量子化学　　Office hour: W 4-5 p.m.　E5-413/412.

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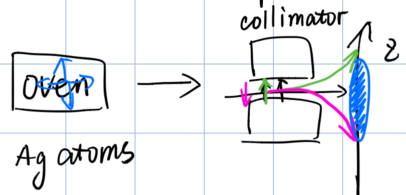
1. Claude Cohen. Tannoudji. Quantum Mechanics I & II.
2. Sakurai Jim Napolitano　Modern Quantum Mechanics.
3. Quantum Chemistry by Levine

Attendice & paitipation	30%
assignment	30%
mid. finals	40%
project	exact 10%

python. Maple. Matlab.

§ (一)

Stern-Gerlach experience.



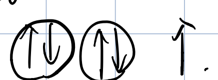
Ag atoms

47 electrons

46 electrons

带有自旋的粒子经过时
不均匀磁场. 才能产生向上/向下的力.

$\frac{\partial B}{\partial z} \neq 0$.　$\frac{\partial B}{\partial z} = 0$.



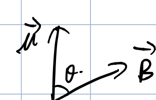
spin.

$\vec{\mu} \propto \vec{S}$

$F_z = \frac{\partial}{\partial z}(\vec{\mu} \cdot \vec{B})$.

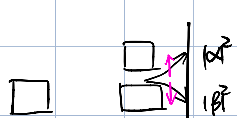
$= \vec{\mu} \cdot \frac{\partial \vec{B}}{\partial z}$

磁矩.



$\mu = eg S_z$. μ的正负取决于 S_z 的正负.

存在自旋时. 会有向上,向下的力.

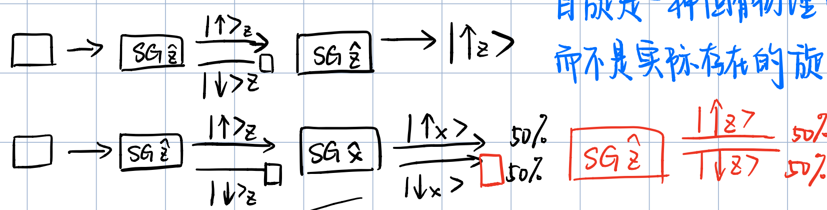


in quantum, only two point, no other choice.

$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$　$|\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

$|\psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$.

$|\alpha|^2+|\beta|^2=1$

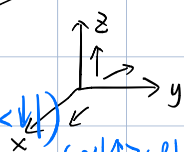


自旋是一种固有物理量. 有两个相反的状态.
而不是实际存在的旋转方向.

$|Ag\rangle=\alpha|\uparrow\rangle+\beta|\downarrow\rangle$

$|\uparrow\rangle_z=\alpha|\uparrow\rangle_x+\beta|\downarrow\rangle_x$

$\langle Ag|Ag\rangle$



$=(\alpha^*\langle\uparrow|+\beta^*\langle\downarrow|)(\alpha|\uparrow\rangle+\beta|\downarrow\rangle)$

$=\alpha^*\alpha\langle\uparrow|\uparrow\rangle+\beta^*\beta\langle\downarrow|\downarrow\rangle+0+0$

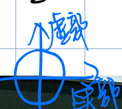
$=|\alpha|^2+|\beta|^2=1$ (归一化).

$|\alpha|^2+|\beta|^2=1.$

实验得到. 朝上与朝下的可能性.

$\alpha=\frac{\sqrt{2}}{2}$. $\beta=\frac{\sqrt{2}}{2}$.

$\alpha=\frac{\sqrt{2}}{2}e^{i\theta}$. $\beta=\frac{\sqrt{2}}{2}e^{i\phi}$.



$e^{i\theta}=\cos\theta+i\sin\theta$.

* 是共轭.

α. β 是复数.

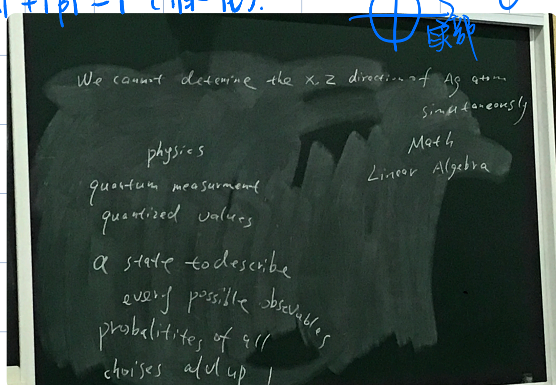
α. β 代表概率.

