,m|l',m'\rangle = \delta_{ll'}\delta_{mm'}$

ii) $\sum_{l,m} |l,m\rangle\langle l,m| = \hat{I}$

Trick: 利用 $(x,y,z) \leftrightarrow (r,\theta,\varphi)$ 代数关系

2. 角动量的代数性质

① $\hat{J}^2 \hat{J}_\pm |j,m\rangle = \hat{J}_\pm \hat{J}^2 |j,m\rangle = l(l+1)\hbar^2 \hat{J}_\pm |j,m\rangle$ with $[\hat{l}^2, \hat{l}_i] = 0$

② $\hat{J}_\pm |j,m\rangle = \sqrt{l(l+1) - m(m\pm1)}\,\hbar\, |j,m\pm1\rangle$

3. 自旋 Spin

$S=\frac{1}{2}$ Pauli Operater $\hat{S}_i = \frac{\hbar}{2}\hat{\sigma}_i$ 在 $\{\hat{S}^2, \hat{S}_z\}$ 表象下

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

对任意 2×2 矩阵总可用 $\{I, \sigma_x, \sigma_y, \sigma_z\}$ 展开.

e.g: 求 $\hat{\sigma}_y$ 算符的本征值与本征态，如电子处于 $\begin{pmatrix} \alpha \\ \beta \end{pmatrix}$ $(\alpha|\uparrow_z\rangle + \beta|\downarrow_z\rangle)$ 自旋态

问测 $\hat{S}_y$ 的可能测值与对应几率

法一: $\sigma_y : \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \Rightarrow \lambda_1 = 1,\ \frac{\sqrt{2}}{2}\begin{pmatrix} 1 \\ i \end{pmatrix} \quad \lambda_2 = -1,\ \frac{\sqrt{2}}{2}\begin{pmatrix} 1 \\ -i \end{pmatrix}$

$\because |\psi\rangle = \langle\uparrow_y|\psi\rangle|\uparrow_y\rangle + \langle\downarrow_y|\psi\rangle|\downarrow_y\rangle$

$\therefore \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \frac{\sqrt{2}}{2}(\alpha - i\beta)\frac{\sqrt{2}}{2}\begin{pmatrix} 1 \\ i \end{pmatrix} + \frac{\sqrt{2}}{2}(\alpha + i\beta)\frac{\sqrt{2}}{2}\begin{pmatrix} 1 \\ -i \end{pmatrix}$

法二: $\underbrace{\frac{\sqrt{2}}{2}\begin{bmatrix} 1 & -i \\ 1 & i \end{bmatrix}}_{U^\dagger}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\underbrace{\frac{\sqrt{2}}{2}\begin{bmatrix} 1 & 1 \\ i & -i \end{bmatrix}}_{U} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$

$\frac{\sqrt{2}}{2}\begin{bmatrix} 1 & 1 \\ i & -i \end{bmatrix}\begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \begin{bmatrix} \frac{\sqrt{2}}{2}(\alpha - i\beta) \\ \frac{\sqrt{2}}{2}(\alpha + i\beta) \end{bmatrix}$

e.g: 转动算符的矩阵表示 $e^{-i\hat{S}\cdot\vec{n}\varphi/\hbar} = e^{-i\hat{\sigma}\cdot\vec{n}\varphi/2}$

with $(\hat{\vec{\sigma}}\cdot\vec{a})(\hat{\vec{\sigma}}\cdot\vec{b}) = \hat{\sigma}_j a_j \hat{\sigma}_k b_k = \left(\frac{1}{2}\{\hat{\sigma}_j, \hat{\sigma}_k\} + \frac{1}{2}[\hat{\sigma}_j, \hat{\sigma}_k]\right) a_j b_k$

& $\{\hat{\sigma}_i, \hat{\sigma}_j\} = 2\delta_{ij}$, $[\hat{\sigma}_i, \hat{\sigma}_j] = 2i\varepsilon_{ijk}\hat{\sigma}_k$

thus $(\hat{\vec{\sigma}}\cdot\vec{a})(\hat{\vec{\sigma}}\cdot\vec{b}) = a_j b_j + i\varepsilon_{jkl}\hat{\sigma}_l a_j b_k = \vec{a}\cdot\vec{b} + i(\vec{a}\times\vec{b})\cdot\hat{\vec{\sigma}}$

noticing that $(\hat{\vec{\sigma}}\cdot\vec{n})^2 = 1$, expanding it:

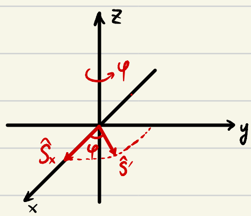
$$e^{-i(\hat{\vec{\sigma}}\cdot\vec{n})\varphi/2} = \left[1 - \frac{(\hat{\vec{\sigma}}\cdot\vec{n})^2}{2!}\left(\frac{\varphi}{2}\right)^2 + \frac{(\hat{\vec{\sigma}}\cdot\vec{n})^4}{4!}\left(\frac{\varphi}{2}\right)^4 + \cdots\right] + \left[-i(\hat{\vec{\sigma}}\cdot\vec{n})\frac{\varphi}{2} + i\frac{(\hat{\vec{\sigma}}\cdot\vec{n})^3}{3!}\left(\frac{\varphi}{2}\right)^3 + \cdots\right]$$

$$= \cos\left(\frac{\varphi}{2}\right)\hat{I} - i(\hat{\vec{\sigma}}\cdot\vec{n})\sin\left(\frac{\varphi}{2}\right)$$

$\Rightarrow e^{-i(\hat{\vec{\sigma}}\cdot\vec{n})\varphi} = \cos\varphi\,\hat{I} - i\sin\varphi(\hat{\vec{\sigma}}\cdot\vec{n})$

e.g: 转动算符

(1) $e^{-i\hat{S}_z\varphi/\hbar}\boxed{\hat{S}_x}e^{i\hat{S}_z\varphi/\hbar} = \frac{\hbar}{2}e^{-i\sigma_z\varphi/2}\sigma_x e^{i\sigma_z\varphi/2} = \overbrace{\boxed{\cos\varphi\,\hat{S}_x + \sin\varphi\,\hat{S}_y}}^{\hat{S}'}$



(2) 在 $\{\hat{S}^2, \hat{S}_z\}$ 的本征基下，求 $\hat{S}$ 在 $\vec{n} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$ 方向上分量的矩阵表示与本征态.

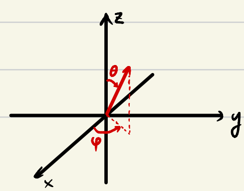
法一: $\hat{S}_n = \hat{\vec{S}}\cdot\vec{n} = \sin\theta\cos\varphi\,\hat{S}_x + \sin\theta\sin\varphi\,\hat{S}_y + \cos\theta\,\hat{S}_z$

$\Rightarrow \frac{\hbar}{2}\begin{bmatrix} \cos\theta & \sin\theta\, e^{-i\varphi} \\ \sin\theta\, e^{i\varphi} & -\cos\theta \end{bmatrix} \Rightarrow \begin{cases} \frac{\hbar}{2}, & \begin{bmatrix} \cos\frac{\theta}{2}e^{i\varphi/2} \\ \sin\frac{\theta}{2}e^{i\varphi/2} \end{bmatrix} \\ -\frac{\hbar}{2}, & \begin{bmatrix} -\sin\frac{\theta}{2}e^{-i\varphi/2} \\ \cos\frac{\theta}{2}e^{i\varphi/2} \end{bmatrix} \end{cases}$

法二: 定义转动算符由两步完成

$\hat{U} = e^{-i\frac{\varphi}{2}\hat{\sigma}_z}e^{-i\frac{\theta}{2}\hat{\sigma}_x}$

$= \begin{bmatrix} \cos\theta/2\, e^{-i\varphi/2} & -\sin\theta/2\, e^{-i\varphi/2} \\ \sin\theta/2\, e^{i\varphi/2} & \cos\theta/2\, e^{i\varphi/2} \end{bmatrix}$



延续法二: $\hat{u}\hat{S}_z\hat{u}^+ = \frac{\hbar}{2}\begin{bmatrix}\cos\theta & \sin\theta\, e^{-i\varphi}\\ \sin\theta\, e^{i\varphi} & -\cos\theta\end{bmatrix}$

同时有 $\begin{cases}|\uparrow_n\rangle = \hat{u}|\uparrow_z\rangle = \hat{u}\begin{pmatrix}1\\0\end{pmatrix} = \begin{bmatrix}\cos\frac{\theta}{2}e^{-i\varphi/2}\\ \sin\frac{\theta}{2}e^{i\varphi/2}\end{bmatrix}\\ |\downarrow_n\rangle = \hat{u}|\downarrow_z\rangle = \hat{u}\begin{pmatrix}0\\1\end{pmatrix} = \begin{bmatrix}-\sin\frac{\theta}{2}e^{-i\varphi/2}\\ \cos\frac{\theta}{2}e^{i\varphi/2}\end{bmatrix}\end{cases}$

e.g.: 自旋 $1/2$ 的电子在外磁场中的 Hamiltonian 为 $\hat{H} = A\hat{\vec{S}}\cdot\vec{B}$ 假设磁场 z 向, 电子初态为 $\hat{S}_x$ 的本征值 $\hbar/2$ 的本征态.
求 t 时刻 $\hat{S}_x\ \hat{S}_y\ \hat{S}_z$ 的期望值及测值几率分布.

$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}\quad |\downarrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$

$|\psi(t)\rangle = \langle\uparrow_x|\psi(t)\rangle|\uparrow_x\rangle + \langle\downarrow_x|\psi(t)\rangle|\downarrow_x\rangle$

$= \cos\frac{\phi t}{2}|\uparrow_x\rangle - i\sin\frac{\phi t}{2}|\downarrow_x\rangle$

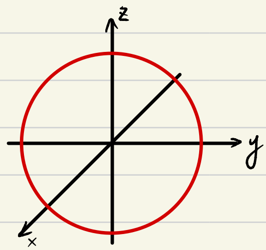
$\hat{H} = AB\hat{S}_z$, $\boxed{\hat{u} = e^{-i\frac{AB}{2}\hat{\sigma}_z t} \Rightarrow \begin{bmatrix}e^{-i\frac{AB}{2}t} & 0\\ 0 & e^{i\frac{AB}{2}t}\end{bmatrix}}$

即 $|\uparrow_x\rangle$ 态绕 z 轴转 $\frac{ABt}{2}$ 角 ($\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$)

$|\psi(t)\rangle = \hat{u}|\uparrow_x\rangle = \frac{\sqrt{2}}{2}\begin{pmatrix}e^{-i\phi t/2}\\ e^{i\phi t/2}\end{pmatrix}$ with $\phi = AB$

测值: $\langle\hat{S}_z\rangle_t = 0$ $\begin{cases}\frac{\hbar}{2}, & P=\frac{1}{2}\\ -\frac{\hbar}{2}, & P=-\frac{1}{2}\end{cases}$ | $\langle\hat{S}_x\rangle_t = \frac{\hbar}{2}\cos\phi t$ $\begin{cases}\frac{\hbar}{2}, & P=\cos^2\frac{\phi t}{2}\\ -\frac{\hbar}{2}, & P=\sin^2\frac{\phi t}{2}\end{cases}$ | $\langle\hat{S}_y\rangle_t = \frac{\hbar}{2}\sin\phi t$ $\begin{cases}\frac{\hbar}{2}, & \frac{1}{2}[1+\sin\phi t]\\ -\frac{\hbar}{2}, & \frac{1}{2}[1-\sin\phi t]\end{cases}$

e.g.: Bloch Sphere ⇔ 2×2 体系动力学



$H_0 = AI + B\sigma_x + C\sigma_y + D\sigma_z$

不就是 $\hat{S}_n$ 吗

选取新势能零点 $H = B\sigma_x + C\sigma_y + D\sigma_z = E\,\hat{\vec{\sigma}}\cdot\vec{n}$

