Ch. 量子力学

QM. 参考书 Griffith. 曾; Note

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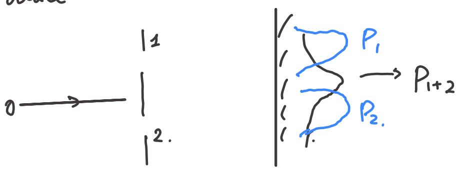
作业: 双周周一 / 教学网 15:35:50

Introduce.



$\Rightarrow$ Inference. $P_{1+2} \neq P_1 + P_2$.

实验: 慢电子

相干 $\Rightarrow$ [波子 $\rightarrow$ 线性.

规律 $\Rightarrow$ 动力学变量 + 参量 + $\underbrace{\text{方程}}_{\hookrightarrow \text{解}}$.

$\hat{L}u=0$

Schrödinger 方程

$$i\hbar \frac{\partial}{\partial t}\psi(x,t) = \hat{H}\psi(x,t) \Rightarrow \begin{cases} \hat{H}(\alpha\psi) = \alpha\hat{H}\psi \\ \hat{H}(\psi_1+\psi_2) = \hat{H}\psi_1 + \hat{H}\psi_2 \end{cases}$$

$\Downarrow$ Planck constant

$\hat{L} = i\hbar\frac{\partial}{\partial t} - \hat{H}$. [$\hat{L}\psi = 0$.]

复函数 v.s. 可观测量.

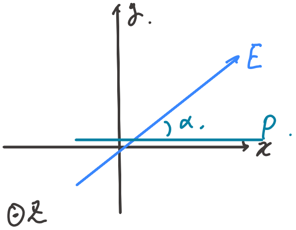
$|\psi|^2$: 几率. Born

$\Leftarrow$ 放弃"确定性"

光量子: $E = h\nu$. Photon.
↳ 全同粒子.

$I = \underline{N}h\underline{\nu}$

单光子，偏振（Dirac）



经典: $\vec{E} = E\cos\alpha\,\hat{e}_x + E\sin\alpha\,\hat{e}_y$.

$$|E|^2 \to \begin{cases} I_0\cos^2\alpha & \text{过} \\ I_0\sin^2\alpha & \text{挡} \end{cases} \qquad \nu_{\text{透}} = \nu_\lambda .$$

Exp Data : 单光子过 / 挡 :

Dirac 符号（波函数）: 沿 x 方向: $|x\rangle$. 沿 y 方向: $|y\rangle$.

沿 α 方向: $|\alpha\rangle$.

[$\Rightarrow P(|x\rangle) = \cos^2\alpha \quad P(|y\rangle) = \sin^2\alpha$]

$$|\alpha\rangle = \cos\alpha\,|x\rangle + \sin\alpha\,|y\rangle .$$

态叠加. Superposition ① 量子处在互斥的状态上

"不确定"

$\Rightarrow$ 测量 $\quad |A\rangle \quad |B\rangle$

$\quad Q. \quad a \quad b$

$$|\psi\rangle = \alpha|A\rangle + \beta|B\rangle$$

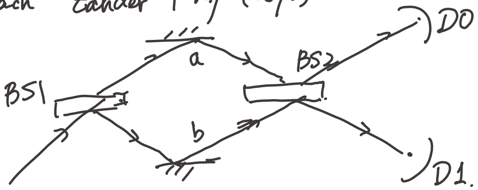
a 或 b.

几率: $|\alpha|^2$, $|\beta|^2$ （完备: $|\alpha|^2 + |\beta|^2 = 1$）

② 态函数与自身叠加不改变物理 （归一化）

$$|A\rangle \cong (\alpha + i\beta)|A\rangle$$

Mach - Zahder 干涉 (1896)

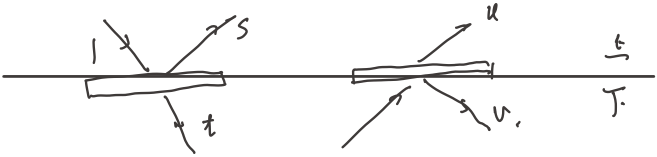


BS: beam splitter.

单光子入射.

a or b.

调 BS. 观测到 $D_0=1$ $D_1=0$ 的现象 ⇒ 干涉

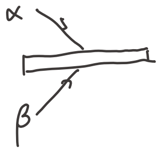


$\begin{pmatrix}1\\0\end{pmatrix}$ 上 $\begin{pmatrix}0\\1\end{pmatrix}$ 下

$$\begin{pmatrix}1\\0\end{pmatrix} \xrightarrow{BS} s\begin{pmatrix}1\\0\end{pmatrix}+t\begin{pmatrix}0\\1\end{pmatrix}. \quad \begin{pmatrix}0\\1\end{pmatrix} \xrightarrow{BS} u\begin{pmatrix}1\\0\end{pmatrix}+v\begin{pmatrix}0\\1\end{pmatrix}.$$

$$s=t=u=v=\frac{1}{\sqrt{2}} \,. \quad (\text{等值}).$$

⇒



$$\begin{pmatrix}\alpha\\\beta\end{pmatrix} = \alpha\begin{pmatrix}1\\0\end{pmatrix}+\beta\begin{pmatrix}0\\1\end{pmatrix}.$$

$$= \alpha\begin{pmatrix}s\\t\end{pmatrix}+\beta\begin{pmatrix}u\\v\end{pmatrix} = \begin{pmatrix}\alpha s+\beta u\\\alpha t+\beta v\end{pmatrix}.$$

$$\underbrace{\begin{pmatrix}s & u\\t & v\end{pmatrix}}_{BS}\begin{pmatrix}\alpha\\\beta\end{pmatrix}.$$

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

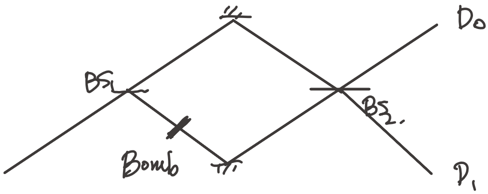
则 $BS\begin{pmatrix}1\\0\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$ $\quad BS\,\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} = \begin{pmatrix}1\\1\end{pmatrix}$ × 不守恒.

令 $BS_1 = \frac{1}{\sqrt{2}}\begin{pmatrix}-1 & 1\\1 & 1\end{pmatrix}$ $\quad BS_2 = \frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\1 & -1\end{pmatrix}.$

$$\begin{pmatrix}\alpha\\ \beta\end{pmatrix} \xrightarrow{BS_1 \otimes BS_2} \frac{1}{2}\begin{pmatrix}0 & 2\\ -2 & 0\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\end{pmatrix} = \begin{pmatrix}\beta\\ -\alpha\end{pmatrix}$$

$\Rightarrow$ $\alpha = 0$ $\beta = 1$ 时 $D0 = 1$ $D1 = 0$.

Elitzur - Vaidaman 炸弹测试



Block $\frac{1}{2}$

好炸弹: $D0$ $\frac{1}{4}$
$D1$ $\frac{1}{4}$

坏炸弹. $D0$ 1
$D1$ 0.

$\Rightarrow$ D_1: 必为好炸弹 (无接触测量)

What's Important? 态叠加. 互斥事件.

测量: 不可逆变化, $|\alpha\rangle \to |x\rangle$ or $|y\rangle$.

interaction-free measurement.

{退相干测量}

$\Rightarrow$ 从测量结果 $\Rightarrow$ 物理

波粒二象性

Local $\left\{ \begin{array}{l} E = \hbar\omega \\ \vec{p} = \hbar\vec{k} \end{array} \right\}$ 广延.

黑体辐射

1859 Kirchhoff

辐射

$$\frac{E(\nu,T)}{A(\nu,T)} = \underbrace{f(\nu,T)}_{\text{和物体无关}}$$

吸收

黑体, $A = 1$.

$f(\nu,T) \to \rho(\nu,T)$

$\Rightarrow$ Wien : $\rho(\nu,T) = c_1\nu^2 \exp\left(-\frac{c_2\nu}{T}\right)$ (低频偏离)

〈思路: $\left\{ \begin{array}{l} \text{能均分定理} \\ \text{态密度 } \nu^2 d\nu. \end{array} \right.$ 〉 Quantum: 并非 $\frac{1}{2}k_B T$.

$h\nu \cdot c_1\nu^2$

Planck : 结合 Th - exp.

$$\rho(\nu,T) = \frac{c_1\nu^3}{\exp\left(\frac{c_2\nu}{T}\right) - 1} = \frac{\overset{h}{k_B c_2}\,\nu}{\exp\left(\frac{k_B c_2 \nu}{k_B T}\right) - 1} \cdot \frac{c_1}{k_B c_2}\nu^2 d\nu$$

$\nu \to 0 \Rightarrow \frac{c_1}{c_2} = \frac{8\pi k_B}{c^3}$

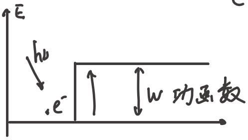
$h\nu$

$m_e c$

Planck 公式

$$\rho(\nu,T) = \frac{8\pi h}{c^3} \frac{\nu^3}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} d\nu$$

光电效应



$h\nu > W \Rightarrow$ 光电子.

Compton 实验 $\Rightarrow$ 动量性质. ($\vec{p} = \hbar\vec{k}$)

$$\lambda' = \lambda + \frac{h}{m_e c}(1 - \cos\theta)$$

Compton 波长 $\lambda_e \sim 2500$ fm

[微观的能, 动量守恒]

里德伯 $\frac{1}{\lambda} = R_H\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$ $\Rightarrow$ 原子光谱.

Bohr 模型.

1) 定态：原子处在分立的稳定能级.

2) 轨道：$m v_n r_n = n\hbar$

3) 跃迁：$E_f - E_i = \pm \hbar\omega_{if}$

$\Rightarrow v_n,\ r_n \rightarrow E_n.$

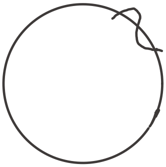
* 对应原理（假设）：n 大，$QM \longrightarrow CM$

$\Downarrow$

$\left(\nu_n = \frac{v_n}{2\pi r_n}\right)$

Sommerfield 量子化 $\dot{q}_a = \frac{\partial H_a}{\partial p_a}$， $\dot{p}_a = -\frac{\partial H_a}{\partial q_a}$，若 q, p 周期变化，

则 $\oint p_a\, dq_a = n_a h$



驻波：$n\lambda = 2\pi r.$

$rmv = n\hbar$

$\Big\} \Rightarrow p = \frac{h}{\lambda}.$

$\psi \sim e^{\frac{i}{\hbar}(px - Et)}.$

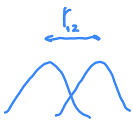
de Brogile (1923)

$\Rightarrow \Delta\varphi = \frac{1}{\hbar}\oint p\,dq = 2n\pi$ $\Rightarrow$ Sommerfield.

周期性

Bose – Einstein condensation (1925)

$\lambda = \frac{h}{p}$ $\Rightarrow mv\downarrow,\ \lambda\uparrow \Rightarrow (\lambda \rightarrow r_{12})$



$T\downarrow,\ v\downarrow.$

$\frac{4\pi}{3}\left(\frac{h}{2mv}\right)^3 \geq \frac{V}{N}$; $\frac{1}{2}mv^2 = \frac{3}{2}k_B T$

$\longrightarrow T_c = \left[\left(\frac{\pi N}{6V}\right)^{2/3}\right]\frac{h^2}{3mk_B} \rightarrow$ Truth: $3.31\left(\frac{N}{V}\right)\frac{\hbar^2}{mk_B}$

$E = \hbar\omega$

$p = \hbar k$ $\Rightarrow$ $\omega = \frac{\hbar k^2}{2m}$ $\longrightarrow$ $\psi(x,t) \sim e^{\frac{i}{\hbar}(px - Et)} \sim e^{i(kx-\omega t)}$

$\frac{\partial}{\partial t}\psi \sim -\frac{i}{\hbar}E\psi$; $\frac{\partial^2}{\partial x^2}\psi \sim -\frac{p^2}{\hbar^2}\psi$.

$\Rightarrow$ $i\hbar\frac{\partial}{\partial t}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi$ (自由空间的) Schrödinger Equation

$\Downarrow$.

$\underbrace{\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right]}_{\hat{H}}\psi$.

$\left\{ \quad i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle \quad \text{Sc. Eqn} . \quad \right\}$

Galileo $v' = v - v_0$

$p' = p - mv_0$

（经典）

$\downarrow$

$\left\{ 要求\ \lambda' = \lambda.\ \ \omega \neq \omega \right\}$.

$\Rightarrow \phi'(x',t') = \phi(x,t)$ 相位性质.

$\frac{2\pi}{\lambda}(x - Vt) = \frac{2\pi}{\lambda}\left(x' - (v-v_0)t'\right)$ $\longrightarrow$ 可观测量条件

Now. $\lambda = \frac{h}{p}$. 放弃? $\Rightarrow$ $\psi(x,t)$ 不是可观测物理量.

则 $\lambda' \neq \lambda$, $\psi'(x',t') \neq \psi(x,t)$.

S. Frame: $i\hbar\frac{\partial}{\partial t}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi + V\psi$

S'. Frame: $i\hbar\frac{\partial}{\partial t'}\psi'(x',t') = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x'^2}\psi'(x',t') + V\psi'(x',t')$

要求: $|\psi|^2 = |\psi'|^2$

则有：

$$\psi(x,t) = e^{-ig(x',t')}\,\psi'(x',t')$$

其中 $g = \dfrac{mV_0 x'}{\hbar} - \dfrac{mV_0^2}{2\hbar}t'$ (homework)

Galileo

S: $\psi = \dfrac{1}{\sqrt{2\pi\hbar}} e^{\frac{ipt}{\hbar}} e^{-\frac{i}{\hbar}\frac{p^2}{2m}t}$

S'. $\psi' = \dfrac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar}(p-mV_0)x} e^{-\frac{i}{\hbar}\frac{(p-mV_0)^2}{2m}t'}$

$$\frac{1}{2}mV^2 = E = h\nu$$

$$mV = p = \frac{h}{\lambda}$$

$$\Rightarrow \quad \frac{1}{2}V_{粒子} = V_{波}$$

De Brogile 波包 Wave Packet

$$\sin\big((k-\Delta k)x-(\omega-\Delta\omega)t\big) + \sin\big((k+\Delta k)x-(\omega+\Delta\omega)t\big)$$

$$= \sin(kx-\omega t)\big[2\cos(\Delta k\cdot x - \Delta\omega\cdot t)\big].$$

不确定关系.

$\Delta x\,\Delta p \sim \dfrac{h}{2}$

$\Delta x \sim \dfrac{\pi}{\Delta k}$

$V_{phase} = \dfrac{\omega}{k}$ $\qquad V_{group} = \dfrac{\Delta\omega}{\Delta k} \to \dfrac{d\omega}{dk}$ $\qquad \omega = \dfrac{\hbar k^2}{2m}$

$$\Rightarrow \quad V_{group} = \frac{\hbar k}{m} = V_{粒子}.$$

传播

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} \phi(k)\, e^{i(kx-\omega t)}\,dk$$

$\phi(k) \to g(k-k_0)$

$$\omega(k)=\omega(k_0)+(k-k_0)\frac{d\omega}{dk}+\frac{1}{2}(k-k_0)^2\underbrace{\frac{d^2\omega}{dk^2}}_{\hbar/m}+\cdots \qquad 0$$

$\Rightarrow$

$$kx-\omega t = k_0x+(k-k_0)x-\left[\omega(k_0)+v_g(k-k_0)+\alpha(k-k_0)^2\right]t$$

$$=\left[k_0x+\omega(k_0)t\right]+(k-k_0)\left[x-\left(v_g+(k-k_0)\alpha\right)t\right]$$

几率波函数性质

可归一化

单值，有界，连续

$[e^{i\alpha}\psi\cong\psi]$ $|\psi|^2$ — 几率密度

相对相位才有意义

$$\rho(x,t)=|\psi(x,t)|^2 \quad \text{几率密度}$$

$$\int_{-\infty}^{+\infty}|\psi(x,t)|^2dx=1 \quad (\text{归一化})$$

若 $\psi\sim r^s$

	$\int\psi^2dx$	$r\to0$	$r\to\infty$
1D	$\sim x^{2s+1}$	$s>-\frac{1}{2}$	$s<-\frac{1}{2}$
2D	$\sim\rho^{2s+2}$	$s>-1$	$s<-1$
3D	$\sim r^{2s+3}$	$s>-\frac{3}{2}$	$s<-\frac{3}{2}$.

$\{nD\to-\frac{n}{2}\}$

S.E 能否保证满足 $|\psi|^2$ 归一化？

验证：$\frac{d}{dt}\int_{-\infty}^{+\infty}|\psi|^2dx=0$

$$\frac{d}{dt}\int_{-\infty}^{+\infty}|\psi|^2dx=\int_{-\infty}^{+\infty}\frac{\partial}{\partial t}|\psi|^2dx$$

$$\frac{\partial}{\partial t}(\psi\psi^*) = \psi\frac{\partial}{\partial t}\psi^* + \psi^*\frac{\partial}{\partial t}\psi$$

$$\begin{cases} \frac{\partial\psi}{\partial t} = \hat{H}\psi\, i\hbar \\ \frac{\partial\psi^*}{\partial t} = (\hat{H}\psi)^*(-i\hbar) \end{cases}$$

$$= \frac{1}{i\hbar}\left[-(\hat{H}\psi)^*\psi + \psi^*\hat{H}\psi\right]$$

$$\therefore 原 = \frac{1}{i\hbar}\left[\int_{-\infty}^{+\infty}\psi^* H\psi\,dx - \int_{-\infty}^{+\infty}(H\psi)^*\psi\,dx\right]$$

$$\Rightarrow 要求 \int_{-\infty}^{+\infty}\psi^* H\psi\,dx = \int_{-\infty}^{+\infty}(H\psi)^*\psi\,dx \quad \Rightarrow 厄米算符$$

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \underbrace{\hat{V}(x,t)}_{\to V(x)}$$

$$\frac{\partial\psi}{\partial t} = \frac{i\hbar}{2m}\frac{\partial^2}{\partial x^2}\psi - \frac{i}{\hbar}V(x)\psi.$$

$$\Rightarrow \frac{\partial}{\partial t}|\psi|^2 = \frac{i\hbar}{2m}\left(\psi^*\frac{\partial^2}{\partial x^2}\psi - \psi\frac{\partial^2}{\partial x^2}\psi^*\right) + \frac{i}{\hbar}\underbrace{(V^*-V)}_{\to 0}\psi^*\psi$$

$$= \frac{\partial}{\partial x}\left(\frac{i\hbar}{2m}\left(\psi^*\frac{\partial}{\partial x}\psi - \psi\frac{\partial}{\partial x}\psi^*\right)\right).$$

$$\therefore \int_{-\infty}^{+\infty}\frac{\partial}{\partial t}|\psi|^2\,dx = \frac{i\hbar}{2m}\left(\psi^*\frac{\partial}{\partial x}\psi - \psi\frac{\partial}{\partial x}\psi^*\right)\Bigg|_{-\infty}^{+\infty} \overset{有界}{=\!=} 0$$

几率流 $j = -\frac{i\hbar}{2m}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)$

$$\frac{\partial\rho}{\partial t} + \frac{\partial}{\partial x}j(x,t) = 0 \quad 连续性方程$$

$$j = -\frac{i\hbar}{2m}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)$$

$$= -\frac{i\hbar}{2m}i2\,\mathrm{Im}\left(\psi^*\frac{\partial\psi}{\partial x}\right) = \frac{1}{2m}2\,\mathrm{Im}\left(i\psi^*\left(-i\hbar\frac{\partial\psi}{\partial x}\right)\right)$$

$$= \frac{1}{m}\mathrm{Im}\left(i\psi^*\hat{p}\psi\right) = \frac{1}{m}\mathrm{Re}\left(\psi^*\hat{p}\psi\right)$$

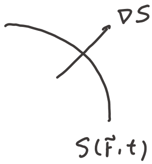
波函数

$$\psi(x,t)=\sqrt{\rho(x,t)}\,e^{\frac{i}{\hbar}S(x,t)} \qquad (\rho,\ S\in R)$$

$$\psi^*\frac{\partial}{\partial x}\psi=\sqrt{\rho}\,e^{-\frac{i}{\hbar}S}\left(e^{\frac{i}{\hbar}S}\frac{\partial}{\partial x}\sqrt{\rho}+\sqrt{\rho}\frac{\partial}{\partial x}e^{iS/\hbar}\right)$$

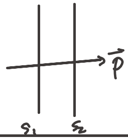
$$=\sqrt{\rho}\frac{\partial}{\partial x}\sqrt{\rho}+\underbrace{\rho\,e^{-\frac{i}{\hbar}S}e^{\frac{i}{\hbar}S}\frac{\partial S}{\partial x}\cdot\frac{i}{\hbar}}_{Im}$$

$$\therefore\ j(x,t)=\frac{\hbar}{m}\frac{\rho}{\hbar}\frac{\partial S}{\partial x}=\frac{\rho(x,t)}{m}\frac{\partial S}{\partial x}$$



* $S(x,t)$ 随空间的变化决定了几率流

eg. 平面波 $\psi\sim e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{r}-Et)}\Rightarrow\nabla S=\vec{p}$



可观测量.

$$\langle x\rangle_t=\int x|\psi|^2dx=\int_{-\infty}^{+\infty}\psi^*x\,\psi\,dx$$

$\hat{x}:\ \hat{x}\psi=x\psi.$ {操作}

$$=\int_{-\infty}^{+\infty}\psi^*\hat{x}\,\psi\,dx$$

验证: $\dfrac{d\langle\hat{x}\rangle}{dt}=\dfrac{\langle\hat{p}_x\rangle}{m}.$

(Ehrenfest 定理)

考虑 $\hat{p}_x=-i\hbar\frac{\partial}{\partial x}$

$$\langle\hat{p}_x\rangle_t=\int\psi^*\left(-i\hbar\frac{\partial\psi}{\partial x}\right)dx$$

$$\frac{d\langle\hat{x}\rangle_t}{dt}=\frac{d}{dt}\int x\,\psi^*\psi\,dx=\int x\left(\frac{\partial\psi^*}{\partial t}\psi+\frac{\partial\psi}{\partial t}\psi^*\right)dx$$

$$\overset{IBP}{=}-\frac{i\hbar}{m}\int\psi^*\frac{\partial}{\partial x}\psi\,dx=\frac{1}{m}\int\psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\,dx$$

任意算符 $\langle\hat{O}\rangle_t=\int\psi^*\hat{O}\,\psi\,dx$

高斯波包 ⟶ 扩散

(选做：Plot)

自由波包 ψ 的 $\langle\hat{x}\rangle$，$\langle\hat{p}_x\rangle$

$$\psi=\frac{1}{\sqrt{\ }}e^{\frac{i}{\hbar}(p_0x-\frac{p_0^2}{2m}t)}e^{-\frac{(x-\frac{p_0}{m}t)^2}{2\alpha^2\hbar^2\tau}},\ \tau=m\hbar\alpha^2$$

HW-2

定态 S.E. (Schrodinger Eqn)

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

$\hookrightarrow \frac{\partial V}{\partial t}=0.$

分离变量

$$\psi(x,t)=\phi(x)T(t)$$

$$\frac{i\hbar}{T}T'=\frac{\hat{H}\phi(x)}{\phi(x)}=E$$

$$\therefore\begin{cases}T(t)=e^{-\frac{i}{\hbar}Et}\\ \hat{H}\phi=E\phi\end{cases}$$

— 本征方程 ⇒ 定态薛定谔方程 TISE

$$\psi(x,t)=\phi_E(x)e^{-\frac{iEt}{\hbar}}\quad\cong\ \phi_{E+\alpha}e^{-\frac{i}{\hbar}(E+\alpha)t}$$

TISE

$$\underbrace{\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right)}_{\hat{H}}\phi_E(x)=\underbrace{E}_{\text{本征值}}\phi_E(x)$$

{斯特姆-刘维尔方程}

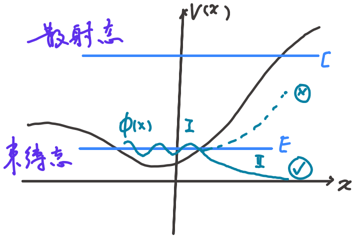
定态下，$\frac{\partial\hat{O}}{\partial t}=0$，则 $\frac{\partial\langle\hat{O}\rangle_t}{\partial t}=0.$

其中 $\langle\hat{O}\rangle_t=\int\psi_E^*(x,t)\,\hat{O}\,\psi_E(x,t)\,dx.$

$$=\int\phi_E^*(x)\,\hat{O}\,\phi_E(x)\,dx.\qquad(=\langle\hat{O}\rangle_{t=0})$$

边界条件：

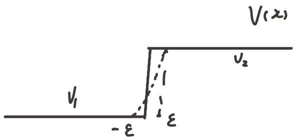
$$\frac{d^2\phi(x)}{dx^2} = \frac{2m}{\hbar^2}[V(x)-E]\,\phi(x)$$



$$\Rightarrow \begin{cases} \phi_{I}(x_2) = \phi_{II}(x_2) \\ \phi_{I}'(x_2) = \phi_{I}'(x_2) \end{cases} \Rightarrow \text{量子化}$$

在 $V(x)$ 有限区域内，$\phi(x)$ 和 $\phi'(x)$ 连续，取有限值

$$\lim_{\varepsilon\to 0}[\phi'(\varepsilon) - \phi'(-\varepsilon)] = \frac{2m}{\hbar}\int_{-\varepsilon}^{+\varepsilon} \underbrace{[E-V(x)]}_{\text{有限}}\phi(x)\,dx = 0.$$



dist theory proves

$$\psi(x) = \underbrace{\tilde{\psi}(x)}_{\text{连续}} + \underbrace{\theta(x)}_{\text{阶跃}}$$

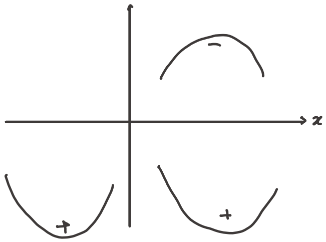
$$\psi'(x) \sim b\,\delta(x) \qquad \psi''(x) \sim b\,\delta'(x)$$

$$\xRightarrow{\text{TISE}} b\,\delta' \sim \tilde{\psi} + \theta$$

$$\Downarrow$$

$$b = 0.$$

波函数形式 $|\psi''(x)|$



$$T = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \sim \frac{-1}{2m}\left(i\hbar\frac{\partial}{\partial x}\right)^2$$

$|\psi''|\uparrow \Rightarrow p\uparrow,\ \lambda\downarrow.$

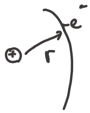
$\psi'' > 0$ 凹，< 0 凸.

分立能级振荡定理

当分立能级按大小顺序排列，一般第 $(n+1)$ 个能级的波函数在取值范围内有 n 个节点（$\phi(x) = 0$），不包括边界和无穷远.

氢原子能级

$n=1.\quad E=\frac{p^2}{2m}$



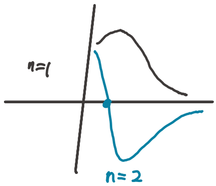
$\Delta x\,\Delta p_x\sim\hbar$

$p=\frac{\hbar}{r}$

$\Rightarrow E=\frac{\hbar^2}{2mr^2}-\frac{e}{r}=\frac{A}{2r^2}-\frac{B}{r}$

$\frac{dE}{dr}=0\Rightarrow r=\frac{A}{B}=\frac{\hbar^2}{me^2}.$ Bohr 半径.

