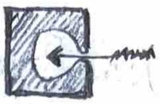
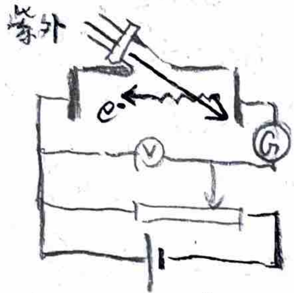
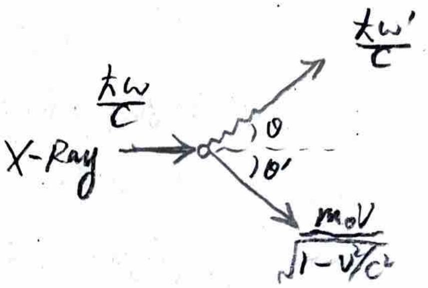
0. 史诗

黑体辐射：Plank ($\varepsilon=h\nu$) ⇒ 辐射量子化.



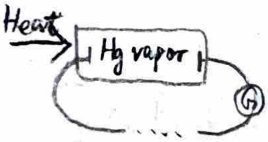
光电效应：Einstein ($\varepsilon=h\nu$) ⇒ 辐射量子化





Compton效应：$\lambda'-\lambda=\frac{h}{m_e c}(1-\cos\theta)$ ⇒ P-E：光的波粒二象性；能量、动量守恒

Franck-Hertz实验：



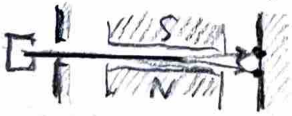
⇒ 原子能量量子化. Hg ($T=4.9V$).

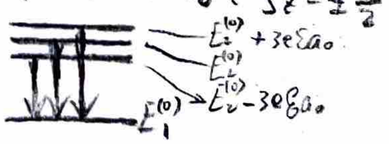
Davisson-Germer电子衍射实验：$n\lambda=d\sin\theta$ ⇒ 电子的波粒二象性 (de Broglie).

氢原子光谱：Rydberg…… $\nu=R_H c(\frac{1}{n_1^2}-\frac{1}{n_2^2})$ ⇒ 原子能量量子化 H. (Bohr：三条假设)

⇒ Sommerfeld：$\oint p\,dq=nh$.

Stern-Gerlach实验：$M_z=\pm M_B$ ⇒ Uhlenbeck-Goudsmit：$S_z=\pm\frac{\hbar}{2}$





Stark效应(一级H)：$H'=e\mathcal{E}z$ ⇒ 简并微扰 (Schrödinger)

简单Zeeman效应：$U=\frac{e}{2\mu c}(\hat{L}_z+2\hat{S}_z)B_s$ ⇒ 强磁场，忽略角动量耦合

$$\omega=\omega_0$$
$$\omega=\omega_0\pm\frac{eB_s}{2\mu c}.$$

一. 线性空间 → 矢量

1. V为域F上的线性空间：V(F) 由矢量 $\{\vec{\alpha}_i\}_m$ 张成

若 $\vec{\alpha}_i \in V$，$\lambda_i \in F$，$\vec{\alpha} = \sum_m \lambda_i \vec{\alpha}_i$，则 $\vec{\alpha}$ 属于 V(F).

2. 线性空间的基：$B = \{\vec{\alpha}_i\}_m$，$L(B) = V(F)$

若 $\vec{\alpha} = \sum_m \lambda_i \vec{\alpha}_i$，则 $(\lambda_1, \dots, \lambda_m)$ 为 $\vec{\alpha}$ 在基B下的坐标

3. 内积空间（不赋范）：函；积分定义内积 $(\vec{\alpha}, \vec{\beta}) = (\vec{\beta}, \vec{\alpha})^*$，$(\vec{\alpha}, \vec{\alpha}) \geq 0$，线性.

单位正交基：$B = \{\vec{\alpha}_i\}_m$，$L(B) = V(F)$，且 $(\vec{\alpha}_i, \vec{\alpha}_j) = \delta_{ij}$

施密特正交化：递归

二. 不同基下的矢量

1. 矢量 $\vec{x} = \sum_i \lambda_i \vec{\alpha}_i = \sum_j \mu_j \vec{\beta}_j$：$\{\vec{\alpha}_i\}_m$ $\{\vec{\beta}_j\}_m$ 单位正交化.

则 $\lambda_i = (\vec{\alpha}_i, \vec{x}) = \sum_j \mu_j (\vec{\alpha}_i, \vec{\beta}_j)$，

即 $(\vec{\alpha}_i, \vec{x}) = \sum_j (\vec{\beta}_j, \vec{x})(\vec{\alpha}_i, \vec{\beta}_j) = \sum_j (\vec{\alpha}_i, \vec{\beta}_j)(\vec{\beta}_j, \vec{x}) = \sum_j S_{ij} (\vec{\beta}_j, \vec{x})$；$\vec{X}_\alpha = S\vec{X}_\beta$，$\vec{X}_\beta = S^{-1}\vec{X}_\alpha$

$\therefore \sum_i (\vec{\alpha}_i, \vec{x}) \vec{\alpha}_i = \sum_{ij} \vec{\alpha}_i S_{ij} (\vec{\beta}_j, \vec{x})$，写成 $\sum_i |\alpha_i\rangle\langle\alpha_i|x\rangle = \sum_{ij} |\alpha_i\rangle\langle\alpha_i|\beta_j\rangle\langle\beta_j|x\rangle$.

2. 定义 $S^\dagger = \tilde{S}^*$ 为S的厄密共轭，则

$$(S^\dagger S)_{ij} = \sum_k (S^\dagger)_{ik} (S)_{kj} = \sum_k S^*_{ki} S_{kj} = \sum_k (\vec{\alpha}_k, \vec{\beta}_i)^* (\vec{\alpha}_k, \vec{\beta}_j) = \sum_k (\vec{\beta}_i, \vec{\alpha}_k)(\vec{\alpha}_k, \vec{\beta}_j)$$

$$= \sum_k \langle\beta_i|\alpha_k\rangle\langle\alpha_k|\beta_j\rangle = \langle\beta_i|\beta_j\rangle = \delta_{ij}$$

即 $S^\dagger S = I$，故 $S^\dagger = S^{-1}$.