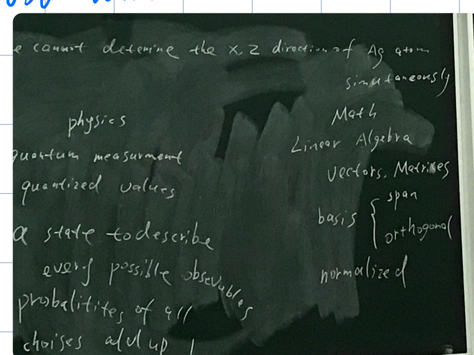
we can't determine the x. z direction of Ag atoms simultaneously

$[\hat{O}_x,\hat{O}_z]\neq 0.$

不对易的时候不能同时测.

交换. commutitive





括号. 用某个记号标定某个状态.

inner product.

bra ket

$\langle\uparrow|\downarrow\rangle=(1,0)\begin{pmatrix}0\\1\end{pmatrix}=0$

$\langle\uparrow|=(1,0)$ 转置.

$\langle\uparrow|\uparrow\rangle=1$

$\langle\downarrow|\downarrow\rangle=1$

ket. bra是ket的转置.

$|\uparrow\rangle=\begin{pmatrix}1\\0\end{pmatrix}$ $|\downarrow\rangle=\begin{pmatrix}0\\1\end{pmatrix}$

bra ket

$\langle\uparrow|\uparrow\rangle=(1,0)\begin{pmatrix}1\\0\end{pmatrix}=1.$

$\langle\downarrow|\downarrow\rangle=(0,1)\begin{pmatrix}0\\1\end{pmatrix}=1.$

$\langle\uparrow|\downarrow\rangle=(1,0)\begin{pmatrix}0\\1\end{pmatrix}=0.$

$|\psi\rangle=\underset{\text{Identity}}{\mathbb{I}}|\psi\rangle$

$\mathbb{I}=\begin{pmatrix}1&0\\0&1\end{pmatrix}$. 用线代表示量子的state.

$=\underbrace{(|\uparrow\rangle\langle\uparrow|+|\downarrow\rangle\langle\downarrow|)}_{\text{outer product}}|\psi\rangle$

$=\boxed{\langle\uparrow|\psi\rangle}|\uparrow\rangle+\boxed{\langle\downarrow|\psi\rangle}|\downarrow\rangle$ states

单位矩阵 $I=|\uparrow\rangle\langle\uparrow|+|\downarrow\rangle\langle\downarrow|$

$=\begin{pmatrix}1\\0\end{pmatrix}(1,0)+\begin{pmatrix}0\\1\end{pmatrix}(0,1)$

$=\begin{pmatrix}1&0\\ \end{pmatrix}+\begin{pmatrix}0&0\\ \end{pmatrix}$

数 数

$= \alpha|\uparrow\rangle + \beta|\downarrow\rangle$

$= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$

1. outer product of normalized vector with itself is a projection operator.
投影

投影算符 $\hat{P}_\uparrow = |\uparrow\rangle\langle\uparrow||\psi\rangle = \underbrace{\langle\uparrow|\psi\rangle}_{\alpha}|\uparrow\rangle$ 数

$= \alpha|\uparrow\rangle$

$\hat{P}_\downarrow = |\downarrow\rangle\langle\downarrow|$

$I = \sum_i V_i V_i^+ = \sum_i P_i$

$= |\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|$

$V_i = \{|\uparrow\rangle, |\downarrow\rangle\}$ $V_i^+ = \{\langle\uparrow|, \langle\downarrow|\}$

vector: 向量.

"+": 共轭转置.

转置: $(a+bi)^* = a-bi$.

$\hat{P}_\uparrow|A_g\rangle = |\uparrow\rangle\langle\uparrow|(\alpha|\uparrow\rangle + \beta|\downarrow\rangle)$

对错原3在↑方向做投影.