$E=-\frac{1}{2}\frac{B^2}{A}=-\frac{me^4}{2\hbar^2}$



n=2 → 有一个节点，get $p=\hbar/(\frac{r}{2})$

$\Rightarrow\cdots\quad E_{n=2}=\frac{4\hbar^2}{2mr^2}-\frac{e^2}{r}$

→ 同理，$r=4a_B$

$E_{n=2}=\frac{1}{4}E_{n=1}.$

$\xrightarrow{\text{推广}}\quad r_n=n^2a_B$

$E_n=\frac{1}{n^2}E_{n=1}$

一般性的 $\psi(x,t=0)\neq\phi_E$，假设只有离散解.

$\hat{H}\phi_n(x)=E_n\phi_n\qquad n=1,2,\cdots\infty.$

定态 $\psi_n(x)=\phi_n e^{-iEt/\hbar}\longrightarrow\{\phi_n\}$完备.

$\psi(x,t=0)=\sum_{n=1}^{\infty}c_n\phi_n(x).$

$c_n=\int\phi_n^*(x)\,\psi(x,0)\,dx.$

演化行为由相互作用 $V(x)$ 决定 ⇐ t

与初态无关).

⇓

动力学.

$\psi(x,t)=\sum_{n=1}^{\infty}c_n\phi_n(x)e^{-iE_nt/\hbar}$

$$\psi(x,t) = \sum_n c_n e^{-\frac{i}{\hbar}E_n t}\phi_n(x)$$

$$= \sum_n c_n e^{-\frac{i}{\hbar}\hat{H}t}\phi_n(x)$$

$$= e^{-\frac{i}{\hbar}\hat{H}t}\underbrace{\sum_n c_n\phi_n(x)}_{\psi(x,0)}$$

$\Longrightarrow$ 结论 $\psi(x,t) = \underbrace{e^{-\frac{i}{\hbar}\hat{H}t}}_{\text{时间演化算符}}\psi(x,0)$

1) 归一化

$$1 = \int_{-\infty}^{+\infty}|\psi(x,t)|^2 dx$$

$$= \sum_{nm} c_n^* c_m e^{\frac{i}{\hbar}(E_n - E_m)t}\underbrace{\int_{-\infty}^{+\infty}\phi_n^*\phi_m dx}_{\delta_{mn}}.$$

$$= \sum_n c_n^* c_n = \sum_n |c_n|^2$$

2) 能量均值

$$\langle\hat{H}\rangle = \int\psi^*\hat{H}\psi\, dx \xlongequal{\text{Dirac符号}} \langle\psi|\hat{H}|\psi\rangle$$

$$= \int\sum_n c_n^*\phi_n^* e^{\frac{i}{\hbar}E_n t}\hat{H}\sum_m c_m\phi_m(x)e^{-\frac{i}{\hbar}E_m t}dx$$

$$= \sum_{nm} c_n^* c_m e^{\frac{i}{\hbar}(E_n - E_m)t}E_m\int\phi_n^*\phi_m dx.$$

$$= \sum_n E_n|c_n|^2$$

类似地，$\langle\hat{x}\rangle = \langle\psi|x|\psi\rangle$

$$= \int x|\psi(x,t)|^2 dx.$$

任意算符 $\hat{O}$

$\langle\hat{O}\rangle = \langle\psi^*|\hat{O}|\psi\rangle \Rightarrow$ 找 $\hat{O}$ 的本征函数. $\langle\hat{O}\rangle = \sum_n O_n|c_n|^2$

双态系统

$$E_2,\ \phi_2$$

$$\hat{H}\phi_{1,2} = E_{1,2}\,\phi_{1,2}$$

$$E_1,\ \phi_1$$

初始时 $\psi(x, t=0) = c_1\phi_1 + c_2\phi_2.$ $\quad (|c_1|^2 + |c_2|^2 = 1)$

$$\langle H\rangle = |c_1|^2 E_1 + |c_2|^2 E_2.$$

$$= E_1\left(|c_1|^2 + |c_2|^2\right) + (E_2 - E_1)|c_2|^2$$

$$= E_1 + (E_2 - E_1)|c_2|^2.$$

令 $c_1 = c_2 = \frac{1}{\sqrt{2}}$

$$\psi(x, t=0) = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

$$P(x,t) = |\psi(x,t)|^2 = \frac{1}{2}|\phi_1|^2 + \frac{1}{2}|\phi_2|^2 + \underline{\underline{\phi_1^*\phi_2 \cos\frac{(E_2 - E_1)t}{\hbar}}}.$$

$$\hat{H} = \frac{1}{2m}\hat{p}_x^2 + V(x). \qquad \hat{p}_x = -i\hbar\frac{\partial}{\partial x}$$

算符的函数

$$\hat{A}\,\phi_i(x) = a_i\phi_i(x)$$

$$\hat{A}^n\phi_i(x) = a_i^n\phi_i(x).$$

$f(\hat{A}) \Rightarrow$ $\quad f(\hat{A})\phi_i(x) = f(a_i)\,\phi_i(x).$

$f(\hat{A})$ 和 $\hat{A}$ 具有相同本征函数

展开：$f(a_i) = \sum_0^{\infty} f^{(n)}(0)\frac{a_i^n}{n!}$ $\qquad f(\hat{A}) = \sum\frac{f^{(n)}(0)\hat{A}^n}{n!}$

$$f(\hat{A})\phi_i(x) = f(a_i)\phi_i(x)$$

动量空间中的 S.E.

$$i\hbar\frac{\partial}{\partial t}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V\psi(x,t).$$

$\int e^{-\frac{ipx}{\hbar}}dx$

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}}\int \phi(p,t)e^{i\frac{px}{\hbar}}dp$$

$$\phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}}\int \psi(x,t)e^{-i\frac{px}{\hbar}}dx.$$

{需要构造}

$$i\hbar\frac{\partial}{\partial t}\phi(p,t) = \frac{p^2}{2m}\phi(p,t) + V(\hat{x})\phi(p,t)$$

$$\frac{1}{\sqrt{2\pi\hbar}}\int V(x)\psi(x,t)e^{-\frac{ipx}{\hbar}}dx = \frac{1}{\sqrt{2\pi\hbar}}\int\sum_{n=0}^{\infty}\frac{V^{(n)}(0)}{n!}\hat{x}^n\psi(x,t)e^{-i\frac{px}{\hbar}}dx.$$

$\hat{x}^n$ 项为

$$\frac{1}{\sqrt{2\pi\hbar}}\int\psi(x,t)\cdot x^n e^{-i\frac{px}{\hbar}}dx.$$

$$= \frac{1}{\sqrt{2\pi\hbar}}\int\psi(x,t)\left(i\hbar\frac{\partial}{\partial p}\right)^n e^{-\frac{ipx}{\hbar}}dx.$$

$$= \left(i\hbar\frac{\partial}{\partial p}\right)^n\phi(p,t).$$

$$\therefore\ V(x)\psi(x,t) = \sum_{n=0}^{\infty}\frac{V^{(n)}(0)}{n!}\left(i\hbar\frac{\partial}{\partial p}\right)^n\phi(p,t)$$

$$= V\left(i\hbar\frac{\partial}{\partial p}\right)\cdot\phi(p,t).$$

$\hat{x} = +i\hbar\frac{\partial}{\partial p}.$

结论：

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

测量假设

物理可观测量 = 算符 $\hat{O}$

实验测量 = $\langle \hat{O} \rangle$

客体与遵从经典规律的仪器之间的相互作用 ⇒ 量子力学

$$\text{量子体系} \xleftrightarrow{\text{与观测者无关}} \text{经典仪器}$$

量子体系	经典仪器
任意测量都会影响量子体系（非仪器误差）	足够精确服从经典规律
测量值是体系的属性.	仪器状态测量前后发生可观测的变化

重复测量

退相干 → Copenhagen.

$$\psi(x,t) \longrightarrow \underset{}{\overset{t_1}{\boxed{A}}} \xrightarrow[\psi?\ \Downarrow\ \phi_1]{a_1} \overset{t_1+\varepsilon}{\boxed{A}} \xrightarrow[\phi_1]{a_1} \overset{t_1+2\varepsilon}{\boxed{A}} \xrightarrow[\phi_1]{a_1} \cdots\cdots$$

$t' = t + \Delta t$.

$$\hat{A}\phi_1(x) = a_1\phi_1(x)$$

实验结论.

⇓

理论：波函数坍缩假设

"系综"

观测 ψ 的 a_n，ϕ_n：制备多个 $\psi(x,t)$，重复观测

测量 N 次，得到 $P(a_i) = \dfrac{N(a_i)}{\sum N(a_i)}$

⇒ QM测量的性质

$$\langle \hat{A} \rangle = \sum_{i=1} P(a_i)\, a_i$$

(续).

$$\hat{A}\phi_i = a_i\phi_i$$

$$\hat{A}\left(e^{-\frac{i}{\hbar}\hat{H}t}\{\phi_i\}\right) \overset{?}{=} a_i e^{-\frac{i}{\hbar}E_n t}\phi_i \qquad \Big]\, t$$

$\Rightarrow$ 要求 $[H, A] = 0$

└ 对易子 $[H, A] = HA - AH$.

独立"自由度"

$$\psi \longrightarrow \boxed{\hat{A}} \xrightarrow[\phi_i]{a_i} \boxed{B} \xrightarrow[f_j]{b_j} \boxed{A} \xrightarrow[\phi_i]{a_i} \boxed{B} \xrightarrow[f_j]{b_j'}$$

$AB = BA$. $\Rightarrow [\hat{A}, \hat{B}] = 0$

$\Rightarrow$ 可同时测出 $\psi \to \boxed{A/B} \xrightarrow[b_j]{a_i} \boxed{A/B} \xrightarrow[b_j]{a_i}$

厄米算符 $\hat{O}$

对任意波函数 ψ 和 ϕ，满足

$$\int \psi^* \hat{O}\phi \, dx = \int (\hat{O}\psi)^* \phi \, dx.$$

取 $\phi = \psi$ 时，$\int \psi^* \hat{O}\psi \, dx = \int (\hat{O}\psi)^* \psi \, dx$

$$= \left[\int \psi^* \hat{O} \psi \, dx\right]^*.$$

$$\therefore \langle \psi | O | \psi \rangle \in \mathrm{Re}.$$

$$\| $$

$$\langle \hat{O}\psi | \psi \rangle$$

内积 $(\psi, \hat{O}\phi) = (\hat{O}\psi, \phi)$

动量

$$\langle \hat{p} \rangle_\psi^* = \int dx\, \psi^* (-i\hbar \frac{\partial}{\partial x} \psi)$$

$$= \underbrace{i\hbar\, \psi^* \psi \Big|_{-\infty}^{+\infty}}_{0.} - \int dx\, \psi (-i\hbar \frac{\partial}{\partial x} \psi)$$

测量要求：

在对体系影响小时，$\hat{A}$ 和 $\hat{B}$ 可以测得极其精确。

涨落：在一定概率分布的状态中，$\hat{A}$ 与均值的偏差

$$\Delta \hat{A} = \sqrt{(\psi, (\hat{A} - \bar{A})^2 \psi)} \geqslant 0 . \qquad (\hat{A}\psi = \bar{A}\psi).$$

极其精确：$\Delta \hat{A} = 0$ 即 $(\hat{A} - \bar{A})\psi = \phi$

测量 $\hat{A}$ 和 $\hat{B}$.

任意两个算符的涨落满足不确定关系。

$$(\Delta \hat{A})^2 (\Delta \hat{B})^2 \geqslant \frac{1}{4} \underbrace{\left(\overline{i[\hat{A}, \hat{B}]} \right)^2}$$

$$\begin{cases} [\hat{A}, \hat{B}] = 0 \\ [\hat{A}, \hat{B}] \neq 0 \quad \underbrace{\text{但 } \overline{i[\hat{A}, \hat{B}]} = 0.}_{\text{特殊的 } \psi.} \end{cases}$$

Schwarz 不等式：

若 ψ_1, ψ_2 平方可积，则有：

$$(\psi_1, \psi_1)(\psi_2, \psi_2) \geqslant |(\psi_1, \psi_2)|^2$$

证：平方可积：$(\psi_{1,2}, \psi_{1,2}) \geq 0$.

考虑任意 ψ，$(\psi, \psi) \geq 0$.

令 $\psi = \psi_1 + \lambda\psi_2$

$\lambda \longrightarrow$ 任意参数 λ.

$$(\psi, \psi) = (\psi_1, \psi_1) + \lambda^*(\psi_2, \psi_1) + \lambda(\psi_1, \psi_2) + |\lambda|^2(\psi_1, \psi_2) \geq 0 .$$

令 $\lambda = -\frac{(\psi_2, \psi_1)}{(\psi_2, \psi_2)}$

$$(\psi, \psi) = (\psi_1, \psi_1) - \frac{(\psi_2, \psi_1)^*(\psi_2, \psi_1)}{(\psi_2, \psi_2)} - \cdots$$

$$= (\psi_1, \psi_1) - \frac{|(\psi_2, \psi_1)|^2}{(\psi_2, \psi_2)} \geq 0$$

$$\therefore (\psi_1, \psi_1)(\psi_2, \psi_2) \geq |(\psi_1, \psi_2)|^2 .$$

$$(\Delta\hat{A})^2 = (\psi, (\hat{A} - \bar{A})^2\psi) \overset{\text{记}}{=} (\psi, \hat{a}^2\psi).$$

$$(\Delta\hat{B})^2 = (\psi, \hat{b}^2\psi)$$

$$(\Delta\hat{A})^2(\Delta\hat{B})^2 = (\hat{a}\psi, \hat{a}\psi)(\hat{b}\psi, \hat{b}\psi) \overset{\text{记为}}{\equiv} (\psi_a, \psi_a)(\psi_b, \psi_b)$$

$$\geq |(\psi_a, \psi_b)|^2$$

$$(\psi_a, \psi_b) \equiv (\hat{a}\psi, \hat{b}\psi) \qquad \{Re + i\,Im\}$$

$$= (\psi, \hat{a}\hat{b}\psi) = (\psi, \tfrac{1}{2}(\hat{a}\hat{b} + \hat{b}\hat{a})\psi) - i(\psi, \underbrace{\tfrac{i}{2}(\hat{a}\hat{b} - \hat{b}\hat{a})}_{\text{厄米}}\psi)$$

$$\therefore |(\psi_a, \psi_b)|^2 \geq |(\psi, \tfrac{i}{2}[\hat{a}, \hat{b}]\psi)|^2$$

$$[\hat{a}, \hat{b}] = [\hat{A} - \bar{A}, \hat{B} - \bar{B}] = [\hat{A}, \hat{B}]$$

$$[\hat{x}, \hat{p}_x]\psi = (\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\psi$$
$$= x(\hat{p}_x\psi) - \hat{p}_x(x\psi)$$
$$= x\left(-i\hbar\frac{\partial}{\partial x}\psi\right) - (-i\hbar)\frac{\partial}{\partial x}(x\psi).$$
$$= i\hbar\psi.$$

$$\Rightarrow [\hat{x}, \hat{p}_x] = i\hbar$$

$$\boxed{\Rightarrow (\Delta x)(\Delta p_x) \geq \frac{\hbar}{2}.}$$

测量不兼容

对易算符性质： $[\hat{A}, \hat{B}] = 0$

① 若 $A\psi_a = a\psi_a$

则 $B\psi_a$ 也是本征函数，属于同一本征值.

$$A(B\psi_a) = BA\psi_a = Ba\psi_a = a(B\psi_a)$$

（若无简并，则 $B\psi_a \sim \psi_a$）

② ψ_1, ψ_2 为 $\hat{A}$ 不同本征值对应的本征函数，

则 $(\psi_1, \hat{B}\psi_2) = 0.$

证：
$$\hat{A}(B\psi_2) = a_2(B\psi_2)$$
$$\hat{A}\psi_1 = a_1\psi_1$$
$$\Rightarrow (\psi_1, \hat{B}\psi_2) = 0$$

③ $\hat{A}$ 和 $\hat{B}$ 共同的本征函数组构成波函数空间的正交归一基 ☆

④ 如果存在由 $\hat{A}$ 和 $\hat{B}$ 的共同本征函数构成的基，则 $[\hat{A}, \hat{B}] = 0$

可测量物理量完全集

如一组算符的集合 $\{\hat{A}, \hat{B}, \cdots\}$ 的共同本征函数构成正交归一基，且这组基是唯一的，则称之为可测量物理量完全集

$\{\}$ 中任意两个 $[\hat{A}_i, \hat{A}_j] = 0$.

$\hat{A}$ ① $\{u_n\}$ 无简并 $\Rightarrow$ 完全集.

② $\{u_n\}$ 有简并　　$a_n \rightarrow \{u_n^i\}$　$i = 1, 2, \cdots g_n$

明确描述物理：解除简并　　　　g_n：a_n 的简并度

考虑 $\hat{B}$，$[\hat{A}, \hat{B}] = 0$

$$\hat{B} u_n^i = b_n^i u_n^i$$
$$\hat{B} u_n^j = b_n^j u_n^j$$

$b_n^i \neq b_n^j \rightarrow \{A, B\}$ 为完全集

若还有简并，依次类推 $\{A, B, C, \cdots\}$.

$\Rightarrow$ 态：$u_{a_n b_m c_i d_j e_k \cdots} \Rightarrow (a_n, b_m, c_i, d_j \cdots)$.

最小可观测量完全集 $\Rightarrow$ 只包含想考虑的物理对象.

$[\hat{A}, \hat{B}] = 0$，　$\hat{A} u_{a_n b_p} = a_n u_{a_n b_p}$

相容.

$\hat{B} u_{a_n b_p} = b_p u_{a_n b_p}$.

任意态：$\psi = \sum_{np} C_{np} u_{np}$

测量ψ：

$$\psi \xrightarrow[a_n]{\hat A} \psi_n' \xrightarrow[b_p]{\hat B} \psi_{np}' = u_{np} \Rightarrow P(np) = |C_{np}|^2$$

$$\downarrow$$

$$\frac{1}{\cdots}\sum_p C_{np} u_{np}$$ 不改变系数.

$$\Downarrow$$

$$\frac{1}{\sqrt{\sum_p |C_{np}|^2}}\sum_p C_{np} u_{np}, \quad P(n) = \sum_p |C_{np}|^2.$$

测量顺序不改变测量结果及概率

若完全集中包含 $\hat H$ ⇒ 守恒量完全集 $\{\hat H, \hat A, \hat B, \cdots\}$

$$i\hbar\frac{\partial}{\partial t}\psi = \hat H\psi \to \frac{\partial \psi}{\partial t} = \frac{\hat H}{i\hbar}\psi \ ; \quad \frac{\partial \psi^*}{\partial t} = \frac{-\hat H}{i\hbar}\psi^*$$

$$\frac{d\langle \hat A\rangle_\psi}{dt} = \frac{d}{dt}\int \psi^* \hat A \psi \, dx$$

$$= \int \frac{\partial \psi^*}{\partial t}\hat A \psi \, dx + \cancel{\int \psi^* \frac{\partial \hat A}{\partial t}\psi \, dx} + \int \psi^* \hat A \frac{\partial \psi}{\partial t} dx$$

$\hat A$ 不含时

$$= \int \frac{-1}{i\hbar}\hat H \psi^* \hat A \psi \, dx + \frac{1}{i\hbar}\psi^* \hat A \hat H \psi \, dx.$$

$$= \frac{1}{i\hbar}\int \psi^* (\hat A \hat H - \hat H \hat A)\psi \, dx. \xrightarrow[{[\hat A, \hat H] = 0}]{} 0.$$ 守恒.

Ehrenfest 定理.

$$\frac{d\langle \hat A\rangle_\psi}{dt} = \frac{1}{i\hbar}\langle [\hat A, \hat H]\rangle_\psi$$

(Notice：与定态（$\hat H$的本征态）区分)

$$\frac{d\langle \hat x\rangle_\psi}{dt} = \frac{1}{i\hbar}\langle [\hat x, \frac{p_x^2}{2m} + V(x)]\rangle_\psi = \frac{1}{i\hbar}\frac{1}{2m}\langle [\hat x, \hat p_x^2]\rangle.$$

$$[\hat A \hat B, \hat C] = [\hat A, \hat C]\hat B + \hat A[\hat B, \hat C]$$

$$[\hat A, \hat B^n] = \sum_{s=0}^{n-1}\hat B^s [\hat A, \hat B]\hat B^{n-s-1}$$

$$[\hat A, f(\hat B)] = \cancel{[\hat A, f_0]} + f'[\hat A, \hat B] + \cdots + \frac{1}{n!}f^{(n)}[\hat A, \hat B^n]$$

若 $[[\hat A, \hat B], \hat B] = 0$

$$[\hat A, f(\hat B)] = [\hat A, \hat B](f' + f''\hat B + \cdots)$$

$$= [\hat A, \hat B]\frac{df(\hat B)}{d\hat B}$$

now $[\hat{x}, \hat{p}_x] = i\hbar$, $[[\hat{x}, \hat{p}_x], \hat{p}_x] = 0$

$$\therefore \quad \frac{d\langle \hat{x} \rangle}{dt} = \frac{\langle p_x \rangle}{m}$$

$$[x, p_x] = i\hbar$$

又. $[\hat{p}_x, \hat{H}] = [\hat{p}_x, V(x)] = -i\hbar \frac{\partial V(x)}{\partial x}$.

$$\frac{d\langle \hat{p}_x \rangle}{dt} = \frac{1}{i\hbar}\left(-i\hbar \left\langle \frac{\partial V}{\partial x} \right\rangle\right) = -\left\langle \frac{\partial V}{\partial x} \right\rangle.$$

算符共轭与转置

$\forall \phi, \psi$, $\quad \phi = \hat{A}\psi$. $\quad \phi^* = \hat{B}\psi^*$

则称 $\hat{B} = \hat{A}^*$

性质: $(\hat{A}\hat{B})^* = \hat{A}^*\hat{B}^*$

$(A^*)^* = \hat{A}$

$\forall \phi, \psi$, $\quad \int \psi^* \hat{A}\phi \, dx = \int \phi \hat{B} \psi^* dx$

则称 $B = \tilde{A}$ or $B = A^T$

$(\widetilde{AB}) = \tilde{B}\tilde{A}$

厄米共轭 $\hat{O}^\dagger = \widetilde{\hat{O}^*}$ $\quad (O^\dagger)^\dagger = O$

$$\int \psi^* O^\dagger \phi \, dx = \int \phi \tilde{O}^* \psi^* dx = \int (O\psi)^* \phi \, dx.$$

即 $(\psi, O^\dagger \phi) = (O\psi, \phi)$

$\forall \phi \Rightarrow \psi^* \hat{O}^\dagger = (\hat{O}\psi)^*$

$(\hat{H}\hat{F}\hat{G}\psi)^* = \psi^* (\hat{H}\hat{F}\hat{G})^\dagger$

$(\hat{H}\hat{F}\hat{G}\psi)^* = (\hat{F}\hat{G}\psi)^* \hat{H}^\dagger = (\hat{G}\psi)^* F^\dagger H^\dagger = \psi^* G^\dagger F^\dagger H^\dagger$

$\Rightarrow (HFG)^\dagger = G^\dagger F^\dagger H^\dagger$

厄米算符 $\int \psi^* \hat{O} \phi \, dx = \int (\hat{O}\psi)^* \phi \, dx = \int \psi^* \hat{O}^+ \phi \, dx$

厄米算符定义

$\Rightarrow$ 即 $\hat{O} = \hat{O}^{+}$

$$(\hat{A}\hat{B})^+ = \hat{B}\hat{A} \xlongequal{[A,B]=0} \hat{A}\hat{B}.$$

1) $\forall \psi$, $\langle \psi | \hat{O} | \psi \rangle = \langle \hat{O} \rangle \in \mathrm{Re}$.

$$\Rightarrow \hat{O}^{+} = \hat{O}$$

$$(\psi, \hat{A}\psi) = (\psi, \hat{A}\psi)^* = (\hat{A}\psi, \psi) = (\psi, \hat{A}^{+}\psi) \Rightarrow \hat{A} = \hat{A}^{+}.$$

2) $\forall \hat{A} = \hat{A}^{+}$, $\langle \hat{A}^2 \rangle_\psi \geq 0$.

$$(\psi, \hat{A}^2\psi) = (\hat{A}\psi, \hat{A}\psi) \geq 0.$$

3) $A = A^{+}$, $B = B^{+}$

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

$$(i[\hat{A}, \hat{B}])^{+} = i[\hat{A}, \hat{B}]$$ $i[\hat{A}, \hat{B}]$ 是厄米的.

任意算符都可表示为两个厄米之和

$$\hat{A} = \hat{A}_+ + i\hat{A}_-$$

$$\begin{cases} \hat{A}_+ = \frac{1}{2}(\hat{A} + \hat{A}^{+}) \\ \hat{A}_- = \frac{-i}{2}(\hat{A} - \hat{A}^{+}) \end{cases}$$

Hamiltonian 构造

$$\hat{H} = -\frac{1}{2m}P_x^2 \to -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}.$$

经典 → 量子过渡.

$$\xrightarrow{?} -\frac{1}{2m}\frac{1}{\sqrt{x}}P_x \, x \, P_x \frac{1}{\sqrt{x}} \to -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \underbrace{\frac{1}{4x^2}}_{?}\right)$$

量子化方案

(1) 对称方案 $\quad xP_x \to$ 对称化. $\dfrac{xP_x + P_x x}{2}$.

(2) Weyl.

(3) Dirac.

(4) Von-Neumann.

① 在直角坐标系. $p_i \to -i\hbar\frac{\partial}{\partial x_i}$ 再转入其它系

② $\sum_i P_i f(x_i) \to \frac{1}{2}[pf + fp]$.

量子力学中的时间 t.

NR, QM. $\quad \frac{\partial}{\partial t} \quad \frac{\partial}{\partial x}. \qquad i\hbar\frac{\partial}{\partial t}\psi = \hat{H}\psi$ $\quad V(x)$

$t \to \hat{t}$? 测量时间?

$x. \, p \to \hat{x}, \hat{p} \to [\hat{x}, \hat{p}]. \Rightarrow \Delta x \Delta p \geq \frac{\hbar}{2}.$

$E. \, t. \to [\hat{E}, \hat{t}] = i\hbar$?

Pauli (1933) 不存在与正则坐标动量对易关系对应的哈密顿算符-时间算符对易关系

证: 若存在 $[\hat{t}, \hat{H}] = i\hbar$, 引入 $F(\hat{t})$

$$[\hat{H}, F(\hat{t})] = [\hat{H}, \hat{t}]\frac{\partial F(\hat{t})}{\partial t}$$

设 $\hat{H}\Phi_E = E\Phi_E$, 且 $F(\hat{t}) = e^{i\alpha\hat{t}}$ $\quad \alpha \to$ Const

$$\hat{H}\left(e^{i\alpha\hat{t}}\phi_E\right) = e^{i\alpha\hat{t}}\hat{H}\phi_E - \left(i\hbar\frac{\partial}{\partial t}e^{i\alpha t}\right)\phi_E$$

$$= E e^{i\alpha\hat{t}}\phi_E + \alpha\hbar e^{i\alpha\hat{t}}\phi_E = (E+\hbar\alpha)\left(e^{i\alpha\hat{t}}\phi_E\right)$$

应与ϕ_E等价　　$\Downarrow$ $E+\hbar\alpha = E$　　㊀ 无离散本征解.

又α可以任取，矛盾.

$\Longrightarrow$ QM中 t 是参数而非算符.