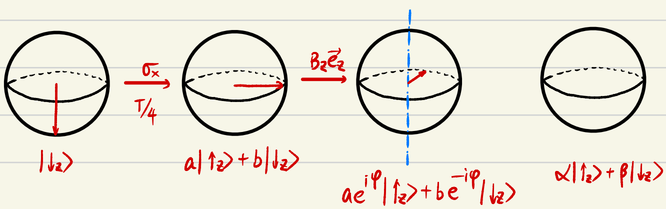
$\Rightarrow$ 其本征态 $E_i\ \begin{bmatrix}\cos\frac{\theta}{2}e^{-i\varphi/2}\\ \sin\frac{\theta}{2}e^{i\varphi/2}\end{bmatrix}$; $-E_i\ \begin{bmatrix}-\sin\frac{\theta}{2}e^{-i\varphi/2}\\ \cos\frac{\theta}{2}e^{i\varphi/2}\end{bmatrix}$

$\begin{pmatrix}1\\0\end{pmatrix} \Rightarrow \theta=0,\ \varphi=0$ 的规范 $\quad \hat{u}(\theta,\varphi)\begin{pmatrix}1\\0\end{pmatrix} = \begin{bmatrix}\cos\frac{\theta}{2}e^{-i\varphi/2}\\ \sin\frac{\theta}{2}e^{i\varphi/2}\end{bmatrix}$

$|\uparrow_n\rangle$

若取 $\vec{n}' = -\vec{n}$, 则 $\begin{cases}\theta\to\pi-\theta\\ \varphi\to\varphi+\pi\end{cases}$ $\quad |\uparrow_{n'}\rangle \to i\begin{bmatrix}\cos\frac{\theta}{2}e^{-i\varphi/2}\\ \sin\frac{\theta}{2}e^{i\varphi/2}\end{bmatrix}$

e.g.(承接上例)
干涉仪



$\sum_m |jm\rangle\langle jm| = \hat{I} \leftarrow 2j+1$ 维

4. 角动量耦合

考虑两独立的角动量 $\hat{\vec{j}}_1$, $\hat{\vec{j}}_2$ 即 $[\hat{j}_{1\alpha}, \hat{j}_{2\beta}] = 0$

定义 $\boxed{\hat{\vec{j}} = \hat{\vec{j}}_1 + \hat{\vec{j}}_2}$，则 $\hat{\vec{j}}$ 亦为角动量算符，服从 $[\hat{j}_\alpha, \hat{j}_\beta] = i\hbar\varepsilon_{\alpha\beta\gamma}\hat{j}_\gamma$

如研究氢原子
$\hat{\vec{l}} + \hat{\vec{s}} = \hat{\vec{j}}$ OR $\hat{\vec{s}}_1 + \hat{\vec{s}}_2 = \hat{\vec{s}}$
轨道 电子自旋

可研究 $\{\hat{j}^2, \hat{j}_z\}$ 的本征问题

老性质仍然满足 $[\hat{j}^2, \hat{j}_i^2] = 0$，$[\hat{j}_\alpha, \hat{j}_i^2] = 0$　　$i = 1,2$

① $\{\hat{j}_1^2, \hat{j}_2^2, \hat{j}_{1z}, \hat{j}_{2z}\}$　　$|\underbrace{j_1 m_1}_{\hat{j}_1^2,\hat{j}_{1z}}\rangle \otimes |\underbrace{j_2 m_2}_{\hat{j}_2^2,\hat{j}_{2z}}\rangle = |j_1 m_1\rangle |j_2 m_2\rangle = \boxed{|j_1 \underset{2j_1+1}{m_1}; j_2 \underset{2j_2+1}{m_2}\rangle}$

非耦合表象

$$\begin{cases} \hat{j}_1^2 |\ \rangle = j_1(j_1+1)\hbar^2 |\ \rangle \\ \hat{j}_{1z} |\ \rangle = m_1\hbar |\ \rangle \\ \hat{j}_2^2 |\ \rangle = j_2(j_2+1)\hbar^2 |\ \rangle \\ \hat{j}_{2z} |\ \rangle = m_2\hbar |\ \rangle \end{cases}$$

② 耦合表象 $\{\hat{j}_1^2, \hat{j}_2^2, \hat{j}^2, \hat{j}_z\}$　　$|j_1 j_2 j m\rangle$

$$\begin{cases} \hat{j}_1^2 |\ \rangle = j_1(j_1+1)\hbar^2 |\ \rangle \\ \hat{j}_2^2 |\ \rangle = j_2(j_2+1)\hbar^2 |\ \rangle \\ \hat{j}^2 |\ \rangle = j(j+1)\hbar^2 |\ \rangle \\ \hat{j}_z |\ \rangle = m\hbar |\ \rangle \end{cases}$$

③ 表象变换与CG系数　　CG系数性质

定义：$|j_1 j_2 j m\rangle = \sum_{m_1 m_2} \underbrace{\langle j_1 m_1; j_2 m_2 | j_1 j_2 j m\rangle}_{\text{CG系数}} |j_1 m_1; j_2 m_2\rangle$

(i) 非零，则 $m = m_1 + m_2$

$(\hat{j}_z - \hat{j}_{1z} - \hat{j}_{2z}) |\ \rangle = 0$

$\Rightarrow \langle\ | (\hat{j}_z - \hat{j}_{1z} - \hat{j}_{2z}) |\ \rangle = 0$

$(m - m_1 - m_2)\langle\ |\ \rangle = 0$　　角动量分量守恒

(ii) $|j_1 - j_2| \leq j \leq j_1 + j_2$

(iii) 规范要求CG系数为实数.

$$\begin{aligned} \hat{j}_+ |jm\rangle &= \sqrt{(j-m)(j+m+1)}\, |j, m+1\rangle \\ \hat{j}_- |jm\rangle &= \sqrt{(j+m)(j-m+1)}\, |j, m-1\rangle \end{aligned}$$

e.g. $\{|j_1 m_1\rangle\}$　　$\{|j_2 = \frac{1}{2}, m_2 = \pm\frac{1}{2}\rangle\}$
轨道　　自旋

$\hat{J}_{2+} | \overset{j_2}{\tfrac{1}{2}}, \overset{m_2}{\tfrac{1}{2}}\rangle = 0$，　$|j_1 \overset{j_2}{\tfrac{1}{2}} j m\rangle = C_{-\frac{1}{2}} |j_1, \overset{m_1}{m+\tfrac{1}{2}}; \overset{j_2}{\tfrac{1}{2}}, \overset{m_2}{-\tfrac{1}{2}}\rangle + C_{\frac{1}{2}} |j_1, \overset{m_1}{m-\tfrac{1}{2}}; \overset{j_2}{\tfrac{1}{2}}, \overset{m_2}{\tfrac{1}{2}}\rangle$ ······ (1)

$\hat{j}^2 = \hat{j}_1^2 + \hat{j}_2^2 + 2\hat{j}_{1z}\hat{j}_{2z} + \hat{j}_{1+}\hat{j}_{2-} + \hat{j}_{1-}\hat{j}_{2+}$ ······ (2)

利用(1)(2)式,可得一大坨

$$\begin{cases} 左乘 \langle j_1\ m+\tfrac12;\ \tfrac12\ -\tfrac12| \\ 左乘 \langle j_1\ m-\tfrac12;\ \tfrac12,\ \tfrac12| \end{cases} \xrightarrow[\text{等价的方程}]{\text{两者得到}} j(j+1)C_{-\frac12} = \left[j_1(j_1+1)+\tfrac14-m\right]C_{-\frac12} + \sqrt{(j_1-m+\tfrac12)(j_1+m+\tfrac12)}\,C_{\frac12}$$

再辅以归一化条件 $C_{\frac12}^2 + C_{-\frac12}^2 = 1$

且有 $|j_1-\overset{\frac12}{j_2}| \le j \le j_1+\overset{\frac12}{j_2} \Rightarrow j = j_1 \pm \frac12$ 即总角动量有2种取值情况

1° 若 $j=j_1+\frac12$,则 $\begin{cases} \sqrt{j_1+m+\frac12}\,C_{-\frac12} = \sqrt{j_1-m+\frac12}\,C_{\frac12} \\ C_{-\frac12}^2 + C_{\frac12}^2 \end{cases} \Rightarrow \begin{pmatrix} C_{-\frac12} \\ C_{\frac12} \end{pmatrix} = \frac{1}{\sqrt{2j_1+1}}\begin{pmatrix} \sqrt{j_1-m+\frac12} \\ \sqrt{j_1+m+\frac12} \end{pmatrix} = \frac{1}{\sqrt{2j}}\begin{pmatrix} \sqrt{j-m} \\ \sqrt{j+m} \end{pmatrix}$

即: $|j_1\ \overset{j_2}{\tfrac12}; j\, m\rangle = \sqrt{\frac{j-m}{2j}}\,|j_1, \overset{m_1}{m+\tfrac12}; \overset{j_2}{\tfrac12}, \overset{m_2}{-\tfrac12}\rangle + \sqrt{\frac{j+m}{2j}}\,|j_1, \overset{m_1}{m-\tfrac12}; \overset{j_2}{\tfrac12}, \overset{m_2}{\tfrac12}\rangle$

2° 若 $j=j_1-\frac12$,则 $\begin{cases} \sqrt{j_1+m+\frac12}\,C_{-\frac12} = \sqrt{j_1-m+\frac12}\,C_{\frac12} \\ C_{-\frac12}^2 + C_{\frac12}^2 \end{cases} \Rightarrow \begin{pmatrix} C_{-\frac12} \\ C_{\frac12} \end{pmatrix} = \frac{1}{\sqrt{2j_1+1}}\begin{pmatrix} \sqrt{j_1+m+\frac12} \\ -\sqrt{j_1-m+\frac12} \end{pmatrix} = \frac{1}{\sqrt{2j+2}}\begin{pmatrix} \sqrt{j+m+1} \\ -\sqrt{j-m+1} \end{pmatrix}$

即: $|j_1\ \overset{j_2}{\tfrac12}; j\, m\rangle = \sqrt{\frac{j+m+1}{2j+2}}\,|j_1, \overset{m_1}{m+\tfrac12}; \overset{j_2}{\tfrac12}, \overset{m_2}{-\tfrac12}\rangle - \sqrt{\frac{j-m+1}{2j+2}}\,|j_1, \overset{m_1}{m-\tfrac12}; \overset{j_2}{\tfrac12}, \overset{m_2}{\tfrac12}\rangle$

省略写法: $\begin{cases} |l\, s\, j\, m_j\rangle = |j\, m_j\rangle \\ \hat{l} + \hat{s} = \hat{j} \end{cases}$

$|m_l m_s\rangle = |l, m_l; s, m_s\rangle$

e.g. ① $\langle j, m_j|\hat{l}_z|j, m_j\rangle$

$= \sum_{m_l m_s} \langle j\, m_j|m_l m_s\rangle\langle m_l m_s|j\, m_j\rangle m_l \hbar$

1° 如 $j = l+\frac12$

$$\langle \hat{l}_z\rangle_{j m_j} = \left(\frac{j-m_j}{2j}\right)(m_j+\tfrac12)\hbar + \left(\frac{j+m_j}{2j}\right)\cdot(m_j-\tfrac12)\hbar = \frac{2j-1}{2j}m_j\hbar$$