三. 线性变换 → 矩阵

1. $\vec{Y} = F \cdot \vec{X}$，设 $F^\dagger = F$ 厄密矩阵

加法；数乘；乘法：$(FG)\vec{X} = F(G\vec{X})$；逆：$FF^{-1} = F^{-1}F = F^\dagger F^{-1} = FF^{\dagger -1} = FF^{-1\dagger} = I$

函数：$h(F) = \sum_{n=0}^{\infty} \frac{h^{(n)}(0)}{n!} F^n$.　　通过矩阵初等变换求矩阵的逆．相抵标准形.

2. $\vec{Y} = F \cdot \vec{X}$，在基B下，$\sum_j \mu_j \vec{\alpha}_j = \sum_i \lambda_i F \cdot \vec{\alpha}_i$，$\{\alpha_i\}_m$ 单位正交化.

则 $\mu_j = (\vec{\alpha}_j, \vec{Y}) = \sum_i \lambda_i (\vec{\alpha}_j, F\vec{\alpha}_i)$.

即 $(\vec{\alpha}_j, \vec{Y}) = \sum_i (\vec{\alpha}_i, \vec{x})(\vec{\alpha}_j, F\vec{\alpha}_i) = \sum_i (\vec{\alpha}_j, F\vec{\alpha}_i)(\vec{\alpha}_i, \vec{x}) = \sum_i F_{ji} (\vec{\alpha}_i, \vec{x})$；$\vec{Y}_\alpha = F \cdot \vec{X}_\alpha$.

$\therefore \sum_j (\vec{\alpha}_j, \vec{Y}) \vec{\alpha}_j = \sum_{ij} \vec{\alpha}_j F_{ji} (\vec{\alpha}_i, \vec{x})$，写成 $\sum_j |\alpha_j\rangle\langle\alpha_j|Y\rangle = \sum_{ij} |\alpha_j\rangle\langle\alpha_j|F|\alpha_i\rangle\langle\alpha_i|X\rangle$.

四. 不同基下的矩阵

1. 由 $\vec{Y}_\alpha = F\vec{X}_\alpha$，$\vec{Y}_\alpha = S\cdot\vec{Y}_\beta$，$\vec{X}_\alpha = S\vec{X}_\beta$． $B=\{\vec{\alpha}_i\}_m$ $B'=\{\vec{\beta}_j\}_m$ 正交完备系，

得 $\vec{Y}_\beta = S^{-1}FS\vec{X}_\beta = (S^{+}FS)\vec{X}_\beta$． 即

在B中，$\sum_j \mu_j \vec{\alpha}_j = \sum_i \lambda_i F\vec{\alpha}_i$，$\mu_j = \sum_i \lambda_i (\vec{\alpha}_j \cdot F\vec{\alpha}_i)$；

在B′中，$\sum_k \eta_k \vec{\beta}_k = \sum_t \gamma_t F\vec{\beta}_t$，$\eta_k = \sum_t \gamma_t (\vec{\beta}_k \cdot F\vec{\beta}_t)$；　在B下展开 $\vec{\beta}_k$ 和 $\vec{\beta}_t$，得

$$\eta_k = \sum_t \gamma_t \left(\sum_i \vec{\alpha}_i(\vec{\alpha}_i,\vec{\beta}_k), \sum_j F\vec{\alpha}_j(\vec{\alpha}_j,\vec{\beta}_t)\right)$$

$$= \sum_t \gamma_t \left[\sum_{ij} (\vec{\alpha}_i,\vec{\beta}_k)^*(\vec{\alpha}_i, F\vec{\alpha}_j)(\vec{\alpha}_j,\vec{\beta}_t)\right]$$

$$= \sum_t \gamma_t \left[\sum_{ij} (\vec{\beta}_k,\vec{\alpha}_i)(\vec{\alpha}_i, F\vec{\alpha}_j)(\vec{\alpha}_j\cdot\vec{\beta}_t)\right]$$

$$= \sum_t \gamma_t \sum_{ij} S_{ik}^*(\vec{\alpha}_i \cdot F\vec{\alpha}_j) S_{jt}$$

$$= \sum_t \gamma_t \sum_{ij} S_{ki}^{+} F_{ij} S_{jt}$$

2. 欲将 $S^{+}FS$ 变为对角阵，即 $\begin{bmatrix}\lambda_1 & & \\ & \ddots & \\ & & \lambda_m\end{bmatrix} = S^{+}FS = S^{-1}FS$，则 $F = S\begin{bmatrix}\lambda_1 & & & \\ & \lambda_i & & \\ & & \ddots & \\ & & & \lambda_m\end{bmatrix}S^{-1}$．

需有 $FS_i = \lambda_i S_i$，λ_i：本征值，S_i：本征矢． λ_i 也记为 F_i

即有 $\det|F-\lambda I| = 0$

反之，对任意厄密F，解 $\det|F-\lambda I|_{m\times m} = 0$，有

① λ 有m个解，λ_i 为实

② 属于不同本征值的本征矢正交

③ 属于相同本征值的本征矢（简并）通过施密特正交化而正交．（常注意Pop）

④ $(\vec{x}, F\vec{x})/(\vec{x},\vec{x})$ 有下界、无上界，则本征矢完备　$\overline{\varepsilon^2}=0$、帕塞瓦尔、封闭性关系

3. 若 F、G 有共同本征矢，且组成完备系，则 $FG = GF$．

若 $FG=GF$，则 F、G 有共同本征矢，且组成完备系．（简并→找新"对易"G′直到本征矢无简并）

若 F、G 无共同本征矢，则 $FG \neq GF$，$\sqrt{\overline{|A-\bar{A}I|^2}\cdot\overline{|B-\bar{B}I|^2}} \geq \frac{1}{2}|\overline{AB-BA}|$． Cauchy-Schwarz证．