1945 Madelstam - Tamn 不确定关系　　Madelstam

$$\Delta\hat{E}\cdot\underbrace{\Delta t}_{\text{not } \Delta\hat{t}.}$$

$$\Delta\hat{A}\cdot\Delta\hat{E} \geq \frac{1}{2}\left|\overline{[\hat{A},\hat{H}]}\right|$$

当 $\hat{A}$ 不含时，$\dfrac{d\langle\hat{A}\rangle}{dt} = \dfrac{1}{i\hbar}\overline{[\hat{A},\hat{H}]}$

$$\Rightarrow \underbrace{\frac{\Delta\hat{A}}{\left|\frac{d\langle\hat{A}\rangle}{dt}\right|}}_{\text{定义为 } \hat{\tau}_A}\cdot\Delta\hat{E} \geq \frac{\hbar}{2}.$$

即 $\tau_A\cdot\Delta\hat{E} \geq \dfrac{\hbar}{2}$.
$\Downarrow$
$\sim\Delta t$

验证：自由波包

$$\tau_A = \frac{\Delta\hat{x}}{\left|\frac{d\langle\hat{x}\rangle}{dt}\right|} = \frac{\Delta x}{v_g} = \frac{m}{p}\Delta x.$$

NR,
$$E = \frac{p^2}{2m} \Rightarrow \Delta\hat{E} = \frac{p}{m}\Delta p.$$

$$\Big\} \ \tau_A\Delta\hat{E} = \Delta\hat{x}\,\Delta\hat{p} \geq \frac{\hbar}{2}.$$

SR,
$$E^2 = p^2c^2 + m^2c^4 \Rightarrow 2\Delta E\cdot E = 2p\Delta p\cdot c^2$$

$$\Rightarrow \Delta E = \frac{pc^2}{E}\Delta p$$

$$\Delta E\,\hat{\tau}_x = \frac{pc^2}{E}\frac{m}{p}\cdot\Delta x\Delta p = \Delta x\Delta p \geq \hbar/2.$$

1) 制备　如果在Δt内制备，则在Δt中，无法确定系统处于$E=E_0\pm\Delta E$.

2) 测量．要求能量测量的精度小于ΔE，从而可以区分E_0 or $E_0\pm\Delta E$

$\longrightarrow$ 测量时间大于Δt

QM．公理化

1) $\psi(x,t)$　　完备，平方可积

描述几率

2) 演化方程　$i\hbar\frac{\partial}{\partial t}\psi=\hat{H}\psi$

定态 $V=V(x)\Rightarrow$ TISE　$\hat{H}\phi_n=E_n\phi_n$

$$\psi(x,t)=\sum c_n\phi_n e^{-\frac{i}{\hbar}E_nt}\quad(\sim\sum c_n(t)\phi_n)$$

3) 物理可测量 $\hat{O}$．测量值 $\langle\hat{O}\rangle_\psi$.

不依赖时间.

$$\frac{d}{dt}\langle\hat{A}\rangle_\psi=\frac{1}{i\hbar}\overline{[\hat{A},\hat{H}]}.\qquad\Rightarrow[\hat{A},\hat{H}]=0\text{ 时},\ \frac{d\langle\hat{A}\rangle}{dt}=0.$$

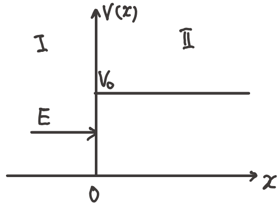
4) 可观测物理守恒量完全集

$$\{\hat{H},\hat{A},\hat{B},\cdots\}\quad\Rightarrow\text{“最小”}$$

5) 测量假设　$\psi(x,t)\xrightarrow[a_n]{\hat{A}}u_n$　　$\hat{A}u_n=a_nu_n$

$$\begin{cases}\psi(x,t)=\sum C_{ij}u_{ij}\\ \hat{A}u_{ij}=a_iu_{ij},\ \hat{B}u_{ij}=b_ju_{ij}\end{cases}\qquad\xrightarrow[a_n]{\hat{A}}\underbrace{\psi'}_{\frac{1}{\sqrt{\ }}\sum_j C_{nj}u_{nj}}\xrightarrow[b_m]{\hat{B}}u_{nm}$$

6) 不确定关系.



$$V(x)=\begin{cases} V_0, & x>0 \\ 0, & x<0. \end{cases}$$

相移.

$$u(x)=\begin{cases} u_I(x)=A\sin(kx+\delta) & \begin{cases} k=\sqrt{2mE/\hbar^2} \\ x<0 \end{cases} \\ u_{II}(x)=Be^{-Kx}+\cancel{Ce^{Kx}}\ \to\infty. & \begin{cases} K=\sqrt{2m(V_0-E)/\hbar^2} \\ x>0 \end{cases} \end{cases}$$

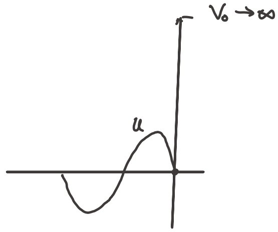
$x=0$ $\quad u_I(0)=u_{II}(0) \qquad A\sin\delta = B.$

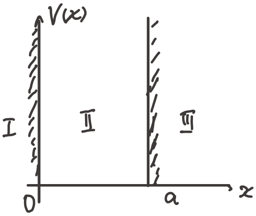
$\quad u_I'(0)=u_{II}'(0) \qquad kA\cos\delta=-KB.$

$\Rightarrow \tan\delta=-\dfrac{k}{K}, \quad \dfrac{A}{B}=\dfrac{1}{\sin\delta}.$

⊛ $V_0\to\infty$, $K \gg k$.

$\tan\delta\to 0 \Rightarrow \delta=0.$





II: $\psi''+k^2\psi=0, \quad k=\sqrt{\dfrac{2mE}{\hbar^2}}$

$\Rightarrow \psi = A\cos kx + B\sin kx.$

I, III: $\psi=0.$

边界 $\Rightarrow \psi_{II}(x=0)=\psi_{II}(x=a)=0.$

$A=0$

$\sin ka = 0. \quad \Rightarrow k=\dfrac{n\pi}{a}$

$\therefore E_n=\dfrac{\hbar^2}{2m}\left(\dfrac{n\pi}{a}\right)^2=\dfrac{n^2\pi^2\hbar^2}{2ma^2} \quad \underline{\propto n^2}$

归一化 $|A|^2\int_0^a \sin^2\left(\frac{n\pi}{a}x\right)dx=1 \Rightarrow A=\sqrt{\frac{2}{a}}. \qquad \psi_n=\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}.$

$$\Rightarrow \langle \hat{x} \rangle = \int_0^a x\psi^2 dx = \frac{a}{2}$$

$$\langle \hat{x}^2 \rangle = \int_0^a x^2\psi^2 dx = \frac{a^2}{3}\left(1 - \frac{3}{2n^2\pi^2}\right)$$

$$\Big\} \langle \Delta x \rangle = a\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}$$

$n \to \infty$, $\langle \hat{x}^2 \rangle_{QM.} \to \langle \hat{x}^2 \rangle_{CL.}$

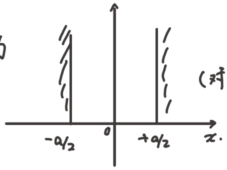
$$\langle \hat{p} \rangle = 0$$

$$\langle \hat{p}^2 \rangle = \frac{n^2\pi^2\hbar^2}{a^2}$$

$$\Big\} \langle \Delta p \rangle = \frac{n\pi\hbar}{a}$$

$$\frac{|E_n - E_{n+1}|}{|E_n|} = \frac{2n+1}{n^2} \xrightarrow[n\to\infty]{} 0 \text{ (连续)}$$

移动



(对称)

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

$$u_n(x) = \begin{cases} \sqrt{\frac{2}{a}}\cos\left(\frac{n\pi}{a}x\right), & n = 1, 3, \cdots \\ \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right), & n = 2, 4, \cdots \end{cases}$$

空间反演 $x \to -x$. (宇称 Parity). $\hat{P}$ $(x \to -x)$.

$V(x)$ 具有空间反演对称性 $V(-x) = V(x)$

如果 $\phi(x)$ 是 SE 对应 "E" 的本征解，则 $\phi(-x)$ 也是.

$\psi(x)$ 是 S.E. 解

$Re(\psi(x))$ 和 $Im(\psi(x))$ 也都是同一本征值的解.

设两个 ψ_1, ψ_2 独立，对应同一个 E.

$$\underbrace{\psi_1\psi_2' - \psi_2\psi_1' = \text{Const.}}_{\text{令}x\to\infty\ =\ \text{Const}=0.} \qquad \left(\frac{\psi_1''}{\psi_1} = \frac{2m}{\hbar}(V-E) = \frac{\psi_2''}{\psi_2}\right)$$

$$\to \frac{\psi_1}{\psi_1'} = \frac{\psi_2}{\psi_2'} \Rightarrow \psi_1 = C\psi_2$$

$\Rightarrow$ 得必不独立 $\Rightarrow$ 一维不简并

从而，一维波函数

$$\boxed{Re(\psi) = C\, Im(\psi).}$$

$V(-x) = V(x)$，对应每个本征值 E 总可找到完备解，其中任一个解都有确定的宇称

$$\begin{cases} \hat{H}\phi(x) = E\phi(x) \\ \hat{H}\phi(-x) = E\phi(-x) \end{cases}$$

$$\begin{cases} \text{偶} & \phi(x) + \phi(-x) \\ \text{奇} & \phi(x) - \phi(-x). \end{cases}$$

2D 势阱

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

$\psi(x,y) = X(x)Y(y)$ 分离变量.

$$\Rightarrow \quad \frac{X''}{X} + \frac{Y''}{Y} = -\frac{2mE}{\hbar^2} \qquad E \Rightarrow E_x + E_y.$$

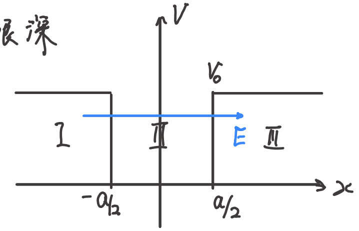
$$\begin{cases} E_{n_x n_y} = \dfrac{\pi^2\hbar^2}{2m}\left(\dfrac{n_x^2}{a^2} + \dfrac{n_y^2}{b^2}\right). \\ \psi_{n_x n_y}(x,y) = \sqrt{\dfrac{4}{ab}}\sin\left(\dfrac{n_x\pi x}{a}\right)\sin\left(\dfrac{n_y\pi y}{b}\right). \end{cases}$$

$a=b$ 时，$\psi = \frac{2}{a}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{a}\right) \qquad x \leftrightarrow y.$

$$E_{n_x n_y} = \frac{\pi^2\hbar^2}{2ma^2}(n_x^2 + n_y^2) \Rightarrow \text{简并}$$

$$\begin{cases} \text{对称性：} (1,2) \leftrightarrow (2,1) \\ \text{偶然简并.} \end{cases}$$

1d 有限深



I $\quad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_1 + V_0\psi_1 = E\psi_1$

II $\quad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_2 = E\psi_2$

III $\quad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_3 + V_0\psi_3 = E\psi_3$

$$q = \sqrt{\frac{2m(V_0-E)}{\hbar}} \qquad k = \sqrt{\frac{2mE}{\hbar}}$$

$$\begin{cases} \psi_I = Ae^{qx} \\ \psi_{II} = Be^{ikx} + Ce^{-ikx} \\ \psi_{III} = De^{-qx} \end{cases}$$

(A.B.C.D.E 4个边界 1个归一化)

奇宇称: $\begin{cases} Ae^{qx} \\ C\sin kx \\ De^{-qx} \end{cases}$

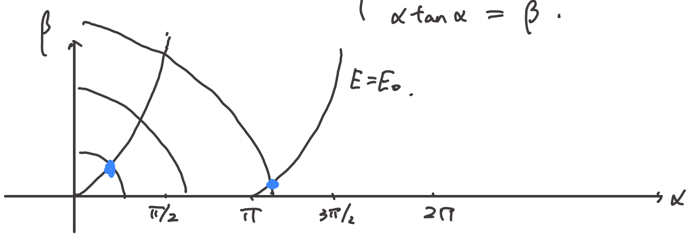
偶宇称: $\begin{cases} Ae^{qx} \\ B\cos kx. \\ De^{-qx} \end{cases}$

奇 $\Rightarrow \cot\left(\frac{ka}{2}\right) = -\frac{q}{k}.$ (numerial: E_n).

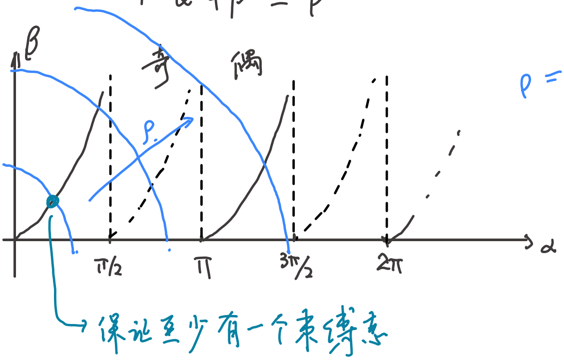
偶 $\Rightarrow \tan\left(\frac{ka}{2}\right) = \frac{q}{k}$ $\quad \left(k^2+q^2 = \frac{2mV_0}{\hbar^2}\right)$

def. $\alpha = \frac{ka}{2}$, $\beta = \frac{qa}{2}.$

$$\begin{cases} \alpha^2+\beta^2 \equiv \rho^2 = \frac{ma^2V_0}{2\hbar^2} \\ \alpha\tan\alpha = \beta. \end{cases}$$



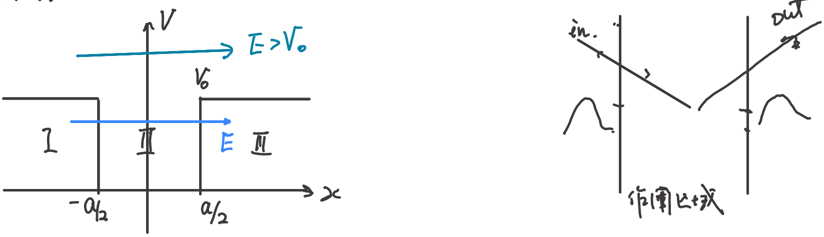
类似地，奇函数 $\begin{cases} \alpha \cot\alpha = -\beta \\ \alpha^2+\beta^2 = \rho^2. \end{cases}$



$\rho = \frac{ma^2V_0}{2\hbar^2}$ ⇒预给定.

当 $V_0\to\infty$. $\rho\to\infty$. 无限深势阱. $\alpha\to\frac{n\pi}{2}$.

散射



平面波近似
$$\psi(x,t) = Ae^{\frac{i}{\hbar}(px-Et)}$$

几率流通量 $j(x,t) = \pm\frac{\hbar k}{m}|A|^2$

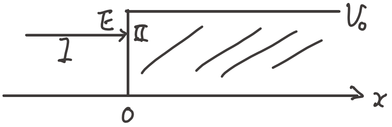
箱归一化. $\int_0^L |A|^2 dx = 1 \;=\!=\!=\; \frac{1}{\sqrt{L}}$

$\Big\}\; j(x,t)\sim\frac{1}{T}.$ 单位时间粒子数

$j_{入}$, $j_{反}$, $j_{透}$ ⇒ 定义：

$$R = \left|\frac{j_{反}}{j_{入}}\right| \quad 反射份额$$

$$T = \left|\frac{j_{透}}{j_{入}}\right| \quad 透射份额.$$



$x<0$: $\psi_1'' + k^2\psi_1 = 0.$

$x>0$: $\psi_2'' - \kappa^2\psi_2 = 0.$

其中 $k^2 = 2mE/\hbar^2$, $\kappa^2 = \frac{2m(V_0-E)}{\hbar^2}$

通解

$$\psi = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x<0 \\ De^{-\kappa x}, & x>0 \end{cases}$$

$$\begin{cases} A + B = D. \\ A - B = i\frac{\kappa}{k}D \end{cases} \Rightarrow \begin{cases} A = \frac{D}{2}\left(1+i\frac{\kappa}{k}\right) \\ B = \frac{D}{2}\left(1-i\frac{\kappa}{k}\right). \end{cases}$$

$$j_{入} = \frac{1}{m}\mathrm{Re}(\psi^*\hat{p}_x\psi) = \frac{\hbar k}{m}\frac{D^2}{4}\left(1+\left(\frac{\kappa}{k}\right)^2\right).$$

$$j_{反} = \frac{1}{m}\mathrm{Re}(\psi^*\hat{p}_x\psi) = -\frac{\hbar k}{m}\frac{D^2}{4}\left(1+\left(\frac{\kappa}{k}\right)^2\right).$$

$$j_{透} = \frac{1}{m}\mathrm{Re}(\psi^*\hat{p}_x\psi) = 0.$$

$$\left.\right\} \quad R = 1, \quad T = 0.$$

若 $E > V_0$

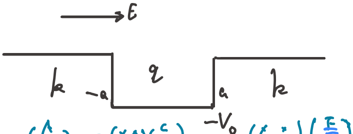
$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x<0. \\ Ce^{iKx} + \cancel{De^{-iKx}}, & x>0. \end{cases}$$

$$\Rightarrow \quad \psi = \begin{cases} A e^{ikx} + A \dfrac{k-K}{k+K} e^{-ikx} \\[2ex] A \dfrac{2k}{k+K} e^{iKx}. \end{cases}$$

$$R = \left(\frac{k-K}{k+K}\right)^2, \quad T = \left(\frac{2k}{k+K}\right)^2 \cdot \left(\frac{K}{k}\right) = \frac{4kK}{(k+K)^2}$$

一维势阱 Ramsauer - Townsend

1D 有限深



$$k = \sqrt{2mE/\hbar^2}$$

$$q = \sqrt{2m(E+V_0)/\hbar^2}$$

$$\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} \times & \times \\ \times & \times \end{pmatrix}\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} \times & \times \\ \times & \times \end{pmatrix}\begin{pmatrix} E \\ G \end{pmatrix}$$

$$\psi = \begin{cases} A e^{ikx} + B e^{-ikx} \\ C e^{iqx} + D e^{-iqx} \\ F e^{iqx} \end{cases}$$

{(物理：3中无左行波)}

边界 $\Rightarrow$

$$\begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} \frac{1}{2}\left(1+\frac{q}{k}\right) e^{i(k-q)a} & \frac{1}{2}\left(1-\frac{q}{k}\right) e^{i(k+q)a} \\ \frac{1}{2}\left(1-\frac{q}{k}\right) e^{-i(k+q)a} & \frac{1}{2}\left(1+\frac{q}{k}\right) e^{i(q-k)a} \end{bmatrix} \begin{bmatrix} C \\ D \end{bmatrix}$$

$$\begin{bmatrix} C \\ D \end{bmatrix} = \begin{bmatrix} \frac{1}{2}\left(1+\frac{k}{q}\right) e^{i(k-q)a} & \frac{1}{2}\left(1-\frac{k}{q}\right) e^{-i(k+q)a} \\ \frac{1}{2}\left(1-\frac{k}{q}\right) e^{i(k+q)a} & \frac{1}{2}\left(1+\frac{k}{q}\right) e^{i(q-k)a} \end{bmatrix} \begin{bmatrix} F \\ G \end{bmatrix}$$

$$\Rightarrow \begin{cases} \dfrac{F}{A} = e^{-i(2ka)} \dfrac{2kq}{2kq\cos(2qa) - i(k^2+q^2)\sin 2qa} = \sqrt{T} \\ \dfrac{B}{A} = i e^{-i(2ka)} \dfrac{(q^2-k^2)\sin 2qa}{2kq\cos 2qa - i(k^2+q^2)\sin 2qa} = \sqrt{R}. \end{cases}$$

令 $\varepsilon = \dfrac{E}{V_0}$, $g^2 = \dfrac{8ma^2V_0}{\hbar^2}$

$$\begin{cases} T = \dfrac{1}{1+\dfrac{1}{4\varepsilon(\varepsilon+1)}\sin^2(g\sqrt{\varepsilon+1})}. \\ R = 1-T = \dfrac{1}{1+\dfrac{4\varepsilon(\varepsilon+1)}{\sin^2(g\sqrt{\varepsilon+1})}}. \end{cases}$$

$$\Rightarrow \underline{E+V_0 = n^2\left(\frac{\pi^2\hbar^2}{8ma^2}\right) \text{ 时}, \ T=1.}$$ "共振透射"

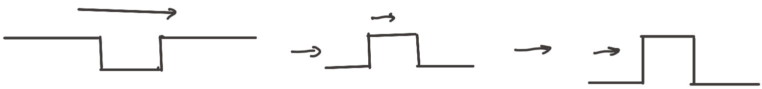
E_1^∞ 无限深基态.

势垒散射: $V_0 \to -V_0$ $(E > V_0)$.

$\varepsilon+1 \to \varepsilon-1$.

$0<E<V_0$ 量子隧穿 $\varepsilon = E/V_0$, $g^2 = \dfrac{8ma^2V_0}{\hbar^2}$

$$T = \left(1+\frac{1}{4\varepsilon(1-\varepsilon)}\sinh^2(g\sqrt{1-\varepsilon})\right)^{-1}; \quad R = T\cdot\frac{1}{4\varepsilon(1-\varepsilon)}\sinh^2(g\sqrt{1-\varepsilon}).$$



$\hbar \to 0$ $(g \gg 1)$. 时趋于经典　　量子效应: 作用量. 大n极限. DB波长.

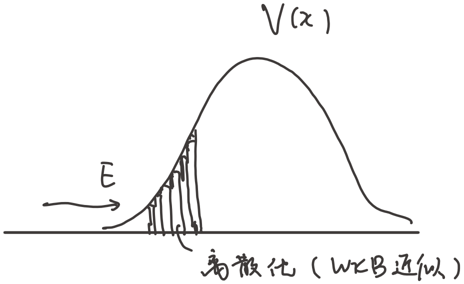
当 $\varepsilon \ll 1$，$g\sqrt{1-\varepsilon} \gg 1$ 时，

$$T \simeq 16\varepsilon(1-\varepsilon)\, e^{-2g\sqrt{1-\varepsilon}}$$

$$= 16\frac{E}{V_0}\left(1-\frac{E}{V_0}\right) e^{-2\left(\frac{2a}{\hbar}\right)\sqrt{2m(V-E)}}$$

$$T \sim \lim_{N\to\infty}\prod_{i=1}^{N} \exp\left[-\frac{2\Delta x_i}{\hbar}\sqrt{2m(V-E)}\right]$$

$$= \exp\left[-\frac{2}{\hbar}\int_{x_1}^{x_2} dx\,\sqrt{2m(V-E)}\right]$$



Wentzel - Kramers - Brillouin

电子在线性势隧穿 $V = e\phi - Fx$.

$$\Rightarrow \phi(x) = T_0\, e^{-\alpha(x)}, \quad \alpha(x) = \frac{\sqrt{2m}}{\hbar}\int_0^x \sqrt{\underbrace{e\phi}_{\text{功函数}} - F\xi - E}\; d\xi$$

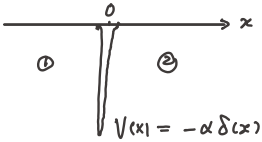
$$\Rightarrow \rho = |T_0|^2 e^{-2\alpha l} = |T_0|^2 e^{-2\frac{2}{3}\frac{\sqrt{2m}}{\hbar F}(e\phi - E)^{3/2}}$$

Fowler - Nordheim 隧穿.

Gamov. 隧道效应 → α 衰变.

δ函数势 $V(x) = -\alpha\delta(x)$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \alpha\delta(x)\psi(x) = E\psi(x)$$



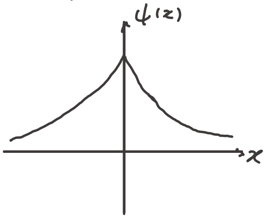
束缚态 $E<0$.

① $\psi_1'' + \frac{2mE}{\hbar^2}\psi_1 = 0$ 令 $k^2 = -\frac{2mE}{\hbar^2}$

$$\psi_1 = Be^{kx} \qquad (x\to-\infty,\ \psi_1\to 0)$$

② 同理 $\psi_2 = Fe^{-kx}$

$$\psi_1(0) = \psi_2(0) \Rightarrow B = F.$$



归一化条件

$$\int_{-\infty}^{\infty}|\psi|^2 dx = 1 \Rightarrow B = \sqrt{k}$$

导数

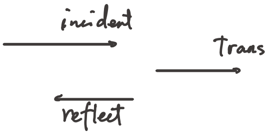
$$\lim_{\varepsilon\to 0}\left[-\frac{\hbar^2}{2m}\int_{-\varepsilon}^{+\varepsilon}\psi'' dx + \int_{-\varepsilon}^{+\varepsilon}\underbrace{V(x)}_{-\alpha\delta(x)}\underbrace{\psi(x)}_{\psi(0)}dx = E\cancel{\int_{-\varepsilon}^{+\varepsilon}\psi(x)dx}\right]$$

$$-2Bk = \lim_{\varepsilon\to 0}\left(\frac{d\psi_2}{dx}\Big|_{\varepsilon} - \frac{d\psi_1}{dx}\Big|_{-\varepsilon}\right) = -\frac{2m}{\hbar^2}\alpha\psi(0) = -\frac{2m\alpha}{\hbar^2}B.$$

$$\therefore\ k = \frac{m\alpha}{\hbar^2}$$

即 $E = -\frac{m\alpha^2}{2\hbar^2}$ 只有一个束缚态.

散射 $E>0$ $kx \to ikx$.



$$\psi_1 = Ae^{ikx} + Be^{-ikx}$$

$$\psi_2 = Fe^{ikx}$$

$$\Rightarrow \begin{cases} A + B = F \\ ikF - (ikA - ikB) = -\frac{2m\alpha}{\hbar^2}F \end{cases}$$

$$\Rightarrow \quad R = \left|\frac{B}{A}\right|^2 = \frac{1}{1+\underbrace{2\hbar^2E/m\alpha^2}}$$

$\longrightarrow E\uparrow, \ R\downarrow.$

$E\to 0$: $R\to 1$ $T\to 0$

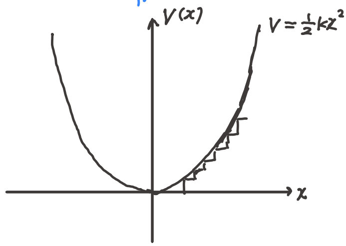
$$T = 1-R = \frac{1}{1+m\alpha^2/2\hbar^2E}$$

$-\alpha \longrightarrow +\alpha$ 正δ势 $\Rightarrow$ R、T 物理意义合理.