2° 如 $j=l-\frac12$

$$\langle \hat{l}_z\rangle_{j m_j} = \left(\frac{j+m_j+1}{2j+2}\right)(m_j+\tfrac12)\hbar + \left(\frac{j-m_j+1}{2j+2}\right)(m_j-\tfrac12)\hbar = \left(m_j + \frac{m_j}{2j+2}\right)\hbar$$

② $\langle \hat{S}_z\rangle_{j,m_j}$: $\begin{cases} j=l+\frac12 & \left(\frac{j-m_j}{2j}\right)(-\frac12)\hbar + \left(\frac{j+m_j}{2j}\right)\frac12\hbar = \frac{m_j}{2j}\hbar \\ j=l-\frac12 & \left(\frac{j+m_j+1}{2j+2}\right)(-\frac12)\hbar + \left(\frac{j-m_j+1}{2j+2}\right)\frac12\hbar = -\frac{m_j}{2j+2}\hbar \end{cases}$

更多

③ $\langle \hat{l}_z\rangle_{j m_j} + \langle \hat{S}_z\rangle_{j m_j} = m_j\hbar \ (= \langle \hat{j}\rangle_{j m_j})$ 是 $m=m_1+m_2$ 的体现

$$\langle \hat{l}_z\rangle_{j m_j} + 2\langle \hat{S}_z\rangle_{j m_j} = \begin{cases} j=l+\frac12: & \left(m_j + \frac{m_j}{2j}\right)\hbar \\ j=l-\frac12: & \left(m_j - \frac{m_j}{2j+2}\right)\hbar \end{cases}$$

e.g: 自旋-自旋耦合（He原子）

$S_1=\frac{1}{2}$, $S_2=\frac{1}{2}$，即 $S=0,1$ （由 $|S_1-S_2|\le \overset{\text{取整数}}{S} \le S_1+S_2$ 给定）

$S=0$, $|\overset{S\ m_s}{0,0}\rangle=\frac{\sqrt{2}}{2}(|\overset{m_1 m_2}{\uparrow\downarrow}\rangle-|\downarrow\uparrow\rangle)$ ～交换反对称态 spin singlet 自旋单态

费米子～电子

$S=1$, $\begin{cases}|\overset{S\ m_s}{1,1}\rangle=|\uparrow\uparrow\rangle \\ |1,0\rangle=\frac{\sqrt{2}}{2}(|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle) \\ |1,-1\rangle=|\downarrow\downarrow\rangle\end{cases}$ ～交换对称态 spin triplet 自旋三重态

玻色子

He原子电子态

全同粒子、 $\psi(\vec{r}_1\vec{r}_2)\chi_{spin}$ ～ $|\psi\rangle\otimes|S_{pin}\rangle$

空间波函数部分

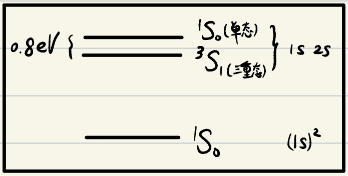
$\begin{cases}\psi(\vec{r}_1\vec{r}_2)\text{ 交换对称}, \chi_{spin}\text{ 交换反对称} \hookrightarrow \text{Singlet} \\ \quad \text{→电子平均间距近，库仑排斥能高} \\ \psi(\vec{r}_1\vec{r}_2)\text{ 交换反对称}, \chi_{spin}\text{ 交换对称} \hookrightarrow \text{triplet} \\ \quad \text{→电子平均间距远，库仑排斥能低}\end{cases}$

引入原子光谱项 $^{2S+1}L_J$ 　1s 2s

定义：对 $(\overset{n=1\ l=0}{1s})^2$ ； with $l=0,1,2$ 　s p d

$\left.\begin{array}{l}\text{考虑轨道角动量 } L：l_1 l_2\text{都零，则}L\text{只能为零}，L=0 \\ \text{考虑自旋角动量 } S：S=0,* \\ \text{最后考虑总角动量 } J：J=0,*\end{array}\right\}$ $^{2S+1}L_J \xRightarrow{\text{写作}} {}^1S_0$

对于 1s 2s ， $\left.\begin{array}{l}L=0 \\ S=0,1 \\ J=0,1\end{array}\right\} \Rightarrow {}^{2S+1}L_J \begin{cases}{}^1S_0 \\ {}^3S_1\end{cases}$



e.g: 耦合量子数

$\hat{\vec{L}}+\hat{\vec{S}}=\hat{\vec{J}}$ 　如 $\begin{cases}L=1 \\ S=\frac{1}{2}\end{cases}$ 　$J=\frac{1}{2}$ 　$m_j=\pm\frac{1}{2}$ 　2个态；$J=\frac{3}{2}$ 　$m_j=\pm\frac{3}{2}\ \pm\frac{1}{2}$ 　4个态 } 6个态

考虑电子构型 1s 2p

$\begin{cases}L=1 \\ S=0\end{cases}$ 　$J=1$ 　$m_j=\pm1,0$ 　3个态

$\begin{cases}L=1 \\ S=1\end{cases}$ 　$J=0$ 　$m_j=0$ 　1；$J=1$ 　$m_j=\pm1,0$ 　3；$J=2$ 　$m_j=\pm2,\pm1,0$ 　5

12个态 直和

非耦合表象下

1s ， $m_s=\pm\frac{1}{2}$ 　2

2p ， $\begin{cases}m_l=\pm1,0 \\ m_s=\pm\frac{1}{2}\end{cases}$ 　$3\times2=6$

$2\times6=12$ 直积

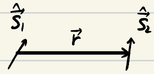
常用代换

$\hat{\vec{j}}_1\cdot\hat{\vec{j}}_2 = \frac{1}{2}(\hat{\vec{J}}^2-\hat{\vec{j}}_1^2-\hat{\vec{j}}_2^2)$ 用于 $|J,m\rangle$ 表象

$= \hat{j}_{1z}\hat{j}_{2z}+\frac{1}{2}(\hat{j}_{1-}\hat{j}_{2+}+\hat{j}_{1+}\hat{j}_{2-})$ 用于 $|m_1,m_2\rangle$ 表象

e.g. 两自旋 $\frac{1}{2}$ 粒子的张量势写做

$$\hat{V}=\frac{4}{\hbar^2}\left[\frac{3(\hat{\vec{S}}_1\cdot\vec{r})(\hat{\vec{S}}_2\cdot\vec{r})}{r^2}-\hat{\vec{S}}_1\cdot\hat{\vec{S}}_2\right]$$



$\vec{r}$ 为相对位矢，将 $\hat{V}$ 表示为 $\hat{\vec{S}}=\hat{\vec{S}}_1+\hat{\vec{S}}_2$ 与 $\vec{r}$ 的函数.

$(\hat{\vec{\sigma}}\cdot\vec{n})^2=1$

$(\hat{\vec{S}}\cdot\vec{n})^2=\frac{\hbar^2}{4}$

$\hat{S}_n \longrightarrow \frac{\hbar}{2}\begin{pmatrix}\cos\theta & \sin\theta e^{-i\varphi}\\ \sin\theta e^{i\varphi} & -\cos\theta\end{pmatrix}$

令 $\vec{n}=\frac{\vec{r}}{r}$，$\hat{S}_n=\hat{\vec{S}}\cdot\vec{n}=\hat{S}_{1n}+\hat{S}_{2n}$

$$\hat{S}_n^2=\hat{S}_{1n}^2+\hat{S}_{2n}^2+2\hat{S}_{1n}\hat{S}_{2n}=(\tfrac{1}{2}\hbar)^2+(\tfrac{1}{2}\hbar)^2+2\hat{S}_{1n}\hat{S}_{2n}=\frac{\hbar^2}{2}+2\hat{S}_{1n}\hat{S}_{2n}$$

$$\Leftrightarrow \hat{S}_{1n}\hat{S}_{2n}=\frac{\hat{S}_n^2-\frac{\hbar^2}{2}}{2}$$

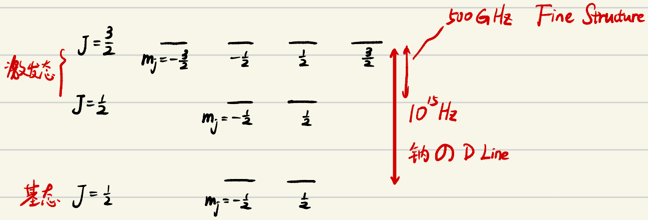
$$\hat{\vec{S}}_1\cdot\hat{\vec{S}}_2=\frac{\hat{\vec{S}}^2-\hat{\vec{S}}_1^2-\hat{\vec{S}}_2^2}{2}=\frac{1}{2}\hat{S}^2-\frac{3}{4}\hbar^2,\quad \hat{V}=\frac{1}{\hbar^2}\left[6(\hat{\vec{S}}\cdot\vec{n})^2-2\hat{S}^2\right]$$

e.g. CG系数在能级跃迁几率中的应用

碱金属 ^{23}Na

3P　$n=3$　$l=1$　$s=\frac{1}{2}$　$^2P_{\frac{1}{2}}$　$^2P_{\frac{3}{2}}$

3S　$n=3$　$l=0$　$s=\frac{1}{2}$　$^2S_{\frac{1}{2}}$



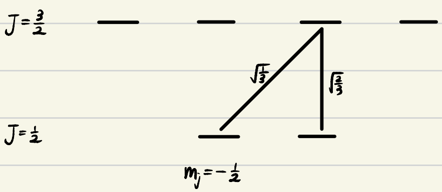
W-E 定理

$$\langle\alpha',j'm'|\hat{T}_q^{(k)}|\alpha,jm\rangle=\langle \overset{j_1 m_1}{j\,m};\overset{j_2 m_2}{k\,q}|\overset{j_1\,j_2\,j\,m}{j\,k\,j'\,m'}\rangle\frac{\langle\alpha',j'||T^{(k)}||\alpha,j\rangle}{\sqrt{2j+1}}$$

光场张量 $k=1,\ q=\pm1,0$

m,q,q' 无关

$\begin{cases} m'=m+q \\ |j-k|\le j'\le j+k \end{cases}$ 选择定则



第八章 近似方法（微扰&变分法）

1. 定态微扰论

求：$\hat{H}|\psi\rangle = E|\psi\rangle$ ？ $\hat{H} = \hat{H}_0 + \lambda\hat{V}$ ～ 微扰项

（λ：小量）

即 已知 $\hat{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle$

$$\begin{cases} |\psi_n^{(0)}\rangle \xrightarrow{\hat{V}} |\psi_n\rangle = \sum_\lambda C_\lambda |\psi_\lambda^{(0)}\rangle \\ E_n^{(0)} \xrightarrow{\hat{V}} E_n \end{cases}$$

a. 非简并微扰论

$\hat{H}|\psi_k\rangle = E_k|\psi_k\rangle$

$$\begin{cases} E_k = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots \\ |\psi_k\rangle = |\psi_k^{(0)}\rangle + \lambda|\psi_k^{(1)}\rangle + \lambda^2|\psi_k^{(2)}\rangle \end{cases} \Rightarrow (\hat{H}_0 + \lambda\hat{V})(|\psi_k^{(0)}\rangle + \lambda|\psi_k^{(1)}\rangle + \lambda^2|\psi_k^{(2)}\rangle + \cdots)$$

$$= (E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots)(|\psi_k^{(0)}\rangle + \lambda|\psi_k^{(1)}\rangle + \lambda^2|\psi_k^{(2)}\rangle + \cdots)$$