若 $FG \neq GF$，则 F、G 无共同本征矢，同有测不准关系．

五. 量子力学

1. 线性空间 → 矢量 → 态矢
2. 线性变换 → 矩阵 → 算符.
3. 统计诠释：$X = \sum_i \lambda_i \alpha_i$，$|\lambda_i|^2$ 概率；平均值 $\overline{F} = \sum_i |\lambda_i|^2 F_i$ 测量到 F_i

   设 $\{\alpha_i\}$ 为 F 的本征矢，则 $\overline{F} = \sum_i \langle X|\alpha_i\rangle\langle\alpha_i|X\rangle F_i = \sum_i \langle X|F_i\alpha_i\rangle\langle\alpha_i|X\rangle$

   $= \sum_i \langle X|F|\alpha_i\rangle\langle\alpha_i|X\rangle = \langle X|F|X\rangle$.
4. 动力学方程：$i\hbar\frac{\partial}{\partial t}|X\rangle = H|X\rangle$　H：哈密顿矩阵.

   当 H 不含时，且 $[F,H] = FH - HF = 0$，$\begin{cases}\frac{d}{dt}\overline{F} = i\hbar\overline{[F,H]} + \overline{\frac{\partial F}{\partial t}} = 0 \\ \frac{\partial}{\partial t}\langle X|X\rangle = -\nabla\cdot\frac{i\hbar}{2\mu}([illegible]\langle\nabla X| - |\nabla X\rangle\langle X|) = 0\end{cases}$ 守恒量
5. 自旋：S Hermitian 算符，本征值 $\pm\frac{\hbar}{2}$，$S\times S = i\hbar S$. 与原态矢空间直积.
6. 全同：质量、电荷、自旋等固有性质完全相同 → 交换无影响.

六. 演绎.

1. 角动量的本征值.

①角动量的定义

$\vec{J}\times\vec{J}=i\hbar\vec{J}$；$J=J^\dagger\Rightarrow[J_x,J_y]=i\hbar J_z$，$[J_y,J_z]=i\hbar J_x$，$[J_z,J_y]=i\hbar J_y$.

由 $J^2=J_x^2+J_y^2+J_z^2$，可得 $[J^2,J_z]=0$。设共同本征态为 $|j,m\rangle$，$J^2|jm\rangle=j_0|jm\rangle$，$J_z|jm\rangle=m|jm\rangle$

② 本征值范围与取值.

定义 $J_+=J_x+iJ_y$，$J_-=J_x-iJ_y$，有 $J_+=J_-^\dagger$，

由于 $[J_z,J_\pm]=\pm\hbar J_\pm$，可得 $J_\pm|jm\rangle\propto|j(m\pm1)\rangle$；

由于 $\langle jm|J^2|jm\rangle=\langle jm|J_x^2|jm\rangle+\langle jm|J_y^2|jm\rangle+\langle jm|J_z^2|jm\rangle\geq\langle jm|J_z^2|jm\rangle=m^2$，可得 $m^2\leq j_0$

故 $\exists\ \bar{m}$、$\underline{m}$

$J_+|j\bar{m}\rangle=0$；$J^2|j\bar{m}\rangle=\{[\frac{1}{2}(J_++J_-)]^2+[\frac{1}{2i}(J_+-J_-)]^2+J_z^2\}|j\bar{m}\rangle=[J_-J_++J_z(J_z+1)]|jm\rangle$ 得 $j_0=\bar{m}(\bar{m}+1)$

取正解，得 $\bar{m}=\sqrt{j_0+\frac{1}{4}}-\frac{1}{2}\triangleq j$

$J_-|j\underline{m}\rangle=0$；$J^2|j\underline{m}\rangle=\{[\frac{1}{2}(J_++J_-)]^2+[\frac{1}{2i}(J_+-J_-)]^2+J_z^2\}|j\underline{m}\rangle=[J_+J_-+J_z(J_z-1)]|jm\rangle$ 得 $j_0=\underline{m}(\underline{m}-1)$

取负解，得 $\underline{m}=-\sqrt{j_0+\frac{1}{4}}+\frac{1}{2}\triangleq -j$

由于 j 到 $-j$ 差整数，故 $j=0,\frac{1}{2},1,\frac{3}{2},\cdots$　$j_0=j(j+1)$.

③ J^2J_z 表象下 J^2、J_x、J_y、J_z、J_+、J_- 的矩阵元.

设 $J_\pm|jm\rangle=k_m|j(m\pm1)\rangle$，有 $J_\mp J_\pm|jm\rangle=k_mJ_\mp|j(m\pm1)\rangle=[j(j+1)-m^2\mp m]|jm\rangle$

$\therefore k_m\langle jm|J_\mp|j(m\pm1)\rangle=j(j+1)-m^2\mp m$，且 $\langle j(m\pm1)|J_\pm|jm\rangle=k_m$

$\therefore|k_m|^2=j(j+1)-m^2\mp m$，令相位为 0，得 $k_m=\sqrt{j(j+1)-m^2\mp m}$，

故 $J_\pm|jm\rangle=\sqrt{j(j+1)-m(m\pm1)}\,|j(m\pm1)\rangle$

$J_x|jm\rangle=\frac{1}{2}\sqrt{j(j+1)-m(m+1)}\,|j(m+1)\rangle+\frac{1}{2}\sqrt{j(j+1)-m(m-1)}\,|j(m-1)\rangle$

$J_y|jm\rangle=\frac{1}{2i}\sqrt{j(j+1)-m(m+1)}\,|j(m+1)\rangle-\frac{1}{2i}\sqrt{j(j+1)-m(m-1)}\,|j(m-1)\rangle$.

2. 耦合角动量的本征值.

① 耦合角动量

$J = J_1 + J_2$, $\Rightarrow J \times J = i\hbar J$; $J = J^{\dagger}$ $\Rightarrow J_1^2, J_2^2, J^2, J_z$ 互相对易，设共同本征态为 $|j_1 j_2 j m\rangle$

② 本征值范围与取值.