思考：为何$\pm\alpha$给出相同结果？束缚与散射关系？

$$V(x) = \underbrace{\cancel{V(x_0)}}_{\text{常数}} + \underbrace{\cancel{V'(x_0)}(x-x_0)}_{\text{平衡点}=0} + \underbrace{\tfrac{1}{2}V''(x_0)(x-x_0)^2}_{\text{谐振子}} + \underbrace{\cdots}_{\text{近似舍弃}}$$

$$\Rightarrow V(x) \sim \frac{1}{2}kx^2$$



S.E. $\quad \dfrac{d^2\psi}{dx^2} = (-\varepsilon + x^2)\psi \qquad$ [Hermite]

渐近行为 $\psi \sim e^{-x^2/2} \quad \to \varepsilon = 1$

$\psi \sim x e^{-x^2/2} \Rightarrow \varepsilon = 3.$

$\psi \sim (x^2+c)e^{-x^2/2} \Rightarrow \varepsilon = 5 \quad ....$

思路

$$\Rightarrow \psi \sim (x^n + a_2 x^{n-2} + a_4 x^{n-4} + \cdots)e^{-x^2/2}$$

$$\Rightarrow (x^2-\varepsilon)\psi = \psi'' = [x^{n+2} + (-n+a_2)x^n + \cdots\cdot]e^{-x^2/2}.$$

简谐振子

令 $\rho = \sqrt{\dfrac{\hbar}{m\omega}}$, $\bar{p} = \sqrt{m\hbar\omega}$, $E_0 = \hbar\omega$

$y = x/\rho \qquad \varepsilon = 2E/E_0$

S.E:
$$\frac{d^2\psi}{dy^2} - y^2\psi(y) = -\varepsilon\psi(y)$$

$y \to +\infty$ 渐近解 $\psi(y) \sim e^{\pm y^2/2}$ $\Rightarrow \psi(y) = H(y)e^{-y^2/2}$

$$H'' - 2yH' + (\varepsilon-1)H = 0$$

偶宇称 $H^{(+)}(y) = \sum_{s=0}^{\infty} a_s y^{2s}$

$$\underbrace{\sum_{s'}}_{s'\to s+1} 2s'(2s'-1)a_{s'}y^{2s'-2} + \sum_s(\varepsilon-1-4s)a_s y^{2s} = 0.$$

$$\sum_s\left[\underbrace{2(s+1)(2s+1)a_{s+1} + (\varepsilon-1-4s)a_s}_{=0}\right]y^{2s} = 0$$

$$a_{s+1} = \frac{4s+1-\varepsilon}{2(s+1)(2s+1)}a_s$$

截断: $\varepsilon = 4s+1$ $\left(\varepsilon = \frac{2E}{\hbar\omega}\right)$ $\Big\} E_s = \hbar\omega\left(2s+\frac{1}{2}\right)$

同理
$$H^{(-1)}(y) = \sum_{s=0}^{\infty} b_s y^{2s+1}, \quad b_{s+1} = b_s\frac{4s+3-\varepsilon}{2(s+1)(2s+3)}.$$

截断: $\varepsilon = 4s+3 \Rightarrow E_s = \hbar\omega\left(2s+\frac{3}{2}\right)$

$$\Rightarrow E_n = \left(n+\underbrace{\tfrac{1}{2}\right)\hbar\omega}_{\text{零点能}}$$

$$\begin{cases} \psi_n(x) = C_n H_n(x) e^{-x^2/2} \\ C_n = \sqrt{\dfrac{\sqrt{m\omega/\pi\hbar}}{2^n\ n!}} \end{cases}$$

递推关系

$$H_n'(x) = 2nH_{n-1}(x)$$

$$H_{n+1}(x) + 2nH_{n-1}(x) = 2xH_n(x)$$

基态: $|\psi_0(0)|^2$ 大 $\to x=0$ 概率大

$n\to\infty$: $|\psi|^2 \to$ Classical.

代数方法：升降算符 (Schrödinger 1941)

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 \qquad \hat{D} = \frac{d}{dx}$$

$$(a_n \hat{D}^n + \cdots + a_1 \hat{D} + a_0)\, y(x) = 0$$

特征根 r_i

$$a_n \Big((\hat{D} - r_n)(\hat{D} - r_{n-1}) \cdots (\hat{D} - r_1) \Big) y(x) = 0$$

独立解 $(\hat{D} - r_i) y = 0 \Rightarrow$ 通解 $y = \sum_{i=1}^{n} c_i e^{r_i x}$.

eg. 自由粒子 $\psi'' + k^2 \psi = 0$.

$$\Rightarrow (\hat{D} + ik)(\hat{D} - ik)\psi = 0$$

$$\Rightarrow \psi = A e^{-ikx} + B e^{ikx}.$$

$$H = \left(\frac{p}{\sqrt{2m}} + i\sqrt{\frac{m\omega^2}{2}} x \right)\left(\frac{p}{\sqrt{2m}} - i\sqrt{\frac{m\omega^2}{2}} x \right)$$

定义非厄米算符

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\, \hat{x} \underset{\Delta}{+} i \frac{\hat{p}}{\sqrt{2m\hbar\omega}}$$

则

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\, \hat{x} \underset{\Delta}{-} i \frac{\hat{p}}{\sqrt{2m\hbar\omega}}.$$

$$\begin{cases} \hat{x} = \sqrt{\frac{\hbar}{m\omega}} (a + a^\dagger) \\ \hat{p} = i\sqrt{\frac{m\hbar\omega}{2}} (a^\dagger - a) \end{cases}$$

$[a, a^\dagger] = 1$. 即 $a a^\dagger = a^\dagger a + 1$.

$$\hat{H} = \frac{\hbar\omega}{2} \big(\underbrace{\hat{a}^\dagger \hat{a}}_{\hat{N}} + \hat{a}\hat{a}^\dagger \big)$$

$$= \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) \quad (\text{or } \hat{a}\hat{a}^\dagger - \frac{1}{2})$$

关联 $\hbar\omega \left(n + \frac{1}{2} \right)$

$$\hat{N} \psi_n(x) = n \psi_n(x).$$

考虑

$$\hat{N}(\hat{a}\psi_n) = a^\dagger a\,(a\psi_n)$$

$$= (aa^\dagger - 1)(a\psi_n)$$

$$= \hat{a}(a^\dagger a)\psi_n - \hat{a}\psi_n.$$

$$= (n-1)\,\hat{a}\psi_n. \qquad \Rightarrow \hat{a}\psi_n \text{ 为本征函数，但 } n \to n-1$$

同理 $\hat{N}(\hat{a}^\dagger\psi_n) = (n+1)\,\hat{a}\psi_n$

物理意义 ⇒ n 粒子数（量子数）.

$\hat{a}$, $\hat{a}^\dagger$ ：消灭／产生算符

基态波函数： $\hat{a}\psi_0 = 0$ 最低能级.

$$\Rightarrow \quad 0 = \left(\sqrt{\frac{m\omega}{2\hbar}}\,x + i\frac{\hat{p}}{\sqrt{2m\hbar\omega}} \right)\psi_0$$

$$= \sqrt{\frac{1}{2m\omega}} \left(\frac{m\omega}{\hbar}x + \frac{d}{dx} \right)\psi_0(x)$$

$$\Rightarrow \quad \psi_0 = C_0 \cdot e^{-x^2/2} \qquad \text{（和解析解相同）}$$

↳ also 不确定关系的下限

迭代关系式 $\psi_n \equiv |n\rangle = C_n (a^\dagger)^n |0\rangle$

↳ 已归一的.

$\langle n| = \langle 0|\, a^n C_n \longrightarrow$ C_n 为实数（Wigner 定理）

$$n = \langle n|\hat{N}|n\rangle = n\langle n|n\rangle = \langle n|a^\dagger a|n\rangle = \langle n|aa^\dagger - 1|n\rangle$$

$$= \langle n|aa^\dagger|n\rangle - 1.$$

即

$$n+1 = \langle n|aa^\dagger|n\rangle$$

$$= C_n^2 \langle 0| \underbrace{(\hat{a})^n(\hat{a}}_{\hat{a}^{n+1}} \underbrace{\hat{a}^\dagger)(\hat{a}^\dagger)^{n+1}}_{(\hat{a}^\dagger)^{n+1}} |0\rangle$$

$$= \frac{C_n^2}{C_{n+1}^2}\langle n+1|n+1\rangle$$

$$= C_n^2 / C_{n+1}^2.$$

$$\therefore\ C_{n+1} = C_n/\sqrt{n+1}$$

$$\Rightarrow\ C_n = \frac{1}{\sqrt{n!}}$$

递推关系:

$$\hat{a}^+|n\rangle = \sqrt{n+1}\,|n+1\rangle$$

$$\hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle.$$

$$\Rightarrow\ |n\rangle = \frac{(\hat{a}^+)^n}{\sqrt{n!}}|0\rangle.$$

测量.

$$\langle n|x|\hat{n}\rangle \sim \langle n|n-1\rangle + \langle n|n+1\rangle = 0$$

$$\hat{x}|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a}|n\rangle + \hat{a}^+|n\rangle\right)$$

$$\langle n|x^2|n\rangle = \frac{\hbar}{2m\omega}\langle n|\hat{a}^2 + (\hat{a}^+)^2 + \hat{a}\hat{a}^+ + \hat{a}^+\hat{a}|n\rangle$$

$$= \frac{\hbar}{2m\omega}\langle n|2\hat{a}^+\hat{a} + 1|n\rangle$$

$$= \frac{\hbar}{m\omega}\left(n+\frac{1}{2}\right)$$

$$\Delta x\cdot\Delta p = \left(n+\frac{1}{2}\right)\hbar.$$

同理 $\langle n|p^2|n\rangle = \hbar m\omega\left(n+\frac{1}{2}\right)$

能量表象 $\{|n\rangle\}$ $\quad \{|0\rangle, |1\rangle, |2\rangle, \cdots\}$

$$\langle n|\hat{a}|n'\rangle = \sqrt{n'}\langle n|n'-1\rangle = \sqrt{n'}\,\delta_{n,n'-1}$$

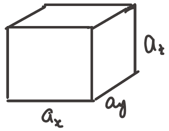
$$\langle n|\hat{a}^+|n'\rangle = \sqrt{n'+1}\,\delta_{n',n'+1}$$

$$\Rightarrow\ \hat{a} = \begin{bmatrix} 0 & 1 & & & \\ & \ddots & \sqrt{2} & & \\ & & \ddots & \sqrt{3} & \\ 0 & & & \ddots & \sqrt{4} \\ & & & & \ddots \end{bmatrix} \qquad \hat{a}^+ = \begin{bmatrix} 0 & & & & \\ 1 & 0 & & & \\ & \sqrt{2} & \ddots & & \\ & & \sqrt{3} & \ddots & \\ & & & \ddots & 0 \end{bmatrix}$$

三维量子系统

自由粒子 3dim. $T = p^2/2m$ $\longrightarrow$ 旋转不变、简并度 $\to \infty$

[1D: 宇称. $\longrightarrow$ 2.]



$$E = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{a_x^2}+\frac{n_y^2}{a_y^2}+\frac{n_z^2}{a_z^2}\right) \xrightarrow[\text{cube}]{\text{简并}} \frac{\pi^2\hbar^2}{2ma^2}(n_x^2+n_y^2+n_z^2)$$

3D 中心力

$$\hat H = \underset{\text{整体}}{\underset{\Downarrow}{\hat H_1}} + \underset{\text{相对}}{\underset{\Downarrow}{\hat H_2}}$$

$$\Rightarrow \psi = \Phi(1)\,\phi(2).$$

$V(\vec r) = V(r)$ 中心势场

描述角向 $\Rightarrow$ 物理量 $\vec L = \vec r\times\vec p$ 角动量. [构造思路: 找个 $\vec A$, 使 $\vec A \sim \theta, \varphi$]

$\downarrow$ 构造 Hermite 算符

$$(\vec r\times\vec p)^\dagger = -\vec p\times\vec r$$

$$\vec L = \left[(\vec r\times\vec p)+(\vec r\times\vec p)^\dagger\right]/2.$$

$$= \vec r\times\vec p \qquad \text{correct.}$$

$[\hat H, \hat{\vec L}] = 0 \Rightarrow \vec L$ 守恒

$$[L_x, L_y] = i\hbar\hat L_z$$

$$[\hat L^2, L_z] = 0 \qquad (L^2 = L_x^2+L_y^2+L_z^2).$$

具体表示

$$\underline{\hat{p}_r = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)} \quad p_r = \frac{1}{2}\left(\frac{\vec{r}}{r}\cdot\vec{p} + \vec{p}\cdot\frac{\vec{r}}{r}\right)$$

角向：$\frac{p^2}{2m} \longrightarrow \frac{L^2}{2mr^2}$

$$\hat{H} = \frac{\hat{p}_r^2}{2m} + \frac{\hat{L}^2}{2mr^2} + V(r).$$

TISE: $\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2\mu r^2} + V(r)\right]\psi(r,\theta,\varphi) = E\psi$

分离变量

$$\psi = R(r)Y(\theta,\varphi)$$

$$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \underbrace{\frac{2\mu(E-V)}{\hbar^2}}_{=k^2}\right]RY = \frac{L^2}{\hbar^2}RY.$$

$$\frac{1}{R}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + k^2r^2\right]R(r) = \frac{1}{\hbar^2}\frac{\hat{L}^2 Y}{Y} = \text{Const}.$$

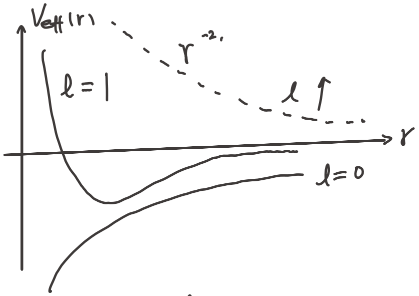
(HW) $\Longrightarrow$
$$\begin{cases} \hat{L}^2 Y_l^m(\theta,\varphi) = l(l+1)\hbar^2 Y_l^m(\theta,\varphi) \\ \hat{L}_z Y_l^m(\theta,\varphi) = m\hbar Y_l^m(\theta,\varphi). \end{cases}$$
m: $2l+1$ 个取值

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

with $P_l^m(\theta,\varphi) = (-1)^{l+m}\frac{(l+m)!}{(l-m)!}\frac{1}{(\sin\theta)^m}\left(\frac{d}{d(\cos\theta)}\right)^{l-m}(\sin\theta)^{2l}$

约化的 S.E.: $R(r)$ 项

$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[V + \underbrace{\frac{(l+1)l\hbar^2}{2\mu r^2}}_{V_{\text{eff}}\text{ 有效势能(离心势)}}\right]R(r) = ER(r)$$



$V(r) = -\frac{A}{r^m}$ 有束缚态条件 $\quad 0<m<2$

位力定理 $\hat{O} = \hat{x}\cdot\hat{p}_x \longrightarrow \hat{O} = \frac{1}{2}(\hat{x}\cdot\hat{p}_x + \hat{p}_x\cdot\hat{p})$.

[伸缩群生成元]

$\hat{O}$ 作用在 $\hat{H}\psi = \lambda\psi$ 上：

$$\frac{d}{dt}\langle\psi|\hat{O}|\psi\rangle = \frac{1}{i\hbar}\langle\psi|[xp_x, H]|\psi\rangle$$

$H\psi = \lambda\psi$.

$$= \frac{1}{i\hbar}\langle\psi|[xp_x, \lambda]|\psi\rangle$$

λ: 数

$$= 0.$$

$$0 = [xp_x, H] = [\hat{x}p_x, \frac{p_x^2}{2m} + V(x)]$$

$$= [\hat{x}, \frac{p_x^2}{2m}]p_x + \hat{x}[\hat{p}_x, V(x)]$$

$$= [x, p_x]\frac{p_x^2}{m} + \hat{x}[p_x, x]\frac{\partial V}{\partial x}.$$

$$= \frac{1}{2}\hat{T} - \hat{x}\frac{\partial V}{\partial x}.$$

(定态！定态！)

$\therefore\ 2\langle\hat{T}\rangle_\psi = \langle\hat{x}\frac{\partial\psi}{\partial x}\rangle_\psi$, now $V\sim r^{-m}$

$$\therefore\ 2\langle\hat{T}\rangle_\psi = -m\langle V\rangle_\psi \qquad (\Rightarrow m>0)$$

$$\therefore\ \langle\hat{H}\rangle = (1-\frac{2}{m})\langle T\rangle < 0$$

束缚态

$$\therefore\ 0<m<2.$$

在 $r\to 0$ 和 $r\to\infty$ 的求解

平方可积

$$\int \psi^2 dV = 1$$

$$4\pi\int_0^\infty |R(r)|^2 r^2 dr = 1. < \infty.$$

束缚态

$$rR(r) \xrightarrow{r\to\infty} 0 \quad (\text{自然边界})$$

$$\xrightarrow{r=0} 0. \quad ?$$

厄米性验证：

$$0 = \langle\psi|\hat{p}_r\psi\rangle - \langle p_r\psi|\psi\rangle. \qquad p_r = \frac{1}{2}\left(\frac{\vec{r}}{r}\cdot\vec{p} + \vec{p}\cdot\frac{\vec{r}}{r}\right).$$

$$= -i\hbar\left(\psi, \frac{\partial\psi}{\partial r} + \frac{\psi}{r}\right) - (+i\hbar)\left(\frac{\partial\psi}{\partial r} + \frac{\psi}{r}, \psi\right)$$

$$0 = \int R^*\left(\frac{\partial R}{\partial r} + \frac{R}{r}\right) r^2 dr + \int\left(\frac{\partial R^*}{\partial r} + \frac{R^*}{r}\right) R r^2 dr$$

$$0 = \int R^*\frac{\partial R}{\partial r} r^2 dr + 2\int |R|^2 r dr + \underbrace{\int \frac{\partial R^*}{\partial r} R r^2 dr}_{\cancel{(RR^*)r^2\Big|_0^\infty} - \int R^*\frac{\partial}{\partial r}(Rr^2) dr.}$$

$0.$

$$= 0 \quad \checkmark$$

令 $R = \frac{1}{r}u(r)$ $\quad u(r)\to 0.$ at $r=0, \infty.$

$$\frac{d^2u}{dr^2} + \frac{2\mu}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]u = 0 \qquad 1\ \text{dim TISE}.$$

$r\to 0$ 时，

$$u'' - \frac{l(l+1)}{r^2}u(r) = 0.$$

$$\Rightarrow u(r)\sim r^s \qquad s(s-1)r^{s-2} - l(l+1)r^{s-2} = 0$$

$$s = \begin{cases} l+1 & \Rightarrow u\sim r^{l+1} \longrightarrow \text{按 } r^l Y_l \text{ 展开} \\ \cancel{-l} & \longrightarrow u\to 0 \text{ 的条件} \end{cases}$$

氢原子

$$\begin{cases} -\frac{\hbar^2}{2M}\nabla_{\vec{z}} K(\vec{z}) = E_K K(\vec{z}) & \text{—— 整体平动} \\ -\frac{\hbar^2}{2\mu}\nabla_{\vec{r}}\psi(\vec{r}) - \frac{e^2}{4\pi\varepsilon_0 r}\psi(\vec{r}) = E_r\psi(\vec{r}) & \text{—— 相对运动} \end{cases}$$

$\hat{p}_r$, $\hat{p}_{\theta,\varphi}$ —— 物理操作

$$p_r \to \frac{\vec{r}}{r}\cdot\vec{p} \xrightarrow{\text{Hermit}} \frac{1}{2}\left(\frac{\vec{r}}{r}\cdot\vec{p} + \vec{p}\cdot\frac{\vec{r}}{r}\right).$$

$$\longrightarrow -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)$$

$$\vec{L} = \vec{r}\times\vec{p} \xrightarrow{\text{Hermit}} \frac{1}{2}\left[\hat{r}\times\hat{p} + (\hat{r}\times\hat{p})^\dagger\right] = \vec{r}\times\vec{p} \quad \checkmark$$

$$\longrightarrow \left(\frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2_{(\theta,\varphi)}}{2\mu r^2} + V(r)\right)\psi(\vec{r}) = E\psi(\vec{r}).$$ 分离变量

$$\frac{1}{R}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{2\mu(E-V)}{\hbar^2}r^2\right]R(r) = \frac{1}{\hbar^2}\frac{\hat{L}^2 Y}{Y} = \text{Const} = l(l+1)$$

空间量子化.

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

m: $2l+1$ 个取值

再令 $u(r) = rR(r)$

$$\frac{d^2u(r)}{dr^2} + \frac{2\mu}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]u = 0$$

具体求解.

① 3D 自由粒子 $V(r) = 0$

$$\frac{d^2u}{dr^2} + \frac{2\mu}{\hbar^2}\left(k^2 - \frac{l(l+1)}{r^2}\right)u = 0$$

$$k^2 = \frac{2\mu E}{\hbar^2}$$

无量纲化. $\rho = kr$

$$\frac{d^2u(\rho)}{d\rho^2} + \left[1 - \frac{l(l+1)}{\rho^2}\right] u(\rho) = 0$$

$$u = \rho R(\rho) \Rightarrow$$

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[1 - \frac{l(l+1)}{\rho^2}\right] R = 0$$ 球 Bessel 方程

通解

$$R_l(\rho) = A_l\, j_l(\rho) + B_l\, n_l(\rho)$$

j_l：球贝塞尔函数　　n_l：球诺伊曼函数

$$j_l(\rho) = (-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \left(\frac{\sin\rho}{\rho}\right)$$ ✓

$$n_l(\rho) = -(-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \left(\frac{\cos\rho}{\rho}\right) \longrightarrow$$ 在 $\rho \to 0$ 发散.

无穷远渐近

$$j_l(\rho) \longrightarrow \frac{1}{\rho}\sin\left(\rho - \frac{l\pi}{2}\right)$$

$$n_l(\rho) \longrightarrow -\frac{1}{\rho}\cos\left(\rho - \frac{l\pi}{2}\right)$$

$$\begin{cases} \psi(r,\theta,\phi) = k\sqrt{\frac{2}{\pi}}\, j_l(kr)\, Y_l^m(\theta,\phi) \\ E = \hbar^2k^2/2\mu \end{cases}$$ 3D 自由粒子 $\longrightarrow$ 平面波按 3D 展开

自由粒子完全集 $\{\hat{p}_x, \hat{p}_y, \hat{p}_z\} \sim \{\hat{p}_r, \hat{L}_z, \hat{L}^2\}$

$$e^{i\vec{k}\cdot\vec{x}} \sim j_l(kr)\, Y_l^m(\theta,\varphi)$$

$$e^{i\vec{k}\cdot\vec{r}} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} a_{lm}\, j_l(kr)\, Y_l^m(\theta,\phi)$$

令 $\vec{k} = k\vec{e}_z$, $m = 0$.

$$e^{ikz} = e^{ikr\cos\theta} = \sum_{l=0}^{\infty} a_{l0}\, j_l(kr)\, P_l(\theta).$$

Hydrogen

$$\left[\frac{\hat{p}_r^2}{2\mu}+\frac{\hat{L}^2}{2\mu r^2}-\frac{e^2}{4\pi\varepsilon_0 r}\right]\psi(\vec{r})=\underbrace{E}_{E<0}\psi(\vec{r})$$

径向方程：令 $\rho=\sqrt{-\frac{8\mu E}{\hbar^2}}\,r$

$$\lambda=\frac{2\mu e^2}{4\pi\varepsilon_0\hbar^2}\sqrt{-\frac{\hbar^2}{8\mu E}}=\frac{1}{\underbrace{a_0}_{\text{Bohr 半径.}}}\sqrt{-\frac{\hbar^2}{2\mu E}}$$

$$\frac{d^2u}{d\rho^2}-\frac{l(l+1)}{\rho^2}u+\frac{\lambda}{\rho}u-\frac{1}{4}u=0.$$

① $\rho\to\infty$ $\quad \frac{d^2u}{d\rho^2}-\frac{1}{4}u=0\longrightarrow u\sim e^{-\frac{1}{2}\rho}$

② $\rho\to 0$ $\quad \frac{d^2u}{d\rho^2}-\frac{(l+1)l}{\rho^2}u=0\longrightarrow u\sim\rho^{l+1}.$ $\quad$ (ρ^{-l} 舍)

通解：$u_l(\rho)\sim\rho^{l+1}e^{-\frac{1}{2}\rho}v_l(\rho).$

代入，

$$\rho v_l''+[2(l+1)-\rho]v_l'-(l+1-\lambda)v_l=0$$ 合流超几何方程

解为

$$v(\rho)=c\underbrace{F(l+1-\lambda,\ 2(l+1),\ \rho)}_{\text{合流超几何级数.}}$$

级数形式：$v=\sum a_i\rho^i$

$$a_{i+1}=\frac{i+l+1-\lambda}{(i+1)(i+2l+2)}a_i$$

截断：$i+l+1-\lambda=0.$ $\Rightarrow$ 能级 E.

$$\lambda=\underbrace{i}_{n_r}+l+1\equiv n\quad(\text{主量子数})$$

故，

$$n=n_r+l+1,\qquad E_n=-\frac{\hbar^2}{2\mu a_0^2n^2}$$

n 给定时， $n_r = n - l - 1 \Rightarrow \begin{cases} n_r = 0, 1, 2, \cdots n-1 \\ l = n-1, \cdots\cdots, 0. \end{cases}$ ← m 简并 $2l+1$.

总简并度 $g_n = \sum_{l=0}^{n-1} (2l+1) = n^2$

⇒ 更强的对称性：LRL 矢量

$$u_{nl}(\rho) = c F(-n_r, 2l+2, \rho_n) \rho_n^{l+1} e^{-\frac{1}{2}\rho_n}, \quad \rho_n = \sqrt{-\frac{8\mu E_n}{\hbar^2}}\, r$$

归一化波函数

$$\psi_{nlm}(\vec{r}) = \frac{u_{nl}(r)}{r} Y_l^m(\theta, \phi).$$

精细结构： $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}$ $\quad E_n = -\frac{1}{2}(\alpha c)^2 M_e \cdot \frac{1}{n^2}$

简并度 n^2（无精细结构）⟶ 更高对称性

计 $[H, F] = [H, G] = 0$, $[F, G] \neq 0$ 则存在简并

$\{H, F\}$ 共同本征 ϕ_F ， $H\phi_f = E\phi_f$

$F\phi_f = f\phi_f$

$\therefore \hat{H}(\hat{G}\phi_f) = G(H\phi_f) = EG\phi_f$

而 $\hat{F}(\hat{G}\phi_f) \neq fG\phi_f$

$\Rightarrow G\phi_f \neq \phi_f$ 简并.

取 $F = L_x$, $G = L_y$ ⇒ 简并

角动量.(算符法)

$$\hat{L}^2 Y_{lm} = l(l+1) Y_{lm}$$

$$\hat{L}_z Y_{lm} = m Y_{lm}$$

总角动量 $\longrightarrow (\vec{L}, \vec{S}, \vec{J})$

轨道 自旋 $\hookrightarrow L+S$.

$$[J_x, J_y] = i\hbar J_z$$

$$[J_i, J_j] = \varepsilon_{ijk} i\hbar J_k$$

算符 $J^2 = J_i J_i$

$$[J_i, J^2] = [J_i, J_k J_k] = [J_i, J_k] J_k + J_k [J_i, J_k]$$

$$= i\hbar \varepsilon_{ikj} J_j J_k + i\hbar \varepsilon_{ikj} J_k J_j$$

$$= i\hbar \varepsilon_{ikj} (J_j J_k + J_k J_j)$$

$$0 = \Leftarrow \quad = i\hbar \varepsilon_{ijk} (J_j J_k + J_k J_j)$$

;交换 j, k.

共同本征函数:

$$J^2 \psi_{jm} = \eta_j \hbar^2 \psi_{jm}$$

$$J_z \psi_{jm} = m\hbar \psi_{jm}$$

(已归一化)

定义 $J_\pm = J_x \pm i J_y$. (非厄米). $(J_+)^+ = J_-$, $(J_-)^+ = J_+$

$$[J_z, J_\pm] = i\hbar J_y \pm (-i\hbar J_z) i$$

$$= \pm \hbar J_\pm$$

$$[J_+, J_-] = [J_x + iJ_y, J_x - iJ_y]$$

$$= (-i)[J_x, J_y] + i[J_y, J_x]$$

$$= 2\hbar J_z$$

则 $J_z(J_-\psi_{jm}) = (J_-J_z - \hbar J_-)\psi_{jm}$

$$= (m-1)\hbar J_-\psi_{jm}$$

$J_-\psi_{jm} \sim \psi_{j,m-1}$ 降算符.

同理: $J_+\psi_{jm} \sim \psi_{j,m+1}$

而 $(J^2 - J_z^2)\psi_{jm} = \underbrace{(\eta_j - m^2)}_{>0}\hbar^2\psi_{jm} \geqslant 0$. , 故 $\eta_j \geqslant m^2 \Rightarrow$ 有界.

$J^2 - J_z^2 = J_x^2 + J_y^2 > 0$

记 $m_+ = \max\{m\}$, $m_- = \min\{m\}$

则 $J_+\psi_{jm_+} = 0$. $J_-\psi_{jm_-} = 0$.