提取命出：

$$\begin{cases} \lambda\text{的0次项} & \hat{H}_0|\psi_k^{(0)}\rangle = E_k^{(0)}|\psi_k^{(0)}\rangle \\ \lambda\text{的1次项} & \hat{H}_0|\psi_k^{(1)}\rangle + \hat{V}|\psi_k^{(0)}\rangle = E_k^{(0)}|\psi_k^{(1)}\rangle + E_k^{(1)}|\psi_k^{(0)}\rangle \\ \lambda\text{的2次项} & \hat{H}_0|\psi_k^{(2)}\rangle + \hat{V}|\psi_k^{(1)}\rangle = E_k^{(0)}|\psi_k^{(2)}\rangle + E_k^{(1)}|\psi_k^{(1)}\rangle + E_k^{(2)}|\psi_k^{(0)}\rangle \end{cases}$$

一级近似解：

用 $\langle\psi_m^{(0)}|$ 作用至 λ 1次项式的两边　设 $|\psi_k^{(1)}\rangle = \sum_n C_n^{(1)}|\psi_n^{(0)}\rangle$

$$\Rightarrow E_m^{(0)}C_m^{(1)} + \underbrace{\langle\psi_m^{(0)}|\hat{V}|\psi_k^{(0)}\rangle}_{V_{mk}} = E_k^{(0)}C_m^{(1)} + E_k^{(1)}\delta_{mk}$$

$$\Rightarrow \begin{cases} m=k\text{时}, & \boxed{E_k^{(1)} = V_{kk} = \langle\psi_k^{(0)}|\hat{V}|\psi_k^{(0)}\rangle} \\ m\neq k\text{时}, & C_m^{(1)} = \dfrac{V_{mk}}{E_k^{(0)} - E_m^{(0)}} \end{cases}$$

$\Rightarrow |\psi_k\rangle \approx |\psi_k^{(0)}\rangle$　波函数0级近似

$E_k \simeq E_k^{(0)} + V_{kk}$　能量1级近似

进而：$|\psi_k\rangle \simeq |\psi_k^{(0)}\rangle + |\psi_k^{(1)}\rangle = |\psi_k^{(0)}\rangle + \boxed{\sum_{n\neq k} \dfrac{V_{nk}}{E_k^{(0)} - E_n^{(0)}}|\psi_n^{(0)}\rangle}$　波函数1级近似

① 非简并的重要性. $E_k^{(0)} \neq E_n^{(0)}$ 对所有 $n\neq k$

② $\langle\psi_k^{(0)}|\psi_k^{(1)}\rangle = 0$

二级近似解：

用 $\langle\psi_m^{(0)}|$ 作用至 λ 1次项式的两边　设 $|\psi_k^{(2)}\rangle = \sum_n C_n^{(2)}|\psi_n^{(0)}\rangle$

$$\hat{H}_0 \sum_n C_n^{(2)}|\psi_n^{(0)}\rangle + \hat{V}\sum_{n\neq k}\frac{V_{nk}}{E_k^{(0)} - E_n^{(0)}}|\psi_n^{(0)}\rangle$$

$$= E_k^{(0)}\sum_n C_n^{(2)}|\psi_n^{(0)}\rangle + V_{kk}\sum_{n\neq k}\frac{V_{nk}}{E_k^{(0)} - E_n^{(0)}}|\psi_n^{(0)}\rangle + E_k^{(2)}|\psi_k^{(0)}\rangle$$

$$\Rightarrow E_m^{(0)}C_m^{(2)} + \sum_{n\neq k}\frac{V_{mn}V_{nk}}{E_k^{(0)} - E_n^{(0)}} = E_k^{(0)}C_m^{(2)} + \frac{V_{kk}V_{mk}}{E_k^{(0)} - E_m^{(0)}}(1 - \delta_{mk}) + E_k^{(2)}\delta_{mk}$$

$$\boxed{\Rightarrow E_k^{(2)} = \sum_{m\neq k}\frac{|V_{mk}|^2}{E_k^{(0)} - E_m^{(0)}}}$$

讨论：(i) 正交归一完备性

(ii) 矩阵图像

e.g. $\hat H = \underbrace{\frac{\hat p^2}{2m} + \frac12 m\omega^2\hat x^2}_{\hat H_0} + \underbrace{\varepsilon \frac12 m\omega^2 \hat x^2}_{\hat V}$ $(\varepsilon \ll 1)$，求问二阶修正？

$$\begin{cases} E_n^{(0)} = (n+\frac12)\hbar\omega \quad |n\rangle \\ E_n = E_n^{(0)} + \langle n|\hat V|n\rangle + \sum\limits_{k\neq n}\frac{|V_{nk}|^2}{E_n^{(0)}-E_k^{(0)}} \end{cases}$$

由 $\hat x^2 = \frac{\hbar}{2m\omega}(\hat a^2 + \hat a^{\dagger 2} + \hat a\hat a^\dagger + \hat a^\dagger \hat a)$，则 $\langle m|\hat x^2|n\rangle = \frac{\hbar^2}{2m\omega}\left[\sqrt{n(n-1)}\,\delta_{m,n-2} + \sqrt{(n+1)(n+2)}\,\delta_{m,n+2} + (2n+1)\,\delta_{mn}\right]$

即 $V_{nn} = \frac14(2n+1)\hbar\omega\varepsilon$，$V_{nk} = \frac14\hbar\omega\varepsilon\left(\sqrt{n(n-1)}\,\delta_{k,n-2} + \sqrt{(n+1)(n+2)}\,\delta_{k,n+2}\right)$ $(k\neq n)$

$$\Rightarrow E_n \simeq (n+\tfrac12)\hbar\omega + \tfrac14(2n+1)\hbar\omega\varepsilon + \frac{\frac1{16}\hbar^2\omega^2\varepsilon^2}{-2\hbar\omega}(n+2)(n+1) + \frac{\frac1{16}\hbar^2\omega^2\varepsilon^2}{2\hbar\omega}n(n-1)$$

$$|\psi_n\rangle \simeq |n\rangle + \frac18\varepsilon\Big[\underbrace{\sqrt{n(n-2)}}_{n\geq 2}|n-2\rangle - \sqrt{(n+1)(n+2)}\,|n+2\rangle\Big] + O(\varepsilon^2)$$

对 $n=0$，$E_0 = \frac12\hbar\omega + \frac14\hbar\omega\varepsilon - \frac1{16}\hbar\omega\varepsilon^2$

$|\psi_0\rangle = |0\rangle - \frac{\sqrt2}{8}\varepsilon|2\rangle$

而精确解为

$E = (n+\frac12)\sqrt{1+\varepsilon}\,\hbar\omega = (n+\frac12)\hbar\omega\left(1+\frac12\varepsilon - \frac18\varepsilon^2+\cdots\right)$

b. 简并微扰论

$\hat H = \hat H_0 + \hat V$ 其中 $\hat H_0$ 的本征态为 $\{|\psi_{m\mu}^{(0)}\rangle, |\psi_n^{(0)}\rangle\}$ $\quad m\neq n$

$m;\mu = 1,2,3,\cdots; g$，标定了一个 g 重简并子空间.

$$\begin{cases} \hat H_0|\psi_{m\mu}^{(0)}\rangle = E_m^{(0)}|\psi_{m\mu}^{(0)}\rangle \\ \hat H_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle \end{cases}$$

① 一般方法：设 $|\psi\rangle = |\psi^{(0)}\rangle + \lambda|\psi^{(1)}\rangle$ $\quad E_m = E_m^{(0)} + E_m^{(1)}$

且 $\begin{cases} |\psi^{(1)}\rangle \text{ 与整个简并子空间正交} \\ |\psi^{(0)}\rangle \text{ 可以用 } \{|\psi_{m\mu}^{(0)}\rangle\} \text{ 展开} \end{cases}$

$\hat H|\psi\rangle = E_m|\psi\rangle$ 的 λ 一次 $|\psi^{(0)}\rangle$ 表达式为：

$$\hat H_0|\psi^{(1)}\rangle + \hat V\sum_\mu C_{m\mu}^{(0)}|\psi_{m\mu}^{(0)}\rangle = E_m^{(0)}|\psi^{(1)}\rangle + E_m^{(1)}\sum_\mu C_{m\mu}^{(0)}|\psi_{m\mu}^{(0)}\rangle$$

左乘 $\langle\psi_{m\nu}^{(0)}|$，有

即在 $\{|\psi_{m\mu}^{(0)}\rangle\}$ 为基的简并子空间内对角化 $\hat{V}$ 的矩阵

$\begin{cases} \text{本征态：简并子空间内新的 0 级波函数} \\ \text{本征值：能量的 1 级修正} \end{cases}$

即
$$\begin{vmatrix} V_{11}-E_n^{(1)} & V_{12} & \cdots & V_{1g} \\ V_{21} & V_{22}-E_n^{(1)} & \cdots & V_{2g} \\ \vdots & \vdots & \ddots & \vdots \\ V_{g1} & V_{g2} & \cdots & V_{gg}-E_n^{(1)} \end{vmatrix} = 0$$

g 为 $E_n^{(0)}$ 的简并度，$\Rightarrow E_{n,i}^{(1)}$ $i=1,2,\cdots,g$

② Practical Methods

1. 寻找算符 $\hat{A}$，使 $[\hat{A},\hat{H}_0]=0$，$[\hat{A},\hat{V}]=0$；$\{\hat{A},\hat{H}_0\}$ 的共同本征态在 $\hat{H}_0$ 的简并子空间无简并.

 则这些本征态是合适的 0 级波函数 $\Rightarrow$ $\hat{V}$ 在这些本征态下对角

 $$\langle\psi_m|\hat{A}\hat{V}-\hat{V}\hat{A}|\psi_n\rangle=0=(A_m-A_n)V_{mn} \Rightarrow V_{mn}=\delta_{mn}V_{nn}$$

e.g.: (Anomalous Zeeman Effect)

考虑 ^{23}Na 原子 $n=3$ 时

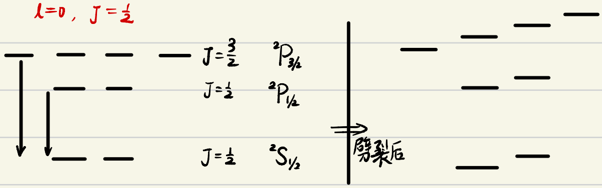
$3p'$ $m_l=\pm1,0$ — — — $l=1$

$3s'$ $m_l=0$ — $l=0$

- 外加磁场，when $B=0$，不变；else if $B\neq0$，3个简并能级分立开来.

- 假设我们不知道 Spin，则三态简并
- 考虑 $s=\frac{1}{2}$，$l=1$，$J=\frac{1}{2},\frac{3}{2}$
  $l=0$，$J=\frac{1}{2}$

$\sim A\hat{\vec{L}}\cdot\hat{\vec{S}}$



下面展示具体运算.

$$\hat{H}= \underbrace{\quad}_{\text{背景项无关心}} A\hat{\vec{L}}\cdot\hat{\vec{S}}+B(\hat{L}_z+2\hat{S}_z)$$ z方向为量子化方向，人为定义

考虑如下情况 (i) $A\gg B$ 强耦合极限
(ii) $A\ll B$ 弱耦合极限

(i) $A\gg B$ 时，$\hat{H}_0=A\hat{\vec{L}}\cdot\hat{\vec{S}}$，$\hat{V}=B(\hat{L}_z+2\hat{S}_z)$

 开始解 $\hat{H}_0$ 的本征问题

 利用 $\hat{\vec{J}}=\hat{\vec{L}}+\hat{\vec{S}}$，$\hat{\vec{L}}\cdot\hat{\vec{S}}=\frac{1}{2}(\hat{\vec{J}}^2-\hat{\vec{L}}^2-\hat{\vec{S}}^2)$ 可知 $[\hat{\vec{J}}^2,\hat{H}_0]=0$，$[\hat{J}_z,\hat{H}_0]=0$

引入 $\{|j m_j\rangle\}$. $E_0=\langle j m_j|A\hat{\vec{L}}\cdot\hat{\vec{S}}|j m_j\rangle=\frac{A}{2}\left[j(j+1)\hbar^2-l(l+1)\hbar^2-s(s+1)\hbar^2\right]$

with $\begin{cases} s=\frac{1}{2},\quad j=l+\frac{1}{2}\Rightarrow E_0=\frac{A}{2}l\hbar^2 \\ s=\frac{1}{2},\quad j=l-\frac{1}{2}\Rightarrow E_0=-\frac{A}{2}(l+1)\hbar^2 \end{cases}$ 这里l取1 OR 0.