将 $J_z = J_{1z} + J_{2z}$ 作用于 $|j_1 j_2 j m\rangle = \sum_{m_1 m_2} |j_1 m_1 j_2 m_2\rangle\langle j_1 m_1 j_2 m_2 | j_1 j_2 j m\rangle$ 两边，得

$m = m_1 + m_2$

由维数不变：耦合表象 $\sum_{\underline{j}}^{\bar{j}} (2j+1)$ = 非耦合表象 $(2j_1+1)(2j_2+1)$，得

$\underline{j}^2 = (j_1 - j_2)^2$，而 $\bar{j} = \bar{m} = \bar{m}_1 + \bar{m}_2 = j_1 + j_2$，故

$j = j_1 + j_2, j_1 + j_2 - 1, \cdots, |j_1 - j_2| + 1, |j_1 - j_2|$.

③ 非耦合表象下耦合角动量的矩阵元：$\langle j_1 m_1 j_2 m_2 | j_1 j_2 j m\rangle$.

例：自旋角动量 s_1 s_2 之耦合在非耦合表象 $|\frac{1}{2} m_1 \frac{1}{2} m_2\rangle$ 下的矩阵元.

设 $\phi(S^2, S_z) = \begin{bmatrix} \quad & \quad \\ \quad & \quad \end{bmatrix}_{4\times4} \begin{pmatrix} |\uparrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \\ |\uparrow\downarrow\rangle \\ |\downarrow\uparrow\rangle \end{pmatrix}$

1) ϕ 是 S_z 的本征态.

$$S_z \phi(S^2, S_z) = (S_{1z} + S_{2z}) \phi(S^2, S_z) = \begin{bmatrix} \quad & \quad \\ \quad & \quad \end{bmatrix} \begin{pmatrix} 1 & |\uparrow\uparrow\rangle \\ -1 & |\downarrow\downarrow\rangle \\ 0 & |\uparrow\downarrow\rangle \\ 0 & |\downarrow\uparrow\rangle \end{pmatrix} = m \begin{bmatrix} \quad & \quad \\ \quad & \quad \end{bmatrix} \begin{pmatrix} |\uparrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \\ |\uparrow\downarrow\rangle \\ |\downarrow\uparrow\rangle \end{pmatrix}.$$

2) ϕ 是 S^2 的本征态.

$$S^2 \phi(S^2, S_z) = (S_1^2 + S_2^2 + S_1 S_2 + S_2 S_1) \phi(S^2, S_z) = \frac{3}{2} + \frac{1}{2}(\sigma_{1x}\sigma_{2x} + \sigma_{1y}\sigma_{2y} + \sigma_{1z}\sigma_{2z}) \phi(S^2, S_z)$$

$$= j(j+1) \begin{bmatrix} \quad & \quad \\ \quad & \quad \end{bmatrix} \begin{pmatrix} |\uparrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \\ |\uparrow\downarrow\rangle \\ |\downarrow\uparrow\rangle \end{pmatrix}.$$

归一化波函数，取 0 相位，得

$$\left.\begin{array}{lll} j=1 & m=1 & \phi = |\uparrow\uparrow\rangle \\ j=1 & m=-1 & \phi = |\downarrow\downarrow\rangle \\ j=1 & m=0 & \phi = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \end{array}\right\} \text{三重态}$$

$j=0$　$m=0$　$\phi = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$　独态.

3. 连续谱表象与表象变换

坐标表象中

本征方程 $\hat{x}|x'\rangle = x'|x'\rangle$

坐标本征矢 $\langle x|x'\rangle = \delta(x-x')$

动量本征矢 $\langle x|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{ip'x/\hbar}$

$$\phi(x) = \langle x|\phi\rangle = \int dp' \langle x|p'\rangle\langle p'|\phi\rangle$$
$$= \int dp' \frac{1}{\sqrt{2\pi\hbar}} e^{ip'x/\hbar} \phi(p')$$

坐标算符 $\langle x'|\hat{x}|x''\rangle = x'\delta(x'-x'')$

动量算符 $\langle x'|\hat{p}|x''\rangle$

$$= \iint dp'dp'' \langle x'|p'\rangle\langle p'|\hat{p}|p''\rangle\langle p''|x''\rangle$$
$$= \frac{1}{2\pi\hbar} \iint dp'dp'' e^{ip'x'/\hbar} p'\delta(p'-p'') e^{-ip''x''/\hbar}$$
$$= \frac{1}{2\pi\hbar} \int dp' p' e^{ip'(x'-x'')/\hbar}$$
$$= \frac{1}{2\pi\hbar} \left(-i\hbar\frac{\partial}{\partial x'}\right) \int dp' e^{ip'(x'-x'')/\hbar}$$
$$= -i\hbar\frac{\partial}{\partial x'} \delta(x'-x'')$$

$\langle x'|F(x)|x''\rangle = F(x')\delta(x'-x'')$

故 $i\hbar\frac{\partial}{\partial t}\langle x|\psi(t)\rangle = \langle x|H|\psi(t)\rangle =$

$\int dx' \langle x|H x'\rangle\langle x'|\psi(t)\rangle =$

$\int dx' \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\delta(x-x') + V(x)\delta(x-x')\right]\psi(x',t) =$

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

动量表象中

本征方程 $\hat{p}|p'\rangle = p'|p'\rangle$

动量本征矢 $\langle p|p'\rangle = \delta(p-p')$

坐标本征矢 $\langle p|x'\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{-ix'p/\hbar}$.

$$\phi(p) = \langle p|\phi\rangle = \int dx' \langle p|x'\rangle\langle x'|\phi\rangle$$
$$= \int dx' \frac{1}{\sqrt{2\pi\hbar}} e^{-ix'p/\hbar} \phi(x')$$

动量算符 $\langle p'|\hat{p}|p''\rangle = p'\delta(p'-p'')$.