$P_\downarrow = |\downarrow\rangle\langle\downarrow|$

2. If I know the eigenstates and eigenvalues, I can form the Matrix by outer product.

矩阵 Matrix

$M = \sum_i \lambda_i V_i V_i^+$ λ是特征值.

$|\uparrow_z\rangle = \alpha|\uparrow_x\rangle + \beta|\downarrow_x\rangle$

$S_z\ \sigma_z = (1\,\underbrace{|\uparrow\rangle\langle\uparrow|}_{|P_\uparrow\rangle} - 1\,\underbrace{|\downarrow\rangle\langle\downarrow|}_{|P_\downarrow\rangle})\frac{\hbar}{2}$ 自旋值.

$= \left\{\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} - \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}\right\}\frac{\hbar}{2}$

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

$S_z = \frac{\hbar}{2}\cdot\sigma_z$.

$\boxed{SG\,\hat{z}}$ $|\uparrow_z\rangle \to |\uparrow_x\rangle$
$\to |\downarrow_x\rangle$

$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ Antate.

$|\downarrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$ $\langle\uparrow_x|\downarrow_x\rangle = 0$

$|\uparrow_x\rangle = \frac{\sqrt{2}}{2}|\uparrow_z\rangle + \frac{\sqrt{2}}{2}|\downarrow_z\rangle$.

$= \frac{\sqrt{2}}{2}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$

$S_x\ \sigma_x = \frac{\hbar}{2}(|\uparrow_x\rangle\langle\uparrow_x| - |\downarrow_x\rangle\langle\downarrow_x|)$

$= \frac{\hbar}{2}\cdot\frac{1}{2}\left[(1,1)\begin{pmatrix} 1 \\ 1 \end{pmatrix} - (1,-1)\begin{pmatrix} 1 \\ -1 \end{pmatrix}\right]$

$= \frac{\hbar}{4}\left[\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} - \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}\right]$

$= \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$.

一般而言. 矩阵中

$A\times B \neq B\times A$. 不可交换

$[\sigma_x, \sigma_z] = \sigma_x\sigma_z - \sigma_z\sigma_x$ Commutator

$$= \frac{\hbar^2}{4}\left[\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}1&0\\0&-1\end{pmatrix}-\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}0&1\\1&0\end{pmatrix}\right]$$

$$= \frac{\hbar^2}{4}\left[\begin{pmatrix}0&-1\\1&0\end{pmatrix}-\begin{pmatrix}0&1\\-1&0\end{pmatrix}\right]$$

$$= \frac{\hbar^2}{2}\begin{pmatrix}0&-1\\1&0\end{pmatrix} = i\hbar\cdot\frac{\hbar}{2}\begin{pmatrix}0&-i\\i&0\end{pmatrix}$$

$$= -i\hbar\sigma_y.$$

$[\sigma_x, \sigma_y] = i\hbar\sigma_z \neq 0$

$[\sigma_y, \sigma_z] = i\hbar\sigma_x \neq 0$

$\begin{pmatrix}a&b\\c&d\end{pmatrix} = \begin{pmatrix}a^*&c^*\\b^*&d^*\end{pmatrix}$.

则a, d是实数.
b, c转换后相等

厄米矩阵

Hermition matrices

$H^+ = (H^*)^T = H$，则

H叫做厄米算符. operator

本征值

eigenvalues of a Hermition matrix are real 实数

Eigenvectors of -- -- can form a basis 基

∴ $AB - BA \neq 0$

写作 $[A, B] \neq 0$. 不对易

当 $[A, B] = 0$ 时.

A, B是同阶方阵.

当 $A|\psi\rangle = a|\psi\rangle$

$B|\psi\rangle = b|\psi\rangle$ 存在时.

(即 $|\psi\rangle$ 同时是A, B的本征态).

$AB|\psi\rangle = Ab|\psi\rangle = ba|\psi\rangle$

$= aB|\psi\rangle = Ba|\psi\rangle = BA|\psi\rangle$

此时

$(AB-BA)|\psi\rangle = 0$.

在 $|\psi\rangle$ 态下 $AB-BA=0$.