H_0的矩阵：

$$\begin{array}{r} j=l-\frac{1}{2} \\ (2j+1=2l\text{ 维}) \\ \text{共 }4l+2\text{ 维} \\ j=l+\frac{1}{2} \\ (2j+1=2l+2\text{ 维}) \end{array}
\begin{bmatrix} \begin{pmatrix} -\frac{A}{2}(l+1)\hbar^2 & & \\ & \ddots & \\ & & -\frac{A}{2}(l+1)\hbar^2 \end{pmatrix} & 0 \\ 0 & \begin{pmatrix} \frac{A}{2}l\hbar^2 & & \\ & \ddots & \\ & & \frac{A}{2}l\hbar^2 \end{pmatrix} \end{bmatrix}$$

$\hat{V}$的矩阵元：

要用到CG系数了!

$$\langle j'm_j'|\hat{V}|j m_j\rangle=B\langle j'm_j'|\hat{L}_z|j m_j\rangle+2B\langle j'm_j'|\hat{S}_z|j m_j\rangle$$

$$=B\delta_{jj'}\delta_{m_j m_j'}m_j\hbar+2B\langle j'm_j'|\hat{S}_z|j m_j\rangle$$

• 同一个j值子空间内，求对角元

$$\begin{cases} j=l+\frac{1}{2} & \langle j m_j|\hat{S}_z|j m_j\rangle=\left[\frac{\hbar}{2}\frac{j+m_j}{2j}+\left(-\frac{\hbar}{2}\right)\frac{j-m_j}{2j}\right]\delta_{m_j' m_j}=\frac{m_j}{2j}\hbar\,\delta_{m_j m_j'} \\ j=l-\frac{1}{2} & \langle j m_j|\hat{S}_z|j m_j\rangle=\left[\frac{\hbar}{2}\frac{j-m_j+1}{2j+2}+\left(-\frac{\hbar}{2}\right)\frac{j+m_j+1}{2j+2}\right]\delta_{m_j m_j'}=-\frac{m_j}{2(j+1)}\hbar\,\delta_{m_j m_j'} \end{cases}$$

• 对于非对角元.(对二阶能量修正有贡献)

正交

$$\langle j'm_j'|\hat{S}_z|j m_j\rangle=\left(\langle m_j'+\tfrac{1}{2},-\tfrac{1}{2}|\sqrt{\frac{j'+m_j'+1}{2j'+2}}-\langle m_j'-\tfrac{1}{2},\tfrac{1}{2}|\sqrt{\frac{j'-m_j'+1}{2j'+2}}\right)\hat{S}_z\left(\sqrt{\frac{j-m_j}{2j}}|m_j+\tfrac{1}{2},-\tfrac{1}{2}\rangle-\sqrt{\frac{j+m_j}{2j}}|m_j-\tfrac{1}{2},\tfrac{1}{2}\rangle\right)$$

$$=\left(-\frac{1}{2}\hbar\sqrt{\frac{j'+m_j+1}{2j'+2}}\sqrt{\frac{j-m_j}{2j}}-\frac{1}{2}\hbar\sqrt{\frac{j'-m_j+1}{2j'+2}}\sqrt{\frac{j+m_j}{2j}}\right)\delta_{j,j'+1}\,\delta_{m_j m_j'}$$

故简并微扰 一级修正为

$$E_1=\langle j m_j|\hat{V}|j m_j\rangle=B m_j\hbar+2B\langle j m_j|\hat{S}_z|j m_j\rangle$$

$$\Rightarrow\begin{cases} j=l+\frac{1}{2} & E_0+E_1=\frac{A}{2}l\hbar^2+B\left(\frac{m_j}{2j}+m_j\right)\hbar \\ j=l-\frac{1}{2} & E_0+E_1=-\frac{A}{2}(l+1)\hbar+B\left(m_j-\frac{m_j}{2(j+1)}\right)\hbar \end{cases}$$

→ 弄出4个能级

→ 弄出2个能级

(取j=1)

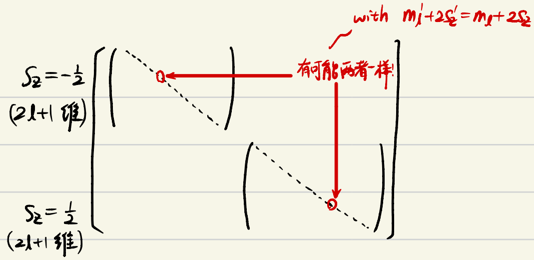
(ii) $A\ll B$

$\hat{H}_0=B(\hat{L}_z+2\hat{S}_z)\qquad \hat{V}=A\hat{\vec{L}}\cdot\hat{\vec{S}}$

自然而然选地非耦合表象基(作为零级波函数) $\{|m_l\, s_z\rangle\}$

$E_0=\langle m_l s_z|\hat{H}_0|m_l s_z\rangle = B(m_l+2s_z)\hbar$

即 $\hat{H}_0$ 的矩阵元如右：



计算 $\hat{V}$ 的矩阵元 $\langle\hat{V}\rangle$：

$$\langle m_l' s_z'|\hat{L}\cdot\hat{S}|m_l s_z\rangle$$
$$=\langle m_l' s_z'|\hat{L}_z\hat{S}_z+\tfrac{1}{2}(\hat{L}_+\hat{S}_-+\hat{L}_-\hat{S}_+)|m_l s_z\rangle$$
$$=m_l s_z\hbar^2\delta_{m_l m_l'}\delta_{s_z s_z'}+C_1\,\delta_{s_z',s_z-1}\delta_{m_l',m_l+1}+C_2\,\delta_{s_z',s_z+1}\delta_{m_l',m_l-1}$$

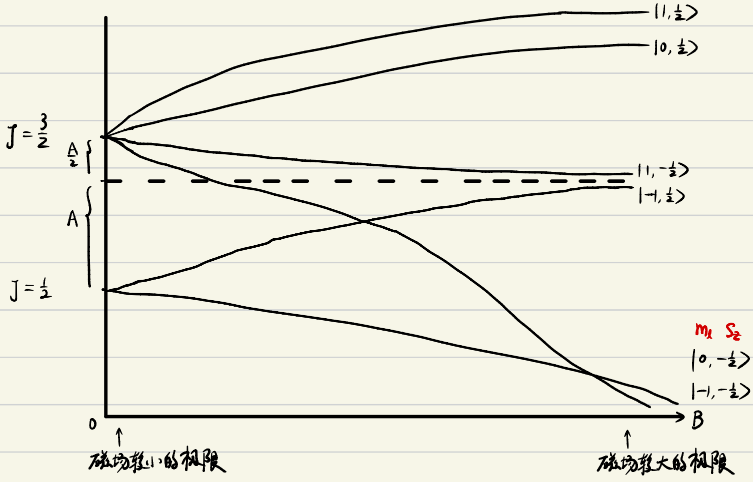
非对角元：$s_z'+m_l'=s_z+m_l$

问题就化为了非简并微扰！

能量的一级修正 $E_1=\langle m_l s_z|A\hat{L}\cdot\hat{S}|m_l s_z\rangle=\langle m_l' s_z'|\hat{L}_z\hat{S}_z+\frac{1}{2}(\hat{L}_+\hat{S}_-+\hat{L}_-\hat{S}_+)|m_l s_z\rangle$

$= A\hbar^2 m_l s_z$

thus $E=E_0+E_1=B(m_l+2s_z)\hbar+A\hbar^2 m_l s_z$



e.g.: (Toy Model) 自旋½的三维各向同性谐振子处于基态

耦合

求在微扰 $\hat{V} = \lambda \hat{\sigma}_x \hat{y}^2$ 作用下的基态能量，精确到二阶.

翻转自旋

$$|000\uparrow\rangle \quad |000\downarrow\rangle \quad \Rightarrow |020\uparrow\rangle \quad |020\downarrow\rangle$$

$$y^2 = \frac{\hbar}{2m\omega}\left(\hat{a}^2 + \hat{a}^{\dagger 2} + 2\hat{a}^\dagger\hat{a} + 1\right)$$

$$\begin{array}{c} \langle 000\uparrow| \\ \langle 000\downarrow| \\ \langle 020\uparrow| \\ \langle 020\downarrow| \end{array} \begin{bmatrix} \frac{3}{2}\hbar\omega & \frac{\hbar}{2m\omega}\lambda & 0 & \frac{\sqrt{2}\hbar}{2m\omega}\lambda \\ \frac{\hbar}{2m\omega}\lambda & \frac{3}{2}\hbar\omega & \frac{\sqrt{2}\hbar}{2m\omega}\lambda & 0 \\ 0 & \frac{\sqrt{2}\hbar}{2m\omega}\lambda & \frac{7}{2}\hbar\omega & \frac{5}{2}\hbar\omega\lambda \\ \frac{\sqrt{2}\hbar}{2m\omega}\lambda & 0 & \frac{5}{2}\hbar\omega\lambda & \frac{7}{2}\hbar\omega \end{bmatrix}$$

Step 1：对角化

一阶（简并微扰） $\frac{3}{2}\hbar\omega \pm \frac{\hbar}{2m\omega}\lambda$

二阶 ⊗ for: $\frac{3}{2}\hbar\omega - \frac{\hbar}{2m\omega}\lambda \Rightarrow |\psi^{(0)}\rangle = \frac{\sqrt{2}}{2}\left(|000\uparrow\rangle - |000\downarrow\rangle\right)$

$$E_2 = \frac{|\langle 020\uparrow|\hat{V}|\psi^{(0)}\rangle|^2 + |\langle 020\downarrow|\hat{V}|\psi^{(0)}\rangle|^2}{\frac{3}{2}\hbar\omega - \frac{7}{2}\hbar\omega} = -\frac{\hbar\lambda^2}{4m^2\omega^3}$$

Intro：近简并微扰论

$$\hat{H} = \begin{pmatrix} a & c \\ c & b \end{pmatrix}$$

with $c \ll a, b$

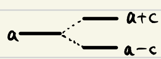
微扰问题其实就是求 $\hat{H}$ 的本征问题，解析地有

$$\frac{a+b}{2} \pm \frac{\sqrt{(a-b)^2 + 4c^2}}{2} \xRightarrow{|c| \ll |a-b|} \begin{cases} a - \frac{c^2}{a-b} \\ b - \frac{c^2}{b-a} \end{cases}$$

$\Rightarrow$

能级的排斥

同样地，$\begin{pmatrix} a & c \\ c & a \end{pmatrix}$



③ 如 $\hat{V}$ 不能消除简并，则需找到合适的零级波函数

$$|\psi\rangle = |\psi^{(0)}\rangle + |\psi^{(1)}\rangle + |\psi^{(2)}\rangle + \cdots$$