坐标算符 $\langle p'|\hat{x}|p''\rangle$

$$= \iint dx'dx'' \langle p'|x'\rangle\langle x'|\hat{x}|x''\rangle\langle x''|p''\rangle$$
$$= \frac{1}{2\pi\hbar} \iint dx'dx'' e^{-ix'p'/\hbar} x'\delta(x'-x'') e^{ip''x''/\hbar}$$
$$= \frac{1}{2\pi\hbar} \int dx' x' e^{-ix'(p'-p'')/\hbar}$$
$$= \frac{1}{2\pi\hbar} \left(i\hbar\frac{\partial}{\partial p'}\right) \int dx' e^{-ix'(p'-p'')/\hbar}$$
$$= i\hbar\frac{\partial}{\partial p'} \delta(p'-p'').$$

$\langle p'|F(x)|p''\rangle = F\left(i\hbar\frac{\partial}{\partial p'}\right)\delta(p'-p'')$

故 $i\hbar\frac{\partial}{\partial t}\langle p|\psi(t)\rangle = \langle p|H|\psi(t)\rangle =$

$\int dp' \langle p|H|p'\rangle\langle p'|\psi(t)\rangle =$

$\int dp' \left[\frac{p^2}{2m}\delta(p-p') + V\left(i\hbar\frac{\partial}{\partial p}\right)\delta(p-p')\right]\psi(p',t) =$

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

4. 一维无限深势阱、方势阱、方势垒、δ势阱、δ势垒、谐振子.

① 一维定态Schrödinger方程 $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + U(x)\psi = E\psi$ ：束缚态：$\psi(x)|_{|x|\to\infty} = 0$；非束缚态：反之

1) 朗斯基定理

$\psi_1(x)$ $\psi_2(x)$ 是能量相同解，则 $\det\begin{vmatrix}\psi_1 & \psi_2 \\ \psi_1' & \psi_2'\end{vmatrix} = \text{constant}$；联立两Schrödinger证.

2) 共轭定理

$\psi(x)$ 是解，则 $\psi^*(x)$ 是另一能量相同解：取两 Schrödinger 共轭证.

3) 反射定理

$U(x)=U(-x)$，则若 $\psi(x)$ 是解，$\psi(-x)$ 是另一能量相同解：取两 Schrödinger 对偶证.

4) 展开定理.

$U(x)=U(-x)$，则 $\forall E$，任何解可由宇称确定解展开.

由反射定理，$\psi(x)$、$\psi(-x)$ 属于同能量解，故 $f(x)=\psi(x)+\psi(-x)$，$g(x)=\psi(x)-\psi(-x)$ 有同能，且宇称确定

5) 束缚态定理.

束缚态：$E<U(+\infty,-\infty)$　非束缚态 $E>U(+\infty)$ 或 $U>U(-\infty)$.

通过 $\frac{d^2}{dx^2}\psi+\frac{2\mu}{\hbar^2}[E-U(x)]\psi=0$ 在 ∞ 处性质证明.

6) 不简并定理

一维束缚态是非简并态.

设 $\psi_1(x)$ $\psi_2(x)$ 是同能量的两解，由朗斯基定理：$\det\begin{vmatrix}\psi_1 & \psi_2\\ \psi_1' & \psi_2'\end{vmatrix}=C$，由于是束缚态，$\psi_1\ \psi_2\big|_{|x|\to\infty}=0$，故 $C=0$，ψ_1 ψ_2 线性相关是同态，与假设矛盾.

7) ~~位相定理~~ 宇称定理

~~一维束缚态波函数的位相是常数~~. 一维束缚态波函数有确定宇称 if $U(-x)=U(x)$

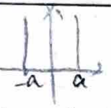
~~设 $\psi(x)=\rho(x)e^{i\theta(x)}$ 代入 Schrödinger 方程~~ 由反射定理，$\psi(x)$ 与 $\psi(-x)$ 是同能解，由不简并定理，$\psi(x)=A\psi(-x)$，取 $x=-x$，有 $\psi(-x)=A\psi(x)$，故 $A^2=1$

$$\begin{cases}A=1 & \text{偶宇称}\\ A=-1 & \text{奇宇称}\end{cases}$$

8) 连续性定理

若 $U(x)$ 连续，则 $\psi'(x)$ 连续，对 Schrödinger 方程小区域积分可证.

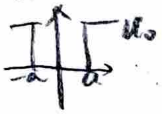
② 无限深方势阱



偶宇称 $\psi(x)=A\cos(n+\frac{1}{2})\frac{\pi x}{a}$　　奇宇称 $\psi(x)=B\sin\frac{n\pi x}{a}$.

合写为 $\psi_n(x)=\frac{1}{\sqrt{a}}\sin\frac{n\pi}{2a}(x+a)$，节点数 $n-1$.

③ 有限深方势阱



束缚态解：$0<E<U_0$

$$\begin{cases} x<-a,\ x>a & \frac{d^2}{dx^2}\psi-\frac{2m(U_0-E)}{\hbar^2}\psi=0,\quad \alpha=\frac{\sqrt{2m(U_0-E)}}{\hbar} \\ -a<x<a & \frac{d^2}{dx^2}\psi+\frac{2mE}{\hbar^2}\psi=0,\quad k=\frac{\sqrt{2mE}}{\hbar} \end{cases} \Rightarrow \psi(x)=\begin{cases} Ce^{\alpha x} & x<-a \\ A\cos kx+B\sin kx & -a<x<a \\ De^{-\alpha x} & x>a. \end{cases}$$

偶宇称

$$\begin{cases} A\cos ka=De^{-\alpha a} \\ -kA\sin ka=-\alpha De^{-\alpha a} \end{cases}$$

奇宇称

$$\begin{cases} B\sin ka=De^{-\alpha a} \\ kB\cos ka=-\alpha De^{-\alpha a} \end{cases}$$

有 $k\tan ka=\alpha$ (1)　$k\cot ka=-\alpha$ (2)　$k^2+\alpha^2=\frac{2mU_0}{\hbar^2}$ (3)

联立(1)(2)(3) 图解法得 $E_n=\frac{\hbar^2}{2m}k_n^2$，$k_n$ 为(1)(2)与(3)交点对应的 k. $0<k_1<\frac{\pi}{2a}<k_2<\frac{\pi}{a}<\cdots$

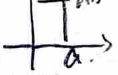
知 $k^2+\alpha^2=\frac{2mU_0}{\hbar^2}\geq(\frac{\pi}{2a}n)^2$，$n$ 为能级数，$n=\lfloor\frac{8mU_0a^2}{\pi^2\hbar^2}\rfloor$.

$$\begin{cases} k^2+\alpha^2\geq(\frac{\pi}{a})^2\text{时，出现第一个偶宇称激发态（束缚态解总存在基态，为偶宇称）} \\ k^2+\alpha^2\geq(\frac{\pi}{2a})^2\text{时，出现第一个奇宇称（激发态）.} \end{cases}$$

① $U_0\gg E$ 时，$\alpha\approx\frac{\sqrt{2mU_0}}{\hbar}$. $k=\frac{\sqrt{2mE}}{\hbar}$，$ka\approx\frac{\pi}{2}+n\pi$.