$\hat{J}_-\hat{J}_+\psi_{jm_+} = 0$, $\hat{J}_+\hat{J}_-\psi_{jm_-} = 0$,

而 $J_\mp J_\pm = J_x^2 + J_y^2 \pm i[J_x, J_y]$

$$= J^2 - J_z^2 \mp \hbar J_z$$

$$0 = (J^2 - J_z^2 \mp \hbar J_z)\psi_{jm_+} = (\eta_j\hbar^2 - m_+^2\hbar^2 - m_+\hbar^2)\psi_{jm_+}$$

$$= [\eta_j - m_+(m_+ + 1)]\hbar^2\psi_{jm_+}$$

同理

$$0 = \hbar^2(\eta_j - m_-^2 + m_-)\psi_{jm_-}$$

故 $\eta_j = m_+^2 + m_+ = m_-^2 - m_-$

$m_+ \geqslant m_-$, 故 $m_- = -m_+$.

令 $m_+ = j$, $\eta_j = j(j+1)$.

$$\Rightarrow \begin{cases} J^2\psi_{jm} = j(j+1)\hbar^2\psi_{jm} \\ J_z\psi_{jm} = m\hbar\psi_{jm} , \quad m \in [-j, j]. \end{cases}$$

设 J_- 作用 N 次后，$\psi_{j,j} \to \psi_{j,-j}$

则 $j = \frac{N}{2} \Longrightarrow$ 半整数

$N=2$: $Y_{1,1} \to Y_{1,0} \longrightarrow Y_{1,-1}$

$N=1$? $j=\frac{1}{2}$. $\phi_{\frac{1}{2},\frac{1}{2}} \longrightarrow \phi_{\frac{1}{2},-\frac{1}{2}}$ spin 自旋

递推关系

$$J_\pm \psi_{jm} = a\,\psi_{jm\pm1}$$

$$(\psi_{jm}, J_\mp J_\pm \psi_{jm}) = ((J_\mp)^\dagger \psi_{jm}, J_\pm \psi_{jm})$$

$$= (J_\pm \psi_{jm}, J_\pm \psi_{jm}) = a^2 \underbrace{(\psi_{jm+1}, \psi_{jm+1})}_{1}$$

$$(\psi_{jm}, (J^2 - J_z^2 - \hbar J_z)\psi_{jm}) = [j(j+1) - m(m+1)]\hbar^2 \underbrace{(\psi_{jm}, \psi_{jm})}_{1}$$

$$\therefore \quad J_+ \psi_{jm} = \sqrt{j(j+1) - m(m+1)}\,\hbar\,\psi_{j,m+1}$$

同理 $$J_- \psi_{jm} = \sqrt{j(j+1) - m(m-1)}\,\hbar\,\psi_{j,m-1}$$

定义 $X_\pm = x \pm iy = r\sin\theta e^{\pm i\phi}$ 即 $X_+ \sim e^{i\phi}$ $X_- \sim e^{-i\phi}$, $z = r\cos\theta$

$$Y_{lm} = (X_+)^{\nu_+}(X_-)^{\nu_-} \cdot z^{\nu_z}, \quad \begin{cases} l = \nu_+ + \nu_- + \nu_z. \\ m = \nu_+ - \nu_- \end{cases}$$

独立多项式数 $N_l = \sum_{\nu_+=0}^{l}\sum_{\nu_-=0}^{l-\nu_+} 1 = \frac{1}{2}(l+1)(l+2). \geqslant 2l+1 \Rightarrow$ 约束.

$D^2(Y_{lm} r^l) = 0 \Rightarrow$

$$l(l+1) r^{l-2} Y_{lm} - l(l+1) r^{l-2} Y_l^m = 0 \qquad N_{l-2} \text{ 个限制}$$

$N_l - N_{l-2} = 2l+1$ ✓

3D 各向同性谐振子

$$\hat{H} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2} + \frac{1}{2}\mu\omega^2 r^2$$

$$= \underbrace{\hat{H}_x}_{\frac{p_x^2}{2\mu} + \frac{1}{2}\mu\omega^2 x^2} + \hat{H}_y + \hat{H}_z$$

$$\psi(x,y,z) = \phi_{n_x}(x)\,\phi_{n_y}(y)\,\phi_{n_z}(z) \qquad \{H_x, H_y, H_z\}$$

算符形式：$\hat{H} = \hbar\omega\left(a_x^\dagger a_x + a_y^\dagger a_y + a_z^\dagger a_z + \frac{3}{2}\right)$

$E = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right)$

$= \left(N + \frac{3}{2}\right)\hbar\omega$

变换 $x', y' \to x, y$:

$$\begin{pmatrix} a_{x'} \\ a_{y'} \end{pmatrix} = U \begin{pmatrix} a_x \\ a_y \end{pmatrix} \qquad \text{2D 旋转} \quad U^\dagger U = 1$$

$$H_{xyz} = \hbar\omega\left(\hat{a}_x^\dagger a_x + \hat{a}_y^\dagger \hat{a}_y\right) + \cdots$$

$$H_{x'y'z} = \hbar\omega\left(\hat{a}_{x'}^\dagger \hat{a}_{x'} + \hat{a}_{y'}^\dagger \hat{a}_{y'}\right) + \cdots$$

$\Rightarrow$ 对称性 $SU(3)$

$x', y', z' \to x, y, z$ 　3D 旋转

同理，$U^\dagger U = 1$

简并度：$\frac{1}{2}(N+1)(N+2)$ 　$(\gg 2l+1 \Rightarrow$ 高对称性$)$

3D 谐振子的解析解

$$\psi_{nlm} = R_{nl}(r)\,Y_{lm}(\theta,\phi) = \frac{u_{nl}}{r}\,Y_{lm}(\theta,\phi) \qquad \{H, L^2, L_z\}$$

得

$$\frac{d^2}{dr^2}u - \frac{l(l+1)}{r^2}u + \frac{2\mu E}{\hbar^2}u - \frac{\mu^2\omega^2 r^2}{\hbar^2}u = 0$$

无量纲化

$$\alpha = \sqrt{\frac{\hbar}{m\omega}}, \quad \rho = \frac{1}{\alpha} r, \quad \lambda = \frac{2E}{\hbar\omega}$$

$$\frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u + \lambda u - \rho^2 u = 0$$

$$\frac{d^2u}{d\rho^2} + \left[\lambda - \rho^2 - \frac{l(l+1)}{\rho^2}\right]u(\rho) = 0$$

渐近形式 $\rho \to \infty \quad u'' - \rho^2 u = 0 \Rightarrow u \sim e^{-\frac{\rho^2}{2}}$ (要收敛)

$\rho \to 0 \quad u \sim \rho^{l+1}$ (收敛. 舍 ρ^{-l})

通解 $u = \rho^{l+1} v(\rho) e^{-\frac{\rho^2}{2}}$.

$$\rho v''(\rho) + \left[2(l+1) - 2\rho^2\right]v'(\rho) + (\lambda - 2l - 3)\rho v(\rho) = 0$$

$y = \rho^2 \Rightarrow$

$$y v'' + \left[(l+\tfrac{3}{2}) - y\right]v' - \frac{2l+3-\lambda}{4} v = 0$$

Hypergeometric:

$y=0$ 处正常解 $v \sim F\left(\frac{2l+3-\lambda}{4}, l+\frac{3}{2}, y\right)$

合流超几何级数

$$F(\alpha, \beta, \rho) = \sum_{n=0}^{\infty} \frac{\Gamma(\alpha+n)}{\Gamma(\alpha)} \frac{\Gamma(\beta)}{\Gamma(\beta+n)} \frac{\rho^n}{n!}$$

故 $\frac{a_{n+1}}{a_n} = \frac{\Gamma(\alpha+n+1)\Gamma(\beta+n)}{\Gamma(\alpha+n)\Gamma(\beta+n+1)} \frac{n!}{(1+n)!} = \frac{1}{n+1}\frac{\alpha+n}{\beta+n} \sim \frac{1}{n+1} \Rightarrow$ 需要截断

截断: $\frac{\Gamma(\alpha+n)}{\Gamma(\alpha)} = (\alpha+n-1)(\alpha+n-2)\cdots\alpha$

$\therefore$ 只要 $\alpha \leq 0$ 且为整数 $(-1)\times(0, 1, 2, \cdots n-1)$

即当 $\frac{2l+3-\lambda}{4} = -n_r \Rightarrow \lambda = \frac{2E}{\hbar\omega} = 4n_r + 2l + 3$. $E = \hbar\omega(\underbrace{2n_r + l}_{N} + \frac{3}{2})$

电磁相互作用

MKSA，Maxwell eqns

$$\nabla\cdot\vec{E} = \frac{1}{\varepsilon_0}\rho \qquad \nabla\cdot\vec{B} = 0$$

$$\nabla\times\vec{E} = -\dot{\vec{B}} \qquad \nabla\times\vec{B} = \frac{1}{c^2}\dot{\vec{E}} + \mu_0\vec{j}$$

标势矢势 $(\phi, \vec{A})$

$$\begin{cases} \vec{E} = -\nabla\phi - \dot{\vec{A}} \\ \vec{B} = \nabla\times\vec{A} \end{cases}$$

自动实现了 $\nabla\cdot\vec{B} = 0$, $\nabla\times\vec{E} = -\dot{\vec{B}}$

则对应地

$$\varepsilon_0\left(\Delta\phi + \nabla\cdot\dot{\vec{A}}\right) = -\rho$$

$$c^2\,\nabla\times(\nabla\times\vec{A}) = -\nabla\dot{\phi} - \ddot{\vec{A}} + \frac{1}{\varepsilon_0}\vec{j}$$

Gauss 制:

$$\nabla\cdot\vec{E} = 4\pi\rho \qquad \nabla\times\vec{B} = \frac{1}{c}\dot{\vec{E}} + \frac{4\pi}{c}\vec{j}$$

$$\nabla\cdot\vec{B} = 0 \qquad \nabla\times\vec{E} = -\frac{1}{c}\dot{\vec{B}}$$

$$A^\mu = (\phi, \vec{A})$$

经典场论，非相对论

$$\mathcal{L}(\vec{r},\vec{v}) = \frac{1}{2}mv^2 - q\phi + \frac{q}{c}(\vec{A}\cdot\vec{v})$$

正则动量 $\vec{p} = \frac{\partial \mathcal{L}}{\partial \vec{v}} = m\vec{v} + \frac{q}{c}\vec{A}$

机械动量 $m\vec{v} = \vec{p} - \frac{q}{c}\vec{A}$

动力学
$$m\frac{d\vec{v}}{dt} = \frac{d\vec{p}}{dt} - \frac{q}{c}\dot{\vec{A}} = \frac{\partial \mathcal{L}}{\partial \vec{r}} - \frac{q}{c}\dot{\vec{A}} = q\left(\vec{E} + \frac{\vec{v}}{c}\times\vec{B}\right)$$

规范不变性

$$\begin{cases} \vec{A} \to \vec{A}' = \vec{A} + \nabla f \\ \phi \to \phi' = \phi - \frac{1}{c}\frac{\partial f}{\partial t} \end{cases}$$

$(E, B) \longrightarrow (E', B') = (E, B)$ —— 规范不变

哈密顿量

$$H = \frac{\partial L}{\partial v}\vec{v} - L$$

$$= \frac{mv^2}{2} + q\phi = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2 + q\phi.$$

量子化（最小替换原则）

$$\hat{p} \to \hat{p} - \frac{q}{c}\hat{A}$$

$$\frac{d}{dt}\langle\vec{r}\rangle = \langle\vec{v}\rangle = \frac{1}{i\hbar}\overline{[\hat{v}, \hat{H}]}_\psi = \frac{\langle p - \frac{q}{c}A\rangle_\psi}{m}$$

$$[\hat{v}_i, \hat{v}_j] = -\frac{q}{m^2c}\left([p_i, A_j] + [A_i, p_j]\right).$$

$$= i\hbar\frac{q}{m^2c}\left(\frac{\partial A_i}{\partial x_j} - \frac{\partial A_j}{\partial x_i}\right) = i\hbar\frac{q}{m^2c}\varepsilon_{ijk}B_k.$$

QM中的规范不变

$$\begin{cases} i\hbar\frac{\partial}{\partial t}\psi = \frac{(\vec{p} - \frac{q}{c}\vec{A})^2}{2m}\psi + q\phi\psi. \\ \Big\downarrow \text{规范变换} \\ i\hbar\frac{\partial}{\partial t}\psi' = \frac{(\vec{p} - \frac{q}{c}\vec{A}')^2}{2m} + q\phi'\psi' \end{cases}$$

$$\underline{\psi \triangleq \psi' = \psi e^{i\gamma(x)}}$$

$\Downarrow$

$\gamma(x)$ 用 $f(x)$ 表示？

$$\left(p - \frac{q}{c}\vec{A} - \frac{q}{c}\nabla f\right)\left(\psi e^{i\gamma(x)}\right) = \left[\left(p - \frac{q}{c}A\right)\psi\right]e^{i\gamma(x)} - \frac{q}{c}\nabla f\,\psi e^{i\gamma}$$

$$- i\hbar(i\nabla\gamma)e^{i\gamma}\psi$$

$$(\vec{p}-\frac{q}{c}\vec{A}-\frac{q}{c}\nabla f)\psi' = [(\vec{p}-\frac{q}{c}\vec{A})\psi]e^{i\gamma} \underbrace{-\frac{q}{c}\nabla f\cdot\psi e^{i\gamma} + \hbar(\nabla\gamma)e^{i\gamma}}_{=0}$$

即要求

$$\gamma(x) \equiv \frac{q}{\hbar c} f(x)$$

时间分量

$$i\hbar\frac{\partial}{\partial t}\psi' = i\hbar\frac{\partial}{\partial t}(\psi e^{i\gamma})$$

$$= i\hbar\dot{\psi}e^{i\gamma} - \hbar\dot{\gamma}\psi e^{i\gamma}$$

而 $\frac{1}{2m}(\vec{p}-q\frac{\vec{A}'}{c})^2\psi' + q\phi'\psi'$

$$= \frac{1}{2m}\left[(\vec{p}-q\frac{\vec{A}}{c})^2\psi\right]e^{i\gamma} + q\phi\psi e^{i\gamma} - \frac{q}{c}\dot{f}\psi e^{i\gamma}$$

即此时 ψ' 确满足

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{(\vec{p}-q\frac{\vec{A}}{c})^2}{2m} + q\phi\psi.$$

外磁场中的氢原子：Zeeman 效应

$$\hat{H} = \frac{1}{2\mu}(p-\frac{q}{c}A)^2 - \frac{e^2}{r}$$

$$=(\frac{1}{2\mu}p^2 - \frac{e^2}{r}) - \frac{q}{2\mu c}(pA+Ap) + \frac{q^2}{2\mu c^2}A^2$$

Coulumb 规范 $\nabla\cdot\vec{A}=0$

故 $(\vec{p}\cdot\vec{A})\psi = -i\hbar\nabla\cdot\vec{A}\psi = (\vec{A}\cdot\vec{p})\psi$

即 $\vec{p}\cdot\vec{A} = \vec{A}\cdot\vec{p}$

又 $\vec{B} = \nabla \times \vec{A} \quad \Rightarrow \quad \vec{A} = \frac{1}{2}\vec{B}\times\vec{r}$

$\therefore \quad \vec{A}\cdot\vec{p} = \frac{1}{2}(\vec{B}\times\vec{r})\cdot\vec{p}$ 　　而 $A^2 = \frac{1}{4}[B^2r^2 - (B\cdot r)^2]$

$= \frac{1}{2}\vec{B}\cdot\vec{L}$, 　　$= \frac{1}{4}B^2\underbrace{(x^2+y^2)}_{\rho^2}$

$$\Rightarrow \hat{H} = \hat{H}_0 - \frac{q}{2\mu c}\vec{B}\cdot\vec{L} + \frac{q^2}{2\mu c^2}\vec{A}^2$$

$(q=-e)$

$$= \hat{H}_0 - \frac{q}{2\mu c}B\hat{L}_z + \frac{e^2}{2\mu c^2}\cdot\frac{1}{4}B^2(x^2+y^2)$$

estimate :

$$\left|\frac{e^2}{2\mu c^2}\cdot\frac{1}{4}B^2a_0^2\Big/\frac{eB}{2\mu c}\hbar\right| \sim 10^{-6}B$$

第三项可略

$$\therefore \quad \hat{H} = \underbrace{\hat{H}_0}_{\{H_0,\, L^2,\, L_z\}} - \frac{qB}{2\mu c}\hat{L}_z$$

对易 $\Rightarrow$ 本征函数不变

$$\hat{H}\psi_{nlm} = \underbrace{\hat{H}_0}_{E_n}\psi_{nlm} - \frac{qB}{2\mu c}m\hbar\cdot\psi_{nlm} \qquad [m=-l,\cdots,l]$$

$$= \left(E_n - \frac{qB}{2\mu c}m\hbar\right)\psi_{nlm}$$

$l=2 \longrightarrow l=1$ 电偶极跃迁 $\Delta m = 0, \pm 1$

$$\Rightarrow \quad \omega = \omega_0 + \begin{cases}\Delta \\ 0 \\ -\Delta\end{cases}$$ 3线.

朗道能级,

考虑一个电子, $\hat{H} = \frac{1}{2\mu}\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2$

$$= \frac{p^2}{2\mu} - \frac{1}{\mu c}(\vec{A}\cdot\vec{p}) + \frac{q^2}{2\mu c^2}A^2$$

朗道规范： $\vec{B} = B\hat{e}_z$

$$\vec{A} = -By\,\hat{e}_x.$$

$$\hat{H} = \frac{1}{2\mu}\left[\left(p_x - \frac{eB}{c}y\right)^2 + p_y^2\right] + \frac{1}{2\mu}p_z^2$$

选 $\{p_x, p_z, H\}$

$$\psi_{np_xp_z} = \frac{1}{2\pi\hbar} e^{i\left(\frac{p_x x}{\hbar} + \frac{p_z z}{\hbar}\right)} \eta_n(y)$$

$$\frac{1}{2\mu}\left[\hat{p}_y^2 + \left(p_x - \frac{eB}{c}y\right)^2\right]\eta_n(y) = \epsilon_n \eta_n(y)$$

$\Rightarrow s = y - \frac{cp_x}{eB}$，谐振子： $\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{ds^2} + \frac{1}{2}\mu^2\omega^2 s^2\right]\eta_n(s) = \epsilon_n \eta_n(s)$

此时，

$$\begin{cases} \omega = \frac{|e|B}{\mu c} = 2\omega_L \quad \text{Lamor 频率} \\ \epsilon_n = (n+\frac{1}{2})\hbar\omega = (2n+1)\hbar\omega_L = (N+1)\hbar\omega_L, \quad N = 0, 2, 4 \end{cases}$$

简并度为 ∞ （p_x 任取）.

$$E_n = p_z^2/2\mu + (N+1)\hbar\omega_L$$

换规范： $A = \frac{1}{2}B(-y, x, 0)$

$$\hat{H} = \frac{1}{2\mu}\left[\left(\hat{p}_x - \frac{eB}{2c}y\right)^2 + \left(p_y + \frac{eB}{2c}x\right)^2\right] + \frac{p_z^2}{2\mu}$$

$$= \underbrace{\frac{1}{2\mu}(p_x^2 + p_y^2) + \frac{1}{2}\mu\omega_L^2(x^2+y^2) + \frac{eB}{2\mu c}\hat{L}_z}_{\hat{H}_{xy}} + \frac{p_z^2}{2\mu}$$

$\{H, L_z, p_z\}$，$\psi = \underbrace{\psi(\rho,\phi)}_{R(\rho)e^{im\phi}} e^{\frac{i}{\hbar}p_z z}$

2D $\nabla^2 = \frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho}$

径向波函数

$$\left[\frac{1}{2\mu}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}-\frac{m^2}{\rho^2}\right)+\frac{1}{2}\mu\omega_L^2\rho^2+m\hbar\omega_L\right]R(\rho)=E\,R(\rho)$$

$$\left[\frac{1}{2\mu}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}-\frac{m^2}{\rho^2}\right)+\frac{1}{2}\mu\omega_L^2\rho^2\right]R(\rho)=E'R(\rho) \qquad (E'=E-m\hbar\omega_L)$$

$$\alpha=\sqrt{\frac{\hbar}{m\omega_L}}\ ,\quad y=\frac{\rho}{\alpha}\ ,\quad \varepsilon=2E'/\hbar\omega_L$$

$$R''+\frac{1}{y}R'+\left(\varepsilon+y^2-\frac{m^2}{y^2}\right)R=0$$

$y\to\infty \qquad R\sim e^{-y^2/2}$

$y\to 0 \qquad R''+\frac{1}{y}R'-\frac{m^2}{y^2}R=0 \quad\Rightarrow\quad R\sim y^{|m|}$

$$\therefore\ R=y^{|m|}v(y)e^{-y^2/2}$$

令 $\eta=y^2$, $\quad \eta\frac{d^2v}{d\eta^2}+(|m|+1-\eta)\frac{dv}{d\eta}-\left[\frac{|m|+1}{2}-\frac{\varepsilon}{4}\right]v=0$

$$v(\eta)\sim F\Big(\underbrace{\frac{|m|+1}{2}-\frac{\varepsilon}{4}}_{\text{截断}},\ |m|+1,\ \eta\Big)$$

$$\frac{|m|+1}{2}-\frac{\varepsilon}{4}=-n_\rho$$

$$\Rightarrow\quad E'=(\underbrace{2n_\rho+|m|}_{N'}+1)\hbar\omega_L$$

$$\therefore\ E'=(N'+1)\hbar\omega_L\ ,\qquad N'=2n_\rho+|m|$$

$$\therefore\ E=E'+m\hbar\omega_L=[\underbrace{2n_\rho+|m|+m}_{N}+1]\hbar\omega_L$$

∞ 简并度 for any $m<0$ same N

给定 N $\begin{cases} m>0 & \text{有物理效应} \\ m<0 & \text{简并} \end{cases}$ —— 经典物理的旋转.

经典极限 $n_\rho = 0$ $|m| \to \infty$. $N \to \infty$

$$P(\rho) = |\psi_{0m}(\rho,\phi)|^2 \rho \sim \rho^{2|m|+1} e^{-\frac{\rho^2}{\alpha^2}}$$

$$\frac{dP}{d\rho} = \left(2|m|+1 - \frac{2\rho^2}{\alpha^2}\right)\rho^{2|m|} e^{-\rho^2/\alpha^2}$$

$$\therefore \rho_{max}^2 = \left(|m|+\frac{1}{2}\right)\alpha^2 = \frac{(|m|+\frac{1}{2})\hbar}{\mu\omega_L} \sim \frac{L_z}{\mu\omega_L}$$

又经典物理中

$$\begin{cases} \frac{1}{c} q v B = \mu B r \\ \mu(\vec{r}\times\vec{v})_z = L_z - \frac{q}{c}\vec{r}\times\frac{1}{2}(\vec{B}\times\vec{r}) \Rightarrow \mu r v = |L_z| + \frac{qBr^2}{2c} \end{cases}$$

$$\therefore r_{经典}^2 = \frac{2c|L_z|}{qB} = \frac{|L_z|}{\mu\omega_L}$$

$$\hat{H}_{xy} = \frac{1}{2\mu}\left[\left(p_x + \frac{qB}{2c}y\right)^2 + \left(p_y - \frac{qB}{2c}x\right)^2\right] = \hbar\omega_L(\Pi_x^2 + \Pi_y^2)$$

$$\omega_L = \frac{qB}{2\mu c}, \quad \Pi_x = \frac{p_x + \mu\omega_L y}{\sqrt{2\mu\hbar\omega_L}} \quad \Pi_y = \frac{p_y - \mu\omega_L x}{\sqrt{2\mu\hbar\omega_L}}$$

$$[\Pi_x, \Pi_y] = \frac{1}{2\hbar}\left\{[p_x, -x] + [y, p_y]\right\} = i \sim \left[x, \frac{p_x}{\hbar}\right]$$

$$\Rightarrow \hat{a} = \frac{1}{\sqrt{2}}(\Pi_x + i\Pi_y)$$

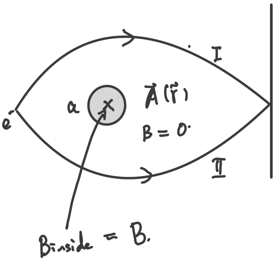
$$\hat{a}^+ = \frac{1}{\sqrt{2}}(\Pi_x - i\Pi_y)$$

$[\hat{a}, \hat{a}^+] = 1$. 升降算符

$$\hat{H}_{xy} = \hbar\omega_L(2a^+a + 1)$$

$$\Rightarrow E_{xy} = \hbar\omega_L(2N+1)$$

Aharonov - Bohm 效应



$$\frac{1}{2\mu}\left[\left(-i\hbar\nabla - \frac{e}{c}\vec{A}\right)^2\right]\psi(x) = E\psi$$

$$\vec{A} \longrightarrow \vec{A}' = \vec{A} + \nabla f(x) = 0.$$

则 $\frac{1}{2\mu}(-i\hbar\nabla)^2\psi'^2 = E\psi'$

$$\psi' = e^{\frac{iq}{\hbar c}f(x)}\psi(x).$$

$$\therefore \psi'(\vec{r}) = e^{\frac{iq}{\hbar c}\int_l \vec{A}\cdot d\vec{r}}\psi(\vec{r})$$

$$\therefore \psi_I + \psi_{II} = e^{-\frac{i}{\hbar}\frac{e}{c}\int_I \vec{A}\cdot d\vec{r}}\psi_I'(r) + e^{-\frac{i}{\hbar}\frac{e}{c}\int_{II}\vec{A}\cdot d\vec{r}}\psi_{II}'(r)$$

$$= e^{-\frac{ie}{\hbar c}\int_I \vec{A}\cdot d\vec{r}}\left[\psi_I' + e^{-\frac{ie}{\hbar c}\left(\int_{II}\vec{A}\cdot d\vec{r} - \int_I \vec{A}\cdot d\vec{r}\right)}\psi_{II}'\right]$$

$$\Downarrow$$

$$\oint_l \vec{A}\cdot d\vec{r} = \Phi.$$

$$\therefore \psi_{I+II} = C\left(\psi_I' + e^{-\frac{ie\Phi}{\hbar c}}\psi_{II}'\right)$$

自旋(Spin)

Zeeman 效应　　$m=0,\pm1$ (2l+1条)　奇数条 ⟶ 正常 Zeeman 效应

反常 ⟶ 偶数条

经典 Hamilton 的几率流 ⇒ 电流

$$\vec{j}_{电} = -\frac{i\hbar}{2\mu}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) \Rightarrow 只有\ e^{im\phi}\ 有效应.$$

$$\longrightarrow\ j_\phi = \frac{ie\hbar}{2\mu}\frac{1}{r\sin\theta}\left(\psi^*\frac{\partial}{\partial\phi}\psi - \psi\frac{\partial}{\partial\phi}\psi^*\right)$$

角量子数

$$= -\frac{e\hbar m}{\mu}\frac{1}{r\sin\theta}\left|\psi_{nlm}\right|^2$$

$$\therefore\ M_z = \int \pi r^2\sin\theta\, j_\phi\, d\sigma = -\frac{e\hbar}{2\mu}m = -\mu_B m$$

Bohr 磁矩　$\mu_B = \frac{e\hbar}{2\mu}$

S-G 实验：梯度磁场 ⟶ 对磁矩施力

⇒ 谱线分裂：空间量子化

(1922, Ag, 正常 Zeeman).