用n作标记

并要求
$$\begin{cases} |\psi^{(0)}\rangle = \sum_\mu C_{m\mu}^{(0)} |\psi_{m\mu}^{(0)}\rangle & \text{简并子空间之内} \\ |\psi^{(1)}\rangle = \sum_{n\neq m} C_n^{(1)} |\psi_n^{(0)}\rangle & \text{简并子空间之外} \\ |\psi^{(2)}\rangle = \sum_{n\neq m} C_n^{(2)} |\psi_n^{(0)}\rangle \end{cases}$$

$$\Rightarrow \begin{cases} O(\lambda): \ (\hat{H}_0 - E_m^{(0)})|\psi^{(1)}\rangle = (E_m^{(1)} - \hat{V})|\psi^{(0)}\rangle \\ O(\lambda^2): \ (\hat{H}_0 - E_m^{(0)})|\psi^{(2)}\rangle = (E_m^{(1)} - \hat{V})|\psi^{(1)}\rangle + E_m^{(2)}|\psi^{(0)}\rangle \end{cases}$$

$\langle \psi_{m\nu}^{(0)}|$ 左乘 $O(\lambda)$： $\sum_\mu \left[V_{m\nu, m\mu} - \delta_{m\mu, m\nu} E_m^{(1)}\right] C_{m\mu}^{(0)} = 0$

如 $V_{m\mu, m\nu}$ 为对角阵，且对角元不相同，则 $|\psi^{(0)}\rangle$ 已为合适的波函数

否则，如 $V_{m\mu,m\nu}$ 为对角阵，且对角元相同，则能级在一级近似下仍简并

接着，$\langle\psi_{m\nu}^{(0)}|$ 左乘 $O(\lambda^2)$：$E_m^{(2)}C_{m\nu}^{(0)}=\sum_{n\neq m}V_{m\nu,n}C_n^{(1)}$

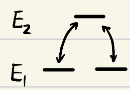
$\langle\psi_n^{(0)}|$ 左乘 $O(\lambda)$：$(E_n^{(0)}-E_m^{(0)})C_n^{(1)}=-\sum_\mu V_{n,m\mu}C_{m\mu}^{(0)} \Rightarrow C_n^{(1)}=\sum_\mu\frac{V_{n,m\mu}}{E_m^{(0)}-E_n^{(0)}}C_{m\mu}^{(0)}$

上两式联立消 $C_n^{(1)}$ 有

$$\sum_\mu\left[\sum_{n\neq m}\frac{V_{m\nu,n}V_{n,m\mu}}{E_m^{(0)}-E_n^{(0)}}-E_m^{(2)}\delta_{m\mu,m\nu}\right]C_{m\mu}^{(0)}=0$$

该矩阵的本征方程决定 $C_{m\mu}^{(0)}$，通过久期方程可求出 $E_{m i}^{(2)}$，$i=1,2,\cdots,g$，(g为简并度)

e.g: $H=H_0+V=\begin{pmatrix}E_1&0&a\\0&E_1&b\\a&b&E_2\end{pmatrix}$ with $|a|,|b|\ll|E_1|,|E_2|,|E_1-E_2|$



取1,2

$$\sum_{n\neq m}\frac{V_{m\nu,n}V_{n,m\mu}}{E_m^{(0)}-E_n^{(0)}}\Rightarrow\begin{pmatrix}\frac{a^2}{E_1-E_2}&\frac{ab}{E_1-E_2}\\\frac{ab}{E_1-E_2}&\frac{b^2}{E_1-E_2}\end{pmatrix}\xRightarrow{\text{对角化}}E_1^{(2)}=0,\ \frac{a^2+b^2}{E_2-E_1}\quad\text{thus}\begin{cases}E_a=E_1\\E_b=E_1+\frac{a^2+b^2}{E_2-E_1}\\E_c=E_2\end{cases}$$

这才更精确!!!

C. 微扰论在氢原子中的应用

零级近似 $\hat{H}_0=-\frac{\hbar^2}{2m}\nabla^2+V(r)\xRightarrow{\text{解析解}}|n\,l\,m\rangle$ $E_n=-\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2}$ 有 n^2 重简并

轨道角动量量子数

主量子数

$$g=\sum_{l=0}^{n-1}(2l+1)=n^2$$

考虑自旋后为 $2n^2$

① Fine Structure

(i) SR 修正 $T=\frac{p^2}{2m}\Leftrightarrow T_{SR}=\sqrt{p^2c^2+m^2c^4}-mc^2\simeq\frac{p^2}{2m}-\frac{p^4}{8m^3c^2}$

量子化 $\hat{V}=-\frac{\hat{p}^4}{8m^3c^2}$ with $[\hat{p}^4,\hat{l}^2]=0$，$[\hat{p}^4,\hat{l}_z]=0$ $\{\hat{l}^2,\hat{l}_z\}$ $|n\,l\,m\rangle$

一级修正

$$E_r=\langle nlm|\hat{V}|nlm\rangle=-\frac{E_n^2}{2mc^2}\left(\frac{4n}{l+\frac{1}{2}}-3\right)$$

已经和角动量有关了，一定程度上破除了简并

(ii) 自旋-轨道耦合

$\hat{H}_{so}=\frac{e^2}{8\pi\varepsilon_0}\frac{1}{m^2}\frac{1}{c^2r^3}\hat{\vec{S}}\cdot\hat{\vec{L}}$ with $[\hat{H}_{so},\hat{L}^2]=0$，$[\hat{H}_{so},\hat{S}^2]=0$

but $[\hat{H}_{so},\hat{L}_z]\neq0$，$[\hat{H}_{so},\hat{S}_z]\neq0$

定义 $\hat{\vec{J}}=\hat{\vec{L}}+\hat{\vec{S}}$，则 $[\hat{H}_{so},\hat{J}^2]=[\hat{H}_{so},\hat{J}_z]=[\hat{H}_0,\hat{J}^2]=[\hat{H}_0,\hat{J}_z]=0$

$\Rightarrow$ 基 $|n\,l\,s\,j\,m_j\rangle$

由而 $E_{so} = \langle n l s j m_j | \hat{H}_{so} | n l s j m_j \rangle = \frac{E_n^2}{mc^2}\left\{ \frac{n[j(j+1) - l(l+1) - \frac{3}{4}]}{l(l+\frac{1}{2})(l+1)} \right\}$ $\Big) \hat{J}^2 - \hat{L}^2 - \hat{S}^2$

得到 Fine Structure

$$E_{nj} = E_n + \frac{E_n^2}{2mc^2}\left(3 - \frac{4n}{j+\frac{1}{2}}\right) = -\frac{13.6\,\mathrm{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$ with $\underline{\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} = \frac{1}{137}}$ <u>Fine Structure Constant</u>

② Zeeman Effect

③ Hipper Fine Structure

考虑核自旋与电子轨道/自旋的相互作用

$$\hat{H}_{hf} = \hat{A}\frac{1}{r^3}\left[3(\hat{\vec{I}}\cdot\vec{e}_r)(\hat{\vec{S}}\cdot\vec{e}_r) - \hat{\vec{I}}\cdot\hat{\vec{S}}\right] + \frac{8\pi}{3}\hat{A}\,\hat{\vec{I}}\cdot\hat{\vec{S}}\,\delta(\vec{r}) + \hat{B}(r)\,\hat{\vec{I}}\cdot\hat{\vec{L}}$$

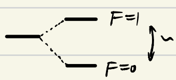
$\sim A\,\hat{\vec{I}}\cdot\hat{\vec{J}}$ ← 只考虑此项

对 $l=0$ 的态(基态) $\hat{H}_{hf} = A\,\hat{\vec{I}}\cdot\hat{\vec{S}}$ 定义 $\overset{\text{Coupling}}{\hat{\vec{F}}} = \hat{\vec{I}} + \hat{\vec{L}} + \hat{\vec{S}}$, with $[\hat{F}^2, \hat{H}_{hf}] = [\hat{F}_z, \hat{H}_{hf}] = 0$

由而得基 $|n l s j I \underline{F m_F}\rangle$

$l=0,\ s=\frac{1}{2},\ I=\frac{1}{2} \xRightarrow{\text{Coupling}} \underline{J=\frac{1}{2}},\ I=\frac{1}{2} \xRightarrow{\text{Coupling}} F=0,1$

$$E_{hf} = \langle F m_F | \hat{H}_{hf} | F m_F \rangle = \frac{1}{2}A\hbar^2[F(F+1) - I(I+1) - S(S+1)] = \begin{cases} \frac{1}{4}A\hbar^2 & F=1 \\ -\frac{3}{4}A\hbar^2 & F=0 \end{cases}$$

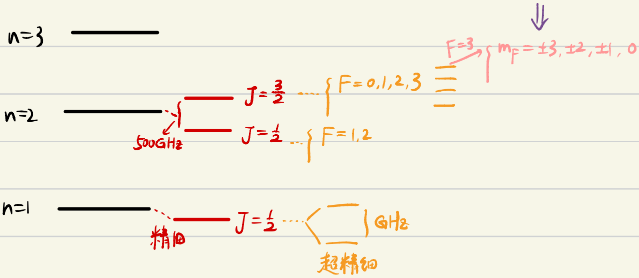
亦即 

, $\lambda = 21\,\mathrm{cm}$

宇宙射线中量常见波长，表明存在大量H.

^{23}Na 一类氢原子 $I = \frac{3}{2}$

加个磁场, Zeeman Effect



2. 变分法

对于给定 $\hat{H}$ 和任意态 $|\psi\rangle$，均有如下关系

$$\langle\psi|\hat{H}|\psi\rangle \geq E_{gs}, \quad \hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

Prove: $|\psi\rangle = \sum C_n|\psi_n\rangle$, $\langle\hat{H}\rangle_\psi = \sum|C_n|^2E_n \geq E_{gs}\underbrace{\sum_n|C_n|^2}_{=1}$

应用：猜基态形式，把求解基态的问题转化为最优化问题 $|\psi(\alpha_n)\rangle$，其中 $\{\alpha_n\}$ 称为变分参数。

BCS 理论

$$E(\alpha_n) = \frac{\langle\psi(\alpha_n)|\hat{H}|\psi(\alpha_n)\rangle}{\langle\psi(\alpha_n)|\psi(\alpha_n)\rangle}$$

由 $\frac{\partial E}{\partial \alpha_n} = 0$，求得 $\{\alpha_n\}$ 及 $E(\alpha_n)$

期望值的极值

e.g. He 原子基态

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1}+\frac{2}{r_2}-\frac{1}{|\vec{r}_1-\vec{r}_2|}\right)$$ ← Born-Oppenheimer 近似

回顾 H 原子基态 $\langle\vec{r}|\overset{1}{n}\,\overset{0}{l}\,\overset{0}{m}\rangle = \frac{1}{\sqrt{\pi a^3}}e^{-r/a}$ ← a 为 Bohr 半径

试探波函数猜成 $\psi(\vec{r}_1,\vec{r}_2) = \frac{Z^3}{\pi a^3}e^{-Z(r_1+r_2)/a}$　　Ze 电量！

于是整理成

$$H = \underbrace{-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{z}{r_1}+\frac{z}{r_2}\right)}_{H_0} + \underbrace{\frac{e^2}{4\pi\varepsilon_0}\left(\frac{z-2}{r_1}+\frac{z-2}{r_2}\right)}_{H_1} + \underbrace{\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1-\vec{r}_2|}}_{V}$$

$$\begin{cases} \langle H_0\rangle_\psi = 2Z^2E_1 & \text{其中 } E_1 = \frac{e^2}{4\pi\varepsilon_0 a} \sim 13.6\,eV \\ \langle H_1\rangle_\psi = 2(z-2)\frac{e^2}{4\pi\varepsilon_0}\frac{z}{a} \\ \langle V\rangle_\psi = -\frac{5}{4}zE_1 \end{cases}$$