即AB可对易.

(在其他态,不一定对易)

A和B对易:

A和B作用到空间内任意状态时. AB均可交换.

怎样能够对易:

该空间的一组基同时是A和B的共同本征态.

厄米算符的性质:

① 本征值都是实数.

② 在自己表象的矩阵表示是一个对角矩阵.

③ 可观测量 (Observable) 对应的算符都是厄米算符

[illegible]

④ 它的本征态构成一组基.

$$\mathbb{I}|\varphi\rangle = (|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|)|\varphi\rangle$$
$$= \underbrace{\langle\uparrow|\varphi\rangle}_{}|\uparrow\rangle + \underbrace{\langle\downarrow|\varphi\rangle}_{}|\downarrow\rangle$$
$$= \alpha|\uparrow\rangle + \beta|\downarrow\rangle$$

$\text{prob} = |\alpha|^2 \cdot |\beta|^2$.

If I make a measurment $|\psi\rangle$

a) find the operator (算符.) that represent the observable (可观测量.) $\hat{O}$

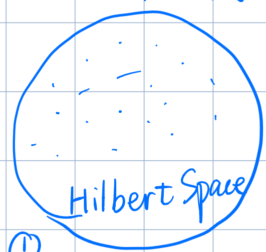
b) find the eigenvalues and eigenvectors of the operator $\hat{O} = \sum_i \lambda_i |\varphi_i\rangle\langle\varphi_i|$

c) expand the state vector into a linear combination of the eigenvector

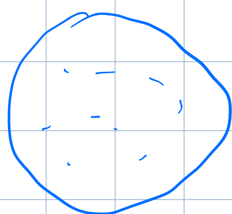
$$|\psi\rangle = \mathbb{I}|\psi\rangle = \sum_i |\varphi_i\rangle\langle\varphi_i|\psi\rangle$$ 系数 x 基矢

d). coefficiences (系数.) of each basis vector give (给出.) the prob. (概率.) of obseving that eigenvalues.

定义线性空间：



①



②

$|\alpha\rangle$. $|\beta\rangle$ 是Hilbert Space内的两个向量. 用竖向量表示.

它们满足 $|\alpha\rangle+|\beta\rangle=|r\rangle$

$a|\alpha\rangle=|\lambda\rangle$

$a(|\alpha\rangle+|\beta\rangle)=|y\rangle$

则Hilbert Space是线性空间.

同时有另一个空间②，①和②完全相同. 一一对应，有共轭转置的关系.

inner product

$\langle\alpha|\beta\rangle$ 是内积. 指 $|\alpha\rangle$ 的对偶与 $|\beta\rangle$ 相乘.

$\langle\beta|\alpha\rangle$ 是 $|\beta\rangle$ 的对偶与 $|\alpha\rangle$ 相乘.

$\langle\alpha|\beta\rangle=\langle\beta|\alpha\rangle^*$.

eg: $|\alpha\rangle=\begin{pmatrix} i \\ 0 \end{pmatrix}$. $|\beta\rangle=\begin{pmatrix} 1 \\ 0 \end{pmatrix}$.

$\therefore \langle\alpha|\beta\rangle=(-i,0)\begin{pmatrix} 1 \\ 0 \end{pmatrix}=-i$

$\langle\beta|\alpha\rangle=(1,0)\begin{pmatrix} i \\ 0 \end{pmatrix}=i$.

外积：$|\alpha\rangle\langle\beta|=\begin{pmatrix} i \\ 0 \end{pmatrix}(1,0)=\begin{pmatrix} i & 0 \\ 0 & 0 \end{pmatrix}$.

out product.

$$\begin{cases} |\uparrow\rangle\langle\uparrow|\alpha\rangle = \langle\uparrow|\alpha\rangle|\uparrow\rangle = C_\uparrow|\uparrow\rangle \\ C_\uparrow 是一个系数，值为\alpha 在\uparrow 方向上的分量. \\ |\downarrow\rangle\langle\downarrow|\alpha\rangle = b|\downarrow\rangle. \end{cases}$$

$\therefore$ $|\uparrow\rangle\langle\downarrow|\uparrow\rangle = 0.$ $\quad(\langle\downarrow|\uparrow\rangle=0)$

$|\uparrow\rangle\langle\downarrow|\downarrow\rangle = |\uparrow\rangle$ $\quad(\langle\downarrow|\downarrow\rangle=1)$

$|\uparrow\rangle\langle\downarrow|$ 作用在↑方向得到0. 作用在↓方向得到$|\uparrow\rangle$.
命名为自旋角动量的升算符 $\hat{\sigma}_+$.