1924-25 双线结构：

Na 黄线 5893 Å $\xrightarrow[B=0]{\text{未加磁场}}$ $\begin{cases}\lambda_1 = 5896\ \text{Å} \\ \lambda_2 = 5890\ \text{Å}\end{cases}$ $\xrightarrow[\text{反常 Zeeman (B)}]{\text{Paschen Backer 1912}}$ $D_1 \to$ 4条，$D_2 \to$ 6条

1918 Bohr-Sommerfield 模型，原子壳层 ($\boxed{2}n^2$)

⇒ 1925 Pauli：在 n, l, m 之外有第四个量子数　$2\times n^2$

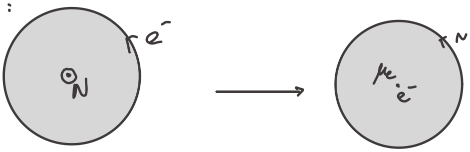
1924 Kronig ⇒ 经典小球模型 

⟹ Lorentz：$\frac{e^2}{r} = m_e c^2 \longrightarrow r_c \sim 10^{-15}m$

$$m v_e r_c = \frac{\hbar}{2} \Rightarrow v_e = \frac{c}{2\alpha} \sim 69c\ !$$

→ 经典线速度与狭义相对论矛盾.

Pauli:



$$\vec{B} = \frac{\vec{v}\times\vec{E}}{c^2} = \frac{Ze\vec{L}}{4\pi\varepsilon_0 m_e c^2}\cdot\frac{1}{r^2}\times\frac{1}{2}.$$

1926 Thomas 旋进

$$\hat{H} = -\mu_e\cdot\vec{B} \quad\Rightarrow\quad \Delta\lambda = \underbrace{12Å\times\tfrac{1}{2}}_{\to\, 6Å!} > 6Å$$

→ 6Å! 碱金属双线 $(\vec{L}\cdot\vec{\mu_e})$

1927 Fraser 银原子基态 $\vec{L} = 0$ ⇒ S-G 实验的现象:

半整数角动量 $\mu_{自旋} = \underbrace{2}\times\left(\frac{q}{2m_e}\right)\left(\frac{\hbar}{2}\right)$

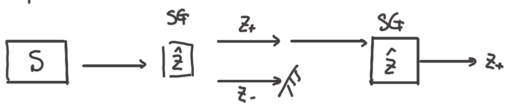
→ Landé factor $g = 2$ (2.000⋯)

1927. Pauli 自旋理论

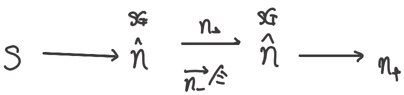
历史回顾

Pauli 矩阵

①



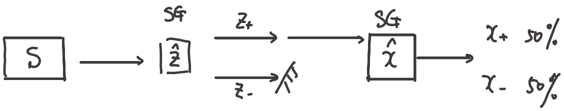
z_+ / z_- 是 SG($\hat{z}$) 的本征态



任意方向 ⇒ 只有±两种状态.

→ μ_s 为 2 维量.

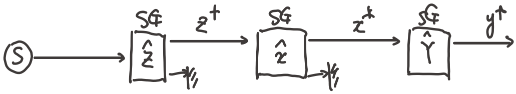
②



x y z 不同时确定

定义 $\vec{\mu} = (\mu_x, \mu_y, \mu_z)$

$\mu_{x,y,z} \longrightarrow$ 2维描述



$$\begin{cases} |z_+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ |z_-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{cases} \longrightarrow \mu_z = \mu_B \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$\mu_z |z_+\rangle = (+1)|z_+\rangle$

$\mu_z |z_-\rangle = (-1)|z_-\rangle.$

构造 μ_x, μ_y

$$\mu_x \longrightarrow \begin{pmatrix} a & b \\ c & d \end{pmatrix} \mu_B. \qquad \mu_x^{\dagger} = \mu_B \begin{pmatrix} a^* & c^* \\ b^* & d^* \end{pmatrix}$$

物理算符 $\mu_x = \mu_x^{\dagger} \Rightarrow \begin{cases} a, d \in R \\ b = c^* \end{cases}$

本征值为 ± 1：
$$\begin{cases} Tr(\hat{\mu}_x) = 0 & (+1+-1) \\ det(\hat{\mu}_x) = -1. & (+1 \times -1) \end{cases} \Rightarrow \begin{cases} a+d=0 \\ ad-bc=-1. \end{cases}$$

$bc=1$ $\qquad d=0$

作用在 $|z_+\rangle$ 上：

$$\langle z_+ | \hat{\mu}_x | z_+ \rangle = \mu_B (1, 0) \begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0 \quad \begin{pmatrix} |x_+\rangle\ 50\% \\ |x_-\rangle\ 50\% \end{pmatrix} \Rightarrow a = 0.$$

则
$$\mu_x = \mu_B \begin{pmatrix} 0 & e^{-i\phi_x} \\ e^{i\phi_x} & 0 \end{pmatrix} \qquad \mu_y = \mu_B \begin{pmatrix} 0 & e^{-i\phi_y} \\ e^{i\phi_y} & 0 \end{pmatrix}$$

再在 $|x_+\rangle$ 中 SG − Y：

$$\mu_x |x_+\rangle = |x_+\rangle \Rightarrow |x_+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ e^{i\phi_x} \end{pmatrix}$$

$$\langle x_+ | \mu_y | x_+ \rangle = \mu_B \cos(\phi_x - \phi_y) = 0.$$

选取 $\phi_x = 0,\ \phi_y = \frac{\pi}{2}$ (Pauli)

→ 定义

$$\mu_x = \mu_B \underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\sigma_x} \qquad \mu_y = \mu_B \underbrace{\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}_{\sigma_y} \qquad \mu_z = \mu_B \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}_{\sigma_z}$$

$\sigma_{x,y,z}$ ～ Pauli 矩阵

$$\begin{cases} S_i = \frac{\hbar}{2}\sigma_i \\ [S_x, S_y] = i\hbar S_z \\ [S^2, S_z] = 0 \end{cases}$$

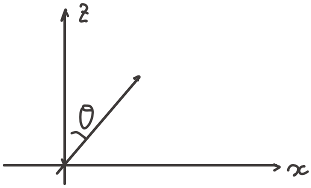
自旋

$\{S^2, S_z\} \longrightarrow |s,m\rangle$

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

电子 $S = \frac{1}{2}$ ， $m = \frac{1}{2}$

沿任意轴 θ 的测量



经典： $\mu_\theta = \mu_x \sin\theta + \mu_z \cos\theta$

$\downarrow$ 假定

$$\hat{\mu}_\theta = \hat{\mu}_x \sin\theta + \hat{\mu}_z \cos\theta$$

$$= \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix} \mu_B .$$

本征函数即为 $|\theta_+\rangle = \begin{pmatrix} \cos\theta/2 \\ \sin\frac{\theta}{2} \end{pmatrix}$ $\quad |\theta_-\rangle = \begin{pmatrix} -\sin\frac{\theta}{2} \\ \cos\frac{\theta}{2} \end{pmatrix}$

$|z_+\rangle$ 中测 $\hat{\mu}_\theta$ ？

$$P_+ = |\langle\theta_+|z_+\rangle|^2 = \cos^2\frac{\theta}{2}.$$

$$P_- = |\langle\theta_-|z_+\rangle|^2 = \sin^2\frac{\theta}{2}.$$

$$\langle z_+|\mu_\theta|z_+\rangle = (+)\cos^2\frac{\theta}{2} + (-)\sin^2\frac{\theta}{2} = \cos\theta.$$

一般地. $\hat{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$

则 $\hat{\mu}_n = \vec{\mu}\cdot\hat{n} = \mu_B \begin{pmatrix} \cos\theta & \sin\theta e^{-i\phi} \\ \sin\theta e^{i\phi} & -\cos\theta \end{pmatrix}$

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

电子波函数 $\{S^2, S_z\}$

记 $|z_+\rangle = |+\rangle$, $|z_-\rangle = |-\rangle$, 空间波函数 $\psi(\vec{r})$

混合表示: ($S=\frac{1}{2}$粒子)

$$|\psi(\vec{r}, S_z)\rangle = \underbrace{|\psi_+(\vec{r})\rangle}\otimes|+\rangle + \underbrace{|\psi_-(\vec{r})\rangle}\otimes|-\rangle$$

($\psi_\pm$ 不一定一样).

$$\langle\psi|\psi\rangle = \langle\psi_+|\psi_+\rangle\langle+|+\rangle + \langle\psi_-|\psi_-\rangle\langle-|-\rangle$$

$$= \langle\psi_+|\psi_+\rangle + \langle\psi_-|\psi_-\rangle$$

{ 在 r 处 dV 内发现自旋为 $+\frac{1}{2}\hbar$ 的几率 }

引入 $|+\rangle, |-\rangle$, 旋量表示:

$$|\psi(r, S_z)\rangle = \begin{pmatrix} \psi_+(\vec{r}) \\ \psi_-(\vec{r}) \end{pmatrix}$$ 旋量 spinor

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验证实验: S-G Exp

自旋空间的单位算符.

$$\hat{H} = \hat{H}_{ext} - \hat{\vec{\mu}}\cdot\hat{\vec{B}} \longrightarrow \hat{H}_{ext}\otimes\hat{I}^{(2)}_{spin} - \vec{\mu}_B\cdot\vec{B}(\vec{r})$$

若 $\vec{B} = B_0\hat{e}_z$, $-\vec{\mu}\cdot\vec{B} = -\mu_z B_0$ $\Rightarrow |\psi(\vec{r}, S_z)\rangle = |\psi(\vec{r})\rangle|S_z\rangle$

若 $\vec{B} = B(\vec{r})$, $\Rightarrow$ 外部 $\otimes$ 内部.

$\hat{H} = \hat{H}_{ext} \otimes \hat{I}_s + \hat{W}$

$$i\hbar \frac{\partial}{\partial t}\left(\psi_+|+\rangle + \psi_-|-\rangle\right) = (\underbrace{\hat{H}_{ext}}_{\psi_+ 或 \psi_-} \otimes \underbrace{\hat{I}_s}_{|+\rangle \text{ or } |-\rangle} + \hat{w})(\psi_+|+\rangle + \psi_-|-\rangle).$$

左乘 $\langle + |$:

$$i\hbar \frac{\partial}{\partial t}\psi_+ \underbrace{\cancel{\langle+|+\rangle}}_{1} = \left(\hat{H}_{ext}\psi_+\right)\underbrace{\cancel{\langle+|+\rangle}}_{1} + \underbrace{\langle+|\hat{w}\psi_+|+\rangle}_{\langle+|\hat{w}|+\rangle\psi_+} + \langle+|\hat{w}\psi_-|-\rangle.$$

$\langle+|I_s|+\rangle$

$$i\hbar \frac{\partial}{\partial t}\psi_+ = \hat{H}_{ext}\psi_+ + \langle+|\hat{w}|+\rangle\psi_+ + \langle+|\hat{W}|-\rangle\psi_-$$

① 匀强场 $\vec{B} = B_0\hat{e}_z$

$$\hat{W} = \hat{\mu}_z B_0, \qquad \psi(\vec{r}, S_z) = \psi(\vec{r})\left(\alpha|+\rangle + \beta|-\rangle\right)$$

$$\begin{cases} i\hbar \frac{\partial}{\partial t}\psi(\vec{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) & \text{—— 自由粒子平动} \\ i\hbar\frac{d}{dt}(\alpha|+\rangle + \beta|-\rangle) = -\hat{\mu}_z B_0(\alpha|+\rangle+\beta|-\rangle) \Rightarrow i\hbar\frac{d}{dt}\begin{pmatrix}\alpha\\ \beta\end{pmatrix} = -\mu_B B_0\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\end{pmatrix} \end{cases}$$

$$= -\mu_B B_0\begin{pmatrix}\alpha\\ -\beta\end{pmatrix}.$$

$$\therefore \begin{cases} i\hbar\frac{d\alpha}{dt} = -\mu_B B_0\alpha \\ i\hbar\frac{d\beta}{dt} = \mu_B B_0\beta \end{cases} \Rightarrow \begin{cases} \alpha = \alpha_0 e^{-\frac{i\omega_0 t}{2}} \\ \beta = \beta_0 e^{i\frac{\omega_0 t}{2}} \end{cases} \qquad \omega_0 = \frac{-2\mu_B B}{\hbar} = -\frac{q}{m_e}B.$$

此时 t 时刻 $\langle\hat{\mu}_x\rangle = ?$

$$|S(t)\rangle = \begin{pmatrix}\alpha(t)\\ \beta(t)\end{pmatrix}$$

$$M_x(t) = \langle s|\mu_x|s\rangle = \mu_B(\alpha^* \ \beta^*)\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\end{pmatrix}.$$

$$= \mu_B(\alpha^*\beta + \beta^*\alpha)$$

$$= \mu_B(2\alpha_0\beta_0\cos\omega_0 t).$$

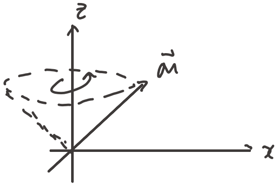
同理,

$$M_y(t) = \mu_B(2\alpha_0\beta_0\sin\omega_0 t).$$

$$M_z(t) = \mu_B(\alpha_0^2 - \beta_0^2)$$

$$[\hat{H}, \hat{\mu}_z] = 0 \Rightarrow \frac{dM_z}{dt} = 0$$

$$\begin{cases} \frac{dM_x}{dt} = -\omega_0 M_y \\ \frac{dM_y}{dt} = \omega_0 M_x \end{cases}$$



$$\Rightarrow \frac{d\vec{M}}{dt} = -\gamma_0 \vec{B} \times \vec{M} \qquad \left(\gamma = \frac{q}{m}\right)$$

经典周期：$T = \frac{2\pi}{\omega_0} \longrightarrow$ 初态

but in QM:

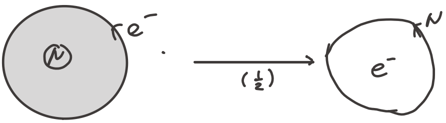
选 $\alpha = \beta$. $|S(t=0)\rangle = |\mu_x, +\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)$

$$|S(t)\rangle = \frac{1}{\sqrt{2}}\left(e^{-i\omega_0 t/2}|+\rangle + e^{i\omega_0 t/2}|-\rangle\right)$$

$t = T$ 时，$|S(t)\rangle = -\frac{1}{\sqrt{2}}(|+\rangle + |-\rangle) \neq |S(t=0)\rangle$.

$T_{QM} = 4\pi/\omega_0$. $|S(t = \frac{4\pi}{\omega_0})\rangle = |S(t=0)\rangle$, $\boxed{SU(2) \quad SO(3)}$

碱金属的双线结构



$$E_1 = -\frac{1}{2}\mu(\alpha c)^2$$

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2} - Z\frac{e^2}{r} + Z\alpha^2 E_1 \left(\frac{a_0}{r}\right)^3 \frac{\vec{S}\cdot\vec{L}}{\hbar^2} \Rightarrow L_z, S_z.$$

$\vec{J} = \vec{L} + \vec{S}$

总角动量.

$\{H, J^2, L^2, S^2, J_z\}$ 动力学量.

$$\hat{H} = \underbrace{\frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2} - Z\frac{e^2}{r}}_{H_0} + Z\alpha^2 E_1 \left(\frac{a_0}{r}\right)^3 \frac{\hat{\vec{S}}\cdot\hat{\vec{L}}}{\hbar^2}$$

$$[\hat{\vec{L}}, \hat{\vec{S}}] = 0$$

$$\begin{cases} [S_i, S_j] = i\hbar\varepsilon_{ijk}S_k \longrightarrow \{S^2, S_z\}. \\ [L_i, L_j] = i\hbar\varepsilon_{ijk}L_k \end{cases}$$

$$[\hat{\vec{L}}, \vec{S}\cdot\vec{L}] = \vec{S}[\hat{\vec{L}}, \hat{\vec{L}}] = S_i[\hat{\vec{L}}, L_i] \neq 0. \Rightarrow \vec{L} \text{ 不守恒.}$$

$\longrightarrow$ 考虑总角动量 $\vec{J} = \vec{L} + \vec{S}$

$$[J_i, J_j] = i\hbar\varepsilon_{ijk}J_k$$

$$[\hat{\vec{J}}, \hat{\vec{S}}\cdot\hat{\vec{L}}] = [\hat{\vec{J}}, S_iL_i]$$

$$= [S_k + L_k, S_iL_i]$$

$$= S_i[L_k, L_i] + [S_k, S_i]L_i$$

$$= i\hbar\varepsilon_{kij}(S_iL_j + S_jL_i) = 0.$$

故 $[\vec{J}, H] = 0$. 总角动量守恒 $\Rightarrow J^2, J_z$.

而 $[L^2, \vec{S}\cdot\vec{L}] = S_i[L^2, L_i] = 0 \Rightarrow L^2$

$[S^2, \vec{S}\cdot\vec{L}] = [S^2, S_i] = 0 \Rightarrow S^2$

$(+H)$ 五个 $\{H, J^2, L^2, S^2, J_z\}$

$\Rightarrow$ 描述体系.

$$\vec{S}\cdot\vec{L} = \frac{1}{2}(J^2 - S^2 - L^2)$$

微扰 $\Rightarrow$ 从 $R_{nl}(r)Y_l^m(\theta,\phi)$ 出发

混合表示: $\psi(r,\theta,\phi) \otimes |S^2, S_z\rangle$

$$S_z = \frac{1}{2} \mapsto \psi_+(r,\theta,\phi)|S_z=+\rangle + \psi_-(r,\theta,\phi)|S_z=-\rangle$$

$\longrightarrow$ 旋量表示 $\begin{pmatrix}\psi_+\\\psi_-\end{pmatrix}$ (or $\begin{pmatrix}\psi_1\\\psi_2\end{pmatrix}$) — 是 S^2 的本征函数 $S^2|+\rangle = \frac{3}{4}\hbar^2|+\rangle$

$S^2|-\rangle = \frac{3}{4}\hbar^2|-\rangle$.

物理目的: 合理的 $\psi_{1,2}$. $\longrightarrow$

L^2:

$$\hat{L}^2\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = c\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} \longrightarrow \psi \text{是} \vec{L} \text{本征函数}$$

$$L^2\psi_{1,2} = l(l+1)\hbar^2\psi_{1,2}.$$

$$\Rightarrow \psi_1 \sim Y_{l,m}, \quad \psi_2 \sim Y_{l,m'} \Rightarrow Y_{l,m+1}.$$

J_z:

$$\hat{J}_z\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = j_z\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}$$

$$(L_z + S_z)\psi_{1,2} = j_z\psi_{1,2}.$$

$$\begin{cases} L_z\psi_1 = m\psi_1 \qquad L_z\psi_2 = m'\psi_2 \\ S_z\,\psi_1\otimes\begin{pmatrix}1\\0\end{pmatrix} = \frac{\hbar}{2}\psi_1\otimes\begin{pmatrix}1\\0\end{pmatrix} \\ S_z\,\psi_2\otimes\begin{pmatrix}0\\1\end{pmatrix} = -\frac{\hbar}{2}\psi_2\otimes\begin{pmatrix}0\\1\end{pmatrix} \end{cases}$$

$$\because j_z = \left(m+\tfrac{1}{2}\right)\hbar = \left(m'-\tfrac{1}{2}\right)\hbar$$

$$\therefore m' = m+1$$

J^2

$$\psi = \begin{pmatrix} aY_{lm} \\ bY_{l\,m+1}\end{pmatrix} \qquad J^2 = L^2 + S^2 + 2\vec{S}\cdot\vec{L}$$

$$= I_{2\times2}\otimes L^2 + S^2 + \hbar(\sigma_x L_x + \sigma_y L_y + \sigma_z L_z)$$

代入,

$$J^2 = \begin{pmatrix} L^2 + \frac{3}{4}\hbar^2 + \hbar L_z & \hbar\underbrace{(L_x - iL_y)}_{L_-} \\ \hbar\underbrace{(L_x + iL_y)}_{L_+} & L^2 + \frac{3}{4}\hbar^2 - \hbar L_z \end{pmatrix} \qquad L_\pm = L_x \pm iL_y.$$

$$\Rightarrow \begin{pmatrix} L^2 + \frac{3}{4}\hbar^2 + \hbar L_z & \hbar L_- \\ \hbar L_+ & L^2 + \frac{3}{4}\hbar^2 - \hbar L_z \end{pmatrix}\begin{pmatrix} aY_{lm} \\ bY_{lm+1}\end{pmatrix} = \lambda\hbar^2\begin{pmatrix} aY_{lm} \\ bY_{lm+1}\end{pmatrix}.$$

利用升降算符的关系：

$$\hat{L}_\pm Y_{lm} = \hbar\sqrt{(l\mp m)(l\pm m+1)}\, Y_{l,m\pm1}$$

即
$$\begin{cases} \hat{L}_- Y_{lm+1} = \hbar\sqrt{(l+m+1)(l-m)}\, Y_{l,m} \\ \hat{L}_+ Y_{lm} = \hbar\sqrt{(l-m)(l+m+1)}\, Y_{l,m+1} \end{cases}$$

得：
$$\begin{pmatrix} [l(l+1)+\frac{3}{4}+m]\hbar^2 a Y_{lm} + \hbar^2\sqrt{(l+m+1)(l-m)}\, b Y_{lm} \\ \\ \sqrt{(l-m)(l+m+1)}\,\hbar^2 a Y_{lm+1} + [l(l+1)+\frac{3}{4}-(m+1)] b Y_{lm+1} \end{pmatrix} = a\hbar^2 \begin{pmatrix} a Y_{lm} \\ \\ b Y_{lm+1} \end{pmatrix}$$

$$\mathrm{Det} = 0 \Rightarrow \begin{matrix} \lambda_1 = (l+\frac{1}{2})(l+\frac{3}{2}) \\ \lambda_2 = (l-\frac{1}{2})(l+\frac{1}{2}) \end{matrix} \Big\} = j(j+1)$$

$$\Rightarrow j_1 = l + \frac{1}{2}, \quad j_2 = l - \frac{1}{2} \qquad (2l+1)\otimes 2 \text{ 个维度.}$$

eg

$l = 1 \qquad S = 1/2$

$m = -1, 0, 1 \qquad S = \pm \qquad \Rightarrow 3\times 2$

$$\left.\begin{matrix} j = l+\frac{1}{2} & l-\frac{1}{2} & \\ 3/2 & 1/2 & \\ \Downarrow & & \\ 2j+1 = 4 & 2 & \Rightarrow 4+2 \end{matrix}\right\} 6.$$

当 $j_1 = l + \frac{1}{2}$, $\quad \frac{a}{b} = \sqrt{\frac{l+m+1}{l-m}} \qquad \psi = \frac{1}{\sqrt{2l+1}}\begin{pmatrix} \sqrt{l+m+1}\; Y_{lm} \\ \sqrt{l-m}\; Y_{l,m+1} \end{pmatrix}$

$j_2 = l - \frac{1}{2}$. $\quad \frac{a}{b} = -\sqrt{\frac{l-m}{l+m+1}} \qquad \psi = \frac{1}{\sqrt{2l+1}}\begin{pmatrix} -\sqrt{l-m}\; Y_{lm} \\ \sqrt{l+m+1}\; Y_{lm+1} \end{pmatrix}$

$$H_{spin-orbit} = Z\alpha^2 E_1 \left(\frac{a_0}{r}\right)^3 \frac{\vec{S}\cdot\vec{L}}{\hbar^2}$$

$$= Z\alpha^2 E_1 \left(\frac{a_0}{r}\right)^3 \frac{1}{\hbar^2}\cdot\frac{1}{2}\left[J^2 - S^2 - L^2\right]$$

$$= Z\alpha^2 E_1 \left(\frac{a_0}{r}\right)^3 \frac{1}{\hbar^2}\frac{1}{2}\underbrace{\left(j(j+1) - l(l+1) - \frac{3}{4}\right)}_{\frac{l}{2},\ \text{当}\ j=l+\frac{1}{2}\ \ \text{or}\ \ -\frac{l+1}{2}\ \text{当}\ j=l-\frac{1}{2}}\hbar^2 \quad ; \quad j = l \pm \frac{1}{2}.$$

$L\uparrow\uparrow S$ $\quad\quad$ $L\uparrow\downarrow S$

而 $\langle nlm | \frac{1}{r^3} | nlm \rangle = \dfrac{Z^3}{a_0^3 n^3 (l+1)(l+\frac{1}{2})}$

$$\Rightarrow \Delta E = \langle nlm | \hat{H}_{so} | nlm \rangle$$

$$= \begin{cases} K_n \dfrac{1}{(l+1)(l+\frac{1}{2})} & j = l+\frac{1}{2} \\ -K_n \dfrac{1}{l(l+\frac{1}{2})} & j = l-\frac{1}{2}. \end{cases} \qquad K_n = \frac{Z^4\alpha^2}{2n^3}E_1$$

角动量耦合（代数结构）[物理问题：超精细结构 H 21cm 线]

两个角动量物理量 $\vec{J}_1$, $\vec{J}_2$

j_1 $\quad$ j_2

$2j_1+1$ $\quad$ $2j_2+1$ $\longrightarrow$ $\vec{J} = \vec{J}_1 + \vec{J}_2$

$(2j_1+1)\otimes(2j_2+1)$

且 ① $[\vec{J}_1, \vec{J}_2] = 0 \Rightarrow \vec{J}$ 也是角动量

$$\vec{J} = \vec{J}_1 \otimes I_2 + I_1 \otimes \vec{J}_2$$

$$\begin{cases} [J_i, J_j] = i\hbar\,\varepsilon_{ijk} J_k. \\ [J^2, J_i] = 0 \end{cases}$$

描述体系 $\rightarrow \{J_1^2, J_{1z};\ J_2^2, J_{2z}\}$ — 因子化基

$\rightarrow \{J_1^2, J_2^2, J^2, J_z\}$ — 耦合基

考虑电子 $\vec{\mu}_e = -\frac{q}{m_e}\vec{S}_e$

而 H^+ $\vec{\mu}_p = \underbrace{2.79}_{g_c}\frac{q}{m_e}\vec{S}_p$

$\Rightarrow \hat{W} = -\frac{2}{3}\mu_0 \underline{\vec{\mu}_e\cdot\vec{\mu}_p}\,\delta(\vec{r})$

$\Downarrow$ 角动量理论

$\{J_1^2, J_{1z};\ J_2^2, J_{2z}\}$ — 因子化基 $\longrightarrow \{|j_1, j_{1z};\ j_2, j_{2z}>\} \Rightarrow \underline{|j_1, j_{1z}> \otimes |j_2, j_{2z}>}$.