② $U_0\approx E$ 时，$\alpha\approx 0$　$k=\frac{\sqrt{2mE}}{\hbar}$，$ka\approx n\pi$.

④ 方势垒



非束缚态解：$E>U(\pm\infty)=0$，设粒子从左入射.

$$\begin{cases} 0<x<a: & \psi''-\alpha^2\psi=0 \\ x<0,\ x>a: & \psi''+k^2\psi=0 \end{cases} \Rightarrow \psi(x)=\begin{cases} e^{ikx}+Re^{-ikx} & x<0 \\ Ae^{\alpha x}+Be^{\alpha x} & 0<x<a\ (E<U_0) \\ Se^{ikx} & x>a. \end{cases}$$

在 $x=0$ 的连续条件：

$$\begin{cases} 1+R=A+B \\ \frac{ik}{\alpha}(1-R)=A-B \end{cases}$$

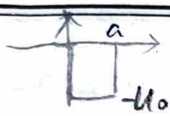
在 $x=a$ 的连续条件：

$$\begin{cases} Ae^{\alpha a}+Be^{-\alpha a}=Se^{ika} \\ Ae^{\alpha a}-Be^{-\alpha a}=\frac{ik}{\alpha}Se^{ika}. \end{cases}$$

解得

$$|S|^2=\frac{4k^2\alpha^2}{(k^2-\alpha^2)^2\mathrm{sh}^2\alpha a+4k^2\alpha^2\mathrm{ch}^2\alpha a}\qquad |R|^2=\frac{(k^2+\alpha^2)^2\mathrm{sh}^2\alpha a}{(k^2+\alpha^2)^2\mathrm{sh}^2\alpha a+4k^2\alpha^2}\qquad |R|^2+|S|^2=1.$$

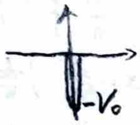
方势阱的透射.



将上式 $U_0 \to -U_0$，$\alpha = \sqrt{2m(E+U_0)}/\hbar$ 得 $T = \left[1 + \frac{\sin^2 \alpha a}{4\frac{E}{U_0}(1+\frac{E}{U_0})}\right]^{-1}$.

若 $E \ll U_0$，$\sin\alpha a = 0$；$\alpha a = n\pi$，共振透射. 能级 $E_n = -U_0 + \frac{n^2\pi^2\hbar^2}{2ma^2}$ $n=1,2,3\cdots$

⑤ δ势阱



$V(x) = -V_0\delta(x)$ $V_0>0$ $\frac{d^2}{dx^2}\psi + \frac{2m}{\hbar^2}[E+V_0\delta(x)]\psi = 0$

在0附近积分：$\int_{-\varepsilon}^{\varepsilon}\frac{d^2}{dx^2}\psi\,dx = \psi'(\varepsilon)-\psi'(-\varepsilon)$，$\int_{-\varepsilon}^{\varepsilon}\psi\,dx = \psi(0)2\varepsilon$，$\int_{\varepsilon}^{\varepsilon}\delta(x)\psi(x)dx = \psi(0)$，故

$\psi'(0^+)-\psi'(0^-) = -\frac{2mV_0}{\hbar^2}\psi(0)$.

束缚态解：$E<0$，令 $k = \frac{\sqrt{-2mE}}{\hbar}$.

$$\begin{cases} x\neq 0 & \psi''-k^2\psi=0 \\ x=0 & \psi(0)=\psi|_{x\to 0} \end{cases} \qquad \psi(x) = \begin{cases} Ae^{-kx}+Be^{kx} & x>0 \\ Ce^{-kx}+De^{kx} & x<0 \end{cases}$$

偶宇称

$$\begin{cases} \psi'(0^+) = -kA,\ \psi'(0^-) = kD\ (A=D) \\ -2Ak = -\frac{2mV_0}{\hbar^2}A. \end{cases}$$

$\therefore E = -\frac{mV_0^2}{2\hbar^2}$：唯一束缚态能级.

奇宇称

无束缚态解.

$$\psi(x) = \begin{cases} \sqrt{k}e^{-kx} & x>0 \\ \sqrt{k}e^{kx} & x<0 \end{cases}$$

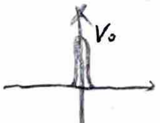
非束缚态解：$E>0$，令 $\beta = \frac{\sqrt{2mE}}{\hbar}$，设粒子从左入射.

$$\begin{cases} x\neq 0 & \psi''+\beta^2\psi=0 \\ x=0 & \psi(0)=\psi|_{x\to 0} \end{cases} \qquad \psi(x) = \begin{cases} e^{i\beta x}+Re^{-i\beta x} & x>0 \\ Se^{i\beta x} & x<0. \end{cases}$$

$$\begin{cases} 1+R=S & \psi\text{连续} \\ 1-R = S+\frac{2mV_0}{i\hbar^2\beta}\cdot S & \psi'\text{跃变} \end{cases} \qquad \begin{cases} |S|^2 = 1/(1+\frac{mV_0^2}{2\hbar^2E}) \\ |R|^2 = \frac{mV_0^2}{2\hbar^2E}/(1+\frac{mV_0^2}{2\hbar^2E}) \end{cases}$$

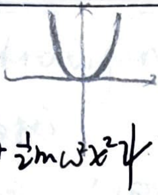
$E \gg \frac{mV_0^2}{\hbar^2}$ 时，$|S|^2 \approx 1$.