$|\downarrow\rangle\langle\uparrow|\uparrow\rangle = |\downarrow\rangle$

$|\downarrow\rangle\langle\uparrow|\downarrow\rangle = 0.$

$|\downarrow\rangle\langle\uparrow|$ 作用在↑方向得到$|\downarrow\rangle$ 作用在↓方向得到0.
命名为自旋角动量的降算符 $\hat{\sigma}_-$.

$$\hat{\sigma}_+ = |\uparrow\rangle\langle\downarrow| = \begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}0 & 1\end{pmatrix} = \begin{pmatrix}0&1\\0&0\end{pmatrix}$$

$$\hat{\sigma}_- = |\downarrow\rangle\langle\uparrow| = \begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}1 & 0\end{pmatrix} = \begin{pmatrix}0&0\\1&0\end{pmatrix}$$

$$|\uparrow\rangle\langle\uparrow|\uparrow\rangle = |\uparrow\rangle.$$

$$|\uparrow\rangle\langle\uparrow|\downarrow\rangle = 0.$$

$$|\downarrow\rangle\langle\downarrow|\uparrow\rangle = 0$$

$$|\downarrow\rangle\langle\downarrow|\downarrow\rangle = |\downarrow\rangle.$$

定义 $\begin{cases} \hat{\sigma}_x = \hat{\sigma}_+ + \hat{\sigma}_- = \begin{pmatrix}0&1\\1&0\end{pmatrix} \\ \hat{\sigma}_y = \dfrac{\hat{\sigma}_+ - \hat{\sigma}_-}{+i} = \begin{pmatrix}0&-i\\i&0\end{pmatrix} \end{cases}$

此时有一σ_z算符. 作用在↑方向得到$|\uparrow\rangle$,
作用在↓方向得到$-|\downarrow\rangle$, 则 $\hat{\sigma}_z = |\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|$

$$= \begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}1&0\end{pmatrix} - \begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}0&1\end{pmatrix}$$

$$= \begin{pmatrix}1&0\\0&-1\end{pmatrix}.$$

$\hat{\sigma}_x$、$\hat{\sigma}_y$、$\hat{\sigma}_z$ 不对易.

$$\hat{\sigma}_x = \begin{pmatrix}0&1\\1&0\end{pmatrix}$$

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \lambda \begin{pmatrix} a \\ b \end{pmatrix}$$ 求$\hat{\sigma}_x$的本征值λ和本征态$\begin{pmatrix} a \\ b \end{pmatrix}$.

$$\left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - \lambda\right]\begin{pmatrix} a \\ b \end{pmatrix} = 0$$

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - \lambda \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} -\lambda & 1 \\ 1 & -\lambda \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = 0$$

即 $\begin{vmatrix} -\lambda & 1 \\ 1 & -\lambda \end{vmatrix} = 0.$

$\lambda^2 - 1 = 0.$

$\lambda = \pm 1.$

$\lambda = 1$时. $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = 1\begin{pmatrix} a \\ b \end{pmatrix}$

$\begin{pmatrix} b \\ a \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix}$.

$\therefore\ a = b$

令 $a = b = 1.$

则本征态为$\begin{pmatrix} 1 \\ 1 \end{pmatrix}$.

归一化后为 $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$.

内积$(1,1)\begin{pmatrix} 1 \\ 1 \end{pmatrix} = 2$. 则每个向量乘$\frac{1}{\sqrt{2}}$

$\lambda = -1$时. $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = -\begin{pmatrix} a \\ b \end{pmatrix}$

$\begin{pmatrix} b \\ a \end{pmatrix} = \begin{pmatrix} -a \\ -b \end{pmatrix}$

$b = -a.$

$\begin{pmatrix} a \\ b \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}.$