$\{J_1^2, J_2^2, J^2, J_z\}$ — 耦合基 $\longrightarrow \{\underline{|j, j_1, j_2, j_z>}\}$

$$\vec{J}_1 = \vec{J} - \vec{J}_2$$

$$\Rightarrow j_1(j_1+1) = j(j+1) - j_2(j_2+1) - \frac{2\vec{J}_2\cdot\vec{J}}{\hbar^2} \leftarrow \text{离散}.$$

基关联：$(m = j_z)$

$$|j, j_1, j_2, m> = \sum_{m_1, m_2} \underbrace{C^{jm}_{j_1m_1j_2m_2}}_{\text{C-G 系数}} |j_1, m_1;\ j_2, m_2>$$

最大值：

$$|j, j_1, j_2, j_1+j_2> = |j_1, j_1> \otimes |j_2, j_2>$$

$j_1+j_2 = j$, m, m_1, m_2

$\downarrow$ 降低

$$|J, j_1, j_2, j_1+j_2-1> = (\alpha_1)|j_1, j_1-1> \otimes |j_2, j_2> + (\alpha_2)|j_1, j_1> \otimes |j_2, j_2-1>$$

具体计算：

$|jj-1>$

$$|jj> = \underline{|j_1 j_1> \otimes |j_2 j_2>}.$$

$$J_\pm = J_x \pm iJ_y$$

$$= (J_{1x} \pm iJ_{1y}) + (J_{2x} \pm iJ_{2y})$$

$$= \underline{J_{1\pm}} + \underline{J_{2\pm}}$$

$$J_-|jj> = (J_{1-} + J_{2-})(|j_1 j_1> \otimes |j_2 j_2>)$$

$$= (J_{1-}|j_1 j_1>) \otimes |j_2 j_2> + |j_1 j_1> \otimes J_{2-}|j_2 j_2>$$

利用 $J_\pm |jm\rangle = \sqrt{(j\mp m)(j\pm m+1)}\,|j,m\pm1\rangle$.

$$\therefore\ \sqrt{2j}\,|j,j-1\rangle = \sqrt{2j_1}\,|j_1,j_1-1\rangle\otimes|j_2\,j_2\rangle + \sqrt{2j_2}\,|j_1\,j_1\rangle\otimes|j_2,j_2-1\rangle.$$

$$|j,j-1\rangle = \sqrt{\frac{j_1}{j}}\,|j_1,j_1-1\rangle\otimes|j_2,j_2\rangle + \sqrt{\frac{j_2}{j}}\,|j_1,j_1\rangle\otimes|j_2,j_2-1\rangle$$

$$\Big\downarrow J_-$$

$$|j,j-2\rangle = \left\{\begin{array}{ll} |j_1,j_1-2\rangle\otimes|j_2,j_2\rangle & |j_1,j_1-1\rangle\otimes|j_2,j_2-1\rangle \\ |j_1,j_1-1\rangle\otimes|j_2,j_2-1\rangle & |j_1,j_1\rangle\otimes|j_2,j_2-1\rangle \end{array}\right\}$$

$$\Big\downarrow J$$

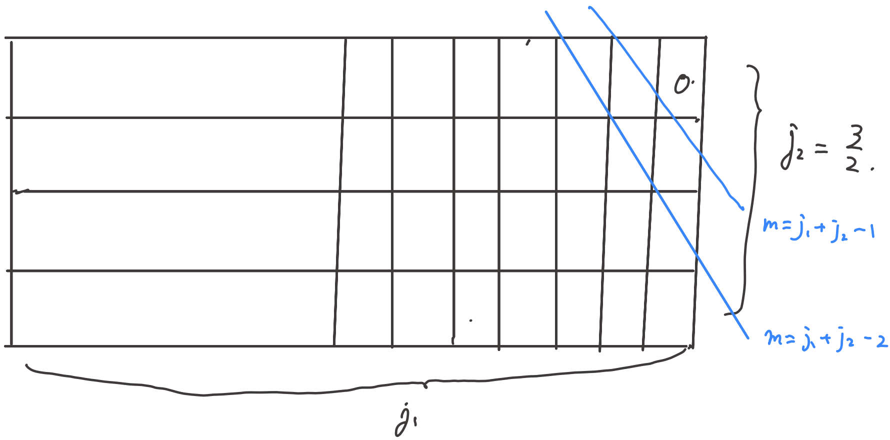
$$|j,j-3\rangle = \cdots\cdots$$

降低 j:

$$|j_1+j_2-1,\ j_1+j_2-1\rangle = \sqrt{\frac{j_2}{j}}\,|j_1,j_1-1\rangle\otimes|j_2,j_2\rangle - \sqrt{\frac{j_1}{j}}\,|j_1,j_1\rangle\otimes|j_2,j_2-1\rangle$$

$\uparrow$

$j = j_1+j_2-1$



特殊地，对于 $s_1, s_2 = \pm\frac{1}{2}$ 的情形.

因子化基 $\{ |+;+\rangle\ |+;-\rangle\ |-;+\rangle\ |-;-\rangle \}$

耦合基 $|\underbrace{s}_{\text{总自旋}},\ m\rangle$

最高态：$|+;+\rangle = |\tfrac{1}{2},\tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2},\tfrac{1}{2}\rangle_2$

即 $|1,1\rangle = |+;+\rangle = |\tfrac{1}{2},\tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2},\tfrac{1}{2}\rangle_2$

⟶降算符作用.

$$\sqrt{2}\,|1,0\rangle = \left(S_{1-}|\tfrac{1}{2},\tfrac{1}{2}\rangle_1\right)\otimes|\tfrac{1}{2},\tfrac{1}{2}\rangle_2 + |\tfrac{1}{2},\tfrac{1}{2}\rangle_1\otimes\left(S_{2-}|\tfrac{1}{2},\tfrac{1}{2}\rangle_2\right)$$

$$= |-;+\rangle + |+;-\rangle$$

$\therefore |1,0\rangle = \frac{1}{\sqrt{2}}\left(|-;+\rangle + |+;-\rangle\right) \longrightarrow |0\ 0\rangle = \frac{1}{\sqrt{2}}\left(|-;+\rangle - |+;-\rangle\right)$

$|1,-1\rangle = |-;-\rangle.$

矩阵表示

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

$$\begin{cases}
|\uparrow;\uparrow\rangle = \begin{pmatrix}1\\0\end{pmatrix}_1 \otimes \begin{pmatrix}1\\0\end{pmatrix}_2 = \begin{pmatrix}1\\0\\0\\0\end{pmatrix} \\
|\uparrow;\downarrow\rangle = \begin{pmatrix}1\\0\end{pmatrix}_1 \otimes \begin{pmatrix}0\\1\end{pmatrix}_2 = \begin{pmatrix}0\\1\\0\\0\end{pmatrix} \\
|\downarrow;\uparrow\rangle = \begin{pmatrix}0\\0\\1\\0\end{pmatrix} \\
|\downarrow;\downarrow\rangle = \begin{pmatrix}0\\0\\0\\1\end{pmatrix}
\end{cases}$$

再考虑 S.

$$S_x = S_{1x} + S_{2x}$$

$$S_{1x} = \frac{\hbar}{2}\hat{\sigma}_x \otimes I_2 = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_2 = \frac{\hbar}{2}\begin{pmatrix} & & 1 & \\ & & & 1 \\ 1 & & & \\ & 1 & & \end{pmatrix}$$

$$S_{2x} = \frac{\hbar}{2} I_1 \otimes \hat{\sigma}_x = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_1 \otimes \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} & 1 & & \\ 1 & & & \\ & & & 1 \\ & & 1 & \end{pmatrix}$$

$$\therefore \quad S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix},$$

$$S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i & -i & 0 \\ i & 0 & 0 & -i \\ i & 0 & 0 & -i \\ 0 & i & i & 0 \end{pmatrix}, \qquad S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & & & \\ & & & \\ & & & \\ & & & -1 \end{pmatrix}.$$

$$\therefore \quad S^2 = \hbar^2\begin{pmatrix} 2 & & & \\ & 1 & 1 & \\ & 1 & 1 & \\ & & & 2 \end{pmatrix}$$

$$\begin{cases} S^2\begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = s(s+1)\begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} \\ S_z\begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = m\hbar\begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} \end{cases} \Rightarrow \begin{cases} s=1,\ m=1 \quad |11\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \\ \qquad m=0 \quad |10\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix} \\ \qquad m=-1 \quad |1-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} \\ s=0 \quad m=0 \quad |00\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix}. \end{cases}$$

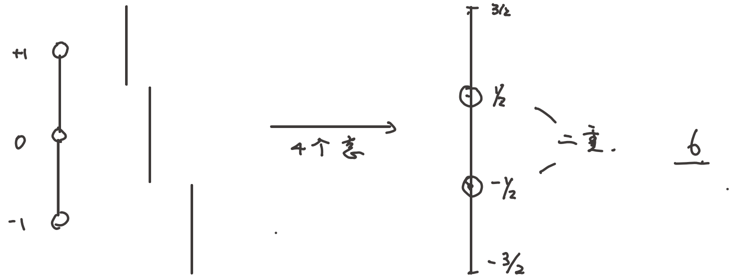
$$U = \begin{pmatrix} 1 & & & \\ & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & \\ & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & \\ & & & 1 \end{pmatrix}$$

则

$$S^2: \begin{pmatrix} 1&&& \\ &\frac{1}{\sqrt2}&\frac{1}{\sqrt2}& \\ &&&1 \\ &\frac{1}{\sqrt2}&-\frac{1}{\sqrt2}& \end{pmatrix} \hbar^2 \begin{pmatrix} 2&&& \\ &1&& \\ &&1& \\ &&&2 \end{pmatrix} \begin{pmatrix} 1&&& \\ &\frac{1}{\sqrt2}&\frac{1}{\sqrt2}& \\ &\frac{1}{\sqrt2}&&-\frac{1}{\sqrt2} \\ &&1& \end{pmatrix} = \hbar^2 \left(\begin{array}{ccc|c} 2&&& \\ &2&& \\ &&2& \\ \hline &&&S \end{array}\right)$$

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

MMA: $l=1 \quad s=\frac{1}{2}$.



直和 $W(m) \quad (\vec{f_1}, \vec{f_2}, \cdots, \vec{f_n})$

$V(n) \quad (\vec{e_1}, \cdots, \vec{e_n})$

直和: $W+V\ (n+m) \quad (\vec{e_1}, \vec{e_2}, \cdots, \vec{f_1}, \cdots)$.

$$\vec{v} \oplus \vec{w} = \left(\begin{array}{c} v_1 \\ v_2 \\ \vdots \\ v_n \\ \hline w_1 \\ \vdots \\ w_m \end{array}\right) = \left(\begin{array}{c} \vec{v} \\ \hline \vec{w} \end{array}\right)_{n+m}.$$

矩阵 $\vec{A}_{nn} \oplus \vec{B}_{mm} = \left(\begin{array}{c|c} \vec{A} & O_{nm} \\ \hline O_{mn} & \vec{B} \end{array}\right)$

直乘 $V \times W$, $\vec{e_i} \otimes \vec{f_j}$ xx线性.

eg. for $V(2) \otimes W(3)$

$$\vec{e_1} \otimes \vec{f_1} = \left(\begin{array}{c} 1 \\ 0 \\ 0 \\ \hline 0 \\ 0 \\ 0 \end{array}\right), \quad \vec{e_2} \otimes \vec{f_1} = \left(\begin{array}{c} 0 \\ 0 \\ 0 \\ \hline 1 \\ 0 \\ 0 \end{array}\right), \quad \cdots$$

性质：$(A\otimes I)(\vec{v}\otimes\vec{w}) = (A\vec{v})\otimes\vec{w}$

$$\downarrow$$

$$A\otimes I = \left(\begin{array}{ccc|ccc} a_{11} & & & a_{12} & & \\ & a_{11} & & & a_{12} & \\ & & a_{11} & & & a_{12} \\ \hline a_{21} & & & a_{22} & & \\ & a_{21} & & & a_{22} & \\ & & a_{21} & & & a_{22} \end{array}\right).$$

同理，$(I\otimes B)(\vec{v}\otimes w) = \vec{v}\otimes(B\vec{w})$

$$\downarrow$$

$$I\otimes B = \left(\begin{array}{ccc|ccc} b_{11} & b_{12} & b_{13} & & & \\ \vdots & & & & 0 & \\ b_{31} & \cdots & b_{33} & & & \\ \hline & & & b_{11} & \cdots & b_{13} \\ & 0 & & & & \\ & & & b_{31} & \cdots & b_{33} \end{array}\right).$$

现有：
$$\begin{cases} S_+ = \hbar\begin{pmatrix} & 1 \\ & \end{pmatrix} \quad S_- = \hbar\begin{pmatrix} & \\ 1 & \end{pmatrix} \quad S_z = \begin{pmatrix} 1 & \\ & 1 \end{pmatrix}\frac{\hbar}{2}. \\ L_+ = \hbar\begin{pmatrix} & \sqrt{2} & \\ & & \sqrt{2} \\ & & \end{pmatrix} \quad L_- = \hbar\begin{pmatrix} & & \\ \sqrt{2} & & \\ & \sqrt{2} & \end{pmatrix} \quad L_z = \begin{pmatrix} 1 & & \\ & & \\ & & -1 \end{pmatrix}\hbar \end{cases} \longrightarrow J = S\otimes I + I\otimes L$$

而 $|\frac{3}{2},\frac{3}{2}\rangle = \begin{pmatrix} 1 \\ \\ \\ \\ \\ \\ \end{pmatrix}$, $|\frac{3}{2},-\frac{3}{2}\rangle = \begin{pmatrix} \\ \\ \\ \\ \\ 1 \end{pmatrix}$.

$$J_+|\tfrac{3}{2},\tfrac{3}{2}\rangle = J_-|\tfrac{3}{2},-\tfrac{3}{2}\rangle = 0.$$

$$J_\pm|j,m\rangle = \sqrt{j(j+1)-m(m\pm1)}\,|j,m\pm1\rangle.$$

$$\Rightarrow J_-|\tfrac{3}{2},\tfrac{3}{2}\rangle = \begin{pmatrix} 0 \\ \sqrt{2} \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = \sqrt{3}\,\underbrace{|\tfrac{3}{2},\tfrac{1}{2}\rangle}_{\text{get}}$$

即 $\sqrt{2}|\frac{1}{2},\frac{1}{2}\rangle\otimes|1,0\rangle + |\frac{1}{2},-\frac{1}{2}\rangle\times|1,1\rangle = \sqrt{3}|\frac{3}{2},\frac{1}{2}\rangle$

正交组合

$\Rightarrow |\frac{1}{2},\frac{1}{2}\rangle.$

再令

$|\frac{1}{2}, \frac{3}{2}\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ \hline 0 \\ 0 \end{pmatrix}$, ······ 构成 U　　$2 \oplus 3 \longrightarrow 4 \oplus 2$.

则 $U J_{z,\pm} U^\dagger \longrightarrow 4 \oplus 2$ 的升降算符.

eg

$$U J_z U^\dagger = \left(\begin{array}{cccc|cc} 3/2 & & & & & \\ & 1/2 & & & & \\ & & -1/2 & & & \\ & & & -3/2 & & \\ \hline & & & & 1/2 & \\ & & & & & -1/2 \end{array}\right) \hbar$$

全同粒子

量子化 $\longrightarrow$ 同种粒子的物理属性完全相同

全同体系的波函数

eg. 1D 谐振子两个

$$\hat{H} = h^{(1)} + h^{(2)} = \frac{p_1^2}{2m} + \frac{1}{2} m\omega^2 x_1^2 + \frac{p_2^2}{2m} + \frac{1}{2} m\omega^2 x_2^2$$

基态 $\longrightarrow \Phi_0(x_1, x_2) = \phi_0(x_1)\,\phi_0(x_2)$

第一激发 $\longrightarrow \underbrace{\phi_1(x_1)\phi_0(x_2) \ \& \ \phi_0(x_1)\phi_1(x_2)}_{\text{应当一样}} = \Phi_1$

态叠加原理:

$$\Phi_1 = \lambda \phi_1 \phi_0 + \mu \phi_0 \phi_1$$

Φ_1 中测 $x_1 \otimes x_2$.

$$\langle x_1 \otimes x_2 \rangle = \frac{\hbar}{2m\omega}(\lambda^* \mu + \lambda \mu^*) = \frac{\hbar}{m\omega} \mathrm{Re}(\lambda^* \mu)$$ $\Rightarrow$ 可观测量.

λ, μ 是可观测的, 而非任意.

$\longrightarrow$ 自然界只允许 $\lambda = \pm\mu$. "$\pm$" 对应自旋.

置换算符 $\hat{P}$

双粒子体系 $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2 \Rightarrow |\psi\rangle = \sum_{kn} C_{kn} |k\rangle \otimes |n\rangle.$

$$\underset{|k\rangle}{\mathcal{H}_1} \quad \underset{|n\rangle}{\mathcal{H}_2}$$

$$\equiv \sum_{kn} C_{kn} |1:k;2:n\rangle.$$

不应依赖于编号

$$\hat{P}_{12} |1:k;2:n\rangle = |2:k;1:n\rangle. = e^{i\delta} |1:k;2:n\rangle.$$

$$\begin{cases} \text{态叠加：} \delta \text{ 不依赖于 } \psi. \\ \hat{P}_{12}^2 = \hat{I} \end{cases} \Rightarrow e^{i\delta} = \pm 1.$$

$[P, H] = 0 \longrightarrow P$ 是运动常数

编号无关

对称： $\hat{P}_{12}|\psi_s\rangle = |\psi_s\rangle$

反对称： $\hat{P}_{12}|\psi_s\rangle = -|\psi_s\rangle$

$\longrightarrow$ Pauli 不相容原理

Fermi, Dirac：自旋为整数：Bose 子．对称

半整数：Fermi 子．反对称

(反)对称化算子 $S_N^{\pm}$

$$\hat{S}_N^{(\pm)} = \frac{1}{\sqrt{N!}} \sum_{\hat{P}_\delta} (\pm 1)^\delta \hat{P}_\delta$$

循环置换 δ 为偶

else 为奇.

$$\begin{cases} (1,2,3) \to (1,3,2): & \delta \text{ odd.} \\ (1,2,3) \to (2,3,1): & \delta \text{ even.} \end{cases}$$

全同费米子，Slater determinant

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} |1:1\rangle & \cdots & |1:n\rangle \\ |n:1\rangle & \cdots & |n:n\rangle \end{vmatrix}$$

全同自由粒子. $p = \hbar k_\alpha,\ \hbar k_\beta.$

$$\phi_k(\vec{r}) = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\vec{k}\cdot\vec{r}}$$

① 非全同.

$$r^2 dr \int |\phi_k|^2 d\Omega = 4\pi r^2 \cdot \frac{1}{(2\pi\hbar)^3} dr = 4\pi r^2 \underbrace{P(r)}_{\text{常数}} dr$$

② 反对称.

$$\Rightarrow \phi_{12}^{(A)} = \frac{1}{\sqrt{2}}\left(1 - \hat{P}_{12}\right)\frac{1}{(2\pi\hbar)^{3/2}} e^{i\vec{k}\cdot\vec{r}}$$

$\hat{P}_{12}$: $r \to -r$

$$= \frac{i\sqrt{2}}{(2\pi\hbar)^{3/2}} \sin(\underbrace{\vec{k}\cdot\vec{r}}_{kr\cos\theta})$$

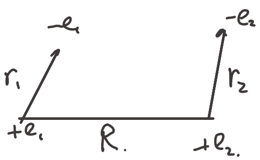
$$\Rightarrow 4\pi r^2 P^{(A)} dr = r^2 dr \int |\phi|^2 d\Omega$$

$$= \frac{4\pi r^2 dr}{(2\pi\hbar)^3} \cdot \underbrace{\left(1 - \frac{\sin 2kr}{2kr}\right)}_{③(\text{对称}:\ 1 + \frac{\sin 2kr}{2kr})}$$

$r \to \infty$ ① - ③ 无区别

氢分子

$$\hat{H} = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} \underbrace{- 2e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right)}_{\text{中心场近似}} + \frac{e^2}{|r_{12}|}$$



H_2^+ 离子: $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R}.$

He 氦原子

$$\hat{H} = \underbrace{\frac{p_1^2}{2m_e} + \frac{p_2^2}{2m_e} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2}}_{} + \underbrace{\frac{e^2}{r_{12}}}_{\text{微扰 } V_{12}}$$

不计微扰和全同性时，

$E_0 = 2\times 4E_{0H} = 108.8\text{eV}.$

实验值 78.975 eV.

① 全同性： $|1;\alpha_1\rangle \otimes |2;\alpha_2\rangle = |n_1l_1m_1;n_2l_2m_2\rangle.$

$$|n_1l_1m_1;n_2l_2m_2\rangle = C\cdot\left(|n_1l_1m_1;n_2l_2m_2\rangle \pm |n_2l_2m_2;n_1l_1m_1\rangle\right)$$

1) 空间反对称自旋对称 $\Rightarrow$ $|11\rangle$, $|10\rangle$, $|1-1\rangle$.

2) 空间对称自旋反对称 $\Rightarrow |00\rangle$

② V_{12}：微扰论.

一维无限深多电子.

$$E = \frac{\hbar^2\pi^2}{ml^2}\left(\frac{N_{max}^3}{3}\right)$$ 最高能级 $\longrightarrow$ Fermi 能级

不全同时 $E = N\cdot\frac{\hbar^2\pi^2}{2mL^2}$.

元素周期表：核外电子排布.

$$\left[{}^{2S+1}L_j\right]$$

$$\langle nlm | \frac{1}{r^3} | nlm \rangle = \frac{Z^3}{a_0^3 n^3 (l+1)(l+\frac{1}{2})}$$

$$\hat{H} = \underbrace{\frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2} - Z\frac{e^2}{r}}_{H_0} + \underbrace{Z\alpha^2 E_1 \left(\frac{a_0}{r}\right)^3 \frac{\hat{S}\cdot\hat{L}}{\hbar^2}}_{W}$$

微扰论

$$\hat{H} = \hat{H}_0 + \lambda \hat{W}$$

λ：标记大小的参数

$\hat{H}_0 |k^{(0)}\rangle = E_k^{(0)} |k^{(0)}\rangle$.

$\longrightarrow$ 求解：$\hat{H}|k\rangle = E_k |k\rangle$.

$|k\rangle$: $|k^{(0)}\rangle + \lambda |k^{(1)}\rangle + \lambda^2 |k^{(2)}\rangle$.

E_k: $E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots$

合理性： $\lambda \to 0 \quad |k\rangle \longrightarrow |k^{(0)}\rangle$

$|k^{(0)}\rangle \xrightarrow{\lambda} |k\rangle$ ：需要验证.(Exp).

$$(\hat{H}_0 + \lambda \hat{W})(|k^0\rangle + \lambda |k^1\rangle + \lambda^2 |k^2\rangle) = (E_k^0 + \lambda E_k^1 + \lambda^2 E_k^2)(|k^0\rangle + \lambda |k^1\rangle + \lambda^2 |k^2\rangle)$$

λ 项：

λ^0： $\hat{H}_0 |k^0\rangle = E_k^0 |k^0\rangle$. $\longrightarrow (\hat{H}_0 - E_k^0)|k^0\rangle = 0$.

λ^1： $\hat{H}_0 |k^1\rangle + \hat{W}|k^0\rangle = E_k^0 |k^1\rangle + E_k^1 |k^0\rangle$

$\longrightarrow (\hat{H}_0 - \hat{E}_k^0)|k^1\rangle = (E_k^1 - \hat{W})|k^0\rangle$.

λ^2： $(\hat{H}_0 - \hat{E}_k^0)|k^2\rangle = E_k^2 |k^0\rangle + (E_k^1 - \hat{W})|k^1\rangle$

(相位自由度：$|k^m\rangle \longrightarrow |k^m\rangle + \varepsilon |k^0\rangle \Rightarrow |k'\rangle = e^{i\alpha\lambda}|k\rangle$

$\langle k^0|$:

$$0 = \langle k^0 | \hat{H}_0 - \hat{E}_k^0 | k^1\rangle = \langle k^0 | E_k^1 - \hat{W} | k^0\rangle = E_k^{(1)} - \langle k^0 | \hat{W} | k^0\rangle$$

$\therefore$ 一阶微扰： $E_k^1 = \langle k^0 | \hat{W} | k^0 \rangle$

二阶微扰：需要 $|k'\rangle$

利用 $\{|k^\circ\rangle\}$ 完备性.

$$|k'\rangle = \sum_m a_m' |m^\circ\rangle.$$

$$(\hat{H}_0 - E_k^\circ)|k'\rangle = (E_k' - \hat{W})|k^\circ\rangle$$

$$(\hat{H}_0 - E_k^\circ)\left[a_k' |k^\circ\rangle + \sum_{m\neq k} a_m' |m^\circ\rangle\right] = (E_k' - \hat{w})|k^\circ\rangle$$

$=0.$

左乘 $\langle n^\circ|$.

$$\sum_{m\neq k} \langle n^\circ|\hat{H}_0 - E_k^\circ|m^\circ\rangle a_m' = \langle n^\circ|E_k' - \hat{w}|k^\circ\rangle.$$

$$\sum_{m\neq k} a_m' (E_n^\circ - E_k^\circ) \underbrace{\langle n^\circ|m^\circ\rangle}_{\delta_{mn}} = \langle n^\circ|E_k' - \hat{w}|k^\circ\rangle$$

$$\therefore \quad a_n' = \frac{\langle n^\circ|E_k' - \hat{w}|k^\circ\rangle}{E_n^\circ - E_k^\circ}$$

$$= \frac{\langle n^\circ|\hat{W}|k^\circ\rangle}{E_k^\circ - E_n^\circ} \qquad (n\neq k)$$

$n=k \quad a_k' = ?$ $\longrightarrow$ 约定

$$\text{Consider} \quad |k\rangle' \equiv e^{i\alpha\lambda}|k\rangle = e^{i\alpha\lambda}\left(|k^\circ\rangle + \lambda|k'\rangle + \lambda^2|k^2\rangle + \cdots\right)$$

$$= |k^\circ\rangle + \lambda\left(a_k'|k^\circ\rangle + i\alpha|k^\circ\rangle\right) + \cdots$$

选 $i\alpha$. (约定)

考虑归一化

$$\langle k^\circ + \lambda k'|k^\circ + \lambda k'\rangle = 1.$$

$$\langle\lambda k'|k^\circ\rangle + \langle\lambda k^\circ|k'\rangle + \cancel{\lambda^2\langle k'|k'\rangle} = 0 \quad \sim\lambda^2$$

$$\longrightarrow \quad a_k' + a_k'^* = 0 \quad \leftarrow a_k' \ \mathrm{Im}$$

可选 $i\alpha$ 抵消之

$\longrightarrow$ 约定：$a_k' = 0$

现有. $\begin{cases} E_k^1 = \langle k^0|\hat{W}|k^0\rangle \\ |k^1\rangle = \sum\limits_{i\neq k} \underbrace{\dfrac{\langle i^0|\hat{W}|k^0\rangle}{E_k^0 - E_i^0}}_{\text{微扰}: \ll 1} |i^0\rangle \end{cases}$ (so $\langle k^1|k^0\rangle = 0$).

λ^2: $(\hat{H}_0 - \hat{E}_k^0)|k^2\rangle = E_k^2|k^0\rangle + (E_k^1 - \hat{W})|k^1\rangle$

$$0 = \langle k^0|(\hat{H}_0 - \hat{E}_k^0)|k^2\rangle = E_k^2 + \langle k^0|(E_k^1 - \hat{W})|k^1\rangle$$
$$= E_k^2 - \langle k^0|\hat{W}|k^1\rangle.$$

$$\therefore E_k^2 = \langle k^0|\hat{W}|k^1\rangle$$
$$= \sum_{i\neq k} \frac{\langle i^0|\hat{W}|k^0\rangle\langle k^0|\hat{W}|i^0\rangle}{E_k^0 - E_i^0}$$
※ 二阶微扰能量.
$$= \sum_{i\neq k} \frac{|\langle i^0|\hat{W}|k^0\rangle|^2}{E_k^0 - E_i^0}$$

λ^j:
$$(\hat{H}_0 - E_n^0)|n^j\rangle = -\hat{W}|n^{j-1}\rangle + \sum_{k=1}^{j} E_n^k |n^{j-k}\rangle$$

归一化: $1 = \langle n^0|n^0\rangle + \lambda[\underbrace{\langle n^1|n^0\rangle + \langle n^0|n^1\rangle}_{=0}]$

$+ \lambda^2[\underbrace{\langle n^0|n^2\rangle + \langle n^1|n^1\rangle + \langle n^2|n^0\rangle}_{=0}] + \cdots$

$+ \lambda^j \boxed{\underbrace{\sum_{k=0}^{j}\langle n^{j-k}|n^k\rangle}_{=0}}$

约定: $\langle n^0|n\rangle \in \mathbb{R}$. $\longrightarrow$ $\langle n^0|n^j\rangle = \langle n^j|n^0\rangle$.