δ势垒.



将 $-V_0 \to V_0$ 即可.

⑤ 谐振子



$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi+\frac12 m\omega^2x^2\psi=E\psi \to \frac12(-\frac{d^2}{dx^2}+x^2)\psi=E\psi$.

1) 居位数算符.

$a_-=\frac{1}{\sqrt2}(-\frac{d}{dx}+x)=\frac{1}{\sqrt2}(\hat{p}+\hat{x})$，$a_+=\frac{1}{\sqrt2}(\frac{d}{dx}+x)=\frac{1}{\sqrt2}(-\hat{p}+\hat{x})$；$a_-=a_+^\dagger$；$[a_-,a_+]=I$.

令 $N=a_+a_-$，有 $H=N+\frac12$，$N|n\rangle=n|n\rangle$，且 $a_-a_+=N+I$.

2) 本征值范围与取值.

~~$\langle n|N|n\rangle=\langle n|a_+a_-|n\rangle=n\geq0$~~

由于 $[N,a_\pm]=\pm a_\pm$，可得 $a_\pm|n\rangle\propto|n\pm1\rangle$.

由于 $\langle n|N|n\rangle=\langle n|a_+a_-|n\rangle=n\geq0$，

故 $\exists|\underline{n}\rangle$.

3) 居位数表象下 N、a_-、a_+、H 的矩阵元.

设 $a_\pm|n\rangle=k_n|n\pm1\rangle$，有 $a_\mp a_\pm|n\rangle=k_na_\mp|n\pm1\rangle=(n+\frac12\pm\frac12)|n\rangle$

∴ $k_n\langle n|a_\mp|n\pm1\rangle=n+\frac12\pm\frac12$，且 $\langle n\pm1|a_\pm|n\rangle=k_n$

∴ $|k_n|^2=n+\frac12\pm\frac12$，令相位为0，得 $k_n=\sqrt{n+\frac12\pm\frac12}$

故 $a_\pm|n\rangle=\sqrt{n+\frac12\pm\frac12}\,|n\pm1\rangle$

$H|n\rangle=(n+\frac12)|n\rangle$

由 $a_-=\frac{1}{\sqrt2}(-\frac{d}{dx}+x)$，得 $\frac{1}{\sqrt2}(-\frac{d}{dx}+x)\cancel{x}|\underline{n}\rangle=0$ 解得 $\psi_{(0)}(x)=\langle x|\underline{n}\rangle=(\frac{m\omega}{\pi\hbar})^{\frac14}e^{-\frac{m\omega}{2\hbar}x^2}$.

由 $a_+=\frac{1}{\sqrt2}(\frac{d}{dx}+x)$，得 $\psi_{(n)}(x)=\frac{1}{\sqrt n}a_+\psi_{(n-1)}(x)=\cdots=\frac{1}{\sqrt{n!}}(\frac{\alpha^2}{\pi})^{\frac14}(\alpha x-\frac{1}{\alpha}\frac{d}{dx})^ne^{-\frac{m\omega}{2\hbar}x^2}$.

5. 氢原子.

$$[-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})+\frac{\hat{L}^2}{2\mu r^2}-\frac{ke^2}{r}]\psi(\theta,\varphi,r)=E\psi(\theta,\varphi,r).$$

$\psi_{nlm}(\theta,\varphi,r)=R_{nl}(r)\cdot Y_{lm}(\theta,\varphi)$　n：主；l：$0\sim n-1$：角；m：$-l\sim l$：磁。$E_n=-\frac{e^2}{2a}\frac{1}{n^2}$（$n^2$简并）

径向概率：$\int_\varphi\int_\theta|\psi|^2r\sin\theta d\theta\, rdrd\varphi=r^2dr\int d\Omega|\psi|^2=|R_{nl}(r)|^2r^2dr$. 最可几半径 $r_n=n^2a$.

角向概率：$\int_r|\psi|^2r\sin\theta d\theta\, rdrd\varphi=|Y_{lm}(\theta,\varphi)|^2d\Omega\propto|P_l^m(\cos\theta)|^2d\Omega$.

电流密度：$\vec{j}=\frac{ie\hbar}{2\mu}(\psi^*\nabla\psi-\psi\nabla\psi^*)$　$j_r=j_\theta=0$；$j_\varphi=-\frac{e\hbar m}{\mu}\frac{1}{r\sin\theta}|\psi|^2$.

磁矩：$M=M_z=\frac1c\int\pi r^2\sin^2\theta\, j_\varphi d\sigma=-\frac{e\hbar m}{2\mu c}$.

6. 微扰 Schrödinger.

① 非简并微扰

已知 $H=H^{(0)}+H'$ 矩阵元，且 $H^{(0)}\psi_n^{(0)}=E_n^{(0)}\psi_n^{(0)}$、$H\psi_n=E_n\psi_n$，设 $E_n^{(0)}$ 不简并，则

$E_n=E_n^{(0)}+E_n^{(1)}+\cdots$；$\psi_n=\psi_n^{(0)}+\psi_n^{(1)}+\cdots$ 由数量级相同，有

$(H^{(0)}-E_n^{(0)})\psi_n^{(1)}=-(H'-E_n^{(1)})\psi_n^{(0)}$　　(1)

$(H^{(0)}-E_n^{(0)})\psi_n^{(2)}=-(H'-E_n^{(1)})\psi_n^{(1)}+E_n^{(2)}\psi_n^{(0)}$　　(2)

……　　　……

由(1)，$E_n^{(1)}=\int\psi_n^{(0)*}H'\psi_n^{(0)}d\tau=\langle n^{(0)}|H'|n^{(0)}\rangle$；$\psi_n^{(1)}=\sum_m^{m\neq n}\frac{\langle m^{(0)}|H'|n^{(0)}\rangle}{E_n^{(0)}-E_m^{(0)}}\psi_m^{(0)}$（m共H阶数-1）

由(2)，$E_n^{(2)}=\sum_m^{m\neq n}\frac{|\langle m^{(0)}|H'|n^{(0)}\rangle|^2}{E_n^{(0)}-E_m^{(0)}}$　　成立条件：$\left|\frac{H'_{mn}}{E_n^{(0)}-E_m^{(0)}}\right|\ll 1$.