组装得到 $\langle H\rangle_\psi = (-2z^2+\frac{27}{4}z)E_1$，求其期望最小值

$$\frac{d\langle H\rangle_\psi}{dz} = 0 \Rightarrow z = \frac{27}{16} \sim 1.69$$ 比 2 小一点的正电荷

此刻 $\langle H\rangle_\psi = -77.5\,eV$（实验：$-78.795\,eV$）

3. 含时微扰

a. 设 $\hat{H} = \hat{H}_0 + \hat{V}(t)$

概率幅在变，这样才能发生跃迁

$$\hat{H}_0|\psi_n\rangle = E_n|\psi_n\rangle \qquad |\psi(t)\rangle = \sum_n C_n(t)|\psi_n\rangle$$

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle \Rightarrow i\hbar\frac{d}{dt}\left(\sum C_n(t)|\psi_n\rangle\right) = (\hat{H}_0+\hat{V})\sum C_n(t)|\psi_n\rangle$$

$$\xrightarrow{\text{左乘}\langle\psi_m|} i\hbar\frac{d}{dt}C_m(t) = E_m C_m(t) + \sum_n V_{mn}(t)\, C_n(t) \quad \text{-------} \quad (1)$$

先做变换 $\tilde{C}_m(t) = e^{iE_m t/\hbar}\, C_m(t)$ (相当于选了一个特定的 Rotating Frame)，两边求导可得

$$i\hbar\frac{d}{dt}\tilde{C}_m(t) = -E_m\tilde{C}_m(t) + e^{-iE_m t/\hbar}\left[i\hbar\frac{d}{dt}C_m(t)\right] \quad \text{-----------} \quad (2)$$

(1)代入(2)可知　　各项吸收进入

$$\Rightarrow i\hbar\frac{d}{dt}\tilde{C}_m(t) = -E_m\tilde{C}_m(t) + E_m e^{iE_m t/\hbar}C_m(t) + \sum_n V_{mn}(t)\, e^{iE_m t/\hbar} e^{-iE_n t/\hbar}\tilde{C}_n(t)$$

$$\Rightarrow i\hbar\frac{d}{dt}\tilde{C}_m(t) = \sum_n V_{mn}(t)\, e^{i(E_m-E_n)t/\hbar}\tilde{C}_n(t) \qquad \text{记 } \omega_{mn} = \frac{E_m-E_n}{\hbar}$$

$$i\hbar\frac{d}{dt}\begin{pmatrix}\tilde{C}_1\\ \tilde{C}_2\\ \vdots\\ \tilde{C}_n\end{pmatrix} = \begin{pmatrix} & & \\ & V_{mn} & \\ & & \end{pmatrix}\begin{pmatrix}\tilde{C}_1\\ \tilde{C}_2\\ \vdots\\ \tilde{C}_n\end{pmatrix}$$

之后只需迭代微扰
- i) 设 $t=0$ 时初态为零级近似
- ii) 把零级近似代入上式右边 $\xrightarrow{\text{积分}}$ 一级修正
- iii) …… $\xrightarrow{\text{积分}}$ 二级修正

e.g. 二能级系统

$$\begin{cases} i\hbar\frac{d}{dt}\tilde{C}_b = V_{bb}\tilde{C}_b + V_{ba}e^{i\omega_{mn}t}\tilde{C}_a \\ i\hbar\frac{d}{dt}\tilde{C}_a = V_{aa}\tilde{C}_a + V_{ab}e^{i\omega_{mn}t}\tilde{C}_b \end{cases}$$

设 $\tilde{C}_a(0)=1$, $\tilde{C}_b(0)=0$. (零级)

$$\begin{cases} i\hbar\frac{d}{dt}\tilde{C}_a^{(1)} = V_{aa} \\ i\hbar\frac{d}{dt}\tilde{C}_b^{(1)} = V_{ba}e^{i\omega_{ba}t} \end{cases} \Rightarrow \begin{cases} \tilde{C}_a^{(1)} = -\frac{i}{\hbar}\int_0^t V_{aa}(t')\,dt' \\ \tilde{C}_b^{(1)} = -\frac{i}{\hbar}\int_0^t V_{ba}(t')\,e^{i\omega_{mn}t'}dt' \end{cases} \quad (\text{一级})$$

故

$$\begin{cases} \tilde{C}_a = 1 - \frac{i}{\hbar}\int_0^t V_{aa}(t')\,dt' \\ \tilde{C}_b = -\frac{i}{\hbar}\int_0^t V_{ba}(t')\,e^{i\omega_{mn}t'}dt' \end{cases} \qquad \text{with } |\tilde{C}_a|^2 + |\tilde{C}_b|^2 = 1 + O(V^2)$$

b. 跃迁

设初态为某 k 态，则零级近似为 $\tilde{C}_n^{(0)} = \delta_{nk}$

$$i\hbar\frac{d}{dt}\tilde{C}_m = \sum_n V_{mn}\,e^{i\omega_{mn}t}\tilde{C}_n$$

一级含时微扰为 $i\hbar\frac{d}{dt}\tilde{C}_m^{(1)} = V_{mk}e^{i\omega_{mk}t} \Rightarrow C_m^{(1)} = -\frac{i}{\hbar}\int_0^t V_{mk}(t')\,e^{i\omega_{mk}t'}dt'$

$$\Rightarrow \tilde{C}_m \simeq \delta_{mk} - \frac{i}{\hbar}\int_0^t V_{mk}(t')\,e^{i\omega_{mk}t'}dt'$$

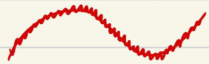
对于 $m\neq k$ 的态，定义跃迁概率为

$$P_{k\to m}(t)=\frac{1}{\hbar^2}\left|\int_0^t V_{mk}(t')e^{i\omega_{mk}t'}dt'\right|^2$$

e.g. 光场与二能级原子的耦合

$|b\rangle$

$|a\rangle$



(旋波近似)

RWA近似

$$V(t)=V(\vec r)\left(e^{i\omega t}+e^{-i\omega t}\right)\qquad E_b-E_a=\hbar\omega_0$$

$$V_{aa}=V_{bb}=0\ ,\quad V_{ab}=\langle a|\hat V(\vec r)|b\rangle$$

(i) 一级修正解

初态 $|a\rangle$，$\tilde C_b(t)=-\frac{i}{\hbar}\int_0^t V_{ba}\left(e^{i\omega t'}+e^{-i\omega t'}\right)e^{i\omega_0 t'}dt'$ $\xlongequal{\text{积分得到}}$ $-\frac{V_{ba}}{\hbar}\left[\underbrace{\frac{e^{i(\omega_0+\omega)t}-1}{\omega_0+\omega}}_{\text{快变项，可省去}}+\underbrace{\frac{e^{i(\omega_0-\omega)t}-1}{\omega_0-\omega}}_{\text{慢变项}}\right]$

$P_{a\to b}(t)=|\tilde C_b|^2$, with $|V_{ba}|\ll\hbar\omega_0,\hbar\omega$, $\hbar(\omega_0-\omega)\ll|V_{ab}|\to\omega_0\sim\omega$ (近共振条件)

利用RWA，可得 $\tilde C_b(t)\approx-\frac{V_{ba}}{\hbar}e^{i(\omega_0-\omega)t/2}\left|\frac{1}{\omega_0-\omega}2i\sin[(\omega_0-\omega)t/2]\right|$

即 $P_{a\to b}(t)\approx\frac{4|V_{ab}|^2}{\hbar^2}\frac{\sin^2\left[\frac{(\omega-\omega_0)t}{2}\right]}{(\omega-\omega_0)^2}$

$$\xlongequal{t\to\infty}\frac{2\pi}{\hbar^2}t|V_{ba}|^2\delta(\omega_0-\omega)\quad\left(\text{with }\frac{1}{|V_{ba}|}\gg t,\ \text{let } P<1\right)$$

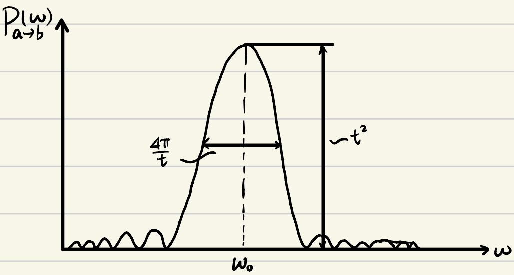
Trick:

$$\lim_{t\to\infty}\frac{\sin^2\left[\frac{(\omega-\omega_0)t}{2}\right]}{(\omega-\omega_0)^2}=\frac{\pi}{4}+\delta\left(\frac{\omega_0-\omega}{2}\right)$$

利用了 $\lim_{\alpha\to\infty}\frac{\sin^2[\alpha x]}{\alpha x^2}=\delta(x)\pi$

单位时间跃迁几率 $w_{a\to b}=\frac{2\pi}{\hbar^2}|V_{ba}|^2\delta(\omega_0-\omega)$

如 $|b\rangle$ 附近有一系列态 $\sum_b P_{a\to b}(t)\Big|_{t\to\infty}=\int dE\,\rho(E)\frac{2\pi}{\hbar}|V_{ab}|^2\delta(E-E_0)t$



Fermi's Golden Rule

试问：会有 $a\to b$，单次测量能量不守恒？计算能量涨落 $\Delta E\cdot\Delta t\simeq\frac{4\pi}{t}\hbar\cdot t\simeq4\pi\hbar$

思考：时间测量尺度越小，能量涨落越大

(ii) 严格解

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}C_a\\C_b\end{pmatrix}=\begin{pmatrix}E_a & V_{ab}\left(e^{i\omega t}+e^{-i\omega t}\right)\\ \cdots & E_b\end{pmatrix}\begin{pmatrix}C_a\\C_b\end{pmatrix}$$

取相互作用绘景 $\begin{cases}\tilde C_a=C_a e^{i\left(\frac{E_a+E_b}{2\hbar}-\frac{\omega}{2}\right)t}\\ \tilde C_b=C_b e^{i\left(\frac{E_a+E_b}{2\hbar}+\frac{\omega}{2}\right)t}\end{cases}$

RWA近似

$$\Rightarrow\ i\frac{\partial}{\partial t}\begin{pmatrix}\tilde C_a\\\tilde C_b\end{pmatrix}=\underbrace{\begin{pmatrix}\delta=\frac{\omega-\omega_0}{2} & \frac{V_{ab}}{\hbar}\left(1+\cancel{e^{-i2\omega t}}\right)\\ \cdots & -\delta=-\frac{\omega-\omega_0}{2}\end{pmatrix}}_{V}\begin{pmatrix}\tilde C_a\\\tilde C_b\end{pmatrix}$$

$\delta\begin{cases}\frac{\delta}{2}\ |a\rangle\\ \text{能量零点}\\ -\frac{\delta}{2}\ |b\rangle\end{cases}$

上述变换后的V矩阵可写成Pauli矩阵和： $\tilde{V} = \frac{\delta}{2}\sigma_z + Re\left(\frac{V_{ab}}{\hbar}\right)\sigma_x - Im\left(\frac{V_{ab}}{\hbar}\right)\sigma_y$, $\begin{pmatrix}\tilde{C}_a(t)\\ \tilde{C}_b(t)\end{pmatrix} = e^{-i\tilde{V}t}\begin{pmatrix}\tilde{C}_a(0)\\ \tilde{C}_b(0)\end{pmatrix}$