逐级逼近: 用 $j-1$ 阶信息逼近 E_n^j, $|n^j\rangle = \sum a_m^j |m^0\rangle$.

$$E_n^j = \langle n^0|\hat{W}|n^{j-1}\rangle - \sum_{k=1}^{j-1} E_n^k \langle n^0|n^{j-k}\rangle.$$

$$a_m^j = -\frac{\langle m^0|\hat{W}|n^{j-1}\rangle}{E_m^0 - E_n^0} + \sum_{k=1}^{j-1} \frac{E_n^k\langle m^0|n^{j-k}\rangle}{E_m^0 - E_n^0} \quad (m\neq n)$$

$m=n$: 归一化.

$$a_n^j = \langle n^0 | n^j \rangle$$
$$= -\frac{1}{2}\sum_{k=1}^{j-1} \langle n^{j-k} | n^k \rangle \qquad (归一化)$$

$$\sum_{k=0}^{j} \langle n^{j-k} | n^k \rangle = 0$$

eg. for $j=2$:

$$\langle n^2 | n^0 \rangle + \langle n^1 | n^1 \rangle + \langle n^0 | n^2 \rangle = 0$$

and $\langle n^2 | n^0 \rangle = \langle n^0 | n^2 \rangle$

利用上述各式迭代 $\longrightarrow$ 所求精度

记 $\langle m^0 | W | n^0 \rangle = W_{mn}$, $E_m^0 - E_n^0 = E_{mn}$

(1+2) 阶总贡献

$$E_n = E_n^0 + W_{nn} - \sum_{m\neq n} \frac{|W_{mn}|^2}{E_{mn}}$$

$$|n\rangle = |n^0\rangle\left[1 - \frac{1}{2}\sum_{m\neq n}\frac{|W_{mn}|^2}{E_{mn}}\right] + \sum_{m\neq n}|m^0\rangle\left[-\frac{W_{mn}}{E_{mn}} + \sum_{m'\neq n}\frac{W_{mm'}W_{m'n}}{E_{mn}E_{m'n}} - \frac{W_{mn}W_{nn}}{E_{mn}^2}\right]$$

简并微扰

微扰 $\longmapsto$ 破坏对称性 $\Rightarrow$ 对称化微扰

eg. 2D 谐振子:

$$\hat{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2(x^2+y^2) + m\alpha\omega^2 xy$$
$$\Downarrow$$
$$\hat{V} + \hat{W} = \frac{1}{2}m\omega^2\left[(1+\alpha)\left(\frac{x+y}{\sqrt{2}}\right)^2 + (1-\alpha)\left(\frac{x-y}{\sqrt{2}}\right)^2\right]$$

普遍地: 选定子空间, 对角化微扰

一阶简并：

$$\langle \psi_b^0 | W | \psi_a^0 \rangle = (E_a^0 - E_b^0)\langle \psi_b^0 | \psi_a^1 \rangle + E_a^1 \langle \psi_b^0 | \psi_a^0 \rangle$$

简并：$E_b^0 = E_a^0$ 时 $\langle \psi_b^0 | \psi_a^0 \rangle = 0$

对 $a=b$，$E_a^1 = \langle \psi_a^0 | \hat{W} | \psi_a^0 \rangle$

对 $a\neq b$，$\langle \psi_b^0 | \hat{W} | \psi_a^0 \rangle = 0$ （对角化条件）.

即：规定对 E_a^0 本征值的一组基矢，使 $\langle \psi_b^0 | \hat{W} | \psi_a^0 \rangle = \lambda_a \delta_{ab}$.

具体地，设 E_l 为 f_l 重简并，

$$\hat{H}_0 \phi_{lk}^{(0)} = E_l^{(0)} \phi_{lk}^{(0)}$$

$$\phi_l^{(0)} = \sum a_{lk}^{(0)} \phi_{lk}^{(0)} \qquad \psi_l^1 = \sum_{k=1}^{f_l} \phi_{lk}^{(0)} a_{lk}^1 + \sum_{l'\neq l} \phi_{l'}^0 a_{l'}^1$$

一阶：$\hat{H}_0 \psi_l^1 + \hat{W}\psi_l^{(0)} = E_l^0 \psi_l^1 + E_l^1 \psi_l^0$，标积 $\phi_{lm}^{(0)}$.

$$\sum_{k=1}^{f_l} \langle \phi_{lm}^0 | \hat{W} | \phi_{lk}^0 \rangle a_{lk}^0 = E_l^1 a_{lm}$$

$$\Rightarrow \sum_{k=1}^{f_l} \Big[\underbrace{\langle \phi_{lm}^0 | \hat{W} | \phi_{lk}^0 \rangle}_{\hat{W}_{mk}} - E_l^1 \delta_{mk}\Big] a_{lk}^0 = 0$$

非零解：$\left| \hat{W}_{mk} - E_l^1 \delta_{mk} \right| = 0 \longmapsto \begin{cases} E = E_l^0 + E_{ln}^1 \\ \psi_{ln}^{(0)} = \sum_k \phi_{lk}^{(0)} a_{lk}^{n(0)} \end{cases}$

eg. 二重简并

$$\begin{pmatrix} E_0^0 + \lambda W_{11} & \lambda W_{12} \\ \lambda W_{21} & E_0^0 + \lambda_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = E \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

$$\longmapsto E_{\pm} = E_0^0 + \frac{\lambda}{2}(W_{11} + W_{22}) \pm \frac{\lambda}{2}\sqrt{(W_{11} - W_{22})^2 + 4W_{12}W_{21}}$$

对应的，

$$\frac{a_1^{\pm}}{a_2^{\pm}} = \frac{2W_{12}}{(W_{22}-W_{11}) \mp \sqrt{(W_{11}-W_{22})^2+4W_{12}W_{21}}}$$

与λ无关，只由W的形式。

$$\psi^{\pm} \sim a_1^{\pm}\psi_1 + a_2^{\pm}\psi_2$$

特殊地，若 $W_{11} = W_{22} = 0$，$W_{12} = W_{21} = V$

$$E_{\pm} = E_0^{0} \pm \lambda V$$

$$a_1^{\pm} = \mp a_2^{\pm} \longrightarrow \begin{cases} \psi_+ = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2) \\ \psi_- = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2) \end{cases}$$

线性 Stark 效应

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}}_{H_0} + \underbrace{e\varepsilon z}_{W}$$

n=2 能级四重简并：$\phi_{nlm} = \phi_{200}, \phi_{210}, \phi_{21-1}, \phi_{211}$

Note：$\begin{cases} [z, \hat{L}_z] = 0 \mapsto \Delta m = 0 \\ z \text{ 为奇宇称.} \end{cases}$

∴ 唯一非零：$\langle\phi_{200}|\hat{z}|\phi_{210}\rangle = \frac{1}{32\pi a_0^2}\int e^{-\frac{r}{a_0}} \frac{1}{a_0} r(2-\frac{r}{a_0}) e\varepsilon r \cos^2\theta \sin\theta \, d\theta \, d\phi \, r^2 dr.$

$$\langle\phi_{200}|\hat{z}|\phi_{210}\rangle = -3e\varepsilon a_0$$

$$\Rightarrow \begin{cases} E_1' = -3a_0 e\varepsilon, & \psi_{21}' = \frac{1}{\sqrt{2}}(\phi_{200} + \phi_{210}) \\ E_2' = +3a_0 e\varepsilon, & \psi_{22}' = \frac{1}{\sqrt{2}}(\phi_{200} - \phi_{210}) \end{cases}$$

另两个无贡献

$H = H_0 + W \qquad H_0 |nm^0\rangle = E_n^0 |nm^0\rangle$

$$(W_n - E_{nm}^1)|nm^0\rangle = 0$$

主方程 $(H_0 - E_n^1)|nm^j\rangle = -W|nm^{j-1}\rangle + \sum_k E_{nm}^k |nm^{j-k}\rangle.$

归一化： $\langle nm^0|nm^j\rangle = -\frac{1}{2}\sum \langle nm^k|nm^{j-k}\rangle$

微扰修正 $\longmapsto \begin{cases} \langle nm| \\ \langle nm'| \\ \langle n'm'| \end{cases}$ 作用于主方程.

以下 carefully 区分 "'" "0" "1"

一阶微扰： $\langle nm^0|nm^1\rangle = 0$

$$\begin{cases} 0 = -\langle nm^0|W|nn^0\rangle + E_{nm}^{(1)} \Rightarrow E_{nm}^1 = W_{nm}. \\ 0 = -\langle nm'^0|W|nm^0\rangle \Rightarrow \text{对角化（在 } H_0 \text{ 简并子空间内）} \\ (E_{n'}^0 - E_n^0)\langle n'm'^0|nm^1\rangle = -\langle n'm'|W|nm^0\rangle \end{cases}$$

$$\Rightarrow \langle n'm'^0|nm^1\rangle = -\frac{W_{n'm'nm}}{\Delta_{n'n}}.$$

Problem: $\langle nm'^0|nm^1\rangle = ?$ ← 2阶

※ 利用 $\sum_{i=1}^n |i\rangle\langle i| = \mathbb{1}_{n\times n}.$

$\langle nm^0|W|\left(\sum |n'm'\rangle\langle n'm'|\right)nm'\rangle$

$$\begin{cases} 0 = -\langle nm^0|W|nm^1\rangle + E_{nm}^2 \\ \Rightarrow E_{nm}^2 = -\sum_{\substack{n'\neq n \\ m'}} W_{nmn'm'} W_{n'm'nm} / \Delta_{n'n} \\ 0 = -\langle nm'^0|W|nm^1\rangle + E_{nm}^1 \langle nm'^0|nm^1\rangle. \\ \Rightarrow \langle nm'^0|nm^1\rangle = \sum_{\substack{n''\neq n \\ m''}} \frac{W_{nm'n''m''} W_{n''m''nm}}{W_{nm'm}\Delta_{n''n}} \end{cases}$$

$W_{nm'm} = W_{nm'} - W_{nm}$

$\langle nm^0|nm^2\rangle = -\frac{1}{2}\langle nm^1|nm^1\rangle \ ; \ \langle n'm'^0|nm^2\rangle = \ldots$

变分法 Rayleigh-Ritz 定理.

$\longmapsto$ 强关联基态.

$\longmapsto$ 不要求小量 / 精确解.

$\longmapsto$ 试探波函数

物理体系在合理的试探波函数中的 $\langle H\rangle$ 必大于基态能量.

$$\langle H\rangle = \frac{\sum_k |C_k|^2 E_k}{\sum_k |C_k|^2} \geq E_0.$$

思路：选 $\psi(\vec{r}, \alpha_1, \cdots \alpha_n)$

求出 $\langle H\rangle \longrightarrow \left.\frac{\partial H}{\partial \alpha_i}\right|_{\alpha_i^{(0)}} = 0$ 确定 $\alpha_i^{(0)}$

$\Rightarrow$ 得到上限 $E_0 \leq \langle \hat{H} \rangle_{\alpha_i^{(0)}}$

eg. H 基态.

试探：$\psi = a^{-3/2} f(\frac{r}{a})$. 收敛 $\Rightarrow \sim e^{-x^n}$

$\psi = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$. $\psi \sim \left(\frac{2}{\pi a^2}\right)^{3/2} e^{-r^2/a^2}$ etc.

$\Rightarrow \langle T \rangle$. $\langle V \rangle$. $\longmapsto$ 对 a 变分 $\Rightarrow a_0$.

基础：

$$\delta\langle H\rangle_\psi = \frac{1}{\langle\psi|\psi\rangle} 2\mathrm{Re}\left[\langle\delta\psi|\hat{H} - \langle\hat{H}\rangle_\psi|\psi\rangle\right]$$

$$\Rightarrow \left.\mathrm{Re}\left[\langle\delta\psi|\hat{H} - \langle\hat{H}\rangle_\psi|\psi\rangle\right]\right|_{\alpha=\alpha_0} = 0 \quad \text{对 } \delta\alpha_i \text{ 成立}$$

$$\langle\delta\psi|\hat{H} - \langle\hat{H}\rangle_\psi|\psi\rangle = 0$$

$\longrightarrow$ 对足够多的 $\delta\alpha \Rightarrow \delta\psi$ 任取

$$\therefore (\hat{H} - \langle\hat{H}\rangle_\psi)|\psi\rangle = 0 \Rightarrow \hat{H}|\psi\rangle = \langle\hat{H}\rangle_\psi|\psi\rangle.$$

估算激发态

Rayleigh-Ritz 定理：厄米算符驻点位于本征态处，且所有本征态都是驻点.

Lagrange 乘子.

$$\begin{cases} F(\alpha_i;\beta) = \langle\psi(\alpha_i)|\hat{H}|\psi(\alpha_i)\rangle - \beta\left(\langle\psi(\alpha_i)|\psi(\alpha_i)\rangle - 1\right) \\ \frac{\partial F}{\partial \alpha_i} = 0 \quad \frac{\partial F}{\partial \beta} = 0 \end{cases}$$

↳ 约束：归一化.

RR方法：增加 α_i 个数 ⟼ 必能降低上限.

Hylleraas-Undheim 定理

$N\times N$ 本征解从小到大为 $\beta_0 = \beta_1 < \beta_2 \cdots \le \beta_{N-1}$ ⟼ 试探解.

利用对称性/精确基态 ⟼ 正交构建激发态.

完备性 ⟼ 有下限态

$E_{min} = E_n$，当 ψ 为 $0 = \langle 0|\psi\rangle = \cdots = \langle n-1|\psi\rangle$ 的任意态.

若 $\hat{A}$ 有下限而无上界，厄米算符 $\hat{A}$ 的本征函数集 $\{|a\rangle\}$ 完备.

含时微扰 $\hat{H} = \hat{H}_0 + \hat{V}(t)$

$|n(t)\rangle = e^{-iE_nt/\hbar}|n\rangle$. $[0,\tau]$内微扰 ⟵ 能量不守恒；考虑跃迁 ⟼ 本征态不变.

无微扰：

$$|\psi(t)\rangle = \sum C_n e^{-i\frac{E_n}{\hbar}t}|n\rangle.$$

有微扰：

$$|\psi(t)\rangle = \sum C_n(t) e^{-i\frac{E_n}{\hbar}t}|n\rangle. \quad , \quad i\hbar\frac{\partial\psi}{\partial t} = \hat{H}|\psi(t)\rangle.$$

$$i\hbar\frac{\partial}{\partial t}\sum C_n(t)e^{-i\frac{E_n}{\hbar}t}|n\rangle = (\hat{H}_0+\hat{V})\sum C_n(t)e^{-i\frac{E_n}{\hbar}t}|n\rangle.$$

$$i\hbar\sum_n\left(\dot{C}_n e^{-i\frac{E_n}{\hbar}t}|n\rangle\right) + \cancel{\sum_n C_nE_ne^{-i\frac{E_n}{\hbar}t}|n\rangle} = \cancel{\sum_n C_nE_ne^{-i\frac{E_n}{\hbar}t}|n\rangle} + \hat{V}\sum_n C_n e^{-i\frac{E_n}{\hbar}t}|n\rangle$$

$$i\hbar\sum_n\left(\dot{C}_n e^{-i\frac{E_n}{\hbar}t}|n\rangle\right) = \hat{V}\sum_n C_n e^{-i\frac{E_n}{\hbar}t}|n\rangle.$$

左乘 $\underline{\langle m|e^{iE_mt/\hbar}}$ ⟵ 相当于 $\langle m(t)|$

$$i\hbar\sum_n\dot{C}_n(t)e^{\frac{i(E_m-E_n)t}{\hbar}}\langle m|n\rangle = \sum_n\langle m|\hat{V}|n\rangle C_n(t)e^{i\frac{(E_m-E_n)t}{\hbar}}$$

$$\therefore\ i\hbar\dot{C}_m = \sum_n \underbrace{\langle m|\hat{V}(t)|n\rangle}_{V_{mn}} C_n(t)e^{i\frac{E_m-E_n}{\hbar}t}$$

$\frac{E_m-E_n}{\hbar}$ ↑ ω_{mn}.

$$i\hbar\frac{dC_m}{dt} = \sum_n V_{mn}e^{i\omega_{mn}t}C_n(t)$$

$V \ll H_0$ 时，微扰论：

$$C_m = C_m^{(0)} + \lambda C_m^{(1)} + \lambda^2 C_m^{(2)}.$$

$$\begin{cases} i\hbar \dfrac{dc_m^{(0)}}{dt} = 0 \\ i\hbar \dfrac{d}{dt}(c_m^{(1)}) = \sum_n V_{mn} e^{i\omega_{mn}t} c_n^{(0)} \\ i\hbar \dfrac{d}{dt}(c_m^{(2)}) = \sum_n V_{mn} e^{i\omega_{mn}t} c_n^{(1)} \\ \vdots \end{cases}$$

$P_{i\to f} = |\langle f|\psi\rangle|^2$

零阶: $c_{fi}^{(0)}(t) = \delta_{fi}$

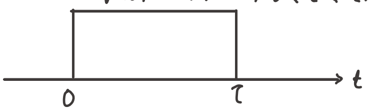
一阶: $c_{fi}^{(1)}(t) = \dfrac{1}{i\hbar}\int_0^t V_{fi}(t')\, e^{i\omega_{fi}t'}\, dt'$

$P_{i\to f} = |c_{fi}(t)|^2$

k级: $\underline{\int_0^t \ k个}$ (PPT)

常微扰

$$\hat{V}(t) = \begin{cases} 0, & t<0 \text{ or } t>\tau \\ \hat{V}, & 0<t<\tau \end{cases}$$



$$P_{i\to f}(t) = \frac{1}{\hbar^2}\left|\langle f|\hat{V}|i\rangle \int_0^t e^{i\omega_{fi}t'}\, dt'\right|^2$$

$$= \frac{1}{\hbar^2}|\langle f|\hat{V}|i\rangle|^2 \left|\frac{e^{i\omega_{fi}t}-1}{\omega_{fi}}\right|^2$$

$$= \frac{4|V_{fi}|^2}{\hbar^2\omega_{fi}^2}\sin^2\left(\frac{\omega_{fi}t}{2}\right)$$ (要求 $|V_{fi}| \ll \Delta E = |E_f - E_i|$)

[$\mapsto$ $t\to 0$ 时 $P \sim \dfrac{|V_{fi}|^2}{\hbar^2}t^2$]

时间尺度

能量标度 ~ $\tau_0 = \frac{\hbar}{E_0}$

跃迁能级 ~ $\tau_{ba} = \omega_{ba}^{-1} = \frac{\hbar}{|E_b - E_a|}$

微扰尺度 ~ $\tau_{pert} \sim \frac{\hbar}{|V_{ba}|}$

$\tau_{pert} \gg \tau_{ba}$ 不改变原有性质

当 $t \to 0$ 时 → 能量不确定，无法区分.

长时间 → $\lim_{t\to\infty} \frac{1}{(\omega_{fi}/2)^2} \sin^2\left(\frac{\omega_{fi}}{2} t\right) = 2\pi t \hbar \delta(E_f - E_i)$

$\therefore P_{i\to f}(t) = \frac{2\pi t}{\hbar} |V_{fi}|^2 \delta(E_f - E_i)$

[线性依赖]

等能量能级

Fermi 黄金定则 $\rho(E_f)$ → 末态密度

$$W_{i\to f} = \int \frac{dP_{if}}{dt} \rho(E_f)\, dE_f$$

$\frac{2\pi}{\hbar} |V_{fi}|^2 \delta(E_f - E_i)$

$$= \frac{2\pi}{\hbar} \sum_{f\neq i} |V_{fi}|^2 \rho(E_i)$$

($W_{i\to f}$ 与 t 无关) ⟶ 小系统到大末态的跃迁速度，$\tau \gg \frac{\hbar}{dE}$

长时间 $P_{i\to f}(t) > 1$ 几率不守恒？

$C_f^{(0)} = 1 \Rightarrow$ 外源保持粒子数

周期微扰：光的吸收和辐射

半经典：电磁场作为经典场 $H' = -\vec{D}\cdot\vec{E}_0\cos\omega t = W\cos\omega t.$

⇒ 微扰

$$V = \hat{v}e^{i\omega t} + \hat{v}^\dagger e^{-i\omega t}.$$

$$\therefore P_{i\to f}(t) = \frac{1}{\hbar^2}\left| \underbrace{\langle f|\hat{v}|i\rangle}_{V_{fi}} \int_0^t e^{i(\omega_f+\omega)t'}dt' + \underbrace{\langle f|\hat{v}^\dagger|i\rangle}_{V_{fi}^*} \int_0^t e^{i(\omega_f-\omega)t'}dt' \right|^2$$

$$= \frac{4}{\hbar^2}\left[\frac{\sin^2\left(\frac{\omega_f+\omega}{2}t\right)}{(\omega_{fi}+\omega)^2}|V_{fi}|^2 + \frac{\sin^2\left(\frac{\omega_f-\omega}{2}t\right)}{(\omega_{fi}-\omega)^2}|V_{fi}^*|^2\right]$$

共振区 $\omega \simeq \pm\omega_{fi}$ $\quad P \sim t^2/\hbar^2 \cdot |\langle f|v|i\rangle|_{\omega=\omega_{fi}}$

表象

$\{\hat{F}, \cdots\}$ 力学量完备集 : $\{\phi_i\}$ ↪ F表象 ↦ 相当于坐标系

$\{\hat{G}, \cdots\}$ ⟶ G表象.

$\Rightarrow \forall \psi,\ |\psi\rangle = \sum_n \underbrace{C_n}_{\text{表象中的坐标}} |\phi_n\rangle \qquad C_n = \langle\phi_n|\psi\rangle$

$\{C_n\}$ 为 $|\psi\rangle$ 在 F 表象中的表示.

$$|\psi\rangle = \sum_n \langle\phi_n|\psi\rangle|\phi_n\rangle$$
$$= \sum_n |\phi_n\rangle\langle\phi_n|\psi\rangle$$

投影算符 $\hat{P}_n = |\phi_n\rangle\langle\phi_n| \qquad (\hat{P}_n^2 = \hat{P}_n).$

$\hat{P}_n$ 的本征值 0 或 1

自然表示(自然展开)

$$\hat{O}|\varphi_n\rangle = \hat{O}_n|\varphi_n\rangle$$

以$\{|\varphi_n\rangle\}$为基底 线性空间.

$$[\hat{O}] = \begin{pmatrix} O_1 & & & \\ & O_2 & & \\ & & \ddots & \\ & & & \ddots \end{pmatrix} = \sum_n |\varphi_n\rangle O_n \langle\varphi_n| = \underline{\sum_n O_n |\varphi_n\rangle\langle\varphi_n|}$$

自然展开.

任意 $\hat{A}$: $A_{mn} = \langle\varphi_m|\hat{A}|\varphi_n\rangle$.

算符函数

$$F(\hat{O}) = \sum_n |\varphi_n\rangle F(O_n)\langle\varphi_n|$$

$$= \sum_n |\varphi_n\rangle \sum_{m=0}^{\infty} \frac{F^{(m)}(0)}{m!}(O_n)^m \langle\varphi_n|.$$

逆 $\hat{O}\hat{O}^{-1} = \hat{O}^{-1}\hat{O} = 1$

$$\hat{O}^{-1} = \sum_n |\varphi_n\rangle \frac{1}{O_n}\langle\varphi_n|$$

表象变换

F表象$\{|\phi_k\rangle\}$, F'表象$\{|\phi_k'\rangle\}$

$$|\phi_\alpha'\rangle = \sum_k |\phi_k\rangle\langle\phi_k|\phi_\alpha'\rangle = \sum_k |\phi_k\rangle S_{k\alpha} = \sum_k |\phi_k\rangle S^*_{\alpha k}$$

F

$$|\phi_\beta'\rangle = \sum_j |\phi_j\rangle S^*_{\beta j}$$

$$A'_{\alpha\beta} = \left(\sum_k \langle\phi_k|S_{\alpha k}\right)\hat{A}\left(\sum_j |\phi_j\rangle S^*_{\beta j}\right) = \left(SAS^\dagger\right)_{\alpha\beta}.$$

S.E: $i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle$, $\psi = \sum a_k(t)|\phi_k\rangle$

$$\Rightarrow \quad i\hbar\dot{a}_j = \sum_k a_k H_{jk}$$

F表象中有$\hat{H} \mapsto E_n$.

$$i\hbar\dot{a}_j = a_j E_j$$

均值 $\langle\psi|\hat{A}|\psi\rangle = \sum_{jk} a_j^* A_{jk} a_k$.

绘景 (picture)

演化算符 $\hat{u}(t, t_0)$

$$|\psi(t)\rangle = \hat{u}\,|\psi(t_0)\rangle. \qquad \hat{u}(t_0, t_0) = 1.$$

$$\hat{u}\left(a|\psi_1(0)\rangle + b|\psi_2(0)\rangle\right) = a\,\hat{u}|\psi_1\rangle + b\,\hat{u}|\psi_2\rangle.$$

$$\langle\psi(t)|\psi(t)\rangle = \langle\psi(0)|\underbrace{\hat{u}^\dagger\hat{u}}|\psi(0)\rangle$$ 幺正: $u^\dagger = u^{-1}$

$$i\hbar\frac{\partial}{\partial t}\left(\hat{u}|\psi(0)\rangle\right) = \hat{H}\hat{u}|\psi(0)\rangle$$

$$\therefore\ i\hbar\frac{\partial \hat{u}}{\partial t} = \hat{H}\hat{u} \qquad \mapsto \qquad \hat{u} = e^{-i\hat{H}t/\hbar}$$

$$\langle\hat{F}\rangle_{\psi(t)} = \langle u\psi|\hat{F}|u\psi\rangle$$
$$= \langle\psi|\underbrace{u^\dagger F u}|\psi\rangle.$$

$F(t) = u^\dagger F u$ {算符随t变}

$$\frac{d\hat{F}}{dt} = -\frac{1}{i\hbar}(u^\dagger H)Fu + \frac{1}{i\hbar}u^\dagger F H u.$$ $\{[u, \hat{H}] = 0\}$

$$= \frac{1}{i\hbar}\left\{-Hu^\dagger F u + u^\dagger F u H\right\}.$$

$$= \frac{1}{i\hbar}[F(t), \hat{H}]$$ — 海森堡方程.

Picture:

$$\begin{array}{ccc}
\psi(0) & \longrightarrow & \psi(t) \\
F & & F \\
 & \Updownarrow & \\
\psi & \longrightarrow & \psi \\
F(0) & & F(t).
\end{array}$$

Dirac 相互作用绘景 (I)

$\hat{H} = \hat{H}_0 + \hat{V}(t)$ （分离含时部分）

S：薛
H：海
I：相互作用.

$|\psi\rangle_I = e^{iH_0t/\hbar}|\psi(t)\rangle_S$.

$i\hbar\frac{d}{dt}|\psi\rangle_I = V_I|\psi\rangle_I$

$V_I(t) = e^{i\hat{H}_0t/\hbar}\hat{H}_0 e^{-i\hat{H}_0t/\hbar}$

$\hat{A}_I = e^{i\hat{H}_0t/\hbar}\hat{A}_s e^{-i\hat{H}_0t/\hbar}$

$\frac{d\hat{A}_I}{dt} = \frac{1}{i\hbar}[\hat{A}_I, \hat{H}_0]$

设 $\psi = \hat{U}\psi(0) \Rightarrow$

$i\hbar\dot{\hat{U}}(t,t_i) = \hat{V}\hat{U} \longrightarrow \hat{U} = 1 - \frac{i}{\hbar}\int_{t_i}^{t}\hat{V}_I(t')\hat{U}_I(t',t_i)dt'$

微扰 $\hat{U}^{(0)} = 1$. $\Rightarrow U^{(1)} = 1 - \frac{i}{\hbar}\int_{t_i}^{t}\hat{V}_I(t')dt'$

— Dyson 序列.

$U^{(i)} = \left(-\frac{i}{\hbar}\right)^n\int_{t_{n-1}}^{t_n}V\int V\cdots\int_{t_1}^{t_1}V\,dt'$

$P_{i\to f}(t) = |\langle f|V_I|i\rangle|^2$. $= \delta_{fi} - \frac{i}{\hbar}\int_0^t\langle f|V(t')|i\rangle e^{i\omega_{fi}t'}dt'$.