② 简并微扰

已知 $H=H^{(0)}+H'$ 矩阵元，且 $H^{(0)}\psi_n^{(0)}=E_n^{(0)}\psi_n^{(0)}$、$H\psi_n=E_n\psi_n$，设 $E_n^{(0)}$ 简并（简并度 $k\leq$ H阶数）.

k个本征矢 $\phi_{n1}^{(0)}\cdots\phi_{nk}^{(0)}$ 满足 $H^{(0)}\phi_{ni}^{(0)}=E_n^{(0)}\phi_{ni}^{(0)}$，$i=1,2,\cdots,k$.

重新组合 $\phi_{ni}^{(0)}$：$\chi_n^{(0)}=\sum_{i=1}^{k}C_i^{(0)}\phi_{ni}^{(0)}$ 使得 $\sum_{i=1}^{k}(H'_{mi}-E_n^{(1)}\delta_{mi})C_i^{(0)}=0$　$m=1,2,\cdots,k$.

解此方程组（k个）即得 k个 $E_n^{(1)}$（假设简并已消除），进而有 k个 $\chi_n^{(0)}$. 其中 $H'_{mi}=\int\phi_{nm}^{(0)*}H'\phi_{ni}^{(0)}d\tau$.

③ 含时微扰.

已知 $H=H_0+H'(t)$ 矩阵元（H_0 不含时，H' 含时，但不含对时间的微分算子），~~且 $i\hbar\frac{\partial}{\partial t}\Psi=H\Psi$~~.

且 $H\Psi=i\hbar\frac{\partial}{\partial t}\Psi$，$H_0\Phi_n=i\hbar\frac{\partial}{\partial t}\Phi_n$，$\Phi_n=\varphi_n e^{\frac{\varepsilon_n t}{i\hbar}}$. 求 Ψ:

将 Ψ 按 H_0 的定态波函数展开：$\Psi=\sum_n a_n(t)\Phi_n(t)$. 代入 $H\Psi=i\hbar\frac{\partial}{\partial t}\Psi$ 有

$$i\hbar\sum_n\Phi_n(t)\frac{da_n(t)}{dt}=\sum_n a_n(t)H'(t)\Phi_n(t)$$

，即

$$i\hbar\frac{da_m(t)}{dt}=\sum_n a_n(t)H'_{mn}(t)e^{\frac{i}{\hbar}(\varepsilon_m-\varepsilon_n)t}.$$

设 $H'(t)$ 在 $t=0$ 引入，此时 $\Psi=\Phi_k(0)$，故 $a_n(0)=\delta_{nk}$. 考虑 $a_n(t)\approx a_n(0)$，则

$$i\hbar\frac{da_m(t)}{dt}=\sum_n\delta_{nk}H'_{mn}(t)e^{\frac{i}{\hbar}(\varepsilon_m-\varepsilon_n)t}=H'_{mk}e^{\frac{i}{\hbar}(\varepsilon_m-\varepsilon_k)t}$$

；即

$$a_m(t)=\frac{1}{i\hbar}\int_0^t H'_{mk}(t)e^{\frac{i}{\hbar}(\varepsilon_m-\varepsilon_k)t}dt$$

由 Φ_k 跃迁到 Φ_m 概率 $W_{km}(t)=|a_m(t)|^2=\frac{1}{\hbar^2}\left|\int_0^t H'_{mk}(t)e^{\frac{i}{\hbar}(\varepsilon_m-\varepsilon_k)t}dt\right|^2$. 其中 $H'_{mk}(t)=\int\varphi_m^*H'(t)\varphi_k d\tau$

七. uncertainty relation

Let us examine any two such Hermitian operators, P, Q with

$$PQ - QP = a \cdot 1$$

Since $(PQ-QP)^* = QP - PQ$, a's pure imaginary. This operator equation is not necessarily understood to include the equality of the domains of definition of both sides: $PQ-QP$ need not have sense everywhere.

For each ϕ then,

$$\operatorname{Im}(P\phi, Q\phi) = -i[(P\phi, Q\phi) - (Q\phi, P\phi)] = -i[(QP\phi, \phi) - (PQ\phi, \phi)]$$
$$= (i[PQ-QP]\phi, \phi) = ia\|\phi\|^2$$

Let $a \neq 0$, then we have

$$\|\phi\|^2 = \frac{-2i}{a}\operatorname{Im}(P\phi, Q\phi) \leq \frac{2}{|a|}|(P\phi, Q\phi)| \leq \frac{2}{|a|}\|P\phi\| \cdot \|Q\phi\|$$

therefore, for $\|\phi\| = 1$

$$\|P\phi\| \cdot \|Q\phi\| \geq \frac{|a|}{2}$$

Since $P - \bar{P}$, $Q - \bar{Q}$ also have the above commutation property, we have similarly

$$\|P\phi - \bar{P}\phi\| \cdot \|Q\phi - \bar{Q}\phi\| \geq \frac{|a|}{2}.$$

and if we introduce the mean values and the dispersions:

$$\rho = (P\phi, \phi), \quad \varepsilon^2 = \|P\phi - \rho \cdot \phi\|^2$$
$$\sigma = (Q\phi, \phi), \quad \eta^2 = \|Q\phi - \sigma\phi\|^2$$

then this becomes:

$$\varepsilon\eta \geq \frac{|a|}{2}.$$

附：若$[A, B]=0$，则A、B可找到共同本征态.（$A\psi_n = \lambda_n \psi_n$）

(1) λ_n不简并，交换本征方程中A、B顺序即证.

(2) λ_n简并，由维数不变，构造幺正阵将λ_n的子空间变换到使B对角化的子空间，这些基由简并态原本征矢构成.

至此，四.3 完备.