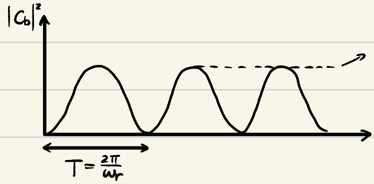
其解

$$\begin{pmatrix}\tilde{C}_a\\ \tilde{C}_b\end{pmatrix} = \begin{pmatrix}\cos\frac{\omega_r}{2}t + i\frac{\delta}{\omega_r}\sin\frac{\omega_r}{2}t & -i\frac{2V_{ab}}{\hbar\omega_r}\sin\frac{\omega_r}{2}t \\ \cdots & \cos\frac{\omega_r}{2}t - i\frac{\delta}{\omega_r}\sin\frac{\omega_r}{2}t\end{pmatrix}\begin{pmatrix}\tilde{C}_a(0)\\ \tilde{C}_b(0)\end{pmatrix}$$

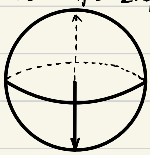
with $\omega_r = \sqrt{\delta^2 + \frac{4|V_{ab}|^2}{\hbar^2}}$ Rabi Frequency

考虑 $\tilde{C}_a(0)=1$, $\tilde{C}_b(0)=1$ 的特殊情况

①: $\begin{cases}\tilde{C}_a(t) = \cos\frac{\omega_r}{2}t + i\frac{\delta}{\omega_r}\sin\frac{\omega_r}{2}t \\ \tilde{C}_b(t) = -i\frac{2V_{ab}^*}{\hbar\omega_r}\sin\frac{\omega_r}{2}t\end{cases}$



②:用Bloch球去理解



$e^{i\varphi(\vec{n}\cdot\vec{\sigma})}$

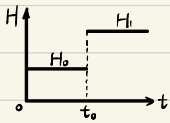
想翻上去，则$\vec{\sigma}$必在xy平面内 ⇒ $\delta=0$，共振

C.含时问题特殊

① 突变近似

$\hat{H}_0|\psi_n\rangle = E_n|\psi_n\rangle$

$\hat{H}_1|\varphi_\alpha\rangle = E_\alpha|\varphi_\alpha\rangle$



在t_0时刻，态近似不变.

$t=0$, $|\psi\rangle = \sum_n C_n|\psi_n\rangle$

$0<t<t_0$, $|\psi\rangle = \sum_n C_n e^{-iE_nt/\hbar}|\psi_n\rangle$

$t=t_0$, $|\psi\rangle = \sum_n C_n e^{-iE_nt_0/\hbar}|\psi_n\rangle$

$t>t_0$, $|\psi\rangle = \sum_\alpha e^{-iE_\alpha(t-t_0)}$

② 绝热近似

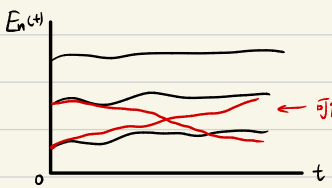
$\hat{H}(t)$缓变，则初始本征态绝热跟随瞬时$\hat{H}(t)$的本征态演化 $\hat{H}(t)|\psi_n(t)\rangle = E_n(t)|\psi_n(t)\rangle$

$t=0$, $|\psi_n\rangle$, $\hat{H}(t=0)|\psi_n\rangle = E_n(0)|\psi_n\rangle$

$t>0$, $|\psi(t)\rangle \approx e^{i\theta_n(t)}e^{i\gamma_n(t)}|\psi_n(t)\rangle$

动力学phase $\theta_n = -\frac{1}{\hbar}\int_0^t E_n(t')dt'$

几何学phase $\gamma_n = i\int_0^t \langle\psi_n(t')|\frac{\partial}{\partial t'}|\psi_n(t')\rangle dt'$



Spin，角动量耦合(CG)；定态微扰 判断 {简并 非简并，{变分 含时 简单

Bonus：拓展论题

1. 全同粒子　详见 Griffith

内禀属性一致为全同粒子

N个粒子体系

$$\hat{P}_{ij}\psi(q_1,\cdots,q_i,\cdots,q_j,\cdots q_N)=\psi(q_1,\cdots,q_j,\cdots,q_i,\cdots q_N)$$

如 $[\hat{P}_{ij},\hat{A}]=0$，有共同本征态

$$\hat{P}_{ij}\psi=\lambda\psi,\quad \hat{P}_{ij}^2\psi=\lambda^2\psi=\psi\Rightarrow\lambda=\pm1$$

定义 $\begin{cases}\hat{P}_{ij}\psi^S=\psi^S & \text{交换对称}\\ \hat{P}_{ij}\psi^A=-\psi^A & \text{交换反对称}\end{cases}$

e.g. 两粒子波函数

$$\hat{H}=\hat{h}_1(q_1)+\hat{h}_2(q_2)\qquad 设\ h_i\varphi_{ki}(q_i)=\varepsilon_{ki}\varphi_{ki}(q_i)\quad i=1,2$$

考虑 $\hat{H}\underbrace{\varphi_{k1}(q_1)\varphi_{k2}(q_2)}_{\text{直积态}}=(\varepsilon_{k1}+\varepsilon_{k2})\varphi_{k1}(q_1)\varphi_{k2}(q_2)$

e.g. 交换作用（参见 Griffith）

直积态 $|a\rangle_1|b\rangle_2$　对称态 $\frac{\sqrt{2}}{2}(|a\rangle_1|b\rangle_2+|b\rangle_1|a\rangle_2)$　反对称态 $\frac{\sqrt{2}}{2}(|a\rangle_1|b\rangle_2-|b\rangle_1|a\rangle_2)$

求 $\langle(\hat{x}_1-\hat{x}_2)^2\rangle$

直积态：$_1\langle a|_2\langle b|(\hat{x}_1^2+\hat{x}_2^2-2\hat{x}_1\hat{x}_2)|a\rangle_1|b\rangle_2=\langle\hat{x}_1^2\rangle_a+\langle\hat{x}_2^2\rangle_b-2\langle\hat{x}_1\rangle_a\langle\hat{x}_2\rangle_b$

设 $\begin{cases}\langle\hat{x}_1^2\rangle_a=\langle\hat{x}_2^2\rangle_a & \langle\hat{x}_1\rangle_a=\langle\hat{x}_2\rangle_a\\ \langle\hat{x}_1^2\rangle_b=\langle\hat{x}_2^2\rangle_b & \langle\hat{x}_1\rangle_b=\langle\hat{x}_2\rangle_b\end{cases}$ $\overset{\langle\cdots\rangle_\psi}{\Longrightarrow}\langle\hat{x}_1^2\rangle_a+\langle\hat{x}_2^2\rangle_b-2\langle\hat{x}_1\rangle_a\langle\hat{x}_2\rangle_b\mp2|\langle\hat{x}\rangle_{ab}|^2$

即 $\begin{cases}\text{对称态　间距小}(-)\ (\text{成键})\\ \text{反对称态　间距大}(+)\ (\text{反键})\end{cases}$

2. 量子信息初步

① 密度矩阵

a. 对于任意态 $|\psi\rangle$　$\hat{\rho}=|\psi\rangle\langle\psi|$ —— 含概了体系的量子信息

力学量期望值：$\langle\psi|\hat{A}|\psi\rangle=\sum_n\langle\psi_n|\hat{A}|\psi\rangle\langle\psi|\psi_n\rangle=Tr(\hat{A}\hat{\rho})$

e.g. a. 二能级体系 (qubit)

$$|\psi\rangle = |\uparrow_x\rangle = \frac{\sqrt{2}}{2}\left(|\uparrow_z\rangle + |\downarrow_z\rangle\right)$$

$$\Rightarrow \hat{\rho} = |\psi\rangle\langle\psi| = \cdots \sim \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix}$$ 相干性 Coherence

$$= \underline{|\uparrow_x\rangle\langle\uparrow_x|}$$ 我很纯

则 $\hat{S}_z$ 测值 $\begin{cases} P=\frac{1}{2} & \uparrow_z \\ P=\frac{1}{2} & \downarrow_z \end{cases}$ $\hat{S}_x$ 测值 $\begin{cases} P=1 & \uparrow_x \\ P=0 & \downarrow_x \end{cases}$ 纯态

再考虑 $$\hat{\rho}' = \frac{1}{2}|\uparrow_z\rangle\langle\uparrow_z| + \frac{1}{2}|\downarrow_z\rangle\langle\downarrow_z| \sim \begin{pmatrix} \frac{1}{2} & \\ & \frac{1}{2} \end{pmatrix}$$

$$= \underline{\frac{1}{2}|\uparrow_x\rangle\langle\uparrow_x| + \frac{1}{2}|\downarrow_x\rangle\langle\downarrow_x|}$$ 我不能化到只有一项纯

则 $\hat{S}_x$ 测值 $\begin{cases} P=\frac{1}{2} & \uparrow_x \\ P=\frac{1}{2} & \downarrow_x \end{cases}$ 混态

应用：随机制备 $\left.\begin{cases} \frac{1}{2} \ \uparrow_z & \begin{cases} \frac{1}{2} & \uparrow_x \\ \frac{1}{2} & \downarrow_x \end{cases} \\ \frac{1}{2} \ \downarrow_z & \begin{cases} \frac{1}{2} & \uparrow_x \\ \frac{1}{2} & \downarrow_x \end{cases} \end{cases}\right\} \Rightarrow \begin{cases} \frac{1}{2} & \uparrow_x \\ \frac{1}{2} & \downarrow_x \end{cases}$

b. 两个二能级体系

$$|\psi_{AB}\rangle = a|\uparrow_z\rangle_A|\uparrow_z\rangle_B + b|\downarrow_z\rangle_A|\downarrow_z\rangle_B \quad \text{with } |a|^2+|b|^2=1$$

对A的态测量 $\begin{cases} P=|a|^2 & |\uparrow_z\rangle_A \\ P=|b|^2 & |\downarrow_z\rangle_A \end{cases}$ 同时态坍缩为 $\begin{cases} |\uparrow_z\rangle_A|\uparrow_z\rangle_B \\ |\downarrow_z\rangle_A|\downarrow_z\rangle_B \end{cases}$

如不关心B的结果，只对A进行测量：

$$\langle\psi_{AB}|\hat{M}_A\otimes\hat{I}_B|\psi_{AB}\rangle = |a|^2\langle\uparrow_z|\hat{M}_A|\uparrow_z\rangle_A + |b|^2\langle\downarrow_z|\hat{M}_A|\downarrow_z\rangle_A$$ ← 插入完备基，$\{|\varphi_0\rangle, |\varphi_1\rangle\}$ 为A的基

$$\xlongequal[\text{相乘顺序}]{\text{交换一下数的}} |a|^2\langle\varphi_0|\uparrow_z\rangle\langle\uparrow_z|\hat{M}_A|\varphi_0\rangle + |a|^2\langle\varphi_1|\uparrow_z\rangle\langle\uparrow_z|\hat{M}_A|\varphi_1\rangle$$

$$+|b|^2\langle\varphi_0|\downarrow_z\rangle\langle\downarrow_z|\hat{M}_A|\varphi_0\rangle + |b|^2\langle\varphi_1|\downarrow_z\rangle\langle\downarrow_z|\hat{M}_A|\varphi_1\rangle$$

定义 $\hat{\rho}_A = |a|^2|\uparrow_z\rangle_A\langle\uparrow_z| + |b|^2|\downarrow_z\rangle_B\langle\downarrow_z|$ ⇒ 混态

$$= \mathrm{Tr}_A(\hat{\rho}_A\hat{M}_A)$$

② 纠缠与纠缠态

可分离的态 $|\psi_{AB}\rangle = |\varphi_A\rangle\otimes|\chi_B\rangle$

$$\hat{\rho}_A = \mathrm{Tr}_B(\hat{\rho}_{AB}) = |\varphi\rangle_A\langle\varphi|\otimes\underbrace{\langle\chi|\chi\rangle_B}_{1} = |\varphi\rangle_A\langle\varphi|$$ 成为纯态

找一组B的完备基，把B作用掉！